Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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1. General considerations

All manipulations were performed under an argon atmosphere in either an MBraun glovebox or using standard Schlenk techniques. Glassware was flame dried prior to use. Solvents were dried by standard methods and distilled under argon. Additionally, deuterated solvents used for NMR were purchased from Cambridge Isotope Laboratories, and dried over CaH_2. Multinuclear NMR data were recorded on a Varian INOVA 500 MHz, Bruker 300 MHz and Jeol 500 MHz spectrometers. NMR signals are listed in ppm. Coupling constants *J* are given in Hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad. EPR spectra were obtained using an X-band Bruker E500 spectrometer. Field calibration was accomplished by using a standard of solid 2,2-diphenyl-1-picrylhydrazyl (DPPH), g = 2.0036.[1] Single crystal X-Ray diffraction data were collected on a Bruker Apex II-CCD detector, using Mo-K_α radiation (λ = 0.71073 Å). Crystals were selected under oil, mounted on nylon loops, then immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL and Olex2 software.[2]

2. Synthesis and characterization

1 CAAC-BH_3:
The literature procedure was followed.[3] ^{1}H {11B}NMR (300 MHz, C_6D_6): δ 7.25 (m, 2 H), 7.15 (m, 1 H), 2.87 (sept, *J* = 6.6 Hz, 2 H), 2.05 (m, 2 H); 1.94 (m, 2 H), 1.63 (s, 2 H), 1.58 (s, 3 H, B*H*$_3$), 1.49 (d, *J* = 6.7 Hz, 6 H), 1.24 (d, *J* = 6.6 Hz, 6 H), 1.02 (s, 6 H), 1.00 (t, *J* = 7.4 Hz, 6 H); ^{13}C NMR (75 MHz, C_6D_6): δ 145.6 (C_q), 134.3 (C_q), 129.3 (CH_{Ar}), 124.7 (CH_{Ar}), 76.1 (C_q), 60.9 (C_q), 41.5 (CH_2), 33.2 (CH_2), 29.7, 28.9, 26.1, 23.4, 9.6, C_{Carb} was not detected; ^{11}B NMR (96 MHz, C_6D_6): δ -28.5 (q, J_{BH} = 87.5 Hz).

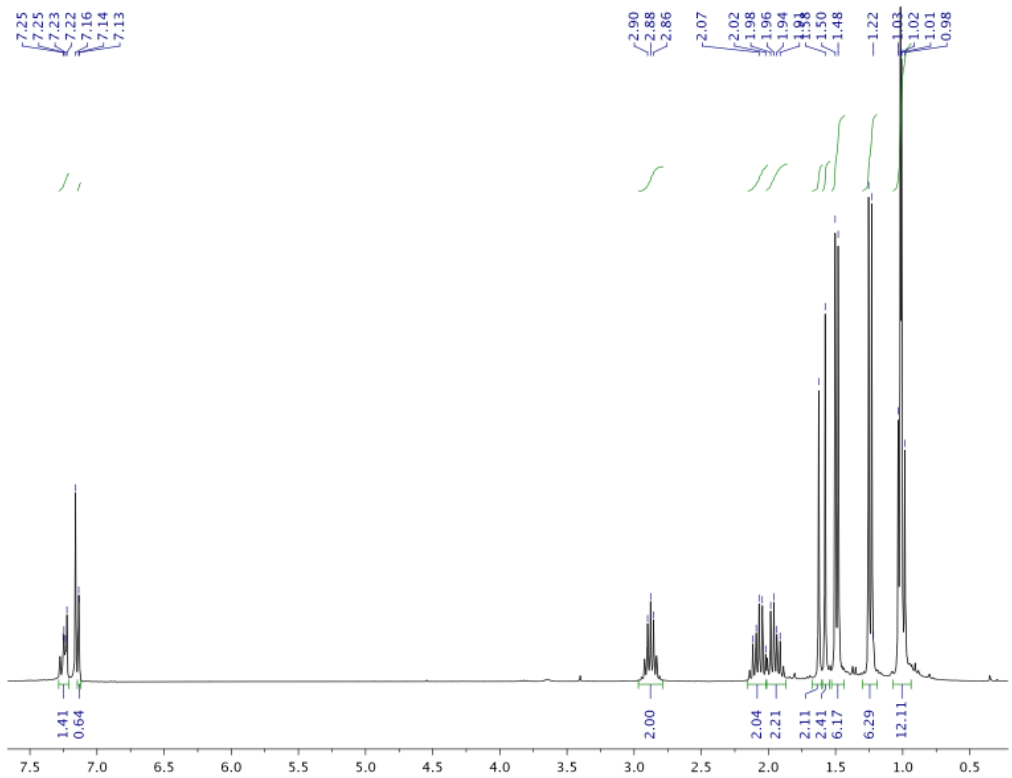

Figure S1 ^{1}H $\{^{11}B\}$ NMR spectrum of **1**

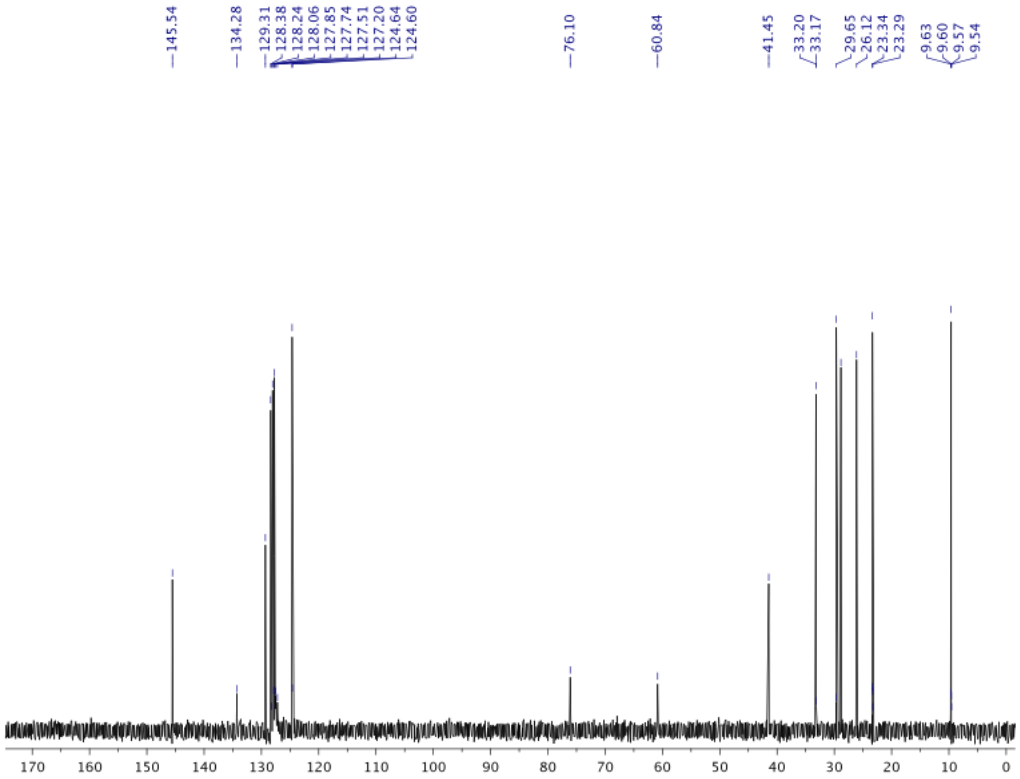

Figure S2 ^{13}C $\{^{1}H\}$ NMR spectrum of **1**

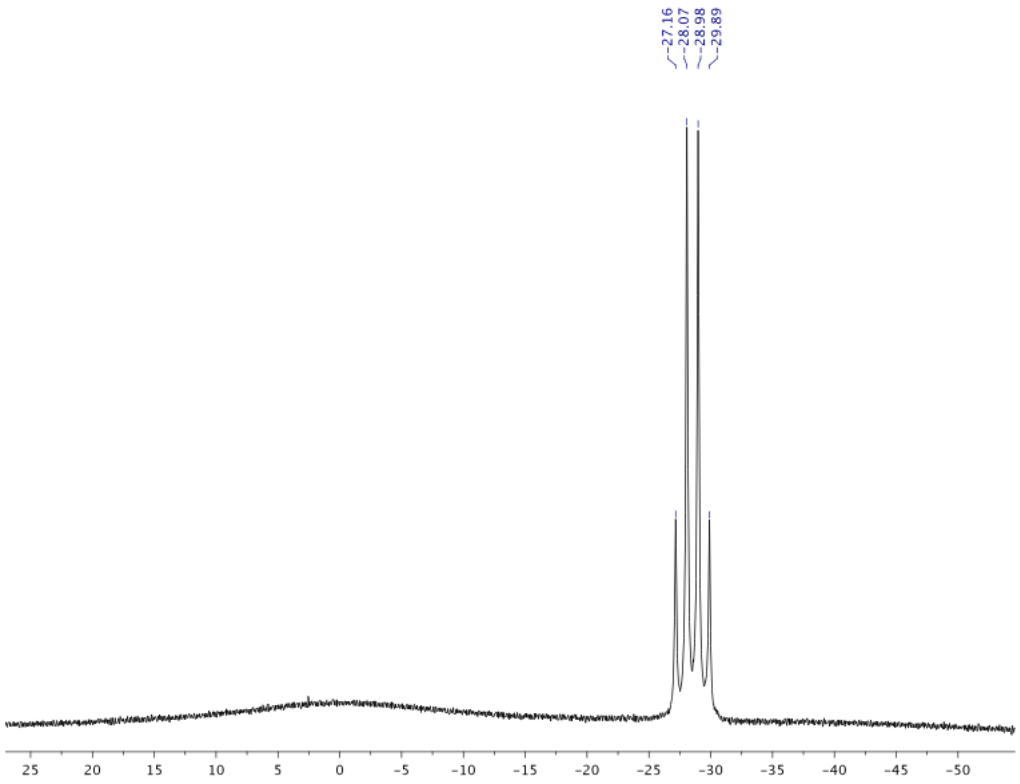

Figure S3 ^{11}B NMR spectrum of **1**

2 CAAC-BH_2OTf:

To a solution of **1** (4.0 g, 12.2 mmol) in 50 mL of benzene MeOTf (2.0 mL, 18.3 mmol) was added slowly, and some bubbling occurred. The reaction was stirred overnight and the volatiles were removed under vacuum. The residue was washed with 60 mL of hexanes, and after drying under vacuum, **2** was isolated as a white solid (5.5 g, 95% yield). Colorless single crystals were obtained by vapor diffusion of pentane in a saturated chloroform solution. ^{1}H {11B} NMR (300 MHz, C_6D_6): δ 7.10 (t, *J* = 7.7 Hz, 1 H), 6.95 (d, *J* = 7.7 Hz, 2 H), 3.24 (br s, 2 H, B*H*$_2$), 2.53 (sept, *J* = 6.6 Hz, 2 H), 2.01 (m, 2 H), 1.80 (m, 2 H), 1.49 (s, 2 H), 1.27 (d, *J* = 6.6 Hz, 6 H), 1.06 (d, *J* = 6.6 Hz, 6 H), 0.88 (t, *J* = 7.4 Hz, 6 H), 0.82 (s, 6 H); ^{13}C NMR (75 MHz, C_6D_6): δ 144.6 (C_q), 132.1 (C_q), 130.3 (CH_{Ar}), 125.4 (CH_{Ar}), 78.6 (C_q), 62.1 (C_q), 42.2 (CH_2), 31.6 (CH_2), 29.4, 28.7, 25.9, 23.9, 9.6, C_{Carb} was not detected; ^{11}B NMR (96 MHz, C_6D_6): δ -6.1 (br s); ^{19}F NMR (283 MHz, C_6D_6) δ -76.2.

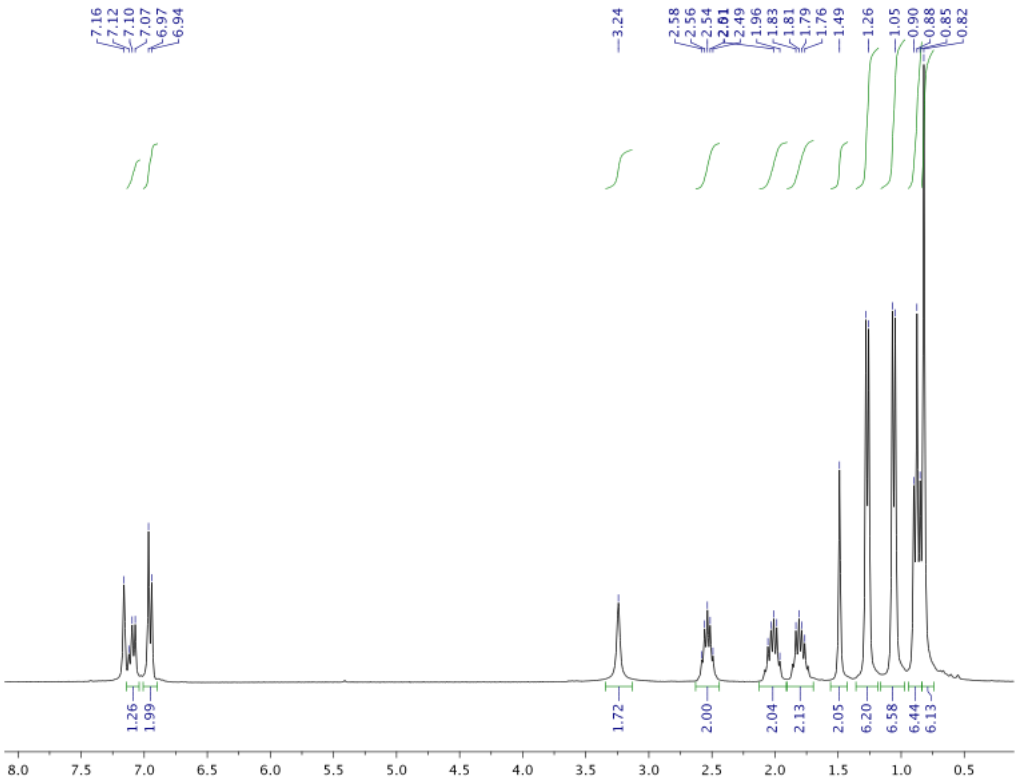

Figure S4 ^{1}H $\{^{11}B\}$ NMR spectrum of **2**

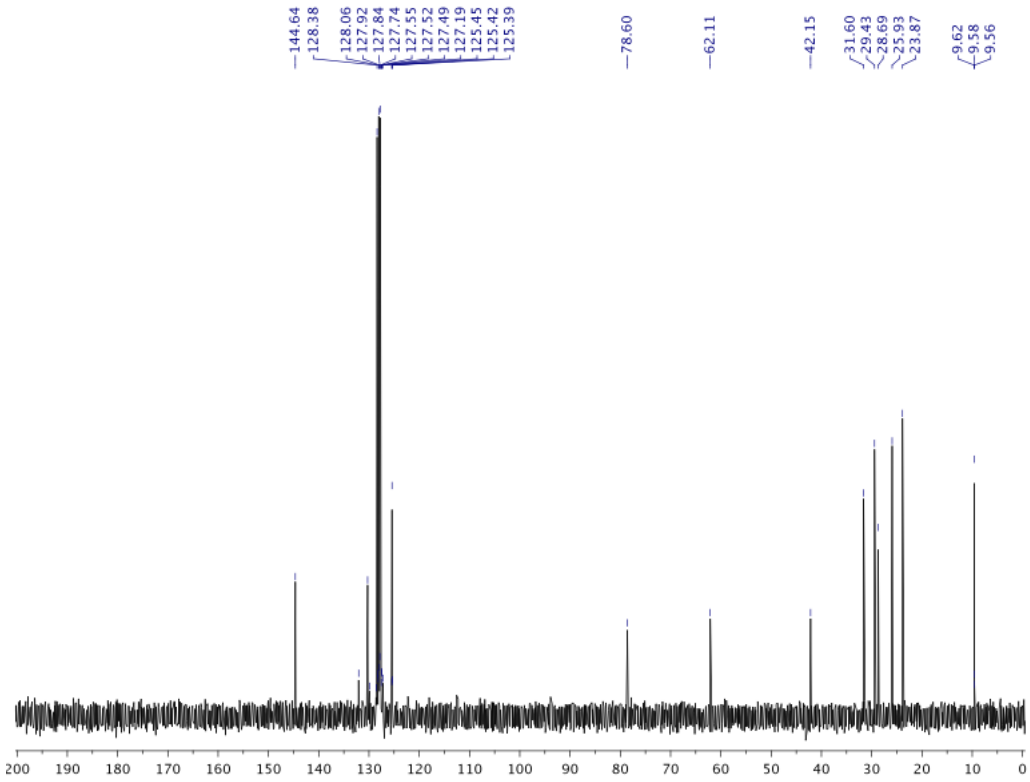

Figure S5 ^{13}C $\{^{1}H\}$ NMR spectrum of **2**

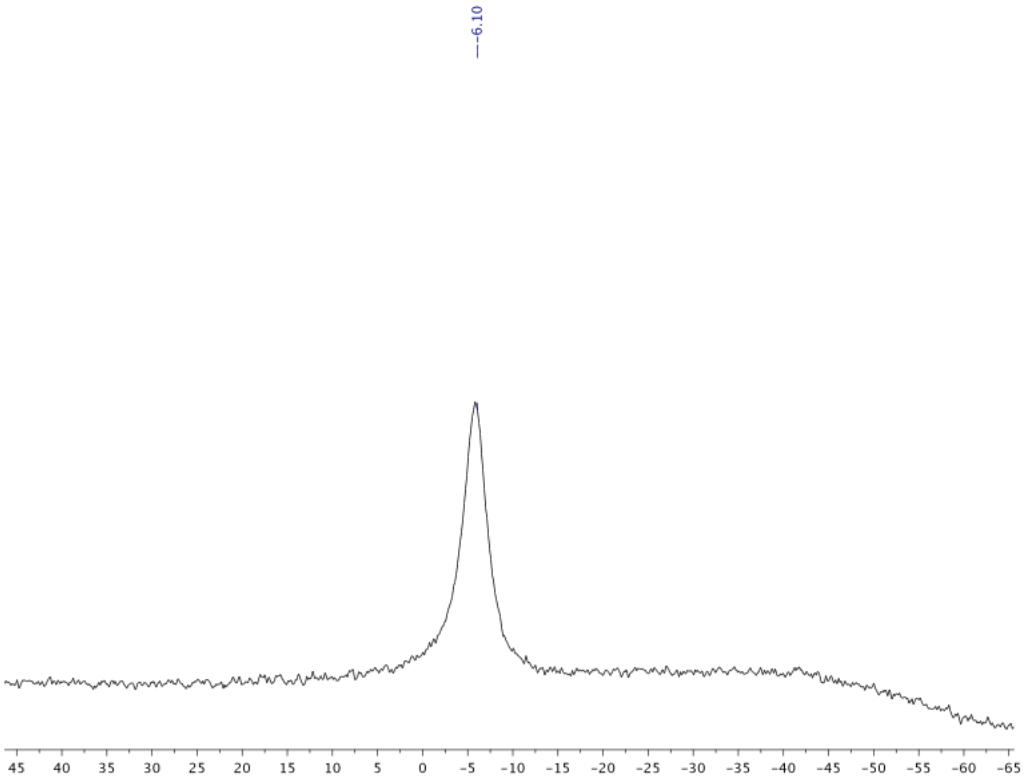

Figure S6 ^{11}B NMR spectrum of **2**

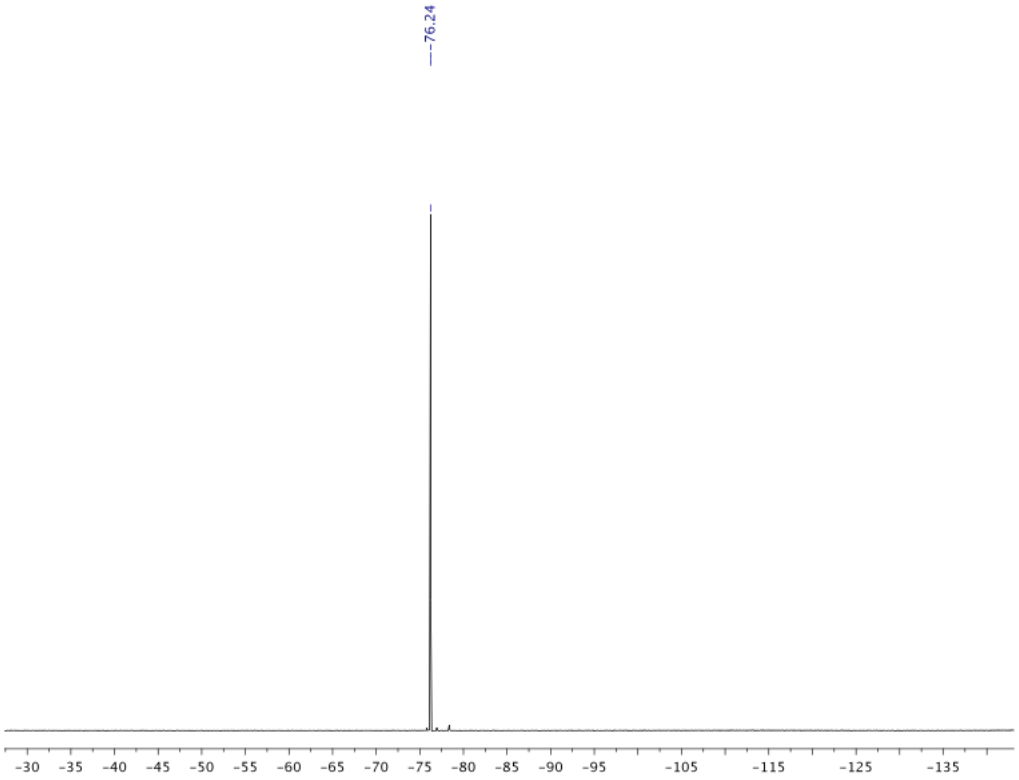

Figure S7 ^{19}F NMR spectrum of **2**

3a [CAAC-BH_2-NHC]OTf:

A Schlenk tube was loaded with **2** (4.9 g, 10.3 mmol), benzimidazolylidene $\mathbf{L_a}$ (2.2 g, 10.1 mmol) and 100 mL of benzene. The reaction was stirred at 80 ºC overnight. A suspension was formed. The mixture was cooled to room temperature, and hexanes (60 mL) was added to further induce precipitation. The solid residue obtained by filtration was washed with hexanes (40 mL), and dried under vacuum to give **3a** (6.7 g, 95% yield). ^{1}H {^{11}B} NMR (300 MHz, $CDCl_3$): δ 7.83 (m, 2 H), 7.47 (m, 3 H), 7.35 (d, J = 8 Hz, 2 H), 4.98 (sept, J = 6.5 Hz, 2 H), 2.72 (sept, J = 6.6 Hz, 2 H), 2.21 (s, 2 H), 1.90 (br s, 2 H, BH_2), 1.62 (m, 16 H), 1.45 (s, 6 H), 1.39 (d, J = 6.6 Hz, 6 H), 1.37 (d, J = 6.5 Hz, 6 H), 1.10 (t, J = 7.4 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3 (C_q), 132.1 (C_q), 131.7 (C_q), 130.4 (CH_{ar}), 126.0 (CH_{ar}), 125.2 (CH_{ar}), 114.8 (CH_{ar}), 80.4 (C_q), 61.6 (C_q), 52.4, 40.4 (CH_2), 31.0 (CH_2), 29.9, 29.6, 26.6, 24.8, 20.9 10.0, C_{Carb_CAAC} and C_{carb_NHC} were not detected; ^{11}B NMR (96 MHz, $CDCl_3$): δ -28.6 (t, J_{BH} = 82.9 Hz); ^{19}F NMR (283 MHz, $CDCl_3$) δ -78.0.

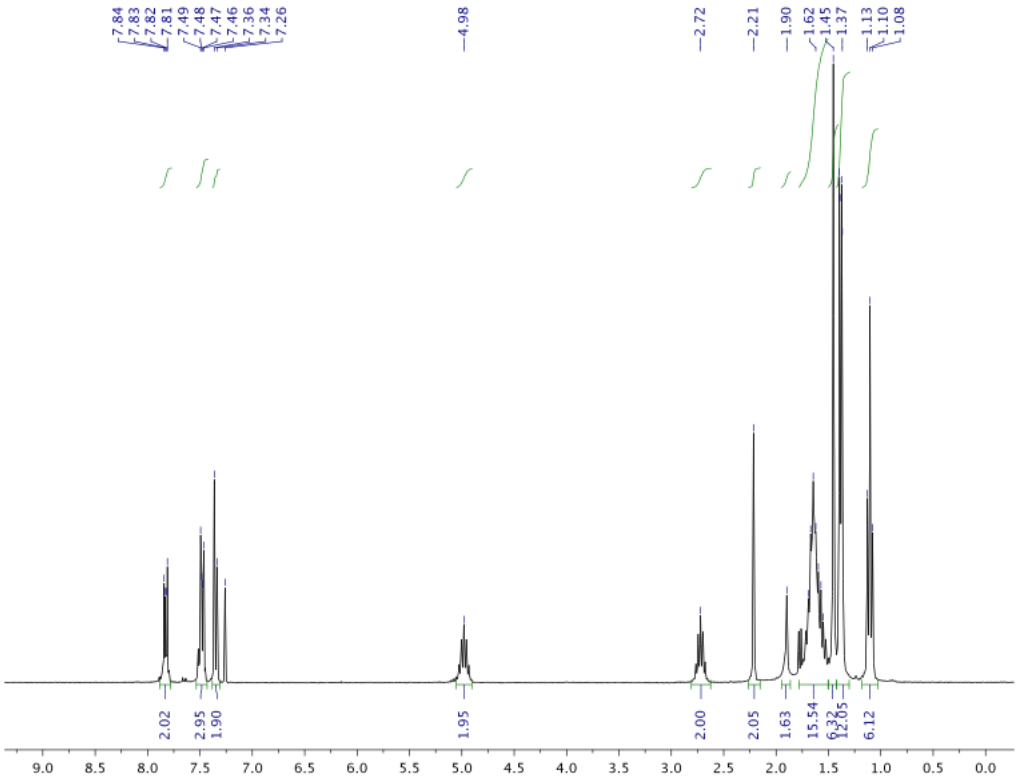

Figure S8 ^{1}H {^{11}B} NMR spectrum of **3a**

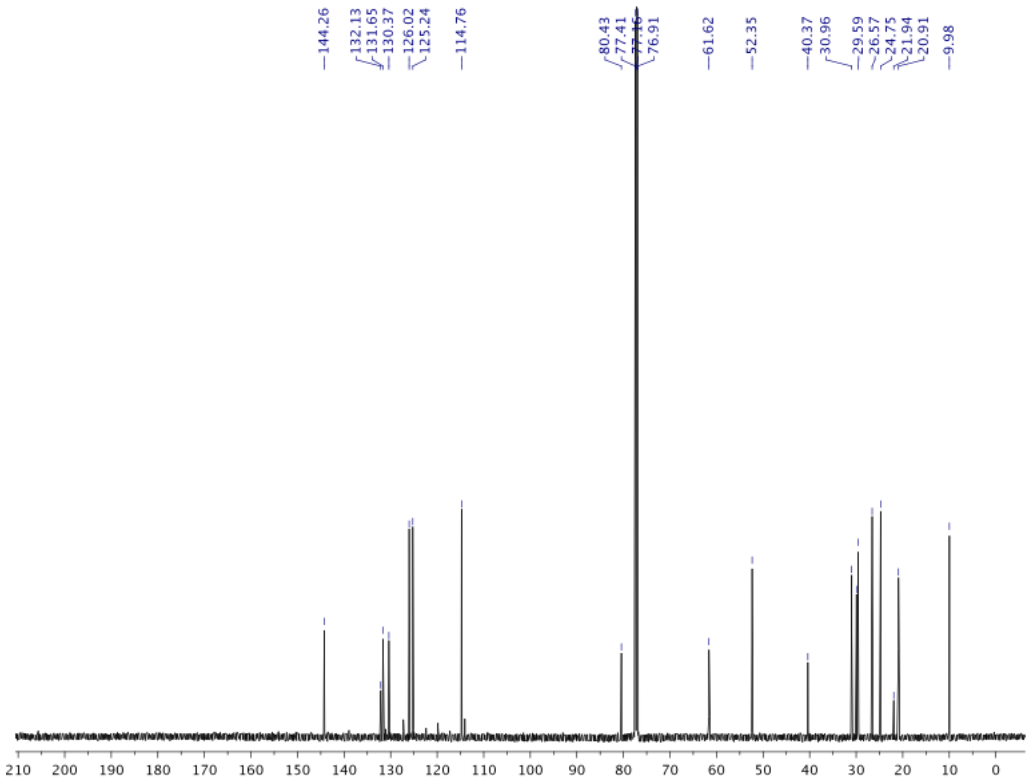

Figure S9 ^{13}C {^{1}H} NMR spectrum of **3a**

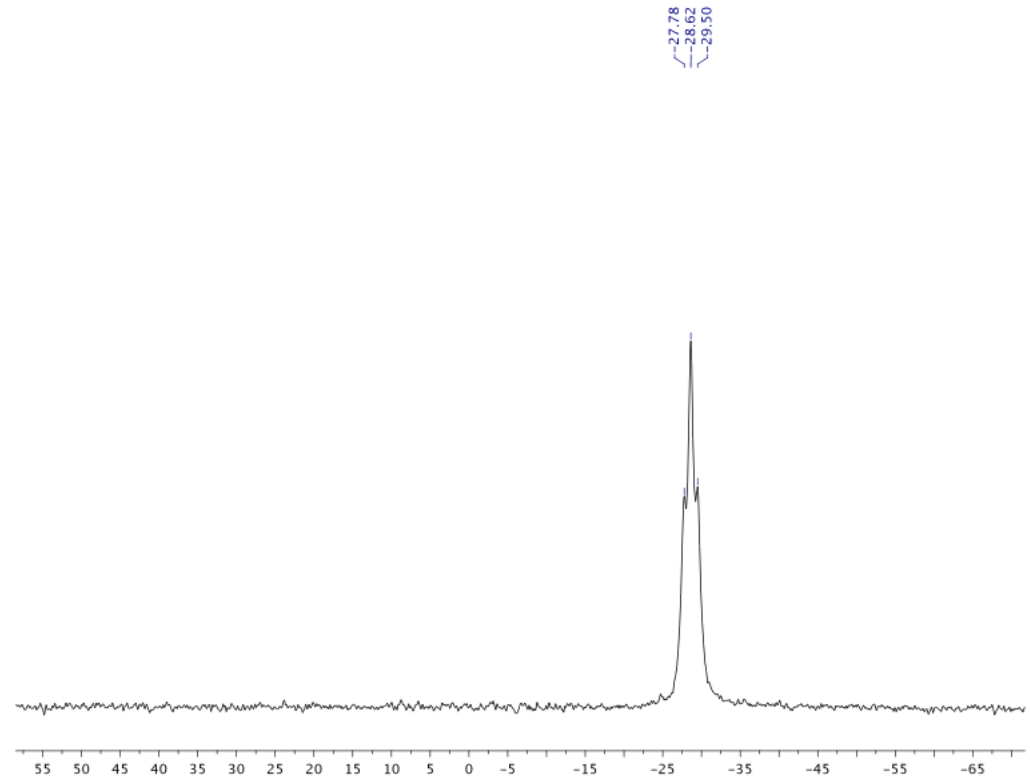

Figure S10 ^{11}B NMR spectrum of **3a**

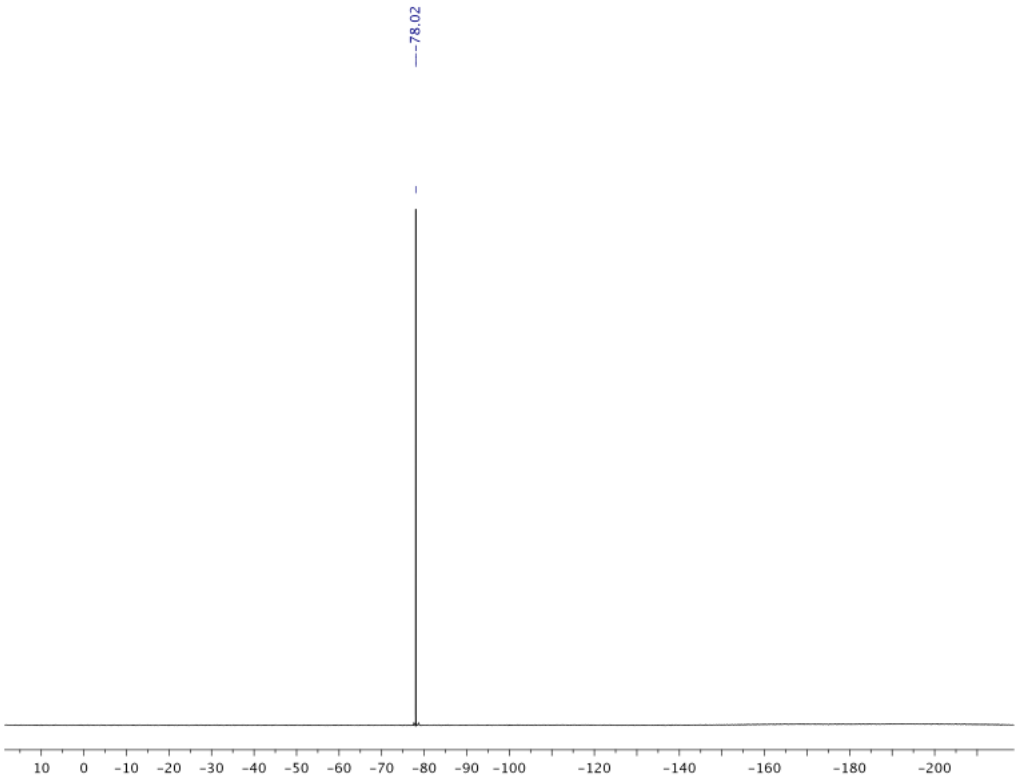

Figure S11 ^{19}F NMR spectrum of **3a**

3b [CAAC-BH_2-BAC]OTf:

A Schlenk tube was loaded with **2** (2.6 g, 5.5 mmol), cyclopropenylidene $\mathbf{L_b}$ (1.1 g, 4.7 mmol) and 80 mL of benzene. The reaction was stirred at 80 ºC overnight. A suspension was formed. The mixture was cooled to room temperature, and hexanes (40 mL) was added to further induce precipitation. The solid obtained by filtration was washed with hexanes (40 mL). The resulting off white solid was dried under vacuum to give **3b** (2.7 g, 80% yield). ^{1}H NMR (300 MHz, CD_3CN): δ 7.45 (t, J = 8 Hz, 1 H), 7.45 (m, 2 H), 4.00 (br s, 4 H), 2.71 (sept, J = 6.5 Hz, 2 H), 2.13 (s, 2 H), 1.74 (br s, 2 H, BH_2), 1.68 (m, 2 H), 1.60 (m, 2 H), 1.36 (s, 6 H), 1.32 (m, 36 H), 1.03 (t, J = 7.4 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.4 (C_q), 141.4 (C_q), 132.5 (C_q), 130.0 (CH_{ar}), 125.6 (CH_{ar}), 79.5 (C_q), 61.3 (C_q), 40.6 (CH_2), 30.8 (CH_2), 29.9, 29.5, 26.6, 24.5, 21.8, 10.0, C_{Carb_CAAC} and C_{carb_BAC} were not detected; ^{11}B NMR (96 MHz, $CDCl_3$): δ -27.7 (t, J_{BH} = 87.9 Hz); ^{19}F NMR (283 MHz, $CDCl_3$) δ -79.3.

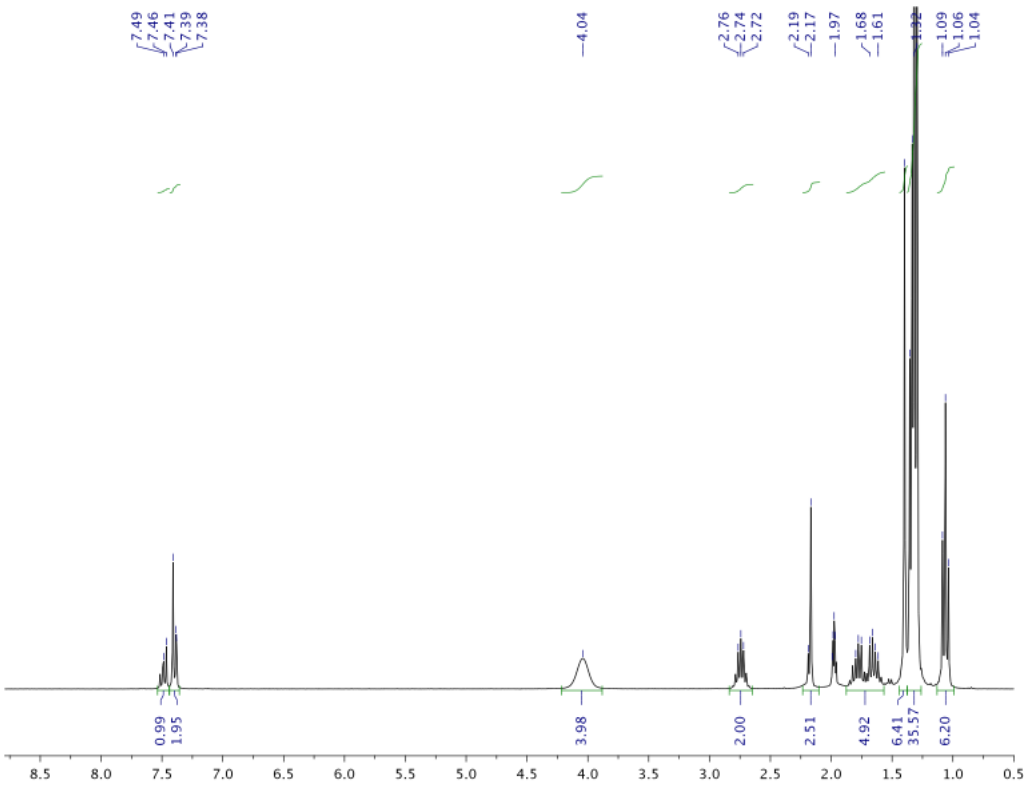

Figure S12 ^{1}H $\{^{11}B\}$ NMR spectrum of **3b**

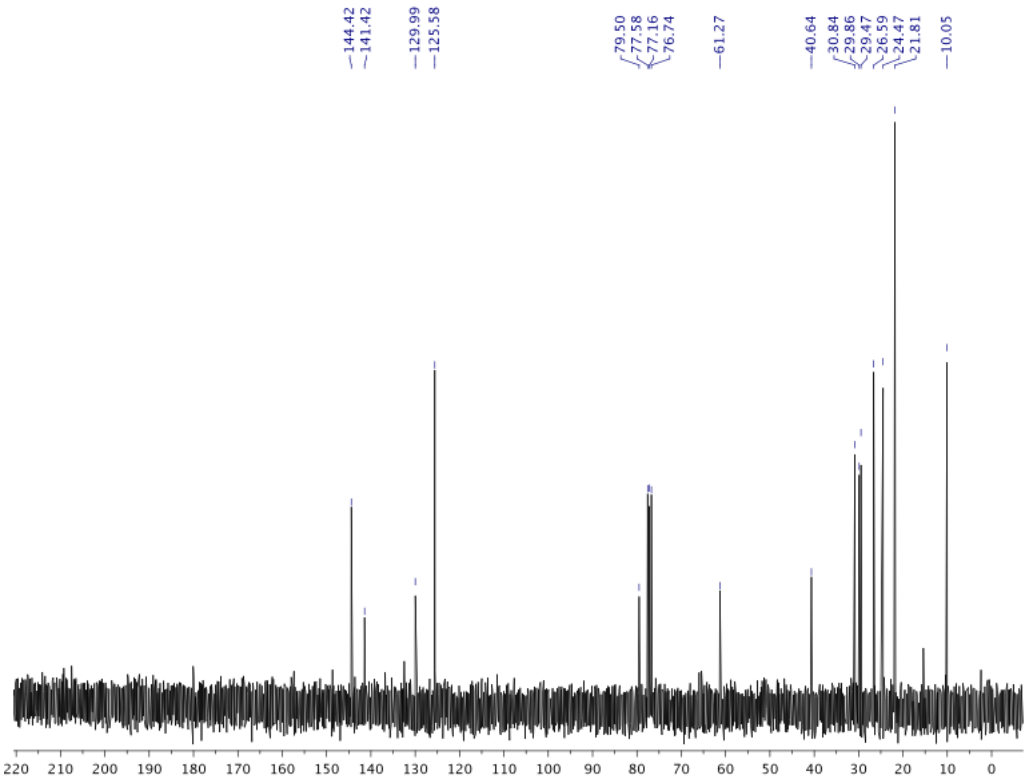

Figure S13 ^{13}C $\{^{1}H\}$ NMR spectrum of **3b**

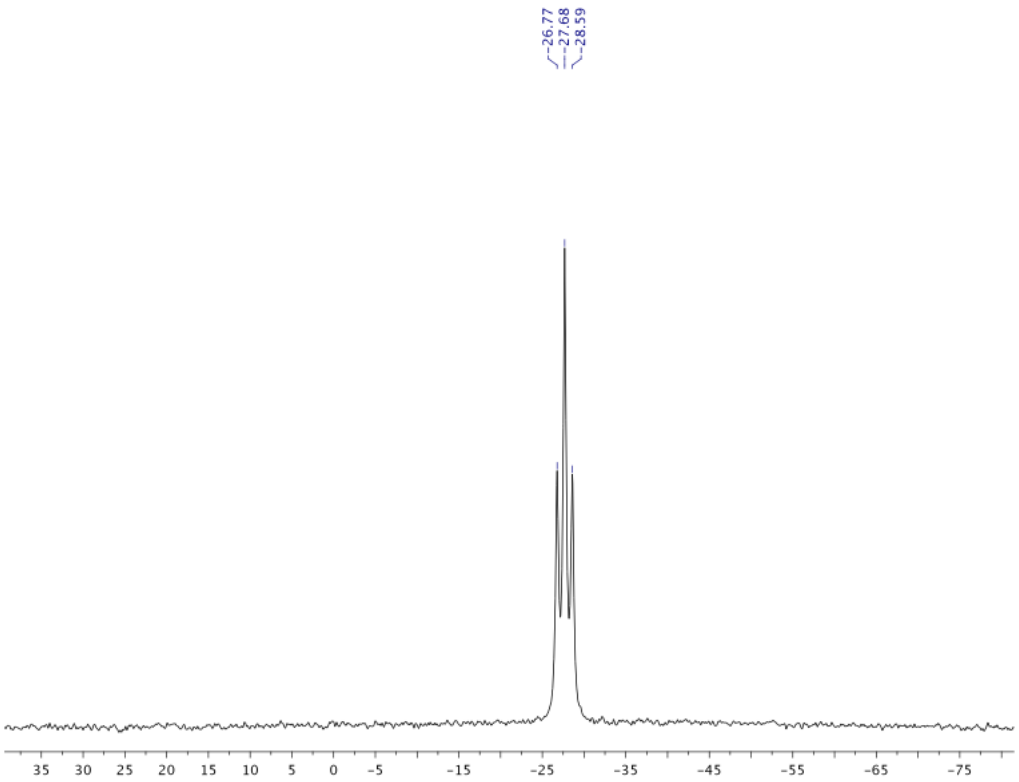

Figure S14 ^{11}B NMR spectrum of **3b**

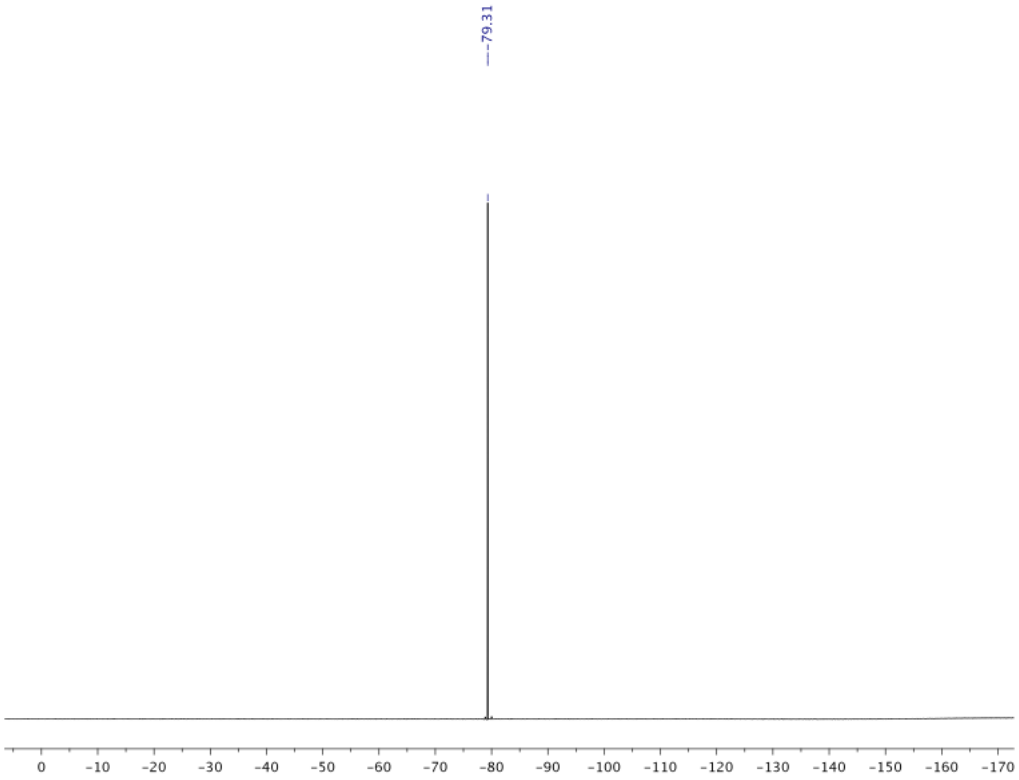

Figure S15 ^{19}F NMR spectrum of **3b**

4a [CAAC-BH(OTf)-NHC]OTf:
3a (3.0 g, 4.3 mmol) was dissolved in 40 mL of CH_2Cl_2. An excess of triflic acid was added (2-5 eqs.). The solution was stirred and the reaction monitored by ^{11}B NMR. In some cases the process was complete overnight, and in others several days elapsed before completion. Then, the mixture was open to air and cooled in an ice bath. Excess triethylamine (6 eq.) was added to neutralize the excess of triflic acid. The mixture was washed with water (4 x 50 mL). The organic phase was collected, dried with $MgSO_4$, filtered, and the volatiles were removed, giving an oily residue. 60 mL of ether was added and the emulsion stirred vigorously for several hours, which induced the formation of a powder. After filtration, the solid was dried under vacuum, and **4a** was obtained as a white solid (2.6 g, 70 % yield). ^1H NMR (500 MHz, $CDCl_3$): δ 8.0 (m, 2 H), 7.9 (m, 2 H), 7.87 (d, *J* = 8.4 Hz, 1 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.62 (m, 4 H), 7.58 (d, *J* = 7.8 Hz, 1 H), 7.54 (t, *J* = 7.0 Hz, 1 H), 7.50 (m, 4 H), 7.35 (m, 3 H), 7.17 (d, *J* = 7.8 Hz, 1 H), 5.48 (sept, *J* = 7.0 Hz, 2 H), 5.06 (sept, *J* = 7.0 Hz, 1 H), 4.59 (sept, *J* = 6.7 Hz, 2 H), 4.01 (sept, *J* = 6.7 Hz, 1 H), 2.84 (sept, *J* = 6.5 Hz, 2 H), 2.71 (sept, *J* = 6.5 Hz, 1 H), 2.59 (sept, *J* = 6.5 Hz, 2 H), 2.46-2.36 (m, 6 H), 2.21 (m, 4 H), 2.12 (m, 1 H), 1.94 (d, *J* = 6.8 Hz, 6 H), 1.91 (d, *J* = 7.0 Hz, 6 H), 1.83 (d, *J* = 7.0 Hz, 6 H), 1.77 (d, *J* = 6.8 Hz, 6 H), 1.73 (s, 6 H) 1.71 (d, *J* = 3.0 Hz, 6 H), 1.70 (d, *J* = 2.7 Hz, 6 H), 1.67 (s, 3 H), 1.54 (d, *J* = 6.5 Hz, 6 H), 1.43 (m, 16 H), 1.37 (m, 18 H), 1.30 (s, 6 H), 1.25 (s, 3 H), 1.21 (d, *J* = 6.5 Hz, 6 H), 1.17 (m, 8 H), 1.00 (t, *J* = 7.3 Hz, 6 H), 0.88 (d, *J* = 7.0 Hz, 6 H), -0.26 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.2, 144.2, 144.1, 143.1, 132.5, 132.4, 131.9, 131.6, 131.2, 131.1, 130.9, 127.6, 127.3, 126.8, 126.6, 126.5, 126.2, 122.3, 119.8, 118.9, 116.2, 115.9, 115.8, 115.3, 83.9, 83.2, 64.5, 61.4, 53.6, 53.1, 52.7, 52.6, 46.3, 42.2, 40.5, 32.2, 32.0, 31.6, 31.5, 30.3, 30.0, 29.9, 29.4, 29.2, 27.4, 27.3, 26.5, 26.3, 25.8, 25.6, 25.4, 25.3, 24.7, 22.5, 22.2, 22.1, 21.3, 21.2, 21.1, 20.8, 20.7, 11.0, 10.7, 10.0, 9.6, 8.9; ^{11}B NMR (96 MHz, $CDCl_3$): δ -7.5 (br s); ^{19}F NMR (283 MHz, $CDCl_3$) δ -75.4, -78.1.
4a and $NaBPh_4$ were stirred for 2 hours at room temperature in CH_2Cl_2. After filtration, the solution was evaporated to give the corresponding BPh_4 salt, which was crystallized by slow diffusion of pentane in a saturated CH_2Cl_2 solution.

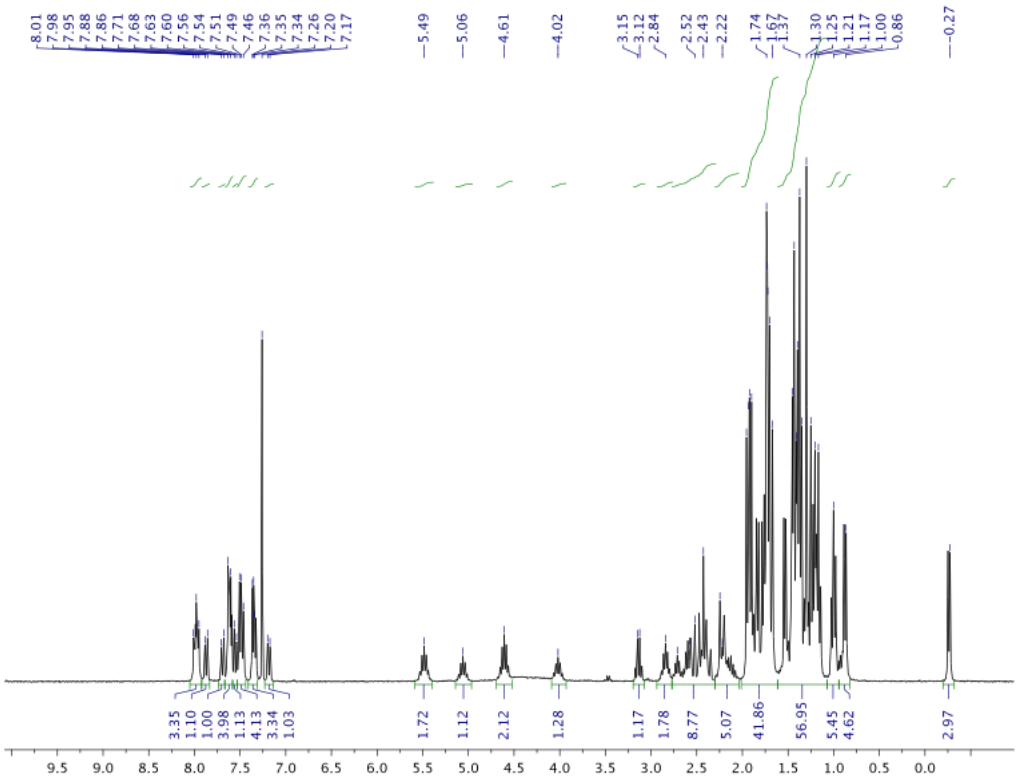

Figure S16 ^{1}H $\{^{11}B\}$ NMR spectrum of **4a**

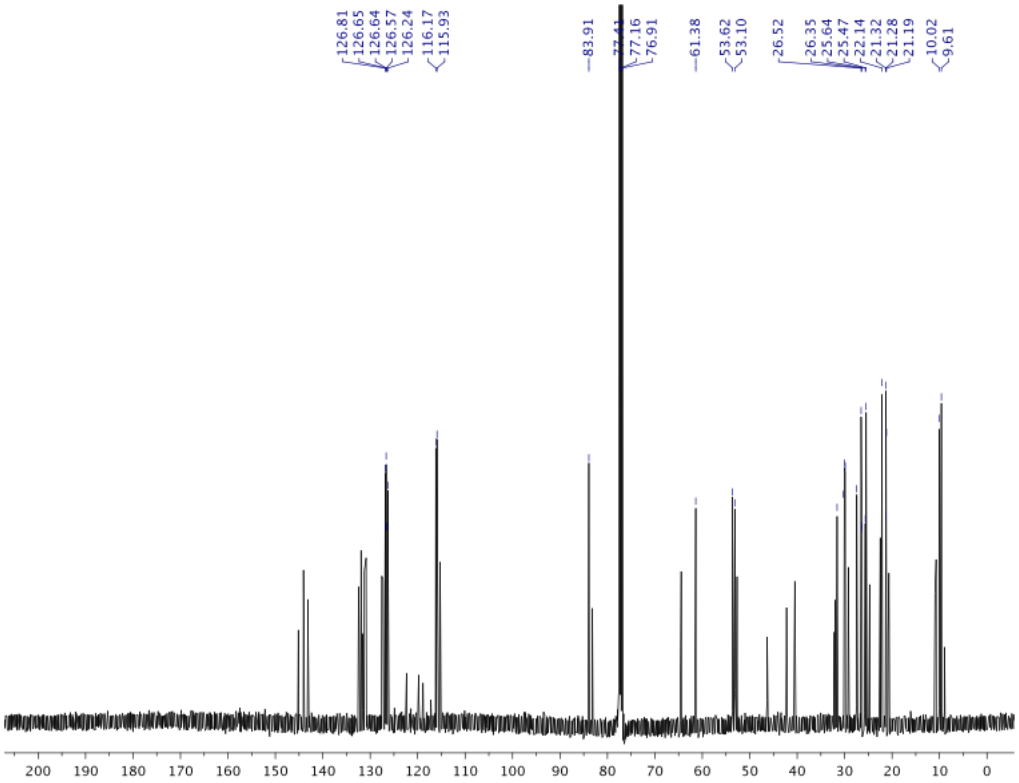

Figure S17 ^{13}C $\{^{1}H\}$ NMR spectrum of **4a**

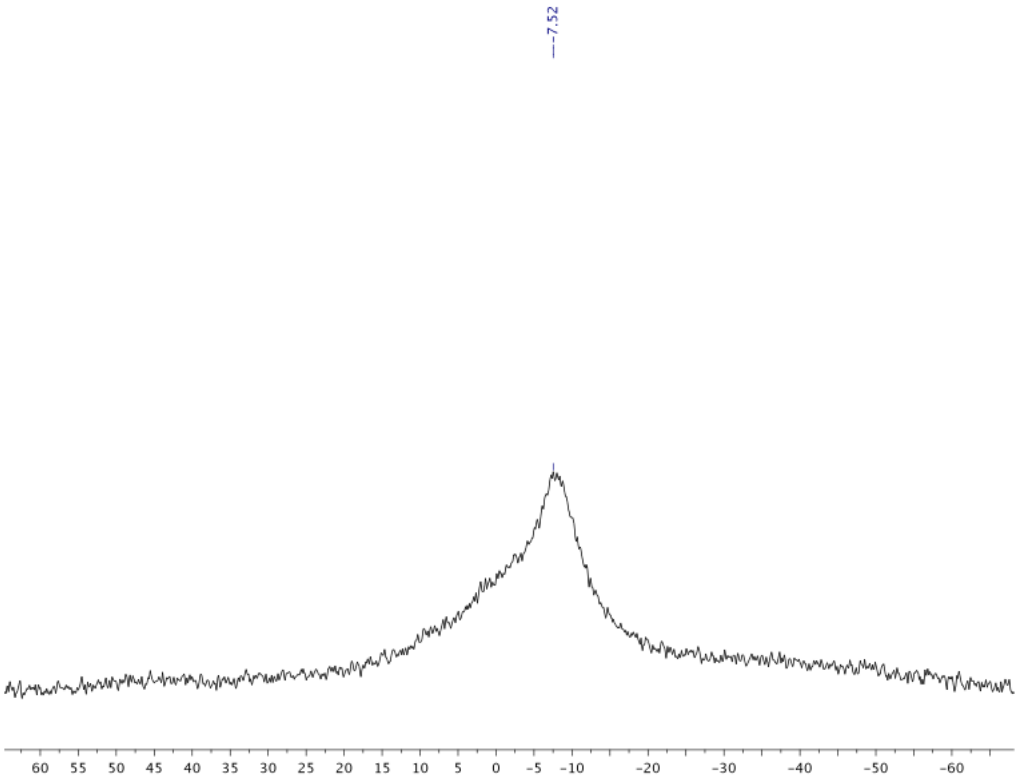

Figure S18 ^{11}B NMR spectrum of **4a**

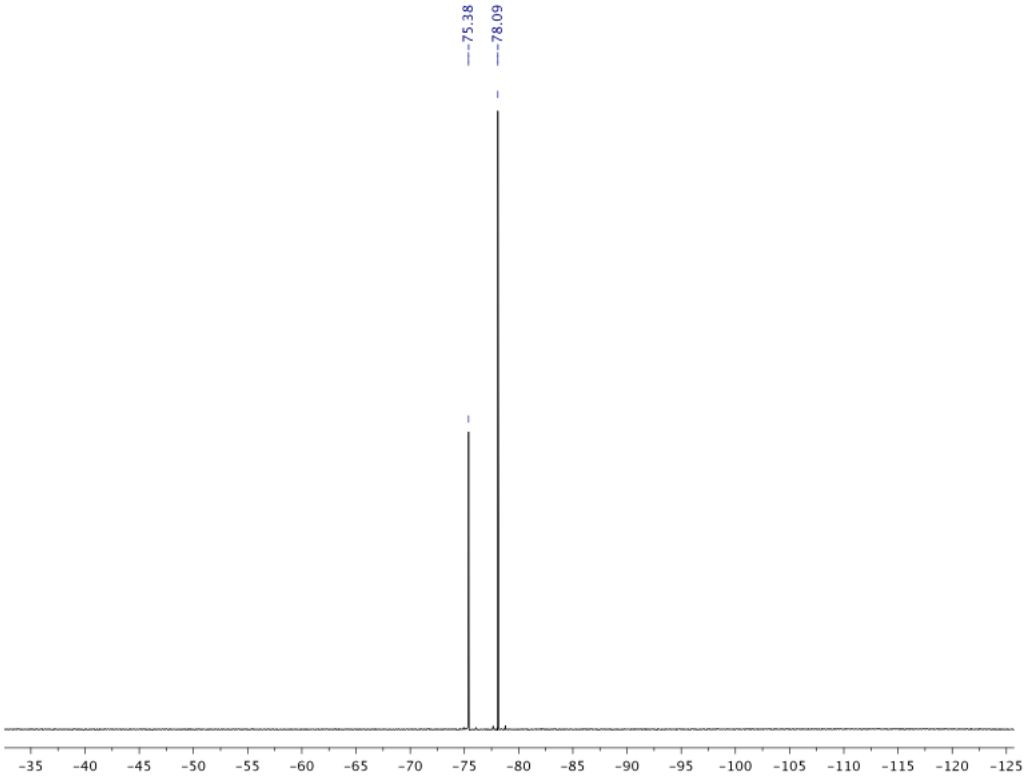

Figure S19 ^{19}F NMR spectrum of **4a**

4b [CAAC-BH(OTf)-BAC]OTf:
3b (2.0 g, 2.8 mmol) was dissolved in 30 mL of CH_2Cl_2, and an excess of triflic acid was added (2-5 eqs.). The solution was stirred and the reaction monitored by ^{11}B NMR. In some cases the process was complete overnight, and in others several days elapsed before completion. Then, the mixture was open to air and cooled in an ice bath. Excess triethylamine (6 eq.) was added to neutralize the excess of triflic acid. The mixture was washed with water (4 x 50 mL). The organic phase was collected, dried with $MgSO_4$, filtered, and the volatiles were removed, giving an oily residue. 60 mL of ether was added and the emulsion stirred vigorously for several hours, which induced the formation of a powder. After filtration, the solid was dried under vacuum, and **4b** was obtained as an off white solid (1.6 g, 67 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.45 (t, *J* = 7.8 Hz, 1H), 7.29 (m, 2H), 4.19 (br, 1 H), 4.04 (sept, *J* = 6.5 Hz, 2 H), 3.80 (br, 1 H, B*H*), 2.66 (sept, *J* = 6.5 Hz, 1 H), 2.52 (sept, *J* = 6.5 Hz, 1 H), 2.24 (m, 2 H), 1.93 (m, 1 H), 1.71 (m, 2 H), 1.45-1.21 (m, 43 H), 1.08 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.9 (C_q), 143.8 (C_q), 141.0 (C_q), 140.5 (C_q), 131.7 (C_q), 130.8 (CH_{Ar}), 126.2 (CH_{Ar}), 126.1 (CH_{Ar}), 82.9 (C_q), 62.1 (C_q), 52.3, 41.0 (CH_2), 31.8 (CH_2), 29.9 (CH_2), 29.5, 29.1, 25.6, 25.4, 25.3, 25.2, 22.7, 22.2, 22.1, 22.0, 21.7, 21.0, 10.0, 9.7, C_{Carb_CAAC} and C_{carb_BAC} were not detected; ^{11}B NMR (96 MHz, $CDCl_3$): δ -5.1 (br s); ^{19}F NMR (283 MHz, $CDCl_3$) δ -76.2, -78.0. **4b** and $NaBPh_4$ were stirred for 2 hours at room temperature in CH_2Cl_2. After filtration, the solution was evaporated to give the corresponding BPh_4 salt, which was crystallized by slow diffusion of pentane in a saturated CH_2Cl_2 solution.

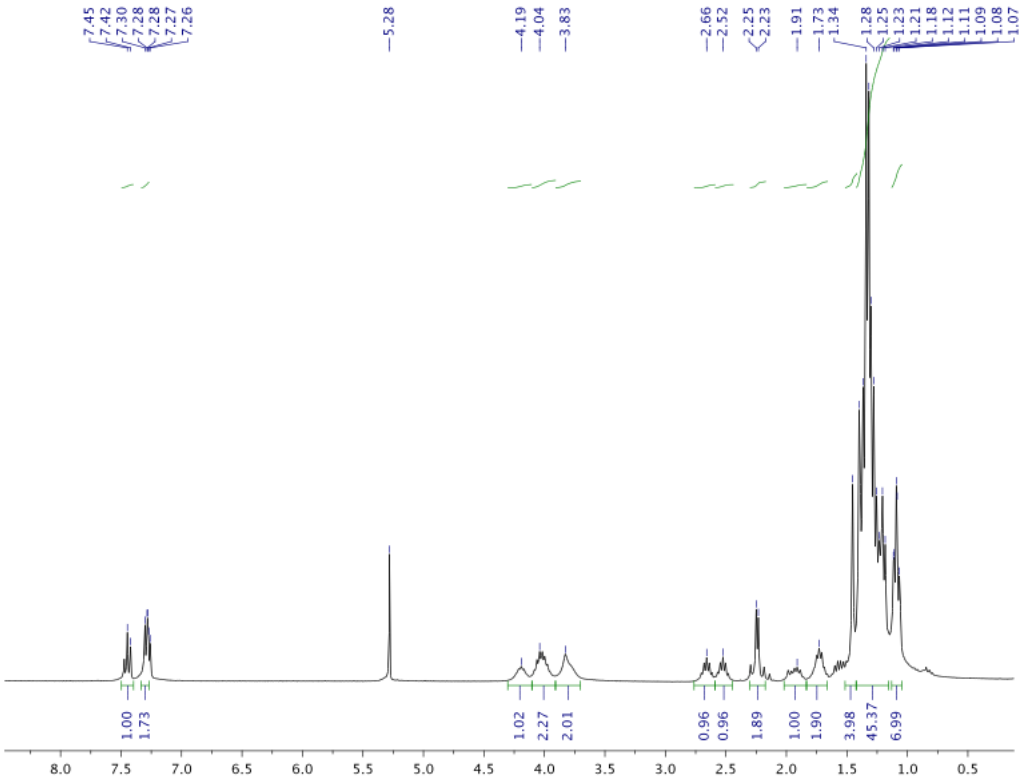

Figure S20 ^{1}H $\{^{11}B\}$ NMR spectrum of **4b**

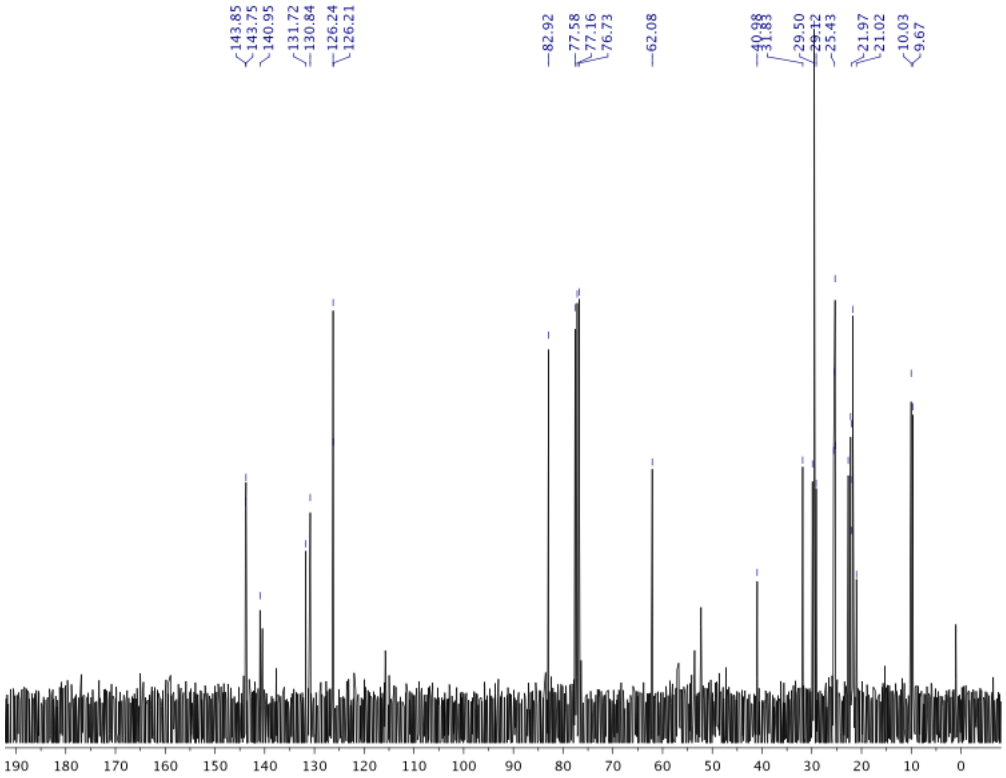

Figure S21 ^{13}C $\{^{1}H\}$ NMR spectrum of **4b**

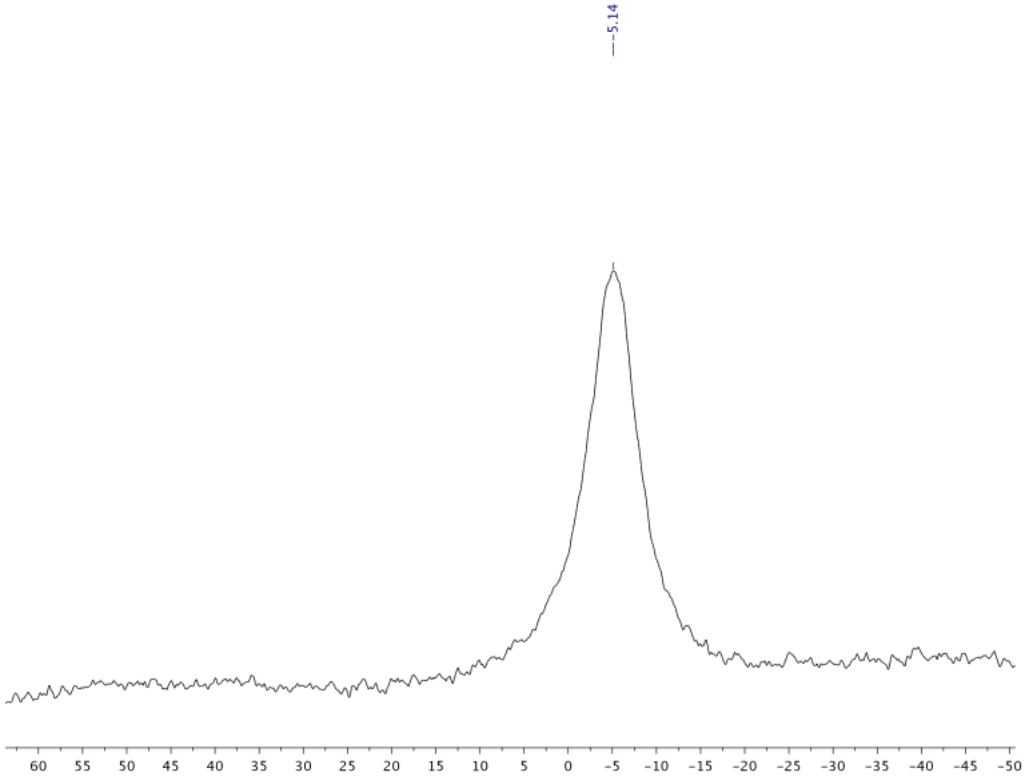

Figure S22 ^{11}B NMR spectrum of **4b**

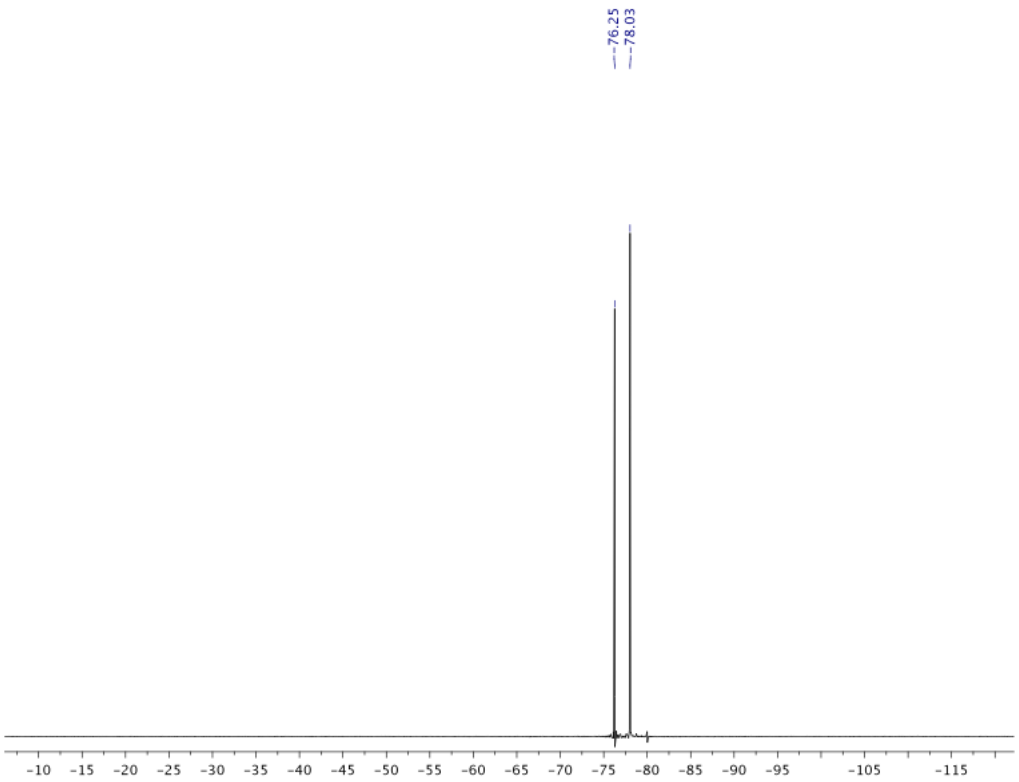

Figure S23 ^{19}F NMR spectrum of **4b**

5a CAAC-BH-NHC:

4a (2.0 g, 2.4 mmol) and KC_8 (800 mg, 5.9 mmol) were loaded into a Schlenk tube. 20 mL of THF was added, which induces an immediate deep blue color. The mixture was stirred for 3 hours. The volatiles were removed, and the residue was extracted with 40 mL of pentane. The solution was evaporated to dryness, which gave **5a** as a blue solid (1.1 g, 87 % yield). Single crystals were obtained by slow evaporation of a saturated pentane solution. M.p.: 112 ^{o}C (dec.); ^{1}H {^{11}B} NMR (300 MHz, C_6D_6): δ 6.99 (br s, 3 H), 6.94 (m, 2 H), 6.71 (m, 2 H), 5.47 (sept, J = 6.7 Hz, 2 H), 3.63 (sept, J = 6.5 Hz, 2 H), 2.51 (s, 1 H, B*H*), 1.86 (s, 2 H), 1.51 (m, 2 H), 1.49 (m, 2 H), 1.40 (d, J = 6.6 Hz, 6 H), 1.35 (d, J = 6.6 Hz, 6 H), 1.20 (s, 6 H), 1.07 (d, J = 7.0, 12 H), 0.97 (t, J = 7.4, 6 H); ^{13}C NMR (75 MHz, C_6D_6): δ 151.4 (C_q), 140.0 (C_q), 133.1 (C_q), 126.6 (CH_{ar}), 124.3 (CH_{ar}), 122.2 (CH_{ar}), 112.7 (CH_{ar}), 63.7 (C_q), 52.1 (C_q), 51.2, 47.3 (CH_2), 35.6 (CH_2), 31.0, 28.8, 28.0, 24.4, 20.5, 10.7, C_{Carb_CAAC} and C_{carb_NHC} were not detected; ^{11}B NMR (96 MHz, $CDCl_3$): δ -1.3 (d, J_{BH} = 82.4 Hz).

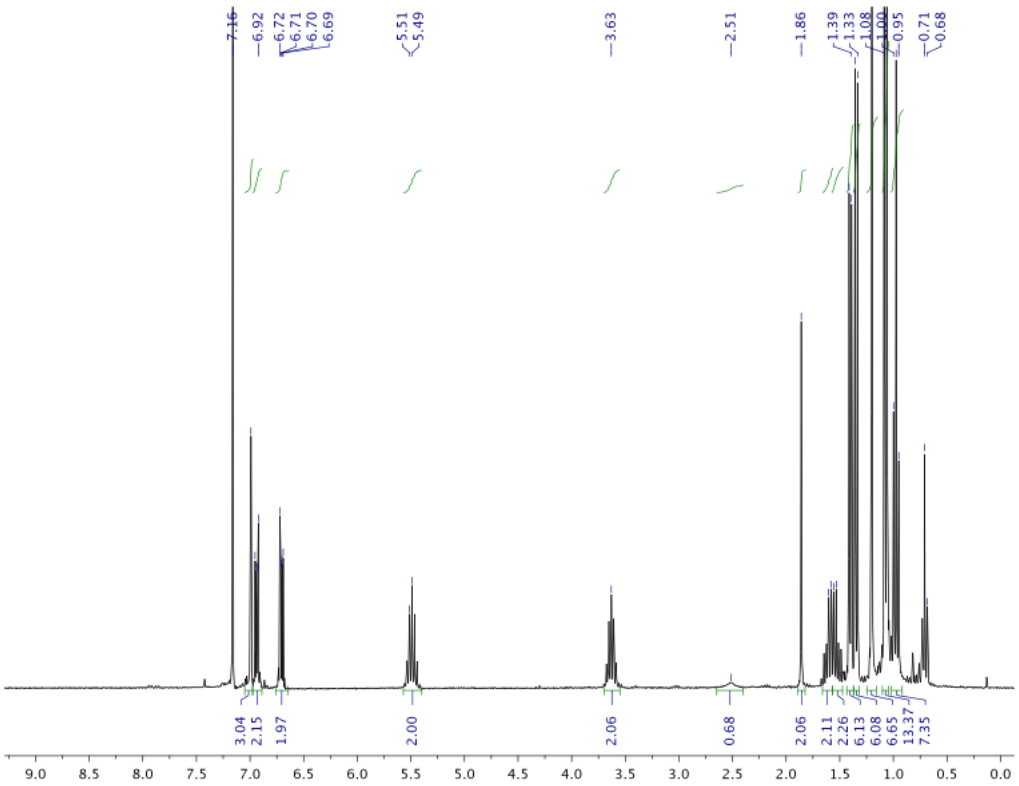

Figure S24 ^{1}H $\{^{11}B\}$ NMR spectrum of **5a**

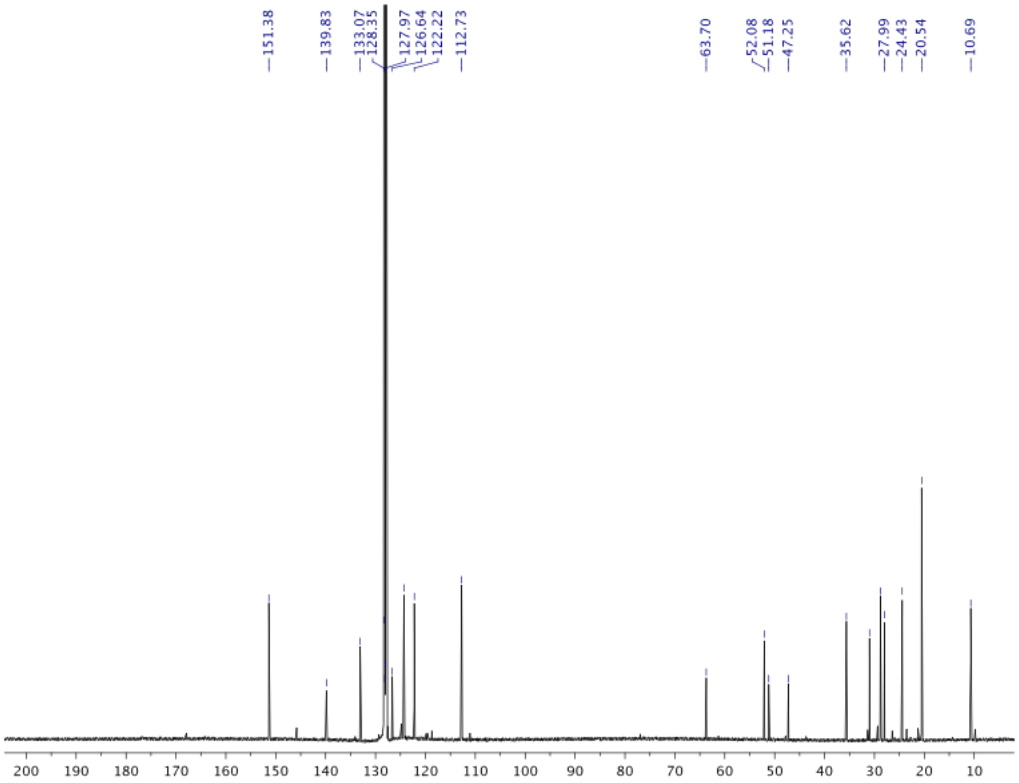

Figure S25 ^{13}C $\{^{1}H\}$ NMR spectrum of **5a**

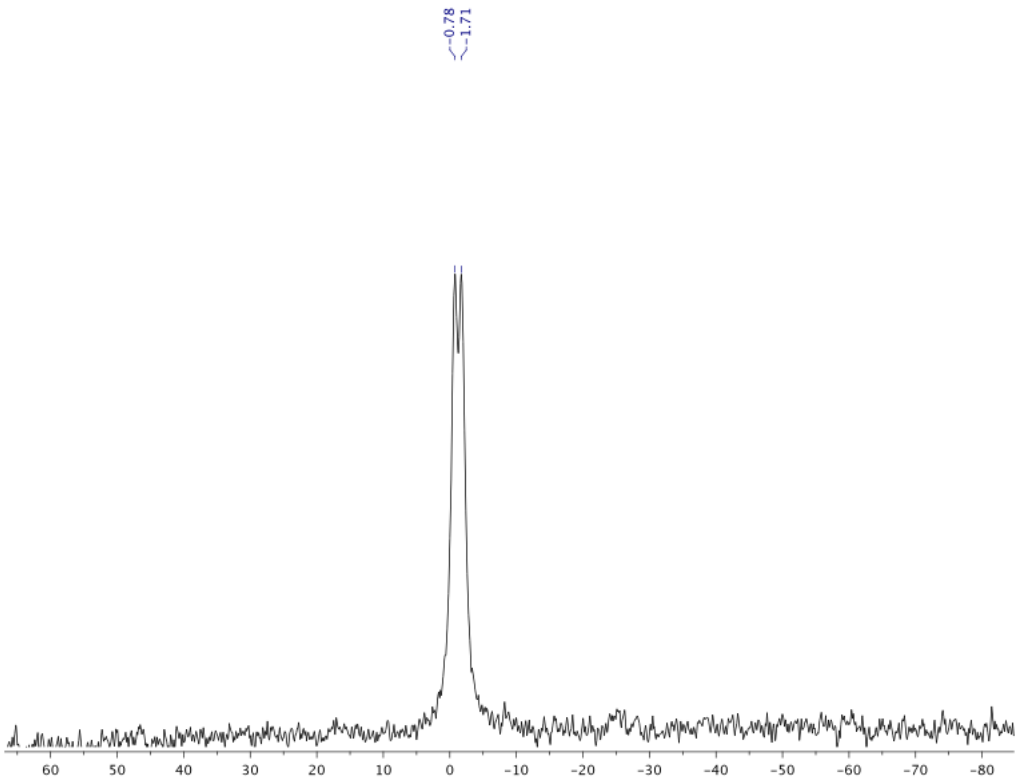

Figure S26 ^{11}B NMR spectrum of **5a**

5b CAAC-BH-BAC:

4b (1.5 g, 1.7 mmol) and KC_8 (600 mg, 4.4 mmol) were loaded into a Schlenk flask. 20 mL of THF was added which induced an immediate deep red color. The mixture was stirred for 3 hours. The volatiles were evaporated, and the residue was extracted with 40 mL of pentane. The solution was evaporated to dryness, which gave **5b** as a red solid (0.8 g, 82 % yield). Single crystals were obtained by slow evaporation of a saturated pentane solution. M.p.: 135 ^{o}C (dec.); ^{1}H {^{11}B} NMR (300 MHz, C_6D_6): δ 7.16 (br, 1 H), 7.00 (br, 2 H), 3.59-3.38 (m, 6 H), 2.73 (s, 1 H, B*H*), 1.98 (q, *J* = 7.4 Hz, 4 H), 1.91 (s, 2 H), 1.49 (d, *J* = 6.6 Hz, 6 H), 1.30 (d, *J* = 6.8 Hz, 6 H), 1.22 (s, 6 H), 1.09 (t, *J* = 7.4 Hz, 6 H), 0.86 (d, *J* = 6.8 Hz, 24 H); ^{13}C NMR (75 MHz, C_6D_6): δ 150.7 (C_q), 140.0 (C_q), 135.1 (C_q), 126.7 (CH_{ar}), 124.2 (CH_{ar}), 64.7 (C_q), 52.2 (C_q), 50.0, 48.3 (CH_2), 34.9 (CH_2), 30.8, 29.0, 27.9, 24.5, 22.3, 10.5, C_{Carb_CAAC} and C_{carb_BAC} were not detected; ^{11}B NMR (96 MHz, C_6D_6): δ 0.8 (d, J_{BH} = 89.7 Hz).

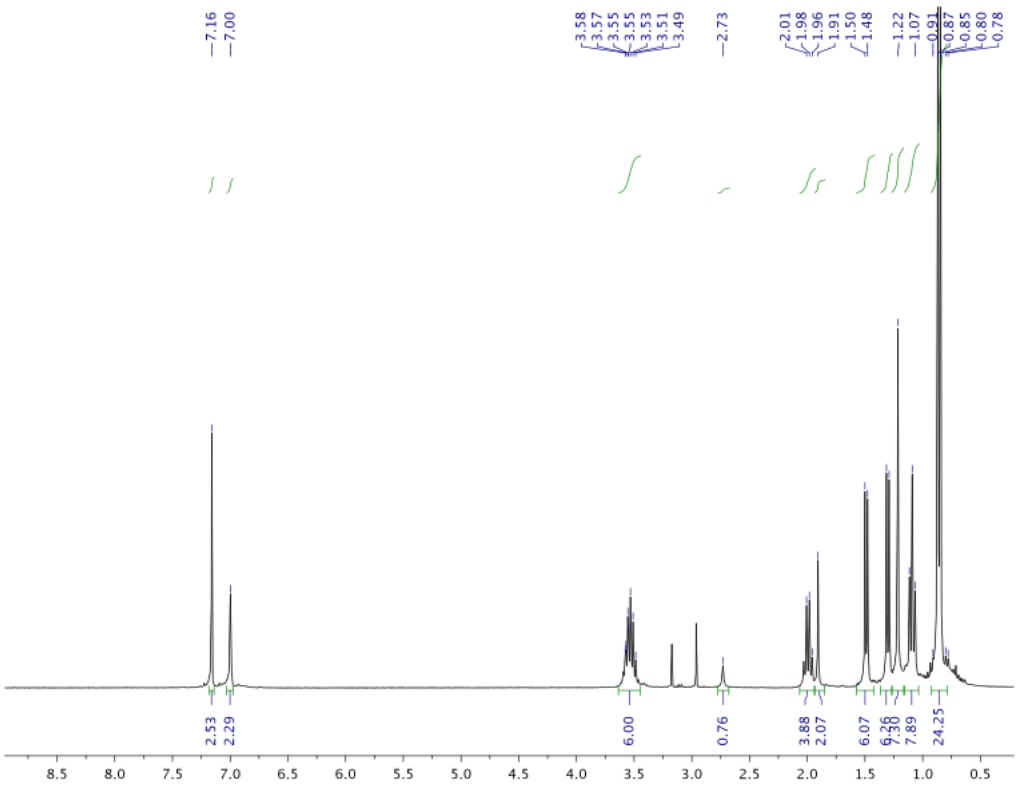

Figure S27 ^{1}H $\{^{11}B\}$ NMR spectrum of **5b**

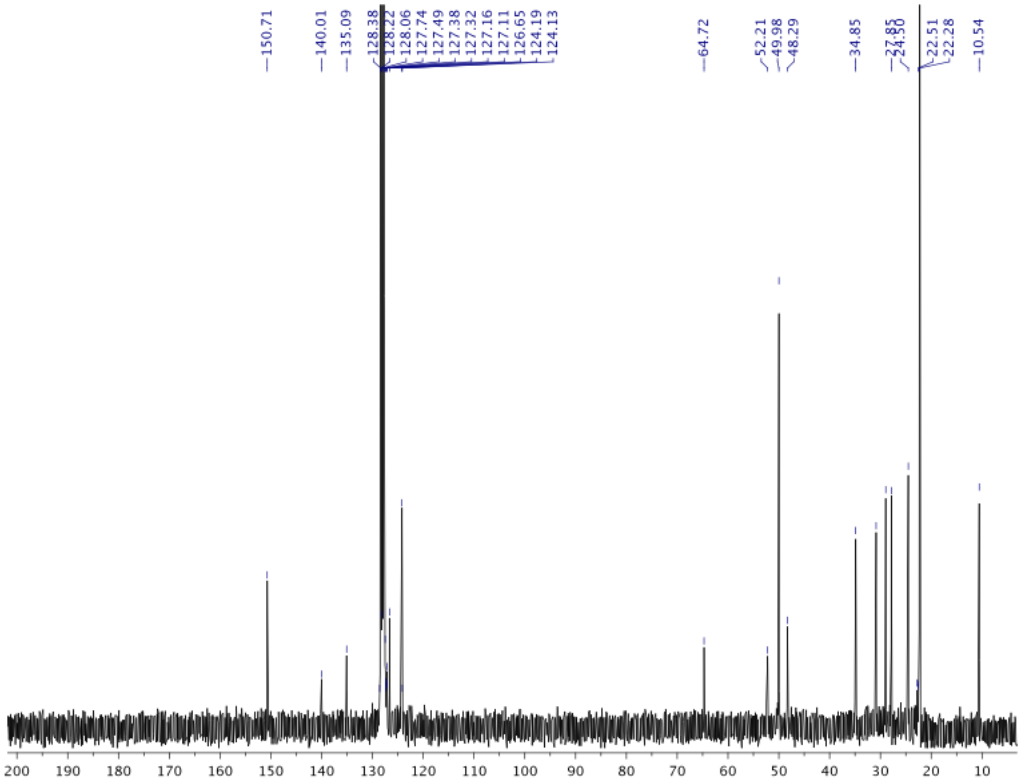

Figure S28 ^{13}C $\{^{1}H\}$ NMR spectrum of **5b**

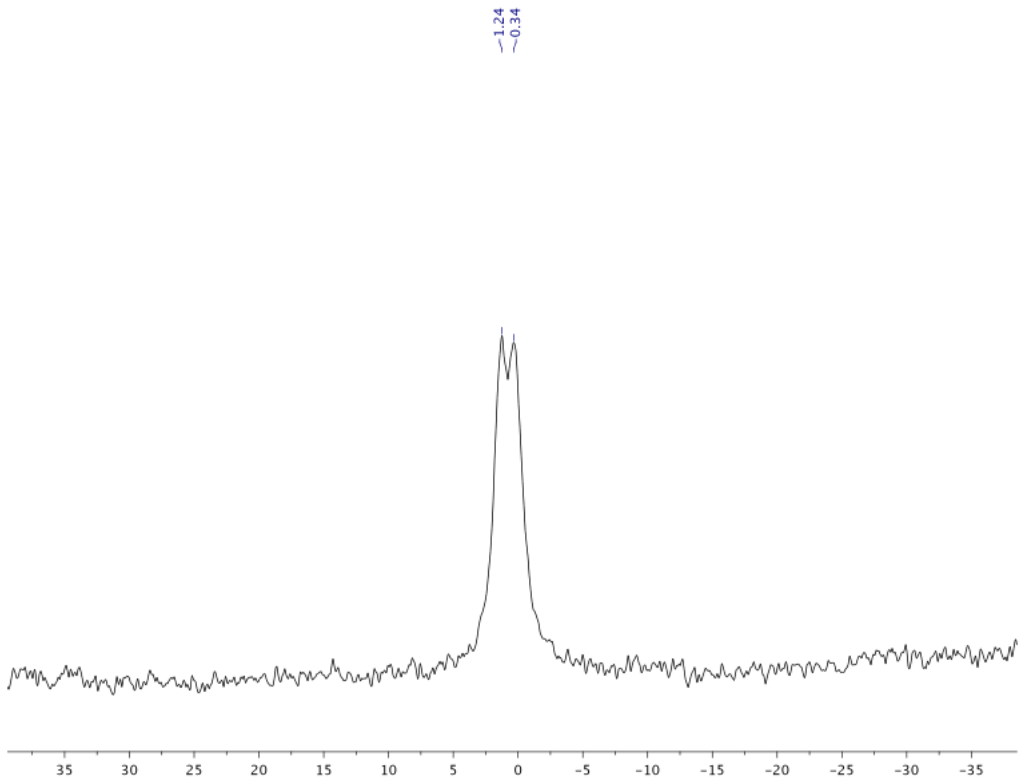

Figure S29 ^{11}B NMR spectrum of **5b**

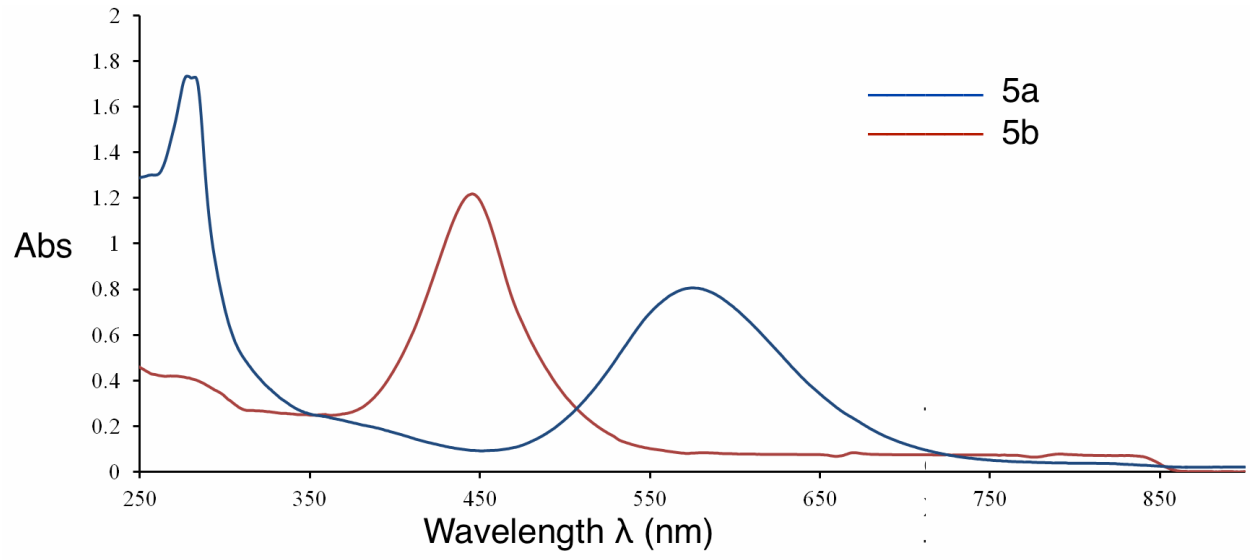

Figure S30 UV-Vis spectra of **5a** and **5b** in THF (1 mg/mL)

Protonation of **5a,b**:
TfOH (1.2 eq) was added at room temperature to a benzene solution (5 mL) of **5a,b** (100 mg, 0.19 mmol; 100 mg, 0.18 mmol). The solution immediately turned colorless. After stirring for 30 minutes, the volatiles were removed under vacuum, and the residue was extracted with 10 mL of dichloromethane. The solvent was removed and the residue was washed with hexanes. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR were identical to those of **3a,b**. **3a:** 110 mg, 86 % yield; **3b**: 107 mg, 85 % yield). Further TfOH addition lead to compounds **4a,b** as described above.

Observation of **6b**:
4b (100 mg, 0.116 mmol) was dissolved in 5 mL of DME. To the stirred solution, one equivalent of KC_8 was added. The colorless solution became red immediately. An aliquot was taken and checked by NMR and EPR. The ^{1}H, ^{13}C and ^{11}B NMR were silent, but one fluorine signal corresponding to a free triflate group was observed (-78.1 ppm).

3. Crystal structure parameters

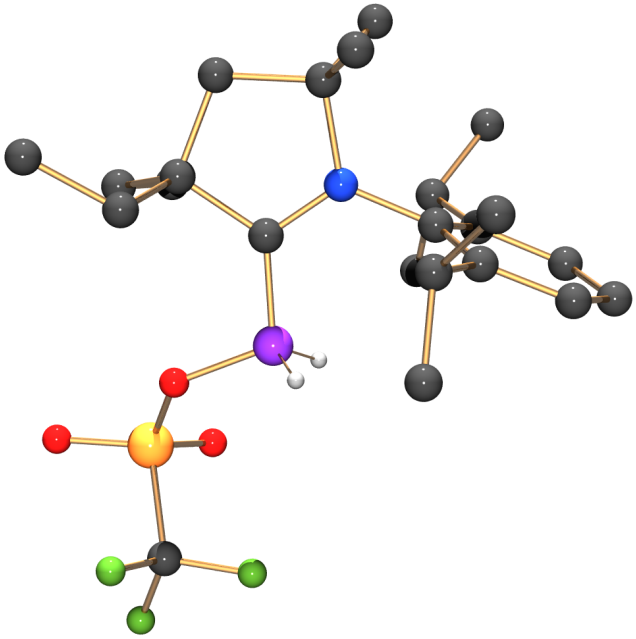

Figure S31 Molecular structure of **2** in the solid state. Hydrogen atoms, except the B-H, are omitted for clarity

2 CCDC (1001687)

Empirical formula	$C_{23}H_{37}BF_3NO_3S$
Formula weight	475.41
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.1389(6)
b/Å	13.5546(7)

c/Å	16.2662(9)
α/°	90.00
β/°	95.4560(10)
γ/°	90.00
Volume/Å^3	2444.8(2)
Z	4
ρ_{calc}mg/mm^3	1.292
m/mm^{-1}	0.180
F(000)	1016.0
Crystal size/mm^3	0.32 × 0.17 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.26 to 58.72°
Index ranges	-15 ≤ h ≤ 14, -18 ≤ k ≤ 13, -21 ≤ l ≤ 22
Reflections collected	19841
Independent reflections	6162 [R_{int} = 0.0132, R_{sigma} = 0.0121]
Data/restraints/parameters	6162/0/401
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0326, wR_2 = 0.0872
Final R indexes [all data]	R_1 = 0.0346, wR_2 = 0.0889
Largest diff. peak/hole / e Å^{-3}	0.44/-0.32

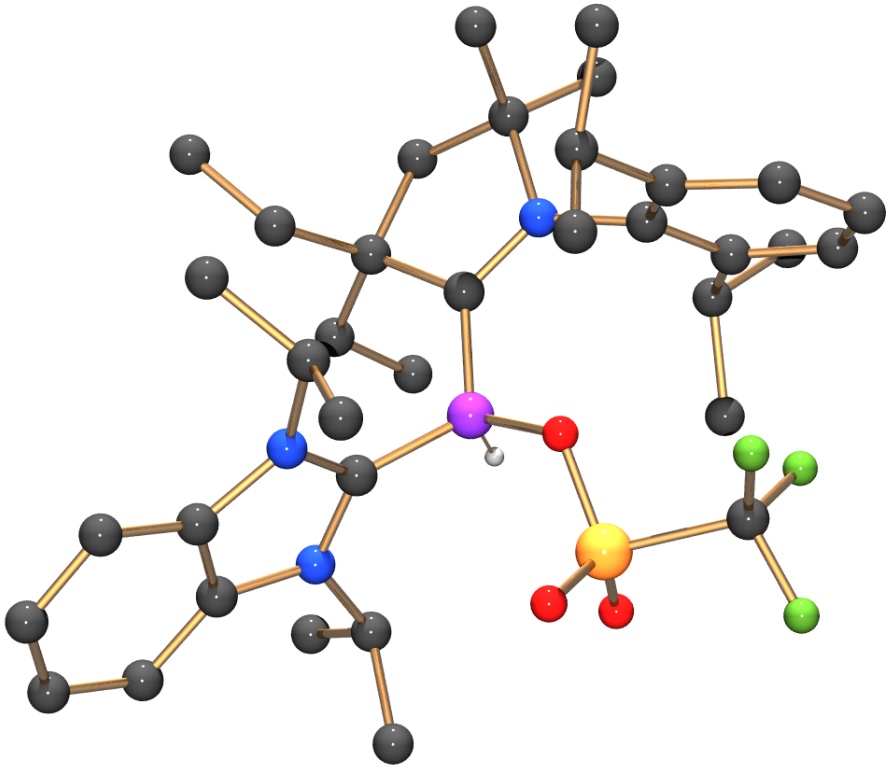

Figure S32 Molecular structure of **4a(BPh$_4$)** in the solid state. Hydrogen atoms, except the B-H, and the BPh$_4$ anion are omitted for clarity.

4a(BPh_4) CCDC (1001686)

Empirical formula	$C_{60}H_{74}B_2F_3N_3O_3S$
Formula weight	995.90
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.2524(5)
b/Å	13.4771(5)
c/Å	28.1965(9)
α/°	90
β/°	91.7220(10)
γ/°	90
Volume/$Å^3$	5413.6(3)
Z	4
$\rho_{calc}mg/mm^3$	1.222
m/mm^{-1}	0.118
F(000)	2128.0
Crystal size/mm^3	0.25 × 0.22 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	5.018 to 52.78°
Index ranges	$-17 \leq h \leq 17$, $-16 \leq k \leq 16$, $-33 \leq l \leq 34$
Reflections collected	34655
Independent reflections	10835 [R_{int} = 0.0671, R_{sigma} = 0.0686]
Data/restraints/parameters	10835/0/661
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0479, wR_2 = 0.1248
Final R indexes [all data]	R_1 = 0.0620, wR_2 = 0.1350
Largest diff. peak/hole / e $Å^{-3}$	0.56/-0.49

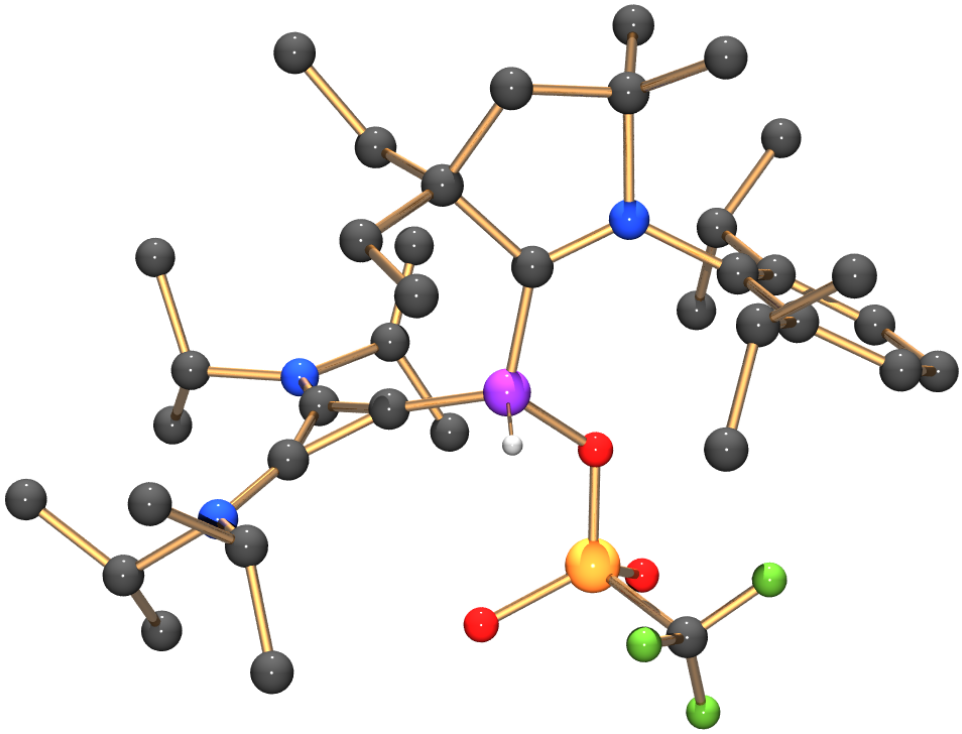

Figure S33 Molecular structure of **4b(BPh$_4$)** in the solid state. Hydrogen atoms, except the B-H, and the BPh$_4$ anion are omitted for clarity.

4b(BPh$_4$) CCDC (1001685)	
Empirical formula	$C_{62}H_{84}B_2F_3N_3O_3S$
Formula weight	1030.00
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	22.260(12)
b/Å	13.788(7)
c/Å	19.769(10)
α/°	90.00
β/°	106.570(7)
γ/°	90.00
Volume/Å^3	5816(5)
Z	4
ρ_{calc}mg/mm^3	1.176
m/mm^{-1}	0.112
F(000)	2216.0
Crystal size/mm^3	0.28 × 0.14 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.82 to 46.56°
Index ranges	$-24 \leq h \leq 24$, $-15 \leq k \leq 13$, $-21 \leq l \leq 20$
Reflections collected	24181

Independent reflections	8342 [R_{int} = 0.1417, R_{sigma} = 0.2426]
Data/restraints/parameters	8342/79/763
Goodness-of-fit on F^2	0.787
Final R indexes [I>=2σ (I)]	R_1 = 0.0522, wR_2 = 0.0744
Final R indexes [all data]	R_1 = 0.1833, wR_2 = 0.0995
Largest diff. peak/hole / e $Å^{-3}$	0.35/-0.30

5a CCDC (1001684)

Empirical formula	$C_{35}H_{54}BN_3$
Formula weight	527.62
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.2182(7)
b/Å	9.3515(4)
c/Å	21.6436(10)
α/°	90
β/°	104.492(2)
γ/°	90
Volume/$Å^3$	3178.1(2)
Z	4
ρ_{calc}mg/mm^3	1.103
m/mm^{-1}	0.063
F(000)	1160.0
Crystal size/mm^3	0.2 × 0.18 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	2.826 to 52.794°
Index ranges	-19 ≤ h ≤ 20, -11 ≤ k ≤ 11, -24 ≤ l ≤ 27
Reflections collected	22614
Independent reflections	6500 [R_{int} = 0.0372, R_{sigma} = 0.0422]
Data/restraints/parameters	6500/0/359
Goodness-of-fit on F^2	1.111
Final R indexes [I>=2σ (I)]	R_1 = 0.0492, wR_2 = 0.1318
Final R indexes [all data]	R_1 = 0.0786, wR_2 = 0.1654
Largest diff. peak/hole / e $Å^{-3}$	0.39/-0.58

5b CCDC (1001683)

Empirical formula	$C_{39.5}H_{70}BN_3$
Formula weight	597.80
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	27.415(5)

b/Å	18.243(4)
c/Å	17.305(3)
α/°	90.00
β/°	114.471(2)
γ/°	90.00
Volume/Å^3	7877(3)
Z	8
ρ_{calc}mg/mm^3	1.008
m/mm^{-1}	0.057
F(000)	2664.0
Crystal size/mm^3	0.20 × 0.18 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.22 to 68.72°
Index ranges	-43 ≤ h ≤ 39, -28 ≤ k ≤ 28, -19 ≤ l ≤ 27
Reflections collected	32951
Independent reflections	15374 [R_{int} = 0.0609, R_{sigma} = 0.0878]
Data/restraints/parameters	15374/0/587
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0629, wR_2 = 0.1547
Final R indexes [all data]	R_1 = 0.1173, wR_2 = 0.1813
Largest diff. peak/hole / e Å^{-3}	0.93/-0.46

4. Computational details

Calculations were performed with the Gaussian 09 program package[4] using the BVP86/6-311+g(2d,p) and (U)BVP86/6-311+g(2d,p)[5] level of theory. All energies were corrected for (unscaled) zero-point vibrational energy contributions with this method. The structures represented here correspond to energetic minima indicated by the absence of negative frequencies. The cartesian coordinates are as follows:

5a

ZPE = -1555.016793 a.u.

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-2.760659	-0.857173	-0.265591
7	-2.580762	1.353835	-0.179798
6	-6.431988	-0.107274	-0.614238
1	-7.417805	-0.560432	-0.731193
6	-5.306048	-0.936664	-0.525217
1	-5.421102	-2.017437	-0.566294
6	-4.052987	-0.332354	-0.377258
6	-1.827142	0.180578	-0.154761
6	0.737070	-0.471513	0.696495

6	2.700331	0.346806	-0.646261
6	3.109515	1.708896	-0.580058
6	2.737818	2.643597	0.569805
1	2.228910	2.039839	1.335354
6	1.736394	3.711162	0.077114
1	2.216539	4.406133	-0.630019
1	1.357756	4.304707	0.924503
1	0.886042	3.244597	-0.436134
6	-6.312163	1.286928	-0.555191
1	-7.205726	1.909634	-0.624704
6	-2.373278	-2.199003	-0.767137
1	-1.290994	-2.234018	-0.582590
6	-2.601163	-2.291612	-2.283309
1	-3.665712	-2.194611	-2.540941
1	-2.249093	-3.265787	-2.653377
1	-2.040983	-1.503865	-2.805553
6	-3.049732	-3.350627	-0.011988
1	-3.043844	-3.190006	1.074317
1	-2.507541	-4.283828	-0.222094
1	-4.090068	-3.504755	-0.329145
6	-1.993030	2.683880	0.066198
1	-0.931651	2.455643	0.243548
6	-2.093856	3.577711	-1.174720
1	-1.627167	3.087977	-2.040822
1	-1.568126	4.526379	-0.992520
1	-3.135863	3.815114	-1.434652
6	-2.553503	3.329942	1.340700
1	-3.619779	3.580723	1.259057
1	-2.004637	4.260442	1.546614
1	-2.423498	2.660175	2.202504
6	-3.933879	1.074633	-0.323305
6	-5.061390	1.899994	-0.413189
1	-4.981084	2.985309	-0.384809
6	0.542209	-1.163138	2.065742
6	1.982120	-1.342697	2.628223
1	2.121823	-0.699822	3.509922
1	2.169221	-2.373820	2.962450
6	3.759728	-2.143896	0.962400
1	3.080182	-2.900739	0.552348
1	4.361238	-2.615093	1.755489
1	4.449292	-1.826876	0.166561
6	2.901760	-0.387395	-1.847837
6	3.597398	0.218379	-2.904964
1	3.764902	-0.348294	-3.823963
6	4.073114	1.523148	-2.812797
1	4.626093	1.969809	-3.642291

6	3.808352	2.261912	-1.663869
1	4.138302	3.301909	-1.608130
6	3.948886	3.350466	1.210877
1	4.708981	2.643052	1.566673
1	3.622735	3.961468	2.067373
1	4.436106	4.030251	0.494735
6	2.336648	-1.785570	-2.079794
1	1.897440	-2.124199	-1.131728
6	1.198410	-1.729433	-3.119590
1	0.419389	-1.023419	-2.799989
1	0.741333	-2.724020	-3.244591
1	1.575993	-1.408230	-4.103266
6	3.400737	-2.809497	-2.521574
1	3.821578	-2.553808	-3.506290
1	2.950444	-3.810695	-2.610766
1	4.235405	-2.875390	-1.809921
6	4.049671	0.027805	2.118327
1	4.739845	0.386492	1.341441
1	4.645708	-0.505039	2.875336
1	3.580774	0.891983	2.605830
6	-0.211515	-2.515117	1.999081
1	-0.302035	-2.903026	3.027901
1	-1.239306	-2.306315	1.669427
6	0.400294	-3.613378	1.126764
1	0.539511	-3.277815	0.087551
1	-0.246428	-4.503937	1.112825
1	1.380678	-3.937135	1.506431
6	-0.268846	-0.199338	2.991913
1	0.251909	0.772894	2.988963
1	-1.245832	-0.016903	2.518192
6	-0.482857	-0.656711	4.443067
1	-1.136498	-1.538492	4.512327
1	-0.959795	0.145443	5.026820
1	0.464969	-0.904581	4.946336
5	-0.282899	0.182652	-0.177492
1	0.137025	1.025567	-0.941961
7	2.116572	-0.287318	0.510741
6	2.998402	-0.932590	1.538171

5b

ZPE = -1637.070368 a.u.

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z

7	2.573481	-0.529452	-0.288128
7	-3.116079	2.168925	-0.099532
7	-3.294795	-1.591727	0.338662
5	0.159875	0.239096	-0.053507
6	-1.364320	0.169519	-0.087023
6	-2.644290	-0.427759	0.090209
6	-2.563973	0.943602	-0.028665
6	1.203408	-0.690494	-0.581087
6	1.129503	-1.757570	-1.689491
6	2.452724	-2.541227	-1.501529
6	3.477599	-1.573404	-0.873535
6	3.066453	0.426608	0.668173
6	3.622436	1.656015	0.220022
6	4.199158	2.524867	1.159456
6	4.201901	2.225130	2.518542
6	3.587743	1.055451	2.959158
6	3.005020	0.147956	2.062160
6	-0.070845	-2.715027	-1.560337
6	-0.143117	-3.813308	-2.632599
6	1.127203	-1.058764	-3.094714
6	-0.186009	-0.404300	-3.531418
6	4.316488	-2.292524	0.199668
6	4.466402	-1.014490	-1.918248
6	3.531759	2.124285	-1.229871
6	4.888206	2.552235	-1.821523
6	2.517398	3.280814	-1.353062
6	2.282137	-1.064929	2.643399
6	3.175320	-1.907500	3.576072
6	1.008198	-0.624151	3.395284
6	-2.254135	3.362007	-0.324546
6	-1.342254	3.642007	0.877788
6	-1.476426	3.250658	-1.640442
6	-4.572459	2.368484	0.058164
6	-5.214724	2.964472	-1.204733
6	-4.919573	3.180443	1.315249
6	-2.489300	-2.678808	0.959388
6	-2.753955	-4.044352	0.313914
6	-2.648431	-2.743477	2.487333
6	-4.770684	-1.701442	0.333373
6	-5.351215	-1.260854	-1.017392
6	-5.455849	-1.017792	1.531868
1	2.278372	-3.375464	-0.801755
1	2.831399	-2.973653	-2.439546
1	4.641526	3.463413	0.816826
1	4.661363	2.910604	3.234673
1	3.554684	0.840031	4.030063

1	-0.008412	-3.189925	-0.567961
1	-1.004297	-2.131743	-1.571137
1	-0.267983	-3.396813	-3.643218
1	-0.996345	-4.483994	-2.448083
1	0.763659	-4.437497	-2.641105
1	1.916023	-0.291811	-3.090360
1	1.431105	-1.804854	-3.851008
1	-0.974513	-1.146310	-3.730875
1	-0.037933	0.172785	-4.457395
1	-0.551341	0.280940	-2.752561
1	4.991720	-1.594915	0.716784
1	4.934710	-3.067787	-0.279107
1	3.677448	-2.782647	0.945040
1	3.960204	-0.519962	-2.756813
1	5.069320	-1.840057	-2.327851
1	5.158074	-0.298391	-1.453542
1	3.140079	1.284841	-1.819778
1	5.283950	3.445935	-1.314093
1	4.777379	2.805318	-2.887679
1	5.647190	1.761375	-1.738581
1	1.539541	2.981155	-0.954665
1	2.390988	3.570891	-2.408462
1	2.860484	4.168418	-0.797641
1	1.955867	-1.690362	1.799726
1	4.110577	-2.216747	3.088761
1	2.640310	-2.814937	3.898322
1	3.444896	-1.348903	4.485849
1	1.255205	0.024549	4.251233
1	0.471859	-1.504499	3.785391
1	0.335826	-0.075692	2.720869
1	-2.960866	4.201692	-0.415937
1	-1.928748	3.756667	1.800878
1	-0.777922	4.572482	0.713011
1	-0.619516	2.825877	1.018922
1	-0.754223	2.421890	-1.596976
1	-0.918444	4.180086	-1.828221
1	-2.157252	3.078505	-2.486799
1	-4.980947	1.358384	0.186665
1	-4.876681	3.994741	-1.390330
1	-6.308770	2.994398	-1.090263
1	-4.977242	2.360656	-2.092023
1	-4.494193	2.716237	2.216286
1	-6.011832	3.238084	1.438948
1	-4.540924	4.211551	1.249166
1	-1.450060	-2.389118	0.749072
1	-3.741858	-4.449656	0.583077

1	-2.005201	-4.768557	0.667127
1	-2.684908	-3.988619	-0.780685
1	-2.471316	-1.760992	2.946554
1	-1.914918	-3.449502	2.906220
1	-3.648515	-3.098315	2.781177
1	-4.967379	-2.780352	0.425027
1	-5.151734	-0.199932	-1.223681
1	-6.441406	-1.406905	-1.029732
1	-4.912193	-1.847711	-1.836212
1	-5.119091	-1.450949	2.482317
1	-6.547476	-1.144998	1.467719
1	-5.244060	0.058952	1.568647
1	0.562126	1.258127	0.466208

6b

ZPE = -1636.908744 a.u.

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-2.554550	-0.425371	0.394967
7	3.169476	2.092631	-0.051597
7	3.195151	-1.650754	-0.452065
5	-0.174242	0.282383	-0.007859
6	1.372791	0.172330	0.015961
6	2.593185	-0.493820	-0.190644
6	2.572120	0.907680	-0.071076
6	-1.243321	-0.502304	0.754141
6	-1.134734	-1.332922	2.042986
6	-2.488206	-2.091008	2.069223
6	-3.496114	-1.272890	1.238316
6	-3.051083	0.316978	-0.754244
6	-3.559200	1.629807	-0.578200
6	-4.123189	2.272120	-1.690796
6	-4.166962	1.662825	-2.940732
6	-3.609194	0.398363	-3.106854
6	-3.036743	-0.298688	-2.032947
6	0.040246	-2.335499	2.022259
6	0.127578	-3.239639	3.260317
6	-1.034817	-0.375264	3.280183
6	0.313916	0.305050	3.524613
6	-4.375379	-2.178849	0.365678
6	-4.428251	-0.417589	2.114120
6	-3.442099	2.424181	0.721404
6	-4.786733	3.006947	1.199471

6	-2.412748	3.563435	0.561069
6	-2.374727	-1.644846	-2.322859
6	-3.311498	-2.630091	-3.049964
6	-1.084840	-1.441130	-3.145538
6	2.358774	3.351009	0.012915
6	1.538122	3.549022	-1.266323
6	1.514779	3.427642	1.287311
6	4.655124	2.221334	-0.080926
6	5.189849	2.816633	1.228174
6	5.138044	2.991484	-1.315921
6	2.347012	-2.862669	-0.676134
6	2.697805	-3.987586	0.303387
6	2.414223	-3.327039	-2.136618
6	4.668481	-1.782590	-0.657320
6	5.445312	-1.464310	0.625676
6	5.154207	-1.026426	-1.900028
1	-2.358865	-3.080706	1.603113
1	-2.856632	-2.256867	3.090329
1	-4.525985	3.279850	-1.573019
1	-4.618717	2.180068	-3.789337
1	-3.614166	-0.062297	-4.096595
1	-0.072514	-2.967977	1.126063
1	0.987058	-1.786526	1.902365
1	0.302630	-2.665840	4.181553
1	0.956314	-3.955393	3.159598
1	-0.790793	-3.827608	3.403617
1	-1.813260	0.396952	3.183337
1	-1.307345	-0.962682	4.172242
1	1.103275	-0.419244	3.773093
1	0.235808	1.004598	4.369718
1	0.646631	0.878670	2.648378
1	-5.045253	-1.595806	-0.281777
1	-5.001401	-2.796353	1.025958
1	-3.777312	-2.855634	-0.256735
1	-3.886539	0.238146	2.807062
1	-5.055724	-1.092474	2.714204
1	-5.099364	0.194760	1.498573
1	-3.061125	1.750427	1.501202
1	-5.154888	3.780934	0.509742
1	-4.665937	3.481686	2.184703
1	-5.570787	2.242131	1.284564
1	-1.435725	3.175772	0.243113
1	-2.283154	4.098175	1.514538
1	-2.748096	4.294061	-0.190549
1	-2.082321	-2.096030	-1.362982
1	-4.261229	-2.769842	-2.515884

1	-2.826481	-3.612998	-3.149747
1	-3.550837	-2.282387	-4.065734
1	-1.308696	-0.986714	-4.122465
1	-0.592618	-2.408128	-3.331683
1	-0.377564	-0.781021	-2.622163
1	3.111365	4.150480	0.060874
1	2.181002	3.541983	-2.157564
1	1.021010	4.518551	-1.228413
1	0.776857	2.764318	-1.378092
1	0.718223	2.670647	1.290757
1	1.034015	4.414208	1.349561
1	2.133256	3.291029	2.185241
1	5.023260	1.191011	-0.156720
1	4.869771	3.859369	1.369199
1	6.289177	2.813653	1.211675
1	4.858473	2.232334	2.098116
1	4.763858	2.539117	-2.245174
1	6.236923	2.980694	-1.348166
1	4.824037	4.045291	-1.294186
1	1.323049	-2.522391	-0.470101
1	3.696145	-4.408146	0.110587
1	1.976782	-4.810013	0.191745
1	2.662305	-3.639970	1.344354
1	2.132939	-2.521217	-2.828073
1	1.716788	-4.163824	-2.286055
1	3.416730	-3.690041	-2.408333
1	4.812039	-2.853430	-0.858322
1	5.290136	-0.430058	0.962585
1	6.522678	-1.604544	0.458108
1	5.137099	-2.131111	1.442780
1	4.642402	-1.386201	-2.802829
1	6.233728	-1.184317	-2.035759
1	4.980858	0.055078	-1.826787
1	-0.563007	1.146233	-0.749704

Mulliken atomic spin densities:

1 N 0.285080	11 C -0.062436	21 C 0.003746
2 N 0.036522	12 C -0.022417	22 C 0.005529
3 N 0.026285	13 C 0.009536	23 C 0.027897
4 B 0.490116	14 C -0.011296	24 C -0.005013
5 C -0.066068	15 C 0.001992	25 C -0.003431
6 C 0.026394	16 C 0.004946	26 C 0.008604
7 C 0.035665	17 C -0.004610	27 C 0.010823
8 C 0.224405	18 C 0.037741	28 C -0.006462
9 C -0.050901	19 C 0.003077	29 C 0.002006
10 C 0.007482	20 C 0.003531	30 C -0.017270

31	C	0.008947
32	C	0.006278
33	C	-0.002930
34	C	0.001730
35	C	0.002345
36	C	0.006848
37	C	0.006286
38	C	0.000806
39	C	-0.003662
40	C	0.001757
41	C	0.001625
42	H	-0.000096
43	H	-0.000513
44	H	0.000778
45	H	-0.000060
46	H	0.000680
47	H	-0.003730
48	H	-0.001569
49	H	0.000305
50	H	0.000389
51	H	-0.000012
52	H	0.000461
53	H	0.001710
54	H	0.000842
55	H	-0.000124
56	H	0.002077
57	H	-0.000553
58	H	0.000626
59	H	0.000009
60	H	-0.000076
61	H	0.002348
62	H	-0.000693
63	H	0.000959
64	H	-0.000031
65	H	0.000001
66	H	0.000000
67	H	-0.001077
68	H	0.000040
69	H	0.000859
70	H	0.000861
71	H	-0.000041
72	H	-0.000055
73	H	-0.000086
74	H	0.001330
75	H	-0.000032
76	H	-0.002004
77	H	0.000212
78	H	-0.000020
79	H	0.000142
80	H	0.000566
81	H	0.001529
82	H	0.000799
83	H	0.000183
84	H	-0.000136
85	H	-0.000110
86	H	0.000005
87	H	-0.000078
88	H	-0.000076
89	H	0.000592
90	H	-0.000088
91	H	-0.001685
92	H	-0.000090
93	H	-0.000061
94	H	-0.000183
95	H	0.000010
96	H	0.000595
97	H	0.000011
98	H	0.000179
99	H	-0.000014
100	H	0.000076
101	H	-0.000059
102	H	-0.000056
103	H	-0.000129
104	H	-0.000028
105	H	-0.037112

Sum of Mulliken atomic spin densities = 1.00

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