Synthesis of Silicon-Based Drugs and Odourants

Dissertation zur Erlangung des

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vorgelegt von

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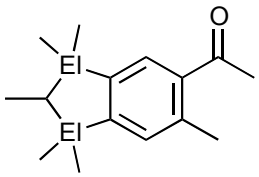
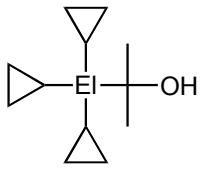
Contents

1 Introduction

One of the major themes tackled in our research group is the synthesis of silicon-containing biologically active organic molecules. The target compounds are most usually drugs (for recent examples, see refs 1 and 2) or odourants (for recent examples, see refs 3–5). Biologically active silicon-containing molecules are most often synthesised using one of the following two methodologies. In the silicon-switch strategy, a quaternary carbon atom of a drug or odourant is replaced with a silicon atom. Practically, this means that an analogue of a known biologically active substance is synthesised where one or more carbon atoms are replaced with silicon, for example the musk odourant phantolide (**1a**) and its silicon-containing analogue disila-phantolide (**1b**).[3b] The second method involves the production of a completely new silicon-containing structural motif. Often the carbon analogues of this second type of molecule are completely unknown or have very long, involved, and thus usually expensive synthetic accesses. This is well illustrated by the C/Si-analogous patchouli odourants **2a** and **2b**. The silicon compound (**2b**) is easily produced in a three-step process starting from tetrachlorosilane, whereas the synthesis of the carbon analogue (**2a**) requires six steps and is comparatively low yielding.[5]



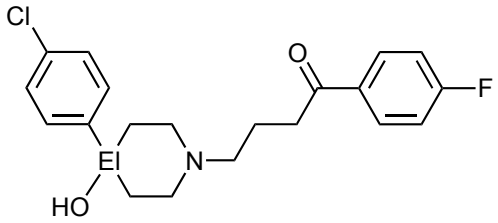
El = C: **1a** (Phantolide)
El = Si: **1b** (Disila-phantolide)



El = C: **2a**
El = Si: **2b**

This piece of work focuses on the first of the two methods outlined above. Located as it is in group 14 of the periodic table, silicon can superficially mimic a quaternary carbon centre. However, the fundamental differences between the two elements are the power behind the silicon-switch strategy. Silicon analogues of known drugs and odourants can display altered pharmacological or olfactory profiles due to the differences between the covalent radius and electronegativity of the carbon and silicon atom. In addition, the bond strength and length, along with the possible bonding modes of a carbon-silicon or silicon-silicon bond when compared with a carbon-carbon bond can affect the biodegradability. Obviously, the aim of

the silicon-switch strategy is to produce an improved version of the target molecule, and a fantastic example of this is the sila-substitution of haloperidol (**3a** → sila-haloperidol, **3b**).



El = C: **3a** (Haloperidol)
El = Si: **3b** (Sila-haloperidol)

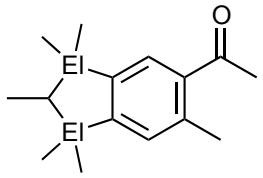
Haloperidol (**3a**) is an antipsychotic drug, and prolonged treatment can result in irreversible side effects with similar symptoms to Parkinson's disease. These side effects are caused by a metabolite with a carbon-carbon double bond formed in the first metabolic step by water elimination in the piperidine ring. Metabolism of sila-haloperidol (**3b**) does not result in an analogue of this compound, as this would require the formation of an energetically unfavourable silicon-carbon double bond,[2b,2d] thus demonstrating that the silicon-switch can potentially have a massive effect on the metabolism of a given molecule.

2 Aims and Objectives

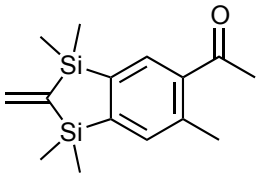
Broadly, the aim of this project was to synthesise silicon-containing bioactive molecules with potential applications as drugs or odourants. In all cases the molecules were analogues of known biologically active carbon compounds, thus allowing comparisons of the pharmacological activities or odour profiles and providing further information on the effectiveness of the silicon-switch strategy. Focus was also given to the effect sila-substitution would have on the biodegradability of a known molecule.

2.1 1,2,3-Trisilaindanes as Phantolide Analogues

Previously, a thorough, systematic investigation into the effect of modification of the saturated portion of the indane skeleton of the musk odourant phantolide (**1a**) on the molecule's odour profile was carried out.[3b] Disila-phantolide (**1b**) and its derivatives **4**–**7** were synthesised and their odour profiles were analysed.



El = C: **1a** (Phantolide)
El = Si: **1b** (Disila-phantolide)



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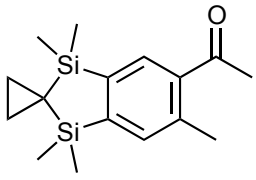

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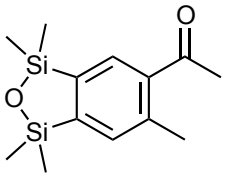

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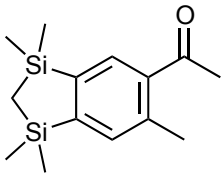

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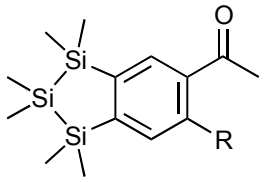
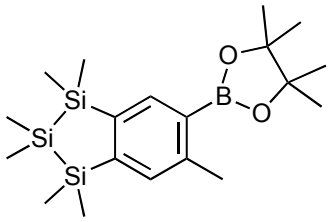
The next logical step was to include a third silicon atom at the 2-position of the indane ring system. This would almost certainly alter the odour profile, as the previous study aptly demonstrated; the substitution pattern or heteroatom at the 2-position of the indane ring has a controlling effect on the odour of the molecule.[3b] However, we hoped for an additional benefit. The biodegradability of the indane and related tetrahydronaphthalene skeletons is

notoriously poor. We intended to take advantage of the relative weakness of the Si–Si single bond in comparison with Si–C and C–C single bonds with a view to the synthesis of musk odorants with enhanced biodegradability. Thus, the potential odourants **8** (2-methyltrisilaphantolide) and **9** were to be synthesised, along with the building block **10**, a potential precursor for silicon-based retinoids (see chapter 2.2). The olfactory properties of compounds **8** and **9** were to be investigated through collaboration with expert perfumers in industry.



R = Me: **8**
R = Et: **9**



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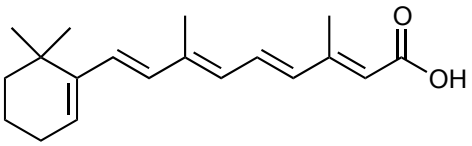
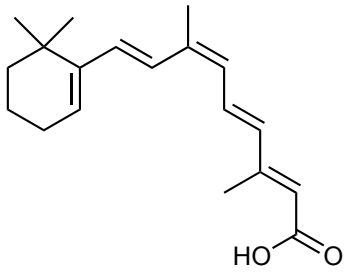
There are few reports on 1,2,3-trisilaindane species in the literature. Molecules of this class have been synthesised with alkyl or aryl substituted silicon atoms[6] and more recently with Si–Cl and Si–H bonds.[7] However, these compounds were all obtained via catalytic or thermal isomerisation reactions. To the best of our knowledge, a targeted synthesis of the 1,2,3-trisilaindane skeleton had not been reported prior to our paper on the subject,[3c] and these compounds are the only examples of 1,2,3-trisilaindane derivatives with substituents at the 5- and 6-positions of the aromatic ring.

2.2 Disila-Retinoids

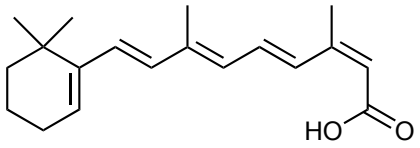
Retinoids are a group of compounds that are metabolites or synthetic analogues of vitamin A (retinol). The term ‘retinoid’ was coined by M. Sporn in the mid 1970s when he reported the first systematic study of a set of vitamin A analogues.[8] Retinoids can be divided into two groups, namely the naturally occurring metabolites of vitamin A and their synthetic analogues. The naturally occurring retinoids all-*trans* retinoic acid (**11**, ATRA), 9-*cis* retinoic acid (**12**, 9*c*RA) and 13-*cis* retinoic acid (**13**, 13*c*RA), along with a few synthetic analogues (e.g. bexarotene), are currently in clinical use for the treatment of proliferative skin diseases and/or cancer.[9]



11: all-*trans* Retinoic Acid



12: 9-*cis* Retinoic Acid



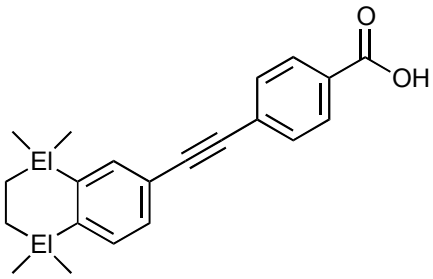
13: 13-*cis* Retinoic Acid

Retinoid activity results from the transcriptional regulation of specific genes. Regulation of these processes occurs through the binding of retinoids with nuclear receptors from the steroid/thyroid superfamily.[10] The retinoid signal is mediated in target cells through RARs (retinoic acid receptors) and RXRs (retinoid X receptors), each of which comprise three isotypes: α, β and γ.[11] RARs and RXRs are divergent in their ligand specificity. For example, ATRA can bind and activate only RAR receptors, whereas 9-*cis* RA binds and activates all three of the RAR and RXR subtypes and shows different affinities for each.[12]

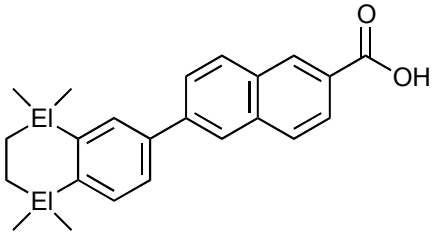
Each of the RAR/RXR subtypes mediate different biological processes.. Additionally, each subtype tends to be associated with one or more particular tissue types. RARγ is primarily expressed in the skin and is associated with photoaging, skin disorders such as acne and psoriasis, and teratogenic effects. RARβ is mainly expressed in the heart, lungs and spleen. As the RARβ receptor plays an important role in limiting the growth of certain cell types, it is a worthwhile target for cancer prevention. RARα is ubiquitous in its distribution and has been associated with triglyceride levels. The RXR isotypes are mostly expressed in adult tissue. RXRβ is present in nearly all tissue types, whereas RXRα is associated with expression in the liver, kidneys and spleen, while the RXRγ subtype tends to be expressed in the brain and muscles.[13]

Generally, retinoids consist of a bulky hydrophobic group connected to a polar group (usually a carboxyl moiety) by a hydrophobic linker.[14] The synthetic retinoids EC23 (**14a**), a close mimic of ATRA (**11**)[15] and TTNN (**15a**),[16] an RARβ,γ-selective retinoid,[17] display these typical structural features, with the 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene

moiety as the bulky hydrophobic group. Previous work has aptly demonstrated that the carbon/silicon switch strategy (C/Si exchange, sila-substitution) is a powerful tool when applied to retinoids based on 1,2,3,4-tetrahydronaphthalene or indane skeletons. Sila-substituition has resulted in an up to ten-fold increase in activity and, in some cases, to changes of the retinoid receptor subtype selectivity.[1] In order to study the effect of the carbon/silicon switch on molecules of this type, silicon analogues of the retinoids EC23 (**14a**→ disila-EC23 (**14b**)) and TTNN (**15a**→ disila-TTNN (**15b**)) were to be synthesised.

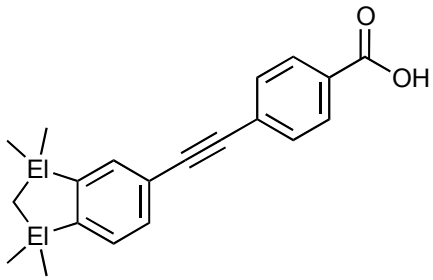


El = C: **14a** (EC23)
El = Si: **14b** (Disila-EC23)

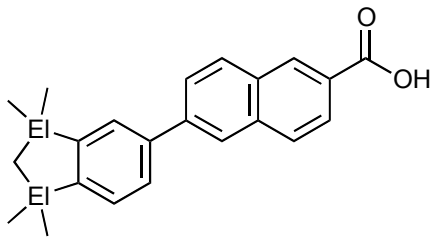


El = C: **15a** (TTNN)
El = Si: **15b** (Disila-TTNN)

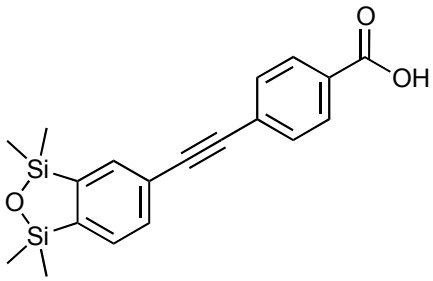
In order to complement this study on C/Si bioisosterism, the related disila-retinoids **16b**, **17**, **18b** and **19** were also to be synthesised, as well as the previously unknown carbon analogues **16a** and **18a**.



El = C: **16a**
El = Si: **16b**



El = C: **18a**
El = Si: **18b**



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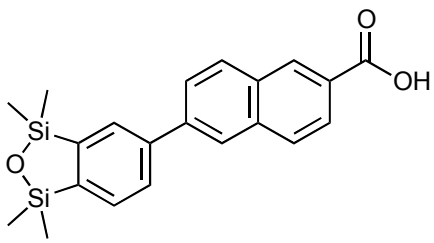


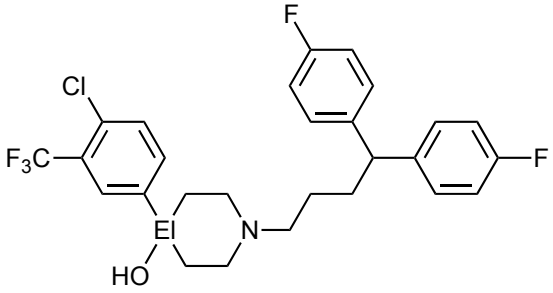
19

In these compounds the 1,2,3,4-tetrahydronaphthalene moiety is replaced with an indane, disilaindane or oxadisilaindane type bicyclic skeleton allowing the study of the effect on receptor binding resulting from the alteration of the steric bulk and/or polarity of the unsaturated portion of the retinoid molecule. These investigations were to be performed with a special emphasis on the comparison of (i) the C/Si analogues **14a**/**14b**, **15a**/**15b**, **16a**/**16b** and **18a**/**18b** (effect of two-fold sila-substitution) and (ii) the CH_2/O analogues **16b**/**17** and **18b**/**19** (effect of replacement of the $SiCH_2Si$ fragment with the more polar SiOSi moiety). The biological activities of **14a**, **14b**, **15a**, **15b**, **16a**, **16b**, **17**, **18a**, **18b**, and **19** were to be investigated through collaboration with colleagues from academia.

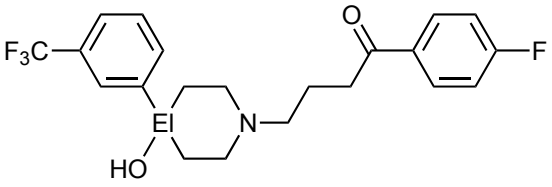
2.3 Sila-penfluridol

Penfluridol (**20a**) is an antipsychotic drug based on a 1,4-substituted piperidine skeleton and derives from the butyrophenone class of molecules. Janssen Pharmaceutica first developed this drug in the early 1970s[18] with the aim of producing an orally administrable antipsychotic that need only be taken once weekly.[19] The strategy chosen to achieve this goal was to produce a molecule with very high lipophilicity that also shared structural features with known butyrophenone antipsychotics, such as haloperidol (**3a**) and trifluperidol (**21a**). High lipophilicity would ease passage of the drug through the blood-brain barrier, resulting in improved potency by increasing the concentration of the drug at the site of action. A second benefit of increased lipophilicity is higher fat solubility of the molecule, this means that the drug can be stored in the lipid tissues and slowly released, resulting in a much longer duration of action.[19] Due to this slow release mechanism, penfluridol is currently in clinical use as a depot medication for treatment of chronic schizophrenics, especially those who do not respond well to daily oral medication.[20] While the synthesis of penfluridol has been the subject of extensive studies,[21] no comprehensive examination of the *in vitro* activity of **20a** exists in the literature. Penfluridol is known to be a dopamine antagonist,[22] however only one receptor specific (D_4) study has been reported.[23] The drug also binds to serotonin[24] and $sigma_1$[25] receptors, and is a calcium channel antagonist.[26] Sila-substitution in structurally similar butyrophenone type antipsychotics has been shown to radically alter their receptor specificity.[2] Previously, several attempts to synthesise the silicon analogue of penfluridol (**20a**), sila-penfluridol (**20b**), have been made.[27,28] However,

chemically pure sila-penfluridol has not been obtained so far due to the difficulties incurred in the isolation of the free silanol.



El = C: **20a** (Penfluridol)
El = Si: **20b** (Sila-penfluridol)

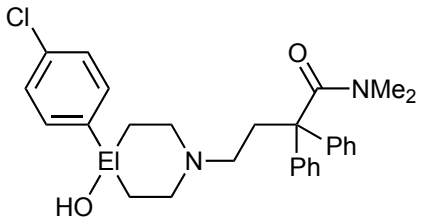


El = C: **21a** (Trifluperidol)
El = Si: **21b** (Sila-trifluperidol)

Following the development of the 2,4,6-trimethoxyphenyl moiety as a protecting group for silicon,[29] syntheses of silicon analogues of the related butyrophenone-type antipsychotics haloperidol (**3a**→ sila-haloperidol, (**3b**)) and trifluperidol (**21a**→ sila-trifluperidol, (**21b**)) were developed using this protecting group to mask the silanol functionality.[2b–2d] Sila-penfluridol (**20b**) was to be synthesised analogously, using the 2,4,6-trimethoxyphenyl protecting group, and its biological properties analysed through collaboration with colleagues from academia.

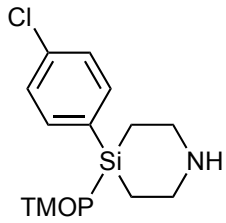
2.4 Sila-loperamide

Similarly to haloperidol (**3a**), loperamide (**22a**) is a drug of the butyrophenone class, also developed by Janssen Pharmaceuticals. The discovery that loperamide displays high antidiarrheal activity was initially surprising given that the 4-aryl-4-pipiridinol moiety is typically found in neuroleptics such as penfluridol and haloperidol.[30] Loperamide was selected from a series of around fifty related compounds as having the optimum balance of high antidiarrheal activity and non-existent analgesic effects.[30] Unlike other opioids, loperamide does not affect the central nervous system; however, the observed antidiarrheal activity is mediated by the μ-opiate receptor.[31]



El = C: **22a** (Loperamide)
El = Si: **22b** (Sila-loperamide)

As with sila-penfluridol, several attempts at the synthesis of sila-loperamide (**22a**) have been made. The target compound has been previously isolated as the corresponding hydrochloride (**22b**·HCl); however, the purity was unsatisfactory.[28] A further attempt to synthesise sila-loperamide using the 2,4,6-trimethoxyphenyl protecting group was made, however, this was unsuccessful as synthesis and isolation of the free base of the piperidine intermediate **23** was not possible.[29b]



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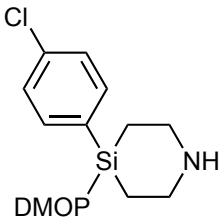

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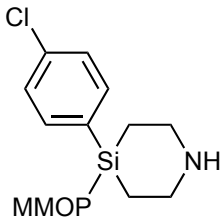

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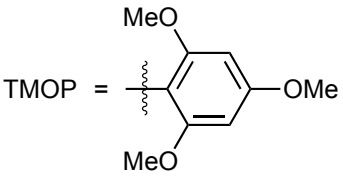
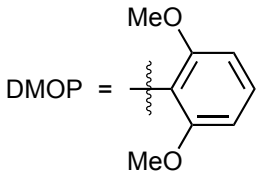
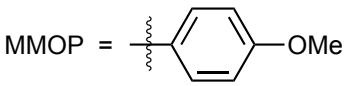




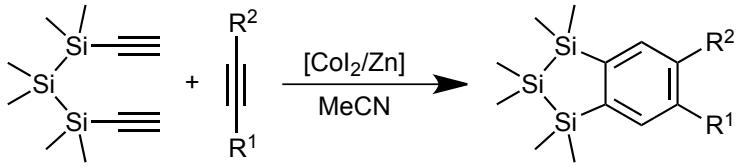


Thus, two projects were to be run concurrently, the free silapiperidines **24** and **25** were to be produced containing the less labile[29a] 2,6-dimethoxyphenyl (DMOP) or 4-methoxyphenyl (MMOP) protecting groups. The sticking point of the previous attempted synthesis, via compound **23**, was the selective deprotection of the amine functionality. Hopefully, a less labile silicon protecting group would alleviate this problem and allow the isolation of the intermediate amine. This piece of work concerns the synthesis of **22a** via compound **24**, the synthesis via compound **25** was to be carried out simultaneously.[32]

3 1,2,3-Trisilaindanes as Phantolide Analogues

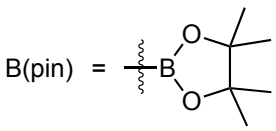
3.1 Syntheses

2-Methyltrisilaphantolide (**8**), along with the related compounds **9**, **10** and **26**, was synthesised according to Scheme 3.1 via a cobalt-catalysed [2+2+2] cycloaddition of 1,3-diethynylhexamethyltrisilane (**27**) and an appropriate monoalkyne (**28**–**31**). The cycloaddition was carried out using a catalytic system comprising cobalt(II) iodide and zinc powder in acetonitrile[33] (yields: **8**, 13%; **9**, 17%; **10**, 25%; **26**, 24%).



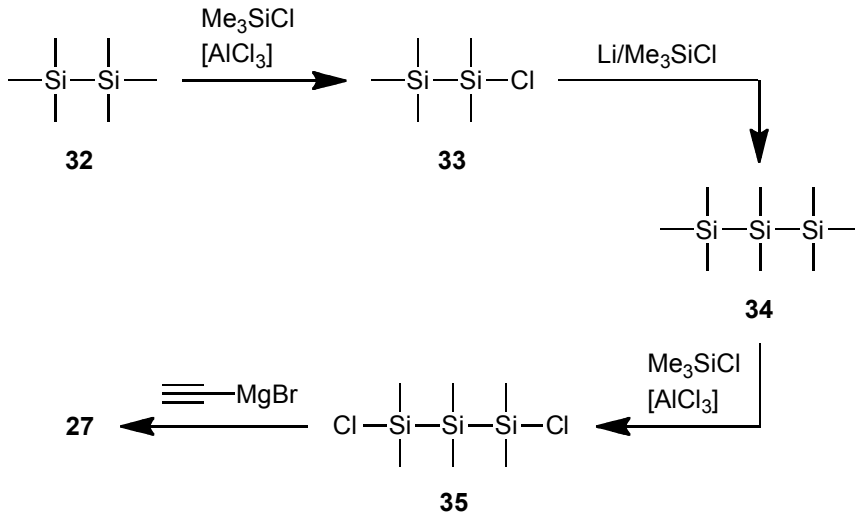
27 **28–31** **8–10**, **26**

	R^1	R^2
8, **28**	Me	C(O)Me
9, **29**	Et	C(O)Me
10, **30**	Me	B(pin)
26, **31**	Me	CH(OH)Me



Scheme 3.1

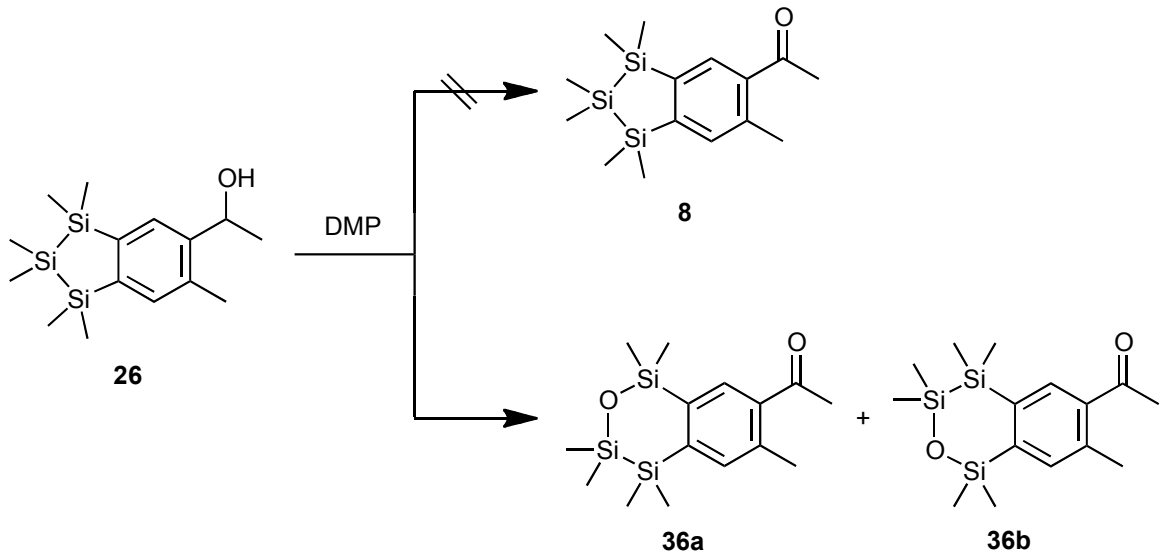
The precursor dialkyne **27** was synthesised in a multi-step procedure according to Scheme 3.2. Commercially available hexamethyldisilane (**32**) was treated with chlorotrimethylsilane and a catalytic amount of aluminium trichloride to produce chloropentamethyldisilane (**33**) in 67% yield. The synthesis of **27** then proceeded via previously described procedures: first, coupling of **33** with chlorotrimethylsilane using lithium powder gave octamethyltrisilane (**34**). 1,3-Dichlorohexamethyltrisilane (**35**) was then produced similarly to **33** by treatment of **34** by treatment with chlorotrimethylsilane and a catalytic amount of aluminium trichloride. Finally, the 1,3-diethynyl trisilane **27** was prepared by reaction of **35** with ethynylmagnesium bromide.



Scheme 3.2

3.2 Stability

Initially, the ketones **8** and **9** were to be synthesised via oxidation of the corresponding alcohols by analogy with previous work.[3b] However, reaction of compound **26** with an oxidising agent (MnO_2, $K_2Cr_2O_7$, pyridinium chlorochromate or the Dess-Martin perioindane[34]) did not result in formation of the desired product **8**. Surprisingly, treatment of **26** with the Dess-Martin perioindane (DMP) yielded compounds **36a** and **36b** (Scheme 3.3).



Scheme 3.3

The novel 1,3,4-trisilaisochroman system (compounds **36a** and **36b**) was isolated in 48% yield as a mixture of the two possible isomers in the molar ratio of 1:0.85 (**36a**:**36b**). Thus, the [2+2+2] cycloaddition was by necessity the last step in the synthesis of the potential odorants **8** and **9**. Any attempts to further derivatise the 1,2,3-trisilaindane skeleton (for example the use of compound **10** as a palladium catalysed cross coupling substrate; see ref. 33b for an example of similar work) resulted in reactions occurring at the silicon atoms rather than at the substituent on the aromatic ring.

3.3 Olfactory Studies*

Compounds **8** and **9** were studied for their olfactory properties. Neither compound displayed a musk odour. An underlying musky effect is only recognizable in the powdery shade of the ethyl-substituted compound **9**. This makes these 1,2,3-trisilaindanes closer in their structure-odor relationship to versalide (1-(3-ethyl-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)ethanone)[3a] than to phantolide, which might be due to the greater volume of the $SiMe_2SiMe_2SiMe_2$ moiety. In the analogous carbon series, the nor-derivative vernolide (1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)ethanone) is also less musky than the parent odorant versalide.[3a] However, both 1,2,3-trisilaindanes **8** and **9** were very weak in

* The olfactory studies were carried out by Dr. Philip Kraft and co-workers at Givaudan Schweiz AG, Fragrance Research, Dübendorf, Switzerland.

odour, with threshold values of 866 ng L^{-1} air (**8**) and 750 ng L^{-1} air (**9**). The weak odour was not due to oxidation or other decomposition as the compounds proved to be stable enough during olfactory evaluation in air (GC analysis), and no off-odours appeared during the evaluation. Of course, an oxidation by cytochrome P450 oxidases in the nasal mucosa[35] cannot be completely ruled out, but the molecular dimensions and the high molecular mass of **8** (306 u) and **9** (320 u) are the most likely reasons for the weak odours of these compounds. The "heaviest" odourant known to date is a linear musk of the formula $C_{20}H_{36}O_3$[36] (325 u), but for polycyclic musks disila-versalide,[3a] $C_{16}H_{26}OSi_2$ (290 u), holds the record. An increase in molecular mass results in a decrease in the volatility and vapour pressure. Yet, the GC threshold values indicate that the weak odour impression is not due to volatility or vapour pressure but inherent to the structural and electronic properties of **8** and **9**.

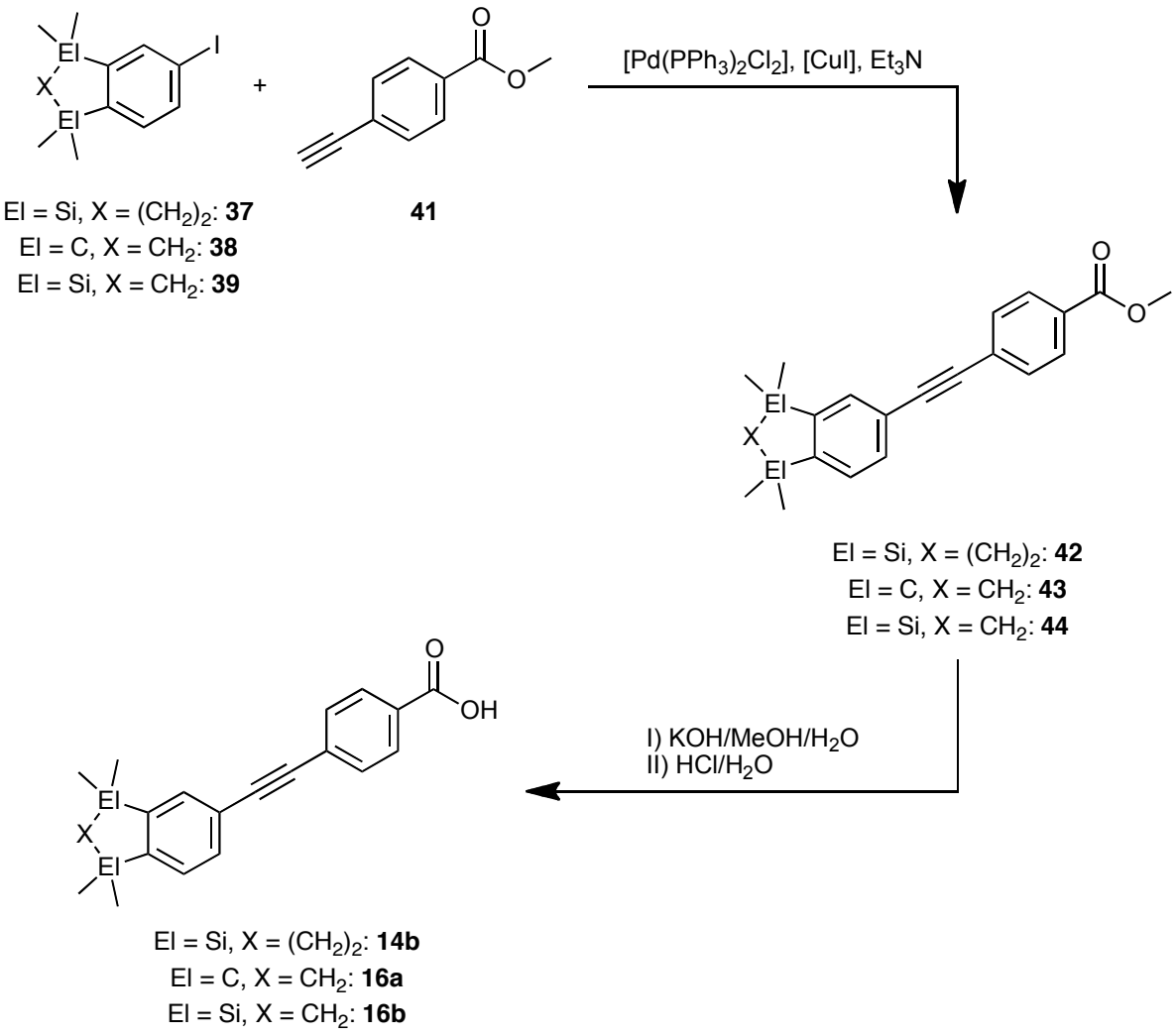
The main odour character of the 1,2,3-trisilaindanes **8** and **9** is creamy-lactonic with some coumarinic aspects. The coumarine note was more pronounced in the slightly more potent ethyl-substituted derivative **9**, which in addition was reminiscent of hay, tonka beans, and tobacco, and had a powdery shade. Together with the high threshold values, the non-musky main characters of **8** and **9** indicate that the molecules exceed the molecular dimensions of the musk odorant receptor binding site(s).

4 Disila-Retinoids

4.1 Retinoid Syntheses

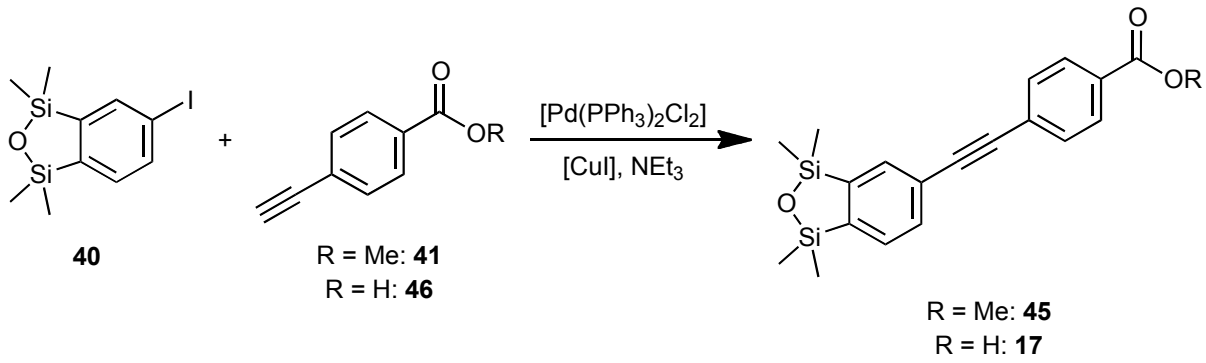
4.1.1 EC23 Derivatives

The series of compounds based on the retinoid EC23[14] (**14b**, **16a**, **16b** and **17**) were synthesised according to Schemes 4.1 and 4.2. A palladium-catalysed Sonogashira cross coupling[37] of an appropriate aryl iodide (**37**–**40**) with methyl 4-ethynylbenzoate (**41**) gave the protected intermediates **42**–**45** (yields: **42**, 82%; **43**, 95%; **44**, 97%; **45**, 96%). The methyl esters of **42**–**44** were then deprotected using potassium hydroxide in methanol/water, followed by acidification with hydrochloric acid (Scheme 4.1), to afford the target compounds (yields: **14b**, 76%; **16a**, 90%; **16b**, 95%).



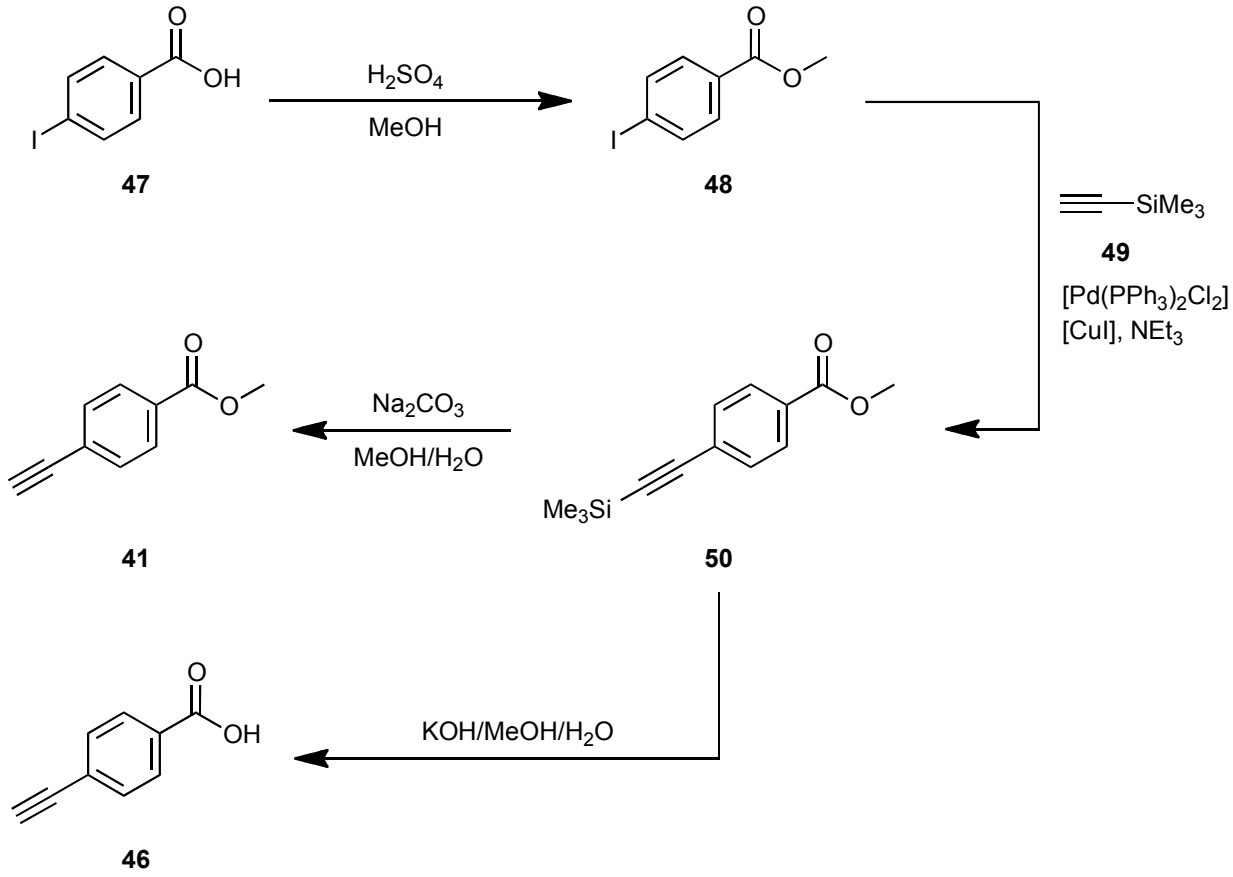
Scheme 4.1

Unfortunately, the conditions of this deprotection step proved to be incompatible with the siloxane backbone of compound **45** and we were unable to obtain a pure sample of **17** using this methodology. Omission of the methyl ester protecting group allowed the direct synthesis of compound **17** in 67% yield by cross coupling of 4-ethynylbenzoic acid (**46**) with the aryl iodide **40** (Scheme 4.2).



Scheme 4.2

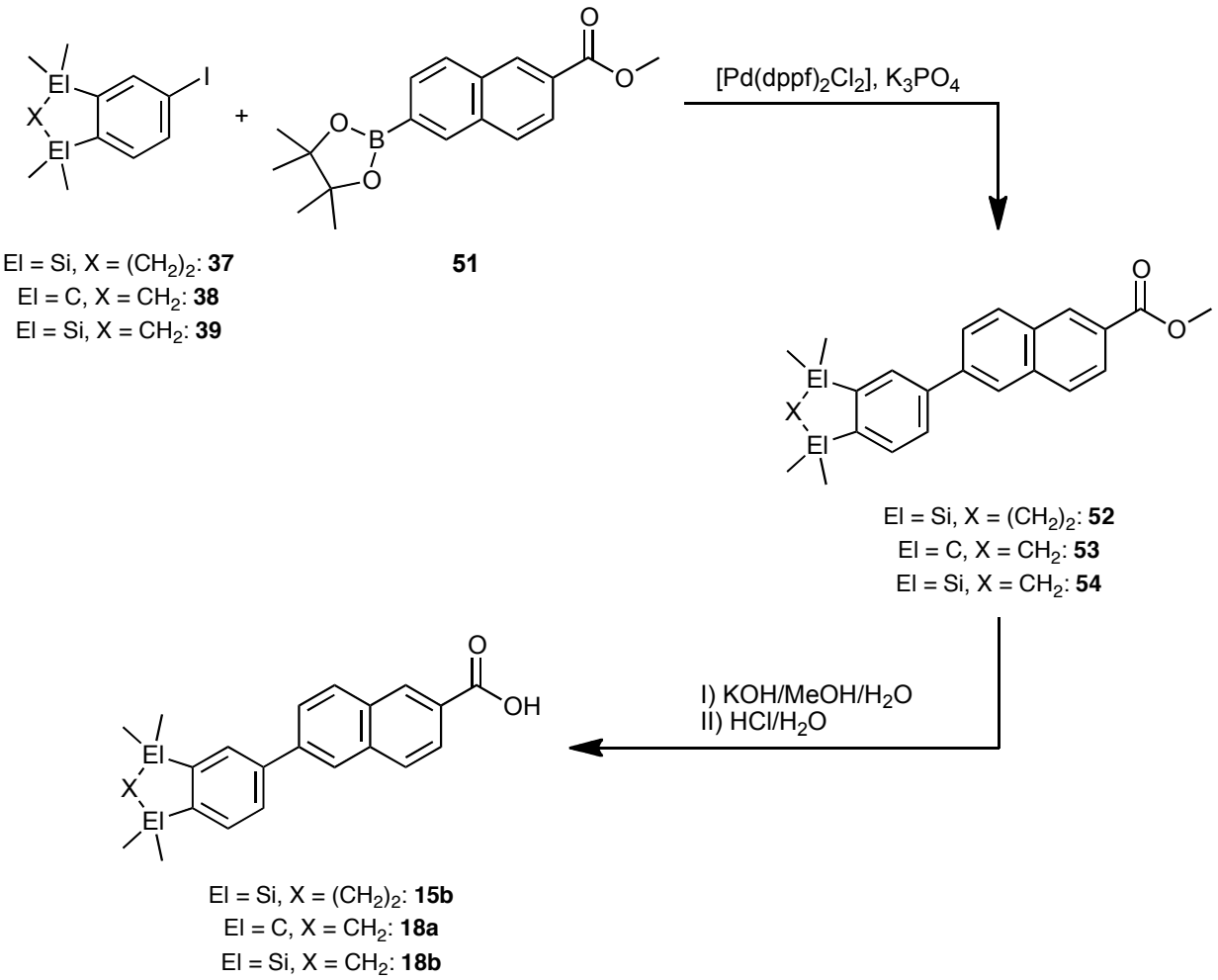
The aryl iodides **37**–**40** were synthesised as described in Chapter 4.2. Compounds **41** and **46** were synthesised according to Scheme 4.3. 4-Iodobenzoic acid (**47**) was protected as the methyl ester (**48**) with sulphuric acid and methanol. Subsequent Sonogashira[37] coupling with ethynyltrimethylsilane (**49**) afforded the trimethylsilyl protected alkyne (**50**). Deprotection of **50** with sodium carbonate in aqueous methanol yielded methyl 4-ethynylbenzoate (**41**), whereas deprotection with potassium hydroxide in aqueous methanol yielded **46**.



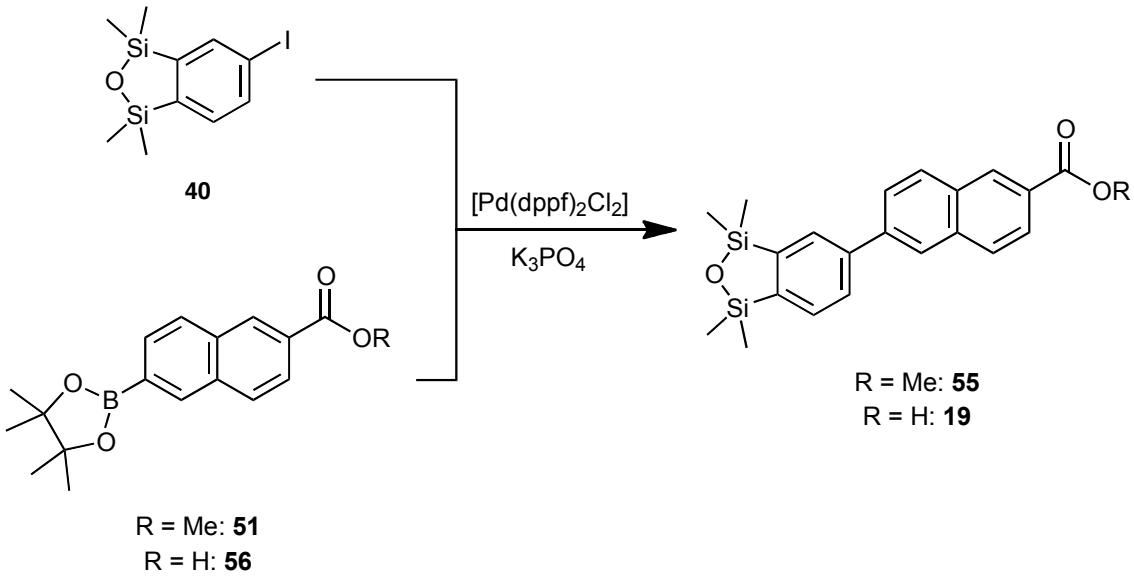
Scheme 4.3

4.1.2 TTNN Derivatives

Three derivatives of the retinoid TTNN[16] (**15b**, **18a** and **18b**) were synthesised according to Schemes 4.4 and 4.5. A palladium-catalysed Suzuki-Miyaura cross coupling[38] of an appropriate aryl iodide (**37**–**40**) with compound **51** gave the methyl protected intermediates **52**–**55** (yields: **52**, 49%; **53**, 62%; **54**, 43%; **55**, 35%). The methyl esters of the non-siloxane systems (**52**–**54**) were then deprotected using potassium hydroxide in methanol/water, followed by acidification with hydrochloric acid, to afford the free retinoids (yields: **15b**, 67%; **18a**, 71%; **18b**, 98%). Unfortunately, these conditions proved to be incompatible with the siloxane backbone of compound **55** and we were unable to obtain a pure sample of **19** using this methodology. Omission of the methyl protecting group allowed the direct synthesis of compound **19** by cross coupling of the naphthoic acid **56** with iodide **40** (Scheme 4.5). However, a pure sample of **19** could not be isolated. The very poor solubility of **19** prevented the effective use of column chromatography and the compound could not be induced to crystallise.

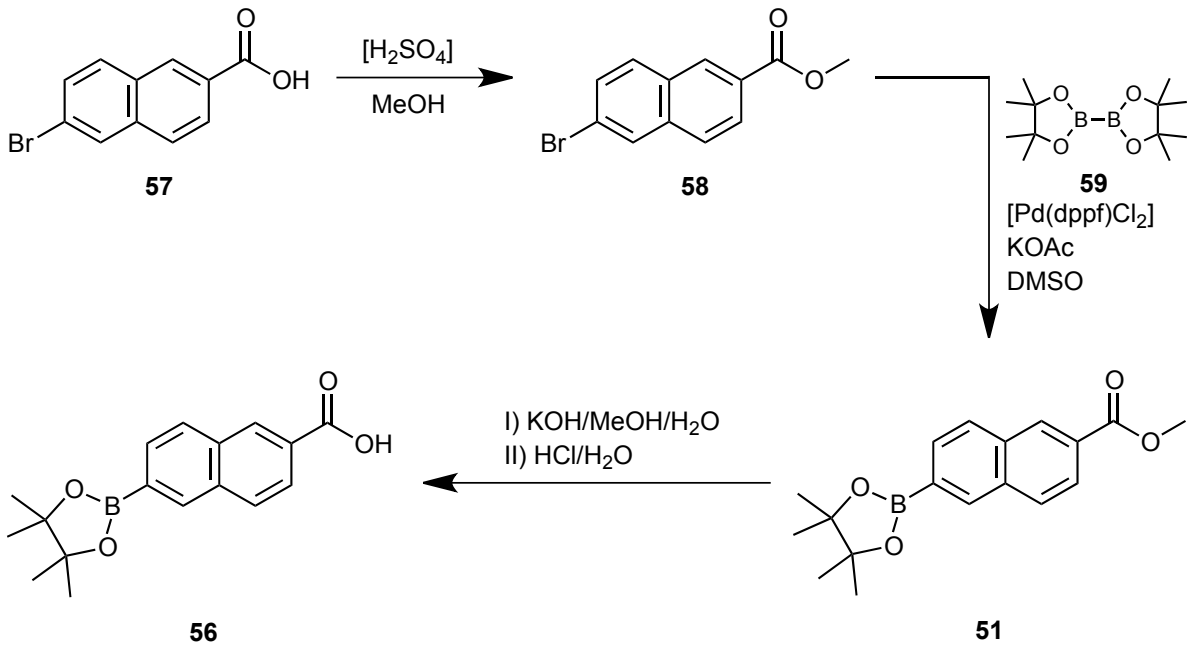


Scheme 4.4



Scheme 4.5

Compound **51** was synthesised according to Scheme 4.6 by protective esterification of 6-bromo-2-naphthoic acid (**57**) with acidified methanol and subsequent palladium-catalysed Miyaura borylation[39] of the protected 2-naphthoic acid **58** with bis(pinacalato)diboron (**59**). Deprotection of compound **51** with potassium hydroxide in aqueous methanol, followed by acidification with hydrochloric acid allowed the preparation of the free acid **56**.

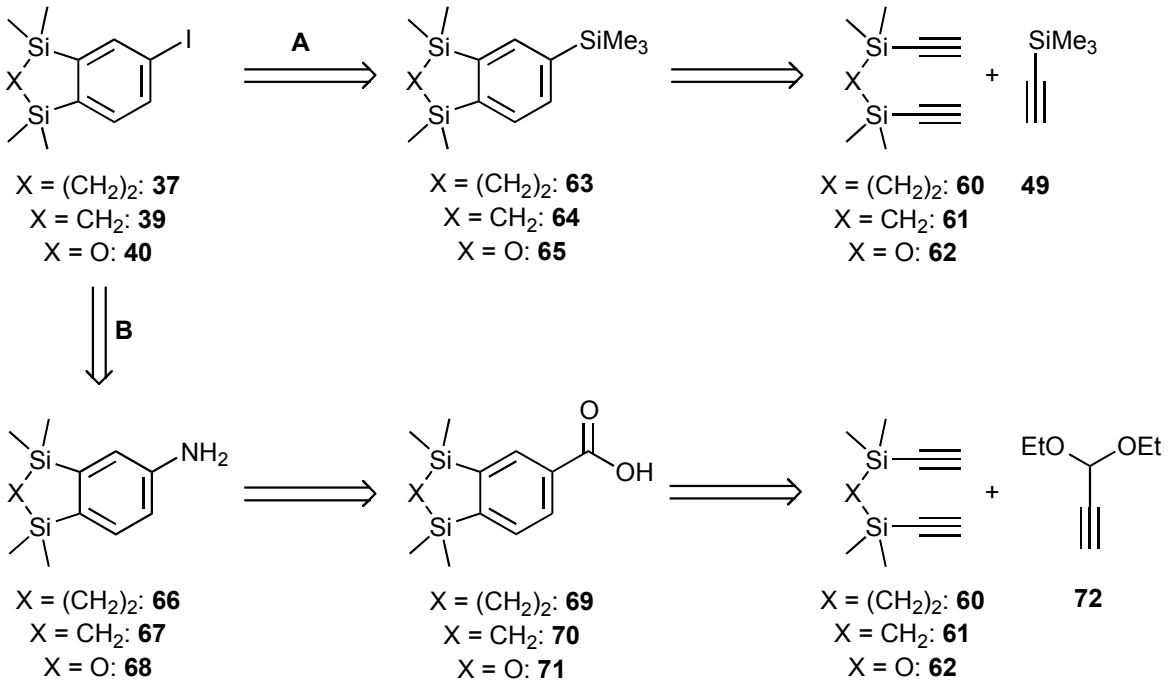


Scheme 4.6

4.2 Syntheses of Aryl Iodide Precursors

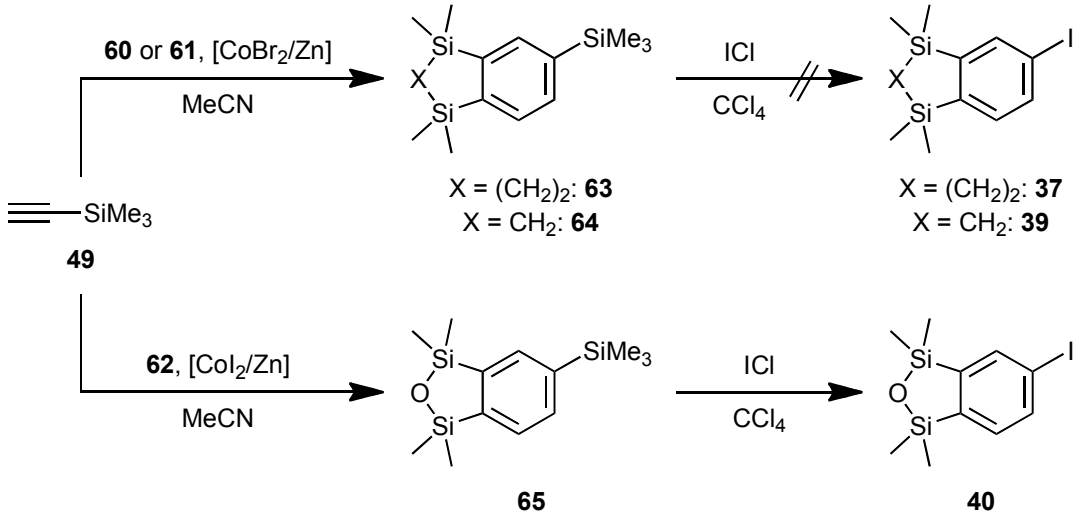
4.2.1 Silicon-Containing Aryl Iodides

The synthetic challenge in this project was the preparation of the silicon-containing aryl iodides **37**, **39** and **40**. As aryl iodides are increasingly important synthetic intermediates, highlighted by the recent award of the Nobel Prize in Chemistry for palladium-catalysed cross-coupling reactions in which aryl iodides are usually the preferred electrophilic coupling partner, there are a wide variety of methods available for their synthesis. However, the production of the desired silicon-containing bicyclic aryl iodides **37**, **39** and **40** was constrained by the necessity of utilising a [2+2+2] alkyne trimerisation as the key step in the construction of the bicyclic ring system. This constraint arises from the required starting materials. Silicon-containing dialkynes, such as **60–62**, have been extensively used as reagents in cyclotrimerisation reactions by our group.[1,3,4,33] On the other hand, not all monoalkynes are good partners for the [2+2+2] cycloaddition reaction. Thus, it is not always possible to build the required functionality into the monoalkyne precursor. For example, while halogenoalkynes have been reported and used successfully in cyclotrimerisation reactions,[40] these syntheses utilise a disubstituted alkyne. The parent compounds of the formula HC≡CX (X = Cl, Br, I) that would be required to directly produce the desired halogenoarenes in a [2+2+2] cyclisation are very oxygen sensitive and tend to decompose, burn or even explode, when exposed to the air.[41] A safe, in-situ preparation of iodoacetylene for use in a [2+3] cyclisation has been reported.[42] However, we doubted that this procedure would be compatible with the temperatures and reagent concentrations sometimes achieved or required in the exothermic [2+2+2] trimerisation reaction. So we considered the potential starting materials that would allow the synthesis of the target aryl iodides **37**, **39** and **40**. Two possible routes were proposed (Scheme 4.7).



Scheme 4.7

Initially, method **A** (Scheme 4.7) seemed the most attractive, using trimethylsilylethyne (**49**) in a cobalt(II)-catalysed [2+2+2] cycloaddition with the dialkynes **60**–**62** to produce the trimethylsilyl-substituted compounds **63**–**65**. The intention here was to utilise iodine monochloride to perform a selective electrophilic aromatic substitution, by analogy with the work of Vollhardt,[43] to produce the desired aryl iodides in a two-step synthesis (Scheme 4.8).

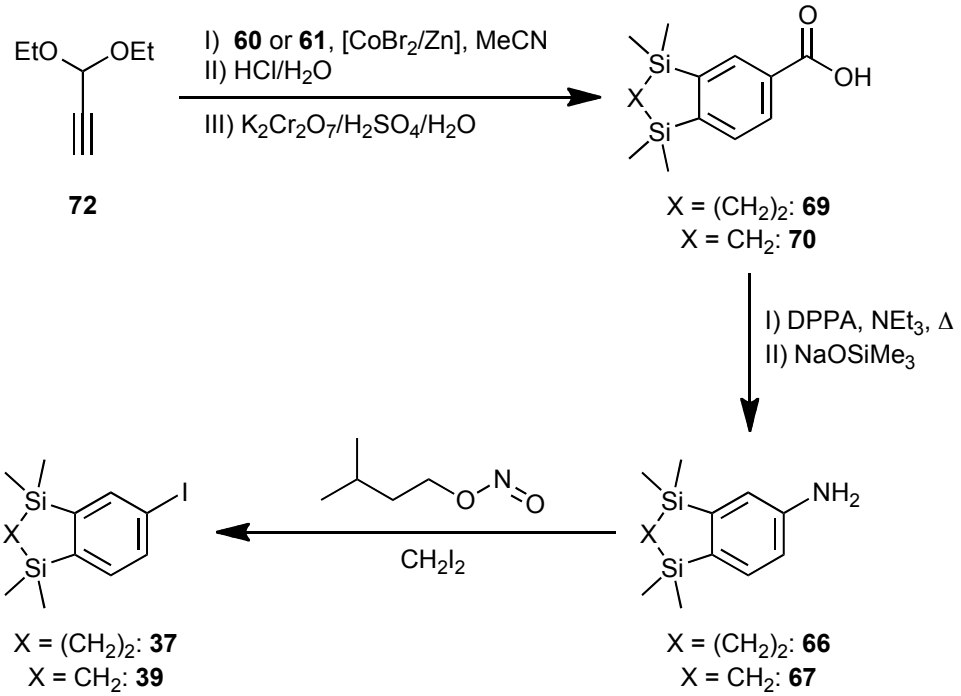


Scheme 4.8

Compounds **63** and **64** were synthesised by a [2+2+2] cycloaddition catalysed by cobalt(II) bromide and zinc in acetonitrile,[44] whereas a system comprising cobalt(II) iodide and zinc in acetonitrile[33] was used in the synthesis of **65** (yields: **63**, 34%; **64**, 9%; **65**, 63%). These reactions provided an interesting comparison of the two catalytic systems: cobalt(II) iodide proved much more effective than cobalt(II) bromide in the synthesis of compound **65**, as the reaction was comparatively selective for the desired product, with little trimerisation of **49** observed. However, in the case of **63** and **64**, the selectivity of the reaction was not noticeably altered by the use of cobalt(II) bromide in place of cobalt(II) iodide, although the use of cobalt(II) bromide resulted in a very slight increase in isolated yield. An additional benefit of the cobalt(II) bromide system is the stability of the catalyst solution. Cobalt(II) iodide in acetonitrile decays to produce elemental iodine, whereas the corresponding bromide does not decompose.[45] This stability allows the preparation of stock catalyst solutions of cobalt(II) bromide that can be stored and used more conveniently. The very low yield of **64** is due to the difficulty of separating the product from the side product tris(trimethylsilyl)benzene formed by the trimerisation of **49**. Fortuitously, it was possible to separate compound **63** from this by-product by crystallisation from ethanol, resulting in a higher yield. Unfortunately, as can be seen from Scheme 4.8, a selective substitution of the trimethylsilyl group of compound **63** or **64** with an iodine atom was not possible. Treatment of these compounds with iodine monochloride resulted in a complex mixture, the major component of which could be identified as triiodobenzene by GC-MS analysis. In contrast, reaction of compound **65** with a slight excess of iodine monochloride in tetrachloromethane

at 0 °C allowed the preparation of the aryl iodide **40** in 34% yield. The difference in the reactivity towards "I^+" observed for **65** compared with that of compounds **63** and **64** is likely to be due to the presence of the electron-withdrawing oxygen atom in the bicyclic ring system. The change in electronic character of the backbone caused by exchange of an $SiCH_2Si$ or $SiCH_2CH_2Si$ moiety for an SiOSi fragment seems to cause the ring silicon atoms to be less susceptible to electrophillic substitution.

As an alternative methodology for the synthesis of the aryl iodides was necessary, we turned towards more traditional iodination chemistry (method **B**, Scheme 4.7). A Sandmeyer[46] iodination of the amines **66**–**68** would allow the synthesis of the target aryl iodides. Compound **66** has been previously synthesised by our group,[1d] though the six-step synthesis with 12% overall yield (relative to **60**) was less than ideal. However, recent studies[44] suggested that it would be possible to produce the carboxylic acids **69**–**71** by a [2+2+2] cycloaddition of the commercially available monoalkyne **72** with the dialkynes **60**–**62**, followed by an in-situ deprotection and subsequent oxidation. A modified one-pot[47] Curtius rearrangement[48] would then allow the direct synthesis of the amines **66**–**68** (Scheme 4.9).

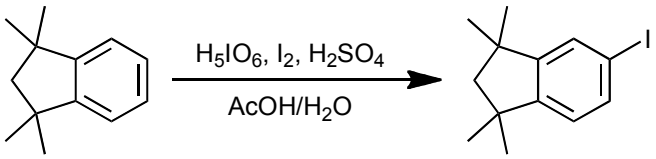


Scheme 4.9

The aryl iodides **37** and **39** were produced according to Scheme 4.9 in a three-step synthesis. A [2+2+2] cycloaddition of 3,3-diethoxypropyne (**72**) and an appropriate dialkyne (**60**, **61**) with a catalytic system comprising cobalt(II) bromide and zinc in acetonitrile,[44] acidification of the reaction mixture with hydrochloric acid and a Jones oxidation[49] of the crude aldehyde intermediate with potassium dichromate yielded the carboxylic acids **69** and **70** (yields: **69**, 19%; **70**, 37%). Treatment of **69** and **70** with diphenoxyphosphoryl azide (DPPA)[47,50] and triethylamine in toluene, followed by addition of a solution of sodium trimethylsilanolate,† afforded the amines **66** and **67** (yields: **66**, 46%; **67**, 63%). Compounds **66** and **67** were then reacted with isoamyl nitrite in diiodomethane,[51] in a modified Sandmeyer[46] reaction, to give the aryl iodides **37** and **39** (yields: **37**, 33%; **39**, 30%). As the aryl iodide **40** was available using the previously discussed electrophilic aromatic substitution route, we did not pursue its synthesis via the Sandmeyer iodination method.

4.2.2 5-Iodo-1,1,3,3-tetramethylindane (38)

Compound **38**, the aryl iodide precursor to the all-carbon EC23 and TTNN analogues **16a** and **18a**, was synthesised from 1,1,3,3-tetramethylindane (**73**) via a conventional aromatic iodination.[52] Treatment of **73** with orthoperiodic acid, iodine, sulphuric acid, glacial acetic acid and water afforded **38** in 64% yield (Scheme 4.10).



73 **38**

Scheme 4.10

†Sodium trimethylsilanolate is commercially available (Acros Organics, Sigma Aldrich) as a solution in dichloromethane or in tetrahydrofuran. We found that the two solutions could be used interchangeably; no significant alteration in yield was observed.

4.3 Biological Activity[‡]

The *in vivo* transcription activity of the retinoids **14a**, **14b**, **15a**, **15b**, **16a**, **16b**, **17**, **18a** and **18b** was investigated using a cell reporter system that has been previously described.[53] Briefly, two chimeric constructs, comprising (i) a chimeric receptor composed of the RAR ligand binding domain (GAL4-RARα,β,γ) and (ii) a luciferase-based reporter gene driven by the GAL4 response element (17-mer-G-Luc) in front of the minimal β-globin promoter, were stably introduced into HeLa cells. Exposure of the three reporter cells to the test compounds resulted in dose response curves that will be discussed below. All experiments were carried out utilising the known potent pan-agonist TTNPB as a control comparison.

4.3.1 EC23 Derivatives

The dose response curves for the ATRA mimic[15] EC23 (**14a**) and the analogous compounds **14b**, **16a**, **16b** and **17** are shown in Figures 4.1–4.3. The activity profiles of the test compounds revealed some important differences. Firstly, the two-fold sila-substitution of EC23 (**14a→14b**) results in a minor loss of RARα activity, whereas in the case of the two other RAR isotypes no significant differences in the activities of **14a** and **14b** are apparent. Secondly, replacement of the CCH_2CH_2C moiety of EC23 with a CCH_2C fragment (**14a→16a**) results in only a moderate decrease in transactivation potential, which is most pronounced for RARα. Thirdly, similarly to the disila-substitution of EC23 (**14a→14b**), two-fold C/Si exchange in **16a** (**→16b**) results in a minor loss of RARα activity, with almost no change in RARβ,γ activation. Introduction of the more polar SiOSi fragment in place of the $SiCH_2Si$ moiety of **16b** (**→17**) leads to a decrease in RARα,β,γ activation at low concentrations, whereas at higher concentrations similar transcription activation capacities of **16b** and **17** were observed.

[‡]The biological investigations of the retinoids discussed herein were carried out by J. Vallet and Prof. H. Gronemeyer of the Department of Cancer Biology, Institut de Génétique et de Biologie Moléculaire et Cellulaire (IGBMC), Illkirch Cedex (France).

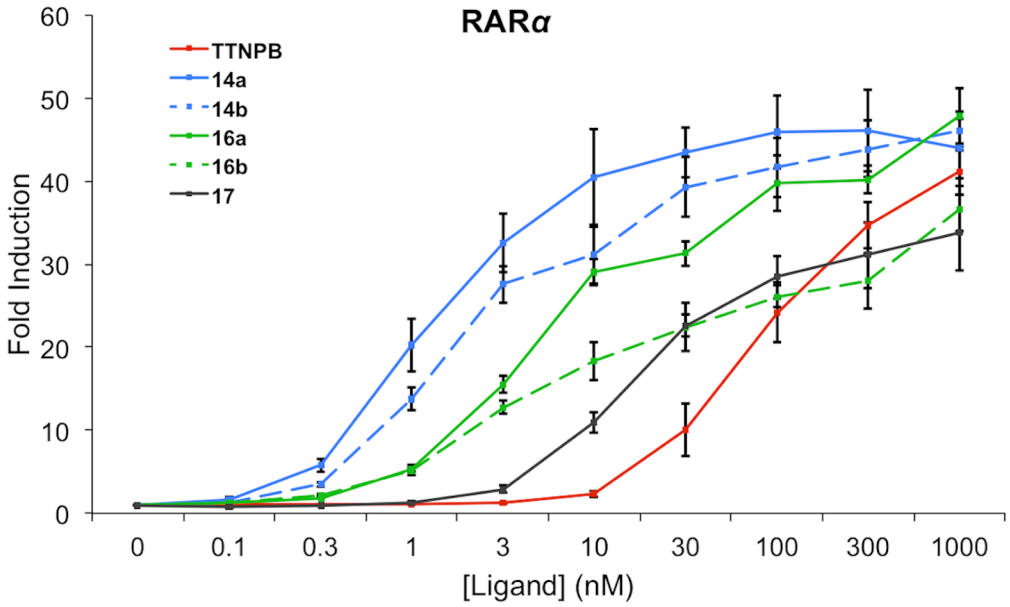


Fig. 4.1 Dose response curves of TTNPB, EC23 (**14a**) and the related retinoids **14b**, **16a**, **16b** and **17** in RARα reporter cells. Cells were exposed to the various ligands and the transcription activation through the RAR isotype was monitored as induced luciferase activity. The data are derived from at least three independent experiments, with duplicates in each of the experiments; the standard deviations (S.E.M.) are indicated.

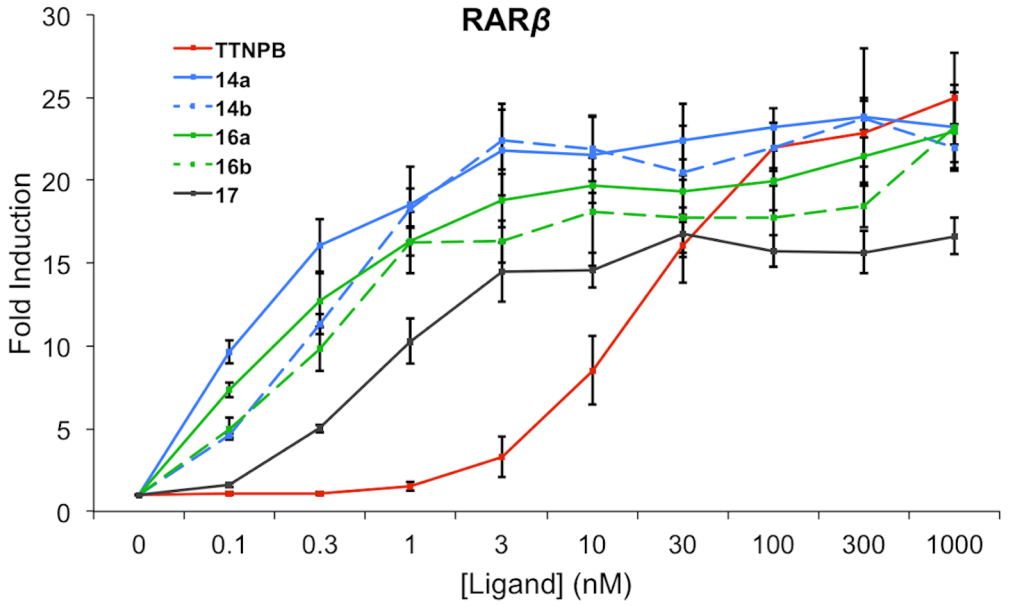


Fig. 4.2 Dose response curves of TTNPB, EC23 (**14a**) and the related retinoids **14b**, **16a**, **16b** and **17** in RARβ reporter cells. Cells were exposed to the various ligands and the transcription activation through the RAR isotype was monitored as induced luciferase activity. The data are derived from at least three independent experiments, with duplicates in each of the experiments; the standard deviations (S.E.M.) are indicated.

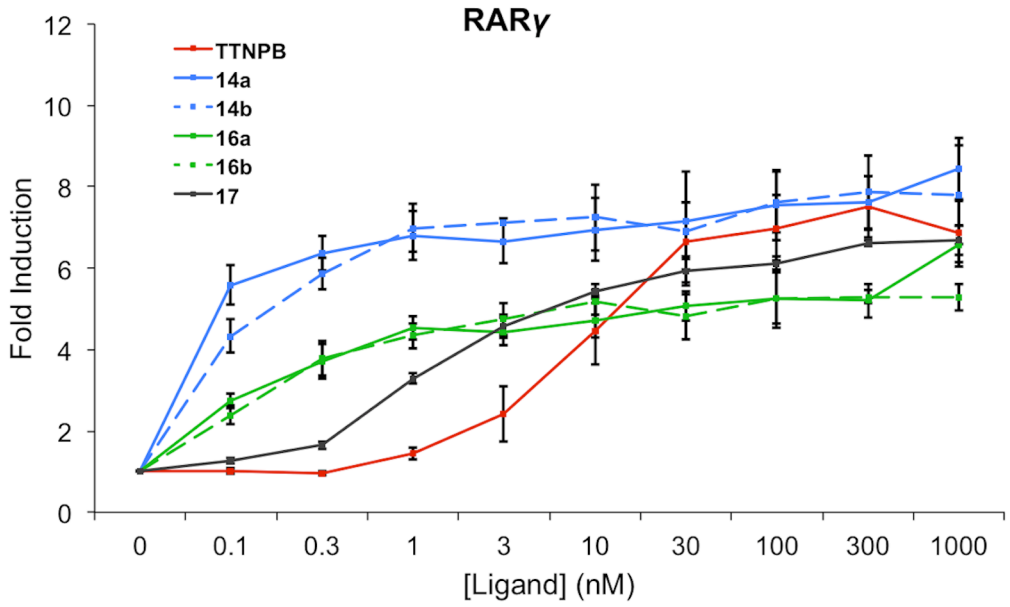


Fig. 4.3 Dose response curves of TTNPB, EC23 (**14a**) and the related retinoids **14b**, **16a**, **16b** and **17** in RARγ reporter cells. Cells were exposed to the various ligands and the transcription activation through the RAR isotype was monitored as induced luciferase activity. The data are derived from at least three independent experiments, with duplicates in each of the experiments; the standard deviations (S.E.M.) are indicated.

In conclusion, EC23 (4a) and its derivatives disila-EC23 (4b), 5a, 5b and 6 are very potent RAR agonists, being even more active than the powerful reference compound TTNPB. Similarly to the disila-substitution of several structurally related retinoids (such as bexarotene, TTNPB, SR11237, AM80 (tamibarotene) and AM580),[1] moderate biological effects have been observed in this study. Further investigations, including the structural characterisation of the receptor–ligand binding interactions, are necessary to fully interpret the structure−activity relationships observed herein.

4.3.2 TTNN Derivatives

The most important message that can be extracted from the comparison of the dose-response profiles given in Figures 4.4–4.6 is that disila-substitution of the weak retinoid agonist TTNN (**15a→15b**) results in a significant gain in transcription activation potential for all three RAR isotypes (increase in potency by factors of ca. 3 (RARβ) or 10 (RARγ)). However, replacement of the CCH_2CH_2C moiety of TTNN with a CCH_2C fragment (**15a→18a**) significantly decreases the activity, and two-fold C/Si exchange in **18a** (**→18b**) does not lead to a gain in activity. Together these results suggest that the lipophilic 1,2,3,4-tetrahydronaphthalene backbone of TTNN (**15a**) and the indane and 1,3-disilaindane

skeletons of **18a** and **18b**, respectively, are unfavourable for RAR binding and/or co-activator interaction; this effect is apparently relieved by disila-substitution of TTNN (**15a→15b**). This generates a retinoid that, while somewhat less active than TTNPB, has considerable RARβ,γ activity above 10 nM; significant RARα activation requires approximately a ten-fold higher concentration of **15b**. The C/Si analogues **18a** (indane skeleton) and **18b** (1,3-disilaindane skeleton) display very similar activities. Like the parent compound **15a** neither **18a** nor **18b** shows significant RARα activity; both display RARβ,γ selectivity but require an approximately 10-fold higher ligand concentration than TTNN (**15a**). In summary, two-fold sila-substitution of **15a** (1,2,3,4-tetrahydronaphthalene skeleton) and **18a** (indane skeleton) leads to considerably different effects: a significant increase (**15a→15b**) and almost no change (**18a→18b**) in transcription activation potential for all three RAR isotypes. Disila-TTNN (**15b**) can be regarded as a powerful RARβ,γ-selective retinoid.

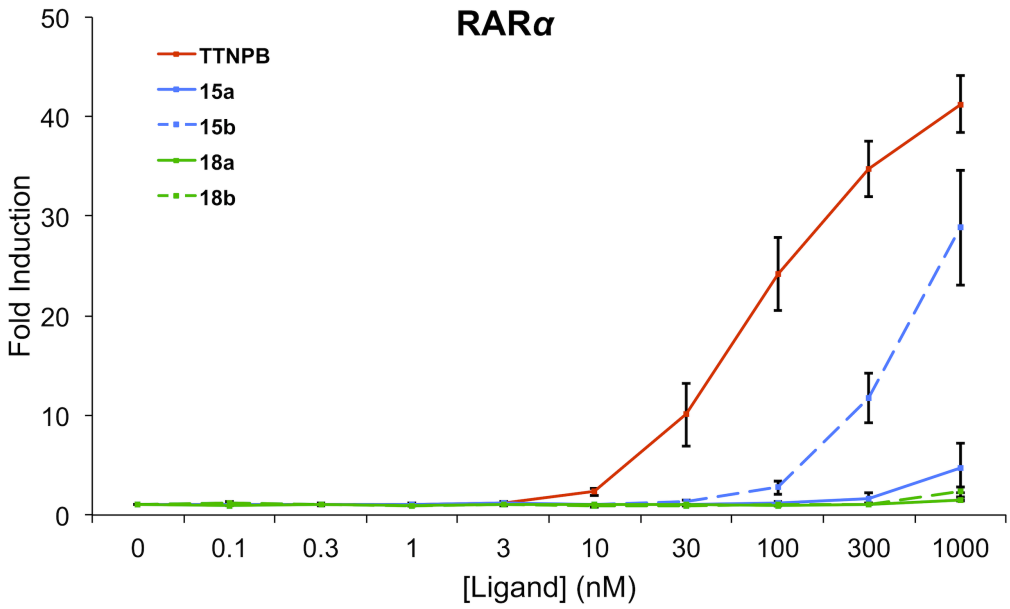


Fig. 4.4 Dose response curves of TTNPB, TTNN (**15a**) and the related retinoids **15b**, **18a** and **18b** in RARα reporter cells. Cells were exposed to the various ligands and the transcription activation through the RAR isotype was monitored as induced luciferase activity. The data are derived from at least three independent experiments, with duplicates in each of the experiments; the standard deviations (S.E.M.) are indicated.

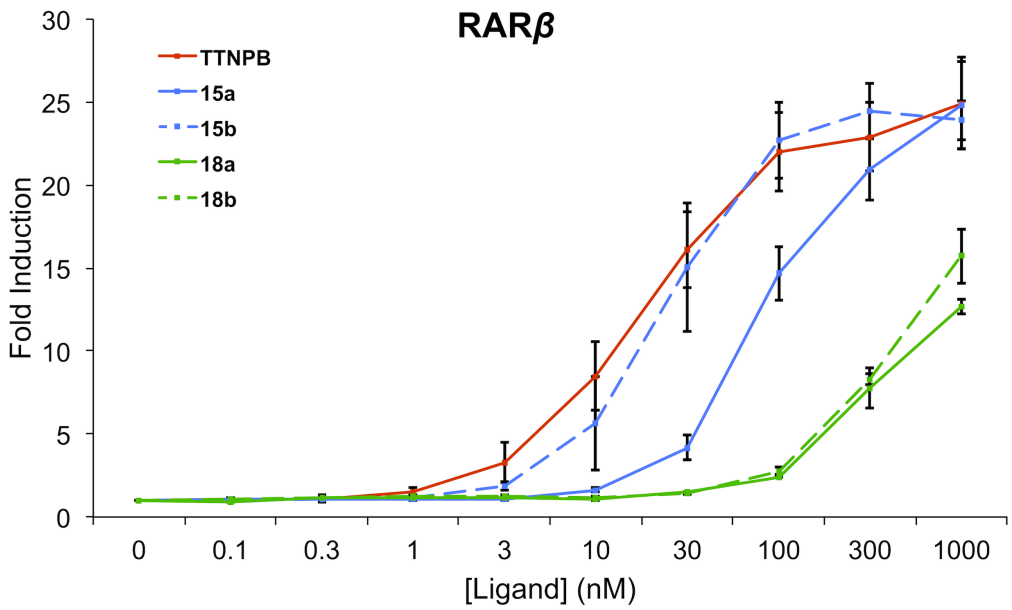


Fig. 4.5 Dose response curves of TTNPB, TTNN (**15a**) and the related retinoids **15b**, **18a** and **18b** in RAR*β* reporter cells. Cells were exposed to the various ligands and the transcription activation through the RAR isotype was monitored as induced luciferase activity. The data are derived from at least three independent experiments, with duplicates in each of the experiments; the standard deviations (S.E.M.) are indicated.

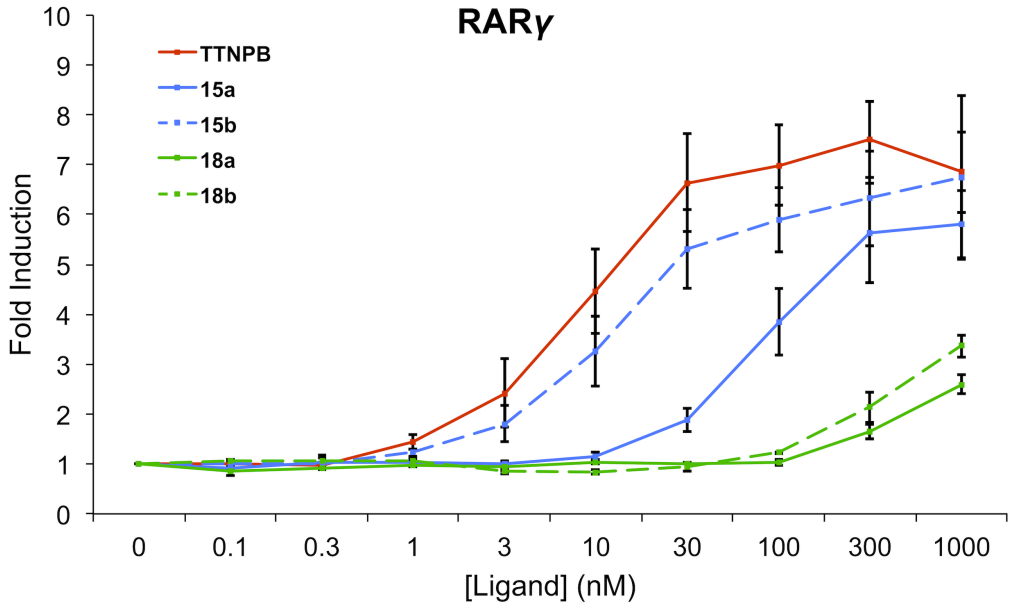
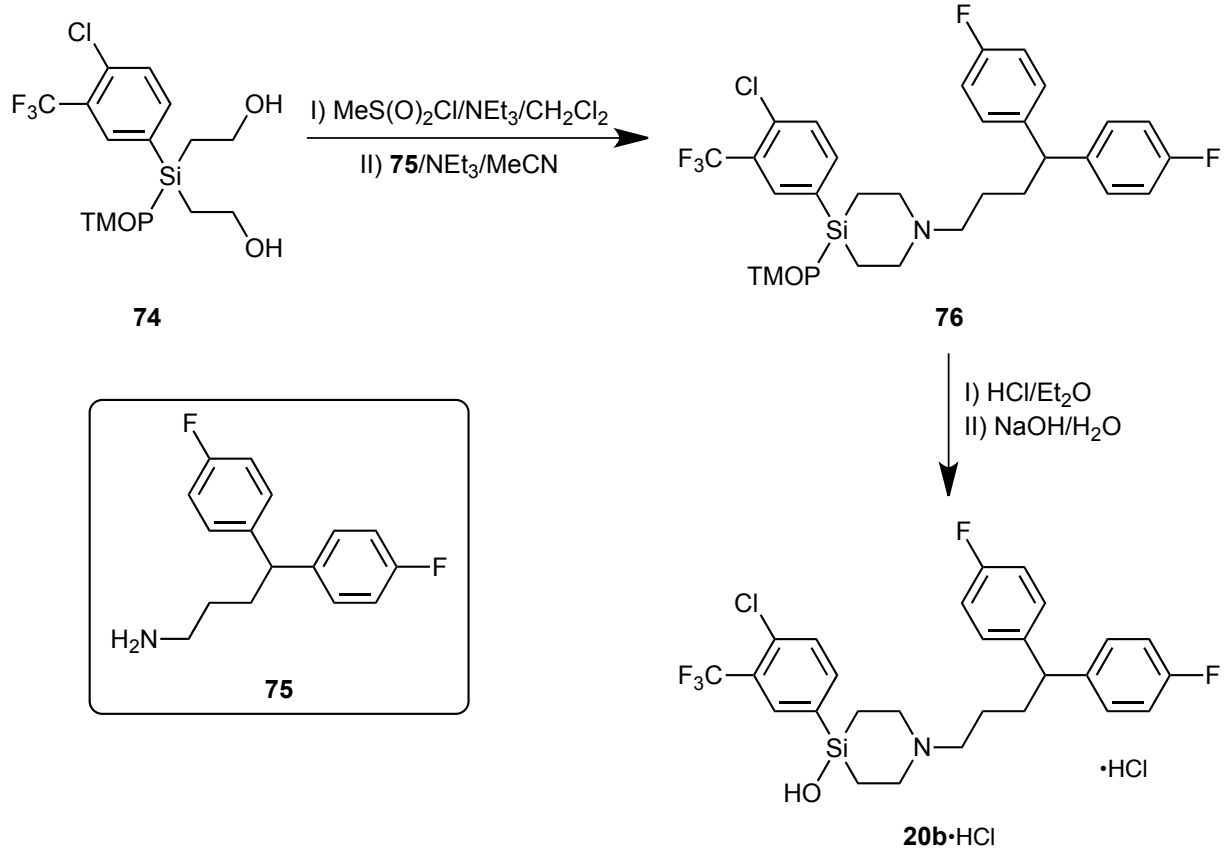


Fig. 4.6 Dose response curves of TTNPB, TTNN (**15a**) and the related retinoids **15b**, **18a** and **18b** in RAR*γ* reporter cells. Cells were exposed to the various ligands and the transcription activation through the RAR isotype was monitored as induced luciferase activity. The data are derived from at least three independent experiments, with duplicates in each of the experiments; the standard deviations (S.E.M.) are indicated.

5 Sila-penfluridol

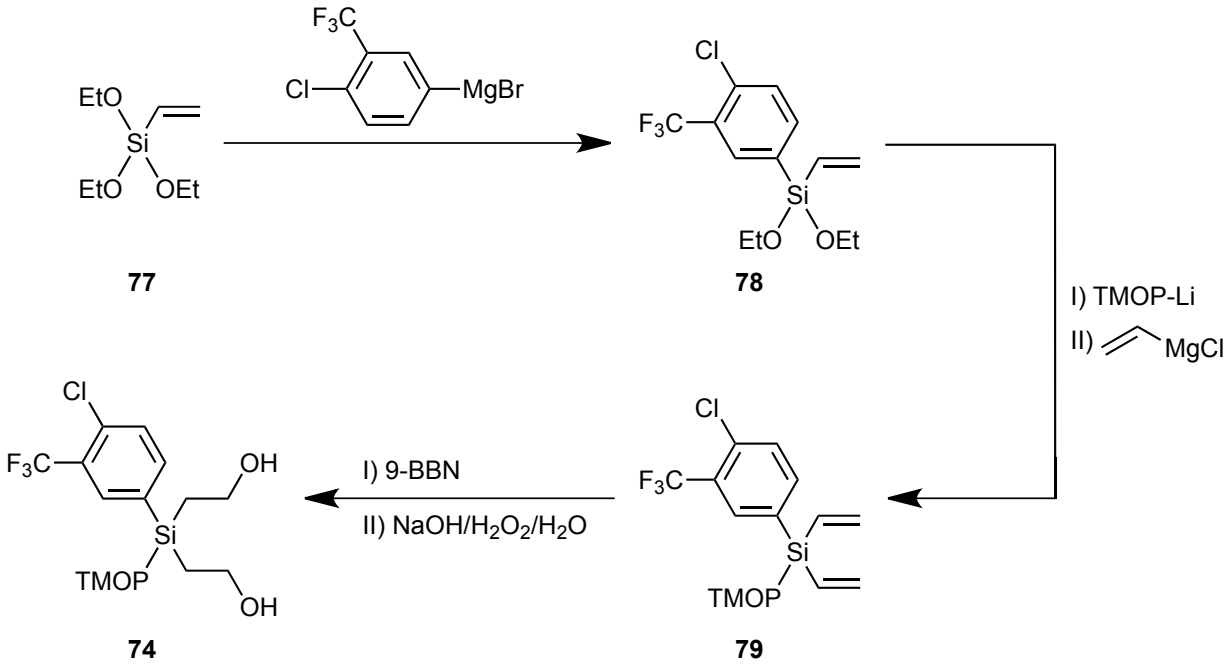
Sila-penfluridol (**20b**) was synthesised according to Scheme 5.1, starting from the bis(2-hydroxyethyl)silane **74**. In the first stage, compound **74** was treated with methanesulphonyl chloride at –25 ºC, followed by addition of the amine **75** and triethylamine at ambient temperature, resulting in a ring closing reaction to give the TMOP protected silapiperidine **76** in 35% yield. Deprotection of **76** with ethereal hydrogen chloride,[29a] followed by addition of the intermediate chlorosilane to water as a solution in isopropanol, allowed the production of **20b**·HCl. However, pure **20b**·HCl could not be obtained due to contamination by the corresponding disiloxane. Rather than directly precipitating as a solid, compound **20b**·HCl initially forms an oil. Presumably, the oil/water miscibility is high enough to allow the condensation of **20b**·HCl leading to the presence of low levels of the siloxane dimer. Compound **20b**·HCl and the corresponding disiloxane could identified by comparison of CI-MS and ^{1}H NMR spectra with existing data.[27] A similar solubility situation was observed in the synthesis of **20a**·HCl though in this case condensation (ether formation) does not occur. Attempts to further purify **20b**·HCl or to control the equilibrium ($2\ R_3SiOH \rightleftharpoons R_3Si–O–SiR_3 + H_2O$)[27,28] failed. The precursors **74** and **75** were synthesised according to Schemes 5.2 and 5.3, respectively. The ring closing reaction of **74** with **75** proceeds via the corresponding bis(2-methanesulphonatoethyl)silane which was not isolated due to the low stability of the crude product. In the syntheses of sila-haloperidol (**3b**) and sila-trifluperidol (**21b**), the yields for the corresponding ring closing reaction were 41%[2b] and 37%,[2c] respectively. In contrast to previous findings, we discovered that the ring closing reaction could be carried out at room temperature. In the case of the synthesis of **76**, a slight increase in yield could be obtained when the reaction was unheated.



Scheme 5.1

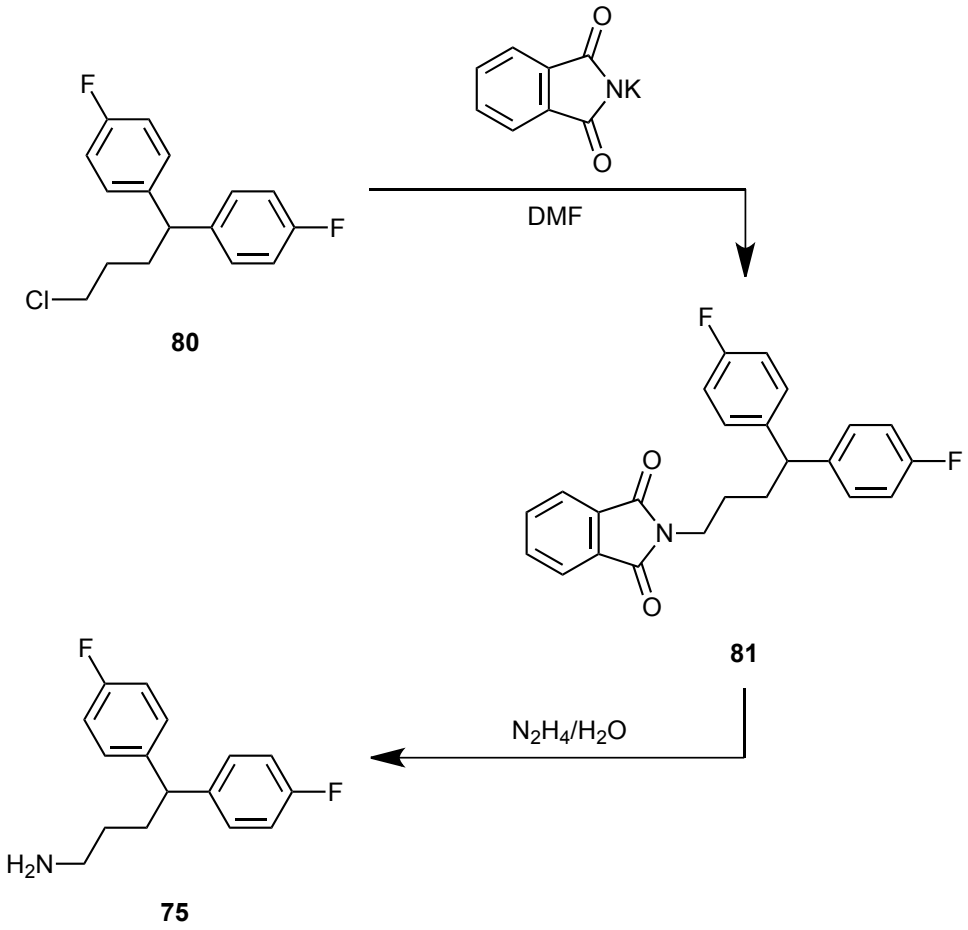
Compound **74** was synthesised according to Scheme 5.2 by treatment of triethoxy(vinyl)silane (**77**) with 4-chloro-3-(trifluoromethyl)phenylmagnesium bromide to give the corresponding diethoxysilane **78** in 53% yield. Sequential treatment of **78** with 2,4,6-trimethoxyphenyllithium and vinylmagnesium bromide allowed the preparation of the divinylsilane **79** in 48% yield. Hydroboration of **79** with the 9-borabicyclo[3.3.1]nonane dimer (9-BBN dimer), followed by workup with aqueous sodium hydroxide and aqueous hydrogen peroxide, gave the target compound **74** in 90% yield. The synthesis of **74** closely follows the preparation of the corresponding sila-trifluperidol precursor.[2c] Triethoxy(vinyl)silane was chosen as the starting material for several reasons. Ethoxysilanes are generally easier to handle than chlorosilanes as they are much more stable with respect to hydrolysis, ethoxysilanes also lack the toxicity associated with analogous methoxysilanes. In addition, from a synthetic point of view, inclusion of a vinyl group in the starting material is more atom efficient and thus more cost efficient, and triethoxy(vinyl)silane is a widely available chemical feedstock. The divinylsilane **79** was synthesised directly from **78** in a

one-pot reaction in order to improve the yield (for examples of similar syntheses, see refs 2b, 28 and 29b).



Scheme 5.2

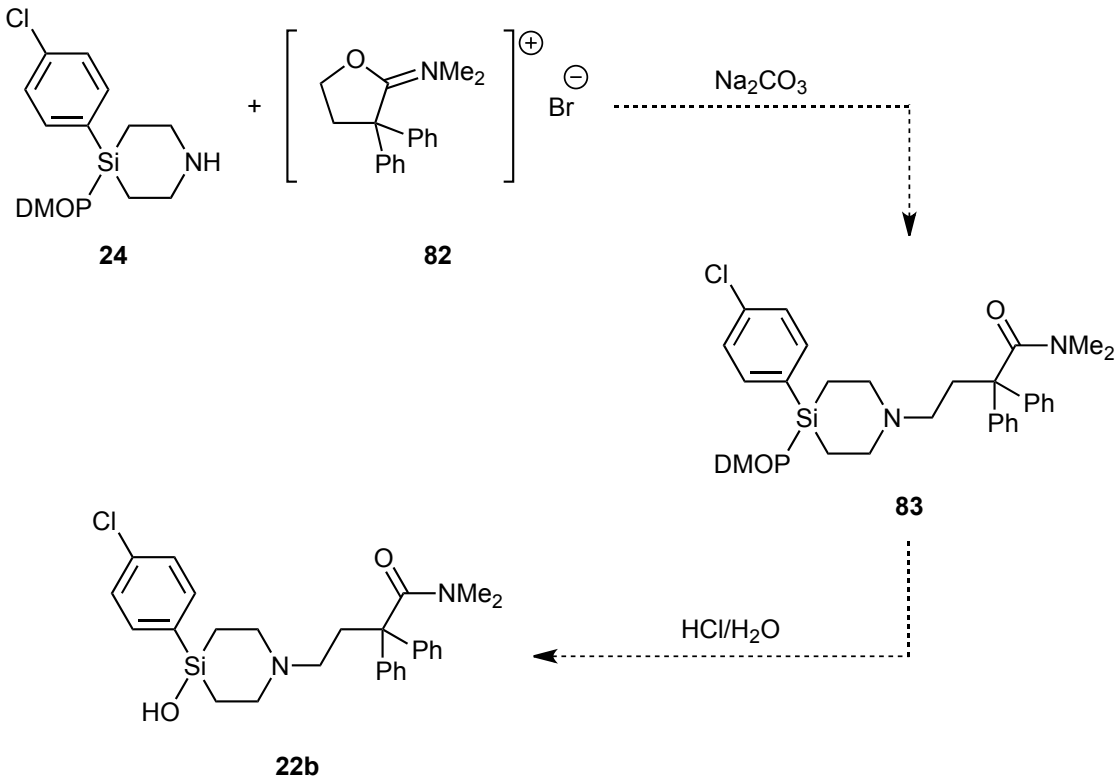
The amine precursor **75** was synthesied according to Scheme 5.3 via a classic Gabriel reaction.[54] 4,4'-(4-Chlorobutan-1,1-diyl)bis(fluorobenzene) (**80**) was treated with potassium phthalimide under reflux in *N*,*N*-dimethylformamide to give the phthalimide protected amine **81** in 73% yield. The free amine was then obtained in 79% yield following hydrazinolysis of **81**.



Scheme 5.3

6 Sila-loperamide

Sila-loperamide (**22b**) was to be synthesised according to Scheme 6.1 by a base mediated nuecleophilic ring opening reaction of the 2,6-dimethoxyphenyl protected silapiperidine **24** with the building block **82**, followed by deprotection of the intermediate **83**, to give the free silanol **22b**. Unfortunately, due to time constraints, the synthesis of **22b** could not be completed.

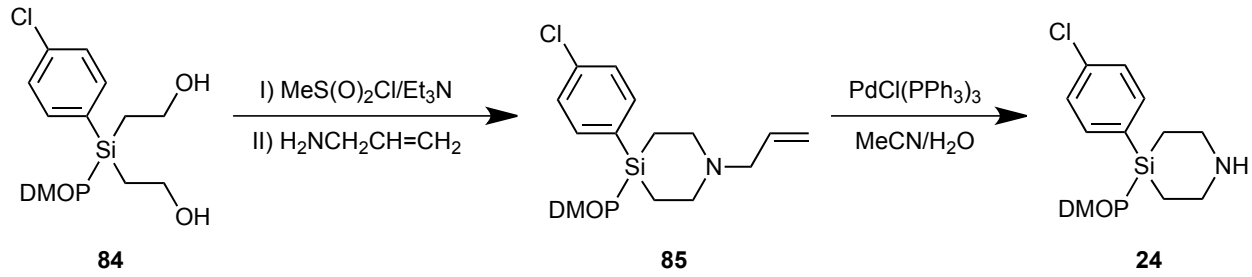


Scheme 6.1

Unlike in the synthesis of sila-penfluridol, a direct ring closing reaction of the corresponding bis(2-hydroxyethylsilane) with a linear amine side chain cannot be carried out as the necessary linear amine is unstable.[28] Therein lay the synthetic challenge of this project. The synthesis of **24** needed to be carried out via an *Si*-protected sila-pipiridine.[29b] However, the deprotection of the amine functionality could not be carried out under acidic conditions as this would be very likely to deprotect the silicon atom as well.[29] Unfortunately, all classical base-labile amine protecting groups are amide based and the necessary ring closing reaction

requires a primary amine to function. Thus, a protecting group was required that could be introduced via a primary amine and that could be removed selectively without interfering with the 2,6-dimethoxyphenyl moiety.

Allylamine was chosen as the ring closing partner following recent work by Yamada *et al.* on the synthesis of 2,5-substituted pyrrolidines. In this report, a ring closing reaction of a diol with allylamine is followed by catalytic deprotection with Wilkinson's catalyst [$PdCl(PPh_3)_3$].[55] This catalytic system is advantageous as it is likely to circumvent the previous problems encountered in this deprotection reaction as the conditions are comparatively mild and, importantly, neutral. In addition, the byproduct is likely to be a propene derivative and thus easily removed from the reaction mixture. Finally, there is no hydrogen source present; previously this has been shown to lead to reaction at the carbon-chlorine bond of the chlorophenyl moiety of the piperidine precursor.[29b] The free silapiperidine **24** was synthesised according to Scheme 6.2 by treatment of the bis(2-hydroxyethylsilane) **84** first with methanesulphonyl chloride and triethylamine followed by addition of allylamine to give the protected silapiperidine **85** in 22% yield. The deprotection of this *N*-allyl silapiperidine was demonstrated using Wilkinson's catalyst [$PdCl(PPh_3)_3$] in a mixture of acetonitrile and water. Unfortunately, time constraints prevented the purification of **24** and only the crude product was obtained (as observed by CI-MS).

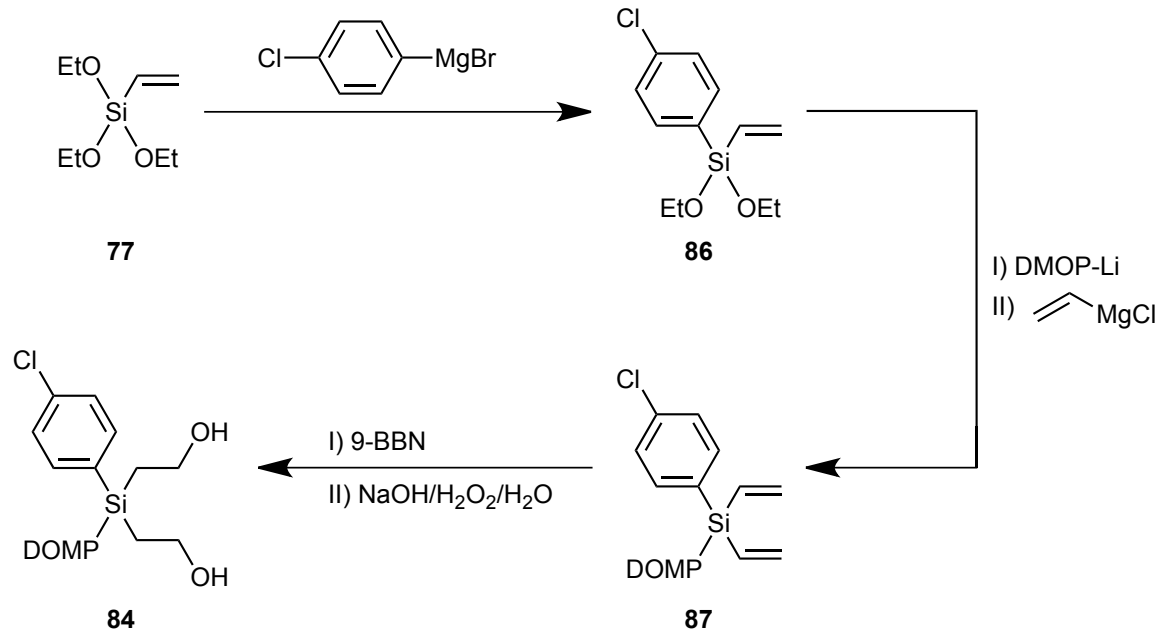


84 **85** **24**

Scheme 6.2

Compound **84** was synthesised according to Scheme 6.3, starting from triethoxy(vinyl)silane (**77**). Triethoxy(vinyl)silane was treated with 4-chlorophenylmagnesium bromide according to ref. 32 to give the (4-chlorophenyl)silane **86**. Compound **86** was then reacted with 2,6-dimethoxyphenyllithium[29a] followed by treatment with vinylmagnesium bromide to give the divinylsilane **87** in 68% yield. Hydroboration of **87** the 9-borabicyclo[3.3.1]nonane

dimer (9-BBN dimer), followed by workup with aqueous sodium hydroxide and aqueous hydrogen peroxide, gave the target compound **84** in 62% yield. This synthesis was carried out analogously to that of the corresponding bis(2-hydroxyethylsilane) **74** used in the synthesis of sila-penfluridol (see chapter 5.1 for further details).



77 **86** **87** **84**

Scheme 6.3

7 Crystal Structure Analyses†

Single crystals of **9**, **10**, **16a**, **16b**, **18b**, **26**, **43**, **45**, **51**, **64**, **65**, **69**, **70**, **81**, **85** and **86** suitable for X-ray diffraction studies were obtained. The crystals were mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fibre and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS (**9**, **10**, **16a**, **16b**, **18b**, **51**, **64**, **65**, **69**, **70**, **81** and **86**; graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å); Bruker Nonius KAPPA APEX II (**26**, **43**, **45** and **85**; Montel mirror, graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å)). The structures were solved by direct methods.[56] The non-hydrogen atoms were refined anisotropically.[56] A riding model was employed in the refinement of the C*H* hydrogen atoms. Bond lengths and angles not explicitly discussed herein lie within the typical range expected for the molecular bonds in question. Selected bond lengths and angles are given in the relevant figure legends. Complete results from these X-ray diffraction studies can be found in Appendix B.

7.1 Crystal Structure Analyses of 1,2,3-Trisilaindanes

7.1.1 Crystal Structure Analysis of 1-(6-Ethyl-1,1,2,2,3,3-hexamethyl-1,2,3-trisilaindan-5-yl)ethanone (9)

A single crystal of **9** suitable for X-ray diffraction study was obtained as described in the Experimental Section. This compound crystallised in the space group $P2_1/c$. The molecular structure of **9** is shown in Fig. 7.1.

† The crystal structure analyses were carried out by Dr. Christian Burschka, Institut für Anorganische Chemie, Universität Würzburg.

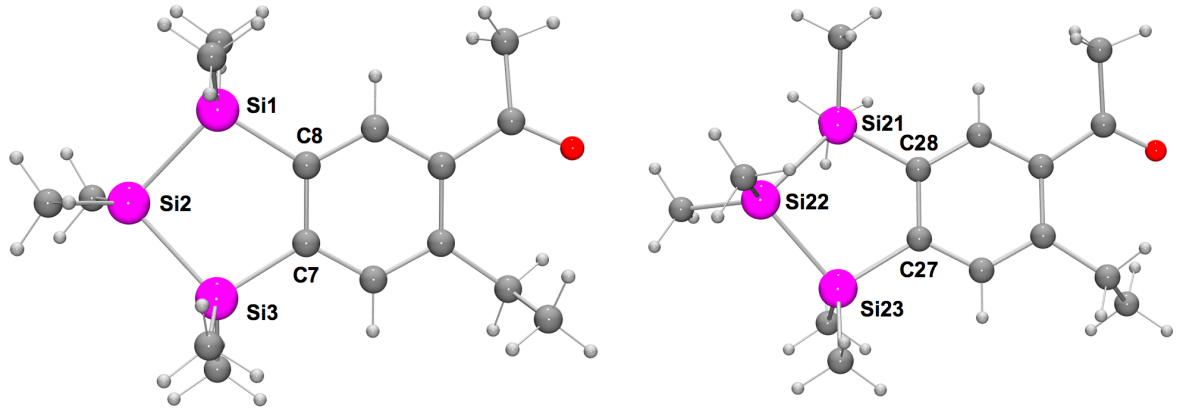


Figure 7.1. Molecular structures of the two crystallographically independent molecules in the crystal of **9**. Selected bond lengths [Å] and angles [deg] (for torsion angles, see Table 7.1): *Molecule I:* Si1−Si2 2.3495(8), Si1−C8 1.8918(18), Si2−Si3 2.3618(8), Si3−C7 1.9066(19), C7−C8 1.414(3); Si1−Si2−Si3 92.50(3), Si1−C8−C7 121.68(13), Si2−Si1−C8 101.54(6), Si2−Si3−C7 100.71(6), Si3−C7−C8 121.41(13). *Molecule II:* Si21−Si22 2.3453(9), Si21−C28 1.8929(18), Si22−Si23 2.3556(8), Si23−C27 1.8988(19), C27−C28 1.417(2); Si21−Si22−Si23 90.89(3), Si21−C28−C27 120.96(13), Si22−Si21−C28 99.25(6), Si22−Si23−C27 99.15(6), Si23−C27−C28 120.32(13).

7.1.2 Crystal Structure Analysis of 2-(1,1,2,2,3,3,6-Heptamethyl-1,2,3-trisilaindan-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)

A single crystal of **10** suitable for X-ray diffraction study was obtained as described in the Experimental Section. This compound crystallised in the space group $P2_1$. The molecular structure of **10** is shown in Fig. 7.2.

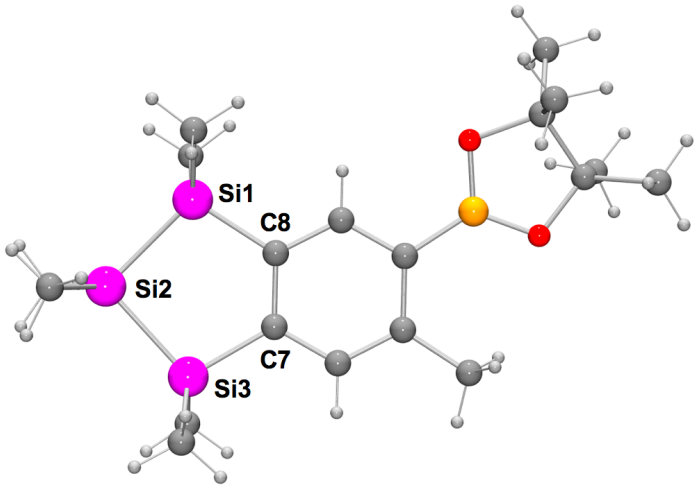


Figure 7.2. Molecular structure of **10** in the crystal (disorder in the tetramethyl-1,3,2-dioxaborolane ring removed for clarity). Selected bond lengths [Å] and angles [deg] (for torsion angles, see Table 7.1): Si1−Si2 2.3512(9), Si1−C8 1.897(2), Si2−Si3 2.3419(9), Si3−C7 1.904(2), C7−C8 1.418(3); Si1−Si2−Si3 93.11(3), Si1−C8−C7 121.90(15), Si2−Si1−C8 101.53(7), Si2−Si3−C7 101.79(7), Si3−C7−C8 121.24(15).

7.1.3 Crystal Structure Analysis of *rac*-1-(1,1,2,2,3,3,6-Heptamethyl-1,2,3-trisilaindan-5-yl)ethanol (26)

A single crystal of **26** suitable for X-ray diffraction study was obtained following crystallisation from a solution in *n*-hexane at –30 ºC over a period of six months. This compound crystallised in the space group $P2_1/c$. The molecular structure of **26** is shown in Fig. 7.3.

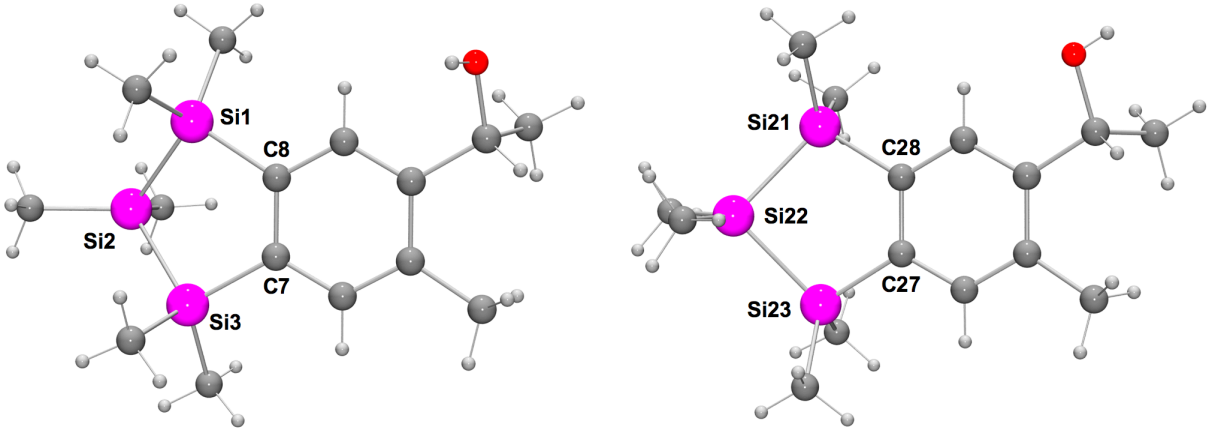


Figure 7.3. Molecular structures of the two crystallographically independent molecules in the crystal of **26**. Selected bond lengths [Å] and angles [deg] (for torsion angles, see Table 7.1): *Molecule I:* Si1−Si2 2.3436(5), Si1−C8 1.8891(12), Si2−Si3 2.3341(5), Si3−C7 1.8912(13), C7−C8 1.4148(16); Si1−Si2−Si3 90.674(18), Si1−C8−C7 120.99(9), Si2−Si1−C8 99.50(4), Si2−Si3−C7 99.69(4), Si3−C7−C8 119.74(9). *Molecule II:* Si21−Si22 2.3334(5), Si21−C28 1.8843(13), Si22−Si23 2.3418(6), Si23−C27 1.8900(13), C27−C28 1.4174(17); Si21−Si22−Si23 91.508(19), Si21−C28−C27 120.69(9), Si22−Si21−C28 100.27(4), Si22−Si23−C27 99.78(4), Si23−C27−C28 120.88(9).

7.1.4 Comparison of the 1,2,3-Trisilaindane Structures

As can be seen from Table 7.1, there is a great deal of conformational flexibility in the 1,2,3-trisilaindane ring. The conformation of the five-membered ring does not appear to depend on the aromatic ring substituents, as the two crystallographically independent molecules of **9** display differing degrees of deviation from planarity. The ring conformations observed range from an almost perfectly planar system (**10**) to the pronounced envelope conformation observed in the crystal of **9** (*Molecule II*) and **26**, indicating that the energy difference between the planar and envelope conformations is very low. These findings demonstrate the profound effect that an exchange of silicon for carbon can have on a molecular framework. In an analogous all-carbon system, a planar ring would be energetically disfavoured compared with the envelope conformation, whereas the energy difference must be less pronounced in the case of the 1,2,3-trisilaindane system. The Si–Si–Si angles of **9**, **10** and **26** are in the range 90.674(18)–93.11(3)°, suggesting that the 1,2,3-trisilaindane ring system is strained. This finding correlates with the high reactivity of the 1,2,3-trisilaindane species (**8**–**10** and **26**) against oxidation reagents.

Table 7.1. Torsion angles [deg] of compounds **9**, **10** and **26** in the crystal.

	9[a]	**9**[b,c]	**10**	**26**[a]	**26**[b,c]
Si1–Si2–Si3–C7	−12.80(6)	25.76(7)	5.78(7)	−26.37(4)	22.18(5)
Si1–C8–C7–Si3	−4.0(2)	−0.3(2)	1.2(2)	−3.47(14)	0.60(15)
Si2–Si1–C8–C7	−7.06(16)	21.02(15)	3.60(17)	−18.15(10)	17.43(11)
Si2–Si3–C7–C8	12.57(16)	−20.55(16)	−5.35(17)	23.17(10)	−18.19(11)
Si3–Si2–Si1–C8	11.45(6)	−25.83(6)	−5.33(7)	24.98(4)	−22.06(4)

[a] *Molecule I*. [b] *Molecule II*. [c] For *Molecule II*, read Si1 as Si21, C1 as C21, etc.

7.2 Crystal Structure Analyses of Retinoids and Precursors

7.2.1 Crystal Structure Analysis of 4-(1,1,3,3-Tetramethylindan-5-ylethynyl)benzoic Acid (16a)

A single crystal of **16a** suitable for X-ray diffraction study was obtained as described in the Experimental Section. This compound crystallised in the space group *P*1. The molecular structure of **16a** is shown in Fig. 7.4.

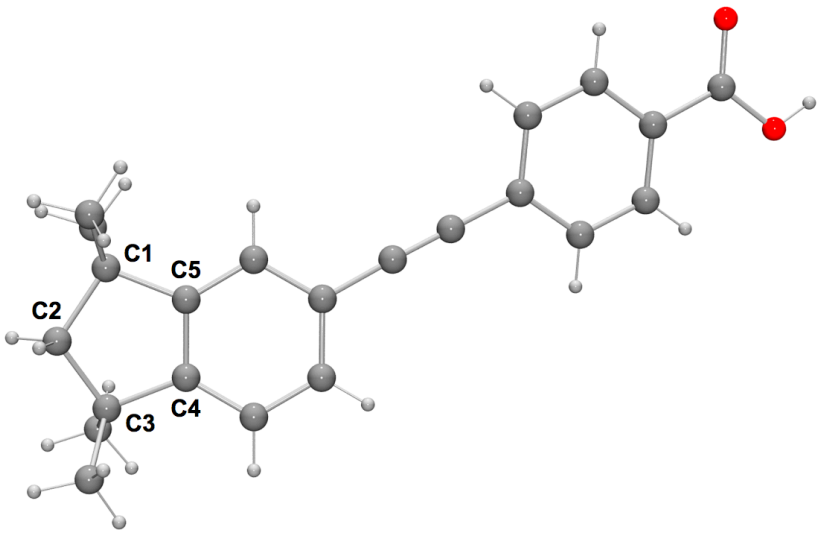


Figure 7.4. Molecular structure of **16a** in the crystal. Selected bond lengths [Å], bond angles [deg] and torsion angles [deg]: C1–C2 1.560(3), C2–C3 1.545(3), C1–C5 1.522(2), C3–C4 1.521(2), C4–C5 1.388(2); C1–C2–C3 107.85(16), C1–C5–C4 111.48(15), C3–C4–C5 111.69(14), C2–C1–C5 101.66(14), C2–C3–C4 101.42(15); C4–C5–C1–C2 10.9(2), C5–C1–C2–C3 –21.9(2), C1–C2–C3–C4 24.2(2), C2–C3–C4–C5 –17.78(19), C3–C4–C5–C1 4.40(19).

7.2.2 Crystal Structure Analysis of 4-(1,1,3,3-Tetramethyl-1,3-disilaindan-5-ylethynyl) benzoic Acid (16b)

A single crystal of **16b** suitable for X-ray diffraction study was obtained following evaporation of a solution of **16b** in dichloromethane at room temperature. This compound crystallised in the space group *Pbca*. The molecular structure of **16b** is shown in Fig. 7.5.

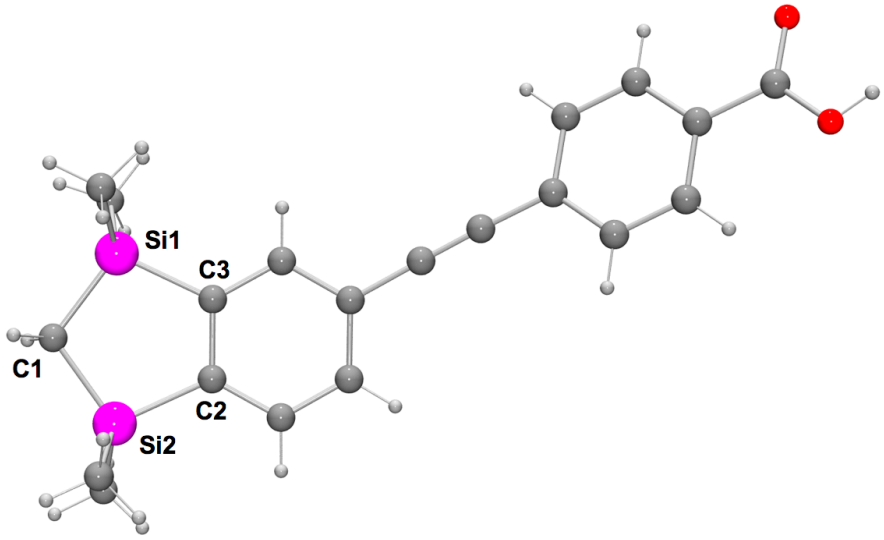


Figure 7.5. Molecular structure of **16b** in the crystal. Selected bond lengths [Å], bond angles [deg] and torsion angles [deg]: Si1–C1 1.870(2), Si2–C1 1.877(2), Si1–C3 1.8824(19), Si2–C2 1.8856(19), C2–C3 1.418(3); Si1–C1–Si2 107.15(11), Si1–C3–C2 115.10(14), Si2–C2–C3 114.98(14), C1–Si1–C3 101.34(9), C1–Si2–C2 101.02(9); C2–C3–Si1–C1 0.18(18), C3–Si1–C1–Si2 3.89(16), Si1–C1–Si2–C2 –5.78(16), C1–Si2–C2–C3 6.51(18), Si2–C2–C3–Si1 –4.37(19).

7.2.3 Crystal Structure Analysis of 6-(1,1,3,3-Tetramethyl-1,3-disilaindan-5-yl)-2-naphthoic Acid (18b)

A single crystal of **18b** suitable for X-ray diffraction study was obtained as described in the Experimental Section. This compound crystallised in the space group *Pbca*. The molecular structure of **18b** is shown in Fig. 7.6.

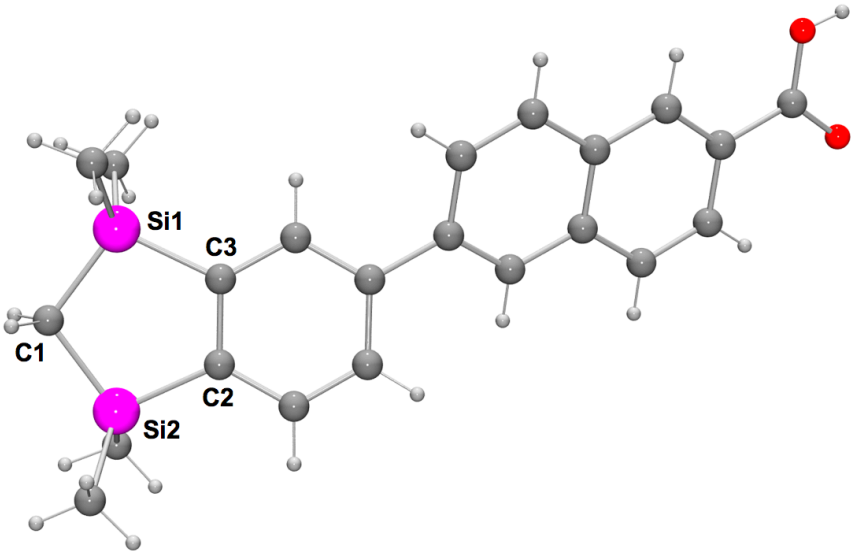


Figure 7.6. Molecular structure of **18b** in the crystal. Selected bond lengths [Å], bond angles [deg] and torsion angles [deg]: Si1–C1 1.880(2), Si2–C1 1.880(3), Si1–C3 1.891(2), Si2–C2 1.891(2), C2–C3 1.412(3); Si1–C1–Si2 107.20(11), Si1–C3–C2 114.93(14), Si2–C2–C3 115.44(15), C1–Si1–C3 100.95(10), C1–Si2–C2 100.51(10); C2–C3–Si1–C1 1.09(19), C3–Si1–C1–Si2 –6.91(17), Si1–C1–Si2–C2 9.25(17), C1–Si2–C2–C3 –9.5(2), Si2–C2–C3–Si1 5.5(2).

7.2.4 Crystal Structure Analysis of Methyl 4-(1,1,3,3-Tetramethylindan-5-ylethynyl) benzoate (43)

A single crystal of **43** suitable for X-ray diffraction study was obtained following evaporation of a solution of **43** in acetonitrile at room temperature. This compound crystallised in the space group $P2_1/c$. The molecular structure of **43** is shown in Fig. 7.7.

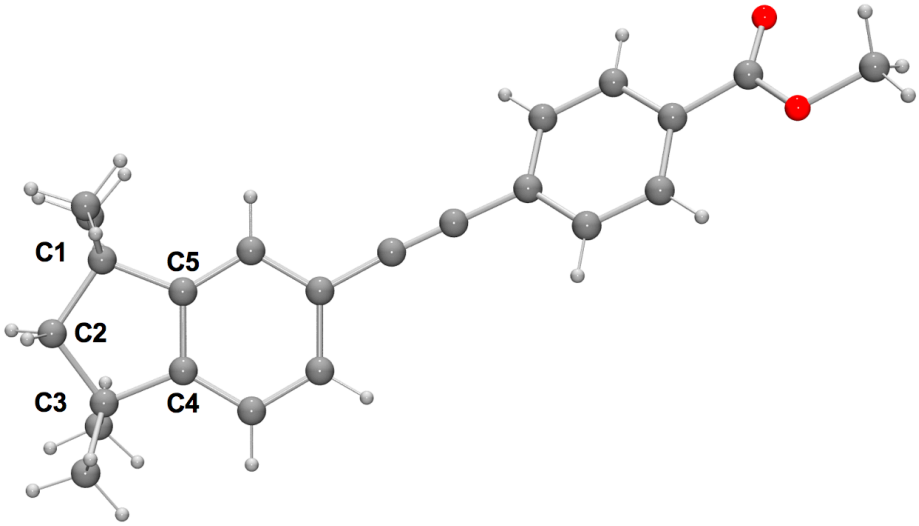


Figure 7.7. Molecular structure of compound **43** in the crystal. Selected bond lengths [Å], bond angles [deg] and torsion angles [deg]: C1–C2 1.5589(12), C3–C2 1.5551(12), C1–C5 1.5196(11), C3–C4 1.5159(11), C4–C5 1.3949(11); C1–C2–C3 108.68(7), C1–C5–C4 112.6(2), C3–C4–C5 112.06(7), C2–C1–C5 102.42(6), C2–C3–C4 102.00(6); C4–C5–C1–C2 6.17(9), C5–C1–C2–C3 –15.02(9), C1–C2–C3–C4 17.77(9), C2–C3–C4–C5 –14.29(9), C3–C4–C5–C1 5.34(10).

7.2.5 Crystal Structure Analysis of Methyl 4-(1,1,3,3-Tetramethyl-2-oxa-1,3-disilaindan-5-ylethynyl)benzoate (45)

A single crystal of **45** suitable for X-ray diffraction study was obtained following evaporation of a solution of **45** in acetonitrile at room temperature. This compound crystallised in the space group *C*2. The asymmetric unit of **45** contained three crystallographically distinct molecules (Molecules I–III), the structures of which are shown in Figs. 7.8–7.10.

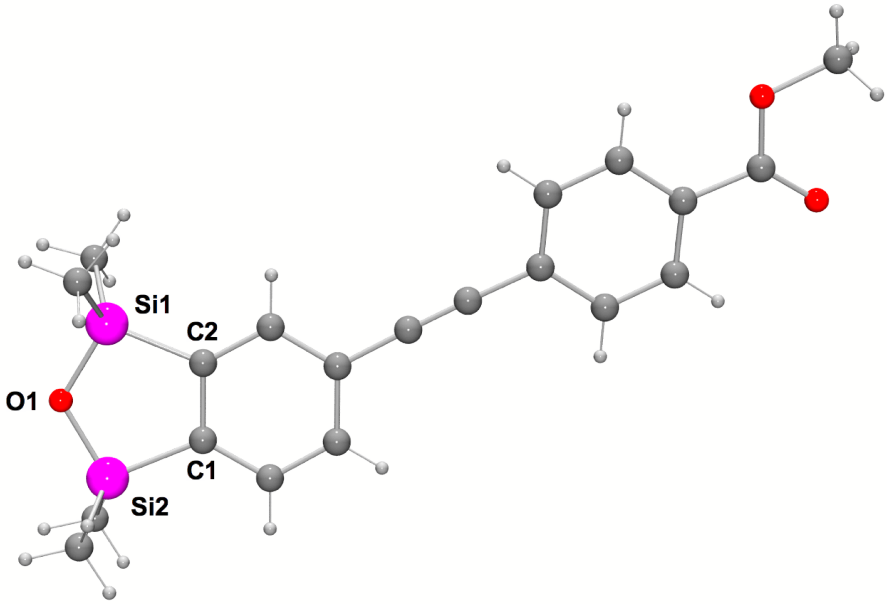


Figure 7.8. Molecular structure of *Molecule I* in the crystal of **45**. Selected bond lengths [Å], bond angles [deg] and torsion angles [deg]: Si1–O1 1.656(2), Si2–O1 1.653(3), Si1–C2 1.878(3), Si2–C1 1.887(3), C1–C2 1.421(4); Si1–O1–Si2 118.36(15), Si1–C2–C1 112.6(2), Si2–C1–C2 111.7(2), O1–Si1–C2 98.48(14), O1–Si2–C1 98.66(13); C1–C2–Si1–O1 1.2(3), C2–Si1–O1–Si2 –3.7(2), Si1–O1–Si2–C1 4.4(2), O1–Si2–C1–C2 –3.3(3), Si2–C1–C2–Si1 1.3(3).

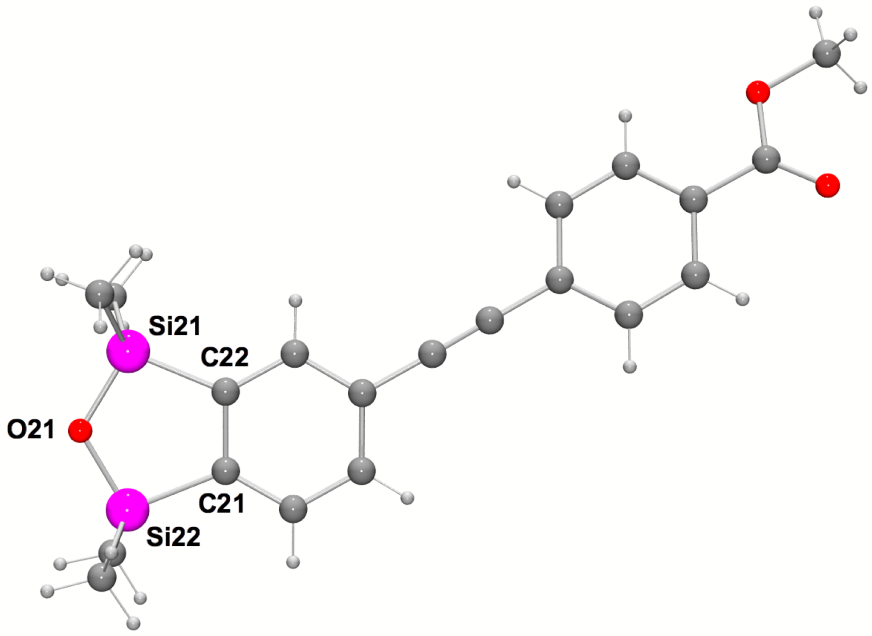


Figure 7.9. Molecular structure of *Molecule II* in the crystal of **45**. Selected bond lengths [Å], bond angles [deg] and torsion angles [deg]: Si21–O21 1.656(2), Si22–O21 1.652(3), Si21–C22 1.868(4), Si22–C21 1.869(3), C21–C22 1.425(4); Si21–O21–Si22 118.31(15), Si21–C22–C21 111.8(2), Si22–C21–C22 112.7(2), O21–Si21–C22 98.72(13), O21–Si22–C21 98.34(13); C21–C22–Si21–O21 –0.7(3), C22–Si21–O21–Si22 3.1(2), Si21–O21–Si22–C21–3.8(2), O21–Si22–C21–C22 –1.5(3), Si22–C21–C22–Si21 –1.5(3).

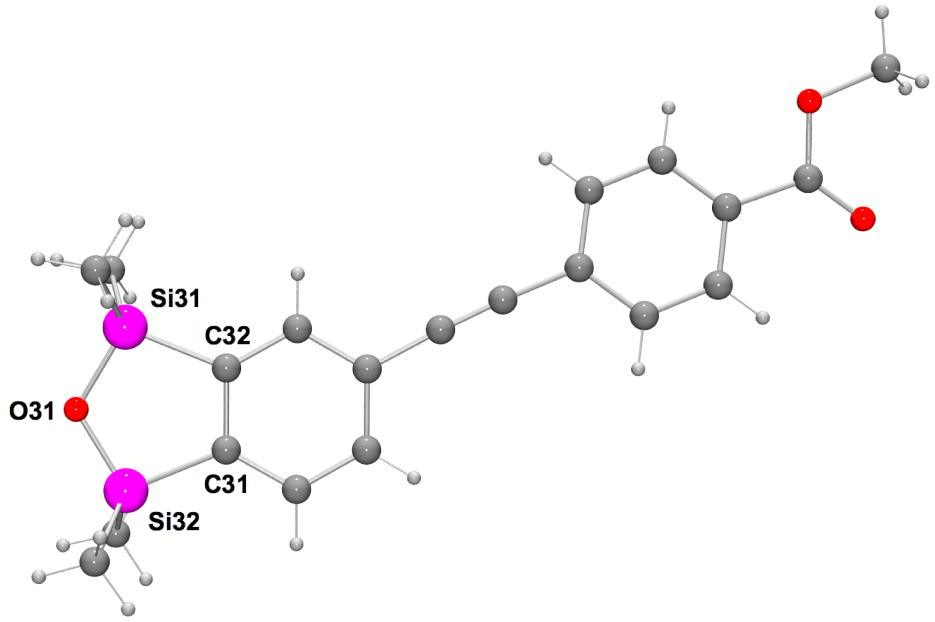


Figure 7.10. Molecular structure of *Molecule III* in the crystal of **45**. Selected bond lengths [Å], bond angles [deg] and torsion angles [deg]: Si31–O31 1.656(2), Si32–O31 1.650(3), Si31–C32 1.883(3), Si32–C31 1.877(3), C31–C32 1.418(4); Si31–O31–Si32 118.31(15), Si31–C32–C31 111.9(2), Si32–C31–C32 112.3(2), O31–Si31–C32 98.79(13), O31–Si32–C31 98.87(13); C31–C32–Si31–O31 –0.6(3), C32–Si31–O31–Si32 –2.0(2), Si31–O31–Si32–C31 3.2(2), O31–Si32–C31–C32 –3.6(3), Si32–C31–C32–Si31 2.6(3).

7.2.6 Crystal Structure Analysis of Methyl 6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthoate (51)

A single crystal of **51** suitable for X-ray diffraction study was obtained following recrystallisation from *n*-hexane (cooling of a hot solution to 20 °C). This compound crystallised in the space group $Pna2_1$. The molecular structure of **51** is shown in Fig. 7.11.

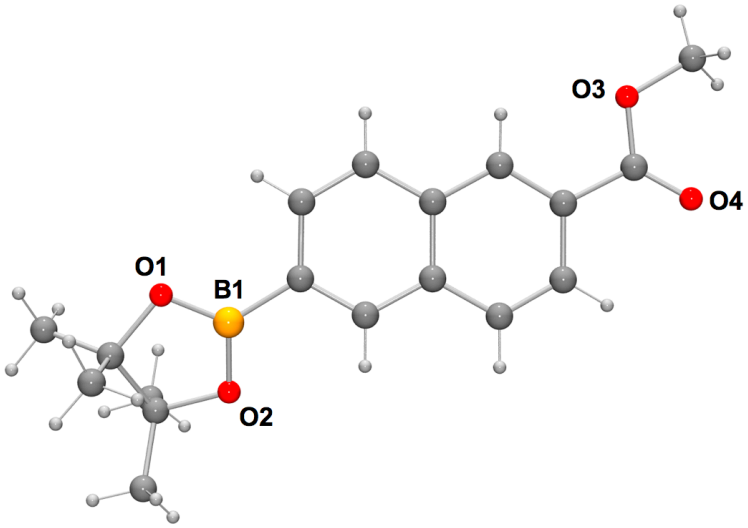


Figure 7.11. Molecular structure of compound **51** in the crystal. The bond lengths and angles observed fall within the ranges expected for the molecular bonds in question. For full details, see Appendix B.

7.2.7 Crystal Structure Analysis of 1,1,3,3-Tetramethyl-5-trimethylsilyl-1,3-disilaindane(64)

A single crystal of **64** suitable for X-ray diffraction study was obtained following evaporation of a solution of **64** in ethanol at room temperature. This compound crystallised in the space group $P2_1/c$. The molecular structure of **64** is shown in Fig. 7.12.

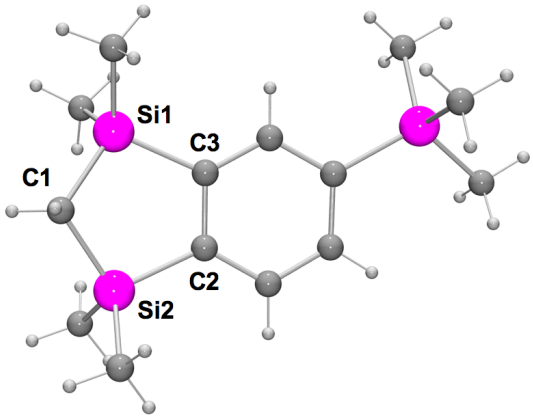


Figure 7.12. Molecular structure of compound **64** in the crystal. Selected bond lengths [Å], bond angles [deg] and torsion angles [deg]: Si1–C1 1.882(2), Si2–C1 1.876(2), Si1–C3 1.894(2), Si2–C2 1.891(2), C2–C3 1.420(3); Si1–C1–Si2 105.22(10), Si1–C3–C2 113.46(15), Si2–C2–C3 115.31(14), C1–Si1–C3 100.05(10), C1–Si2–C2 99.96(10); C2–C3–Si1–C1 18.42(16), C3–Si1–C1–Si2 –23.63(13), Si1–C1–Si2–C2 21.42(13), C1–Si2–C2–C3 –11.11(17), Si2–C2–C3–Si1 –4.76(19).

7.2.8 Crystal Structure Analysis of 1,1,3,3-Tetramethyl-5-trimethylsilyl-2-oxa-1,3-disilaindane (65)

A single crystal of **65** suitable for X-ray diffraction study was obtained following evaporation of a solution of **65** in ethanol at room temperature. This compound crystallised in the space group $P2_1$. The molecular structure of **65** is shown in Fig. 7.13.

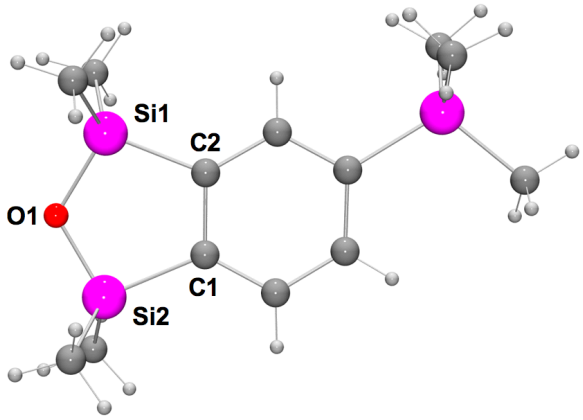


Figure 7.13. Molecular structure of compound **65** in the crystal (disorder in the trimethylsilyl group removed for clarity). Selected bond lengths [Å], bond angles [deg] and torsion angles [deg]: Si1–O1 1.6913(18), Si2–O1 1.6664(19), Si1–C2 1.882(3), Si2–C1 1.915(2), C1–C2 1.436(3); Si1–O1–Si2 117.50(10), Si1–C2–C1 111.01(17), Si2–C1–C2 113.37(17), O1–Si1–C2 99.87(9), O1–Si2–C1 98.00(9); C1–C2–Si1–O1 –3.42(18), C2–Si1–O1–Si2 5.40(14), Si1–O1–Si2–C1 –4.97(14), O1–Si2–C1–C2 2.37(19), Si2–C1–C2–Si1 0.7(2).

7.2.9 Crystal Structure Analysis of 1,1,4,4-Tetramethyl-1,2,3,4-tetrahydro-1,4-disila-6-naphthoic Acid (69)

A single crystal of **69** suitable for X-ray diffraction study was obtained following evaporation of a solution of **69** in *n*-hexane at room temperature. This compound crystallised in the space group $P2_1/c$. The molecular structure of **69** is shown in Fig. 7.14.

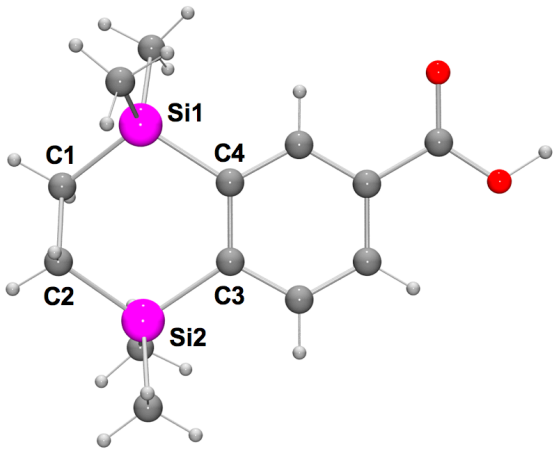


Figure 7.14. Molecular structure of compound **69** in the crystal. Selected bond lengths [Å], bond angles [deg] and torsion angles [deg]: Si1–C1 1.8731(17), Si1–C4 1.8937(15), Si2–C2 1.8754(17), Si2–C3 1.8880(15), C1–C2 1.546(2), C3–C4 1.415(2); Si1–C1–C2 112.23(11), Si1–C4–C3 123.13(11), Si2–C2–C1 111.82(11), Si2–C3–C4 123.93(11), C1–Si1–C4 108.67(7), C2–Si2–C3 108.49(7); Si1–C1–C2–Si2 –65.99(15), Si1–C4–C3–Si2 5.09(19), C1–Si1–C4–C3 –16.84(15), C1–C2–Si2–C3 49.13(14), C2–C1–Si1–C4 48.72(13), C2–Si2–C3–C4 –17.55(15).

7.2.10 Crystal Structure Analysis of 1,1,3,3-Tetramethyl-1,3-disila-5-indanoic Acid (70)

A single crystal of **70** suitable for X-ray diffraction study was obtained following evaporation of a solution of **70** in *n*-hexane at room temperature. This compound crystallised in the space group *C*2/*c*. The molecular structure of **70** is shown in Figs 7.15 and 7.16.

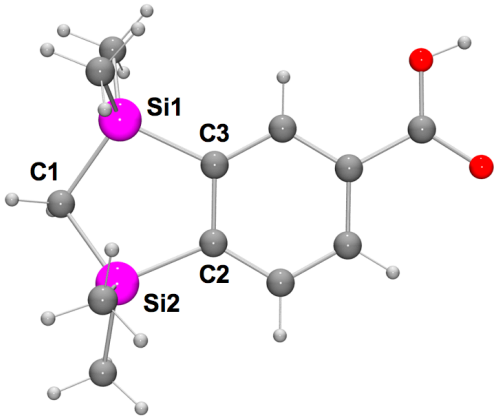


Figure 7.15. Molecular structure of compound **70** in the crystal. Selected bond lengths [Å], bond angles [deg] and torsion angles [deg]: Si1–C1 1.8774(13), Si2–C1 1.8739(13), Si1–C3 1.8901(13), Si2–C2 1.8870(13), C2–C3 1.4155(16); Si1–C1–Si2 104.21(7), Si1–C3–C2 114.10(9), Si2–C2–C3 114.11(9), C1–Si1–C3 99.53(6), C1–Si2–C2 99.18(6); C2–C3–Si1–C1 –15.15(11), C3–Si1–C1–Si2 26.66(8), Si1–C1–Si2–C2 –28.30(7), C1–Si2–C2–C3 21.04(11), Si2–C2–C3–Si1 –3.80(12).

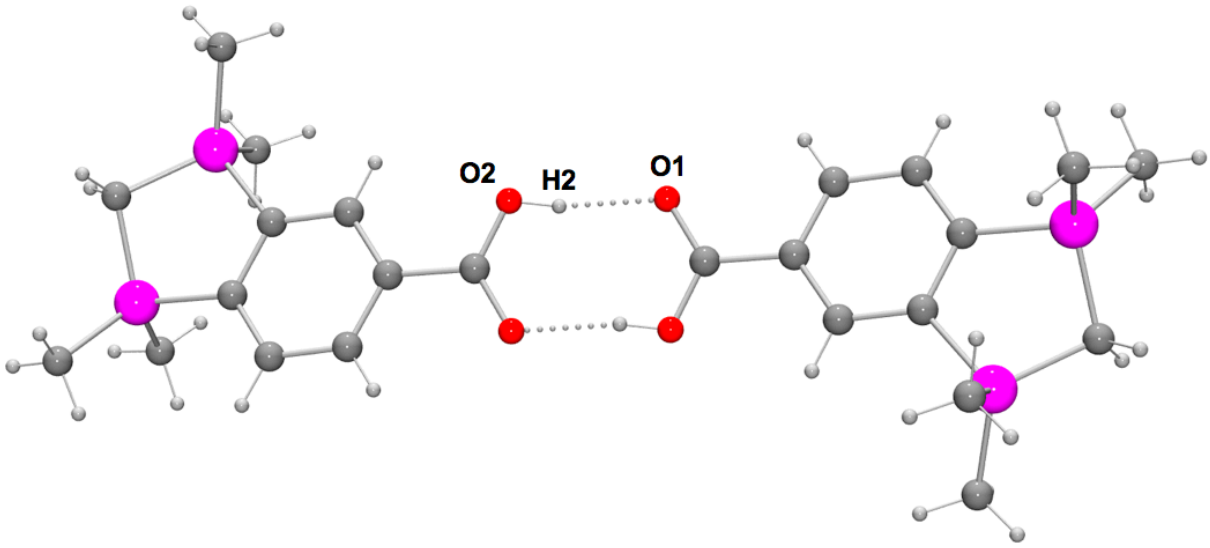


Figure 7.16. Hydrogen bonding system in the crystal of **70**. Selected bond lengths [Å] and angles [deg]: O2–H2 0.840 (1), H2···O1 1.798(1), O2···O1 2.629(2), O2–H2···O1 169.87(8).

7.3 Crystal Structure Analyses of Sila-penfluridol and Sila-loperamide Precursors

7.3.1 Crystal Structure Analysis of 2-(4,4-Bis(4-fluorophenyl)butyl)isoindoline-1,3-dione (81)

A single crystal of **81** suitable for X-ray diffraction study was obtained following recrystallisation from ethanol (standing of a room temperature solution for 16 h). This compound crystallised in the space group $P2_1/c$. The molecular structure of **81** is shown in Fig. 7.17.

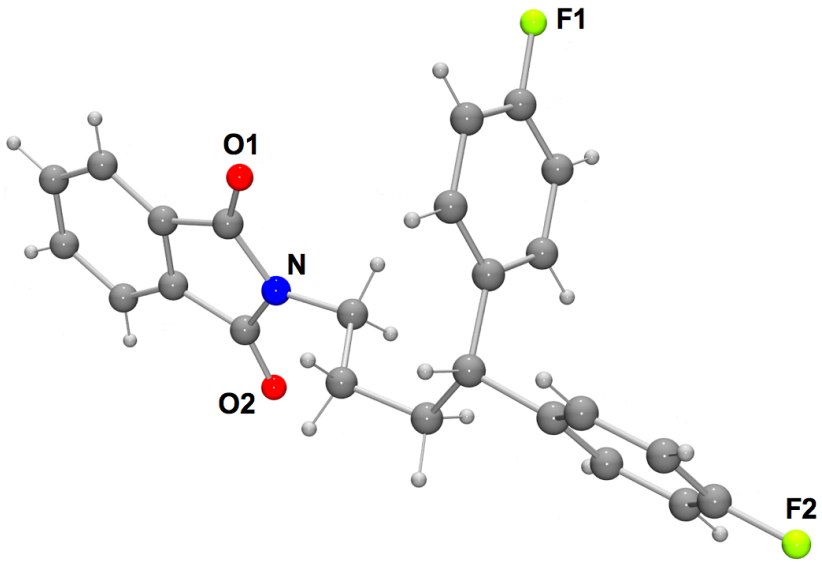


Figure 7.17. Molecular structure of compound **81** in the crystal. The bond lengths and angles observed fall within the expected ranges for the molecular bonds in question. For full details, see Appendix B.

7.3.2 Crystal Structure Analysis of (4-Chlorophenyl)(2,6-dimethoxyphenyl)bis(2-hydroxyethyl)silane (84)

A single crystal of **84** suitable for X-ray diffraction study was obtained following evaporation of a solution of **84** in diethyl ether at room temperature. This compound crystallised in the space group $P\bar{1}$. The molecular structure of **84** is shown in Fig. 7.18.

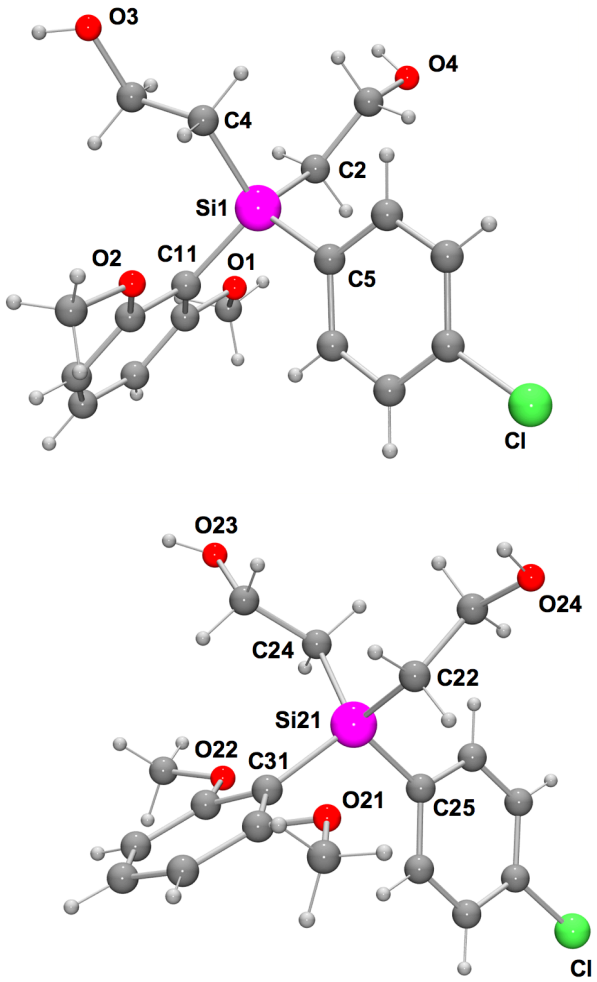


Figure 7.18. Molecular structures of the two crystallographically independent molecules in the crystal of **84**. Selected bond lengths [Å] bond angles [deg]: *Molecule I:* Si1–C2 1.8894(16), Si1–C4 1.8867(15), Si1–C5 1.8777(15), Si1–C11 1.8829(15); C2–Si1–C4 108.33(8), C2–Si1–C5 109.48(7), C2–Si1–C11 112.07(7), C4–Si1–C5 110.14(7), C4–Si1–C11 110.56(7), C5–Si1–C11 106.24(7). *Molecule II:* Si21–C22 1.8880(15), Si21–C24 1.8843(14), Si21–C25 1.8785(15), Si21–C31 18873(15); C22–Si21–C24 108.07(7), C22–Si21–C25 108.74(7), C22–Si21–C31 111.29(7), C24–Si21–C25 108.99(6), C24–Si21–C31 112.21(7), C25–Si21–C31 107.47(7).

7.3.3 Crystal Structure Analysis of 1-Allyl-4-(4-chlorophenyl)-4-(2,6-dimethoxy-phenyl)-4-silapiperidine (85)

A single crystal of **85** suitable for X-ray diffraction study was obtained following evaporation of a solution of **85** in *n*-hexane at room temperature. This compound crystallised in the space group *Cc*. The molecular structure of **85** is shown in Fig. 7.19.

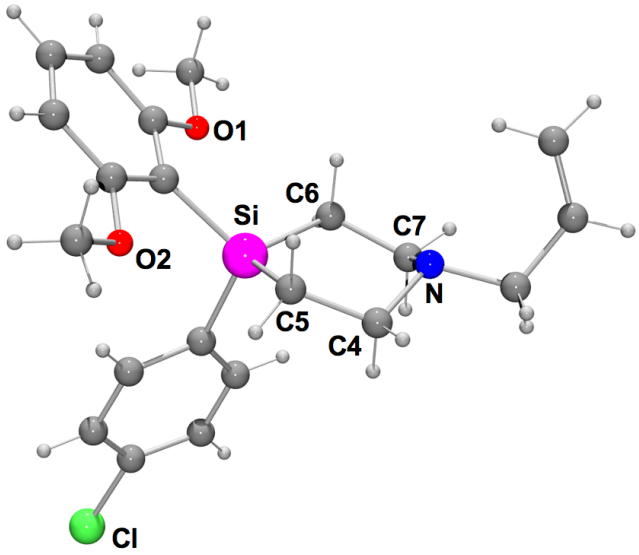


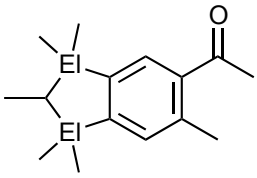
Figure 7.19. Molecular structure of compound **85** in the crystal. Selected bond lengths [Å], bond angles [deg] and torsion angles [deg]: Si–C5 1.8799(15), Si–C6 1.8824(15), N–C4 1.468(2), N–C7 1.468(2), C4–C5 1.535(2), C6–C7 1.539(2); Si–C5–C4 111.76(11), Si–C6–C7 113.58(10), N–C4–C5 112.72(12), N–C7–C6 113.48(12), C4–N–C7 111.39(13), C5–Si–C6 103.35(7); Si–C5–C4–N 56.82(16), Si–C6–C7–N –50.68(17), C4–N–C7–C6 70.78(17), C5–Si–C6–C7 32.79(13), C6–Si–C5–C4 –35.35(12), C7–N–C4–C5 –74.75(17).

8 Summary

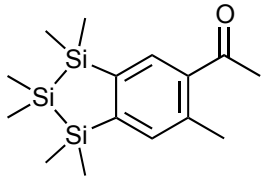
This thesis concerns (i) the synthesis and olfactory characterisation of silicon-containing analogues of the musk odourant phantolide, (ii) the synthesis and pharmacological investigation of silicon-containing analogues of retinoids of the EC23 and TTNN type and (iii) the attempted syntheses of silicon-containing analogues of the antipsychotic penfluridol and the antidiarrhoeal agent loperamide. All target compounds and intermediates were characterised by multinuclear NMR studies (^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si) and elemental analyses or high-resolution mass spectrometry. Additionally, some of these compounds were characterized by single crystal X-ray diffraction studies.

5,6-Disubstituted 1,2,3-Trisilaindanes as Analogues of the Musk Odourant Phantolide

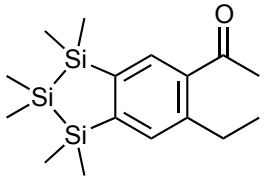
The 1,2,3-trisilaindanes **8** and **9** were synthesised as silicon analogues of the musk odourant phantolide (**1a**), along with the related compounds **10** and **26**. These syntheses were carried out using a [2+2+2] cycloaddition reaction as the key step.



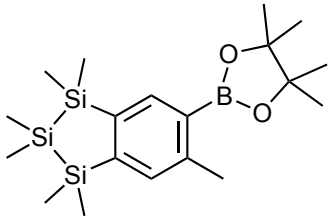
El = C: **1a** (Phantolide)
El = Si: **1b** (Disila-phantolide)



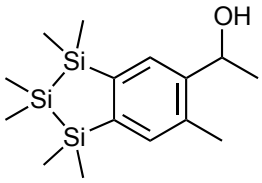
8



9

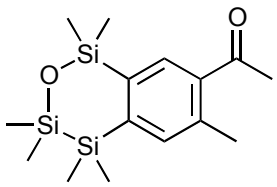


10

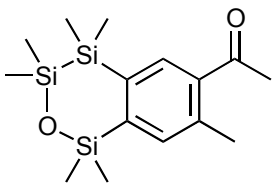


26

The [2+2+2] cycloaddition was by necessity the final stage in the synthesis of **8**–**10** and **26** because the 1,2,3-trisilaindane skeleton proved to be rather unstable. Treatment of **26** with an oxidation reagent (the Dess-Martin perioindane) resulted in the novel 1,3,4-trisilaisochroman isomers **36a** and **36b**.



36a

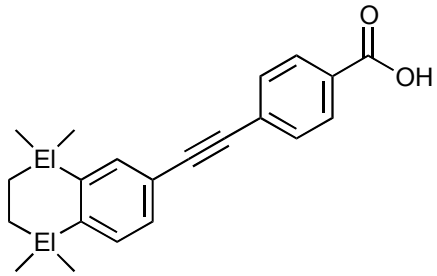


36b

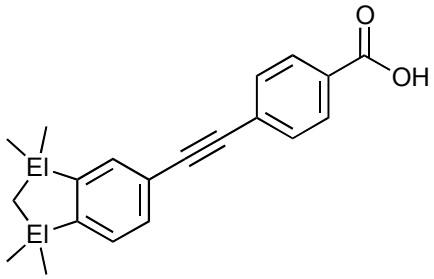
Compounds **8** and **9** were studied for their olfactory properties and were found to display no musk odour. Indeed both compounds are, strictly speaking, odourless.

Analogues of the Retinoid Agonist EC23

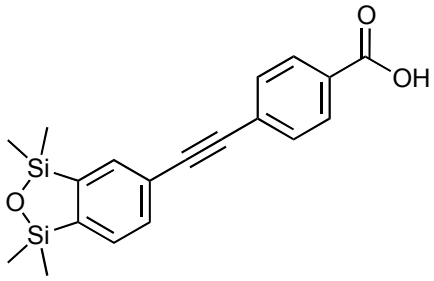
Four novel analogues of the retinoid agonist EC23 (**14a**) (compounds **14b**, **16a**, **16b** and **17**) were synthesised via Sonogashira cross coupling reactions.



El = C: **14a** (EC23)
El = Si: **14b** (Disila-EC23)

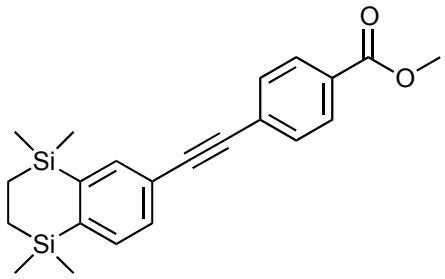


El = C: **16a**
El = Si: **16b**

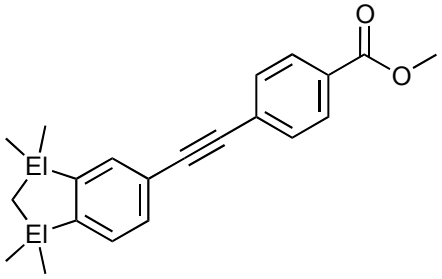


17

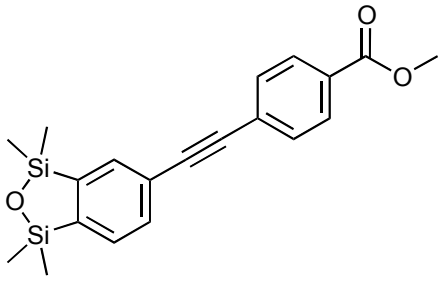
Deprotection of the methyl ester intermediates **42**–**44** in the final step allowed the synthesis of **14b**, **16a** and **16b**. However, the synthesis of **17** could not be carried out by deprotection of the relevant methyl ester **45** due to the relatively high reactivity of the 2-oxa-1,3-disilaindane backbone to strong acids and bases. Instead, the methyl ester protecting group was removed in an earlier synthetic step, prior to the introduction of the 2-oxa-1,3-disilaindane moiety.



42



El = C: **43**
El = Si: **44**

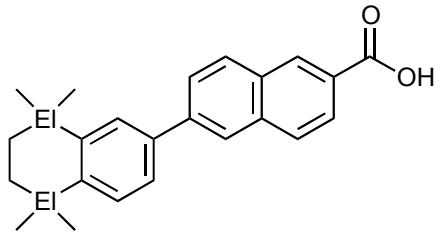


45

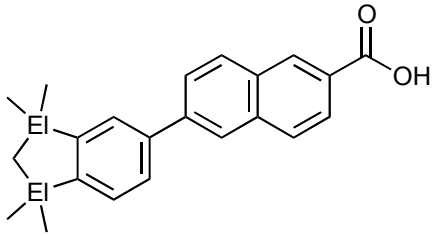
Comparative pharmacological studies of the retinoids **14a**, **14b**, **16a**, **16b** and **17** with respect to their transactivation activity revealed significant differences in the activity and selectivity profiles of the respective C/Si analogues. Replacement of the CCH_2CH_2C moiety of EC23 with a CCH_2C fragment (**14a→16a**) results in only a moderate decrease in transactivation potential, which is most pronounced for RARα. Two-fold sila-substitution of **14a** (→**14b**) and **16a** (→**16b**) leads to a moderate decrease in RARα activation, whereas the RARβ,γ activation is almost not affected. Replacement of the $SiCH_2Si$ moiety of **16b** with an SiOSi fragment (→**17**) results in a moderate decrease in activity at low concentrations, whereas similar transcription activation potentials are observed at higher concentrations.

Analogues of the Retinoid Agonist TTNN

Three analogues of the retinoid agonist TTNN (**15a**) (compounds **15b**, **18a** and **18b**) were synthesised via Suzuki-Miyaura cross coupling reactions.

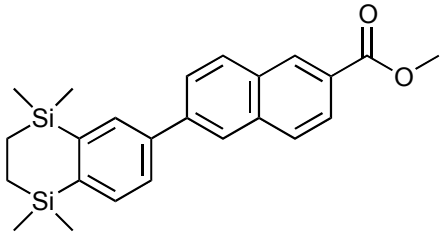


El = C: **15a** (TTNN)
El = Si: **15b** (Disila-TTNN)

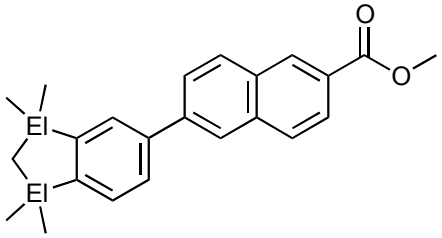


El = C: **18a**
El = Si: **18b**

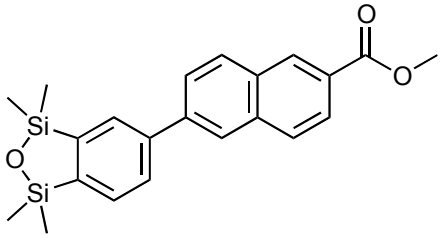
Compounds **15b**, **18a** and **18b** were obtained by deprotection of the methyl ester intermediates **52**–**54** in the final step. The protected retinoid precursor **55** was also synthesised. However, as previously indicated the 2-oxa-1,3-disilaindane backbone is reactive towards strong acids and bases thus preventing deprotection of the methyl ester. Unfortunately, a direct synthesis of the corresponding free acid, analogously to the synthesis of **17**, failed.



52



El = C: **53**
El = Si: **54**



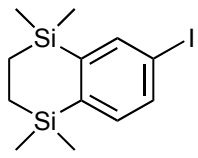
55

Comparative pharmacological studies of the retinoids **15a**, **15b**, **18a** and **18b** with respect to their transactivation activity revealed differences in the selectivity and activity profiles of the respective C/Si analogues. Two-fold sila-substitution of **15a** (1,2,3,4-tetrahydronaphthalene skeleton) and **18a** (indane skeleton) resulted in considerably different effects: a significant increase (**15a→15b**) and almost no change (**18a→18b**) in transcription activation potential

for all three RAR isotypes. Disila-TTNN can be regarded as a powerful RARβ,γ-selective retinoid.

Aryl Iodides as Building Blocks

In order to construct the retinoids described above, the corresponding aryl iodides **37**–**40** were required. These were synthesised by a variety of methods as the properties of the saturated portion of the 1,2,3,4-tetrahydro-1,4-disilanaphthalene, indane, 1,3-disilaindane and 2-oxa-1,3-disilaindane skeletons had a controlling influence on the effectiveness of the synthesis.



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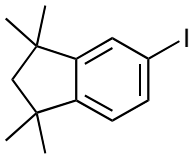

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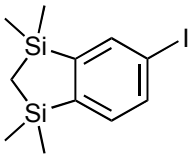

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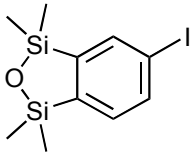
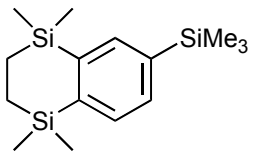


40

In context with these aryl iodide syntheses, the precursors **63**–**65**, **67** and **70** were synthesised for the first time. In addition, a new synthetic route to the known compounds **66** and **69** was developed.



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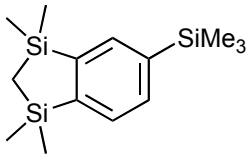

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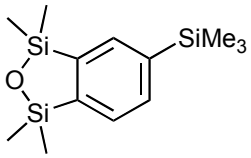

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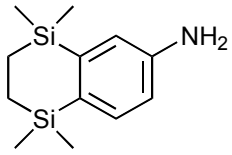

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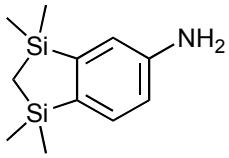

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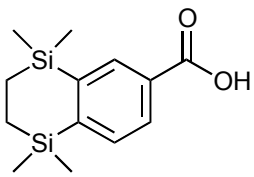

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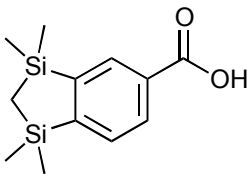
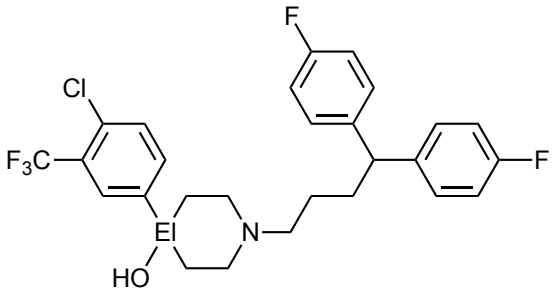


70

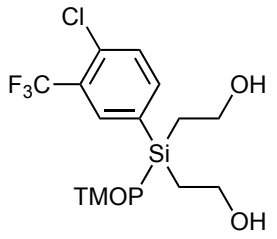
A Silicon Analogue of the Antipsychotic Penfluridol

Sila-penfluridol (**20b**), a silicon analogue of the antipsychotic penfluridol (**20a**), was synthesised using the 2,4,6-trimethoxyphenyl (TMOP) protecting group to mask the silanol functionality. Unfortunately, **20b** could not be obtained as a pure product and was always contaminated to a greater or lesser extent with the corresponding disiloxane.



El = C: **20a** (Penfluridol)
El = Si: **20b** (Sila-penfluridol)

Over the course of the attempted synthesis of sila-penfluridol (**20b**), the novel intermediates **74**–**76**, **78**, **79** and **81** were synthesied.



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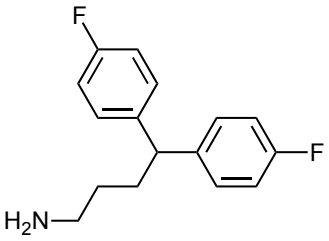

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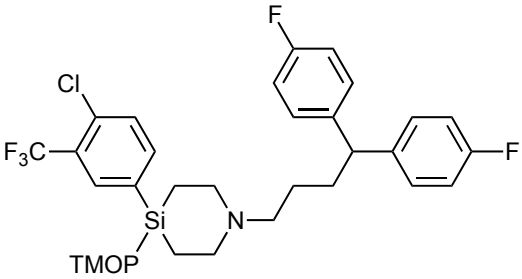

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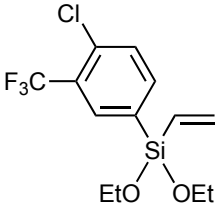

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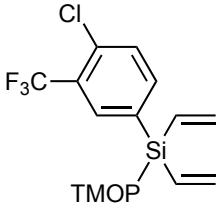

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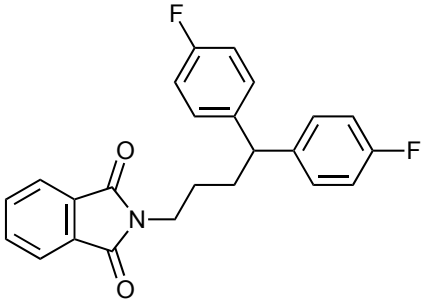
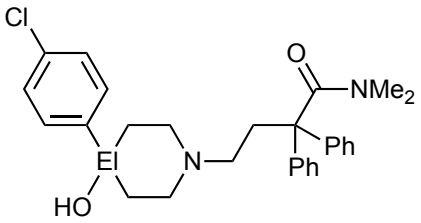


81

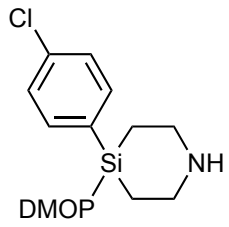
A Silicon Analogue of the Antidiarrhoeal Loperamide

Due to time constraints the synthesis of sila-loperamide (**22b**), a silicon analogue of the antidiarrhoeal drug loperamide (**22a**), could not be brought to conclusion.



El = C: **22a** (Loperamide)
El = Si: **22b** (Sila-loperamide)

In the attempt to produce sila-loperamide (**22b**) the synthesis of the building block **24** was developed, using the 2,6-dimethoxyphenyl (DMOP) protecting group. Selective *N*-deprotection of the intermediate **86** to give **24** was demonstrated. Unfortunately, due to time constraints, compound **24** could only be obtained as a crude product. During the synthesis of **24**, the novel intermediates **84**, **85** and **87** were synthesised.



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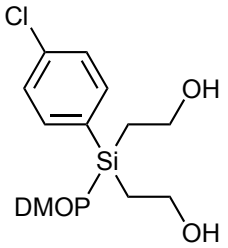
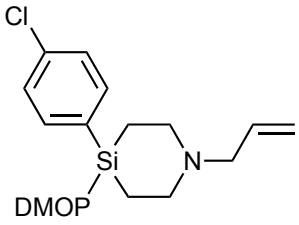


84



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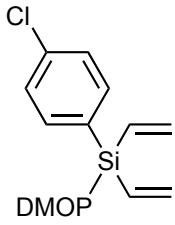


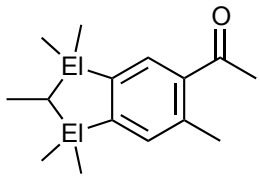
87

9 Zusammenfassung

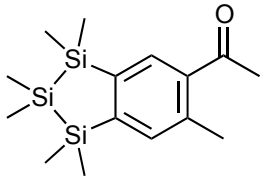
Die vorliegende Arbeit beschreibt (i) die Synthese und olfaktorische Charakterisierung von siliciumhaltigen Derivaten des Moschus-Riechstoffes Phantolid, (ii) die Synthese und pharmakologische Charakterisierung siliciumhaltiger Derivate von Retinoiden des EC23- und TTNN-Typs, und (iii) die Versuche zur Darstellung siliciumhaltiger Analoga der Wirkstoffe Penfluridol und Loperamid. Die Charakterisierung der Zielverbindungen sowie aller auftretenden Zwischenstufen erfolgte durch NMR-Spektroskopie (^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si) und Elementaranalyse bzw. hochaufgelöste Massenspektrometrie. Außerdem wurden einige der Verbindungen durch Kristallstrukturanalyse charakterisiert.

5,6-Disubstituierte 1,2,3-Trisilaindane als Analoga des Moschus-Riechstoffes Phantolid

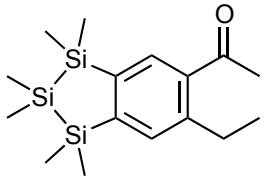
Die 1,2,3-Trisilaindane **8** und **9** wurden als Analoga des Moschus-Riechstoffes Phantolid (**1a**) – zusammen mit den Derivate **10** und **26** - synthetisiert. Für diese Synthesen stellte der Aufbau des 1,2,3-Trisilaindan-gerüsts durch eine [2+2+2]-Cycloaddition den Schlüsselschritt dar.



El = C: **1a** (Phantolid)
El = Si: **1b** (Disila-phantolid)



8



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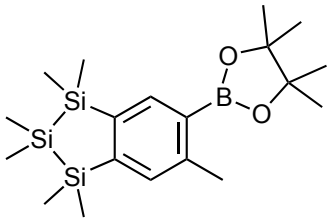

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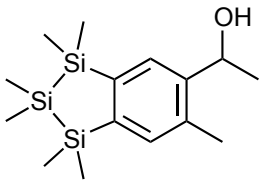
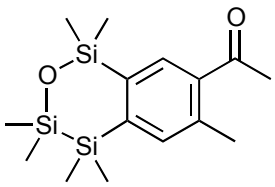
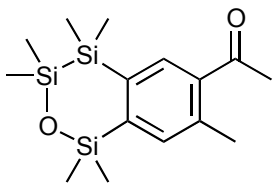


26

Die [2+2+2]-Cycloaddition musste die letzte Stufe in den Synthesen von **8**–**10** und **26** sein, da sich das 1,2,3-Trisilaindan-gerüst als instabil gegen Oxidationsmittlen erwies. Die Umsetzung von **26** mit dem Dess-Martin-Reagenz lieferte die beiden 1,3,4-Trisilaisochroman-Isomere **36a** und **36b**.



36a

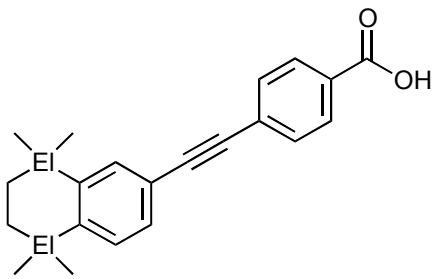


36b

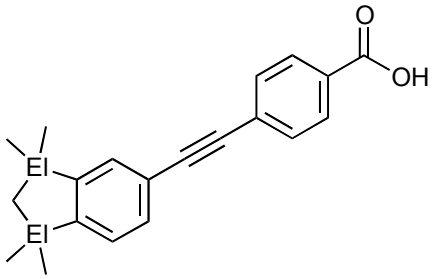
Die olfaktorische Charakterisierung von **8** und **9** ergab, dass beide Verbindungen keinen typischen Moschusgeruch zeigen und praktisch geruchlos sind.

Derivate des Retinoid-Agonisten EC23

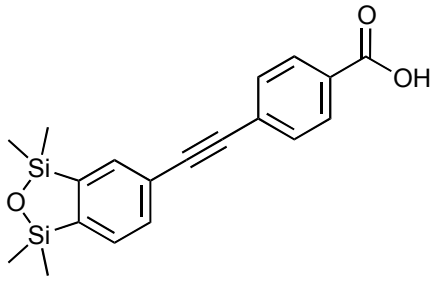
Vier Derivate des Retinoid-Agonisten EC23 (**14a**), die Verbindungen **14b**, **16a**, **16b**, und **17**, konnten mit Hilfe einer Sonogashira-Kreuzkupplung synthetisiert werden.



El = C: **14a** (EC23)
El = Si: **14b** (Disila-EC23)

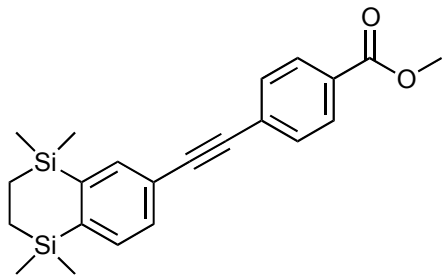


El = C: **16a**
El = Si: **16b**

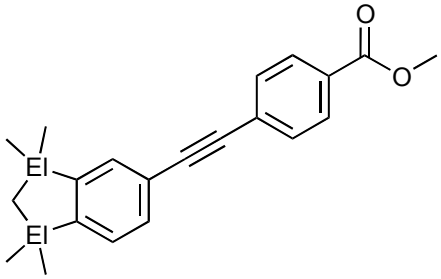


17

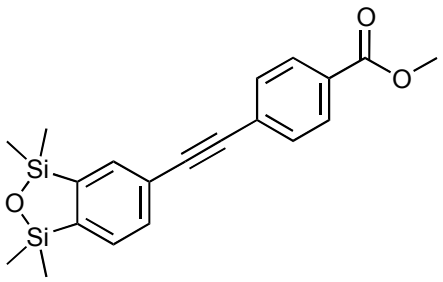
Die Verbindungen **14b**, **16a** und **16b** konnten im letzten syntheseschritt durch Entschützung der Methylester-Intermediate **42**–**44** erhalten werden. Verbindung **17** konnte unter Verwendung dieser Methode nicht dargestellt werden, da das 2-Oxa-1,3-disilaindan-Gerüst gegen Säuren und Basen labil ist. Daher wurde die Methylester-Funktion in einem früheren Reaktionsschritt - vor dem Einbau des 2-Oxa-1,3-disilaindan-Gerüstes - gespalten.



42



El = C: **43**
El = Si: **44**

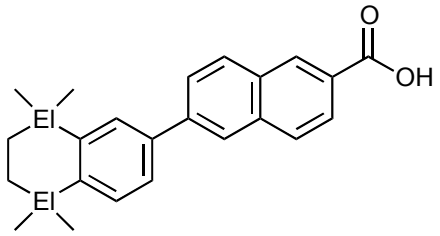


45

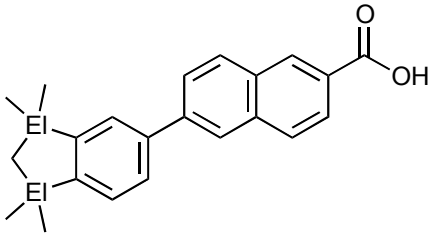
Die vergleichenden pharmakologischen Untersuchungen der Retinoide **14a**, **14b**, **16a**, **16b**, und **17** hinsichtlich ihres Transaktivierungs-Potentials ergaben in alle Fällen eine Veränderung der Selektivitätsprofile der jeweiligen C/Si-Analoga. Austausch der CCH_2CH_2C-Einheit durch eine CCH_2C-Einheit (**14a→16a**) ergab nur einer kleine Verringerung der RAR Aktivität. Im Fall von **14a** (→**14b**) und **16a** (→**16b**) führt die Sila-Substitution zu einer Verringerung der RARα Aktivität jedoch werde durch die Sila-Substitution die Aktivität an RARβ und RARγ unverändert. Der Austausch der CCH_2C-Einheit durch eine SiOSi-Einheit (**16a→17**) führt die Sila-Substitution zu einer Verringerung der RAR Aktivität bei niedrige Konzentrationen, dahingegen bei höhere Konzentrationen der Wirkungsprofil ist ähnlich als die andere untersuchtet Substanzen.

Derivate des Retinoid-Agonisten TTNN

Drei Derivate des Retinoid-Agonisten TTNN (**15a**), die Verbindungen **15b**, **18a** und **18b**, konnten mit Hilfe einer Suzuki-Miyaura-Kreuzkupplung synthetisiert werden.

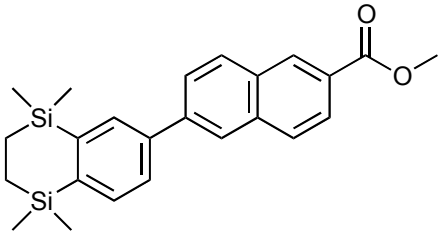


El = C: **15a** (TTNN)
El = Si: **15b** (Disila-TTNN)

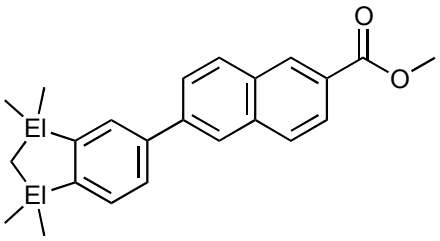


El = C: **18a**
El = Si: **18b**

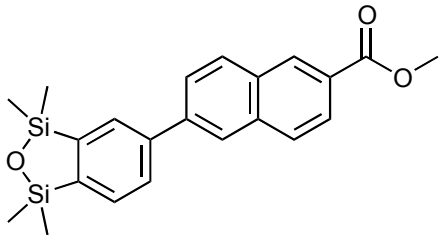
Die Verbindungen **15b**, **18a** und **18b** konnten im letzten Synthese-Schritt durch Entschützung der Methylester-Intermediate **52**–**54** erhalten werden. Der Methylester **55** konnte ebenfalls synthetisiert werden, allerdings konnte die freie Säure bisher nicht dargestellt werden.



52



El = C: **53**
El = Si: **54**

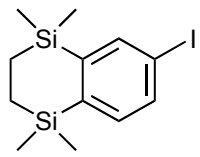


55

Die vergleichenden pharmakologischen Untersuchungen der Retinoide **15a**, **15b 18a**, und **18b** hinsichtlich ihres Transaktivierungs-Potentials ergaben in beiden Fällen eine Veränderung der Selektivitätsprofile der jeweiligen C/Si-Analoga. Zwar ist die TTNN-Analog **15b** viel aktiver als die Muttersubstanz **15a**, jedoch wurde durch die Sila-Substitution die Aktivität an RARβ und RARγ von **15b** mehr erhöht im als die Aktivität an RARα. Im vergleich, der Austausch der CCH_2C-Einheit durch eine $SiCH_2Si$-Einheit (**18a→18b**) führt die Sila-Substitution nur eine kleine Änderung der RAR Aktivität.

Aryliodide als Synthesebausteine

Für die Synthese der zuvor beschriebenen Retinoide stellte der Aufbau der Aryliodide **37**–**40** den Schlüsselschritt dar. Diese Verbindungen wurden über verschiedene Methoden synthetisiert, da die Eigenschaften der 1,2,3,4-Tetrahydro-1,4-disilanaphthalin-, Indan-, 1,3-Disilaindan- und 2-Oxa-1,3-disilaindan-Gerüste einen großen Einfluss auf die Effizienz der jeweiligen Synthesen haben.



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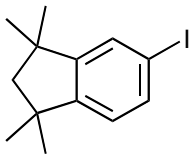

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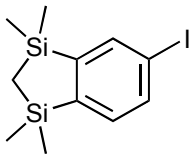
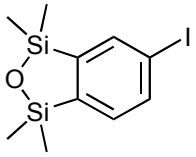
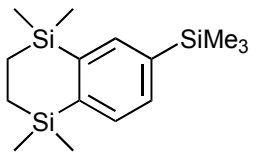


39



40

Im Rahmen dieser Arbeiten wurden die Verbindungen **63–65**, **67** und **70** erstmalig synthetisiert. Zusätzlich wurden die schon bekannten Verbindungen **66** und **69** über eine neue Synthese methode dargestellt.



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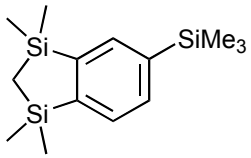

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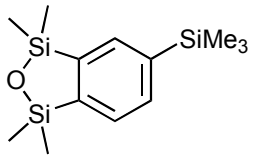

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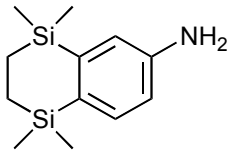

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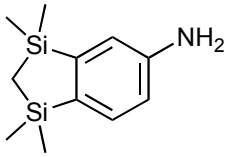

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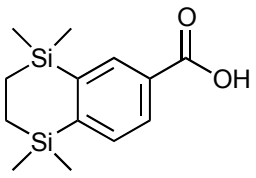

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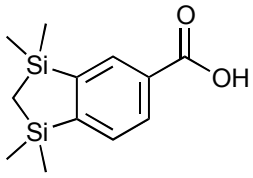
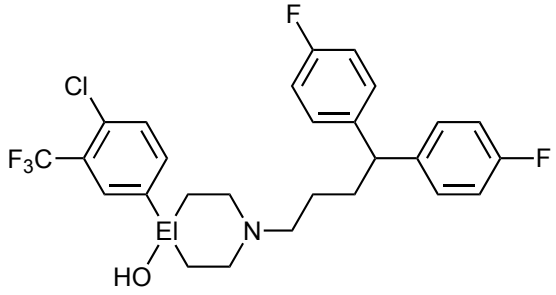


70

Ein Sila-Analogon des Antipsychoticums Penfluridol

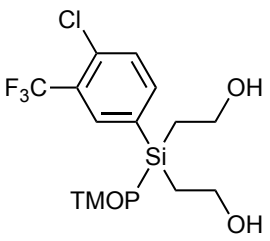
Sila-Penfluridol (**20b**), ein Silicium-Analogon des Antipsychoticums Penfluridol (**20a**), wurde in einer neuen Synthese unter Verwendung der 2,4,6-Trimethoxyphenyl-Schutzgruppe

dargestellt. Leider konnte Sila-penfluridol nur in ungenügender Reinheit isoliert werden (**20b** war immer mit dem entsprechenden Disiloxan verunreinigt).

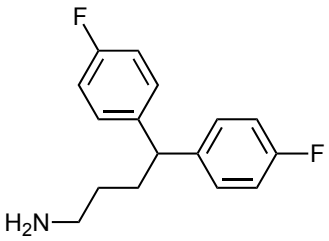


El = C: **20a** (Penfluridol)
El = Si: **20b** (Sila-penfluridol)

Im Rahmen dieser Arbeiten wurden die Zwischenstufen **74–76**, **78**, **79** und **81** erstmalig synthetisiert und charakterisiert.



74



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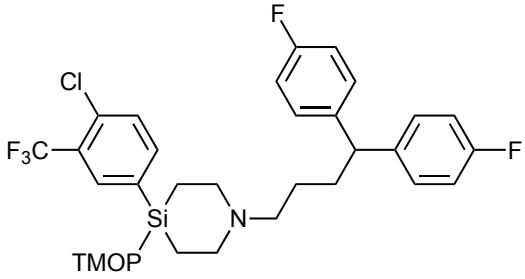

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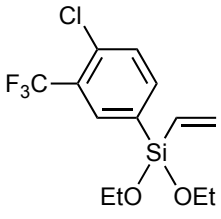

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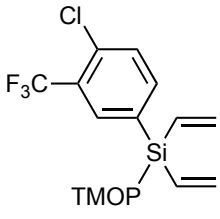

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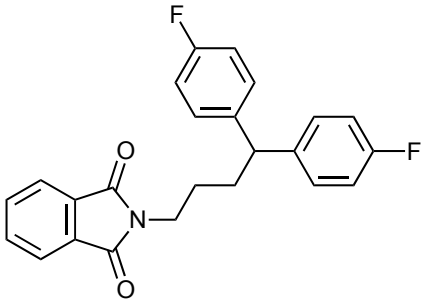
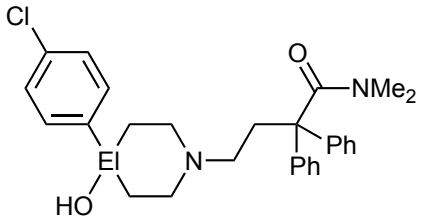


81

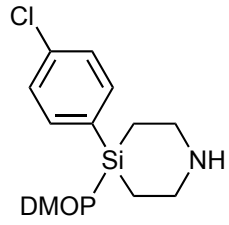
Ein Sila-Analogon des Durchfallmedikamentes Loperamid

Die Synthese von Sila-loperamid (**22b**), ein Silicium-Analogen des Durchfallmedikamentes Loperamid (**22a**) konnte aus zeitlichen Gründen nicht abgeschlossen werden.

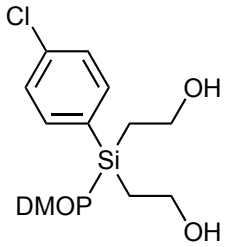


El = C: **22a** (Loperamid)
El = Si: **22b** (Sila-loperamid)

Für die Darstellung von Sila-loperamid (**22b**) wurde das bisher unbekannte 4-Silapiperidin-Derivat **24** unter Verwendung der 2,6-Dimethoxyphenyl-Schutzgruppe synthetisiert. Aus zeitlichen Gründen konnte **24** nicht in ausreichender Reinheit erhalten werden, die selektive *N*-Entschützung von **85** konnte aber nachgewiesen werden. Im Zuge dieser Synthese wurden die bisher unbekannten Verbindungen **84**, **85** und **87** als Zwischenstufen dargestellt.



24



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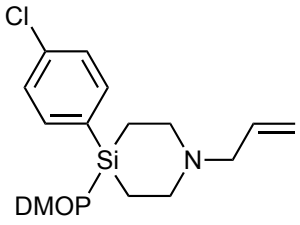

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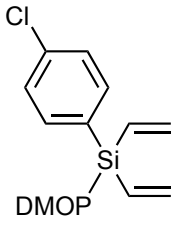

87

10 Experimental Section

10.1 General Procedures

10.1.1 General Synthetic Techniques

Chemical Syntheses:

Unless otherwise indicated, all reactions were carried out in dry, oxygen free solvents under a dry argon atmosphere. In order to completely exclude moisture,s the argon was first passed through three columns; two filled with a mixture of phosphorus pentoxide and pumice stone, and the third filled with silica gel and a moisture indicator. Reaction workup was carried out in air with no specific precautions against oxygen or moisture.

The sodium sulphate and magnesium sulphate used to dry organic phases following aqueous workup were anhydrous and of "purum" quality; all other commercial reagents were of analytical (p.a.) quality and were used as received.

Solvents:

All of the solvents used for synthesis were dried and distilled according to standard procedures and stored under dry nitrogen. Solvents used for reaction workup or column chromatography were distilled prior to use or purchased with analytical purity. The solvents used for RP-MPLC (including water) were purchased as HPLC grade and were used without further purification. For general synthetic purposes, deionised water was used. The deuterated solvents used for NMR spectroscopy were purchased in individual glass ampoules and were used as received.

Bulb-to-Bulb Distillations:

Bulb-to-bulb distillations were accomplished using a Büchi GKR-50, GKR-51 or a Büchi B-580 Glass Oven apparatus. The temperatures quoted are internal oven temperatures.

Reversed Phase Medium Pressure Liquid Chromatography (RP-MPLC):

Pressure, 16 bar; column dimensions, 50 × 2.5 cm; RP-18 silica gel, YMC ODS-A, 15 μm; detector, Knauer Variable Wavelength Monitor.

Column Chromatography:

Column chromatography and flash column chromatography were carried out using silica gel (40–63 μm; Merck) or aluminium oxide (neutral; 150 mesh, 58 Å; Brockmann activity III; Sigma Aldrich and Macherey-Nagel). Silica gel masses for chromatography were determined according to ref. 57.

10.1.2 Analytical Techniques

^{1}H NMR Spectra:

Spectrometers: Bruker DRX-300 (300.1 MHz), Avance 400 (400.1 MHz) and Avance 500 (500.1 MHz); Solvents and reference signals: $CDCl_3$ (internal standard $CHCl_3$, δ = 7.24), CD_2Cl_2 (internal standard $CHDCl_2$, δ = 5.32), C_6D_6 (internal standard C_6HD_5, δ = 7.28) and [D_6]DMSO (internal standard [D_5]DMSO, δ = 2.49); Measurement temperature 23 °C. Assignment of the ^{1}H NMR data was supported by ^{1}H,^{1}H gradient selected COSY, ^{13}C,^{1}H HMQC and HMBC, and gradient-selected ^{1}H,^{29}Si HMQC (optimised for $^{2}J_{SiH}$ = 7 Hz) experiments.

^{11}B NMR Spectra:

Spectrometers: Bruker DRX-300 (96.3 MHz) and Avance 500 (160.5 MHz); Solvents and reference signal: $CDCl_3$ and [D_6]DMSO (external standard $BF_3{\cdot}Et_2O$, δ = 0.0); Measurement temperature 23 °C. All ^{11}B NMR spectra were ^{1}H broadband decoupled.

^{13}C NMR Spectra:

Spectrometers: Bruker DRX-300 (75.5 MHz), Avance 400 (100.6 MHz) and Avance 500 (125.8 MHz); Solvents and reference signals: $CDCl_3$ (internal standard $CDCl_3$, δ = 77.00), CD_2Cl_2 (internal standard CD_2Cl_2, δ = 53.80), C_6D_6 (internal standard C_6D_6, δ = 128.00) and [D_6]DMSO (internal standard [D_6]DMSO, δ = 39.50); Measurement temperature 23 °C. All ^{13}C NMR spectra were ^{1}H broadband decoupled. Assignment of the ^{13}C NMR data was supported by DEPT-135, ^{1}H,^{1}H gradient selected COSY, gradient selected ^{13}C,^{1}H HMQC and HMBC, and gradient-selected ^{1}H,^{29}Si HMQC (optimised for $^{2}J_{Si\text{-}H}$ = 7 Hz) experiments, along with examination of both the characteristic carbon–fluorine coupling constants[58] and ^{13}C NMR substituent effects.[59]

^{15}N NMR Spectra:

Spectrometers: Bruker DRX-300 (30.4 MHz), Avance 400 (40.6 MHz) and Avance 500 (50.7 MHz); Solvents and reference signal: $CDCl_3$, C_6D_6 and [D_6]DMSO [external standard $H_2NC(O)H$ (90% in [D_6]DMSO), δ = –268.0]; Measurement temperature 23 °C. All ^{15}N NMR spectra were obtained using inverse correlation ^{15}N,^{1}H HMQC or HMBC experiments.

^{19}F NMR Spectra:

Spectrometer: Bruker Avance 400 (376.5 MHz); Solvents and reference signal: $CDCl_3$, C_6D_6 and [D_6]DMSO (external standard $CFCl_3$, δ = 0); Measurement temperature 23 °C. All ^{19}F NMR spectra were ^{1}H broadband decoupled

^{29}Si NMR Spectra:

Spectrometers: Bruker DRX-300 (59.6 MHz), Avance 400 (79.5 MHz) and Avance 500 (99.4 MHz); Solvents and reference signal: $CDCl_3$, CD_2Cl_2, C_6D_6 and [D_6]DMSO (external standard TMS, δ = 0); Measurement temperature 23 °C. All ^{29}Si NMR spectra were ^{1}H broadband decoupled. Assignment of the ^{29}Si NMR data was supported by gradient-selected ^{1}H,^{29}Si HMQC (optimised for $^{2}J_{Si\text{-}H}$ = 7 Hz) experiments.

NMR Structural Assignment:

In the assignment of the ^{1}H and ^{13}C NMR data the underlying skeletons of the differing bicyclic ring systems of **14b**, **15b**, **16**–**18**, **42**–**45** and **52**–**55** are indicated by the following abbreviations and numbered conventionally: Benz, benzoic acid; Benz', methyl benzoate; Naph, naphthoic acid; Naph', methyl naphthoate; Ind, indan-5-yl; Ind', 1,3-disilaindan-5-yl; Ind'', 2-oxa-1,3-disilaindan-5-yl; THN, 1,2,3,4-tetrahydro-1,4-disilanaphthalen-6-yl.

Elemental Analyses:

Instruments: VarioMicro apparatus (Elementar Analysensysteme GmbH) or EURO EA Elemental Analyzer (EuroVector), Institut für Anorganische Chemie, Universität Würzburg.

Gas Chromatography:

Instrument: Hewlett Packard 5890 Series II; Column: Phenomenex Zebron ZB-1 (15 m, inside diameter 0.32 mm); Flow rate: 0.67 mL min^{-1}; Injector: split ratio 1:10, 220 °C; Detector; FID, 320 °C; Carrier gas N_2.

Gas Chromatography/Mass Spectrometry (GC-MS Coupling):

I) a) Gas Chromatograph: Thermo Electron Corporation MS-8060; Column: Phenomenex Zebron ZB-1 (15 m, inside diameter 0.32 mm); Flow rate 0.73 mL min^{-1}; Injector: split ratio 1:25, 200 °C; Carrier gas: He.

b) Quadrupole Mass Spectrometer: Thermo Electron Corporation TRIO-1000; Electron impact ionisation (EI-MS), 70 eV.

II) a) Gas Chromatograph: Varian 450-GC; Column: Varian FactorFour VF-5ms (30 m, inside diameter 0.25 mm); Flow rate 1.0 mL min^{-1}; Injector: split ratio 1:25, 220 °C; Carrier gas: He.

b) Quadrupole Mass Spectrometer: Varian 320-MS; Electron impact ionisation (EI-MS), 70 eV; Chemical ionisation (CI-MS) reactant gas: methane.

High-Resolution Mass Spectrometry:

ESI-HRMS spectra (**14b**, **16a**, **16b** and **17**: negative mode; **15b**, **18a**, **18b** and **52**–**55**: positive mode) were recorded on a Bruker MicrOTOF instrument using solutions in trichloromethane/acetonitrile (1:1 (v/v)). EI-HRMS spectra were recorded on a Finnigan MAT90 instrument.

Melting Points:

Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in open glass capillaries, or by differential scanning calorimetery using a Mettler Toledo DSC 823 apparatus.

10.2 Syntheses

*1-(1,1,2,2,3,3,6-Heptamethyl-1,2,3-trisilaindan-5-yl)ethanone (**8**, methyltrisilaphantolide).*

A solution of iodine in acetonitrile (0.01 M, 10.0 mL, 100 μmol of iodine) was added to zinc powder (64.0 mg, 979 μmol) in a single portion at 20 °C. The mixture was stirred and heated at 80 °C until the brown colouration disappeared and a grey suspension was observed. Compound **27** (980 mg, 4.36 mmol), compound **28** (570 mg, 6.94 mmol) and a solution of cobalt(II) iodide in acetonitrile (0.1 M, 2.50 mL, 250 μmol of CoI_2) were then added sequentially in single portions. The resulting brown solution was stirred at 80 °C for 45 min, whereupon GC analysis indicated complete consumption of the starting materials. Following

cooling to 20 °C, the reaction mixture was passed through a short silica column (eluent, *n*-hexane/ethyl acetate (90:10 (v/v))). The residue resulting following removal of the solvent under reduced pressure was purified by flash column chromatography (silica gel; eluent, *n*-hexane/diethyl ether (90:10 (v/v))). The relevant fractions (GC analysis) were combined and concentrated under reduced pressure to yield a yellow oil, which crystallised as it cooled. Twofold recrystallisation from methanol (−30 °C) yielded fine, colourless, acicular crystals. The solvent was decanted and the crystals were washed with cold (−30 °C) methanol (4 × 1 mL) affording **8** in 13% yield (176 mg, 574 μmol); mp 94−96 °C. — ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.26 (s, 6 H, SiCH_3), 0.33 (s, 6 H, SiCH_3), 0.34 (s, 6 H, SiCH_3), 2.54 (s, 3 H, CCH_3), 2.80 (s, 3 H, C(O)CH_3), 7.44 (s, 1 H, *H*-7), 7.82 (s, 1 H, *H*-4). — ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = −8.2 (Si*C*H_3), −1.9 (Si*C*H_3), −1.6 (Si*C*H_3), 21.7 (C*C*H_3), 29.9 (C(O)*C*H_3), 133.3 (*C*-4), 136.9 (*C*-7), 137.4 (*C*-6), 138.8 (*C*-5), 147.8 (*C*-3a or *C*-7a), 155.5 (*C*-3a or *C*-7a), 202.7 (*C*(O)CH_3). — ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ = −52.8, −13.0, −12.8. — EI-MS: *m/z* (%) 306 (46) [M^+], 291 (50) [$M^+ - CH_3$], 73 (100). Odour description: very weak, with only a slightly creamy-lactonic impression and some coumarine facets, but no musk character. Odour threshold: 866 ng L^{-1} air.

$C_{15}H_{26}OSi_3$ (306.63)	Calculated:	C 58.76	H, 8.55
	Found:	C 58.5	H, 8.5

*1-(6-Ethyl-1,1,2,2,3,3-hexamethyl-1,2,3-trisilaindan-5-yl)ethanone (**9**)*.

A solution of iodine in acetonitrile (0.01 M, 10.0 mL, 100 μmol of iodine) was added to zinc powder (64.0 mg, 979 μmol in a single portion at 20 °C. The mixture was stirred and heated at 80 °C until the brown colouration disappeared and a grey suspension was observed. Compound **27** (1.12 g, 4.99 mmol), compound **29** (671 mg, 6.98 mmol) and a solution of cobalt(II) iodide in acetonitrile (0.1 M, 2.50 mL, 250 μmol of CoI_2) were then added sequentially in single portions. The resulting brown solution was stirred at 80 °C for 90 min, whereupon GC analysis indicated complete consumption of the starting materials. Following cooling to 20 °C, the reaction mixture was passed through a short silica column (eluent, *n*-hexane/ethyl acetate (90:10 (v/v))). The residue resulting following the removal of the solvent under reduced pressure was purified by flash column chromatography (silica gel; eluent, *n*-hexane/diethyl ether (90:10 (v/v))). The relevant fractions (GC analysis) were combined and concentrated under reduced pressure to give a yellow oil. This oil was further purified by RP-MPLC (eluent, methanol/water (90:10 (v/v)); flow rate, 31 mL min^{-1}; detector wavelength, 250 nm) yielding a colourless oil, which crystallised as it cooled,

affording **9** in 17% yield (280 mg, 873 μmol); mp 39−42 °C. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 0.25 (s, 6 H, SiCH_3), 0.30 (s, 6 H, SiCH_3), 0.32 (s, 6 H, SiCH_3), 1.11 (t, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 3 H, CCH$_2$CH_3), 2.57 (s, 3 H, C(O)CH_3), 2.73 (q, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 2 H, CCH_2CH$_3$), 7.49 (s, 1 H, *H*-7), 7.82 (s, 1 H, *H*-4). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = −8.5 (Si*C*H$_3$), −2.1 (Si*C*H$_3$), −1.9 (Si*C*H$_3$), 16.2 (CCH$_2$*C*H$_3$), 26.2 (C*C*H$_2$CH$_3$), 30.2 (C(O)*C*H$_3$), 132.5 (*C*-4), 134.7 (*C*-7), 138.3 (*C*-5), 141.9 (*C*-6), 147.1 (*C*-3a or *C*-7a), 154.1 (*C*-3a or *C*-7a), 203.2 (*C*(O)CH$_3$). — ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = −53.6, −12.91, −12.88. — EI-MS: *m/z* (%) 320 (34) [M$^+$], 305 (21) [M$^+$ − CH$_3$], 291 (25) [M$^+$ − CH$_2$CH$_3$], 73 (100). Odour description: very weak, slightly stronger than compound **8**, with a slightly powdery, creamy-lactonic impression and some slightly hay-like, coumarinic aspects reminiscent of tonka beans and tobacco. In the powdery shade, some underlying musk effects can be recognized, albeit not very apparent. Odour threshold: 750 ng L^{-1} air.

$C_{16}H_{28}OSi_3$ (320.65)	Calculated:	C 59.93	H 8.80
	Found:	C 59.7	H 8.7

*2-(1,1,2,2,3,3,6-Heptamethyl-1,2,3-trisilaindan-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**).*

A solution of iodine in acetonitrile (0.01 M, 40.0 mL, 400 μmol of iodine) was added to zinc powder (256 mg, 3.92 mmol) in a single portion at 20 °C. The mixture was then stirred at this temperature until the brown colouration disappeared and a grey suspension was observed. Compound **27** (4.48 g, 20.0 mmol), compound **30** (4.64 g, 27.9 mmol) and a solution of cobalt(II) iodide in acetonitrile (0.1 M, 10.0 mL 1.00 mmol of CoI$_2$) were then added sequentially in single portions. The resulting dark brown solution was stirred at 20 °C for 30 min, whereupon GC analysis indicated complete consumption of the starting materials. The reaction mixture was then passed through a short silica gel column (eluent, *n*-hexane/ethyl acetate (80:20 (v/v)). The brown residue resulting following removal of the solvent was purified by flash column chromatography (silica gel; eluent, *n*-hexane/ethyl acetate (96:4 (v/v))). The relevant fractions (GC analysis) were combined and concentrated under reduced pressure to give a yellow oil. This was crystallised from methanol (−30 °C), followed by recrystallisation, once from methanol (−30 °C) and twice from *n*-hexane (20 °C), to afford **10** as a colourless crystalline solid in 25% yield (1.94 g, 4.97 mmol); mp 287 °C (decomp.). — ^{1}H NMR (500.1 MHz, CDCl$_3$): δ = 0.26 (s, 6 H, SiCH_3), 0.30 (s, 6 H, SiCH_3), 0.33 (s, 6 H, SiCH_3), 1.33 (s, 12 H, C(CH_3)$_2$), 2.54 (s, 3 H, CCH_3), 7.37 (s, 1 H, *H*-4), 7.97 (s, 1 H, *H*-7). — ^{11}B NMR (160.5 MHz, CDCl$_3$): δ = 30.6. — ^{13}C NMR

(125.8 MHz, $CDCl_3$): δ −8.2 (Si*C*H_3), −1.9 (Si*C*H_3), −1.6 (Si*C*H_3), 22.6 (C*C*H_3), 25.0 (C(*C*H_3)$_2$), 83.4 (*C*(CH$_3$)$_2$), 14.7 (*C*-4), 140.6 (*C*-7), 144.5 (*C*-3a or *C*-7a), 145.7 (*C*-3a or *C*-7a), 154.1 (*C*-6), *C*-5 not detected. — ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ = −53.3, −13.5, −13.3. — EI-MS: *m/z* (%) 390 (84) [M^+], 375 (48) [$M^+ - CH_3$], 73 (100).

$C_{19}H_{35}BSi_3O_2$ (390.55)	Calculated:	C 58.43	H 9.03
	Found:	C 58.7	H 8.7

*4-(5,5,8,8-Tetramethyl-5,6,7,8-tetrahydronaphthalen-2-ylethynyl)benzoic acid (**14a**, EC23).*
This compound was generously donated by Reinnervate Ltd. (for synthesis see ref 14a).

*4-(1,1,4,4-Tetramethyl-1,2,3,4-tetrahydro-1,4-disilanaphthalen-6-ylethynyl)benzoic acid (**14b**, disila-EC23).*

A mixture of **42** (144 mg, 380 μmol), potassium hydroxide (213 mg, 3.80 mmol) and methanol/water (3:1 (v/v), 8 mL) was heated under reflux for 6 h. Hydrochloric acid (4 M, 10 mL) was then added to the reaction mixture, followed by ethyl acetate (60 mL). Separation of the organic layer, drying over sodium sulphate, filtration and concentration under reduced pressure gave a white powder, which was crystallised from acetonitrile (cooling of a boiling solution to 20 °C) to afford **14b** in 76% yield (105 mg, 288 μmol) as a colourless crystalline solid. — ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 0.24 (s, 6 H, Si(CH_3)$_2$), 0.26 (s, 6 H, Si(CH_3)$_2$), 1.04 (s, 4 H, SiCH_2C), 7.50 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^4J_{H\text{-}H}$ = 1.5 Hz, *H*-7, THN), 7.52 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^5J_{H\text{-}H}$ = 1.0 Hz, *H*-8, THN), 7.66 (m, 2 H, *H*-3/*H*-5, Benz), 7.68 (m, 1 H, *H*-5, THN) 8.10 ppm (m, 2 H, *H*-2/*H*-6, Benz), COO*H* not observed. — ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = –1.64 (Si(*C*H_3)$_2$), –1.59 (Si(*C*H_3)$_2$), 7.58 (Si*C*H_2C), 7.62 (Si*C*H_2C), 89.0 (THN-C≡*C*), 93.6 (THN-*C*≡C), 122.4 (*C*-6, THN), 128.7 (*C*-1, Benz), 129.3 (*C*-4, Benz), 130.4 (*C*-2/*C*-6, Benz), 131.0 (*C*-7, THN), 132.0 (*C*-3/*C*-5, Benz), 133.7 (*C*-8, THN), 136.6 (*C*-5, THN), 146.6 (*C*-4a or C-8a, THN), 147.6 (*C*-4a or C-8a, THN), 170.7 ppm (*C*OOH). — ^{29}Si NMR (99.4 MHz, CD_2Cl_2): δ = –6.6, –6.5 ppm. — EI-MS: *m/z* (%) 364 (30) [M^+], 349 (29) [$M^+ - CH_3$], 73 (100).

$C_{21}H_{24}O_2Si_2$ (364.59)	Calculated:	363.12421 $[M - H]^-$
	Found:	363.12398 $[M - H]^-$

*6-(5,5,8,8-Tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-2-naphthoic acid (**15a**, TTNN).*
This compound was kindly provided by Prof. Todd Marder (Universität Würzburg); for synthesis see ref 16.

*6-(1,1,4,4-Tetramethyl-1,2,3,4-tetrahydro-1,4-disilanaphthalen-6-yl)-2-naphthoic acid (**15b**, disila-TTNN).*

A mixture of **52** (172 mg, 425 μmol), potassium hydroxide (238 mg, 4.24 mmol) and methanol/water (3:1 (v/v), 8.5 mL) was heated under reflux for 1 h. Hydrochloric acid (4 M, 10 mL) was then added to the reaction mixture, followed by dichloromethane (25 mL). The organic layer was separated, dried over magnesium sulphate, filtered and allowed to slowly evaporate (20 °C) to give pale yellow crystals. These were washed with acetone (2 mL) and dried under reduced pressure (20 °C, 0.03 mbar) to afford **15b** in 67% yield (111 mg, 284 μmol) as a colourless crystalline solid. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 0.25 (s, 6 H, Si(C*H*$_3$)$_2$), 0.27 (s, 6 H, Si(C*H*$_3$)$_2$), 1.00 (s, 4 H, SiC*H*$_2$C), 7.64 (d, 1 H, $^{3}J_{\text{H-H}}$ = 7.5 Hz, *H*-8, THN), 7.77 (dd, 1 H, $^{3}J_{\text{H-H}}$ = 7.5 Hz, $^{4}J_{\text{H-H}}$ = 2.0 Hz, *H*-7, THN), 7.90 (m, 1 H, *H*-5, THN), 7.92 (m, 1 H, *H*-7, Naph), 8.00 (m, 1 H, *H*-3, Naph), 8.09 (m, 1 H, *H*-4, Naph), 8.20 (m, 1 H, *H*-8, Naph), 8.29 (m, 1 H, *H*-5, Naph), 8.62 (m, 1 H, *H*-1, Naph), 13.08 (s, 1 H, COO*H*). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = –1.53 (Si(*C*H$_3$)$_2$), –1.51 (Si(*C*H$_3$)$_2$), 7.0 (Si*C*H$_2$C), 7.1 (Si*C*H$_2$C), 125.1 (*C*-5, Naph), 125.6 (*C*-3, Naph), 126.1 (*C*-7, Naph), 127.0 (*C*-7, THN) 128.0 (*C*-2, Naph), 128.6 (*C*-4, Naph), 130.0 (*C*-8, Naph), 130.3 (*C*-1, Naph), 131.4 (*C*-8a, Naph), 131.8 (*C*-5, THN), 134.1 (*C*-8, THN), 135.3 (*C*-4a, Naph), 139.1 (*C*-6, THN), 140.0 (*C*-6, Naph), 144.7 (*C*-8a, THN), 146.1 (*C*-4a, THN), 167.4 (*C*OOH). — ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = –6.9, –6.6. — EI-MS: *m/z* (%) 390 (64) [M$^+$], 375 (72) [M$^+$ − CH$_3$], 73 (100).

$C_{23}H_{26}O_2Si_2$ (390.63)	Calculated:	391.15441 $[M + H]^+$
	Found:	391.15431 $[M + H]^+$

*4-(1,1,3,3-Tetramethylindan-5-ylethynyl)benzoic acid (**16a**).*

A mixture of **43** (264 mg, 794 μmol), potassium hydroxide (446 mg, 7.95 mmol) and methanol/water (3:1 (v/v), 20 mL) was heated under reflux for 2 h. The reaction mixture was then concentrated under reduced pressure to approximately one quarter of the original volume and ethyl acetate (30 mL) was added. Separation of the organic phase, washing with hydrochloric acid (1 M, 30 mL), drying over sodium sulphate, filtration and concentration under reduced pressure gave a white powder. The product was dissolved in diethyl ether/acetonitrile (1:1 (v/v), 30 mL) and the solvents were allowed to slowly evaporate until approximately 5 mL of liquid remained. The remaining solvent was removed by decantation, and the crystals were dried under reduced pressure (20 °C, 0.01 mbar) to afford **16a** in 90% yield (228 mg, 716 μmol) as a colourless crystalline solid. — ^{1}H NMR (500.1 MHz,

[D$_6$]DMSO): δ = 1.26 (s, 6 H, C(CH_3)$_2$), 1.28 (s, 6 H, C(CH_3)$_2$), 1.88 (s, 2 H, CCH_2C), 7.22 (d, 1 H, $^3J_{H\text{-}H}$ = 8.5 Hz, *H*-7, Ind), 7.39–7.40 (m, 2 H, *H*-4 and *H*-6, Ind), 7.65 (m, 2 H, *H*-3/*H*-5, Benz), 7.95 (m, 2 H, *H*-2/*H*-6, Benz), 13.11 (br. s, 1 H, COO*H*). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 31.0 (C(CH_3)$_2$), 31.1 (C(CH_3)$_2$), 42.2 (*C*-1 or *C*-3, Ind), 42.4 (*C*-1 or *C*-3, Ind), 55.8 (C*C*H$_2$C), 87.7 (Ind-C≡*C*), 92.8 (Ind-*C*≡C), 120.0 (*C*-5, Ind), 123.0 (*C*-7, Ind), 125.8 (*C*-4, Ind), 126.9 (*C*-4, Benz), 129.5 (*C*-2/*C*-6, Benz), 130.3 (*C*-1, Benz), 130.4 (*C*-6, Ind), 131.4 (*C*-3/*C*-5, Benz), 151.4 (*C*-3a, Ind), 152.3 (*C*-7a, Ind), 166.6 (*C*OOH). — EI-MS: *m/z* (%) 318 (44) [M$^+$], 303 (100) [M$^+$ − CH$_3$].

$C_{22}H_{22}O_2$ (318.42)	Calculated:	317.15470 [M − H]$^-$
	Found:	317.15484 [M − H]$^-$

*4-(1,1,3,3-Tetramethyl-1,3-disilaindan-5-ylethynyl)benzoic acid (**16b**).*

A mixture of **44** (82.0 mg, 224 μmol), potassium hydroxide (126 mg, 2.25 mmol) and methanol/water (3:1 (v/v), 5 mL) was heated under reflux for 2 h. Subsequently, ethyl acetate (20 mL) and hydrochloric acid (4 M, 10 mL) were added. Separation of the organic phase, drying over sodium sulphate, filtration and concentration under reduced pressure gave a white powder. The product was crystallised from acetonitrile (cooling of a boiling solution to 20 °C) to afford **16b** in 96% yield (75.0 mg, 214 μmol) as a colourless crystalline solid. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = –0.02 (s, 2 H, SiCH_2Si), 0.27 (s, 6 H, Si(CH_3)$_2$), 0.29 (s, 6 H, Si(CH_3)$_2$), 7.54 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^4J_{H\text{-}H}$ = 1.5 Hz, *H*-6, Ind'), 7.63–7.67 (m, 3 H, *H*-7 (Ind') and *H*-3/*H*-5 (Benz)), 7.78 (m, 1 H, *H*-4, Ind'), 7.96 (m, 2 H *H*-2/*H*-6, Benz), 13.14 (br. s, 1 H, COO*H*). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = –2.9 (Si*C*H$_2$Si), 0.36 (Si(*C*H$_3$)$_2$), 0.37 (Si(*C*H$_3$)$_2$), 89.0 (Ind'-C≡*C*), 92.5 (Ind'-*C*≡C), 122.0 (*C*-5, Ind'), 126.6 (*C*-4, Benz), 129.6 (*C*-2/*C*-6, Benz), 130.5 (*C*-1, Benz), 131.2 (*C*-6, Ind'), 131.5 (*C*-3/*C*-5, Benz), 131.9 (*C*-7, Ind'), 134.5 (*C*-4, Ind'), 150.5 (*C*-3a, Ind'), 151.3 (*C*-7a, Ind'), 166.6 (*C*OOH). — ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = 9.2, 9.4 . — EI-MS: *m/z* (%) 350 (42) [M$^+$], 335 (100) [M$^+$ − CH$_3$].

$C_{20}H_{22}O_2Si_2$ (350.56)	Calculated:	349.10856 [M − H]$^-$
	Found:	349.10841 [M − H]$^-$

*4-(1,1,3,3-Tetramethyl-2-oxa-1,3-disilaindan-5-ylethynyl)benzoic acid (**17**).*

Compound **41** (72.0 mg, 493 μmol), compound **40** (150 mg, 449 μmol), Pd(PPh$_3$)$_2$Cl$_2$[60] (3.15 mg, 4.49 μmol) and copper(I) iodide (855 μg, 4.49 μmol) were dissolved in triethylamine (10 mL) at 20 °C. The reaction mixture was stirred at this temperature for 2 d,

whereupon GC analysis indicated complete consumption of the starting materials. The solvent was then removed under reduced pressure, and the residue was dissolved in a mixture of tetrahydrofuran (20 mL) and water (10 mL). Acetic acid was added to this mixture until it reached pH 6 (pH paper test), followed by addition of dichloromethane (20 mL) and water (20 mL). The aqueous layer was separated, washed with dichloromethane (2 × 20 mL) and discarded. Drying of the combined organic extracts over magnesium sulphate, filtration and concentration under reduced pressure gave a brown solid. Purification of the crude product by flash column chromatography (eluent, dichloromethane/methanol (99:1 (v/v))), followed by crystallisation from tetrahydro-furan/acetonitrile (1:2 (v/v); slow evaporation of the solvents at 20 °C), afforded **17** in 67% yield (106 mg, 301 μmol) as a colourless crystalline solid. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 0.32 (s, 6 H, Si(CH_3)$_2$), 0.33 (s, 6 H, Si(CH_3)$_2$), 7.60 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{4}J_{H\text{-}H}$ = 2.0 Hz, *H*-6, Ind''), 7.66 (m, 2 H, *H*-3/*H*-5, Benz), 7.72 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{5}J_{H\text{-}H}$ = 1.0 Hz, *H*-7, Ind''), 7.90 (m, 1 H, *H*-4, Ind''), 7.97 (m, 2 H, *H*-2/*H*-6, Benz), 12.94 (br. s, 1 H, COO*H*). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 0.88 (Si(*C*H$_3$)$_2$), 0.89 (Si(*C*H$_3$)$_2$), 89.2 (Ind''-C≡*C*), 92.3 (Ind''-*C*≡C), 122.4 (*C*-5, Ind''), 126.5 (*C*-4, Benz), 129.6 (*C*-1 and *C*-2/*C*-6, Benz), 131.3 (*C*-7, Ind''), 131.5 (*C*-3/*C*-5, Benz), 131.6 (*C*-6, Ind''), 134.0 (*C*-4, Ind''), 148.2 (*C*-3a, Ind''), 148.8 (*C*-7a, Ind''), 166.7 (*C*OOH). — ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = 14.90, 14.93 . — EI-MS: *m/z* (%) 352 (40) [M$^+$], 337 (100) [M$^+$ − CH$_3$].

$C_{19}H_{20}O_3Si_2$ (352.54) Calculated: 351.08782 [M − H]$^-$

Found: 351.08791 [M − H]$^-$

*6-(1,1,3,3-Tetramethylindan-5-yl)-2-naphthoic acid (**18a**).*

A mixture of **53** (122 mg, 340 μmol), potassium hydroxide (191 mg, 3.40 mmol) and methanol/water (3:1 (v/v), 17 mL) was heated under reflux for 7 h. Hydrochloric acid (4 M, 10 mL) was then added to the reaction mixture, followed by ethyl acetate (60 mL). The organic layer was separated, dried over magnesium sulphate, filtered and concentrated under reduced pressure to yield a fine, white powder. This product was dissolved in dichloromethane (15 mL) and the solvents were allowed to slowly evaporate (20 °C) until approximately 3 mL of liquid remained. The remaining solvent was decanted to afford **18a** in 72% yield (84.0 mg, 244 μmol) as a colourless crystalline solid. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 1.31 (s, 6 H, C(CH_3)$_2$), 1.35 (s, 6 H, C(CH_3)$_2$), 1.93 (s, 2 H, CCH_2C), 7.29 (d, 1 H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, *H*-7, Ind), 7.61–7.65 (m, 2 H, *H*-4 and *H*-6, Ind), 7.92 (m, 1 H, *H*-7, Naph), 7.98 (m, 1 H, *H*-3, Naph), 8.06 (m, 1 H, *H*-4, Naph), 8.17 (m, 1 H, *H*-8, Naph), 8.26

(m, 1 H, *H*-5, Naph), 8.61 (m, 1 H, *H*-1, Naph), 13.04 (s, 1 H, COO*H*). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 31.3 (C(*C*H$_3$)$_2$), 31.4 (C(*C*H$_3$)$_2$), 42.0 (*C*-1 or *C*-3, Ind), 42.3 (*C*-1 or *C*-3, Ind), 56.3 (C*C*H$_2$C), 121.3 (*C*-4, Ind), 123.0 (*C*-7, Ind) 124.8 (*C*-5, Naph), 125.5 (*C*-3, Naph), 126.1 (*C*-6, Ind), 126.2 (*C*-7, Naph), 127.8 (*C*-2, Naph), 128.4 (*C*-4, Naph), 129.8 (*C*-8, Naph), 130.3 (*C*-1, Naph), 131.2 (*C*-8a, Naph), 135.4 (*C*-4a, Naph), 138.4 (*C*-5, Ind), 140.4 (*C*-6, Naph), 150.7 (*C*-7a, Ind), 151.7 (*C*-3a, Ind), 167.4 (*C*OOH). — EI-MS: *m/z* (%) 344 (46) [M$^+$], 329 (100) [M$^+$ − CH$_3$].

$C_{24}H_{24}O_2$ (344.45)	Calculated:	345.18491 $[M + H]^+$
	Found:	345.18503 $[M + H]^+$

*6-(1,1,3,3-Tetramethyl-1,3-disilaindan-5-yl)-2-naphthoic acid (**18b**).*

A mixture of **54** (85.0 mg, 218 μmol), potassium hydroxide (122 mg, 2.17 mmol) and methanol/tetrahydrofuran/water (3:2:1 (v/v), 15 mL) was heated under reflux for 4 h. Dichloromethane (20 mL) and hydrochloric acid (4 M, 10 mL) were then added sequentially to the reaction mixture. The aqueous phase was separated and extracted with dichloromethane (2 × 20 mL). Combination of the organic phases, drying over magnesium sulphate, filtration and concentration to approximately one third of the original volume under reduced pressure gave a colourless solution. The remaining solvent was then allowed to slowly evaporate (20 °C), and the resulting crystals were washed with acetone (5 mL)[†] and dried under reduced pressure (20 °C, 0.03 mbar) to afford **18b** in 96% yield (79.0 mg, 210 μmol) as a colourless crystalline solid. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 0.00 (s, 2 H, SiC*H*$_2$Si), 0.30 (s, 6 H, Si(C*H*$_3$)$_2$), 0.34 (s, 6 H, Si(C*H*$_3$)$_2$), 7.71 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^5J_{H\text{-}H}$ = 1.0 Hz, *H*-7, Ind'), 7.81 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^4J_{H\text{-}H}$ = 2.0 Hz, *H*-6, Ind'), 7.94 (m, 1 H, *H*-7, Naph), 8.00 (m, 1 H, *H*-3, Naph), 8.02 (m, 1 H, *H*-4, Ind'), 8.10 (m, 1 H, *H*-4, Naph), 8.20 (m, 1 H, *H*-8, Naph), 8.31 (m, 1 H, *H*-5, Naph), 8.62 (m, 1 H, *H*-1, Naph) 13.07 (s, 1 H, COO*H*). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = –2.6 (Si*C*H$_2$Si), 0.56 (Si(*C*H$_3$)$_2$), 0.60 (Si(*C*H$_3$)$_2$), 125.2 (*C*-5, Naph), 125.6 (*C*-3, Naph), 126.2 (*C*-7, Naph), 127.6 (*C*-6, Ind'), 128.0 (*C*-2, Naph), 128.5 (*C*-4, Naph), 129.9 (*C*-8, Naph), 130.26 (*C*-1, Naph, or *C*-4, Ind') 130.7 (*C*-1, Naph, or *C*-4, Ind'), 131.4 (*C*-8a, Naph), 132.4 (*C*-7, Ind'), 135.3 (*C*-4a, Naph), 139.8 (*C*-5, Ind'), 140.2 (*C*-6, Naph), 149.5 (*C*-7a, Ind'), 150.9 (*C*-3a, Ind') 167.4 (*C*OOH). — ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = 8.6, 9.0. — EI-MS: *m/z* (%) 376 (42) [M$^+$], 361 (100) [M$^+$ − CH$_3$].

[†]Storage of this wash solution at –35 °C for a period of seven months yielded a single crystal of **18b** suitable for X-ray diffraction studies.

$C_{22}H_{24}O_2Si_2$ (376.60) Calculated: 377.13876 $[M + H]^+$

Found: 377.13912 $[M + H]^+$

*rac-1-(1,1,2,2,3,3,6-Heptamethyl-1,2,3-trisilaindan-5-yl)ethanol (**26**).*

A solution of iodine in acetonitrile (0.01 M, 10.0 mL, 100 μmol of iodine) was added to zinc powder (64.0 mg, 979 μmol) in a single portion at 20 °C. The mixture was then stirred at this temperature until the brown colouration disappeared and a grey suspension was observed. Compound **27** (1.12 g, 4.99 mmol), compound **31** (587 mg, 6.98 mmol), and a solution of cobalt(II) iodide in acetonitrile (0.1 M, 2.50 mL, 250 μmol of CoI_2) were then added sequentially in single portions. The resulting dark brown solution was stirred at 20 °C for 30 min, whereupon GC analysis indicated complete consumption of the starting materials. Removal of the solvent under reduced pressure resulted in a dark green-black solid. This residue was purified by flash column chromatography (silica gel; eluent, *n*-hexane/ethyl acetate (90:10 (v/v)). The relevant fractions (GC analysis) were combined and concentrated under reduced pressure to yield an off-white solid. This was recrystallised from *n*-hexane (−30 °C) to afford **26** as a fine, colourless, microcrystalline powder in 24% yield (371 mg, 1.20 mmol); mp 108−109 °C. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 0.22 (s, 3 H, SiCH_3), 0.23 (s, 3 H, SiCH_3), 0.25 (s, 3 H, SiCH_3), 0.26 (s, 3 H, SiCH_3), 0.270 (s, 3 H, SiCH_3), 0.272 (s, 3 H, SiCH_3), 1.28 (d, 3 H, $^3J_{H\text{-}H}$ = 6.4 Hz, CH(OH)CH_3), 2.27 (s, 3 H, CCH_3), 4.86−4.91 (m, 1 H, C*H*(OH)CH$_3$), 5.00 (d, 1 H, $^3J_{H\text{-}H}$ = 4.0 Hz, O*H*), 7.29 (s, 1 H, *H*-7), 7.66 (s, 1 H, *H*-4). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = −8.40 (Si*C*H$_3$), –8.38 (Si(*C*H$_3$)$_2$), −1.8 (Si(*C*H$_3$)$_2$), −1.69 (Si(*C*H$_3$)$_2$), –1.65 (2 C, Si*C*H$_3$), 18.7 (C*C*H$_3$), 24.5 (CH(OH)*C*H$_3$), 65.1 (*C*H(OH)CH$_3$), 129.2 (*C*-4), 133.9 (*C*-6), 134.6 (*C*-7), 145.3 (*C*-5), 146.5 (*C*-3a or *C*-7a), 147.3 (*C*-3a or *C*-7a). — ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = −53.6, −14.0, −13.9. — EI-MS: *m/z* (%) 308 (37) [M^+], 293 (11) [$M^+ - CH_3$], 73 (100).

$C_{15}H_{28}OSi_3$ (308.64) Calculated: C 58.37 H 9.14

Found: C 58.4 H 9.0

*1,3-Diethynylhexamethyltrisilane (**27**).*

This compound was synthesised from **29** according to ref 61.

*Pent-3-yne-2-one (**28**).*

This compound was synthesised according to ref 62.

*Hex-3-yne-2-one (**29**).*

This compound was commercially available (ABCR). It was distilled prior to use and stored under argon.

*4,4,5,5-Tetramethyl-2-prop-1-ynyl-1,3,2-dioxaborolane (**30**).*

This compound was synthesised according to ref 33b.

*rac-Pent-3-yne-2-ol (**31**).*

This compound was synthesised according to ref 63.

*Hexamethyldisilane (**32**).*

This compound was commercially available (ABCR) and was used as received.

*Chloropentamethyldisilane (**33**).*

A mixture of compound **32** (99.7 g, 681 mmol), chlorotrimethylsilane (81.8 g, 753 mmol) and aluminium trichloride (1.82 g, 13.6 mmol) was heated such as to distill off the accruing tetramethylsilane (bp 28 °C, 1 bar) fractionating using a spinning band column. When the rate of formation of the dichlorinated side product (dichlorotetramethyldisilane), as observed by GC, exceeded the rate of consumption of **32**, dry acetone (5.00 mL) was added to deactivate the aluminium trichloride. The distillation was continued to remove the remaining tetramethylsilane and chlorotrimethylsilane (bp 57−58 °C, 1 bar). Vacuum distillation of the remaining liquid over a spinning band column afforded **33** in 67% yield (76.0 g, 456 mmol) as a colourless liquid; bp 76−77 °C, 170 mbar. — ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.16 (s, 9 H, $Si(CH_3)_3$), 0.47 (s, 6 H, $Si(CH_3)_2Cl$). — ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = −2.9 ($Si(CH_3)_3$), 2.2 ($Si(CH_3)_2Cl$). — ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ = −18.2, 23.9. — EI-MS: *m/z* (%) 166 (23) [M^+], 151 (27) [$M^+ - CH_3$], 131 (35) [$M^+ - Cl$], 73 (100). ^{1}H NMR data were in good agreement with those reported in ref 64.

$C_5H_{15}ClSi_2$ (166.80)	Calculated:	C 36.00	H 9.06
	Found:	C 35.4	H 9.0

*Octamethyltrisilane (**34**).*

This compound was synthesised from **27** according to ref 65.

*1,3-Dichlorohexamethyltrisilane (**35**).*

This compound was synthesised from **28** according to ref 66.

*1-(1,1,3,3,4,4,6-Heptamethyl-1,3,4-trisilaisochroman-7-yl)ethanone (**36a**) and 1-(1,1,3,3,4,4,7-heptamethyl-1,3,4-trisilaisochroman-6-yl)ethanone (**36b**).*

A single aliquot of **26** (300 mg, 972 μmol) as a solution in dichloromethane (5 mL) was added to a stirred solution of the Dess–Martin periodinane[34] in dichloromethane (0.1 M, 11.6 mL, 1.16 mmol) at 20 °C. Stirring was continued for 2.5 h, whereupon GC analysis indicated complete consumption of **26**. An aqueous solution of sodium hydroxide (1.0 M, 5.00 mL, 5.00 mmol) and diethyl ether (20 mL) were added sequentially, and the reaction mixture was stirred at 20 °C for a further 15 min. The aqueous layer was separated, extracted with diethyl ether (2 × 20 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulphate and passed through a short silica gel column (eluent, *n*-hexane/ethyl acetate (10:90 (v/v)). The solvent was removed under reduced pressure, and the resultant yellow oily residue was purified by RP-MPLC (eluent, methanol/water (90:10 (v/v)); flow rate, 23 mL min^{-1}; detector wavelength, 240 nm) to yield a very viscous colourless oil, which solidified on standing, to afford **36** in 48% yield as a colourless waxy solid (152 mg, 471 μmol; molar ratio **36a**:**36b**, 1:0.85). — NMR data for **36a**: ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.29 (s, 6 H, SiSi(CH_3)$_2$O), 0.32 (s, 6 H, CSi(CH_3)$_2$Si), 0.34 (s, 6 H, CSi(CH_3)$_2$O), 2.51 (s, 3 H, CCH_3), 2.56 (s, 3 H, C(O)CH_3), 7.44 (s, 1 H, *H*-5), 7.68 (s, 1 H, *H*-8). — ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = −2.6 (CSi(*C*H$_3$)$_2$Si), 1.99 (SiSi(*C*H$_3$)$_2$O), 2.02 (CSi(*C*H$_3$)$_2$O), 21.5 (C*C*H$_3$), 29.5 (C(O)*C*H$_3$), 133.2 (*C*-8), 137.2 (*C*-8a), 137.4 (*C*-4a), 137.6 (*C*-5), 143.7 (*C*-7), 150.6 (*C*-6), 202.2 (*C*(O)CH$_3$). — ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ = −33.2 (C*Si*Si), 1.1 (C*Si*O), 8.9 (Si*Si*O). — NMR data for **36b**: ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.29 (s, 6 H, SiSi(CH_3)$_2$O), 0.33 (s, 12 H, CSi(CH_3)$_2$Si and CSi(CH_3)$_2$O), 2.49 (s, 3 H, CCH_3), 2.58 (s, 3 H, C(O)CH_3), 7.28 (s, 1 H, *H*-8), 7.82 (s, 1 H, *H*-5). — ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = −2.3 (CSi(*C*H$_3$)$_2$Si), 1.9 (CSi(*C*H$_3$)$_2$O), 1.98 (SiSi(*C*H$_3$)$_2$O), 21.5 (C*C*H$_3$), 29.6 (C(O)*C*H$_3$), 134.0 (*C*-5), 136.8 (*C*-8), 136.9 (*C*-8a), 137.8 (*C*-4a), 142.8 (*C*-6), 151.0 (*C*-7), 202.3 (*C*(O)CH$_3$). — ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ = −33.4 (C*Si*Si), 1.0 (C*Si*O), 9.0 (Si*Si*O). — EI-MS (mixture of **36a** and **36b**): *m/z* (%) 322 (10) [M^+], 307 (100) [$M^+ - CH_3$].

$C_{15}H_{26}O_2Si_3$ (322.63)	Calculated:	C 55.84	H 8.12
	Found:	C 55.7	H 8.1

*6-Iodo-1,1,4,4-tetramethyl-1,2,3,4-tetrahydro-1,4-disilanaphthalene (**37**).*

A solution of **63** (1.07 g, 4.54 mmol) and isoamylnitrite (1.06 g, 9.07 mmol) in diiodomethane (5.0 mL) was stirred at 20 °C for 20 h. The excess diiodomethane was removed via bulb-to-bulb distillation (40 °C, 1.5 mbar) and discarded. The crude product was purified by further bulb-to-bulb distillation (100–130 °C, 0.05 mbar), followed by RP-MPLC (eluent, methanol/water (95:05 (v/v)); flow rate, 25 mL min^{-1}; detector wavelength, 240 nm), to give a pale yellow oil. This was passed through a short silica gel column (eluent, *n*-hexane) to afford **37** in 33% yield (527 mg, 1.52 mmol) as a colourless oil. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = –0.17 (s, 6 H, Si(CH_3)$_2$), –0.19 (s, 6 H, Si(CH_3)$_2$), 0.94 (s, 4 H, SiCH_2C), 7.28 (d, 1 H, $^3J_{H\text{-}H}$ = 8.0 Hz, *H*-8), 7.69 (dd, 1 H, $^3J_{H\text{-}H}$ = 8.0 Hz, $^4J_{H\text{-}H}$ = 2.0 Hz, *H*-7), 7.78 (d, 1 H, $^3J_{H\text{-}H}$ = 2.0 Hz, *H*-5). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = –1.77 (Si(*C*H$_3$)$_2$), –1.75 (Si(*C*H$_3$)$_2$), 6.71 (Si*C*H$_2$C), 6.73 (Si*C*H$_2$C), 97.1 (*C*-6), 135.5 (*C*-8), 136.7 (*C*-7), 141.2 (*C*-5), 144.2 (*C*-8a), 148.7 (*C*-4a). — ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = –6.5, –6.4. — EI-MS: *m/z* (%) 346 (38) [M^+], 331 (100) [$M^+ - CH_3$].

$C_{12}H_{19}ISi_2$ (346.36)	Calculated:	C 41.61	H 5.53
	Found:	C 42.2	H 5.6

*5-Iodo-1,1,3,3-tetramethylindane (**38**).*

Glacial acetic acid (15.0 mL), concentrated sulphuric acid (98%, 0.8 mL) and water (3.0 mL) were added to a mixture of **73** (3.00 g, 17.2 mmol), orthoperiodic acid (785 mg, 3.44 mmol) and iodine (1.75 g, 6.89 mmol of I_2). This mixture was stirred at 70 °C for 10 h and then allowed to cool to 20 °C, whereupon it was diluted with water (20 mL). Extraction of the mixture with *n*-hexane (2 × 20 mL), followed by washing of the combined extracts first with an aqueous sodium thiosulphate solution (1 M, 40 mL) and then with an aqueous sodium hydroxide solution (1 M, 40 mL), drying of the combined organic phases (magnesium sulphate), filtration and removal of the solvent under reduced pressure yielded a yellow liquid. This was distilled under reduced pressure to afford **38** in 64% yield (3.30 g, 11.0 mmol) as a colourless liquid; bp 63 °C (0.16 mbar). — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 1.23 (s, 6 H, C(CH_3)$_2$), 1.24 (s, 6 H, C(CH_3)$_2$), 1.82 (s, 2 H, CCH_2C), 6.98 (d, 1 H, $^3J_{H\text{-}H}$ = 8.3 Hz, *H*-7), 7.49 (m, 2 H, *H*-4 and *H*-6). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 31.0 (C(*C*H$_3$)$_2$), 31.1 (C(*C*H$_3$)$_2$), 42.0 (*C*-1), 42.2 (*C*-3), 55.8 (C*C*H$_2$C), 92.3 (*C*-5), 125.0 (*C*-7), 131.3 (*C*-4 or *C*-6), 135.4 (*C*-4 or *C*-6), 150.6 (*C*-7a), 153.7 (*C*-3a). — EI-MS: *m/z* (%) 300 (36) [M^+], 285 (100) [$M^+ - CH_3$].

$C_{13}H_{17}I$ (300.18)	Calculated:	300.03695 [M^+]
	Found:	300.03683 [M^+]

*5-Iodo-1,1,3,3-tetramethyl-1,3-disilaindane (**39**).*

A solution of **64** (822 mg, 3.71 mmol) and isoamylnitrite (870 mg, 7.43 mmol) in diiodomethane (3.7 mL) was stirred at 20 °C for 22 h. The excess diiodomethane was removed via bulb-to-bulb distillation (46 °C, 1.0 mbar) and discarded. The crude product was purified by further bulb-to-bulb distillation (100–124 °C, 0.1 mbar), followed by RP-MPLC (eluent, methanol/water (95:05 (v/v)); flow rate, 22 mL min^{-1}; detector wavelength, 250 nm), to afford **39** in 30% yield (364 mg, 1.10 mmol) as a colourless oil. — ^{1}H NMR (500.1 MHz, [D_6]DMSO): δ = –0.06 (s, 2 H, SiCH_2Si), 0.23 (s, 6 H, Si(CH_3)$_2$), 0.25 (s, 6 H, Si(CH_3)$_2$), 7.36 (d, 1 H, $^3J_{H\text{-}H}$ = 8.0 Hz, *H*-7), 7.69 (dd, 1 H, $^3J_{H\text{-}H}$ = 8.0 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz, *H*-6), 7.92 (d, 1 H, $^4J_{H\text{-}H}$ = 1.8 Hz, *H*-4). — ^{13}C NMR (125.8 MHz, [D_6]DMSO): δ = –3.0 (Si*C*H$_2$Si), 0.34 (Si(*C*H$_3$)$_2$), 0.36 (Si(*C*H$_3$)$_2$), 97.9 (*C*-5), 133.8 (*C*-7), 137.0 (*C*-6), 140.0 (*C*-4), 149.0 (*C*-3a), 153.5 (*C*-7a). — ^{29}Si NMR (99.4 MHz, [D_6]DMSO): δ = 9.2, 9.3. — EI-MS: *m/z* 332 (20) [M^+], 317 (100) [$M^+ - CH_3$].

$C_{11}H_{17}ISi_2$ (332.33)	Calculated:	C 39.76	H 5.16
	Found:	C 39.9	H 5.2

*5-Iodo-1,1,3,3-tetramethyl-2-oxa-1,3-disilaindane (**40**).*

A solution of **65** (1.72 g, 6.13 mmol) in tetrachloromethane (2 mL) was added in one smooth injection to a stirred solution of iodine monochloride (1.10 g, 6.78 mmol) in tetrachloromethane (6 mL) at 0 °C. The reaction mixture was stirred at this temperature for 10 min, diluted with diethyl ether (15 mL), washed with an aqueous sodium thiosulphate solution (20 mL) and concentrated under reduced pressure. The resulting yellow oil was purified by RP-MPLC (eluent, methanol/water (90:10 (v/v)); flow rate, 20 mL min^{-1}; detector wavelength, 240 nm), followed by bulb-to-bulb distillation (40 °C, 0.03 mbar), to afford **40** in 36% yield (736 mg, 2.20 mmol) as a colourless crystalline solid; mp 75−76 °C. — ^{1}H NMR (400.1 MHz, [D_6]DMSO): δ = 0.29 (s, 6 H, Si(CH_3)$_2$), 0.31 (s, 6 H, Si(CH_3)$_2$), 7.46 (d, 1 H, $^3J_{H\text{-}H}$ = 7.7 Hz, *H*-7), 7.77 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.7 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz, *H*-6), 8.06 (d, 1 H, $^4J_{H\text{-}H}$ = 1.6 Hz, *H*-4). — ^{13}C NMR (100.6 MHz, [D_6]DMSO): δ = 0.9 (4 C, Si(*C*H$_3$)$_2$), 98.3 (*C*-5), 133.2 (*C*-7), 137.4 (*C*-6), 139.5 (*C*-4), 146.7 (*C*-7a), 151.2 (*C*-3a). — ^{29}Si NMR (99.4 MHz, [D_6]DMSO): δ = 14.3, 15.1. — EI-MS: *m/z* (%) 334 (22) [M^+], 319 (100) [$M^+ - CH_3$].

$C_{10}H_{15}OISi_2$ (334.30)	Calculated:	C 35.93	H 4.52
	Found:	C 35.9	H 4.5

*Methyl 4-ethynylbenzoate (**41**).*

This compound was synthesised according to ref 67.

*Methyl 4-(1,1,4,4-tetramethyl-1,2,3,4-tetrahydro-1,4-disilanaphthalen-6-ylethynyl)benzoate (**42**).*

Compound **41** (81.0 mg, 506 μmol), compound **37** (160 mg, 462 μmol), $Pd(PPh_3)_2Cl_2$[60] (3.24 mg, 4.62 μmol) and copper(I) iodide (880 μg, 4.62 μmol) were dissolved in triethylamine (10 mL) at 20 °C. The reaction mixture was stirred at this temperature for 2.5 h, whereupon GC analysis indicated complete consumption of the starting materials. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography (silica gel; eluent, *n*-hexane/ethyl acetate (90:10 (v/v))), followed by recrystallisation from acetonitrile (20 °C), to afford **42** in 82% yield (144 mg, 380 μmol) as a colourless crystalline solid; mp 93−94 °C. — ^{1}H NMR (400.1 MHz, [D$_6$]DMSO): δ = 0.20 (s, 6 H, Si(CH_3)$_2$), 0.22 (s, 6 H, Si(CH_3)$_2$), 0.94 (s, 4 H, SiCH_2C), 3.86 (s, 3 H, C(O)OCH_3), 7.52 (d, 1 H, $^3J_{H\text{-}H}$ = 7.6 Hz, *H*-7, THN), 7.56 (d, 1 H, $^3J_{H\text{-}H}$ = 7.6 Hz, *H*-8, THN), 7.69 (m, 3 H, *H*-5 (THN) and *H*-3/*H*-5 (Benz')), 7.98 (m, 2 H, *H*-2/*H*-6, Benz'). — ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = –1.72 (Si(*C*H$_3$)$_2$), 6.8 (Si*C*H$_2$C), 6.9 (Si*C*H$_2$C), 52.3 (C(O)O*C*H$_3$), 88.9 (THN-C≡*C*), 92.7 (THN-*C*≡C), 121.5 (*C*-6, THN), 127.0 (*C*-4, Benz'), 129.3 (*C*-1, Benz'), 129.4 (*C*-2/*C*-6, Benz'), 130.7 (*C*-7, THN), 131.7 (*C*-3/*C*-5, Benz'), 133.5 (*C*-8, THN), 135.8 (*C*-5, THN) 145.9 (*C*-4a, THN), 146.8 (*C*-8a, THN), 165.6 (*C*(O)OCH$_3$). — ^{29}Si NMR (79.5 MHz, [D$_6$]DMSO): δ = –6.54, –6.46 ppm. — EI-MS: *m/z* (%) 378 (30) [M$^+$], 363 (36) [M$^+$ − CH$_3$], 73 (100).

$C_{22}H_{26}O_2Si_2$ (378.62)	Calculated:	C 69.79	H 6.92
	Found:	C 69.8	H 6.9

*Methyl 4-(1,1,3,3-tetramethylindan-5-ylethynyl)benzoate (**43**).*

Compound **41** (270 mg, 1.69 mmol), compound **38** (460 mg, 1.53 mmol), $Pd(PPh_3)_2Cl_2$[60] (10.8 mg, 15.4 mmol) and copper(I) iodide (2.92 mg, 15.3 mmol) were dissolved in triethylamine (20 mL) at 20 °C. The reaction mixture was stirred at this temperature for 16 h, whereupon GC analysis indicated complete consumption of the starting materials. The solvent was then removed under reduced pressure and the residue was purified by flash

column chromatography (silica gel; eluent, *n*-hexane/ethyl acetate (90:10 (v/v))), followed by crystallisation from acetonitrile (cooling of a hot solution to 20 °C), to afford **43** in 95% yield (482 mg, 1.45 mmol) as a colourless crystalline solid; mp 105 °C. — ^{1}H NMR (400.1 MHz, [D$_6$]DMSO): δ = 1.27 (s, 6 H, C(C*H*$_3$)$_2$), 1.28 (s, 6 H, C(C*H*$_3$)$_2$), 1.88 (s, 2 H, CC*H*$_2$C), 3.86 (s, 3 H, C(O)OC*H*$_3$), 7.23 (d, 1 H, $^{3}J_{H\text{-}H}$ = 8.6 Hz, *H*-7, Ind), 7.40 (m, 2 H, *H* 4 and *H* 6, Ind), 7.66 (m, 2 H, *H*-3/*H*-5, Benz'), 7.97 (m, 2 H, *H*-2/*H*-6, Benz'). — ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = 31.0 (C(*C*H$_3$)$_2$), 31.1 (C(*C*H$_3$)$_2$), 42.2 (*C*-3, Ind), 42.4 (*C*-1, Ind), 52.3 (C(O)O*C*H$_3$), 55.8 (C*C*H$_2$C), 87.5 (Ind-C≡*C*), 93.2 (Ind-*C*≡C), 120.0 (*C*-5, Ind), 123.0 (*C*-7, Ind), 125.9 (*C*-4, Ind), 127.3 (*C*-4, Benz'), 129.0 (*C*-1 Benz'), 129.4 (*C*-2/*C*-6, Benz'), 130.4 (*C*-6, Ind), 131.5 (*C*-3/*C*-5, Benz'), 151.4 (*C*-3a, Ind), 152.4 (*C*-7a, Ind), 165.6 (*C*(O)OCH$_3$). — EI-MS: *m/z* (%) 332 (46) [M$^+$], 317 (100) [M$^+$ − CH$_3$].

$C_{23}H_{24}O_2$ (332.44)	Calculated:	C 83.10	H 7.28
	Found:	C 83.0	H 7.3

*Methyl 4-(1,1,3,3-tetramethyl-1,3-disilaindan-5-ylethynyl)benzoate (**44**).*

Compound **41** (71.0 mg, 443 μmol), compound **39** (134 mg, 403 μmol), Pd(PPh$_3$)$_2$Cl$_2$[60] (2.83 mg, 4.03 μmol) and copper(I) iodide (760 μg, 4.03 μmol) were dissolved in triethylamine (5 mL) at 20 °C. The reaction mixture was stirred at this temperature for 17 h, whereupon GC analysis indicated complete consumption of the starting materials. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography (silica gel; eluent, *n*-hexane/ethyl acetate (90:10 (v/v))) to give a colourless oil. This oil was crystallised from acetonitrile (10 mL, slow evaporation of the solvent at 20 °C) to afford **44** in 97% yield (142 mg, 389 μmol) as a colourless crystalline solid; mp 97–98 °C. — ^{1}H NMR (500.1 MHz, CD$_2$Cl$_2$): δ = –0.01 (s, 2 H, SiC*H*$_2$Si), 0.31 (s, 6 H, Si(C*H*$_3$)$_2$), 0.32 (s, 6 H, Si(C*H*$_3$)$_2$), 3.91 (s, 3 H, C(O)OC*H*$_3$), 7.52 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{4}J_{H\text{-}H}$ = 1.5 Hz, *H*-6, Ind'), 7.57 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{5}J_{H\text{-}H}$ = 1.0 Hz, *H*-7, Ind'), 7.61 (m, 2 H, *H*-3/*H*-5, Benz'), 7.74 (m, 1 H, *H*-4, Ind') 8.02 (m, 2 H, *H*-2/*H*-6, Benz'). — ^{13}C NMR (125.8 MHz, CD$_2$Cl$_2$): δ = –2.5 (Si*C*H$_2$Si), 0.42 (Si(*C*H$_3$)$_2$), 0.45 (Si(*C*H$_3$)$_2$), 52.5 (C(O)O*C*H$_3$), 89.1 (Ind'-C≡*C*), 93.2 (Ind'-*C*≡C), 122.9 (*C*-5, Ind'), 128.3 (*C*-4, Benz'), 129.8 (*C*-2/*C*-6, Benz'), 130.0 (*C*-1, Benz'), 131.6 (*C*-6, Ind'), 131.8 (*C*-3/*C*-5, Benz'), 132.0 (*C*-7, Ind'), 135.1 (*C*-4, Ind'), 151.2 (*C*-3a, Ind'), 152.1 (*C*-7a, Ind'), 166.6 (*C*(O)OCH$_3$). — ^{29}Si NMR (99.4 MHz, CD$_2$Cl$_2$): δ = 9.4, 9.5. — EI-MS: *m/z* (%) 364 (33) [M$^+$], 349 (100) [M$^+$ − CH$_3$].

$C_{21}H_{24}O_2Si_2$ (364.59)	Calculated:	C 69.18	H 6.63
	Found:	C 69.4	H 6.6

*Methyl 4-(1,1,3,3-tetramethyl-2-oxa-1,3-disilaindan-5-ylethynyl)benzoate (**45**).*

Compound **41** (53.0 mg, 331 μmol), compound **40** (100 mg, 299 μmol), $Pd(PPh_3)_2Cl_2$[60] (2.10 mg, 2.99 μmol) and copper(I) iodide (570 μg, 2.99 μmol) were dissolved in triethylamine (15 mL) at 20 °C. The reaction mixture was stirred at this temperature for 1 h, whereupon GC analysis indicated complete consumption of the starting materials. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography (silica gel; eluent, *n*-hexane/ethyl acetate (90:10 (v/v))), followed by crystallisation from ethanol (20 °C) to afford **45** in 96% yield (105 mg, 286 μmol) as a colourless crystalline solid; mp 123−125 °C. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 0.32 (s, 6 H, Si(CH_3)$_2$), 0.33 (s, 6 H, Si(CH_3)$_2$), 3.86 (s, 3 H, C(O)OCH_3), 7.60 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^4J_{H\text{-}H}$ = 1.5 Hz, *H*-6, Ind''), 7.69 (m, 2 H, *H*-3/*H*-5, Benz'), 7.72 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^5J_{H\text{-}H}$ = 1.0 Hz, *H*-7, Ind''), 7.90 (dd, 1 H, $^4J_{H\text{-}H}$ = 1.5 Hz, $^5J_{H\text{-}H}$ = 1.0 Hz, *H*-4, Ind''), 7.99 (m, 2 H, *H*-2/*H*-6, Benz'). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 0.88 (Si(*C*H$_3$)$_2$), 0.89 (Si(*C*H$_3$)$_2$), 52.3 (C(O)O*C*H$_3$), 89.0 (Ind''-C≡*C*), 92.7 (Ind''-*C*≡C), 122.3 (*C*-5, Ind''), 127.0 (*C*-4, Benz'), 129.3 (*C*-1, Benz'), 129.5 (*C*-2/*C*-6, Benz'), 131.2 (*C*-7, Ind''), 131.67 (*C*-6, Ind''), 131.68 (*C*-3/*C*-5, Benz'), 134.0 (*C*-4, Ind''), 148.3 (*C*-3a, Ind''), 148.9 (*C*-7a, Ind''), 165.6 (*C*(O)OCH$_3$). — ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = 14.91, 14.93. — EI-MS: *m/z* 366 (%) (28) [M$^+$], 351 (100) [M$^+$ − CH$_3$].

$C_{20}H_{22}O_3Si_2$ (366.56)	Calculated:	C 65.53	H 6.05
	Found:	C 65.4	H 6.0

*4-Ethynylbenzoic acid (**46**).*

This compound was synthesised from **50** according to ref 68.

*4-Iodobenzoic acid (**47**).*

This compound was commercially available (ABCR) and was used as received.

*Methyl 4-iodobenzoate (**48**).*

This compound was synthesised according to ref 67.

*Ethynyltrimethylsilane (**49**).*

This compound was commercially available (ABCR) and was used as received.

*Methyl 4-((trimethylsilyl)ethynyl)benzoate (**50**).*

This compound was synthesised according to ref 67.

*Methyl 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthoate (**51**).*

This compound was synthesised from **58** according to ref 69.

*Methyl 6-(1,1,4,4-tetramethyl-1,2,3,4-tetrahydro-1,4-disilanaphthalen-6-yl)-2-naphthoate (**52**).*

Compound **51** (205 mg, 657 mmol), compound **37** (250 mg, 722 mmol), Pd(dppf)Cl_2 (19.2 mg, 26.2 μmol) and potassium phosphate (348 mg, 1.64 mmol) were combined with degassed *N*,*N*-dimethylformamide (15 mL) and degassed water (2 mL) in a schlenk bomb at 20 °C utilising a dry, argon filled glovebox. The tube was sealed and heated at 80 °C for 16 h, whereupon GC analysis indicated complete consumption of **51**. The reaction mixture was poured onto a mixture of dichloromethane (50 mL) and hydrochloric acid (4 M, 10 mL). The organic layer was separated and washed with an aqueous sodium chloride solution (2 × 25 mL). Separation of the organic layer, drying over magnesium sulphate, filtration and concentration under reduced pressure yielded a brown residue, which was purified by flash column chromatography (silica gel; eluent, *n*-hexane/ethyl acetate (90:10 (v/v))). Concentration of the relevant fractions to one third of the original volume and subsequent cooling of the resulting solution to –30 °C afforded **52** in 47% yield (126 mg, 311 μmol) as a colourless crystalline solid following isolation by filtration; mp 167 °C. — ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 0.28 (s, 6 H, Si(CH_3)$_2$), 0.30 (s, 6 H, Si(CH_3)$_2$), 1.08 (s, 4 H, SiCH_2C), 3.97 (s, 3 H, C(O)OCH_3), 7.64 (m, 1 H, *H*-8, THN), 7.70 (m, 1 H, *H*-7, THN), 7.81–7.86 (m, 2 H, *H*-5, THN, and *H*-7, Naph'), 7.98 (m, 1 H, *H*-4, Naph'), 8.05–8.09 (m, 2 H, *H*-3 and *H*-8, Naph'), 8.10 (m, 1 H, *H*-5, Naph'), 8.62 (m, 1 H, *H*-1, Naph'). — ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = –1.48 (Si(*C*H_3)$_2$), –1.43 (Si(*C*H_3)$_2$), 7.7 (Si*C*H_2C), 7.8 (Si*C*H_2C), 52.5 (C(O)O*C*H_3), 125.8 (*C*-5, Naph'), 126.0 (*C*-3, Naph'), 126.8 (*C*-7, Naph'), 127.4 (*C*-7, THN) 127.9 (*C*-2, Naph'), 128.7 (*C*-4, Naph'), 130.1 (*C*-8, Naph'), 131.0 (*C*-1, Naph'), 132.0 (*C*-8a, Naph'), 132.6 (*C*-5, THN), 134.5 (*C*-8, THN), 136.2 (*C*-4a, Naph'), 140.2 (*C*-6, THN), 141.5 (*C*-6, Naph'), 145.8 (*C*-8a, THN), 147.2 (*C*-4a, THN) 167.3

(*C*(O)OCH$_3$). — ^{29}Si NMR (99.4 MHz, CD_2Cl_2): δ = –6.8, –6.6. — EI-MS: *m/z* (%) 404 (24) [M^+], 389 (26) [$M^+ - CH_3$], 73 (100).

$C_{24}H_{28}O_2Si_2$ (404.66) Calculated: 405.17006 $[M + H]^+$

Found: 405.16991 $[M + H]^+$

*Methyl 6-(1,1,3,3-tetramethylindan-5-yl)-2-naphthoate (**53**).*

Compound **51** (250 mg, 801 mmol), compound **38** (200 mg, 666 mmol), Pd(dppf)Cl_2 (19.5 mg, 26.6 μmol) and potassium phosphate (354 mg, 1.67 mmol) were combined with degassed *N*,*N*-dimethylformamide (10 mL) and degassed water (2 mL) in a schlenk bomb at 20 °C utilising a dry, argon filled glovebox. The tube was sealed and heated at 80 °C for 19 h, whereupon GC analysis indicated complete consumption of **38**. The reaction mixture was poured onto ethyl acetate (50 mL), the resulting mixture was washed with hydrochloric acid (1 M, 2 × 50 mL) and the combined aqueous washings were extracted with a further portion of ethyl acetate (50 mL) and discarded. Combination of the organic extracts, drying over magnesium sulphate, filtration and concentration under reduced pressure yielded a brown residue. Purification of this residue by flash column chromatography (silica gel; eluent, *n*-hexane/ethyl acetate (90:10 (v/v))) and subsequent recrystallisation from *n*-hexane (slow cooling of a hot solution to 20 °C) afforded **53** in 62% yield (147 mg, 410 μmol) as a fluffy, white, crystalline solid; mp 156 °C. — ^{1}H NMR (500.1 MHz, [D_6]DMSO): δ = 1.31 (s, 6 H, C(C*H*$_3$)$_2$), 1.35 (s, 6 H, C(C*H*$_3$)$_2$), 1.92 (s, 2 H, CC*H*$_2$C), 3.92 (s, 3 H, C(O)OC*H*$_3$), 7.29 (d, 1 H, $^3J_{H\text{-}H}$ = 8.0 Hz, *H*-7, Ind), 7.61–7.64 (m, 2 H, *H*-4 and *H*-6, Ind), 7.93 (m, 1 H, *H*-7, Naph'), 7.99 (m, 1 H, *H*-3, Naph'), 8.09 (m, 1 H, *H*-4, Naph'), 8.20 (m, 1 H, *H*-8, Naph'), 8.28 (s, 1 H, *H*-5, Naph'), 8.65 (s, 1 H, *H*-1, Naph'). — ^{13}C NMR (125.8 MHz, [D_6]DMSO): δ = 31.3 (C(*C*H$_3$)$_2$), 31.4 (C(*C*H$_3$)$_2$), 42.0 (*C*-1 or *C*-3, Ind), 42.3 (*C*-1 or *C*-3, Ind), 52.2 (C(O)O*C*H$_3$), 56.3 (C*C*H$_2$C), 121.3 (*C*-4, Ind), 123.0 (*C*-7, Ind) 124.8 (*C*-5, Naph'), 125.1 (*C*-3, Naph'), 126.1 (*C*-6, Ind), 126.4 (*C*-7, Naph'), 126.6 (*C*-2, Naph'), 128.7 (*C*-4, Naph'), 129.9 (*C*-8, Naph'), 130.3 (*C*-1, Naph'), 131.1 (*C*-8a, Naph'), 135.5 (*C*-4a, Naph'), 138.4 (*C*-5, Ind), 140.7 (*C*-6, Naph'), 150.8 (*C*-7a, Ind), 151.7 (*C*-3a, Ind), 166.3 (*C*(O)OCH$_3$). — EI-MS: *m/z* (%) 358 (41) [M^+], 343 (100) [$M^+ - CH_3$].

$C_{25}H_{26}O_2$ (358.48) Calculated: 359.20056 $[M + H]^+$

Found: 359.20030 $[M + H]^+$

*Methyl 6-(1,1,3,3-tetramethyl-1,3-disilaindan-5-yl)-2-naphthoate (**54**).*

Compound **51** (251 mg, 804 mmol), compound **39** (294 mg, 885 mmol), Pd(dppf)Cl_2 (23.5 mg, 32.1 μmol) and potassium phosphate (427 mg, 2.01 mmol) were combined with degassed *N*,*N*-dimethylformamide (10 mL) and degassed water (2 mL) in a schlenk bomb at 20 °C utilising a dry, argon filled glovebox. The tube was sealed and heated at 80 °C for 24 h, whereupon GC analysis indicated complete consumption of **51**. The reaction mixture was poured onto a mixture of ethyl acetate (40 mL) and hydrochloric acid (4 M, 10 mL), and the resulting mixture was washed with an aqueous sodium chloride solution (30 mL). Separation of the organic layer, drying over sodium sulphate, filtration and concentration under reduced pressure yielded a brown residue. Purification of this residue by flash column chromatography (silica gel; eluent, *n*-hexane/ethyl acetate (90:10 (v/v))) and subsequent crystallisation from acetonitrile (slow cooling of a boiling solution to 20 °C) afforded **54** in 43% yield (135 mg, 346 μmol) as a fluffy, white, crystalline solid; mp 152 °C. — ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 0.05 (s, 2 H, SiCH_2Si), 0.34 (s, 6 H, Si(CH_3)$_2$), 0.36 (s, 6 H, Si(CH_3)$_2$), 3.97 (s, 3 H, C(O)OCH_3), 7.70 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^5J_{H\text{-}H}$ = 1.0 Hz, *H*-7, Ind'), 7.74 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^4J_{H\text{-}H}$ = 1.5 Hz, *H*-6, Ind'), 7.86 (m, 1 H, *H*-7, Naph'), 7.92 (dd, 1 H, $^4J_{H\text{-}H}$ = 1.5 Hz, $^5J_{H\text{-}H}$ = 1.0 Hz, *H*-4, Ind'), 7.97 (m, 1 H, *H*-4, Naph'), 8.05–8.08 (m, 2 H, *H*-3 and *H*-8, Naph'), 8.13 (m, 1 H, *H*-5, Naph'), 8.63 (m, 1 H, *H*-1, Naph'). — ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = –2.2 (Si*C*H$_2$Si), 0.59 (Si(*C*H$_3$)$_2$), 0.62 (Si(*C*H$_3$)$_2$), 52.5 (C(O)O*C*H$_3$), 125.92 (*C*-3 or *C*-5, Naph'), 125.94 (*C*-3 or *C*-5, Naph'), 126.9 (*C*-7, Naph'), 127.9 (*C*-2, Naph'), 128.1 (*C*-6, Ind'), 128.7 (*C*-4, Naph'), 130.1 (*C*-8, Naph'), 131.0 (*C*-1, Naph', and *C*-4, Ind'), 132.0 (*C*-8a, Naph'), 132.7 (*C*-7, Ind'), 136.2 (*C*-4a, Naph'), 140.8 (*C*-5, Ind'), 141.7 (*C*-6, Naph'), 150.5 (*C*-7a, Ind'), 152.0 (*C*-3a, Ind'), 167.3 (*C*(O)OCH$_3$). — ^{29}Si NMR (99.4 MHz, CD_2Cl_2): δ = 8.9, 9.3. — EI-MS: *m/z* (%) 390 (38) [M^+], 375 (100) [$M^+ - CH_3$].

$C_{23}H_{27}O_2Si_2$ (391.64)	Calculated:	391.15441 $[M + H]^+$
	Found:	391.15461 $[M + H]^+$

*Methyl 6-(1,1,3,3-tetramethyl-2-oxa-1,3-disilaindan-2-yl)-2-naphthoate (**55**).*

Compound **51** (148 mg, 474 mmol), compound **40** (174 mg, 522 mmol), Pd(dppf)Cl_2 (13.9 mg, 19.0 mmol) and potassium phosphate (252 mg, 1.19 mmol) were combined with degassed *N*,*N*-dimethylformamide (10 mL) and degassed water (2 mL) in a schlenk bomb at 20 °C utilising a dry, argon filled glovebox. The tube was sealed and heated at 80 °C for 18 h, whereupon GC analysis indicated complete consumption of **51**. The reaction mixture

was poured onto a mixture of diethylether (40 mL) and hydrochloric acid (4 M, 10 mL). The organic layer was separated and washed with an aqueous sodium chloride solution (20 mL). Separation of the organic layer, drying over magnesium sulphate, filtration and concentration under reduced pressure yielded a brown residue. Purification of the residue by flash column chromatography (silica gel; eluent, *n*-hexane/ethyl acetate (90:10 (v/v))) and subsequent crystallisation from acetonitrile (cooling of a boiling solution to 20 °C) afforded **55** as a fluffy, white, crystalline solid in 35% yield (66.0 mg, 158 μmol); mp 147 °C. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 0.36 (s, 6 H, Si(CH_3)$_2$), 0.38 (s, 6 H, Si(CH_3)$_2$), 3.94 (s, 3 H, C(O)OCH_3), 7.78 (m, 1 H, *H*-7, Ind), 7.86 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 9.4 Hz, $^{4}J_{H\text{-}H}$ = 1.8 Hz, *H*-6, Ind), 7.96 (m, 1 H, *H*-7, Naph), 8.01 (m, 1 H, *H*-3, Naph), 8.09–9.11 (m, 2 H, *H*-4, Ind and *H*-4, Naph), 8.20 (m, 1 H, *H*-8, Naph), 8.31 (m, 1 H, *H*-5, Naph), 8.64 (m, 1 H, *H*-5, Naph). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 0.60 (Si(*C*H$_3$)$_2$), 0.62 (Si(*C*H$_3$)$_2$), 51.7 (C(O)O*C*H$_3$), 124.9 (*C*-3, Naph), 125.0 (*C*-5, Naph), 126.0 (*C*-7, Naph), 126.8 (*C*-2, Naph), 127.7 (*C*-6, Ind), 128.3 (*C*-4, Naph), 129.3 (*C*-8, Naph), 129.8 (*C*-1, Naph and *C*-4, Ind), 131.1 (*C*-8a, Naph), 131.2 (*C*-7, Ind), 135.1 (*C*-4a, Naph), 139.8 (*C*-5, Ind), 140.1 (*C*-6, Naph), 146.9 (*C*-3a, Ind), 148.5 (*C*-7a, Ind), 166.0 (*C*(O)OCH$_3$). — ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = 14.5, 14.6. — EI-MS: *m/z* (%) 392 (35) [M$^+$], 377 (100) [M$^+$ − CH$_3$].

$C_{22}H_{24}O_3Si_2$ (392.60)	Calculated:	393.13367 $[M + H]^+$
	Found:	393.13347 $[M + H]^+$

*6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthoic acid (**56**).*

A mixture of **51** (341 mg, 1.09 mmol), potassium hydroxide (613 mg, 10.9 mmol) and methanol/water (3:1 (v/v), 20.0 mL) was stirred at 20 °C for 3 d. Hydrochloric acid (4 M, 25 mL) was then added to the reaction mixture, followed by dichloromethane (25 mL). The aqueous layer was separated, extracted with dichloromethane (2 × 25 mL) and discarded. The combined organic extracts were dried over sodium sulphate, filtered and concentrated to afford **56** as a colourless crystalline solid in 71% yield (321 mg, 775 μmol); mp 231°C. — ^{1}H NMR (300.1 MHz, [D$_6$]DMSO): δ = 1.33 (s, 12 H, CH_3), 7.77 (m, 1 H, *H*-7), 7.97 (m, 1 H, *H*-3), 8.06–8.12 (m, 2 H, *H*-4 and *H*-8), 8.37 (m, 1 H, *H*-5), 8.59 (m, 1 H, *H*-1), 13.14 (s, 1 H, COO*H*). — ^{11}B NMR (96.3 MHz, [D$_6$]DMSO): δ = –5.2. — ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 24.7 (*C*H$_3$), 84.0 (*C*(CH$_3$)$_2$), 125.3 (*C*-3), 128.5 (*C*-4 or *C*-8), 128.9 (*C*-4 or *C*-8), 129.2 (*C*-2), 130.2 (*C*-1), 130.7 (*C*-7), 133.7 (*C*-8a), 134.2 (*C*-5a), 135.6 (*C*-5), 167.3 (*C*OOH).

$C_{17}H_{19}BO_4$ (298.15)	Calculated:	C 68.49	H 6.42
	Found:	C 68.6	H 6.4

*6-Bromo-2-naphthoic acid (**57**).*

This compound was commercially available (ABCR) and was used as received.

*Methyl 6-Bromo-2-naphthoate (**58**).*

A mixture of compound **57** (10.0 g, 39.8 mmol), concentrated sulphuric acid (2.00 g, 20.4 mmol) and methanol (125 mL) was heated under reflux for 8.5 hours. Following cooling to 20 °C, the reaction mixture was diluted with diethyl ether (400 mL), washed with both water (2 × 250 mL) and saturated $NaHCO_3$ solution (250 mL), dried over magnesium sulphate, filtered, and evaporated to dryness to afford **47** as an amorphous, off-white solid in 94% yield (9.90 g, 37.4 mmol); mp 125−126 °C (lit. 125−127 °C[70]). — ^{1}H NMR (300.1 MHz, [D$_6$]DMSO): δ = 3.92 (s, 3 H, C(O)OC*H*$_3$), 7.74 (m, 1 H, $^4J_{H\text{-}H}$ = 2.0 Hz, *H*-7), 8.02 (s, 1 H, *H*-3 or *H*-4), 8.03 (s, 1 H, *H*-3 or *H*-4), 8.12 (m, 1 H, *H*-8), 8.32 (m, 1 H, *H*-5), 8.66 (s, 1 H, *H*-1). — ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 52.4 (C(O)O*C*H$_3$), 122.1 (*C*-6), 125.9 (*C*-3 or *C*-4), 127.4 (*C*-2), 127.7 (*C*-3 or *C*-4), 129.7 (*C*-5), 130.1 (*C*-7), 130.6 (*C*-1), 130.7 (*C*-8a), 131.5 (*C*-8), 136.1 (*C*-4a), 166.1 (*C*(O)OCH$_3$). — EI-MS *m/z* (%) 264 (38) [M^+], 233 (49) [$M^+ - OCH_3$], 126 (100).

*Bis(pinacalato)diboron (**59**).*

This compound was commercially available (ABCR); except for storage in a dry glovebox it was used as received.

*1,2-Bis(ethynyldimethylsilyl)ethane (**60**).*

This compound was synthesised according to ref 1a.

*Bis(ethynyldimethylsilyl)methane (**61**).*

This compound was synthesised according to ref 71.

*1,3-Diethynyl-1,1,3,3-tetramethyldisiloxane (**62**).*

This compound was synthesised according to ref 72.

*1,1,4,4-Tetramethyl-6-trimethylsilyl-1,2,3,4-tetrahydro-1,4-disilanaphthalene (**63**).*

A mixture of iodine (51.0 mg, 201 μmol of I_2), zinc (131 mg, 2.00 mmol) and acetonitrile (40 mL) was stirred at 20 °C until the brown colouration disappeared and a grey suspension was observed. Compound **60** (3.89 g, 20.0 mmol), compound **49** (2.75 g, 28.0 mmol) and a solution of cobalt(II) bromide in acetonitrile (0.2 M, 5.00 mL, 1.00 mmol of $CoBr_2$) were then added sequentially in single portions at 20 °C. The resulting dark brown solution was stirred at this temperature for 2 h, whereupon GC analysis indicated complete consumption of **60**. The reaction mixture was filtered through a short silica gel column (eluent, *n*-hexane) and the filtrate was concentrated under reduced pressure to give a yellow oil. Purification by RP-MPLC (eluent, methanol; flow rate, 38 mL min^{-1}; detector wavelength, 240 nm) gave a white solid, which was crystallised from ethanol (cooling of a hot solution to 20 °C) to afford **63** in 34% yield (2.01 g, 6.87 mmol) as a colourless crystalline solid; mp 60 °C. — ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.21 (s, 6 H, Si(CH_3)$_2$), 0.22 (s, 6 H, Si(CH_3)$_2$), 0.25 (s, 9 H, Si(CH_3)$_3$), 0.99 (s, 4 H, SiCH_2C), 7.54 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.3 Hz, $^5J_{H\text{-}H}$ = 0.9 Hz, *H*-8), 7.49 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.3 Hz, $^4J_{H\text{-}H}$ = 1.0 Hz, *H*-7), 7.62 ("t", 1 H, $^4J_{H\text{-}H}$ = $^5J_{H\text{-}H}$ = 1.0 Hz, *H*-5). — ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = –1.54 (Si(*C*H_3)$_2$), –1.45 (Si(*C*H_3)$_2$), –1.2 (Si(*C*H_3)$_3$), 7.4 (Si*C*H_2C), 7.6 (Si*C*H_2C), 132.6 (*C*-8), 132.9 (*C*-7), 138.2 (*C*-5), 139.8 (*C*-6), 144.7 (*C*-4a or *C*-8a), 146.3 (*C*-4a or *C*-8a). — ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ = −7.3, –7.2, –4.2 ppm. — EI-MS: *m/z* (%) 292 (23) [M^+], 277 (100) [$M^+ - CH_3$].

$C_{15}H_{28}Si_3$ (292.64)	Calculated:	C 61.56	H 9.64
	Found:	C 61.4	H 9.6

*1,1,3,3-Tetramethyl-5-trimethylsilyl-1,3-disilaindane (**64**).*

A mixture of iodine (51.0 mg, 201 μmol of I_2), zinc (131 mg, 2.00 mmol) and acetonitrile (10 mL) was stirred at 20 °C until the brown colouration disappeared and a grey suspension was observed. Compound **61** (3.61 g, 20.0 mmol), compound **49** (1.97 g, 20.1 mmol) and a solution of cobalt(II) bromide in acetonitrile (0.1 M, 10.0 mL, 1.00 mmol of $CoBr_2$) were then added sequentially in single portions at 20 °C. The resulting dark brown solution was stirred at this temperature for 2 h, whereupon GC analysis indicated complete consumption of **61**. The reaction mixture was filtered through a short silica gel colunm (eluent, *n*-hexane) and the filtrate was concentrated under reduced pressure to give a yellow oil. Purification by RP-MPLC (eluent, methanol; flow rate, 34 mL min^{-1}; detector wavelength, 240 nm) gave a white solid, which was crystallised from ethanol (cooling of a hot solution to 20 °C) to afford **64** in 9% yield (490 mg, 1.76 mmol) as a colourless crystalline solid; mp 38 °C. — ^{1}H NMR

(500.1 MHz, $CDCl_3$): δ = –0.06 (s, 2 H, SiCH_2Si), 0.28 (s, 9 H, Si(CH_3)$_3$), 0.29 (s, 6 H, Si(CH_3)$_2$), 0.30 (s, 6 H, Si(CH_3)$_2$), 7.55 (m, 2 H, *H*-6 and *H*-7), 7.71 (m, 1 H, *H*-4). — ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = –2.5 (Si*C*H$_2$Si), −1.1 (Si(*C*H$_3$)$_3$), 0.5 (Si(*C*H$_3$)$_2$), 0.6 (Si(*C*H$_3$)$_2$), 130.9 (*C*-7), 133.5 (*C*-6), 136.6 (*C*-4), 140.3 (*C*-5), 149.4 (*C*-3a or *C*-7a), 151.1 (*C*-3a or *C*-7a). — ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ = −4.1, 8.7, 8.9. — EI-MS: *m/z* (%) 278 (5) [M^+], 263 (100) [$M^+ - CH_3$].

$C_{14}H_{26}Si_3$ (278.62)	Calculated:	C 60.35	H 9.41
	Found:	C 60.4	H 9.4

*1,1,3,3-Tetramethyl-5-trimethylsilyl-2-oxa-1,3-disilaindane (**65**).*

A mixture of iodine (51.0 mg, 201 μmol of I_2), zinc (130 mg, 2.00 mmol) and acetonitrile (10 mL) was stirred at 20 °C until the brown colouration disappeared and a grey suspension was observed. Compound **62** (3.64 g, 20.0 mmol), compound **49** (2.75 g, 28.0 mmol) and a solution of cobalt(II) iodide in acetonitrile (0.1 M, 10.0 mL, 1.00 mmol of CoI_2) were then added sequentially in single portions at 20 °C. The resulting dark brown solution was stirred at this temperature for 18 h, whereupon GC analysis indicated complete consumption of **62**. The reaction mixture was concentrated under reduced pressure and the residue was purified by bulb-to-bulb distillation (71−114 °C, 0.15 mbar) to afford **65** in 63% yield (3.50 g, 12.5 mmol) as a colourless crystalline solid; mp 49−51 °C. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 0.24 (s, 9 H, Si(CH_3)$_3$), 0.28 (s, 6 H, Si(CH_3)$_2$), 0.29 (s, 6 H, Si(CH_3)$_2$), 7.54 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.2 Hz, $^4J_{H\text{-}H}$ = 1.1 Hz, *H*-6), 7.60 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.2 Hz, $^5J_{H\text{-}H}$ = 1.0 Hz, *H*-7), 7.77 ("t", 1 H, $^4J_{H\text{-}H}$ = $^5J_{H\text{-}H}$ = 1.1 Hz, *H*-4). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = −1.1 (Si(*C*H$_3$)$_3$), 1.0 (Si(*C*H$_3$)$_2$), 1.1 (Si(*C*H$_3$)$_2$), 130.2 (*C*-7), 133.7 (*C*-6), 135.6 (*C*-4), 140.4 (*C*-5), 146.6 (*C*-3a), 148.2 (*C*-7a). — ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = −4.0, 14.4, 14.7 ppm. — EI-MS: *m/z* (%) 280 (7) [M^+], 265 (100) [$M^+ - CH_3$].

$C_{13}H_{24}OSi_3$ (280.59)	Calculated:	C 55.65	H 8.62
	Found:	C 55.4	H 8.6

*(1,1,4,4-Tetramethyl-1,2,3,4-tetrahydro-1,4-disilanaphthalen-6-yl)amine (**66**).*

A solution of **69** (2.63 g, 9.94 mmol), diphenoxyphosphoryl azide (3.01 g, 10.9 mmol) and triethylamine (1.1 mL) in toluene (250 mL) was heated under reflux for 17 h, whereupon GC analysis indicated complete consumption of **66**. Following cooling to 0 °C, a solution of sodium trimethylsilanolate in dichloromethane (1.0 M, 27.0 mL, 27.0 mmol of $NaOSiMe_3$) was added over a period of 5 min to the stirred solution. The reaction mixture was stirred at

0 °C for 30 min and hydrochloric acid (4 M, 20 mL) was added. The aqueous phase was adjusted to pH 6 (pH paper test) by gradual addition of an aqueous sodium hydroxide solution (4 M). Separation of the organic layer and concentration under reduced pressure gave a brown solid, which was purified by RP-MPLC (eluent, methanol/water (85:15 (v/v)); flow rate, 18 mL min^{-1}; detector wavelength, 240 nm) and subsequent bulb-to-bulb distillation (65 °C, 0.05 mbar) to afford **66** in 46% yield (1.07 g, 4.54 mmol) as a colourless crystalline solid; mp 66 °C. — ^{1}H NMR (300.1 MHz, [D$_6$]DMSO): δ = 0.10 (s, 6 H, Si(CH_3)$_2$), 0.13 (s, 6 H, Si(CH_3)$_2$), 0.88 (s, 4 H, SiCH_2C), 5.09 (s, 2 H, NH_2), 6.54 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 7.8 Hz, $^{4}J_{H\text{-}H}$ = 2.1 Hz, *H*-7), 6.68 (d, 1 H, $^{4}J_{H\text{-}H}$ = 2.1 Hz, *H*-5), 7.12 (d, 1 H, $^{3}J_{H\text{-}H}$ = 7.8 Hz, *H*-8). — ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = –1.4 (Si(*C*H$_3$)$_2$), –1.0 (Si(*C*H$_3$)$_2$), 7.3 (Si*C*H$_2$C), 7.5 (Si*C*H$_2$C), 114.4 (*C*-7), 118.5 (*C*-5), 128.8 (*C*-6), 134.3 (*C*-8), 145.3 (*C*-8a), 148.5 (*C*-4a). — ^{15}N NMR (30.4 MHz, [D$_6$]DMSO): δ = –319.5. — ^{29}Si NMR (59.6 MHz, [D$_6$]DMSO): δ = –8.6, –7.7. — EI-MS: *m/z* (%) 235 (55) [M^+], 220 (93) [$M^+ - CH_3$], 160 (100). — ^{1}H, ^{13}C and ^{29}Si NMR data were in agreement with those reported in ref. 1d.

*(1,1,3,3-Tetramethyl-1,3-disilaindan-5-yl)amine (**67**).*

A solution of **70** (1.82 g, 7.26 mmol), diphenoxyphosphoryl azide (2.20 g, 7.99 mmol) and triethylamine (1.2 mL) in toluene (180 mL) was heated under reflux for 17 h, whereupon GC analysis indicated complete consumption of **70**. Following cooling to 0 °C, a solution of sodium trimethylsilanolate in dichloromethane (1.0 M, 20.0 mL, 20.0 mmol of $NaOSiMe_3$) was added over a period of 10 min to the stirred solution. The reaction mixture was stirred at 0 °C for 30 min and hydrochloric acid (4 M, 10 mL) was added. The reaction mixture was concentrated under reduced pressure and the residue was purified by bulb-to-bulb distillation (110–125 °C, 0.2 mbar) to afford **67** in 63% yield (1.02 g, 4.61 mmol) as a colourless crystalline solid; mp 37 °C. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = –0.15 (s, 2 H, SiCH_2Si), 0.17 (s, 6 H, Si(CH_3)$_2$), 0.19 (s, 6 H, Si(CH_3)$_2$), 5.10 (s, 2 H, NH_2), 6.57 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, $^{4}J_{H\text{-}H}$ = 2.0 Hz, *H*-6), 6.71 (d, 1 H, $^{4}J_{H\text{-}H}$ = 2.0 Hz, *H*-4), 7.19 (d, 1 H, $^{4}J_{H\text{-}H}$ = 8.0 Hz, *H*-7). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = –2.4 (Si*C*H$_2$Si), 0.6 (Si(*C*H$_3$)$_2$), 1.2 (Si(*C*H$_3$)$_2$), 115.3 (*C*-6), 116.3 (*C*-4), 132.4 (*C*-7), 134.0 (*C*-5), 149.1 (*C*-3a), 150.6 (*C*-7a). — ^{15}N NMR (40.6 MHz, [D$_6$]DMSO): δ = –319.3. — ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = 6.5, 7.5. — EI-MS: *m/z* (%) 221 (25) [M^+], 206 (100) [$M^+ - CH_3$].

$C_{11}H_{19}NSi_2$ (221.44)	Calculated:	C 59.66	H 8.65	N 6.33
	Found:	C 59.8	H 8.6	N 6.3

*1,1,4,4-Tetramethyl-1,2,3,4-tetrahydro-1,4-disila-6-naphthoic acid (**69**).*

A mixture of iodine (102 mg, 402 μmol of I_2), zinc (262 mg, 4.00 mmol) and acetonitrile (20 mL) was stirred at 20 °C until the brown colouration disappeared and a grey suspension was observed. Compound **60** (3.89 g, 20.0 mmol), compound **72** (3.59 g, 28.0 mmol) and a solution of cobalt(II) bromide in acetonitrile (0.2 M, 10.0 mL, 2.00 mmol of $CoBr_2$) were then added sequentially in single portions to the stirred mixture. The resulting dark green solution was stirred at 20 °C for 16 h, whereupon GC analysis indicated complete consumption of **60**. Hydrochloric acid (4 M, 10 mL) was then added and the reaction mixture was stirred at 20 °C for 30 min. Subsequently, ethyl acetate (100 mL) was added and the organic phase was separated and washed with aqueous sodium chloride solution (3 × 60 mL). The aqueous phases were combined, extracted with a further portion of ethyl acetate (100 mL) and discarded. Both of the organic phases were combined, dried over magnesium sulphate, filtered and concentrated. The resulting brown oil was purified by flash column chromatography (silica gel; eluent, *n*-hexane) to yield 2.51 g of a yellow oil. This oil was dissolved in acetone (25 mL) and the solution was added dropwise over 5 min to a stirred mixture of potassium dichromate (3.97 g, 13.5 mmol), concentrated sulphuric acid (4.00 mL), water (12.0 mL) and acetone (50 mL) at 0 °C. This mixture was stirred and allowed to warm to 20 °C over a period of 4 h and then poured onto a mixture of *n*-hexane (100 mL) and an aqueous solution of sodium hydroxide (4 M, 100 mL). The organic layer was separated and discarded. Concentrated hydrochloric acid was carefully added to the aqueous phase until it reached pH 2, and this solution was extracted with dichloromethane (2 × 100 mL). Combination of the organic washings, drying over magnesium sulphate, filtration and concentration of the filtrate under reduced pressure yielded a yellow oil. Purification of the crude product by column chromatography (silica gel; eluent, *n*-hexane/diethyl ether/acetic acid (80:20:2 (v/v/v))) afforded **69** in 19% yield (1.03 g, 3.89 mmol, relative to compound **60**) as an amorphous white solid. — ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 0.26 (s, 6 H, Si(CH_3)$_2$), 0.28 (s, 6 H, Si(CH_3)$_2$), 1.06 (s, 4 H, SiCH_2C), 7.64 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^5J_{H\text{-}H}$ = 0.5 Hz, *H*-8), 8.01 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^4J_{H\text{-}H}$ = 2.0 Hz, *H*-7), 8.21 (dd, 1 H, $^4J_{H\text{-}H}$ = 2.0 Hz, $^5J_{H\text{-}H}$ = 0.5 Hz, *H*-5), COO*H* not observed. — ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = –1.7 (Si(*C*H$_3$)$_2$), –1.6 (Si(*C*H$_3$)$_2$), 7.5 (Si*C*H$_2$C), 7.6 (Si*C*H$_2$C), 128.6 (*C*-6), 129.2 (*C*-7), 133.9 (*C*-8), 134.8 (*C*-5), 147.0 (*C*-8a), 154.1 (*C*-4a), 172.7 (*C*(O)OH). — ^{29}Si NMR (99.4 MHz, CD_2Cl_2): δ = –6.2, –6.1. — EI-MS: *m/z* (%) 264 (18) [M^+], 249 (100) [$M^+ - CH_3$]. — ^{1}H, ^{13}C and ^{29}Si NMR data were in agreement with those reported in ref. 1d.

*1,1,3,3-Tetramethyl-1,3-disila-5-indanoic acid (**70**).*

A mixture of iodine (102 mg, 402 μmol of I_2), zinc (262 mg, 4.01 mmol) and acetonitrile (20 mL) was heated under reflux until the brown colouration disappeared and a grey suspension was observed. Compound **61** (3.61 g, 20.0 mmol), compound **72** (3.59 g, 28.0 mmol) and a solution of cobalt(II) bromide in acetonitrile (0.2 M, 10.0 mL, 2.00 mmol of $CoBr_2$) were then added sequentially in single portions to the refluxing mixture. The resulting dark green solution was stirred under reflux for 3.5 h and then at 20 °C for 22 h, whereupon GC analysis indicated complete consumption of **61**. Hydrochloric acid (1 M, 40 mL) was then added and the reaction mixture was stirred at 20 °C for 1 h. Subsequently, ethyl acetate (60 mL) was added and the organic phase was separated and washed with an aqueous sodium chloride solution (2 × 40 mL). The aqueous phases were combined, extracted with a further portion of ethyl acetate (60 mL) and discarded. Both of the organic phases were combined, dried over magnesium sulphate, filtered and concentrated. The resulting brown oil was purified by flash column chromatography (silica gel; eluent, *n*-hexane) to yield 3.47 g of a yellow oil. This oil was dissolved in acetone (25 mL) and the solution was added dropwise over 5 min to a stirred mixture of potassium dichromate (5.82 g, 19.3 mmol), concentrated sulphuric acid (5.80 mL), water (17.5 mL) and acetone (50 mL) at 0 °C. This mixture was stirred and allowed to warm to 20 °C over a period of 18 h and then passed through a short silica gel column (silica gel; eluent, *n*-hexane, 250 mL). The organic solution was washed with an aqueous solution of sodium hydroxide (4 M, 100 mL) and discarded. Concentrated hydrochloric acid was added to the aqueous phase until it reached pH 2, and this solution was extracted sequentially with *n*-hexane (3 × 150 mL) and diethyl ether (100 mL). Combination of the organic washings, drying over magnesium sulphate, filtration and concentration of the filtrate under reduced pressure yielded a greeny-yellow solid. Purification of the crude product by column chromatography (eluent, *n*-hexane/diethyl ether/acetic acid (80:20:2 (v/v/v))) afforded **70** in 37% yield (1.86 g, 7.43 mmol, relative to compound **61**) as an amorphous white solid. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 0.00 (s, 2 H, SiC*H*$_2$Si), 0.27 (s, 6 H, Si(C*H*$_3$)$_2$), 0.28 (s, 6 H, Si(C*H*$_3$)$_2$), 7.67 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.6 Hz, $^5J_{H\text{-}H}$ = 0.8 Hz, *H*-7), 7.89 (dd, 1 H, $^3J_{H\text{-}H}$ = 7.6 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz, *H*-6), 8.10 (dd, 1 H, $^4J_{H\text{-}H}$ = 1.6 Hz, $^5J_{H\text{-}H}$ = 0.8 Hz, *H*-4), 12.90 (C(O)O*H*). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = –2.8 (Si*C*H$_2$Si), 0.3 (Si(*C*H$_3$)$_2$), 0.4 (Si(*C*H$_3$)$_2$), 129.1 (*C*-6), 130.7 (*C*-5), 131.8 (*C*-7), 132.0 (*C*-4), 150.2 (*C*-3a), 155.8 (*C*-7a), 167.8 (*C*(O)OH). — ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = 9.0, 9.1. — EI-MS: *m/z* (%) 250 (4) [M^+], 235 (100) [$M^+ - CH_3$].

$C_{12}H_{18}O_2Si_2$ (250.44)	Calculated:	C 57.55	H 7.24
	Found:	C 57.4	H 7.2

*3,3-Diethoxyprop-1-yne (**72**).*

This compound was commercially available (ABCR); it was distilled before use and stored at 4 °C under dry argon.

*1,1,3,3-Tetramethylindane (**73**).*

This compound was synthesised according to ref 73.

*4-Chloro-3-(trifluoromethyl)phenyl-bis(2-hydroxyethyl)-(2,4,6-trimethoxyphenyl)silane (**74**).*

A solution of 9-borabicyclo[3.3.1]nonane (4.98 g, 20.4 mmol (based on the 9-BBN dimer)) and **79** (7.00 g, 16.3 mmol) in tetrahydrofuran (80 mL) was stirred at 20 °C for 22 h, followed by sequential addition of water (16 mL) and an aqueous sodium hydroxide solution (4 M, 24 mL). Subsequently, an aqueous hydrogen peroxide solution (30 wt %, 32 mL) was added dropwise at 20 °C within 1 h to the stirred reaction mixture and the resulting mixture was then heated under reflux for 3 h. Following cooling to 20 °C, an aqueous solution of potassium carbonate (0.1 M, 75 mL) and dichloromethane (50 mL) were added. The organic layer was separated; the aqueous layer was then extracted with dichloromethane (2 × 50 mL) and discarded. Combination of the organic phases, drying over anhydrous sodium sulphate and concentration under reduced pressure yielded a light yellow oil. The byproduct cyclooctane-1,5-diol was separated from this crude product by bulb-to-bulb distillation (140 °C/0.07 mbar) and the residue was purified by column chromatography (Al_2O_3, Brockmann III; eluent, *n*-hexane/dichloromethane/ethanol (20:50:4 (v/v/v))) The relevant fractions were combined and the solvents were removed under reduced pressure to afford **74** in 90% yield as a colourless viscous oil (6.82 g, 14.7 mmol) that solidified after being left undisturbed at 20 °C for one month to give a colourless crystalline solid; mp 58 °C. — ^{1}H NMR (500.1 MHz, C_6D_6): δ = 1.60–1.78 (m, 6 H, SiC*H*$_2$CH$_2$OH and SiCH$_2$CH$_2$O*H*), 3.16 (s, 6 H, *o*-C*H*$_3$, $C_6H_2(OCH_3)_3$), 3.42 (s, 3 H, *p*-C*H*$_3$, $C_6H_2(OCH_3)_3$), 3.82 (m, 4 H, SiCH$_2$C*H*$_2$OH), 6.05 (s, 2 H, $C_6H_2(OCH_3)_3$), 7.23 (m, 1 H, *H*-6, $C_6H_3Cl(CF_3)$), 7.52 (m, 1 H, *H*-5, $C_6H_3Cl(CF_3)$), 8.21 (m, 1 H, *H*-2, $C_6H_3Cl(CF_3)$). — ^{13}C NMR (125.8 MHz, C_6D_6): δ = 20.4 (Si*C*H$_2$CH$_2$OH), 55.4 (*o*-*C*H$_3$, $C_6H_2(OCH_3)_3$), 54.7 (*p*-*C*H$_3$, $C_6H_2(OCH_3)_3$), 59.8 (SiCH$_2$*C*H$_2$OH), 91.1 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 100.3 (*C*-1, $C_6H_2(OCH_3)_3$), 124.2 (q, $^1J_{C\text{-}F}$ = 270.7 Hz, *C*F$_3$), 130.5 (*C*-6, $C_6H_3Cl(CF_3)$), 132.5 (m, *C*-4, $C_6H_3Cl(CF_3)$), 133.0 (q,

$^{3}J_{C\text{-}F}$ = 5.2 Hz *C*-2, $C_6H_3Cl(CF_3)$), 138.8 (m, *C*-5, $C_6H_3Cl(CF_3)$), 139.9 (*C*-1, $C_6H_3Cl(CF_3)$) *C*-3 $C_6H_3Cl(CF_3)$ not observed. — ^{19}F NMR (376.5 MHz, C_6D_6): δ = –61.7. — ^{29}Si NMR (99.4 MHz, C_6D_6): δ = −10.9.

$C_{20}H_{24}ClF_3O_5Si$ (464.94)	Calculated:	C 51.64	H 5.20
	Found:	C 52.0	H 5.2

*4,4-Bis(4-fluorophenyl)butylamine (**75**).*

A mixture of **81** (4.57 g, 11.7 mmol), hydrazine hydrate solution (80 wt %, 7 mL) and absolute ethanol (300 mL) was heated under reflux for 2 h and then allowed to cool to 20 °C. The white precipitate was removed by filtration and the resulting colourless solution was concentrated under reduced pressure to give an off-white solid. Diethyl ether (75 mL) and a half-saturated aqueous potassium carbonate solution (50 mL) were added to this residue. The resulting mixture was stirred for 10 min and the aqueous phase was separated, extracted with diethyl ether (2 × 50 mL) and discarded. Combination of the organic phases, drying over sodium sulphate, filtration and concentration under reduced pressure gave a yellow tinged oil. This oil was purified by bulb-to-bulb distillation (140–160 °C/0.05 mbar) to afford **75** in 79% yield (2.41 g, 9.22 mmol) as a colourless liquid. — ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.12 (br. s, 2 H, N*H*$_2$), 1.36 (m, 2 H, *H*-2, Butyl), 1.99 (m, 2 H, *H*-3, Butyl), 2.68 (m, 2 H, *H*-1, Butyl), 3.84 (m, 2 H, *H*-4, Butyl), 6.92–6.96 (m, 4 H, *H*-3/*H*-5, C_6H_4F), 7.12–7.15 (m, 4 H, *H*-2/*H*-6, C_6H_4F). — ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 26.6 (*C*-2, Butyl), 32.1 (*C*-3, Butyl), 42.1 (*C*-1, Butyl), 49.7 (*C*-4, Butyl), 115.2 (d, $^{2}J_{C\text{-}F}$ = 21.1 Hz, *C*-3/*C*-5, C_6H_4F), 129.0 (d, $^{3}J_{C\text{-}F}$ = 8.5 Hz, *C*-2/*C*-6, C_6H_4F), 140.50 (d, $^{4}J_{C\text{-}F}$ = 0.7 Hz, *C*-1, C_6H_4F), 140.53 (d, $^{4}J_{C\text{-}F}$ = 0.7 Hz, *C*-1', C_6H_4F), 161.3 (d, $^{1}J_{C\text{-}F}$ = 245.0 Hz, *C*-4, C_6H_4F). — ^{15}N NMR (50.7 MHz, $CDCl_3$): δ = –358.0. — ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −117.0. — EI-MS: *m/z* (%) 261 (25) [M^+], 216 (26), 45 (100).

$C_{16}H_{17}F_2N$ (261.31)	Calculated:	C 73.54	H 6.56	N 5.36
	Found:	C 73.5	H 6.6	N 5.4

*4-[4-chloro-3-(trifluoromethyl)phenyl]-1-[4,4-bis(4-Fluorophenyl)butyl]-4-(2,4,6trimethoxy-phenyl)-4-silapiperidine (**76**).*

Methanesulphonyl chloride (2.78 g, 24.3 mmol) was added dropwise at –25 °C within 5 min to a stirred solution of **74** (5.54 g, 11.9 mmol) and triethylamine (5 mL) in dichloromethane (80 mL). After the addition was complete, the reaction mixture was stirred at –25 °C for a further 25 min. The mixture was then allowed to warm to 20 °C, and *n*-pentane (80 mL) was

added. The resulting suspension was stirred at 20 °C for 5 min, and the precipitate was removed by filtration and discarded. The volatile components of the filtrate were removed under reduced pressure and the residue was dried *in vacuo* (0.1 mbar, 30 min). This crude intermediate was dissolved in acetonitrile (80 mL), then triethylamine (5 mL) and **75** (3.11 g, 11.9 mmol) were added at 20 °C, and the reaction mixture was stirred at this temperature for 3 d. The volatile components of the reaction mixture were removed under reduced pressure, followed by addition of dichloromethane (100 mL) and an aqueous solution of potassium carbonate (0.1 M, 50 mL). The organic layer was separated, the aqueous layer was extracted with dichloromethane (2 × 50 mL), the combined organic phases were dried over sodium sulphate and the solvent was removed under reduced pressure. The residue was purified by column chromatography (Al_2O_3, Brockmann III; eluent, *n*-hexane/ethyl acetate/triethylamine (70:30:1 (v/v/v))) to give a colourless viscous oil which crystallised upon drying under reduced pressure (0.1 mbar, 30 min) to afford **76** in 35% yield as a white crystalline solid (2.91 g, 4.22 mmol); mp 131 °C. — ^{1}H NMR (300.1 MHz, C_6D_6): δ = 1.45–1.55 (m, 2 H, *H*-2, Butyl), 1.62–1.89 (m, 4 H, SiCH_2CH_2N), 1.97–2.07 (m, 2 H, *H*-3, Butyl), 3.57 (t, 2 H, $^3J_{H\text{-}H}$ = 7.3 Hz, *H*-1, Butyl), 2.67–2.78 (m, 2 H SiCH$_2$CH_2N), 3.02–3.12 (m, 2 H SiCH$_2$CH_2N), 3.29 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.42 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 3.74 (t, 2 H, $^3J_{H\text{-}H}$ = 7.3 Hz, *H*-4, Butyl), 6.06 (s, 2 H, $C_6H_2(OCH_3)_3$), 6.87–7.01 (m, 8 H, *H*-2/*H*-6 and *H*-3/*H*-5, C_6H_4F), 7.22 (m, 1 H, *H*-6, $C_6H_3Cl(CF_3)$), 7.67 (m, 1 H, *H*-5, $C_6H_3Cl(CF_3)$), 8.40 (m, 1 H, *H*-2, $C_6H_3Cl(CF_3)$). — ^{13}C NMR (75.5 MHz, C_6D_6): δ = 14.5 (Si*C*H$_2$CH$_2$N), 26.5 (*C*-2, Butyl), 34.0 (*C*-3, Butyl), 49.9 (*C*-4, Butyl), 53.4 (SiCH$_2$*C*H$_2$N), 54.6 (*o*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 54.7 (*p*-O*C*H$_3$, $C_6H_2(OCH_3)_3$), 58.6 (*C*-1, Butyl), 91.0 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 101.3 (*C*-1, $C_6H_2(OCH_3)_3$), 115.5 (d, $^2J_{C\text{-}F}$ = 20.0 Hz, *C*-3/*C*-5, C_6H_4F), 124.2 (q, $^1J_{C\text{-}F}$ = 273.3 Hz, *C*F$_3$), 129.5 (d, $^3J_{C\text{-}F}$ = 7.7 Hz, *C*-2/*C*-6, C_6H_4F), 130.8 (*C*-6, $C_6H_3Cl(CF_3)$), 132.9 (q, $^3J_{C\text{-}F}$ = 2.3 Hz, *C*-4, $C_6H_3Cl(CF_3)$), 133.5 (q, $^3J_{C\text{-}F}$ = 5.2 Hz, *C*-2, $C_6H_3Cl(CF_3)$), 139.1 (*C*-1, $C_6H_3Cl(CF_3)$), 139.2 (q, $^4J_{C\text{-}F}$ = 1.1 Hz, *C*-5, $C_6H_3Cl(CF_3)$), 141.11 (d, $^4J_{C\text{-}F}$ = 0.7 Hz, *C*-1, C_6H_4F), 141.15 (d, $^4J_{C\text{-}F}$ = 0.7 Hz, *C*-1', C_6H_4F), 161.8 (d, $^1J_{C\text{-}F}$ = 244.4 Hz, *C*-4, C_6H_4F), 164.8 (*C*-4, $C_6H_2(OCH_3)_3$), 166.9 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$) *C*-3 $C_6H_3Cl(CF_3)$ not observed. — ^{15}N NMR (50.7 MHz, C_6D_6): δ = –330.6. — ^{19}F NMR (376.5 MHz, C_6D_6): δ = −116.8 (2 F, C_6H_4F), –61.8 (3 F, CF_3). — ^{29}Si NMR (59.6 MHz, C_6D_6): δ = −17.0.

$C_{36}H_{37}ClF_5NO_3Si$ (690.22)	Calculated:	C 62.65	H 5.40	N 2.03
	Found:	C 62.7	H 5.4	N 2.0

*Triethoxy(vinyl)silane (**77**).*

This compound was commercially available (Johnson Matthey) and was distilled before use.

*[4-Chloro-3-(trifluoromethyl)phenyl]diethoxyvinylsilane (**78**).*

A solution of [4-chloro-3-(trifluoromethyl)phenyl]magnesium bromide (prepared from 1-bromo-4-chloro-(3-trifluoromethyl)benzene (25.0 g, 96.4 mmol) and magnesium turnings (2.44 g, 100 mmol)) in diethyl ether (150 mL) was added dropwise at 0 °C within 1 h to a stirred solution of **77** (67.9 g, 357 mmol) in diethyl ether (200 mL). After the addition was complete, the reaction mixture was allowed to warm to 20 °C and was then stirred at this temperature for a further 17 h. *n*-Pentane (350 mL) was added, and the resulting suspension was stirred at 20 °C for 1 h. The precipitate was removed by filtration, washed with *n*-pentane (100 mL), and discarded. The filtrate and the wash solutions were combined, the solvents were removed under reduced pressure, and the residue was distilled under reduced pressure to give 45.0 g (236 mmol) of unreacted starting material **77** (72–74 °C/48 mbar). The higher boiling residue was purified by bulb-to-bulb distillation (88–92 °C/0.1 mbar) to afford **78** in 53% yield as a colourless liquid (16.6 g, 51.1 mmol). — ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 1.23 (δ_X), 3.80 (δ_A) and 3.85 (δ_B) (ABX_3 system, $^{2}J_{A\text{-}B}$ = 9.3 Hz, $^{3}J_{A\text{-}X,B\text{-}X}$ = 7.0 Hz, 10 H, $SiOCH_AH_BC(H_X)_3$), 5.93 (δ_A), 6.08 (δ_M) and 6.19 (δ_X) (AMX system, $^{2}J_{A\text{-}X}$ = 4.6 Hz, $^{3}J_{A\text{-}M}$ = 20.1 Hz, $^{3}J_{M\text{-}X}$ = 14.6 Hz, 3 H, $SiCH_M{=}CH_XH_A$), 7.49 (m, 1 H, *H*-6, $SiC_6H_3Cl(CF_3)$), 7.71 (m, 1 H, *H*-5, $SiC_6H_3Cl(CF_3)$), 7.92 (m, 1 H, *H*-6, $SiC_6H_3Cl(CF_3)$). — ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.1 ($SiOCH_2CH_3$), 58.5 ($SiOCH_2CH_3$), 123.0 (q, $^{1}J_{C\text{-}F}$ = 273.4 Hz, CF_3), 127.8 (q, $^{2}J_{C\text{-}F}$ = 30.6 Hz *C*-3, $SiC_6H_3Cl(CF_3)$), 130.8 (*C*-6, $SiC_6H_3Cl(CF_3)$), 130.9 ($SiCH{=}CH_2$), 132.9 (*C*-1, $SiC_6H_3Cl(CF_3)$), 133.3 (q, $^{3}J_{C\text{-}F}$ = 5.7 Hz *C*-2, $SiC_6H_3Cl(CF_3)$), 134.4 (m, *C*-4, $SiC_6H_3Cl(CF_3)$), 138.0 ($SiCH{=}CH_2$), 139.0 (m, *C*-5, $SiC_6H_3Cl(CF_3)$). — ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –62.5. — ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ = −34.7. — EI-MS: *m/z* (%) 324 (1) [M^+], 305 (4) [M^+ − F], 297 (25) [M^+ − $CH{=}CH_2$], 152 (100).

$C_{13}H_{16}ClF_3O_2Si$ (324.80)	Calculated:	C 48.07	H 4.97
	Found:	C 48.1	H 5.0

*[4-Chloro-3-(trifluoromethyl)phenyl](2,4,6-trimethoxyphenyl)divinylsilane (**79**).*

A solution of *n*-butyllithium in hexanes (2.5 M, 40 mL, 100 mmol of *n*-BuLi) was added dropwise at 20 °C within 15 min to a stirred mixture of 1,3,5-trimethoxybenzene (13.3 g, 79.1 mmol), 1,2-bis(dimethylamino)ethane (TMEDA; 13 mL), *n*-hexane (15 mL) and diethyl

ether (50 mL). The resulting suspension was stirred at 20 °C for 21 h and was then added dropwise at 0 °C within 30 min to a stirred solution of **78** (24.5 g, 75.6 mmol) in diethyl ether (80 mL). When the addition was complete, the resulting mixture was stirred at 20 °C for 21 h. Subsequently, a solution of vinylmagnesium chloride (15 wt %, d = 0.97 g/mL; 68.0 mL, 114 mmol of CH_2=CHMgCl) in tetrahydrofuran was added dropwise at 20 °C within 25 min to the reaction mixture. After the addition was complete, the reaction mixture was stirred at 20 °C for 2 d, followed by sequential addition of ice (50 g) and water (100 mL). The mixture was stirred for 30 min, and the aqueous layer was separated and extracted with diethyl ether (3 × 150 mL). The organic extracts were combined, dried over sodium sulphate, filtered and concentrated under reduced pressure to yield a brown oil. The lower boiling contaminants were removed by bulb-to-bulb distillation (100 °C/0.4 mbar) and the remaining oil was purified by column chromatography (Al_2O_3, Brockmann III; eluent, *n*-hexane/dichloromethane/triethylamine (100:10:0.1 (v/v/v))) to give **79** in 48% yield as a colourless viscous liquid (15.7 g, 36.6 mmol). — ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.58 (s, 6 H, *o*-CH_3, $C_6H_2(OCH_3)_3$), 3.81 (s, 3 H, *p*-CH_3, $C_6H_2(OCH_3)_3$), 5.61 (δ_A), 6.09 (δ_M) and 6.53 (δ_X) (AMX system, $^2J_{A\text{-}X}$ = 3.3 Hz, $^3J_{A\text{-}M}$ = 20.7 Hz, $^3J_{M\text{-}X}$ = 14.1 Hz, 6 H, SiCH_M=C$H_X H_A$) 6.06 (s, 2 H, $C_6H_2(OCH_3)_3$), 7.39 (m, 1 H, *H*-6, $C_6H_3Cl(CF_3)$), 7.56 (m, 1 H, *H*-5, $C_6H_3Cl(CF_3)$), 7.78 (m, 1 H, *H*-2, $C_6H_3Cl(CF_3)$). — ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.1 (*o*-CH_3, $C_6H_2(OCH_3)_3$), 55.2 (*p*-CH_3, $C_6H_2(OCH_3)_3$), 90.8 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 99.8 (*C*-1, $C_6H_2(OCH_3)_3$), 123.2 (q, $^1J_{C\text{-}F}$ = 273.3 Hz, CF_3), 127.0 (q, $^2J_{C\text{-}F}$ = 30.6 Hz, *C*-3, $C_6H_3Cl(CF_3)$), 130.0 (*C*-6, $C_6H_3Cl(CF_3)$), 132.3 (q, $^3J_{C\text{-}F}$ = 1.9 Hz, *C*-4, $C_6H_3Cl(CF_3)$), 133.5 (q, $^3J_{C\text{-}F}$ = 5.7 Hz, *C*-2, $C_6H_3Cl(CF_3)$), 133.7 (SiCH=CH_2), 135.6 (SiCH=CH_2), 137.1 (*C*-1, $C_6H_3Cl(CF_3)$), 139.3 (m, *C*-5, $C_6H_3Cl(CF_3)$), 164.4 (*C*-4, $C_6H_2(OCH_3)_3$), 166.6 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). — ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –62.1. — ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ = −24.7. — EI-MS: *m/z* (%) 428 (17) [M^+], 413 (100) [$M^+ - CH_3$].

$C_{20}H_{20}ClF_3O_3Si$ (428.91)	Calculated:	C 56.01	H 4.70
	Found:	C 56.0	H 4.6

*4,4'-(4-Chlorobutan-1,1-diyl)bis(fluorobenzene) (**80**).*

This compound was commercially available (Acros Organics) and was distilled before use.

*2-(4,4-Bis(4-fluorophenyl)butyl)isoindoline-1,3-dione (**81**).*

A mixture of potassium phthalimide (5.23 g, 28.2 mmol), compound **80** (7.50 g, 26.7 mmol) and *N*,*N*-dimethylformamide (30 mL) was heated under reflux for 3 h and then allowed to

cool to 20 °C. The reaction mixture was diluted with dichloromethane (40 mL) and then water (100 mL) was added. The aqueous phase was separated, extracted with dichloromethane (2 × 30 mL) and discarded. Combination of the organic phases, washing with an aqueous sodium hydroxide solution (0.1 M, 40 mL), drying over magnesium sulphate and concentration under reduced pressure gave a yellow oil. This residue was passed through a short silica gel column (eluent, *n*-hexane) and the solvents were evaporated under reduced pressure to give a thick, colourless, sticky, resinous substance, which crystallised on standing at ambient temperature for one month to afford **81** in 73% yield (7.67 g, 19.6 mmol) as a colourless crystalline solid; mp 80 °C. — ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 1.43–1.49 (m, 2 H, *H*-2, Butyl), 1.97–2.07 (m, 2 H, *H*-3, Butyl), 3.57 (m, 2 H, *H*-1, Butyl), 3.99 (m, 2 H, *H*-4, Butyl), 7.04–7.07 (m, 4 H, *H*-3/*H*-5, C_6H_5F), 7.27–7.32 (m, 4 H, *H*-2/*H*-6, C_6H_4F), 7.78–7.84 (m, 4 H, $C_8H_4NO_2$). — ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 26.6 (*C*-2, Butyl), 32.1 (*C*-3, Butyl), 37.2 (*C*-1, Butyl), 48.4 (*C*-4, Butyl), 115.0 (d, $^{2}J_{C\text{-}F}$ = 21.1 Hz, *C*-3/*C*-5, C_6H_4F), 122.9 (*C*-4/*C*-7 or *C*-5/*C*-6, $C_8H_4NO_2$), 129.2 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz, *C*-2/*C*-6, C_6H_4F), 131.6 (*C*-3a/*C*-7a, $C_8H_4NO_2$), 134.3 (*C*-4/*C*-7 or *C*-5/*C*-6, $C_8H_4NO_2$), 140.9 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz, *C*-1, C_6H_4F), 160.6 (d, $^{1}J_{C\text{-}F}$ = 242.2 Hz, *C*-4, C_6H_4F), 167.9 (*C*(O)N). — ^{15}N NMR (30.4 MHz, [D$_6$]DMSO): δ = –218.9. — ^{19}F NMR (376.5 MHz, [D$_6$]DMSO): δ = −117.1. — EI-MS: *m/z* (%) 391 (4) [M$^+$], 203 (100).

$C_{24}H_{19}NO_2F_2$ (391.41)	Calculated:	C 73.65	H 4.89	N 3.58
	Found:	C 73.6	H 4.9	N 3.6

*3,3-Diphenyldihydrofuran-2-yl(dimethyliminium)bromide (**82**).*

This compound was synthesised according to ref 30.

*(4-Chlorophenyl)(2,6-dimethoxyphenyl)bis(2-hydroxyethyl)silane (**84**).*

A solution of 9-borabicyclo[3.3.1]nonane (4.04 g, 16.6 mmol (based on the 9-BBN dimer)) and **87** (4.39 g, 13.3 mmol) in tetrahydrofuran (70 mL) was stirred at 20 °C for 19 h, followed by the addition of water (30 mL) and an aqueous sodium hydroxide solution (4 M, 30 mL). Subsequently, an aqueous hydrogen peroxide solution (30 wt %, 30 mL) was added dropwise at 20 °C within 30 min to the stirred reaction mixture and the resulting mixture was then heated under reflux for 3 h. Following cooling to 20 °C, an aqueous solution of potassium carbonate (0.1 M, 130 mL) and dichloromethane (50 mL) were added. The organic layer was separated; the aqueous layer was then extracted with dichloromethane (3 × 50 mL) and discarded. Combination of the organic phases, drying over anhydrous

sodium sulphate and concentration under reduced pressure yielded a light yellow oil. The byproduct cyclooctane-1,5-diol was separated from the crude product by bulb-to-bulb distillation (160–170 °C/0.46 mbar), and the residue was purified by column chromatography (Al_2O_3, Brockmann III; eluent, *n*-hexane/dichloromethane/methanol (20:50:4 (v/v/v))). The relevant fractions were combined and the solvents were removed under reduced pressure to afford **74** in 62% yield as a colourless viscous oil (3.00 g, 8.18 mmol) that solidified after being left undisturbed at 20 °C for 8 d to give a white crystalline solid; mp 78 °C. — ^{1}H NMR (300.1 MHz, [D$_6$]DMSO): δ = 1.35–1.44 (m, 4 H, SiC*H*$_2$CH$_2$OH), 3.41 (m, 4 H, SiCH$_2$C*H*$_2$OH), 3.58 (s, 6 H, SiC$_6$H$_3$(OC*H*$_3$)$_2$), 4.30 (t, $^3J_{H\text{-}H}$ = 5.0 Hz, 2 H, O*H*), 6.57 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2 H, *H*-3/*H*-5, SiC$_6$H$_3$(OCH$_3$)$_2$), 7.30–7.39 (m, 5 H, *H*-4, SiC$_6$H$_3$(OCH$_3$)$_2$), *H*-2/*H*-6 and *H*-3/*H*-5, SiC$_6$H$_4$Cl). ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 20.1 (Si*C*H$_2$CH$_2$OH), 55.2 (SiC$_6$H$_3$(O*C*H$_3$)$_2$), 57.9 (SiCH$_2$*C*H$_2$OH), 104.0 (*C*-3/*C*-5, SiC$_6$H$_3$(OCH$_3$)$_2$), 108.7 (*C*-1, SiC$_6$H$_3$(OCH$_3$)$_2$), 127.3 (*C*-2/*C*-6 or *C*-3/*C*-5, SiC$_6$H$_4$Cl), 137.6 (*C*-2/*C*-6 or *C*-3/*C*-5, SiC$_6$H$_4$Cl), 132.6 (*C*-1, SiC$_6$H$_4$Cl), 133.3 (*C*-4, SiC$_6$H$_3$(OCH$_3$)$_2$), 137.6 (*C*-4, SiC$_6$H$_4$Cl), (*C*-2/*C*-6, SiC$_6$H$_3$(OCH$_3$)$_2$). — ^{29}Si NMR (59.6 MHz, [D$_6$]DMSO): δ = –12.9.

$C_{18}H_{23}ClO_4Si$ (366.91)	Calculated:	C 58.92	H 6.32
	Found:	C 58.9	H 6.6

*1-Allyl-4-(4-chlorophenyl)-4-(2,6-dimethoxyphenyl)-4-silapiperidine (**85**)*

Methanesulphonyl chloride (916 mg, 8.00 mmol) was added dropwise at –25 °C within 5 min to a stirred solution of **84** (1.17 g, 3.19 mmol) and triethylamine (1 mL) in dichloromethane (70 mL). After the addition was complete, the reaction mixture was stirred for a further 1.5 h at –25 °C, the mixture was then allowed to warm to 20 °C, and allyl amine (17.6 g, 308 mmol) was added. The resulting mixture was stirred at 20 °C temperature for 16 h. The volatile components of the reaction mixture were then removed under reduced pressure, followed by addition of ethyl acetate (40 mL) and an aqueous solution of potassium carbonate (0.1 M, 50 mL). The organic layer was separated, the aqueous layer was extracted with ethyl acetate (3 × 40 mL), the combined organic phases were dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure. The residue was purified by column chromatography (Al_2O_3, Brockmann III; eluent, *n*-hexane/ethyl acetate/triethylamine (70:30:1 (v/v/v))) to give a colourless viscous oil which crystallised on standing at ambient temperature for 1 d to afford **85** in 22% yield as a colourless crystalline solid (276 mg, 711 μmol); mp 81 °C. — ^{1}H NMR (300.1 MHz, C$_6$D$_6$): δ = 1.66–1.90 (m,

4 H, SiC*H*$_2$CH$_2$N), 2.80 (m, 2 H, SiCH$_2$C*H*$_2$N), 3.10–3.31 (m, 4 H, NC*H*$_2$CH=CH$_2$ and SiCH$_2$C*H*$_2$N), 3.31 (s, 6 H, SiC$_6$H$_3$(OC*H*$_3$)$_2$), 5.23 (m, 2 H, NCH$_2$CH=C*H*$_2$), 6.09 (m, 1 H, NCH$_2$C*H*=CH$_2$), 6.34 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, *H*-3/*H*-5, SiC$_6$H$_3$(OCH$_3$)$_2$), 7.24 (t, $^3J_{H\text{-}H}$ = 8.2 Hz, *H*-4, SiC$_6$H$_3$(OCH$_3$)$_2$), 7.32 (m, 2 H, *H*-2/*H*-6 or *H*-3/*H*-5, SiC$_6$H$_4$Cl), 7.67 (m, 2 H, *H*-2/*H*-6 or *H*-3/*H*-5, SiC$_6$H$_4$Cl). — ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ = 14.8 (Si*C*H$_2$CH$_2$N), 53.3 (SiCH$_2$*C*H$_2$N), 54.8 (SiC$_6$H$_3$(O*C*H$_3$)$_2$), 62.4 (N*C*H$_2$CH=CH$_2$), 103.9 (*C*-3/*C*-5, SiC$_6$H$_3$(OCH$_3$)$_2$), 111.0 (*C*-1, SiC$_6$H$_3$(OCH$_3$)$_2$), 116.2 (NCH$_2$CH=*C*H$_2$), 128.1 (*C*-3/*C*-5 or *C*-2/*C*-6, SiC$_6$H$_4$Cl), 132.4 (*C*-4, SiC$_6$H$_3$(OCH$_3$)$_2$), 135.2 (*C*-1, SiC$_6$H$_4$Cl), 136.3 (*C*-3/*C*-5 or *C*-2/*C*-6, SiC$_6$H$_4$Cl), 137.2 (*C*-4, SiC$_6$H$_4$Cl), 137.5 (NCH$_2$*C*H=CH$_2$), 165.9 (*C*-2/*C*-6, SiC$_6$H$_3$(OCH$_3$)$_2$). — ^{15}N NMR (13.4 MHz, C$_6$D$_6$): δ = –330.7. — ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ = –17.2.

$C_{21}H_{26}ClNO_2Si$ (387.98)	Calculated:	C 65.01	H 6.75	N 3.61
	Found:	C 64.9	H 6.9	N 3.9

*(4-Chlorophenyl)diethoxyvinylsilane (**86**).*

This compound was synthesised according to ref 32; the synthesis was carried out by M. Geyer, Institut für Anorganische Chemie, Universität Würzburg.

*(4-Chlorophenyl)(2,6-dimethoxyphenyl)divinylsilane (**87**)*

A solution of *n*-butyllithium in hexanes (2.5 M, 8.18 mL, 20.5 mmol of *n*-BuLi) was added dropwise at 20 °C within 15 min to a stirred mixture of 1,3-dimethoxybenzene (2.82 g, 20.4 mmol), 1,2-bis(dimethylamino)ethane (TMEDA; 2.42 g, 20.8 mmol) and *n*-hexane (40 mL). The resulting suspension was stirred at 20 °C for 15 h and was then added dropwise at 0 °C within 10 min to a stirred solution of **86** (5.00 g, 19.5 mmol) in diethyl ether (20 mL). When the addition was complete, the resulting mixture was stirred under reflux for 2.5 h. Subsequently, a solution of vinylmagnesium bromide (0.7 M, 36.1 mL, 25.3 mmol of CH$_2$=CHMgBr) in tetrahydrofuran was added dropwise at 20 °C within 1 h to the stirred reaction mixture. After the addition was complete, the reaction mixture was stirred under reflux for 15 h. Following cooling to 20 °C, a saturated solution of sodium carbonate (40 mL) and diethylether (50 mL) were added and the aqueous layer was separated and extracted with diethyl ether (3 × 50 mL). The organic extracts were combined, dried over sodium sulphate, filtered and concentrated under reduced pressure to yield a brown oil, which was purified by bulb-to-bulb distillation (150–155 °C/0.43 mbar) to give **87** in 68% yield as a colourless viscous liquid (4.39 g, 13.3 mmol). — ^{1}H NMR (500.1 MHz, C$_6$D$_6$):

δ = 3.31 (s, 6 H, $SiC_6H_3(OCH_3)_2$), 5.94 (δ_A), 6.28 (δ_M) and 6.93 (δ_X) (AMX system, $^2J_{A\text{-}M}$ = 5.0 Hz, $^3J_{M\text{-}X}$ = 15.0 Hz, $^3J_{A\text{-}X}$ = 20.0 Hz, 6 H, $SiCH_X{=}CH_MH_A$), 6.40 (d, $^2J_{H\text{-}H}$ = 5.0 Hz, 2 H, *H*-3/*H*-5, $SiC_6H_3(OCH_3)_2$), 7.28–7.33 (m, 3 H, *H*-2/*H*-6, SiC_6H_4Cl and *H*-4, $SiC_6H_3(OCH_3)_2$), 7.61 (m, 2 H, *H*-2/*H*-6, $SiC_6H_3(OCH_3)_2$). — ^{13}C NMR (125.8 MHz, C_6D_6): δ = 54.9 ($SiC_6H_3(OCH_3)_2$), 104.3 (*C*-3/*C*-5, $SiC_6H_3(OCH_3)_2$), 127.9 (*C*-3/*C*-5, SiC_6H_4Cl), 132.9 (*C*-4, $SiC_6H_4(OCH_3)_2$), 133.4 ($SiCH{=}CH_2$), 135.1 (*C*-4, SiC_6H_5Cl), 135.7 (*C*-1, $SiC_6H_4(OCH_3)_2$), 136.8 (*C*-2/*C*-7, SiC_6H_4Cl), 136.9 ($SiCH{=}CH_2$). — ^{29}Si NMR (99.4 MHz, C_6D_6): δ = –24.0.

$C_{18}H_{19}ClO_2Si$ (330.89)	Calculated:	C 65.34	H 5.79
	Found:	C 65.6	H 5.8

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Appendix A: Abbreviations

13*c*RA	13-*cis* Retinoic Acid
9-BBN	9-Borabicyclo[3.3.1]nonane
9*c*RA	9-*cis* Retinoic Acid
Ac	Acetyl
ATRA	all-*trans* Retinoic Acid
B(pin)	4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl
b.p.	Boiling Point
Benz	Benzoic Acid
Benz'	Methyl Benzoate
Bu	*n*-Butyl
CI	Chemical Ionisation
COSY	Correlated Spectroscopy
d	Day(s)
DEPT	Distortionless Enhancement by Polarisation Transfer
DMOP	2,6-Dimethoxyphenyl
DMP	Dess-Martin Perioindane
DMSO	Dimethylsulphoxide
DPPA	Diphenoxyphosphoryl Azide
dppf	1,1'-Bis(diphenylphosphino)ferrocene
DSC	Differential Scanning Calorimetry
EC23	4-(5,5,8,8-Tetramethyl-5,6,7,8-tetrahydronaphthalen-2-ylethynyl)benzoic Acid
EI	Electron Impact Ionisation
ESI	Electrospray Ionisation
Et	Ethyl
GC	Gas Chromatography
h	Hour(s)
HMBC	Heteronuclear Multiple Bond Correlation
HMQC	Heteronuclear Multiple Quantum Coherence
HRMS	High Resolution Mass Spectrometry
IBMK	Isobutylmethylketone (4-Methylpentan-2-one)

Ind	Indan-5-yl
Ind’	1,3-Disilaindan-5-yl
Ind’’	2-Oxa-1,3-disilaindan-5-yl
m.p.	Melting Point
Me	Methyl
min	Minute(s)
MMOP	4-Methoxyphenyl
Ms	Mesyl
MS	Mass Spectrometry
Naph	Naphthoic Acid
Naph’	Methyl Naphthoate
NMR	Nuclear Magnetic Resonance
Ph	Phenyl
rac	Racemic
RAR	Retinoic Acid Receptor
RP-MPLC	Reversed Phase Medium Pressure Liquid Chromatography
RXR	Retinoid X Receptor
THN	1,2,3,4-Tetrahydro-1,4-disilanaphthalen-6-yl
TMEDA	Tetramethylethylenediamine
TMS	Tetramethylsilane
TMOP	2,4,6-Trimethoxyphenyl
TTNN	6-(5,5,8,8-Tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-2-naphthoic Acid
TTNPB	4-[(*E*)-2-(5,6,7,8-Tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-1-propenyl] Benzoic Acid

br.	Broad
d	Doublet
dd	Doublet of Doublets
J	Coupling Constant
m	Multiplet
q	Quartet
s	Singlet
t	Triplet

Appendix B: Crystal Structure Data

Table A1. Crystallographic data and experimental parameters for the crystal structure analyses of **9**, **10** and **16a**.

	9	**10**	**16a**
empirical formula	$C_{16}H_{28}OSi_3$	$C_{19}H_{35}BO_2Si_3$	$C_{22}H_{22}O_2$
formula mass, g mol^{-1}	320.65	390.55	318.40
collection *T*, K	173(2)	173(2)	173(2)
$\lambda(Mo_{K\alpha})$, Å	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic
space group (No.)	$P2_1/c$ (14)	$P2_1$ (4)	$P\bar{1}$ (1)
a, Å	10.8718(13)	9.9177(17)	6.6502(19)
b, Å	35.093(4)	11.9574(12)	8.0811(19)
c, Å	10.3208(12)	10.3355(16)	18.466(5)
α, deg	90	90	80.28(3)
β, deg	89.999(14)	98.14(2)	84.36(3)
γ, deg	90	90	66.24(3)
V, Å^3	3937.6(8)	1213.3(3)	894.7(4)
Z	8	2	2
D_{calcd}, g cm^{-3}	1.082	1.069	1.182
μ, mm^{-1}	0.236	0.205	0.074
F(000)	1392	424	340
crystal dimensions, mm	0.5 × 0.5 × 0.3	0.5 × 0.4 × 0.3	0.50 × 0.20 × 0.02
2θ range, deg	4.40−55.92	7.90−58.24	5.56–58.34
index ranges	$-14 \le h \le 14$,	$-13 \le h \le 13$,	$-9 \le h \le 9$,
	$-46 \le k \le 46$,	$-15 \le k \le 15$,	$-10 \le k \le 10$,
	$-13 \le l \le 13$	$-14 \le l \le 14$	$-25 \le l \le 25$
no. of collected reflections	47192	16219	12799
no. of independent reflections	9388	6149	4485
R_{int}	0.0518	0.0295	0.0927
no. of reflections used	9388	6149	4485
no. of parameters	378	273	232
no. of restraints	0	67	12
S[a]	1.050	1.070	0.900
weight parameters *a*/*b*[b]	0.0672/0.9943	0.0824/0.2881	0.1005/0.0000
R_1[c] [$I > 2\sigma(I)$]	0.0438	0.0454	0.0579
wR_2[d] (all data)	0.1091	0.1270	0.1664
max./min. residual electron density, e Å^{-3}	+0.588/−0.295	+0.763/−0.391	+0.368/−0.261

[a] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; *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] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Table A2. Crystallographic data and experimental parameters for the crystal structure analyses of **16b**, **18b** and **26**.

	16b	**18b**	**26**
empirical formula	$C_{20}H_{22}O_2Si_2$	$C_{22}H_{24}O_2Si_2$	$C_{15}H_{28}OSi_3$
formula mass, g mol^{-1}	350.56	376.59	308.64
collection T, K	173(2)	173(2)	100(2)
λ(Mo$_{K\alpha}$), Å	0.71073	0.71073	0.71073
crystal system	orthorhombic	orthorhombic	monoclinic
space group (No.)	*Pbca* (61)	*Pbca* (61)	$P2_1/c$ (14)
a, Å	9.7328(10)	10.3734(6)	13.3164(13)
b, Å	11.2756(8)	11.1736(7)	8.2981(8)
c, Å	35.715(4)	36.103(2)	34.292(3)
β, deg	90	90	93.436(5)
V, Å^3	3919.5(6)	4184.6(4)	3782.5(6)
Z	8	8	8
D_{calcd}, g cm^{-3}	1.188	1.196	1.084
μ, mm^{-1}	0.190	0.182	0.244
F(000)	1488	1600	1344
crystal dimensions, mm	0.5 × 0.4 × 0.1	0.4 × 0.3 × 0.2	0.3 × 0.1 × 0.04
2θ range, deg	4.76–53.84	4.52–53.72	3.06−56.68
index ranges	$-12 \le h \le 12$, $-13 \le k \le 12$, $-45 \le l \le 26$	$-13 \le h \le 13$, $-14 \le k \le 14$, $-45 \le l \le 45$	$-17 \le h \le 16$, $-11 \le k \le 11$, $-45 \le l \le 45$
no. of collected reflections	19094	30629	79455
no. of independent reflections	3971	4474	9416
R_{int}	0.0456	0.0654	0.0380
no. of reflections used	3971	4474	9416
no. of parameters	224	240	365
no. of restraints	0	0	0
S^a	1.014	1.03	1.052
weight parameters a/b^b	0.0665/0.2200	0.054/2.6001	0.0383/1.6447
$R_1{}^c$ [$I > 2\sigma(I)$]	0.0402	0.0469	0.0308
$wR_2{}^d$ (all data)	0.1109	0.1229	0.0836
max./min. residual electron density, e Å^{-3}	+0.232/−0.284	+0.271/–0.301	+0.512/−0.305

[a] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; 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] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Table A3. Crystallographic data and experimental parameters for the crystal structure analyses of **43**, **45** and **51**.

	43	**45**	**51**
empirical formula	$C_{23}H_{24}O_2$	$C_{20}H_{22}O_3Si_2$	$C_{18}H_{21}BO_4$
formula mass, g mol^{-1}	332.42	366.56	312.16
collection T, K	100(2)	100(2)	173(2)
λ(Mo$_{K\alpha}$), Å	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	orthorhombic
space group (No.)	$P2_1/c$ (14)	$C2$ (5)	$Pna2_1$ (33)
a, Å	20.5765(9)	60.024(5)	22.368(3)
b, Å	11.1441(5)	11.4478(8)	12.108(2)
c, Å	8.1245(4)	8.7407(6)	6.0975(7)
β, deg	98.9270(10)	95.534(4)	90
V, Å^3	1840.43(15)	5978.1(7)	1651.4(4)
Z	4	12	4
D_{calcd}, g cm^{-3}	1.200	1.222	1.256
μ, mm^{-1}	0.075	0.193	0.086
F(000)	712	2328	664
crystal dimensions, mm	0.30 × 0.22 × 0.10	0.47 × 0.20 × 0.03	0.5 × 0.2 × 0.2
2θ range, deg	2.00−66.28	2.72−52.74	6.42–58.44
index ranges	$-31 \le h \le 31$, $-17 \le k \le 16$, $-9 \le l \le 12$	$-72 \le h \le 74$, $-14 \le k \le 14$, $-10 \le l \le 10$	$-30 \le h \le 30$, $-16 \le k \le 16$, $-8 \le l \le 8$
no. of collected reflections	38468	39207	22231
no. of independent reflections	6772	12031	4437
R_{int}	0.0313	0.0454	0.0401
no. of reflections used	6772	12031	4437
no. of parameters	231	692	213
no. of restraints	0	1	1
S^a	1.072	1.020	1.083
weight parameters a/b^b	0.0565/0.5356	0.0909/2.7879	0.0456/0.2541
$R_1{}^c$ [$I > 2\sigma(I)$]	0.0422	0.0549	0.0357
$wR_2{}^d$ (all data)	0.1216	0.1458	0.0956
absolute structure parameter		0.00(15)	
max./min. residual electron density, e Å^{-3}	+0.558/−0.184	+1.103/−0.295	+0.182/–0.140

[a] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; 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] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Table A4. Crystallographic data and experimental parameters for the crystal structure analyses of **64**, **65** and **69**.

	64	**65**	**69**
empirical formula	$C_{14}H_{26}Si_3$	$C_{13}H_{24}OSi_3$	$C_{13}H_{20}O_2Si_2$
formula mass, g mol^{-1}	278.62	280.59	264.47
collection T, K	173(2)	173(2)	173(2)
λ(Mo$_{K\alpha}$), Å	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group (No.)	$P2_1/c$ (14)	$P2_1$ (4)	$P2_1/c$ (14)
a, Å	14.635(4)	6.2270(8)	12.8871(17)
b, Å	10.5599(16)	10.0764(18)	8.8099(11)
c, Å	11.643(3)	14.0512(19)	14.4156(14)
β, deg	94.50(3)	91.347(16)	116.374(12)
V, Å^3	1793.9(7)	881.4(2)	1466.3(3)
Z	4	2	4
D_{calcd}, g cm^{-3}	1.032	1.057	1.198
μ, mm^{-1}	0.247	0.256	0.231
F(000)	608	304	568
crystal dimensions, mm	0.50 × 0.30 × 0.15	0.5 × 0.2 × 0.2	0.4 × 0.4 × 0.2
2θ range, deg	4.76–54.96	5.80–59.04	5.60−58.50
index ranges	$-19 \le h \le 19$, $-12 \le k \le 12$, $-15 \le l \le 15$	$-8 \le h \le 8$, $-13 \le k \le 13$, $-19 \le l \le 19$	$-17 \le h \le 17$, $-11 \le k \le 12$, $-19 \le l \le 19$
no. of collected reflections	21879	11609	18328
no. of independent reflections	3958	4562	3938
R_{int}	0.0949	0.0605	0.0410
no. of reflections used	3958	4562	3938
no. of parameters	161	193	180
no. of restraints	0	51	0
S^a	0.913	1.053	1.060
weight parameters a/b^b	0.0588/0.0000	0.0778/0.0000	0.0769/0.3474
$R_1{}^c$ [$I > 2\sigma(I)$]	0.0425	0.0433	0.0446
$wR_2{}^d$ (all data)	0.1084	0.1232	0.1252
absolute structure parameter		0.01(13)	
max./min. residual electron density, e Å^{-3}	+0.357/−0.278	+0.365/−0.381	+0.382/−0.403

^{a} $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; 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} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{d} $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Table A5. Crystallographic data and experimental parameters for the crystal structure analyses of **70** and **81**.

	70	**81**
empirical formula	$C_{12}H_{18}O_2Si_2$	$C_{24}H_{19}F_2NO_2$
formula mass, g mol^{-1}	250.44	391.4
collection *T*, K	173(2)	173(2)
$\lambda(Mo_{K\alpha})$, Å	0.71073	0.71073
crystal system	monoclinic	monoclinic
space group (No.)	*C*2/*c* (15)	$P2_1/c$ (14)
a, Å	17.973(4)	8.7133(10)
b, Å	5.5806(8)	23.458(2)
c, Å	27.605(6)	9.3958(12)
β, deg	90.75(3)	90.231(15)
V, Å^3	2768.5(9)	1920.5(4)
Z	8	4
D_{calcd}, g cm^{-3}	1.202	1.354
μ, mm^{-1}	0.241	0.099
F(000)	1072	816
crystal dimensions, mm	0.50 × 0.40 × 0.15	0.5 × 0.4 × 0.4
2*θ* range, deg	7.64−58.32	4.98–58.42
index ranges	$-24 \le h \le 24$, $-7 \le k \le 7$, $-37 \le l \le 37$	$-11 \le h \le 11$, $-32 \le k \le 32$, $-12 \le l \le 12$
no. of collected reflections	19009	27755
no. of independent reflections	3545	5159
R_{int}	0.0368	0.0452
no. of reflections used	3545	5159
no. of parameters	150	262
no. of restraints	0	0
S[a]	1.104	1.065
weight parameters *a*/*b*[b]	0.0619/1.4934	0.0723/0.3141
R_1[c] [$I > 2\sigma(I)$]	0.0370	0.0469
wR_2[d] (all data)	0.1080	0.1367
max./min. residual electron density, e Å^{-3}	+0.364/−0.242	+0.156/–0.247

[a] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; *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] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Table A6. Crystallographic data and experimental parameters for the crystal structure analyses of **84** and **85**.

	84	**85**
empirical formula	$C_{18}H_{23}ClO_4Si$	$C_{21}H_{26}ClNO_2Si$
formula mass, g mol^{-1}	366.9	387.97
collection T, K	173(2)	273(2)
$\lambda(Mo_{K\alpha})$, Å	0.71073	0.71073
crystal system	triclinic	monoclinic
space group (No.)	$P\bar{1}$ (2)	Cc (9)
a, Å	8.3446(7)	14.4129(18)
b, Å	12.1666(10)	20.0148(18)
c, Å	19.1885(16)	7.2757(9)
α, deg	90.259(2)	90
β, deg	98.132(2)	102.949(14)
γ, deg	97.485(2)	90
V, Å^3	1911.6(3)	2045.5(4)
Z	4	4
D_{calcd}, g cm^{-3}	1.275	1.26
μ, mm^{-1}	0.28	0.26
F(000)	776	824
crystal dimensions, mm	0.45 × 0.40 × 0.40	0.5 × 0.4 × 0.4
2θ range, deg	3.38–58.32	5.8–58.24
index ranges	$-11 \le h \le 11$, $-16 \le k \le 16$, $-26 \le l \le 26$	$-19 \le h \le 19$, $-27 \le k \le 27$, $-9 \le l \le 9$
no. of collected reflections	6201	14474
no. of independent reflections	10218	5404
R_{int}	0.0213	0.0339
no. of reflections used	10218	5404
no. of parameters	441	238
no. of restraints	0	2
S^a	1.026	1.065
weight parameters a/b^b	0.0573/0.1151	0.0455/0.8142
$R_1{}^c$ [$I > 2\sigma(I)$]	0.0455	0.0321
$wR_2{}^d$ (all data)	0.1236	0.0836
max./min. residual electron density, e Å^{-3}	+0.869/–0.565	+0.261/–0.171

^{a} $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; 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} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{d} $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

*1-(6-Ethyl-1,1,2,2,3,3-hexamethyl-1,2,3-trisilaindan-5-yl)ethanone (**9**).*

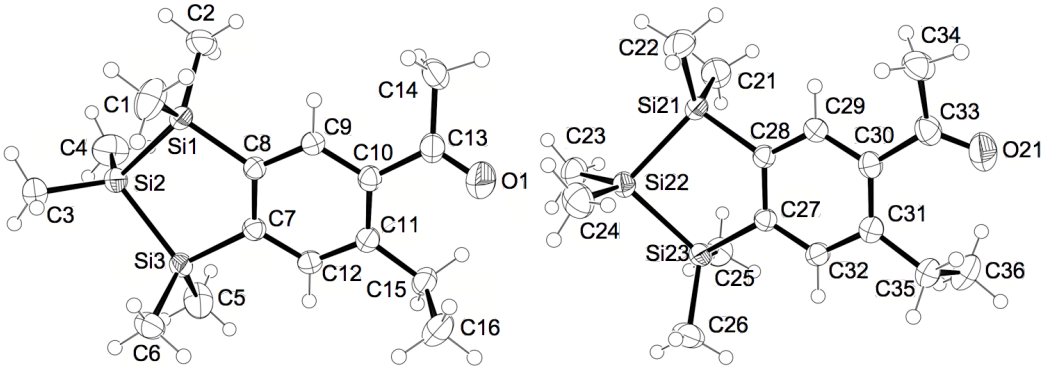


Figure A1. Molecular structures of the two crystallographically independent molecules in the crystal of **9** (probability level of displacement ellipsoids 50%).

Table A7. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **9**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Si1	9392(1)	737(1)	4658(1)	29(1)
Si2	7690(1)	611(1)	5993(1)	33(1)
Si3	7158(1)	1263(1)	6121(1)	30(1)
C1	9156(3)	598(1)	2917(2)	55(1)
C2	10885(2)	523(1)	5241(3)	50(1)
C3	6487(2)	305(1)	5175(3)	51(1)
C4	8171(3)	397(1)	7600(3)	59(1)
C5	5842(2)	1363(1)	4979(2)	44(1)
C6	6814(3)	1469(1)	7764(3)	55(1)
C7	8606(2)	1492(1)	5430(2)	27(1)
C8	9511(2)	1274(1)	4784(2)	26(1)
C9	10534(2)	1464(1)	4247(2)	27(1)
C10	10683(2)	1860(1)	4316(2)	28(1)
C11	9791(2)	2079(1)	4978(2)	29(1)
C12	8779(2)	1888(1)	5524(2)	30(1)
C13	11792(2)	2037(1)	3674(2)	36(1)
C16	9168(3)	2719(1)	4068(3)	47(1)
C15	9849(2)	2508(1)	5142(2)	36(1)
C14	12880(2)	1785(1)	3354(2)	43(1)
O1	11821(2)	2371(1)	3389(3)	74(1)

	x	*y*	*z*	U_{eq}
Si21	4184(1)	757(1)	810(1)	31(1)
Si22	2851(1)	658(1)	–945(1)	33(1)
Si23	2202(1)	1298(1)	–862(1)	30(1)
C22	5710(2)	501(1)	762(3)	57(1)
C21	3428(3)	666(1)	2435(3)	53(1)
C24	3792(3)	558(1)	–2455(3)	52(1)
C23	1604(2)	292(1)	–686(3)	47(1)
C26	1845(3)	1544(1)	–2430(2)	50(1)
C25	849(2)	1351(1)	291(3)	44(1)
C27	3618(2)	1517(1)	–86(2)	27(1)
C28	4455(2)	1287(1)	617(2)	26(1)
C29	5498(2)	1461(1)	1159(2)	28(1)
C30	5711(2)	1854(1)	1078(2)	30(1)
C31	4872(2)	2085(1)	393(2)	30(1)
C32	3854(2)	1909(1)	–181(2)	29(1)
C33	6838(2)	2013(1)	1732(2)	37(1)
O21	6889(2)	2348(1)	2050(2)	68(1)
C34	7913(2)	1752(1)	1986(2)	44(1)
C35	4982(2)	2513(1)	255(2)	36(1)
C36	4291(3)	2723(1)	1323(3)	51(1)

Table A8. Bond lengths [Å] and angles [deg] for **9**.

Si1–C1	1.879(3)	C33–O21	1.219(3)	C11–C15–C16	112.40(17)
Si1–C2	1.887(2)	C33–C34	1.509(3)	C22–Si21–C28	109.15(11)
Si1–C8	1.8918(18)	C35–C36	1.524(3)	C22–Si21–C21	108.91(14)
Si1–Si2	2.3495(8)			C28–Si21–C21	109.00(10)
Si2–C3	1.892(2)	C1–Si1–C2	108.59(14)	C22–Si21–Si22	116.89(10)
Si2–C4	1.894(3)	C1–Si1–C8	109.48(10)	C28–Si21–Si22	99.25(6)
Si2–Si3	2.3618(8)	C2–Si1–C8	108.41(10)	C21–Si21–Si22	113.02(10)
Si3–C6	1.881(2)	C1–Si1–Si2	113.86(10)	C23–Si22–C24	112.23(13)
Si3–C5	1.886(2)	C2–Si1–Si2	114.57(9)	C23–Si22–Si21	115.81(9)
Si3–C7	1.9066(19)	C8–Si1–Si2	101.54(6)	C24–Si22–Si21	109.20(9)
C7–C12	1.405(3)	C3–Si2–C4	110.88(14)	C23–Si22–Si23	115.33(9)
C7–C8	1.414(3)	C3–Si2–Si1	112.92(9)	C24–Si22–Si23	111.61(10)
C8–C9	1.410(3)	C4–Si2–Si1	111.74(10)	Si21–Si22–Si23	90.89(3)
C9–C10	1.402(2)	C3–Si2–Si3	113.93(8)	C26–Si23–C27	110.09(10)
C10–C11	1.414(3)	C4–Si2–Si3	113.76(11)	C26–Si23–C25	109.59(13)
C10–C13	1.509(3)	Si1–Si2–Si3	92.50(3)	C27–Si23–C25	108.89(10)
C11–C12	1.406(3)	C6–Si3–C5	109.92(13)	C26–Si23–Si22	118.06(9)
C11–C15	1.516(3)	C6–Si3–C7	109.79(11)	C27–Si23–Si22	99.15(6)
C13–O1	1.210(3)	C5–Si3–C7	108.33(10)	C25–Si23–Si22	110.38(8)
C13–C14	1.512(3)	C6–Si3–Si2	118.10(10)	C32–C27–C28	118.54(16)
C16–C15	1.525(3)	C5–Si3–Si2	109.32(8)	C32–C27–Si23	121.14(14)
Si21–C22	1.888(2)	C7–Si3–Si2	100.71(6)	C28–C27–Si23	120.32(13)
Si21–C28	1.8929(18)	C12–C7–C8	118.43(17)	C29–C28–C27	118.19(16)
Si21–C21	1.894(3)	C12–C7–Si3	120.13(14)	C29–C28–Si21	120.85(14)
Si21–Si22	2.3453(9)	C8–C7–Si3	121.41(13)	C27–C28–Si21	120.96(13)
Si22–C23	1.886(2)	C9–C8–C7	118.47(16)	C30–C29–C28	122.67(17)
Si22–C24	1.897(3)	C9–C8–Si1	119.84(13)	C29–C30–C31	119.23(17)
Si22–Si23	2.3556(8)	C7–C8–Si1	121.68(13)	C29–C30–C33	118.25(17)
Si23–C26	1.876(2)	C10–C9–C8	122.75(17)	C31–C30–C33	122.52(17)
Si23–C27	1.8988(19)	C9–C10–C11	118.97(17)	C32–C31–C30	118.03(17)
Si23–C25	1.900(2)	C9–C10–C13	118.56(17)	C32–C31–C35	117.50(17)
C27–C32	1.402(2)	C11–C10–C13	122.47(17)	C30–C31–C35	124.46(17)
C27–C28	1.417(2)	C12–C11–C10	118.10(17)	C31–C32–C27	123.28(17)
C28–C29	1.406(3)	C12–C11–C15	117.51(17)	O21–C33–C30	121.0(2)
C29–C30	1.400(3)	C10–C11–C15	124.39(17)	O21–C33–C34	120.2(2)
C30–C31	1.411(3)	C7–C12–C11	123.25(17)	C30–C33–C34	118.82(18)
C30–C33	1.506(3)	O1–C13–C10	121.8(2)	C31–C35–C36	111.92(17)
C31–C32	1.399(3)	O1–C13–C14	119.5(2)		
C31–C35	1.514(3)	C10–C13–C14	118.76(17)		

*2-(1,1,2,2,3,3,6-Heptamethyl-1,2,3-trisilaindan-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**).*

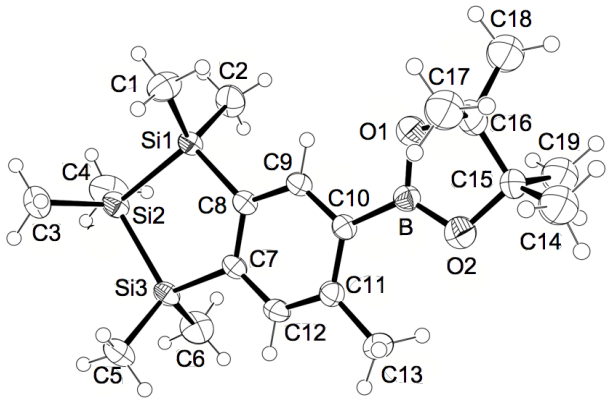


Figure A2. Molecular structure of **10** in the crystal (probability level of displacement ellipsoids 50%, disorder in the 1,3,2-dioxaborolane ring removed for clarity).

Table A9. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **10**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
B	1746(2)	6043(2)	1105(2)	30(1)
O1	753(4)	6621(3)	1619(4)	42(1)
C16	466(5)	7632(5)	821(5)	46(1)
C15	992(5)	7290(5)	–461(5)	50(2)
O2	2029(4)	6467(4)	–27(4)	46(1)
B1B	1746(2)	6043(2)	1105(2)	30(1)
O1B	395(4)	6290(4)	1104(5)	40(1)
C16B	–2(5)	7209(4)	216(5)	34(1)
C15B	1417(6)	7743(5)	50(6)	41(1)
O2B	2339(4)	6785(4)	319(4)	35(1)
C1	1783(3)	4755(2)	6357(3)	44(1)
C2	42(3)	2892(3)	4947(3)	50(1)
C3	4513(3)	2494(3)	7762(3)	51(1)
C4	2475(4)	673(3)	6544(4)	63(1)
C5	6384(2)	2314(2)	4857(3)	45(1)
C6	4239(4)	697(3)	3436(3)	54(1)
C7	3672(2)	3228(2)	3429(2)	27(1)

	x	*y*	*z*	U_{eq}
C8	2548(2)	3808(2)	3814(2)	26(1)
C9	1985(2)	4693(2)	3019(2)	29(1)
C10	2478(2)	5032(2)	1877(2)	27(1)
C11	3617(2)	4453(2)	1512(2)	30(1)
C12	4176(2)	3567(2)	2291(2)	31(1)
C13	4228(3)	4772(2)	308(2)	41(1)
Si1	1828(1)	3439(1)	5365(1)	28(1)
Si2	3346(1)	2038(1)	6256(1)	34(1)
Si3	4508(1)	2016(1)	4435(1)	31(1)
C17	1358(6)	8564(5)	1563(6)	56(1)
C18	–1090(6)	7814(6)	692(7)	56(1)
C14	1614(6)	8344(6)	–1073(6)	56(1)
C19	–165(6)	6742(5)	–1447(6)	56(1)
C20	1973(8)	8601(7)	1048(7)	56(1)
C21	1538(8)	8046(8)	–1387(7)	56(1)
C22	–754(8)	6718(7)	–1047(7)	56(1)
C23	–810(8)	8104(7)	882(8)	56(1)

Table A10. Bond lengths [Å] and angles [deg] for **10**.

B–O2	1.341(4)	C11–C13	1.507(3)	C12–C11–C10	118.77(18)
B–O1	1.370(4)	Si1–Si2	2.3512(9)	C12–C11–C13	119.64(19)
B–C10	1.570(3)	Si2–Si3	2.3419(9)	C10–C11–C13	121.60(19)
O1–C16	1.468(6)			C11–C12–C7	122.98(18)
C16–C15	1.546(7)	O2–B–O1	113.5(3)	C2–Si1–C1	108.76(15)
C15–O2	1.448(6)	O2–B–C10	126.6(2)	C2–Si1–C8	109.98(11)
O1B–C16B	1.449(6)	O1–B–C10	119.8(2)	C1–Si1–C8	107.84(11)
C16B–C15B	1.576(8)	B–O1–C16	106.9(3)	C2–Si1–Si2	111.87(11)
C15B–O2B	1.467(7)	O1–C16–C15	101.6(4)	C1–Si1–Si2	116.49(10)
C1–Si1	1.882(3)	O2–C15–C16	103.1(3)	C8–Si1–Si2	101.53(7)
C2–Si1	1.881(3)	B–O2–C15	107.4(3)	C3–Si2–C4	111.16(17)
C3–Si2	1.884(3)	O1B–C16B–C15B	102.1(4)	C3–Si2–Si3	110.64(10)
C4–Si2	1.890(3)	O2B–C15B–C16B	101.9(4)	C4–Si2–Si3	113.88(13)
C5–Si3	1.884(3)	C12–C7–C8	118.79(18)	C3–Si2–Si1	113.66(11)
C6–Si3	1.883(3)	C12–C7–Si3	119.97(15)	C4–Si2–Si1	113.30(11)
C7–C12	1.402(3)	C8–C7–Si3	121.23(15)	Si3–Si2–Si1	93.11(3)
C7–C8	1.418(3)	C9–C8–C7	117.89(18)	C6–Si3–C5	110.12(14)
C7–Si3	1.904(2)	C9–C8–Si1	120.20(15)	C6–Si3–C7	108.73(12)
C8–C9	1.405(3)	C7–C8–Si1	121.90(15)	C5–Si3–C7	108.76(11)
C8–Si1	1.897(2)	C10–C9–C8	123.59(18)	C6–Si3–Si2	113.75(12)
C9–C10	1.400(3)	C9–C10–C11	117.97(18)	C5–Si3–Si2	113.22(10)
C10–C11	1.421(3)	C9–C10–B	117.41(17)	C7–Si3–Si2	101.79(7)
C11–C12	1.397(3)	C11–C10–B	124.61(18)		

*4-(1,1,3,3-Tetramethylindan-5-ylethynyl)benzoic acid (**16a**).*

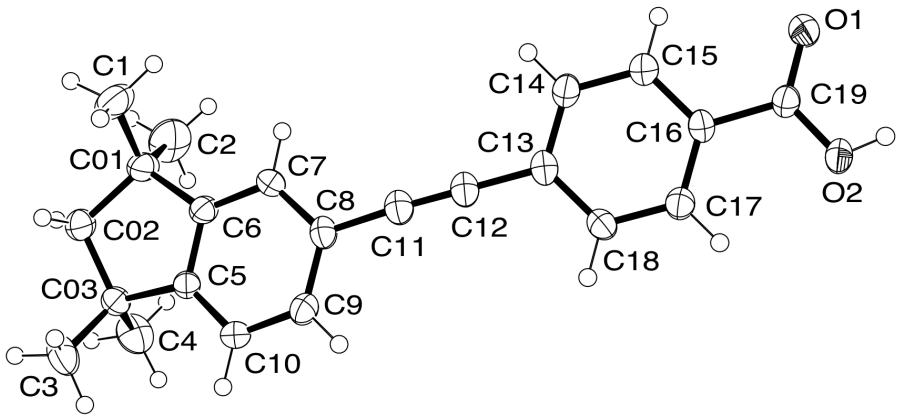


Figure A3. Molecular structure of **16a** in the crystal (probability level of displacement ellipsoids 50%, disorder at C02 removed for clarity).

Table A11. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **16a**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
C1	4022(4)	3730(3)	6256(1)	56(1)
C2	7245(4)	2118(4)	5462(1)	64(1)
C3	4774(3)	–2254(3)	6994(1)	48(1)
C4	7919(4)	–2683(3)	6099(1)	49(1)
C5	7390(3)	–715(2)	7066(1)	27(1)
C6	7263(3)	1041(2)	6815(1)	28(1)
C7	8366(3)	1808(2)	7163(1)	30(1)
C8	9610(3)	800(2)	7777(1)	29(1)
C9	9632(3)	–929(3)	8048(1)	32(1)
C10	8537(3)	–1691(2)	7694(1)	31(1)
C11	10943(3)	1478(3)	8107(1)	33(1)
C12	12197(3)	1939(3)	8360(1)	33(1)
C13	13685(3)	2498(3)	8671(1)	30(1)
C14	13586(3)	4271(3)	8490(1)	35(1)

	x	*y*	*z*	U_{eq}
C15	15016(3)	4804(3)	8794(1)	33(1)
C16	16581(3)	3558(2)	9281(1)	27(1)
C17	16703(3)	1793(3)	9461(1)	32(1)
C18	15275(3)	1253(3)	9158(1)	32(1)
C19	18113(3)	4165(2)	9587(1)	28(1)
C01	5847(3)	1895(3)	6144(1)	36(1)
C02	4767(4)	509(3)	6131(1)	37(1)
C03	6228(3)	–1333(2)	6564(1)	32(1)
C01B	5847(3)	1895(3)	6144(1)	36(1)
C02B	6060(30)	156(15)	5837(7)	28(5)
C03B	6228(3)	–1333(2)	6564(1)	32(1)
O1	18032(2)	5748(2)	9392(1)	38(1)
O2	19490(2)	2986(2)	10056(1)	36(1)

Table A12. Bond lengths [Å] and angles [deg] for **16a**.

C1–C01	1.523(3)	C19–O2	1.2929(19)	C17–C16–C15	119.88(16)
C2–C01	1.520(3)	C01–C02	1.560(3)	C17–C16–C19	121.42(14)
C3–C03	1.532(3)	C02–C03	1.545(3)	C15–C16–C19	118.70(16)
C4–C03	1.526(3)			C16–C17–C18	120.28(15)
C5–C6	1.388(2)	C6–C5–C10	119.95(16)	C17–C18–C13	120.35(17)
C5–C10	1.389(2)	C6–C5–C03	111.69(14)	O1–C19–O2	123.05(15)
C5–C03	1.521(2)	C10–C5–C03	128.33(16)	O1–C19–C16	120.24(14)
C6–C7	1.388(2)	C5–C6–C7	120.75(14)	O2–C19–C16	116.71(15)
C6–C01	1.522(2)	C5–C6–C01	111.48(15)	C2–C01–C6	110.74(16)
C7–C8	1.402(2)	C7–C6–C01	127.77(16)	C2–C01–C1	110.07(18)
C8–C9	1.397(3)	C6–C7–C8	119.62(16)	C6–C01–C1	111.58(15)
C8–C11	1.438(2)	C9–C8–C7	119.14(16)	C2–C01–C02	114.59(18)
C9–C10	1.389(2)	C9–C8–C11	119.70(15)	C6–C01–C02	101.66(14)
C11–C12	1.199(2)	C7–C8–C11	121.09(16)	C1–C01–C02	107.95(18)
C12–C13	1.439(2)	C10–C9–C8	120.81(14)	C03–C02–C01	107.85(16)
C13–C14	1.391(3)	C9–C10–C5	119.58(16)	C5–C03–C4	109.91(15)
C13–C18	1.401(2)	C12–C11–C8	174.84(18)	C5–C03–C3	112.39(14)
C14–C15	1.387(2)	C11–C12–C13	179.35(18)	C4–C03–C3	108.41(17)
C15–C16	1.392(2)	C14–C13–C18	118.90(16)	C5–C03–C02	101.42(15)
C16–C17	1.380(3)	C14–C13–C12	120.78(15)	C4–C03–C02	115.14(16)
C16–C19	1.487(2)	C18–C13–C12	120.32(17)	C3–C03–C02	109.54(17)
C17–C18	1.387(2)	C15–C14–C13	120.52(16)		
C19–O1	1.250(2)	C14–C15–C16	120.07(17)		

*4-(1,1,3,3-Tetramethyl-1,3-disilaindan-5-ylethynyl)benzoic acid (**16b**).*

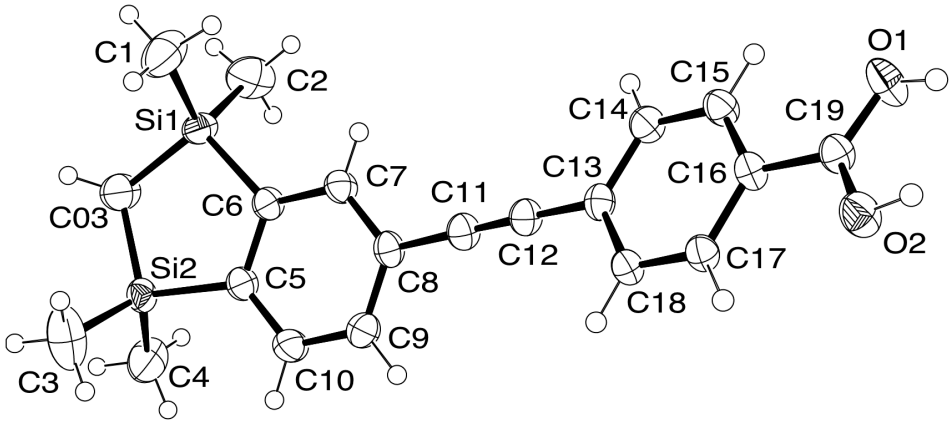


Figure A4. Molecular structure of **16b** in the crystal (probability level of displacement ellipsoids 50%).

Table A13. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **16b**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
C1	8937(3)	5698(2)	2346(1)	66(1)
C2	6778(2)	4382(2)	1893(1)	63(1)
C3	12687(3)	3146(3)	1871(1)	75(1)
C4	10806(3)	1621(2)	1408(1)	60(1)
C5	10527(2)	4348(2)	1380(1)	31(1)
C6	9502(2)	5114(2)	1525(1)	30(1)
C7	9235(2)	6188(2)	1344(1)	32(1)
C8	9966(2)	6525(2)	1023(1)	30(1)
C9	10936(2)	5738(2)	874(1)	38(1)
C10	11207(2)	4672(2)	1051(1)	39(1)
C11	9792(2)	7675(2)	860(1)	32(1)
C12	9715(2)	8661(2)	732(1)	31(1)

	x	*y*	*z*	U_{eq}
C13	9723(2)	9842(2)	589(1)	27(1)
C14	8603(2)	10608(2)	638(1)	31(1)
C15	8656(2)	11756(2)	507(1)	31(1)
C16	9831(2)	12174(2)	325(1)	27(1)
C17	10936(2)	11408(2)	268(1)	28(1)
C18	10883(2)	10259(2)	396(1)	28(1)
C19	9897(2)	13403(2)	186(1)	28(1)
C03	9563(3)	3151(2)	2050(1)	55(1)
O1	8844(1)	14055(1)	202(1)	40(1)
O2	11045(1)	13768(1)	52(1)	38(1)
Si1	8649(1)	4586(1)	1968(1)	36(1)
Si2	10921(1)	3014(1)	1680(1)	33(1)

Table A14. Bond lengths [Å] and angles [deg] for **16b**.

C2–Si1	1.855(2)	C19–O2	1.283(2)	C17–C16–C15	119.32(16)
C1–Si1	1.865(3)	C03–Si1	1.870(2)	C17–C16–C19	120.01(15)
C4–Si2	1.850(3)	C03–Si2	1.877(2)	C15–C16–C19	120.66(15)
C3–Si2	1.855(2)			C18–C17–C16	120.44(15)
C5–C10	1.397(3)	C10–C5–C6	118.75(17)	C17–C18–C13	120.61(16)
C5–C6	1.418(3)	C10–C5–Si2	126.12(14)	O1–C19–O2	122.51(17)
C5–Si2	1.8856(19)	C6–C5–Si2	114.98(14)	O1–C19–C16	119.77(15)
C6–C7	1.397(3)	C7–C6–C5	119.32(17)	O2–C19–C16	117.72(15)
C6–Si1	1.8824(19)	C7–C6–Si1	125.54(14)	Si1–C03–Si2	107.15(11)
C7–C8	1.400(3)	C5–C6–Si1	115.10(14)	C2–Si1–C1	109.61(13)
C8–C9	1.401(3)	C6–C7–C8	121.32(17)	C2–Si1–C03	112.46(12)
C8–C11	1.433(3)	C7–C8–C9	118.78(17)	C1–Si1–C03	113.31(13)
C9–C10	1.385(3)	C7–C8–C11	121.25(17)	C2–Si1–C6	110.53(11)
C11–C12	1.203(3)	C9–C8–C11	119.89(17)	C1–Si1–C6	109.32(11)
C12–C13	1.427(3)	C10–C9–C8	120.30(18)	C03–Si1–C6	101.34(9)
C13–C14	1.402(2)	C9–C10–C5	121.42(18)	C4–Si2–C3	108.53(14)
C13–C18	1.403(2)	C12–C11–C8	176.19(18)	C4–Si2–C03	113.44(12)
C14–C15	1.378(3)	C11–C12–C13	175.96(17)	C3–Si2–C03	112.75(15)
C15–C16	1.398(2)	C14–C13–C18	118.76(16)	C4–Si2–C5	111.48(11)
C16–C17	1.395(2)	C14–C13–C12	121.69(15)	C3–Si2–C5	109.45(11)
C16–C19	1.473(3)	C18–C13–C12	119.55(16)	C03–Si2–C5	101.02(9)
C17–C18	1.374(3)	C15–C14–C13	120.45(16)		
C19–O1	1.263(2)	C14–C15–C16	120.39(16)		

*6-(1,1,3,3-Tetramethyl-1,3-disilaindan-5-yl)-2-naphthoic acid (**18b**).*

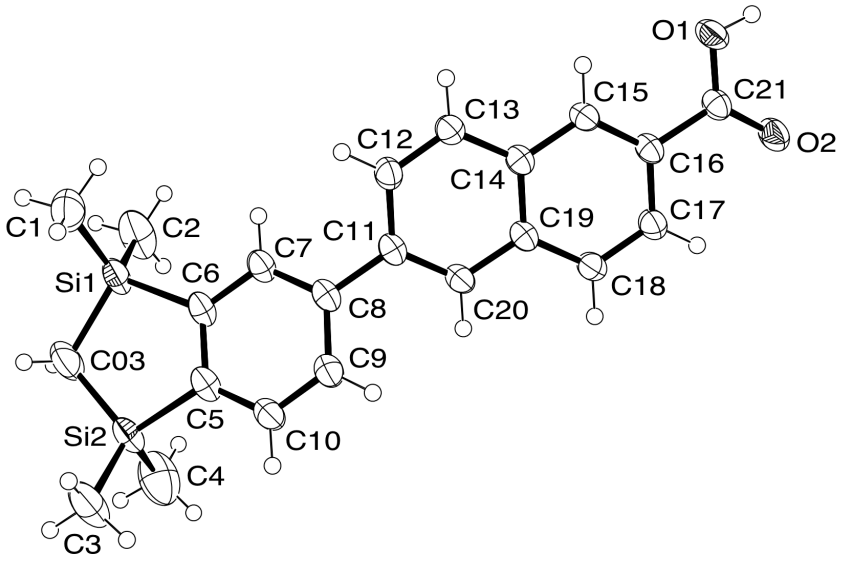


Figure A5. Molecular structure of **18b** in the crystal (probability level of displacement ellipsoids 50%).

Table A15. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **18b**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
C1	3113(3)	5340(2)	3044(1)	62(1)
C2	923(4)	4111(2)	2632(1)	69(1)
C3	–647(4)	8212(2)	3603(1)	71(1)
C4	–2406(4)	6616(3)	3148(1)	86(1)
C5	–317(2)	5439(2)	3620(1)	39(1)
C6	593(2)	4654(2)	3460(1)	36(1)
C7	854(2)	3549(2)	3631(1)	35(1)
C8	240(2)	3205(2)	3959(1)	33(1)
C9	–617(2)	4016(2)	4123(1)	39(1)
C10	–895(2)	5108(2)	3956(1)	42(1)
C11	446(2)	1991(2)	4123(1)	32(1)
C12	1632(2)	1369(2)	4080(1)	34(1)
C13	1801(2)	233(2)	4217(1)	33(1)

	x	*y*	*z*	U_{eq}
C14	783(2)	–363(2)	4407(1)	30(1)
C15	896(2)	–1552(2)	4540(1)	30(1)
C16	–129(2)	–2098(2)	4716(1)	30(1)
C17	–1300(2)	–1468(2)	4773(1)	34(1)
C18	–1426(2)	–318(2)	4648(1)	35(1)
C19	–401(2)	258(2)	4458(1)	30(1)
C20	–540(2)	1430(2)	4313(1)	32(1)
C21	–57(2)	–3356(2)	4846(1)	31(1)
C03	505(3)	6684(2)	2956(1)	62(1)
O1	1013(1)	–3916(1)	4784(1)	43(1)
O2	–1000(1)	–3832(1)	5004(1)	42(1)
Si1	1322(1)	5193(1)	3010(1)	43(1)
Si2	–742(1)	6797(1)	3332(1)	42(1)

Table A16. Bond lengths [Å] and angles [deg] for **18b**.

C1–Si1	1.869(3)	C21–O1	1.293(2)	C15–C16–C21	121.64(17)
C2–Si1	1.869(3)	C03–Si2	1.880(3)	C17–C16–C21	117.82(17)
C3–Si2	1.861(3)	C03–Si1	1.880(2)	C18–C17–C16	119.89(18)
C4–Si2	1.862(3)			C17–C18–C19	120.96(18)
C5–C10	1.404(3)	C10–C5–C6	118.42(18)	C20–C19–C18	121.37(17)
C5–C6	1.412(3)	C10–C5–Si2	125.93(16)	C20–C19–C14	119.40(17)
C5–Si2	1.891(2)	C6–C5–Si2	115.44(15)	C18–C19–C14	119.22(16)
C6–C7	1.406(3)	C7–C6–C5	119.64(18)	C11–C20–C19	121.78(18)
C6–Si1	1.891(2)	C7–C6–Si1	125.39(16)	O2–C21–O1	122.96(17)
C7–C8	1.399(3)	C5–C6–Si1	114.93(14)	O2–C21–C16	120.48(17)
C8–C9	1.401(3)	C8–C7–C6	121.68(19)	O1–C21–C16	116.56(16)
C8–C11	1.495(2)	C7–C8–C9	117.94(17)	Si2–C03–Si1	107.20(11)
C9–C10	1.390(3)	C7–C8–C11	121.33(17)	C1–Si1–C2	109.02(15)
C11–C20	1.382(3)	C9–C8–C11	120.68(17)	C1–Si1–C03	112.15(13)
C11–C12	1.422(3)	C10–C9–C8	121.12(19)	C2–Si1–C03	113.48(14)
C12–C13	1.374(3)	C9–C10–C5	121.1(2)	C1–Si1–C6	111.60(11)
C13–C14	1.424(3)	C20–C11–C12	118.22(17)	C2–Si1–C6	109.46(11)
C14–C15	1.419(2)	C20–C11–C8	120.16(18)	C03–Si1–C6	100.95(10)
C14–C19	1.422(3)	C12–C11–C8	121.59(17)	C3–Si2–C4	109.22(17)
C15–C16	1.379(3)	C13–C12–C11	121.53(18)	C3–Si2–C03	113.59(14)
C16–C17	1.419(3)	C12–C13–C14	120.71(18)	C4–Si2–C03	111.85(16)
C16–C21	1.484(2)	C15–C14–C19	118.96(17)	C3–Si2–C5	112.40(10)
C17–C18	1.370(3)	C15–C14–C13	122.70(17)	C4–Si2–C5	108.99(12)
C18–C19	1.419(3)	C19–C14–C13	118.34(16)	C03–Si2–C5	100.51(10)
C19–C20	1.418(2)	C16–C15–C14	120.41(17)		
C21–O2	1.252(2)	C15–C16–C17	120.53(16)		

*rac-1-(1,1,2,2,3,3,6-Heptamethyl-1,2,3-trisilaindan-5-yl)ethanol (**26**).*

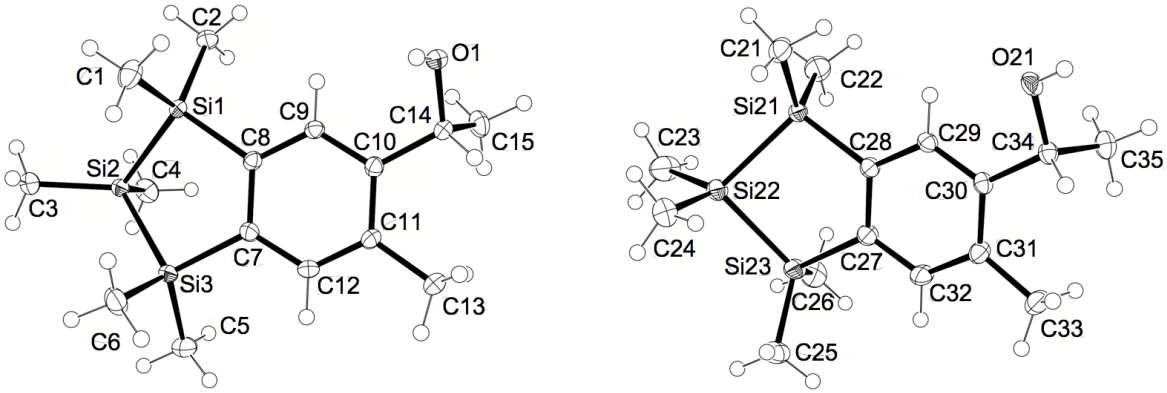


Figure A6. Molecular structure of the two crystallographically independent molecules in the crystal of **26** (probability level of displacement ellipsoids 50%).

Table A17. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **26**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Si1	9392(1)	737(1)	4658(1)	29(1)
Si2	7690(1)	611(1)	5993(1)	33(1)
Si3	7158(1)	1263(1)	6121(1)	30(1)
C1	9156(3)	598(1)	2917(2)	55(1)
C2	10885(2)	523(1)	5241(3)	50(1)
C3	6487(2)	305(1)	5175(3)	51(1)
C4	8171(3)	397(1)	7600(3)	59(1)
C5	5842(2)	1363(1)	4979(2)	44(1)
C6	6814(3)	1469(1)	7764(3)	55(1)
C7	8606(2)	1492(1)	5430(2)	27(1)
C8	9511(2)	1274(1)	4784(2)	26(1)
C9	10534(2)	1464(1)	4247(2)	27(1)
C10	10683(2)	1860(1)	4316(2)	28(1)
C11	9791(2)	2079(1)	4978(2)	29(1)
C12	8779(2)	1888(1)	5524(2)	30(1)
C13	11792(2)	2037(1)	3674(2)	36(1)
C16	9168(3)	2719(1)	4068(3)	47(1)
C15	9849(2)	2508(1)	5142(2)	36(1)
C14	12880(2)	1785(1)	3354(2)	43(1)

	x	*y*	*z*	U_{eq}
Si21	4184(1)	757(1)	810(1)	31(1)
Si22	2851(1)	658(1)	–945(1)	33(1)
Si23	2202(1)	1298(1)	–862(1)	30(1)
C22	5710(2)	501(1)	762(3)	57(1)
C21	3428(3)	666(1)	2435(3)	53(1)
C24	3792(3)	558(1)	–2455(3)	52(1)
C23	1604(2)	292(1)	–686(3)	47(1)
C26	1845(3)	1544(1)	–2430(2)	50(1)
C25	849(2)	1351(1)	291(3)	44(1)
C27	3618(2)	1517(1)	–86(2)	27(1)
C28	4455(2)	1287(1)	617(2)	26(1)
C29	5498(2)	1461(1)	1159(2)	28(1)
C30	5711(2)	1854(1)	1078(2)	30(1)
C31	4872(2)	2085(1)	393(2)	30(1)
C32	3854(2)	1909(1)	–181(2)	29(1)
C33	6838(2)	2013(1)	1732(2)	37(1)
O21	6889(2)	2348(1)	2050(2)	68(1)
C34	7913(2)	1752(1)	1986(2)	44(1)
C35	4982(2)	2513(1)	255(2)	36(1)

Table A18. Bond lengths [Å] and angles [deg] for **26**.

Si1–C1	1.879(3)	C33–O21	1.219(3)	C11–C15–C16	112.40(17)
Si1–C2	1.887(2)	C33–C34	1.509(3)	C22–Si21–C28	109.15(11)
Si1–C8	1.8918(18)	C35–C36	1.524(3)	C22–Si21–C21	108.91(14)
Si1–Si2	2.3495(8)			C28–Si21–C21	109.00(10)
Si2–C3	1.892(2)	C1–Si1–C2	108.59(14)	C22–Si21–Si22	116.89(10)
Si2–C4	1.894(3)	C1–Si1–C8	109.48(10)	C28–Si21–Si22	99.25(6)
Si2–Si3	2.3618(8)	C2–Si1–C8	108.41(10)	C21–Si21–Si22	113.02(10)
Si3–C6	1.881(2)	C1–Si1–Si2	113.86(10)	C23–Si22–C24	112.23(13)
Si3–C5	1.886(2)	C2–Si1–Si2	114.57(9)	C23–Si22–Si21	115.81(9)
Si3–C7	1.9066(19)	C8–Si1–Si2	101.54(6)	C24–Si22–Si21	109.20(9)
C7–C12	1.405(3)	C3–Si2–C4	110.88(14)	C23–Si22–Si23	115.33(9)
C7–C8	1.414(3)	C3–Si2–Si1	112.92(9)	C24–Si22–Si23	111.61(10)
C8–C9	1.410(3)	C4–Si2–Si1	111.74(10)	Si21–Si22–Si23	90.89(3)
C9–C10	1.402(2)	C3–Si2–Si3	113.93(8)	C26–Si23–C27	110.09(10)
C10–C11	1.414(3)	C4–Si2–Si3	113.76(11)	C26–Si23–C25	109.59(13)
C10–C13	1.509(3)	Si1–Si2–Si3	92.50(3)	C27–Si23–C25	108.89(10)
C11–C12	1.406(3)	C6–Si3–C5	109.92(13)	C26–Si23–Si22	118.06(9)
C11–C15	1.516(3)	C6–Si3–C7	109.79(11)	C27–Si23–Si22	99.15(6)
C13–O1	1.210(3)	C5–Si3–C7	108.33(10)	C25–Si23–Si22	110.38(8)
C13–C14	1.512(3)	C6–Si3–Si2	118.10(10)	C32–C27–C28	118.54(16)
C16–C15	1.525(3)	C5–Si3–Si2	109.32(8)	C32–C27–Si23	121.14(14)
Si21–C22	1.888(2)	C7–Si3–Si2	100.71(6)	C28–C27–Si23	120.32(13)
Si21–C28	1.8929(18)	C12–C7–C8	118.43(17)	C29–C28–C27	118.19(16)
Si21–C21	1.894(3)	C12–C7–Si3	120.13(14)	C29–C28–Si21	120.85(14)
Si21–Si22	2.3453(9)	C8–C7–Si3	121.41(13)	C27–C28–Si21	120.96(13)
Si22–C23	1.886(2)	C9–C8–C7	118.47(16)	C30–C29–C28	122.67(17)
Si22–C24	1.897(3)	C9–C8–Si1	119.84(13)	C29–C30–C31	119.23(17)
Si22–Si23	2.3556(8)	C7–C8–Si1	121.68(13)	C29–C30–C33	118.25(17)
Si23–C26	1.876(2)	C10–C9–C8	122.75(17)	C31–C30–C33	122.52(17)
Si23–C27	1.8988(19)	C9–C10–C11	118.97(17)	C32–C31–C30	118.03(17)
Si23–C25	1.900(2)	C9–C10–C13	118.56(17)	C32–C31–C35	117.50(17)
C27–C32	1.402(2)	C11–C10–C13	122.47(17)	C30–C31–C35	124.46(17)
C27–C28	1.417(2)	C12–C11–C10	118.10(17)	C31–C32–C27	123.28(17)
C28–C29	1.406(3)	C12–C11–C15	117.51(17)	O21–C33–C30	121.0(2)
C29–C30	1.400(3)	C10–C11–C15	124.39(17)	O21–C33–C34	120.2(2)
C30–C31	1.411(3)	C7–C12–C11	123.25(17)	C30–C33–C34	118.82(18)
C30–C33	1.506(3)	O1–C13–C10	121.8(2)	C31–C35–C36	111.92(17)
C31–C32	1.399(3)	O1–C13–C14	119.5(2)		
C31–C35	1.514(3)	C10–C13–C14	118.76(17)		

*Methyl 4-(1,1,3,3-tetramethylindan-5-ylethynyl)benzoate (**43**).*

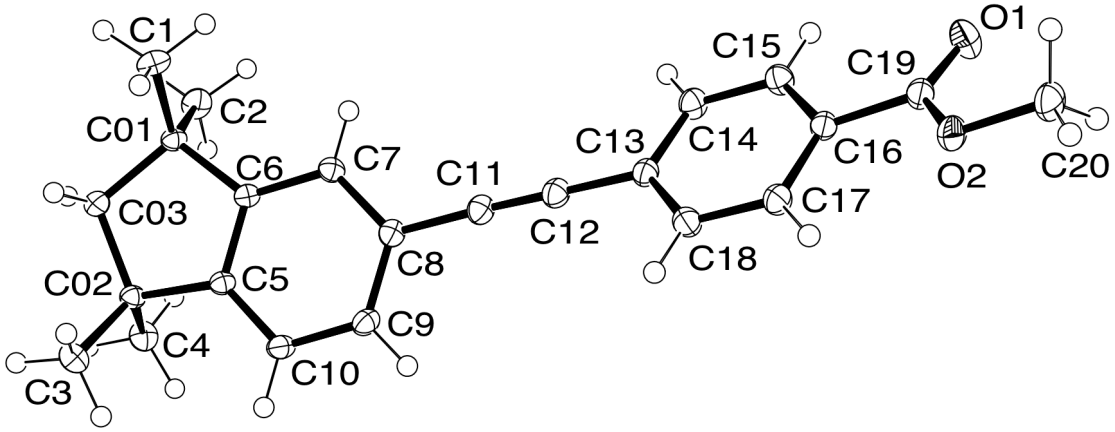


Figure A7. Molecular structure of **43** in the crystal (probability level of displacement ellipsoids 50%).

Table A19. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **43**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
C1	6242(1)	–604(1)	4759(1)	22(1)
C2	6564(1)	–1794(1)	7364(1)	22(1)
C3	5459(1)	1967(1)	8485(1)	21(1)
C4	5989(1)	395(1)	10449(1)	20(1)
C5	6615(1)	1227(1)	8338(1)	14(1)
C6	6860(1)	395(1)	7308(1)	14(1)
C7	7504(1)	480(1)	6986(1)	16(1)
C8	7896(1)	1443(1)	7666(1)	16(1)
C9	7639(1)	2296(1)	8668(1)	18(1)
C10	7003(1)	2181(1)	9024(1)	17(1)
C11	8550(1)	1611(1)	7312(1)	19(1)
C12	9089(1)	1839(1)	6983(1)	20(1)
C13	9712(1)	2148(1)	6523(1)	17(1)
C14	10156(1)	1256(1)	6214(1)	20(1)
C15	10744(1)	1560(1)	5678(1)	20(1)
C16	10901(1)	2760(1)	5474(1)	17(1)
C17	10470(1)	3658(1)	5831(1)	20(1)
C18	9877(1)	3354(1)	6340(1)	20(1)
C19	11521(1)	3042(1)	4817(1)	19(1)
C20	12121(1)	4538(1)	3656(1)	28(1)
C01	6351(1)	–550(1)	6670(1)	15(1)
C02	5932(1)	896(1)	8667(1)	15(1)
C03	5723(1)	–78(1)	7316(1)	20(1)
O1	11946(1)	2315(1)	4672(1)	28(1)
O2	11548(1)	4199(1)	4375(1)	23(1)

Table A20. Bond lengths [Å] and angles [deg] for **43**.

C1–C01	1.5348(12)	C19–O2	1.3420(12)	C14–C15–C16	120.11(8)
C2–C01	1.5348(12)	C20–O2	1.4454(11)	C15–C16–C17	119.74(8)
C3–C02	1.5334(12)	C01–C03	1.5589(12)	C15–C16–C19	118.20(8)
C4–C02	1.5391(12)	C02–C03	1.5551(12)	C17–C16–C19	122.02(8)
C5–C10	1.3931(12)			C18–C17–C16	120.16(8)
C5–C6	1.3949(11)	C10–C5–C6	120.61(8)	C17–C18–C13	120.28(8)
C5–C02	1.5159(11)	C10–C5–C02	127.19(7)	O1–C19–O2	123.84(8)
C6–C7	1.3931(11)	C6–C5–C02	112.06(7)	O1–C19–C16	124.38(9)
C6–C01	1.5196(11)	C7–C6–C5	120.75(7)	O2–C19–C16	111.77(8)
C7–C8	1.4031(12)	C7–C6–C01	127.52(7)	C6–C01–C2	110.92(7)
C8–C9	1.4069(12)	C5–C6–C01	111.72(7)	C6–C01–C1	110.89(7)
C8–C11	1.4328(12)	C6–C7–C8	118.83(8)	C2–C01–C1	108.95(7)
C9–C10	1.3899(12)	C7–C8–C9	120.07(8)	C6–C01–C03	102.42(6)
C11–C12	1.2064(12)	C7–C8–C11	121.40(8)	C2–C01–C03	112.73(7)
C12–C13	1.4334(12)	C9–C8–C11	118.49(8)	C1–C01–C03	110.83(7)
C13–C14	1.3987(13)	C10–C9–C8	120.56(8)	C5–C02–C3	112.69(7)
C13–C18	1.3992(13)	C9–C10–C5	119.12(8)	C5–C02–C4	108.49(7)
C14–C15	1.3899(12)	C12–C11–C8	175.16(10)	C3–C02–C4	109.07(7)
C15–C16	1.3919(13)	C11–C12–C13	177.01(10)	C5–C02–C03	102.00(6)
C16–C17	1.3979(13)	C14–C13–C18	119.24(8)	C3–C02–C03	111.92(7)
C16–C19	1.4909(12)	C14–C13–C12	120.73(8)	C4–C02–C03	112.52(7)
C17–C18	1.3887(12)	C18–C13–C12	120.02(8)	C02–C03–C01	108.68(7)
C19–O1	1.2106(12)	C15–C14–C13	120.42(8)	C19–O2–C20	115.41(8)

*Methyl 4-(1,1,3,3-tetramethyl-2-oxa-1,3-disilaindan-5-ylethynyl)benzoate (**45**).*

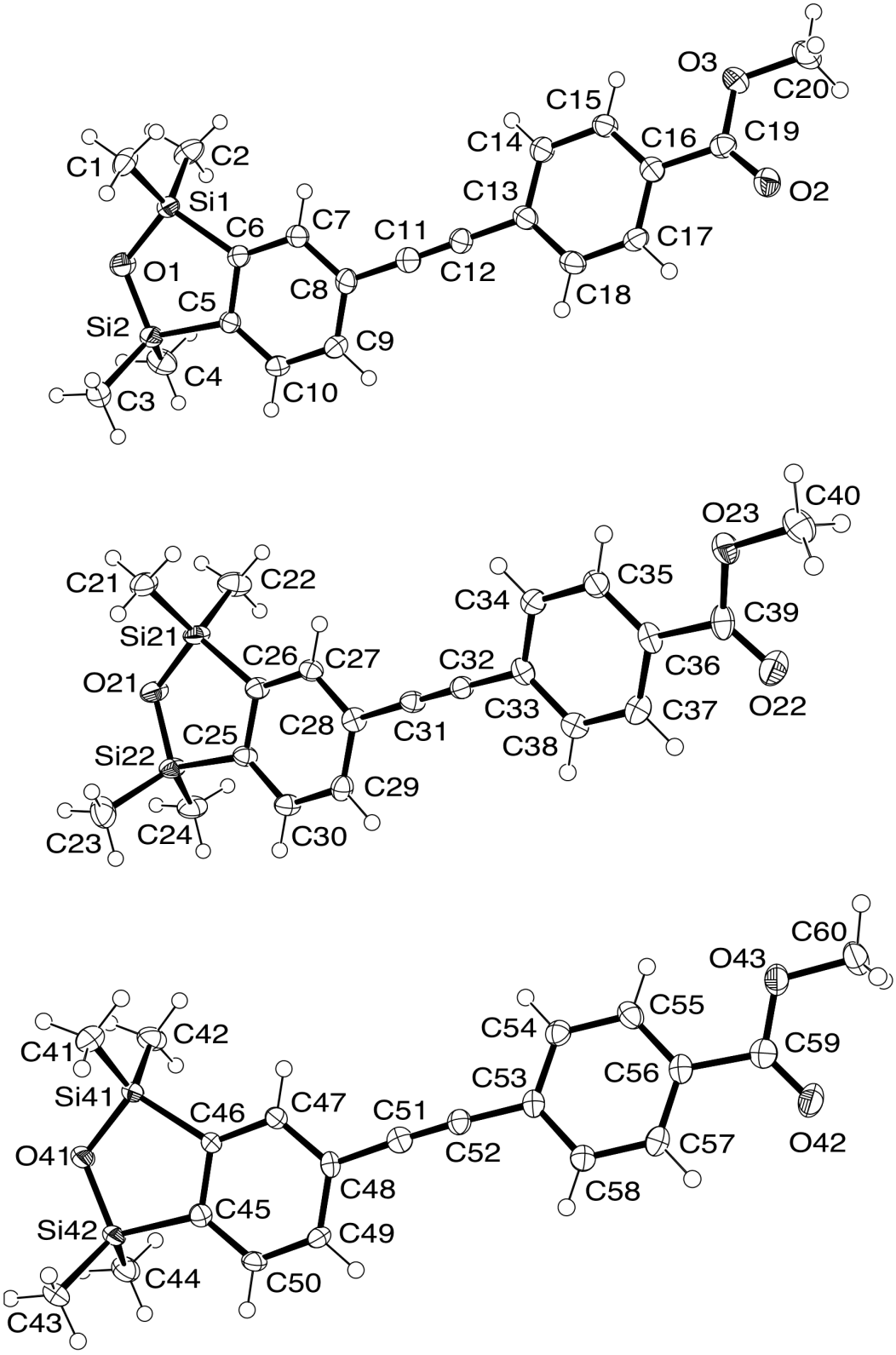


Figure A8. Molecular structures of the three crystallographically independent molecules of **45** in the crystal (probability level of displacement ellipsoids 50%).

Table A21. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **45**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Si1	2499(1)	8828(1)	3779(1)	23(1)
Si2	2423(1)	7237(1)	1287(1)	25(1)
O1	2568(1)	8337(2)	2106(3)	31(1)
O2	879(1)	6858(2)	11892(3)	31(1)
O3	1169(1)	7571(2)	13435(2)	30(1)
C1	2437(1)	10416(3)	3646(4)	32(1)
C2	2725(1)	8568(3)	5333(4)	37(1)
C3	2296(1)	7648(3)	–657(4)	35(1)
C4	2598(1)	5922(4)	1189(4)	38(1)
C5	2207(1)	7087(3)	2707(3)	22(1)
C6	2248(1)	7873(3)	3960(3)	22(1)
C7	2103(1)	7860(3)	5135(3)	22(1)
C8	1920(1)	7102(3)	5065(4)	23(1)
C9	1879(1)	6350(3)	3815(4)	26(1)
C10	2024(1)	6347(3)	2653(4)	26(1)
C11	1774(1)	7090(3)	6273(4)	25(1)
C12	1659(1)	7071(3)	7309(4)	25(1)
C13	1513(1)	7080(3)	8532(3)	25(1)
C14	1586(1)	7596(3)	9949(4)	27(1)
C15	1443(1)	7632(3)	11109(4)	25(1)
C16	1228(1)	7171(3)	10872(3)	23(1)
C17	1156(1)	6642(3)	9466(4)	24(1)
C18	1297(1)	6594(3)	8321(4)	26(1)
C19	1072(1)	7184(3)	12083(4)	24(1)
C20	1030(1)	7527(4)	14682(4)	35(1)
Si21	342(1)	–930(1)	3728(1)	25(1)
Si22	456(1)	659(1)	6174(1)	25(1)
O21	286(1)	–360(2)	5391(3)	32(1)
O22	1952(1)	889(2)	–4680(3)	33(1)
O23	1673(1)	–21(2)	–6137(2)	28(1)
C21	120(1)	–581(4)	2156(4)	31(1)
C22	380(1)	–2525(3)	3939(4)	37(1)
C23	309(1)	2083(4)	6236(4)	37(1)

	x	*y*	*z*	U_{eq}
C29	1001(1)	1207(3)	3567(4)	23(1)
C30	864(1)	1299(3)	4756(4)	24(1)
C31	1083(1)	403(3)	1089(3)	21(1)
C32	1199(1)	400(3)	42(3)	21(1)
C33	1340(1)	416(3)	–1193(3)	21(1)
C34	1271(1)	–114(3)	–2588(4)	25(1)
C35	1408(1)	–108(3)	–3780(4)	26(1)
C36	1616(1)	425(3)	–3581(3)	23(1)
C37	1686(1)	968(3)	–2185(4)	25(1)
C38	1550(1)	972(3)	–995(4)	23(1)
C39	1768(1)	464(3)	–4819(4)	26(1)
C40	1813(1)	–20(3)	–7399(4)	32(1)
Si41	359(1)	5542(1)	8765(1)	24(1)
Si42	465(1)	3971(1)	11233(1)	23(1)
O41	300(1)	5001(2)	10436(2)	31(1)
O42	1974(1)	2860(2)	613(3)	34(1)
O43	1770(1)	4245(2)	–717(3)	34(1)
C41	412(1)	7141(3)	8927(4)	37(1)
C42	130(1)	5232(4)	7237(4)	33(1)
C43	583(1)	4388(3)	13193(3)	30(1)
C44	311(1)	2571(4)	11275(4)	33(1)
C45	677(1)	3924(3)	9788(3)	22(1)
C46	621(1)	4683(3)	8527(3)	18(1)
C47	758(1)	4719(3)	7324(3)	19(1)
C48	949(1)	4023(3)	7355(3)	19(1)
C49	1004(1)	3279(3)	8608(3)	21(1)
C50	868(1)	3233(3)	9801(3)	22(1)
C51	1092(1)	4039(3)	6125(3)	22(1)
C52	1214(1)	4009(3)	5125(3)	21(1)
C53	1363(1)	3902(3)	3939(3)	20(1)
C54	1309(1)	4394(3)	2487(4)	23(1)
C55	1455(1)	4297(3)	1364(4)	26(1)
C56	1654(1)	3677(3)	1665(3)	21(1)

Table A21. Continued

C24	573(1)	240(4)	8143(4)	33(1)	C57	1708(1)	3167(3)	3098(4)	23(1)
C25	667(1)	641(3)	4739(3)	21(1)	C58	1564(1)	3284(3)	4240(4)	22(1)
C26	609(1)	–140(3)	3496(3)	22(1)	C59	1820(1)	3526(3)	485(4)	25(1)
C27	746(1)	–214(3)	2305(3)	21(1)	C60	1925(1)	4192(4)	–1884(4)	40(1)
C28	942(1)	454(3)	2333(3)	21(1)					

Table A22. Bond lengths [Å] and angles [deg] for **45**.

Si1–O1	1.656(2)	C52–C53	1.440(4)	C27–C26–C25	119.2(3)
Si1–C2	1.851(4)	C53–C54	1.397(4)	C27–C26–Si21	129.0(2)
Si1–C1	1.857(4)	C53–C58	1.401(5)	C25–C26–Si21	111.8(2)
Si1–C6	1.878(3)	C54–C55	1.382(4)	C26–C27–C28	120.8(3)
Si2–O1	1.653(3)	C55–C56	1.392(5)	C27–C28–C29	120.1(3)
Si2–C4	1.843(4)	C56–C57	1.392(4)	C27–C28–C31	121.2(3)
Si2–C3	1.855(4)	C56–C59	1.511(4)	C29–C28–C31	118.8(3)
Si2–C5	1.887(3)	C57–C58	1.390(4)	C30–C29–C28	119.9(3)
O2–C19	1.214(4)			C29–C30–C25	120.7(3)
O3–C19	1.342(4)	O1–Si1–C2	111.43(17)	C32–C31–C28	177.7(4)
O3–C20	1.437(4)	O1–Si1–C1	110.03(16)	C31–C32–C33	178.8(4)
C5–C10	1.386(5)	C2–Si1–C1	109.38(18)	C34–C33–C38	119.5(3)
C5–C6	1.421(4)	O1–Si1–C6	98.48(14)	C34–C33–C32	120.5(3)
C6–C7	1.408(4)	C2–Si1–C6	112.46(16)	C38–C33–C32	120.0(3)
C7–C8	1.397(5)	C1–Si1–C6	114.67(16)	C35–C34–C33	120.6(3)
C8–C9	1.395(5)	O1–Si2–C4	111.35(17)	C36–C35–C34	120.0(3)
C8–C11	1.433(4)	O1–Si2–C3	110.87(16)	C35–C36–C37	119.8(3)
C9–C10	1.399(5)	C4–Si2–C3	110.50(18)	C35–C36–C39	122.2(3)
C11–C12	1.194(5)	O1–Si2–C5	98.66(13)	C37–C36–C39	118.0(3)
C12–C13	1.447(4)	C4–Si2–C5	112.77(17)	C38–C37–C36	120.7(3)
C13–C14	1.403(4)	C3–Si2–C5	112.20(17)	C37–C38–C33	119.5(3)
C13–C18	1.406(5)	Si2–O1–Si1	118.36(15)	O22–C39–O23	124.0(3)
C14–C15	1.390(4)	C19–O3–C20	115.0(3)	O22–C39–C36	124.2(3)
C15–C16	1.389(5)	C10–C5–C6	119.5(3)	O23–C39–C36	111.7(3)
C16–C17	1.402(4)	C10–C5–Si2	128.8(2)	O41–Si41–C42	111.05(15)
C16–C19	1.479(4)	C6–C5–Si2	111.7(2)	O41–Si41–C41	110.48(16)
C17–C18	1.373(5)	C7–C6–C5	118.8(3)	C42–Si41–C41	110.68(18)
Si21–O21	1.656(2)	C7–C6–Si1	128.6(2)	O41–Si41–C46	98.79(13)
Si21–C22	1.847(4)	C5–C6–Si1	112.6(2)	C42–Si41–C46	112.82(16)
Si21–C21	1.863(4)	C8–C7–C6	120.9(3)	C41–Si41–C46	112.50(17)
Si21–C26	1.868(4)	C9–C8–C7	119.8(3)	O41–Si41–Si42	30.94(9)
Si21–Si22	2.8398(12)	C9–C8–C11	119.8(3)	C42–Si41–Si42	121.57(13)
Si22–O21	1.652(3)	C7–C8–C11	120.4(3)	C41–Si41–Si42	122.80(12)
Si22–C23	1.856(4)	C8–C9–C10	119.7(3)	C46–Si41–Si42	67.88(9)
Si22–C24	1.858(3)	C5–C10–C9	121.3(3)	O41–Si42–C44	110.31(16)
Si22–C25	1.869(3)	C12–C11–C8	178.0(4)	O41–Si42–C43	111.52(15)
O22–C39	1.202(4)	C11–C12–C13	177.8(4)	C44–Si42–C43	110.61(17)
O23–C39	1.354(4)	C14–C13–C18	119.2(3)	O41–Si42–C45	98.87(13)
O23–C40	1.447(4)	C14–C13–C12	119.6(3)	C44–Si42–C45	111.09(16)

Table A22. Continued

C25–C30	1.402(5)	C18–C13–C12	121.1(3)	C43–Si42–C45	113.92(16)
C25–C26	1.425(4)	C15–C14–C13	119.6(3)	O41–Si42–Si41	31.05(8)
C26–C27	1.394(4)	C16–C15–C14	120.5(3)	C44–Si42–Si41	119.23(12)
C27–C28	1.398(5)	C15–C16–C17	120.1(3)	C43–Si42–Si41	125.35(13)
C28–C29	1.400(5)	C15–C16–C19	122.1(3)	C45–Si42–Si41	67.87(10)
C28–C31	1.444(4)	C17–C16–C19	117.8(3)	Si42–O41–Si41	118.01(14)
C29–C30	1.389(4)	C18–C17–C16	119.6(3)	C59–O43–C60	114.4(3)
C31–C32	1.200(4)	C17–C18–C13	121.0(3)	C50–C45–C46	119.2(3)
C32–C33	1.436(4)	O2–C19–O3	123.4(3)	C50–C45–Si42	128.4(2)
C33–C34	1.388(4)	O2–C19–C16	124.1(3)	C46–C45–Si42	112.3(2)
C33–C38	1.409(5)	O3–C19–C16	112.5(3)	C47–C46–C45	119.3(3)
C34–C35	1.388(4)	O21–Si21–C22	109.58(16)	C47–C46–Si41	128.9(2)
C35–C36	1.385(5)	O21–Si21–C21	111.87(15)	C45–C46–Si41	111.9(2)
C36–C37	1.397(5)	C22–Si21–C21	111.04(18)	C48–C47–C46	120.8(3)
C36–C39	1.483(4)	O21–Si21–C26	98.72(13)	C47–C48–C49	119.6(3)
C37–C38	1.381(4)	C22–Si21–C26	112.93(18)	C47–C48–C51	121.7(3)
Si41–O41	1.656(2)	C21–Si21–C26	112.12(16)	C49–C48–C51	118.6(3)
Si41–C42	1.853(4)	O21–Si21–Si22	30.81(9)	C50–C49–C48	119.9(3)
Si41–C41	1.862(4)	C22–Si21–Si22	122.62(13)	C49–C50–C45	121.2(3)
Si41–C46	1.883(3)	C21–Si21–Si22	121.40(13)	C52–C51–C48	177.3(4)
Si41–Si42	2.8338(12)	C26–Si21–Si22	67.96(10)	C51–C52–C53	176.7(4)
Si42–O41	1.650(3)	O21–Si22–C23	110.99(17)	C54–C53–C58	119.6(3)
Si42–C44	1.852(4)	O21–Si22–C24	111.40(16)	C54–C53–C52	120.9(3)
Si42–C43	1.853(3)	C23–Si22–C24	109.71(18)	C58–C53–C52	119.5(3)
Si42–C45	1.877(3)	O21–Si22–C25	98.34(13)	C55–C54–C53	120.3(3)
O42–C59	1.193(4)	C23–Si22–C25	112.56(16)	C54–C55–C56	119.9(3)
O43–C59	1.346(4)	C24–Si22–C25	113.45(16)	C57–C56–C55	120.4(3)
O43–C60	1.448(4)	O21–Si22–Si21	30.89(8)	C57–C56–C59	117.0(3)
C45–C50	1.391(5)	C23–Si22–Si21	120.30(13)	C55–C56–C59	122.7(3)
C45–C46	1.418(4)	C24–Si22–Si21	125.06(13)	C58–C57–C56	119.9(3)
C46–C47	1.399(4)	C25–Si22–Si21	67.52(10)	C57–C58–C53	119.9(3)
C47–C48	1.394(4)	Si22–O21–Si21	118.31(15)	O42–C59–O43	125.2(3)
C48–C49	1.401(4)	C39–O23–C40	114.9(3)	O42–C59–C56	124.3(3)
C48–C51	1.438(4)	C30–C25–C26	119.4(3)	O43–C59–C56	110.5(3)
C49–C50	1.389(4)	C30–C25–Si22	127.9(2)		
C51–C52	1.194(4)	C26–C25–Si22	112.7(2)		

*Methyl 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-2-naphthoate (**51**).*

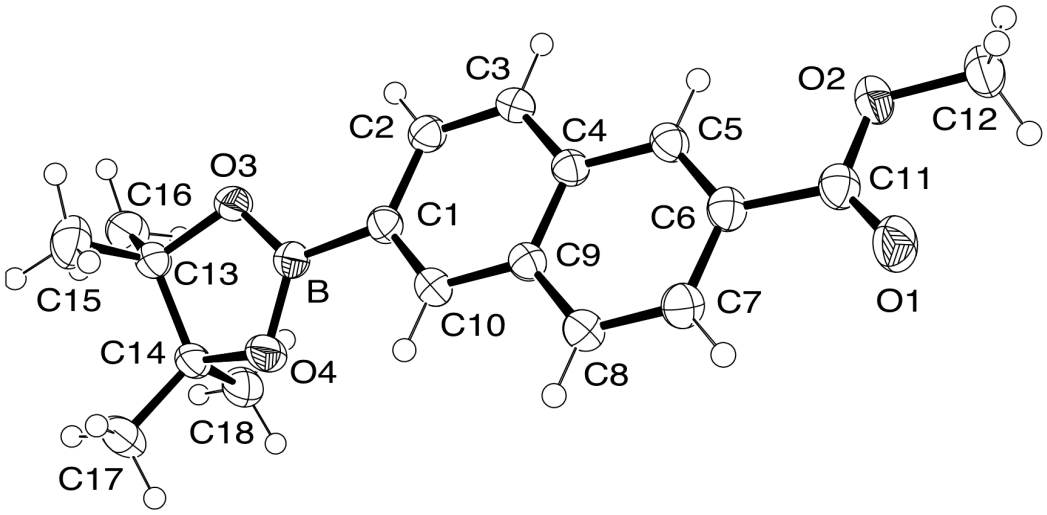


Figure A9. Molecular structure of compound **51** in the crystal (probability level of displacement ellipsoids 50%).

Table A23. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **51**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
B	8177(1)	1366(1)	5242(3)	28(1)
C1	8656(1)	602(1)	4140(2)	28(1)
C2	8920(1)	855(1)	2074(2)	29(1)
C3	9307(1)	135(1)	1067(2)	28(1)
C4	9454(1)	–890(1)	2072(2)	26(1)
C5	9832(1)	–1678(1)	1047(2)	28(1)
C6	9956(1)	–2673(1)	2052(3)	30(1)
C7	9720(1)	–2911(1)	4165(2)	32(1)
C8	9356(1)	–2164(1)	5191(2)	30(1)
C9	9208(1)	–1143(1)	4173(2)	26(1)
C10	8808(1)	–381(1)	5147(2)	28(1)
C11	10333(1)	–3539(1)	992(3)	32(1)
C12	10846(1)	–4077(1)	–2218(3)	39(1)
C13	7649(1)	2883(1)	6262(2)	30(1)
C14	7351(1)	1818(1)	7211(2)	31(1)
C15	8021(1)	3501(2)	7956(3)	49(1)
C16	7224(1)	3661(1)	5103(3)	42(1)
C17	7198(1)	1862(1)	9629(3)	43(1)
C18	6814(1)	1430(1)	5886(3)	43(1)
O1	10479(1)	–4390(1)	1893(2)	45(1)
O2	10484(1)	–3278(1)	–1068(2)	38(1)
O3	8065(1)	2428(1)	4641(2)	32(1)
O4	7818(1)	992(1)	6890(2)	38(1)

Table A24. Bond lengths [Å] and angles [deg] for **51**.

B–O3	1.3600(16)	C14–O4	1.4604(15)	C10–C9–C4	118.68(11)
B–O4	1.3641(18)	C14–C17	1.515(2)	C8–C9–C4	119.23(11)
B–C1	1.5665(18)	C14–C18	1.522(2)	C1–C10–C9	122.04(12)
C1–C10	1.3819(18)			O1–C11–O2	123.95(13)
C1–C2	1.4247(19)	O3–B–O4	113.85(11)	O1–C11–C6	123.55(14)
C2–C3	1.3738(18)	O3–B–C1	124.65(12)	O2–C11–C6	112.49(12)
C3–C4	1.4224(17)	O4–B–C1	121.47(11)	O3–C13–C16	108.55(12)
C4–C5	1.4197(17)	C10–C1–C2	118.44(11)	O3–C13–C15	107.17(11)
C4–C9	1.4279(18)	C10–C1–B	119.10(12)	C16–C13–C15	110.75(13)
C5–C6	1.3798(19)	C2–C1–B	122.39(11)	O3–C13–C14	102.16(10)
C6–C7	1.422(2)	C3–C2–C1	121.33(12)	C16–C13–C14	114.74(12)
C6–C11	1.4937(18)	C2–C3–C4	120.46(12)	C15–C13–C14	112.77(13)
C7–C8	1.3673(18)	C5–C4–C3	122.29(12)	O4–C14–C17	108.44(12)
C8–C9	1.4219(18)	C5–C4–C9	118.70(11)	O4–C14–C18	106.44(12)
C9–C10	1.4158(17)	C3–C4–C9	119.01(11)	C17–C14–C18	110.42(13)
C11–O1	1.2119(18)	C6–C5–C4	120.72(13)	O4–C14–C13	102.12(10)
C11–O2	1.3382(19)	C5–C6–C7	120.31(12)	C17–C14–C13	115.36(12)
C12–O2	1.4436(17)	C5–C6–C11	122.31(13)	C18–C14–C13	113.25(12)
C13–O3	1.4653(16)	C7–C6–C11	117.38(12)	C11–O2–C12	116.05(12)
C13–C16	1.5130(19)	C8–C7–C6	120.09(12)	B–O3–C13	106.91(11)
C13–C15	1.523(2)	C7–C8–C9	120.92(13)	B–O4–C14	107.00(10)
C13–C14	1.5631(18)	C10–C9–C8	122.06(12)		

*1,1,3,3-Tetramethyl-5-trimethylsilyl-1,3-disilaindane (**64**)*

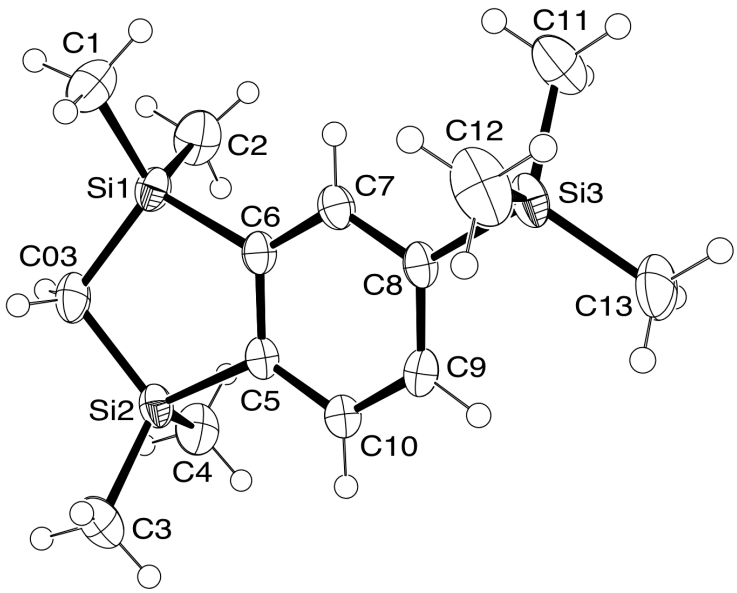


Figure A10. Molecular structure of compound **64** in the crystal (probability level of displacement ellipsoids 50%).

Table A25. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **64**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
C1	5543(2)	834(3)	6305(2)	48(1)
C2	6073(2)	3120(3)	7797(2)	51(1)
C03	7340(2)	2370(2)	5908(2)	38(1)
C3	9414(2)	1680(3)	5769(2)	49(1)
C4	8864(2)	3817(2)	7356(2)	44(1)
C5	8281(1)	1058(2)	7825(1)	25(1)
C6	7343(1)	769(2)	7924(2)	27(1)
C7	7115(1)	–173(2)	8700(2)	28(1)
C8	7781(1)	–847(2)	9392(1)	26(1)

	x	*y*	*z*	U_{eq}
C9	8700(2)	–517(2)	9294(2)	29(1)
C10	8949(1)	406(2)	8532(2)	28(1)
C11	6385(2)	–1798(3)	11023(2)	56(1)
C12	7294(2)	–3659(3)	9440(2)	57(1)
C13	8409(2)	–2509(3)	11484(2)	50(1)
Si1	6530(1)	1775(1)	6964(1)	30(1)
Si2	8510(1)	2268(1)	6687(1)	30(1)
Si3	7463(1)	–2200(1)	10348(1)	33(1)

Table A26. Bond lengths [Å] and angles [deg] for **64**.

C1–Si1	1.867(2)	C13–Si3	1.867(2)	C2–Si1–C03	110.74(13)
C2–Si1	1.873(3)			C1–Si1–C6	111.95(11)
C03–Si2	1.876(2)	Si2–C03–Si1	105.22(10)	C2–Si1–C6	110.65(10)
C03–Si1	1.882(2)	C10–C5–C6	118.65(18)	C03–Si1–C6	100.05(10)
C3–Si2	1.872(3)	C10–C5–Si2	126.00(16)	C4–Si2–C3	110.09(13)
C4–Si2	1.868(3)	C6–C5–Si2	115.31(14)	C4–Si2–C03	111.36(12)
C5–C10	1.407(3)	C7–C6–C5	119.02(18)	C3–Si2–C03	113.75(11)
C5–C6	1.420(3)	C7–C6–Si1	127.51(16)	C4–Si2–C5	110.98(10)
C5–Si2	1.891(2)	C5–C6–Si1	113.46(15)	C3–Si2–C5	110.35(11)
C6–C7	1.401(3)	C6–C7–C8	122.64(19)	C03–Si2–C5	99.96(10)
C6–Si1	1.894(2)	C9–C8–C7	116.90(18)	C11–Si3–C13	110.20(12)
C7–C8	1.408(3)	C9–C8–Si3	121.13(15)	C11–Si3–C12	110.24(15)
C8–C9	1.404(3)	C7–C8–Si3	121.88(16)	C13–Si3–C12	108.30(14)
C8–Si3	1.891(2)	C10–C9–C8	121.90(18)	C11–Si3–C8	109.33(12)
C9–C10	1.386(3)	C9–C10–C5	120.86(19)	C13–Si3–C8	110.25(11)
C11–Si3	1.866(3)	C1–Si1–C2	108.69(13)	C12–Si3–C8	108.50(11)
C12–Si3	1.873(3)	C1–Si1–C03	114.56(11)		

*1,1,3,3-Tetramethyl-5-trimethylsilyl-2-oxa-1,3-disilaindane (**65**).*

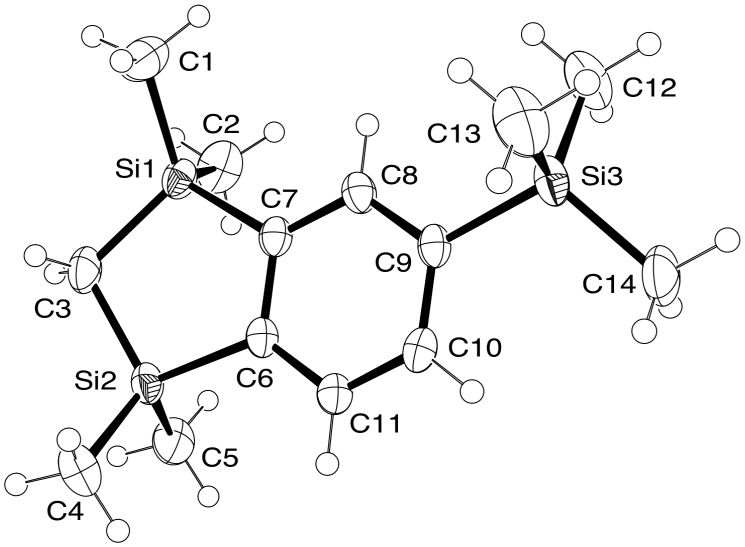


Figure A11. Molecular structure of compound **65** in the crystal (probability level of displacement ellipsoids 50%), disorder in the trimethylsilyl group removed for clarity).

Table A27. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **65**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
C1	5280(6)	889(3)	2988(2)	53(1)
C2	1161(6)	6(3)	2014(3)	54(1)
C3	7405(5)	3574(3)	461(2)	44(1)
C4	3438(5)	2916(3)	–705(2)	43(1)
C5	2881(4)	3851(2)	1403(2)	29(1)
C6	2203(4)	3022(2)	2171(2)	28(1)
C7	836(5)	3552(2)	2891(2)	32(1)
C8	167(5)	4875(2)	2886(2)	34(1)
C9	874(5)	5672(3)	2117(2)	36(1)
C10	2185(4)	5175(2)	1390(2)	34(1)
Si3	–1592(1)	5543(1)	3889(1)	40(1)

	x	*y*	*z*	U_{eq}
C11	–	4516(15)	4055(10)	66(3)
C12	–	7331(10)	3671(9)	73(3)
C13	158(17)	5478(14)	5013(6)	51(2)
Si3B	–1592(1)	5543(1)	3889(1)	40(1)
C11B	–	4213(9)	4309(8)	60(2)
C12B	–	6958(10)	3463(6)	73(3)
C13B	98(17)	6054(15)	4874(7)	76(3)
O1	4542(3)	1437(2)	999(1)	36(1)
Si1	3294(1)	1289(1)	2049(1)	32(1)
Si2	4621(1)	2940(1)	506(1)	29(1)

Table A28. Bond lengths [Å] and angles [deg] for **65**.

C1–Si1	1.832(3)	O1–Si1	1.6913(18)	C11–Si3–C8	111.8(4)
C2–Si1	1.853(3)			C12–Si3–C8	109.2(4)
C3–Si2	1.850(3)	C10–C5–C6	117.8(2)	C13–Si3–C8	105.7(4)
C4–Si2	1.838(3)	C10–C5–Si2	128.81(18)	Si2–O1–Si1	117.50(10)
C5–C10	1.403(3)	C6–C5–Si2	113.37(17)	O1–Si1–C1	109.37(13)
C5–C6	1.436(3)	C5–C6–C7	120.1(2)	O1–Si1–C2	112.45(12)
C5–Si2	1.915(2)	C5–C6–Si1	111.01(17)	C1–Si1–C2	109.72(17)
C6–C7	1.440(3)	C7–C6–Si1	128.91(18)	O1–Si1–C6	99.87(9)
C6–Si1	1.882(3)	C8–C7–C6	122.1(2)	C1–Si1–C6	112.18(12)
C7–C8	1.397(3)	C7–C8–C9	116.4(2)	C2–Si1–C6	112.93(15)
C8–C9	1.423(4)	C7–C8–Si3	120.28(19)	O1–Si2–C4	110.94(13)
C8–Si3	1.927(3)	C9–C8–Si3	123.30(19)	O1–Si2–C3	111.42(12)
C9–C10	1.414(4)	C10–C9–C8	122.9(2)	C4–Si2–C3	109.19(13)
Si3–C11	1.819(11)	C5–C10–C9	120.7(2)	O1–Si2–C5	98.00(9)
Si3–C12	1.861(9)	C11–Si3–C12	114.7(6)	C4–Si2–C5	113.23(12)
Si3–C13	1.899(8)	C11–Si3–C13	108.9(5)	C3–Si2–C5	113.70(12)
O1–Si2	1.6664(19)	C12–Si3–C13	106.0(6)		

*1,1,4,4-Tetramethyl-1,2,3,4-tetrahydro-1,4-disila-6-naphthoic acid (**69**).*

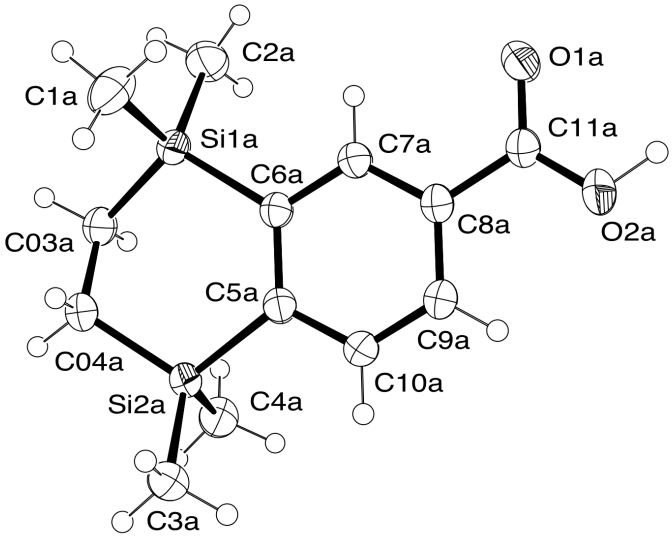


Figure A12. Molecular structure of compound **69** in the crystal (probability level of displacement ellipsoids 50%).

Table A29. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **69**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
C1A	4911(2)	2138(3)	10108(2)	51(1)
C4A	1404(2)	–153(2)	11463(1)	40(1)
C3A	3138(2)	–2652(2)	11634(1)	39(1)
C5A	2185(1)	–460(2)	9784(1)	28(1)
C6A	2462(1)	793(2)	9321(1)	28(1)
C7A	1972(1)	863(2)	8237(1)	30(1)
C8A	1227(1)	–269(2)	7620(1)	29(1)
C9A	967(1)	–1509(2)	8076(1)	33(1)

	x	*y*	*z*	U_{eq}
C10A	1446(1)	–1592(2)	9146(1)	33(1)
C11A	703(1)	–145(2)	6476(1)	29(1)
C03A	3621(2)	2309(2)	11450(1)	36(1)
C04A	3902(2)	693(2)	11915(1)	37(1)
O1A	895(1)	1011(2)	6064(1)	41(1)
O2A	62(1)	–1250(2)	5954(1)	43(1)
Si1A	3463(1)	2380(1)	10095(1)	31(1)
Si2A	2670(1)	–654(1)	11221(1)	29(1)

Table A30. Bond lengths [Å] and angles [deg] for **69**.

C2A–Si1A	1.866(2)	C04A–Si2A	1.8754(17)	O2A–C11A–C8A	116.92(14)
C1A–Si1A	1.871(2)	O2A–H2O	0.98(3)	C04A–C03A–	112.23(11)
C4A–Si2A	1.8667(18)			C03A–C04A–	111.82(11)
C3A–Si2A	1.8701(18)	C10A–C5A–C6A	119.04(13)	C11A–O2A–H2O	114.4(17)
C5A–C10A	1.403(2)	C10A–C5A–Si2A	116.90(11)	C2A–Si1A–C1A	108.17(11)
C5A–C6A	1.415(2)	C6A–C5A–Si2A	123.93(11)	C2A–Si1A–C03A	110.50(9)
C5A–Si2A	1.8880(15)	C7A–C6A–C5A	118.47(13)	C1A–Si1A–C03A	109.92(9)
C6A–C7A	1.402(2)	C7A–C6A–Si1A	118.40(11)	C2A–Si1A–C6A	109.89(8)
C6A–Si1A	1.8937(15)	C5A–C6A–Si1A	123.13(11)	C1A–Si1A–C6A	109.68(8)
C7A–C8A	1.396(2)	C8A–C7A–C6A	121.32(14)	C03A–Si1A–C6A	108.67(7)
C8A–C9A	1.390(2)	C9A–C8A–C7A	120.18(13)	C4A–Si2A–C3A	110.39(9)
C8A–C11A	1.483(2)	C9A–C8A–C11A	119.79(13)	C4A–Si2A–C04A	110.74(9)
C9A–C10A	1.386(2)	C7A–C8A–C11A	120.03(14)	C3A–Si2A–C04A	110.42(8)
C11A–O1A	1.257(2)	C10A–C9A–C8A	119.00(14)	C4A–Si2A–C5A	107.03(7)
C11A–O2A	1.2823(19)	C9A–C10A–C5A	121.98(15)	C3A–Si2A–C5A	109.68(8)
C03A–C04A	1.546(2)	O1A–C11A–O2A	123.31(14)	C04A–Si2A–C5A	108.49(7)
C03A–Si1A	1.8731(17)	O1A–C11A–C8A	119.77(13)		

*1,1,3,3-Tetramethyl-1,3-disila-5-indanoic acid (**70**).*

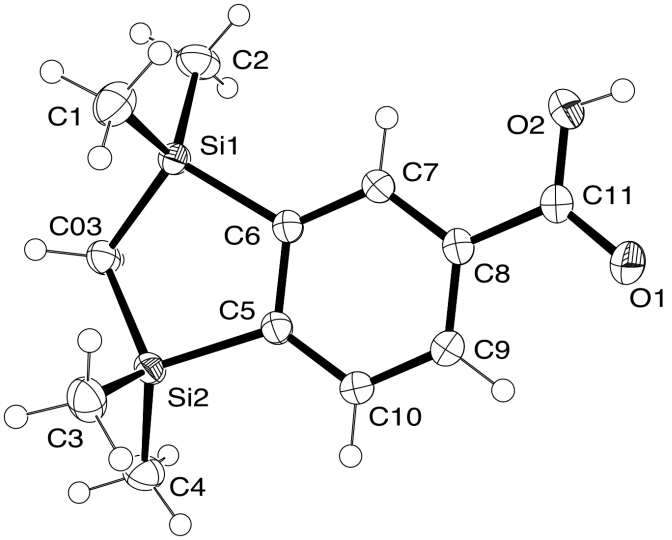


Figure A13. Molecular structure of compound **70** in the crystal (probability level of displacement ellipsoids 50%).

Table A31. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **70**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
C1	1110(1)	3057(3)	2238(1)	36(1)
C2	238(1)	–573(3)	1652(1)	36(1)
C03	2000(1)	–928(2)	1723(1)	26(1)
C3	3197(1)	3036(3)	1822(1)	34(1)
C4	3456(1)	–868(3)	1087(1)	35(1)
C5	2099(1)	2640(2)	981(1)	22(1)
C6	1352(1)	2794(2)	1133(1)	22(1)
C7	854(1)	4286(2)	882(1)	24(1)

	x	*y*	*z*	U_{eq}
C8	1097(1)	5658(2)	491(1)	25(1)
C9	1827(1)	5434(3)	331(1)	28(1)
C10	2323(1)	3927(3)	572(1)	26(1)
C11	600(1)	7461(3)	258(1)	27(1)
O2	–75(1)	7541(2)	393(1)	39(1)
O1	870(1)	8866(2)	–53(1)	40(1)
Si1	1148(1)	1019(1)	1699(1)	23(1)
Si2	2724(1)	867(1)	1403(1)	23(1)

Table A32. Bond lengths [Å] and angles [deg] for **70**.

C1–Si1	1.8747(16)	C11–O2	1.2729(16)	O1–C11–C8	118.59(12)
C2–Si1	1.8639(15)			O2–C11–C8	117.84(11)
C03–Si2	1.8739(13)	Si2–C03–Si1	104.21(7)	C2–Si1–C1	107.63(7)
C03–Si1	1.8774(13)	C10–C5–C6	119.43(11)	C2–Si1–C03	116.15(7)
C3–Si2	1.8717(16)	C10–C5–Si2	126.21(9)	C1–Si1–C03	111.23(7)
C4–Si2	1.8600(15)	C6–C5–Si2	114.11(9)	C2–Si1–C6	111.81(7)
C5–C10	1.4026(17)	C7–C6–C5	119.44(11)	C1–Si1–C6	110.34(7)
C5–C6	1.4155(16)	C7–C6–Si1	126.35(9)	C03–Si1–C6	99.53(6)
C5–Si2	1.8870(13)	C5–C6–Si1	114.10(9)	C4–Si2–C3	107.99(7)
C6–C7	1.3990(16)	C8–C7–C6	120.38(11)	C4–Si2–C03	116.33(7)
C6–Si1	1.8901(13)	C9–C8–C7	119.89(12)	C3–Si2–C03	111.48(7)
C7–C8	1.3977(17)	C9–C8–C11	119.15(11)	C4–Si2–C5	113.73(6)
C8–C9	1.3948(17)	C7–C8–C11	120.87(11)	C3–Si2–C5	107.71(7)
C8–C11	1.4863(17)	C10–C9–C8	120.31(12)	C03–Si2–C5	99.18(6)
C9–C10	1.3883(18)	C9–C10–C5	120.39(11)		
C11–O1	1.2646(16)	O1–C11–O2	123.55(12)		

*2-(4,4-Bis(4-fluorophenyl)butyl)isoindoline-1,3-dione (**81**).*

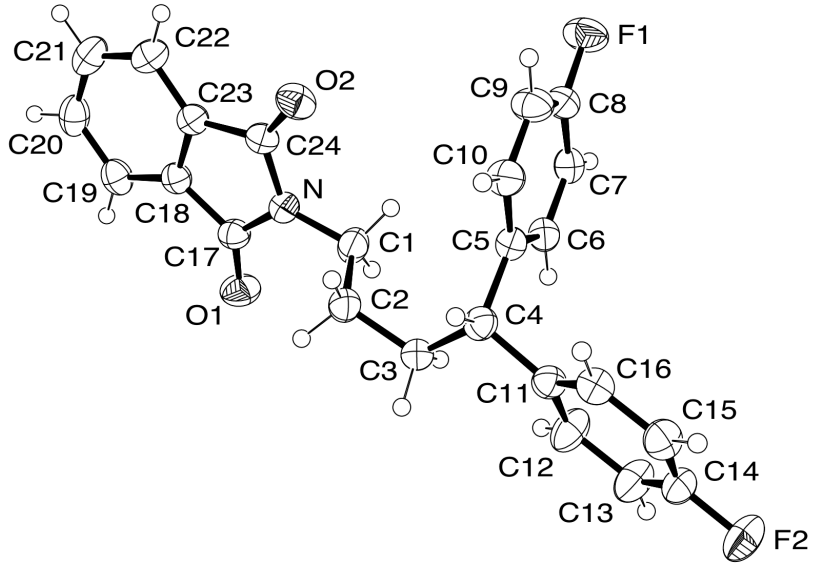


Figure A14. Molecular structure of compound **81** in the crystal (probability level of displacement ellipsoids 50%).

Table A33. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **81**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
C1	9534(2)	3987(1)	5174(2)	41(1)
C2	10387(2)	3855(1)	6556(2)	41(1)
C3	9622(2)	4119(1)	7879(2)	38(1)
C4	8365(2)	3752(1)	8583(1)	35(1)
C5	7009(2)	3621(1)	7595(1)	33(1)
C6	6115(2)	4057(1)	7004(2)	34(1)
C7	4896(2)	3934(1)	6093(1)	35(1)
C8	4586(2)	3372(1)	5789(2)	38(1)
C9	5420(2)	2928(1)	6364(2)	45(1)
C10	6640(2)	3059(1)	7274(2)	40(1)
C11	7796(2)	4016(1)	9976(1)	35(1)
C12	7728(2)	4602(1)	10194(2)	50(1)
C13	7156(2)	4830(1)	11460(2)	50(1)
C14	6666(2)	4464(1)	12501(2)	40(1)
C15	6710(2)	3883(1)	12337(2)	42(1)
C16	7278(2)	3663(1)	11063(2)	38(1)
C17	11481(2)	4137(1)	3215(2)	35(1)
C18	11973(2)	3803(1)	1942(1)	33(1)
C19	13039(2)	3926(1)	894(2)	41(1)
C20	13204(2)	3531(1)	–214(2)	46(1)
C21	12326(2)	3039(1)	–260(2)	47(1)
C22	11275(2)	2909(1)	817(2)	42(1)
C23	11127(2)	3301(1)	1913(1)	33(1)
C24	10125(2)	3292(1)	3200(1)	33(1)
F1	3418(1)	3251(1)	4863(1)	54(1)
F2	6119(1)	4690(1)	13736(1)	56(1)
O1	11911(1)	4604(1)	3607(1)	50(1)
O2	9259(1)	2917(1)	3606(1)	44(1)
N	10368(1)	3807(1)	3900(1)	34(1)

Table A34. Bond lengths [Å] and angles [deg] for **81**.

C1–N	1.4649(17)	C20–C21	1.386(3)	C11–C12–C13	121.27(14)
C1–C2	1.526(2)	C21–C22	1.401(2)	C14–C13–C12	118.70(15)
C2–C3	1.5418(19)	C22–C23	1.3861(19)	F2–C14–C13	118.33(14)
C3–C4	1.543(2)	C23–C24	1.4946(18)	F2–C14–C15	119.46(13)
C4–C5	1.5305(19)	C24–O2	1.2198(16)	C13–C14–C15	122.21(14)
C4–C11	1.5328(19)	C24–N	1.3932(18)	C14–C15–C16	118.30(13)
C5–C10	1.391(2)			C11–C16–C15	121.71(14)
C5–C6	1.3986(19)	N–C1–C2	113.31(12)	O1–C17–N	124.93(13)
C6–C7	1.3917(19)	C1–C2–C3	113.19(12)	O1–C17–C18	128.77(13)
C7–C8	1.375(2)	C2–C3–C4	115.60(13)	N–C17–C18	106.30(11)
C8–F1	1.3667(16)	C5–C4–C11	110.32(11)	C19–C18–C23	121.30(13)
C8–C9	1.380(2)	C5–C4–C3	113.52(11)	C19–C18–C17	130.88(13)
C9–C10	1.396(2)	C11–C4–C3	111.92(12)	C23–C18–C17	107.81(11)
C11–C12	1.391(2)	C10–C5–C6	118.63(13)	C18–C19–C20	117.44(14)
C11–C16	1.392(2)	C10–C5–C4	119.91(12)	C21–C20–C19	121.04(14)
C12–C13	1.398(2)	C6–C5–C4	121.46(12)	C20–C21–C22	121.36(14)
C13–C14	1.372(2)	C7–C6–C5	121.04(13)	C23–C22–C21	117.13(15)
C14–F2	1.3635(16)	C8–C7–C6	118.32(13)	C22–C23–C18	121.68(13)
C14–C15	1.373(2)	F1–C8–C7	118.45(13)	C22–C23–C24	130.37(13)
C15–C16	1.396(2)	F1–C8–C9	118.80(14)	C18–C23–C24	107.95(11)
C17–O1	1.2143(17)	C7–C8–C9	122.74(13)	O2–C24–N	124.80(13)
C17–N	1.3986(17)	C8–C9–C10	118.14(14)	O2–C24–C23	128.88(13)
C17–C18	1.4942(19)	C5–C10–C9	121.10(13)	N–C24–C23	106.32(11)
C18–C19	1.3866(19)	C12–C11–C16	117.80(13)	C24–N–C17	111.53(11)
C18–C23	1.3897(19)	C12–C11–C4	122.65(13)	C24–N–C1	124.13(12)
C19–C20	1.401(2)	C16–C11–C4	119.52(13)	C17–N–C1	124.32(12)

*(4-Chlorophenyl)(2,6-dimethoxyphenyl)bis(2-hydroxyethyl)silane (**84**).*

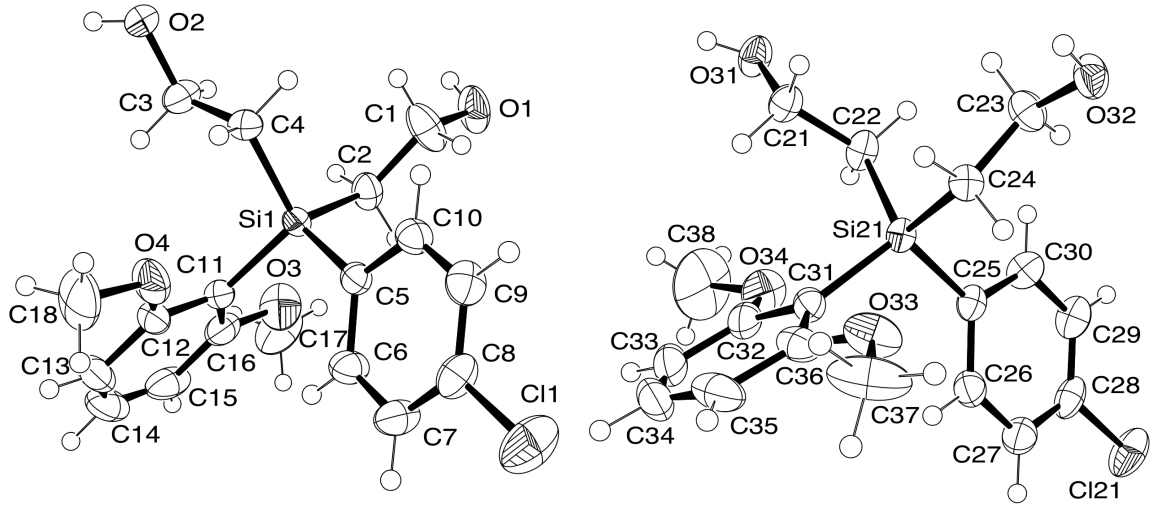


Figure A15. Molecular structures of the two crystallographically independent molecules in the crystal of **84** (probability level of displacement ellipsoids 50%).

Table A35. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **84**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	*y*	*z*	U_{eq}
C1	3490(3)	1446(2)	3102(1)	54(1)
C2	4109(2)	919(1)	2498(1)	36(1)
C3	8501(2)	1454(1)	3085(1)	38(1)
C4	7441(2)	2336(1)	2856(1)	33(1)
C5	4904(2)	3025(1)	1664(1)	28(1)
C6	4637(2)	3067(1)	928(1)	38(1)
C7	3956(2)	3924(2)	578(1)	43(1)
C8	3521(2)	4759(1)	967(1)	39(1)
C9	3780(2)	4769(1)	1693(1)	40(1)
C10	4460(2)	3904(1)	2037(1)	34(1)
C11	6614(2)	1058(1)	1423(1)	31(1)
C12	7969(2)	1601(2)	1150(1)	39(1)
C13	8653(3)	1143(2)	613(1)	56(1)
C14	7952(3)	133(2)	331(1)	63(1)
C15	6633(3)	–440(2)	570(1)	56(1)
C16	5965(2)	18(2)	1122(1)	40(1)
C17	4080(3)	–1629(2)	1179(2)	70(1)
C18	9952(3)	3241(2)	1228(2)	72(1)
C21	4611(2)	8509(1)	4415(1)	33(1)
C22	5666(2)	8585(1)	3831(1)	33(1)
C23	9550(2)	8551(1)	4547(1)	36(1)
C24	8557(2)	7415(1)	4440(1)	28(1)
C25	7461(2)	7366(1)	2846(1)	28(1)
C26	7346(2)	6398(1)	2441(1)	36(1)
C27	7891(2)	6400(2)	1787(1)	41(1)
C28	8585(2)	7387(2)	1542(1)	38(1)
C29	8725(2)	8365(2)	1921(1)	40(1)
C30	8155(2)	8348(1)	2568(1)	36(1)
C31	5300(2)	6003(1)	3760(1)	31(1)
C32	3669(2)	5975(2)	3435(1)	44(1)
C33	2486(3)	5079(2)	3478(1)	62(1)
C34	2925(3)	4179(2)	3839(1)	69(1)
C35	4523(3)	4124(2)	4145(1)	59(1)
C36	5718(2)	5035(1)	4089(1)	39(1)
C37	7839(4)	4089(2)	4678(1)	70(1)
C38	1733(3)	7103(4)	2863(2)	116(1)
Cl1	2600(1)	5813(1)	528(1)	67(1)
Cl21	9329(1)	7398(1)	738(1)	59(1)
O1	2225(2)	728(1)	3376(1)	53(1)
O2	9756(1)	1830(1)	3659(1)	37(1)
O3	4664(2)	–499(1)	1391(1)	58(1)
O4	8546(2)	2621(1)	1447(1)	49(1)
O31	3614(1)	9387(1)	4366(1)	39(1)
O32	11048(1)	8548(1)	5018(1)	39(1)
O33	7329(2)	5049(1)	4333(1)	48(1)
O34	3373(2)	6892(1)	3054(1)	56(1)
Si1	5771(1)	1822(1)	2115(1)	27(1)
Si21	6735(1)	7330(1)	3730(1)	25(1)

Table A36. Bond lengths [Å] and angles [deg] for **84**.

C1–O1	1.440(2)	C31–C32	1.410(2)	C23–C24–Si21	114.57(10)
C1–C2	1.506(2)	C31–Si21	1.8873(15)	C26–C25–C30	117.01(14)
C2–Si1	1.8894(16)	C32–O34	1.367(3)	C26–C25–Si21	120.71(11)
C3–O2	1.4358(19)	C32–C33	1.383(3)	C30–C25–Si21	122.27(12)
C3–C4	1.506(2)	C33–C34	1.361(4)	C25–C26–C27	121.86(16)
C4–Si1	1.8867(15)	C34–C35	1.389(4)	C28–C27–C26	118.72(16)
C5–C6	1.400(2)	C35–C36	1.407(2)	C29–C28–C27	121.73(15)
C5–C10	1.400(2)	C36–O33	1.357(2)	C29–C28–Cl21	118.92(14)
C5–Si1	1.8777(15)	C37–O33	1.429(2)	C27–C28–Cl21	119.35(14)
C6–C7	1.384(2)	C38–O34	1.422(3)	C28–C29–C30	118.64(16)
C7–C8	1.374(3)			C29–C30–C25	122.02(16)
C8–C9	1.379(3)	O1–C1–C2	112.73(17)	C36–C31–C32	116.68(15)
C8–Cl1	1.7405(17)	C1–C2–Si1	114.76(12)	C36–C31–Si21	125.10(12)
C9–C10	1.386(2)	O2–C3–C4	112.11(13)	C32–C31–Si21	118.22(13)
C11–C16	1.398(2)	C3–C4–Si1	111.71(11)	O34–C32–C33	122.93(19)
C11–C12	1.402(2)	C6–C5–C10	116.79(14)	O34–C32–C31	114.21(15)
C11–Si1	1.8829(15)	C6–C5–Si1	120.64(11)	C33–C32–C31	122.8(2)
C12–O4	1.363(2)	C10–C5–Si1	122.55(11)	C34–C33–C32	118.4(2)
C12–C13	1.393(2)	C7–C6–C5	122.29(15)	C33–C34–C35	122.11(18)
C13–C14	1.365(4)	C8–C7–C6	118.69(16)	C34–C35–C36	118.9(2)
C14–C15	1.361(4)	C7–C8–C9	121.44(16)	O33–C36–C31	115.21(14)
C15–C16	1.409(3)	C7–C8–Cl1	118.83(14)	O33–C36–C35	123.94(18)
C16–O3	1.351(2)	C9–C8–Cl1	119.72(14)	C31–C36–C35	120.85(19)
C17–O3	1.434(2)	C8–C9–C10	119.22(15)	C16–O3–C17	118.48(19)
C18–O4	1.425(2)	C9–C10–C5	121.56(15)	C12–O4–C18	119.56(18)
C21–O31	1.4328(17)	C16–C11–C12	116.08(15)	C36–O33–C37	118.08(17)
C21–C22	1.515(2)	C16–C11–Si1	126.29(13)	C32–O34–C38	119.2(2)
C22–Si21	1.8880(15)	C12–C11–Si1	117.53(12)	C5–Si1–C11	106.24(7)
C23–O32	1.4351(18)	O4–C12–C13	122.88(18)	C5–Si1–C4	110.14(7)
C23–C24	1.514(2)	O4–C12–C11	114.31(14)	C11–Si1–C4	110.56(7)
C24–Si21	1.8843(14)	C13–C12–C11	122.80(19)	C5–Si1–C2	109.48(7)
C25–C26	1.393(2)	C14–C13–C12	118.6(2)	C11–Si1–C2	112.07(7)
C25–C30	1.400(2)	C15–C14–C13	121.68(18)	C4–Si1–C2	108.33(8)
C25–Si21	1.8785(15)	C14–C15–C16	119.5(2)	C25–Si21–C24	108.99(6)
C26–C27	1.394(2)	O3–C16–C11	115.54(15)	C25–Si21–C31	107.47(7)
C27–C28	1.378(3)	O3–C16–C15	123.14(18)	C24–Si21–C31	112.21(7)
C28–C29	1.374(3)	C11–C16–C15	121.31(19)	C25–Si21–C22	108.74(7)
C28–Cl21	1.7428(16)	O31–C21–C22	110.41(12)	C24–Si21–C22	108.07(7)

Table A36. Continued

C29–C30	1.391(2)	C21–C22–Si21	114.45(10)	C31–Si21–C22	111.29(7)
C31–C36	1.400(2)	O32–C23–C24	112.87(13)		

*1-Allyl-4-(4-chlorophenyl)-4-(2,6-dimethoxyphenyl)-4-silapiperidine (**85**).*

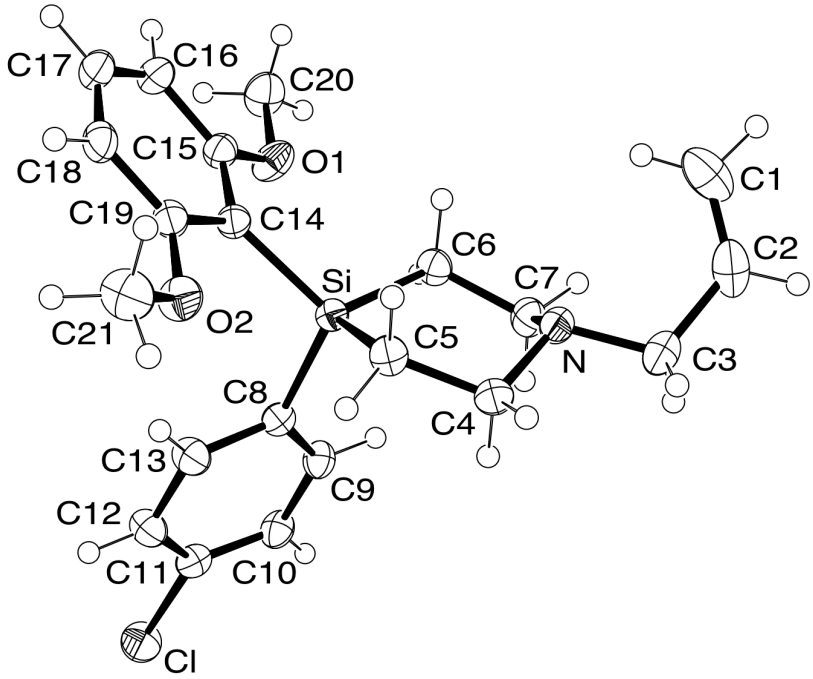


Figure A16. Molecular structure of **85** in the crystal (probability level of displacement ellipsoids 50%).

Table A37. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$A^2 \times 10^3$] for the non-hydrogen atoms of **85**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

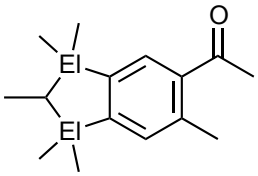
	x	*y*	*z*	U_{eq}
C1	–1491(2)	509(1)	–4372(3)	49(1)
C2	–2188(1)	839(1)	–3888(3)	44(1)
C3	–2144(1)	1186(1)	–2038(3)	38(1)
C4	–1178(1)	1329(1)	1122(2)	31(1)
C5	–198(1)	1199(1)	2415(2)	27(1)
C6	371(1)	1866(1)	–780(2)	27(1)
C7	–714(1)	1844(1)	–1555(2)	30(1)
C8	711(1)	2597(1)	3103(2)	24(1)
C9	332(1)	3187(1)	2193(2)	27(1)
C10	356(1)	3793(1)	3167(2)	29(1)
C11	778(1)	3804(1)	5079(2)	26(1)
C12	1143(1)	3232(1)	6050(2)	30(1)
C13	1103(1)	2634(1)	5052(2)	30(1)

	x	*y*	*z*	U_{eq}
C14	1982(1)	1408(1)	2654(2)	24(1)
C15	2694(1)	1514(1)	1643(2)	27(1)
C16	3575(1)	1182(1)	2107(2)	33(1)
C17	3761(1)	759(1)	3662(2)	35(1)
C18	3104(1)	667(1)	4775(2)	32(1)
C19	2224(1)	998(1)	4262(2)	26(1)
C20	3153(1)	2065(1)	–944(3)	40(1)
C21	1653(2)	446(1)	6722(3)	42(1)
Cl	863(1)	4565(1)	6303(1)	38(1)
N	–1173(1)	1266(1)	–887(2)	28(1)
O1	2468(1)	1957(1)	178(2)	35(1)
O2	1535(1)	945(1)	5285(2)	34(1)
Si	737(1)	1771(1)	1857(1)	21(1)

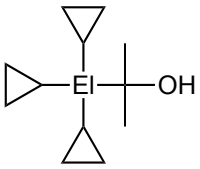
Table A38. Bond lengths [Å] and angles [deg] for **85**.

C1–C2	1.315(3)	C17–C18	1.388(3)	C15–C14–Si	122.14(11)
C2–C3	1.503(3)	C18–C19	1.406(2)	C19–C14–Si	121.12(11)
C3–N	1.470(2)	C19–O2	1.3715(19)	O1–C15–C14	115.54(13)
C4–N	1.468(2)	C20–O1	1.431(2)	O1–C15–C16	122.57(14)
C4–C5	1.535(2)	C21–O2	1.4280(19)	C14–C15–C16	121.88(15)
C5–Si	1.8799(15)			C17–C16–C15	118.87(15)
C6–C7	1.539(2)	C1–C2–C3	126.19(17)	C18–C17–C16	121.50(14)
C6–Si	1.8824(15)	N–C3–C2	113.85(14)	C17–C18–C19	118.43(14)
C7–N	1.468(2)	N–C4–C5	112.72(12)	O2–C19–C18	122.67(14)
C8–C9	1.403(2)	C4–C5–Si	111.76(11)	O2–C19–C14	114.94(13)
C8–C13	1.406(2)	C7–C6–Si	113.58(10)	C18–C19–C14	122.40(14)
C8–Si	1.8898(15)	N–C7–C6	113.48(12)	C7–N–C4	111.39(13)
C9–C10	1.401(2)	C9–C8–C13	117.27(14)	C7–N–C3	109.86(13)
C10–C11	1.388(2)	C9–C8–Si	123.87(11)	C4–N–C3	111.10(13)
C11–C12	1.386(2)	C13–C8–Si	118.85(11)	C15–O1–C20	117.87(13)
C11–Cl	1.7548(16)	C10–C9–C8	121.75(14)	C19–O2–C21	118.04(13)
C12–C13	1.395(2)	C11–C10–C9	118.55(14)	C5–Si–C6	103.35(7)
C14–C15	1.406(2)	C12–C11–C10	121.85(14)	C5–Si–C8	109.70(7)
C14–C19	1.408(2)	C12–C11–Cl	118.91(12)	C6–Si–C8	111.66(7)
C14–Si	1.9022(14)	C10–C11–Cl	119.24(12)	C5–Si–C14	112.01(7)
C15–O1	1.368(2)	C11–C12–C13	118.52(15)	C6–Si–C14	112.28(7)
C15–C16	1.406(2)	C12–C13–C8	122.02(14)	C8–Si–C14	107.85(6)
C16–C17	1.390(3)	C15–C14–C19	116.70(13)		

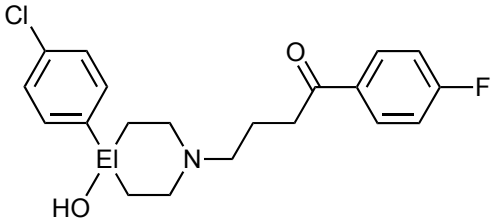
Appendix C: Compound Index



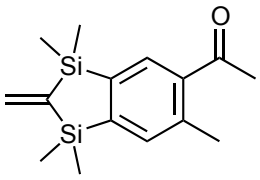
El = C: **1a** (Phantolide)
El = Si: **1b** (Disila-phantolide)



El = C: **2a**
El = Si: **2b**



El = C: **3a** (Haloperidol)
El = Si: **3b** (Sila-haloperidol)



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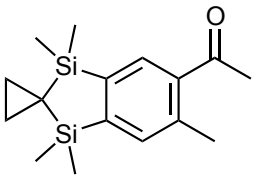

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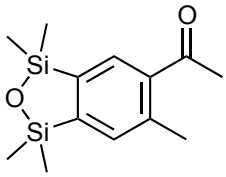

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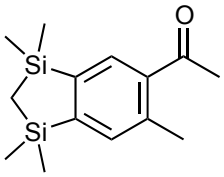

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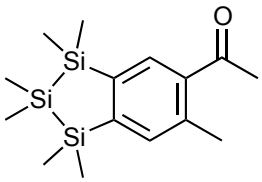

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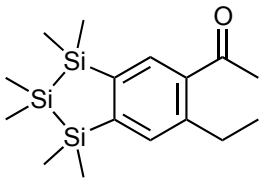

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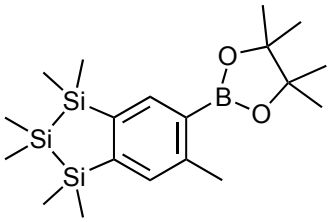

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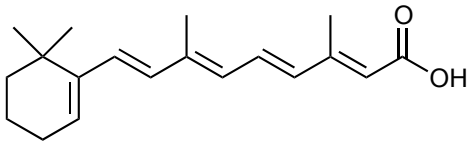
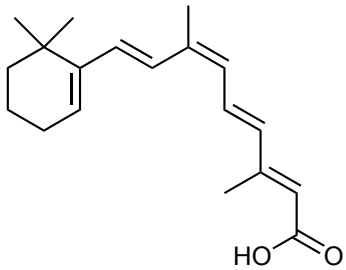
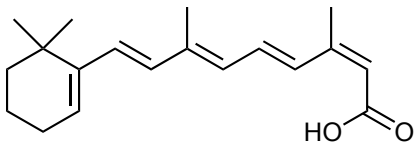


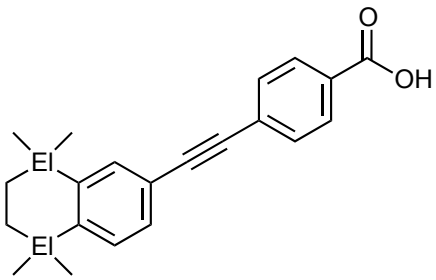
11: all-*trans* Retinoic Acid



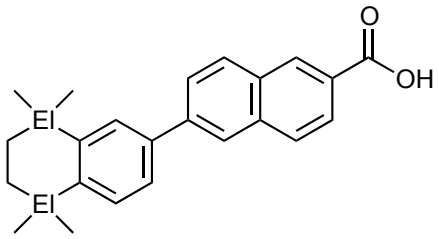
12: 9-*cis* Retinoic Acid



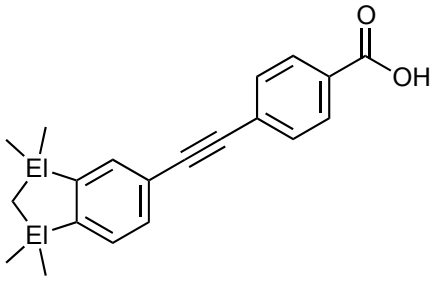
13: 13-*cis* Retinoic Acid



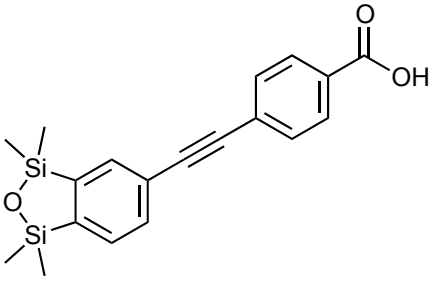
El = C: **14a** (EC23)
El = Si: **14b** (Disila-EC23)



El = C: **15a** (TTNN)
El = Si: **15b** (Disila-TTNN)



El = C: **16a**
El = Si: **16b**



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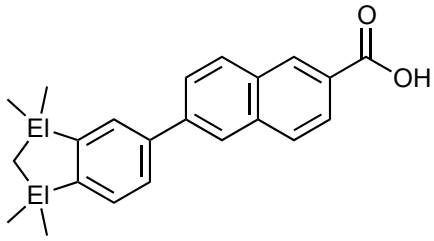
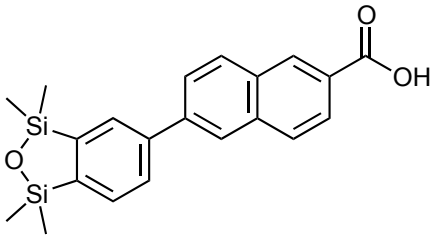


El = C: **18a**
El = Si: **18b**



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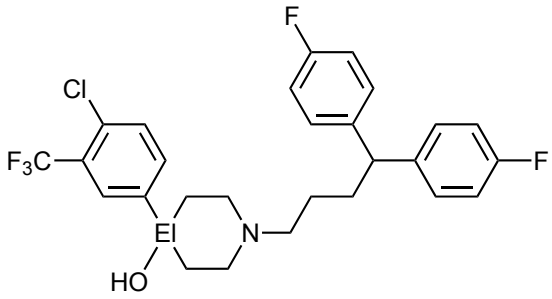
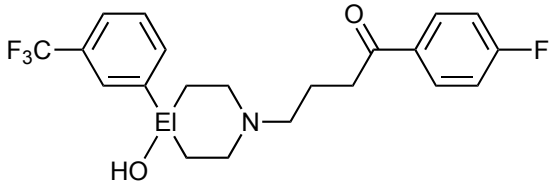
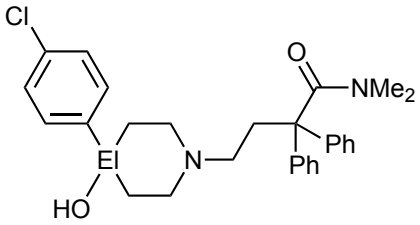


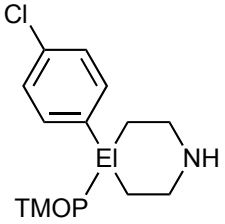
El = C: **20a** (Penfluridol)
El = Si: **20b** (Sila-penfluridol)



El = C: **21a** (Trifluperidol)
El = Si: **21b** (Sila-trifluperidol)



El = C: **22a** (Loperamide)
El = Si: **22b** (Sila-loperamide)



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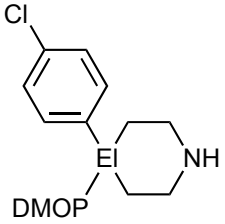

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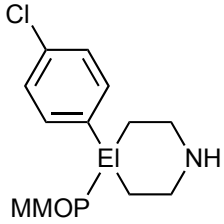

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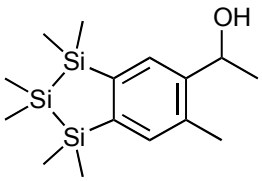

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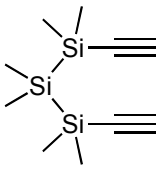

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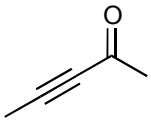

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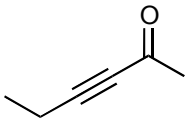

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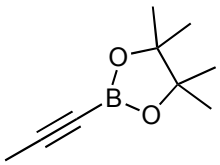

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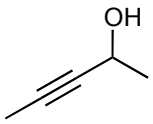

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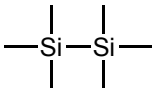

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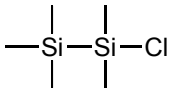

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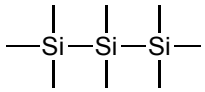

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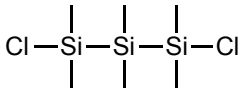

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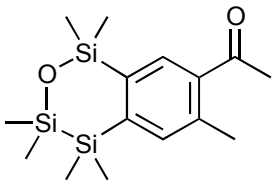

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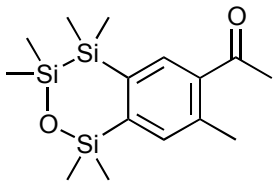

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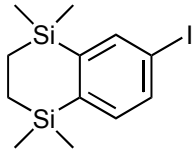

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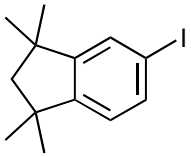

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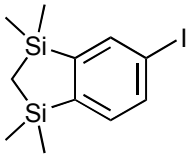

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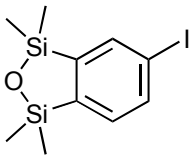

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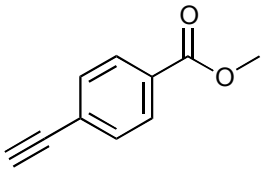

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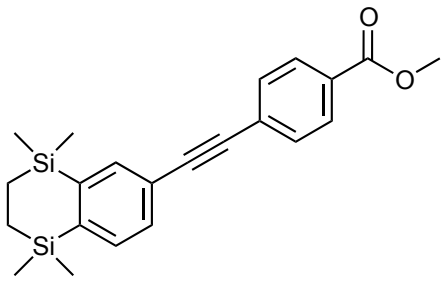

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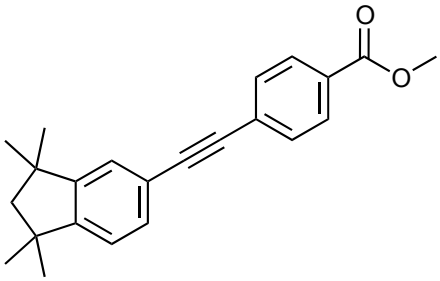

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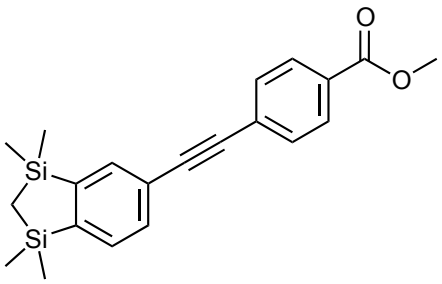

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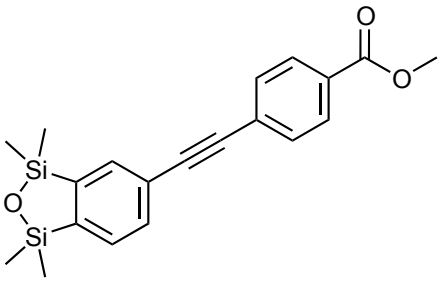

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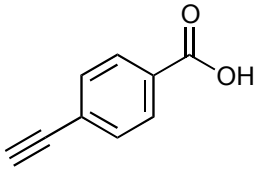

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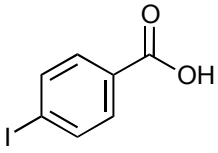

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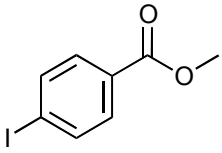

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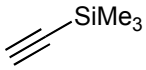

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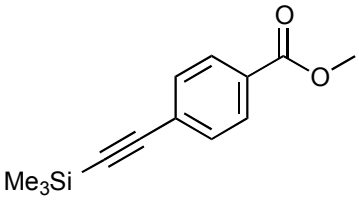

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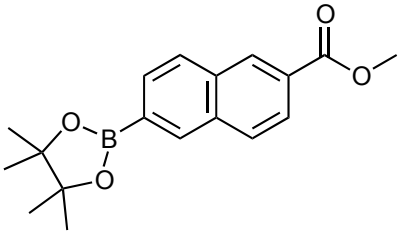

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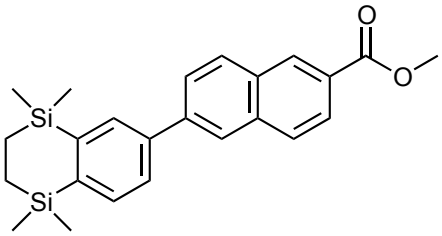

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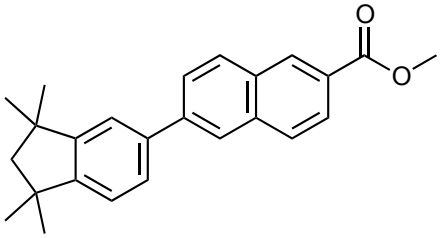

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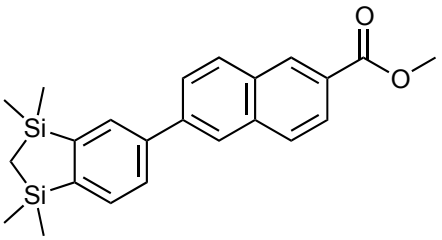

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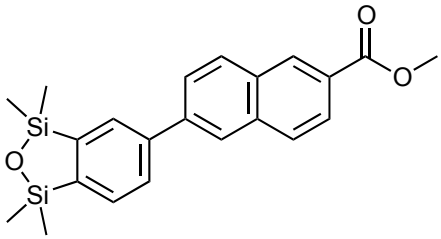

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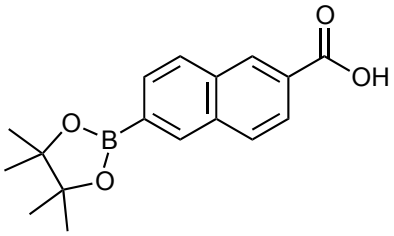

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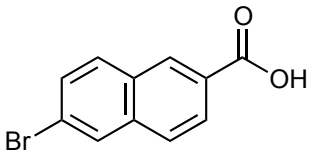

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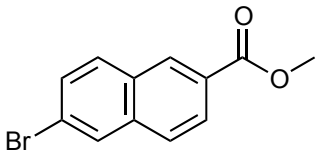

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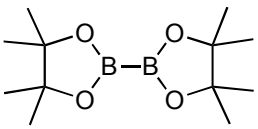

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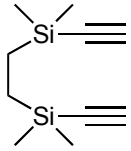

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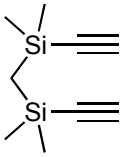

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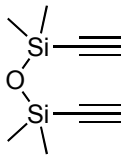

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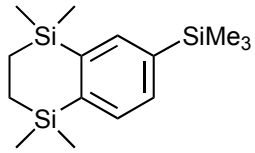

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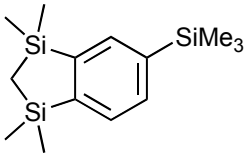

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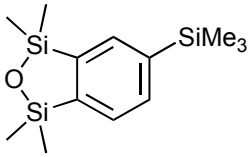

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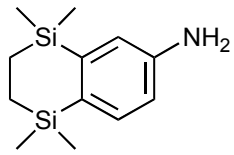

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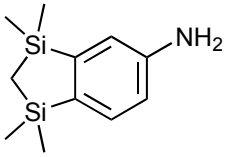

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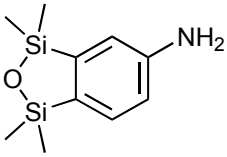

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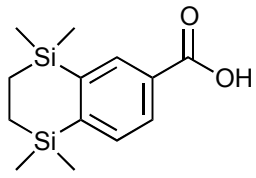

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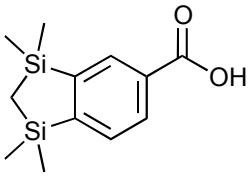

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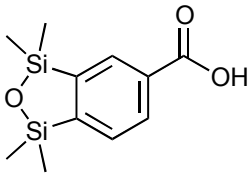

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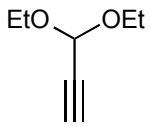

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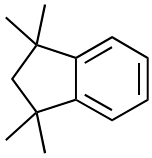

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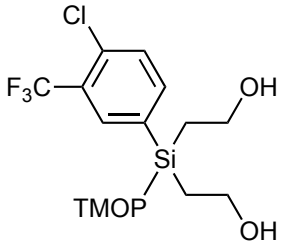

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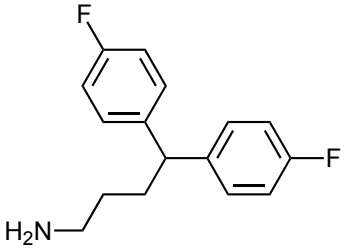

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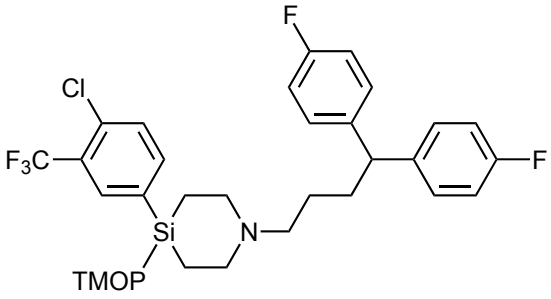

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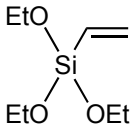

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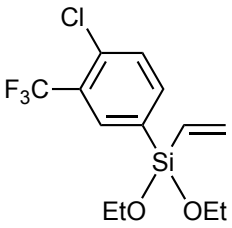

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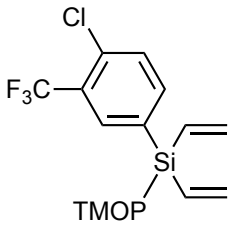

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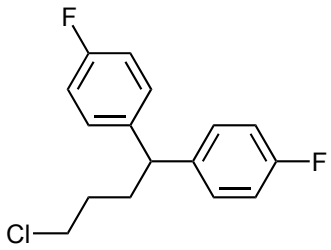

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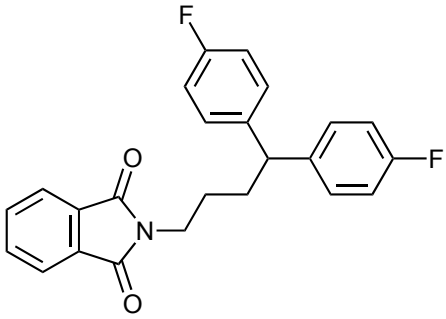

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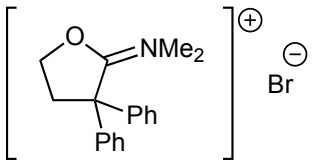

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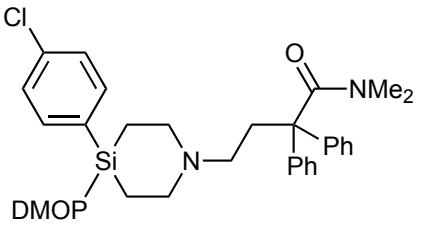

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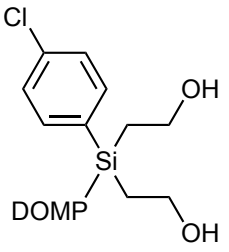

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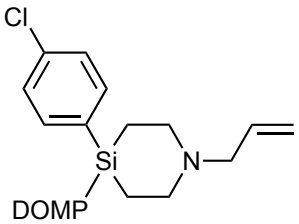

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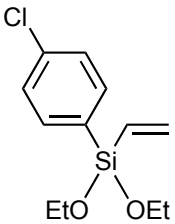

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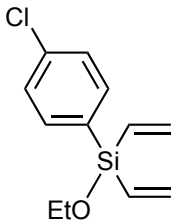

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Acknowledgements

First a *caveat lector* to the acknowledgements: they are in English despite the fact that those being thanked are, for the most part, native German speakers. However, those who will be reading this know how awful my written German is and so hopefully will understand!

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