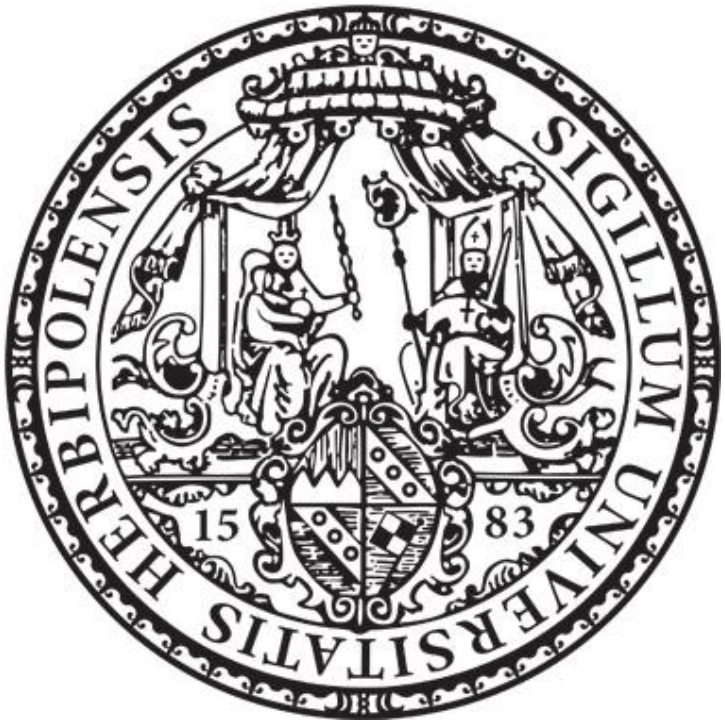
C–S Bond Borylation and Diborylation of Alkyl Halides, Tosylates, and Alcohols



Dissertation zur Erlangung des naturwissenschaftlichen Doktorgrades

der Julius-Maximilians-Universität Würzburg

vorgelegt von

Mingming Huang

aus Jiangsu, V.R. China

Würzburg, 2022

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Eingereicht bei der Fakultät für Chemie und Pharmazie am

_____

Gutachter der schriftlichen Arbeit

1. Gutachter: Prof. Dr. Dr. h. c. Todd B. Marder

2. Gutachter: Prof. Dr. Florian Beuerle

Prüfer des öffentlichen Promotionskolloquiums

1. Prüfer: Prof. Dr. Dr. h. c. Todd B. Marder

2. Prüfer: Prof. Dr. Florian Beuerle

3. Prüfer: Prof. Dr. Udo Radius

Datum des öffentlichen Promotionskolloquiums

_____

Doktorurkunde ausgehändigt am

_____

"Those times when you get up early and you work hard, those times when you stay up late and work hard. Those times when you don't feel like working, your're too tired and you don't want to push yourself but you do it anyway. That is actually the dream!"

-- Kobe Bryant

谨此献给我的家人

Für meine Familie

Die Experimente zur vorliegenden Arbeit wurden in der Zeit von Oktober 2017 bis Dezember 2021 am Institut für Anorganische Chemie der Julius - Maximilians - Universität Würzburg unter der Aufsicht von Prof. Dr. Dr. h. c. Todd B. Marder und Prof. Dr. rer. nat. habil. Udo Radius durchgeführt.

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List of Publications

The publications listed below are reproduced in this dissertation with permission from Wiley-VCH and Royal Society of Chemistry. The table itemizes at which position in this work the paper has been reproduced.

Publication	**Position**
M. Huang, Z. Wu, J. Krebs, A. Friedrich, X. Luo*, S. A. Westcott, U. Radius*, T. B. Marder*, *Chem. Eur. J.* **2021**, *27*, 8149–8158.	Chapter 2
M. Huang, J. Hu*, I. Krummenacher, A. Friedrich, H. Braunschweig, S. A. Westcott, U. Radius*, T. B. Marder*, *Chem. Eur. J.* **2022**, DOI: 10.1002/chem.202103866.	Chapter 3
M. Huang, M. Tang, J. Hu*, S. A. Westcott, U. Radius*, T. B. Marder*, *Chem. Commun.* **2022**, *58*, 395–398.	Chapter 4
M. Huang, J. Hu*, S. Shi, A. Friedrich, J. Krebs, S. A. Westcott, U. Radius*, T. B. Marder*, *Submitted*.	Chapter 5

Further publications:

1. L. Kuehn, M. Huang, U. Radius, T. B. Marder, *Org. Biomol. Chem.* **2019**, *17*, 6601–6606.
2. Z. Liu, Y. P. Budiman, Y. M. Tian, A. Friedrich, M. Huang, S. A. Westcott, U. Radius, T. B. Marder, *Chem. Eur. J.* **2020**, *26*, 17267–17274.
3. W. Ming, X. Liu, A. Friedrich, J. Krebs, Y. P. Budiman, M. Huang, T. B. Marder*, *Green Chem.* **2020**, *22*, 2184–2190.

List of Abbreviations

Aq	Aqueous
Ar	Argon
B_2cat_2	Bis(catecholato)diboron
BHT	Butylated hydroxytoluene
$B_2(OH)_4$	Tetrahydroxydiboron
B_2pin_2	Bis(pinacolato)diboron
B_2neop_2	Bis(neopentyl glycolato)diboron
bpy	2,2′-Bipyridine
COD	1,5-Cyclooctadiene
CPME	cyclopentyl methyl ether
CV	Cyclic voltammetry
DABCO	1,4-Diazabicyclo[2.2.2]octane
dan	1,8-Diaminonaphthalene
dba	Dibenzylideneacetone
DCM	Dichloromethane
DEMS	Methyldiethoxysilane
DFT	Density functional theory
DMA	*N*,*N*-dimethylacetamide
DMAP	4-Dimethylaminopyridine
DMF	*N*,*N*-Dimethylformamide
DMPO	Dimethyl-1-pyrroline *N*-oxide
DMSO	Dimethyl sulfoxide
dppf	1,1'-Bis(diphenylphosphino)ferrocene
dtbpy	4,4′-Di-*tert*-butyl-2,2′-dipyridyl
EDA	Energy decomposition analysis
EPR	Electron paramagnetic resonance

Et_3N	Triethylamine
EtOAc	Ethyl acetate
equiv	Equivalents
GC-MS	Gas chromatography-mass spectrometry
HAT	Hydrogen atom transfer
HPLC	High-performance liquid chromatography
HRMS	High-resolution mass spectrometry
ICy	1,3-Dicyclohexylimidazol-2-ylidene
IMe	1,3,4,5-tetramethylimidazolin-2-ylidene
IMes	1,3-Dimesitylimidazol-2-ylidene
IPr	1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene
KI	Potassium iodide
KO^tBu	Potassium *tert*-butoxide
LED	Light-emitting diode
$LiN(SiMe_3)_2$	Lithium-bis-(trimethylsilyl)-amid
MeCN	Acetonitrile
MIDA	Trivalent *N*-methyliminodiacetic acid
MTBE	Methyl *tert*-butyl ether
NBS	*N*-Bromosuccinimide
n.d.	Not detected
NHC	*N*-Heterocyclic carbene
NMR	Nuclear magnetic resonance
$P(o\text{-tol})_3$	Tris(*o*-tolyl)phosphine
PCy_3	Tricyclohexylphosphine
PPh_3	Triphenylphosphine
$PnBu_3$	Tri-*n*-butylphosphine
rt	Room temperature

SET	Single electron transfer
TCT	Cyanuric chloride
TEMPO	2,2,6,6-Tetramethylpiperidinyloxyl
TET	Triplet energy transfer
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TMEDA	Tetramethylethylenediamine
UV	Ultraviolet
XantPhos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene

Table of Contents

Chapter 1

Introduction

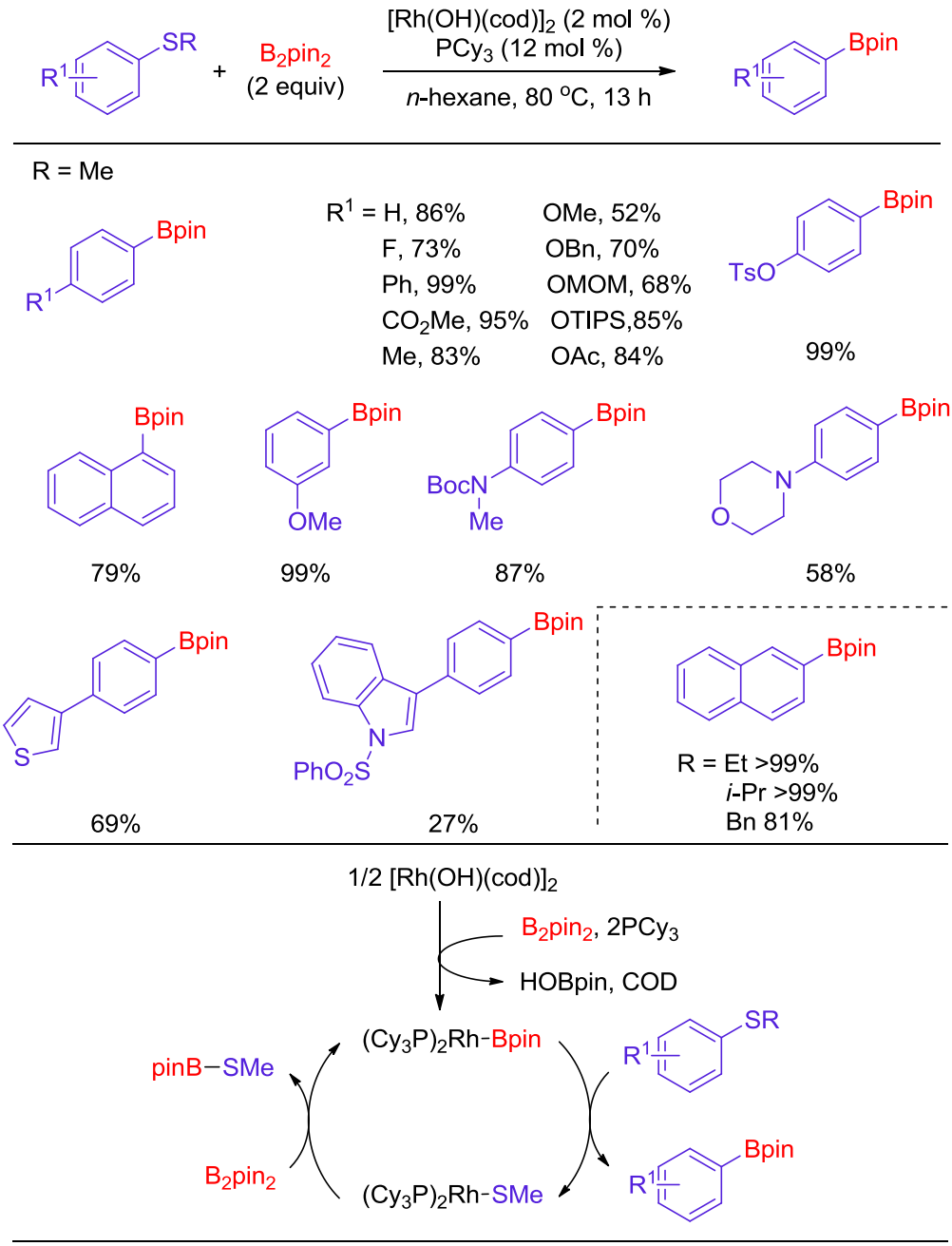
1 Introduction

1.1 C–S Bond Borylation

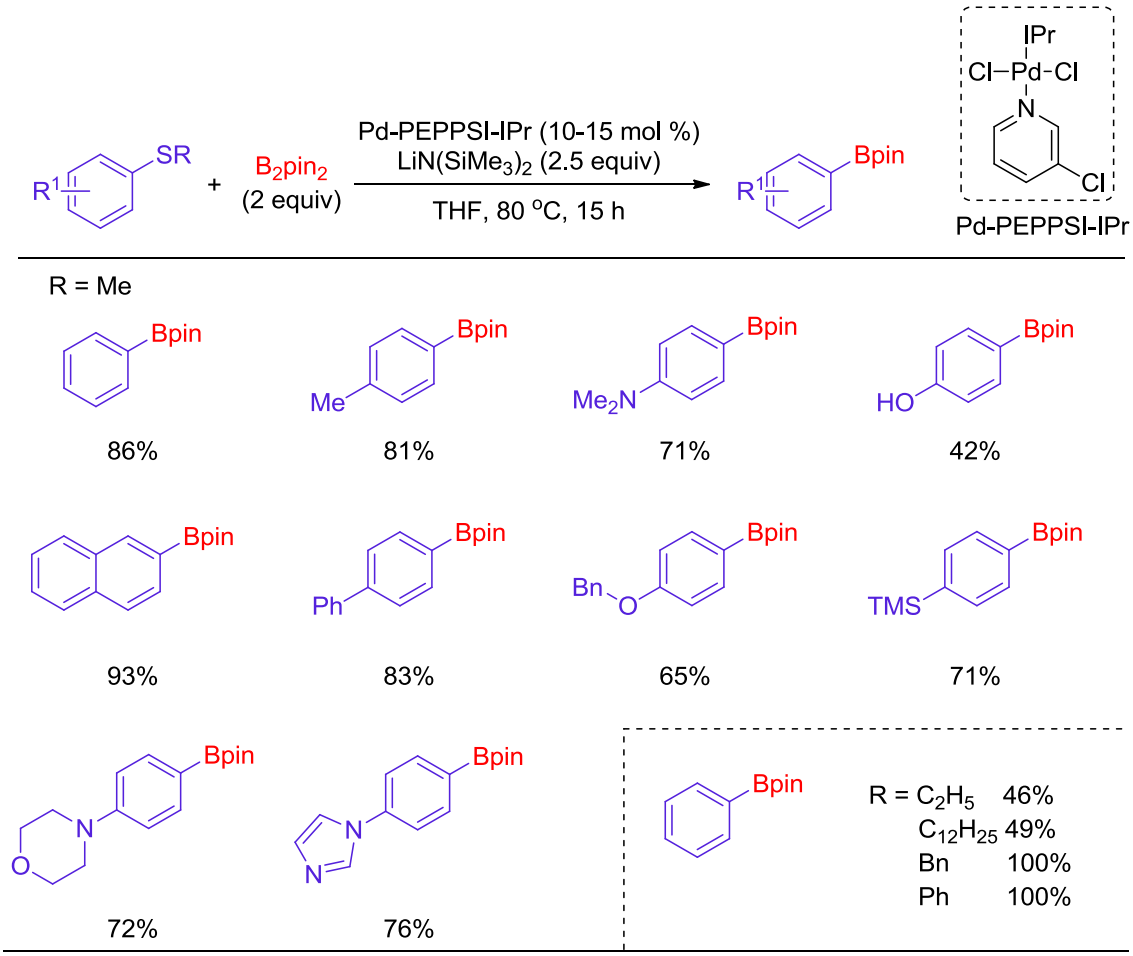
1.1.1 Sulfide C–S Bond Borylation

Hosoya *et al.* reported the rhodium-catalyzed aryl C–S bond borylation of aryl alkyl sulfides in 2016 (Scheme 1-1).[1] PCy_3 as the ligand played an important role in the reaction. Thioanisoles, bearing different electron-withdrawing or electron-donating groups, yielded the corresponding arylboronic esters in good to excellent yields. Various heteroarylsulfides were also borylated smoothly with this system. The strategy was also suitable for the transformation of alkylthioarenes with leaving groups other than SMe. Substrates bearing Et, *i*Pr, or Bn groups on the sulfur atom were borylated to the target products in good yields. The catalytic cycle was found to start from a Rh-boryl complex by ^{31}P NMR and ESI-MS analysis.

At the same time, Yorimitsu *et al.* independently described a Pd-NHC-catalyzed borylation of aryl alkyl sulfides with diboron reagents (Scheme 1-2).[2] $LiN(SiMe_3)_2$ was essential to the success of this borylation. This method was capable of borylating a wide range of aryl alkyl sulfides.

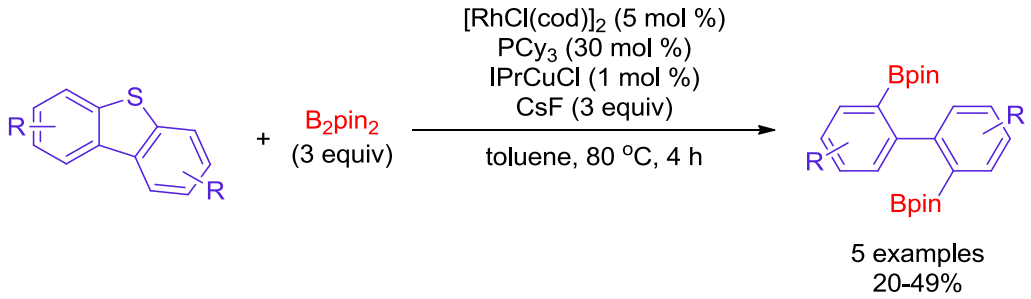


Scheme 1-1. Rh-catalyzed borylation of aryl alkyl sulfides.



Scheme 1-2. Pd-catalyzed borylation of aryl alkyl sulfides.

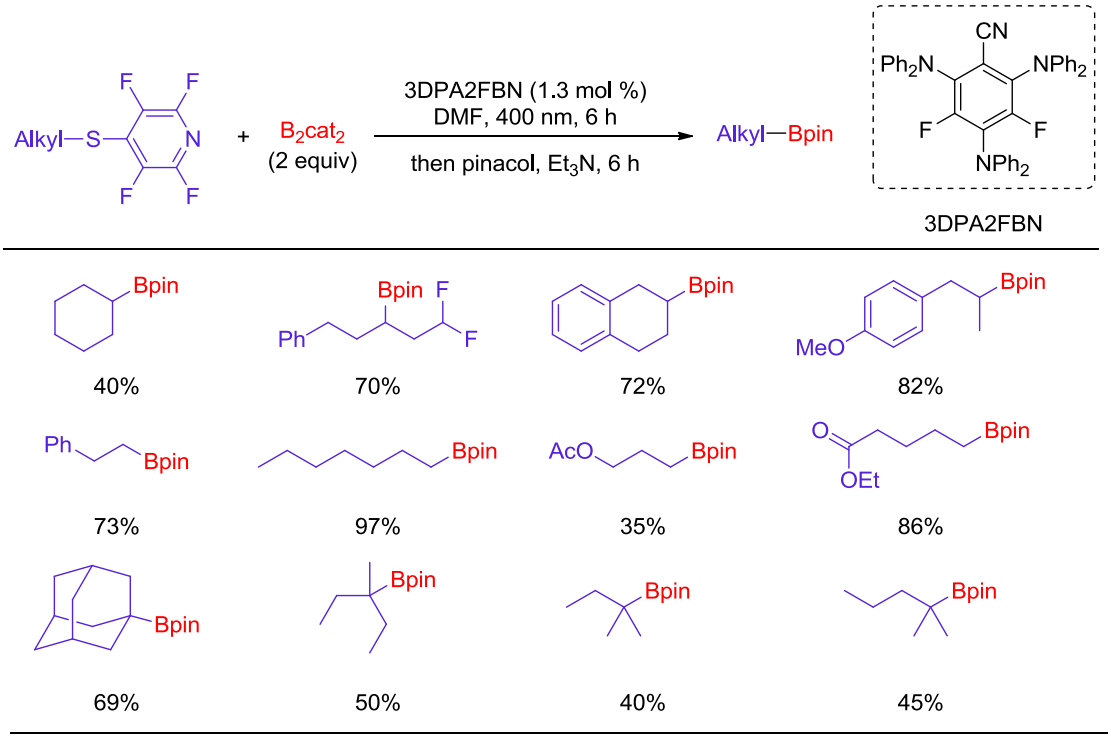
They also developed a ring-opening diborylation of dibenzothiophenes with rhodium and copper complexes as co-catalysts in 2017 (Scheme 1-3).[3] Stepwise borylation of the two C–S bonds of dibenzothiophenes led to the corresponding 2,2'-diborylaryls in the presence of 30 mol% PCy_3, 1 mol% IPrCuCl, and 5 mol% $[RhCl(cod)]_2$ as co-catalysts, and CsF in toluene.



Scheme 1-3. Rhodium-catalyzed ring-opening borylation of dibenzothiophenes.

Recently, the Dilman group reported a radical borylation of sulfides containing a

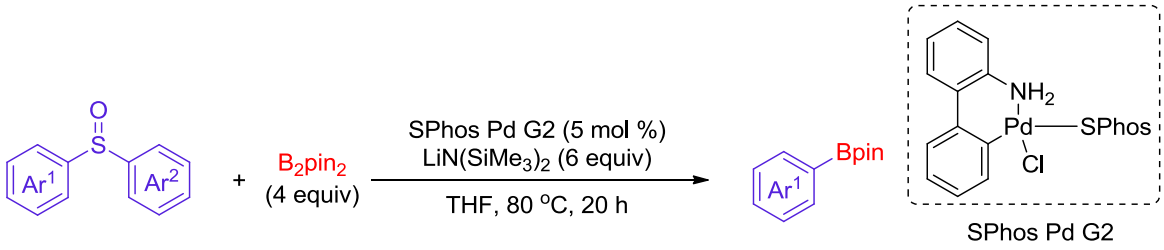
tetrafluoropyridinyl (PyfS) group using 3DPA2FBN as a photoredox catalyst and B_2cat_2 as boron source in DMF under 400 nm irradiation (Scheme 1-4).[4] This protocol was compatible with a wide range of primary, secondary, and tertiary sulfides. Ester and acetoxy groups were tolerated under the reaction conditions. The electron-withdrawing nature of the fluorinated motif plays a crucial role for generation of alkyl radicals, which prefer to generate an EDA complex.



Scheme 1-4. Light-mediated sulfur-boron exchange.

1.1.2 Sulfoxide C–SO Bond Borylation

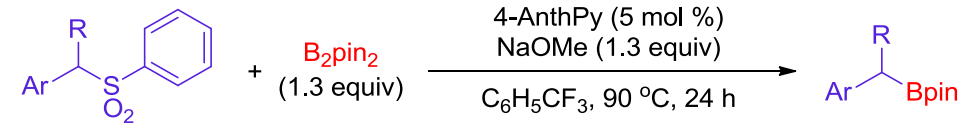
In 2017, Yorimitsu and co-workers developed the first borylation of diaryl sulfoxides in the presence of a phosphine-ligated palladium catalyst and $LiN(SiMe_3)_2$ as the base (Scheme 1-5).[5] The addition of $LiN(SiMe_3)_2$ significantly increased the reactivity of the reaction, and both of the aromatic rings of the diaryl sulfoxides were transformed into the corresponding arylboronate esters. Electronically-biased unsymmetrical diaryl sulfoxides were applied to intramolecular competition reactions to indicate that an electron-deficient aryl fragment reacted preferentially.



Scheme 1-5. Pd-catalyzed borylation of aryl sulfoxides.

1.1.3 Sulfone C–SO_2 Bond Borylation

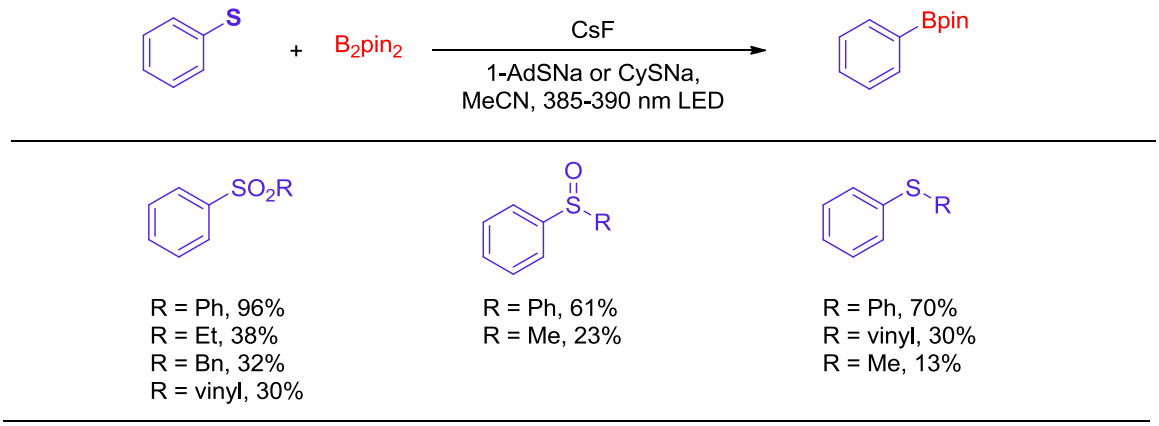
In 2019, Nambo and Crudden's group reported a transition metal-free, 4-arylpyridine-catalyzed borylation of benzyl sulfones using B_2pin_2 in $C_6H_5CF_3$ at 90 °C for 48 h (Scheme 1-6).[6] This method realized the selective borylation of benzyl C–SO_2 bonds, with SO_2Ph as the leaving group. When cyclic sulfones were subjected to this process, the benzyl borylated sulfinated salts were generated through cleavage of the benzyl(C)–SO_2 bonds for further functionalization.



(R = H, aryl, alkyl)

Scheme 1-6. Pyridine-catalyzed benzyl C–SO_2 bonds borylation of benzyl sulfones.

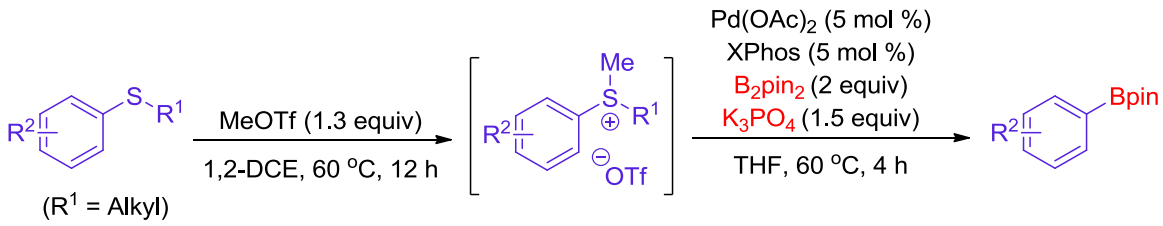
Later, König's group developed a novel photocatalytic method involving single electron transfer (SET) for the borylation of various inert substituted arenes using thiolate as a photoredox catalyst and B_2pin_2 as the boron source in MeCN under LED irraditation (Scheme 1-7).[7] The reactivity of benzyl phenyl sulfones occurred predominately at the C(sp^2)–SO_2 site which was different from Nambo and Crudden's catalytic system.[6] Other than aryl sulfones, aryl sulfoxides and sulfides can also act as the phenyl radical precursors to convert to aryl boronic esters smoothly under this radical process.



Scheme 1-7. Photoinduced thiolate-catalyzed borylation of organosulfur compounds.

1.1.4 Sulfonium Salt C–S Bond Borylation

Previous palladium- and rhodium-catalyzed borylation of aryl alkyl sulfides suffered from the requirement of a strong base $LiN(SiMe_3)_2$ and poor functional group tolerance. In 2018, the Yorimitsu group reported the $Pd(OAc)_2$-catalyzed borylation of aryl sulfonium salts generated *in situ* from aryl sulfides with methyl triflate (Scheme 1-8).[8] Aryl sulfoniums proved to be more reactive than the corresponding aryl sulfides and were less poisonous to the catalyst. This borylation was conducted under milder reaction conditions than previous ones, and the reaction tolerated various useful functional groups, such as acetyl, cyano, nitro, and hydroxyl groups.

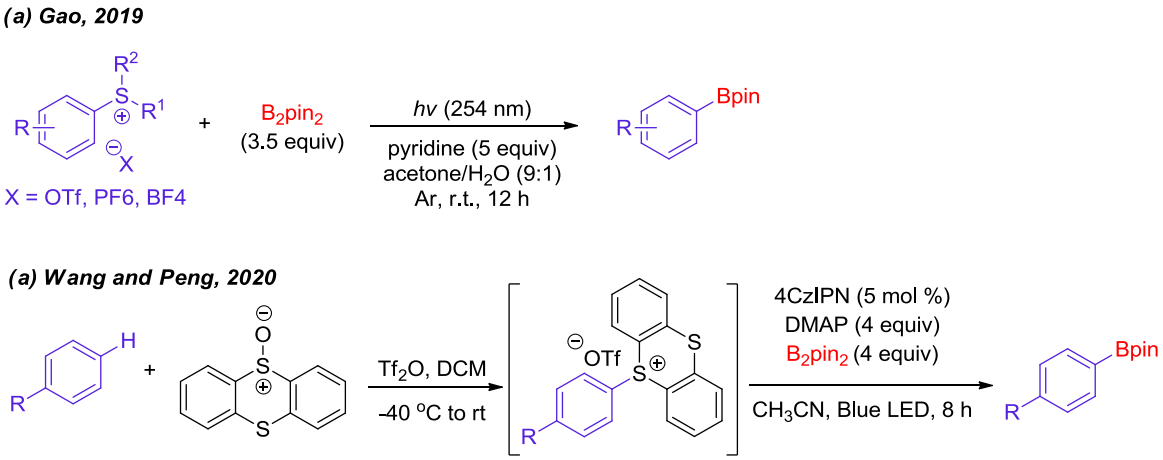


Scheme 1-8. Pd-catalyzed borylation of aryl sulfonium salts.

Later on, an efficient photoinduced borylation process was reported by Gao for the synthesis of arylboronate esters from various aryl sulfonium salts (Scheme 1-9a).[9a] This transition metal-free strategy exploited redox-neutral aromatic sulfonium salts to access aryl radicals through C–S bond activation under UV irradiation (254 nm).

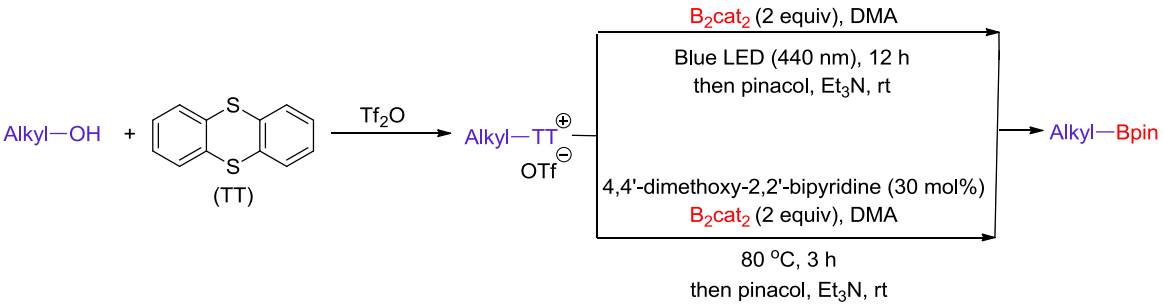
Aryl sulfonium salts bearing a thianthrene fragement were generated from their sulfoxide

precursors with trifluoromethanesulfonic anhydride which has the potential for the *para*-selective C−H functionalization of mono-substituted arenes. Recently, Wang and Peng's group described the photocatalyzed C−S *para*-borylation of different monosubstituted arenes *via* aryl sulfonium salts bearing a thianthrene fragement (Scheme 1-9b).[9b]



Scheme 1-9. Photoinduced borylation of aryl sulfonium salts.

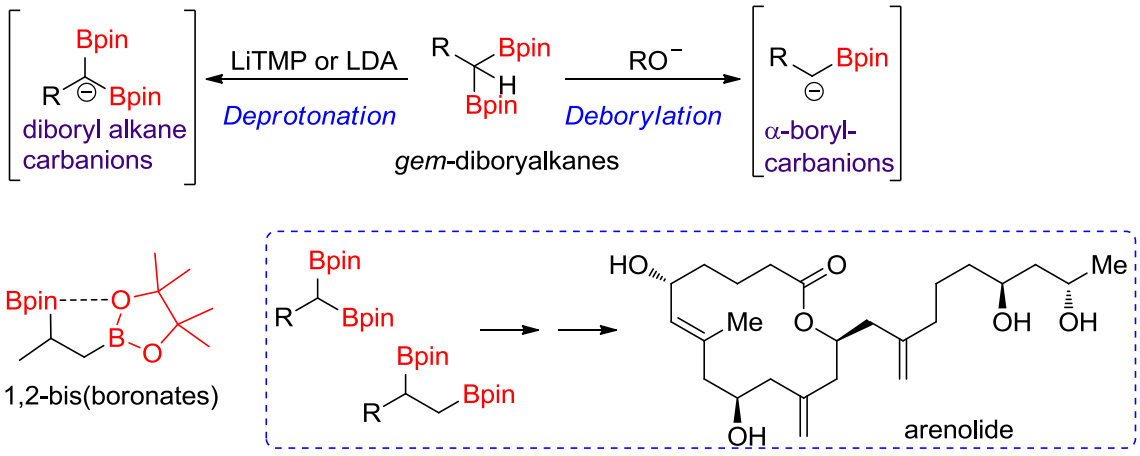
Shi *et al.* developed a method for the production of non-stabilized alkyl radicals from alkyl sulfonium salts *via* single-electron reduction (Scheme 1-10).[10] The *S*-(alkyl) thianthrenium salts were easily prepared from the corresponding alkyl alcohols and TT. They reported a radical borylation of *S*-(alkyl) thianthrenium salts using B_2cat_2 as the boron source in DMA under photoredox or Lewis base-catalyzed conditions to generate alkylboronates. These sulfonium salts can be also used for other transformations, such as heteroarylation, alkylation, alkenylation, and alkynylation.



Scheme 1-10. Borylation of alkyl sulfonium salts.

1.2 C(sp^3)−Het, C(sp^3)−H, and C(sp^3)−C Bond Multiborylation

The preparation of alkylboronates is a vital and valuable subject in organic synthesis because these organoboron compounds play an important role in organic chemistry, drug discovery and materials science.[11] Their good air and moisture stability leads to them being easy to handle and they can easily be further functionalized under mild reaction conditions.[12] In particular, multiborylalkanes are emerging as indispensable synthetic modules for preparing multifunctionalized complex molecules due to their ready accessibility, high functional group tolerance, and stability.[13] Boron moieties in a single molecule can be selectively differentiated, allowing the synthesis of a wide variety of complex molecules for drugs, natural products, and functional materials (Scheme 1-11).[14] For example, in the alkylation of electrophiles using *gem*-diborylalkanes, the boryl-group can stabilize an α-boryl carbanion, which is generated by a metal alkoxide/hydroxide base, through hyperconjugation.[15] The deprotonation process of *gem*-diborylalkanes *via* diboryl alkane carbanion species will take place when a stronger and bulkier base is used.[16] In addition, the reactivity and Lewis acidity of 1,2-bis(boronates) can be improved by internal chelation.[14] As one example, the total synthesis of the natural product arenolide was accomplished based on a diborylalkane reaction (Scheme 1-11).[14c] Some of the organomultiboryl compounds show vital biological activities and are used as antineoplastic drugs.[17] Therefore, it is of great significance to develop efficient and atom-economical strategies for the preparation of multiborylalkanes.



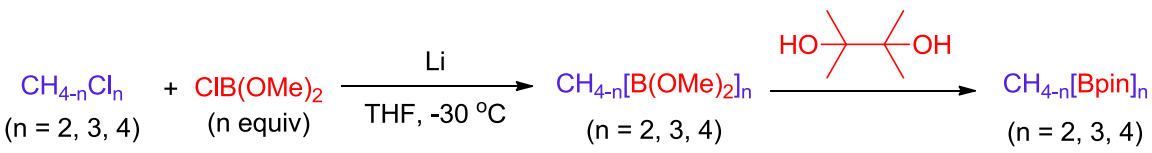
Scheme 1-11. Transformations and applications of multiborylalkanes.

Over the past few decades, many straightforward methods for the synthesis of organomultiboryl compounds from alkenes and alkynes *via* hydroboration and ploy borylation processes have been developed.[13,18] In 1998, an early review by Marder and Norman described the homogeneous transition metal-catalyzed diborylation of unsaturated hydrocarbons.[19] Iwasawa also reported the transition metal catalyzed diborylation of unsaturated hydrocarbons with diboron(4) reagents in 2012, focusing on vicinal diboronates.[20] Much work has been reported for the creation of geminal diboronates, vicinal diboronates, and triboronates through transition-metal or base-catalyzed multiborylation of alkenes and alkynes. The direct monoborylation of $C(sp^3)$−Het, $C(sp^3)$−H, and $C(sp^3)$−C bonds has also advanced significantly in the past decade.[21] Importantly, significant improvements have been made in the multiborylation of saturated alkyl derivatives under mild reaction conditions. Alkyl substrates with $C(sp^3)$−Het, $C(sp^3)$−H, and $C(sp^3)$−C bonds have been extensively studied as multiborylation coupling partners to create organoboronates. Despite these accomplishments, the published review papers only cover parts of the current research topics in this highly burgeoning area.

1.2.1 $C(sp^3)$−X (X = I, Br, Cl, F) Bond Multiborylation

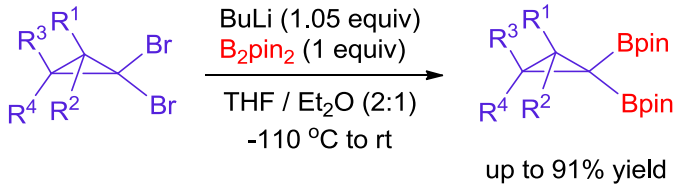
1.2.1.1 Multiborylation of Polyhalides

Multi(dimethoxyboryl)methane was originally discovered by the Matteson group *via* reaction of dimethoxyboron chloride with Li and various chlorinated reagents such as CH_2Cl_2, $CHCl_3$, CCl_4 in THF (Scheme 1-12).[22] The lability of dimethoxyboryl moieties resulted in difficulties in isolating the corresponding multiborylalkane species and, consequently, cyclic boronic esters were then prepared by transesterification as they are generally more stable towards hydrolysis (Scheme 1-12).



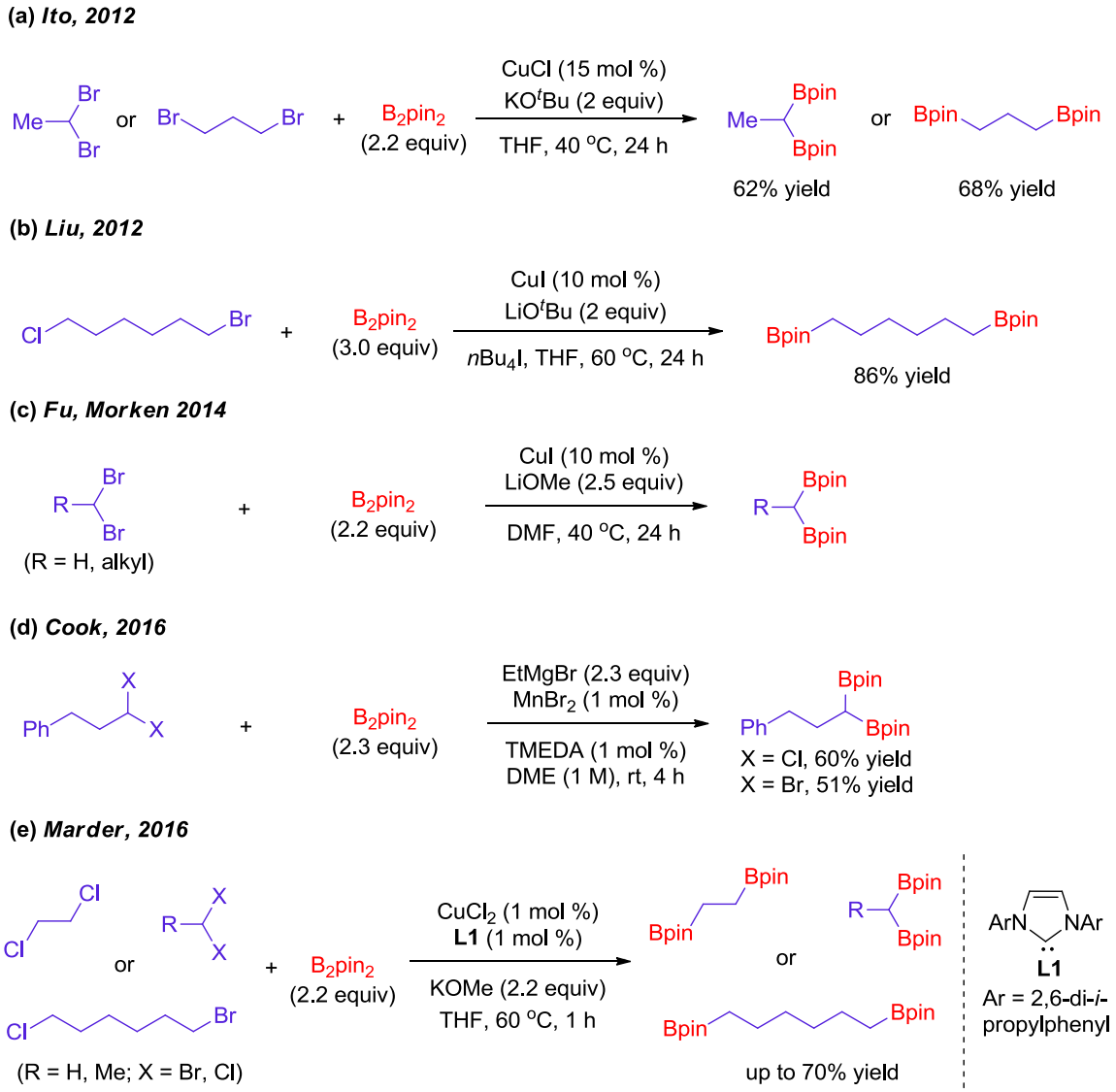
Scheme 1-12. Multiborylation of $CH_{4-n}Cl_n$.

In 2006, a reliable synthetic protocol for the preparation of 1,1-diborylated cyclopropanes by *gem*-diboration of dibromocyclopropanes with BuLi and B_2pin_2 in THF / Et_2O at −110 °C was developed by the Shimizu group (Scheme 1-13).[23]



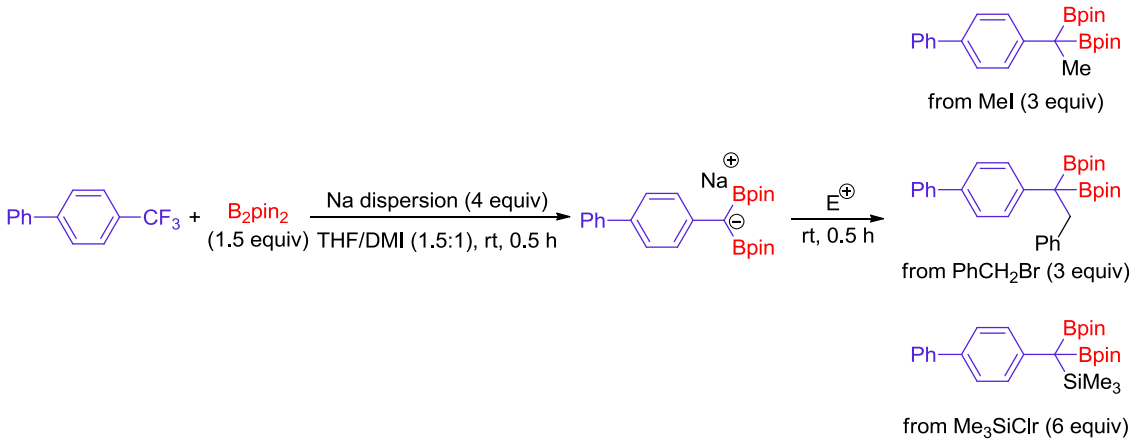
Scheme 1-13. Synthesis of 1,1-diborylated cyclopropanes.

In 2012, the Ito[24] and Liu[25] groups reported the Cu-catalyzed borylation of dihalides with B_2pin_2 to form diborylalkanes (Scheme 1-14a and 1-14b). Later, the Fu[26] and Morken[15b] groups employed this copper-catalyzed approach to generate a series of alkyl-substituted *gem*-diborylalkanes from the corresponding dibromides in good yields under mild reaction conditions (Scheme 1-14c). Cook *et al.*[27] described another method to synthesize diborylalkanes from dihalides and B_2pin_2 using manganese(II) bromide as the catalyst, tetramethylethylenediamine (TMEDA), and a Grignard reagent (Scheme 1-14d). Then, the Marder group developed an efficient Cu(II)-catalyzed borylation of unactivated alkyl dichlorides with B_2pin_2 in good yields even when open to the air (Scheme 1-14e).[28]



Scheme 1-14. Diborylation of dihalides for the synthesis of diborylated compounds.

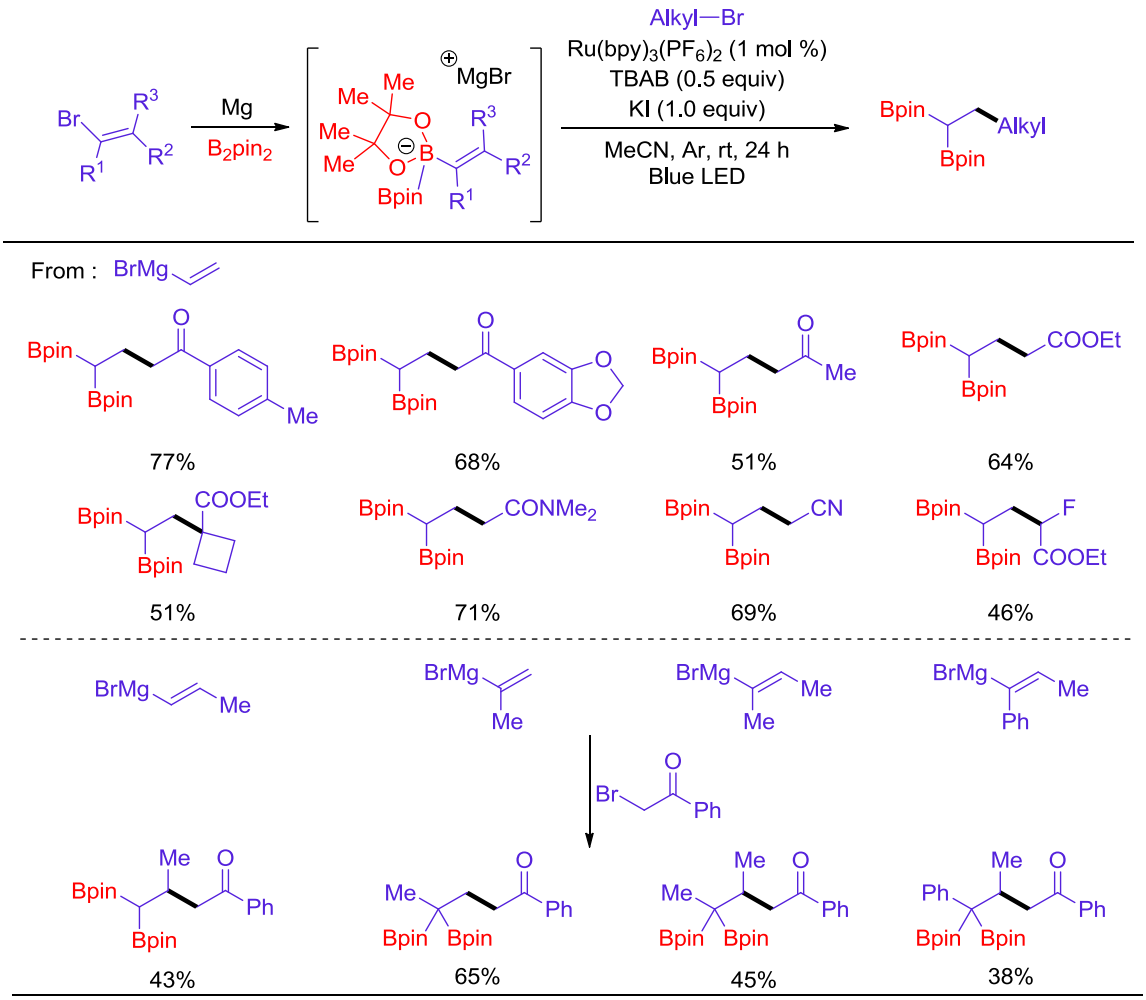
Very recently, Yorimitsu's group reported the reductive diborylation of benzotrifluorides with B_2pin_2 in the presence of sodium dispersion to afford the corresponding diborylbenzylsodium species, which could be further derivatized to yield *gem*-diboryl products with reactive halides (Scheme 1-15).[29] Methylation after the reductive borylation provided a series of diborylated products. The intermediate benzylic anion can be also functionalized *via* benzylation and silylation. Other simple alkyl halides showed no reactivity under the reaction systems. Reduction of benzotrifluorides with sodium dispersion provides access to unstable difluorobenzyl- sodium, which reacts immediately with B_2pin_2 *via* a 1,2-boryl shift to generate *gem*-diborylfluoro species, and further reduction affords the diboryl-stabilized benzylic anion.



Scheme 1-15. Defluorinative diborylation of benzotrifluorides (Yorimitsu, 2021).

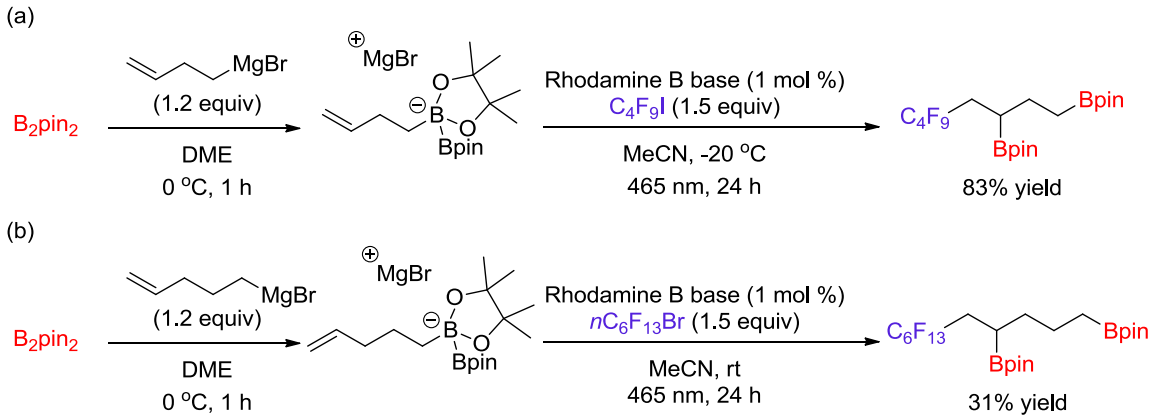
1.2.1.2 Diborylation of Mono Halides

In 2019, Shi *et al.* reported a photoinduced strategy for the generation of 1,1-diboronates *via* an olefinic 1,2-boryl-migration (Scheme 1-16).[30] An array of alkenyl diboronate compounds, which were obtained *in situ* by reaction of the alkenyl Grignard reagent with B_2pin_2 in THF at −78 °C, reacted with a variety of alkyl halides using a Ru photoredox catalyst under visible light. This diborylation showed good functional group tolerance and can act as an effective and reliable tool for late-stage modification. A variety of 2-bromoacetophenone derivatives, aliphatic ketones, aliphatic esters, and substrates bearing amide, cyano, and fluorine were all tolerated when using vinyl magnesium bromide as the precursor of the alkenyl diboronate species. Other alkenyl Grignard reagents were also employed for the synthesis of the corresponding alkenyl diboronate species to access *gem*-bis(boryl)alkanes. In the reaction, alkyl radicals added efficiently to alkenyl diboronate intermediates, leading to a 1,2-boryl-migration from boron to the α-carbon sp^2 center.



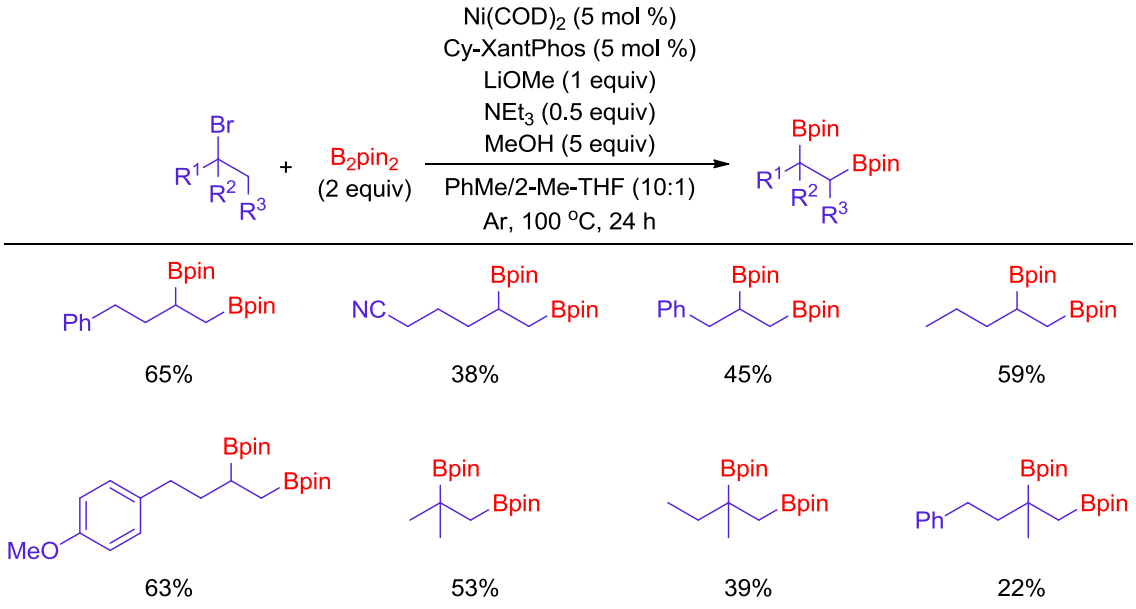
Scheme 1-16. Olefinic 1,2-boryl-migration to construct *gem*-bis(boryl)alkanes (Shi, 2019).

Studer's group extended this process to involve 1,4-boron migration using but-3-enylmagnesium bromide as a model substrate with B_2pin_2 using Rhodamine B base (1 mol%) as an initiator under visible light irradiation (465 nm) in the presence of C_4F_9I (1.5 equiv) in CH_3CN to access the 1,3-bisborylalkane (Scheme 1-17).[31] A series of *n*-perfluoroalkyl iodides afforded the trifunctionalized 1,3-diboronates in good to excellent yields. The 1,5-boron migration process was also achieved in moderate yields when using 4-pentenylmagnesium bromide and *n*-perfluorohexyl bromide as C-radical precursors. This remote radical B-migration process provided an efficient method to prepare 1,n-bisborylalkanes from B_2pin_2 and Grignard reagents which can readily be prepared from the corresponding alkyl bromides.



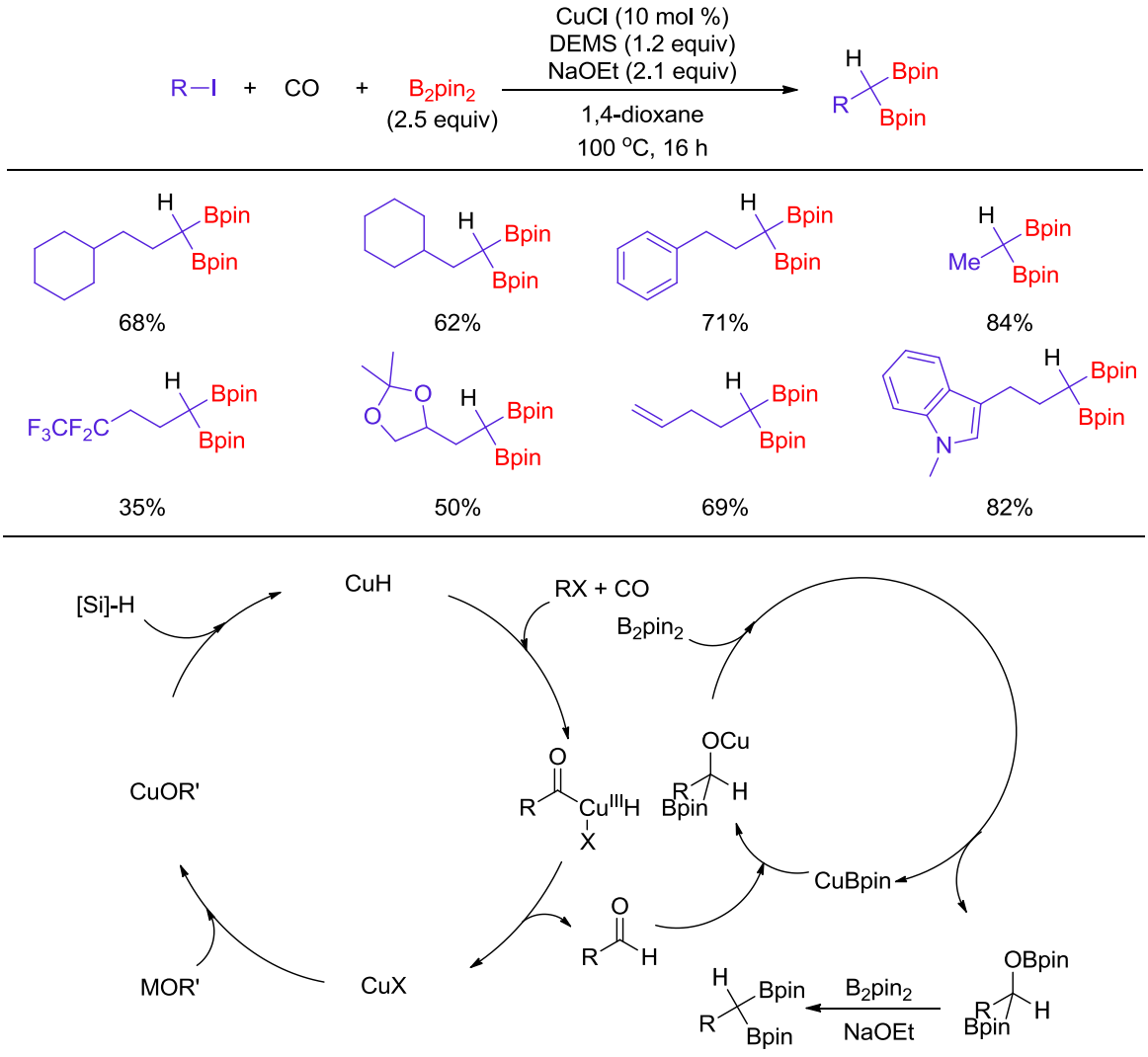
Scheme 1-17. 1,4- and 1,5-boron migration reactions (Studer, 2020).

Fu and co-workers then developed a nickel-catalyzed vicinal diborylation of alkyl bromides for the synthesis of 1,2-diborylalkanes in the presence of Cy-XantPhos, MeOH, and Et_3N (Scheme 1-18).[32] This regioselective diborylation was compatible with diverse primary, secondary, and tertiary bromides. However, the products were obtained in moderate yields (20%−65%) and the reaction was limited to terminal 1,2-bis(boronate esters) under the Ni tandem-catalyzed process. A series of mechanistic studies indicated that terminal alkenes were formed from the corresponding alkyl bromides selectively *via* Ni-catalyzed dehydrohalogenation followed by a Lewis acid-base adduct-promoted 1,2-diborylation to generate the 1,2-bis(boronate esters).



Scheme 1-18. Ni-catalyzed vicinal diboration of alkyl bromides (Fu, 2019).

Very recently, Wu's group developed a CuBpin and CuH catalyzed borylative methylation of alkyl iodides using CO as the C1 source in the presence of methyldiethoxysilane (DEMS) (Scheme 1-19).[33] Various 1,1-diboronates, elongated by one carbon atom, were obtained from the corresponding alkyl iodides in good yields. Alkyl iodides bearing different carbon chains, and different functional groups, such as trifluoromethyl, alkene, and ether, were tolerated. Heterocycles were also compatible with these conditions. In this cooperative borylative methylation, CuH reacted with the alkyl iodide faster than CuBpin. Initially, CuH was formed from the copper catalyst, metal alkoxide MOR' and silane. Subsequently, CuH reacted with alkyl iodide and CO *via* radical intermediates to generate acyl-CuH complexes. The intermediate aldehyde was then generated after reductive elimination. Afterwards, the α-boryl-oxo-copper complexes reacted with B_2pin_2 to give α-OBpin boronate, which were generated from CuBpin and the aldehyde. Then, the 1,1-diboronates can be obtained from the α-OBpin boronates in the presence of base and B_2pin_2.

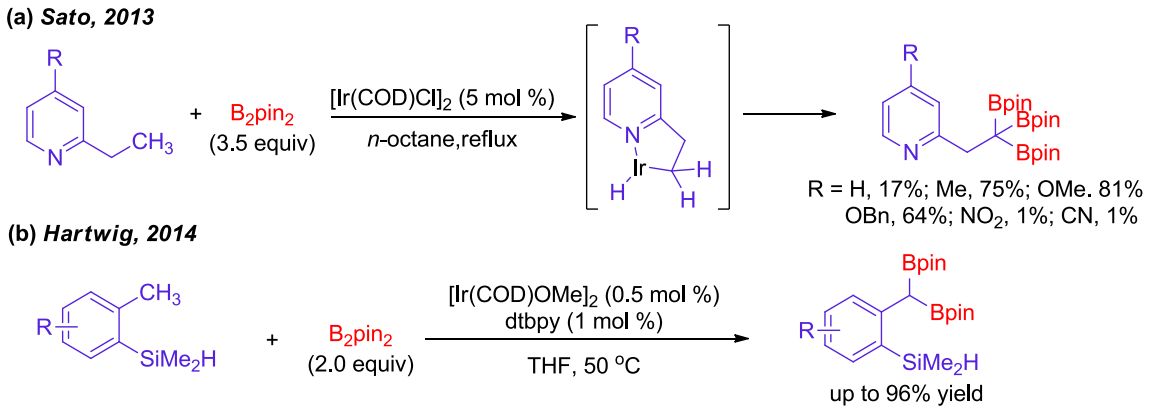


Scheme 1-19. Cu-catalyzed borylative methylation of alkyl iodides with CO (Wu, 2021).

1.2.2 C(sp^3)−H Bond Multiborylation

Marder *et al.* reported a very early example of the Rh-catalyzed benzylic product-H diborylation of toluene, but the benzyl bis(boronate) was obtained in only 7% yield.[34] In 2013, Sawamura disclosed an example of an Ir-catalyzed pyridine-directed diboration of C(sp^3)−H bonds.[35] At the same time, Sato and Mita's groups reported the first triple borylation at a single carbon of terminal primary C(sp^3)−H bonds with the aid of a nitrogen directing group (Scheme 1-20a).[36] Substrates containing electron-withdrawing groups such as nitro, cyano, and chloro showed lower reactivity under the reaction conditions, while the borylation of electron-donating substituted compounds proceeded in excellent yields within 10-30 min. This Ir-catalyzed site-selective C(sp^3)−H bonds borylation of the model substrate 2-ethylpyridine proceeded through a five-membered metallacycle

intermediate which reacted with B_2pin_2 affording the triborylated products. Hartwig's group developed an iridium-catalyzed site-selective diboration of primary benzylic C(sp^3)–H bonds with the assistance of a hydrosilyl directing group using 1 mol% of dtbpy and 2.0 equiv. of B_2pin_2 (Scheme 1-20b).[37a] This method gave a variety of 1,1-benzyldiboronate esters in good to excellent yields. With the latter strategy, the substrate without directing group, 4-CF_3-toluene, was diborylated to give the corresponding product.[37b]

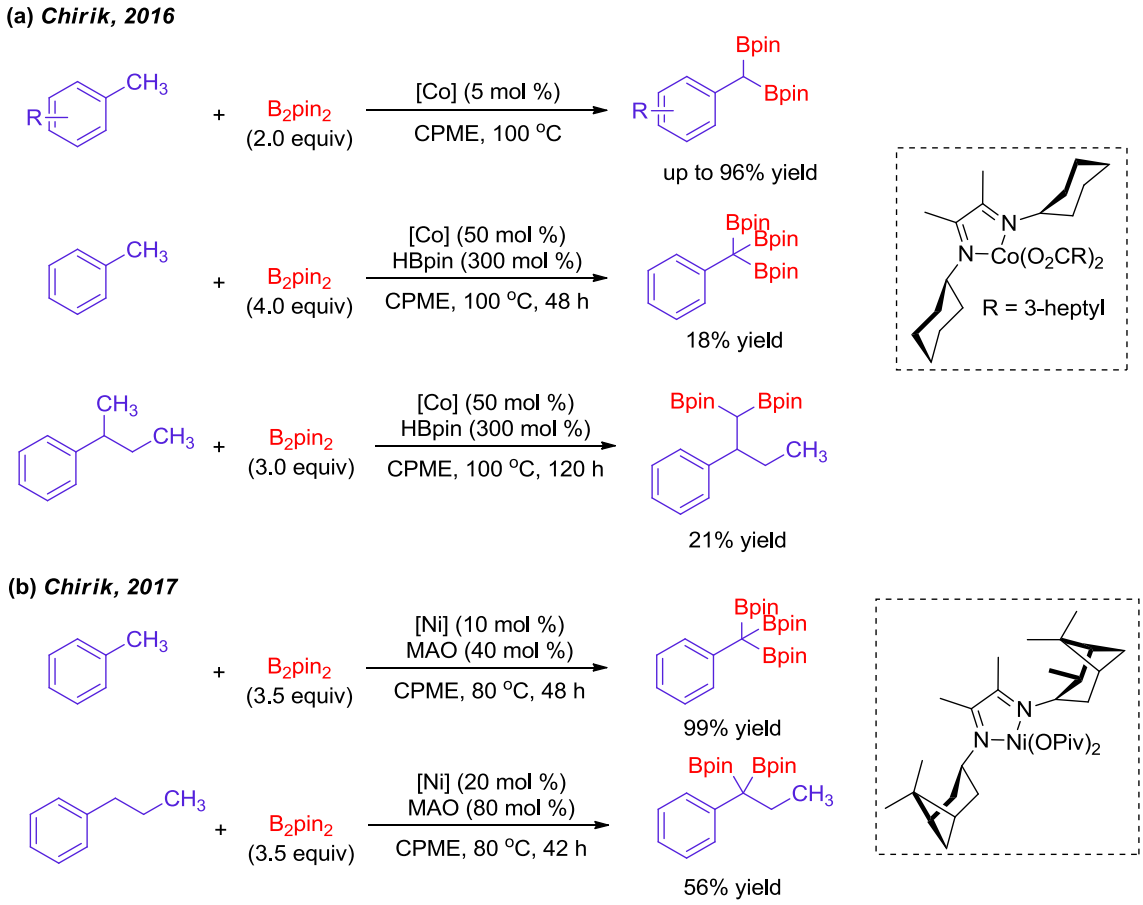


Scheme 1-20. Ir-catalyzed multiboration of C(sp^3)–H bonds.

Chirik and co-workers reported an α-diimine cobalt-catalyzed selective borylation of C(sp^3)–H bonds of alkylarene with B_2pin_2 (Scheme 1-21a).[38] A range of methylarenes reacted with the respective indicated co-catalyst loadings, 2 equiv. of B_2pin_2, and 4 equiv. of HBpin with respect to the Co-catalyst at 100 °C in cyclopentyl methyl ether (CPME) to access 1,1-diboronates in good yields. Interestingly, increased catalyst loading and 4 equiv. of B_2pin_2 led to an 18% yield of the triborylation product of toluene. This method was also extended to other branched alkylarenes. The selective diborylation of *sec*-butyl benzene at the terminal benzylic position required a high catalyst loading (50 mol%), 3 equiv. of B_2pin_2, and 300 mol% HBpin at 100 °C in CPME for 120 h, which seemingly results from a consecutive benzylic activation/isomerization/borylation sequence.

Furthermore, they also reported an α-diimine nickel catalyst for the preparation of benzyltriboronates *via* triborylation of a series of benzylic C(sp^3)–H bonds of methylarenes (Scheme 1-21b).[39] The benzyltriboronates are useful building blocks, which could undergo

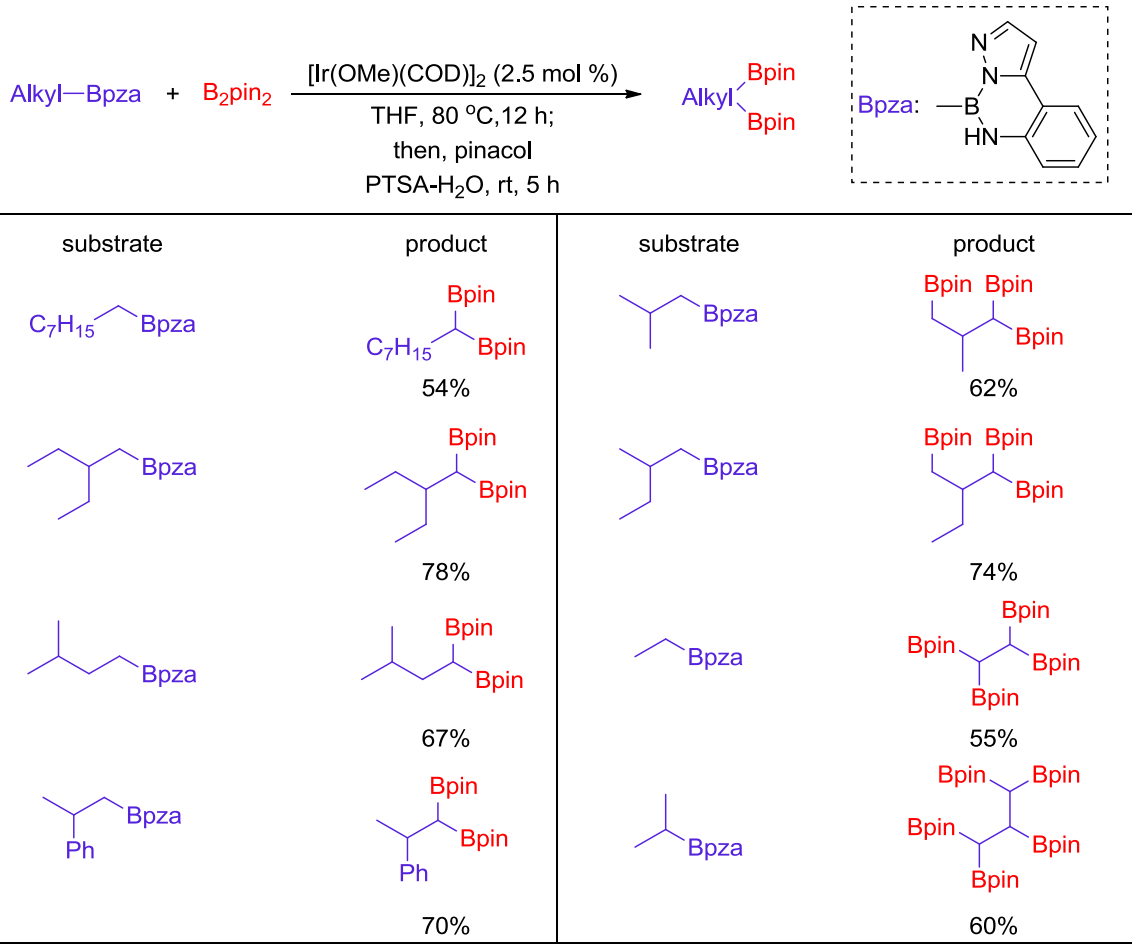
deborylative conjugate addition with (*E*)-methylcrotonate *via* C−C bond-forming reactions to provide products with high diastereoselectivities. The diborylation of secondary C(sp^3)−H bond of linear alkyl arene was also achieved using 20 mol% of a nickel catalyst and excess B_2pin_2. *n*-propylbenzene, *n*-pentylbenzene, and trimethylsilyl-protected substrates were compatible with the catalytic system, giving products in moderate yields.



Scheme 1-21. α-Diimine cobalt- and nickel-catalyzed multiborylation of C(sp^3)−H bonds.

In 2019, the Suginome and Yamamoto groups described Ir-catalyzed C(sp^3)−H borylations of alkylboronate acids by attaching pyrazolylaniline (pza) as a temporary directing group on the boron (Scheme 1-22).[40] A series of primary alkylboronic acids were subjected to the Bpza-directed C(sp^3)−H borylation to produce 1,1-alkyldiboronate esters selectively. β- and γ-branched substrates were also tolerated to give the corresponding α-borylated products. When β- and γ-branched primary alkylboronic acids were subjected to increased loadings of Ir-catalyst and excess B_2pin_2, various multiboryl products were obtained in 55%−74% yields through C(sp^3)−H

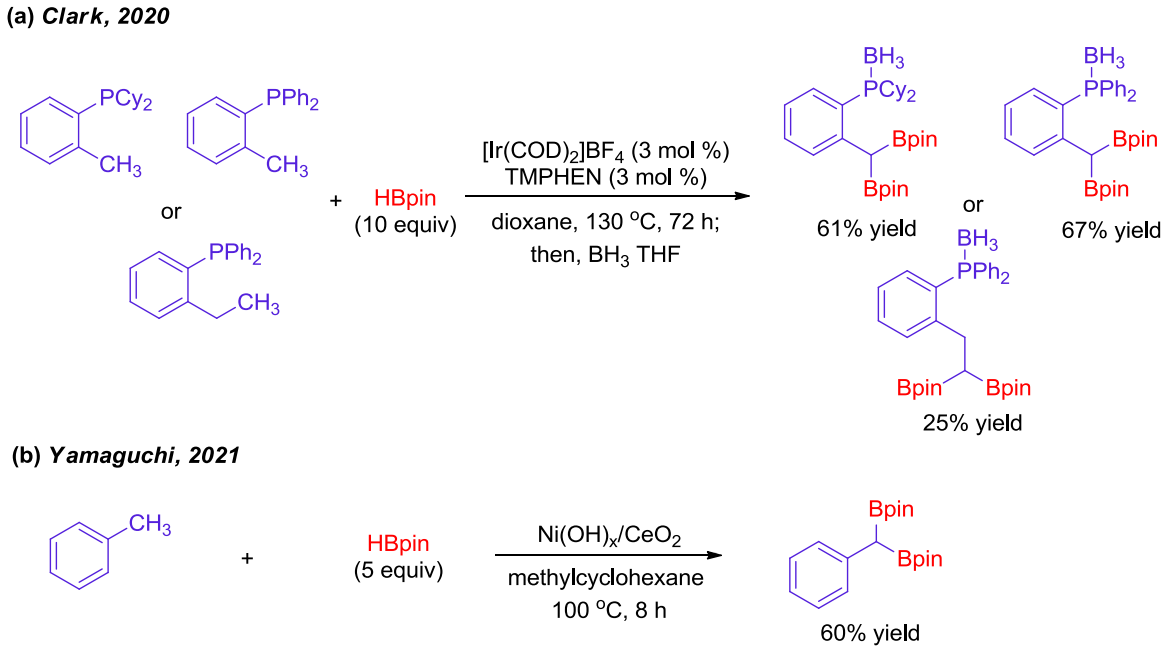
multiborylation at the α-, β- and γ-positions.



Scheme 1-22. Boryl-directed, Ir-catalyzed selective multiborylation of C(sp^3)−H bonds.

Subsequently, Clark *et al.* developed a phosphine-directed cationic iridium-catalyzed benzylic C(sp^3)−H diborylation (Scheme 1-23a).[41] The selective diborylation of dicyclohexyl(2-methylphenyl)phosphine proceeds with an excess (10 equiv.) of HBpin in the presence of $[Ir(COD)_2]BF_4$ (3 mol%) at 130 °C for 72 h to afford the diborylated product in moderate yield. Replacing the dicyclohexyl substituents with diphenyl substituents also provided the bisborylation product in a 67% yield. With an ethyl in place of the methyl, the bisborylation occurred at the terminal methyl position rather than the benzylic position.

Very recently, the Yamaguchi group described a selective diborylation of benzylic C(sp^3)−H of methylarenes with HBpin in the presence of highly dispersed Ni hydroxide species supported on CeO_2 as the active heterogeneous catalyst in moderate yields (Scheme 1-23b).[42]

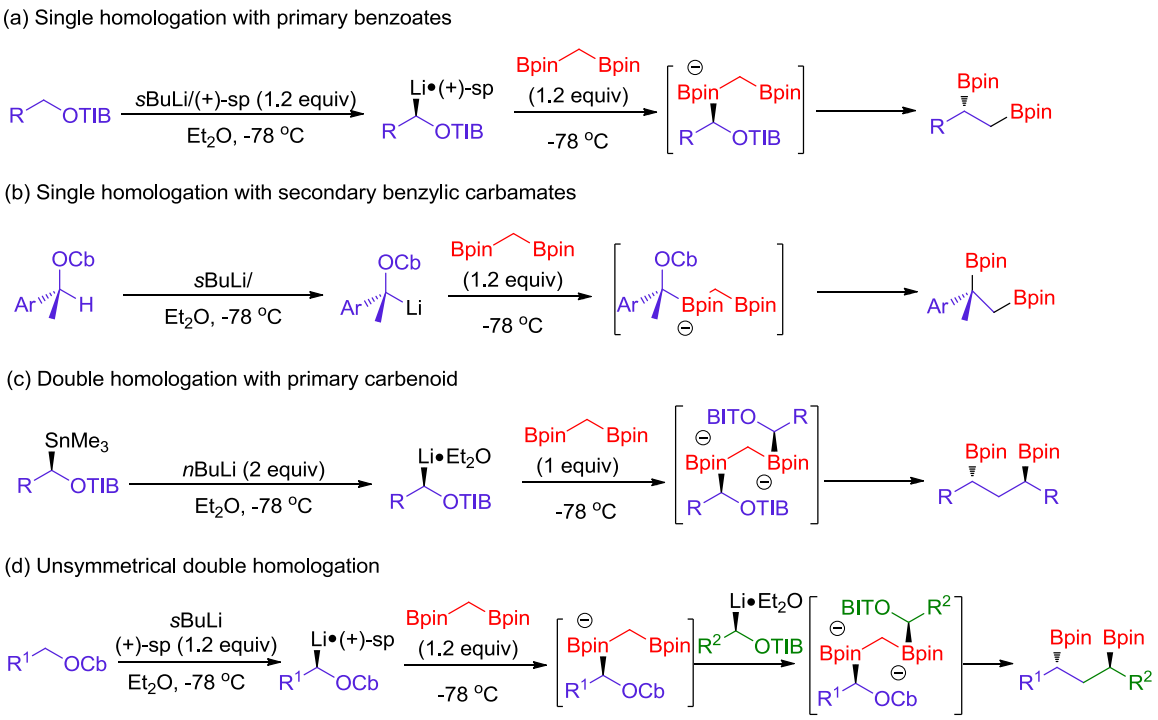


Scheme 1-23. Selective diborylation of C(sp^3)–H bonds.

1.2.3 C(sp^3)–O and C(sp^3)–N Bond Multiborylation

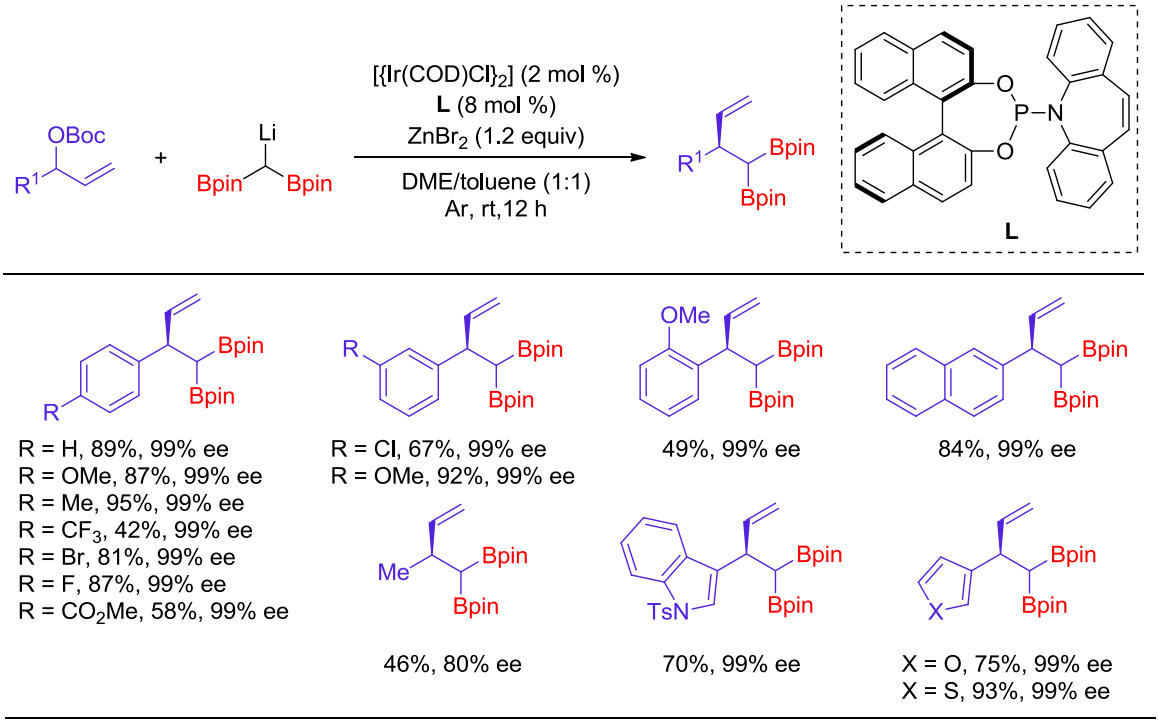
1,2- and 1,3-Bis(boronic esters) are interesting intermediates for the preparation of various functional groups. In 2017, Aggarwal *et al.* reported an alternative stereospecific homologation of diborylmethane by reaction with enantioenriched lithiated benzoates or carbamates to access 1,2- and 1,3-bis(boronate esters) with high levels of enantiopurity (Scheme 1-24).[43] The single homologation of diborylmethane with a variety of (+)-sparteine-ligated lithiated primary benzoates through a stereodefined carbenoid followed by 1,2-metallate rearrangement produced the primary–secondary 1,2-bis(boronate esters) in good yields with excellent enantiopurity (Scheme 1-24a). The single homologation of sterically hindered enantiopure (S)-1-phenylethanol-derived lithiated carbamate with diborylmethane also proceeded successfully to give a series of primary–tertiary benzylic 1,2-bis(boronate esters) in up to 85% yields with excellent enantioselectivity (up to > 99:1 er) (Scheme 1-24b). Some C_2-symmetric secondary–secondary 1,3-bis(boronate esters) were produced exclusively from the corresponding primary diamine-free lithiated benzoates through one-pot double homologation with excellent diastereoselectivity (> 95:5 dr) (Scheme 1-24c). This strategy can be also exploited for the three-component coupling of diborylmethane with sparteine-ligated lithiated carbamate and a range of secondary lithiated benzoates to generate non-symmetric

1,3-bis(boronate esters) directly in a one-pot non-symmetric carbenoid-carbenoid double homologation (Scheme 1-24d).



Scheme 1-24. Homologation of diborylmethane (Aggarwal, 2017).

Recently, the Cho group developed a (diborylmethyl)zinc(II) species which was generated *in situ* by treating the (diborylmethyl)lithium with zinc(II) halides (Scheme 1-25).[44] The (diborylmethyl)zinc(II) species were utilized in the preparation of enantioenriched *gem*-diborylalkanes *via* an iridium-catalyzed asymmetric allylic alkylation of Boc-protected racemic allylic alcohols in the presence of a phosphoramidite ligand. The operationally simple and productive protocol was compatible with a variety of functional groups, and diverse enantioenriched *gem*-diborylalkanes were produced in good yields with excellent enantioselectivity. Further stereospecific transformations of the enantioenriched *gem*-diborylalkanes products were also established to afford a series of useful enantioenriched compounds. Later, the first two examples of an Ir-catalyzed C(sp^3)–O and C(sp^3)–N diborylation were achieved using Clark's strategy.[31]

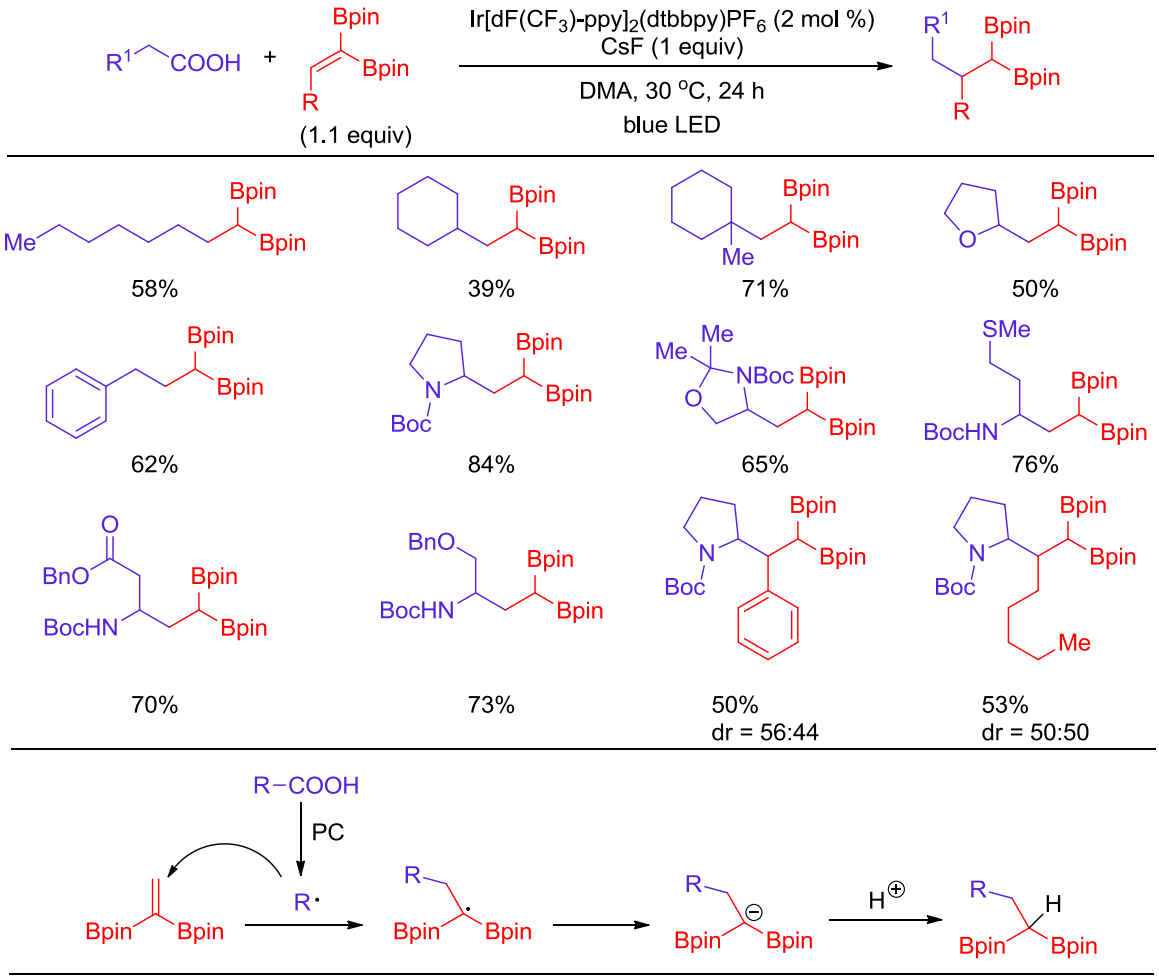


Scheme 1-25. Iridium-catalyzed asymmetric allylic alkylation reaction (Cho, 2018).

1.2.4 C(sp^3)−C Bond Multiborylation

Carboxylic acids are prevalent and abundant in natural products, bioactive compounds, and drugs. Thus, decarboxylative borylation act as an effective tool for late-stage modification. Very recently, Masarwa's group developed a *gem*-diborylalkene as a radical-reactive group, the double bond of which could couple with carbon-centered radicals (from carboxylic acids) to generate a *gem*-diboryl radical under visible light (Scheme 1-26).[45] A variety of γ-amino *gem*-diborylated products were obtained smoothly using tris[2-phenylpyridinato-C2,*N*]iridium(III) (Ir[dF(CF_3)-ppy]$_2$(dtbbpy)PF_6) as a photoredox catalyst and CsF as a base in *N,N*-dimethylacetamide under 427 nm LED irraditation. Other primary, secondary, and tertiary aliphatic carboxylic acids also worked well under the reaction conditions. Phenylacetic acids and cyclic α-oxy group-containing carboxylic acids afforded the corresponding diboryl products in moderate yields. A range of (*iso*)dipeptides and natural products were also investigated leading to useful *gem*-diboryl products in synthetically acceptable yields. Furthermore, tri-substituted diborylalkenes also gave the desired products in high regioselectivity. This decarboxylative conjugate addition reaction started with the formation of the alkyl radical *via* initial SET (single-electron transfer) between the photoexcited

photocatalyst PC* and carboxylic acids. Then, the alkyl radical added to the *gem*-diborylalkene gave the stabilized *gem*-diborylmethane radical, which subsequently underwent SET to afford the *gem*-diboryl anion followed by protonation to give the *gem*-diborylalkane product.



Scheme 1-26. Photoinduced reaction of *gem*-diborylalkenes (Masarwa, 2020).

1.2.5 Conclusions and Perspective

Multi(boronate esters) represent a class of useful organoboron compounds, including bis(boronate esters) and tri(boronate esters), which serve as valuable synthetic precursors for preparing various multifunctionalised complex molecules. Previous substrates to access to multi(boronate) esters mainly focused on unsaturated alkenes and alkynes, as more unsaturated hydrocarbons offer more possibilities. As alkyl precursors are prevalent and readily available, the development of multiborylations of saturated C(sp^3) bond is also valuable. Recent methods for selective

multiborylation of various alkyl C(sp^3) bonds were described, including C(sp^3)−X (I, Cl, Br, F), C(sp^3)−H, C(sp^3)−O, C(sp^3)−N, and C(sp^3)−C bonds. Still, the development of new catalytic systems for the construction of multi(boronate esters) from saturated C(sp^3) bonds is desirable.

1.3 References

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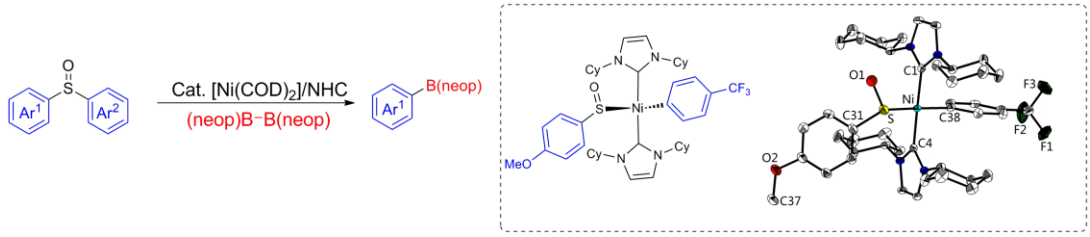
Chapter 2

Ni-Catalyzed Borylation of Aryl Sulfoxides



2 Ni-Catalyzed Borylation of Aryl Sulfoxides

2.1 Abstract

A nickel/*N*-heterocyclic carbene (NHC) catalytic system has been developed for the borylation of aryl sulfoxides with $B_2(neop)_2$ (neop = neopentyl glycolato). A wide range of aryl sulfoxides with different electronic and steric properties were converted into the corresponding arylboronic esters in good yields. The regioselective borylation of unsymmetric diaryl sulfoxides was also feasible leading to borylation of the sterically less encumbered aryl substituent. Competition experiments demonstrated that an electron-deficient aryl moiety reacts preferentially. The origin of the selectivity in the Ni-catalyzed borylation of electronically biased unsymmetrical diaryl sulfoxide lies in the oxidative addition step of the catalytic cycle, as oxidative addition of methoxyphenyl 4-(trifluoromethyl)phenyl sulfoxide to the Ni(0) complex occurs selectively to give the structurally characterized complex *trans*-[Ni(ICy)$_2$(4-CF$_3$-C$_6$H$_4$){(SO)-4-MeO-C$_6$H$_4$}] **2-4**. For complex **2-5**, an isomer, namely *trans*-[Ni(ICy)$_2$(C$_6$H$_5$)(OSC$_6$H$_5$)] **2-5-I**, was structurally characterized in which the phenyl sulfinyl ligand is bound *via* the oxygen atom to nickel. DFT calculations and experimental observations both revealed both isomers, *trans*-[Ni(ICy)$_2$(C$_6$H$_5$)(OSC$_6$H$_5$)] **2-5-I** and S-bonded isomer *trans*-[Ni(ICy)$_2$(C$_6$H$_5$)(SOC$_6$H$_5$)] **2-5** are in equilibrium, and that both isomers are connected *via* a transition state *trans*-[Ni(ICy)$_2$(C$_6$H$_5$)(η^2-{SO}-C$_6$H$_5$)], which lies only 10.8 kcal/mol above **2-5**.

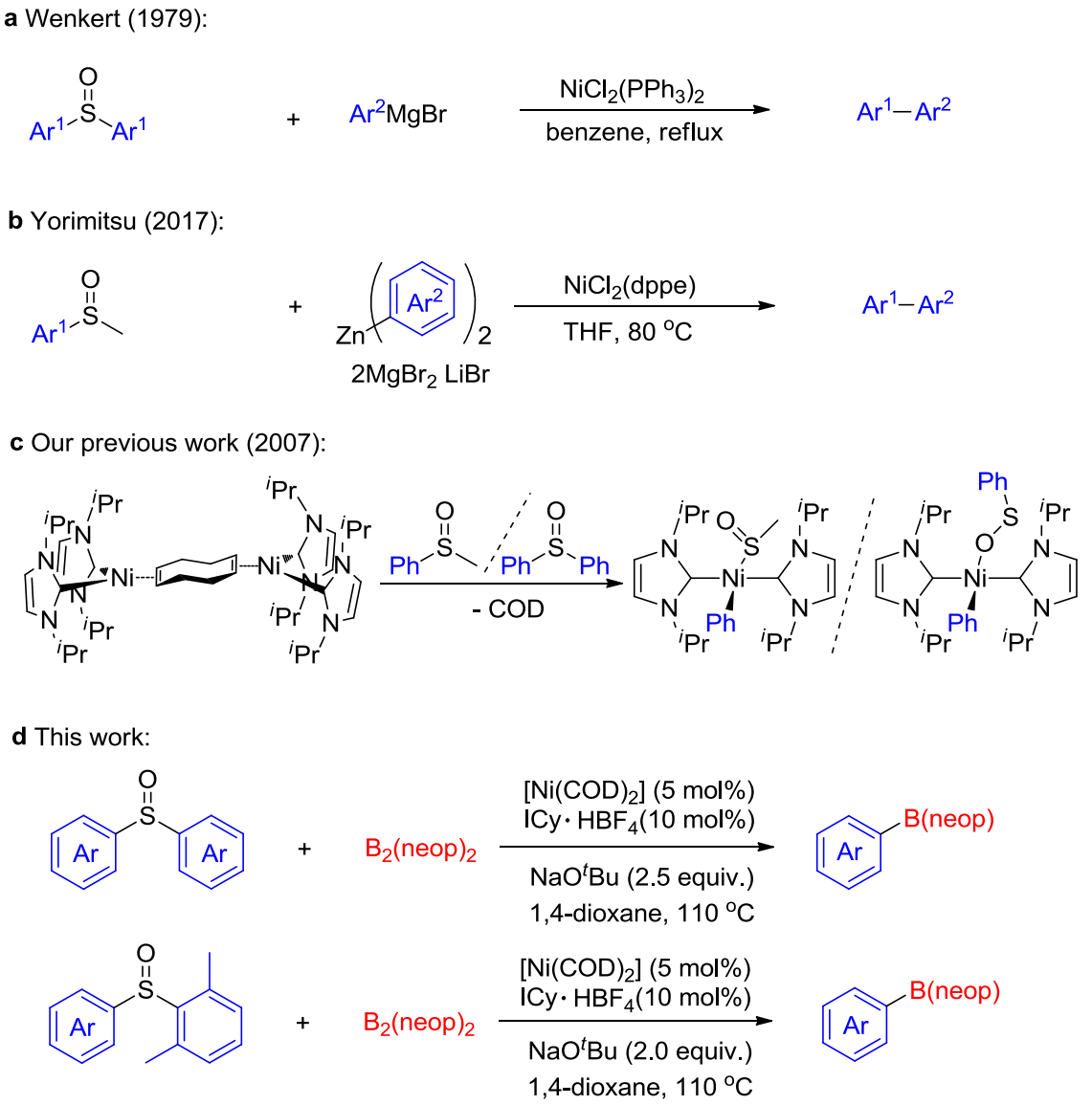
2.2 Introduction

The expansion of the range of alternative electrophilic coupling partners is an important and valuable topic in research on transition metal-catalyzed cross-coupling reactions.[1] Recently, cross-coupling of organosulfur compounds as electrophiles has gained much attention.[2,3] Due to their ubiquity and versatility in synthetic organic chemistry, organosulfur compounds are expected to be useful surrogates for aryl halides in transition metal-catalyzed coupling reactions. In contrast, cross-coupling of aryl sulfoxides has rarely been explored.[4] Sulfoxides are prevalent in nature and can be found in bioactive products and pharmaceuticals, and they are also useful as synthetic

intermediates.[5,6] Due to the electron deficiency of the sulfur atoms in the sulfoxide groups, the C–S bonds are considered to be easily cleavable and more reactive than aryl sulfides.

Previous work described C–S bond cleavage of sulfoxides by nickel-catalyzed reactions using Grignard reagents.[7] The groups of Wenkert and Enthaler developed Kumada-type cross-coupling reactions of aryl sulfoxides with aryl magnesium reagents and nickel catalysts (Scheme 2-1a).[8] Recently, the Yorimitsu group reported the $NiCl_2$(dppe)-catalyzed Negishi-type cross-coupling of aryl methyl sulfoxides with aryl zinc reagents (Scheme 2-1b).[9] However, a large amount of homocoupling byproducts of the aryl zinc reagents is formed along with the desired heterocoupling products. In 2007, one of our groups investigated the reactivity of the NHC-stabilized nickel(0) complex $[Ni_2(I^iPr)_4\{\mu\text{-}(\eta^2{:}\eta^2)\text{-COD}\}]$ (I^iPr = 1,3-di-*iso*-propylimidazolin-2-ylidene; COD = 1,5-cyclooctadiene) with sulfoxides in stoichiometric bond-activation reactions. We first demonstrated the transition metal-mediated C–S cleavage of sulfoxides containing sp^2- and sp^3-hybridized carbon bonds attached to the sulfur atom, leading to a [Ni–S(=O)R] structure, and reported the first structurally characterized complex *trans*-$[Ni(I^iPr)_2(Ph)(OSPh)]$ featuring an oxygen-bound sulfinyl ligand (Scheme 2-1c).[10] We then extended our work to C–S bond activation in thioethers, benzothiophene and dibenzothiophene using $[Ni_2(I^iPr)_4\{\mu\text{-}(\eta^2{:}\eta^2)\text{-COD}\}]$.[11]

Aryl- and heteroboronate esters are extremely important because of their exceptional utility as synthetic building blocks,[12] especially in C–C, C–O, C–N and C–X bond-forming reactions, as exemplified by the Suzuki−Miyaura coupling reaction.[13] To date, numerous methodologies have been developed for the synthesis of arylboronate esters.[14,15] In recent years, the development of transition metal-catalyzed Miyaura-type borylation reactions has allowed the synthesis of arylboronate esters under mild reaction conditions.[15]



Scheme 2-1. Nickel-mediated C–S activation of sulfoxides

As first row "Earth-abundant" metal catalysts have become of increasing interest for chemists due to their low cost and toxicity, recent research has enabled nickel-catalyzed borylation of less reactive C–Cl,[16] C–F,[17] C–O,[18] C–N,[19] and C–C bonds.[20] Our groups have reported the reactivity of the nickel(0)-NHC complex $[Ni_2(I^iPr)_4\{\mu\text{-}(\eta^2{:}\eta^2)\text{-COD}\}]$ towards organic halides and other substrates in stoichiometric bond-activations.[21] Recently, we demonstrated efficient thermal[22a] as well as photocatalytic[22b] procedures for the borylation of C–F bonds of aryl fluorides in the presence of $[Ni(IMes)_2]$ (IMes = 1,3-dimesitylimidazolin-2-ylidene) and a Ni/Rh tandem catalyst system, respectively. Subsequently, by applying a readily prepared NHC-stabilized nickel(0) catalyst precursor $[Ni_2(ICy)_4\{\mu\text{-}(\eta^2{:}\eta^2)\text{-COD}\}]$ (ICy = 1,3-dicyclohexylimidazolin-2-

ylidene) and the base NaOAc, we demonstrated the catalytic C–Cl borylation of aryl chlorides.[23] Very recently, we reported an efficient [Ni(IMes)$_2$]-catalyzed directed C3-selective C–H borylation of indoles.[24] In 2006, Hosoya[25a] and Yorimitsu[25b] independently demonstrated the borylation of aryl sulfides employing rhodium and palladium-NHC catalysts, respectively. Yorimitsu's group continued to develop the borylation of diaryl sulfoxides using a phosphine-ligated palladium catalyst and LiN(SiMe$_3$)$_2$ as the base.[26] Very recently, Pd-catalyzed as well as photoinduced strategies for the borylation of C–S bonds in aryl sulfonium salts were reported by Yorimitsu[27a] and Gao,[27b] respectively.

With the first demonstration of a Ni-mediated C–S bond cleavage of sulfoxides by our group,[10,11] and our successful previous work on the NHC nickel-catalyzed borylation of aryl halides,[22,23] we envisioned transforming aryl sulfoxides to arylboronate esters using an NHC nickel catalyst. Inexpensive Ni and ligand were used in place of expensive Rh and Pd metals which were employed previously. We note that the prices of those 2 metals have increased drastically over the past year. Furthermore, compared with conventional groups, such as aryl (pseudo)halides or alcohols, sulfoxides represent an alternative and complimentary substitute in coupling reactions, as aryl sulfoxides can be prepared directly from arenes by reaction with thionyl chloride. Herein, we report initial results on the NHC Ni-catalyzed borylation of aryl sulfoxides.

2.3 Result and Discussion

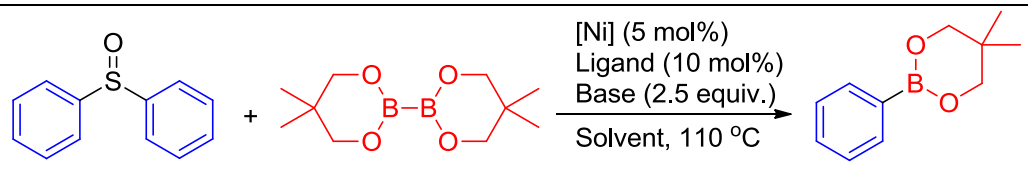
2.3.1 Optimization of Reaction Conditions

Our initial studies involved evaluation of the borylation of diphenyl sulfoxide **2-1a** with B$_2$(neop)$_2$[28] (Table 2-1), noting that B$_2$pin$_2$ proved unreactive under our conditions. In the presence of 5 mol% of [Ni(COD)$_2$], 10 mol% of IMes, and 2.5 equivalents of KO^{t}Bu, at 110 °C under an argon atmosphere in toluene solvent, the desired borylated product **2-3a** was obtained in 26% yield (entry 1 in Table 2-1). With this promising first result, we screened a range of ligands, bases, solvents, catalysts and boron sources to determine the scope and limitations of this reaction (Table 2-1). The reaction was accompanied by the reduction of sulfoxides to sulfides.[29] Among

the various NHC ligands we examined (entries 1-4 in Table 2-1), a dramatic effect of ICy•HBF_4 is notable, affording a 61% yield of **2-3a**. Employing the free carbene ICy instead of ICy•HBF_4 and a base did not affect the reactivity within experimental error (entry 2 in Table 2-1). However, the reaction was sensitive to the nature of the alkoxide under these conditions, as KOMe was not as effective as KO^{t}Bu (entry 5 in Table 2-1), and no reaction took place with NaOMe or LiO^{t}Bu (entries 6 and 7 in Table 2-1). The replacement of KO^{t}Bu with NaO^{t}Bu resulted in an increased yield of 73% (entry 8 in Table 2-1). Solvent screening showed 1,4-dioxane to be the most effective among those examined (entry 9 in Table 2-1). Polar solvents, such as THF, MTBE (methyl *tert*-butyl ether), CH_3CN and DMF, were not suitable for this borylation reaction.

We then investigated the catalytic activity of different NHC nickel complexes for the borylation using NaO^{t}Bu as a base and 1,4-dioxane as the solvent at 110°C for 20 h. The complex $[Ni_2(I^iPr)_4\{\mu\text{-}(\eta^2\text{:}\eta^2)\text{-COD}\}]$[23] also afforded the borylated compound **2-3a** in a very good yield of 79% (entry 10 in Table 2-1). The reaction of $[Ni(COD)_2]$ with two equivalents of the free carbene ICy in THF, which affords the dinuclear, COD-bridged complex $[Ni_2(ICy)_4\{\mu\text{-}(\eta^2\text{:}\eta^2)\text{-COD}\}]$, led to formation of the borylation product **2-3a** in a similar high yield of 88% (entry 11 in Table 2-1). The application of $[Ni(IMes)_2]$, however, containing the sterically more demanding NHC IMes, turned out to be less efficient, showing only moderate catalytic activity (26% yield) for the borylation of sulfoxides under the current conditions (entry 12 in Table 2-1). Other commercially available nickel sources such as $[NiCl_2]$, $[Ni(acac)_2]$ and $[Ni(OAc)_2]$ as catalyst precursors also proved successful in this coupling reaction (entries 13-15 in Table 2-1). Notably, decreasing the $[Ni(COD)_2]$ loading to 1 mol% still resulted in 70% yield (entry 16 in Table 2-1), and no product was observed in the absence of Ni catalyst.

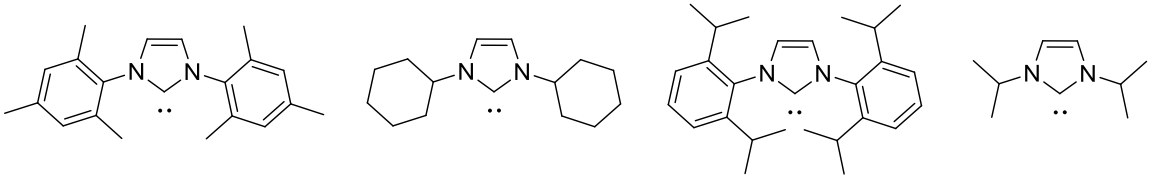
Table 2-1. Screening of reaction conditions for the Ni-catalyzed borylation of diphenyl sulfoxide **2-1a**.[a]



2-1a + **2-2a** → **2-3a**

Entry	Base	Catalyst	Ligand	Solvent	Yield of **2-3a** (%)[b]
1	KO^{t}Bu	[Ni(COD)$_2$]	IMes	toluene	26
2	KO^{t}Bu	[Ni(COD)$_2$]	ICy	toluene	58
3	KO^{t}Bu	[Ni(COD)$_2$]	ICy•HBF$_4$	toluene	61
4	KO^{t}Bu	[Ni(COD)$_2$]	IDipp•HBF$_4$	toluene	37
5	KOMe	[Ni(COD)$_2$]	ICy•HBF$_4$	toluene	22
6	NaOMe	[Ni(COD)$_2$]	ICy•HBF$_4$	toluene	0
7	LiO^{t}Bu	[Ni(COD)$_2$]	ICy•HBF$_4$	toluene	0
8	NaO^{t}Bu	[Ni(COD)$_2$]	ICy•HBF$_4$	toluene	73
9	**NaO^{t}Bu**	**[Ni(COD)$_2$]**	**ICy•HBF$_4$**	**1,4-dioxane**	**93 (81)**[c]
10	NaO^{t}Bu	[Ni$_2$(I^{i}Pr)$_4$\{μ-(η^2:η^2)-COD\}]	-	1,4-dioxane	79
11	NaO^{t}Bu	[Ni$_2$(ICy)$_4$\{μ-(η^2:η^2)-COD\}]	-	1,4-dioxane	88
12	NaO^{t}Bu	[Ni(IMes)$_2$]	-	1,4-dioxane	26
13	NaO^{t}Bu	[NiCl$_2$]	ICy•HBF$_4$	1,4-dioxane	63
14	NaO^{t}Bu	[Ni(OAc)$_2$]	ICy•HBF$_4$	1,4-dioxane	66
15	NaO^{t}Bu	[Ni(acac)$_2$]	ICy•HBF$_4$	1,4-dioxane	62
16[d]	NaO^{t}Bu	[Ni(COD)$_2$]	ICy•HBF$_4$	1,4-dioxane	70

[a] Reaction conditions, unless otherwise stated: diphenyl sulfoxide **2-1a** (0.5 mmol, 1.0 equiv.), [Ni]-catalyst precursor (5 mol%), ligand (10 mol%), $B_2(neop)_2$ (2.5 equiv.), base (2.5 equiv.), solvent (3 mL), 110 °C, 20 h. [b] The yields were determined by GC-MS of a diluted and filtred aliquot of the reaction mixture using dodecane as the internal standard (average of two runs). [c] Isolated yield. [d] [Ni(COD)$_2$] (1 mol%), ICy•HBF$_4$ (2 mol%).



IMes ICy IDipp I^{i}Pr

2.3.2 Investigation of Reaction Scope

Having identified the optimized conditions with diphenyl sulfoxide **2-1a** as the standard substrate, we then conducted the borylation of a series of diaryl sulfoxides **2-1b** – **2-1n** (Figure 2-1). Diaryl sulfoxides bearing electron-donating substituents (**2-1b,c,g,h,i**) gave the borylated products in yields up to 86%. Electron-rich substrates containing a *p*-OMe or *p*-SMe group (**2-1c** and **2-1g**) were converted into their corresponding arylboronic esters in 49% and 67% yield, respectively. Unfortunately, the attempted borylation of *ortho*-tolyl sulfoxide $(2\text{-}CH_3\text{-}C_6H_4)_2S{=}O$ **1i** gave the product **3i** in only 16% GC yield, whereas bis(1,3,5-trimethylphenyl) sulfoxide **2-1j** (disubstituted at both *ortho* positions) failed to give the product **2-3j**, and only unreacted starting material was identified by GC-MS. Electron-poor diaryl sulfoxides (**2-1d** – **2-1f, 2-1k**) were also borylated in satisfying to good yields. Thus, chloro- or fluoro- moieties on **2-1d** or **2-1e**, respectively, were compatible with the borylation reaction, undergoing selective cleavage of the C–S(=O) bond over that of the C–F or C–Cl bond. Applying *para*-substituted **2-3f**, and the sulfoxide **2-3k**, substituted in both *meta*-positions with $\text{-}CF_3$ groups, gave the products in 73% and 68% yields, respectively. In an analogous fashion, biphenyl sulfoxide **2-1l** reacted well under the standard conditions. The π-extended dinaphthyl sulfoxide **2-1m** also underwent the reaction to furnish **2-3m** in 71 % yield. Interestingly, a substrate containing benzothiophene moieties was also tolerated, demonstrated by the synthesis of borylated compound **2-3n** in 76% yield.

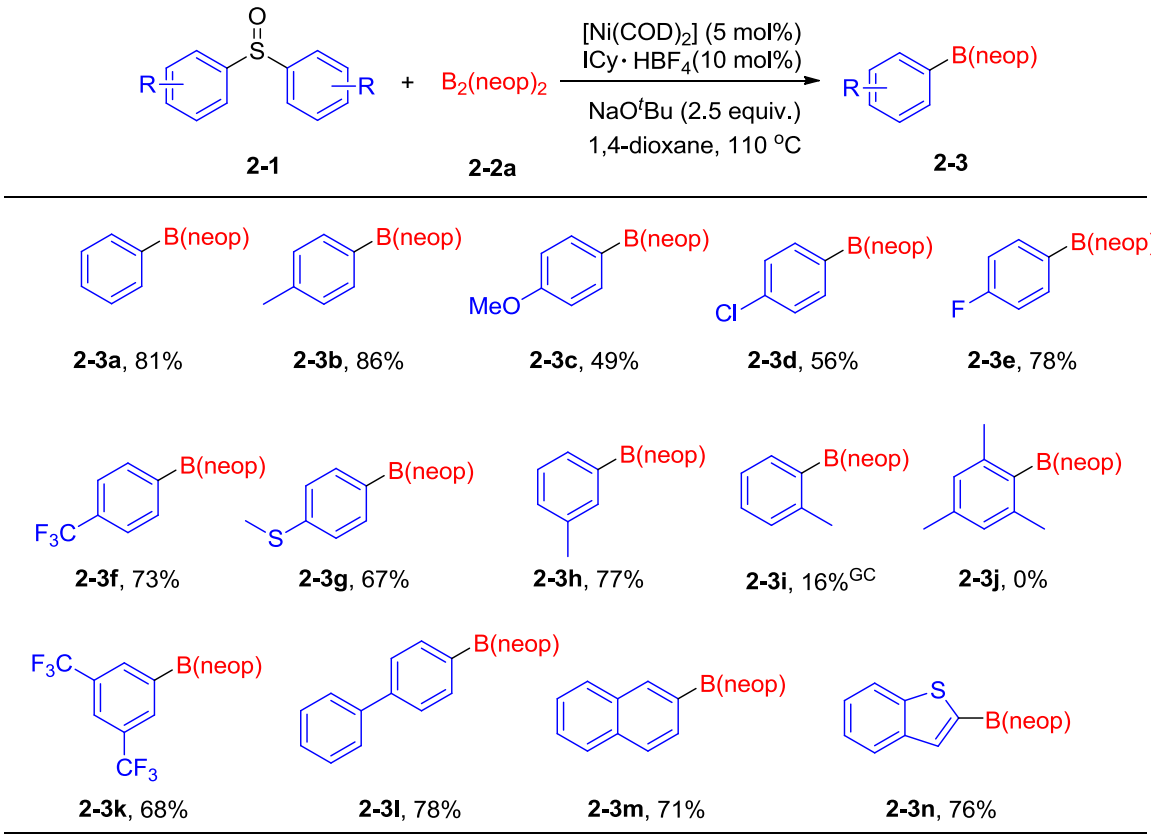


Figure 2-1. Screening of diaryl sulfoxides for the Ni-catalyzed borylation reaction.[a] [a] Reaction conditions, unless otherwise stated: diaryl sulfoxides **2-1** (0.5 mmol, 1.0 equiv.), $[Ni(COD)_2]$ (5 mol%), ICy•HBF_4 (10 mol%), $B_2(neop)_2$ (2.5 equiv.), NaO^{t}Bu (2.5 equiv.), 1,4-dioxane (3 mL), 110 °C, 20 h. Isolated yield after chromatographic workup. The yield with a "GC" superscript is the GC-MS yield with dodecane as the internal standard.

Considering the failure when utilizing **2-1j** (disubstituted at both *ortho* positions) as the substrate, we anticipated that regioselective borylation of unsymmetrical diaryl sulfoxides would be feasible by means of steric bias (Figure 2-2). The borylation of sterically-biased fluoro-substituted **2-1o** and methoxy-substituted **2-1p** with **2-2a** proceeded smoothly to afford **2-3e** and **2-3c** in 82% and 57% yields, respectively. Using a substrate containing a trimethylsilyl moiety, under the conditions employed, generated borylated **2-3q** in 85% yield. Furthermore, a wide variety of π-extended systems participated in the reaction to afford the borylated products **2-3r** – **2-3v** in good yields, and the presence of substituted nitrogen- and oxygen-containing heterocycles did not interfere with productive C–B bond formation. This nickel-catalyzed method was also applicable to the borylation of 3-((2,6-dimethylphenyl)sulfinyl)pyridine **2-1w** and 2-((2,6-dimethylphenyl)sulfinyl)thiophene **2-1x** derivatives. Although the reaction shows a broad scope,

there are some functional groups which were not tolerated. Cyano-, amino-, ester- and indole-substituted substrates failed to provide borylated products, and the starting materials were recovered. As expected, 2-((2,6-difluorophenyl)sulfinyl)-1,3-dimethylbenzene (substituted at four *ortho* positions) was also unsuccessful. Furthermore, an aryl alkyl sulfoxide also proved to be ineffective in this Ni-NHC system, as alkanesulfenate anions are more labile than arenesulfenate anions.[9, 30]

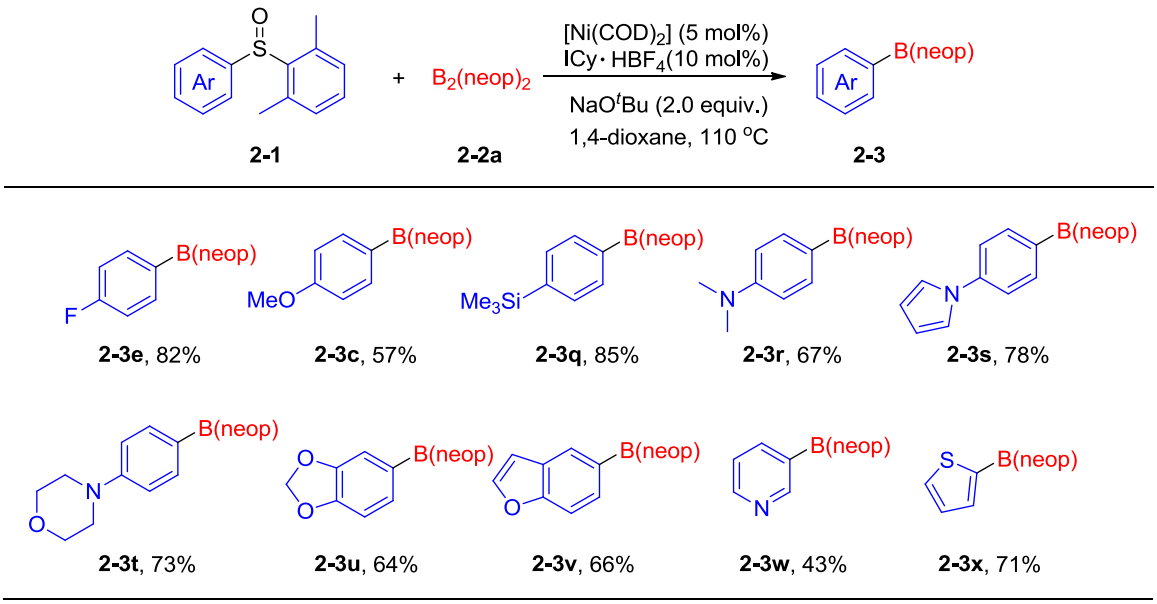
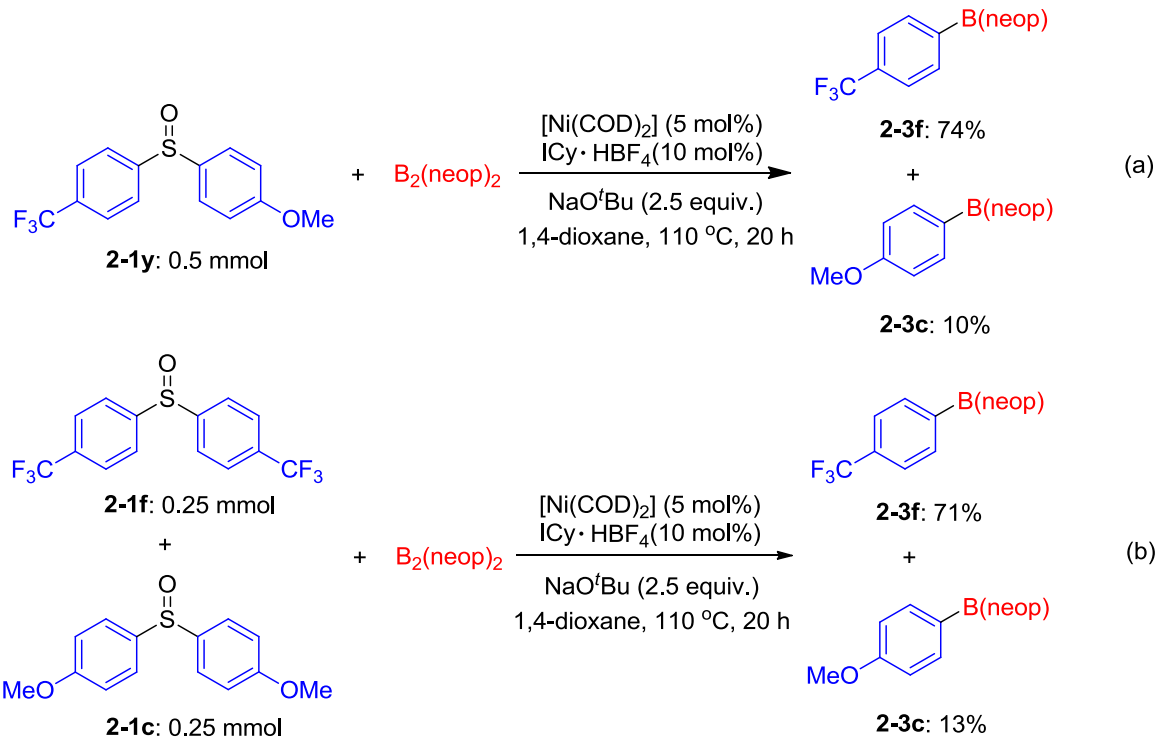


Figure 2-2. Regioselective borylation of unsymmetrical diaryl sulfoxides.[a] [a] Reaction conditions, unless otherwise stated: diaryl sulfoxides **2-1** (0.5 mmol, 1.0 equiv.), [Ni(COD)$_2$] (5 mol%), ICy•HBF$_4$ (10 mol%), B$_2$(neop)$_2$ (2.0 equiv.), NaO^{t}Bu (2.0 equiv.), 1,4-dioxane (3 mL), 110 °C, 20 h. Isolated yield after chromatographic workup.

2.3.3 Competition Experiments and Ni Complex Analysis

Next, we conducted competition experiments to gain additional insight into the effect of the electronic properties of aryl sulfoxides on the reaction (Scheme 2-2). First, the intramolecular competition reaction of electronically-biased unsymmetrical diaryl sulfoxide **2-1y** was conducted with B$_2$(neop)$_2$ (Scheme 2-2a). The electron-deficient aryl moiety reacted preferentially to afford **2-3f** in 74% yield accompanied by 10% of **2-3c** as a minor product. A similar trend was found for the intermolecular version. Thus, in the same vessel, 0.25 mmol of electron-deficient and -rich aryl sulfoxides **2-1f** and **2-1c** were treated with 2.5 equivalents of B$_2$(neop)$_2$, and the reaction

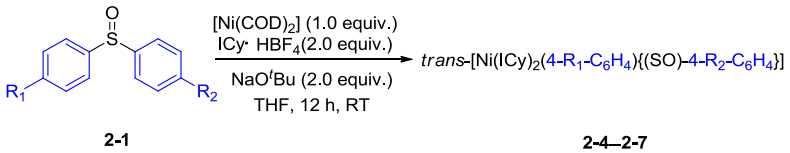
predominantly consumed electron-deficient **2-1f** providing **2-3f** in 71% yield (Scheme 2-2b). To examine the origin of the selectivity in the Ni-catalyzed borylation of the electronically biased unsymmetrical diaryl sulfoxide, we reacted methoxyphenyl-4-(trifluoromethyl)phenyl sulfoxide (**2-1y**) with a Ni(0)-NHC complex, and the oxidative addition product *trans*-[Ni(ICy)$_2$(4-CF$_3$-C$_6$H$_4$){(SO)-4-MeO-C$_6$H$_4$}] **2-4** was isolated in 86% yield (Scheme 2-3, left). Single-crystal X-ray diffraction analysis of **2-4** showed that the C–S oxidative addition to Ni proceeded mainly at the side of electron-poor (trifluoromethyl)phenyl group (Scheme 2-3, right).

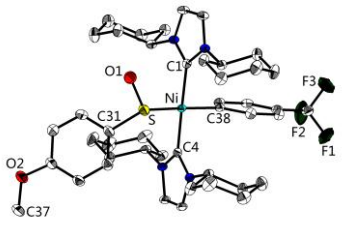


Scheme 2-2. Competition experiments. (a) Intramolecular competitive borylation of unsymmetrical diaryl sulfoxide **2-1y**. (b) Intermolecular competitive borylation of **2-1c** and **2-1f** in the same vessel.

We therefore investigated further the first step of a possible catalytic cycle, namely the oxidative addition of the C–(S=O) bond. According to our previous work, we prepared *trans*-[Ni(ICy)$_2$(C$_6$H$_5$){(SO)-C$_6$H$_5$}] **2-5** by treatment of diphenyl sulfoxide **2-1a** with [Ni(COD)$_2$], ICy•HBF$_4$ and NaO^{t}Bu in THF at room temperature, which was isolated as a yellow solid in 78% yield (Scheme 2-3). In analogous reactions utilizing bis(4-methylphenyl) sulfoxide **2-1b** and bis(4-fluorophenyl) sulfoxide **2-1e**, we isolated the oxidative addition products *trans*-[Ni(ICy)$_2$(4-CH$_3$-

C_6H_4){(SO)-4-CH_3-C_6H_4}] **2-6** and *trans*-[Ni(ICy)$_2$(4-F-C_6H_4){(SO)-4-F-C_6H_4}] **2-7** in 73% and 63% yields, respectively. Complexes **2-4** – **2-7** were characterized by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy, elemental analysis, HRMS, IR spectroscopy and, for **2-4** and **2-5**, by single-crystal X-ray diffraction[31]. In all cases, the ensuing Ni(II)-(Ar){(SO)-Ar'} complexes were found to be stable both in the solid state and in solution. Remarkably, in contrast with previously reported phosphine ligated Ni(II) aryl complexes, which rapidly decompose to nickel(I) species, complexes **2-4** – **2-7** are stable in solution even upon heating at 110 °C for several hours.[32]

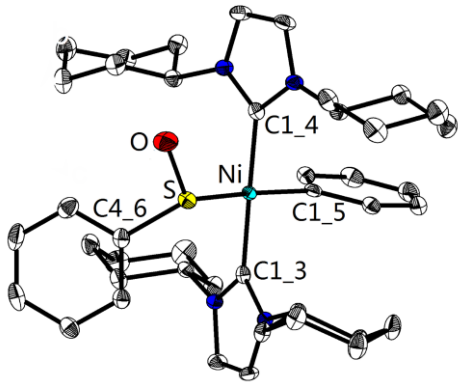




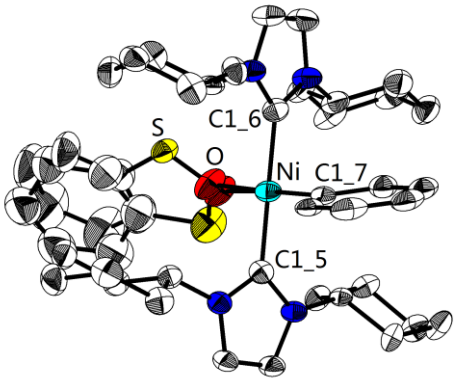
Molecular structure of ***2-4***

Scheme 2-3. Synthesis of the oxidative-addition products of the type *trans*-[Ni(ICy)$_2$(Ar^1){(SO)Ar^2}] **2-4** – **2-7**. Molecular structure of **2-4** shown with thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **2-4**: Ni–C1 1.894(2), Ni–C4 1.907(2), Ni–C38 1.925(2), Ni–S 2.2259(8), S–C31 1.801(2), S=O1 1.535(2); C1-Ni-C4 176.16(7), C1-Ni-C38 88.31(7), C4-Ni-C38 88.59(7), C1-Ni-S 91.09(6), C4-Ni-S 92.37(6), C38-Ni-S 169.45(5).

Surprisingly, we found a small number of single crystals of another compound which had also grown from a solution of **2-5**, namely *trans*-[Ni(ICy)$_2$(C_6H_5)(OSC_6H_5)] **2-5-I**, a product in which the phenyl sulfinyl ligand is bound *via* oxygen to the nickel atom, which was confirmed by X-ray diffraction (Figure 2-3).[31] In both structures, the coordination around the Ni atom is nearly perfectly square-planar with the sum of the angles around Ni being 360° in each case (within 3 esd's, see Table 2-S1). In addition, the *trans*-influence of the O- and S-bound ligands appears to be the same, as the Ni–C(phenyl) bond lengths of 1.929(2) and1.930(4) Å for **2-5** and **2-5-I**, respectively, are identical within less than 1 esd (see Table 2-S1).



Molecular structure of ***2-5***



Molecular structure of ***2-5-I***

Figure 2-3. Molecular structures of **2-5** and **2-5-I** shown with thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **2-5**: Ni–C1_4 1.894(2), Ni–C1_3 1.900(2), Ni–C1_5 1.929(2), Ni–S 2.2284(8), S–C4_6 1.798(2), S=O 1.537(2); C1_4-Ni-C1_3 177.73(9), C1_4-Ni-C1_5 89.93(9), C1_3-Ni-C1_5 88.08(9), C1_5-Ni-S 170.33(7), C1_4-Ni-S 90.87(7), C1_3-Ni-S 91.27(7). Selected bond lengths [Å] and angles [°] of **2-5-I**: Ni–C1_5 1.895(4), Ni–C1_6 1.901(4), Ni–C1_7 1.930(4), Ni–O 1.924(7) / 1.91(2), S–O 1.606(8) / 1.611(13); C1_5-Ni-C1_6 178.66(18), C1_5-Ni-C1_7 90.02(17), C1_6-Ni-C1_7 88.79(18), C1_7-Ni-O 173.5(2) / 175.8(7), C1_5-Ni-O 87.3(5) / 91.6(16), C1_6-Ni-O 94.0(5) / 89.5(16).

We performed DFT calculations to address the relative energies of both isomers and to investigate a possible transition state connecting them (Figure 2-4). The calculated results show that the relative energies of both isomers are similar. Both isomers are connected *via* a transition state (**TS-iso**) with the *trans*-[Ni(ICy)$_2$(C$_6$H$_5$)(η^2-{SO}-C$_6$H$_5$)] structure, in which the sulfoxide ligand is η^2-bound to the nickel center, which lies only 10.8 kcal/mol above **2-5**. As the barrier for the interconversion is low, we expect that both Ni complexes can easily interconvert and are thus in equilibrium, which is consistent with the low temperature NMR spectra of **2-5** (see Figures 2-S11 and 2-S12), in which both isomers were observed at –90 °C.

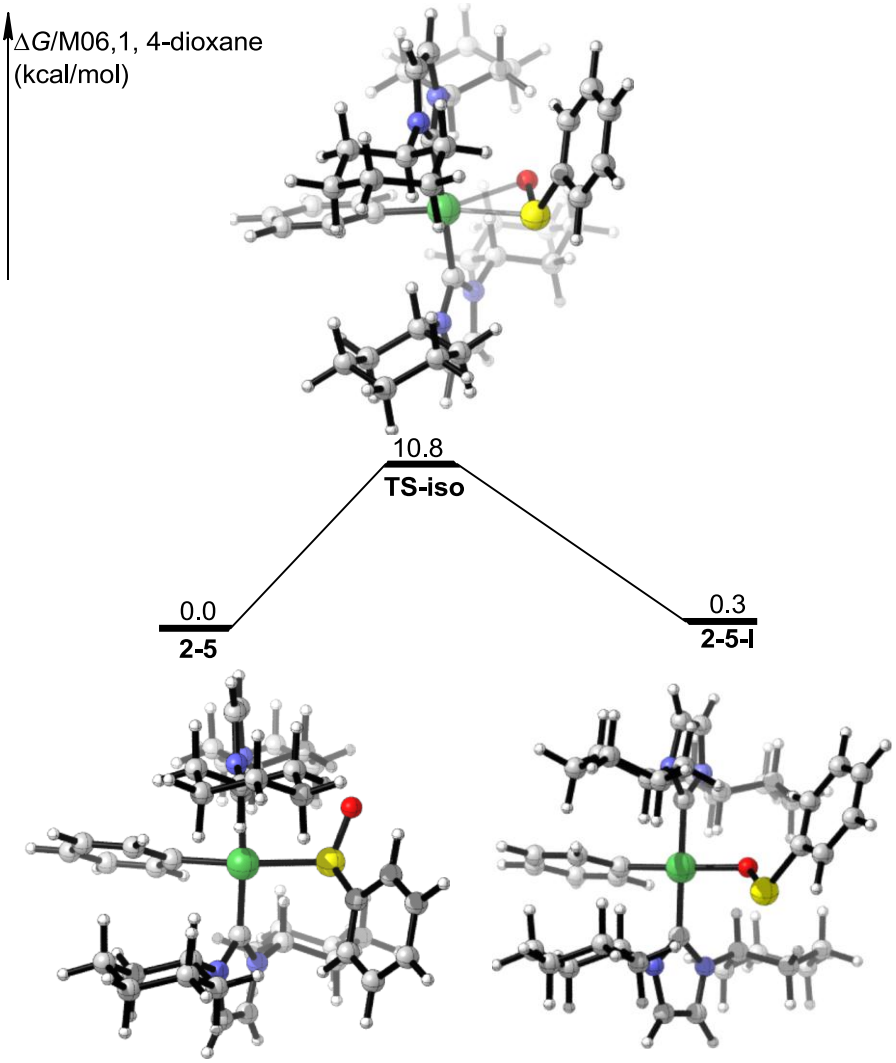
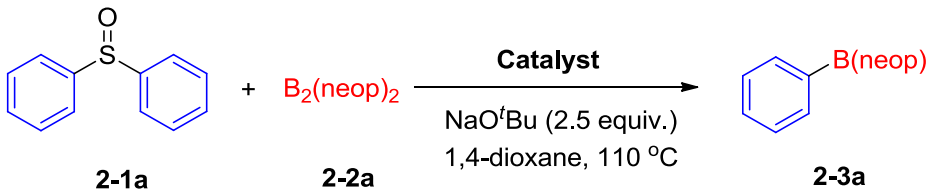


Figure 2-4. Free energy profile for the isomerization of *trans*-[Ni(ICy)$_2$(C$_6$H$_5$)(SOC$_6$H$_5$)] **2-5** to *trans*-[Ni(ICy)$_2$(C$_6$H$_5$)(OSC$_6$H$_5$)] **2-5-I** calculated at the (M06/def2-TZVP, SMD//B3-LYP/def2-SVP) level of theory. Energies relative to **2-5** is given in kcal/mol.

2.3.4 Mechanistic Studies

We next evaluated the catalytic behavior of different Ni(0) and Ni(II) species for the borylation of diphenyl sulfoxide (Scheme 2-4). The isolated COD-bridged Ni(0) complex [Ni$_2$(ICy)$_4${μ-(η^2:η^2)-COD}] showed high reactivity for the borylation, similar to that of a mixture of [Ni(COD)$_2$] with ICy. Ni(II) complex **2-5** was also capable of facilitating the catalytic borylation with approximately identical efficiency to that of a combination of [Ni(COD)$_2$] and ICy. To evaluate a possible resting state of the catalytic cycle, and thus gather information about the turnover-limiting step, we performed an *in situ* NMR study. The reaction of [Ni(COD)$_2$] and ICy with an aryl sulfoxide leads

to rapid oxidative addition of the C–S bond with formation of *trans*-[Ni(ICy)$_2$(Ar^1)(SOAr^2)] as a mixture of S- and O-bound isomers within one hour at room temperature. The oxidative addition product *trans*-[Ni(ICy)$_2$(Ar^1)(SOAr^2)] is the resting state of the catalytic cycle (see Figures 2-S6-2-S9). The reaction of [Ni(COD)$_2$], ICy with stoichiometric amounts of B$_2$(neop)$_2$ did not show any evidence for the formation of a likely nickel-boryl complex intermediate (see Figure 2-S10). Heating a mixture of [Ni(ICy)$_2$(Ar)(SOR)}] and B$_2$(neop)$_2$ to 110 °C for 1 h revealed the formation of a small amount of ArB(neop) formed by ^{19}F and ^{11}B NMR spectroscopy (see Figures 2-S4 and 2-S5), but no Ni-boryl intermediate was observed. It was not possible to isolate or observe *trans*-[Ni(ICy)$_2$(Bneop)(Ar)], as Ni-boryls are fairly unstable, and reductive elimination of the product is fast, as expected.[33]

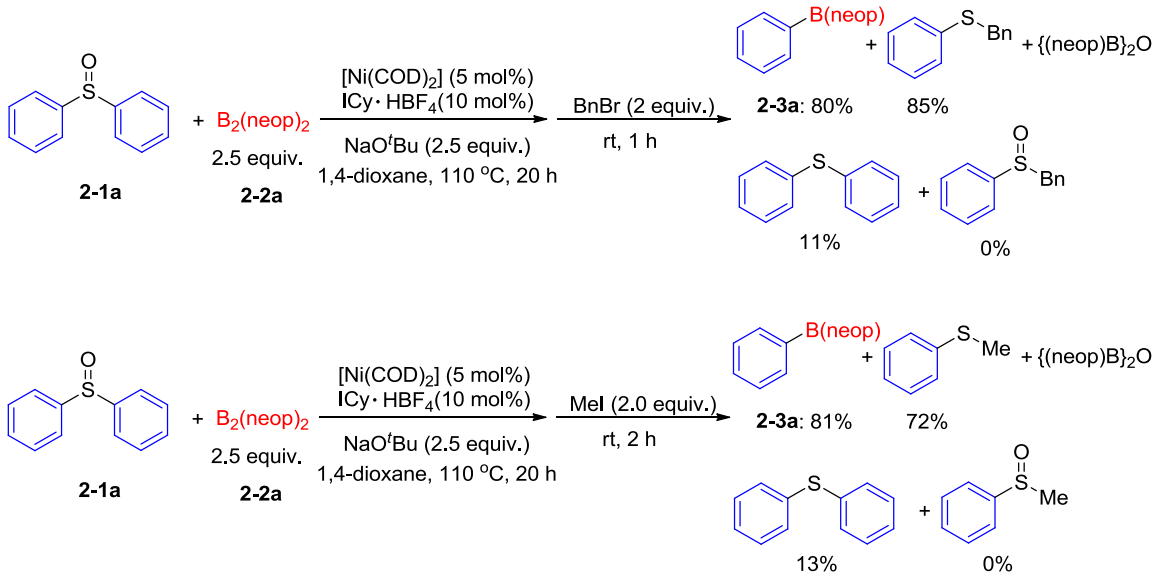


Catalyst	[Ni$_2$(ICy)$_4$COD] (5 mol%)	Ni(II) complex 2-5 (5 mol%)	Ni(II) complex 5/ICy·HBF$_4$ (5 mol%)/(10 mol%)
3a	88%	67%	81%

Scheme 2-4. Catalytic activity of Ni(0) and Ni(II) species.

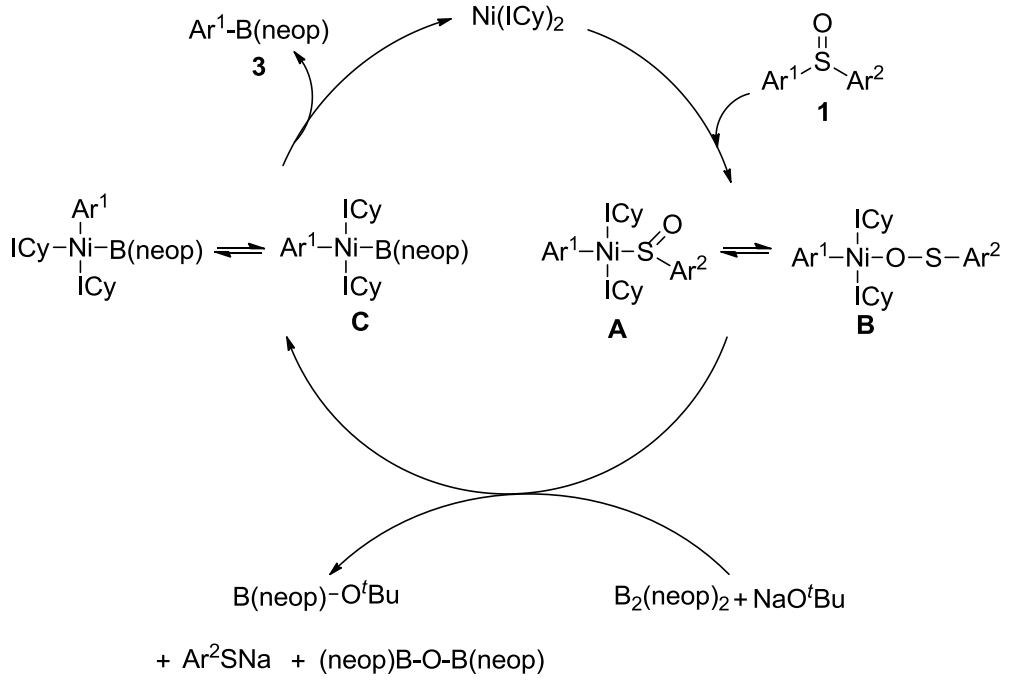
To probe the fate of the leaving groups, we conducted experiments to trap the sulfur-containing products (Scheme 2-5). The borylation of **2-1a** with B$_2$(neop)$_2$ was carried out under standard conditions, and then the reaction mixture was treated with 2.0 equiv. of benzyl bromide or iodomethane, respectively. Interestingly, in the first case, benzyl phenyl sulfide was obtained in 85% yield accompanied by the desired borylated product **2-3a**, and benzyl phenyl sulfoxide was not observed. Likewise, in the second case, methyl phenyl sulfide was formed in 72 % yield, along with **2-3a**. As sulfides rather than sufloxides were observed as byproducts, reduction of the latter by the diboron was accompanied by the formation of {(neop)B}$_2$O (see Figure 2-S3).[29] In order to explore whether the mechanism is a one-step nickel-catalyzed borylation of the sulfoxide or

involves reduction of the sulfoxide to a sulfide with $B_2(neop)_2$ followed by nickel-catalyzed borylation of the sulfide, we reacted diphenylsulfide as a potential substrate under the standard conditions. However, diphenylsulfide failed to give the borylated product and 91% of the diphenylsulfide was recovered. When a mixture of diphenyl sulfoxide **2-1a** and di-*p*-tolylsulfide were reacted under the standard conditions, PhB(neop) **2-3a** was still obtained in good (78%) yield. These results prove that a diarylsulfide is neither a catalyst poison nor inhibitor in this reaction and is also unlikely to be an intermediate.



Scheme 2-5. Electrophilic trapping of the anionic sulfur fragments.

The isolation and characterization of the key intermediates and products of the C–S borylation of diaryl sulfoxides leads us to propose the following mechanism (Scheme 2-6). In the first step, the *in situ* formed [Ni(ICy)$_2$] reacts with aryl sulfoxide **2-1** *via* oxidative addition of the C–S bond forming *trans*-[Ni(ICy)$_2$(Ar^1)(SOAr^2)] (**2-A**), which is in equilibrium with *trans*-[Ni(ICy)$_2$(Ar^1)(OSAr^2)] (**2-B**). This is followed by boryl transfer to generate *trans*-[Ni(ICy)$_2${B(neop)}(Ar^1)] (**2-C**) and B(neop)-O^{t}Bu[34] assisted by the base, and subsequent rapid reductive elimination from a *cis* isomer delivers the target product **2-3** and regenerates the [Ni(ICy)$_2$] species.



Scheme 2-6. Proposed mechanism for the NHC-nickel-catalyzed borylation of aryl sulfoxides.

2.4 Conclusions

In summary, we have developed an efficient nickel-catalyzed borylation of diaryl sulfoxides via C–S bond activation producing a variety of useful organoboronates. This simple procedure has a wide substrate scope, including electron-rich aryl sulfoxides, and broad functional group tolerance, using an inexpensive, and a relatively low toxicity first-row transition metal. Elucidation of key mechanistic features of this newly developed reaction led to the identification of fully characterized nickel intermediates. The molecular structures of **2-5** and **2-5-I** demonstrate the ambivalence of O versus S binding of sulfoxide ligands. The nickel sulfinyl moieties may be of significance to bioinorganic chemists regarding the deactivation of nickel-containing enzymes.[35] Further mechanistic studies of this borylation process, as well as expansion of the scope of this transformation, are underway in our laboratory.

2.5 Detailed Experiments and Characterization Data

2.5.1 General Information

All reactions and subsequent manipulations were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox (Innovative Technology Inc. and Braun Uni Lab). All

reactions were carried out in oven-dried glassware. Reagent grade solvents (Fisher Scientific and J.T. Baker) were nitrogen saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System, and further deoxygenated using the freeze-pump-thaw method. C_6D_6 and $CDCl_3$ were purchased from Sigma-Aldrich. [Ni(COD)$_2$],[36] [Ni(IMes)$_2$],[37] [Ni$_2$(ICy)$_4${μ-(η^2:η^2)-COD}],[38] [Ni$_2$(I^{i}Pr)$_4${μ-(η^2:η^2)-COD}],[40a-b] ICy•HBF$_4$,[39] ICy•HCl,[39] ICy,[39] IDipp•HBF$_4$,[40a-b] IMes,[40c] were prepared according to published procedures. The diboron reagents B_2pin_2 and $B_2(neop)_2$ were a generous gift from AllyChem Co. Ltd. All other reagents were purchased from Sigma-Aldrich or ABCR.

NMR spectra were recorded at 298 K using Bruker Avance 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz, ^{11}B, 96 MHz), Bruker DPX-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz, ^{11}B, 128 MHz; ^{19}F, 376 MHz), or Bruker Avance 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz, ^{11}B, 160 MHz; ^{19}F, 470 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm; C_6D_6: 7.16 ppm) whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS using the natural-abundance carbon resonances ($CDCl_3$: 77.2 ppm; C_6D_6: 128.0 ppm). ^{11}B and ^{19}F NMR chemical shifts are reported relative to external BF_3•OEt_3 or $CFCl_3$, respectively. Coupling constants are given in Hertz. Elemental analyses were performed in the microanalytical laboratory of the Institute of Inorganic Chemistry, Universität Würzburg, using an Elementar vario micro cube instrument. Automated flash chromatography was performed using a Biotage® Isolera Four system, on silica gel (Biotage SNAP cartridge KP-Sil 10 g and KP-Sil 25 g). Commercially available, precoated TLC plates (Polygram® Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 30 °C. GC-MS analyses were performed using a Thermo Fisher Scientific Trace 1310 gas chromatograph (column: TG-SQC 5% phenyl methyl siloxane, 15 m, Ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C; carrier gas: He (1.2 mL min^{-1}) or an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 30 m, Ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C (20 °C min^{-1}); carrier gas: He (1.2 mL min^{-1}) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A

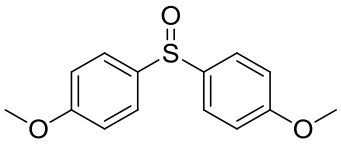
series auto sampler/injector. High-resolution mass spectra were obtained using a Thermo Scientific Exactive Plus spectrometer equipped with an Orbitrap Mass Analyzer. Measurements were accomplished using an ASAP/APCI source with a corona needle, and a carrier-gas (N_2) temperature of 250 °C.

2.5.2 General Procedure for the Synthesis of Sulfoxides

Synthesis of 2-1c-2-1e, 2-1j

These compounds were prepared as described previously.[41] A Schlenk flask was charged with thionyl chloride (0.73 mL, 10 mmol) and corresponding aromatic (25 mL) under argon. The mixture was cooled to 0 °C and stirred while 3.8 mL (43.0 mmol) of triflic acid was added. After 1 h, the resulting mixture was allowed to further stir at room temperature overnight. After the completion of the reaction, ice and saturated aqueous $NaHCO_3$ were added and the resulting biphasic solution was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layer was dried over $MgSO_4$, and filtred through a pad of Celite (Ø 3 mm × 8 mm) followed by rotary evaporation. The product was isolated by flash column chromatography (hexane/ethyl acetate: 10/1).

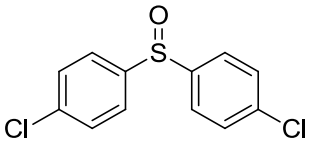
Bis(4-methoxyphenyl) sulfoxide 2-1c



Prepared from 10 mmol thionyl chloride and 25 mL of anisole. White solid (1.96 g, 7.5 mmol, 75%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.54 – 7.49 (m, 4H), 6.96 – 6.91 (m, 4H), 3.79 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 161.9, 137.1, 127.0, 114.8, 55.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{15}O_3S$ $[M+H]^+$ 263.0736 (263.0728).

The spectroscopic data for **2-1c** match those reported in the literature.[41]

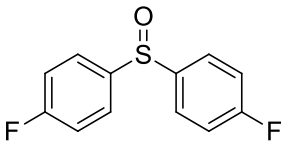
Bis(4-chlorophenyl) sulfoxide 2-1d



Prepared from 10 mmol thionyl chloride and 25 mL of chlorobenzene. White solid (1.92 g, 7.1 mmol, 71%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.59 – 7.54 (m, 4H), 7.46 – 7.42 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 144.0, 137.8, 129.9, 126.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_9Cl_2OS$ $[M+H]^+$ 270.9746 (270.9737).

The spectroscopic data for 2-**1d** match those reported in the literature.[41]

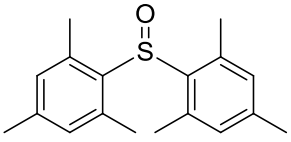
Bis(4-fluorophenyl) sulfoxide 2-1e



Prepared from 5 mmol thionyl chloride and 10 mL of fluorobenzene. White solid (0.61 g, 2.55 mmol, 51%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.64 – 7.60 (m, 4H), 7.18 – 7.13 (m, 4H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 164.5 (d, J = 251 Hz), 141.1 (d, J = 4 Hz), 127.2 (d, J = 10 Hz), 116.9 (d, J = 23 Hz). **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -108.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_9F_2OS$ $[M+H]^+$ 239.0337 (239.0328).

The spectroscopic data for **2-1e** match those reported in the literature.[41]

Bis(1,3,5-trimethylphenyl) sulfoxide 2-1j



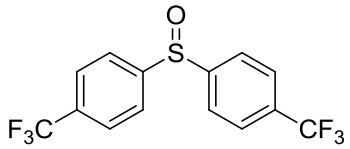
Prepared from 5 mmol thionyl chloride and 10 mL of mesitylene. White solid (0.66 g, 2.3 mmol, 46%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 6.81 (s, 4H), 2.41 (s, 12H), 2.26 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 140.6, 138.6, 136.6, 131.3, 21.0, 19.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{23}OS$ $[M+H]^+$ 287.1464 (287.1456).

The spectroscopic data for **2-1j** match those reported in the literature.[41]

Synthesis of 2-1f-2-1i, 2-1k

These compounds were prepared as described previously.[42] A Schlenk flask was charged with thionyl chloride (0.40 mL, 5.5 mmol) and THF (5 mL) under argon. The mixture was cooled to 0 °C. 4-(Trifluoromethyl)phenylmagnesium bromide (ca. 1 M in THF, 10 mL) prepared from the corresponding aryl bromide (10 mmol) was added slowly and the resulting mixture was allowed to warm to room temperature. After the completion of the reaction, ice and saturated aqueous $NaHCO_3$ were added and the resulting biphasic solution was extracted with EtOAc (20 mL × 3). The combined organic layer was dried over $MgSO_4$, and filtred through a pad of Celite (Ø 3 mm × 8 mm) followed by rotary evaporation. The product was isolated by flash column chromatography (hexane/ethyl acetate: 10/1).

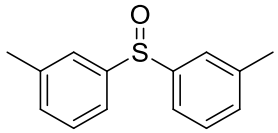
Bis[4-(trifluoromethyl)phenyl] sulfoxide 2-1f



Prepared from 10 mmol of 1-bromo-4-(trifluoromethyl)benzene. White solid (1.23 g, 3.65 mmol, 73%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.82 – 7.79 (m, 4H), 7.76 – 7.73 (m, 4H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 149.3, 133.6 (q, J = 33 Hz), 126.8 (q, J = 4 Hz), 125.0, 123.4 (q, J = 271 Hz). **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -63.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_9F_6OS$ $[M+H]^+$ 339.0273 (339.0263).

The spectroscopic data for **2-1f** match those reported in the literature.[43]

Bis(3-methylphenyl) sulfoxide 2-1h

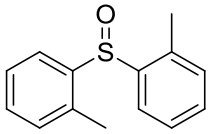


Prepared from 10 mmol of 1-bromo-3-methylbenzene. White solid (0.78 g, 3.4 mmol, 68%). **^{1}H**

NMR (300 MHz, $CDCl_3$): δ = 7.47 (s, 2H), 7.43 – 7.39 (m, 2H), 7.33 (t, J = 9 Hz, 2H), 7.25 – 7.21 (m, 2H), 2.37 (s, 6H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 145.5, 139.6, 132.0, 129.2, 125.1, 122.1, 21.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{15}OS$ $[M+H]^+$ 231.0838 (231.0834).

The spectroscopic data for **2-1h** match those reported in the literature.[42]

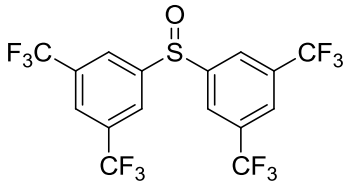
Bis(2-methylphenyl) sulfoxide 2-1i



Prepared from 10 mmol of 1-bromo-2-methylbenzene. White solid (0.61 g, 2.65 mmol, 53%). **^1H NMR** (300 MHz, $CDCl_3$): δ = 7.70 – 7.66 (m, 2H), 7.37 – 7.34 (m, 4H), 7.21 – 7.18 (m, 2H), 2.41 (s, 6H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 141.9, 136.8, 131.2, 131.0, 127.3, 126.2, 18.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{15}OS$ $[M+H]^+$ 231.0838 (231.0834).

The spectroscopic data for **2-1i** match those reported in the literature.[42]

5,5'-Sulfinylbis(1,3-bis(trifluoromethyl)benzene) 2-1k



Prepared from 10 mmol of 1-bromo-3,5-bis(trifluoromethyl)benzene. White solid (1.30 g, 2.75 mmol, 55%). **^1H NMR** (400 MHz, $CDCl_3$): δ = 8.16 (s, 4H), 8.02 (s, 2H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ = 147.8, 133.8 (q, J = 34 Hz), 126.0, 124.7, 122.5 (q, J = 272 Hz). **$^{19}F\{^1H\}$ NMR** (376 MHz, $CDCl_3$): δ = -63.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{16}F_{12}OS$ $[M]^+$ 473.9953 (473.9949).

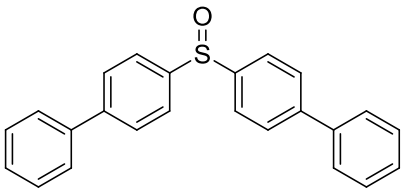
The spectroscopic data for **2-1k** match those reported in the literature.[44]

Synthesis of 2-1l

This compound was prepared as described previously.[41] A Schlenk flask was charged with

biphenyl (3.08 g, 20 mmol) and CH_2Cl_2 (15 mL) under argon. The mixture was cooled to 0 °C and stirred while thionyl chloride (0.37 mL, 5 mmol) and 1.9 mL (21.5 mmol) and triflic acid were added. After 1 h, the resulting mixture was allowed to further stir at room temperature overnight. After the completion of the reaction, ice and saturated aqueous $NaHCO_3$ were added and the resulting biphasic solution was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layer was dried over $MgSO_4$, and filtred through a pad of Celite (Ø 3 mm x 8 mm) followed by rotary evaporation. The product was isolated by flash column chromatography (hexane/ethyl acetate: 10/1).

4,4''-Sulfinyldi-1,1'-biphenyl 2-1l



White solid (1.19 g, 3.35 mmol, 67%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.78 – 7.74 (m, 4H), 7.71 – 7.67 (m, 4H), 7.59 – 7.55 (m, 4H), 7.48 – 7.42 (m, 4H), 7.40 – 7.35 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 144.5, 144.3, 139.9, 129.1, 128.3, 128.25, 127.4, 125.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{23}OS$ $[M+H]^+$ 355.1151 (355.1140).

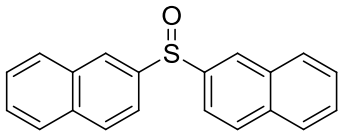
The spectroscopic data for **2-1l** match those reported in the literature.[41]

Synthesis of 2-1m

This compound was prepared as described previously.[45] A Schlenk flask was charged with 2-bromonaphthalene (1.04 g, 5 mmol) and THF (15 mL) under argon. The mixture was cooled to -78 °C and stirred while *n*-BuLi (2.5 M solution in hexane, 2.2 mL, 5.5 mmol) was added dropwise. After 30 min, a solution of thionyl chloride (0.20 mL, 2.75 mmol) in THF (4 mL) was added dropwise. The reaction mixture was stirred at -78 °C for another 2 h. After 2 h, the resulting mixture was allowed to further stir at room temperature for 2 h. After completion of the reaction, *t*-BuOMe (20 mL), ice water (20 mL) and saturated aqueous $NaHCO_3$ were added and the resulting

biphasic solution was extracted with *t*-BuOMe (3 x 20 mL). The combined organic layer was dried over $MgSO_4$, and filtred through a pad of Celite (Ø 3 mm x 8 mm) followed by rotary evaporation. The product was isolated by flash column chromatography (hexane/ethyl acetate: 4/1).

Bis(2-naphthyl) sulfoxide 2-1m



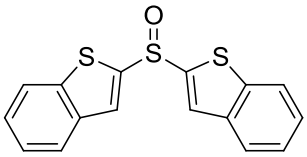
White solid (0.33 g, 1.1 mmol, 44%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.38 – 8.37 (m, 2H), 7.98 – 7.95 (m, 2H), 7.86 – 7.82 (m, 4H), 7.59 – 7.56 (m, 4H), 7.54 – 7.51 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 142.5, 134.5, 132.9, 129.9, 128.8, 128.2, 128.1, 127.4, 125.8, 121.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{20}H_{15}OS$ $[M+H]^+$ 303.0838 (303.0829).

The spectroscopic data for **2-1m** match those reported in the literature.[45]

Synthesis of 2-1n

This compound was prepared as described previously.[46] A Schlenk flask was charged with benzo[*b*]thiophene (1.3 g, 10 mmol) and THF (30 mL) under argon. The mixture was cooled to -78 °C and stirred while *n*-BuLi (2.5 M solution in hexane, 4.0 mL, 10 mmol) was added dropwise. After 30 min, a solution of thionyl chloride (0.40 mL, 5.5 mmol) in THF (5 mL) was added dropwise. After another 30 min at -78 °C, the reaction was warmed to room temperature. The reaction was quenched after 1 h with aqueous sat. NH_4Cl solution (20 mL). The resulting biphasic solution was extracted with *t*-BuOMe (3 x 20 mL). The combined organic layer was dried over $MgSO_4$, and filtred through a pad of Celite (Ø 3 mm x 8 mm) followed by rotary evaporation. The product was isolated by flash column chromatography (hexane/ethyl acetate: 4/1).

Bis(2-benzo[*b*]thienyl) sulfoxide 2-1n



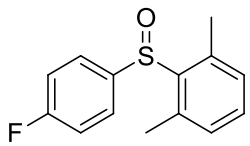
White solid (0.487 g, 1.55 mmol, 31%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.88 – 7.81 (m, 6H), 7.45 – 7.39 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 148.0, 142.2, 138.2, 127.2, 126.8, 125.40, 125.38, 123.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{11}S_3O$ $[M+H]^+$ 314.9967 (314.9960).

The spectroscopic data for **2-1n** match those reported in the literature.[46]

Synthesis of 2-1o-2-1x

These compounds were prepared as described previously.[47] Synthesis of **1o** is representative. A glass tube was charged with K_2CO_3 (0.456 g, 3.3 mmol), CuI (2.5 mol%, 0.0143g), and *N*-methylpyrrolidinone (0.6 mL). The compounds 1-fluoro-4-iodobenzene (3 mmol, 0.67 g) and 2,6-dimethylbenzenethiol (3.6 mmol, 0.50 g) were added, and mixture was stirred at 100 °C for 16 h. After completion, the mixture was passed through a pad of Celite, and the filtrate was concentrated. The crude aryl sulfide was dissolved in DCM (10 mL) in an ice-water bath before *m*-CPBA (contains *ca*. 23 wt%, 3 mmol, 0.67 g) was added in portions. The mixture was allowed to warm to room temperature. After 12 h, saturated aqueous Na_2CO_3 were added and the resulting solution was extracted with EtOAc (3 x 30 mL). The combined organic layer was dried over $MgSO_4$, and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product was isolated by flash column chromatography (hexane/ethyl acetate: 5/1).

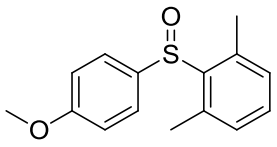
2,6-Dimethylphenyl 4-fluorophenyl sulfoxide 2-1o



White solid (0.66 g, 2.64 mmol, 88%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.43 – 7.40 (m, 2H), 7.27

(t, *J* = 8 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.06 (d, *J* = 8 Hz, 2H), 2.46 (s, 6H). **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ = 163.6 (d, *J* = 249 Hz), 140.0, 139.7 (d, *J* = 4 Hz), 139.5, 132.0, 130.3, 126.8 (d, *J* = 9 Hz), 116.3 (d, *J* = 23 Hz), 19.5. **$^{19}F\{^1H\}$ NMR** (470 MHz, $CDCl_3$): δ = -111.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{14}FOS$ $[M+H]^+$ 249.0744 (249.0738).

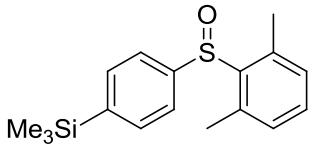
2,6-Dimethylphenyl 4-methoxyphenyl sulfoxide 2-1p



Prepared from 3 mmol of 1-iodo-4-methoxybenzene. White solid (0.67 g, 2.58 mmol, 86%). **^1H NMR** (300 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8 Hz, 2H), 7.25 (t, *J* = 8 Hz, 1H), 7.05 (d, *J* = 8 Hz, 2H), 6.95 (d, *J* = 8 Hz, 2H), 3.82 (s, 3H), 2.47 (s, 6H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 160.9, 140.0, 139.8, 135.1, 131.7, 130.2, 126.3, 114.6, 55.6, 19.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{17}O_2S$ $[M+H]^+$ 261.0944 (261.0933).

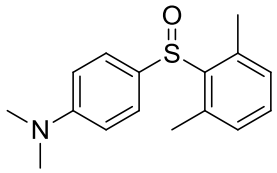
The spectroscopic data for **2-1p** match those reported in the literature.[42]

2,6-Dimethylphenyl 4-(trimethylsilyl)phenyl sulfoxide 2-1q



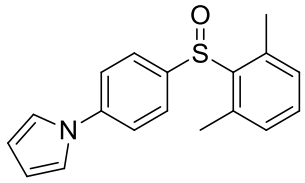
Prepared from 3 mmol of (4-iodophenyl)trimethylsilane. White solid (0.64 g, 2.13 mmol, 71%). **^1H NMR** (300 MHz, $CDCl_3$): δ = 7.59 – 7.55 (m, 2H), 7.42 – 7.38 (m, 2H), 7.26 (t, *J* = 8 Hz, 1H), 7.06 (d, *J* = 8 Hz, 2H), 2.48 (s, 6H), 0.26 (s, 9H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 144.7, 142.9, 140.1, 139.8, 133.9, 131.8, 130.1, 123.8, 19.6, -1.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{23}OSSi$ $[M+H]^+$ 303.1233 (303.1221).

4-((2,6-Dimethylphenyl)sulfinyl)-*N,N*-dimethylaniline 2-1r



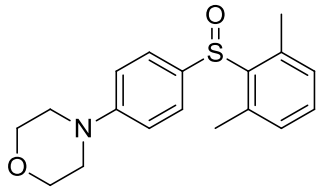
Prepared from 3 mmol of 4-iodo-*N,N*-dimethylaniline. White solid (0.43 g, 1.59 mmol, 53%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.21 – 7.12 (m, 2H), 7.16 (t, *J* = 9 Hz, 1H), 6.93 (d, *J* = 9 Hz, 2H), 6.62 (d, *J* = 9 Hz, 2H), 2.89 (s, 6H), 2.46 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 148.7, 143.5, 132.9, 128.7, 128.67, 128.4, 113.6, 40.8, 22.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{20}NOS$ $[M+H]^+$ 274.1260 (274.1248).

1-(4-((2,6-Dimethylphenyl)sulfinyl)phenyl)-1*H*-pyrrole 2-1s



Prepared from 3 mmol of 1-(4-iodophenyl)-1*H*-pyrrole. White solid (0.66 g, 2.25 mmol, 75%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.50 – 7.47 (m, 2H), 7.47– 7.44 (m, 2H), 7.29 (t, *J* = 8 Hz, 1H), 7.10 (t, *J* = 3 Hz, 2H), 7.08 (d, *J* = 8 Hz, 2H), 6.36 (t, *J* = 3 Hz, 2H), 2.50 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 141.8, 140.8, 140.1, 139.6, 132.0, 130.3, 126.2, 120.5, 119.2, 111.4, 19.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{18}NOS$ $[M+H]^+$ 296.1104 (296.1090).

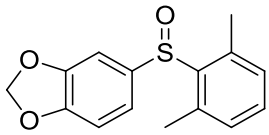
4-(4-((2,6-Dimethylphenyl)sulfinyl)phenyl)morpholine 2-1t



Prepared from 3 mmol of 4-(4-iodophenyl)morpholine. White solid (0.64 g, 2.04 mmol, 68%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8 Hz, 2H), 7.25 (t, *J* = 8 Hz, 1H), 7.04 (d, *J* = 8 Hz, 2H), 6.92 (d, *J* = 8 Hz, 2H), 3.84 (t, *J* = 5 Hz, 4H), 3.19 (t, *J* = 5 Hz, 4H), 2.48 (s, 6H). **^{13}C{^{1}H}**

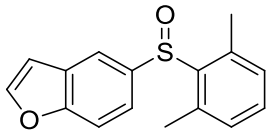
NMR (75 MHz, $CDCl_3$): δ = 152.2, 140.0, 139.8, 131.6, 130.1, 128.6, 126.1, 115.3, 66.8, 48.6, 19.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{22}NO_2S$ $[M+H]^+$ 316.1366 (316.1352).

5-((2,6-Dimethylphenyl)sulfinyl)benzo[*d*][1,3]dioxole 2-1u



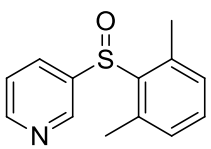
Prepared from 3 mmol of 5-iodobenzo[*d*][1,3]dioxole. White solid (0.62 g, 2.25 mmol, 75%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.26 (t, J = 8 Hz, 1H), 7.06 (s, 1H), 7.06 – 7.04 (m, 1H), 6.97 – 6.94 (m, 1H), 6.87 – 6.82 (m, 2H), 5.99 (s, 2H), 2.48 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 149.2, 148.5, 140.0, 139.6, 137.3, 131.8, 130.2, 119.1, 108.8, 105.2, 101.9, 19.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{15}O_3S$ $[M+H]^+$ 275.0736 (275.0725).

5-((2,6-Dimethylphenyl)sulfinyl)benzofuran 2-1v



Prepared from 3 mmol of 5-iodobenzofuran. White solid (0.50 g, 1.86 mmol, 62%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.69 – 7.68 (m, 1H), 7.53 (d, J = 9 Hz, 1H), 7.27 (t, J = 9 Hz, 1H), 7.26 (d, J = 9 Hz, 1H), 7.07 (d, J = 9 Hz, 2H), 6.80 – 6.79 (m, 1H), 2.49 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 155.6, 146.7, 140.1, 140.0, 138.4, 131.8, 130.2, 128.2, 120.6, 118.3, 112.2, 106.9, 19.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{15}O_2S$ $[M+H]^+$ 271.0787 (271.0781).

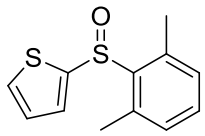
3-((2,6-Dimethylphenyl)sulfinyl)pyridine 2-1w



Prepared from 3 mmol of 3-iodopyridine. White solid (0.37 g, 1.59 mmol, 53%). **^{1}H NMR**

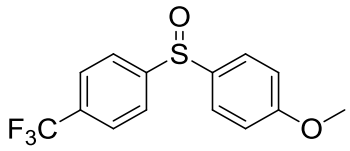
(300 MHz, $CDCl_3$): δ = 8.64 (d, J = 5 Hz, 1H), 8.50 (s, 1H), 7.92 – 7.88 (m, 1H), 7.41 (dd, J = 8, 5 Hz, 1H), 7.29 (t, J = 8 Hz, 1H), 7.08 (d, J = 8 Hz, 2H), 2.47 (s, 6H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 150.7, 146.0, 141.0, 140.0, 138.9, 132.9, 132.4, 130.4, 123.8, 19.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{14}NOS$ $[M+H]^+$ 232.0791 (232.0786).

2-((2,6-Dimethylphenyl)sulfinyl)thiophene 2-1x



Prepared from 3 mmol of 2-iodothiophene. White solid (0.47 g, 1.98 mmol, 66%). **^1H NMR** (300 MHz, $CDCl_3$): δ = 7.54 – 7.51 (m, 1H), 7.31 – 7.28 (m, 2H), 7.10 – 7.07 (m, 3H), 2.55 (s, 6H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 145.9, 139.7, 139.3, 131.8, 130.7, 130.3, 129.5, 128.0, 19.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{13}OS_2$ $[M+H]^+$ 237.0402 (237.0398).

1-Methoxy-4-((4-(trifluoromethyl)phenyl)sulfinyl)benzene 2-1y



Prepared from 3 mmol of 1-iodo-4-(trifluoromethyl)benzene and 3.6 mmol of 4-methoxybenzenethiol. White solid (0.73 g, 2.43 mmol, 81%). **^1H NMR** (500 MHz, $CDCl_3$): δ = 7.74 – 7.69 (m, 4H), 7.59 – 7.56 (m, 2H), 6.98 – 6.95 (m, 2H), 3.82 (s, 3H). **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ = 162.6, 150.4 (q, J = 1 Hz), 136.1, 132.7 (q, J = 33 Hz), 127.6, 126.3 (q, J = 4 Hz), 124.9, 123.6 (q, J = 270 Hz), 115.2, 55.7. **$^{19}F\{^1H\}$ NMR** (470 MHz, $CDCl_3$): δ = -62.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{12}F_3O_2S$ $[M+H]^+$ 301.0505 (301.0492).

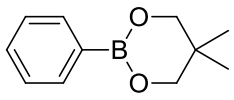
The spectroscopic data for **2-1y** match those reported in the literature.[48]

2.5.3 Details of the Catalytic Borylation of Aryl Sulfoxides

In an argon-filled glovebox, $[Ni(COD)_2]$ (5 mol%), ICy•HBF_4 (10 mol%) and 1,4-dioxane (3 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^tBu

(1.25 mmol, 2.5 equiv.), the boron reagent (1.25 mmol, 2.5 equiv.) and the aryl sulfoxide (0.5 mmol, 1.0 equiv.) were added. The reaction mixture was stirred at 110 °C for 20 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product was isolated by flash column chromatography (hexane/ethyl acetate (95/5)) after careful removal of the solvent *in vacuo*. The reactions were commonly performed on a 500 µmol scale. All aryl boronate products were reported previously and were unambiguously identified by comparison of HRMS and ^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$ and/or $^{19}F\{^{1}H\}$ NMR spectra with literature data. The boron-bonded carbon atom was not detected for all compounds, due to quadrupolar broadening by the ^{11}B nucleus.

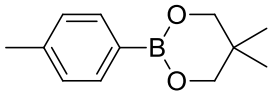
5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane 2-3a



Yield: 77.0 mg (405 µmol, 81%) of a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.81 (d, J = 8 Hz, 2H), 7.43 – 7.41 (m, 1H), 7.38 – 7.32 (m, 2H), 3.78 (s, 4H), 1.03 (s, 6H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$): δ = 134.0, 130.8, 127.7, 72.5, 32.0, 22.1. **$^{11}B\{^{1}H\}$ NMR** (96 MHz, $CDCl_3$): δ = 26.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{15}BO_2$ $[M]^+$ 190.1160 (190.1157).

The spectroscopic data for **2-3a** match those reported in the literature.[49]

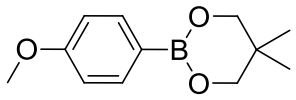
2-(4-Methyl-phenyl)-5,5-dimethyl-[1,3,2]dioxaborinane 2-3b



Yield: 87.8 mg (430 µmol, 86%) of a colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.71 (d, J = 8 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 3.77 (s, 4H), 2.37 (s, 3H), 1.03 (s, 6H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$): δ = 140.8, 134.0, 128.5, 72.4, 32.0, 22.1, 21.8. **$^{11}B\{^{1}H\}$ NMR** (160 MHz, $CDCl_3$): δ = 27.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}BO_2$ $[M]^+$ 204.1316 (204.1315).

The spectroscopic data for **2-3b** match those reported in the literature.[49]

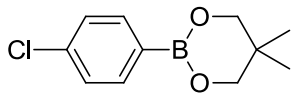
2-(4-Methoxyphenyl)-5,5-dimethyl-[1,3,2]dioxaborinane 2-3c



Yield: 54.0 mg (245 µmol, 49%) of a colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.74 (d, J = 9 Hz, 2H), 6.89 (d, J = 9 Hz, 2H), 3.82 (s, 3H), 3.75 (s, 4H), 1.02 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 161.9, 135.7, 113.3, 72.4, 55.2, 32.1, 22.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 27.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{18}BO_3$ $[M+H]^+$ 221.1344 (221.1336).

The spectroscopic data for **2-3c** match those reported in the literature.[49]

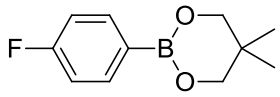
2-(4-Chlorophenyl)-5,5-dimethyl-[1,3,2]dioxaborinane 2-3d



Yield: 63.0 mg (280 µmol, 56%) of a colorless solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.72 (d, J = 8 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 3.76 (s, 4H), 1.02 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 137.0, 135.4, 128.0, 72.5, 32.0, 22.0. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 26.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{15}BClO_2$ $[M+H]^+$ 225.0848 (225.0842).

The spectroscopic data for **2-3d** match those reported in the literature.[50]

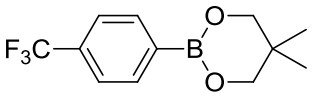
2-(4-Fluorophenyl)-5,5-dimethyl-[1,3,2]dioxaborinane 2-3e



Yield: 81.1 mg (390 µmol, 78%) of a colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.81 – 7.77 (m, 2H), 7.05 – 7.01 (m, 2H), 3.76 (s, 4H), 1.02 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 165.0 (d, J = 248 Hz), 136.1 (d, J = 8 Hz), 114.7 (d, J = 20 Hz), 72.5, 32.0, 22.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 26.6. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -109.9 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{15}BFO_2$ $[M+H]^+$ 209.1144 (209.1137).

The spectroscopic data for **2-3e** match those reported in the literature.[49]

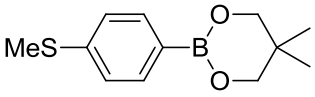
2-(4-Trifluoromethyl-phenyl)-5,5-dimethyl-[1,3,2]dioxaborinane 2-3f



Yield: 94.0 mg (365 µmol, 73%) of a pale yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.90 (d, J = 8 Hz, 2H), 7.60 (d, J = 8 Hz, 2H), 3.79 (s, 4H), 1.03 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 134.2, 132.4 (q, J = 32 Hz), 124.3 (q, J = 4 Hz), 124.4 (q, J = 272 Hz), 72.5, 32.0, 22.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 26.5. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -62.9 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{14}BF_3O_2$ $[M]^+$ 258.1033 (258.1021).

The spectroscopic data for **2-3f** match those reported in the literature.[51]

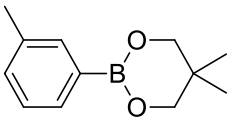
2-(4-(Methylthio)phenyl)-5,5-dimethyl-[1,3,2]dioxaborinane 2-3g



Yield: 79.1 mg (335 µmol, 67%) of a colorless solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.71 (d, J = 8 Hz, 2H), 7.22 (d, J = 8 Hz, 2H), 3.76 (s, 4H), 2.49 (s, 3H), 1.02 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 141.8, 134.4, 125.2, 72.4, 32.0, 22.1, 15.3. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 26.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{18}BOS$ $[M+H]^+$ 237.1115 (237.1106).

The spectroscopic data for **2-3g** match those reported in the literature.[52]

2-(3-Methyl-phenyl)-5,5-dimethyl-[1,3,2]dioxaborinane 2-3h

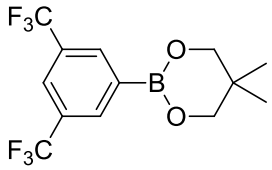


Yield: 78.6 mg (385 µmol, 77%) of a colorless solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.65 – 7.61 (m, 2H), 7.31 – 7.26 (m, 2H), 3.79 (s, 4H), 2.37 (s, 3H), 1.04 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 137.1, 134.6, 131.6, 131.0, 127.7, 72.5, 32.0, 22.0, 21.5. **^{11}B{^{1}H} NMR** (96 MHz,

$CDCl_3$): δ = 26.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{18}BOS$ $[M+H]^+$ 205.1394 (205.1389).

The spectroscopic data for **2-3h** match those reported in the literature.[49]

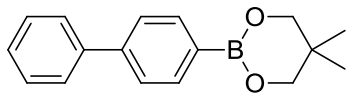
2-(3,5-Bis(trifluoromethyl)phenyl)-5,5-dimethyl-1,3,2-dioxaborinane 2-3k



Yield: 110.8 mg (340 µmol, 68%) of a pale yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.23 (s, 2H), 7.91 (s, 1H), 3.81 (s, 4H), 1.04 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 134.0 (m), 130.8 (q, J = 34 Hz), 124.3 (q, J = 5 Hz), 123.8 (q, J = 271 Hz), 72.6, 32.1, 22.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 26.1. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -62.8 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{14}BF_6O_2$ $[M]^+$ 327.0986 (327.0975).

The spectroscopic data for **2-3k** match those reported in the literature.[53]

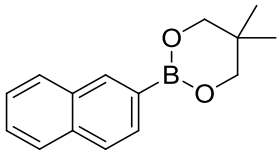
2-(Biphenyl-4-yl)-5,5-dimethyl-[1,3,2]dioxaborinane 2-3l



Yield: 103.8 mg (390 µmol, 78%) of a colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.91 – 7.89 (m, 2H), 7.65 – 7.61 (m, 4H), 7.47 – 7.44 (m, 2H), 7.38 – 7.35 (m, 1H), 3.81 (s, 4H), 1.04 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 143.4, 141.3, 134.5, 128.9, 127.5, 127.3, 126.5, 72.5, 32.0, 22.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 27.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{20}BO_2$ $[M+H]^+$ 267.1551 (267.1541).

The spectroscopic data for **2-3l** match those reported in the literature.[52]

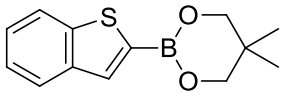
2-(Naphthalen-2-yl)-5,5-dimethyl-[1,3,2]dioxaborinane 2-3m



Yield: 85.0 mg (355 µmol, 71%) of a colorless solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.35 (s, 1H), 7.90 – 7.80 (m, 4H), 7.50 – 7.43 (m, 2H), 3.84 (s, 4H), 1.06 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 135.2, 135.0, 133.1, 130.1, 128.8, 127.8, 126.9, 126.8, 125.7, 72.6, 32.1, 22.1. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 27.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{18}BO_2$ $[M+H]^+$ 241.1394 (241.1386).

The spectroscopic data for **2-3m** match those reported in the literature.[52]

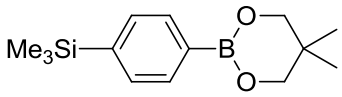
2-(Benzo[*b*]thiophen-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane 2-3n



Yield: 93.5 mg (380 µmol, 76%) of a colorless solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.91 – 7.88 (m, 1H), 7.86 – 7.81 (m, 2H) 7.36 – 7.33 (m, 2H), 3.81 (s, 4H), 1.06 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 143.5, 140.8, 133.0, 125.1, 124.4, 124.1, 122.7, 72.7, 32.2, 22.1. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 25.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{16}BO_2S$ $[M+H]^+$ 247.0959 (247.0953).

The spectroscopic data for **2-3n** match those reported in the literature.[54]

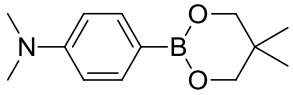
(4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)trimethylsilane 2-3q



Yield: 111.4 mg (425 µmol, 85%) of a colorless solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.78 (d, J = 8 Hz, 2H), 7.53 (d, J = 8 Hz, 2H), 3.77 (s, 4H), 1.02 (s, 6H), 0.27 (s, 9H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 143.5, 133.1, 132.7, 72.4, 32.0, 22.0, -1.1. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 26.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{24}BO_2Si$ $[M+H]^+$ 263.1633 (263.1627).

The spectroscopic data for **2-3q** match those reported in the literature.[55]

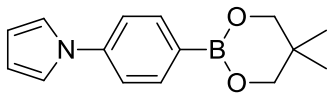
4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-*N*,*N*-dimethylaniline 2-3r



Yield: 78.1 mg (335 µmol, 67%) of a colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.69 (d, J = 9 Hz, 2H), 6.71 (d, J = 9 Hz, 2H), 3.75 (s, 4H), 2.99 (s, 6H), 1.02 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 152.4, 135.3, 111.5, 72.4, 40.4, 32.1, 22.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 27.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{21}BNO_2$ $[M+H]^+$ 234.1660 (234.1656).

The spectroscopic data for **2-3r** match those reported in the literature.[56]

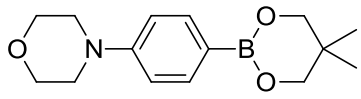
1-(4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)-1*H*-pyrrole 2-3s



Yield: 99.5 mg (390 µmol, 78%) of a colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.86 (d, J = 9 Hz, 2H), 7.39 (d, J = 9 Hz, 2H), 7.14 (t, J = 3 Hz, 2H), 6.35 (t, J = 3 Hz, 2H), 3.79 (s, 4H), 1.04 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 142.6, 135.4, 119.4, 119.3, 110.7, 72.5, 32.1, 22.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 26.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{19}BNO_2$ $[M+H]^+$ 256.1503 (256.1494).

The spectroscopic data for **2-3s** match those reported in the literature.[56]

4-(4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)morpholine 2-3t

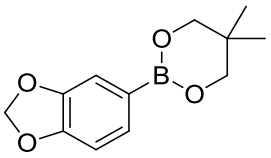


Yield: 100.4 mg (365 µmol, 73%) of a colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.72 (d, J = 9 Hz, 2H), 6.89 (d, J = 9 Hz, 2H), 3.86 (t, J = 5 Hz, 4H), 3.75 (s, 4H), 3.22 (t, J = 5 Hz, 4H), 1.01 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 153.1, 135.3, 114.3, 72.4, 67.0, 48.7, 32.0,

22.1. **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$): δ = 26.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{23}BNO_3$ $[M+H]^+$ 276.1766 (276.1756).

The spectroscopic data for **2-3t** match those reported in the literature.[57]

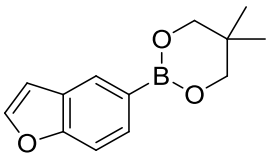
2-(Benzo[*d*][1,3]dioxol-5-yl)-5,5-dimethyl-1,3,2-dioxaborinane 2-3u



Yield: 74.9 mg (320 µmol, 64%) of a colorless solid. **^1H NMR** (300 MHz, $CDCl_3$): δ = 7.35 (d, J = 8 Hz, 1H), 7.24 (s, 1H), 6.82 (d, J = 8 Hz, 1H), 5.94 (s, 2H), 3.74 (s, 4H), 1.01 (s, 6H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 149.8, 147.3, 128.7, 113.4, 108.2, 100.8, 72.4, 32.0, 22.0. **$^{11}B\{^1H\}$ NMR** (96 MHz, $CDCl_3$): δ = 26.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{16}BO_4$ $[M+H]^+$ 235.1136 (235.1127).

The spectroscopic data for **2-3u** match those reported in the literature.[52]

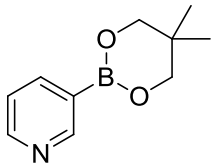
2-(Benzofuran-5-yl)-5,5-dimethyl-1,3,2-dioxaborinane 2-3v



Yield: 75.9 mg (330 µmol, 66%) of a colorless solid. **^1H NMR** (300 MHz, $CDCl_3$): δ = 8.10 (s, 1H), 7.77 (dd, J = 8, 1 Hz, 1H), 7.60 (d, J = 2 Hz, 1H), 7.49 (d, J = 8 Hz, 1H), 6.77 (dd, J = 2, 1 Hz, 1H), 3.80 (s, 4H), 1.04 (s, 6H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 157.0, 144.8, 130.1, 127.7, 127.2, 110.8, 106.9, 72.5, 32.1, 22.1. **$^{11}B\{^1H\}$ NMR** (96 MHz, $CDCl_3$): δ = 26.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{16}BO_3$ $[M+H]^+$ 231.1187 (231.1179).

The spectroscopic data for **2-3v** match those reported in the literature.[56]

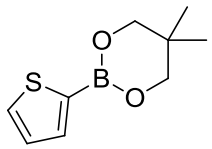
3-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)pyridine 2-3w



Yield: 41.1 mg (215 µmol, 43%) of a colorless solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.94 (s, 1H), 8.64 (d, J = 8 Hz, 1H), 8.04 (d, J = 8 Hz, 1H), 7.28 – 7.24 (m, 1H), 3.77 (s, 4H), 1.03 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 154.9, 151.4, 141.7, 123.2, 72.5, 32.1, 22.0. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 26.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{14}BNO_2$ $[M+H]^+$ 192.1190 (192.1185).

The spectroscopic data for **2-3w** match those reported in the literature.[52]

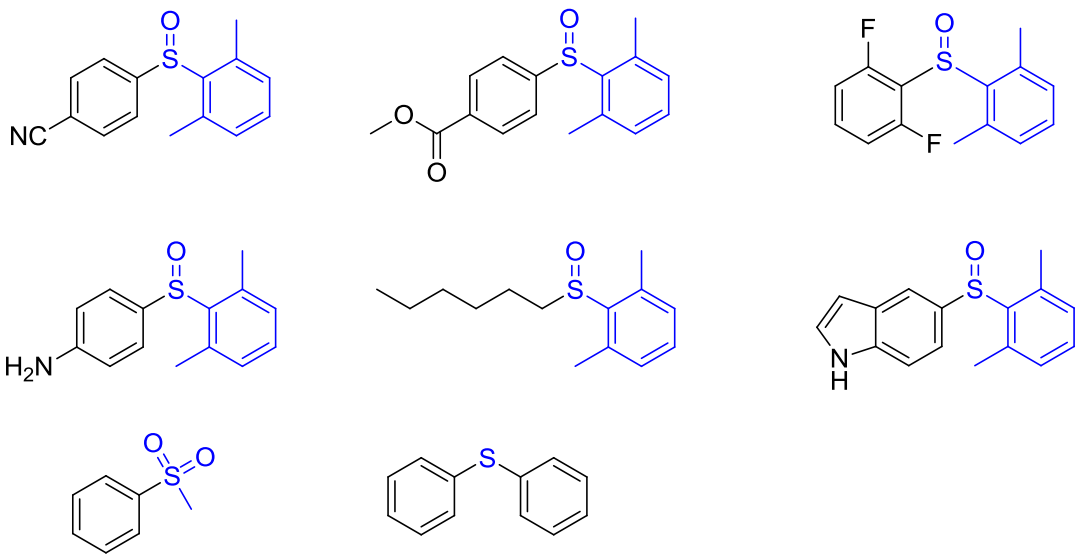
5,5-Dimethyl-2-(thiophen-2-yl)-1,3,2-dioxaborinane 2-3x



Yield: 69.2 mg (355 µmol, 71%) of a colorless solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.60 – 7.57 (m, 2H), 7.17 (dd, J = 5, 4 Hz, 1H), 3.77 (s, 4H), 1.03 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 135.8, 131.5, 128.2, 72.5, 32.2, 22.1. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 25.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{14}BO_2S$ $[M+H]^+$ 197.0802 (197.0796).

The spectroscopic data for **2-3x** match those reported in the literature.[52]

2.5.4 Unsuccessful Substrates



2.5.5 Synthesis and Characterization of *trans*-[Ni(ICy)$_2$(Ar^1){(SO)Ar^2}]

***trans*-[Ni(ICy)$_2$(4-CF$_3$-C$_6$H$_4$){(SO)-4-MeO-C$_6$H$_4$}] (2-4)**: In an argon-filled glovebox, 1-methoxy-4-((4-(trifluoromethyl)phenyl)sulfinyl)benzene **2-1y** (0.5 mmol, 1.0 equiv., 150 mg), [Ni(COD)$_2$] (0.5 mmol, 1.0 equiv., 138 mg), ICy•HBF$_4$ (1 mmol, 2.0 equiv., 320 mg), NaO^{t}Bu (1 mmol, 2.0 equiv., 96 mg) and THF (10 mL) were added to a 50 mL round-bottom flask equipped with a magnetic stirring bar. The reaction mixture was stirred overnight at room temperature. All volatiles were removed *in vacuo* and the resulting yellow residue was suspended in 25 mL of hexane. The product was collected by filtration and dried *in vacuo* to give **2-4** (354 mg, 86%) as a yellow powder. **Elemental analysis** for [C$_{44}$H$_{59}$F$_3$N$_4$NiO$_2$S] [823.72 g/mol]: Calc. (found) C 64.16 (63.88), H 7.22 (7.38), N 6.80 (6.83), S 3.89 (4.16). **^{1}H NMR** (400 MHz, 25 °C, C$_6$D$_6$): δ = 7.52 (d, J = 8 Hz, 2H), 7.01 (dd, J = 12 Hz, 8 Hz, 4H), 6.76 (d, J = 8 Hz, 2H), 6.35 (s, 4H), 5.98 (t, J = 12 Hz, 4H), 3.33 (s, 3H), 2.60 (d, J = 12 Hz, 4H), 1.82-1.56 (m, 24H), 1.35-1.18 (m, 8H), 1.09-1.00 (m, 4H). **^{13}C{^{1}H} NMR** (100 MHz, 25 °C, C$_6$D$_6$): δ = 182.3, 147.4, 138.7, 134.1, 121.0, 116.9, 116.6, 114.2, 113.2, 59.9, 55.0, 34.7, 34.3, 26.6, 26.4, 25.8. **^{19}F{^{1}H} NMR** (376 MHz, C$_6$D$_6$): δ = -61.2. **HRMS-LIFDI** (m/z): Calculated (found) for C$_{37}$H$_{52}$F$_3$N$_4$Ni [*M*-(SO)4-OMePh]$^+$ 667.3492 (667.3488). **IR (ATR)**: 624 (w), 699 (s), 810 (s), 897 (w), 1008

(m),1037 (vw), 1061 (s) 1111 (s), 1152 (m), 1194 (w), 1235 (s), 1318 (s), 1420 (m), 1441 (w), 1478 (m), 1577 (vw), 2852 (vw), 2930 (w).

***trans*-[Ni(ICy)$_2$(C$_6$H$_5$){(SO)-C$_6$H$_5$}] (2-5)**: In an argon-filled glovebox, diphenyl sulfoxide **2-1a** (0.5 mmol, 1.0 equiv., 101 mg), [Ni(COD)$_2$] (0.5 mmol, 1.0 equiv., 138 mg), ICy•HBF$_4$ (1.0 mmol, 2.0 equiv., 320 mg), NaO^{t}Bu (1.0 mmol, 2.0 equiv., 96 mg) and THF (10 mL) were added to a 50 mL round-bottom flask equipped with a magnetic stirring bar. The reaction mixture was stirred overnight at room temperature. All volatiles were removed *in vacuo* and the resulting yellow residue was suspended in 25 mL of hexane. The product was collected by filtration and dried *in vacuo* to give **2-5** (282 mg, 78%) as a yellow powder. **Elemental analysis** for [C$_{42}$H$_{58}$N$_4$NiOS] [725.69 g/mol]: Calc. (found) C 69.51 (69.36), H 8.06 (8.27), N 7.72 (7.73), S 4.42 (4.26). **^{1}H NMR** (400 MHz, 25 °C, C$_6$D$_6$): δ = 7.43 (d, J = 7 Hz, 2H), 7.16-7.10 (m, 4H), 6.84 (t, J = 7 Hz, 2H), 6.75-6.72 (m, 2H), 6.39 (s, 4H), 6.11 (t, J = 11 Hz, 4H), 2.64 (d, J = 11 Hz, 4H), 1.94-1.66 (m, 24H), 1.35-1.05 (m, 12H). **^{13}C{^{1}H} NMR** (100 MHz, 25 °C, C$_6$D$_6$): δ = 183.8, 157.2, 139.2, 125.4, 120.8, 119.9, 118.5, 116.3, 59.7, 34.8, 34.2, 26.6, 26.5, 25.9. **HRMS-LIFDI** (m/z): Calculated (found) for C$_{42}$H$_{57}$N$_4$NiSO [M]$^+$ 723.3601 (723.3594). **IR (ATR)**: 509 (w), 566 (vw), 692 (m), 703 (s), 733 (s), 821 (m), 836 (m), 896 (w), 986 (vw), 1018 (w), 1083 (vw), 1196 (w), 1235 (m), 1266 (vw), 1383 (vw), 1424 (m), 1446 (w), 1464 (m), 1560 (w), 1577 (m), 2852 (w), 2923 (m).

***trans*-[Ni(ICy)$_2$(4-CH$_3$-C$_6$H$_4$){(SO)-4-CH$_3$-C$_6$H$_4$}] (2-6)**: In an argon-filled glovebox, bis(4-methylphenyl) sulfoxide **2-1b** (0.5 mmol, 1.0 equiv., 115 mg), [Ni(COD)$_2$] (0.5 mmol, 1.0 equiv., 138 mg), ICy•HBF$_4$ (1.0 mmol, 2.0 equiv., 320 mg), NaO^{t}Bu (1.0 mmol, 2.0 equiv., 96 mg) and THF (10 mL) were added to a 50 mL round-bottom flask equipped with a magnetic stirring bar. The reaction mixture was stirred overnight at room temperature. All volatiles were removed *in vacuo* and the resulting yellow residue was suspended in 25 mL of hexane. The product was collected by filtration and dried *in vacuo* to give **2-6** (275 mg, 73%) as a yellow powder. **Elemental analysis** for [C$_{44}$H$_{62}$N$_4$NiOS] [753.75 g/mol]: Calc. (found) C 70.11 (70.00), H 8.29 (8.42), N 7.43 (7.39), S 4.25 (4.52). **^{1}H NMR** (400 MHz, 25 °C, C$_6$D$_6$): δ = 7.35 (d, J = 8 Hz, 2H),

7.07 (d, *J* = 8 Hz, 2H), 6.93 (d, *J* = 8 Hz, 2H), 6.69 (d, *J* = 8 Hz, 2H), 6.39 (s, 4H), 6.15 (t, *J* = 12 Hz, 4H), 2.67 (d, *J* = 12 Hz, 4H), 2.14 (s, 3H), 2.07 (s, 3H), 1.99 (d, *J* = 12 Hz, 4H), 1.81-1.68 (m, 20H), 1.36-1.25 (m, 8H), 1.36-1.25 (m, 8H), 1.13-1.05 (m, 4H). **^{13}C{^{1}H} NMR** (100 MHz, 25 °C, C_6D_6): δ = 184.1, 153.8, 138.6, 129.1, 128.6, 126.5, 119.1, 116.3, 59.7, 34.8, 34.3, 26.63, 26.56, 26.0, 21.0, 20.9. **HRMS-LIFDI** (m/z): Calculated (found) for $C_{37}H_{55}N_4Ni$ [*M*-(SO)4-MePh]$^+$ 613.3775 (613.3768). **IR (ATR)**: 475 (m), 501 (m), 562 (vw), 624 (w), 702 (s), 727 (vw), 756 (vw), 793 (s), 826 (s), 897 (m), 995 (vw), 1037 (vw), 1078 (m), 1144 (vw), 1193 (m), 1235 (m), 1264 (vw), 1292 (vw), 1383 (w), 1424 (m), 1445 (m), 1482 (m), 1548 (vw), 1594 (vw), 2852 (m), 2926 (m).

***trans*-[Ni(ICy)$_2$(4-F-C$_6$H$_4$){(SO)-4-F-C$_6$H$_4$}] (2-7)**: In an argon-filled glovebox, bis(4-fluorophenyl) sulfoxide **2-1e** (0.5 mmol, 1.0 equiv., 119 mg), [Ni(COD)$_2$] (0.5 mmol, 1.0 equiv., 138 mg), ICy•HBF$_4$ (1 mmol, 2.0 equiv., 320 mg), NaO^{t}Bu (1 mmol, 2.0 equiv., 96 mg) and THF (10 mL) were added to a 50 mL round-bottom flask equipped with a magnetic stirring bar. The reaction mixture was stirred overnight at room temperature. All volatiles were removed *in vacuo* and the resulting yellow residue was suspended in 25 mL of hexane. The product was collected by filtration and dried *in vacuo* to give **7** (239 mg, 63%) as a yellow powder. **Elemental analysis** for [$C_{42}H_{56}F_2N_4NiOS$] [761.68 g/mol]: Calc. (found) C 66.23 (66.51), H 7.41 (7.67), N 7.36 (7.49), S 4.21 (4.17). **^{1}H NMR** (400 MHz, 25 °C, C_6D_6): δ = 7.20 (t, *J* = 9 Hz, 2H), 6.92-6.88 (m, 2H), 6.80 (t, *J* = 9 Hz, 2H), 6.63 (t, *J* = 9 Hz, 2H), 6.36 (s, 4H), 5.99 (t, *J* = 12 Hz, 4H), 2.56 (d, *J* = 12 Hz, 4H), 1.86-1.55 (m, 24H), 1.35-1.20 (m, 8H), 1.09-0.99 (m, 4H). **^{13}C{^{1}H} NMR** (100 MHz, 25 °C, C_6D_6): δ = 183.1, 161.2, 159.3, 151.8, 138.8 (d, *J* = 5 Hz), 116.5, 114.7 (d, *J* = 21 Hz), 112.3 (d, *J* = 18 Hz), 59.8, 34.8, 34.2, 26.54, 26.47, 25.8. **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ = -125.0, -125.4. **HRMS-LIFDI** (m/z): Calculated (found) for $C_{36}H_{52}FN_4Ni$ [M-(SO)-4-FPh]$^+$ 617.3524 (617.3518). **IR (ATR)**: 414 (w), 488 (m), 509 (w), 567 (w), 620 (m), 702 (s), 733 (s), 723 (vw), 756 (vw), 810 (s), 892 (m), 983 (vw), 1000 (vw), 1025 (vw), 1082 (w), 1144 (w), 1201 (s), 1235 (m), 1379 (vw), 1424 (m), 1445 (w), 1474 (s), 1565 (vw), 2852 (m), 2926 (m).

2.5.6 Investigations Concerning the Reaction Mechanism

a) $B_2(neop)_2$ Itself is Stable Under These Conditions (1 h at 110 °C in C_6D_6, see Figure 2-S1).

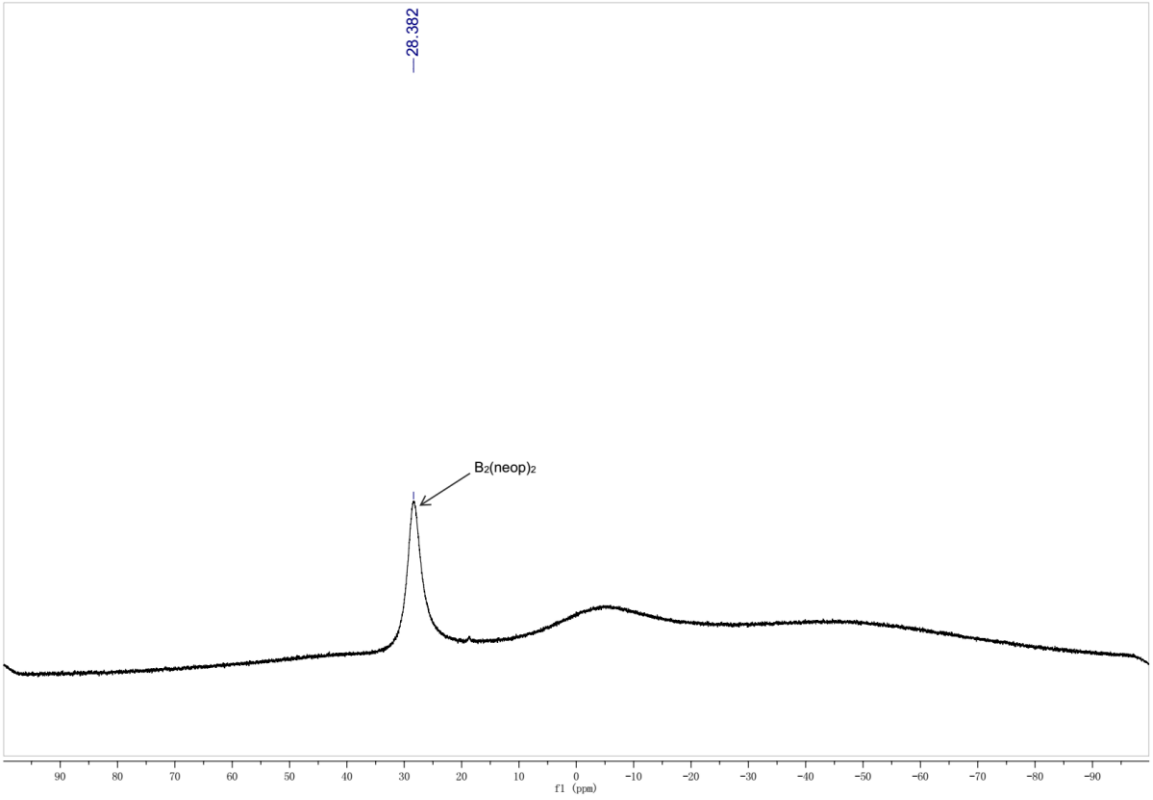
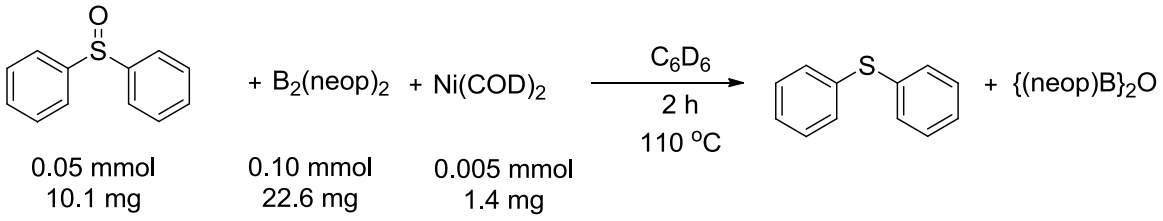


Figure 2-S1. ^{11}B NMR spectrum after heating the starting material $B_2(neop)_2$ to 110 °C for 1 h without forming any decomposition product.

b) Reduction of Sulfoxide to Sulfide

In a Young's tap NMR tube, diphenyl sulfoxide (0.05 mmol, 10.1 mg), $B_2(neop)_2$ (0.10 mmol, 22.6 mg) and $[Ni(COD)_2]$ (1.4 mg, 0.005 mmol) were added to C_6D_6 (0.7 mL). After measurement of $^{11}B\{^1H\}$ NMR at room temperature, the resulting solution was heated at 110 °C for 2 h, and $^{11}B\{^1H\}$ NMR of the mixture was measured again.

The signal corresponding to $B_2(neop)_2$ (δ = 28.3) was observed before heating.



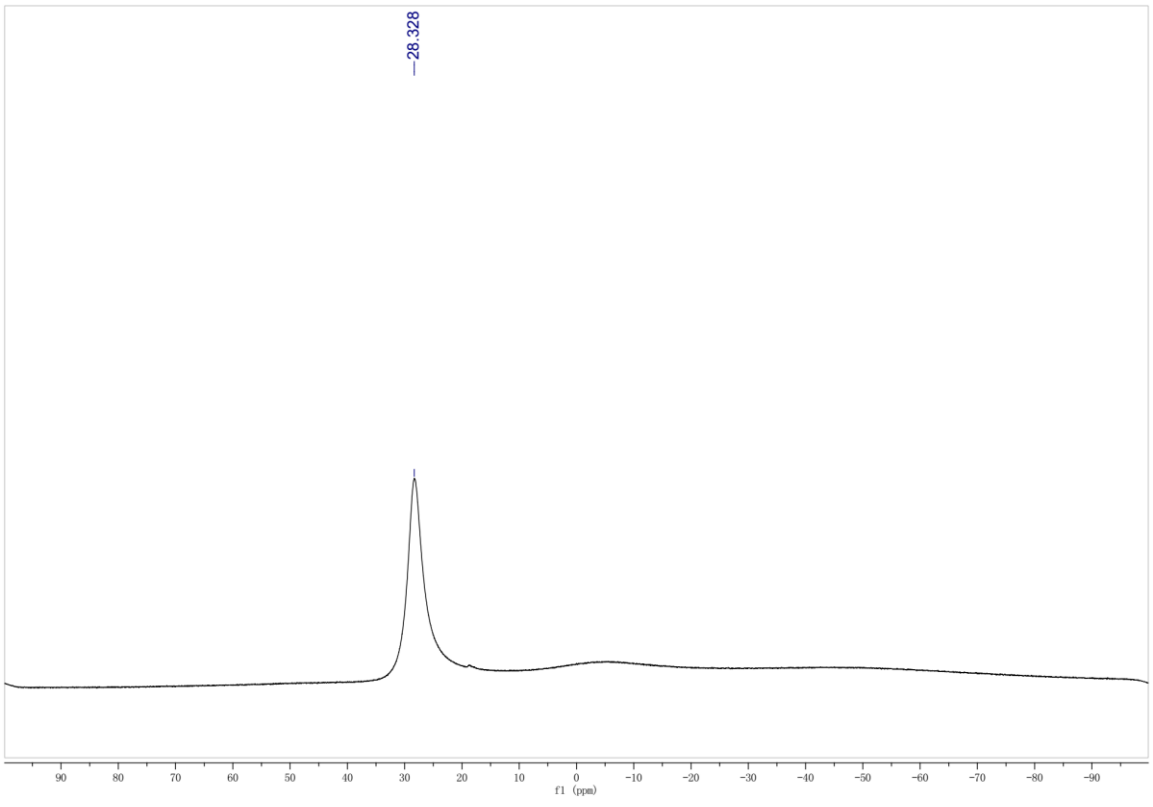


Figure 2-S2. ^{11}B NMR spectrum of diphenyl sulfoxide, $B_2(neop)_2$ and $[Ni(COD)_2]$ in C_6D_6 at room temperature.

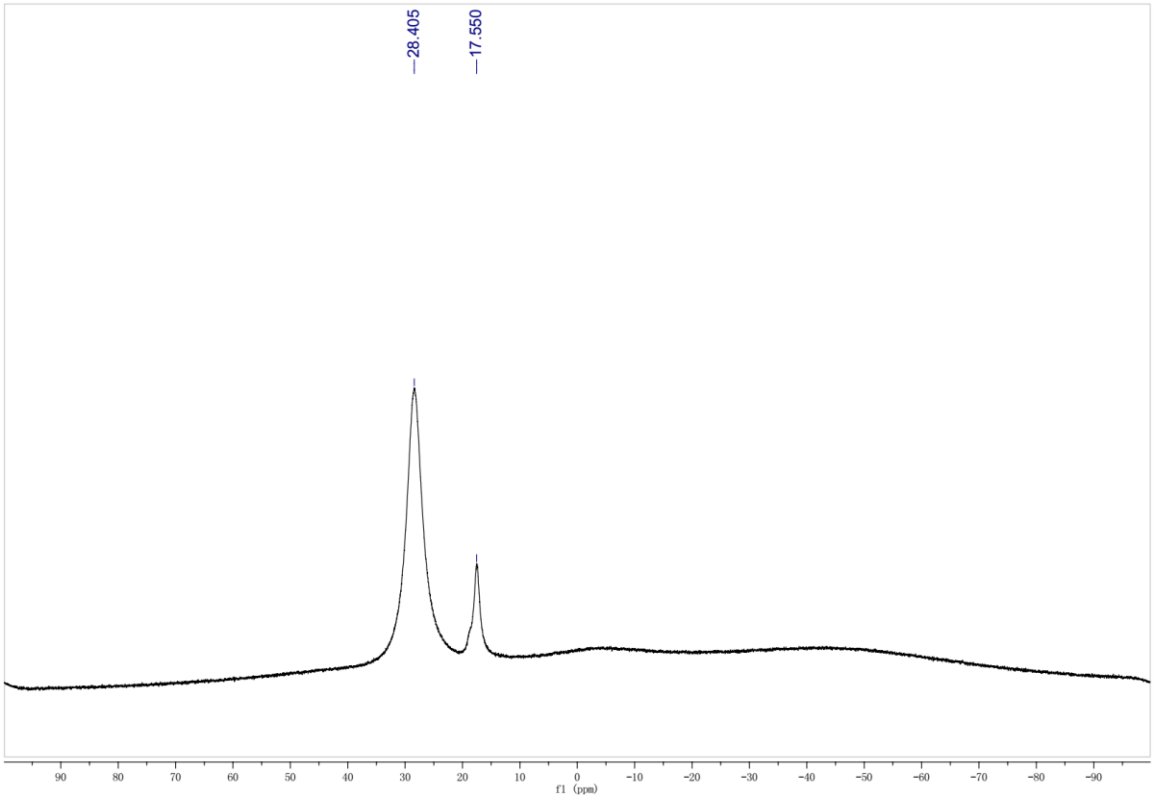
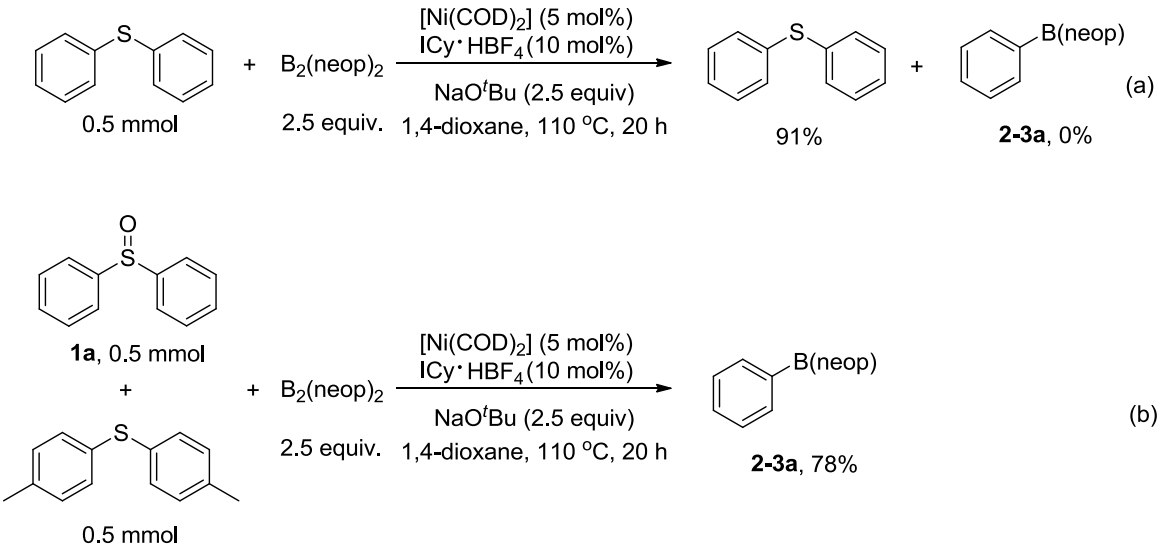


Figure 2-S3. ^{11}B NMR spectrum of diphenyl sulfoxide, $B_2(neop)_2$ and $[Ni(COD)_2]$ in C_6D_6 at 110 °C for 2 h. After heating, a new sharp signal attributed to $\{(neop)B\}_2O$ ($\delta = 17.6$) emerged.

c) Reactivity Tests Involving Diaryl Sulfides



In an argon-filled glovebox, [Ni(COD)$_2$] (5 mol%), ICy•HBF$_4$ (10 mol%) and 1,4-dioxane (3 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (1.25 mmol, 2.5 equiv.), B$_2$(neop)$_2$ (1.25 mmol, 2.5 equiv.) and [(a): diphenylsulfide (0.5 mmol); (b): di-*p*-tolylsulfide (0.5 mmol), **2-1a** (0.5 mmol)] were added. The reaction mixture was stirred at 110 °C for 20 h, then diluted with Et$_2$O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product was isolated by flash column chromatography (hexane/ethyl acetate (95/5)) after careful removal of the solvent *in vacuo*.

d) Reactivity Tests of *trans*-[Ni(ICy)$_2$(4-CF$_3$-C$_6$H$_4$){(SO)-4-MeO-C$_6$H$_4$}] 2-4 with B$_2$(neop)$_2$.

We studied the reactivity of [Ni^{II}] with stoichiometric amounts of B$_2$(neop)$_2$. In a Young's tap NMR tube *trans*-[Ni(ICy)$_2$(4-CF$_3$-C$_6$H$_4$){(SO)-4-MeO-C$_6$H$_4$}] **2-4** (24.7 mg, 30.0 µmol, 1.0 equiv.) and B$_2$(neop)$_2$ (6.8 mg, 30 µmol, 1.0 equiv.) were dissolved in C$_6$D$_6$ (0.7 mL). Investigating the reaction mixture by NMR spectroscopy after 1 h at room temperature did not show any borylated product. Heating the reaction mixture to 110 °C for 1 h revealed small amounts of **2-3e** in the ^{19}F and ^{11}B NMR spectra.

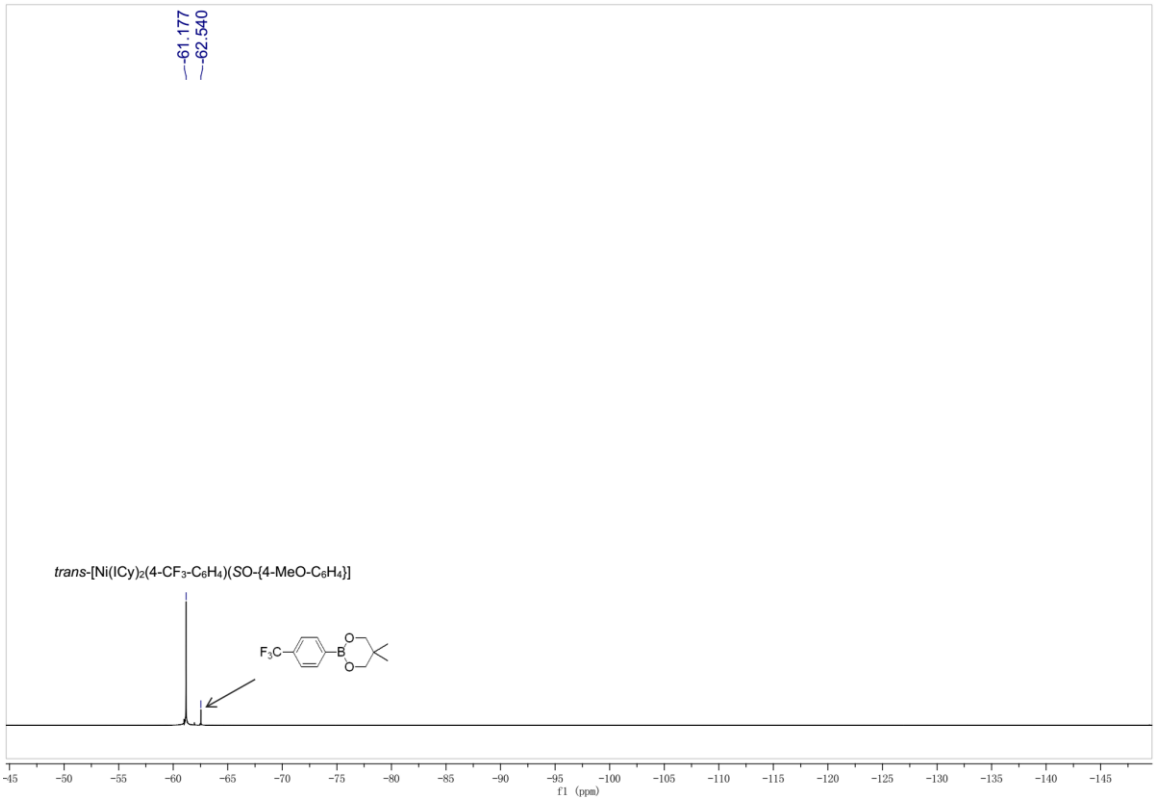


Figure 2-S4. ^{19}F NMR spectrum (recorded in C$_6$D$_6$; 470 MHz) of the reaction mixture of *trans*-[Ni(ICy)$_2$(4-CF$_3$-C$_6$H$_4$){(SO)-4-MeO-C$_6$H$_4$}] **2-4** and B$_2$(neop)$_2$ (110 °C, 1h).

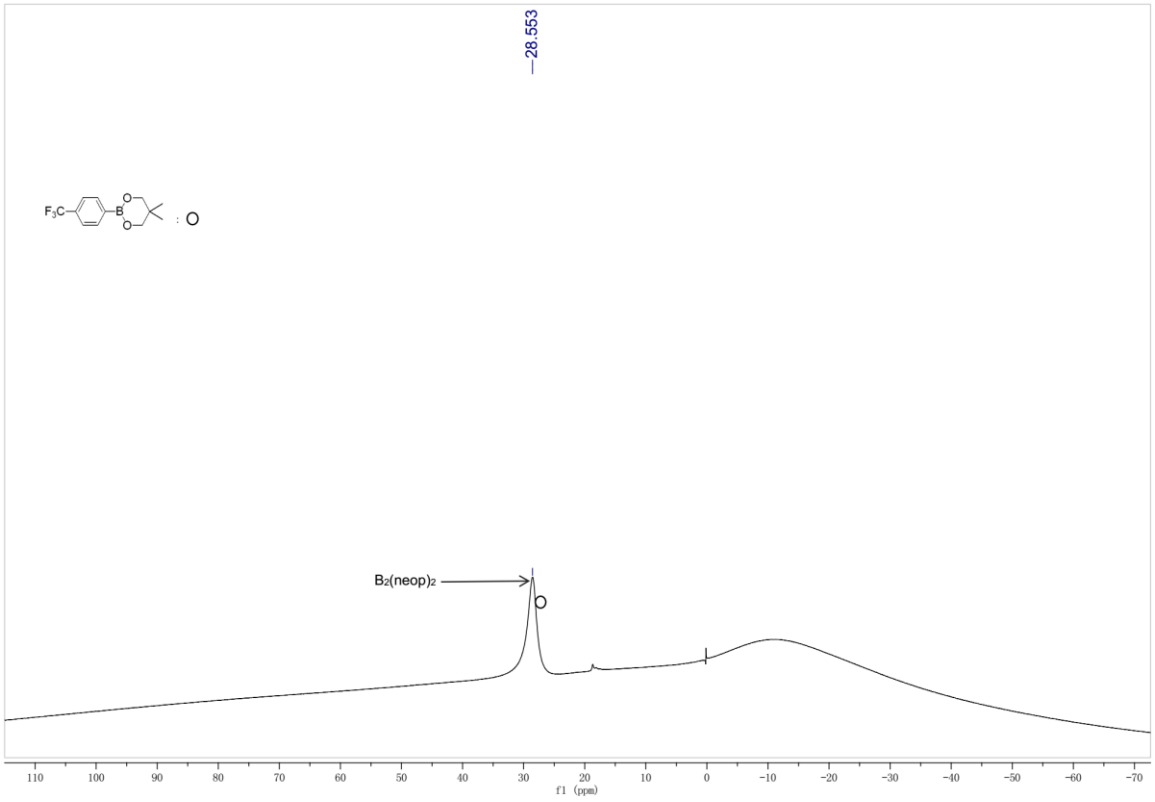
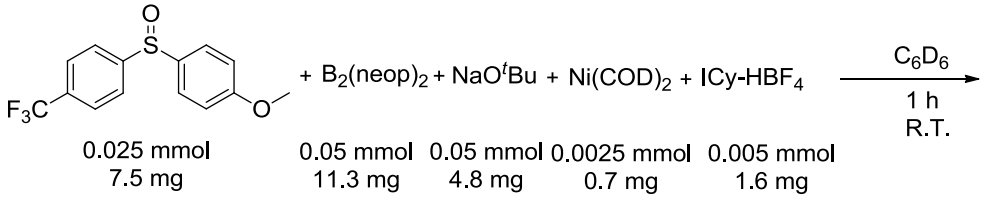
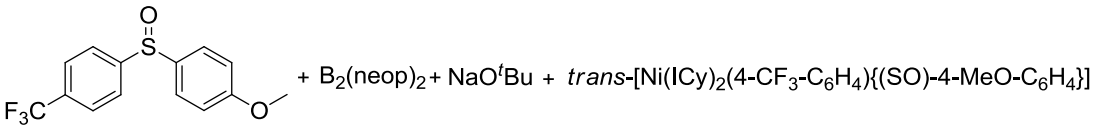


Figure 2-S5. ^{11}B NMR spectrum (recorded in C_6D_6; 160 MHz) of the reaction mixture of *trans*-[Ni(ICy)$_2$(4-CF$_3$-C$_6$H$_4$){(SO)-4-MeO-C$_6$H$_4$}] **2-4** and $B_2(neop)_2$ (110 °C, 1h).

e) Catalytic Test Reaction Using [Ni(COD)$_2$]

A mixture of 1-methoxy-4-((4-(trifluoromethyl)phenyl)sulfinyl)benzene **2-1y** (0.025 mmol, 7.5 mg), $B_2(neop)_2$ (0.05 mmol, 11.3 mg, 2 eq.), NaO^{t}Bu (0.05 mmol, 4.8 mg, 2.0 eq.), [Ni(COD)$_2$] (0.0025 mmol, 0.7 mg, 10 mol%) and ICy•HBF$_4$ (0.005 mmol, 1.6 mg, 20 mol%) was suspended in 0.7 mL C_6D_6 in a Young's tap NMR tube. Then the mixture was studied by NMR spectroscopy after 1 h at room temperature, which revealed only the formation of *trans*-[Ni(ICy)$_2$(4-CF$_3$-C$_6$H$_4$){(SO)-4-MeO-C$_6$H$_4$}] **2-4**; however, Heating the reaction mixture to 110 °C for 2 h, it showed significant borylation product and the presence of **2-4**.





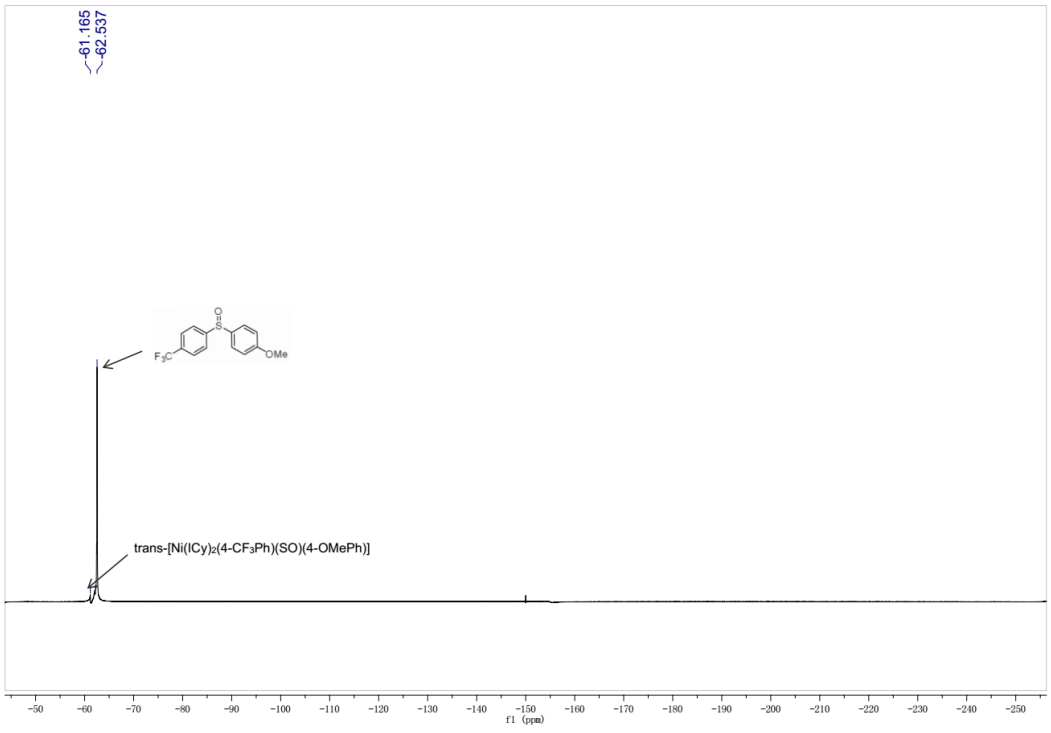


Figure 2-S6. ^{19}F NMR spectrum (recorded in C_6D_6; 470 MHz) after 1 h at room temperature.

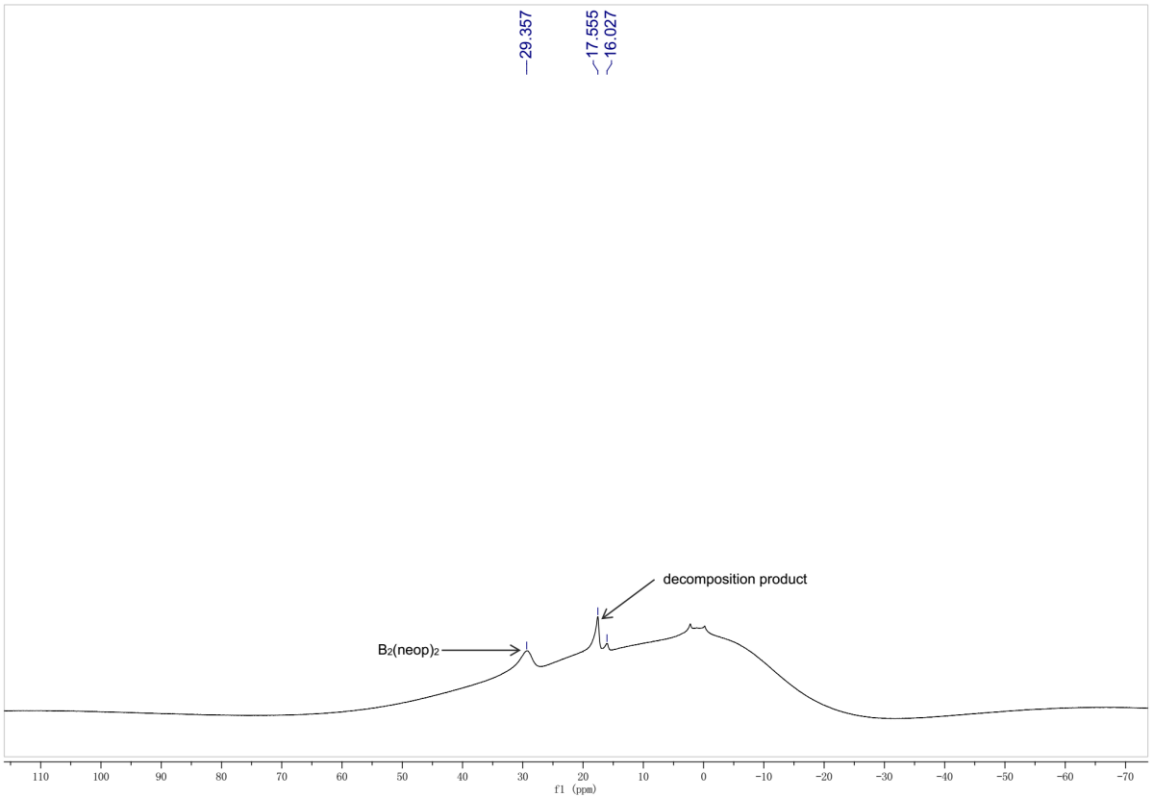
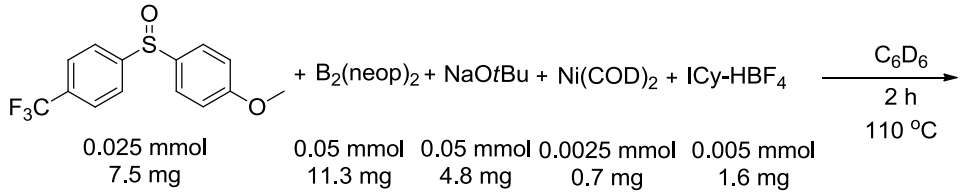
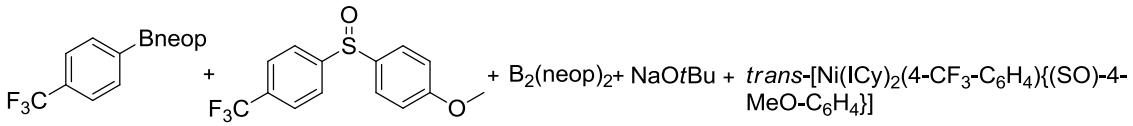


Figure 2-S7. ^{11}B NMR spectrum (recorded in C_6D_6; 160 MHz) after 1 h at room temperature.





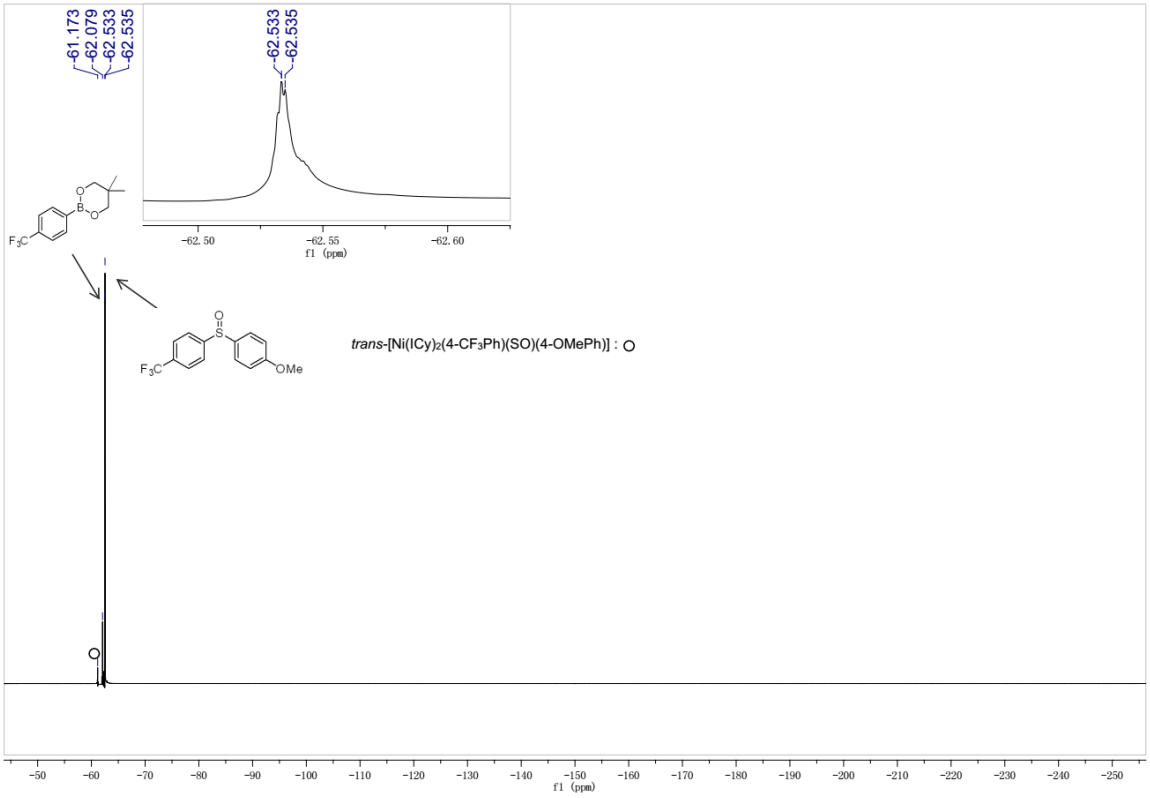


Figure 2-S8. ^{19}F NMR spectrum (recorded in C_6D_6; 470 MHz) at 110 ^{o}C for 2 h.

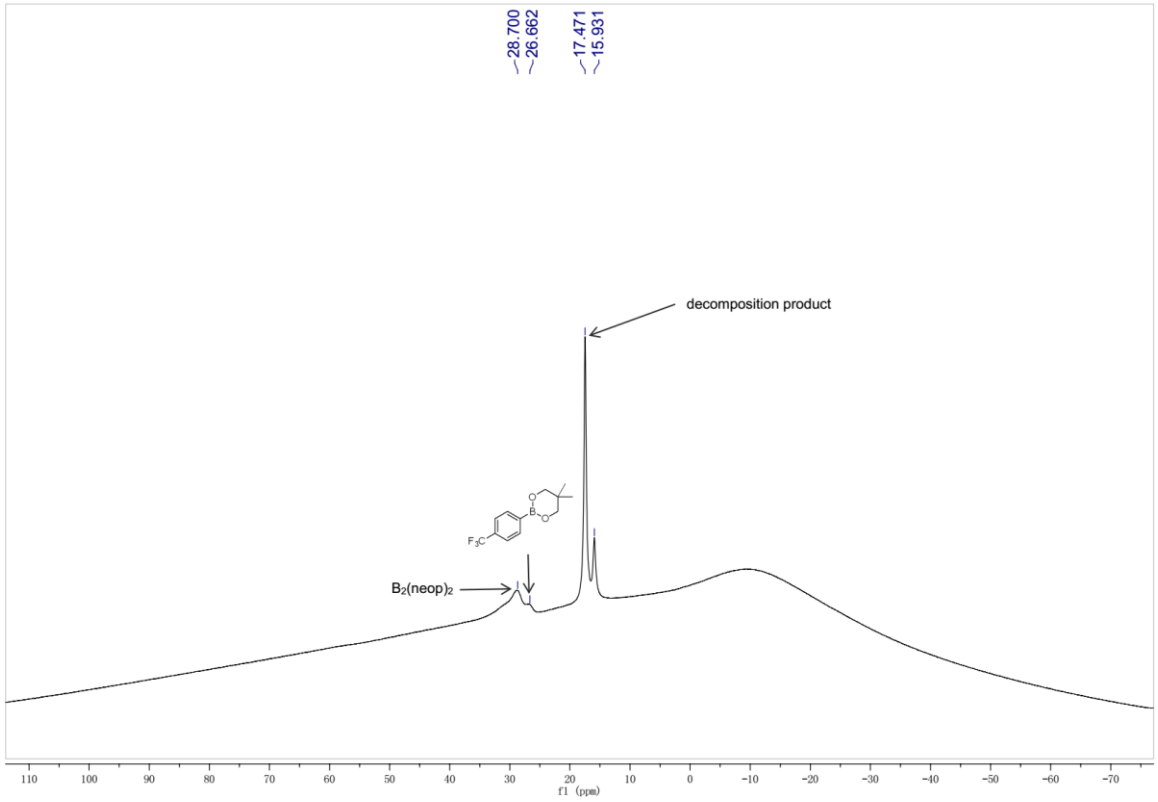


Figure 2-S9. ^{11}B NMR spectrum (recorded in C_6D_6; 160 MHz) at 110 ^{o}C for 2 h.

f) Stoichiometric Reaction of [Ni(COD)$_2$], ICy with B$_2$(neop)$_2$

In a Young's tap NMR tube, B$_2$(neop)$_2$ (6.7 mg, 30.0 µmol, 1.0 equiv.), ICy (13.9 mg, 60.0 µmol, 2.0 equiv.) and [Ni(COD)$_2$] (8.3 mg, 30.0 µmol, 1.0 equiv.) were added to 1,4-dioxane (0.7 mL). Investigation of the reaction mixture by $^{11}B\{^1H\}$ NMR spectroscopy revealed no nickel-boryl complex.

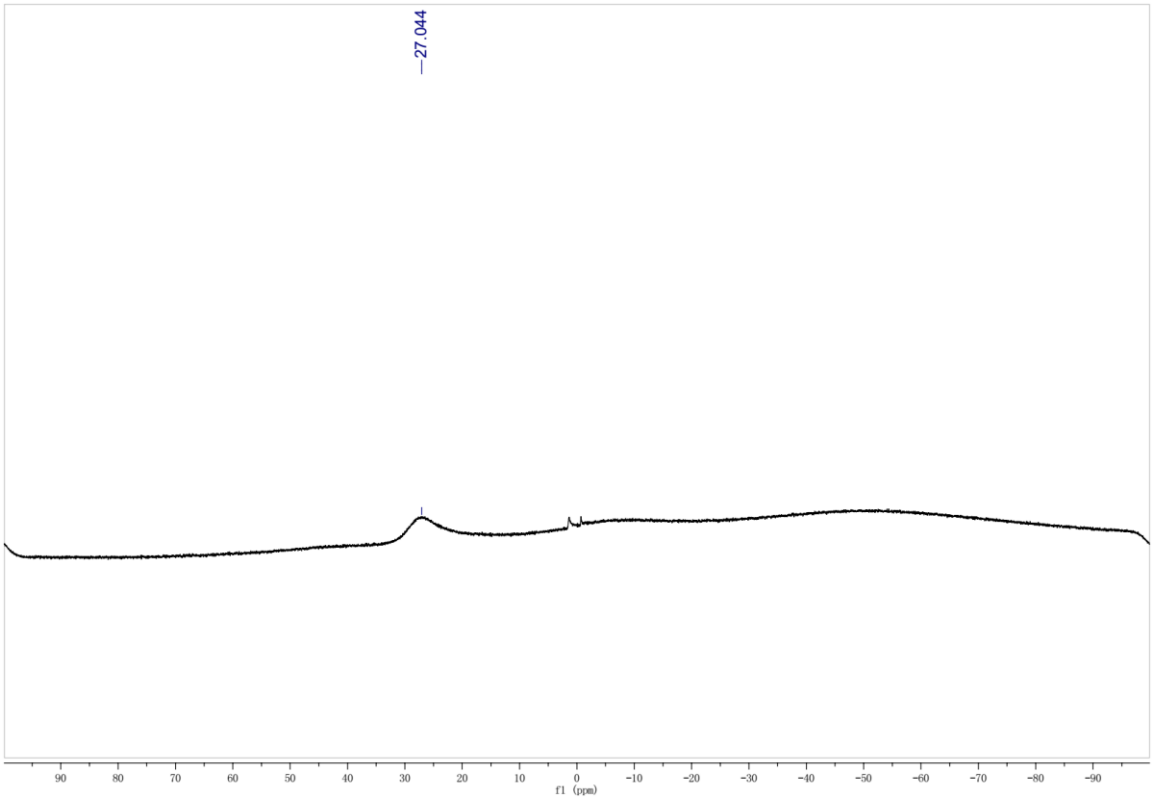
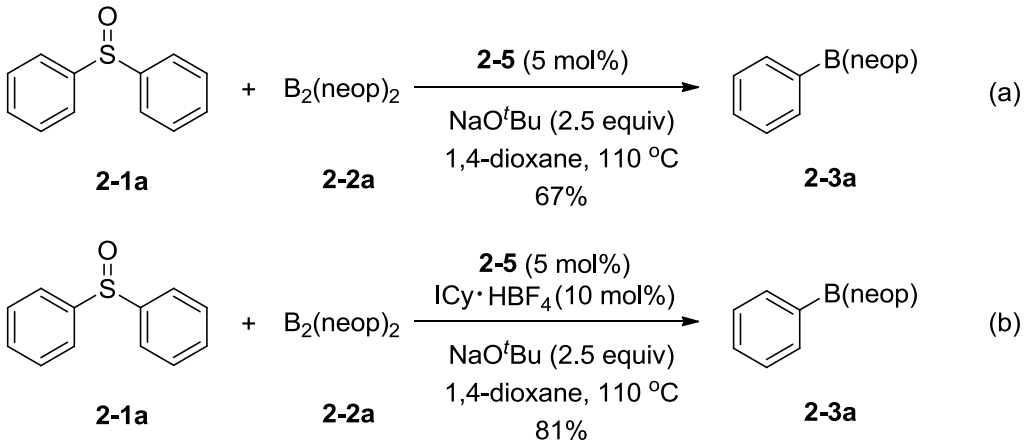


Figure 2-S10. ^{11}B NMR spectrum (recorded in 1,4-dioxane; 96 MHz) at room temperature.

g) Reactivity of *trans*-[Ni(ICy)$_2$(C$_6$H$_5$){(SO)-C$_6$H$_5$}]



In an argon-filled glovebox, *trans*-[Ni(ICy)$_2$(C$_6$H$_5$){(SO)-C$_6$H$_5$}] **2-5** (5 mol%), [(a): no ICy•HBF$_4$; (b): 10 mol% ICy•HBF$_4$] and 1,4-dioxane (3 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (1.25 mmol, 2.5 equiv.), B$_2$(neop)$_2$ (1.25 mmol, 2.5 equiv.) and the aryl sulfoxide (0.5 mmol, 1.0 equiv.) were added. The reaction mixture was stirred at 110 °C for 20 h, then diluted with Et$_2$O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product was isolated by flash column chromatography (hexane/ethyl acetate (95/5)) after careful removal of the solvent *in vacuo* (especially noting that volatile arylboronates can evaporate with the solvent).

h) VT-NMR spectra of 2-5 in THF-d_8

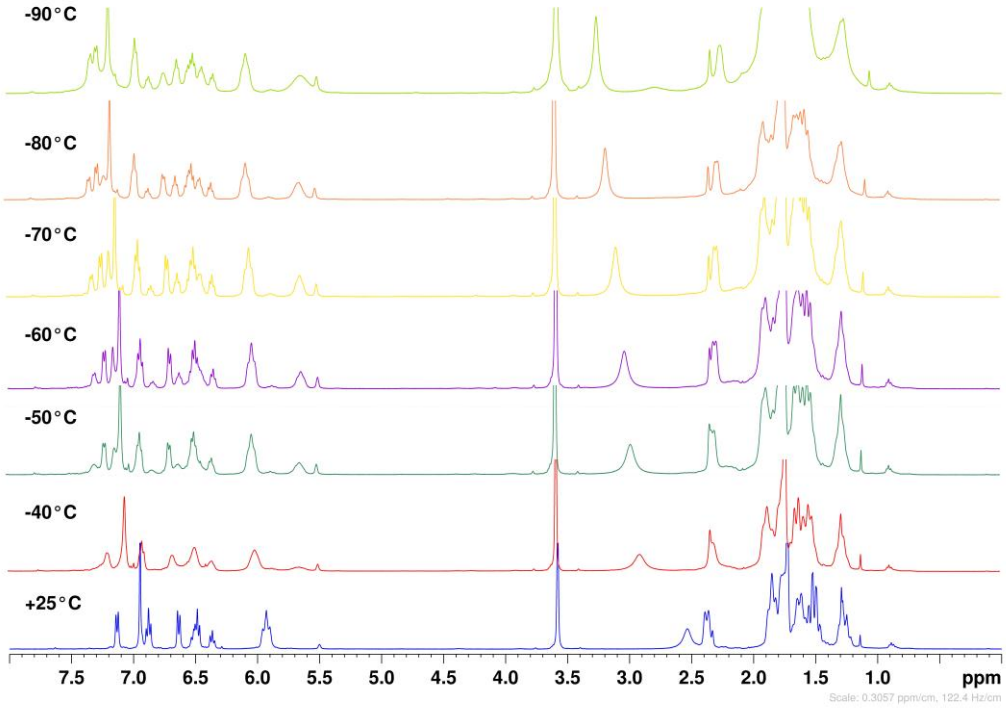


Figure 2-S11. ^{1}H VT-NMR spectra of **2-5** in THF-d_8.

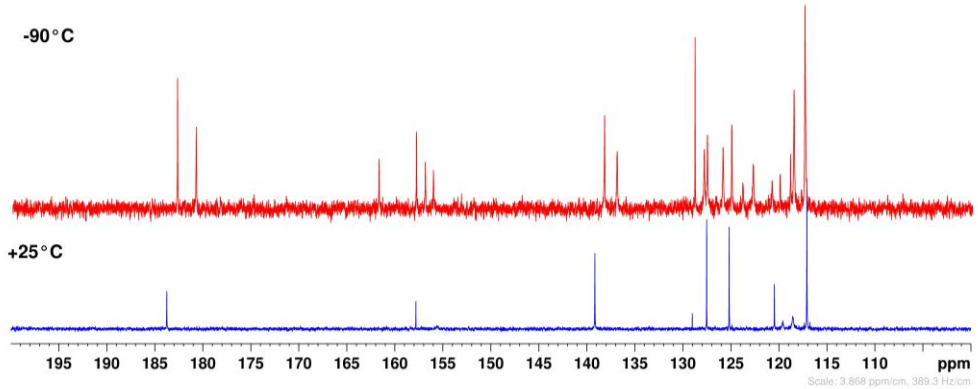


Figure 2-S12. ^{13}C{^{1}H} VT-NMR spectra of 2-**5** in THF-d_8.

2.5.7 Crystallographic Details

Crystals were immersed in a film of perfluoropolyether oil, mounted on MiTeGen sample holders, and transferred to a Bruker X8 Apex-2 diffractometer, with CCD area detector and mirror-monochromated Mo-K_α radiation. Data were collected at 100 K, using an Oxford Cryosystems low-temperature device. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method (SHELXT)[57] and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against F^2 of all data, using SHELXL[58] software and the SHELXLE graphical user interface.[59] Diamond[60] software was used for graphical representation. Crystal data and experimental details are listed in Table 2-S1; full structural information has been deposited with Cambridge Crystallographic Data Centre. CCDC-1997417 (**2-5-I**), 1997418 (**2-5**) and 2022071 (**2-4**).

Table S5: Crystal data and structure refinements for **2-5**, **2-5-I** and **2-4**.

Compound	**2-5**	**2-5-I**	**2-4**
CCDC number	1997418	1997417	2022071
Empirical formula	$C_{42}H_{58}N_4NiOS·2(CH_2Cl_2)$	$C_{42}H_{58}N_4NiOS$	$C_{40}H_{59}F_3N_4NiO_2S·C_4H_8O_5$
Formula weight ($g·mol^{-1}$)	895.54	725.69	895.82
Temperature (K)	100(2)	100(2)	100(2)
Radiation, λ (Å)	Mo-K_α 0.71073	Mo-K_α 0.71073	Mo-K_α 0.71073
Crystal size (mm^3)	0.20×0.24×0.29	0.08×0.16×0.33	0.43 × 0.39 × 0.19
Crystal color, habit	Yellow block	Yellow block	Yellow block
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	11.488(4)	12.990(4)	9.519(3)
b (Å)	30.107(8)	20.882(7)	12.442(6)
c (Å)	13.646(5)	15.209(5)	20.272(7)
α (°)	90	90	79.01(3)
β (°)	106.006(17)	106.228(8)	86.851(12)
γ (°)	90	90	74.603(10)
Volume ($Å^3$)	4537(2)	3961(2)	2272.2(16)
Z	4	4	2
ρ_{calc} ($g·cm^{-3}$)	1.311	1.217	1.309
μ (mm^{-1})	0.747	0.579	0.530
F(000)	1896	1560	956.0
θ range (°)	1.353 - 26.738	1.702 - 26.360	3.454 - 55.694
Reflections collected	66732	67257	59217
Unique reflections	9640	8083	10784
Parameters / restraints	496 / 0	564 / 389	542 / 0
GooF on F^2	1.019	1.052	1.042
R_1 [I>2σ(I)]	0.0418	0.0711	0.0419
wR^2 (all data)	0.1031	0.1703	0.1140
Max./min. residual electron density ($e·Å^{-3}$)	0.551 / –0.526	1.955 / –0.815	1.88 / –0.70

Table S6: Bond lengths (Å) and angles (°) of **2-5**, **2-5-I** and **2-4**.

	2-5	**2-5-I**	**2-4**
Ni – C (NHC)	1.900(2)	1.895(4)	1.8940(17)
Ni – C (NHC)	1.894(2)	1.901(4)	1.9066(17)
Ni – C (phenyl)	1.929(2)	1.930(4)	1.9254(18)
Ni – S (**2-5**) / O (**2-5-I**)	2.2284(8)	1.924(7) / 1.91(2)	2.2259(8)
C – Ni – C	177.73(9)	178.66(18)	176.16(7)
	89.93(9)	90.02(17)	88.31(7)
	88.08(9)	88.79(18)	88.59(7)
C – Ni – S (**2-4**, **2-5**) / O (**2-5-I**)	170.33(7)	173.5(2) / 175.8(7)	169.45(5)
	90.87(7)	94.0(5) / 89.5(16)	91.09(6)
	91.27(7)	87.3(5) / 91.6(16)	92.37(6)
Sum ∠ C – Ni – C / O / S	360.15(10)	360.1(4) / 359.9(17)	360.36(7)

2.5.8 Crystallographic Details

DFT calculations were carried out with the Gaussian09 package.[61] The geometries of the different structures were optimized at the DFT level using the B3LYP[62] hybrid functional with the def2-SVP basis set.[63] Frequency analysis was carried out at the same level to verify the stationary points as an intermediate or transition state and to obtain the thermodynamic energy corrections assuming a standard state of 1 atm and 298.15 K. Solvent effects were taken into consideration by single point calculations of the gas-phase stationary points with the SMD[64] continuum solvation model with 1,4-dioxane as the solvent. To obtain more accurate energy information, solvation single-point energy calculations were performed at the M06[65] level of theory using the larger def2-TZVP basis set.[63] All of the three-dimensional molecular diagrams of the molecules were generated with CYLView.[66]

Table S7: Absolute calculated electronic energies, correction of enthalpies, and free energies.

Geometry	$E_{(elec\text{-}B3LYP)}$[a]	$G_{(corr\text{-}B3LYP)}$[b]	$H_{(corr\text{-}B3LYP)}$[c]	$E_{(M06\ 1,4\text{-}dioxane)}$[d]	IF[e]
2-5-I	-3834.557506	0.84834	0.982195	-3835.429856	
TS-iso	-3834.527749	0.850293	0.980803	-3835.415038	-190.90
2-5	-3834.537444	0.849771	0.982028	-3835.431747	

[a] Electronic energy calculated by B3LYP/def2-SVP in gas phase. [b] Thermal correction to Gibbs free energy calculated by B3LYP/def2-SVP in the gas phase. [c] Thermal correction to enthalpy calculated by B3LYP/def2-SVP in the gas phase [d] Electronic energy calculated by M06/def2-TZVP in 1,4-dioxane. [e] B3LYP calculated imaginary frequencies for the transition states.

2.6 References

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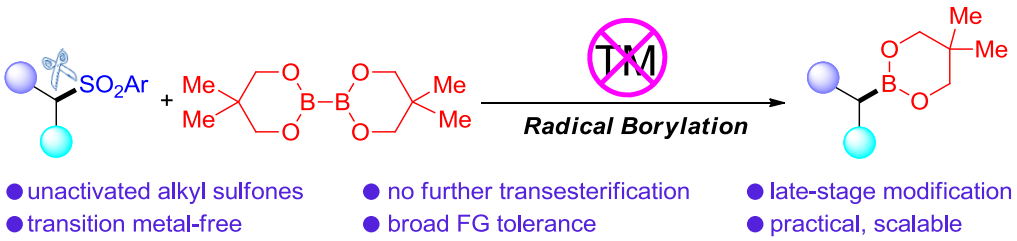
Chapter 3

Base-Mediated Radical Borylation of Alkyl Sulfones



3 Base-Mediated Radical Borylation of Alkyl Sulfones

3.1 Abstract

A practical and direct method was developed for the production of versatile alkylboronic esters *via* transition metal-free borylation of primary and secondary alkyl sulfones. The key to the success of the strategy is the use of bis(neopentyl glycolato) diboron (B_2neop_2), with a stoichiometric amount of base as a promoter. The practicality and industrial potential of this protocol are highlighted by its wide functional group tolerance, the late-stage modification of complex compounds, no need for further transesterification, and operational simplicity. Radical clock, radical trap experiments, and EPR studies were conducted which show that the borylation process involves radical intermediates.

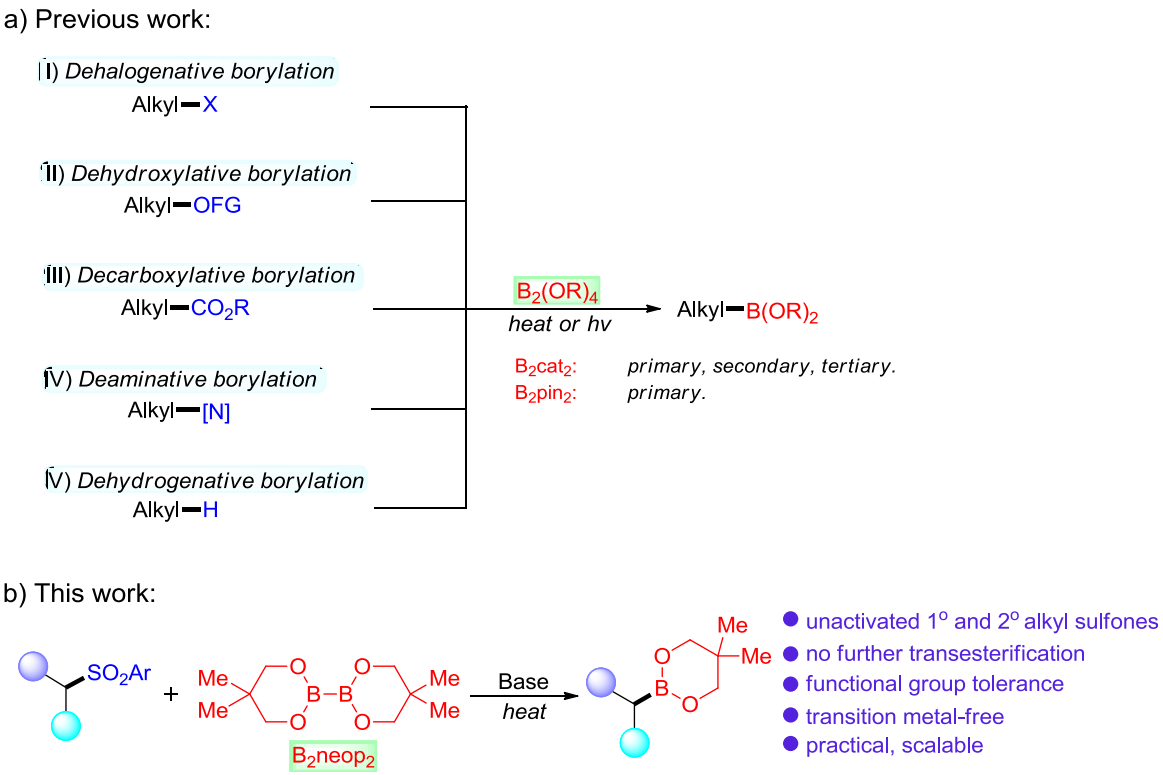
3.2 Introduction

The preparation of alkylboronates is an important and valuable process in organic synthesis because these compounds play an essential role in synthetic chemistry, drug discovery, and materials science.[1] Early research typically focused on transmetalation using organolithium or Grignard reagents,[2] and the metal-catalyzed hydroboration[3] or diboration of alkenes.[4] More recently, transition metal-catalyzed cross-coupling strategies for the direct borylation of alkyl halides have been well-developed by Marder, Steel and Liu,[5] Fu,[6] Ito,[7] Cook,[8] and others.[9] This Miyaura-type borylation has now been widely applied using sustainable chemical feedstocks, such as alcohols,[10] carboxylic acids[11] and amine derivatives.[12] With increasing attention to sustainable chemistry, transition metal-free radical borylation protocols have emerged as an important tool to access alkyl boronic compounds (Scheme 3-1I-V).[13] Bis(catecholato)diboron (B_2cat_2)[14] is an efficient diboron(4) compound for the borylation of redox-active esters in the presence of amide-based solvents, as first reported by Aggarwal and co-workers.[15] As the catechol boronate esters are sensitive to hydrolysis, transesterification with pinacol in the presence of Et_3N is employed. Then, Studer[16] and Jiao[17] independently reported the transition metal-free radical borylation of primary and secondary alkyl bromides and iodides employing B_2cat_2 under blue LED

irradiation, providing a broad range of alkylboronate esters. In addition, visible light-mediated approaches for deoxygenative borylation[18] and decarboxylative borylation[15,19] using B_2cat_2 as the boron source in *N,N*-dimethylformamide (DMF) or *N,N*-dimethylacetamide (DMA) were introduced by Studer and Aggarwal. Interestingly, Shi,[20a] Aggarwal,[21] and Glorius[22] independently reported metal-free deaminative borylations of pyridinium salt-activated alkylamines with a proposed B_2cat_2-DMA sp^2-sp^3 adduct[23] under visible light or with heating. In 2020, a photochemical method for the dehydrogenative borylation of non-activated alkanes using a chloride source as a hydrogen atom transfer (HAT) catalyst was described.[24] The trapping of alkyl radicals with B_2pin_2[25] without transesterification was also reported; however, the substrates for this method are limited to primary alkyl halides.[26] The sustained expansion of transition metal-free direct radical borylation without transesterification is extremely desirable but challenging.

Sulfone functionalities are important and fundamental structural motifs in chemistry.[27] In general transition metal-catalyzed cross-coupling processes, they are commonly used as electrophiles to construct C–C and C–heteroatom bonds. Generally, studies in this area have mainly concentrated on aryl-,[28] vinyl-,[29] allylic-[30] and benzylic sulfones.[31] In contrast, the desulfonative transformation of unactivated alkyl sulfones is scarce and challenging because of the inherent low reactivity of the C–SO_2 bond.[32] Notably, alkyl sulfones present several advantages over alkylhalides, including the tolerance of α-functionalization before coupling, as well as their stability and crystallinity, which allow for convenient manipulation. Pragmatically speaking, alkyl sulfones can be easily synthesized from alkyl alcohols or halides with inexpensive and odorless sodium arenesulfinate or diphenyl disulphide to produce highly crystalline products. In 2018, Scheidt *et al.* developed a Cu-catalyzed approach for the hydroboration of aldimines with B_2pin_2 using *N*-benzoyl-protected *α*-tosylamines as starting materials, providing enantioenriched *α*-amidoboronates.[33] In the same year, Baran and co-workers reported a breakthrough in the desulfonative radical process of alkyl sulfones in the presence of aryl zinc reagents using nickel(II) acetylacetonate and a bipyridine-type ligand as catalyst precursor.[34] Recently, transition metal-free, pyridine-catalyzed borylation of benzyl sulfones with B_2pin_2 was reported by Crudden

group,[31d] however, it was mainly focused on the benzyl substrates. In view of recent progress and our interest in borylation reactions,[35] we postulated that if a transient alkyl radical could be generated from an alkyl sulfone using light or heat, this species might undergo radical borylation with an appropriate diboron reagent for the construction of C(sp^3)–B bonds. Herein, we report our initial results on the utilization of alkyl sulfones as alkyl radical precursors in a base-mediated borylation reaction with B_2neop_2, thus allowing for direct access to valuable alkylboronate esters without transesterification.



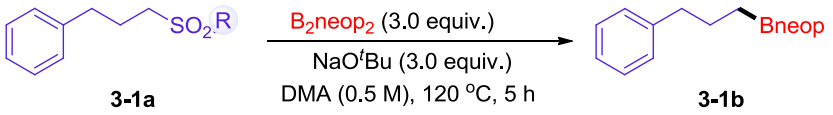
Scheme 3-1. Transition metal-free radical borylation reaction.

3.3 Results and Discussion

3.3.1 Optimization of Reaction Conditions

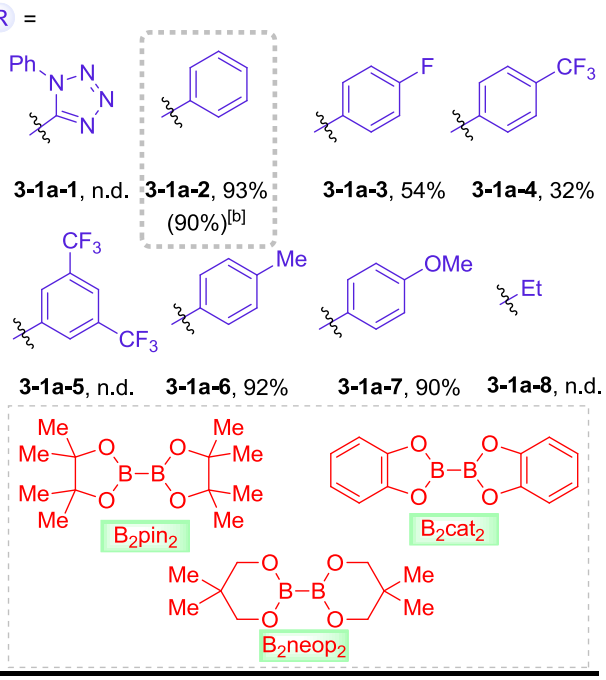
We initiated this study by investigating a sulfone bearing a phenyl-tetrazole moiety, **3-1a-1**, previously reported by Baran, for potential borylation using B_2neop_2,[36] but the target product **3-1b** was not detected by GC-MS in the presence of NaO^{t}Bu in DMA at 120 °C. However, alkyl aryl sulfone **3-1a-2** was effectively converted to alkylboronic ester **3-1b** under these conditions with an isolated yield of 90%. Other sulfones (**3-1a-3** – **3-1a-7**) with different electronic properties and

sizes were also explored in this system, and we found that substrates with electron-withdrawing groups gave low yields and reaction with **3-1a-8** was unsuccessful (Scheme 3-2). Subsequently, we began to study the influence of other parameters on this borylation reaction by using ((3-phenylpropyl)sulfonyl)benzene **3-1a-2** as the model substrate. Upon removal of the base from this system, alkylboronates were not formed, leaving only unreacted starting materials (entry 1). Other alkoxides, such as KO^{t}Bu, LiO^{t}Bu, KOMe and LiOMe, gave lower yields (entries 2–5), and no reaction took place with NaOMe, K_3PO_4 and Et_3N under these conditions (entries 6–8). In the presence of 3.0 equivalents of NaO^{t}Bu, we observed moderate reactivity in other organic solvents, for example DMF, DMSO, toluene, and 1,4-dioxane (entries 9–12). Lowering the reaction temperature to 100 °C resulted in a slightly diminished yield of **3-1b** under the otherwise optimal conditions (entry 13). At a lower temperature (80 °C), the results were inferior (entry 14). B_2pin_2 and B_2cat_2 are commonly used sources of boron in radical borylation reactions. However, B_2pin_2 failed to afford any product under our conditions (entry 15), as the formation of a base-diboron complex might be promoted when B_2neop_2 was used due to a steric factor (B_2pin_2 vs B_2neop_2). The reaction also resulted in poor conversion using B_2cat_2 instead of B_2neop_2 (entry 16), unfavorable decomposition of such a complex might be suppressed at high temperature in the case of B_2neop_2 (B_2cat_2 vs B_2neop_2).



3-1a **3-1b**

Entry	Deviation from above[c]	Yield of **3-1b** (%)
1	w/o NaO^{t}Bu	0
2	with KO^{t}Bu	65
3	with LiO^{t}Bu	25
4	with KOMe	40
5	with LiOMe	17
6	with NaOMe	0
7	with K_3PO_4	0
8	with Et_3N	0
9	DMF	26
10	DMSO	72
11	toluene	56
12	1,4-dioxane	50
13	at 100 °C	86
14	at 80 °C	61
15	with B_2pin_2	0
16	with B_2cat_2	13

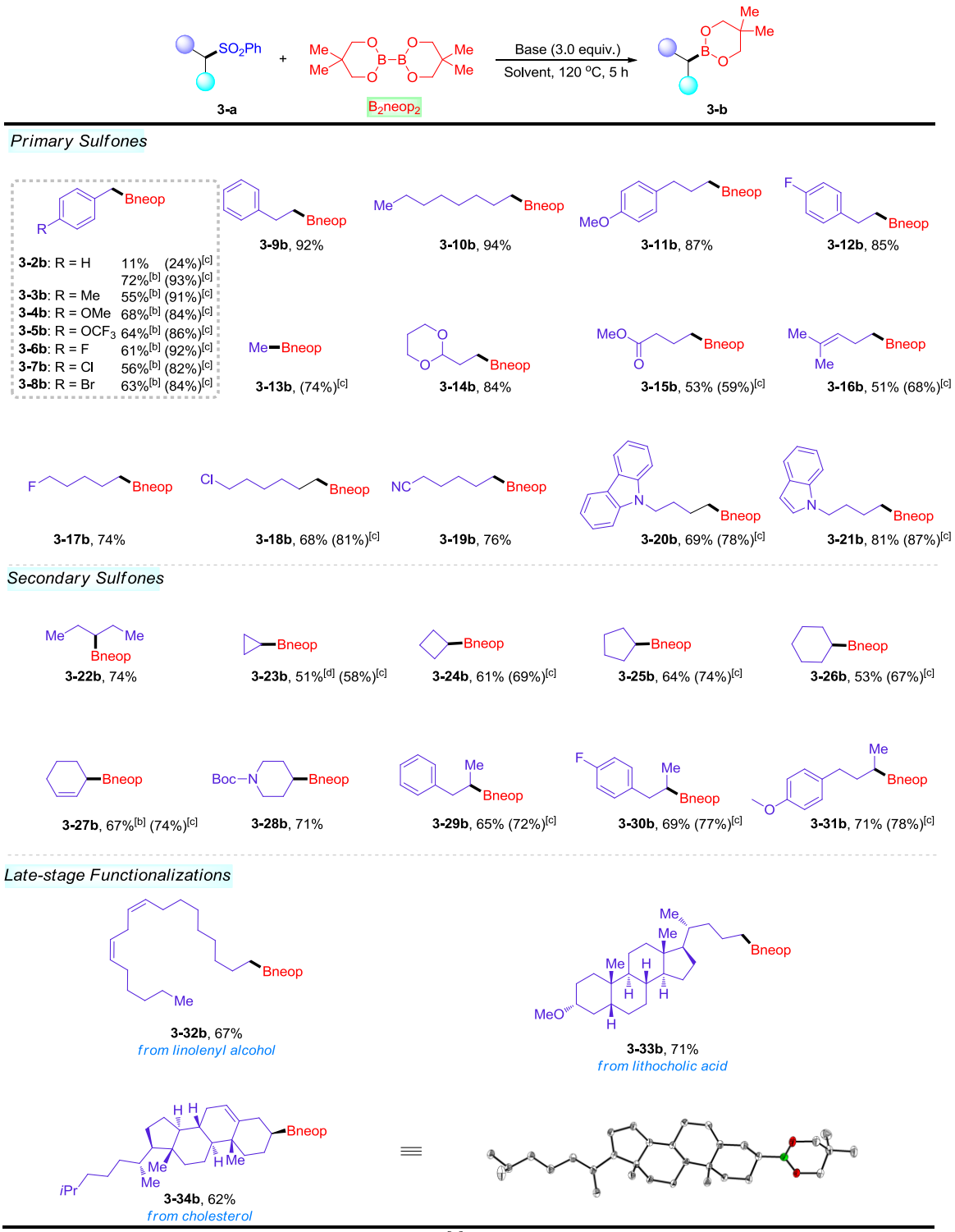


Scheme 3-2. Optimization of reaction conditions for the borylation of alkyl sulfones[a] [a] Reaction conditions: a mixture of alkyl sulfone **3-1a** (0.5 mmol, 1.0 equiv.), B_2neop_2 (3.0 equiv.), and NaO^{t}Bu (3.0 equiv.), DMA (1.0 mL), 120 °C, 5 h, under Ar. The yields were determined by GC-MS analysis using an internal standard and are averages of two runs. [b] Yield of Isolated product after chromatographic workup. [c] Using **3-1a-2** as starting material. n.d. = not detected.

3.3.2 Investigation of Reaction Scope

Under optimized reaction conditions, we proceeded to investigate the scope of alkyl aryl sulfones using B_2neop_2 as a coupling reagent (Scheme 3-3). Initially, (benzylsulfonyl)benzene **3-2a** was examined in reactions with B_2neop_2 under standard conditions, affording the corresponding product **3-2b** in 24% NMR yield. In order to improve the conversion efficiency of the transformation, modified conditions were applied to the desulfonative borylation of benzyl sulfones (see Table 3-S2 for a survey of the reaction conditions). The borylation reaction is tolerant to OCF_3 (**3-5b**) and F, Cl, and Br groups (**3-6b**, **3-7b**, **3-8b**). Aryl halide substrates worked well in the process, exhibiting selective cleavage of the C(sp^3)–SO_2 bonds over the aryl C–X bonds (**3-6b** – **3-8b**). Sulfone substrates with different carbon chains were successfully borylated using NaO^{t}Bu as the base (**3-9b** – **3-12b**, 85–94%). In particular, methyl boronate ester **3-13b**, which decomposes

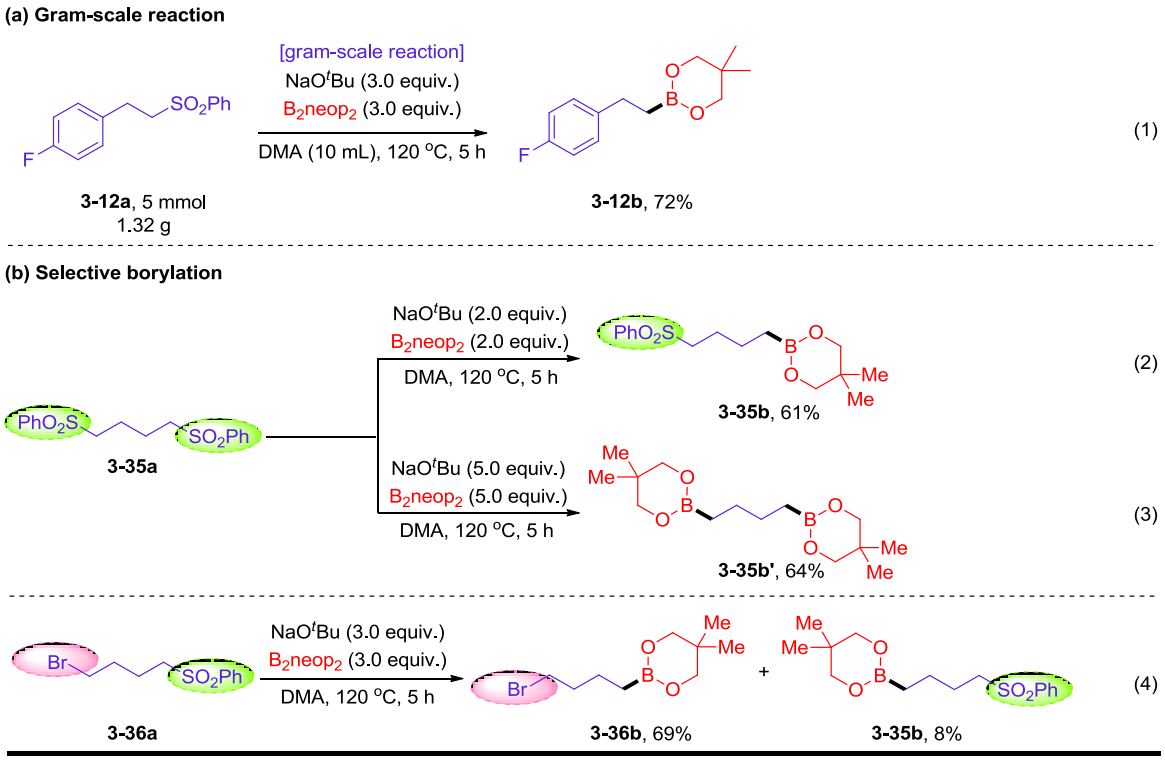
readily on silica gel, was formed from methyl phenyl sulfone in 74% NMR yield under our conditions. In addition, under these conditions, other functionalities, such as ether, ester, olefin, F and Cl, were well-tolerated and proceeded to generate the desired alkylboronates in moderate to high isolated yields (**3-14b** – **3-18b**). The sulfone bearing a cyano motif also worked well in this system, giving **3-19b** in 76% yield. Heterocycles, including carbazole and indole, exhibited high levels of reactivity, delivering **3-20b** and **3-21b**, respectively. A range of secondary alkyl sulfones were also efficiently transformed into the corresponding alkylboronates **3-22b** – **3-31b** in good yields (51%–74%). Interestingly, this method could be used for the late-stage derivatization of complex compounds. Linolenyl alcohol derivative **3-32a**, bearing two *cis*-alkene groups, reacted with B_2neop_2 under our conditions, providing product **3-32b** in 67% yield. The lithocholic acid derivative **3-33a** afforded the borylation product **3-33b** in 71% yield, and the complex sulfone derivative **3-34a** was also readily converted into alkylboronic ester **3-34b** without observation of other isomers. The molecular structure of **3-34b** was determined by single-crystal X-ray diffraction. The tertiary sulfone substrates were also examined, no desired borylated products were observed.



Scheme 3-3. Alkyl sulfones substrate scope.[a] [a] Reaction conditions: A mixture of alkyl aryl sulfone **3-a** (0.5 mmol, 1.0 equiv.), B_2neop_2 (3.0 equiv.), and NaO^{t}Bu (3.0 equiv.) in DMA (1 mL) was stirred for 5 h at 120 °C under Ar; isolated yields after chromatography. [b] Using KOMe (1.2 equiv.) and B_2neop_2 (1.2 equiv.) in 1,4-dioxane (2.0 mL) at 110 °C for 2 h under Ar. [c] Yields in parentheses were determined by ^{1}H NMR analysis. [d] From sulfone substrate 1-(cyclopropylsulfonyl)-4-methylbenzene.

3.3.3 Gram-Scale Reaction and Selective Borylation

To showcase the applicability of the process, a 1 g scale reaction was performed with **3-12a** giving a 72% isolated yield of borylated product **3-12b**, indicating the viability of this strategy for the large-scale production of alkylboronic esters (Scheme 3-4a, eq1). The borylation of 1,4-bis(phenylsulfonyl)butane **3-35a** selectively generated the mono-borylated product **3-35b** or di-borylated product **3-35b'** under different reaction conditions (Scheme 3-4b, eq 2 and 3). Different from substrate **3-18a**, **3-36a** bears both alkyl bromide and alkyl aryl sulfone sites, afforded **3-36b** as the main product, accompanied by only 8% yield of the debromination product **3-35b** (Scheme 3-4b, eq 4).

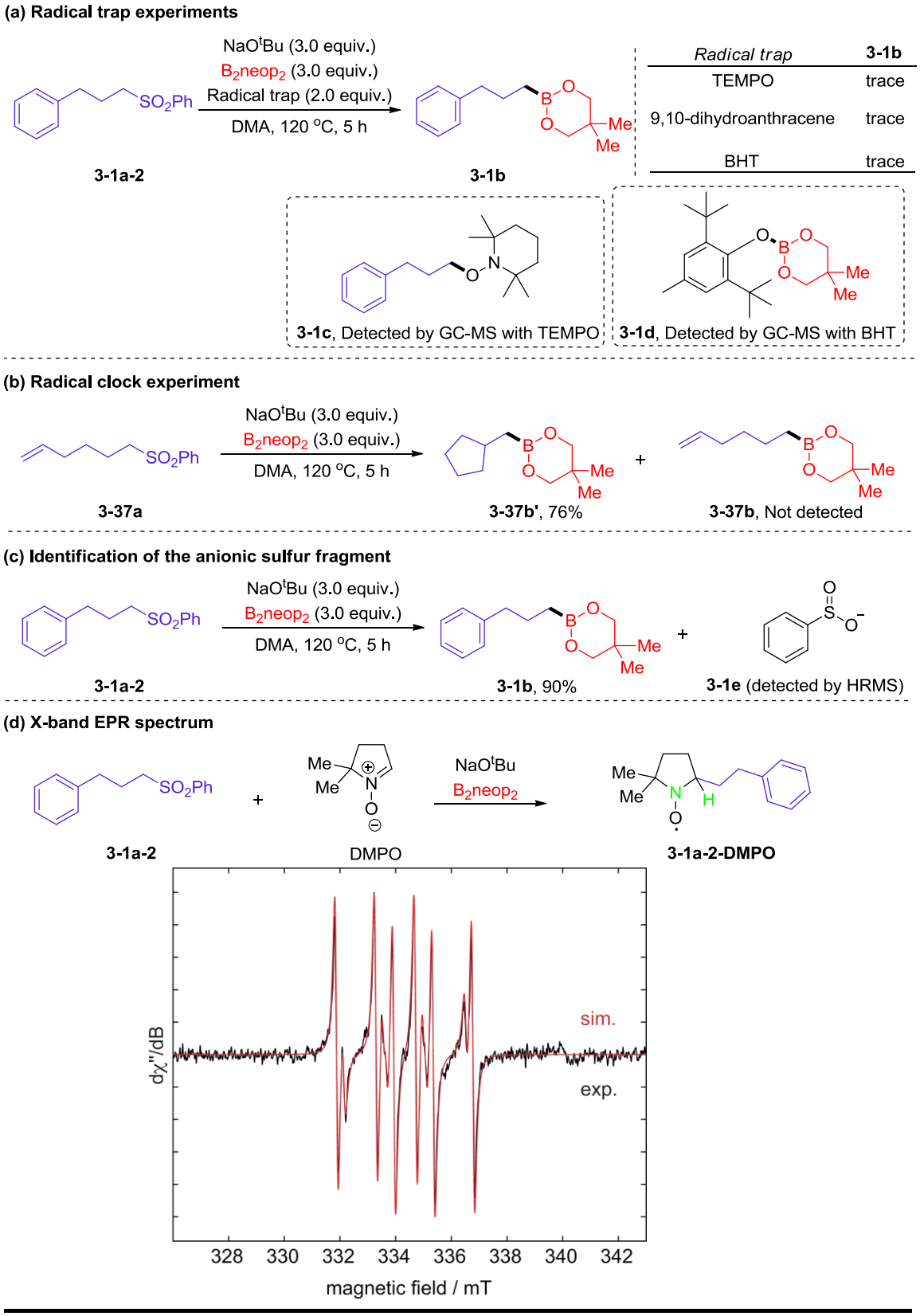


Scheme 3-4. Gram-scale reaction and selective borylation.

3.3.4 Mechanistic Studies

We next conducted some control experiments to explore this borylation process. Firstly, when 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO), 9,10-dihydroanthracene, or butylated hydroxytoluene (BHT) were added as radical traps, **3-1b** was barely detected by GC-MS (Scheme 3-5a). Additionally, TEMPO-trapped product **3-1c** and BHT-Bneop adduct **3-1d** were observed by

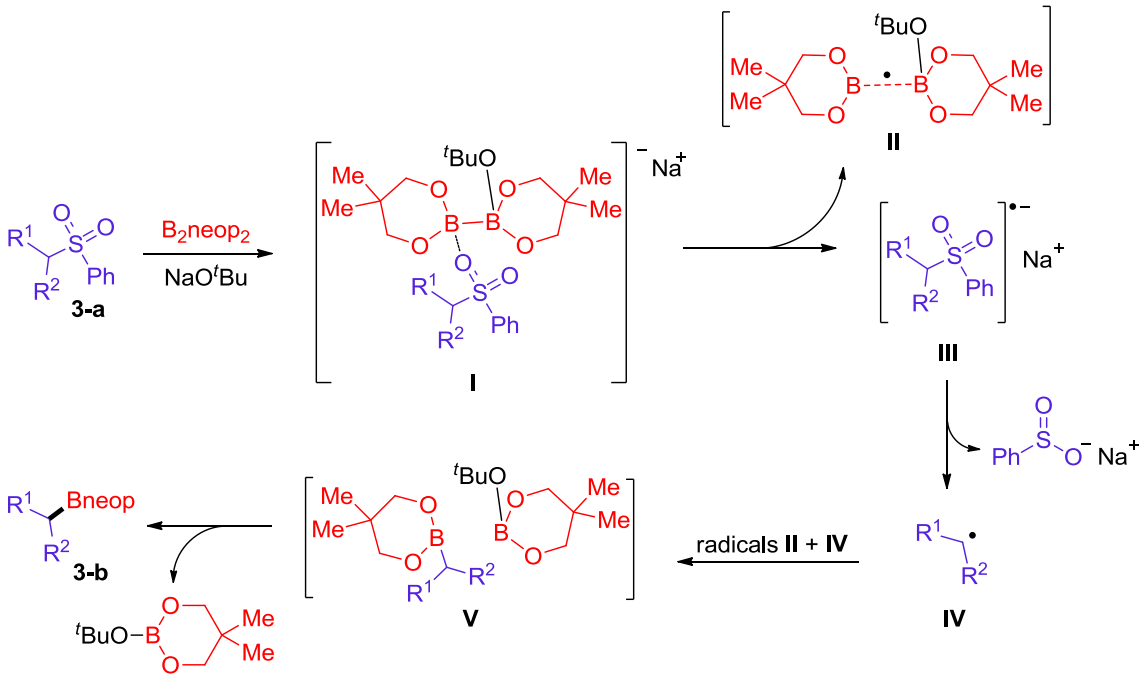
GC−MS and HRMS analysis. The formation of a boron radical is suggested during the reaction based on the observation of adduct **3-1d**. Secondly, a radical clock experiment was carried out with hex-5-en-1-ylsulfonylbenzene **3-37a** as the substrate, and the cyclic boronate ester **3-37b'** was isolated exclusively in 76% yield (Scheme 3-5b). These results support a radical borylation mechanism. In addition, after the reaction completed, we detected phenylsulfinate by HRMS, which was generated by cleavage of the C–S bond (Scheme 3-5c). We also used electron paramagnetic resonance (EPR) spectroscopy to investigate the nature of the radicals in the process (Scheme 3-5d). 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) was added to act as a spin-trap, which reacts with short-lived alkyl radicals to produce the more stable and observable DMPO-trapped radical. The EPR signal depicted in Scheme 3-5d shows a g_{iso} value of 2.0053 with a hyperfine splitting which is in accordance with coupling to the adjacent hydrogen and nitrogen atoms (highlighted in green in Scheme 3-5d). The major alkyl-DMPO adduct is accompanied by a second minor species of unknown composition. A sulfonyl radical seems reasonable based on the *g* factor and observed couplings; we can definitely exclude a phenyl radical, which could also be generated by extrusion of sulfur dioxide from a putative sulfonyl radical. The trapping experiment was also conducted under the same conditions without the addition of B_2neop_2, and no EPR signal was observed.



Scheme 3-5. Mechanistic studies. (a) Radical trap experiments. (b) Radical clock experiment. (c) Identification of the anionic sulfur fragment. (d) Experimental (black) and simulated (red) continuous-wave (CW) X-band EPR spectra of the DMPO spin trapping experiment. Best-fit simulation parameters: g_{iso} = 2.0053, $a(^{14}N)$ = 40 MHz (14.3 G) and $a(^{1}H)$ = 58 MHz (20.6 G,

major species); g_{iso} = 2.0053, $a(^{14}N)$ = 40 MHz (14.3 G) and $a(^{1}H)$ = 43 MHz (15.4 G, minor species).

Based on the above observations and previous work on radical borylations, a possible mechanism is shown in Scheme 3-6. We propose a possible ate complex **I**, which is generated from **3-a**, B_2neop_2, and alkoxide.[23, 37] This intermediate undergoes intramolecular electron transfer to release radical **II** and sulfone radical anion **III**. Then, alkyl radical **IV** is formed by elimination of phenylsulfinate from sulfone radical anion **III**. Subsequently, alkyl radicals **II** and **IV** combine to produce species **V**, leading to the borylated product and ^{t}BuOBneop.[38] While we have previously explored the electronic properties of B_2neop_2, B_2cat_2, and B_2pin_2,[36b, 39a] or their monoboron counterparts Bneop, Bcat, and Bpin,[39b] in various contexts, the reaction mixtures in the present work are likely more complex than depicted in our proposed mechanism, and it is not clear to us why B_2neop_2[37a] shows such unique reactivity among the diboron compounds investigated in our newly developed process. Thus, while our proposal is consistent with our observations, further experimental and theoretical studies will be required to gain a complete understanding of the nature of all species present during the reaction.



Scheme 3-6. Proposed mechanism.

3.4 Conclusions

In summary, we have successfully achieved the base-promoted radical borylation of alkyl sulfones using B_2neop_2, which displayed enhanced reactivity compared with the diboron reagents B_2cat_2 and B_2pin_2. This approach is tolerant to a variety of functional groups and substrates, including complex molecules. Preliminary mechanistic studies revealed a plausible reaction pathway involving the formation of alkyl radicals. Additional studies are required to achieve a more detailed understanding of the intimate mechanism of the process and the reason that B_2neop_2 shows optimum reactivity among the diboron(4) reagents examined. We anticipate that these findings will prompt further development of desulfonative radical cross-coupling reactions.

3.5 Detailed Experiments and Characterization Data

3.5.1 General Information

All reactions and subsequent manipulations were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox (Innovative Technology Inc. and Braun Uni Lab). All reactions were carried out in oven-dried glassware. Reagent grade solvents (Fisher Scientific and J.T. Baker) were nitrogen saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System, and further deoxygenated using the freeze-pump-thaw method. $CDCl_3$ was purchased from Sigma-Aldrich. The diboron reagents B_2neop_2, B_2cat_2 and B_2pin_2 were a generous gift from AllyChem Co. Ltd. All other reagents were purchased from Alfa-Aesar, Sigma-Aldrich or ABCR, and were checked for purity by GC-MS and/or ^1H NMR spectroscopy and used as received.

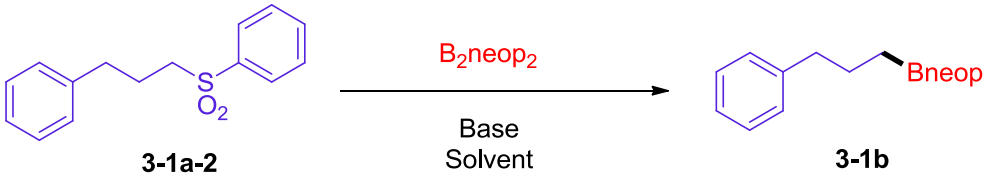
NMR spectra were recorded at 298 K using Bruker Avance 300 (^1H, 300 MHz; ^{13}C, 75 MHz, ^{11}B, 96 MHz), Bruker DPX-400 (^1H, 400 MHz; ^{13}C, 100 MHz, ^{11}B, 128 MHz; ^{19}F, 376 MHz), or Bruker Avance 500 (^1H, 500 MHz; ^{13}C, 125 MHz, ^{11}B, 160 MHz; ^{19}F, 470 MHz) spectrometers. ^1H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas $^{13}C\{^1H\}$ NMR spectra are reported relative to TMS using the natural-abundance carbon resonances ($CDCl_3$:

77.16 ppm). However, signals for the carbon attach to boron, C-B, are usually too broad to observe in the $^{13}C\{^{1}H\}$ NMR spectra. ^{11}B and ^{19}F NMR chemical shifts are reported relative to external BF_3•OEt_3 or $CFCl_3$, respectively. Coupling constants are given in Hertz. Elemental analyses were performed in the microanalytical laboratory of the Institute of Inorganic Chemistry, Universität Würzburg, using an Elementar vario micro cube instrument. Automated flash chromatography was performed using a Biotage® Isolera Four system, on silica gel (Biotage SNAP cartridge KP-Sil 10 g and KP-Sil 25 g). Commercially available, precoated TLC plates (Polygram® Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 30 °C. GC-MS analyses were performed using a Thermo Fisher Scientific Trace 1310 gas chromatograph (column: TG-SQC 5% phenyl methyl siloxane, 15 m, Ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C; carrier gas: He (1.2 mL min^{-1}) or an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 30 m, Ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C (20 °C min^{-1}); carrier gas: He (1.2 mL min^{-1}) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. High-resolution mass spectra were obtained using a Thermo Scientific Exactive Plus spectrometer equipped with an Orbitrap Mass Analyzer. Measurements were accomplished using an ASAP/APCI source with a corona needle, and a carrier-gas (N_2) temperature of 250 °C.

3.5.2 Deatiled Optimization of the Reaction Conditions

General procedure of optimization for Table 3-S1. In an argon-filled glovebox, the alkyl sulfone **3-1a-2** (0.5 mmol, 1.0 equiv.), dissolved in solvent (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. Base and the boron source were added. The reaction mixture was stirred at indicated temperature for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The solvent was evaporated under reduced pressure and dodecane was added as an internal standard and the crude reaction mixture was analyzed by GC-MS.

Table 3-S1: Optimization of reaction conditions for the borylation of ((3-phenylpropyl)sulfonyl)benzene **3-1a-2**.



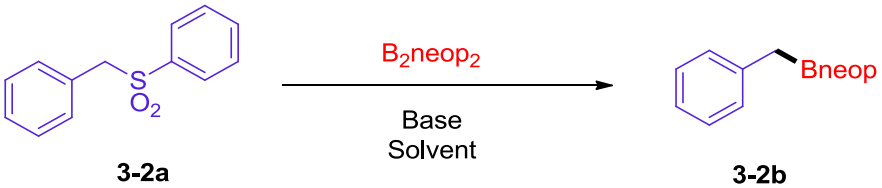
3-1a-2 **3-1b**

Entry	Base (eq.)	Solvent	B_2neop_2 (eq.)	T (℃)	Yield of **3-1b** (%)[a]
1	KOMe (3.0)	DMA	3.0	120	40
2	KO^{t}Bu (3.0)	DMA	3.0	120	65
3	NaO^{t}Bu (3.0)	DMA	3.0	120	93 (90)[b]
4	NaOMe (3.0)	DMA	3.0	120	0
5	CsF (3.0)	DMA	3.0	120	28
6	K_3PO_4 (3.0)	DMA	3.0	120	0
7	LiOMe (3.0)	DMA	3.0	120	17
8	LiO^{t}Bu (3.0)	DMA	3.0	120	25
9	NaO^{t}Bu (3.0)	DMF	3.0	120	26
10	NaO^{t}Bu (3.0)	DMSO	3.0	120	72
11	NaO^{t}Bu (3.0)	Me-Cy	3.0	120	68
12	NaO^{t}Bu (3.0)	MTBE	3.0	120	69
13	NaO^{t}Bu (3.0)	toluene	3.0	120	56
14	NaO^{t}Bu (3.0)	1,4-dioxane	3.0	120	50
15	NaO^{t}Bu (1.5)	DMA	1.5	120	47
16	NaO^{t}Bu (2.0)	DMA	2.0	120	67
17	NaO^{t}Bu (2.5)	DMA	2.5	120	76
18	NaO^{t}Bu (3.5)	DMA	3.5	120	83
19	NaO^{t}Bu (3.0)	DMA	3.0	80	61
20	NaO^{t}Bu (3.0)	DMA	3.0	90	81
21	NaO^{t}Bu (3.0)	DMA	3.0	100	86
22	NaO^{t}Bu (3.0)	DMA	3.0	110	89
23[c]	NaO^{t}Bu (3.0)	DMA	3.0	120	83
24[d]	NaO^{t}Bu (3.0)	DMA	3.0	120	0
25[e]	NaO^{t}Bu (3.0)	DMA	3.0	120	13

[a] Reaction conditions: **3-1a-2** (0.5 mmol, 1.0 equiv.) in solvent (0.5 M) for 5 h unless otherwise stated. The yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two runs. [b] Isolated yield. [c] 3 h. [d] B_2pin_2 instead of B_2neop_2. [e] B_2cat_2 instead of B_2neop_2.

General procedure of optimization for Table 3-S2. In an argon-filled glovebox, the alkyl aryl sulfone **3-2a** (0.5 mmol, 1.0 equiv.), dissolved in solvent (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. Base and the boron source were added. The reaction mixture was stirred at indicated temperature for 2 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). *n*-Dodecane was added as an internal standard and crude reaction mixture was analysed by GC-MS.

Table 3-S2: Optimization of reaction conditions for the borylation of (benzylsulfonyl)benzene **3-2a**.



3-2a **3-2b**

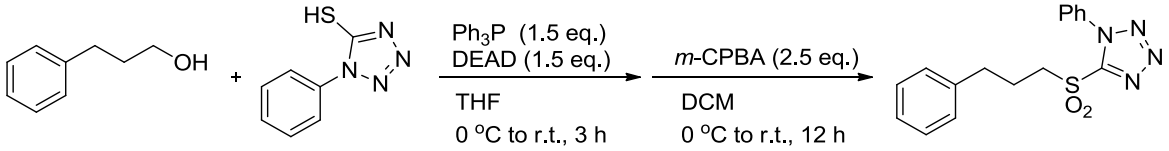
Entry	Base (eq.)	Solvent	B_2neop_2 (eq.)	T (℃)	Yield of **3-2b** (%)[a]
1	NaO^{t}Bu (3.0)	DMA	3.0	120	24
2	NaO^{t}Bu (1.5)	toluene	1.5	110	57
3	NaO^{t}Bu (1.5)	THF	1.5	110	66
4	NaO^{t}Bu (1.5)	MTBE	1.5	110	49
5	NaO^{t}Bu (1.5)	Me-Cy	1.5	110	53
6	NaO^{t}Bu (1.5)	1,4-dioxane	1.5	110	71
7	NaO^{t}Bu (1.5)	hexane	1.5	110	52
8	KO^{t}Bu (1.5)	1,4-dioxane	1.5	110	70
9	LiO^{t}Bu (1.5)	1,4-dioxane	1.5	110	67
10	LiOMe (1.5)	1,4-dioxane	1.5	110	36
11	KOMe (1.5)	1,4-dioxane	1.5	110	93
12	NaOMe (1.5)	1,4-dioxane	1.5	110	0
13	NaOAc (1.5)	1,4-dioxane	1.5	110	0
14	K_3PO_4 (1.5)	1,4-dioxane	1.5	110	0
15	KF (1.5)	1,4-dioxane	1.5	110	0
16	CsF (1.5)	1,4-dioxane	1.5	100	62
17	KOMe (1.5)	1,4-dioxane	1.5	60	10
18	KOMe (1.5)	1,4-dioxane	1.5	80	78
19	KOMe (1.5)	1,4-dioxane	1.5	100	90
21[b]	KOMe (1.1)	1,4-dioxane	1.1	110	73
22[c]	KOMe (1.2)	1,4-dioxane	1.2	110	93 (72)[e]
23[d]	KOMe (1.2)	1,4-dioxane	-	110	0

[a] Reaction conditions: **3-2a** (0.5 mmol, 1.0 equiv.) in solvent (1.0 M) for 2 h unless otherwise stated. The yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are

averages of two runs. [b] 1.1 equiv. KOMe and 1.1 equiv. B_2neop_2 were added. [c] 1.2 equiv. KOMe and 1.2 equiv. B_2neop_2 were added. [d] 1.2 equiv. B_2pin_2 was added. [e] isolated yield.

3.5.3 Synthesis of Sulfone Substrates

1-Phenyl-5-({3-phenylpropyl}sulfonyl)-1*H*-tetrazole 3-1a-1

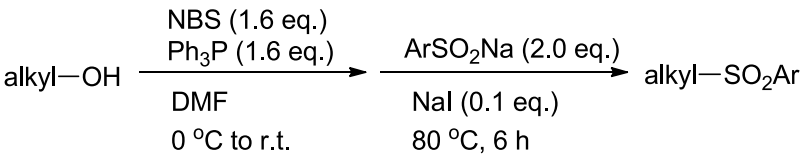


Compound **3-1a-1** was synthesized according to reported literature.[40] A glass tube was charged with alcohol (0.545 g, 4.0 mmol), PPh_3 (1.574 g, 6.0 mmol) and 1-phenyl-1*H*-tetrazole-5-thiol (1.069 g, 6.0 mmol) in THF (15 mL). DEAD (1.10 mL, 6.0 mmol) was slowly added at 0 ℃ to the solution, and mixture was stirred at room temperature for 3 h before the solvent was evaporated. The crude aryl sulfide was dissolved in DCM (12 mL) in an ice-water bath before *m*-CPBA (contains *ca*. 23 wt%, 10.0 mmol, 2.24 g) was added in portions. The mixture was allowed to warm to room temperature. After 12 h, saturated aqueous Na_2CO_3 was added, and the resulting solution was extracted with EtOAc (3 x 30 mL). The combined organic layer was dried over Na_2SO_4 and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product was isolated by flash column chromatography (hexane/ethyl acetate: 10/1) to afford compound **3-1a-1**.

Yield: 960 mg (2.92 mmol, 73%) of a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.68 – 7.57 (m, 5H), 7.32 (t, J = 7 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.20 – 7.18 (m, 2H), 3.73 – 3.69 (m, 2H), 2.84 (t, J = 7 Hz, 2H), 2.35 – 2.27 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 153.5, 139.3, 133.1, 131.6, 129.9, 128.9, 128.6, 126.9, 125.2, 55.3, 34.0, 23.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{17}N_4O_2S$ $[M+H]^+$ 329.1067 (329.1063).

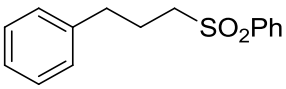
The spectroscopic data for **3-1a-1** match those reported in the literature.[40]

General procedure 1:



This method was based on the literature.[41] The alkyl alcohol (3.0 mmol), Ph_3P (4.8 mmol) and anhydrous DMF (10 mL) were added to a Schlenk flask equipped with a magnetic stirring bar at 0 ℃ under Ar. NBS (4.8 mmol) was added in small portions over 15 min. The reaction mixture was stirred while warming from 0 ℃ to r.t. over 30 min. To this solution was added a mixture of $PhSO_2Na$ (6.0 mmol) and NaI (0.3 mmol) in 3 portions over 10 min. The mixture was stirred for 6 h at 80 ℃, then diluted with EtOAc (20 mL) and 3% aq $Na_2S_2O_3$ (20 mL). The layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The organic layer was washed with water and brine, and then dried over anhydrous Na_2SO_4, filtred and the solvent removed under vacuum. The crude product was purified by recrystallization or flash column chromatography on silica gel with hexane/EtOAc to afford the sulfone.

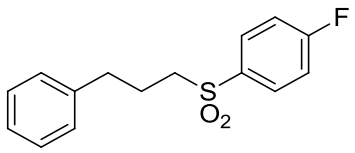
({3-Phenylpropyl}sulfonyl)benzene 3-1a-2



According to **General procedure 1** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and $PhSO_2Na$ (985 mg, 6.0 mmol, 2.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-1a-2** as a white solid (633 mg, 2.43 mmol, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.90 – 7.87 (m, 2H), 7.68 – 7.64 (m, 1H), 7.58 – 7.54 (m, 2H), 7.29 – 7.25 (m, 2H), 7.22 – 7.18 (m, 1H), 7.11 – 7.09 (m, 2H), 3.10 – 3.06 (m, 2H), 2.70 (t, J = 7 Hz, 2H), 2.09 – 2.01 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 139.9, 139.0, 133.8, 129.4, 128.7, 128.5, 128.1, 126.5, 55.5, 34.2, 24.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{17}O_2S$ $[M+H]^+$ 261.0944 (261.0943).

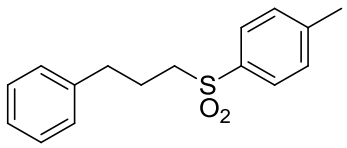
The spectroscopic data for **3-1a-2** match those reported in the literature.[43]

1-Fluoro-4-({3-phenylpropyl}sulfonyl)benzene 3-1a-3



According to **General procedure 1** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and 4-F$PhSO_2Na$ (1.093 g, 6.0 mmol, 2.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-1a-3** as a white solid (559 mg, 2.01 mmol, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.93 – 7.88 (m, 2H), 7.31 – 7.19 (m, 5H), 7.12 – 7.10 (m, 2H), 3.10 – 3.06 (m, 2H), 2.71 (t, *J* = 7 Hz, 2H), 2.09 – 2.01 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 165.9 (d, *J* = 254 Hz), 139.8, 135.1 (d, *J* = 3 Hz), 131.0 (d, *J* = 9 Hz), 128.7, 128.5, 126.6, 116.7 (d, *J* = 23 Hz), 55.6, 34.1, 24.4. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -103.3 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{16}FO_2S$ $[M+H]^+$ 279.0850 (279.0848).

1-Methyl-4-({3-phenylpropyl}sulfonyl)benzene 3-1a-6

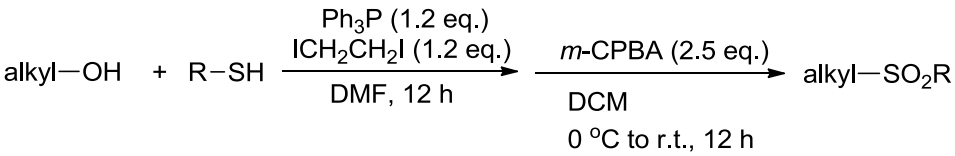


According to **General procedure 1** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and 4-Me$PhSO_2Na$ (1.069 g, 6.0 mmol, 2.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-1a-6** as a white solid (633 mg, 2.31 mmol, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8 Hz, 2H), 7.34 (d, *J* = 8 Hz, 2H), 7.27 (dd, *J* = 6, 9 Hz, 2H), 7.20 (dd, *J* = 6, 9 Hz, 1H), 7.10 (dd, *J* = 7 Hz, 2H), 3.08 – 3.04 (m, 2H), 2.69 (t, *J* = 7 Hz, 2H), 2.45 (s, 3H), 2.07 – 1.99 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 144.8,

140.0, 136.1, 130.0, 128.7, 128.5, 128.2, 126.5, 55.6, 34.2, 24.4, 21.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}O_2S$ $[M+H]^+$ 275.1100 (275.1098).

The spectroscopic data for **3-1a-6** match those reported in the literature.[42]

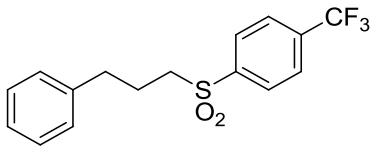
General procedure 2:



This method was based on the literature.[44] The alkyl alcohol (3.0 mmol), Ph_3P (3.6 mmol) and anhydrous DMF (10 mL) were added to a Schlenk flask equipped with a magnetic stirring bar under Ar. 1,2-Diiodoethane (3.6 mmol) was then added and the mixture was stirred for 2 min until the 1,2-diiodoethane was completely dissolved. Thiol (9.0 mmol) was added subsequently and the mixture was stirred at room temperature for 12 h, then diluted with DCM (20 mL). The mixture was washed with water (3 x 20 mL), the combined organic phases were dried over anhydrous Na_2SO_4, filtred and the solvent was removed under vacuum.

The crude aryl sulfide was dissolved in DCM (10 mL) in an ice-water bath before *m*-CPBA (contains *ca*. 23 wt%, 7.5 mmol, 1.68 g) was added in portions. The mixture was allowed to warm to room temperature. After 12 h, saturated aqueous Na_2CO_3 was added and the resulting solution was extracted with EtOAc (3 x 20 mL). The combined organic layer was dried over Na_2SO_4, and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product was purified by flash column chromatography (hexane/ethyl acetate: 10/1).

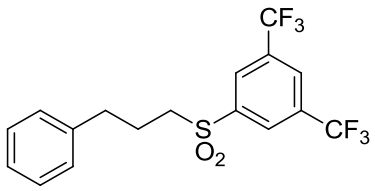
1-({3-Phenylpropyl}sulfonyl)-4-(trifluoromethyl)benzene 3-1a-4



According to **General procedure 2** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and 4-CF_3PhSH (1.603 g, 9.0 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-1a-4** as a white solid (630 mg, 1.92 mmol, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.02 (d, J = 8 Hz, 2H), 7.83 (d, J = 8 Hz, 2H), 7.27 (t, J = 7 Hz, 2H), 7.21 (dd, J = 6, 9 Hz, 1H), 7.10 (d, J = 7 Hz, 2H), 3.11 – 3.08 (m, 2H), 2.72 (t, J = 7 Hz, 2H), 2.10 – 2.03 (m, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 142.7, 139.7, 135.6 (q, J = 33 Hz), 128.9, 128.8, 128.5, 126.7, 126.6 (q, J = 4 Hz), 123.2 (q, J = 273 Hz), 55.4, 34.2, 24.2. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -63.2 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{16}F_3O_2S$ $[M+H]^+$ 329.0818 (329.0814).

The spectroscopic data for **3-1a-4** match those reported in the literature.[42]

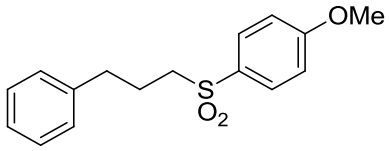
1-({3-Phenylpropyl}sulfonyl)-3,5-bis(trifluoromethyl)benzene 3-1a-5



According to **General procedure 2** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and 3,5-CF_3PhSH (2.215 g, 9.0 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-1a-5** as a white solid (654 mg, 1.65 mmol, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.33 (s, 2H), 8.15 (s, 1H), 7.30 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 7.11 – 7.09 (m, 2H), 3.15 – 3.12 (m, 2H), 2.76 (t, J = 8 Hz, 2H), 2.15 – 2.09 (m, 2H). **^{13}C{^{1}H} NMR** (120 MHz, $CDCl_3$): δ = 142.2, 139.3, 133.5 (q, J =

34 Hz), 128.9, 128.6 (q, J = 4 Hz), 128.5, 127.6, 126.9, 122.5 (q, J = 273 Hz), 55.4, 34.0, 23.9. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -62.9 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{15}F_6O_2S$ $[M+H]^+$ 397.0691 (397.0687).

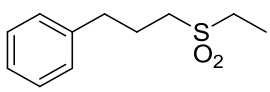
1-Methoxy-4-({3-phenylpropyl}sulfonyl)benzene 3-1a-7



According to **General procedure 2** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and 4-OMePhSH (1.262 g, 9.0 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-1a-7** as a white solid (633 mg, 2.31 mmol, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 9 Hz, 2H), 7.27 (dd, J = 6, 9 Hz, 2H), 7.20 (dd, J = 6, 9 Hz, 1H), 7.12 – 7.10 (m, 2H), 7.00 (d, J = 9 Hz, 2H), 3.87 (s, 3H), 3.08 – 3.04 (m, 2H), 2.69 (t, J = 7 Hz, 2H), 2.07 – 1.99 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 163.7, 140.0, 130.5, 130.2, 128.6, 128.4, 126.4, 114.5, 55.77, 55.75, 34.1, 24.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}O_3S$ $[M+H]^+$ 291.1049 (291.1044).

The spectroscopic data for **3-1a-7** match those reported in the literature.[42]

(3-{Ethylsulfonyl}propyl)benzene 3-1a-8

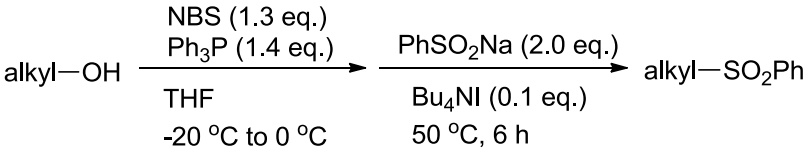


According to **General procedure 2** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and ethanethiol (559 mg, 9.0 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-1a-8** as a white solid (535 mg, 2.52 mmol, 84%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.32 – 7.29 (m, 2H), 7.24 – 7.17 (m,

3H), 2.98 – 2.90 (m, 4H), 2.78 (t, J = 7 Hz, 2H), 2.21 – 2.13 (m, 2H), 1.34 (t, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 139.9, 128.7, 128.5, 126.6, 50.9, 47.1, 34.3, 23.4, 6.62. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{17}O_2S$ $[M+H]^+$ 213.0944 (213.0938).

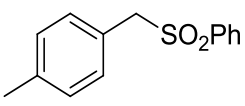
The spectroscopic data for **3-1a-8** match those reported in the literature.[43]

General procedure 3:



This method was according to reported literature.[2] Alkyl alcohol (3.0 mmol), Ph_3P (4.2 mmol) and THF (10 mL) were added to a Schlenk flask equipped with a magnetic stirring bar at –20 ℃ under Ar. NBS (3.9 mmol) was added in small portions over 15 min. The reaction mixture was stirred while warming from –20 ℃ to 0 ℃ for 30 min. A mixture of $PhSO_2Na$ (6.0 mmol) and Bu_4NI (0.3 mmol) was added in 3 portions over 10 min to this solution. The mixture was stirred for 6 h at 50 ℃, then diluted with EtOAc (20 mL) and 3% aqueous $Na_2S_2O_3$ (20 mL). The layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The organic layer was washed with water and brine, and then dried over anhydrous Na_2SO_4, filtred and the solvent was removed under vacuum. The crude product was purified by recrystallization or flash column chromatography on silica gel with hexane/EtOAc to afford the sulfone.

1-Methyl-4-({phenylsulfonyl}methyl)benzene 3-3a

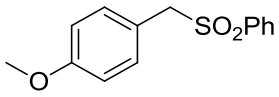


According to **General procedure 3** with *p*-tolylmethanol (366 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-3a** as a

white solid (672 mg, 2.73 mmol, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 8 Hz, 2H), 7.60 (t, J = 8 Hz, 1H), 7.44 (t, J = 8 Hz, 2H), 7.06 (d, J = 8 Hz, 2H), 6.95 (d, J = 8 Hz, 2H), 4.27 (s, 2H), 2.31 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 138.8, 137.9, 133.8, 130.7, 129.3, 128.9, 128.7, 124.9, 62.6, 21.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{15}O_2S$ $[M+H]^+$ 247.0787 (247.0785).

The spectroscopic data for **3-3a** match those reported in the literature.[45]

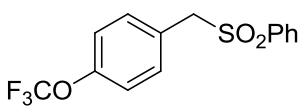
1-Methoxy-4-({phenylsulfonyl}methyl)benzene 3-4a



According to **General procedure 3** with (4-methoxyphenyl)methanol (414 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-4a** as a white solid (684 mg, 2.61 mmol, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 7 Hz, 2H), 7.60 (t, J = 8 Hz, 1H), 7.45 (t, J = 8 Hz, 2H), 6.99 (d, J = 9 Hz, 2H), 6.78 (d, J = 9 Hz, 2H), 4.25 (s, 2H), 3.78 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 160.0, 137.9, 133.8, 132.1, 129.0, 128.7, 120.0, 114.1, 62.3, 55.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{15}O_3S$ $[M+H]^+$ 263.0736 (263.0728).

The spectroscopic data for **3-4a** match those reported in the literature.[45]

1-({Phenylsulfonyl}methyl)-4-(trifluoromethoxy)benzene 3-5a

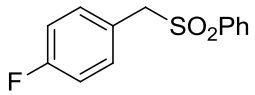


According to **General procedure 3** with (4-(trifluoromethoxy)phenyl)methanol (576 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield

the product **3-5a** as a white solid (692 mg, 2.19 mmol, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.66 – 7.61 (m, 3H), 7.47 (t, J = 8 Hz, 2H), 7.14 – 7.10 (m, 4H), 4.30 (s, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 149.8 (q, J = 3 Hz), 137.8, 134.1, 132.5, 129.2, 128.7, 127.0, 121.1, 120.5 (q, J = 256 Hz), 62.2. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -57.9 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{12}F_3O_3S$ $[M+H]^+$ 317.0454 (317.0449).

The spectroscopic data for **3-5a** match those reported in the literature.[46]

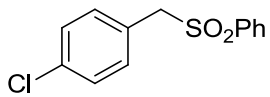
1-Fluoro-4-({phenylsulfonyl}methyl)benzene 3-6a



According to **General procedure 3** with (4-fluorophenyl)methanol (378 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-6a** as a white solid (630 mg, 2.52 mmol, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.65 – 7.60 (m, 3H), 7.47 (t, J = 8 Hz, 2H), 7.08 – 7.03 (m, 2H), 6.95 (t, J = 8 Hz, 2H), 4.28 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 163.1 (d, J = 247 Hz), 137.6, 134.0, 132.7 (d, J = 8 Hz), 129.1, 128.7, 124.0 (d, J = 3 Hz), 115.8 (d, J = 22 Hz), 62.1. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -112.3 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{12}FO_2S$ $[M+H]^+$ 251.0537 (251.0534).

The spectroscopic data for **3-6a** match those reported in the literature.[45]

1-Chloro-4-({phenylsulfonyl}methyl)benzene 3-7a

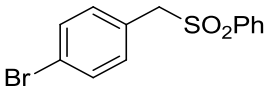


According to **General procedure 3** with (4-chlorophenyl)methanol (428 mg, 3.0 mmol, 1.0

equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-7a** as a white solid (664 mg, 2.49 mmol, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.66 – 7.60 (m, 3H), 7.47 (t, *J* = 8 Hz, 2H), 7.23 (d, *J* = 8 Hz, 2H), 7.01 (d, *J* = 8 Hz, 2H), 4.27 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 137.7, 135.1, 134.1, 132.2, 129.2, 128.9, 128.7, 126.7, 62.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{12}ClO_2S$ $[M+H]^+$ 267.0241 (267.0235).

The spectroscopic data for **3-7a** match those reported in the literature.[46]

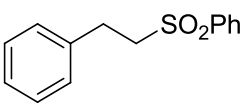
1-Bromo-4-({phenylsulfonyl}methyl)benzene 3-8a



According to **General procedure 3** with (4-bromophenyl)methanol (561 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-8a** as a white solid (644 mg, 2.07 mmol, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.66 – 7.61 (m, 3H), 7.48 (t, *J* = 8 Hz, 2H), 7.39 (d, *J* = 8 Hz, 2H), 6.95 (d, *J* = 8 Hz, 2H), 4.26 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 137.6, 134.1, 132.5, 131.9, 129.2, 128.7, 127.2, 123.4, 62.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{12}BrO_2S$ $[M+H]^+$ 310.9736 (310.9730).

The spectroscopic data for **3-8a** match those reported in the literature.[46]

({2-Phenylethyl}sulfonyl)benzene 3-9a

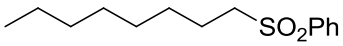


According to **General procedure 1** with 2-phenylethanol (366 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-9a** as a white solid (554 mg, 2.25 mmol, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.95 – 7.92 (m,

2H), 7.69 – 7.64 (m, 1H), 7.60 – 7.55 (m, 2H), 7.28 – 7.23 (m, 2H), 7.21 – 7.17 (m, 1H), 7.12 – 7.09 (m, 2H), 3.37 – 3.33 (m, 2H), 3.06 – 3.02 (m, 2H). **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ = 139.0, 137.5, 134.0, 129.5, 128.9, 128.4, 128.2, 127.0, 57.6, 28.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{15}O_2S$ $[M+H]^+$ 247.0787 (247.0782).

The spectroscopic data for **3-9a** match those reported in the literature.[47]

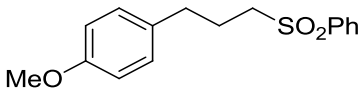
(Octylsulfonyl)benzene 3-10a



According to **General procedure 1** with octan-1-ol (390 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-10a** as a white solid (587 mg, 2.31 mmol, 77% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.93 – 7.89 (m, 2H), 7.68 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 3.10 – 3.05 (m, 2H), 1.75 – 1.65 (m, 2H), 1.36 – 1.22 (m, 10H), 0.85 (t, J = 7 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$): δ = 139.4, 133.8, 129.4, 128.2, 56.5, 31.8, 29.1, 29.0, 28.4, 22.8, 22.7, 14.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{23}O_2S$ $[M+H]^+$ 255.1413 (255.1409).

The spectroscopic data for **3-10a** match those reported in the literature.[48]

1-Methoxy-4-(3-{phenylsulfonyl}propyl)benzene 3-11a

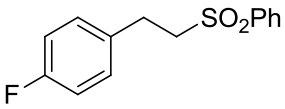


According to **General procedure 1** with 3-(4-methoxyphenyl)propan-1-ol (499 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-11a** as a white solid (653 mg, 2.25 mmol, 75% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.91 – 7.87 (m, 2H), 7.68 – 7.62 (m, 1H), 7.59 – 7.53 (m, 2H), 7.02 (d, J = 9 Hz, 2H), 6.81 (d, J = 9 Hz,

2H), 3.78 (s, 3H), 3.08 – 3.03 (m, 2H), 2.64 (t, J = 6 Hz, 2H), 2.06 – 1.96 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 158.3, 139.3, 133.8, 132.0, 129.5, 129.4, 128.2, 114.1, 55.6, 55.4, 33.3, 24.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}O_3S$ $[M+H]^+$ 291.1049 (291.1045).

The spectroscopic data for **3-11a** match those reported in the literature.[49]

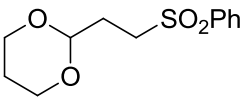
1-Fluoro-4-(2-{phenylsulfonyl}ethyl)benzene 3-12a



According to **General procedure 1** with 2-(4-fluorophenyl)ethanol (420 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-12a** as a white solid (554 mg, 2.13 mmol, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.94 – 7.91 (m, 2H), 7.69 – 7.65 (m, 1H), 7.60 – 7.55 (m, 2H), 7.10 – 7.05 (m, 2H), 6.97 – 6.91 (m, 2H), 3.35 – 3.31 (m, 2H), 3.05 – 3.01 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 161.9 (d, J = 244 Hz), 139.0, 134.0, 133.2 (d, J = 3 Hz), 129.9 (d, J = 8 Hz), 129.5, 128.2, 115.8 (d, J = 22 Hz), 57.6, 28.0. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -115.6 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{14}FO_2S$ $[M+H]^+$ 265.0693 (265.0691).

The spectroscopic data for **3-12a** match those reported in the literature.[47]

2-(2-{Phenylsulfonyl}ethyl)-1,3-dioxane 3-14a

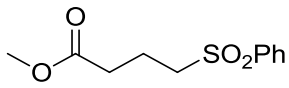


According to **General procedure 1** with 2-(1,3-dioxan-2-yl)ethanol (396 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-14a** as a white solid (599 mg, 2.34 mmol, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.91 –

7.88 (m, 2H), 7.67 – 7.62 (m, 1H), 7.58 – 7.53 (m, 2H), 4.62 (t, *J* = 4 Hz, 1H), 4.03 (dd, *J* = 5, 11 Hz, 2H), 3.70 (td, *J* = 2, 12 Hz, 2H), 3.26 – 3.22 (m, 2H), 2.02 – 1.91 (m, 3H), 1.33 – 1.28 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 138.9, 133.8, 129.4, 128.2, 99.3, 66.9, 51.1, 28.5, 25.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}O_4S$ $[M+H]^+$ 257.0842 (257.0838).

The spectroscopic data for **3-14a** match those reported in the literature.[50]

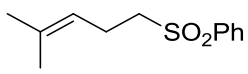
Methyl 4-(phenylsulfonyl)butanoate 3-15a



According to **General procedure 1** with methyl 4-hydroxybutanoate (354 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 5/1) to yield the product **3-15a** as a white solid (378 mg, 1.56 mmol, 52% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.93 – 7.89 (m, 2H), 7.69 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 3.64 (s, 3H), 3.20 – 3.15 (m, 2H), 2.46 (t, *J* = 7 Hz, 2H), 2.07 – 1.98 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 172.6, 139.0, 133.9, 129.5, 128.2, 55.2, 51.9, 32.1, 18.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{15}O_4S$ $[M+H]^+$ 243.0686 (243.0681).

The spectroscopic data for **3-15a** match those reported in the literature.[51]

({4-Methylpent-3-en-1-yl)sulfonyl)benzene 3-16a

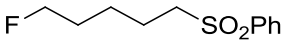


According to **General procedure 3** with 4-methylpent-3-en-1-ol (300 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-16a** as a white solid (430 mg, 1.92 mmol, 64% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.94 – 7.90 (m, 2H), 7.69 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 5.00 – 4.93 (m, 1H),

3.11 – 3.05 (m, 2H), 2.40 (dd, *J* = 8, 16 Hz, 2H), 1.63 (d, *J* = 1 Hz, 3H), 1.54 (s, 3H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$): δ = 139.4, 135.2, 133.8, 129.4, 128.2, 119.4, 56.1, 25.7, 21.8, 17.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}O_2S$ $[M+H]^+$ 225.0944 (225.0939).

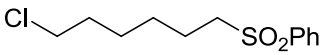
The spectroscopic data for **3-16a** match those reported in the literature.[52]

({5-fluoropentyl}sulfonyl)benzene 3-17a



According to **General procedure 1** with 5-fluoropentan-1-ol (318 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-17a** as a white solid (497 mg, 2.16 mmol, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.92 – 7.89 (m, 2H), 7.69 – 7.64 (m, 1H), 7.60 – 7.55 (m, 2H), 4.46 (t, *J* = 6 Hz, 1H), 4.34 (t, *J* = 6 Hz, 1H), 3.12 – 3.08 (m, 2H), 1.80 – 1.60 (m, 4H), 1.53 – 1.45 (m, 2H). **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ = 139.1, 133.9, 129.4, 128.1, 83.5 (d, *J* = 164 Hz), 55.2, 29.9 (d, *J* = 19 Hz), 24.3 (d, *J* = 5 Hz), 22.4. **$^{19}F\{^{1}H\}$ NMR** (376 MHz, $CDCl_3$): δ = -218.8 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{16}FO_2S$ $[M+H]^+$ 231.0850 (231.0844).

({6-Chlorohexyl}sulfonyl)benzene 3-18a

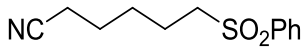


According to **General procedure 1** with 6-chlorohexan-1-ol (410 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-18a** as a white solid (594 mg, 2.28 mmol, 76% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.93 – 7.89 (m, 2H), 7.69 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 3.52 – 3.34 (m, 2H), 3.11 – 3.06 (m, 2H), 1.86 – 1.68 (m, 4H), 1.48 – 1.33 (m, 4H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$): δ

= 139.3, 133.8, 129.4, 128.2, 56.2, 44.9, 32.2, 27.7, 26.4, 22.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{18}ClO_2S$ $[M+H]^+$ 261.0711 (261.0708).

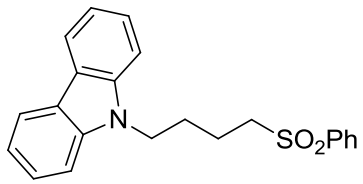
The spectroscopic data for **3-18a** match those reported in the literature.[53]

6-(Phenylsulfonyl)hexanenitrile 3-19a



According to **General procedure 1** with 6-hydroxyhexanenitrile (339 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-19a** as a white solid (470 mg, 1.98 mmol, 66% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.93 – 7.89 (m, 2H), 7.79 – 7.65 (m, 1H), 7.61 – 7.55 (m, 2H), 3.12 – 3.07 (m, 2H), 2.33 (t, J = 7 Hz, 2H), 1.81 – 1.51 (m, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 139.2, 134.0, 129.5, 128.1, 119.3, 55.9, 27.4, 25.0, 22.1, 17.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{16}NO_2S$ $[M+H]^+$ 238.0896 (238.0890).

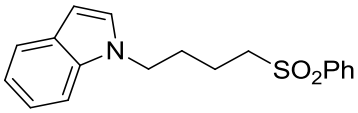
9-(4-{Phenylsulfonyl}butyl)-9*H*-carbazole 3-20a



According to **General procedure 1** with 4-(9*H*-carbazol-9-yl)butan-1-ol (718 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-20a** as a white solid (806 mg, 2.22 mmol, 74% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.12 – 8.08 (m, 2H), 7.67 – 7.63 (m, 2H), 7.52 – 7.43 (m, 5H), 7.38 – 7.35 (m, 2H), 7.26 – 7.21 (m, 2H), 4.32 (t, J = 7 Hz, 2H), 4.07 – 3.99 (m, 1H), 3.67 – 3.54 (m, 1H), 2.00 – 1.91 (m, 2H), 1.72 – 1.63 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 144.5, 140.4,

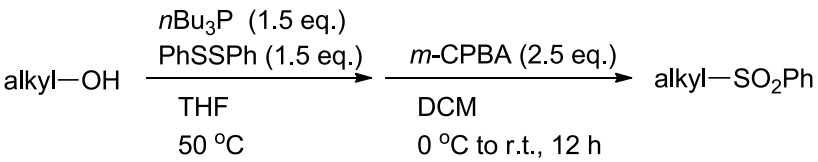
132.3, 129.2, 125.8, 125.3, 123.0, 120.5, 119.0, 108.7, 64.0, 42.5, 27.5, 25.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{22}NO_2S$ $[M+H]^+$ 364.1366 (364.1362).

1-(4-{Phenylsulfonyl}butyl)-1*H*-indole 3-21a



According to **General procedure 1** with 4-(1*H*-indol-1-yl)butan-1-ol (568 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-21a** as a white solid (667 mg, 2.13 mmol, 71% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.82 – 7.78 (m, 2H), 7.66 – 7.60 (m, 1H), 7.54 – 7.48 (m, 2H), 7.28 – 7.25 (m, 1H), 7.22 – 7.16 (m, 1H), 7.13 – 7.07 (m, 1H), 7.00 (d, *J* = 3 Hz, 1H), 6.46 (dd, *J* = 3, 1 Hz, 1H), 4.12 (t, *J* = 7 Hz, 2H), 3.03 – 2.98 (m, 2H), 2.00 – 1.90 (m, 2H), 1.78 – 1.67 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 139.0, 135.9, 133.9, 129.4, 128.8, 128.1, 127.7, 121.7, 121.3, 119.6, 109.3, 101.6, 55.7, 45.8, 28.9, 20.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{20}NO_2S$ $[M+H]^+$ 314.1209 (314.1207).

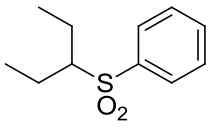
General procedure 4:



A glass tube was charged with alkyl alcohol (3.0 mmol, 1.0 equiv.), diphenyl disulfide (983 mg, 4.5 mmol, 1.5 equiv.) and *n*Bu_3P (1.12 mL, 4.5 mmol, 1.5 equiv.) in dry THF (10 mL) at room temperature, and the mixture was heated at 50 ℃ for 12 h. The mixture was quenched with 2N NaOH and extracted with EtOAc three times. The combined organic phase was washed with brine and concentrated under reduced pressure.

The crude aryl sulfide was dissolved in DCM (9 mL) in an ice-water bath before *m*-CPBA (*ca*. 23 wt%, 7.5 mmol, 1.68 g) was added in portions. The mixture was allowed to warm to room temperature. After 12 h, saturated aqueous Na_2CO_3 was added, and the resulting solution was extracted with EtOAc (3 x 30 mL). The combined organic layer was dried over Na_2SO_4 and filtred through a pad of Celite (Ø 3 mm x 8 mm). The crude product was purified by flash column chromatography on silica gel with hexane/EtOAc to afford the sulfone.

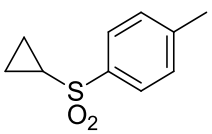
(Pentan-3-ylsulfonyl)benzene 3-22a



According to **General procedure 4** with pentan-3-ol (264 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-22a** as a white solid (350 mg, 1.65 mmol, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.88 – 7.86 (m, 2H), 7.65 – 7.61 (m, 1H), 7.56 – 7.52 (m, 2H), 2.82 – 2.76 (m, 1H), 1.91 – 1.81 (m, 2H), 1.72 – 1.61 (m, 2H), 0.98 (t, J = 8 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 138.5, 133.6, 129.2, 128.8, 67.1, 20.3, 11.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{17}O_2S$ $[M+H]^+$ 213.0944 (213.0939).

The spectroscopic data for **3-22a** match those reported in the literature.[54]

1-(Cyclopropylsulfonyl)-4-methylbenzene 3-23a

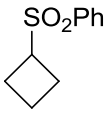


According to **General procedure 4** with cyclopropanol (174 mg, 3.0 mmol, 1.0 equiv.) and 4-$MePhSO_2Na$ (3.3 mmol, 1.1 equiv.), the reaction mixture was purified by column chromatography

on silica gel (hexane/EtOAc = 10/1) to yield the product **3-23a** as a white solid (312 mg, 1.59 mmol, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 2.46 – 2.39 (m, 1H), 2.42 (s, 3H), 1.32 – 1.27 (m, 2H), 1.02 – 0.96 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 144.3, 137.7, 129.9, 127.6, 33.1, 21.7, 6.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{13}O_2S$ $[M+H]^+$ 197.0631 (197.0627).

The spectroscopic data for **3-23a** match those reported in the literature.[55]

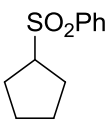
(Cyclobutylsulfonyl)benzene 3-24a



According to **General procedure 4** with cyclobutanol (216 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-24a** as a white solid (283 mg, 1.44 mmol, 48% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.87 – 7.85 (m, 2H), 7.65 – 7.61 (m, 1H), 7.56 – 7.52 (m, 2H), 3.84 – 3.76 (m, 1H), 2.61 – 2.51 (m, 2H), 2.21 – 2.13 (m, 2H), 2.01 – 1.95 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 138.3, 133.7, 129.3, 128.4, 57.0, 22.9, 16.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{13}O_2S$ $[M+H]^+$ 197.0631 (197.0627).

The spectroscopic data for **3-24a** match those reported in the literature.[56]

(Cyclopentylsulfonyl)benzene 3-25a

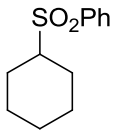


According to **General procedure 4** with cyclopentanol (258 mg, 3.0 mmol, 1.0 equiv.), the

reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-25a** as a white solid (309 mg (1.47 mmol, 49% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.91 – 7.89 (m, 2H), 7.66 – 7.62 (m, 1H), 7.58 – 7.53 (m, 1H), 3.53 – 3.45 (m, 1H), 2.11 – 2.02 (m, 2H), 1.91 – 1.82 (m, 2H), 1.81 – 1.71 (m, 2H), 1.64 – 1.54 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 139.0, 133.6, 129.3, 128.5, 64.2, 27.3, 26.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{15}O_2S$ $[M+H]^+$ 211.0787 (211.0781).

The spectroscopic data for **3-25a** match those reported in the literature.[42]

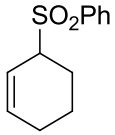
(Cyclohexylsulfonyl)benzene 3-26a



According to **General procedure 4** with cyclohexanol (300 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-26a** as a white solid (376 mg, 1.68 mmol, 56% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.89 – 7.85 (m, 2H), 7.68 – 7.62 (m, 1H), 7.59 – 7.53 (m, 2H), 2.95 – 2.85 (m, 1H), 2.09 – 2.03 (m, 2H), 1.90 – 1.83 (m, 2H), 1.69 – 1.62 (m, 1H), 1.47 – 1.34 (m, 2H), 1.29 – 1.09 (m, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 137.4, 133.7, 129.2, 129.1, 63.6, 25.6, 25.23, 25.19. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}O_2S$ $[M+H]^+$ 225.0944 (225.0938).

The spectroscopic data for **3-26a** match those reported in the literature.[57]

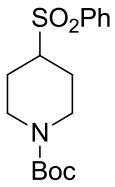
(Cyclohex-2-en-1-ylsulfonyl)benzene 3-27a



According to **General procedure 4** with cyclohex-2-enol (294 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-27a** as a colorless liquid (280 mg, 1.26 mmol, 42% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.90 – 7.86 (m, 2H), 7.68 – 7.62 (m, 1H), 7.58 – 7.52 (m, 2H), 6.12 – 6.05 (m, 1H), 5.78 (d, J = 10 Hz, 1H), 3.80 – 3.72 (m, 1H), 2.01 – 1.72 (m, 5H), 1.56 – 1.43 (m, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 137.5, 135.5, 133.8, 129.3, 129.1, 118.6, 61.9, 24.5, 22.8, 19.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{15}O_2S$ $[M+H]^+$ 223.0787 (223.0786).

The spectroscopic data for **3-27a** match those reported in the literature.[57]

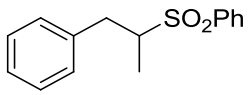
<u>*tert*-Butyl 4-(phenylsulfonyl)piperidine-1-carboxylate 3-28a</u>



According to **General procedure 4** with N-Boc 4-hydroxupiperidine (604 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-28a** as a white solid (498 mg, 1.53 mmol, 51% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.89 – 7.85 (m, 2H), 7.71 – 7.65 (m, 1H), 7.61 – 7.55 (m, 2H), 4.22 (d, J = 13.5 Hz, 2H), 3.08 – 2.98 (m, 1H), 2.65 (t, J = 13 Hz, 2H), 1.97 (d, J = 13 Hz, 2H), 1.67 – 1.53 (m, 2H), 1.42 (s, 9H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 154.5, 136.8, 134.1, 129.4, 129.2, 80.3, 61.9, 42.7, 28.5, 25.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{24}NO_4S$ $[M+H]^+$ 326.1421 (326.1415).

The spectroscopic data for **3-28a** match those reported in the literature.[58]

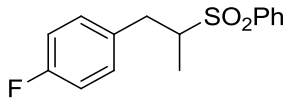
((1-Phenylpropan-2-yl)sulfonyl)benzene 3-29a



According to **General procedure 4** with 1-phenylpropan-2-ol (408 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-29a** as a white solid (421 mg, 1.62 mmol, 54% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.95 – 7.93 (m, 2H), 7.71 – 7.66 (m, 1H), 7.62 – 7.58 (m, 2H), 7.30 – 7.20 (m, 3H), 7.11 – 7.09 (m, 2H), 3.43 (dd, *J* = 3, 13 Hz, 1H), 3.31 – 3.22 (m, 1H), 2.54 (dd, *J* = 11, 13 Hz, 1H), 1.15 (d, *J* = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 137.1, 137.0, 133.9, 129.3, 129.2, 129.1, 128.8, 127.0, 61.7, 35.4, 12.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{17}O_2S$ $[M+H]^+$ 261.0944 (261.09337).

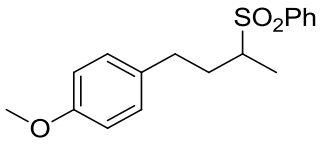
The spectroscopic data for **3-29a** match those reported in the literature.[59]

1-Fluoro-4-(2-(phenylsulfonyl)propyl)benzene 3-30a



According to **General procedure 4** with 1-(4-fluorophenyl)propan-2-ol (462 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-30a** as a white solid (417 mg, 1.50 mmol, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.95 – 7.92 (m, 2H), 7.71 – 7.66 (m, 1H), 7.62 – 7.57 (m, 2H), 7.08 – 7.04 (m, 2H), 6.99 – 6.94 (m, 2H), 3.40 (dd, *J* = 3, 13 Hz, 1H), 3.26 – 3.17 (m, 1H), 2.54 (dd, *J* = 11, 13 Hz, 1H), 1.14 (d, *J* = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 161.9 (d, *J* = 244 Hz), 137.1, 134.0, 132.7 (d, *J* = 3 Hz), 130.7 (d, *J* = 8 Hz), 129.4, 129.1, 115.7 (d, *J* = 22 Hz), 61.7 (d, *J* = 2 Hz), 34.6, 12.8. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -115.6 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{16}FO_2S$ $[M+H]^+$ 279.0850 (279.0847).

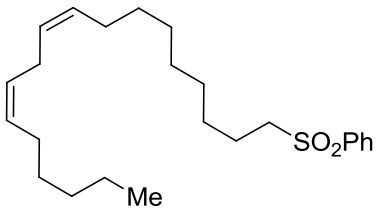
1-Methoxy-4-(3-(phenylsulfonyl)butyl)benzene 3-31a



According to **General procedure 4** with 1-methoxy-4-(3-(phenylsulfonyl)butyl)benzene (462 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-31a** as a white solid (557 mg, 1.83 mmol, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.85 – 7.83 (m, 2H), 7.64 (t, J = 7 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.01 (d, J = 8 Hz, 2H), 6.80 (d, J = 8 Hz, 2H), 3.78 (s, 3H), 3.06 – 2.97 (m, 1H), 2.79 – 2.72 (m, 1H), 2.56 – 2.49 (m, 1H), 2.32 – 2.23 (m, 1H), 1.73 – 1.63 (m, 1H), 1.30 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 158.2, 137.3, 133.7, 132.2, 129.3, 129.2, 129.1, 114.1, 59.2, 55.4, 31.6, 31.0, 13.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{21}O_3S$ $[M+H]^+$ 305.1206 (305.1203).

The spectroscopic data for **3-31a** match those reported in the literature.[60]

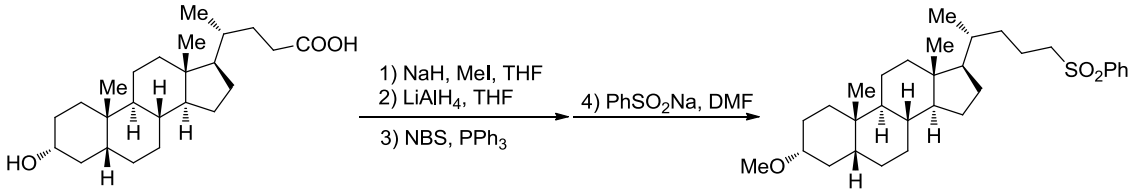
((9*Z*,12*Z*)-octadeca-9,12-dien-1-ylsulfonyl)benzene 3-32a



According to **General procedure 3** with linolenyl alcohol (792 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-32a** as a colorless oil (656 mg, 1.68 mmol, 56% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.92 – 7.89 (m, 2H), 7.67 – 7.63 (m, 1H), 7.59 – 7.54 (m, 2H), 5.44 – 5.31 (m, 4H), 3.09 – 3.05 (m, 2H), 2.77 – 2.64 (m, 2H), 2.04 – 1.92 (m, 4H), 1.73 – 1.65 (m, 2H), 1.35 – 1.22

(m, 16H), 0.87 (t, J = 8 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ = 139.2, 133.7, 131.2, 131.0, 129.4, 128.8, 128.6, 128.1, 56.4, 35.7, 32.64, 32.60, 31.5, 29.5, 29.3, 29.2, 29.1, 29.0, 28.3, 22.7, 22.6, 14.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{24}H_{39}O_2S$ $[M+H]^+$ 391.2665 (391.2657). **Anal.** for $C_{24}H_{38}O_2S$ calcd: C, 73.79; H, 9.81; S, 8.21. found: C, 73.70; H, 9.69; S, 8.40.

The synthesis of substrate 3-33a

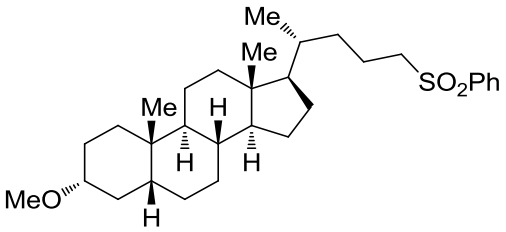


NaH (9 mmol, 3.0 equiv., 60 % dispersion in mineral oil) was added at 0 ℃ in portions to a solution of hyodeoxycholic acid (3 mmol, 1.0 equiv.) in THF (30 mL, 0.1 M). The reaction mixture was stirred for 3 h at room temperature. Afterwards, MeI (6 mmol, 2 equiv.) was slowly added and the mixture was stirred at 45 ^{o}C for 24 hours. The reaction mixture was quenched with saturated aqueous NH_4Cl at 0 ^{o}C. The aqueous layer was extracted three times with EtOAc and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

$LiAlH_4$ (9 mmol, 3 equiv.) was added slowly at 0 ℃ to a solution of the crude product in 20 mL anhydrous THF. The mixture was allowed to warm to room temperature and stirred for another 4 h, then quenched with 1.0 M NaOH. We extracted the mixture three times with CH_2Cl_2 and the combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. PPh_3 (1.2 equiv.) and NBS (1.2 equiv.) were added sequentially to a solution of the crude alcohol in 10 mL DCM in an ice bath. After 0.5 h stirring at room temperature, the reaction mixture was concentrated, and the crude material was purified by silica gel to deliver the primary bromide as a white solid.

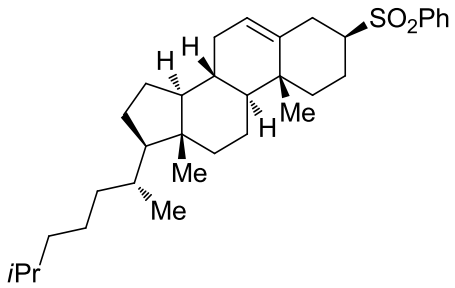
The primary bromide (1.5 mmol, 1.0 equiv.) and $PhSO_2Na$ (2.25 mmol, 1.5 equiv.) was dissolved in 5 mL DMF. The mixture was stirred for 12 h at 85 ℃, then diluted with EtOAc (20 mL) and 3% aqueous $Na_2S_2O_3$ (20 mL). The layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The organic layer was washed with water and brine, and then dried over anhydrous Na_2SO_4, filtred, and the solvent was removed under vacuum. The crude product was purified by flash column chromatography on silica gel with hexane/EtOAc: 5/1 to afford **3-33a**.

(3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-methoxy-10,13-dimethyl-17-((*R*)-5-(phenylsulfonyl)pentan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene 3-33a



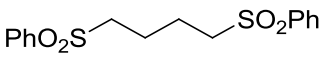
Yield: 631 mg (1.26 mmol, 42%) of a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.93 – 7.90 (m, 2H), 7.68 – 7.64 (m, 1H), 7.60 – 7.55 (m, 2H), 3.34 (s, 3H), 3.19 – 2.97 (m, 3H), 1.93 – 1.49 (m, 9H), 1.43 – 0.95 (m, 19H), 0.90 (s, 3H), 0.85 (d, J = 6 Hz, 3H), 0.59 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 139.3, 133.8, 129.4, 128.2, 80.5, 56.8, 56.5, 56.0, 55.7, 42.8, 42.1, 40.4, 40.2, 35.9, 35.6, 35.4, 35.0, 34.6, 32.8, 28.4, 27.4, 26.9, 26.5, 24.3, 23.5, 20.9, 19.6, 18.4, 12.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{31}H_{49}O_3S$ $[M+H]^+$ 501.3397 (501.3389). **Anal.** for $C_{31}H_{48}O_3S$ calcd: C, 74.35; H, 9.66; S, 6.40. found: C, 74.51; H, 9.71; S, 6.28.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-3-(phenylsulfonyl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene 3-34a



According to **General procedure 4** with cholesterol (1.16 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 5/1) to yield the product **3-34a** as a white solid (429 mg, 0.84 mmol, 28% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.73 – 7.71 (m, 2H), 7.54 – 7.52 (m, 3H), 5.41 – 5.25 (m, 1H), 4.25 – 4.17 (m, 1H), 2.50 – 2.18 (m, 2H), 2.06 – 1.69 (m, 6H), 1.60 – 1.23 (m, 10H), 1.21 – 0.91 (m, 10H), 0.99 (s, 3H), 0.90 (d, *J* = 7 Hz, 3H), 0.86 (dd, *J* = 2, 7 Hz, 6H), 0.66 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 145.7, 139.6, 132.1, 129.1, 125.2, 123.1, 79.5, 56.8, 56.2, 50.0, 42.4, 40.4, 40.3, 39.8, 39.6, 37.3, 36.6, 36.3, 35.9, 32.0, 31.9, 30.1, 30.0, 28.4, 28.1, 24.4, 23.9, 23.0, 22.7, 21.1, 19.4, 18.8, 12.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{33}H_{51}O_2S$ $[M+H]^+$ 511.3604 (511.3602). **Anal.** for $C_{33}H_{50}O_2S$ calcd: C, 77.59; H, 9.87; S, 6.28. found: C, 77.50; H, 9.78; S, 6.40.

1,4-Bis(phenylsulfonyl)butane 3-35a



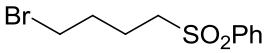
A glass tube was charged with KOH (0.387 g, 6.9 mmol) and thiopheol (0.68 mL, 6.6 mmol) in ethanol (10 mL) and stirred for 1 h. 1,4-Dibromobutane (0.36 mL, 3.0 mmol) in ethanol (5 mL) was slowly added at 0 ℃ to the solution, and the mixture was stirred at room temperature for 12 h and filtred through a pad of Celite (Ø 3 mm x 8 mm) before the solvent was evaporated. The crude aryl sulfide was dissolved in DCM (12 mL) in an ice-water bath before *m*-CPBA (contains *ca*. 23 wt%, 15.0 mmol, 3.36 g) was added in portions. The mixture was allowed to warm to room

temperature. After 12 h, saturated aqueous Na_2CO_3 was added, and the resulting solution was extracted with EtOAc (3 x 30 mL). The combined organic layer was dried over Na_2SO_4 and filtred through a pad of Celite (Ø 3 mm x 8 mm). The reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3-35a** as a white solid (720 mg, 2.13 mmol, 71% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 – 7.85 (m, 4H), 7.69 – 7.63 (m, 2H), 7.59 – 7.53 (m, 4H), 3.09 – 3.04 (m, 2H), 1.86 – 1.81 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 138.9, 134.0, 129.5, 128.1, 55.5, 21.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}O_4S_2$ $[M+H]^+$ 339.0719 (339.0710).

The spectroscopic data for **3-35a** match those reported in the literature.[61]

((4-Bromobutyl)sulfonyl)benzene 3-36a



According to **General procedure 1** with 1,4-dibromobutane (410 mg, 3.0 mmol, 1.0 equiv.), $PhSO_2Na$ (492 mg, 3.0 mmol, 1.0 equiv.) and NaI (45 mg, 0.3 mmol, 0.1 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-36a** as a white solid (565 mg, 2.04 mmol, 68% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.93 – 7.91 (m, 2H), 7.71 – 7.65 (m, 1H), 7.61 – 7.56 (m, 2H), 3.37 (t, J = 6 Hz, 2H), 3.12 (t, J = 8 Hz, 2H), 2.02 – 1.84 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 139.1, 134.0, 129.5, 128.2, 55.4, 32.3, 31.1, 21.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{14}BrO_2S$ $[M+H]^+$ 276.9892 (276.9885).

The spectroscopic data for **3-36a** match those reported in the literature.[62]

3.5.4 Details of the Borylation of Alkyl Sulfones

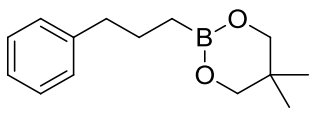
General procedure 5:

In an argon-filled glovebox, the alkyl sulfone (0.5 mmol, 1.0 equiv.), dissolved in DMA (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv.) and B_2neop_2 (339 mg, 1.5 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 120 °C for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the product was purified by flash column chromatography (hexane/EtOAc). All alkyl boronate products were unambiguously identified by comparison of HRMS and ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ and/or $^{19}F\{^1H\}$ NMR spectra with literature data.

General procedure 6:

In an argon-filled glovebox, alkyl sulfone (0.5 mmol, 1.0 equiv.), dissolved in 1,4-dioxane (2 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. KOMe (42 mg, 0.6 mmol, 1.2 equiv.) and B_2neop_2 (135.5 mg, 0.6 mmol, 1.2 equiv.) were added. The reaction mixture was stirred at 110 °C for 2 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product was purified by flash column chromatography (hexane/EtOAc) after careful removal of the solvent *in vacuo*. All alkyl boronate products were unambiguously identified by comparison of HRMS and ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ and/or $^{19}F\{^1H\}$ NMR spectra with literature data.

2-(3-Phenylpropyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-1b

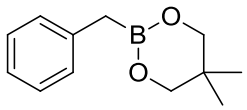


According to **General procedure 5** with **3-1a-2** (130 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **3-1b** as a white solid (104 mg, 450 µmol, 90% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ =

7.30 – 7.14 (m, 5H), 3.58 (s, 4H), 2.62 (t, *J* = 8 Hz, 2H), 1.77 – 1.67 (m, 2H), 0.96 (s, 6H), 0.78 (t, *J* = 8 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$): δ = 143.1, 128.7, 128.2, 125.6, 72.1, 38.8, 31.7, 26.3, 22.0. **$^{11}B\{^{1}H\}$ NMR** (96 MHz, $CDCl_3$): δ = 30.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{22}BO_2$ $[M+H]^+$ 233.1707 (233.1701).

The spectroscopic data for **3-1b** match those reported in the literature.[64]

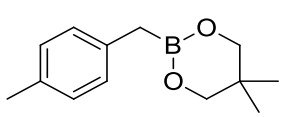
2-Benzyl-5,5-dimethyl-1,3,2-dioxaborinane 3-2b



According to **General procedure 6** with **3-2a** (116 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-2b** as a colorless oil (73 mg, 360 µmol, 72% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.24 – 7.08 (m, 5H), 3.59 (s, 4H), 2.23 (s, 2H), 0.93 (s, 6H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$): δ = 140.0, 129.0, 128.3, 124.7, 72.4, 31.8, 21.9. **$^{11}B\{^{1}H\}$ NMR** (96 MHz, $CDCl_3$): δ = 29.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{18}BO_2$ $[M+H]^+$ 205.1394 (205.1387).

The spectroscopic data for **3-2b** match those reported in the literature.[65]

2-(4-Methylbenzyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-3b

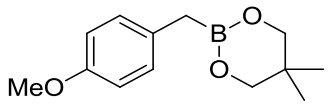


According to **General procedure 6** with **3-3a** (123 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-3b** as a colorless oil (60 mg, 275 µmol, 55% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.06 (m, 4H), 3.59 (s, 4H), 2.30 (s, 3H), 2.19 (s, 2H), 0.94 (s, 6H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz,

$CDCl_3$): δ = 136.8, 134.0, 129.0, 128.9, 72.4, 31.8, 21.9, 21.1. **$^{11}B\{^1H\}$ NMR** (96 MHz, $CDCl_3$): δ = 29.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_2$ $[M+H]^+$ 219.1551 (219.1545).

The spectroscopic data for **3-3b** match those reported in the literature.[65]

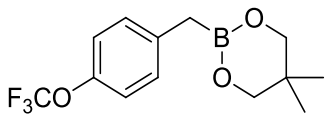
2-(4-Methoxybenzyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-4b



According to **General procedure 6** with **3-4a** (131 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-4b** as a colorless oil (80 mg, 340 µmol, 68% yield). **^1H NMR** (300 MHz, $CDCl_3$): δ = 7.09 (d, J = 9 Hz, 2H), 6.80 (d, J = 9 Hz, 2H), 3.77 (s, 3H), 3.59 (s, 4H), 2.16 (s, 2H), 0.94 (s, 6H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 157.1, 131.9, 129.8, 113.8, 72.3, 55.3, 31.8, 21.9. **$^{11}B\{^1H\}$ NMR** (96 MHz, $CDCl_3$): δ = 29.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_3$ $[M+H]^+$ 235.1500 (235.1492).

The spectroscopic data for **3-4b** match those reported in the literature.[66]

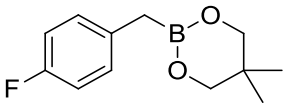
2-(4-(Trifluoromethoxy)benzyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-5b



According to **General procedure 6** with **3-5a** (158 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-5b** as a colorless oil (92 mg, 320 µmol, 64% yield). **^1H NMR** (500 MHz, $CDCl_3$): δ = 7.16 (d, J = 9 Hz, 2H), 7.07 (d, J = 9 Hz, 2H), 360 (s, 4H), 2.22 (s, 2H), 0.93 (s, 6H). **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ = 146.7 (q, J = 1.25 Hz), 138.9, 130.1, 120.9, 120.7 (q, J = 255 Hz),

72.4, 31.8, 21.9. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 29.3. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -57.9 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{17}BF_3O_3$ $[M+H]^+$ 289.1217 (289.1209). **Anal.** for $C_{13}H_{16}BF_3O_3$ calcd: C, 54.20; H, 5.60. found: C, 54.13; H, 5.58.

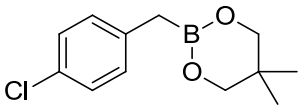
2-(4-Fluorobenzyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-6b



According to **General procedure 6** with **3-6a** (125 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-6b** as a colorless oil (67 mg, 305 μmol, 61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.12 – 7.08 (m, 2H), 6.94 – 6.89 (m, 2H), 3.59 (s, 4H), 2.19 (s, 2H), 0.93 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 160.8 (d, J = 240 Hz), 135.5 (d, J = 3.75 Hz), 130.2 (d, J = 8.75 Hz), 115.0 (d, J = 20 Hz), 72.4, 31.8, 21.9. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 29.3. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -119.8 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}BFO_2$ $[M+H]^+$ 223.1300 (223.1294).

The spectroscopic data for **3-6b** match those reported in the literature.[65]

2-(4-Chlorobenzyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-7b

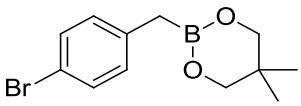


According to **General procedure 6** with **3-7a** (133 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-7b** as a colorless oil (67 mg, 280 μmol, 56% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.19 (d, J = 9 Hz, 2H), 7.09 (d, J = 9 Hz, 2H), 3.59 (s, 4H), 2.19 (s, 2H), 0.93 (s, 6H). **^{13}C{^{1}H}**

NMR (75 MHz, $CDCl_3$): δ = 138.5, 130.41, 130.35, 128.3, 72.4, 31.8, 21.9. **$^{11}B\{^1H\}$ NMR** (96 MHz, $CDCl_3$): δ = 29.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}BClO_2$ $[M+H]^+$ 239.1005 (239.0999).

The spectroscopic data for **3-7b** match those reported in the literature.[65]

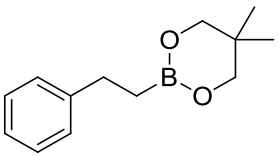
2-(4-Bromobenzyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-8b



According to **General procedure 6** with **3-8a** (156 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-8b** as a colorless oil (89 mg, 315 µmol, 63% yield). **^1H NMR** (300 MHz, $CDCl_3$): δ = 7.34 (d, J = 9 Hz, 2H), 7.04 (d, J = 9 Hz, 2H), 3.59 (s, 4H), 2.17 (s, 2H), 0.93 (s, 6H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 139.1, 131.3, 130.8, 118.4, 72.4, 31.8, 21.9. **$^{11}B\{^1H\}$ NMR** (96 MHz, $CDCl_3$): δ = 29.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}BBrO_2$ $[M+H]^+$ 283.0499 (283.0495).

The spectroscopic data for **3-8b** match those reported in the literature.[65]

2-Phenethyl-5,5-dimethyl-1,3,2-dioxaborinane 3-9b

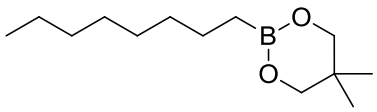


According to **General procedure 5** with **3-9a** (123 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-9b** as a colorless oil (100 mg, 460 µmol, 92% yield). **^1H NMR** (400 MHz, $CDCl_3$): δ =

7.29 – 7.13 (m, 5H), 3.60 (s, 4H), 2.71 (t, *J* = 8 Hz, 2H), 1.09 (t, *J* = 8 Hz, 2H), 0.94 (s, 6H). **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ = 145.1, 128.3, 128.1, 125.5, 72.1, 31.8, 30.2, 21.9. **$^{11}B\{^{1}H\}$ NMR** (128 MHz, $CDCl_3$): δ = 29.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_2$ $[M+H]^+$ 219.1551 (219.1547).

The spectroscopic data for **3-9b** match those reported in the literature.[67,72]

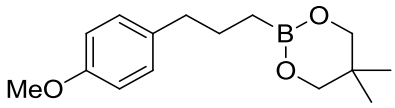
5,5-Dimethyl-2-octyl-1,3,2-dioxaborinane 3-10b



According to **General procedure 5** with **3-10a** (127 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-10b** as a colorless oil (106 mg, 470 µmol, 94% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 3.58 (s, 4H), 1.38 – 1.26 (m, 12H), 0.95 (s, 6H), 0.89 – 0.85 (m, 3H), 0.69 (t, *J* = 7 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$): δ = 72.1, 32.7, 32.1, 31.8, 29.6, 29.4, 24.3, 22.8, 22.0, 14.3. **$^{11}B\{^{1}H\}$ NMR** (96 MHz, $CDCl_3$): δ = 30.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{28}BO_2$ $[M+H]^+$ 227.2177 (227.2169).

The spectroscopic data for **3-10b** match those reported in the literature.[66]

2-(3-(4-Methoxyphenyl)propyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-11b

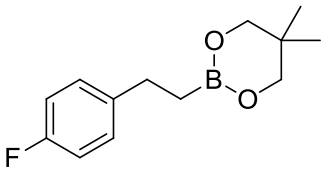


According to **General procedure 5** with **3-11a** (145 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the

product **3-11b** as a colorless oil (114 mg, 435 µmol, 87% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.12 – 7.07 (m, 2H), 6.84 – 6.79 (m, 2H), 3.78 (s, 3H), 3.57 (s, 4H), 2.54 (t, *J* = 8 Hz, 2H), 1.72 – 1.61 (m, 2H), 0.95 (s, 6H), 0.75 (t, *J* = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 157.7, 135.3, 129.6, 113.7, 72.1, 55.4, 37.9, 31.7, 26.5, 22.0. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{24}BO_3$ $[M+H]^+$ 263.1813 (263.1808).

The spectroscopic data for **3-11b** match those reported in the literature.[67]

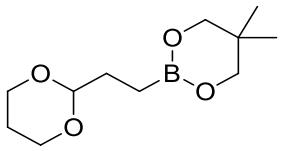
2-(4-Fluorophenethyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-12b



According to **General procedure 5** with **3-12a** (132 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-12b** as a white solid (100 mg, 425 µmol, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.18 – 7.13 (m, 2H), 6.96 – 6.90 (m, 2H), 3.59 (s, 4H), 2.67 (t, *J* = 8 Hz, 2H), 1.05 (t, *J* = 8 Hz, 2H), 0.92 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 161.1 (d, *J* = 240 Hz), 140.6 (d, *J* = 3 Hz), 129.4 (d, *J* = 8 Hz), 114.9 (d, *J* = 21 Hz), 72.1, 31.8, 29.4, 21.9. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -118.6 (s). **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 30.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{19}BFO_2$ $[M+H]^+$ 237.1457 (237.1455).

The spectroscopic data for **3-12b** match those reported in the literature.[68]

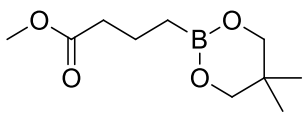
2-(2-(1,3-Dioxan-2-yl)ethyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-14b



According to **General procedure 5** with **3-14a** (128 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-14b** as a colorless oil (95 mg, 420 μmol, 84% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 4.45 (t, J = 5 Hz, 1H), 4.08 (dd, J = 5, 11 Hz, 2H), 3.74 (dt, J = 2, 12 Hz, 2H), 3.57 (s, 4H), 2.15 – 1.99 (m, 1H), 1.70 – 1.64 (m, 2H), 1.34 – 1.27 (m, 1H), 0.94 (s, 6H), 0.75 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 103.7, 72.1, 67.0, 31.8, 29.7, 26.0, 22.0. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{22}BO_4$ $[M+H]^+$ 229.1606 (229.1602).

The spectroscopic data for **3-14b** match those reported in the literature.[67]

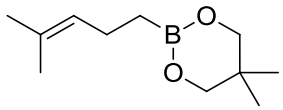
Methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)butanoate 3-15b



According to **General procedure 5** with **3-15a** (121 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 96/4) to yield the product **3-15b** as a colorless oil (56 mg, 265 μmol, 53% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.64 (s, 3H), 3.57 (s, 4H), 2.30 (t, J = 8 Hz, 2H), 1.73 – 1.67 (m, 2H), 0.94 (s, 6H), 0.74 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 174.5, 72.1, 51.5, 36.6, 31.8, 22.0, 19.9. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{20}BO_4$ $[M+H]^+$ 215.1449 (215.1441).

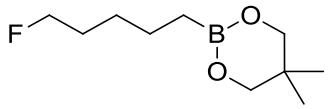
The spectroscopic data for **3-15b** match those reported in the literature.[69]

5,5-Dimethyl-2-(4-methylpent-3-en-1-yl)-1,3,2-dioxaborinane 3-16b



According to **General procedure 5** with **3-16a** (112 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-16b** as a colorless oil (50 mg, 255 µmol, 51% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 5.15 – 5.11 (m, 1H), 3.59 (s, 4H), 2.07 – 2.02 (m, 2H), 1.66 (s, 3H), 1.60 (s, 3H), 0.95 (s, 6H), 0.75 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 130.3, 127.4, 72.1, 31.8, 25.9, 22.7, 22.0, 17.7. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{22}BO_2$ $[M+H]^+$ 197.1707 (197.1701). **Anal.** for $C_{11}H_{21}BO_2$ calcd: C, 67.37; H, 10.79. found: C, 67.21; H, 10.81.

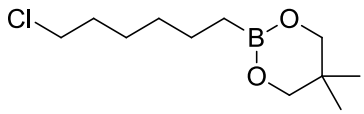
2-(5-Fluoropentyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-17b



According to **General procedure 5** with **3-17a** (115 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-17b** as a colorless oil (75 mg, 370 µmol, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.48 (t, J = 6 Hz, 1H), 4.37 (t, J = 6 Hz, 1H), 3.58 (s, 4H), 1.75 – 1.62 (m, 2H), 1.40 – 1.38 (m, 4H), 0.95 (s, 6H), 0.72 (t, J = 7 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 84.4 (d, J = 163 Hz), 72.1, 31.8, 30.4 (d, J = 19 Hz), 28.0 (d, J = 6 Hz), 23.9, 22.0. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -217.8 (s). **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 30.7. **HRMS-ASAP** (m/z):

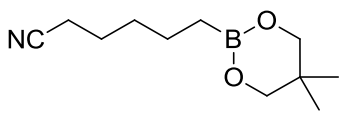
Calculated (found) for $C_{10}H_{21}BFO_2$ $[M+H]^+$ 203.1613 (203.1610). **Anal.** for $C_{10}H_{21}BFO_2$ calcd: C, 59.44; H, 9.98. found: C, 59.53; H, 10.03.

2-(6-Chlorohexyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-18b



According to **General procedure 5** with **3-18a** (130 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3-18b** as a colorless oil (79 mg, 340 µmol, 68% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 3.59 (s, 4H), 3.52 (t, J = 7 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.44 – 1.24 (m, 6H), 0.95 (s, 6H), 0.71 (t, J = 7 Hz, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 72.1, 45.4, 32.7, 31.82, 31.76, 26.9, 24.1, 22.0. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{23}BClO_2$ $[M+H]^+$ 233.1474 (233.1477). **Anal.** for $C_{11}H_{22}BClO_2$ calcd: C, 56.81; H, 9.54. found: C, 56.88; H, 9.51.

6-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)hexanenitrile 3-19b

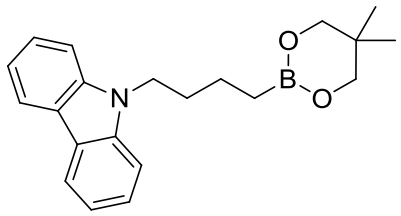


According to **General procedure 5** with **3-19a** (119 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 95/5) to yield the product **3-19b** as a colorless oil (79 mg, 380 µmol, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.58 (s, 4H), 2.32 (t, J = 8 Hz, 2H), 1.68 – 1.62 (m, 2H), 1.47 – 1.36 (m, 4H), 0.95 (s, 6H), 0.72 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 120.1, 72.1, 31.8, 31.4, 25.4, 23.3, 22.0,

17.2. **$^{11}B\{^{1}H\}$ NMR** (160 MHz, $CDCl_3$): δ = 30.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{21}BNO_2$ $[M+H]^+$ 210.1660 (210.1658).

The spectroscopic data for **3-19b** match those reported in the literature.[69]

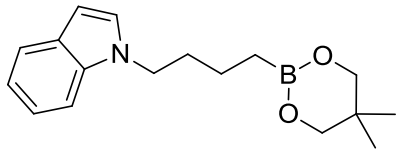
9-(4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)butyl)-9*H*-carbazole 3-20b



According to **General procedure 5** with **3-20a** (182 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 95/5) to yield the product **3-20b** as a colorless oil (115 mg, 345 μmol, 69% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.12 – 8.10 (m, 2H), 7.48 – 7.42 (m, 4H), 7.24 – 7.21 (m, 2H), 4.30 (t, J = 7 Hz, 2H), 3.57 (s, 4H), 1.92 – 1.85 (m, 2H), 1.56 – 1.49 (m, 2H), 0.94 (s, 6H), 0.82 – 0.79 (m, 2H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$): δ = 140.6, 125.6, 122.9, 120.4, 118.7, 108.9, 72.1, 43.1, 31.7, 31.6, 22.0, 21.9. **$^{11}B\{^{1}H\}$ NMR** (160 MHz, $CDCl_3$): δ = 30.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{27}BNO_2$ $[M+H]^+$ 336.2129 (336.2119).

The spectroscopic data for **3-20b** match those reported in the literature.[64]

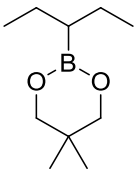
1-(4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)butyl)-1*H*-indole 3-21b



According to **General procedure 5** with **3-21a** (157 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 95/5) to yield the product **3-21b** as a colorless oil (115 mg, 405 µmol, 81% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7 Hz, 1H), 7.36 (d, *J* = 7 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.12 – 7.06 (m, 2H), 6.48 (d, *J* = 3 Hz, 1H), 4.11 (t, *J* = 7 Hz, 2H), 3.58 (s, 4H), 1.90 – 1.80 (m, 2H), 1.49 – 1.39 (m, 2H), 0.95 (s, 6H), 0.77 (t, *J* = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 136.1, 128.7, 127.9, 121.3, 121.0, 119.2, 109.6, 100.8, 72.1, 46.5, 32.9, 31.7, 22.0, 21.7. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{25}BNO_2$ $[M+H]^+$ 286.1973 (286.1969).

The spectroscopic data for **3-21b** match those reported in the literature.[64]

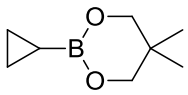
2-(Pentan-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane 3-22b



According to **General procedure 5** with **3-22a** (106 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 99/1) to yield the product **3-22b** as a colorless oil (68 mg, 370 µmol, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.59 (s, 4H), 1.44 – 1.31 (m, 4H), 0.96 (s, 6H), 0.88 (t, *J* = 7 Hz, 6H), 0.73 – 0.65 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 72.0, 31.7, 24.1, 22.1, 14.0. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 29.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{22}BO_2$ $[M+H]^+$ 185.1707 (185.1702).

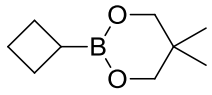
The spectroscopic data for **3-22b** match those reported in the literature.[70]

2-Cyclopropyl-5,5-dimethyl-1,3,2-dioxaborinane 3-23b



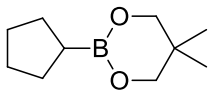
According to **General procedure 5** with **3-23a** (91 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 99/1) to yield the product **3-23b** as a colorless oil (39 mg, 255 μmol, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.55 (s, 4H), 0.94 (s, 6H), 0.54 – 0.50 (m, 2H), 0.44 – 0.40 (m, 2H), -0.27 – -0.35 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 72.1, 31.9, 21.9, 3.54. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 28.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_8H_{16}BO_2$ $[M+H]^+$ 155.1238 (155.1232).

2-Cyclobutyl-5,5-dimethyl-1,3,2-dioxaborinane 3-24b



According to **General procedure 5** with **3-24a** (98 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 99/1) to yield the product **3-24b** as a colorless oil (51 mg, 305 μmol, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.60 (s, 4H), 2.09 – 1.98 (m, 5H), 1.96 – 1.81 (m, 2H), 0.96 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 72.2, 31.8, 24.1, 22.6, 21.9. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 29.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{18}BO_2$ $[M+H]^+$ 169.1394 (169.1387).

2-Cyclopentyl-5,5-dimethyl-1,3,2-dioxaborinane 3-25b

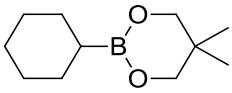


According to **General procedure 5** with **3-25a** (105 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 99/1) to yield the

product **3-25b** as a colorless oil (58 mg, 320 µmol, 64% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.59 (s, 4H), 1.76 – 1.68 (m, 2H), 1.62 – 1.40 (m, 6H), 1.12 – 1.05 (m, 1H), 0.95 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 72.2, 31.6, 28.8, 27.0, 21.9. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 30.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{20}BO_2$ $[M+H]^+$ 183.1551 (183.1545).

The spectroscopic data for **3-25b** match those reported in the literature.[67,70]

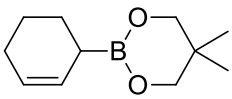
2-Cyclohexyl-5,5-dimethyl-1,3,2-dioxaborinane 3-26b



According to **General procedure 5** with **3-26a** (112 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 99/1) to yield the product **3-26b** as a colorless oil (52 mg, 265 µmol, 53% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 3.58 (s, 4H), 1.68 – 1.59 (m, 5H), 1.28 – 1.23 (m, 5H), 0.94 (s, 6H), 0.89 – 0.80 (m, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 72.1, 31.8, 28.3, 27.6, 27.1, 21.9. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{22}BO_2$ $[M+H]^+$ 197.1707 (197.1701).

The spectroscopic data for **3-26b** match those reported in the literature.[64,67]

2-(Cyclohex-2-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane 3-27b

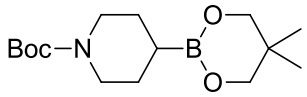


According to **General procedure 6** with **3-27a** (111 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 99/1) to yield the product **3-27b** as a colorless oil (65 mg, 335 µmol, 67% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 5.77 – 5.72 (m, 1H), 5.68 – 5.62 (m, 1H), 3.60 (s, 4H), 2.01 – 1.96 (m, 2H), 1.73 – 1.62 (m, 4H),

0.95 (s, 6H), 0.89 – 0.81 (m, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 128.9, 125.6, 72.3, 31.8, 25.3, 24.4, 22.8, 21.9. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 29.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{20}BO_2$ $[M+H]^+$ 195.1551 (195.1550).

The spectroscopic data for **3-27b** match those reported in the literature.[70]

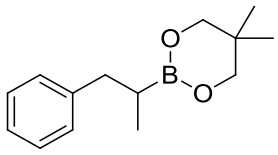
<u>*tert*-Butyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)piperidine-1-carboxylate 3-28b</u>



According to **General procedure 5** with **3-28a** (163 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 95/5) to yield the product **3-28b** as a colorless oil (105 mg, 355 µmol, 71% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 3.86 (dt, J = 4, 13 Hz, 2H), 3.57 (s, 4H), 2.85 – 2.76 (m, 2H), 1.65 – 1.57 (m, 2H), 1.44 (s, 9H), 1.42 – 1.33 (m, 2H), 1.01 – 0.96 (m, 1H), 0.93 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 155.1, 79.1, 72.1, 45.2, 31.8, 28.6, 27.3, 21.9. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{29}BNO_4$ $[M+H]^+$ 298.2184 (298.2179).

The spectroscopic data for **3-28b** match those reported in the literature.[71]

<u>2-(1-Phenylpropan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane 3-29b</u>

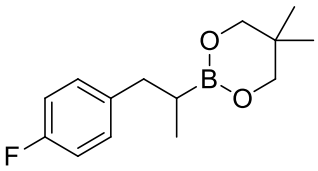


According to **General procedure 5** with **3-29a** (130 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 95/5) to yield the product **3-29b** as a colorless oil (75 mg, 325 µmol, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ =

7.24 (d, *J* = 7 Hz, 2H), 7.18 (d, *J* = 7 Hz, 2H), 7.15 (t, *J* = 7 Hz, 1H), 3.57 (s, 4H), 2.82 (dd, *J* = 7, 14 Hz, 1H), 2.46 (dd, *J* = 9, 14 Hz, 1H), 1.27 – 1.22 (m, 1H), 0.92 (d, *J* = 7 Hz, 3H), 0.90 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 143.1, 129.0, 128.1, 125.5, 72.1, 39,2, 31.7, 21.9, 15.5. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 29.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{22}BO_2$ $[M+H]^+$ 233.1707 (233.1704).

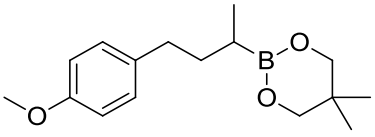
The spectroscopic data for **3-29b** match those reported in the literature.[72]

2-(1-(4-Fluorophenyl)propan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane 3-30b



According to **General procedure 5** with **3-30a** (139 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 95/5) to yield the product **3-30b** as a colorless oil (86 mg, 345 µmol, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.15 – 7.10 (m, 2H), 6.96 – 6.90 (m, 2H), 3.56 (s, 4H), 2.79 – 2.73 (m, 1H), 2.46 – 2.41 (m, 1H), 1.23 – 1.67 (m, 1H), 0.91 (d, *J* = 7 Hz, 3H), 0.89 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 161.2 (d, *J* = 241 Hz), 138.6 (d, *J* = 3 Hz), 130.2 (d, *J* = 8 Hz), 114.8 (d, *J* = 21 Hz), 72.1, 38.4, 31.7, 21.9, 15.5. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -118.6 (s). **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 30.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{21}BFO_2$ $[M+H]^+$ 251.1613 (251.1610). **Anal.** for $C_{14}H_{20}BFO_2$ calcd: C, 67.23; H, 8.06. found: C, 67.17; H, 8.20.

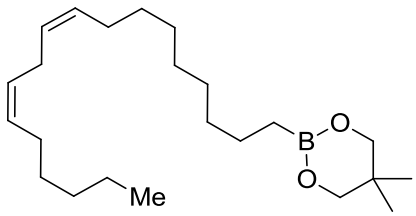
2-(4-(4-Methoxyphenyl)butan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane 3-31b



According to **General procedure 5** with **3-31a** (152 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 95/5) to yield the product **3-31b** as a colorless oil (98 mg, 355 µmol, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 8 Hz, 2H), 6.82 (d, *J* = 8 Hz, 2H), 3.78 (s, 3H), 3.57 (s, 4H), 2.63 – 2.49 (m, 2H), 1.79 – 1.70 (m, 1H), 1.55 – 1.47 (m, 1H), 0.99 – 0.96 (m, 1H), 0.98 (s, 3H), 0.95 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 157.6, 135.5, 129.5, 113.7, 72.0, 55.4, 35.7, 34.6, 31.7, 21.9, 15.8. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 29.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{26}BO_3$ $[M+H]^+$ 277.1970 (277.1966).

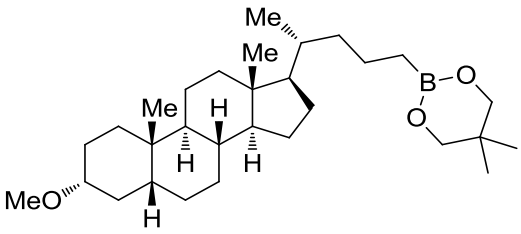
The spectroscopic data for **3-31b** match those reported in the literature.[64]

2-((9*Z*,12*Z*)-Octadeca-9,12-dien-1-yl)- 5,5-dimethyl-1,3,2-dioxaborinane 3-32b



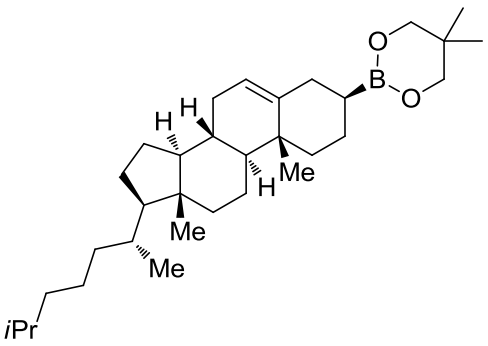
According to **General procedure 5** with **3-32a** (78 mg, 0.2 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 95/5) to yield the product **3-32b** as a colorless oil (48.5 mg, 134 µmol, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.42 – 5.29 (m, 4H), 3.59 (s, 4H), 2.77 (t, *J* = 6 Hz, 2H), 2.07 – 2.01 (m, 4H), 1.39 – 1.26 (m, 18H), 0.95 (s, 6H), 0.89 (t, *J* = 7 Hz, 3H), 0.70 (t, *J* = 7 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 130.4, 130.3, 128.1, 128.0, 72.1, 32.8, 32.7, 31.8, 31.7, 29.9, 29.7, 29.51, 29.49, 27.4, 27.3, 25.8, 24.3, 22.7, 22.0, 14.2. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 29.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{23}H_{44}BO_2$ $[M+H]^+$ 363.3429 (363.3424). **Anal.** for $C_{23}H_{43}BO_2$ calcd: C, 76.23; H, 11.96. found: C, 76.44; H, 12.18.

2-((*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-methoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-33b



According to **General procedure 5** with **3-33a** (100 mg, 0.2 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 93/7) to yield the product **3-33b** as a colorless oil (67 mg, 142 μmol, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.58 (s, 4H), 3.34 (s, 3H), 3.19 – 3.11 (m, 1H), 1.96 – 1.92 (m, 1H), 1.88 – 1.73 (m, 4H), 1.70 – 1.47 (m, 4H), 1.42 – 0.99 (m, 19H), 0.95 (s, 6H), 0.90 (s, 3H), 0.88 (d, J = 6 Hz, 3H), 0.75 – 0.63 (m, 2H), 0.61 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 80.6, 72.1, 56.6, 56.2, 55.7, 42.8, 42.2, 40.4, 40.3, 39.1, 36.0, 35.9, 35.4, 35.0, 32.9, 31.7, 28.4, 27.5, 26.9, 26.5, 24.4, 23.6, 22.0, 20.9, 20.7, 18.3, 12.1. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 30.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{30}H_{54}BO_3$ $[M+H]^+$ 473.4161 (473.4155). **Anal.** for $C_{30}H_{53}BO_3$ calcd: C, 76.25; H, 11.30. found: C, 76.08; H, 11.47.

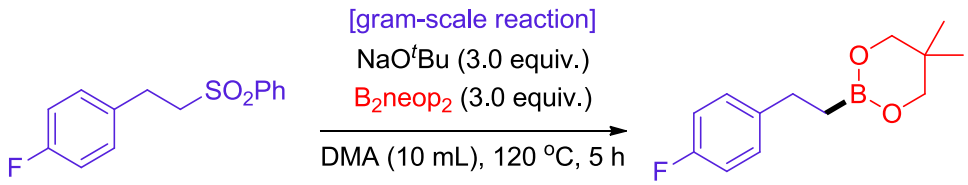
2-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane 3-34b



According to **General procedure 5** with **3-34a** (102 mg, 0.2 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 93/7) to yield the product **3-34b** as a colorless oil (60 mg, 124 µmol, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.26 – 5.25 (m, 1H), 3.58 (s, 4H), 2.21 – 2.13 (m, 1H), 2.01 – 1.77 (m, 6H), 1.56 – 0.99 (m, 22H), 0.98 (s, 3H), 0.94 (s, 6H), 0.90 (d, J = 6 Hz, 3H), 0.86 (dd, J = 2, 7 Hz, 6H), 0.66 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 144.5, 118.4, 72.1, 57.0, 56.3, 53.6, 50.7, 42.4, 41.2, 40.0, 39.7, 37.5, 36.3, 35.9, 34.3, 32.1, 32.0, 31.8, 28.4, 28.2, 24.42, 24.37, 24.0, 23.0, 22.7, 21.9, 20.9, 19.7, 18.9, 12.0. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 30.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{32}H_{56}O_2S$ $[M+H]^+$ 483.4368 (483.4366). **Anal.** for $C_{32}H_{55}BO_2$ calcd: C, 79.64; H, 11.49. found: C, 79.81; H, 11.56.

3.5.5 Unsuccessful Tertiary Sulfone Substrates

3.5.6 Gram-scale Reaction

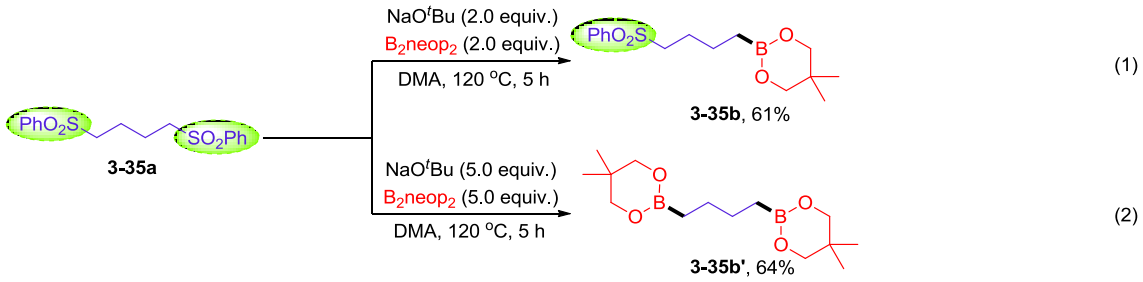


3-12a, 5 mmol
1.32 g

3-12b, 72%

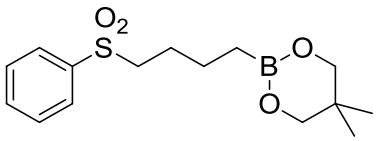
In an argon-filled glovebox, the alkyl sulfone **12a** (1.32 g, 5 mmol, 1.0 equiv.), dissolved in DMA (10 mL), was added to a 20 mL Schlenk tube equipped with a magnetic stirring bar. NaO^{t}Bu (1.44 mg, 15 mmol, 3.0 equiv.) and B_2neop_2 (3.39 g, 15 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 120 ℃ for 5 h, then diluted with Et_2O (20 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (98/2)) to yield the product **12b** as a white solid (0.85 g, 3.6 mmol, 72%).

3.5.7 Selective Borylation



In an argon-filled glovebox, the sulfone **3-35a** (169 mg, 0.5 mmol, 1.0 equiv.), dissolved in DMA (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (96 mg, 1.0 mmol, 2.0 equiv.) and B_2neop_2 (226 mg, 1.0 mmol, 2.0 equiv.) were added. The reaction mixture was stirred at 120 ℃ for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (10/1)) to yield the product **3-35b** as a white solid (94.6 mg, 305 µmol, 61% yield).

5,5-Dimethyl-2-(4-(phenylsulfonyl)butyl)-1,3,2-dioxaborinane 3-35b

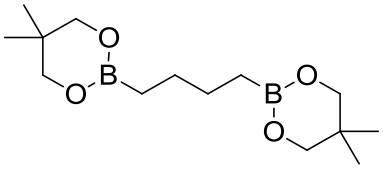


^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 – 7.88 (m, 2H), 7.65 – 7.62 (m, 1H), 7.57 – 7.53 (m, 2H), 3.53 (s, 4H), 3.09 – 3.05 (m, 2H), 1.70 – 1.64 (m, 2H), 1.44 – 1.38 (m, 2H), 0.90 (s, 6H), 0.66 (t, *J* = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 139.3, 133.6, 129.3, 128.2, 72.1, 56.4, 31.7, 25.2, 23.0, 21.9. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{24}BO_4S$ $[M+H]^+$ 311.1483 (311.1476). **Anal.** for $C_{15}H_{23}BO_4S$ calcd: C, 58.08; H, 7.47; S, 10.34. found: C, 57.82; H, 7.34; S, 10.41.

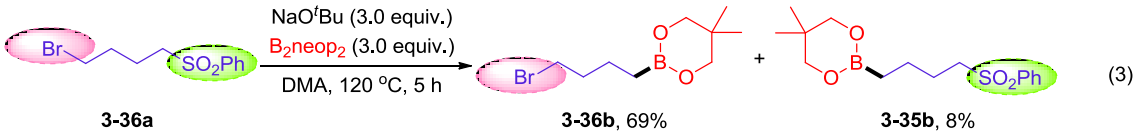
In an argon-filled glovebox, the sulfone **3-35a** (169 mg, 0.5 mmol, 1.0 equiv.), dissolved in DMA (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (240 mg, 2.5 mmol, 5.0 equiv.) and B_2neop_2 (565 mg, 2.5 mmol, 5.0 equiv.) were added. The reaction mixture was stirred at 120 ℃ for 5 h, then diluted with Et_2O (2 mL) and filtred

through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (97/3)) to yield the product **35b'** as a white solid (90.2 mg, 320 µmol, 64% yield).

1,4-Bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)butane 3-35b'



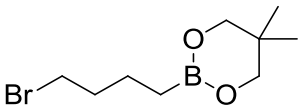
^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.57 (s, 8H), 1.36 – 1.33 (m, 4H), 0.94 (s, 12H), 0.71 – 0.68 (m, 4H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 72.1, 31.7, 27.3, 22.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{29}B_2O_4$ $[M+H]^+$ 283.2246 (283.2240). **Anal.** for $C_{14}H_{28}B_2O_4$ calcd: C, 59.63; H, 10.01. found: C, 59.71; H, 9.88.



(3)

In an argon-filled glovebox, the sulfone **3-36a** (138 mg, 0.5 mmol, 1.0 equiv.), dissolved in DMA (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv.) and B_2neop_2 (339 mg, 1.5 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 120 ℃ for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc) to yield the product **3-36b** as colorless oil (86 mg, 345 µmol, 69% yield) and **3-35b** as a white solid (12 mg, 40 µmol, 8% yield).

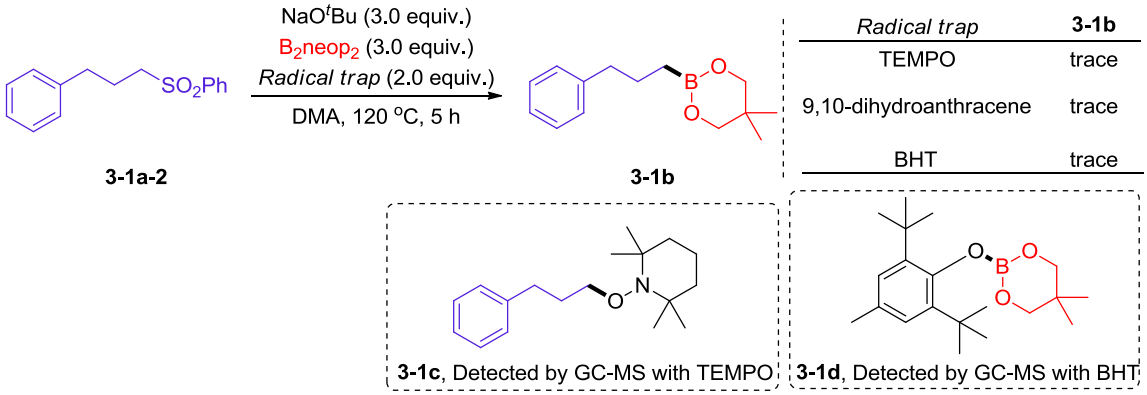
2-(4-Bromobutyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-36b



^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.58 (s, 4H), 3.40 (t, J = 7 Hz, 2H), 1.90 – 1.81 (m, 2H), 1.55 – 1.45 (m, 2H), 0.95 (s, 6H), 0.72 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 72.1, 35.6, 34.1, 31.8, 23.0, 22.0. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{19}BBrO_2$ $[M+H]^+$ 249.0656 (249.0648).

3.5.8 Preliminary Mechanistic Investigations

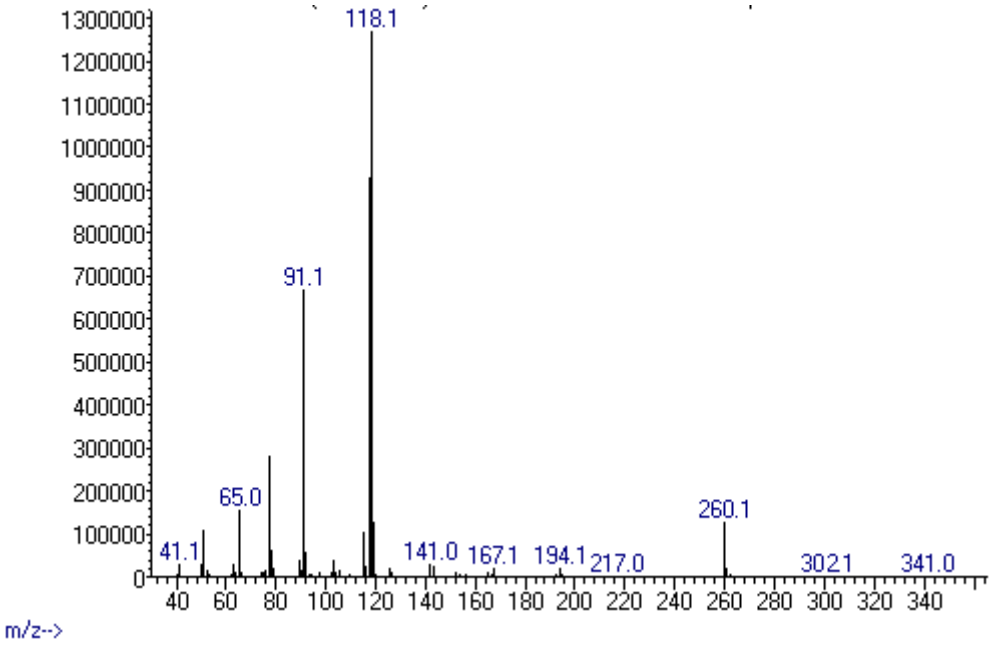
3.5.8.1 Radical Trap Experiments



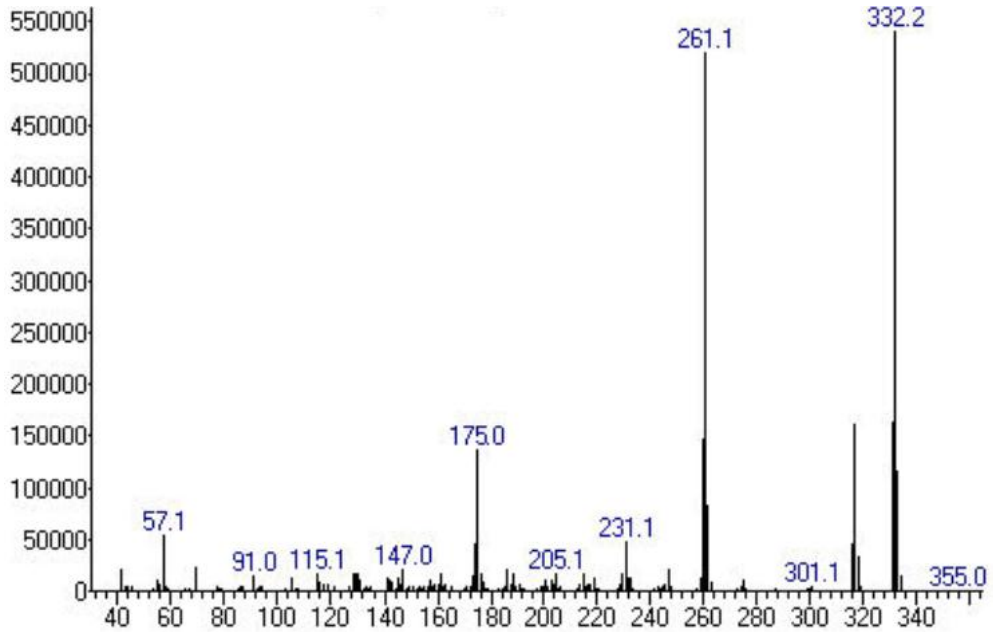
In an argon-filled glovebox, ((3-phenylpropyl)sulfonyl)benzene **3-1a-2** (130 mg, 0.5 mmol, 1.0 equiv.) in DMA (1 mL) was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv.), B_2neop_2 (339 mg, 1.5 mmol, 3.0 equiv.) and radical trap [TEMPO (117 mg, 0.75 mmol, 1.5 equiv.), 9,10-dihydroanthracene (135 mg, 0.75 mmol, 1.5 equiv.) or BHT (165.3 mg, 0.75 mmol, 1.5 equiv.)] were added. The reaction mixture was stirred at 120 °C for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The solvent was evaporated under reduced pressure, dodecane was added as an internal standard and the crude reaction mixture was analyzed by GC-MS.

3-1c was detected by GC-MS when TEMPO was added, GC-MS: m/z 260 (M^+-CH_3).[73] **HRMS-**

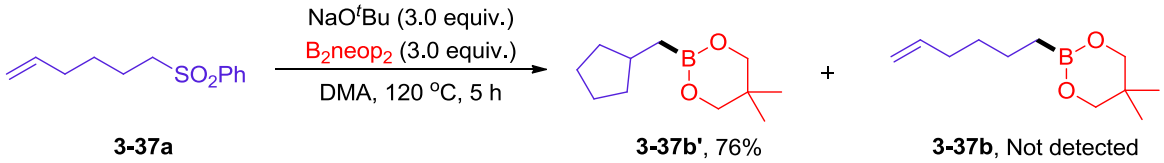
ASAP (m/z): Calculated (found) for $C_{18}H_{30}NO$ $[M+H]^+$ 276.2322 (276.2316).



3-1d was detected by GC-MS when BHT was added, GC-MS: m/z 332 (M^+). **HRMS-ASAP** (m/z): Calculated (found) for $C_{20}H_{33}BO_3$ $[M]^+$ 332.2517 (332.2508).



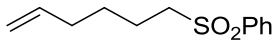
3.5.8.2 Radical Clock Experiment



3-37a **3-37b'**, 76% **3-37b**, Not detected

In an argon-filled glovebox, (hex-5-en-1-ylsulfonyl)benzene **3-37a** (112 mg, 0.5 mmol, 1.0 equiv.) in DMA (1 mL) was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv.) and B_2neop_2 (339 mg, 1.5 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 120 °C for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The cyclized product was isolated exclusively in 76% yield following flash column chromatography (hexane/EtOAc (98/2)) after careful removal of the solvent *in vacuo*.

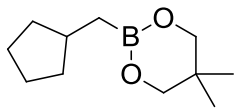
(Hex-5-en-1-ylsulfonyl)benzene 3-37a



According to **General procedure 1** with hex-5-en-1-ol (300 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **3-37a** as a colorless oil (505 mg, 2.25 mmol, 75% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.93 – 7.89 (m, 2H), 7.69 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 5.78 – 5.64 (m, 1H), 5.00 – 4.91 (m, 2H), 3.11 – 3.06 (m, 2H), 2.06 – 1.99 (m, 2H), 1.78 – 1.68 (m, 2H), 1.51 – 1.41 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 139.3, 137.6, 133.8, 129.4, 128.2, 115.5, 56.3, 33.2, 27.6, 22.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}O_2S$ $[M+H]^+$ 225.0944 (225.0938).

The spectroscopic data for **3-37a** match those reported in the literature.[74]

2-(Cyclopentylmethyl)-5,5-dimethyl-1,3,2-dioxaborinane 3-37b'



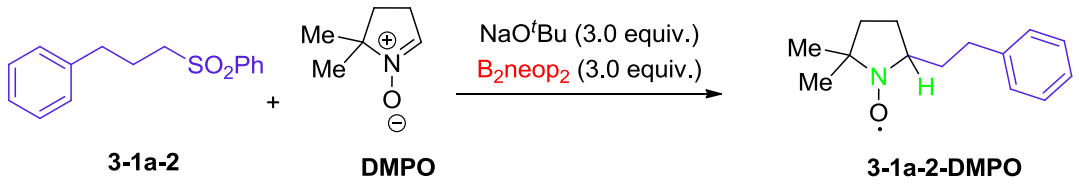
Yield: 74 mg (380 μmol, 76%) of a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 3.59 (s, 4H), 1.97 – 1.87 (m, 1H), 1.82 – 1.72 (m, 2H), 1.63 – 1.45 (m, 4H), 1.11 – 1.00 (m, 2H), 0.95 (s, 6H), 0.77 (d, J = 7 Hz, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 72.1, 36.4, 35.3, 31.8, 25.3, 22.0. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{22}BO_2$ $[M+H]^+$ 197.1707 (197.1706).

The spectroscopic data for **3-37b'** match those reported in the literature.[65]

3.5.8.3 EPR Spectroscopic Study

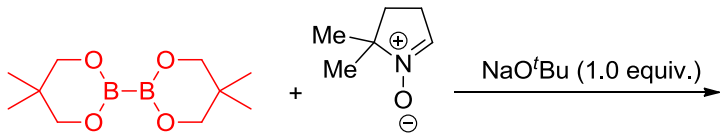
X-band EPR measurements (9.38 GHz) were carried out at room temperature using a Bruker ELEXSYS E580 CW EPR spectrometer. CW EPR spectra were measured using 2 mW microwave power and 0.5 G field modulation at 100 kHz, with a conversion time of 20 ms. The spectral simulations were performed using MATLAB R2021a and the EasySpin 6.0.0 toolbox.[75]

Sample (a)



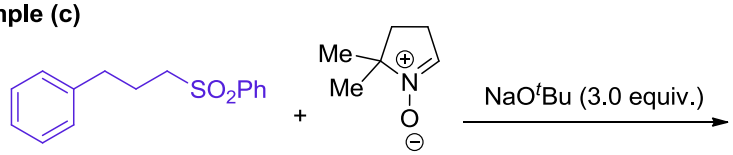
3-1a-2 + **DMPO** → **3-1a-2-DMPO**

Sample (b)



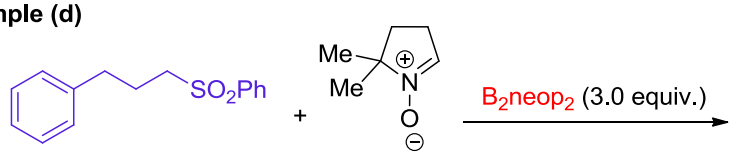
DMPO

Sample (c)



3-1a-2 + **DMPO**

Sample (d)



3-1a-2 + **DMPO**

In an argon-filled glovebox, each of the samples was prepared in a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar and stirred for 10 min at 120 °C. The reaction mixtures were transferred into Young's tap tubes. In sample (a), **3-1a-2** (13 mg, 0.05 mmol, 1.0 equiv.), B_2neop_2 (33.9 mg, 0.15 mmol, 3.0 equiv.), NaO^{t}Bu (14.4 mg, 0.15 mmol, 3.0 equiv.), DMPO (11.3 mg, 0.10 mmol, 2.0 equiv.) and dry 1,4-dioxane (0.5 mL) were used. In sample (b), B_2neop_2 (33.9 mg, 0.15 mmol, 1.0 equiv.), NaO^{t}Bu (14.4 mg, 0.15 mmol, 1.0 equiv.), DMPO (17.0 mg, 0.15 mmol, 1.0 equiv.) and dry 1,4-dioxane (0.5 mL) were used. In sample (c), **3-1a-2** (13 mg, 0.05 mmol, 1.0 equiv.), NaO^{t}Bu (14.4 mg, 0.15 mmol, 3.0 equiv.), DMPO (11.3 mg, 0.10 mmol, 2.0 equiv.) and dry 1,4-dioxane (0.5 mL) were used. In sample (d), **3-1a-2** (13 mg, 0.05 mmol, 1.0 equiv.), B_2neop_2 (33.9 mg, 0.15 mmol, 3.0 equiv.), DMPO (11.3 mg, 0.10 mmol, 2.0 equiv.) and dry 1,4-dioxane (0.5 mL) were used.

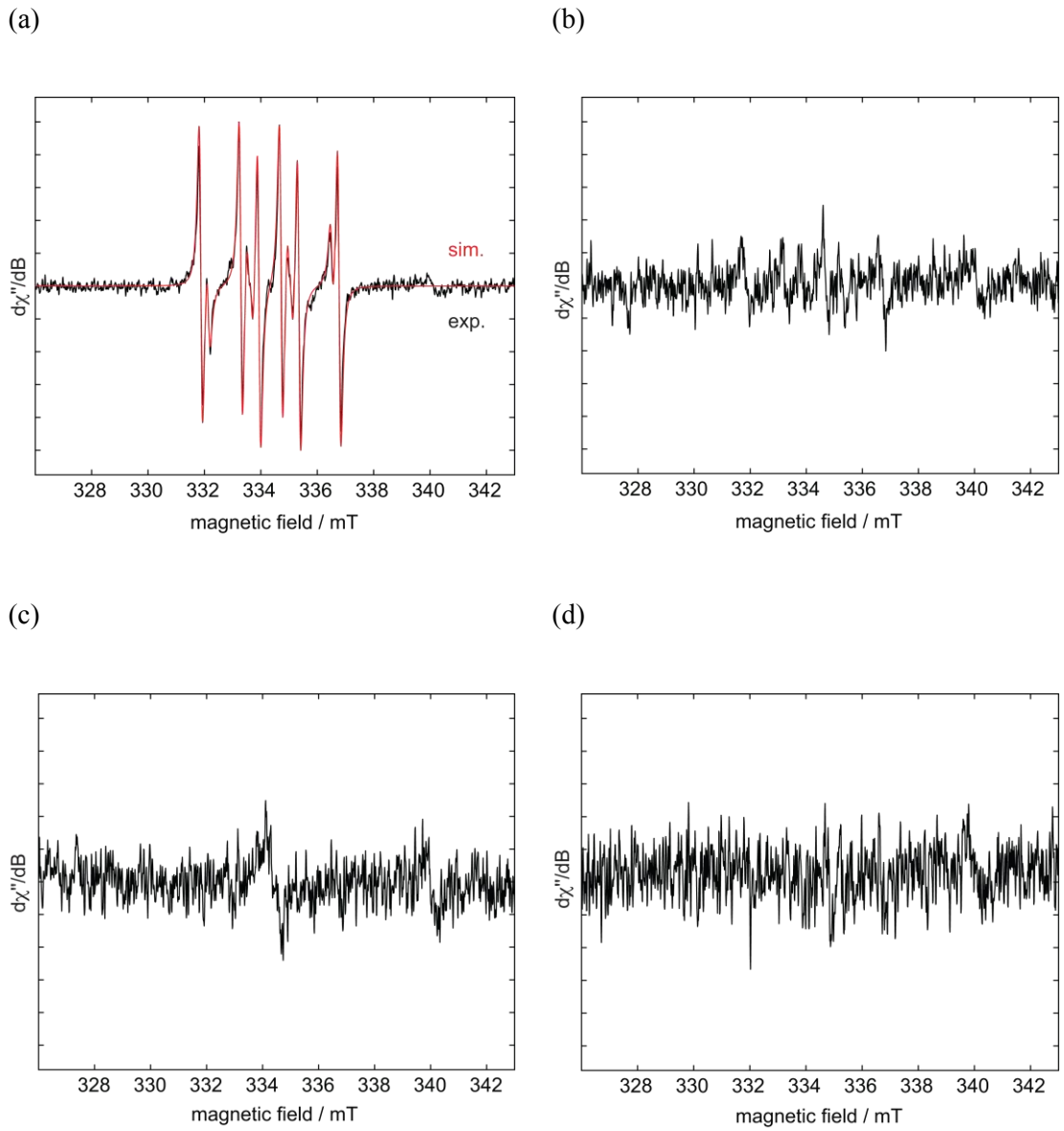


Figure 3-S1. (a) Experimental (black) and simulated (red) continuous-wave (CW) X-band EPR spectra of the DMPO spin trapping experiment in 1,4-dioxane at room temperature: **3-1a-2** + B_2neop_2 + NaO^{t}Bu. Best-fit simulation parameters: g_{iso} = 2.0053, $a(^{14}N)$ = 40 MHz (14.3 G) and $a(^{1}H)$ = 58 MHz (20.6 G, major species); g_{iso} = 2.0053, $a(^{14}N)$ = 40 MHz (14.3 G) and $a(^{1}H)$ = 43 MHz (15.4 G, minor species). **(b)** CW X-band EPR spectra of the DMPO spin trapping experiment in 1,4-dioxane at room temperature: B_2neop_2 + NaO^{t}Bu. **(c)** CW X-band EPR spectra of the DMPO spin trapping experiment in 1,4-dioxane at room temperature: **3-1a-2** + NaO^{t}Bu. **(d)** CW X-band EPR spectra of the DMPO spin trapping experiment in 1,4-dioxane at room temperature: **3-1a-2** + B_2neop_2.

3.5.9 Single-Crystal X-ray Diffraction Analysis

A crystal suitable for single-crystal X-ray diffraction was selected, coated in perfluoropolyether oil, and mounted on a microloop. Diffraction data of **3-34b** was collected on a RIGAKU OXFORD DIFFRACTION XTALAB Synergy diffractometer with a semiconductor HPA-detector (HyPix-6000) and multi-layer mirror monochromated Cu-K_α radiation. The crystal was cooled at 100 K using an Oxford Cryostream 800 low-temperature device. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the CrysAlis^{Pro} software. The structure was solved using the intrinsic phasing method (SHELXT)[76] and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' on idealised positions by full-matrix least squares against F^2 of all data, using SHELXL software[77] and the SHELXLE graphical user interface[78]. The crystal structure was solved as a superstructure of a smaller, commensurately modulated monoclinic structure with lattice parameters a = 12.7032 Å, b = 9.1345 Å, c = 12.9947 Å, and β = 103.01 °, with a modulation (q) vector of [0.25, 0, 0.5] and is obtained from the smaller cell by applying the transformation matrix [2 0 1, 0 -1 0, 0 0 -2]. The smaller unit cell is obtained from the large one by applying the transformation matrix [0.5 0 0.25, 0 -1 0, 0 0 -0.5]. Diamond[79] software was used for graphical representation. Crystal data and experimental details are listed in Table 3-S3; full structural information has been deposited with Cambridge Crystallographic Data Centre. CCDC-2079501. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 3-S3: Single-crystal X-ray diffraction data and refinement details of **3-34b**.

Data	**3-34b**
CCDC number	2079501
Empirical formula	$C_{32}H_{55}BO_2$
Formula weight / g·mol^{-1}	482.57
T / K	100(2)
Radiation, λ / Å	Cu-K_α 1.54184
Crystal size / mm³	0.03×0.07×0.17
Crystal color, habit	Colorless needle
μ / mm^{-1}	0.485
Crystal system	Monoclinic
Space group	$P2_1$
a / Å	25.8010(4)
b / Å	9.13450(10)
c / Å	25.9893(4)
α / °	90
β / °	106.377(2)
γ / °	90
Volume / Å^3	5876.62(15)
Z	8
ρ_{calc} / g·cm^{-3}	1.091
F(000)	2144
θ range / °	2.131 – 68.249
Reflections collected	37525
Unique reflections	18290
Parameters / restraints	1324 / 76
GooF on F^2	1.026
R_1 [I>2σ (I)]	0.0482
wR^2 (all data)	0.1307
Max. / min. residual electron density / e·Å^{-3}	0.356 / –0.183

3.6 References

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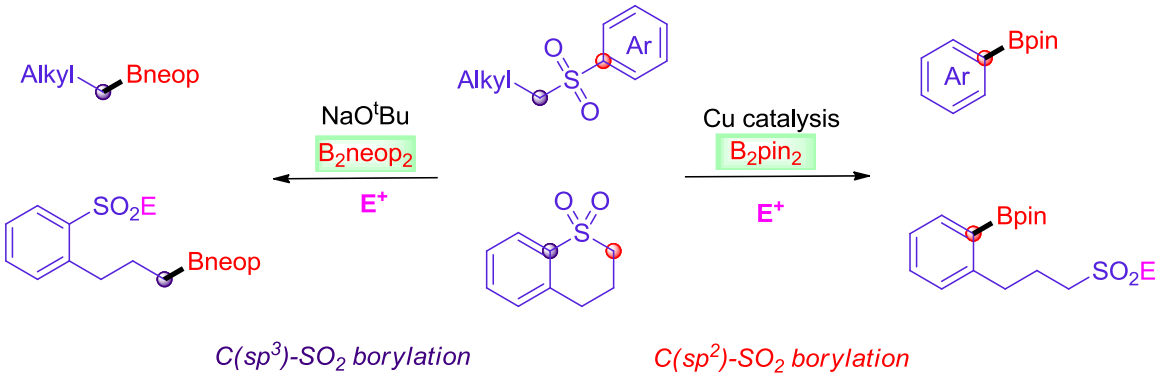
Chapter 4

Cu-mediated *vs* Cu-free Selective Borylation of Aryl Alkyl Sulfones



4 Cu-mediated *vs* Cu-free Selective Borylation of Aryl Alkyl Sulfones

4.1 Abstract

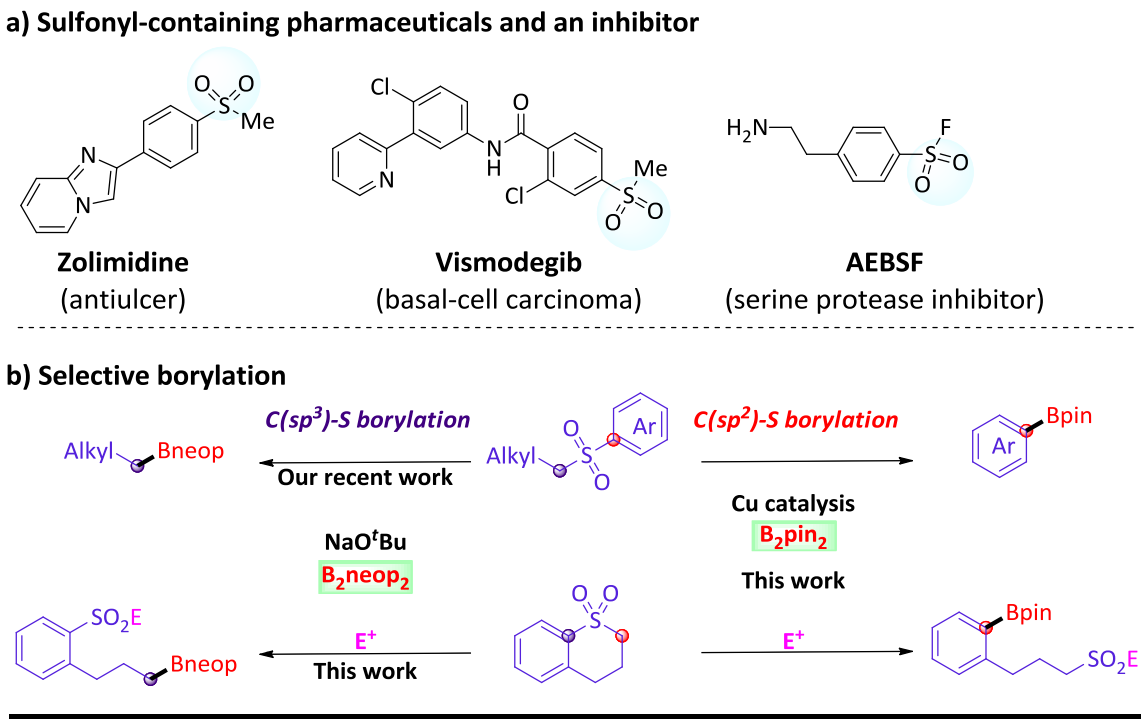
A Cu-catalysed borylation of aryl alkyl sulfones was developed for the high yield synthesis of versatile arylboronic esters using a readily prepared NHC-Cu catalyst. In addition, the selective cleavage of either alkyl(C)-sulfonyl or aryl(C)-sulfonyl bonds of a cyclic sulfone *via* Cu-free or Cu-mediated processes generates the corresponding sulfinate salts, which can be further derivatised to provide sulfonyl-containing boronate esters, such as sulfones and sulfonyl fluorides.

4.2 Introduction

Organosulfur compounds are synthetically valuable and fundamental compounds in chemistry.[1] Molecules incorporating sulfonyl-based (–SO_2–) functional groups such as sulfones and sulfonyl fluorides are commercially available and of paramount importance in drug discovery.[2] Aryl alkyl sulfones are widespread, show a high degree of stability and crystallinity, and can be easily synthesised from alcohols and halides with inexpensive and odorless sodium arenesulfinate, allowing for convenient manipulation. A selection of recognised sulfonyl-containing drugs in clinical trials include the anti-ulcer drug Zolimidine,[3] the basal-cell carcinoma drug Vismodegib,[4] and the serine protease inhibitor (2-aminoethyl)benzenesulfonyl fluoride (AEBSF)[5] (Scheme 4-1a).

Recently, our group developed a base-mediated, transition metal-free radical borylation of unactivated primary and secondary alkyl sulfones using $B_2(neop)_2$ (neop = neopentyl glycolato). This approach proved practical and straightforward for the construction of versatile alkylboronate esters without further transesterification (Scheme 4-1b, upper left).[6] Under the base-mediated reaction system, we realised the selective cleavage of alkyl(C)–SO_2 bonds, with SO_2Ar as the leaving group, without the observation of cleavage of aryl(C)–SO_2 bonds. Generally, C(sp^2)–SO_2 bond cleavage of sulfones is more often observed using transition metals, such as Pd[7] and Ni,[8] or

visible light.[9] In general, in transition metal-catalysed cross-coupling processes, the cleavage of C(sp^2)–S bonds can be used to construct C–C and C–heteroatom bonds.[10] N-heterocyclic carbene (NHC)-nickel(0) complexes were previously shown by our group to undergo stoichiometric bond-activation reactions with sulfoxides.[11] Most recently, we developed a $Ni(COD)_2$/NHC catalytic process for the borylation of C(sp^2)–SO bonds of aryl sulfoxides with $B_2(neop)_2$ to afford arylboronate esters. Oxidative addition of the C–SO bond in unsymmetrical diaryl sulfoxide to the Ni(0) complex proceeded mainly at the side of the electron-poor group.[12]



Scheme 4-1. Relevance and selective cleavage of C–SO_2 bonds.

Arylboronates play a highly important and valuable role in drug discovery, materials science, and synthetic chemistry,[13] as exemplified by the Suzuki-Miyaura cross-coupling reaction.[14] The development of transition metal-catalysed Miyaura-type borylation reactions has been well-developed to allow access to arylboronate esters.[15] As first row "Earth-abundant" metal catalysts are of increasing interest due to their low cost and toxicity, much work has been done on aryl borylation reactions using Cu catalysis,[16] which works well for many aryl C–X (Cl, Br, I),[17] C–F,[18] and C–N bonds.[19] Our group reported the first Cu-catalysed borylation of aryl bromides using a Cu(I)I/P^{n}Bu$_3$ catalyst under mild conditions.[20] Later, we also reported the first Cu-

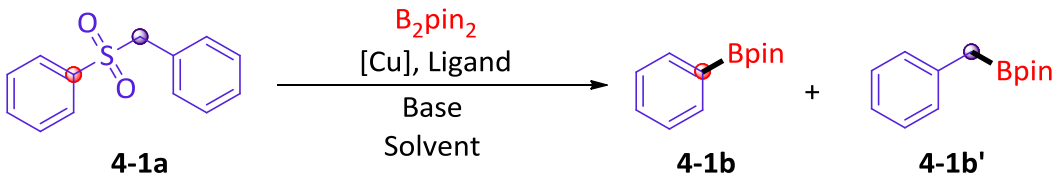
catalysed borylation of a variety of aryl chlorides using a readily prepared NHC-Cu-catalyst with B_2pin_2 as the diboron reagent.[21] With our successful previous work on NHC-copper-catalysed borylation reactions,[22] and development of synthetic routes to and characterisation of diverse Cu(I)-complexes of the type (NHC)CuCl,[23] herein, we report initial results on the NHC Cu-catalysed borylation of $C(sp^2)$–SO_2 bonds of aryl alkyl sulfones. Compared with our recent $C(sp^3)$–SO_2Ar bond cleavage under transition metal-free conditions, the new copper-mediated strategy shows the opposite selectivity.

4.3 Results and Discussion

4.3.1 Optimization of Reaction Conditions

We initiated this study using (benzylsulfonyl)benzene **4-1a**, B_2pin_2 as the diboron reagent, KO^{t}Bu as the base, toluene as the solvent, and ICyCuCl (ICy = 1,3-dicyclohexylimidazolin-2-ylidene) as the catalyst at 100 °C for 5 h, affording benzyl-Bpin **4-1b'** as the main product, accompanied by only an 18% yield of the desired phenyl-Bpin **4-1b** (Table 4-1, entry 1). With this promising first result, a range of catalysts and ligands, including NHC-copper complexes and a variety of phosphine or nitrogen ligands, was screened. Only IMesCuCl (IMes = 1,3-dimesitylimidazolin-2-ylidene) revealed a significantly higher catalytic activity, providing the desired product **4-1b** in excellent yield (entry 6), while no products were observed using other copper complexes (entries 2−5). Other bases were also examined in the presence of IMesCuCl, but KOMe, KF, LiO^{t}Bu, NaOMe, and NaO^{t}Bu, all gave lower yields (entries 7–11). We observed good reactivity in other organic solvents, e.g., THF, ^{n}hexane, DMF, and MTBE (entries 12–15). Decreasing the IMesCuCl loading to 5 mol % resulted in a slightly diminished yield of **4-1b** under the otherwise optimal conditions (entry 16). However, B_2cat_2 and B_2neop_2 gave the mixture of products **4-1b** and **4-1b'** under our conditions, with only slight preferences for **4-1b** (entries 17 and 18).

Table 4-1. Screening of reaction conditions.[a]



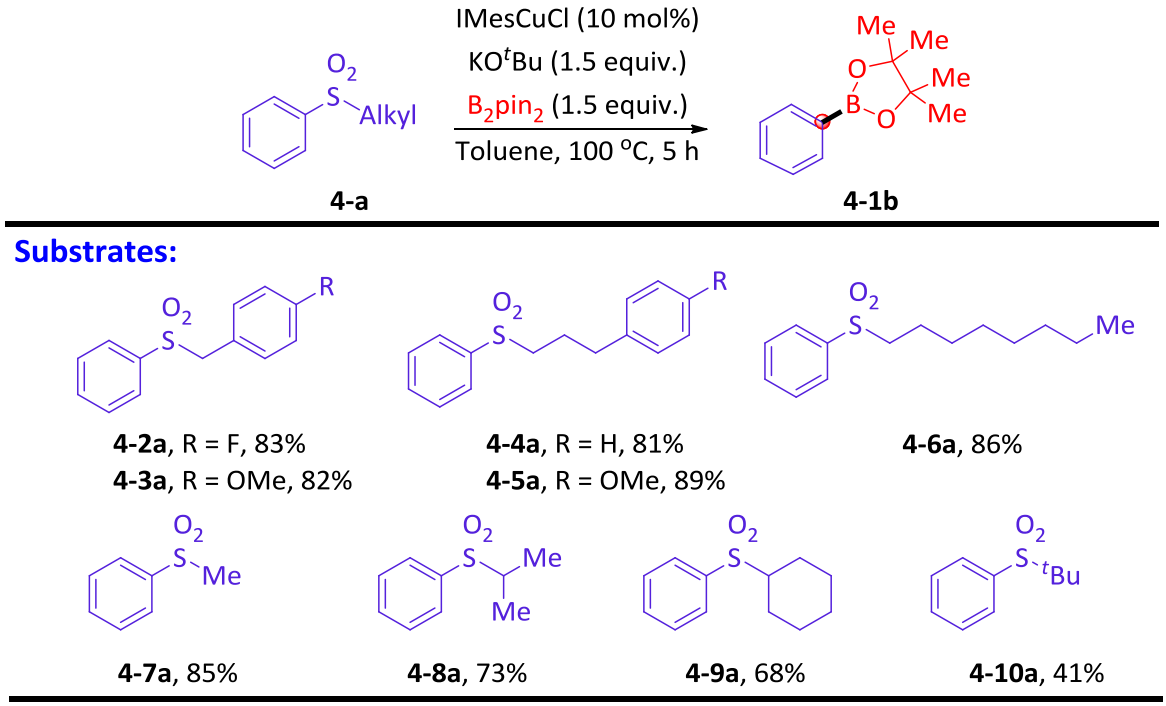
4-1a **4-1b** **4-1b'**

Entry	Catalyst	Base	Solvent	Yield of **1b**	Yield of **1b'**
1	ICyCuCl	KO^{t}Bu	toluene	18	86
2	IPrCuCl	KO^{t}Bu	toluene	0	15
3	IMeCuCl	KO^{t}Bu	toluene	0	28
4	bpyCuCl	KO^{t}Bu	toluene	0	0
5	$(PCy_3)_2CuCl$	KO^{t}Bu	toluene	0	0
6	**IMesCuCl**	**KO^{t}Bu**	**toluene**	**98(87)**[e]	**3**
7	IMesCuCl	KOMe	toluene	71	34
8	IMesCuCl	KF	toluene	7	0
9	IMesCuCl	LiO^{t}Bu	toluene	67	36
10	IMesCuCl	NaOMe	toluene	22	9
11	IMesCuCl	NaO^{t}Bu	toluene	49	15
12	IMesCuCl	KO^{t}Bu	THF	67	0
13	IMesCuCl	KO^{t}Bu	^{n}hexane	81	16
14	IMesCuCl	KO^{t}Bu	DMF	15	9
15	IMesCuCl	KO^{t}Bu	MTBE	93	4
16[b]	IMesCuCl	KO^{t}Bu	toluene	78	5
17[c]	IMesCuCl	KO^{t}Bu	toluene	42	31
18[d]	IMesCuCl	KO^{t}Bu	toluene	21	14

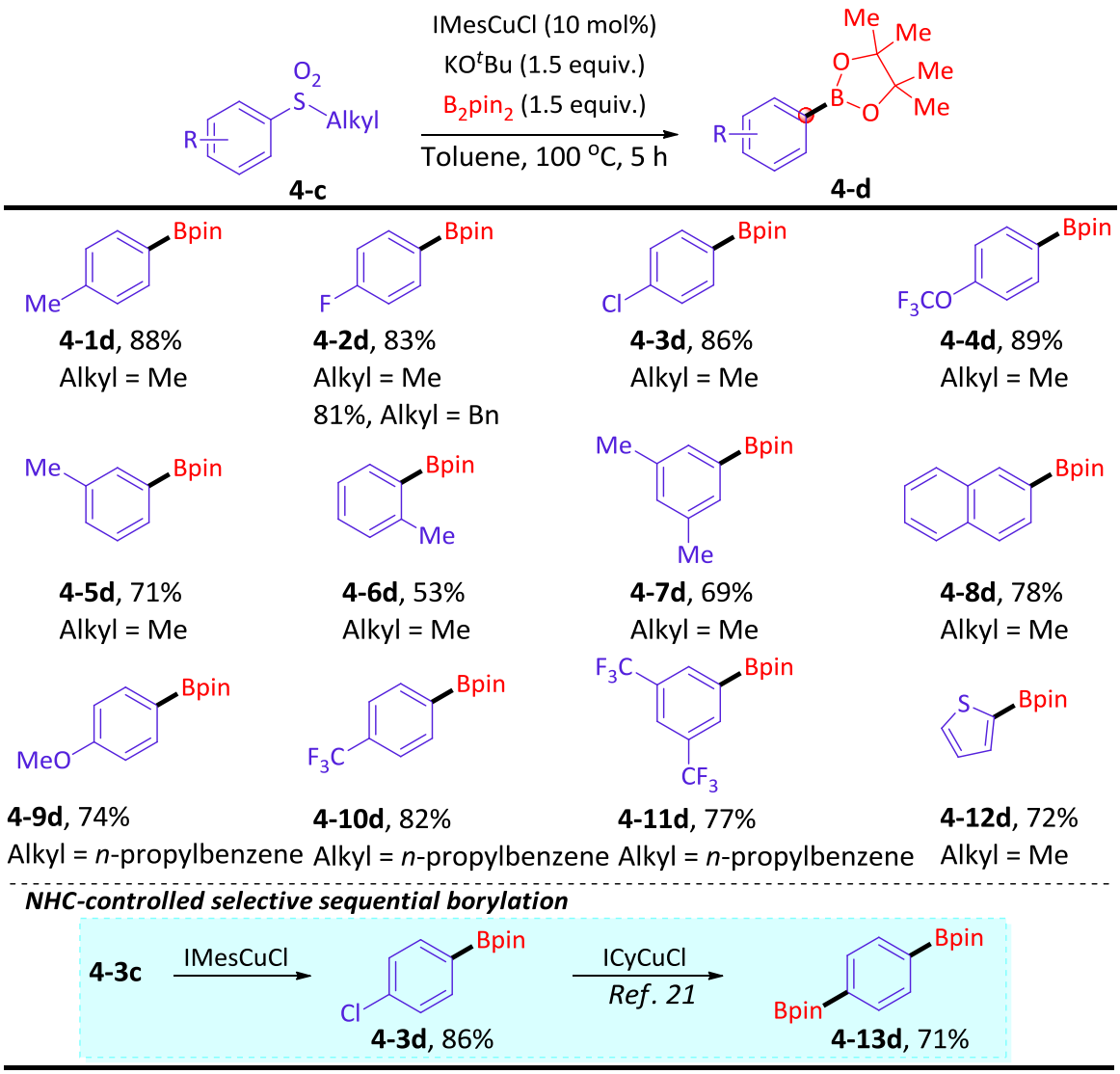
[a] Reaction conditions: **4-1a** (0.5 mmol, 1.0 equiv.), B_2pin_2 (1.5 equiv.), catalyst (10 mol%), base (1.5 equiv.), solvent (2 mL), at 100 °C for 5 h unless otherwise stated. The yields were determined by GC-MS analysis *vs* a calibrated internal standard and are averages of two runs. [b] 5 mol% IMesCuCl. [c] B_2neop_2 instead of B_2pin_2. [d] B_2cat_2 instead of B_2pin_2. [d] Isolated yield. Abbreviations: IMe, 1,3,4,5-tetramethylimidazolin-2-ylidene; bpy, 2,2'-bipyridine.

4.3.2 Investigation of Reaction Scope

Initially, under optimised reaction conditions, we proceeded to investigate the feasibility of this catalytic system with aryl substrates bearing different alkyl leaving groups (Scheme 4-2). A series of primary phenyl alkyl sulfones (**4-2a** – **4-7a**) with different alkyl functional groups, electronic properties, and carbon chains were efficiently transformed into phenyl boronate ester **4-1b** in excellent isolated yields (81%–89%), with borylation occurring selectively at the phenyl–SO_2 bonds, whereas the alkyl boronate esters were only observed in trace amounts by GC-MS. The secondary phenyl alkyl chain and cyclic sulfones **4-8a** and **4-9a** could generate the desired products in good yield, whereas tertiary sulfones **4-10a** showed lower reactivity.



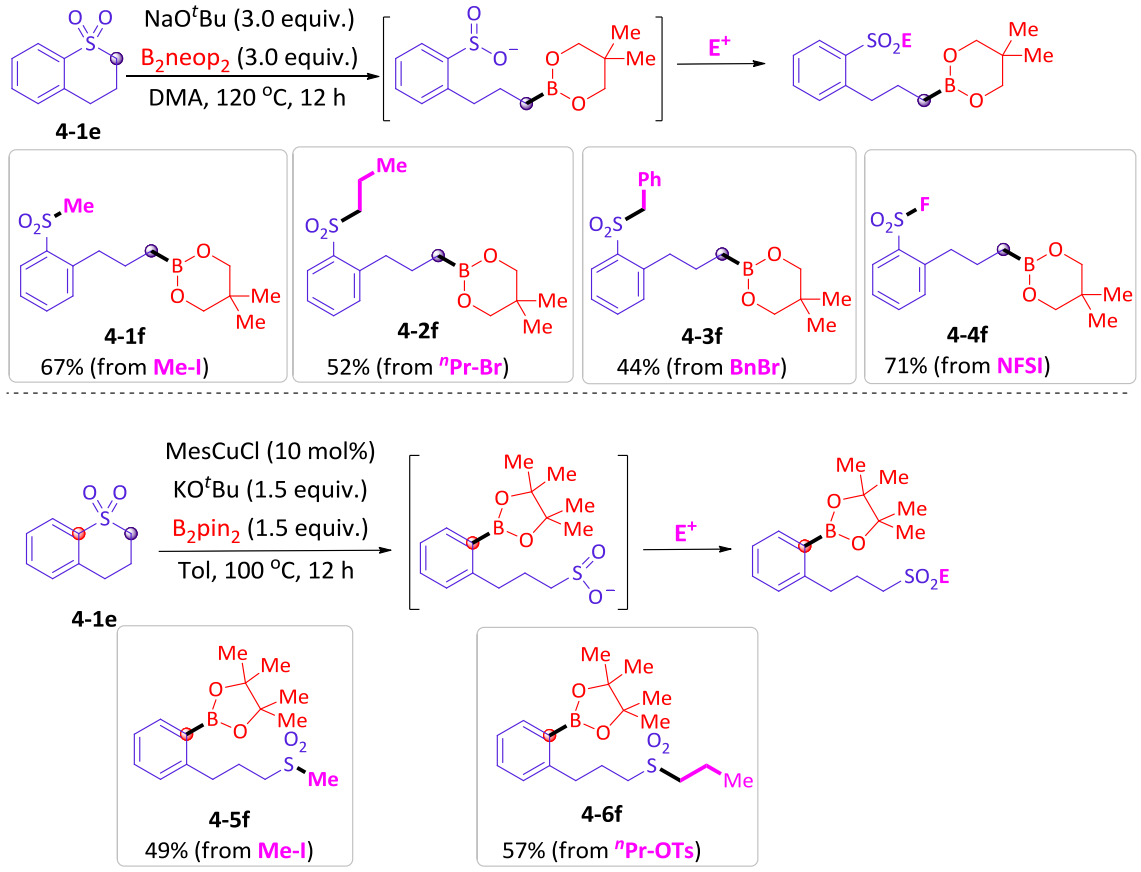
Scheme 4-2. Leaving-group scope for the copper-catalysed borylation of phenyl alkyl sulfones.



Scheme 4-3. Aryl alkyl sulfone substrate scope.

To evaluate the utility of this desulfonative borylation process, a series of aryl sulfones were examined (Scheme 4-3). The borylation had good functional group tolerance, as Me (**4-1d**), F (**4-2d**), Cl (**4-3d**), OCF_3 (**4-4d**), OMe (**4-9d**) or CF_3 (**4-10d**) groups were compatible. Halides on the benzene ring worked well in this process, exhibiting selective cleavage of the C(sp^2)–SO_2 bonds without any competitive C–Cl or C–F bond borylation. The sterically hindered, *meta*- and *ortho*-substituted tolyl-compounds **4-5c** and **4-6c** were also borylated smoothly in moderated yields (53%−71%). The compound 2-(methylsulfonyl)naphthalene **4-8c** was also successfully converted into the corresponding arylboronate ester **4-8d** in 78% yield. Bis-substituted aryl sulfones bearing electron-donating Me (**4-7c**) or electron-withdrawing CF_3 (**4-11c**) groups in both *meta*-positions gave the desired products **4-7d** and **4-11d** in 69% and 77% yields, respectively. This method was

also compatible with heteroaryl sulfone **4-12c**, generating borylated thiophene **4-12d** in 72% yield. Furthermore, by harnessing the chemoselectivity of the current reaction, in combination with our previously reported NHC-Cu systems,[23] the sequential borylation of the bifunctional 1-chloro-4-(methylsulfonyl)benzene **4-3c** became feasible. Thus, after the IMesCuCl-catalysed C(sp^2)–SO_2 borylation protocol afforded the 4-chlorophenylboronate ester **4-3d**, leaving the C(sp^2)–Cl bond intact, subsequent borylation using ICyCuCl as catalyst afforded the bisborylated product **4-13d**, based on our previously developed reaction conditions.[21] We observed poor reactivity for a diaryl sulfoxide in this reaction.



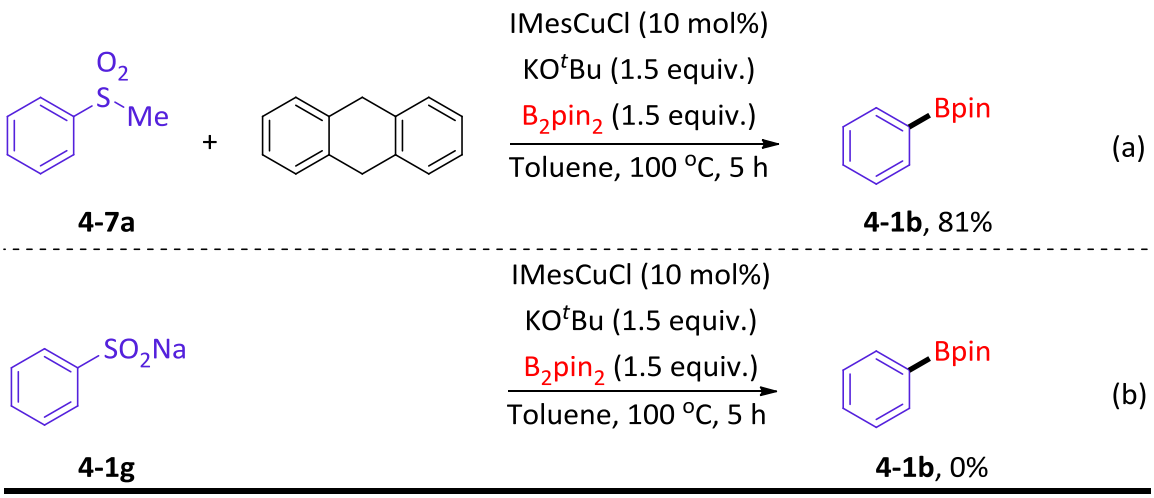
Scheme 4-4. Selective (sp^3-C–S (top) and sp^2-C–S (bottom)) ring-opening borylation of a cyclic sulfone and diverse products obtained by subsequent functionalisation of the sulfinate salt.

Cyclic sulfones are attractive scaffolds for the construction of sulfone-containing products. Cyclic sulfone **4-1e** has both alkyl C(sp^3)–SO_2 and aryl C(sp^2)–SO_2 bonds, which provides the possibility for diversity via selective borylation. Thus, **4-1e** was subjected to our

recently reported metal-free borylation conditions,[6] and the *in situ* formed alkyl borylated sulfinate salt was generated through cleavage of the alkyl C(sp^3)–SO_2 bond. Scheme 4-4 (top) outlines the aryl sulfones and sulfonyl fluoride molecules containing alkyl boronate groups that can be synthesised by further functionalising the sulfinate intermediates with diverse electrophiles in a one-pot, two-step fashion, including methyl iodide (**4-1f**), 1-bromopropane (**4-2f**), benzyl bromide (**4-3f**), and *N*-fluorobenzenesulfonimide (NFSI) (**4-4f**). In contrast, we also achieved selective borylation of the aryl C(sp^2)–SO_2 bond of cyclic sulfone **4-1e** using our optimised ICyCuCl-catalysed process (Scheme 4-4, bottom), and **4-5f** and **4-6f**, containing both alkyl sulfone and aryl boronate groups were generated selectively by treatment with iodomethane or propyl 4-methylbenzene-sulfonate, respectively, after *in situ* formation of the aryl borylated sulfinate salt.

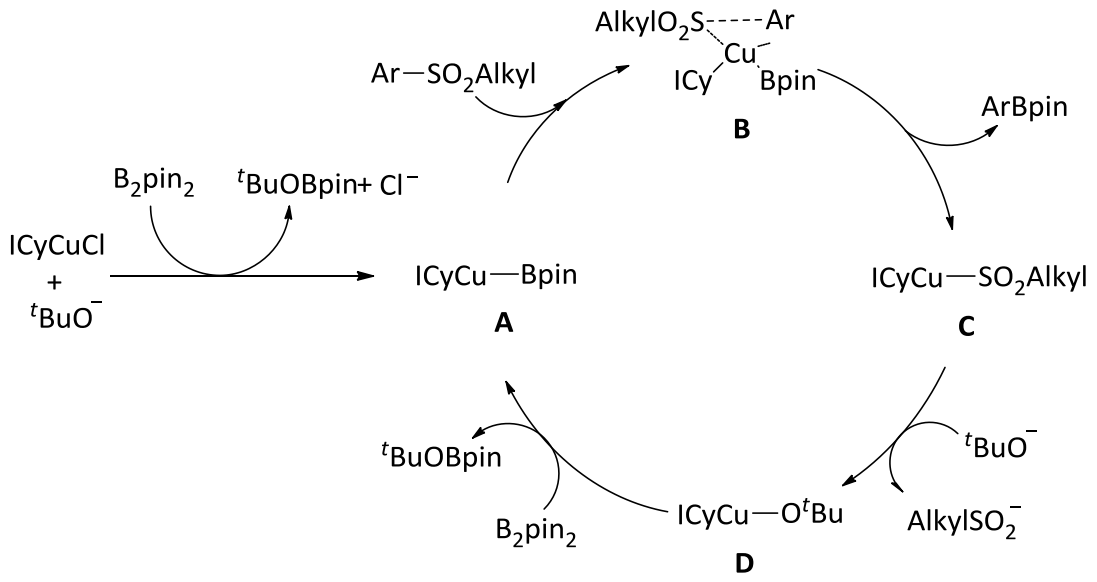
4.3.3 Mechanistic Studies

We next conducted some experiments to explore the mechanism of this Cu-catalysed borylation process. When the radical trap 9,10-dihydroanthracene (2.0 equiv.) was added to the reaction of **4-7a**, the yield of borylated product **4-1b** was essentially unaffected (Scheme 4-5a). Additionally, reaction of benzenesulfinic acid sodium salt **4-1g** failed to afford any borylated product, which ruled out the possibility of an aryl sulfinate salt intermediate to produce the arylboronates (Scheme 4-5b).



Scheme 4-5. Mechanistic studies.

Based on our previously proposed mechanism for the Cu-catalysed borylation of aryl halides,[20] we propose a catalytic cycle starting with the reaction of the alkoxy-activated $[ROB_2pin_2]^-$ anionic sp^2-sp^3 adduct[13a,24] with ICyCuCl, or ICyCuO^{t}Bu with B_2pin_2, forming ^{t}BuOBpin and ICyCuBpin (Scheme 4-6). Subsequently, copper boryl complex **A** reacts with the aryl sulfone generating the desired aryl boronate and ICyCu–SO_2Alkyl **C**, which then reacts with the ^{t}BuO$^-$ base forming ICyCuO^{t}Bu **D**. Copper boryl complex **A** is regenerated by reaction with B_2pin_2 forming ^{t}BuOBpin. Further studies regarding the mechanism are under way.



Scheme 4-6. Proposed mechanism.

4.4 Conclusions

In summary, we have successfully achieved the copper-catalysed selective borylation of aryl alkyl sulfones using a readily prepared NHC-Cu-catalyst. A wide range of aryl sulfones with various functional groups, electronic properties, and alkyl carbon chains are efficiently transformed into aryl boronate esters in good yields. The selective cleavage of alkyl(C)-sulfonyl or aryl(C)-sulfonyl bonds of cyclic sulfones under different reaction systems delivers versatile sulfinate intermediates *in situ*, which readily react with alkyl halides or electrophilic fluorine sources in a one-pot, two-step sequence to generate sulfonyl-containing boronate esters, including sulfones and sulfonyl fluorides.

4.5 Detailed Experiments and Characterization Data

4.5.1 General Information

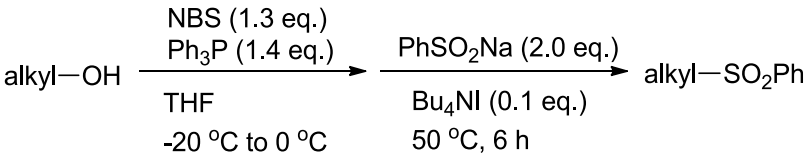
All reactions and subsequent manipulations were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox (Innovative Technology Inc. and Braun Uni Lab). All reactions were carried out in oven-dried glassware. Reagent grade solvents (Fisher Scientific and J.T. Baker) were nitrogen saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System, and further deoxygenated using the freeze-pump-thaw method. $CDCl_3$ was purchased from Sigma-Aldrich. The diboron reagents B_2neop_2, B_2cat_2 and B_2pin_2 were a generous gift from AllyChem Co. Ltd. All other reagents were purchased from Alfa-Aesar, Sigma-Aldrich or ABCR, and were checked for purity by GC-MS and/or ^1H NMR spectroscopy and used as received.

NMR spectra were recorded at 298 K using Bruker Avance 300 (^1H, 300 MHz; ^{13}C, 75 MHz, ^{11}B, 96 MHz), Bruker DPX-400 (^1H, 400 MHz; ^{13}C, 100 MHz, ^{11}B, 128 MHz; ^{19}F, 376 MHz), or Bruker Avance 500 (^1H, 500 MHz; ^{13}C, 125 MHz, ^{11}B, 160 MHz; ^{19}F, 470 MHz) spectrometers. ^1H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas $^{13}C\{^1H\}$ NMR spectra are reported relative to TMS using the natural-abundance carbon resonances ($CDCl_3$: 77.16 ppm). However, signals for the carbon attached to boron, C-B, are usually too broad to observe in the $^{13}C\{^1H\}$ NMR spectra. ^{11}B and ^{19}F NMR chemical shifts are reported relative to external $BF_3{\bullet}OEt_3$ or $CFCl_3$, respectively. Coupling constants are given in Hertz. Elemental analyses were performed in the microanalytical laboratory of the Institute of Inorganic Chemistry, Universität Würzburg, using an Elementar vario micro cube instrument. Automated flash chromatography was performed using a Biotage® Isolera Four system, on silica gel (Biotage SNAP cartridge KP-Sil 10 g and KP-Sil 25 g). Commercially available, precoated TLC plates (Polygram® Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 30 °C. GC-MS analyses were performed using a Thermo Fisher Scientific Trace 1310 gas chromatograph (column: TG-

SQC 5% phenyl methyl siloxane, 15 m, ∅ 0.25 mm, film 0.25 μm; injector: 250 ℃; oven: 40 ℃ (2 min), 40 ℃ to 280 ℃; carrier gas: He (1.2 mL min^{-1}) or an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 30 m, Ø 0.25 mm, film 0.25 μm; injector: 250 ℃; oven: 40 ℃ (2 min), 40 ℃ to 280 ℃ (20 ℃ min^{-1}); carrier gas: He (1.2 mL min^{-1}) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. High-resolution mass spectra were obtained using a Thermo Scientific Exactive Plus spectrometer equipped with an Orbitrap Mass Analyzer. Measurements were accomplished using an ASAP/APCI source with a corona needle, and a carrier-gas (N_2) at the temperature of 250 ℃.

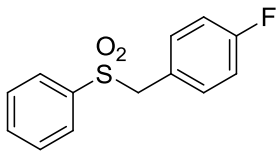
4.5.2 Synthesis of Sulfone Substrates

General procedure 1:



The compound was synthesized according to the literature.[25] Alkyl alcohol (3.0 mmol), Ph_3P (4.2 mmol) and THF (10 mL) were added to a Schlenk flask equipped with a magnetic stirring bar at –20 ℃ under argon. NBS (3.9 mmol) was added in small portions over 15 min. The reaction mixture was stirred while warming from –20 ℃ to 0 ℃ for 30 min. A mixture of $PhSO_2Na$ (6.0 mmol) and Bu_4NI (0.3 mmol) was added in 3 portions over 10 min to this solution. The mixture was stirred for 6 h at 50 ℃, then diluted with EtOAc (20 mL) and 3% aqueous $Na_2S_2O_3$ (20 mL). The layers were separated, and the aqueous phase was extracted with EtOAc (2 x 30 mL). The organic layer was washed with water and brine, and then dried over anhydrous Na_2SO_4, filtred and the solvent was removed under vacuum. The crude product was purified by recrystallization or flash column chromatography on silica gel with hexane/EtOAc to afford the sulfone.

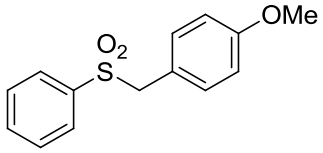
1-Fluoro-4-({phenylsulfonyl}methyl)benzene 4-2a



According to **General procedure 1** with (4-fluorophenyl)methanol (378 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **4-2a** as a white solid (630 mg, 2.52 mmol, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.65 – 7.60 (m, 3H), 7.47 (t, J = 8 Hz, 2H), 7.08 – 7.03 (m, 2H), 6.95 (t, J = 8 Hz, 2H), 4.28 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 163.1 (d, J = 247 Hz), 137.6, 134.0, 132.7 (d, J = 8 Hz), 129.1, 128.7, 124.0 (d, J = 3 Hz), 115.8 (d, J = 22 Hz), 62.1. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -112.3 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{12}FO_2S$ $[M+H]^+$ 251.0537 (251.0534).

The spectroscopic data for **4-2a** match those reported in the literature.[26]

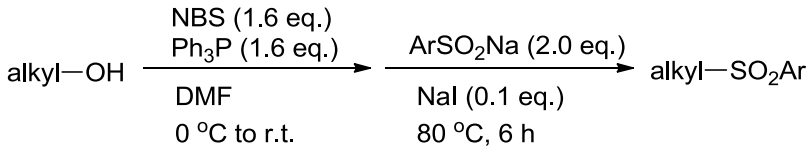
1-Methoxy-4-({phenylsulfonyl}methyl)benzene 4-3a



According to **General procedure 1** with (4-methoxyphenyl)methanol (414 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **4-3a** as a white solid (684 mg, 2.61 mmol, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 7 Hz, 2H), 7.60 (t, J = 7 Hz, 1H), 7.45 (t, J = 7 Hz, 2H), 6.99 (d, J = 9 Hz, 2H), 6.78 (d, J = 9 Hz, 2H), 4.25 (s, 2H), 3.78 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 160.0, 137.9, 133.8, 132.1, 129.0, 128.7, 120.0, 114.1, 62.3, 55.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{15}O_3S$ $[M+H]^+$ 263.0736 (263.0728).

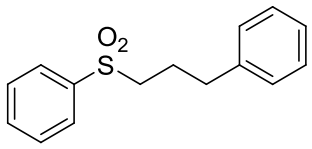
The spectroscopic data for **4-3a** match those reported in the literature.[26]

General procedure 2:



This method was based on the literature.[25] The alkyl alcohol (3.0 mmol), Ph_3P (4.8 mmol) and anhydrous DMF (10 mL) were added to a Schlenk flask equipped with a magnetic stirring bar at 0 ℃ under Ar. NBS (4.8 mmol) was added in small portions over 15 min. The reaction mixture was stirred while warming from 0 ℃ to r.t. over 30 min. To this solution was added a mixture of $PhSO_2Na$ (6.0 mmol) and NaI (0.3 mmol) in 3 portions over 10 min. The mixture was stirred for 6 h at 80 ℃, then diluted with EtOAc (20 mL) and 3% aq $Na_2S_2O_3$ (20 mL). The layers were separated, and the aqueous phase was extracted with EtOAc (2 x 30 mL). The organic layer was washed with water and brine, and then dried over anhydrous Na_2SO_4, filtred and the solvent removed under vacuum. The crude product was purified by recrystallization or flash column chromatography on silica gel with hexane/EtOAc to afford the sulfone.

<u>({3-Phenylpropyl}sulfonyl)benzene 4-4a</u>

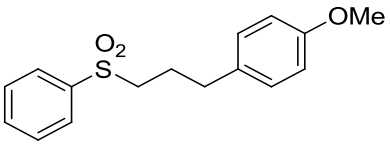


According to **General procedure 2** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and $PhSO_2Na$ (985 mg, 6.0 mmol, 2.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **4-4a** as a white solid (633 mg, 2.43 mmol, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.90 – 7.87 (m, 2H), 7.68 – 7.64 (m, 1H), 7.58 – 7.54 (m, 2H), 7.29

– 7.25 (m, 2H), 7.22 – 7.18 (m, 1H), 7.11 – 7.09 (m, 2H), 3.10 – 3.06 (m, 2H), 2.70 (t, *J* = 7 Hz, 2H), 2.09 – 2.01 (m, 2H). **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ = 139.9, 139.0, 133.8, 129.4, 128.7, 128.5, 128.1, 126.5, 55.5, 34.2, 24.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{17}O_2S$ $[M+H]^+$ 261.0944 (261.0943).

The spectroscopic data for **4-4a** match those reported in the literature.[27]

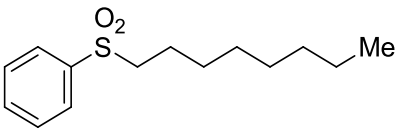
1-Methoxy-4-(3-{phenylsulfonyl}propyl)benzene 4-5a



According to **General procedure 2** with 3-(4-methoxyphenyl)propan-1-ol (499 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **4-5a** as a white solid (653 mg, 2.25 mmol, 75% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.91 – 7.87 (m, 2H), 7.68 – 7.62 (m, 1H), 7.59 – 7.53 (m, 2H), 7.03 – 6.99 (m, 2H), 6.82 – 6.78 (m, 2H), 3.78 (s, 3H), 3.08 – 3.03 (m, 2H), 2.64 (t, *J* = 7 Hz, 2H), 2.06 – 1.96 (m, 2H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$): δ = 158.3, 139.3, 133.8, 132.0, 129.5, 129.4, 128.2, 114.1, 55.6, 55.4, 33.3, 24.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}O_3S$ $[M+H]^+$ 291.1049 (291.1045).

The spectroscopic data for **4-5a** match those reported in the literature.[28]

(Octylsulfonyl)benzene 4-6a

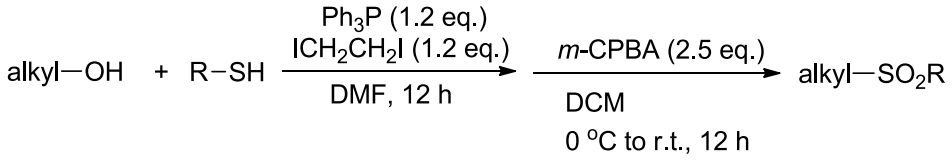


According to **General procedure 1** with octan-1-ol (390 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the

product **4-6a** as a white solid (587 mg, 2.31 mmol, 77% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.93 – 7.89 (m, 2H), 7.68 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 3.10 – 3.05 (m, 2H), 1.75 – 1.65 (m, 2H), 1.36 – 1.22 (m, 10H), 0.85 (t, *J* = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 139.4, 133.8, 129.4, 128.2, 56.5, 31.8, 29.1, 29.0, 28.4, 22.8, 22.7, 14.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{23}O_2S$ $[M+H]^+$ 255.1413 (255.1409).

The spectroscopic data for **4-6a** match those reported in the literature.[29]

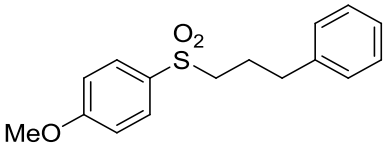
General procedure 3:



This method was based on the literature.[30] The alkyl alcohol (3.0 mmol), Ph_3P (3.6 mmol) and anhydrous DMF (10 mL) were added to a Schlenk flask equipped with a magnetic stirring bar under argon. The compound 1,2-diiodoethane (3.6 mmol) was then added and the mixture was stirred for 2 min until the 1,2-diiodoethane was completely dissolved. Thiol (9.0 mmol) was added subsequently and the mixture was stirred at room temperature for 12 h, then diluted with CH_2Cl_2 (20 mL). The mixture was washed with water (3 x 20 mL), the combined organic phases were dried over anhydrous Na_2SO_4, filtred and the solvent was removed under vacuum.

The crude aryl sulfide was dissolved in CH_2Cl_2 (10 mL) in an ice-water bath before *m*-CPBA (contains *ca*. 23 wt%, 7.5 mmol, 1.68 g) was added in portions. The mixture was allowed to warm to room temperature. After 12 h, saturated aqueous Na_2CO_3 was added and the resulting solution was extracted with EtOAc (3 x 20 mL). The combined organic layer was dried over Na_2SO_4 and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product was purified by flash column chromatography (hexane/ethyl acetate: 10/1).

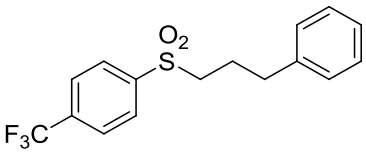
1-Methoxy-4-({3-phenylpropyl}sulfonyl)benzene 4-9c



According to **General procedure 3** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and 4-OMePhSH (1.262 g, 9.0 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **4-9c** as a white solid (633 mg, 2.31 mmol, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 9 Hz, 2H), 7.27 (dd, J = 6, 9 Hz, 2H), 7.20 (dd, J = 6, 9 Hz, 1H), 7.12 – 7.10 (m, 2H), 7.00 (d, J = 9 Hz, 2H), 3.87 (s, 3H), 3.08 – 3.04 (m, 2H), 2.69 (t, J = 7 Hz, 2H), 2.07 – 1.99 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 163.7, 140.0, 130.5, 130.2, 128.6, 128.4, 126.4, 114.5, 55.77, 55.75, 34.1, 24.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}O_3S$ $[M+H]^+$ 291.1049 (291.1044).

The spectroscopic data for **4-9c** match those reported in the literature.[31]

1-({3-Phenylpropyl}sulfonyl)-4-(trifluoromethyl)benzene 4-10c

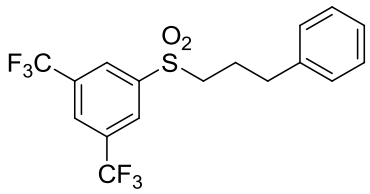


According to **General procedure 3** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and 4-CF_3PhSH (1.603 g, 9.0 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **4-10c** as a white solid (630 mg, 1.92 mmol, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.02 (d, J = 8 Hz, 2H), 7.83 (d, J = 8 Hz, 2H), 7.27 (t, J = 7 Hz, 2H), 7.21 (dd, J = 6, 9 Hz, 1H), 7.10 (d, J = 7 Hz, 2H), 3.11 – 3.08 (m, 2H), 2.72 (t, J = 7 Hz, 2H), 2.10 – 2.03 (m, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 142.7, 139.7, 135.6 (q, J = 33 Hz), 128.9, 128.8, 128.5, 126.7, 126.6 (q, J = 4 Hz), 123.2 (q, J = 273 Hz),

55.4, 34.2, 24.2. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -63.2 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{16}F_3O_2S$ $[M+H]^+$ 329.0818 (329.0814).

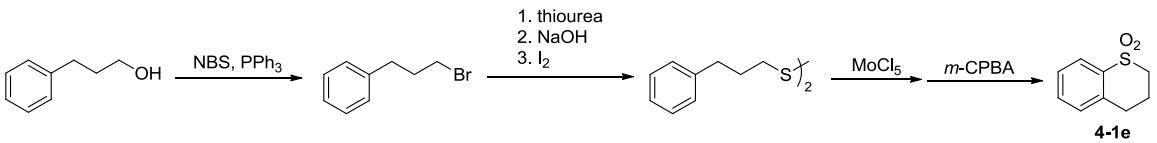
The spectroscopic data for **4-10c** match those reported in the literature.[31]

1-({3-Phenylpropyl}sulfonyl)-3,5-bis(trifluoromethyl)benzene 4-11c



According to **General procedure 3** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and 3,5-CF_3PhSH (2.215 g, 9.0 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **4-11c** as a white solid (654 mg, 1.65 mmol, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.33 (s, 2H), 8.15 (s, 1H), 7.30 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 7.11 – 7.09 (m, 2H), 3.15 – 3.12 (m, 2H), 2.76 (t, J = 8 Hz, 2H), 2.15 – 2.09 (m, 2H). **^{13}C{^{1}H} NMR** (120 MHz, $CDCl_3$): δ = 142.2, 139.3, 133.5 (q, J = 34 Hz), 128.9, 128.6 (q, J = 4 Hz), 128.5, 127.6, 126.9, 122.5 (q, J = 273 Hz), 55.4, 34.0, 23.9. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -62.9 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{15}F_6O_2S$ $[M+H]^+$ 397.0691 (397.0687).

The synthesis of thiochroman 1,1-dioxide 4-1e



3-Phenylpropan-1-ol (1.36 g, 10 mmol, 1.0 equiv.) was dissolved in anhydrous CH_2Cl_2 (20 mL) under an argon atmosphere. Triphenylphosphine (3.15 g, 12 mmol, 1.2 equiv.) and *N*-bromosuccinimide (2.14 g, 12 mmol, 1.2 equiv.) were added to the solution at 0 ℃ and the

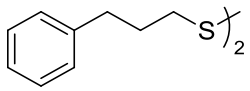
mixture was stirred for 2 h. A saturated aqueous solution of $NaHCO_3$ (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by flash column chromatography (hexane/ethyl acetate: 100/1) to afford (3-bromopropyl)benzene (1.83 g, 9.2 mmol, 92%).

(3-Bromopropyl)benzene (1.19 g, 6 mmol, 1.0 equiv.) was dissolved in ethanol (10 mL) and thiourea (0.5 g, 6.6 mmol, 1.1 equiv.) was added. The mixture was heated to reflux for 16 h and subsequently cooled to room temperature. Then, 2 N NaOH (20 mL) was added, and the reaction was stirred at room temperature for 20 min. Afterwards, the solution was acidified with a 2 N H_2SO_4 and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was dried over $MgSO_4$ and evaporated to dryness. The crude thiol was dissolved in methanol (20 mL) and a saturated solution of iodine in methanol was added until the colour of the solution maintained yellow. A saturated aqueous solution of $Na_2S_2O_3$ (20 mL) was added to remove the excess iodine and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by flash column chromatography (hexane/ethyl acetate: 100/1) to afford the disulfide (1.54 g, 5.1 mmol, 85%).

The disulfide (1.54 g, 5.1 mmol, 1.0 equiv.) was dissolved in anhydrous CH_2Cl_2 (10 mL) at argon atmosphere. $MoCl_5$ (2.79 g, 10.2 mmol, 2.0 equiv.) was added and the reaction mixture was stirred at room temperature for the 5 min. After 5 min, the reaction mixture was filtred through a pad of Celite (Ø 3 mm x 8 mm) and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ethyl acetate: 100/1) to afford the sulfide (0.53 g, 3.5 mmol, 69%). The sulfide (0.53 g, 3.5 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (9 mL) in an ice-water bath before *m*-CPBA (*ca*. 23 wt%, 8.75 mmol, 1.96 g) was added in portions. The mixture was allowed to warm to room temperature. After 12 h, saturated aqueous Na_2CO_3 were added, and the resulting solution was extracted with EtOAc (3 x 30 mL). The combined organic layer was dried over Na_2SO_4 and filtred through a pad of Celite (Ø 3 mm x 8 mm). The reaction mixture was

purified by recrystallisation (hexane/EtOAc) to yield the product **4-1e** as a white solid (492 mg, 2.70 mmol, 77% yield).

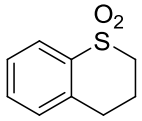
1,2-Bis(3-phenylpropyl)disulfane



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 – 7.26 (m, 4H), 7.22 – 7.16 (m, 6H), 2.75 – 2.66 (m, 8H), 2.06 – 1.97 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 141.5, 128.63, 128.56, 126.1, 38.3, 34.5, 30.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{11}O_2S$ $[M+H]^+$ 303.1236 (303.1226).

The spectroscopic data match those reported in the literature.[32]

Thiochroman 1,1-dioxide 4-1e



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 – 7.90 (m, 1H), 7.49 – 7.37 (m, 2H), 7.25 – 7.22 (m, 1H), 3.38 – 3.34 (m, 2H), 3.03 (t, J = 6 Hz, 2H), 2.54 – 2.46 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 139.1, 136.5, 132.4, 129.7, 127.8, 123.8, 50.9, 28.5, 21.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{11}O_2S$ $[M+H]^+$ 183.0474 (183.0467).

The spectroscopic data for **4-1e** match those reported in the literature.[32]

4.5.3 Details of the Borylation of Aryl Alkyl Sulfones

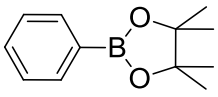
General procedure of optimization:

In an argon-filled glovebox, the aryl sulfone **4-1a** (0.5 mmol, 1.0 equiv.), dissolved in solvent (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. Base, catalyst and the boron source were added. The reaction mixture was stirred at 100 °C for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The solvent was evaporated under reduced pressure and dodecane was added as an internal standard and the crude reaction mixture was analysed by GC-MS.

General procedures 4:

In an argon-filled glovebox, the sulfone (0.5 mmol, 1.0 equiv.), dissolved in toluene (2 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. IMesCuCl (20.2 mg, 10 mol%), KO^{t}Bu (84.2 mg, 0.75 mmol, 1.5 equiv.), and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 equiv.) were added. The reaction mixture was stirred at 100 ℃ for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product was purified by flash column chromatography (hexane/EtOAc) after careful removal of the solvent *in vacuo*. All aryl boronate products were unambiguously identified by comparison of HRMS and ^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H} and/or ^{19}F{^{1}H} NMR spectra with literature data.

2-Phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4-1b

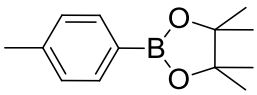


According to **General procedure 4**, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4-1b** as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.85 – 7.82 (m, 2H), 7.51 – 7.45 (m, 1H), 7.41 – 7.36 (m, 2H), 1.37 (s, 12H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 134.9, 131.4, 127.8, 83.9, 25.0. **^{11}B{^{1}H} NMR**

(96 MHz, $CDCl_3$): δ = 30.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{18}BO_2$ $[M+H]^+$ 205.1394 (205.1386).

The spectroscopic data for **4-1b** match with those reported in the literature.[33]

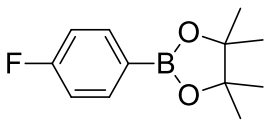
2-(*p*-Tolyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4-1d



According to **General procedure 4** with 1-methyl-4-(methylsulfonyl)benzene **4-1c** (85.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4-1d** as a colorless solid (96.0 mg, 440 µmol, 88% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.71 (d, J = 8 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 2.37 (s, 3H) 1.34 (s, 12H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 141.5, 134.9, 128.7, 83.8, 25.0, 21.9. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_2$ $[M+H]^+$ 219.1551 (219.1548).

The spectroscopic data for **4-1d** match those reported in the literature.[34]

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4-2d

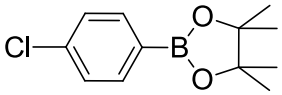


According to **General procedure 4** with 1-fluoro-4-(methylsulfonyl)benzene **4-2c** (87.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4-2d** as a colorless solid (92.2 mg, 415 µmol, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.83 – 7.79 (m, 2H), 7.07 – 7.03 (m, 2H), 1.34 (s, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 165.2 (d, J = 250 Hz), 137.2 (d, J = 8 Hz), 125.1 (br),

115.0 (d, *J* = 20 Hz), 114.8 (d, *J* = 21 Hz), 84.0, 25.0. **$^{11}B\{^{1}H\}$ NMR** (160 MHz, $CDCl_3$): δ = 30.7. **$^{19}F\{^{1}H\}$ NMR** (470 MHz, $CDCl_3$): δ = -108.4 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}BFO_2$ $[M+H]^+$ 223.1300 (223.1298).

The spectroscopic data for **4-2d** match those reported in the literature.[35]

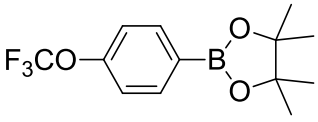
2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4-3d



According to **General procedure 4** with 1-chloro-4-(methylsulfonyl)benzene **4-3c** (95.3 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4-3d** as a colorless solid (102.5 mg, 430 µmol, 86% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8 Hz, 2H), 7.34 (d, *J* = 8 Hz, 2H), 1.34 (s, 12H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$): δ = 137.7, 136.3, 128.1, 84.1, 25.0. **$^{11}B\{^{1}H\}$ NMR** (96 MHz, $CDCl_3$): δ = 30.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}BClO_2$ $[M+H]^+$ 239.1005 (239.1001).

The spectroscopic data for **4-3d** match those reported in the literature.[36]

2-(4-(Trifluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4-4d

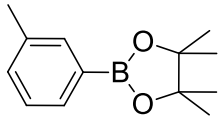


According to **General procedure 4** with 1-trifluoromethoxy-4-(methylsulfonyl)benzene **4-4c** (120.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4-4d** as a colorless solid (128.2 mg, 445 µmol, 89% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8 Hz, 2H), 7.20 (d, *J* = 8 Hz,

2H), 1.34 (s, 12H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$): δ = 151.8, 136.7, 120.6 (q, J = 258 Hz), 120.0, 84.2, 25.0. **$^{11}B\{^{1}H\}$ NMR** (160 MHz, $CDCl_3$): δ = 30.6. **$^{19}F\{^{1}H\}$ NMR** (470 MHz, $CDCl_3$): δ = -57.6 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{16}BF_3O_3$ $[M]^+$ 288.1139 (288.1133).

The spectroscopic data for **4-4d** match those reported in the literature.[37]

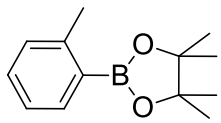
2-(3-Methyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 4-5d



According to **General procedure 4** with 1-methyl-3-(methylsulfonyl)benzene **4-5c** (85.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4-5d** as a colorless solid (77.4 mg, 355 µmol, 71% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.64 – 7.58 (m, 2H), 7.28 – 7.26 (m, 2H), 2.36 (s, 3H), 1.35 (s, 12H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$): δ = 137.3, 135.5, 132.2, 131.9, 127.8, 83.9, 25.0, 21.4. **$^{11}B\{^{1}H\}$ NMR** (96 MHz, $CDCl_3$): δ = 31.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_2$ $[M+H]^+$ 219.1551 (219.1547).

The spectroscopic data for **4-5d** match those reported in the literature.[38]

2-(2-Methyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 4-6d

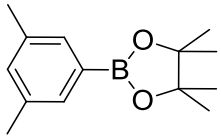


According to **General procedure 4** with 1-methyl-2-(methylsulfonyl)benzene **4-6c** (85.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel

(hexane/EtOAc = 98/2) to yield the product **4-6d** as a colorless solid (57.8 mg, 265 µmol, 53% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.79 – 7.76 (m, 1H), 7.33 (td, J = 8 Hz, 1H), 7.19 – 7.14 (m, 2H), 2.55 (s, 3H), 1.35 (s, 12H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 145.0, 136.0, 130.9, 129.9, 124.8, 83.5, 25.0, 22.4. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 31.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_2$ $[M+H]^+$ 219.1551 (219.1552).

The spectroscopic data for **4-6d** match those reported in the literature.[43]

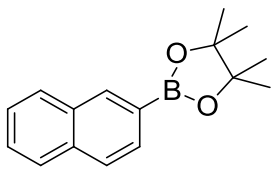
2-(3,5-Dimethylphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 4-7d



According to **General procedure 4** with 1,3-dimethyl-5-(methylsulfonyl)benzene **4-7c** (92.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4-7d** as a colorless solid (80.1 mg, 345 µmol, 69% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.44 (m, 2H). 7.10 (m, 1H), 2.32 (d, J = 1 Hz, 6H),1.34 (s, 12H), **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 137.3, 133.1, 132.5, 83.8, 25.0, 21.3. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{22}BO_2$ $[M+H]^+$ 233.1707 (233.1702).

The spectroscopic data for **4-7d** match those reported in the literature.[36]

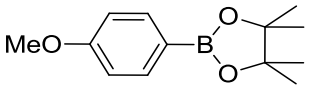
2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)naphthalene 4-8d



According to **General procedure 4** with 2-(methylsulfonyl)naphthalene **4-8c** (103.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4-8d** as a colorless solid (99.1 mg, 390 µmol, 78% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.38 (s, 1H), 7.90 – 7.82 (m, 4H), 7.54 – 7.45 (m, 2H), 1.40 (s, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 136.4, 135.2, 133.0, 130.5, 128.8, 127.8, 127.1, 127.1, 125.9, 84.1, 25.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 31.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}BO_2$ $[M]^+$ 254.1473 (254.1471).

The spectroscopic data for **4-8d** match those reported in the literature.[39]

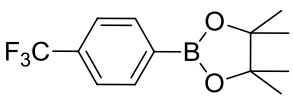
2-(4-Methoxy-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 4-9d



According to **General procedure 4** with 1-methoxy-4-((3-phenylpropyl)sulfonyl)benzene **4-9c** (145.2 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4-9d** as a colorless solid (86.6 mg, 370 µmol, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.76 (d, J = 9 Hz, 2H), 6.90 (d, J = 9 Hz, 2H), 3.82 (s, 3H), 1.34 (s, 12H),. **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 162.3, 136.6, 120.5 (br), 113.4, 83.7, 55.2, 25.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_3$ $[M+H]^+$ 235.1500 (235.1489).

The spectroscopic data for **4-9d** match those reported in the literature.[34]

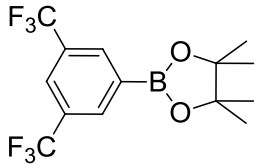
2-(4-Trifluoromethyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 4-10d



According to **General procedure 4** with 1-((3-phenylpropyl)sulfonyl)-4-(trifluoromethyl)benzene **4-10c** (164.2mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4-10d** as a colorless solid (111.5 mg, 410 μmol, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.91 (d, J = 8 Hz, 2H), 7.61 (d, J = 8 Hz, 2H), 1.36 (s, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 135.2, 133.0 (q, J = 32 Hz), 124.7 (q, J = 4 Hz), 124.7 (q, J = 272 Hz), 84.7, 25.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.7. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -63.0(s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{17}BF_3O_2$ $[M+H]^+$ 273.1268 (273.1255).

The spectroscopic data for **4-10d** match those reported in the literature.[40]

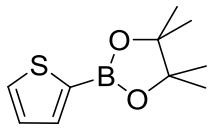
2-(3,5-Trifluoromethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4-11d



According to **General procedure 4** with 1-((3-phenylpropyl)sulfonyl)-3,5-bis(trifluoromethyl)benzene **4-11c** (198.2 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4-11d** as a colorless solid (131.0 mg, 385 μmol, 77% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.23 (m, 2H), 7.94 (m, 1H), 1.37 (s, 12 H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 134.8 (m), 131.0 (q, J = 33 Hz), 124.9 (m), 123.6 (q, J = 272 Hz), 85.0, 25.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.3. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -62.8 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{16}BF_6O_2$ $[M+H]^+$ 341.1142 (341.1135).

The spectroscopic data for **4-11d** match those reported in the literature.[41]

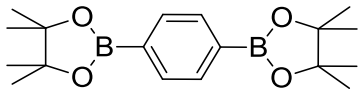
2-(Thiophene-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 4-12d



According to **General procedure 4** with 2-(methylsulfonyl)thiophene **4-12c** (81.5 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4-12d** as a yield solid (75.6 mg, 360 μmol, 72% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.63 – 7.67 (m, 2H), 7.20 (m, 1H), 1.35 (s, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 137.3, 132.5, 128.4, 84.2, 24.9. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 29.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{16}BO_2$ $[M+H]^+$ 211.0959 (211.0949).

The spectroscopic data for **4-12d** match those reported in the literature.[43]

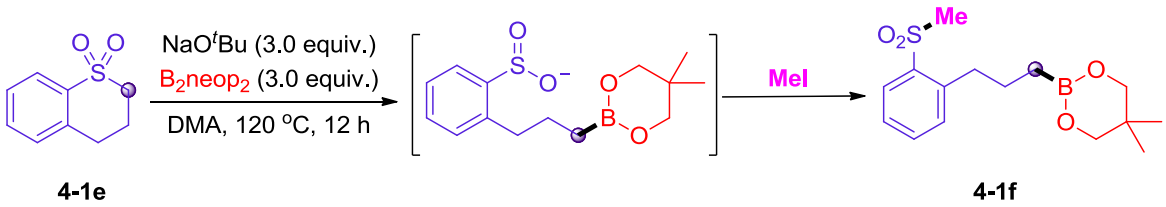
2,2'-(1,4-Phenylene)-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 4-13d



Yield: 117.2 mg (325 μmol, 71%) of a colorless solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.80 (s, 4H), 1.35 (s, 24H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 134.0, 84.0, 25.0. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{29}B_2O_4$ $[M+H]^+$ 331.2246 (331.2241).

The spectroscopic data for **4-13d** match those reported in the literature.[42]

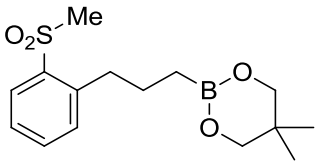
4.5.4 Ring-opening Borylation of Cyclic Sulfones



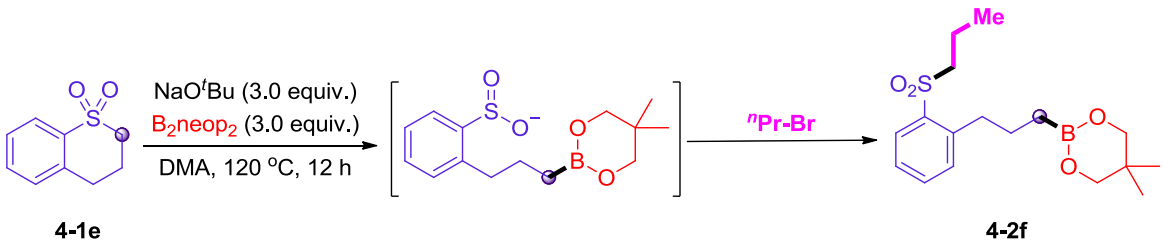
4-1e **4-1f**

In an argon-filled glovebox, the cyclic sulfone **4-1e** (54.7 mg, 0.3 mmol, 1.0 equiv.), dissolved in DMA (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (86.5 mg, 0.9 mmol, 3.0 equiv.) and B_2neop_2 (203.3 mg, 0.9 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 120 ℃ for 12 h. After 12 h, iodomethane (85.2 mg, 0.6 mmol, 2.0 equiv.) was added into the reaction tube under argon. The reaction mixture was stirred at room temperature for extra 6 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (5/1)) to yield the product **4-1f**.

2-(3-(2-(Methylsulfonyl)phenyl)propyl)-5,5-dimethyl-1,3,2-dioxaborinane 4-1f

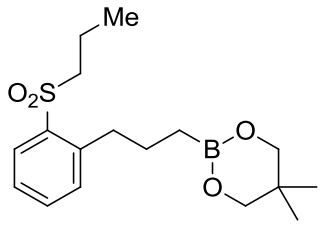


Yield: 62.3 mg (201 µmol, 67%) of a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.03 – 8.01 (m, 1H), 7.55 – 7.51 (m, 1H), 7.42 – 7.40 (m, 1H), 7.36 – 7.32 (m, 1H), 3.58 (s, 4H), 3.11 (s, 3H), 3.06 – 3.02 (m, 2H), 1.81 – 1.74 (m, 2H), 0.95 (s, 6H), 0.87 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 143.1, 138.6, 133.6, 131.9, 129.4, 126.5, 72.1, 44.7, 35.2, 31.8, 26.7, 22.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{24}BO_4S$ $[M+H]^+$ 311.1483 (311.1471). **Anal.** for $C_{15}H_{23}BO_4S$ calcd: C, 58.08; H, 7.47; S, 10.34. found: C, 58.22; H, 7.58; S, 10.52.

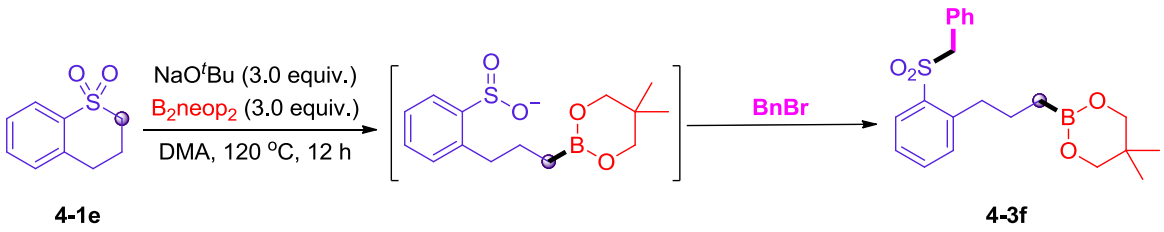


In an argon-filled glovebox, the cyclic sulfone **4-1e** (54.7 mg, 0.3 mmol, 1.0 equiv.), dissolved in DMA (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (86.5 mg, 0.9 mmol, 3.0 equiv.) and B_2neop_2 (203.3 mg, 0.9 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 120 ℃ for 12 h. After 12 h, 1-bromopropane (73.8 mg, 0.6 mmol, 2.0 equiv.) was added into the reaction tube under argon. The reaction mixture was stirred at room temperature for extra 12 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (5/1)) to yield the product **4-2f**.

2-(3-(2-(Propylsulfonyl)phenyl)propyl)-5,5-dimethyl-1,3,2-dioxaborinane 4-2f

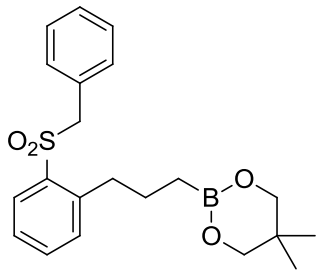


Yield: 52,8 mg (156 µmol, 52%) of a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.99 – 7.97 (m, 1H), 7.54 – 7.50 (m, 1H), 7.41 – 7.39 (m, 1H), 7.35 – 7.32 (m, 1H), 3.59 (s, 4H), 3.15 – 3.12 (m, 2H), 3.03 – 3.00 (m, 2H), 1.79 – 1.68 (m, 4H), 0.99 (t, J = 8 Hz, 3H), 0.96 (s, 6H), 0.87 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 143.4, 137.1, 133.5, 131.9, 130.4, 126.3, 72.1, 58.1, 35.4, 31.8, 26.9, 22.0, 16.6, 13.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{28}BO_4S$ $[M+H]^+$ 339.1796 (339.1784). **Anal.** for $C_{17}H_{27}BO_4S$ calcd: C, 60.36; H, 8.05; S, 9.48. found: C, 60.51; H, 7.92; S, 9.61.

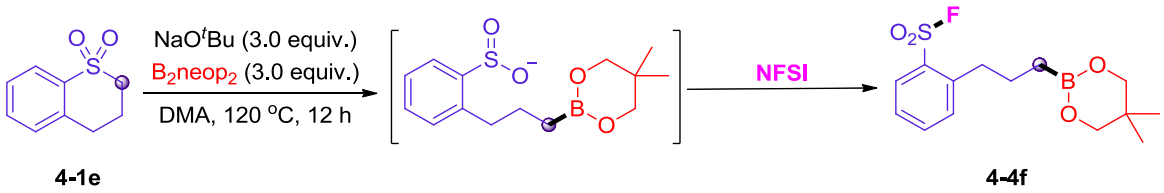


In an argon-filled glovebox, the cyclic sulfone **4-1e** (54.7 mg, 0.3 mmol, 1.0 equiv.), dissolved in DMA (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (86.5 mg, 0.9 mmol, 3.0 equiv.) and B_2neop_2 (203.3 mg, 0.9 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 120 ℃ for 12 h. After 12 h, (bromomethyl)benzene (102.6 mg, 0.6 mmol, 2.0 equiv.) was added into the reaction tube under argon. The reaction mixture was stirred at room temperature for an additional 12 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (5/1)) to yield the product **4-3f**.

2-(3-(2-(Benzylsulfonyl)phenyl)propyl)-5,5-dimethyl-1,3,2-dioxaborinane 4-3f

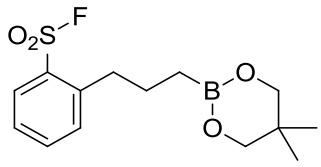


Yield: 51.0 mg (132 µmol, 44%) of a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.64 – 7.62 (m, 1H), 7.49 – 7.46 (m, 1H), 7.38 – 7.36 (m, 1H), 7.30 – 7.27 (m, 1H), 7.25 – 7.21 (m, 2H), 7.19 – 7.16 (m, 1H), 7.09 – 7.07 (m, 2H), 4.36 (s, 2H), 3.59 (s, 4H), 2.95 – 2.92 (m, 2H), 1.80 – 1.74 (m, 2H), 0.96 (s, 6H), 0.85 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 143.9, 135.9, 133.6, 131.7, 131.1, 131.0, 128.8, 128.6, 128.3, 126.1, 72.1, 62.9, 35.4, 31.8, 26.7, 22.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{28}BO_4S$ $[M+H]^+$ 387.1796 (387.1786). **Anal.** for $C_{21}H_{27}BO_4S$ calcd: C, 65.29; H, 7.04; S, 8.30. found: C, 65.46; H, 7.19; S, 8.33.

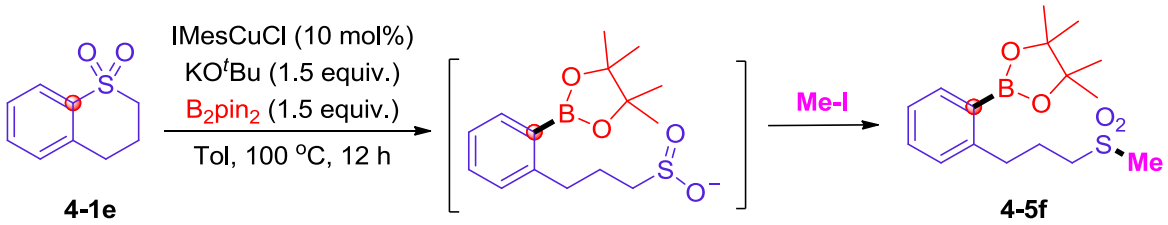


In an argon-filled glovebox, the cyclic sulfone **4-1e** (54.7 mg, 0.3 mmol, 1.0 equiv.), dissolved in DMA (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (86.5 mg, 0.9 mmol, 3.0 equiv.) and B_2neop_2 (203.3 mg, 0.9 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 120 ℃ for 12 h. After 12 h, N-fluorobenzenesulfonimide (189.2 mg, 0.6 mmol, 2.0 equiv.) was added into the reaction tube under argon. The reaction mixture was stirred at room temperature for an additional 6 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (10/1)) to yield the product **4-4f**.

2-(3-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)propyl)benzene-1-sulfonyl fluoride 4-4f

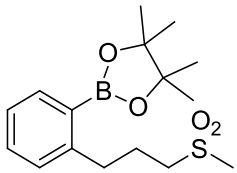


Yield: 67.0 mg (213 µmol, 71%) of a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.02 (d, J = 8 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.48 (d, J = 8 Hz, 1H), 7.40 – 7.36 (m, 1H), 3.59 (s, 4H), 3.02 – 2.99 (m, 2H), 1.80 – 1.74 (m, 2H), 0.96 (s, 6H), 0.85 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 144.3, 135.2, 132.2, 132.15 (d, J = 23 Hz), 130.2, 126.5, 72.1, 35.6, 31.8, 26.0, 22.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.3. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -150.0 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{21}BFO_4S$ $[M+H]^+$ 315.1232 (339.1221). **Anal.** for $C_{14}H_{20}BFO_4S$ calcd: C, 53.52; H, 6.42; S, 10.21. found: C, 53.66; H, 6.38; S, 10.28.

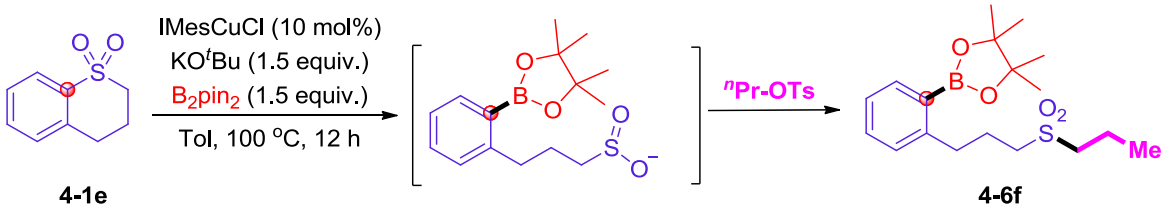


In an argon-filled glovebox, the cyclic sulfone **4-1e** (54.7 mg, 0.3 mmol, 1.0 equiv.), dissolved in toluene (2 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. IMesCuCl (12.1 mg, 10 mol%), KO^{t}Bu (50.5 mg, 0.45 mmol, 1.5 equiv.) and B_2pin_2 (114.3 mg, 0.45 mmol, 1.5 equiv.) were added. The reaction mixture was stirred at 100 ℃ for 12 h. After 12 h, iodomethane (85.2 mg, 0.6 mmol, 2.0 equiv.) was added into the reaction tube under argon. The reaction mixture was stirred at room temperature for an additional 6 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (10/1)) to yield the product **4-5f**.

4,4,5,5-Tetramethyl-2-(2-(3-(methylsulfonyl)propyl)phenyl)-1,3,2-dioxaborolane 4-5f



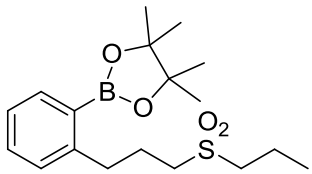
Yield: 47.7 mg (147 µmol, 49%) of a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.84 – 7.82 (m, 1H), 7.39 – 7.36 (m, 1H), 7.24 – 7.21 (m, 1H), 7.18 – 7.16 (m, 1H), 3.04 – 3.01 (m, 4H), 2.84 (s, 3H), 2.17 – 2.11 (m, 2H), 1.35 (s, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 147.2, 136.8, 131.4, 129.4, 126.0, 83.8, 54.7, 40.4, 34.2, 25.9, 25.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 31.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{26}BO_4S$ $[M+H]^+$ 325.1639 (325.1629). **Anal.** for $C_{16}H_{25}BO_4S$ calcd: C, 59.27; H, 7.77; S, 9.89. found: C, 59.34; H, 7.66; S, 9.73.



4-1e **4-6f**

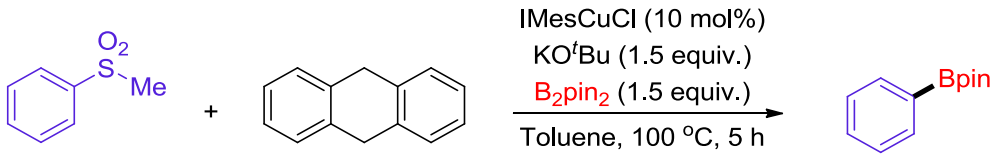
In an argon-filled glovebox, the cyclic sulfone **4-1e** (54.7 mg, 0.3 mmol, 1.0 equiv.), dissolved in toluene (2 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. IMesCuCl (12.1 mg, 10 mol%), KO^{t}Bu (50.5 mg, 0.45 mmol, 1.5 equiv.) and B_2pin_2 (114.3 mg, 0.45 mmol, 1.5 equiv.) were added. The reaction mixture was stirred at 100 ℃ for 12 h. After 12 h, propyl 4-methylbenzenesulfonate (128.6 mg, 0.6 mmol, 2.0 equiv.) was added into the reaction tube under argon. The reaction mixture was stirred at 100 ℃ for extra 3 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (10/1)) to yield the product **4-6f**.

4,4,5,5-Tetramethyl-2-(2-(3-(propylsulfonyl)propyl)phenyl)-1,3,2-dioxaborolane 4-6f



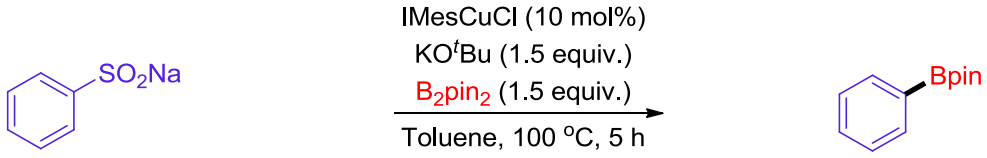
Yield: 60.2 mg (171 µmol, 57%) of a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.83 – 7.81 (m, 1H), 7.39 – 7.35 (m, 1H), 7.24 – 7.21 (m, 1H), 7.18 – 7.16 (m, 1H), 3.01 (t, J = 8 Hz, 2H), 2.98 – 2.94 (m, 2H), 2.89 – 2.86 (m, 2H), 2.15 – 2.08 (m, 2H), 1.86 – 1.78 (m, 2H), 1.35 (s, 12H), 1.04 (t, J = 8 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 147.2, 136.8, 131.4, 129.4, 125.9, 83.8, 54.3, 52.5, 34.3, 25.4, 25.1, 15.9, 13.3. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 31.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{30}BO_4S$ $[M+H]^+$ 353.1952 (353.1942). **Anal.** for $C_{18}H_{29}BO_4S$ calcd: C, 61.37; H, 8.30; S, 9.10. found: C, 61.42; H, 8.15; S, 9.18.

4.5.5 Preliminary Mechanistic Investigations



4-7a 2.0 equiv. **4-1b**, 81%

In an argon-filled glovebox, (methylsulfonyl)benzene **4-7a** (78.1 mg, 0.5 mmol, 1.0 equiv.), dissolved in toluene (2 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. IMesCuCl (20.2 mg, 10 mol%), KO^{t}Bu (84.2 mg, 0.75 mmol, 1.5 equiv.), B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 equiv.), and 9,10-dihydroanthracene (180.2 mg,1.0 mmol, 2.0 equiv.) were added. The reaction mixture was stirred at 100 ℃ for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product **4-1b** was isolated in 81% yield following flash column chromatography (hexane/EtOAc (98/2)) after careful removal of the solvent *in vacuo*.



4-1g **4-1b**, 0%

In an argon-filled glovebox, benzenesulfinic acid sodium salt **4-1g** (82.1 mg, 0.5 mmol, 1.0 equiv.), dissolved in toluene (2 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. IMesCuCl (20.2 mg, 10 mol%), KO^{t}Bu (84.2 mg, 0.75 mmol, 1.5 equiv.), and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 equiv.) were added. The reaction mixture was stirred at 100 ℃ for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product **4-1b** was not observed by GC-MS.

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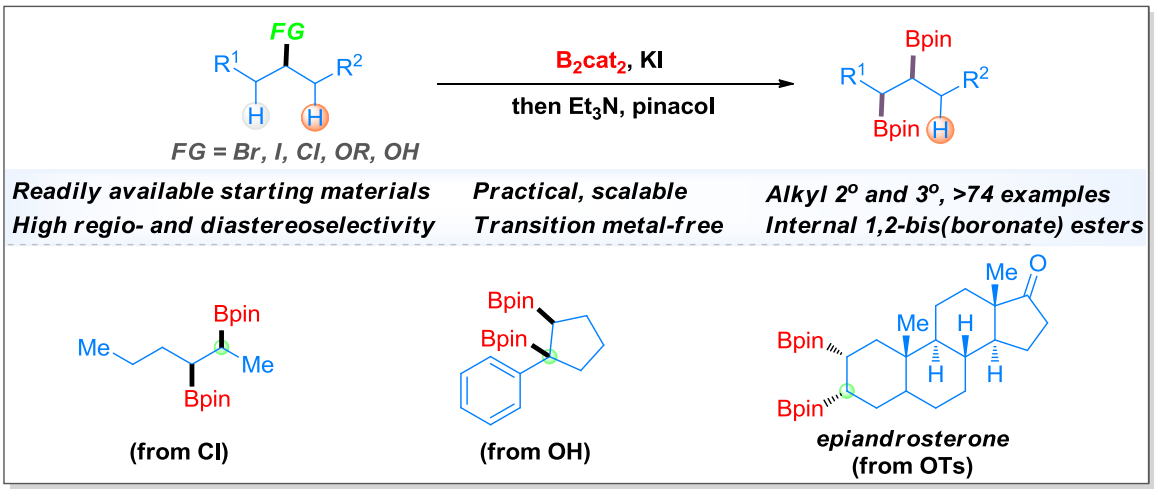
Chapter 5

Selective, Transition Metal-free 1,2-Diboration of Alkyl Halides, Tosylates, and Alcohols



5 Selective, Transition Metal-free 1,2-Diboration of Alkyl Halides, Tosylates, and Alcohols

5.1 Abstract

Defunctionalization of readily available feedstocks to provide alkenes for the synthesis of multifunctional molecules represents an extremely useful process in organic synthesis. Herein, we describe a transition metal-free, simple and efficient strategy to access alkyl 1,2-bis(boronate esters) via regio- and diastereoselective diboration of secondary and tertiary alkyl halides (Br, Cl, I), tosylates, and alcohols. Control experiments demonstrated that the key to this high reactivity and selectivity is the addition of a combination of potassium iodide and *N*,*N*-dimethylacetamide (DMA). The practicality and industrial potential of this transformation are demonstrated by its operational simplicity, wide functional group tolerance, and the late-stage modification of complex molecules. From a drug discovery perspective, this synthetic method offers control of the position of diversification and diastereoselectivity in complex ring scaffolds, which would be especially useful in a lead optimization program.

5.2 Introduction

Alkylboronates play an important role in synthetic chemistry, materials science and drug discovery.[1] They are easy to handle due to their good air and moisture stability, and can be readily employed to form carbon–carbon and carbon–heteroatom bonds and converted to various functional groups under mild reaction conditions.[2] The early approach to generate alkyl boronates typically focused on transmetalation using organolithium or Grignard reagents,[3] or the classical hydroboration of olefins,[4] which was followed by the development of metal-catalyzed olefin hydroboration.[5] Notably, the diboration of alkenes has attracted much attention because 1,2-bis(boronate esters) are emerging as important synthetic intermediates for preparing 1,2-difunctional compounds.[6] In addition, the boryl moieties in different environments in a 1,2-bis(boronate ester) can be differentiated and converted selectively, allowing the synthesis of a wide

variety of complex molecules.[7] From the emergence of diboron(4) compounds, the addition of diboron tetrachloride to ethylene was reported by Schlesinger.[8] Compared with diboron tetrahalide species, diboron(4) esters are much easier to handle, and are now commercially available in ton quantities.[9] Shortly after the initial report on the diboration of alkynes with bis(pinacolato)diboron (B_2pin_2) by Miyaura and Suzuki in 1993,[10] the first examples of the 1,2-diboration of alkenes using rhodium and gold catalysts were reported by Baker, Westcott, Marder and co-workers.[11] Subsequently, transition metal-catalyzed syntheses of 1,2-diborylalkanes from terminal or internal alkenes and alkynes have been widely reported by Marder,[12] Fernández,[13] Yun,[14] and others,[15] and enantioselective diboration[12b] was subsequently developed by Morken[16] and Hoveyda[17] (Figure 5-1A). Recently, Fernández and co-workers employed a Lewis acid-base adduct,[18] formed from an alkoxide and a diboron(4) reagent, which enabled the first transition metal-free 1,2-diboration of nonactivated alkenes.[19] Furthermore, other transition metal-free protocols have been developed for this 1,2-diboration process, such as amine-catalyzed or mediated,[20a,20b] hydroxyl-directed,[20c] carbohydrate-catalyzed enantioselective 1,2-diboration,[20d] unidirectional homologation of diborylmethane,[20e] and the reductive diboration of aryl alkenes with Na dispersion.[20f] Later, this strategy was also employed by Song's group to the base-catalyzed, selective diboration of alkynes in the presence of MeOH.[21]

As the most prevalent and readily available alkyl source, alkyl halides, alcohols, and their derivatives have recently been utilized in borylation reactions catalyzed by transition metals.[22,23] Despite the rapid development of these methods, diboration of these substrates is extremely rare. In 2019, Fu and co-workers developed a nickel-catalyzed vicinal diboration of alkyl bromides for the synthesis of 1,2-diborylalkanes; however, the products obtained were limited to terminal 1,2-bis(boronate esters).[23m] With increasing attention to sustainable chemistry, transition metal-free protocols[19e,24–27] have emerged as practical tools for the direct conversion of alkyl (pseudo)halides to alkyl boronates. The Studer,[28] Melchiorre,[29] and Jiao[30] groups independently reported the metal-free radical borylation of primary and secondary or benzylic alkyl halides using B_2cat_2 under blue LED irradiation, providing a broad range of alkylboronate esters. This protocol was later

extended by Mo, et al.[31] to the thermal borylation of primary alkyl iodides using B_2pin_2. Interestingly, deoxygenative monoborylations of secondary and tertiary alcohol derivatives, including xanthates, thionocarbamates, and methyl oxalate esters, using B_2cat_2 in DMF were disclosed by Studer[32] and Aggarwal.[33] Surprisingly, despite much effort on the metal-free borylation of alkyl precursors (including Br, I, and alcohol derivatives) (*vide supra*): 1) the transition metal-free direct borylation of unactivated alkyl chlorides and alcohols remains an unsolved problem, as most such reactions require transition metals;[23] and 2) almost all metal-free borylations of alkyl precursors focus on monoborylation. To the best of our knowledge, the metal-free diboration of alkyl halides and alcohols has not been achieved to date.

Defunctionalization of readily available feedstocks has emerged as one of the most valuable strategies for the generation of alkenes.[34] However, most of these transformations require a transition metal catalyst, a ligand, a strong base, or an expensive photocatalyst. Additionally, it is difficult to the control of regio- and stereoselectivities of the reactions; thus, four isomers of the alkenes were generally obtained restricting the selectivity of further transformations (Figure 5-1B). Therefore, we set as a goal the development of practical methods to solve these challenges. Given the easy accessibility and abundance of alkyl halides (including iodides, bromides and chlorides) and alcohols, we report, herein, the transition metal-free diboration of C–X and C–O bonds as a highly selective synthetic approach to useful 1,2-bis(boronate esters) (Figure 5-1C).

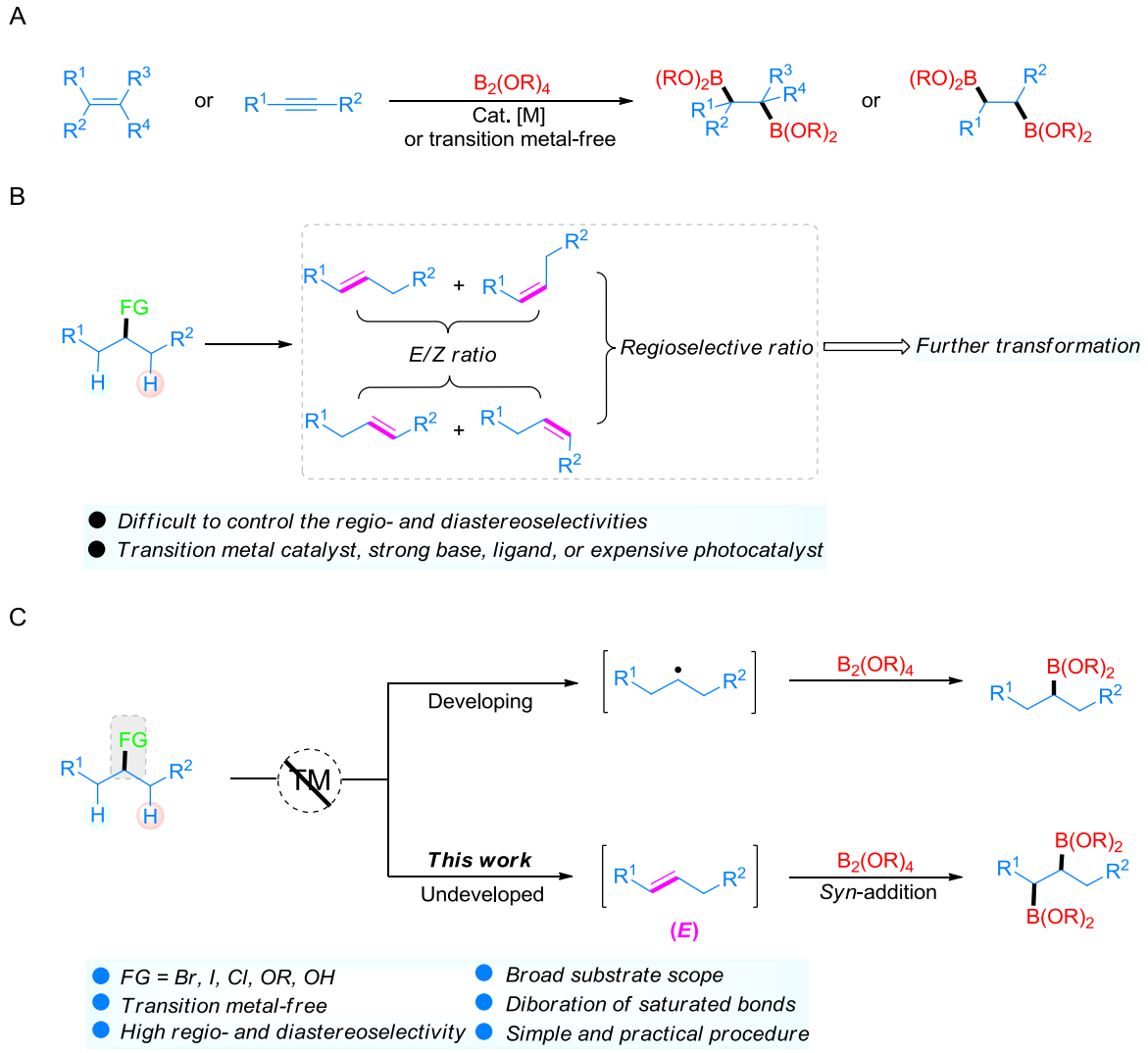


Figure 5-1. (A) Diboration of unsaturated bonds. (B) Challenges in olefin synthesis via defunctionalization processes. (C) This work: direct site-selective diboration of alkyl (pseudo)halides and alcohols.

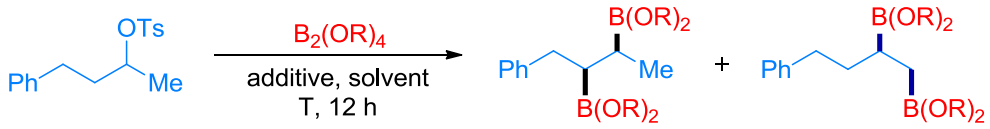
5.3 Results and Discussion

5.3.1 Optimization of Reaction Conditions

We set out to explore the possibility of metal-free diboration using the secondary alkyl tosylate (**5-1a)** as a model substrate (Table 5-1). As commonly used sources of diboron reagent in borylation reactions, bis(pinacolato)diboron (B_2pin_2), bis(neopentyl glycolato)diboron (B_2neop_2), and tetrahydroxydiboron ($B_2(OH)_4$) failed to afford any product in DMA at 80 °C for 12 h, whereas when bis(catecholato)diboron (B_2cat_2) was applied to this reaction, only trace amounts of 1,2-bisboronate pinacol ester were detected by GC-MS after transesterification of the crude catechol

boronate ester with pinacol in Et_3N (entries 1−4). When the reaction time was extended to 72 h, 1,2-bisboronate pinacol ester regioisomers (**5-1b**/**5-1b'** = 58/42) were obtained in 18% yield (entries 5). By screening solvents such as DMF, 1,4-dioxane, MeCN, and toluene (entries 6−9), we found that only an amide-based solvent was effective for this transformation. To improve the reactivity, we next tested a variety of bases or other additives. In view of the fact that strong bases can promote radical borylation,[31] we tested some strong bases, including LiO^{t}Bu and NaOMe, which were not efficient for our diboration reaction, and the monoboration product was also not detected in our system (entries 10 and 11). Neutral Lewis base additives, 4-PhPy and PPh_3, proved ineffective (entries 12 and 13). As the addition of KOAc showed a slightly increase in reactivity (entry 14), other alkali salts were screened (entries 15−17). Thus, upon addition of a stoichiometric amount of NaI to the reaction at 80 °C, a 62% yield of 1,2-diborylalkanes was obtained with the ratio of the internal and terminal borylation products **5-1b** and **5-1b'**, respectively, being 77:23 (entry 16). Interestingly, KI showed a dramatically increased yield and excellent regioselectivity of **5-1b**/**5-1b'** (entry 18). Further study showed that a slight temperature increase (90 °C) provided a higher isolated yield (95 %), rr = 95:5, dr > 10:1 (entry 19). This result suggested that KI could serve as an effective additive to promote the yield significantly with competitive regioselectivity.

Table 5-1: Optimization of the reaction conditions.[a]



5-1a **5-1b** **5-1b'**

entry	$B_2(OR)_4$	solvent	additive	temperature (°C)	yield (%)[b]	**5-1b/5-1b'**[c]
1	B_2pin_2	DMA	-	80	0	-
2	B_2neop_2	DMA	-	80	0	-
3	$B_2(OH)_4$	DMA	-	80	0	-
4	B_2cat_2	DMA	-	80	trace	-
5[d]	B_2cat_2	DMA	-	80	18	58/42
6[d]	B_2cat_2	DMF	-	80	10	55/45
7	B_2cat_2	1,4-dioxane	-	80	0	-
8	B_2cat_2	MeCN	-	80	0	-
9	B_2cat_2	toluene	-	80	0	-
10	B_2cat_2	DMA	LiO^tBu	80	27	54/46
11	B_2cat_2	DMA	NaOMe	80	trace	-
12	B_2cat_2	DMA	4-PhPy	80	0	-
13	B_2cat_2	DMA	PPh_3	80	0	-
14	B_2cat_2	DMA	KOAc	80	24	57/43
15	B_2cat_2	DMA	KCl	80	27	61/39
16	B_2cat_2	DMA	NaI	80	62	77/23
17	B_2cat_2	DMA	TBAI	80	39	71/28
18	B_2cat_2	DMA	KI	80	84	94/6
19	**B_2cat_2**	**DMA**	**KI**	**90**	**95**	**95/5**

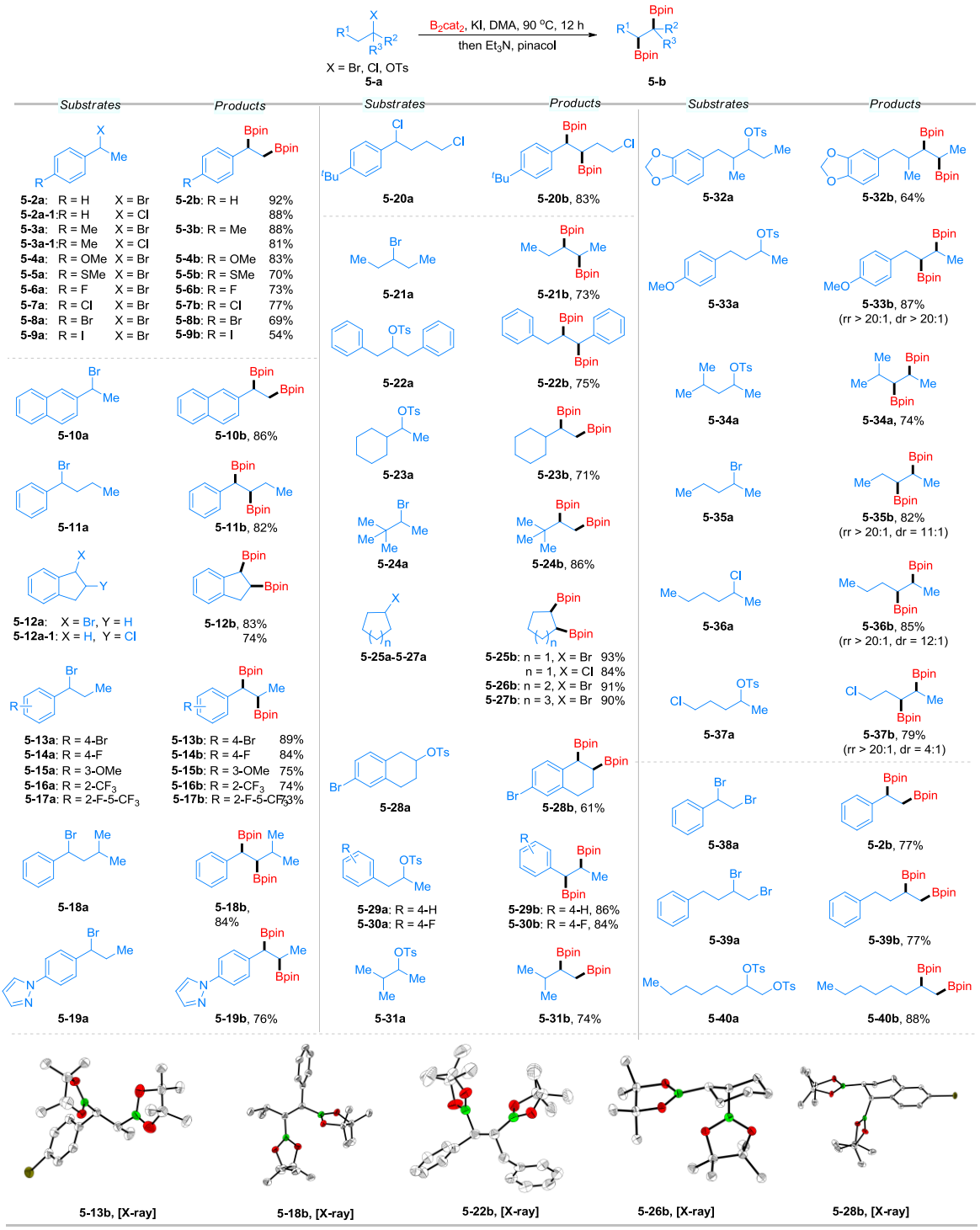
[a] Reaction conditions: alkyl tosylates **5-1a** (0.3 mmol, 1.0 equiv.), $B_2(OR)_4$ (2.5 equiv.), additive (1.0 equiv.), solvent (1.0 mL), 12 h, under argon; then pinacol (0.9 mmol), Et_3N (1.0 mL), rt, 1 h. [b] Isolated yield of **5-1b** and **5-1b'** after chromatographic workup. [c] The ratio of **5-1b** and **5-1b'** was determined of the crude reaction mixture by GC-MS analysis *vs* a calibrated internal standard and are averages of two runs. [d] 80 °C, 72 h. 4-PhPy, 4-Phenylpyridine. DMA, *N,N*-Dimethylacetamide. DMF, *N,N*-Dimethylformamide.

5.3.2 Investigation of Reaction Scope

With the optimal reaction conditions in hand, we proceeded to investigate the substrate scope of this transformation using various alkyl halides and tosylates. As shown in Scheme 5-1, secondary alkyl halides and tosylates could easily be diborylated with good to excellent yields. Thus, 1-(bromoethyl)arenes (**5-2a** − **5-5a**), bearing a *para*-Me, OMe, or SMe substituent, were converted into the corresponding alkylboronate esters in excellent isolated yields (**5-2b** − **5-5b**). Halide substituents (F, Cl, Br and I) on the benzene rings of the substrates were compatible with the

diboration reaction, exhibiting selective cleavage of the alkyl C–Br bond over the aryl C–X bond (**5-6b** − **5-9b**). We also investigated the compatibility of alkyl chlorides, as examples of the borylation of these substrates remain rare and usually require transition metals. Strikingly, the diboration of alkyl chlorides (**5-2a-1** and **5-3a-1**) preceded well under our conditions, giving the corresponding diboration products. Diboration of 2-(1-bromoethyl)naphthalene **5-10a** was also successful, and **5-10b** was obtained in 86% yield. A series of other linear and cyclic benzyl bromides also worked well to generate the internal 1,2-bisboronate pinacol esters bearing two stereocenters (**5-11a** − **5-19a**). Regarding the effect of steric hindrance, substituents in the alkyl branch did not affect the reaction efficiency (**5-11a**, **5-18a**). *Para*-, *meta*-, and even *ortho*-substituted (1-bromopropyl)arenes **5-13a** − **5-17a** performed well to deliver the corresponding diborylated products. Substrate **5-19a** containing an *N*-heterocycle was also compatible under standard conditions. The relative stereochemistries of the racemic diborylated products were assessed by analogy with single-crystal X-ray diffraction studies performed on **5-13b** and **5-18b**. Similar to the previously reported transition metal-free nucleophilic 1,2-diborations of non-activated olefins, which occurs in a *syn* fashion,[19,20] our racemic diborylated products were formed in a *syn*-configuration. Notably, substrate **5-20a**, containing both a primary and a secondary chloro group, also exhibited excellent chemoselectivity giving an 83% yield of **5-20b**. The synthesis of products bearing two secondary alkyl boronate esters were also performed in 73 and 75% yields, respectively, from symmetrical substrates **5-21a** and **5-22a**. It is worth noting the regioselective transformations of 1-cyclohexylethanol derivative **5-23a** and hindered halide **5-24a** to the corresponding sole products in 71 and 86% yields, respectively. Similarly to **5-12b**, cyclopentyl, cyclohexyl, and cycloheptyl halides (bromides and chlorides) reacted efficiently with B_2cat_2 to produce vicinal diboronates with a *syn*-configuration (**5-25b** − **5-27b**). The stereochemistry of **5-26b** was determined by single-crystal X-ray diffraction (Scheme 1). For the unsymmetrical six-membered ring substrate **5-28a**, *cis*-diboronate **5-28b** was obtained with complete regioselectivity, with the second boryl moiety at the benzylic site. The *syn* stereochemistry and site-selectivity of **5-28b** was determined by single crystal X-ray diffraction. We also performed DFT calculations to examine the relative energies of stereoisomers of **5-28b**.

The results showed that the energies of the *syn*-configurations were lower than those of the *anti*-configurations.



Scheme 5-1. Diboration of secondary alkyl halides and tosylates.[a] [a] All reaction were conducted on 0.3 mmol scale; isolated yield after chromatography; rr's were determined by GC-MS analysis of the crude reaction mixture *vs.* a calibrated internal standard and are averages of two runs, and

dr's were determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture *vs.* a calibrated internal standard and are averages of two runs.

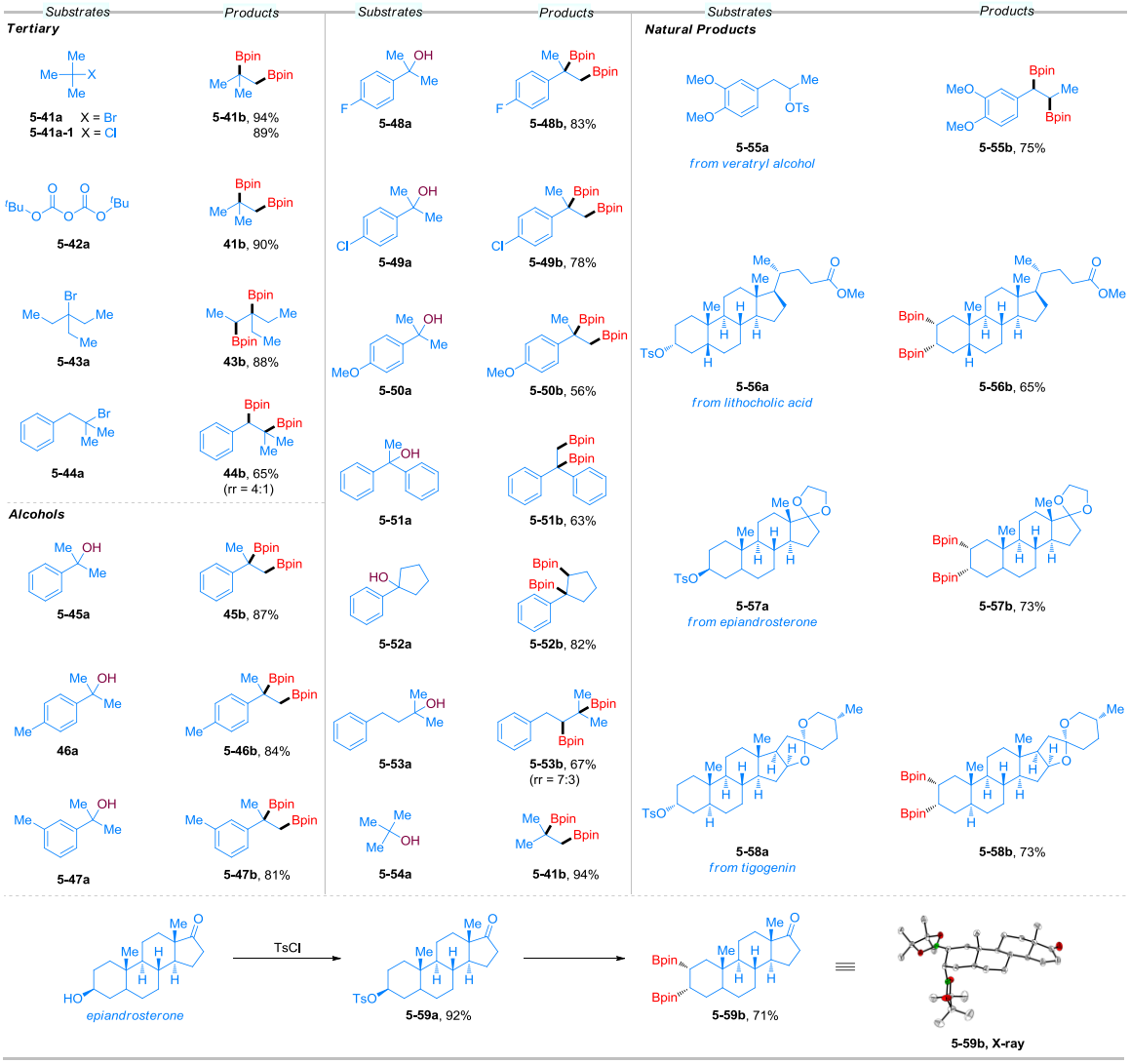
Another series of unsymmetrical substrates **5-29a** − **5-36a** was also studied to examine site-selectivity under our reaction conditions. Among them, for substrates possessing two alternative β sites (internal or terminal sites) (**5-29a**, **5-30a** and **5-33a** − **5-36a**), the second Bpin moiety was preferentially incorporated at the internal position to generate the internal 1,2-bisboronate pinacol ester with excellent regio- and diastereoselectivities. Interestingly, when the internal position was substituted with a methyl group, such as in **5-31a** and **5-32a**, the second boryl group was installed at the terminal position. This implies that the reaction occurs at the site with less steric hindrance. In addition to unactivated secondary alkyl chloride **5-36a**, which can efficiently produce internal 1,2-bis(boronate esters), substrate **5-37a** with both primary alkyl chloride and secondary alkyl tosylate sites exhibited similar reactivity, high regioselectivity, and good stereoselectivity. Interestingly, using 1,2-dibromo (**5-38a**, **5-39a**) or 1,2-ditosyl (**5-40a**) substrates, we obtained chemoselective diborylated products. This process also provides an efficient method to control the reaction sites for 1,2-difunctionalization. The corresponding alkenes were observed in the absence of B_2cat_2 when 1,2-dibromo (**5-38a**, **5-39a**) or 1,2-ditosyl (**5-40a**) substrates were employed under the standard conditions.[35]

Furthermore, various *tert*-alkyl substrates and complex natural products were examined (Scheme 5-2). The simple and commercially available *tert*-butyl halides (Br and Cl) (**5-41a** and **5-41a-1**) and Boc_2O (**5-42a**) both afforded diborylated compound **5-41b** in 89-94% yields. A slightly more sterically hindered *tert*-alkyl bromide **5-43a** also performed well. Substrate **5-44a** showed good regioselectivity (rr = 4:1) to afford the internal diboronated products.

In light of the above results, we wondered whether our diboration reaction could be applied directly to alkyl alcohols. In fact, a variety of benzyl *tert*-alkyl alcohols possessing Me, F, Cl, and OMe groups were well tolerated, giving good yields of **5-45b** –**5-50b** in all cases. The more sterically hindered substrate **5-51a** did not interfere with productive C–B bond formation (**5-51b**).

The internal cyclic product **5-52b** was also obtained from the corresponding tertiary alcohol, and **5-53b**, along with another terminal regioisomer, was obtained from alcohol **5-53a** under our conditions. Intriguingly, *tert*-butanol **5-54a** smoothly afforded the diborylated product in 94% yield.

The site-selective diboration of complex molecules is highly relevant to late-stage functionalization in total synthesis and drug discovery. Thus, veratryl alcohol derivative **5-55a** was subjected to our reaction conditions, delivering **5-55b** in 75% yield. Functional groups such as esters, acetals and ethers, as found in lithocholic acid (**5-56a**), epiandrosterone (**5-57a**), and tigogenin (**5-58a**), respectively, were tolerated, and excellent regio- and stereocontrol was achieved. The second boronate ester moieties are incorporated at the less sterically hindered sites to generate **5-56b** − **5-59b** as single *syn* regioisomers. The relative stereochemistries of **5-56b** − **5-59b** were assessed by analogy with single crystal X-ray diffraction studies of **5-59b**, which showed that **5-59b** was the only isolated stereoisomer present in the solid-state. From the viewpoint of drug development, this synthetic technique provides control over the selectivity for diversification and diastereoselectivity in the reactions of natural products, which should be crucial for lead optimization processes.

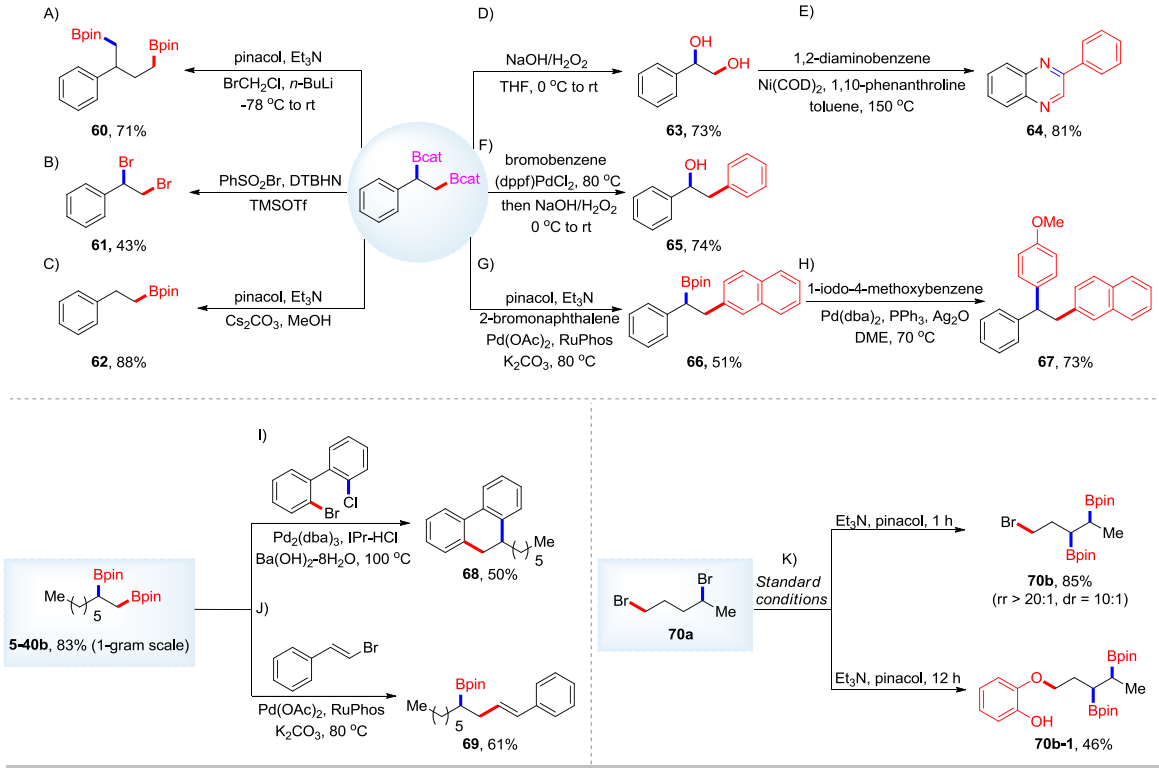


Scheme 5-2. Diboration of tertiary (pseudo)halides, alcohols and natural product derivatives.

5.3.3 Applications of the 1,2-Diborylalkane Products

To demonstrate further the synthetic value of this strategy, we carried out a series of reactions of the 1,2-diborylalkane products (Scheme 5-3). Subjection to standard Matteson homologation and deboronative bromination[36] gave the corresponding difunctionalization products **60** and **61**, respectively, in 71 and 43% yields. We were also particularly interested in whether selective functionalization of either the primary or the secondary boronate ester could be achieved. Selective protodeboronation occurred at the benzylic position, which eventually led to homobenzylic boronate **62**.[7g] Quinoxaline **64** was prepared readily from 1,2-diaminobenzene and 1,2-diol **63**,[37] which was formed under standard oxidation conditions. Alternatively, the 1,2-diboronate ester can be reacted, *in situ*, with bromobenzene in a one-pot reaction wherein the less hindered C–B bond

participates in the Suzuki-Miyaura cross-coupling.[7a] Then, the remaining C–B bond was oxidized to produce **65** during the reaction workup. For **5-2b**, the primary linear C–B bond could be coupled with an aryl bromide in the presence of $Pd(OAc)_2$ and RuPhos to give **66**. The remaining branched, secondary C–B bond was available for further cross-coupling under Ag_2O-promoted conditions to deliver compound **67**.[7f] According to recent work from the Morandi group,[6e] we conducted the stereospecific cascade Suzuki-Miyaura annulation of alkyl 1,2-bisboronate ester **40b** with 2-bromo-2'-chloro biaryl giving rise to 9,10-dihydrophenanthrene **68**. The secondary alkylboronate ester **69** could also be prepared from **5-40b** by reaction with (*E*)-(2-bromovinyl)benzene. Regarding chemoselectivity, an intramolecular competition experiment with secondary and primary alkyl bromide sites showed that the former functionality was more reactive. Thus, diboration of **70a** smoothly provided **70b** in 85% yield with excellent regioselectivity, and the primary alkyl bromide moiety was retained. Interestingly, after adding pinacol and trimethylamine to the reaction with stirring for 12 hours, we isolated the catechol-containing product (**70b-1**) in which the catechol moiety had displaced the bromide at the primary alkyl site.

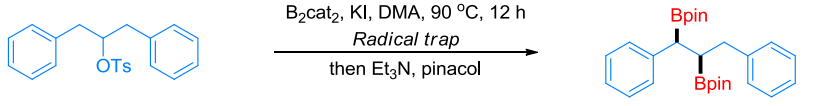


Scheme 5-3. Applications of the 1,2-diborylalkane products. DTBHN, *trans*-Di-*t*-butylhyponitrite. DME, Dimethoxyethane.

5.3.4 Mechanistic Studies

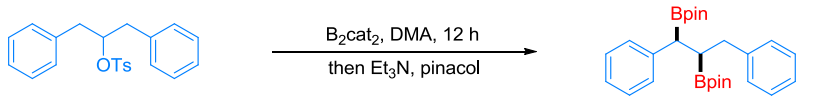
We next conducted several experiments to explore the mechanism of this diboration process. Firstly, when 9,10-dihydroanthracene or butylated hydroxytoluene (BHT) were added as radical traps, the yield of diboryl product **5-22b** remained largely unaffected (Scheme 5-4a). This result implies that radical process may not be involved. Secondly, without the addition of KI, only a trace amount of diborylated product **5-22b** was detected, and **5-22a** was almost completely recovered (Scheme 5-4b). Clearly, KI plays a crucial role for the generation of the diborylated products. When tosylate **5-22a** was reacted in DMA without addition of B_2cat_2, olefin **5-22c** was obtained in 19% yield with low stereoselectivity. Upon addition of KI, olefin **5-22c** was isolated in 78% yield with an excellent *E/Z* ratio at 80 °C. The results also implied that alkyl alkenes might be the active intermediates of this transformation. Immediately afterwards, **5-22c** could be converted into **5-22b** in similarly high yields regardless of the presence or absence of KI under the standard conditions. In order to confirm whether the process undergoes replacement of the OTs in **5-22a** by iodide, we synthesized alkyl iodide (**71a**), which was subjected to our conditions (Scheme 5-4c). In the absence of B_2cat_2, KI promoted the formation of *E*-alkenes (**5-22c**). When KI and B_2cat_2 were added to the reaction at the same time, the yield of the target product increased significantly. These results indicated that the presence of KI enhanced both the reactivity and regioselectivity and diastereoselectivity of the reaction. However, this does not rule out the possibility of initial iodide exchange taking place. Finally, we explored the role of DMA in this system (Scheme 5-4d). Only an amide solvent afforded the desired product, which was in accordance with literature reports, suggesting the weak complexation of B_2cat_2 with DMA.[25a,26a] However, 4-dimethylaminopydidine (DMAP) was somewhat effective as a base additive, indicating that a nitrogen base can promote the diboration process to some extent.[20a,38] Based on the above experiments, we propose a plausible mechanism (Scheme 5-4e). Alkyl (pseudo)halides are initially dehydrohalogenated to form alkenes with high selectivity using a combination of KI and DMA. Subsequently, the alkenes undergo *syn*-selective diboration[19a,20a] with DMA-activated B_2cat_2, providing the target product.

(a) Radical trap experiments

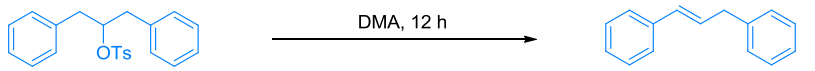


Radical trap	**5-22b**
None	81%
9,10-dihydroanthracene	75%
BHT	76%

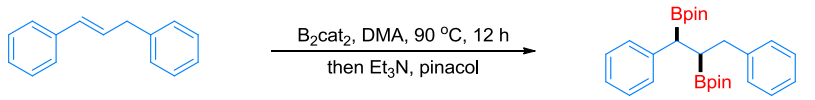
(b) Role of KI



T/°C	KI	**5-22b**
80	✗	trace
80	✓	72%

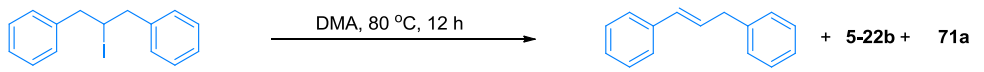


T/°C	KI	**5-22c** (*E*/*Z*)
80	✗	19% (59/41)
80	✓	78% (98/2)
90	✓	85% (98/2)



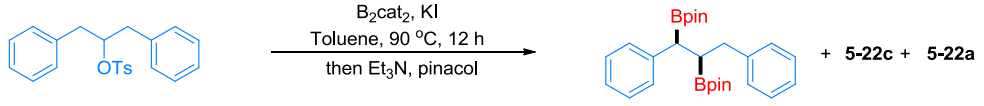
KI	**5-22b**
✗	78%
✓	81%

(c) Diboration of iodides



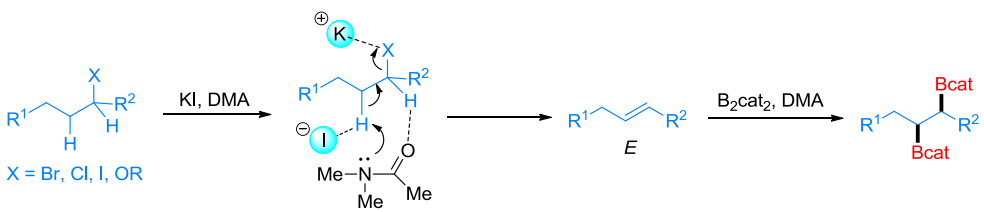
KI	B_2cat_2	**5-22c** (*E*/*Z*)		
✗	✗	18% (61/39)	-	71%
✓	✗	74% (95/5)	-	0%
✗	✓	0%	12%	79%
✓	✓	0%	78%	0%

(d) Role of DMA



Additive	**5-22b**		
None	0%	0%	92%
DMA (3.0 equiv.)	19%	0%	74%
DMAP (3.0 equiv.)	11%	0%	76%

(e) Plausible mechanism



Scheme 5-4. Mechanistic studies.

5.4 Conclusion

We have developed a direct and selective diboration of C–X and C–O bonds, thus efficiently synthesizing 1,2-bis(boronate esters). The use of KI and DMA is critical to the methodology, which circumvents the regio- and diastereoselectivity problems. The method shows a broad substrate scope with high yields and selectivities, and practicality for the late-stage modification of natural molecules. Experimental studies of the reaction mechanism of the selective diborylation process were also carried out. Given how widespread halogen and hydroxyl groups are, we anticipate that this approach will simplify the preparation of diborylalkane targets for research in chemistry, materials, bioactive compounds, and other applications.

5.5 Detailed Experiments and Characterization Data

5.5.1 General Information

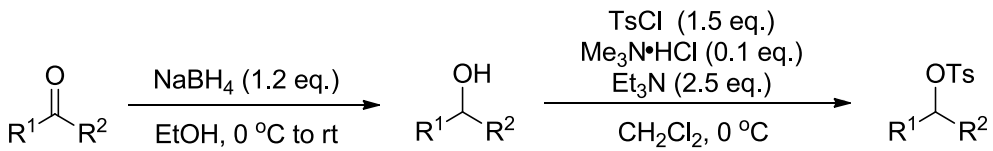
All reactions and subsequent manipulations were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox (Innovative Technology Inc. and Braun Uni Lab). All reactions were carried out in oven-dried glassware. Reagent grade solvents (Fisher Scientific and J.T. Baker) were nitrogen saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System, and further deoxygenated using the freeze-pump-thaw method. C_6D_6 and $CDCl_3$ were purchased from Sigma-Aldrich. The diboron reagents B_2pin_2, B_2neop_2, and $B_2(OH)_4$ were a generous gift from AllyChem Co. Ltd. All other reagents were purchased from Sigma-Aldrich or ABCR.

NMR spectra were recorded at 298 K using Bruker Avance 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz, ^{11}B, 96 MHz), Bruker DPX-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz, ^{11}B, 128 MHz; ^{19}F, 376 MHz), or Bruker Avance 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz, ^{11}B, 160 MHz; ^{19}F, 470 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm; C_6D_6: 7.16 ppm) whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS using the natural-abundance carbon resonances ($CDCl_3$: 77.16 ppm, C_6D_6: 128.0 ppm). ^{11}B and ^{19}F NMR chemical shifts are reported relative to

external BF_3•OEt_3 or $CFCl_3$, respectively. Coupling constants are given in Hertz. Elemental analyses were performed in the microanalytical laboratory of the Institute of Inorganic Chemistry, Universität Würzburg, using an Elementar vario micro cube instrument. Automated flash chromatography was performed using a Biotage® Isolera Four system, on silica gel (Biotage SNAP cartridge KP-Sil 10 g and KP-Sil 25 g). Commercially available, precoated TLC plates (Polygram® Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 30 °C. GC-MS analyses were performed using a Thermo Fisher Scientific Trace 1310 gas chromatograph (column: TG-SQC 5% phenyl methyl siloxane, 15 m, Ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C; carrier gas: He (1.2 mL min^{-1}) or an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 30 m, Ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C (20 °C min^{-1}); carrier gas: He (1.2 mL min^{-1}) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. High-resolution mass spectra were obtained using a Thermo Scientific Exactive Plus spectrometer equipped with an Orbitrap Mass Analyzer. Measurements were accomplished using an ASAP/APCI source with a corona needle, and a carrier-gas (N_2) temperature of 250 °C.

5.5.2 Preparation of Substrates

General procedure 1: Preparation of secondary alkyl tosylates

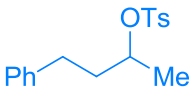


To a solution of ketone (3.0 mmol, 1.0 equiv.) in EtOH (9.0 mL) was added $NaBH_4$ (136.8 mg, 3.6 mmol, 1.2 equiv.) at 0 °C and the reaction mixture was stirred at room temperature for 2 h. The reaction was then quenched with water, diluted with CH_2Cl_2, and extracted with CH_2Cl_2 three times. The combined organic layer was washed by brine, dried over Na_2SO_4, filtred, and

concentrated under reduced pressure to afford the corresponding alcohol, which was directly used in the next step without further purification.

Tosylates were synthesized according to reported literature.[39] A glass tube was charged with *p*-toluene sulfonyl chloride (857.9 mg, 4.5 mmol, 1.5 equiv.) and trimethylamine hydrochloride (28.7 mg, 0.3 mmol, 0.1 equiv.) in CH_2Cl_2 (1 M with respect to the alcohol). Triethylamine (1.04 mL, 7.5 mmol, 2.5 equiv.) was added dropwise at 0 °C to the solution. To the resulting mixture was added a solution of the alcohol obtained above (3.0 mmol, 1.0 equiv.) in CH_2Cl_2 (1 M), and the mixture was then stirred at 0 °C for 2 h. The reaction was quenched by addition of *N,N*-dimethylethylenediamine (0.49 mL, 4.5 mmol, 1.5 equiv.) and stirred for 10 min. The reaction was mixed with water and extracted 3 times with CH_2Cl_2. The organic layer was washed sequentially with 1 M HCl, saturated aqueous Na_2CO_3 and brine. The combined organic layer was dried over Na_2SO_4, and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product was isolated by flash column chromatography.

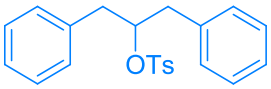
4-Phenylbutan-2-yl 4-methylbenzenesulfonate 5-1a



According to **General procedure 1** with 4-phenylbutan-2-one (444.6 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-1a** as a white solid (785.4 mg, 2.58 mmol, 86% yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8 Hz, 2H), 7.31 (d, J = 8 Hz, 2H), 7.26 – 7.16 (m, 3H), 7.05 (d, J = 7 Hz, 2H), 4.69 – 4.58 (m, 1H), 2.65 – 2.47 (m, 2H), 2.43 (s, 3H), 1.99 – 1.73 (m, 2H), 1.29 (d, J = 6 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 144.6, 141.0, 134.6, 129.9, 128.6, 128.4, 127.9, 126.2, 80.0, 38.3, 31.3, 21.8, 21.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{21}O_3S$ $[M+H]^+$ 305.1206 (305.1201).

The spectroscopic data for **5-1a** match those reported in the literature.[39]

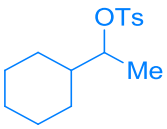
1,3-Diphenylpropan-2-yl 4-methylbenzenesulfonate 5-22a



According to **General procedure 1** with 1,3-diphenylpropan-2-one (630.8 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-22a** as a white solid (802.6 mg, 2.19 mmol, 73% yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.41 – 7.38 (m, 2H), 7.22 – 7.18 (m, 6H), 7.07 – 7.05 (m, 6H), 4.85 – 4.79 (m, 1H), 2.99 – 2.89 (m, 4H), 2.37 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 144.1, 136.4, 133.4, 129.7, 129.6, 128.6, 127.6, 126.8, 84.7, 40.6, 21.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{23}O_3S$ $[M+H]^+$ 367.1362 (367.1358).

The spectroscopic data for **5-22a** match those reported in the literature.[39]

1-Cyclohexylethyl 4-methylbenzenesulfonate 5-23a

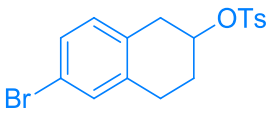


According to **General procedure 1** with 1-cyclohexylethanone (378.6 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-23a** as a white solid (601.5 mg, 2.13 mmol, 71% yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 4.47 – 4.41 (m, 1H), 2.44 (s, 3H), 1.73 – 1.55 (m, 6H), 1.49 – 1.41 (m, 1H), 1.19 (d, J = 6 Hz, 3H), 1.17 – 0.80 (m, 4H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 144.5, 134.7, 129.8, 127.8, 84.7, 43.2, 28.3, 28.1, 26.3,

26.0, 25.9, 21.8, 17.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{23}O_3S$ $[M+H]^+$ 283.1362 (283.1659).

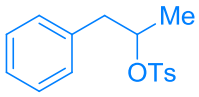
The spectroscopic data for **5-23a** match those reported in the literature.[39]

6-Bromo-1,2,3,4-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate 5-28a



According to **General procedure 1** with 6-bromo-3,4-dihydronaphthalen-2(1*H*)-one (675.2 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-28a** as a white solid (823.6 mg, 2.16 mmol, 72% yield over two steps). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.80 (d, J = 8 Hz, 2H), 7.34 (d, J = 8 Hz, 2H), 7.23 – 7.19 (m, 2H), 6.85 – 6.83 (m, 1H), 4.97 – 4.90 (m, 1H), 3.00 – 2.68 (m, 4H), 2.46 (s, 3H), 2.06 – 1.96 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 144.9, 137.3, 134.5, 131.49, 131.48, 130.9, 130.0, 129.3, 127.8, 120.1, 34.8, 28.2, 25.8, 21.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{18}BrO_3S$ $[M+H]^+$ 381.0155 (381.0151). **Anal.** for $C_{17}H_{17}BrO_3S$ calcd: C, 53.55; H, 4.49; S, 8.41. found: C, 53.46; H, 4.36; S, 8.46.

1-Phenylpropan-2-yl 4-methylbenzenesulfonate 5-29a

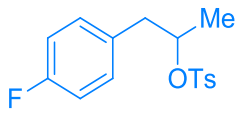


According to **General procedure 1** with 1-phenylpropan-2-one (402.5 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-29a** as a white solid (740.5 mg, 2.55 mmol, 85% yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 8 Hz, 2H), 7.23 – 7.18 (m, 5H), 7.04 – 7.02 (m, 2H),

4.77 – 4.69 (m, 1H), 2.91 (dd, J = 7, 14 Hz, 1H), 2.78 (dd, J = 7, 14 Hz, 1H), 2.41 (s, 3H), 1.30 (d, J = 6 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 144.4, 136.4, 134.0, 129.8, 129.6, 128.5, 127.7, 126.8, 80.8, 43.0, 21.7, 20.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}O_3S$ $[M+H]^+$ 291.1049 (291.1047).

The spectroscopic data for **5-29a** match those reported in the literature.[40]

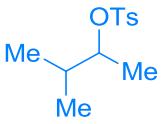
1-(4-Fluorophenyl)propan-2-yl 4-methylbenzenesulfonate 5-30a



According to **General procedure 1** with 1-(4-fluorophenyl)propan-2-one (456.5 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-30a** as a white solid (721.6 mg, 2.34 mmol, 78% yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 8 Hz, 2H), 7.20 (d, J = 8 Hz, 2H), 6.99 – 6.94 (m, 2H), 6.86 – 6.80 (m, 2H), 4.72 – 4.64 (m, 1H), 2.84 (dd, J = 7, 14 Hz, 1H), 2.76 (dd, J = 7, 14 Hz, 1H), 2.42 (s, 3H), 1.33 (d, J = 6 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 161.9 (d, J = 244 Hz), 144.5, 133.9, 132.1 (d, J = 3 Hz), 130.9 (d, J = 8 Hz), 129.7, 127.7, 115.3 (d, J = 21 Hz), 80.8 (d, J = 2 Hz), 42.2, 21.7, 20.9. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -116.2 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{18}FO_3S$ $[M+H]^+$ 309.0955 (309.0951).

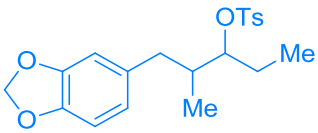
The spectroscopic data for **5-30a** match those reported in the literature.[40]

3-Methylbutan-2-yl 4-methylbenzenesulfonate 5-31a



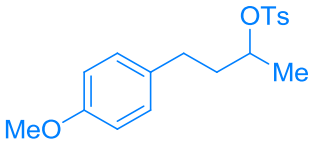
According to **General procedure 1** with 3-methylbutan-2-one (258.4 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to yield the product **5-31a** as a white solid (625.2 mg, 2.58 mmol, 86% yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 4.48 – 4.42 (m, 1H), 2.44 (s, 3H), 1.83 – 1.75 (m, 1H), 1.20 (d, J = 6 Hz, 3H), 0.83 (dd, J = 5, 7 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 144.5, 134.7, 129.8, 127.8, 85.0, 33.4, 21.8, 17.9, 17.7, 17.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{19}O_3S$ $[M+H]^+$ 243.1049 (243.1045). **Anal.** for $C_{12}H_{18}O_3S$ calcd: C, 59.47; H, 7.49; S, 13.23. found: C, 59.54; H, 7.41; S, 13.37.

1-(Benzo[*d*][1,3]dioxol-5-yl)-2-methylpentan-3-yl 4-methylbenzenesulfonate 5-32a



According to **General procedure 1** with 1-(benzo[*d*][1,3]dioxol-5-yl)-2-methylpentan-3-one (660.8 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-32a** as a white solid (835.8 mg, 2.22 mmol, 74% yield over two steps). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.82 (d, J = 8 Hz, 2H), 7.34 (d, J = 8 Hz, 2H), 6.70 (d, J = 8 Hz, 1H), 6.50 – 6.49 (m, 2H), 5.93 (dd, J = 2, 5 Hz, 2H), 4.56 – 4.53 (m, 1H), 2.68 (dd, J = 5, 14 Hz, 1H), 2.45 (s, 3H), 2.21 – 2.18 (m, 1H), 2.02 – 1.98 (m, 1H), 1.69 – 1.64 (m, 2H), 0.84 (q, J = 7 Hz, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 147.7, 146.0, 144.6, 135.2, 134.1, 129.9, 127.9, 122.1, 109.4, 108.2, 101.0, 89.1, 38.6, 38.3, 24.0, 21.8, 14.3, 10.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{20}H_{25}O_5S$ $[M+H]^+$ 377.1417 (377.1412). **Anal.** for $C_{20}H_{24}O_5S$ calcd: C, 63.81; H, 6.43; S, 8.52. found: C, 63.92; H, 6.40; S, 8.59.

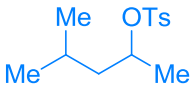
4-(4-Methoxyphenyl)butan-2-yl 4-methylbenzenesulfonate 5-33a



According to **General procedure 1** with 4-(4-methoxyphenyl)butan-2-one (534.7 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-33a** as a white solid (822.7 mg, 2.46 mmol, 82% yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.81 – 7.78 (m, 2H), 7.34 – 7.32 (m, 2H), 6.99 – 6.96 (m, 2H), 6.81 – 6.77 (m, 2H), 4.66 – 4.59 (m, 1H), 3.78 (s, 3H), 2.58 – 2.51 (m, 1H), 2.47 – 2.40 (m, 4H), 1.94 – 1.85 (m, 1H), 1.80 – 1.72 (m, 1H), 1.29 (d, J = 6 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 158.0, 144.6, 134.5, 133.0, 129.9, 129.3, 127.9, 113.9, 80.1, 55.4, 38.5, 30.4, 21.8, 21.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{23}O_4S$ $[M+H]^+$ 335.1312 (335.1310).

The spectroscopic data for **5-33a** match those reported in the literature.[39]

4-Methylpentan-2-yl 4-methylbenzenesulfonate 5-34a

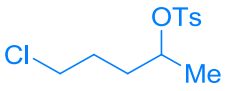


According to **General procedure 1** with 4-methylpentan-2-ol (306.5 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-34a** as a white solid (707.6 mg, 2.76 mmol, 92% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.80 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 4.73 – 4.63 (m, 1H), 2.44 (s, 3H), 1.62 – 1.52 (m, 2H), 1.31 – 1.20 (m, 4H), 0.81 (d, J = 6 Hz, 3H), 0.75 (d, J = 6 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 144.5, 134.8, 129.8, 127.9, 79.3, 46.0, 24.4, 22.9, 22.1, 21.8, 21.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{21}O_3S$ $[M+H]^+$ 257.1206 (257.1201).

The spectroscopic data for **5-34a** match those reported in the literature.[41]

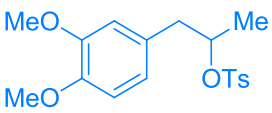
5-Chloropentan-2-yl 4-methylbenzenesulfonate 5-37a



According to **General procedure 1** with 5-chloropentan-2-one (361.7 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-37a** as a white solid (622.7 mg, 2.25 mmol, 75% yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 4.66 – 4.59 (m, 1H), 3.49 – 3.40 (m, 2H), 2.43 (s, 3H), 1.81 – 1.63 (m, 4H), 1.24 (d, J = 6 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ = 144.8, 134.3, 129.9, 127.8, 79.5, 44.5, 33.8, 27.9, 21.7, 21.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{18}ClO_3S$ $[M+H]^+$ 277.0660 (277.0654).

The spectroscopic data for **5-37a** match those reported in the literature.[39]

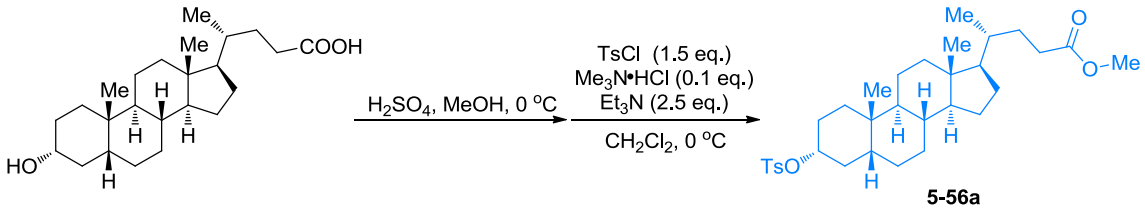
1-(3,4-Dimethoxyphenyl)propan-2-yl 4-methylbenzenesulfonate 5-55a



According to **General procedure 1** with 1-(3,4-dimethoxyphenyl)propan-2-one (582.7 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 5/1) to yield the product **5-55a** as a white solid (735.9 mg, 2.10 mmol, 70% yield over two steps). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 8 Hz, 2H), 7.18 (d, J = 8 Hz, 2H), 6.68 (d, J = 8 Hz, 1H), 6.58 (dd, J = 2, 8 Hz, 1H), 6.464 – 6.458 (m, 1H), 4.75 – 4.64 (m,

1H), 3.85 (s, 3H), 3.75 (s, 3H), 2.86 – 2.68 (m, 2H), 2.40 (s, 3H), 1.34 (d, J = 6 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 148.8, 148.0, 144.4, 134.1, 129.6, 129.0, 127.7, 121.6, 112.4, 111.1, 81.1, 55.9, 55.7, 42.7, 21.7, 21.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{22}O_5S$ [M] 350.1182 (350.1175). **Anal.** for $C_{18}H_{22}O_5S$ calcd: C, 61.69; H, 6.33; S, 9.15. found: C, 61.54; H, 6.42; S, 9.16.

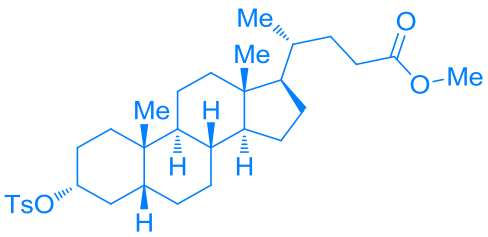
The synthesis of substrate 5-56a



5-56a

Conc. H_2SO_4 (0.50 mL) was added in portions to a solution of lithocholic acid (1.13 g, 3 mmol, 1.0 equiv.) in MeOH (12 mL). The reaction mixture was stirred for 24 h at 70 °C. Afterwards, the reaction mixture was neutralized with diluted solution of $NaHCO_3$ and the aqueous layer was extracted three times with CH_2Cl_2 and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Then, a glass tube was charged with *p*-toluene sulfonyl chloride (857.9 mg, 4.5 mmol, 1.5 equiv.) and trimethylamine hydrochloride (28.7 mg, 0.3 mmol, 0.1 equiv.) in CH_2Cl_2 (1 M with respect to the alcohol). Triethylamine (1.04 mL, 7.5 mmol, 2.5 equiv.) was added dropwise at 0 °C to the solution. To the resulting mixture was added a solution of the alcohol obtained above (3.0 mmol, 1.0 equiv.) in CH_2Cl_2 (1 M), and the mixture was then stirred at 0 °C for 2 h. The reaction was quenched by addition of *N,N*-dimethylethylenediamine (0.49 mL, 4.5 mmol, 1.5 equiv.) and stirred for 10 min. The reaction was mixed with water and extracted 3 times with CH_2Cl_2. The organic layer was washed sequentially with 1 M HCl, saturated aqueous Na_2CO_3 and brine. The combined organic layer was dried over Na_2SO_4, and filtred through a pad of Celite (Ø 3 mm x 8 mm). The reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 90/10) to yield the product **5-56a** as a white solid (1.03 mg, 1.89 mmol, 63% yield over two steps).

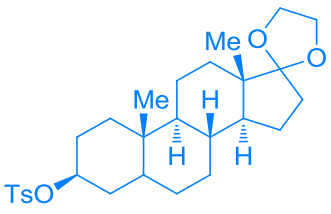
(*R*)-methyl 4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3-(tosyloxy)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate 5-56a



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, J = 8 Hz, 2H), 7.31 (d, J = 8 Hz, 2H), 4.50 – 4.39 (m, 1H), 3.65 (s, 3H), 2.43 (s, 3H), 2.37 – 2.15 (m, 2H), 2.03 – 0.94 (m, 26H), 0.90– 0.87 (m, 6H), 0.61 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 174.8, 144.4, 134.9, 129.8, 127.7, 83.3, 56.5, 56.0, 51.6, 42.8, 42.2, 40.4, 40.1, 35.8, 35.4, 35.1, 34.4, 33.2, 31.14, 31.1, 28.3, 27.7, 26.9, 26.3, 24.3, 23.2, 21.7, 20.9, 18.4, 12.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{32}H_{49}O_5S$ $[M+H]^+$ 545.3295 (545.3288).

The spectroscopic data for **5-56a** match those reported in the literature.[42]

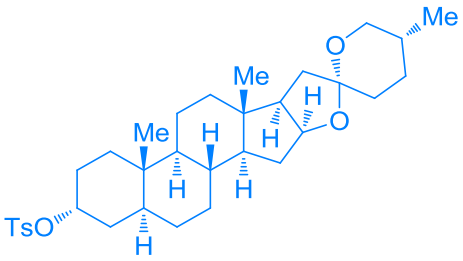
(3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethylhexadecahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl 4-methylbenzenesulfonate 5-57a



According to **General procedure 1** with (3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethylhexadecahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-ol (1.003 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 90/10) to yield the product **5-57a** as a white solid (1.085 g, 2.22 mmol, 74%

yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.78 (d, J = 8 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 4.49 – 4.46 (m, 1H), 4.43 – 4.35 (m, 1H), 4.24 – 4.20 (m, 1H), 4.14 – 4.09 (m, 1H), 3.98 – 3.87 (m, 2H), 2.44 (s, 3H), 2.08 – 2.00 (m, 1H), 1.98 – 1.92 (m, 1H), 1.79 – 1.44 (m, 10H), 1.37 – 1.13 (m, 6H), 0.94 – 0.86 (m, 2H), 0.84 (s, 3H), 0.76 (s, 3H), 0.66 – 0.60 (m, 1H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 144.5, 134.8, 129.9, 127.7, 116.9, 82.4, 66.6, 66.3, 55.5, 53.8, 48.4, 45.6, 44.8, 36.8, 35.5, 35.4, 35.2, 34.9, 31.0, 30.6, 28.4, 28.2, 21.8, 20.4, 14.8, 12.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{28}H_{41}O_5S$ $[M+H]^+$ 489.2669 (489.2663). **Anal.** for $C_{28}H_{40}O_5S$ calcd: C, 68.82; H, 8.25; S, 6.56. found: C, 68.67; H, 8.11; S, 6.74.

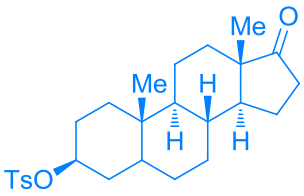
(2a*S*,2'*R*,4*R*,5'*R*,6a*S*,6b*S*,8a*S*,8b*R*,11a*S*,12a*S*,12b*R*)-5',6a,8a-Trimethyldocosahydrospiro[naphtho[2',1':4,5]indeno[2,1-*b*]furan-10,2'-pyran]-4-yl 4-methylbenzenesulfonate 5-58a



According to **General procedure 1** with (2a*S*,2'*R*,4*R*,5'*R*,6a*S*,6b*S*,8a*S*,8b*R*,11a*S*,12a*S*,12b*R*)-5',6a,8a-trimethyldocosahydrospiro[naphtho[2',1':4,5]indeno[2,1-*b*]furan-10,2'-pyran]-4-ol (1.208 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 90/10) to yield the product **5-58a** as a white solid (1.186 g, 2.13 mmol, 71% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.78 (d, J = 8 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 4.46 – 4.33 (m, 2H), 3.49 – 3.32 (m, 2H), 2.44 (s, 3H), 1.99 – 1.91 (m, 1H), 1.89 – 1.82 (m, 1H), 1.76 – 1.40 (m, 13H), 1.28 – 1.00 (m, 7H), 0.95 (d, J = 7 Hz, 3H), 0.91 – 0.83 (m, 2H), 0.79 – 0.77 (m, 6H), 0.74 (s, 3H), 0.64 – 0.55 (m, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 144.5, 134.9, 129.9, 127.7, 109.4, 82.6, 80.9, 67.0, 62.3, 56.3, 54.2, 44.9, 41.7, 40.7, 40.1, 36.9, 35.5, 35.1, 35.0, 32.2, 31.9, 31.5, 30.4, 28.9, 28.5, 21.8, 21.1, 17.3, 16.6, 14.6, 12.3. **HRMS-ASAP** (m/z): Calculated

(found) for $C_{33}H_{49}O_5S$ $[M+H]^+$ 557.3295 (557.3287). **Anal.** for $C_{33}H_{48}O_5S$ calcd: C, 71.18; H, 8.69; S, 5.76. found: C, 71.26; H, 8.68; S, 5.89.

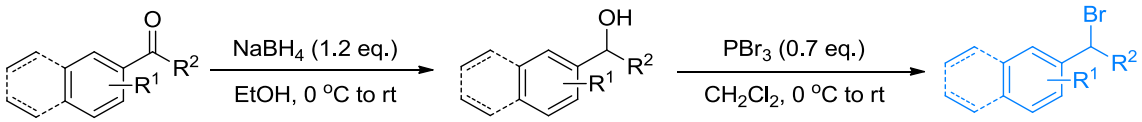
(3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-methylbenzenesulfonate 5-59a



According to **General procedure 1** with (3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-3-hydroxy-10,13-dimethyltetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17(2*H*)-one (871.3 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 90/10) to yield the product **5-59a** as a white solid (973.7 mg, 2.19 mmol, 73% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.78 (d, J = 8 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 4.46 – 4.35 (m, 1H), 2.47 – 2.38 (m, 4H), 2.11 – 1.99 (m, 1H), 1.95 – 1.86 (m, 1H), 1.79 – 1.44 (m, 10H), 1.30 – 1.04 (m, 6H), 0.99 – 0.88 (m, 2H), 0.83 (s, 3H), 0.80 (s, 3H), 0.68 – 0.60 (m, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 221.2, 144.5, 134.8, 129.9, 127.7, 82.3, 54.3, 51.5, 47.9, 44.9, 36.8, 35.9, 35.5, 35.1, 34.9, 31.6, 30.8, 28.4, 28.2, 21.9, 21.8, 20.6, 13.9, 12.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{26}H_{37}O_4S$ $[M+H]^+$ 445.2407 (445.2401). **Anal.** for $C_{26}H_{36}O_4S$ calcd: C, 70.23; H, 8.16; S, 7.21. found: C, 70.11; H, 8.23; S, 7.37.

The spectroscopic data for **5-59a** match those reported in the literature.[43]

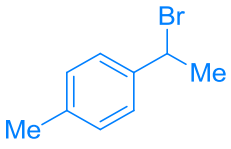
General procedure 2: Preparation of secondary alkyl bromides



To a solution of ketone (3.0 mmol, 1.0 equiv.) in EtOH (9.0 mL) was added $NaBH_4$ (136.8 mg, 3.6 mmol, 1.2 equiv.) at 0 °C and the reaction mixture was stirred at room temperature for 2 h. The reaction was then quenched with water, diluted with CH_2Cl_2, and extracted with CH_2Cl_2 three times. The combined organic layer was washed by brine, dried over Na_2SO_4, filtred, and concentrated under reduced pressure to afford the corresponding alcohol, which was directly used in the next step without further purification.

To a solution of the residue obtained above (if it is a commercially available alcohol, skip the above step and use it directly in this step) in CH_2Cl_2 (9.0 mL) was added PBr_3 (0.20 mL, 2.1 mmol, 0.70 equiv.) under argon at 0 °C and the resulting reaction mixture was stirred at room temperature overnight. The reaction was then quenched with water and extracted 3 times with CH_2Cl_2. The organic layer was washed with brine, and then dried over Na_2SO_4, and filtred through a pad of Celite (Ø 3 mm x 8 mm), concentrated under reduced pressure to afford the corresponding crude alkyl bromide, which was directly used in the next step without further purification or stored in a refrigerator. (The product readily decomposed in air or on silica gel).

1-(1-Bromoethyl)-4-methylbenzene 5-3a

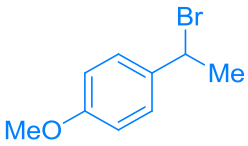


According to **General procedure 2** with 1-(p-tolyl)ethanone (402.5 mg, 3.0 mmol, 1.0 equiv.), **5-3a** was obtained as a yellow oil (513.7 mg, 2.58 mmol, 86% crude yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.35 (d, J = 8 Hz, 2H), 7.17 (d, J = 8 Hz, 2H), 5.23 (q, J = 7 Hz, 1H), 2.36

(s, 3H), 2.06 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 140.5, 138.4, 129.5, 126.8, 50.0, 26.9, 21.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{12}Br$ $[M+H]^+$ 199.0117 (199.0114).

The spectroscopic data for **5-3a** match those reported in the literature.[44]

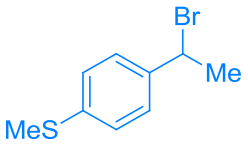
1-(1-Bromoethyl)-4-methoxybenzene 5-4a



According to **General procedure 2** with 1-(4-methoxyphenyl)ethanol (456.6 mg, 3.0 mmol, 1.0 equiv.), **5-4a** was obtained as a yellow oil (529.1 mg, 2.46 mmol, 82% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.38 (d, J = 9 Hz, 2H), 6.87 (d, J = 9 Hz, 2H), 5.26 (q, J = 7 Hz, 1H), 3.81 (s, 3H), 2.05 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 159.6, 135.6, 128.2, 114.1, 55.5, 50.2, 27.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{12}BrO$ $[M+H]^+$ 215.0066 (215.0061).

The spectroscopic data for **5-4a** match those reported in the literature.[45]

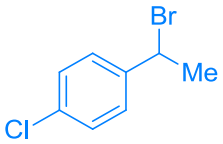
(4-(1-Bromoethyl)phenyl)(methyl)sulfane 5-5a



According to **General procedure 2** with 1-(4-(methylthio)phenyl)ethanone (498.7 mg, 3.0 mmol, 1.0 equiv.), **5-5a** was obtained as a white solid (610.2 mg, 2.64 mmol, 88% crude yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.37 – 7.34 (m, 2H), 7.23 – 7.19 (m, 2H), 5.21 (q, J = 7 Hz, 1H), 2.48 (s, 3H), 2.03 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 140.0, 139.1, 127.4, 126.5, 49.6, 26.8, 15.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{12}BrS$ $[M+H]^+$

230.9838 (230.9832). **Anal.** for $C_9H_{11}BrS$ calcd: C, 46.76; H, 4.80; S, 13.87. found: C, 46.71; H, 4.91; S, 13.86.

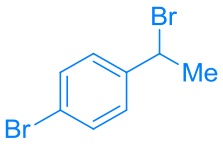
1-(1-Bromoethyl)-4-chlorobenzene 5-7a



According to **General procedure 2** with 1-(4-chlorophenyl)ethanone (463.8 mg, 3.0 mmol, 1.0 equiv.), **5-7a** was obtained as a yellow oil (533.4 mg, 2.43 mmol, 81% crude yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.40 – 7.36 (m, 2H), 7.33 – 7.30 (m, 2H), 5.18 (q, J = 7 Hz, 1H), 2.03 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 141.8, 134.1, 128.9, 128.3, 48.4, 26.8. **HRMS-ASAP** (m/z): Calculated (found) for C_8H_9BrCl $[M+H]^+$ 218.9571 (218.9567).

The spectroscopic data for **5-7a** match those reported in the literature.[45]

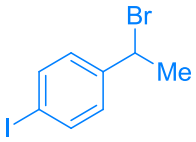
1-Bromo-4-(1-bromoethyl)benzene 5-8a



According to **General procedure 2** with 1-(4-bromophenyl)ethanone (597.1 mg, 3.0 mmol, 1.0 equiv.), **5-8a** was obtained as a yellow oil (681.0 mg, 2.58 mmol, 86% crude yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.49 – 7.45 (m, 2H), 7.33 – 7.30 (m, 2H), 5.15 (q, J = 7 Hz, 1H), 2.02 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 142.4, 132.0, 128.6, 122.3, 48.4, 26.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_8H_9Br_2$ $[M+H]^+$ 262.9066 (262.9061).

The spectroscopic data for **5-8a** match those reported in the literature.[46]

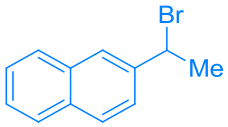
1-(1-Bromoethyl)-4-iodobenzene 5-9a



According to **General procedure 2** with 1-(4-iodophenyl)ethanone (738.1 mg, 3.0 mmol, 1.0 equiv.), **5-9a** was obtained as a yellow oil (932.9 mg, 2.34 mmol, 78% crude yield over two steps). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.68 (d, J = 8 Hz, 2H), 7.18 (d, J = 8 Hz, 2H), 5.13 (q, J = 7 Hz, 1H), 2.01 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 143.1, 137.9, 128.8, 94.0, 48.4, 26.8. **HRMS-ASAP** (m/z): Calculated (found) for C_8H_9BrI $[M+H]^+$ 310.8927 (310.8923).

The spectroscopic data for **5-9a** match those reported in the literature.[47]

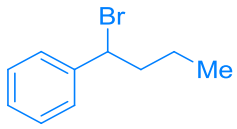
2-(1-Bromoethyl)naphthalene 5-10a



According to **General procedure 2** with 1-(naphthalen-2-yl)ethanone (510.6 mg, 3.0 mmol, 1.0 equiv.), **5-10a** was obtained as a white solid (557.2 mg, 2.37 mmol, 79% crude yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.87 – 7.81 (m, 4H), 7.61 (dd, J = 8, 2 Hz, 1H), 7.53 – 7.48 (m, 2H), 5.41 (q, J = 7 Hz, 1H), 2.16 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 140.5, 133.3, 133.1, 128.8, 128.2, 127.8, 126.62, 126.60, 125.3, 125.2, 50.2, 26.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{12}Br$ $[M+H]^+$ 235.0117 (235.0114).

The spectroscopic data for **5-10a** match those reported in the literature.[44]

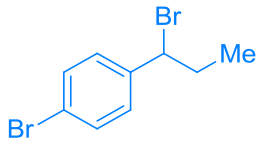
(1-Bromobutyl)benzene 5-11a



According to **General procedure 2** with 1-phenylbutan-1-one (444.6 mg, 3.0 mmol, 1.0 equiv.), **5-11a** was obtained as a colorless oil (537.0 mg, 2.52 mmol, 84% crude yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.43 – 7.40 (m, 2H), 7.38 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 5.00 (t, J = 7 Hz, 1H), 2.35 – 2.26 (m, 1H), 2.18 – 2.09 (m, 1H), 1.58 – 1.48 (m, 1H), 1.41 – 1.31 (m, 1H), 0.96 (t, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 142.4, 128.8, 128.4, 127.4, 55.6, 42.1, 21.6, 13.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{14}Br$ $[M+H]^+$ 213.0273 (213.0269).

The spectroscopic data for **5-11a** match those reported in the literature.[44]

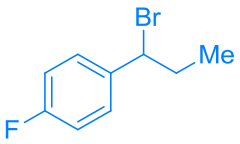
1-Bromo-4-(1-bromopropyl)benzene 5-13a



According to **General procedure 2** with 1-(4-bromophenyl)propan-1-one (639.2, 3.0 mmol, 1.0 equiv.), **5-13a** was obtained as a colorless oil (683.8 mg, 2.46 mmol, 82% crude yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.49 – 7.45 (m, 2H), 7.28 – 7.25 (m, 2H), 4.82 (t, J = 7 Hz, 1H), 2.32 – 2.21 (m, 1H), 2.18 – 2.07 (m, 1H), 0.99 (t, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 141.3, 131.9, 129.1, 122.2, 56.3, 33.3, 13.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{11}Br_2$ $[M+H]^+$ 276.9222 (276.9218).

The spectroscopic data for **5-13a** match those reported in the literature.[44]

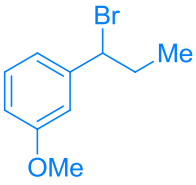
1-(1-Bromopropyl)-4-fluorobenzene 5-14a



According to **General procedure 2** with 1-(4-fluorophenyl)propan-1-one (456.5 mg, 3.0 mmol, 1.0 equiv.), **5-14a** was obtained as a colorless oil (566.6 mg, 2.61 mmol, 87% crude yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.40 – 7.35 (m, 2H), 7.06 – 7.00 (m, 2H), 4.88 (t, J = 7 Hz, 1H), 2.34 – 2.23 (m, 1H), 2.20 – 2.09 (m, 1H), 1.00 (t, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 162.4 (d, J = 246 Hz), 138.2 (d, J = 3 Hz), 129.1 (d, J = 8 Hz), 115.7 (d, J = 21 Hz), 56.6, 33.6, 13.1. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -116.2 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{11}BrF$ $[M+H]^+$ 217.0023 (217.0018).

The spectroscopic data for **5-14a** match those reported in the literature.[48]

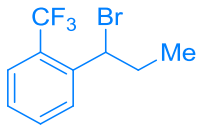
1-(1-Bromopropyl)-3-methoxybenzene 5-15a



According to **General procedure 2** with 1-(3-methoxyphenyl)propan-1-one (492.6 mg, 3.0 mmol, 1.0 equiv.), **5-15a** was obtained as a colorless oil (556.7 mg, 2.43 mmol, 81% crude yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.27 (t, J = 8 Hz, 1H), 6.99 (d, J = 8 Hz, 1H), 6.96 – 6.95 (m, 1H), 6.85 – 6.83 (m, 1H), 4.86 (t, J = 8 Hz, 1H), 3.83 (s, 3H), 2.35 – 2.24 (m, 1H), 2.23 – 2.12 (m, 1H), 1.02 (t, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 159.8, 143.7, 129.8, 119.7, 113.8, 113.1, 57.6, 55.4, 33.4, 13.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{14}Br$ $[M+H]^+$ 229.0223 (229.0220).

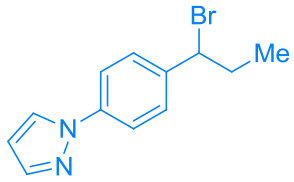
The spectroscopic data for **5-15a** match those reported in the literature.[44]

1-(1-Bromopropyl)-2-(trifluoromethyl)benzene 5-16a



According to **General procedure 2** with 1-(2-(trifluoromethyl)phenyl)propan-1-one (606.5 mg, 3.0 mmol, 1.0 equiv.), **5-16a** was obtained as a colorless oil (577.0 mg, 2.16 mmol, 72% crude yield over two steps). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.71 (d, J = 8 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.40 (t, J = 7 Hz, 1H), 5.65 – 5.61 (m, 1H), 1.93 – 1.81 (m, 2H), 0.99 (t, J = 8 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 139.6 (q, J = 2 Hz), 132.4, 128.3, 128.2 126.8 (q, J = 30 Hz), 125.6 (q, J = 6 Hz), 125.2 (q, J = 272 Hz), 75.9 (q, J = 3 Hz), 32.2, 10.1. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -58.1 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{11}BrF_3$ $[M+H]^+$ 266.9991 (266.9983). **Anal.** for $C_{10}H_{10}BrF_3$ calcd: C, 44.97; H, 3.77. found: C, 44.84; H, 3.82.

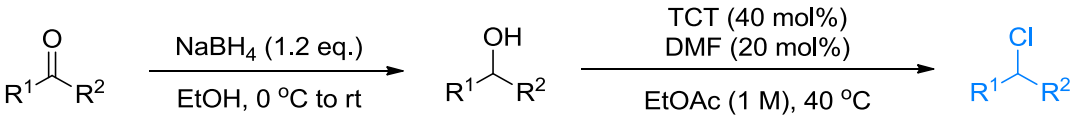
1-(4-(1-Bromopropyl)phenyl)-1*H*-pyrazole 5-19a



According to **General procedure 2** with 1-(4-(1*H*-pyrazol-1-yl)phenyl)propan-1-one (600.7 mg, 3.0 mmol, 1.0 equiv.), **5-19a** was obtained as a colorless oil (588.6 mg, 2.22 mmol, 74% crude yield over two steps). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.96 (d, J = 3 Hz, 1H), 7.80 (d, J = 2 Hz, 1H), 7.70 (d, J = 9 Hz, 2H), 7.49 (d, J = 9 Hz, 2H), 6.52 (t, J = 2 Hz, 1H), 4.90 (t, J = 7 Hz, 1H), 2.38 – 2.25 (m, 1H), 2.23 – 2.10 (m, 1H), 1.01 (t, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 141.1, 140.6, 139.0, 128.7, 127.1, 119.8, 108.1, 56.5, 33.3, 13.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{14}BrN_2$ $[M+H]^+$ 265.0335 (265.0331).

The spectroscopic data for **5-19a** match those reported in the literature.[44]

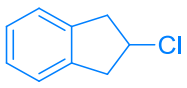
General procedure 3: Preparation of alkyl chlorides



Alkyl chlorides were synthesized according to reported literature.[49a] To a solution of ketone (3.0 mmol, 1.0 equiv.) in EtOH (9.0 mL) was added $NaBH_4$ (136.8 mg, 3.6 mmol, 1.2 equiv.) at 0 °C and the reaction mixture was stirred at room temperature for 2 h. The reaction was then quenched with water, diluted with CH_2Cl_2, and extracted with CH_2Cl_2 three times. The combined organic layer was washed by brine, dried over Na_2SO_4, filtred, and concentrated under reduced pressure to afford the corresponding alcohol, which was directly used in the next step without further purification.

To a solution of the residue obtained above (if it is a commercially available alcohol, skip the above step and use it directly in this step) in EtOAc (3.0 mL) was added DMF (44.0 mg, 0.6 mmol, 20 mol%). Next, cyanuric chloride (TCT) (221.3 mg, 1.2 mmol, 40 mol%) was added in one portion and the resulting reaction mixture was stirred at 0 °C for 6 h. After completion of reaction, the reaction mixture was filtred through a pad of Celite (Ø 3 mm x 8 mm), concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the corresponding chlorides.

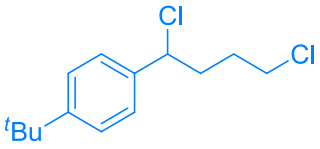
2-Chloro-2,3-dihydro-1*H*-indene 5-12a-1



According to **General procedure 3** with 1*H*-inden-2(3*H*)-one (396.5 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **5-12a-1** as a colorless oil (325.0 mg, 213 mmol, 71% yield over two steps). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.29 – 7.21 (m, 4H), 4.78 – 4.71 (m, 1H), 3.50 – 3.42 (m, 2H), 3.27 – 3.20 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 140.3, 127.1, 124.7, 59.3, 44.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{10}Cl$ $[M+H]^+$ 153.0466 (153.0461).

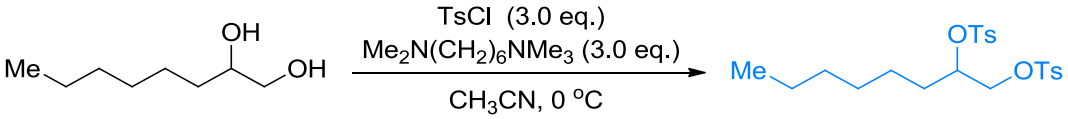
The spectroscopic data for **5-12-1** match those reported in the literature.[49b]

1-(*tert*-Butyl)-4-(1,4-dichlorobutyl)benzene 5-20a

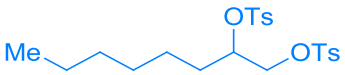


According to **General procedure 3** with 1-(4-(*tert*-butyl)phenyl)-4-chlorobutan-1-one (716.3 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **5-20a** as a colorless oil (482.1 mg, 1.86 mmol, 62% yield over two steps). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.39 (d, J = 8 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 4.89 (t, J = 7 Hz, 1H), 3.60 – 3.56 (m, 2H), 2.29 – 2.21 (m, 2H), 2.10 – 1.96 (m, 1H), 1.92 – 1.78 (m, 1H), 1.33 (s, 9H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 151.6, 138.5, 126.7, 125.8, 63.0, 44.4, 37.3, 34.8, 31.4, 30.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{21}Cl_2$ $[M+H]^+$ 259.1015 (259.1008). **Anal.** for $C_{14}H_{20}Cl_2$ calcd: C, 64.87; H, 7.78. found: C, 64.95; H, 7.74.

Octane-1,2-diyl bis(4-methylbenzenesulfonate) 5-40a



Tosylates were synthesized according to reported literature.[50] *p*-Toluene sulfonyl chloride (857.9 mg, 4.5 mmol, 3.0 equiv.) in CH_3CN (1.5 mL) was added to a stirred solution of the octane-1,2-diol (219.3 mg, 1.5 mmol, 1.0 equiv.) and $Me_2N(CH_2)_6NMe_2$ (775.4 mg, 4.5 mmol, 3.0 equiv.) in CH_3CN (1.5 mL) at 0 °C for 1 h. The reaction was quenched by addition of *N,N*-dimethylethylenediamine (0.49 mL, 4.5 mmol, 1.5 equiv.) and stirred for 10 min. The reaction was mixed with water and extracted 3 times with CH_2Cl_2. The organic layer was washed sequentially with 1 M HCl, saturated aqueous Na_2CO_3 and brine. The combined organic layer was dried over Na_2SO_4, and filtred through a pad of Celite (Ø 3 mm x 8 mm). The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-40a** as a white solid (392.0 mg, 1.305 mmol, 87% yield).



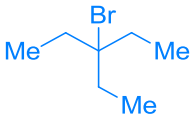
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 – 7.69 (m, 4H), 7.34 – 7.30 (m, 4H), 4.60 – 4.55 (m, 1H), 4.06 – 3.99 (m, 2H), 2.45 (d, J = 4 Hz, 6H), 1.63 – 1.56 (m, 2H), 1.25 – 1.04 (m, 8H), 0.84 (t, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 145.3, 145.1, 133.6, 132.4, 130.1, 129.9, 128.1, 128.0, 79.0, 69.5, 31.6, 31.1, 28.8, 24.5, 22.5, 21.80, 21.78, 14.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{31}O_6S_2$ $[M+H]^+$ 455.1557 (455.1555).

The spectroscopic data for **5-40a** match those reported in the literature.[50]

General procedure 4: Preparation of tertiary alkyl bromides.

To a solution of alcohol (3.0 mmol, 1.0 equiv.) in CH_2Cl_2 was added LiBr (521 mg, 6.0 mmol, 2.0 equiv.) in 48 wt% aqueous HBr at 0 °C and the reaction mixture was stirred at room temperature for overnight. The reaction was then diluted with Et_2O, washed with water, saturated $NaHCO_3$, and brine, dried over Na_2SO_4, filtred, and concentrated under reduced pressure. The residue was purified by column chromatography to afford the product.

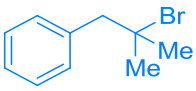
3-Bromo-3-ethylpentane 5-43a



According to **General procedure 4** with 3-ethylpentan-3-ol (348.6 mg, 3.0 mmol, 1.0 equiv.), **5-43a** was obtained as a colorless oil (472.8 mg, 2.64 mmol, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.87 (q, J = 7 Hz, 6H), 0.97 (t, J = 7 Hz, 9H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 81.8, 34.3, 9.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_7H_{16}Br$ $[M+H]^+$ 179.0430 (179.0425).

The spectroscopic data for **5-43a** match those reported in the literature.[51]

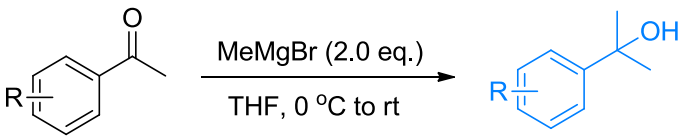
(2-Bromo-2-methylpropyl)benzene 5-44a



According to **General procedure 4** with 2-methyl-1-phenylpropan-2-ol (450.7 mg, 3.0 mmol, 1.0 equiv.), **5-44a** was obtained as a colorless oil (581.8 mg, 2.73 mmol, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.27 (m, 4H), 3.22 (s, 2H), 1.78 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 137.2, 130.9, 128.1, 127.0, 66.7, 53.3, 33.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{14}Br$ $[M+H]^+$ 213.0273 (213.0268).

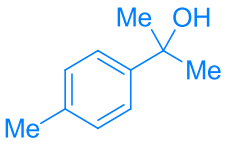
The spectroscopic data for **5-44a** match those reported in the literature.[51]

General procedure 5:



To a solution of ketone (3.0 mmol, 1.0 equiv.) in anhydrous THF (3.0 mL) was slowly added MeMgBr (1.0 M in THF, 2.0 equiv.) at 0 °C under argon atmosphere. Then the reaction mixture was warmed up to room temperature and stirred until the ketone was completely consumed (monitored by TLC). The reaction was quenched by 3.0 M HCl and extracted with CH_2Cl_2 three times. The combined organic layer was dried over Na_2SO_4, filtred, and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the corresponding product.

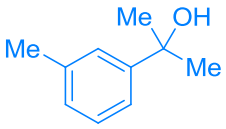
2-(*p*-Tolyl)propan-2-ol 5-46a



According to **General procedure 5** with 1-(*p*-tolyl)ethanone (402.6 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-46a** as a colorless oil (374.0 mg, 2.49 mmol, 83% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.39 (d, J = 8 Hz, 2H), 7.16 (d, J = 8 Hz, 2H), 2.35 (s, 3H), 1.71 (s, 1H), 1.58 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 146.4, 136.4, 129.0, 124.4, 72.5, 31.9, 21.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{15}O$ $[M+H]^+$ 151.1117 (151.1114).

The spectroscopic data for **5-46a** match those reported in the literature.[52]

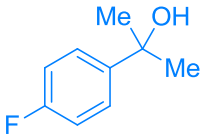
2-(*m*-Tolyl)propan-2-ol 5-47a



According to **General procedure 5** with 1-(*m*-tolyl)ethanone (402.6 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-47a** as a colorless oil (328.9 mg, 2.19 mmol, 73% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.32 – 7.21 (m, 3H), 7.09 – 7.05 (m, 1H), 2.37 (s, 3H), 1.73 – 1.66 (m, 1H), 1.58 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 149.2, 137.9, 128.3, 127.6, 125.3, 121.5, 72.6, 31.9, 21.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{15}O$ $[M+H]^+$ 151.1117 (151.1115).

The spectroscopic data for **5-47a** match those reported in the literature.[53]

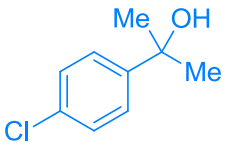
2-(4-Fluorophenyl)propan-2-ol 5-48a



According to **General procedure 5** with 1-(4-fluorophenyl)ethanone (414.4 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-48a** as a colorless oil (328.4 mg, 2.13 mmol, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.47 – 7.44 (m, 2H), 7.03 – 6.99 (m, 2H), 1.68 (s, 1H), 1.57 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 161.8 (d, J = 242 Hz), 145.0 (d, J = 4 Hz), 126.3 (d, J = 8 Hz), 115.0 (d, J = 21 Hz), 72.4, 32.0. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -116.8 (m). **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{12}FO$ $[M+H]^+$ 155.0867 (155.0861).

The spectroscopic data for **5-48a** match those reported in the literature.[54]

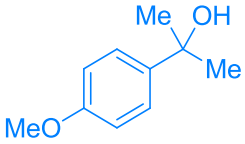
2-(4-Chlorophenyl)propan-2-ol 5-49a



According to **General procedure 5** with 1-(4-chlorophenyl)ethanone (463.8 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-49a** as a colorless oil (404.0 mg, 2.37 mmol, 79% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.42 (d, J = 9 Hz, 2H), 7.30 (d, J = 9 Hz, 2H), 1.69 (s, 1H), 1.57 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 147.7, 132.6, 128.4, 126.1, 72.4, 31.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{12}ClO$ $[M+H]^+$ 171.0571 (171.0568).

The spectroscopic data for **5-49a** match those reported in the literature.[54]

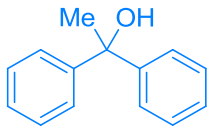
2-(4-Methoxyphenyl)propan-2-ol 5-50a



According to **General procedure 5** with 1-(4-methoxyphenyl)ethanone (450.5 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-50a** as a colorless oil (349.0 mg, 2.10 mmol, 70% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.41 (d, J = 9 Hz, 2H), 6.87 (d, J = 9 Hz, 2H), 3.80 (s, 3H), 1.73 (s, 1H), 1.57 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 158.5, 141.5, 125.7, 113.6, 72.3, 55.4, 31.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{15}O_2$ $[M+H]^+$ 167.1067 (167.1064).

The spectroscopic data for **5-50a** match those reported in the literature.[52]

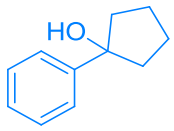
1,1-Diphenylethanol 5-51a



According to **General procedure 5** with benzophenone (546.7 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **5-51a** as a white solid (487.7 mg, 2.46 mmol, 82% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.44 (d, J = 7 Hz, 4H), 7.34 (t, J = 7 Hz, 4H), 7.26 (t, J = 7 Hz, 2H), 2.24 (s, 1H), 1.97 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 148.1, 128.3, 127.1, 126.0, 76.3, 31.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{15}O$ $[M+H]^+$ 199.1117 (199.1112).

The spectroscopic data for **5-51a** match those reported in the literature.[55]

1-Phenylcyclopentanol 5-52a



To a solution of cyclopentanone (3.0 mmol, 1.0 equiv.) in anhydrous THF (3.0 mL) was slowly added PhMgBr (1.0 M in THF, 2.0 equiv.) at 0 °C under argon atmosphere. Then the reaction mixture was warmed up to room temperature and stirred until the ketone was completely consumed (monitored by TLC). The reaction was quenched by 3.0 M HCl and extracted with CH_2Cl_2 three times. The combined organic layer was dried over Na_2SO_4, filtred, and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the corresponding product **5-52a** as a white solid (408.8 mg, 2.52 mmol, 84% yield). **^{1}H NMR** (300 MHz, C_6D_6): δ = 7.41 – 7.37 (m, 2H), 7.23 – 7.18 (m, 2H), 7.13 – 7.07 (m, 1H), 1.92 –

1.75 (m, 6H), 1.64 – 1.57 (m, 2H), 1.00 (s, 1H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, C_6D_6): δ = 147.8, 129.7, 126.8, 125.4, 83.1, 42.3, 24.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{11}H_{15}O$ $[M+H]^+$ 163.1117 (163.1114).

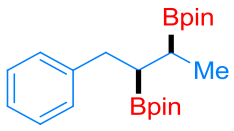
The spectroscopic data for **5-52a** match those reported in the literature.[56]

5.5.3 Details of the Diboration of Alkyl Halides, Tosylates, and Alcohols

General procedure 6:

In an argon-filled glovebox, alkyl halides, tosylates, or alcohols (0.3 mmol, 1.0 equiv.) in DMA (1 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. KI (49.8 mg, 0.3 mmol, 1.0 equiv.) and B_2cat_2 (178 mg, 0.75 mmol, 2.5 equiv.) were added. The reaction mixture was stirred at 90 °C for 12 h, then a solution of pinacol (106 mg, 0.9 mmol, 3.0 equiv.) in Et_3N (1 mL) was added to the reaction mixture, which was stirred at room temperature for 1 h. Then water was added, and the reaction mixture was extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtred, and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the corresponding product.

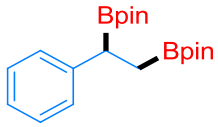
2,2'-(1-Phenylbutane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-1b



According to **General procedure 6** with 4-phenylbutan-2-yl 4-methylbenzenesulfonate **5-1a** (91.3 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-1b** as a colorless oil (99.6 mg, 258 µmol, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.25 – 7.19 (m, 4H), 7.13 – 7.10 (m, 1H), 2.77 – 2.76 (m,

2H), 1.45 – 1.41 (m, 1H), 1.26 (s, 12H), 1.19 – 1.16 (m, 1H), 1.14 (s, 6H), 1.12 (s, 6H), 1.03 (d, *J* = 8 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 143.2, 129.2, 128.0, 125.5, 83.0, 82.9, 36.0, 25.1, 25.0, 24.91, 24.88, 15.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{37}B_2O_4$ $[M+H]^+$ 387.2872 (387.2866). **Anal.** for $C_{22}H_{36}B_2O_4$ calcd: C, 68.43; H, 9.40. found: C, 68.56; H, 9.39.

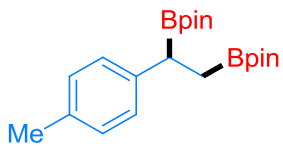
2,2'-(1-Phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-2b



According to **General procedure 6** with (1-bromoethyl)benzene **5-2a** (55.5 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-2b** as a colorless oil (98.8 mg, 276 µmol, 92% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.23 – 7.22 (m, 4H), 7.13 – 7.07 (m, 1H), 2.52 (dd, *J* = 6, 11 Hz, 1H), 1.38 (dd, *J* = 11, 16 Hz, 1H), 1.20 (s, 12H), 1.19 (s, 6H), 1.17 (s, 6H), 1.11 (dd, *J* = 6, 16 Hz, 1H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 145.5, 128.3, 128.1, 125.0, 83.3, 83.2, 25.1, 24.84, 24.81, 24.6. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 33.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{20}H_{33}B_2O_4$ $[M+H]^+$ 359.2559 (359.2556).

The spectroscopic data for **5-2b** match those reported in the literature.[57]

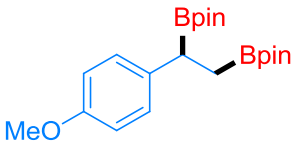
2,2'-(1-(*p*-Tolyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-3b



According to **General procedure 6** with 1-(1-bromoethyl)-4-methylbenzene **5-3a** (59.7 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-3b** as a colorless oil (98.2 mg, 264 µmol, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.13 – 7.10 (m, 2H), 7.05 – 7.03 (m, 2H), 2.47 (dd, J = 6, 11 Hz, 1H), 2.28 (s, 3H), 1.36 (dd, J = 11, 16 Hz, 1H), 1.22 (s, 12H), 1.20 (s, 6H), 1.18 (s, 6H), 1.08 (dd, J = 6, 16 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 142.4, 134.3, 129.0, 127.8, 83.2, 83.1, 25.1, 24.8, 24.7, 24.6, 21.1. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{35}B_2O_4$ $[M+H]^+$ 373.2716 (373.2712).

The spectroscopic data for **5-3b** match those reported in the literature.[57]

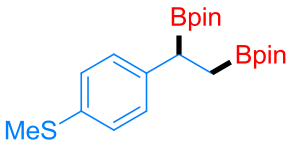
2,2'-(1-(4-Methoxyphenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-4b



According to **General procedure 6** with 1-(1-bromoethyl)-4-methoxybenzene **5-4a** (64.5 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-4b** as a colorless oil (96.6 mg, 249 µmol, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.15 – 7.12 (m, 2H), 6.80 – 6.76 (m, 2H), 3.76 (s, 3H), 2.45 (dd, J = 6, 11 Hz, 1H), 1.33 (dd, J = 11, 16 Hz, 1H), 1.20 (s, 12H), 1.19 (s, 6H), 1.17 (s, 6H), 1.07 (dd, J = 6, 16 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 157.2, 137.4, 128.8, 113.7, 83.3, 83.1, 55.3, 25.1, 24.82, 24.78, 24.6. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{35}B_2O_5$ $[M+H]^+$ 389.2665 (389.2661).

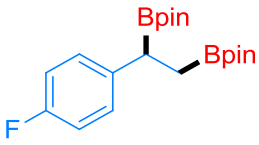
The spectroscopic data for **5-4b** match those reported in the literature.[58]

2,2'-(1-(4-(Methylthio)phenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-5b



According to **General procedure 6** with (4-(1-bromoethyl)phenyl)(methyl)sulfane **5-5a** (69.3 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-5b** as a colorless oil (84.9 mg, 210 µmol, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.15 (m, 3H), 2.47 (dd, J = 6, 11 Hz, 1H), 2.44 (s, 3H), 1.34 (dd, J = 11, 16 Hz, 1H), 1.20 (s, 12H), 1.18 (s, 6H), 1.17 (s, 6H), 1.07 (dd, J = 6, 16 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 142.8, 134.0, 128.6, 127.2, 83.4, 83.2, 25.1, 24.82, 24.77, 24.6. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 32.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{35}B_2O_4S$ $[M+H]^+$ 405.2437 (405.2433). **Anal.** for $C_{21}H_{34}B_2O_4S$ calcd: C, 62.40; H, 8.48; S, 7.93. found: C, 62.29; H, 8.56; S, 7.98.

2,2'-(1-(4-Fluorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-6b

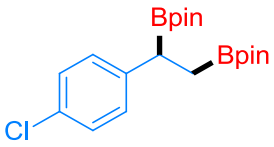


According to **General procedure 6** with 1-(1-bromoethyl)-4-fluorobenzene **5-6a** (60.9 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-6b** as a colorless oil (82.4 mg, 219 µmol, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.17 – 7.13 (m, 2H), 6.93 – 6.87 (m, 2H), 2.49 (dd, J = 6, 11 Hz, 1H), 1.32 (dd, J = 11, 16 Hz, 1H), 1.184 (s, 12H), 1.176 (s, 6H), 1.16 (s, 6H), 1.08 (dd, J = 6, 16 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 160.9 (d, J = 240 Hz), 141.0 (d, J = 3 Hz), 129.2 (d, J = 8 Hz), 114.9 (d, J = 21 Hz), 83.4, 83.2, 25.1, 25.0, 24.8, 24.6. **^{19}F{^{1}H} NMR**

(376 MHz, $CDCl_3$): δ = -119.3 (s). **$^{11}B\{^1H\}$ NMR** (128 MHz, $CDCl_3$): δ = 33.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{20}H_{32}B_2FO_4$ $[M+H]^+$ 377.2465 (377.2459).

The spectroscopic data for **5-6b** match those reported in the literature.[57]

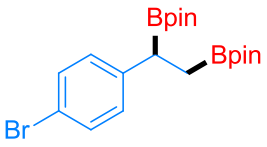
2,2'-(1-(4-Chlorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-7b



According to **General procedure 6** with 1-(1-bromoethyl)-4-chlorobenzene **5-7a** (65.9 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-7b** as a colorless oil (90.7 mg, 231 µmol, 77% yield). **^1H NMR** (400 MHz, $CDCl_3$): δ = 7.21 – 7.17 (m, 2H), 7.16 – 7.13 (m, 2H), 2.49 (dd, J = 6, 11 Hz, 1H), 1.34 (dd, J = 11, 16 Hz, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 1.18 (s, 6H), 1.17 (s, 6H), 1.07 (dd, J = 6, 16 Hz, 1H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ = 144.0, 130.6, 129.4, 128.3, 83.5, 83.3, 25.1, 24.80, 24.77, 24.6. **$^{11}B\{^1H\}$ NMR** (128 MHz, $CDCl_3$): δ = 33.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{20}H_{32}B_2ClO_4$ $[M+H]^+$ 393.2170 (393.2168).

The spectroscopic data for **5-7b** match those reported in the literature.[59]

2,2'-(1-(4-Bromophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-8b

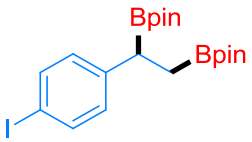


According to **General procedure 6** with 1-bromo-4-(1-bromoethyl)benzene **5-8a** (79.2 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-8b** as a colorless oil (90.5 mg, 207 µmol, 69%

yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.35 – 7.32 (m, 2H), 7.11 – 7.07 (m, 2H), 2.47 (dd, J = 6, 11 Hz, 1H), 1.33 (dd, J = 11, 16 Hz, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 1.18 (s, 6H), 1.17 (s, 6H), 1.07 (dd, J = 6, 16 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 144.5, 131.2, 129.8, 118.7, 83.5, 83.2, 25.1, 24.8, 24.7, 24.6. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 32.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{20}H_{32}B_2BrO_4$ $[M+H]^+$ 437.1665 (437.1661).

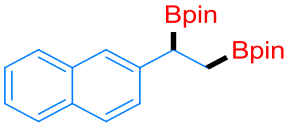
The spectroscopic data for **5-8b** match those reported in the literature.[59]

2,2'-(1-(4-Iodophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-9b



According to **General procedure 6** with 1-(1-bromoethyl)-4-iodobenzene **5-9a** (93.3 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-9b** as a colorless oil (78.4 mg, 162 µmol, 54% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.55 – 7.51 (m, 2H), 6.99 – 6.96 (m, 2H), 2.46 (dd, J = 6, 11 Hz, 1H), 1.33 (dd, J = 11, 16 Hz, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 1.18 (s, 6H), 1.17 (s, 6H), 1.06 (dd, J = 6, 16 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 145.3, 137.2, 130.2, 90.0, 83.5, 83.3, 25.1, 24.81, 24.78, 24.6. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{20}H_{32}B_2IO_4$ $[M+H]^+$ 485.1526 (485.1521). **Anal.** for $C_{20}H_{31}B_2IO_4$ calcd: C, 49.63; H, 6.46. found: C, 49.71; H, 6.61.

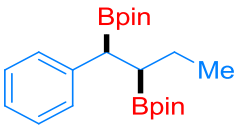
2,2'-(1-(Naphthalen-2-yl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-10b



According to **General procedure 6** with 2-(1-bromoethyl)naphthalene **5-10a** (70.5 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-10b** as a colorless oil (105.3 mg, 258 µmol, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.78 – 7.71 (m, 3H), 7.66 (s, 1H), 7.43 – 7.35 (m, 3H), 2.71 (dd, J = 6, 11 Hz, 1H), 1.50 (dd, J = 11, 16 Hz, 1H), 1.21 (dd, J = 6, 16 Hz, 1H), 1.21 (s, 12H), 1.20 (s, 6H), 1.18 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 143.1, 133.9, 131.8, 127.64, 127.61, 127.59, 127.5, 125.6, 125.5, 124.8, 83.4, 83.2, 25.1, 24.83, 24.77, 24.6. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{24}H_{35}B_2O_4$ $[M+H]^+$ 409.2716 (409.2712).

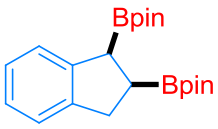
The spectroscopic data for **5-10b** match those reported in the literature.[57]

2,2'-(1-Phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-11b



According to **General procedure 6** with (1-bromobutyl)benzene **5-11a** (63.9 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-11b** as a colorless oil (95.0 mg, 246 µmol, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.24 – 7.16 (m, 4H), 7.12 – 7.08 (m, 1H), 2.40 (d, J = 13 Hz, 1H), 1.60 – 1.54 (m, 1H), 1.33 – 1.29 (m, 1H), 1.27 (s, 12H), 1.15 (s, 6H), 1.14 (s, 6H), 1.11 – 1.08 (m, 1H), 0.76 (t, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 142.9, 128.9, 128.2, 125.0, 83.2, 25.3, 25.1, 24.8, 24.3, 21.8, 12.5. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{37}B_2O_4$ $[M+H]^+$ 387.2872 (387.2866). **Anal.** for $C_{22}H_{36}B_2O_4$ calcd: C, 68.43; H, 9.40. found: C, 68.33; H, 9.52.

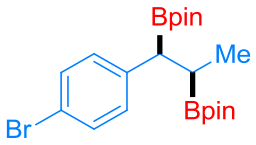
2,2'-(2,3-Dihydro-1*H*-indene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-12b



According to **General procedure 6** with 1-bromo-2,3-dihydro-1*H*-indene **5-12a** (59.1 mg, 0.3 mmol, 1.0 equiv.) or 2-chloro-2,3-dihydro-1*H*-indene **5-12a-1** (45.8 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-12b** as a colorless oil (92.2 mg, 249 µmol, 83% yield from Br or 82.1 mg, 222 µmol, 74% yield from Cl). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.25 – 7.23 (m, 1H), 7.19 – 7.17 (m, 1H), 7.09 – 7.02 (m, 2H), 3.10 – 2.95 (m, 2H), 2.89 (d, J = 9 Hz, 1H), 2.02 – 1.95 (m, 1H), 1.27 (s, 12H), 1.17 (s, 6H), 1.09 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 146.2, 144.5, 125.8, 125.2, 124.1, 124.0, 83.3, 83.2, 35.0, 25.4, 25.0, 24.6, 24.3. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 32.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{33}B_2O_4$ $[M+H]^+$ 371.2559 (371.2556).

The spectroscopic data for **5-12b** match those reported in the literature.[60]

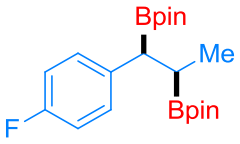
2,2'-(1-(4-Bromophenyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-13b



According to **General procedure 6** with 1-bromo-4-(1-bromopropyl)benzene **5-13a** (83.4 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-13b** as a colorless oil (120.4 mg, 267 µmol, 89% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.33 (d, J = 8 Hz, 2H), 7.04 (d, J = 8 Hz, 2H), 2.19 (d, J = 12 Hz, 1H), 1.48 (dd, J = 8, 12 Hz, 1H), 1.24 (s, 12H), 1.16 (s, 6H), 1.15 (s, 6H), 0.73 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 142.2, 131.2, 130.8, 118.8, 83.3, 83.2, 25.1, 25.0,

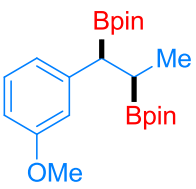
24.7, 24.4, 14.7. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 33.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{34}B_2BrO_4$ $[M+H]^+$ 451.1821 (451.1815). **Anal.** for $C_{21}H_{33}B_2BrO_4$ calcd: C, 55.92; H, 7.38. found: C, 55.84; H, 7.52.

2,2'-(1-(4-Fluorophenyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-14b



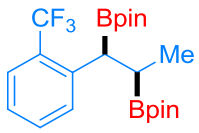
According to **General procedure 6** with 1-(1-bromopropyl)-4-fluorobenzene **5-14a** (65.1 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-14b** as a colorless oil (98.3 mg, 252 µmol, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.12 – 7.09 (m, 2H), 6.93 – 6.88 (m, 2H), 2.20 (d, J = 12 Hz, 1H), 1.48 (dd, J = 8, 12 Hz, 1H), 1.24 (s, 12H), 1.16 (s, 6H), 1.15 (s, 6H), 0.73 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 161.0 (d, J = 240 Hz), 138.5 (d, J = 3 Hz), 130.2 (d, J = 8 Hz), 114.9 (d, J = 21 Hz), 83.3, 83.2, 25.1, 25.0, 24.7, 24.4. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -119.0 (s). **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{34}B_2FO_4$ $[M+H]^+$ 391.2622 (391.2617). **Anal.** for $C_{21}H_{33}B_2FO_4$ calcd: C, 64.66; H, 8.53. found: C, 64.68; H, 8.41.

2,2'-(1-(3-Methoxyphenyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-15b



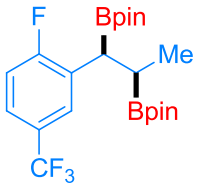
According to **General procedure 6** with 1-(1-bromopropyl)-3-methoxybenzene **5-15a** (68.7 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-15b** as a colorless oil (90.5 mg, 225 µmol, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.14 (t, J = 8 Hz, 1H), 6.77 – 6.73 (m, 2H), 6.68 – 6.65 (m, 1H), 3.77 (s, 3H), 2.19 (d, J = 12 Hz, 1H), 1.52 (dd, J = 8, 12 Hz, 1H), 1.25 (s, 12H), 1.18 (s, 6H), 1.17 (s, 6H), 0.75 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 159.6, 144.7, 129.1, 121.7, 114.3, 110.9, 83.3, 83.2, 55.2, 25.2, 25.1, 24.7, 24.4, 14.7. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{37}B_2O_5$ $[M+H]^+$ 403.2822 (403.2815). **Anal.** for $C_{22}H_{36}B_2O_5$ calcd: C, 65.71; H, 9.02. found: C, 65.84; H, 8.91.

2,2'-(1-(2-(Trifluoromethyl)phenyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-16b



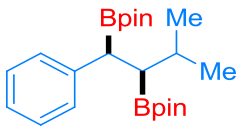
According to **General procedure 6** with 1-(1-bromopropyl)-2-(trifluoromethyl)benzene **5-16a** (80.1 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-16b** as a colorless oil (97.7 mg, 222 µmol, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.57 (d, J = 8 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.20 – 7.16 (m, 1H), 2.73 (d, J = 12 Hz, 1H), 1.63 – 1.56 (m, 1H), 1.26 (s, 12H), 1.16 (s, 6H), 1.14 (s, 6H), 0.71 (d, J = 8 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 143.2, 131.5, 129.9, 129.6 (q, J = 29 Hz), 125.7 (q, J = 6 Hz), 124.78 (q, J = 272 Hz), 124.82, 83.3, 83.2, 25.1, 24.9, 24.7, 24.5, 14.6. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -58.1 (s). **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{34}B_2F_3O_4$ $[M+H]^+$ 441.1196 (441.1191). **Anal.** for $C_{22}H_{33}B_2F_3O_4$ calcd: C, 60.04; H, 7.56. found: C, 60.11; H, 7.43.

2,2'-(1-(2-Fluoro-5-(trifluoromethyl)phenyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-17b



According to **General procedure 6** with 2-(1-bromopropyl)-1-fluoro-4-(trifluoromethyl)benzene **5-17a** (85.5 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-17b** as a white solid (100.3 mg, 219 µmol, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.53 (dd, J = 7, 2 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.06 (t, J = 9 Hz, 1H), 2.58 (d, J = 12 Hz, 1H), 1.55 – 1.48 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.21 (s, 6H), 1.20 (s, 6H), 0.78 (d, J = 8 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 163.3 (dd, J = 2, 248 Hz), 131.6 (d, J = 18 Hz), 128.8 (q, J = 4 Hz), 126.3 (q, J = 32 Hz), 124.3 (q, J = 4 Hz), 124.2 (q, J = 270 Hz), 115.6 (d, J = 25 Hz), 25.1, 25.0, 24.7, 24.5, 14.9. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -61.9 (q), -111.0 (s). **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 33.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{33}B_2F_4O_4$ $[M+H]^+$ 459.2496 (459.2491). **Anal.** for $C_{22}H_{32}B_2F_4O_4$ calcd: C, 57.68; H, 7.04. found: C, 57.61; H, 7.22.

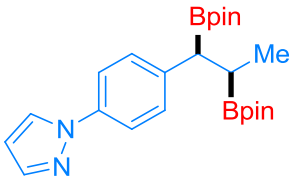
2,2'-(3-Methyl-1-phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-18b



According to **General procedure 6** with (1-bromo-3-methylbutyl)benzene **5-18a** (68.1 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-18b** as a colorless oil (100.8 mg, 252 µmol, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.25 – 7.15 (m, 4H), 7.12 – 7.06 (m, 1H), 2.52 (d, J = 13 Hz, 1H), 1.61 (dd, J = 3, 13 Hz, 1H), 1.44 – 1.38 (m, 1H), 1.28 (s, 12H), 1.14 (s, 6H), 1.13 (s,

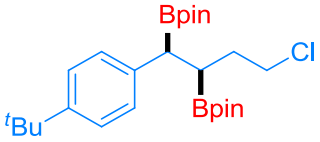
6H), 0.92 (d, J = 7 Hz, 3H), 0.77 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 143.2, 128.8, 128.3, 125.0, 83.2, 83.1, 26.8, 25.7, 25.2, 24.8, 24.2, 23.5, 18.6. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 33.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{23}H_{39}B_2O_4$ $[M+H]^+$ 401.3029 (401.3022). **Anal.** for $C_{23}H_{38}B_2O_4$ calcd: C, 69.03; H, 9.57. found: C, 69.14; H, 9.53.

1-(4-(1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)-1*H*-pyrazole 5-19b



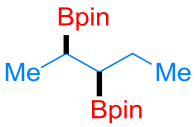
According to **General procedure 6** with 1-(4-(1-bromopropyl)phenyl)-1*H*-pyrazole **5-19a** (79.5 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 90/10) to yield the product **5-19b** as a colorless oil (100.0 mg, 228 µmol, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.88 (d, J = 2 Hz, 1H), 7.70 (d, J = 2 Hz, 1H), 7.55 (d, J = 9 Hz, 2H), 7.26 (d, J = 9 Hz, 2H), 6.43 (t, J = 2 Hz, 1H), 2.28 (d, J = 12 Hz, 1H), 1.55 (dd, J = 8, 12 Hz, 1H), 1.26 (s, 12H), 1.18 (s, 6H), 1.16 (s, 6H), 0.78 (d, J = 8 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 141.8, 140.6, 137.7, 129.9, 126.9, 119.4, 107.3, 83.4, 83.3, 25.2, 25.1, 24.7, 24.4, 14.7. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 33.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{24}H_{37}B_2N_2O_4$ $[M+H]^+$ 439.2934 (439.2931). **Anal.** for $C_{24}H_{36}B_2N_2O_4$ calcd: C, 65.79; H, 8.28; N, 6.39. found: C, 65.88; H, 8.21; N, 6.33.

2,2'-(1-(4-(*tert*-Butyl)phenyl)-4-chlorobutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-20b



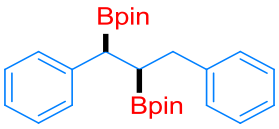
According to **General procedure 6** with 1-(*tert*-butyl)-4-(1,4-dichlorobutyl)benzene **5-20a** (77.8 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-20b** as a colorless oil (118.7 mg, 249 µmol, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.23 (d, J = 8 Hz, 2H), 7.08 (d, J = 8 Hz, 2H), 3.53 – 3.48 (m, 1H), 3.38 – 3.32 (m, 1H), 2.33 – 2.30 (m, 1H), 1.73 – 1.64 (m, 2H), 1.35 – 1.31 (m, 1H), 1.28 (s, 9H), 1.26 (s, 12H), 1.16 (s, 6H), 1.15 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 148.1, 138.6, 128.5, 125.3, 83.5, 83.4, 44.6, 34.4, 32.9, 31.6, 25.3, 25.1, 24.8, 24.4. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 33.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{26}H_{44}B_2ClO_4$ $[M+H]^+$ 477.3109 (477.3099). **Anal.** for $C_{26}H_{43}B_2ClO_4$ calcd: C, 65.51; H, 9.09. found: C, 65.43; H, 9.12.

2,2'-(Pentane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-21b



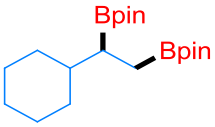
According to **General procedure 6** with 3-bromopentane **5-21a** (45.3 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **5-21b** as a colorless oil (71.0 mg, 219 µmol, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.56 – 1.47 (m, 1H), 1.43 – 1.33 (m, 1H), 1.23 – 1.21 (m, 24H), 1.18 – 1.14 (m, 1H), 1.01 – 0.96 (m, 1H), 0.95 (d, J = 8 Hz, 3H), 0.87 (t, J = 8 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 82.9, 82.8, 25.2, 25.1, 24.83, 24.76, 22.4, 14.5, 13.8. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{35}B_2O_4$ $[M+H]^+$ 325.2716 (325.2710). **Anal.** for $C_{17}H_{34}B_2O_4$ calcd: C, 63.01; H, 10.57. found: C, 62.94; H, 10.66.

2,2'-(1,3-Diphenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-22b



According to **General procedure 6** with 1,3-diphenylpropan-2-yl 4-methylbenzenesulfonate **5-22a** (109.9 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-22b** as a colorless oil (100.8 mg, 225 µmol, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.28 – 7.24 (m, 4H), 7.19 – 7.07 (m, 6H), 2.64 (dd, J = 5, 14 Hz, 1H), 2.43 (t, J = 12 Hz, 2H), 2.02 – 1.93 (m, 1H), 1.16 (s, 12H), 1.15 (s, 6H), 1.10 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 142.6, 142.2, 129.3, 129.1, 128.3, 127.8, 125.5, 125.3, 83.3, 83.2, 35.8, 25.1, 25.0, 24.9, 24.5. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{27}H_{39}B_2O_4$ $[M+H]^+$ 449.3029 (449.3021). **Anal.** for $C_{27}H_{38}B_2O_4$ calcd: C, 72.35; H, 8.55. found: C, 72.38; H, 8.67.

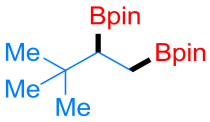
2,2'-(1-Cyclohexylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-23b



According to **General procedure 6** with 1-cyclohexylethyl 4-methylbenzenesulfonate **5-23a** (84.7 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-23b** as a colorless oil (77.6 mg, 213 µmol, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.98 (d, J = 12 Hz, 1H), 1.90 (d, J = 12 Hz, 1H), 1.65 – 1.61 (m, 2H), 1.41 – 1.29 (m, 1H), 1.25 (s, 12H), 1.23 (s, 12H), 1.18 – 0.93 (m, 9H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 83.0, 82.8, 35.4, 34.1, 26.9, 25.9, 25.6, 25.3, 25.1, 24.9, 24.8, 11.9. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 34.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{20}H_{39}B_2O_4$ $[M+H]^+$ 365.3029 (365.3026).

The spectroscopic data for **5-23b** match those reported in the literature.[60]

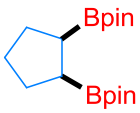
2,2'-(3,3-Dimethylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-24b



According to **General procedure 6** with 3-bromo-2,2-dimethylbutane **5-24a** (49.5 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **5-24b** as a colorless oil (87.2 mg, 258 µmol, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.24 (s, 12H), 1.21 (s, 6H), 1.20 (s, 6H), 0.95 (dd, J = 4, 12 Hz, 1H), 0.90 (s, 9H), 0.84 – 0.77 (m, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 82.9, 82.8, 32.5, 29.2, 25.3, 25.2, 25.0, 24.8. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{37}B_2O_4$ $[M+H]^+$ 339.2872 (339.2870).

The spectroscopic data for **5-24b** match those reported in the literature.[61]

1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane 5-25b

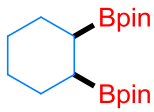


According to **General procedure 6** with bromocyclopentane **5-25a** (44.7 mg, 0.3 mmol, 1.0 equiv.) or chlorocyclopentane **5-25a-1** (31.4 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **25b** as a colorless oil (89.9 mg, 279 µmol, 93% yield from Br) or (81.2 mg, 252 µmol, 84% yield from Cl). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.76 – 1.50 (m, 6H), 1.44 – 1.37 (m, 2H), 1.23 (s, 24H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 82.9, 28.8, 25.8, 25.0, 24.9. **^{11}B{^{1}H} NMR** (96 MHz,

$CDCl_3$): δ = 34.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{33}B_2O_4$ $[M+H]^+$ 323.2559 (323,2552).

The spectroscopic data for **5-25b** match those reported in the literature.[62]

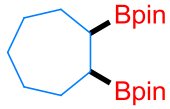
1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane 5-26b



According to **General procedure 6** with bromocyclohexane **5-26a** (48.9 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-26b** as a colorless oil (91.7 mg, 273 µmol, 91% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.65 – 1.52 (m, 5H), 1.47 – 1.35 (m, 5H), 1.231 (s, 12H), 1.228 (s, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 82.9, 28.2, 27.0, 25.1, 25.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{35}B_2O_4$ $[M+H]^+$ 337.2716 (337.2711).

The spectroscopic data for **5-26b** match those reported in the literature.[63]

1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cycloheptane 5-27b

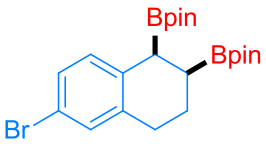


According to **General procedure 6** with bromocycloheptane **5-27a** (53.1 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-27b** as a colorless oil (94.5 mg, 270 µmol, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.81 – 1.75 (m, 2H), 1.69 – 1.62 (m, 2H), 1.55 – 1.42 (m, 6H), 1.35 – 1.33

(m, 2H), 1.228 (s, 12H), 1.226 (s, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 82.9, 30.6, 28.5, 27.9, 25.00, 24.97. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{19}H_{37}B_2O_4$ $[M+H]^+$ 351.2872 (351.2866).

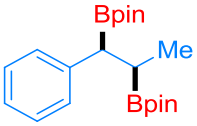
The spectroscopic data for **5-27b** match those reported in the literature.[63]

2,2'-(1,2,3,4-Tetrahydronaphthalene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-28b



According to **General procedure 6** with 6-bromo-1,2,3,4-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate **5-28a** (114.4 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-28b** as a colorless oil (84.7 mg, 183 µmol, 61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.16 – 7.12 (m, 2H), 7.00 (d, J = 8 Hz, 1H), 2.75 – 2.73 (m, 1H), 2.64 – 2.63 (m, 1H), 2.01 – 1.96 (m, 1H), 1.94 – 1.85 (m, 1H), 1.33 – 1.30 (m, 1H), 1.27 (s, 6H), 1.26 (s, 6H), 1.24 – 1.20 (m, 1H), 1.16 (s, 6H), 1.15 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 139.0, 138.5, 132.0, 130.8, 128.0, 118.1, 83.4, 83.3, 30.0, 25.3, 25.0, 24.8, 24.7, 22.6. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 33.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{34}B_2BrO_4$ $[M+H]^+$463.1821 (463.1814). **Anal.** for $C_{22}H_{33}B_2BrO_4$ calcd: C, 57.07; H, 7.18. found: C, 57.13; H, 7.26.

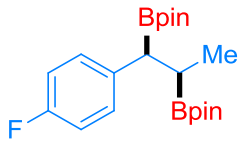
2,2'-(1-Phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-29b



According to **General procedure 6** with 1-phenylpropan-2-yl 4-methylbenzenesulfonate **5-29a** (87.1 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-29b** as a colorless oil (96.0 mg, 258 µmol, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.23 (t, J = 7 Hz, 2H), 7.16 (d, J = 7 Hz, 2H), 7.11 (t, J = 7 Hz, 1H), 2.22 (d, J = 12 Hz, 1H), 1.53 (dd, J = 8, 12 Hz, 1H), 1.26 (s, 12H), 1.17 (s, 6H), 1.15 (s, 6H), 0.74 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 143.0, 129.1, 128.2, 125.1, 83.3, 83.2, 25.2, 25.0, 24.7, 24.4, 14.7. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{35}B_2O_4$ $[M+H]^+$ 373.2716 (373.2710).

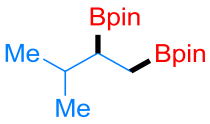
The spectroscopic data for **5-29b** match those reported in the literature.[64]

2,2'-(1-(4-Fluorophenyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-30b



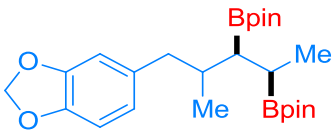
According to **General procedure 6** with 1-(4-fluorophenyl)propan-2-yl 4-methylbenzenesulfonate **5-30a** (92.5 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-30b** as a colorless oil (98.3 mg, 252 µmol, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.12 – 7.09 (m, 2H), 6.93 – 6.88 (m, 2H), 2.20 (d, J = 12 Hz, 1H), 1.48 (dd, J = 8, 12 Hz, 1H), 1.24 (s, 12H), 1.16 (s, 6H), 1.15 (s, 6H), 0.73 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 161.0 (d, J = 240 Hz), 138.5 (d, J = 3 Hz), 130.2 (d, J = 8 Hz), 114.9 (d, J = 21 Hz), 83.3, 83.2, 25.1, 25.0, 24.7, 24.4. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -119.0 (s). **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{34}B_2FO_4$ $[M+H]^+$ 391.2622 (391.2617). **Anal.** for $C_{21}H_{33}B_2FO_4$ calcd: C, 64.66; H, 8.53. found: C, 64.68; H, 8.41.

2,2'-(3-Methylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-31b



According to **General procedure 6** with 3-methylbutan-2-yl 4-methylbenzenesulfonate **5-31a** (72.7 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **5-31b** as a colorless oil (71.9 mg, 222 µmol, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.25 – 1.23 (m, 1H), 1.22 (s, 12H), 1.21 (s, 12H), 1.07 (dd, J = 7, 15 Hz, 1H), 0.94 (s, 3H), 0.93 (s, 3H), 0.93 – 0.91 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 82.8, 82.8, 25.0, 24.94, 24.87, 24.8, 23.7, 23.4, 11.1. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{35}B_2O_4$ $[M+H]^+$ 325.2716 (325.2708). **Anal.** for $C_{17}H_{34}B_2O_4$ calcd: C, 63.01; H, 10.57. found: C, 62.92; H, 10.70.

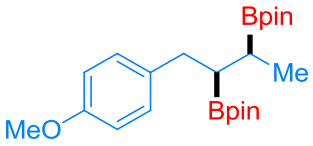
2,2'-(5-(Benzo[*d*][1,3]dioxol-5-yl)-4-methylpentane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-32b



According to **General procedure 6** with 1-(benzo[*d*][1,3]dioxol-5-yl)-2-methylpentan-3-yl 4-methylbenzenesulfonate **5-32a** (112.9 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-32b** as a colorless oil (88.0 mg, 192 µmol, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.82 (s, 1H), 6.70 (d, J = 8 Hz, 1H), 6.66 (d, J = 8 Hz, 1H), 5.88 (s, 2H), 2.90 (d, J = 14 Hz, 1H), 2.46 (d, J = 14 Hz, 1H), 1.63 – 1.58 (m, 1H), 1.50 – 1.43 (m, 1H), 1.28 (s, 6H), 1.27 (s, 6H), 1.22 (s, 6H), 1.18 (s, 6H), 0.93 (dd, J = 4, 12 Hz, 1H), 0.90 – 0.87 (m, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 146.9, 145.4, 135.2, 123.5, 111.2, 107.5, 100.6, 83.2, 83.0, 42.8, 25.23, 25.15, 25.14, 25.11, 21.6, 20.2, 14.9. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.3. **HRMS-ASAP** (m/z): Calculated (found)

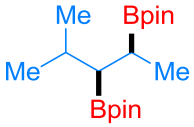
for $C_{25}H_{41}B_2O_6$ $[M+H]^+$ 459.3084 (459.3077). **Anal.** for $C_{25}H_{40}B_2O_6$ calcd: C, 65.53; H, 8.80. found: C, 65.67; H, 8.78.

2,2'-(1-(4-Methoxyphenyl)butane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-33b



According to **General procedure 6** with 4-(4-methoxyphenyl)butan-2-yl 4-methylbenzenesulfonate **5-33a** (100.3 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-33b** as a colorless oil (108.6 mg, 261 µmol, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.15 (d, J = 8 Hz, 2H), 6.77 (d, J = 8 Hz, 2H), 3.76 (s, 3H), 2.71 – 2.69 (m, 2H), 1.64 – 1.63 (m, 1H), 1.40 – 1.35 (m, 1H), 1.25 (s, 12H), 1.15 (s, 6H), 1.13 (s, 6H), 1.02 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 157.6, 135.3, 130.1, 113.4, 83.0, 82.9, 55.4, 35.0, 25.1, 25.0, 24.9, 24.8, 15.1. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{23}H_{39}B_2O_5$ $[M+H]^+$ 417.2978 (417.2972). **Anal.** for $C_{23}H_{38}B_2O_5$ calcd: C, 66.38; H, 9.20. found: C, 66.41; H, 9.29.

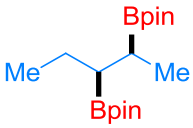
2,2'-(4-Methylpentane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-34b



According to **General procedure 6** with 4-methylpentan-2-yl 4-methylbenzenesulfonate **5-34a** (76.9 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **5-34b** as a colorless oil (82.2 mg, 243 µmol, 81% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.96 – 1.90 (m, 1H), 1.27 (s, 6H), 1.26 (s, 6H), 1.25

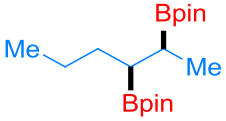
(s, 6H), 1.24 (s, 6H), 1.23 – 1.21 (m, 1H), 0.97 (dd, J = 4, 8 Hz, 6H), 0.91 – 090 (m, 1H), 0.89 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 82.83, 82.79, 26.8, 25.3, 25.2, 25.0, 24.7, 23.2, 21.2, 14.8. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{37}B_2O_4$ $[M+H]^+$ 339.2872 (339.2870). **Anal.** for $C_{18}H_{36}B_2O_4$ calcd: C, 63.94; H, 10.73. found: C, 63.87; H, 10.84.

2,2'-(Pentane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-35b



According to **General procedure 6** with 2-bromopentane **5-35a** (45.3 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **5-35b** as a colorless oil (79.7 mg, 246 µmol, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.56 – 1.47 (m, 1H), 1.44 – 1.34 (m, 1H), 1.23 – 1.21 (m, 24H), 1.18 – 1.14 (m, 1H), 1.05 – 0.98 (m, 1H), 0.96 – 0.93 (m, 3H), 0.87 (t, J = 8 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 82.9, 82.8, 25.2, 25.1, 24.83, 24.77, 22.4, 14.5, 13.8. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{35}B_2O_4$ $[M+H]^+$ 325.2716 (325.2712). **Anal.** for $C_{17}H_{34}B_2O_4$ calcd: C, 63.01; H, 10.57. found: C, 62.94; H, 10.66.

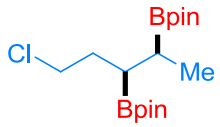
2,2'-(Hexane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-36b



According to **General procedure 6** with 2-chlorohexane **5-36a** (36.2 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **5-36b** as a colorless oil (86.2 mg, 255 µmol, 85% yield). **^{1}H NMR** (500 MHz,

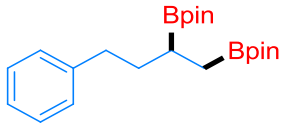
$CDCl_3$): δ = 1.51 – 1.44 (m, 1H), 1.37 – 1.28 (m, 2H), 1.27 – 1.24 (m, 1H), 1.22 – 1.21 (m, 24H), 1.18 – 1.13 (m, 1H), 1.10 – 1.04 (m, 1H), 0.87 (d, J = 8 Hz, 3H), 0.87 (t, J = 8 Hz, 3H). **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ = 82.8, 82.8, 31.9, 25.14, 25.10, 24.84, 24.76, 22.6, 14.7, 14.5. **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$): δ = 34.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{37}B_2O_4$ $[M+H]^+$ 339.2872 (339.2863). **Anal.** for $C_{18}H_{36}B_2O_4$ calcd: C, 63.94; H, 10.73. found: C, 63.83; H, 10.89.

2,2'-(5-Chloropentane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-37b



According to **General procedure 6** with 5-chloropentan-2-yl 4-methylbenzenesulfonate **5-37a** (36.2 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **5-37b** as a colorless oil (85.0 mg, 237 µmol, 79% yield). **^1H NMR** (500 MHz, $CDCl_3$): δ = 3.65 – 3.60 (m, 1H), 3.55 – 3.50 (m, 1H), 2.05 – 1.96 (m, 1H), 1.84 – 1.74 (m, 1H), 1.30 – 1.25 (m, 1H), 1.23 – 1.22 (m, 24H), 1.20 – 1.17 (m, 1H), 0.99 (d, J = 7 Hz, 3H). **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ = 83.2, 83.1, 45.4, 33.2, 25.11, 25.07, 24.8, 24.8, 14.7. **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$): δ = 34.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{34}B_2ClO_4$ $[M+H]^+$ 359.2326 (359.2321). **Anal.** for $C_{17}H_{33}$ B_2ClO_4 calcd: C, 56.95; H, 9.28. found: C, 57.03; H, 9.14.

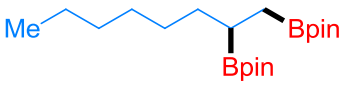
2,2'-(4-Phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-39b



According to **General procedure 6** with (3,4-dibromobutyl)benzene **5-39a** (87.6 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-39b** as a colorless oil (84.6 mg, 219 µmol, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.27 – 7.23 (m, 2H), 7.19 – 7.13 (m, 3H), 2.62 (t, J = 8 Hz, 2H), 1.82 – 1.75 (m, 1H), 1.67 – 1.60 (m, 1H), 1.25 (s, 12H), 1.23 (s, 12H), 1.21 – 1.18 (m, 1H), 0.97 – 0.85 (m, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 143.5, 128.6, 128.3, 125.6, 83.0, 36.1, 35.5, 25.1, 25.0, 24.94, 24.92, 18.5, 12.7. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{37}B_2O_4$ $[M+H]^+$ 387.2872 (387.2865).

The spectroscopic data for **5-39b** match those reported in the literature.[65]

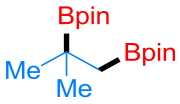
2,2'-(Octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-40b



According to **General procedure 6** with octane-1,2-diyl bis(4-methylbenzenesulfonate) **5-40a** (136.4 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **5-40b** as a colorless oil (96.7 mg, 264 µmol, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.46 – 1.37 (m, 1H), 1.32 – 1.24 (m, 8H), 1.22 (s, 12H), 1.21 (s, 12H), 1.13 – 1.06 (m, 2H), 0.89 – 0.79 (m, 5H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 82.93, 82.86, 34.0, 32.0, 29.7, 29.0, 25.03, 24.96, 24.89, 24.86, 22.8, 14.3. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{20}H_{41}B_2O_4$ $[M+H]^+$ 367.3185 (367.3180).

The spectroscopic data for **5-40b** match those reported in the literature.[63]

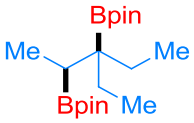
2,2'-(2-Methylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-41b



According to **General procedure 6** with 2-bromo-2-methylpropane **5-41a** (41.1 mg, 0.3 mmol, 1.0 equiv.), or 2-chloro-2-methylpropane **5-41a-1** (27.8 mg, 0.3 mmol, 1.0 equiv.), or di-*tert*-butyl dicarbonate **5-42a** (65.5 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-41b** as a colorless oil (from **5-41a**: 87.4 mg, 282 µmol, 94% yield; from **5-41a-1**: 82.8 mg, 267 µmol, 89% yield; from **5-42a**: 83.7 mg, 270 µmol, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.22 (d, J = 7 Hz, 24H), 0.97 (s, 6H), 0.81 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 83.0, 82.9, 27.6, 25.0, 24.8. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{33}B_2O_4$ $[M+H]^+$ 311.2559 (311.2551).

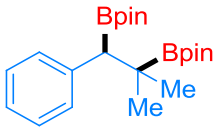
The spectroscopic data for **5-41b** match those reported in the literature.[63]

2,2'-(3-Ethylpentane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 4-43b



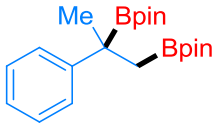
According to **General procedure 6** with 3-bromo-3-ethylpentane **5-43a** (53.7 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-43b** as a colorless oil (92.9 mg, 264 µmol, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.59 – 1.32 (m, 4H), 1.23 (s, 12H), 1.223 (s, 6H), 1.219 (s, 6H), 1.13 (dd, J = 8, 16 Hz, 3H), 0.91 (d, J = 8 Hz, 3H), 0.82 – 0.75 (m, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 82.8, 82.7, 26.3, 25.3, 25.1, 24.9, 24.8, 24.3, 11.6, 9.7, 8.8. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 34.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{19}H_{39}B_2O_4$ $[M+H]^+$ 353.3029 (353.3026). **Anal.** for $C_{19}H_{38}B_2O_4$ calcd: C, 64.81; H, 10.88. found: C, 64.77; H, 10.97.

2,2'-(2-Methyl-1-phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-44b



According to **General procedure 6** with (2-bromo-2-methylpropyl)benzene **5-44a** (63.9 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-44b** as a colorless oil (75.3 mg, 195 µmol, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.23 – 7.18 (m, 4H), 7.15 – 7.12 (m, 1H), 2.47 (s, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.22 (s, 12H), 0.98 (s, 3H), 0.83 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 140.5, 131.7, 127.4, 125.3, 83.3, 83.1, 29.9, 25.1, 25.0, 24.8, 24.7, 24.6, 22.9, 14.3. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{37}B_2O_4$ $[M+H]^+$ 387.2872 (387.2866). **Anal.** for $C_{22}H_{36}B_2O_4$ calcd: C, 68.43; H, 9.40. found: C, 68.35; H, 9.42.

2,2'-(2-Phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-45b

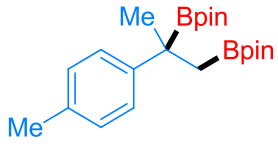


According to **General procedure 6** with 2-phenylpropan-2-ol **5-45a** (40.8 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-45b** as a colorless oil (97.1 mg, 261 µmol, 87% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.40 – 7.37 (m, 2H), 7.27 – 7.23 (m, 2H), 7.12 – 7.08 (m, 1H), 1.48 (d, J = 16 Hz, 1H), 1.41 (s, 3H), 1.211 (s, 6H), 1.207 (s, 6H), 1.20 (s, 6H), 1.18 (s, 6H), 1.14 (d, J = 16 Hz, 1H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 149.1, 127.9, 126.4, 124.8, 83.3, 83.0, 25.1,

24.70, 24.68, 24.6, 24.4. **$^{11}B\{^{1}H\}$ NMR** (160 MHz, $CDCl_3$): δ = 33.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{35}B_2O_4$ $[M+H]^+$ 373.2716 (373.2711).

The spectroscopic data for **5-45b** match those reported in the literature.[66]

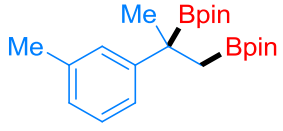
2,2'-(2-(*p*-Tolyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-46b



According to **General procedure 6** with 2-(*p*-tolyl)propan-2-ol **5-46a** (45.1 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-46b** as a colorless oil (97.3 mg, 252 µmol, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.27 (d, J = 8 Hz, 2H), 7.06 (d, J = 8 Hz, 2H), 2.29 (s, 3H), 1.47 (d, J = 16 Hz, 1H), 1.38 (s, 3H), 1.22 (s, 6H), 1.21 (s, 6H), 1.20 (s, 6H), 1.18 (s, 6H), 1.10 (d, J = 16 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$): δ = 146.3, 134.2, 128.8, 126.4, 83.3, 83.1, 25.3, 25.0, 24.9, 24.7, 24.6, 21.0. **$^{11}B\{^{1}H\}$ NMR** (160 MHz, $CDCl_3$): δ = 34.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{37}B_2O_4$ $[M+H]^+$ 387.2872 (387.2866).

The spectroscopic data for **5-46b** match those reported in the literature.[66]

2,2'-(2-(*m*-Tolyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-47b

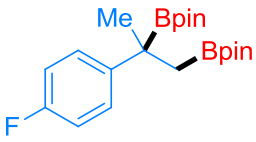


According to **General procedure 6** with 2-(*m*-tolyl)propan-2-ol **5-47a** (45.1 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-47b** as a colorless oil (93.8 mg, 243 µmol, 81% yield). **^{1}H NMR**

(500 MHz, $CDCl_3$): δ = 7.21 – 7.17 (m, 2H), 7.14 (t, J = 8 Hz, 1H), 6.93 – 6.91 (m, 1H), 2.31 (s, 3H), 1.47 (d, J = 16 Hz, 1H), 1.39 (s, 3H), 1.221 (s, 6H), 1.216 (s, 6H), 1.21 (s, 6H), 1.19 (s, 6H), 1.13 (d, J = 16 Hz, 1H). **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ = 149.2, 137.3, 127.9, 127.3, 125.7, 123.7, 83.4, 83.1, 25.2, 24.84, 24.83, 24.7, 24.6, 21.8. **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$): δ = 33.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{37}B_2O_4$ $[M+H]^+$ 387.2872 (387.2866).

The spectroscopic data for **5-47b** match those reported in the literature.[66]

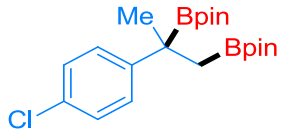
2,2'-(2-(4-Fluorophenyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-48b



According to **General procedure 6** with 2-(4-fluorophenyl)propan-2-ol **5-48a** (46.3 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-48b** as a colorless oil (97.1 mg, 249 µmol, 83% yield). **^1H NMR** (500 MHz, $CDCl_3$): δ = 7.35 – 7.31 (m, 2H), 6.95 – 6.91 (m, 2H), 1.42 (d, J = 16 Hz, 1H), 1.38 (s, 3H), 1.20 (s, 6H), 1.19 (s, 12H), 1.18 (s, 6H), 1.13 (d, J = 16 Hz, 1H). **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ = 160.8 (d, J = 240 Hz), 144.9 (d, J = 3 Hz), 128.0 (d, J = 8 Hz), 114.6 (d, J = 20 Hz), 83.5, 83.2, 25.2, 25.0, 24.8, 24.7, 24.6. **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$): δ = 33.8. **$^{19}F\{^1H\}$ NMR** (470 MHz, $CDCl_3$): δ = -119.6 (m). **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{34}B_2FO_4$ $[M+H]^+$ 391.2622 (391.2615). **Anal.** for $C_{21}H_{33}B_2FO_4$ calcd: C, 64.66; H, 8.53. found: C, 64.53; H, 8.66.

The spectroscopic data for **5-48b** match those reported in the literature.[66]

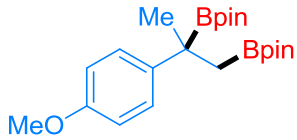
2,2'-(2-(4-Chlorophenyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-49b



According to **General procedure 6** with 2-(4-chlorophenyl)propan-2-ol **5-49a** (51.2 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-49b** as a colorless oil (95.1 mg, 234 µmol, 78% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.31 (d, J = 9 Hz, 2H), 7.21 (d, J = 9 Hz, 2H), 1.42 (d, J = 16 Hz, 1H), 1.37 (s, 3H), 1.20 (s, 6H), 1.195 (s, 6H), 1.19 (s, 6H), 1.18 (s, 6H), 1.12 (d, J = 16 Hz, 1H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 147.9, 130.7, 128.1, 128.0, 83.5, 83.2, 25.2, 24.82, 24.78, 24.7, 24.6. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 33.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{34}B_2ClO_4$ $[M+H]^+$ 407.2326 (407.2322). **Anal.** for $C_{21}H_{33}B_2ClO_4$ calcd: C, 62.04; H, 8.18. found: C, 62.68; H, 8.19.

The spectroscopic data for **5-49b** match those reported in the literature.[66]

2,2'-(2-(4-Methoxyphenyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-50b

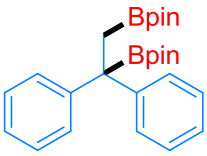


According to **General procedure 6** with 2-(4-methoxyphenyl)propan-2-ol **5-50a** (49.9 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-50b** as a colorless oil (67.6 mg, 168 µmol, 56% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.30 (d, J = 9 Hz, 2H), 6.81 (d, J = 9 Hz, 2H), 3.77 (s, 3H), 1.45 (d, J = 16 Hz, 1H), 1.37 (s, 3H), 1.210 (s, 6H), 1.206 (s, 6H), 1.19 (s, 6H), 1.18 (s, 6H), 1.10 (d, J = 16 Hz, 1H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 157.1, 141.4, 127.5, 113.4, 83.3,

83.1, 55.3, 25.2, 25.0, 24.8, 24.7, 24.6. **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$): δ = 33.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{37}B_2O_5$ $[M+H]^+$ 403.2822 (403.2813). **Anal.** for $C_{22}H_{36}B_2O_5$ calcd: C, 65.71; H, 9.02. found: C, 65.58; H, 9.14.

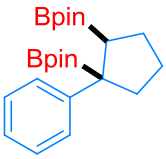
The spectroscopic data for **5-50b** match those reported in the literature.[66]

2,2'-(1,1-Diphenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-51b



According to **General procedure 6** with 1,1-diphenylethanol **5-51a** (59.5 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-51b** as a colorless oil (82.1 mg, 189 µmol, 63% yield). **^1H NMR** (500 MHz, $CDCl_3$): δ = 7.35 – 7.33 (m, 4H), 7.21 – 7.17 (m, 4H), 7.11 – 7.07 (m, 2H), 1.73 (s, 2H), 1.16 (s, 12H), 1.05 (s, 12H). **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ = 148.3, 129.4, 127.7, 125.2, 83.6, 83.1, 24.9, 24.5. **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$): δ = 33.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{26}H_{37}B_2O_4$ $[M+H]^+$ 435.2872 (435.2865). **Anal.** for $C_{26}H_{36}B_2O_4$ calcd: C, 71.92; H, 8.36. found: C, 71.75; H, 8.47.

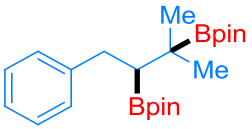
2,2'-(1-Phenylcyclopentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-52b



According to **General procedure 6** with 1-phenylcyclopentanol **5-52a** (48.7 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-52b** as a colorless oil (98.0 mg, 246 µmol, 82% yield). **^1H NMR**

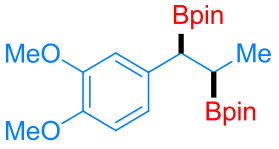
(500 MHz, $CDCl_3$): δ = 7.41 – 7.38 (m, 2H), 7.25 – 7.21 (m, 2H), 7.11 – 7.07 (m, 1H), 2.25 – 2.20 (m, 1H), 198 – 1.93 (m, 1H), 1.84 – 1.73 (m, 2H), 1.70 – 1.60 (m, 2H), 1.26 (s, 6H), 1.25 (s, 6H), 1.17 (s, 6H), 1.14 (s, 6H), 0.89 (t, J = 7 Hz, 1H). **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ = 147.5, 127.8, 127.4, 124.7, 83.3, 83.0, 36.5, 27.7, 25.2, 24.8, 24.7, 24.5, 24.0. **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$): δ = 34.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{23}H_{37}B_2O_4$ $[M+H]^+$ 399.2872 (399.2865). **Anal.** for $C_{26}H_{36}B_2O_4$ calcd: C, 69.38; H, 9.11. found: C, 69.31; H, 9.24.

2,2'-(3-Methyl-1-phenylbutane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-53b



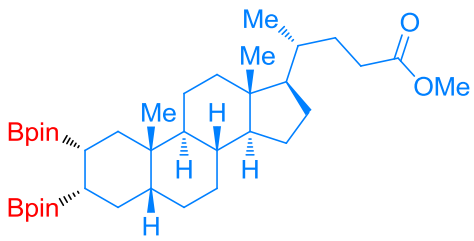
According to **General procedure 6** with 2-methyl-4-phenylbutan-2-ol **5-53a** (49.3 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-53b** as a colorless oil (80.4 mg, 201 µmol, 67% yield). **^1H NMR** (500 MHz, $CDCl_3$): δ = 7.25 – 7.18 (m, 4H), 7.12 – 7.08 (m, 1H), 2.72 – 2.70 (m, 1H), 1.50 (dd, J = 6, 11 Hz, 1H), 1.25 (s, 12H), 1.08 (s, 6H), 1.06 (s, 3H), 1.04 (s, 3H), 1.01 (s, 6H), 0.88 (t, J = 7 Hz, 1H). **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ = 143.4, 129.3, 128.0, 125.5, 83.1, 82.9, 35.1, 25.5, 25.2, 25.1, 24.9, 24.8, 23.1, 22.5, 14.2. **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$): δ = 34.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{23}H_{39}B_2O_4$ $[M+H]^+$ 401.3029 (401.3022). **Anal.** for $C_{23}H_{38}B_2O_4$ calcd: C, 69.03; H, 9.57. found: C, 68.95; H, 9.55.

2,2'-(1-(3,4-Dimethoxyphenyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-55b



According to **General procedure 6** with 1-(3,4-dimethoxyphenyl)propan-2-yl 4-methylbenzenesulfonate **5-55a** (105.1 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **5-55b** as a colorless oil (97.2 mg, 225 µmol, 75% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 6.74 – 6.68 (m, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 2.13 (d, J = 12 Hz, 1H), 1.47 (dq, J = 7, 12 Hz, 1H), 1.25 (s, 12H), 1.18 (s, 6H), 1.17 (s, 6H), 0.76 (d, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 148.7, 146.7, 135.5, 121.2, 111.9, 111.1, 83.23, 83.16, 55.9, 55.8, 25.2, 24.7, 24.4, 14.7. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 33.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{23}H_{38}B_2O_6$ $[M]^+$ 432.2849 (432.2843). **Anal.** for $C_{23}H_{38}B_2O_4$ calcd: C, 63.92; H, 8.86. found: C, 64.04; H, 8.95.

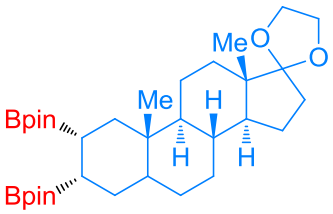
(*R*)-Methyl 4-((2*R*,3*S*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate 5-56b



According to **General procedure 6** with (*R*)-methyl 4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3-(tosyloxy)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate **5-56a** (163.4 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 90/10) to yield the product **5-56b** as a white solid (122.2 mg, 195 µmol, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.65 (s, 3H), 2.37 – 2.31 (m, 1H), 2.24 – 2.17 (m, 1H), 1.97 – 1.91 (m, 2H), 1.86 – 1.74 (m, 4H), 1.66 – 0.84 (m, 50H), 0.62 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 175.0, 83.1, 82.7, 56.8, 56.2, 51.6, 42.9, 42.7, 40.5, 40.2, 37.0, 36.1, 35.5, 35.4, 31.21, 31.18, 29.5, 28.4, 27.9, 26.7, 25.2, 25.0, 24.7, 24.6, 24.4, 20.9, 18.4, 12.2. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.0. **HRMS-ASAP** (m/z): Calculated (found) for

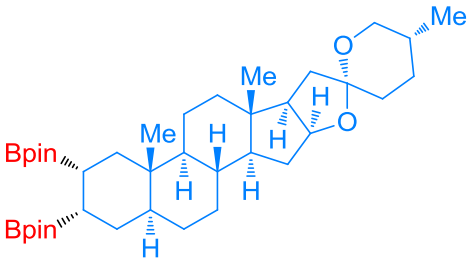
$C_{37}H_{65}B_2O_6$ $[M+H]^+$ 627.4962 (627.4951). **Anal.** for $C_{37}H_{64}B_2O_6$ calcd: C, 70.93; H, 10.30. found: C, 70.87; H, 10.43.

2,2'-((2*R*,3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethylhexadecahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolane]-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-57b



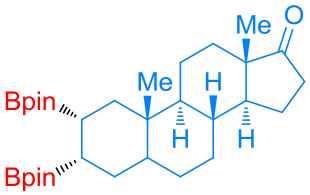
According to **General procedure 6** with (3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethylhexadecahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl 4-methylbenzenesulfonate **5-57a** (146.6 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 90/10) to yield the product **5-57b** as a white solid (124.9 mg, 219 µmol, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 4.49 (dd, J = 4, 11 Hz, 1H), 4.24 – 4.20 (m, 1H), 4.14 – 4.09 (m, 1H), 3.95 – 3.89 (m, 1H), 2.10 – 2.02 (m, 1H), 1.98 – 1.93 (m, 1H), 1.74 – 1.65 (m, 4H), 1.57 – 1.52 (m, 2H), 1.49 – 1.46 (m, 1H), 1.43 – 1.40 (m, 2H), 1.35 – 1.06 (m, 30H), 0.98 – 0.83 (m, 7H), 0.74 (S, 3H), 0.69 – 0.64 (m, 1H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 117.1, 83.1, 82.7, 66.6, 66.2, 56.0, 54.8, 48.9, 46.4, 45.8, 38.4, 36.4, 35.63, 35.6, 31.5, 31.3, 30.8, 28.9, 25.14, 25.08, 24.9, 24.8, 20.1, 14.9, 12.3. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{33}H_{57}B_2O_6$ $[M+H]^+$ 571.4336 (571.4331). **Anal.** for $C_{33}H_{56}B_2O_6$ calcd: C, 69.48; H, 9.90. found: C, 69.70; H, 9.86.

2,2'-((2a*S*,2'*R*,4*S*,5*R*,5'*R*,6a*S*,6b*S*,8a*S*,8b*R*,11a*S*,12a*S*,12b*R*)-5',6a,8a-Trimethyldocosahydrospiro[naphtho[2',1':4,5]indeno[2,1-*b*]furan-10,2'-pyran]-4,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 5-58b



According to **General procedure 6** with (2a*S*,2'*R*,4*R*,5'*R*,6a*S*,6b*S*,8a*S*,8b*R*,11a*S*,12a*S*,12b*R*)-5',6a,8a-trimethyldocosahydrospiro[naphtho[2',1':4,5]indeno[2,1-*b*]furan-10,2'-pyran]-4-yl 4-methylbenzenesulfonate **5-58a** (167.0 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 90/10) to yield the product **5-58b** as a white solid (140.0 mg, 219 µmol, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.40 – 4.33 (m, 1H), 3.49 – 3.44 (m, 1H), 3.36 (d, J = 11 Hz, 1H), 2.31 – 2.17 (m, 1H), 1.99 – 1.91 (m, 1H), 1.88 – 1.81 (m, 1H), 1.76 – 1.41 (m, 10H), 1.25 – .075 (m, 48H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 109.4, 83.1, 82.7, 81.1, 67.0, 62.4, 56.7, 55.2, 46.4, 41.8, 40.7, 40.2, 38.5, 36.5, 35.6, 32.6, 31.9, 31.6, 30.5, 29.3, 29.0, 25.2, 25.1, 24.9, 24.8, 20.8, 17.3, 16.7, 14.7, 12.4. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{38}H_{65}B_2O_6$ $[M+H]^+$ 639.4962 (639.4954). **Anal.** for $C_{38}H_{64}B_2O_6$ calcd: C, 71.48; H, 10.10. found: C, 71.55; H, 10.03.

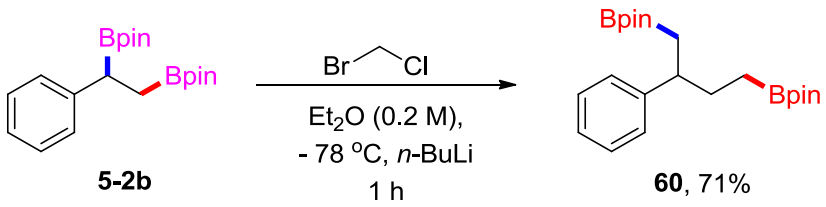
(2*R*,3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17(2*H*)-one 5-59b



According to **General procedure 6** with (3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-methylbenzenesulfonate **5-59a** (133.3 mg, 0.3 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 90/10) to yield the product **5-59b** as a white solid (112.1 mg, 213 µmol, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.41 (dd, J = 9, 19 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.92 – 1.87 (m, 1H), 1.80 – 1.67 (m, 4H), 1.56 – 1.43 (m, 5H), 1.30 – 1.21 (m, 29H), 1.11 – 0.61 (m, 11H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 221.9, 83.1, 82.7, 55.3, 51.7, 48.0, 46.4, 38.5, 36.6, 36.0, 35.5, 31.7, 31.4, 31.3, 29.0, 25.14, 25.10, 24.9, 24.7, 22.8, 21.9, 20.3, 14.2, 14.0, 12.3. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{31}H_{53}B_2O_5$ $[M+H]^+$ 527.4074 (527.4066). **Anal.** for $C_{31}H_{52}B_2O_5$ calcd: C, 70.74; H, 9.96. found: C, 70.82; H, 9.84.

5.5.4 Details of the Application of 1,2-Diborylalkane

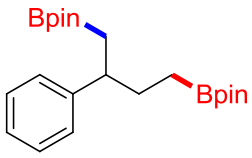
Procedure A:



To a solution of the 1,2-bis(boronic ester) **5-2b** (71.6 mg, 0.2 mmol, 1.0 equiv.) in anhydrous Et_2O (0.2 M) was added bromochloromethane (155 mg, 1.2 mmol, 6.0 equiv.) under argon. The reaction mixture was cooled to -78 °C. nBuLi (2.5 M in hexane, 5.0 equiv.) was added dropwise to the reaction mixture at -78 °C. The reaction mixture was stirred at -78 °C for 20 min and the resulting reaction mixture was stirred at room temperature for 1 h. The reaction was then diluted with water and extracted 3 times with Et_2O. The organic layer was washed with brine, and then dried over Na_2SO_4, and filtred through a pad of Celite (Ø 3 mm x 8 mm), concentrated under reduced

pressure and the residue was purified by flash column chromatography on silica gel to provide double homologation product **60**.

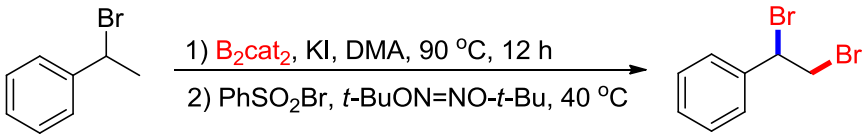
2,2'-(2-Phenylbutane-1,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 60



The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **60** as a colorless oil (54.8 mg, 142 µmol, 71% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.25 – 7.08 (m, 5H), 2.79 – 2.69 (m, 1H), 1.77 – 1.55 (m, 2H), 1.27 – 1.24 (m, 2H), 1.20 (s, 12H), 1.06 (s, 6H), 1.05 (s, 6H), 0.68 – 0.59 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 147.2, 128.1, 127.8, 125.8, 83.0, 82.9, 44.1, 34.1, 25.0, 24.9, 24.8, 24.7. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 33.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{22}H_{37}B_2O_4$ $[M+H]^+$ 387.2872 (387.2863).

The spectroscopic data for **60** match those reported in the literature.[67]

Procedure B:

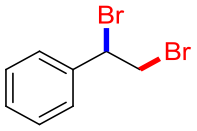


5-2a **61**, 43%

Based on the procedure described previously in literature,[68] in an argon-filled glovebox, (1-bromoethyl)benzene **5-2a** (55.5 mg, 0.3 mmol, 1.0 equiv.) in DMA (1 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. KI (49.8 mg, 0.3 mmol, 1.0 equiv.) and B_2cat_2 (178 mg, 0.75 mmol, 2.5 equiv.) were added. The reaction mixture was

stirred at 90 °C for 12 h. MeOH (58 µL, 1.44 mmol) was added at 0 °C and the solution was stirred for 15 min at room temperature. $PhSO_2Br$ (1.2 mmol) and di-*tert*-butyl hyponitrite (3.4 mg, 0.02 mmol) was added every 1h and the solution was warmed to 40 °C for 3 h. The crude product was purified by flash column chromatography on silica gel to provide the product **61**.

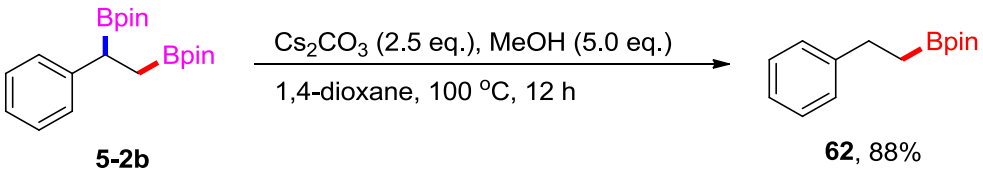
(1,2-Dibromoethyl)benzene 61



The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **61** as a colorless oil (34.1 mg, 129 µmol, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.44 – 7.34 (m, 5H), 5.16 (dd, J = 5, 8 Hz, 1H), 4.12 – 4.02 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 138.7, 129.3, 129.0, 127.8, 51.0, 35.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_8H_9Br_2$ $[M+H]^+$ 262.9066 (262.9061).

The spectroscopic data for **61** match those reported in the literature.[69]

Procedure C:

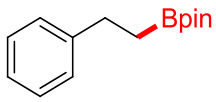


5-2b **62**, 88%

Based on the procedure described previously in literature,[70] to a solution of the 1,2-bis(boronic ester) **5-2b** (71.6 mg, 0.2 mmol, 1.0 equiv.) in anhydrous 1,4-dioxane (0.2 M), Cs_2CO_3 (163 mg, 0.5 mmol, 2.5 equiv.) and MeOH (41 µL, 1.0 mmol, 5.0 equiv.) were added under argon. The reaction mixture was stirred at 100 °C for 12 h. The reaction was then diluted with ethyl acetate,

and filtred through a pad of Celite (Ø 3 mm x 8 mm), concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel to provide the product **62**.

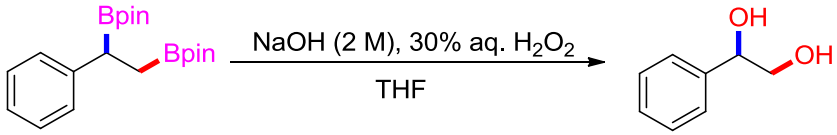
4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane 62



The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **62** as a colorless oil (40.8 mg, 176 µmol, 88% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.28 – 7.21 (m, 4H), 7.17 – 7.14 (m, 1H), 2.75 (t, J = 8 Hz, 2H), 1.22 (s, 12H), 1.15 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 144.5, 128.3, 128.1, 125.6, 83.2, 30.1, 24.9. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 33.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{22}BO_2$ $[M+H]^+$ 233.1707 (233.1703).

The spectroscopic data for **62** match those reported in the literature.[70]

Procedure D:

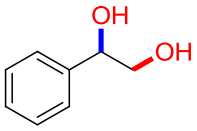


5-2b **63**, 73%

A premixed solution of 2 M aq. NaOH/30% aq. H_2O_2 (2:1, 3 mL) was added dropwise to a solution of the 1,2-bis(boronic ester) **5-2b** (71.6 mg, 0.2 mmol, 1.0 equiv.) in THF (2 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 4 h. The reaction was then diluted with water (2 mL) and Et_2O (2 mL), and extracted 3 times with Et_2O. The organic layer was washed with brine, and then dried over Na_2SO_4, and filtred through a pad of Celite (Ø 3 mm x

8 mm), concentrated under reduced pressure and the residue was purified by column chromatography to provide diol **63**.

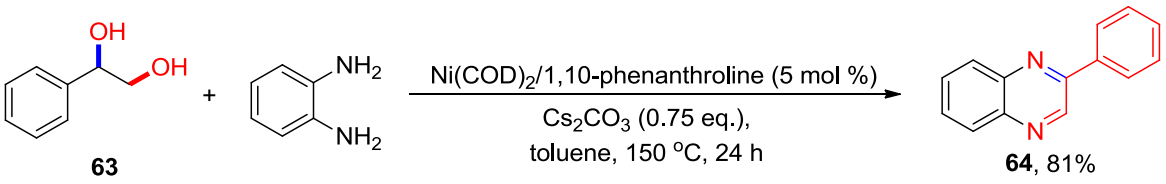
1-Phenylethane-1,2-diol 63



The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 1/2) to yield the product **63** as a white solid (20.2 mg, 146 µmol, 73% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.37 – 7.27 (m, 5H), 4.82 (dd, J = 4, 8 Hz, 1H), 3.76 (dd, J = 4, 11 Hz, 1H), 3.66 (dd, J = 8, 11 Hz, 1H), 2.44 – 2.36 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 140.6, 128.7, 128.2, 126.2, 74.8, 68.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_8H_{11}O_2$ $[M+H]^+$ 139.0754 (139.0745).

The spectroscopic data for **63** match those reported in the literature.[71]

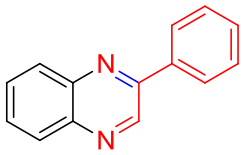
Procedure E:



Based on the procedure described previously in literature,[72] 1,2-diamine (54.1 mg, 0.5 mmol, 1.0 equiv.), vicinal diol **63** (54.1 mg, 1.0 mmol, 2.0 equiv.), $Ni(COD)_2$ (6.9 mg, 5 mol %), 1,10-phenanthroline (4.5 mg, 5 mol %), Cs_2CO_3 (122.2 mg, 0.375 mmol, 0.75 equiv.), and 2 mL of toluene were taken in a pressure tube, and the tube was sealed under an argon atmosphere. The reaction mixture was stirred at 150 °C for 24 h. The reaction was then diluted with water (8 mL),

and extracted 3 times with ethyl acetate, and filtred through a pad of Celite (Ø 3 mm x 8 mm), concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the quinoxaline **64**.

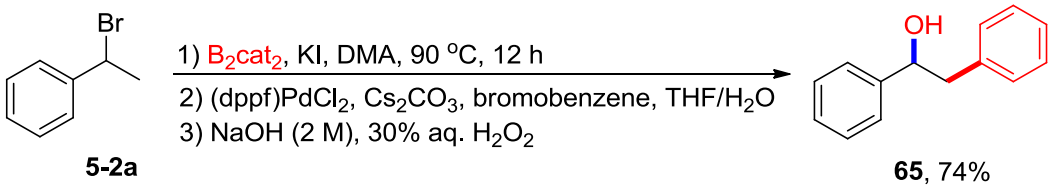
2-Phenylquinoxaline 64



The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **64** as a yellow solid (83.5 mg, 405 µmol, 81% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 9.34 (s, 1H), 8.22 – 8.13 (m, 4H), 7.83 – 7.73 (m, 2H), 7.61 – 7.53 (m, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 152.1, 143.1, 142.5, 141.3, 136.7, 130.6, 130.5, 129.9, 129.7, 129.4, 129.0, 127.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{11}N_2$ $[M+H]^+$ 207.0917 (207.0911).

The spectroscopic data for **64** match those reported in the literature.[72]

Procedure F:



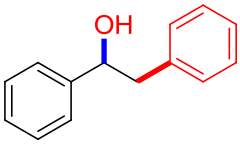
5-2a

65, 74%

Based on the procedure described previously in literature,[73] in an argon-filled glovebox, (1-bromoethyl)benzene **5-2a** (55.5 mg, 0.3 mmol, 1.0 equiv.) in DMA (1 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. KI (49.8 mg, 0.3 mmol, 1.0 equiv.) and B_2cat_2 (178 mg, 0.75 mmol, 2.5 equiv.) were added. The reaction mixture was stirred at 90 °C for 12 h. After completion of reaction, DMA was removed in vacuo. $(dppf)PdCl_2$

(22 mg, 10 mol%), Cs_2CO_3 (293 mg, 0.9 mmol, 3.0 equiv.), bromobenzene (94.2 mg, 0.6 mmol, 2.0 equiv.) and THF (2 mL) were added and the solution was stirred for 1 min. 200 µL of deoxygenated water was added to the mixture and the solution was heated to 80 °C for 18 h. After this time, a premixed solution of 2 M aq. NaOH/30% aq. H_2O_2 (2:1, 4.5 mL) was added dropwise to the mixture at 0 °C. The reaction mixture was warmed to room temperature and stirred for 6 h. The reaction was then diluted with H_2O (2 mL) and Et_2O (2 mL), and extracted 3 times with Et_2O. The organic layer was washed with brine, and then dried over Na_2SO_4, and filtred through a pad of Celite (Ø 3 mm x 8 mm), concentrated under reduced pressure and the residue was purified by column chromatography to provide **65**.

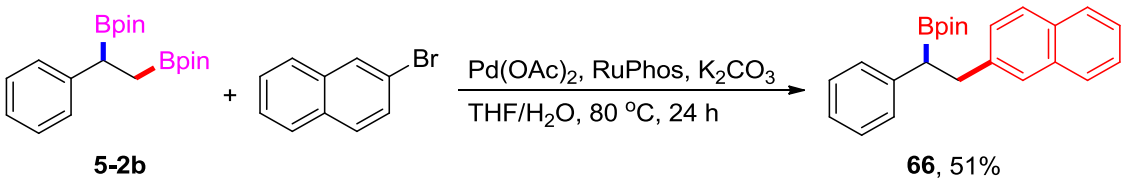
1,2-Diphenylethanol 65



The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **65** as a white solid (44 mg, 222 µmol, 74% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.38 – 7.19 (m, 10H), 4.91 (d, J = 5, 8 Hz, 1H), 3.10 – 2.96 (m, 2H), 1.93 – 1.89 (m, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 143.9, 138.2, 129.6, 128.6, 128.5, 127.7, 126.7, 126.0, 75.5, 46.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{15}O$ $[M+H]^+$ 199.1117 (199.1115).

The spectroscopic data for **65** match those reported in the literature.[73]

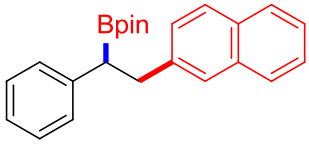
Procedure G:



5-2b **66**, 51%

Based on the procedure described previously in literature,[74] in an argon-filled glovebox, 1,2-bis(boronic ester) **5-2b** (143.2 mg, 0.4 mmol, 1.0 equiv.), 2-bromonaphthalene (99.4 mg, 0.48 mmol, 1.2 equiv.), $Pd(OAc)_2$ (9 mg, 0.04 mmol, 0.1 equiv.), Ruphos (46.7 mg, 0.1 mmol, 0.25 equiv.) and K_2CO_3 (110.6 mg, 0.8 mmol, 2.0 equiv.) were weighed into a 10 mL thick-walled reaction tube and THF (2 mL) was added. Degassed water was added (20:1, organic:water) and the reaction mixture was stirred at 80 °C for 24 h. After completion of reaction, the reaction mixture was filtred through a plug of silica, washed through with EtOAc and concentrated under reduced pressure and the residue was purified by column chromatography to provide **66**.

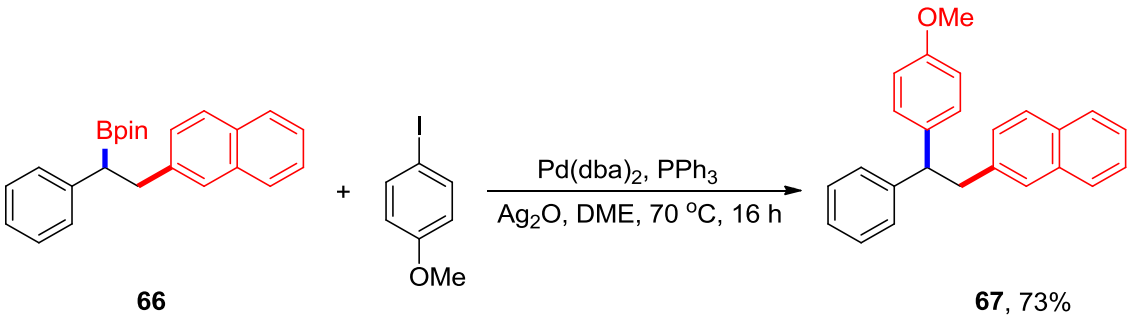
4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)-1-phenylethyl)-1,3,2-dioxaborolane 66



The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 97/3) to yield the product **66** as a colorless oil (73.1 mg, 204 µmol, 51% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.78 – 7.76 (m, 1H), 7.74 – 7.70 (m, 2H), 7.64 – 7.63 (m, 1H), 7.43 – 7.38 (m, 2H), 7.33 (dd, J = 2, 9 Hz, 1H), 7.29 – 7.24 (m, 4H), 7.16 – 7.13 (m, 1H), 3.34 (dd, J = 10, 14 Hz, 1H), 3.12 (dd, J = 7, 14 Hz, 1H), 2.79 (dd, J = 7, 10 Hz, 1H), 1.09 (d, J = 7 Hz, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 142.7, 139.5, 133.6, 132.1, 128.6, 128.5, 127.9, 127.7, 127.6, 127.0, 125.8, 125.6, 125.1, 83.6, 39.1, 24.71, 24.68. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 33.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{24}H_{28}BO_2$ $[M+H]^+$ 359.2177 (359.2171).

The spectroscopic data for **66** match those reported in the literature.[74]

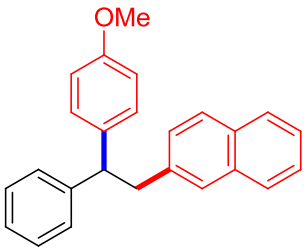
Procedure H:



66 **67**, 73%

Based on the procedure described previously in literature,[74] in an argon-filled glovebox, boronic ester **66** (71.6 mg, 0.2 mmol, 1.0 equiv.), 1-iodo-4-methoxybenzene (70.2 mg, 0.3 mmol, 1.5 equiv.), $Pd(dba)_2$ (9 mg, 0.016 mmol, 0.08 equiv.), PPh_3 (33.6 mg, 0.128 mmol, 0.64 equiv.) and Ag_2O (69.5 mg, 0.3 mmol, 1.5 equiv.) were weighed into a 10 mL thick-walled reaction tube and dimethoxyethane (DME) (2 mL) was added. The reaction mixture was stirred at 70 °C for 16 h. After completion of reaction, the reaction mixture was filtred through a plug of silica, washed through with EtOAc and concentrated under reduced pressure and the residue was purified by column chromatography to provide **67**.

2-(2-(4-Methoxyphenyl)-2-phenylethyl)naphthalene 67

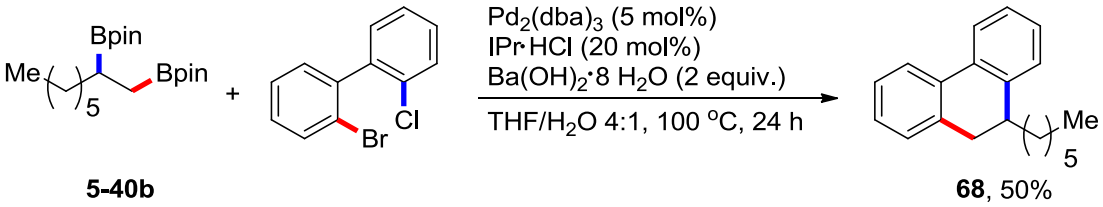


The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **67** as a colorless oil (49.4 mg, 146 µmol, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.77 – 7.75 (m, 1H), 7.69 – 7.66 (m, 2H), 7.45 – 7.39 (m, 3H), 7.25 – 7.22 (m, 4H),

7.17 – 7.14 (m, 4H), 6.79 (d, J = 8 Hz, 2H), 4.31 (t, J = 8 Hz, 1H), 3.76 (s, 3H), 3.50 (d, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 158.1, 145.0, 138.1, 136.7, 133.6, 132.1, 129.1, 128.5, 128.1, 127.88, 127.86, 127.67, 127.65, 127.6, 126.3, 125.8, 125.3, 113.9, 55.3, 52.3, 42.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{25}H_{23}O$ $[M+H]^+$ 339.1743 (339.1737).

The spectroscopic data for **67** match those reported in the literature.[74]

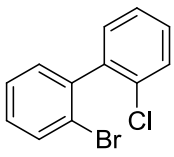
Procedure I:



5-40b **68**, 50%

Based on the procedure described previously in literature,[75] in an argon-filled glovebox, boronic ester **5-40b** (183 mg, 0.5 mmol, 1.0 equiv.), 2-bromo-2'-chloro biaryl (133.8 mg, 0.5 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (23 mg, 0.025 mmol, 5 mol%), IPr•HCl (42.7 mg, 0.1 mmol, 20 mol%) and $Ba(OH)_2$•$8H_2O$ (315.5 mg, 1.0 mmol, 2.0 equiv.) were weighed into a 50 mL Schlenk flask and THF (10 mL)/water (2.5 mL) was added. The reaction mixture was stirred at 100 °C for 24 h. The reaction was then diluted with water (5 mL) and MTBE (10 mL). The organic phase was extracted 3 times with MTBE, and then dried over Na_2SO_4, and filtred through a pad of Celite (Ø 3 mm x 8 mm), concentrated under reduced pressure and the residue was purified by column chromatography to provide compound **68**.

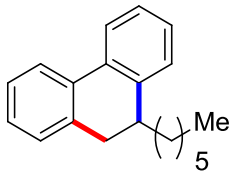
2-Bromo-2'-chloro biaryl



The synthesis was performed according to Morandi *et al*.[75] To a solution of 1-bromo-2-chlorobenzene (2.35 mL, 20 mmol, 2.0 equiv.) in THF (40 mL) was added a hexane solution of *n*-butyllithium (4.0 mL, 2.5 M, 10 mmol, 1.0 equiv.) slowly under argon at -78 °C and the resulting reaction mixture was stirred at room temperature for 4 h. The reaction was quenched by aqueous HCl solution (25 mL, 2M). The organic layer was extracted with DCM, washed with brine, and then dried over Na_2SO_4, and filtred through a pad of Celite (Ø 3 mm x 8 mm), concentrated under reduced pressure and the residue was purified by column chromatography to provide the product. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.71 – 7.67 (m, 1H), 7.51 – 7.48 (m, 1H), 7.42 – 7.33 (m, 3H), 7.29 – 7.24 (m, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 140.6, 140.2, 133.5, 132.7, 131.22, 131.20, 129.6, 129.5, 129.4, 127.3, 126.6, 123.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_9BrCl$ $[M+H]^+$ 266.9571 (266.9566).

The spectroscopic data for **2-Bromo-2'-chloro biaryl** match those reported in the literature.[75]

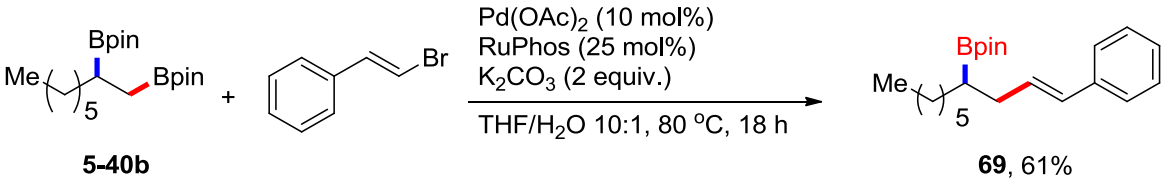
9-Hexyl-9,10-dihydrophenanthrene 68



The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **68** as a colorless oil (66 mg, 250 µmol, 50% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.75 (t, J = 8 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.26 – 7.20 (m, 4H), 3.10 (dd, J = 5, 15 Hz, 1H), 2.86 – 2.81 (m, 1H), 2.78 (dd, J = 5, 15 Hz, 1H), 1.41 – 1.21 (m, 10H), 0.85 (t, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 141.5, 135.7, 134.2, 133.6, 129.1, 128.3, 127.6, 127.4, 127.0, 126.9, 124.1, 123.5, 38.7, 34.1, 33.5, 32.0, 29.5, 27.7, 22.8, 14.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{20}H_{25}$ $[M+H]^+$ 265.1951 (265.1943).

The spectroscopic data for **68** match those reported in the literature.[75]

Procedure J:

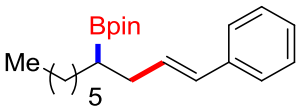


5-40b

69, 61%

In an argon-filled glovebox, boronic ester **5-40b** (183 mg, 0.5 mmol, 1.0 equiv.), (*E*)-(2-bromovinyl)benzene (109.8 mg, 0.6 mmol, 1.2 equiv.), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 10 mol%), RuPhos (58.3 mg, 0.125 mmol, 25 mol%) and K_2CO_3 (138.2 mg, 1.0 mmol, 2.0 equiv.) were weighed into a 10 mL Schlenk flask and THF (5 mL)/water (0.5 mL) was added. The reaction mixture was stirred at 80 °C for 18 h. The reaction was then diluted with water (5 mL) and MTBE (10 mL). The organic phase was extracted 3 times with MTBE, and then dried over Na_2SO_4, and filtred through a pad of Celite (Ø 3 mm x 8 mm), concentrated under reduced pressure and the residue was purified by column chromatography to provide compound **69**.

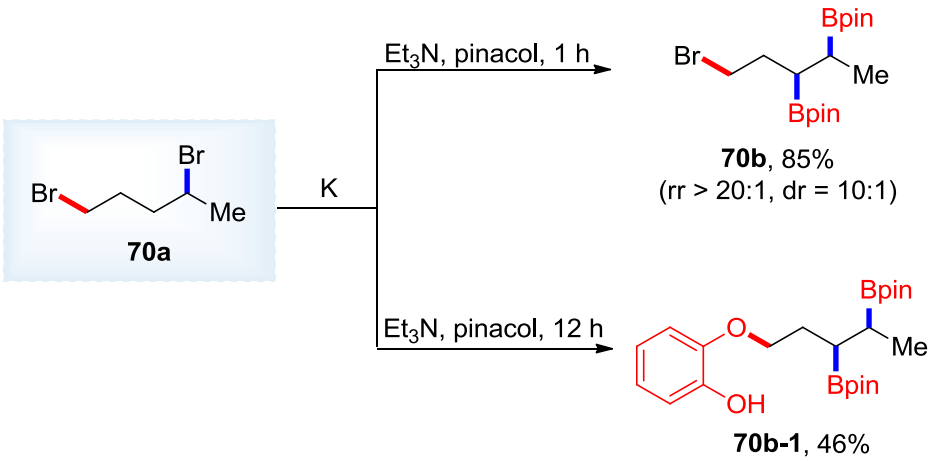
(*E*)-4,4,5,5-Tetramethyl-2-(1-phenyldec-1-en-4-yl)-1,3,2-dioxaborolane 69



The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **69** as a colorless oil (104.4 mg, 305 µmol, 61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.33 – 7.27 (m, 4H), 7.19 – 7.16 (m, 1H), 6.39 (d, J = 16 Hz, 1H), 6.26 – 6.20 (m, 1H), 2.33 – 2.28 (m, 1H), 1.49– 1.25 (m, 12H), 1.22 (s, 6H), 1.22 (s, 6H), 0.88 (t, J = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 138.1, 131.0, 130.2, 128.5, 126.8, 126.1, 83.1, 34.9, 32.0, 31.2, 29.7, 29.3, 25.0, 24.96, 22.8, 14.2. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.4. **HRMS-**

ASAP (m/z): Calculated (found) for $C_{22}H_{36}BO_2$ $[M+H]^+$ 343.2803 (343.2796). **Anal.** for $C_{22}H_{35}BO_2$ calcd: C, 77.19; H, 10.31. found: C, 77.32; H, 10.26.

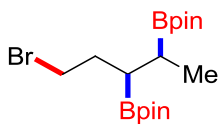
Procedure K:



In an argon-filled glovebox, 1,4-dibromopentane (69.0 mg, 0.3 mmol, 1.0 equiv.) in DMA (1 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. KI (49.8 mg, 0.3 mmol, 1.0 equiv.) and B_2cat_2 (178 mg, 0.75 mmol, 2.5 equiv.) were added. The reaction mixture was stirred at 90 °C for 12 h.

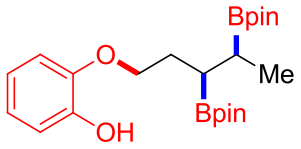
Then a solution of pinacol (106 mg, 0.9 mmol, 3.0 equiv.) in Et_3N (1 mL) was added to the reaction mixture, which was stirred at room temperature for 1 h or 12 h. Then water was added, and the reaction mixture was extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtred, and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide product **70b** or **70b-1**.

2,2'-(5-Bromopentane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 70b



The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **70b** as a colorless oil (102.7 mg, 255 μmol, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.54 – 3.46 (m, 1H), 3.44 – 3.36 (m, 1H), 2.16 – 2.01 (m, 1H), 1.94 – 1.79 (m, 1H), 1.32 – 1.25 (m, 1H), 1.22 (m, 24H), 1.19 – 1.16 (m, 1H), 0.99 – 0.95 (m, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 83.2, 83.1, 34.3, 33.5, 25.1, 25.06, 24.8, 24.8, 14.7. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ = 33.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{34}B_2BrO_4$ $[M+H]^+$ 403.1821 (403.1817). **Anal.** $C_{17}H_{33}B_2BrO_4$ calcd: C, 50.67; H, 8.25. found: C, 50.73; H, 8.12.

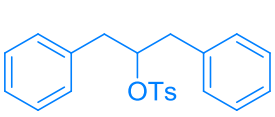
2-((3,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)oxy)phenol 70b-1



The reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 4/1) to yield the product **70b-1** as a white solid (59.6 mg, 138 μmol, 46% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.92 – 6.90 (m, 1H), 6.87 – 6.82 (m, 2H), 6.80 – 6.77 (m, 1H), 6.69 (s, 1H), 4.09 – 4.04 (m, 1H), 4.03 – 3.99 (m, 1H), 2.06 – 1.99 (m, 1H), 1.83 – 1.77 (m, 1H), 1.35 – 1.30 (m, 2H), 1.25 – 1.24 (m, 24H), 1.00 (d, J = 8 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 146.7, 146.6, 121.5, 119.8, 114.8, 112.8, 83.4, 83.2, 69.9, 29.5, 25.1, 25.0, 24.8, 24.7, 14.5. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 34.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{23}H_{39}B_2O_6$ $[M+H]^+$ 433.2927 (433.2921). **Anal.** $C_{23}H_{38}B_2O_6$ calcd: C, 63.92; H, 8.86. found: C, 63.85; H, 8.97.

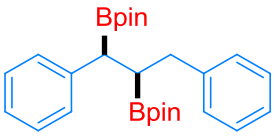
5.5.5 Preliminary Mechanistic Investigations

a) Radical trap experiments



5-22a

B_2cat_2, KI, DMA, 90 °C, 12 h
Radical trap
then Et_3N, pinacol

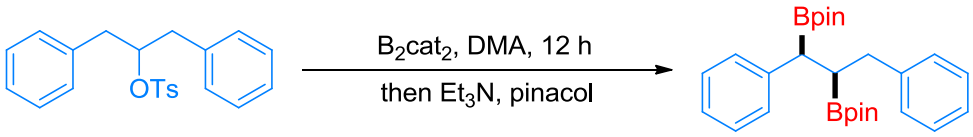


5-22b

Radical trap	**5-22b**
None	81%
9,10-dihydroanthracene	75%
BHT	76%

In an argon-filled glovebox, 1,3-diphenylpropan-2-yl 4-methylbenzenesulfonate **5-22a** (109.9 mg, 0.3 mmol, 1.0 equiv.) in DMA (1 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. KI (49.8 mg, 0.3 mmol, 1.0 equiv.), B_2cat_2 (178 mg, 0.75 mmol, 2.5 equiv.), and radical trap [9,10-dihydroanthracene (108.2 mg, 0.6 mmol, 2.0 equiv.) or BHT (132.2 mg, 0.6 mmol, 2.0 equiv.)] were added. The reaction mixture was stirred at 90 °C for 12 h. Then a solution of pinacol (106 mg, 0.9 mmol, 3.0 equiv.) in Et_3N (1 mL) was added to the reaction mixture, which was stirred at room temperature for 1 h. Then water was added, and the reaction mixture was extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtred, and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide product **5-22b** in 75% or 76% yield, respectively.

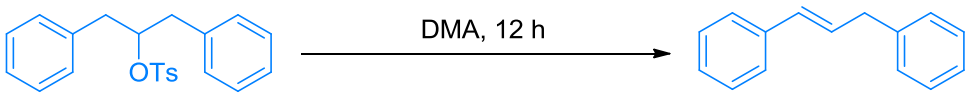
b) Role of KI



5-22a **5-22b**

T/°C	KI	
80	✗	trace
80	✓	72%

In an argon-filled glovebox, 1,3-diphenylpropan-2-yl 4-methylbenzenesulfonate **5-22a** (109.9 mg, 0.3 mmol, 1.0 equiv.) in DMA (1 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. B_2cat_2 (178 mg, 0.75 mmol, 2.5 equiv.) was added with or without addition of KI (49.8 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was stirred at 80 °C for 12 h. Then a solution of pinacol (106 mg, 0.9 mmol, 3.0 equiv.) in Et_3N (1 mL) was added to the reaction mixture, which was stirred at room temperature for 1 h. Then water was added, and the reaction mixture was extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtred, and concentrated under reduced pressure, *n*-dodecane was added as an internal standard and the crude reaction mixture was analyzed by GC-MS. Trace amount of the diborylated product **5-22b** was observed by GC-MS without the addition of KI. However, 72% yield of **5-22b** was obtained with the addition of KI. It suggested KI played a crucial role for the generation of diborylated products.

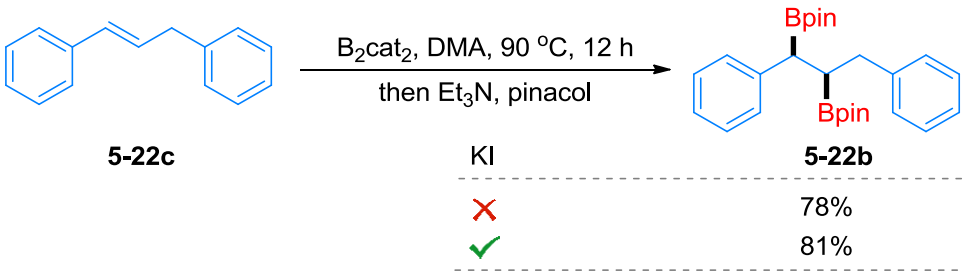


5-22a

T/°C	KI	**5-22c**	*E/Z*
80	✗	19%	59/41
80	✓	78%	98/2
90	✓	85%	98/2

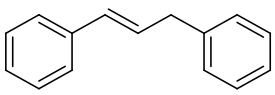
In an argon-filled glovebox, 1,3-diphenylpropan-2-yl 4-methylbenzenesulfonate **5-22a** (109.9 mg, 0.3 mmol, 1.0 equiv.) in DMA (1 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. The reaction mixture was stirred at indicated temperature for 12 h.

Then the reaction mixture was purified by column chromatography on silica gel to provide product olefin **5-22c**. 1) The olefin **5-22c** was obtained in only 19% yield with an average stereoselectivity. 2) Upon addition of KI, the olefin **5-22c** was isolated in 78% yield with excellent *E/Z* ratio at 80 °C. The results implied that alkyl alkenes might be the active intermediates of this transformation.



In an argon-filled glovebox, olefin **5-22c** (58.3 mg, 0.3 mmol, 1.0 equiv.) in DMA (1 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. B_2cat_2 (178 mg, 0.75 mmol, 2.5 equiv.) was added with or without addition of KI (49.8 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was stirred at 90 °C for 12 h. Then a solution of pinacol (106 mg, 0.9 mmol, 3.0 equiv.) in Et_3N (1 mL) was added to the reaction mixture, which was stirred at room temperature for 1 h. Then water was added, and the reaction mixture was extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtred, and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide diborylated product **5-22b** in 78% or 81% yield, respectively. **5-22b** was obtained in similar high yields regardless of the presence or absence of KI under the standard conditions.

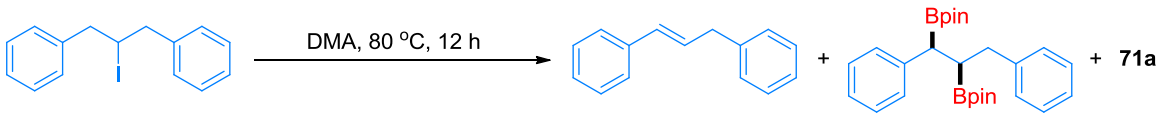
(*E*)-Prop-1-ene-1,3-diyldibenzene 5-22c



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 – 7.20 (m, 10H), 6.49 – 6.35 (m, 2H), 3.57 (d, J = 7 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 140.3, 137.6, 131.2, 129.4, 128.8, 128.64, 128.63, 127.2, 126.32, 126.26, 39.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{15}$ $[M+H]^+$ 195.1168 (195.1165).

The spectroscopic data for **5-22c** match those reported in the literature.[76]

c) Diboration of iodides



71a

KI	B_2cat_2	**5-22c**	**5-22b**	
✗	✗	18% (*E*/*Z*, 61/39)	-	71%
✓	✗	74% (*E*/*Z*, 95/5)	-	0%
✗	✓	0%	12%	79%
✓	✓	0%	78%	0%

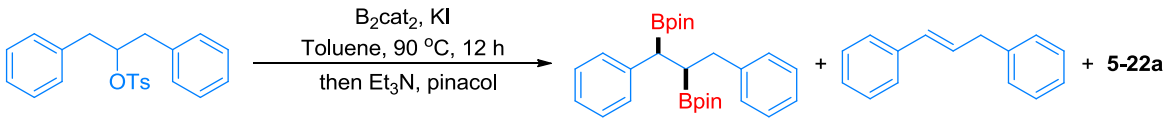
In order to confirm whether the process undergoes iodine replacement (the replacement of iodine in KI with OTs in **5-22a**), the alkyl iodide (**71a**) was subjected to standard conditions.

In the absence of B_2cat_2, we observed a similar phenomenon, and KI promoted the formation of *E*-alkenes (**5-22c**).

When KI and B_2cat_2 were added into the reaction at the same time, the yield of the target product increased sharply.

These results indicated that the presence of KI enhanced both the reactivity and regioselectivity and diastereoselectivity of the reaction. However, this does not rule out the possibility of initial iodide exchange taking place.

d) Role of DMA



5-22a

Additive	**5-22b**	**5-22c**	
None	0%	0%	92%
DMA (3.0 equiv.)	19%	0%	74%
DMAP (3.0 equiv.)	11%	0%	76%

In an argon-filled glovebox, 1,3-diphenylpropan-2-yl 4-methylbenzenesulfonate **5-22a** (109.9 mg, 0.3 mmol, 1.0 equiv.) in toluene (1 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. KI (49.8 mg, 0.3 mmol, 1.0 equiv.) and B_2cat_2 (178 mg, 0.75 mmol, 2.5 equiv.), were added. The reaction mixture was stirred at 90 °C for 12 h. Then a solution of pinacol (106 mg, 0.9 mmol, 3.0 equiv.) in Et_3N (1 mL) was added to the reaction mixture, which was stirred at room temperature for 1 h. Then water was added, and the reaction mixture was extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtred, and concentrated under reduced pressure, *n*-dodecane was added as an internal standard and the crude reaction mixture was analyzed by GC-MS. The diborylated product **5-22b** was not observed by GC-MS. When DMA (3.0 equiv.) or DMAP (3.0 equiv.) was added to the reaction mixture, the diborylated product **5-22b** was generated.

5.5.6 Single-Crystal X-ray Diffraction Analysis

A crystal suitable for single-crystal X-ray diffraction was selected, coated in perfluoropolyether oil, and mounted on a microloop. Diffraction data of **5-13b**, **5-18b**, **5-22b**, **5-26b**, **5-28b**, and **5-59b** were collected on a RIGAKU OXFORD DIFFRACTION XTALAB Synergy-S, Dualflex, four-circle diffractometer with a semiconductor HPA-detector (HyPix-6000) and micro-focus sealed X-ray tubes providing multi-layer mirror monochromated Cu-K_α radiation and, for compound **5-18b**, Mo-K_α radiation. The crystals were cooled at 100 K, or 173 K for compound **5-22b**, using an Oxford Cryostream 800 low-temperature device. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the CrysAlis^{Pro} software. The structures were solved using the intrinsic phasing method (SHELXT)[77] and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' on idealised positions by full-matrix least squares against F^2 of all data, using SHELXL software[78] and the SHELXLE graphical user interface[79]. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Diamond[80] software was used for graphical representation. Crystal data and experimental details are listed in Tables S2 and S3; full structural information has been deposited with Cambridge Crystallographic Data Centre. CCDC-2119847 (**5-13b**), 2119849 (**5-18b**), 2119873 (**5-22b**), 2119851 (**5-26b**), 2119856 (**5-28b**), and 2119852 (**5-59b**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 5-S1: Single-crystal X-ray diffraction data and refinement details of **5-13b**, **5-18b**, and **5-22b**.

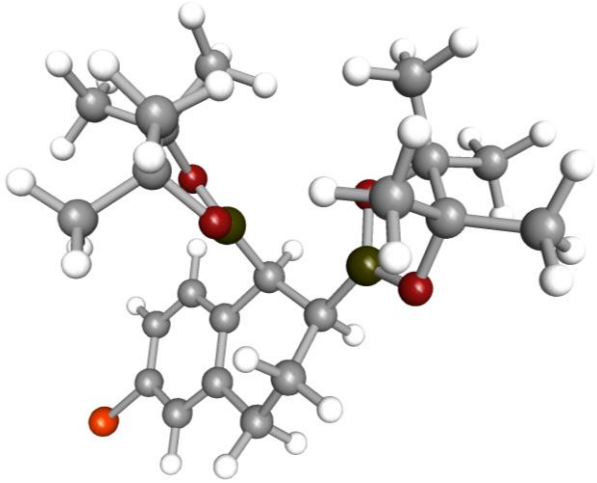
Data	**5-13b**	**5-18b**	**5-22b**
CCDC number	2119847	2119849	2119873
Empirical formula	$C_{21}H_{33}B_2BrO_4$	$C_{23}H_{38}B_2O_4$	$C_{27}H_{38}B_2O_4$
Formula weight / g·mol^{-1}	451.00	400.15	448.19
T / K	100(2)	100(2)	173(2)
Radiation, λ / Å	Cu-K_α 1.54184	Mo-K_α 0.71073	Cu-K_α 1.54184
Crystal size / mm³	0.057×0.097×0.329	0.155×0.298×0.543	0.465×0.230×0.214
Crystal color, habit	Colorless needle	Colorless plate	Colorless block
μ / mm^{-1}	2.604	0.073	0.564
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a / Å	9.04840(10)	6.6217(2)	20.4392(3)
b / Å	21.9005(4)	40.7610(13)	9.80950(10)
c / Å	11.9134(2)	9.0118(3)	26.8903(3)
α / °	90	90	90
β / °	102.4160(10)	104.716(4)	99.0130(10)
γ / °	90	90	90
Volume / Å^3	2305.60(6)	2352.55(15)	5324.89(11)
Z	4	4	8
ρ_{calc} / g·cm^{-3}	1.299	1.130	1.118
F(000)	944	872	1936
θ range / °	4.037 – 74.503	1.998 – 26.370	2.189 – 80.217
Reflections collected	24717	17800	50427
Unique reflections	4722	4817	11417
Parameters / restraints	560 / 661	532 / 1032	1054 / 1920
GooF on F^2	1.065	1.097	1.056
R_1 [I>2σ (I)]	0.0402	0.0712	0.0719
wR^2 (all data)	0.1098	0.1685	0.1782
Max. / min. residual electron density / e·Å^{-3}	0.525 / –0.426	0.419 / –0.247	0.284 / –0.275

Table 5-S2: Single-crystal X-ray diffraction data and refinement details of **26b**, **28b**, and **59b**.

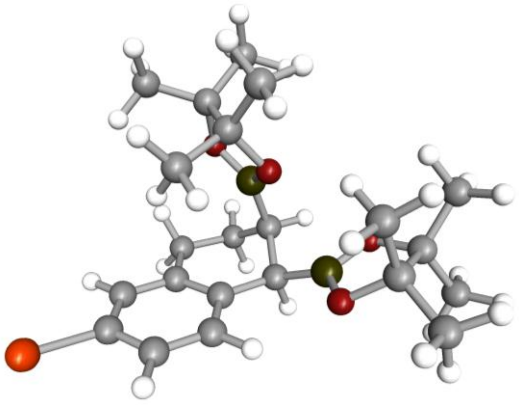
Data	**26b**	**28b**	**59b**
CCDC number	2119851	2119856	2119852
Empirical formula	$C_{18}H_{34}B_2O_4$	$C_{22}H_{33}B_2BrO_4$	$C_{31}H_{52}B_2O_5$
Formula weight / g·mol^{-1}	336.07	463.01	526.34
T / K	100(2)	100(2)	100(2)
Radiation, λ / Å	Cu-K$_\alpha$ 1.54184	Cu-K$_\alpha$ 1.54184	Mo-K$_\alpha$ 0.71073
Crystal size / mm³	0.021×0.104×0.202	0.122×0.240×0.334	0.157×0.321×0.403
Crystal color, habit	Colorless plate	Colorless plate	Colorless block
μ / mm^{-1}	0.609	2.601	0.073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1$	$P2_1$
a / Å	9.7006(2)	12.98450(10)	14.0122(4)
b / Å	10.0093(3)	12.24660(10)	7.93797(17)
c / Å	11.9545(2)	14.83570(10)	14.5453(4)
α / °	72.544(2)	90	90
β / °	68.499(2)	100.1580(10)	106.337(3)
γ / °	65.208(3)	90	90
Volume / Å^3	965.61(5)	2322.13(3)	1552.53(7)
Z	2	4	2
ρ_{calc} / g·cm^{-3}	1.156	1.324	1.126
F(000)	368	968	576
θ range / °	4.035 – 74.478	3.026 – 74.491	2.380 – 26.370
Reflections collected	20282	45749	31892
Unique reflections	3946	9474	6338
Parameters / restraints	225 / 0	539 / 1	430 / 229
GooF on F^2	1.060	1.041	1.044
R$_1$ [I>2σ (I)]	0.0483	0.0231	0.0406
wR^2 (all data)	0.1407	0.0582	0.1070
Max. / min. residual electron density / e·Å^{-3}	0.511 / –0.302	0.205 / –0.361	0.348 / –0.302

5.5.7 Computational Details

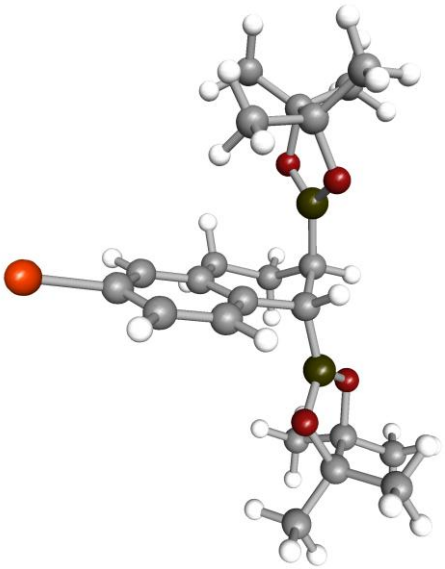
Calculations were carried out using the TURBOMOLE V7.2 2017 program suite, a development of the University of Karlsruhe and the Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.[81] Geometry optimizations were performed using (RI-)DFT calculations[82] on a m4 grid employing the M06-2x[83] functional and def2-SVP basis sets for all atoms.[84]



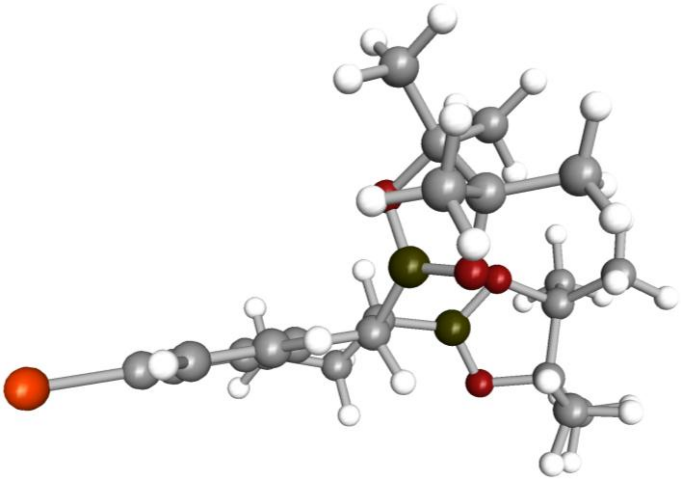
*syn*1_**5-28**, 0.00 kJ/mol



*syn*2_**5-28**, +4.70 kJ/mol



*anti*1_**5-28**, +12.86 kJ/mol



*anti*2_**5-28**, +12.07 kJ/mol

Cartesian Coordinates and Energies of the Geometry-optimized Compounds

*syn*1_**5-28**
Energy = -3781.560489237

C	-0.6194207	-0.9585494	0.7869554
C	0.6469402	-0.8111406	0.2370732
C	1.1459198	0.4613875	-0.0740491
C	0.3516134	1.5940189	0.1739037
C	-0.9193480	1.4161588	0.7426579
C	-1.4174442	0.1549278	1.0472415
H	1.2605669	-1.6935025	0.0444791
H	-1.5255943	2.2995388	0.9563602
H	-2.4094149	0.0324306	1.4821997
C	0.8458051	3.0034695	-0.1168927
H	0.0285709	3.5465465	-0.6200424
C	2.1095347	3.0438621	-0.9937517
H	1.8201181	2.8051160	-2.0366240
C	3.1170077	1.9758572	-0.5501854
H	4.0410566	2.0594664	-1.1398815
H	3.3919238	2.1582142	0.5015210
C	2.5195127	0.5818653	-0.6985499
H	2.4358728	0.3365047	-1.7718893
H	3.1834955	-0.1796558	-0.2620991
Br	-1.2683369	-2.6935473	1.1958327
B	1.0498771	3.7304951	1.2698432
O	2.2742571	3.9977666	1.8346981
O	0.0108890	4.1061781	2.0783525
C	2.0395656	4.3594850	3.2095452
C	0.5599639	4.8740047	3.1632080
C	3.0575045	5.4000338	3.6420070
C	2.1927243	3.0837899	4.0332633
C	-0.2438712	4.6087157	4.4241077
C	0.4621296	6.3408288	2.7545299
H	2.8454658	5.7424623	4.6658745
H	4.0646619	4.9601830	3.6267105
H	3.0505156	6.2691511	2.9725530
H	3.1939548	2.6681253	3.8556172
H	2.0784959	3.2805437	5.1081738
H	1.4500907	2.3310412	3.7290656
H	0.2157697	5.1106430	5.2887759
H	-1.2614515	5.0028566	4.2978718
H	-0.3167466	3.5345708	4.6325996
H	-0.5905680	6.5780875	2.5487484
H	0.8260316	7.0098861	3.5469150
H	1.0376582	6.5172720	1.8342630
B	2.7466920	4.4804623	-1.0287091
O	4.0329208	4.7362206	-1.4233459
O	2.0701206	5.6271949	-0.6839785
C	4.3277001	6.1001415	-1.0767434
C	2.8998501	6.7464431	-1.0470030
C	5.2716461	6.6901054	-2.1095575
C	4.9828494	6.0669524	0.3017654
C	2.7331842	7.8559224	-0.0232990
C	2.4379841	7.2201863	-2.4224391

H	5.4408419	7.7593432	-1.9124302
H	6.2395326	6.1731898	-2.0574329
H	4.8762141	6.5730734	-3.1257026
H	5.8775377	5.4318342	0.2481288
H	5.2824730	7.0703793	0.6361755
H	4.2939370	5.6265301	1.0377206
H	3.4202063	8.6868949	-0.2417770
H	1.7040026	8.2402882	-0.0578324
H	2.9327805	7.4929428	0.9923567
H	1.3676354	7.4616021	-2.3709811
H	2.9860730	8.1161018	-2.7456985
H	2.5772218	6.4307034	-3.1745986

*syn*2_**5-28**

Energy = -3781.558700435

C	-1.5939106	-1.1203933	-0.6922543
C	-0.2844731	-0.9599296	-0.2621846
C	0.2404965	0.3197513	-0.0298772
C	-0.5662227	1.4540871	-0.2531578
C	-1.8924946	1.2571713	-0.6700583
C	-2.4146440	-0.0125502	-0.8928968
H	0.3449938	-1.8374468	-0.0993208
H	-2.5257878	2.1265243	-0.8425569
H	-3.4447965	-0.1430627	-1.2244690
C	0.0083134	2.8487823	-0.0485758
H	-0.1700845	3.1336423	1.0094673
C	1.5387158	2.8212340	-0.2681832
H	1.9359299	3.8327195	-0.0861551
C	2.1780748	1.8263112	0.7020143
H	3.2749914	1.8503977	0.6259527
H	1.9202162	2.1237018	1.7319323
C	1.6849956	0.4045877	0.4277601
H	2.3100327	-0.0484280	-0.3576762
H	1.8091862	-0.2261019	1.3217510
Br	-2.2734433	-2.8639031	-1.0044583
B	-0.6103408	4.0437165	-0.8800595
O	0.1121427	5.1961810	-1.0597730
O	-1.8784842	4.1490970	-1.3924754
C	-0.7680333	6.2017410	-1.5830391
C	-1.9307059	5.3437899	-2.1942301
C	-0.0100275	7.0472216	-2.5932496
C	-1.2215547	7.0595433	-0.4048159
C	-3.3115472	5.9652479	-2.0754964
C	-1.6521219	4.9207105	-3.6331798
H	-0.6851122	7.7620706	-3.0867611
H	0.7772395	7.6143163	-2.0777047
H	0.4648270	6.4175527	-3.3553453
H	-0.3321122	7.4649739	0.0963879
H	-1.8531564	7.8969015	-0.7328524
H	-1.7828518	6.4584996	0.3248717
H	-3.3457502	6.9286525	-2.6054463
H	-4.0543463	5.2956566	-2.5303285
H	-3.5921587	6.1264328	-1.0277356
H	-2.3921385	4.1613853	-3.9240711
H	-1.7269558	5.7698405	-4.3267064

H	-0.6514661	4.4738025	-3.7051075
B	1.7961920	2.4454861	-1.7787253
O	2.7750954	1.5967810	-2.2176805
O	0.9732511	2.8588646	-2.8029250
C	2.7006221	1.5358393	-3.6539120
C	1.2268424	1.9937955	-3.9276468
C	3.0142388	0.1200973	-4.1059809
C	3.7337795	2.5180773	-4.1988889
C	1.0443316	2.7637178	-5.2253081
C	0.2191750	0.8502232	-3.8379180
H	2.8645662	0.0184872	-5.1911477
H	4.0630561	-0.1146323	-3.8781653
H	2.3785849	-0.6102924	-3.5906564
H	4.7186401	2.2555355	-3.7894806
H	3.7879323	2.4810109	-5.2956999
H	3.4955671	3.5462559	-3.8908513
H	1.3951122	2.1619571	-6.0771031
H	-0.0199126	2.9848984	-5.3839572
H	1.5972657	3.7113649	-5.2098993
H	-0.7928544	1.2792672	-3.8155205
H	0.2993509	0.1720489	-4.6988055
H	0.3542288	0.2709888	-2.9111640

*anti*1_**5-28**
Energy = -3781.555590293

C	-1.4299663	-0.7711859	0.4283595
C	-0.0509114	-0.9022737	0.3473685
C	0.7710208	0.2323334	0.2672463
C	0.1825753	1.5089895	0.2581480
C	-1.2130962	1.6113446	0.3537875
C	-2.0277832	0.4895893	0.4371345
H	0.4014757	-1.8962903	0.3459638
H	-1.6674405	2.6047788	0.3597763
H	-3.1113288	0.5852349	0.5052552
C	1.0306227	2.7596126	0.1398157
H	0.4605847	3.4752453	-0.4795692
C	2.3685822	2.4490954	-0.5571170
H	2.9972154	3.3551751	-0.5304885
C	3.0799208	1.3254174	0.2061156
H	4.0810640	1.1427470	-0.2101633
H	3.2227839	1.6466316	1.2516938
C	2.2698962	0.0289105	0.1539637
H	2.4717565	-0.4808963	-0.8020132
H	2.5970177	-0.6620210	0.9467037
Br	-2.5164650	-2.3233503	0.5306313
B	1.2175093	3.4693107	1.5357326
O	2.3878941	4.0649778	1.9271924
O	0.2283250	3.5940053	2.4735605
C	2.2511038	4.4111118	3.3171565
C	0.6949947	4.5157981	3.4755589
C	3.0087237	5.6988119	3.5909019
C	2.8469126	3.2582152	4.1210469
C	0.1639370	4.0907218	4.8333095
C	0.1585722	5.8944988	3.0993140
H	2.8433670	6.0320441	4.6262334

H	4.0846451	5.5261187	3.4510132
H	2.6992453	6.4977825	2.9065695
H	3.8879685	3.1095777	3.8028888
H	2.8347189	3.4674904	5.1996158
H	2.2940016	2.3253637	3.9356215
H	0.5892872	4.7209108	5.6285379
H	-0.9285546	4.2032618	4.8506410
H	0.4020662	3.0412414	5.0434924
H	-0.9350078	5.8345891	3.0168407
H	0.4141151	6.6483248	3.8568638
H	0.5597924	6.2199686	2.1286245
B	2.0820171	2.0685532	-2.0591247
O	1.0754944	2.6428316	-2.7925110
O	2.7408884	1.0907294	-2.7579456
C	0.8511032	1.8011667	-3.9370101
C	2.2472450	1.1102895	-4.1102609
C	0.4134275	2.6547502	-5.1136908
C	-0.2483782	0.8163903	-3.5435169
C	2.1878366	-0.3123908	-4.6392955
C	3.2222361	1.9481928	-4.9327580
H	0.3252150	2.0422485	-6.0233370
H	-0.5691697	3.0967409	-4.8992725
H	1.1218033	3.4707497	-5.3006185
H	-1.1320107	1.3868748	-3.2257245
H	-0.5308905	0.1633701	-4.3810795
H	0.0687754	0.1930229	-2.6931011
H	1.7100961	-0.3357303	-5.6300433
H	3.2066975	-0.7114976	-4.7380365
H	1.6270988	-0.9654302	-3.9595228
H	4.2282559	1.5186603	-4.8312563
H	2.9478521	1.9562818	-5.9967957
H	3.2517655	2.9849839	-4.5678268

*anti*2_**5-28**
Energy = -3781.555890345

C	-1.3273104	-0.0523731	0.7635485
C	-0.0258090	-0.1914408	0.2986737
C	0.7232874	0.9328322	-0.0735375
C	0.1437792	2.2086625	0.0186573
C	-1.1660341	2.3204086	0.5079275
C	-1.9115802	1.2079177	0.8805432
H	0.4215667	-1.1850084	0.2294466
H	-1.6095733	3.3157660	0.6088781
H	-2.9286320	1.3123417	1.2584586
C	0.9022048	3.4701786	-0.3618279
H	1.1369097	3.9971877	0.5831387
C	2.2335400	3.1856413	-1.1086840
H	1.9881643	2.9193009	-2.1515950
C	2.9723535	2.0224210	-0.4483869
H	3.9585846	1.8692166	-0.9119540
H	3.1561170	2.2661447	0.6112145
C	2.1443913	0.7468319	-0.5603019
H	2.1174797	0.4266544	-1.6164283
H	2.6109470	-0.0776456	-0.0001809
Br	-2.3164582	-1.5927713	1.2581306

B	-0.0159574	4.4285665	-1.2207412
O	-0.4754421	5.6459812	-0.7864520
O	-0.4611451	4.1130917	-2.4726603
C	-1.4692720	6.0930089	-1.7302289
C	-1.0962522	5.2814372	-3.0220169
C	-1.3763258	7.6014283	-1.8806387
C	-2.8290418	5.6977387	-1.1592675
C	-2.2864327	4.8510841	-3.8631784
C	-0.0607426	5.9924449	-3.8883365
H	-2.0836131	7.9559239	-2.6451484
H	-1.6303079	8.0820534	-0.9256272
H	-0.3644543	7.9119145	-2.1672930
H	-2.9308571	6.1337644	-0.1557579
H	-3.6531498	6.0630830	-1.7873347
H	-2.9141161	4.6046434	-1.0728361
H	-2.8481836	5.7295044	-4.2142397
H	-1.9294782	4.2970618	-4.7419502
H	-2.9618539	4.1964508	-3.2998149
H	0.2876641	5.2929865	-4.6607823
H	-0.4897176	6.8763346	-4.3814468
H	0.8098691	6.2880061	-3.2873622
B	2.9784826	4.5628048	-1.0745196
O	3.8405157	4.9524165	-0.0851235
O	2.6801223	5.5867443	-1.9391398
C	3.8910910	6.3921055	-0.1086073
C	3.5111765	6.7113556	-1.5952172
C	5.2756879	6.8530816	0.3096513
C	2.8336806	6.8834795	0.8784466
C	2.7137293	7.9917630	-1.7796685
C	4.7135664	6.6862614	-2.5339046
H	5.3655197	7.9449233	0.2097088
H	5.4468979	6.5872501	1.3616601
H	6.0557691	6.3746398	-0.2947361
H	3.0386743	6.4366104	1.8608218
H	2.8526650	7.9775860	0.9793300
H	1.8249609	6.5762252	0.5603249
H	3.2827317	8.8590110	-1.4124420
H	2.5039315	8.1482046	-2.8476381
H	1.7588047	7.9375217	-1.2419406
H	4.3517196	6.7027212	-3.5710084
H	5.3658411	7.5562419	-2.3750730
H	5.3051148	5.7707793	-2.3897322

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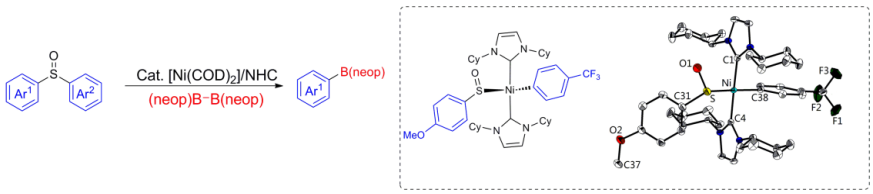
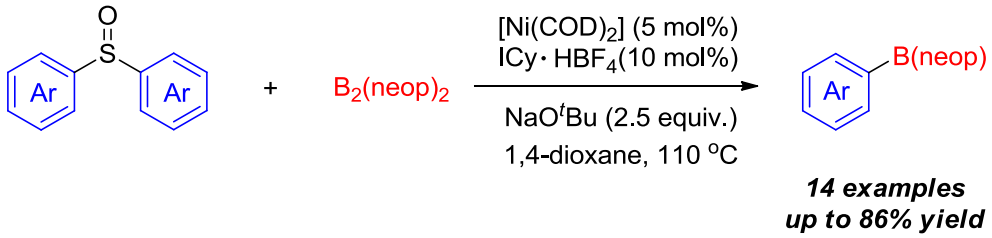
Summary

Alkylboronates play an important role in synthetic chemistry, materials science and drug discovery. They are easy to handle due to their good air and moisture stability, and can be readily employed to form carbon–carbon and carbon–heteroatom bonds and can be converted to various functional groups under mild reaction conditions. Compared with conventional groups, such as aryl (pseudo)halides or alcohols, organosulfur compounds represent an alternative and complimentary substitute in coupling reactions. The construction of C–B bond from C–SO bond of aryl sulfoxide is presented in Chapter 2. The selective cleavage of either alkyl(C)-sulfonyl or aryl(C)-sulfonyl bonds of an aryl alkyl sulfone *via* Cu-free or Cu-mediated processes generates the corresponding boronate esters, which are presented in Chapter 3 and Chapter 4. 1,2-Bis(boronate esters) are emerging as important synthetic intermediates for preparing 1,2-difunctional compounds. In addition, the boryl moieties in different environments in a 1,2-bis(boronate ester) can be differentiated and converted selectively, allowing the synthesis of a wide variety of complex molecules. A direct and selective diboration of C–X and C–O bonds for the preparation of 1,2-bis(boronate esters) is presented in Chapter 5.

Chapter 2

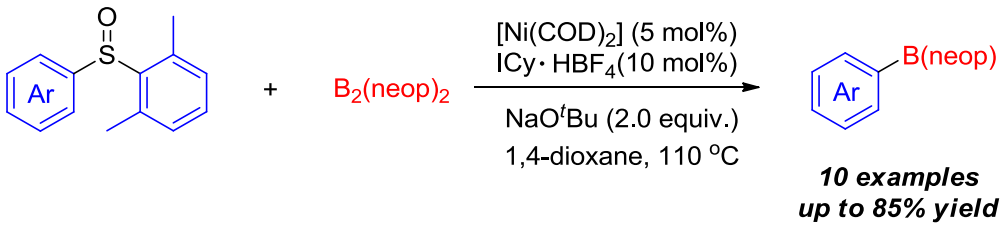


In this chapter, a nickel/NHC catalytic system has been developed for the efficient borylation of aryl sulfoxides *via* C–SO bond activation using $B_2(neop)_2$ as boron source in the presence of NaO^{t}Bu. A wide range of symmetric diaryl sulfoxides bearing different electronic and steric properties were converted into the corresponding arylboronic esters in good yields (Scheme S-1). The attempted borylation of *ortho*-tolyl sulfoxide gave the product in only 16% GC yield, whereas bis(1,3,5-trimethylphenyl) sulfoxide (disubstituted at both *ortho* positions) failed to give the corresponding product, and only unreacted starting material was identified by GC-MS.



Scheme S-1. Screening of diaryl sulfoxides for the Ni-catalyzed borylation reaction.

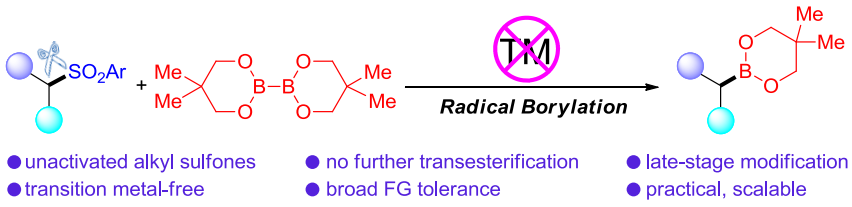
The regioselective borylation of unsymmetric diaryl sulfoxides was also feasible leading to borylation of the sterically less encumbered aryl substituent by means of steric bias (Scheme S-2). This process was compatible with various important functional groups, such as fluoro, methoxy, trimethylsilyl, nitrogen- and oxygen-containing heterocycles.



Scheme S-2. Regioselective borylation of unsymmetrical diaryl sulfoxides.

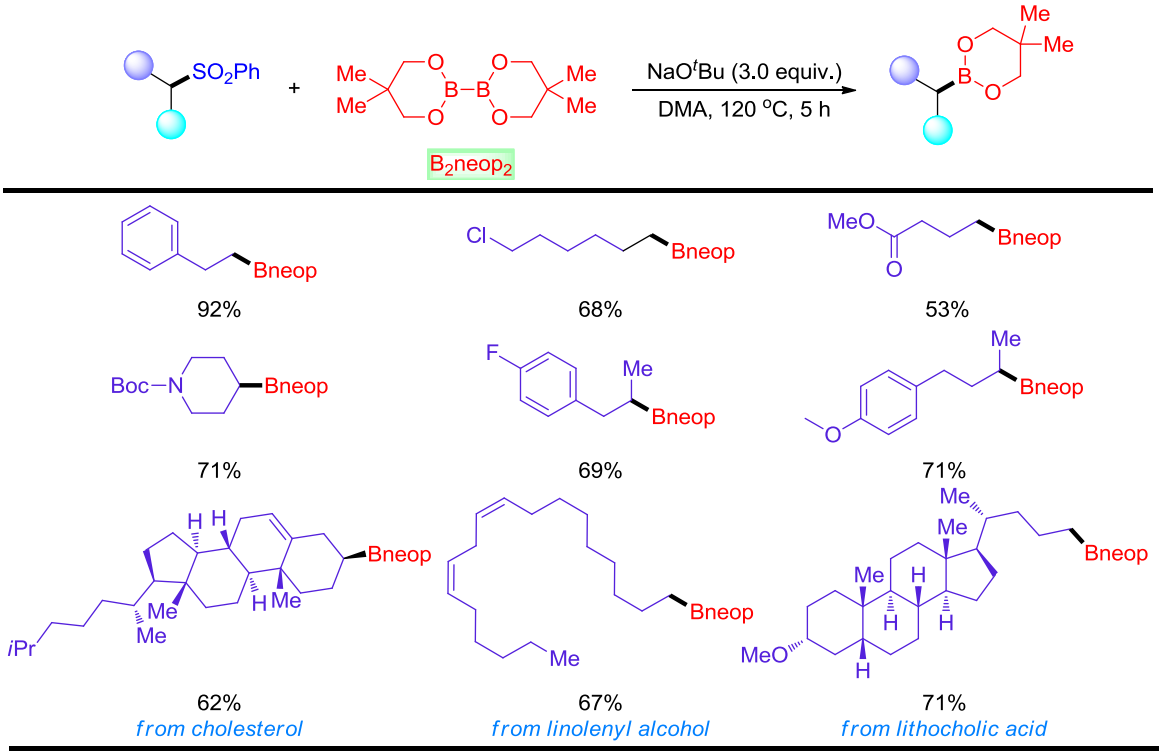
Competition experiments demonstrated that an electron-deficient aryl moiety reacts preferentially. The origin of the selectivity in the Ni-catalyzed borylation of electronically biased unsymmetrical diaryl sulfoxide lies in the oxidative addition step of the catalytic cycle, as oxidative addition of methoxyphenyl 4-(trifluoromethyl)phenyl sulfoxide to the Ni(0) complex occurs selectively to give the structurally characterized complex *trans*-[Ni(ICy)$_2$(4-CF$_3$-C$_6$H$_4$){(SO)-4-MeO-C$_6$H$_4$}].

Chapter 3



In this chapter, a practical and direct method for the production of versatile alkylboronic esters *via* transition metal-free borylation of primary and secondary alkyl sulfones is presented. A broad range of alkyl aryl sulfones were transformed to corresponding alkylboronic esters in the presence

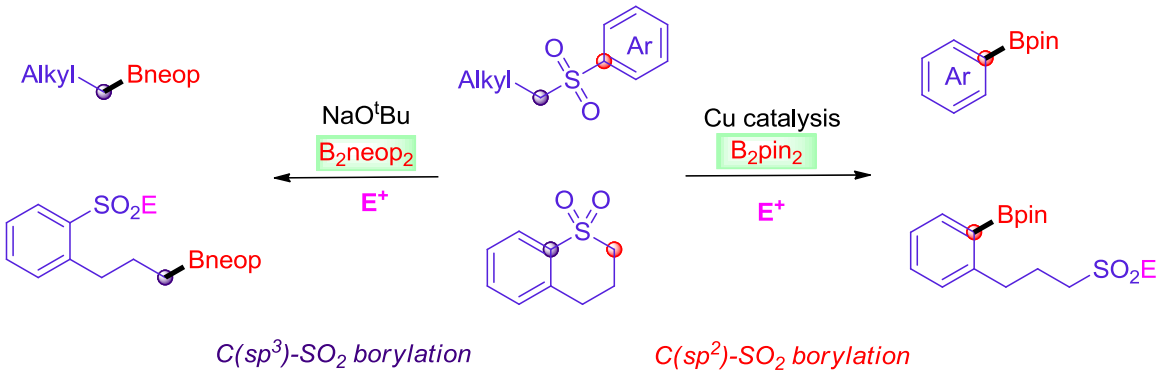
of 3.0 equiv. of NaO^{t}Bu in DMA at 120 °C using $B_2(neop)_2$ as the boron source (Scheme S-3). The practicality and industrial potential of this protocol are highlighted by its wide functional group tolerance, the late-stage modification of complex compounds, no need for further transesterification, and operational simplicity. This chapter showed 34 examples under the reaction conditions.



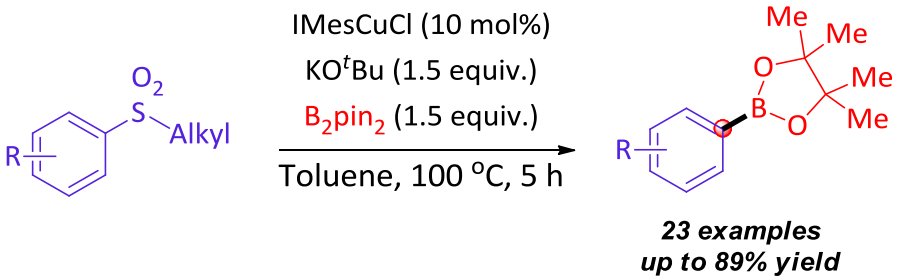
Scheme S-3. Alkyl sulfones substrate scope.

Radical trap experiments using 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO), 9,10-dihydroanthracene, or butylated hydroxytoluene (BHT) as radical traps, radical clock experiments was carried out with hex-5-en-1-ylsulfonylbenzene as the substrate, and EPR studies using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a spin-trap showed that this desulfonative borylation process involves radical intermediates. Additional studies are required to achieve a more detailed understanding of the intimate mechanism of the process and the reason that B_2neop_2 shows optimum reactivity among the diboron(4) reagents examined. We anticipate that these findings will prompt further development of desulfonative radical cross-coupling reactions.

Chapter 4



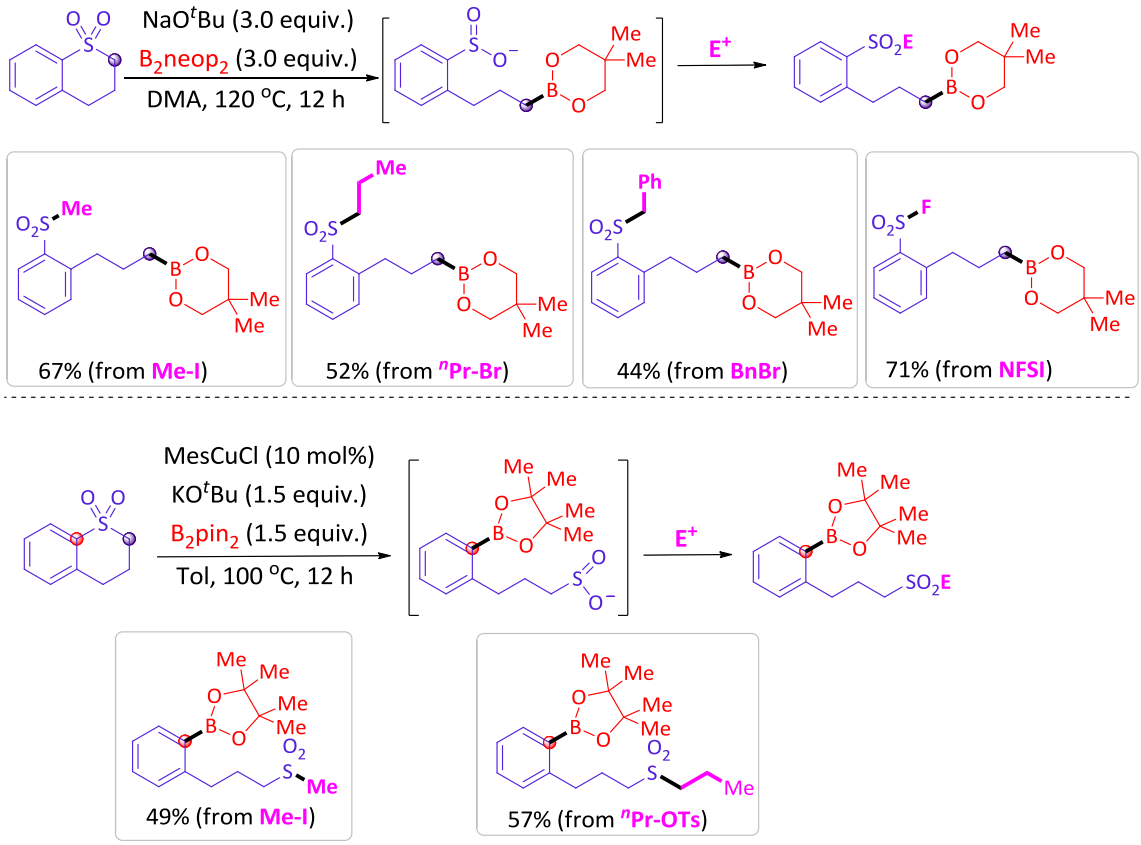
In this chapter, a process of NHC-Cu-catalysed borylation of aryl alkyl sulfones for the the high yield synthesis of versatile arylboronic esters via selective C(sp^2)–SO_2 bond cleavage is presented. This new copper-catalysed strategy showed the opposite selectivity compared with our developed base-mediated transition metal-free radical borylation of unactivated primary and secondary alkyl sulfones of Chapter 3. In general, a variety of aryl sulfones with various functional groups, electronic properties, and alkyl carbon chains are efficiently transformed into aryl boronate esters in good yields (Scheme S-4).



Scheme S-4. Aryl alkyl sulfone substrate scope.

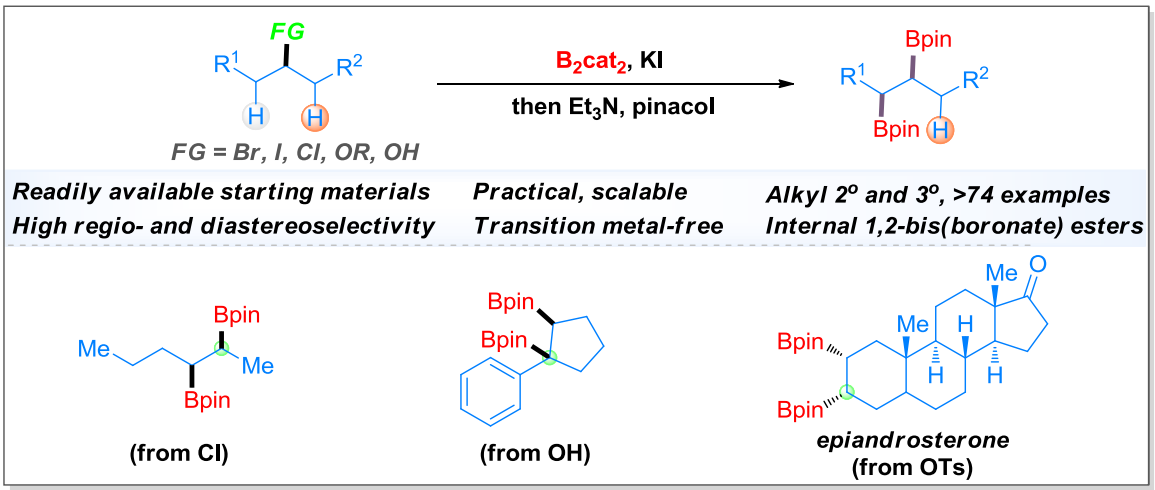
Moreover, diverse products can be obtained by subsequent functionalisation of the sulfinate salt. Cyclic sulfone has both alkyl C(sp^3)–SO_2 and aryl C(sp^2)–SO_2 bonds, which provides the possibility for diversity via selective borylation. Thus, cyclic sulfone was subjected to metal-free borylation conditions of Chapter 3, and the *in situ* formed alkyl borylated sulfinate salt was generated through cleavage of the alkyl C(sp^3)–SO_2 bond followed by subsequent functionalisation in a one-pot, two-step fashion. In contrast, the selective borylation of the aryl C(sp^2)–SO_2 bond of cyclic sulfone using ICyCuCl-catalysed process (Scheme S-5), and the products containing both

alkyl sulfone and aryl boronate groups were generated selectively by treatment with iodomethane or propyl 4-methylbenzene-sulfonate, respectively, after *in situ* formation of the aryl borylated sulfinate salt (Scheme S-5).



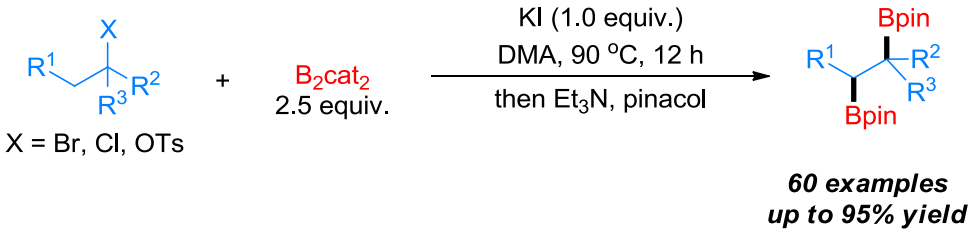
Scheme S-5. Selective (sp^3-C-S (top) and sp^2-C-S (bottom)) ring-opening borylation of a cyclic sulfone and diverse products obtained by subsequent functionalisation of the sulfinate salt.

Chapter 5



In this chapter, a transition metal-free, simple and efficient strategy to access alkyl 1,2-

bis(boronate) esters via regio- and diastereoselective diboration of secondary and tertiary alkyl halides (Br, Cl, I), tosylates, and alcohols is presented. The use of KI and DMA is critical to the methodology, which circumvents the regio- and diastereoselectivity problem. The method showed a broad substrate scope (75 examples) with high yields and selectivities, and practicality for the late-stage modification of natural molecules. This synthetic method offers control of the position of diversification and diastereoselectivity in complex rings scaffolds, which would be especially useful in a lead optimization program (Scheme S-6).



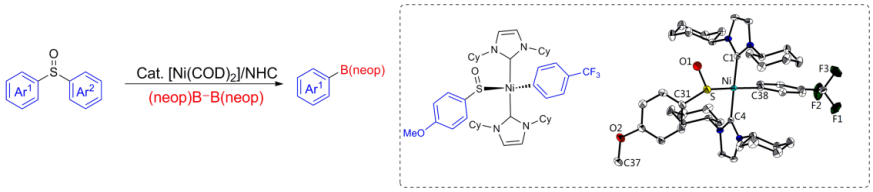
Scheme S-6. Diboration of secondary alkyl halides, tosylates, and alcohols.

As the boryl moieties in different environments in 1,2-diborylalkanes can be differentiated and converted selectively, allowing the synthesis of a wide variety of complex molecules. A series of reactions of the 1,2-diborylalkane products demonstrated the further synthetic value of this strategy. Experimental studies of the reaction mechanism showed alkyl (pseudo)halides are initially dehydrohalogenated to form alkenes with high selectivity using a combination of KI and DMA. Subsequently, the alkenes undergo *syn*-selective diboration with DMA-activated B_2cat_2, providing the target product.

Zusammenfassung

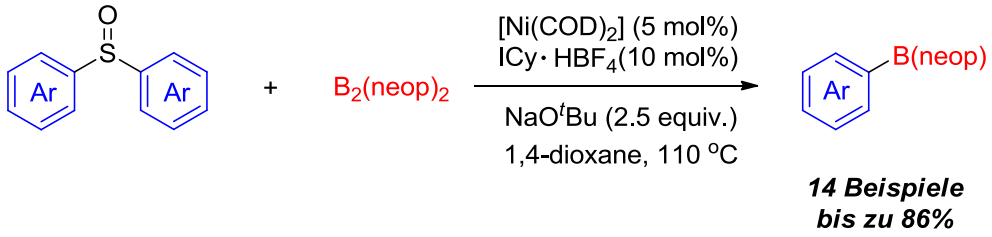
Alkylboronate spielen eine wichtige Rolle in der Synthesechemie, den Materialwissenschaften und der Wirkstoffforschung. Sie sind aufgrund ihrer guten Luft- und Feuchtigkeitsstabilität einfach zu handhaben und können leicht zur Bildung von Kohlenstoff-Kohlenstoff- und Kohlenstoff-Heteroatom-Bindungen verwendet und unter milden Reaktionsbedingungen in verschiedene funktionelle Gruppen umgewandelt werden. Gegenüber herkömmlichen Gruppen wie Aryl(Pseudo)halogeniden oder Alkoholen stellen Organoschwefelverbindungen einen alternativen und komplementären Ersatz bei Kupplungsreaktionen dar. Der Aufbau einer C–B-Bindung aus einer C–SO-Bindung von Arylsulfoxid wird in Kapitel 2 vorgestellt. Die selektive Spaltung von entweder Alkyl(C)-Sulfonyl- oder Aryl(C)-Sulfonyl-Bindungen eines Arylalkylsulfons über Cu-freie oder Cu-vermittelte Prozesse erzeugen die entsprechenden Boronatester und werden in Kapitel 3 und Kapitel 4 vorgestellt. 1,2-Bis(Boronatester) entwickeln sich als wichtige Synthesezwischenprodukte zur Herstellung von 1,2-difunktionellen Verbindungen. Darüber hinaus können die Boryleinheiten in verschiedenen Umgebungen in einem 1,2-Bis(boronatester) differenziert und selektiv umgewandelt werden, was die Synthese einer Vielzahl komplexer Moleküle ermöglicht. Eine direkte und selektive Diborierung von C–X- und C–O-Bindungen zur Herstellung von 1,2-Bis(boronatestern) wird in Kapitel 5 vorgestellt.

Kapitel 2



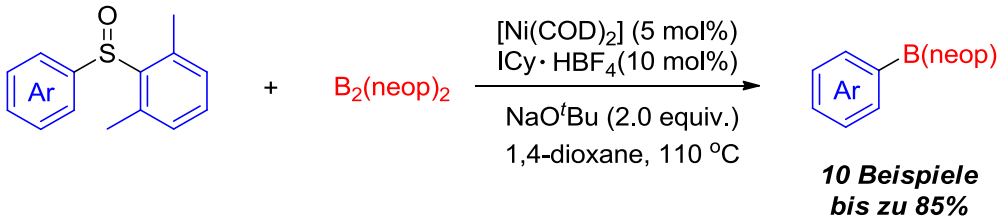
In diesem Kapitel wurde ein Nickel/NHC-Katalysatorsystem für die effiziente Borylierung von Arylsulfoxiden über die C–SO-Bindungsaktivierung mit $B_2(neop)_2$ als Borquelle in Gegenwart von NaO^{t}Bu entwickelt. Eine breite Palette symmetrischer Diarylsulfoxide mit unterschiedlichen elektronischen und sterischen Eigenschaften wurde in guten Ausbeuten in die entsprechenden Arylboronsäureester umgewandelt (Schema S-1). Die versuchte Borylierung von ortho-

Tolylsulfoxid ergab das Produkt in nur 16% GC-Ausbeute, wohingegen Bis(1,3,5-trimethylphenyl)sulfoxid (in beiden ortho-Positionen disubstituiert) nicht das entsprechende Produkt ergab und es wurde nur nicht umgesetztes Ausgangsmaterial durch GC-MS identifiziert.



Schema S-1. Screening von Diarylsulfoxiden für die Ni-katalysierte Borylierungsreaktion.

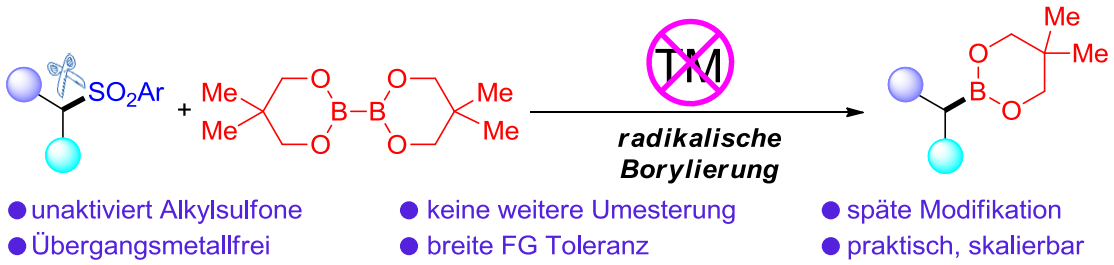
Die regioselektive Borylierung von unsymmetrischen Diarylsulfoxiden war ebenfalls möglich und führte zur Borylierung des sterisch weniger belasteten Arylsubstituenten durch sterische Vorspannung (Schema S-2). Dieses Verfahren war mit verschiedenen wichtigen funktionellen Gruppen kompatibel, wie Fluor-, Methoxy-, Trimethylsilyl-, stickstoff- und sauerstoffhaltigen Heterocyclen.



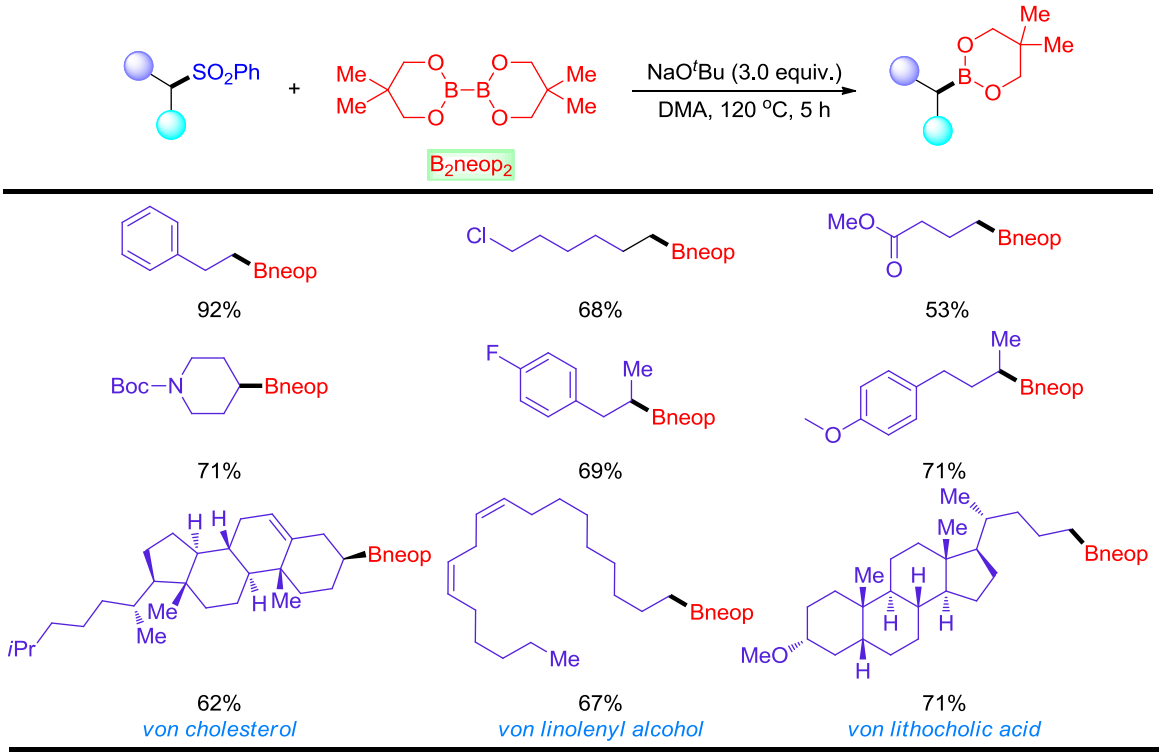
Schema S-2. Regioselektive Borylierung unsymmetrischer Diarylsulfoxide.

Konkurrenzexperimente zeigten, dass eine elektronenarme Aryleinheit bevorzugt reagiert. Der Ursprung der Selektivität bei der Ni-katalysierten Borylierung von elektronisch vorgespanntem unsymmetrischem Diarylsulfoxid liegt im oxidativen Additionsschritt des Katalysezyklus, da die oxidative Addition von Methoxyphenyl-4-(trifluormethyl)phenylsulfoxid an den Ni(0)-Komplex selektiv stattfindet und dann den strukturell charakterisierten Komplex *trans*-[Ni(ICy)$_2$(4-CF$_3$-C$_6$H$_4$){(SO)-4-MeO-C$_6$H$_4$}] ergibt.

Kapitel 3



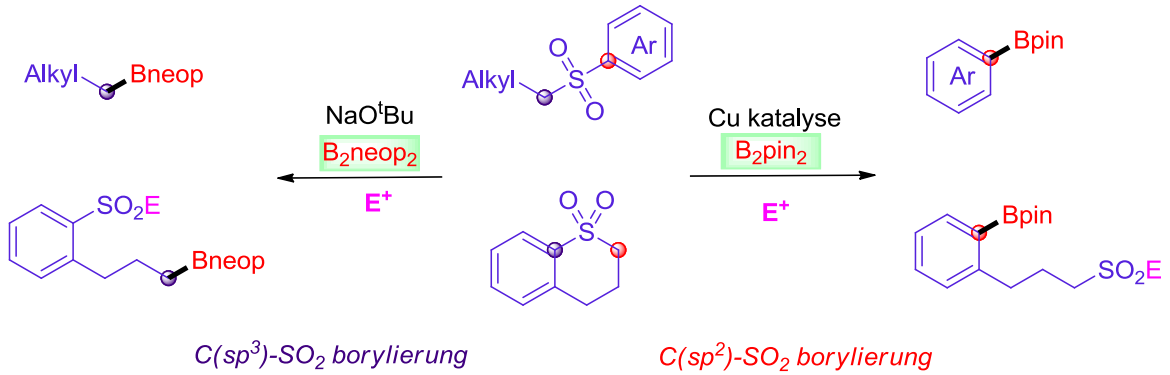
In diesem Kapitel wird eine praktische und direkte Methode zur Herstellung vielseitiger Alkylboronsäureester durch übergangsmetallfreie Borylierung von primären und sekundären Alkylsulfonen vorgestellt. Eine breite Palette von Alkylarylsulfonen wurde in Gegenwart von 3.0 Äquiv. zu entsprechenden Alkylboronsäureestern umgewandelt. von NaO^{t}Bu in DMA bei 120 °C mit $B_2(neop)_2$ als Borquelle (Schema S-3). Die Praktikabilität und das industrielle Potenzial dieses Protokolls werden durch seine breite Toleranz gegenüber funktionellen Gruppen, die späte Modifikation komplexer Verbindungen, keine Notwendigkeit für eine weitere Umesterung und die einfache Bedienung unterstrichen. Dieses Kapitel zeigte 34 Beispiele unter den Reaktionsbedingungen.



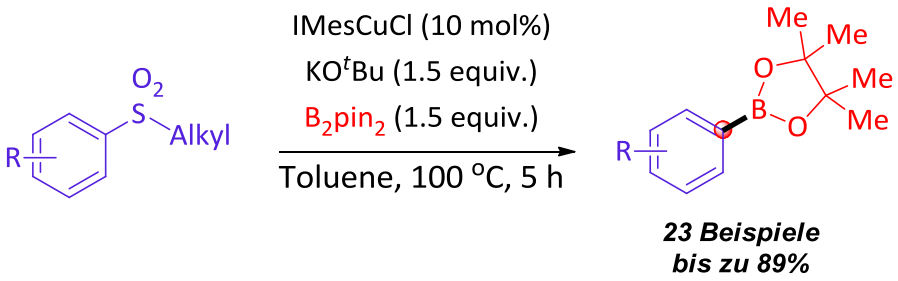
Schema S-3. Substratspektrum von Alkylsulfonen.

Radikalfängerexperimente mit 2,2,6,6-Tetramethyl-1-piperidinyloxyl (TEMPO), 9,10-Dihydroanthracen oder butyliertem Hydroxytoluol (BHT) als Radikalfänger, Radikaluhrexperimente mit Hex-5-en-1-ylsulfonylbenzol als Substrat und EPR-Studien mit 5,5-Dimethyl-1-pyrrolin-N-oxid (DMPO) als Spin-Trap zeigten, dass dieser desulfonierende Borylierungsprozess radikalische Zwischenstufen umfasst. Weitere Studien sind erforderlich, um den detaillierten Mechanismus des Prozesses und den Grund für die optimale Reaktivität von B_2neop_2 unter den untersuchten Dibor(4)-Reagenzien genauer zu verstehen. Wir gehen davon aus, dass diese Ergebnisse die Entwicklung desulfonativer radikalischer Kreuzkupplungen vorantreiben werden.

Kapitel 4

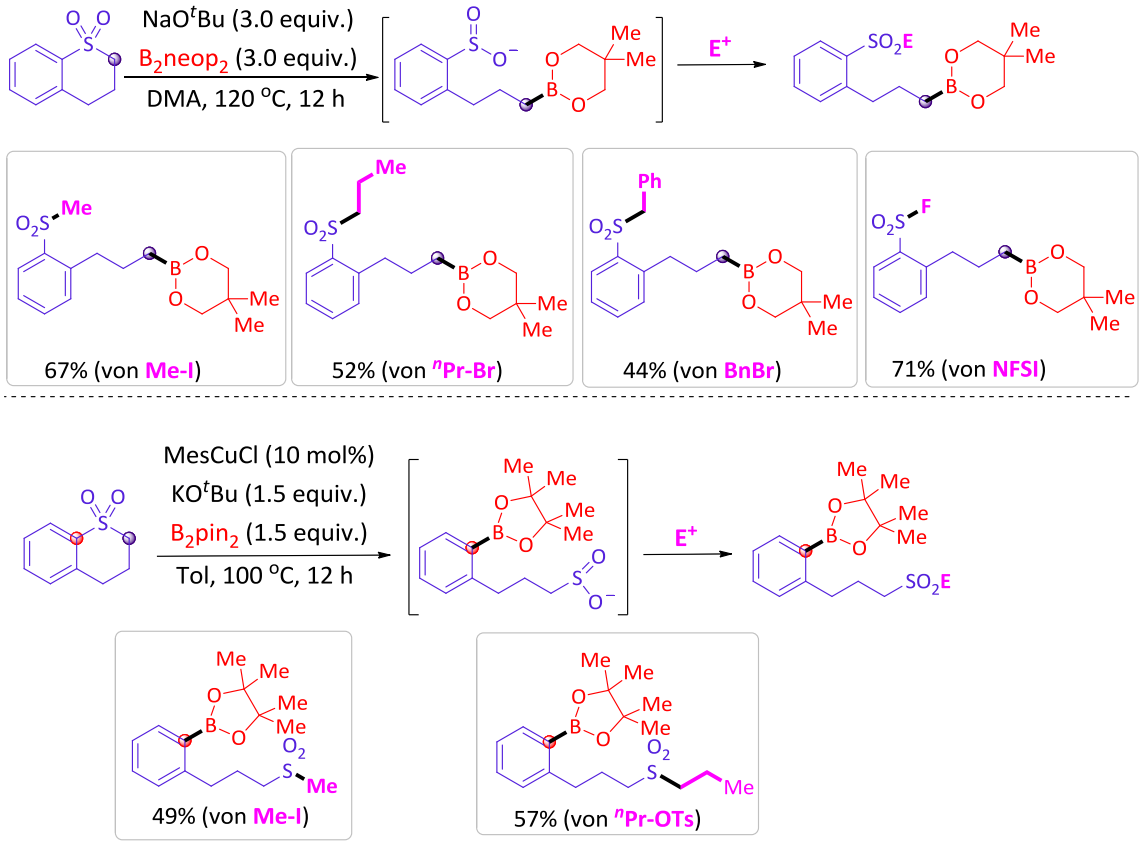


In diesem Kapitel wird ein Verfahren zur NHC-Cu-katalysierten Borylierung von Arylalkylsulfonen für die Synthese vielseitiger Arylboronsäureester in hoher Ausbeute über selektive C(sp^2)-SO_2-Bindungsspaltung vorgestellt. Diese neue kupferkatalysierte Strategie zeigte die entgegengesetzte Selektivität im Vergleich zu unserer entwickelten basenvermittelten Übergangsmetall-Radikalborylierung von nichtaktivierten primären und sekundären Alkylsulfonen aus Kapitel 3. Eine Vielzahl von Arylsulfonen mit verschiedenen funktionellen Gruppen, elektronischen Eigenschaften, und Alkylkohlenstoffketten werden in guten Ausbeuten effizient in Arylboronatester umgewandelt (Schema S-4).



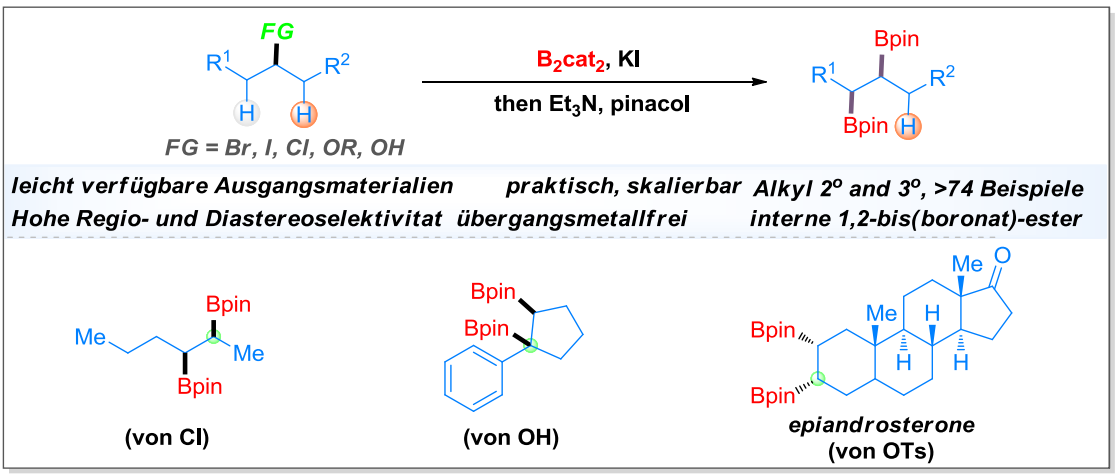
Schema S-4. Substratspektrum von Arylalkylsulfon.

Darüber hinaus können durch nachträgliche Funktionalisierung des Sulfinatsalzes diverse Produkte erhalten werden. Cyclisches Sulfon weist sowohl Alkyl-C(sp^3)-SO_2- als auch Aryl-C(sp^2)-SO_2-Bindungen auf, was die Diversität durch selektive Borylierung ermöglicht. So wurde cyclisches Sulfon den metallfreien Borylierungsbedingungen von Kapitel 3 unterworfen, und das in situ gebildete alkylborylierte Sulfinatsalz wurde durch Spaltung der Alkyl-C(sp^3)-SO_2-Bindung und anschließende Funktionalisierung in einem Eintopf-Zwei-Schritt-Modus erhalten. Im Gegensatz dazu wurde die selektive Borylierung der Aryl-C(sp^2)-SO_2-Bindung eines cyclischen Sulfons mithilfe eines ICyCuCl-katalysierten Prozesses (Schema S-5) durchgeführt. Die Produkte mit sowohl Alkylsulfon- als auch Arylboronatgruppen wurden selektiv durch Behandlung mit Iodmethan oder Propyl-4-methylbenzolsulfonat bzw. nach in situ-Bildung des arylborylierten Sulfinatsalzes (Schema S-5) erhalten.



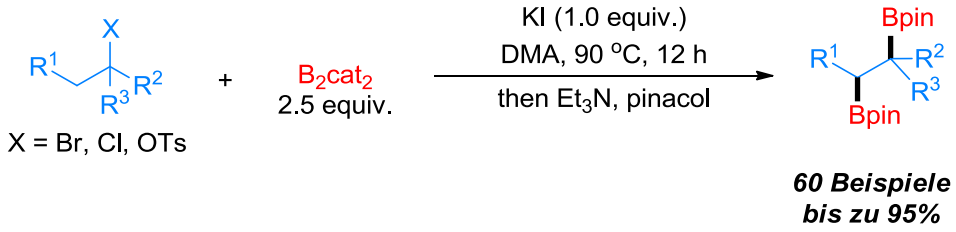
Schema S-5. Selektive (sp^3-C-S (oben) und sp^2-C-S (unten)) Ringöffnungsborylierung eines cyclischen Sulfons und diverser Produkte, die durch anschließende Funktionalisierung des Sulfinatsalzes erhalten werden.

Kapitel 5



In diesem Kapitel wird eine übergangsmetallfreie, einfache und effiziente Strategie zum Zugang zu Alkyl-1,2-bis(boronat)-estern über regio- und diastereoselektive Diborierung von sekundären und tertiären Alkylhalogeniden (Br, Cl, I), Tosylaten und Alkoholen vorgestellt wird vorgestellt. Die

Verwendung von KI und DMA ist entscheidend für die Methodik, die das Regio- und Diastereoselektivitätsproblem umgeht. Die Methode zeigte eine breite Substratbreite (75 Beispiele) mit hohen Ausbeuten und Selektivitäten und war praktisch für die späte Modifikation natürlicher Moleküle. Diese Synthesemethode bietet die Kontrolle über die Position der Diversifikation und Diastereoselektivität in komplexen Ringgerüsten, was besonders in einem Leitstrukturoptimierungsprogramm nützlich wäre (Schema S-6).



Schema S-6. Diborierung sekundärer Alkylhalogenide, Tosylate und Alkohole.

Da die Boryleinheiten in unterschiedlichen Umgebungen in 1,2-Diborylalkanen differenziert und selektiv umgewandelt werden können, ist die Synthese einer Vielzahl komplexer Moleküle möglich. Eine Reihe von Reaktionen der 1,2-Diborylalkan-Produkte demonstrierten den weiteren synthetischen Wert dieser Strategie (12 Anwendungen werden vorgestellt). Experimentelle Studien zum Reaktionsmechanismus zeigten, dass Alkyl(Pseudo)halogenide zunächst mit hoher Selektivität unter Verwendung einer Kombination von KI und DMA zu Alkenen dehydrohalogeniert werden. Anschließend durchlaufen die Alkene eine syn-selektive Diborierung mit DMA-aktiviertem B_2cat_2, was das Zielprodukt liefert.

Appendix

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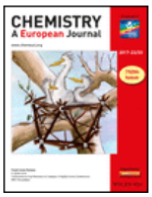

Ni-Catalyzed Borylation of Aryl Sulfoxides

Author: Todd B. Marder, Udo Radius, Stephen A. Westcott, et al

Publication: Chemistry - A European Journal

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Base-Mediated Radical Borylation of Alkyl Sulfones

Author: Mingming Huang, Jiefeng Hu, Ivo Krummenacher, et al

Publication: Chemistry - A European Journal

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