Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

"Successive Carbene Insertion into 9-Phenyl-9-Borafluorene"

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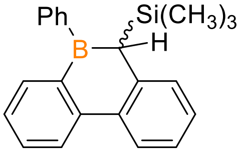
Experimental details

General Considerations: All manipulations were performed under an inert atmosphere in a nitrogen-filled MBraun Unilab glove box or using standard Schlenk techniques. Benzene was purchased as ACS grade from Millipore Corporation, and C_6D_6 for NMR spectroscopy was purchased from Cambridge Isotope Laboratories. Both were dried by stirring for 3 days over CaH_2, distilled, and stored over 4 Å molecular sieves. All other solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents, and stored over 4Å molecular sieves. 9-Phenyl-9-borafluorene (**2Ph**) was prepared by the literature procedure.[1] Trimethylsilyldiazomethane solution (2 M in hexanes) was purchased from Acros Organics and used as received. Multinuclear NMR spectra (^1H, $^{13}C\{^1H\}$, ^{11}B) were recorded on a Bruker Ascend 400 MHz instrument. High resolution mass spectra (HRMS) were obtained at the University of Texas at Austin Mass Spectrometry Center on a Micromass Autospec Ultima spectrometer using CI. Melting points were measured with a Thomas Hoover Uni-melt capilliary melting point apparatus and are uncorrected. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Crystals were selected under paratone oil, mounted on MiTeGen micromounts, and immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL and figures produced using OLEX2.[2,3]



Synthesis of **3:** To a solution of **2Ph** (28.0 mg, 0.117 mmol) in *n*-pentane (1 mL), trimethylsilyldiazomethane (2 M in hexanes, 0.067 mL, 0.134 mmol) was added dropwise at room temperature while stirring. The reaction mixture was stirred for an additional 10 min, after which the volatiles were removed *in vacuo*. The product, a pale yellow solid, was determined to be pure by ^{1}H NMR with no additional work-up. Single crystals for X-ray diffraction studies were grown from an *n*-pentane solution of **3** at -35 ºC. Yield: 38.0 mg (quantitative). d.p. 66-68 ºC.

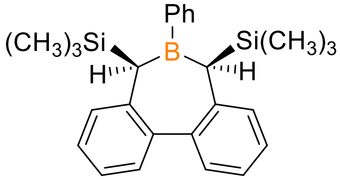
^{1}H NMR (400 MHz, C_6D_6): δ 8.13 (dd, *J* = 7.5, 1.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 8.03-8.00 (m, 1H), 7.80 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.46-7.42 (m, 1H), 7.35-7.29 (m, 3H), 7.26-7.12 (m, *C_6D_6*, 5H), 3.88 (s, 1H), -0.30 (s, 9H)

$^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6): δ 144.65, 140.59, 136.01, 135.15, 134.42, 133.37, 130.14, 129.80, 127.20, 126.76, 125.61, 124.79, 123.98, 48.87, -0.20

^{11}B NMR (128 MHz, C_6D_6): δ 65.8

FT-IR (cm^{-1} (ranked intensity)): 1593 (5), 1476 (12), 1439 (7), 1247 (2), 1038 (6), 952 (9), 826 (1), 766 (15), 746 (10), 730 (3), 702 (4), 659 (8), 544 (14), 486 (13), 439 (11)

High-resolution mass spectrometry (HRMS) chemical ionization (CI): calcd for $C_{22}H_{23}BSi$ $[M]^+$, 326.1662; found, 326.1667.



Synthesis of **4:** To a solution of **3** (83.0 mg, 0.254 mmol) in benzene (1.5 mL), trimethylsilyldiazomethane (2 M in hexanes, 0.128 mL, 0.256 mmol) was added dropwise at room temperature while stirring.

After 20 minutes of stirring, the volatiles were removed *in vacuo* to yield **4** as a white solid. The solid was then redissolved in a minimal amount of toluene, recrystallized at -35 ºC, and dried *in vacuo*. Yield: 47.0 mg (45%). d.p. 66-68 ºC.

Synthesis of **4** directly from **2Ph**: To a solution of **2Ph** (429.0 mg, 1.787 mmol) in benzene (5 mL), trimethylsilyldiazomethane (2 M in hexanes, 1.787 mL, 3.574 mmol) was added dropwise at room temperature while stirring. The reaction mixture was then heated for 1 d at 80 ºC, after which the solvent was evaporated *in vacuo* to afford a pale yellow oil. Lyophilization of the crude oil from benzene (1 mL) provided a white powder, which was dissolved in a minimal amount of toluene and recrystallized at -35 ºC. Crystals for X-ray diffraction studies were grown from the crude product oil at -35 ºC. Yield: 136.0 mg (18%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.54 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.46-7.43 (m, 3H), 7.25-7.20 (m, 3H), 7.19-7.13 (m, C_6D_6, 7H), 7.03 (dd, *J* = 7.0, 2.0 Hz, 1H), 3.24 (s, 1H), 2.70 (s, 1H), -0.07 (s, 9H), -0.59 (s, 9H)

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 144.32, 142.76, 140.12, 138.08, 130.77, 130.61, 129.53, 129.09, 128.96, 128.59, 127.54, 127.42, 126.00, 125.03, 49.78, 37.75, 0.61, 0.38

^{11}B NMR (128 MHz, C_6D_6): δ 75.4

FT-IR (cm^{-1} (ranked intensity)): 2954 (10), 1695 (5), 1596 (8), 1473 (14), 1436 (12), 1311 (9), 1247 (2), 1197 (11), 1026 (6), 834 (1), 749 (3), 700 (4), 579 (13), 499 (7), 479 (15)

High-resolution mass spectrometry (HRMS) chemical ionization (CI): calcd for $C_{26}H_{33}BSi_2$ $[M]^+$, 412.2214; found, 412.2218.

Figure S-1: ^{1}H NMR spectrum of **3** in C_6D_6.

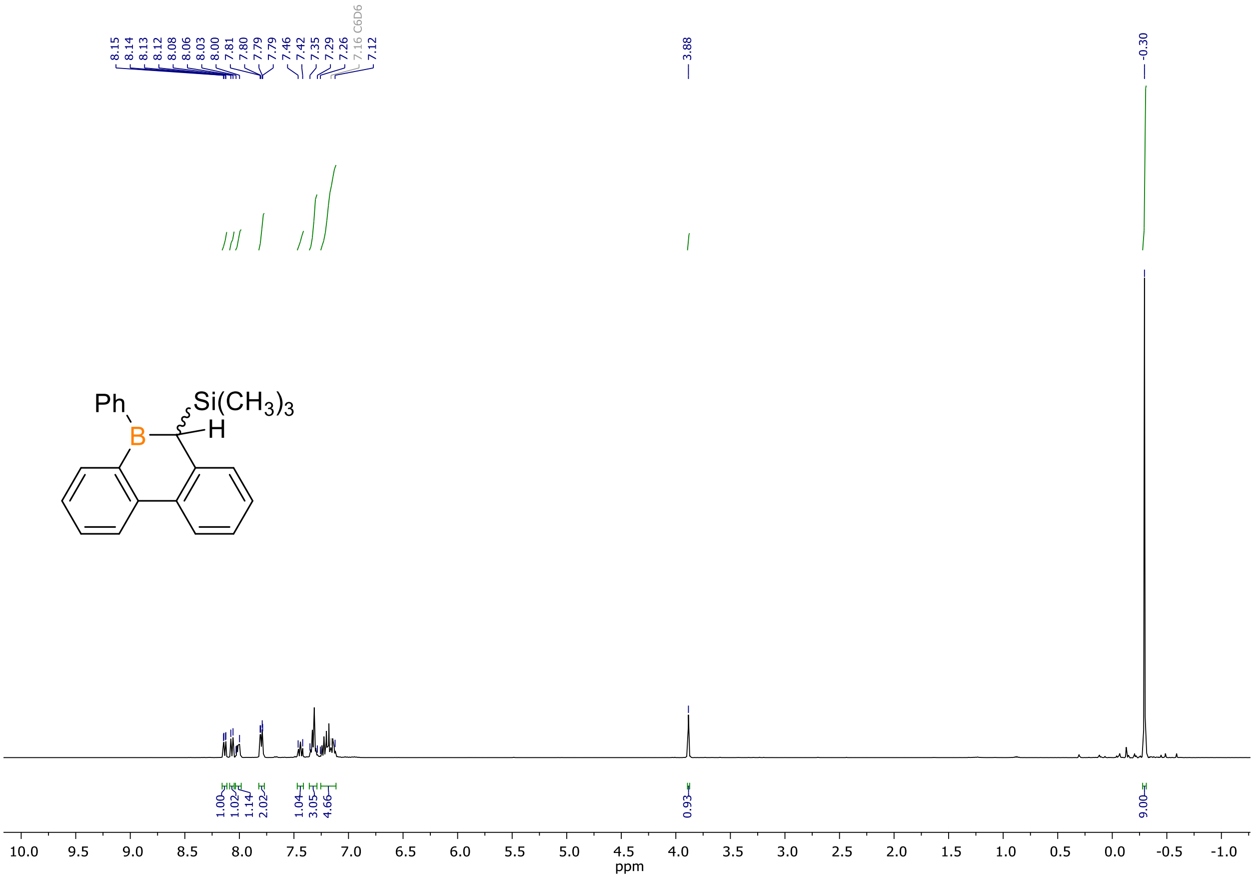


Figure S-2: Expansion of ^{1}H NMR spectrum of **3** in C_6D_6 (aryl region).

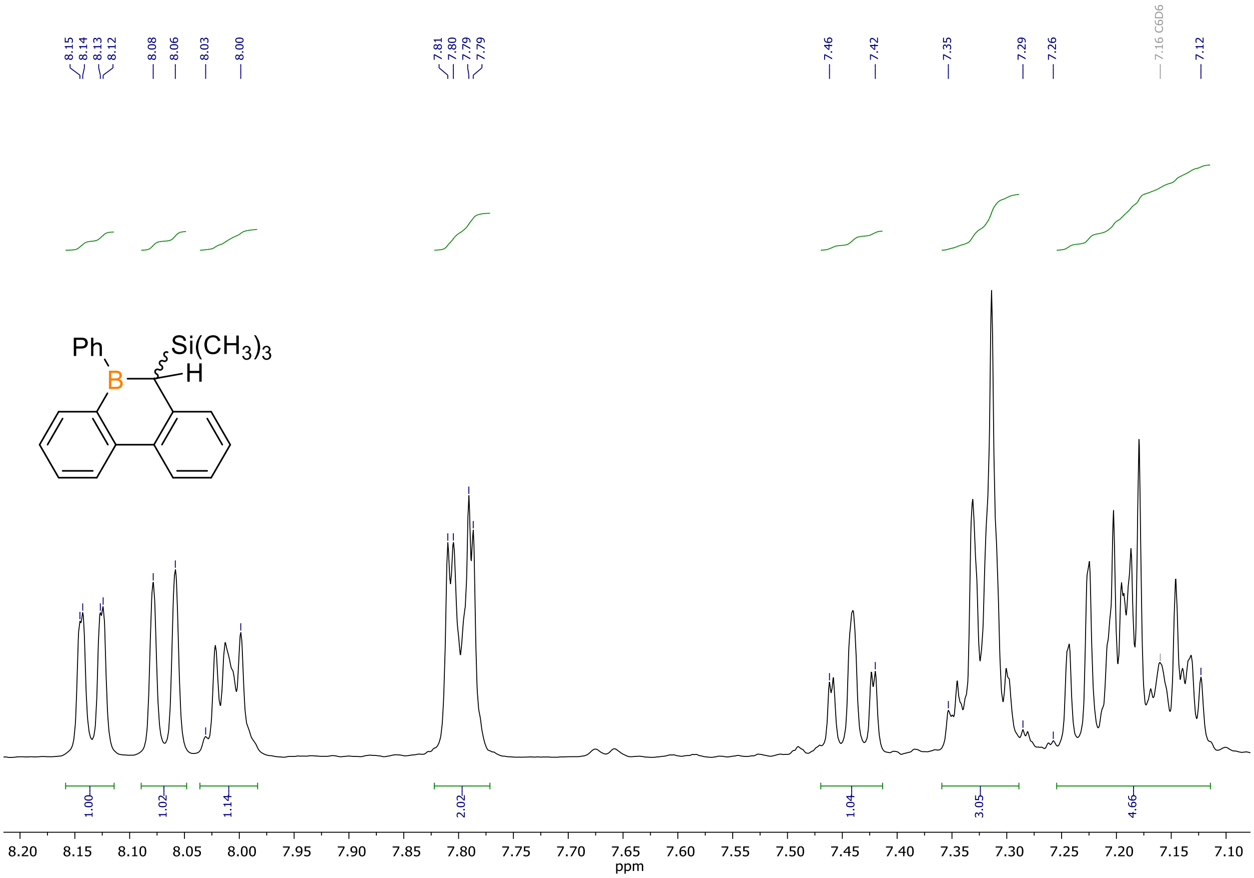


Figure S-3: $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.

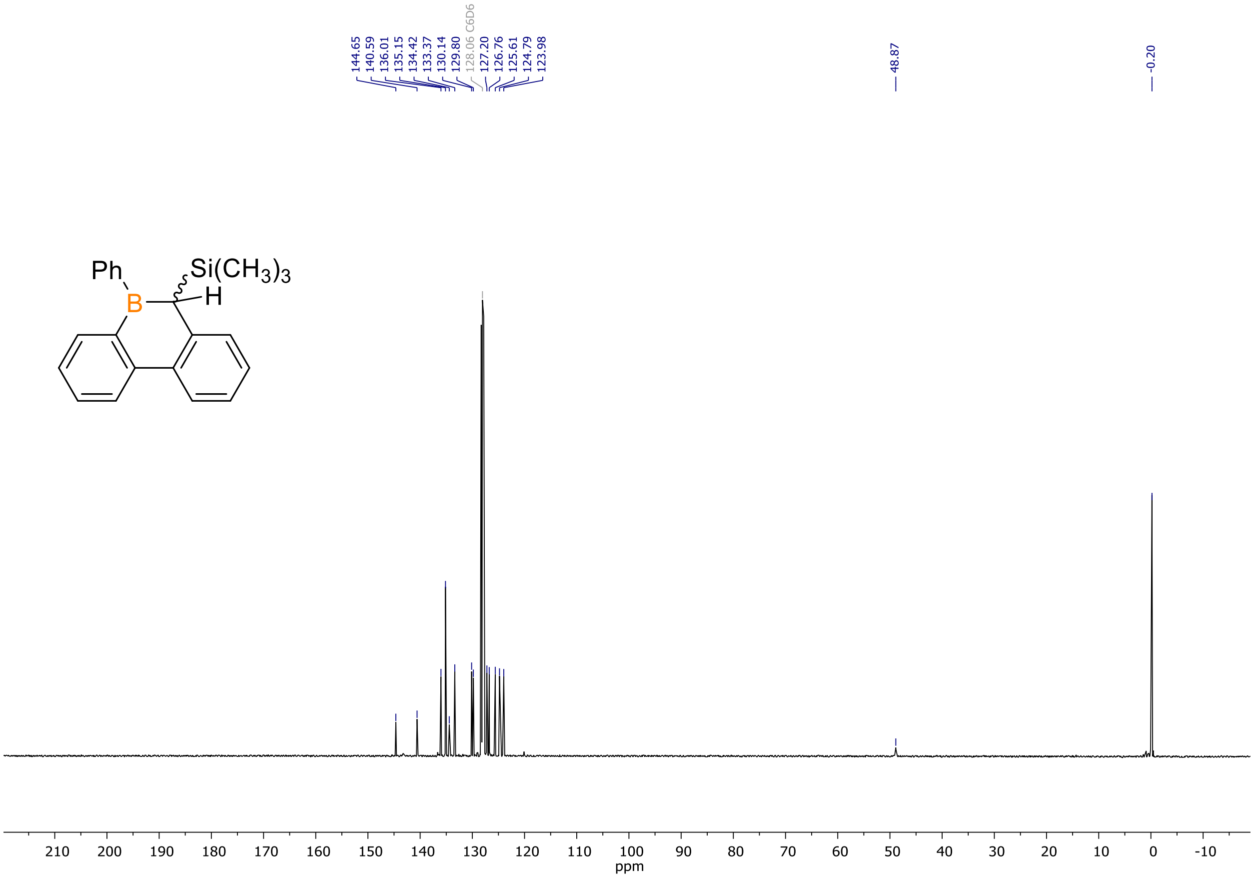


Figure S-4: Expansion of $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 (aryl region).

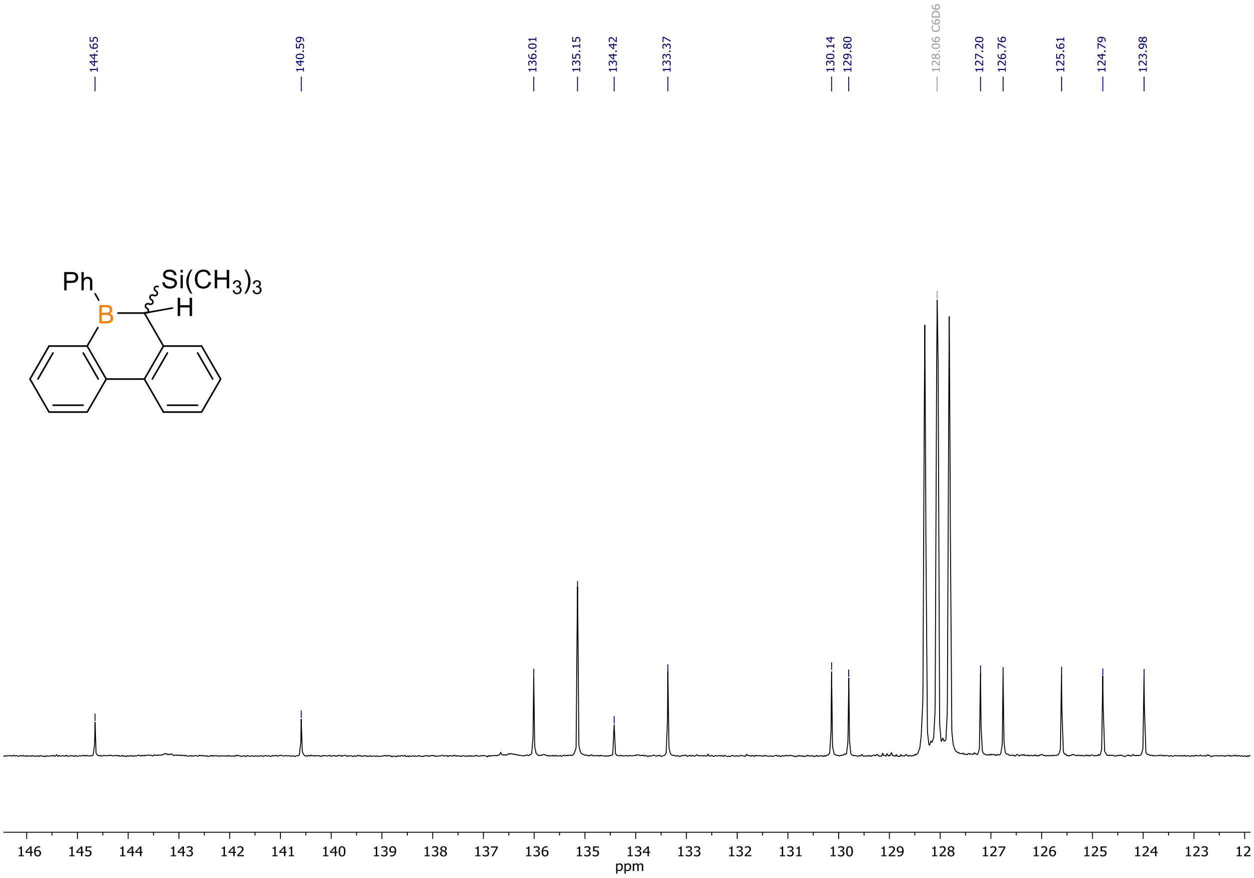


Figure S-5: ^{11}B NMR spectrum of **3** in C_6D_6.

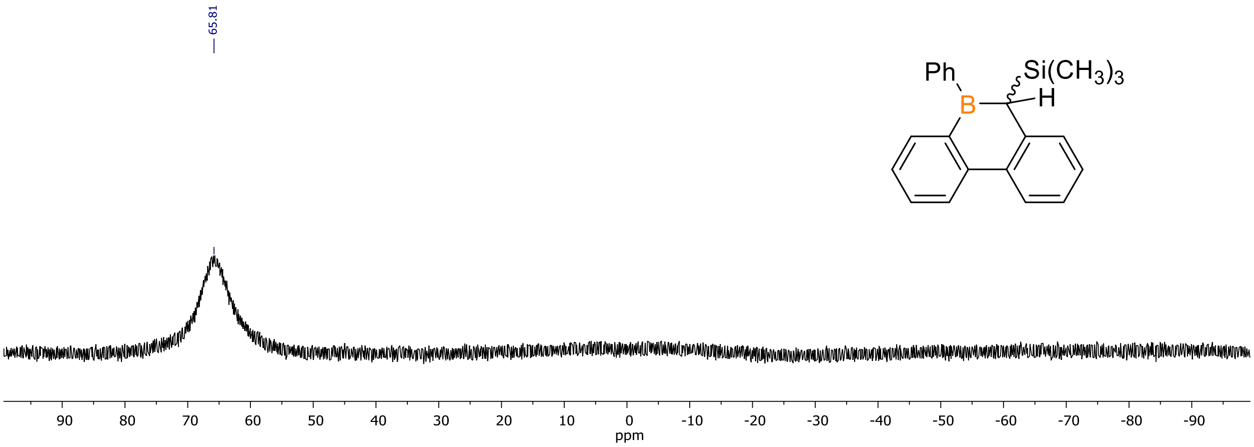


Figure S-6: FT-IR spectrum of **3**.

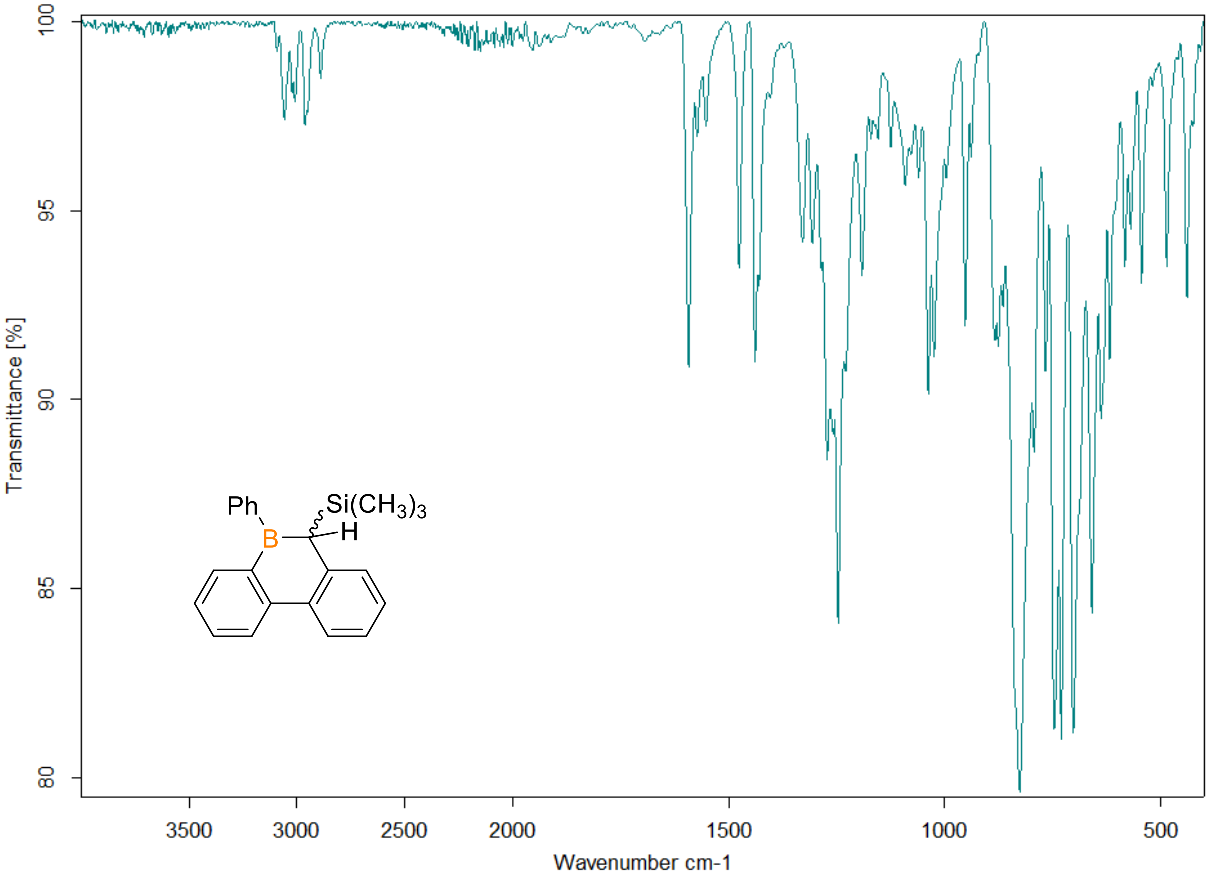
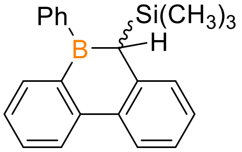


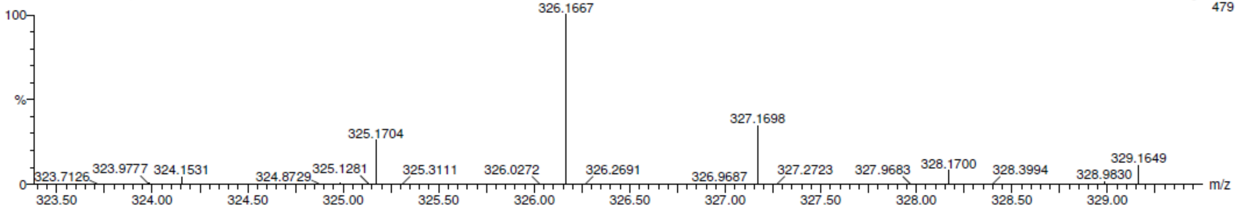
Figure S-7: High resolution mass spectrum of **3**.

Multiple Mass Analysis: 4 mass(es) processed - displaying only valid results
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None



Monoisotopic Mass, Odd and Even Electron Ions
77 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 Si: 1-1 10B: 0-1 11B: 0-1

TB-1-26
MSF19-TB-1-26_hrClpos1 427 (4.285) Cn (Cen,1, 10.00, Ar); Sm (Mn, 2x2.00); Cm (422:427)



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Minimum:   10.00                          -1.5
Maximum:   100.00             5.0    5.0   50.0

Mass       RA       Calc. Mass   mDa    PPM    DBE    i-FIT       Formula

325.1704   25.79    325.1698     0.6    1.8    13.0   1.5         C22  H23  Si  10B
326.1667   100.00   326.1662     0.5    1.5    13.0   1.3         C22  H23  Si  11B
```

Figure S-8: ^{1}H NMR spectrum of **4** in C_6D_6 (* indicates grease).

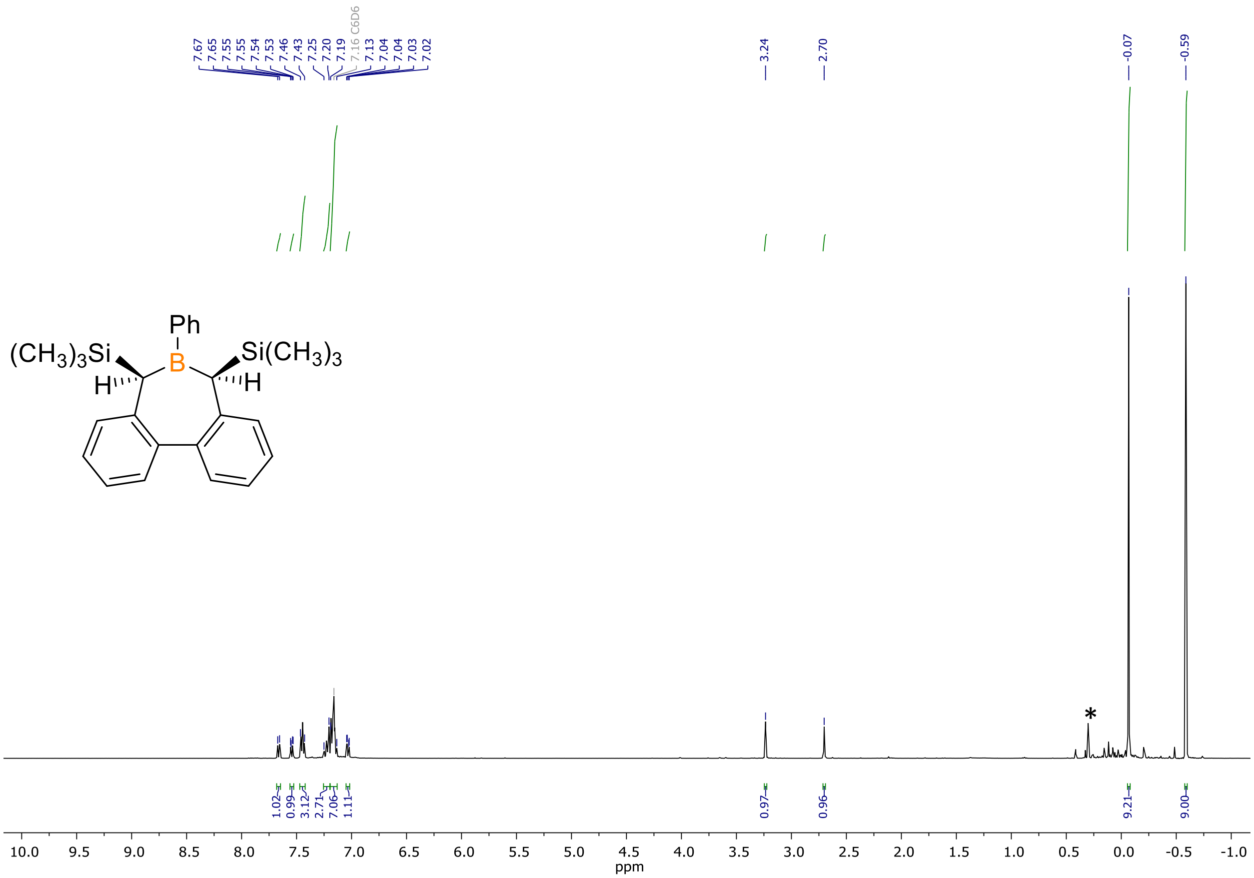


Figure S-9: Expansion of ^{1}H NMR spectrum of **4** in C_6D_6 (aryl region).

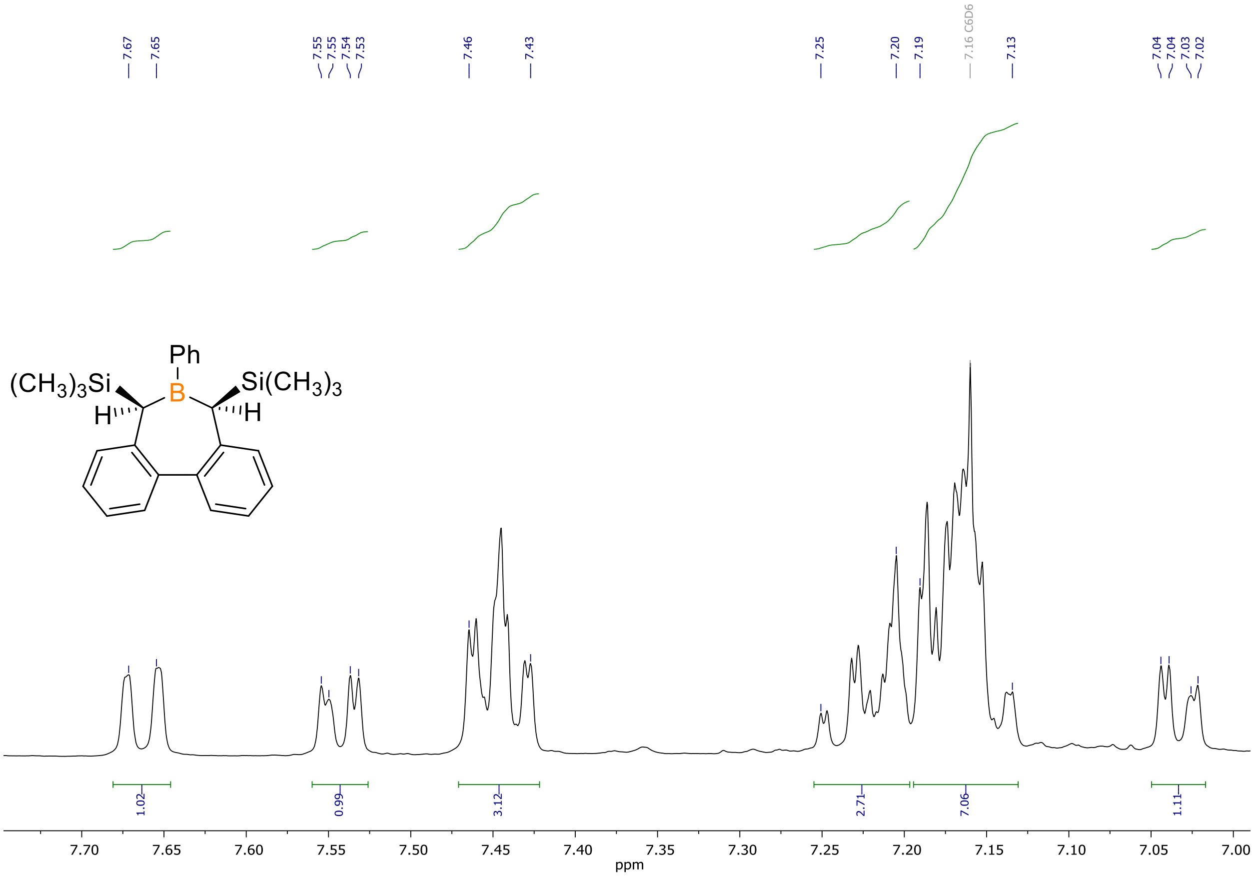


Figure S-10: Expansion of ^{1}H NMR spectrum of **4** in C_6D_6 (aliphatic region, * indicates grease).

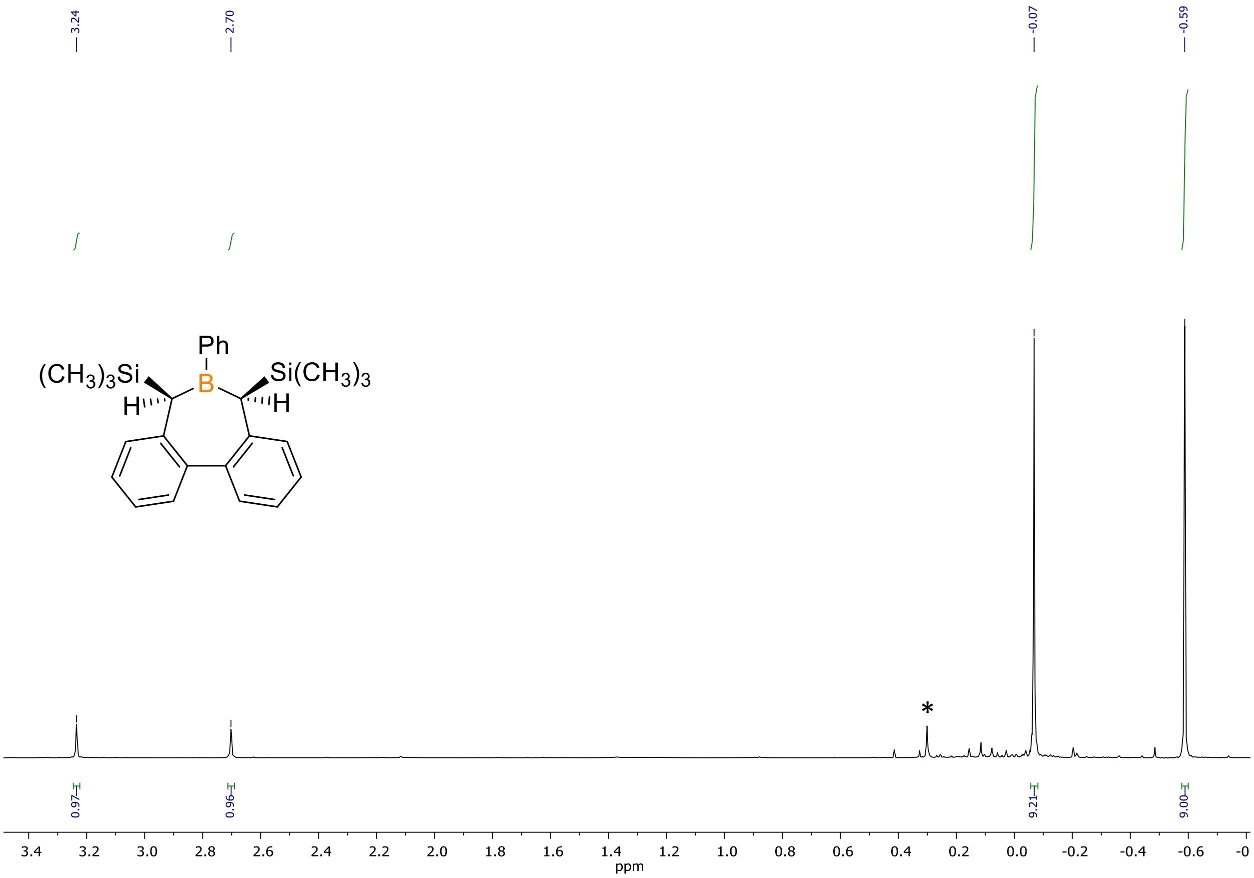


Figure S-11: $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 (* indicates grease).

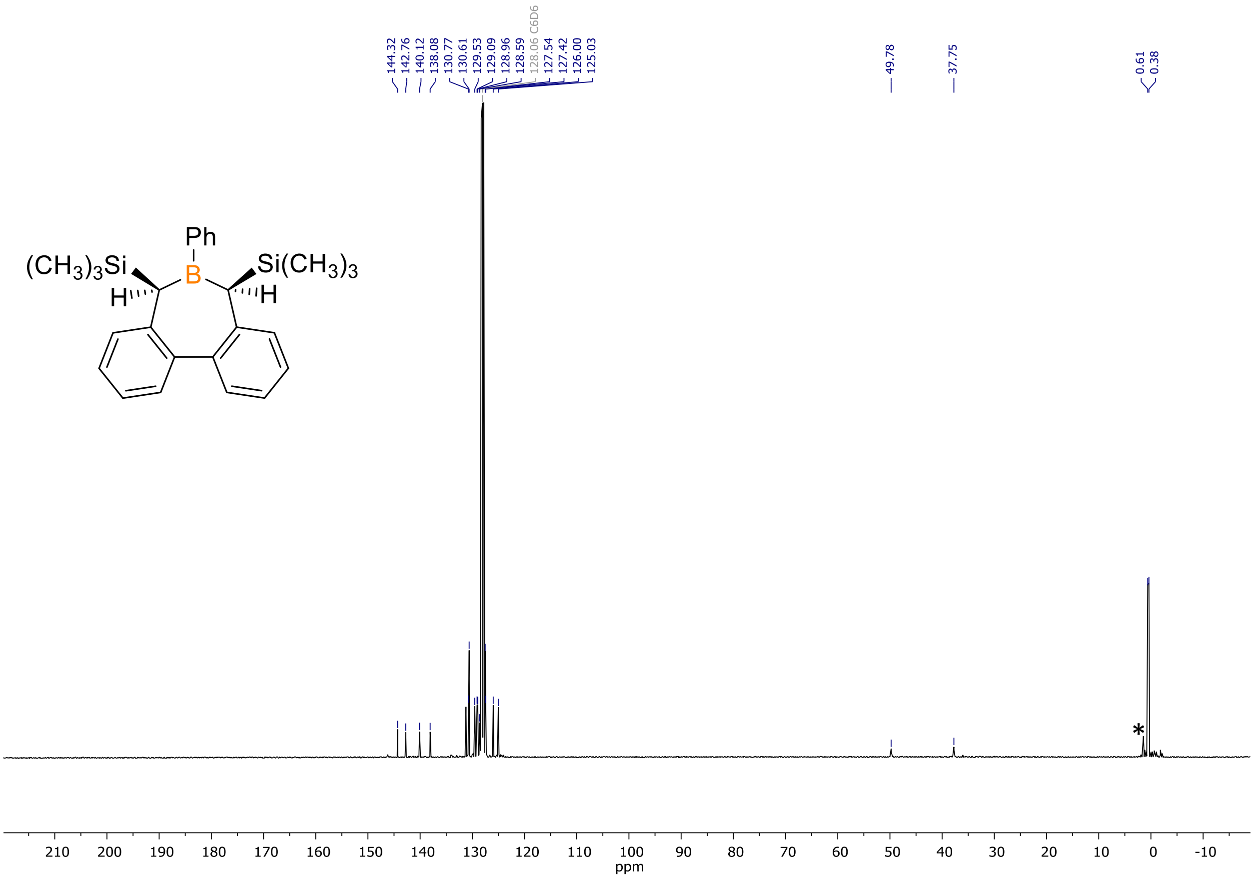


Figure S-12: Expansion of $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 (aryl region).

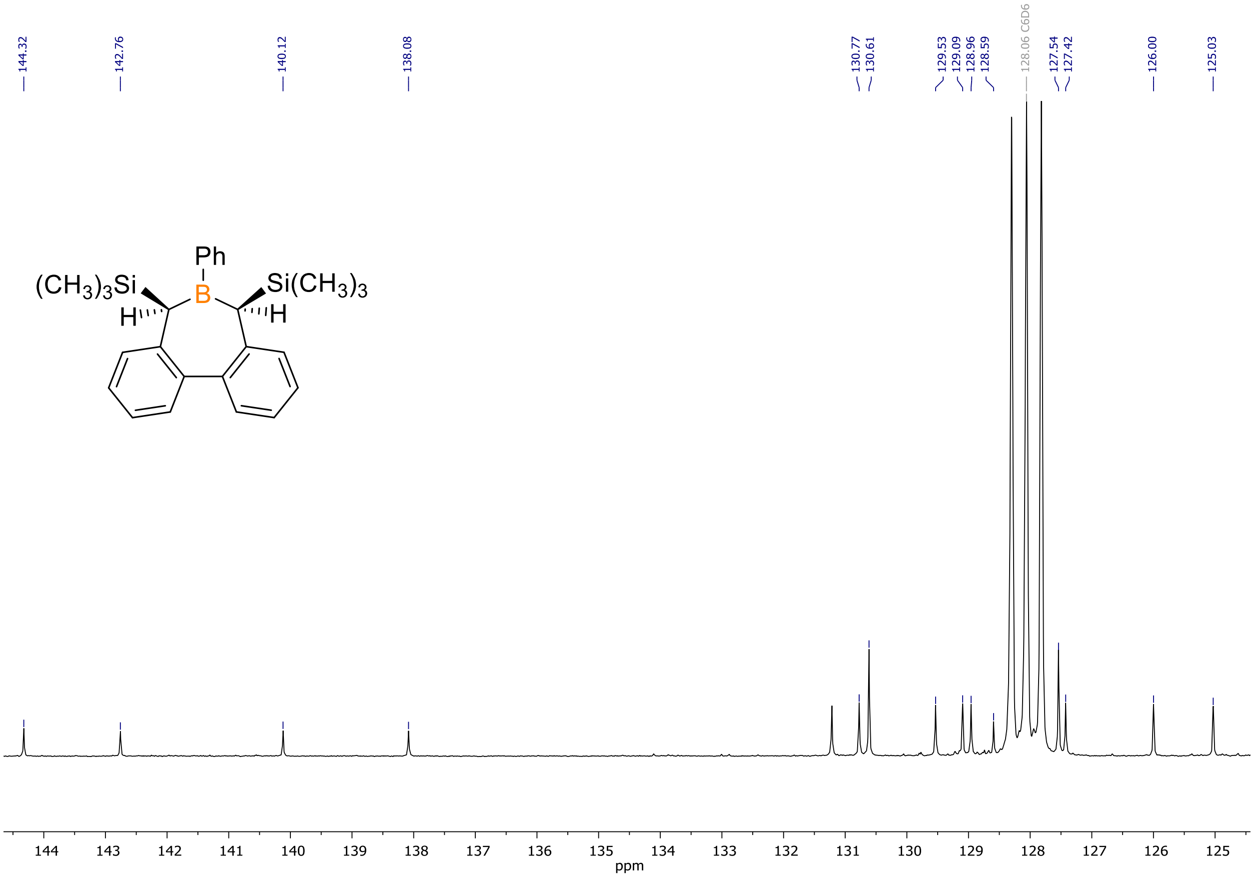


Figure S-13: ^{11}B NMR spectrum of **4** in C_6D_6.

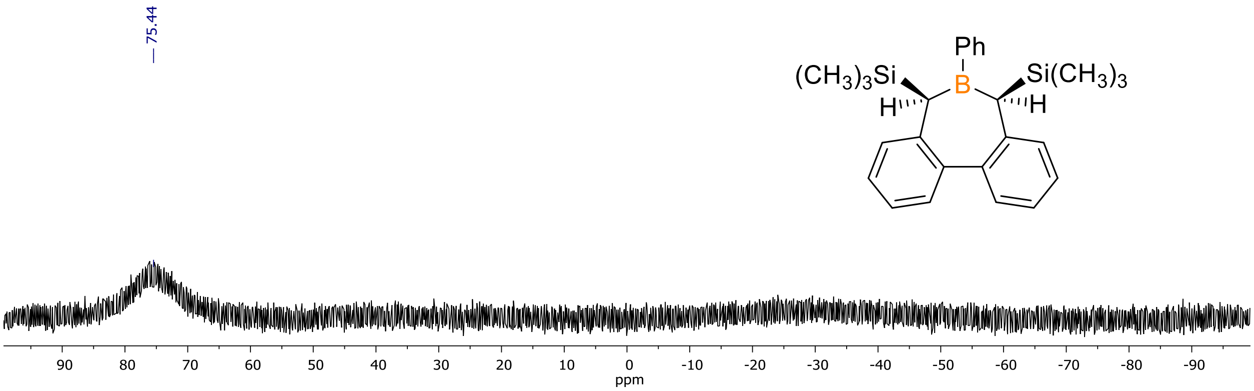


Figure S-14: FT-IR spectrum of **4**.

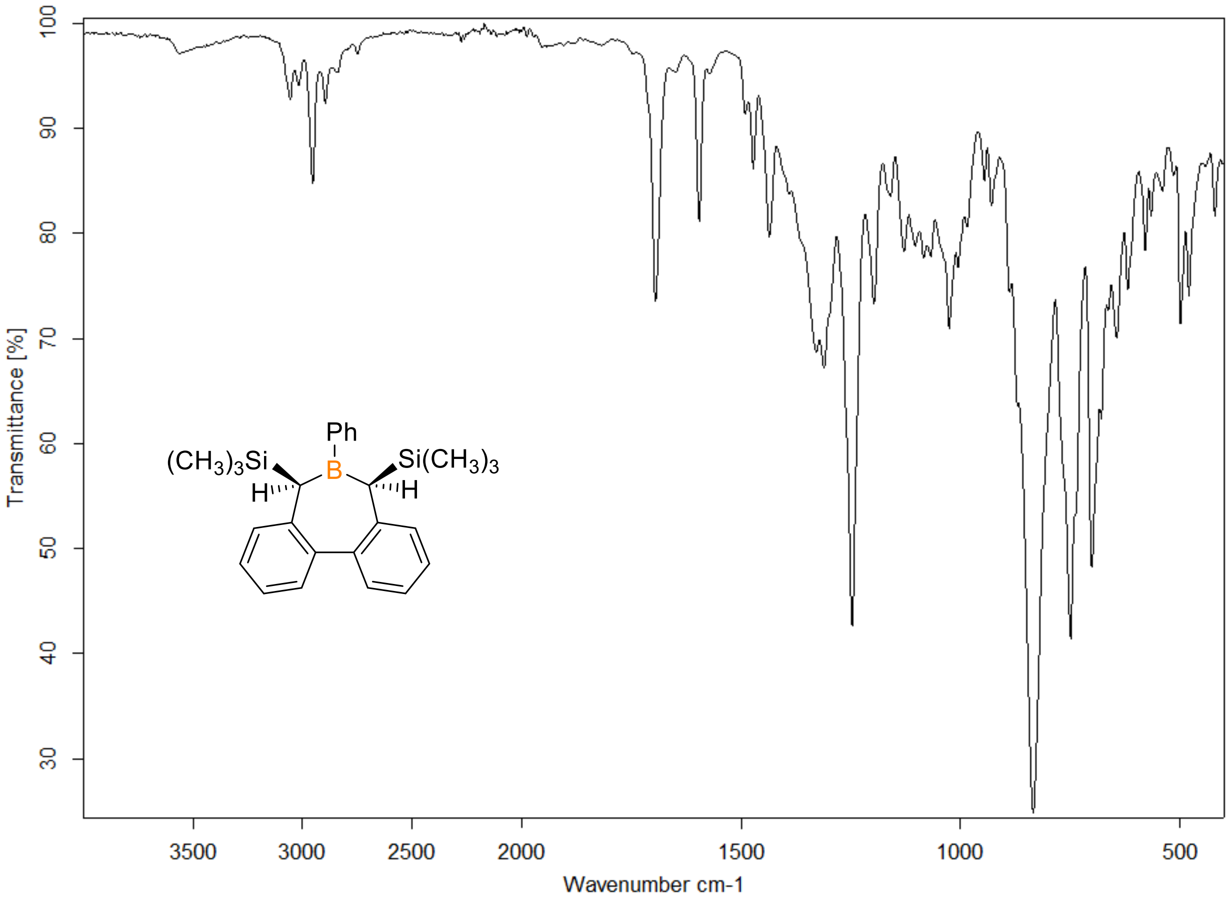
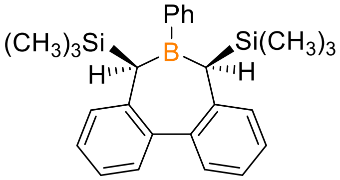


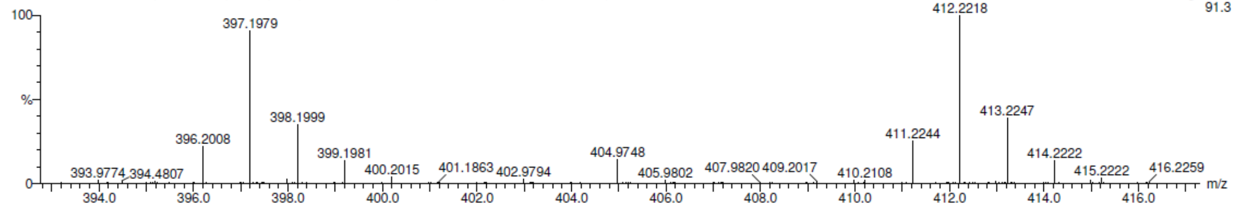
Figure S-15: High resolution mass spectrum of **4**.



Multiple Mass Analysis: 6 mass(es) processed - displaying only valid results
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
123 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 10B: 0-1 11B: 0-1 Si: 2-2

TB-1-15-10
MSF19-TB-1-15-10_hrClpos1 1361 (13.677) Cn (Cen,1, 20.00, Ar); Sm (Mn, 2x2.00); Cm (1358:1444)



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Minimum:   20.00                                    -1.5
Maximum:   100.00                 5.0        5.0    50.0

Mass       RA         Calc. Mass  mDa        PPM    DBE      i-FIT      Formula

396.2008   21.96      396.2015    -0.7       -1.8   13.5     0.0        C25  H30  10B  Si2
397.1979   90.79      397.1979    0.0        0.0    13.5     0.1        C25  H30  11B  Si2
411.2244   25.43      411.2250    -0.6       -1.5   13.0     0.1        C26  H33  10B  Si2
412.2218   100.00     412.2214    0.4        1.0    13.0     0.0        C26  H33  11B  Si2
```
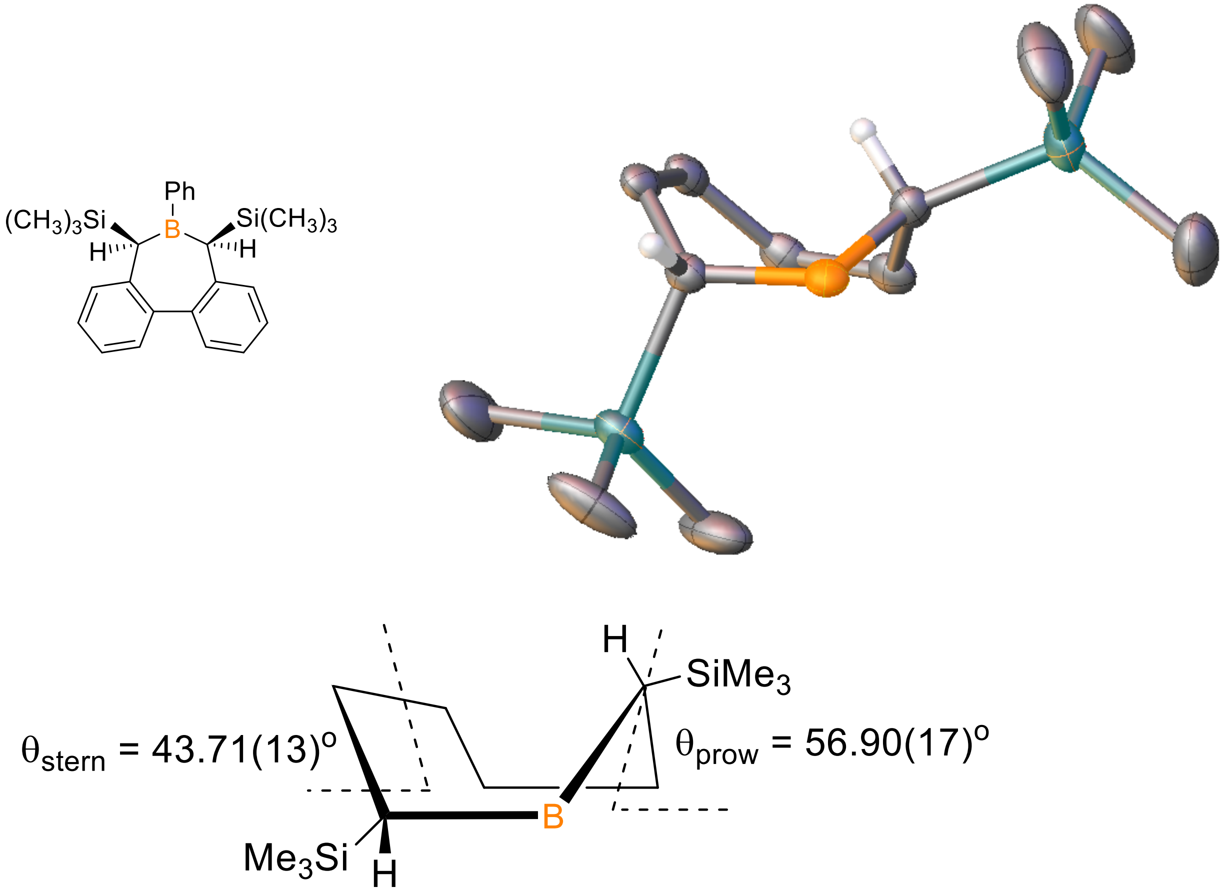

Table S-1: X-ray crystallographic details for **3** and **4**.

	3	**4**
CCDC	1901552	1901553
Empirical Formula	$C_{22}H_{23}BSi$	$C_{26}H_{33}BSi_2$
FW (g/mol)	326.30	412.51
Crystal System	Triclinic	Monoclinic
Space Group	P -1	I 2/a
a (Å)	7.2004(11)	17.718(4)
b (Å)	9.8166(16)	10.3253(17)
c (Å)	13.857(2)	28.130(7)
α (deg)	86.856(5)	90
β (deg)	79.281(5)	103.693(10)
γ (deg)	74.582(5)	90
V (Å^3)	927.7(3)	4999.9(19)
Z	2	8
D_c (g cm^{-3})	1.168	1.096
Radiation λ (Å)	0.71073	0.71073
Temp (K)	150	150
R1 [I>2(σ)I]^{a}	0.0487	0.0406
wR2 (F^2)^{a}	0.1068	0.1066
GOF (S)^{a}	1.029	1.056

^{a} $R1(F[I > 2(I)]) = \sum\|F_o| - |F_c\|/\sum |F_o|$; $wR2(F^2$ [all data]) = $[w(F_o^2 - F_c^2)^2]^{1/2}$; S(all data) = $[w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

Figure S-16: Diagram of **4** illustrating the dihedral planes θ_{prow} and θ_{stern} defining the deviation of the ring from planarity into a boat-like conformation.



References

1. P. E. Romero, W. E. Piers, S. A. Decker, D. Chau, T. K. Woo, M. Parvez, *Organometallics*, **2003**, *22*, 1266-1274.
2. G. M. Sheldrick, *Acta. Cryst.,* **2009**, *A64*, 112-122.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, **2009**, *42*, 229-341