

Electronic Supplementary Information

Synthesis, Structure and Reactivity of Iminoborane Radical

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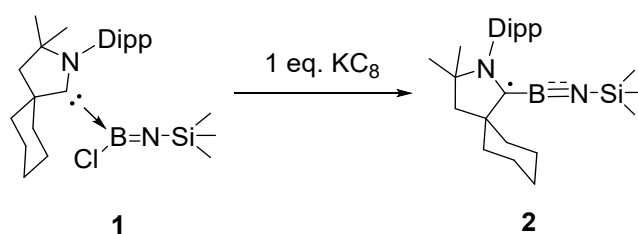
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Table of Contents

Experimental Section	S2
Crystal Data and Summary of Data Collection and Refinement	S3
Computational Details	S5
EPR Spectra and Simulations	S7
NMR Spectrum	S8
References	S12

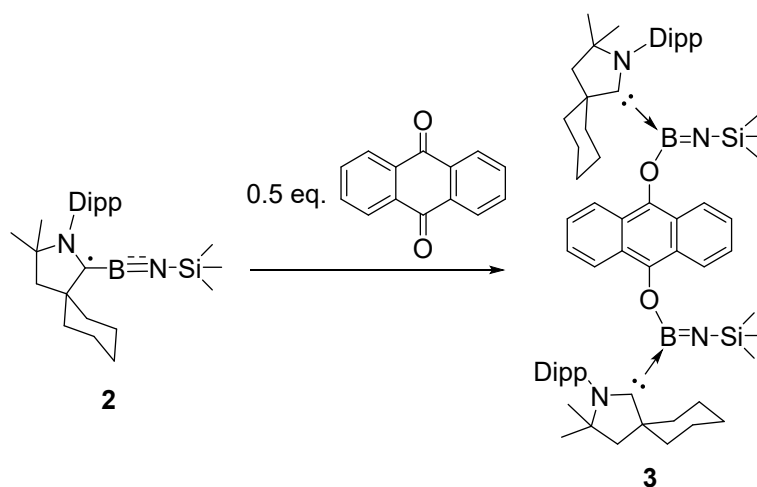
General Procedures. All operations were carried out under a dry argon atmosphere using standard Schlenk and glovebox techniques. ^1H , ^{13}C , and ^{11}B NMR spectra were recorded on a Bruker DPX 400/500 spectrometer at 400/500 MHz, 100/125 MHz and 128/160 MHz, respectively. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, and to external $\text{BF}_3 \cdot \text{OEt}_2$ (0.00 ppm) for boron chemical shifts. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Mass spectrum were obtained on solariX XR spectrometer. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Imino(chloro)borane–carbene adduct **1** was prepared according to the literature procedure.^[1] All other chemicals were purchased from either Aldrich, J&K or Acros Chemical Co. and used as received unless otherwise specified.

Experimental Section

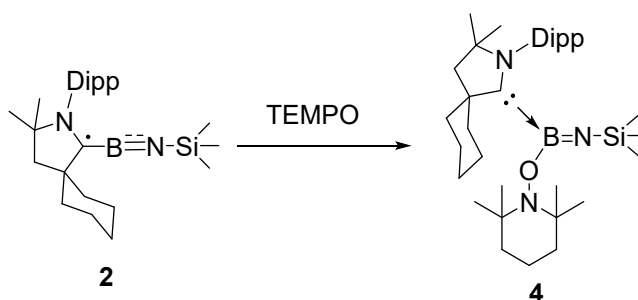


Preparation of 1. A toluene solution (10 mL) of **1** (916 mg, 2.0 mmol) was slowly added to the toluene solution of KC_8 (270 mg, 2.0 mmol) at room temperature and the reaction mixture was stirred overnight. The color of the solution was changed to deep red. After filtration, the red filtrate was concentrated to about 5 mL. Compound **2** was isolated as red crystals after this solution stood at room temperature (541 mg, 64 %).

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{44}\text{BN}_2\text{Si}^-(\text{M}-\text{H})^-$: 422.3299. Found: 422.3309.



Preparation of 2. To a mixture of **2** (424 mg, 1.0 mmol) and Anthraquinone (104 mg, 0.5 mmol) was added toluene (10 mL) at room temperature. The reaction mixture was stirred overnight. After removal of the volatiles under reduced pressure, the residue was extracted with toluene (3 x 3 mL) and then recrystallized from toluene (5 mL) at room temperature via slow evaporation to give compound **3** as red crystals. (231 mg, 28 %). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.19-6.61 (br, 8H; aromatic CH), 7.59 (m, 2H; aromatic CH), 7.40 (br, 4H; aromatic CH), 2.94 (br, 4H; CHMe₂), 2.29 (br, 4H; C₆H₁₀), 1.88 (br, 6H; C₆H₁₀), 1.81 (m, 4H; C₆H₁₀), 1.49 (s, 22H; C₆H₁₀ + CHMe₂+CMe₂), 1.29 (s, 12H; CHMe₂), 1.14 (br, 12H; CMe₂), -1.22 (s, 18H; CMe₃). ^{13}C { ^1H } NMR (100 MHz, CD_2Cl_2): δ 147.0, (NCN), 143.6, 133.3, 130.2, 126.1, 124.8, 124.3, 122.3 (aromatic C), 79.6 (CHMe₂), 57.9, 46.1, (C₆H₁₀), 29.7 (CHMe₂), 25.9 (C₆H₁₀), 25.0 (CHMe₂), 3.4 (CMe₃). ^{11}B NMR (128 MHz, CD_2Cl_2): δ 18.3 (br, 1B). ^{11}Si NMR: no observed. HRMS: m/z calcd for C₂₉H₄₆N₂B₁₂Br₄⁻ (M)⁻: 1055.7352. Found: 1055.7361.



Preparation of 3. To a mixture of **2** (212 mg, 0.5 mmol) and TEMPO (78 mg, 0.5 mmol) was added toluene (10 mL) at room temperature. The reaction mixture was stirred overnight. After removal of the volatiles under reduced pressure, the residue was extracted with hexane (3 x 3 mL) and then recrystallized from toluene (5 mL) at room temperature via slow evaporation to give compound **4** as yellow crystals. (235 mg, 81 %). ^1H NMR (500 MHz, CD_2Cl_2): δ 7.32 (m, 1H; aromatic CH), 7.24 (m, 2H; aromatic CH), 2.93 (m, 4H; CHMe₂), 2.19 (s, 2H; C₆H₁₀), 2.11 (s, 2H; C₆H₁₀), 1.76-1.73 (br, 4H; C₆H₁₀), 1.39 (s, 20H; CHMe₂ + C₆H₁₀+C₅NH₆), 1.22 (s, 8H; C₆H₁₀+C₅NH₆), 0.76 (s, 12H; CMe₂), -0.04 (s, 9H; CMe₃). ^{13}C { ^1H } NMR (125 MHz, CD_2Cl_2): δ 146.8 (NCC), 134.9, 129.4, 125.6 (aromatic C), 76.4 (CHMe₂), 58.3, 56.5, 47.5, 40.5, 38.5, 34.1 (C₆H₁₀+C₅NH₆), 29.3 (CHMe₂), 25.9, 25.6 (CHMe₂), 23.2, 20.7, 17.9 (CMe₂), 5.0 (CMe₃). ^{11}B NMR (160 MHz, CD_2Cl_2): δ 19.4 (s, 1B). ^{11}Si NMR: no observed. HRMS: m/z calcd for C₃₅H₆₂BN₃OSi (M+H)⁺: 580.4834. Found: 580.4837.

Crystal Data and Summary of Data Collection and Refinement

X-ray Structure Determination. Single crystals were immersed in Paraton-N oil and sealed under argon in thin-walled glass capillaries. All data were collected at 296 K or 173 K on a Bruker Kappa ApexII Duo Diffractometer using Mo-K α radiation. An

empirical absorption correction was applied using the SADABS program.^[2] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.^[3] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and refinement are given in **Table S1**. Details of the crystal structures were deposited in the Cambridge Crystallographic Data Centre with CCDC 2329996-2329998 for **2**, **3** and **4**, respectively.

Table S1 Crystal Data, Summary of Data Collection and Refinement for **1**, **2** and **3**.

Compound	2	3	4
Formula	C ₂₆ H ₄₄ BN ₂ Si	C ₆₆ H ₉₆ B ₂ N ₄ O ₂ Si ₂	C ₃₅ H ₆₂ BN ₃ OSi
MW	423.53	1055.26	579.77
Crystal size (mm ³)	0.50x0.40x0.30	0.50x0.40x0.30	0.50x0.40x0.30
Crystal system	Triclinic	Monoclinic	Monoclinic
Space Group	P-1	C2/c	P2 ₁ /n
a, Å	10.212(3)	16.183(2)	10.257(1)
b, Å	11.708(5)	30.376(3)	18.663(1)
c, Å	12.522(4)	17.536(2)	19.582(1)
α, deg	106.89(2)	90	90
β, deg	100.52(2)	113.97(1)	99.64(1)
γ, deg	90.38(2)	90	90
V, Å ³	1405.7(9)	7876.9(2)	3695.7(2)
Z	2	4	4
D _{calcd} Mg/m ³	1.001	0.890	1.042
Radiation (Å)	0.71073	0.71073	0.71073
2θrange, deg	5.54 to 50.50	5.36 to 50.50	6.58 to 136.7
μ, mm ⁻¹	0.097	0.081	0.760
F(000)	466	2296	1280
No. of obsd rflns	5080	7130	6711
No. of params refnd	271	343	370
Goodness of fit	1.011	1.055	1.059
R1	0.0750	0.0997	0.0521
wR2	0.2089	0.2803	0.1526

Computational detail: All of these calculations were carried out with the Gaussian 16 program.^[4] Optimization of the ground state structures were performed at B3LYP/6-31+G (d,p)^[5] level of theory. Orbital energies of compound **2** were calculated at the B3LYP/6-31G+(d,p) level of theory. NBO analysis at the B3LYP/6-31G+(d,p) level of theory was carried out using the NBO program implemented in the Gaussian 16 package.^[6] The graphics of the molecular orbitals were produced by using the visualizing software VMD.^[7] Spin population by Hirshfeld method was calculated with Multiwfn package.^[7]

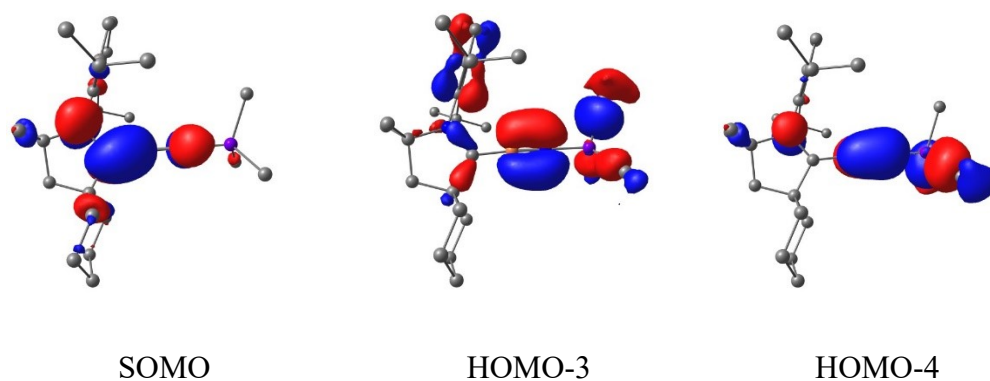


Figure S1. Plot of the SOMO (-4.08 eV) of **2** calculated at the B3LYP/6-31G+ (d, p) level of theory, where red and blue indicate different phases of the wave functions. (Contour value for isosurface: 0.036)

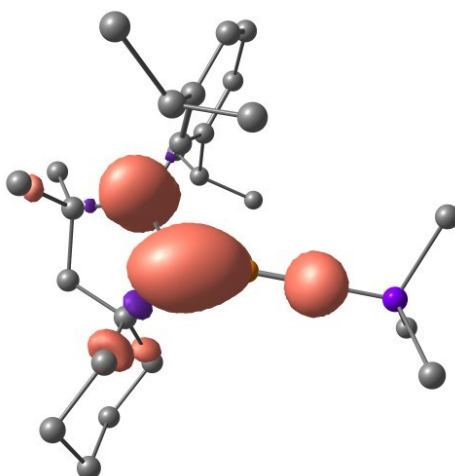


Figure S2. Spin population plot of the optimized structure of **2**. (Contour value for isosurface: 0.0026)

Cartesian coordinates:

2			
Si	0.400158000	4.080059000	0.002746000

B	-0.370004000	1.193523000	-0.009523000
N	-0.015220000	-1.331554000	-0.035620000
N	-0.037916000	2.420860000	-0.010479000
C	1.421311000	-1.222019000	0.020751000
C	2.177248000	-1.107025000	-1.173790000
C	3.575027000	-1.053521000	-1.075696000
H	4.168386000	-0.972970000	-1.981590000
C	4.217391000	-1.078791000	0.157721000
H	5.301907000	-1.038935000	0.210124000
C	3.461300000	-1.122674000	1.325523000
H	3.966927000	-1.098082000	2.286195000
C	2.062081000	-1.181554000	1.287403000
C	1.541007000	-0.952799000	-2.553460000
H	0.464339000	-1.084971000	-2.440363000
C	2.047461000	-1.997560000	-3.567530000
H	1.493786000	-1.909612000	-4.509068000
H	3.108518000	-1.852473000	-3.798198000
H	1.927778000	-3.020828000	-3.198162000
C	1.762705000	0.473882000	-3.101816000
H	1.250485000	0.592035000	-4.063864000
H	1.374794000	1.228778000	-2.412552000
H	2.827716000	0.676287000	-3.262763000
C	1.294999000	-1.121645000	2.607464000
H	0.237934000	-1.286008000	2.387080000
C	1.745852000	-2.198545000	3.614417000
H	1.101898000	-2.178193000	4.500961000
H	1.703754000	-3.204251000	3.185335000
H	2.772538000	-2.026909000	3.955399000
C	1.408508000	0.282274000	3.240964000
H	0.809489000	0.333585000	4.157688000
H	2.446798000	0.512653000	3.505998000
H	1.053945000	1.057846000	2.556699000
C	-0.775186000	-2.623137000	-0.104715000
C	-0.205122000	-3.688241000	0.843891000
H	-0.797075000	-4.604872000	0.752062000
H	0.831658000	-3.933655000	0.593565000
H	-0.245370000	-3.367806000	1.886168000
C	-0.782865000	-3.215190000	-1.530330000
H	-1.404979000	-4.116868000	-1.545378000
H	-1.187663000	-2.515799000	-2.264856000
H	0.224464000	-3.501647000	-1.842693000
C	-2.191209000	-2.167315000	0.328976000
H	-2.309631000	-2.346531000	1.403743000
H	-2.961853000	-2.752242000	-0.180149000

C	-2.307756000	-0.640327000	0.051155000
C	-0.843408000	-0.218997000	0.000647000
C	-3.033874000	-0.317746000	-1.290067000
H	-2.552571000	-0.853297000	-2.115634000
H	-2.893701000	0.751653000	-1.496942000
C	-4.540838000	-0.626913000	-1.265613000
H	-4.988239000	-0.327597000	-2.221590000
H	-4.700694000	-1.711101000	-1.180299000
C	-5.247321000	0.081128000	-0.100532000
H	-6.306742000	-0.201624000	-0.068115000
H	-5.216593000	1.167794000	-0.266330000
C	-4.563967000	-0.242118000	1.236028000
H	-4.702636000	-1.307748000	1.469197000
H	-5.039881000	0.315424000	2.052142000
C	-3.064000000	0.091247000	1.192845000
H	-2.945616000	1.174204000	1.051133000
H	-2.588553000	-0.149186000	2.151610000
C	2.236259000	4.250999000	-0.418795000
H	2.549565000	5.302145000	-0.406431000
H	2.856118000	3.705380000	0.301561000
H	2.451084000	3.847342000	-1.414651000
C	0.079426000	4.817652000	1.716751000
H	0.341773000	5.882401000	1.747951000
H	-0.977220000	4.723527000	1.992589000
H	0.670381000	4.302782000	2.482787000
C	-0.633045000	5.018720000	-1.275809000
H	-0.380654000	6.086192000	-1.286729000
H	-0.465281000	4.622067000	-2.283609000
H	-1.703229000	4.928802000	-1.056441000

EPR Spectra and Simulations

Room temperature solution EPR measurement was carried out on a Bruker EMXPlus-10/12 spectrometer. Samples containing around 0.001 M of radical species were transferred to a quartz J-Young's tube under nitrogen atmosphere. EPR spectra of **2** were obtained with a microwave power of 0.5024 mW, modulation amplitude of 0.2 G, time constant of 0.01 ms, and sweep time of 60 s. Spectral simulations were performed using the Easypin 5.2.35 toolbox^[8-9].

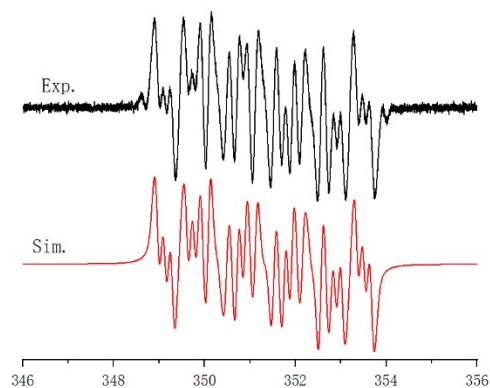


Figure S3. EPR spectrum of **2** in toluene at room temperature. The simulation parameters are $g_{\text{iso}} = 2.0015$, $a(^{11,10}\text{B}) = 10.36/3.45$ G, $a(^{14}\text{N}_{\text{CAAC}}) = 6.39$ G, and $a(^{14}\text{N}_{\text{BN}}) = 1.622$ G.

NMR spectrum

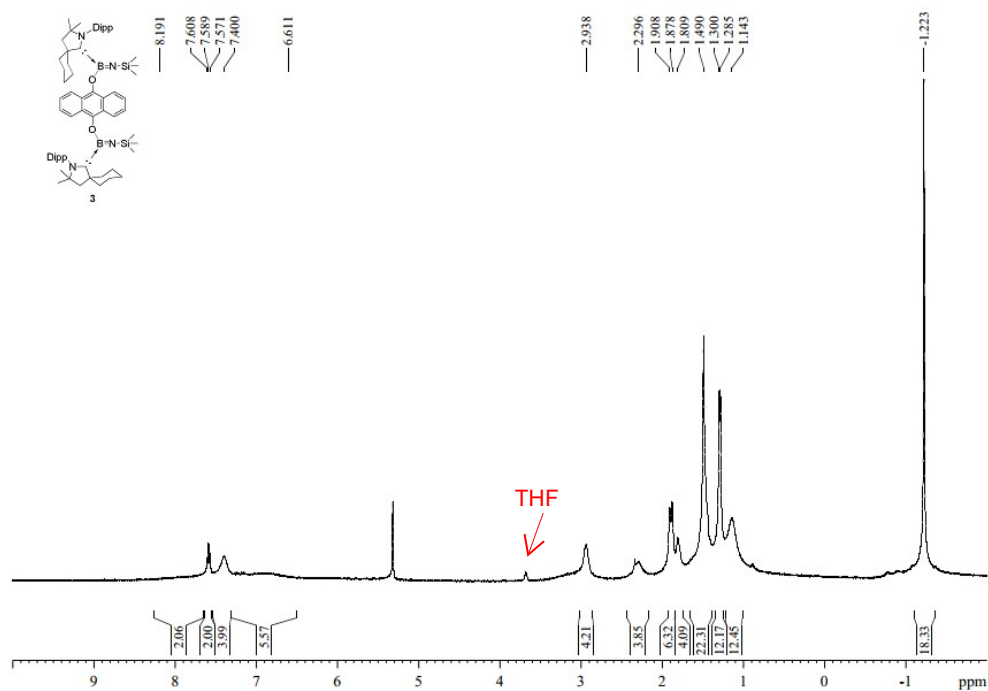


Figure S4. ^1H NMR spectrum of compound **3** in CD_2Cl_2 .

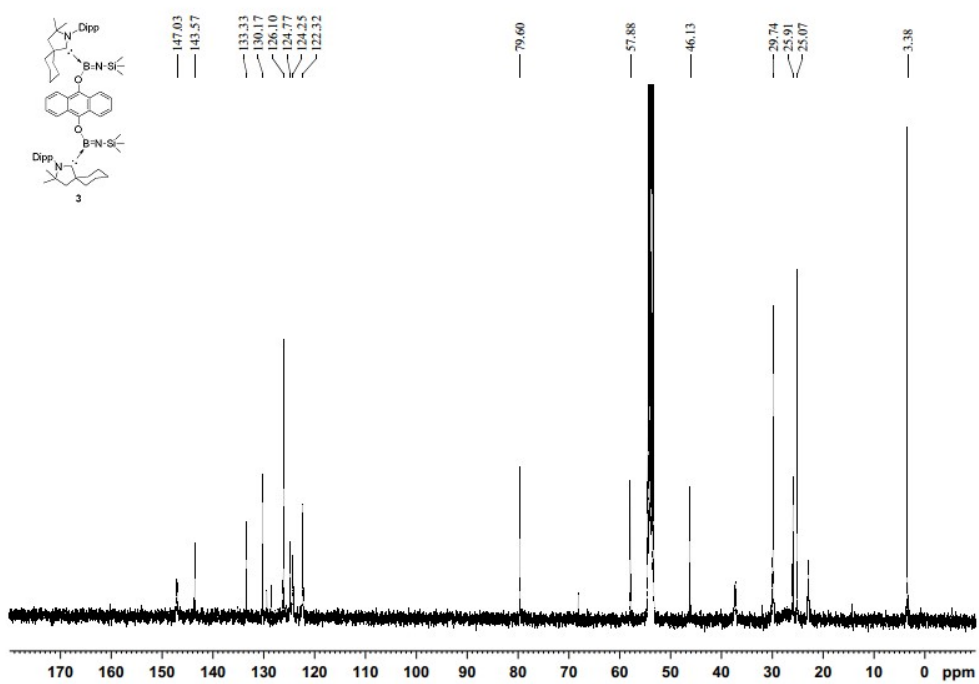


Figure S5. ¹³C NMR spectrum of compound **3** in CD₂Cl₂.

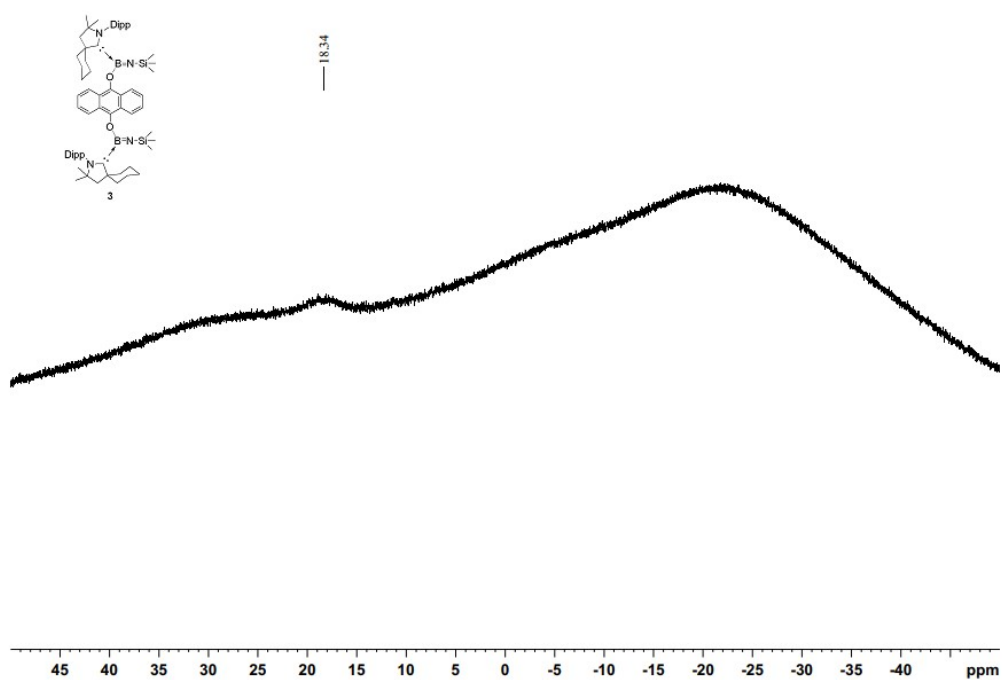


Figure S6. ¹¹B {¹H} NMR spectrum of compound **3** in CD₂Cl₂.

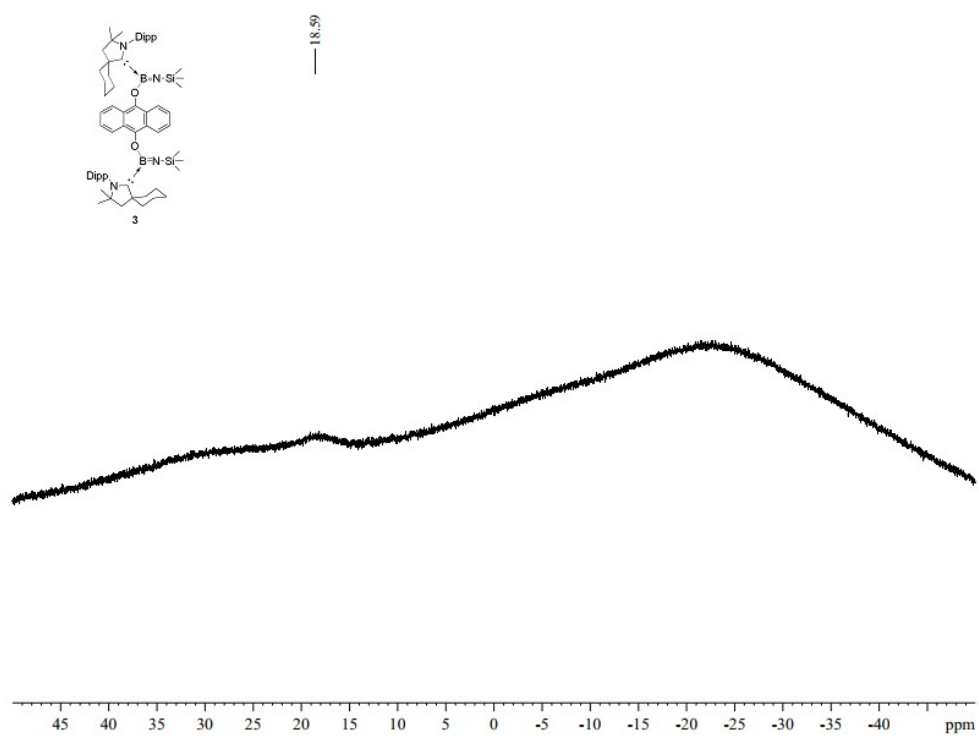


Figure S7. ^{11}B NMR spectrum of compound **3** in CD_2Cl_2 .

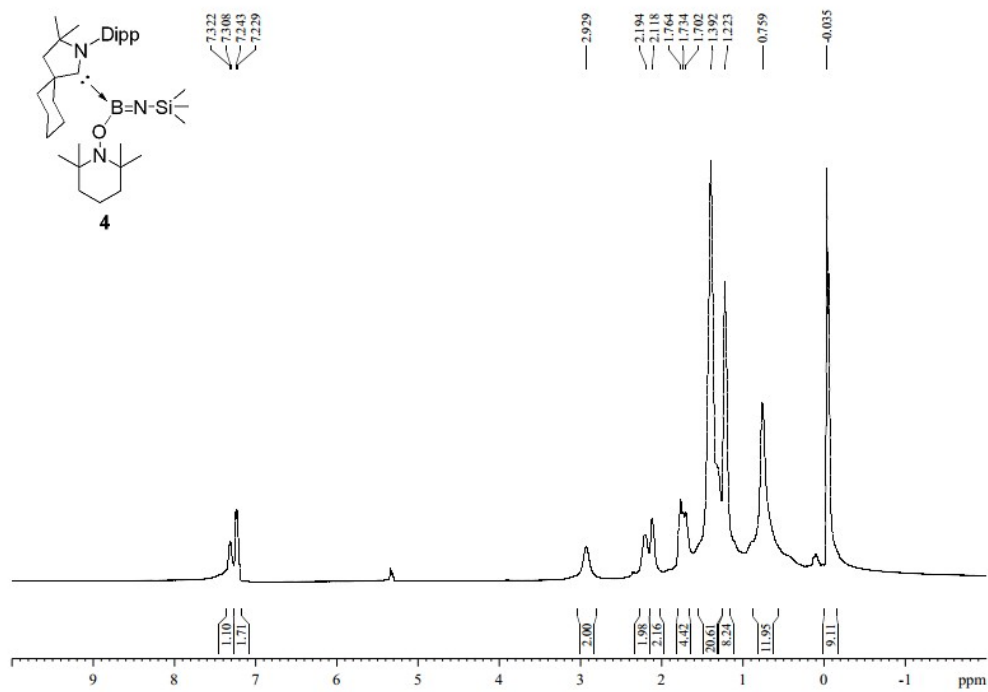


Figure S8. ^1H NMR spectrum of compound **4** in CD_2Cl_2 .

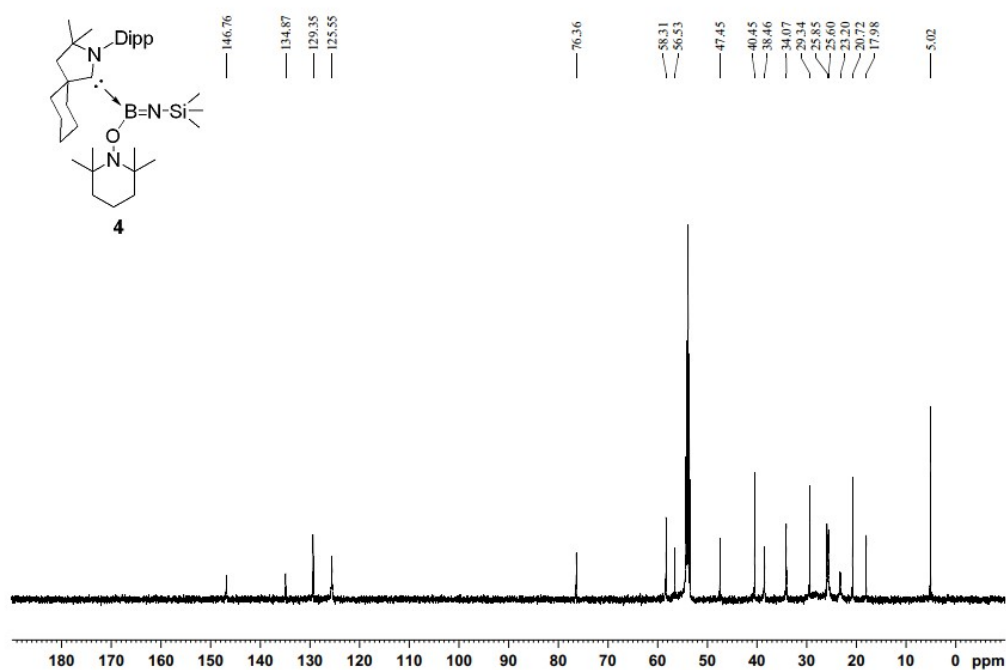


Figure S9. ^{13}C NMR spectrum of compound **4** in CD_2Cl_2 .

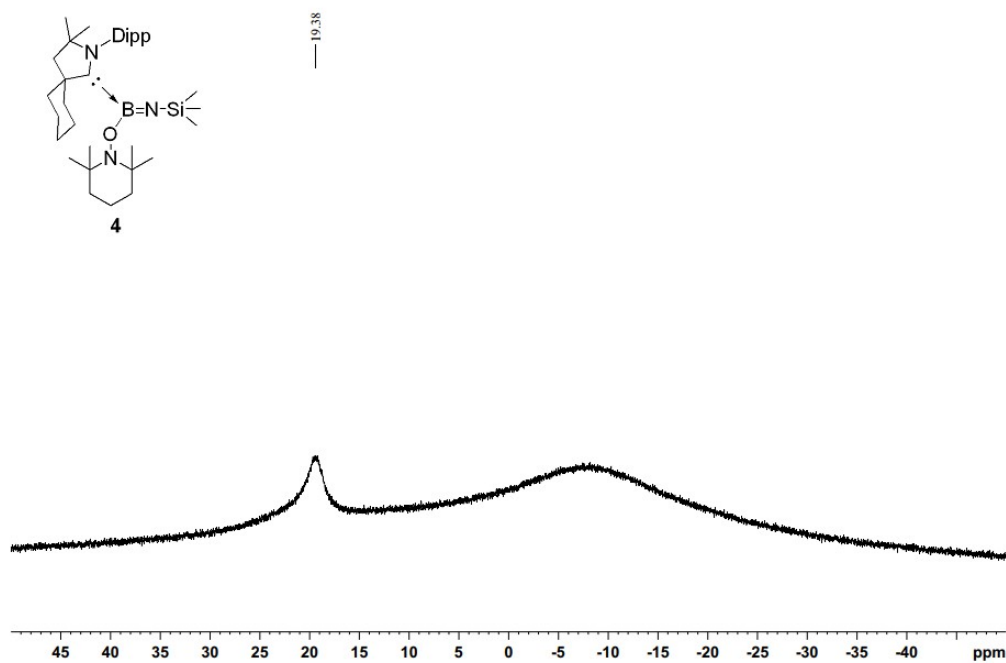


Figure S10. ^{11}B $\{^1\text{H}\}$ NMR spectrum of compound **4** in CD_2Cl_2 .

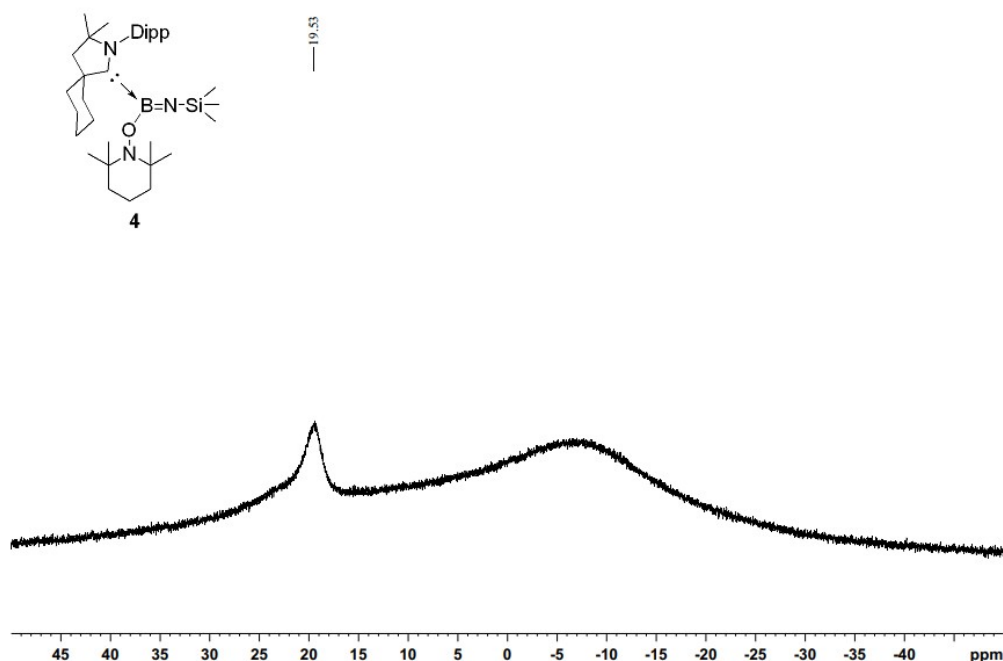


Figure S11. ^{11}B NMR spectrum of compound **4** in CD_2Cl_2 .

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