Synthesis of Sila-Analogs and Silicon-Containing Derivatives of Drugs and Development and Application of the *Si*-2,4,6-Trimethoxyphenyl Moiety as a Novel Protecting Group in Organosilicon Chemistry

Dissertation

zur Erlangung des naturwissenschaftlichen Doktorgrades
der Bayerischen Julius-Maximilians-Universität Würzburg

Vorgelegt von
Diplom-Chemiker
Jürgen Oliver Daiß
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1 Introduction

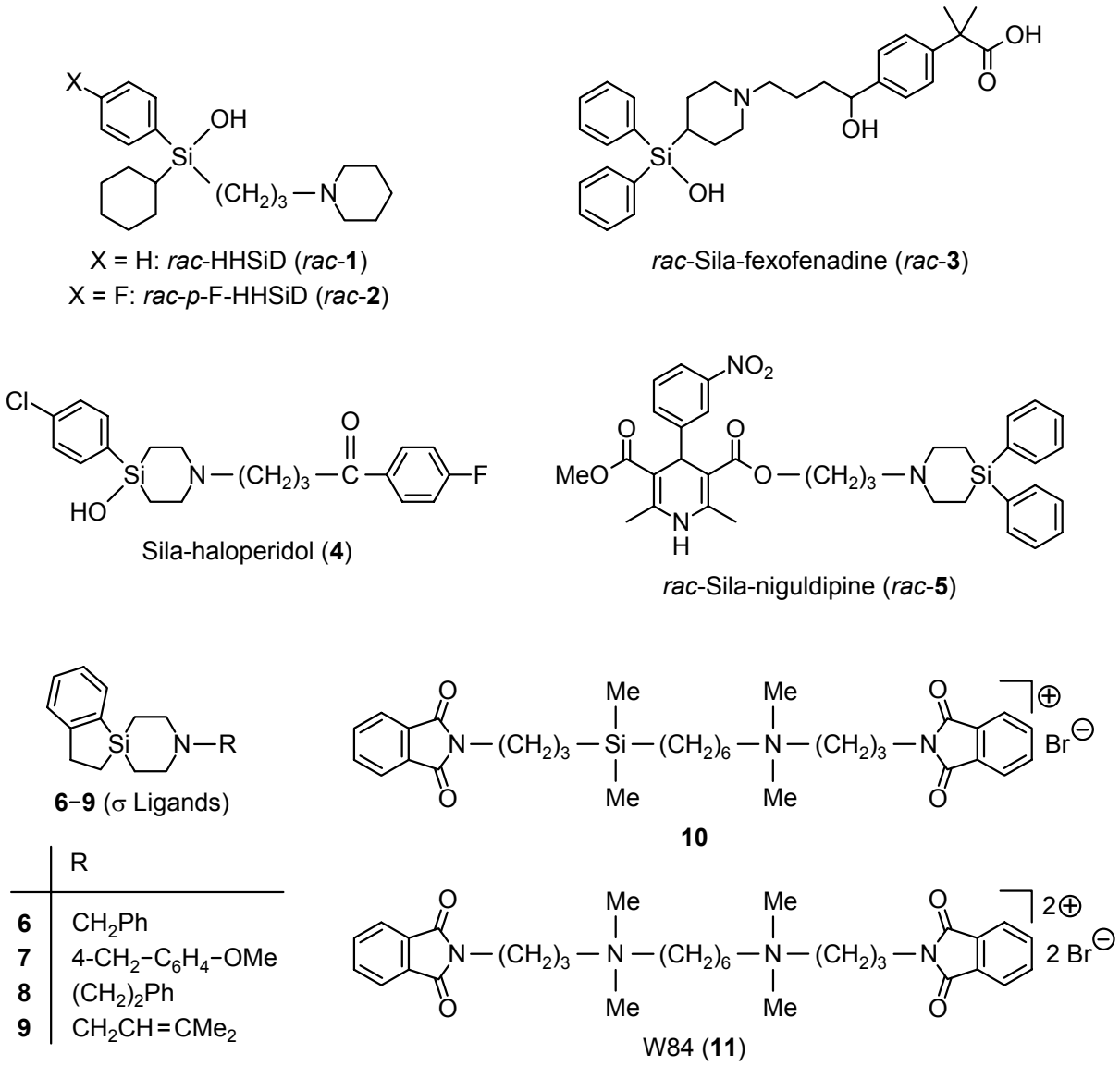
Within organic chemistry, the synthesis of natural products has been a stimulus for the development of new and selective preparative methods for many decades,[1] and these methods have found manifold use in countless industrial processes of high economic interest and revenue. Within the field of medicinal chemistry, these methods are being used to prepare libraries of thousands of structural variations of pharmacologically more or less useful compounds, only about one or two out of ten thousand of which finds its way through pre-clinical and clinical testing to become a new medicine ingredient, which means enormous research and development (R&D) costs.[2]

At this very point, the concept of sila-substitution of such pharmacologically active compounds (i.e., the exchange of one or more selected carbon atom(s) at specific positions of the parent carbon-based drug) comes into play.[3,4] By application of this concept, which has been developed by our group for decades[5] (and still is being developed further), to a prevailing compound of such traditional pre-clinical and clinical testing processes, there is an opportunity to improve the properties of a drug even further without synthesizing large numbers of compounds. Still, almost all the experience of those traditional processes which have lead to the specific molecular shape of the parent carbon compound flows into the development of its silicon derivative, since the organic side chains remain untouched, providing the conclusion that the concept of sila-substitution of drugs offers the opportunity to obtain economically profitable drugs on a cost-effective and short time scale.

Among the properties of a drug which can be influenced by a C/Si exchange are not only its pharmacodynamics, but also its ADMET properties, i.e., its *a*bsorption into, *d*istribution and *m*etabolism in, *e*xcretion from, and *t*oxicology within a biological system like the human body; hence, there are numerous parameters to be addressed.

Some of the most prominent and successful examples of a C/Si switch are the silanols *rac*-hexahydro-sila-difenidol (*rac*-HHSiD) (*rac*-**1**) and *rac*-*p*-fluoro-hexahydro-sila-difenidol (*rac*-*p*-F-HHSiD) (*rac*-**2**),[6] which have excellent functional muscarinc M_3 receptor subtype selectivity and therefore are in use as commercially available pharmacological tools for the characterization of muscarinic receptor subtypes, whereas our group´s most recent developments in the field of silicon-based drugs include the silanols (C_3COH/C_3SiOH exchange) *rac*-sila-fexofenadine (*rac*-**3**)[7] and sila-haloperidol (**4**)[8] as well as compounds with a C_4Si backbone (C_4C/C_4Si exchange), e.g., *rac*-sila-niguldipine (*rac*-**5**)[9] and a series of σ ligands (**6**–**9**)[10]. In addition, the C/Si exchange concept was extended to the substitution of quaternary formally positively charged ammonium nitrogen atoms for electrostatically neutral silicon atoms (N^+/Si exchange) (prototype: compound **10**), which

resulted in a tremendous change of the allosteric action of **10** compared to its parent alkanediaminium compound, the allosteric modulator W84 (**11**):[11,12] Whereas **11** decreased equilibrium binding of the orthosteric ligand [^{3}H]*N*-methylscopolamine ([^{3}H]NMS) at muscarinic M_2 receptors (negative cooperativity), **10** significantly enhanced [^{3}H]NMS binding (positive cooperativity).[13,14]



	R
6	CH_2Ph
7	4-CH_2-C_6H_4-OMe
8	$(CH_2)_2Ph$
9	$CH_2CH=CMe_2$

Chart 1. Examples for a successful C/Si or N^+/Si exchange in drugs.

Although parts of the syntheses of these silicon compounds can be accomplished by the application of known methods, the aim to prepare them stimulates chemists to develop new methods, as the synthesis of natural products does in organic chemistry, or leads to unexpected observations. This actually happened to be, for instance, in the case of sila-haloperidol, where an unexpected ease of the hydrolytic cleavage of sila-haloperidol disiloxane was observed.[8b]

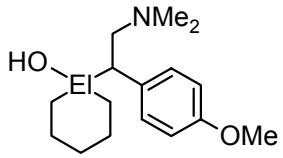
2 Aim

Within the frame of aiming at the synthesis of specific target structures which represent sila-analogs of biologically active molecules, these targets were to be used as a stimulus to search for novel and unconventional methods wherever the opportunity to do so would present itself, which parallels the role of the synthesis of natural products as a stimulus for method development in organic chemistry (cf. Section 1).

In continuation of our studies on the concept of sila-substitution of biologically active compounds, this concept was to be applied on a spectrum of targets including a carbinol/silanol (C_3COH/C_3SiOH) exchange, the exchange of quaternary carbon atoms for silicon atoms (C_4C/C_4Si exchange), and the exchange of formally positively charged nitrogen atoms for electrostatically neutral silicon atoms (C_4N^+/C_4Si exchange). In cases where interesting biological data was obtained for the resulting silicon compounds, scale-up was to be included in this work up to a scale of tens of grams. In addition, the studies on carbinol/silanol switches lead to the development of the *Si*-2,4,6-trimethoxyphenyl group as a novel protecting group in organosilicon chemistry, which was found to be extremely useful for the preparation of functionalized (chloromethyl)silanes; therefore, several compounds of this type were included as preparative targets. These aims are presented in detail in the following sections.

2.1 Sila-venlafaxine

Racemic venlafaxine hydrochloride (*rac*-**12a**·HCl) (Effexor™, Wyeth-Ayerst; Efexor™, Wyeth, Wyeth-Lederle; Trevilor™, Wyeth) is a serotonin/noradrenaline reuptake inhibitor[15] which is in clinical use as an antidepressant.[16]



El = C: Venlafaxine (*rac*-**12a**)
El = Si: Sila-venlafaxine (*rac*-**12b**)

Its silicon derivative sila-venlafaxine (*rac*-**12b**) was chosen as a target since sila-substitution of *rac*-**12a** (→ *rac*-**12b**) was expected to affect the chemical and physicochemical properties and the structure of *rac*-**12a** and therefore to alter its biological properties. For example, (i) the higher OH acidity of silanols (compared to analogous carbinols) should increase the strength of hydrogen-bonding interactions with biomolecules (receptors) and thus should enhance receptor binding. (ii) As the covalent radius of silicon is larger than that of carbon, the C/Si analogs *rac*-**12a** and *rac*-**12b**

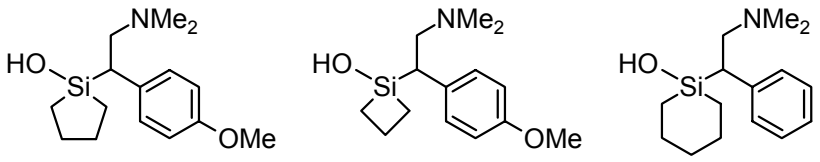
are expected to differ in their structure (size and shape) and in their stereodynamics, which may also affect receptor binding. (iii) Furthermore, differences in the lipophilicity of *rac*-**12a** and *rac*-**12b** can be assumed, which could alter the ADMET properties.

Once methods for the preparation of *rac*-**12b** have been established, the resolution of racemic sila-venlafaxine (*rac*-**12b**) was to be accomplished including the determination of the absolute configuration of the sila-venlafaxine enantiomers (*R*)-**12b** and (*S*)-**12b**. All these compounds (*rac*-**12b**, (*R*)-**12b**, and (*S*)-**12b**) were to be prepared as pharmacologically acceptable salts, preferably as the hydrochlorides, and to be compared to their parent carbon compounds *rac*-**12a**, (*R*)-**12a**, and (*S*)-**12a** [17] concerning their pharmacological profile (i.e., reuptake inhibition of serotonin, noradrenaline, and dopamine). In addition, the methods for the preparation of *rac*-**12b**, (*R*)-**12b**, and (*S*)-**12b** were to be planned and chosen concerning heat flow, gas flow, toxicity, safety, and ecological and economical aspects in order to facilitate scale-up on a multi-kilogram scale.[18]

2.1.1 Derivatives of sila-venlafaxine

Studies on the structure-activity relationships (SARs) of carbon-based venlafaxine derivatives have shown that the receptor affinities crucially depended on (i) the substituents attached to the nitrogen atom, with other patterns apart from the dimethylamino group leading to a detrimental effect on the biological activity in most cases, (ii) the size of the cycloalkanol ring, with the highest affinities being observed for five- and six-membered ring systems, and (iii) the substituents attached to the phenyl group, with the highest affinities being observed for 4-OMe, 4-OH, 4-Cl, and 4-Br substituents.

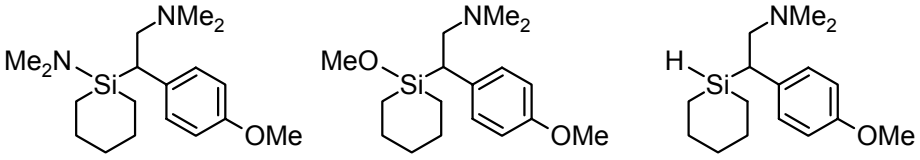
Hence, to get further insight into the structure-activity relationships of silicon-based sila-venlafaxine derivatives, *rac*-**13**–*rac*-**15** were chosen as target compounds for several reasons. (i) The amino moiety was chosen to be dimethylamino in all cases, since an entirely detrimental effect on the biological activity of the silicon-based venlafaxine derivatives was to be avoided. (ii) The most interesting question was what influence variation of the 1-silacycloalkan-1-ol ring size would have, since, due to the larger covalent radius of silicon compared to that of carbon, the maximum receptor affinity may shift from the six- and five-membered ring systems in the case of carbon to the five- and four-membered ring systems *rac*-**13** and *rac*-**14** in the case of silicon. In addition, compound *rac*-**14** was of special interest since the strain of the four-membered ring system was expected to influence the acidity of the OH group significantly. (iii) The 4-H derivative *rac*-**15** was chosen as a target for a negative crosscheck. Since the absence of any substituent in the 4-position of the phenyl group lead to a lower receptor affinity in the SAR of the parent carbon-based venlafaxine derivatives, *rac*-**15** presented itself for a crosscheck to see if the corresponding silicon derivatives would follow similar SARs.



rac-**13** *rac*-**14** *rac*-**15**

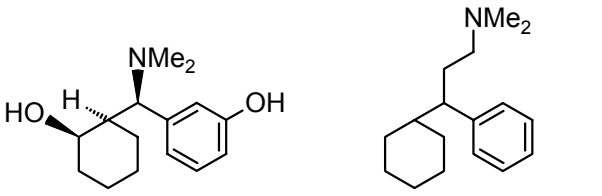
2.1.2 Prodrugs of sila-venlafaxine

Silanols can be formed easily by hydrolysis of halosilanes, alkoxysilanes, aminosilanes, and hydridosilanes under the conditions of an *in vivo* environment.[5,19] This chemistry, which is intrinsic to silicon, but not to carbon, offers the possibility to use these non-enzymatic hydrolysis reactions *in vivo* when a prodrug of a silanol is applied to an organism. Hence, the sila-venlafaxine prodrugs *rac*-**16**–*rac*-**18** were additional targets.



rac-**16** *rac*-**17** *rac*-**18**

The hydrolysis reactions of *rac*-**16**, *rac*-**17**, and *rac*-**18** are bioactivation processes with respect to the biological activity of *rac*-sila-venlafaxine (*rac*-**12b**). However, it should be noted that venlafaxine (**12a**) was developed by hybridizing the molecular shapes of the mixed opiate agonist-antagonist ciramadol (**19**) and of the antidepressant *rac*-gamfexine (*rac*-**20**).[15c] The close structural analogy of *rac*-**18** and *rac*-**20** suggests that, if *rac*-**18** should have similar efficacies like *rac*-gamfexine (*rac*-**20**) *in vivo*, an interesting change in the pharmacological action of *rac*-**18** can be expected *in vivo* over a certain time scale, since the hydrolysis reaction *rac*-**18** → *rac*-**12b** would then mean a simultaneous bioinactivation of the gamfexine-like action and a bioactivation of the sila-venlafaxine action.

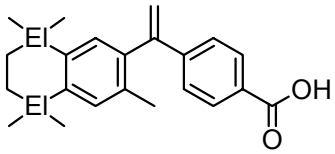


Ciramadol (**19**) *rac*-Gamfexine (*rac*-**20**)

2.2 Disila-bexarotene

Bexarotene (Targretin™, **21a**) is an RXR-selective retinoid that is in therapeutic use for treatment of cutaneous T-cell lymphoma.[20–23] As almost all sila-analogs of drugs studied so far are

antagonists,[5] the twofold sila-substitution of the retinoid agonist bexarotene was particularly challenging.



El = C: Bexarotene (**21a**)
El = Si: Disila-bexarotene (**21b**)

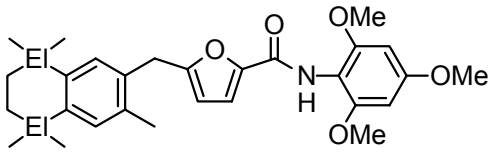
The molecular events by which RXR and other members of the nuclear receptor family regulate transcription of cognate gene programs are, at least in principle, reasonably well understood.[24] The signalling cascade relies on a precisely orchestrated recruitment and dissociation of transcription factors and molecular machineries to target gene promoters, which is initiated upon ligand binding. Multiple transcription activation, protein interaction, and crystallographic studies have revealed structural features of nuclear receptor ligand binding domains that are generated upon binding of agonists, antagonists, mixed agonists/antagonists, or inverse agonists, demonstrating an unexpected potential to modulate nuclear receptor action by ligand design.[25] Here we explore for the first time the activity of a ligand with a silicon-containing backbone.

Due to the different covalent radii of carbon and silicon, disila-substitution of the tetrahydronaphthalene skeleton of bexarotene was expected to change the structure (conformation) of the saturated ring and also to increase the lipophilicity (in this context, see ref. 5). This effect was expected to be more pronounced in the case of disila-bexarotene (**21b**) than in the case of sila-venlafaxine (**12b**) since four Si–C bonds are present in the six-membered ring system of **21b** after a twofold C/Si exchange. This point is underlined by the following estimation: Usual bond lengths are 1.54 Å (C–C bond) and 1.87 Å (Si–C bond).[26] With four Si–C bonds being present within the saturated ring of **21b**, this difference should cause an enlargement of approximately $4 \times (1.87 - 1.54)$ Å = 1.32 Å, which nearly equals an additional C–C bond within this ring system. As a result, the molecular shape of **21b** should be similar to a carbon-based seven-membered ring system, and, therefore, disila-bexarotene (**21b**) makes a highly interesting target for testing its biological retinoid agonist activity. Finally, as carbon and silicon differ in their electronegativity, differences in the electronic properties (electrostatic potential) have also to be considered. All these changes could lead to different biological properties of the C/Si analogs **21a** and **21b**.

The aim of the present work was to synthesize reasonable amounts of **21b**[27] to be used in biological studies on the C/Si pair **21a**/**21b** including *in vitro* studies (ligand binding to RXR receptors and RXR activation) as well as *in vivo* studies.

2.3 Disila-AG-045572 (disila-CMPD1)

While peptide-type gonadotropin-releasing hormone (GnRH) antagonists and agonists are already in clinical use for the treatment of reproductive disorders and steroid hormone-dependent tumors, nonpeptide-type GnRH antagonists have appeared in the literature very recently, and several advantages over peptide-type GnRH agonists and antagonists have been discussed.[28] AG-045572 (CMPD1, **22a**) is a very recent example of a potent orally active nonpeptide GnRH antagonist.[29,30] The sila-substitution approach was applied to **22a** with the aim to optimize the pharmacodynamic and pharmacokinetic properties of **22a** by a twofold carbon/silicon exchange in its 3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydro-2-naphthyl group, and the same considerations apply as those discussed for the C/Si-pair **21a**/**21b**, except for the fact that AG-045572 (**22a**) is an antagonist, not an agonist (different from the retinoid agonist bexarotene (**21a**)).



El = C: AG-045572 (**22a**)
El = Si: Disila-AG-045572 (**22b**)

Compound **22b** should be synthesized on a gram-scale[31] to allow for comparison of the C/Si pair **22a**/**22b** regarding their antagonizing effects at the GnRH receptor.

2.4 (Chloromethyl)silanes

2.4.1 Tris(chloromethyl)silanes

(Chloromethyl)silanes are versatile starting materials for the synthesis of organofunctional silanes.[32] The coupling reaction between chlorosilanes and (chloromethyl)lithium, generated in situ from bromochloromethane and *n*-butyllithium in THF, has been demonstrated to be an excellent preparative method for the synthesis of (chloromethyl)silanes.[33,34] Silanes with more than one $SiCH_2Cl$ moiety and compounds of this type with additional *Si*-functional groups are of great interest for synthetic organosilicon chemistry. There is a need for convenient and reliable preparative methods for the synthesis of such compounds, for instance for the development of new silicon-based drugs that contain more than one *Si*-bound organofunctional group.

Investigations prior to this work have shown that neither the photochlorination of methylsilanes[35] nor the reaction of chlorosilanes with diazomethane[36,37] are convenient methods for the preparation of such compounds, since both methods suffer from their lack of selectivity and broad applicability to a wide range of chloro(organyl)silanes. In addition, the diazomethane method

is problematic due to its dangerous handling and the toxicity of this reagent. On the other hand, previous attempts to prepare chlortris(chloromethyl)silane (**23**) and tris(chloromethyl)methoxysilane (**24**), starting from trichloro(chloromethyl)silane and using the reagent system $BrCH_2Cl$/*n*-BuLi, were unsuccessful, since the only product which could be isolated was terakis(chloromethyl)silane.[38] This clearly points at the necessity to protect one out of the four valencies at the silicon atom using a protecting group. In context with the studies on sila-venlafaxine (**12b**), the *Si*-2,4,6-trimethoxyphenyl (*Si*-2,4,6-TMOP) group was developed as a novel protecting group in organosilicon chemistry, and therefore it should be used to develop methods for the synthesis of chlortris(chloromethyl)silane (**23**) and tris(chloromethyl)methoxysilane (**24**)[39] (although (2,4,6-trimethoxyphenyl)silanes have been synthesized and studied before,[40] these studies were not aimed at the development of the *Si*-2,4,6-TMOP moiety as a protecting group).

$ClSi(CH_2Cl)_3$ **23** $MeOSi(CH_2Cl)_3$ **24**

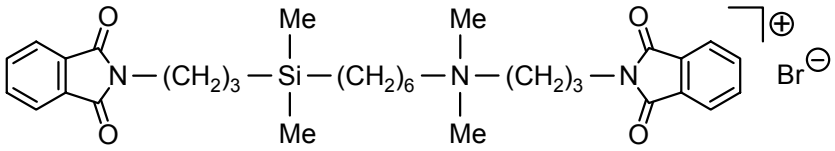
2.4.2 Dichlorobis(chloromethyl)silane

Dichlorobis(chloromethyl)silane (**25**) is accessible either by stepwise chloromethylation of tetrachlorosilane using diazomethane[37] or by chloromethylation of dichlorodiphenylsilane using $BrCH_2Cl$/*n*-BuLi[34], followed by cleavage of the Ph–Si-bonds using triflic acid and subseqent treatment with triethylammonium chloride. Since these methods both involve dangerous (i.e., diazomethane) or aggressive (i.e., triflic acid) reagents, it was to be explored if the use of the *Si*-2,4,6-TMOP group would offer a better alternative for the preparation of dichlorobis(chloromethyl)silane (**25**).

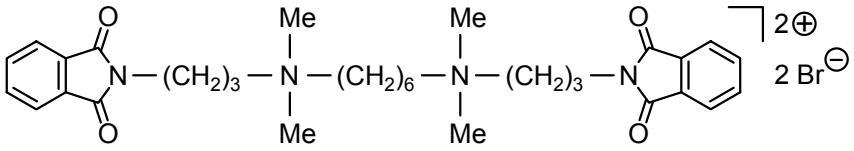
$Cl_2Si(CH_2Cl)_2$
25

2.5 Silicon-based allosteric modulators of muscarinic M_2 receptors

W84 (**11**) is an allosteric agent for the ”common allosteric site“ of muscarinic M_2 receptors, its allosteric action being characterized by an inhibition of the dissociation of the orthosteric ligand [^{3}H]NMS and by a decrease of [^{3}H]NMS equilibrium binding. Previous studies have lead to the development of **10** as a new lead structure for allosteric modulators of muscarinic M_2 receptors (N^+/Si exchange), since, in contrast to the parent alkanediaminium type compound W84 (**11**), the allosteric action of **10** was characterized by an enhancement of [^{3}H]NMS equilibrium binding to muscarinic M_2 receptors.[13]

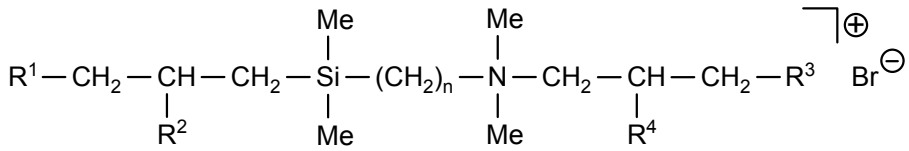


10

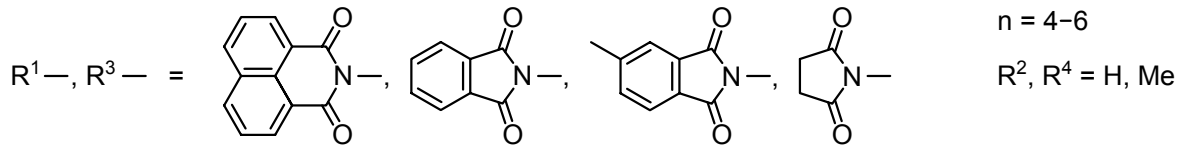


W84 (**11**)

Whereas there are plenty of data on W84-type allosteric modulators and related compounds,[41,42] only five silicon-based allosteric modulators of the "**10**-type" are known so far (variation of the number of CH_2 groups of the central $(CH_2)_6$ spacer ranging from four to eight CH_2 groups).[13] Hence, a number of structural modifications of **10** were to be prepared (compounds **26**–**50**, *rac*-**51**, and *rac*-**52**; see Chart 3 (page 27) for a detailed list of all target structures) in order to establish SAR studies of the silicon-based allosteric modulators of the "**10**-type". The moieties to be modified were (i) the central $(CH_2)_6$ spacer; the $(CH_2)_n$ spacer length of the target molecules was chosen to be n = 4–6 (→ compounds **26**–**45**), since the most interesting pharmacological activity of this type of compound had been found for a spacer length of and around five methylene groups.[13] (ii) Instead of the lateral phthalimido moieties, which are part of the molecular structure of **10**, molecules with lateral 1,8-naphthalimido, phthalimido, 4-methylphthalimido, and succinimido moieties were to be synthesized. Since the highest biological activities were found for the 1,8-naphthalimido group in the case of the W84-type compounds,[42] this group was chosen as a "standard" (or "reference") group, and non-symmetrical derivatives of **10** containing different lateral imido moieties should be varied against the 1,8-naphthalimido group to be present at the opposite terminus of the target cations (→ compounds **26**–**48**).[43] (iii) Recently, compounds appeared in the literature in which the lateral phthalimido moieties in the molecular structure of W84 (**11**) were substituted for 4-methylphthalimido moieties and/or the lateral $(CH_2)_3$ spacers were

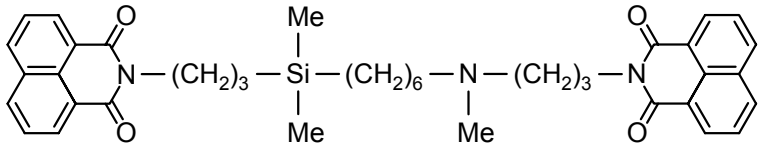


26–**50**, *rac*-**51**, and *rac*-**52**



substituted for $CH_2CH(CH_3)CH_2$ spacers resulting in a switch of the allosteric action of this type of compound from negative to positive cooperativity.[12e,41r,42c] The same structural variation was to be applied to the silicon-based "**10**-type" allosteric modulators to elucidate whether synergetic effects could be used to augment the positive cooperativity of **10** (→ compounds **49**, **50**, *rac*-**51**, and *rac*-**52**).

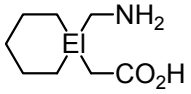
In addition to the synthesis of the allosteric modulators **26**–**50**, *rac*-**51**, and *rac*-**52**, which contain a permanently positively charged quaternary nitrogen atom, the tertiary derivative **53** was to be synthesized, since tertiary amines are in a dynamic equilibrium with their corresponding protonated ammonium salts under physiological conditions and the free base is expected to show a high propensity to penetrate the blood-brain barrier. The lateral moieties of **53** were chosen to be 1,8-naphthalimido groups (for which the highest biological activities in the SAR of the W84-type compounds had been observed,[41] see above), and the length of the central spacer was chosen to be $(CH_2)_6$, since SAR data for the W84-type compounds is most plentiful for this spacer length, thus ensuring the best comparability of the W84-type SAR data to that of **53**.



53

2.6 Sila-gabapentin

Gabapentin (**54a**), an analog of 4-aminobutyric acid, currently is in clinical use as an antiepileptic. The synthesis of its silicon analog sila-gabapentin (**54b**)[44] was especially challenging, since it has a carbonyl moiety in the β-position to the silicon atom.[45,46] The reactivity of β-carbonylsilanes is mainly based on the weakness of the Si–$CH_2C(O)R$ bond, which is an intrinsic obstacle when tranformations of *C*-functionalized organyl groups at the silicon atom are intended. Therefore, most of the publications on the reactivity of β-carbonylsilanes report on reactions involving cleavage of the Si–$CH_2C(O)R$ bond.[47] A typical example of this is the use of $Me_3SiCH_2CO_2Et$ as a silylating agent. Despite this intrinsic obstacle, sila-gabapentin (**54b**) was to be synthesized, if possible, in reasonable quantities for its pharmacological characterization.



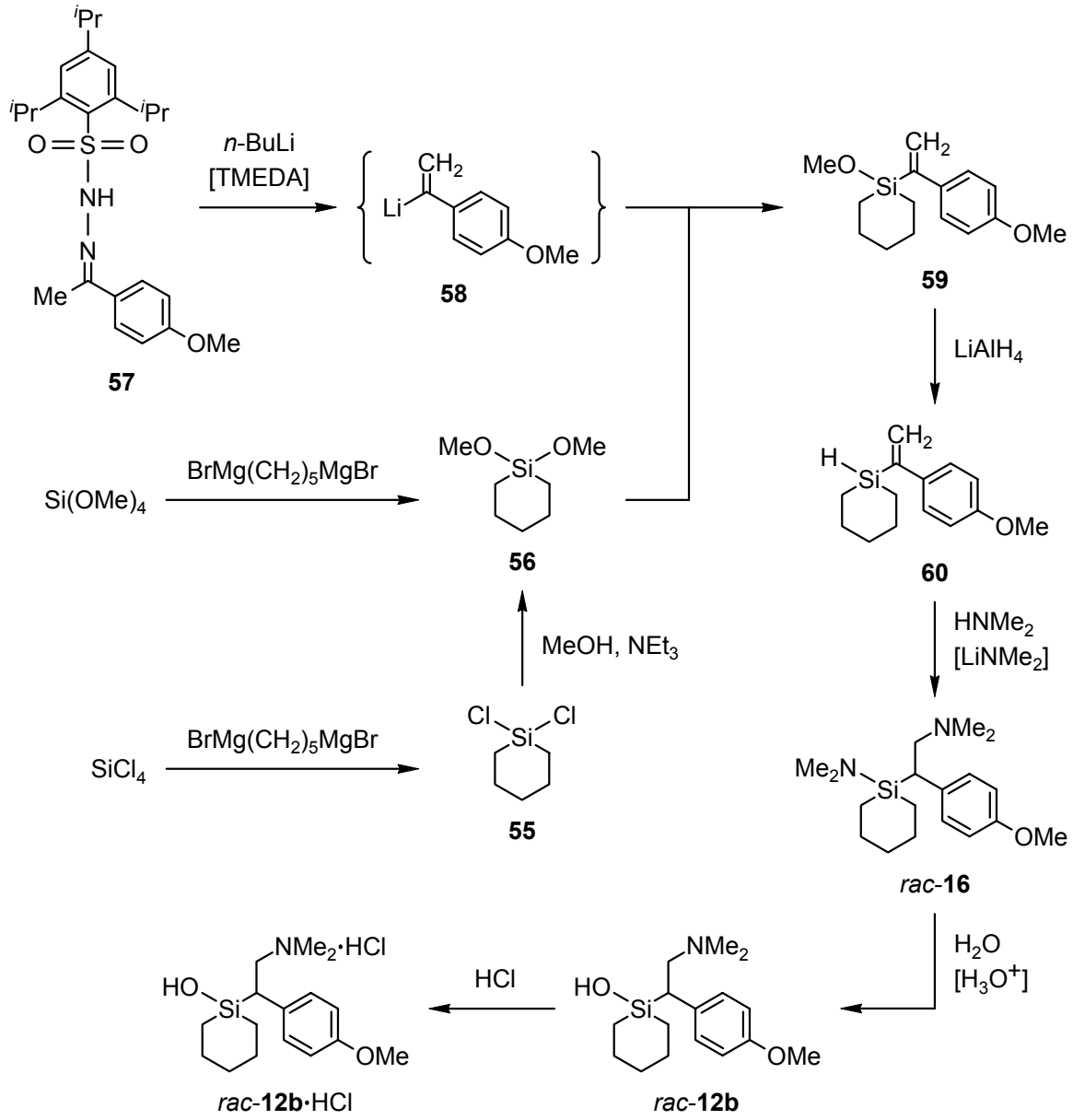
El = C: Gabapentin (**54a**)
El = Si: Sila-gabapentin (**54b**)

3 Synthesis of sila-venlafaxine and derivatives

3.1 Synthesis of racemic and non-racemic sila-venlafaxine

3.1.1 Method A: synthesis of *rac*-sila-venlafaxine (*rac*-12b) *via* a hydridosilane

rac-Sila-venlafaxine hydrochloride (*rac*-**12b**·HCl) was prepared in 15% overall yield in a multistep synthesis, starting from tetrachlorosilane (Scheme 1). Thus, treatment of tetrachlorosilane with 1,5-bis(bromomagnesio)pentane gave 1,1-dichloro-1-silacyclohexane (**55**) (yield 62%), which upon methanolysis, in the presence of triethylamine, afforded 1,1-dimethoxy-1-silacyclohexane (**56**) (yield 80%). Alternatively, compound **56** was synthesized by reaction of tetramethoxysilane with 1,5-bis(bromomagnesio)pentane (yield 43%). Treatment of 4-methoxyacetophenone 2,4,6-



Scheme 1. Synthesis of *rac*-sila-venlafaxine (*rac*-**12b**) *via* a hydridosilane.

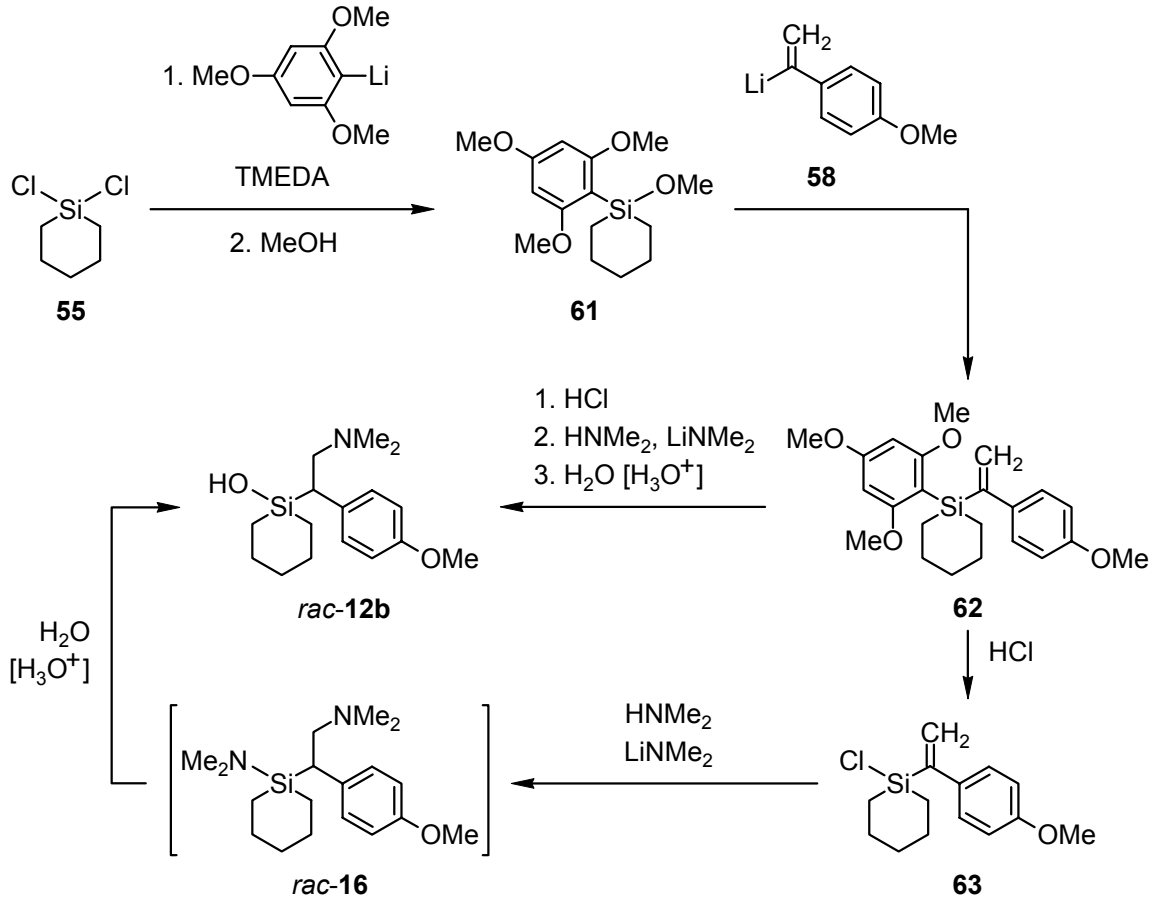
triisopropylbenzenesulfonylhydrazone (**57**) with *n*-butyllithium, in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), gave the intermediate [1-(4-methoxyphenyl)vinyl]lithium (**58**) (Shapiro reaction), which upon reaction with **56** afforded 1-methoxy-1-[1-(4-methoxyphenyl)vinyl]-1-silacyclohexane (**59**) (yield 45%), which was then reacted with lithium aluminum hydride to give 1-[1-(4-methoxyphenyl)vinyl]-1-silacyclohexane (**60**) (yield 82%). The lithium dimethylamide-catalyzed reaction of **60** with dimethylamine (→ *rac*-**16**), followed by hydrolysis, yielded *rac*-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclohexan-1-ol (*rac*-sila-venlafaxine, *rac*-**12b**) (yield 90%). The isolation and purification of the intermediate *rac*-**16** in the transformation **60** → *rac*-**12b** was not necessary. Treatment of *rac*-**12b** with an ethereal hydrogen chloride solution finally afforded the hydrochloride *rac*-**12b**·HCl (yield 90%). To characterize the intermediate *rac*-1-(dimethylamino)-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclohexane (*rac*-**16**), this compound was also isolated and purified (yield 76%).

3.1.2 Method B: synthesis of *rac*-sila-venlafaxine (*rac*-12b) using the *Si*-2,4,6-trimethoxyphenyl group as a protecting group

As shown below in Scheme 5 (p. 15, Section 3.3), the reaction pathways which were successful for the preparation of *rac*-sila-venlafaxine (*rac*-**12b**) (as displayed in Scheme 1 (p. 11, Section 3.1.1)) could not be applied to synthesize its four-membered ring system derivative *rac*-**14**; cf. Scheme 5 (p. 15, Section 3.3). Nevertheless, the problems which were encountered during the attempted synthesis of *rac*-**14** according to Scheme 5 were a stimulus to search for unconventional alternatives, resulting in the development of the *Si*-2,4,6-trimethoxyphenyl moiety as a novel protecting group; cf. Scheme 6 (p. 17, Section 3.3). Concomitantly, the synthesis of *rac*-sila-venlafaxine (*rac*-**12b**) as shown in Scheme 1 suffered from the drawback that large amounts of iodomethane had to be used during the workup of the intermediate **59** and the fact that hydridosilanes (such as **60**) pose a danger in large-scale syntheses.

The methods shown in Scheme 6 were suitable to circumvent these problems, and, therefore, *rac*-sila-venlafaxine (*rac*-**12b**) was synthesized according to Scheme 2 using analogous reaction pathways as those shown in Scheme 6 in a multistep synthesis in 21% or 27% (without isolation of **63**) overall yield, starting from 1,1-dichloro-1-silacyclohexane (**55**). Thus, reaction of **55** with one molar equivalent of (2,4,6-trimethoxyphenyl)lithium, followed by methanolysis of the remaining Si–Cl bond, yielded 1-methoxy-1-(2,4,6-trimethoxyphenyl)-1-silacyclohexane (**61**) (yield 66%). Treatment of **61** with [1-(4-methoxyphenyl)vinyl]lithium (**58**) gave 1-[1-(4-methoxyphenyl)vinyl]-1-(2,4,6-trimethoxyphenyl)-1-silacyclohexane (**62**) (yield 47%), which in turn was used to prepare

1-chloro-1-[1-(4-methoxyphenyl)vinyl]-1-silacyclohexane (**63**) (yield 77%) by treatment with an ethereal hydrogen chloride solution (selective cleavage of the *Si*-2,4,6-TMOP protecting group; no side products arising from cleavage of the other Si–C bonds could be detected by GC-MS analysis). Reaction of **63** with dimethylamine/lithium dimethylamide, followed by hydrolysis, finally afforded *rac*-**12b** (yield 86%). Alternatively, *rac*-**12b** was prepared directly from **62** by treatment with an ethereal hydrogen chloride solution (no isolation of the resulting chlorosilane **63**), followed by reaction with dimethylamine/lithium dimethylamide and subsequent hydrolysis (yield 86%). In the transformation **63** → *rac*-**12b**, *rac*-1-(dimethylamino)-1-[2-(dimethylamino)-1-(4-methoxyphenyl)-ethyl]-1-silacyclohexane (*rac*-**16**) was shown to be an intermediate (comparison with an authentic sample; GC-MS analysis).

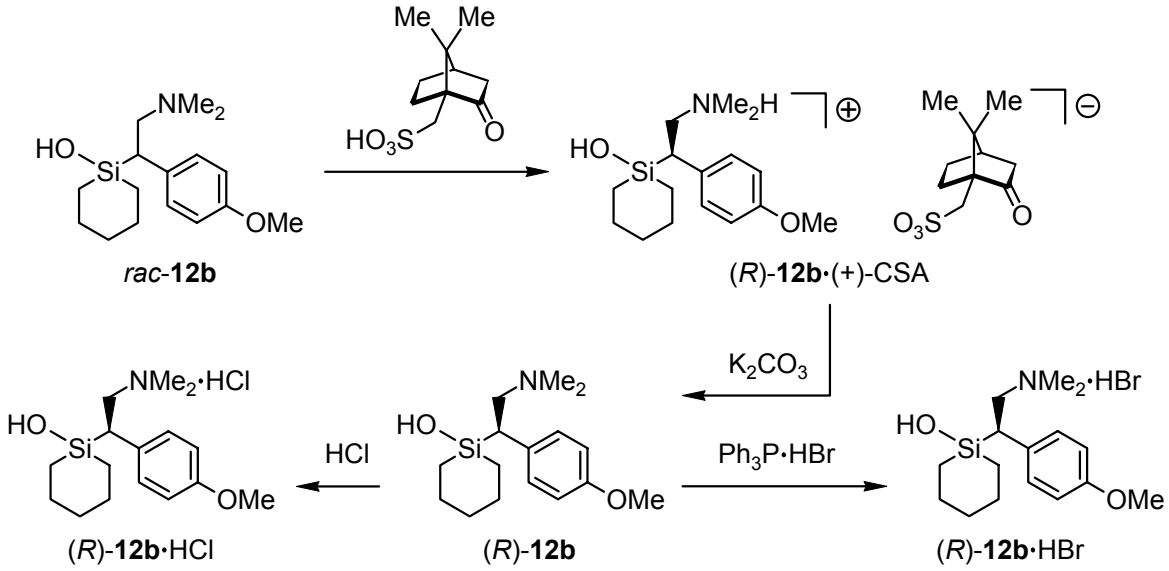


Scheme 2. Synthesis of *rac*-sila-venlafaxine (*rac*-**12b**) using the *Si*-2,4,6-trimethoxyphenyl moiety as a novel protecting group.

3.1.3 Resolution of *rac*-sila-venlafaxine (*rac*-12b)

(*R*)-Sila-venlafaxine ((*R*)-**12b**) was prepared according to Scheme 3 by resolution of *rac*-**12b**, using (+)-10-camphorsulfonic acid ((+)-CSA) as the resolving agent (→ (*R*)-**12b**·(+)-CSA; yield 30%, related to *rac*-**12b**). Treatment of the diastereomerically pure salt (*R*)-**12b**·(+)-CSA with an aqueous potassium carbonate solution gave (*R*)-**12b** (yield 99%). The antipode (*S*)-**12b** was

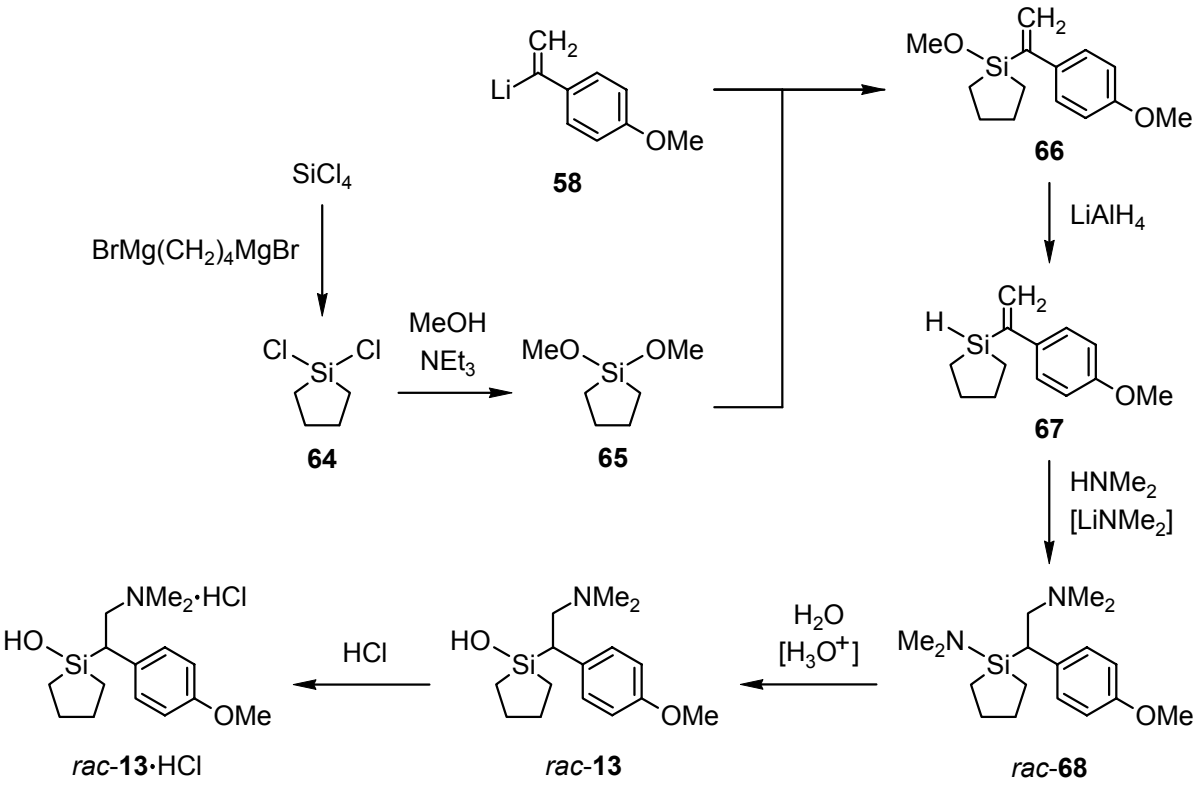
prepared analogously, starting from the mother liquor obtained in the preparation of (*R*)-**12b**·(+)-CSA and using (–)-CSA as the resolving agent (→ (*S*)-**12b**·(–)-CSA). The enantiopure hydrochlorides (*R*)-**12b**·HCl and (*S*)-**12b**·HCl were prepared by treatment of (*R*)-**12b** and (*S*)-**12b**, respectively, with an ethereal hydrogen chloride solution (yield 27–28%, related to *rac*-**12b**).[48] Reaction of (*R*)-**12b** with triphenylphosphonium bromide afforded (*R*)-**12b**·HBr (yield 90%),[49] the crystal structure analysis of which allowed the assignment of the absolute configurations of the sila-venlafaxine enantiomers (see below).



Scheme 3. Resolution of *rac*-sila-venlafaxine (*rac*-**12b**).

3.2 Synthesis of the *rac*-sila-venlafaxine derivative *rac*-1-[2-(dimethyl-amino)-1-(4-methoxyphenyl)ethyl]-1-silacyclopentan-1-ol (*rac*-13)

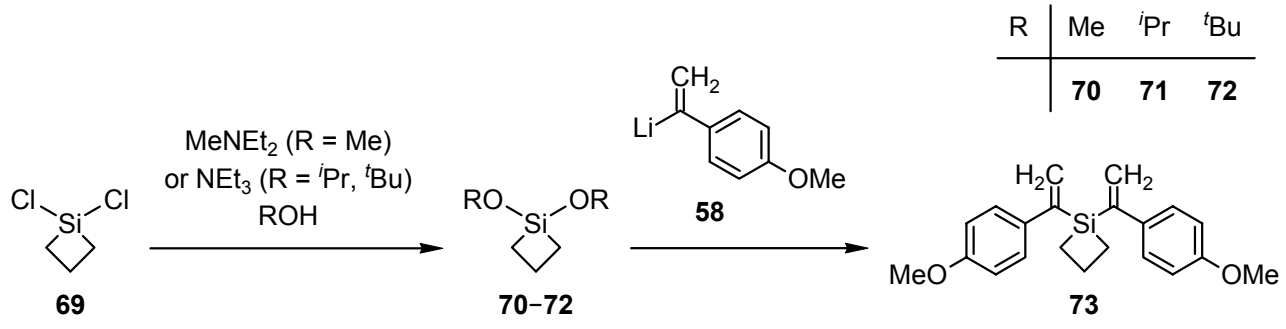
The sila-venlafaxine derivative *rac*-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-sila-cyclopentan-1-ol (*rac*-**13**) and its hydrochloride *rac*-**13**·HCl were prepared analogous to the synthesis of *rac*-**12b**·HCl *via* the intermediates **64**–**67** and *rac*-**68**, starting from tetrachlorosilane, and were isolated in 5% overall yield (Scheme 4).



Scheme 4. Synthesis of the sila-venlafaxine derivative *rac*-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-sila-cyclopentan-1-ol (*rac*-**13**).

3.3 Attempted synthesis of the *rac*-sila-venlafaxine derivative *rac*-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclobutan-1-ol (*rac*-14)

The reaction pathways that were established for the synthesis of *rac*-sila-venlafaxine (*rac*-**12b**) as shown in Scheme 1 (p. 11, Section 3.1.1) have also been applied to 1,1-dichloro-1-silacyclobutane (**69**) in an attempt to prepare the *rac*-sila-venlafaxine derivative *rac*-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclobutan-1-ol (*rac*-**14**). In this context, 1,1-dimethoxy-1-silacyclobutane (**70**) (yield 55%), 1,1-diisopropoxy-1-silacyclobutane (**71**) (yield 62%), and 1,1-di-*tert*-butoxy-1-silacyclobutane (**72**) (yield 56%) were synthesized from **69**.[50]



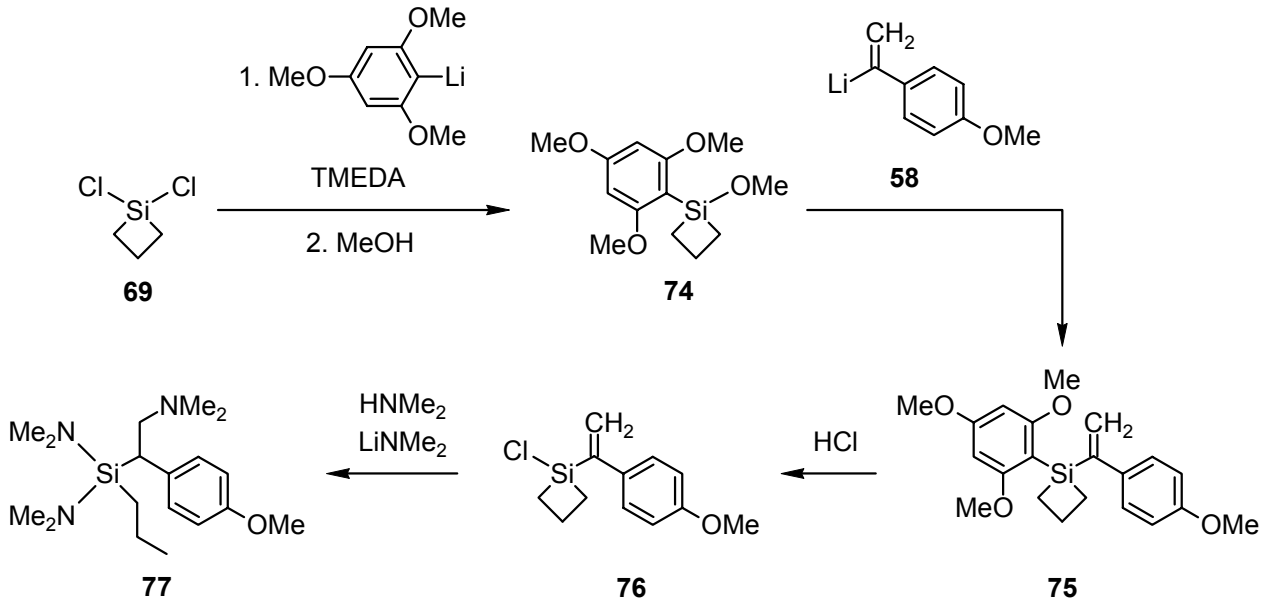
Scheme 5. Reaction of **58** with equimolar amounts of the 1,1-dialkoxy-1-silacyclobutanes **70**–**72**.

Twofold substitution took place when equimolar amounts of **58** and **70** were reacted according to Scheme 5, even at low temperature (–78 °C),[51] affording 1,1-bis-[1-(4-methoxyphenyl)vinyl]-1-silacyclobutane (**73**; yield 70% (related to **58**)[52]/33% (related to **70**)). Very similar results were obtained in experiments using equimolar amounts of **58** and **71** or **72** (GC control, no further workup). Considering these results, a preparation of *rac*-**14** analogous to the synthesis of *rac*-**12b** did not seem to be promising.

Instead, a different approach was pursued. The unexpected ease of substitution of the second alkoxy functionality in the 1,1-dialkoxy-1-silacyclobutanes **70**–**72** clearly warranted the use of a blocking (or protecting) group attached to the silacyclobutane backbone before treatment with **58**. It was decided to use the *Si*-2,4,6-trimethoxyphenyl (*Si*-2,4,6-TMOP) group for several reasons: (i) (2,4,6-trimethoxyphenyl)lithium, required for the preparation of (2,4,6-trimethoxyphenyl)silanes, can be prepared very easily by deprotonation of 1,3,5-trimethoxybenzene with *n*-butyllithium/TMEDA. (ii) The *ortho*-methoxy groups, which are present adjacent to the silicon atom after one of the two leaving groups in **69** has been displaced by a *Si*-2,4,6-TMOP group, were expected to pose significant steric demand, thus leading to a high selectivity (no twofold substitution of both chlorine atoms in **69** by (2,4,6-trimethoxyphenyl)lithium). (iii) Since methoxy groups attached to a benzene ring significantly facilitate electrophilic substitution reactions in their *ortho* and *para* position(s), the Si–2,4,6-TMOP bond of the protected (2,4,6-trimethoxyphenyl)silanes was expected to be easily cleavable by electrophilic reagents, especially by Brønsted acids.

Thus, treatment of 1,1-dichloro-1-silacyclobutane (**69**) with one molar equivalent of (2,4,6-trimethoxyphenyl)lithium, followed by methanolysis of the remaining Si–Cl bond, afforded 1-methoxy-1-(2,4,6-trimethoxyphenyl)-1-silacyclobutane (**74**) (yield 58%) (Scheme 6). No side products were detected (GC), indicating that twofold substitution did not take place in the reaction of **69** with (2,4,6-trimethoxyphenyl)lithium. Treatment of **74** with [1-(4-methoxyphenyl)vinyl]lithium (**58**) gave 1-[1-(4-methoxyphenyl)vinyl]-1-(2,4,6-trimethoxyphenyl)-1-silacyclobutane (**75**) (yield 62%), which in turn was used to prepare 1-chloro-1-[1-(4-methoxyphenyl)vinyl]-1-silacyclobutane (**76**) (yield 53%) by treatment with an ethereal hydrogen chloride solution (selective cleavage of the *Si*-2,4,6-TMOP protecting group; no side products arising from cleavage of the other Si–C bonds could be detected by GC-MS analysis). Subsequent treatment of **76** with dimethylamine/lithium dimethylamide (analogous to the transformation **63** → *rac*-**12b**) surprisingly afforded bis(dimethylamino)[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]propylsilane (**77**) (yield 57%); i.e., in addition to the attempted chloro/dimethylamino exchange at the silicon atom and the amine addition to the vinyl group, ring

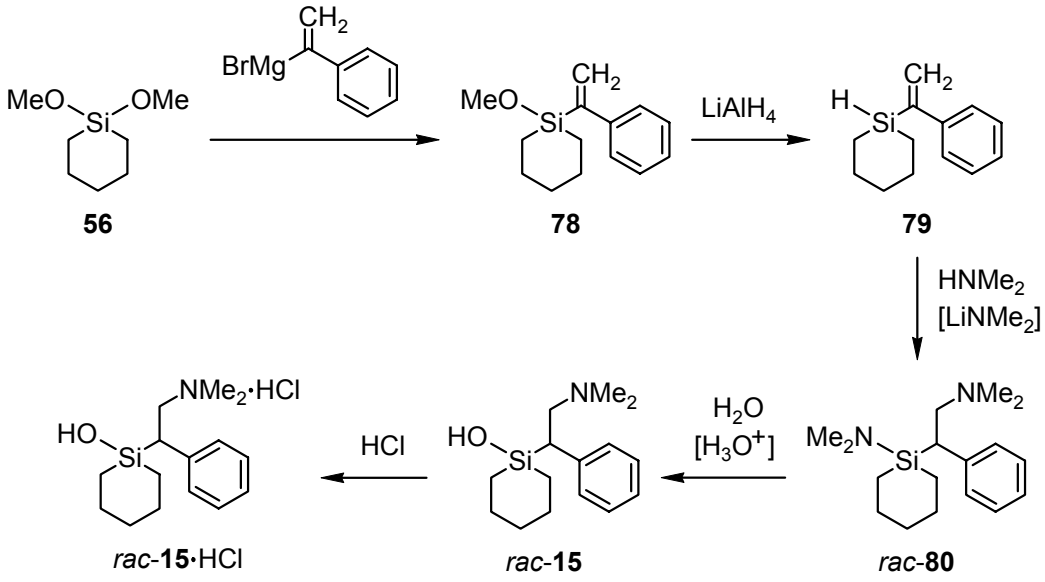
opening (Si–C cleavage) of the silacyclobutane skeleton took place. This ring opening, which can be explained by the higher ring strain compared to that of the silacyclohexane skeleton, prevented the synthesis of *rac*-**14** by this route.



Scheme 6. Attempted synthesis of *rac*-**14** using the *Si*-2,4,6-trimethoxyphenyl moiety as a novel protecting group.

3.4 Synthesis of *rac*-desmethoxy-sila-venlafaxine (*rac*-1-[2-(dimethyl-amino)-1-phenylethyl]-1-silacyclohexan-1-ol, *rac*-15)

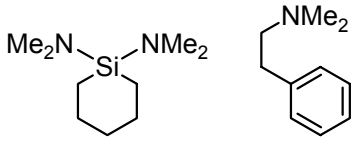
rac-Desmethoxy-sila-venlafaxine (*rac*-1-[2-(dimethylamino)-1-phenylethyl]-1-silacyclo-hexan-1-ol, *rac*-**15**) and its hydrochloride *rac*-**15**·HCl were prepared in multistep syntheses, starting from 1,1-dimethoxy-1-silacyclohexane (**56**) (Scheme 7). Thus, reaction of **56**



Scheme 7. Synthesis of *rac*-desmethoxy-sila-venlafaxine (*rac*-**15**).

with (1-phenylvinyl)magnesium bromide[53] gave 1-methoxy-1-(1-phenylvinyl)-1-silacyclohexane (**78**) (yield 59%), which upon treatment with lithium aluminum hydride afforded 1-(1-phenylvinyl)-1-silacyclohexane (**79**) (yield 83%). Compound **79** was then reacted with dimethylamine, in the presence of lithium dimethylamide, to give *rac*-1-(dimethylamino)-1-[2-(dimethylamino)-1-phenylethyl]-1-silacyclohexane (*rac*-**80**) (yield 40%). Hydrolysis of *rac*-**80** afforded *rac*-**15** (yield 91%), which upon treatment with an ethereal hydrogen chloride solution gave the corresponding hydrochloride *rac*-**15**·HCl (yield 93%).

In the course of the synthesis of *rac*-**80**, the formation of 1,1-bis(dimethylamino)-1-silacyclohexane (**81**) and dimethyl-(2-phenylethyl)amine (**82**) was observed (comparison with authentic samples, GC-MS analysis of the reaction mixture), resulting from an Si–C bond cleavage induced by a nucleophilic attack of $LiNMe_2$ at the silicon atom. This cleavage reaction is mainly responsible for the poor yield of *rac*-**80**. Interestingly, no cleavage of the corresponding Si–C(H)(Aryl) bonds was observed in the course of the comparable reactions **60** → *rac*-**16**, **63** → *rac*-**16**, **67** → *rac*-**68**, or **76** → **77**.

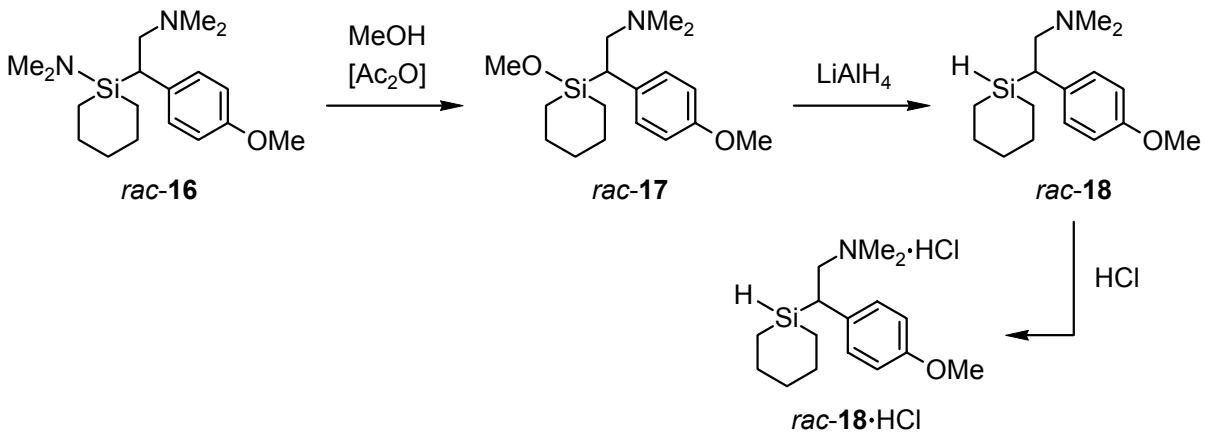


81 **82**

Chart 2. Side products formed in the course of the synthesis of *rac*-**80**.

3.5 Synthesis of sila-venlafaxine prodrugs

The sila-venlafaxine prodrugs *rac*-**17** and *rac*-**18** were synthesized according to Scheme 8, starting from *rac*-**16**, which is an intermediate in the synthesis of *rac*-sila-venlafaxine (*rac*-**12b**); cf. Scheme 1 (p. 11, Section 3.1.1). Thus, acetic acid anhydride-catalyzed[54] reaction of *rac*-**16** in



rac-**16** *rac*-**17** *rac*-**18**

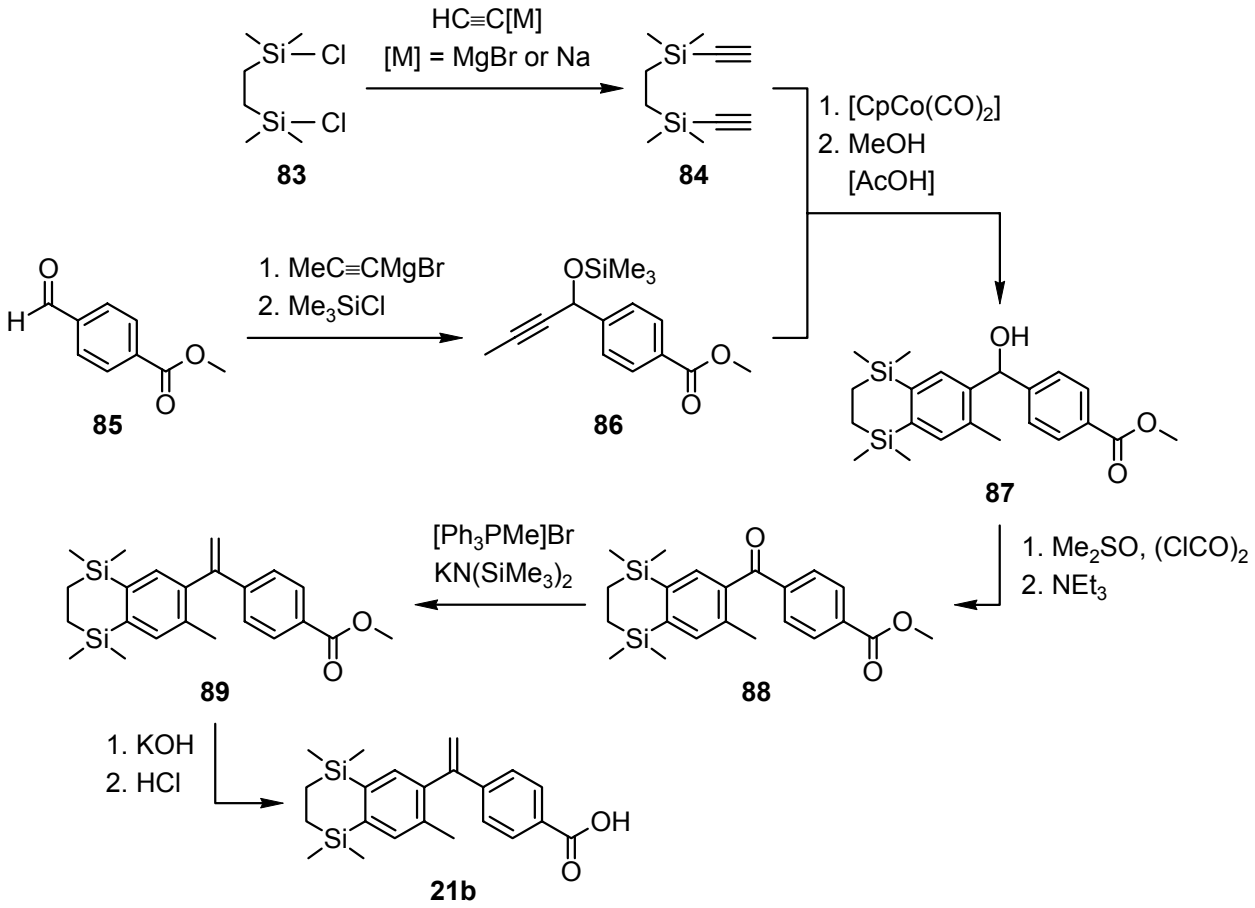
rac-**18**·HCl

Scheme 8. Synthesis of the *rac*-sila-venlafaxine prodrugs *rac*-**17**, *rac*-**18**, and *rac*-**18**·HCl.

methanol gave *rac*-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-methoxy-1-silacyclohexane (*rac*-**17**) (yield 87%), which was then reacted with lithium aluminum hydride to give *rac*-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclohexane (*rac*-**18**) (yield 73%). In order to obtain a stable storage form of *rac*-**18** (rapid base-catalyzed hydrolysis of Si–H bonds in the presence of atmospheric moisture), the corresponding hydrochloride *rac*-**18**·HCl was prepared by treatment of *rac*-**18** with an ethereal hydrogen chloride solution (yield 79%), thus inactivating the basic amino moiety present in the molecule.

4 Synthesis of disila-bexarotene

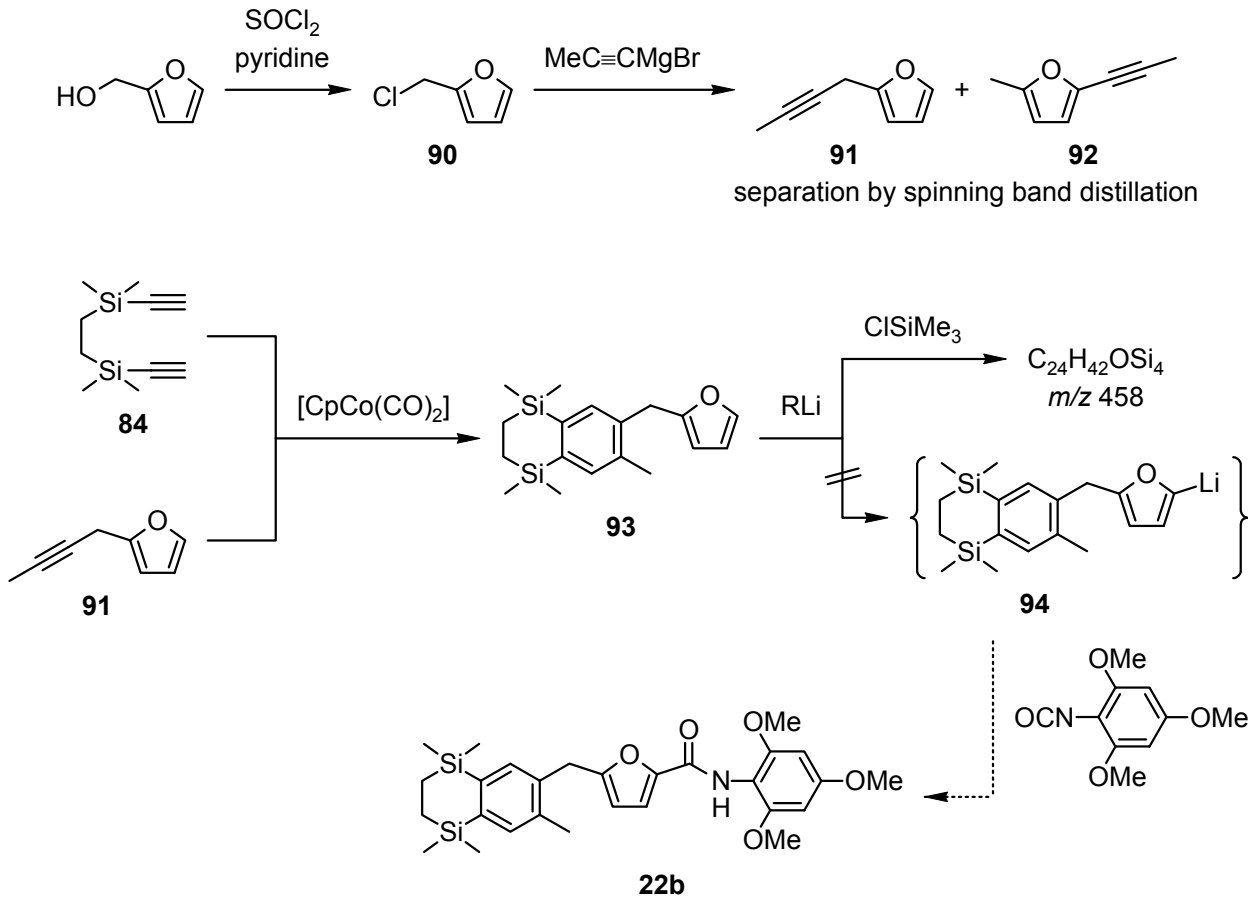
Disila-bexarotene (**21b**) was synthesized in a multistep synthesis, starting from 1,2-bis(chlorodimethylsilyl)ethane (**83**) (Scheme 9). Thus, treatment of **83** with ethynylmagnesium bromide gave 1,2-bis(ethynyldimethylsilyl)ethane (**84**) (yield 80%). Alternatively, sodium acetylide instead of ethynylmagnesium bromide was used for this preparation (yield 71%). Treatment of methyl 4-formylbenzoate (**85**) with 1-propynylmagnesium bromide, followed by reaction with chlorotrimethylsilane, afforded methyl 4-[1-(trimethylsiloxy)but-2-ynyl]benzoate (**86**) (yield 61%). Compounds **84** and **86** were then reacted in a cobalt-catalyzed [$CpCo(CO)_2$] Vollhardt cyclization,[55] followed by treatment with methanol in the presence of acetic acid, to give methyl 4-[hydroxy-(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)methyl]benzoate (**87**) (yield 22%). Oxidation of the alcohol **87** using Swern conditions (oxalyl chloride, dimethyl sulfoxide, triethylamine) afforded the corresponding ketone **88** (yield 87%), which was transformed into the corresponding olefin **89** using a Wittig-type reaction (yield 90%). Treatment of **89** with potassium hydroxide in methanol/water and subsequent acidification with hydrochloric acid finally afforded the title compound **21b** (yield 96%).[48]



Scheme 9. Synthesis of disila-bexarotene (**21b**).

5 Synthesis of disila-AG045572

Two different methods were pursued for the synthesis of disila-AG045572 (**22b**). The first one was planned using a lithiation reaction by deprotonation of a furan moiety as the key step (Scheme 10). Thus, 2-(chloromethyl)furan (**90**) was prepared according to a literature method[56] from 2-furylmethanol by reaction with thionyl chloride in the presence of pyridine. Treatment of **90** with 1-propynylmagnesium bromide yielded a mixture of 2-(but-2-ynyl)furan (**91**) (29% yield) and 5-methyl-2-prop-1-ynylfuran (**92**) (10% yield), which were separated by distillation with a spinning band column. Compounds **84** and **91** were then reacted in a cobalt-catalyzed [$CpCo(CO)_2$] Vollhardt cyclization[55] to give 2-[(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)-methyl]furan (**93**) (41% yield). Compound **93** was then treated with one molar equivalent of various common lithiation reagents (e.g., *n*-BuLi/TMEDA) under various reaction conditions with the aim to lithiate the 5-position of the furan moiety. The reactions were monitored by quenching an aliquot of the reaction mixture with chlorotrimethylsilane and subsequent GC/EI MS analysis, which clearly showed that half of the amount of the starting material had been lithiated and silylated twice ($\rightarrow C_{24}H_{42}OSi_4$, m/z = 458, at least two products, cf. Figure 1; for reaction conditions, see Table 1),



Scheme 10. Attempted synthesis of disila-AG045572 (**22b**) using a deprotonation reaction as the key step.

whereas the second half of **93** had remained unreacted.[57] This result prevented the preparation of {5-[(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)methyl]-2-furyl}lithium (**94**) by this route, which was planned to be reacted with 2-isocyanato-1,3,5-trimethoxybenzene to yield **22b** after aqueous workup.

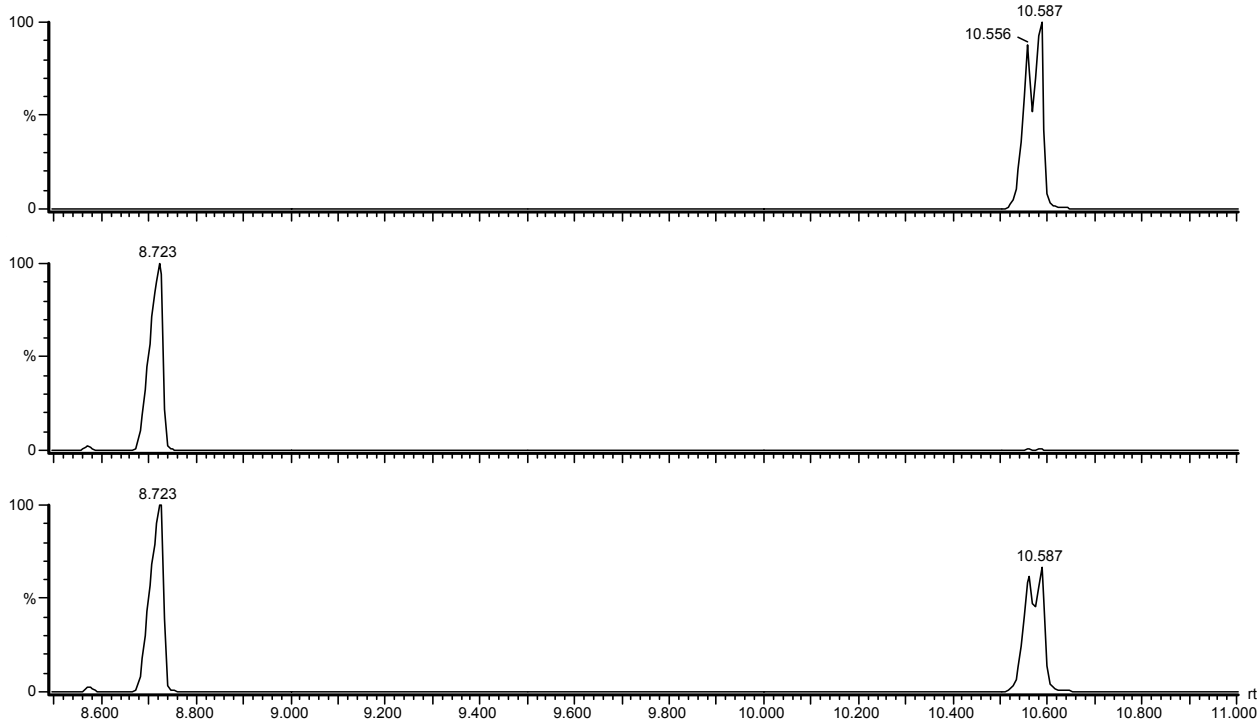
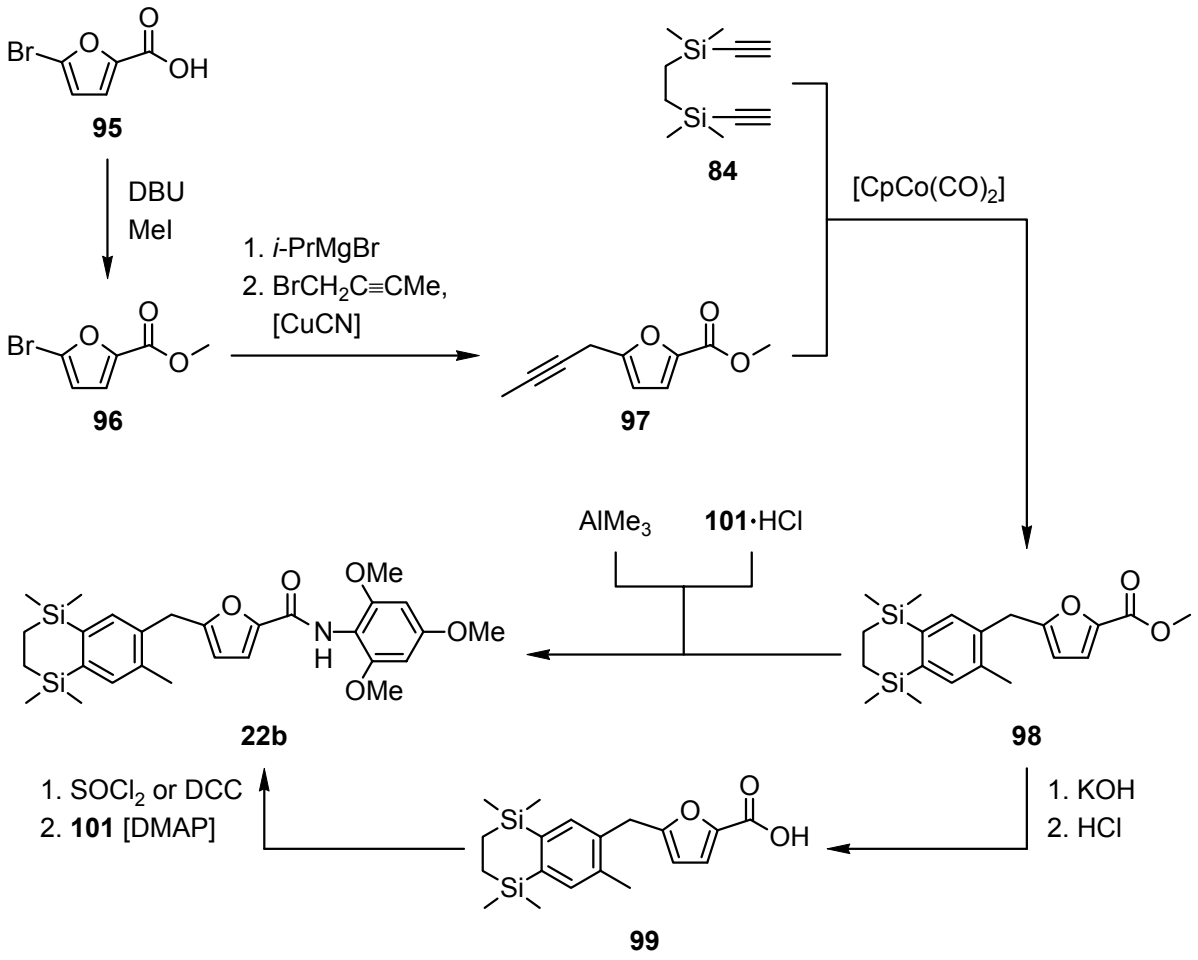


Figure 1. GC/EI MS analysis of a representative lithiation/silylation sequence of compound **93**. Top, trace of m/z = 458 (i.e., products obtained from a twofold lithiation/silylation sequence); middle, trace of m/z = 314 (i.e., starting material); bottom, integration of all positive ions detected ($m/z \geq 50$). The isotope pattern of the peaks with m/z = 458 (top) were in excellent agreement with the formula $C_{24}H_{42}OSi_4$; no ions with $m/z > 458$ were detected except for the isotope peaks within the pattern.

Table 1. Reagents and conditions used for the lithiation of **93** and results obtained from these experiments.

Reagent(s)	Solvent	Temperature	Result
n-BuLi	Et_2O	1. –78 °C; 2. 0 °C	no reaction
s-BuLi	THF	1. –78 °C; 2. 0 °C	twofold lithiation
t-BuLi	THF	1. –78 °C; 2. 0 °C	twofold lithiation
n-BuLi, TMEDA	*n*-hexane	0 °C	twofold lithiation
n-BuLi, TMEDA	*n*-hexane, THF	0 °C	twofold lithiation
n-BuLi, cat. *i*-Pr_2NH	THF	0 °C	twofold lithiation
n-BuLi, TMEDA	*n*-hexane	–78 °C	no reaction
i-Pr_2NLi	THF	1. 0 °C; 2. 20 °C	no reaction

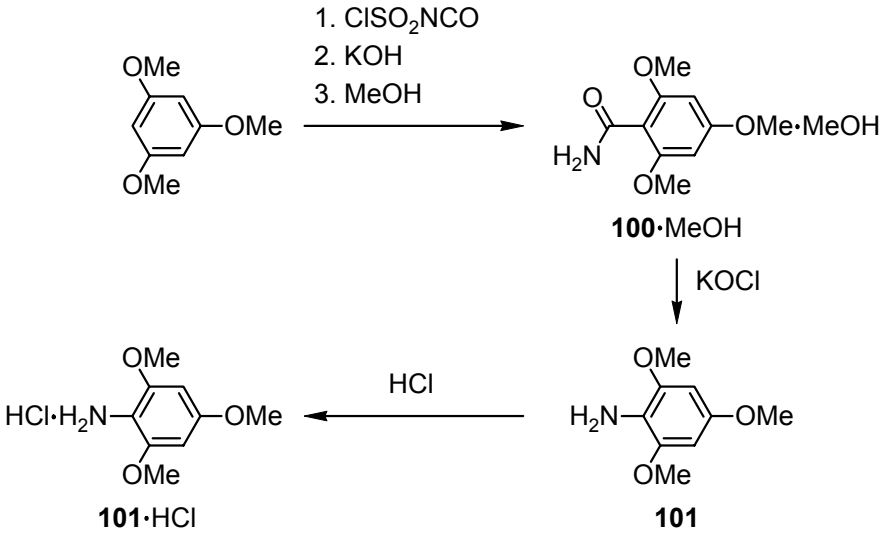
The second approach to synthesize disila-AG-045572 (**22b**) proceeded *via* a halogen/metal exchange.[58] The target compound **22b** was prepared by various methods in multistep syntheses, starting from 1,2-bis(ethynyldimethylsilyl)ethane (**84**) and 5-bromo-2-furoic acid (**95**) (Scheme 11). Reaction of **95** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and iodomethane gave methyl 5-bromo-2-furoate (**96**) (82% yield), which was treated with (i) isopropylmagnesium bromide and (ii) 1-bromobut-2-yne in the presence of copper(I) cyanide to give methyl 5-(but-2-ynyl)-2-furoate (**97**) (62% yield). Compounds **84** and **97** were then reacted in a cobalt-catalyzed ($CpCo(CO)_2$) Vollhardt cyclization[55] to afford methyl 5-[(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)-methyl]-2-furoate (**98**) (39% yield). Reaction of **98** with potassium hydroxide, followed by treatment with hydrochloric acid, gave the corresponding acid **99** (92% yield). Treatment of **99** with thionyl chloride and pyridine, in the presence of 4-(dimethylamino)pyridine (DMAP), and subsequent reaction with 2,4,6-trimethoxyaniline (**101**) gave the target compound 5-[(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)methyl]-*N*-(2,4,6-trimethoxyphenyl)furan-2-carboxamide (disila-AG-045572, **22b**) (22% yield). Treatment of **99** with dicyclohexylcarbodiimide (DCC) and pyridine, in the presence of DMAP, and subsequent reaction with **101** afforded **22b** as



Scheme 11. Preparation of disila-AG-045572 (**22b**) using a halogen/metal exchange as the key step.[58]

well (37% yield). Alternatively, compound **22b** was synthesized by treatment of **98** with a reagent obtained from trimethylaluminum and **101**·HCl (83% yield).

Compounds **101** and **101**·HCl were obtained from 2,4,6-trimethoxybenzamide–methanol (**100**·MeOH) (Scheme 12). Treatment of **100**·MeOH with an aqueous potassium hypochlorite solution gave **101** (38% yield), which upon reaction with hydrogen chloride in diethyl ether afforded **101**·HCl (98% yield).

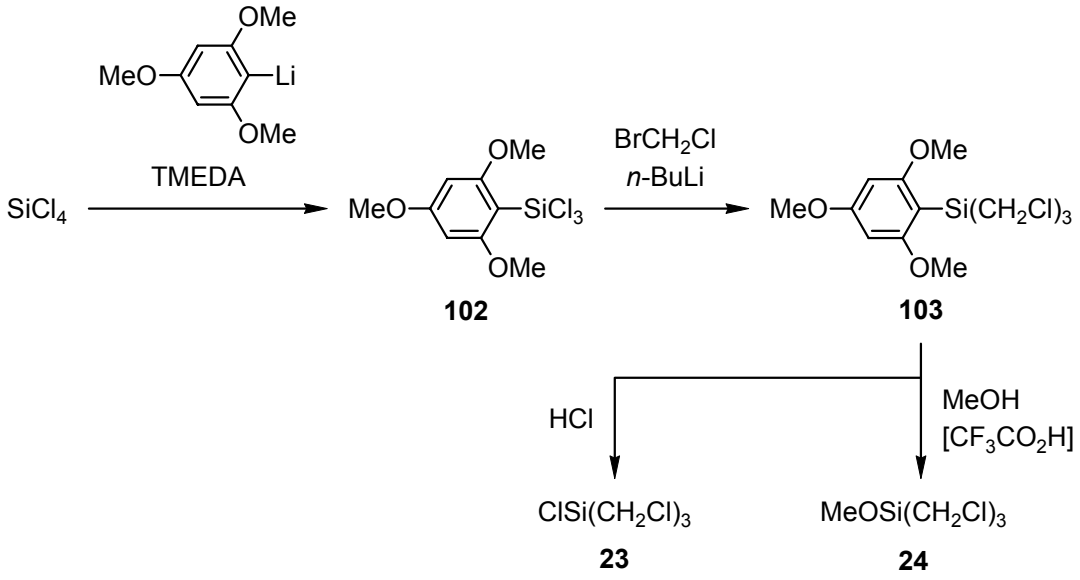


Scheme 12. Preparation of 2,4,6-trimethoxyaniline (**101**) and 2,4,6-trimethoxyanilinium chloride (**101**·HCl).

6 Synthesis of (chloromethyl)silanes

6.1 Synthesis of chlorotris(chloromethyl)silane (23) and tris(chloromethyl)-methoxysilane (24)

The chlorotris(chloromethyl)silane (**23**) and tris(chloromethyl)methoxysilane (**24**) were synthesized according to Scheme 13, starting from tetrachlorosilane. Thus, reaction of $SiCl_4$ with one molar equivalent of (2,4,6-trimethoxyphenyl)lithium yielded trichloro(2,4,6-trimethoxyphenyl)-silane (**102**) (yield 65%), which upon treatment with $BrCH_2Cl$/*n*-BuLi gave tris(chloromethyl)(2,4,6-trimethoxyphenyl)silane (**103**) (yield 39%). Treatment of **103** with an ethereal hydrogen chloride solution finally afforded **23** (yield 65%), whereas methanolysis of **103**, in the presence of trifluoroacetic acid, gave **24** (yield 69%). The substitution of more than one chlorine atom of tetrachlorosilane was observed only in trace amounts (formation of dichlorobis(2,4,6-trimethoxyphenyl)silane (**104**); GC control) during the preparation of **102** when a 1:1 stoichiometry of tetrachlorosilane and (2,4,6-trimethoxyphenyl)lithium was maintained.

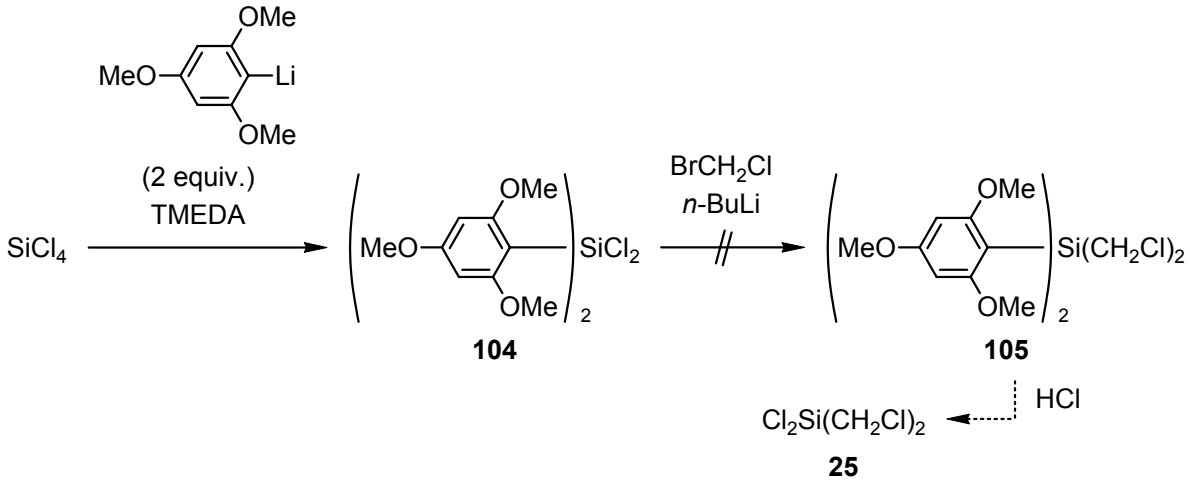


Scheme 13. Synthesis of chlorotris(chloromethyl)silane (**23**) and tris(chloromethyl)methoxysilane (**24**) using the *Si*-2,4,6-trimethoxyphenyl moiety as a protecting group.

6.2 Synthesis of dichlorobis(2,4,6-trimethoxyphenyl)silane (104) and attempted synthesis of dichlorobis(chloromethyl)silane (25) *via* 104

Dichlorobis(2,4,6-trimethoxyphenyl)silane (**104**) was synthesized by reaction of tetrachlorosilane with two molar equivalents of (2,4,6-trimethoxyphenyl)lithium (yield 67%). Treatment of **104** with $BrCH_2Cl$/*n*-BuLi, however, did not yield bis(chloromethyl)bis(2,4,6-trimethoxyphenyl)silane (**105**), which can be explained by the poor solubility of **104** in

tetrahydrofuran (THF) at –70 °C.[59] After the reaction mixture was warmed to 20 °C, GC analysis showed that **104** had remained untouched.

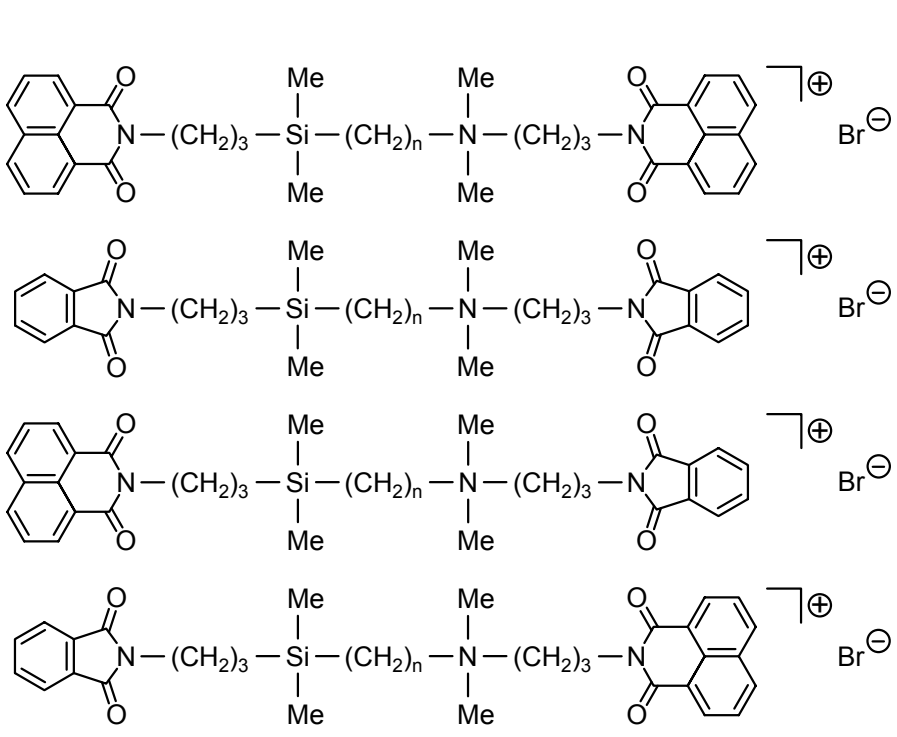


Scheme 14. Synthesis of dichlorobis(2,4,6-trimethoxyphenyl)silane (**104**) and attempted synthesis of dichlorobis(chloromethyl)silane (**25**) *via* **104**.

7 Synthesis of W84-type silicon-based allosteric modulators of muscarinic M_2 receptors

7.1 Synthesis of silicon-based allosteric modulators containing a quaternary ammonium nitrogen atom

The allosteric modulators **10**, **26**–**50**, *rac*-**51**, and *rac*-**52**[60] (Chart 3) were synthesized, starting from chlorodimethylsilane, in multistep syntheses according to Scheme 15. Thus, platinum-catalyzed (H_2PtCl_6) hydrosilylation of the ω-bromo-1-alkenes $H_2C{=}CH(CH_2)_{n-2}Br$ (n = 2–4) with chlorodimethylsilane afforded the (ω-bromoalkyl)chlorodimethylsilanes **106**–**108** (yield 70% (**106**, n = 4), 77% (**107**, n = 5), or 83% (**108**, n = 6)), which upon reaction with lithium aluminum hydride gave the (ω-bromoalkyl)dimethylsilanes **109**–**111** (yield 84% (**109**, n = 4), 87% (**110**, n = 5), or 91% (**111**, n = 6)) (see Chart 4). Subsequent platinum-catalyzed (H_2PtCl_6) hydrosilylation of the *N*-allylimides **112**–**116** (synthesized according to Scheme 16; for yields, see also Scheme 16) with the (ω-bromoalkyl)dimethylsilanes **109**–**111** gave the (ω-bromoalkyl)dimethyl(3-imidopropyl)silanes **117**–**126** and *rac*-**127** (for the yields, see Chart 5), which were then reacted with the (3-imido-propyl)dimethylamines[61] **128**–**131** and *rac*-**132** (synthesized according to Scheme 16; compound *rac*-**132** was synthesized *via* the intermediates *rac*-**133** and *rac*-**134**; for the yields, see also Scheme 16) to afford the allosteric modulators **10**, **26**–**50**, *rac*-**51**, and *rac*-**52** (for the yields, see Chart 3).[60]



n	Cpd. No.	Yield
4	**26**	79%
5	**27**	51%
6	**28**	73%
4	**29**	70%
5	**30**	41%
6	**10**	56%
4	**31**	49%
5	**32**	70%
6	**33**	45%
4	**34**	88%
5	**35**	53%
6	**36**	56%

Chart 3. Structures of the silicon-based W84-type allosteric modulators **10**, **26**–**50**, *rac*-**51**, and *rac*-**52**.[60]

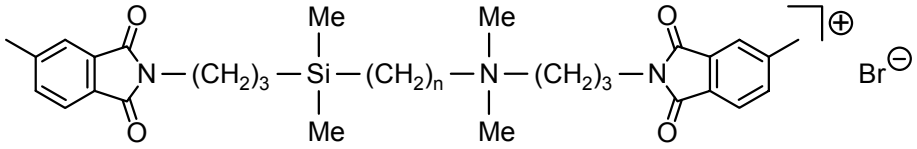
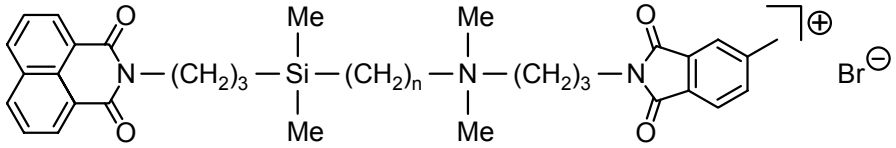
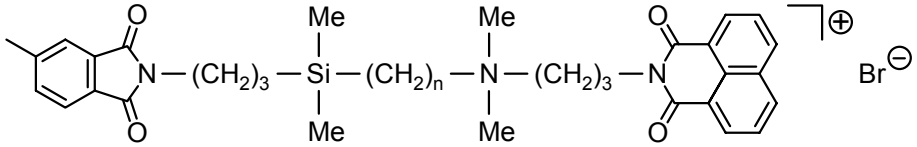
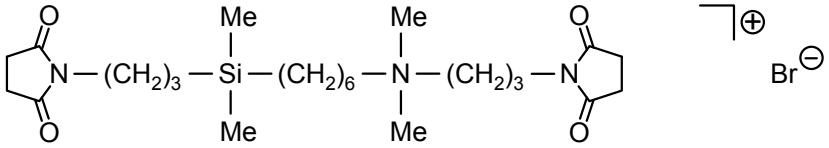
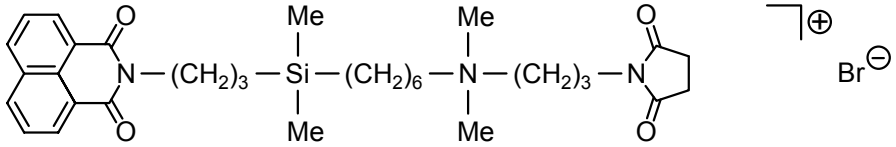
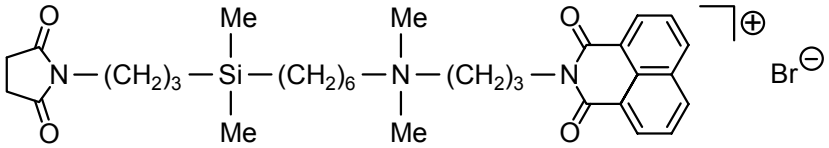
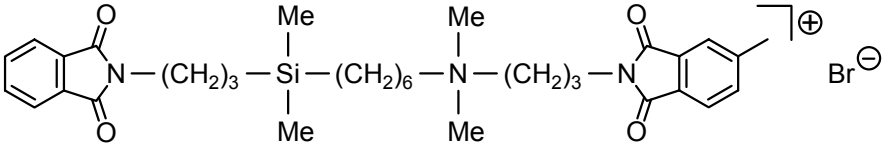
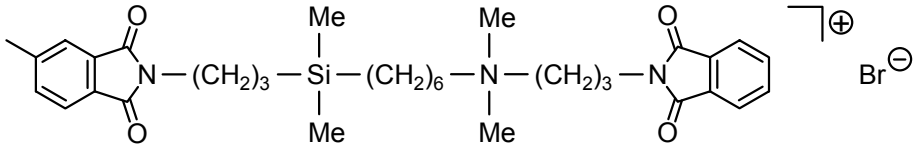
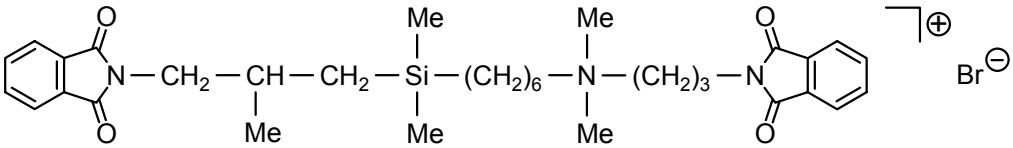
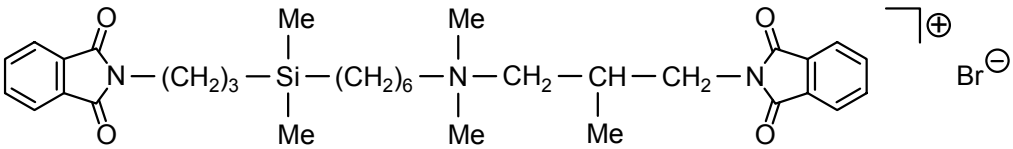
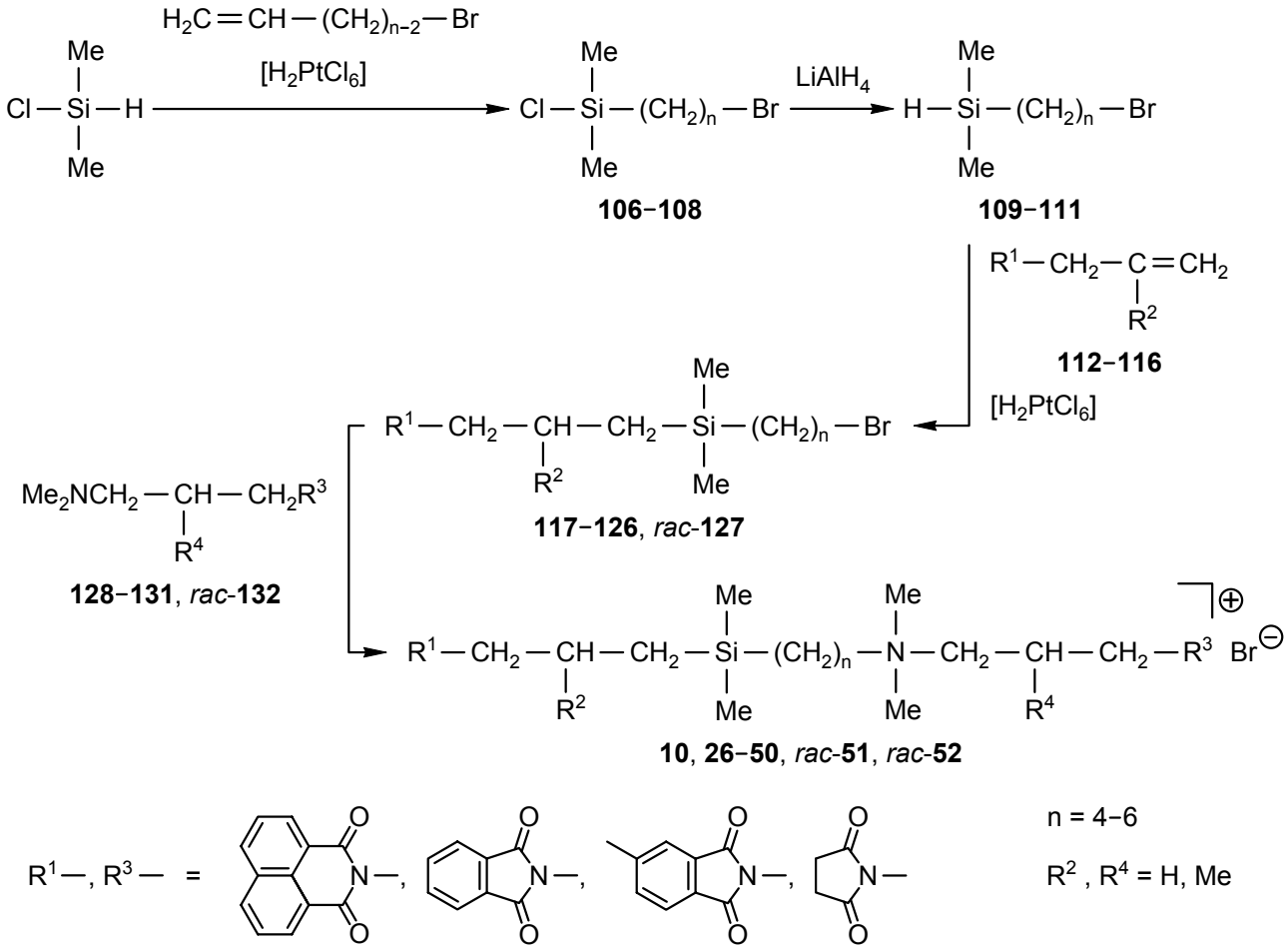
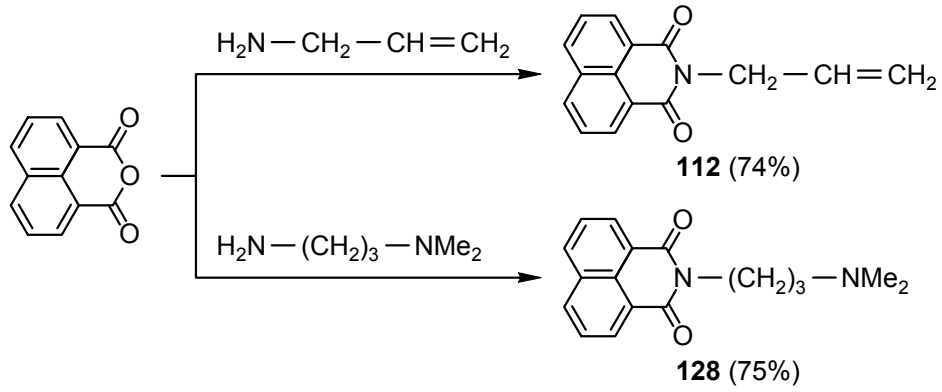
	n	Cpd. No.	Yield
	4	**37**	58%
	5	**38**	58%
	6	**39**	56%
	4	**40**	59%
	5	**41**	84%
	6	**42**	57%
	4	**43**	80%
	5	**44**	71%
	6	**45**	69%
		**46**	62%
		**47**	60%
		**48**	81%
		**49**	57%
		**50**	65%
		*rac*-**51**	44%
		*rac*-**52**	56%

Chart 3 (continued).

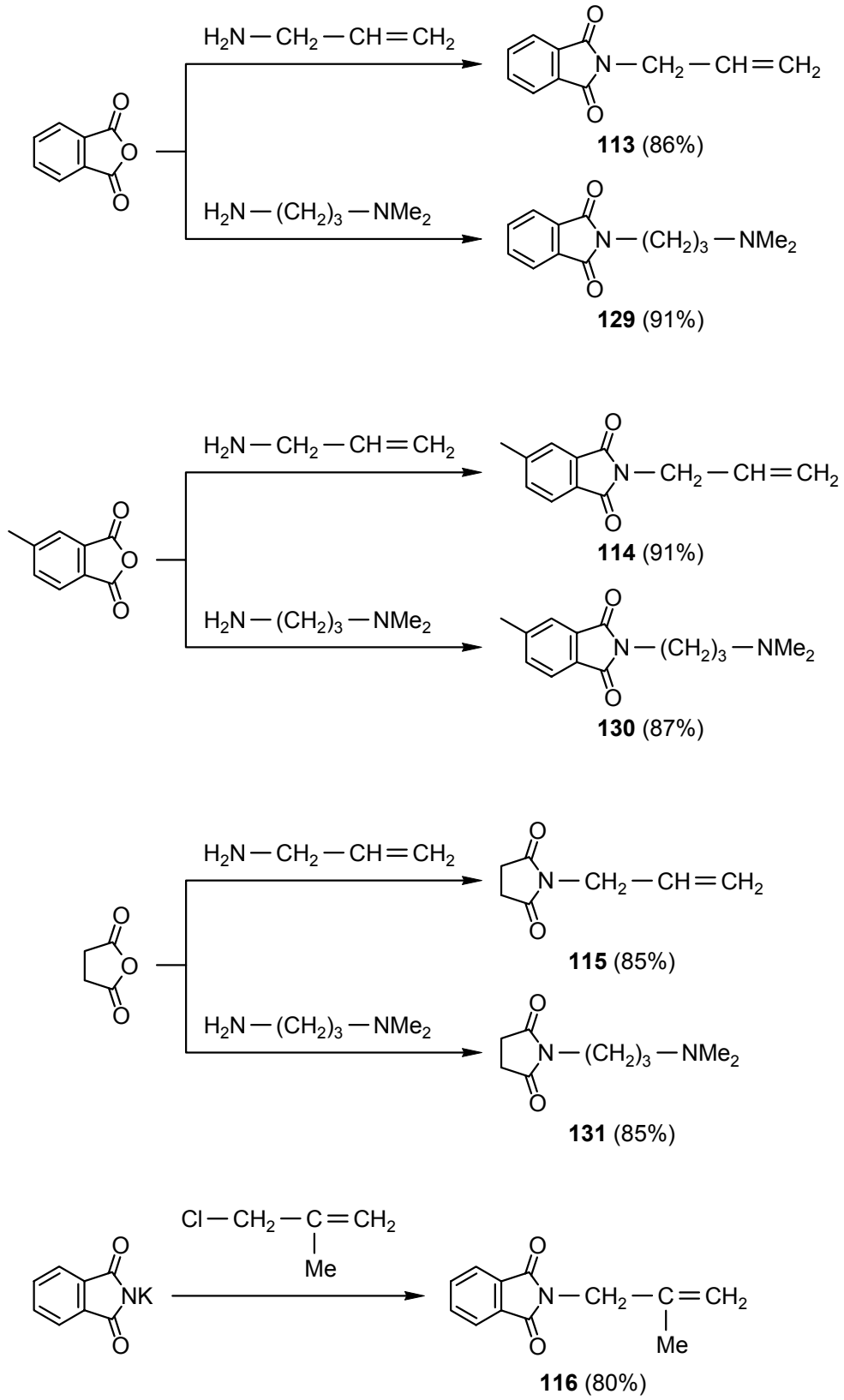


Scheme 15. Synthesis of the allosteric modulators **10**, **26**–**50**, *rac*-**51**, and *rac*-**52** containing a quaternary nitrogen atom. For the combinations of R^1, R^2, R^3, R^4, and n synthesized, see Charts 3 and 5.

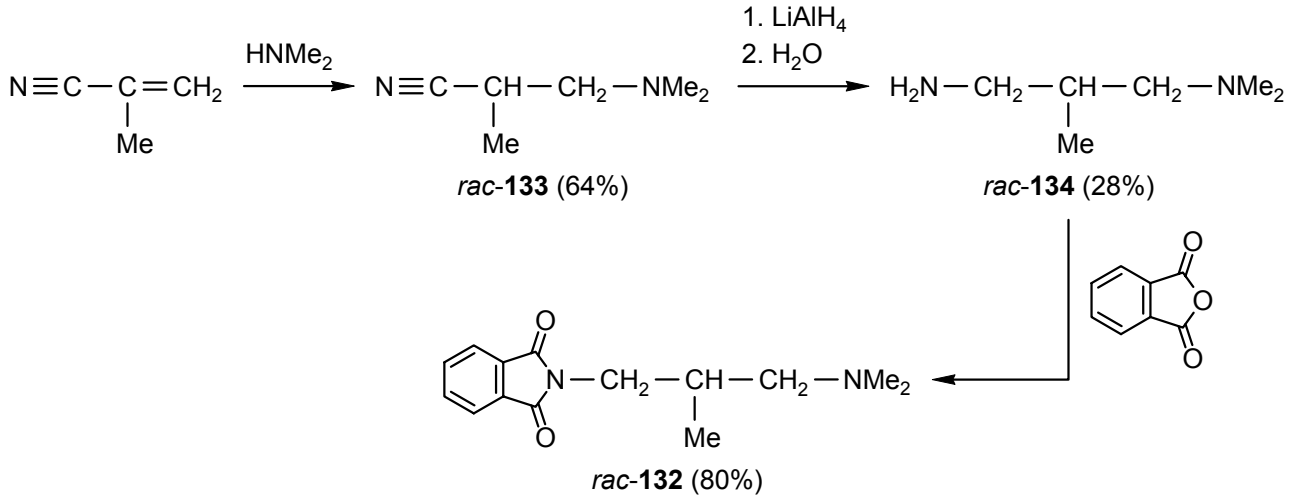
Chart 4. The (ω-bromoalkyl)chlorodimethylsilanes **106**–**108** and the (ω-bromoalkyl)dimethylsilanes **109**–**111**.



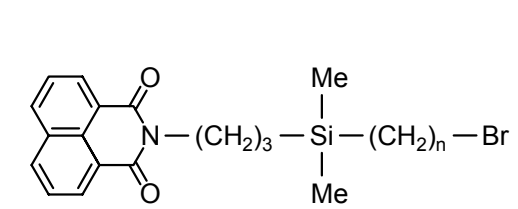
Scheme 16. Synthesis of the *N*-allylimides **112**–**116** and of the (3-imidopropyl)dimethylamines **128**–**131** and *rac*-**132**.



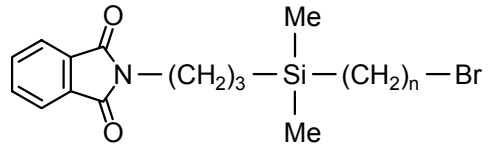
Scheme 16 (continued).



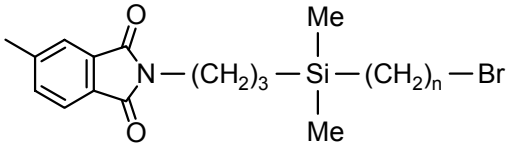
Scheme 16 (continued).



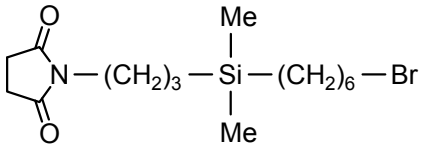
n	cpd. no.	Yield
4	**117**	84%
5	**118**	71%
6	**119**	81%



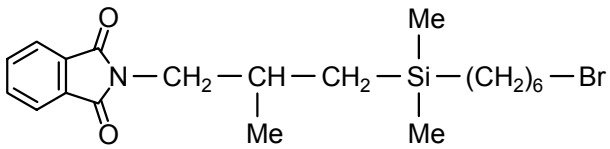
n	cpd. no.	Yield
4	**120**	57%
5	**121**	76%
6	**122**	86%



n	cpd. no.	Yield
4	**123**	76%
5	**124**	79%
6	**125**	67%



	126	82%



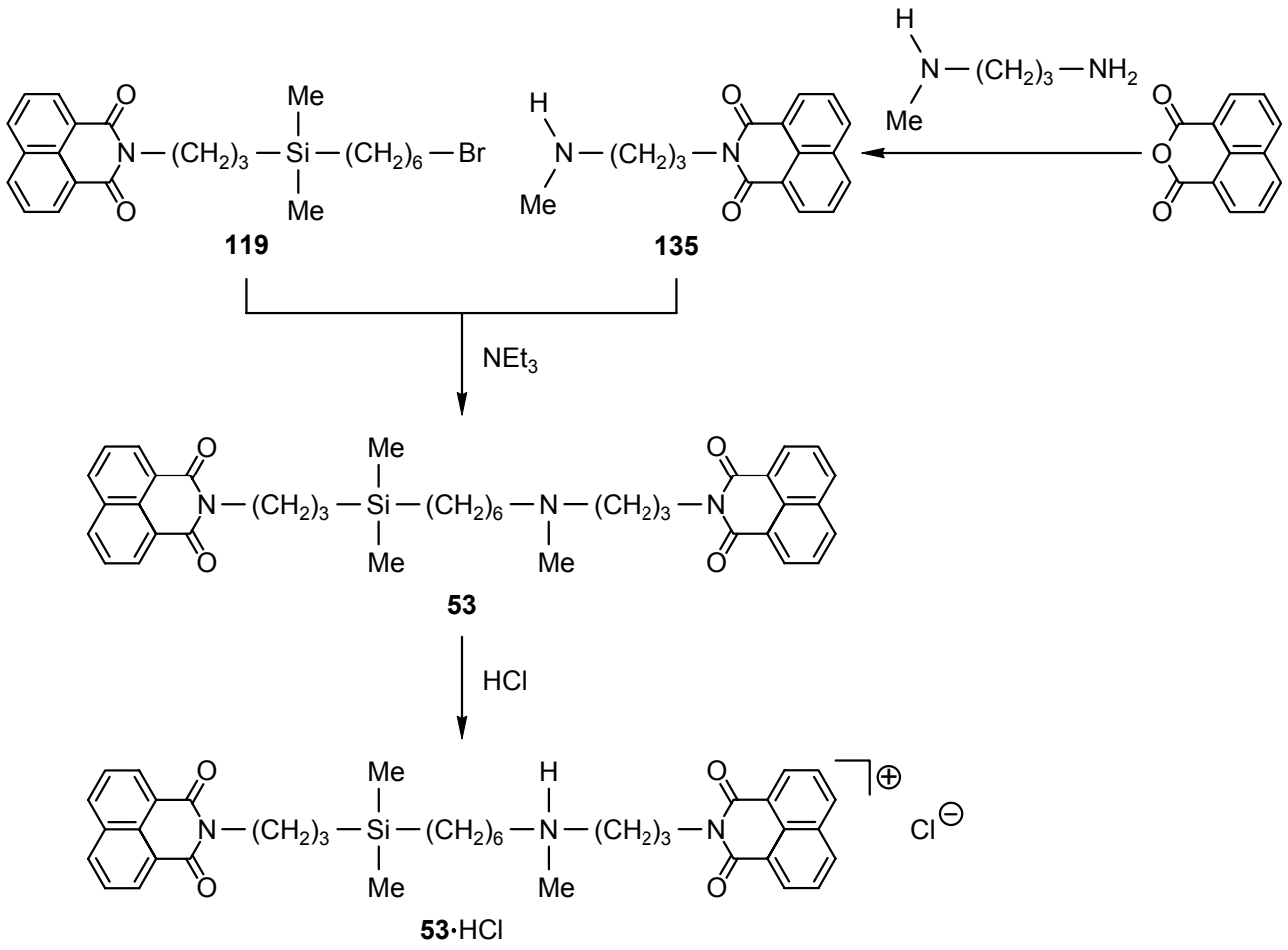
	rac-**127**	58%

Chart 5. The (ω-bromoalkyl)dimethyl(3-imidopropyl)silanes **117**–**126** and *rac*-**127**.

7.2 Synthesis of a silicon-based allosteric modulator containing a tertiary nitrogen atom

(6-Bromohexyl)dimethyl[3-(1,8-naphthalimido)propyl]silane (**119**) was reacted with methyl[3-(1,8-naphthalimido)propyl]amine (**135**) in the presence of excess triethylamine to afford **53**.[62] Treatment of **53** with an ethereal hydrogen chloride solution gave the corresponding hydrochloride **53**·HCl (yield 56%, related to **119**).

Compound **135** was synthesized by reaction of 1,8-naphthalic acid anhydride with *N*-methylpropane-1,3-diamine in refluxing glacial acetic acid (yield 70%).

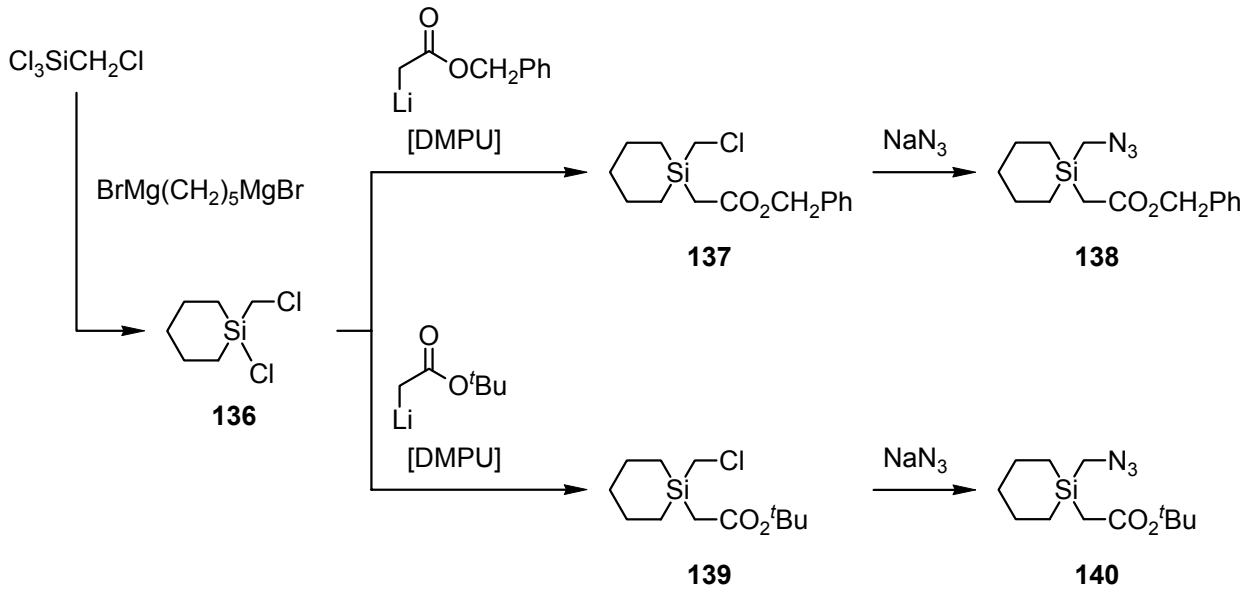


Scheme 17. Synthesis of an allosteric modulator containing a tertiary nitrogen atom.

8 Synthesis of β-carbonylsilanes: partial synthesis of sila-gabapentin

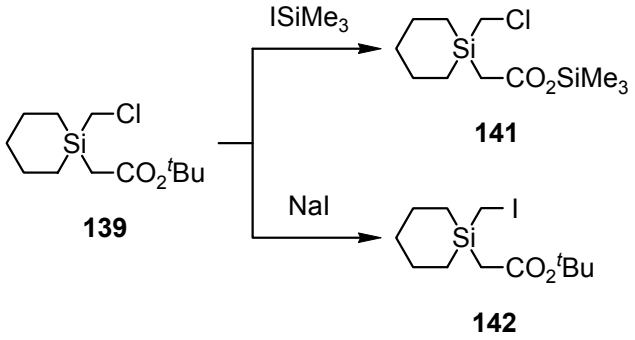
As discussed in Section 2.6 (p. 10), the weakness of the Si–$CH_2C(O)R$ bond is an intrinsic obstacle when tranformations of *C*-functionalized organyl groups at the silicon atom are intended. The synthesis of sila-gabapentin (**54b**) was not achieved within this work, and this can be ascribed to that problem. Nevertheless, novel methods have been developed and known methods have been optimized and applied for (i) the synthesis of β-carbonylsilanes, with a silacyclohexane skeleton and an additional *C*-functionalized organyl group at the silicon atom, and for (ii) reactions of these compounds involving functional group transformations within the *C*-functionalized group without cleavage of the Si–$CH_2C(O)R$ bond. The resulting preparative methods and data are documented below and in the Experimental Section.

The β-carbonylsilanes benzyl 2-[1-(chloromethyl)-1-sila-1-cyclohexyl]acetate (**137**) and *tert*-butyl 2-[1-(chloromethyl)-1-sila-1-cyclohexyl]acetate (**139**) were synthesized according to Scheme 18 by reaction of 1-chloro-1-(chloromethyl)-1-silacyclohexane (**136**) (prepared from trichloro(chloromethyl)silane in 52% yield by reaction with 1,5-bis(bromomagnesio)pentane[63,64]) with the lithium reagents $LiCH_2CO_2CH_2Ph$ (→ **137**, yield 43%) or $LiCH_2CO_2{}^tBu$ (→ **139**, yield 79%) in the presence of 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU). Treatment of **137** and **139** with sodium azide gave benzyl 2-[1-(azidomethyl)-1-sila-1-cyclohexyl]acetate (**138**, yield 86%)[65] and *tert*-butyl 2-[1-(azidomethyl)-1-sila-1-cyclohexyl]acetate (**140**, yield 89%), respectively (Scheme 18).



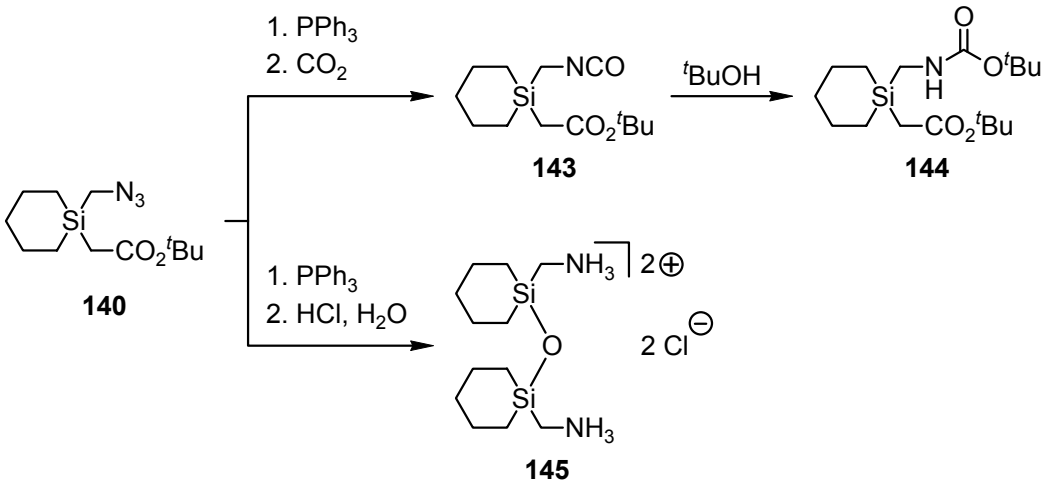
Scheme 18. Synthesis of the β-carbonylsilanes **137**–**140**.

Further transformations of **139** (see Scheme 19) include (i) the displacement of the *tert*-butyl group by a trimethylsilyl moiety by reaction with iodotrimethylsilane to give trimethylsilyl 2-[1-(chloromethyl)-1-sila-1-cyclohexyl]acetate (**141**, yield 85%) and (ii) a chlorine/iodine exchange by reaction with sodium iodide to give *tert*-butyl 2-[1-(iodomethyl)-1-sila-1-cyclohexyl]acetate (**142**, yield 88%).



Scheme 19. Synthesis of the β-carbonylsilanes **141** and **142**.

Reaction of **140** with triphenylphosphine, followed by treatment with carbon dioxide, gave *tert*-butyl 2-[1-(isocyanatomethyl)-1-sila-1-cyclohexyl]acetate (**143**, yield 34%), which upon reaction with *tert*-butanol afforded *tert*-butyl 2-{1-[((*tert*-butoxycarbonyl)amino)methyl]-1-sila-1-cyclohexyl}acetate (**144**, yield 44%) (Scheme 20). In addition, compound **140** was reacted with triphenylphosphine according to Scheme 20, followed by treatment with hydrochloric acid, to give 1,1′-oxybis{[(1-sila-1-cyclohexyl)methyl]ammonium} dichloride (**145**, yield 38%). Thus, the attempted transformation of the $SiCH_2N_3$ group into the $SiCH_2NH_2$ moiety and the transformation of the $SiCH_2CO_2{}^tBu$ group into the $SiCH_2COOH$ moiety in a one-pot synthesis (→ formation of **54b**) resulted in an Si–C bond cleavage.



Scheme 20. Synthesis of the β-carbonylsilanes **143** and **144** and of the disiloxane **145**.

9 Biological studies

9.1 Sila-venlafaxine and derivatives

Compounds *rac*-**12a**, *rac*-**12b**, *rac*-**13**, and *rac*-**15** were studied for their *in vitro* efficacy regarding serotonin, noradrenaline, and dopamine reuptake inhibition using the corresponding hydrochlorides. The monoamine reuptake inhibition profiles of *rac*-**12a**, *rac*-**12b**, *rac*-**13**, and *rac*-**15** were generated *via* radioligand transporter assays using recombinant human monoamine transporter proteins. The data represent the mean of duplicate analyses. The studies were performed by Amedis Pharmaceuticals Ltd., Cambridge.

As can be seen from Figure 2, sila-substitution of *rac*-**12a** (→ *rac*-**12b**) substantially affects the pharmacological profile with respect to serotonin reuptake inhibition. The other (major) structural changes in the molecular shape of *rac*-**12b** (→ *rac*-**13**, *rac*-**15**) also influenced the pharmacological profile with respect to monoamine selectivity (*rac*-**13**) and/or absolute potency (*rac*-**15**). These results clearly demonstrate that the carbon/silicon switch strategy is a powerful tool for drug design.

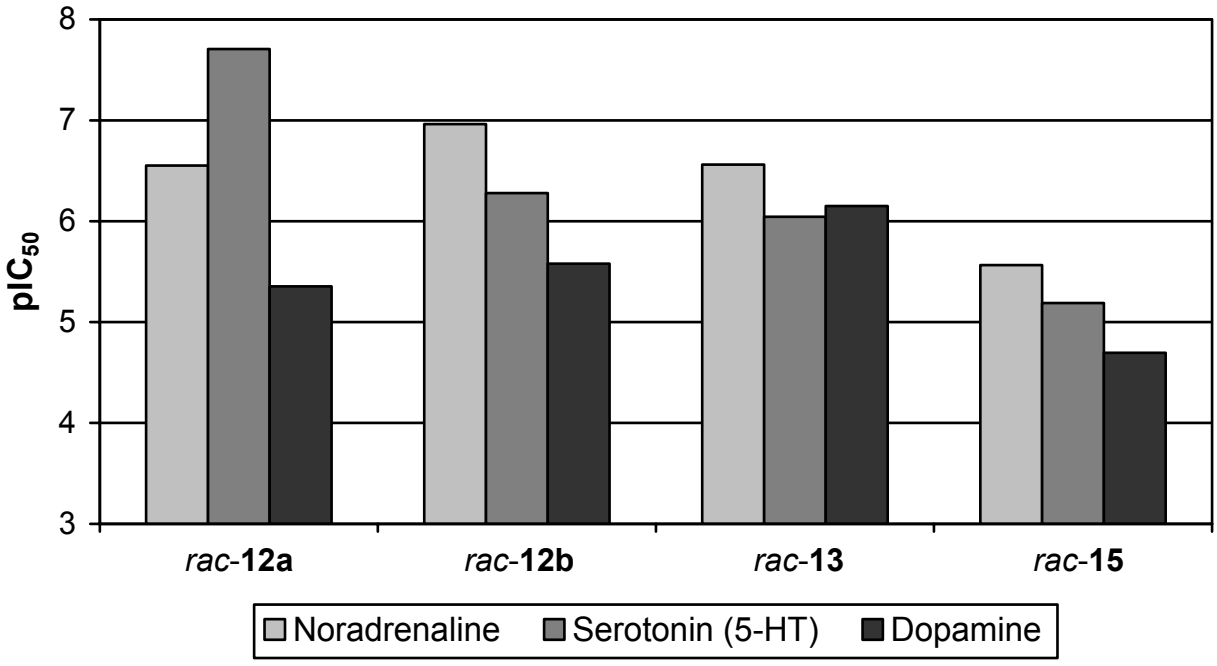


Figure 2. *In vitro* efficacy of compounds *rac*-**12a**, *rac*-**12b**, *rac*-**13**, and *rac*-**15** regarding serotonin, noradrenaline, and dopamine reuptake inhibition (preliminary data). pIC_{50} denotes the negative decadic logarithm of the half-maximum effect concentration [M]; cf. Table 44 (Appendix B, p. 184).

9.2 Silicon-based allosteric modulators of muscarinic receptors

The allosteric effects of the test compounds **10**, **11**, **27**–**30**, **32**, **33**, **35**, **36**, **39**, **42**, **45**–**50**, *rac*-**51**, *rac*-**52**, and **53** (tested as the hydrochloride **53**·HCl) on [^{3}H]NMS dissociation and [^{3}H]NMS equilibrium binding were tested at muscarinic M_2 receptors of porcine heart homogenates.[66] The data were measured by Dr. Seraina Duda-Johner and Marc Albrecht, Universität Bonn.

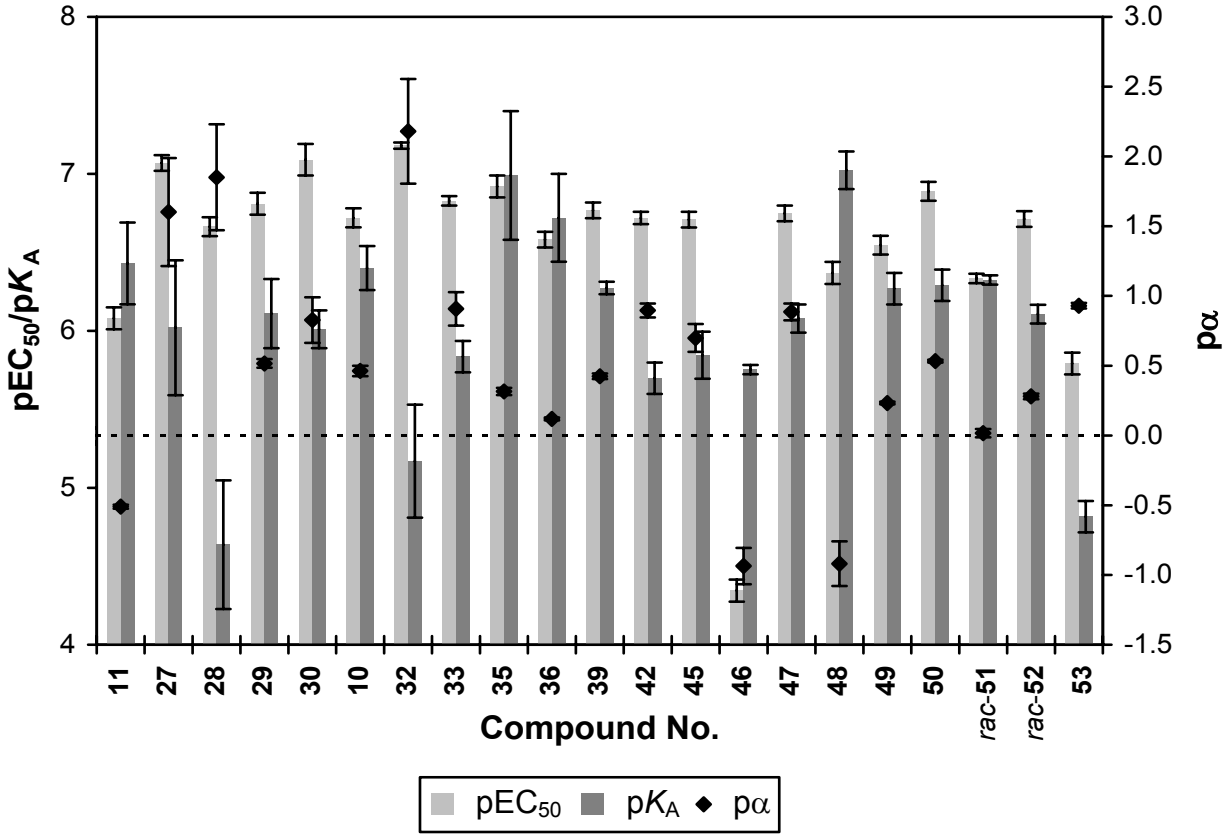


Figure 3. $pEC_{50,diss}$, pK_A, and pα values obtained from the interaction studies of the respective allosteric modulators **10**, **11**, **27**–**30**, **32**, **33**, **35**, **36**, **39**, **42**, **45**–**50**, *rac*-**51**, *rac*-**52**, and **53** (tested as the hydrochloride **53**·HCl) with [^{3}H]NMS at muscarinic M_2 receptors of porcine heart homogenates. For further data, see Table 45 (Appendix B, p. 184). The order of the compounds reflects the order in Chart 3, and the data for W84 (**11**) was included for comparison.

The apparent rate constant k_{-1} of [^{3}H]NMS dissociation was reduced concentration-dependently by the test compounds. The inflection points of the resulting concentration-effect curves ($EC_{50,diss}$ value) is a measure of the allosteric potency of the respective test compounds (for concentration-effect curves, see refs. 13 and 43). $EC_{50,diss}$ corresponds to a 50% occupancy of the [^{3}H]NMS-occupied receptor by the test compound and denotes the dissociation constant of allosteric agent binding to a ligand-occupied receptor; thus, the $pEC_{50,diss}$ values are a measure for the binding affinity of the allosteric test compounds to [^{3}H]NMS-occupied receptors.[41m] The Hill coefficient n_H, characterizing the slope of the concentration-effect curves, was significantly different from –1 for compounds **27**, **28**, **32**, **33**, and *rac*-**51**. This may point to a different way of

interaction of these silicon compounds with muscarinic acetylcholine receptors compared to the modulators of the W84-diaminium type ("**11**-type").

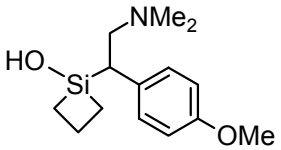
Equilibrium binding experiments provide the factor of cooperativity (α) between the respective modulator and [^{3}H]NMS and the binding constant pK_A for allosteric modulator binding to ligand-free receptors. pα > 0 indicates a positive cooperativity (i.e., enhancement of [^{3}H]NMS equilibrium binding) and *vice versa*. The allosteric modulator W84 (**11**) reduced [^{3}H]NMS equilibrium binding, indicating a negative cooperativity (pα = –0.51). This result is in agreement with data published previously.[411] In contrast, most of the silicon-based allosteric modulators increased [^{3}H]NMS equilibrium binding, which reflects positive cooperativity. Thus, the SAR studies based on the availability of the broad range of structural variations of the silicon-based allosteric modulators synthesized within this work clearly demonstrate that a positive cooperativity is a very common characteristic of the allosteric action of the silicon-based allosteric modulators. This positive cooperativity is found to be most pronounced for compounds **27**, **28**, and **32**, all of which bear 1,8-naphthalimido moieties. This high positive cooperativity can (in the case of **28** and **32**) be ascribed to the low affinity of these compounds for ligand-free receptors (low pK_A value), whereas the only negative cooperativities were found for **46** and **48**, both bearing succinimido moieties.

The development of allosteric modulators which increase binding of the endogenous ligand acetylcholine is a primary aim, hence, the different mode of action of the silicon-based allosteric modulators with [^{3}H]NMS at muscarinic M_2 receptors (frequent pattern: positive cooperativity) compared to modulators of the W84-diaminium type (frequent pattern: negative cooperativity) points to a novel lead structure, in which one of the positive ammonium centers of W84 is replaced by a hydrophobic electrostatically neutral group. This novel lead structure of the "**11**-type" may exhibit the desired mode of interaction (positive cooperativity) with acetylcholine at certain muscarinic receptor subtypes.[67]

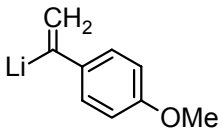
10 The performance of the *Si*-2,4,6-trimethoxyphenyl moiety as a novel protecting group in organosilicon chemistry

10.1 Discussion

The selectivity problems which were encountered in context with the work on the synthesis of the sila-venlafaxine derivative *rac*-**14** in the reactions of **70**–**72** with **58** (twofold substitution of the alkoxy groups by organic moieties to give **73**) lead to the development of the *Si*-2,4,6-trimethoxyphenyl (*Si*-2,4,6-TMOP) moiety as a novel protecting group in organosilicon chemistry, which in turn was used for developing an alternative synthesis of *rac*-sila-venlafaxine (*rac*-**12b**), chlorotris(chloromethyl)silane (**23**), and tris(chloromethyl)methoxysilane (**24**).



rac-**14**



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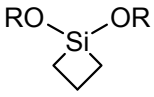
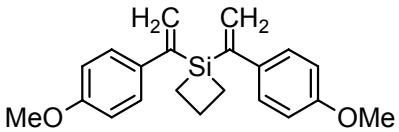
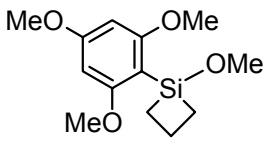


R = Me: **70**
R = ^{i}Pr: **71**
R = ^{t}Bu: **72**



73

The use of the *Si*-2,4,6-TMOP moiety as a protecing group in silacyclobutane chemistry is of special interest: (i) (2,4,6-Trimethoxyphenyl)lithium reacts selectively (monosubstitution) with 1,1-dichloro-1-silacyclobutane to give **74** after treatment with methanol. (ii) The presence of the bulky *Si*-2,4,6-TMOP group does not render the *Si*-methoxy group in compound **74** unreactive, thus allowing the transformation **74** → **75**. (iii) Most importantly, the *Si*-2,4,6-TMOP group can be cleaved selectively with hydrogen chloride from the silacyclobutane ring (transformation **75** → **76**) without any other Si–C bond cleavage. This is especially remarkable as numerous Si–C bond cleavage reactions with hydrogen chloride, leading to ring opening of the silacyclobutane backbone, have been reported in the literature.[68]



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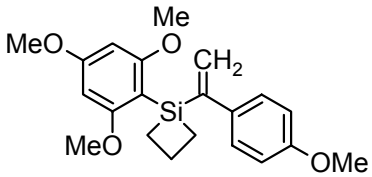

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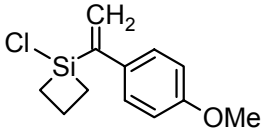
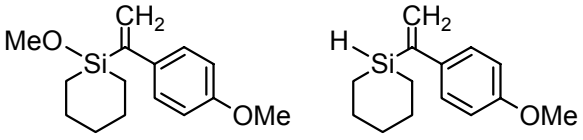


76

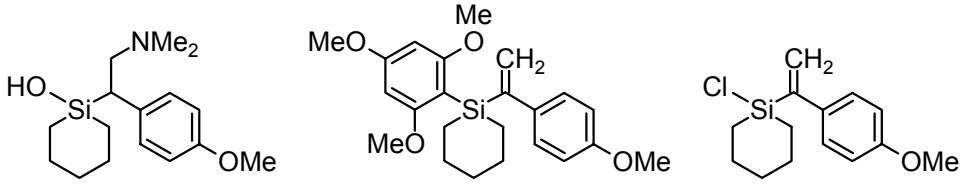
In context with the synthesis of *rac*-sila-venlafaxine (*rac*-**12b**), the synthetic route using the *Si*-2,4,6-TMOP group as shown in Scheme 2 (p. 13, Section 3.1.2) has several advantages over the "conventional" way as shown in Scheme 1 (p. 11, Section 3.1.1), since (i) it can be carried out in

three steps instead of four (starting from 1,1-dichloro-1-silacyclohexane), (ii) it avoids the use of toxic and volatile iodomethane, which was used for the workup of **59**, and (iii) it avoids the preparation of a dangerous intermediate, such as the hydridosilane **60**.



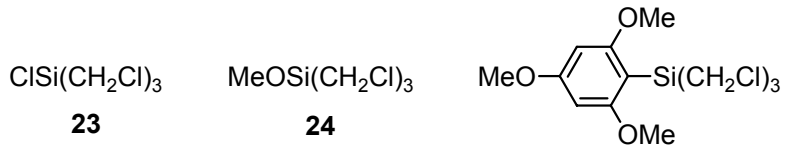
59 **60**

The reaction conditions which were used to remove the *Si*-2,4,6-TMOP group (reaction **62** → **63**) were remarkably mild (room temperature, only a tiny excess of HCl) to give an Si–Cl group, the only detectable by-product being 1,3,5-trimethoxybenzene. Since the 1,3,5-trimethoxybenzene formed is inert to many reagents, further transformations of the resulting chlorosilane are possible without isolation of the intermediate chlorosilane, which was demonstrated by the direct transformation **62** → *rac*-**12b** (no isolation of **63**). In addition, the by-product 1,3,5-trimethoxybenzene could be removed very easily from *rac*-**12b** by washing an aqueous solution of *rac*-**12b** with diethyl ether at an acidic pH value.



rac-**12b** **62** **63**

As stated above, the *Si*-2,4,6-TMOP group was also applied to the synthesis of chlorotris(chloromethyl)silane (**23**) and tris(chloromethyl)methoxysilane (**24**) *via* **103**.

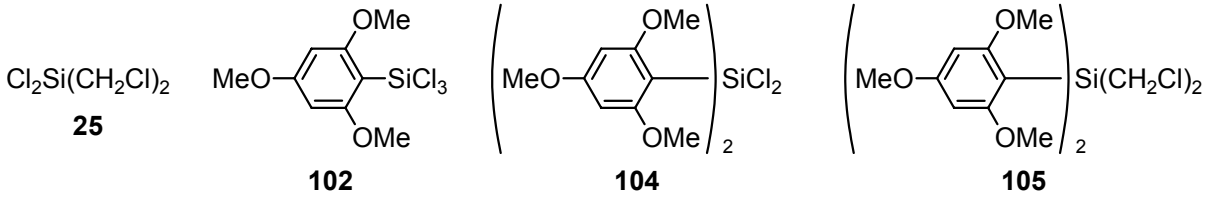


23 **24** **103**

In these syntheses, the reaction conditions used to remove the *Si*-2,4,6-trimethoxyphenyl group again were remarkably mild (room temperature, HCl or MeOH/[$CF_3C(O)OH$]) to give Si–Cl or Si–OMe groups, the only detectable by-product being 1,3,5-trimethoxybenzene (same as in the synthesis of *rac*-**12b** *via* **62**). The workup of **23** and **24** included twofold distillation (separation from the 1,3,5-trimethoxybenzene formed), and some product was lost during the distillation process to impure side fractions. This points at minor limitations of the *Si*-2,4,6-trimethoxyphenyl protecting group whenever isolation of a chloro- or methoxysilane is desired after cleavage of the Si–2,4,6-TMOP bond in case the respective chloro- or methoxysilane has a boiling point close to

that of 1,3,5-trimethoxybenzene; however, the direct further transformation of the resulting chloro- or methoxysilane without isolation is an easy, fast, and effective way to circumvent this problem. This was demonstrated exemplarily by the transformation **62** → *rac*-**12b** in the sila-venlafaxine synthesis (see above).

In an attempt to prepare dichlorobis(chloromethyl)silane (**25**) using the *Si*-2,4,6-TMOP group, dichlorobis(2,4,6-trimethoxyphenyl)silane (**104**) was prepared. However, the further transfomation using $BrCH_2Cl$/*n*-Buli to give the intermediate **105** failed, which prevented the synthesis of **25** by this route.



Nevertheless, the preparation of **104** from tetrachlorosilane gave insight into the selectivity of the reaction of tetrachlorosilane with two molar equivalents of (2,4,6-trimethoxyphenyl)lithium. The reaction $SiCl_4$ → **104** was shown to be highly selective by GC analysis. Apart from trace amounts of the monosubstitution product **102**, compound **104** was the only detectable product. Since side reactions involving substitution of three or four chlorine atoms of the starting material tetrachlorosilane would lead to a unproportional high consumption of (2,4,6-trimethoxyphenyl)lithium, and, hence, to the formation of significant amounts of **102** (which then would not find (2,4,6-trimethoxyphenyl)lithium to react with), the experimentally established presence of only trace amounts of **102** unequivocally proves that this reaction is highly selective, even though the products of threefold or tetrafold substitution reactions (i.e., chlorotris(2,4,6-trimethoxyphenyl)silane and tetrakis(2,4,6-trimethoxyphenyl)silane) are unlikely to pass the GC column and, therefore, cannot be expected to be detectable by this method.[69] On the other hand, when tetrachlorosilane was reacted with one molar equivalent of (2,4,6-trimethoxyphenyl)lithium, compound **102** was the main product, and **104** was detected only in traces (GC). Hence, the selectivities found for the reactions of tetrachlorosilane with one or two molar equivalents of (2,4,6-trimethoxyphenyl)lithium demonstrate the high performance of the *Si*-2,4,6-TMOP chemistry.

10.2 Conclusions

The *Si*-2,4,6-TMOP moiety was demonstrated to be an effective protecting group for synthetic organosilicon chemistry. It fulfils all the major requirements that have been claimed to be necessary for a good protecting group:[70] (i) The reagents for its introduction and cleavage are

commercially available; (ii) its introduction is easy and effective and does not lead to additional stereogenic centers; (iii) it is easy to characterize (^{1}H and ^{13}C NMR spectroscopy); (iv) it is stable to a wide range of workup and reaction conditions including chromatography on silica gel; (v) it can be removed efficiently and selectively; and (vi) the by-product of the deprotection (1,3,5-trimethoxybenzene) can be separated easily from the substrate.

In addition to the above-mentioned profile, (vii) (2,4,6-trimethoxyphenyl)silanes exhibit a high tendency for crystallization, making their isolation, purification, and characterization (crystal structure analysis) very easy, and (viii) they have low UV detection limits.

The Si–C cleavage of the *Si*-2,4,6-TMOP moiety has been demonstrated to occur with hydrogen chloride in diethyl ether at 0 °C, without use of any catalyst (such as $AlCl_3$), to yield a chlorosilane. The *Si*-allyl group and other *Si*-aryl moieties have also been reported to be removable by Si–C cleavage; however, these cleavage reactions have been accomplished with triflic acid[8,71] or trifluoroacetic acid[72].Thus, the easily and selectively removable *Si*-2,4,6-TMOP group complements the toolbox of protecting groups in organosilicon chemistry that can be removed by acid-induced Si–C cleavage.

11 Results of the single-crystal X-ray diffraction studies

Compounds *rac*-**12b**·HCl, (*R*)-**12b**·HBr, *rac*-**13**, *rac*-**15**, *rac*-**15**·HCl, **21a**, **21b**, **22b**, **61**, **62**, **74**, **75**, **89**, **99**, **103**, **104**, **145**·2H_2O, and **146** were structurally characterized by single-crystal X-ray diffraction.[73] The crystal data and experimental parameters used for these studies are given in Appendix A. The structures were solved by direct methods.[74] All non-hydrogen atoms were refined anisotropically.[75] The N*H*, CO*H*, and HO*H* hydrogen atoms were localized in difference Fourier syntheses and refined freely. A riding model was employed in the refinement of the C*H* and SiO*H* hydrogen atoms. All bond lengths and angles which are not discussed explicitly in the following sections are in the expected range and therefore do not need further discussion.

11.1 *rac*-Sila-venlafaxine hydrochloride (*rac*-12b·HCl)

Suitable single crystals of *rac*-**12b**·HCl were obtained by cooling of a boiling saturated solution of *rac*-**12b**·HCl in dichloromethane to 4 °C. Compound *rac*-**12b**·HCl crystallizes in the space group $Pca2_1$. As would be expected, the silacyclohexane skeleton in *rac*-**12b**·HCl adopts a chair conformation (Figure 4). The structure is characterized by a relatively long Si–C6 distance (1.9041(14) Å), the reason for this elongation being unclear. Similar structural features are observed

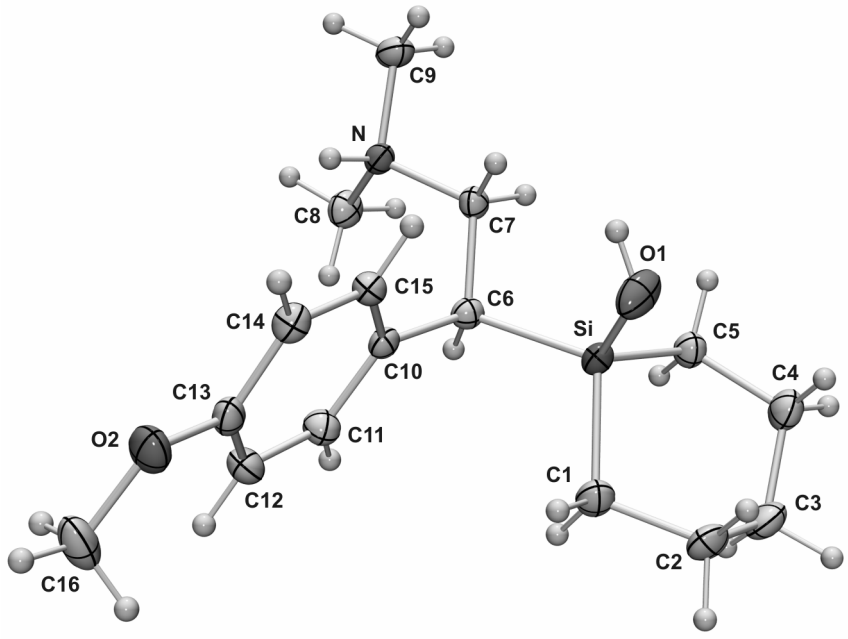


Figure 4. Structure of the cation of *rac*-**12b**·HCl in the crystal (only one enantiomer depicted; probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg): Si–O1 1.6286(12), Si–C1 1.8549(14), Si–C5 1.8610(14), Si–C6 1.9041(14), C1–C2 1.539(2), C2–C3 1.529(2), C3–C4 1.526(2), C4–C5 1.5386(19), O1–Si–C1 106.38(7), O1–Si–C5 110.98(7), O1–Si–C6 111.08(6), C1–Si–C5 104.93(7), C1–Si–C6 111.31(7), C5–Si–C6 111.88(6), Si–C1–C2 110.46(10), C1–C2–C3 113.04(12), C2–C3–C4 113.91(13), C3–C4–C5 113.23(12), C4–C5–Si 110.38(10).

for the Si–C6 (Si–C5) distances in the range 1.8931(15) to 1.909(3) Å in the molecular structures of (*R*)-**12b**·HBr, *rac*-**13**, *rac*-**15**, and *rac*-**15**·HCl. Interestingly, the corresponding C–C distance in (*S*)-**12a**·HBr is less elongated (1.56 Å),[15c] indicating that the steric demand of the equatorial 2-(dimethylammonio)- or 2-(dimethylamino)-1-(4-methoxyphenyl)ethyl substituent is not responsible for the long Si–C6 (Si–C5) distances observed for *rac*-**12b**·HCl, (*R*)-**12b**·HBr, *rac*-**13**, *rac*-**15**, and *rac*-**15**·HCl.

The crystal structure of *rac*-**12b**·HCl is governed by hydrogen bonds.[76] Compound *rac*-**12b**·HCl forms O1–H*O*···Cl and N–H*N*···Cl hydrogen bonds, leading to the formation of infinite chains along [0 0 1] (Figure 5). These chains are built up by the ammonium cations and chloride anions, the absolute configurations of all the cations in a given chain being identical.

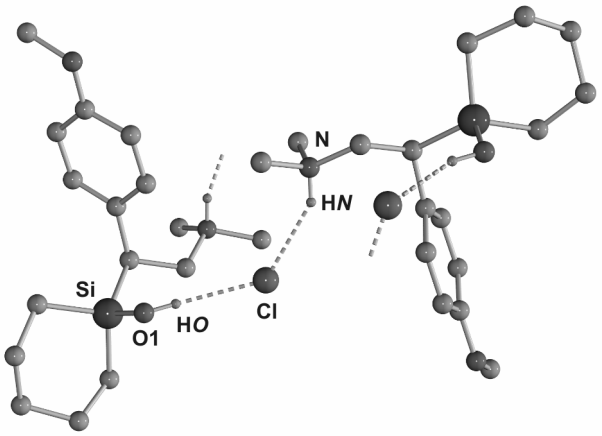


Figure 5. Hydrogen-bonding system in the crystal of *rac*-**12b**·HCl. Selected distances (Å) and angles (deg): O1–H*O* 0.84, H*O*···Cl 2.34, O1···Cl 3.1246(13), O1–H*O*···Cl 156, N···H*N* 0.863(18), H*N*···Cl 2.305(17), N···Cl 3.0680(13), N–H*N*···Cl 147.5(14).[76] The hydrogen atoms (except for the H*O* and H*N* atoms) are omitted for clarity.

Figure 6 shows a superposition of the cyclohexane skeleton of (*S*)-**12a**·HBr[15c] and the 1-silacyclohexane skeleton of the (*S*)-enantiomer of *rac*-**12b**·HCl. Due to the longer covalent radius of the silicon atom, the 1-silacyclohexane ring is more "flattened" than the cyclohexane ring. As a further consequence, the OH group and the ammonio moiety of the C/Si analogs differ in their relative orientation. These structural features might be important for the ligand-receptor interactions of the venlafaxine and sila-venlafaxine enantiomers.

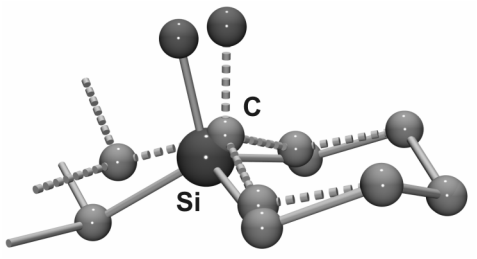


Figure 6. Superposition of the cyclohexane skeleton of (*S*)-**12a**·HBr and the 1-silacyclohexane skeleton of the (*S*)-enantiomer of *rac*-**12b**·HCl. The hydrogen atoms are omitted for clarity.

11.2 (*R*)-Sila-venlafaxine hydrobromide ((*R*)-12b·HBr)

Suitable single crystals of (*R*)-**12b**·HBr were obtained directly from the preparation of this compound (see Experimental Section). Compound (*R*)-**12b**·HBr crystallizes in the space group $P2_1$. Similar to *rac*-**12b**·HCl, the silacyclohexane skeleton of (*R*)-**12b**·HBr adopts a chair conformation, and the Si–C6 bond is elongated significantly (1.909(3) Å) (Figure 7).

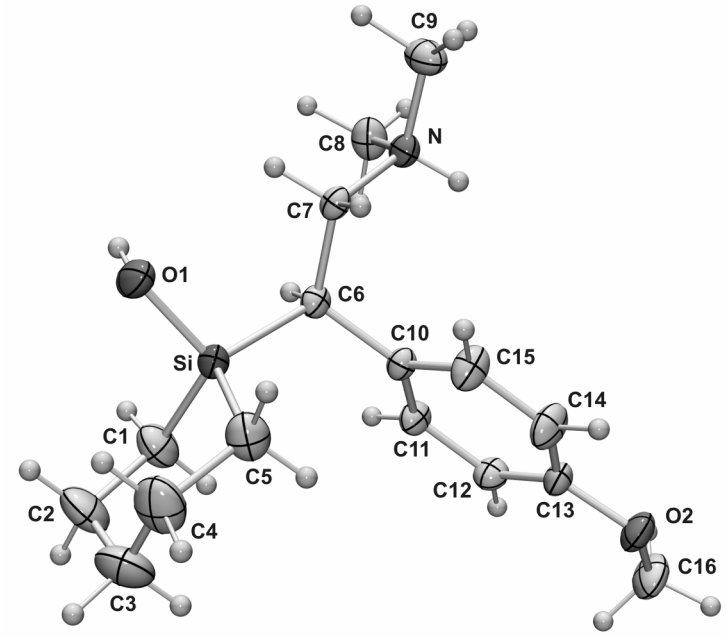


Figure 7. Structure of the cation of (*R*)-**12b**·HBr in the crystal (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg): Si–O1 1.637(3), Si–C1 1.845(3), Si–C5 1.854(3), Si–C6 1.909(3), C1–C2 1.534(5), C2–C3 1.510(6), C3–C4 1.506(7), C4–C5 1.525(5), O1–Si–C1 111.38(15), O1–Si–C5 106.75(16), O1–Si–C6 109.18(12), C1–Si–C5 104.72(16), C1–Si–C6 109.49(15), C5–Si–C6 115.26(13), Si–C1–C2 110.3(3), C1–C2–C3 113.6(3), C2–C3–C4 115.1(3), C3–C4–C5 114.0(4), C4–C5–Si 110.1(2).

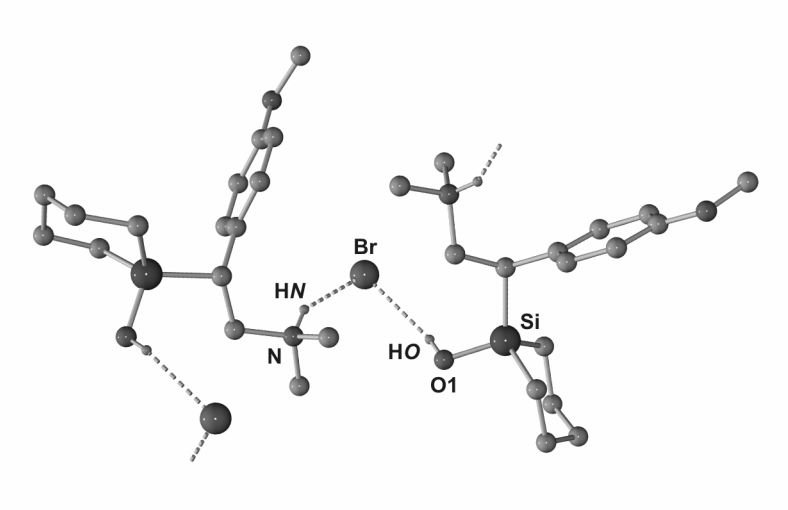


Figure 8. Hydrogen-bonding system in the crystal of (*R*)-**12b**·HBr. Selected distances (Å) and angles (deg): O1–H*O* 0.84, H*O*···Br 2.48, O1···Br 3.261(2), O1–H*O*···Br 154, N···H*N* 0.89(4), H*N*···Br 2.48(4), N···Br 3.290(3), N–H*N*···Br 151(2).[76] The hydrogen atoms (except for the H*O* and H*N* atoms) are omitted for clarity.

The absolute configuration of (*R*)-**12b**·HBr was reliably determined by refinement of the Flack parameter, leading to a value of 0.000(7) for the reported structure and to a value of 1.018(7) for the inverted structure and thus revealing sufficiently strong inversion distinguishing power of the dataset.[77]

Compound (*R*)-**12b** forms O1–H*O*···Br and N–H*N*···Br hydrogen bonds that lead to infinite chains of the ammonium cations and bromide anions along [0 1 0] (Figure 8).

11.3 *rac*-1-[2-(Dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclopentan-1-ol (*rac*-13)

Single crystals of *rac*-**13** were grown by cooling of a solution of *rac*-**13** (934 mg) in *n*-pentane (3 mL) to 4 °C. Compound *rac*-**13** crystallizes in the space group $P2_1/c$. The silacyclopentane ring in *rac*-**13** adopts two different envelope conformations (disorder of the carbon atoms C2 and C3), with occupancy factors of 0.76 and 0.24, and the silacyclopentane skeleton shows some significant deviations from the tetrahedral angle, which is most pronounced for the angle C1–Si–C4 (96.22(10) deg). Similar to *rac*-**12b**·HCl, the Si–C5 bond of *rac*-**13** (corresponding to the Si–C6 bond in compound *rac*-**12b**·HCl) is elongated significantly (1.9056(13) Å) (Figure 9).

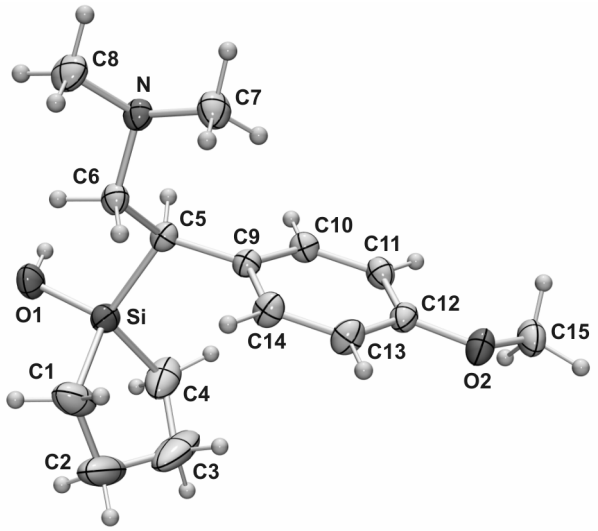


Figure 9. Molecular structure of *rac*-**13** in the crystal (only one enantiomer depicted; probability level of displacement ellipsoids 50%). Due to the presence of two different envelope conformations of the silacyclopentane ring, the crystal structure of *rac*-**13** is characterized by a disorder. The structure shown represents the dominating conformer (occupancy 76%). Selected bond distances (Å) and angles (deg): Si–O1 1.6286(11), Si–C1 1.8834(18), Si–C4 1.8683(17), Si–C5 1.9056(13), C1–C2 1.552(5), C2–C3 1.530(6), C3–C4 1.503(4), O1–Si–C1 109.30(7), O1–Si–C4 115.45(7), O1–Si–C5 108.39(6), C1–Si–C4 96.22(10), C1–Si–C5 114.37(7), C4–Si–C5 112.83(7), Si–C1–C2 101.9(3), C1–C2–C3 109.5(3), C2–C3–C4 107.9(3), C3–C4–Si 104.30(19).

Compound *rac*-**13** forms intermolecular O1–H*O*···N hydrogen bonds, leading to the formation of centrosymmetric dimers (Figure 10).

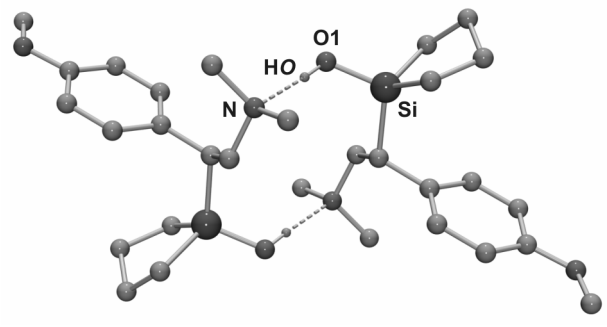


Figure 10. Hydrogen-bonding system in the crystal of *rac*-**13** (dominating conformer). Selected distances (Å) and angles (deg): O1–H*O* 0.84, H*O*···N 1.90, O1···N 2.7338(16), O1–H*O*···N 169.[76] The hydrogen atoms (except for the H*O* atoms) are omitted for clarity.

11.4 *rac*-Desmethoxy-sila-venlafaxine (*rac*-1-[2-(dimethylamino)-1-phenyl-ethyl]-1-silacyclohexan-1-ol, *rac*-15)

Suitable single crystals of *rac*-**15** were obtained directly from the preparation of this compound (see Experimental Section). Compound *rac*-**15** crystallizes in the space group $P2_1/n$. The asymmetric unit contains two molecules (A and B), with very similar structures (Figure 11). Similar to *rac*-**12b**·HCl, the silacyclohexane skeleton of *rac*-**15** adopts a chair conformation, and the Si–C6 (Si–C26) bond is elongated significantly (molecule A, 1.8931(15) Å; molecule B, 1.8988(15) Å).

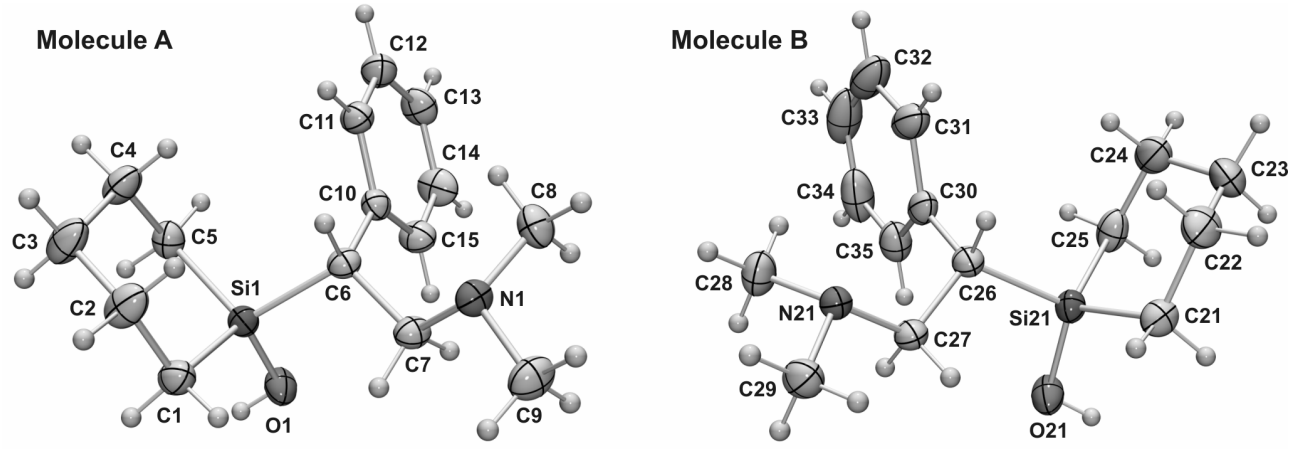


Figure 11. Structure of *rac*-**15** in the crystal (only one enantiomer of molecules A and B depicted; probability level of displacement ellipsoids 50%; the depiction does not reflect the relative orientation of molecules A and B in the crystal). Selected bond distances (Å) and angles (deg); data for molecule A: Si1–O1 1.6200(11), Si1–C1 1.8655(17), Si1–C5 1.8608(16), Si1–C6 1.8931(15), C1–C2 1.529(2), C2–C3 1.524(2), C3–C4 1.519(2), C4–C5 1.533(2), O1–Si1–C1 113.78(7), O1–Si1–C5 115.47(7), O1–Si1–C6 105.45(6), C1–Si1–C5 103.76(7), C1–Si1–C6 109.26(7), C5–Si1–C6 109.03(7), Si1–C1–C2 110.99(11), C1–C2–C3 113.03(15), C2–C3–C4 114.65(15), C3–C4–C5 113.42(15), C4–C5–Si1 110.50(11). Data for molecule B (the atoms are labelled by adding "20" to the label number of the corresponding atoms in molecule A): Si21–O21 1.6259(12), Si21–C21 1.8609(16), Si21–C25 1.8560(18), Si21–C26 1.8988(15), C21–C22 1.528(2), C22–C23 1.518(3), C23–C24 1.515(3), C24–C25 1.536(3), O21–Si21–C21 111.95(7), O21–Si21–C25 113.66(8), O21–Si21–C26 108.25(7), C21–Si21–C25 103.91(8), C21–Si21–C26 109.09(7), C25–Si21–C26 109.87(7), Si21–C21–C22 112.40(12), C21–C22–C23 113.44(15), C22–C23–C24 114.22(16), C23–C24–C25 112.50(15), C24–C25–Si21 111.13(13).

In contrast to the closely related compounds *rac*-**12b**·HCl, (*R*)-**12b**·HBr, and *rac*-**13**, the silanol OH group occupies an equatorial position of the silacyclohexane skeleton of *rac*-**15** in the crystal, which also applies to the corresponding hydrochloride *rac*-**15**·HCl (see below).

The crystal structure of *rac*-**15** is governed by hydrogen bonds.[76] Compound *rac*-**15** forms intermolecular O1–H*O1*···N21 and O21–H*O21*···N1 hydrogen bonds that lead to infinite chains of the molecules along [1 0 0] (Figure 12). These chains are built up by molecules A and B in an alternating manner (···A···B···A···B···), the absolute configurations of A and B in a given chain being opposite.

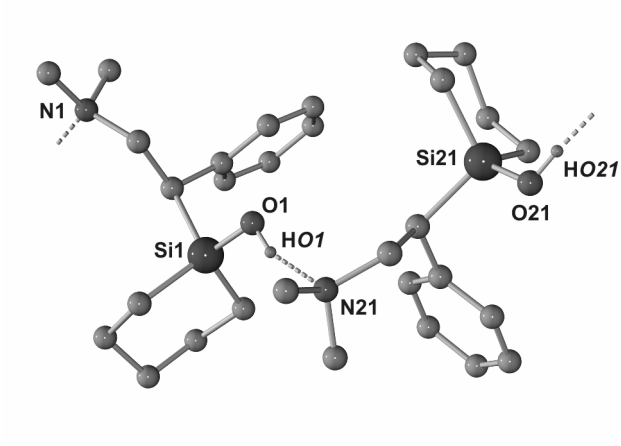


Figure 12. Hydrogen-bonding system in the crystal of *rac*-**15**. Selected distances (Å) and angles (deg): O1–H*O1* 0.84, H*O1*···N21 1.91, O1···N21 2.6996(18), O1–H*O1*···N 157; O21–H*O21* 0.84, H*O21*···N1 1.95, O21···N1 2.7878(17), O21–H*O21*···N1 175.[76] The hydrogen atoms (except for the H*O1* and H*O21* atoms) are omitted for clarity.

11.5 *rac*-Desmethoxy-sila-venlafaxine hydrochloride (*rac*-[2-(1-hydroxy-1-sila-1-cyclohexyl)-2-phenylethyl]dimethylammonium chloride, *rac*-15·HCl)

Suitable single crystals of *rac*-**15**·HCl were obtained directly from the preparation of this compound (see Experimental Section). Compound *rac*-**15**·HCl crystallizes in the space group $P2_1/n$. Similar structural features as discussed for *rac*-**15** apply, with the silacyclohexane ring adopting a chair conformation, the Si–C6 bond being elongated significantly (1.9041(14) Å), and the silanol OH group being in an equatorial position (Figure 13).

The crystal structure of *rac*-**15**·HCl is governed by hydrogen bonds.[76] Compound *rac*-**15**·HCl forms O–H*O*···Cl and N–H*N*···Cl hydrogen bonds, leading to the formation of infinite chains along [1 0 0] (Figure 14). These chains are built up by the ammonium cations and chloride anions, the absolute configurations of all the cations in a given chain being identical.

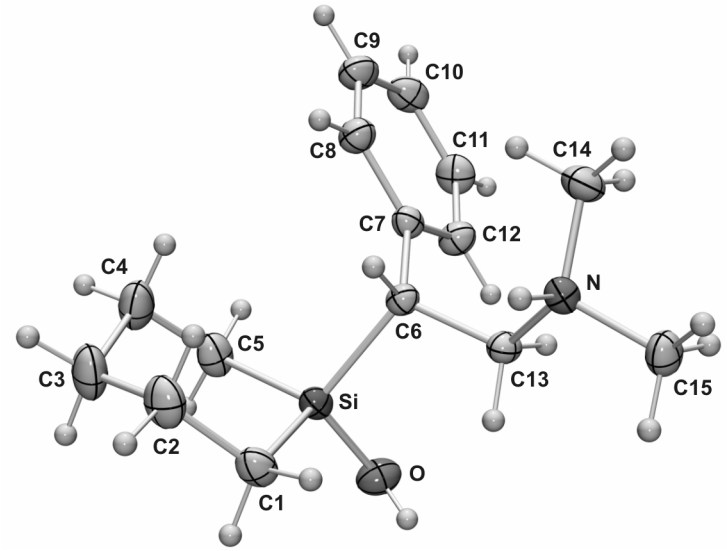


Figure 13. Structure of the cation of *rac*-**15**·HCl in the crystal (only one enantiomer depicted). Selected bond distances (Å) and angles (deg): Si–O 1.6348(12), Si–C1 1.8602(15), Si–C5 1.8481(15), Si–C6 1.9041(14), C1–C2 1.537(2), C2–C3 1.524(2), C3–C4 1.531(2), C4–C5 1.526(2), O–Si–C1 113.03(7), O–Si–C5 110.04(7), O–Si–C6 108.25(6), C1–Si–C5 105.73(7), C1–Si–C6 108.34(7), C5–Si–C6 111.47(7), Si–C1–C2 111.57(10), C1–C2–C3 113.39(15), C2–C3–C4 114.23(13), C3–C4–C5 113.42(15), C4–C5–Si 110.93(11).

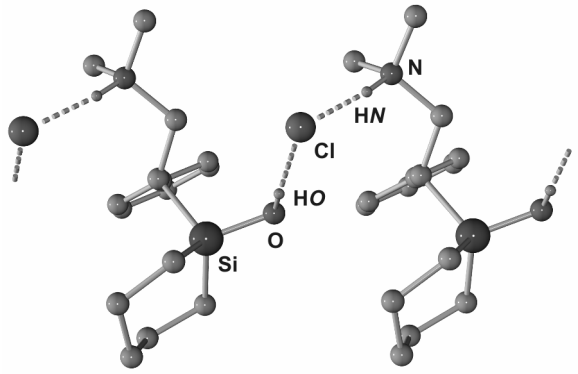


Figure 14. Hydrogen-bonding system in the crystal of *rac*-**15**·HCl. Selected distances (Å) and angles (deg): O–H*O* 0.84, H*O*···Cl 2.25, O···Cl 3.0762(12), O–H*O*···Cl 170; N···H*N* 0.929(18), H*N*···Cl 2.119(18), N···Cl 3.0444(13), N–H*N*···Cl 173.8(15).[76] The hydrogen atoms (except for the H*O* and H*N* atoms) are omitted for clarity.

11.6 Bexarotene (21a)

Suitable single crystals of **21a** (mp 224–225 °C) were obtained by crystallization from a solution of **21a** (130 mg) in dichloromethane (5 mL) (slow evaporation of the solvent at 20 °C). Compound **21a** crystallizes in the space group $P\bar{1}$ and forms intermolecular O2–H2···O1A hydrogen bonds in the crystal, leading to the formation of centrosymmetric dimers (Figure 15).

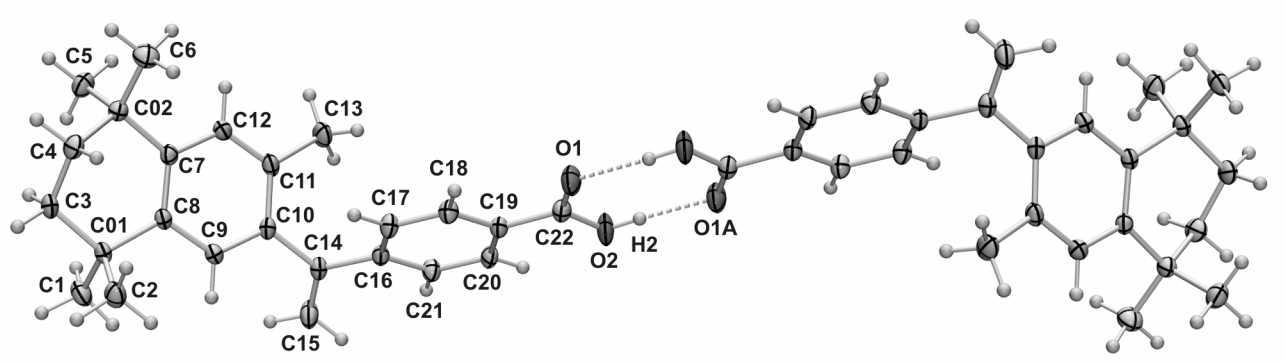


Figure 15. Centrosymmetric dimer in the crystal of **21a** (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg) and selected torsion angles (deg): C01–C1 1.5331(18), C01–C2 1.5332(19), C01–C3 1.5407(16), C01–C8 1.5380(15), C02–C4 1.5367(18), C02–C5 1.532(2), C02–C6 1.5347(18), C02–C7 1.5281(16), C3–C4 1.5170(18), C7–C8 1.4005(15), C1–C01–C2 109.05(10), C1–C01–C3 107.85(10), C1–C01–C8 109.18(10), C2–C01–C3 109.28(11), C2–C01–C8 110.27(10), C3–C01–C8 111.16(9), C4–C02–C5 111.44(10), C4–C02–C6 107.28(12), C4–C02–C7 108.79(9), C5–C02–C6 108.38(11), C5–C02–C7 109.37(11), C6–C02–C7 111.60(10), C01–C3–C4 112.70(10), C01–C8–C7 123.39(10), C02–C4–C3 111.57(11), C02–C7–C8 122.67(10), C01–C3–C4–C02 –64.15(15), C01–C8–C7–C02 6.08(19), C3–C01–C8–C7 2.63(17), C8–C01–C3–C4 –36.55(15), C4–C02–C7–C8 18.69(16), C7–C02–C4–C3 –52.40(14), C9–C10–C14–C15 51.66(19), C9–C10–C14–C16 –126.74(13), C10–C14–C16–C17 26.45(17). Data for the hydrogen-bonding system:[76] O2–H2 0.89(2), H2···O1A 1.772(19), O2···O1A 2.6593(15), O2–H2···O1A 176(2).

11.7 Disila-bexarotene (21b)

Suitable single crystals of **21b** were obtained directly from the preparation of this compound (see Experimental Section). Compound **21b** crystallizes in the space group $P\bar{1}$ and forms

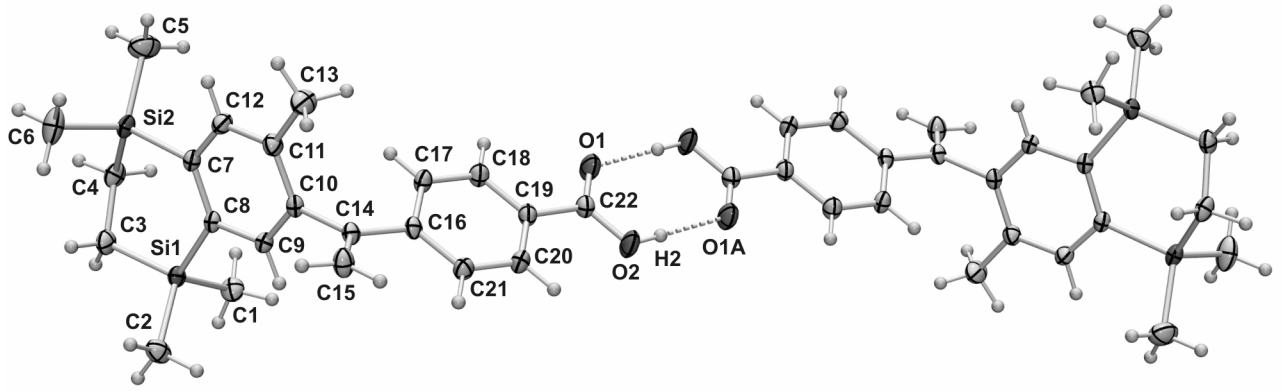


Figure 16. Centrosymmetric dimer in the crystal of **21b** (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg) and selected torsion angles (deg): Si1–C1 1.8665(15), Si1–C2 1.8706(15), Si1–C3 1.8735(14), Si1–C8 1.8877(14), Si2–C4 1.8752(16), Si2–C5 1.8640(17), Si2–C6 1.8711(17), Si2–C7 1.8863(14), C3–C4 1.548(2), C7–C8 1.4145(17), C1–Si1–C2 109.49(7), C1–Si1–C3 109.32(7), C1–Si1–C8 108.49(6), C2–Si1–C3 110.39(7), C2–Si1–C8 109.59(7), C3–Si1–C8 109.53(6), C4–Si2–C5 110.23(8), C4–Si2–C6 110.38(8), C4–Si2–C7 108.04(6), C5–Si2–C6 109.30(9), C5–Si2–C7 110.58(7), C6–Si2–C7 108.28(8), Si1–C3–C4 112.09(9), Si1–C8–C7 124.53(9), Si2–C4–C3 111.65(10), Si2–C7–C8 122.54(10), Si1–C3–C4–Si2 –65.85(12), Si1–C8–C7–Si2 1.09(16), C3–Si1–C8–C7 –7.41(13), C8–Si1–C3–C4 42.37(13), C4–Si2–C7–C8 –18.21(13), C7–Si2–C4–C3 53.34(11), C9–C10–C14–C15 –92.78(16), C9–C10–C14–C16 86.41(14), C10–C14–C16–C17 23.62(17). Data for the hydrogen-bonding system:[76] O2–H2 0.83(2), H2···O1A 1.83(2), O2···O1A 2.6582(16), O2–H2···O1A 174(2).

intermolecular O2–H2···O1A hydrogen bonds in the crystal, leading to the formation of centrosymmetric dimers (Figure 16).

As can be seen from the figure legends of Figures 16, 18, 23, and 24, the conformations of the 5,8-disila-5,6,7,8-tetrahydronaphthalene skeletons of **21b**, **22b**, **89**, and **99** are very similar, but differ significantly from the conformation of the 5,6,7,8-tetrahydronaphthalene moiety of **21a** (Figure 15). This is demonstrated in Figure 17 by the superposition of the respective partial structures of the C/Si analogs **21a** and **21b**. These differences result from the different covalent radii of carbon and silicon.

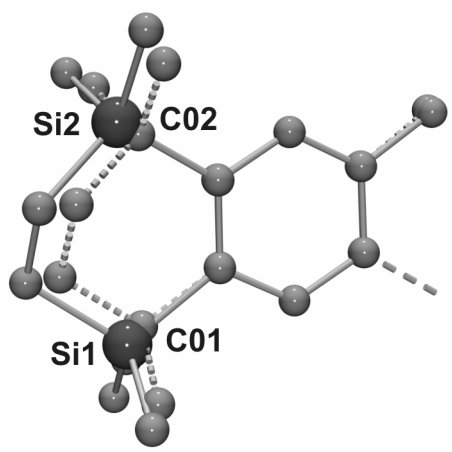


Figure 17. Superposition of the 3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydro-2-naphthyl group of **21a** (dashed bonds) and the 3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl group of **21b** (solid bonds). The hydrogen atoms are omitted for clarity.

As can be seen from Figures 15, 16, and 23 and from the torsion angles listed in the respective figure legends, the sp^2-hybridized carbon atoms C9, C10, C14, C15, C16, and C17 of **21a**, **21b**, and **89** are not localized in one plane, probably due to the steric requirements of the C13-methyl group. The different torsion angles C9–C10–C14–C15, C9–C10–C14–C16, and C10–C14–C16–C17 reflect the conformational flexibility of these compounds, which might be very important for receptor binding.

11.8 Disila-AG-045572 (22b)

Suitable single crystals of **22b** were obtained by vapor diffusion of *n*-pentane into a solution of **22b** (100 mg) in diethyl ether (30 mL) (colorless plates, mp 158 °C).[78] Compound **22b** crystallizes in the space group *C*2/*c* and forms intermolecular N–H···O hydrogen bonds in the crystal, leading to infinite chains along [0 1 0].

The sp^2-hybridized atoms C17, C18, C19, and O2 of **22b** are not localized in one plane (C17–C18–C19–O2 –162.8(2) deg), and the torsion angle C19–N–C20–C21 (64.9(2) deg) indicates that there is hardly any interaction of the lone pair of the nitrogen atom with the π electrons of the

adjacent aromatic moiety. In contrast, the torsion angle C18–C19–N–C20 (177.08(15) deg) and the sum of bond angles around the nitrogen atom (ca. 359 deg) indicate a high degree of interaction between the lone pair of the nitrogen atom and the carbonyl group. All these structural features might be of importance for the active conformation of **22b** at the receptor.

As can be seen from the torsion angles listed in the figure legends of Figures 18 and 24, the conformations of the 3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl groups of **22b** and **99** are rather similar. These conformations are also similar to that of the corresponding framework of disila-bexarotene (**21b**), but differ significantly from the conformation of the 3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydro-2-naphthyl group of bexarotene (**21a**).[79] This difference might be important for the receptor binding of the C/Si analogs **22a** and **22b**.

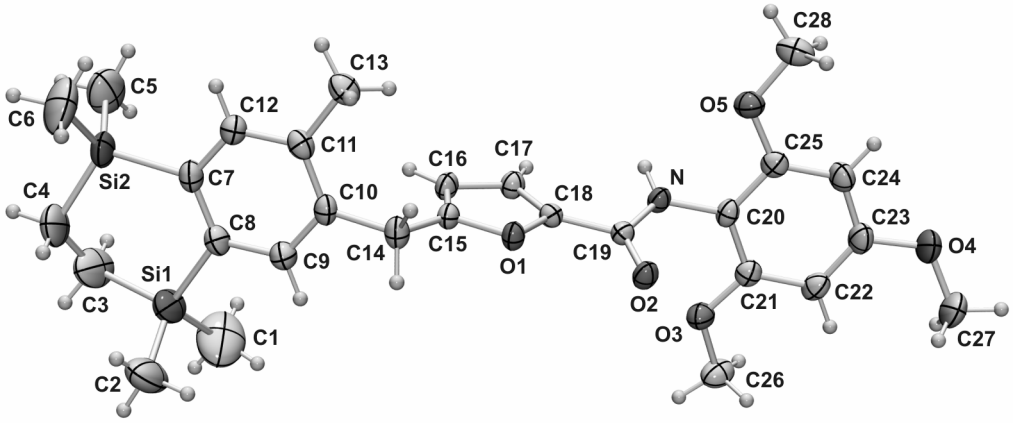


Figure 18. Molecular structure of **22b** in the crystal (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg) and selected torsion angles (deg): Si1–C1 1.863(4), Si1–C2 1.853(4), Si1–C3 1.862(3), Si1–C8 1.879(2), Si2–C4 1.870(3), Si2–C5 1.852(3), Si2–C6 1.858(3), Si2–C7 1.8814(18), C3–C4 1.522(4), C7–C8 1.408(3), C1–Si1–C2 109.0(2), C1–Si1–C3 110.04(18), C1–Si1–C8 109.96(14), C2–Si1–C3 110.51(16), C2–Si1–C8 108.82(13), C3–Si1–C8 108.50(12), C4–Si2–C5 109.54(16), C4–Si2–C6 110.81(16), C4–Si2–C7 108.33(11), C5–Si2–C6 108.59(18), C5–Si2–C7 110.02(12), C6–Si2–C7 109.55(12), Si1–C3–C4 112.5(2), Si1–C8–C7 124.00(14), Si2–C4–C3 112.69(19), Si2–C7–C8 123.54(14), Si1–C3–C4–Si2 65.8(3), Si1–C8–C7–Si2 –1.8(3), C3–Si1–C8–C7 11.9(2), C8–Si1–C3–C4 –47.2(3), C4–Si2–C7–C8 12.0(2), C7–Si2–C4–C3 –47.4(3). Data for the hydrogen-bonding system:[76] N–H 0.845(19), H···O2A 2.202(19), N···O2A 3.029(2), N–H···O2A 166.2(18).

11.9 1-Methoxy-1-(2,4,6-trimethoxyphenyl)-1-silacyclohexane (61)

Suitable single crystals of **61** were obtained directly from the preparation of this compound (see Experimental Section). Compound **61** crystallizes in the space group $P2_12_12_1$. It exhibits an approximately tetrahedral coordination at the silicon atom, and silacyclohexane ring of **61** adopts a chair conformation (Figure 19). Compound **61** exhibits short intramolecular distances between the silicon atoms and the oxygen atoms in the *ortho*-methoxy groups. These Si···O distances are all shorter than the sum of the van der Waals radii of silicon (2.1 Å) and oxygen (1.5 Å) but significantly longer than a typical covalent Si–O bond (1.64 Å)[80] of a tetracoordinate silicon

compound. The *Si*-2,4,6-TMOP group exhibits one shorter and one longer Si···O contact (Si···O1 2.9001(16) Å, Si···O3 3.1189(15) Å). Very similar results are observed for the 2,4,6-trimethoxyphenyl)silanes **62**, **74**, **75**, **103**, **104**, and **146**, with Si···O distances in the range 2.76–3.17 Å, and have also been reported for a series of other (2,4,6-trimethoxyphenyl)silanes.[40e]

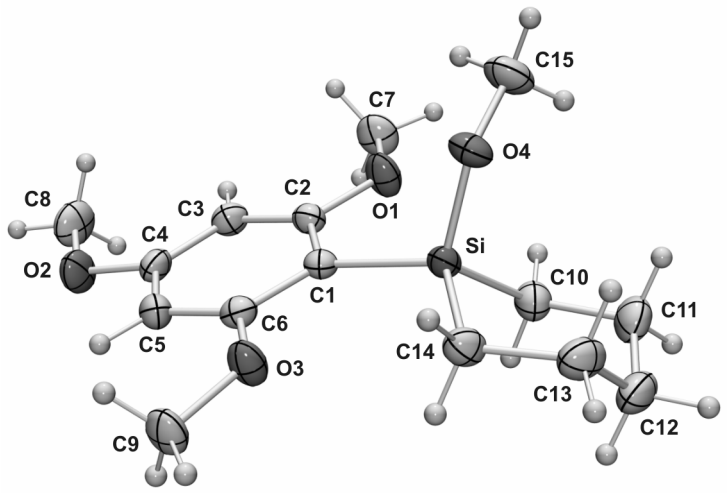


Figure 19. Molecular structure of **61** in the crystal (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg): Si–C1 1.888(2), Si–C10 1.867(2), Si–C14 1.864(2), Si–O4 1.6509(14), Si···O1 2.9001(16), Si···O3 3.1189(15), C1–Si–C10 111.92(10), C1–Si–C14 115.04(10), C1–Si–O4 110.07(8), C10–Si–C14 104.35(11), C10–Si–O4 110.54(9), C14–Si–O4 104.56(9).

11.10 1-[1-(4-Methoxyphenyl)vinyl]-1-(2,4,6-trimethoxyphenyl)-1-silacyclohexane (62)

Suitable single crystals of **62** were obtained from an undercooled (20 °C) melt of this compound (1.3 g) after addition of two drops of *n*-hexane; the resulting mixture was kept at 20 °C for 16 h to afford colorless crystals (mp 45–46 °C). Compound **62** crystallizes in the space group $P\bar{1}$. The asymmetric unit contains two molecules (A and B) with similar structures (Figure 20). Similar structural features as discussed for **61** apply, with the silacyclohexane ring adopting a chair conformation and the Si···O distances between the silicon atoms and the oxygen atoms in the *ortho*-methoxy groups being smaller than the sum of the van der Waals radii of oxygen and silicon.

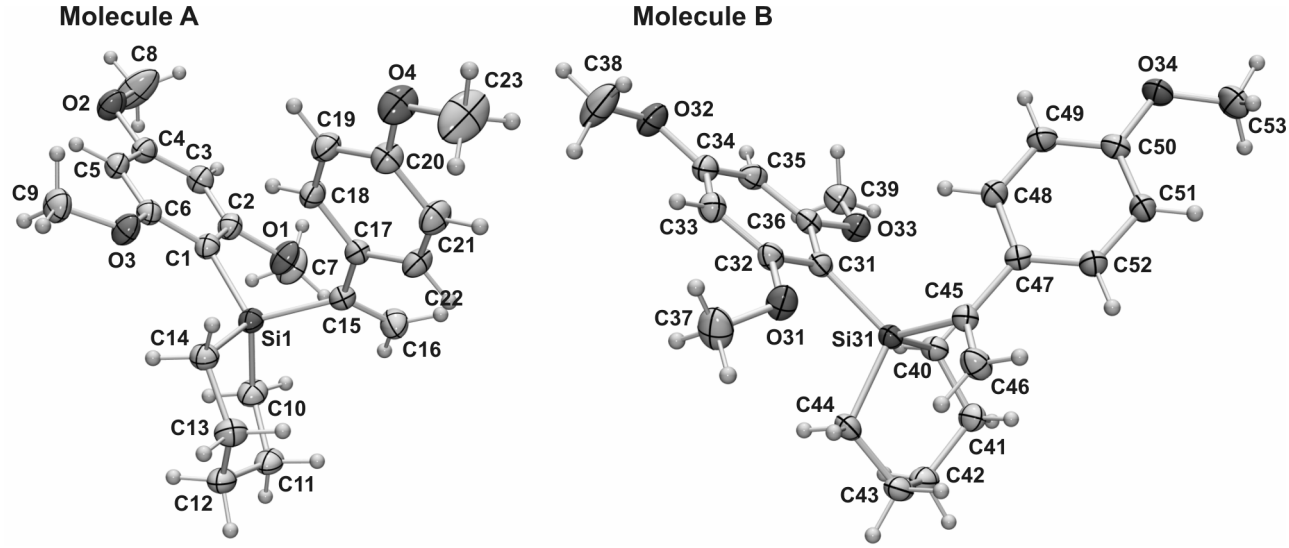


Figure 20. Structure of **62** in the crystal (probability level of displacement ellipsoids 50%; the depiction does not reflect the relative orientation of molecules A and B in the crystal). Selected interatomic distances (Å) and bond angles (deg); data for molecule A: Si1–C1 1.8838(19), Si1–C10 1.8890(19), Si1–C14 1.881(2), Si1–C15 1.8903(19), Si1···O1 2.9037(17), Si1···O3 3.1249(15), C1–Si1–C10 110.62(9), C1–Si1–C14 113.44(9), C1–Si1–C15 111.16(8), C10–Si1–C14 104.01(9), C10–Si1–C15 109.80(9), C14–Si1–C15 107.52(9). Data for molecule B (the atoms are labelled by adding "30" to the label number of the corresponding atoms in molecule A): Si31–C31 1.8942(18), Si31–C40 1.877(2), Si31–C44 1.8870(18), Si31–C45 1.8968(19), Si31···O31 2.9125(17), Si31···O33 3.1268(14), C31–Si31–C40 113.09(8), C31–Si31–C44 110.49(8), C31–Si31–C45 112.37(8), C40–Si31–C44 104.14(9), C40–Si31–C45 106.98(9), C44–Si31–C45 109.39(8).

11.11 1-Methoxy-1-(2,4,6-trimethoxyphenyl)-1-silacyclobutane (74)

Suitable single crystals of **74** were obtained directly from the preparation of this compound (see Experimental Section). Compound **74** crystallizes in the space group $P2_1/n$. The Si-coordination polyhedron of **74** is a strongly distorted tetrahedron (Figure 21). This distortion is forced by the geometry of the four-membered silacyclobutane ring, which adopts a butterfly

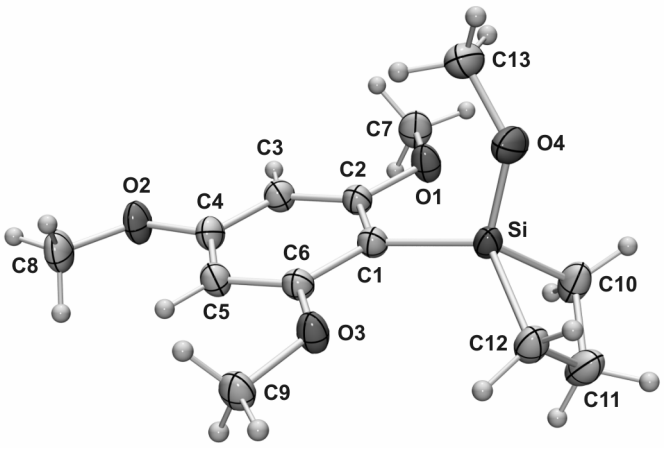


Figure 21. Molecular structure of **74** in the crystal (probability level of displacement ellipsoids 50%). Selected interatomic distances (Å) and bond angles (deg): Si–C1 1.8678(17), Si–C10 1.873(2), Si–C12 1.8720(18), Si–O4 1.6450(15), Si···C11 2.387(2), Si···O1 2.9339(14), Si···O3 3.0580(14), C1–Si–C10 116.95(9), C1–Si–C12 119.52(8), C1–Si–O4 110.13(8), C10–Si–C12 79.98(8), C10–Si–O4 116.07(9), C12–Si–O4 111.50(9).

conformation. The Si···C11 distance is remarkably short (2.387(2) Å), which also reflects the geometry that is forced by this butterfly conformation. Apart from the geometry of the silacyclobutane skeleton, similar structural features as discussed for **61** apply, with the Si···O distances between the silicon atom and the oxygen atoms in the *ortho*-methoxy groups being smaller than the sum of the van der Waals radii of oxygen and silicon.

11.12 1-[1-(4-Methoxyphenyl)vinyl]-1-(2,4,6-trimethoxyphenyl)-1-silacyclobutane (75)

Suitable single crystals of **75** were obtained directly from the preparation of this compound (see Experimental Section). Compound **75** crystallizes in the space group $P2_1/n$. Similar structural features as discussed for **61** and **74** apply, with the silacyclohexane ring adopting a a butterfly conformation (Si···C11, 2.4012(14) Å) and the Si···O distances between the silicon atom and the oxygen atoms in the *ortho*-methoxy groups being smaller than the sum of the van der Waals radii of oxygen and silicon.

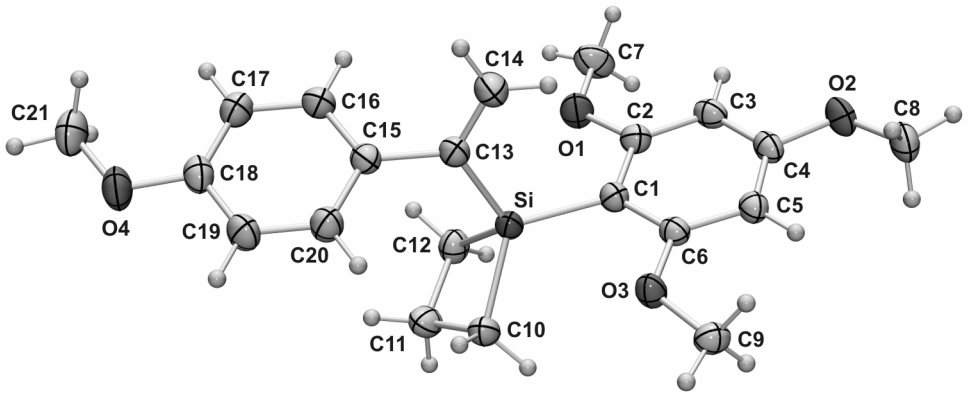


Figure 22. Molecular structure of **75** in the crystal (probability level of displacement ellipsoids 50%). Selected interatomic distances (Å) and bond angles (deg): Si–C1 1.8681(13), Si–C10 1.8829(14), Si–C12 1.8803(14), Si–C13 1.8850(14), Si···C11 2.4012(14), Si···O1 2.9226(11), Si···O3 3.0136(10), C1–Si–C10 118.49(6), C1–Si–C12 120.79(6), C1–Si–C13 109.26(6), C10–Si–C12 79.00(6), C10–Si–C13 115.73(6), C12–Si–C13 110.96(6).

11.13 Methyl 4-[1-(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)vinyl]benzoate (89)

Suitable single crystals of **89** were obtained directly from the preparation of this compound (see Experimental Section). Compound **89** crystallizes in the space group $P2_1/c$. For a discussion of structural features of **89**, see Section 11.7 (p. 49).

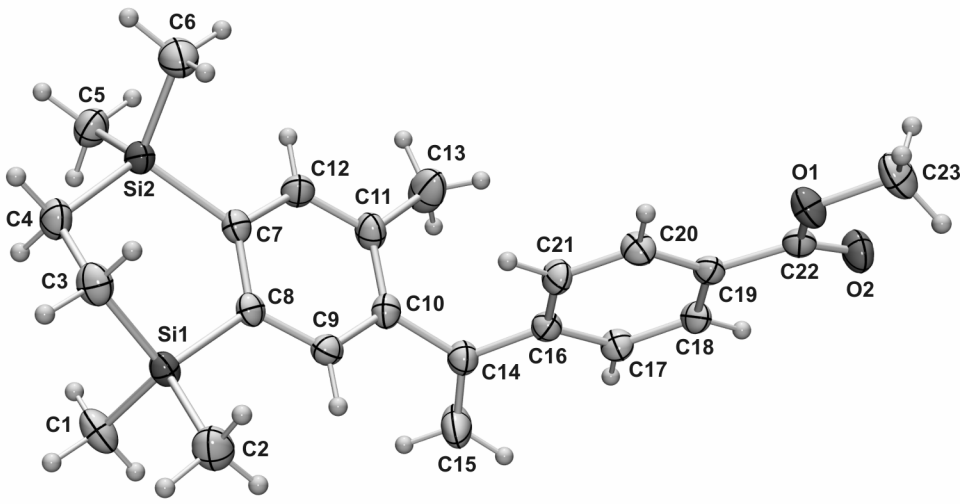


Figure 23. Molecular structure of **89** in the crystal (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg) and selected torsion angles (deg): Si1–C1 1.859(2), Si1–C2 1.869(2), Si1–C3 1.873(2), Si1–C8 1.8892(18), Si2–C4 1.875(2), Si2–C5 1.864(2), Si2–C6 1.865(2), Si2–C7 1.8874(19), C3–C4 1.544(3), C7–C8 1.411(3), C1–Si1–C2 108.77(11), C1–Si1–C3 110.82(10), C1–Si1–C8 107.96(9), C2–Si1–C3 108.86(11), C2–Si1–C8 112.67(9), C3–Si1–C8 107.77(9), C4–Si2–C5 108.27(9), C4–Si2–C6 112.11(11), C4–Si2–C7 110.28(9), C5–Si2–C6 109.38(11), C5–Si2–C7 109.70(9), C6–Si2–C7 107.07(9), Si1–C3–C4 111.66(15), Si1–C8–C7 121.27(13), Si2–C4–C3 114.03(13), Si2–C7–C8 125.11(13), Si1–C3–C4–Si2 –61.61(18), Si1–C8–C7–Si2 –5.2(2), C3–Si1–C8–C7 –27.50(18), C8–Si1–C3–C4 56.99(15), C4–Si2–C7–C8 –5.3(2), C7–Si2–C4–C3 35.26(19), C9–C10–C14–C15 62.3(3), C9–C10–C14–C16 –114.2(2), C10–C14–C16–C17 –155.64(18).

11.14 5-[(3,5,5,8,8-Pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)methyl]-2-furoic acid (99)

Suitable single crystals of **99** were obtained directly from the preparation of this compound (see Experimental Section). Compound **99** crystallizes in the space group *C*2/*c* and forms

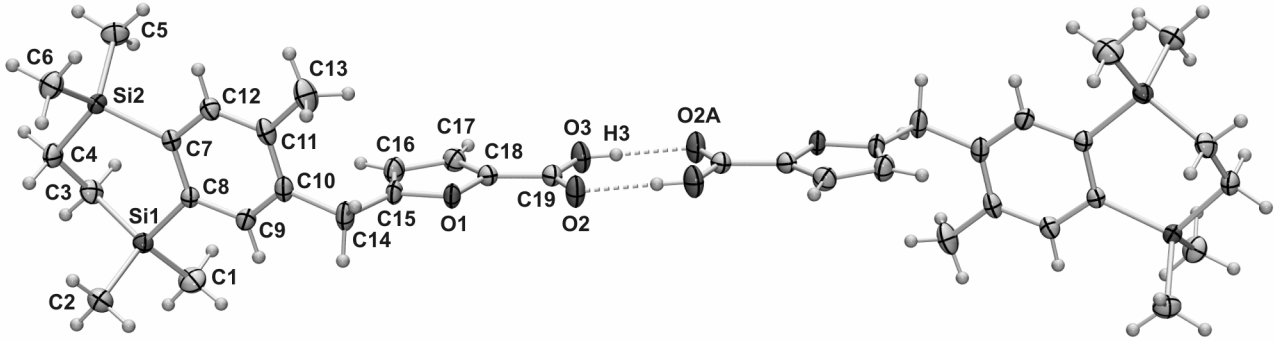


Figure 24. Centrosymmetric dimer in the crystal of **99** (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg) and selected torsion angles (deg): Si1–C1 1.8696(15), Si1–C2 1.8696(17), Si1–C3 1.8690(15), Si1–C8 1.8837(14), Si2–C4 1.8732(15), Si2–C5 1.8635(16), Si2–C6 1.8682(15), Si2–C7 1.8870(13), C3–C4 1.544(2), C7–C8 1.4150(18), C1–Si1–C2 109.45(8), C1–Si1–C3 110.63(8), C1–Si1–C8 109.59(7), C2–Si1–C3 110.96(7), C2–Si1–C8 108.57(7), C3–Si1–C8 107.59(6), C4–Si2–C5 110.94(7), C4–Si2–C6 109.20(7), C4–Si2–C7 109.82(6), C5–Si2–C6 109.33(7), C5–Si2–C7 107.85(7), C6–Si2–C7 109.68(7), Si1–C3–C4 111.35(10), Si1–C8–C7 122.75(10), Si2–C4–C3 114.16(10), Si2–C7–C8 124.22(10), Si1–C3–C4–Si2 63.22(13), Si1–C8–C7–Si2 –0.43(17), C3–Si1–C8–C7 22.65(13), C8–Si1–C3–C4 –55.45(11), C4–Si2–C7–C8 2.69(14), C7–Si2–C4–C3 –36.48(13). Data for the hydrogen-bonding system:[76] O3–H 0.82(3), H···O2A 1.84(3), O3···O2A 2.6583(18), O3–H···O2A 178(3).

intermolecular O3–H3···O2A hydrogen bonds in the crystal, leading to the formation of centrosymmetric dimers (Figure 24). For a discussion of structural features of **99**, see Section 11.8 (p. 50).

11.15 Tris(chloromethyl)(2,4,6-trimethoxyphenyl)silane (103)

Suitable single crystals of **103** were obtained directly from the preparation of this compound (see Experimental Section). Compound **103** crystallizes in the space group $P\bar{1}$. The Si–C12–Cl31(Cl32) group in **103** adopts two different conformations (disorder of the chlorine atoms Cl31 and Cl32), with occupancy factors of 0.65 and 0.35, respectively. The molecular structure is characterized by short intramolecular distances between the silicon atom and the oxygen atoms in the *ortho*-methoxy groups (Figure 25). These Si···O distances amount to 2.8708(15) Å and 3.0679(14) Å, respectively, which parallels the findings for compounds **61**, **62**, **74**, **75**, **104**, and **146**, cf. Section 11.9 (p. 51).

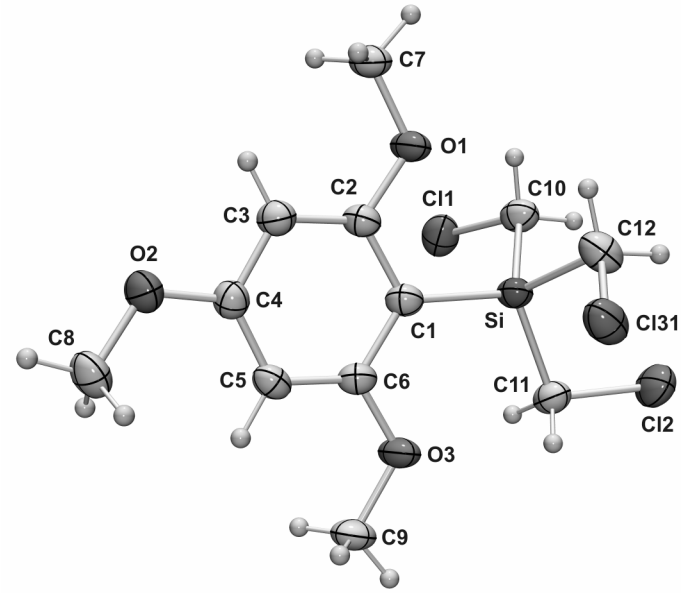


Figure 25. Molecular structure of **103** in the crystal (probability level of displacement ellipsoids 50%). Due to the presence of two different conformations of the Si–C12–Cl31(Cl32) group, the crystal structure of **103** is characterized by a disorder. The structure shown represents the dominating conformer (occupancy 65%). Selected interatomic distances (Å) and bond angles (deg): Si–C1 1.854(2), Si–C10 1.8750(19), Si–C11 1.8735(19), Si–C12 1.876(2), C10–Cl1 1.789(2), C11–Cl2 1.803(2), C12–Cl31 1.802(4), Si···O1 2.8708(15), Si···O3 3.0679(14), C1–Si–C10 113.46(9), C1–Si–C11 112.88(8), C1–Si–C12 110.51(10), C10–Si–C11 107.13(9), C10–Si–C12 104.40(9), C11–Si–C12 107.96(10), Si–C10–Cl1 111.08(10), Si–C11–Cl2 110.52(10), Si–C12–Cl31 111.42(14).

11.16 Dichlorobis(2,4,6-trimethoxyphenyl)silane (104)

Suitable single crystals of **104** were obtained directly from the preparation of this compound (see Experimental Section). Compound **104** crystallizes in the space group *C*2/*c*. The Si-coordination polyhedron of **104** is a strongly distorted tetrahedron (Figure 26), with the largest

angle at the silicon atom being observed for C1–Si–C10 (117.62(6) deg) and the smallest for Cl1–Si–Cl2 (103.98(2) deg), thus clearly reflecting the different steric demands of the bulky *Si*-2,4,6-TMOP groups and the smaller chlorine atoms attached to the silicon atom.

Similar to the closely related compounds **61**, **62**, **74**, **75**, **103**, and **146**, the molecular structure of **104** is characterized by short intramolecular distances between the silicon atom and the oxygen atoms in the *ortho*-methoxy groups. Within this series of crystal structures of analogous (2,4,6-trimethoxyphenyl)silanes, the smallest and largest Si···O-distances are observed for compound **104** (Si···O4 2.7558(11), Si···O6 3.1700(11)). These extremes may be explained by the fact that **104** is the only compound within this series of (2,4,6-trimethoxyphenyl)silanes which bears two *Si*-2,4,6-TMOP moieties, which infers a special steric situation to the coordination sphere at the silicon atom.

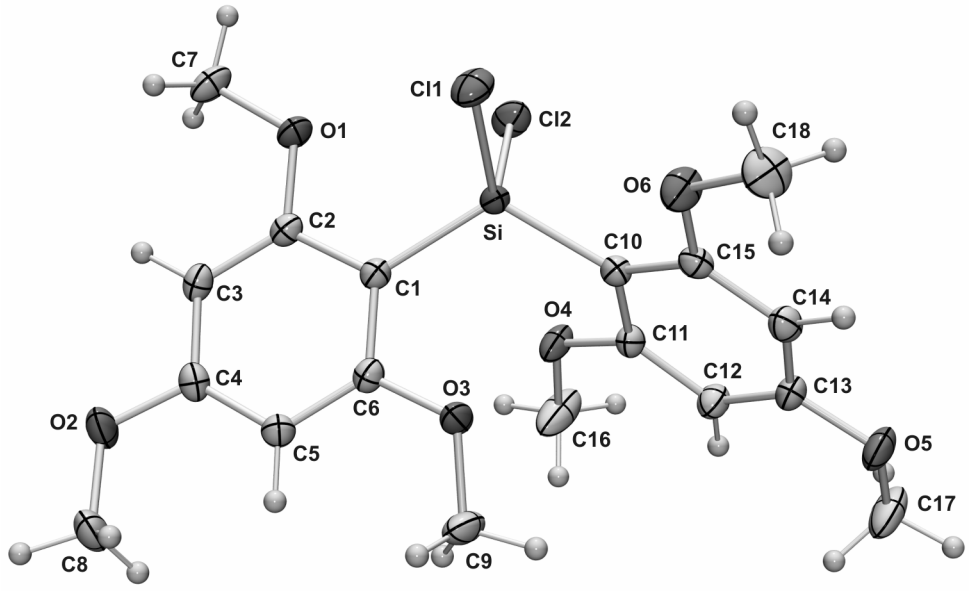


Figure 26. Molecular structure of **104** in the crystal (probability level of displacement ellipsoids 50%). Selected interatomic distances (Å) and bond angles (deg): Si–C1 1.8528(14), Si–C10 1.8536(13), Si–Cl1 2.0593(5), Si–Cl2 2.0608(6), Si···O1 2.9623(11), Si···O3 3.0034(12), Si···O4 2.7558(11), Si···O6 3.1700(11), C1–Si–C10 117.62(6), C1–Si–Cl1 105.15(5), C1–Si–Cl2 111.13(5), C10–Si–Cl1 112.48(5), C10–Si–Cl2 105.74(5), Cl1–Si–Cl2 103.98(2).

11.17 1,1´-Oxybis{[(1-sila-1-cyclohexyl)methyl]ammonium} dichloride dihydrate (145·2H_2O)

Suitable single crystals of **145**·2H_2O were obtained directly from the preparation of this compound (see Experimental Section; crystallization from 6 M hydrochloric acid at –20 °C; no subsequent drying to avoid loss of the water of crystallization). Compound **145**·2H_2O crystallizes in the space group $P2_1/c$. The crystal structure of **145**·2H_2O is governed by hydrogen bonds, leading to an infinite two-dimensional network along the base vectors [0 1 0] and [0 0 1]. All six NH groups of

the dication and all OH groups of the two crystallographically independent water molecules act as proton donors, whereas both chloride anions and the oxygen atoms of both water molecules act as proton acceptors.

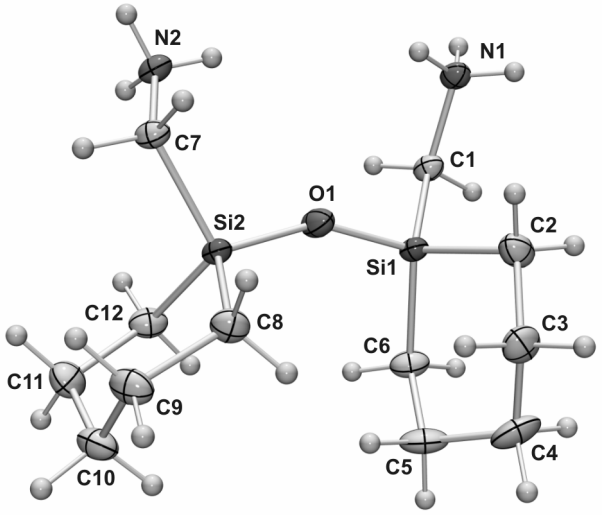


Figure 27. Structure of the dication in the crystal of **145**·2H_2O. Selected bond distances (Å) and angles (deg): Si1–O1 1.6317(9), Si2–O1 1.6360(9), Si1–C1 1.8826(12), Si1–C2 1.8574(14), Si1–C6 1.8677(12), Si2–C7 1.8859(12), Si2–C8 1.8589(13), Si2–C12 1.8584(13), Si1–O1–Si2 152.05(6), O1–Si1–C1 107.67(5), O1–Si1–C2 110.54(6), O1–Si1–C6 111.88(6), O1–Si2–C7 106.47(5), O1–Si2–C8 112.94(6), O1–Si2–C12 111.04(6), C1–Si1–C2 112.33(6), C1–Si1–C6 109.22(6), C2–Si1–C6 105.25(6), C7–Si2–C8 108.66(6), C7–Si2–C12 111.11(6), C8–Si2–C12 106.67(6).

11.18 1,1'-(Oxybis-1-silacyclobutane-1,1-diyl)bis(2,4,6-trimethoxybenzene) (146)

Suitable single crystals of **146** were obtained from the mother liquor of the crystallization of compound **74**. After evaporation of the solvent of this solution under ambient conditions (humid air, 20 °C), a few crystals formed at the surface of the liquid phase.[81] Compound **146** crystallizes in the space group *Pbcn*. The asymmetric unit contains half of the molecule (symmetry transformations used to generate equivalent atoms: #1 –x + 2, y, –z +½). The arrangement of the *Si*-2,4,6-TMOP moieties may be ascribed to a π stacking effect (Figure 28). Apart from that, similar considerations as discussed for **61**, **62**, **74**, **75**, **103**, and **104** apply to compound **146** concerning the Si···O contacts between the silicon atom and the oxygen atoms in the *ortho*-methoxy groups and the conformation of the silacyclobutane ring skeleton; cf. Sections 11.9 and 11.11 (p. 51 and 53).

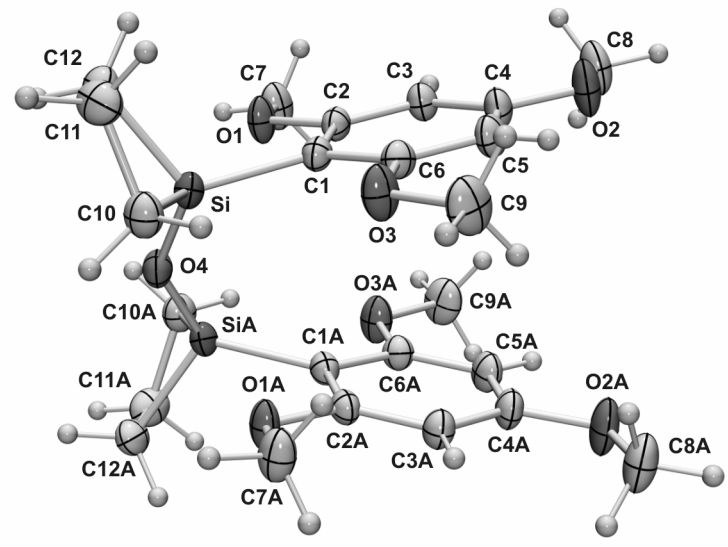


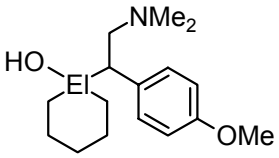
Figure 28. Molecular structure of **146** in the crystal (probability level of displacement ellipsoids 50%). Selected interatomic distances (Å) and bond angles (deg): Si–C1 1.8767(13), Si–C10 1.8735(15), Si–C12 1.8730(14), Si–O4 1.6321(6), Si···C11 2.3756(16), Si···O1 2.8795(10), Si···O3 3.1008(11), C1–Si–C10 119.43(6), C1–Si–C12 114.77(6), C1–Si–O4 110.02(6), C10–Si–C12 79.70(7), C10–Si–O4 115.19(6), C12–Si–O4 114.96(6). The O4 oxygen atom lies on a special position (1.000, 0.374, 0.250), and the molecule shows C_2 symmetry.

12 Summary

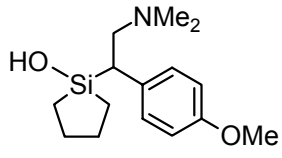
This work describes (i) the synthesis of sila-analogs (C/Si-exchange) and silicon-containing derivatives of the drugs venlafaxine and bexarotene, the GnRH antagonist AG-045572, and the allosteric modulator W84, (ii) a partial synthesis of sila-gabapentin, and (iii) the development of the *Si*-2,4,6-trimethoxyphenyl (*Si*-2,4,6-TMOP) moiety as a novel protecting group in organosilicon chemistry and its application in the synthesis of chlorotris(chloromethyl)silane and tris(chloromethyl)methoxysilane.

12.1 Sila-venlafaxine and derivatives

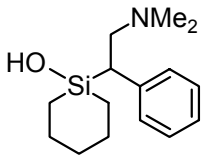
In context with the synthesis of a sila-analog and silicon-containing derivatives of the serotonin/noradrenaline reuptake inhibitor venlafaxine (**12a**), racemic and non-racemic sila-venlafaxine (*rac*-**12b**, (*R*)-**12b**, and (*S*)-**12b**), its racemic derivatives *rac*-**13** and *rac*-**15**, and its racemic prodrugs *rac*-**16**, *rac*-**17**, *rac*-**18**, and *rac*-**18**·HCl were prepared. Compound *rac*-**12b** was prepared by three different preparation protocols.



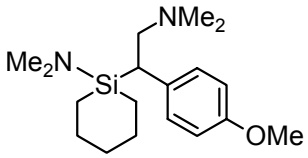
El = C: *rac*-Venlafaxine (*rac*-**12a**)
El = Si: *rac*-Sila-venlafaxine (*rac*-**12b**)



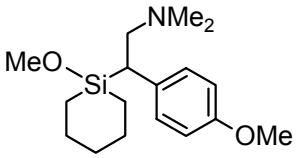
rac-**13**



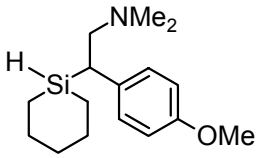
rac-**15**



rac-**16**

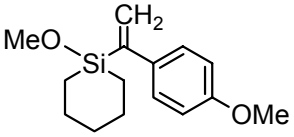


rac-**17**

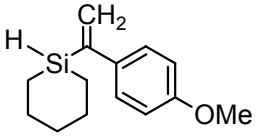


rac-**18**

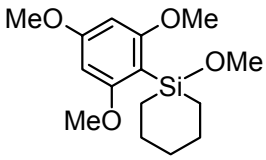
In the course of these syntheses, the intermediates **59**–**63**, **66**, **67**, *rac*-**68**, **78**, **79**, and *rac*-**80** were prepared.



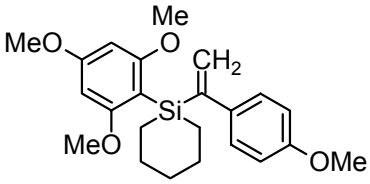
59



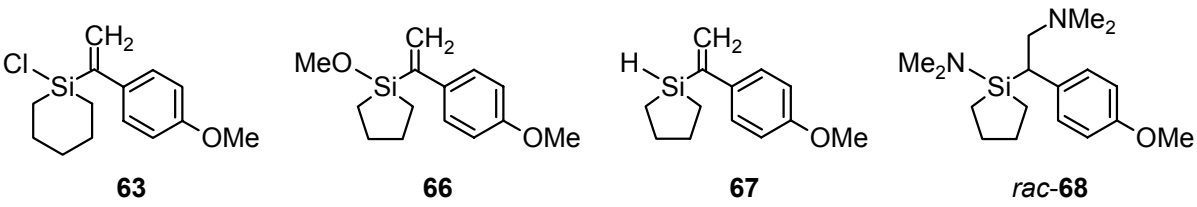
60



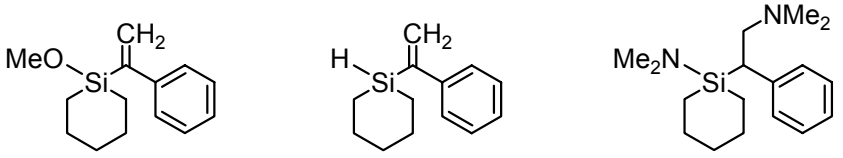
61



62

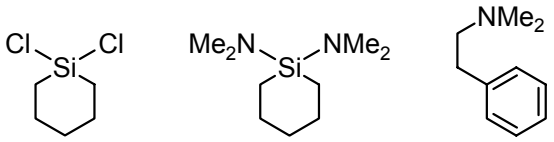


63 **66** **67** ***rac*-68**



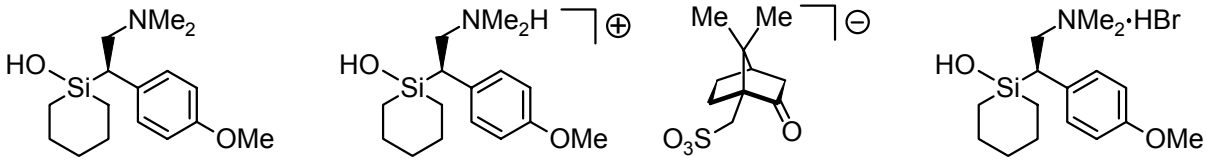
78 **79** ***rac*-80**

In addition, compound **81** was obtained in admixture with **82** in the synthesis of *rac*-**15**, and pure **81** was prepared from the known compound **55** (**82** is commercially available).

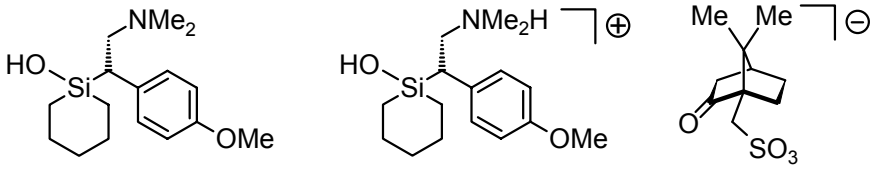


55 **81** **82**

The sila-venlafaxine enantiomers (*R*)-**12b** and (*S*)-**12b** were prepared from *rac*-**12b** by resolution of the racemate using (+)- or (–)-camphor-10-sulfonic acid ((+)- or (–)-CSA) as the resolving agent *via* (*R*)-**12b**·(+)-CSA and (*S*)-**12b**·(–)-CSA as the isolated intermediates, and the enantiomeric purities of (*R*)-**12b** and (*S*)-**12b** were determined by ^{1}H NMR spectroscopy in the presence of (*R*)-(–)-1-(9-anthryl)-2,2,2-trifluoroethanol ((*R*)-(–)-TFAE) as a chiral solvating agent (in both cases, only one enantiomer of **12b** was detected; probe, NCH_3 resonance). The absolute configuration of (*R*)-**12b** was determined by single-crystal X-ray diffraction using the hydrobromide (*R*)-**12b**·HBr.

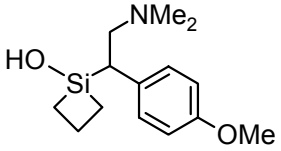


(*R*)-**12b** (*R*)-**12b**·(+)-CSA (*R*)-**12b**·HBr

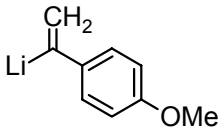


(*S*)-**12b** (*S*)-**12b**·(−)-CSA

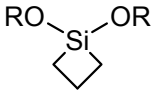
In the attempts to synthesize the sila-venlafaxine derivative *rac*-**14**, the novel silacyclobutane derivatives **72**–**76** were prepared, and compound **77** was obtained from the reaction of **76** with $HNMe_2$/[$LiNMe_2$].



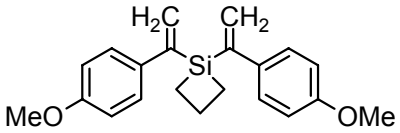
rac-**14**



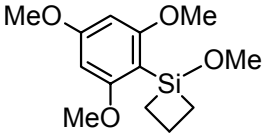
58



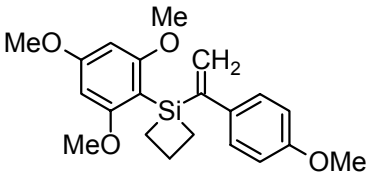
R = Me: **70**
R = ^{i}Pr: **71**
R = ^{t}Bu: **72**



73



74



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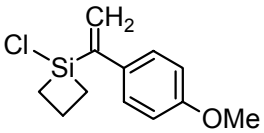

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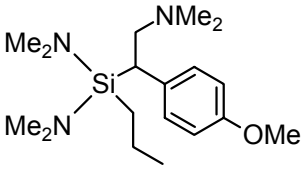
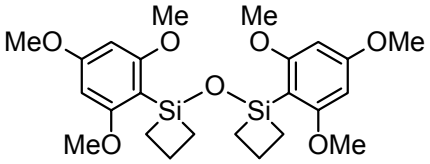


77

The selectivity problems which were encountered in the reactions of **70**–**72** with **58** (twofold substitution of the alkoxy groups to give compound **73**) lead to the development of the *Si*-2,4,6-trimethoxyphenyl (*Si*-2,4,6-TMOP) moiety as a novel protecting group in organosilicon chemistry, which in turn was used for developing an alternative synthesis of *rac*-sila-venlafaxine (*rac*-**12b**) (see above) and applied to the syntheses of chlorotris(chloromethyl)silane (**23**) and tris(chloromethyl)methoxysilane (**24**) (see below).

The hydrochlorides of *rac*-**12b**, (*R*)-**12b**, (*S*)-**12b**, *rac*-**13**, and *rac*-**15** were prepared to obtain water-soluble compounds for their pharmacological characterization, and compounds *rac*-**12b**·HCl, *rac*-**13**·HCl, and *rac*-**15**·HCl were studied for their *in vitro* serotonin, noradrenaline, and dopamine reuptake inhibition efficacy.

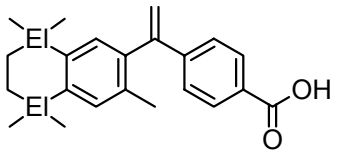
All compounds synthesized were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si (and partially ^{15}N)) and elemental analyses, and compounds *rac*-**12b**·HCl, (*R*)-**12b**·HBr, *rac*-**13**, *rac*-**15**, *rac*-**15**·HCl, **61**, **62**, **74**, **75**, and the disiloxane **146** (obtained by hydrolysis of **74** and subsequent condensation) were additionally characterized by single-crystal X-ray diffraction. Furthermore, the syntheses of *rac*-**12b**·HCl, (*R*)-**12b**·HCl, and (*S*)-**12b**·HCl were scaled up to scales of tens of grams.



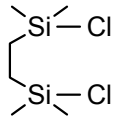
146

12.2 Disila-bexarotene

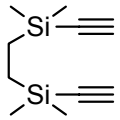
Disila-bexarotene (**21b**), a silicon analog of the retinoid bexarotene (**21a**), was synthesized *via* the intermediates **84**–**89**. 1,2-Bis(ethynyldimethylsilyl)ethane (**84**) has already been reported in the literature (preparation from **83** using ethynylmagnesium bromide), whereas the use of sodium acetylide for the reaction **83** → **84** was established within this work and represents a more cost-effective way for the preparation of **84** compared to the use of ethynylmagnesium bromide.



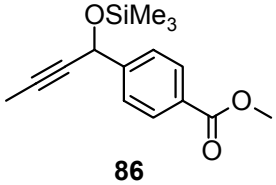
El = C: Bexarotene (**21a**)
El = Si: Disila-bexarotene (**21b**)



83



84



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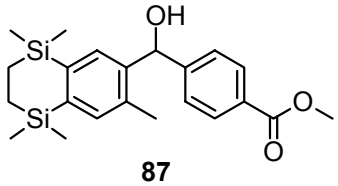

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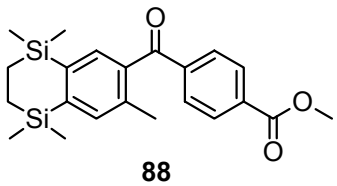
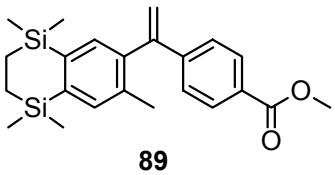


88

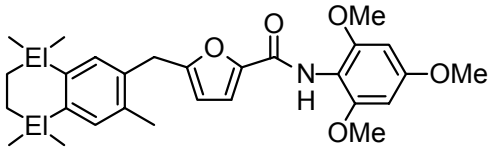


89

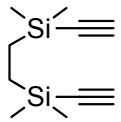
The target compound **21b** and all the intermediates were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si) and elemental analyses, and compounds **21a**, **21b**, and **89** were additionally characterized by single-crystal X-ray diffraction. The synthesis of **21b** was scaled up successfully to a scale of ca. 30 g.

12.3 Disila-AG045572

The first attempt to synthesize disila-AG-045572 (**22b**), a disila-analog of the non-peptide GnRH antagonist AG-045572 (**22a**), started from compound **91**, which was reacted successfully with **84** in a cobalt-catalyzed ($CpCo(CO)_2$) Vollhardt cyclization to give **93**. Surprisingly, **93** was deprotonated twice upon treatment with one molar equivalent of various common lithiation reagents (e.g., *n*-BuLi/TMEDA) under various reaction conditions (reaction control by silylation with chlorotrimethylsilane followed by GC/EI MS analysis). Monolithiation (which would give **94**) was never observed.



El = C: AG-045572 (**22a**)
El = Si: Disila-AG-045572 (**22b**)



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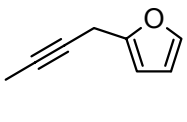
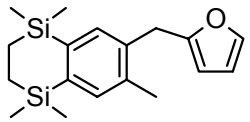


91



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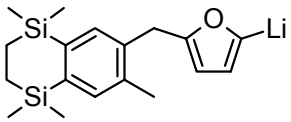
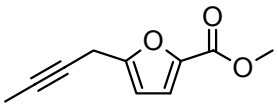


94

Although this result prevented the synthesis of disila-AG-045572 (**22b**) by this route, the preparation of **93** was the first successful synthesis of a molecule with a 3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl moiety starting from **84**, and this method was then, in turn, applied by Amedis Pharmaceuticals Ltd., Cambridge, U.K. to a Vollhardt cyclization using **84** and **97** as the starting materials, which enabled the synthesis of **22b** *via* **98** and **99** using a reaction of **99** with thionyl chloride and then with **101** in the final step.



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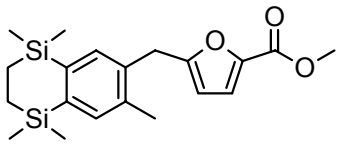

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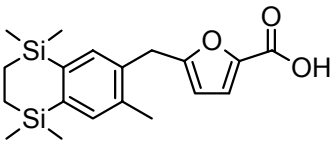
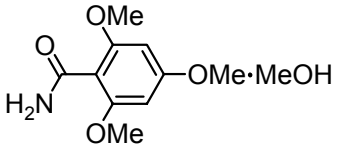


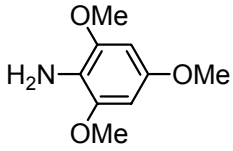
99

These methods which had been developed jointly in cooperation with Amedis Pharmaceuticals Ltd., Cambridge, U.K. were then finally optimized in this work regarding yield and purity of the intermediates **97**–**99** and of the target compound **22b**, and additional methods for the preparation of **22b** starting from **99** and using dicyclohexylcarbodiimide (DCC) instead of thionyl chloride or starting from **98** and using a reagent prepared from **101**·HCl and trimethylaluminum were developed as well in this work, thereby leading to a pronounced improvement of the total yield of this synthesis.

The known compound **101** as well as **101**·HCl were prepared starting from **100**·MeOH by a Hofmann rearrangement using potassium hypochlorite, which represents a novel and cost-effective method for the preparation of **101**.



100·MeOH

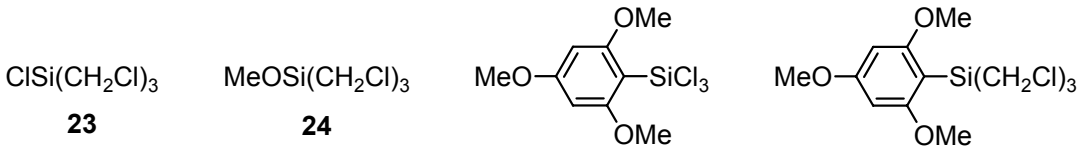


101

The target compound **22b** and all the intermediates were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{15}N (only in the case of **22b**), ^{29}Si) and elemental analyses, and compounds **22b** and **99** were additionally characterized by single-crystal X-ray diffraction.

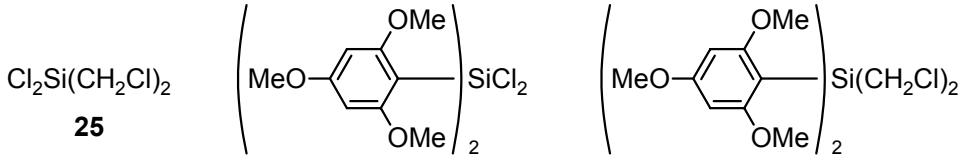
12.4 (Chloromethyl)silanes

The *Si*-2,4,6-TMOP group, which had been developed as a novel protecting group in organosilicon chemistry in context with the synthesis of sila-venlafaxine, was applied successfully to the synthesis of chlorotris(chloromethyl)silane (**23**) and tris(chloromethyl)methoxysilane (**24**) *via* the intermediates trichloro(2,4,6-trimethoxyphenyl)silane (**102**) and tris(chloromethyl)(2,4,6-trimethoxyphenyl)silane (**103**).



23 **24** **102** **103**

In an attempt to synthesize dichlorobis(chloromethyl)silane (**25**) using the *Si*-2,4,6-TMOP group, dichlorobis(2,4,6-trimethoxyphenyl)silane (**104**) was prepared. However, the further transformation of **104** with $BrCH_2Cl$/*n*-Buli to the intermediate **105** failed, which prevented the synthesis of **25** by this route.



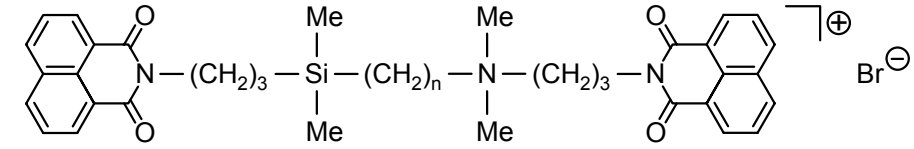
25 **104** **105**

The target compounds **23** and **24** and all the intermediates were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si) and elemental analyses, and compounds **103** and **104** were additionally characterized by single-crystal X-ray diffraction.

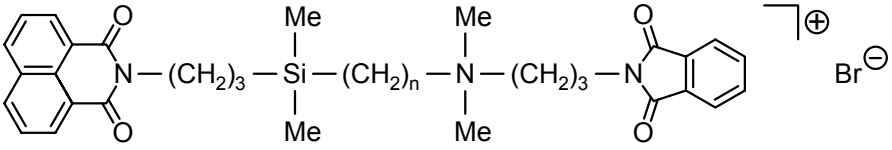
12.5 Silicon-based allosteric modulators of muscarinic M_2 receptors

In continuation of earlier studies of silicon-based allosteric modulators of muscarinic M_2 receptors, compounds **26**–**28**, **31**–**50**, *rac*-**51**, *rac*-**52**, and **53** (isolated as **53**·HCl) were synthesized. In addition, the hitherto unknown intermediates **114**, **117**–**126**, *rac*-**127**, and *rac*-**132** were prepared.

n	Cpd. No.
4	**26**
5	**27**
6	**28**



n	Cpd. No.
4	**31**
5	**32**
6	**33**



n	Cpd. No.
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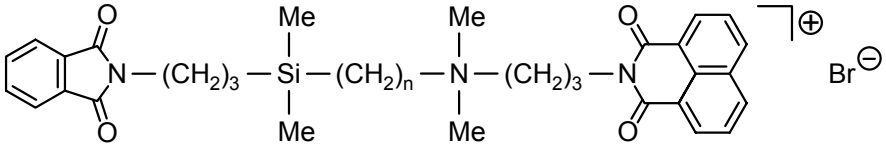
5	**35**
6	**36**



n	Cpd. No.
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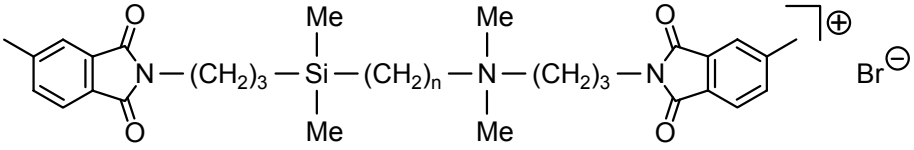
5	**38**
6	**39**



n	Cpd. No.
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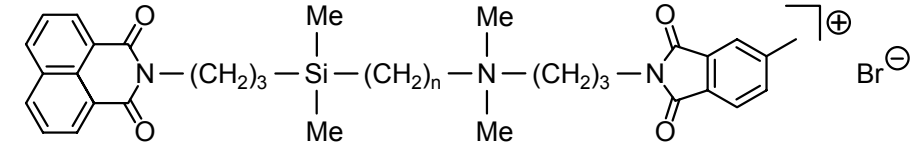
5	**41**
6	**42**



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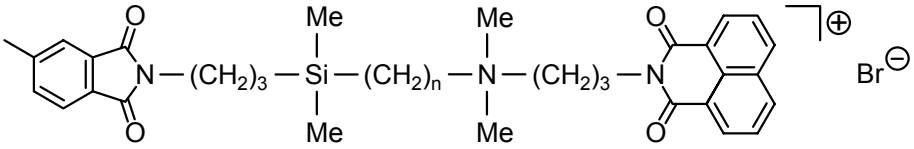
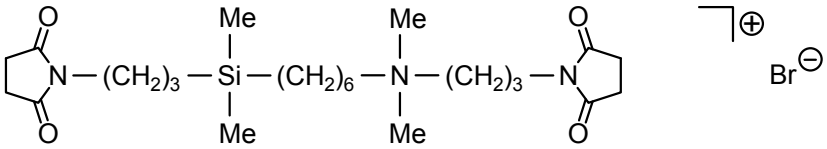
5	**44**
6	**45**



Cpd. No.
46



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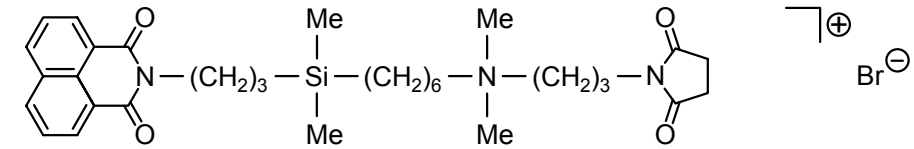
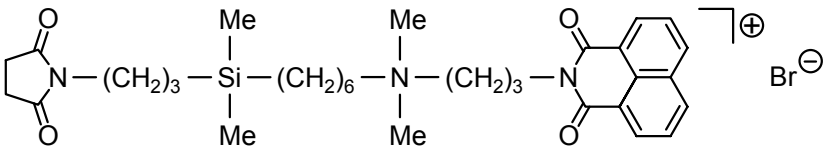
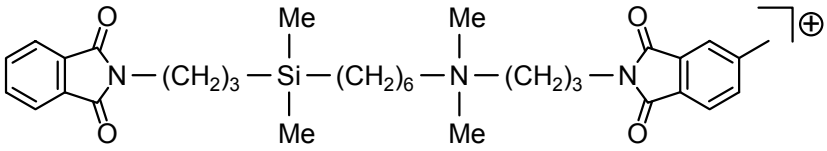
47



Cpd. No.
48





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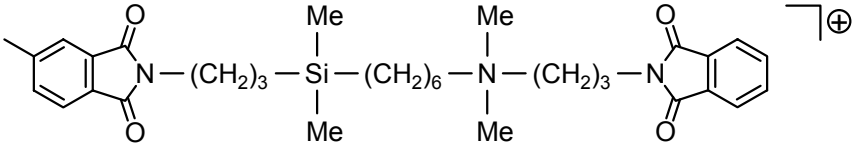

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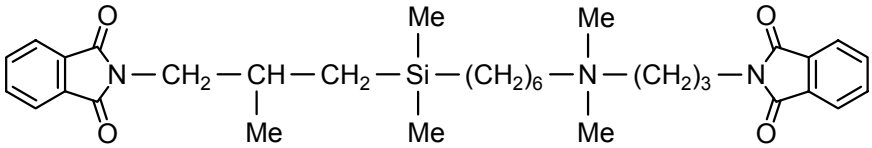
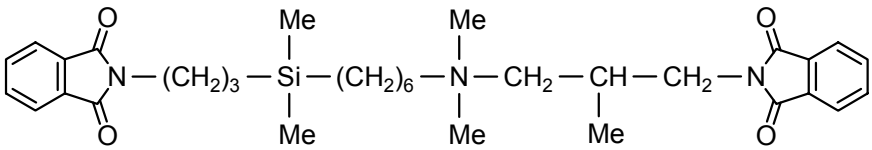
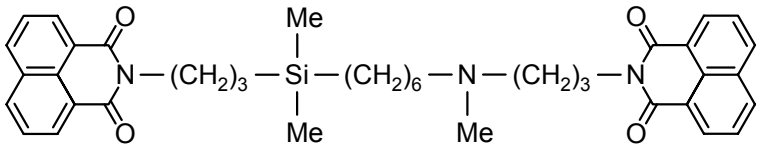


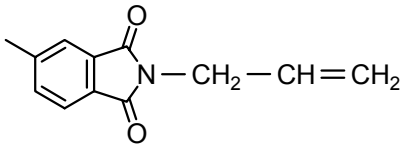
rac-**51**



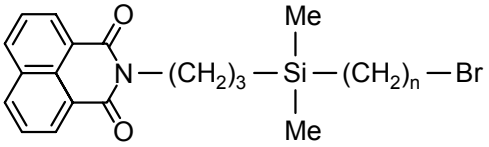
rac-**52**

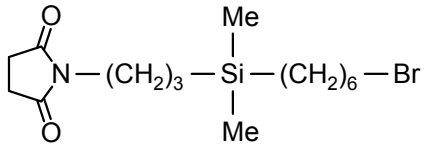


53

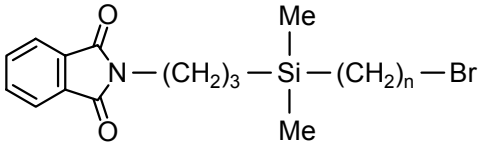


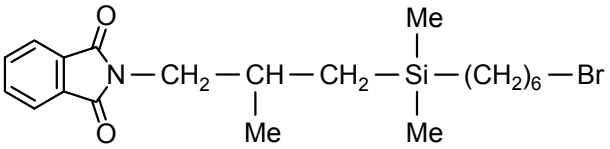
114

	n	Cpd. no.
	4	**117**
	5	**118**
	6	**119**

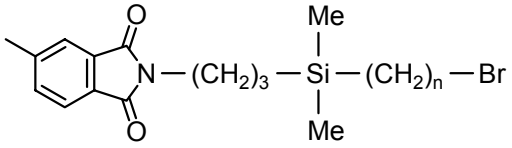


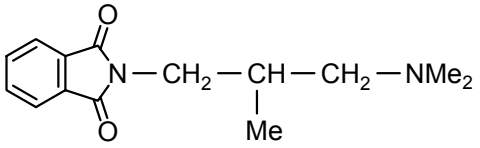
126

	n	Cpd. no.
	4	**120**
	5	**121**
	6	**122**



rac-**127**

	n	Cpd. no.
	4	**123**
	5	**124**
	6	**125**

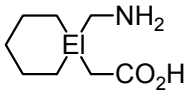


rac-**132**

All target compounds and the intermediates were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{15}N (partially), ^{29}Si) and elemental analyses. Compounds **27**, **28**, **32**, **33**, **35**, **36**, **39**, **42**, **45**–**50**, *rac*-**51**, *rac*-**52**, and **53** (tested as the hydrochloride **53**·HCl) were studied for their allosteric effects on [^{3}H]NMS dissociation and [^{3}H]NMS equilibrium binding at muscarinic M_2 receptors of porcine heart homogenates (SAR studies). For most of these compounds, positive cooperativity was found in this test system (exceptions: compounds **46** and **48**), i.e., an enhancement of [^{3}H]NMS equilibrium binding was observed.

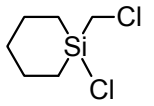
12.6 β-Carbonylsilanes

In context with the partial synthesis of sila-gabapentin (**54b**) (a sila-analog of the antiepileptic gabapentin (**54a**)), a series of β-carbonylsilanes with a silacyclohexane backbone was synthesized (compounds **137**–**144**), starting from **136**, and several methods for functional group transformations within the organic side chains of these molecules in the very presence of the sensitive Si–$CH_2C(O)R$ bond were established.



El = C: Gabapentin (**54a**)
El = Si: Sila-gabapentin (**54b**)

Treatment of **140** with triphenylphosphine (Staudinger reaction), followed by acidic hydrolysis, gave the disiloxane **145** (Si–$CH_2C(O)R$ bond cleavage), the dihydrate **145**·2H_2O of which was characterized by single-crystal X-ray diffraction. Compounds **137**–**145** were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{15}N (partially), ^{29}Si) and elemental analyses.



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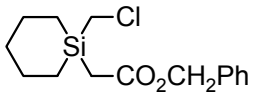

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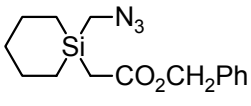

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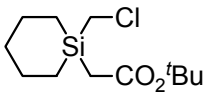

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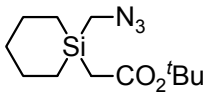

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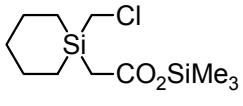

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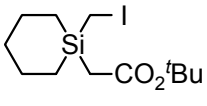

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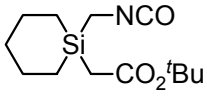

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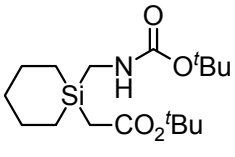

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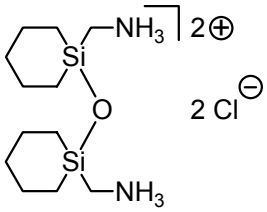


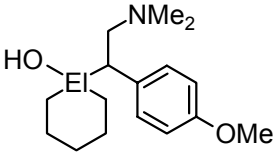
145

13 Zusammenfassung

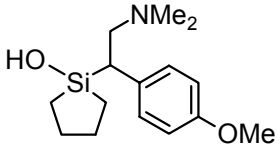
Die vorliegende Arbeit beschreibt (i) die Synthese siliciumhaltiger Analoga (C/Si-Austausch) und siliciumhaltiger Derivate der Wirkstoffe Venlafaxin und Bexarotene, des GnRH Antagonisten AG-045572 und des allosteren Modulators W84, (ii) eine Partialsynthese von Sila-Gabapentin und (iii) die Entwicklung der *Si*-2,4,6-Trimethoxyphenyl-Gruppe (*Si*-2,4,6-TMOP-Gruppe) als neuartige Schutzgruppe in der Organosiliciumchemie und ihre Anwendung in der Synthese von Chlortris(chlormethyl)silan und Tris(chlormethyl)methoxysilan.

13.1 Sila-venlafaxin und Derivative

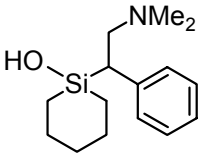
Im Zusammenhang mit der Synthese eines Sila-Analogons und siliciumhaltiger Derivate des Serotonin/Noradrenalin-Wiederaufnahmehemmers Venlafaxin (**12a**) wurden racemisches und nichtracemisches Sila-venlafaxin (*rac*-**12b**, (*R*)-**12b** und (*S*)-**12b**), dessen racemische Derivate *rac*-**13** und *rac*-**15** und dessen racemische „Prodrugs“ *rac*-**16**, *rac*-**17**, *rac*-**18** und *rac*-**18**·HCl dargestellt. Verbindung *rac*-**12b** wurde nach drei verschiedenen präparativen Methoden dargestellt.



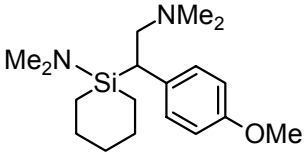
El = C: *rac*-Venlafaxin (*rac*-**12a**)
El = Si: *rac*-Sila-venlafaxin (*rac*-**12b**)



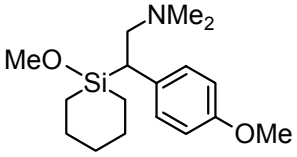
rac-**13**



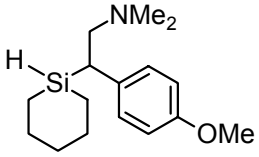
rac-**15**



rac-**16**

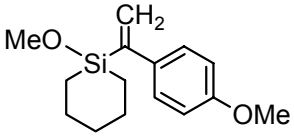


rac-**17**



rac-**18**

Im Verlauf dieser Synthesen wurden die Intermediate **59**–**63**, **66**, **67**, *rac*-**68**, **78**, **79** und *rac*-**80** dargestellt.



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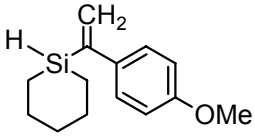

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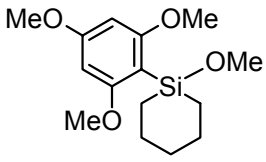

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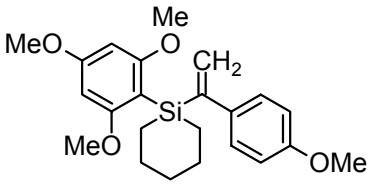

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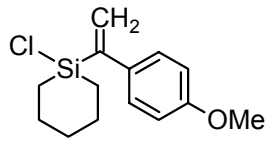

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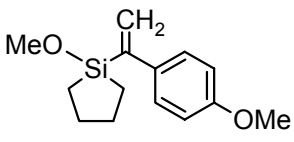

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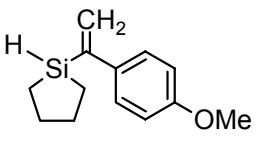

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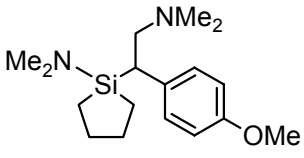
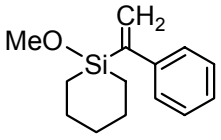


rac-**68**



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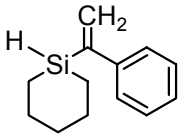

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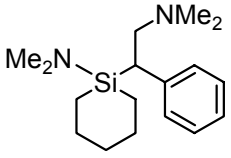
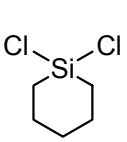


rac-**80**

Ferner wurde **81** bei der Synthese von *rac*-**15** als Gemisch mit **82** erhalten und die reine Verbindung **81** wurde aus der literaturbekannten Verbindung **55** dargestellt (**82** ist als Handelsprodukt verfügbar).



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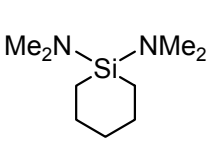

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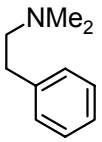
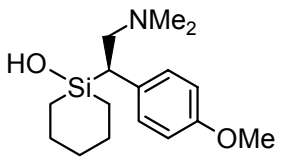
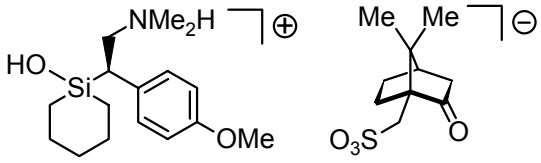


82

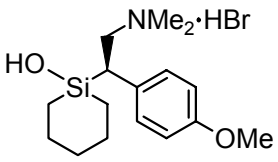
Die Sila-venlafaxin-Enantiomere (*R*)-**12b** und (*S*)-**12b** wurden aus *rac*-**12b** durch Racematspaltung mit (+)- bzw. (–)-Campher-10-sulfonsäure ((+)- bzw. (–)-CSA) als Spaltungsreagenz über die isolierten Intermediate (*R*)-**12b**·(+)-CSA und (*S*)-**12b**·(–)-CSA dargestellt. Die Enantiomerenreinheit von (*R*)-**12b** und (*S*)-**12b** wurde durch ^{1}H-NMR-Spektroskopie in Gegenwart von (*R*)-(–)-1-(9-Anthryl)-2,2,2-trifluorethanol ((*R*)-(–)-TFAE) als chiralem Solvatationsreagenz bestimmt (in beiden Fällen wurde nur ein Enantiomer von **12b** detektiert; Sonde: NCH_3-Resonanz). Die absolute Konfiguration von (*R*)-**12b** wurde durch Einkristall-Röntgenbeugung des Hydrobromids (*R*)-**12b**·HBr ermittelt.



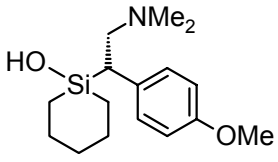
(*R*)-**12b**



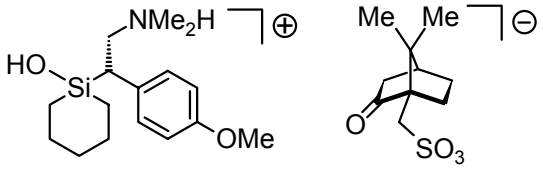
(*R*)-**12b**·(+)-CSA



(*R*)-**12b**·HBr

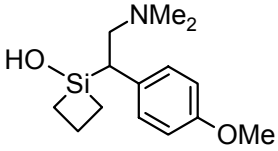


(*S*)-**12b**

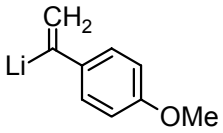


(*S*)-**12b**·(−)-CSA

Bei den Versuchen, das Sila-venlafaxin-Derivat *rac*-**14** zu synthetisieren, wurden die neuartigen Silacyclobutan-Derivate **72**–**76** dargestellt, und Verbindung **77** wurde aus der Reaktion von **76** mit $HNMe_2$/[$LiNMe_2$] erhalten.



rac-**14**



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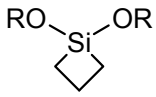
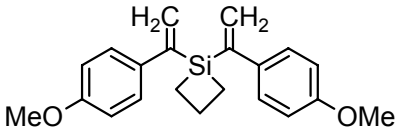


R = Me: **70**
R = ^{i}Pr: **71**
R = ^{t}Bu: **72**



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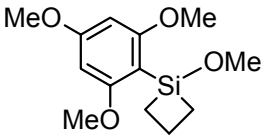

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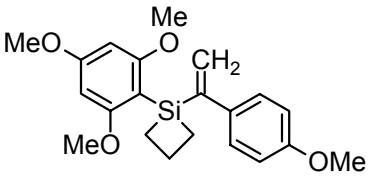

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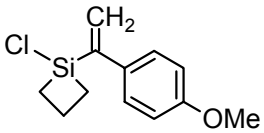

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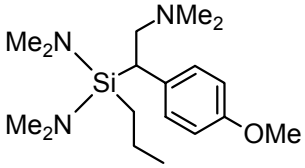
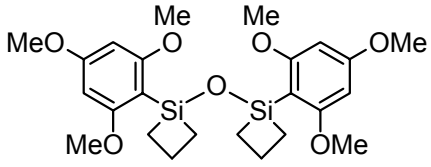


77

Die Selektivitätsprobleme, die sich bei den Reaktionen von **70**–**72** mit **58** stellten (Zweifachsubstitution der Alkoxygruppen, was Verbindung **73** ergab) führten zur Entwicklung der *Si*-2,4,6-Trimethoxyphenyl-Gruppe (*Si*-2,4,6-TMOP-Gruppe) als neuartige Schutzgruppe in der Organosiliciumchemie. Diese Schutzgruppe wurde für die Entwicklung einer alternativen Synthese von *rac*-Sila-venlafaxin (*rac*-**12b**) (siehe oben) sowie zur Synthese von Chlortris(chlormethyl)silan (**23**) und Tris(chlormethyl)methoxysilan (**24**) (siehe unten) verwendet.

Die Hydrochloride der Verbindungen *rac*-**12b**, (*R*)-**12b**, (*S*)-**12b**, *rac*-**13**, and *rac*-**15** wurden dargestellt, um wasserlösliche Verbindungen für deren pharmakologische Charakterisierung zu erhalten. Die Verbindungen *rac*-**12b**·HCl, *rac*-**13**·HCl und *rac*-**15**·HCl wurden hinsichtlich ihrer *in vitro*-Aktivität bezüglich der Wiederaufnahmehemmung von Serotonin, Noradrenalin und Dopamin untersucht.

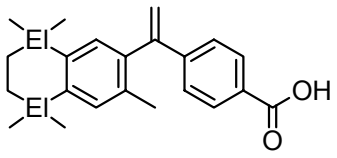
Alle synthetisierten Verbindungen wurden durch NMR-Spektroskopie (^{1}H, ^{13}C, ^{29}Si (und teilweise ^{15}N)) und Elementaranalysen charakterisiert. Zusätzlich wurden die Verbindungen *rac*-**12b**·HCl, (*R*)-**12b**·HBr, *rac*-**13**, *rac*-**15**, *rac*-**15**·HCl, **61**, **62**, **74**, **75** und das Disiloxan **146** (erhalten durch Hydrolyse von **74** und nachfolgende Kondensation) durch Röntgenbeugung an Einkristallen charakterisiert. Des weiteren wurden die Synthesen von *rac*-**12b**·HCl, (*R*)-**12b**·HCl und (*S*)-**12b**·HCl in den zweistelligen Gramm-Bereich hochskaliert.



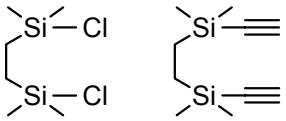
146

13.2 Disila-bexarotene

Disila-bexarotene (**21b**), ein Silicium-Analogon des Retinoids Bexarotene (**21a**), wurde über die Intermediate **84**–**89** dargestellt. 1,2-Bis(ethinyldimethylsilyl)ethan (**84**) wurde bereits in der Literatur beschrieben (Darstellung aus **83** unter Verwendung von Ethinylmagnesiumbromid), wohingegen die Verwendung von Natriumacetylid für die Reaktion **83** → **84** im Rahmen dieser Arbeit etabliert wurde und – verglichen mit der Verwendung von Ethinylmagnesiumbromid – einen kostengünstigeren Weg für die Darstellung von **84** repräsentiert.

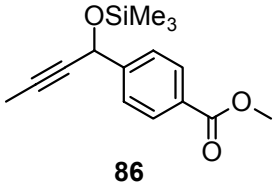


El = C: Bexarotene (**21a**)
El = Si: Disila-bexarotene (**21b**)

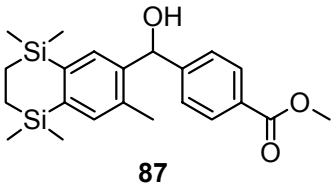


83

84



86



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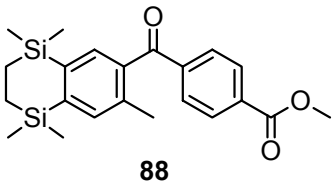

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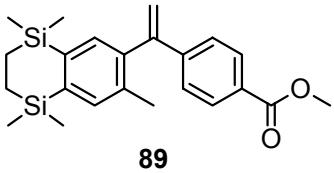
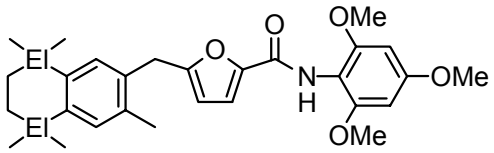


89

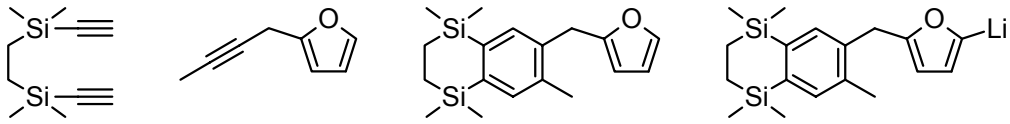
Die Zielverbindung **21b** und die genannten Intermediate wurden durch NMR-Spektroskopie (^{1}H, ^{13}C, ^{29}Si) und Elementaranalysen charakterisiert. Zusätzlich wurden die Verbindungen **21a**, **21b** und **89** durch Röntgenbeugung an Einkristallen charakterisiert. Die Synthese von **21b** wurde erfolgreich auf ca. 30 g hochskaliert.

13.3 Disila-AG-045572

Der erste Versuch zur Synthese von Disila-AG-045572 (**22b**), ein Disila-Analogon des nichtpeptidischen GnRH-Antagonisten AG-045572 (**22a**), erfolgte ausgehend von Verbindung **91**, welche erfolgreich mit **84** in einer kobaltkatalysierten ($CpCo(CO)_2$) Vollhardt-Cyclisierung zu **93** umgesetzt wurde. Überraschenderweise wurde **93** bei Behandlung mit einem Mol-Äquivalent verschiedener gängiger Lithiierungsreagenzien (z.B. *n*-BuLi/TMEDA) unter variierenden Reaktionsbedingungen zweifach deprotoniert (Reaktionskontrolle mittels Silylierung mit Chlortrimethylsilan und nachfolgende GC/EI-MS Analytik). Monolithiierung (die zu **94** führen würde) wurde nie beobachtet.

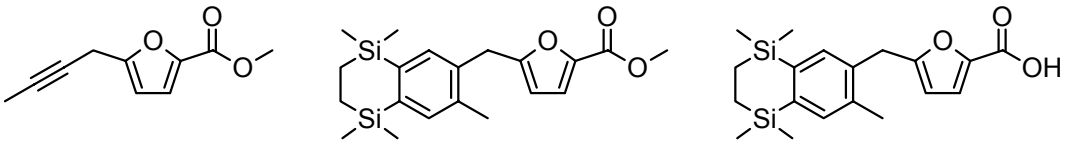


El = C: AG-045572 (**22a**)
El = Si: Disila-AG-045572 (**22b**)



84 **91** **93** **94**

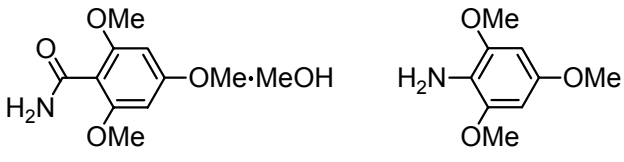
Obwohl dieses Ergebnis die Synthese von Disila-AG-045572 (**22b**) auf diesem Weg verhinderte, war die Darstellung von **93** die erste erfolgreiche Synthese eines Moleküls mit einer 3,5,5,8,8-Pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl-Gruppe ausgehend von **84**. Diese Methode wurde nachfolgend von Amedis Pharmaceuticals Ltd., Cambridge, U.K., auf eine Vollhardt-Cyclisierung unter Verwendung von **84** und **97** als Ausgangsmaterialien angewendet, was die Synthese von **22b** *via* **98** und **99** unter Verwendung einer Reaktion von **99** mit Thionylchlorid und nachfolgend mit **101** im letzten Schritt ermöglichte.



97 **98** **99**

Diese Methoden, die zusammen mit Amedis Pharmaceuticals Ltd., Cambridge, U.K., entwickelt worden waren, wurden dann schließlich im Rahmen dieser Arbeit bezüglich der Ausbeute und Reinheit der Zwischenstufen **97**–**99** und der Zielverbindung **22b** optimiert. Ebenso wurden im Rahmen dieser Arbeit weitere Methoden zur Darstellung von **22b** entwickelt, ausgehend von **99** unter Verwendung von Dicyclohexylcarbodiimid (DCC) anstelle von Thionylchlorid oder ausgehend von **98** unter Verwendung eines Reagenzes dargestellt aus **101**·HCl und Trimethylaluminium, was zu einer deutlichen Verbesserung der Gesamtausbeute dieser Synthese führte.

Die bekannte Verbindung **101** sowie **101**·HCl wurden ausgehend von **100**·MeOH durch Hofmann-Umlagerung unter Verwendung von Kaliumhypochlorit dargestellt, was einen neuen und kostengünstigen Weg für die Darstellung von **101** repräsentiert.

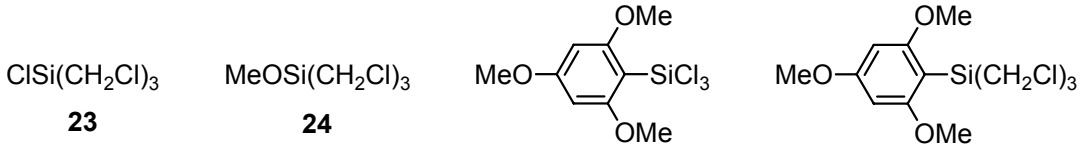


100·MeOH **101**

Die Zielverbindung **22b** und die genannten Zwischenstufen wurden durch NMR-Spektroskopie (^{1}H, ^{13}C, ^{15}N (nur im Falle von **22b**), ^{29}Si) und Elementaranalysen charakterisiert. Zusätzlich wurden die Verbindungen **22b** und **99** durch Röntgenbeugung an Einkristallen charakterisiert.

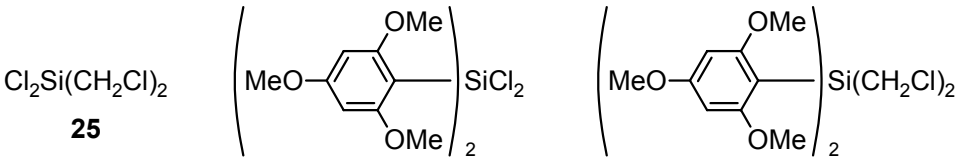
13.4 (Chlormethyl)silane

Die *Si*-2,4,6-TMOP-Gruppe, die im Zusammenhang mit der Sila-venlafaxin-Synthese als neuartige Schutzgruppe für die Organosiliciumchemie entwickelt worden war, wurde erfolgreich auf die Synthese von Chlortris(chlormethyl)silan (**23**) und Tris(chlormethyl)methoxysilan (**24**) über die Intermediate Trichlor(2,4,6-trimethoxyphenyl)silan (**102**) und Tris(chlormethyl)(2,4,6-trimethoxyphenyl)silan (**103**) angewendet.



23 **24** **102** **103**

Im Zuge von Bemühungen, Dichlorbis(chlormethyl)silan (**25**) unter Verwendung der *Si*-2,4,6-TMOP-Gruppe zu synthetisieren, wurde Dichlorbis(2,4,6-trimethoxyphenyl)silan (**104**) dargestellt. Jedoch schlug dessen weitere Umsetzung mit $BrCH_2Cl$/*n*-BuLi zu **105** fehl, was die Synthese von **25** auf diesem Weg verhinderte.

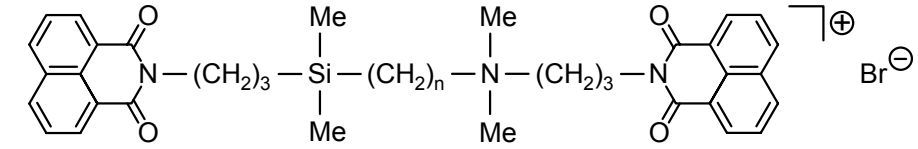
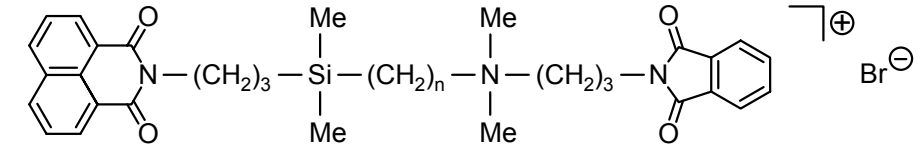
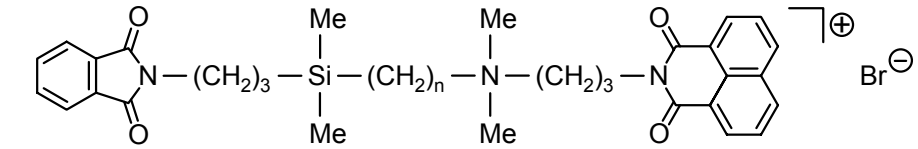
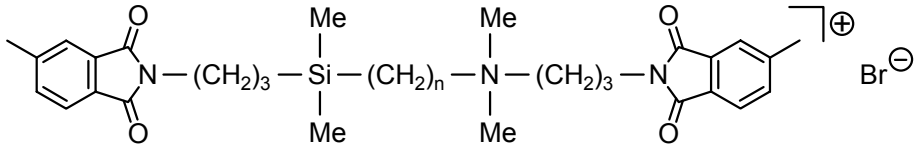
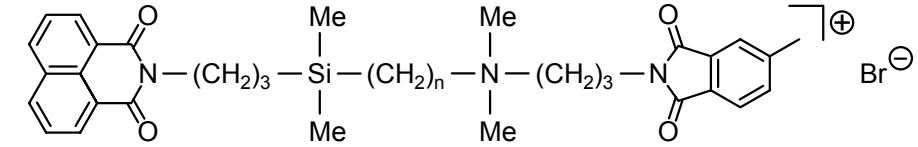
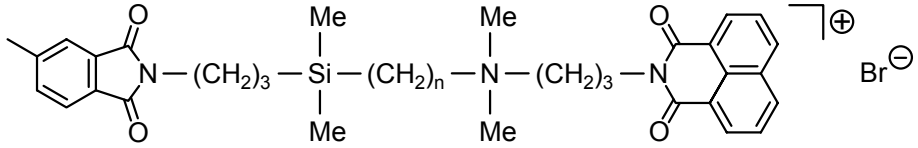
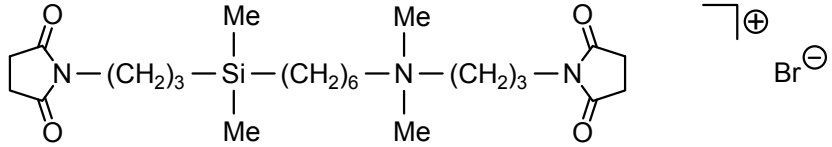
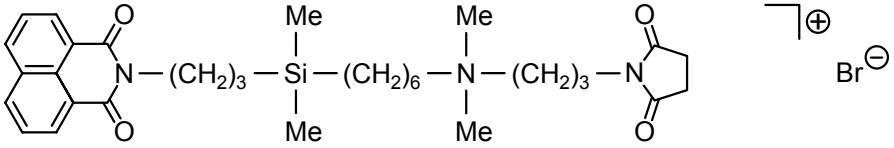
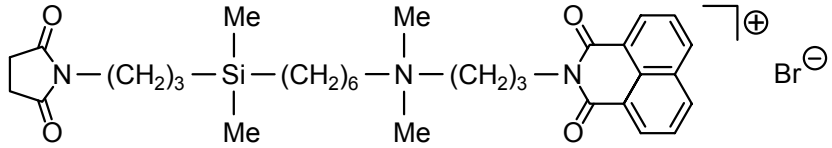


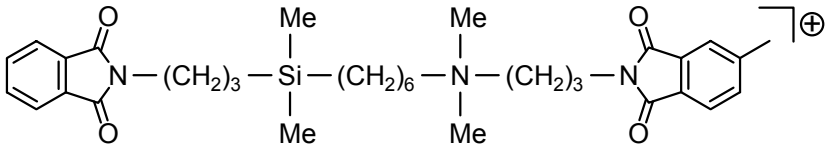
25 **104** **105**

Die Zielverbindungen **23** und **24** und die genannten Zwischenstufen wurden durch NMR-Spektroskopie (^{1}H, ^{13}C, ^{29}Si) und Elementaranalysen charakterisiert. Zusätzlich wurden die Verbindungen **103** und **104** durch Röntgenbeugung an Einkristallen charakterisiert.

13.5 Allostere M_2-Muscarinrezeptor-Modulatoren auf Siliciumbasis

Im Rahmen der Weiterführung früherer Studien über allostere M_2-Muscarinrezeptor-Modulatoren auf Siliciumbasis wurden die Verbindungen **26**–**28**, **31**–**50**, *rac*-**51**, *rac*-**52** und **53** (isoliert als **53**·HCl) synthetisiert. Ferner wurden die bisher nicht literaturbekannten Zwischenstufen **114**, **117**–**126**, *rac*-**127** und *rac*-**132** dargestellt.

	n	Verb.-Nr.
	4	**26**
	5	**27**
	6	**28**
	4	**31**
	5	**32**
	6	**33**
	4	**34**
	5	**35**
	6	**36**
	4	**37**
	5	**38**
	6	**39**
	4	**40**
	5	**41**
	6	**42**
	4	**43**
	5	**44**
	6	**45**
		**46**
		**47**
		**48**



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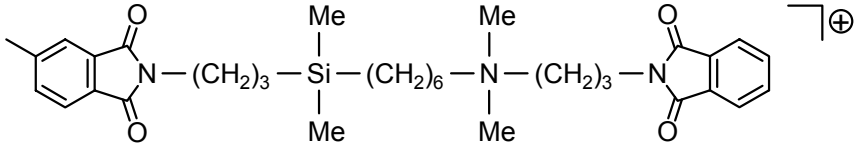

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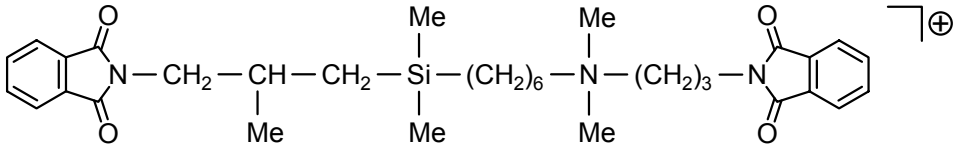
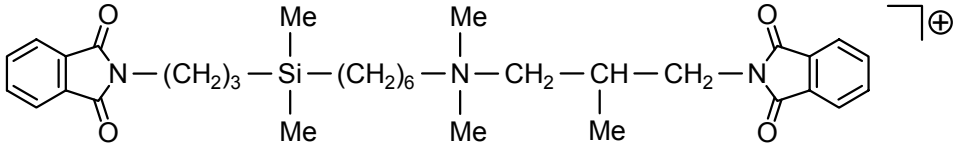
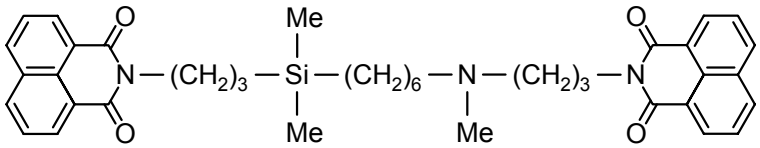


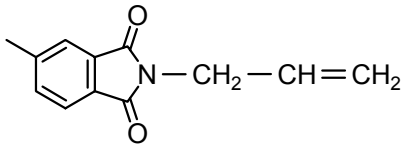
rac-**51**



rac-**52**

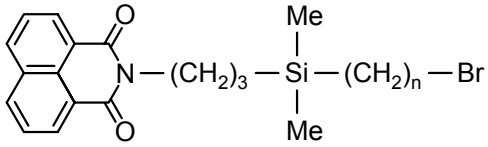


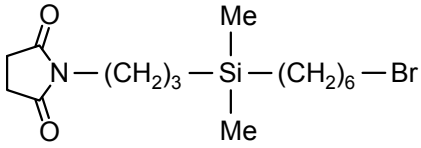
53



114

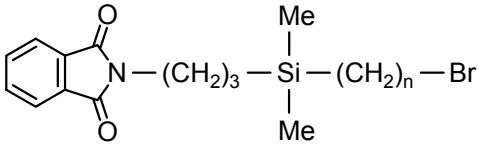
n	Verb.-Nr.
4	**117**
5	**118**
6	**119**

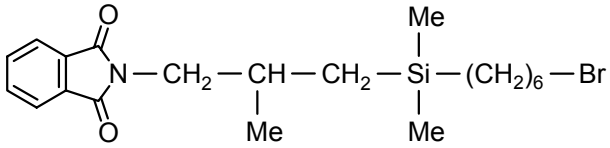




126

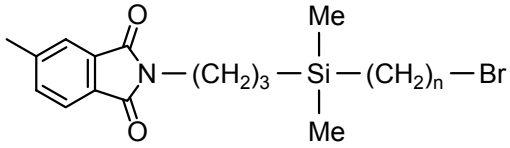
n	Verb.-Nr.
4	**120**
5	**121**
6	**122**

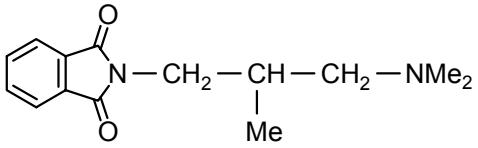




rac-**127**

n	Verb.-Nr.
4	**123**
5	**124**
6	**125**



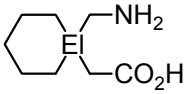


rac-**132**

Alle Zielverbindungen und Zwischenstufen wurden durch NMR-Spektroskopie (^{1}H, ^{13}C, ^{15}N (partiell), ^{29}Si) und Elementaranalysen charakterisiert. Die Verbindungen **27**, **28**, **32**, **33**, **35**, **36**, **39**, **42**, **45**–**50**, *rac*-**51**, *rac*-**52** und **53** (als Hydrochlorid **53**·HCl getestet) wurden hinsichtlich ihres allosterischen Effekts auf die [^{3}H]NMS-Dissoziation und [^{3}H]NMS-Gleichgewichtsbindung an muscarinischen M_2-Rezeptoren von Herzhomogenaten des Hausschweins untersucht („SAR"-Studien). Für die meisten dieser Verbindungen wurde positive Kooperativität in diesem Testsystem gefunden (Ausnahmen: Verbindungen **46** und **48**), d.h. eine Steigerung der [^{3}H]NMS-Gleichgewichtsbindung wurde beobachtet.

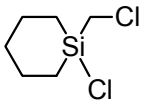
13.6 β-Carbonylsilane

Im Zusammenhang mit der Partialsynthese von Sila-gabapentin (**54b**) (ein Sila-Analogon des Antiepileptikums Gabapentin (**54a**)) wurde ausgehend von **136** eine Reihe von β-Carbonylsilanen mit einem Silacyclohexan-Grundgerüst synthetisiert (Verbindungen **137**–**144**). Mehrere Methoden für Umwandlungen funktioneller Gruppen in den organischen Seitenketten dieser Moleküle in Gegenwart der empfindlichen Si–CH_2C(O)R-Bindung wurden etabliert.

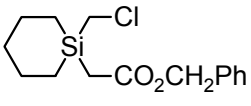


El = C: Gabapentin (**54a**)
El = Si: Sila-gabapentin (**54b**)

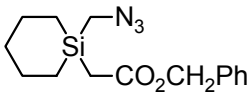
Behandlung von **140** mit Triphenylphosphin (Staudinger-Reaktion) – gefolgt durch saure Hydrolyse – ergab das Disiloxan **145** (Si–CH_2C(O)R-Bindungsbruch), dessen Dihydrat **145**·2H_2O durch Röntgenbeugung an Einkristallen charakterisiert wurde. Die Verbindungen **137**–**145** wurden durch NMR-Spektroskopie (^{1}H, ^{13}C, ^{15}N (partiell), ^{29}Si) und Elementaranalysen charakterisiert.



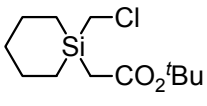
136



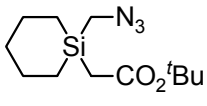
137



138



139



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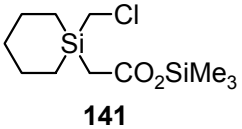
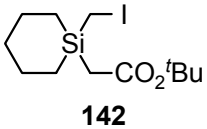


141



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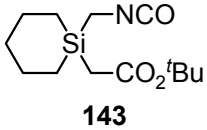
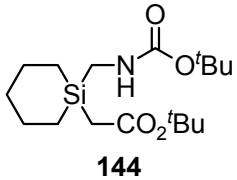


143



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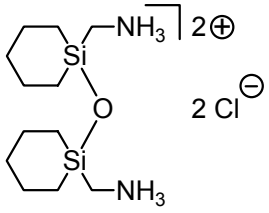

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14 Experimental section

14.1 General procedures

Syntheses. All syntheses (except for the hydrolyses yielding *rac*-**12b**, *rac*-**13**, *rac*-**15**, **21b**, **99**, and **146** and the preparation of most hydrochlorides,[82] hydrobromides, and camphor-10-sulfonates) were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under dry nitrogen. A Büchi GKR 50 apparatus was used for the bulb-to-bulb distillations. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in open glass capillaries except for compounds **102** and **104**, for which sealed glass capillaries were used.

NMR spectroscopy. The ^{1}H, ^{13}C, ^{15}N, and ^{29}Si solution NMR spectra were recorded on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{15}N, 30.4 MHz; ^{29}Si, 59.6 MHz). $CDCl_3$, CD_2Cl_2, C_6D_6, [D_8]THF, or [D_6]DMSO were used as the solvent. Unless otherwise stated, spectra were recorded at 22 °C. Chemical shifts were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24; $CDCl_3$), $CDCl_3$ (^{13}C, δ 77.0; $CDCl_3$), $CHDCl_2$ (^{1}H, δ 5.32; CD_2Cl_2), CD_2Cl_2 (^{13}C, δ 53.8; CD_2Cl_2), C_6HD_5 (^{1}H, δ 7.28; C_6D_6), C_6D_6 (^{13}C, δ 128.0; C_6D_6), [D_7]THF (^{1}H, δ 1.73; [D_8]THF), [D_8]THF (^{13}C, δ 25.3; [D_8]THF), [D_5]DMSO (^{1}H, δ 2.49; [D_6]DMSO), [D_6]DMSO (^{13}C, δ 39.5; [D_6]DMSO), external formamide (^{15}N, δ –268.0; $CDCl_3$, CD_2Cl_2, C_6D_6, [D_6]DMSO), or external TMS (^{29}Si, δ 0; $CDCl_3$, CD_2Cl_2, C_6D_6, [D_8]THF, [D_6]DMSO). The reported chemical shifts refer to the δ scale and are given in [ppm]. Analysis and assignment of the ^{1}H NMR data was supported by $^{1}H,^{1}H$, $^{13}C,^{1}H$, $^{15}N,^{1}H$, and $^{29}Si,^{1}H$ correlation experiments and partially by simulations using the WIN-DAISY software package (version 4.05, Bruker).[83] Assignment of the ^{13}C NMR data was supported by DEPT 90, DEPT 135, and $^{13}C,^{1}H$ correlation experiments. The $^{2}J_{HH}$ coupling constants reported for the C=CH_2 groups represent absolute values. Abbreviations for the signal assignments: Fu = Furyl; Me-phth = 4-methylphthalimido; Naph = 3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl; Naph′ = 3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydro-2-naphthyl; Naphth = 1,8-naphthalimido; Phe = 1-carboxyphenyl; Phe′ = 1-(methoxycarbonyl)phenyl; Phth = phthalimido; Succ = succinimido; Tri = 2,4,6-trimethoxyphenyl.

Mass spectrometry. The GC/EI MS studies were performed with a ThermoQuest gas chromatograph MS-8060 (phenomenex Zebron ZB-1 capillary column, 15 m, i.d. 0.25 mm, film thickness 0.25 μm; injector, split (1:10), 220 °C; carrier gas, helium) and a ThermoQuest mass spectrometer TRIO 1000 (EI MS, 70 eV).

Polarimetry. Specific optical rotations were determined with a Jasco P-1030 Polarimeter using a 10 cm cuvette; dichloromethane (spectroscopy grade, stabilized with amylene (25 mg/L); Riedel-deHaën, art. no. 34908) was used as the solvent.

IR spectroscopy. The IR spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer. The sample preparations are specified in the respective preparation protocols.

Determination of enantiomeric purities. Compounds *rac*-**12b**, (*R*)-**12b**, or (*S*)-**12b** (10.0 mg, 34.1 μmol) and (*R*)-(–)-TFAE (26.4 mg, 95.6 μmol; 2.8 molar equivalents) were dissolved in $CDCl_3$ (700 μL), and the solutions were studied at 22 °C by ^{1}H NMR spectroscopy (300.1 MHz). The ^{1}H NMR resonance signals for the NCH_3 groups were used as the probe to determine the enantiomeric purities of (*R*)-**12b** and (*S*)-**12b**. When measuring a sample of *rac*-**12b**, base line separation for the NCH_3 signals was found for the diastereomeric solvates (*R*)-**12b**·(*R*)-(–)-TFAE (δ 2.13 ppm) and (*S*)-**12b**·(*R*)-(–)-TFAE (δ 2.10 ppm).

14.2 Syntheses

Preparation of {6-[dimethyl(3-phthalimidopropyl)silyl]hexyl}dimethyl(3-phthalimidopropyl)ammonium bromide (10).[60] Compound **10** was prepared from **122** (1.25 g, 3.05 mmol) and **129** (868 mg, 3.74 mmol) in ethanol (12 mL) and was purified according to a procedure very similar to the workup Protocol A (see pp. 96–97) (for details, see ref. 13) (precipitation for 1 day at 20 °C, then for 3 days at –25 °C) to give **10** in 56% yield as an amorphous white solid (1.10 g, 1.71 mmol); mp 174–175 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.07 (s, 6 H, SiCH_3), 0.39–0.52 (m, 4 H, CCH_2SiCH_2C), 1.13–1.33 (m, 6 H, $SiCH_2(CH_2)_3(CH_2)_2N^+$), 1.49–1.65 (m, 4 H, $NCH_2CH_2CH_2Si$ and $Si(CH_2)_4CH_2CH_2N^+$), 1.95–2.10 (m, 2 H, $N^+CH_2CH_2CH_2N$), 2.97 (s, 6 H, N^+CH_3), 3.16–3.26 (m, 2 H, $Si(CH_2)_5CH_2N^+$), 3.27–3.38 (m, 2 H, $N^+CH_2(CH_2)_2N$), 3.52 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, $NCH_2(CH_2)_2Si$), 3.64 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, $N^+(CH_2)_2CH_2N$), 7.79–7.90 (m, 8 H, *H*-3/*H*-6, *H*-4/*H*-5, Phth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 ($SiCH_3$), 11.7 ($N(CH_2)_2CH_2Si$), 14.4 ($SiCH_2(CH_2)_5N^+$), 21.58 ($Si(CH_2)_4CH_2CH_2N^+$ or $N^+CH_2CH_2CH_2N$), 21.59 ($Si(CH_2)_4CH_2CH_2N^+$ or $N^+CH_2CH_2CH_2N$), 22.5 ($NCH_2CH_2CH_2Si$), 23.1 ($SiCH_2CH_2(CH_2)_4N^+$), 25.4 ($Si(CH_2)_3CH_2(CH_2)_2N^+$), 32.4 ($Si(CH_2)_2CH_2(CH_2)_3N^+$), 34.6 ($N^+(CH_2)_2CH_2N$), 40.4 ($NCH_2(CH_2)_2Si$), 49.9 ($N^+CH_3$), 60.6 ($N^+CH_2(CH_2)_2N$), 63.1 ($Si(CH_2)_5CH_2N^+$), 122.98 (*C*-3/*C*-6, Phth), 123.04 (*C*-3/*C*-6, Phth), 131.5 (*C*-1/*C*-2, Phth), 131.7 (*C*-1/*C*-2, Phth), 134.39 (*C*-4/*C*-5, Phth), 134.41 (*C*-4/*C*-5, Phth), 167.9 (*C*=O, Phth), 168.0 (*C*=O, Phth). ^{15}N NMR ([D$_6$]DMSO): δ –328 (N^+), –221 ($N^+(CH_2)_3N$), –218 ($N(CH_2)_3Si$). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for $C_{32}H_{44}BrN_3O_4Si$: C, 59.80; H, 6.90; N, 6.54. Found: C, 59.5; H, 6.9; N, 6.5.

Preparation of *rac*-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclohexan-1-ol (*rac*-sila-venlafaxine, *rac*-12b).

Protocol A. A 2.7 M solution of *n*-butyllithium in *n*-heptane (35 mL, 94.5 mmol of *n*-BuLi) was added dropwise at –50 °C within 10 min to a stirred solution of dimethylamine (21.6 g, 479 mmol) in THF (100 mL). The resulting mixture was warmed to –10 °C within 2 h and then cooled to –40 °C, followed by dropwise addition of **60** (20.0 g, 86.1 mmol) within a period of 15 min (evolution of hydrogen; rise in temperature from –40 to –35 °C). The resulting stirred yellow solution was warmed to –20 °C within 2 h and then kept undisturbed at –26 °C for 16 h. Subsequently, the solvent was removed under reduced pressure in a water bath (5–15 °C) until a residual volume of 50 mL was obtained. This solution was diluted with diethyl ether (200 mL) and then added in one single portion at 0 °C to a stirred two-phase mixture of diethyl ether (50 mL) and 2 M potassium acetate/acetic acid buffer (pH 4.5) (300 mL). The pH of the aqueous phase changed to pH 7.2 within 10 min and was readjusted to pH 5.0 by addition of small portions of glacial acetic acid. The mixture was stirred at 0 °C for a further 1 h, with the pH of the aqueous phase remaining constantly at pH 5.0 during this time. The aqueous layer was separated, the organic phase was extracted with 1 M potassium acetate/acetic acid buffer (pH 5.0) (3 × 100 mL), and the aqueous solutions were combined. Diethyl ether (150 mL) was added, and the pH of the aqueous phase was adjusted to pH 10.5 by addition of small portions of a saturated aqueous potassium carbonate solution. The organic layer was separated, the aqueous phase was extracted with diethyl ether (5 × 100 mL), and the organic extracts were combined, followed by addition of *n*-hexane (200 mL). The solvent was removed under reduced pressure in a water bath (5–15 °C) until a residual volume of 100 mL was obtained, whereupon residual water separated from the organic phase (formation of a two-phase system). The organic layer was separated, the aqueous phase was extracted with *n*-hexane (2 × 100 mL), and the organic solutions were combined. The solvent was removed completely under reduced pressure in a water bath (5–15 °C) to give a colorless oil. Crystallization of this oil from *n*-pentane (400 mL) at –26 °C using seed crystals (obtained by cooling of a solution of oily *rac*-**12b** (3.20 g) in *n*-pentane (5 mL) to –26 °C) afforded *rac*-**12b** in 90% yield as a colorless crystalline solid (22.8 g, 77.7 mmol) (isolated by quick decantation of the cold solvent, followed by drying in vacuo (0.001 mbar, 20 °C, 6 h)); mp 33 °C. ^{1}H NMR ($CDCl_3$): δ 0.44–0.78, 1.00–1.15, and 1.19–1.69 (m, 10 H, Si(CH_2)$_5$), 2.29 (s, 6 H, NCH_3), 2.44 (δ_C), 2.52 (δ_A), and 3.12 (δ_B), (3 H, $^{2}J_{AB}$ = –12.1 Hz, $^{3}J_{AC}$ = 5.0 Hz, $^{3}J_{BC}$ = 12.1 Hz, SiCH_CC$H_A$$H_B$N), 3.75 (s, 3 H, OC$H_3$), 5.6 (br s, 1 H, SiO*H*), 6.75–6.83 (m, 2 H, *H*-3/*H*-5, Aryl), 6.91–6.98 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR ($CDCl_3$): δ 12.1 (Si*C*H$_2$C), 14.2 (Si*C*H$_2$C), 24.06 (SiCH$_2$*C*H$_2$C), 24.13 (SiCH$_2$*C*H$_2$C), 29.4 (Si(CH$_2$)$_2$*C*H$_2$C), 32.6 (Si*C*HC$_2$), 45.4 (N*C*H$_3$), 55.2 (O*C*H$_3$), 61.8 (N*C*H$_2$C), 113.8 (*C*-3/*C*-5, Aryl),

128.2 (*C*-2/*C*-6, Aryl), 133.0 (*C*-1, Aryl), 157.1 (*C*-4, Aryl). ^{15}N NMR ($CDCl_3$): δ –353. ^{29}Si NMR ($CDCl_3$): δ 10.3. Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.48; H, 9.27; N, 4.77. Found: C, 65.5; H, 9.3; N, 4.8.

Protocol B. A 2.5 M solution of *n*-butyllithium in *n*-hexane (4.2 mL, 10.5 mmol of *n*-BuLi) was added dropwise at –50 °C within 2 min to a stirred solution of dimethylamine (6.91 g, 153 mmol) in THF (20 mL). The resulting mixture was warmed to –25 °C within 90 min and then cooled to –40 °C, followed by dropwise addition of a solution of **63** (1.35 g, 5.06 mmol) in THF (8 mL) within a period of 4 min. The stirred mixture was warmed to –20 °C within 2 h and then stirred at 0 °C for a further 1 h (complete conversion **63** → *rac*-**16**; GC control). Subsequently, the mixture was warmed to 20 °C within 1 h, and the solvent was removed under reduced pressure at 5–15 °C until a residual volume of ca. 10 mL was obtained. This solution was diluted with diethyl ether (20 mL) and then added in one single portion at 0 °C to a stirred two-phase mixture of diethyl ether (10 mL) and 2 M potassium acetate/acetic acid buffer (pH 4.5, 50 mL). The pH of the aqueous phase changed to pH 5.7 within ca. 10 min and was readjusted to pH 5.0 by addition of small portions of glacial acetic acid. The mixture was stirred at 0 °C for a further 1 h, with the pH of the aqueous phase remaining constantly at pH 5.0 during this time. The aqueous layer was separated, the organic phase was extracted with 1 M potassium acetate/acetic acid buffer (pH 5.0, 3 × 20 mL), and the aqueous solutions were combined. Diethyl ether (20 mL) was added to the combined aqueous extracts, and the pH of the aqueous phase was adjusted to pH 10.5 by addition of small portions of a saturated aqueous potassium carbonate solution. The organic layer was separated, the aqueous phase was extracted with diethyl ether (4 × 20 mL), and the organic extracts were combined, followed by addition of *n*-hexane (80 mL). The solvent was removed under reduced pressure at 5–15 °C until a residual volume of ca. 50 mL was obtained, whereupon residual water separated from the organic phase (formation of a two-phase system). The organic layer was separated, the aqueous phase was extracted with *n*-hexane (2 × 15 mL), and the organic solutions were combined. The solvent was removed completely under reduced pressure at 5–15 °C to give a colorless oil, which was dried in vacuo (0.001 mbar, 20 °C, 1 h) and then crystallized from *n*-pentane (25 mL; crystallization at –26 °C over a period of 3 days) using seed crystals (see Protocol A). The product was isolated by quick decantation of the cold solvent, followed by drying in vacuo (0.001 mbar, 20 °C, 6 h) to give *rac*-**12b** in 86% yield as a colorless crystalline solid (1.27 g, 4.33 mmol); mp 33 °C. Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.48; H, 9.27; N, 4.77. Found: C, 65.6; H, 9.5; N, 4.7. For NMR data, see Protocol A.

Protocol C. *Solution A:* A 2.0 M ethereal hydrogen chloride solution (12.5 mL, 25.0 mmol of HCl) was added to a solution of **62** (9.39 g, 23.6 mmol) in diethyl ether (25 mL) in one single

portion at 0 °C, and the resulting mixture was stirred at 0 °C for 10 min (complete conversion **62** → **63**; GC control). The solvent and the excess hydrogen chloride were removed under reduced pressure at 5–15 °C, and the oily residue was dried in vacuo (0.001 mbar, 20 °C, 10 min) and then dissolved in THF (25 mL). *Solution B:* A 2.5 M solution of *n*-butyllithium in *n*-hexane (20.0 mL, 50.0 mmol of *n*-BuLi) was added dropwise at –50 °C within 10 min to a stirred solution of dimethylamine (13.7 g, 304 mmol) in THF (50 mL). The resulting mixture was warmed to –10 °C within 2 h.

Solution B was then cooled to –40 °C, followed by dropwise addition of *Solution A* within a period of 4 min. The resulting stirred mixture was warmed to –20 °C within 2 h and then stirred at 0 °C for a further 2 h (complete conversion **63** → *rac*-**16**; GC control). Subsequently, the solution was warmed to 20 °C within 1 h, and the solvent was removed under reduced pressure at 5–15 °C until a residual volume of ca. 35 mL was obtained. This solution was diluted with diethyl ether (50 mL) and then added in one single portion at 0 °C to a stirred two-phase mixture of diethyl ether (50 mL) and 2 M potassium acetate/acetic acid buffer (pH 4.5, 100 mL). The pH of the aqueous phase changed to pH 6.0 within ca. 10 min and was readjusted to pH 5.0 by addition of small portions of glacial acetic acid. The mixture was stirred at 0 °C for a further 1 h, with the pH of the aqueous phase remaining constantly at pH 5.0 during this time. The aqueous layer was separated, the organic phase was extracted with 1 M potassium acetate/acetic acid buffer (pH 5.0, 3 × 50 mL), and the aqueous solutions were combined and then extracted with diethyl ether (100 mL). The aqueous layer was separated, the organic phase was extracted with 1 M potassium acetate/acetic acid buffer (pH 5.0, 2 × 50 mL), and the aqueous solutions were combined. Diethyl ether (100 mL) was added to the combined aqueous extracts, and the pH of the aqueous phase was adjusted to pH 10.5 by addition of small portions of a saturated aqueous potassium carbonate solution. The organic layer was separated, the aqueous phase was extracted with diethyl ether (5 × 150 mL), and the organic extracts were combined, followed by addition of *n*-hexane (200 mL). The solvent was removed under reduced pressure at 5–15 °C until a residual volume of ca. 150 mL was obtained, whereupon residual water separated from the organic phase (formation of a two-phase system). The organic layer was separated, the aqueous phase was extracted with *n*-hexane (2 × 50 mL), and the organic solutions were combined. The solvent was removed completely under reduced pressure at 5–15 °C to give a colorless oil, which was dried in vacuo (0.001 mbar, 20 °C, 1 h) and then crystallized from *n*-pentane (110 mL; crystallization at –26 °C over a period of 3 days) using seed crystals (see Protocol A). The product was isolated by quick decantation of the cold solvent, followed by drying in vacuo (0.001 mbar, 20 °C, 6 h) to give *rac*-**12b** in 86% yield as a colorless crystalline solid (5.98

g, 20.4 mmol); mp 33 °C. Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.48; H, 9.27; N, 4.77. Found: C, 65.4; H, 9.1; N, 4.7. For NMR data, see Protocol A.

Preparation of (*R*)-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclohexan-1-ol ((*R*)-sila-venlafaxine, (*R*)-12b).

(a) Preparation of seed crystals of (*R*)-sila-venlafaxine·(+)-10-camphorsulfonic acid ((*R*)-12b·(+)-CSA). A solution of (+)-10-camphorsulfonic acid ((+)-CSA) (792 mg, 3.41 mmol) in acetone (25 mL) was added at 0 °C to a solution of *rac*-**12b** (1.00 g, 3.41 mmol) in acetone (25 mL). After the mixture was shaken briefly, it was kept undisturbed at 0 °C. After ca. 10 min, thin needle-shaped crystals precipitated. A further 40 mL of acetone were added immediately, and the mixture was then kept undisturbed at 4 °C for 2 days. The precipitate was isolated by filtration, washed with acetone (20 mL), and then recrystallized twice from boiling acetone (45 mL; crystallization at 4 °C over a period of 2 days). (To leave a few seed crystals, the solid was not allowed to dissolve completely in both recrystallization steps.) The product was finally isolated by filtration, washed with acetone (3 mL), and dried in vacuo (0.001 mbar, 20 °C, 6 h) to give 629 mg of a colorless crystalline solid. This material (long, very thin needles) was used as seed crystals in the following protocol.

(b) Preparation of (*R*)-sila-venlafaxine·(+)-10-camphorsulfonic acid ((*R*)-12b·(+)-CSA). A solution of (+)-CSA (4.55 g, 19.6 mmol) in acetone (120 mL) was added at 20 °C to a solution of *rac*-**12b** (5.75 g, 19.6 mmol) in acetone (375 mL). After the mixture was shaken briefly, it was kept undisturbed at 4 °C for 2 h. Subsequently, a few seed crystals (see above) were added, and the mixture was then kept undisturbed at 4 °C for 2 days. The resulting precipitate was isolated by filtration, washed with acetone (2 × 20 mL), and then recrystallized twice from boiling acetone (280 mL; crystallization at 4 °C over a period of 2 days). (To leave a few seed crystals, the solid was not allowed to dissolve completely in these recrystallization steps.) The product was isolated and washed as described above and finally dried in vacuo (0.001 mbar, 20 °C, 6 h) to give (*R*)-**12b**·(+)-CSA in 30% yield (related to *rac*-**1b**) as a colorless crystalline solid (3.10 g, 5.90 mmol); mp 164 °C; $[\alpha]_{589}^{20}$ = +7.7 (*c* = 2.50, CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 0.40–0.75, 0.49–0.69, 0.99–1.17, 1.29–1.45, and 1.47–1.72 (m, 12 H, Si(CH_2)$_5$ and CCH_OH$_P$CH_QH$_R$CCH$_S$H$_T$SO$_3^-$, CSA), 0.83 (s, 3 H, CCH_3, CSA), 1.06 (s, 3 H, CCH_3, CSA), 1.86 (d, 1 H, $^2J_{XY}$ = –18.2 Hz, (CHCH_XH$_Y$C=O, CSA), 1.93–2.03 (m, 1 H, CCH$_O$$H_PCH_QH_RCCH_SH_TSO_3^-$, CSA), 2.03–2.08 (m, 1 H, C$_3$CH, CSA), 2.25–2.36 (m, 1 H, CHCH$_X$$H_Y$C=O, CSA), 2.49–2.62 (m, 1 H, CCH$_O$H$_P$CH$_Q$$H_RCCH_SH_TSO_3^-$, CSA), 2.7 (br s, 6 H, HNCH_3), 2.74 (δ_S) and 3.20 (δ_T) ($^2J_{ST}$ = –14.6 Hz, 2 H, CC$H_S$$H_TSO_3^-$, CSA), 2.84 ($\delta_C$), 3.47 ($\delta_A$), and 3.84 ($\delta_B$) ($^2J_{AB}$ = –13.3 Hz, $^3J_{AC}$ = 10.6 Hz, $^3J_{BC}$ = 2.5 Hz, 3 H, SiCH_CC$H_A$$H_B$N), 3.77 (s, 3 H, OC$H_3$), 5.1 (br s, 1 H, SiO$H$), 6.82–6.89 (m, 2 H, *H*-3/*H*-5, Aryl), 7.08–7.15 (m, 2 H,

H-2/*H*-6, Aryl), 10.0 (br s, 1 H, N*H*). ^{13}C NMR (CD_2Cl_2): δ 11.7 (Si*C*H_2C), 13.5 (Si*C*H_2C), 19.9 (2 C) (C(*C*H_3)$_2$, CSA), 24.3 (SiCH$_2$*C*H_2C), 24.4 (SiCH$_2$*C*H_2C), 25.0 (CCH$_2$*C*H_2CCH$_2$SO$_3^-$), 27.3 (C*C*H_2CH$_2$CCH$_2$SO$_3^-$), 29.7 (Si(CH$_2$)$_2$*C*H_2C), 33.7 (Si*C*HC$_2$), 43.1 (C$_3$*C*H, CSA), 43.2 (CH*C*H_2C=O, CSA), 43.5 (br, N*C*H_3), 44.9 (br, N*C*H_3), 47.6 (C*C*H_2SO$_3^-$, CSA), 48.2 (C$_2$*C*Me$_2$, CSA), 55.5 (O*C*H_3), 58.7 (C$_2$*C*CH$_2$SO$_3^-$, CSA), 59.8 (C*C*H_2N), 114.8 (*C*-3/*C*-5, Aryl), 128.7 (*C*-2/*C*-6, Aryl), 131.6 (*C*-1, C_6H_4), 158.2 (*C*-4, Aryl), 217.0 (*C*=O). ^{29}Si NMR (CD_2Cl_2): δ 4.7. Anal. Calcd for $C_{26}H_{43}NO_6SSi$: C, 59.39; H, 8.24; N, 2.66; S, 6.10. Found: C, 59.4; H, 8.2; N, 2.7; S, 6.0.

(c) Preparation of (*R*)-sila-venlafaxine ((*R*)-12b). Diethyl ether (5 mL) was added at 20 °C to a stirred solution of (*R*)-**12b**·(+)-CSA (3.05 g, 5.80 mmol) in water (85 mL), and the pH of the aqueous phase was adjusted to pH 10.5 by addition of a saturated aqueous potassium carbonate solution. The resulting mixture was extracted with diethyl ether (4 × 100 mL), and the organic layers were combined, followed by addition of *n*-hexane (200 mL). The solvent was removed under reduced pressure in a water bath (5–15 °C) until a residual volume of 50 mL was obtained. The mixture was then kept at –20 °C for 3 h (crystallization of the residual water), and the organic supernatant was quickly isolated by decantation and stored separately. The ice was allowed to melt, the resulting aqueous phase was shaken with *n*-hexane (60 mL), and the two-phase system was again kept at –20 °C for 3 h. The decantation procedure was repeated, the organic solutions were combined, and the solvent was removed under reduced pressure in a water bath (5–15 °C). The resulting colorless oil was dissolved in *n*-pentane (35 mL), and the solution was kept undisturbed at –20 °C. After a period of ca. 2–3 h, an oil separated, and a few crystals grew within the oil drops. The mixture was then warmed to 20 °C, whereupon the oil dissolved rapidly, whereas the crystals dissolved only slowly. After most of the crystals were dissolved (except for a few seed crystals), the mixture was again kept undisturbed at –20 °C for 3 days. The resulting product was isolated by decantation and then dried in vacuo (0.001 mbar, 20 °C, 6 h) to give (*R*)-**12b** in 99% yield as a colorless crystalline solid (1.68 g, 5.72 mmol; including workup of the mother liquor by concentrating it to a volume of 10 mL and using the crystallization protocol described above); mp 64–65 °C; $[\alpha]_{589}^{20}$ = –40.3 (*c* = 2.50, CH_2Cl_2). The NMR data of the product were identical with those obtained for *rac*-**12b**. Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.48; H, 9.27; N, 4.77. Found: C, 65.2; H, 9.1; N, 4.7.

Preparation of (*S*)-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclohexan-1-ol ((*S*)-sila-venlafaxine, (*S*)-12b).

(a) Preparation of (*S*)-sila-venlafaxine·(–)-10-camphorsulfonic acid ((*S*)-12b·(–)-CSA). The combined mother liquors obtained in the preparation of (*R*)-**12b**·(+)-CSA (see above) were used to prepare (*S*)-**12b**·(–)-CSA. For this purpose, the mother liquors were concentrated under

reduced pressure, treated with potassium carbonate as described for the preparation of (*R*)-**12b**, and concentrated again, and the oily residue was then reacted with (–)-CSA analogous to the protocol described for the preparation of (*R*)-**12b**·(+)-CSA. Compound (*S*)-**12b**·(–)-CSA was obtained in 32% yield (related to *rac*-**12b**) as a colorless crystalline solid (3.29 g, 6.26 mmol); mp 164 °C; $[\alpha]_{589}^{20}$ = –7.6 (*c* = 2.50, CH_2Cl_2). The NMR data of the product were identical with those obtained for (*R*)-**12b**·(+)-CSA. Anal. Calcd for $C_{26}H_{43}NO_6SSi$: C, 59.39; H, 8.24; N, 2.66; S, 6.10. Found: C, 59.3; H, 7.9; N, 2.4; S, 5.9.

(b) Preparation of (*S*)-sila-venlafaxine ((*S*)-12b). Compound (*S*)-**12b** was prepared from (*S*)-**12b**·(–)-CSA (3.23 g, 6.14 mmol) analogous to the synthesis of (*R*)-**12b** and was isolated in 94% yield as a colorless crystalline solid (1.70 g, 5.79 mmol); mp 64–65 °C; $[\alpha]_{589}^{20}$ = +40.3 (*c* = 2.50, CH_2Cl_2). The NMR data of the product were identical with those obtained for *rac*-**12b**. Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.48; H, 9.27; N, 4.77. Found: C, 65.2; H, 9.1; N, 4.8.

Preparation of *rac*-[2-(1-hydroxy-1-sila-1-cyclohexyl)-2-(4-methoxyphenyl)ethyl]-dimethylammonium chloride (*rac*-sila-venlafaxine hydrochloride, *rac*-12b·HCl). A 2 M ethereal hydrogen chloride solution (23 mL, 46.0 mmol of HCl) was added in one single portion at 20 °C to a stirred solution of *rac*-**12b** (12.9 g, 44.0 mmol) in dichloromethane (200 mL). The resulting solution was cooled to –11 °C, and a few seed crystals (obtained from 20 μL of the reaction mixture by slow evaporation of the solvent at 20 °C) were added. The mixture was kept undisturbed at –11 °C for 1 day and then at –27 °C for a further 1 day. The resulting precipitate was isolated by filtration at –27 °C, washed with ice-cold acetone (20 mL), and dried in vacuo (0.001 mbar, 20 °C, 6 h) to give *rac*-**12b**·HCl in 90% yield (including workup of the mother liquor) as a colorless crystalline solid (13.0 g, 39.4 mmol); mp 160 °C. ^{1}H NMR ([D$_6$]DMSO):[84] δ 0.25–0.41, 0.50–0.69, and 1.13–1.70 (m, 10 H, Si(CH_2)$_5$), 2.56 (δ_M), 2.61 (δ_N), 2.74 (δ_C), 3.38 (δ_A), 3.73 (δ_B), and 9.6 (br, δ_G) (10 H, $^2J_{AB}$ = –13.8 Hz, $^3J_{AC}$ = 2.5 Hz, $^3J_{BC}$ = 12.7 Hz, $^3J_{GM}$ = 3.2 Hz, $^3J_{GN}$ = 3.5 Hz, SiCH_CC$H_A$$H_BNH_G$(C($H_M$)$_3$)(C($H_N$)$_3$)), 3.71 (s, 3 H, OC$H_3$), 6.01 (s, 1 H, SiO*H*), 6.83–6.91 (m, 2 H, *H*-3/*H*-5, Aryl), 7.14–7.22 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR ([D$_6$]DMSO): δ 12.4 (Si*C*H$_2$C), 13.2 (Si*C*H$_2$C), 23.6 (SiCH$_2$*C*H$_2$C), 23.7 (SiCH$_2$*C*H$_2$C), 29.2 (Si(CH$_2$)$_2$*C*H$_2$C), 30.8 (Si*C*HC$_2$), 41.4 (NCH_3), 43.0 (NCH_3), 54.9 (OCH_3), 57.6 (C*C*H$_2$N), 114.0 (*C*-3/*C*-5, Aryl), 128.7 (*C*-2/*C*-6, Aryl), 130.5 (*C*-1, Aryl), 157.2 (*C*-4, Aryl). ^{15}N NMR ([D$_6$]DMSO): δ –338. ^{29}Si NMR ([D$_6$]DMSO): δ 2.8. Anal. Calcd for $C_{16}H_{28}ClNO_2Si$: C, 58.25; H, 8.55; N, 4.25. Found: C, 58.1; H, 8.4; N, 4.3.

Preparation of (*R*)-[2-(1-hydroxy-1-sila-1-cyclohexyl)-2-(4-methoxyphenyl)ethyl]-dimethylammonium chloride ((*R*)-sila-venlafaxine hydrochloride, (*R*)-12b·HCl).

Protocol A. A 2 M ethereal hydrogen chloride solution (1.8 mL, 3.6 mmol of HCl) was added at 20 °C to a solution of (*R*)-**12b** (1.00 g, 3.41 mmol) in dichloromethane (19 mL), and the resulting mixture was shaken briefly. Upon vapor diffusion of diethyl ether into this mixture at 20 °C over a period of 6 days, a crystalline product was obtained, which was isolated by filtration, washed with diethyl ether (40 mL), and finally dried in vacuo (0.001 mbar, 20 °C, 6 h) to give (*R*)-**12b**·HCl in 93% yield as a colorless crystalline solid (1.04 g, 3.15 mmol); mp 174 °C; $[\alpha]_{589}^{20} = -29.3$ (*c* = 1.00, CH_2Cl_2). ^{1}H NMR ([D$_6$]DMSO):[84,85] δ 0.25–0.41, 0.50–0.69, and 1.13–1.70 (m, 10 H, Si(CH_2)$_5$), 2.56 (br, δ_M), 2.61 (br, δ_N), 2.74 (δ_C), 3.38 (δ_A), 3.73 (δ_B), and 9.6 (br, δ_G) (10 H, $^2J_{AB}$ = –14.2 Hz, $^3J_{AC}$ = 2.6 Hz, $^3J_{BC}$ = 12.7 Hz, $^3J_{GM}$ and $^3J_{GN}$ not resolved, SiCH_CC$H_A H_B$NH_G(C(H_M)$_3$)(C(H_N)$_3$)), 3.71 (s, 3 H, OCH_3), 6.01 (s, 1 H, SiO*H*), 6.83–6.91 (m, 2 H, *H*-3/*H*-5, Aryl), 7.14–7.22 (m, 2 H, *H*-2/*H*-6, Aryl). The ^{13}C and ^{29}Si NMR data were identical with those obtained for *rac*-**12b**·HCl. Anal. Calcd for $C_{16}H_{28}ClNO_2Si$: C, 58.25; H, 8.55; N, 4.25. Found: C, 58.4; H, 8.4; N, 4.4.

Protocol B. A 2.1 M ethereal hydrogen chloride solution (17.5 mL, 36.8 mmol of HCl) was added at 20 °C (water bath) to a stirred solution of (*R*)-**12b** (10.2 g, 34.8 mmol) in THF/dichloromethane (9/1, v/v) (228 mL), and the resulting mixture was stirred moderately for 5 seconds and then cooled to 0 °C (spontaneous crystallization). The mixture was kept undisturbed at 0 °C for 1 h and then at 4 °C for 16 h. The precipitate was isolated by suction filtration, washed with diethyl ether (2 × 40 mL), and dried in vacuo (0.001 mbar, 20 °C, 4 h) to give (*R*)-**12b**·HCl in 95% yield as a colorless crystalline solid (10.9 g, 33.0 mmol); mp 180–181 °C; $[\alpha]_{589}^{20} = -29.3$ (*c* = 1.00, CH_2Cl_2). The NMR data of the product were identical with those obtained for (*R*)-**12b**·HCl synthesized according to Protocol A. Anal. Calcd for $C_{16}H_{28}ClNO_2Si$: C, 58.25; H, 8.55; N, 4.25. Found: C, 58.1; H, 8.5; N, 4.3.

Preparation of (*R*)-[2-(1-hydroxy-1-sila-1-cyclohexyl)-2-(4-methoxyphenyl)ethyl]-dimethylammonium bromide ((*R*)-sila-venlafaxine hydrobromide, (*R*)-12b·HBr). A solution of triphenylphosphonium bromide (586 mg, 1.71 mmol) in dichloromethane (10 mL) was added at 20 °C in one single portion to a solution of (*R*)-**12b** (501 mg, 1.71 mmol) in dichloromethane (5 mL). The resulting mixture was stirred at 20 °C for 10 min, ethyl acetate was added (30 mL), and the solvent was removed under reduced pressure in a water bath (5–15 °C) until a residual volume of 15 mL was obtained (partial precipitation of (*R*)-**12b**·HBr). A further 30 mL of ethyl acetate were added, and the solution was concentrated again under reduced pressure (water bath, 5–15 °C) until a residual volume of 15 mL was obtained (almost quantitative precipitation of (*R*)-**12b**·HBr). The solvent was removed by decantation, and the precipitate was washed with diethyl ether (2 × 10 mL; separation by decantation), dried in vacuo (0.001 mbar, 20 °C, 1 h), and then redissolved in

dichloromethane (6 mL). Upon vapor diffusion of diethyl ether into the resulting solution at 20 °C, crystals precipitated, which were isolated by filtration to give (*R*)-**12b**·HBr in 90% yield as a colorless crystalline solid (573 mg, 1.53 mmol); mp 152–153 °C; $[\alpha]_{589}^{20}$ = –20.8 (*c* = 2.50, CH_2Cl_2). ^{1}H NMR ([D$_6$]DMSO): δ 0.26–0.43, 0.50–0.70, and 1.13–1.70 (m, 10 H, Si(CH_2)$_5$), 2.65 (br s, 6 H, NCH_3), 2.68 (δ_C), 3.36 (δ_A), and 3.79 (δ_B) (3 H, $^2J_{AB}$ = –13.6 Hz, $^3J_{AC}$ = 2.9 Hz, $^3J_{BC}$ = 13.3 Hz, SiCH_CC$H_A$$H_B$N), 3.72 (s, 3 H, OC$H_3$), 5.9 (br s, 1 H, SiO*H*), 6.84–6.92 (m, 2 H, *H*-3/*H*-5, Aryl), 7.15–7.23 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR ([D$_6$]DMSO): δ 12.4 (Si*C*H$_2$C), 13.2 (Si*C*H$_2$C), 23.5 (SiCH$_2$*C*H$_2$C), 23.7 (SiCH$_2$*C*H$_2$C), 29.1 (Si(CH$_2$)$_2$*C*H$_2$C), 30.7 (Si*C*HC$_2$), 40.8 (N*C*H$_3$), 43.8 (N*C*H$_3$), 55.0 (O*C*H$_3$), 57.7 (C*C*H$_2$N), 114.1 (*C*-3/*C*-5, Aryl), 128.8 (*C*-2/*C*-6, Aryl), 129.7 (*C*-1, Aryl), 157.3 (*C*-4, Aryl). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for $C_{16}H_{28}BrNO_2Si$: C, 51.33; H, 7.54; N, 3.74. Found: C, 51.0; H, 7.3; N, 3.8.

Preparation of (*S*)-[2-(1-hydroxy-1-sila-1-cyclohexyl)-2-(4-methoxyphenyl)ethyl]-dimethylammonium chloride ((*S*)-sila-venlafaxine hydrochloride, (*S*)-12b·HCl). This compound was prepared from (*S*)-**12b** analogous to the protocols used for the preparation of (*R*)-**12b**·HCl.

Protocol A. Compound (*S*)-**12b**·HCl was synthesized from (*S*)-**12b** (1.00 g, 3.41 mmol) and isolated in 92% yield as a colorless crystalline solid (1.03 g, 3.12 mmol); mp 174 °C; $[\alpha]_{589}^{20}$ = +29.3 (*c* = 1.00, CH_2Cl_2). The NMR data of the product were identical with those obtained for (*R*)-**12b**·HCl. Anal. Calcd for $C_{16}H_{28}ClNO_2Si$: C, 58.25; H, 8.55; N, 4.25. Found: C, 58.0; H, 8.2; N, 4.0.

Protocol B. Compound (*S*)-**12b**·HCl was synthesized from (*S*)-**12b** (8.95 g, 30.5 mmol) and isolated in 89% yield as a colorless crystalline solid (8.93 g, 27.1 mmol); mp 180–181 °C; $[\alpha]_{589}^{20}$ = +29.3 (*c* = 1.00, CH_2Cl_2). The NMR data of the product were identical with those obtained for (*R*)-**12b**·HCl. Anal. Calcd for $C_{16}H_{28}ClNO_2Si$: C, 58.25; H, 8.55; N, 4.25. Found: C, 58.0; H, 8.3; N, 4.3.

Preparation of *rac*-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclopentan-1-ol (*rac*-13). This compound was prepared analogous to the synthesis of *rac*-**12b** according to Protocol A (**67** (2.54 g, 11.6 mmol), dimethylamine (8.07 g, 179 mmol), a 1.6 M solution of *n*-butyllithium in *n*-hexane (8.0 mL, 12.8 mmol of *n*-BuLi), THF (65 mL)). The oily crude product crystallized from *n*-pentane (45 mL; –11 °C (1 h) → –26 °C (1 day)), and compound *rac*-**13** was isolated in 54% yield as a colorless crystalline solid (1.77 g, 6.33 mmol); mp 37 °C. ^{1}H NMR ($CDCl_3$): [86] δ 0.32–0.65 (m, 4 H, SiCH_2C), 0.70–0.88, 0.95–1.11, and 1.31–1.49 (m, 4 H, SiCH$_2$CH_2C), 2.32 (s, 6 H, NCH_3), 2.52–2.68 (m, 2 H, SiC*H*C*H*HN), 3.12–3.28 (m, 1 H,

SiCHCH*H*N), 3.75 (s, 3 H, OC*H*$_3$), 6.3 (br s, 1 H, SiO*H*), 6.74–6.81 (m, 2 H, *H*-3/*H*-5, Aryl), 6.91–6.98 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR ($CDCl_3$): δ 9.8 (Si*C*H$_2$C), 11.0 (Si*C*H$_2$C), 25.56 (SiCH$_2$*C*H$_2$C), 25.60 (SiCH$_2$*C*H$_2$C), 31.1 (Si*C*HC$_2$), 45.4 (N*C*H$_3$), 55.1 (O*C*H$_3$), 61.9 (C*C*H$_2$N), 113.5 (*C*-3/*C*-5, Aryl), 128.0 (*C*-2/*C*-6, Aryl), 132.0 (*C*-1, Aryl), 156.6 (*C*-4, Aryl). ^{29}Si NMR ($CDCl_3$): δ 34.4. Anal. Calcd for $C_{15}H_{25}NO_2Si$: C, 64.47; H, 9.02; N, 5.01. Found: C, 64.6; H, 9.1; N, 5.1.

Preparation of [2-(1-hydroxy-1-sila-1-cyclopentyl)-2-(4-methoxyphenyl)ethyl]dimethylammonium chloride (*rac*-13·HCl). A 2 M ethereal hydrogen chloride solution (2.0 mL, 4.0 mmol of HCl) was added at 20 °C in one single portion to a stirred solution of *rac*-**13** (1.02 g, 3.65 mmol) in dichloromethane (16 mL). The mixture was kept undisturbed at –27 °C for 2 h, and a few seed crystals (obtained from 20 μL of the reaction mixture by slow evaporation of the solvent at 20 °C, followed by cooling of the resulting oil to –27 °C) were added. The resulting mixture was kept undisturbed at –27 °C for three days, and the precipitate was isolated by filtration at –27 °C, washed with ice-cold acetone (10 mL) and then dried in vacuo (0.001 mbar, 20 °C, 6 h) to give *rac*-**13**·HCl in 52% yield as a colorless crystalline solid (598 mg, 1.89 mmol); mp 153–154 °C. ^{1}H NMR ([D$_6$]DMSO): δ 0.18–0.62 (m, 4 H, SiC*H*$_2$C), 1.06–1.27 and 1.32–1.55 (m, 4 H, SiCH$_2$C*H*$_2$C), 2.6 (br s, 6 H, NC*H*$_3$), 2.82 (δ_C), 3.43 (δ_A), and 3.82 (δ_B) (3 H, $^2J_{AB}$ = –13.5 Hz, $^3J_{AC}$ = 2.6 Hz, $^3J_{BC}$ = 12.7 Hz, SiC*H*$_C$C*H*$_A$*H*$_B$N), 3.71 (s, 3 H, OC*H*$_3$), 6.2 (br s, 1 H, SiO*H*), 6.82–6.90 (m, 2 H, *H*-3/*H*-5, Aryl), 7.17–7.25 (m, 2 H, *H*-2/*H*-6, Aryl), 9.5 (br s, 1 H, N*H*). ^{13}C NMR ([D$_6$]DMSO): δ 10.4 (Si*C*H$_2$C), 10.9 (Si*C*H$_2$C), 25.36 (SiCH$_2$*C*H$_2$C), 25.43 (SiCH$_2$*C*H$_2$C), 31.7 (Si*C*HC$_2$), 41.5 (N*C*H$_3$), 43.1 (N*C*H$_3$), 55.0 (O*C*H$_3$), 57.5 (C*C*H$_2$N), 114.1 (*C*-3/*C*-5, Aryl), 128.9 (*C*-2/*C*-6, Aryl), 130.0 (*C*-1, Aryl), 157.3 (*C*-4, Aryl). ^{29}Si NMR ([D$_6$]DMSO): δ 25.1. Anal. Calcd for $C_{15}H_{26}ClNO_2Si$: C, 57.03; H, 8.30; N, 4.43. Found: C, 56.6; H, 7.9; N, 4.4.

Preparation of *rac*-1-[2-(dimethylamino)-1-phenylethyl]-1-silacyclohexan-1-ol (*rac*-desmethoxy-sila-venlafaxine, *rac*-15). A solution of *rac*-**80** (7.88 g, 27.1 mmol) in diethyl ether (50 mL) was added in one single portion at 0 °C to a stirred two-phase mixture of diethyl ether (50 mL) and 2 M potassium acetate/acetic acid buffer (pH 4.5, 150 mL). The pH of the aqueous phase changed to pH ca. 7 within 10 min and was readjusted to pH 5.0 by addition of small portions of glacial acetic acid. The mixture was stirred at 0 °C for a further 1 h, with the pH of the aqueous phase remaining constantly at pH 5.0 during this time. The aqueous layer was separated, the organic phase was extracted with 1 M potassium acetate/acetic acid buffer (pH 5.0) (3 × 100 mL), and the aqueous solutions were combined. Diethyl ether (50 mL) was added, and the pH of the aqueous phase was adjusted to pH 10.5 by addition of small portions of a saturated aqueous potassium carbonate solution. The organic layer was separated, the aqueous phase was extracted with diethyl

ether (5 × 100 mL), and the organic extracts were combined, followed by addition of *n*-hexane (200 mL). The solvent was removed under reduced pressure in a water bath (5–15 °C) until a residual volume of 150 mL was obtained, whereupon residual water separated from the organic phase (formation of a two-phase system). The organic layer was separated, the aqueous phase was extracted with *n*-hexane (2 × 100 mL), and the organic solutions were combined. The solvent was removed completely under reduced pressure in a water bath (5–15 °C) to give a colorless oil. Crystallization of this oil from *n*-pentane (120 mL) at 4 °C over a period of 1 day and then at –20 °C for a further 6 days afforded *rac*-**15** in 91% yield as a colorless crystalline solid (6.50 g, 24.7 mmol) (isolated by quick decantation of the cold solvent, followed by drying in vacuo (0.001 mbar, 20 °C, 6 h)); mp 63 °C. ^{1}H NMR (CD_2Cl_2): δ 0.45–0.78 and 1.00–1.69 (m, 10 H, Si(CH_2)$_5$), 2.30 (s, 6 H, NCH_3), 2.54 (δ_C), 2.58 (δ_A), and 3.16 (δ_B), (3 H, $^{2}J_{AB}$ = –12.0 Hz, $^{3}J_{AC}$ = 5.3 Hz, $^{3}J_{BC}$ = 12.1 Hz, SiCH_CC$H_A$$H_B$N), 5.1 (br s, 1 H, SiO$H$), 7.03–7.09 (m, 2 H, *H*-2/*H*-6, Aryl), 7.09–7.14 (m, 1 H, *H*-4, Aryl), 7.20–7.29 (m, 2 H, *H*-3/*H*-5, Aryl). ^{13}C NMR (CD_2Cl_2): δ 12.5 (Si*C*H$_2$C), 14.5 (Si*C*H$_2$C), 24.5 (SiCH$_2$*C*H$_2$C), 24.6 (SiCH$_2$*C*H$_2$C), 29.9 (Si(CH$_2$)$_2$*C*H$_2$C), 34.3 (Si*C*HC$_2$), 45.5 (N*C*H$_3$), 61.6 (N*C*H$_2$C), 125.2 (*C*-4, Aryl), 127.9 (*C*-2/*C*-6, Aryl), 128.6 (*C*-3/*C*-5, Aryl), 141.9 (*C*-1, Aryl). ^{29}Si NMR (CD_2Cl_2): δ 9.5. Anal. Calcd for $C_{15}H_{25}NOSi$: C, 68.39; H, 9.56; N, 5.32. Found: C, 68.0; H, 9.7; N, 5.5.

Preparation of *rac*-[2-(1-hydroxy-1-sila-1-cyclohexyl)-2-phenylethyl]dimethylammonium chloride (*rac*-desmethoxy-sila-venlafaxine hydrochloride, *rac*-15·HCl). A 2 M ethereal hydrogen chloride solution (10.5 mL, 21.0 mmol of HCl) was added in one single portion at 20 °C to a stirred solution of *rac*-**15** (5.27 g, 20.0 mmol) in dichloromethane (50 mL). The resulting solid was dissolved in dichloromethane (150 mL) at reflux temperature, and the solution was then kept undisturbed at 4 °C for 1 day and at –20 °C for a further 3 days. The precipitate was isolated by filtration at –20 °C, washed with diethyl ether (20 mL), and dried in vacuo (0.001 mbar, 20 °C, 6 h) to give *rac*-**15**·HCl in 93% yield (including workup of the mother liquor) as a colorless crystalline solid (5.60 g, 18.7 mmol); mp 186–187 °C (dec.). ^{1}H NMR ([D$_6$]DMSO): δ 0.24–0.41, 0.51–0.71, and 1.12–1.59 (m, 10 H, Si(CH_2)$_5$), 2.56 (δ_M), 2.61 (δ_N), 2.83 (δ_C), 3.42 (δ_A), 3.81 (δ_B), and 9.8 (br, δ_G) (10 H, $^{2}J_{AB}$ = –13.1 Hz, $^{3}J_{AC}$ = 2.5 Hz, $^{3}J_{BC}$ = 12.5 Hz, $^{3}J_{GM}$ and $^{3}J_{GN}$ not resolved, SiCH_CC$H_A$$H_BNH_G$(C($H_M$)$_3$)(C($H_N$)$_3$)), 6.06 (s, 1 H, SiO$H$), 7.11–7.19 (m, 1 H, *H*-4, Aryl), 7.23–7.34 (m, 4 H, *H*-2/*H*-6, *H*-3/*H*-5, Aryl). ^{13}C NMR ([D$_6$]DMSO): δ 12.3 (Si*C*H$_2$C), 13.2 (Si*C*H$_2$C), 23.6 (SiCH$_2$*C*H$_2$C), 23.7 (SiCH$_2$*C*H$_2$C), 29.1 (Si(CH$_2$)$_2$*C*H$_2$C), 32.1 (Si*C*HC$_2$), 41.6 (N*C*H$_3$), 42.9 (N*C*H$_3$), 57.3 (C*C*H$_2$N), 125.4 (*C*-4, Aryl), 127.7 (*C*-2/*C*-6, Aryl), 128.5 (*C*-3/*C*-5, Aryl), 139.1 (*C*-

1, Aryl). ^{29}Si NMR ([D$_6$]DMSO): δ 2.8. Anal. Calcd for $C_{15}H_{26}ClNOSi$: C, 60.07; H, 8.74; N, 4.67. Found: C, 60.0; H, 8.9; N, 4.8.

Preparation of *rac*-1-(dimethylamino)-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclohexane (*rac*-16). A 1.6 M solution of *n*-butyllithium in *n*-hexane (9.5 mL, 15.2 mmol of *n*-BuLi) was added dropwise at –50 °C within 5 min to a stirred solution of dimethylamine (5.51 g, 122 mmol) in THF (150 mL). The resulting mixture was warmed to –15 °C within 4 h and then cooled to –35 °C, followed by dropwise addition of **60** (3.20 g, 13.8 mmol) within 10 min (evolution of hydrogen; rise in temperature from –35 to –30 °C). The resulting yellow solution was stirred at –30 °C for 3 h and then kept undisturbed at –26 °C for 16 h. Subsequently, the solution was placed in an ice bath and stirred again, followed by addition of chlorotrimethylsilane (1.72 g, 15.8 mmol) in one single portion (change of color from yellow to colorless). The mixture was stirred at 0 °C for 30 min, and the solvent was removed completely under reduced pressure in a water bath (5–15 °C), followed by addition of *n*-hexane (40 mL). The mixture was stirred at 20 °C for 30 min, the resulting precipitate was separated by filtration, and the filter cake was washed with *n*-hexane (20 mL). The filtrate and the wash solution were combined, the solvent was removed completely under reduced pressure in a water bath (5–15 °C), and the residue was distilled in vacuo (Vigreux column, 5 cm) to give *rac*-**16** in 76% yield as a colorless oily liquid (3.37 g, 10.5 mmol); bp 115–118 °C/0.003 mbar. ^{1}H NMR ([D$_8$]THF): δ 0.35–0.75, 0.84–0.97, and 1.12–1.79 (m, 10 H, Si(CH_2)$_5$), 2.12 (s, 6 H, CNCH_3), 2.34 (δ_C), 2.618 (δ_A), and 2.623 (δ_B) (3 H, $^2J_{AB}$ = 0.0 Hz, $^3J_{AC}$ = 7.8 Hz, $^3J_{BC}$ = 9.2 Hz, SiCH_CC$H_A$$H_B$N), 2.44 (s, 6 H, SiNC$H_3$), 3.71 (s, 3 H, OC$H_3$), 6.71–6.78 (m, 2 H, *H*-3/*H*-5, Aryl), 6.89–6.96 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR ([D$_8$]THF): δ 12.0 (Si*C*H$_2$C), 12.8 (Si*C*H$_2$C), 24.9 (SiCH$_2$*C*H$_2$C), 25.0 (SiCH$_2$*C*H$_2$C), 31.1 (Si(CH$_2$)$_2$*C*H$_2$C), 36.1 (Si*C*HC$_2$), 38.7 (SiNCH$_3$), 45.7 (CNCH$_3$), 55.1 (OCH$_3$), 61.6 (C*C*H$_2$N), 114.0 (*C*-3/*C*-5, Aryl), 129.4 (*C*-2/*C*-6, Aryl), 135.4 (*C*-1, Aryl), 159.2 (*C*-4, Aryl). ^{29}Si NMR ([D$_8$]THF): δ 0.8. Anal. Calcd for $C_{18}H_{32}N_2OSi$: C, 67.45; H, 10.06; N, 8.74. Found: C, 67.3; H, 9.8; N, 8.6.

Preparation of *rac*-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-methoxy-1-silacyclohexane (*rac*-17). A mixture of acetic acid anhydride (108 mg, 1.06 mmol) in methanol (35 mL) was stirred at 20 °C for 30 min. The mixture was cooled to 0 °C, and *rac*-**16** (6.53 g, 20.4 mmol) was added within 5 min. The mixture was stirred at 0 °C for 30 min and then warmed to 20 °C within a further 30 min (quantitative conversion *rac*-**16** → *rac*-**17**; GC control). The solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation in vacuo (Kugelrohr apparatus, 130 °C/0.001 mbar) to give *rac*-**17** in 87% yield as a colorless oily liquid (5.43 g, 17.7 mmol). ^{1}H NMR ($CDCl_3$): δ 0.36–0.70, 0.73–0.88, 1.11–1.29, and 1.37–1.73 (m, 10 H, Si(CH_2)$_5$), 2.14 (s, 6 H, NCH_3), 2.40 (δ_C), 2.52 (δ_A), and 2.85 (δ_B) (3 H, $^2J_{AB}$ = –12.4 Hz, $^3J_{AC}$ =

5.3 Hz, $^{3}J_{BC}$ = 11.0 Hz, SiCH_CC$H_A$$H_B$N), 3.39 (s, 3 H, SiOC$H_3$), 3.73 (s, 3 H, COC$H_3$), 6.74–6.81 (m, 2 H, *H*-3/*H*-5, Aryl), 6.96–7.04 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR ($CDCl_3$): δ 10.9 (Si*C*H_2C), 11.3 (Si*C*H_2C), 24.1 (2 C, SiCH$_2$*C*H_2C), 29.5 (Si(CH$_2$)$_2$*C*H_2C), 33.7 (Si*C*HC$_2$), 45.3 (N*C*H_3), 51.0 (SiO*C*H_3), 55.0 (CO*C*H_3), 59.6 (C*C*H_2N), 113.7 (*C*-3/*C*-5, Aryl), 128.4 (*C*-2/*C*-6, Aryl), 133.1 (*C*-1, Aryl), 156.9 (*C*-4, Aryl). ^{29}Si NMR ($CDCl_3$): δ 10.0. Anal. Calcd for $C_{17}H_{29}NO_2Si$: C, 66.40; H, 9.51; N, 4.55. Found: C, 66.4; H, 9.4; N, 4.8.

Preparation of *rac*-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclohexane (*rac*-18). A solution of *rac*-**17** (3.48 g, 11.3 mmol) in diethyl ether (10 mL) was added at 20 °C within 10 min to a suspension of lithium aluminum hydride (LAH) (253 mg, 6.67 mmol) in diethyl ether (50 mL). The mixture was heated under reflux for 90 min and then cooled to 20 °C, the solid was removed by filtration, and the filter cake was washed with diethyl ether (10 mL). The filtrate and the wash solution were combined, chlorotrimethylsilane (123 mg, 1.13 mmol) was added at 20 °C, and the resulting mixture was stirred at 20 °C for 30 min (a drop of the mixture gave a strongly acidic reaction on wet pH indicator paper, thus ensuring that any basic impurities were absent). The solvent was removed under reduced pressure, followed by addition of *n*-pentane (40 mL) to the residue and subsequent filtration. The filter cake was washed with *n*-pentane (10 mL), the filtrate and the wash solution were combined, and the solvent was removed under reduced pressure. The residue was distilled in vacuo (Vigreux column, 5 cm) to give *rac*-**18** in 73% yield as a colorless oily liquid (2.28 g, 8.22 mmol); bp 110–113 C/0.001 mbar. ^{1}H NMR ($CDCl_3$): δ 0.31–0.67, 0.75–0.89, 1.08–1.28, 1.35–1.58, and 1.67–1.85 (m, 10 H, Si(CH_2)$_5$), 2.16 (s, 6 H, NCH_3), 2.46 (δ_C), 2.52 (δ_A), and 2.82 (δ_B) (3 H, $^{2}J_{AB}$ = –11.7 Hz, $^{3}J_{AC}$ = 5.9 Hz, $^{3}J_{BC}$ = 10.1 Hz, SiCH_CC$H_A$$H_B$N), 3.69–3.80 (m, 1 H, Si*H*), 3.75 (s, 3 H, OCH_3), 6.76–6.83 (m, 2 H, *H*-3/*H*-5, Aryl), 6.94–7.02 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR ($CDCl_3$): δ 8.9 (Si*C*H_2C), 9.8 (Si*C*H_2C), 24.83 (SiCH$_2$*C*H_2C), 24.84 (SiCH$_2$*C*H_2C), 29.6 (Si(CH$_2$)$_2$*C*H_2C), 31.2 (Si*C*HC$_2$), 45.4 (N*C*H_3), 55.1 (O*C*H_3), 61.1 (C*C*H_2N), 113.9 (*C*-3/*C*-5, Aryl), 128.2 (*C*-2/*C*-6, Aryl), 134.1 (*C*-1, Aryl), 156.9 (*C*-4, Aryl). ^{29}Si NMR ($CDCl_3$): δ –9.0. Anal. Calcd for $C_{16}H_{27}NOSi$: C, 69.26; H, 9.81; N, 5.05. Found: C, 69.4; H, 9.8; N, 5.2.

Preparation of *rac*-[2-(4-methoxyphenyl)-2-(1-sila-1-cyclohexyl)ethyl]dimethylammonium chloride (*rac*-18·HCl). A 2 M ethereal hydrogen chloride solution (1.00 mL, 2.00 mmol of HCl) was added in one single portion at 20 °C to a stirred solution of *rac*-**18** (541 mg, 1.95 mmol) in dichloromethane (3 mL), and the resulting precipitate was redissolved by addition of dichloromethane (4 mL). Upon vapor diffusion of diethyl ether into this mixture at 20 °C over a period of 8 days, a crystalline product was obtained, which was isolated by filtration, washed with diethyl ether (2 × 10 mL), and finally dried in vacuo (0.001 mbar, 20 °C, 4 h) to give *rac*-**18**·HCl in

79% yield as a colorless crystalline solid (486 mg, 1.55 mmol); mp 167 °C (dec. with gas evolution). ^{1}H NMR (CD_2Cl_2): δ 0.32–0.47, 0.50–0.75, 0.83–0.96, 1.17–1.33, 1.37–1.62, and 1.67–1.90 (m, 10 H, Si(C*H*$_2$)$_5$), 2.47 (d, $^3J_{HH}$ = 4.9 Hz, 3 H, NC*H*$_3$), 2.59 (d, $^3J_{HH}$ = 5.0 Hz, 3 H, NC*H*$_3$), 2.97–3.06 (m, 1 H, SiC*H*C$_2$), 3.37–3.54 (m, 2 H, CC*H*$_2$N), 3.71–3.82 (m, 1 H, Si*H*), 3.76 (s, 3 H, OC*H*$_3$), 6.83–6.91 (m, 2 H, *H*-3/*H*-5, Aryl), 7.06–7.15 (m, 2 H, *H*-2/*H*-6, Aryl), 12.4 (br s, 1 H, N*H*). ^{13}C NMR (CD_2Cl_2): δ 8.4 (Si*C*H$_2$C), 9.4 (Si*C*H$_2$C), 24.70 (SiCH$_2$*C*H$_2$C), 24.75 (SiCH$_2$*C*H$_2$C), 29.1 (Si*C*HC$_2$), 29.6 (Si(CH$_2$)$_2$*C*H$_2$C), 42.3 (N*C*H$_3$), 44.5 (N*C*H$_3$), 55.5 (O*C*H$_3$), 59.6 (C*C*H$_2$N), 115.0 (*C*-3/*C*-5, Aryl), 128.6 (*C*-2/*C*-6, Aryl), 131.6 (*C*-1, Aryl), 158.4 (*C*-4, Aryl). ^{29}Si NMR (CD_2Cl_2): δ –9.0. Anal. Calcd for $C_{16}H_{28}ClNOSi$: C, 61.21; H, 8.99; N, 4.46. Found: C, 60.7; H, 8.9; N, 4.4.

4-[1-(3,5,5,8,8-Pentamethyl-5,6,7,8-tetrahydro-2-naphthyl)vinyl]benzoic acid (bexarotene, 21a). This compound was kindly provided by Amedis Pharmaceuticals Ltd., Cambridge, U.K. ^{1}H NMR (CD_2Cl_2): δ 1.28 (s, 6 H, Alkyl-C*H*$_3$), 1.30 (s, 6 H, Alkyl-C*H*$_3$), 1.71 (s, 4 H, CC*H*$_2$C), 1.95 (br "s", 3 H, Aryl-C*H*$_3$), 5.33 (d, $^2J_{HH}$ = 1.3 Hz, 1 H, C=C*H*$_A$H$_B$), 5.87 (d, $^2J_{HH}$ = 1.3 Hz, 1 H, C=CH$_A$*H*$_B$), 7.11 (br "s", 1 H, *H*-4, Naph′), 7.15 (s, 1 H, *H*-1, Naph′), 7.36–7.43 (m, 2 H, *H*-3/*H*-5, Phe), 7.99–8.06 (m, 2 H, *H*-2/*H*-6, Phe), 10.7 (br s, 1 H, C(O)O*H*). ^{13}C NMR (CD_2Cl_2): δ 19.9 (Aryl-*C*H$_3$), 31.95 (2 C, Alkyl-*C*H$_3$), 32.00 (2 C, Alkyl-*C*H$_3$), 34.2 (Aryl-*C*C$_3$), 34.3 (Aryl-*C*C$_3$), 35.47 (C*C*H$_2$C), 35.49 (C*C*H$_2$C), 117.4 (C=*C*H$_2$), 127.1 (*C*-3/*C*-5, Phe), 128.35 (*C*-1 or *C*-4, Naph′), 128.37 (*C*-1, Phe), 128.44 (*C*-1 or *C*-4, Naph′), 130.6 (*C*-2/*C*-6, Phe), 133.1 (*C*-3, Naph′), 138.4 (*C*-2, Naph′), 142.8 (*C*-8a, Naph′), 144.9 (*C*-4a, Naph′), 146.9 (*C*-4, Phe), 149.5 (*C*=CH$_2$), 172.1 (*C*(O)OH).

Preparation of 4-[1-(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)-vinyl]benzoic acid (disila-bexarotene, 21b). A mixture of methanol (120 mL), water (40 mL), potassium hydroxide (5.54 g, 98.7 mmol), and **89** (3.94 g, 9.98 mmol) was heated under reflux for 45 min (slow dissolution of **89**, quantitative conversion **89** → **21b** (HPLC)). The mixture was cooled in an ice bath, followed by addition of dichloromethane (100 mL), and the aqueous phase was acidified to ca. pH 1 by addition of 1 M hydrochloric acid (130 mL) (formation of a precipitate). The ice bath was removed, and the mixture was stirred at 20 °C for 5 min (dissolution of the precipitate). The organic phase was separated, the aqueous layer was extracted with dichloromethane (3 × 100 mL), and the organic extracts were combined and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was dried in vacuo (10 mbar, 20 °C, 1 h) to give 3.73 g of a white amorphous solid. This solid was dissolved in diethyl ether (85 mL), and **21b** was crystallized at 20 °C by vapor diffusion of *n*-pentane into this solution over a period of 2 weeks. The precipitate was isolated by decantation of the solvent,

washed with *n*-pentane (2 × 20 mL), and dried in vacuo (0.001 mbar, 20 °C, 4 h) to give **21b** in 96% yield as a colorless crystalline solid (3.65 g, 9.59 mmol); mp 221 °C. ^{1}H NMR (CD_2Cl_2): δ 0.23 (s, 6 H, SiCH_3), 0.26 (s, 6 H, SiCH_3), 1.05 (s, 4 H, SiCH_2C), 2.00–2.02 (m, 3 H, CCH_3), 5.35 (d, $^{2}J_{HH}$ = 1.1 Hz, 1 H, C=CH_AH$_B$), 5.91 (d, $^{2}J_{HH}$ = 1.1 Hz, 1 H, C=CH$_A$$H_B$), 7.32–7.34 (m, 1 H, *H*-4, Naph), 7.35 (br "s", 1 H, *H*-1, Naph), 7.37–7.43 (m, 2 H, *H*-3/*H*-5, Phe), 8.01–8.07 (m, 2 H, *H*-2/*H*-6, Phe), 11.4 (br s, 1 H, C(O)O*H*). ^{13}C NMR (CD_2Cl_2): δ –1.41 (2 C, Si*C*H$_3$), –1.39 (2 C, Si*C*H$_3$), 7.87 (Si*C*H$_2$C), 7.89 (Si*C*H$_2$C), 20.2 (C*C*H$_3$), 117.7 (C=*C*H$_2$), 127.0 (*C*-3/*C*-5, Phe), 128.5 (*C*-1, Phe), 130.6 (*C*-2/*C*-6, Phe), 135.2 (*C*-1, Naph), 135.7 (*C*-4, Naph), 136.0 (*C*-3, Naph), 141.0 (*C*-2, Naph), 143.3 (*C*-4a, Naph), 145.8 (*C*-8a, Naph), 146.5 (*C*-4, Phe), 149.3 (*C*=CH$_2$), 172.2 (*C*(O)OH). ^{29}Si NMR (CD_2Cl_2): δ –7.03, –6.98. Anal. Calcd for $C_{22}H_{28}O_2Si_2$: C, 69.42; H, 7.41. Found: C, 69.2; H, 7.4.

Preparation of 5-[(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)-methyl]-*N*-(2,4,6-trimethoxyphenyl)furan-2-carboxamide (disila-AG-045572, 22b).

Protocol A. *Solution I.* A solution of **99** (1.00 g, 2.79 mmol) and thionyl chloride (6.85 g, 57.6 mmol) in dichloromethane (9 mL) was heated under reflux for 5 h. All volatile components were removed in vacuo (0.001 mbar, 20 °C, 1 h), and the oily residue was redissolved in dichloromethane (4 mL).

Solution II. Compound **101** (572 mg, 3.12 mmol; freshly distilled by bulb-to-bulb distillation directly before use), pyridine (245 mg, 3.10 mmol), and 4-(dimethylamino)pyridine (DMAP; 7.0 mg, 57 μmol) were dissolved in dichloromethane (5 mL).

Solution I was added dropwise at 0 °C within 10 min to the stirred *solution II* (formation of a precipitate which redissolved later; change of color from colorless to orange). The mixture was stirred at 0 °C for a further 10 min and then at 20 °C for 16 h, followed by addition of dichloromethane (20 mL). The resulting solution was washed successively with a 5 vol-% aqueous acetic acid solution (solution A, 20 mL), a half-saturated aqueous sodium hydrogen carbonate solution (solution B, 20 mL), and water (solution C, 20 mL). The first aqueous wash solution (A) was extracted with dichloromethane (20 mL), the resulting organic extract was used to extract the second aqueous wash solution (B), the resulting organic extract was used to extract the third aqueous wash solution (C), and the organic extract was separated, followed by a second extraction of the aqueous wash solutions A, B and C with a fresh portion of dichloromethane (20 mL), using the same protocol as described for the first extraction sequence. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was dried in vacuo (10 mbar, 20 °C, 30 min) and then purified by column chromatography on silica gel (column dimensions, 66 × 3.5 cm; silica gel (15–40 μm, Merck 1.15111), 235 g;

eluent, ethyl acetate/*n*-hexane (55:45, v/v)). The relevant fractions (TLC control) were combined, the solvent was removed under reduced pressure, and the residue was dried in vacuo (0.01 mbar, 20 °C, 1 h) to give 548 mg of an oil which was dissolved in diethyl ether (5 mL). The product crystallized from the resulting solution at 4 °C within 7 days, and the precipitate was isolated by decantation, washed with *n*-pentane (2 mL), and dried in vacuo (0.01 mbar, 20 °C, 4 h) to give **22b** in 22% yield as a colorless crystalline solid (318 mg, 607 μmol); mp 139–140 °C. ^{1}H NMR (C_6D_6): δ 0.38 (s, 6 H, SiCH_3), 0.39 (s, 6 H, SiCH_3), 1.15 ("s", 4 H, SiCH_2C), 2.14 (s, 3 H, CCH_3), 3.45 (s, 6 H, *o*-OCH_3, Tri), 3.51 (s, 3 H, *p*-OCH_3, Tri), 3.70 (br "s", 2 H, CCH_2C), 5.61 (d, $^{3}J_{HH}$ = 3.4 Hz, 1 H, *H*-4, Fu (= furyl)), 6.23 (s, 2 H, *H*-3/*H*-5, Tri), 7.14 (d, $^{3}J_{HH}$ = 3.4 Hz, 1 H, *H*-3, Fu), 7.41 (s, 1 H, *H*-1, Naph), 7.46 (s, 1 H, *H*-4, Naph), 7.5 (br s, 1 H, N*H*). ^{13}C NMR (C_6D_6): δ –1.31 (2 C, SiCH_3), –1.28 (2 C, SiCH_3), 8.00 (SiCH_2C), 8.01 (SiCH_2C), 19.3 (CCH_3), 32.6 (CCH_2C), 55.0 (*p*-OCH_3, Tri), 55.5 (*o*-OCH_3, Tri), 91.5 (*C*-3/*C*-5, Tri), 108.0 (*C*-1, Tri), 109.1 (*C*-4, Fu), 115.4 (*C*-3, Fu), 135.2 (*C*-1, Naph), 135.7 (*C*-2, Naph), 135.9 (*C*-4, Naph), 136.7 (*C*-3, Naph), 143.3 (*C*-4a, Naph), 144.3 (*C*-8a, Naph), 148.4 (*C*-2, Fu), 156.1 (*C*-5, Fu), 156.6 (*C*(O)N), 157.3 (*C*-2/*C*-6, Tri), 160.4 (*C*-4, Tri). ^{15}N NMR (C_6D_6): δ –281.8. ^{29}Si NMR (C_6D_6): δ –7.34, –7.30. Anal. Calcd for $C_{28}H_{37}NO_5Si_2$: C, 64.21; H, 7.12; N, 2.67. Found: C, 64.6; H, 7.1; N, 2.7.

Protocol B. A solution of **99** (584 mg, 1.63 mmol) in dichloromethane (10 mL) was added dropwise at 20 °C within 10 min to a stirred solution of dicyclohexylcarbodiimide (DCC; 370 mg, 1.79 mmol) and pyridine (265 mg, 3.35 mmol) in dichloromethane (10 mL). The mixture was stirred at 20 °C for a further 24 h, followed by addition of DMAP (4.0 mg, 33 μmol) in one single portion. Subsequently, a solution of **101** (358 mg, 1.95 mmol; freshly distilled by bulb-to-bulb distillation directly before use) in dichloromethane (5 mL) was added to the stirred mixture at 20 °C within 10 min, and stirring was continued at 20 °C for a further 3 days (formation of a precipitate). The mixture was washed with water (2 × 25 mL), and the organic layer was separated. The first aqueous wash solution (A) was extracted with dichloromethane (20 mL), the resulting organic extract was used to extract the second aqueous wash solution (B), and the organic extract was separated, followed by a second extraction of the aqueous wash solutions A and B with a fresh portion of dichloromethane (20 mL), using the same protocol as described for the first extraction sequence, and all organic extracts were combined and dried over anhydrous sodium sulfate (remaining solids that did not dissolve in neither phase were filtered off along with the sodium sulfate). The solvent was removed under reduced pressure, and the residue was dried in vacuo (10 mbar, 20 °C, 30 min) and then purified by column chromatography on silica gel (column dimensions, 70 × 3.5 cm; silica gel (15–40 μm, Merck 1.15111), 250 g; eluent, ethyl acetate/*n*-hexane (55:45, v/v)). The relevant fractions (TLC control) were combined, the solvent was removed

under reduced pressure, and the residue was dried in vacuo (0.01 mbar, 20 °C, 1 h) to give 454 mg of an oil which was dissolved in diethyl ether (8 mL). The resulting solution was then kept undisturbed at 4 °C for 2 days and at –20 °C for a further 4 days (formation of a precipitate). The precipitate was isolated by decantation, washed with *n*-pentane (3 mL), and dried in vacuo (0.01 mbar, 20 °C, 4 h) to give **22b** in 37% yield as a colorless crystalline solid (318 mg, 607 μmol); mp 139 °C. The NMR data of the product (^{1}H, ^{13}C, ^{29}Si) were identical with those obtained for the product prepared according to Protocol A (see above). Anal. Calcd for $C_{28}H_{37}NO_5Si_2$: C, 64.21; H, 7.12; N, 2.67. Found: C, 64.2; H, 7.1; N, 2.7.

Protocol C. A 2.0 M solution of trimethylaluminum in toluene (5.00 mL, 10.0 mmol of $AlMe_3$) was added dropwise at –30 °C within 8 min to a stirred suspension of **101**·HCl (2.20 g, 10.0 mmol) in toluene (20 mL) (dissolution of **101**·HCl, followed by the formation of a precipitate). The stirred mixture was warmed to –20 °C within 25 min and then to 20 °C within a further 1 h (dissolution of the precipitate), and the resulting solution was then added dropwise at 0 °C within 10 min to a stirred solution of **98** (1.86 g, 4.99 mmol) in dichloromethane (20 mL). The resulting mixture was stirred at 0 °C for a further 1 h and then at 20 °C for 3 days (quantitative conversion (HPLC control), change of color from colorless to black), followed by addition of a half-saturated aqueous ammonium acetate solution (solution A, 100 mL) (formation of a precipitate). The precipitate was separated by filtration and washed with ethyl acetate (5 × 20 mL), the filtrate and the wash solutions were combined, and the organic layer was separated and washed with water (solution B, 100 mL). The first aqueous wash solution (A) was extracted with ethyl acetate (50 mL), the resulting organic extract was used to extract the second aqueous wash solution (B), and the organic extract was separated, followed by a second and third extraction of the aqueous wash solutions A and B with fresh portions of ethyl acetate (2 × 50 mL), using the same protocol as described for the first extraction sequence. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue (4.0 g of a dark brown viscous oil) was purified by column chromatography on silica gel (column dimensions, 80 × 3.0 cm; silica gel (32–63 μm, ICN 02826), 230 g; eluent, ethyl acetate/*n*-hexane (55:45, v/v)). The relevant fractions (TLC control) were combined, the solvent was removed under reduced pressure, and the residue was dried in vacuo (0.001 mbar, 20 °C, 1 h) to give 2.77 g of a brown oil. The product was crystallized and then recrystallized from diethyl ether (54 mL for each crystallization (sonication was necessary to achieve complete dissolution); crystallization at 4 °C over a period of 1 day and then at –20 °C over a period of 3 days). The crystalline solid was isolated by decantation, washed with *n*-pentane (5 mL), and dried in vacuo (0.001 mbar, 20 °C, 4 h) to give 1.58 g of **22b**. The solvent of the combined mother liquors was removed to yield 1.06 g of a brown

oily product which was crystallized twice from diethyl ether (19 mL) to give a further 580 mg of **22b**. Compound **22b** was obtained in a total yield of 83% as a colorless crystalline solid (2.16 g, 4.12 mmol); mp 139 °C. The NMR data of the product (^{1}H, ^{13}C, ^{29}Si) were identical with those obtained for the product prepared according to Protocol A (see above). Anal. Calcd for $C_{28}H_{37}NO_5Si_2$: C, 64.21; H, 7.12; N, 2.67. Found: C, 64.2; H, 7.1; N, 2.7.

Preparation of chlorotris(chloromethyl)silane (23). A 2.0 M ethereal hydrogen chloride solution (24.0 mL, 48 mmol of HCl) was added dropwise at 0 °C within 2 min to a stirred suspension of **103** (14.4 g, 41.9 mmol) in diethyl ether (10 mL), and the resulting mixture was stirred at 0 °C for 1 min. After the cooling bath was removed, the temperature increased to 20 °C within ca. 5 min (concomitant dissolution of **103**), and the mixture was stirred at this temperature for a further 20 min (quantitative conversion **103** → **23** (GC control)). The solvent was removed under reduced pressure, the residue was distilled in vacuo (Vigreux column, 5 cm) to remove most of the 1,3,5-trimethoxybenzene formed, and the fraction boiling at 86–117 °C/1 mbar was collected (8.1 g) and then redistilled in vacuo (Vigreux column, 13 cm) to give **23** in 65% yield as a colorless liquid (5.77 g, 27.2 mmol); bp 85 °C/1 mbar. ^{1}H NMR (C_6D_6): δ 2.70 (s, SiC*H*$_2$Cl). ^{13}C NMR (C_6D_6): δ 24.8 (Si*C*H$_2$Cl). ^{29}Si NMR (C_6D_6): δ 10.5. Anal. Calcd for $C_3H_6Cl_4Si$: C, 17.00; H, 2.85. Found: C, 17.3; H, 3.0; Cl, 66.7.

Preparation of tris(chloromethyl)methoxysilane (24). Trifluoroacetic acid (179 mg, 1.57 mmol) was added at 20 °C to a stirred suspension of **103** (10.2 g, 29.7 mmol) in methanol (30 mL), and the resulting mixture was stirred at this temperature for 22 h (dissolution of **103** and quantitative conversion **103** → **24** (GC control)). The solvent was removed under reduced pressure, the residue was distilled in vacuo (Vigreux column, 5 cm) to remove most of the 1,3,5-trimethoxybenzene formed, and the fraction boiling at 90–127 °C/1 mbar was collected (6.3 g) and then redistilled in vacuo (Vigreux column, 8 cm) to give **24** in 69% yield as a colorless liquid (4.24 g, 20.4 mmol); bp 94 °C/1 mbar. ^{1}H NMR (C_6D_6): δ 2.74 (s, 6 H, SiC*H*$_2$Cl), 3.38 (s, 3 H, OC*H*$_3$). ^{13}C NMR (C_6D_6): δ 23.9 (Si*C*H$_2$Cl), 52.3 (O*C*H$_3$). ^{29}Si NMR (C_6D_6): δ –4.9. Anal. Calcd for $C_4H_9Cl_3OSi$: C, 23.15; H, 4.37; Cl, 51.24. Found: C, 23.4; H, 4.3; Cl, 51.1.

Preparation of the {ω-[dimethyl(3-imidopropyl)silyl]alkyl}dimethyl(3-imidopropyl)-ammonium bromides 10, 26–50, *rac*-51, and *rac*-52. General method. A solution of one of the (ω-bromoalkyl)(3-imidopropyl)dimethylsilanes **117**–**126** or *rac*-**127** and one of the amines **128**–**131** or *rac*-**132** (in this context, see Charts 3 and 5 and Schemes 15 and 16) in ethanol was heated under reflux for 48 h. After the mixture was cooled to 20 °C, the solvent was removed at 30 mbar, and ethyl acetate (50 mL) was added. The solution was concentrated in vacuo to a volume of 3 mL per mmol silane by lowering the pressure slowly from 200 mbar to 30 mbar. The addition of ethyl

acetate and subsequent evaporation of the solvent were repeated until the product precipitated almost quantitatively as a white amorphous solid. This product was isolated by centrifugation (1100 × g, 5 min), washed with *n*-pentane (2 × 20 mL), and dried in vacuo (2 h, 0.001 mbar, 20 °C) to give the desired (3-imidopropyl){ω-[(3-imidopropyl)dimethylsilyl]alkyl}dimethylammonium bromide as a white amorphous solid. Depending on the solubility of the product prepared, one of the following workup protocols (Protocols A–C) was applied. **Protocol A.** To purify the crude product, a boiling saturated solution in acetone was concentrated by distillation at atmospheric pressure until the product precipitated significantly (in cases where no precipitation occured in the heat, a minimum amount of solvent of 10 mL/g was used; as a rule, the rank order of solubilities of the (3-imidopropyl){ω-[(3-imidopropyl)dimethylsilyl]alkyl}dimethylammonium bromides in acetone was succinimido > 4-methylphthalimido > phthalimido >> 1,8-naphthalimido, with the amount of boiling acetone required to dissolve 1 g of the respective substance generally ranging from ca. 10 mL to 1 L). The precipitation was completed by storing the suspension for several days (for the precipiation time and temperature, see the respective preparation protocol). The product was isolated by centrifugation and washed with acetone (2 × 20 mL), the purification procedure (i.e., dissolution in boiling acetone, followed by concentration, precipitation, and centrifugation) was repeated twice, and the product was then dried in vacuo (0.001 mbar, 60 °C, 8 h) to give the desired (3-imidopropyl){ω-[(3-imidopropyl)dimethylsilyl]alkyl}dimethylammonium bromide as an amorphous white solid. **Protocol B.** The crude product was dissolved in boiling acetone (40 mL), the solvent was removed at 500 mbar until a residual volume of ca. 15 mL was obtained, ethyl acetate (40 mL) was added at 20 °C, and the mixture was concentrated at 20 °C under reduced pressure until a trace amount of a white precipitate was observed. The mixture was then kept undisturbed at 4 °C for 1 day, the resulting precipitate was isolated by filtration, washed with ethyl acetate (2 × 20 mL), and the purification protocol was repeated twice. The product was finally washed with *n*-pentane (2 × 20 mL) and dried in vacuo (0.001 mbar, 60 °C, 8 h). **Protocol C.** The crude product was dissolved in boiling acetone (80 mL), the solvent was removed by distillation at atmospheric pressure until a residual volume of ca. 15 mL was obtained, and ethyl acetate (10 mL) was added to the warm mixture directly after removing the heat source. The mixture was cooled to 20 °C within 1 h (formation of a precipitate), a further portion of ethyl acetate (30 mL) was added, and the resulting mixture was shaken gently and then kept undisturbed at 4 °C for 1 day. The resulting precipitate was isolated by filtration, and the purification protocol was repeated twice. The product was finally washed with *n*-pentane (2 × 20 mL) and dried in vacuo (0.001 mbar, 60 °C, 8 h).

In some cases, residual acetone was retained in the products prepared according to the Protocols A–C; therefore, additional subsequent crystallization steps from different solvents became necessary. Generally, vapor diffusion of diethyl ether into a solution of the respective (3-imidopropyl){ω-[(3-imidopropyl)dimethylsilyl]alkyl}dimethylammonium bromide in dichloromethane, followed by decantation or centrifugation and drying in vacuo (0.001 mbar, 20 °C, 4 h), gave satisfying results.

Preparation of {4-[dimethyl(3-(1,8-naphthalimido)propyl)silyl]butyl}dimethyl[3-(1,8-naphthalimido)propyl]ammonium bromide (26). Compound **26** was prepared from **117** (1.14 g, 2.64 mmol) and **128** (773 mg, 2.74 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day), followed by twofold purification by vapor diffusion of diethyl ether into a solution of **26** in dichloromethane, isolation of the resulting precipitate by decantation, and drying in vacuo (0.001 mbar, 20 °C, 4 h) to give **26** in 79% yield as an amorphous white solid (1.48 g, 2.07 mmol); mp 211 °C (dec). ^{1}H NMR ([D$_6$]DMSO): δ –0.09 (s, 6 H, SiCH_3), 0.38–0.56 (m, 4 H, CCH_2SiCH_2C), 1.14–1.32 (m, 2 H, SiCH$_2$CH_2(CH$_2$)$_2$N$^+$), 1.45–1.70 (m, 4 H, NCH$_2$CH_2CH$_2$Si and Si(CH$_2$)$_2$CH_2CH$_2$N$^+$), 2.00–2.18 (m, 2 H, N$^+$CH$_2$CH_2CH$_2$N), 3.03 (s, 6 H, N$^+$CH_3), 3.20–3.34 (m, 2 H, Si(CH$_2$)$_3$CH_2N$^+$), 3.34–3.49 (m, 2 H, N$^+$CH_2(CH$_2$)$_2$N), 3.78–3.91 (m, 2 H, NCH_2(CH$_2$)$_2$Si), 4.04 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, N$^+$(CH$_2$)$_2$CH_2N), 7.68–7.79 (m, 4 H, *H*-3/*H*-6, Naphth), 8.26–8.35 (m, 8 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.6 (Si*C*H$_3$), 11.8 (N(CH$_2$)$_2$*C*H$_2$Si), 14.1 (Si*C*H$_2$(CH$_2$)$_3$N$^+$), 20.3 (SiCH$_2$*C*H$_2$(CH$_2$)$_2$N$^+$), 21.2 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 21.9 (NCH$_2$*C*H$_2$CH$_2$Si), 25.3 (Si(CH$_2$)$_2$*C*H$_2$CH$_2$N$^+$), 36.8 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 42.4 (N*C*H$_2$(CH$_2$)$_2$Si), 50.0 (N$^+$*C*H$_3$), 60.8 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 62.6 (Si(CH$_2$)$_3$*C*H$_2$N$^+$), 121.6 (*C*-1/*C*-8, Naphth), 121.7 (*C*-1/*C*-8, Naphth), 127.0 (5 C, *C*-8a and *C*-3/*C*-6, Naphth), 127.1 (*C*-8a, Naphth), 130.46 (*C*-2/*C*-7, Naphth), 130.50 (*C*-2/*C*-7, Naphth), 130.98 (*C*-4a, Naphth), 131.03 (*C*-4a, Naphth), 134.1 (*C*-4/*C*-5, Naphth), 134.2 (*C*-4/*C*-5, Naphth), 163.0 ((*C*=O)$_2$N(CH$_2$)$_3$Si), 163.4 (N$^+$(CH$_2$)$_3$N(*C*=O)$_2$). ^{29}Si NMR ([D$_6$]DMSO): δ 3.0. Anal. Calcd for $C_{38}H_{44}BrN_3O_4Si$: C, 63.85; H, 6.20; N, 5.88. Found: C, 63.5; H, 6.3; N, 5.8.

Preparation of {5-[dimethyl(3-(1,8-naphthalimido)propyl)silyl]pentyl}dimethyl[3-(1,8-naphthalimido)propyl]ammonium bromide (27). Compound **27** was prepared from **118** (1.36 g, 3.05 mmol) and **128** (968 mg, 3.43 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day, then at –20 °C for 3 days), followed by twofold crystallization by vapor diffusion of diethyl ether into a solution of **27** in dichloromethane, isolation of the resulting precipitate by centrifugation, and drying in vacuo (0.001 mbar, 20 °C, 4 h) to give **27** in 51% yield as a crystalline white solid (1.13 g, 1.55 mmol); mp 123–125 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.10 (s, 6 H, SiCH_3), 0.32–0.55 (m, 4 H, CCH_2SiCH_2C), 1.09–1.32 (m, 4 H,

$SiCH_2(CH_2)_2(CH_2)_2N^+$), 1.41–1.71 (m, 4 H, $NCH_2CH_2CH_2Si$ and $Si(CH_2)_3CH_2CH_2N^+$), 1.98–2.18 (m, 2 H, $N^+CH_2CH_2CH_2N$), 3.05 (s, 6 H, N^+CH_3), 3.21–3.34 (m, 2 H, $Si(CH_2)_4CH_2N^+$), 3.34–3.49 (m, 2 H, $N^+CH_2(CH_2)_2N$), 3.77–3.88 (m, 2 H, $NCH_2(CH_2)_2Si$), 3.97–4.08 (m, 2 H, $N^+(CH_2)_2CH_2N$), 7.66–7.75 (m, 4 H, *H*-3/*H*-6, Naphth), 8.23–8.32 (m, 8 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 ($SiCH_3$), 11.8 ($N(CH_2)_2CH_2Si$), 14.2 ($SiCH_2(CH_2)_4N^+$), 21.2 ($N^+CH_2CH_2CH_2N$), 21.3 ($Si(CH_2)_3CH_2CH_2N^+$), 21.9 ($NCH_2CH_2CH_2Si$), 22.8 ($SiCH_2CH_2(CH_2)_3N^+$), 29.4 ($Si(CH_2)_2CH_2(CH_2)_2N^+$), 36.7 ($N^+(CH_2)_2CH_2N$), 42.4 ($NCH_2(CH_2)_2Si$), 50.0 ($N^+CH_3$), 60.7 ($N^+CH_2(CH_2)_2N$), 62.8 ($Si(CH_2)_4CH_2N^+$), 121.56 (*C*-1/*C*-8, Naphth), 121.65 (*C*-1/*C*-8, Naphth), 126.90 (*C*-8a, Naphth), 126.92 (4 C) (*C*-3/*C*-6, Naphth), 127.1 (*C*-8a, Naphth), 130.40 (*C*-2/*C*-7, Naphth), 130.44 (*C*-2/*C*-7, Naphth), 130.9 (*C*-4a, Naphth), 131.0 (*C*-4a, Naphth), 134.1 (*C*-4/*C*-5, Naphth), 134.2 (*C*-4/*C*-5, Naphth), 163.0 ($(C{=}O)_2N(CH_2)_3Si$), 163.4 ($N^+(CH_2)_3N(C{=}O)_2$). ^{15}N NMR ([D$_6$]DMSO): δ –327 (N^+), –205 ($N(CH_2)_3Si$ or $(N^+(CH_2)_3N$), –206 ($N(CH_2)_3Si$ or $(N^+(CH_2)_3N$). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for $C_{39}H_{46}BrN_3O_4Si$: C, 64.27; H, 6.36; N, 5.77. Found: C, 64.0; H, 6.5; N, 5.7.

Preparation of {6-[dimethyl(3-(1,8-naphthalimido)propyl)silyl]hexyl}dimethyl[3-(1,8-naphthalimido)propyl]ammonium bromide (28). Compound **28** was prepared from **119** (1.11 g, 2.41 mmol) and **128** (710 mg, 2.51 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day) to give **28** in 73% yield as an amorphous white solid (1.31 g, 1.76 mmol); mp 189 °C (dec). ^{1}H NMR ([D$_6$]DMSO): δ –0.07 (s, 6 H, $SiCH_3$), 0.37–0.47 (m, 2 H, $SiCH_2(CH_2)_5N^+$), 0.47–0.58 (m, 2 H, $N(CH_2)_2CH_2Si$), 1.13–1.30 (m, 6 H, $SiCH_2(CH_2)_3(CH_2)_2N^+$), 1.48–1.68 (m, 4 H, $NCH_2CH_2CH_2Si$ and $Si(CH_2)_4CH_2CH_2N^+$), 2.01–2.18 (m, 2 H, $N^+CH_2CH_2CH_2N$), 2.99 (s, 6 H, N^+CH_3), 3.15–3.29 (m, 2 H, $Si(CH_2)_5CH_2N^+$), 3.35–3.46 (m, 2 H, $N^+CH_2(CH_2)_2N$), 3.88–3.99 (m, 2 H, $NCH_2(CH_2)_2Si$), 4.08 (t, $^3J_{HH}$ = 6.3 Hz, 2 H, $N^+(CH_2)_2CH_2N$), 7.76–7.85 (m, 4 H, *H*-3/*H*-6, Naphth), 8.35–8.45 (m, 8 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.4 ($SiCH_3$), 12.0 ($N(CH_2)_2CH_2Si$), 14.4 ($SiCH_2(CH_2)_5N^+$), 21.2 ($N^+CH_2CH_2CH_2N$), 21.6 ($Si(CH_2)_4CH_2CH_2N^+$), 22.0 ($NCH_2CH_2CH_2Si$), 23.0 ($SiCH_2CH_2(CH_2)_4N^+$), 25.4 ($Si(CH_2)_3CH_2(CH_2)_2N^+$), 32.3 ($Si(CH_2)_2CH_2(CH_2)_3N^+$), 36.9 ($N^+(CH_2)_2CH_2N$), 42.5 ($NCH_2(CH_2)_2Si$), 50.0 ($N^+CH_3$), 60.8 ($N^+CH_2(CH_2)_2N$), 63.0 ($Si(CH_2)_5CH_2N^+$), 121.9 (*C*-1/*C*-8, Naphth), 122.0 (*C*-1/*C*-8, Naphth), 127.1 (5 C, *C*-8a and *C*-3/*C*-6, Naphth), 127.3 (*C*-8a, Naphth), 130.59 (*C*-2/*C*-7, Naphth), 130.63 (*C*-2/*C*-7, Naphth), 131.1 (*C*-4a, Naphth), 131.2 (*C*-4a, Naphth), 134.2 (*C*-4/*C*-5, Naphth), 134.3 (*C*-4/*C*-5, Naphth), 163.2 ($(O{=}C)_2N(CH_2)_3Si$), 163.6 ($N^+(CH_2)_3N(C{=}O)_2$). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for $C_{40}H_{48}BrN_3O_4Si$: C, 64.68; H, 6.51; N, 5.66. Found: C, 64.6; H, 6.6; N, 5.6.

Preparation of {4-[dimethyl(3-phthalimidopropyl)silyl]butyl}dimethyl(3-phthalimidopropyl)ammonium bromide (29).[60] Compound **29** was prepared from **120** (1.18 g, 3.09 mmol) and **129** (923 mg, 3.97 mmol) in ethanol (12 mL) and was purified according to a procedure very similar to Protocol A (for details, see ref. 13) (precipitation at 20 °C for 1 day, then at –25 °C for 3 days) to give **29** in 70% yield as an amorphous white solid (1.33 g, 2.16 mmol) containing trace amounts of residual acetone which could not be removed by drying in vacuo at elevated temperature (up to 80 °C). A solvent-free sample was prepared by subsequent precipitation from ethanol/ethyl acetate; mp 138–139 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.08 (s, 6 H, SiCH_3), 0.38–0.55 (m, 4 H, CCH_2SiCH_2C), 1.15–1.30 (m, 2 H, SiCH$_2$CH_2(CH$_2$)$_2$N$^+$), 1.47–1.69 (m, 4 H, NCH$_2$CH_2CH$_2$Si and Si(CH$_2$)$_2$CH_2CH$_2$N$^+$), 1.95–2.12 (m, 2 H, N$^+$CH$_2$CH_2CH$_2$N), 2.99 (s, 6 H, N$^+$CH_3), 3.19–3.30 (m, 2 H, Si(CH$_2$)$_3$CH_2N$^+$), 3.30–3.41 (m, 2 H, N$^+$CH_2(CH$_2$)$_2$N), 3.51 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, NCH_2(CH$_2$)$_2$Si), 3.64 (t, $^3J_{HH}$ = 6.0 Hz, 2 H, N$^+$(CH$_2$)$_2$CH_2N), 7.78–7.89 (m, 8 H, *H*-3/*H*-6, *H*-4/*H*-5, Phth). ^{13}C NMR ([D$_6$]DMSO): δ –3.6 (Si*C*H$_3$), 11.6 (N(CH$_2$)$_2$*C*H$_2$Si), 14.1 (Si*C*H$_2$(CH$_2$)$_3$N$^+$), 20.3 (SiCH$_2$*C*H$_2$(CH$_2$)$_2$N$^+$), 21.6 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 25.3 (Si(CH$_2$)$_2$*C*H$_2$CH$_2$N$^+$), 34.6 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 40.4 (N*C*H$_2$(CH$_2$)$_2$Si), 49.9 (N$^+$*C*H$_3$), 60.7 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 62.8 (Si(CH$_2$)$_3$*C*H$_2$N$^+$), 122.9 (*C*-3/*C*-6, Phth), 123.0 (*C*-3/*C*-6, Phth), 131.5 (*C*-1/*C*-2, Phth), 131.7 (*C*-1/*C*-2, Phth), 134.4 (4 C, *C*-4/*C*-5, Phth), 167.89 (*C*=O, Phth), 167.93 (*C*=O, Phth). ^{29}Si NMR ([D$_6$]DMSO): δ 3.1. ^{15}N NMR ([D$_6$]DMSO): δ –327 (*N*$^+$), –222 (N$^+$(CH$_2$)$_3$*N*), –218 (*N*(CH$_2$)$_3$Si). Anal. Calcd for C$_{30}$H$_{40}$BrN$_3$O$_4$Si: C, 58.62; H, 6.56; N, 6.84. Found: C, 58.2; H, 6.5; N, 6.8.

Preparation of {5-[dimethyl(3-phthalimidopropyl)silyl]pentyl}dimethyl(3-phthalimidopropyl)ammonium bromide (30).[60] Compound **30** was prepared from **121** (1.31 g, 3.30 mmol) and **129** (996 mg, 4.29 mmol) in ethanol (12 mL) and was purified according to a procedure very similar to Protocol A (for details, see ref. 13) (precipitation at 20 °C for 1 day, then at –25 °C for 3 days) to give **30** in 41% yield as a crystalline white solid (851 mg, 1.35 mmol); mp 175 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.09 (s, 6 H, SiCH_3), 0.36–0.52 (m, 4 H, CCH_2SiCH_2C), 1.15–1.32 (m, 4 H, SiCH$_2$(CH_2)$_2$(CH$_2$)$_2$N$^+$), 1.46–1.68 (m, 4 H, NCH$_2$CH_2CH$_2$Si and Si(CH$_2$)$_3$CH_2CH$_2$N$^+$), 1.95–2.11 (m, 2 H, N$^+$CH$_2$CH_2CH$_2$N), 3.01 (s, 6 H, N$^+$CH_3), 3.19–3.31 (m, 2 H, Si(CH$_2$)$_4$CH_2N$^+$), 3.31–3.42 (m, 2 H, N$^+$CH_2(CH$_2$)$_2$N), 3.63 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, N$^+$(CH$_2$)$_2$CH_2N), 3.49 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, NCH_2(CH$_2$)$_2$Si), 7.79–7.87 (m, 8 H, *H*-3/*H*-6, *H*-4/*H*-5, Phth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 (Si*C*H$_3$), 11.6 (N(CH$_2$)$_2$*C*H$_2$Si), 14.3 (Si*C*H$_2$(CH$_2$)$_4$N$^+$), 21.4 (Si(CH$_2$)$_3$*C*H$_2$CH$_2$N$^+$), 21.6 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 22.9 (SiCH$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 29.5 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$N$^+$), 34.6 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 40.4 (N*C*H$_2$(CH$_2$)$_2$Si), 49.9 (N$^+$*C*H$_3$), 60.5 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 63.0 (Si(CH$_2$)$_4$*C*H$_2$N$^+$), 122.9 (*C*-3/*C*-6, Phth), 123.0 (*C*-3/*C*-6, Phth), 131.4 (*C*-

1/*C*-2, Phth), 131.6 (*C*-1/*C*-2, Phth), 134.4 (4 C, *C*-4/*C*-5, Phth), 167.86 (*C*=O, Phth), 167.90 (*C*=O, Phth). ^{15}N NMR ([D$_6$]DMSO): δ –327 (*N*$^+$), –221 (N$^+$(CH$_2$)$_3$*N*), –218 (*N*(CH$_2$)$_3$Si). ^{29}Si NMR ([D$_6$]DMSO): δ 3.0. Anal. Calcd for $C_{31}H_{42}BrN_3O_4Si$: C, 59.23; H, 6.73; N, 6.68. Found: C, 58.7; H, 6.7; N, 6.6.

Preparation of {4-[dimethyl(3-(1,8-naphthalimido)propyl)silyl]butyl}dimethyl(3-phthalimidopropyl)ammonium bromide (31). Compound **31** was prepared from **117** (1.14 g, 2.64 mmol) and **129** (631 mg, 2.72 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 4 °C for 1 day) to give **31** in 49% yield as an amorphous white solid (858 mg, 1.29 mmol); mp 166–167 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.06 (s, 6 H, SiC*H*$_3$), 0.42–0.58 (m, 4 H, CC*H*$_2$SiC*H*$_2$C), 1.16–1.32 (m, 2 H, SiCH$_2$C*H*$_2$(CH$_2$)$_2$N$^+$), 1.49–1.70 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$Si and Si(CH$_2$)$_2$C*H*$_2$CH$_2$N$^+$), 1.95–2.11 (m, 2 H, N$^+$CH$_2$C*H*$_2$CH$_2$N), 3.00 (s, 6 H, N$^+$C*H*$_3$), 3.19–3.31 (m, 2 H, Si(CH$_2$)$_3$C*H*$_2$N$^+$), 3.31–3.43 (m, 2 H, N$^+$C*H*$_2$(CH$_2$)$_2$N), 3.62 (t, $^3J_{HH}$ = 6.1 Hz, 2 H, N$^+$(CH$_2$)$_2$C*H*$_2$N), 3.86–3.99 (m, 2 H, NC*H*$_2$(CH$_2$)$_2$Si), 7.75–7.84 (m, 6 H, *H*-3/*H*-6, *H*-4/*H*-5, Phth, and *H*-3/*H*-6, Naphth), 8.35–8.42 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 (Si*C*H$_3$), 11.8 (N(CH$_2$)$_2$*C*H$_2$Si), 14.2 (Si*C*H$_2$(CH$_2$)$_3$N$^+$), 20.3 (SiCH$_2$*C*H$_2$(CH$_2$)$_2$N$^+$), 21.6 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 21.9 (NCH$_2$*C*H$_2$CH$_2$Si), 25.3 (Si(CH$_2$)$_2$*C*H$_2$CH$_2$N$^+$), 34.6 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 42.5 (N*C*H$_2$(CH$_2$)$_2$Si), 50.0 (N$^+$*C*H$_3$), 60.7 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 62.8 (Si(CH$_2$)$_3$*C*H$_2$N$^+$), 121.8 (*C*-1/*C*-8, Naphth), 123.0 (*C*-3/*C*-6, Phth), 127.11 (*C*-3/*C*-6, Naphth), 127.14 (*C*-8a, Naphth), 130.6 (*C*-2/*C*-7, Naphth), 131.1 (*C*-4a, Naphth), 131.6 (*C*-1/*C*-2, Phth), 134.2 (*C*-4/*C*-5, Naphth or *C*-4/*C*-5, Phth), 134.3 (*C*-4/*C*-5, Naphth or *C*-4/*C*-5, Phth), 163.2 (*C*=O, Naphth), 167.9 (*C*=O, Phth). ^{29}Si NMR ([D$_6$]DMSO): δ 3.1. Anal. Calcd for $C_{34}H_{42}BrN_3O_4Si$: C, 61.44; H, 6.37; N, 6.32. Found: C, 60.7; H, 6.4; N, 6.3.

Preparation of {5-[dimethyl(3-(1,8-naphthalimido)propyl)silyl]pentyl}dimethyl(3-phthalimidopropyl)ammonium bromide (32). Compound **32** was prepared from **118** (2.38 g, 5.33 mmol) and **129** (1.49 g, 6.41 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day), followed by twofold crystallization by vapor diffusion of diethyl ether into a solution of **32** in dichloromethane, isolation of the resulting precipitate by centrifugation, and drying in vacuo (0.001 mbar, 20 °C, 4 h) to give **32** in 70% yield as a crystalline white solid (2.53 g, 3.73 mmol); mp 201–202 °C (dec). ^{1}H NMR ([D$_6$]DMSO): δ –0.07 (s, 6 H, SiC*H*$_3$), 0.36–0.58 (m, 4 H, CC*H*$_2$SiC*H*$_2$C), 1.13–1.34 (m, 4 H, SiCH$_2$(C*H*$_2$)$_2$(CH$_2$)$_2$N$^+$), 1.47–1.70 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$Si and Si(CH$_2$)$_3$C*H*$_2$CH$_2$N$^+$), 1.93–2.11 (m, 2 H, N$^+$CH$_2$C*H*$_2$CH$_2$N), 3.01 (s, 6 H, N$^+$C*H*$_3$), 3.20–3.30 (m, 2 H, Si(CH$_2$)$_4$C*H*$_2$N$^+$), 3.30–3.41 (m, 2 H, N$^+$C*H*$_2$(CH$_2$)$_2$N), 3.61 (t, $^3J_{HH}$ = 6.1 Hz, 2 H, N$^+$(CH$_2$)$_2$C*H*$_2$N), 3.86–3.97 (m, 2 H, NC*H*$_2$(CH$_2$)$_2$Si), 7.74–7.83 (m, 6 H, *H*-3/*H*-6, *H*-4/*H*-5, Phth, and *H*-3/*H*-6, Naphth), 8.33–8.41 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth).

^{13}C NMR ([D$_6$]DMSO): δ –3.5 (Si*C*H$_3$), 11.9 (N(CH$_2$)$_2$*C*H$_2$Si), 14.3 (Si*C*H$_2$(CH$_2$)$_4$N$^+$), 21.4 (Si(CH$_2$)$_3$*C*H$_2$CH$_2$N$^+$ or N$^+$CH$_2$*C*H$_2$CH$_2$N), 21.6 (Si(CH$_2$)$_3$*C*H$_2$CH$_2$N$^+$ or N$^+$CH$_2$*C*H$_2$CH$_2$N), 21.9 (NCH$_2$*C*H$_2$CH$_2$Si), 22.9 (SiCH$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 29.5 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$N$^+$), 34.6 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 42.5 (N*C*H$_2$(CH$_2$)$_2$Si), 50.0 (N$^+$*C*H$_3$), 60.5 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 63.0 (Si(CH$_2$)$_4$*C*H$_2$N$^+$), 121.8 (*C*-1/*C*-8, Naphth), 122.9 (*C*-3/*C*-6, Phth), 127.07 (*C*-3/*C*-6, Naphth), 127.11 (*C*-8a, Naphth), 130.6 (*C*-2/*C*-7, Naphth), 131.1 (*C*-4a, Naphth), 131.6 (*C*-1/*C*-2, Phth), 134.2 (*C*-4/*C*-5, Naphth or *C*-4/*C*-5, Phth), 134.3 (*C*-4/*C*-5, Naphth or *C*-4/*C*-5, Phth), 163.2 (*C*=O, Naphth), 167.8 (*C*=O, Phth). ^{15}N NMR ([D$_6$]DMSO): δ –326 (*N*$^+$), –221 (N$^+$(CH$_2$)$_3$*N*), *N*(CH$_2$)$_3$Si not detected. ^{29}Si NMR ([D$_6$]DMSO): δ 3.0. Anal. Calcd for C$_{35}$H$_{44}$BrN$_3$O$_4$Si: C, 61.94; H, 6.53; N, 6.19. Found: C, 61.9; H, 6.5; N, 6.2.

Preparation of {6-[dimethyl(3-(1,8-naphthalimido)propyl)silyl]hexyl}dimethyl(3-phthalimidopropyl)ammonium bromide (33). Compound **33** was prepared from **119** (1.11 g, 2.41 mmol) and **129** (590 mg, 2.54 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day) to give **33** in 45% yield as an amorphous white solid (752 mg, 1.09 mmol); mp 190–191 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.06 (s, 6 H, SiC*H*$_3$), 0.37–0.49 (m, 2 H, SiC*H*$_2$(CH$_2$)$_5$N$^+$), 0.49–0.60 (m, 2 H, N(CH$_2$)$_2$C*H*$_2$Si), 1.13–1.33 (m, 6 H, SiCH$_2$(C*H*$_2$)$_3$(CH$_2$)$_2$N$^+$), 1.49–1.68 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$Si and Si(CH$_2$)$_4$C*H*$_2$CH$_2$N$^+$), 1.96–2.10 (m, 2 H, N$^+$CH$_2$C*H*$_2$CH$_2$N), 2.98 (s, 6 H, N$^+$C*H*$_3$), 3.15–3.28 (m, 2 H, Si(CH$_2$)$_5$C*H*$_2$N$^+$), 3.28–3.41 (m, 2 H, N$^+$C*H*$_2$(CH$_2$)$_2$N), 3.63 (t, $^3J_{HH}$ = 6.1 Hz, 2 H, N$^+$(CH$_2$)$_2$C*H*$_2$N), 3.90–4.03 (m, 2 H, NC*H*$_2$(CH$_2$)$_2$Si), 7.77–7.89 (m, 6 H, *H*-3/*H*-6, *H*-4/*H*-5, Phth, and *H*-3/*H*-6, Naphth), 8.38–8.47 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.4 (Si*C*H$_3$), 12.0 (N(CH$_2$)$_2$*C*H$_2$Si), 14.4 (Si*C*H$_2$(CH$_2$)$_5$N$^+$), 21.6 (2 C, N$^+$CH$_2$*C*H$_2$CH$_2$N, Si(CH$_2$)$_4$*C*H$_2$CH$_2$N$^+$), 22.0 (NCH$_2$*C*H$_2$CH$_2$Si), 23.1 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$N$^+$), 25.4 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$N$^+$), 32.3 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 34.6 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 42.5 (N*C*H$_2$(CH$_2$)$_2$Si), 49.9 (N$^+$*C*H$_3$), 60.6 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 63.1 (Si(CH$_2$)$_5$*C*H$_2$N$^+$), 121.9 (*C*-1/*C*-8, Naphth), 123.0 (*C*-3/*C*-6, Phth), 127.17 (*C*-3/*C*-6, Naphth), 127.25 (*C*-8a, Naphth), 130.6 (*C*-2/*C*-7, Naphth), 131.2 (*C*-4a, Naphth), 131.7 (*C*-1/*C*-2, Phth), 134.3 (*C*-4/*C*-5, Naphth or *C*-4/*C*-5, Phth), 134.4 (*C*-4/*C*-5, Naphth or *C*-4/*C*-5, Phth), 163.3 (*C*=O, Naphth), 167.9 (*C*=O, Phth). ^{29}Si NMR ([D$_6$]DMSO): δ 3.0. Anal. Calcd for C$_{36}$H$_{46}$BrN$_3$O$_4$Si: C, 62.42; H, 6.69; N, 6.07. Found: C, 62.2; H, 6.7; N, 6.0.

Preparation of {4-[dimethyl(3-phthalimidopropyl)silyl]butyl}dimethyl[3-(1,8-naphthalimido)propyl]ammonium bromide (34). Compound **34** was prepared from **120** (1.15 g, 3.01 mmol) and **128** (927 mg, 3.28 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day) to give **34** in 88% yield as an amorphous white solid (1.75 g, 2.63 mmol); mp 186–187 °C (dec). ^{1}H NMR ([D$_6$]DMSO): δ –0.09 (s, 6 H, SiC*H*$_3$), 0.37–

0.50 (m, 4 H, CC*H*$_2$SiC*H*$_2$C), 1.13–1.30 (m, 2 H, SiCH$_2$C*H*$_2$(CH$_2$)$_2$N$^+$), 1.45–1.70 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$Si and Si(CH$_2$)$_2$C*H*$_2$CH$_2$N$^+$), 2.00–2.20 (m, 2 H, N$^+$CH$_2$C*H*$_2$CH$_2$N), 3.00 (s, 6 H, N$^+$C*H*$_3$), 3.19–3.31 (m, 2 H, Si(CH$_2$)$_3$C*H*$_2$N$^+$), 3.33–3.44 (m, 2 H, N$^+$C*H*$_2$(CH$_2$)$_2$N), 3.48 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, NC*H*$_2$(CH$_2$)$_2$Si), 4.09 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, N$^+$(CH$_2$)$_2$C*H*$_2$N), 7.78–7.87 (m, 6 H, *H*-3/*H*-6, *H*-4/*H*-5, Phth, and *H*-3/*H*-6, Naphth), 8.40–8.46 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.6 (Si*C*H$_3$), 11.6 (N(CH$_2$)$_2$*C*H$_2$Si), 14.1 (Si*C*H$_2$(CH$_2$)$_3$N$^+$), 20.3 (SiCH$_2$*C*H$_2$(CH$_2$)$_2$N$^+$), 21.3 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 25.3 (Si(CH$_2$)$_2$*C*H$_2$CH$_2$N$^+$), 36.9 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 40.3 (N*C*H$_2$(CH$_2$)$_2$Si), 50.0 (N$^+$*C*H$_3$), 60.9 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 62.6 (Si(CH$_2$)$_3$*C*H$_2$N$^+$), 122.0 (*C*-1/*C*-8, Naphth), 122.9 (*C*-3/*C*-6, Phth), 127.1 (*C*-3/*C*-6, Naphth), 127.4 (*C*-8a, Naphth), 130.7 (*C*-2/*C*-7, Naphth), 131.2 (*C*-4a, Naphth), 131.4 (*C*-1/*C*-2, Phth), 134.3 (4 C, *C*-4/*C*-5, Naphth and *C*-4/*C*-5, Phth), 163.6 (*C*=O, Naphth), 167.9 (*C*=O, Phth). ^{29}Si NMR ([D$_6$]DMSO): δ 3.0. Anal. Calcd for C$_{34}$H$_{42}$BrN$_3$O$_4$Si: C, 61.44; H, 6.37; N, 6.32. Found: C, 60.8; H, 6.4; N, 6.2.

Preparation of {5-[dimethyl(3-phthalimidopropyl)silyl]pentyl}dimethyl[3-(1,8-naphthalimido)propyl]ammonium bromide (35). Compound **35** was prepared from **121** (1.24 g, 3.13 mmol) and **128** (971 mg, 3.44 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day) to give **35** in 53% yield as an amorphous white solid (1.13 g, 1.66 mmol); mp 147–148 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.12 (s, 6 H, SiC*H*$_3$), 0.33–0.48 (m, 4 H, CC*H*$_2$SiC*H*$_2$C), 1.12–1.30 (m, 4 H, SiCH$_2$(C*H*$_2$)$_2$(CH$_2$)$_2$N$^+$), 1.42–1.69 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$Si and Si(CH$_2$)$_3$C*H*$_2$CH$_2$N$^+$), 2.00–2.19 (m, 2 H, N$^+$CH$_2$C*H*$_2$CH$_2$N), 3.04 (s, 6 H, N$^+$C*H*$_3$), 3.21–3.33 (m, 2 H, Si(CH$_2$)$_4$C*H*$_2$N$^+$), 3.36–3.50 (m, 4 H, N$^+$C*H*$_2$(CH$_2$)$_2$N and NC*H*$_2$(CH$_2$)$_2$Si), 4.01–4.13 (m, 2 H, N$^+$(CH$_2$)$_2$C*H*$_2$N), 7.73–7.83 (m, 6 H, *H*-3/*H*-6, *H*-4/*H*-5, Phth, and *H*-3/*H*-6, Naphth), 8.34–8.43 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.6 (Si*C*H$_3$), 11.6 (N(CH$_2$)$_2$*C*H$_2$Si), 14.2 (Si*C*H$_2$(CH$_2$)$_4$N$^+$), 21.2 (Si(CH$_2$)$_3$*C*H$_2$CH$_2$N$^+$ or N$^+$CH$_2$*C*H$_2$CH$_2$N), 21.4 (Si(CH$_2$)$_3$*C*H$_2$CH$_2$N$^+$ or N$^+$CH$_2$*C*H$_2$CH$_2$N), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 22.9 (SiCH$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 29.5 (Si(CH$_2$)$_2$*C*H$_2$(CH)$_2$N$^+$), 36.9 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 40.3 (N*C*H$_2$(CH$_2$)$_2$Si), 49.9 (N$^+$*C*H$_3$), 60.7 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 62.8 (Si(CH$_2$)$_4$*C*H$_2$N$^+$), 121.8 (*C*-1/*C*-8, Naphth), 122.8 (*C*-3/*C*-6, Phth), 127.1 (*C*-3/*C*-6, Naphth), 127.2 (*C*-8a, Naphth), 130.6 (*C*-2/*C*-7, Naphth), 131.1 (*C*-4a, Naphth), 131.3 (*C*-1/*C*-2, Phth), 134.3 (4 C, *C*-4/*C*-5, Naphth, and *C*-4/*C*-5, Phth), 163.5 (*C*=O, Naphth), 167.8 (*C*=O, Phth). ^{15}N NMR ([D$_6$]DMSO): δ –327 (*N*$^+$), –218 (*N*(CH$_2$)$_3$Si), –208 (N$^+$(CH$_2$)$_3$*N*). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for C$_{35}$H$_{44}$BrN$_3$O$_4$Si: C, 61.94; H, 6.53; N, 6.19. Found: C, 61.8; H, 6.5; N, 6.3.

Preparation of {6-[dimethyl(3-phthalimidopropyl)silyl]hexyl}dimethyl[3-(1,8-naphthalimido)propyl]ammonium bromide (36). Compound **36** was prepared from **122** (1.21 g,

2.95 mmol) and **128** (910 mg, 3.22 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day) to give **36** in 56% yield as an amorphous white solid (1.14 g, 1.65 mmol); mp 140–141 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.09 (s, 6 H, SiCH_3), 0.35–0.49 (m, 4 H, CCH_2SiCH_2C), 1.12–1.29 (m, 6 H, SiCH$_2$(CH_2)$_3$(CH$_2$)$_2$N$^+$), 1.47–1.65 (m, 4 H, NCH$_2$CH_2CH$_2$Si and Si(CH$_2$)$_4$CH_2CH$_2$N$^+$), 2.03–2.18 (m, 2 H, N$^+$CH$_2$CH_2CH$_2$N), 3.00 (s, 6 H, N$^+$CH_3), 3.17–3.29 (m, 2 H, Si(CH$_2$)$_5$CH_2N$^+$), 3.35–3.44 (m, 2 H, N$^+$CH_2(CH$_2$)$_2$N), 3.48 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, NCH_2(CH$_2$)$_2$Si), 4.11 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, N$^+$(CH$_2$)$_2$CH_2N), 7.79–7.82 (m, 4 H, *H*-3/*H*-6, *H*-4/*H*-5, Phth), 7.82–7.89 (m, 2 H, *H*-3/*H*-6, Naphth), 8.42–8.49 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 (Si*C*H$_3$), 11.7 (N(CH$_2$)$_2$*C*H$_2$Si), 14.3 (Si*C*H$_2$(CH$_2$)$_5$N$^+$), 21.3 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 21.6 (Si(CH$_2$)$_4$*C*H$_2$CH$_2$N$^+$), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 23.0 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$N$^+$), 25.4 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$N$^+$), 32.3 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 36.9 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 40.4 (N*C*H$_2$(CH$_2$)$_2$Si), 49.9 (N$^+$*C*H$_3$), 60.9 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 63.0 (Si(CH$_2$)$_5$*C*H$_2$N$^+$), 122.0 (*C*-1/*C*-8, Naphth), 122.9 (*C*-3/*C*-6, Phth), 127.2 (*C*-3/*C*-6, Naphth), 127.4 (*C*-8a, Naphth), 130.7 (*C*-2/*C*-7, Naphth), 131.3 (*C*-4a, Naphth), 131.5 (*C*-1/*C*-2, Phth), 134.3 (*C*-4/*C*-5, Naphth or *C*-4/*C*-5, Phth), 134.4 (*C*-4/*C*-5, Naphth or *C*-4/*C*-5, Phth), 163.7 (*C*=O, Naphth), 167.9 (*C*=O, Phth). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for C$_{36}$H$_{46}$BrN$_3$O$_4$Si: C, 62.42; H, 6.69; N, 6.07. Found: C, 62.2; H, 6.6; N, 6.1.

Preparation of {4-[dimethyl(3-(4-methylphthalimido)propyl)silyl]butyl}dimethyl[3-(4-methylphthalimido)propyl]ammonium bromide (37). Compound **37** was prepared from **123** (1.14 g, 2.88 mmol) and **130** (752 mg, 3.05 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 4 °C for 1 day) to give **37** in 58% yield as an amorphous white solid (1.08 g, 1.68 mmol); mp 170 °C °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.08 (s, 6 H, SiCH_3), 0.38–0.53 (m, 4 H, CCH_2SiCH_2C), 1.14–1.30 (m, 2 H, SiCH$_2$CH_2(CH$_2$)$_2$N$^+$), 1.45–1.69 (m, 4 H, NCH$_2$CH_2CH$_2$Si and Si(CH$_2$)$_2$CH_2CH$_2$N$^+$), 1.93–2.12 (m, 2 H, N$^+$CH$_2$CH_2CH$_2$N), 2.445 (s, 3 H, Aryl-CH_3), 2.453 (s, 3 H, Aryl-CH_3), 3.00 (s, 6 H, N$^+$CH_3), 3.19–3.29 (m, 2 H, Si(CH$_2$)$_3$CH_2N$^+$), 3.29–3.40 (m, 2 H, N$^+$CH_2(CH$_2$)$_2$N), 3.48 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, NCH_2(CH$_2$)$_2$Si), 3.61 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, N$^+$(CH$_2$)$_2$CH_2N), 7.56–7.67 (m, 4 H, *H*-3, *H*-5, Me-phth), 7.67–7.75 (m, 2 H, *H*-6, Me-phth). ^{13}C NMR ([D$_6$]DMSO): δ –3.6 (Si*C*H$_3$), 11.6 (N(CH$_2$)$_2$*C*H$_2$Si), 14.1 (Si*C*H$_2$(CH$_2$)$_3$N$^+$), 20.3 (SiCH$_2$*C*H$_2$(CH$_2$)$_2$N$^+$), 21.3 (2 C, Aryl-*C*H$_3$), 21.6 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 25.3 (Si(CH$_2$)$_2$*C*H$_2$CH$_2$N$^+$), 34.5 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 40.3 (N*C*H$_2$(CH$_2$)$_2$Si), 50.0 (N$^+$*C*H$_3$), 60.6 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 62.8 (Si(CH$_2$)$_3$*C*H$_2$N$^+$), 122.85 (*C*-6, Me-phth), 122.94 (*C*-6, Me-phth), 123.36 (*C*-3, Me-phth), 123.42 (*C*-3, Me-phth), 128.8 (*C*-1, Me-phth), 129.0 (*C*-1, Me-phth), 131.8 (*C*-2, Me-phth), 132.0 (*C*-2, Me-phth), 134.6 (2 C, *C*-5, Me-phth), 145.2 (*C*-4, Me-phth), 145.3 (*C*-4, Me-

phth), 167.85 (*C*=O), 167.88 (*C*=O), 167.94 (*C*=O), 167.98 (*C*=O). ^{29}Si NMR ([D$_6$]DMSO): δ 3.0. Anal. Calcd for $C_{32}H_{44}BrN_3O_4Si$: C, 59.80; H, 6.90; N, 6.54. Found: C, 60.1; H, 7.1; N, 6.6.

Preparation of {5-[dimethyl(3-(4-methylphthalimido)propyl)silyl]pentyl}dimethyl[3-(4-methylphthalimido)propyl]ammonium bromide (38). Compound **38** was prepared from **124** (1.08 g, 2.63 mmol) and **130** (734 mg, 2.98 mmol) in ethanol (12 mL) and was purified according to Protocol B (precipitation at 4 °C for 1 day) to give **38** in 58% yield as an amorphous white solid (997 mg, 1.52 mmol); mp 130–131 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.07 (s, 6 H, SiC*H*$_3$), 0.39–0.52 (m, 4 H, CC*H*$_2$SiC*H*$_2$C), 1.17–1.32 (m, 4 H, SiCH$_2$(C*H*$_2$)$_2$(CH$_2$)$_2$N$^+$), 1.47–1.67 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$Si and Si(CH$_2$)$_3$C*H*$_2$CH$_2$N$^+$), 2.04–2.09 (m, 2 H, N$^+$CH$_2$C*H*$_2$CH$_2$N), 2.45 (s, 3 H, Aryl-C*H*$_3$), 2.46 (s, 3 H, Aryl-C*H*$_3$), 2.99 (s, 6 H, N$^+$C*H*$_3$), 3.16–3.27 (m, 2 H, Si(CH$_2$)$_4$C*H*$_2$N$^+$), 3.27–3.39 (m, 2 H, N$^+$C*H*$_2$(CH$_2$)$_2$N), 3.48 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, NC*H*$_2$(CH$_2$)$_2$Si), 3.62 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, N$^+$(CH$_2$)$_2$C*H*$_2$N), 7.57–7.67 (m, 4 H, *H*-3, *H*-5, Me-phth), 7.67–7.75 (m, 2 H, *H*-6, Me-phth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 (Si*C*H$_3$), 11.7 (N(CH$_2$)$_2$*C*H$_2$Si), 14.3 (Si*C*H$_2$(CH$_2$)$_4$N$^+$), 21.3 (2 C, Aryl-*C*H$_3$), 21.4 Si(CH$_2$)$_3$*C*H$_2$CH$_2$N$^+$), 21.6 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 22.9 (SiCH$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 29.5 (Si(CH$_2$)$_2$*C*H$_2$(CH)$_2$N$^+$), 34.5 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 40.3 (N*C*H$_2$(CH$_2$)$_2$Si), 50.0 (N$^+$*C*H$_3$), 60.5 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 63.0 (Si(CH$_2$)$_4$*C*H$_2$N$^+$), 122.87 (*C*-6, Me-phth), 122.94 (*C*-6, Me-phth), 123.38 (*C*-3, Me-phth), 123.43 (*C*-3, Me-phth), 128.9 (*C*-1, Me-phth), 129.0 (*C*-1, Me-phth), 131.9 (*C*-2, Me-phth), 132.0 (*C*-2, Me-phth), 134.7 (2 C, *C*-5, Me-phth), 145.25 (*C*-4, Me-phth), 145.28 (*C*-4, Me-phth), 167.895 (*C*=O), 167.905 (*C*=O), 167.98 (*C*=O), 168.01 (*C*=O). ^{29}Si NMR ([D$_6$]DMSO): δ 3.0. Anal. Calcd for $C_{33}H_{46}BrN_3O_4Si$: C, 60.35; H, 7.06; N, 6.40. Found: C, 60.3; H, 6.9; N, 6.2.

Preparation of {6-[dimethyl(3-(4-methylphthalimido)propyl)silyl]hexyl}dimethyl[3-(4-methylphthalimido)propyl]ammonium bromide (39). Compound **39** was prepared from **125** (1.11 g, 2.62 mmol) and **130** (658 mg, 2.67 mmol) in ethanol (12 mL) and was purified according to Protocol B (precipitation at 4 °C for 1 day) to give **39** in 56% yield as an amorphous white solid (1.04 g, 1.55 mmol); mp 131–132 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.08 (s, 6 H, SiC*H*$_3$), 0.37–0.50 (m, 4 H, CC*H*$_2$SiC*H*$_2$C), 1.12–1.32 (m, 6 H, SiCH$_2$(C*H*$_2$)$_3$(CH$_2$)$_2$N$^+$), 1.46–1.65 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$Si and Si(CH$_2$)$_4$C*H*$_2$CH$_2$N$^+$), 1.96–2.10 (m, 2 H, N$^+$CH$_2$C*H*$_2$CH$_2$N), 2.45 (s, 3 H, Aryl-C*H*$_3$), 2.46 (s, 3 H, Aryl-C*H*$_3$), 2.99 (s, 6 H, N$^+$C*H*$_3$), 3.17–3.28 (m, 2 H, Si(CH$_2$)$_5$C*H*$_2$N$^+$), 3.28–3.39 (m, 2 H, N$^+$C*H*$_2$(CH$_2$)$_2$N), 3.48 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, NC*H*$_2$(CH$_2$)$_2$Si), 3.62 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, N$^+$(CH$_2$)$_2$C*H*$_2$N), 7.57–7.67 (m, 4 H, *H*-3, *H*-5, Me-phth), 7.67–7.75 (m, 2 H, *H*-6, Me-phth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 (Si*C*H$_3$), 11.7 (N(CH$_2$)$_2$*C*H$_2$Si), 14.4 (Si*C*H$_2$(CH$_2$)$_5$N$^+$), 21.3 (2 C, Aryl-*C*H$_3$), 21.60 (Si(CH$_2$)$_4$*C*H$_2$CH$_2$N$^+$ or N$^+$CH$_2$*C*H$_2$CH$_2$N), 21.62 (Si(CH$_2$)$_4$*C*H$_2$CH$_2$N$^+$ or N$^+$CH$_2$*C*H$_2$CH$_2$N), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 23.1 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$N$^+$), 25.4

($Si(CH_2)_3CH_2(CH_2)_2N^+$), 32.4 ($Si(CH_2)_2CH_2(CH_2)_3N^+$), 34.5 ($N^+(CH_2)_2CH_2N$), 40.3 ($NCH_2(CH_2)_2Si$), 50.0 ($N^+CH_3$), 60.6 ($N^+CH_2(CH_2)_2N$), 63.1 ($Si(CH_2)_5CH_2N^+$), 122.9 (*C*-6, Me-phth), 123.0 (*C*-6, Me-phth), 123.37 (*C*-3, Me-phth), 123.44 (*C*-3, Me-phth), 128.9 (*C*-1, Me-phth), 129.0 (*C*-1, Me-phth), 131.9 (*C*-2, Me-phth), 132.0 (*C*-2, Me-phth), 134.7 (2 C, *C*-5, Me-phth), 145.25 (*C*-4, Me-phth), 145.28 (*C*-4, Me-phth), 167.89 (*C*=O), 167.91 (*C*=O), 167.97 (*C*=O), 168.01 (*C*=O). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for $C_{34}H_{48}BrN_3O_4Si$: C, 60.88; H, 7.21; N, 6.26. Found: C, 59.4; H, 7.2; N, 6.1.

Preparation of {4-[dimethyl(3-(1,8-naphthalimido)propyl)silyl]butyl}dimethyl[3-(4-methylphthalimido)propyl]ammonium bromide (40). Compound **40** was prepared from **117** (1.10 g, 2.54 mmol) and **130** (650 mg, 2.64 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day) to give **40** in 59% yield as an amorphous white solid (1.02 g, 1.50 mmol); mp 98–99 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.05 (s, 6 H, $SiCH_3$), 0.44–0.59 (m, 4 H, CCH_2SiCH_2C), 1.17–1.33 (m, 2 H, $SiCH_2CH_2(CH_2)_2N^+$), 1.52–1.69 (m, 4 H, $NCH_2CH_2CH_2Si$ and $Si(CH_2)_2CH_2CH_2N^+$), 1.95–2.10 (m, 2 H, $N^+CH_2CH_2CH_2N$), 2.42 (s, 3 H, Aryl-CH_3), 2.99 (s, 6 H, N^+CH_3), 3.19–3.29 (m, 2 H, $Si(CH_2)_3CH_2N^+$), 3.29–3.40 (m, 2 H, $N^+CH_2(CH_2)_2N$), 3.60 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, $N^+(CH_2)_2CH_2N$), 3.89–4.00 (m, 2 H, $NCH_2(CH_2)_2Si$), 7.53–7.58 (m, 1 H, *H*-5, Me-phth), 7.58–7.62 (m, 1 H, *H*-3, Me-phth), 7.67 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, *H*-6, Me-phth), 7.82 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 7.4 Hz, 2 H, *H*-3/*H*-6, Naphth), 8.37–8.45 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 ($SiCH_3$), 11.9 ($N(CH_2)_2CH_2Si$), 14.2 ($SiCH_2(CH_2)_3N^+$), 20.3 ($SiCH_2CH_2(CH_2)_2N^+$), 21.3 (Aryl-CH_3), 21.6 ($N^+CH_2CH_2CH_2N$), 22.0 ($NCH_2CH_2CH_2Si$), 25.3 ($Si(CH_2)_2CH_2CH_2N^+$), 34.5 ($N^+(CH_2)_2CH_2N$), 42.5 ($NCH_2(CH_2)_2Si$), 50.0 (N^+CH_3), 60.6 ($N^+CH_2(CH_2)_2N$), 62.8 ($Si(CH_2)_3CH_2N^+$), 121.9 (*C*-1/*C*-8, Naphth), 122.9 (*C*-6, Me-phth), 123.4 (*C*-3, Me-phth), 127.1 (*C*-3/*C*-6, Naphth), 127.2 (*C*-8a, Naphth), 129.0 (*C*-1, Me-phth), 130.6 (*C*-2/*C*-7, Naphth), 131.2 (*C*-4a, Naphth), 131.9 (*C*-2, Me-phth), 134.3 (*C*-4/*C*-5, Naphth), 134.6 (*C*-5, Me-phth), 145.2 (*C*-4, Me-phth), 163.3 (*C*=O, Naphth), 167.9 (*C*=O, Me-phth), 168.0 (*C*=O, Me-phth). ^{29}Si NMR ([D$_6$]DMSO): δ 3.1. Anal. Calcd for $C_{35}H_{44}BrN_3O_4Si$: C, 61.94; H, 6.53; N, 6.19. Found: C, 60.9; H, 6.6; N, 6.0.

Preparation of {5-[dimethyl(3-(1,8-naphthalimido)propyl)silyl]pentyl}dimethyl[3-(4-methylphthalimido)propyl]ammonium bromide (41). Compound **41** was prepared from **118** (2.38 g, 5.33 mmol) and **130** (1.69 g, 6.86 mmol) in ethanol (15 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day) to give **41** in 84% yield as an amorphous white solid (3.09 g, 4.46 mmol); mp 134–135 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.06 (s, 6 H, $SiCH_3$), 0.40–0.58 (m, 4 H, CCH_2SiCH_2C), 1.15–1.34 (m, 4 H, $SiCH_2(CH_2)_2(CH_2)_2N^+$), 1.49–1.68 (m, 4 H, $NCH_2CH_2CH_2Si$ and $Si(CH_2)_3CH_2CH_2N^+$), 1.94–2.09 (m, 2 H, $N^+CH_2CH_2CH_2N$), 2.41 (s, 3 H,

Aryl-CH_3), 3.00 (s, 6 H, N^+CH_3), 3.16–3.29 (m, 2 H, $Si(CH_2)_4CH_2N^+$), 3.29–3.42 (m, 2 H, $N^+CH_2(CH_2)_2N$), 3.59 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, $N^+(CH_2)_2CH_2N$), 3.87–3.99 (m, 2 H, $NCH_2(CH_2)_2Si$), 7.51–7.56 (m, 1 H, *H*-5, Me-phth), 7.56–7.59 (m, 1 H, *H*-3, Me-phth), 7.64 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, *H*-6, Me-phth), 7.82 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz, 2 H, *H*-3/*H*-6, Naphth), 8.36–8.43 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.4 ($SiCH_3$), 11.9 ($N(CH_2)_2CH_2Si$), 14.3 ($SiCH_2(CH_2)_4N^+$), 21.28 (Aryl-CH_3), 21.33 ($Si(CH_2)_3CH_2CH_2N^+$ or $N^+CH_2CH_2CH_2N$), 21.6 ($Si(CH_2)_3CH_2CH_2N^+$ or $N^+CH_2CH_2CH_2N$), 22.0 ($NCH_2CH_2CH_2Si$), 22.9 ($SiCH_2CH_2(CH_2)_3N^+$), 29.5 ($Si(CH_2)_2CH_2(CH_2)_2N^+$), 34.5 ($N^+(CH_2)_2CH_2N$), 42.5 ($NCH_2(CH_2)_2Si$), 50.0 ($N^+CH_3$), 60.5 ($N^+CH_2(CH_2)_2N$), 62.9 ($Si(CH_2)_4CH_2N^+$), 121.8 (*C*-1/*C*-8, Naphth), 122.8 (*C*-6, Me-phth), 123.3 (*C*-3, Me-phth), 127.1 (*C*-3/*C*-6, Naphth), 127.2 (*C*-8a, Naphth), 128.9 (*C*-1, Me-phth), 130.6 (*C*-2/*C*-7, Naphth), 131.1 (*C*-4a, Naphth), 131.9 (*C*-2, Me-phth), 134.2 (*C*-4/*C*-5, Naphth), 134.5 (*C*-5, Me-phth), 145.2 (*C*-4, Me-phth), 163.2 (*C*=O, Naphth), 167.8 (*C*=O, Me-phth), 167.9 (*C*=O, Me-phth). ^{29}Si NMR ([D$_6$]DMSO): δ 3.0. Anal. Calcd for $C_{36}H_{46}BrN_3O_4Si$: C, 62.42; H, 6.69; N, 6.07. Found: C, 62.0; H, 6.7; N, 5.9.

Preparation of {6-[dimethyl(3-(1,8-naphthalimido)propyl)silyl]hexyl}dimethyl[3-(4-methylphthalimido)propyl]ammonium bromide (42). Compound **42** was prepared from **119** (1.10 g, 2.39 mmol) and **130** (619 mg, 2.51 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day) to give **42** in 57% yield as an amorphous white solid (966 mg, 1.37 mmol); mp 171–173 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.06 (s, 6 H, $SiCH_3$), 0.38–0.48 (m, 2 H, $SiCH_2(CH_2)_5N^+$), 0.48–0.58 (m, 2 H, $N(CH_2)_2CH_2Si$), 1.12–1.31 (m, 6 H, $SiCH_2(CH_2)_3(CH_2)_2N^+$), 1.49–1.67 (m, 4 H, $NCH_2CH_2CH_2Si$ and $Si(CH_2)_4CH_2CH_2N^+$), 1.93–2.09 (m, 2 H, $N^+CH_2CH_2CH_2N$), 2.43 (s, 3 H, Aryl-CH_3), 2.99 (s, 6 H, N^+CH_3), 3.16–3.28 (m, 2 H, $Si(CH_2)_5CH_2N^+$), 3.28–3.40 (m, 2 H, $N^+CH_2(CH_2)_2N$), 3.60 (t, $^3J_{HH}$ = 6.1 Hz, 2 H, $N^+(CH_2)_2CH_2N$), 3.89–4.00 (m, 2 H, $NCH_2(CH_2)_2Si$), 7.54–7.60 (m, 1 H, *H*-5, Me-phth), 7.60–7.64 (m, 1 H, *H*-3, Me-phth), 7.68 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, *H*-6, Me-phth), 7.82 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.4 Hz, 2 H, *H*-3/*H*-6, Naphth), 8.37–8.44 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.4 ($SiCH_3$), 12.0 ($N(CH_2)_2CH_2Si$), 14.4 ($SiCH_2(CH_2)_5N^+$), 21.3 ($ArCH_3$), 21.59 ($Si(CH_2)_4CH_2CH_2N^+$ or $N^+CH_2CH_2CH_2N$), 21.60 ($Si(CH_2)_4CH_2CH_2N^+$ or $N^+CH_2CH_2CH_2N$), 22.0 ($NCH_2CH_2CH_2Si$), 23.1 ($SiCH_2CH_2(CH_2)_4N^+$), 25.4 ($Si(CH_2)_3CH_2(CH_2)_2N^+$), 32.3 ($Si(CH_2)_2CH_2(CH_2)_3N^+$), 34.5 ($N^+(CH_2)_2CH_2N$), 42.5 ($NCH_2(CH_2)_2Si$), 50.0 ($N^+CH_3$), 60.6 ($N^+CH_2(CH_2)_2N$), 63.1 ($Si(CH_2)_5CH_2N^+$), 121.9 (*C*-1/*C*-8, Naphth), 122.9 (*C*-6, Me-phth), 123.4 (*C*-3, Me-phth), 127.1 (*C*-3/*C*-6, Naphth), 127.2 (*C*-8a, Naphth), 129.0 (*C*-1, Me-phth), 130.6 (*C*-2/*C*-7, Naphth), 131.2 (*C*-4a, Naphth), 132.0 (*C*-2, Me-phth), 134.3 (*C*-4/*C*-5, Naphth), 134.6 (*C*-5, Me-phth), 145.2 (*C*-4, Me-phth), 163.3 (*C*=O, Naphth), 167.9 (*C*=O, Me-phth), 168.0 (*C*=O, Me-

phth). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for $C_{37}H_{48}BrN_3O_4Si$: C, 62.88; H, 6.85; N, 5.95. Found: C, 61.4; H, 6.9; N, 5.8.

Preparation of {4-[dimethyl(3-(4-methylphthalimido)propyl)silyl]butyl}dimethyl[3-(1,8-naphthalimido)propyl]ammonium bromide (43). Compound **43** was prepared from **123** (1.19 g, 3.00 mmol) and **128** (879 mg, 3.11 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day) to give **43** in 80% yield as an amorphous white solid (1.62 g, 2.39 mmol); mp 203 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.09 (s, 6 H, SiCH_3), 0.36–0.52 (m, 4 H, CCH_2SiCH_2C), 1.13–1.30 (m, 2 H, SiCH$_2$CH_2(CH$_2$)$_2$N$^+$), 1.44–1.69 (m, 4 H, NCH$_2$CH_2CH$_2$Si and Si(CH$_2$)$_2$CH_2CH$_2$N$^+$), 2.03–2.18 (m, 2 H, N$^+$CH$_2$CH_2CH$_2$N), 2.41 (s, 3 H, Aryl-CH_3), 3.01 (s, 6 H, N$^+$CH_3), 3.20–3.32 (m, 2 H, Si(CH$_2$)$_3$CH_2N$^+$), 3.32–3.50 (m, 4 H, NCH_2(CH$_2$)$_2$Si and N$^+$CH_2(CH$_2$)$_2$N), 4.08 (t, $^3J_{HH}$ = 6.3 Hz, 2 H, N$^+$(CH$_2$)$_2$CH_2N), 7.51–7.58 (m, 2 H, *H*-3, *H*-5, Me-phth), 7.63 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, *H*-6, Me-phth), 7.82 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, 2 H, *H*-3/*H*-6, Naphth), 8.39–8.45 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.6 (Si*C*H$_3$), 11.6 (N(CH$_2$)$_2$*C*H$_2$Si), 14.1 (Si*C*H$_2$(CH$_2$)$_3$N$^+$), 20.3 (SiCH$_2$*C*H$_2$(CH$_2$)$_2$N$^+$), 21.2 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 21.3 (Aryl-*C*H$_3$), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 25.3 (Si(CH$_2$)$_2$*C*H$_2$CH$_2$N$^+$), 36.9 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 40.2 (N*C*H$_2$(CH$_2$)$_2$Si), 50.0 (N$^+$*C*H$_3$), 60.8 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 62.6 (Si(CH$_2$)$_3$*C*H$_2$N$^+$), 121.9 (*C*-1/*C*-8, Naphth), 122.8 (*C*-6, Me-phth), 123.3 (*C*-3, Me-phth), 127.1 (*C*-3/*C*-6, Naphth), 127.3 (*C*-8a, Naphth), 128.8 (*C*-1, Me-phth), 130.6 (*C*-2/*C*-7, Naphth), 131.2 (*C*-4a, Naphth), 131.7 (*C*-2, Me-phth), 134.3 (*C*-4/*C*-5, Naphth), 134.6 (*C*-5, Me-phth), 145.2 (*C*-4, Me-phth), 163.6 (*C*=O, Naphth), 167.8 (*C*=O, Me-phth), 167.9 (*C*=O, Me-phth). ^{29}Si NMR ([D$_6$]DMSO): δ 3.0. Anal. Calcd for $C_{35}H_{44}BrN_3O_4Si$: C, 61.94; H, 6.53; N, 6.19. Found: C, 62.0; H, 6.4; N, 6.2.

Preparation of {5-[dimethyl(3-(4-methylphthalimido)propyl)silyl]pentyl}dimethyl[3-(1,8-naphthalimido)propyl]ammonium bromide (44). Compound **44** was prepared from **124** (1.24 g, 3.02 mmol) and **128** (937 mg, 3.32 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day) to give **44** in 71% yield as an amorphous white solid (1.49 g, 2.15 mmol); mp 184–185 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.08 (s, 6 H, SiCH_3), 0.37–0.51 (m, 4 H, CCH_2SiCH_2C), 1.25–1.32 (m, 4 H, SiCH$_2$(CH_2)$_2$(CH$_2$)$_2$N$^+$), 1.45–1.58 (m, 4 H, NCH$_2$CH_2CH$_2$Si and Si(CH$_2$)$_3$CH_2CH$_2$N$^+$), 2.02–2.18 (m, 2 H, N$^+$CH$_2$CH_2CH$_2$N), 2.42 (s, 3 H, Aryl-CH_3), 3.00 (s, 6 H, N$^+$CH_3), 3.18–3.28 (m, 2 H, Si(CH$_2$)$_4$CH_2N$^+$), 3.35–3.50 (m, 4 H, NCH_2(CH$_2$)$_2$Si and N$^+$CH_2(CH$_2$)$_2$N), 4.10 (t, $^3J_{HH}$ = 6.3 Hz, 2 H, N$^+$(CH$_2$)$_2$CH_2N), 7.51–7.60 (m, 2 H, *H*-3, *H*-5, Me-phth), 7.64 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, *H*-6, Me-phth), 7.84 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz, 2 H, *H*-3/*H*-6, Naphth), 8.41–8.47 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 (Si*C*H$_3$), 11.6 (N(CH$_2$)$_2$*C*H$_2$Si), 14.2 (Si*C*H$_2$(CH$_2$)$_4$N$^+$), 21.2

($Si(CH_2)_3CH_2CH_2N^+$ or $N^+CH_2CH_2CH_2N$), 21.31 (Aryl-CH_3), 21.35 ($Si(CH_2)_3CH_2CH_2N^+$ or $N^+CH_2CH_2CH_2N$), 22.5 ($NCH_2CH_2CH_2Si$), 22.9 ($SiCH_2CH_2(CH_2)_3N^+$), 29.5 ($Si(CH_2)_2CH_2(CH)_2N^+$), 36.9 ($N^+(CH_2)_2CH_2N$), 40.3 ($NCH_2(CH_2)_2Si$), 50.0 (N^+CH_3), 60.7 ($N^+CH_2(CH_2)_2N$), 62.8 ($Si(CH_2)_4CH_2N^+$), 122.0 (*C*-1/*C*-8, Naphth), 122.8 (*C*-6, Me-phth), 123.3 (*C*-3, Me-phth), 127.2 (*C*-3/*C*-6, Naphth), 127.4 (*C*-8a, Naphth), 128.8 (*C*-1, Me-phth), 130.6 (*C*-2/*C*-7, Naphth), 131.2 (*C*-4a, Naphth), 131.8 (*C*-2, Me-phth), 134.4 (*C*-4/*C*-5, Naphth), 134.6 (*C*-5, Me-phth), 145.2 (*C*-4, Me-phth), 163.6 (*C*=O, Naphth), 167.8 (*C*=O, Me-phth), 167.9 (*C*=O, Me-phth). ^{29}Si NMR ([D$_6$]DMSO): δ 3.0. Anal. Calcd for $C_{36}H_{46}BrN_3O_4Si$: C, 62.42; H, 6.69; N, 6.07. Found: C, 62.2; H, 6.5; N, 6.0.

Preparation of {6-[dimethyl(3-(4-methylphthalimido)propyl)silyl]hexyl}dimethyl[3-(1,8-naphthalimido)propyl]ammonium bromide (45). Compound **45** was prepared from **125** (1.21 g, 2.85 mmol) and **128** (827 mg, 2.93 mmol) in ethanol (12 mL) and was purified according to Protocol B, followed by twofold purification by vapor diffusion of diethyl ether into a solution of **45** in dichloromethane, isolation of the resulting precipitate by centrifugation, and drying in vacuo (0.001 mbar, 20 °C, 4 h) to give **45** in 69% yield as an amorphous white solid (1.40 g, 1.98 mmol); mp 174–175 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.09 (s, 6 H, $SiCH_3$), 0.34–0.49 (m, 4 H, CCH_2SiCH_2C), 1.11–1.30 (m, 6 H, $SiCH_2(CH_2)_3(CH_2)_2N^+$), 1.45–1.70 (m, 4 H, $NCH_2CH_2CH_2Si$ and $Si(CH_2)_4CH_2CH_2N^+$), 2.02–2.18 (m, 2 H, $N^+CH_2CH_2CH_2N$), 2.42 (s, 3 H, Aryl-CH_3), 3.01 (s, 6 H, N^+CH_3), 3.18–3.30 (m, 2 H, $Si(CH_2)_5CH_2N^+$), 3.36–3.50 (m, 4 H, $NCH_2(CH_2)_2Si$ and $N^+CH_2(CH_2)_2N$), 4.10 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, $N^+(CH_2)_2CH_2N$), 7.53–7.60 (m, 2 H, *H*-3, *H*-5, Me-phth), 7.65 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, *H*-6, Me-phth), 7.84 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz, 2 H, *H*-3/*H*-6, Naphth), 8.41–8.47 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 ($SiCH_3$), 11.7 ($N(CH_2)_2CH_2Si$), 14.3 ($SiCH_2(CH_2)_5N^+$), 21.2 ($N^+CH_2CH_2CH_2N$), 21.3 (Aryl-CH_3), 21.6 ($Si(CH_2)_4CH_2CH_2N^+$), 22.5 ($NCH_2CH_2CH_2Si$), 23.0 ($SiCH_2CH_2(CH_2)_4N^+$), 25.4 ($Si(CH_2)_3CH_2(CH_2)_2N^+$), 32.3 ($Si(CH_2)_2CH_2(CH_2)_3N^+$), 36.9 ($N^+(CH_2)_2CH_2N$), 40.3 ($NCH_2(CH_2)_2Si$), 49.9 ($N^+CH_3$), 60.8 ($N^+CH_2(CH_2)_2N$), 62.9 ($Si(CH_2)_5CH_2N^+$), 122.0 (*C*-1/*C*-8, Naphth), 122.8 (*C*-6, Me-phth), 123.3 (*C*-3, Me-phth), 127.1 (*C*-3/*C*-6, Naphth), 127.4 (*C*-8a, Naphth), 128.8 (*C*-1, Me-phth), 130.6 (*C*-2/*C*-7, Naphth), 131.2 (*C*-4a, Naphth), 131.8 (*C*-2, Me-phth), 134.4 (*C*-4/*C*-5, Naphth), 134.6 (*C*-5, Me-phth), 145.2 (*C*-4, Me-phth), 163.6 (*C*=O, Naphth), 167.8 (*C*=O, Me-phth), 167.9 (*C*=O, Me-phth). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for $C_{37}H_{48}BrN_3O_4Si$: C, 62.88; H, 6.85; N, 5.95. Found: C, 62.7; H, 6.8; N, 6.0.

Preparation of {6-[dimethyl(3-succinimidopropyl)silyl]hexyl}dimethyl(3-succinimidopropyl)ammonium bromide (46). Compound **46** was prepared from **126** (1.18 g, 3.26 mmol) and **131** (631 mg, 3.42 mmol) in ethanol (12 mL) and was purified according to Protocol C

(precipitation at 4 °C for 1 day) to give **46** in 62% yield as an amorphous white solid (1.11 g, 2.03 mmol); mp 143–145 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.07 (s, 6 H, SiC*H*$_3$), 0.36–0.51 (m, 4 H, CC*H*$_2$SiC*H*$_2$C), 1.16–1.35 (m, 6 H, SiCH$_2$(C*H*$_2$)$_3$(CH$_2$)$_2$N$^+$), 1.35–1.48 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$Si), 1.52–1.67 (m, 2 H, Si(CH$_2$)$_4$C*H*$_2$CH$_2$N$^+$), 1.82–1.96 (m, 2 H, N$^+$CH$_2$C*H*$_2$CH$_2$N), 2.60 (s, 4 H, C(O)C*H*$_2$), 2.64 (s, 4 H, C(O)C*H*$_2$), 3.00 (s, 6 H, N$^+$C*H*$_3$), 3.19–3.36 (m, 6 H, NC*H*$_2$(CH$_2$)$_2$Si, Si(CH$_2$)$_5$C*H*$_2$N$^+$, and N$^+$C*H*$_2$(CH$_2$)$_2$N), 3.41 (t, $^{3}J_{HH}$ = 6.3 Hz, 2 H, N$^+$(CH$_2$)$_2$C*H*$_2$N). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 (Si*C*H$_3$), 11.7 (N(CH$_2$)$_2$*C*H$_2$Si), 14.4 (Si*C*H$_2$(CH$_2$)$_5$N$^+$), 20.7 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 21.6 (Si(CH$_2$)$_4$*C*H$_2$CH$_2$N$^+$), 21.7 (NCH$_2$*C*H$_2$CH$_2$Si), 23.1 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$N$^+$), 25.4 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$N$^+$), 28.0 (C(O)*C*H$_2$), 28.2 (C(O)*C*H$_2$), 32.4 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 34.9 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 40.8 (N*C*H$_2$(CH$_2$)$_2$Si), 49.8 (N$^+$*C*H$_3$), 60.5 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 63.1 (Si(CH$_2$)$_5$*C*H$_2$N$^+$), 177.7 (*C*=O), 177.9 (*C*=O). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for C$_{24}$H$_{44}$BrN$_3$O$_4$Si: C, 52.74; H, 8.11; N, 7.69. Found: C, 52.4; H, 8.3; N, 7.7.

Preparation of {6-[dimethyl(3-(1,8-naphthalimido)propyl)silyl]hexyl}dimethyl(3-succinimidopropyl)ammonium bromide (47). Compound **47** was prepared from **119** (1.07 g, 2.32 mmol) and **131** (499 mg, 2.71 mmol) in ethanol (12 mL) and was purified according to Protocol C (precipitation at 4 °C for 1 day) to give **47** in 60% yield as an amorphous white solid (899 mg, 1.39 mmol); mp 135–136 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.07 (s, 6 H, SiC*H*$_3$), 0.37–0.57 (m, 4 H, CC*H*$_2$SiC*H*$_2$C), 1.12–1.33 (m, 6 H, SiCH$_2$(C*H*$_2$)$_3$(CH$_2$)$_2$N$^+$), 1.50–1.65 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$Si and Si(CH$_2$)$_4$C*H*$_2$CH$_2$N$^+$), 1.83–1.97 (m, 2 H, N$^+$CH$_2$C*H*$_2$CH$_2$N), 2.64 (s, 4 H, C(O)C*H*$_2$), 3.01 (s, 6 H, N$^+$C*H*$_3$), 3.17–3.36 (m, 4 H, Si(CH$_2$)$_5$C*H*$_2$N$^+$ and N$^+$C*H*$_2$(CH$_2$)$_2$N), 3.40 (t, $^{3}J_{HH}$ = 6.2 Hz, 2 H, N$^+$(CH$_2$)$_2$C*H*$_2$N), 3.88–3.99 (m, 2 H, NC*H*$_2$(CH$_2$)$_2$Si), 7.80 (dd, $^{3}J_{HH}$ = 8.1 Hz, $^{3}J_{HH}$ = 7.4 Hz, 2 H, *H*-3/*H*-6, Naphth), 8.36–8.43 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.4 (Si*C*H$_3$), 11.9 (N(CH$_2$)$_2$*C*H$_2$Si), 14.4 (Si*C*H$_2$(CH$_2$)$_5$N$^+$), 20.7 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 21.6 (Si(CH$_2$)$_4$*C*H$_2$CH$_2$N$^+$), 22.0 (NCH$_2$*C*H$_2$CH$_2$Si), 23.1 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$N$^+$), 25.4 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$N$^+$), 28.2 (C(O)*C*H$_2$), 32.4 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 34.9 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 42.5 (N*C*H$_2$(CH$_2$)$_2$Si), 49.8 (N$^+$*C*H$_3$), 60.6 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 63.1 (Si(CH$_2$)$_5$*C*H$_2$N$^+$), 121.9 (*C*-1/*C*-8, Naphth), 127.1 (*C*-3/*C*-6, Naphth), 127.2 (*C*-8a, Naphth), 130.6 (*C*-2/*C*-7, Naphth), 131.2 (*C*-4a, Naphth), 134.2 (*C*-4/*C*-5, Naphth), 163.2 (*C*=O, Naphth), 177.8 (*C*=O, Succ). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for C$_{32}$H$_{46}$BrN$_3$O$_4$Si: C, 59.61; H, 7.19; N, 6.52. Found: C, 59.7; H, 7.4; N, 6.5.

Preparation of {6-[dimethyl(3-succinimidopropyl)silyl]hexyl}dimethyl[3-(1,8-naphthalimido)propyl]ammonium bromide (48). Compound **48** was prepared from **126** (1.07 g, 2.95 mmol) and **128** (861 mg, 3.05 mmol) in ethanol (12 mL) and was purified according to Workup protocol B (precipitation at 4 °C for 1 day) to give **48** in 81% yield as an amorphous white

solid (1.55 g, 2.40 mmol); mp 133–135 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.09 (s, 6 H, SiC*H*$_3$), 0.33–0.46 (m, 4 H, CC*H*$_2$SiC*H*$_2$C), 1.13–1.32 (m, 6 H, SiCH$_2$(C*H*$_2$)$_3$(CH$_2$)$_2$N$^+$), 1.32–1.47 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$Si), 1.51–1.66 (m, 2 H, Si(CH$_2$)$_4$C*H*$_2$CH$_2$N$^+$), 2.01–2.20 (m, 2 H, N$^+$CH$_2$C*H*$_2$CH$_2$N), 2.60 (s, 4 H, C(O)C*H*$_2$), 3.01 (s, 6 H, N$^+$C*H*$_3$), 3.19–3.31 (m, 4 H, NC*H*$_2$(CH$_2$)$_2$Si and Si(CH$_2$)$_5$C*H*$_2$N$^+$), 3.36–3.47 (m, 2 H, N$^+$C*H*$_2$(CH$_2$)$_2$N), 4.10 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, N$^+$(CH$_2$)$_2$C*H*$_2$N), 7.85 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, 2 H, *H*-3/*H*-6, Naphth), 8.42–8.49 (m, 4 H, *H*-2/*H*-7 and *H*-4/*H*-5, Naphth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 (Si*C*H$_3$), 11.7 (N(CH$_2$)$_2$*C*H$_2$Si), 14.4 (Si*C*H$_2$(CH$_2$)$_5$N$^+$), 21.3 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 21.6 (Si(CH$_2$)$_4$*C*H$_2$CH$_2$N$^+$), 21.7 (NCH$_2$*C*H$_2$CH$_2$Si), 23.0 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$N$^+$), 25.4 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$N$^+$), 28.0 (C(O)*C*H$_2$), 32.3 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 36.9 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 40.8 (N*C*H$_2$(CH$_2$)$_2$Si), 49.9 (N$^+$*C*H$_3$), 60.8 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 62.9 (Si(CH$_2$)$_5$*C*H$_2$N$^+$), 122.0 (*C*-1/*C*-8, Naphth), 127.2 (*C*-3/*C*-6, Naphth), 127.4 (*C*-8a, Naphth), 130.7 (*C*-2/*C*-7, Naphth), 131.2 (*C*-4a, Naphth), 134.4 (*C*-4/*C*-5, Naphth), 163.6 (*C*=O, Naphth), 177.7 (*C*=O, Succ). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for C$_{32}$H$_{46}$BrN$_3$O$_4$Si: C, 59.61; H, 7.19; N, 6.52. Found: C, 59.2; H, 7.0; N, 6.5.

Preparation of {6-[dimethyl(3-phthalimidopropyl)silyl]hexyl}dimethyl[3-(4-methylphthalimido)propyl]ammonium bromide (49). Compound **49** was prepared from **122** (1.39 g, 3.39 mmol) and **130** (897 mg, 3.64 mmol) in ethanol (12 mL) and was purified according to Protocol A (precipitation at 20 °C for 1 day) to give **49** in 57% yield as an amorphous white solid (1.26 g, 1.92 mmol); mp 173–174 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.09 (s, 6 H, SiC*H*$_3$), 0.35–0.49 (m, 4 H, CC*H*$_2$SiC*H*$_2$C), 1.10–1.31 (m, 6 H, SiCH$_2$(C*H*$_2$)$_3$(CH$_2$)$_2$N$^+$), 1.46–1.65 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$Si and Si(CH$_2$)$_4$C*H*$_2$CH$_2$N$^+$), 1.95–2.10 (m, 2 H, N$^+$CH$_2$C*H*$_2$CH$_2$N), 2.45 (s, 3 H, Aryl-C*H*$_3$), 3.02 (s, 6 H, N$^+$C*H*$_3$), 3.20–3.30 (m, 2 H, Si(CH$_2$)$_5$C*H*$_2$N$^+$), 3.30–3.42 (m, 2 H, N$^+$C*H*$_2$(CH$_2$)$_2$N), 3.49 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, NC*H*$_2$(CH$_2$)$_2$Si), 3.62 (t, $^3J_{HH}$ = 6.2 Hz, N$^+$(CH$_2$)$_2$C*H*$_2$N), 7.57–7.66 (m, 2 H, *H*-3, *H*-5, Me-phth), 7.70 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, *H*-6, Me-phth), 7.80–7.83 (br s, 4 H, *H*-3/*H*-6, *H*-4/*H*-5, Phth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 (Si*C*H$_3$), 11.7 (N(CH$_2$)$_2$*C*H$_2$Si), 14.4 (Si*C*H$_2$(CH$_2$)$_5$N$^+$), 21.3 (Aryl-*C*H$_3$), 21.6 (2 C, Si(CH$_2$)$_4$*C*H$_2$CH$_2$N$^+$ and N$^+$CH$_2$*C*H$_2$CH$_2$N), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 23.1 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$N$^+$), 25.4 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$N$^+$), 32.4 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 34.5 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 40.4 (N*C*H$_2$(CH$_2$)$_2$Si), 49.9 (N$^+$*C*H$_3$), 60.5 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 63.1 (Si(CH$_2$)$_5$*C*H$_2$N$^+$), 122.9 (3 C, *C*-3/*C*-6, Phth, and *C*-6, Me-phth), 123.4 (*C*-3, Me-phth), 129.0 (*C*-1, Me-phth), 131.4 (*C*-1/*C*-2, Phth), 132.0 (*C*-2, Me-phth), 134.4 (*C*-4/*C*-5, Phth), 134.6 (*C*-5, Me-phth), 145.2 (*C*-4, Me-phth), 167.9 (3 C, *C*=O, Phth and Me-phth), 168.0 (*C*=O, Me-phth). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for C$_{33}$H$_{46}$BrN$_3$O$_4$Si: C, 60.35; H, 7.06; N, 6.40. Found: C, 60.2; H, 7.2; N, 6.4.

Preparation of {6-[dimethyl(3-(4-methylphthalimido)propyl)silyl]hexyl}dimethyl(3-phthalimidopropyl)ammonium bromide (50). Compound **50** was prepared from **125** (1.11 g, 2.62 mmol) and **129** (634 mg, 2.73 mmol) in ethanol (12 mL) and was purified according to Protocol B, followed by twofold crystallization by vapor diffusion of diethyl ether into a solution of **50** in dichloromethane, isolation of the resulting precipitate by centrifugation, and drying in vacuo (0.001 mbar, 20 °C, 4 h) to give **50** in 65% yield as a crystalline white solid (1.11 g, 1.69 mmol); mp 126–127 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.08 (s, 6 H, SiCH_3), 0.37–0.50 (m, 4 H, CCH_2SiCH_2C), 1.12–1.32 (m, 6 H, SiCH$_2$(CH_2)$_3$(CH$_2$)$_2$N$^+$), 1.46–1.66 (m, 4 H, NCH$_2$CH_2CH$_2$Si and Si(CH$_2$)$_4$CH_2CH$_2$N$^+$), 1.96–2.10 (m, 2 H, N$^+$CH$_2$CH_2CH$_2$N), 2.45 (s, 3 H, Aryl-CH_3), 2.99 (s, 6 H, N$^+$CH_3), 3.17–3.28 (m, 2 H, Si(CH$_2$)$_5$CH_2N$^+$), 3.30–3.41 (m, 2 H, N$^+$CH_2(CH$_2$)$_2$N), 3.49 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, NCH_2(CH$_2$)$_2$Si), 3.64 (t, $^3J_{HH}$ = 6.2 Hz, N$^+$(CH$_2$)$_2$CH_2N), 7.57–7.66 (m, 2 H, *H*-3, *H*-5, Me-phth), 7.70 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, *H*-6, Me-phth), 7.80–7.89 (m, 4 H, *H*-3/*H*-6, *H*-4/*H*-5, Phth). ^{13}C NMR ([D$_6$]DMSO): δ –3.5 (Si*C*H$_3$), 11.7 (N(CH$_2$)$_2$*C*H$_2$Si), 14.4 (Si*C*H$_2$(CH$_2$)$_5$N$^+$), 21.3 (Aryl-*C*H$_3$), 21.6 (2 C, Si(CH$_2$)$_4$*C*H$_2$CH$_2$N$^+$ and N$^+$CH$_2$*C*H$_2$CH$_2$N), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 23.1 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$N$^+$), 25.4 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$N$^+$), 32.4 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 34.6 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 40.3 (N*C*H$_2$(CH$_2$)$_2$Si), 49.9 (N$^+$*C*H$_3$), 60.6 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 63.1 (Si(CH$_2$)$_5$*C*H$_2$N$^+$), 122.9 (*C*-6, Me-phth), 123.0 (*C*-3/*C*-6, Phth), 123.4 (*C*-3, Me-phth), 128.9 (*C*-1, Me-phth), 131.7 (*C*-1/*C*-2, Phth), 131.9 (*C*-2, Me-phth), 134.4 (*C*-4/*C*-5, Phth), 134.7 (*C*-5, Me-phth), 145.2 (*C*-4, Me-phth), 167.89 (*C*=O, Me-phth), 167.95 (*C*=O, Phth), 167.98 (*C*=O, Me-phth). ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for C$_{33}$H$_{46}$BrN$_3$O$_4$Si: C, 60.35; H, 7.06; N, 6.40. Found: C, 59.7; H, 6.9; N, 6.5.

Preparation of *rac*-{6-[dimethyl(2-methyl-3-phthalimidopropyl)silyl]hexyl}dimethyl(3-phthalimidopropyl)ammonium bromide (*rac*-51). Compound *rac*-**51** was prepared from *rac*-**127** (1.21 g, 2.85 mmol) and **129** (677 mg, 2.91 mmol) in ethanol (12 mL) and was purified according to Protocol B, followed by twofold purification by vapor diffusion of diethyl ether into a solution of *rac*-**51** in dichloromethane, isolation of the resulting precipitate by centrifugation, and drying in vacuo (0.001 mbar, 20 °C, 4 h) to give *rac*-**51** in 44% yield as an amorphous white solid (817 mg, 1.24 mmol); mp 118–120 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.04 (s, 6 H, SiCH_3), 0.38 (dd, $^2J_{HH}$ = –14.7 Hz, $^3J_{HH}$ = 9.2 Hz, 1 H, NCH$_2$CH(CH$_3$)CH_AH$_B$Si), 0.40–0.51 (m, 2 H, SiCH_2(CH$_2$)$_5$N$^+$), 0.60 (dd, $^2J_{HH}$ = –14.7 Hz, $^3J_{HH}$ = 4.7 Hz, 1 H, NCH$_2$CH(CH$_3$)CH$_A$H$_B$Si), 0.84 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, NCH$_2$CH(CH_3)CH$_2$Si), 1.10–1.32 (m, 6 H, SiCH$_2$(CH_2)$_3$(CH$_2$)$_2$N$^+$), 1.50–1.64 (m, 2 H, Si(CH$_2$)$_4$CH_2CH$_2$N$^+$), 1.91–2.10 (m, 3 H, NCH$_2$C*H*(CH$_3$)CH$_2$Si and N$^+$CH$_2$CH_2CH$_2$N), 2.98 (s, 6 H, N$^+$CH_3), 3.16–3.26 (m, 2 H, Si(CH$_2$)$_5$CH_2N$^+$), 3.28–3.44 (m, 4 H, NCH_2CH(CH$_3$)CH$_2$Si and N$^+$CH_2(CH$_2$)$_2$N), 3.59–3.69 (m, 2 H, N$^+$(CH$_2$)$_2$CH_2N), 7.79–7.90 (m, 8 H, *H*-3/*H*-6, *H*-4/*H*-5,

Phth).[87a] ^{13}C NMR ([D$_6$]DMSO): δ –2.5 (Si*C*H$_3$), –2.4 (Si*C*H$_3$), 15.2 (Si*C*H$_2$(CH$_2$)$_5$N$^+$), 20.2 (NCH$_2$CH(CH$_3$)*C*H$_2$Si), 20.5 (NCH$_2$CH(*C*H$_3$)CH$_2$Si), 21.6 (2 C, Si(CH$_2$)$_4$*C*H$_2$CH$_2$N$^+$ and N$^+$CH$_2$*C*H$_2$CH$_2$N), 23.1 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$N$^+$), 25.4 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$N$^+$), 28.7 (NCH$_2$*C*H(CH$_3$)CH$_2$Si), 32.4 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 34.6 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 46.3 (N*C*H$_2$CH(CH$_3$)CH$_2$Si), 49.9 (N$^+$*C*H$_3$), 60.7 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 63.1 (Si(CH$_2$)$_5$*C*H$_2$N$^+$), 123.0 (4 C, *C*-3/*C*-6, Phth), 131.4 (*C*-1/*C*-2, Phth), 131.7 (*C*-1/*C*-2, Phth), 134.4 (*C*-4/*C*-5, Phth), 134.5 (*C*-4/*C*-5, Phth), 168.0 (*C*=O), 168.2 (*C*=O).[87b] ^{29}Si NMR ([D$_6$]DMSO): δ 2.1. Anal. Calcd for C$_{33}$H$_{46}$BrN$_3$O$_4$Si: C, 60.35; H, 7.06; N, 6.40. Found: C, 58.4; H, 7.0; N, 6.5.

Preparation of *rac*-{6-[dimethyl(3-phtalimidopropyl)silyl]hexyl}dimethyl(2-methyl-3-phthalimidopropyl)ammonium bromide (*rac*-52). Compound *rac*-**52** was prepared from **122** (1.24 g, 3.02 mmol) and *rac*-**132** (761 mg, 3.09 mmol) in ethanol (12 mL) and was purified according to Protocol B (precipitation at 20 °C for 1 day, then at 4 °C for 1 day) to give *rac*-**52** in 56% yield as an amorphous white solid (1.11 g, 1.69 mmol); mp 107–108 °C. ^{1}H NMR ([D$_6$]DMSO): δ –0.10 (s, 6 H, SiC*H*$_3$), 0.35–0.49 (m, 4 H, CC*H*$_2$SiC*H*$_2$C), 1.05 (d, $^3J_{HH}$ = 6.8 Hz, 1 H, N$^+$CH$_2$CH(C*H*$_3$)CH$_2$N), 1.12–1.28 (m, 6 H, SiCH$_2$(C*H*$_2$)$_3$(CH$_2$)$_2$N$^+$), 1.47–1.68 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$Si and Si(CH$_2$)$_4$C*H*$_2$CH$_2$N$^+$), 2.42–2.58 (m, 1 H, N$^+$CH$_2$C*H*(CH$_3$)CH$_2$N), 3.10 (s, 6 H, N$^+$C*H*$_3$), 3.26–3.63 (m, 8 H, NC*H*$_2$(CH$_2$)$_2$Si(CH$_2$)$_5$C*H*$_2$N$^+$C*H*$_2$CH(CH$_3$)C*H*$_2$N), 7.79–7.88 (m, 8 H, *H*-3/*H*-6, *H*-4/*H*-5, Phth).[88a] ^{13}C NMR ([D$_6$]DMSO): δ –3.5 (Si*C*H$_3$), 11.6 (N(CH$_2$)$_2$*C*H$_2$Si), 14.3 (Si*C*H$_2$(CH$_2$)$_5$N$^+$), 18.6 (N$^+$CH$_2$CH(*C*H$_3$)CH$_2$N), 21.7 (Si(CH$_2$)$_4$*C*H$_2$CH$_2$N$^+$), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 23.1 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$N$^+$), 25.4 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$N$^+$), 27.6 (N$^+$CH$_2$*C*H(CH$_3$)CH$_2$N), 32.3 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 40.4 (N*C*H$_2$(CH$_2$)$_2$Si), 42.6 (N$^+$CH$_2$CH(CH$_3$)*C*H$_2$N), 49.9 (N$^+$*C*H$_3$), 50.1 (N$^+$*C*H$_3$), 63.4 (Si(CH$_2$)$_5$*C*H$_2$N$^+$), 66.6 (N$^+$*C*H$_2$CH(CH$_3$)CH$_2$N), 122.9 (*C*-3/*C*-6, Phth), 123.1 (*C*-3/*C*-6, Phth), 131.43 (*C*-1/*C*-2, Phth), 131.44 (*C*-1/*C*-2, Phth), 134.4 (*C*-4/*C*-5, Phth), 134.5 (*C*-4/*C*-5, Phth), 167.9 (*C*=O), 168.2 (*C*=O).[88b] ^{29}Si NMR ([D$_6$]DMSO): δ 2.9. Anal. Calcd for C$_{33}$H$_{46}$BrN$_3$O$_4$Si: C, 60.35; H, 7.06; N, 6.40. Found: C, 59.2; H, 7.0; N, 6.7.

Preparation of {6-[dimethyl(3-(1,8-naphthalimido)propyl)silyl]hexyl}methyl[3-(1,8-naphthalimido)propyl]ammonium chloride (53·HCl). A mixture of **119** (1.60 g, 3.47 mmol), **135** (930 mg, 3.47 mmol), triethylamine (3.52 g, 34.8 mmol), and acetonitrile (25 mL) was heated under reflux for 3 days and was then cooled to 20 °C, diluted with ethyl acetate (50 mL), and washed with a 1 M aqueous potassium carbonate solution (50 mL). The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (2 × 50 mL). All organic solutions were combined and dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the oily residue was purified by column chromatography on silica gel (column dimensions, 81 × 3 cm;

silica gel (32–63 μm, ICN 02826), 250 g; eluent, ethyl acetate/triethylamine 99:1 (v/v)). The relevant fractions (TLC control) were combined, and the solvent was removed in vacuo (0.001 mbar, 20 °C, 2 days) to give 1.4 g of a highly viscous, yellowish oil (compound **53**).[62] This product was dissolved in dichloromethane (66 mL), and 1.06 mL of a 2 M ethereal hydrogen chloride solution (2.12 mmol of HCl) were added at 20 °C. The resulting hydrochloride was crystallized by vapor diffusion of diethyl ether into this solution at 20 °C over a period of ca. 2 weeks, the product was isolated by decantation, redissolved in dichloromethane (61 mL), recrystallized and isolated as described above, and finally dried in vacuo (0.001 mbar, 20 °C, 4 h) to give **53**·HCl in 56% yield (related to **119**) as a colorless crystalline solid (1.34 g, 1.96 mmol); mp 222–223 °C. ^{1}H NMR (CD_2Cl_2[89]): δ –0.04 (s, 6 H, SiCH_3), 0.43–0.54 (m, 2 H, SiCH_2(CH$_2$)$_5$N$^+$), 0.54–0.64 (m, 2 H, N(CH$_2$)$_2$CH_2Si), 1.21–1.41 (m, 6 H, SiCH$_2$(CH_2)$_3$(CH$_2$)$_2$N$^+$), 1.58–1.72 (m, 2 H, NCH$_2$CH_2CH$_2$Si), 1.72–1.92 (m, 2 H, Si(CH$_2$)$_4$CH_2CH$_2$N$^+$), 2.18–2.45 (m, 2 H, N$^+$CH$_2$CH_2CH$_2$N), 2.74 (d, $^{3}J_{HH}$ = 4.2 Hz, 3 H, N$^+$CH_3), 2.85–3.31 (m, 4 H, Si(CH$_2$)$_5$CH_2N$^+$, N$^+$CH_2(CH$_2$)$_2$N), 3.98–4.08 (m, 2 H, NCH_2(CH$_2$)$_2$Si), 4.25 (t, $^{3}J_{HH}$ = 6.8 Hz, 2 H, N$^+$(CH$_2$)$_2$CH_2N), 7.65–7.76 (m, 4 H, *H*-3/*H*-6, Naphth), 8.13–8.22 (m, 4 H, *H*-4/*H*-5, Naphth), 8.46–8.53 (m, 4 H, *H*-2/*H*-7, Naphth), 12.4 (br s, 1 H, N*H*). ^{13}C NMR (CD_2Cl_2): δ –3.4 (Si*C*H$_3$), 12.8 (N(CH$_2$)$_2$*C*H$_2$Si), 15.1 (Si*C*H$_2$(CH$_2$)$_5$N$^+$), 22.8 (NCH$_2$C*H*$_2$CH$_2$Si), 23.3 (N$^+$CH$_2$*C*H$_2$CH$_2$N), 23.6 (Si(CH$_2$)$_4$*C*H$_2$CH$_2$N$^+$), 23.9 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$N$^+$), 26.7 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$N$^+$), 33.1 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$N$^+$), 37.9 (N$^+$(CH$_2$)$_2$*C*H$_2$N), 39.8 (N$^+$*C*H$_3$), 43.5 (N*C*H$_2$(CH$_2$)$_2$Si), 53.7 (N$^+$*C*H$_2$(CH$_2$)$_2$N), 56.0 (Si(CH$_2$)$_5$*C*H$_2$N$^+$), 122.5 (*C*-1/*C*-8, Naphth), 123.0 (*C*-1/*C*-8, Naphth), 127.19 (*C*-3/*C*-6, Naphth), 127.22 (*C*-3/*C*-6, Naphth), 128.27 (*C*-8a, Naphth), 128.28 (*C*-8a, Naphth), 131.1 (*C*-2/*C*-7, Naphth), 131.4 (*C*-2/*C*-7, Naphth), 131.83 (*C*-4a, Naphth), 131.86 (*C*-4a, Naphth), 134.1 (*C*-4/*C*-5, Naphth), 134.5 (*C*-4/*C*-5, Naphth), 164.2 ((O=*C*)$_2$N(CH$_2$)$_3$Si), 164.4 (N$^+$(CH$_2$)$_3$N(*C*=O)$_2$). ^{15}N NMR (CD_2Cl_2): δ –331 (*N*$^+$), –204 (*N*(CH$_2$)$_3$Si or N$^+$(CH$_2$)$_3$*N*), –206 (*N*(CH$_2$)$_3$Si or N$^+$(CH$_2$)$_3$*N*). ^{29}Si NMR (CD_2Cl_2): δ 2.9. Anal. Calcd for $C_{39}H_{46}ClN_3O_4Si$: C, 68.45; H, 6.78; N, 6.14; Cl, 5.18. Found: C, 68.3; H, 6.8; N, 6.2; Cl, 5.1.

NMR data for 53. ^{1}H NMR (CD_2Cl_2): δ –0.03 (s, 6 H, SiCH_3), 0.45–0.56 (m, 2 H, SiCH_2(CH$_2$)$_5$N), 0.56–0.66 (m, 2 H, N(CH$_2$)$_2$CH_2Si), 1.18–1.33 (m, 6 H, SiCH$_2$(CH_2)$_3$(CH$_2$)$_2$N), 1.33–1.45 (m, 2 H, Si(CH$_2$)$_4$CH_2CH$_2$N), 1.62–1.76 (m, 2 H, NCH$_2$CH_2CH$_2$Si), 1.79–1.91 (m, 2 H, N(CH$_3$)CH$_2$CH_2CH$_2$N), 2.18 (s, 3 H, NCH_3), 2.24–2.33 (m, 2 H, Si(CH$_2$)$_5$CH_2N), 2.44 (t, $^{3}J_{HH}$ = 7.1 Hz, 2 H, N(CH$_3$)CH_2(CH$_2$)$_2$N), 4.03–4.20 (m, 4 H, NCH_2(CH$_2$)$_2$Si, N(CH$_3$)(CH$_2$)$_2$CH_2N), 7.69–7.77 (m, 4 H, *H*-3/*H*-6, Naphth), 8.17–8.23 (m, 4 H, *H*-4/*H*-5, Naphth), 8.50–8.56 (m, 4 H, *H*-2/*H*-7, Naphth). ^{13}C NMR (CD_2Cl_2): δ –3.4 (Si*C*H$_3$), 12.8 (N(CH$_2$)$_2$*C*H$_2$Si), 15.4 (Si*C*H$_2$(CH$_2$)$_5$N), 22.9 (NCH$_2$C*H*$_2$CH$_2$Si), 24.2 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$N), 26.1 (N(CH$_3$)CH$_2$*C*H$_2$CH$_2$N), 27.5

($Si(CH_2)_3CH_2(CH_2)_2N$ or $Si(CH_2)_4CH_2CH_2N$), 27.7 ($Si(CH_2)_3CH_2(CH_2)_2N$ or $Si(CH_2)_4CH_2CH_2N$), 34.0 ($Si(CH_2)_2CH_2(CH_2)_3N$), 39.2 ($N(CH_3)(CH_2)_2CH_2N$), 42.1 (NCH_3), 43.6 ($NCH_2(CH_2)_2Si$), 55.8 ($N(CH_3)CH_2(CH_2)_2N$), 58.3 ($Si(CH_2)_5CH_2N$), 123.19 (*C*-1/*C*-8, Naphth), 123.20 (*C*-1/*C*-8, Naphth), 127.2 (4 C, *C*-3/*C*-6, Naphth), 128.4 (2 C, *C*-8a, Naphth), 131.13 (*C*-2/*C*-7, Naphth), 131.14 (*C*-2/*C*-7, Naphth), 131.9 (2 C, *C*-4a, Naphth), 134.1 (4 C, *C*-4/*C*-5, Naphth), 164.26 ($N(C{=}O)_2$), 164.31 ($N(C{=}O)_2$). ^{29}Si NMR (CD_2Cl_2): δ 2.9.

Preparation of 1,1-dichloro-1-silacyclohexane (55).[90] 50 mL of a solution of 1,5-dibromopentane (161 g, 700 mmol) in diethyl ether (300 mL) were added to a stirred suspension of magnesium turnings (37.4 g, 1.54 mol) in diethyl ether (400 mL), and the reaction was started by gentle heating. Subsequently, the remaining 1,5-dibromopentane solution was added within 2 h, causing the mixture to boil under reflux. After the addition was complete, the mixture was heated under reflux for a further 90 min and then cooled to 20 °C within 1 h. The resulting two-phase Grignard reagent (which was separated from residual magnesium turnings by decantation, followed by washing of the magnesium with diethyl ether (2 × 50 mL)) was added dropwise within 2 h to a solution of tetrachlorosilane (131 g, 771 mmol) in diethyl ether (300 mL), causing the mixture to boil under reflux. During the addition, the mixture was stirred vigorously with a mechanical stirrer (formation of a precipitate). The mixture was stirred at 20 °C for 16 h, and the precipitate was separated by filtration and washed with diethyl ether (2 × 200 mL). The filtrate and the wash solutions were combined, and the solvent was removed by distillation under atmospheric pressure, causing a postprecipitation. The precipitate was separated by decantation and washed with *n*-pentane (2 × 50 mL), and the organic solutions were combined. The solvent was removed as described above, and the crude product was isolated by distillation under atmospheric pressure; bp 166–178 °C. Redistillation (Vigreux column, 30 cm) under reduced pressure afforded **55** in 62% yield (related to 1,5-dibromopentane) as a colorless liquid (72.9 g, 431 mmol); bp 70–71 °C/37 mbar. ^{1}H NMR ($CDCl_3$): δ 1.13–1.22 (m, 4 H, $SiCH_2C$), 1.43–1.52 (m, 2 H, $Si(CH_2)_2CH_2C$), 1.77–1.87 (m, 4 H, $SiCH_2CH_2C$). ^{13}C NMR ($CDCl_3$): δ 20.2 ($SiCH_2C$), 24.0 ($SiCH_2CH_2C$), 28.6 ($Si(CH_2)_2CH_2C$). ^{29}Si NMR ($CDCl_3$): δ 28.8. Anal. Calcd for $C_5H_{10}Cl_2Si$: C, 35.51; H, 5.96; Cl, 41.92. Found: C, 35.8; H, 6.1; Cl, 42.2.

Preparation of 1,1-dimethoxy-1-silacyclohexane (56). Protocol A.[90] Methanol (34.8 g, 1.09 mol) was added dropwise within 10 min to a stirred solution of **55** (83.2 g, 492 mmol) and triethylamine (110 g, 1.09 mol) in *n*-hexane (500 mL), causing the mixture to boil under reflux (formation of a precipitate). After the addition was complete, the mixture was heated under reflux for a further 2 h and was then cooled to 20 °C within 1 h and left undisturbed at this temperature for 16 h. The precipitate was separated by suction filtration and washed thoroughly with *n*-hexane (1.5

L). The filtrate and the wash solutions were combined, the solvent was removed by distillation under atmospheric pressure (Vigreux column, 20 cm), and the residue was distilled in vacuo (Vigreux column, 20 cm) to give **56** as a crude product (69 g; bp 70–75 °C/30 mbar) that contained small amounts of a solid. The distillate was diluted with *n*-pentane (150 mL), the mixture was kept undisturbed at 4 °C for 16 h, the resulting precipitate was separated by filtration, the filter cake was washed with *n*-pentane (20 mL), and the filtrate and the wash solution were combined. The solvent was removed by distillation under atmospheric pressure (Vigreux column, 30 cm), and the residue was distilled in vacuo (Vigreux column, 30 cm) to give **56** in 80% yield as a colorless liquid (62.8 g, 392 mmol); bp 62 °C/20 mbar. ^{1}H NMR ($CDCl_3$): δ 0.63–0.72 (m, 4 H, SiCH_2C), 1.32–1.43 (m, 2 H, Si(CH_2)$_2$CH_2C), 1.62–1.75 (m, 4 H, SiCH_2CH_2C), 3.50 (s, 6 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 11.0 (Si*C*H$_2$C), 24.6 (SiCH$_2$*C*H$_2$C), 29.6 (Si(CH$_2$)$_2$*C*H$_2$C), 50.1 (O*C*H$_3$). ^{29}Si NMR ($CDCl_3$): δ –5.1. Anal. Calcd for $C_7H_{16}O_2Si$: C, 52.45; H, 10.06. Found: C, 52.6; H, 9.9. **Protocol B.**[90] A 1,5-bis(bromomagnesio)pentane reagent was prepared from magnesium turnings (22.0 g, 905 mmol), 1,5-dibromopentane (46.0 g, 200 mmol), and diethyl ether (200 mL) analogous to Protocol A (see above). The two-phase Grignard reagent was then added at 0 °C over a period of 1 h to a vigorously stirred solution of tetramethoxysilane (45.7 g, 300 mmol) in diethyl ether (500 mL) (formation of a precipitate). After the addition was complete, the mixture was heated under reflux for 16 h and was then cooled to 20 °C within 1 h. The precipitate was separated by filtration and washed with diethyl ether (3 × 50 mL), the filtrate and the wash solutions were combined, the solvent was removed under reduced pressure, and the residue was distilled and then redistilled in vacuo to give **56** in 43% yield (related to 1,5-dibromopentane) as a colorless liquid (13.9 g, 86.7 mmol); bp 75 °C/36 mbar. The NMR data of the product were identical with those obtained for **56** synthesized according to Protocol A. Anal. Calcd for $C_7H_{16}O_2Si$: C, 52.45; H, 10.06. Found: C, 51.7; H, 9.9.

Preparation of 4-methoxyacetophenone 2,4,6-triisopropylbenzenesulfonylhydrazone (57). This compound was synthesized according to ref. 91 and was isolated, after recrystallization from boiling methanol (crystallization at 4 °C over a period of 16 h), as a colorless crystalline solid; mp 152–153 °C (dec). ^{1}H NMR (CD_2Cl_2):[92] δ 1.25 (d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, *p*-CH(CH_3)$_2$), 1.30 (d, $^{3}J_{HH}$ = 6.8 Hz, 12 H, *o*-CH(CH_3)$_2$), 2.16 (s, 3 H, C(=N)CH_3), 2.92 (septett, $^{3}J_{HH}$ = 6.8 Hz, 1 H, *p*-C*H*(CH$_3$)$_2$), 3.80 (s, 3 H, OCH_3), 4.31 (septett, $^{3}J_{HH}$ = 6.8 Hz, 2 H, *o*-C*H*(CH$_3$)$_2$), 6.81–6.89 (m, 2 H, *H*-3/*H*-5, C(=N)-Aryl), 7.22 (s, 2 H, S-Aryl), 7.56–7.64 (m, 2 H, *H*-2/*H*-6, C(=N)-Aryl), 7.7 (br s, 1 H, N*H*). ^{13}C NMR (CD_2Cl_2): δ 13.3 (C(=N)*C*H$_3$), 23.6 (*p*-CH(*C*H$_3$)$_2$), 24.9 (*o*-CH(*C*H$_3$)$_2$), 30.4 (*o*-*C*H(CH$_3$)$_2$), 34.6 (*p*-*C*H(CH$_3$)$_2$), 55.6 (O*C*H$_3$), 113.9 (*C*-3/*C*-5, C(=N)-Aryl), 124.2 (*C*-3/*C*-5, S-Aryl), 128.0 (*C*-2/*C*-6, C(=N)-Aryl), 130.2 (*C*-1, C(=N)-Aryl), 131.9 (*C*-1, S-Aryl), 151.5

(*C*(=N)CH_3), 151.6 (*C*-2/*C*-6, S-Aryl), 153.9 (*C*-4, S-Aryl), 161.2 (*C*-4, C(=N)-Aryl). Anal. Calcd for $C_{24}H_{34}N_2O_3S$: C, 66.94; H, 7.96; N, 6.51; S, 7.45. Found: C, 67.0; H, 8.0; N, 6.6; S, 7.6.

Preparation of 1-methoxy-1-[1-(4-methoxyphenyl)vinyl]-1-silacyclohexane (59). A 2.7 M solution of *n*-butyllithium in *n*-heptane (70 mL, 189 mmol of *n*-BuLi) was added dropwise at –78 °C within 50 min to a stirred mixture of finely ground **57** (40.0 g, 92.9 mmol), TMEDA (31.0 g, 267 mmol), and *n*-hexane (360 mL). The resulting yellow mixture was stirred at –78 °C for 2 h and then warmed to 0 °C within 90 min (evolution of nitrogen; change of color to orange; formation of [1-(4-methoxyphenyl)vinyl]lithium (**58**)). After the nitrogen evolution was finished, the mixture was stirred at 20 °C for a further 10 min and then added dropwise at 0 °C within 30 min to a stirred solution of **56** (15.0 g, 93.6 mmol) in *n*-hexane (100 mL). The resulting mixture was warmed to 20 °C within 1 h (change of color from orange to yellow within ca. 12 h) and stirred at this temperature for 3 days. The resulting clear yellow solution was cooled in an ice bath, and iodomethane (125 g, 881 mmol) was added (formation of a precipitate). After a period of 2 h, the ice bath was removed and stirring was continued at 20 °C for 1 day. The precipitate was separated by filtration and washed with *n*-hexane (4 × 250 mL), and the filtrate and the wash solutions were combined. The solvent was removed under reduced pressure, and the residue was distilled in vacuo (Kugelrohr apparatus; first fraction, ≤ 90 °C/0.001 mbar, discarded; second fraction, 90–145 °C/0.001 mbar, crude product). The crude products of three identical runs of this preparation were combined (→ 43.0 g) and distilled in vacuo (Vigreux column, 15 cm) to give **59** in 45% yield (related to **56**) as a colorless oily liquid (33.2 g, 127 mmol); bp 105 °C/0.001 mbar. ^{1}H NMR (CD_2Cl_2): δ 0.71–0.98 (m, 4 H, SiCH_2C), 1.34–1.58 (m, 2 H, Si(CH_2)$_2$CH_2C), 1.62–1.82 (m, 4 H, SiCH_2CH_2C), 3.44 (s, 3 H, SiOCH_3), 3.79 (s, 3 H, COCH_3), 5.64 (δ_A) and 6.02 (δ_B) (2 H, $^2J_{AB}$ = 2.7 Hz, C=C$H_A H_B$), 6.83–6.90 (m, 2 H, *H*-3/*H*-5, Aryl), 7.26–7.33 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR (CD_2Cl_2): δ 12.6 (Si*C*H_2C), 24.7 (SiCH_2*C*H_2C), 30.2 (Si(CH_2)$_2$*C*H_2C), 50.6 (SiO*C*H_3), 55.5 (CO*C*H_3), 114.0 (*C*-3/*C*-5, Aryl), 128.00 (C=*C*H_2), 128.05 (*C*-2/*C*-6, Aryl), 135.9 (*C*-1, Aryl), 147.8 (*C*=CH_2), 159.1 (*C*-4, Aryl). ^{29}Si NMR (CD_2Cl_2): δ 3.7. Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.8; H, 8.5.

Preparation of 1-[1-(4-methoxyphenyl)vinyl]-1-silacyclohexane (60). A solution of **59** (32.0 g, 122 mmol) in diethyl ether (50 mL) was added at 20 °C within 10 min to a stirred suspension of LAH (2.48 g, 65.3 mmol) in diethyl ether (200 mL). The mixture was heated under reflux for 2 h and then added carefully at 0 °C to a stirred mixture of 4 M hydrochloric acid (210 mL) and diethyl ether (100 mL). The organic phase was separated, the aqueous layer was extracted with diethyl ether (3 × 100 mL), and the organic solutions were combined and dried over anhydrous magnesium sulfate in an ice bath, followed by an additional thorough dynamic drying using a

chromatographic column densely packed with anhydrous magnesium sulfate (column diameter, 3.5 cm; column length, 15 cm). The magnesium sulfate was finally washed with diethyl ether (500 mL), the organic solutions were combined, the solvent was removed under reduced pressure, and the residue was distilled in vacuo (Vigreux column, 15 cm) to give **60** in 82% yield as a colorless oily liquid (23.3 g, 100 mmol); bp 91–92 °C/0.001 mbar. IR (film): $\tilde{\nu}$ 2110 cm^{-1} (SiH). ^{1}H NMR (CD_2Cl_2): δ 0.68–0.85 and 0.92–1.05 (m, 4 H, SiCH_2C), 1.25–1.41, 1.51–1.72, and 1.80–1.96 (m, 6 H, SiCH$_2$CH_2CH_2C), 3.80 (s, 3 H, OCH_3), 4.26–4.33 (δ_X), 5.60 (δ_A), and 6.00 (δ_B), (3 H, $^2J_{AB}$ = 2.6 Hz, $^4J_{BX}$ = 0.5 Hz, H_XSiC=C$H_A H_B$), 6.83–6.90 (m, 2 H, *H*-3/*H*-5, Aryl), 7.24–7.31 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR (CD_2Cl_2): δ 10.8 (Si*C*H$_2$C), 25.2 (SiCH$_2$*C*H$_2$C), 30.1 (Si(CH$_2$)$_2$*C*H$_2$C), 55.5 (O*C*H$_3$), 114.1 (*C*-3/*C*-5, Aryl), 126.9 (C=*C*H$_2$), 127.8 (*C*-2/*C*-6, Aryl), 136.1 (*C*-1, Aryl), 147.6 (*C*=CH$_2$), 159.2 (*C*-4, Aryl). ^{29}Si NMR (CD_2Cl_2): δ –20.1. Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 72.1; H, 8.7.

Preparation of 1-methoxy-1-(2,4,6-trimethoxyphenyl)-1-silacyclohexane (61). A suspension of 1,3,5-trimethoxybenzene (50.0 g, 297 mmol) in a mixture of *n*-hexane (175 mL) and TMEDA (35.7 g, 307 mmol) was heated to ca. 50 °C to dissolve the 1,3,5-trimethoxybenzene. After the heat source was removed, a 2.5 M solution of *n*-butyllithium in *n*-hexane (121 mL, 303 mmol of *n*-BuLi) was added dropwise within 30 min to the vigorously stirred mixture. During the addition, the heat of reaction caused the mixture to boil under reflux, and a white precipitate was formed. After the addition was complete, the mixture was stirred vigorously (to prevent agglomeration) at 20 °C for 3 days (formation of (2,4,6-trimethoxyphenyl)lithium), and the resulting suspension was then added *via* a dropping funnel at 0 °C within 20 min to a vigorously stirred solution of **55** (50.3 g, 297 mmol) in *n*-hexane (150 mL). The mixture was stirred at 0 °C for a further 15 min and then at 20 °C for 6 h, followed by dropwise addition of methanol (13.1 g, 409 mmol) within a period of 5 min (warming to ca. 30–40 °C; formation of a precipitate). The stirred mixture was cooled to 20 °C within 1 h and then stirred at this temperature for a further 16 h. The resulting suspension was filtered, the filter cake was washed with *n*-hexane (2 × 300 mL), and the filtrate and wash solutions were combined. The solvent was removed under reduced pressure, and the liquid residue was distilled in vacuo (Kugelrohr apparatus; first fraction, ≤120 °C/0.001 mbar, discarded; second fraction, 120–170 °C/0.001 mbar, crude product (65.2 g of a colorless liquid)). The crude product was redistilled in vacuo (Vigreux column, 10 cm) to give **61** in 66% yield as a colorless oily liquid (58.3 g, 197 mmol); bp 105 °C/0.001 mbar. After the liquid was kept at 15–20 °C for 7 days, it solidified to give a colorless crystalline solid; mp 24–25 °C. ^{1}H NMR (CD_2Cl_2): δ 0.75–0.89, 1.08–1.20, 1.23–1.35, 1.53–1.67, and 1.73–1.87 (m, 10 H, Si(CH_2)$_5$), 3.41 (s, 3 H, SiOCH_3), 3.73 (s, 6 H, *o*-OCH_3, Tri), 3.81 (s, 3 H, *p*-OCH_3, Tri), 6.07 (s, 2 H, *H*-3/*H*-5, Tri). ^{13}C NMR (CD_2Cl_2): δ 16.0

(Si*C*H$_2$C), 25.0 (SiCH$_2$*C*H$_2$C), 30.4 (Si(CH$_2$)$_2$*C*H$_2$C), 50.8 (SiO*C*H$_3$), 55.4 (*o*-O*C*H$_3$, Tri), 55.5 (*p*-O*C*H$_3$, Tri), 90.5 (*C*-3/*C*-5, Tri), 102.9 (*C*-1, Tri), 164.2 (*C*-4, Tri), 167.3 (*C*-2/*C*-6, Tri). ^{29}Si NMR (CD_2Cl_2): δ 2.5. Anal. Calcd for $C_{15}H_{24}O_4Si$: C, 60.78; H, 8.16. Found: C, 60.7; H, 7.8.

Preparation of 1-[1-(4-methoxyphenyl)vinyl]-1-(2,4,6-trimethoxyphenyl)-1-silacyclohexane (62). A 2.5 M solution of *n*-butyllithium in *n*-hexane (75.0 mL, 188 mmol of *n*-BuLi) was added dropwise at –78 °C within 20 min to a stirred mixture consisting of finely ground **57** (40.0 g, 92.9 mmol), TMEDA (31.0 g, 267 mmol), and *n*-hexane (300 mL). The resulting yellow mixture was stirred at –78 °C for 2 h and then warmed to 0 °C within 90 min (evolution of nitrogen; change of color to orange; formation of [1-(4-methoxyphenyl)vinyl]lithium) (**58**)). After the nitrogen evolution had finished, the resulting clear solution was stirred at 20 °C for a further 10 min and then added dropwise at 20 °C within 25 min to a solution of **61** (27.5 g, 92.8 mmol) in *n*-hexane (200 mL). During the addition, the mixture warmed to ca. 30 °C. The solution was then cooled to 20 °C and stirred at this temperature for 16 h (change of color from orange to yellow), followed by the addition of silica gel (50 g; 32–63 μm, ICN 02826). The resulting suspension was shaken for 2 min and then subjected to flash chromatography (column diameter, 5.5 cm; column length, 50 cm; silica gel, 520 g (32–63 μm, ICN 02826); the silica gel that was added before shaking the mixture was allowed to sediment on the top of the column in this step), using petroleum ether (40–65 °C)/diethyl ether/triethylamine (55:40:5 (v/v/v)) as the eluent. The relevant fraction that contained the crude product was concentrated under reduced pressure, the liquid residue was distilled in vacuo (Kugelrohr apparatus; first fraction, ≤160 °C/0.001 mbar, discarded; second fraction, 160–220 °C/0.001 mbar, crude product (31.3 g of a colorless liquid)), and the crude product was crystallized from *n*-hexane (120 mL; crystallization at –20 °C over a period 3 days). The resulting product was isolated by decantation, washed with cold (–20 °C) *n*-pentane (10 mL), recrystallized from *n*-hexane (90 mL; crystallization at –20 °C over a period of 4 days), washed with cold (–20 °C) *n*-pentane (10 mL), and dried in vacuo (0.001 mbar, 20 °C, 2 h) to give **62** in 47% yield as a colorless crystalline solid (17.5 g, 43.9 mmol); mp 45–46 °C. ^{1}H NMR (CD_2Cl_2): δ 1.05–1.13, 1.26–1.41, and 1.43–1.78 (m, 10 H, Si(C*H*$_2$)$_5$), 3.70 (s, 6 H, *o*-OC*H*$_3$, Tri), 3.76 (s, 3 H, *p*-OC*H*$_3$, $C_6H_4OCH_3$), 3.80 (s, 3 H, *p*-OC*H*$_3$, Tri), 5.65 (δ_A) and 5.88 (δ_B) ($^2J_{AB}$ = 3.2 Hz, 2 H, C=C*H*$_A$*H*$_B$), 6.08 (s, 2 H, *H*-3/*H*-5, Tri), 6.73–6.79 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 7.13–7.19 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$). ^{13}C NMR (CD_2Cl_2): δ 15.0 (Si*C*H$_2$C), 25.2 (SiCH$_2$*C*H$_2$C), 30.6 (Si(CH$_2$)$_2$*C*H$_2$C), 55.37 (*o*-O*C*H$_3$, Tri), 55.44 (*p*-O*C*H$_3$, Tri, or *p*-O*C*H$_3$, $C_6H_4OCH_3$), 55.5 (*p*-O*C*H$_3$, Tri, or *p*-O*C*H$_3$, $C_6H_4OCH_3$), 90.8 (*C*-3/*C*-5, Tri), 103.6 (*C*-1, Tri), 113.5 (*C*-3/*C*-5, $C_6H_4OCH_3$), 126.2 (C=*C*H$_2$), 128.1 (*C*-2/*C*-6, $C_6H_4OCH_3$), 137.7 (*C*-1, $C_6H_4OCH_3$), 150.4 (*C*=CH$_2$), 158.6 (*C*-4, $C_6H_4OCH_3$), 164.0 (*C*-4, Tri),

167.0 (*C*-2/*C*-6, Tri). ^{29}Si NMR (CD_2Cl_2): δ –15.4. Anal. Calcd for $C_{23}H_{30}O_4Si$: C, 69.31; H, 7.59. Found: C, 69.1; H, 7.5.

Preparation of 1-chloro-1-[1-(4-methoxyphenyl)vinyl]-1-silacyclohexane (63). A 2.0 M ethereal hydrogen chloride solution (11.5 mL, 23.0 mmol of HCl) was added to a solution of **62** (8.70 g, 21.8 mmol) in diethyl ether (30 mL) in one single portion at 0 °C, and the resulting mixture was stirred at 0 °C for 10 min (complete conversion **62** → **63**, GC control). The solvent and the excess hydrogen chloride were removed under reduced pressure at 5–15 °C, the oily residue was dried in vacuo (0.001 mbar, 20 °C, 1 h) and dissolved in *n*-hexane (40 mL), and the resulting solution was then kept undisturbed at –20 °C for 2 days (crystallization of 1,3,5-trimethoxybenzene). The precipitate was separated by filtration and washed with cold (–20 °C) *n*-hexane (20 mL), the filtrate and wash solution were combined, and the solvent was removed under reduced pressure at 5–15 °C. The oily residue was distilled in vacuo (Vigreux column, 5 cm) to give **63** in 77% yield as a colorless liquid (4.46 g, 16.7 mmol); bp 120–122 °C/0.001 mbar. ^{1}H NMR ($CDCl_3$): δ 0.87–1.02, 1.05–1.17, 1.19–1.34, and 1.57–1.92 (m, 10 H, Si(CH_2)$_5$), 3.79 (s, 3 H, OCH_3), 5.73 (δ_A) and 6.00 (δ_B) ($^2J_{AB}$ = 2.2 Hz, 2 H, C=C$H_A H_B$), 6.82–6.89 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 7.23–7.30 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$). ^{13}C NMR ($CDCl_3$): δ 15.7 (Si*C*H$_2$C), 23.5 (SiCH$_2$*C*H$_2$C), 29.2 (Si(CH$_2$)$_2$*C*H$_2$C), 55.2 (O*C*H$_3$), 113.8 (*C*-3/*C*-5, $C_6H_4OCH_3$), 128.0 (*C*-2/*C*-6, $C_6H_4OCH_3$), 129.0 (C=*C*H$_2$), 134.2 (*C*-1, $C_6H_4OCH_3$), 147.1 (*C*=CH$_2$), 158.9 (*C*-4, $C_6H_4OCH_3$). ^{29}Si NMR ($CDCl_3$): δ 14.7. Anal. Calcd for $C_{14}H_{19}ClOSi$: C, 63.02; H, 7.18. Found: C, 62.9; H, 7.2.

Preparation of 1,1-dichloro-1-silacyclopentane (64).[90] This compound was prepared analogous to the synthesis of **55** (1,4-dibromobutane (151 g, 699 mmol), magnesium turnings (37.4 g, 1.54 mol), tetrachlorosilane (131 g, 771 mmol)). After distillation under atmospheric pressure (Vigreux column, 15 cm; 71 g of isolated crude product; bp 141–145 °C) and redistillation in vacuo (Vigreux column, 30 cm), compound **64** was obtained in 61% yield (related to 1,4-dibromobutane) as a colorless liquid (66.2 g, 427 mmol); bp 71–73 °C/100 mbar. ^{1}H NMR ($CDCl_3$): δ 1.09–1.17 (m, 4 H, SiCH_2C), 1.69–1.81 (m, 4 H, SiCH$_2$CH_2C). ^{13}C NMR ($CDCl_3$): δ 17.9 (Si*C*H$_2$C), 24.8 (SiCH$_2$*C*H$_2$C). ^{29}Si NMR ($CDCl_3$): δ 45.5. Anal. Calcd for $C_4H_8Cl_2Si$: C, 30.98; H, 5.20; Cl, 45.72. Found: C, 31.3; H, 5.2; Cl, 45.5.

Preparation of 1,1-dimethoxy-1-silacyclopentane (65).[90] This compound was prepared analogous to the synthesis of **56**, Protocol A (**64** (66.2 g, 427 mmol), methanol (30.4 g, 949 mmol), triethylamine (96.1 g, 950 mmol)). After distillation under atmospheric pressure (Vigreux column, 15 cm; 53 g of isolated crude product; bp 136–144 °C) and redistillation in vacuo, compound **65** was isolated in 74% yield as a colorless liquid (46.2 g, 316 mmol); bp 73 °C/100 mbar. ^{1}H NMR ($CDCl_3$): δ 0.48–0.56 (m, 4 H, SiCH_2C), 1.53–1.62 (m, 4 H, SiCH$_2$CH_2C), 3.52 (s, 6 H, OCH_3). ^{13}C

NMR ($CDCl_3$): δ 7.4 (Si*C*H_2C), 24.7 (SiCH$_2$*C*H_2C), 50.7 (O*C*H_3). ^{29}Si NMR ($CDCl_3$): δ 16.4. Anal. Calcd for $C_6H_{14}O_2Si$: C, 49.27; H, 9.65. Found: C, 49.1; H, 9.6.

Preparation of 1-methoxy-1-[1-(4-methoxyphenyl)vinyl]-1-silacyclopentane (66). A 2.7 M solution of *n*-butyllithium in *n*-heptane (70 mL, 189 mmol of *n*-BuLi) was added dropwise at –78 °C within 50 min to a stirred mixture of **57** (40.0 g, 92.9 mmol), TMEDA (31.0 g, 267 mmol), and *n*-hexane (360 mL). The resulting yellow solution was stirred at –78 °C for 2 h and then warmed to 0 °C within 90 min (evolution of nitrogen; change of color to orange; formation of [1-(4-methoxyphenyl)vinyl]lithium (**58**)). After the nitrogen evolution was finished, the mixture was stirred at 20 °C for a further 10 min and then added dropwise at –55 ±5 °C within 30 min to a solution of **65** (14.3 g, 97.8 mmol) in *n*-hexane (200 mL). The resulting mixture was warmed to –30 °C within 2 h and then to 10 °C within a further 15 h, and was finally stirred at 20 °C for 1 day. The resulting clear yellow solution was cooled in an ice bath, and iodomethane (125 g, 881 mmol) was added (formation of a precipitate). After a period of 2 h, the ice bath was removed and stirring was continued at 20 °C for 1 day. The precipitate was separated by filtration and washed with *n*-hexane (4 × 250 mL), and the filtrate and the wash solutions were combined. The solvent was removed under reduced pressure, and the residue was distilled in vacuo (Kugelrohr apparatus; first fraction, ≤ 90 °C/0.001 mbar, discarded; second fraction, 90–140 °C/0.001 mbar, crude product (15.8 g)). Distillation of this crude product in vacuo (Vigreux column, 15 cm) gave **66** in 45% yield (related to **65**) as a colorless oily liquid (10.9 g, 43.9 mmol); bp 90 °C/0.001 mbar. ^{1}H NMR ($CDCl_3$): δ 0.66–0.89 (m, 4 H, SiC*H*$_2$C), 1.52–1.79 (m, 4 H, SiCH$_2$C*H*$_2$C), 3.42 (s, 3 H, SiOC*H*$_3$), 3.79 (s, 3 H, COC*H*$_3$), 5.70 (δ_A) and 6.05 (δ_B) (2 H, $^2J_{AB}$ = 2.5 Hz, C=C*H*$_A$*H*$_B$), 6.83–6.89 (m, 2 H, *H*-3/*H*-5, Aryl), 7.28–7.35 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR ($CDCl_3$): δ 10.8 (Si*C*H$_2$C), 26.1 (SiCH$_2$*C*H$_2$C), 51.0 (SiO*C*H$_3$), 55.2 (CO*C*H$_3$), 113.8 (*C*-3/*C*-5, Aryl), 127.4 (C=*C*H$_2$), 127.6 (*C*-2/*C*-6, Aryl), 134.9 (*C*-1, Aryl), 147.0 (*C*=CH$_2$), 158.8 (*C*-4, Aryl). ^{29}Si NMR ($CDCl_3$): δ 26.8. Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.70; H, 8.12. Found: C, 67.8; H, 8.0.

Preparation of 1-[1-(4-methoxyphenyl)vinyl]-1-silacyclopentane (67). This compound was prepared analogous to the synthesis of **60** (**66** (10.7 g, 43.1 mmol), LAH (820 mg, 21.6 mmol), diethyl ether (100 mL)) and was isolated in 79% yield as a colorless oily liquid (7.45 g, 34.1 mmol); bp 77 °C/0.001 mbar. IR (film): $\tilde{\nu}$ 2123 cm^{-1} (SiH). ^{1}H NMR (CD_2Cl_2): δ 0.72–1.04 (m, 4 H, SiC*H*$_2$C), 1.61–1.73 (m, 4 H, SiCH$_2$C*H*$_2$C), 3.80 (s, 3 H, OC*H*$_3$), 4.39–4.46 (δ_X), 5.67 (δ_A), and 6.02 (δ_B) (3 H, $^2J_{AB}$ = 2.4 Hz, $^4J_{BX}$ = 0.7 Hz, 2 H, *H*$_X$SiC=C*H*$_A$*H*$_B$), 6.84–6.91 (m, 2 H, *H*-3/*H*-5, Aryl), 7.25–7.32 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR (CD_2Cl_2): δ 10.2 (Si*C*H$_2$C), 27.6 (SiCH$_2$*C*H$_2$C), 55.6 (O*C*H$_3$), 114.1 (*C*-3/*C*-5, Aryl), 126.6 (C=*C*H$_2$), 127.8 (*C*-2/*C*-6, Aryl), 135.9 (*C*-1, Aryl), 147.3

(*C*=CH_2), 159.3 (*C*-4, Aryl). ^{29}Si NMR (CD_2Cl_2): δ –3.2. Anal. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31. Found: C, 71.8; H, 8.3.

Preparation of *rac*-1-(dimethylamino)-1-[2-(dimethylamino)-1-(4-methoxyphenyl)-ethyl]-1-silacyclopentane (*rac*-68). This compound was prepared analogous to the synthesis of *rac*-**16** (**67** (2.52 g, 11.5 mmol), dimethylamine (7.07 g, 157 mmol), a 1.6 M solution of *n*-butyllithium in *n*-hexane (7.9 mL, 12.6 mmol of *n*-BuLi), chlorotrimethylsilane (1.46 g, 13.4 mmol), THF (45 mL)) and was isolated in 60% yield as a colorless oily liquid (2.13 g, 6.95 mmol); bp 112–113 °C/0.001 mbar. ^{1}H NMR ([D$_8$]THF): δ 0.48–0.67 (m, 4 H, SiCH_2C), 1.29–1.59 (m, 4 H, SiCH$_2$CH_2C), 2.12 (s, 6 H, CNCH_3), 2.42 (s, 6 H, SiNCH_3), 2.51 (δ_C), 2.60 (δ_A), and 2.71 (δ_B) (3 H, $^2J_{AB}$ = –12.0 Hz, $^3J_{AC}$ = 6.7 Hz, $^3J_{BC}$ = 9.6 Hz, SiCH_CC$H_A$$H_B$N), 3.70 (s, 3 H, OC$H_3$), 6.71–6.78 (m, 2 H, *H*-3/*H*-5, Aryl), 6.95–7.01 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR ([D$_8$]THF): δ 10.6 (Si*C*H$_2$C), 11.1 (Si*C*H$_2$C), 27.3 (SiCH$_2$*C*H$_2$C), 27.5 (SiCH$_2$*C*H$_2$C), 35.8 (Si*C*HC$_2$), 39.4 (SiN*C*H$_3$), 45.7 (CN*C*H$_3$), 55.1 (O*C*H$_3$), 61.7 (C*C*H$_2$N), 114.1 (*C*-3/*C*-5, Aryl), 129.5 (*C*-2/*C*-6, Aryl), 135.4 (*C*-1, Aryl), 158.1 (*C*-4, Aryl). ^{29}Si NMR ([D$_8$]THF): δ 23.8. Anal. Calcd for $C_{17}H_{30}N_2OSi$: C, 66.61; H, 9.86; N, 9.14. Found: C, 66.2; H, 9.6, N, 8.8.

1,1-Dichloro-1-silacyclobutane (69). This compound was commercially available (ABCR/Gelest, SIC2568.0)

Preparation of 1,1-dimethoxy-1-silacyclobutane (70). This compound was prepared analogous to the synthesis of **56**, Protocol A (**69** (29.1 g, 206 mmol), methanol (14.5 g, 453 mmol), diethylmethylamine[93] (39.6 g, 454 mmol)). After distillation in vacuo (Vigreux column, 10 cm; 17.7 g of isolated crude product; bp 78–80 °C/202 mbar) and redistillation in vacuo (Vigreux column, 10 cm), compound **70** was isolated in 55% yield as a colorless liquid (15.1 g, 114 mmol); bp 78 °C/202 mbar. ^{1}H NMR ($CDCl_3$): δ 1.34–1.45 (m, 4 H, SiCH_2C), 1.57–1.70 (m, 2 H, SiCH$_2$CH_2C), 3.54 (s, 6 H, SiOCH_3). ^{13}C NMR ($CDCl_3$): δ 11.2 (SiCH$_2$*C*H$_2$C), 19.6 (Si*C*H$_2$C), 49.9 (SiO*C*H$_3$). ^{29}Si NMR ($CDCl_3$): δ –12.2. Anal. Calcd for $C_5H_{12}O_2Si$: C, 45.42; H, 9.15. Found: C, 45.9; H, 9.0.

Preparation of 1,1-diisopropoxy-1-silacyclobutane (71). This compound was prepared analogous to the synthesis of **56**, Protocol A (**69** (15.0 g, 106 mmol), propan-2-ol (14.1 g, 235 mmol), triethylamine (23.7 g, 234 mmol)). After distillation in vacuo (Vigreux column, 10 cm; 15.9 g of isolated crude product; bp 55–58 °C/5 mbar) and redistillation in vacuo (Vigreux column, 8 cm), compound **71** was isolated in 62% yield as a colorless liquid (12.5 g, 66.4 mmol); bp 66 °C/13 mbar. ^{1}H NMR ($CDCl_3$): δ 1.20 (d, $^3J_{HH}$ = 6.1 Hz, 12 H, CH_3), 1.30–1.40 (m, 4 H, SiCH_2C), 1.55–1.67 (m, 2 H, SiCH$_2$CH_2C), 4.23 (septett, $^3J_{HH}$ = 6.1 Hz, 2 H, OC*H*). ^{13}C NMR ($CDCl_3$): δ 11.7

(SiCH$_2$*C*H$_2$C), 21.3 (Si*C*H$_2$C), 25.6 (*C*H$_3$), 65.3 (O*C*H). ^{29}Si NMR (CDCl$_3$): δ –19.1. Anal. Calcd for $C_9H_{20}O_2Si$: C, 57.40; H, 10.70. Found: C, 57.1; H, 10.7.

Preparation of 1,1-di-*tert*-butoxy-1-silacyclobutane (72). This compound was prepared similar to the synthesis of **56**, Protocol A (**69** (9.07 g, 64.3 mmol), *tert*-butanol (10.5 g, 142 mmol), triethylamine (14.3 g, 141 mmol); reaction time under reflux, 3 h). After distillation in vacuo (Vigreux column, 5 cm; 9.37 g of isolated crude product; bp 72–74 °C/5 mbar) and redistillation in vacuo (Vigreux column, 5 cm), compound **72** was isolated in 56% yield as a colorless liquid (7.84 g, 36.2 mmol); bp 73 °C/5 mbar. ^{1}H NMR (CDCl$_3$): δ 1.30–1.42 (m, 4 H, SiC*H*$_2$C), 1.33 (s, 18 H, C*H*$_3$), 1.61–1.74 (m, 2 H, SiCH$_2$C*H*$_2$C). ^{13}C NMR (CDCl$_3$): δ 12.1 (SiCH$_2$*C*H$_2$C), 24.3 (Si*C*H$_2$C), 31.9 (*C*H$_3$), 73.4 (O*C*). ^{29}Si NMR (CDCl$_3$): δ –29.4. Anal. Calcd for $C_{11}H_{24}O_2Si$: C, 61.06; H, 11.18. Found: C, 60.9; H, 11.1.

Preparation of 1,1-bis-[1-(4-methoxyphenyl)vinyl]-1-silacyclobutane (73). A 2.7 M solution of *n*-butyllithium in *n*-heptane (70 mL, 189 mmol of *n*-BuLi) was added dropwise at –78 °C within 50 min to a stirred mixture of **57** (40.0 g, 92.9 mmol), TMEDA (31.0 g, 267 mmol), and *n*-hexane (360 mL). The resulting yellow solution was stirred at –78 °C for 2 h and then warmed to 0 °C within 90 min (evolution of nitrogen; change of color to orange; formation of [1-(4-methoxyphenyl)vinyl]lithium (**58**)). After the nitrogen evolution was finished, the mixture was stirred at 20 °C for a further 10 min and then added dropwise at –78 °C within 70 min to a solution of **70** (12.9 g, 97.6 mmol) in *n*-hexane (200 mL). The mixture was stirred at –78 °C for another 3 h and was then warmed to 20 °C within 13 h. The resulting mixture was washed with water (2 × 200 mL), and the organic layer was separated. The first aqueous wash solution (A) was extracted with diethyl ether (100 mL), the resulting ethereal extract was used to extract the second aqueous wash solution (B), and the organic extract was separated, followed by a second extraction of the wash solutions A and B with *n*-hexane (100 mL), using the same protocol as described for the first extraction sequence. All organic extracts were combined, dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The liquid residue was distilled in vacuo (Kugelrohr apparatus; first fraction, ≤150 °C/0.001 mbar, discarded; second fraction, 150–185 °C/0.001 mbar, crude product (11.6 g of a colorless liquid)). The crude product was redistilled in vacuo (vigreux column, 5 cm) to give **73** in 70% yield (related to **57**)/33% yield (related to **70**) as a colorless oily liquid (10.9 g, 32.4 mmol); bp. 166–167 °C/0.001 mbar. ^{1}H NMR (CDCl$_3$): δ 1.32–1.42 (m, 4 H, SiC*H*$_2$C), 2.09–2.22 (m, 2 H, SiCH$_2$C*H*$_2$C), 3.78 (s, 3 H, OC*H*$_3$), 5.73 (δ_A) and 6.06 (δ_B) ($^2J_{AB}$ = 2.5 Hz, 2 H, C=C*H*$_A$*H*$_B$), 6.77–6.83 (m, 2 H, *H*-3/*H*-5, Aryl), 7.17–7.23 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR (CDCl$_3$): δ 14.5 (Si*C*H$_2$C), 18.0 (SiCH$_2$*C*H$_2$C), 55.2 (O*C*H$_3$), 113.6 (*C*-3/*C*-5, Aryl), 127.6 (C=*C*H$_2$), 127.7 (*C*-2/*C*-6, Aryl), 135.0 (*C*-1, Aryl), 148.0 (*C*=CH$_2$), 158.6 (*C*-4,

Aryl) ^{29}Si NMR ($CDCl_3$): δ 6.3. Anal. Calcd for $C_{21}H_{24}O_2Si$: C, 74.96; H, 7.19. Found: C, 74.9; H, 7.2.

Preparation of 1-methoxy-1-(2,4,6-trimethoxyphenyl)-1-silacyclobutane (74). A suspension of 1,3,5-trimethoxybenzene (57.2 g, 340 mmol) in a mixture of *n*-hexane (200 mL) and TMEDA (40.0 g, 344 mmol) was heated to ca. 50 °C to dissolve the 1,3,5-trimethoxybenzene. After the heat source was removed, a 2.5 M solution of *n*-butyllithium in *n*-hexane (138 mL, 345 mmol of *n*-BuLi) was added dropwise within 30 min to the vigorously stirred mixture. During the addition, the heat of reaction caused the mixture to boil under reflux, and a white precipitate was formed. After the addition was complete, the mixture was stirred vigorously (to prevent agglomeration) at 20 °C for 3 days (formation of (2,4,6-trimethoxyphenyl)lithium), and the resulting suspension was then added *via* a dropping funnel at 0 °C within 30 min to a vigorously stirred solution of **69** (48.0 g, 340 mmol) in *n*-hexane (150 mL). The mixture was stirred at 0 °C for a further 15 min and then at 20 °C for 3 h, followed by dropwise addition of methanol (12.7 g, 396 mmol) within a period of 5 min (warming to ca. 30–40 °C; formation of a precipitate). The stirred mixture was cooled to 20 °C within 1 h and then stirred at this temperature for a further 5 h. The resulting suspension was filtered, the filter cake was washed with *n*-hexane (200 mL) and resuspended in *n*-hexane (250 mL), and the resulting mixture was heated under reflux for 5 min and filtered in the heat. The filter cake was washed again with *n*-hexane (100 mL), and all the filtrates and wash solutions were combined. The solvent was removed under reduced pressure, and the liquid residue was distilled in vacuo (Kugelrohr apparatus; first fraction, ≤145 °C/0.001 mbar, discarded; second fraction, 145–165 °C/0.001 mbar, crude product (57.1 g of a colorless solid)). The solid distillate was recrystallized from boiling *n*-hexane (300 mL; crystallization at 4 °C over a period of 16 h) to give **74** in 58% yield as a colorless crystalline solid (53.1 g, 198 mmol); mp 76–77 °C. ^{1}H NMR (CD_2Cl_2): δ 1.31–1.55 (m, 4 H, SiCH_2C), 1.66–2.00 (m, 2 H, CCH_2C), 3.49 (s, 3 H, SiOCH_3), 3.75 (s, 6 H, *o*-OCH_3, Tri), 3.82 (s, 3 H, *p*-OCH_3, Tri), 6.09 (s, 2 H, *H*-3/*H*-5, Tri). ^{13}C NMR (CD_2Cl_2): δ 15.3 (C*C*H$_2$C), 20.2 (Si*C*H$_2$C), 51.0 (SiO*C*H$_3$), 55.6 (*o*-O*C*H$_3$, Tri), 55.8 (*p*-O*C*H$_3$, Tri), 90.6 (*C*-3/*C*-5, Tri), 102.7 (*C*-1, Tri), 164.8 (*C*-4, Tri), 166.9 (*C*-2/*C*-6, Tri). ^{29}Si NMR (CD_2Cl_2): δ 7.7. Anal. Calcd for $C_{13}H_{20}O_4Si$: C, 58.18; H, 7.51. Found: C, 58.1; H, 7.4.

Preparation of 1-[1-(4-methoxyphenyl)vinyl]-1-(2,4,6-trimethoxyphenyl)-1-silacyclobutane (75). A 2.5 M solution of *n*-butyllithium in *n*-hexane (75.0 mL, 188 mmol of *n*-BuLi) was added dropwise at –78 °C within 20 min to a stirred mixture consisting of finely ground **57** (40.0 g, 92.9 mmol), TMEDA (31.0 g, 267 mmol), and *n*-hexane (300 mL). The resulting yellow mixture was stirred at –78 °C for 2 h and then warmed to 0 °C within 90 min (evolution of nitrogen; change of color to orange; formation of [1-(4-methoxyphenyl)vinyl]lithium (**58**)). After the nitrogen

evolution had finished, the resulting clear solution was stirred at 20 °C for a further 10 min and then added dropwise within 25 min to a gently refluxing[94] solution of **74** (24.9 g, 92.8 mmol) in *n*-hexane (200 mL). The solution was then cooled to 20 °C and stirred at this temperature for 16 h (change of color from orange to yellow), followed by the addition of silica gel (50 g; 32–63 μm, ICN 02826). The resulting suspension was shaken for 2 min and then subjected to flash chromatography (column diameter, 5.5 cm; column length, 50 cm; silica gel, 520 g (32–63 μm, ICN 02826); the silica gel that was added before shaking the mixture was allowed to sediment on the top of the column in this step), using petroleum ether (40–65 °C)/diethyl ether/triethylamine (55:40:5 (v/v/v)) as the eluent. The relevant fraction that contained the crude product was concentrated under reduced pressure, the liquid residue was distilled in vacuo (Kugelrohr apparatus; first fraction, ≤180 °C/0.001 mbar, discarded; second fraction, 180–200 °C/0.001 mbar, crude product (21.9 g of a yellowish oily liquid)), and the crude product was crystallized from *n*-hexane (145 mL; crystallization at 4 °C over a period of 3 days). The resulting product was isolated by decantation, washed with cold (4 °C) *n*-pentane (10 mL), and dried in vacuo (0.001 mbar, 20 °C, 2 h) to give **75** in 62% yield as a colorless crystalline solid (21.3 g, 57.5 mmol); mp 45–46 °C. ^{1}H NMR (CD_2Cl_2): δ 1.31–1.54 (m, 4 H, SiCH_2C), 1.92–2.23 (m, 2 H, CCH_2C), 3.72 (s, 6 H, *o*-OCH_3, Tri), 3.77 (s, 3 H, *p*-OCH_3, $C_6H_4OCH_3$), 3.80 (s, 3 H, *p*-OCH_3, Tri), 5.73 (δ_A) and 6.03 (δ_B) ($^2J_{AB}$ = 2.8 Hz, 2 H, C=CH_AH_B), 6.08 (s, 2 H, *H*-3/*H*-5, Tri), 6.77–6.84 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 7.31–7.39 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$). ^{13}C NMR (CD_2Cl_2): δ 16.9 (SiCH_2C), 19.2 (CCH_2C), 55.5 (*p*-OCH_3, Tri, or *p*-OCH_3, $C_6H_4OCH_3$), 55.6 (*p*-OCH_3, Tri, or *p*-OCH_3, $C_6H_4OCH_3$), 55.7 (*o*-OCH_3, Tri), 90.8 (*C*-3/*C*-5, Tri), 103.9 (*C*-1, Tri), 113.7 (*C*-3/*C*-5, $C_6H_4OCH_3$), 125.4 (C=CH_2), 128.1 (*C*-2/*C*-6, $C_6H_4OCH_3$), 135.9 (*C*-1, $C_6H_4OCH_3$), 149.7 (*C*=CH_2), 158.9 (*C*-4, $C_6H_4OCH_3$), 164.4 (*C*-4, Tri), 166.3 (*C*-2/*C*-6, Tri). ^{29}Si NMR (CD_2Cl_2): δ 1.4. Anal. Calcd for $C_{21}H_{26}O_4Si$: C, 68.07; H, 7.07. Found: C, 68.1; H, 7.2.

Preparation of 1-chloro-1-[1-(4-methoxyphenyl)vinyl]-1-silacyclobutane (76). A 2.0 M ethereal hydrogen chloride solution (10.0 mL, 20.0 mmol of HCl) was added to a solution of **75** (7.24 g, 19.5 mmol) in diethyl ether (25 mL) in one single portion at 0 °C, and the resulting mixture was stirred at 0 °C for 10 min (complete conversion **75** → **76**, GC control). The solvent and the excess hydrogen chloride were removed under reduced pressure at 5–15 °C, the oily residue was dried in vacuo (0.001 mbar, 20 °C, 1 h) and dissolved in *n*-hexane (35 mL), and the resulting solution was then kept undisturbed at –20 °C for 2 days (crystallization of 1,3,5-trimethoxybenzene). The precipitate was separated by filtration and washed with cold (–20 °C) *n*-hexane (20 mL), the filtrate and wash solution were combined, and the solvent was removed under reduced pressure at 5–15 °C. The oily residue was distilled in vacuo (Vigreux column, 5 cm) to give

76 in 53% yield as a colorless liquid (2.48 g, 10.4 mmol); bp 93–95 °C/0.001 mbar. ^{1}H NMR ($CDCl_3$): δ 1.59–1.67 (m, 4 H, SiCH_2C), 1.94–2.11 and 2.19–2.37 (m, 2 H, CCH_2C), 3.80 (s, 3 H, OCH_3), 5.83 (δ_A) and 6.17 (δ_B) ($^2J_{AB}$ = 1.8 Hz, 2 H, C=C$H_A H_B$), 6.85–6.92 (m, 2 H, *H*-3/*H*-5, Aryl), 7.29–7.36 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR ($CDCl_3$): δ 16.0 (C*C*H$_2$C), 20.3 (Si*C*H$_2$C), 55.2 (O*C*H$_3$), 114.0 (*C*-3/*C*-5, Aryl), 127.76 (*C*-2/*C*-6, Aryl), 127.83 (C=*C*H$_2$), 132.5 (*C*-1, Aryl), 146.6 (*C*=CH$_2$), 159.2 (*C*-4, Aryl). ^{29}Si NMR ($CDCl_3$): δ 21.0. Anal. Calcd for $C_{12}H_{15}ClOSi$: C, 60.36; H, 6.33. Found: C, 60.2; H, 6.4.

Preparation of bis(dimethylamino)[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-propylsilane (77). A 2.5 M solution of *n*-butyllithium in *n*-hexane (8.7 mL, 21.8 mmol of *n*-BuLi) was added dropwise at –50 °C within 10 min to a stirred solution of dimethylamine (6.05 g, 134 mmol) in THF (20 mL). The resulting mixture was warmed to –10 °C within 2 h and then cooled to –40 °C, followed by dropwise addition of a solution of **76** (2.48 g, 10.4 mmol) in THF (8 mL) within a period of 10 min. The stirred mixture was warmed to –20 °C within 2 h and then to 20 °C within 4 h and was stirred at 20 °C for a further 10 h (complete conversion **76** → **77**; GC control). The mixture was then cooled to 0 °C, chlorotrimethylsilane (2.32 g, 21.4 mmol) was added in one single portion, and the resulting mixture was stirred at 0 °C for 30 min. The solvent was removed under reduced pressure at 5–15 °C, *n*-hexane (20 mL) was added, and the mixture was stirred at 20 °C for 10 min (formation of a precipitate). The mixture was filtered, the filter cake was washed with *n*-hexane (10 mL), the filtrate and wash solutions were combined, the solvent was removed under reduced pressure, and the residue was distilled in vacuo (Vigreux column, 5 cm) to give **77** in 57% yield as a colorless liquid (1.99 g, 5.89 mmol); bp 112–115 °C/0.001 mbar. ^{1}H NMR ([D$_8$]THF): δ 0.28–0.50 (m, 2 H, SiCH_2C), 0.88 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CCH_3), 1.19–1.44 (m, 2 H, CCH_2C), 2.06 (s, 6 H, CNCH_3), 2.44 (s, 6 H, SiNCH_3), 2.47 (s, 6 H, SiNCH_3), 2.55 (δ_A), 2.59 (δ_C), and 2.81 (δ_B) ($^2J_{AB}$ = –13.0 Hz, $^3J_{AC}$ = 3.0 Hz, $^3J_{BC}$ = 12.2 Hz, 3 H, SiCH_CC$H_A H_B$N), 3.71 (s, 3 H, OCH_3), 6.71–6.78 (m, 2 H, *H*-3/*H*-5, Aryl), 6.93–7.00 (m, 2 H, *H*-2/*H*-6, Aryl). ^{13}C NMR ([D$_8$]THF): δ 16.4 (Si*C*H$_2$C), 17.7 (C*C*H$_2$C), 18.8 (C*C*H$_3$), 35.3 (Si*C*HC$_2$), 38.4 (SiN*C*H$_3$), 38.9 (SiN*C*H$_3$), 45.7 (CN*C*H$_3$), 55.1 (O*C*H$_3$), 61.2 (C*C*H$_2$N), 114.0 (*C*-3/*C*-5, Aryl), 129.9 (*C*-2/*C*-6, Aryl), 136.1 (*C*-1, Aryl), 158.0 (*C*-4, Aryl). ^{29}Si NMR ([D$_8$]THF): δ –5.4. Anal. Calcd for $C_{18}H_{35}N_3OSi$: C, 64.04; H, 10.45; N, 12.45. Found: C, 64.3; H, 10.2; N, 12.7.

Preparation of 1-methoxy-1-(1-phenylvinyl)-1-silacyclohexane (78). A solution of 1-bromo-1-phenylethene (28.0 g, 153 mmol) in diethyl ether (140 mL) was added dropwise within 15 min to a suspension of magnesium turnings (4.10 g, 169 mmol) in diethyl ether (10 mL), followed by heating under reflux for an additional 1 h. (The Grignard reaction proceeded smoothly, but required gentle heating to get started.) The resulting dark brown Grignard reagent was cooled to 20

°C, separated from the excess magnesium turnings by decantation, and then added dropwise at 20 °C within 10 min to a stirred solution of **56** (24.6 g, 153 mmol) in diethyl ether (50 mL). The resulting mixture was heated under reflux for 3 days (precipiation of magnesium salts) and was then cooled to 20 °C, followed by filtration. The filter cake was washed with *n*-hexane (300 mL), the filtrate and the wash solution were combined, and the solution was concentrated under reduced pressure at 5–15 °C to a volume of 200 mL and then kept undisturbed at 20 °C for 1 day (postprecipitation of magnesium salts). The precipitate was separated by filtration, the filter cake was washed with *n*-hexane (50 mL), the filtrate and the wash solution were combined, the solvent was removed completely under reduced pressure at 5–15 °C, and the residue was distilled in vacuo to give **78** in 59% yield as a colorless liquid (21.2 g, 91.2 mmol), bp 80–81 °C/0.001 mbar. ^{1}H NMR (CD_2Cl_2): δ 0.71–0.98 (m, 4 H, SiCH_2C), 1.31–1.57 (m, 2 H, Si(CH_2)$_2$CH_2C), 1.60–1.81 (m, 4 H, SiCH$_2$CH_2C), 3.45 (s, 3 H, OCH_3), 5.73 (δ_A) and 6.05 (δ_B) (2 H, $^{2}J_{AB}$ = 2.8 Hz, C=C$H_A H_B$), 7.21–7.28 (m, 1 H, *H*-4, Aryl), 7.28–7.34 (m, 4 H, *H*-2/*H*-6, *H*-3/*H*-5, Aryl). ^{13}C NMR (CD_2Cl_2): δ 12.5 (Si*C*H$_2$C), 24.6 (SiCH$_2$*C*H$_2$C), 30.2 (Si(CH_2)$_2$*C*H$_2$C), 50.6 (O*C*H$_3$), 126.99 (*C*-2/*C*-6, Aryl), 127.00 (*C*-4, Aryl), 128.6 (*C*-3/*C*-5, Aryl), 129.5 (C=*C*H$_2$), 143.7 (*C*-1, Aryl), 148.9 (*C*=CH$_2$). ^{29}Si NMR (CD_2Cl_2): δ 3.4. Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 72.4; H, 8.8.

Preparatiion of 1-(1-phenylvinyl)-1-silacyclohexane (79). A solution of **78** (20.8 g, 89.5 mmol) in diethyl ether (40 mL) was added at 20 °C within 10 min to a stirred suspension of LAH (1.70 g, 44.8 mmol) in diethyl ether (145 mL). The mixture was heated under reflux for 6.5 h and then added carefully at 0 °C to a stirred mixture of 4 M hydrochloric acid (165 mL) and diethyl ether (80 mL). The organic phase was separated, the aqueous layer was extracted with diethyl ether (3 × 100 mL), and the organic solutions were combined and dried over anhydrous magnesium sulfate in an ice bath, followed by an additional thorough dynamic drying using a chromatographic column densely packed with anhydrous magnesium sulfate (column diameter, 3.5 cm; column length, 15 cm). The magnesium sulfate was finally washed with diethyl ether (2 × 200 mL), the organic solutions were combined, the solvent was removed under reduced pressure, and the residue was distilled in vacuo (Vigreux column, 15 cm) to give **79** in 83% yield as a colorless liquid (15.1 g, 74.6 mmol); bp 60–61 °C/0.001 mbar. IR (film): $\tilde{\nu}$ 2112 cm^{-1} (SiH). ^{1}H NMR (CD_2Cl_2): δ 0.69–0.85, 0.92–1.05, 1.25–1.41, 1.51–1.70, and 1.79–1.94 (m, 10 H, Si(CH_2)$_5$), 4.26–4.33 (δ_X), 5.69 (δ_A), and 6.03 (δ_B) (3 H, $^{2}J_{AB}$ = 2.6 Hz, $^{4}J_{BX}$ = 0.4 Hz, H_XSiC=C$H_A H_B$), 7.21–7.28 (m, 1 H, *H*-4, Aryl), 7.28–7.36 (m, 4 H, *H*-2/*H*-6, *H*-3/*H*-5, Aryl). ^{13}C NMR (CD_2Cl_2): δ 10.8 (Si*C*H$_2$C), 25.2 (SiCH$_2$*C*H$_2$C), 30.1 (Si(CH_2)$_2$*C*H$_2$C), 126.8 (*C*-2/*C*-6, Aryl), 127.1 (*C*-4, Aryl), 128.5 (C=*C*H$_2$), 128.7 (*C*-3/*C*-5, Aryl), 144.0 (*C*-1, Aryl), 148.7 (*C*=CH$_2$). ^{29}Si NMR (CD_2Cl_2): δ –19.8. Anal. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97. Found: C, 77.0; H, 9.2.

Preparation of *rac*-1-(dimethylamino)-1-[2-(dimethylamino)-1-phenylethyl]-1-silacyclohexane (*rac*-80). A 2.5 M solution of *n*-butyllithium in *n*-hexane (32.4 mL, 81.0 mmol of *n*-BuLi) was added dropwise at –50 °C within 15 min to a stirred solution of dimethylamine (17.3 g, 384 mmol) in THF (100 mL). The resulting mixture was warmed to –12 °C within 2 h and then cooled to –40 °C, followed by dropwise addition of a solution of **79** (14.9 g, 73.6 mmol) in THF (20 mL) within a period of 20 min (evolution of hydrogen; rise in temperature from –40 °C to –33 °C; change of color from colorless to scarlet red). The resulting solution was stirred at –30 °C for 3 h and then kept undisturbed at 4 °C for 16 h. Subsequently, the solution was placed in an ice bath and stirred again, followed by addition of chlorotrimethylsilane (16.0 g, 147 mmol) in one single portion (change of color from scarlet red to colorless). The mixture was stirred at 0 °C for 5 min, warmed to 20 °C within 30 min, and then stirred at 20 °C for a further 30 min. The solvent was removed completely under reduced pressure at 5–15 °C, followed by addition of *n*-hexane (70 mL). The mixture was stirred at 20 °C for 15 min, the resulting precipitate was separated by filtration, and the filter cake was washed with *n*-hexane (20 mL). The filtrate and the wash solution were combined, the solvent was removed completely under reduced pressure at 5–15 °C, and the residue was distilled in vacuo in a Kugelrohr apparatus (first fraction, ≤90 °C/0.002 mbar, 8.3 g (mainly consisting of **81** and **82**);[95] second fraction, 90–125 °C/0.0005 mbar, 12.5 g (crude product)). The crude product was redistilled in vacuo (Vigreux column, 5 cm) to give *rac*-**80** in 40% yield as a colorless oily liquid (8.63 g, 29.7 mmol); bp 112–114 °C/0.02 mbar. ^{1}H NMR ([D$_8$]THF): δ 0.36–0.71, 0.85–0.98, 1.12–1.30, and 1.35–1.79 (m, 10 H, Si(CH_2)$_5$), 2.12 (s, 6 H, CNCH_3), 2.36–2.46 (m, 1 H, SiCHC$_2$), 2.42 (s, 6 H, SiNCH_3), 2.59–2.76 (m, 2 H, CCH_2N), 6.96–7.05 (m, 3 H, *H*-2/*H*-6, *H*-4, Aryl), 7.11–7.20 (m, 2 H, *H*-3/*H*-5, Aryl). ^{13}C NMR ([D$_8$]THF): δ 11.9 (Si*C*H$_2$C), 12.7 (Si*C*H$_2$C), 24.90 (SiCH$_2$*C*H$_2$C), 24.93 (SiCH$_2$*C*H$_2$C), 31.1 (Si(CH$_2$)$_2$*C*H$_2$C), 37.4 (Si*C*HC$_2$), 38.6 (SiN*C*H$_3$), 45.7 (CN*C*H$_3$), 61.2 (C*C*H$_2$N), 124.9 (*C*-4, Aryl), 128.5 (*C*-3/*C*-5, Aryl), 128.7 (*C*-2/*C*-6, Aryl), 143.9 (*C*-1, Aryl). ^{29}Si NMR ([D$_8$]THF): δ 0.8. Anal. Calcd for C$_{17}$H$_{30}$N$_2$Si: C, 70.28; H, 10.41; N, 9.64. Found: C, 70.0; H, 10.3; N, 9.5.

Preparation of 1,1-bis(dimethylamino)-1-silacyclohexane (81). A 2.5 M solution of *n*-butyllithium in *n*-hexane (18.0 mL, 45.0 mmol of *n*-BuLi) was added dropwise at –50 °C within 15 min to a stirred solution of dimethylamine (7.12 g, 158 mmol) in THF (70 mL). The resulting mixture was warmed to –15 °C within 2 h, followed by dropwise addition of **55** (3.73 g, 22.1 mmol) at –15 °C within a period of 25 min. The resulting solution was warmed to 20 °C within 4 h and then stirred at 20 °C for a further 12 h. The solvent was removed completely under reduced pressure at 5–15 °C, followed by addition of *n*-hexane (100 mL) (formation of a precipitate). The mixture was stirred at 20 °C for 1 day, the resulting precipitate was separated by filtration, and the filter

cake was washed with *n*-hexane (20 mL). The filtrate and the wash solution were combined, the solvent was removed completely under reduced pressure at 5–15 °C, and the residue was distilled in vacuo (Vigreux column, 5 cm) to give **81** in 75% yield as a colorless liquid (3.07 g, 16.5 mmol); bp 69–70 °C/3 mbar. ^{1}H NMR (CD_2Cl_2): δ 0.61–0.70 (m, 4 H, SiCH_2C), 1.33–1.44 (m, 2 H, Si(CH$_2$)$_2$CH_2C), 1.57–1.67 (m, 4 H, SiCH$_2$CH_2C), 2.46 (s, 12 H, NCH_3). ^{13}C NMR (CD_2Cl_2): δ 11.7 (Si*C*H$_2$C), 25.1 (SiCH$_2$*C*H$_2$C), 30.7 (Si(CH$_2$)$_2$*C*H$_2$C), 37.8 (N*C*H$_3$). ^{29}Si NMR (CD_2Cl_2): δ –6.0. Anal. Calcd for $C_9H_{22}N_2Si$: C, 58.00; H, 11.90; N, 15.03. Found: C, 57.9; H, 12.0; N, 15.1.

Dimethyl-(2-phenylethyl)amine (82). This compound was commercially available (Aldrich, 52,380-1).

1,2-Bis(chlorodimethylsilyl)ethane (83). This compound was a gift from the Wacker-Chemie GmbH, Burghausen, Germany.[96]

Preparation of 1,2-bis(ethynyldimethylsilyl)ethane (84).

Protocol A. This compound was synthesized according to ref. 97.

Protocol B. A mixture of **83** (121 g, 562 mmol), sodium acetylide (300 g of an 18% suspension of NaC≡CH in xylene (mixture of isomers), 1.12 mol of NaC≡CH), and THF (THF) (360 mL) was heated under reflux for 3 h. The mixture was cooled to 20 °C and washed with water (2 × 450 mL), and the organic layer was separated. The first aqueous wash solution (A) was extracted with diethyl ether (300 mL), the resulting ethereal extract was used to extract the second aqueous wash solution (B), and the organic extract was separated, followed by a second extraction of the wash solutions A and B with a fresh portion of diethyl ether (300 mL), using the same protocol as described for the first extraction sequence. All organic extracts were combined and dried over anhydrous sodium sulfate, most of the solvent was removed under reduced pressure, and the remaining xylene was then removed by vacuum distillation (30–50 °C/15 mbar) using a Vigreux column (40 cm). The residues from four identical runs of this preparation were combined and distilled in vacuo (Vigreux column, 40 cm) to give 245 g of pure (GC control) **84** (75–77 °C/20 mbar) and 126 g of a lower-boiling fraction containing **84** and xylene (50–75 °C/20 mbar). The latter fraction was redistilled (Vigreux column, 80 cm) to give a further 65 g of **84** (75–77 °C/20 mbar). Compound **84** was obtained in a total yield of 71% as a colorless liquid (310 g, 1.59 mol). ^{1}H NMR ($CDCl_3$): δ 0.16 (s, 12 H, SiCH_3), 0.60 (s, 4 H, SiCH_2C), 2.36 (s, 2 H, SiC≡C*H*). ^{13}C NMR ($CDCl_3$): δ –2.5 (Si*C*H$_3$), 8.1 (Si*C*H$_2$C), 89.1 (Si*C*≡CH), 93.6 (SiC≡*C*H). ^{29}Si NMR ($CDCl_3$): δ –12.8. Anal. Calcd for $C_{10}H_{18}Si_2$: C, 61.78; H, 9.33. Found: C, 61.6; H, 9.2.

Methyl 4-formylbenzoate (85). This compound was commercially available (Fluka, 47717).

Preparation of methyl 4-[1-(trimethylsilyloxy)but-2-ynyl]benzoate (86). A 0.5 M solution of 1-propynylmagnesium bromide in THF (422 mL, 211 mmol of MeC≡CMgBr) was added

dropwise at –20 °C to –15 °C within 105 min to a stirred solution of **85** (34.6 g, 211 mmol) in THF (250 mL), and the mixture was then warmed to –10 °C within 2 h. Subsequently, chlorotrimethylsilane (27.5 g, 253 mmol) was added dropwise at –10 °C over a period of 30 min, and the mixture was warmed to 15 °C within 15 h. Most of the solvent was removed under reduced pressure at 5–15 °C, followed by addition of *n*-hexane (500 mL). The resulting precipitate was separated by filtration and washed with *n*-hexane (2 × 250 mL), and the organic solutions were combined. The solvent was removed under reduced pressure at 5–15 °C, and the residue was distilled in vacuo to give **86** in 61% yield as a colorless liquid (35.3 g, 128 mmol); bp 113 °C/0.0005 mbar. ^{1}H NMR (CD_2Cl_2): δ 0.20 (s, 9 H, SiC*H*$_3$), 1.87 (d, $^{5}J_{HH}$ = 2.2 Hz, 3 H, CC*H*$_3$), 3.89 (s, 3 H, C(O)OC*H*$_3$), 5.49 (q, $^{5}J_{HH}$ = 2.2 Hz, 1 H, SiOC*H*), 7.52–7.59 (m, 2 H, *H*-3/*H*-5, Phe′), 7.97–8.04 (m, 2 H, *H*-2/*H*-6, Phe′). ^{13}C NMR (CD_2Cl_2): δ 0.2 (Si*C*H$_3$), 3.7 (C*C*H$_3$), 52.3 (O*C*H$_3$), 64.7 (SiO*C*H), 79.6 (*C*≡C), 83.1 (C≡*C*), 126.6 (*C*-3/*C*-5, Phe′), 129.9 (*C*-2/*C*-6, Phe′), 130.0 (*C*-1, Phe′), 147.6 (*C*-4, Phe′), 167.0 (*C*(O)OCH$_3$). ^{29}Si NMR (CD_2Cl_2): δ 20.5. Anal. Calcd for $C_{15}H_{20}O_3Si$: C, 65.18; H, 7.29. Found: C, 64.9; H, 7.2.

Preparation of methyl 4-[hydroxy-(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)methyl]benzoate (87). A solution of cyclopentadienylcobaltdicarbonyl ($CpCo(CO)_2$; 13.9 g, 77.2 mmol) in *m*-xylene (100 mL) was added dropwise within 16 h to a stirred boiling solution of **84** (149 g, 766 mmol) and **86** (212 g, 767 mmol) in *m*-xylene (1 L), followed (i) by addition of **84** (74.6 g, 384 mmol) in one single portion at 20 °C, (ii) then by dropwise addition of a solution of $CpCo(CO)_2$ (14.0 g, 77.8 mmol) in *m*-xylene (100 mL) within 11 h at reflux temperature, (iii) then by addition of **84** (74.5 g, 383 mmol) in one single portion at 20 °C, and (iv) finally by dropwise addition of a solution of $CpCo(CO)_2$ (14.0 g, 77.8 mmol) in *m*-xylene (100 mL) within 11 h at reflux temperature. (To avoid heating of the $CpCo(CO)_2$ solution before its addition, the dropping funnel containing this catalyst was separated from the refluxing reaction mixture by a glass tube (length, 20 cm), through which the $CpCo(CO)_2$ solution was allowed to drop freely into the refluxing mixture.) 1 L of the solvent was removed by distillation at atmospheric pressure, methanol (1 L) and acetic acid (2.31 g, 38.5 mmol) were added, and the mixture was heated under reflux for 8 days. The mixture was cooled to 20 °C and then diluted with diethyl ether (1.5 L) and washed with a saturated aqueous sodium hydrogen carbonate solution (4 L). The organic layer was separated, the aqueous phase was extracted with diethyl ether (3 × 1 L), the organic solutions were combined and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The black tarry residue (982 g) was diluted with *n*-hexane/ethyl acetate (83:17 (v/v)) (1 L), followed by treatment with ultrasound at 20 °C for 1 h. The resulting mixture was divided into two equal portions, and each portion was purified by column chromatography on silica gel (column

dimensions, 60 × 5 cm; silica gel (32–63 μm, ICN 02826), 600 g). The impurities (GC control) were eluted with *n*-hexane/ethyl acetate (83:17 (v/v)), and the product was eluted with *n*-hexane/ethyl acetate (80:20 (v/v)). The relevant fractions (GC control) of both chromatographic separations were combined, the solvent was removed under reduced pressure, and the residue was dried in vacuo (10 mbar, 20 °C, 1 h) to give 125 g of a brown solid, which was recrystallized twice from boiling *n*-heptane (6.25 L were used for each crystallization step; crystallization at 4 °C over a period of 1 day). The crystalline product was isolated by suction filtration, washed with cold (4 °C) *n*-heptane (600 mL), and dried in vacuo (0.001 mbar, 20 °C, 4 h) to give 54.2 g of **87**. The mother liquors, the wash solution, and the impure fractions (GC control) obtained from the chromatographic workup were combined, and the resulting solution was concentrated under reduced pressure and then dried in vacuo (0.001 mbar, 20 °C, 1 h) to give 112 g of a brown solid, which was purified by chromatography as described above. The resulting product (54.6 g) was recrystallized twice from *n*-heptane (2.73 L were used for each crystallization step) to give a further 12.4 g of **87**. Compound **87** was obtained in a total yield of 22% (related to **86**) as a colorless crystalline solid (66.6 g, 167 mmol); mp 166 °C. ^{1}H NMR (CD_2Cl_2): δ 0.17 (s, 3 H, SiCH_3), 0.22 (s, 9 H, SiCH_3), 1.01 (s, 4 H, SiCH_2C), 2.24 (br s, 3 H, CCH_3), 2.45 (d, $^3J_{HH}$ = 3.8 Hz, 1 H, O*H*), 3.87 (s, 3 H, C(O)OCH_3), 6.04 (d, $^3J_{HH}$ = 3.8 Hz, 1 H, OC*H*), 7.27 (br s, 1 H, *H*-4, Naph), 7.40–7.47 (m, 2 H, *H*-3/*H*-5, Phe′), 7.56 (br s, 1 H, *H*-1, Naph), 7.94–8.01 (m, 2 H, *H*-2/*H*-6, Phe′). ^{13}C NMR (CD_2Cl_2): δ –1.53 (Si*C*H$_3$), –1.46 (2 C, Si*C*H$_3$), –1.41 (Si*C*H$_3$), 7.78 (Si*C*H$_2$C), 7.83 (Si*C*H$_2$C), 19.5 (C*C*H$_3$), 52.3 (C(O)O*C*H$_3$), 73.7 (O*C*H), 127.1 (*C*-3/*C*-5, Phe′), 129.6 (*C*-1, Phe′), 129.9 (*C*-2/*C*-6, Phe′), 131.8 (*C*-1, Naph), 135.7 (*C*-3, Naph), 136.3 (*C*-4, Naph), 141.3 (*C*-2, Naph), 143.7 (*C*-4a or *C*-8a, Naph), 145.8 (*C*-4a or *C*-8a, Naph), 148.6 (*C*-4, Phe′), 167.1 (*C*(O)OCH$_3$). ^{29}Si NMR (CD_2Cl_2): δ –7.05, –6.95. Anal. Calcd for $C_{22}H_{30}O_3Si_2$: C, 66.28; H, 7.59. Found: C, 66.2; H, 7.6.

Preparation of methyl 4-[(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)carbonyl]benzoate (88). A solution of dimethyl sulfoxide (13.6 g, 174 mmol) in dichloromethane (55 mL) was added dropwise at –55 °C (±5 °C) within 60 min to a stirred solution of oxalyl chloride (11.0 g, 86.7 mmol) in dichloromethane (185 mL) (gas evolution), and the mixture was stirred for 15 min. Subsequently, a solution of **87** (31.5 g, 79.0 mmol) in dichloromethane (100 mL) was added dropwise at –55 °C (±5 °C) within 75 min, the mixture was stirred for 30 min, and triethylamine (40.0 g, 395 mmol) was added dropwise at the same temperature over a period of 30 min. (To avoid cooling of the solution of **87** before its addition, which would result in crystallization of **87** and incomplete conversion, the dropping funnel containing this solution was separated from the cold reaction mixture by a glass tube (length, 20 cm), through which the solution was allowed to drop freely into the cold mixture). The mixture was

stirred at –55 °C for a further 15 min and then warmed to 5 °C within 90 min (>97% conversion, GC control). The mixture was washed with water (2 × 400 mL), the organic phase was separated, the first aqueous wash solution (A) was extracted with diethyl ether (500 mL), the resulting ethereal extract was used to extract the second aqueous wash solution (B), and the organic extract was separated, followed by a second extraction of the wash solutions A and B with a fresh portion of diethyl ether (500 mL), using the same protocol as described for the first extraction sequence. The combined organic solutions were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was dried in vacuo (10 mbar, 20 °C, 1 h) to give a brown amorphous solid (30.3 g), which was purified by column chromatography on silica gel (column dimensions, 71 × 4 cm; silica gel (32–63 μm, ICN 02826), 480 g; eluent, *n*-hexane/ethyl acetate (87:13 (v/v)) to afford **7** as an amorphous colorless solid. The product was crystallized from boiling *n*-heptane (815 mL; crystallization at –20 °C over a period of 2 days), isolated by suction filtration, washed with cold (–20 °C) *n*-pentane (200 mL), and dried in vacuo (0.001 mbar, 20 °C, 6 h) to give 25.6 g of **88**. The mother liquor and the wash solution were combined, the resulting solution was concentrated under reduced pressure to a volume of 180 mL, and a further 1.7 g of the product were obtained by crystallization using the same method as described above. Compound **88** was obtained in a total yield of 87% as a colorless crystalline solid (27.3 g, 68.8 mmol); mp 118 °C. ^{1}H NMR (CD_2Cl_2): δ 0.17 (s, 6 H, SiCH_3), 0.28 (s, 6 H, SiCH_3), 1.05 (s, 4 H, SiCH_2C), 2.30–2.32 (m, 3 H, CCH_3), 3.93 (s, 3 H, C(O)OCH_3), 7.40 (s, 1 H, *H*-1, Naph), 7.43–7.46 (m, 1 H, *H*-4, Naph), 7.81–7.88 (m, 2 H, *H*-3/*H*-5, Phe′), 8.08–8.15 (m, 2 H, *H*-2/*H*-6, Phe′). ^{13}C NMR (CD_2Cl_2): δ –1.63 (2 C, SiCH_3), –1.59 (2 C, SiCH_3), 7.65 (SiCH_2C), 7.68 (SiCH_2C), 20.2 (CCH_3), 52.7 (C(O)OCH_3), 129.8 (*C*-2/*C*-6, Phe′), 130.3 (*C*-3/*C*-5, Phe′), 133.7 (*C*-1, Naph), 134.2 (*C*-1, Phe′), 136.46 (*C*-3, Naph), 136.49 (*C*-4, Naph), 137.9 (*C*-2, Naph), 141.7 (*C*-4, Phe′), 142.8 (*C*-4a, Naph), 149.8 (*C*-8a, Naph), 166.5 (*C*(O)OCH_3), 198.3 (C_2C=O). ^{29}Si NMR (CD_2Cl_2): δ –6.48, –6.42. Anal. Calcd for $C_{22}H_{28}O_3Si_2$: C, 66.62; H, 7.12. Found: C, 66.5; H, 7.0.

Preparation of methyl 4-[1-(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)vinyl]benzoate (89). A 0.5 M solution of potassium bis(trimethylsilyl)amide in toluene (29.7 mL, 14.9 mmol of $KN(SiMe_3)_2$) was added dropwise at 20 °C within 25 min to a stirred suspension of methyltriphenylphosphonium bromide (5.31 g, 14.9 mmol) in toluene (55 mL). The mixture was stirred at 20 °C for 45 min (initially, dissolution of $[Ph_3PMe]Br$; later, formation of a precipitate) and then added dropwise at 20 °C within 30 min to a solution of **88** (5.61 g, 14.1 mmol) in toluene (85 mL). The resulting mixture was stirred at 20 °C for a further 45 min and then added to a stirred mixture of a saturated aqueous ammonium chloride solution (200 mL) (= solution A) and diethyl ether (150 mL), and the organic phase was separated and washed with water (200 mL)

(= solution B). The first aqueous wash solution A was extracted with diethyl ether (150 mL), the resulting ethereal extract was used to extract the second aqueous wash solution B, and the organic extract was separated, followed by a second extraction of the wash solutions A and B with a fresh portion of diethyl ether (150 mL), using the same protocol as described for the first extraction sequence. All organic extracts were combined and dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure at 5–15 °C, and the solid colorless residue was dried in vacuo (0.001 mbar, 20 °C, 20 min). The crude product (11.1 g) was suspended in *n*-hexane/diethyl ether (70:30 (v/v)) (20 mL) and treated with ultrasound at 20 °C for 30 min (dissolution of **89** out of the nearly insoluble triphenylphosphine oxide). The resulting suspension was filtered over silica gel (32–63 μm, ICN 02826; column dimensions, 23 × 4 cm), which was washed with *n*-hexane/diethyl ether (70:30 (v/v)) (1 L). The filtrate and wash solution were combined (no residual Ph_3PO detected by GC), the solvent was removed under reduced pressure, and the residue was dried in vacuo (0.001 mbar, 20 °C, 1 h) to give a white amorphous solid (5.54 g), which was then crystallized from boiling *n*-hexane (165 mL; crystallization at –20 °C over a period of 3 days) to give **89** in 90% yield as a colorless crystalline solid (5.00 g, 12.7 mmol); mp 130 °C. ^{1}H NMR (CD_2Cl_2): δ 0.22 (s, 6 H, SiCH_3), 0.25 (s, 6 H, SiCH_3), 1.04 (s, 4 H, SiCH_2C), 1.98–2.00 (m, 3 H, CCH_3), 3.88 (s, 3 H, C(O)OCH_3), 5.31 (d, $^2J_{HH}$ = 1.2 Hz, 1 H, C=CH_AH$_B$), 5.87 (d, $^2J_{HH}$ = 1.2 Hz, 1 H, C=CH$_A$$H_B$), 7.30–7.38 (m, 4 H, *H*-3/*H*-5, Phe′, *H*-1/*H*-4, Naph), 7.92–7.97 (m, 2 H, *H*-2/*H*-6, Phe′). ^{13}C NMR (CD_2Cl_2): δ –1.42 (2 C, Si*C*H$_3$), –1.40 (2 C, Si*C*H$_3$), 7.86 (Si*C*H$_2$C), 7.89 (Si*C*H$_2$C), 20.2 (C*C*H$_3$), 52.3 (C(O)O*C*H$_3$), 117.2 (C=*C*H$_2$), 126.8 (*C*-3/*C*-5, Phe′), 129.6 (*C*-1, Phe′), 129.9 (*C*-2/*C*-6, Phe′), 135.1 (*C*-1, Naph), 135.7 (*C*-4, Naph), 136.0 (*C*-3, Naph), 141.1 (*C*-2, Naph), 143.3 (*C*-4a, Naph), 145.4 (*C*-4, Phe′), 145.7 (*C*-8a, Naph), 149.4 (*C*=CH$_2$), 167.0 (*C*(O)OCH$_3$). ^{29}Si NMR (CD_2Cl_2): δ –7.06, –7.01. Anal. Calcd for $C_{23}H_{30}O_2Si_2$: C, 70.00; H, 7.66. Found: C, 70.0; H, 7.6.

Preparation of 2-(chloromethyl)furan (90). This compound was synthesized according to ref. 56.

Preparation of 2-(but-2-ynyl)furan (91) and 5-methyl-2-prop-1-ynylfuran (92). A 0.5 M solution of 1-propynylmagnesium bromide in THF (746 mL, 373 mmol of MeC≡CMgBr) was added dropwise at 0 °C within 2 h to a stirred solution of **90** (41.0 g, 352 mmol) in THF (175 mL), and the mixture was then warmed to 20 °C within 30 min, followed by heating under reflux for 2 h (quantitative conversion, GC control). The mixture was cooled to 20 °C, diluted with diethyl ether (350 mL), and washed with a saturated aqueous ammonium chloride solution (700 mL) (= solution A) and water (700 mL) (= solution B). The first aqueous wash solution A was extracted with ethyl acetate (350 mL), the resulting organic extract was used to extract the second aqueous wash solution B, and the organic extract was separated, followed by a second extraction of the wash

solutions A and B with a fresh portion of ethyl acetate (350 mL), using the same protocol as described for the first extraction sequence. All organic extracts were combined and dried over anhydrous sodium sulfate, the solvent was removed by distillation at atmospheric pressure (maximum bath temperature 100 °C), and the residue was distilled in vacuo (Vigreux column, 10 cm) to give 25 g of crude product, bp 38–50 °C/2 mbar, which was redistilled (spinning band column) to give **91** and **92** as colorless liquids; **91**, 29% yield (12.2 g, 102 mmol), bp 53 °C/9 mbar; **92**, 10% yield (4.15 g, 34.5 mmol), bp 60 °C/9 mbar.

Data for **91**. ^{1}H NMR ($CDCl_3$): δ 1.81 (t, $^{5}J_{HH}$ = 2.6 Hz, 3 H, CCH_3), 3.49–3.53 (m, 2 H, CCH_2C), 6.13–6.17 (m, 1 H, *H*-3, Fu), 6.27–6.30 (m, 1 H, *H*-4, Fu), 7.29–7.32 (m, 1 H, *H*-5, Fu). ^{13}C NMR ($CDCl_3$): δ 3.5 (CCH_3), 18.6 (CCH_2C), 73.8 (C≡*C*), 77.2 (*C*≡C), 105.8 (*C*-3, Fu), 110.3 (*C*-4, Fu), 141.5 (*C*-5, Fu), 151.1 (*C*-2, Fu). Anal. Calcd for C_8H_8O: C, 79.97; H, 6.71. Found: C, 79.6; H, 7.2.

Data for **92**. ^{1}H NMR ($CDCl_3$): δ 2.03 (s, 3 H, C≡CCH_3), 2.23–2.25 (m, 3 H, Aryl-CH_3), 5.87–5.90 (m, 1 H, *H*-4, Fu), 6.30–6.33 (m, 1 H, *H*-3, Fu). ^{13}C NMR ($CDCl_3$): δ 4.3 (C≡CCH_3), 13.6 (Aryl-CH_3), 70.4 (*C*≡CCH_3), 89.7 (C≡*C*CH_3), 106.5 (*C*-4, Fu), 114.6 (*C*-3, Fu), 135.7 (*C*-2, Fu), 152.6 (*C*-5, Fu). Anal. Calcd for C_8H_8O: C, 79.97; H, 6.71. Found: C, 79.8; H, 6.9.

Preparation of 2-[(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)-methyl]furan (93). A solution of cyclopentadienylcobaltdicarbonyl ($CpCo(CO)_2$; 383 mg, 2.13 mmol) in *m*-xylene (115 mL) was added dropwise within 2 h to a stirred boiling solution of **84** (6.19 g, 31.8 mmol), **91** (6.89 g, 57.3 mmol), and $CpCo(CO)_2$ (383 mg, 2.13 mmol) in *m*-xylene (65 mL), followed (i) by heating under reflux for 3h, (ii) then by addition of $CpCo(CO)_2$ (383 mg, 2.13 mmol) in one single portion, and (iii) finally by heating under reflux for 16 h (complete conversion, GC control). (To avoid heating of the $CpCo(CO)_2$ solution before its addition, the dropping funnel containing this catalyst was separated from the refluxing reaction mixture by a glass tube (length, 20 cm), through which the $CpCo(CO)_2$ solution was allowed to drop freely into the refluxing mixture.) The mixture was cooled to 20 °C and filtered over silica gel using a standard chromatographic column (column dimensions, 20 × 3.5 cm; silica gel (32–63 μm, ICN 02826)). The silica gel was washed with diethyl ether (500 mL), the filtrate and the wash solution were combined, and the solvent was removed under reduced pressure. The residue (13 g of a yellow oil) was purified by column chromatography on silica gel (column dimensions, 50 × 3.5 cm; silica gel (15–40 μm, Merck 1.15111); eluent, *n*-hexane). The relevant fractions (TLC control) were combined, the solvent was removed under reduced pressure, and the residue was dried in vacuo (0.001 mbar, 20 °C, 6 h) to give **93** in 41% yield (related to **84**) (including workup of impure fractions using the same chromatographic methods) as a colorless oil (4.14 g, 13.2 mmol), which

was pure by NMR and GC. ^{1}H NMR (C_6D_6): δ 0.36 (s, 6 H, SiCH_3), 0.37 (s, 6 H, SiCH_3), 1.14 ("s", 4 H, SiCH_2C), 2.24 (br "s", 3 H, Aryl-CH_3), 3.91 (br "s", 2 H, CCH_2C), 5.85–5.89 (m, 1 H, *H*-3, Fu), 6.13–6.16 (m, 1 H, *H*-4, Fu), 7.17–7.19 (m, 1 H, *H*-5, Fu), 7.46 (br "s", 1 H, *H*-4, Naph), 7.50 (br "s", 1 H, *H*-1, Naph). ^{13}C NMR (C_6D_6): δ –1.3 (4 C, Si*C*H$_3$), 8.00 (Si*C*H$_2$C), 8.02 (Si*C*H$_2$C), 19.3 (C*C*H$_3$), 32.6 (C*C*H$_2$C), 106.4 (*C*-3, Fu), 110.5 (*C*-4, Fu), 135.3 (*C*-1, Naph), 135.8 (*C*-4, Naph), 136.69 (*C*-2 or *C*-3, Naph), 136.74 (*C*-2 or *C*-3, Naph), 141.4 (*C*-5, Fu), 143.1 (*C*-4a, Naph), 144.0 (*C*-8a, Naph), 154.6 (*C*-2, Fu). ^{29}Si NMR (C_6D_6): δ –7.41, –7.38. Anal. Calcd for $C_{18}H_{26}OSi_2$: C, 68.73; H, 8.33. Found: C, 68.8; H, 8.3.

Attempted preparation of {5-[(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)methyl]-2-furyl}lithium (94) (representative experiment). A 1.6 M solution of *n*-butyllithium in *n*-hexane (300 μL, 480 μmol of *n*-BuLi) was added at 0 °C to a stirred mixture of **93** (140 mg, 445 μmol) and diisopropylamine (10 mg, 98.8 μmol) in THF (3 mL) (change of color from colorless to red). The mixture was stirred at 0 °C for a further 20 min, followed by quenching with chlorotrimethylsilane (86 mg, 791 μmol). The result of the subsequent GC/EI MS analysis is shown in Figure 1 (p. 22, Section 5). The result of this reaction sequence did not depend on the mode of addition of the chlorotrimethylsilane (i.e., addition of the chlorotrimethylsilane to the reaction mixture or addition of an aliquot of the reaction mixture to a solution of chlorotrimethylsilane in THF).

5-Bromo-2-furoic acid (95). This compound was commercially available (Aldrich, B6,740-6).

Preparation of methyl 5-bromo-2-furoate (96). A mixture of dichloromethane (700 mL), **95** (146 g, 764 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 122 g, 801 mmol), and iodomethane (130 g, 916 mmol) was heated under reflux for 22 h. The mixture was cooled to 20 °C and was then successively washed with a saturated aqueous ammonium chloride solution (solution A, 300 mL), a saturated aqueous sodium hydrogen carbonate solution (solution B, 300 mL), and water (solution C, 300 mL). The first aqueous wash solution (A) was extracted with ethyl acetate (200 mL), the resulting organic extract was used to extract the second aqueous wash solution (B), the resulting organic extract was used to extract the third aqueous wash solution (C), and the organic extract was separated, followed by a second extraction of the aqueous wash solutions A, B and C with a fresh portion of ethyl acetate (200 mL), using the same protocol as described for the first extraction sequence. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was dried in vacuo (10 mbar, 20 °C, 30 min). *n*-Hexane (1.1 L) was added to the residue, and the resulting mixture was heated under reflux for 5 min, followed by filtration of the hot mixture. The filter cake was washed with boiling *n*-hexane

(160 mL), the filtrate and the wash solution were combined, and the resulting solution was cooled to 20 °C within 2 h and then kept undisturbed at 4 °C for 2 days (formation of a crystalline precipitate). The precipitate was separated by decantation and recrystallized from boiling *n*-hexane (720 mL, crystallization at 4 °C over a period of 4 days). The product was again isolated by decantation and dried in vacuo (0.01 mbar, 20 °C, 4 h) to give 112 g of a yellowish crystalline solid. The mother liquors of the crystallization steps were combined and concentrated under reduced pressure to a volume of 250 mL, and a further 17 g of the product were obtained by crystallization, using the same method as described above. Compound **96** was obtained in a total yield of 82% as a yellowish crystalline solid (129 g, 629 mmol); mp 64–65 °C. ^{1}H NMR ($CDCl_3$): δ 3.87 (s, 3 H, OCH_3), 6.43 (d, $^{3}J_{HH}$ = 3.5 Hz, 1 H, *H*-4, Fu), 7.10 (d, $^{3}J_{HH}$ = 3.5 Hz, 1 H, *H*-3, Fu). ^{13}C NMR ($CDCl_3$): δ 52.1 (O*C*H$_3$), 113.9 (*C*-4, Fu), 120.1 (*C*-3, Fu), 127.5 (*C*-5, Fu), 146.2 (*C*-2, Fu), 158.0 (*C*(O)O). Anal. Calcd for $C_6H_5BrO_3$: C, 35.15; H, 2.46; Br, 38.98. Found: C, 35.4; H, 2.7; Br, 38.8.

Preparation of methyl 5-(but-2-ynyl)-2-furoate (97). A 0.68 M solution of isopropylmagnesium bromide in THF (552 mL, 375 mmol of *i*-PrMgBr) was added dropwise at –40 °C (±5 °C, temperature measured within the flask) within 110 min to a solution of **96** (70.0 g, 341 mmol) in THF (1.0 L). The resulting mixture was stirred at –40 °C (±5 °C) for a further 3 h, followed by sequential addition of copper(I) cyanide (7.70 g, 86.0 mmol) in one single portion and of 1-bromo-2-butyne (64.8 g, 487 mmol) dropwise within 5 min (temperature increase to –20 °C). The mixture was stirred at –35 °C for 2 h and kept undisturbed at –20 °C for a further 16 h, and the cold (–20 °C) mixture was then added to a cold (0 °C) vigorously stirred emulsion consisting of a saturated aqueous ammonium chloride solution (400 mL) and ethyl acetate (200 mL). The resulting mixture was stirred at 0 °C for 30 min, followed by filtration at the same temperature. The filter cake was washed with ethyl acetate (2 × 100 mL), and the two-phase filtrate and the wash solutions were combined. The organic layer was separated, the aqueous phase was extracted with ethyl acetate (3 × 100 mL), and the organic extracts were combined and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (Kugelrohr apparatus; first fraction (<100 °C, 1.03 g), discarded; second fraction (100–130 °C, 51.7 g), crude product). The second fraction (yellowish oil) was crystallized from boiling *n*-hexane (265 mL, crystallization at 4 °C over a period of 4 days), and the crystalline solid was separated by decantation and recrystallized from boiling *n*-hexane (190 mL, crystallization at 4 °C over a period of 2 days). The product was again isolated by decantation and dried in vacuo (0.01 mbar, 20 °C, 4 h) to give 34.2 g of a colorless crystalline solid. The mother liquors of the crystallization steps were combined, the solvent was removed under reduced pressure, and a further 3.4 g of the product were obtained by crystallization of the oily residue using the same method as

described above. Compound **97** was obtained in a total yield of 62% as a colorless crystalline solid (37.6 g, 211 mmol); mp 44 °C. ^{1}H NMR (CD_2Cl_2): δ 1.81–1.84 (m, 3 H, CC*H*$_3$), 3.57–3.62 (m, 2 H, CC*H*$_2$C), 3.83 (s, 3 H, OC*H*$_3$), 6.33–6.36 (m, 1 H, *H*-4, Fu), 7.08–7.11 (m, 1 H, *H*-3, Fu). ^{13}C NMR (CD_2Cl_2): δ 3.5 (C*C*H$_3$), 19.4 (C*C*H$_2$C), 52.0 (O*C*H$_3$), 72.7 (CH$_3$C≡*C*CH$_2$), 78.4 (CH$_3$*C*≡CCH$_2$), 108.8 (*C*-4, Fu), 119.3 (*C*-3, Fu), 144.0 (*C*-2, Fu), 156.5 (*C*-5, Fu), 159.2 (*C*(O)O). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.3; H, 5.7.

Preparation of methyl 5-[(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)methyl]-2-furoate (98). A solution of cyclopentadienylcobaltdicarbonyl ($CpCo(CO)_2$; 1.53 g, 8.50 mmol) in *m*-xylene (90 mL) was added dropwise within 14 h to a boiling solution of **84** (10.9 g, 56.1 mmol) and **97** (10.0 g, 56.1 mmol) in *m*-xylene (100 mL), followed by addition of **84** (5.47 g, 28.1 mmol) in one single portion at 20 °C and then by dropwise addition of a solution of $CpCo(CO)_2$ (1.03 g, 5.72 mmol) in *m*-xylene (60 mL) at reflux temperature within 12 h. (To avoid heating of the $CpCo(CO)_2$ solution before its addition, the dropping funnel containing this catalyst was separated from the refluxing reaction mixture by a glass tube (length, 20 cm), through which the $CpCo(CO)_2$ solution was allowed to drop freely into the refluxing mixture.) The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (column dimensions, 65 × 4.5 cm; silica gel (15–40 μm, Merck 1.15111), 425 g; eluent, ethyl acetate/*n*-hexane (5:95, v/v)). The relevant fractions (GC control) were combined, the solvent was removed under reduced pressure, and the residue was dried in vacuo (0.01 mbar, 20 °C, 1 h) to give 11.1 g of a yellowish oil, which was redissolved in *n*-hexane (95 mL). The resulting solution was kept at –20 °C over a period of 7 days (formation of a precipitate), and the precipitate was isolated by decantation, washed with cold (–20 °C) *n*-hexane (70 mL), and dried in vacuo (0.001 mbar, 20 °C, 2 h) to give 6.83 g of a colorless crystalline solid. The mother liquor was concentrated under reduced pressure to a volume of 25 mL, and a further 1.28 g of the product were obtained by crystallization, using the same method as described above. Compound **98** was obtained in a total yield of 39% as a colorless crystalline solid (8.11 g, 21.8 mmol); mp 75–76 °C. ^{1}H NMR (C_6D_6): δ 0.359 (s, 6 H, SiC*H*$_3$), 0.361 (s, 6 H, SiC*H*$_3$), 1.13 ("s", 4 H, SiC*H*$_2$C), 2.16 (br "s", 3 H, CC*H*$_3$), 3.55 (s, 3 H, OC*H*$_3$), 3.77 (br "s", 2 H, CC*H*$_2$C), 5.66 (dt, $^3J_{HH}$ = 3.4 Hz, $^4J_{HH}$ = 1.0 Hz, 1 H, *H*-4, Fu), 7.03 (d, $^3J_{HH}$ = 3.4 Hz, 1 H, *H*-3, Fu), 7.42 (s, 1 H, *H*-1, Naph), 7.43 (br "s", 1 H, *H*-4, Naph). ^{13}C NMR (C_6D_6): δ –1.34 (2 C, Si*C*H$_3$), –1.31 (2 C, Si*C*H$_3$), 7.94 (Si*C*H$_2$C), 7.95 (Si*C*H$_2$C), 19.3 (C*C*H$_3$), 32.7 (C*C*H$_2$C), 51.0 (O*C*H$_3$), 108.7 (*C*-4, Fu), 119.0 (*C*-3, Fu), 135.3 (*C*-1, Naph), 135.5 (*C*-2, Naph), 135.9 (*C*-4, Naph), 136.7 (*C*-3, Naph), 143.4 (*C*-4a, Naph), 144.1 (*C*-2, Fu), 144.5 (*C*-8a, Naph), 158.9 (*C*(O)O), 159.2 (*C*-5, Fu). ^{29}Si NMR (C_6D_6): δ –7.32, –7.28. Anal. Calcd for $C_{20}H_{28}O_3Si_2$: C, 64.47; H, 7.57. Found: C, 64.2; H, 7.7.

Preparation of 5-[(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)-methyl]-2-furoic acid (99). A mixture of water (48 mL), methanol (143 mL), potassium hydroxide (6.90 g, 123 mmol), and **98** (4.34 g, 11.6 mmol) was heated under reflux for 20 min (slow dissolution of **98**) and was then stirred at 0 °C for 1 min, followed by addition of dichloromethane (50 mL) and 1 M hydrochloric acid to adjust a pH of 1. The resulting two-phase mixture was stirred at 0 °C for 5 min and then at 20 °C for a further 15 min. The organic phase was separated, the aqueous layer was extracted with dichloromethane (3 × 50 mL), and the organic extracts were combined and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the solid residue was dried in vacuo (0.01 mbar, 20 °C, 1 h) and dissolved in diethyl ether (140 mL). The product was crystallized by vapor diffusion of *n*-pentane into this solution at 20 °C over a period of 14 days and was isolated by decantation, washed with *n*-pentane (20 mL), and dried in vacuo (0.01 mbar, 20 °C, 4 h) to give 3.42 g of a colorless crystalline solid. The solvent of the mother liquor was removed under reduced pressure, the residue was redissolved in diethyl ether (30 mL), and a further 420 mg of the product were obtained by crystallization, using the same method as described above. Compound **99** was obtained in a total yield of 92% as a colorless crystalline solid (3.84 g, 10.7 mmol); mp 171 °C. ^{1}H NMR (C_6D_6): δ 0.36 (s, 6 H, SiC*H*$_3$), 0.37 (s, 6 H, SiC*H*$_3$), 1.13 ("s", 4 H, SiC*H*$_2$C), 2.14 (s, 3 H, CC*H*$_3$), 3.72 (s, 2 H, CC*H*$_2$C), 5.58 (dt, $^{3}J_{HH}$ = 3.5 Hz, $^{4}J_{HH}$ = 0.8 Hz, 1 H, *H*-4, Fu), 7.04 (d, $^{3}J_{HH}$ = 3.5 Hz, 1 H, *H*-3, Fu), 7.40 (s, 1 H, *H*-1, Naph), 7.44 (s, 1 H, *H*-4, Naph), 10.1 (br s, 1 H, CO(O)*H*). ^{13}C NMR (C_6D_6): δ –1.4 (2 C, Si*C*H$_3$), –1.3 (2 C, Si*C*H$_3$), 7.92 (Si*C*H$_2$C), 7.94 (Si*C*H$_2$C), 19.2 (C*C*H$_3$), 32.7 (C*C*H$_2$C), 109.1 (*C*-4, Fu), 121.5 (*C*-3, Fu), 135.2 (*C*-2, Naph), 135.3 (*C*-1, Naph), 135.9 (*C*-4, Naph), 136.7 (*C*-3, Naph), 143.1 (*C*-2, Fu), 143.5 (*C*-4a, Naph), 144.6 (*C*-8a, Naph), 160.6 (*C*-5, Fu), 163.9 (*C*(O)O). ^{29}Si NMR (C_6D_6): δ –7.30, –7.25. Anal. Calcd for $C_{19}H_{26}O_3Si_2$: C, 63.64; H, 7.31. Found: C, 63.8; H, 7.3.

Preparation of 2,4,6-trimethoxybenzamide–methanol (100·MeOH). Compound **100** was prepared according to ref. 98 and isolated, after recrystallization from methanol at 4 °C, as the solvate **100**·MeOH; mp 187–188 °C. ^{1}H NMR ([D$_6$]DMSO): δ 3.16 (d, $^{3}J_{HH}$ = 5.2 Hz, 3 H, HOC*H*$_3$), 3.71 (s, 6 H, *o*-OC*H*$_3$, Tri), 3.77 (s, 3 H, *p*-OC*H*$_3$, Tri), 4.10 (q, $^{3}J_{HH}$ = 5.2 Hz, 3 H, *H*OCH$_3$), 6.20 (s, 2 H, *H*-3/*H*-5, Tri), 7.1 (br s, 1 H, N*H*), 7.3 (br s, 1 H, N*H*). ^{13}C NMR ([D$_6$]DMSO): δ 48.6 (HO*C*H$_3$), 55.4 (*p*-O*C*H$_3$, Tri), 55.6 (*o*-O*C*H$_3$, Tri), 90.8 (*C*-3/*C*-5, Tri), 110.3 (*C*-1, Tri), 157.3 (*C*-2/*C*-6, Tri), 160.9 (*C*-4, Tri), 166.6 (*C*(O)N). Anal. Calcd for $C_{10}H_{13}NO_4$·CH_4O: C, 54.31; H, 7.04; N, 5.76. Found: C, 54.2; H, 6.9; N, 5.8.

Preparation of 2,4,6-trimethoxyaniline (101). 12 M Hydrochloric acid (84.0 mL, 1.01 mol of HCl) was added dropwise at 20 °C within 40 min to potassium permanganate (12.8 g, 81.0 mmol) (temperature increase), and the resulting chlorine gas was passed through a stirred solution

of potassium hydroxide (50.5 g, 900 mmol) in water (300 mL) at 0 °C. After the addition of hydrochloric acid was complete, the residual chlorine gas was passed into the aqueous solution by a nitrogen gas stream for 45 min, followed by addition of **100**·MeOH (48.7 g, 200 mmol) at 0 °C in one single portion. The mixture was stirred at 0 °C for a further 6 h and then at 20 °C for 12 h (change of color from colorless to dark brown), followed by addition of sodium sulfite (12.7 g, 101 mmol) at 20 °C in one single portion. The mixture was stirred at 20 °C for 15 min, the resulting precipitate was separated by suction filtration, and the filter cake was washed successively with water (100 mL) and diethyl ether (200 mL). The filtrate and the wash solutions were combined, the two-phase mixture was shaken thoroughly, the organic layer was separated, and the aqueous phase was extracted with diethyl ether (2 × 200 mL). The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the dark-brown residue was purified by bulb-to-bulb distillation (Kugelrohr apparatus, 110–140 °C/0.1 mbar) to give **101** in 38% yield as a colorless liquid (13.9 g, 75.9 mmol), which crystallized at 4 °C; mp 29–31 °C. ^{1}H NMR (C_6D_6): δ 3.47 (s, 6 H, *o*-OC*H*$_3$, Tri), 3.58 (s, 3 H, *p*-OC*H*$_3$, Tri), 3.6 (br s, 2 H, N*H*$_2$), 6.32 (s, 2 H, *H*-3/*H*-5, Tri). ^{13}C NMR (C_6D_6): δ 55.3 (*o*-O*C*H$_3$, Tri), 55.4 (*p*-O*C*H$_3$, Tri), 92.1 (*C*-3/*C*-5, Tri), 120.3 (*C*-1, Tri), 148.1 (*C*-2/*C*-6, Tri), 152.7 (*C*-4, Tri). Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 58.9; H, 7.1; N, 7.5.

Preparation of 2,4,6-trimethoxyanilinium chloride (101·HCl). A 2 M ethereal hydrogen chloride solution (15.5 mL, 31.0 mmol of HCl) was added dropwise at 20 °C to a stirred solution of **101** (5.34 g, 29.1 mmol) in dichloromethane (110 mL). The mixture was shaken briefly and then kept undisturbed at 20 °C for 1 h (formation of a precipitate) and at 4 °C for a further 16 h. The product was isolated by suction filtration, washed with diethyl ether (20 mL), and dried in vacuo (0.01 mbar, 20 °C, 4 h) to give **101**·HCl in 98% yield as a colorless crystalline solid (6.28 g, 28.6 mmol); mp 241–242 °C (dec). ^{1}H NMR ([D$_6$]DMSO): δ 3.79 (s, 3 H, *p*-OC*H*$_3$, Tri), 3.85 (s, 6 H, *o*-OC*H*$_3$, Tri), 6.38 (s, 2 H, *H*-3/*H*-5, Tri), 9.6 (br s, 3 H, N*H*$_3$). ^{13}C NMR ([D$_6$]DMSO): δ 55.7 (*p*-O*C*H$_3$, Tri), 56.4 (*o*-O*C*H$_3$, Tri), 91.5 (*C*-3/*C*-5, Tri), 101.4 (*C*-1, Tri), 153.7 (*C*-2/*C*-6, Tri), 160.3 (*C*-4, Tri). Anal. Calcd for $C_9H_{14}ClNO_3$: C, 49.21; H, 6.42; N, 6.38. Found: C, 49.2; H, 6.3; N, 6.3.

Preparation of trichloro(2,4,6-trimethoxyphenyl)silane (102). A suspension of 1,3,5-trimethoxybenzene (100 g, 595 mmol) in a mixture of *n*-hexane (350 mL) and TMEDA (71.4 g, 614 mmol) was heated to ca. 50 °C to dissolve the 1,3,5-trimethoxybenzene. After the heat source was removed, a 2.5 M solution of *n*-butyllithium in *n*-hexane (244 mL, 610 mmol of *n*-BuLi) was added dropwise within 20 min to the vigorously stirred mixture. During the addition, the heat of reaction caused the mixture to boil under reflux, and a white precipitate was formed. After the addition was complete, the mixture was stirred vigorously (to prevent agglomeration) at 20 °C for 3 days

(formation of (2,4,6-trimethoxyphenyl)lithium), and the resulting suspension was then added *via* a dropping funnel at 0 °C within 30 min to a vigorously stirred solution of tetrachlorosilane (101 g, 594 mmol) in *n*-hexane (200 mL). The mixture was stirred at 0 °C for a further 15 min and then at 20 °C for 16 h. Diethyl ether (700 mL) was added, the resulting mixture was stirred at 20 °C for a further 1 h, the precipitate was separated by filtration and washed with diethyl ether (3 × 100 mL), and the filtrate and the wash solutions were combined. The solvent was removed under reduced pressure, the residue was dissolved in boiling *n*-heptane (1 L), and the resulting solution was filtered hot. The filtrate was cooled to 20 °C within 3 h and then kept undisturbed at this temperature for 16 h, and the resulting precipitate was isolated by filtration and recrystallized from boiling *n*-heptane (700 mL; including hot filtration, cooling to 20 °C within 3 h, and undisturbed storage at 20 °C for 16 h). The product was isolated by filtration and dried in vacuo (0.001 mbar, 20 °C, 5 h) to give **102** in 65% yield as a colorless crystalline solid (116 g, 385 mmol); mp 102 °C. ^{1}H NMR (C_6D_6): δ 3.30 (s, 6 H, *o*-OC*H*$_3$), 3.33 (s, 3 H, *p*-OC*H*$_3$), 5.89 (s, 2 H, *H*-3/*H*-5, Tri). ^{13}C NMR (C_6D_6): δ 54.8 (*p*-O*C*H$_3$), 55.1 (*o*-O*C*H$_3$), 91.0 (*C*-3/*C*-5, Tri), 98.9 (*C*-1, Tri), 166.7 (*C*-4, Tri), 166.8 (*C*-2/*C*-6, Tri). ^{29}Si NMR (C_6D_6): δ –6.7. Anal. Calcd for $C_9H_{11}Cl_3O_3Si$: C, 35.84; H, 3.68. Found: C, 36.0; H, 3.7.

Preparation of tris(chloromethyl)(2,4,6-trimethoxyphenyl)silane (103). A 2.5 M solution of *n*-butyllithium in *n*-hexane (110 mL, 275 mmol of *n*-BuLi) was added dropwise at –70 °C (± 3 °C, temperature measurement within the flask) within 4 h to a stirred mixture of **102** (27.2 g, 90.2 mmol), bromochloromethane (52.8 g, 408 mmol), and THF (150 mL) (the *n*-butyllithium solution was added *via* a special horizontally elongated side neck of the three-necked flask, which itself was immersed in the cooling bath to ensure pre-cooling of the *n*-butyllithium solution before making contact with the reaction mixture). After the addition was complete, the mixture was stirred at –70 °C for 6 h and then warmed to –25 °C within 11 h. The cold (–25 °C) mixture was poured into a cold (0 °C) stirred two-phase mixture of half-saturated aqueous sodium hydrogen carbonate solution (200 mL, solution A) and ethyl acetate (100 mL). The resulting mixture was stirred at 0 °C for 5 min, and the organic phase was separated and washed with water (200 mL, solution B). The first aqueous wash solution (A) was extracted with ethyl acetate (100 mL), the resulting organic extract was used to extract the second aqueous wash solution (B), and the organic extract was separated, followed by a second and third extraction of the wash solutions A and B with fresh portions of ethyl acetate (2 × 100 mL) using the same protocol as described for the first extraction sequence. All organic extracts were combined and dried briefly over anhydrous sodium sulfate, followed by an additional thorough dynamic drying over anhydrous sodium sulfate using a standard chromatographic column densely packed with anhydrous sodium sulfate (column dimensions, 20

cm × 3.5 cm). The sodium sulfate was finally washed with ethyl acetate (3 × 300 mL), all organic solutions were combined, the solvent was removed under reduced pressure, and the oily residue (30 g) was purified by column chromatography on silica gel (column dimensions, 61 cm × 5.5 cm; silica gel (32–63 μm, ICN 02826), 640 g; eluent, *n*-hexane/diethyl ether/1,8-diazabicyclo[5.4.0]undec-7-ene (59:40:1 (v/v/v))). The relevant fractions (GC control) were combined, and the solvent was removed under reduced pressure to give 16 g of a colorless oily product, which was crystallized and then recrystallized twice from boiling *n*-hexane. 200 mL were used for each crystallization step, and the crystallizations were carried out at 4 °C over a period of 1 day. The precipitate was isolated by filtration and washed with cold (0 °C) *n*-pentane (40 mL) after each crystallization step, and the product was finally dried in vacuo (0.001 mbar, 20 °C, 2 h) to give **103** in 39% yield (including workup of the combined mother liquors) as a colorless crystalline solid (12.1 g, 35.2 mmol); mp 88 °C. ^{1}H NMR (C_6D_6): δ 3.18 (s, 6 H, *o*-OC*H*$_3$), 3.40 (s, 3 H, *p*-OC*H*$_3$), 3.50 (s, 6 H, SiC*H*$_2$Cl), 5.97 (s, 2 H, *H*-3/*H*-5, Tri). ^{13}C NMR (C_6D_6): δ 26.8 (Si*C*H$_2$Cl), 54.72 (*p*-O*C*H$_3$), 54.75 (*o*-O*C*H$_3$), 90.9 (*C*-3/*C*-5, Tri), 95.9 (*C*-1, Tri), 165.4 (*C*-4, Tri), 167.3 (*C*-2/*C*-6, Tri). ^{29}Si NMR (C_6D_6): δ –7.0. Anal. Calcd for $C_{12}H_{17}Cl_3O_3Si$: C, 41.93; H, 4.99; Cl, 30.94. Found: C, 41.9; H, 5.1; Cl, 31.1.

Preparation of dichlorobis(2,4,6-trimethoxyphenyl)silane (104). A suspension of 1,3,5-trimethoxybenzene (100 g, 595 mmol) in a mixture of *n*-hexane (350 mL) and TMEDA (71.4 g, 614 mmol) was heated to ca. 50 °C to dissolve the 1,3,5-trimethoxybenzene. After the heat source was removed, a 2.5 M solution of *n*-butyllithium in *n*-hexane (244 mL, 610 mmol of *n*-BuLi) was added dropwise within 20 min to the vigorously stirred mixture. During the addition, the heat of reaction caused the mixture to boil under reflux, and a white precipitate was formed. After the addition was complete, the mixture was stirred vigorously (to prevent agglomeration) at 20 °C for 3 days (formation of (2,4,6-trimethoxyphenyl)lithium), and the resulting suspension was then added *via* a dropping funnel at 0 °C within 30 min to a vigorously stirred solution of tetrachlorosilane (50.4 g, 297 mmol) in *n*-hexane (200 mL). The mixture was stirred at 0 °C for a further 1 h (exclusive formation of **102** at this temperature, GC control) and then at 20 °C for 2 h. Significant warming (no reflux; ca. 50–60 °C) was observed at this point (selective formation of **104** and nearly complete conversion **102** $\rightarrow$ **104**, GC control), followed by cooling to 20 °C within 1 h and stirring at this temperature for a further 16 h. The solid product was collected by filtration (the filtrate contained tiny amounts of residual **102**, but virtually no **104**; GC control), the filter cake was dissolved in boiling dichloromethane (1 L) and filtered hot, the resulting filter cake (mainly consisting of lithium salts) was washed with dichloromethane (60 mL), the filtrate and the wash solution were combined, and the solvent was partially removed by distillation at atmospheric pressure until a residual volume

of ca. 600 mL was obtained. The residue was then kept undisturbed at –25 °C for seven days. The resulting precipitate was isolated by filtration and recrystallized from boiling dichloromethane (500 mL; including hot filtration and undisturbed storage at –25 °C for seven days), and the product was isolated by filtration at –25 °C, washed with cold (–25 °C) dichloromethane (100 mL), and dried in vacuo (0.001 mbar, 20 °C, 5 h) to give **104** in 67% yield (including workup of the mother liquor) as a colorless crystalline solid (85.6 g, 198 mmol); mp 156–157 °C. ^{1}H NMR (CD_2Cl_2): δ 3.66 (s, 12 H, *o*-OC*H*$_3$), 3.81 (s, 6 H, *p*-OC*H*$_3$), 6.09 (s, 4 H, *H*-3/*H*-5, Tri). ^{13}C NMR (CD_2Cl_2): δ 55.6 (*p*-O*C*H$_3$), 56.0 (*o*-O*C*H$_3$), 91.4 (*C*-3/*C*-5, Tri), 104.3 (*C*-1, Tri), 164.9 (*C*-4, Tri), 166.1 (*C*-2/*C*-6, Tri). ^{29}Si NMR (CD_2Cl_2): δ –5.9. Anal. Calcd for $C_{18}H_{22}Cl_2O_6Si$: C, 49.89; H, 5.12; Cl, 16.36. Found: C, 49.5; H, 5.2; Cl, 16.6.

Treatment of 104 with (chloromethyl)lithium (attempted preparation of bis(chloromethyl)bis(2,4,6-trimethoxyphenyl)silane (105)). A suspension of **104** (26.8 g, 61.8 mmol) in a mixture of THF (150 mL) and bromochloromethane (23.9 g, 185 mmol) was heated under reflux for 5 min to dissolve **104**. The vigorously stirred mixture was cooled slowly to –78 °C (precipitation of **104** was observed at a temperature of ca. 20 °C and below). A 2.5 M solution of *n*-butyllithium in *n*-hexane (52.0 mL, 130 mmol of *n*-BuLi) was added dropwise at –70 °C (± 3 °C, temperature measurement within the flask) within 3 h to the stirred mixture (the *n*-butyllithium solution was added *via* a special horizontally elongated side neck of the three-necked flask, which itself was immersed in the cooling bath to ensure pre-cooling of the *n*-butyllithium solution before making contact with the reaction mixture). After the addition was complete, the mixture was stirred at –70 °C for 6 h and then warmed to 0 °C within 15 h. Reaction control (GC) revealed that the starting material **104** had remained untouched (no further workup).[99]

Preparation of (4-bromobutyl)chlorodimethylsilane (106). This compound was prepared analogous to the preparation of (6-bromohexyl)chlorodimethylsilane (**108**) (see below) from 4-bromobut-1-ene (25.0 g, 185 mmol) and chlorodimethylsilane (29 g, 307 mmol)[100] in 70% yield (29.9 g, 130 mmol) (related to 4-bromobut-1-ene); bp 88 °C/9 mbar. ^{1}H NMR ($CDCl_3$): δ 0.40 (s, 6 H, SiC*H*$_3$), 0.76–0.86 (m, 2 H, SiC*H*$_2$(CH$_2$)$_3$Br), 1.49–1.62 (m, 2 H, SiCH$_2$C*H*$_2$(CH$_2$)$_2$Br), 1.84–1.95 (m, 2 H, Si(CH$_2$)$_2$C*H*$_2$CH$_2$Br), 3.40 (t, $^{3}J_{HH}$ = 6.7 Hz, 2 H, Si(CH$_2$)$_3$C*H*$_2$Br). ^{13}C NMR ($CDCl_3$): δ 1.6 (Si*C*H$_3$), 18.0 (Si*C*H$_2$(CH$_2$)$_3$Br), 21.6 (SiCH$_2$*C*H$_2$(CH$_2$)$_2$Br), 33.2 (Si(CH$_2$)$_3$*C*H$_2$Br), 35.5 (Si(CH$_2$)$_2$*C*H$_2$CH$_2$Br). ^{29}Si NMR ($CDCl_3$): δ 31.9. Anal. Calcd for $C_6H_{14}BrClSi$: C, 31.38; H, 6.15. Found: C, 31.3; H, 6.2.

Preparation of (5-bromopentyl)chlorodimethylsilane (107). This compound was prepared analogous to the preparation of (6-bromohexyl)chlorodimethylsilane (**108**) (see below) from 5-bromopent-1-ene (25.1 g, 168 mmol) and chlorodimethylsilane (27.8 g, 294 mmol)[100] in 77% yield

(related to 5-bromopent-1-ene) as a colorless liquid (31.5 g, 129 mmol); bp 92–93 °C/2 mbar. ^{1}H NMR ($CDCl_3$): δ 0.38 (s, 6 H, SiCH_3), 0.75–0.86 (m, 2 H, SiCH_2(CH$_2$)$_4$Br), 1.34–1.53 (m, 4 H, SiCH$_2$(CH_2)$_2$(CH$_2$)$_2$Br), 1.78–1.90 (m, 2 H, Si(CH$_2$)$_3$CH_2CH$_2$Br), 3.37 (t, $^3J_{HH}$ = 6.8 Hz, 2 H, Si(CH$_2$)$_4$CH_2Br). ^{13}C NMR ($CDCl_3$): δ 1.6 (Si*C*H$_3$), 18.7 (Si*C*H$_2$(CH$_2$)$_4$Br), 22.2 (SiCH$_2$*C*H$_2$(CH$_2$)$_3$Br), 31.3 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$Br), 32.3 (Si(CH$_2$)$_3$*C*H$_2$CH$_2$Br), 33.7 (Si(CH$_2$)$_4$*C*H$_2$Br). ^{29}Si NMR ($CDCl_3$): δ 32.0. Anal. Calcd for $C_7H_{16}BrClSi$: C, 34.51; H, 6.62 Found: C, 34.1; H, 6.4.

Preparation of (6-bromohexyl)chlorodimethylsilane (108). $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) was added at 20 °C to a solution of chlorodimethylsilane (19.1 g, 202 mmol) and 6-bromohex-1-ene (27.4 g, 168 mmol) in toluene (200 mL), and the mixture was heated immediately in a pre-heated oil bath (140 °C). After the reaction had started, the oil bath was removed. As soon as the reaction started to become less vigorous, the mixture was heated under reflux (no drop in temperature below reflux temperature at any time), and further portions of $H_2PtCl_6{\cdot}6H_2O$ and chlorodimethylsilane were added sequentially: first portion (after 30 min), addition of $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol; dissolved in propan-2-ol (50 μL)), followed by addition of chlorodimethylsilane (5.00 g, 52.8 mmol); second to fifth portion (after 40, 50, 60, and 70 min), $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol; dissolved in propan-2-ol (50 μL)) and chlorodimethylsilane (1.00 g, 10.6 mmol). After addition of the last portion, the mixture was heated under reflux for a further 50 min. The solvent was removed by distillation under normal pressure, and the residue was distilled in vacuo (Vigreux column, 30 cm) to give **108** in 83% yield (related to 6-bromohex-1-ene) as a colorless liquid (35.8 g, 139 mmol); bp 100–101 °C/3 mbar. ^{1}H NMR ($CDCl_3$): δ 0.38 (s, 6 H, SiCH_3), 0.74–0.84 (m, 2 H, SiCH_2(CH$_2$)$_5$Br), 1.28–1.49 (m, 6 H, SiCH$_2$(CH_2)$_3$(CH$_2$)$_2$Br), 1.77–1.89 (m, 2 H, Si(CH$_2$)$_4$CH_2CH$_2$Br), 3.38 (t, $^3J_{HH}$ = 6.8 Hz, 2 H, Si(CH$_2$)$_5$CH_2Br). ^{13}C NMR ($CDCl_3$): δ 1.6 (Si*C*H$_3$), 18.8 (Si*C*H$_2$(CH$_2$)$_5$Br), 22.8 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$Br), 27.7 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Br), 32.0 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Br), 32.6 (Si(CH$_2$)$_4$*C*H$_2$CH$_2$Br), 33.9 (Si(CH$_2$)$_5$*C*H$_2$Br). ^{29}Si NMR ($CDCl_3$): δ 32.1. Anal. Calcd for $C_8H_{18}BrClSi$: C, 37.29; H, 7.04. Found: C, 37.5; H, 7.1.

Preparation of (4-bromobutyl)dimethylsilane (109) (danger of explosion!) [101] This compound was prepared analogous to the preparation of (6-bromohexyl)dimethylsilane (**111**) (see below) from **106** (28.9 g, 126 mmol) and LAH (2.50 g, 65.9 mmol) in 84% yield as a colorless liquid (20.7 g, 106 mmol); bp 71 °C/17 mbar. IR (film): $\tilde{\nu}$ 2113 cm^{-1} (SiH). ^{1}H NMR ($CDCl_3$): δ 0.06 (d, $^3J_{HH}$ = 3.7 Hz, 6 H, SiCH_3), 0.53–0.63 (m, 2 H, SiCH_2(CH$_2$)$_3$Br), 1.41–1.54 (m, 2 H, SiCH$_2$CH_2(CH$_2$)$_2$Br), 1.87 (”quint“, $^3J_{HH}$ = 6.9 Hz, 2 H, Si(CH$_2$)$_2$CH_2CH$_2$Br), 3.40 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, Si(CH$_2$)$_3$CH_2Br), 3.83 (”nonett“, $^3J_{HH}$ = 3.7 Hz, 1 H, Si*H*). ^{13}C NMR ($CDCl_3$): δ –4.5

(Si*C*H$_3$), 13.2 (Si*C*H$_2$(CH$_2$)$_3$Br), 23.0 (SiCH$_2$*C*H$_2$(CH$_2$)$_2$Br), 33.6 (Si(CH$_2$)$_3$*C*H$_2$Br), 35.9 (Si(CH$_2$)$_2$*C*H$_2$CH$_2$Br). ^{29}Si NMR (CDCl$_3$): δ –12.8. Anal. Calcd for $C_6H_{15}BrSi$: C, 36.92; H, 7.75. Found: C, 36.6; H, 7.7.

Preparation of (5-bromopentyl)dimethylsilane (110). This compound was prepared analogous to the preparation of (6-bromohexyl)dimethylsilane (**111**) (see below) from **107** (30.3 g, 124 mmol) and LAH (2.72 g, 71.7 mmol) in 87% yield as a colorless liquid (22.6 g, 108 mmol); bp 74–75 °C/6 mbar. IR (film): $\tilde{\nu}$ 2110 cm^{-1} (SiH). ^{1}H NMR (CDCl$_3$): δ 0.04 (d, $^3J_{HH}$ = 3.6 Hz, 6 H, SiC*H*$_3$), 0.52–0.61 (m, 2 H, SiC*H*$_2$(CH$_2$)$_4$Br), 1.28–1.51 (m, 4 H, SiCH$_2$(C*H*$_2$)$_2$(CH$_2$)$_2$Br), 1.84 (”quint“, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_3$C*H*$_2$CH$_2$Br), 3.38 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_4$C*H*$_2$Br), 3.82 (”nonett“, $^3J_{HH}$ = 3.6 Hz, 1 H, Si*H*). ^{13}C NMR (CDCl$_3$): δ –4.5 (Si*C*H$_3$), 14.0 (Si*C*H$_2$(CH$_2$)$_4$Br), 23.6 (SiCH$_2$*C*H$_2$(CH$_2$)$_3$Br), 31.6 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$Br), 32.5 (Si(CH$_2$)$_3$*C*H$_2$CH$_2$Br), 33.8 (Si(CH$_2$)$_4$*C*H$_2$Br). ^{29}Si NMR (CDCl$_3$): δ –12.9. Anal. Calcd for $C_7H_{17}BrSi$: C, 40.19; H, 8.19. Found: C, 40.1; H, 7.9.

Preparation of (6-bromohexyl)dimethylsilane (111). Compound **108** (34.9 g, 135 mmol) was added at 20 °C within a period of 5 min to a stirred suspension of LAH (3.74 g, 98.5 mmol) in diethyl ether (250 mL), causing the mixture to boil under reflux during the addition. The resulting mixture was heated under reflux for 30 min, cooled to 20 °C, and then added dropwise to a stirred mixture of concentrated hydrochloric acid (100 mL), diethyl ether (200 mL), and ice (200 g) (to avoid ignition, this step was also performed under a nitrogen atmosphere). The organic layer was separated, the aqueous phase was extracted with diethyl ether (3 × 100 mL), and the combined organic extracts were dried over anhydrous magnesium sulfate in an ice bath, followed by additional thorough dynamic drying over anhydrous magnesium sulfate using a standard chromatographic column densely packed with anhydrous magnesium sulfate (column dimensions, 15 × 3.5 cm). The magnesium sulfate was finally washed with diethyl ether (300 mL), the organic solutions were combined, the solvent was removed under reduced pressure, and the residue was distilled in vacuo (Vigreux column, 30 cm) to give **111** in 91% yield as a colorless liquid (27.6 g, 124 mmol); bp 80 °C/3 mbar. IR (film): $\tilde{\nu}$ 2110 cm^{-1} (SiH). ^{1}H NMR (CDCl$_3$): δ 0.04 (d, $^3J_{HH}$ = 3.7 Hz, 6 H, SiC*H*$_3$), 0.50–0.62 (m, 2 H, SiC*H*$_2$(CH$_2$)$_5$Br), 1.25–1.48 (m, 6 H, SiCH$_2$(C*H*$_2$)$_3$(CH$_2$)$_2$Br), 1.83 (”quint“, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_4$C*H*$_2$CH$_2$Br), 3.38 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_5$C*H*$_2$Br), 3.82 (”nonett“, $^3J_{HH}$ = 3.7 Hz, 1 H, Si*H*). ^{13}C NMR (CDCl$_3$): δ –4.5 (Si*C*H$_3$), 14.0 (Si*C*H$_2$(CH$_2$)$_5$Br), 24.2 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$Br), 27.9 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Br), 32.2 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Br), 32.7 (Si(CH$_2$)$_4$*C*H$_2$CH$_2$Br), 34.0 (Si(CH$_2$)$_5$*C*H$_2$Br). ^{29}Si NMR (CDCl$_3$): δ –12.9. Anal. Calcd for $C_8H_{19}BrSi$: C, 43.04; H, 8.58. Found: C, 43.0; H, 8.5.

Preparation of *N*-allyl-1,8-naphthalimide (112). Allylamine (14.4 g, 252 mmol) was added at 20 °C in one single portion to a suspension of 1,8-naphthalic acid anhydride (50.0 g, 252 mmol) in toluene (250 mL), and the mixture was then stirred at 20 °C for 16 h and heated under reflux for a further 14 h (removal of the resulting water using a water separator). The solvent was removed under reduced pressure, and the solid residue was purified by twofold crystallization from boiling methanol (700 mL for each crystallization; crystallization over a period of 1 day at 20 °C, then 1 day at –26 °C). The product was isolated by filtration and dried in vacuo (0.0001 mbar, 20 °C, 8 h) to give **112** in 74% yield as a yellowish crystalline solid (44.2 g, 186 mmol); mp 135 °C. ^{1}H NMR ($CDCl_3$): δ 4.74 (δ_M), 5.17 (δ_A), 5.29 (δ_B), and 5.96 (δ_G) ($^{2}J_{AB}$ = 1.3 Hz, $^{3}J_{AG,cis}$ = 10.2 Hz, $^{4}J_{AM}$ = 1.3 Hz, $^{3}J_{BG,trans}$ = 17.2 Hz, $^{4}J_{BM}$ = 1.5 Hz, $^{3}J_{GM}$ = 5.9 Hz, 5 H, $NC(H_M)_2CH_G{=}CH_AH_B$), 7.66 (dd, $^{3}J_{HH}$ = 7.4 Hz, $^{3}J_{HH}$ = 8.1 Hz, 2 H, *H*-3/*H*-6, Naphth), 8.11 (dd, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 1.1 Hz, 2 H, *H*-4/*H*-5, Naphth), 8.49 (dd, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ = 1.1 Hz, 2 H, *H*-2/*H*-7, Naphth). ^{13}C NMR ($CDCl_3$): δ 42.3 (NCH_2C), 117.5 ($NCH_2CH{=}CH_2$), 122.3 (*C*-1/*C*-8, Naphth), 126.8 (*C*-3/*C*-6, Naphth), 127.9 (*C*-8a, Naphth), 131.1 (*C*-2/*C*-7, Naphth), 131.4 (*C*-4a, Naphth), 132.1 ($NCH_2CH{=}CH_2$), 133.8 (*C*-4/*C*-5, Naphth), 163.7 (*C*=O). Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.8; H, 4.8; N, 5.9.

Preparation of *N*-allylphthalimide (113). Allylamine (10.4 g, 182 mmol) was added at 20 °C in one single portion to a suspension of phthalic acid anhydride (27.0 g, 182 mmol) in toluene (200 mL), and the mixture was then stirred at 20 °C for 16 h and heated under reflux for a further 3 h (removal of the resulting water using a water separator). The solvent was removed under reduced pressure, and the solid residue was recrystallized from boiling methanol (250 mL); crystallization at –25 °C over a period of 1 day. The product was isolated by filtration and dried in vacuo (0.001 mbar, 20 °C, 8 h) to give **113** in 86% yield as a colorless crystalline solid (29.5 g, 158 mmol); mp 69 °C. ^{1}H NMR ($CDCl_3$): δ 4.27 (δ_M), 5.17 (δ_A), 5.23 (δ_B), and 5.87 (δ_G) ($^{2}J_{AB}$ = 1.5 Hz, $^{3}J_{AG,cis}$ = 10.2 Hz, $^{4}J_{AM}$ = 1.5 Hz, $^{3}J_{BG,trans}$ = 17.2 Hz, $^{4}J_{BM}$ = 1.5 Hz, $^{3}J_{GM}$ = 5.7 Hz, 5 H, $NC(H_M)_2CH_G{=}CH_AH_B$), 7.66–7.73 (m, 2 H, *H*-4/*H*-5, Phth), 7.79–7.87 (m, 2 H, *H*-3/*H*-6, Phth). ^{13}C NMR ($CDCl_3$): δ 40.0 (NCH_2C), 117.7 ($NCH_2CH{=}CH_2$), 123.3 (*C*-3/*C*-6, Phth), 131.5 ($NCH_2CH{=}CH_2$), 132.1 (*C*-1/*C*-2, Phth), 134.0 (*C*-4/*C*-5, Phth), 167.9 (*C*=O). Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.2; H, 5.1; N, 7.4.

Preparation of *N*-allyl-4-methylphthalimide (114). Preparation analogous to the synthesis of **113** from 4-methylphthalic acid anhydride (19.5 g, 120 mmol) and allylamine (6.85 g, 120 mmol) in toluene (100 mL). The solvent was removed under reduced pressure, and the solid residue was purified by bulb-to-bulb distillation in vacuo (110–125 °C/0.001 mbar). Upon cooling to 20 °C, the distillate solidified to give **114** in 91% yield as a colorless crystalline solid (22.1 g, 110 mmol);

mp 67–68 °C. ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 3 H, CH_3), 4.22 (δ_M), 5.13 (δ_A), 5.18 (δ_B), and 5.83 (δ_G) ($^2J_{AB}$ = 1.5 Hz, $^3J_{AG,cis}$ = 10.2 Hz, $^4J_{AM}$ = 1.5 Hz, $^3J_{BG,trans}$ = 17.2 Hz, $^4J_{BM}$ = 1.5 Hz, $^3J_{GM}$ = 5.6 Hz, 5 H, N(C(H_M)$_2$)CH_G=C$H_A H_B$), 7.43–7.48 (m, 1 H, *H*-5, Me-phth), 7.58–7.61 (m, 1 H, *H*-3, Me-phth), 7.67 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, *H*-6, Me-phth). ^{13}C NMR ($CDCl_3$): δ 21.9 (*C*H$_3$), 39.9 (N*C*H$_2$C), 117.5 (NCH$_2$CH=*C*H$_2$), 123.1 (*C*-6, Me-phth), 123.7 (*C*-3, Me-phth), 129.4 (*C*-1, Me-phth), 131.6 (NCH$_2$*C*H=CH$_2$), 132.4 (*C*-2, Me-phth), 134.4 (*C*-5, Me-phth), 145.2 (*C*-4, Me-phth), 167.9 (*C*=O), 168.0 (*C*=O). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.3; H, 5.6; N, 6.9.

Preparation of *N*-allylsuccinimide (115). Preparation analogous to the synthesis of **113** from succinic acid anhydride (15.0 g, 150 mmol) and allylamine (8.56 g, 150 mmol) in toluene (100 mL). The solvent was removed under reduced pressure, and the residue was distilled in vacuo (Vigreux column, 8 cm) to give **115** in 85% yield as a colorless liquid (17.8 g, 128 mmol); bp 73 °C/0.08 mbar. ^{1}H NMR ($CDCl_3$): δ 2.68 (s, 4 H, C(O)CH_2), 4.06 (δ_M), 5.13 (δ_A), 5.17 (δ_B), and 5.74 (δ_G) ($^2J_{AB}$ = 1.2 Hz, $^3J_{AG,cis}$ = 10.2 Hz, $^4J_{AM}$ = 1.2 Hz, $^3J_{BG,trans}$ = 17.1 Hz, $^4J_{BM}$ = 1.4 Hz, $^3J_{GM}$ = 5.9 Hz, 5 H, N(C(H_M)$_2$)CH_G=C$H_A H_B$). ^{13}C NMR ($CDCl_3$): δ 28.1 (C(O)*C*H$_2$), 40.8 (N*C*H$_2$C), 118.3 (NCH$_2$CH=*C*H$_2$), 130.6 (NCH$_2$*C*H=CH$_2$), 176.7 (*C*=O). Anal. Calcd for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.5; H, 6.5; N, 10.2.

Preparation of *N*-(2-methylallyl)phthalimide (116). A mixture of *N*,*N*-dimethylformamide (200 mL), potassium phthalimide (46.3 g, 250 mmol), and 2-methylallyl chloride (22.6 g, 250 mmol) was heated under reflux for 16 h. The mixture was cooled to 20 °C, followed by addition of ice (ca. 100 g) and water (500 mL), and the resulting mixture was extracted with toluene (4 × 100 mL). The organic extracts were combined and dried over anhydrous magnesium sulfate, the solvent was removed under reduced pressure, and the solid residue was recrystallized from methanol (400 mL) at –25 °C over a period of 1 day. The product was isolated by filtration and dried in vacuo (0.001 mbar, 20 °C, 8 h) to give **116** in 80% yield as a colorless crystalline solid (40.0 g, 199 mmol); mp 88–89 °C. ^{1}H NMR ($CDCl_3$): δ 1.74–1.77 (m, 3 H, CCH_3), 4.18–4.21 (m, 2 H, NCH_2C), 4.77–4.81 (m, 1 H, C=CH_AH$_B$), 4.85–4.88 (m, 1 H, C=CH$_A H_B$), 7.66–7.74 (m, 2 H, *H*-4/*H*-5, Phth), 7.80–7.88 (m, 2 H, *H*-3/*H*-6, Phth). ^{13}C NMR ($CDCl_3$): δ 20.4 (C*C*H$_3$), 43.2 (N*C*H$_2$C), 111.9 (NCH$_2$CH=*C*H$_2$), 123.3 (*C*-3/*C*-6, Phth), 132.0 (*C*-1/*C*-2, Phth), 134.0 (*C*-4/*C*-5, Phth), 139.3 (NCH$_2$*C*(CH$_3$)=CH$_2$), 168.0 (*C*=O). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.5; H, 5.6; N, 7.0.

Preparation of the (ω-bromoalkyl)(3-imidopropyl)dimethylsilanes 117–126 and *rac*-127. Protocol A. $H_2PtCl_6 \cdot 6H_2O$ (catalytic, as solid or dissolved in propan-2-ol) was added at 20 °C to a solution of the (ω-bromoalkyl)dimethylsilane and the *N*-allylimide in toluene, and the mixture was

heated immediately in a pre-heated oil bath (140 °C) for 30 min, followed by addition of another portion of $H_2PtCl_6{\cdot}6H_2O$ (catalytic, dissolved in propan-2-ol)[102] and heating under reflux for a further 1 h (complete disappearance of the Si–H IR absorption band at 2110–2113 cm^{-1}; measured as a film of the reaction mixture). The reaction mixture was filtered over silica gel using a standard chromatographic column (column diameter, 3.5 cm; silica gel (63–200 μm; Fluka 60741), 30 g). The silica gel was then washed with ethyl acetate (500 mL), and the organic solutions were combined. The solvent was removed under reduced pressure, and the product was finally purified by column chromatography on silica gel using diethyl ether/*n*-hexane (the appropriate mixture was chosen according to TLC analysis in order to achieve an R_f value of ca. 0.5) as the eluent. The relevant fractions (TLC, GC) were combined, and the solvent was removed under reduced pressure. After bulb-to-bulb-distillation in vacuo, the desired (ω-bromoalkyl)(3-imidopropyl)dimethylsilane was obtained as an NMR-spectroscopically pure colorless viscous liquid. **Protocol B.** The success of this method is based on the complete conversion of the *N*-allylimide, which frequently was found to be difficult to separate from the product by bulb-to-bulb distillation without preceeding separation by column chromatography. Use of an excess of the (ω-bromoalkyl)dimethylsilane (usually approx. 1.02–1.05 molar equivalents related to the *N*-allylimide) ensured complete conversion of the *N*-allylimide when this method was used similar to the protocol described in Protocol A, followed by the same workup as described; i.e., the reaction mixture was filtered over silica gel using a standard chromatographic column (column diameter, 3.5 cm; silica gel (63–200 μm; Fluka 60741), 30 g). The silica gel was then washed with ethyl acetate (500 mL), and the organic solutions were combined. The solvent was removed under reduced pressure, and the product was finally purified by bulb-to-bulb distillation in vacuo (no column chromatography) to give the desired (ω-bromoalkyl)(3-imidopropyl)dimethylsilane as an NMR-spectroscopically pure colorless or yellowish viscous liquid.

Preparation of (4-bromobutyl)dimethyl[3-(1,8-naphthalimido)propyl]silane (117). Compound **117** was prepared according to Protocol B (**109** (3.98 g, 20.4 mmol); **112** (4.75 g, 20.0 mmol); toluene (50 mL); $H_2PtCl_6{\cdot}6H_2O$ (20 mg, 38.6 μmol) (first portion, solid); $H_2PtCl_6{\cdot}6H_2O$ (10 mg, 19.3 μmol) (second portion, dissolved in propan-2-ol (50 μL); added after 30 min)). After bulb-to-bulb-distillation (210–240 °C/0.001 mbar), compound **117** was obtained in 84% yield (related to **109**) as a yellowish viscous liquid (7.41 g, 17.1 mmol). ^{1}H NMR ($CDCl_3$): δ –0.05 (s, 6 H, SiCH_3), 0.42–0.52 (m, 2 H, SiCH_2(CH$_2$)$_3$Br), 0.54–0.65 (m, 2 H, N(CH$_2$)$_2$CH_2Si), 1.32–1.46 (m, 2 H, SiCH$_2$CH_2(CH$_2$)$_2$Br), 1.61–1.75 (m, 2 H, NCH$_2$CH_2CH$_2$Si), 1.81 (”quint“, $^3J_{HH}$ = 6.9 Hz, 2 H, Si(CH$_2$)$_2$CH_2CH$_2$Br), 3.35 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, Si(CH$_2$)$_3$CH_2Br), 4.05–4.14 (m, 2 H, NCH_2(CH$_2$)$_2$Si), 7.68 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.3 Hz, 2 H, *H*-3/*H*-6, Naphth), 8.14 (dd, $^3J_{HH}$ = 8.3

Hz, $^4J_{HH}$ = 1.1 Hz, 2 H, *H*-4/*H*-5, Naphth), 8.52 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.1 Hz, 2 H, *H*-2/*H*-7, Naphth). ^{13}C NMR ($CDCl_3$): δ –3.5 (Si*C*H$_3$), 12.4 (N(CH$_2$)$_2$*C*H$_2$Si), 14.1 (Si*C*H$_2$(CH$_2$)$_3$Br), 22.4 (SiCH$_2$*C*H$_2$(CH$_2$)$_2$Br), 22.5 (NCH$_2$*C*H$_2$CH$_2$Si), 33.5 (Si(CH$_2$)$_3$*C*H$_2$Br), 36.2 (Si(CH$_2$)$_2$*C*H$_2$CH$_2$Br), 43.2 (N*C*H$_2$(CH$_2$)$_2$Si), 122.6 (*C*-1/*C*-8, Naphth), 126.8 (*C*-3/*C*-6, Naphth), 128.0 (*C*-8a, Naphth), 131.0 (*C*-2/*C*-7, Naphth), 131.4 (*C*-4a, Naphth), 133.7 (*C*-4/*C*-5, Naphth), 164.0 (*C*=O). ^{29}Si NMR ($CDCl_3$): δ 3.1. Anal. Calcd for $C_{21}H_{26}BrNO_2Si$: C, 58.33; H, 6.06; N, 3.24. Found: C, 58.0; H, 6.2; N, 3.3.

Preparation of (5-bromopentyl)dimethyl[3-(1,8-naphthalimido)propyl]silane (118). Preparation according to Protocol A (**110** (1.01 g, 4.83 mmol); **112** (1.14 g, 4.80 mmol); toluene (20 mL); $H_2PtCl_6{\cdot}6H_2O$ (10 mg, 19.3 μmol) (dissolved in propan-2-ol (50 μL)); workup including column chromatography on silica gel (column diameter, 4.5 cm; silica gel (63–200 μm; Fluka, 60741), 300 g; eluent, diethyl ether/*n*-hexane (1:1 (v/v))). After bulb-to-bulb-distillation (210–240 °C/0.001 mbar), compound **118** was obtained in 71% yield (related to **110**) as a colorless viscous liquid (1.54 g, 3.45 mmol). ^{1}H NMR ($CDCl_3$): δ –0.05 (s, 6 H, SiC*H*$_3$), 0.43–0.53 (m, 2 H, SiC*H*$_2$(CH$_2$)$_4$Br), 0.54–0.65 (m, 2 H, N(CH$_2$)$_2$C*H*$_2$Si), 1.23–1.34 (m, 2 H, SiCH$_2$C*H*$_2$(CH$_2$)$_3$Br), 1.34–1.46 (m, 2 H, Si(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_2$Br), 1.61–1.75 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$Si), 1.81 (”quint“, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_3$C*H*$_2$CH$_2$Br), 3.36 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_4$C*H*$_2$Br), 4.08–4.16 (m, 2 H, NC*H*$_2$(CH$_2$)$_2$Si), 7.72 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.3 Hz, 2 H, *H*-3/*H*-6, Naphth), 8.17 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.1 Hz, 2 H, *H*-4/*H*-5, Naphth), 8.57 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.1 Hz, 2 H, *H*-2/*H*-7, Naphth). ^{13}C NMR ($CDCl_3$): δ –3.5 (Si*C*H$_3$), 12.5 (N(CH$_2$)$_2$*C*H$_2$Si), 15.0 (Si*C*H$_2$(CH$_2$)$_4$Br), 22.6 (NCH$_2$*C*H$_2$CH$_2$Si), 23.1 (SiCH$_2$*C*H$_2$(CH$_2$)$_3$Br), 32.0 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$Br), 32.5 (Si(CH$_2$)$_3$*C*H$_2$CH$_2$Br), 34.0 (Si(CH$_2$)$_4$*C*H$_2$Br), 43.3 (N*C*H$_2$(CH$_2$)$_2$Si), 122.7 (*C*-1/*C*-8, Naphth), 126.9 (*C*-3/*C*-6, Naphth), 128.1 (*C*-8a, Naphth), 131.1 (*C*-2/*C*-7, Naphth), 131.5 (*C*-4a, Naphth), 133.8 (*C*-4/*C*-5, Naphth), 164.1 (*C*=O). ^{29}Si NMR ($CDCl_3$): δ 3.0. Anal. Calcd for $C_{22}H_{28}BrNO_2Si$: C, 59.19; H, 6.32; N, 3.14. Found: C, 59.2; H, 6.5; N, 3.2.

Preparation of (6-bromohexyl)dimethyl[3-(1,8-naphthalimido)propyl]silane (119). Compound **119** was prepared according to Protocol B (**111** (4.07 g, 18.2 mmol); **112** (4.12 g, 17.4 mmol); toluene (60 mL); $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) (first portion, solid); $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) (second portion, dissolved in propan-2-ol (50 μL); added after 30 min)). After bulb-to-bulb-distillation (240–250 °C/0.001 mbar), compound **119** was obtained in 81% yield (related to **111**) as a slightly yellowish viscous liquid (6.84 g, 14.9 mmol). ^{1}H NMR ($CDCl_3$): δ –0.06 (s, 6 H, SiC*H*$_3$), 0.42–0.52 (m, 2 H, SiC*H*$_2$(CH$_2$)$_5$Br), 0.54–0.64 (m, 2 H, N(CH$_2$)$_2$C*H*$_2$Si), 1.20–1.31 (m, 4 H, SiCH$_2$(C*H*$_2$)$_2$(CH$_2$)$_3$Br), 1.31–1.43 (m, 2 H, Si(CH$_2$)$_3$C*H*$_2$(CH$_2$)$_2$Br), 1.62–1.75 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$Si), 1.80 (”quint“, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_4$C*H*$_2$CH$_2$Br), 3.36 (t, $^3J_{HH}$ = 7.0 Hz, 2

H, $Si(CH_2)_5CH_2Br$), 4.07–4.16 (m, 2 H, $NCH_2(CH_2)_2Si$), 7.71 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.2 Hz, 2 H, *H*-3/*H*-6, Naphth), 8.16 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.1 Hz, 2 H, *H*-4/*H*-5, Naphth), 8.55 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.1 Hz, 2 H, *H*-2/*H*-7, Naphth). ^{13}C NMR ($CDCl_3$): δ –3.5 ($SiCH_3$), 12.5 ($N(CH_2)_2CH_2Si$), 15.0 ($SiCH_2(CH_2)_5Br$), 22.6 ($NCH_2CH_2CH_2Si$), 23.6 ($SiCH_2CH_2(CH_2)_4Br$), 27.8 ($Si(CH_2)_3CH_2(CH_2)_2Br$), 32.65 ($Si(CH_2)_2CH_2(CH_2)_3Br$) or ($Si(CH_2)_4CH_2CH_2Br$), 32.73 ($Si(CH_2)_2CH_2(CH_2)_3Br$) or ($Si(CH_2)_4CH_2CH_2Br$), 34.1 ($Si(CH_2)_5CH_2Br$), 43.3 ($NCH_2(CH_2)_2Si$), 122.7 (*C*-1/*C*-8, Naphth), 126.8 (*C*-3/*C*-6, Naphth), 128.1 (*C*-8a, Naphth), 131.1 (*C*-2/*C*-7, Naphth), 131.5 (*C*-4a, Naphth), 133.8 (*C*-4/*C*-5, Naphth), 164.1 (*C*=O). ^{29}Si NMR ($CDCl_3$): δ 2.9. Anal. Calcd for $C_{23}H_{30}BrNO_2Si$: C, 59.99; H, 6.57; N, 3.04. Found: C, 60.1; H, 6.5; N, 3.1.

Preparation of (4-bromobutyl)dimethyl(3-phthalimidopropyl)silane (120). Compound **120** was prepared according to Protocol B (**109** (2.42 g, 12.4 mmol); **113** (1.69 g, 9.03 mmol); toluene (30 mL); $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) (first portion, solid); $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) (second portion, dissolved in propan-2-ol (50 μL); added after 30 min)). After bulb-to-bulb-distillation (200 °C/0.001 mbar), compound **120** was obtained in 57% yield (related to **109**) as a slightly yellowish viscous liquid (2.69 g, 7.04 mmol). ^{1}H NMR ($CDCl_3$): δ –0.06 (s, 6 H, $SiCH_3$), 0.41–0.55 (m, 4 H, CH_2SiCH_2), 1.31–1.44 (m, 2 H, $SiCH_2CH_2(CH_2)_2Br$), 1.56–1.69 (m, 2 H, $NCH_2CH_2CH_2Si$), 1.81 (”quint“, $^3J_{HH}$ = 7.0 Hz, 2 H, $Si(CH_2)_2CH_2CH_2Br$), 3.36 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, $Si(CH_2)_3CH_2Br$), 3.62 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, $NCH_2(CH_2)_2Si$), 7.64–7.71 (m, 2 H, *H*-4/*H*-5, Phth), 7.77–7.84 (m, 2 H, *H*-3/*H*-6, Phth). ^{13}C NMR ($CDCl_3$): δ –3.6 ($SiCH_3$), 12.2 ($N(CH_2)_2CH_2Si$), 14.0 ($SiCH_2(CH_2)_3Br$), 22.3 ($SiCH_2CH_2(CH_2)_2Br$), 23.1 ($NCH_2CH_2CH_2Si$), 33.5 ($Si(CH_2)_3CH_2Br$), 36.2 ($Si(CH_2)_2CH_2CH_2Br$), 41.0 ($NCH_2(CH_2)_2Si$), 123.1 (*C*-3/*C*-6, Phth), 132.1 (*C*-1/*C*-2, Phth), 133.8 (*C*-4/*C*-5, Phth), 168.4 (*C*=O). ^{15}N NMR ($CDCl_3$): δ –217. ^{29}Si NMR ($CDCl_3$): δ 3.1. Anal. Calcd for $C_{17}H_{24}BrNO_2Si$: C, 53.40; H, 6.33; N, 3.66. Found: C, 53.0; H, 6.1; N, 3.6.

Preparation of (5-bromopentyl)dimethyl(3-phthalimidopropyl)silane (121). Compound **121** was prepared according to Protocol A (**110** (1.62 g, 7.74 mmol); **113** (1.29 g, 6.89 mmol); toluene (20 mL); $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) (first portion, solid); $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) (second portion, dissolved in propan-2-ol (50 μL); added after 30 min)); workup including column chromatography on silica gel (column diameter, 5.5 cm; silica gel (15–40 μm; Merck, 1.15111), 615 g; eluent, diethyl ether/*n*-hexane (1:1 (v/v))). After bulb-to-bulb-distillation (200–220 °C/0.001 mbar), compound **121** was obtained in 76% yield (related to **110**) as a colorless viscous liquid (2.34 g, 5.90 mmol). ^{1}H NMR ($CDCl_3$): δ –0.08 (s, 6 H, $SiCH_3$), 0.40–0.53 (m, 4 H, CH_2SiCH_2), 1.18–1.31 (m, 2 H, $SiCH_2CH_2(CH_2)_3Br$), 1.32–1.44 (m, 2 H, $Si(CH_2)_2CH_2(CH_2)_2Br$), 1.54–1.67 (m, 2 H, $NCH_2CH_2CH_2Si$), 1.79 (”quint“, $^3J_{HH}$ = 7.0 Hz, 2 H, $Si(CH_2)_3CH_2CH_2Br$), 3.34

(t, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_4$C*H*$_2$Br), 3.61 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, NC*H*$_2$(CH$_2$)$_2$Si), 7.63–7.70 (m, 2 H, *H*-4/*H*-5, Phth), 7.76–7.83 (m, 2 H, *H*-3/*H*-6, Phth). ^{13}C NMR (CDCl$_3$): δ –3.6 (Si*C*H$_3$), 12.2 (N(CH$_2$)$_2$*C*H$_2$Si), 14.8 (Si*C*H$_2$(CH$_2$)$_4$Br), 23.0 (SiCH$_2$*C*H$_2$(CH$_2$)$_3$Br), 23.1 (NCH$_2$*C*H$_2$CH$_2$Si), 31.9 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$Br), 32.4 (Si(CH$_2$)$_3$*C*H$_2$CH$_2$Br), 33.9 (Si(CH$_2$)$_4$*C*H$_2$Br), 41.0 (N*C*H$_2$(CH$_2$)$_2$Si), 123.1 (*C*-3/*C*-6, Phth), 132.1 (*C*-1/*C*-2, Phth), 133.8 (*C*-4/*C*-5, Phth), 168.4 (*C*=O). ^{15}N NMR (CDCl$_3$): δ –217. ^{29}Si NMR (CDCl$_3$): δ 2.9. Anal. Calcd for C$_{18}$H$_{26}$BrNO$_2$Si: C, 54.54; H, 6.61; N, 3.53%. Found: C, 54.5; H, 6.6; N, 3.6.

Preparation of (6-bromohexyl)dimethyl(3-phthalimidopropyl)silane (122). Compound **122** was prepared according to Protocol A (**111** (11.2 g, 50.2 mmol); **113** (9.00 g, 48.1 mmol); toluene (200 mL); H$_2$PtCl$_6$·6H$_2$O (5 mg, 9.7 μmol) (first portion, solid); H$_2$PtCl$_6$·6H$_2$O (5 mg, 9.7 μmol) (second portion, dissolved in propan-2-ol (50 μL); added after 30 min)); workup including column chromatography on silica gel (column diameter, 5.5 cm; silica gel (15–40 μm; Merck, 1.15111), 615 g; eluent, diethyl ether/*n*-hexane (1:2 (v/v))). After bulb-to-bulb-distillation (220–250 °C/0.005 mbar), compound **122** was obtained in 86% yield (related to **111**) as a colorless viscous liquid (17.6 g, 43.0 mmol). ^{1}H NMR (CDCl$_3$): δ –0.08 (s, 6 H, SiC*H*$_3$), 0.40–0.54 (m, 4 H, C*H*$_2$SiC*H*$_2$), 1.17–1.31 (m, 4 H, SiCH$_2$(C*H*$_2$)$_2$(CH$_2$)$_3$Br), 1.31–1.43 (m, 2 H, Si(CH$_2$)$_3$C*H*$_2$(CH$_2$)$_2$Br), 1.55–1.68 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$Si), 1.80 (”quint“, $^3J_{HH}$ = 7.1 Hz, 2 H, Si(CH$_2$)$_4$C*H*$_2$CH$_2$Br), 3.36 (t, $^3J_{HH}$ = 7.1 Hz, 2 H, Si(CH$_2$)$_5$C*H*$_2$Br), 3.62 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, NC*H*$_2$(CH$_2$)$_2$Si), 7.64–7.71 (m, 2 H, *H*-4/*H*-5, Phth), 7.77–7.84 (m, 2 H, *H*-3/*H*-6, Phth). ^{13}C NMR (CDCl$_3$): δ –3.5 (Si*C*H$_3$), 12.3 (N(CH$_2$)$_2$*C*H$_2$Si), 14.9 (Si*C*H$_2$(CH$_2$)$_5$Br), 23.2 (NCH$_2$*C*H$_2$CH$_2$Si), 23.6 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$Br), 27.8 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Br), 32.6 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Br), 32.7 (Si(CH$_2$)$_4$*C*H$_2$CH$_2$Br), 34.0 (Si(CH$_2$)$_5$*C*H$_2$Br), 41.0 (N*C*H$_2$(CH$_2$)$_2$Si), 123.1 (*C*-3/*C*-6, Phth), 132.1 (*C*-1/*C*-2, Phth), 133.8 (*C*-4/*C*-5, Phth), 168.4 (*C*=O). ^{15}N NMR (CDCl$_3$): δ –218. ^{29}Si NMR (CDCl$_3$): δ 2.9. Anal. Calcd for C$_{19}$H$_{28}$BrNO$_2$Si: C, 55.60; H, 6.88; N, 3.41. Found: C, 55.2; H, 6.6; N, 3.4.

Preparation of (4-bromobutyl)dimethyl[3-(4-methylphthalimido)propyl]silane (123). Compound **123** was prepared according to Protocol B (**109** (3.03 g, 15.5 mmol); **114** (2.82 g, 14.0 mmol); toluene (60 mL); H$_2$PtCl$_6$·6H$_2$O (5 mg, 9.7 μmol) (first portion, solid); H$_2$PtCl$_6$·6H$_2$O (5 mg, 9.7 μmol) (second portion, dissolved in propan-2-ol (50 μL); added after 30 min)). After bulb-to-bulb-distillation (215–225 °C/0.001 mbar), compound **123** was obtained in 76% yield (related to **109**) as a slightly yellowish viscous liquid (4.70 g, 11.9 mmol). ^{1}H NMR (CDCl$_3$): δ –0.06 (s, 6 H, SiC*H*$_3$), 0.40–0.54 (m, 4 H, C*H*$_2$SiC*H*$_2$), 1.31–1.44 (m, 2 H, SiCH$_2$C*H*$_2$(CH$_2$)$_2$Br), 1.54–1.69 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$Si), 1.81 (”quint“, $^3J_{HH}$ = 6.9 Hz, 2 H, Si(CH$_2$)$_2$C*H*$_2$CH$_2$Br), 2.47 (s, 3 H, Aryl-C*H*$_3$) 3.36 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, Si(CH$_2$)$_3$C*H*$_2$Br), 3.60 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, NC*H*$_2$(CH$_2$)$_2$Si),

7.43–7.49 (m, 1 H, *H*-5, Me-phth), 7.58–7.62 (m, 1 H, *H*-3, Me-phth), 7.68 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, *H*-6, Me-phth). ^{13}C NMR ($CDCl_3$): δ –3.6 (Si*C*H$_3$), 12.2 (N(CH$_2$)$_2$*C*H$_2$Si), 14.0 (Si*C*H$_2$(CH$_2$)$_3$Br), 22.0 (Aryl-*C*H$_3$), 22.3 (SiCH$_2$*C*H$_2$(CH$_2$)$_2$Br), 23.1 (NCH$_2$*C*H$_2$CH$_2$Si), 33.5 (Si(CH$_2$)$_3$*C*H$_2$Br), 36.2 (Si(CH$_2$)$_2$*C*H$_2$CH$_2$Br), 40.9 (N*C*H$_2$(CH$_2$)$_2$Si), 123.0 (*C*-6, Me-phth), 123.7 (*C*-3, Me-phth), 129.5 (*C*-1, Me-phth), 132.5 (*C*-2, Me-phth), 134.3 (*C*-5, Me-phth), 145.0 (*C*-4, Me-phth), 168.5 (*C*=O), 168.6 (*C*=O). ^{29}Si NMR ($CDCl_3$): δ 3.1. Anal. Calcd for $C_{18}H_{26}BrNO_2Si$: C, 54.54; H, 6.61; N, 3.53. Found: C, 54.4; H, 6.6; N, 3.6.

Preparation of (5-bromopentyl)dimethyl[3-(4-methylphthalimido)propyl]silane (124). Compound **124** was prepared according to Protocol A (**110** (3.29 g, 15.7 mmol); **114** (2.92 g, 14.5 mmol); toluene (50 mL); $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) (first portion, solid); $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) (second portion, dissolved in propan-2-ol (50 μL); added after 30 min)); workup including column chromatography on silica gel (column diameter, 5.5 cm; silica gel (15–40 μm; Merck, 1.15111), 615 g; eluent, diethyl ether/*n*-hexane (1:1 (v/v))). After bulb-to-bulb-distillation (180–200 °C/0.0005 mbar), compound **124** was obtained in 79% yield (related to **110**) as a colorless viscous liquid (5.10 g, 12.4 mmol). ^{1}H NMR ($CDCl_3$): δ –0.08 (s, 6 H, SiC*H*$_3$), 0.40–0.53 (m, 4 H, C*H*$_2$SiC*H*$_2$), 1.18–1.32 (m, 2 H, SiCH$_2$C*H*$_2$(CH$_2$)$_3$Br), 1.32–1.45 (m, 2 H, Si(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_2$Br), 1.53–1.66 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$Si), 1.80 (”quint“, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_3$C*H*$_2$CH$_2$Br), 2.47 (s, 3 H, Aryl-C*H*$_3$), 3.35 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_4$C*H*$_2$Br), 3.60 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, NC*H*$_2$(CH$_2$)$_2$Si), 7.43–7.49 (m, 1 H, *H*-5, Me-phth), 7.58–7.62 (m, 1 H, *H*-3, Me-phth), 7.68 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, *H*-6, Me-phth). ^{13}C NMR ($CDCl_3$): δ –3.6 (Si*C*H$_3$), 12.3 (N(CH$_2$)$_2$*C*H$_2$Si), 14.9 (Si*C*H$_2$(CH$_2$)$_4$Br), 22.0 (Aryl-*C*H$_3$), 23.0 (SiCH$_2$*C*H$_2$(CH$_2$)$_3$Br), 23.1 (NCH$_2$*C*H$_2$CH$_2$Si), 32.0 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$Br), 32.5 (Si(CH$_2$)$_3$*C*H$_2$CH$_2$Br), 33.9 (Si(CH$_2$)$_4$*C*H$_2$Br), 40.9 (N*C*H$_2$(CH$_2$)$_2$Si), 123.0 (*C*-6, Me-phth), 123.7 (*C*-3, Me-phth), 129.5 (*C*-1, Me-phth), 132.5 (*C*-2, Me-phth), 134.3 (*C*-5, Me-phth), 145.0 (*C*-4, Me-phth), 168.5 (*C*=O), 168.6 (*C*=O). ^{29}Si NMR ($CDCl_3$): δ 2.9. Anal. Calcd for $C_{19}H_{28}BrNO_2Si$: C, 55.60; H, 6.88; N, 3.41%. Found: C, 55.7; H, 6.9; N, 3.5.

Preparation of (6-bromohexyl)dimethyl[3-(4-methylphthalimido)propyl]silane (125). Compound **125** was prepared according to Protocol B (**111** (3.26 g, 14.6 mmol); **114** (2.85 g, 14.2 mmol); toluene (50 mL); $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) (first portion, solid); $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) (second portion, dissolved in propan-2-ol (50 μL); added after 30 min)). After bulb-to-bulb-distillation (200–210 °C/0.001 mbar), compound **125** was obtained in 67% yield (related to **111**) as a slightly yellowish viscous liquid (4.13 g, 9.73 mmol). ^{1}H NMR ($CDCl_3$): δ –0.08 (s, 6 H, SiC*H*$_3$), 0.40–0.53 (m, 4 H, C*H*$_2$SiC*H*$_2$), 1.17–1.44 (m, 6 H, SiCH$_2$(C*H*$_2$)$_3$(CH$_2$)$_2$Br), 1.54–1.68 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$Si), 1.81 (”quint“, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_4$C*H*$_2$CH$_2$Br), 2.48 (s, 3 H, Aryl-C*H*$_3$), 3.37 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_5$C*H*$_2$Br), 3.61 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, NC*H*$_2$(CH$_2$)$_2$Si),

7.43–7.50 (m, 1 H, *H*-5, Me-phth), 7.59–7.63 (m, 1 H, *H*-3, Me-phth), 7.69 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, *H*-6, Me-phth). ^{13}C NMR ($CDCl_3$): δ –3.5 (Si*C*H$_3$), 12.3 (N(CH$_2$)$_2$*C*H$_2$Si), 15.0 (Si*C*H$_2$(CH$_2$)$_5$Br), 22.0 (Aryl-*C*H$_3$), 23.2 (NCH$_2$*C*H$_2$CH$_2$Si), 23.6 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$Br), 27.8 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Br), 32.67 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Br or Si(CH$_2$)$_4$*C*H$_2$CH$_2$Br), 32.75 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Br or Si(CH$_2$)$_4$*C*H$_2$CH$_2$Br), 34.1 (Si(CH$_2$)$_5$*C*H$_2$Br), 41.0 (N*C*H$_2$(CH$_2$)$_2$Si), 123.1 (*C*-6, Me-phth), 123.7 (*C*-3, Me-phth), 129.5 (*C*-1, Me-phth), 132.5 (*C*-2, Me-phth), 134.3 (*C*-5, Me-phth), 145.1 (*C*-4, Me-phth), 168.6 (*C*=O), 168.7 (*C*=O). ^{29}Si NMR ($CDCl_3$): δ 2.9. Anal. Calcd for $C_{20}H_{30}BrNO_2Si$: C, 56.60; H, 7.12; N, 3.30. Found: C, 56.5; H, 7.1; N, 3.4.

Preparation of (6-bromohexyl)dimethyl(3-succinimidopropyl)silane (126). Compound **126** was prepared according to Protocol B (**111** (2.73 g, 12.2 mmol); **115** (1.67 g, 12.0 mmol); toluene (20 mL); $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) (first portion, solid); $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) (second portion, dissolved in propan-2-ol (50 μL); added after 30 min)). After bulb-to-bulb-distillation (185–190 °C/0.001 mbar), compound **126** was obtained in 82% yield (related to **111**) as a slightly yellowish viscous liquid (3.63 g, 10.0 mmol). ^{1}H NMR ($CDCl_3$): δ –0.08 (s, 6 H, SiC*H*$_3$), 0.38–0.49 (m, 4 H, C*H*$_2$SiC*H*$_2$), 1.16–1.42 (m, 6 H, SiCH$_2$(C*H*$_2$)$_3$(CH$_2$)$_2$Br), 1.42–1.56 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$Si), 1.81 (”quint“, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_4$C*H*$_2$CH$_2$Br), 2.67 (s, 4 H, C(O)C*H*$_2$), 3.37 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, Si(CH$_2$)$_5$C*H*$_2$Br), 3.40–3.47 (m, 2 H, NC*H*$_2$(CH$_2$)$_2$Si). ^{13}C NMR ($CDCl_3$): δ –3.6 (Si*C*H$_3$), 12.3 (N(CH$_2$)$_2$*C*H$_2$Si), 14.9 (Si*C*H$_2$(CH$_2$)$_5$Br), 22.3 (NCH$_2$*C*H$_2$CH$_2$Si), 23.6 (SiCH$_2$*C*H$_2$(CH$_2$)$_4$Br), 27.8 (Si(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$Br), 28.1 (C(O)*C*H$_2$), 32.6 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Br or Si(CH$_2$)$_4$*C*H$_2$CH$_2$Br), 32.7 (Si(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$Br or Si(CH$_2$)$_4$*C*H$_2$CH$_2$Br), 34.1 (Si(CH$_2$)$_5$*C*H$_2$Br), 41.8 (N*C*H$_2$(CH$_2$)$_2$Si), 177.3 (*C*=O). ^{29}Si NMR ($CDCl_3$): δ 2.9. Anal. Calcd for $C_{15}H_{28}BrNO_2Si$: C, 49.72; H, 7.79; N, 3.87. Found: C, 49.5; H, 7.9; N, 3.8.

Preparation of *rac*-(6-bromohexyl)dimethyl(2-methyl-3-phthalimidopropyl)silane (*rac*-127). $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol) was added at 20 °C to a solution of **111** (1.29 g, 5.78 mmol) and **116** 1.11 g, 5.52 mmol) in toluene (15 mL), and the mixture was heated immediately in a pre-heated oil bath (140 °C) for 30 min, followed by addition of a second portion of $H_2PtCl_6{\cdot}6H_2O$ (5 mg, 9.7 μmol; dissolved in propan-2-ol (50 μL)), heating under reflux for 1 h, addition of a third portion of of $H_2PtCl_6{\cdot}6H_2O$ (25 mg, 48.3 μmol; dissolved in propan-2-ol (50 μL)), and heating under reflux for a further 13 h. The reaction mixture was filtered over silica gel using a standard chromatographic column (column diameter, 3.5 cm; silica gel (63–200 μm; Fluka 60741), 30 g). The silica gel was then washed with ethyl acetate (500 mL), and the organic solutions were combined. The solvent was removed under reduced pressure, and the product was purified by bulb-to-bulb-distillation in vacuo (220–240 °C/0.001 mbar) to give *rac*-**127** as a slightly yellowish

viscous liquid in 58% yield (related to **111**) (1.43 g, 3.37 mmol). ^{1}H NMR ($CDCl_3$): δ –0.03 (s, 3 H, SiCH_3), –0.02 (s, 3 H, SiCH_3), 0.42 (δ_A), 0.60 (δ_B), 2.00–2.18 (δ_X) (3 H, $^{2}J_{AB}$ = –14.6 Hz, $^{3}J_{AX}$ = 9.5 Hz, $^{3}J_{BX}$ = 4.4 Hz, $NCH_2CH_X(CH_3)CH_AH_BSi$), 0.43–0.53 (m, 2 H, $SiCH_2(CH_2)_5Br$), 0.89 (d, 3 H, $^{3}J_{HH}$ = 6.8 Hz, $NCH_2CH(CH_3)CH_2Si$), 1.18–1.44 (m, 6 H, $SiCH_2(CH_2)_3(CH_2)_2Br$), 1.80 (”quint“, $^{3}J_{HH}$ = 7.0 Hz, 2 H, $Si(CH_2)_4CH_2CH_2Br$), 3.36 (t, $^{3}J_{HH}$ = 7.0 Hz, 2 H, $Si(CH_2)_5CH_2Br$), 3.39–3.54 (m, 2 H, $NCH_2CH(CH_3)CH_2Si$), 7.65–7.72 (m, 2 H, *H*-4/*H*-5, Phth), 7.78–7.85 (m, 2 H, *H*-3/*H*-6, Phth). ^{13}C NMR ($CDCl_3$): δ –2.6 ($SiCH_3$), –2.5 ($SiCH_3$), 15.8 ($SiCH_2(CH_2)_5Br$), 20.5 ($NCH_2CH(CH_3)CH_2Si$), 20.8 ($NCH_2CH(CH_3)CH_2Si$), 23.6 ($SiCH_2CH_2(CH_2)_4Br$), 27.8 ($Si(CH_2)_3CH_2(CH_2)_2Br$), 29.2 ($NCH_2CH(CH_3)CH_2Si$), 32.68 ($Si(CH_2)_2CH_2(CH_2)_3Br$ or $Si(CH_2)_4CH_2CH_2Br$), 32.72 ($Si(CH_2)_2CH_2(CH_2)_3Br$ or $Si(CH_2)_4CH_2CH_2Br$), 34.0 ($Si(CH_2)_5CH_2Br$), 46.8 ($NCH_2CH(CH_3)CH_2Si$), 123.1 (*C*-3/*C*-6, Phth), 132.0 (*C*-1/*C*-2, Phth), 133.8 (*C*-4/*C*-5, Phth), 168.6 (*C*=O). ^{29}Si NMR ($CDCl_3$): δ 2.1. Anal. Calcd for $C_{20}H_{30}BrNO_2Si$: C, 56.60; H, 7.12; N, 3.30. Found: C, 56.4; H, 7.2; N, 3.2.

Preparation of dimethyl[3-(1,8-naphthalimido)propyl]amine (128). A solution of 1,8-naphthalic acid anhydride (30.0 g, 151 mmol) and *N*,*N*-dimethylpropane-1,3-diamine (15.5 g, 152 mmol) in toluene (300 mL) was heated under reflux for 14 h, and the resulting water was removed using a water separator. The solvent was removed under reduced pressure, and the residue was distilled quickly (solidification of the distillate upon cooling to 0 °C). The solid brown distillate was purified by twofold crystallization from boiling ethanol (500 mL for each crystallization; 1 week at –26 °C; crystallization was initiated by addition of a tiny amount of the solid distillate to the solution at –26 °C). The product was isolated in 75% yield as a yellowish crystalline solid (32.1 g, 114 mmol); mp 113–115 °C. ^{1}H NMR ($CDCl_3$): δ 1.80–1.93 (m, 2 H, $NCH_2CH_2CH_2N$), 2.20 (s, 6 H, NCH_3), 2.38 (t, $^{3}J_{HH}$ = 7.3 Hz, 2 H, $N(CH_2)_2CH_2N(CH_3)_2$), 4.11–4.21 (m, 2 H, $NCH_2(CH_2)_2N(CH_3)_2$), 7.66 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 7.3 Hz, 2 H, *H*-3/*H*-6, naphth), 8.11 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{4}J_{HH}$ = 1.1 Hz, 2 H, *H*-4/*H*-5, naphth), 8.49 (dd, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HH}$ = 1.1 Hz, 2 H, *H*-2/*H*-7, naphth). ^{13}C NMR ($CDCl_3$): δ 26.0 ($NCH_2CH_2CH_2N$), 38.7 ($NCH_2(CH_2)_2N(CH_3)_2$), 45.3 (NCH_3), 57.2 ($N(CH_2)_2CH_2N(CH_3)_2$), 122.5 (*C*-1/*C*-8, naphth), 126.8 (*C*-3/*C*-6, naphth), 127.9 (*C*-8a, naphth), 131.0 (*C*-2/*C*-7, naphth), 131.4 (*C*-4a, naphth), 133.7 (*C*-4/*C*-5, naphth), 164.0 (*C*=O). Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.1; H, 6.4; N, 9.8.

Preparation of dimethyl(3-phthalimidopropyl)amine (129). [103] Compound **129** was prepared according to a literature method[41d] from phthalic acid anhydride (56.4 g, 381 mmol) and *N*,*N*-dimethylpropane-1,3-diamine (40.9 g, 400 mmol). The crude product was distilled in vacuo (bp 118 °C/0.0005 mbar) to give **129** in 91% yield as a slightly yellowish colored liquid (80.1 g, 345 mmol). ^{1}H NMR ($CDCl_3$): δ 1.70–1.81 (m, 2 H, $NCH_2CH_2CH_2N$), 2.13 (s, 6 H, NCH_3), 2.26 (t,

$^3J_{HH}$ = 7.2 Hz, 2 H, N(CH$_2$)$_2$C*H*$_2$N(CH$_3$)$_2$), 3.65 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, NC*H*$_2$(CH$_2$)$_2$N(CH$_3$)$_2$), 7.58–7.66 (m, 2 H, *H*-4/*H*-5, phth), 7.71–7.78 (m, 2 H, *H*-3/*H*-6, phth). ^{13}C NMR (CDCl$_3$): δ 26.4 (NCH$_2$*C*H$_2$CH$_2$N), 36.0 (N*C*H$_2$(CH$_2$)$_2$N(CH$_3$)$_2$), 45.1 (N*C*H$_3$), 56.8 (N(CH$_2$)$_2$*C*H$_2$N(CH$_3$)$_2$), 122.9 (*C*-3/*C*-6, phth), 131.9 (*C*-1/*C*-2, phth), 133.6 (*C*-4/*C*-5, phth), 168.1 (*C*=O). ^{15}N NMR (CDCl$_3$): δ –356 (NCH$_2$(CH$_2$)$_2$*N*(CH$_3$)$_2$), –218 (*N*CH$_2$(CH$_2$)$_2$N(CH$_3$)$_2$). Anal. Calcd for C$_{13}$H$_{16}$N$_2$O$_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.2; H, 6.9; N, 12.1.

Preparation of dimethyl[3-(4-methylphthalimido)propyl]amine (130). A solution of 4-methylphthalic acid anhydride (10.0 g, 61.7 mmol) and *N*,*N*-dimethylpropane-1,3-diamine (6.30 g, 61.7 mmol) in toluene (100 mL) was heated under reflux for 3 h, and the resulting water was removed using a water separator. The solvent was removed under reduced pressure, and the residue was distilled in vacuo (Vigreux column, 10 cm) to give **130** in 87% yield as a slightly yellowish oily liquid (13.2 g, 53.6 mmol); bp 130 °C/0.001 mbar. ^{1}H NMR (CDCl$_3$): δ 1.66 (quint, $^3J_{HH}$ = 7.2 Hz, 2 H, NCH$_2$C*H*$_2$CH$_2$N), 2.05 (s, 6 H, NC*H*$_3$), 2.18 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, N(CH$_2$)$_2$C*H*$_2$N(CH$_3$)$_2$), 2.31 (s, 3 H, Aryl-C*H*$_3$), 3.52 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, NC*H*$_2$(CH$_2$)$_2$N(CH$_3$)$_2$), 7.27–7.33 (m, 1 H, *H*-5, Me-phth), 7.39–7.42 (m, 1 H, *H*-3, Me-phth), 7.49 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, *H*-6, Me-phth). ^{13}C NMR (CDCl$_3$): δ 21.6 (Aryl-*C*H$_3$), 26.2 (NCH$_2$*C*H$_2$CH$_2$N), 35.7 (N*C*H$_2$(CH$_2$)$_2$N(CH$_3$)$_2$), 44.9 (N*C*H$_3$), 56.6 (N(CH$_2$)$_2$*C*H$_2$N(CH$_3$)$_2$), 122.6 (*C*-6, Me-phth), 123.2 (*C*-3, Me-phth), 129.2 (*C*-1, Me-phth), 132.1 (*C*-2, Me-phth), 134.0 (*C*-5, Me-phth), 144.6 (*C*-4, Me-phth), 167.9 (*C*=O), 168.0 (*C*=O). Anal. Calcd for C$_{14}$H$_{18}$N$_2$O$_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.1; H, 7.3; N, 11.1.

Preparation of dimethyl(3-succinimidopropyl)amine (131). A solution of succinic acid anhydride (15.0 g, 150 mmol) and *N*,*N*-dimethylpropane-1,3-diamine (15.3 g, 150 mmol) in toluene (100 mL) was heated under reflux for 3 h, and the resulting water was removed using a water separator. The solvent was removed under reduced pressure, and the residue was distilled in vacuo (Vigreux column, 10 cm) to give **131** in 85% yield as a colorless liquid (23.6 g, 128 mmol); bp 90 °C/0.001 mbar. ^{1}H NMR (CDCl$_3$): δ 1.62 (quint, $^3J_{HH}$ = 7.2 Hz, 2 H, NCH$_2$C*H*$_2$CH$_2$N), 2.09 (s, 6 H, NC*H*$_3$), 2.18 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, N(CH$_2$)$_2$C*H*$_2$N(CH$_3$)$_2$), 2.59 (s, 4 H, C(O)C*H*$_2$), 3.45 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, NC*H*$_2$(CH$_2$)$_2$N(CH$_3$)$_2$). ^{13}C NMR (CDCl$_3$): δ 25.5 (NCH$_2$*C*H$_2$CH$_2$N), 28.0 (C(O)*C*H$_2$), 37.0 (N*C*H$_2$(CH$_2$)$_2$N(CH$_3$)$_2$), 45.2 (N*C*H$_3$), 56.9 (N(CH$_2$)$_2$*C*H$_2$N(CH$_3$)$_2$), 177.1 (*C*=O). Anal. Calcd for C$_9$H$_{16}$N$_2$O$_2$: C, 58.67; H, 8.75; N, 15.21. Found: C, 58.4; H, 8.7; N, 15.3.

Preparation of *rac*-dimethyl(2-methyl-3-phthalimidopropyl)amine (*rac*-132). A solution of phthalic acid anhydride (6.16 g, 41.6 mmol) and *rac*-*N*,*N*,2-trimethylpropane-1,3-diamine (*rac*-**134**) (4.83 g, 41.6 mmol) in toluene (100 mL) was heated under reflux for 3 h, and the resulting water was removed using a water separator. The solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation in vacuo (135–145 °C/0.001 mbar). Upon

cooling to 20 °C, the distillate solidified to give *rac*-**132** in 80% yield as a colorless crystalline solid (8.16 g, 33.1 mmol); mp 60–61 °C. ^{1}H NMR ($CDCl_3$): δ 0.86 (d, $^3J_{HH}$ = 6.4 Hz, 3 H, CC*H*$_3$), 2.01–2.25 (m, 3 H, NCH$_2$C*H*(CH$_3$)C*H*$_2$N(CH$_3$)$_2$), 2.13 (s, 6 H, NC*H*$_3$), 3.39–3.52 (m, 1 H, NC*H*$_A$H$_B$CH(CH$_3$)CH$_2$N(CH$_3$)$_2$), 3.66–3.76 (m, 1 H, NCH$_A$*H*$_B$CH(CH$_3$)CH$_2$N(CH$_3$)$_2$), 7.63–7.70 (m, 2 H, *H*-4/*H*-5, phth), 7.75–7.83 (m, 2 H, *H*-3/*H*-6, phth). ^{13}C NMR ($CDCl_3$): δ 16.5 (C*C*H$_3$), 30.3 (NCH$_2$*C*H(CH$_3$)CH$_2$N), 42.6 (N*C*H$_2$CH(CH$_3$)CH$_2$N(CH$_3$)$_2$), 45.6 (N*C*H$_3$), 64.6 (NCH$_2$CH(CH$_3$)*C*H$_2$N(CH$_3$)$_2$), 123.0 (*C*-3/*C*-6, phth), 132.1 (*C*-1/*C*-2, phth), 133.7 (*C*-4/*C*-5, phth), 168.6 (*C*=O). Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.5; H, 7.3; N, 11.1.

Preparation of *rac*-3-(dimethylamino)-2-methylpropionitrile (*rac*-133). 2-Methylacrylonitrile (77.4 g, 1.15 mol) was added dropwise at ≤30 °C (cooling in a water bath was necessary to maintain this temperature) within 2 h to a stirred mixture of an aqueous solution of dimethylamine (40%, 143 g) (57.2 g, 1.27 mol of dimethylamine) and ethanol (170 mL). After the addition was complete, the mixture was stirred at 0 °C for 1 h and at 20 °C for a further 16 h. The solvent was removed under reduced pressure, and the residue was distilled in vacuo (Vigreux column, 15 cm) to give *rac*-**133** in 64% yield as a colorless liquid (83.1 g, 741 mmol); bp 54–55 °C/9 mbar. ^{1}H NMR ($CDCl_3$): δ 1.25 (δ_X), 2.27 (δ_A), 2.53 (δ_B), and 2.70 (δ_G) ($^2J_{AB}$ = –12.3 Hz, $^3J_{AG}$ = 6.2 Hz, $^3J_{BG}$ = 8.7 Hz, $^3J_{GX}$ = 6.8 Hz, 6 H, N≡CCH$_G$(C(H$_X$)$_3$)CH$_A$H$_B$N(CH$_3$)$_2$), 2.23 (s, 6 H, NC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 15.8 (C*C*H$_3$), 24.5 (N≡C*C*H(CH$_3$)CH$_2$N(CH$_3$)$_2$), 45.4 (N*C*H$_3$), 62.3 (C*C*H$_2$N(CH$_3$)$_2$), 122.4 (N≡*C*). Anal. Calcd for $C_6H_{12}N_2$: C, 64.24; H, 10.78; N, 24.97. Found: C, 64.4; H, 10.8; N, 25.0.

Preparation of *rac*-*N*,*N*,2-trimethylpropane-1,3-diamine (*rac*-134). A solution of *rac*-**133** (73.7 g, 657 mmol) in diethyl ether (250 mL) was added dropwise within 70 min to a stirred suspension of LAH (13.7 g, 361 mmol) in diethyl ether (300 mL), causing the solvent to boil under reflux during the addition. After the addition was complete, the mixture was heated under reflux for 1 h and then cooled to 0 °C, followed by cautious addition of water (150 mL) (formation of a precipitate). The two-phase mixture was filtered, the filter cake was washed with diethyl ether (3 × 50 mL), the two-phase filtrate and the wash solutions were combined, ethane-1,2-diamine (150 mL) was added, and the resulting two-phase mixture was extracted continuously for 2 days using a perforator. The organic phase was dried over anhydrous potassium carbonate, the solvent was removed under reduced pressure, and the residue was distilled under atmospheric pressure to give 62 g of a yellow liquid; bp 110–150 °C. Redistillation using a spinning band column gave *rac*-**134** in 28% yield as a colorless liquid (21.5 g, 185 mmol); bp 140–141 °C/981 mbar (significant decomposition was observed during the distillation).[104] ^{1}H NMR ($CDCl_3$): δ 0.84 (δ_X), 1.57 (δ_G),

1.98 (δ_A), 2.13 (δ_B), 2.50 (δ_M), and 2.63 (δ_N) ($^2J_{AB}$ = –12.0 Hz, $^3J_{AG}$ = 6.7 Hz, $^3J_{BG}$ = 7.9 Hz, $^3J_{GM}$ = 6.2 Hz, $^3J_{GN}$ = 5.5 Hz, $^3J_{GX}$ = 6.6 Hz, $^2J_{MN}$ = –12.5 Hz, 8 H, $H_2NCH_MH_NCH_G(C(H_X)_3)CH_AH_BN(CH_3)_2$), 1.47 (s, 2 H, N$H_2$), 2.14 (s, 6 H, NC$H_3$). ^{13}C NMR ($CDCl_3$): δ 16.4 (CCH_3), 33.9 ($H_2NCH_2CH(CH_3)CH_2N(CH_3)_2$), 45.9 (N$CH_3$), 47.3 ($H_2NCH_2C$), 65.2 ($CCH_2N(CH_3)_2$). Anal. Calcd for $C_6H_{16}N_2$: C, 62.02; H, 13.88; N, 24.11. Found: C, 61.41; H, 13.7; N, 25.1.

Preparation of methyl[3-(1,8-naphthalimido)propyl]amine (135). A mixture of 1,8-naphthalic acid anhydride (4.93 g, 24.9 mmol) and *N*-methylpropane-1,3-diamine (2.23 g, 25.3 mmol) in glacial acetic acid (20 mL) was heated under reflux for 90 min. The solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation in vacuo[105] (Kugelrohr apparatus, 220 °C/0.05 mbar) to give **135** in 70% yield as a yellow solid (4.65 g, 17.3 mmol); mp 103–106 °C.[106] ^{1}H NMR (CD_2Cl_2): δ 1.89 ("quint", $^3J_{HH}$ = 6.9 Hz, 2 H, $NCH_2CH_2CH_2N$), 2.2 (br s, 1 H, N*H*), 2.40 (s, 3 H, NCH_3), 2.64 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, $N(CH_2)_2CH_2NCH_3$), 4.15–4.23 (m, 2 H, $NCH_2(CH_2)_2NCH_3$), 7.74 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 8.3 Hz, 2 H, *H*-3/*H*-6, naphth), 8.21 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.1 Hz, 2 H, *H*-4/*H*-5, naphth), 8.53 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.1 Hz, 2 H, *H*-2/*H*-7, naphth). ^{13}C NMR (CD_2Cl_2): δ 28.4 ($NCH_2CH_2CH_2N$), 36.4 (NCH_3), 38.6 ($NCH_2(CH_2)_2NCH_3$), 49.5 ($N(CH_2)_2CH_2NCH_3$), 123.1 (*C*-1/*C*-8, naphth), 127.2 (*C*-3/*C*-6, naphth), 128.4 (*C*-8a, naphth), 131.2 (*C*-2/*C*-7, naphth), 131.9 (*C*-4a, naphth), 134.2 (*C*-4/*C*-5, naphth), 164.4 (*C*=O). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 70.9; H, 6.2; N, 10.4.

Preparation of 1-chloro-1-(chloromethyl)-1-silacyclohexane (136). 50 mL of a solution of 1,5-dibromopentane (161 g, 700 mmol) in diethyl ether (500 mL) were added to a stirred suspension of magnesium turnings (37.4 g, 1.54 mol) in diethyl ether (200 mL), and the reaction was started by gentle heating. Subsequently, the remaining ethereal 1,5-dibromopentane solution was added within 90 min, causing the mixture to boil under reflux. After the addition was complete, the mixture was heated under reflux for a further 90 min and then cooled to 20 °C within 1 h. The resulting two-phase Grignard reagent (which was separated from residual magnesium turnings by decantation, followed by washing of the magnesium with diethyl ether (2 × 50 mL)) was added dropwise within 90 min to a solution of trichloro(chloromethyl)silane (129 g, 701 mmol) in diethyl ether (300 mL), causing the mixture to boil under reflux. During the addition, the mixture was stirred vigorously with a mechanical stirrer (formation of a precipitate). After the addition was complete, the mixture was stirred at 20 °C for 16 h, the precipitate was separated by filtration and washed with diethyl ether (2 × 200 mL), the filtrate and the wash solutions were combined, and the solvent was removed by distillation under atmospheric pressure, causing a postprecipitation. The

precipitate was separated by decantation and washed with *n*-pentane (2 × 50 mL), and all organic solutions were combined. The solvent was removed as described above, and the crude product (79 g) was isolated by distillation in vacuo (Vigreux column, 30 cm; bp 80–95 °C/18 mbar) and then further purified by redistillation to afford **136** in 52% yield (related to 1,5-dibromopentane) as a colorless liquid (67.4 g, 368 mmol); bp 88–90 °C/18 mbar. ^{1}H NMR ($CDCl_3$): δ 0.92–1.12 (m, 4 H, SiC*H*$_2$C), 1.21–1.37, 1.56–1.79, and 1.81–1.95 (m, 6 H, $SiCH_2(CH_2)_2C$), 2.98 (s, 2 H, SiC*H*$_2$Cl). ^{13}C NMR ($CDCl_3$): δ 13.4 (Si*C*H$_2$C), 23.3 ($SiCH_2CH_2C$), 28.9 ($Si(CH_2)_2CH_2C$), 29.0 (Si*C*H$_2$Cl). ^{29}Si NMR ($CDCl_3$): δ 20.8. Anal. Calc. for $C_6H_{12}Cl_2Si$: C, 39.35; H, 6.60. Found: C, 39.0; H, 6.3.

Preparation of benzyl 2-[1-(chloromethyl)-1-sila-1-cyclohexyl]acetate (137). A 2.5 M solution of *n*-butyllithium in *n*-hexane (45.6 mL, 114 mmol of *n*-BuLi) was added dropwise[107] at 0 °C within 10 min to a stirred (mechanical stirrer) solution of diisopropylamine (12.5 g, 124 mmol) in THF (100 mL), and the mixture was stirred at the same temperature for a further 15 min and then cooled to –80 °C, followed by dropwise addition of benzyl acetate (17.2 g, 115 mmol) within 15 min while the reaction temperature was kept at –75 °C (±5 °C). The mixture was stirred at this temperature for a further 15 min, followed by dropwise addition of 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU) (58.5 g, 456 mmol) at –75 °C (±5 °C) within 30 min (formation of a slurry), and the mixture was then cooled to –100 °C, followed by dropwise addition of **136** (20.8 g, 114 mmol) within 75 min while the temperature was kept at –95 °C (±5 °C) (formation of a highly viscous slurry). The mixture was warmed to –30 °C within 4 h (formation of a clear solution), and the cold solution was poured into a stirred two-phase mixture of a saturated aqueous sodium hydrogen carbonate solution (300 mL, solution A) and diethyl ether (200 mL) (formation of a precipitate which remained in the aqueous phase). The organic phase was separated and washed with a saturated aqueous sodium hydrogen carbonate solution (300 mL, solution B), the organic phase was separated, the first aqueous wash solution (A) was extracted with diethyl ether (200 mL), the resulting ethereal extract was used to extract the second aqueous wash solution (B), and the organic extract was separated, followed by a second extraction of the wash solutions A and B with a fresh portion of diethyl ether (200 mL), using the same protocol as described for the first extraction sequence. The combined organic solutions were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the oily residue was purified by rapid bulb-to-bulb distillation in vacuo (Kugelrohr apparatus). The distillate (33 g, 140–155 °C/0.001 mbar) was redistilled in vacuo (Vigreux column, 10 cm) to give **137** in 43% yield as a colorless liquid (14.4 g, 48.5 mmol); bp 137–138 °C/0.001 mbar. ^{1}H NMR ($CDCl_3$): δ 0.65–0.87 (m, 4 H, SiC*H*$_2$C), 1.32–1.43 (m, 2 H, $Si(CH_2)_2CH_2C$), 1.56–1.74 (m, 4 H, $SiCH_2CH_2C$), 2.10 (s, 2 H, SiC*H*$_2$C(O)), 2.86 (s, 2 H, SiC*H*$_2$Cl), 5.07 (s, 2 H, OC*H*$_2$Ph), 7.26–7.38 (m, 5 H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 9.7

(Si*C*H$_2$C), 21.7 (Si*C*H$_2$C(O)), 23.8 (SiCH$_2$*C*H$_2$C), 27.4 (Si*C*H$_2$Cl), 29.2 (Si(CH$_2$)$_2$*C*H$_2$C), 66.2 (O*C*H$_2$Ph), 128.2 (*C*-4, Ph), 128.4 (*C*-2/*C*-6 or *C*-3/*C*-5, Ph), 128.5 (*C*-2/*C*-6 or *C*-3/*C*-5, Ph), 136.0 (*C*-1, Ph), 171.9 (*C*=O). ^{29}Si NMR (CDCl$_3$): δ –0.8. Anal. Calcd for $C_{15}H_{21}ClO_2Si$: C, 60.69; H, 7.13. Found: C, 60.7; H, 7.0.

Preparation of benzyl 2-[1-(azidomethyl)-1-sila-1-cyclohexyl]acetate (138). A stirred mixture of **137** (10.8 g, 36.4 mmol), sulfolane (25 mL), and sodium azide (4.94 g, 76.0 mmol) was heated at 55 °C for 3 days and was then cooled to 20 °C and poured into a stirred two-phase mixture of diethyl ether (100 mL) and water (200 mL) containing 500 mg of sodium carbonate. The organic layer was separated, the aqueous phase was extracted with diethyl ether (2 × 100 mL), all organic extracts were combined and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (column dimensions, 60 × 5.5 cm; silica gel (15–40 μm, Merck 1.15111), 590 g; eluent, *n*-hexane/diethyl ether 86:14 (v/v)). The relevant fractions (TLC control) were combined, and the solvent was completely removed under reduced pressure to give **138** in 86% yield as a colorless oily liquid (9.50 g, 31.3 mmol). ^{1}H NMR (CD$_2$Cl$_2$): δ 0.67–0.85 (m, 4 H, SiC*H*$_2$C), 1.36–1.46 (m, 2 H, Si(CH$_2$)$_2$C*H*$_2$C), 1.63–1.75 (m, 4 H, SiCH$_2$C*H*$_2$C), 2.07 (s, 2 H, SiC*H*$_2$C(O)), 2.92 (s, 2 H, SiC*H*$_2$N$_3$), 5.08 (s, 2 H, OC*H*$_2$Ph), 7.29–7.40 (m, 5 H, C$_6$*H*$_5$). ^{13}C NMR (CD$_2$Cl$_2$): δ 10.3 (Si*C*H$_2$C), 22.3 (Si*C*H$_2$C(O)), 24.2 (SiCH$_2$*C*H$_2$C), 29.6 (Si(CH$_2$)$_2$*C*H$_2$C), 39.0 (Si*C*H$_2$N$_3$), 66.5 (O*C*H$_2$Ph), 128.5 (*C*-4, Ph), 128.78 (*C*-2/*C*-6 or *C*-3/*C*-5, Ph), 128.81 (*C*-2/*C*-6 or *C*-3/*C*-5, Ph), 136.8 (*C*-1, Ph), 171.9 (*C*=O). ^{15}N NMR (CD$_2$Cl$_2$): δ –319.8 (CH$_2$*N*NN), –172.7 (CH$_2$NN*N*), –130.0 (CH$_2$N*N*N). ^{29}Si NMR (CD$_2$Cl$_2$): δ –1.3. Anal. Calcd for $C_{15}H_{21}N_3O_2Si$: C, 59.37; H, 6.98; N, 13.85. Found: C, 59.7; H, 6.9; N, 13.6.

Preparation of *tert*-butyl 2-[1-(chloromethyl)-1-sila-1-cyclohexyl]acetate (139). Compound **139** was prepared analogous to the preparation of **137** (see above): THF, 100 mL; 2.7 M solution of *n*-butyllithium in *n*-hexane, 41.4 mL (112 mmol of *n*-BuLi); diisopropylamine, 12.5 g (124 mmol); *tert*-butyl acetate, 13.0 g (112 mmol); DMPU, 57.4 g (448 mmol); **136**, 20.9 g (114 mmol); distillate after bulb-to-bulb distillation, 28 g (100–130 °C/0.001 mbar). The product was redistilled in vacuo (Vigreux column, 20 cm) to give **139** in 79% yield (related to **136**) as a colorless liquid (23.8 g, 90.5 mmol); bp 70 °C/0.001 mbar. ^{1}H NMR (CDCl$_3$): δ 0.68–0.91 (m, 4 H, SiC*H*$_2$C), 1.34–1.46 (m, 2 H, Si(CH$_2$)$_2$C*H*$_2$C), 1.41 (s, 9 H, CC*H*$_3$), 1.60–1.76 (m, 4 H, SiCH$_2$C*H*$_2$C), 1.94 (s, 2 H, SiC*H*$_2$C(O)), 2.90 (s, 2 H, SiC*H*$_2$Cl). ^{13}C NMR (CDCl$_3$): δ 9.7 (Si*C*H$_2$C), 23.0 (Si*C*H$_2$C(O)), 23.9 (SiCH$_2$*C*H$_2$C), 27.5 (Si*C*H$_2$Cl), 28.2 (C*C*H$_3$), 29.3 (Si(CH$_2$)$_2$*C*H$_2$C), 80.1 (*C*CH$_3$), 171.4 (*C*=O). ^{29}Si NMR (CDCl$_3$): δ –1.2. Anal. Calcd for $C_{12}H_{23}ClO_2Si$: C, 54.83; H, 8.82. Found: C, 54.5; H, 8.5.

Preparation of *tert*-butyl 2-[1-(azidomethyl)-1-sila-1-cyclohexyl]acetate (140). Compound **140** was prepared analogous to the preparation of **138** (see above): **139**, 11.5 g (43.8 mmol); sulfolane, 25 mL; sodium azide, 5.74 g (88.3 mmol). The product was isolated in 89% yield as a colorless oily liquid (10.5 g, 39.0 mmol). ^{1}H NMR (CD_2Cl_2): δ 0.70–0.87 (m, 4 H, SiC*H*$_2$C), 1.35–1.51 (m, 2 H, Si(CH$_2$)$_2$C*H*$_2$C), 1.43 (s, 9 H, CC*H*$_3$), 1.65–1.80 (m, 4 H, SiCH$_2$C*H*$_2$C), 1.92 (s, 2 H, SiC*H*$_2$C(O)), 2.97 (s, 2 H, SiC*H*$_2$N$_3$). ^{13}C NMR (CD_2Cl_2): δ 10.4 (Si*C*H$_2$C), 23.6 (Si*C*H$_2$C(O)), 24.3 (SiCH$_2$*C*H$_2$C), 28.3 (C*C*H$_3$), 29.7 (Si(CH$_2$)$_2$*C*H$_2$C), 39.3 (Si*C*H$_2$N$_3$), 80.3 (*C*CH$_3$), 171.4 (*C*=O). ^{15}N NMR (CD_2Cl_2): δ –319.5 (CH$_2$*N*NN), –172.0 (CH$_2$NN*N*), –129.5 (CH$_2$N*N*N). ^{29}Si NMR (CD_2Cl_2): δ –1.6. Anal. Calcd for $C_{12}H_{23}N_3O_2Si$: C, 53.50; H, 8.60; N, 15.60. Found: C, 53.6; H, 8.4; N, 15.8.

Preparation of trimethylsilyl 2-[1-(chloromethyl)-1-sila-1-cyclohexyl]acetate (141). Iodotrimethylsilane (5.15 g, 25.7 mmol) was added in one single portion at 20 °C to a stirred solution of **139** (6.00 g, 22.8 mmol) in dichloromethane (20 mL). The mixture was heated under reflux for 30 min (quantitative conversion (GC control)), the solvent was removed under reduced pressure, and the residue was distilled in vacuo (Vigreux column, 5 cm) from copper powder (116 mg, 1.83 mmol) to give **141** in 85% yield (5.44 g, 19.5 mmol) as a colorless liquid; bp 73–74 °C/0.001 mbar. ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 9 H, SiC*H*$_3$), 0.69–0.91 (m, 4 H, SiC*H*$_2$C), 1.35–1.46 (m, 2 H, Si(CH$_2$)$_2$C*H*$_2$C), 1.61–1.76 (m, 4 H, SiCH$_2$C*H*$_2$C), 2.05 (s, 2 H, SiC*H*$_2$C(O)), 2.89 (s, 2 H, SiC*H*$_2$Cl). ^{13}C NMR ($CDCl_3$): δ –0.2 (Si*C*H$_3$), 9.7 (Si*C*H$_2$C), 23.8 (Si*C*H$_2$C(O)), 23.9 (SiCH$_2$*C*H$_2$C), 27.5 (Si*C*H$_2$Cl), 29.3 (Si(CH$_2$)$_2$*C*H$_2$C), 172.6 (*C*=O). ^{29}Si NMR ($CDCl_3$): δ –1.2 (*Si*C$_4$), 23.0 (O*Si*C$_3$). Anal. Calcd for $C_{11}H_{23}ClO_2Si_2$: C, 47.37; H, 8.31. Found: C, 47.1; H, 8.1.

Preparation of *tert*-butyl 2-[1-(iodomethyl)-1-sila-1-cyclohexyl]acetate (142). A stirred mixture of **139** (6.11 g, 23.2 mmol), sodium iodide (4.30 g, 28.7 mmol), and acetone (40 mL) was heated under reflux for 2 h (quantitative conversion (GC control)). The solids were removed by filtration and washed with *n*-heptane (2 × 50 mL), the filtrate and the wash solutions were combined, and the solvent was removed under reduced pressure until a residual volume of ca. 100 mL was obtained (postprecipitation), followed by addition of water (100 mL). The organic phase was separated, the aqueous layer was extracted with diethyl ether (2 × 50 mL), all organic extracts were combined and dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was distilled in vacuo (Vigreux column, 5 cm) from copper powder (122 mg, 1.92 mmol) to give **142** in 88% yield as a colorless liquid (7.24 g, 20.4 mmol); bp 87 °C/0.002 mbar. ^{1}H NMR ($CDCl_3$): δ 0.71–0.90 (m, 4 H, SiC*H*$_2$C), 1.32–1.46 (m, 2 H, Si(CH$_2$)$_2$C*H*$_2$C), 1.41 (s, 9 H, CC*H*$_3$), 1.61–1.72 (m, 4 H, SiCH$_2$C*H*$_2$C), 1.96 (s, 2 H, SiC*H*$_2$C(O)), 2.11 (s, 2 H, SiC*H*$_2$I). ^{13}C NMR ($CDCl_3$): δ –17.2 (Si*C*H$_2$I), 11.4 (Si*C*H$_2$C), 23.9 (Si*C*H$_2$C(O)), 24.0 (SiCH$_2$*C*H$_2$C), 28.2

(C*C*H$_3$), 29.4 (Si(CH$_2$)$_2$*C*H$_2$C), 80.0 (*C*CH$_3$), 171.4 (*C*=O). ^{29}Si NMR (CDCl$_3$): δ 0.3. Anal. Calcd for $C_{12}H_{23}IO_2Si$: C, 40.68; H, 6.54. Found: C, 40.9; H, 6.3.

Preparation of *tert*-butyl 2-[1-(isocyanatomethyl)-1-sila-1-cyclohexyl]acetate (143). Compound **140** (9.26 g, 34.4 mmol) was added in one single portion to a solution of triphenylphosphine (9.30 g, 35.5 mmol) in toluene (300 mL), and the mixture was stirred at 20 °C for 1 day. Subsequently, a gas stream of carbon dioxide (ca. 100 g; prepared from dry ice and dried by passing the gas stream through a column packed with anhydrous calcium chloride) was passed through the stirred solution over a period of 3 h. The solvent was removed under reduced pressure, the residue was purified by bulb-to-bulb distillation in vacuo (Kugelrohr apparatus), and the distillate (4.4 g, 100–175 °C/0.001 mbar) was redistilled in vacuo (Vigreux column, 5 cm) to give **143** in 34% yield as a colorless liquid (3.16 g, 11.7 mmol); bp 98–99 °C/0.002 mbar. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.75–0.85 (m, 4 H, SiC*H*$_2$C), 1.38–1.49 (m, 2 H, Si(CH$_2$)$_2$C*H*$_2$C), 1.43 (s, 9 H, CC*H*$_3$), 1.62–1.82 (m, 4 H, SiCH$_2$C*H*$_2$C), 1.93 (s, 2 H, SiC*H*$_2$C(O)), 2.93 (s, 2 H, SiC*H*$_2$N). ^{13}C NMR (CD$_2$Cl$_2$): δ 10.0 (Si*C*H$_2$C), 23.3 (Si*C*H$_2$C(O)), 24.3 (SiCH$_2$*C*H$_2$C), 28.3 (C*C*H$_3$), 29.0 (Si*C*H$_2$N), 29.7 (Si(CH$_2$)$_2$*C*H$_2$C), 80.4 (*C*CH$_3$), 120.5 (N*C*O), 171.2 (C*C*(=O)O). ^{15}N NMR (CD$_2$Cl$_2$): δ –361.3. ^{29}Si NMR (CD$_2$Cl$_2$): δ –0.8. Anal. Calcd for $C_{13}H_{23}NO_3Si$: C, 57.96; H, 8.60; N, 5.20. Found: C, 57.9; H, 8.5; N, 5.4.

Preparation of *tert*-butyl 2-{1-[((*tert*-butoxycarbonyl)amino)methyl]-1-sila-1-cyclohexyl}acetate (144). A solution of **143** (802 mg, 2.98 mmol) in *tert*-butanol (5 mL) was heated under reflux for 1 day. The solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation in vacuo (Kugelrohr apparatus). The fraction collected at 110–130 °C/0.001 mbar (717 mg) was crystallized from diethyl ether (25 mL) at –27 °C over a period of 3 days. The product was isolated by filtration, washed with cold (–27 °C) *n*-pentane (5 mL), and dried in vacuo (0.001 mbar, 20 °C, 4 h) to give **144** in 44% yield as a colorless crystalline solid (450 mg, 1.31 mmol); mp 84–85 °C. ^{1}H NMR (C$_6$D$_6$): δ 0.64–0.74 (m, 4 H, SiC*H*$_2$C), 1.27–1.39 (m, 2 H, Si(CH$_2$)$_2$C*H*$_2$C), 1.50 (s, 9 H, CC*H*$_3$), 1.59 (s, 9 H, CC*H*$_3$), 1.61–1.73 (m, 4 H, SiCH$_2$C*H*$_2$C), 1.90 (s, 2 H, SiC*H*$_2$C(O)), 2.96 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, SiC*H*$_2$N), 5.1 (br s, 1 H, N*H*). ^{13}C NMR (C$_6$D$_6$): δ 10.5 (Si*C*H$_2$C), 23.7 (Si*C*H$_2$C(O)), 24.2 (SiCH$_2$*C*H$_2$C), 27.9 (Si*C*H$_2$N), 28.2 (C*C*H$_3$), 28.5 (C*C*H$_3$), 29.7 (Si(CH$_2$)$_2$*C*H$_2$C), 78.4 (*C*CH$_3$), 79.9 (*C*CH$_3$), 156.8 (N*C*(=O)O), 171.9 (C*C*(=O)O). ^{15}N NMR (C$_6$D$_6$): δ –310.4. ^{29}Si NMR (C$_6$D$_6$): δ –3.0. Anal. Calcd for $C_{17}H_{33}NO_4Si$: C, 59.44; H, 9.68; N, 4.08. Found: C, 59.5; H, 9.5; N, 4.1.

Preparation of 1,1′-oxybis{[(1-sila-1-cyclohexyl)methyl]ammonium} dichloride (145). A solution of **140** (720 mg, 2.67 mmol) in toluene (5 mL) was added at 20 °C in one single portion to a solution of triphenylphosphine (722 mg, 2.75 mmol) in toluene (5 mL), and the mixture was

stirred at 20 °C for 1 day. The solvent was removed under reduced pressure, 6 M hydrochloric acid (20 mL) was added to the residue, and the mixture was then heated under reflux for 2 h,[108] cooled to 20 °C, and washed with dichloromethane (2 × 10 mL) to remove any triphenylphosphine oxide formed. The aqueous phase was kept undisturbed at –20 °C for 2 days, and the resulting precipitate was isolated by filtration and recrystallized from 6 M hydrochloric acid at –20 °C over a period of 2 days. The product was isolated by filtration and dried in vacuo (0.001 mbar, 20 °C, 8 h) to give **145** in 38% yield (including workup of the mother liquor) as a colorless crystalline solid (177 mg, 512 μmol); mp 256–257 °C (dec.). ^{1}H NMR ([D$_6$]DMSO): δ 0.62–0.78 and 0.82–0.96 (m, 8 H, SiC*H*$_2$C), 1.25–1.46 (m, 4 H, Si(CH$_2$)$_2$C*H*$_2$C), 1.49–1.76 (m, 8 H, SiCH$_2$C*H*$_2$C), 2.29 (q, $^{3}J_{HH}$ = 5.9 Hz, 4 H, SiC*H*$_2$N), 8.1 (br s, 6 H, N*H*$_3$). ^{13}C NMR ([D$_6$]DMSO): δ 13.7 (Si*C*H$_2$C), 23.7 (SiCH$_2$*C*H$_2$C), 25.5 (Si*C*H$_2$N), 28.8 (Si(CH$_2$)$_2$*C*H$_2$C). ^{29}Si NMR ([D$_6$]DMSO): δ 0.7. Anal. Calcd for C$_{12}$H$_{30}$Cl$_2$N$_2$OSi$_2$: C, 41.72; H, 8.75; N, 8.11. Found: C, 41.4; H, 8.3; N, 8.0.

1,1'-(Oxybis-1-silacyclobutane-1,1-diyl)bis(2,4,6-trimethoxybenzene) (146). The mother liquor of the crystallization of compound **74** was evaporated slowly under ambient conditions (humid air, 20 °C), upon which a few crystals formed at the surface of the liquid phase. These crystals were suitable for single-crystal X-ray diffraction analysis; however, the crystals of **146** crystallized as a conglomerate with crystals of compound **74**. Therefore, the crystal structure analysis of **146** (cf. Section 11.18, p. 58) was successful, but no further characterization (mp, NMR) was obtained from this mixture.

15 Appendix A: crystal structure data

Table 2. Crystal data and exp. parameters for the crystal structure analyses of *rac*-**12b**·HCl, (*R*)-**12b**·HBr, and *rac*-**13**.

	rac-**12b**·HCl	(*R*)-**12b**·HBr	*rac*-**13**
empirical formula	$C_{16}H_{28}ClNO_2Si$	$C_{16}H_{28}BrNO_2Si$	$C_{15}H_{25}NO_2Si$
formula mass, g mol^{-1}	329.93	374.39	279.45
collection *T*, K	173(2)	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
crystal system	orthorhombic	monoclinic	monoclinic
space group (no.)	$Pca2_1$ (29)	$P2_1$ (4)	$P2_1/c$ (14)
a, Å	12.8309(16)	6.6309(10)	14.0274(13)
b, Å	14.209(2)	10.3142(11)	10.7234(16)
c, Å	9.8055(11)	13.713(2)	10.7269(17)
β, deg	90	92.637(19)	99.752(14)
V, Å^3	1787.7(4)	936.9(2)	1590.2(4)
Z	4	2	4
D(calcd), g cm^{-3}	1.226	1.327	1.167
μ, mm^{-1}	0.285	2.262	0.147
F(000)	712	392	608
cryst. dimens., mm	0.4 × 0.3 × 0.1	0.4 × 0.3 × 0.1	0.3 × 0.3 × 0.2
2θ range, deg	4.28–53.94	4.94–52.94	4.80–56.00
index ranges	$-16 \le h \le 16$,	$-8 \le h \le 8$,	$-18 \le h \le 18$,
	$-18 \le k \le 18$,	$-12 \le k \le 11$,	$-14 \le k \le 14$,
	$-12 \le l \le 12$	$-17 \le l \le 17$	$-14 \le l \le 14$
no. of coll. reflns.	20273	8706	18884
no. of indep. reflns.	3853	3648	3738
R_{int}	0.0358	0.0586	0.0411
no. of reflections used	3853	3648	3738
no. of restraints	1	1	14
no. of parameters	197	201	195
S[a]	1.061	0.986	1.041
weight parameters *a*/*b*[b]	0.0388/0.1601	0.0502/0.0000	0.0644/0.2725
*R*1[c] [$I > 2\sigma(I)$]	0.0257	0.0310	0.0398
*wR*2[d] (all data)	0.0627	0.0782	0.1096
absolute structure parameter	–0.03(4)	–0.018(7)	
max./min. res. el. dens., e Å^{-3}	+0.246/–0.134	+0.549/–0.363	+0.293/–0.227

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{0.5}$; *n* = no. of reflections; *p* = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2] / 3$. [c] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$.

Table 3. Crystal data and experimental parameters for the crystal structure analyses of *rac*-**15**, *rac*-**15**·HCl, and **21a**.

	rac-**15**	*rac*-**15**·HCl	**21a**
empirical formula	$C_{15}H_{25}NOSi$	$C_{15}H_{26}ClNOSi$	$C_{24}H_{28}O_2$
formula mass, g mol^{-1}	263.45	299.91	348.46
collection T, K	173(2)	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic
space group (no.)	$P2_1/n$ (14)	$P2_1/n$ (14)	$P\bar{1}$ (2)
a, Å	11.9830(10)	6.0012(5)	5.8732(12)
b, Å	11.1445(10)	26.724(3)	9.3259(19)
c, Å	23.160(2)	10.7674(9)	18.156(4)
α, deg	90	90	98.96(3)
β, deg	99.162(11)	103.940(9)	94.03(3)
γ, deg	90	90	98.87(3)
V, Å^3	3053.5(5)	1676.0(3)	966.0(3)
Z	8	4	2
D(calcd), g cm^{-3}	1.146	1.189	1.198
μ, mm^{-1}	0.144	0.293	0.074
F(000)	1152	648	376
cryst. dimens., mm	0.5 × 0.5 × 0.3	0.5 × 0.4 × 0.2	0.5 × 0.4 × 0.2
2θ range, deg	5.02–54.16	4.94–53.92	4.48–56.02
index ranges	$-15 \le h \le 15$,	$-7 \le h \le 7$,	$-7 \le h \le 7$,
	$-14 \le k \le 14$,	$-34 \le k \le 34$,	$-12 \le k \le 12$,
	$-29 \le l \le 19$	$-13 \le l \le 13$	$-23 \le l \le 23$
no. of coll. reflns.	17801	14764	12700
no. of indep. reflns.	6592	3483	4306
R_{int}	0.0441	0.0515	0.0370
no. of reflections used	6592	3483	4306
no. of parameters	331	178	243
S^a	1.016	1.040	0.993
weight parameters a/b^b	0.0572/0.4079	0.0551/0.4269	0.0754/0.0000
$R1^c$ [$I > 2\sigma(I)$]	0.0391	0.0355	0.0407
$wR2^d$ (all data)	0.1063	0.0972	0.1152
max./min. res. el. dens., e Å^{-3}	+0.272/–0.315	+0.307/–0.361	+0.267/–0.193

$^a S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. $^b w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2] / 3$. $^c R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $^d wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$.

Table 4. Crystal data and experimental parameters for the crystal structure analyses of **21b**, **22b**, and **61**.

	21b	**22b**	**61**
empirical formula	$C_{22}H_{28}O_2Si_2$	$C_{28}H_{37}NO_5Si_2$	$C_{15}H_{24}O_4Si$
formula mass, g mol^{-1}	380.62	523.77	296.43
collection T, K	173(2)	243(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
crystal system	triclinic	monoclinic	orthorhombic
space group (no.)	$P\bar{1}$ (2)	$C2/c$ (15)	$P2_12_12_1$ (19)
a, Å	6.1056(10)	46.264(5)	6.7418(6)
b, Å	13.279(2)	9.5779(7)	12.8308(14)
c, Å	13.314(2)	13.6161(17)	18.615(3)
α, deg	97.06(2)	90	90
β, deg	94.99(2)	91.347(14)	90
γ, deg	95.04(2)	90	90
V, Å^3	1061.9(3)	6031.7(11)	1610.3(3)
Z	2	8	4
D(calcd), g cm^{-3}	1.190	1.154	1.223
μ, mm^{-1}	0.180	0.152	0.156
F(000)	408	2240	640
cryst. dimens., mm	0.5 × 0.2 × 0.1	0.5 × 0.3 × 0.1	0.5 × 0.15 × 0.07
2θ range, deg	4.66–56.06	5.00–55.94	5.40–52.74
index ranges	$-7 \le h \le 7$,	$-60 \le h \le 60$,	$-8 \le h \le 7$,
	$-17 \le k \le 17$,	$-11 \le k \le 11$,	$-16 \le k \le 15$,
	$-17 \le l \le 17$	$-17 \le l \le 17$	$-21 \le l \le 23$
no. of coll. reflns.	13959	28091	7361
no. of indep. reflns.	4735	6789	3241
R_{int}	0.0406	0.0706	0.0475
absorption correction	numerical	none	none
max./min. transmission	0.9726/0.9108		
no. of reflections used	4735	6789	3241
no. of parameters	243	336	185
S^a	1.061	0.918	0.914
weight parameters a/b^b	0.0546/0.2327	0.0589/0.0000	0.0305/0.0000
$R1^c$ [$I > 2\sigma(I)$]	0.0349	0.0448	0.0354
$wR2^d$ (all data)	0.0985	0.1146	0.0710
absolute structure parameter			0.06(14)
max./min. res. el. dens., e Å^{-3}	+0.394/–0.272	+0.236/–0.243	+0.185 /–0.191

$^a S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. $^b w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2] / 3$. $^c R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $^d wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$.

Table 5. Crystal data and experimental parameters for the crystal structure analyses of **62**, **74**, and **75**.

	62	**74**	**75**
empirical formula	$C_{23}H_{30}O_4Si$	$C_{13}H_{20}O_4Si$	$C_{21}H_{26}O_4Si$
formula mass, g mol^{-1}	398.56	268.38	370.51
collection T, K	173(2)	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
crystal system	triclinic	monoclinic	monoclinic
space group (no.)	$P\bar{1}$ (2)	$P2_1/n$ (14)	$P2_1/n$ (14)
a, Å	8.3831(12)	7.1214(14)	12.3183(15)
b, Å	9.2713(12)	16.462(3)	7.3965(11)
c, Å	28.720(4)	11.891(2)	21.489(3)
α, deg	95.090(16)	90	90
β, deg	95.010(17)	97.78(3)	97.044(15)
γ, deg	100.338(16)	90	90
V, Å^3	2175.1(5)	1381.2(5)	1943.1(4)
Z	4	4	4
D(calcd), g cm^{-3}	1.217	1.291	1.267
μ, mm^{-1}	0.133	0.174	0.144
F(000)	856	576	792
cryst. dimens., mm	0.4 × 0.4 × 0.4	0.4 × 0.3 × 0.2	0.5 × 0.5 × 0.3
2θ range, deg	5.02–56.04	4.26–53.96	5.82–52.84
index ranges	$-11 \le h \le 11$,	$-9 \le h \le 9$,	$-15 \le h \le 15$,
	$-12 \le k \le 11$,	$-20 \le k \le 20$,	$-9 \le k \le 9$,
	$-37 \le l \le 37$	$-15 \le l \le 15$	$-26 \le l \le 26$
no. of coll. reflns.	20546	19626	26008
no. of indep. reflns.	9605	2968	3959
R_{int}	0.0700	0.1643	0.0483
no. of reflections used	9605	2968	3959
no. of parameters	513	167	239
S^a	1.083	1.030	1.058
weight parameters a/b^b	0.0452/1.0800	0.0845/0.3400	0.0627/0.4654
$R1^c$ [$I > 2\sigma(I)$]	0.0501	0.0502	0.0376
$wR2^d$ (all data)	0.1376	0.1436	0.1073
max./min. res. el. dens., e Å^{-3}	+0.386/–0.299	0.329/–0.394	+0.317/–0.232

$^a S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. $^b w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2] / 3$. $^c R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $^d wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$.

Table 6. Crystal data and experimental parameters for the crystal structure analyses of **89**, **99**, and **103**.

	89	**99**	**103**
empirical formula	$C_{23}H_{30}O_2Si_2$	$C_{19}H_{26}O_3Si_2$	$C_{12}H_{17}Cl_3O_3Si$
formula mass, g mol^{-1}	394.65	358.58	343.70
collection T, K	173(2)	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic
space group (no.)	$P2_1/c$ (14)	$C2/c$ (15)	$P\bar{1}$ (2)
a, Å	15.398(2)	29.567(2)	7.8786(12)
b, Å	24.713(4)	5.9168(4)	8.0041(11)
c, Å	5.9517(7)	24.3353(19)	12.4129(19)
α, deg	90	90	92.665(17)
β, deg	95.485(16)	110.810(8)	90.158(18)
γ, deg	90	90	93.517(17)
V, Å^3	2254.5(5)	3979.6(5)	780.4(2)
Z	4	8	2
D(calcd), g cm^{-3}	1.163	1.197	1.463
μ, mm^{-1}	0.172	0.191	0.664
F(000)	848	1536	356
cryst. dimens., mm	0.4 × 0.2 × 0.1	0.5 × 0.3 × 0.1	0.3 × 0.3 × 0.1
2θ range, deg	4.24–49.54	5.70–55.96	5.18–54.00
index ranges	$-18 \le h \le 18$,	$-38 \le h \le 38$,	$-10 \le h \le 9$,
	$-29 \le k \le 28$,	$-7 \le k \le 7$,	$-10 \le k \le 9$,
	$-6 \le l \le 6$	$-31 \le l \le 31$	$-15 \le l \le 15$
no. of coll. reflns.	11326	12731	5891
no. of indep. reflns.	3822	4718	3095
R_{int}	0.0463	0.0314	0.0226
no. of reflections used	3822	4718	3095
no. of restraints			7
no. of parameters	250	225	186
S^a	0.915	0.959	1.053
weight parameters a/b^b	0.0475/0.0000	0.0612/0.0000	0.0614/0.1586
$R1^c$ [$I > 2\sigma(I)$]	0.0342	0.0348	0.0353
$wR2^d$ (all data)	0.0831	0.0920	0.1007
max./min. res. el. dens., e Å^{-3}	+0.221/–0.143	+0.267/–0.299	+0.322/–0.332

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2] / 3$. [c] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$.

Table 7. Crystal data and experimental parameters for the crystal structure analyses of **104**, **145**·2H_2O, and **146**.

	104	**145**·2H_2O	**146**
empirical formula	$C_{18}H_{22}Cl_2O_6Si$	$C_{12}H_{34}Cl_2N_2O_3Si_2$	$C_{24}H_{34}O_7Si_2$
formula mass, g mol^{-1}	433.35	381.49	490.69
collection T, K	173(2)	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	orthorhombic
space group (no.)	$C2/c$ (15)	$P2_1/c$ (14)	$Pbcn$ (60)
a, Å	23.184(3)	16.5887(19)	13.1773(10)
b, Å	13.2630(10)	6.6154(6)	17.5456(14)
c, Å	13.889(2)	19.072(2)	10.7724(11)
β, deg	111.460(13)	103.955(14)	90
V, Å^3	3974.6(8)	2031.2(4)	2490.6(4)
Z	8	4	4
D(calcd), g cm^{-3}	1.448	1.248	1.309
μ, mm^{-1}	0.419	0.447	0.184
F(000)	1808	824	1048
cryst. dimens., mm	0.5 × 0.5 × 0.3	0.5 × 0.2 × 0.2	0.3 × 0.3 × 0.3
2θ range, deg	4.30–54.04	4.52–55.96	5.98–53.98
index ranges	$-29 \le h \le 29$,	$-21 \le h \le 21$,	$-16 \le h \le 16$,
	$-16 \le k \le 13$,	$-8 \le k \le 8$,	$-22 \le k \le 22$,
	$-17 \le l \le 17$	$-25 \le l \le 25$	$-10 \le l \le 13$
no. of coll. reflns.	12695	17341	10791
no. of indep. reflns.	4232	4847	2685
R_{int}	0.0435	0.0379	0.0281
no. of reflections used	4232	4847	2685
no. of parameters	250	220	153
S^a	1.048	0.974	1.055
weight parameters a/b^b	0.0484/2.1053	0.0537/0.0000	0.0585/0.4817
$R1^c$ [$I > 2\sigma(I)$]	0.0309	0.0287	0.0338
$wR2^d$ (all data)	0.0858	0.0757	0.0961
max./min. res. el. dens., e Å^{-3}	+0.333/–0.258	+0.408/–0.415	+0.304/–0.232

$^a S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. $^b w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2] / 3$. $^c R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $^d wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$.

Table 8. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for *rac*-**12b**·HCl. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
C1	908(1)	4230(1)	2425(2)	29(1)	C12	–1906(1)	2901(1)	4368(2)	28(1)
C2	1551(1)	4943(1)	1596(2)	32(1)	C13	–2430(1)	2494(1)	3290(2)	24(1)
C3	2697(1)	4974(1)	2020(2)	34(1)	C14	–1883(1)	1943(1)	2360(2)	24(1)
C4	3294(1)	4069(1)	1717(2)	31(1)	C15	–816(1)	1829(1)	2488(1)	22(1)
C5	2912(1)	3223(1)	2560(2)	24(1)	C16	–4080(1)	3100(1)	4003(2)	40(1)
C6	916(1)	2210(1)	3627(1)	20(1)	O1	1250(1)	2666(1)	760(1)	36(1)
C7	1376(1)	1235(1)	3426(1)	20(1)	O2	–3476(1)	2579(1)	3040(1)	33(1)
C9	1447(1)	–433(1)	4027(2)	29(1)	N	978(1)	494(1)	4395(1)	20(1)
C8	1160(1)	725(1)	5851(2)	28(1)	Si	1490(1)	3039(1)	2299(1)	20(1)
C10	–268(1)	2255(1)	3553(1)	19(1)	Cl	–1076(1)	–573(1)	4812(1)	35(1)
C11	–833(1)	2775(1)	4493(1)	25(1)					

Table 9. Bond lengths (Å) and angles (deg) for *rac*-**12b**·HCl.

C1–C2	1.539(2)	C16–O2	1.429(2)	O2–C13–C14	115.27(13)
C1–Si	1.8549(14)	O1–Si	1.6286(12)	C12–C13–C14	119.47(13)
C2–C3	1.529(2)	N–HN	0.863(18)	C15–C14–C13	120.32(14)
C3–C4	1.526(2)			C14–C15–C10	121.05(12)
C4–C5	1.5386(19)	C2–C1–Si	110.46(10)	C13–O2–C16	117.36(13)
C5–Si	1.8610(14)	C3–C2–C1	113.04(12)	HN–N–C8	106.4(11)
C6–C7	1.5191(18)	C4–C3–C2	113.91(13)	HN–N–C9	102.8(11)
C6–C10	1.5211(17)	C3–C4–C5	113.23(12)	C8–N–C9	111.40(12)
C6–Si	1.9041(14)	C4–C5–Si	110.38(10)	HN–N–C7	113.2(11)
C7–N	1.5068(17)	C7–C6–C10	114.83(11)	C8–N–C7	113.47(11)
C9–N	1.4917(18)	C7–C6–Si	108.96(9)	C9–N–C7	109.13(11)
C8–N	1.484(2)	C10–C6–Si	109.14(9)	O1–Si–C1	106.38(7)
C10–C11	1.3867(19)	N–C7–C6	115.06(11)	O1–Si–C5	110.98(7)
C10–C15	1.3967(19)	C11–C10–C15	117.68(12)	C1–Si–C5	104.93(7)
C11–C12	1.3942(19)	C11–C10–C6	120.82(12)	O1–Si–C6	111.08(6)
C12–C13	1.380(2)	C15–C10–C6	121.35(12)	C1–Si–C6	111.31(7)
C13–O2	1.3695(17)	C10–C11–C12	121.77(13)	C5–Si–C6	111.88(6)
C13–C14	1.392(2)	C13–C12–C11	119.65(13)		
C14–C15	1.3840(18)	O2–C13–C12	125.25(13)		

Table 10. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (*R*)-**12b**·HBr. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
C1	–1352(5)	–396(4)	8740(2)	40(1)	C13	4674(4)	–4046(3)	7590(2)	26(1)
C2	–1252(6)	451(5)	9661(3)	53(1)	C14	5361(4)	–2895(3)	7228(3)	35(1)
C3	863(7)	633(5)	10095(3)	63(1)	C15	4059(4)	–1902(3)	6969(2)	33(1)
C4	2282(6)	1346(6)	9457(3)	55(1)	C10	1986(4)	–2045(3)	7063(2)	21(1)
C5	2715(5)	637(4)	8513(2)	40(1)	C16	5456(6)	–6205(4)	8106(3)	45(1)
C6	531(4)	–955(3)	6783(2)	21(1)	Br	6002(1)	1479(1)	5607(1)	36(1)
C7	991(4)	–273(3)	5842(2)	21(1)	N	934(3)	–1159(3)	4964(2)	24(1)
C8	–1085(4)	–1719(3)	4760(3)	33(1)	O1	–546(4)	1639(3)	7375(2)	41(1)
C9	1589(5)	–416(3)	4111(2)	37(1)	O2	6124(3)	–4959(2)	7815(2)	36(1)
C11	1322(4)	–3204(3)	7432(2)	24(1)	Si	317(1)	264(1)	7821(1)	24(1)
C12	2628(4)	–4218(3)	7693(2)	26(1)					

Table 11. Bond lengths (Å) and angles (deg) for (*R*)-**12b**·HBr.

C1–C2	1.534(5)	C14–C15	1.375(4)	O2–C13–C12	124.8(3)
C1–Si	1.845(3)	C15–C10	1.395(4)	C14–C13–C12	119.4(3)
C2–C3	1.510(6)	C16–O2	1.423(4)	C13–C14–C15	121.5(3)
C3–C4	1.506(7)	O1–Si	1.637(3)	C14–C15–C10	120.5(3)
C4–C5	1.525(5)			C11–C10–C15	117.2(3)
C5–Si	1.854(3)	C2–C1–Si	110.3(3)	C11–C10–C6	121.6(2)
C6–C7	1.514(4)	C3–C2–C1	113.6(3)	C15–C10–C6	121.1(2)
C6–C10	1.518(4)	C4–C3–C2	115.1(3)	C8–N–C9	110.5(2)
C6–Si	1.909(3)	C3–C4–C5	114.0(4)	C8–N–C7	112.2(2)
C7–N	1.511(4)	C4–C5–Si	110.1(2)	C9–N–C7	108.6(2)
C8–N	1.473(4)	C7–C6–C10	114.1(2)	C13–O2–C16	117.4(3)
C9–N	1.481(4)	C7–C6–Si	110.7(2)	O1–Si–C1	111.38(15)
C11–C10	1.379(4)	C10–C6–Si	111.57(18)	O1–Si–C5	106.75(16)
C11–C12	1.394(4)	N–C7–C6	113.5(2)	C1–Si–C5	104.72(16)
C12–C13	1.382(4)	C10–C11–C12	122.7(2)	O1–Si–C6	109.18(12)
C13–O2	1.370(3)	C13–C12–C11	118.6(3)	C1–Si–C6	109.49(15)
C13–C14	1.373(5)	O2–C13–C14	115.8(2)	C5–Si–C6	115.26(13)

Table 12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for *rac*-**13**. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
C9	2797(1)	–743(1)	3103(1)	24(1)	C2	1308(3)	1185(6)	5851(5)	80(2)
C5	3534(1)	–491(1)	4277(1)	25(1)	C3	1306(2)	1655(4)	4504(5)	83(2)
C6	3897(1)	–1618(1)	5111(1)	26(1)	C4	2331(2)	1969(2)	4383(2)	53(1)
C12	1407(1)	–1096(1)	906(1)	28(1)	C1A	2092(1)	161(2)	6179(2)	51(1)
C10	2881(1)	–167(1)	1965(1)	27(1)	C2A	1155(8)	751(11)	5575(16)	67(4)
C11	2197(1)	–333(1)	873(1)	29(1)	C3A	1441(7)	2045(9)	5190(14)	56(3)
C14	1983(1)	–1496(1)	3112(1)	30(1)	C4A	2331(2)	1969(2)	4383(2)	53(1)
C13	1303(1)	–1678(1)	2037(1)	32(1)	N	4583(1)	–2447(1)	4606(1)	27(1)
C15	695(1)	–625(2)	–1220(1)	40(1)	O1	3983(1)	1232(1)	6341(1)	36(1)
C7	4093(1)	–3263(1)	3602(1)	36(1)	O2	692(1)	–1340(1)	–104(1)	37(1)
C8	5103(1)	–3217(1)	5636(2)	38(1)	Si	3072(1)	732(1)	5317(1)	29(1)
C1	2092(1)	161(2)	6179(2)	51(1)					

Table 13. Bond lengths (Å) and angles (deg) for *rac*-**13**.

C9–C10	1.3903(17)	C1–Si	1.8834(18)	O2–C12–C13	115.59(12)
C9–C14	1.3994(18)	C2–C3	1.530(6)	C11–C12–C13	119.34(13)
C9–C5	1.5122(18)	C3–C4	1.503(4)	C9–C10–C11	122.11(12)
C5–C6	1.5377(17)	C4–Si	1.8683(17)	C12–C11–C10	119.66(12)
C5–Si	1.9056(13)	C2A–C3A	1.521(12)	C13–C14–C9	121.64(12)
C6–N	1.4783(17)	O1–Si	1.6286(11)	C14–C13–C12	120.29(13)
C12–O2	1.3716(17)			C2–C1–Si	101.9(3)
C12–C11	1.382(2)	C10–C9–C14	116.96(12)	C3–C2–C1	109.5(3)
C12–C13	1.3932(19)	C10–C9–C5	120.27(12)	C4–C3–C2	107.9(3)
C10–C11	1.3946(19)	C14–C9–C5	122.67(11)	C3–C4–Si	104.30(19)
C14–C13	1.381(2)	C9–C5–C6	117.16(10)	C7–N–C8	109.17(11)
C15–O2	1.4220(18)	C9–C5–Si	111.00(9)	C7–N–C6	112.05(11)
C7–N	1.4651(18)	C6–C5–Si	108.22(8)	C8–N–C6	109.48(11)
C8–N	1.4699(17)	N–C6–C5	115.58(10)	C12–O2–C15	117.14(12)
C1–C2	1.552(5)	O2–C12–C11	125.08(12)	O1–Si–C4	115.45(7)

O1–Si–C1	109.30(7)	O1–Si–C5	108.39(6)	C1–Si–C5	114.37(7)
C4–Si–C1	96.22(10)	C4–Si–C5	112.83(7)		

Table 14. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for *rac*-**15** (molecules A and B). U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
C1	8026(2)	7519(1)	61(1)	34(1)	C21	3046(1)	10522(1)	1415(1)	34(1)
C2	9046(2)	6677(2)	151(1)	40(1)	C22	4005(2)	10597(2)	1934(1)	44(1)
C3	8794(2)	5468(2)	409(1)	45(1)	C23	3703(2)	10065(2)	2493(1)	49(1)
C4	8509(2)	5530(2)	1025(1)	38(1)	C24	3481(2)	8726(2)	2463(1)	47(1)
C5	7408(1)	6205(1)	1061(1)	32(1)	C25	2409(2)	8404(2)	2035(1)	39(1)
C6	8507(1)	8674(1)	1277(1)	25(1)	C26	3536(1)	8041(1)	945(1)	28(1)
C10	8202(1)	8574(1)	1881(1)	25(1)	C30	3543(1)	6752(1)	1137(1)	32(1)
C11	8782(1)	7789(1)	2287(1)	30(1)	C31	4515(2)	6261(2)	1459(1)	46(1)
C12	8465(2)	7616(2)	2827(1)	36(1)	C32	4540(3)	5071(2)	1624(1)	67(1)
C13	7568(2)	8244(2)	2983(1)	39(1)	C33	3607(3)	4361(2)	1482(1)	72(1)
C14	6986(2)	9035(2)	2587(1)	41(1)	C34	2629(2)	4845(2)	1176(1)	59(1)
C15	7288(1)	9192(2)	2044(1)	34(1)	C35	2596(2)	6030(2)	1006(1)	41(1)
C7	8580(1)	9944(1)	1031(1)	29(1)	C27	3375(1)	8226(1)	282(1)	28(1)
C8	9919(1)	10762(2)	1824(1)	36(1)	C28	4329(2)	6540(1)	–109(1)	40(1)
C9	9739(2)	11613(2)	866(1)	41(1)	C29	4348(2)	8453(2)	–549(1)	38(1)
N1	9692(1)	10507(1)	1198(1)	28(1)	N21	4341(1)	7827(1)	5(1)	26(1)
O1	6287(1)	8490(1)	683(1)	35(1)	O21	1281(1)	8948(1)	852(1)	40(1)
Si1	7464(1)	7748(1)	760(1)	25(1)	Si21	2487(1)	8970(1)	1289(1)	27(1)

Table 15. Bond lengths (Å) and angles (deg) for *rac*-**15** (molecules A and B).

C1–C2	1.529(2)	C26–C27	1.531(2)	C12–C13–C14	118.95(17)
C1–Si1	1.8655(17)	C26–Si21	1.8988(15)	C15–C14–C13	120.68(16)
C2–C3	1.524(2)	C30–C35	1.384(3)	C14–C15–C10	121.18(15)
C3–C4	1.519(2)	C30–C31	1.391(2)	N1–C7–C6	113.61(12)
C4–C5	1.533(2)	C31–C32	1.379(3)	C9–N1–C8	110.07(14)
C5–Si1	1.8608(16)	C32–C33	1.367(4)	C9–N1–C7	109.35(13)
C6–C10	1.505(2)	C33–C34	1.379(4)	C8–N1–C7	111.26(12)
C6–C7	1.534(2)	C34–C35	1.377(3)	O1–Si1–C5	115.47(7)
C6–Si1	1.8931(15)	C27–N21	1.4784(19)	O1–Si1–C1	113.78(7)
C10–C11	1.387(2)	C28–N21	1.458(2)	C5–Si1–C1	103.76(7)
C10–C15	1.396(2)	C29–N21	1.460(2)	O1–Si1–C6	105.45(6)
C11–C12	1.378(2)	O21–Si21	1.6259(12)	C5–Si1–C6	109.03(7)
C12–C13	1.378(2)			C1–Si1–C6	109.26(7)
C13–C14	1.379(3)	C2–C1–Si1	110.99(11)	C22–C21–Si21	112.40(12)
C14–C15	1.375(3)	C3–C2–C1	113.03(15)	C23–C22–C21	113.44(15)
C7–N1	1.4679(19)	C4–C3–C2	114.65(15)	C24–C23–C22	114.22(16)
C8–N1	1.459(2)	C3–C4–C5	113.42(15)	C23–C24–C25	112.50(15)
C9–N1	1.458(2)	C4–C5–Si1	110.50(11)	C24–C25–Si21	111.13(13)
O1–Si1	1.6200(11)	C10–C6–C7	116.70(12)	C30–C26–C27	114.80(13)
C21–C22	1.528(2)	C10–C6–Si1	108.29(10)	C30–C26–Si21	111.70(11)
C21–Si21	1.8609(16)	C7–C6–Si1	109.87(10)	C27–C26–Si21	111.18(10)
C22–C23	1.518(3)	C11–C10–C15	117.22(15)	C35–C30–C31	118.44(17)
C23–C24	1.515(3)	C11–C10–C6	120.44(13)	C35–C30–C26	121.64(15)
C24–C25	1.536(3)	C15–C10–C6	122.19(13)	C31–C30–C26	119.91(16)
C25–Si21	1.8560(18)	C12–C11–C10	121.53(15)	C32–C31–C30	120.4(2)
C26–C30	1.504(2)	C11–C12–C13	120.41(16)	C33–C32–C31	120.6(2)

C32–C33–C34	119.6(2)	C28–N21–C27	112.86(13)	O21–Si21–C26	108.25(7)
C35–C34–C33	120.4(2)	C29–N21–C27	110.55(12)	C25–Si21–C26	109.87(7)
C34–C35–C30	120.6(2)	O21–Si21–C25	113.66(8)	C21–Si21–C26	109.09(7)
N21–C27–C26	114.35(12)	O21–Si21–C21	111.95(7)		
C28–N21–C29	108.25(13)	C25–Si21–C21	103.91(8)		

Table 16. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for *rac*-**15**·HCl. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Si	6527(1)	1075(1)	6931(1)	22(1)	C9	666(3)	881(1)	2941(2)	33(1)
Cl	959(1)	2183(1)	8373(1)	34(1)	C12	4749(3)	1399(1)	3703(1)	28(1)
O	9004(2)	1269(1)	6735(1)	32(1)	C14	1328(3)	2420(1)	5057(2)	33(1)
N	3261(2)	2412(1)	6208(1)	23(1)	C11	4037(3)	1216(1)	2464(1)	33(1)
C6	4192(3)	1498(1)	5959(1)	21(1)	C15	4292(3)	2919(1)	6465(1)	31(1)
C13	5078(2)	2036(1)	6140(1)	22(1)	C2	4368(3)	764(1)	8848(2)	37(1)
C7	3412(3)	1325(1)	4582(1)	22(1)	C4	4105(4)	185(1)	6917(2)	40(1)
C8	1360(3)	1064(1)	4180(1)	28(1)	C3	4444(4)	229(1)	8368(2)	42(1)
C1	6340(3)	1092(1)	8630(1)	30(1)	C10	2003(3)	957(1)	2080(1)	33(1)
C5	6061(3)	415(1)	6428(1)	32(1)					

Table 17. Bond lengths (Å) and angles (deg) for *rac*-**15**·HCl.

Si–O	1.6348(12)	C11–C10	1.377(2)	C7–C6–Si	111.69(9)
Si–C5	1.8481(15)	C2–C3	1.524(2)	C13–C6–Si	107.48(9)
Si–C1	1.8602(15)	C4–C3	1.531(2)	N–C13–C6	113.74(12)
Si–C6	1.9041(14)			C8–C7–C12	118.10(13)
N–HN	0.929(19)	O–Si–C5	110.04(7)	C8–C7–C6	119.94(13)
N–C14	1.4798(19)	O–Si–C1	113.03(7)	C12–C7–C6	121.89(13)
N–C15	1.4863(18)	C5–Si–C1	105.73(7)	C9–C8–C7	120.95(15)
N–C13	1.4984(17)	O–Si–C6	108.25(6)	C2–C1–Si	111.57(10)
C6–C7	1.5155(17)	C5–Si–C6	111.47(7)	C4–C5–Si	110.93(11)
C6–C13	1.5293(18)	C1–Si–C6	108.34(7)	C10–C9–C8	120.37(16)
C7–C8	1.390(2)	HN–N–C14	106.9(12)	C11–C12–C7	120.57(15)
C7–C12	1.394(2)	HN–N–C15	107.7(11)	C10–C11–C12	120.68(15)
C8–C9	1.388(2)	C14–N–C15	110.55(12)	C3–C2–C1	113.39(15)
C1–C2	1.537(2)	HN–N–C13	107.6(11)	C5–C4–C3	113.42(15)
C5–C4	1.526(2)	C14–N–C13	113.64(11)	C2–C3–C4	114.23(13)
C9–C10	1.379(2)	C15–N–C13	110.20(12)	C11–C10–C9	119.33(14)
C12–C11	1.388(2)	C7–C6–C13	115.29(11)		

Table 18. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **21a**. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
C01	12685(2)	5355(1)	2033(1)	22(1)	C5	11074(3)	2979(1)	80(1)	32(1)
C02	12717(2)	2801(1)	741(1)	23(1)	C6	13868(3)	1454(1)	504(1)	35(1)
O1	11151(2)	–3835(1)	4476(1)	36(1)	C7	11352(2)	2631(1)	1417(1)	20(1)
O2	7829(2)	–3802(1)	5007(1)	38(1)	C8	11425(2)	3777(1)	2022(1)	20(1)
C1	10948(3)	6422(1)	2142(1)	32(1)	C9	10268(2)	3469(1)	2642(1)	22(1)
C2	14618(3)	5783(1)	2679(1)	31(1)	C10	8940(2)	2103(1)	2667(1)	21(1)
C3	13730(2)	5506(1)	1289(1)	28(1)	C11	8695(2)	997(1)	2029(1)	24(1)
C4	14659(2)	4141(1)	957(1)	28(1)	C12	9932(2)	1287(1)	1433(1)	24(1)

C13	7086(3)	–456(1)	1969(1)	34(1)	C18	10640(2)	–1267(1)	3898(1)	24(1)
C14	7809(2)	1858(1)	3359(1)	23(1)	C19	8985(2)	–1941(1)	4303(1)	23(1)
C15	6502(3)	2782(1)	3670(1)	37(1)	C20	6974(2)	–1363(1)	4410(1)	25(1)
C16	8256(2)	558(1)	3700(1)	21(1)	C21	6616(2)	–125(1)	4112(1)	24(1)
C17	10277(2)	–28(1)	3600(1)	24(1)	C22	9420(2)	–3278(1)	4604(1)	26(1)

Table 19. Bond lengths (Å) and angles (deg) for **21a**.

C01–C1	1.5331(18)	C18–C19	1.3914(17)	C8–C7–C02	122.67(10)
C01–C2	1.5332(19)	C19–C20	1.3854(18)	C11–C12–C7	123.86(10)
C01–C8	1.5380(15)	C19–C22	1.4862(17)	C12–C11–C10	117.95(10)
C01–C3	1.5407(16)	C20–C21	1.3878(17)	C12–C11–C13	119.64(11)
C02–C7	1.5281(16)			C10–C11–C13	122.38(11)
C02–C5	1.532(2)	C1–C01–C2	109.05(10)	C9–C10–C11	118.42(10)
C02–C6	1.5347(18)	C1–C01–C8	109.18(10)	C9–C10–C14	119.59(10)
C02–C4	1.5367(18)	C2–C01–C8	110.27(10)	C11–C10–C14	121.99(10)
O1–C22	1.2309(16)	C1–C01–C3	107.85(10)	C10–C9–C8	123.13(10)
O2–H2	0.89(2)	C2–C01–C3	109.28(11)	C15–C14–C16	121.28(11)
O2–C22	1.3088(16)	C8–C01–C3	111.16(9)	C15–C14–C10	121.22(11)
C4–C3	1.5170(18)	C7–C02–C5	109.37(11)	C16–C14–C10	117.48(10)
C8–C7	1.4005(15)	C7–C02–C6	111.60(10)	C17–C16–C21	118.33(10)
C8–C9	1.4006(16)	C5–C02–C6	108.38(11)	C17–C16–C14	121.19(10)
C7–C12	1.3996(16)	C7–C02–C4	108.79(9)	C21–C16–C14	120.46(11)
C12–C11	1.3825(17)	C5–C02–C4	111.44(10)	C18–C17–C16	120.71(11)
C11–C10	1.4089(16)	C6–C02–C4	107.28(12)	C17–C18–C19	120.32(12)
C11–C13	1.5114(16)	H2–O2–C22	109.2(13)	C20–C19–C18	119.55(11)
C10–C9	1.3962(16)	C3–C4–C02	111.57(11)	C20–C19–C22	121.71(11)
C10–C14	1.4949(16)	C4–C3–C01	112.70(10)	C18–C19–C22	118.74(12)
C14–C15	1.3278(19)	C7–C8–C9	118.06(10)	C19–C20–C21	120.00(11)
C14–C16	1.4928(16)	C7–C8–C01	123.39(10)	C20–C21–C16	121.10(12)
C16–C17	1.3928(18)	C9–C8–C01	118.55(10)	O1–C22–O2	123.55(11)
C16–C21	1.3974(16)	C12–C7–C8	118.16(10)	O1–C22–C19	121.68(11)
C17–C18	1.3888(17)	C12–C7–C02	119.16(10)	O2–C22–C19	114.77(12)

Table 20. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **21b**. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Si1	11599(1)	4971(1)	2132(1)	20(1)	C10	7251(2)	2451(1)	886(1)	19(1)
Si2	12501(1)	3135(1)	3756(1)	23(1)	C11	7518(2)	1725(1)	1559(1)	23(1)
O1	10583(2)	194(1)	–3771(1)	35(1)	C12	9107(2)	1968(1)	2391(1)	24(1)
O2	7715(2)	739(1)	–4638(1)	38(1)	C13	6126(3)	710(1)	1394(1)	34(1)
C1	13442(3)	5060(1)	1092(1)	29(1)	C14	5612(2)	2251(1)	–43(1)	20(1)
C2	9570(3)	5943(1)	2072(1)	32(1)	C15	3532(2)	2445(1)	25(1)	29(1)
C3	13316(3)	5189(1)	3390(1)	28(1)	C16	6423(2)	1850(1)	–1021(1)	20(1)
C4	14510(2)	4245(1)	3604(1)	28(1)	C17	8305(2)	1326(1)	–1017(1)	23(1)
C5	13980(3)	1980(1)	3881(2)	44(1)	C18	9087(2)	934(1)	–1916(1)	25(1)
C6	11007(3)	3431(2)	4909(1)	44(1)	C19	7990(2)	1056(1)	–2848(1)	23(1)
C7	10407(2)	2906(1)	2604(1)	20(1)	C20	6106(3)	1573(1)	–2867(1)	27(1)
C8	10073(2)	3652(1)	1948(1)	19(1)	C21	5339(2)	1970(1)	–1965(1)	25(1)
C9	8520(2)	3390(1)	1093(1)	19(1)	C22	8891(3)	629(1)	–3792(1)	26(1)

Table 21. Bond lengths (Å) and angles (deg) for **21b**.

Si1–C1	1.8665(15)	C18–C19	1.3934(18)	C7–C8–Si1	124.53(9)
Si1–C2	1.8706(15)	C19–C20	1.390(2)	C10–C9–C8	123.10(11)
Si1–C3	1.8735(14)	C19–C22	1.4845(18)	C9–C10–C11	119.04(11)
Si1–C8	1.8877(14)	C20–C21	1.3873(19)	C9–C10–C14	118.92(11)
Si2–C5	1.8640(17)			C11–C10–C14	122.03(11)
Si2–C6	1.8711(17)	C1–Si1–C2	109.49(7)	C12–C11–C10	118.12(12)
Si2–C4	1.8752(16)	C1–Si1–C3	109.32(7)	C12–C11–C13	120.61(12)
Si2–C7	1.8863(14)	C2–Si1–C3	110.39(7)	C10–C11–C13	121.27(12)
O1–C22	1.2269(18)	C1–Si1–C8	108.49(6)	C11–C12–C7	123.41(12)
O2–H2	0.83(2)	C2–Si1–C8	109.59(7)	C15–C14–C16	122.34(12)
O2–C22	1.3121(17)	C3–Si1–C8	109.53(6)	C15–C14–C10	120.00(11)
C3–C4	1.548(2)	C5–Si2–C6	109.30(9)	C16–C14–C10	117.66(11)
C7–C12	1.4015(19)	C5–Si2–C4	110.23(8)	C17–C16–C21	117.92(12)
C7–C8	1.4145(17)	C6–Si2–C4	110.38(8)	C17–C16–C14	119.97(11)
C8–C9	1.4047(17)	C5–Si2–C7	110.58(7)	C21–C16–C14	122.10(12)
C9–C10	1.3929(18)	C6–Si2–C7	108.28(8)	C18–C17–C16	121.30(12)
C10–C11	1.4045(17)	C4–Si2–C7	108.04(6)	C17–C18–C19	120.15(13)
C10–C14	1.5034(17)	H2–O2–C22	106.4(15)	C20–C19–C18	119.36(12)
C11–C12	1.3932(19)	C4–C3–Si1	112.09(9)	C20–C19–C22	122.25(12)
C11–C13	1.5103(19)	C3–C4–Si2	111.65(10)	C18–C19–C22	118.39(13)
C14–C15	1.326(2)	C12–C7–C8	118.40(11)	C21–C20–C19	120.22(12)
C14–C16	1.4871(17)	C12–C7–Si2	119.06(9)	C20–C21–C16	121.04(13)
C16–C17	1.3946(19)	C8–C7–Si2	122.54(10)	O1–C22–O2	123.35(12)
C16–C21	1.4022(17)	C9–C8–C7	117.85(11)	O1–C22–C19	121.95(12)
C17–C18	1.3856(18)	C9–C8–Si1	117.62(9)	O2–C22–C19	114.69(13)

Table 22. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **22b**. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Si1	598(1)	1041(1)	9418(1)	59(1)	C11	1389(1)	3268(2)	10993(1)	33(1)
Si2	496(1)	3613(1)	11201(1)	49(1)	C12	1106(1)	3641(2)	11222(1)	36(1)
O1	2133(1)	1960(1)	9021(1)	29(1)	C13	1639(1)	4021(2)	11488(2)	41(1)
O2	2631(1)	1349(1)	8057(1)	33(1)	C14	1727(1)	1646(2)	10071(1)	35(1)
O3	2687(1)	1641(2)	5877(1)	38(1)	C15	1865(1)	2431(2)	9263(1)	28(1)
O4	3710(1)	2760(2)	5711(1)	63(1)	C16	1790(1)	3527(2)	8696(1)	31(1)
O5	3090(1)	5077(2)	7905(1)	38(1)	C17	2027(1)	3796(2)	8069(1)	30(1)
N	2631(1)	3506(2)	7357(1)	29(1)	C18	2228(1)	2824(2)	8287(1)	26(1)
C1	667(1)	996(6)	8075(3)	122(2)	C19	2515(1)	2477(2)	7896(1)	26(1)
C2	579(1)	–774(3)	9884(3)	94(1)	C20	2901(1)	3322(2)	6888(1)	28(1)
C3	255(1)	1988(4)	9650(3)	85(1)	C21	2930(1)	2348(2)	6141(1)	31(1)
C4	220(1)	2338(4)	10731(2)	80(1)	C22	3201(1)	2127(2)	5718(1)	37(1)
C5	413(1)	5370(3)	10700(3)	85(1)	C23	3434(1)	2903(2)	6061(2)	40(1)
C6	495(1)	3706(5)	12564(2)	95(1)	C24	3409(1)	3909(2)	6780(1)	38(1)
C7	862(1)	3024(2)	10790(1)	37(1)	C25	3141(1)	4116(2)	7190(1)	31(1)
C8	902(1)	1973(2)	10083(1)	38(1)	C26	2689(1)	784(2)	5010(2)	44(1)
C9	1187(1)	1573(2)	9881(1)	38(1)	C27	3769(1)	1608(3)	5099(2)	79(1)
C10	1429(1)	2194(2)	10320(1)	32(1)	C28	3323(1)	5941(3)	8230(2)	47(1)

Table 23. Bond lengths (Å) and angles (deg) for **22b**.

Si1–C2	1.853(4)	C20–C21	1.388(3)	C10–C9–C8	123.25(19)
Si1–C3	1.862(3)	C20–C25	1.398(3)	C9–C10–C11	118.81(16)
Si1–C1	1.863(4)	C21–C22	1.409(2)	C9–C10–C14	118.80(18)
Si1–C8	1.879(2)	C22–C23	1.381(3)	C11–C10–C14	122.37(17)
Si2–C5	1.852(3)	C23–C24	1.380(3)	C10–C11–C12	118.24(17)
Si2–C6	1.858(3)	C24–C25	1.386(2)	C10–C11–C13	122.48(17)
Si2–C4	1.870(3)			C12–C11–C13	119.27(18)
Si2–C7	1.8814(18)	C2–Si1–C3	110.51(16)	C7–C12–C11	123.57(19)
O1–C15	1.3694(19)	C2–Si1–C1	109.0(2)	C15–C14–C10	113.44(16)
O1–C18	1.377(2)	C3–Si1–C1	110.04(18)	C16–C15–O1	110.10(14)
O2–C19	1.225(2)	C2–Si1–C8	108.82(13)	C16–C15–C14	135.12(15)
O3–C21	1.354(2)	C3–Si1–C8	108.50(12)	O1–C15–C14	114.77(15)
O3–C26	1.438(2)	C1–Si1–C8	109.96(14)	C15–C16–C17	106.94(15)
O4–C23	1.382(2)	C5–Si2–C6	108.59(18)	C18–C17–C16	106.27(16)
O4–C27	1.412(3)	C5–Si2–C4	109.54(16)	C17–C18–O1	110.31(14)
O5–C25	1.364(2)	C6–Si2–C4	110.81(16)	C17–C18–C19	134.30(16)
O5–C28	1.425(2)	C5–Si2–C7	110.02(12)	O1–C18–C19	115.37(15)
N–HN	0.85(2)	C6–Si2–C7	109.55(12)	O2–C19–N	124.11(15)
N–C19	1.350(2)	C4–Si2–C7	108.33(11)	O2–C19–C18	121.98(15)
N–C20	1.427(2)	C15–O1–C18	106.36(13)	N–C19–C18	113.91(15)
C3–C4	1.522(4)	C21–O3–C26	118.90(14)	C21–C20–C25	119.49(15)
C7–C12	1.395(3)	C23–O4–C27	118.21(18)	C21–C20–N	120.74(16)
C7–C8	1.408(3)	C25–O5–C28	118.09(15)	C25–C20–N	119.76(16)
C8–C9	1.405(2)	HN–N–C19	123.0(13)	O3–C21–C20	115.94(15)
C9–C10	1.390(3)	HN–N–C20	115.1(14)	O3–C21–C22	123.92(17)
C10–C11	1.393(3)	C19–N–C20	121.26(15)	C20–C21–C22	120.13(17)
C10–C14	1.520(2)	C4–C3–Si1	112.5(2)	C23–C22–C21	118.40(18)
C11–C12	1.398(2)	C3–C4–Si2	112.69(19)	C24–C23–C22	122.53(17)
C11–C13	1.506(3)	C12–C7–C8	118.08(16)	C24–C23–O4	114.09(18)
C14–C15	1.489(2)	C12–C7–Si2	118.37(15)	C22–C23–O4	123.38(19)
C15–C16	1.344(3)	C8–C7–Si2	123.54(14)	C23–C24–C25	118.45(18)
C16–C17	1.430(2)	C9–C8–C7	117.97(17)	O5–C25–C24	123.75(17)
C17–C18	1.344(2)	C9–C8–Si1	118.01(15)	O5–C25–C20	115.31(15)
C18–C19	1.479(2)	C7–C8–Si1	124.00(14)	C24–C25–C20	120.94(18)

Table 24. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **61**. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Si	1468(1)	7853(1)	7671(1)	24(1)	C6	1712(3)	9047(2)	6323(1)	26(1)
O1	–1972(2)	7170(1)	6863(1)	37(1)	C7	–3792(4)	6737(2)	6620(1)	40(1)
O2	–1345(3)	9330(1)	4744(1)	41(1)	C8	–3050(4)	8871(2)	4422(1)	47(1)
O3	3406(3)	9441(1)	6614(1)	35(1)	C9	4318(4)	10315(2)	6270(1)	40(1)
O4	2215(2)	6629(1)	7638(1)	33(1)	C10	–568(4)	8008(2)	8342(1)	36(1)
C1	693(3)	8306(2)	6748(1)	24(1)	C11	182(4)	7848(2)	9116(1)	42(1)
C2	–1034(3)	7902(2)	6448(1)	26(1)	C12	1952(4)	8535(2)	9309(1)	44(1)
C3	–1791(3)	8207(2)	5781(1)	30(1)	C13	3812(4)	8314(2)	8874(1)	40(1)
C4	–738(4)	8949(2)	5398(1)	29(1)	C14	3601(4)	8573(2)	8069(1)	33(1)
C5	1016(3)	9360(2)	5657(1)	29(1)	C15	1004(4)	5726(2)	7696(2)	47(1)

Table 25. Bond lengths (Å) and angles (deg) for **61**.

Si–O4	1.6509(14)	C13–C14	1.541(3)	C6–O3–Si	69.97(10)
Si–C14	1.864(2)			C9–O3–Si	167.11(13)
Si–C10	1.867(2)	O4–Si–C14	104.56(9)	C15–O4–Si	126.69(15)
Si–C1	1.888(2)	O4–Si–C10	110.54(9)	C2–C1–C6	115.60(18)
Si–O1	2.9001(16)	C14–Si–C10	104.35(11)	C2–C1–Si	118.84(15)
Si–O3	3.1189(15)	O4–Si–C1	110.07(8)	C6–C1–Si	125.55(16)
O1–C2	1.371(2)	C14–Si–C1	115.04(10)	O1–C2–C1	114.51(17)
O1–C7	1.421(3)	C10–Si–C1	111.92(10)	O1–C2–C3	121.63(19)
O2–C4	1.374(2)	O4–Si–O1	86.39(7)	C1–C2–C3	123.86(19)
O2–C8	1.424(3)	C14–Si–O1	166.79(8)	C4–C3–C2	117.6(2)
O3–C6	1.362(3)	C10–Si–O1	77.97(8)	O2–C4–C5	115.38(19)
O3–C9	1.431(3)	C1–Si–O1	53.10(7)	O2–C4–C3	123.2(2)
O4–C15	1.421(3)	O4–Si–O3	118.05(7)	C5–C4–C3	121.38(19)
C1–C2	1.392(3)	C14–Si–O3	66.64(7)	C4–C5–C6	119.48(19)
C1–C6	1.415(3)	C10–Si–O3	131.33(8)	O3–C6–C5	122.23(19)
C2–C3	1.398(3)	C1–Si–O3	48.76(7)	O3–C6–C1	115.71(18)
C3–C4	1.385(3)	O1–Si–O3	101.86(4)	C5–C6–C1	122.1(2)
C4–C5	1.382(3)	C2–O1–C7	119.10(17)	C11–C10–Si	111.74(17)
C5–C6	1.385(3)	C2–O1–Si	73.52(10)	C12–C11–C10	113.6(2)
C10–C11	1.540(3)	C7–O1–Si	166.92(13)	C13–C12–C11	114.40(19)
C11–C12	1.526(4)	C4–O2–C8	117.80(18)	C12–C13–C14	113.7(2)
C12–C13	1.519(4)	C6–O3–C9	118.20(17)	C13–C14–Si	110.56(17)

Table 26. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **62** (molecules A and B). U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Si1	1654(1)	3968(1)	1175(1)	27(1)	C21	–1088(2)	211(2)	2291(1)	37(1)
O1	1160(2)	6883(2)	1515(1)	42(1)	C22	153(2)	1362(2)	2214(1)	34(1)
O2	–3166(2)	7453(2)	354(1)	43(1)	C23	–3655(4)	–2124(3)	2384(1)	71(1)
O3	–1186(2)	2987(2)	368(1)	35(1)	Si31	10849(1)	8188(1)	3830(1)	25(1)
O4	–3881(2)	–1105(2)	2051(1)	45(1)	O31	10173(2)	10924(2)	3502(1)	36(1)
C1	38(2)	4953(2)	932(1)	27(1)	O32	6545(2)	12205(2)	4628(1)	41(1)
C2	40(2)	6393(2)	1127(1)	31(1)	O33	8546(2)	7745(2)	4626(1)	33(1)
C3	–999(2)	7282(2)	954(1)	34(1)	O34	4597(2)	2635(2)	2961(1)	40(1)
C4	–2078(2)	6702(2)	561(1)	33(1)	C31	9396(2)	9346(2)	4068(1)	26(1)
C5	–2144(2)	5284(2)	349(1)	31(1)	C32	9278(2)	10655(2)	3875(1)	27(1)
C6	–1125(2)	4420(2)	541(1)	28(1)	C33	8340(2)	11650(2)	4043(1)	31(1)
C7	1821(3)	8398(3)	1600(1)	51(1)	C34	7515(2)	11326(2)	4430(1)	30(1)
C8	–3182(4)	8896(3)	556(1)	76(1)	C35	7599(2)	10049(2)	4643(1)	30(1)
C9	–2104(3)	2471(3)	–74(1)	40(1)	C36	8497(2)	9065(2)	4454(1)	26(1)
C10	3753(2)	5120(2)	1170(1)	35(1)	C37	10810(3)	12413(3)	3449(1)	48(1)
C11	5108(2)	4205(3)	1230(1)	36(1)	C38	6369(4)	13495(3)	4416(1)	68(1)
C12	4844(2)	2850(3)	873(1)	37(1)	C39	7950(3)	7522(3)	5068(1)	38(1)
C13	3349(2)	1684(2)	940(1)	36(1)	C40	11178(2)	6675(2)	4200(1)	30(1)
C14	1733(2)	2196(2)	813(1)	31(1)	C41	12709(2)	6077(2)	4082(1)	33(1)
C15	1330(2)	3518(2)	1793(1)	28(1)	C42	14254(2)	7291(2)	4148(1)	34(1)
C16	2350(2)	4232(3)	2159(1)	39(1)	C43	14268(2)	8390(2)	3785(1)	33(1)
C17	–19(2)	2295(2)	1870(1)	26(1)	C44	12949(2)	9345(2)	3838(1)	32(1)
C18	–1531(2)	2051(2)	1598(1)	32(1)	C45	10121(2)	7286(2)	3211(1)	26(1)
C19	–2788(2)	918(2)	1671(1)	33(1)	C46	10978(2)	7657(2)	2853(1)	34(1)
C20	–2568(2)	–8(2)	2011(1)	32(1)	C47	8666(2)	6063(2)	3128(1)	25(1)

C48	7321(2)	6086(2)	3384(1)	32(1)	C51	7248(2)	3694(2)	2724(1)	37(1)
C49	5970(2)	4946(2)	3310(1)	34(1)	C52	8589(2)	4861(2)	2797(1)	33(1)
C50	5949(2)	3740(2)	2989(1)	30(1)	C53	4632(3)	1319(3)	2673(1)	50(1)

Table 27. Bond lengths (Å) and angles (deg) for **62** (molecules A and B).

Si1–C14	1.881(2)	C31–C36	1.411(2)	C4–C3–C2	117.47(19)
Si1–C1	1.8838(19)	C32–C33	1.396(3)	O2–C4–C3	123.59(19)
Si1–C10	1.8890(19)	C33–C34	1.387(3)	O2–C4–C5	114.72(17)
Si1–C15	1.8903(19)	C34–C35	1.390(3)	C3–C4–C5	121.68(18)
Si1–O1	2.9037(17)	C35–C36	1.388(3)	C6–C5–C4	119.07(17)
Si1–O3	3.1249(15)	C40–C41	1.538(2)	O3–C6–C5	122.28(16)
O1–C2	1.378(2)	C41–C42	1.541(3)	O3–C6–C1	115.38(17)
O1–C7	1.405(3)	C42–C43	1.521(3)	C5–C6–C1	122.34(18)
O2–C4	1.370(2)	C43–C44	1.545(3)	C11–C10–Si1	112.14(15)
O2–C8	1.413(3)	C45–C46	1.338(3)	C12–C11–C10	112.80(16)
O3–C6	1.368(2)	C45–C47	1.495(2)	C11–C12–C13	113.28(16)
O3–C9	1.421(2)	C47–C52	1.387(3)	C14–C13–C12	112.29(18)
O4–C20	1.379(2)	C47–C48	1.401(2)	C13–C14–Si1	110.71(13)
O4–C23	1.426(3)	C52–C51	1.400(3)	C16–C15–C17	119.92(17)
C1–C2	1.401(3)	C51–C50	1.387(3)	C16–C15–Si1	120.30(15)
C1–C6	1.412(2)	C50–C49	1.381(3)	C17–C15–Si1	119.68(13)
C2–C3	1.394(3)	C49–C48	1.390(3)	C22–C17–C18	116.68(17)
C3–C4	1.386(3)			C22–C17–C15	122.11(16)
C4–C5	1.388(3)	C14–Si1–C1	113.44(9)	C18–C17–C15	121.21(17)
C5–C6	1.385(3)	C14–Si1–C10	104.01(9)	C19–C18–C17	121.27(18)
C10–C11	1.542(3)	C1–Si1–C10	110.62(9)	C20–C19–C18	120.58(17)
C11–C12	1.521(3)	C14–Si1–C15	107.52(9)	O4–C20–C19	116.10(17)
C12–C13	1.540(3)	C1–Si1–C15	111.16(8)	O4–C20–C21	124.18(19)
C13–C14	1.539(3)	C10–Si1–C15	109.80(9)	C19–C20–C21	119.71(18)
C15–C16	1.337(3)	C14–Si1–O1	165.60(7)	C20–C21–C22	118.66(19)
C15–C17	1.496(3)	C1–Si1–O1	53.52(6)	C17–C22–C21	123.09(17)
C17–C22	1.383(3)	C10–Si1–O1	78.12(8)	C40–Si31–C44	104.14(9)
C17–C18	1.400(2)	C15–Si1–O1	84.65(7)	C40–Si31–C31	113.09(8)
C18–C19	1.392(3)	C14–Si1–O3	65.49(6)	C44–Si31–C31	110.49(8)
C19–C20	1.379(3)	C1–Si1–O3	48.55(6)	C40–Si31–C45	106.98(9)
C20–C21	1.390(3)	C10–Si1–O3	130.20(8)	C44–Si31–C45	109.39(8)
C21–C22	1.398(3)	C15–Si1–O3	119.86(6)	C31–Si31–C45	112.37(8)
Si31–C40	1.877(2)	O1–Si1–O3	102.04(4)	C40–Si31–O31	164.21(7)
Si31–C44	1.8870(18)	C2–O1–C7	118.55(18)	C44–Si31–O31	76.99(7)
Si31–C31	1.8942(18)	C2–O1–Si1	73.21(11)	C31–Si31–O31	53.23(6)
Si31–C45	1.8968(19)	C7–O1–Si1	146.95(15)	C45–Si31–O31	87.07(7)
Si31–O31	2.9125(17)	C4–O2–C8	117.65(19)	C40–Si31–O33	65.28(6)
Si31–O33	3.1268(14)	C6–O3–C9	117.89(16)	C44–Si31–O33	130.68(7)
O31–C32	1.375(2)	C6–O3–Si1	69.68(9)	C31–Si31–O33	48.54(6)
O31–C37	1.414(3)	C9–O3–Si1	163.61(12)	C45–Si31–O33	119.85(6)
O32–C34	1.373(2)	C20–O4–C23	117.16(17)	O31–Si31–O33	101.75(4)
O32–C38	1.416(3)	C2–C1–C6	115.49(17)	C32–O31–C37	117.28(16)
O33–C36	1.365(2)	C2–C1–Si1	118.35(13)	C32–O31–Si31	73.07(10)
O33–C39	1.425(2)	C6–C1–Si1	125.96(15)	C37–O31–Si31	146.24(15)
O34–C50	1.376(2)	O1–C2–C3	121.43(18)	C34–O32–C38	117.24(17)
O34–C53	1.418(3)	O1–C2–C1	114.68(17)	C36–O33–C39	118.09(16)
C31–C32	1.394(3)	C3–C2–C1	123.88(17)	C36–O33–Si31	69.82(9)

C39–O33–Si31	162.61(12)	C36–C35–C34	118.72(17)	C52–C47–C48	117.24(16)
C50–O34–C53	116.66(15)	O33–C36–C35	121.91(16)	C52–C47–C45	121.67(15)
C32–C31–C36	115.78(16)	O33–C36–C31	115.59(16)	C48–C47–C45	121.09(16)
C32–C31–Si31	118.39(13)	C35–C36–C31	122.50(18)	C47–C52–C51	122.14(16)
C36–C31–Si31	125.64(15)	C41–C40–Si31	110.75(13)	C50–C51–C52	119.11(18)
O31–C32–C31	115.21(16)	C40–C41–C42	112.43(17)	O34–C50–C49	115.81(16)
O31–C32–C33	121.14(18)	C43–C42–C41	113.36(16)	O34–C50–C51	124.28(18)
C31–C32–C33	123.65(17)	C42–C43–C44	112.46(16)	C49–C50–C51	119.90(17)
C34–C33–C32	117.74(19)	C43–C44–Si31	112.13(14)	C50–C49–C48	120.30(16)
O32–C34–C33	123.71(19)	C46–C45–C47	119.74(17)	C49–C48–C47	121.24(17)
O32–C34–C35	114.75(17)	C46–C45–Si31	120.27(14)		
C33–C34–C35	121.53(17)	C47–C45–Si31	119.76(13)		

Table 28. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **74**. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Si	1915(1)	6374(1)	2982(1)	26(1)	C5	2594(2)	5210(1)	–85(1)	28(1)
O1	3219(2)	7507(1)	1348(1)	34(1)	C6	2253(2)	5359(1)	1024(1)	25(1)
O2	3435(2)	5787(1)	–1831(1)	37(1)	C7	3974(3)	8152(1)	742(2)	37(1)
O3	1696(2)	4759(1)	1701(1)	32(1)	C8	2972(3)	5032(1)	–2394(2)	39(1)
O4	–208(2)	6779(1)	2924(1)	45(1)	C9	1709(3)	3937(1)	1298(2)	33(1)
C1	2442(2)	6137(1)	1521(1)	26(1)	C10	3843(3)	6875(1)	3970(2)	38(1)
C2	3050(2)	6759(1)	840(1)	26(1)	C11	4099(3)	6064(1)	4631(2)	42(1)
C3	3413(2)	6631(1)	–265(1)	28(1)	C12	2326(3)	5580(1)	4117(2)	34(1)
C4	3138(2)	5853(1)	–717(1)	28(1)	C13	–1274(3)	7176(1)	1993(2)	44(1)

Table 29. Bond lengths (Å) and angles (deg) for **74**.

Si–O4	1.6450(15)	O4–Si–C12	111.50(9)	C6–O3–C9	117.92(13)
Si–C1	1.8678(17)	C1–Si–C12	119.52(8)	C6–O3–Si	70.48(8)
Si–C12	1.8720(18)	O4–Si–C10	116.07(9)	C9–O3–Si	169.61(10)
Si–C10	1.873(2)	C1–Si–C10	116.95(9)	C13–O4–Si	127.84(13)
Si–C11	2.387(2)	C12–Si–C10	79.98(8)	C6–C1–C2	116.01(15)
Si–O1	2.9339(14)	O4–Si–C11	127.92(8)	C6–C1–Si	124.10(12)
Si–O3	3.0580(14)	C1–Si–C11	121.93(8)	C2–C1–Si	119.89(12)
O1–C2	1.369(2)	C12–Si–C11	40.37(7)	O1–C2–C3	122.54(15)
O1–C7	1.429(2)	C10–Si–C11	40.40(7)	O1–C2–C1	114.54(14)
O2–C4	1.3725(19)	O4–Si–O1	94.92(7)	C3–C2–C1	122.91(15)
O2–C8	1.429(2)	C1–Si–O1	52.79(6)	C2–C3–C4	118.11(15)
O3–C6	1.367(2)	C12–Si–O1	152.66(7)	O2–C4–C5	123.66(15)
O3–C9	1.435(2)	C10–Si–O1	82.22(7)	O2–C4–C3	114.42(15)
O4–C13	1.414(2)	C11–Si–O1	116.78(6)	C5–C4–C3	121.91(15)
C1–C6	1.409(2)	O4–Si–O3	110.28(7)	C4–C5–C6	118.49(15)
C1–C2	1.410(2)	C1–Si–O3	50.05(6)	O3–C6–C5	122.13(15)
C2–C3	1.389(2)	C12–Si–O3	75.18(6)	O3–C6–C1	115.35(14)
C3–C4	1.392(2)	C10–Si–O3	132.77(7)	C5–C6–C1	122.51(15)
C4–C5	1.383(2)	C11–Si–O3	101.93(6)	C11–C10–Si	87.96(12)
C5–C6	1.395(2)	O1–Si–O3	102.83(4)	C12–C11–C10	102.08(15)
C10–C11	1.548(3)	C2–O1–C7	117.57(13)	C12–C11–Si	51.62(8)
C11–C12	1.547(3)	C2–O1–Si	72.78(9)	C10–C11–Si	51.64(9)
		C7–O1–Si	168.84(11)	C11–C12–Si	88.01(11)
O4–Si–C1	110.13(8)	C4–O2–C8	117.71(14)		

Table 30. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **75**. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Si	7917(1)	7297(1)	1045(1)	28(1)	C9	4365(1)	6302(2)	946(1)	35(1)
O1	8280(1)	8930(2)	–151(1)	45(1)	C10	7515(1)	7607(2)	1856(1)	35(1)
O2	4715(1)	8596(1)	–1266(1)	42(1)	C11	8597(1)	8679(2)	2027(1)	39(1)
O3	5491(1)	6579(1)	887(1)	35(1)	C12	8906(1)	9104(2)	1363(1)	36(1)
O4	12253(1)	3447(2)	2721(1)	49(1)	C13	8657(1)	5128(2)	909(1)	32(1)
C1	6873(1)	7753(2)	356(1)	30(1)	C14	8412(1)	4152(2)	392(1)	46(1)
C2	7192(1)	8518(2)	–192(1)	32(1)	C15	9614(1)	4629(2)	1373(1)	32(1)
C3	6462(1)	8802(2)	–727(1)	34(1)	C16	10665(1)	4655(2)	1210(1)	39(1)
C4	5374(1)	8331(2)	–714(1)	32(1)	C17	11573(1)	4260(2)	1642(1)	41(1)
C5	5001(1)	7620(2)	–181(1)	31(1)	C18	11422(1)	3823(2)	2252(1)	37(1)
C6	5768(1)	7334(2)	346(1)	29(1)	C19	10375(1)	3773(2)	2422(1)	41(1)
C7	8659(1)	9899(2)	–654(1)	48(1)	C20	9485(1)	4169(2)	1989(1)	39(1)
C8	3625(1)	7921(2)	–1304(1)	45(1)	C21	13342(1)	3538(2)	2567(1)	52(1)

Table 31. Bond lengths (Å) and angles (deg) for **75**.

Si–C1	1.8681(13)			C6–C1–Si	123.30(10)
Si–C12	1.8803(14)	C1–Si–C12	120.79(6)	C2–C1–Si	120.03(10)
Si–C10	1.8829(14)	C1–Si–C10	118.49(6)	O1–C2–C3	123.45(12)
Si–C13	1.8850(14)	C12–Si–C10	79.00(6)	O1–C2–C1	114.09(11)
Si–C11	2.4012(14)	C1–Si–C13	109.26(6)	C3–C2–C1	122.45(12)
Si–O1	2.9226(11)	C12–Si–C13	110.96(6)	C2–C3–C4	118.34(12)
Si–O3	3.0136(10)	C10–Si–C13	115.73(6)	O2–C4–C5	123.24(13)
O1–C2	1.3668(16)	C1–Si–C11	138.67(6)	O2–C4–C3	114.70(12)
O1–C7	1.4237(17)	C12–Si–C11	40.29(5)	C5–C4–C3	122.05(12)
O2–C4	1.3678(15)	C10–Si–C11	40.34(5)	C4–C5–C6	117.71(12)
O2–C8	1.4257(19)	C13–Si–C11	112.07(6)	O3–C6–C1	114.90(11)
O3–C6	1.3711(15)	C1–Si–O1	52.69(5)	O3–C6–C5	122.32(12)
O3–C9	1.4227(16)	C12–Si–O1	82.17(5)	C1–C6–C5	122.76(12)
O4–C18	1.3743(16)	C10–Si–O1	148.12(5)	C11–C10–Si	88.06(8)
O4–C21	1.422(2)	C13–Si–O1	94.96(5)	C12–C11–C10	100.71(10)
C1–C6	1.3937(18)	C11–Si–O1	121.49(5)	C12–C11–Si	51.51(6)
C1–C2	1.4056(18)	C1–Si–O3	50.65(4)	C10–C11–Si	51.60(6)
C2–C3	1.3861(18)	C12–Si–O3	139.07(5)	C11–C12–Si	88.20(8)
C3–C4	1.388(2)	C10–Si–O3	75.85(5)	C14–C13–C15	120.22(13)
C4–C5	1.3878(19)	C13–Si–O3	108.91(5)	C14–C13–Si	121.87(11)
C5–C6	1.3994(17)	C11–Si–O3	114.05(4)	C15–C13–Si	117.61(9)
C10–C11	1.5552(19)	O1–Si–O3	103.33(3)	C16–C15–C20	117.56(12)
C11–C12	1.5535(19)	C2–O1–C7	118.27(11)	C16–C15–C13	120.99(12)
C13–C14	1.328(2)	C2–O1–Si	73.15(7)	C20–C15–C13	121.43(12)
C13–C15	1.4938(17)	C7–O1–Si	167.44(9)	C15–C16–C17	121.88(13)
C15–C16	1.382(2)	C4–O2–C8	117.05(11)	C18–C17–C16	119.32(13)
C15–C20	1.3952(18)	C6–O3–C9	118.70(10)	O4–C18–C17	124.56(13)
C16–C17	1.3952(19)	C6–O3–Si	71.15(7)	O4–C18–C19	115.77(13)
C17–C18	1.383(2)	C9–O3–Si	168.43(8)	C17–C18–C19	119.67(12)
C18–C19	1.384(2)	C18–O4–C21	117.30(12)	C20–C19–C18	120.29(13)
C19–C20	1.380(2)	C6–C1–C2	116.65(11)	C19–C20–C15	121.28(13)

Table 32. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **89**. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Si1	3487(1)	3699(1)	2952(1)	28(1)	C11	1063(1)	4273(1)	6654(4)	34(1)
Si2	3050(1)	5063(1)	3766(1)	28(1)	C12	1644(1)	4642(1)	5881(4)	33(1)
O1	–3046(1)	3296(1)	726(2)	35(1)	C13	333(2)	4470(1)	7975(5)	54(1)
O2	–3558(1)	3041(1)	3972(3)	40(1)	C14	593(1)	3300(1)	7011(3)	31(1)
C1	4367(1)	3544(1)	5222(4)	43(1)	C15	883(1)	2932(1)	8504(5)	53(1)
C2	3261(1)	3079(1)	1195(4)	45(1)	C16	–323(1)	3286(1)	5959(3)	26(1)
C3	3825(1)	4258(1)	1101(4)	37(1)	C17	–987(1)	3058(1)	7104(3)	29(1)
C4	4015(1)	4786(1)	2444(4)	37(1)	C18	–1835(1)	3035(1)	6098(3)	28(1)
C5	3460(1)	5486(1)	6236(4)	40(1)	C19	–2041(1)	3229(1)	3943(3)	25(1)
C6	2333(1)	5482(1)	1749(4)	47(1)	C20	–1389(1)	3466(1)	2791(3)	29(1)
C7	2360(1)	4493(1)	4729(3)	27(1)	C21	–544(1)	3495(1)	3811(3)	30(1)
C8	2501(1)	3938(1)	4334(3)	25(1)	C22	–2960(1)	3179(1)	2920(3)	28(1)
C9	1906(1)	3567(1)	5101(3)	28(1)	C23	–3925(1)	3269(1)	–370(4)	44(1)
C10	1193(1)	3724(1)	6235(3)	29(1)					

Table 33. Bond lengths (Å) and angles (deg) for **89**.

Si1–C1	1.859(2)	C18–C19	1.378(3)	C7–C8–Si1	121.27(13)
Si1–C2	1.869(2)	C19–C20	1.397(3)	C10–C9–C8	122.93(17)
Si1–C3	1.873(2)	C19–C22	1.492(2)	C11–C10–C9	119.26(17)
Si1–C8	1.8892(18)	C20–C21	1.384(3)	C11–C10–C14	121.38(16)
Si2–C5	1.864(2)			C9–C10–C14	119.35(17)
Si2–C6	1.865(2)	C1–Si1–C2	108.77(11)	C12–C11–C10	118.14(17)
Si2–C4	1.875(2)	C1–Si1–C3	110.82(10)	C12–C11–C13	119.70(18)
Si2–C7	1.8874(19)	C2–Si1–C3	108.86(11)	C10–C11–C13	122.13(18)
O1–C22	1.332(2)	C1–Si1–C8	107.96(9)	C11–C12–C7	123.43(18)
O1–C23	1.447(2)	C2–Si1–C8	112.67(9)	C15–C14–C16	120.82(17)
O2–C22	1.209(2)	C3–Si1–C8	107.77(9)	C15–C14–C10	120.79(17)
C3–C4	1.544(3)	C5–Si2–C6	109.38(11)	C16–C14–C10	118.30(16)
C7–C12	1.403(3)	C5–Si2–C4	108.27(9)	C21–C16–C17	118.15(16)
C7–C8	1.411(3)	C6–Si2–C4	112.11(11)	C21–C16–C14	121.09(16)
C8–C9	1.402(3)	C5–Si2–C7	109.70(9)	C17–C16–C14	120.75(17)
C9–C10	1.397(3)	C6–Si2–C7	107.07(9)	C18–C17–C16	120.53(18)
C10–C11	1.396(3)	C4–Si2–C7	110.28(9)	C19–C18–C17	120.77(17)
C10–C14	1.499(3)	C22–O1–C23	115.61(16)	C18–C19–C20	119.37(16)
C11–C12	1.387(3)	C4–C3–Si1	111.66(15)	C18–C19–C22	118.38(16)
C11–C13	1.513(3)	C3–C4–Si2	114.03(13)	C20–C19–C22	122.25(18)
C14–C15	1.320(3)	C12–C7–C8	118.54(16)	C21–C20–C19	119.75(18)
C14–C16	1.489(2)	C12–C7–Si2	116.33(14)	C20–C21–C16	121.39(17)
C16–C21	1.390(3)	C8–C7–Si2	125.11(13)	O2–C22–O1	124.03(17)
C16–C17	1.400(3)	C9–C8–C7	117.69(16)	O2–C22–C19	123.48(19)
C17–C18	1.385(3)	C9–C8–Si1	120.97(14)	O1–C22–C19	112.49(16)

Table 34. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **99**. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Si1	1300(1)	3749(1)	2538(1)	23(1)	O2	–1949(1)	–3356(2)	390(1)	38(1)
Si2	1696(1)	3048(1)	1356(1)	21(1)	O3	–2189(1)	239(2)	142(1)	38(1)
O1	–1008(1)	–1916(2)	882(1)	27(1)	C1	848(1)	5197(3)	2793(1)	40(1)

C2	1699(1)	1910(3)	3141(1)	36(1)
C3	1665(1)	5865(2)	2304(1)	29(1)
C4	2010(1)	4698(3)	2043(1)	29(1)
C6	2117(1)	848(3)	1264(1)	35(1)
C5	1501(1)	4933(3)	699(1)	35(1)
C7	1138(1)	1650(2)	1405(1)	21(1)
C8	976(1)	1917(2)	1883(1)	22(1)
C9	561(1)	717(2)	1865(1)	26(1)
C10	309(1)	–720(2)	1408(1)	27(1)
C11	466(1)	–977(2)	933(1)	28(1)
C12	874(1)	228(2)	944(1)	26(1)
C13	214(1)	–2554(3)	430(1)	43(1)
C14	–140(1)	–1925(3)	1419(1)	35(1)
C15	–592(1)	–672(2)	1078(1)	27(1)
C16	–688(1)	1528(3)	937(1)	32(1)
C17	–1198(1)	1709(3)	639(1)	31(1)
C18	–1375(1)	–404(3)	615(1)	26(1)
C19	–1864(1)	–1330(3)	374(1)	28(1)

Table 35. Bond lengths (Å) and angles (deg) for **99**.

Si1–C3	1.8690(15)	C16–C17	1.427(2)	C9–C8–Si1	119.58(10)
Si1–C2	1.8696(17)	C17–C18	1.348(2)	C7–C8–Si1	122.75(10)
Si1–C1	1.8696(15)	C18–C19	1.4602(19)	C10–C9–C8	123.34(13)
Si1–C8	1.8837(14)			C9–C10–C11	119.14(12)
Si2–C5	1.8635(16)	C3–Si1–C2	110.96(7)	C9–C10–C14	119.89(14)
Si2–C6	1.8682(15)	C3–Si1–C1	110.63(8)	C11–C10–C14	120.95(14)
Si2–C4	1.8732(15)	C2–Si1–C1	109.45(8)	C12–C11–C10	117.90(13)
Si2–C7	1.8870(13)	C3–Si1–C8	107.59(6)	C12–C11–C13	120.53(14)
O1–C15	1.3659(16)	C2–Si1–C8	108.57(7)	C10–C11–C13	121.55(13)
O1–C18	1.3767(17)	C1–Si1–C8	109.59(7)	C11–C12–C7	123.79(13)
O2–C19	1.229(2)	C5–Si2–C6	109.33(7)	C15–C14–C10	111.89(12)
O3–H3	0.82(2)	C5–Si2–C4	110.94(7)	C16–C15–O1	110.42(12)
O3–C19	1.3118(18)	C6–Si2–C4	109.20(7)	C16–C15–C14	133.13(13)
C3–C4	1.544(2)	C5–Si2–C7	107.85(7)	O1–C15–C14	116.38(12)
C7–C12	1.3987(19)	C6–Si2–C7	109.68(7)	C15–C16–C17	106.81(13)
C7–C8	1.4150(18)	C4–Si2–C7	109.82(6)	C18–C17–C16	106.04(13)
C8–C9	1.4045(18)	C15–O1–C18	105.97(11)	C17–C18–O1	110.74(12)
C9–C10	1.389(2)	H3–O3–C19	110.4(17)	C17–C18–C19	132.72(14)
C10–C11	1.399(2)	C4–C3–Si1	111.35(10)	O1–C18–C19	116.54(12)
C10–C14	1.5138(18)	C3–C4–Si2	114.16(10)	O2–C19–O3	125.23(13)
C11–C12	1.3926(19)	C12–C7–C8	118.14(12)	O2–C19–C18	122.56(13)
C11–C13	1.509(2)	C12–C7–Si2	117.62(10)	O3–C19–C18	112.21(13)
C14–C15	1.497(2)	C8–C7–Si2	124.22(10)		
C15–C16	1.351(2)	C9–C8–C7	117.67(12)		

Table 36. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **103**. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}
Si	3616(1)	7376(1)	1954(1)	30(1)
Cl1	84(1)	5828(1)	1476(1)	46(1)
Cl2	5269(1)	4067(1)	1760(1)	55(1)
C12	5466(3)	8277(3)	1177(2)	45(1)
Cl31	7068(4)	9295(5)	2063(2)	47(1)
Cl32	6897(14)	9476(15)	1976(8)	84(2)
O1	1941(2)	10257(2)	1309(1)	37(1)
O2	890(2)	13016(2)	4668(1)	43(1)
O3	3578(2)	7740(2)	4425(1)	41(1)
C1	2751(2)	9009(2)	2869(1)	30(1)
C2	1992(2)	10359(2)	2412(1)	31(1)
C3	1361(2)	11655(2)	3021(1)	35(1)
C4	1509(2)	11664(2)	4136(1)	32(1)
C5	2248(2)	10367(2)	4642(1)	32(1)
C6	2847(2)	9071(2)	3999(1)	31(1)
C7	1144(3)	11555(3)	790(2)	38(1)
C8	1056(3)	13175(3)	5811(2)	44(1)
C9	3581(3)	7613(3)	5567(2)	43(1)
C10	2066(2)	6510(3)	891(2)	37(1)
C11	4347(2)	5554(3)	2688(2)	36(1)

Table 37. Bond lengths (Å) and angles (deg) for **103**.

Si–C1	1.854(2)	C1–Si–C11	112.88(8)	C9–O3–C11	133.85(13)
Si–C11	1.8735(19)	C1–Si–C10	113.46(9)	C6–O3–Si	70.21(9)
Si–C10	1.8750(19)	C11–Si–C10	107.13(9)	C9–O3–Si	170.40(13)
Si–C12	1.876(2)	C1–Si–C12	110.51(10)	C11–O3–Si	36.86(4)
Si–O1	2.8708(15)	C11–Si–C12	107.96(10)	C6–C1–C2	115.73(17)
Si–O3	3.0679(14)	C10–Si–C12	104.40(9)	C6–C1–Si	125.67(14)
Cl1–C10	1.789(2)	C1–Si–O1	53.89(6)	C2–C1–Si	118.53(13)
Cl2–C11	1.803(2)	C11–Si–O1	165.15(7)	O1–C2–C3	123.37(16)
C12–Cl32	1.717(8)	C10–Si–O1	76.06(7)	O1–C2–C1	113.79(16)
C12–Cl31	1.802(4)	C12–Si–O1	84.73(8)	C3–C2–C1	122.84(16)
O1–C2	1.367(2)	C1–Si–O3	49.39(6)	C2–C3–C4	118.98(17)
O1–C7	1.424(2)	C11–Si–O3	63.92(7)	O2–C4–C3	114.72(16)
O2–C4	1.358(2)	C10–Si–O3	134.97(7)	O2–C4–C5	124.13(16)
O2–C8	1.424(2)	C12–Si–O3	120.50(7)	C3–C4–C5	121.15(18)
O3–C6	1.368(2)	O1–Si–O3	103.28(4)	C6–C5–C4	118.09(16)
O3–C9	1.425(2)	Cl32–C12–Cl31	7.1(5)	O3–C6–C5	122.15(15)
O3–C11	2.805(2)	Cl32–C12–Si	112.9(3)	O3–C6–C1	114.67(17)
C1–C6	1.403(2)	Cl31–C12–Si	111.42(14)	C5–C6–C1	123.19(16)
C1–C2	1.408(2)	C2–O1–C7	116.93(15)	Cl1–C10–Si	111.08(10)
C2–C3	1.374(3)	C2–O1–Si	73.75(10)	Cl2–C11–Si	110.52(10)
C3–C4	1.388(3)	C7–O1–Si	169.30(12)	Cl2–C11–O3	166.65(10)
C4–C5	1.394(3)	C4–O2–C8	118.83(16)	Si–C11–O3	79.22(7)
C5–C6	1.385(3)	C6–O3–C9	118.60(16)		
		C6–O3–C11	106.86(11)		

Table 38. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **104**. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Si	1436(1)	6716(1)	1721(1)	17(1)	O6	800(1)	6039(1)	3286(1)	31(1)
Cl1	1355(1)	5179(1)	1844(1)	29(1)	C7	2319(1)	5746(1)	–413(1)	30(1)
O1	2106(1)	6112(1)	360(1)	27(1)	C8	4539(1)	7671(2)	3290(1)	39(1)
C1	2262(1)	6933(1)	1923(1)	19(1)	C9	2779(1)	8317(1)	4349(1)	34(1)
Cl2	871(1)	7031(1)	218(1)	29(1)	C10	1107(1)	7428(1)	2549(1)	19(1)
O2	4119(1)	7284(1)	2332(1)	33(1)	C11	1149(1)	8477(1)	2492(1)	21(1)
C2	2512(1)	6606(1)	1190(1)	20(1)	C12	938(1)	9143(1)	3059(1)	24(1)
O3	2436(1)	7658(1)	3537(1)	29(1)	C13	661(1)	8736(1)	3704(1)	25(1)
C3	3125(1)	6762(1)	1319(1)	22(1)	C14	604(1)	7702(1)	3791(1)	24(1)
O4	1421(1)	8790(1)	1823(1)	26(1)	C15	829(1)	7059(1)	3222(1)	20(1)
C4	3512(1)	7213(1)	2227(1)	23(1)	C16	1548(1)	9827(1)	1775(2)	48(1)
O5	431(1)	9302(1)	4298(1)	34(1)	C17	452(1)	10373(1)	4210(2)	46(1)
C5	3296(1)	7530(1)	2983(1)	22(1)	C18	517(1)	5613(1)	3944(1)	36(1)
C6	2674(1)	7390(1)	2815(1)	21(1)					

Table 39. Bond lengths (Å) and angles (deg) for **104**.

Si–C1	1.8528(14)	Si–O1	2.9623(11)	C1–C6	1.396(2)
Si–C10	1.8536(13)	Si–O3	3.0034(12)	C1–C2	1.4112(18)
Si–Cl1	2.0593(5)	Si–O6	3.1700(11)	O2–C4	1.3642(17)
Si–Cl2	2.0608(6)	O1–C2	1.3610(17)	O2–C8	1.426(2)
Si–O4	2.7558(11)	O1–C7	1.4217(16)	C2–C3	1.381(2)

O3–C6	1.3576(16)	Cl1–Si–O1	82.53(3)	C11–O4–C16	118.97(11)
O3–C9	1.4181(18)	Cl2–Si–O1	72.29(3)	C11–O4–Si	75.42(7)
C3–C4	1.388(2)	O4–Si–O1	108.79(3)	C16–O4–Si	164.28(10)
O4–C11	1.3653(16)	C1–Si–O3	50.99(5)	O2–C4–C5	122.93(14)
O4–C16	1.4124(19)	C10–Si–O3	68.52(5)	O2–C4–C3	115.20(12)
C4–C5	1.3825(19)	Cl1–Si–O3	114.07(3)	C5–C4–C3	121.83(13)
O5–C13	1.3616(16)	Cl2–Si–O3	140.83(3)	C13–O5–C17	117.55(12)
O5–C17	1.428(2)	O4–Si–O3	64.01(4)	C4–C5–C6	118.31(13)
C5–C6	1.386(2)	O1–Si–O3	102.97(3)	O3–C6–C5	121.32(13)
O6–C15	1.3597(17)	C1–Si–O6	130.86(5)	O3–C6–C1	115.88(12)
O6–C18	1.4212(17)	C10–Si–O6	47.08(5)	C5–C6–C1	122.74(12)
C10–C11	1.3985(19)	Cl1–Si–O6	65.40(2)	C15–O6–C18	118.98(12)
C10–C15	1.4023(18)	Cl2–Si–O6	117.98(3)	C15–O6–Si	68.02(7)
C11–C12	1.3869(19)	O4–Si–O6	103.29(3)	C18–O6–Si	172.94(9)
C12–C13	1.3867(19)	O1–Si–O6	147.66(3)	C11–C10–C15	116.26(12)
C13–C14	1.388(2)	O3–Si–O6	87.26(3)	C11–C10–Si	114.78(9)
C14–C15	1.387(2)	C2–O1–C7	118.74(11)	C15–C10–Si	128.96(10)
		C2–O1–Si	71.96(7)	O4–C11–C12	122.67(12)
C1–Si–C10	117.62(6)	C7–O1–Si	169.29(9)	O4–C11–C10	113.59(11)
C1–Si–Cl1	105.15(5)	C6–C1–C2	116.32(12)	C12–C11–C10	123.74(12)
C10–Si–Cl1	112.48(5)	C6–C1–Si	122.47(10)	C13–C12–C11	117.47(13)
C1–Si–Cl2	111.13(5)	C2–C1–Si	121.17(10)	O5–C13–C12	123.61(13)
C10–Si–Cl2	105.74(5)	C4–O2–C8	116.77(11)	O5–C13–C14	114.92(12)
Cl1–Si–Cl2	103.98(2)	O1–C2–C3	122.80(12)	C12–C13–C14	121.48(13)
C1–Si–O4	82.45(5)	O1–C2–C1	114.81(12)	C15–C14–C13	119.32(12)
C10–Si–O4	56.21(5)	C3–C2–C1	122.38(13)	O6–C15–C14	122.34(12)
Cl1–Si–O4	168.68(3)	C6–O3–C9	119.21(11)	O6–C15–C10	115.93(12)
Cl2–Si–O4	80.44(3)	C6–O3–Si	70.65(8)	C14–C15–C10	121.73(13)
C1–Si–O1	52.04(5)	C9–O3–Si	163.73(10)		
C10–Si–O1	164.61(5)	C2–C3–C4	118.35(12)		

Table 40. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **145**·2H_2O. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Si1	2198(1)	3781(1)	3646(1)	17(1)	C5	494(1)	4625(2)	3152(1)	34(1)
Cl1	4285(1)	9548(1)	3249(1)	24(1)	C6	1103(1)	2854(2)	3383(1)	26(1)
Cl2	3558(1)	4909(1)	5940(1)	24(1)	C7	3486(1)	5201(2)	1920(1)	21(1)
Si2	2416(1)	4984(1)	2093(1)	17(1)	C8	1873(1)	7444(2)	1874(1)	24(1)
O1	2551(1)	4351(2)	2943(1)	25(1)	C9	1483(1)	7665(2)	1056(1)	29(1)
N1	3730(1)	2392(2)	4562(1)	21(1)	C10	931(1)	5885(2)	732(1)	30(1)
N2	4046(1)	3465(2)	2195(1)	22(1)	C11	1403(1)	3911(2)	729(1)	31(1)
C1	2882(1)	1734(2)	4160(1)	20(1)	C12	1782(1)	3066(2)	1491(1)	25(1)
C2	2169(1)	6060(2)	4208(1)	27(1)	O2	4486(1)	4937(2)	3705(1)	26(1)
C4	589(1)	6282(3)	3726(1)	40(1)	O3	4356(1)	–1096(2)	5371(1)	33(1)
C3	1418(1)	7406(2)	3875(1)	29(1)					

Table 41. Bond lengths (Å) and angles (deg) for **145**·2H_2O.

Si1–O1	1.6317(9)	Si2–C12	1.8584(13)	C2–C3	1.5393(17)
Si1–C2	1.8574(14)	Si2–C8	1.8589(13)	C3–C4	1.529(2)
Si1–C6	1.8677(12)	Si2–C7	1.8859(12)	C4–C5	1.529(2)
Si1–C1	1.8826(12)	N1–C1	1.4956(15)	C5–C6	1.5405(19)
Si2–O1	1.6360(9)	N2–C7	1.4903(16)	C8–C9	1.5439(18)

C9–C10	1.528(2)	O1–Si2–C12	111.04(6)	C3–C4–C5	114.51(12)
C10–C11	1.524(2)	O1–Si2–C8	112.94(6)	C4–C5–C6	113.17(12)
C11–C12	1.5427(19)	C12–Si2–C8	106.67(6)	C5–C6–Si1	110.87(10)
		O1–Si2–C7	106.47(5)	N2–C7–Si2	114.39(8)
O1–Si1–C2	110.54(6)	C12–Si2–C7	111.11(6)	C9–C8–Si2	111.89(10)
O1–Si1–C6	111.88(6)	C8–Si2–C7	108.66(6)	C10–C9–C8	113.57(11)
C2–Si1–C6	105.25(6)	Si1–O1–Si2	152.05(6)	C11–C10–C9	113.83(11)
O1–Si1–C1	107.67(5)	N1–C1–Si1	115.61(9)	C10–C11–C12	113.57(12)
C2–Si1–C1	112.33(6)	C3–C2–Si1	111.25(9)	C11–C12–Si2	112.10(10)
C6–Si1–C1	109.22(6)	C4–C3–C2	113.47(12)		

Table 42. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **146**. U_{eq} is defined as 1/3 of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
C11	9639(1)	3988(1)	–876(2)	37(1)	C9	10902(1)	1324(1)	–799(2)	43(1)
C12	8857(1)	4069(1)	198(1)	31(1)	C7	7344(1)	2768(1)	3637(2)	37(1)
C10	10586(1)	3694(1)	–154(1)	33(1)	C8	7473(1)	–1(1)	2666(2)	45(1)
C1	9236(1)	2412(1)	1242(1)	23(1)	O4	10000	3740(1)	2500	28(1)
C2	8440(1)	2251(1)	2062(1)	24(1)	O2	8227(1)	176(1)	1766(1)	44(1)
C3	8067(1)	1520(1)	2284(1)	28(1)	O3	10425(1)	1945(1)	–179(1)	37(1)
C4	8515(1)	922(1)	1642(1)	30(1)	O1	8047(1)	2882(1)	2647(1)	32(1)
C5	9301(1)	1044(1)	805(1)	31(1)	Si	9694(1)	3422(1)	1126(1)	23(1)
C6	9651(1)	1781(1)	619(1)	26(1)					

Table 43. Bond lengths (Å) and angles (deg) for **146**.

C11–C12	1.555(2)	O4–Si#1	1.6321(6)	C6–C5–C4	119.03(12)
C11–C10	1.557(2)	O4–Si	1.6321(6)	O3–C6–C5	122.40(12)
C11–Si	2.3756(16)			O3–C6–C1	115.20(12)
C12–Si	1.8730(14)	C12–C11–C10	100.95(11)	C5–C6–C1	122.39(12)
C10–Si	1.8735(15)	C12–C11–Si	51.95(7)	Si#1–O4–Si	139.97(9)
C1–C2	1.3994(18)	C10–C11–Si	51.97(7)	C4–O2–C8	118.02(11)
C1–C6	1.4042(18)	C11–C12–Si	87.22(9)	C6–O3–C9	117.60(12)
C1–Si	1.8767(13)	C11–C10–Si	87.13(9)	C2–O1–C7	118.38(10)
C2–O1	1.3745(15)	C2–C1–C6	115.77(12)	O4–Si–C12	114.96(6)
C2–C3	1.3943(18)	C2–C1–Si	118.22(9)	O4–Si–C10	115.19(6)
C3–C4	1.3888(19)	C6–C1–Si	125.94(10)	C12–Si–C10	79.70(7)
C4–O2	1.3691(16)	O1–C2–C3	121.94(12)	O4–Si–C1	110.02(6)
C4–C5	1.389(2)	O1–C2–C1	114.20(11)	C12–Si–C1	114.77(6)
C5–C6	1.3877(19)	C3–C2–C1	123.86(12)	C10–Si–C1	119.43(6)
C6–O3	1.3646(16)	C4–C3–C2	117.41(12)	O4–Si–C11	133.42(6)
C9–O3	1.4251(17)	O2–C4–C3	123.75(13)	C12–Si–C11	40.83(6)
C7–O1	1.4262(17)	O2–C4–C5	114.71(12)	C10–Si–C11	40.90(6)
C8–O2	1.4221(19)	C3–C4–C5	121.54(12)	C1–Si–C11	116.47(6)

Symmetry transformations used to generate equivalent atoms: #1 –x + 2, y, –z + ½.

16 Appendix B: data of the biological studies

Table 44. *In vitro* efficacy (IC_{50} values) of compounds *rac*-**12a**, *rac*-**12b**, *rac*-**13**, and *rac*-**15** regarding serotonin, noradrenaline, and dopamine reuptake inhibition (preliminary data).

	IC_{50} (pIC_{50})		
Compd No.	Noradrenaline	Serotonin	Dopamine
rac-**12a**	281 (6.55)	19.6 (7.71)	4430 (5.35)
rac-**12b**	109 (6.96)	525 (6.28)	2630 (5.58)
rac-**13**	275 (6.56)	904 (6.04)	707 (6.15)
rac-**15**	2720 (5.57)	6480 (5.19)	20200 (4.69)

IC_{50} denotes the half-maximum effect concentration [nM]. The data represent the mean of duplicate analyses. The pIC_{50} (= –log IC_{50}) values given in parentheses are the basis for Figure 2 (Section 9.1, p. 35).

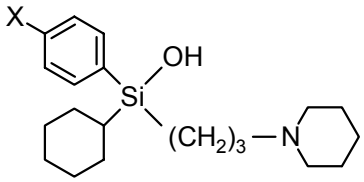
Table 45. Compilation of the parameters to characterize the interaction of the allosteric test compounds W84 (**11**) and **10**, **27**–**30**, **32**, **33**, **35**, **36**, **39**, **42**, **45**–**50**, *rac*-**51**, *rac*-**52**, and **53**[a] with [^{3}H]NMS-occupied and unoccupied muscarinic M_2 receptors.

Compd No.[b]	$pEC_{50,diss}$[c]	n_H	pK_A[e]	pα[f]
11	6.08 ± 0.07	–0.98	6.43 ± 0.26	–0.51 ±0.02
27	7.07 ± 0.05	–2.3[d]	6.02 ± 0.43	1.602 ± 0.39
28	6.664 ± 0.06	–1.535[d]	4.638 ± 0.41	1.851 ± 0.38
29	6.81 ± 0.07	–0.76	6.11 ± 0.22	0.516 ± 0.03
30	7.09 ± 0.10	–1.06	6.01 ± 0.12	0.827 ± 0.16
10	6.72 ± 0.06	–1.27	6.4 ± 0.14	0.463 ± 0.04
32	7.18 ± 0.02	–1.5[d]	5.17 ± 0.36	2.18 ± 0.38
33	6.828 ± 0.03	–1.306[d]	5.836 ± 0.10	0.908 ± 0.12
35	6.92 ± 0.07	–1.1	6.99 ± 0.41	0.316 ± 0.03
36	6.581 ± 0.05	–1.025	6.72 ± 0.28	0.119 ± 0.01
39	6.768 ± 0.05	–1.103	6.273 ± 0.04	0.425 ± 0.02
42	6.719 ± 0.04	–1.161	5.698 ± 0.10	0.896 ± 0.05
45	6.709 ± 0.05	–1.092	5.845 ± 0.15	0.699 ± 0.10
46	4.345 ± 0.07	–0.84	5.753 ± 0.03	–0.936 ± 0.13
47	6.748 ± 0.05	–1.124	6.079 ± 0.09	0.886 ± 0.06
48	6.369 ± 0.07	–1.043	7.023 ± 0.12	–0.919 ± 0.16
49	6.546 ± 0.06	–1.196	6.269 ± 0.10	0.233 ± 0.01
50	6.889 ± 0.06	–0.856	6.29 ± 0.10	0.533 ± 0.01
rac-**51**	6.334 ± 0.03	–1.357[d]	6.324 ± 0.03	0.017 ± 0.03
rac-**52**	6.713 ± 0.05	–1.027	6.107 ± 0.06	0.28 ± 0.02
53	5.792 ± 0.07	–0.994	4.816 ± 0.10	0.930 ± 0.02

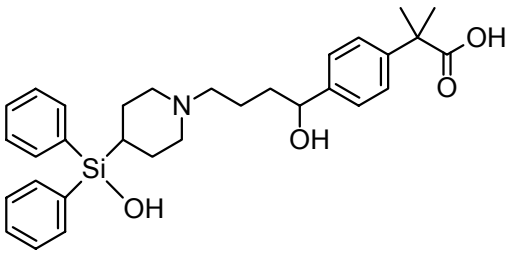
[a] Tested as the hydrochloride **53**·HCl. [b] The order of the test compounds compiled in Table 45 reflects the order as shown in Chart 3. [c] $pEC_{50,diss}$ indicates the –log concentration of the test compound at which orthosteric radioligand dissociation was reduced to 50% compared with control conditions and reflects the affinity of the modulator to NMS-occupied M_2 receptors. [d] Significantly different from –1. [e] pK_A is the –log value of the equilibrium dissociation constant of the test compound and reflects its affinity for free receptors. Mean values ± S.E.M., n = 2–6 independent experiments. [f] pα is the –log factor of cooperativity between [^{3}H]NMS and the test compound; a positive sign indicates an enhancement of [^{3}H]NMS equilibrium binding by the modulator (positive cooperativity), whereas a negative sign denotes a reduction of [^{3}H]NMS equilibrium binding (negative cooperativity).

17 Appendix C: formula index

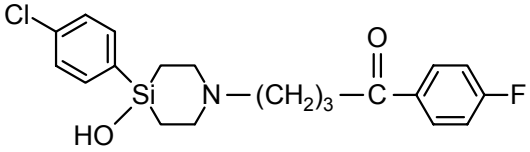
Hydrochlorides, hydrobromides, and solvates are not reported in this section. The depicted structures refer exclusively to the formulas of the analogous respective free amine bases or of the solvate-free compounds.



X = H: *rac*-**1**
X = F: *rac*-**2**



rac-**3**



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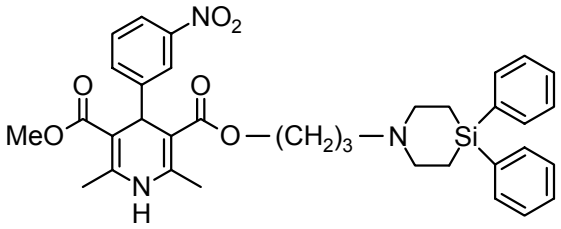
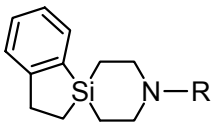
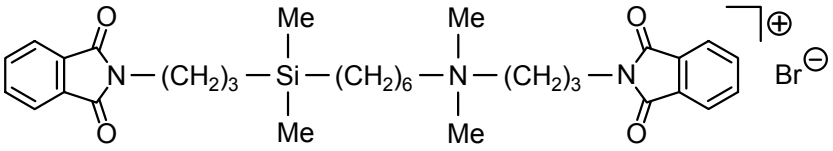


rac-**5**



6–**9**

	R
6	CH_2Ph
7	4-CH_2-C_6H_4-OMe
8	$(CH_2)_2Ph$
9	$CH_2CH=CMe_2$



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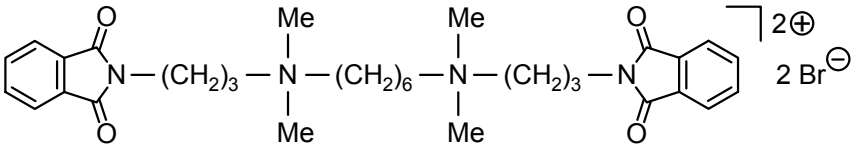

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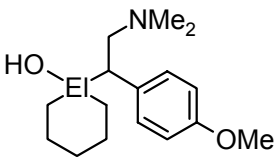

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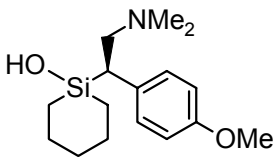
El = Si: *rac*-**12b**



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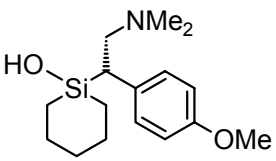

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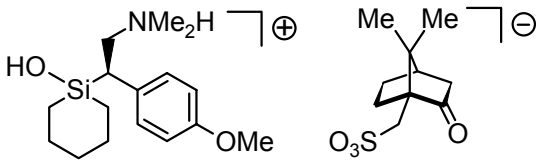
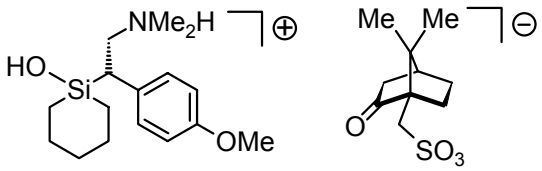
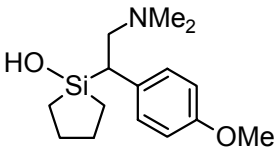


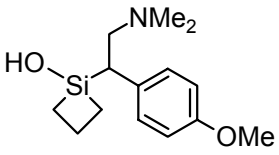
(*R*)-**12b**·(+)-CSA



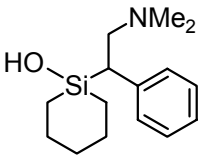
(*S*)-**12b**·(−)-CSA



rac-**13**



rac-**14**



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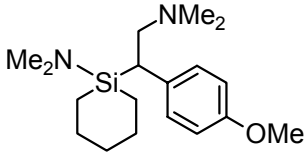
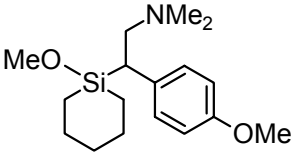
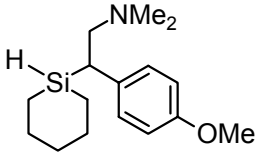


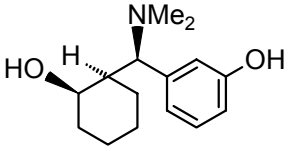
rac-**16**



rac-**17**



rac-**18**



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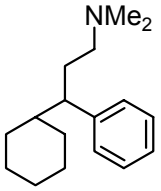
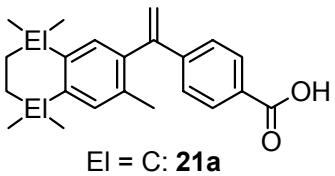


rac-**20**



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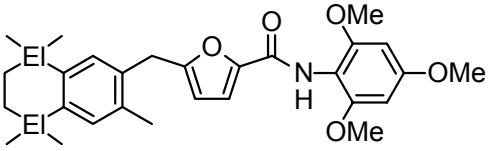
El = Si: **21b**



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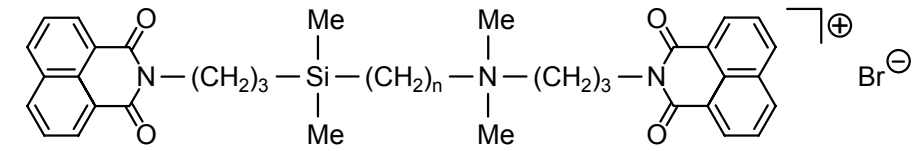
El = Si: **22b**

$ClSi(CH_2Cl)_3$ **23**

$MeOSi(CH_2Cl)_3$ **24**

$Cl_2Si(CH_2Cl)_2$ **25**

n	Cpd. No.
4	**26**
5	**27**
6	**28**



n	Cpd. No.
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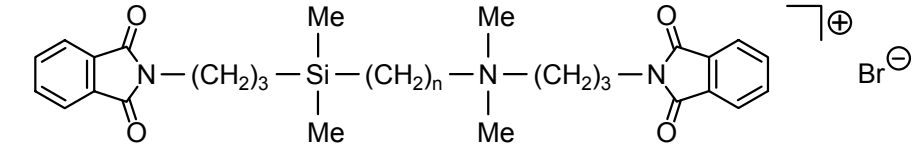
5	**30**
6	**10**



n	Cpd. No.
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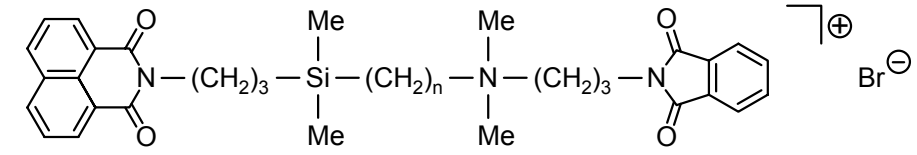
5	**32**
6	**33**



n	Cpd. No.
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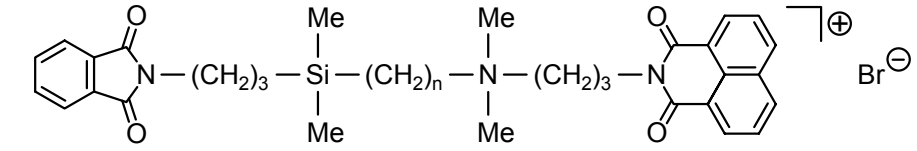
6	**36**



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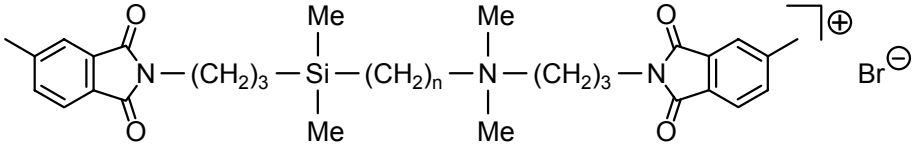

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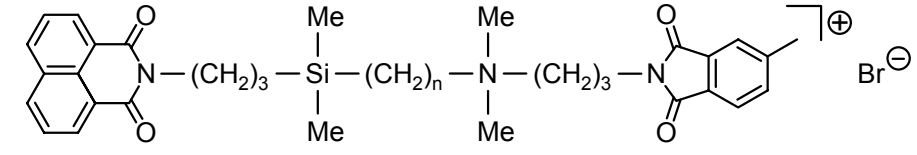

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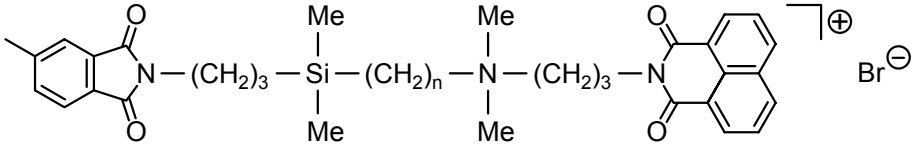

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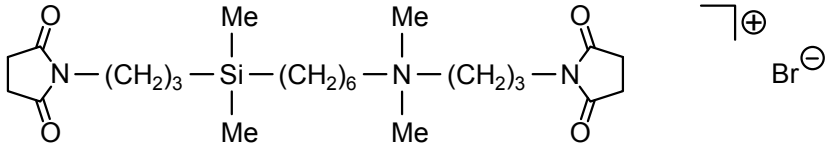

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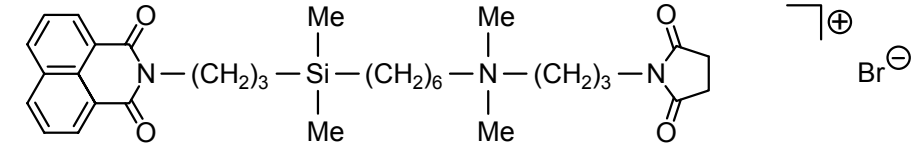

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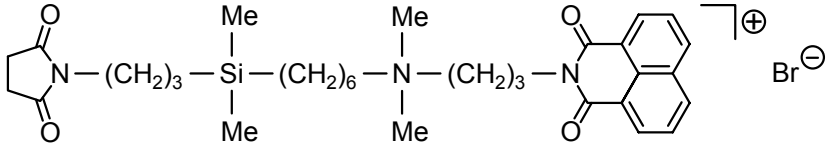

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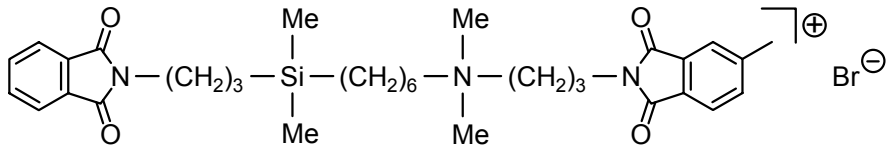

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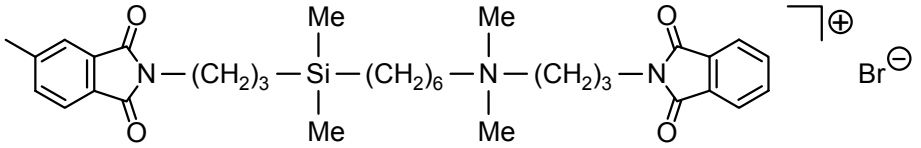

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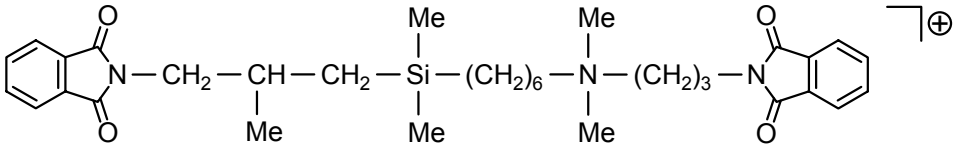
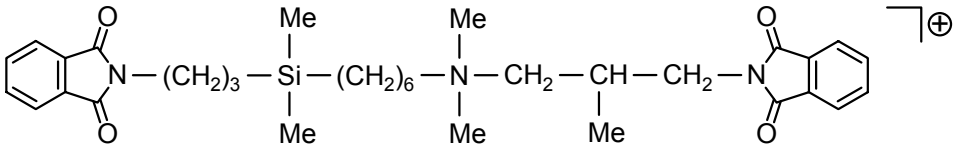
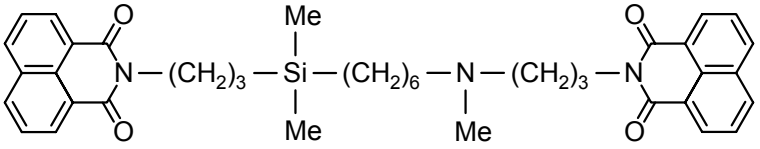


rac-**51**



rac-**52**



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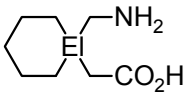
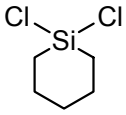


El = C: **54a**
El = Si: **54b**



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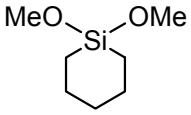

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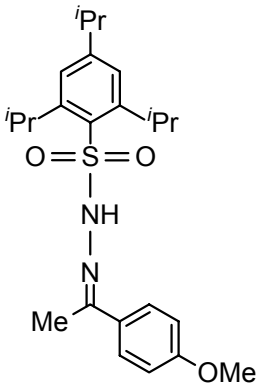

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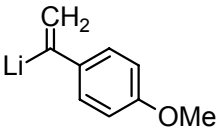

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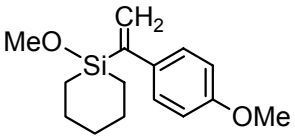

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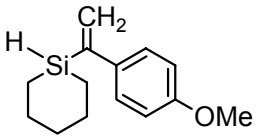

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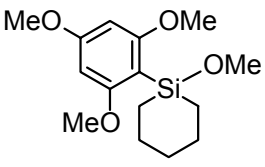

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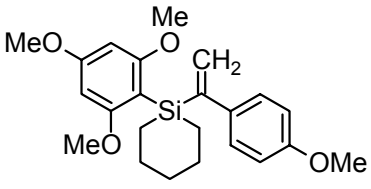

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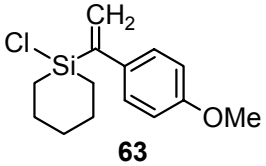

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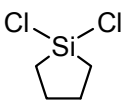

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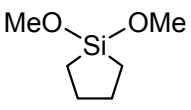

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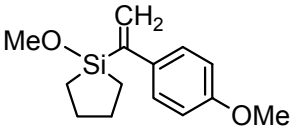

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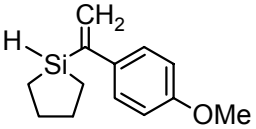

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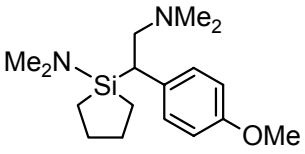
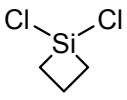


rac-**68**



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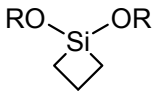
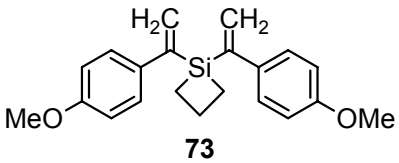


R = Me: **70**
R = ^{i}Pr: **71**
R = ^{t}Bu: **72**



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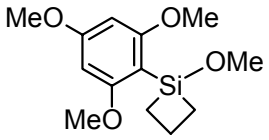

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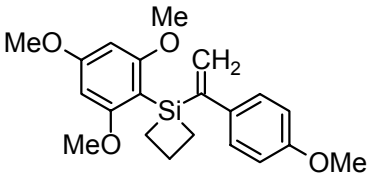

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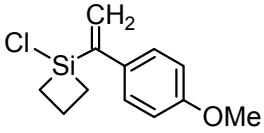

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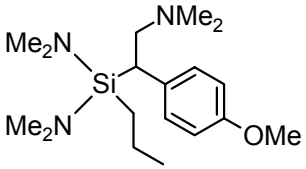

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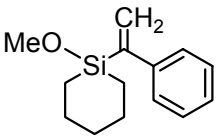

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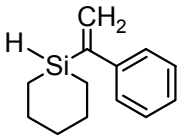

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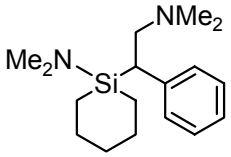
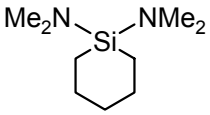


rac-**80**



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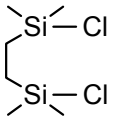

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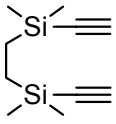

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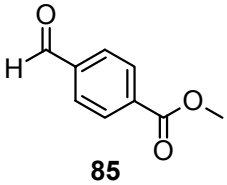

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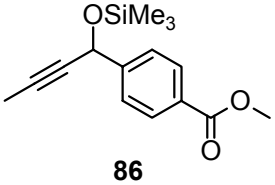

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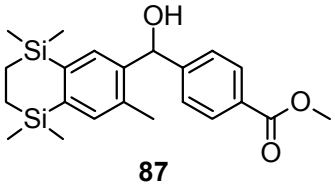

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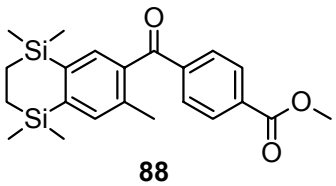

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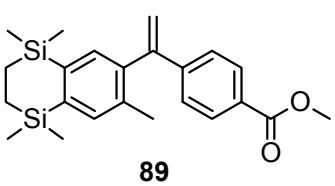

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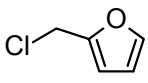

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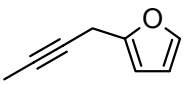

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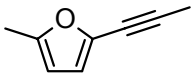

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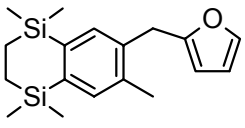

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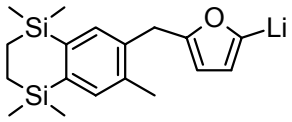

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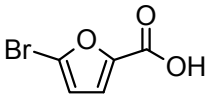

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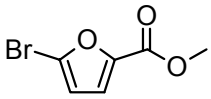

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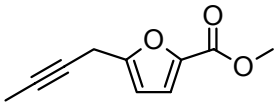

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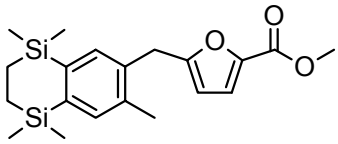

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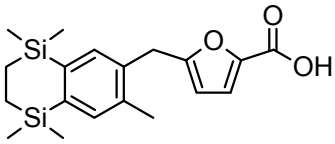

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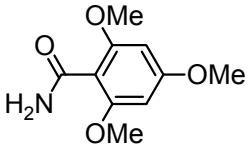

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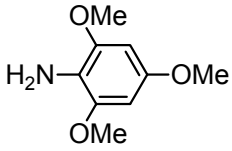

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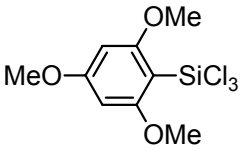

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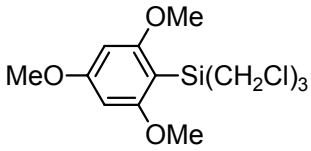

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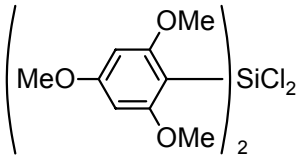

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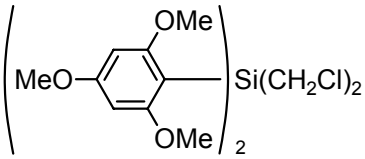

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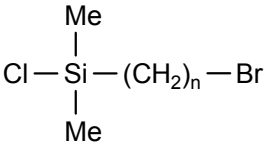

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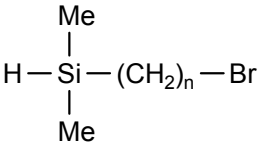

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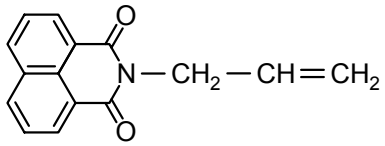

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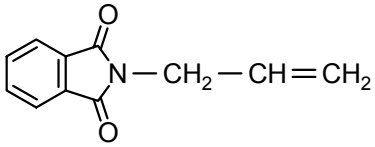

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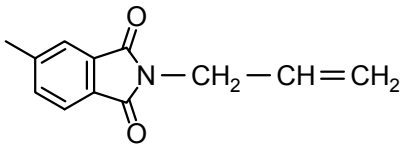

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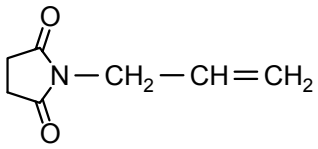

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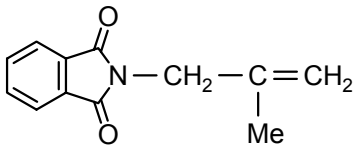

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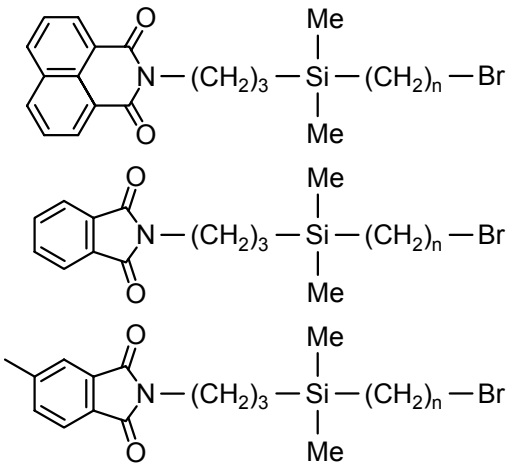

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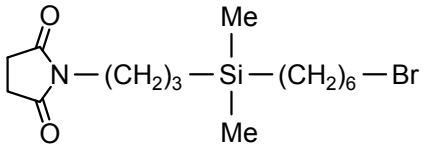

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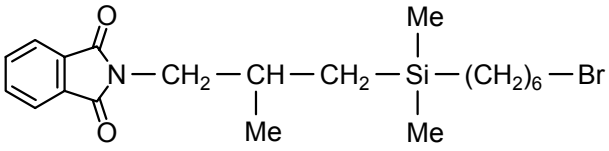

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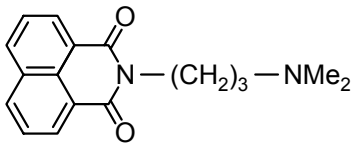

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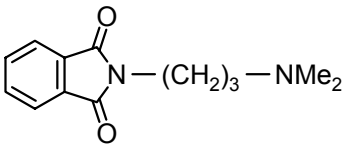

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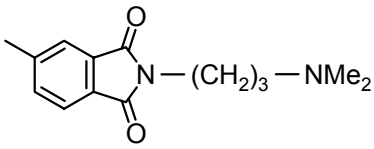

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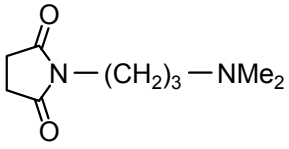

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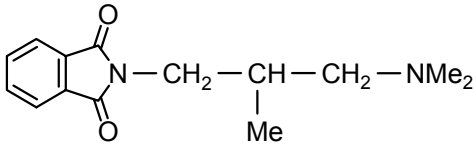

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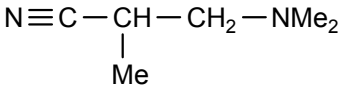

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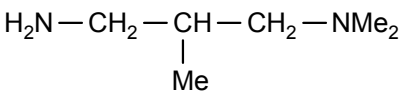

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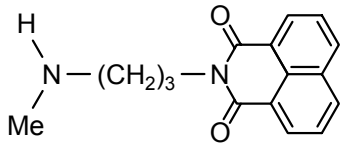

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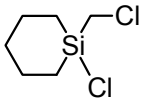

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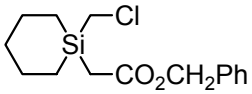

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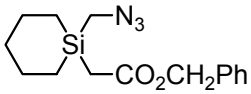

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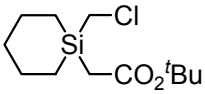

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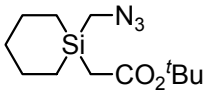

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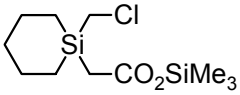

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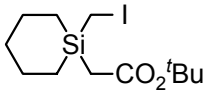

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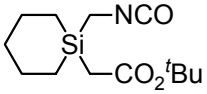

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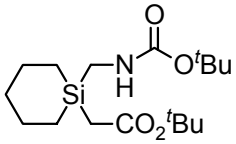

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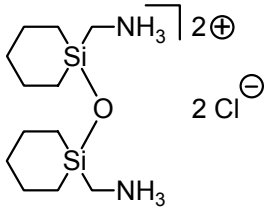

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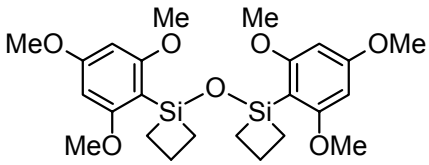

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18 References and notes

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(2) Nevertheless, the highest costs in the course of this process accumulate in phase III clinical testing.

(3) The concept of sila-substitution was not only applied successfully to drugs, but also to other biologically active compounds like amino acids and peptides prepared thereof (some of these may also act as drugs) (a–d), fungicides (e), acaricides (f, g), insect pheromones (h), and fragrance ingredients (i–l): (a) Handmann, V. I.; Merget, M.; Tacke, R. *Z. Naturforsch.* **2000**, *55b*, 133–138. (b) Tacke, R.; Merget, M.; Bertermann, R.; Bernd, M.; Beckers, T.; Reissmann, T. *Organometallics* **2000**, *19*, 3486–3497. (c) Merget, M.; Günther, K.; Bernd, M.; Günther, E.; Tacke, R. *J. Organomet. Chem.* **2001**, *628*, 183–194. (d) Tacke, R.; Handmann, V. I. *Organometallics* **2002**, *21*, 2619–2626. (e) Tacke, R.; Becker, B.; Schomburg, D. *Appl. Organomet. Chem.* **1989**, *3*, 133–139. (f) Tacke, R.; Link, M.; Joppien, H.; Ernst, L. *Z. Naturforsch.* **1986**, *41b*, 1123–1128. (g) Schomburg, D.; Link, M.; Linoh, H.; Tacke, R. *J. Organomet. Chem.* **1988**, *339*, 69–80. (h) Tacke, R.; Schmid, T.; Hofmann, M.; Tolasch, T.; Francke, W. *Organometallics* **2003**, *22*, 370–372. (i) Wrobel, D.; Tacke, R.; Wannagat, U.; Harder, U. *Chem. Ber.* **1982**, *115*, 1694–1704. (j) Tacke, R.; Wiesenberger, F. *Z. Naturforsch.* **1991**, *46b*, 275–279. (k) Tacke, R.; Schmid, T.; Burschka, C.; Penka, M. Surburg, H. *Organometallics* **2002**, *21*, 113–120. (l) Schmid, T.; Daiss, J. O.; Ilg, R.; Surburg, H.; Tacke, R. *Organometallics* **2003**, *22*, 4343–4346.

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(49) $Ph_3P{\cdot}HBr$ is a mild, stable, and precisely weighable source of HBr, which is important with respect to the acid-sensitive Si–OH moiety of (*R*)-**12b**. To the most recent knowledge, the use of $Ph_3P{\cdot}HBr$ for the preparation of ammonium bromides from amines has hitherto not been reported.

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(52) Assuming that **58** is formed quantitatively in the course of the Shapiro reaction **57** → **58**.

(53) Surprisingly, this Grignard reagent did not react with 1,1-dichloro-1-silacyclohexane in refluxing diethyl ether (analogous reaction conditions, GC control).

(54) It is very likely that acetic acid is the active catalyst in this reaction, formed by reaction of acetic acid anhydride with the solvent methanol giving acetic acid and methyl acetate. Hence, the advantage of using acetic acid anhydride in this reaction instead of acetic acid is the fact that the use of the anhydride ensures the absence of any water.

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(58) The methods for the preparation of **22b** using the halogen/metal exchange of **96** with isopropylmagnesium bromide and using thionyl chloride in the final step (Scheme 11) were

developed by Amedis Pharmaceuticals Ltd., Cambridge, U.K., using the information on the Vollhardt-cyclization gained in the course of this work; cf. Scheme 10 (p. 21, section 5). The methods developed by Amedis Pharmaceuticals Ltd. were optimized in this work and additional methods for the preparation of **22b** (starting from **99** and using DCC or starting from **98** and using trimethylaluminum) were developed in this work; cf. Scheme 11 (p. 23, section 5).

(59) Both the use of THF as the solvent and performing the reaction at low temperature are essential for the successful use of $BrCH_2Cl$/*n*-BuLi as a chloromethylation reagent.[33]

(60) Compounds **10**, **29**, and **30** were prepared within the experimental work of the Diplomarbeit[13a] using the same methods in the last step, but a different strategy for the preparation of the earlier steps of their synthesis. The respective preparation protocols were published in ref. 13b. The pharmacological, experimental, and NMR data of **10**, **29**, and **30** are given in the respective sections for comparison and completeness.

(61) Although the imido moiety has seniority over the amino functionality in the nomenclature of these compounds, the use of the amine nomenclature produces analogous names in the course of the following step of the synthesis and thus follows the recommendations of IUPAC, Commission on Nomenclature of Organic Chemistry. *A Guide to IUPAC Nomenclature of Organic Compounds (Recommendations 1993)*, 1993, Blackwell Scientific publications, Oxford.

(62) After chromatographic purification, compound **53** was isolated in ca. 60% yield as a highly viscous, yellowish oil, which contained some residual ethyl acetate (ca. 5% by weight) that could not be removed in vacuo.

(63) Nametkin, N. S.; Vdovin, V. M.; Pushchevaya, K. S.; Egorochkin, A. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 2530; *Chem. Abstr.* **1968**, *69*, 59325n.

(64) When a mixture of Cl_3SiCH_2Cl and $Cl_2(Me)SiCH_2Cl$ (approx. 70:30 (aceotropic mixture)) was used for the preparation of **136**, pure **136** was obtained after distillation with a spinning band column. This represents a cost-effective way for the preparation of **136**.

(65) Treatment of **138** with Pd/C (dried in vacuo prior to use) in a hydrogen atmosphere (3 bar) for 16 h in methanol or THF afforded toluene and benzyl acetate as the main products (preparative HPLC purification of a representative sample). The presence of the latter compound clearly indicates that Si–C bond cleavage took place under these reaction conditions. Additionally, the ^{29}Si NMR spectrum of the mixture (after filtration and evaporation of the solvent in vacuo) showed several peaks.

(66) The data for compounds **10**, **11**, **27**, **29**, **30**, **32**, and **35** were taken from Duda-Johner, S. *Dissertation*, Universität Bonn, **2002**; the data for compounds **28**, **33**, **36**, **39**, **42**, **45**–**50**, *rac*-**51**, and *rac*-**52** were taken from Albrecht, M. *Dissertation*, Universität Bonn, in preparation.

(67) Further investigations are necessary to elucidate the effect of the most interesting test compounds of this series on the binding of [^{3}H]NMS and acetylcholine to muscarinic receptor subtypes. For investigations of muscarinic receptor subtype profiles of **27**, **30**, **32**, and **35** using [^{3}H]NMS, see ref. 43.

(68) Damrauer, R. *Organomet. Chem. Rev. A* **1972**, *8*, 67–133.

(69) For the reaction of trichlorosilane with with one, two, or three molar equivalents of (2,4,6-trimethoxyphenyl)lithium, see ref. 40e.

(70) Kocienski, P. J. *Protecting Groups*; Georg Thieme Verlag: Stuttgart, Germany, 2000; p 2.

(71) (a) Bassindale, A. R.; Stout, T. *J. Organomet. Chem.* **1984**, *271*, C1–C3. (b) Uhlig, W.; Tzschach, A. *J. Organomet. Chem.* **1989**, *378*, C1–C5. (c) Uhlig, W. *J. Organomet. Chem.* **1991**, *402*, C45–C49. (d) Uhlig, W. *J. Organomet. Chem.* **1991**, *409*, 377–383. (e) Uhlig, W. *Chem. Ber.* **1992**, *125*, 47–53. (f) Uhlig, W. *J. Organomet. Chem.* **1993**, *452*, 29–32. (g) Uhlig, W. *J. Organomet. Chem.* **1993**, *463*, 73–76. (h) Uhlig, W. *Z. Naturforsch.* **1994**, *49b*, 609–614. (i) Uhlig, W. *Chem. Ber.* **1996**, *129*, 733–739. (j) Chen, C.-A.; Sieburth, S. McN.; Glekas, A.; Hewitt, G. W.; Trainor, G. L.; Erickson-Viitanen, S.; Garber, S. S.; Cordova, B.; Jeffry, S.; Klabe, R. M. *Chem. Biol.* **2001**, *8*, 1161–1166. (k) Kim, J.; Glekas, A.; Sieburth, S. McN. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 3625–3627. (l) wa Mutahi, M.; Nittoli, T.; Guo, L.; Sieburth, S. McN. *J. Am. Chem. Soc.* **2002**, *124*, 7363–7375. (m) Kim, J.; Sieburth, S. McN. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 2853–2856.

(72) (a) Häbich, D.; Effenberger, F. *Synthesis* **1978**, 755–756. (b) Eaborn, C.; Lickiss, P. D.; Ramadan, N. A. *J. Chem. Soc. Perkin Trans. 2* **1984**, 267–270. (c) Coppi, L.; Ricci, A.; Taddei, M. *Tetrahedron Lett.* **1987**, *28*, 965–968. (d) Eaborn, C.; Jones, K. L.; Lickiss, P. D. *J. Organomet. Chem.* **1993**, *461*, 31–34. (e) Showell, G. A.; Chadwick, J. A.; Higgs, C.; Hunt, H. J.; MacKenzie, R. E.; Price, S.; Wilkinson, T. J.; Montana, J. G. In *Organosilicon Chemistry VI*; Auner, N., Weis, J., Eds. Wiley-VCH: Weinheim, Germany, in press.

(73) The crystal structure analyses were performed by Martin Penka (compounds **74** and **75**) and Dr. Christian Burschka (all the other crystal structure analyses).

(74) (a) Sheldrick, G. M. SHELXS-97; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *Acta Crystallogr., Sect A* **1990**, *46*, 467–473.

(75) Sheldrick, G. M. SHELXL-97; University of Göttingen: Göttingen, Germany, 1997.

(76) The hydrogen-bonding systems were analyzed by using the program system PLATON: Spek, A. L. PLATON; University of Utrecht: Utrecht, The Netherlands, 1998. In this context, see also: Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, Germany, 1991; pp 15–24.

(77) (a) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876–881. (b) Flack, H. D.; Bernardinelli, G. *Acta Crystallogr., Sect. A* **1999**, *55*, 908–915. (c) Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, *33*, 1143–1148.

(78) Interestingly, the melting point of a sample of **22b** that had been crystallized from diethyl ether at 4 to –20 °C was 139 °C (see Experimental section). A finely ground 1:1 (w/w) mixture of the modifications of **22b** melting at 139 °C and 158 °C showed melting of half of the material at 139 °C (heating rate 1 °C min^{-1}), followed by recrystallization of all of the molten material at 140–142 °C (heating rate 1 °C min^{-1}) and, finally, a very sharp melting point of all of the material at 157.6–157.9 °C (heating rate 0.5 °C min^{-1}).

(79) All attempts to characterize **22a** by single-crystal X-ray diffraction failed, but very similar conformations of the 3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydro-2-naphthyl group of **21a** and **22a** can be expected.

(80) Rademacher, P. *Strukturen organischer Moleküle*; VCH Verlagsgesellschaft: Weinheim, Germany, 1987; p 56.

(81) The single crystals of **146** were obtained as a conglomerate with crystals of compound **74**. Therefore, the crystal structure analysis of **146** was performed successfully, but no further characterization (mp, NMR) was obtained from this conglomerate.

(82) The moisture-sensitive hydrochloride *rac*-**18**·HCl was prepared and stored under nitrogen.

(83) (a) Program WIN-DAISY 4.05, Bruker-Franzen GmbH, Bremen, Germany, 1998. (b) Weber, U.; Germanus, A.; Thiele, H. *Fresenius J. Anal. Chem.* **1997**, *359*, 46–49.

(84) The ^{1}H NMR data of *rac*-**12b**·HCl, (*R*)-**12b**·HCl, (*S*)-**12b**·HCl, (*R*)-**12b**·HBr, *rac*-**13**·HCl, and *rac*-**15**·HCl depend significantly on the concentration of these compounds, especially for the $SiCH_CCH_AH_BNH_G(C(H_M)_3(C(H_N)_3)$ moiety. The data given were obtained at a concentration of 80 mM. The $^3J_{AG}$ and $^3J_{BG}$ couplings are not resolved, but recognizable by line broadening of the signals for the CH_AH_BN protons.

(85) The ^{1}H NMR spectra of (*R*)-**12b**·HCl and (*S*)-**12b**·HCl differ slightly from the ^{1}H NMR spectrum of *rac*-**12b**·HCl in the $SiCH_CCH_AH_BNH_G(C(H_M)_3)(C(H_N)_3)$ region. This could be explained by the existence of different aggregates in solution ((*R*)-**12b**·HCl and (*S*)-**12b**·HCl, exclusively (*R*,*R*)- or (*S*,*S*)-aggregates; *rac*-**12b**·HCl, (*R*,*R*)-, (*S*,*S*)-, and (*R*,*S*)-aggregates).

(86) As significant disiloxane formation was observed at 22 °C in $CDCl_3$, the NMR spectra of *rac*-**13** were recorded at –20 °C.

(87) (a) The ^{1}H NMR spectrum showed minor impurities at δ 2.72 (s) and 3.06–3.14 (m), which could not be removed by fractional crystallization. (b) The ^{13}C NMR spectrum showed minor impurities at δ 23.3, 42.1, and 54.2, which could not be removed by fractional crystallization.

(88) (a) The ^{1}H NMR spectrum showed minor impurities at δ 0.98 (d, J_{HH} = 6.6 Hz, 1 H), 2.22–2.40 (m), and 2.78 (dd, J_{HH} = 20.8 Hz, J_{HH} = 4.0 Hz), which could not be removed by fractional crystallization. (b) The ^{13}C NMR spectrum showed minor impurities at δ 15.8, 28.9, 40.9, 41.8, 43.4, 59.8, 123.05, 131.5, and 134.40, which could not be removed by fractional crystallization.

(89) Absence of dichloromethane as the solvent of crystallization was verified by recording a ^{1}H NMR spectrum of **53**·HCl in [D_6]DMSO. However, due to the poor solubility of **53**·HCl in [D_6]DMSO, this solvent was not suitable for recording ^{13}C, ^{15}N, and ^{29}Si NMR spectra of this compound.

(90) For a similar method, see: West, R. *J. Am. Chem. Soc.* **1954**, *76*, 6012–6014.

(91) This procedure follows a general protocol described in: Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147–154 (there referred to as Method A). In this context, see also: Yu, W.-Y.; Bensimon, C.; Alper, H. *Chem. Eur. J.* **1997**, *3*, 417–423.

(92) Significant decomposition of **57** was observed in $CDCl_3$ at 20 °C.

(93) Diethyl(methyl)amine was used for the preparation of **70** instead of triethylamine since the latter is hard to separate from the product by distillation. In addition, the precipitate of Et_2NMe·HCl, which is formed during the reaction, is much less voluminous than the corresponding salt Et_3N·HCl and therefore can be separated much easier by filtration.

(94) As **74** does not dissolve in *n*-hexane at ambient temperature, heating is required.

(95) Attempts to separate **81** and **82** by distillation were unsuccessful. However, the identities of **81** and **82** could be established unequivocally by comparing the GC-MS data of the mixture with those of authentic samples.

(96) The 1,2-bis(chlorodimethylsilyl)ethane (**83**) obtained from the Wacker-Chemie GmbH did not contain the isomer 1,1-bis(chlorodimethylsilyl)ethane in detectable amounts (GC).

(97) Kusumoto, T.; Hiyama, T. *Chem. Lett.* **1988**, 1149–1152.

(98) Effenberger, F.; Gleiter, R.; Heider, L.; Niess, R. *Chem. Ber.* **1968**, *101*, 502–511.

(99) A representative sample of the precipitated solids was dissolved in dichloromethane and analyzed by GC to ensure that the desired product **105** had not formed and then precipitated quantitatively.

(100) This amount includes the portions of chlorodimethylsilane which were added after 30 (5.00 g) and after 40, 50, 60, and 70 min (4 × 1.00 g); cf. the preparation protocol for **108**.

(101) Care should be taken during the distillation of compound **109**, and the acidic aqueous workup described in the protocol should never be omitted. A violent explosion occurred when the excess lithium aluminum hydride and other precipitates were removed after the reaction by centrifugation (no acidic aqueous workup), followed by removing the solvent under reduced pressure and subsequent distillation.

(102) Using solid $H_2PtCl_6 \cdot 6H_2O$ as the first portion has the advantage that only a tiny amount of the catalyst dissolves in the reaction mixture. This helps to keep the reaction under control, which, in some cases, can be very vigorous, especially when done at larger scales. In certain cases, more (cf. preparation of *rac*-**127**) or fewer portions (cf. preparation of **118**) may be necessary, depending on the nature of the starting materials and on the reaction scales; the exact amount of $H_2PtCl_6 \cdot 6H_2O$ used is given in the respective preparation protocols.

(103) Compound **129** was prepared within the experimental work of the Diplomarbeit.[13a] The experimental and NMR data are given for comparison and completeness.

(104) The distillation could not be performed under reduced pressure owing to excessive foaming.

(105) After the solvent was removed under reduced pressure, the salt **135**$\cdot CH_3C(O)OH$ was obtained. During the subsequent bulb-to-bulb distillation, dissociation of this salt occurred, and acetic acid was collected at <150 °C/0.05 mbar as a lower-boiling fraction in a cooled trap.

(106) Attempts to recrystallize the NMR-spectroscopically almost pure product from various organic solvents (ethyl acetate, dichloromethane, propan-2-ol) failed due to the instability of **135** in solution. Meanwhile, compound **135** has been described in the literature, stating that it can be recrystallized successfully from a mixture of dichloromethane and hexane; see Jones, G., II; Kumar, S. *J. Photochem. Photobiol. A: Chemistry* **2003**, *160*, 139–149.

(107) The same dropping funnel was used for the addition of this and of all the following reagents and was flushed with THF (10 mL) after the addition of each reagent, thus diluting the reagent mixture by a small extent.

(108) Under milder reaction conditions (20 °C), the same product was obtained, but it was formed at a much slower rate.

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Daiß, J. O.; Tacke, R.; Bains, W.; Warneck, J. Synthesis and Pharmacological Characterization of Sila-venlafaxine, a Silicon Analogue of the Antidepressant Venlafaxine. *2nd European Organosilicon Days*, München, Deutschland, 11.–12. September 2003; Nr. A 8.

Erklärung

Hiermit erkläre ich an Eides statt, daß ich die Dissertation

Synthesis of Sila-Analogs and Silicon-Containing Derivatives of Drugs and Development and Application of the *Si*-2,4,6-Trimethoxyphenyl Moiety as a Novel Protecting Group in Organosilicon Chemistry

selbständig angefertigt und keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt habe.

Ich erkläre außerdem, daß diese Dissertation weder in gleicher oder anderer Form bereits in einem anderen Prüfungsverfahren vorgelegen hat.

Ich habe früher außer den mit dem Zulassungsgesuch urkundlich vorgelegten Graden keine weiteren akademischen Grade erworben oder zu erwerben versucht.

Würzburg, den

(Jürgen Oliver Daiß)