Supporting Information

2,5-bis-Trimethylsilyl substituted Boroles

Tobias Heitkemper, Leonard Naß, Christian P. Sindlinger[a,*]

[a]Institut für Anorganische Chemie, Tammannstr. 4, 37077 Göttingen, Germany

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Experimental Details

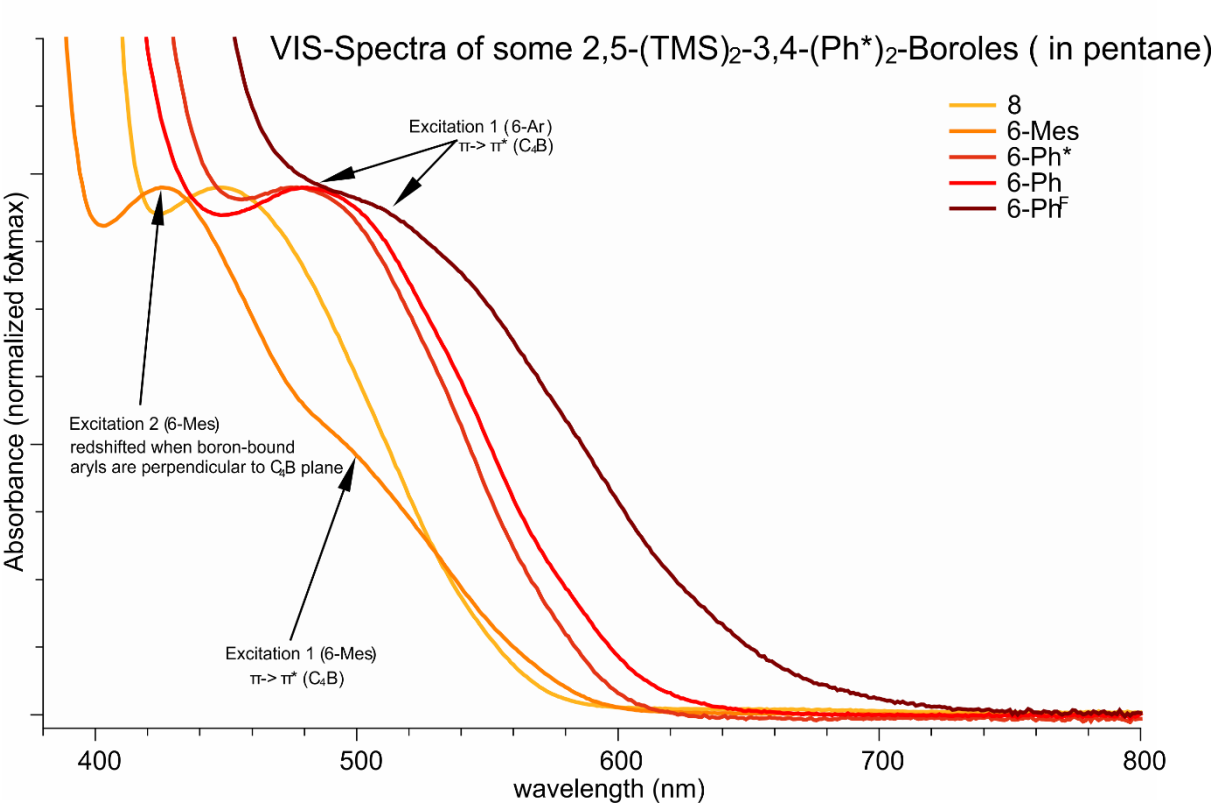
General Information

All manipulations requiring handling under inert conditions were carried out under argon atmosphere using standard Schlenk techniques or an MBraun Glovebox with an Ar atmosphere. Benzene was obtained from an MBraun SPS and stored over molecular sieves, toluene and ether were distilled from sodium. Hexane and pentane were distilled from Na/K alloy. THF was distilled from potassium. NEt_3 was distilled from CaH_2. d_8-THF was distilled from $LiAlD_4$ and stored in a dry box. Benzene-d_6 and toluene-d_8 were distilled from potassium, degassed and stored in a glove box. All solvents were routinely degassed three times using freeze-pump-thaw cycles.

Elemental analysis was performed by the Analytisches Labor, Institut für Anorganische Chemie, Universität Göttingen

UVVis spectroscopy

UV/Vis spectra were recorded on an Agilent Cary 60 or an Agilent Cary 50 spectrometer using quartz cuvettes fitted with Young-type teflon-valves in pentane.



Mass spectrometry

Mass spectra were recorded by the Zentrale Analytik within the Faculty of Chemistry, Göttingen applying a Liquid Injection Field Desorption Ionisation-technique on a JEOL accuTOF instrument with an inert-sample application setup under argon atmosphere. The injection capillary was washed several times with dry, distilled and inertly injected toluene before the samples were injected. Samples usually had a concentration of 1 – 2 mmol/L in toluene and were prepared in a glovebox. HR-ESI spectra were obtained from a BRUKER micrOTOF instrument.

NMR spectroscopy

NMR spectra were recorded with either a Bruker Avance III 400 NMR spectrometer equipped with a 5 mm BBFO ATM probe head and operating at 400.13 (^{1}H), 100.61 (^{13}C), 128.38 (^{11}B) and 376.45 MHz (^{19}F) along with a variable temperature set-up or a Bruker Avance Neo 400 NMR spectrometer with a CryoProbeProdigy BB ATM probe head operating at 400.25 MHz (^{1}H) or a Bruker AVIII HD 500 NMR spectrometer with a CryoProbeProdigy ATM probe head and operating at 500.13 (^{1}H) and 130.35 MHz (^{27}Al). Chemical shifts are reported in δ values in ppm relative to external Me_4Si and, if not otherwise stated, referenced using the chemical shift of the solvent ^{2}H lock resonance frequency and Ξ = 25.145020% for ^{13}C, Ξ = 32.083974% for ^{11}B and Ξ = 94.094011 % for ^{19}F.[1] ^{1}H and ^{13}C spectra have been referenced on specific values for the respective solvent signal. The proton and carbon signals were assigned where possible via a detailed analysis of ^{1}H, ^{13}C, ^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC NMR spectra.

Young-type teflon-valve borosilicate NMR tubes have been used throughout the study.

Gutmann-Beckett Analysis

Assessments of the Lewis-acidity of the presented borole derivatives were studied using the Gutmann-Beckett method, analogously to a previously reported assessment of pentaphenylborole.[2] To samples of the boroles in C_6D_6 was added with an Eppendorf-Pipette an equimolar amount of $Et_3P{=}O$ (stock solution in C_6D_6) and ^{31}P-NMR chemical shifts were determined. The acceptor numbers (AN) were calculated according to $2.21\times(\delta_{measured} - 41)$.[3-5]

In all cases, the intensely red-orange borole solutions immediatedly turned colorless upon addition of 1 equiv. $Et_3P{=}O$. To test the sensitivity of the method regarding the amount of phosphinoxide relative to the borole we added 0.5/1.0/1.5 equiv. of Et_3PO to **6-Ph*** and obtained essentially the same ^{31}P-NMR shift for 0.5 equiv. (δ_{31P} = 73.67 ppm, pale orange solution, broad ^{1}H-NMR spectra) as when 1.5 equiv. of Et_3PO were added (δ_{31P} = 73.64 ppm, colorless solutions, sharp ^{1}H NMR spectra).

In case of **6-Ph**, $Et_3P{=}O$ was added to an orange-red sample solution that still contained 0.65 equiv. of THF and the ^{31}P-NMR spectra were recorded. In order to estimate the impact of the THF contamination on the ^{31}P-shift we then added one further equivalent of THF to the solution which did not affect the ^{31}P-NMR spectrum at all and we therefore consider the THF contamination to be negligible with regards to the Lewis-acidity assessment.

Starting materials and reagents

Cp_2ZrCl_2, $PhBCl_2$ (97%), CuCl, $Zn(C_6F_5)_2$ and BCl_3 (1 M in Hexane) were obtained from Sigma Aldrich, Germany. Et_3PO was obtained from ABCR, Germany. $ZnPh_2$ was obtained from STREM.

1-Bromo-3,5-di-(*t*-butyl)$_2$-benzene was prepared following a known literature procedure.[6, 7]

Rosenthal's reagent was prepared following the literature.[8]

Ph*C_2TMS was prepared as previously described.[9]

MesLi was prepared following a literature procedure.[10]

$MesBCl_2$ was prepared following a literature procedure.[11]

Ph_2Mg was prepared following a literature procedure.[12]

Synthesis of (3,5-di-*t*Bu-phenyl)lithium Ph*Li

In a Schlenk flask, 1-Bromo-3,5-di-*t*Bu-benzene (2.20 g, 8.17 mmol, 1 eq) was dissolved in dry hexane (20 mL). The solution was cooled to 0 °C and *n*-BuLi (3.27 mL, 2.5 M in hexane, 8.17 mmol, 1 eq) was added dropwise with a syringe. Stirring at 0 °C was continued for 60 min and then the solution was allowed to warm to ambient temperature and was stirred for further 2 h. Afterwards the solvent was removed in vacuo to yield an off-white solid. This solid was washed with hexane (3 x 5 mL) and dried in vacuo to give of (3,5-di-*t*Bu-phenyl)lithium Ph*Li (1.15 g, 5.86 mmol, 72 %) as a white solid.

^{1}H (300.13 MHz, 298 K, C_6D_6, C_6D_5H at 7.15 ppm): 7.84 (d, $^4J_{HH}$ = 1.89 Hz, 2H, *o*-H_{ar}), 7.50 (t, $^4J_{HH}$ = 1.89 Hz, 1H, *p*-H_{ar}), 1.28 (s, 18H, C(*Me*)$_3$). Due to poor solubility, no ^{13}C-NMR data was obtained.

^{7}Li{^{1}H} (116.64 MHz, 298 K, C_6D_6): 3.54 (s).

Synthesis of (3',5'-di-*t*Bu-phenyl)trimethylsilane Ph*SiMe$_3$

In a Schlenk flask, a solution of 1-Bromo-3,5-di-*t*Bu-Benzene (9.50 g, 35.29 mmol, 1 eq) in dry THF (100 mL) was prepared and cooled down to –78 °C. At this temperature n-BuLi (15.52 ml, 2.5 M in hexane, 38.81 mmol, 1.1 eq) was slowly added over the course of 45 min to give a deep yellow solution. Stirring at –78 °C was continued for further 4 h. and then a solution of TMSCl (4.22 g, 38.81 mmol, 1.1 eq) in dry THF (5 mL) was added slowly and the solution was allowed to warm to ambient temperature overnight. The light-yellow solution was quenched by addition of a saturated NH_4Cl solution (25 mL), the phases were separated and the organic phase was extracted with Et_2O (3 x 25 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under vacuum to give a yellow oil. After distillation ($5\cdot10^{-3}$ mbar, 108 °C (oil bath)) with a Vigreux column (11 cm) (3,5-di-tert-butylphenyl) trimethylsilane (5.09 g, 19.41 mmol, 55 %) was obtained as a colourless liquid.

^{1}H (300.13 MHz, 300 K, $CDCl_3$, $CHCl_3$ at 7.15 ppm): 7.46 (t, $^4J_{HH}$ = 1.94 Hz, 1H, *p*-H_{ar}), 7.40 (d, $^4J_{HH}$ = 1.94 Hz, 2H, *o*-H_{ar}), 1.36 (s, 18H, C(*Me*)$_3$), 0.29 (s, 9H, Si*Me*$_3$).

Synthesis of (3,5-di-*t*Bu-phenyl)boron dichloride Ph*BCl_2

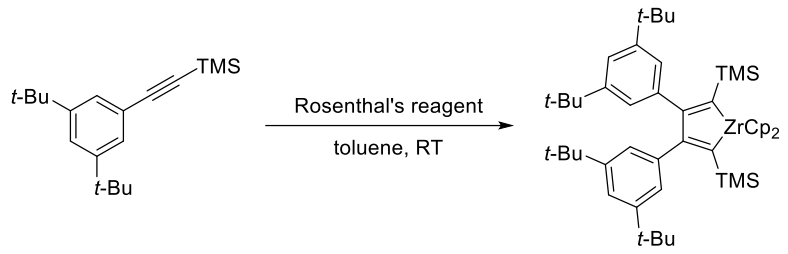
In a Schlenk A solution of BCl_3 in CH_2Cl_2 (15.4 mL, 1 M in CH_2Cl_2, 15.43 mmol, 1.5 eq) was cooled to –78 °C and (3,5-di-tert-butylphenyl)trimethylsilane (2.7 g, 10.29 mmol, 1 eq) was added portion-wise over the course of 30 min. The reaction mixture was allowed to warm to ambient temperature overnight. ^{1}H-NMR analysis of an aliquot of the reaction mixture indicated no full consumption of the starting material even after 12 days. Therefore, additional BCl_3 (7.7 mL, 1 M in CH_2Cl_2, 7.71 mmol, 0.75 eq) was added at ambient temperature. After 4 additional days, ^{1}H-NMR analysis indicated complete consumption of the starting material. All volatiles were removed in vacuo to yield a brown oil, which was purified by distillation ($7\cdot10^{-3}$ mbar, 103 °C (oil bath)) to yield (3,5-di-*t*Bu-phenyl)BCl_2 Ph*BCl_2 (1.34 g, 4.94 mmol, 48 %) as a colourless liquid .

^{1}H (300.13 MHz, 300 K, C_6D_6, C_6D_5H at 7.15 ppm): 8.18 (d, $^4J_{HH}$ = 1.94 Hz, 2H, *o*-H_{ar}), 7.75 (t, $^4J_{HH}$ = 1.94 Hz, 1H, *p*-H_{ar}), 1.23 (s, 18 H, C(*Me*)$_3$)

^{11}B (96.29 MHz, 300 K, C_6D_6): 56.1.

Synthesis and Analytical Data

Compound 1



Molecular Weight: 286,53 Molecular Weight: 573,07

In a glovebox, 3,5-di-*tert*-butylphenyl-trimethylsilyl acetylene **C** (400.0 mg, 1.4 mmol, 1 eq) was dissolved in dry degassed toluene. To this solution was added with a syringe a toluene solution of Rosenthal's reagent (368.1 mg, 0.78 mmol, 0.56 eq). The reaction mixture was stirred for 2.5 h at ambient temperature and subsequently the solvent was removed in vacuo. The residue was redissolved in hexane (2 mL) and then all volatiles were thoroughly removed in vacuo once again to yield an orange-yellow powder (1.08 g, 1.36 mmol, 97%). This powder was pure enough for further reactions as indicated by NMR Spectroscopy and was therefore not further purified.

Crystals of the title compound were grown from a saturated toluene solution by slow evaporation of the solvent at ambient temperature.

Please note: Experimental insight into zirconacyclopentadiene **1** suggests, that the free alkyne can be liberated from the five-membered ring to a certain degree. This is strongly supported by the LIFDI-MS spectra of pure **1** which only reveals a signal for a complex that contains $Cp_2Zr(TMS\text{-}C_2\text{-}Ph^*)$. Also synthetic indications are observed:

a) In one attempt to form the stannole out of **1** by Cu(I) catalyzed Zr/Sn exchange we re-isolated 100% of pure acetylene.
b) NMR samples after a few hours revealed signal sets corresponding to the acetylene.

Analytical Data for Compound 1

NMR:

^{1}H (300.13 MHz, 300 K, C_6D_6, C_6D_5H at 7.15 ppm): 7.09 (t, $^{4}J_{HH}$ = 1.88 Hz, 2H, *p*-H_{ar}), 6.67 (d, $^{4}J_{HH}$ = 1.88 Hz, 4H, *o*-H_{ar}), 6.18 (s, 10H, Cp-*H*), 1.25 (s, 36H, C(*Me*)$_3$), –0.11 (s, 18H, Si(*Me*)$_3$).

^{13}C{^{1}H} (100.65 MHz, 298 K, solvent signal at 128.0 ppm): 203.5 (*C*=C-Zr), 151.3 (*ipso*-C_{ar}), 148.7 (*m*-C_{ar}), 145.3 (C=*C*-Zr), 124.0 (*o*-C_{ar}), 119.1 (*p*-C_{ar}), 111.3 (Cp-*C*), 34.6 (*C*(CH$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 3.1 (Si(*C*H$_3$)$_3$).

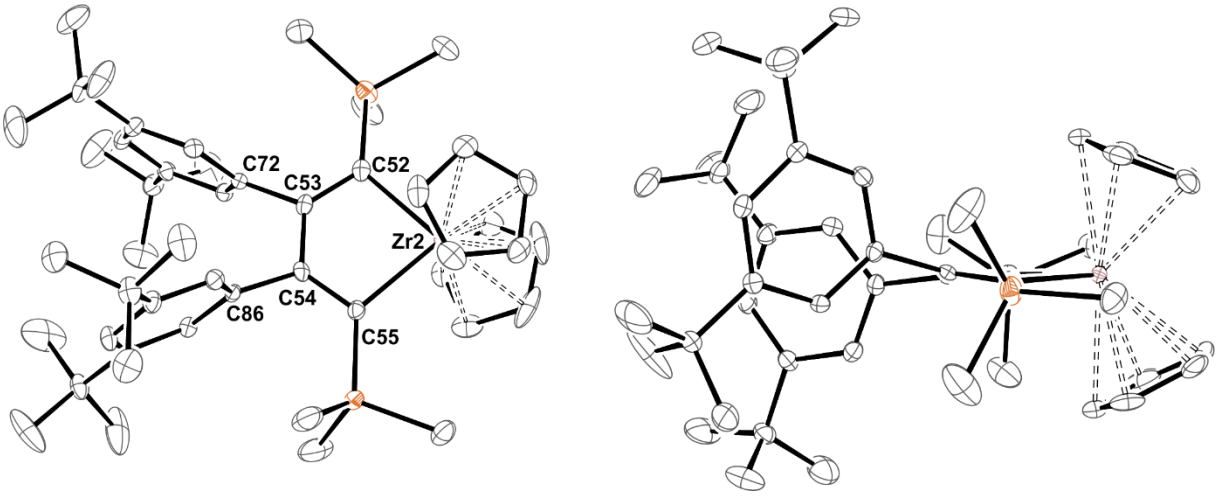
^{29}Si-INEPT (79.49 MHz, 300 K, C_6D_6): –18.4.

Elemental Analysis: $C_{48}H_{70}Si_2Zr$ calcd C 72.57, H 8.88; observed C 73.06, H 9.04.

LIFDI-MS: calcd exact mass: 792.41 m/z; observed m/z: 506.8 $[Cp_2Zr(TMSC_2Ph^*)]^+$.

Crystal structure of Compound 1

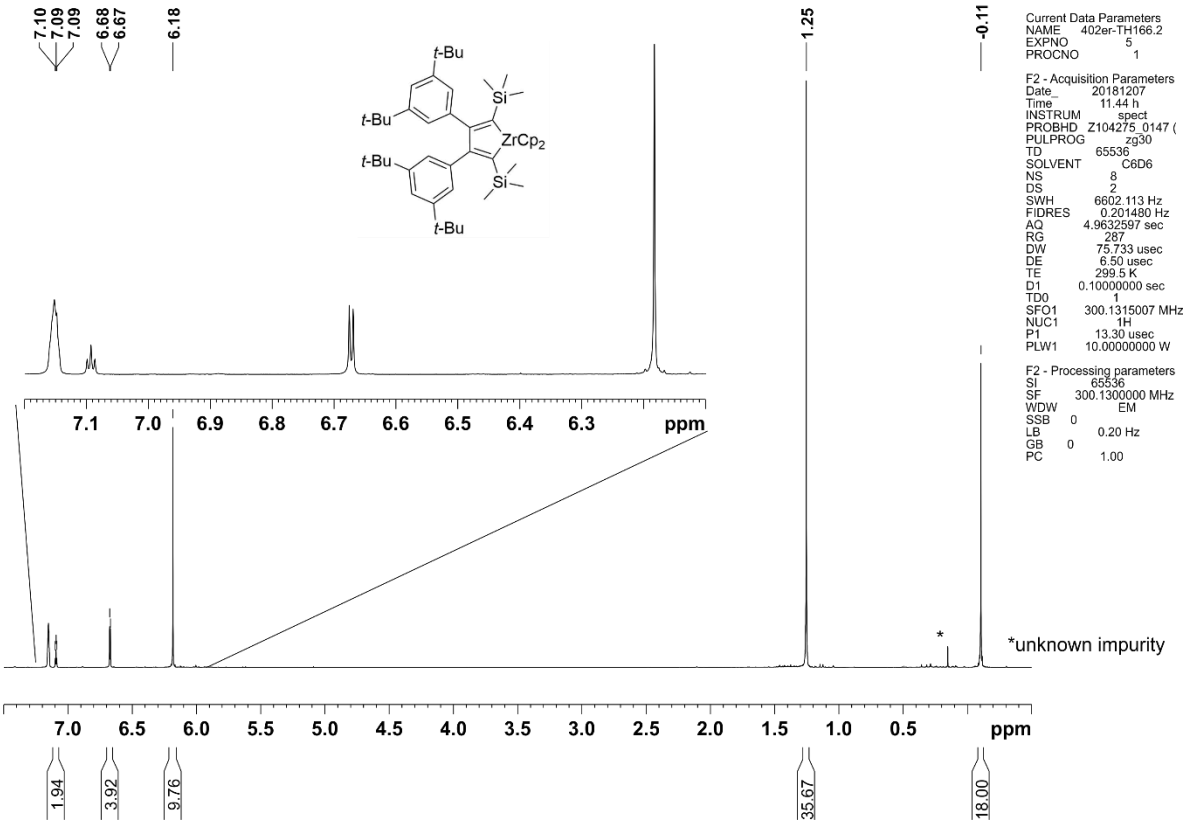
1 crystallised from concentrated pentane solutions in a freezer (-40°C) with two independent molecules in the asymmetric unit. Only one is depicted from two perspectives



ORTEP plot of the molecular structure of **1**. Atomic displacement parameters are drawn at 50% probability level. Only one molecule within the asymmetric unit is depicted. Selected bond length: Zr2—C52 2.248 (2), C52—C53 1.360 (3), C53—C54 1.508 (3), C54—C55 1.363 (3), Zr2—C55 2.238 (2).

Spectra Plots for Compound 1

1H-NMR-spectrum of 1,1-Dicyclopentadienyl-2,5-(SiMe3)-3,4-(3',5'-tBu2(C6H3))-zirconacyclopentadiene in C6D6



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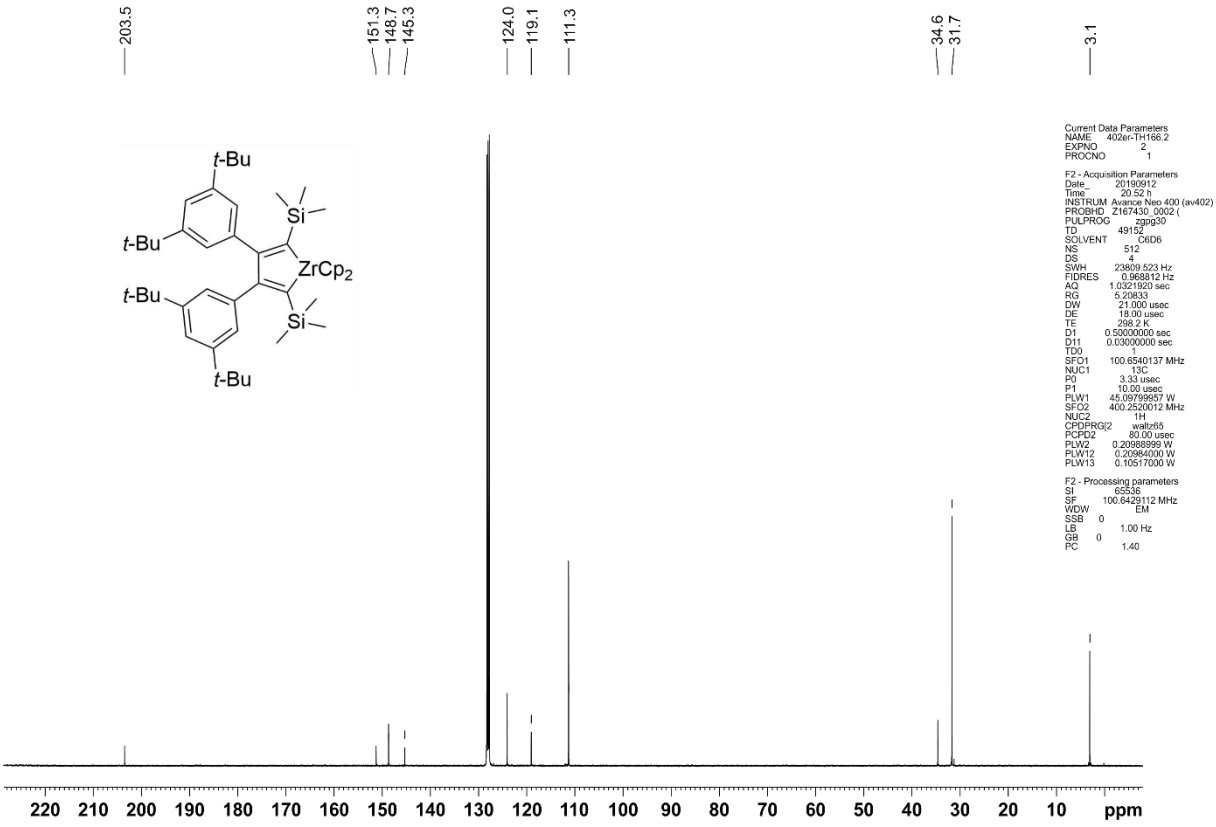
13C{1H}-NMR-spectrum of 1,1-Dicyclopentadienyl-2,5-(SiMe3)-3,4-(3',5'-tBu2(C6H3))-zirconacyclopentadiene in C6D6



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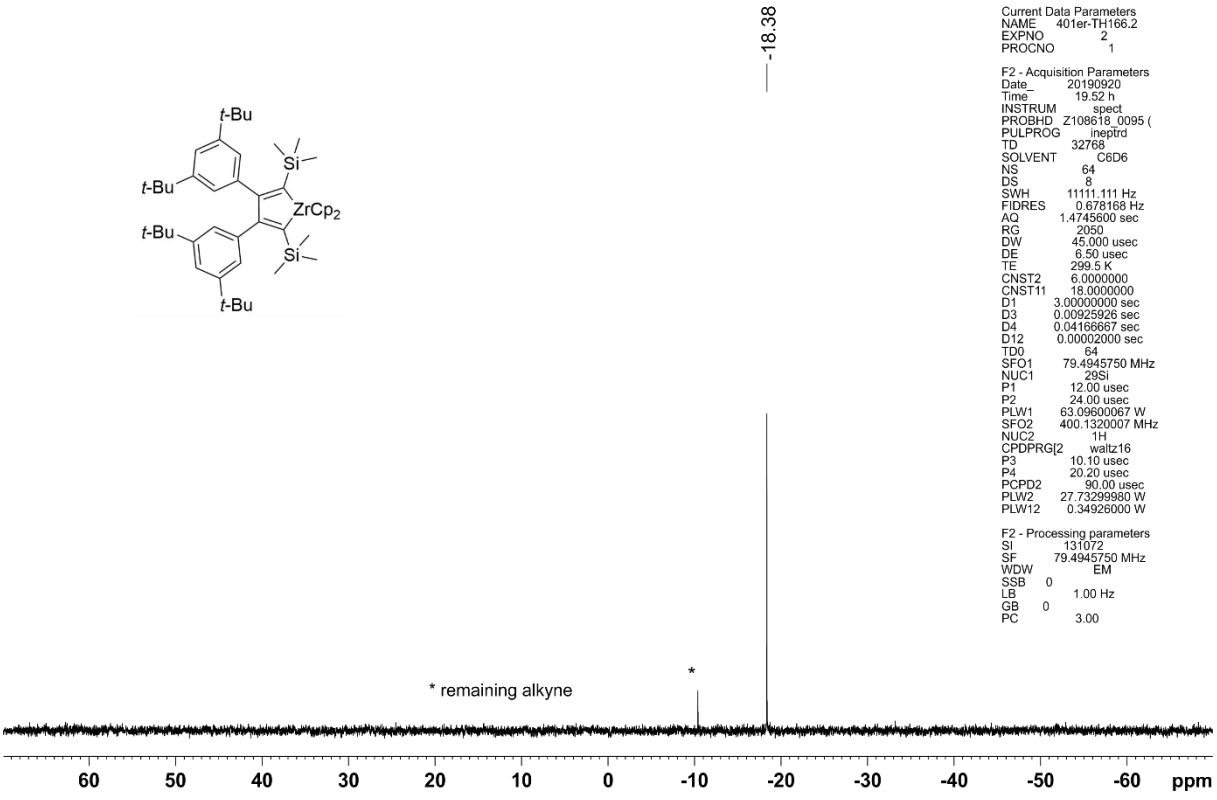
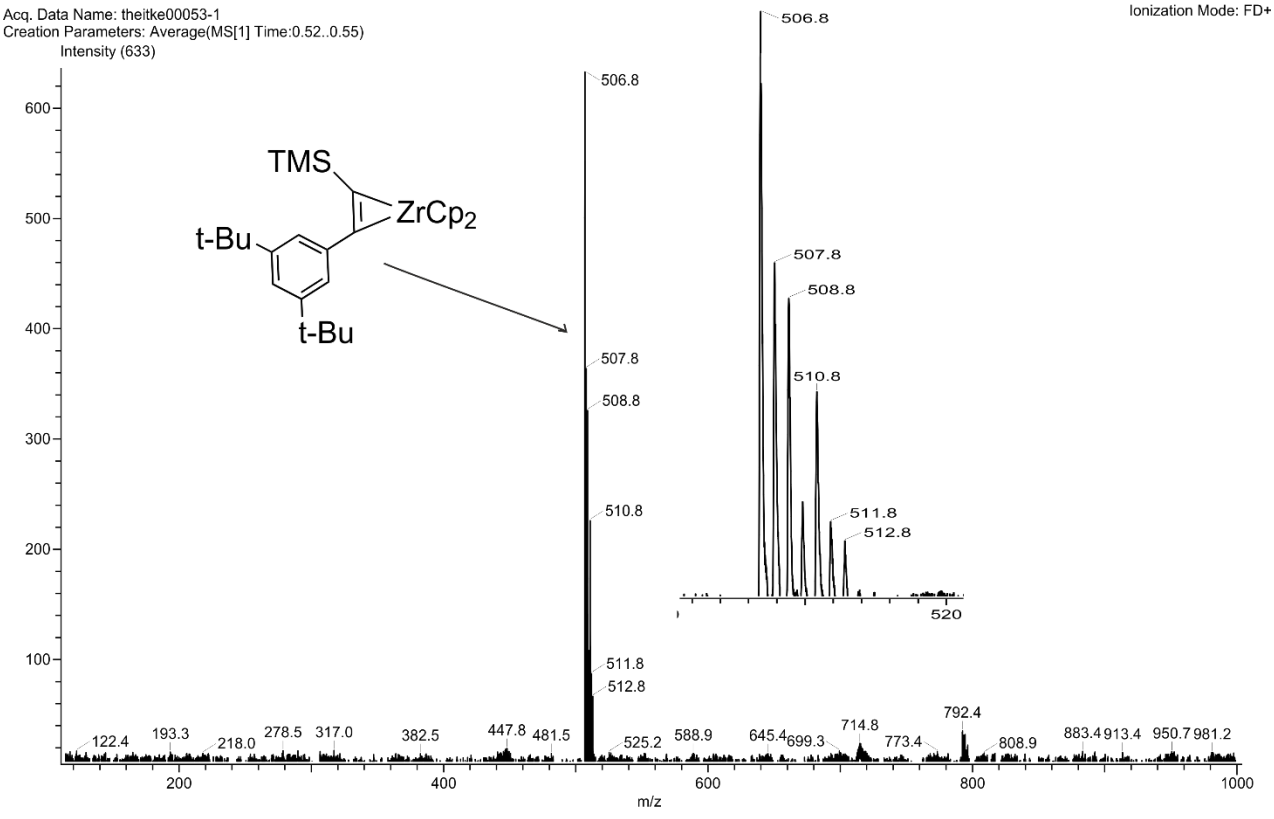
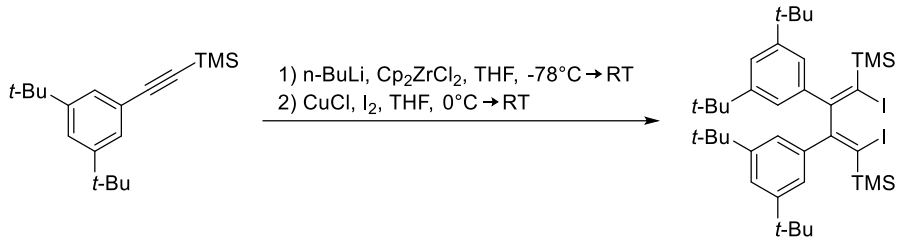
29Si-INEPT-NMR-spectrum of
1,1-Dicyclopentadienyl-2,5-(SiMe3)-3,4-(3',5'-tBu2(C6H3))-zirconacyclopentadiene in C6D6



LIFDI-MS of dilute solutions of zirconacyclopentadiene 1



Compound 2-Z,Z



Molecular Weight: 286,53 Molecular Weight: 826,88

In a Schlenk flask Cp_2ZrCl_2 (3.80 g, 13.02 mmol, 0.56 eq) was dissolved in dry THF (50 mL). The solution was cooled to –78 °C and *n*-BuLi (10.4 mL, 2.5 M in hexane, 26.03 mmol, 1.11 eq) was added with a syringe. The resulting yellow solution was further stirred at –78 °C for 1 h and then acetylene **C** (6.72 g, 23.45 mmol, 1 eq) was added at once. The reaction mixture was allowed to slowly warm to ambient temperature overnight, in which the colour changed to deep red. At 0 °C CuCl (1.22 g, 12.32 mmol, 0.53 eq) was added and afterwards a solution of I_2 (6.25 g, 24.63 mmol, 1.05 eq) in THF (15 mL) was added dropwise over the course of 30 min to yield a dark brown solution. The solution was allowed to warm to ambient temperature and stirred for 3 days. After this time the reaction mixture was quenched with aqueous $Na_2S_2O_4$ (400 mg in 20 mL H_2O) and was afterwards extracted with Et_2O (3 x 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The resulting brown residue was redissolved in hexane (65 mL) and filtered over a short plug of silica gel (Ø 10 cm, length 4 cm, hexane). The solvent was once again removed under reduced pressure and the resulting yellow solid was recrystallized from hot acetone (80 mL) to yield compound **2** (8.20 g, 9.92 mmol, 85 % with respect to the alkyne) as yellow crystals.

Analytical Data for Compound 2-Z,Z

NMR:

^{1}H (300.13 MHz, 298 K, C_6D_6, C_6D_5H at 7.15 ppm): 7.41 (t, $^4J_{HH}$ = 1.82 Hz, 2H, *p*-H_{ar}), 7.37 – 7.19 (br, 4H, *o*-H_{ar}), 1.21 (s, 36H, C(*Me*)$_3$), 0.13 (s, 18H, Si(*Me*)$_3$).

^{13}C{^{1}H} (75.48 MHz, 298 K, solvent signal at 128.0 ppm): 165.2, 150.4 (*m*-C_{ar}), 139.2, 124.4 (*o*-C_{ar}), 122.1 (*p*-C_{ar}), 111.5 (*C*-I), 34.8 (*C*(CH$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 1.1 (Si(*C*H$_3$)$_3$).

^{29}Si-INEPT (79.49 MHz, 301 K, C_6D_6): 2.8.

Elemental Analysis: $C_{38}H_{60}Si_2I_2$ calcd C 55.20, H 7.31; observed C 54.75, H 7.27

HR-ESI-MS (positive mode): *m*/*z* = 827.2399 $[M+H]^+$, 844.2667 $[M+NH_4]^+$, 849.2218 $[M+Na]^+$.

HR-ESI-MS (positive mode): *m*/*z* calcd for $[C_{38}H_{61}Si_2I_2]^+$: 827.2396 $[M+H]^+$; found: 827.2399.

Note: We observed the above described route *via in situ* generated zirconacyclopentadiene **1** to be the most reliable route to the Z,Z-1,4-diiodobutadiene **2**. When the iodination was conducted under otherwise identical (Cu-facilitated) conditions on zirconacyclopentadiene that had been isolated and purified by crystallisation prior to its derivatisation, significant amounts of the **2-E,Z**-isomer form. **2-E,Z** and **2-Z,Z** can be separated by column chromatography (silica gel, hexane R_f(Z,Z) = 0.52 ; R_f(E,Z) = 0.38), however this is a very inefficient route. In case of one-pot iodination the **2-E,Z** isomer was not observed.

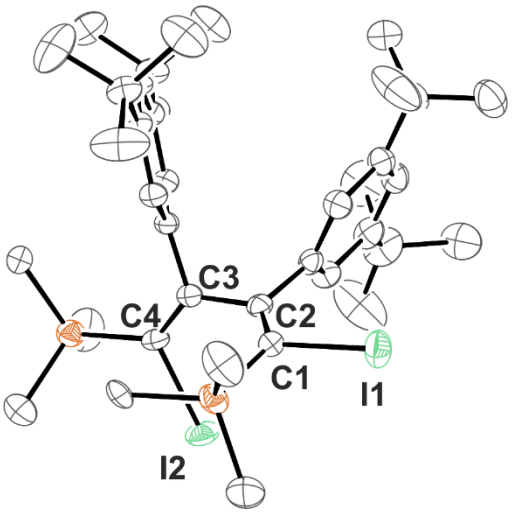
NMR-spectroscopic data of **2-E,Z**: **^{1}H** (400.25 MHz, 298 K, $CDCl_3$, $CHCl_3$ at 7.26 ppm): 7.22(t, $^4J_{HH}$ = 1.75 Hz, 1H, *p*-H_{ar}), 7.14(t, $^4J_{HH}$ = 1.75 Hz, 1H, *p*-H_{ar}), 6.84 (br, 2H, *o*-H_{ar}), 6.73 (br, 2H, *o*-H_{ar}), 1.19 (s, 18H, C(*Me*)$_3$), 1.17 (s, 18H, C(*Me*)$_3$), 0.50 (s, 9H, Si(*Me*)$_3$), -0.05 (s, 9H, Si(*Me*)$_3$). **^{13}C** (100.64 MHz, 298 K, $CDCl_3$, *C*DCl_3 at 77.0 ppm):164.6, 161.5, 150.0, 149.4, 144.6, 138.9, 123.6, 122.6, 121.6, 120.3, 113.8, 110.8, 34.69, 34.68, 31.38, 31.35, 1.5, 0.77.

Note: Formation of the mono-iodo-butadiene as a sideproduct was observed when the iodination was worked up too early. It is beneficial to allow the reaction to stir over a weekend.

Note: Care must be taken upon reductive work-up of the iodination mixture. If excessive amounts of reducing agents such as $(Na_2S_2O_3)_{aq}$ are applied, the organic products (even after column chromatography or recrystallisation) contain a source of sulfur. Subsequent attempts to lithiate these batches of **2-Z,Z** lead to the formation of the respective thiophene in considerable amounts (10-15%).

Crystal structure of Compound 2-E,Z

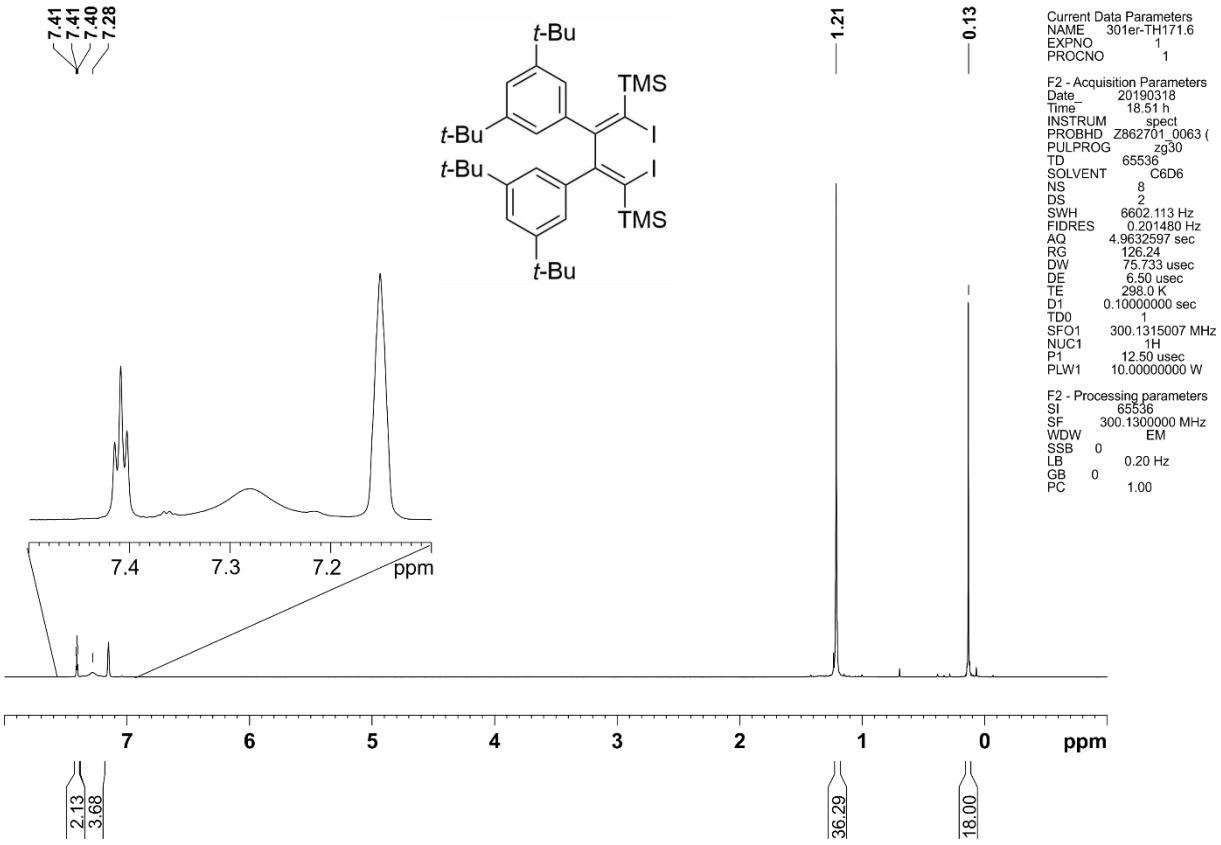
Crystals of the E,Z-stereoisomer of **2-E,Z** crystallised from acetone at room temperature. The E,Z-Isomer was obtained as a side-product of the synthesis of **2-Z,Z.** X-Ray data was collected to confirm the identity of the asymmetric side product. The structure is reported only for completeness.



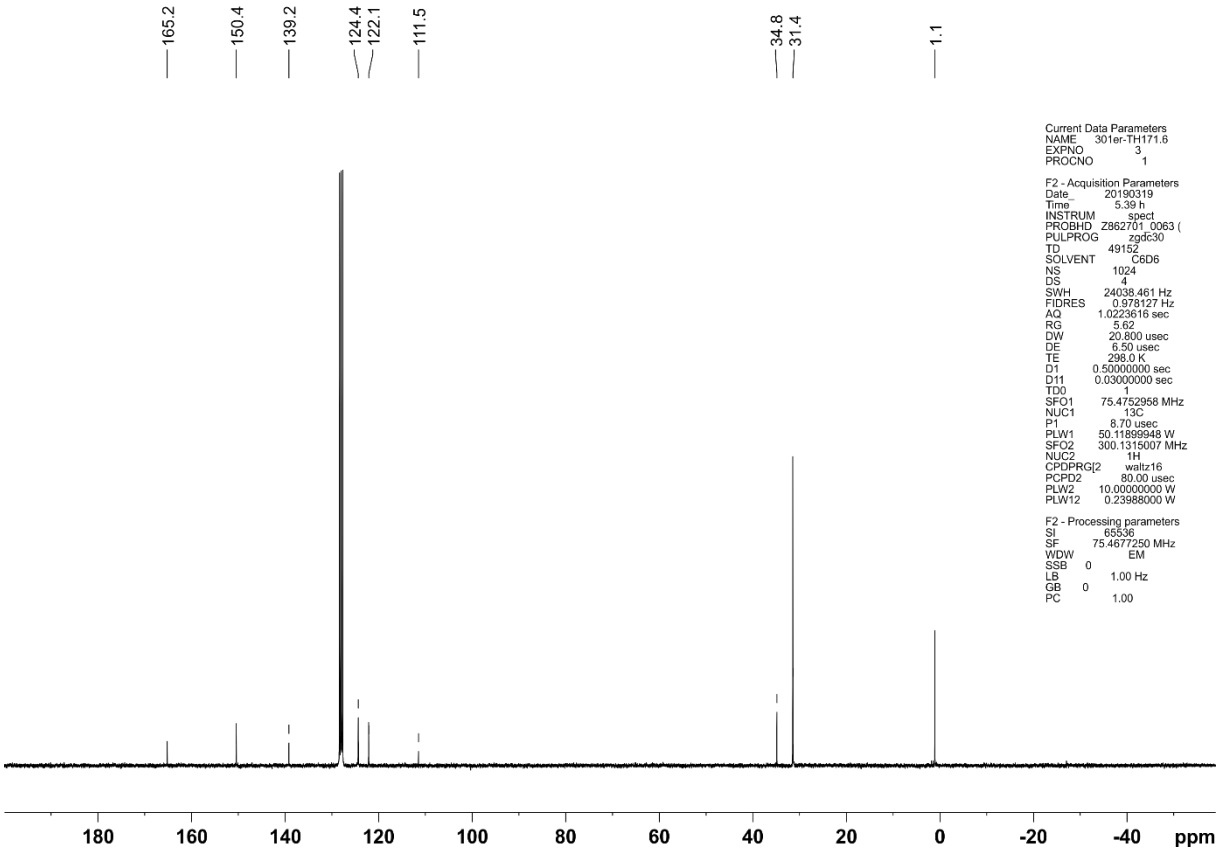
ORTEP plot of the molecular structure of **2-E,Z**. Atomic displacement parameters are drawn at 50% probability level. Disorder in *t*-Bu groups is not shown. Selected bond length: I1-C1 2.145(3), C1-C2 1.335(4), C2-C3 1.505(4), C3-C4 1.337(6), C4-I2 2.1373(3).

Spectra Plots for Compound 2

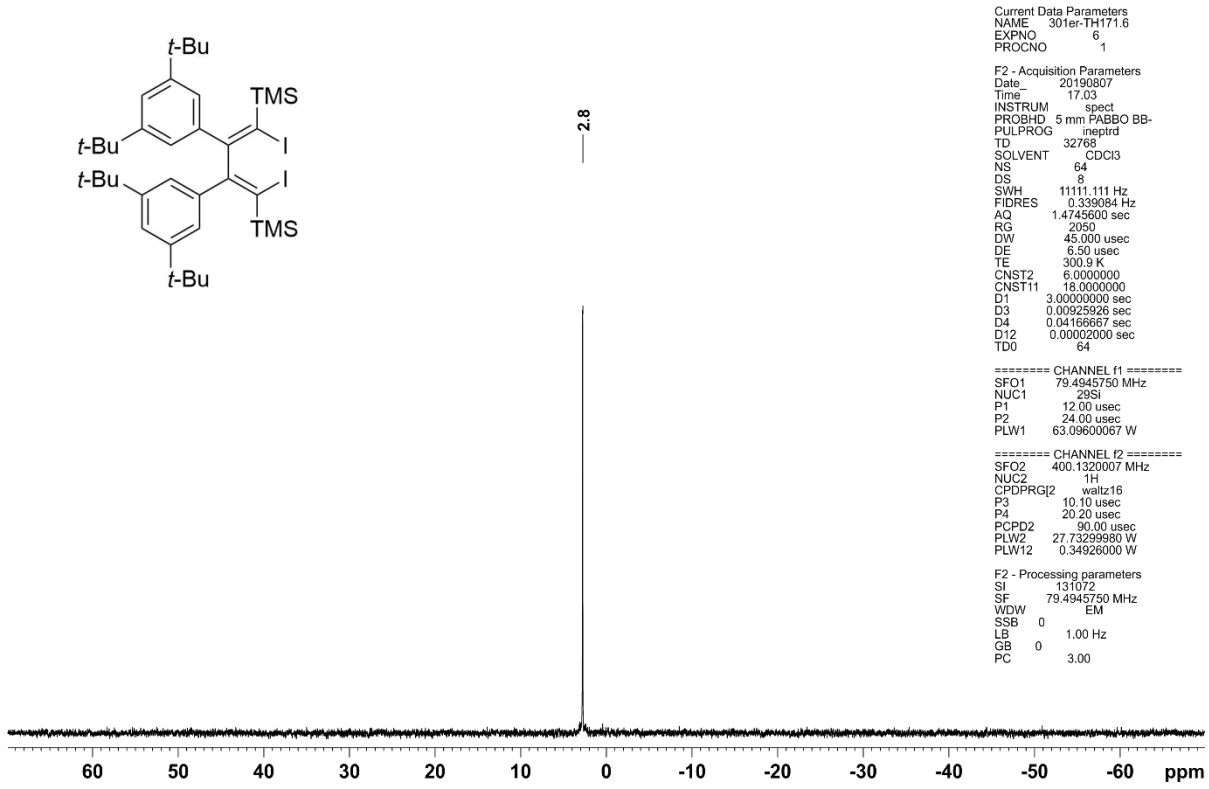
1H-NMR-spectrum of 1,4-(SiMe3)2-2,3-(3',5'-tBu2Ph)-1,4-diiodobutadiene in C6D6



13C{1H}-NMR-spectrum of 1,4-(SiMe3)2-2,3-(3',5'-tBu2C6H3)-1,4-diiodobutadiene in C6D6



29Si-INEPT-NMR-spectrum of 1,4-(SiMe3)2-2,3-(3',5'-tBu2Ph)-1,4-diiodobutadiene in C6D6



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P2 24.00 usec
PLW1 63.09600067 W

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NUC2 1H
CPDPRG[2 waltz16
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PCPD2 90.00 usec
PLW2 27.73299980 W
PLW12 0.34926000 W

F2 - Processing parameters
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WDW EM
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LB 1.00 Hz
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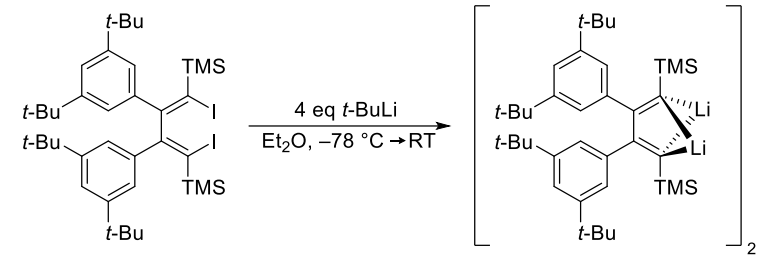
Compound 3



Molecular Weight: 826,88 Molecular Weight: 1173,90

In a Schlenk flask a solution of compound **2** (3.01 g, 3.64 mmol, 1 eq) in dry Et_2O (40 mL) was prepared and cooled to –78 °C. At this temperature *t*-BuLi (7.66 mL, 1.9 M in pentane, 14.56 mmol, 4 eq) was added with a syringe. The resulting deep red solution was kept at –78 °C for 1 h and was then allowed to warm to ambient temperature over the course of 1 h. The solvents were removed in vacuo and the Schlenk flask was transferred into a glovebox. The orange residue was suspended in hexane (15 mL) and filtered through a syringe filter equipped with a thin plug of glass fibre. The filter was washed with hexane (3 x 5 mL) until the remaining solid was colourless. Removal of all volatiles in vacuo yielded compound **3** (2.1 g, 3.58 mmol, 98 %) as an orange solid material, which was pure enough for further reactions according to NMR and elemental analysis.

Crystals suitable for X-ray analysis were grown from a saturated hexane solution at –40 °C.

N. B. In some cases, after filtration of LiI and removal of all volatiles, the resulting solid could not be completely redissolved in hexane. In this case, the filtration was repeated.

Analytical Data for Compound 3

NMR:

^{1}H (400.25 MHz, 298 K, C_6D_6, C_6D_5H at 7.15 ppm): 7.16 (t, $^{4}J_{HH}$ = 1.88 Hz, 2H, *p*-H_{ar}), 6.83 (d, $^{4}J_{HH}$ = 1.88 Hz, 4H, *o*-H_{ar}), 1.30 (s, 36H, C(*Me*)$_3$), 0.03 (s, 18H, Si(*Me*)$_3$).

^{13}C{^{1}H} (100.65 MHz, 300 K, solvent signal at 128.0 ppm): 194.9 (br, *C*-Li), 172.0 (*C*=C-Li), 149.2 (*m*-C_{ar}), 149.0 (*ipso*-C_{Ar}), 122.6 (*o*-C_{ar}), 118.5 (*p*-C_{ar}), 34.7 (*C*(CH$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 0.8 (Si(*C*H$_3$)$_3$).

^{7}Li{^{1}H} (155.51 MHz, 299 K, C_6D_6): 2.26.

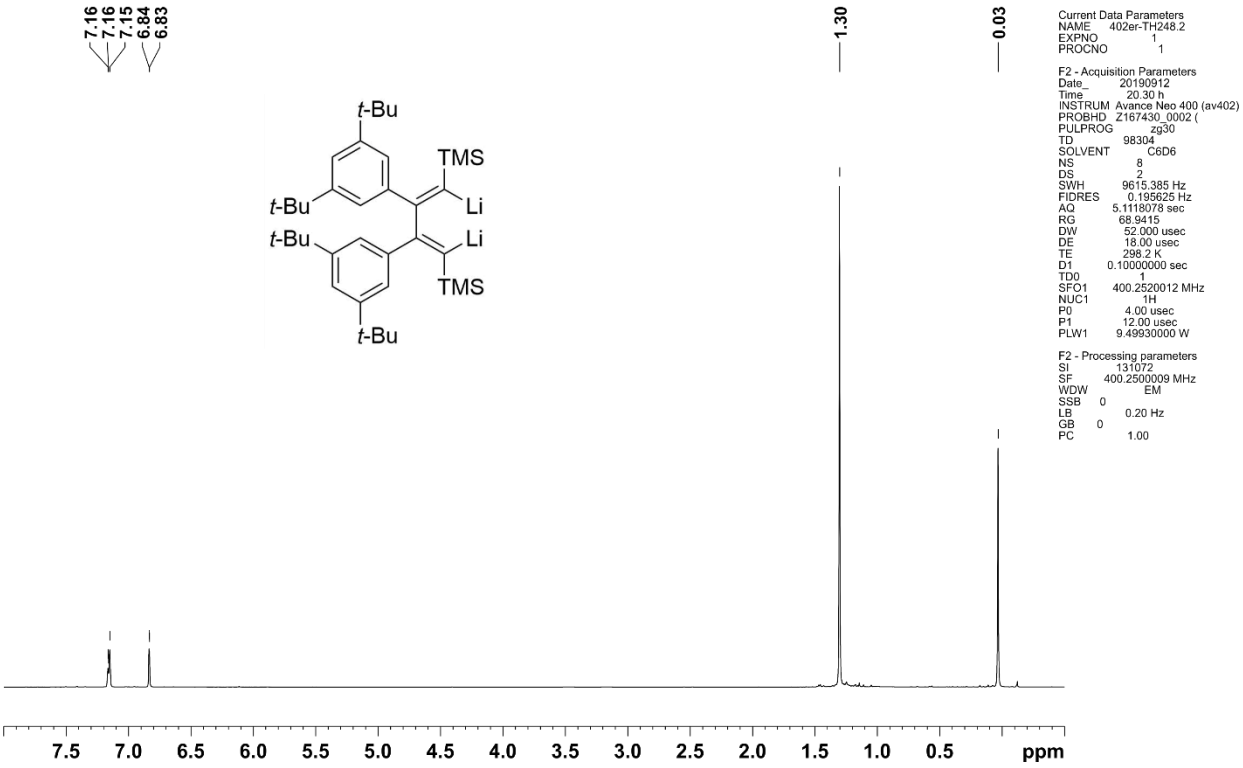
^{29}Si-INEPT (79.49 MHz, 298 K, C_6D_6): –16.0.

Elemental Analysis: $C_{38}H_{60}Li_2Si_2$ calcd C 77.76; H 10.30; observed C 77.85, H 10.31.

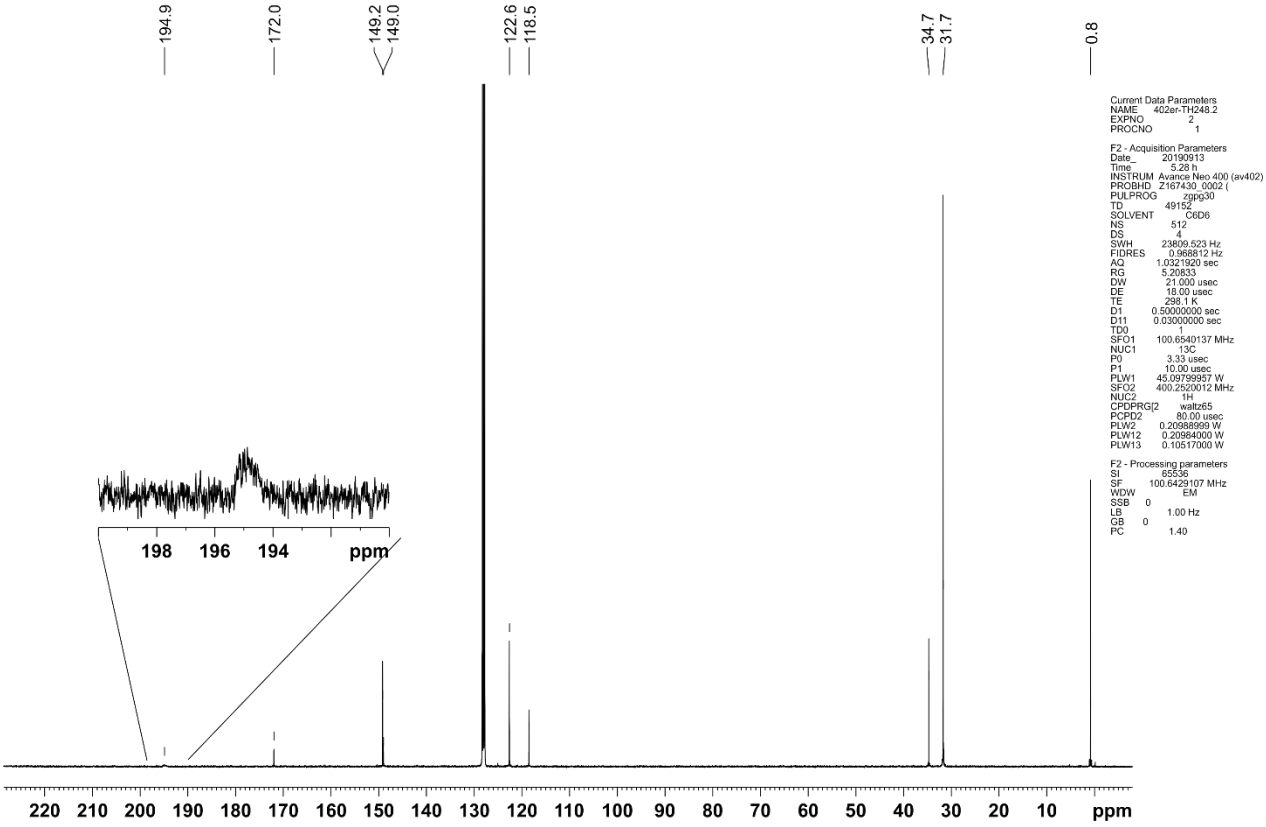
LIFDI-MS: Attempts to obtain mass spectrometric data from an inert sample application set-up for liquid injection FD-mass spectrometry only gave signals for the doubly protonated butadiene (m/z (100%) 574.7)

Spectra Plots for Compound 3

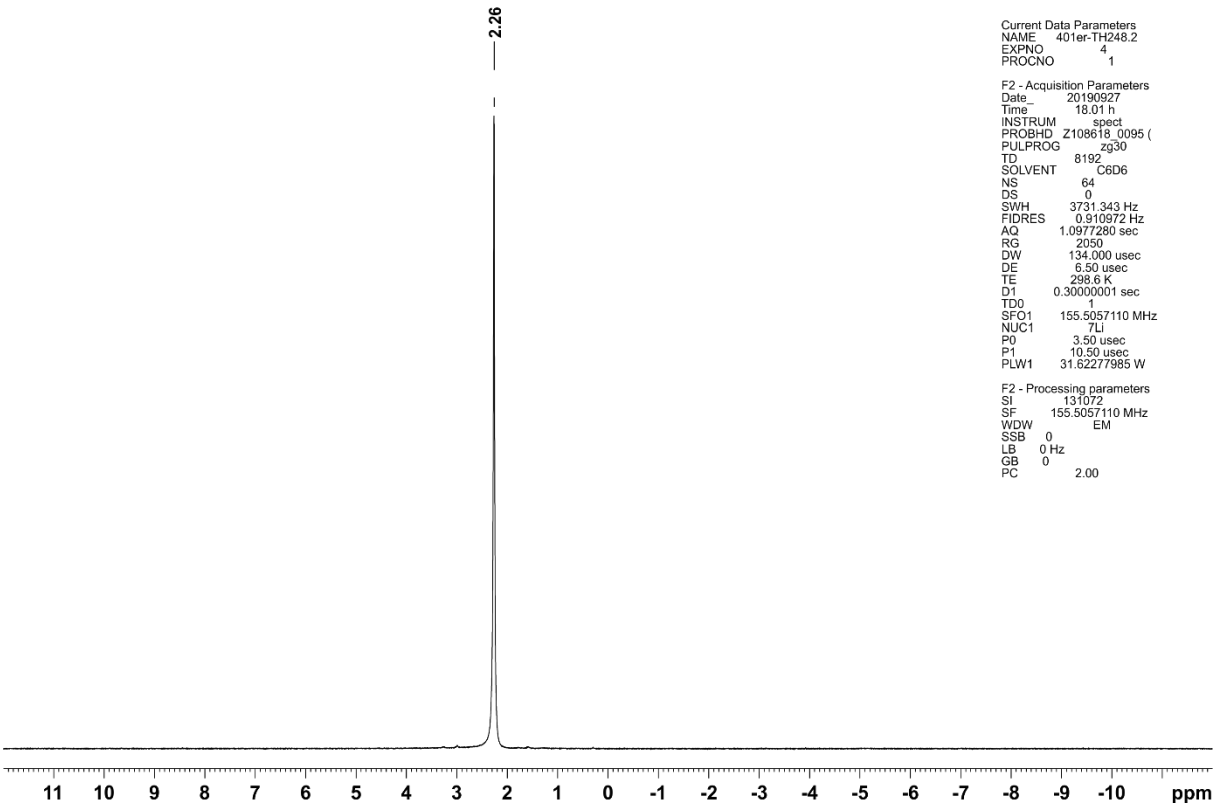
1H-NMR-spectrum of 2,5-(SiMe3)-3,4-(3',5'-tBu2C6H3)-1,4-dilithio-1,3-butadiene in C6D6



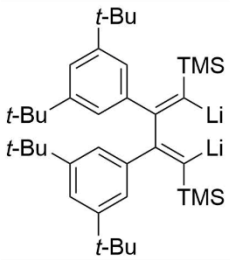
13C{1H}-NMR-spectrum of 2,5-(SiMe3)-3,4-(3',5'-tBu2C6H3)-1,4-dilithio-1,3-butadiene in C6D6



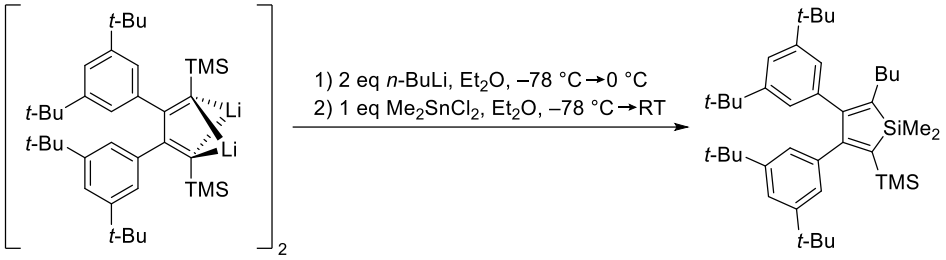
7Li{1H}-NMR-spectrum of 2,5-(SiMe3)-3,4-(3',5'-tBu2C6H3)-1,4-dilithio-1,3-butadiene in C6D6



29Si-INEPT-NMR-spectrum of 2,5-(SiMe3)-3,4-(3',5'-tBu2C6H3)-1,4-dilithio-1,3-butadiene in C6D6



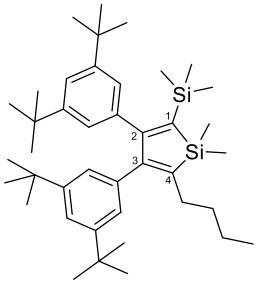
Compound 4



Molecular Weight: 1173,90 Molecular Weight: 615,15

A solution of **Diiodobutadien** (453 mg, 0.55 mmol, 1 eq) in Et_2O (10 mL) was prepared in a Schlenk flask. The mixture was cooled to –78 °C and n-BuLi (0.44 mL, 2.5 M in hexane, 1.1 mmol, 2 eq) was added dropwise with a syringe. After stirring for 1 h at –78 °C, the solution was warmed to 0 °C and stirred at this temperature for 30 min. Afterwards the solution was once again cooled to –78 °C and Me_2SnCl_2 (120 mg, 0.55 mmol, 1 eq) was added and the reaction was allowed to warm to ambient temperature overnight. The reaction mixture was then quenched with water (10 mL), the layers were separated, and the aqueous layer extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure to yield a yellow Oil. Recrystallization from hot acetone (1 mL) afforded compound **4** (102 mg, 0.17 mmol, 30 %) as colourless crystals.

Analytical Data for Compound 4



^{1}H (400.25 MHz, 298 K, $CDCl_3$, $CHCl_3$ at 7.26 ppm): 7.04 (t, $^4J_{HH}$ = 1.76 Hz, 2H, *p*-$H_{ar,3}$), 7.02 (t, $^4J_{HH}$ = 1.77 Hz, 2H, *p*-$H_{ar,4}$), 6.62 (d, $^4J_{HH}$ = 1.76 Hz, 4H, *o*-$H_{ar,3}$), 6.56 (d, $^4J_{HH}$ = 1.77 Hz, 4H, *o*-$H_{ar,4}$), 2.28 – 2.24 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.53 – 1.42 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.31 – 1.19 (m, partially superimposed, 2H, $CH_2CH_2CH_2CH_3$), 1.12 (s, 18H, C(Me)$_3$), 1.12 (s, 18H, C(Me)$_3$), 0.82 (t, $^3J_{HH}$ = 7.32 Hz, 3H, $CH_2CH_2CH_2CH_3$), 0.4 (s, 6H, SiMe_2), –0.14 (s, 9H, Si(Me)$_3$).

^{13}C{^{1}H} (100.65 MHz, 298 K, solvent signal at 77.16 ppm): 170.3 (silole-C_3), 156.0 (silole-C_4), 149.1 (*m*-$C_{ar,3}$), 149.0 (*m*-$C_{ar,2}$), 146.4 (silole-C_5), 142.5 (ipso-C_{ar}), 138.2 (ipso-C_{ar}), 135.7 (silole-C_2), 124.0 (*o*-$C_{ar,4}$), 123.1 (*o*-$C_{ar,3}$), 119.8 (*p*-$C_{ar,3}$), 119.2 (*p*-$C_{ar,4}$), 34.7 (C(CH$_3$)$_3$), 34.6 (C(CH$_3$)$_3$), 33.0 ($CH_2CH_2CH_2CH_3$), 31.62 (C(CH$_3$)$_3$), 31.58 (C(CH$_3$)$_3$), 30.8 ($CH_2CH_2CH_2CH_3$), 23.2 ($CH_2CH_2CH_2CH_3$), 14.1 ($CH_2CH_2CH_2CH_3$), 1.2 (Si(CH$_3$)$_3$), –2.7 (Si(CH$_3$)$_2$,).

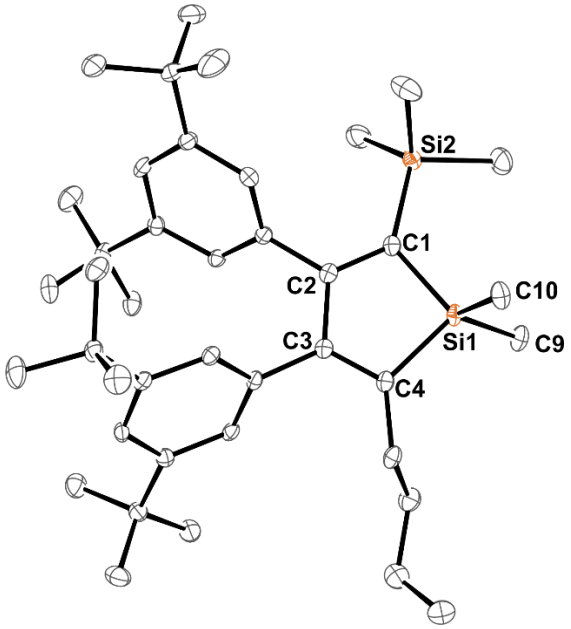
^{29}Si-INEPT (79.49 MHz, 300 K, C6D6): 12.1 (s, *Si*Me$_2$), –10.3 (s, *Si*Me$_3$)

Elemental Analysis: $C_{41}H_{66}Si_2$ calcd C 80.05, H 10.81; observed C 79.60, H 10.84.

HR-ESI-MS (positive mode): *m/z* = 615.4777 $[M+H]^+$, 637.4595 $[M+Na]^+$.

Crystal structure of Compound 4

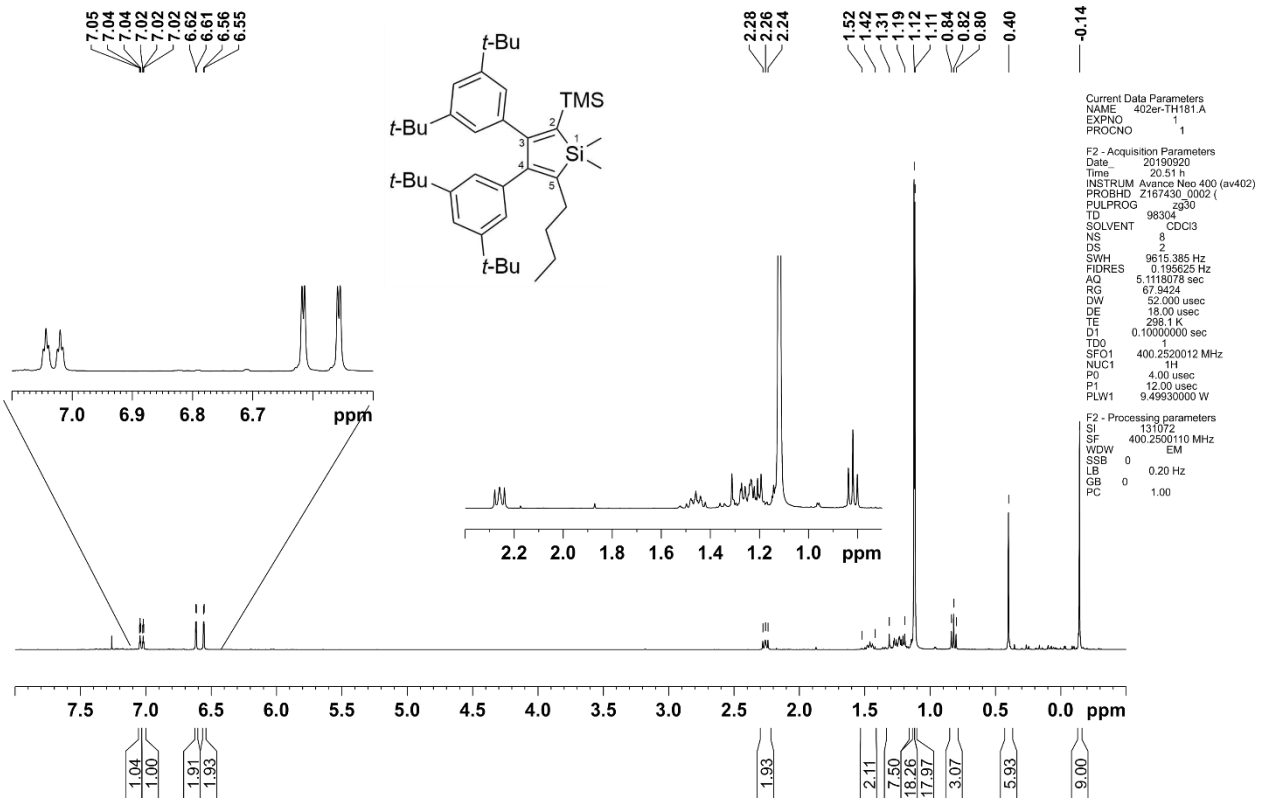
Crystals of **4** were obtained from recrystallisation in hot acetone.



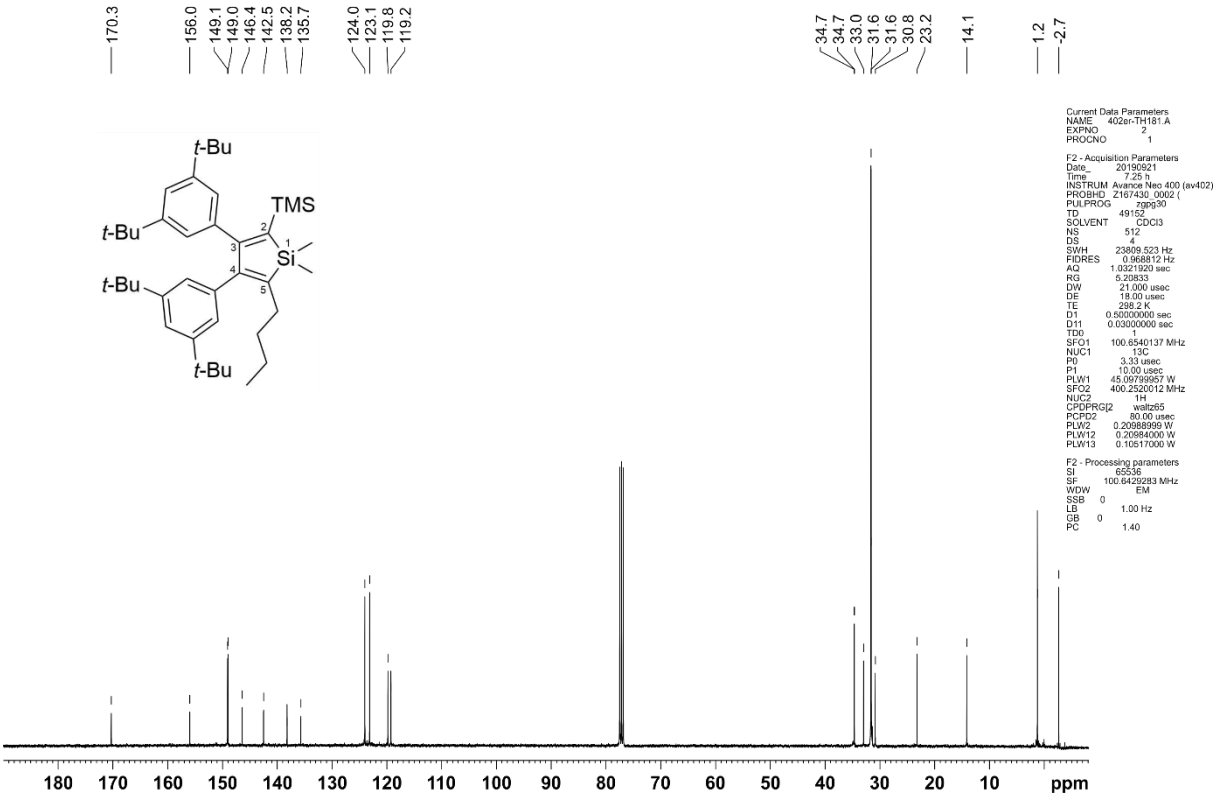
ORTEP plot of the molecular structure of **4.** Atomic displacement parameters are drawn at 50% probability level. Selected bond length: Si1—C10 1.8641 (18), Si1—C9 1.8660 (19), Si1—C1 1.8735 (18), C1—C2 1.363 (2), C2—C3 1.514 (2), C3—C4 1.355 (2).

Spectra Plots for Compound 4

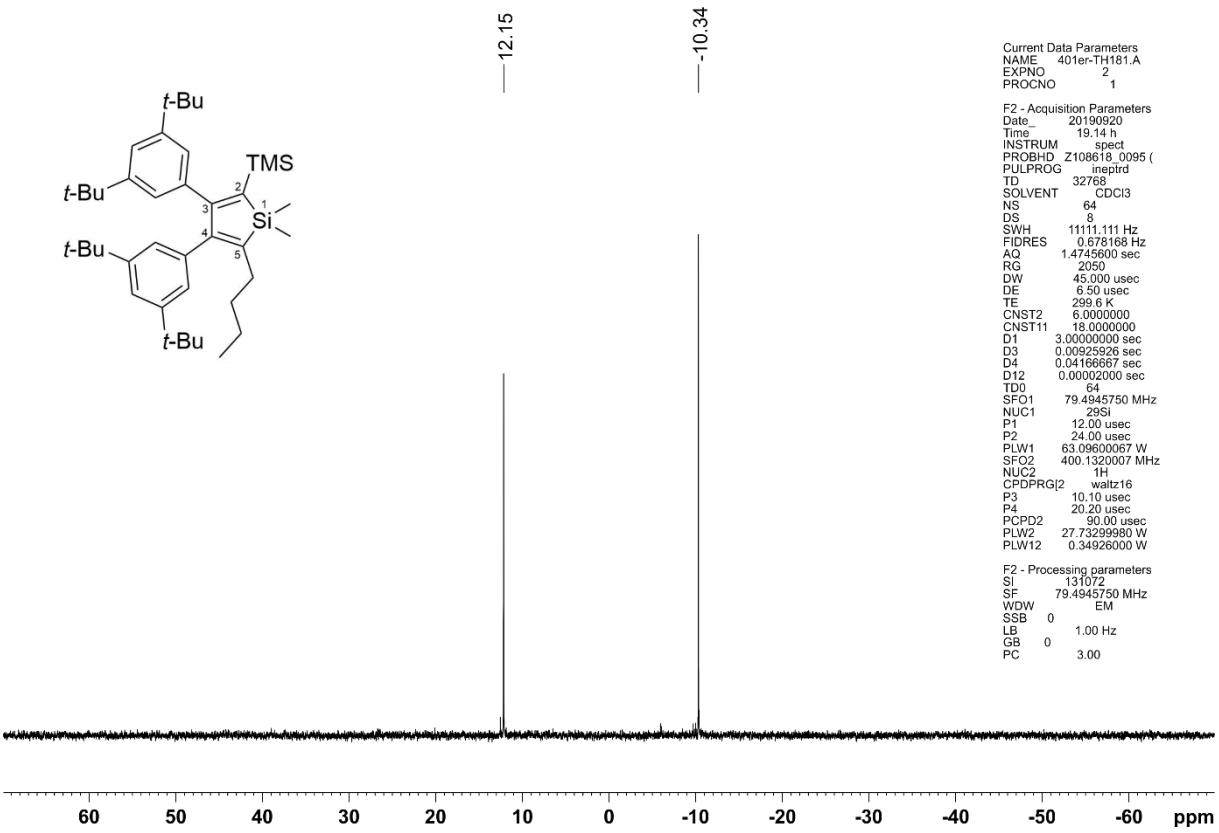
1H-NMR-spectrum of 1,1-Dimethyl-2-(SiMe3)-3,4-(3',5'-tBu2C6H3)-5-butyl-silole in C6D6



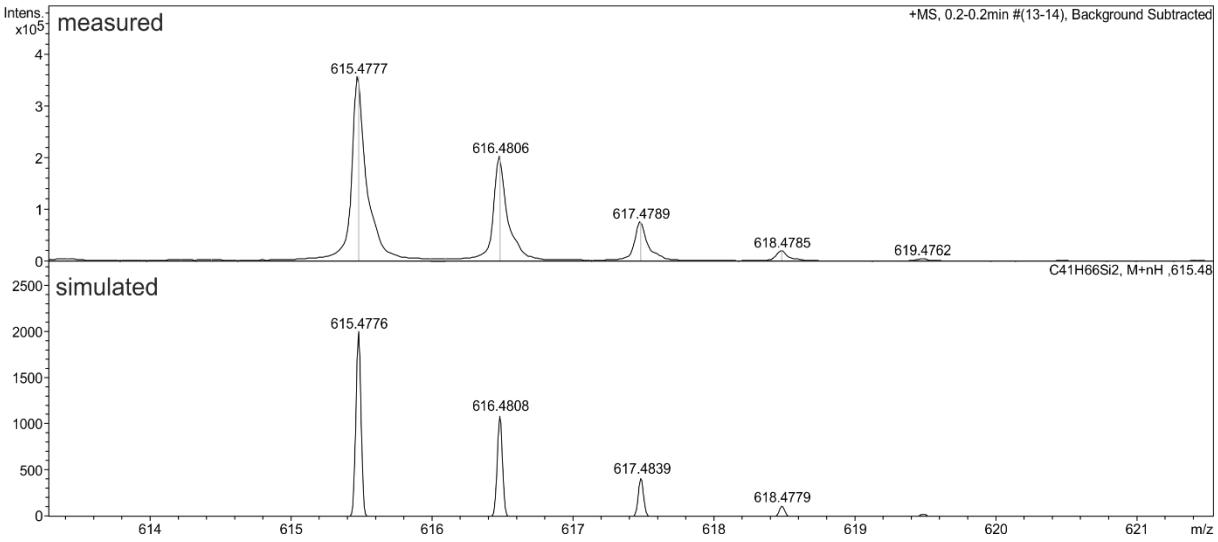
13C{1H}-NMR-spectrum of 1,1-Dimethyl-2-(SiMe3)-3,4-(3',5'-tBu2C6H3)-5-butyl-silole in C6D6



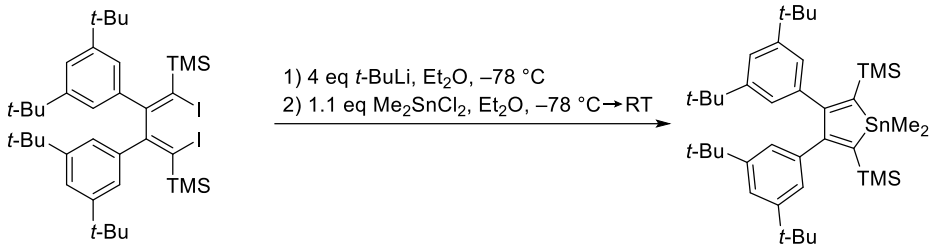
29Si-INEPT-NMR-spectrum of
1,1-Dimethyl-2-(SiMe3)-3,4-(3',5'-tBu2C6H3)-5-butyl-silole in C6D6



HR-ESI $(M-H)^+$



Compound 5



Molecular Weight: 826,88

Molecular Weight: 721,85

In a Schlenk flask compound **2** (528 mg, 0.64 mmol, 1 eq) was dissolved in dry Et_2O (8 mL). The solution was cooled to –78 °C and *t*-BuLi (1.34 mL, 1.9 M in pentane, 2.55 mmol, 4 eq) was added at once with a syringe, resulting in a deep red solution. After stirring at –78 °C for 1 h, Me_2SnCl_2 (154 mg, 0.70 mmol, 1.1 eq) was added and the solution was allowed to warm to ambient temperature overnight, yielding a turbid, almost colourless solution. The solvents were removed thoroughly and the resulting residue was extracted with pentane (3 x 2 mL). The combined filtrates were stored at –40 °C overnight to yield 190 mg of colourless to pale-yellow crystals. After a second crystallisation compound **5** (266 mg, 0.39 mmol, 58 %) was obtained as an off-white powder.

Analytical Data for Compound 5

NMR:

^{1}H (400.25 MHz, 299 K, C_6D_6, C_6D_5H at 7.15 ppm): 7.17 (t, $^{4}J_{HH}$ = 1.84 Hz, 2H, *p*-H_{ar}), 6.89 (d, $^{4}J_{HH}$ = 1.84 Hz, 4H, *o*-H_{ar}), 1.17 (s, 36H, C(*Me*)$_3$),0.50 (s, 6H, Sn*Me*$_2$ ^{2}J(^{1}H–$^{117/119}$Sn) = 51.0/53.1 Hz), 0.07 (s, 18H, Si(*Me*)$_3$).

^{13}C{^{1}H} (100.65 MHz, 298 K, solvent signal at 128.0 ppm): 168.4 (^{2}J(^{13}C–$^{117/119}$Sn) = 53.6 Hz, stannole-$C_{3,4}$), 149.4 (*m*-C_{ar}), 146.7 (^{1}J(^{13}C–$^{117/119}$Sn) = 221.0/231.0 Hz, stannole-$C_{2,5}$), 144.6 (^{3}J(^{13}C–$^{117/119}$Sn) = 98.3/102.8 Hz, ipso-C_{ar}), 123.9 (*o*-C_{ar}), 119.7 (*p*-C_{ar}), 34.7 (*C*(CH$_3$)$_3$), 31.6 (C(*C*H$_3$)$_3$), 1.4 (Si(*C*H$_3$)$_3$), –6.8 (^{1}J(^{13}C–$^{117/119}$Sn) = 277.5/290.4 Hz, Sn(*C*H$_3$)$_2$,)

^{29}Si (79.49 MHz, 300 K, C_6D_6): –7.6 (^{2}J(^{29}Si–$^{117/119}$Sn) = 76.5/80.0 Hz).

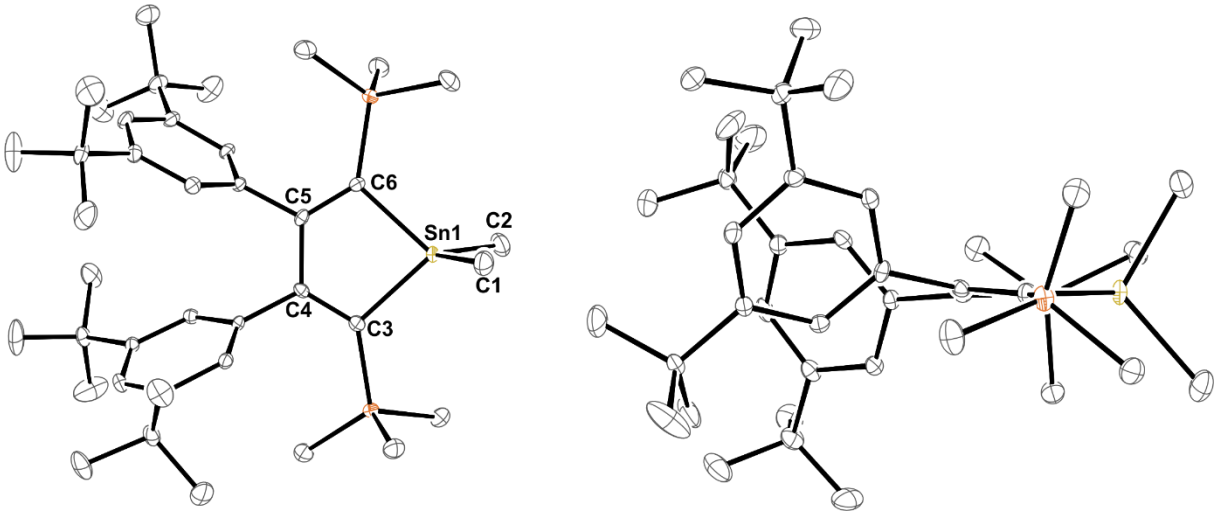
^{119}Sn{^{1}H} (149.21 MHz, 298 K, C_6D_6): 69.1 (s).

Elemental Analysis: $C_{40}H_{66}Si_2Sn$ calcd C 66.56, H 9.22; observed C 66.18, H 9.33.

HR-ESI-MS (positive mode): *m/z* = 723.3786 $[M+H]^+$, 745.3603 $[M+Na]^+$, 761. 3351 $[M+K]^+$.

Crystal structure of Compound 5

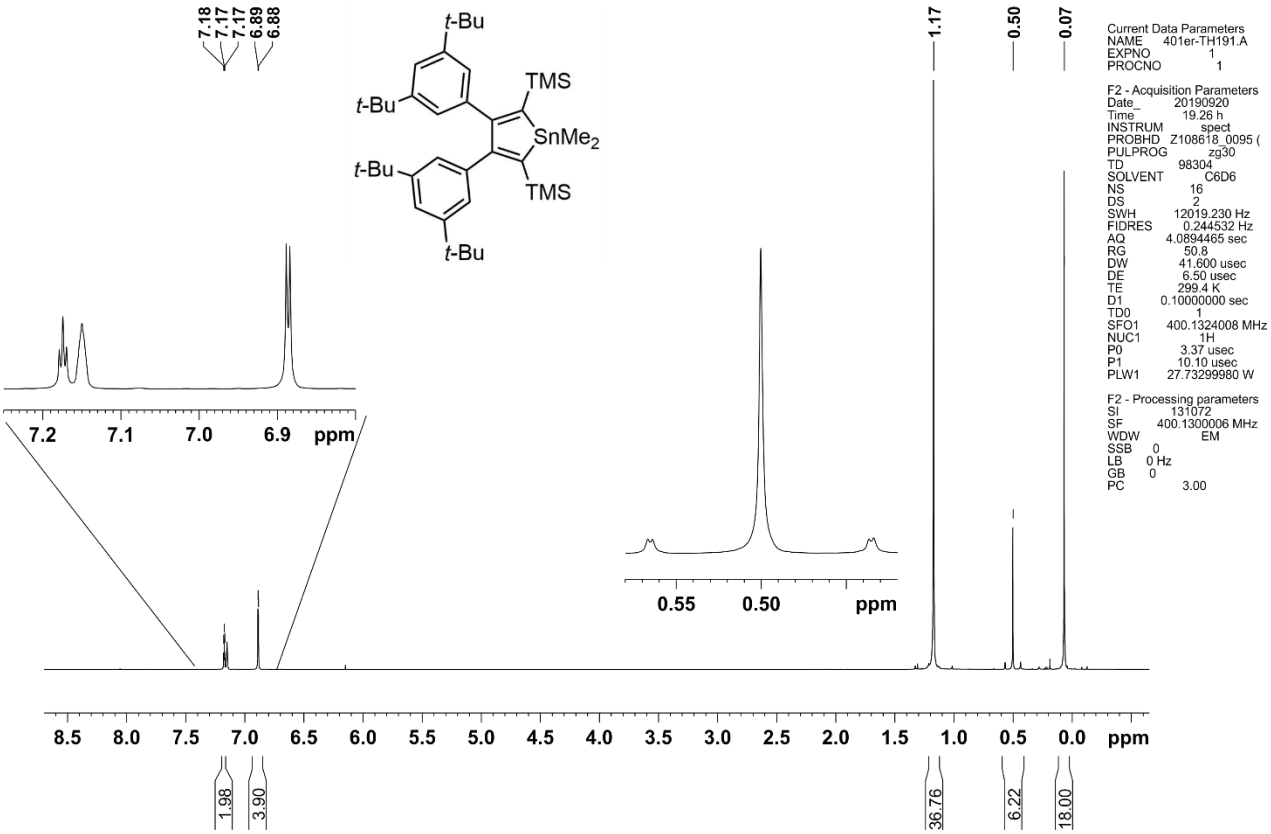
Crystals of **5** were obtained from concentrated solutions in pentane in the cold (-40°C)



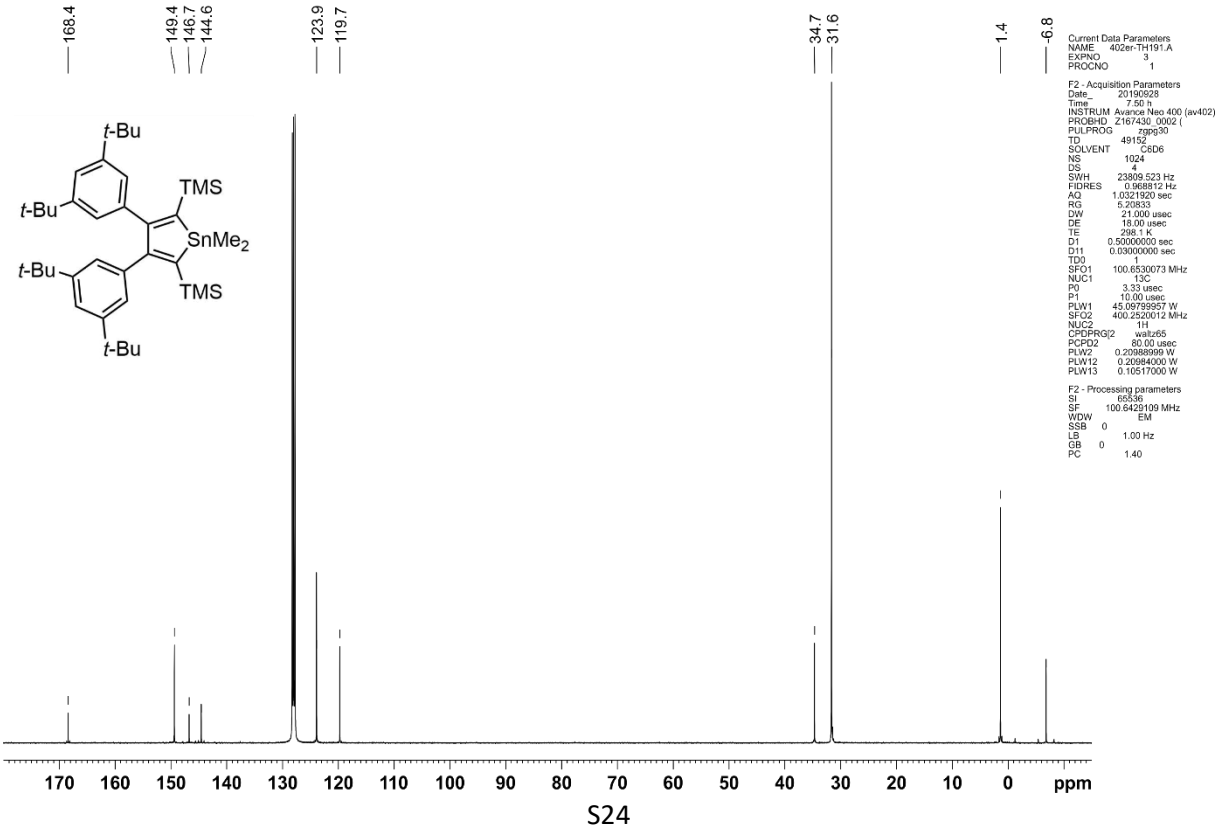
ORTEP plot of two perspectives on the molecular structure of **5.** Atomic displacement parameters are drawn at 50% probability level. Selected bond length: C1—Sn1 2.154 (3), Sn1—C2 2.153 (3), Sn1—C3 2.146 (3), 7 C3—C4 1.353 (4), C4—C5 1.523 (3), C5—C6 1.348 (4), 6 Sn1—C6 2.144 (2).

Spectra Plots for Compound 5

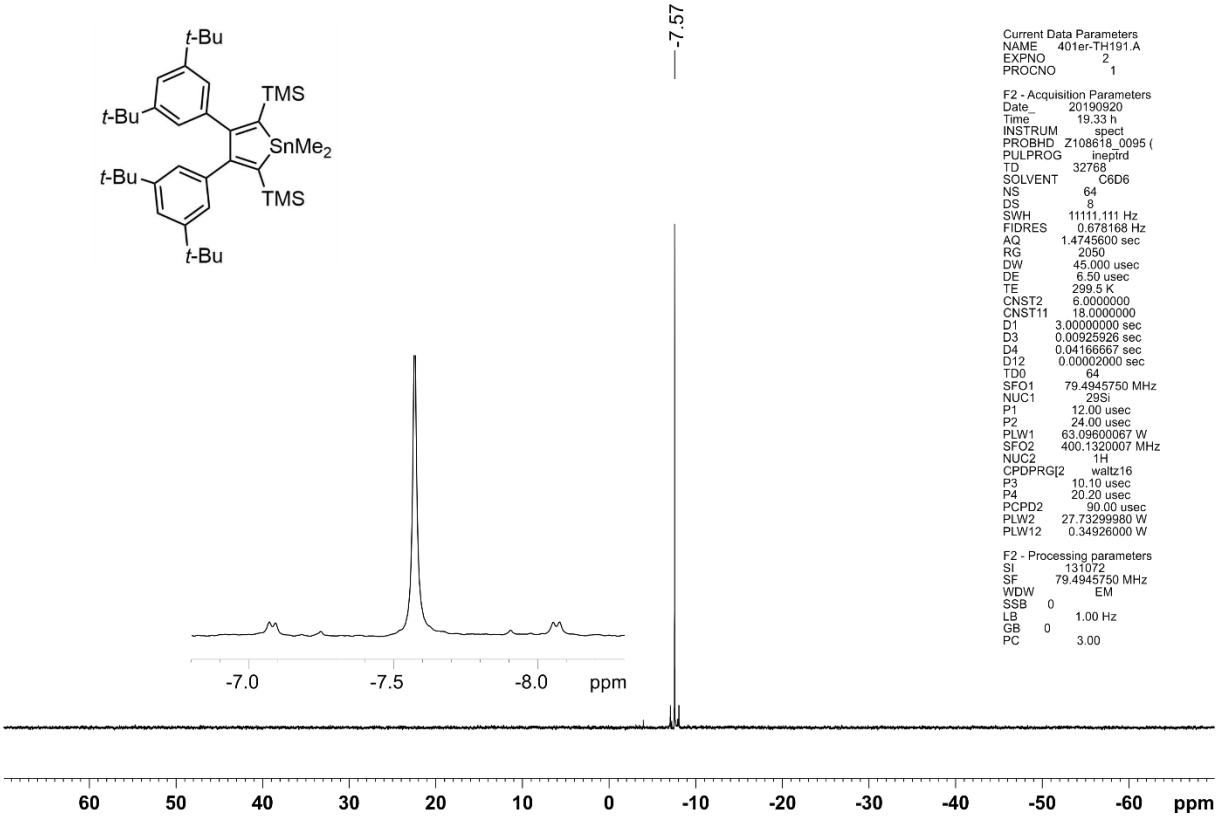
1H-NMR-spectrum of 1,1-Dimethyl-2,5-(SiMe3)-3,4-(3',5'-tBu2C6H3)-stannole in C6D6



13C{1H}-NMR-spectrum of 1,1-Dimethyl-2,5-(SiMe3)-3,4-(3',5'-tBu2C6H3)-stannole in C6D6



29Si-INEPT-NMR-spectrum of 1,1-Dimethyl-2,5-(SiMe3)-3,4-(3',5'-tBu2C6H3)-stannole in C6D6



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PROCNO 1

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CNST11 18.0000000
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P1 12.00 usec
P2 24.00 usec
PLW1 63.09600067 W
SFO2 400.1320007 MHz
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F2 - Processing parameters
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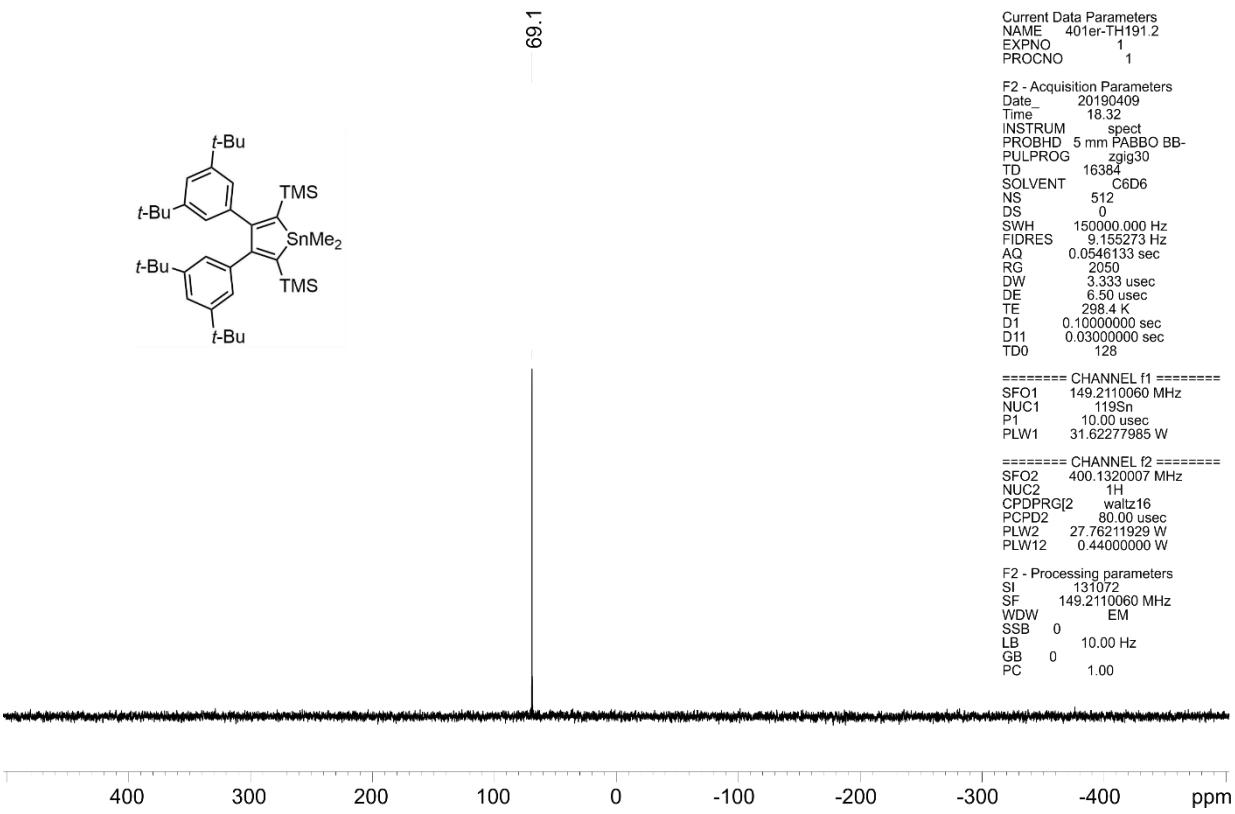
119Sn{1H} NMR of 1,1-Dimethyl-2,5-(SiMe3)-3,4-(3',5'-tBu2C6H3)-stannole in C6D6



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======== CHANNEL f2 ========
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PLW12 0.44000000 W

F2 - Processing parameters
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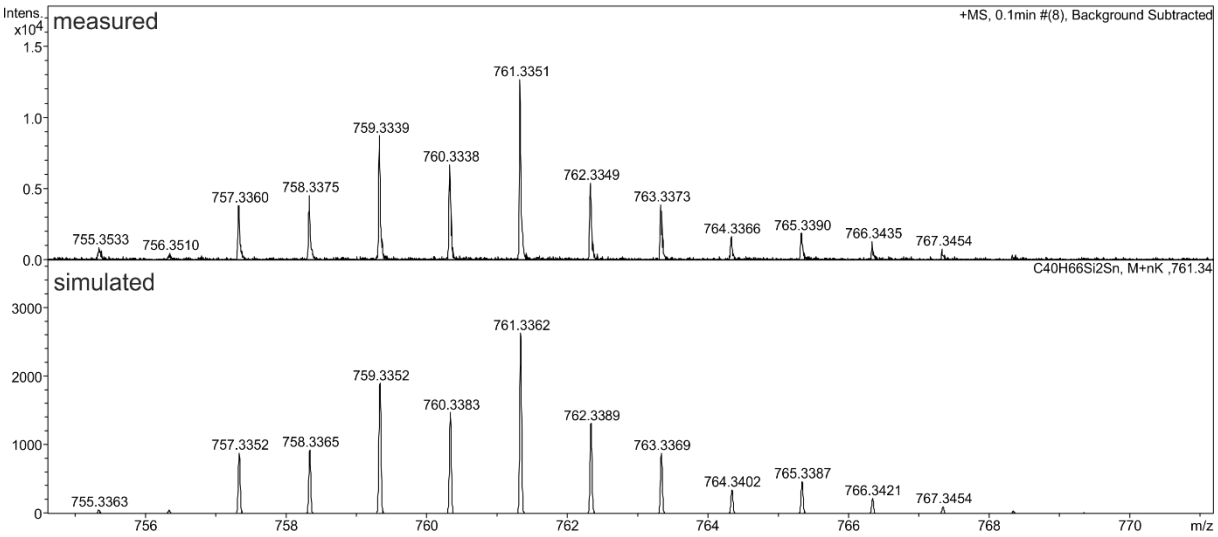
HR-ESI $(M-K)^+$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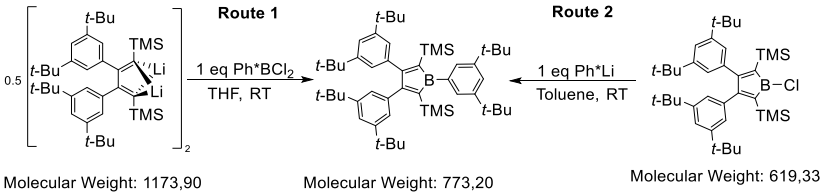
m/z

Compound 6-Ph*



Molecular Weight: 1173,90 Molecular Weight: 773,20 Molecular Weight: 619,33

Route 1: In a glovebox, to a stirred solution of 1,4-dilithiobutadiene **3** (200 mg, 0.34 mmol, 1 eq) in THF (4 mL) was added a solution of Ph*BCl_2 (92.4 mg, 0.34 mmol, 1 eq) in THF (1 mL) at once. The opaque faintly grey-greenish mixture was stirred at room temperature over two days and all volatiles were removed under reduced pressure to give an orange solid. The solid was redissolved in pentane twice followed by removal of solvents to force precipitation of LiCl. The solid is extracted with pentane (4 mL, 2 mL, 2 mL) and the extracts are filtered through a syringe equipped with a thin plug of glass fibre and all solvents are removed under reduced pressure. The solid is repeatedly redissolved in pentane and dried for several hours under reduced pressure to co-evaporate residual THF (5 cycles). When NMR monitoring confirmed the absence of THF, **6-Ph*** (234 mg) were crystallised from concentrated solutions in pentane at –40°C to give **6-Ph*** (120 mg, 0.16 mmol, 46%) as red-orange crystalline material.

Route 2: To a solution of the chloroborole **8** (154 mg, 0.25 mmol, 1 eq) in dry, degassed toluene (10 mL) in a glovebox, 3,5-*t*-$Bu_2(C_6H_3)Li$ (Ph*Li) (73 mg, 0.37 mmol, 1.5 eq) was added at once, and the resulting suspension was left stirring at ambient temperature for 48 h. In the course of the reaction the colour of the solution changed from red to deep green and the suspended is slowly consumed. The solvent was removed in vacuo to yield a deep green powder, which was extracted with pentane (4 x 2 mL) and filtered through a syringe filter equipped with a thin plug of glass fiber. After removal of the solvent in vacuo, **6-Ph*** (172 mg) was obtained as a deep green powder. NMR spectroscopic examination of this crude powder reveals >95% purity. Upon crystallization of **6-Ph*** from concentrated cold pentane (3-4 mL, –40°C) orange-red crystals and crystalline powder (ca. 50 mg) separated which were isolated. Attempts to get hands on the intensely green byproduct remained unsuccessful.

Analytical Data for Compound 6-Ph*

NMR:

^{1}H (400.25 MHz, 299 K, C_6D_6, C_6D_5H at 7.15 ppm): 7.86 (d, $^{4}J_{HH}$ = 1.88 Hz, 2H, o-H_{ar1}), 7.64 (t, $^{4}J_{HH}$ = 1.88 Hz, 1H, *p*-H_{ar1}), 7.29 (t, $^{4}J_{HH}$ = 1.79 Hz, 2H, *p*-$H_{ar3,4}$), 6.92 (d, $^{4}J_{HH}$ = 1.79 Hz, 4H, o-$H_{ar3,4}$), 1.44 (s, 18H, Ar_1-C(Me)$_3$), 1.20 (s, 36H, $Ar_{3,4}$-C(Me)$_3$), 0.00 (s, 18H, Si(Me)$_3$).

^{13}C{^{1}H} (100.65 MHz, 298 K, solvent signal at 128.0 ppm): 182.8 (borole-$C_{3,4}$), 149.7 (m-C_{ar1}), 149.6 (m-$C_{ar3,4}$), 144.6 (*ipso*-C_{ar1}), 140.1 (*ipso*-$C_{ar3,4}$), 139.2 (borole-$C_{2,5}$), 125.2 (o-C_{ar1}), 123.9 (*p*-C_{ar1}), 123.3 (o-$C_{ar3,4}$), 121.1 (*p*-$C_{ar3,4}$), 35.1 (Ar_1-C(CH_3)$_3$), 34.8 ($Ar_{3,4}$-C(CH_3)$_3$), 31.7 (Ar_1-C(CH_3)$_3$), 31.6 ($Ar_{3,4}$-C(CH_3)$_3$), 1.5 (Si(CH_3)$_3$).

^{11}B (128.38 MHz, 299 K, C_6D_6): 77.1 (br, $\varpi_{1/2}$ ≈ 2700 Hz).

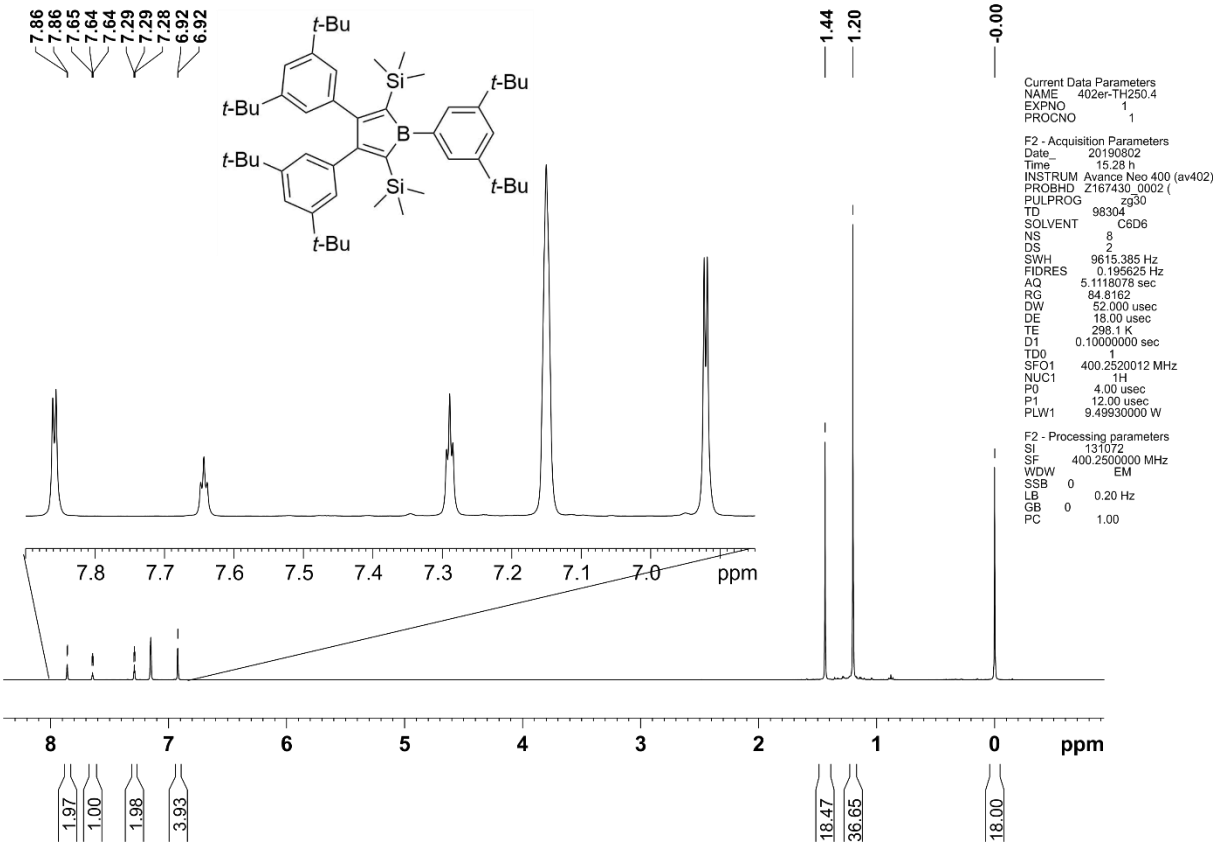
^{29}Si-INEPT (79.49 MHz, 300 K, C_6D_6): –9.2.

Elemental Analysis: $C_{52}H_{81}Si_2B$ calcd C 80.78, H 10.56; observed C 81.19 H 11.09.

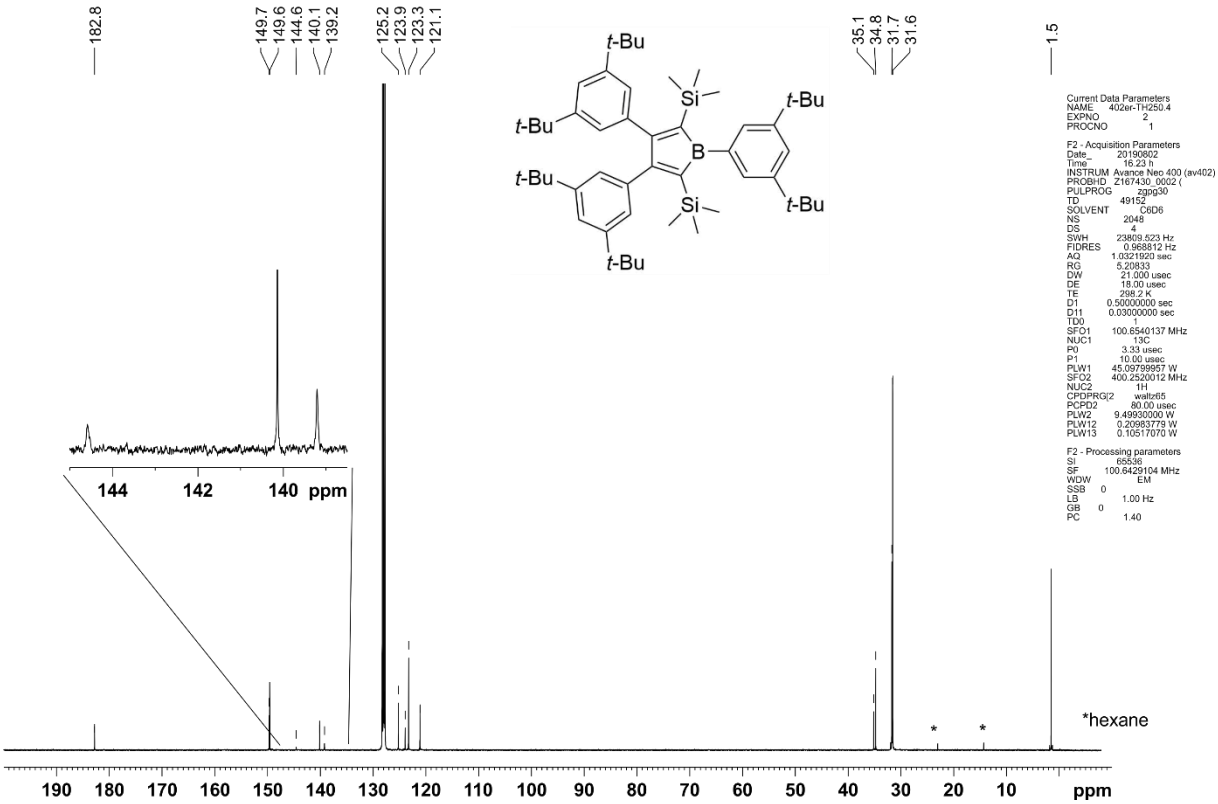
LIFDI-MS (positive mode): *m/z* =[M]$^+$ 772.6 (minor); [M+(H_2O)]$^+$. 790.5 (major)

Spectra Plots for Compound 6-Ph*

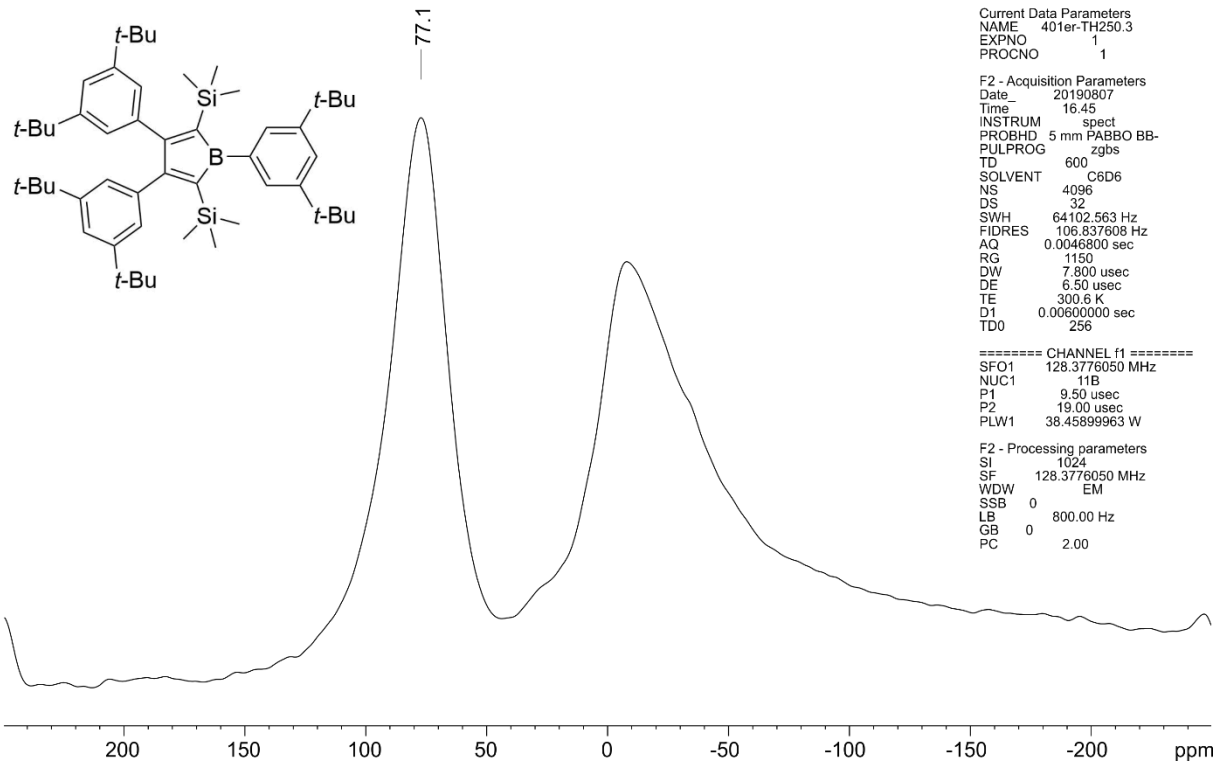
1H-NMR-spectrum of 1-(3',5'-tBu2(C6H3))-2,5-(SiMe3)2-3,4-(3',5'-tBu2(C6H3))2-borole in C6D6



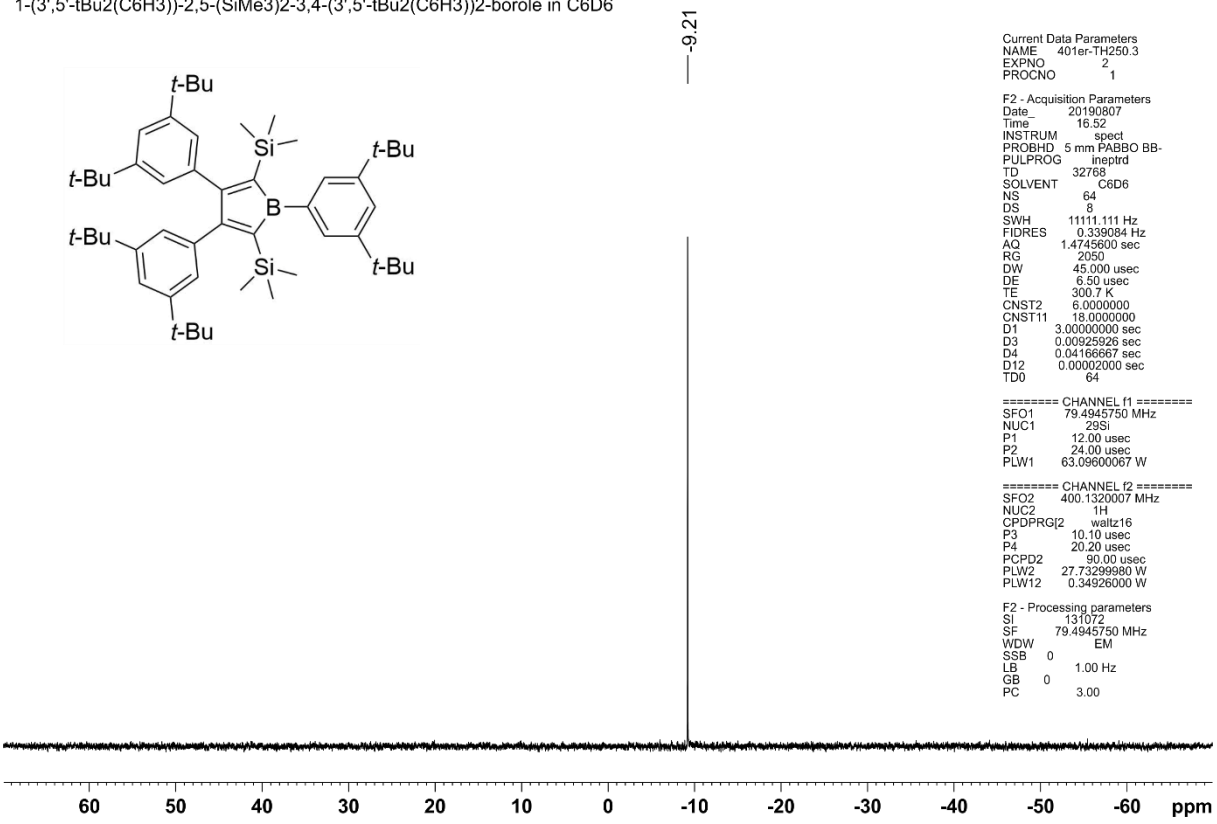
13C{1H}-NMR-spectrum of 1-(3',5'-tBu2(C6H3))-2,5-(SiMe3)2-3,4-(3',5'-tBu2(C6H3))2-borole in C6D6

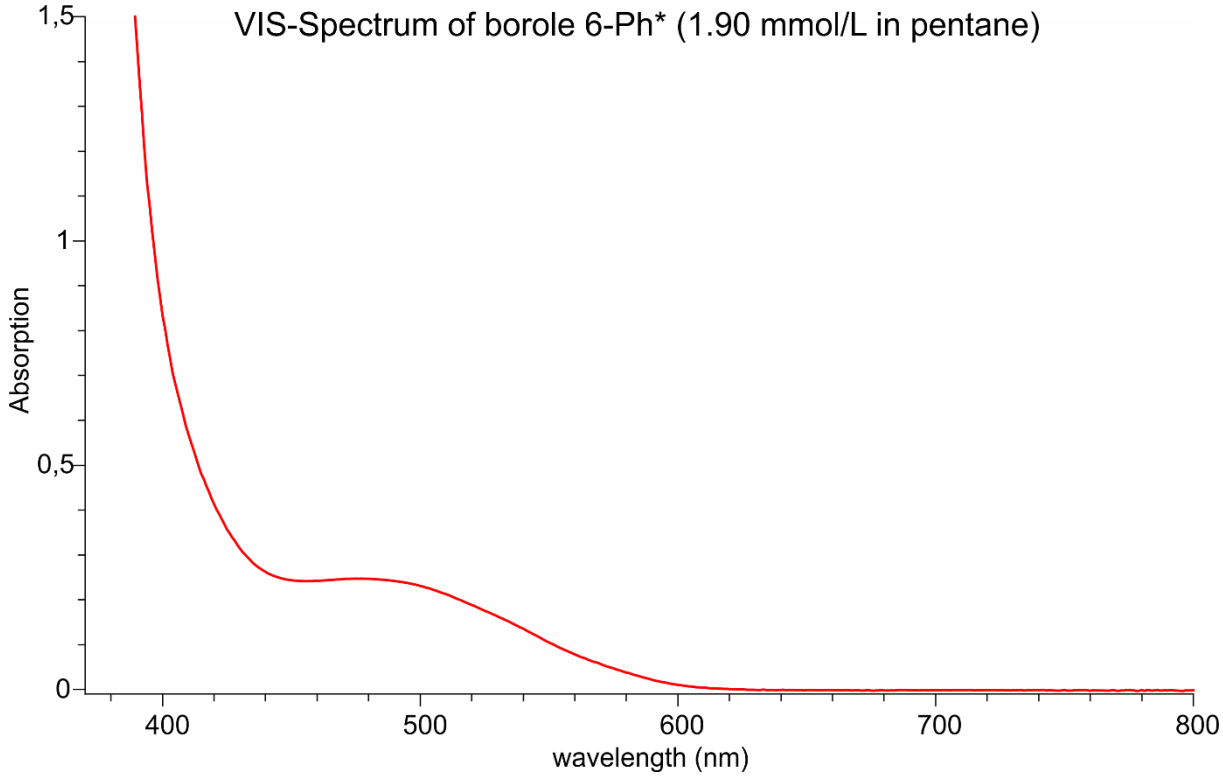


11B-NMR spectrum (background suppressed) of
1-(3',5'-tBu2(C6H3))-2,5-(SiMe3)2-3,4-(3',5'-tBu2(C6H3))2-borole in C6D6

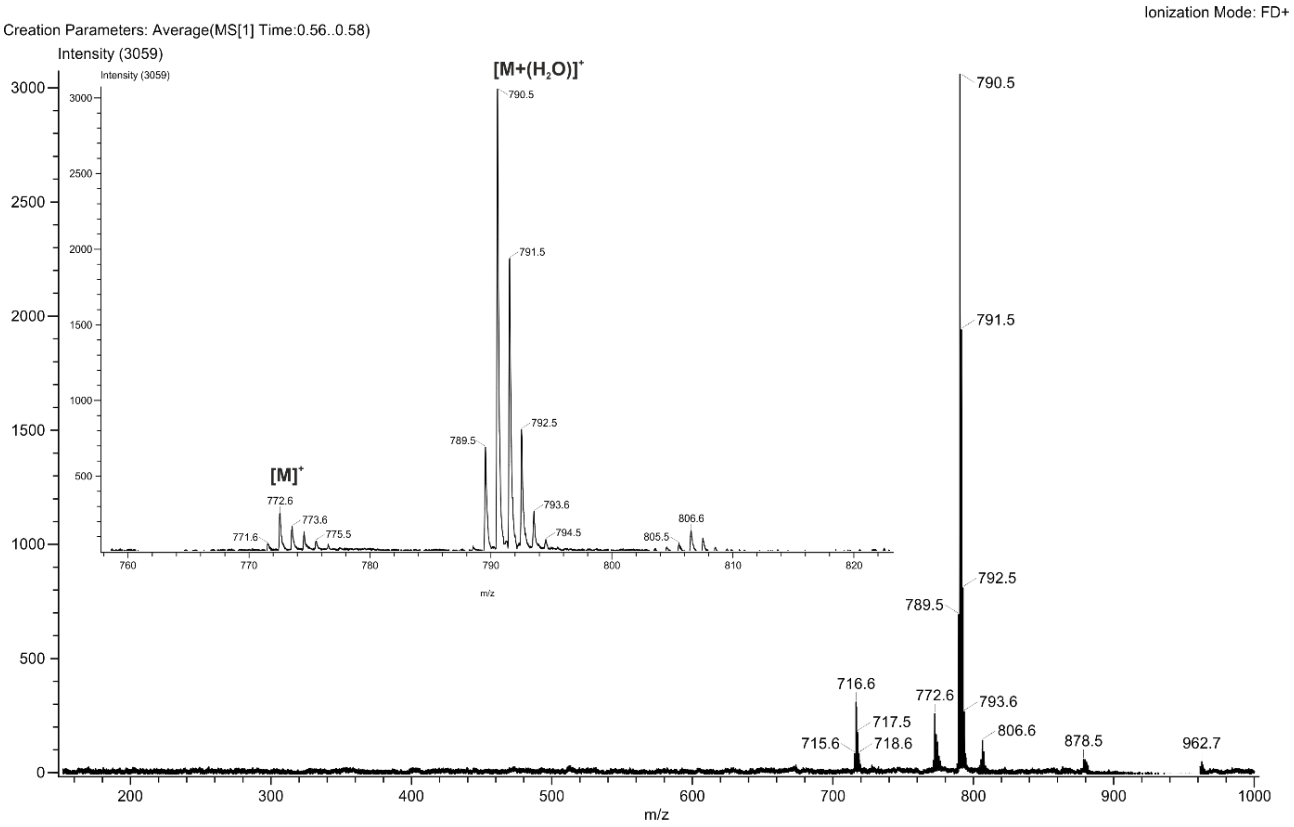


29Si-INEPT-NMR-spectrum of
1-(3',5'-tBu2(C6H3))-2,5-(SiMe3)2-3,4-(3',5'-tBu2(C6H3))2-borole in C6D6




VIS-Spectrum of borole 6-Ph* (1.90 mmol/L in pentane)
Absorption
wavelength (nm)
1,5
1
0,5
0
400
500
600
700
800

LIFDI-MS


Ionization Mode: FD+
Creation Parameters: Average(MS[1] Time:0.56..0.58)
Intensity (3059)
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[M]+
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791.5
792.5
789.5
793.6
772.6
773.6
771.6
775.5
794.5
806.6
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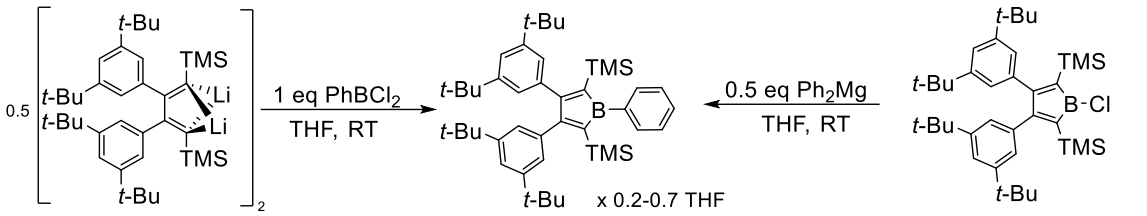
718.6
878.5
962.7
m/z

Compound 6-Ph



Molecular Weight: 1173,90 Molecular Weight: 660,98 Molecular Weight: 619,33

ROUTE 1 In a glovebox, to a stirred solution of 1,4-dilithiobutadiene **3** (220 mg, 0.375 mmol, 1 eq) in THF (4 mL) was added a solution of $PhBCl_2$ (60 mg, 0.39 mmol, 1 eq) in THF (2 mL) over the course of 10 min. The opaque faintly grey-orange mixture was stirred at room temperature for 24 h and all volatiles were removed under reduced pressure to give a beige solid. The solid was redissolved in pentane (2 × 2 mL) and toluene (2 × 2 mL) each time followed by removal of solvents to force precipitation of LiCl and co-evaporation of THF. The hydrocarbon extracts turn increasingly orange red. The waxy deep red solid is extracted with pentane (4 mL, 2 mL) and the extracts are filtered through a syringe equipped with a thin plug of glass fibre and all volatiles are removed under reduced pressure. The solid is again repeatedly redissolved in pentane and toluene and dried for several hours under reduced pressure to co-evaporate residual THF (5 cycles). The crude intensely red waxy material (ca. 255 mg) contained **6-Ph**•$(THF)_1$ in about 90-95% NMR purity. Fractional crystallisation from pentane afforded intensely red crystals of **6-Ph**•$(THF)_{0.6\text{-}0.7}$ (THF content assigned by NMR) in a combined yield of (150 mg, 0.21 mmol, 56%).

Please note: Even after prolonged drying the samples still contained 0.25 equivalents of THF per **6-Ph** and quantitative removal has not been achieved. Please note: Drying the borole **6-Ph** under reduced pressure (10^{-3} mbar) at mild oil bath temperatures (40°C) lead to complete removal of THF but also to substantial formation of a few unknown side products (25% after 4h). **6-Ph** crystallises from these mixtures from cold pentane (–40°), however, colorless crystals of the side products could not be satisfyingly removed.

ROUTE 2: In a glovebox, to a mixture of chloroborole **8** (100 mg, 0.161 mmol, 1 eq) and Ph_2Mg (14.4 mg, 0.081 mmol, 0.5 eq) THF (2 mL) was added and the mixture was stirred at room temperature for six days. All volatiles were then removed from the pale green mixture and the resulting solid was extracted into pentane (3 mL). The extracts were filtered through a syringe filter equipped with a thin pad of glass fibre and dried under reduced pressure (10^{-3} mbar) for several days to give **6-Ph (**91 mg, 0.138 mmol, 86%) that still contained ca. 0.25 equiv. of THF.

Please note: Drying the borole **6-Ph** under reduced pressure (10^{-3} mbar) at mild oil bath temperatures (40°C) lead to complete removal of THF but also to substantial formation of a few unknown side products (25% after 4h). **6-Ph** crystallises from these mixtures from cold pentane (–40°), however, colorless crystals of the side products could not be satisfyingly removed.

Analytical Data for Compound 6-Ph

NMR for 6-Ph•$(THF)_{0.6}$

^{1}H (300.13 MHz, 302 K, C_6D_6, C_6D_5H at 7.15 ppm): 7.82-7.79 (m, 2H, o-H_{Ph}), 7.33-7.27 superimposed signals (m, 2H, *m*-H_{Ph}) and (t, 2H, *p*-$H_{ar3,4}$), 2.23-2.18 (m, 1H, p-H_{Ph}), 6.89 (d, $^{4}J_{HH}$ = 1.86 Hz, *o*-$H_{ar3,4}$), 3.31 (m, THF OCH_2), 1.69 (m, THF OCH_2CH_2), 1.18 (s, 36H, $Ar_{3,4}$-C(Me)$_3$), -0.05 (s, 18H, Si(Me)$_3$).

^{13}C{^{1}H} (100.65 MHz, 298 K, solvent signal at 128.0 ppm): 183.1 (borole-$C_{3,4}$), 149.6 (m-$C_{ar3,4}$), 145.4(*ipso*-C_{Ph}), 139.9 (*ipso*-$C_{ar3,4}$), 139.2 (borole-$C_{2,5}$), 130.2 (o-C_{Ph}), 130.0 (*p*-C_{Ph}), 127.9(*m*-C_{Ph}), 123.2 (o-$C_{ar3,4}$), 121.2 (*p*-$C_{ar3,4}$), 70.8 (THF, OCH_2), 34.8 ($Ar_{3,4}$-$C(CH_3)_3$), 31.5 ($Ar_{3,4}$-C(CH_3)$_3$), 27.2 (THF, OCH_2CH_2), 1.4 (Si(CH_3)$_3$).

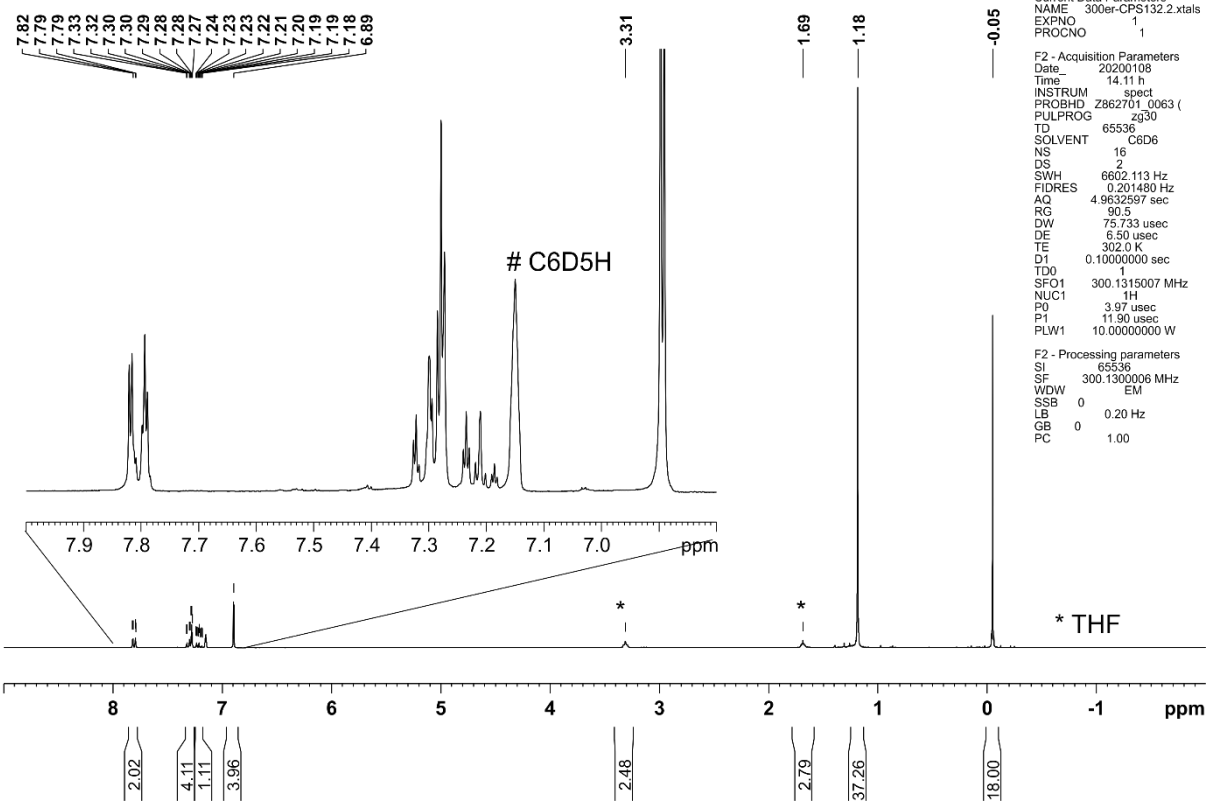
^{11}B (128.38 MHz, 299 K, C_6D_6): 76.6 (br, major, $\varpi_{1/2}$ ≈ 2100 Hz), 27.7 (br, minor, $\omega_{1/2}$ ≈ 320 Hz)

^{29}Si-INEPT (79.49 MHz, 300 K, C_6D_6): –9.2.

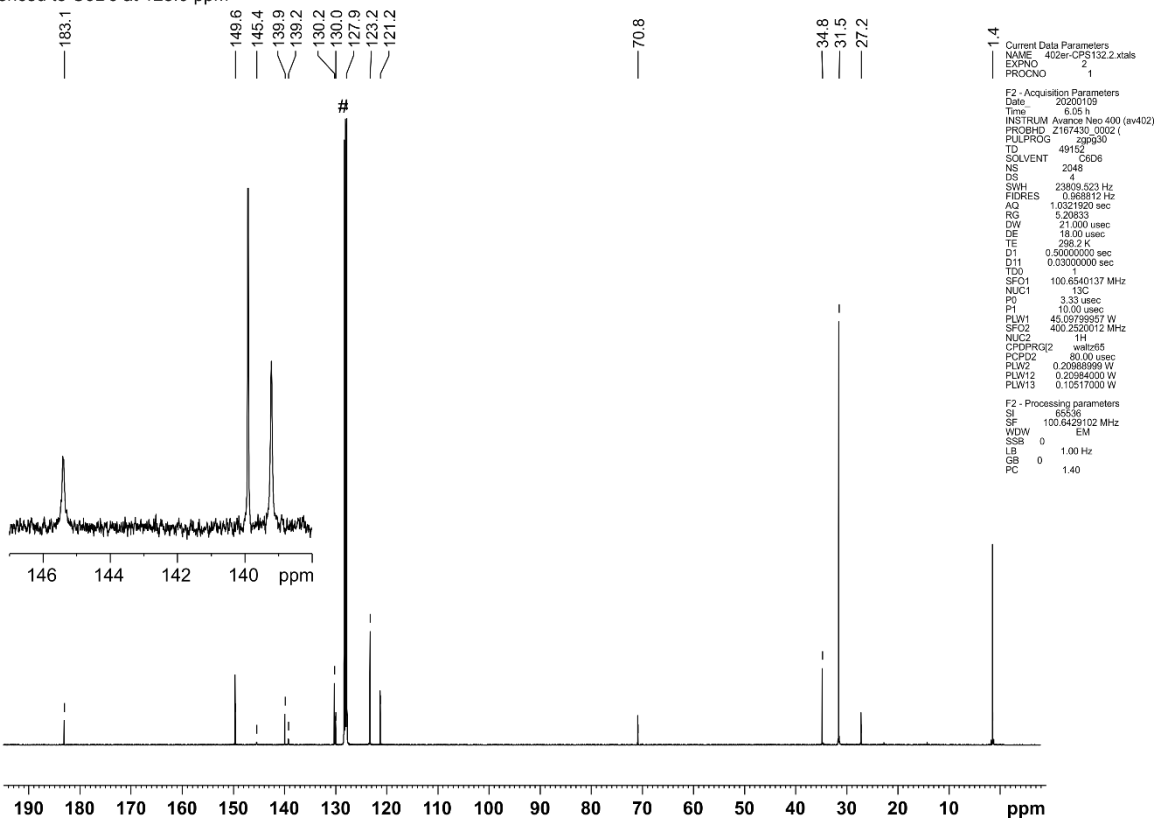
LIFDI-MS (positive mode): *m/z* =$[M]^+$ 660.6 (major); $[M+(H_2O)]^+$. 678.5 (minor)

Spectra Plots for Compound 6-Ph

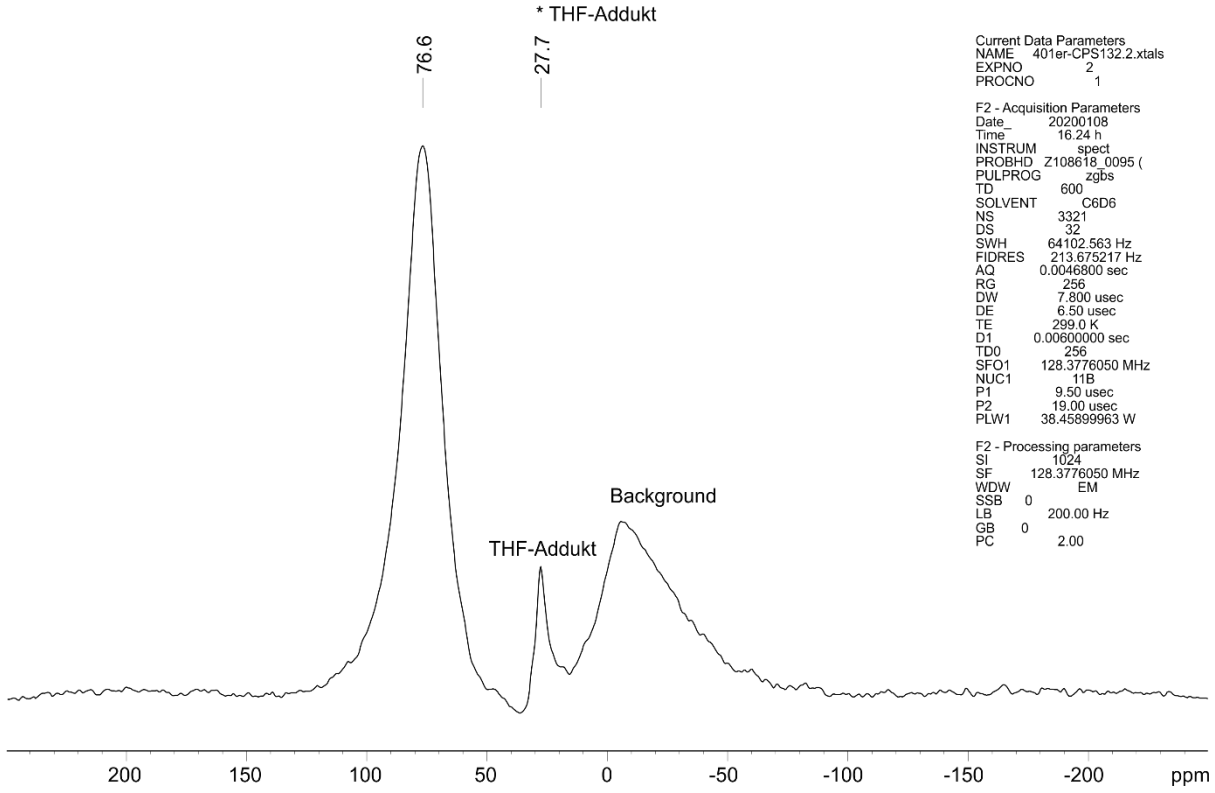
1H-NMR-spectrum of 1-[Ph]-2,5-(SiMe3)-3,4-(3',5'-tBu2Ph)-borole in C6D6
THF contamination after crystallisation from pentane and drying



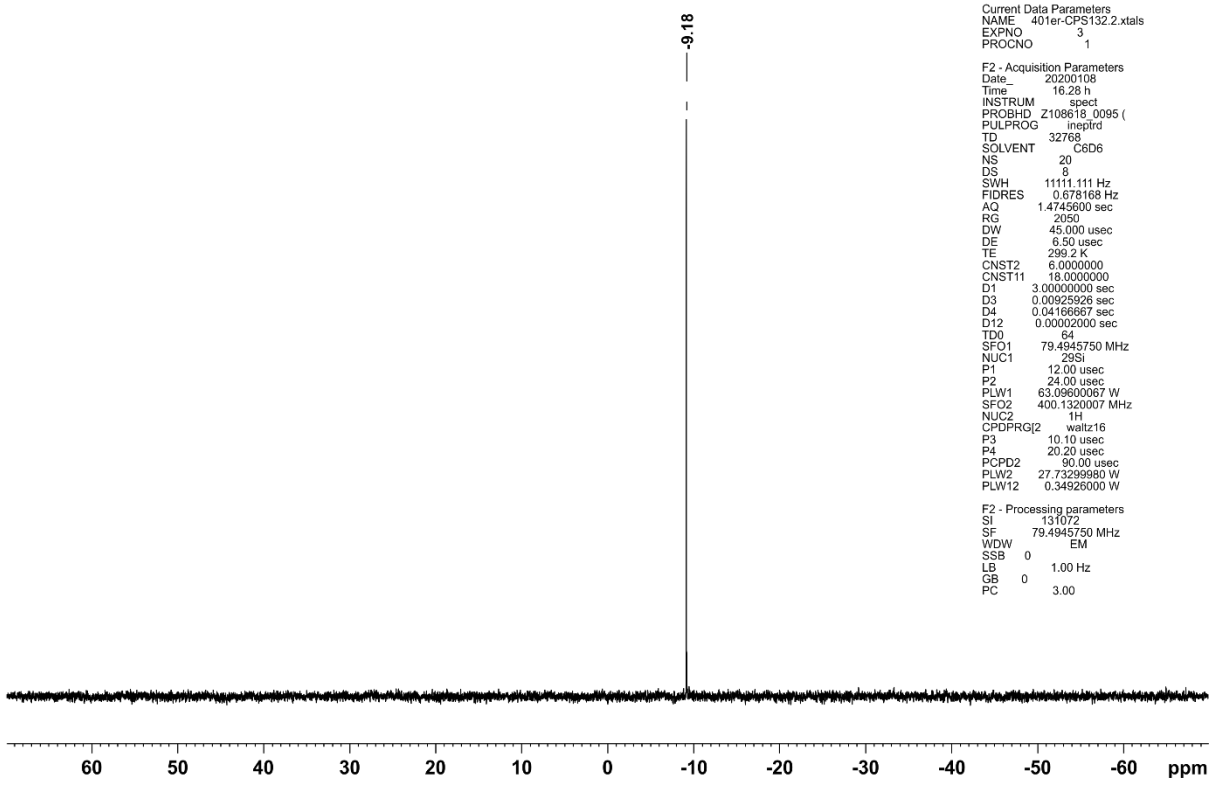
13C{1H}-NMR-spectrum of 1-[Ph]-2,5-(SiMe3)-3,4-[3',5'-tBu2(C6H3)]-borole x 0.6(THF) in C6D6
referenced to C6D6 at 128.0 ppm

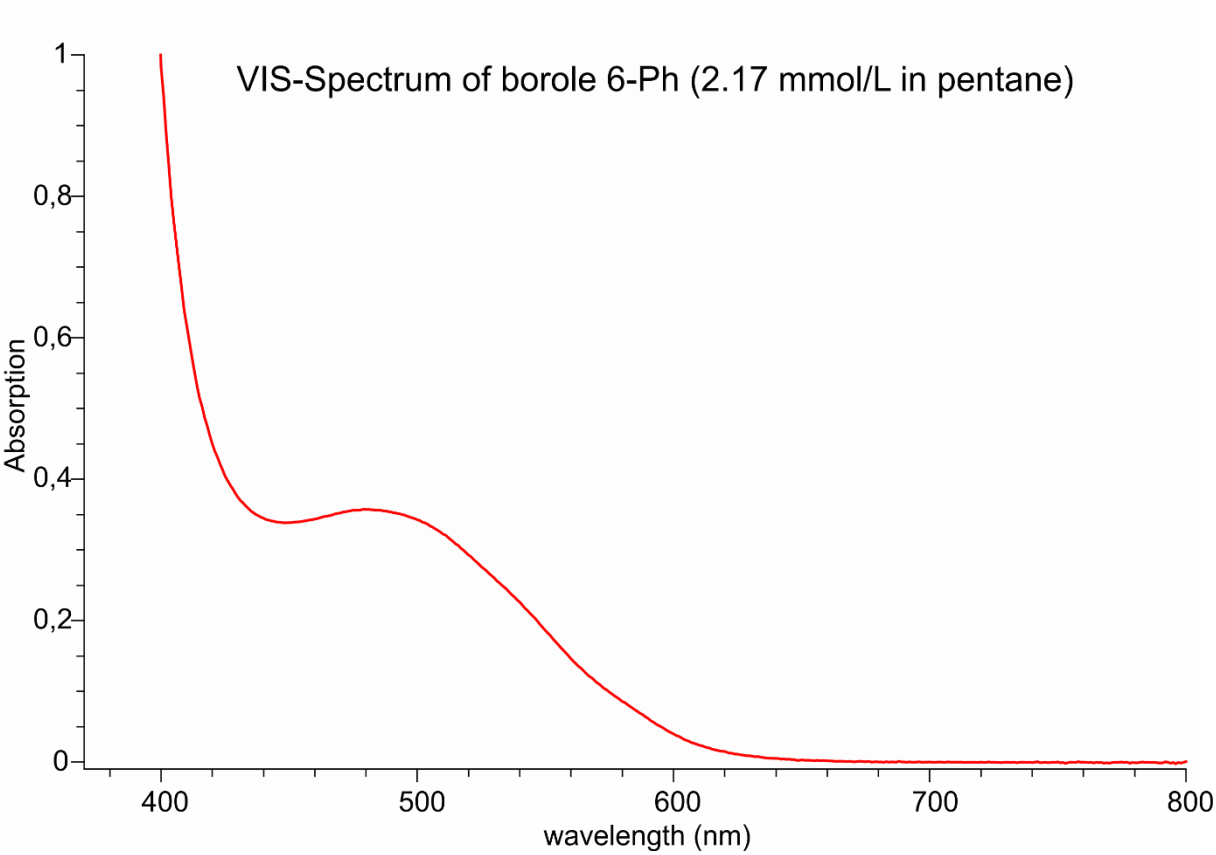


11B-NMR spectrum (background suppressed) of 1-Ph-2,5-(SiMe3)2-3,4-(3',5'-tBu2Ph)2-Borole in C6D6



29Si-Inept-NMR-spectrum of 1-Ph-2,5-(SiMe3)2-3,4-(3',5'-tBu2Ph)2-Borole in C6D6





LIFDI-MS of compound 6-Ph

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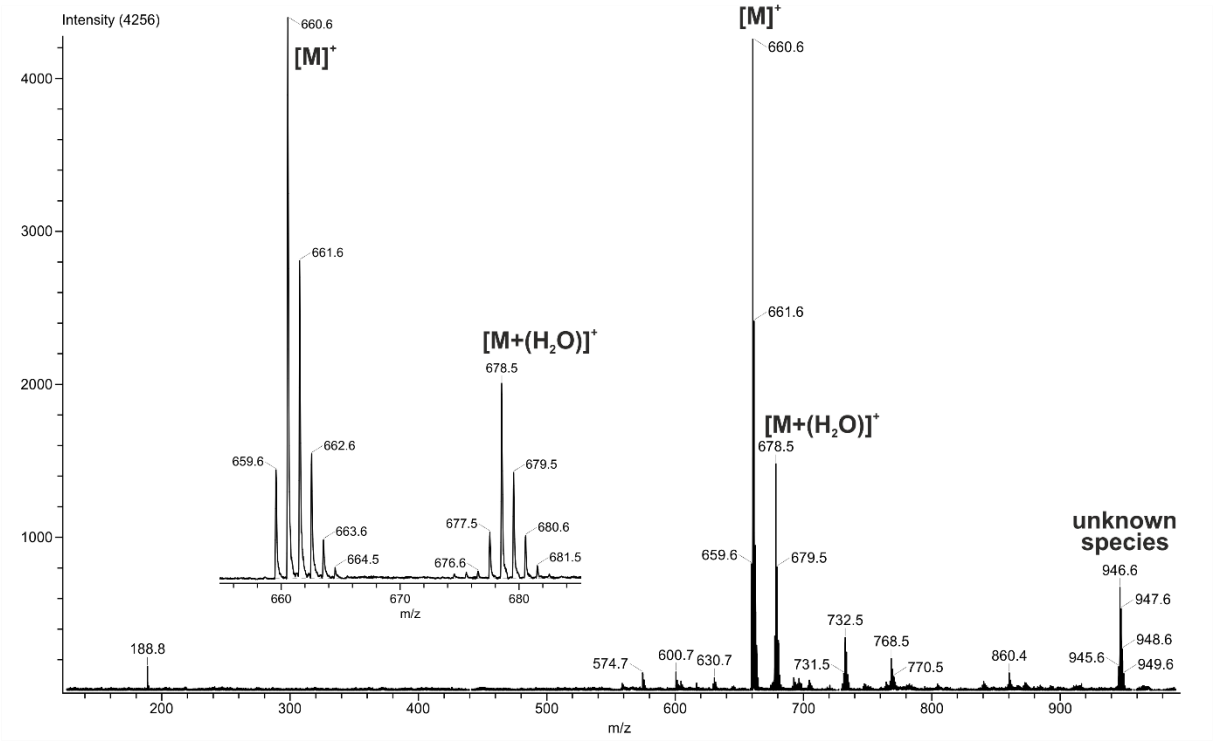
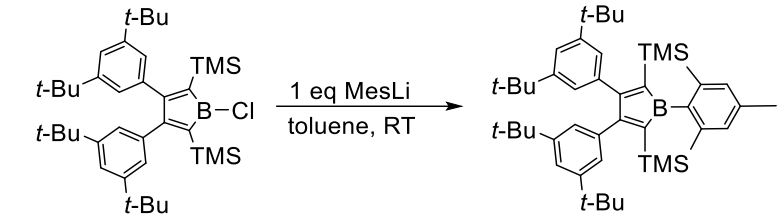
Creation Parameters: Average(MS[1] Time:0.59..0.61)

Ionization Mode: FD+



Compound 6-Mes



Molecular Weight: 619,33 Molecular Weight: 703,07

To a solution of chloroborole **8** (80 mg, 0.13 mmol, 1 eq) in dry, degassed toluene (3 mL) in a glovebox, MesLi (26 mg, 0.21 mmol, 1.6 eq) was added at once, and the resulting suspension was left stirring at ambient temperature for 24 h. In the course of the reaction the colour of the solution changed to deep red. The suspension was filtered through a syringe filter equipped with a thin plug of glass fiber and the remaining solid was washed with pentane (2 x 1 mL). The solvent was removed under reduced pressure to yield a red solid (92 mg). This solid was dissolved in a minimal amount of pentane (ca 0.8 mL) and stored at –40 °C for 2 days to give red crystals of mesityl borole **6-Mes**. The supernatant was removed with a syringe and the crystals dried in vacuo to yield **6-Mes** (66 mg, 0.09 mmol, 73 %) as a red crystalline material.

Analytical Data for Compound 6-Mes

NMR:

^{1}H (400.13 MHz, 299 K, C_6D_6, C_6D_5H at 7.15 ppm): 7.29 (t, $^{4}J_{HH}$ = 1.85 Hz, 2H, *p*-$H_{ar3,4}$), 6.99 (d, $^{4}J_{HH}$ = 1.79 Hz, 4H, *o*-$H_{ar3,4}$), 6.77 (s, 2H, *m*-H_{ar1}), 2.41 (s, 6H, 2',6'-Mes-CH_3), 2.18 (s, 3H, 4'-Mes-CH_3), 1.17 (s, 36H, C(*Me*)$_3$), –0.02 (s, 18H, Si(*Me*)$_3$).

^{13}C{^{1}H} (100.65 MHz, 298 K, solvent signal at 128.0 ppm): 181.4 (borole-$C_{3,4}$), 149.7 (*m*-$C_{ar3,4}$), 142.7 (ipso-C_{Mes}), 139.6 (ipso-$C_{ar3,4}$), 138.8 (borole-$C_{2,5}$), 137.2 (*p*-C_{Mes}), 135.6 (*o*-C_{Mes}), 127.5 (*m*-C_{Mes}), 123.1 (*o*-$C_{ar3,4}$), 121.3 (*p*-$C_{ar3,4}$), 34.8 (*C*(CH$_3$)$_3$), 31.5 (C(*C*H$_3$)$_3$), 22.2 (2',6'-Mes-*C*H$_3$), 21.3 (4'-Mes-*C*H$_3$), 0.9 (Si(*C*H$_3$)$_3$).

^{11}B (128.38 MHz, 299 K, C_6D_6): 79.9 (br, $\varpi_{1/2}$ ≈ 2100 Hz).

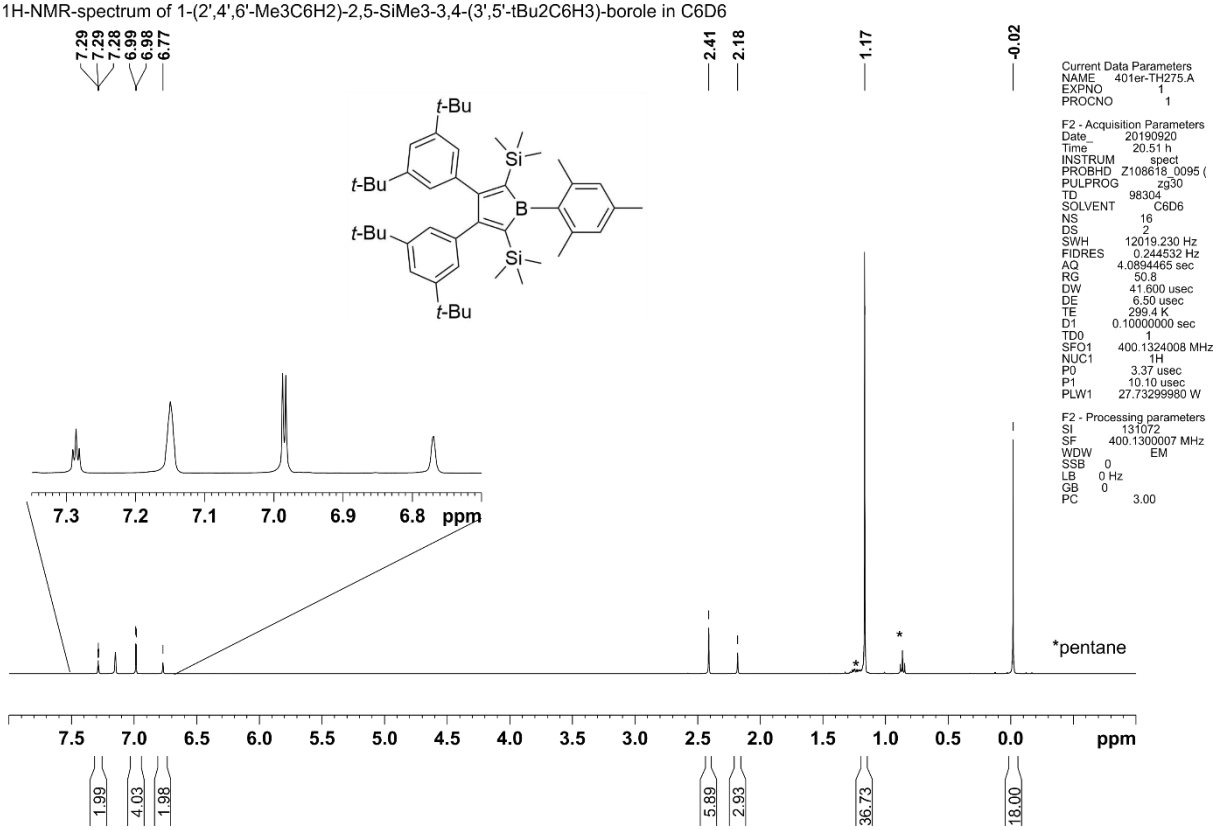
^{29}Si-INEPT (79.49 MHz, 300 K, C_6D_6): –9.2.

Elemental Analysis: $C_{47}H_{71}Si_2B$ calcd C 80.29, H 10.18; observed C 80.58 H 10.23.

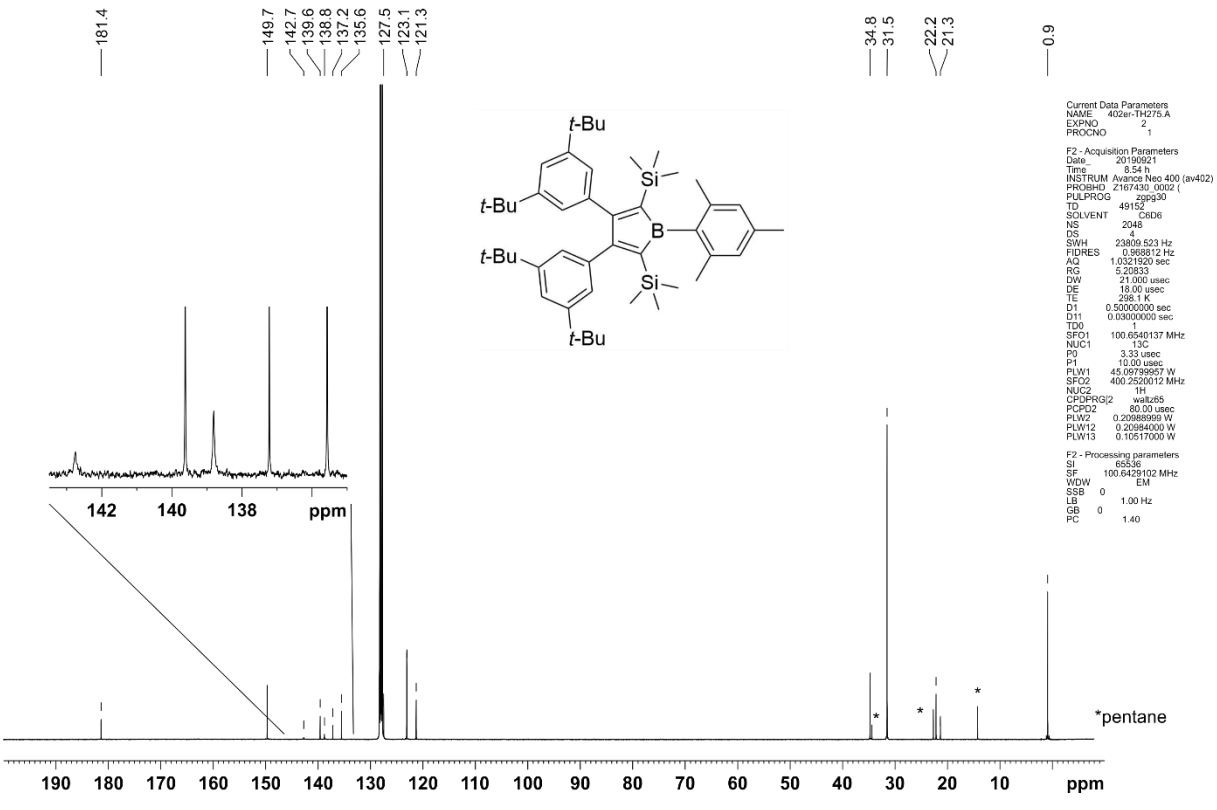
LIFDI-MS (positive mode): *m/z* =[M]$^{+}$ 702.5

Spectra Plots for Compound 6-Mes

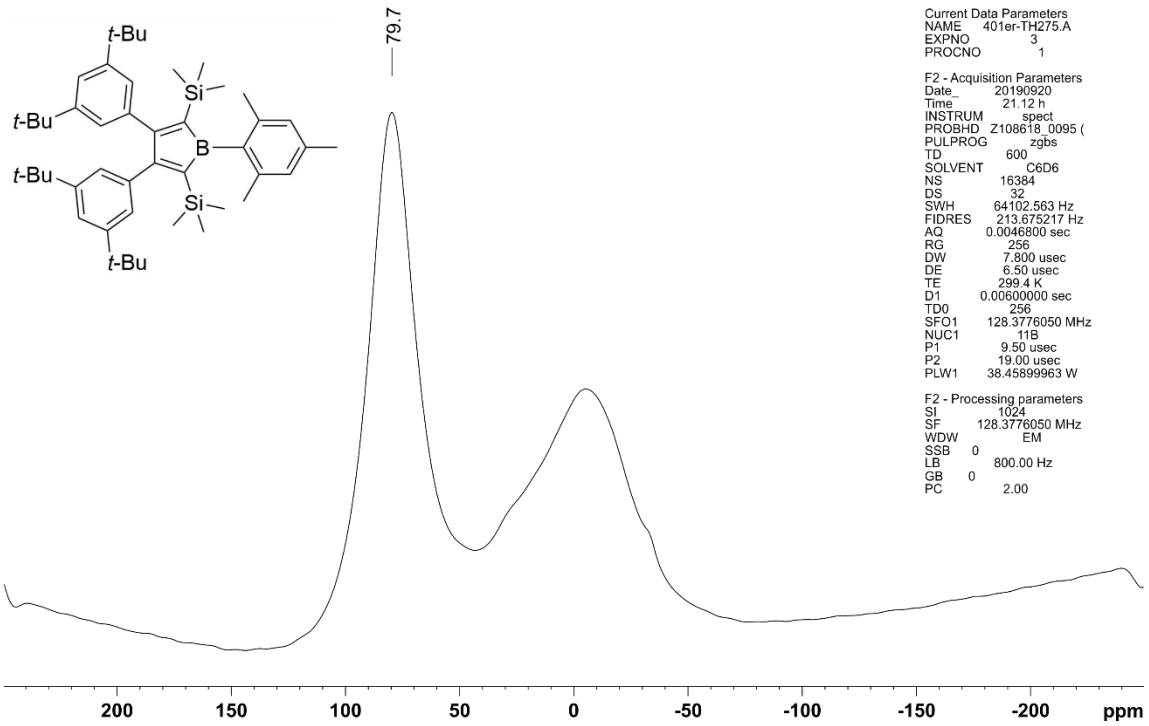
1H-NMR-spectrum of 1-(2',4',6'-Me3C6H2)-2,5-SiMe3-3,4-(3',5'-tBu2C6H3)-borole in C6D6



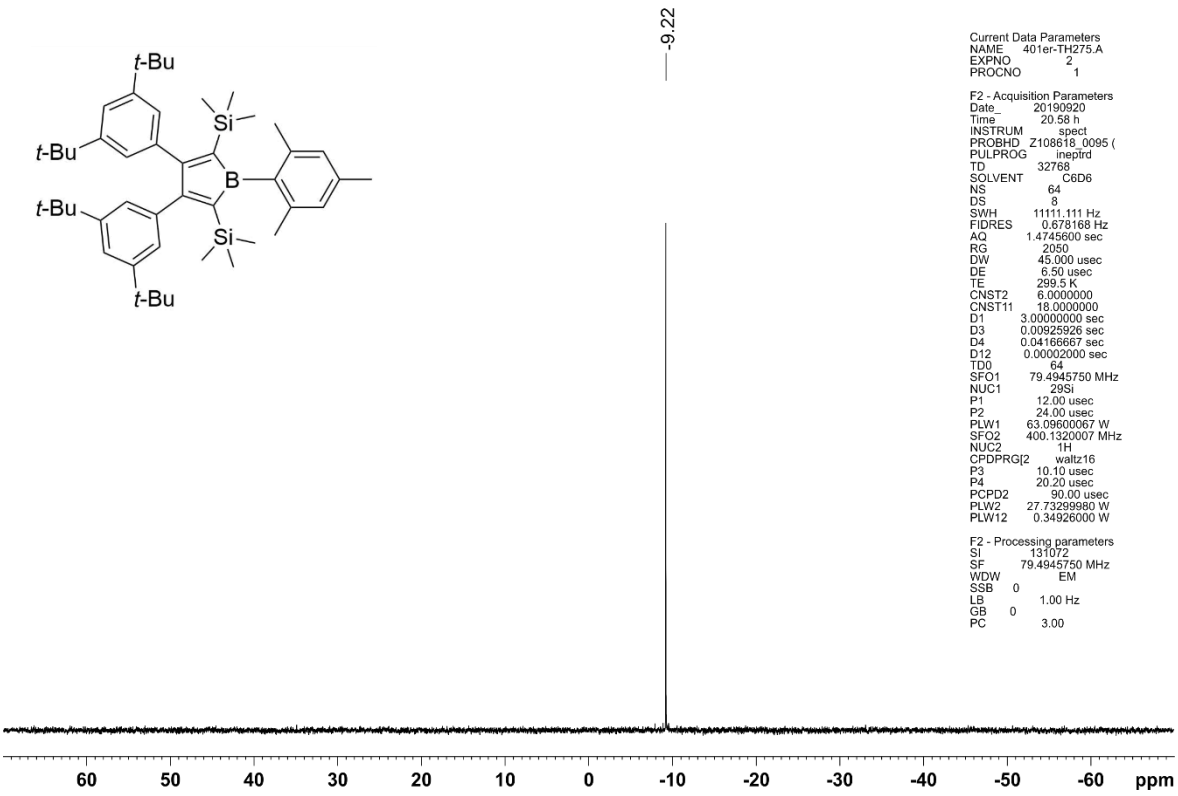
13C{1H}-NMR-spectrum of 1-(2',4',6'-Me3C6H2)-2,5-SiMe3-3,4-(3',5'-tBu2C6H3)-borole in C6D6

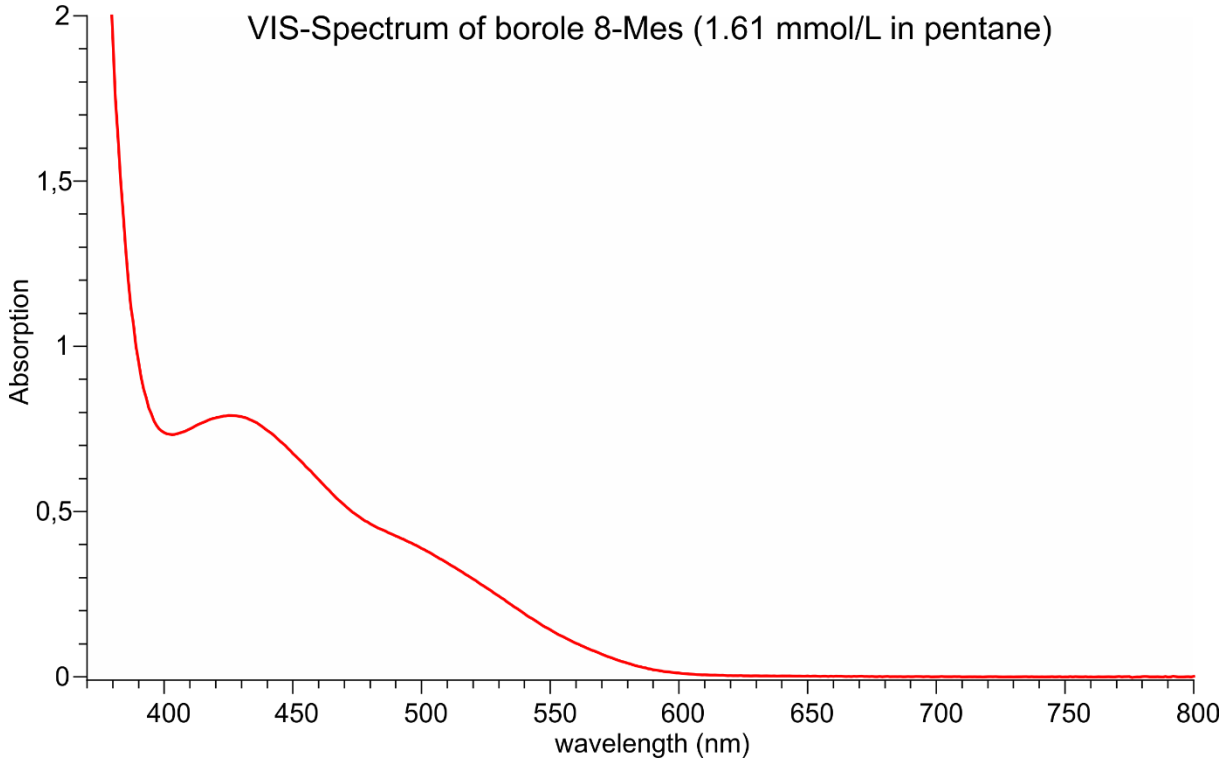


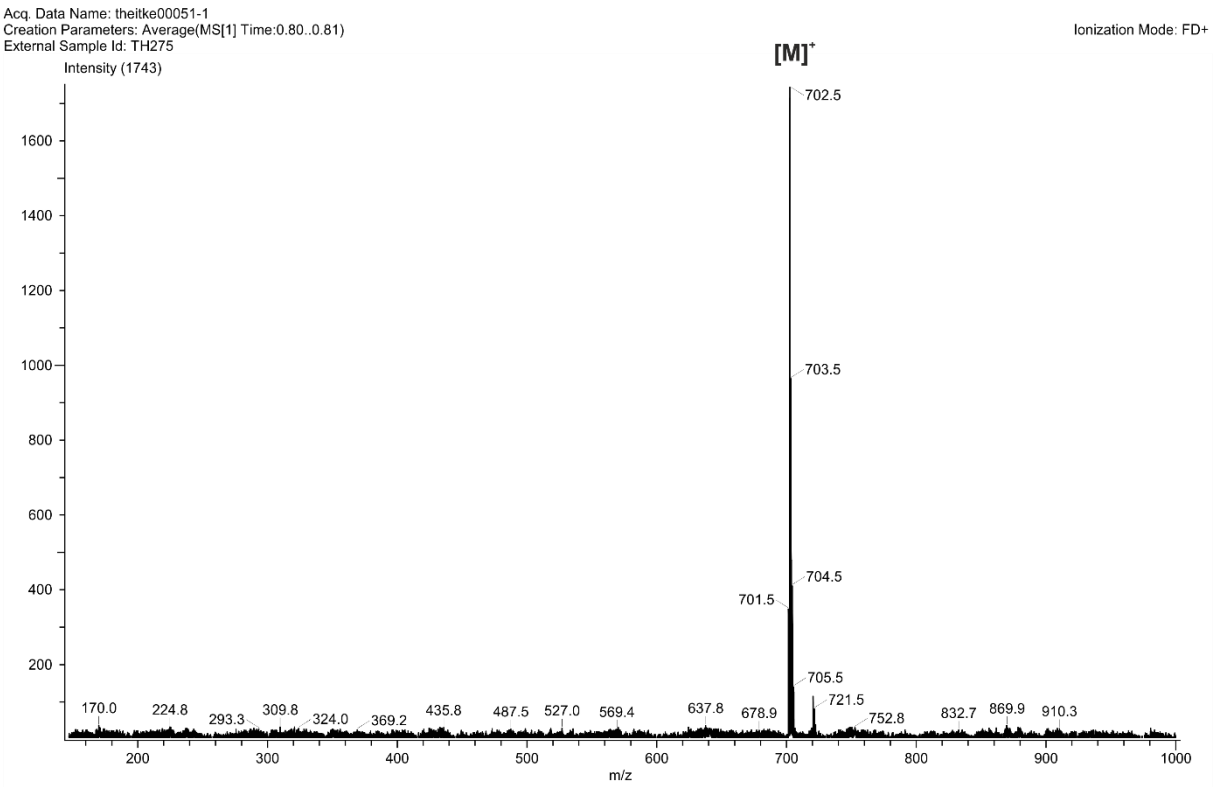
11B-NMR spectrum (background suppressed) of
1-(2',4',6'-Me3C6H2)-2,5-SiMe3-3,4-(3',5'-tBu2C6H3)-borole in C6D6



29Si-INEPT-NMR-spectrum of 1-(2',4',6'-Me3C6H2)-2,5-SiMe3-3,4-(3',5'-tBu2C6H3)-borole in C6D6




VIS-Spectrum of borole 8-Mes (1.61 mmol/L in pentane)
Absorption
wavelength (nm)
2
1,5
1
0,5
0
400
450
500
550
600
650
700
750
800


Acq. Data Name: theitke00051-1
Creation Parameters: Average(MS[1] Time:0.80..0.81)
External Sample Id: TH275
Ionization Mode: FD+
Intensity (1743)
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721.5
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832.7
869.9
910.3
170.0
224.8
293.3
309.8
324.0
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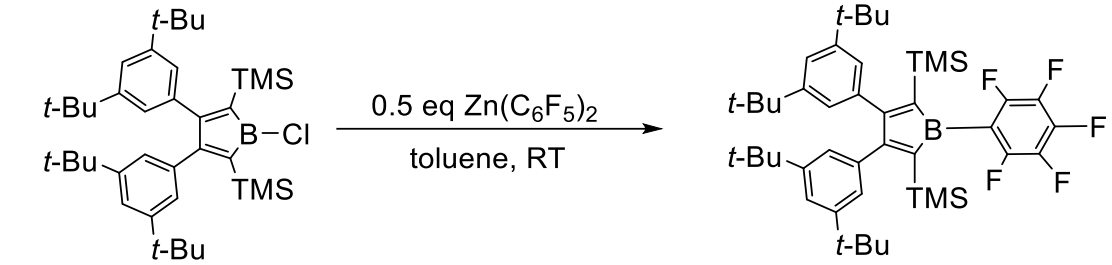
487.5
527.0
569.4
637.8
678.9
m/z

Compound 6-Ph^F



Molecular Weight: 619,33 Molecular Weight: 750,94

To a suspension of chloroborole **8** (260.7 mg, 0.42 mmol, 1 eq) in dry, degassed toluene (8 mL) in a glovebox, a solution of $Zn(C_6F_5)_2$ (84.1 mg, 0.21 mmol, 0.5 eq) in toluene (4 mL) was added dropwise over 15 minutes upon which the mixture turned dark red. The resulting mixture was stirred at ambient temperature for 16 h and all volatiles were removed in vacuo. The brown-red residue was extracted with pentane (3 mL, 2 × 1 mL) and the pentane extracts were filtered through a syringe filter equipped with a thin pad of glass fiber. After removal of pentane under reduced pressure a red-brown solid is obtained (ca. 300 mg). NMR reveals two compounds **6-Ph^F** (ca. 75 %) and an unknown side product (ca. 25 %). The solid is highly soluble in hydrocarbons and ether. Crystals grow from concentrate solutions in pentane, toluene or ether. However, the side product always co-crystallises. After three re-crystallisations from Et_2O 140 mg of **6-Ph^F** were obtained that contained 10% of unknown the impurity.

Analytical Data for Compound 6-Ph^F

NMR:

^{1}H (400.25 MHz, 299 K, C_6D_6, C_6D_5H at 7.15 ppm): 7.28 (t, $^4J_{HH}$ = 1.81 Hz, 2H, *p*-H_{Ph*}), 6.92 (d, $^4J_{HH}$ = 1.81 Hz, 4H, o-H_{Ph*}), 1.13 (s, 36H, C(*Me*)$_3$), 0.08 (s, 18H, Si(*Me*)$_3$).

^{13}C{^{1}H} (100.65 MHz, 298 K, solvent signal at 128.0 ppm): 184.8 (borole-$C_{3,4}$), 149.8 (m-C_{Ph*}), 144.9 (dm, $^1J_{FC}$ = ca. 240 Hz) presumably *p*-$C_{Ph}{}^F$), 138.7 (*ipso*-C_{Ph*}), 137.6 (br, borole-$C_{2,5}$), 122.9 (o-C_{Ph*}), 120.9 (*p*-C_{Ph*}), 34.7 ($C(CH_3)_3$), 31.4 (C(CH_3)$_3$), 0.6 (Si(CH_3)$_3$). Weak or obscured ^{13}C-NMR data did not allow unambiguous identification of the *ipso*-$C_{Ph}{}^F$, *o*-$C_{Ph}{}^F$, and *m*-$C_{Ph}{}^F$.

^{11}B (128.38 MHz, 299 K, C_6D_6): 77.4 (br, $\varpi_{1/2} \approx 2700$ Hz).

^{19}F (376.91 MHz, 298 K, C_6D_6): –130.20 (m, 2F, *ortho*), –152.23 (m, 1F, *para*), –161.12 (m, 2F, *meta*)

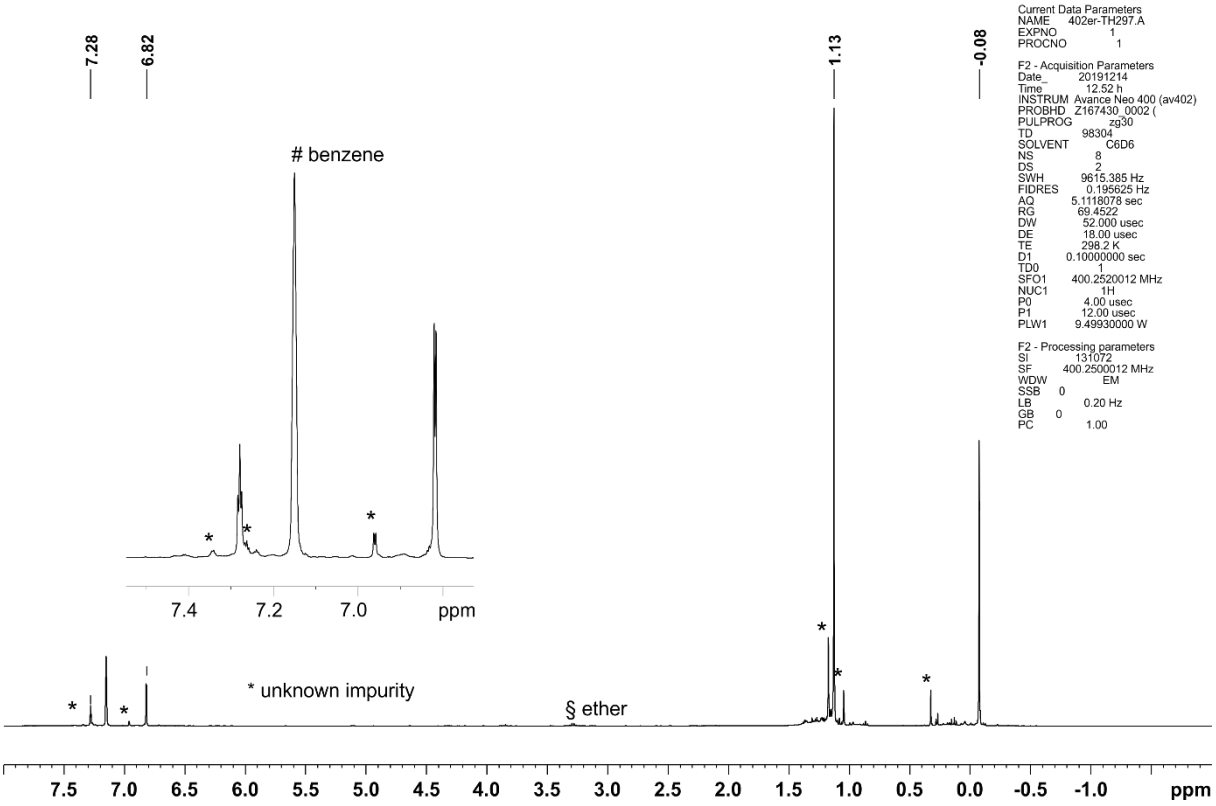
^{29}Si-INEPT (79.49 MHz, 300 K, C_6D_6): –9.2.

Elemental Analysis: due to obvious impurities, no elemental analysis was conducted.

LIFDI-MS (positive mode): *m/z* =$[M]^+$ 750.4 (major); $[M+(H_2O)]^+$. 768.4 (minor)

Spectra Plots for Compound 6-Ph^F

1H-NMR-spectrum of 1-[C6F5]-2,5-(TMS)2-3,4(3',5'-tBu2Ph)-borole in C6D6
a contamination of approx. 10% with an unknown impurity remained after several recrystallisations



Current Data Parameters
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PROCNO 1

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PULPROG zg30
TD 98304
SOLVENT C6D6
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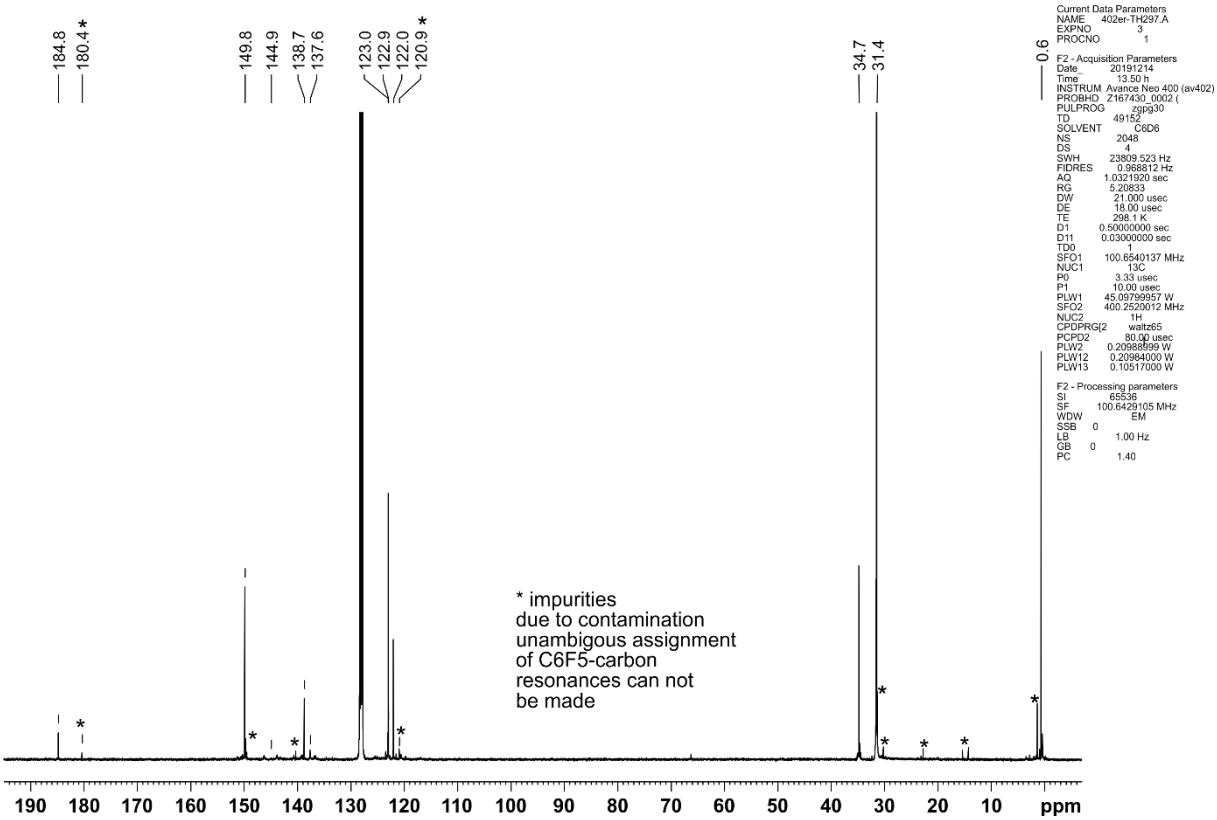
DS 2
SWH 9615.385 Hz
FIDRES 0.195625 Hz
AQ 5.1118078 sec
RG 69.4522
DW 52.000 usec
DE 18.00 usec
TE 298.2 K
D1 0.10000000 sec
TD0 1
SFO1 400.2520012 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 9.49930000 W

F2 - Processing parameters
SI 131072
SF 400.2500012 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

13C{1H}-NMR-spectrum of 1-[C6F5]-2,5-(TMS)2-3,4-[3',5'-tBu2(C6H3)]-borole in C6D6
referenced to C6D6 at 128.0 ppm



Current Data Parameters
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EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191214
Time 13.50 h
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PULPROG zgpg30
TD 49152
SOLVENT C6D6
NS 2048
DS 4
SWH 23809.523 Hz
FIDRES 0.968812 Hz
AQ 1.0321920 sec
RG 5.20833
DW 21.000 usec
DE 18.00 usec
TE 298.1 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6540137 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 45.09799957 W
SFO2 400.2520012 MHz
NUC2 1H
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PLW13 0.10517000 W

F2 - Processing parameters
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SSB 0
LB 1.00 Hz
GB 0
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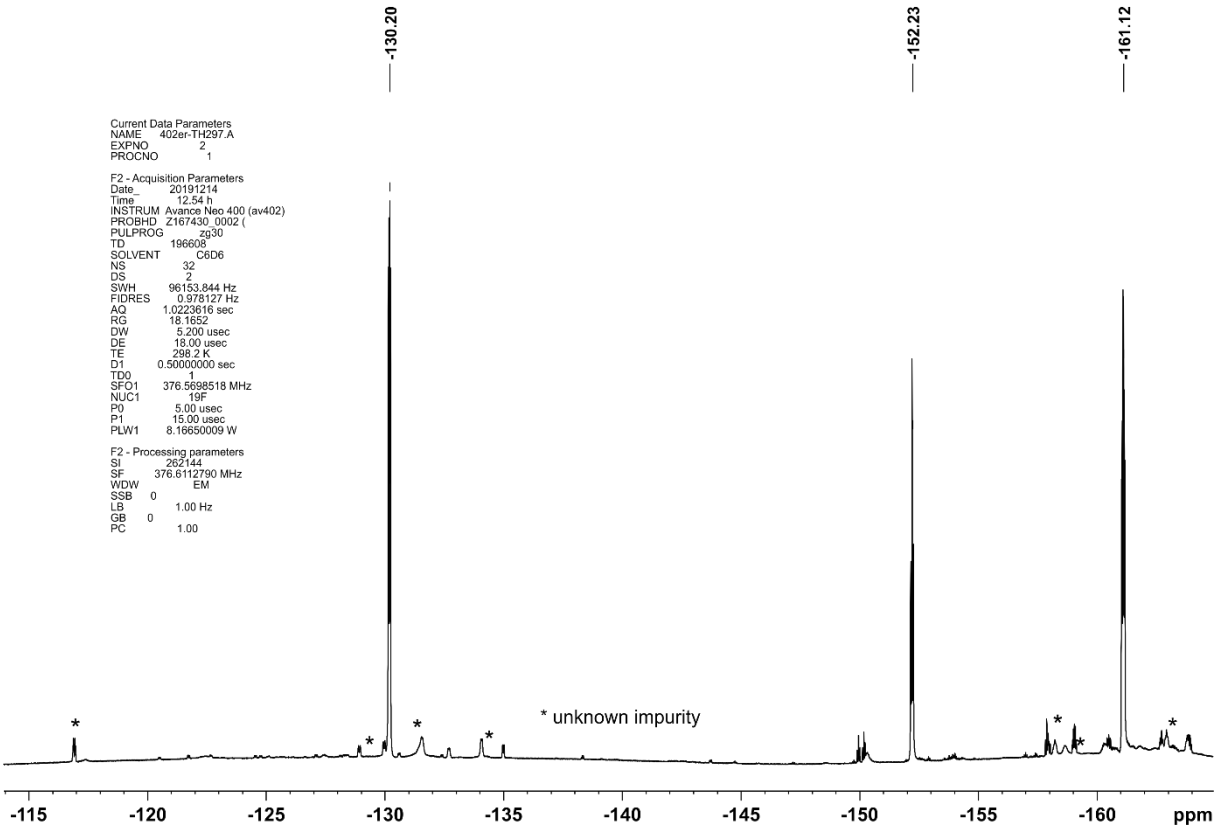
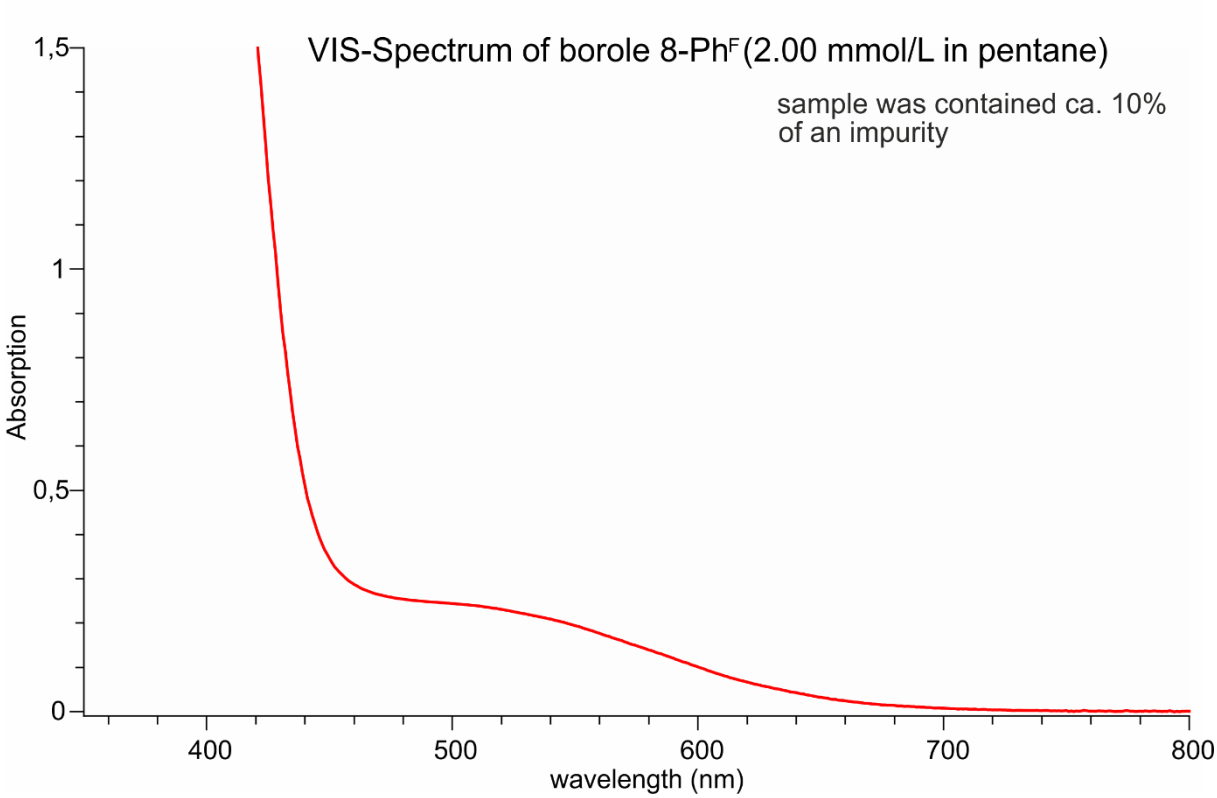
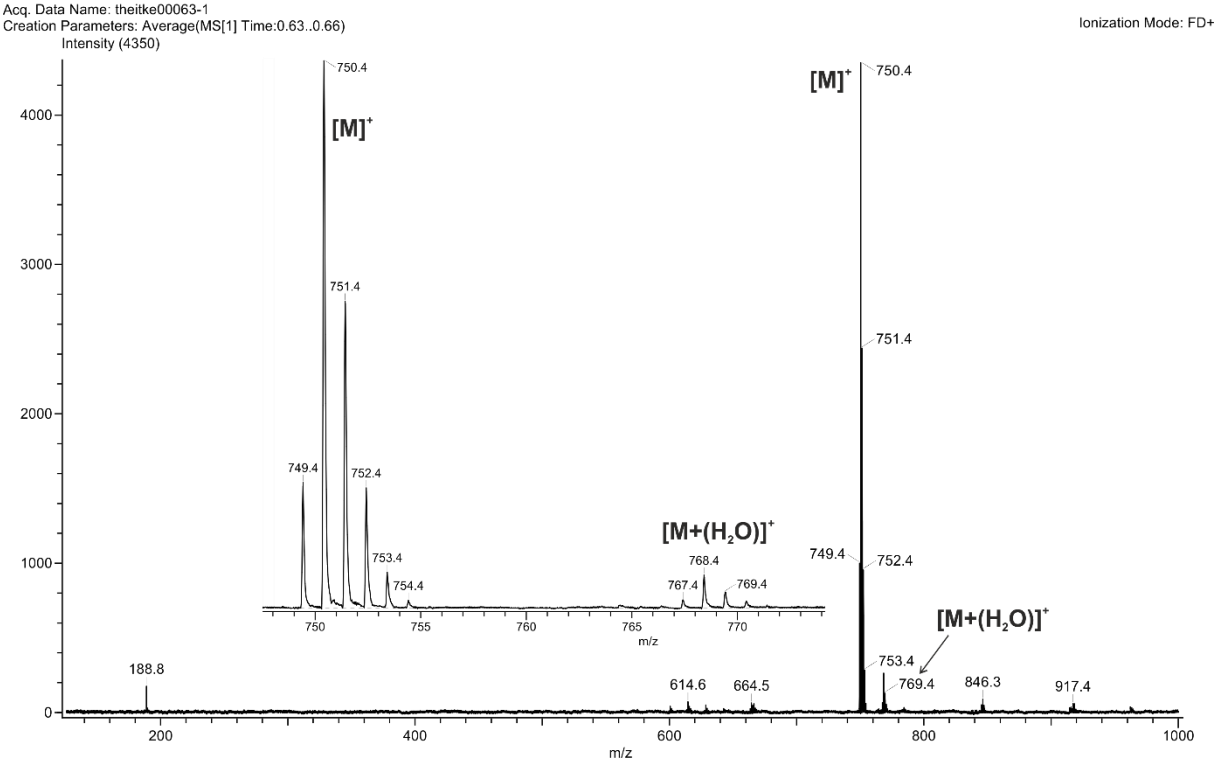
19F{1H}-NMR-spectrum of 1-[C6F5]-2,5-(TMS)2-3,4-(3',5'-tBu2Ph)-borole in C6D6

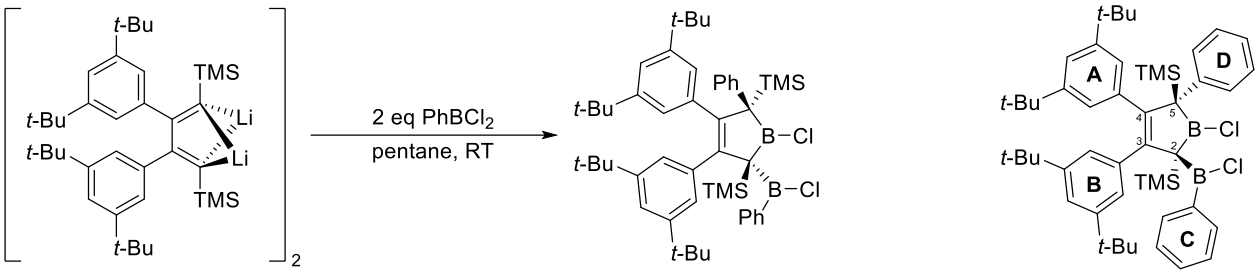




LIFDI-MS of 6-Ph^F



Compound 7-Ph



Molecular Weight: 1173,90 | Molecular Weight: 819,80 | For NMR assignment

In a glovebox, compound **3** (133.9 mg, 0.228 mmol, 1 eq) was dissolved in dry and degassed pentane (4 mL). To this solution was added a solution of $PhBCl_2$ (72.5 mg, 0.456 mmol, 2 eq) in pentane (1 mL) dropwise with a syringe over the course of approximately 3 mins. A white solid immediately precipitated and the solution turned orange. The reaction mixture was stirred at ambient temperature overnight and during this time the solution decolorized to a pale green-yellow. It was then filtered through a syringe filter equipped with a thin plug of glass fiber and the filter was washed with pentane (3 x 0.5 mL). The solvent of the filtrate was removed in vacuo to yield a pale yellow-green solid. This solid was redissolved in pentane (0.3 mL) and stored at –40 °C overnight to yield pale yellow crystals of the title compound. After decanting the solvent with a syringe and drying the crystals, compound **7** (53.6 mg, 0.065 mmol, 29 %) was isolated as a colorless powder.

Analytical Data for Compound 7-Ph

NMR:

^{1}H (300.13 MHz, 302 K, C_6D_6, C_6D_5H at 7.15 ppm): 8.73 – 8.70 (m, 2H, *o*-$H_{ar,\,C}$), 7.92 – 7.88 (m, 2H, *o*-$H_{ar,\,D}$), 7.40 (d, $^{4}J_{HH}$ = 1.79 Hz, 2H, *o*-$H_{ar,\,A}$), 7.38 – 7.21 (m, 8H), 7.14 (*p*-$H_{ar,\,B}$, superimposed by solvent signal), 7.09 (tt, $^{3}J_{HH}$ = 7.34 Hz, $^{4}J_{HH}$ = 1.15 Hz, 1H, *o*-$H_{ar,\,D}$), 1.19 (s, 18H, C(*Me*)$_3$ at Ar_A), 1.04 (s, 18H, C(*Me*)$_3$ at Ar_B), 0.26 (s, 9H, Si(*Me*)$_3$ at C_2), 0.09 (s, 9H, Si(*Me*)$_3$ at C_5).

^{13}C{^{1}H} (100.65 MHz, 298 K, solvent signal at 128.0 ppm): 149.7 (*m*-$C_{ar,A}$), 149.4 (*ipso*-$C_{ar,\,B}$), 149.1 (*m*-$C_{ar,\,B}$), 145.4 (*ispo*-$C_{ar,\,A}$), 141.3 (br, *ipso*-$C_{ar,\,C}$), 141.2 (*ipso*-$C_{ar,\,D}$), 140.6 (C_3 or C_4), 138.8 (C_3 or C_4), 137.3 (*o*-$C_{ar,\,C}$), 133.3 (*para*-$C_{ar,\,C}$), 131.3 (*o*-$C_{ar,\,D}$), 128.9 (*o*-$C_{ar,\,B}$), 128.1 (*m*-$C_{ar,\,D}$), 127.9 (*m*-$C_{ar,\,C}$), 126.8 (*o*-$C_{ar,\,A}$), 126.0 (*p*-$C_{ar,\,D}$), 120.2 (*p*-$C_{ar,\,A}$), 120.1 (*p*-$C_{ar,\,B}$), 73.9 (C_2), 61.0 (C_5), 34.8 (*C*(CH$_3$)$_3$ at Ar_A), 34.6 (*C*(CH$_3$)$_3$ at Ar_B), 31.5 (C(*C*H$_3$)$_3$ at Ar_B), 31.3 (C(*C*H$_3$)$_3$ at Ar_A), 4.1 (Si(*C*H$_3$)$_3$ at C_2), 2.6 (Si(*C*H$_3$)$_3$ at C_5)

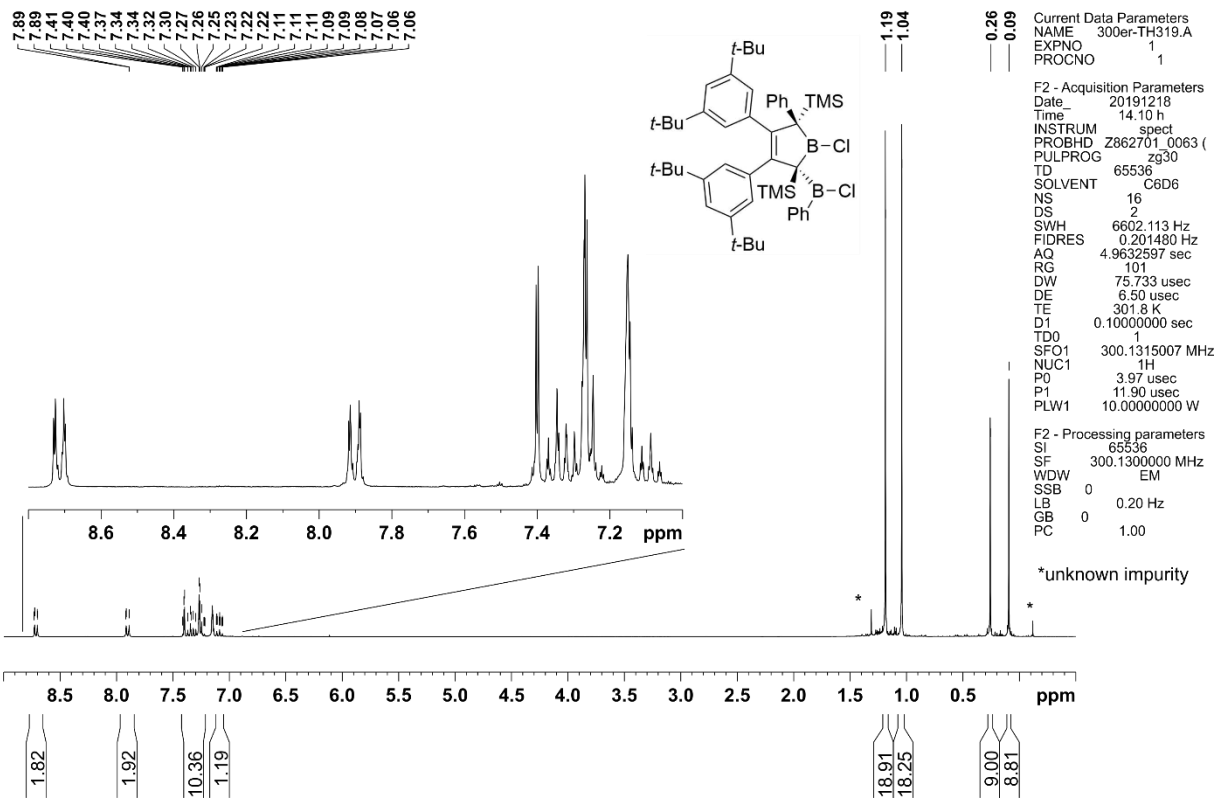
^{11}B (128.38 MHz, 299 K, C_6D_6): 70.2, 64.0.

^{29}Si (79.49 MHz, 298 K, C_6D_6): 4.8 (s), 7.8 (s).

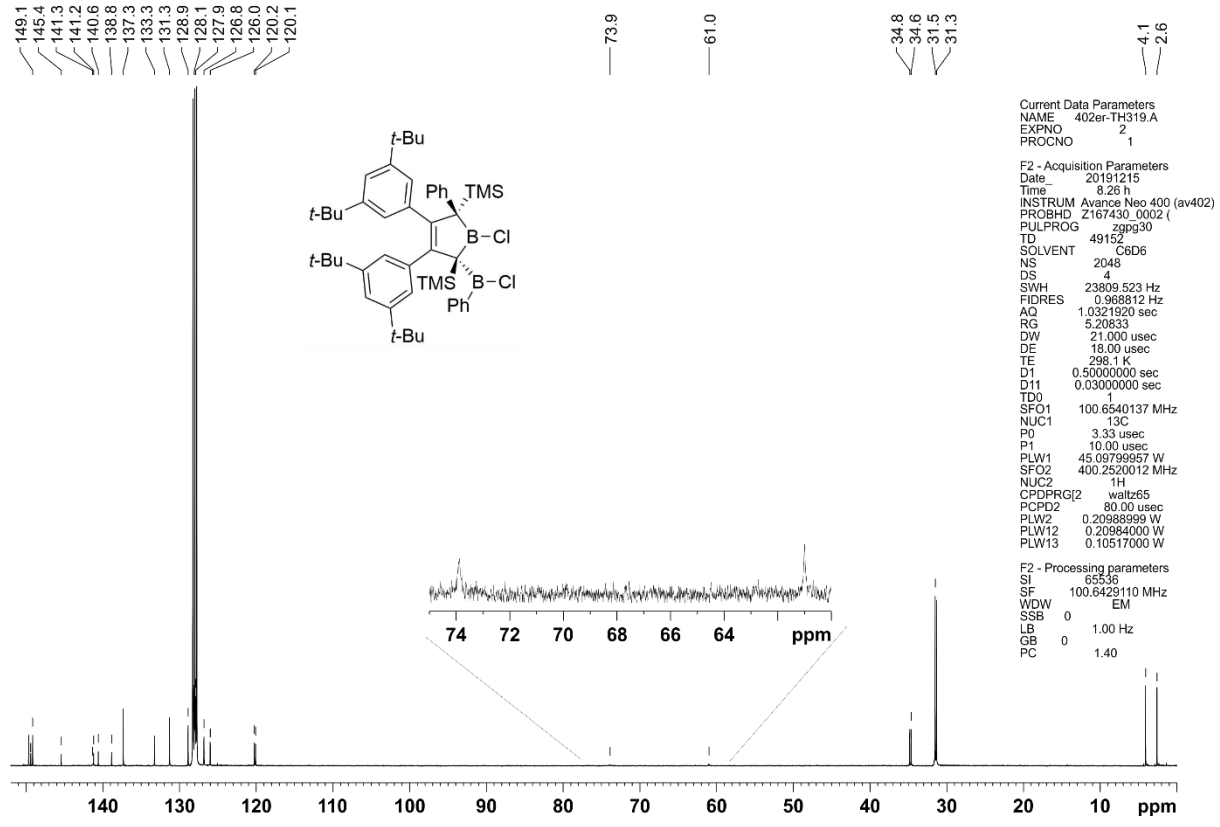
Elemental Analysis: $C_{50}H_{70}Si_2B_2Cl_2$ calcd C 73.26, H 8.61; observed C 73.21 H 8.63.

Spectra Plots for Compound 7-Ph

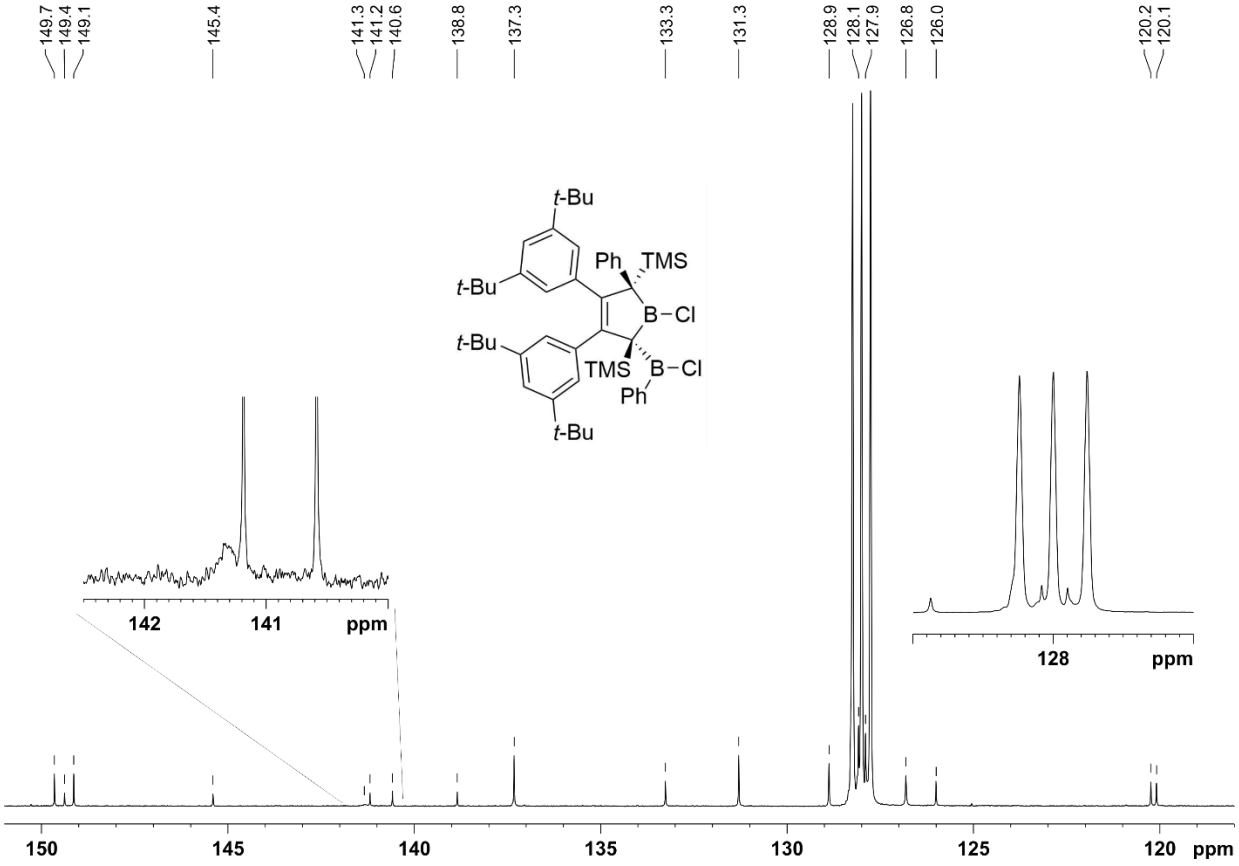
1H-NMR-spectrum of 1-Cl-2,5-(SiMe3)2-2-Ph-3,4-Ph*-5-(BClPh)-3-borolen in C6D6



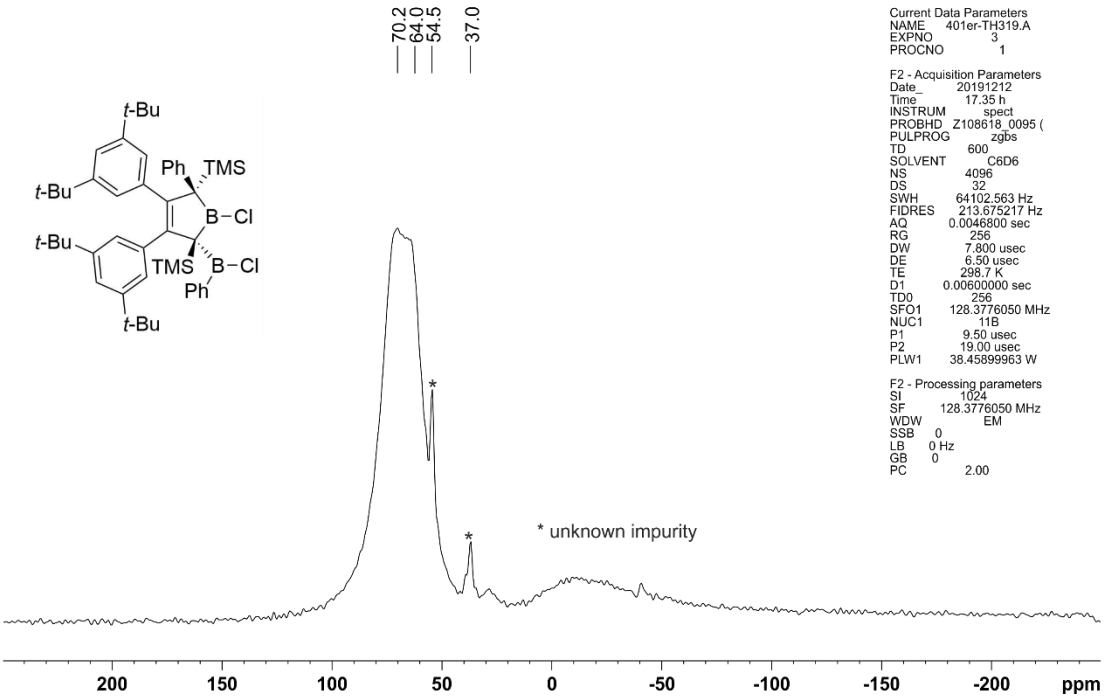
13C{1H}-NMR-spectrum of compound 1-Cl-2,5-(SiMe3)2-2-Ph-3,4-Ph*-5-(BClPh)-3-borolene in C6D6



Extension of 13C{1H}-NMR-spectrum of compound 1-Cl-2,5-(SiMe3)2-2-Ph-3,4-Ph*-5-(BClPh)-3-borolene in C6D6



11B-NMR spectrum (background suppressed) of compound 1-Cl-2,5-(SiMe3)2-2-Ph-3,4-Ph*-5-(BClPh)-3-borolene in C6D6



Current Data Parameters
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EXPNO 3
PROCNO 1

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SOLVENT C6D6
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RG 256
DW 7.800 usec
DE 6.50 usec
TE 298.7 K
D1 0.00600000 sec
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SFO1 128.3776050 MHz
NUC1 11B
P1 9.50 usec
P2 19.00 usec
PLW1 38.45899963 W

F2 - Processing parameters
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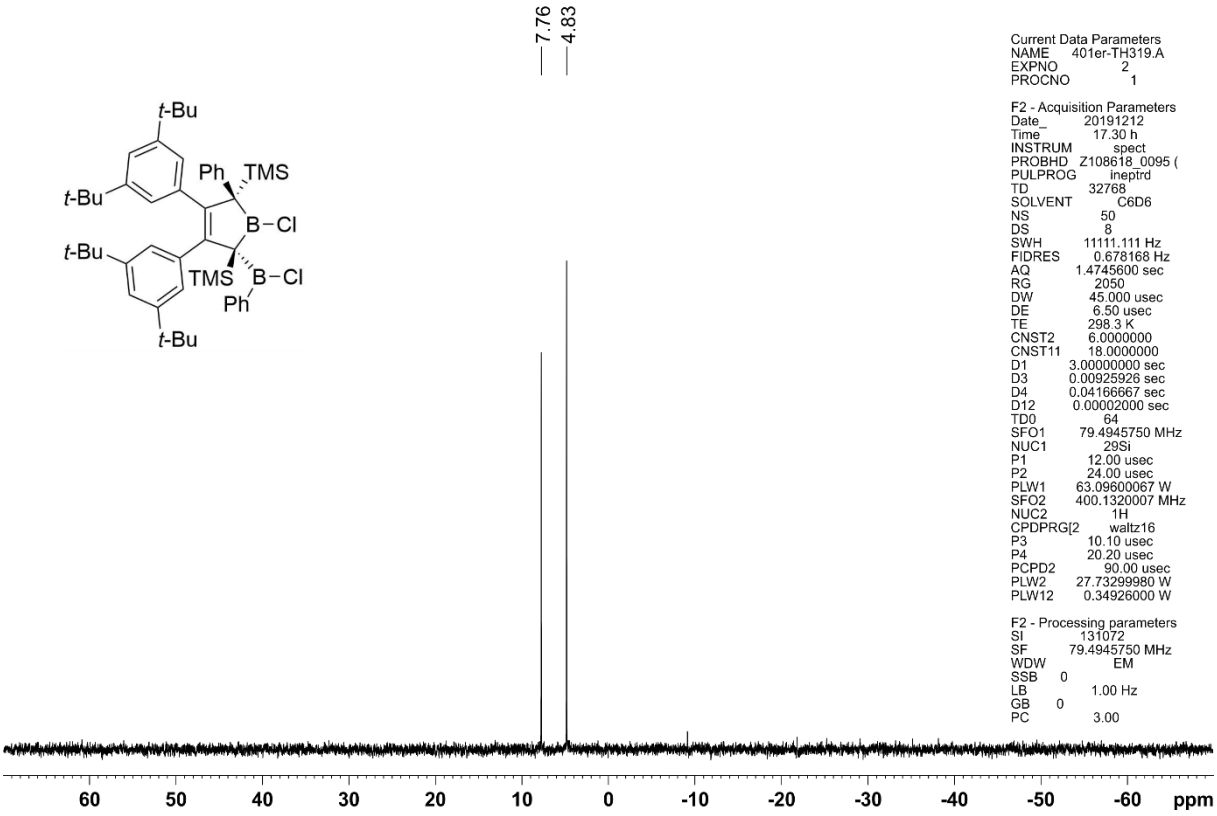
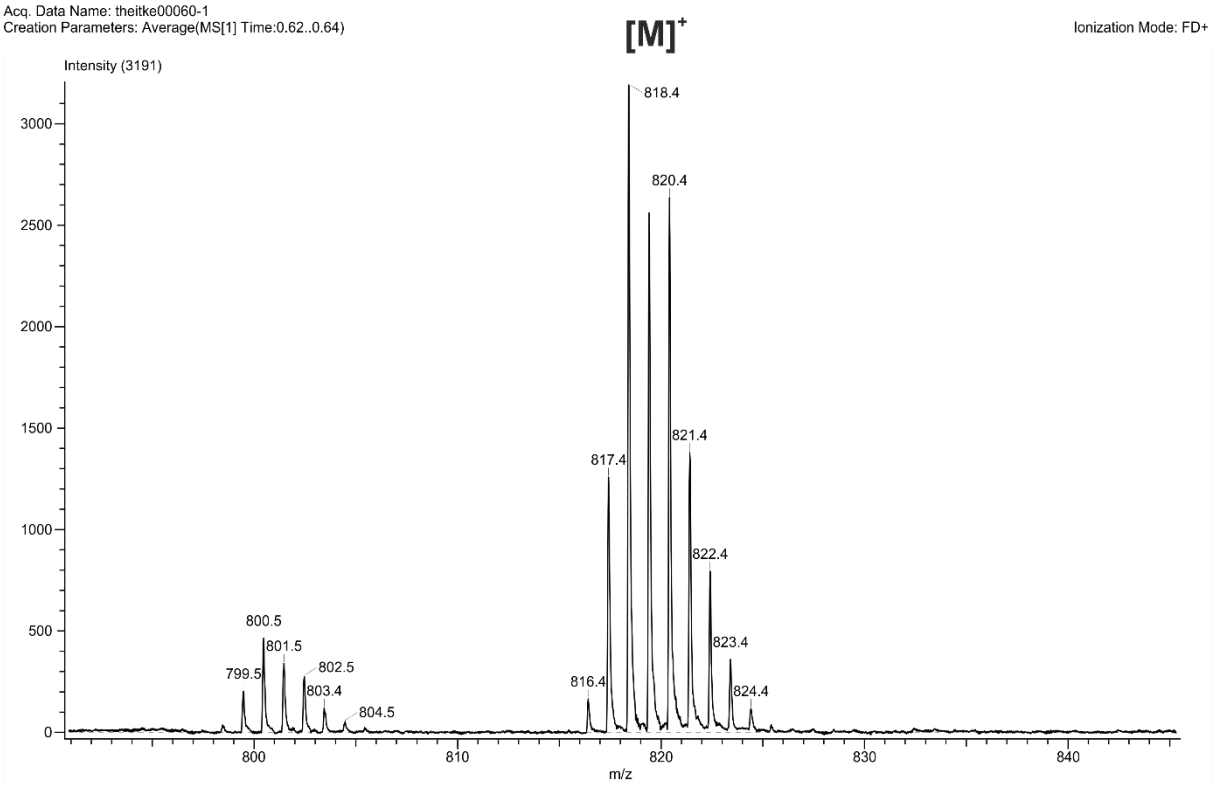
SF 128.3776050 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 2.00

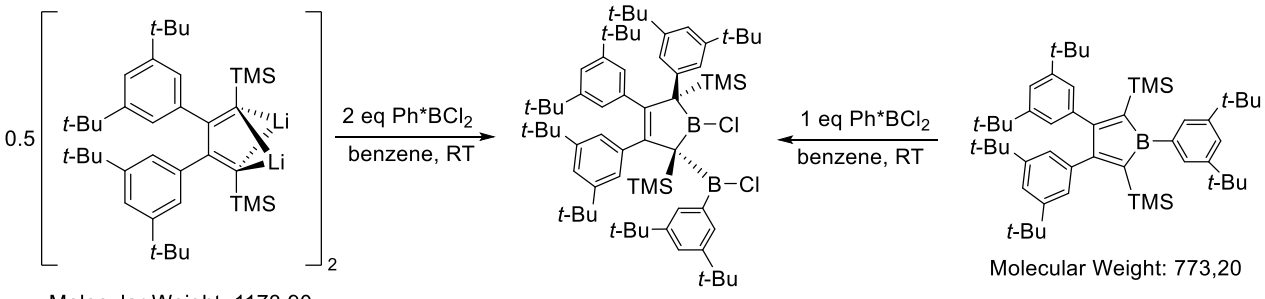
29Si-INEPT-NMR-spectrum of compound 1-Cl-2,5-(SiMe3)2-2-Ph-3,4-Ph*-5-(BClPh)-3-borolene in C6D6



Excerpt of the LIFDI-MS spectrum



Compound 7-Ph*



Molecular Weight: 1173,90

Molecular Weight: 1044,23

Molecular Weight: 773,20

Route 1 In a glovebox, compound **3** (19.9 mg, 0.034 mmol, 1 eq) was suspended in C_6D_6 (0.4 mL). To the red mixture was added a solution of Ph*BCl_2 (18.4 mg, 0.068 mmol, 2 eq) in C_6D_6 (0.2 mL) at once. The reaction progress was monitored by NMR. Conversions after 3h: ca. 40 %, after 20 h: ca 90%. After 2 days full conversion was observed. The mixture was filtered through a pad of glass fibre, and evaporated to dryness and crystallised from pentane (0.3 mL) at –40°C and the colorless thin needle-shaped crystals were isolated and dried in vacuo to give **7-Ph*** (25.3 mg, 0.024 mmol, 70%) as an off-white powder.

Route 2 In an NMR experiment, **6-Ph*** (12.4 mg, 0.016 mmol, 1 eq) was dissolved in C_6D_6 (0.4 mL) and a solution of Ph*BCl_2 (4.4 mg, 0.016 mmol, 1 eq) in C_6D_6 (0.3 mL) was added. The initially intensely dark red solution turned dark green after 5 minutes and decolorized over the course of 15 minutes. NMR monitoring revealed the reaction to be complete after half an hour and formation of **7-Ph*** as the main product (see NMR).

Analytical Data for Compound 7-Ph*

NMR:

^{1}H (400.25 MHz, 299 K, C_6D_6, C_6D_5H at 7.15 ppm): 8.24 (d, 2H, ^{4}J= 1.88 Hz, o-$H_{B\text{-}Ph*}$), 7.83 (d, 2H, ^{4}J= 1.68 Hz, o-$H_{C5\text{-}Ph*}$), 7.65 (t, 1H, ^{4}J= 1.84 Hz, o-$H_{B\text{-}Ph*}$), 7.58 (d, 2H, ^{4}J= 1.79 Hz, o-$H_{C3\text{-}Ph*}$), 7.56 (d, 2H, ^{4}J= 1.79 Hz, o-$H_{C4\text{-}Ph*}$), 7.45 (t, 1H, ^{4}J= 1.67 Hz, o-$H_{C5\text{-}Ph*}$), 7.29 (t, 1H, ^{4}J= 1.80 Hz, o-$H_{C4\text{-}Ph*}$), 7.27 (t, 1H, ^{4}J= 1.79 Hz, o-$H_{C3\text{-}Ph*}$), 1.46 (s, 18H, CMe_3(C5-Ph*)), 1.38 (s, 18H, CMe_3(B-Ph*)), 1.26 (s, 18H, CMe_3(C3-Ph*)), 1.21 (s, 18H, CMe_3(C4-Ph*)), 0.32 (s, 9H, SiMe_3(C5)), 0.00 (s, 9H, SiMe_3(C2)).

^{13}C{^{1}H} (100.65 MHz, 298 K, solvent signal at 128.0 ppm): 150.3 (C_3=C_4), 149.7 (*m*-C_{Ph*}), 149.6 (*m*-C_{Ph*}), 149.6 (*m*-C_{Ph*}), 149.4 (*m*-C_{Ph*}), 146.1 (C_3=C_4), 142.1 (*ipso*-$C_{B\text{-}Ph*}$), 140.5 (*ipso*-C_{Ph*}), 139.8 (*ipso*-C_{Ph*}), 139.7 (*ipso*-C_{Ph*}), 128.4 (*o*-$C_{B\text{-}Ph*}$), 127.9 (*p*-$C_{C3\text{-}Ph*}$), 127.5 (*p*-$C_{C4\text{-}Ph*}$), 125.5 (*o*-$C_{C5\text{-}Ph*}$), 125.1 (*p*-$C_{B\text{-}Ph*}$), 120.5 (*o*-$C_{C4\text{-}Ph*}$), 120.2 (*o*-$C_{C3\text{-}Ph*}$), 119.2 (*p*-$C_{C5\text{-}Ph*}$), 72.9 (C_2), 62.7 (C_5), 35.3 (*C*Me_3-B-Ph*), 35.2 (*C*Me_3-C_5-Ph*), 34.9 (*C*Me_3-C_3-Ph*), 34.9 (*C*Me_3-C_4-Ph*), 31.8 (CMe_3-C_5-Ph*), 31.7 (CMe_3-Ph*), 31.6 (CMe_3-Ph*), 31.6 (CMe_3-Ph*), 3.6 (Si$Me_{3,}$ C_2), 3.1 (Si$Me_{3,}$ C_5).

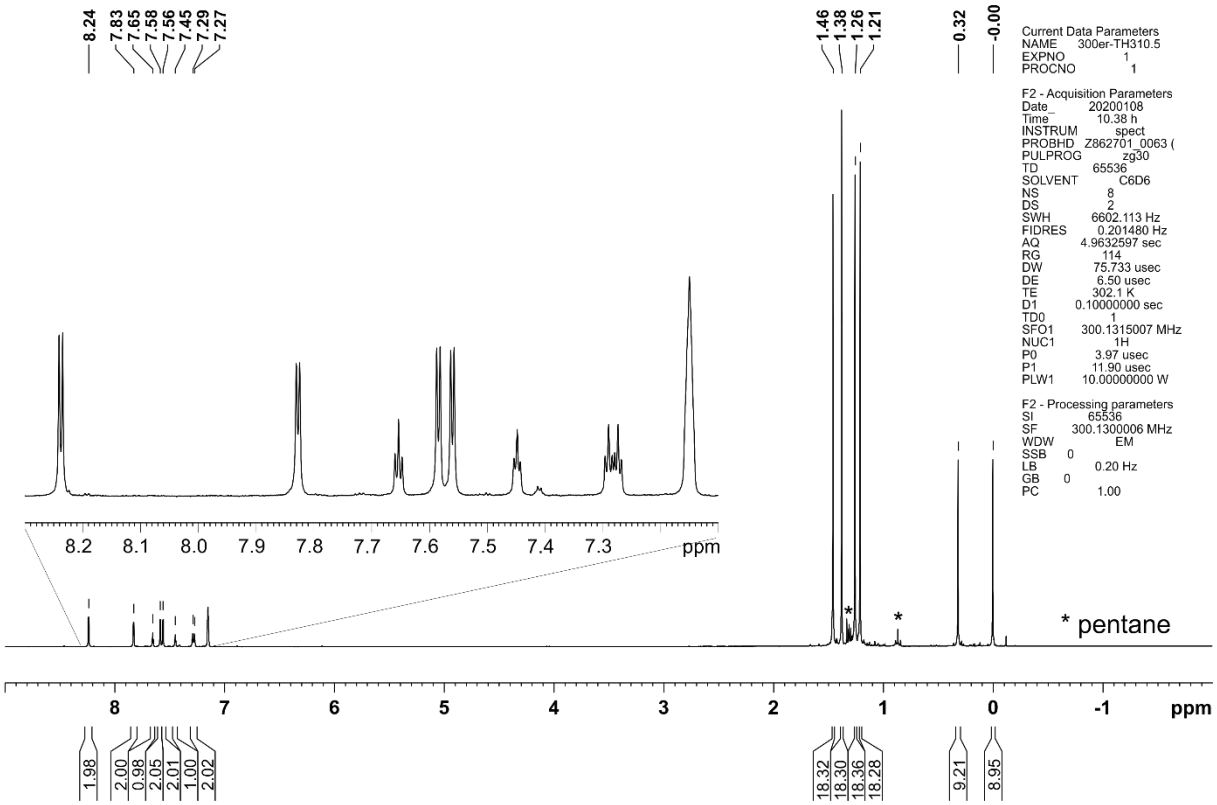
^{11}B (128.38 MHz, 299 K, C_6D_6): one broad major signal at 71.2 (br, $\varpi_{1/2}$ ≈ 2900 Hz), minor signal at 37.6 ppm.

^{29}Si-INEPT (79.49 MHz, 300 K, C_6D_6): 5.6, 3.7.

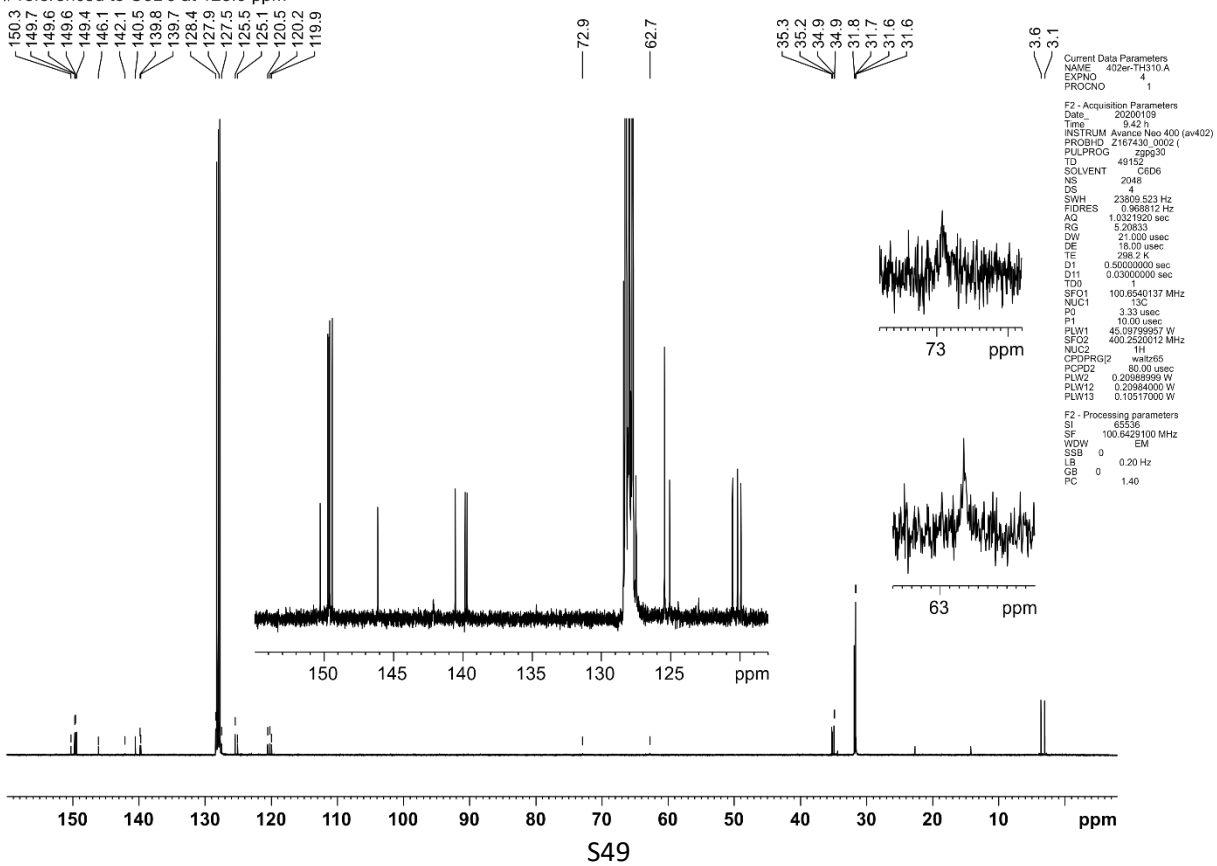
Elemental Analysis: $C_{66}H_{102}Si_2B_2Cl_2$ calcd C 75.91, H 9.85; observed C 76.42 H 9.85.

Spectra Plots for 7-Ph*

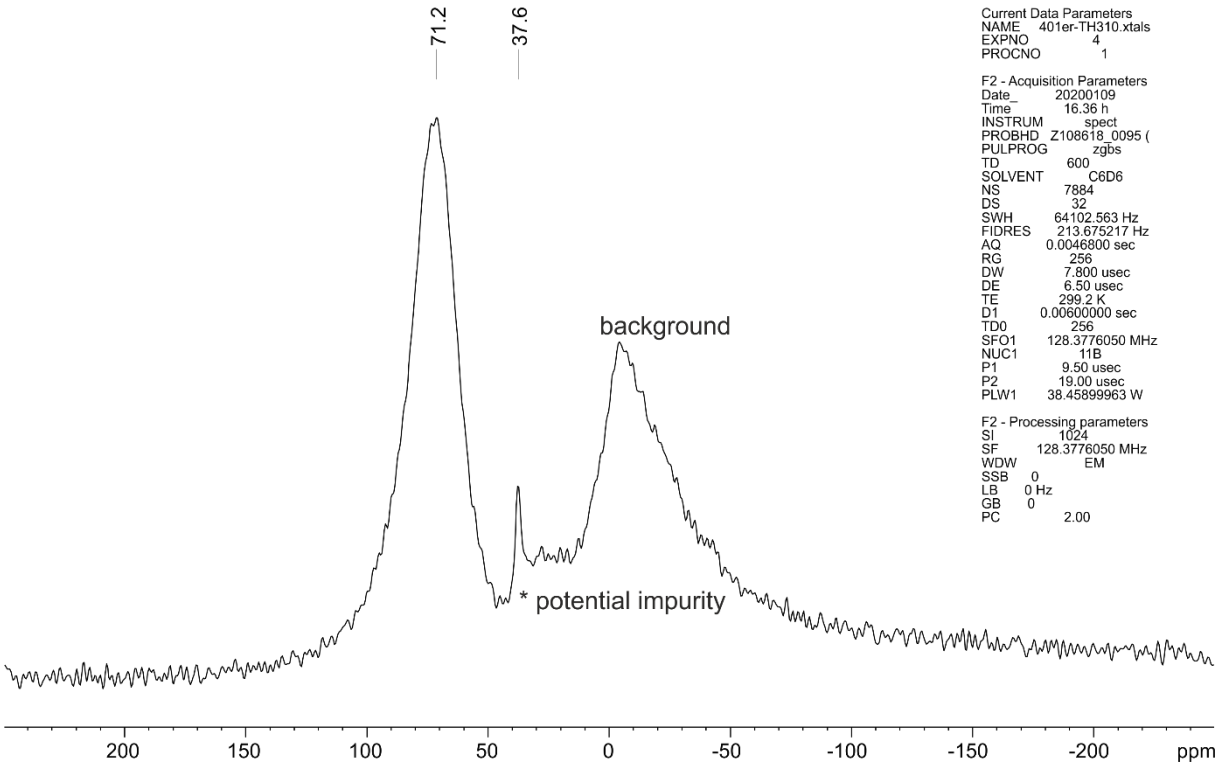
1H-NMR-spectrum of 2-Boryl-3-borolene 7-Ph* in C6D6



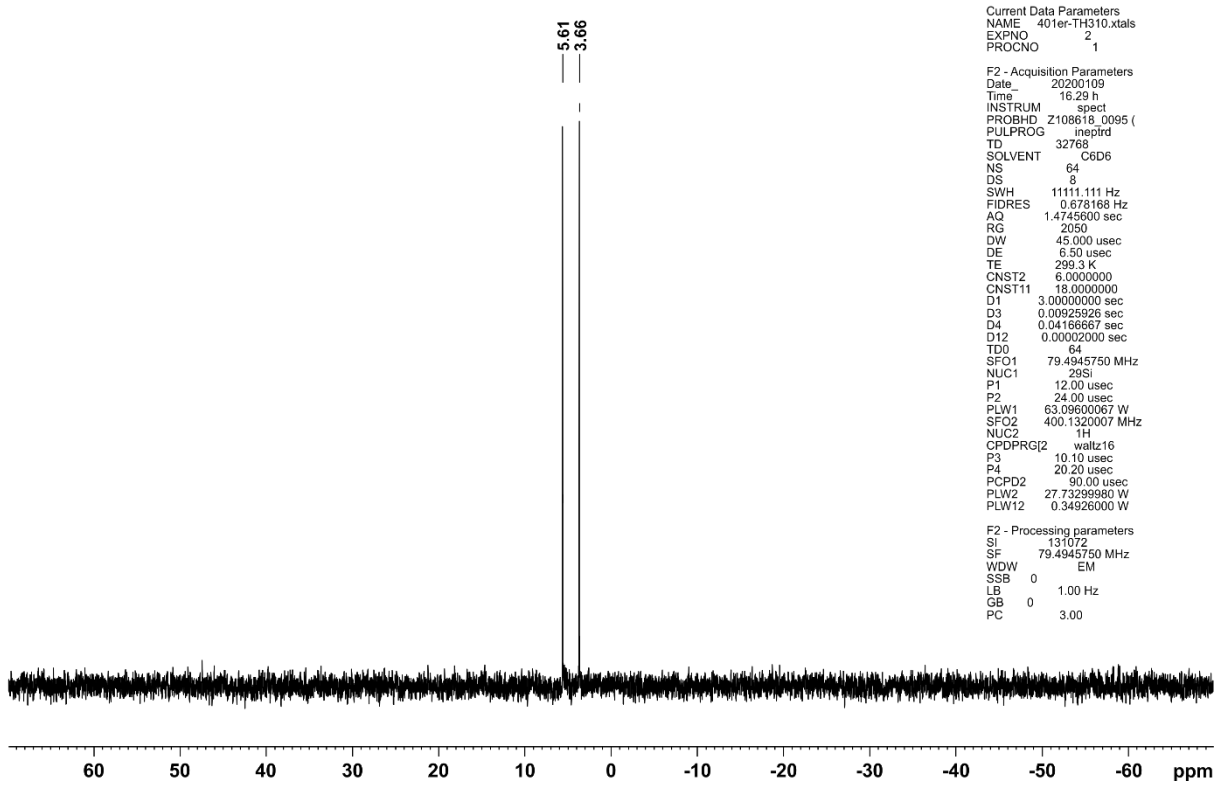
13C{1H}-NMR-spectrum of 7-Ph (Ph*-2-Boryl-3-Borolene) in C6D6
referenced to C6D6 at 128.0 ppm



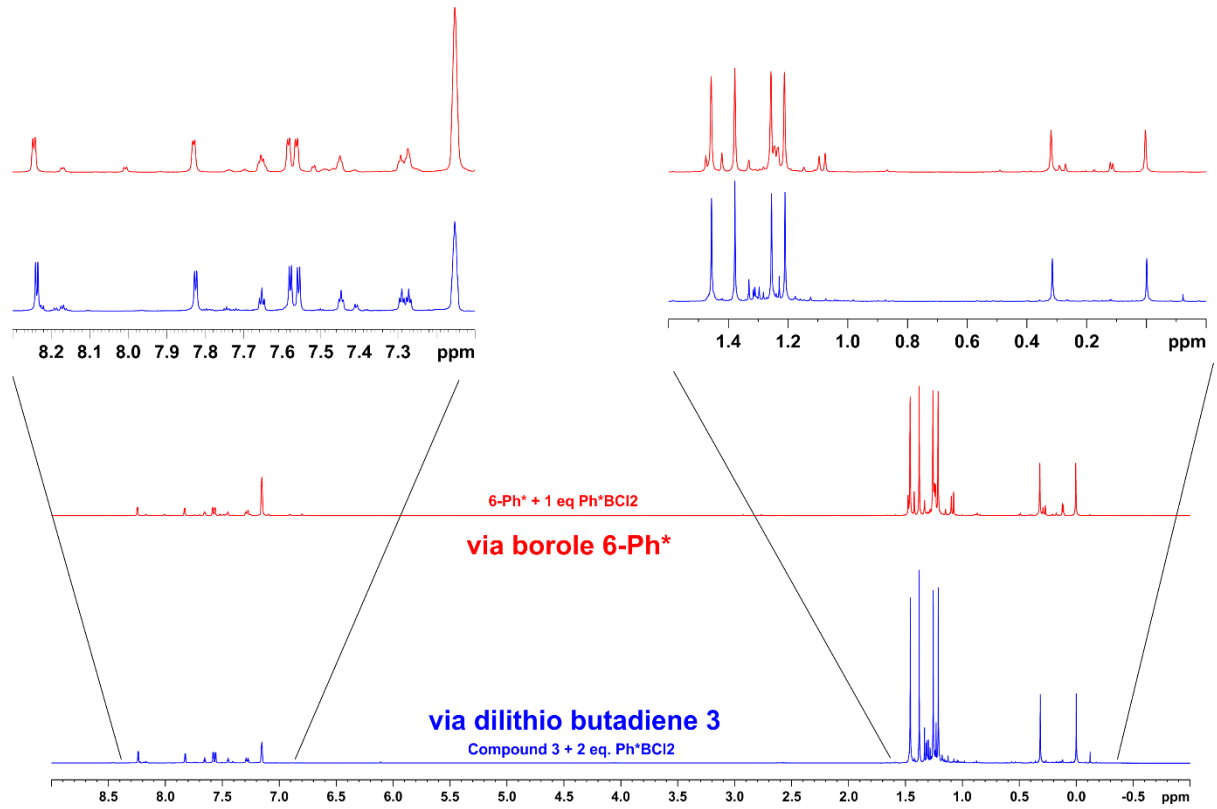
11B-NMR spectrum (background suppressed) of 7-Ph* (Ph*-2-Boryl-3-borolene)in C6D6



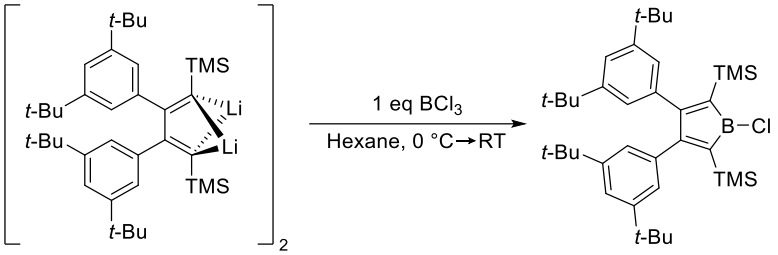
29Si-Inept-NMR-spectrum of 7-Ph* (Ph*-2-Boryl-3-borolene) in C6D6



Comparison of different reaction routes to 7-Ph*



Compound 8



Molecular Weight: 1173,90 Molecular Weight: 619,33

In a Schlenk flask compound **3** (1.54 g, 2.62 mmol, 1 eq) was dissolved in dry and degassed hexane (35 mL). The solution was cooled to 0°C and BCl_3 (2.62 mL, 1 M in hexane, 2.62 mmol, 1 eq) was added with a syringe. The mixture instantly became turbid and turned from deep red to brown. The mixture was allowed to warm to ambient temperature and was stirred overnight. The solvent was then removed in vacuo and the remaining red-brown solid was transferred into a glovebox. The solid was washed with hexane (2 x 15 mL) until the washing phase had a red colour. The remaining red solid was extracted with hexane (80 mL in total) until the remaining solid was white. The solvent of the red solution was removed in vacuo to yield compound **6** (0.95 g, 1.53 mmol, 60 %) as a red solid.

Crystals suitable for X-ray analysis were grown from a saturated hexane solution at –40 °C.

Analytical Data for Compound 8

^{1}H (400.25 MHz, 298 K, C_6D_6, C_6D_5H at 7.15 ppm): 7.25 (t, $^{4}J_{HH}$ = 1.79 Hz, 2H, *p*-H_{ar}), 6.76 (d, $^{4}J_{HH}$ = 1.79 Hz, 4H, *o*-H_{ar}), 1.15 (s, 36H, C(*Me*)$_3$), 0.17 (s, 18H, Si(*Me*)$_3$).

^{13}C{^{1}H} (100.65 MHz, 298 K, solvent signal at 128.0 ppm): 182.1 (borole-$C_{3,4}$), 149.7 (*m*-C_{ar}), 138.8 (*ipso*-C_{ar}), 134.8 (br, borole-$C_{2,5}$), 122.8 (*o*-C_{ar}), 121.3 (*p*-C_{ar}), 34.7 (*C*(CH$_3$)$_3$), 31.5 (C(*C*H$_3$)$_3$), 1.0 (Si(*C*H$_3$)$_3$).

^{11}B (128.38 MHz, 298 K, C6D6): 70.8 (br, $\varpi_{1/2}$ ≈ 1370 Hz).

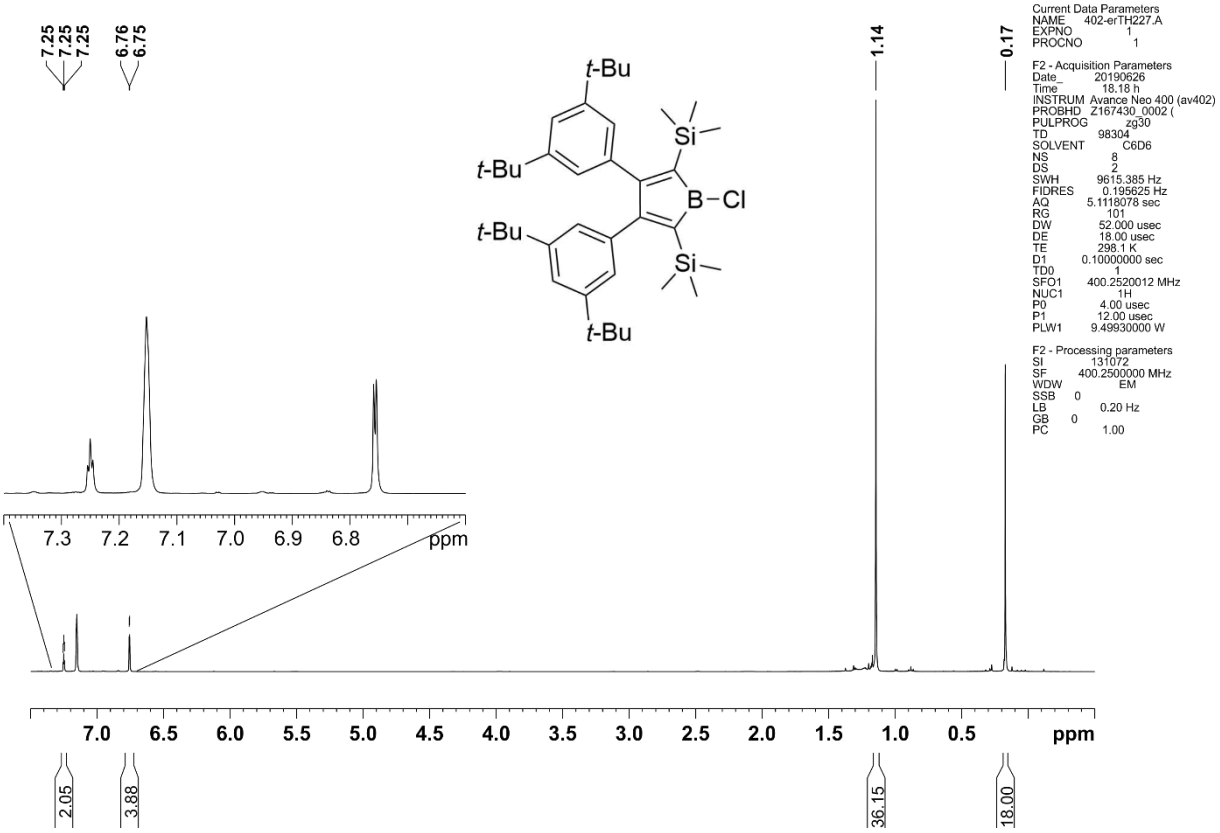
^{29}Si (79.49 MHz, 301 K, C_6D_6): –9.0.

Elemental Analysis: $C_{38}H_{60}BSi_2Cl$ calcd C 73.70, H 9.77; observed C 73.86, H 9.82.

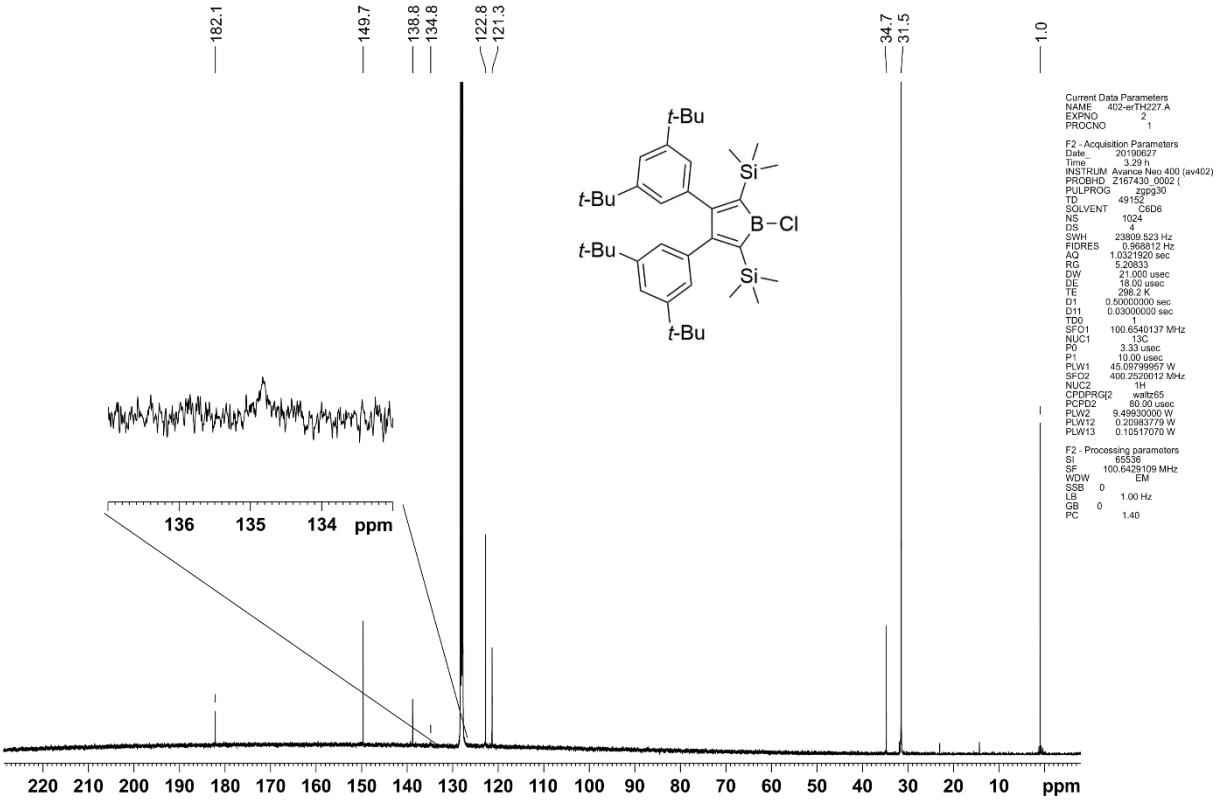
LIFDI-MS (positive mode): *m/z* =[M]$^+$ 600.4 (major); [M+(OH)-(Cl)]$^+$. 618.3 [M]$^+$ (minor).

Spectra Plots for Compound 8

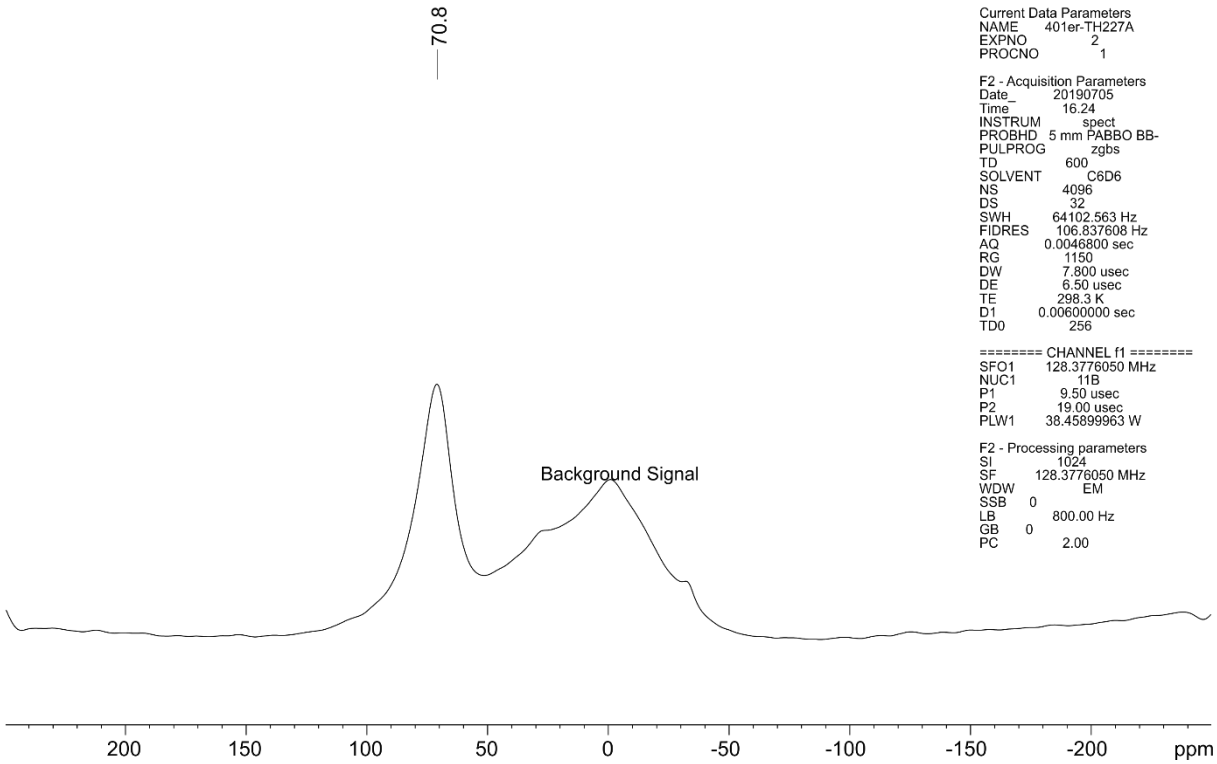
1H-NMR-spectrum of 1-Cl-2,5-(SiMe3)2-3,4-(3',5'-tBu2(C6H3))2-borole in C6D6



13C{1H}-NMR-spectrum of 1-Cl-2,5-(SiMe3)2-3,4-(3',5'-tBu2(C6H3))2-borole in C6D6



11B-NMR spectrum (background suppressed) of 1-Cl-2,5-(SiMe3)2-3,4-(3',5'-tBu2(C6H3))2-borole in C6D6

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DE             6.50 usec
TE             298.3 K
D1          0.00600000 sec
TD0              256

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P1              9.50 usec
P2             19.00 usec
PLW1       38.45899963 W

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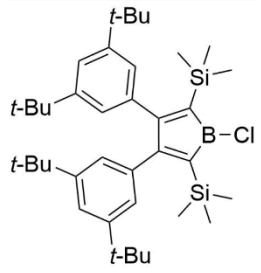
29Si-INEPT-NMR-spectrum of 1-Cl-2,5-(SiMe3)2-3,4-(3',5'-tBu2(C6H3))-borole in C6D6

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PROCNO            1

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CNST11        18.0000000
D1          3.00000000 sec
D3          0.00925926 sec
D4          0.04166667 sec
D12         0.00002000 sec
TD0              64

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P2              24.00 usec
PLW1       63.09600067 W

======== CHANNEL f2 ========
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NUC2             1H
CPDPRG[2       waltz16
P3              10.10 usec
P4              20.20 usec
PCPD2           90.00 usec
PLW2       27.73299980 W
PLW12       0.34926000 W

F2 - Processing parameters
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SF         79.4945750 MHz
WDW              EM
SSB      0
LB            1.00 Hz
GB       0
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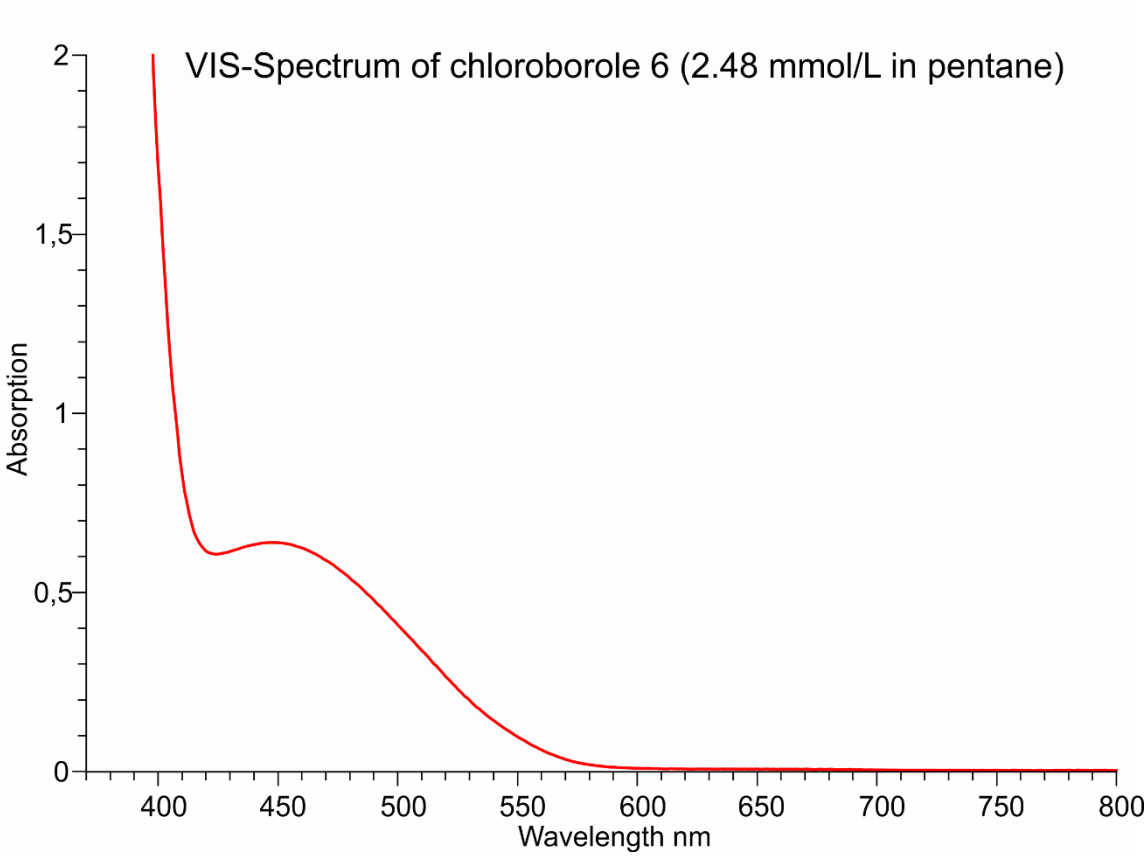
VIS-Spectrum of chloroborole 6 (2.48 mmol/L in pentane)
Absorption
Wavelength nm
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1
0,5
0
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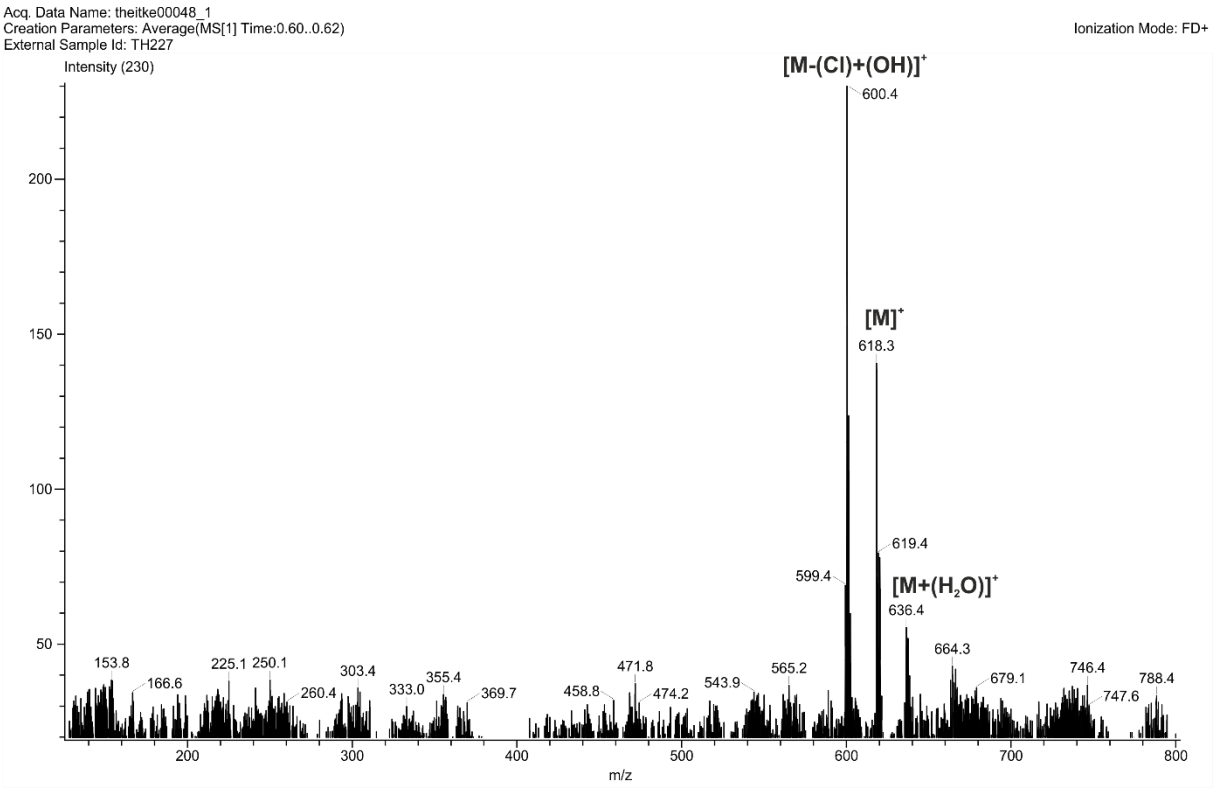
450
500
550
600
650
700
750
800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[M]+
618.3
619.4
599.4
[M+(H2O)]+
636.4
664.3
153.8
166.6
225.1
250.1
260.4
303.4
333.0
355.4
369.7
458.8
471.8
474.2
543.9
565.2
679.1
746.4
747.6
788.4
m/z

Crystallographic Details

General Data Acquisition and Processing

X-ray data for **1, 2-E,Z, 3, 4, 5, 6-Ph*, 6-Mes, 6-Ph^F, 7-Ph and 8** were collected on Bruker APEX II CCD diffractometers with either Mo or Ag Kα radiation. The data were integrated using SAINT implemented in Brukers APEX3 programme suite.[13] SADABS was used for multi-scan absorption correction.[14] Structure solution was performed with SHELXT[15] and refined using SHELXL[16] along the graphical user interphase of ShelXle.[17] In some cases DSR has been applied to treat disordered solvent molecules.[18] All hydrogen atoms were placed with a riding model. Further details on the individual data sets are tabulated in the analytical section of each compound.

X-ray data acquisition for **7** and **8-Ph** was attempted. Data collection for **7** was aborted preliminary and no full data set to allow publication could be collected. However, the data allowed to preliminarily assign the structure which is in perfect agreement with NMR spectroscopic data. Thin needle-shaped crystals of **8-Ph** were repeatedly found to be twinned and diffract insufficiently.

Crystallographic and Refinement Details 1

A *t*-Bu group was found to be disordered over two positions and modelled using SAME, SIMU and RIGU restraints.

Crystallographic and Refinement Details 2-E,Z

Three *t*-Bu group were found to be disordered over two positions and modelled using SAME, SIMU and RIGU restraints. The E,Z-Isomer of compound **2** was not used for the syntheses described in this manuscript and only forms as a minor side product when deviating from the synthetic procedure to obtain the **2-Z,Z** isomer discussed in this manuscript.

Crystallographic and Refinement Details 3

A *t*-Bu group was found to be disordered over two positions and modelled using SAME, SIMU and RIGU restraints. The crystallographic density of the material is below 1 as the structure contains light lithium atoms.

Crystallographic and Refinement Details 5

The crystal was found to be twinned. Two domains were identified and the structure was refined taking two domains into account.

Crystallographic and Refinement Details 6-Ph*

One molecule of lattice pentane was found to be disordered over two positions on a special position and modelled over two positions in PART-1 and PART-2 using SAME, SIMU and RIGU restraints.

Crystallographic and Refinement Details 6-Ph^F

Two *t*-Bu groups were found to be disordered over two positions and modelled using SAME, SIMU and RIGU restraints.

Crystallographic and Refinement Details 7-Ph

The crystal was found to be twinned. Two domains and a twin law were identified and the structure was refined taking two domains into consideration (BASF 0.51).

	1	**2-E,Z**	**3**	**4**	**5**	**6-Ph***	**6-Mes**	**6-Ph^F**	**7-Ph**	**8**
CCDC number	1976852	1976853	1976859	1976857	1976856	1976854	1976860	1976858	1976855	1976861
empirical formula	$C_{48}H_{70}Si_2Zr$	$C_{38}H_{60}I_2Si_2$	$C_{76}H_{120}Li_4Si_4$	$C_{40}H_{66}Si_2Sn$	$C_{41}H_{66}Si_2$ (C_5H_{12})	$C_{51}H_{81}BSi_2$	$C_{47}H_{71}BSi_2$, 0.5(C_6H_{14})	$C_{44}H_{60}BSi_2F_5$, (OC_2H_{10})	$C_{50}H_{70}B_2Cl_2Si_2$	$C_{38}H_{60}BClSi_2$
formula weight	794.44	826.84	1173.83	721.79	615.11	845.30	746.11	825.03	819.76	619.30
T / K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
λ / Å	0.56086, Ag	0.56086	0.71073	0.56086	0.56086	0.71073	0.71073	0.71073	0.71073	0.56086
crystal system	Triclinic	Triclinic	Triclinic	Triclinic	monoclinic	monoclinic	Triclinic	Triclinic	triclinic	monoclinic
space group	*P-1*	*P-1*	*P-1*	*P-1*	$P2_1/c$	*C2/c*	*P-1*	*P-1*	*P-1*	$P2_1/c$
a / Å	12.5487(9)	10.4219(5)	12.1327(9)	11.8487(5)	12.9527(10)	17.5775(17)	13.7584(9)	13.5409(7)	12.0043(7)	11.7378(4)
b / Å	17.0980(12)	11.1194(5)	17.9330(13)	12.8443(5)	26.578(2)	21.320(2)	14.0442(9)	13.9254(7)	20.4730(12)	12.4676(4)
c / Å	21.7789(16)	19.8329(9)	19.8813(14)	15.9399(7)	12.2730(10)	16.318(3)	14.1442(9)	14.2996(7)	20.6672(12)	26.4693(9)
α	79.764(2)	74.0185(19)	78.173(2)	84.482(2)	90	90	67.3410(10)	108.309(2)	101.047(3)	90
β / °	87.198(2)	79.046(2)	73.231(2)	70.627(2)	114.341(2)	114.605(2)	73.0980(10)	108.132(2)	90.377(3)	99.1270(10)
γ	88.546(2)	72.581(2)	73.259(2)	62.6790(10)	90	90	87.9940(10)	90.795(2)	91.410(3)	90
V / Å^3	4592.3(6)(4)	2093.63(17)	3931.0(5)	2028.67(15)	3849.6(5)	5560.2(11)	2403.9(3)	2414.1(2)	4983.3(5)	3824.5(2)
Z	4	2	2	2	4	4	2	2	4	4
ρ / Mg m^{-3}	1.149	1.312	0.992	1.182	1.061	1.010	1.031	1.135	1.093	1.076
μ / mm^{-1}	0.80	0.842	0.112	0.383	0.068	0.096	0.104	0.125	0.209	0.102
F(000)	1704	844	1288	768	1360	1872	822	888	1768	1352
crystal size / mm^3	0.21/0.16/0.11	0.44/0.21/0.19	0.41/0.33/0.24	0.46/0.30/0.13	0.60/0.23/0.23	0.37/0.19/0.10	0.24/0.14/0.09	0.51/0.20/0.15	0.22/0.16/0.07	0.40/0.24/0.15
θ range / °	1.3 to 20.8	1.6 to 20.7	1.1 to 26.6	1.1 to 21.1	1.6 to 20.9	1.6 to 25.1	1.6 to 25.7	1.6 to 30.7	1.0 to 25.2	1.2 to 21.7
index ranges	$-15 \le h \le 15$	$-13 \le h \le 13$	$-15 \le h \le 15$	$-14 \le h \le 15$	$-15 \le h \le 16$	$-20 \le h \le 20$	$-16 \le h \le 15$	$-19 \le h \le 19$	$-15 \le h \le 15$	$-15 \le h \le 15$
	$-21 \le k \le 21$	$-13 \le k \le 13$	$-22 \le k \le 22$	$-16 \le k \le 16$	$-33 \le k \le 33$	$-25 \le k \le 25$	$-17 \le k \le 17$	$-19 \le k \le 19$	$-26 \le k \le 26$	$-16 \le k \le 16$
	$-27 \le l \le 27$	$-24 \le l \le 24$	$-25 \le l \le 24$	$-0 \le l \le 20$	$-15 \le l \le 12$	$-19 \le l \le 19$	$-17 \le l \le 16$	$-20 \le l \le 20$	$0 \le l \le 26$	$34 \le l \le 34$
refl. Collected	71186	64782	73908	9050	36804	76308	19910	69372	91559	92892
indep. reflections/ R_{int}	19626 / 0.052	8671 / 0.043	16374 / 0.028	8672 / 0.026	8200 / 0.065	4929 / 0.08	9124 / 0.04	14725 /0.04	26326 /0.054	9164 /0.047
completeness to θ_{max}	99.9 %	99.5 %	99.6%	99.9%	99.4 %	100 %	99.4%	98.7%	99.1%	99.3%
data/restraints/ parameters	19626/180/986	8671/408/490	16374/138/824	9050/0/409	8200/0/406	4929/187/357	9124/0/500	14725/360/596	26310/153/1071	9164/0/397
GooF	1.02	1.02	1.02	1.11	1.04	1.05	1.02	1.02	1.03	1.08
final R indices [I>2sigma(I)] R_1 / wR_2	0.039 / 0.090	0.033 / 0.082	0.039 / 0.104	0.026 / 0.072	0.047 / 0.113	0.066/0.202	0.053/0.140	0.049/0.137	0.065/0.161	0.042/0.107
R indices (all data) R_1 / wR_2	0.065 / 0.082	0.045 / 0.075	0.050 / 0.0962	0.029 / 0.069	0.078 / 0.100	0.076/0.185	0.085/0.125	0.065/0.125	0.0909/ 0.148	0.057/0.100
largest diff. peak and hole / eÅ^{-3}	0.68/ -0.61	1.65 / - 1.41	0.37 / - 0.26	0.38 / -0.44	0.35 / -032	0.81/-0.56	0.92/-0.40	0.45/-0.47	0.84/-0.61	0.42/-0.28
absorption correction	multiscan	multiscan	multiscan	multiscan	multiscan	multiscan	multiscan	multiscan	multiscan	multiscan
miscellaneous				2 comp. twin					2-comp.twin	

Computational Details

Structure Optimisation, Frequency Calculation and Thermochemical Approximations

Computational examination was performed using ORCA (version 4.1.).[19, 20] All structures were optimised on RI-BP86-D3BJ[21] def2SVP/J model chemistry[22-26] in the gas phase followed by a frequency calculation on the same level of theory and thermochemical corrections were taken from these frequency calculations. For all compounds, except for **6-Mes** no imaginary frequencies were observed confirming true minima. For **6-Mes** a negligible imaginary frequency at i11 cm^{-1} was observed related to a methyl rotation. All structures were then reoptimized using BP86-D3BJ-def2TZVP/J model chemistry and all energies and spectroscopic properties were subsequently calculated based on these structures. Graphical depictions were created using ChemCraft.[27]

Computational assessment of spectroscopic features

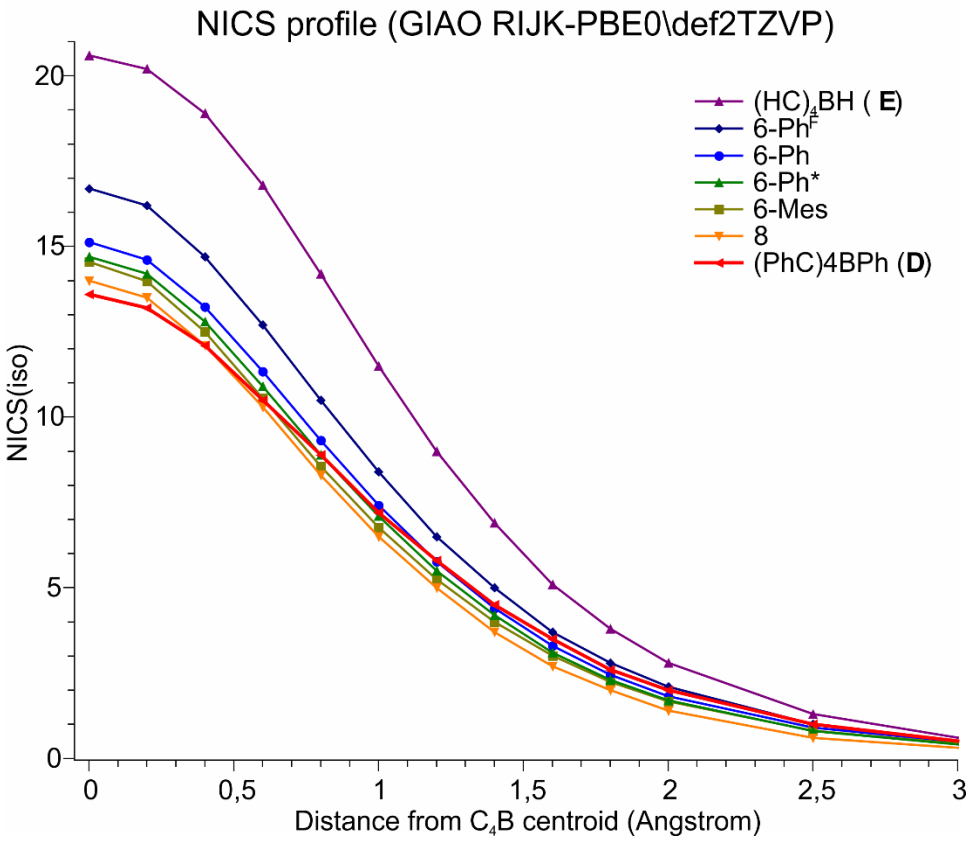
GIAO-NMR spectroscopic properties including NICS[28, 29] values were calculated as implemented as the default in ORCA4.1 applying RIJK-PBE0[30] functional on structures previously optimised using the RI-BP86-D3BJ-def2TZVP/J model chemistry.[22-26] NICS scans were performed determining the centroid of the C_4B plane (in ChemCraft) (NICS0) and on a series of points along an orthogonal vector to C_4B starting from there.

UVVis-spectroscopic features TD-DFT calculations for 10 states using RIJCOSX-approximation with CAM-B3LYP[31] functional and def2-SVP basis sets on all atoms were performed.

Qualitative TDDFT study of C_4B-Ph torsion angle influence on the absorption in pentaphenyl borole.

To probe the effect of torsion angles and thus on the extent of π-interaction to the visible light absorptions in boroles, we optimised the structure of pentaphenyl borole[32] according to the procedures described above. Starting from this paddlewheel structure, all C_4B-Ph torsions were manually set to 90°. The C_4B-Ph torsion angle for each set of Ph-groups (C_α-bound, C_β-bound and B-bound) was then incrementally (10° steps) lowered with the other groups remaining perpendicular. At each step, a TD-DFT single point calculations was performed (see above). In this model scenario, C_β-bound phenyl groups eventually collapse and thus only torsions up to 30° were taken into account.

NICS Profiles



XYZ-coordinates of optimised structures

All structures optimised at BP86-D3BJ\def2TZVP level of theory.

6-Ph (E = -2320.6615106 H)

Si	5.701121000	4.102174000	3.937392000
C	7.468143000	4.725620000	3.883930000
B	8.327805000	5.356984000	5.063862000
Si	11.289750000	6.299572000	5.349916000
C	8.385505000	4.450789000	2.910791000
C	10.927553000	4.643469000	2.400625000
C	7.787085000	5.856381000	6.426418000
C	9.844580000	5.382651000	4.585408000
H	9.302154000	4.864101000	7.609069000
C	8.414903000	5.499722000	7.637186000
C	7.915029000	5.925688000	8.867400000
H	8.403746000	5.617188000	9.793036000
C	6.799693000	6.768119000	8.912228000
H	6.418466000	7.120177000	9.872058000
C	6.174159000	7.158229000	7.723869000
H	5.305341000	7.817767000	7.755230000
C	6.648634000	6.684471000	6.501104000
H	6.138722000	6.971775000	5.579425000
C	5.299096000	3.571181000	5.704936000
H	4.298665000	3.113351000	5.740163000
H	5.318221000	4.410823000	6.411241000
H	6.022888000	2.822580000	6.060350000
C	4.485889000	5.453332000	3.411009000
H	4.681867000	5.784556000	2.380741000
H	4.550692000	6.336602000	4.062419000
H	3.450597000	5.081934000	3.453136000
C	5.428640000	2.580908000	2.850966000
H	5.441398000	2.808203000	1.778174000
H	4.452827000	2.133147000	3.095343000
H	6.203507000	1.823072000	3.037500000
C	12.225534000	5.197147000	6.570001000
H	12.636100000	4.308697000	6.068283000
H	11.576254000	4.848034000	7.385643000
H	13.065789000	5.745428000	7.022669000
C	12.508261000	6.952722000	4.062363000
H	13.105838000	6.162319000	3.592429000
H	13.197500000	7.662272000	4.546038000
H	11.980557000	7.489197000	3.260344000
C	10.630634000	7.811820000	6.270003000
H	10.033116000	8.445734000	5.597889000
H	11.470072000	8.417750000	6.644038000
H	9.994341000	7.542253000	7.122430000
C	8.154272000	3.838380000	1.596272000
C	7.223976000	4.396409000	0.709170000
H	6.674344000	5.281074000	1.033138000
C	7.020397000	3.855728000	-0.565211000
C	5.998167000	4.506523000	-1.505808000
C	6.378095000	5.985954000	-1.728012000
H	7.371629000	6.067596000	-2.191785000
H	6.399381000	6.545252000	-0.782892000
H	5.647224000	6.472101000	-2.391587000
C	4.600127000	4.427554000	-0.856294000
H	3.847453000	4.898013000	-1.506819000
H	4.576680000	4.940894000	0.114647000
H	4.306061000	3.381358000	-0.689259000
C	5.939829000	3.812923000	-2.874936000
H	5.200978000	4.319028000	-3.512647000
H	5.636862000	2.759627000	-2.786257000
H	6.910158000	3.851509000	-3.391092000
C	7.767973000	2.726283000	-0.928992000
H	7.626013000	2.299246000	-1.918236000
C	8.707853000	2.141208000	-0.067078000
C	9.535208000	0.908925000	-0.453743000
C	9.175546000	-0.249749000	0.501056000
H	8.107067000	-0.498481000	0.427766000
H	9.389402000	0.013217000	1.546083000
H	9.758914000	-1.148536000	0.249736000
C	9.269521000	0.455932000	-1.896830000
H	9.515250000	1.245846000	-2.621747000
H	8.220156000	0.163675000	-2.047398000
H	9.895026000	-0.417668000	-2.129870000
C	11.037096000	1.236111000	-0.314002000
H	11.642863000	0.349585000	-0.555608000
H	11.293686000	1.558695000	0.703194000
H	11.329000000	2.048107000	-0.994116000
C	8.895887000	2.719810000	1.189488000
H	9.627725000	2.301730000	1.880144000
C	9.808959000	4.847424000	3.329885000
C	10.865238000	5.137328000	1.089621000
H	9.981174000	5.697422000	0.786160000
C	11.906967000	4.928078000	0.184046000
C	11.792295000	5.504467000	-1.232691000
C	11.743116000	7.044683000	-1.138913000
H	11.655796000	7.487196000	-2.142836000
H	12.655143000	7.436173000	-0.665801000
H	10.883501000	7.380848000	-0.543053000
C	10.492947000	4.992780000	-1.890093000
H	10.380075000	5.425863000	-2.895552000
H	9.604296000	5.256743000	-1.302495000
H	10.503733000	3.898377000	-1.985987000
C	12.977162000	5.104549000	-2.123970000
H	12.841176000	5.527725000	-3.129549000
H	13.055457000	4.012420000	-2.228731000
H	13.931631000	5.482729000	-1.730008000
C	13.016326000	4.184808000	0.614681000
H	13.825495000	3.995969000	-0.085840000
C	13.107179000	3.659533000	1.911871000
C	14.312049000	2.837252000	2.386597000
C	13.828092000	1.451581000	2.864338000
H	13.341796000	0.904583000	2.043877000
H	13.106716000	1.536302000	3.688329000
H	14.679190000	0.852187000	3.221008000
C	15.351095000	2.628186000	1.274990000
H	14.923786000	2.090876000	0.415843000
H	16.188217000	2.029464000	1.661613000
H	15.762506000	3.582667000	0.916109000
C	14.990814000	3.576169000	3.559570000
H	15.853695000	3.000923000	3.927732000
H	14.297944000	3.722026000	4.399475000
H	15.346713000	4.567097000	3.242909000
C	12.051093000	3.905334000	2.796242000
H	12.070899000	3.507618000	3.811694000

6-Ph* (E= -2635.3146871 H)

Si	5.607122000	4.430342000	3.804433000
C	7.418505000	4.913841000	3.838794000
B	8.289049000	5.449330000	5.060438000
Si	11.321395000	6.138380000	5.433203000
C	8.340789000	4.590583000	2.885069000
C	10.901156000	4.593480000	2.446315000
C	7.750597000	5.954743000	6.417564000
C	9.817821000	5.366891000	4.620929000
H	9.279838000	4.981676000	7.573701000
C	8.390552000	5.608971000	7.623163000
C	7.907932000	6.036511000	8.863164000
C	6.777068000	6.866400000	8.867632000
H	6.395885000	7.222982000	9.826468000
C	6.113763000	7.258572000	7.695536000
C	6.606386000	6.772855000	6.481191000
H	6.106853000	7.034575000	5.549125000
C	5.064683000	3.915298000	5.539843000
H	4.034709000	3.528047000	5.508151000
H	5.102315000	4.741995000	6.260145000

H	5.712743000	3.113978000	5.925303000
C	4.531363000	5.873123000	3.219596000
H	4.756945000	6.129315000	2.174130000
H	4.690560000	6.778576000	3.821743000
H	3.463188000	5.613868000	3.277534000
C	5.269394000	2.939243000	2.693443000
H	5.357938000	3.167761000	1.624479000
H	4.248709000	2.571911000	2.882567000
H	5.968667000	2.119963000	2.915704000
C	12.162555000	4.913207000	6.604757000
H	12.569155000	4.056369000	6.047960000
H	11.466923000	4.516098000	7.357197000
H	12.997720000	5.392226000	7.138264000
C	12.598739000	6.746075000	4.180007000
H	13.135100000	5.930709000	3.679776000
H	13.338404000	7.377943000	4.695879000
H	12.120904000	7.355770000	3.399280000
C	10.788457000	7.665094000	6.411040000
H	10.247479000	8.370172000	5.762288000
H	11.676010000	8.184058000	6.804395000
H	10.128011000	7.421200000	7.252470000
C	8.103432000	4.027515000	1.548626000
C	7.255956000	4.680879000	0.643900000
H	6.772455000	5.602724000	0.969472000
C	7.051525000	4.184920000	-0.648622000
C	6.119647000	4.937263000	-1.607340000
C	6.613427000	6.390783000	-1.767605000
H	7.628242000	6.413326000	-2.190027000
H	6.636036000	6.920309000	-0.805572000
H	5.946840000	6.947481000	-2.443331000
C	4.694000000	4.941942000	-1.015768000
H	4.004441000	5.485919000	-1.678896000
H	4.668642000	5.426096000	-0.030027000
H	4.318552000	3.915704000	-0.894299000
C	6.067929000	4.290341000	-2.999483000
H	5.398338000	4.870760000	-3.650281000
H	5.681478000	3.261773000	-2.957774000
H	7.060028000	4.268106000	-3.473491000
C	7.712658000	3.003168000	-1.013297000
H	7.569723000	2.609621000	-2.016172000
C	8.569554000	2.323614000	-0.134584000
C	9.307035000	1.036210000	-0.523415000
C	8.836490000	-0.106119000	0.402274000
H	7.754091000	-0.270184000	0.300360000
H	9.044825000	0.122361000	1.456432000
H	9.354776000	-1.043196000	0.148164000
C	9.041744000	0.627513000	-1.979704000
H	9.368510000	1.405173000	-2.685572000
H	7.976130000	0.423995000	-2.159611000
H	9.600127000	-0.290548000	-2.212473000
C	10.825690000	1.244786000	-0.343486000
H	11.368074000	0.317976000	-0.584783000
H	11.080367000	1.533058000	0.684439000
H	11.195167000	2.041660000	-1.003536000
C	8.761441000	2.858503000	1.140669000
H	9.431846000	2.366416000	1.844892000
C	9.775990000	4.864481000	3.351861000
C	10.917792000	5.128206000	1.150253000
H	10.091835000	5.768422000	0.841347000
C	11.962860000	4.856804000	0.265166000
C	11.933542000	5.476027000	-1.137687000
C	11.994295000	7.012882000	-1.004779000
H	11.969367000	7.484714000	-1.998800000
H	12.918153000	7.324355000	-0.496466000
H	11.144435000	7.397545000	-0.424521000
C	10.620055000	5.077167000	-1.843346000
H	10.567726000	5.541068000	-2.840047000
H	9.736875000	5.391355000	-1.272531000
H	10.553899000	3.987398000	-1.966609000
C	13.111879000	5.012108000	-2.006298000
H	13.038599000	5.471416000	-3.002526000
H	13.111753000	3.920456000	-2.140896000
H	14.079337000	5.306372000	-1.574166000
C	12.993904000	4.010974000	0.700840000
H	13.803558000	3.774375000	0.015593000
C	13.003731000	3.442949000	1.982971000
C	14.123110000	2.509863000	2.462502000
C	13.513291000	1.161379000	2.900761000
H	12.998573000	0.674778000	2.059879000
H	12.785634000	1.290294000	3.713379000
H	14.303059000	0.484251000	3.259424000
C	15.163657000	2.234372000	1.366831000
H	14.709287000	1.756480000	0.486720000
H	15.936102000	1.555376000	1.755496000
H	15.665522000	3.156273000	1.039283000
C	14.837762000	3.164370000	3.663815000
H	15.641435000	2.510972000	4.035706000
H	14.141999000	3.351037000	4.493114000
H	15.281797000	4.128147000	3.375973000
C	11.946994000	3.751336000	2.847061000
H	11.904470000	3.323601000	3.849474000
C	8.572923000	5.658621000	10.192313000
C	4.881836000	8.166691000	7.792310000
C	5.286212000	9.501538000	8.453026000
H	5.693392000	9.346260000	9.461700000
H	6.053542000	10.014635000	7.855709000
H	4.413212000	10.166082000	8.538908000
C	4.275477000	8.468738000	6.414072000
H	4.993913000	8.977511000	5.755171000
H	3.934878000	7.552364000	5.911407000
H	3.403654000	9.128361000	6.530780000
C	3.805050000	7.470405000	8.651920000
H	3.506610000	6.513066000	8.201033000
H	4.167272000	7.265394000	9.668684000
H	2.911289000	8.107195000	8.733776000
C	9.018821000	6.945075000	10.919942000
H	9.499516000	6.694884000	11.877724000
H	9.739164000	7.507685000	10.308845000
H	8.168128000	7.607035000	11.132481000
C	7.557448000	4.895338000	11.068766000
H	7.226807000	3.973869000	10.568346000
H	8.013284000	4.621181000	12.032185000
H	6.666152000	5.503152000	11.277297000
C	9.807885000	4.768529000	9.989562000
H	10.244971000	4.515531000	10.966167000
H	9.552784000	3.826339000	9.483253000
H	10.582884000	5.278560000	9.399926000

6-Mes (E= -2438.6680808))

Si	5.638760000	4.293796000	3.916575000
C	7.438765000	4.809694000	3.861877000
B	8.299552000	5.416415000	5.053754000
Si	11.265261000	6.253367000	5.428153000
C	8.356801000	4.513247000	2.896419000
C	10.900713000	4.713248000	2.387325000
C	7.755065000	5.924624000	6.415087000
C	9.819560000	5.410465000	4.586024000
C	8.692628000	3.859726000	7.527823000
H	7.973526000	3.039648000	7.368974000
H	9.241112000	3.640574000	8.454593000
H	9.402075000	3.829203000	6.686387000
C	7.981990000	5.187680000	7.596548000
C	7.483244000	5.659019000	8.815181000
H	7.658749000	5.076812000	9.724444000
C	6.757751000	6.852634000	8.898201000
C	6.204177000	7.336650000	10.213504000
H	6.351137000	8.419343000	10.336859000
H	6.682653000	6.826636000	11.060356000
H	5.120937000	7.146719000	10.280321000
C	6.541930000	7.578327000	7.719008000
H	5.990266000	8.521921000	7.765025000
C	7.026380000	7.132842000	6.487127000
C	6.849690000	7.974350000	5.248507000
H	6.814368000	7.349383000	4.342703000

H	7.697072000	8.668087000	5.123810000
H	5.933025000	8.578810000	5.291378000
C	5.147194000	3.977038000	5.710547000
H	4.107007000	3.619886000	5.757233000
H	5.229793000	4.883387000	6.324908000
H	5.785090000	3.206644000	6.168153000
C	4.513697000	5.659079000	3.245501000
H	4.775975000	5.938370000	2.215014000
H	4.577728000	6.565029000	3.864469000
H	3.464606000	5.325806000	3.245940000
C	5.326184000	2.696673000	2.957944000
H	5.427264000	2.821994000	1.872764000
H	4.308265000	2.333515000	3.167898000
H	6.034183000	1.914214000	3.268520000
C	12.222266000	5.039594000	6.519328000
H	12.594365000	4.178192000	5.946432000
H	11.589804000	4.653639000	7.331110000
H	13.090172000	5.537853000	6.977699000
C	12.447937000	7.047356000	4.187877000
H	13.009848000	6.310455000	3.600725000
H	13.170495000	7.683478000	4.722072000
H	11.896507000	7.683901000	3.480286000
C	10.610502000	7.630338000	6.539629000
H	10.021773000	8.360396000	5.964975000
H	11.451032000	8.170003000	7.002259000
H	9.966425000	7.242037000	7.339676000
C	8.125471000	3.881982000	1.591235000
C	7.177902000	4.406655000	0.702046000
H	6.615241000	5.287151000	1.013320000
C	6.975518000	3.841503000	-0.561714000
C	5.931568000	4.454668000	-1.503682000
C	6.260081000	5.945229000	-1.732736000
H	7.250722000	6.059379000	-2.195861000
H	6.260017000	6.510525000	-0.791008000
H	5.513396000	6.401880000	-2.399557000
C	4.538184000	4.330332000	-0.850998000
H	3.768700000	4.773328000	-1.501186000
H	4.499588000	4.844558000	0.118902000
H	4.280251000	3.275145000	-0.680881000
C	5.895274000	3.754374000	-2.870213000
H	5.142689000	4.236177000	-3.510652000
H	5.622793000	2.693098000	-2.778233000
H	6.864901000	3.819234000	-3.385112000
C	7.743185000	2.721627000	-0.913683000
H	7.603473000	2.277086000	-1.895514000
C	8.700308000	2.168866000	-0.049588000
C	9.552601000	0.949913000	-0.424260000
C	9.227511000	-0.202332000	0.550395000
H	8.164823000	-0.477609000	0.488761000
H	9.442426000	0.081392000	1.589748000
H	9.830419000	-1.090649000	0.308193000
C	9.286437000	0.469411000	-1.858318000
H	9.508897000	1.253559000	-2.596856000
H	8.242823000	0.151482000	-1.996345000
H	9.929684000	-0.393366000	-2.083178000
C	11.047543000	1.314009000	-0.301342000
H	11.671991000	0.438884000	-0.536837000
H	11.304944000	1.655395000	0.709517000
H	11.314821000	2.123805000	-0.994130000
C	8.884535000	2.770192000	1.196790000
H	9.629365000	2.377043000	1.888086000
C	9.783778000	4.894717000	3.322781000
C	10.814864000	5.209420000	1.078084000
H	9.914502000	5.747903000	0.783826000
C	11.851856000	5.027000000	0.161497000
C	11.706534000	5.599114000	-1.254164000
C	11.621817000	7.137795000	-1.161497000
H	11.510155000	7.576607000	-2.164623000
H	12.530604000	7.551761000	-0.701472000
H	10.762632000	7.454090000	-0.554243000
C	10.411747000	5.055743000	-1.895122000
H	10.278785000	5.481201000	-2.901364000
H	9.523598000	5.303406000	-1.299667000
H	10.445386000	3.961355000	-1.985783000
C	12.889648000	5.225978000	-2.159279000
H	12.731494000	5.644162000	-3.163685000
H	12.992584000	4.135848000	-2.263447000
H	13.839616000	5.627341000	-1.777567000
C	12.983796000	4.311539000	0.580012000
H	13.790313000	4.143516000	-0.128827000
C	13.100673000	3.787488000	1.875775000
C	14.332099000	2.998215000	2.338157000
C	13.890375000	1.605556000	2.835890000
H	13.403925000	1.039361000	2.028635000
H	13.181452000	1.679388000	3.671609000
H	14.761954000	1.030624000	3.183101000
C	15.358131000	2.804020000	1.211840000
H	14.929415000	2.251469000	0.363100000
H	16.214131000	2.226639000	1.589439000
H	15.743151000	3.764576000	0.840171000
C	15.010610000	3.764925000	3.493405000
H	15.893142000	3.214644000	3.853104000
H	14.327553000	3.902328000	4.342574000
H	15.336848000	4.761093000	3.161626000
C	12.046862000	4.003838000	2.770398000
H	12.086816000	3.602168000	3.783260000

6-Ph^{F} (E = -2817.0674395 H)

Si	5.665602000	4.238617000	3.898146000
C	7.468819000	4.750516000	3.852775000
B	8.342197000	5.342469000	5.026940000
Si	11.308364000	6.181157000	5.421758000
C	8.387152000	4.452223000	2.886636000
C	10.936322000	4.640572000	2.384532000
C	7.796284000	5.846667000	6.407142000
C	9.856626000	5.343287000	4.581378000
F	8.987276000	4.166435000	7.588510000
C	8.157695000	5.236047000	7.608766000
C	7.677441000	5.660853000	8.846571000
F	8.033171000	5.036973000	9.982048000
C	6.812061000	6.757468000	8.898162000
F	6.345712000	7.189087000	10.078547000
C	6.433388000	7.403611000	7.717822000
F	5.607874000	8.462260000	7.771413000
C	6.922876000	6.930952000	6.501161000
F	6.546125000	7.581573000	5.375340000
C	5.177969000	3.906896000	5.694101000
H	4.166589000	3.474308000	5.729537000
H	5.171047000	4.821553000	6.301889000
H	5.863851000	3.191643000	6.171378000
C	4.554879000	5.612542000	3.232383000
H	4.767473000	5.830469000	2.176025000
H	4.698919000	6.542096000	3.800429000
H	3.494930000	5.326010000	3.308637000
C	5.358813000	2.639569000	2.943480000
H	5.472926000	2.760266000	1.859192000
H	4.336368000	2.283180000	3.142288000
H	6.058240000	1.854471000	3.266320000
C	12.249756000	4.965339000	6.517225000
H	12.685551000	4.144070000	5.930549000
H	11.584253000	4.520889000	7.270264000
H	13.071504000	5.473546000	7.044339000
C	12.484938000	6.975087000	4.177728000
H	13.039682000	6.238025000	3.584209000
H	13.214369000	7.604009000	4.710923000
H	11.932872000	7.618737000	3.477218000
C	10.649127000	7.572222000	6.518804000
H	9.997975000	8.255502000	5.954065000
H	11.489835000	8.162395000	6.913993000
H	10.075493000	7.193586000	7.375337000
C	8.156529000	3.824667000	1.582165000
C	7.206838000	4.349461000	0.694259000
H	6.644207000	5.229679000	1.006085000
C	7.007345000	3.786349000	-0.570603000

C	5.966091000	4.400520000	-1.514796000
C	6.292376000	5.892621000	-1.736934000
H	7.285136000	6.010797000	-2.194505000
H	6.285373000	6.455368000	-0.793734000
H	5.548236000	6.349276000	-2.406411000
C	4.570303000	4.270294000	-0.868498000
H	3.802710000	4.713381000	-1.520663000
H	4.525845000	4.781875000	0.102551000
H	4.314117000	3.213977000	-0.702798000
C	5.937515000	3.704821000	-2.883895000
H	5.187317000	4.187926000	-3.526006000
H	5.665781000	2.642891000	-2.797390000
H	6.909391000	3.773068000	-3.394115000
C	7.775520000	2.666310000	-0.922154000
H	7.636266000	2.222648000	-1.904423000
C	8.732326000	2.112096000	-0.058667000
C	9.580728000	0.890288000	-0.432553000
C	9.245479000	-0.261916000	0.538822000
H	8.181652000	-0.531560000	0.472534000
H	9.458025000	0.018484000	1.579592000
H	9.844519000	-1.152884000	0.297154000
C	9.317698000	0.414354000	-1.868720000
H	9.545625000	1.199361000	-2.604704000
H	8.273572000	0.100191000	-2.011196000
H	9.958570000	-0.450156000	-2.093331000
C	11.077072000	1.246132000	-0.302897000
H	11.697173000	0.367922000	-0.537892000
H	11.332883000	1.583139000	0.709859000
H	11.351786000	2.055658000	-0.993058000
C	8.918397000	2.714227000	1.186825000
H	9.662406000	2.320175000	1.878223000
C	9.820976000	4.827421000	3.317171000
C	10.849745000	5.130607000	1.072269000
H	9.950193000	5.668678000	0.775418000
C	11.889086000	4.947867000	0.158656000
C	11.748335000	5.519614000	-1.257559000
C	11.668498000	7.058613000	-1.164728000
H	11.561361000	7.497649000	-2.168151000
H	12.577311000	7.469642000	-0.702187000
H	10.808483000	7.378040000	-0.560262000
C	10.453229000	4.980760000	-1.901613000
H	10.324161000	5.407687000	-2.907629000
H	9.564349000	5.231211000	-1.308389000
H	10.483705000	3.886399000	-1.993668000
C	12.932429000	5.142323000	-2.159672000
H	12.777540000	5.560164000	-3.164648000
H	13.032631000	4.051843000	-2.262992000
H	13.882673000	5.541563000	-1.776499000
C	13.020050000	4.233425000	0.581457000
H	13.827336000	4.063062000	-0.125917000
C	13.136317000	3.712849000	1.879002000
C	14.366914000	2.923358000	2.342988000
C	13.922813000	1.535069000	2.850721000
H	13.431703000	0.965365000	2.048758000
H	13.217871000	1.615317000	3.689183000
H	14.794217000	0.959878000	3.197597000
C	15.389180000	2.719598000	1.214898000
H	14.956483000	2.163704000	0.370361000
H	16.244011000	2.141359000	1.593585000
H	15.777065000	3.676566000	0.836996000
C	15.050461000	3.696002000	3.491273000
H	15.932530000	3.145824000	3.851921000
H	14.370365000	3.840017000	4.341725000
H	15.378344000	4.689240000	3.152394000
C	12.083267000	3.933985000	2.772915000
H	12.121978000	3.535860000	3.787140000

8 (E = -2549.2123803 H)

Si	5.062242000	10.445321000	15.187055000
C	3.261130000	9.937435000	15.287548000
C	5.186868000	12.311097000	15.441418000
H	4.677475000	12.868943000	14.645258000
H	6.243957000	12.617425000	15.454408000
H	4.738960000	12.610390000	16.400501000
C	0.681604000	9.959850000	15.287493000
C	1.192278000	8.857349000	15.907666000
Si	-1.124525000	10.319350000	14.935977000
C	2.733664000	8.830008000	15.887622000
C	6.130527000	9.641434000	16.519889000
H	6.307688000	8.573165000	16.345587000
H	5.664103000	9.740123000	17.510917000
H	7.106086000	10.150619000	16.554294000
C	5.735628000	10.016845000	13.475291000
H	5.135630000	10.499001000	12.689770000
H	5.712331000	8.932030000	13.295816000
H	6.776704000	10.355974000	13.363808000
C	-1.276470000	11.184411000	13.266647000
H	-0.821679000	10.584001000	12.465109000
H	-0.786450000	12.166562000	13.266908000
H	-2.338497000	11.329663000	13.016657000
C	-1.804374000	11.465551000	16.275253000
H	-1.215209000	12.392523000	16.331704000
H	-1.772786000	10.988351000	17.265584000
H	-2.849545000	11.739674000	16.066225000
C	-2.166520000	8.748432000	14.843733000
H	-3.161047000	8.996247000	14.441682000
H	-2.302865000	8.265210000	15.818786000
H	-1.705096000	8.011492000	14.170309000
B	1.978658000	10.735120000	14.838491000
Cl	1.993401000	12.257844000	13.945602000
C	4.379545000	6.967258000	15.722036000
H	4.563637000	7.284975000	14.697286000
C	3.446645000	7.690554000	16.479264000
C	5.038085000	5.856642000	16.258553000
C	6.073772000	5.052394000	15.463407000
C	6.256276000	5.593812000	14.037632000
H	7.003400000	4.987900000	13.505577000
H	6.612005000	6.634260000	14.039730000
H	5.319822000	5.550369000	13.462798000
C	7.432885000	5.131322000	16.191508000
H	8.194824000	4.558245000	15.642034000
H	7.369865000	4.723065000	17.209496000
H	7.773917000	6.173767000	16.267823000
C	5.622371000	3.579770000	15.372003000
H	4.657923000	3.499060000	14.851174000
H	5.504796000	3.129102000	16.366900000
H	6.365114000	2.986717000	14.817641000
C	4.734108000	5.487161000	17.576542000
H	5.235632000	4.617625000	18.004927000
C	3.801004000	6.180623000	18.361076000
C	3.493595000	5.709915000	19.788031000
C	4.785049000	5.761888000	20.629962000
H	5.566997000	5.114100000	20.209900000
H	4.585089000	5.427646000	21.659146000
H	5.182302000	6.786207000	20.670136000
C	2.960906000	4.262541000	19.743753000
H	2.016371000	4.220148000	19.182997000
H	2.770709000	3.895580000	20.763556000
H	3.673718000	3.576944000	19.265259000
C	2.423649000	6.581841000	20.461768000
H	2.747218000	7.628245000	20.558088000
H	2.220512000	6.200319000	21.472821000
H	1.480799000	6.562422000	19.896366000
C	3.160589000	7.281390000	17.791504000
H	2.422739000	7.841423000	18.360529000
C	0.462301000	7.752730000	16.545200000
C	0.684796000	6.432383000	16.131220000
H	1.364291000	6.258303000	15.297907000
C	0.059863000	5.357406000	16.765461000
C	0.289187000	3.935184000	16.238730000
C	-0.458865000	3.796400000	14.894238000
H	-0.091609000	4.528796000	14.161766000
H	-1.537243000	3.964505000	15.027353000
H	-0.313602000	2.788747000	14.475841000

C	1.794162000	3.686089000	16.007861000
H	1.952959000	2.660995000	15.641534000
H	2.367521000	3.815302000	16.934673000
H	2.217184000	4.374537000	15.264871000
C	-0.234996000	2.864061000	17.207734000
H	-1.323924000	2.929428000	17.343550000
H	0.241157000	2.943661000	18.195880000
H	-0.012497000	1.864746000	16.807315000
C	-0.787397000	5.635778000	17.850341000
H	-1.265096000	4.808201000	18.368374000
C	-1.038846000	6.944393000	18.288625000
C	-2.000282000	7.259153000	19.442238000
C	-1.279343000	8.106523000	20.511332000
H	-0.428374000	7.558124000	20.938829000
H	-1.973127000	8.355292000	21.328172000
H	-0.898475000	9.049241000	20.096193000
C	-3.194043000	8.059578000	18.877236000
H	-2.863491000	8.998521000	18.412042000
H	-3.903554000	8.309425000	19.680466000
H	-3.728560000	7.476603000	18.113477000
C	-2.538096000	5.988465000	20.116879000
H	-3.113779000	5.366172000	19.416734000
H	-3.208915000	6.265936000	20.942441000
H	-1.725796000	5.376742000	20.535902000
C	-0.403989000	7.996223000	17.617523000
H	-0.553682000	9.028841000	17.934390000

E (E= -180.2796198 H)

B	8.259187000	10.371774000	18.565844000
C	8.954166000	11.278422000	19.664956000
C	9.459150000	10.428778000	20.581878000
C	9.176530000	8.980309000	20.218073000
C	8.486980000	8.884009000	19.063562000
H	7.687712000	10.732255000	17.574540000
H	9.044969000	12.361457000	19.733466000
H	10.009333000	10.697047000	21.487726000
H	9.512971000	8.153118000	20.848782000
H	8.181595000	7.936522000	18.622074000

D (E= -1336.1109803 H)

B	-0.042365000	1.345380000	-0.007989000
C	1.242249000	0.421504000	-0.038641000
C	0.787846000	-0.869142000	-0.024614000
C	-0.735345000	-0.915853000	0.006111000
C	-1.267977000	0.344500000	0.021597000
C	2.646910000	0.843992000	-0.008841000
C	3.103778000	1.844774000	-0.889133000
H	2.400547000	2.289050000	-1.594524000
C	4.434788000	2.262163000	-0.874235000
H	4.766989000	3.032428000	-1.572140000
C	5.337946000	1.701280000	0.032582000
H	6.377399000	2.031681000	0.049509000
C	4.896244000	0.717740000	0.924224000
H	5.591221000	0.280924000	1.643295000
C	3.569450000	0.292966000	0.902819000
H	3.230305000	-0.471987000	1.601899000
C	1.611265000	-2.085458000	-0.025147000
C	2.673371000	-2.225149000	-0.938696000
H	2.866137000	-1.423264000	-1.651364000
C	3.464310000	-3.371331000	-0.939983000
H	4.277064000	-3.466274000	-1.661476000
C	3.219836000	-4.396486000	-0.019731000
H	3.842280000	-5.292313000	-0.018982000
C	2.171640000	-4.268943000	0.895192000
H	1.974044000	-5.063646000	1.615896000
C	1.366490000	-3.130411000	0.886233000
H	0.546695000	-3.039601000	1.598557000
C	-1.482801000	-2.180266000	0.005631000
C	-1.175004000	-3.207436000	-0.906855000
H	-0.362649000	-3.065996000	-1.619452000
C	-1.908998000	-4.393087000	-0.916545000
H	-1.663485000	-5.173554000	-1.638077000
C	-2.947032000	-4.585339000	-0.001346000
H	-3.513512000	-5.517563000	-0.002704000
C	-3.253369000	-3.577884000	0.919933000
H	-4.058502000	-3.723005000	1.641623000
C	-2.533988000	-2.385488000	0.919433000
H	-2.775122000	-1.597510000	1.632887000
C	-2.695921000	0.680049000	-0.007569000
C	-3.583010000	0.074334000	-0.919722000
H	-3.197528000	-0.667552000	-1.619644000
C	-4.933430000	0.416660000	-0.940460000
H	-5.600366000	-0.061316000	-1.659906000
C	-5.434618000	1.370165000	-0.047646000
H	-6.492440000	1.635978000	-0.064022000
C	-4.567483000	1.984544000	0.859673000
H	-4.946316000	2.732093000	1.558523000
C	-3.213307000	1.649835000	0.873926000
H	-2.538617000	2.135660000	1.579797000
C	-0.089581000	2.885415000	-0.006693000
C	0.904483000	3.648372000	0.650319000
H	1.721123000	3.135892000	1.159533000
C	0.850589000	5.040666000	0.670843000
H	1.616972000	5.608886000	1.200317000
C	-0.176243000	5.709424000	-0.003955000
H	-0.209735000	6.800344000	-0.002880000
C	-1.160158000	4.980268000	-0.680137000
H	-1.959983000	5.501449000	-1.208542000
C	-1.128568000	3.587256000	-0.662320000
H	-1.912294000	3.026643000	-1.172539000

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