Supporting information for:

Trapping of a Borirane Intermediate in the Reductive Coupling of an Arylborane to a Diborene

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Contents

General considerations

All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Solvents (both deuterated and non-deuterated) were stored under argon over activated 4 Å molecular sieves. NMR spectra were acquired on a Bruker Avance 500 NMR spectrometer (^{1}H: 500.1 MHz, ^{1}H{^{11}B}: 400.1 MHz, ^{11}B{^{1}H}: 160.5 MHz, ^{13}C{^{1}H}: 125.8 MHz, ^{19}F{^{1}H}: 470.6 MHz or 367.5 MHz, ^{31}P{^{1}H}: 202.5 MHz). Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei (^{13}C{^{1}H}) or residual protons (^{1}H) of the solvent. ^{11}B{^{1}H} NMR spectra were referenced to [$BF_3 \cdot OEt_2$], ^{19}F{^{1}H} NMR to CCl_3F and ^{31}P{^{1}H} NMR to 85% H_3PO_4 as an external standard. ^{1}H NMR and ^{13}C{^{1}H} NMR resonances were assigned with assistance from DEPT-135, HSQC, HMBC, HMQC and ROESY experiments. Microanalyses (C, H, N) were performed on an Elementar vario MICRO cube elemental analyzer. UV-vis spectra were acquired on a JASCO-V660 UV-vis spectrometer. Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a *Vycor* tip, serving as the reference electrode. Formal redox potentials are referenced to the ferrocene/ferrocenium (Fc/Fc^{+}) redox couple. Tetra-*n*-butylammonium hexafluorophosphate ([nBu$_4$N][PF_6]) was employed as the supporting electrolyte. Compensation for resistive losses (*iR* drop) was employed for all measurements.

Solvents and reagents were purchased from Sigma Aldrich or Alfa Aesar. Deuterated solvents were degassed with three freeze-pump-thaw cycles and stored over molecular sieves in J. Young-style ampoules or in a glovebox. I*i*Pr (1,3-di*iso*propylimidazol-2-ylidene)[1] and CAAC (1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene)[2] were synthesized using literature procedures. Potassium graphite (KC_8) was prepared by heating graphite (20.36 g, 1.695 mol; first heated to 180 °C under reduced pressure for ten hours) and freshly-cut potassium (8.35 g, 214 mmol) at 180 °C with stirring for two days, followed by filtering the powder through a tea strainer.

Synthetic procedures

BAr^FCat

A solution of 1-Br-Ar^F (5.00 mL, 8.50 g, 29.0 mmol, Ar^F = 3,5-trifluoromethylphenyl) in Et_2O (80 mL) was cooled to −78 °C, *n*Buli (18.1 mL, 29.0 mmol, 1.60 M in hexane) was added slowly and the reaction mixture stirred for 15 min before addition of $BH_3(SMe_2)$ (2.75 mL, 29.0 mmol). The reaction mixture was stirred at −78 °C for another 45 min, then warmed to rt. Upon addition of Me_3SiCl (3.69 mL, 29.0 mmol) a white precipitate formed and the mixture was stirred for another 30 min at rt. Catechol (3.19 g, 29.0 mmol) in Et_2O (40 mL) was added slowly and the reaction mixture was stirred under a flow of argon until evolution of H_2 ceased. All volatiles were removed in vacuo and the residue was extracted with toluene (4 x 25 mL). After crystallization at −30 °C BAr^FCat (Cat = catecholate) was isolated as a colorless, crystalline solid (8.39 g, 25.3 mmol, 87%). NMR data obtained were consistent with reported data.[3] ^{1}H NMR (400.1 MHz, 296 K, C_6D_6): δ = 8.19 (s, 2H, *o*-Ar^F-*H*), 7.80 (s, 1H, *p*-Ar^F-*H*), 7.09-7.04 (m, 2H, Cat-*H*), 6.89-6.84 (m, 2H, Cat-*H*) ppm. $^{11}B\{^1H\}$ NMR (128.4 MHz, 296 K, C_6D_6): δ = 31.4 (s) ppm. $^{19}F\{^1H\}$ NMR (367.5 MHz, 296 K, C_6D_6): δ = −62.8 (s) ppm.

(I*i*Pr)BAr^FCat

BAr^FCat (2.96 g, 8.91 mmol) was suspended in hexanes (20 mL) and cooled to −50 °C. A solution of I*i*Pr (1.36 g, 8.91 mmol) in hexanes was added dropwise and the mixture was stirred for 1 h at rt. The pink suspension was centrifuged and the isolated solid washed with hexanes (2 x 15 mL) and dried in vacuo to yield **(I*i*Pr)BAr^FCat** as a colorless solid (3.99 g, 8.24 mmol, 93%). ^{1}H NMR (500.1 MHz, 296 K, C_6D_6): δ = 8.18 (s, 2H, *o*-Ar^F-*H*), 7.83 (s, 1H, *p*-Ar^F-*H*), 7.05–7.03 (m, 2H, Cat-*H*), 6.86–6.85 (m, 2H, Cat-*H*), 5.95 (s, 2H, C*H*=C*H*), 5.49 (sept, ^3J = 6.7 Hz, 2H, C*H*$(CH_3)_2$), 0.80 (d, ^3J = 6.7 Hz, 12H, CH(C*H*$_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, 296 K, C_6D_6): δ = 153.6 (Ar-*C*-O), 131.8 (*o*-Ar^F-*C*), 130.9 (q, $^2J_{13C\text{-}19F}$ = 32.1 Hz, *m*-Ar^F-*C*), 124.9 (q, $^1J_{13C\text{-}19F}$ = 273 Hz, *C*F_3), 120.9 (sept, $^3J_{13C\text{-}19F}$ = 3.8 Hz, *p*-Ar^F-*C*), 119.6 (Cat-*C*H), 116.8 (*C*H=*C*H), 109.9 (Cat-*C*H), 50.3 (N*C*H$(CH_3)_2$), 22.9 (CH(*C*H$_3)_2$) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, 296 K, C_6D_6): δ = 8.7 (s) ppm. $^{19}F\{^1H\}$ NMR (367.5 MHz, 296 K, C_6D_6): δ = −62.2 (s) ppm. Elemental analysis: calculated for $C_{23}H_{23}BN_2O_2F_6$: C 57.05, H 4.79, N 5.79; found: C 56.59, H 4.70, N 5.87%.

(I*i*Pr)BAr^{F}Br$_2$, 1

A suspension of **(I*i*Pr)BAr^{F}Cat** (1.24 g, 2.55 mmol) in hexanes (20 mL) was cooled to –78 °C. BBr_3 (0.64 g, 2.25 mmol) was added dropwise and the suspension turned orange. After stirring for 1 h at rt the suspension was centrifuged, the solid was washed with hexanes (2 x 15 mL) and compound **1** dried in *vacuo* (1.22 g, 2.28 mmol, 89%). ^{1}H NMR (500.1 MHz, 296 K, C_6D_6): δ = 8.76 (s, 2H, *o*-Ar-*H*), 7.75 (s, 1H, *p*-Ar-*H*), 5.97 (s, 2H, C*H*=C*H*), 5.04 (sept, ^{3}J = 6.7 Hz, 2H, C*H*(CH_3)$_2$), 0.73 (d, ^{3}J = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, 296 K, C_6D_6): δ = 134.1 (*o*-Ar-*C*), 131.0 (q, $^{2}J_{13C\text{-}19F}$ = 32.5 Hz, *m*-Ar-*C*$_q$), 124.6 (q, $^{1}J_{13C\text{-}19F}$ = 273 Hz, *C*F$_3$), 120.9 (sept, $^{3}J_{13C\text{-}19F}$ = 3.8 Hz, *p*-Ar-*C*), 117.8 (*C*H=*C*H), 50.9 (N*C*H(CH_3)$_2$), 22.3 (CH(*C*H$_3$)$_2$) ppm. ^{11}B{^{1}H} NMR (160.5 MHz, 296 K, C_6D_6): δ = –5.6 (s) ppm. ^{19}F{^{1}H} NMR (470.6 MHz, 296 K, C_6D_6): δ = –62.4 (s) ppm. Elemental analysis: calculated for $C_{17}H_{19}BN_2F_6$: C 38.10, H 3.57, N 5.23; found: C 38.88, H 3.45, N 5.82%.

(I*i*Pr)$_2$B$_2$Ar$^{F}_2$, 2

In a round-bottomed flask **1** (1.25 g, 2.33 mmol) and KC_8 (3.17 g, 23.3 mmol) were combined in benzene (15 mL), whereupon the suspension turned deep purple. The mixture was stirred 4.5 h at rt, filtered and the residue washed with benzene (3 x 15 mL). The solvent was removed in vacuo to yield the crude diborene as a 3:1 mixture of two isomers, **2a** (*trans*) and **2b** (*cis*). **2a** was selectively recrystallized from a saturated benzene solution as a deep purple solid (0.47 g, 0.62 mmol, 53%). No crystals of **2b** could be obtained. NMR data given here for isolated **2a** (see reduction of **3a/3b** below for ^{1}H and ^{19}F NMR data of **2b**). ^{1}H NMR (500.1 MHz, 296 K, C_6D_6): δ = 7.29 (s, 2H, *o*-Ar-*H*), 6.91 (s, 4H, *p*-Ar-*H*), 6.39 (s, 4H, C*H*=C*H*), 5.14 (sept, ^{3}J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 0.94 (d, ^{3}J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 0.91 (d, ^{3}J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, 296 K, C_6D_6): δ = 130.2 (*o*-Ar-*C*), 129.8 (q, $^{2}J_{13C\text{-}19F}$ = 30.9 Hz, *m*-Ar-C), 125.5 (q, $^{1}J_{13C\text{-}19F}$ = 272 Hz, *C*F$_3$), 116.2 (*C*H=*C*H), 112.3 (sept, $^{3}J_{13C\text{-}19F}$ = 3.9 Hz, *p*-Ar-*C*), 50.3 (N-*C*H(CH_3)$_2$), 23.2 (CH(*C*H$_3$)$_2$), 21.9 (CH(*C*H$_3$)$_2$) ppm. ^{11}B{^{1}H} NMR (160.5 MHz, 296 K, C_6D_6): δ = 26.1 (br) ppm. ^{19}F{^{1}H} NMR (470.6 MHz, 296 K, C_6D_6): δ = –62.9 (s) ppm. UV-vis (benzene): λ_{max} = 576 nm. Elemental analysis: calculated for $C_{34}H_{38}B_2N_4F_{12}$: C 54.28, H 5.09, N 7.45; found: C 54.57, H 5.35, N 7.46%.

(I*i*Pr)B(2,3-{BAr^{F}(I*i*Pr)}Ar^{F}Br$_2$, 3a/3b

Path A) Compound **3a/3b** was first obtained as a minor by-product of the above synthesis of **2a/2b**. As **3a/3b** is significantly less soluble in benzene than **2a/2b** it was isolated selectively

as large colorless crystals in the first crystallization fraction of the diborene crude product in benzene at rt. Subsequent washing of the isolated crystals with hexanes or recrystallization from benzene yielded analytically pure **3a/3b** as a colorless mixture of isomers of two diastereomers, **3a** and **3b**, in a 3:1 ratio (73 mg, 80 μmol, 7%).

Path B) Alternatively, **3a/3b** can be synthesized selectively as the same mixture of diastereomers using the following synthetic procedure. In a Schlenk flask **1** (0.20 g, 0.37 mmol) and KC_8 (0.50 g, 3.73 mmol) were combined in benzene (25 mL). The mixture was stirred 4 h at rt, filtered and the residue washed with benzene (3 x 15 mL). The solution was concentrated in vacuo, affording **3a/3b** as colorless crystals by slow diffusion of hexanes into the saturated benzene solution (71 mg, 78 μmol, 42%). *Note: The dilution of the reaction mixture is crucial for controlling the reaction selectivity. In a concentrated reaction mixture (0.15 M) diborene **2a/2b** is obtained as the main product, whereas in highly diluted reaction mixtures (0.015 M) borirane-borane **3a/3b** is obtained as the major product.* **3a (major isomer):** ^{1}H NMR (500.1 MHz, 296 K, C_6D_6): δ = 8.90 (s, 2H, *o*-Ar-*H*), 7.77 (s, 1H, *p*-Ar-*H*), 7.04 (s, 1H, *p*-Ar-*H*), 6.85 (d, ^{1}J = 1.2 Hz, 1H, CF_3C=C*H*CCF_3), 6.06 (d, ^{3}J = 2.1 Hz, 1H, C*H*=C*H*), 6.05 (s, 2H, C*H*=C*H*), 6.00 (d, ^{3}J = 2.1 Hz, 1H, C*H*=C*H*), 5.96 (sept, ^{3}J = 6.0 Hz, 1H, C*H*$(CH_3)_2$), 5.57 (sept, ^{3}J = 6.4 Hz, 2H, C*H*$(CH_3)_2$), 5.47 (sept, ^{3}J = 6.4 Hz, 1H, C*H*$(CH_3)_2$), 2.99 (s, 1H, BCC*H*B), 1.51 (d, ^{3}J = 6.6 Hz, 3H, CH(C*H*$_3)_2$), 1.14 (d, ^{3}J = 6.6 Hz, 3H, CH(C*H*$_3)_2$), 1.08 (d, ^{3}J = 6.4 Hz, 6H, CH(C*H*$_3)_2$), 1.03-1.00 (m, 12H, CH(C*H*$_3)_2$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, 296 K, C_6D_6): δ = 136.5 (Ar-*C*), 130.7 (q, $^{2}J_{13C\text{-}19F}$ = 31.8 Hz, Ar-C_q), 127.9 (q, $^{1}J_{13C\text{-}19F}$ = 270 Hz, HCC*C*F_3), 126.9 (q, $^{1}J_{13C\text{-}19F}$ = 269 Hz, C=CC*C*F_3), 125.7 (m, C=*C*CCF_3), 125.1 (q, $^{1}J_{13C\text{-}19F}$ = 273 Hz, *C*F_3), 122.5 (q, $^{2}J_{13C\text{-}19F}$ = 29.1 Hz, HC*C*CF_3), 119.6 (sept, $^{3}J_{13C\text{-}19F}$ = 3.8 Hz, Ar-*C*), 119.3 (m, C=*C*CCF_3) 117.5 (*C*H=*C*H), 117.2 (CH=*C*H), 116.8 (*C*H=CH), 51.1 (*C*H$(CH_3)_2$), 50.4 (*C*H$(CH_3)_2$), 49.3 (*C*H$(CH_3)_2$), 24.4 (CH(*C*H$_3)_2$), 23.7 (CH(*C*H$_3)_2$), 23.6 (CH(*C*H$_3)_2$), 22.5 (CH(*C*H$_3)_2$), ppm. ^{11}B{^{1}H} NMR (160.5 MHz, 296 K, C_6D_6): δ = –3.1 (br), –27.8 (s) ppm. ^{19}F{^{1}H} NMR (470.6 MHz, 296 K, C_6D_6): δ = –58.0 (s, 3F, CCC*F*$_3$), –62.2 (s, 6F, Ar-C*F*$_3$), –65.6 (s, 3H, C=CCC*F*$_3$) ppm. **3b (minor isomer):** ^{1}H NMR (500.1 MHz, 296 K, C_6D_6): δ = 8.34 (s, 2H, *o*-Ar-*H*), 7.70 (s, 1H, *p*-Ar-*H*), 7.13 (s, 1H, C*H*C=CF_3), 7.00 (sept, ^{3}J = 6.4 Hz, 1H, C*H*$(CH_3)_2$), 6.12 (d, ^{3}J = 2.1 Hz, 1H, C*H*=C*H*), 6.03 (s, 2H, C*H*=C*H*), 5.97 (2, ^{3}J = 2.1 H, 1H, C*H*=C*H*), 5.78 (sept, ^{3}J = 6.7 Hz, 2H, C*H*$(CH_3)_2$), 5.28 (sept, ^{3}J = 6.7 Hz, 1H, C*H*$(CH_3)_2$), 5.01 (s, 1H, CC*H*CCF_3), 3.26 (s, 1H, BCC*H*B), 1.47 (d, ^{3}J = 6.6 Hz, 3H, CH(C*H*$_3)_2$), 1.39 (d, ^{3}J = 6.7 Hz, 3H, CH(C*H*$_3)_2$), 1.03-1.00 (m, 9H, CH(C*H*$_3)_2$), 0.90 (d, ^{3}J = 6.6 Hz, 6H, CH(C*H*$_3)_2$), 0.51 (d, ^{3}J = 6.6 Hz, 3H, CH(C*H*$_3)_2$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, 296 K, C_6D_6): δ = 137.7 (Ar-*C*), 129.9 (q, $^{2}J_{13C\text{-}19F}$ = 31.7 Hz, Ar-C_q), 126.9 (q, $^{1}J_{13C\text{-}19F}$ = 270 Hz, HCC*C*F_3), 125.3 (m,

C=*C*CCF$_3$), 125.2 (q, $^1J_{13C-19F}$ = 271 Hz, Ar-*C*F$_3$), 125.1 (q, $^1J_{13C-19F}$ = 271 Hz, C=CC*C*F$_3$), 123.5 (q, $^2J_{13C-19F}$ = 29.3 Hz, HC*C*CF$_3$), 118.9 (sept, $^3J_{13C-19F}$ = 3.8 Hz, *p*-Ar-*C*), 117.3 (CH=*C*H), 116.7 (CH=*C*H), 114.0 (m, C=CC*C*F$_3$), 51.5 (*C*H(CH$_3$)$_2$), 50.7 (*C*H(CH$_3$)$_2$), 50.3 (*C*H(CH$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$), 22.9 (CH(*C*H$_3$)$_2$), 22.8 (CH(*C*H$_3$)$_2$), 22.1 (CH(*C*H$_3$)$_2$) ppm. ^{11}B{^{1}H} NMR (160.5 MHz, 296 K, C$_6$D$_6$): δ = –3.1 (br), –26.4 (s) ppm. ^{19}F{^{1}H} NMR (470.6 MHz, 296 K, C$_6$D$_6$): δ = –62.1 (s, 6F, Ar-C*F*$_3$), –62.6 (s, 3H, C=CCC*F*$_3$), –66.6 (s, 3F, CCC*F*$_3$) ppm. Elemental analysis: calculated for C$_{34}$H$_{38}$B$_2$N$_4$F$_{12}$Br$_2$ (isomer mixture): C 44.77, H 4.20, N 6.14; found: C 45.71, H 4.48, N 6.32%.

Irradiation of a 1:1 mixture of 2a and 1

In a sealable NMR tube **2a** (4.40 mg, 5.85 μmol) and **1** (6.27 mg, 11.7 μmol) were combined in C$_6$D$_6$ (0.5 mL). The mixture was irradiated for three days at rt and the reaction was monitored by ^{1}H and ^{11}B{^{1}H} NMR spectroscopy, evidencing the formation of compounds **3a/3b**.

Reduction of 3a/3b

KC$_8$ (38.5 mg, 0.29 mmol) and isolated **3a/3b** (3:1 mixture, 26.0 mg, 29 μmol) were combined in a sealable NMR tube in C$_6$D$_6$ (0.5 mL). The reaction mixture turned purple after 1 h at rt and the reaction was monitored by ^{1}H and ^{11}B{^{1}H} NMR spectroscopy. After 36 h the reaction was complete, providing quantitative conversion to the diborene as a mixture of two isomers, **2a** as described above and **2b**, the NMR data of which are as follows: ^{1}H NMR (400.1 MHz, 296 K, C$_6$D$_6$): δ = 7.96 (s, 4H, *o*-Ar-*H*), 7.61 (s, 2H, *p*-Ar-*H*), 6.07 (s, 4H, C*H*=C*H*), 4.99 (sept, ^3J = 6.5 Hz, 4H, C*H*(CH$_3$)$_2$), 0.73 (d, ^3J = 6.5 Hz, 12H, CH(C*H*$_3$)$_2$), 0.52 (d, ^3J = 6.5 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. ^{11}B{^{1}H} NMR (160.5 MHz, 296 K, C$_6$D$_6$): δ = 26.1 (br) ppm. ^{19}F{^{1}H} NMR (470.6 MHz, 296 K, C$_6$D$_6$): δ = –62.6 (s) ppm.

(CAAC)BAr^{F}Cat

BAr^{F}Cat (0.64 g, 1.93 mmol) was suspended in hexanes (10 mL) and cooled to –50 °C. A solution of CAAC (0.55 g, 1.93 mmol) in hexanes was added dropwise and the mixture stirred 1 h at rt. The yellow suspension was centrifuged and the isolated solid washed with hexanes (2 x 10 mL) and dried in *vacuo* to yield **(CAAC)BAr^{F}Cat** as a bright yellow solid (1.08 g, 1.75 mmol, 91%). ^{1}H NMR (500.1 MHz, 296 K, C$_6$D$_6$): δ = 7.87 (s, 2H, Ar^F-*H*), 7.65 (s, 1H, Ar^F-*H*), 7.18–7.15 (m, 1H, Dip-*H*), 6.94–6.92 (m, 2H, Dip-*H*), 6.78–6.75 (m, 2H, Cat-*H*), 6.69-6.65 (m, 2H, Cat-*H*), 2.58 (sept, ^3J = 6.6 Hz, 2H, C*H*(CH$_3$)$_2$), 1.33 (s, 6H, NC(C*H*$_3$)$_2$), 1.26 (s, 2H,

*C*H$_2$), 1.04 (d, ^3J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.98 (d, ^3J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.81 (s, 6H, C(*C*H$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, 296 K, C$_6$D$_6$): δ = 152.9 (Ar-*C*$_q$-O), 145.1 (Ar-*C*$_q$-N), 133.7 (Ar^F-*C*$_q$), 132.5 (Ar^F-*C*), 130.6 (Dip-*C*), 130.0 (q, $^2J_{13C\text{-}19F}$ = 32.4 Hz, Ar^F-*C*$_q$), 125.7 (Dip-*C*), 124.9 (q, $^1J_{13C\text{-}19F}$ = 273 Hz, *C*F$_3$), 120.5 (sept, $^3J_{13C\text{-}19F}$ = 4.0 Hz, Ar^F-*C*), 119.1 (Cat-*C*H), 109.8 (Cat-*C*H), 80.6 (N*C*(CH$_3$)$_2$), 53.5 (*C*(CH$_3$)$_2$), 52.1 (*C*H$_2$), 29.4 (*C*H(CH$_3$)$_2$), 28.6 (NC(*C*H$_3$)$_2$), 28.3 (C(*C*H$_3$)$_2$), 26.1 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$) ppm. ^{11}B{^{1}H} NMR (160.5 MHz, 296 K, C$_6$D$_6$): δ = 8.3 (s) ppm. ^{19}F{^{1}H} NMR (470.6 MHz, 296 K, C$_6$D$_6$): δ = –62.1 (s) ppm. Elemental analysis: calculated for C$_{34}$H$_{38}$BNO$_2$F$_6$: C 66.14, H 6.20, N 2.27; found: C 66.45, H 6.30, N 2.38%.

(CAAC)BAr^{F}Cl$_2$, 4

A suspension of **(CAAC)BAr^{F}Cat** (1.05 g, 1.70 mmol) in hexanes (15 mL) was cooled to −78 °C and a solution of BCl$_3$ in hexanes (1 M, 1.70 mL, 1.70 mmol) was added dropwise. After stirring 1 h at rt the suspension was centrifuged, the solid washed with hexanes (2 x 15 mL) and dried in vacuo. The crude product was extracted with toluene and concentrated. Crystallization overnight at –30 °C yielded colorless crystals of **4** (0.40 g, 0.69 mmol, 41%). ^{1}H NMR (500.1 MHz, 296 K, C$_6$D$_6$): δ = 8.61 (s, 2H, Ar^F-*H*), 7.77 (s, 1H, Ar^F-*H*), 7.12–7.09 (m, 1H, Dip-*H*), 7.00–6.99 (m, 2H, Ar-*H*), 2.81 (sept, ^3J = 6.5 Hz, 2H, C*H*(CH$_3$)$_2$), 1.64 (d, ^3J = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.23 (s, 2H, *C*H$_2$), 1.12 (d, ^3J = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 0.96 (s, 6H, NC(C*H*$_3$)$_2$)), 0.76 (s, 6H, C(*C*H$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, 296 K, C$_6$D$_6$): δ = 145.1 (Ar-*C*$_q$-N), 134.0 (Dip-*C*), 133.4 (Ar^F-*C*$_q$), 130.2 (q, $^2J_{13C\text{-}19F}$ = 32.1 Hz, Ar^F-*C*$_q$), 130.1 (Dip-*C*), 125.5 (Dip-*C*), 124.8 (q, $^1J_{13C\text{-}19F}$ = 273 Hz, *C*F$_3$), 120.6 (sept, $^3J_{13C\text{-}19F}$ = 4.0 Hz, Ar^F-*C*), 79.8 (N*C*(CH$_3$)$_2$), 53.7 (*C*(CH$_3$)$_2$), 51.5 (*C*H$_2$), 30.8 (NC(*C*H$_3$)$_2$), 29.6 (*C*H(CH$_3$)$_2$), 28.5 (C(*C*H$_3$)$_2$), 27.0 (CH(*C*H$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$) ppm. ^{11}B{^{1}H} NMR (160.5 MHz, 296 K, C$_6$D$_6$): δ = 1.5 (s) ppm. ^{19}F{^{1}H} NMR (470.6 MHz, 296 K, C$_6$D$_6$): δ = –62.3 (s) ppm. Elemental analysis: calculated for [C$_{28}$H$_{34}$BCl$_2$N$_2$F$_6$ + 0.5 C$_6$H$_6$]: C 59.83, H 6.48, N 2.25; found: C 60.09, H 6.36, N 2.54%.

(CAAC)(I*i*Pr)BAr^F, 5

A solution of I*i*Pr (41.0 mg, 0.27 mmol) in benzene (4 mL) was added dropwise to a mixture of **5** (0.10 g, 0.17 mmol) and KC$_8$ (0.23 g, 1.72 mmol). The reaction mixture was stirred for 2 h, filtered and the solvent removed in vacuo. The residue was dissolved in hexanes (4 mL), filtered again and stored overnight at –30 °C to yield **5** as a deep red, crystalline solid (90.1 mg, 0.14 mmol, 79%). ^{1}H NMR (500.1 MHz, 296 K, C$_6$D$_6$): δ = 7.38–7.35 (m, 1H, Dip-*H*), 7.30 (s,

1H, Ar^F-*H*), 7.14 (s, 2H, Dip-*H*), 6.69 (m, 2H, Ar^F-*H*), 6.10 (s, 2H, C*H*=C*H*), 5.23 (sept, ^3J = 6.8 Hz, 2H, I*i*Pr-C*H*(CH_3)$_2$), 3.78 (sept, ^3J = 6.8 Hz, 2H, Dip-C*H*(CH_3)$_2$), 1.99 (s, 2H, CH_2), 1.34 (d, ^3J = 6.8 Hz, 6H, I*i*Pr-CH(C*H*$_3$)$_2$), 1.33 (s, 6H, NC(C*H*$_3$)$_2$), 1.25 (s, 6H, C(C*H*$_3$)$_2$), 1.19 (d, ^3J = 6.8 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 0.96 (d, ^3J = 6.8 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 0.72 (d, ^3J = 6.8 Hz, 6H, I*i*Pr-CH(C*H*$_3$)$_2$) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, 296 K, C_6D_6): δ = 150.6 (Ar-C_q-N), 143.5 (Dip-C_q), 134.5 (Ar^F-*C*), 130.2 (q, $^2J_{13C\text{-}19F}$ = 31.3 Hz, Ar^F-C_q), 127.5 (Dip-*C*), 125.3 (q, $^1J_{13C\text{-}19F}$ = 273 Hz, *C*F_3), 124.5 (Dip-*C*), 116.2 (*C*H=*C*H), 114.5 (sept, $^3J_{13C\text{-}19F}$ = 4.1 Hz, Ar^F-*C*), 63.1 (N*C*(CH_3)$_2$), 60.2 (*C*H_2), 50.4 (I*i*Pr-*C*H(CH_3)$_2$), 44.7 (C(*C*H_3)$_2$), 35.2 (C(*C*H_3)$_2$), 28.4 (NC(*C*H_3)$_2$), 28.3 (Dip-*C*H(CH_3)$_2$), 26.0 (I*i*Pr-CH(*C*H_3)$_2$), 24.7 (Dip-CH(*C*H_3)$_2$), 23.6 (I*i*Pr-CH(*C*H_3)$_2$), 21.8 (Dip-CH(*C*H_3)$_2$) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, 296 K, C_6D_6): δ = 6.9 (s) ppm. $^{19}F\{^1H\}$ NMR (470.6 MHz, 296 K, C_6D_6): δ = –61.6 (s) ppm. UV-vis (benzene): λ_{max} = 482 nm. Elemental analysis: calculated for $C_{37}H_{50}BN_3F_6$: C 67.17 H 7.62, N 6.35; found: C 67.51, H 7.52, N 6.24%.

Reduction of 1 in the presence of CAAC

A solution of CAAC (26.6 mg, 93 μmol) was added to a mixture of **1** (50.0 mg, 93 μmol) and KC_8 (50.4 g, 0.37 mmol). The deep purple reaction mixture was stirred for 12 h and filtered. The ^{11}B NMR spectrum showed two resonances, the first at 26.1 ppm, corresponding to diborene **2**, and the second at 12.6 (s) ppm. The latter does not fit the expected borylene **5** (δ_{11B} = 6.9 ppm, see above) and could not be further identified.

NMR spectra of isolated new compounds

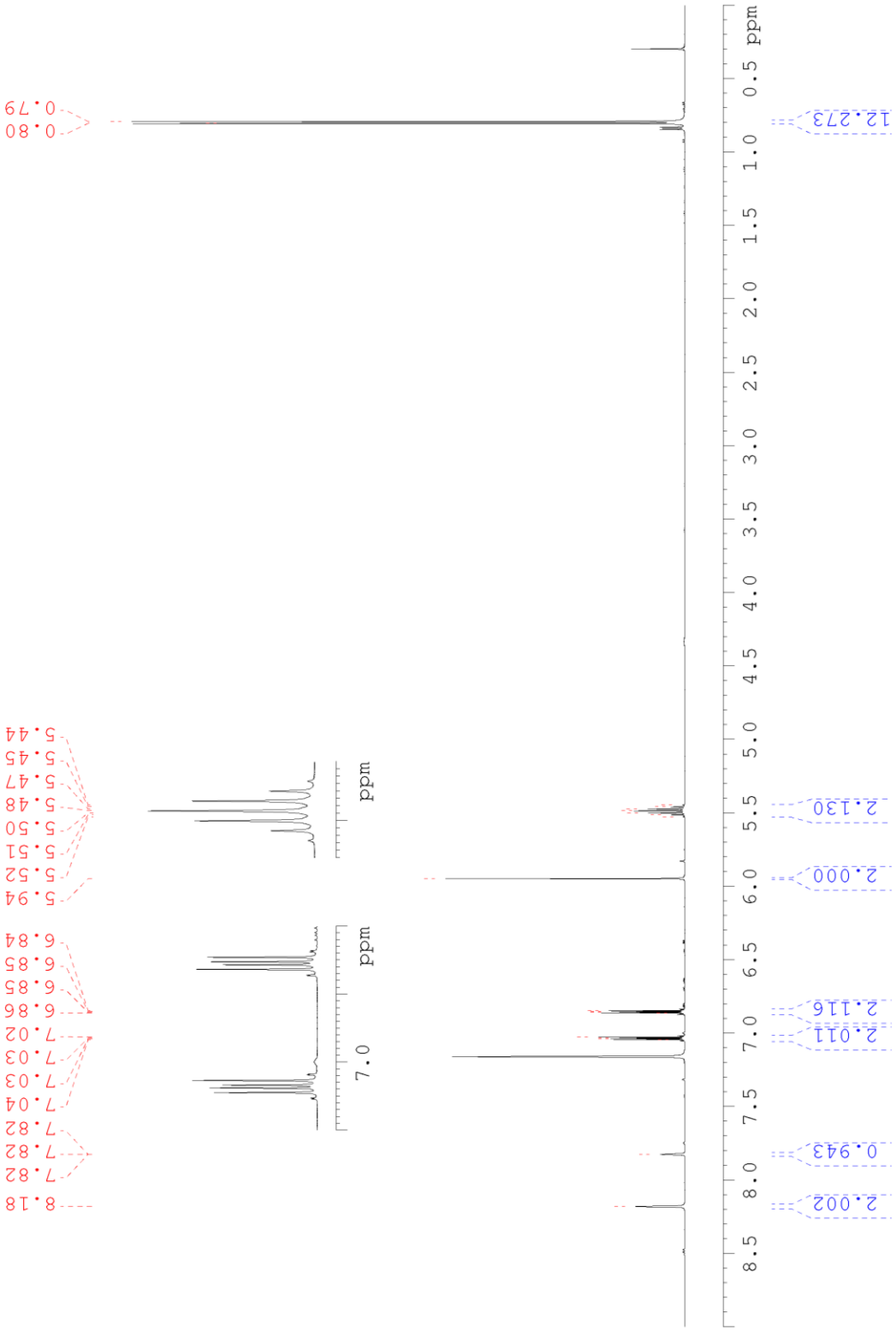


Figure S1. ^{1}H NMR spectrum of **(I*i*Pr)BAr^{F}Cat** in C_6D_6.

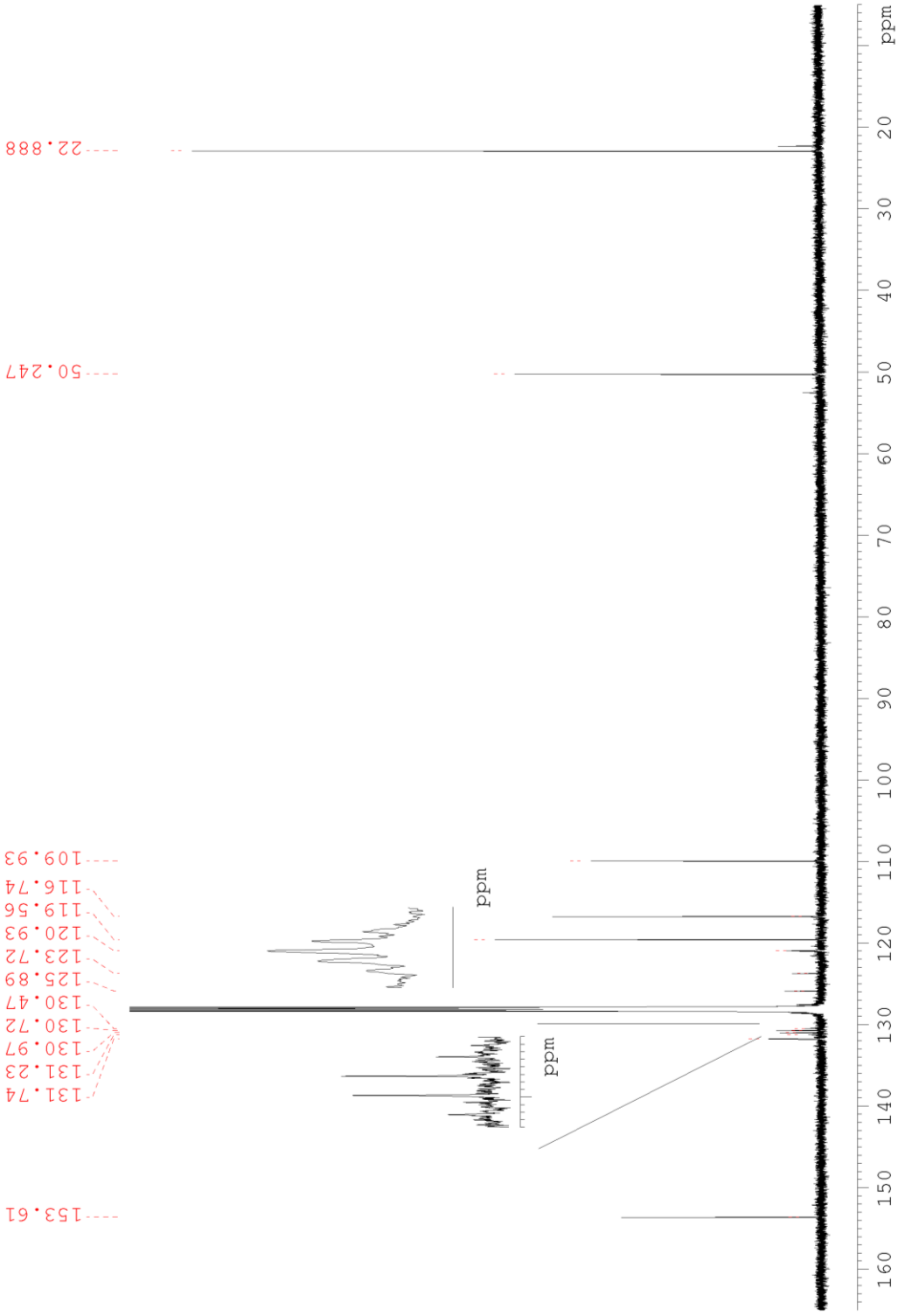


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **(I*i*Pr)BAr^{F}Cat** in C_6D_6.

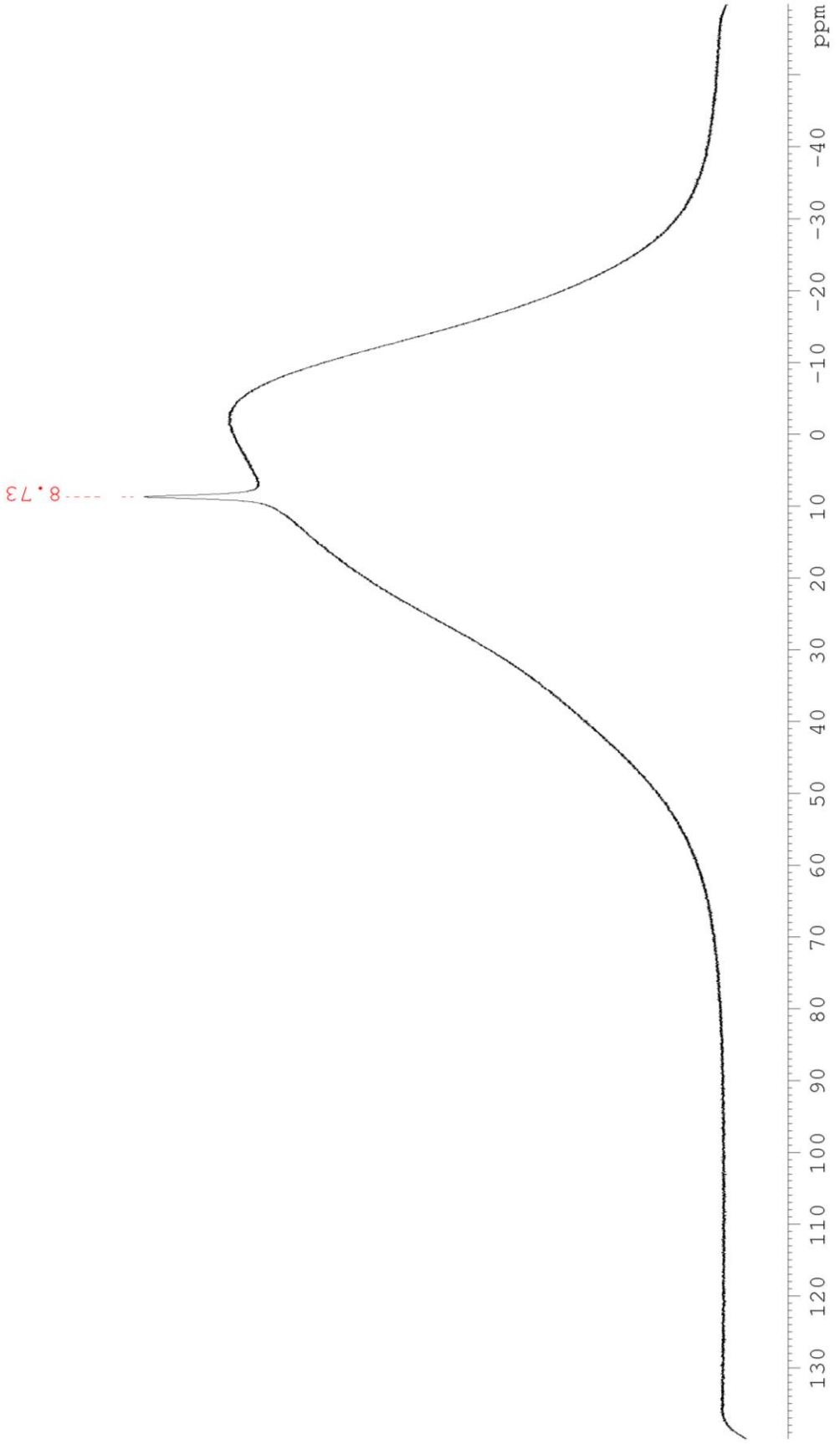


Figure S3. $^{11}B\{^{1}H\}$ NMR spectrum of **(I*i*Pr)BAr^{F}Cat** in C_6D_6.

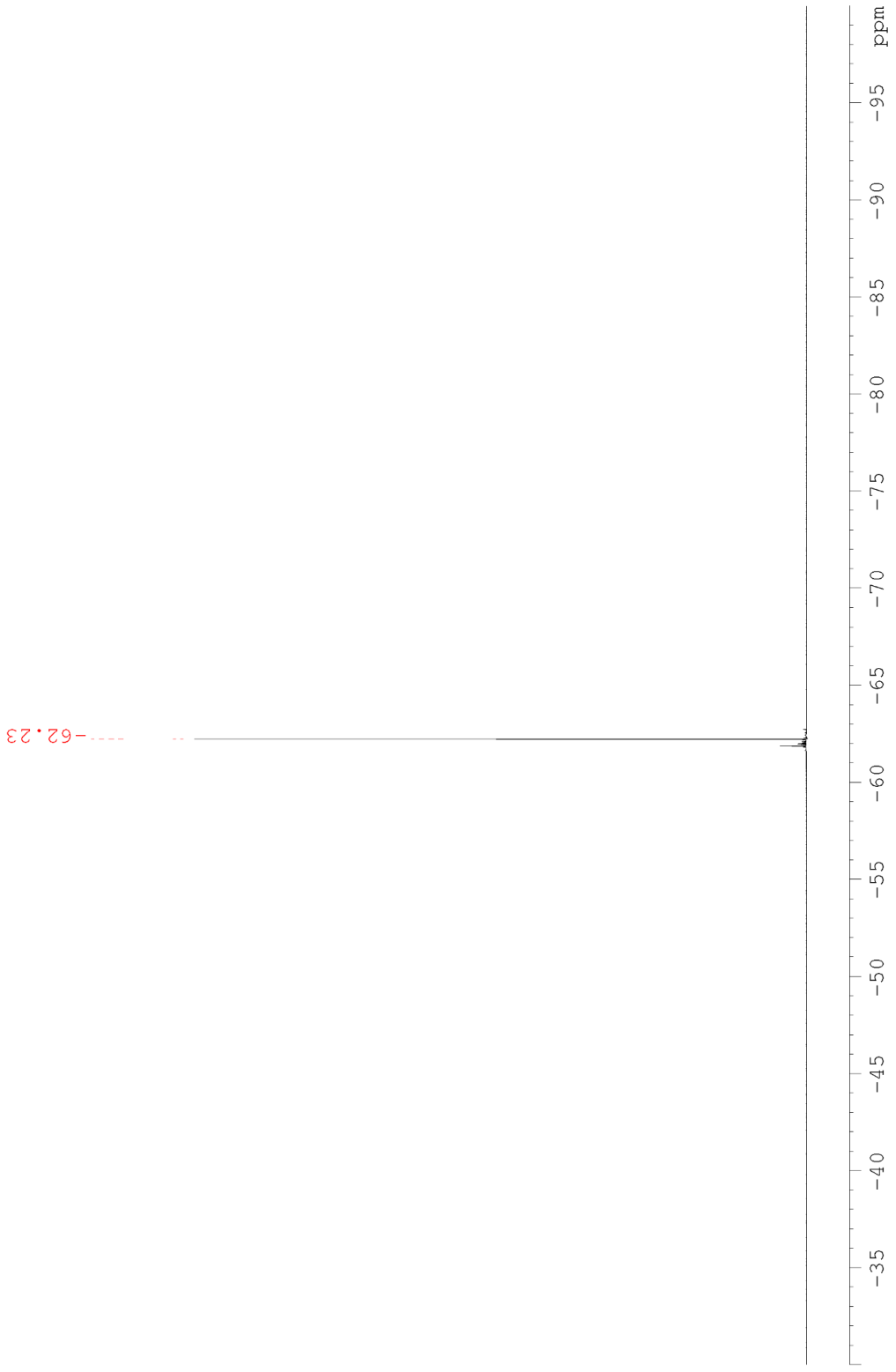


Figure S4. $^{19}F\{^{1}H\}$ NMR spectrum of **(I*i*Pr)BAr^{F}Cat** in C_6D_6.

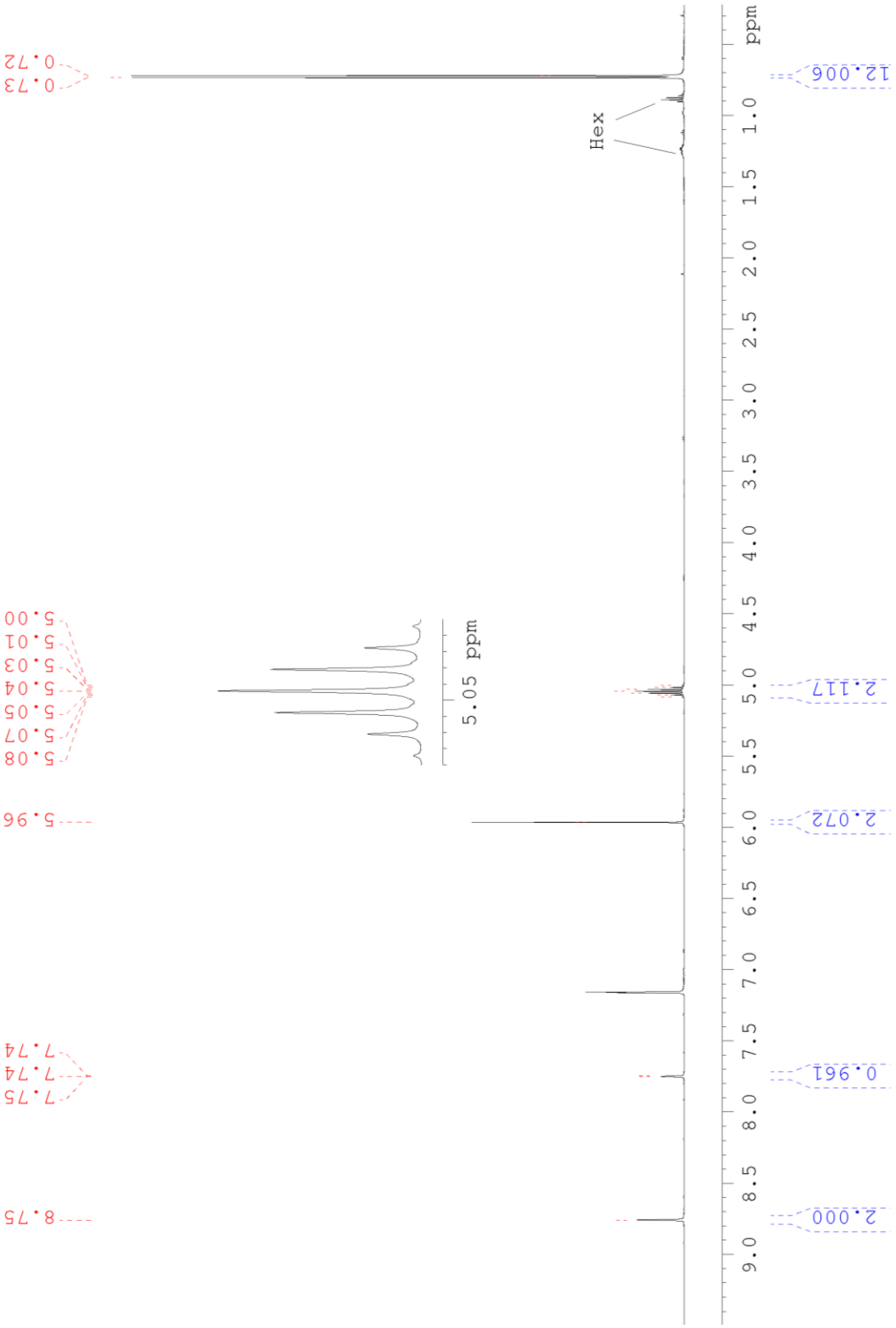


Figure S5. ^{1}H NMR spectrum of **1** in C_6D_6.

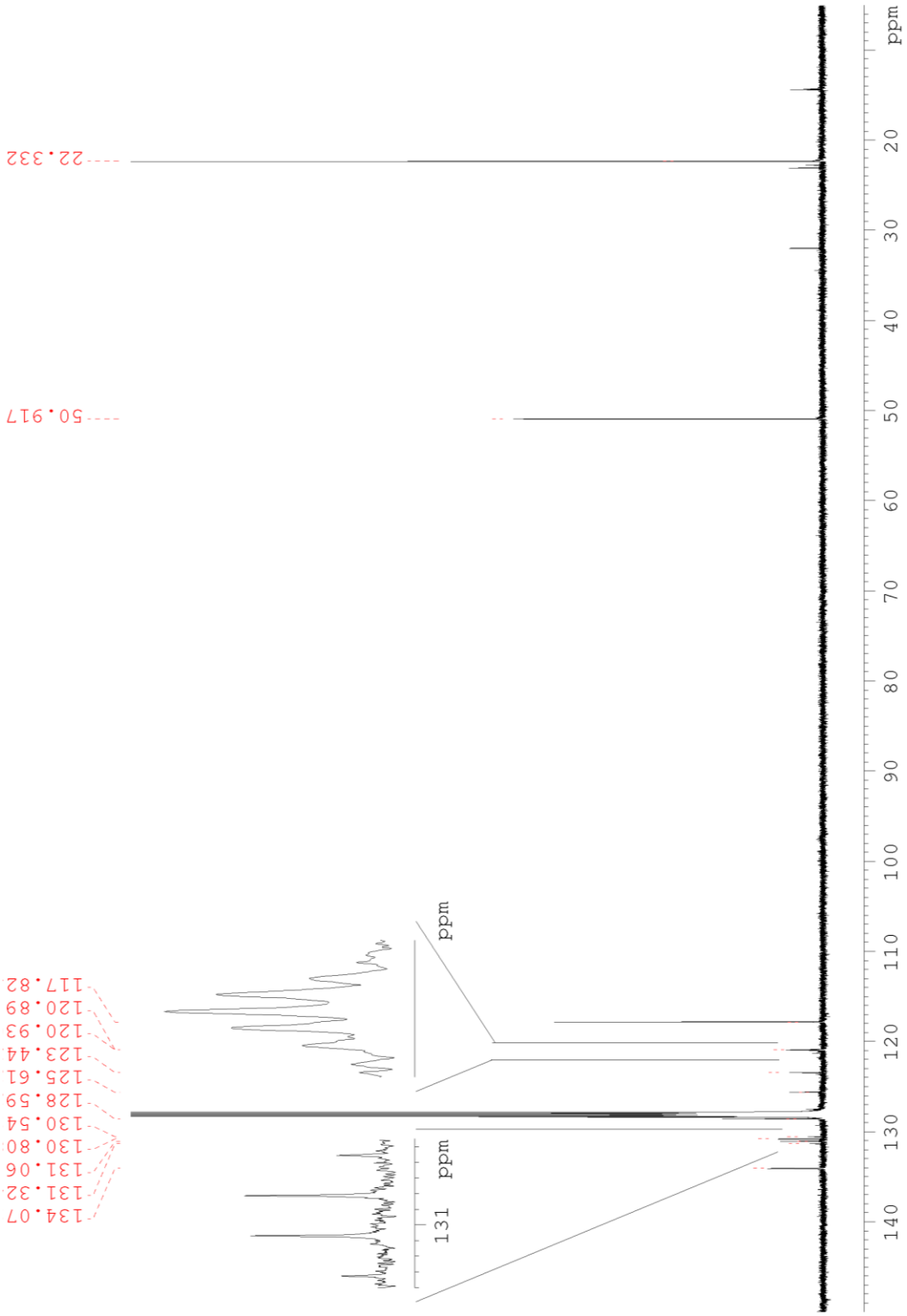


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6.

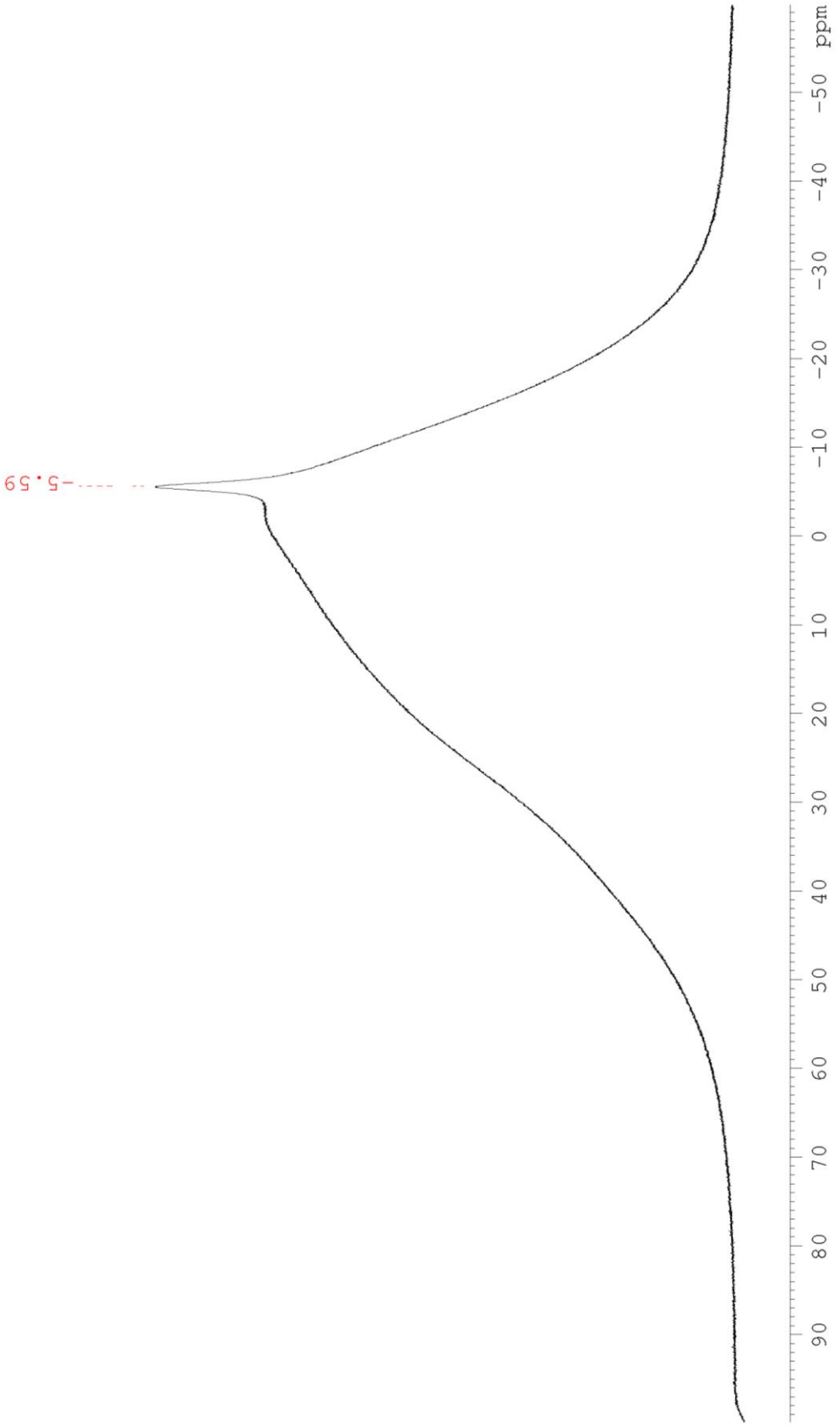


Figure S7. $^{11}B\{^{1}H\}$ NMR spectrum of **1** in C_6D_6.

Figure S8. $^{19}F\{^{1}H\}$ NMR spectrum of **1** in C_6D_6.

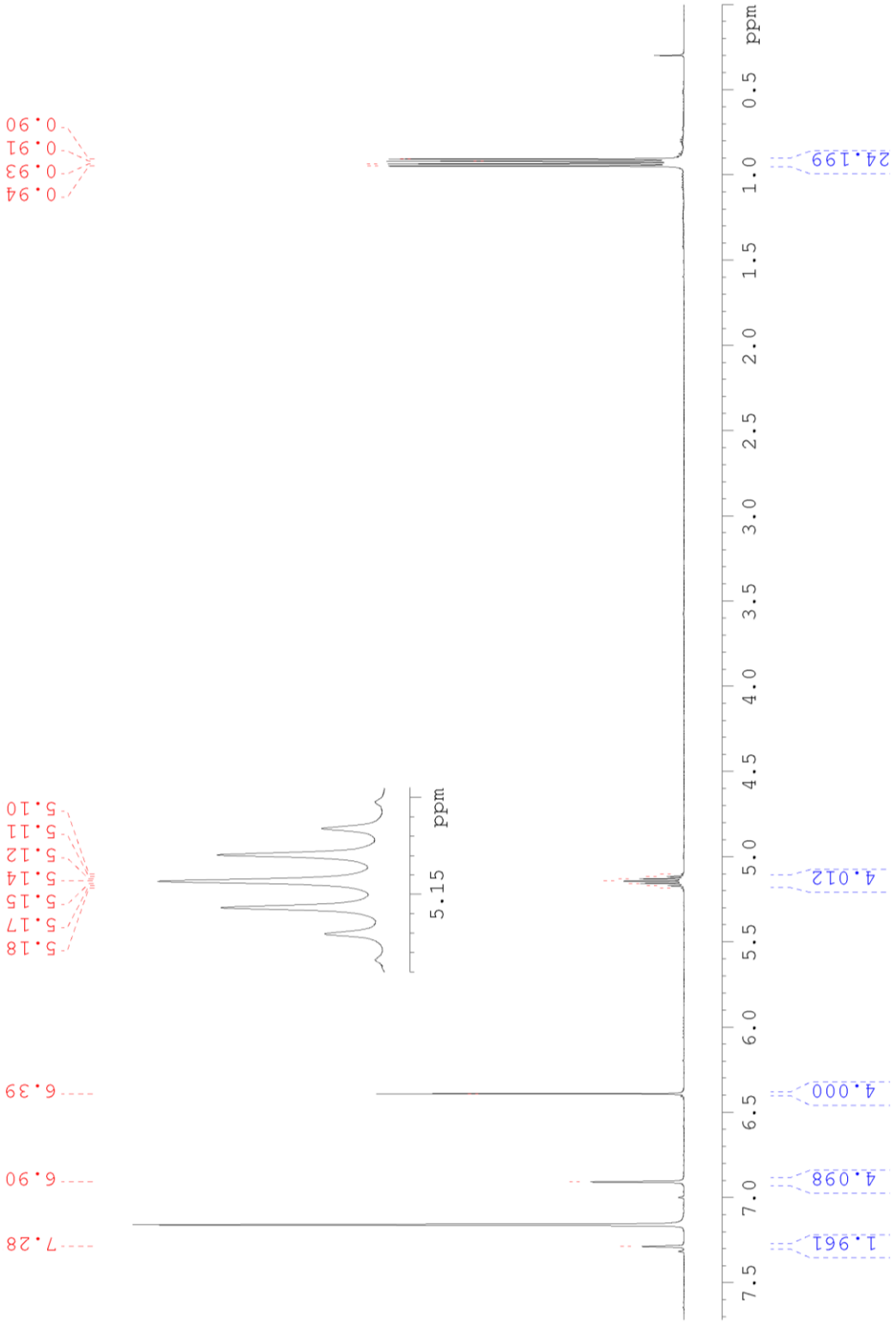


Figure S9. ^{1}H NMR spectrum of **2a** in C_6D_6.

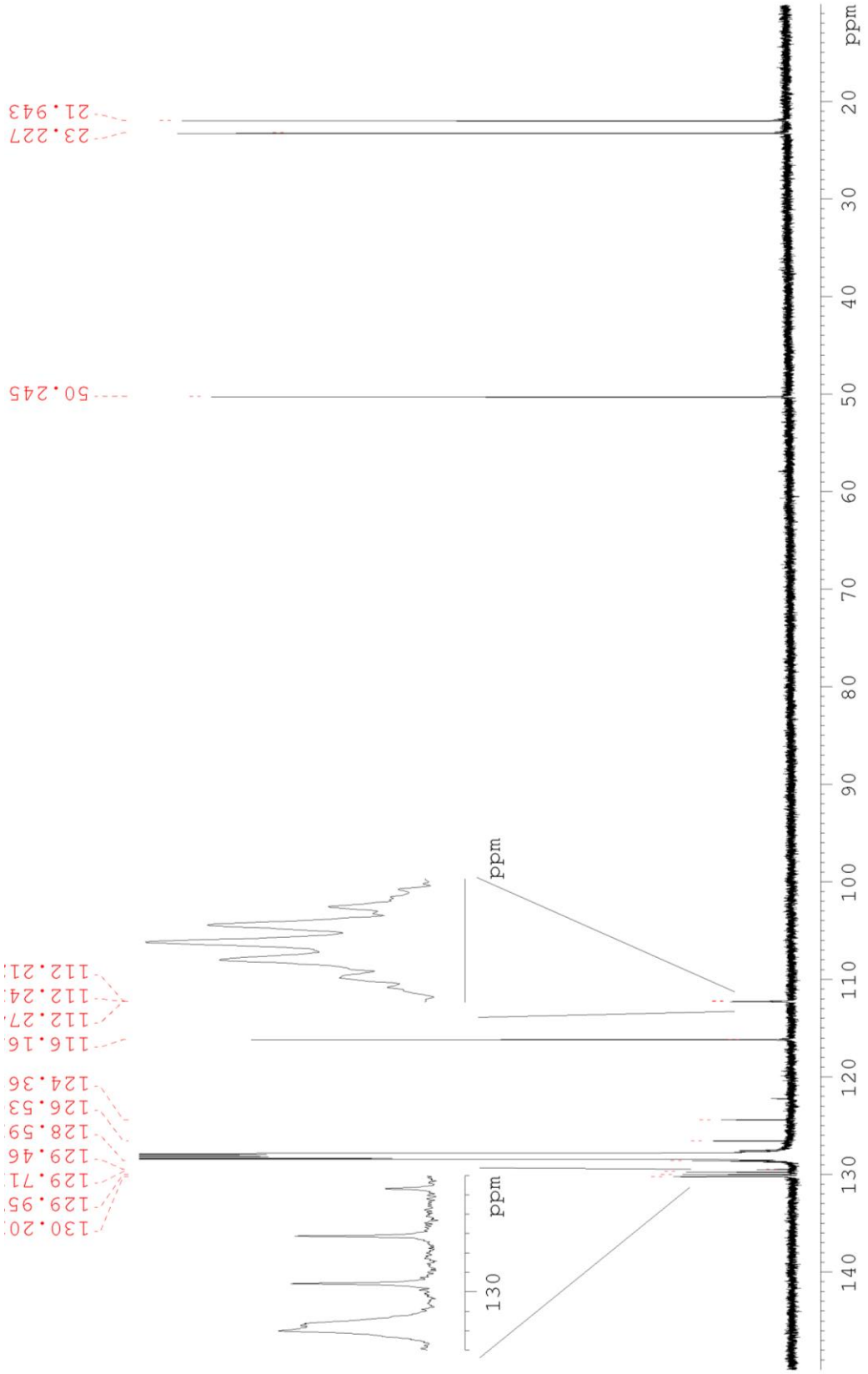


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

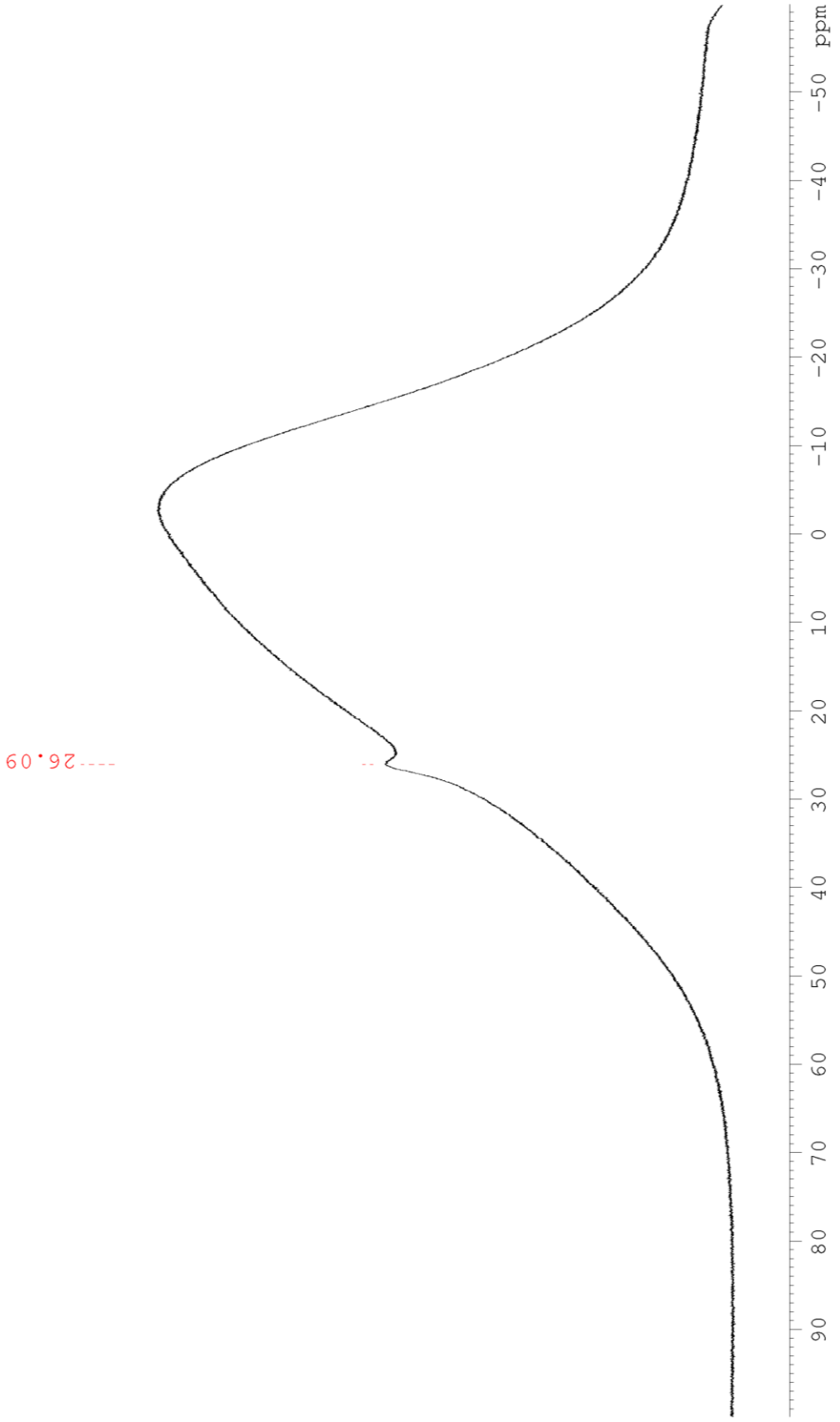


Figure S11. $^{11}B\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

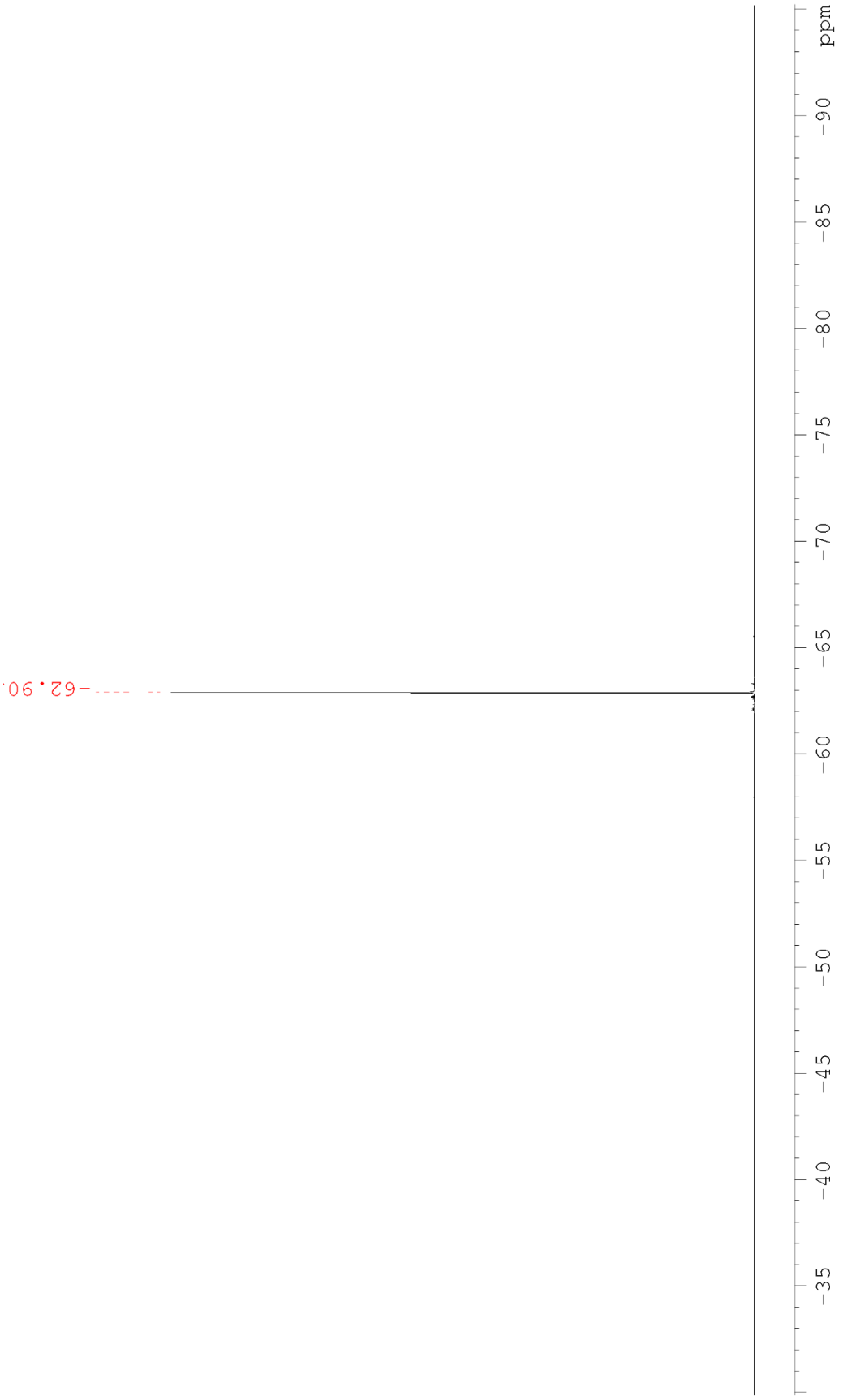


Figure S12. $^{19}F\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

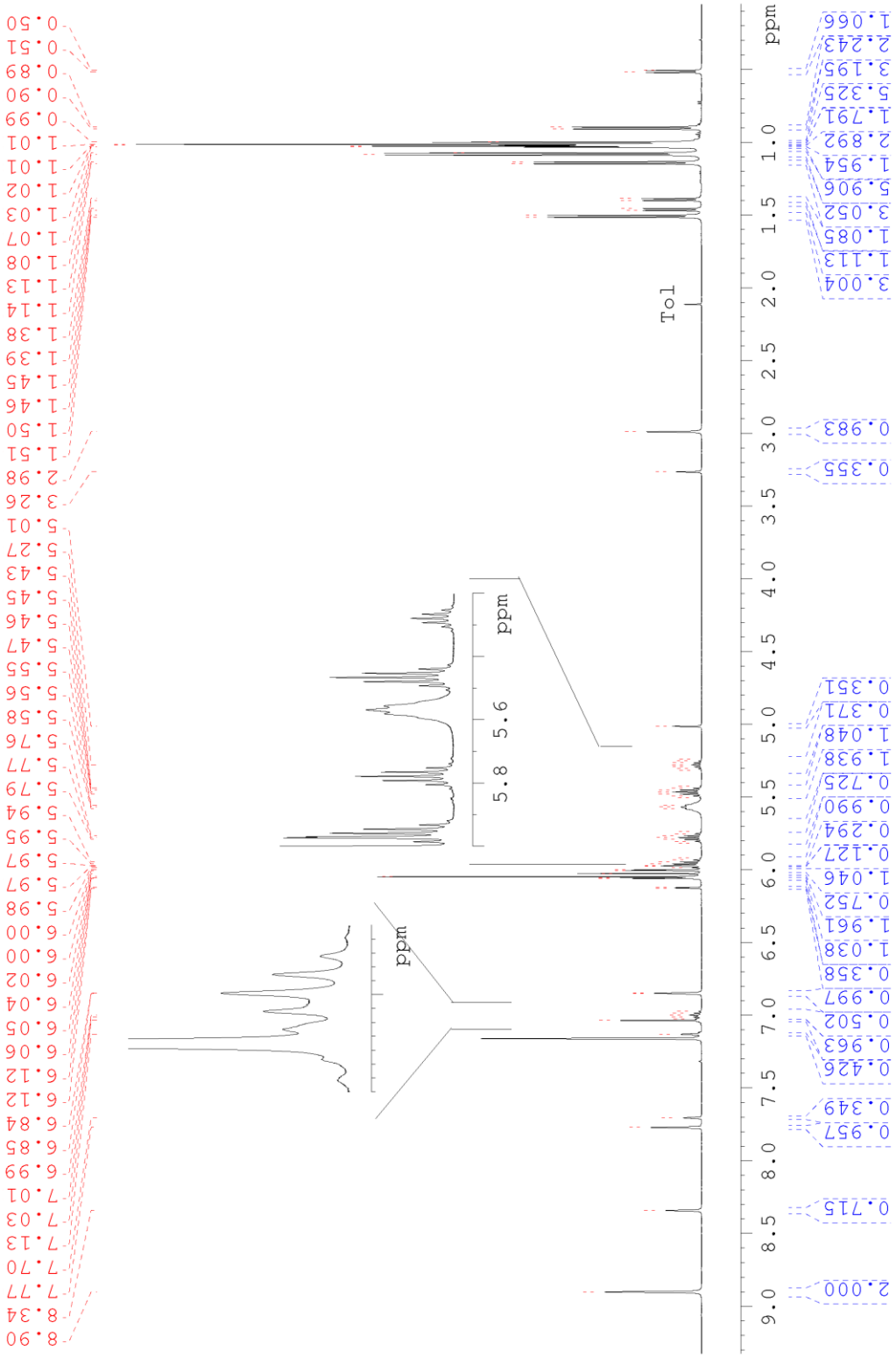


Figure S13. ^{1}H NMR spectrum of **3** in C_6D_6.

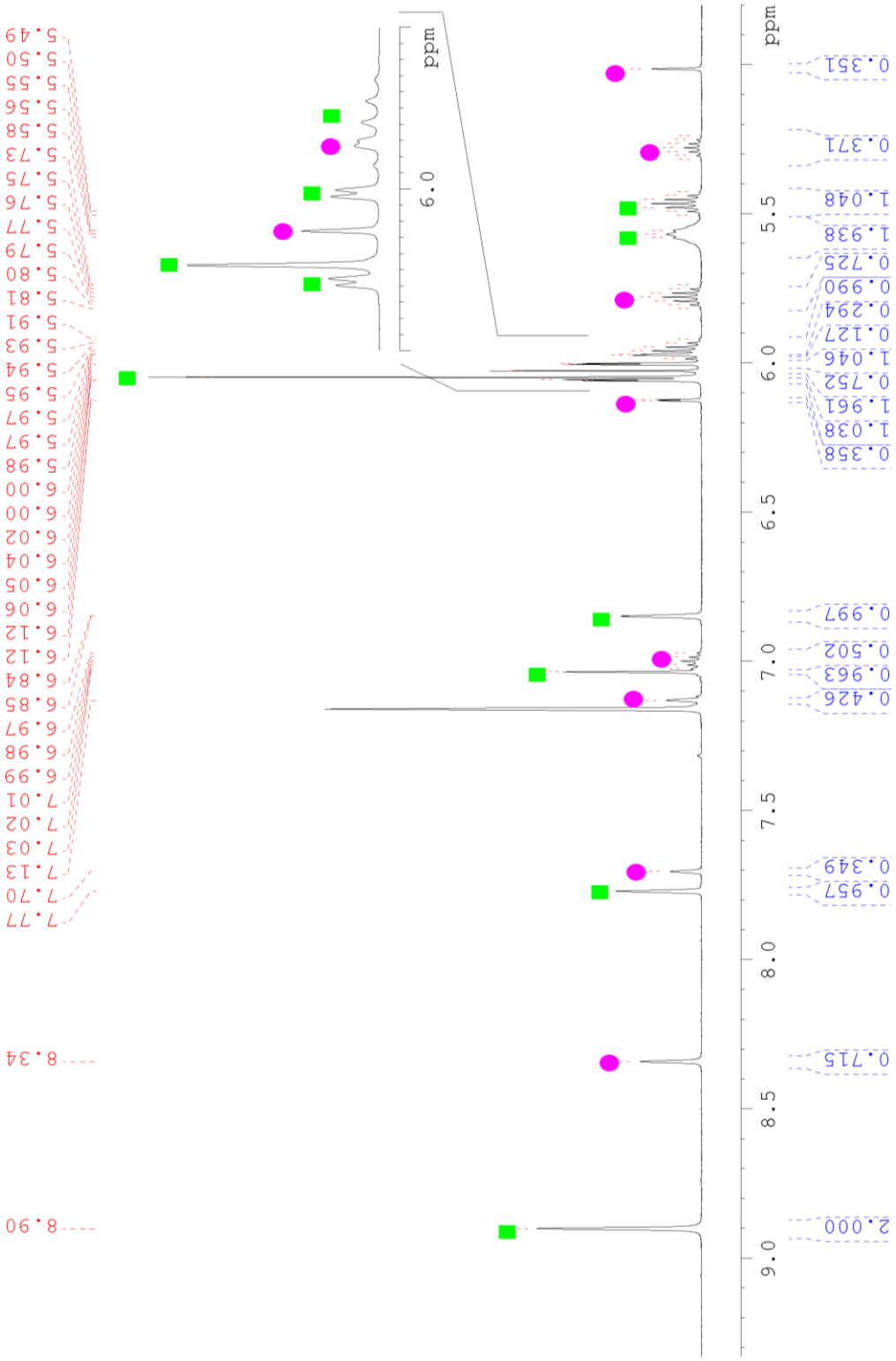


Figure S14. ^{1}H NMR spectrum of **3** in C_6D_6 in the region of 9.33–4.80 ppm with corresponding signals of **3a** (green) and **3b** (pink).

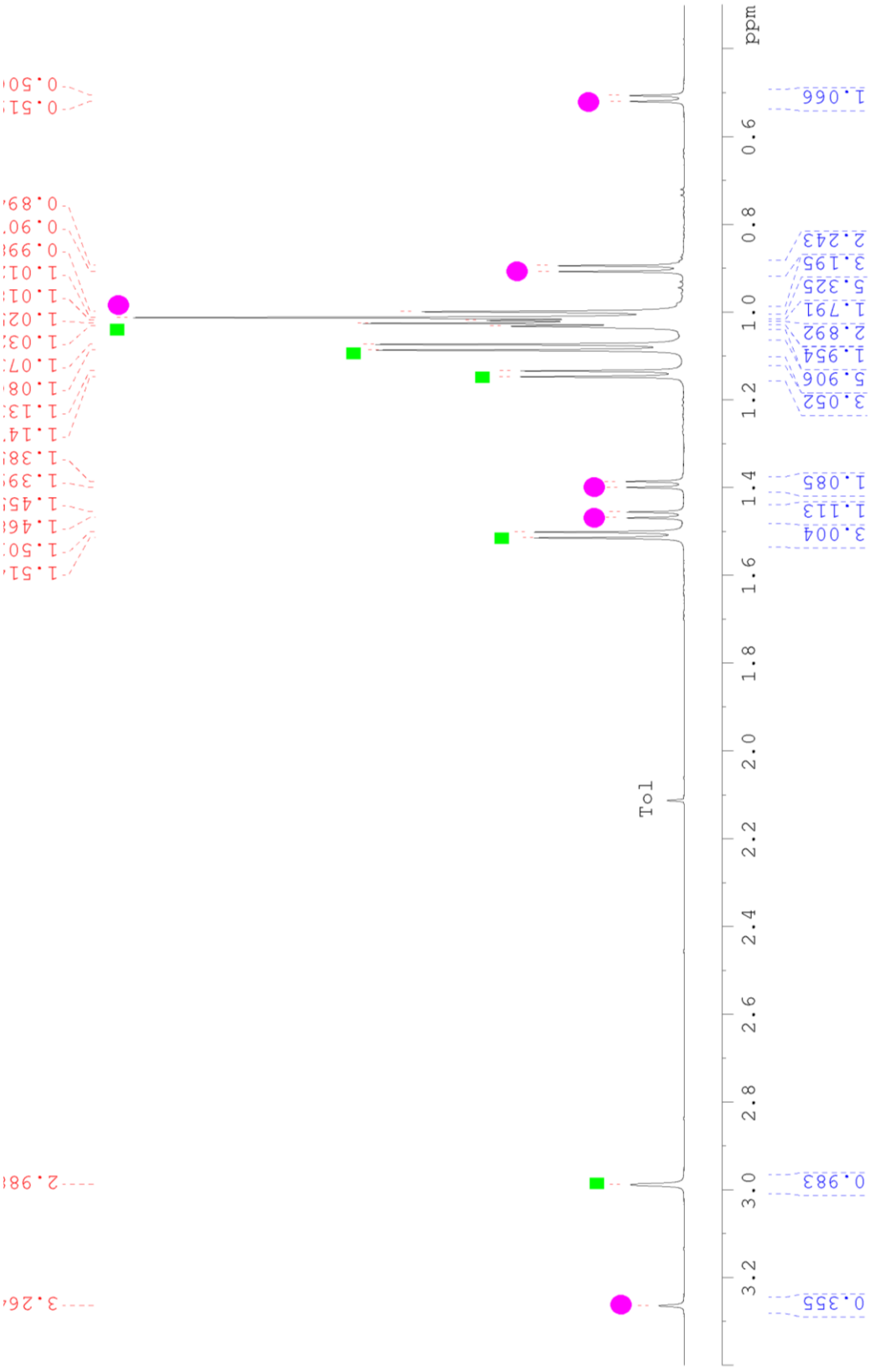


Figure S15. ^{1}H NMR spectrum of **3** in C_6D_6 in the region of 3.40–0.30 ppm with corresponding signals of **3a** (green) and **3b** (pink).

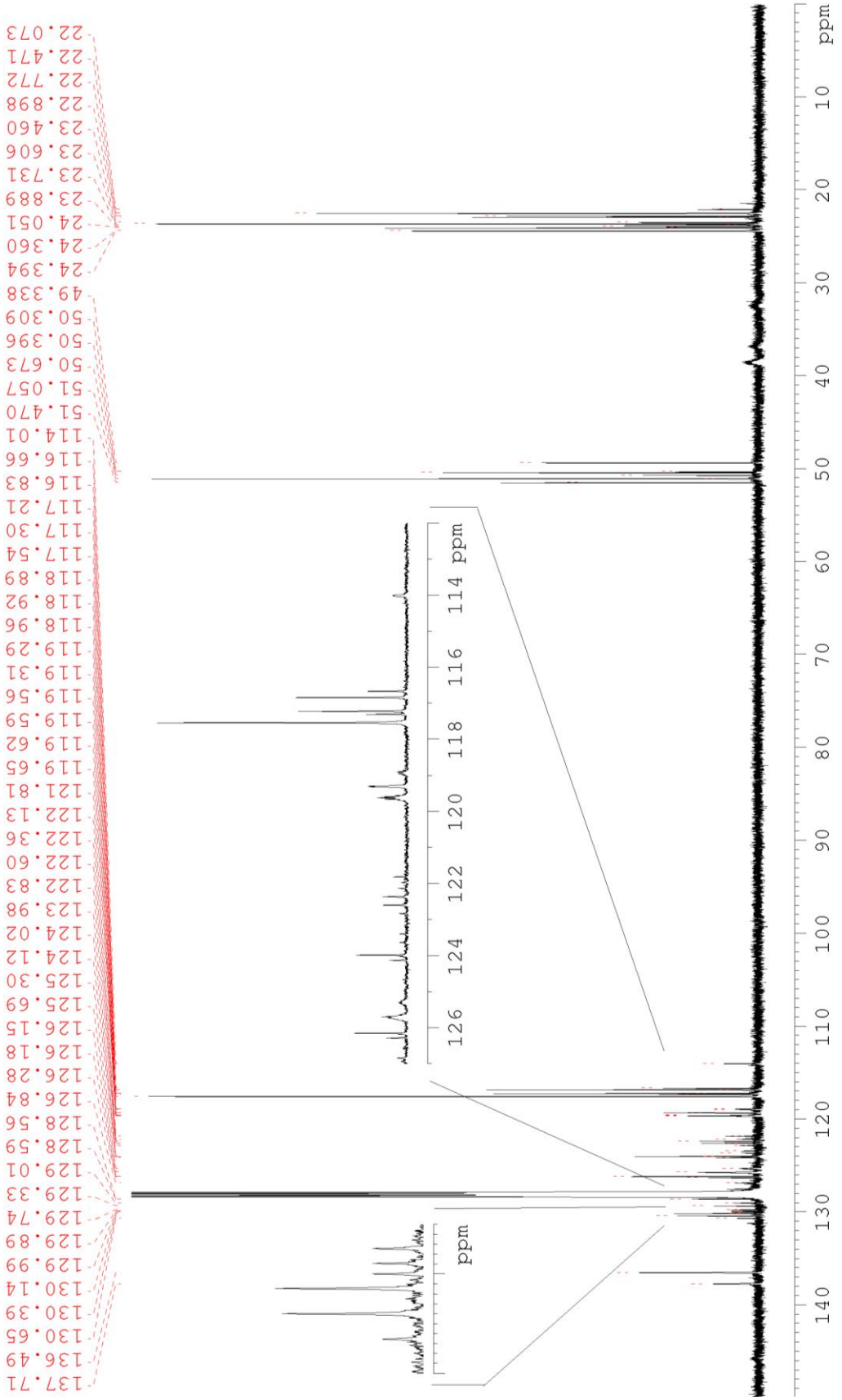


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.

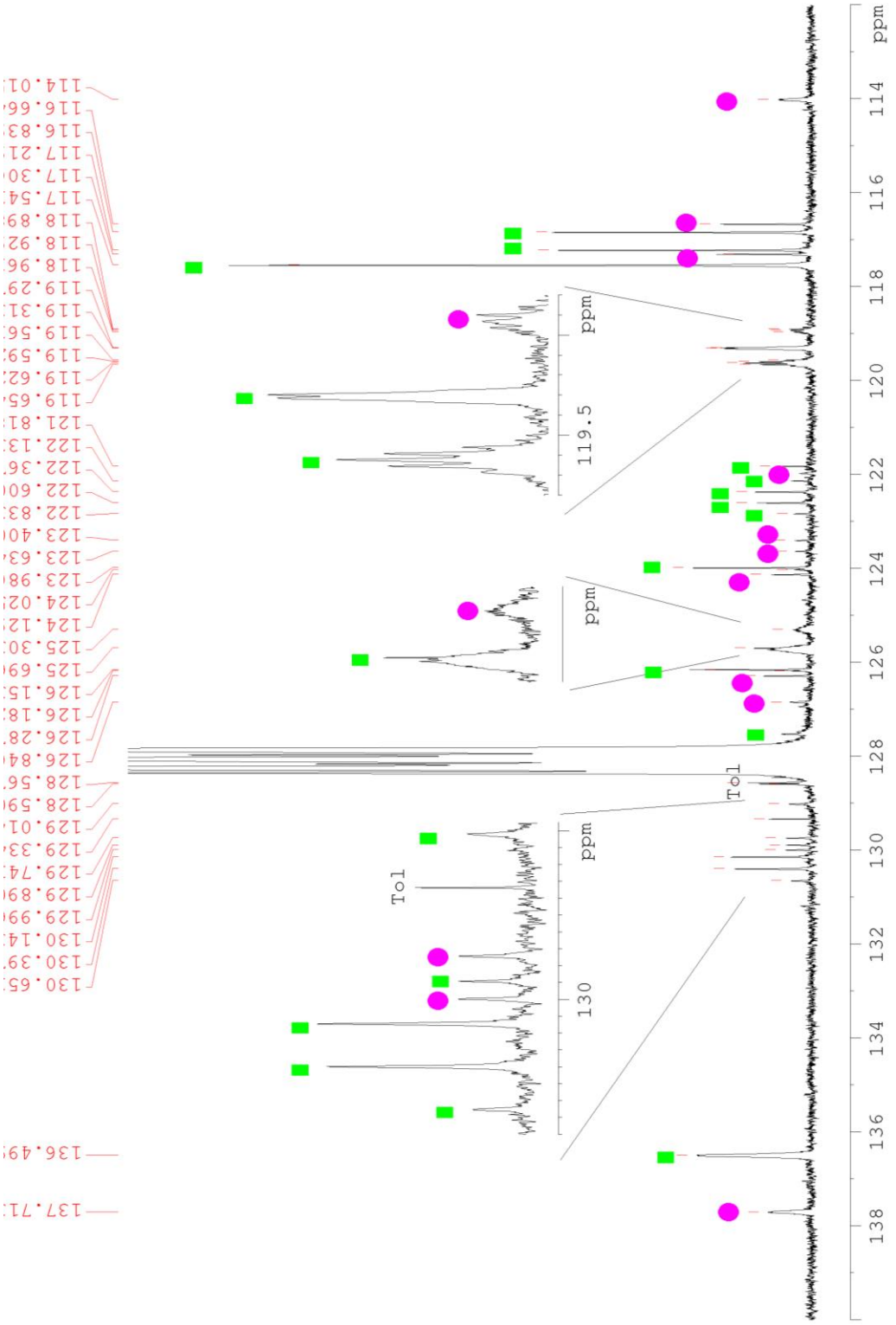


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 in the region of 140.0–112.0 ppm with corresponding signals of **3a** (green) and **3b** (pink).

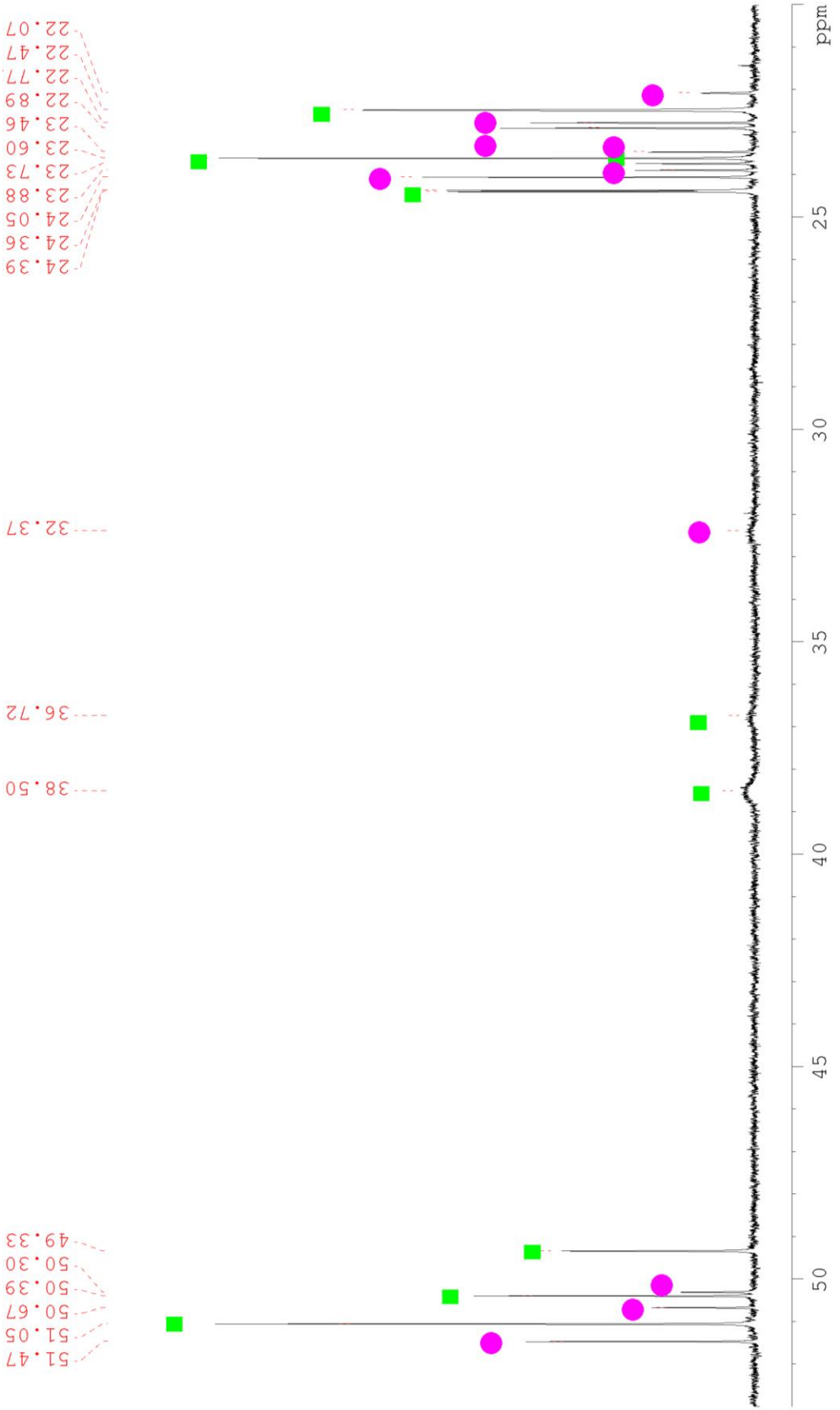


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 in the region of 53.0–20.0 ppm with corresponding signals of **3a** (green) and **3b** (pink).

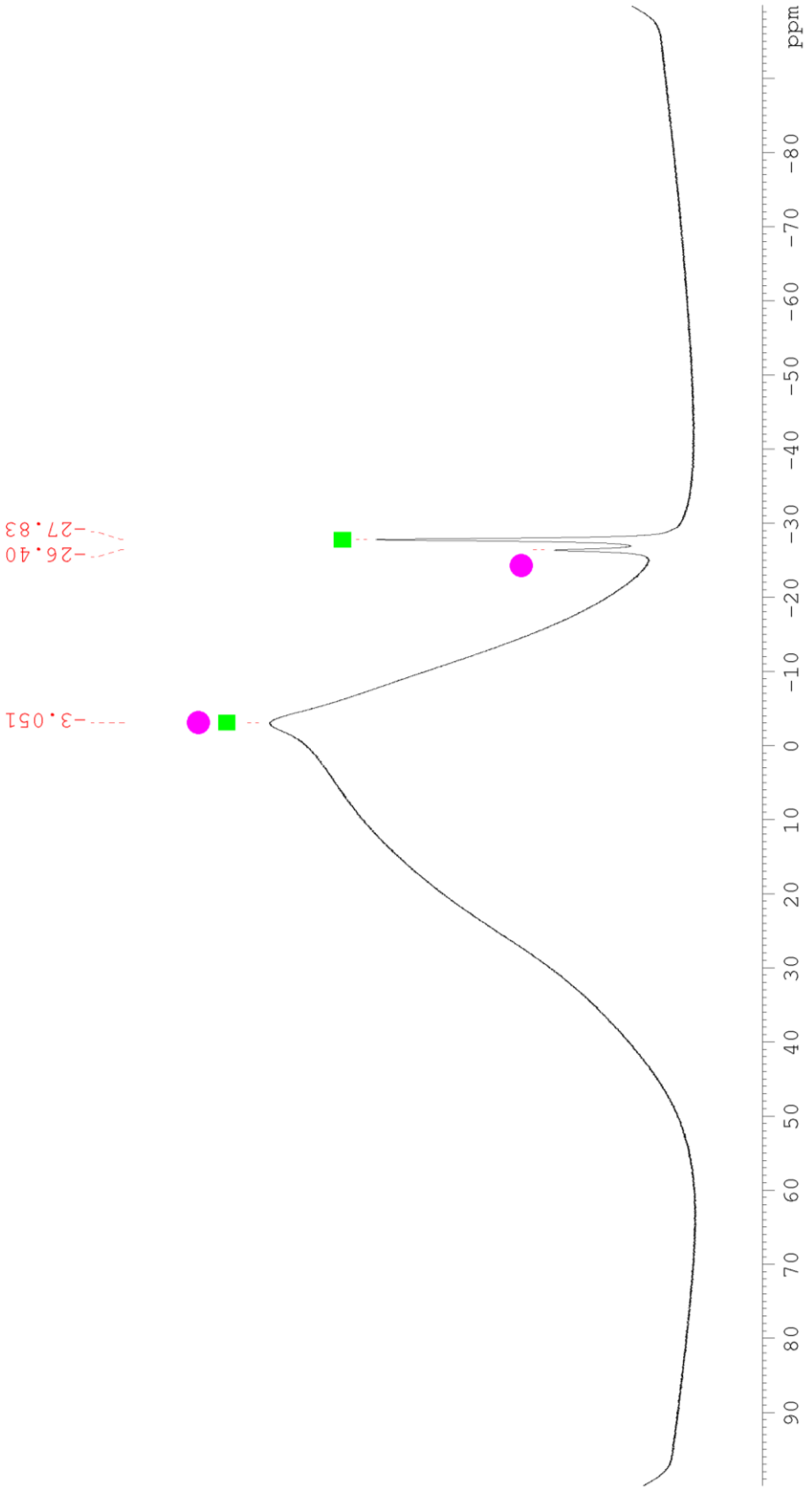


Figure S19. $^{11}B\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 with corresponding signals of **3a** (green) and **3b** (pink).

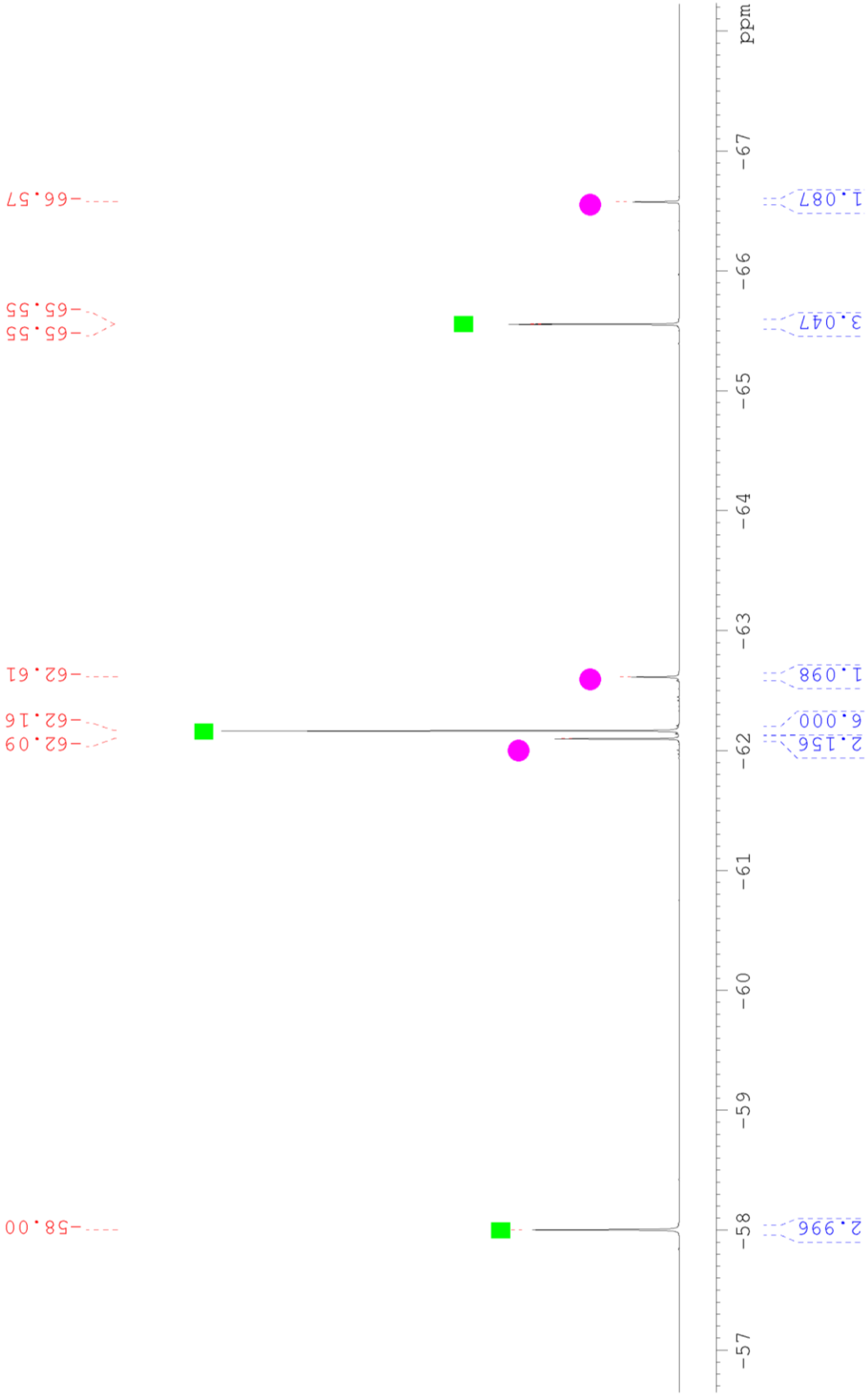


Figure S20. $^{19}F\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 with corresponding signals of **3a** (green) and **3b** (pink).

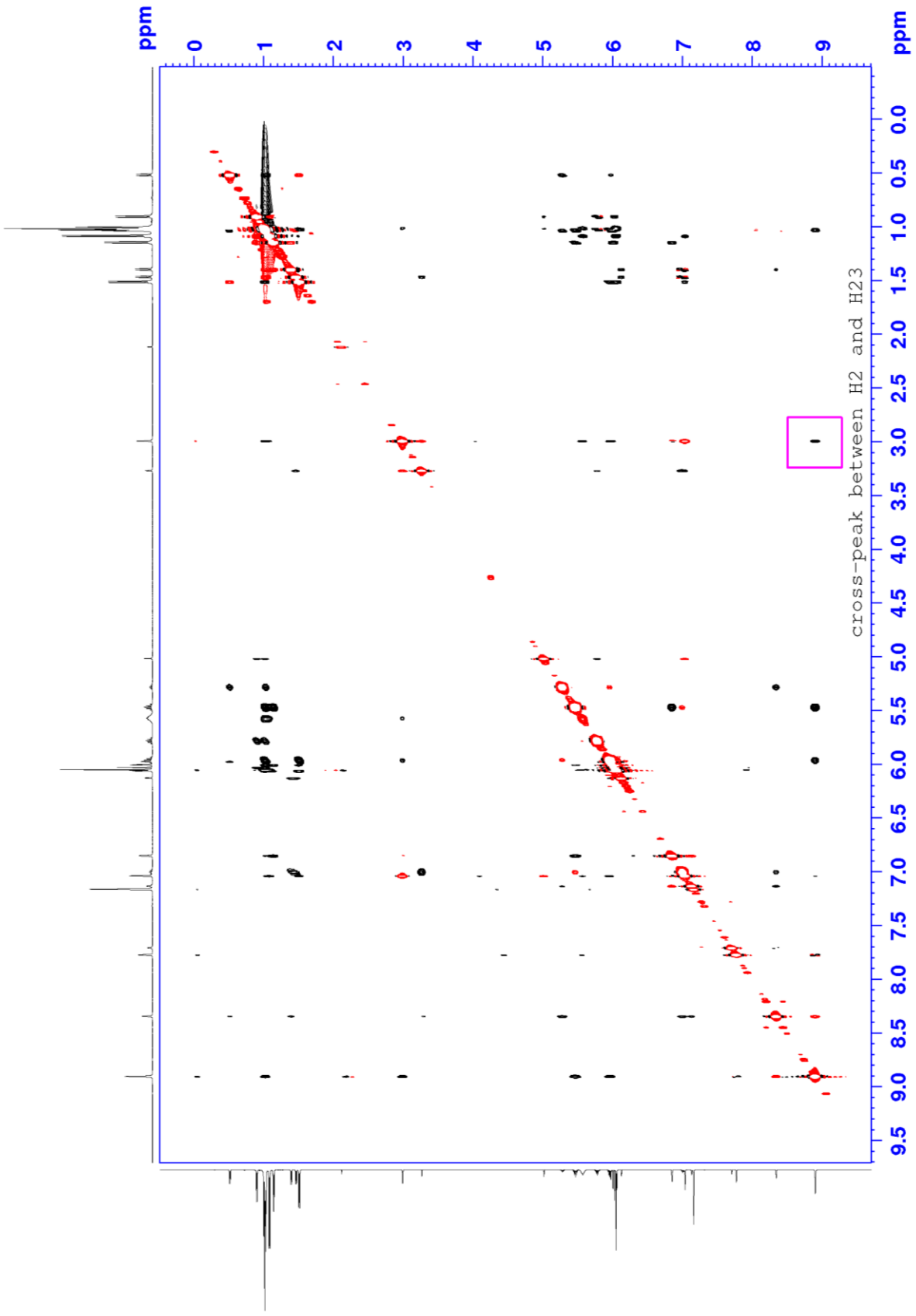


Figure S21. ^{1}H,^{1}H-ROESY of **3** in C_6D_6.

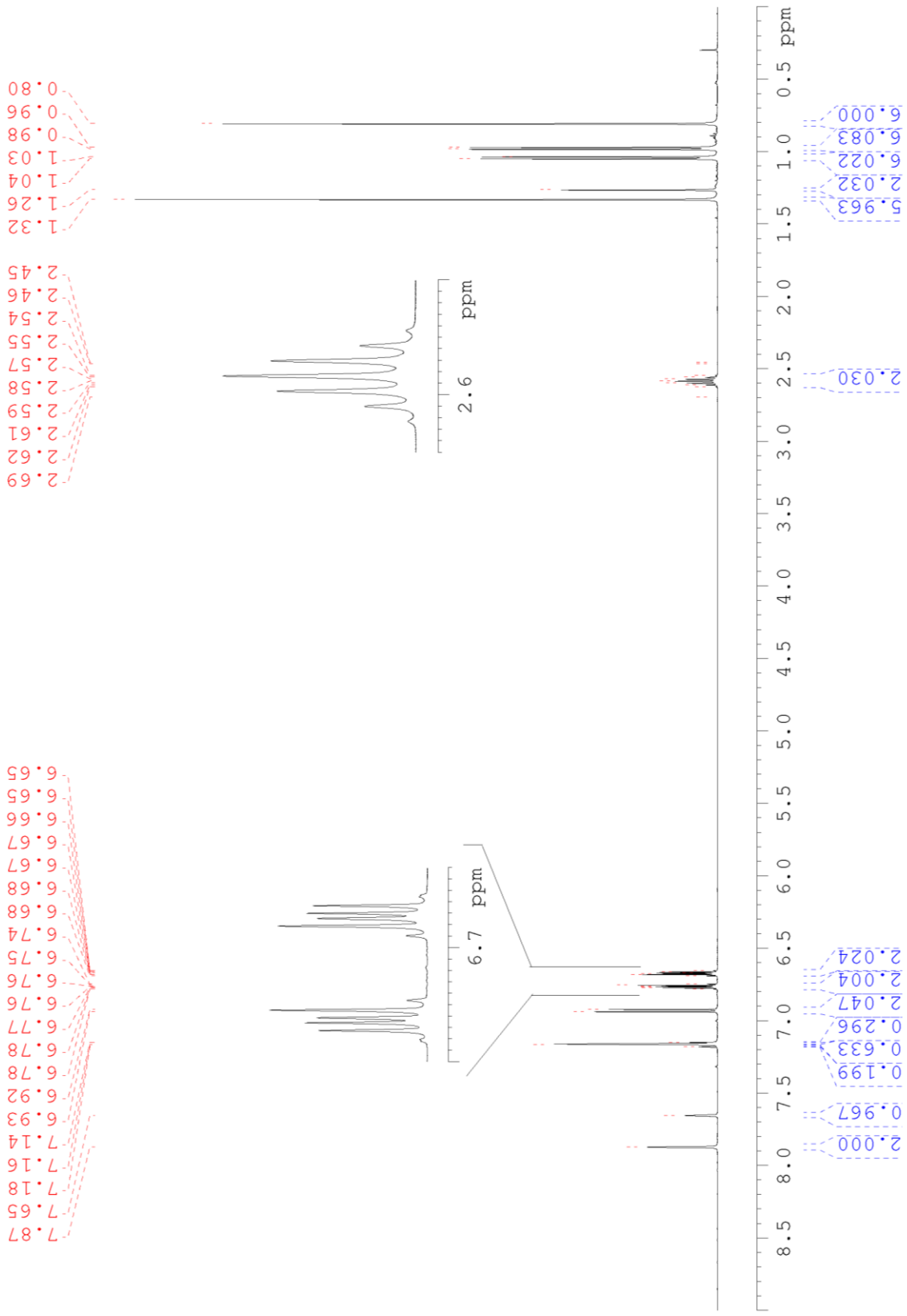


Figure S22. ^{1}H NMR spectrum of **(CAAC)BAr^{F}Cat** in C_6D_6.

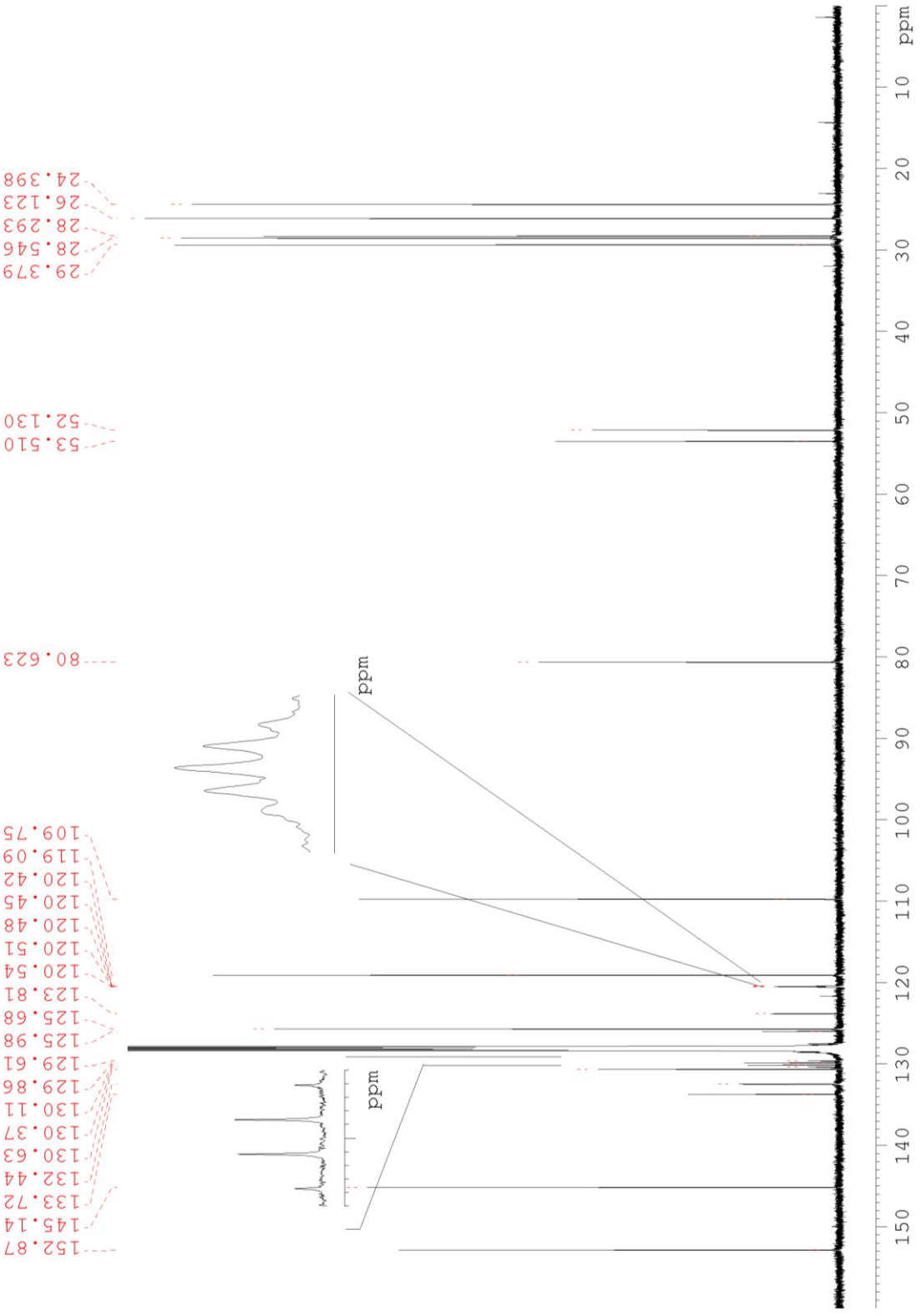


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **(CAAC)BAr^{F}Cat** in C_6D_6.

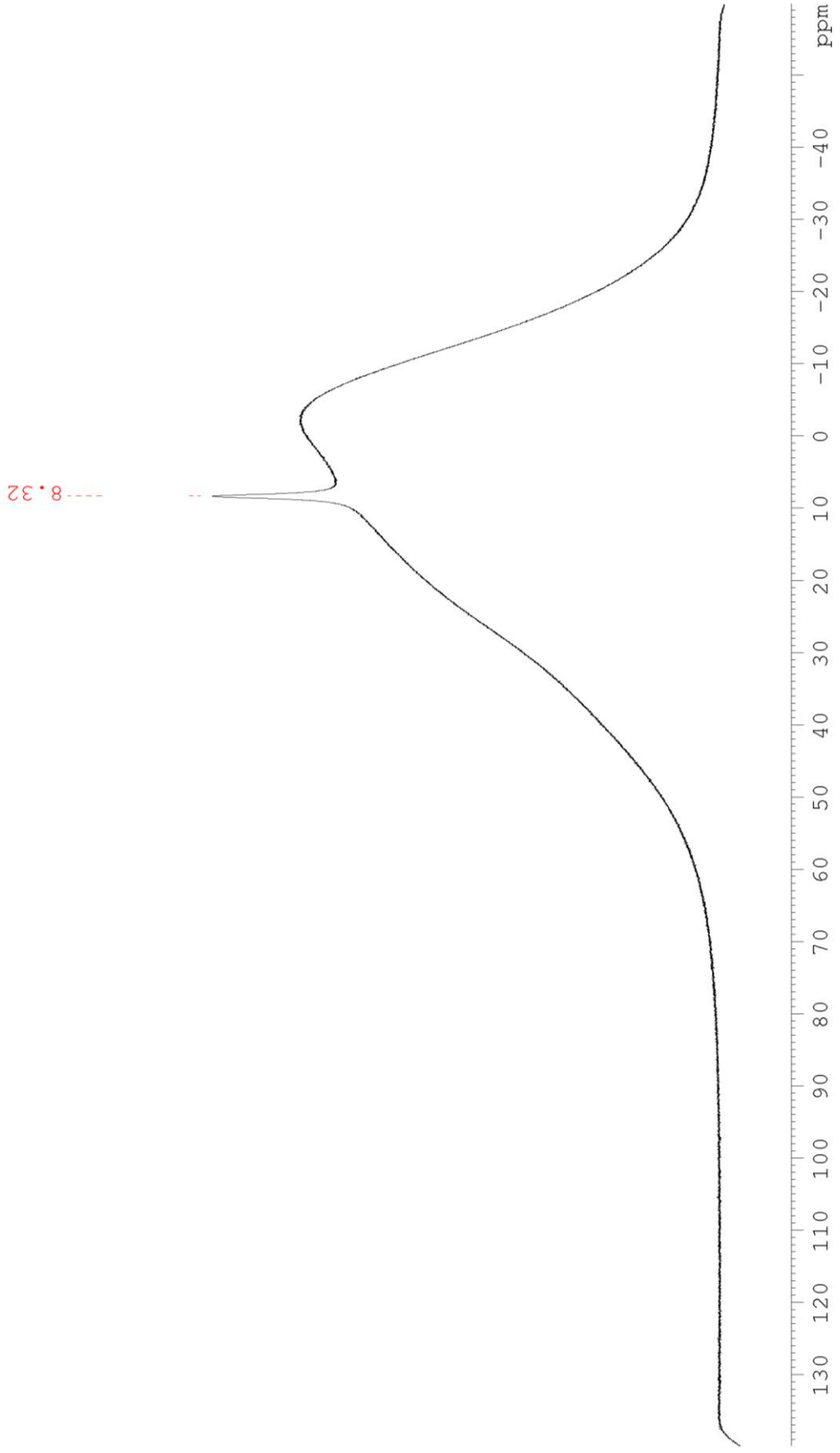


Figure S24. $^{11}B\{^{1}H\}$ NMR spectrum of **(CAAC)BAr^{F}Cat** in C_6D_6.

Figure S25. $^{19}F\{^{1}H\}$ NMR spectrum of **(CAAC)BAr^{F}Cat** in C_6D_6.

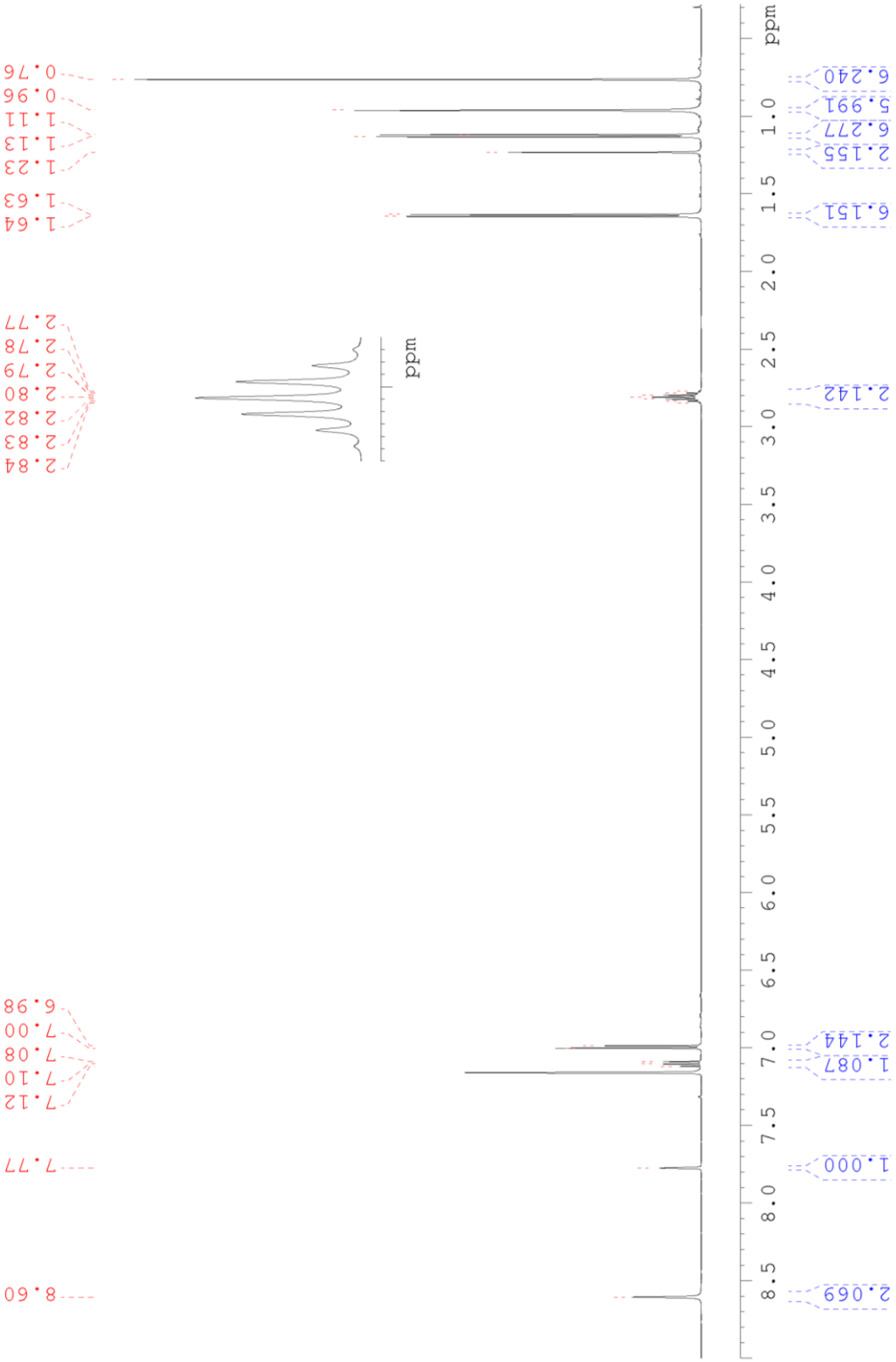


Figure S26. ^{1}H NMR spectrum of **4** in C_6D_6.

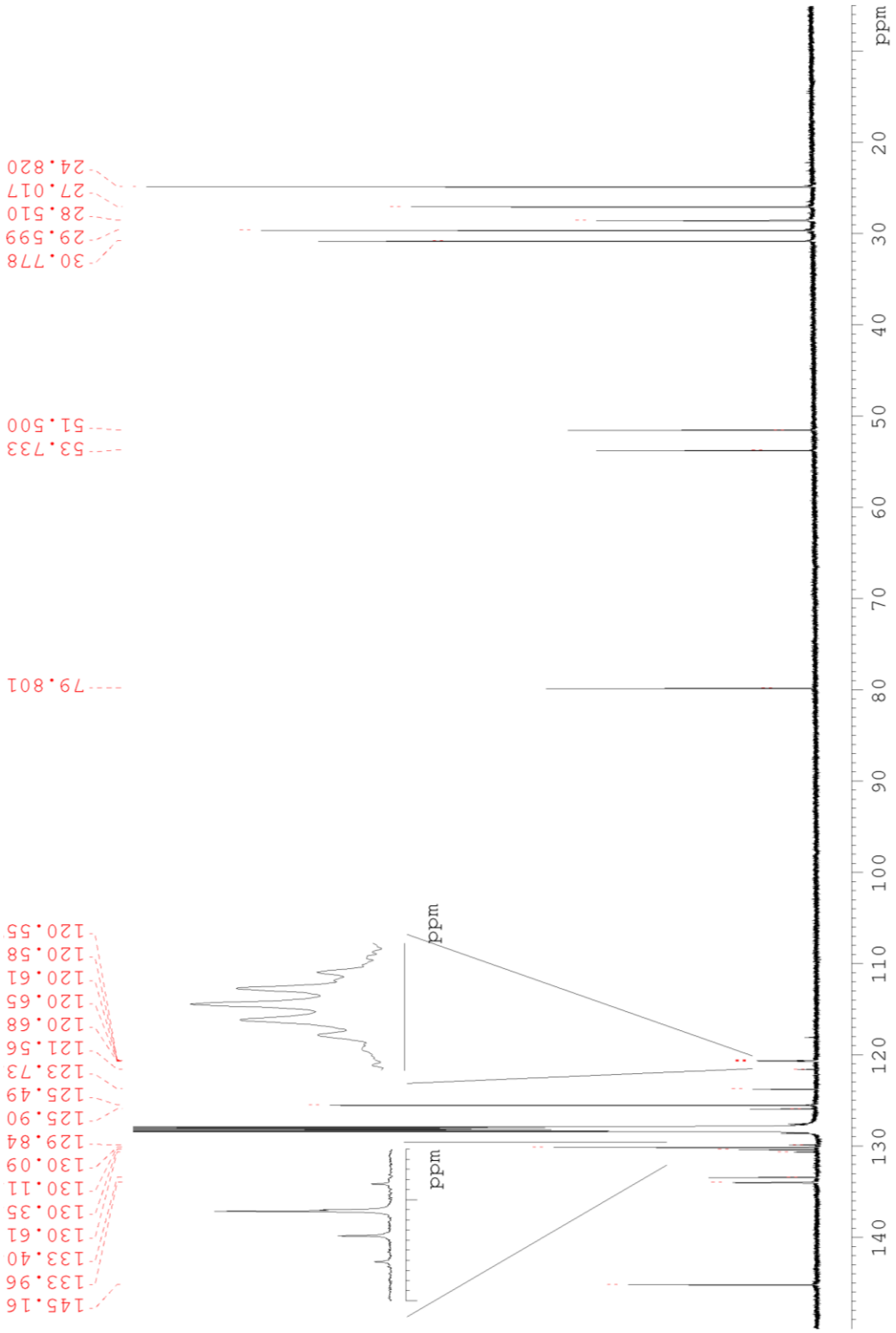


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

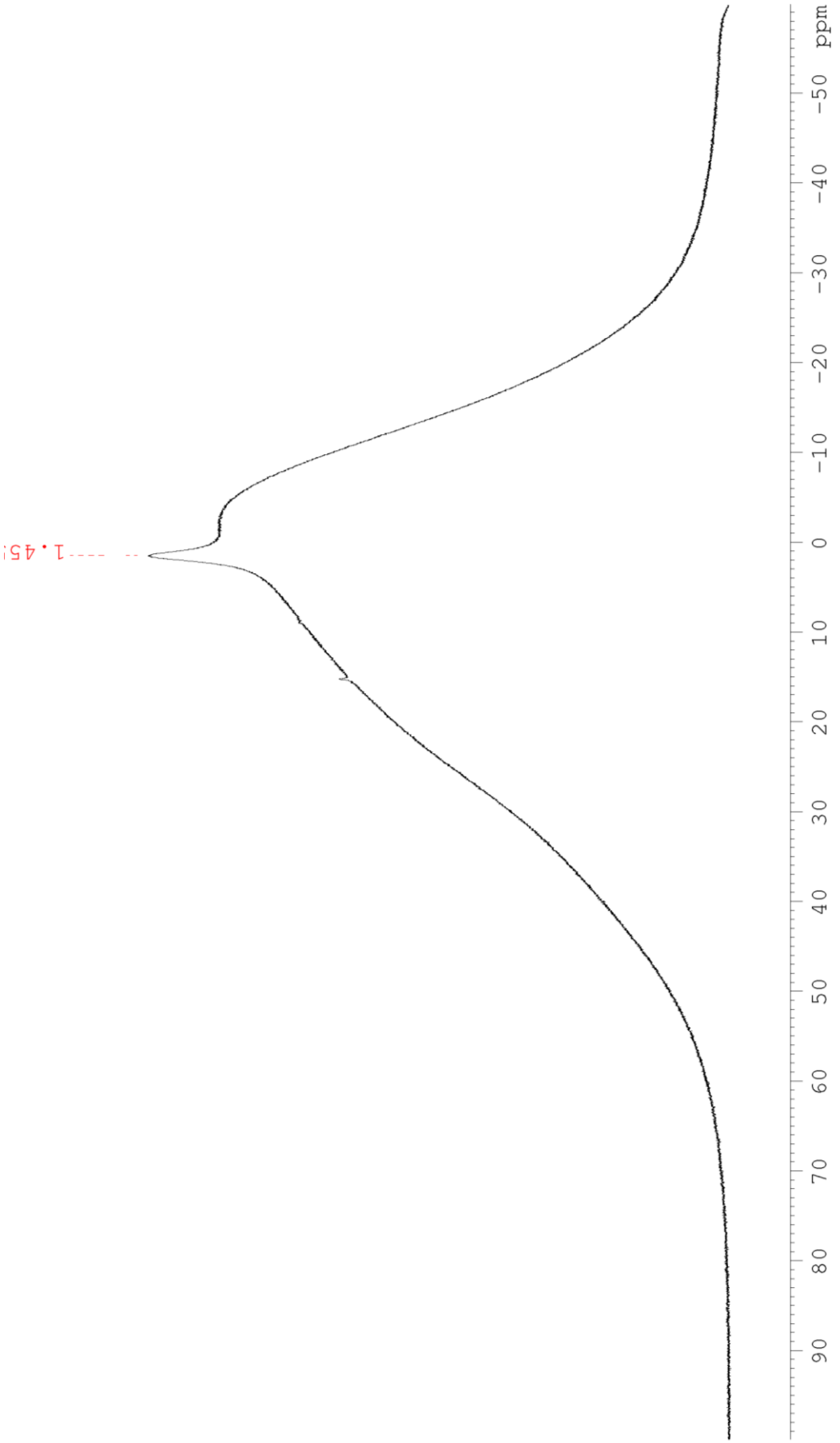


Figure S28. $^{11}B\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

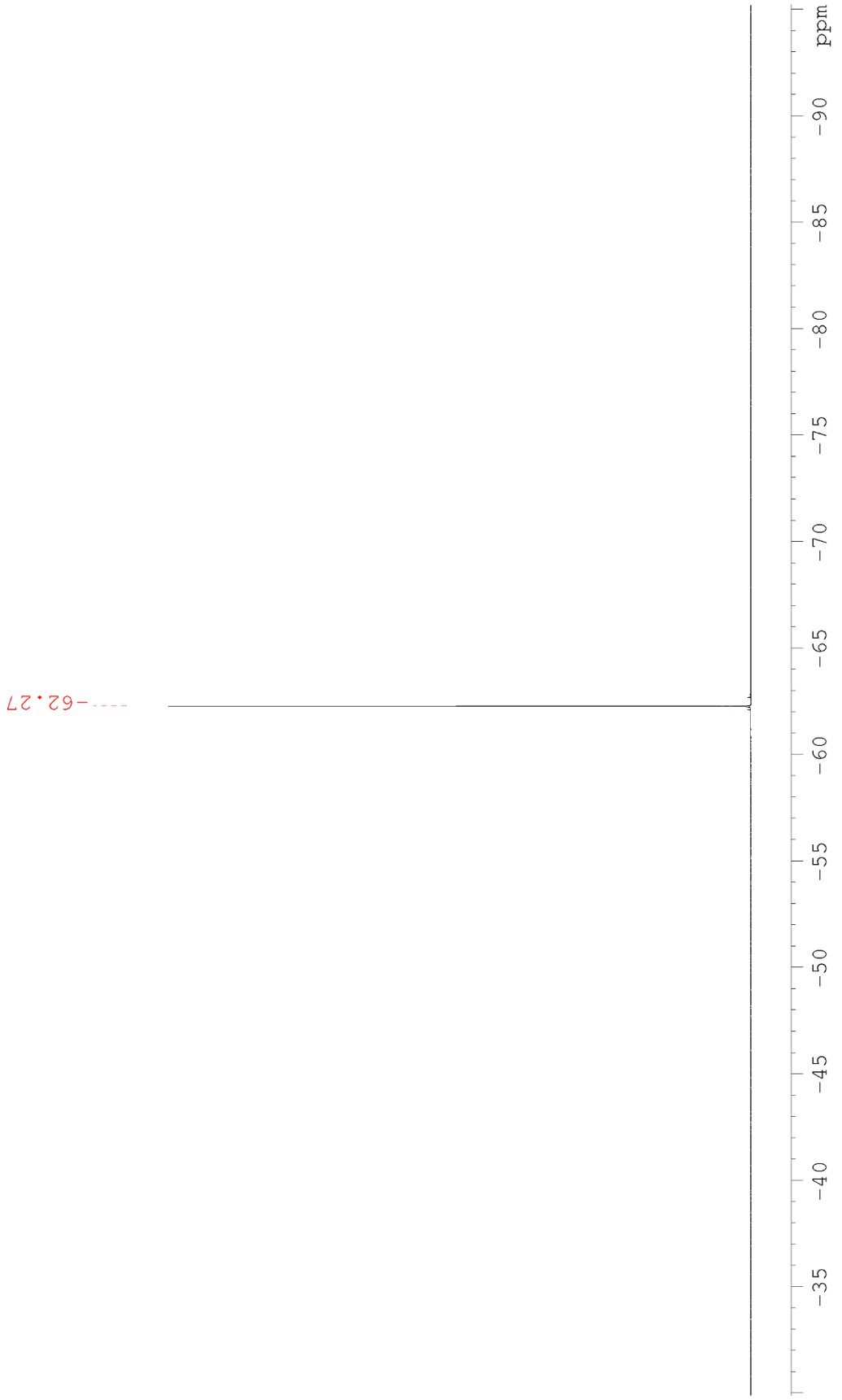


Figure S29. $^{19}F\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

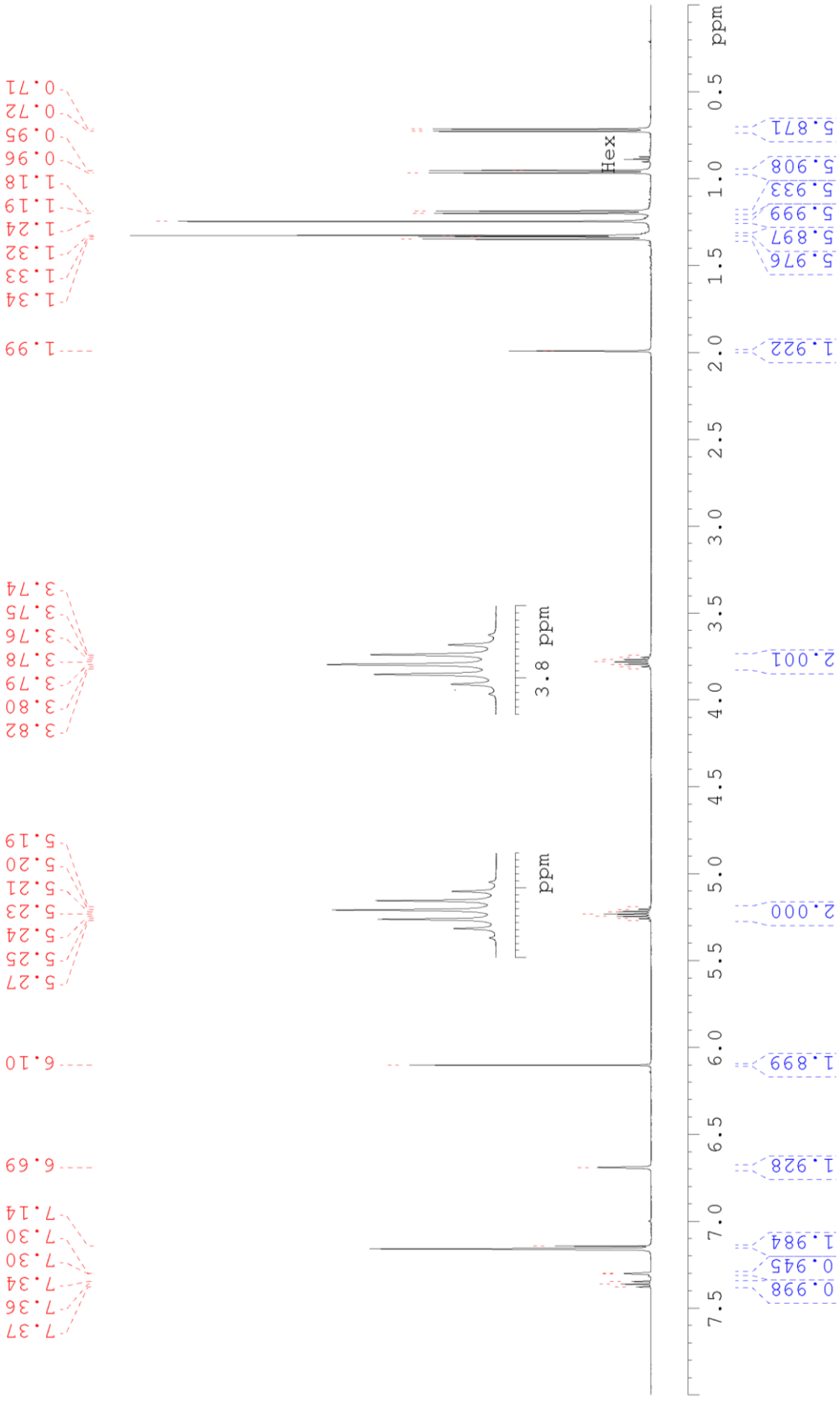


Figure S30. ^{1}H NMR spectrum of **5** in C_6D_6.

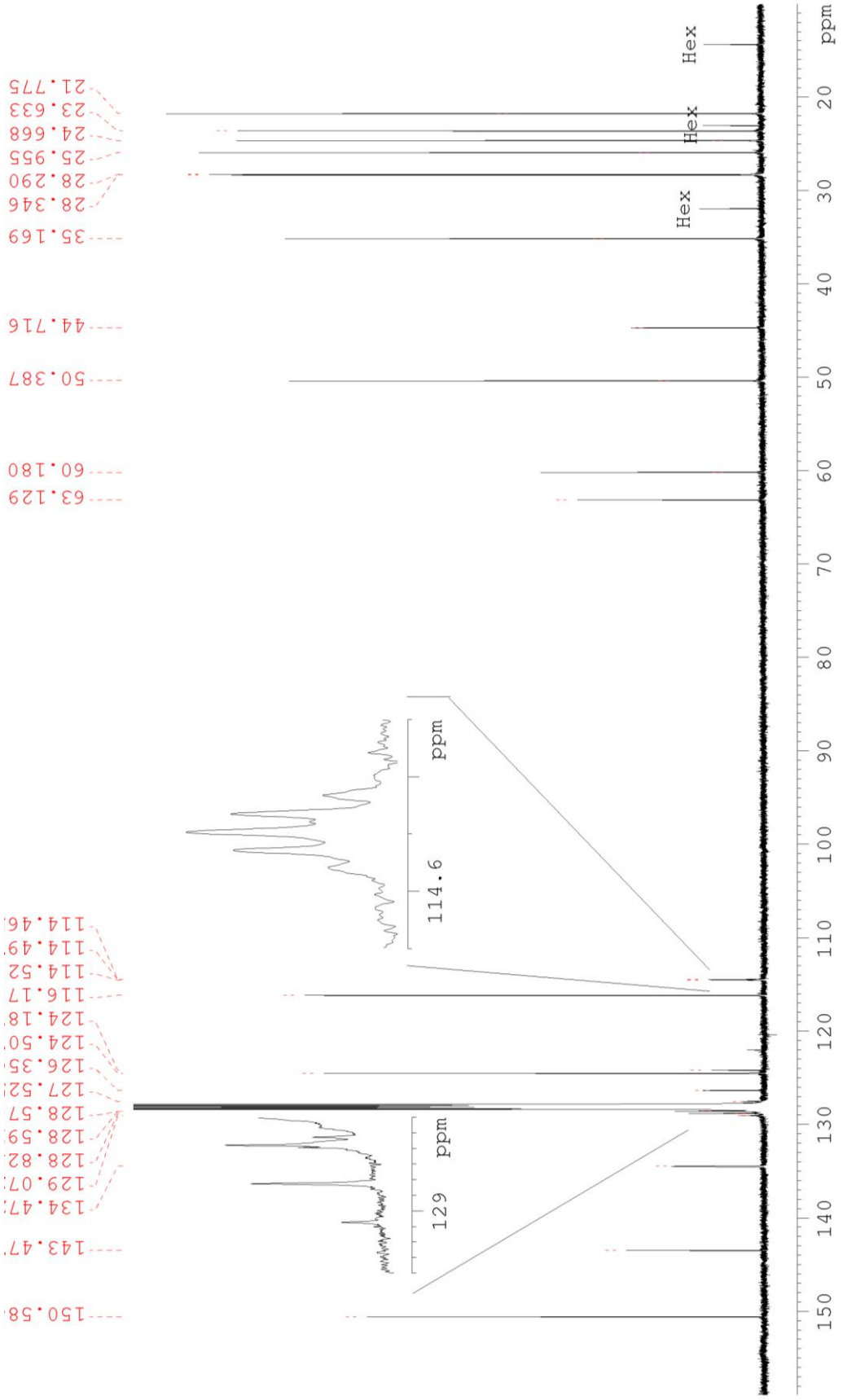


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6.

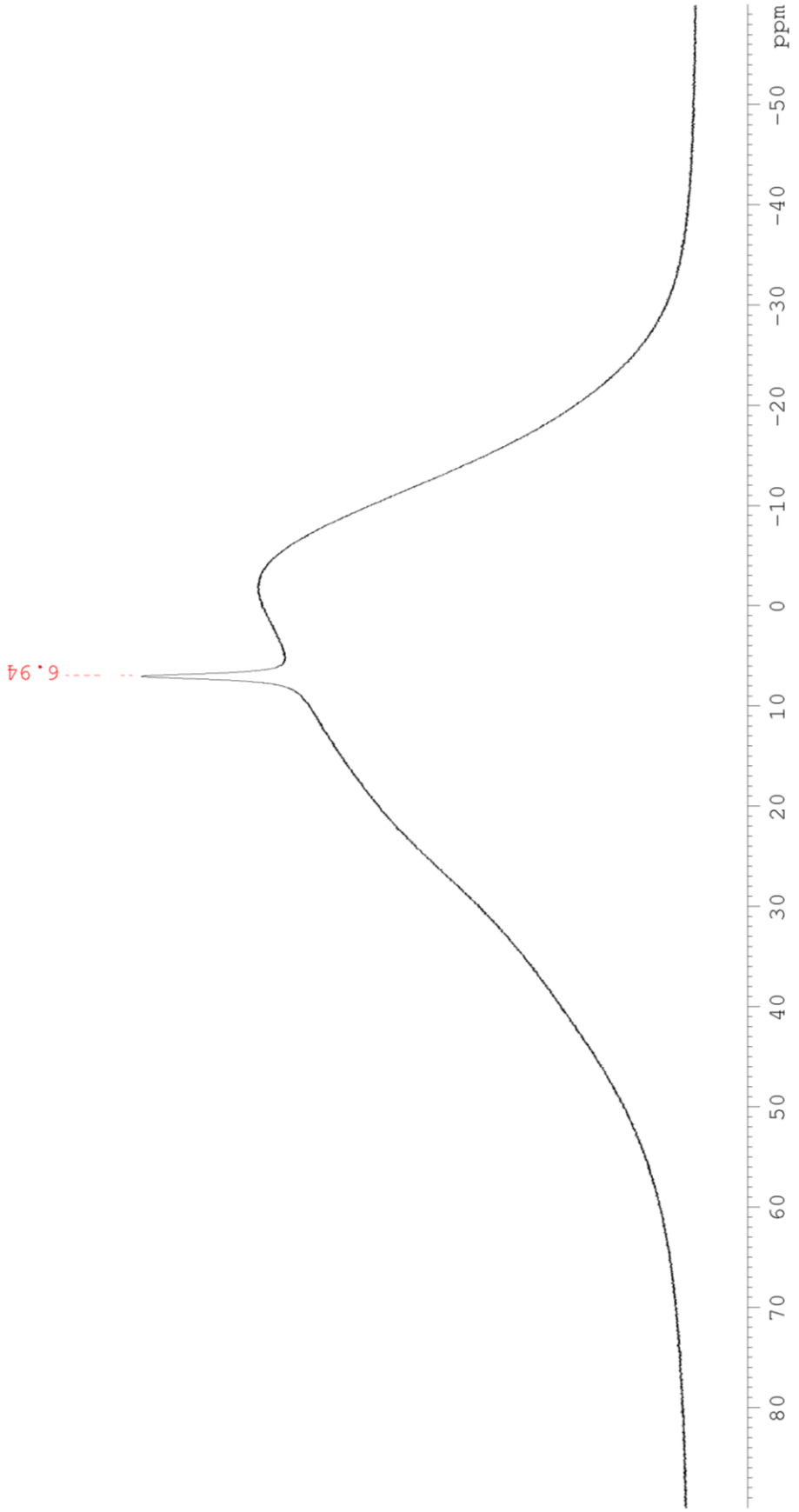


Figure S32. $^{11}B\{^{1}H\}$ NMR spectrum of **5** in C_6D_6.

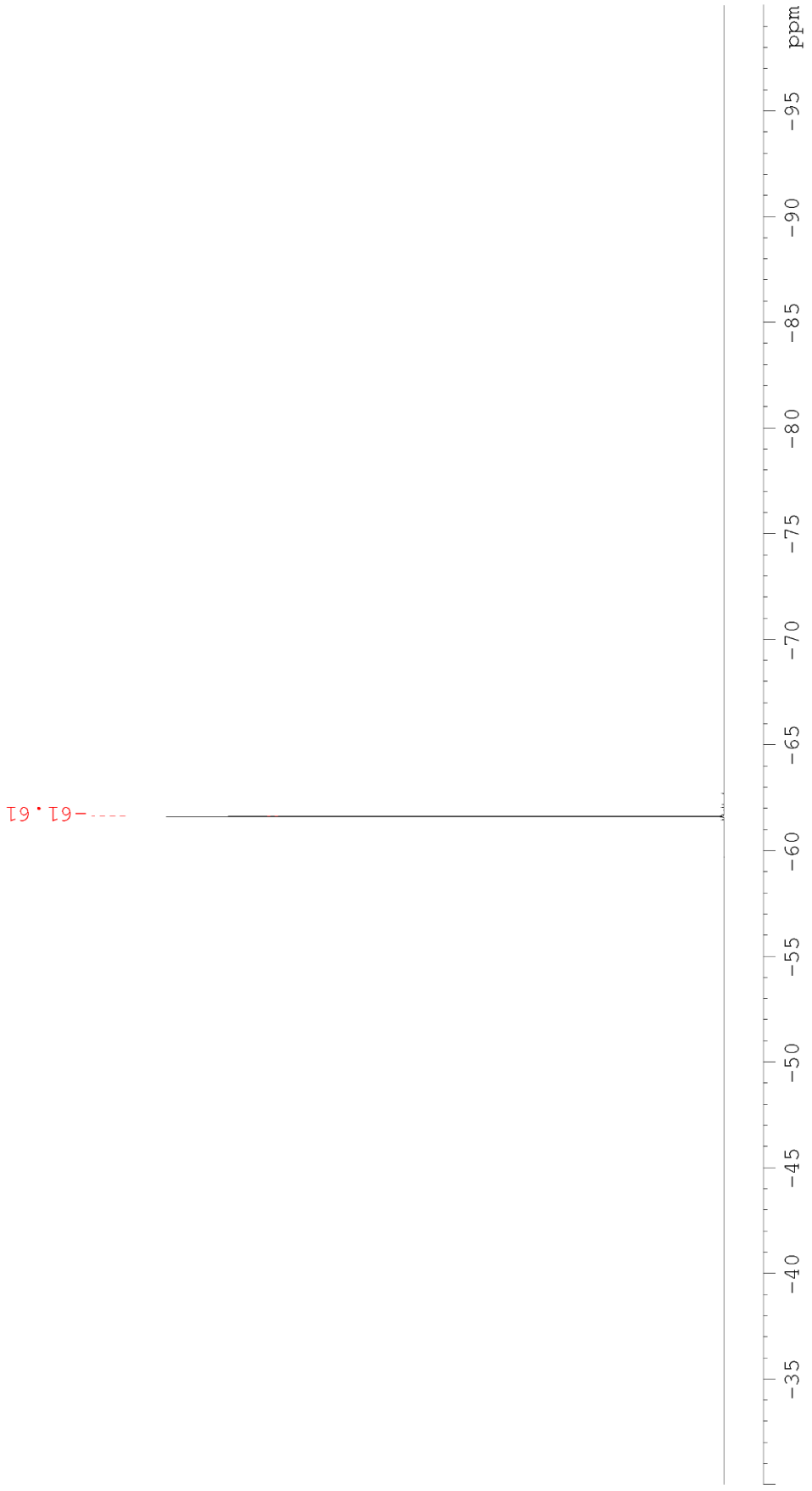


Figure S33. $^{19}F\{^{1}H\}$ NMR spectrum of **5** in C_6D_6.

NMR spectra of reaction mixtures

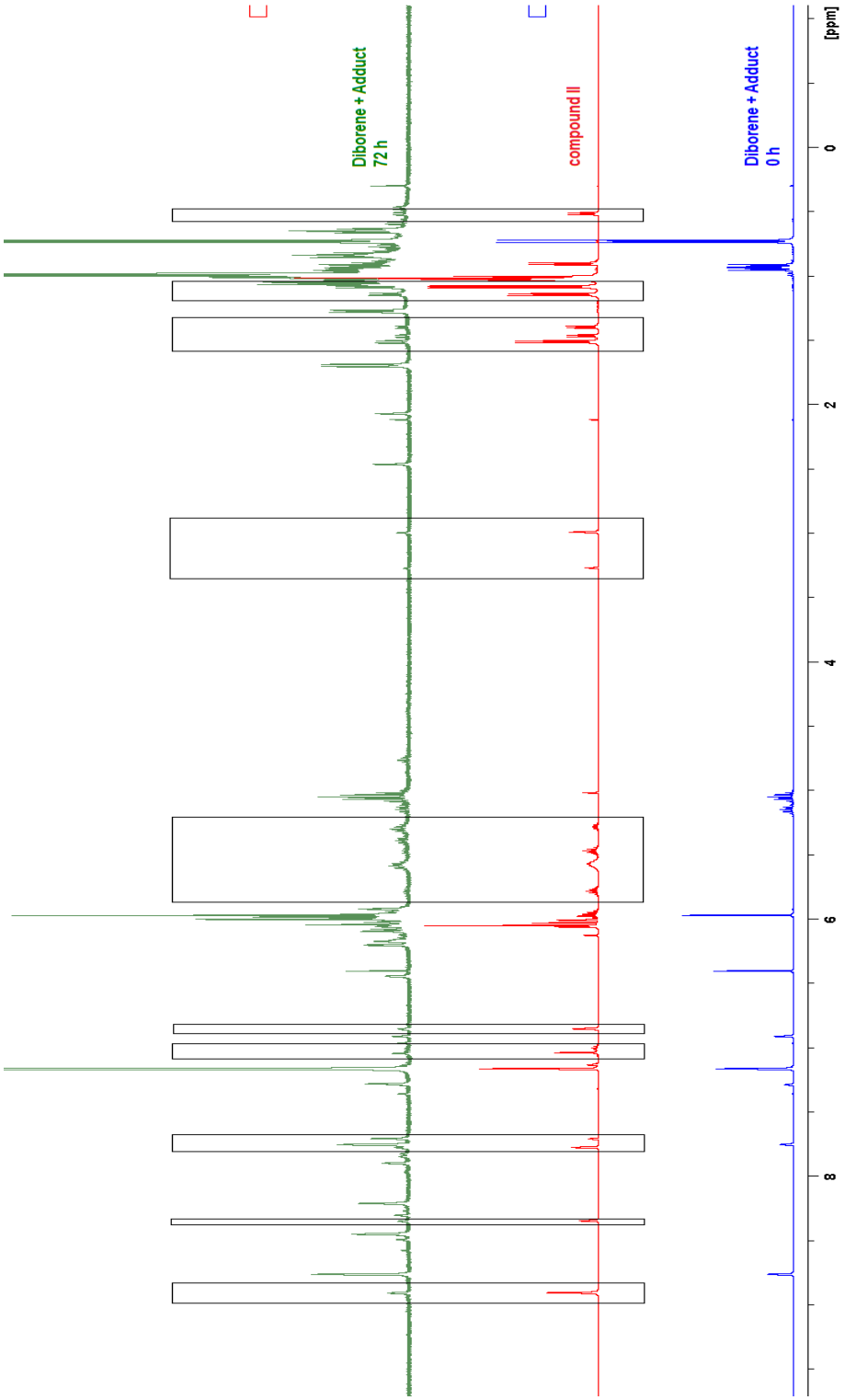


Figure S34. Stackplot of ^{1}H NMR spectra in C_6D_6 of the reaction mixture of diborene **2a** with two equivalents of borane **1** before irradiation (blue), after 72 h irradiation (green), and isolated **3** for comparison (red).

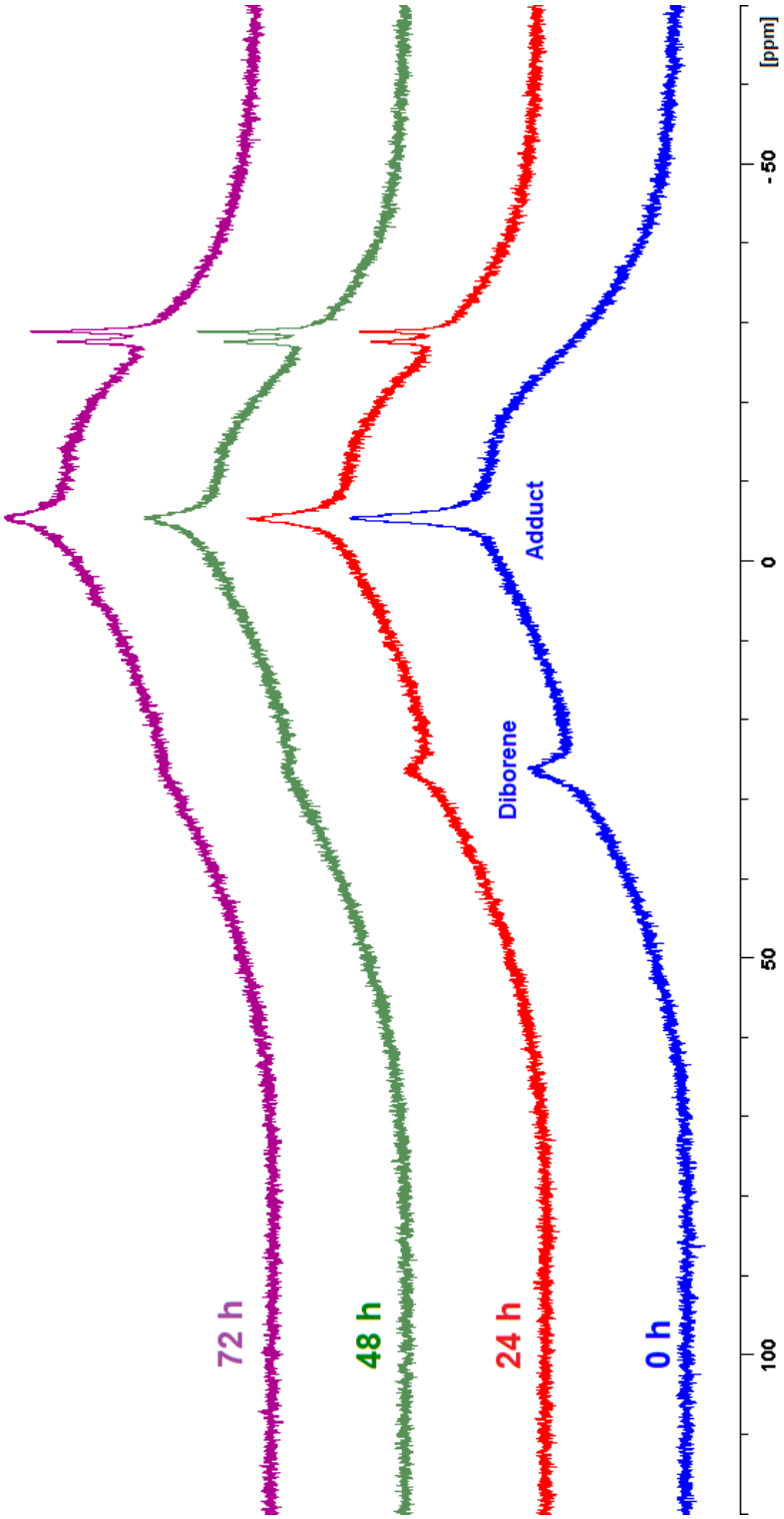


Figure S35. Stackplot of $^{11}B\{^{1}H\}$ NMR spectrum in C_6D_6 of the reaction mixture of diborene **2a** with two equivalents of borane **1** before irradiation (blue), after 24 h irradiation (red), 48 h (green) and 72 h (purple).

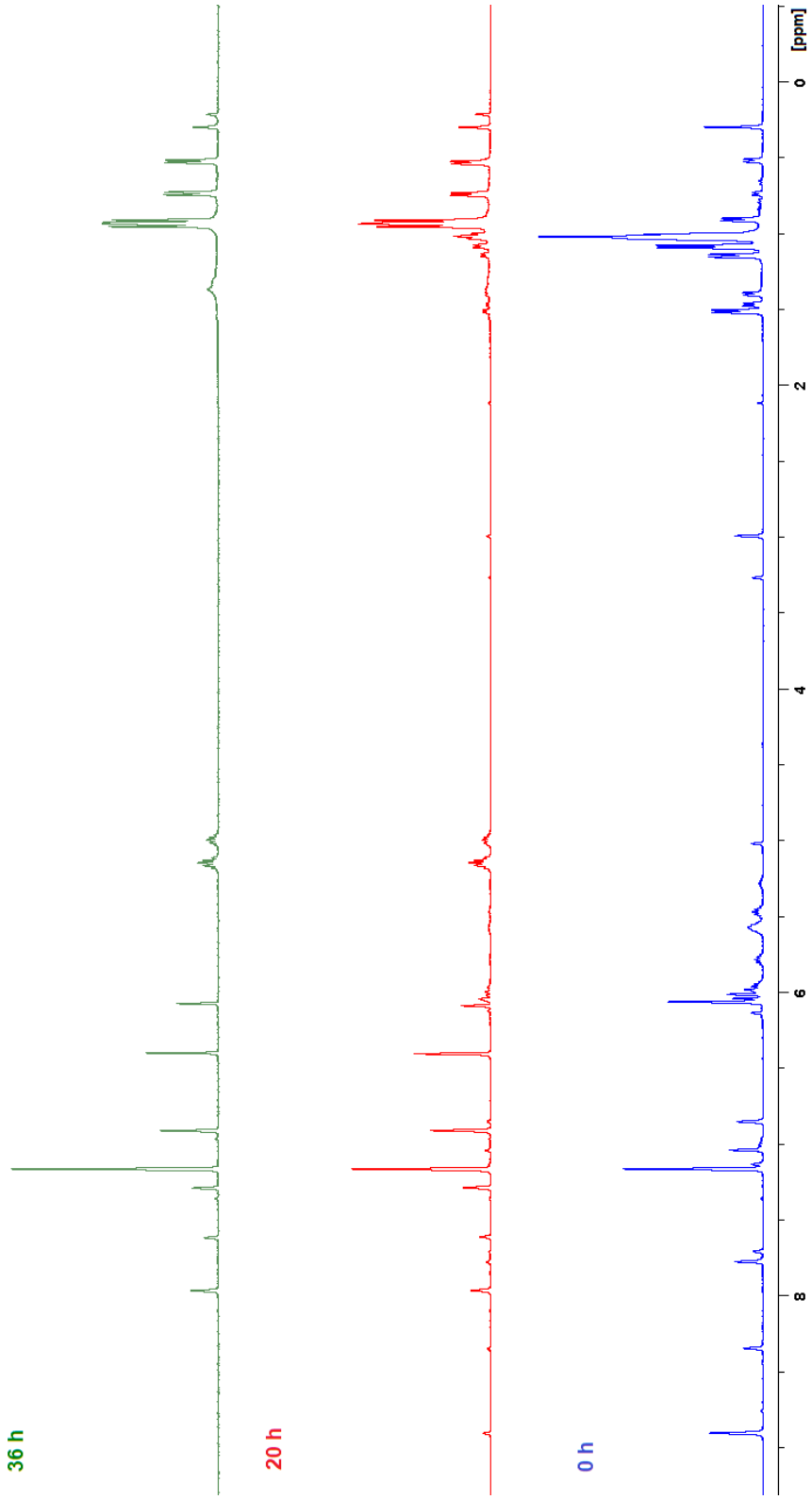


Figure S36. Stackplot of ^{1}H NMR spectrum in C_6D_6 of the reduction of **3** with KC_8 at the start of the reaction (blue), after 20 h at rt (red) and 36 h at rt (green).

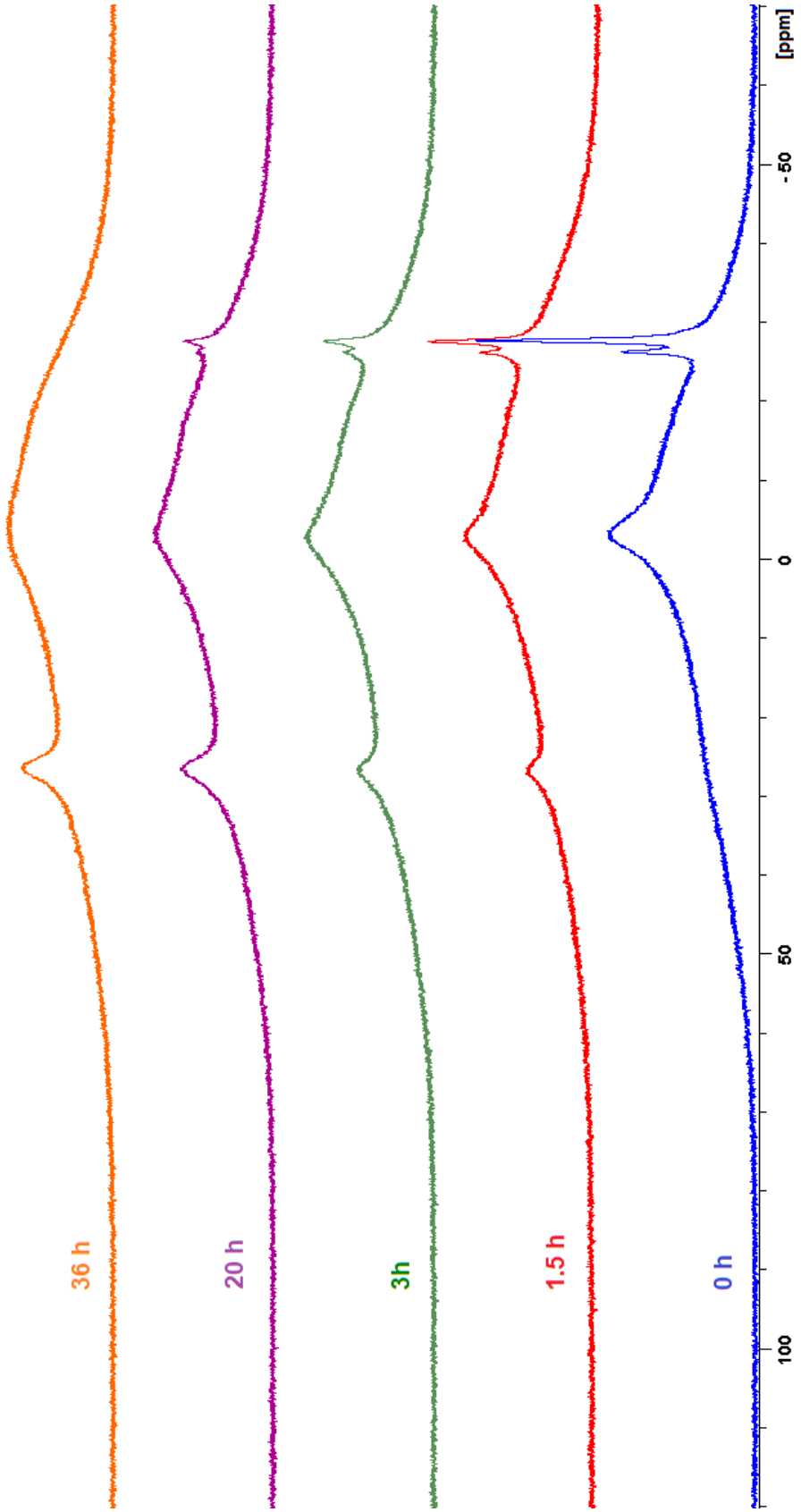


Figure S37. Stackplot of $^{11}B\{^{1}H\}$ NMR spectra in C_6D_6 of the reduction of **3** with KC_8 at the start of the reaction (blue), after 1.5 h (red), 3 h (green), 20 h (purple) and 36 h (orange) at rt.

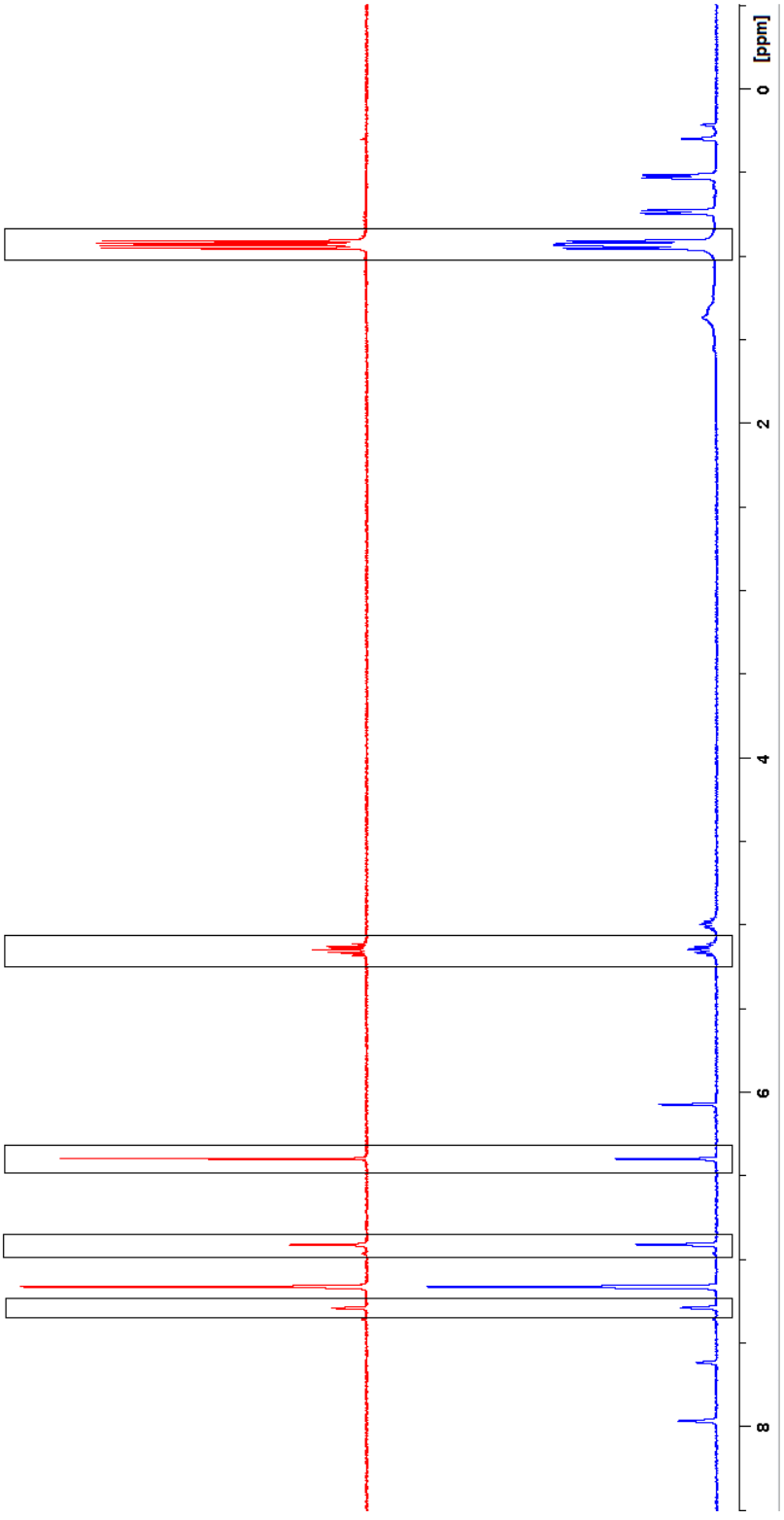


Figure S38. Stackplot of ^{1}H NMR spectra in C_6D_6 after completion of the reduction of **3** with KC_8 (blue) and isolated **2a** for comparison (red).

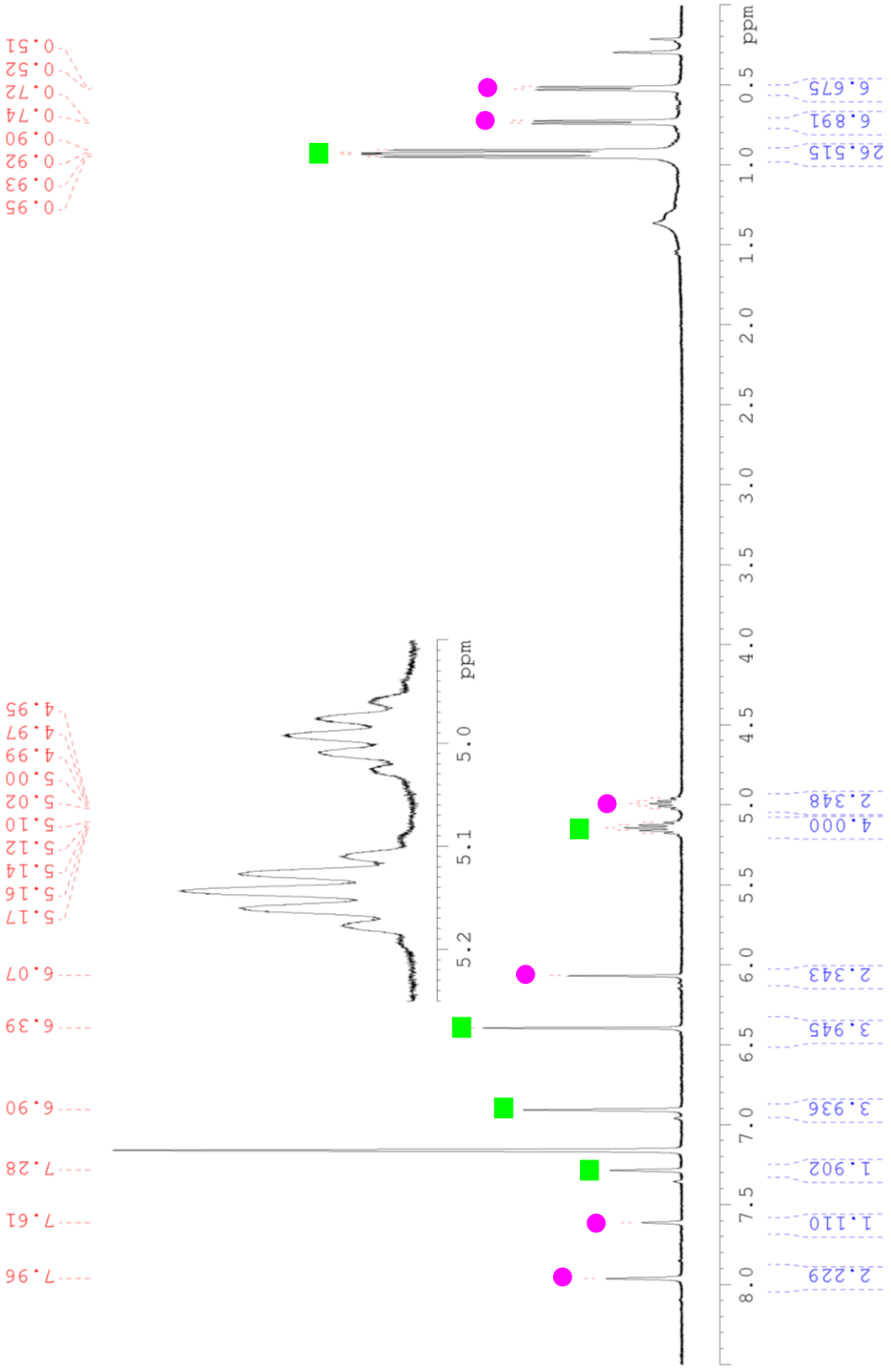


Figure S39. ^{1}H NMR spectrum in C_6D_6 after completion of the reduction of **3** with KC_8, showing clean conversion to isomers **2a** (green) and **2b** (pink).

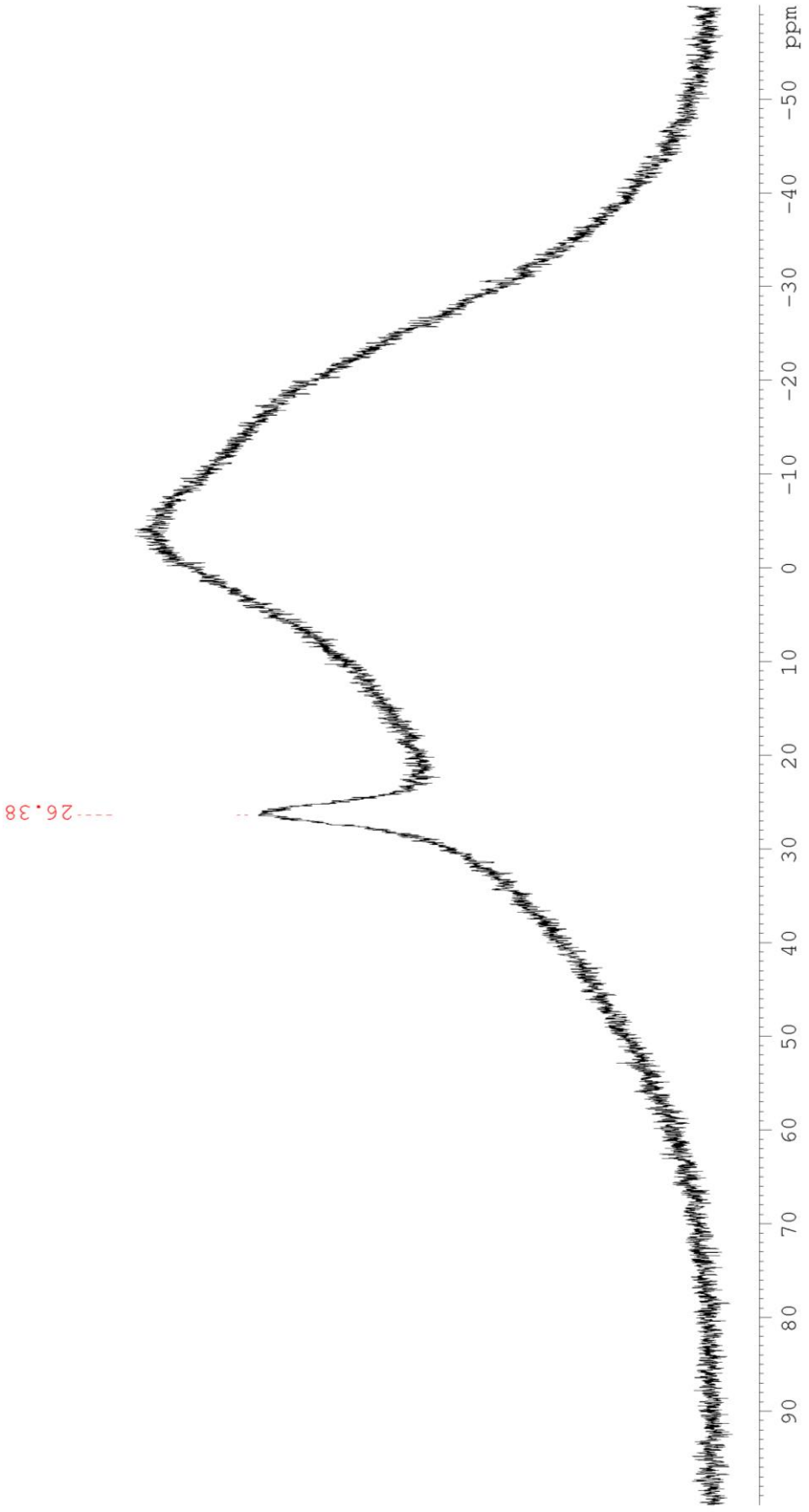


Figure S40. $^{11}B\{^{1}H\}$ NMR spectrum in C_6D_6 after completion of the reduction of **3** with KC_8.

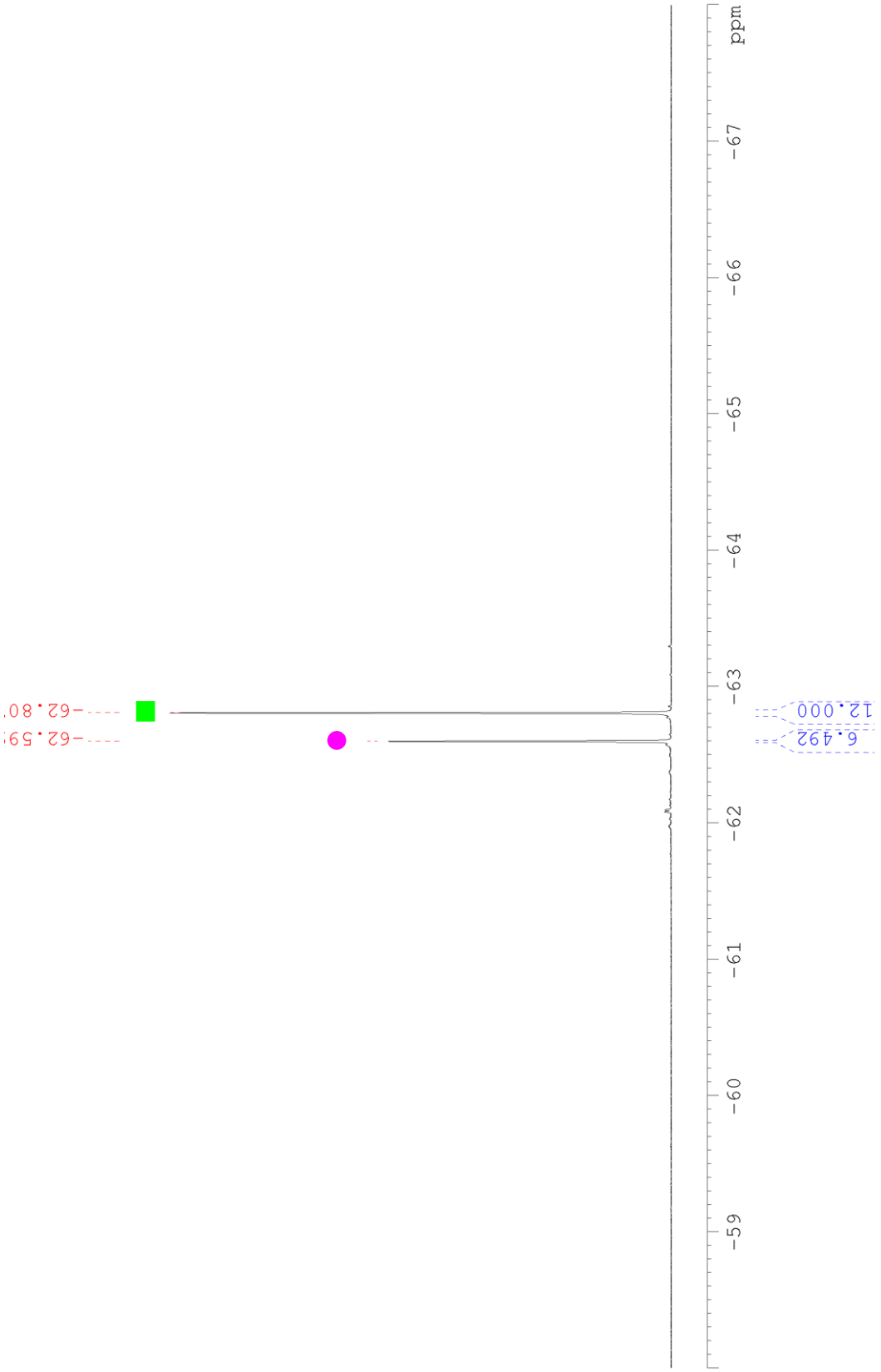


Figure S41. $^{19}F\{^{1}H\}$ NMR spectrum in C_6D_6 after completion of the reduction of **3** with KC_8 showing clean conversion to isomers **2a** (green) and **2b** (pink).

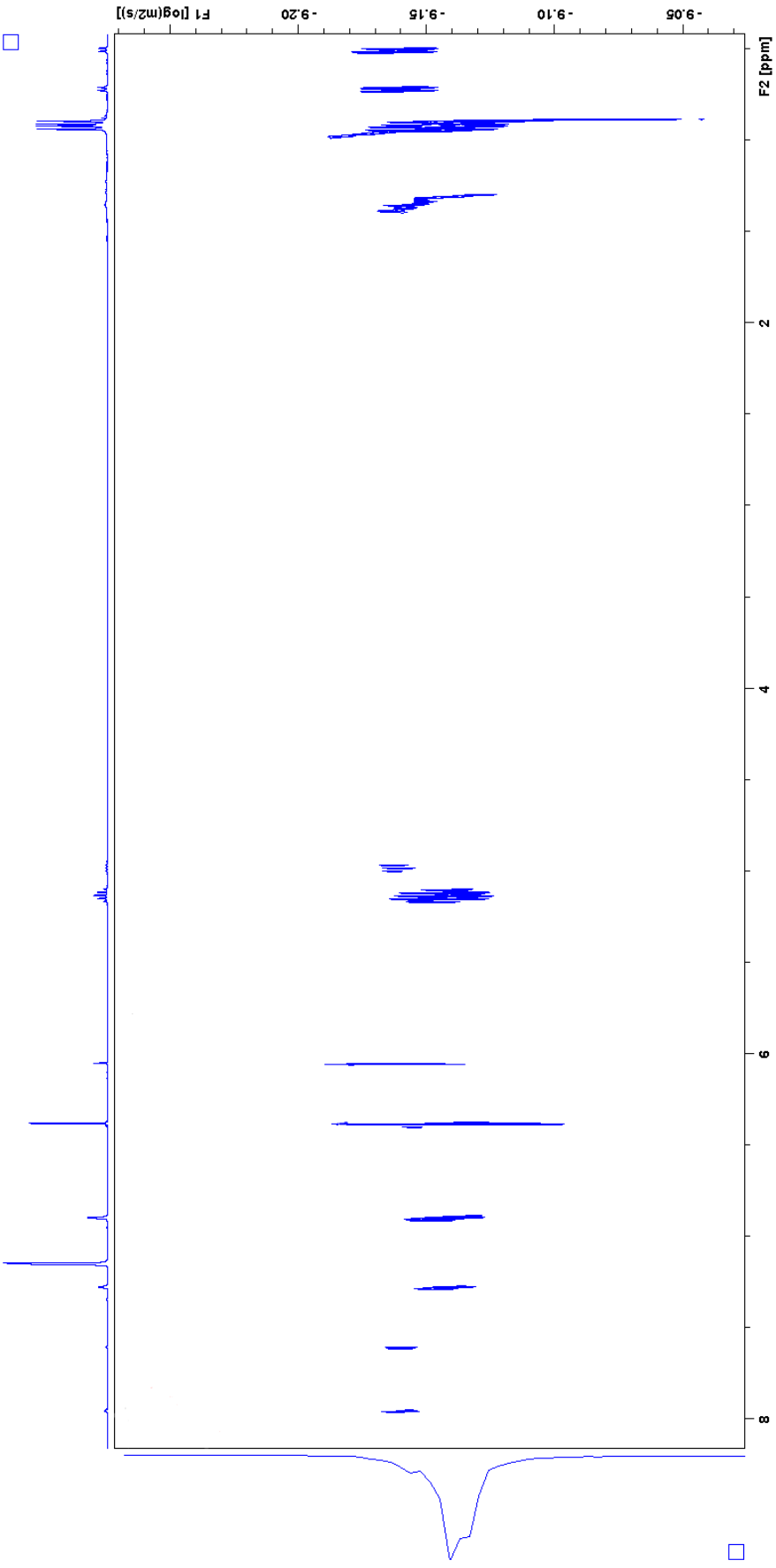


Figure S42. ^{1}H DOSY spectrum in C_6D_6 after completion of the reduction of **3** with KC_8.

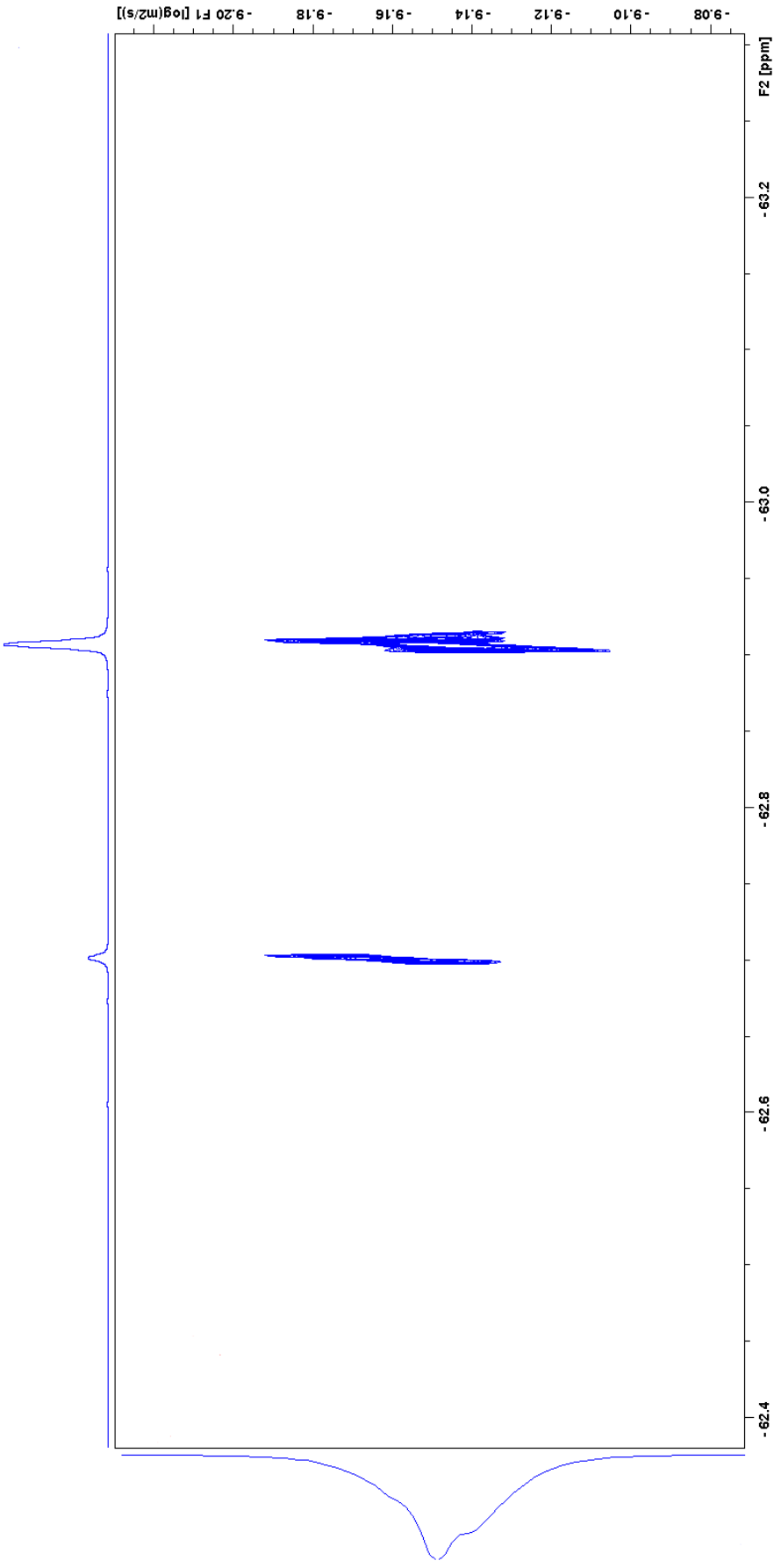


Figure S43. ^{19}F DOSY spectrum in C_6D_6 after completion of the reduction of **3** with KC_8.

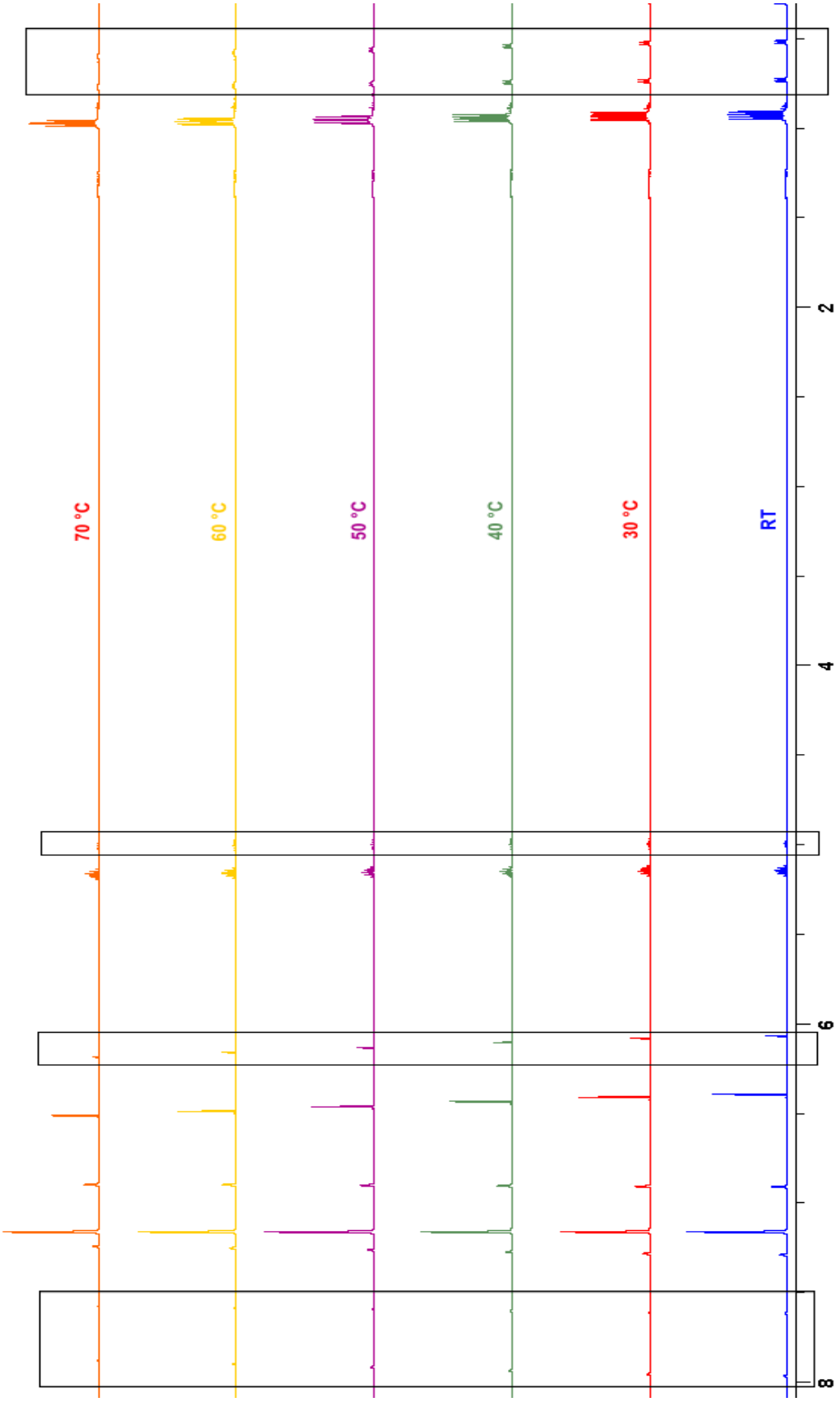


Figure S44. Stackplot of ^{1}H NMR spectra of **2a**/**2b** in C_6D_6 from rt to 70 °C showing the conversion of **2b** (highlighted) to **2a** above 70 °C.

UV-vis spectra

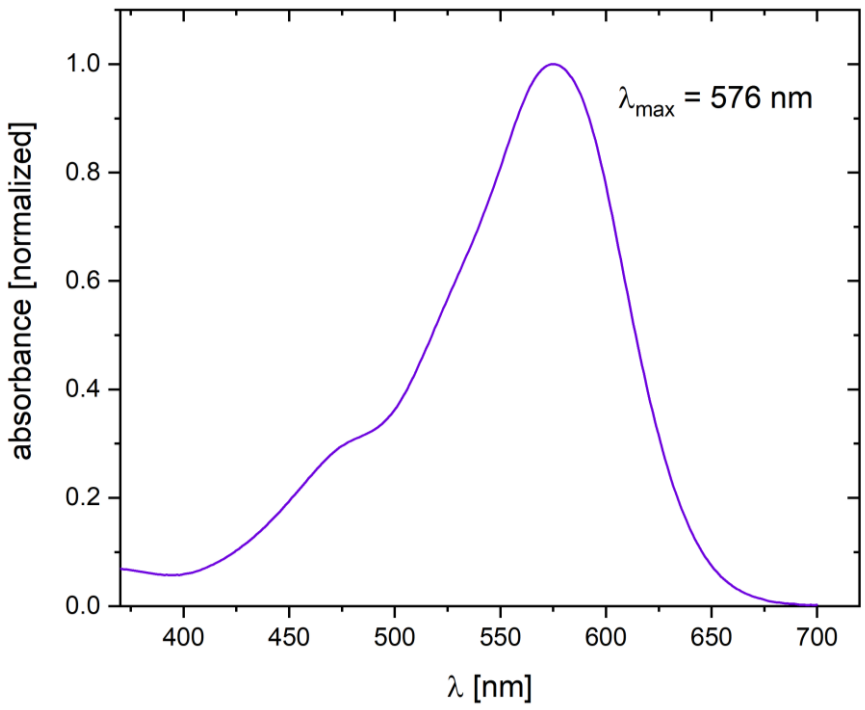


Figure S45. UV-vis absorption spectrum of **2a** in benzene (6.84 x 10^{-5} M): ε_{max} = 14620 M^{-1} cm^{-1}.

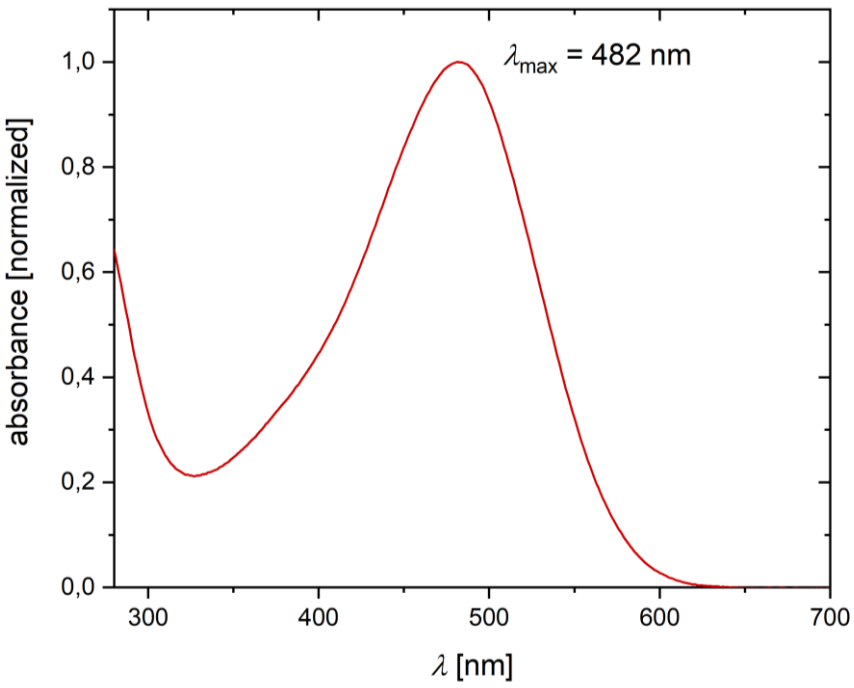


Figure S46. UV-vis absorption spectrum of **5** in benzene (5.89 x 10^{-5} M): ε_{max} = 16978 M^{-1} cm^{-1}.

Cyclic voltammetry

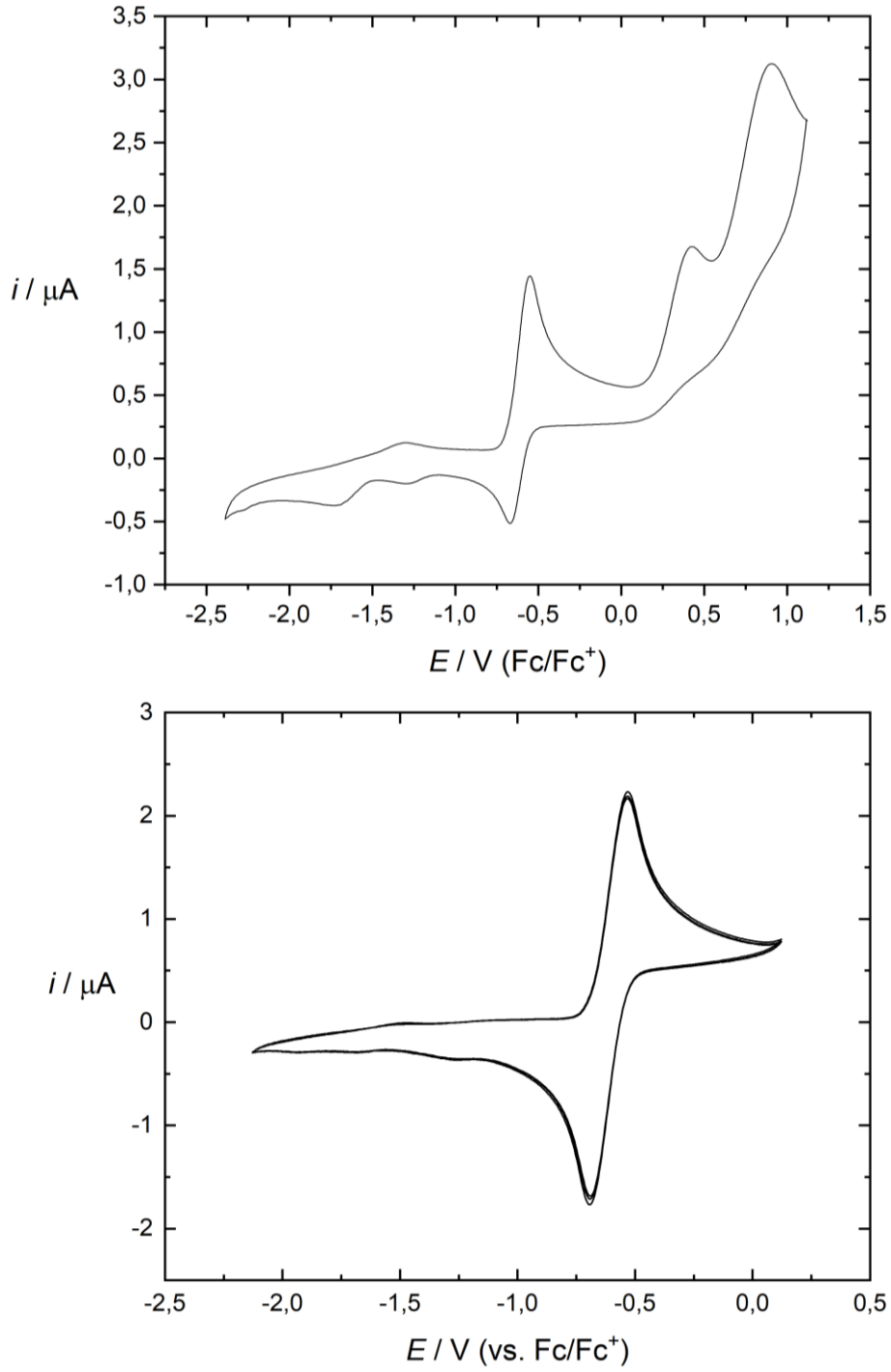


Figure S47. Cyclic voltamogramm of **3** in THF with 0.1 M [*n*Bu$_4$N][PF$_6$] as the supporting electrolyte. Formal potential at peak current: E_{PA} = 0.43, 0.91 V, E_{PC} = –1.73, –1.30 V and $E_{1/2}$ = –0.61 (relative to Fc/Fc$^+$ couple, scan rate 250 mV/s).

Crystallographic details

The crystal data of **(I*i*Pr)BAr^{F}Cat**, **2a**, **(CAAC)BAr^{F}Cat**, **4** and **5** were collected on a Bruker D8 Quest diffractometer with a CCD-area detector or a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The crystal data of **1** and **3a** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated MoKα radiation. The structures were solved using intrinsic phasing method,[4] refined with the ShelXL program[5] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 1985025-1985031. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Refinement details for (I*i*Pr)BAr^{F}Cat: Refined as a two-component inversion twin using TWIN keyword. The BASF parameter was refined to 34%. Both CF_3 groups were disordered. The first (RESI 1 and 11 CF3) was modelled as twofold disordered in a 71:29 ratio. The second (RESI 2, 21, 22 CF3) was modelled as threefold disordered with three free variables summed up to 1 in a 80:9:11 ratio. ADPS in both groups were restrained with SIMU 0.005 to the ADP of the carbon atom. One *i*Pr group of the NHC ligand was modelled as twofold disordered in a 72:28 ratio. ADPs within this group were restrained with SIMU 0.003.

Crystal data for (I*i*Pr)BAr^{F}Cat: $C_{23}H_{23}BF_6N_2O_2$, M_r = 484.24, colorless block, 0.208×0.185×0.143 mm^3, orthorhombic space group $P2_12_12_1$, a = 8.4650(19) Å, b = 11.3157(18) Å, c = 23.879(5) Å, V = 2287.3(8) Å^3, Z = 4, ρ_{calcd} = 1.406 g·cm^{-3}, μ = 0.122 mm^{-1}, $F(000)$ = 1000, T = 100(2) K, R_1 = 0.0257, wR^2 = 0.0651, 4500 independent reflections [$2\theta \leq 52.044°$] and 427 parameters.

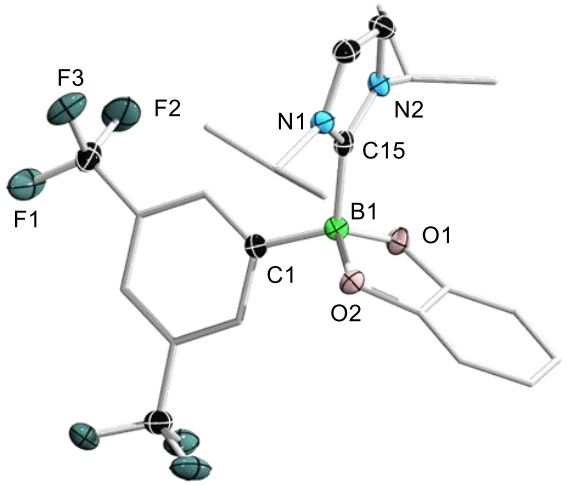


Figure S48. Crystallographically derived molecular structure of **(I*i*Pr)BAr^{F}Cat**. Thermal ellipsoids set at 50% probability. Thermal ellipsoids of ligand periphery and hydrogen atoms omitted for clarity. Selected bond lengths (Å): B1-C1 1.617(2), B1-C15 1.659(3).

Refinement details for 1: Both CF_3 groups were disordered. The first (RESI 1 and 11 CF3) was modelled as twofold disordered in a 57:43 ratio. The second (RESI 2, 21, 22 CF3) was modelled as threefold disordered with three free variable summed up to 1 in a 58:28:14 ratio. ADPS in both groups were restrained with SIMU 0.005 to the ADP of the carbon atom.

Crystal data for 1: $C_{17}H_{19}BBr_2F_6N_2$, M_r = 535.97, colorless block, 0.25×0.239×0.164 mm^3, monoclinic space group $P2_1/c$, a = 12.566(3) Å, b = 8.2909(8) Å, c = 20.179(4) Å, β = 104.595(16)°, V = 2034.5(7) Å^3, Z = 4, ρ_{calcd} = 1.750 g·cm^{-3}, μ = 4.043 mm^{-1}, F(000) = 1056, T = 100(2) K, R_1 = 0.0179, wR^2 = 0.0446, 4007 independent reflections [2θ ≤ 52.036°] and 342 parameters.

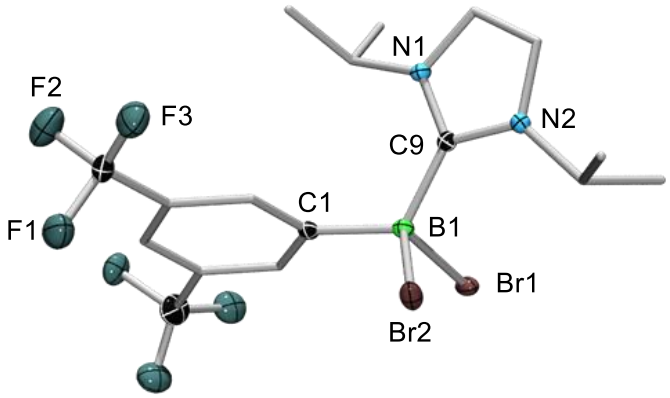


Figure S49. Crystallographically derived molecular structure of **1**. Thermal ellipsoids set at 50% probability. Thermal ellipsoids of ligand periphery and hydrogen atoms omitted for clarity. Selected bond lengths (Å): B1-C1 1.610(2), B1-C9 1.625(2).

Refinement details for 2a: The entire molecule is twofold disordered in a 89:11 ratio via a mirror plane perpendicular to the ArBBAr plane traversing the center of the B=B bond and including N1 and N2. 1,2- and 1,3-distances in both parts were restrained to be similar using SAME. Within the minor part all ADPs were restrained with SIMU 0.004, those of the benzene ring with ISOR 0.005 and those of the CF3 groups with ISOR 0.003. The iPr groups were not included in the disordered parts and the ADPs in one of them (C12 > C14) were restrained with ISOR 0.002.

Crystal data for 2a: $C_{34}H_{38}B_2F_{12}N_4$, M_r = 752.30, purple plate, 0.242×0.227×0.111 mm^3, Triclinic space group $P\,\bar{1}$, a = 8.849(3) Å, b = 10.927(4) Å, c = 10.940(4) Å, α = 114.541(18)°, β = 102.10(3)°, γ = 97.48(3)°, V = 912.4(6) Å^3, Z = 1, ρ_{calcd} = 1.369 g·cm^{-3}, μ = 0.123 mm^{-1}, F(000) = 388, T = 100(2) K, R_1 = 0.1323, wR^2 = 0.2092, 3569 independent reflections [$2\theta \leq 51.992°$] and 396 parameters.

Refinement details for 3a: The asymmetric unit contains two half and one entire benzene molecules. The latter (RESI BENZ) was modelled as twofold disordered in a 57:43 ratio. The rings within BENZ were idealized with AFIX 66 and ADPs restrained with SIMU 0.005. Furthermore, the otherwise oblate ADP of C9 was restrained to similarity with B1, N1, N2 using SIMU 0.005.

Crystal data for 3a: $C_{34}H_{38}B_2Br_2F_{12}N_4{\cdot}(C_6H_6)_2$, M_r = 1068.34, colorless block, 0.158×0.136×0.124 mm^3, triclinic space group $P\,\bar{1}$, a = 10.477(7) Å, b = 11.414(8) Å, c = 21.469(18) Å, α = 75.850(15)°, β = 85.729(8)°, γ = 72.776(19)°, V = 2378(3) Å^3, Z = 2, ρ_{calcd} = 1.492 g·cm^{-3}, μ = 1.789 mm^{-1}, F(000) = 1084, T = 173(2) K, R_1 = 0.0518, wR^2 = 0.1131, 9343 independent reflections [$2\theta \leq 52.042°$] and 646 parameters.

Refinement details for (CAAC)BAr^{F}Cat: The CF_3 group at C7 was modelled as twofold disordered in a 55:45 ratio. ADPs were restrained to similarity with C7 using SIMU 0.005.

Crystal data for (CAAC)BAr^{F}Cat: $C_{34}H_{38}BF_6NO_2$, M_r = 617.46, yellow block, 0.474×0.453×0.142 mm^3, monoclinic space group *C*2/*c*, *a* = 24.208(9) Å, *b* = 16.720(8) Å, *c* = 20.187(7) Å, β = 130.261(7)°, *V* = 6235(4) Å^3, *Z* = 8, ρ_{calcd} = 1.316 g·cm^{-3}, μ = 0.105 mm^{-1}, *F*(000) = 2592, *T* = 100(2) K, R_1 = 0.0610, wR^2 = 0.1663, 6056 independent reflections [2θ ≤ 52.044°] and 433 parameters.

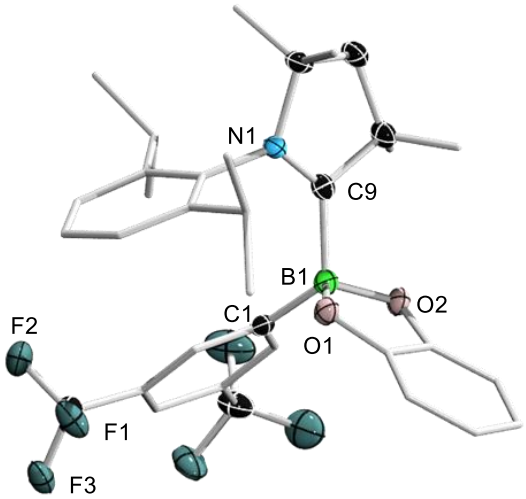


Figure S50. Crystallographically derived molecular structure of **(CAAC)BAr^{F}Cat**. Thermal ellipsoids set at 50% probability. Thermal ellipsoids of ligand periphery and hydrogen atoms omitted for clarity. Selected bond lengths (Å): B1-C1 1.663(4), B1-C15 1.676(4), C15-N1 1.247(3).

Refinement details for 4: The asymmetric unit contains half a benzene molecule (RESI BZ) positioned by an inversion center and refined as PART -1. ADPS withing BZ were restrained with SIMU 0.005. Both CF_3 groups were disordered. The first (RESI 1, 11, 12 CF3) was modelled as threefold disordered with three free variable summed up to 1 in a 61:12:27 ratio. The second (RESI 2, 21 CF3) was modelled as twofold disordered in a 53:47 ratio. ADPS in both groups were restrained with SIMU 0.005 to the ADP of the carbon atom.

Crystal data for 4: $C_{28}H_{34}BCl_2F_6N\cdot(C_6H_6)_{0.5}$, M_r = 619.32, colorless block, 0.323×0.192×0.098 mm^3, monoclinic space group *C*2/*c*, *a* = 15.8864(6) Å, *b* = 9.1579(3) Å, *c* = 42.8822(16) Å, β = 99.7830(10)°, *V* = 6148.0(4) Å^3, *Z* = 8, ρ_{calcd} = 1.338 g·cm^{-3}, μ = 0.269 mm^{-1}, *F*(000) = 2584, *T* = 100(2) K, R_1 = 0.0350, wR^2 = 0.0878, 6063 independent reflections [2θ ≤ 52.042°] and 478 parameters.

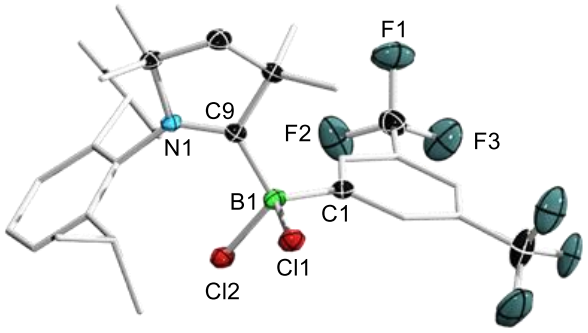


Figure S51. Crystallographically derived molecular structure of **4**. Thermal ellipsoids set at 50% probability. Thermal ellipsoids of ligand periphery and hydrogen atoms omitted for clarity. Selected bond lengths (Å): B1-C1 1.611(3), B1-C9 1.638(2), C9-N1 1.303(2).

Crystal data for 5: $C_{37}H_{50}BF_6N_3$, M_r = 661.61, red block, 0.162×0.119×0.118 mm^3, triclinic space group $P\ \bar{1}$, a = 11.5551(19) Å, b = 12.353(3) Å, c = 13.320(3) Å, α = 85.773(16)°, β = 69.850(10)°, γ = 81.738(13)°, V = 1765.8(7) Å^3, Z = 2, ρ_{calcd} = 1.244 g·cm^{-3}, μ = 0.094 mm^{-1}, F(000) = 704, T = 100(2) K, R_1 = 0.0591, wR^2 = 0.0983, 6963 independent reflections [2θ≤52.044°] and 436 parameters.

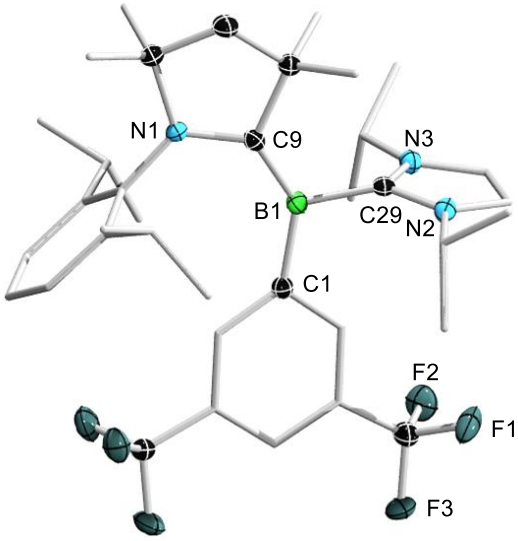


Figure S52. Crystallographically derived molecular structure of **5**. Thermal ellipsoids set at 50% probability. Thermal ellipsoids of ligand periphery and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles: B1-C1 1.605(2), B1-C9 1.481(2), B1-C29 1.609(2), C9-N1 1.4175(18), $\Sigma\angle_{B1}$ 359.97(12), dihedral angle (N1,C9,B1,C1) 7.1(3), (N2,C29,B1,C1) 85.45(16).

Computational details

Geometry optimizations of 2a in the gas phase at the OLYP/ZORA/TZ2P level of theory

Geometry optimizations and further analysis were carried out using the Amsterdam Density Functional (ADF)[6-8] program at the OLYP/ZORA/TZ2P[9-13] level of theory. To obtain the singlet state, spin-restricted calculations were performed constraining the projection of the total electronic spin along a reference axis to 0. Frequency calculations were conducted to determine if each stationary point corresponds to a minimum.[14-16]

At this level of theory the aryl rings of **2a** are not coplanar with the >B=B< plane and the NHCs not perpendicular to the >B=B< plane. The HOMO is mainly composed of the B=B π system and of the pure p orbitals on the aryl carbon and NHC nitrogen atoms (Fig. S53). Closer inspection reveals that these p orbitals would be interacting in a highly anti-bonding configuration with the BB π system, hence in the absence of external constraints, e.g. crystal packing, further stabilization can be gained by adopting a slightly non-coplanar geometry. The LUMO corresponds to B-C_{aryl} π bonding and retains the pure p character of the other aryl carbon and NHC nitrogen centres. In the gas phase, the planar configuration in agreement with the solid-state structure corresponds to a low-lying transition state.

Despite the non-planar geometry of optimized **2a** its calculated UV-vis spectrum reproduces the experimental absorptions quite well, albeit slightly red-shifted, which is not unusual in qualitative Time-Dependent Density Functional Theory (TDDFT). The main absorption corresponds to the HOMO-LUMO transition while the shoulder at lower energy corresponds to the HOMO-LUMO-3 transition (Fig. S54). It is noteworthy that the calculated UV-vis spectrum of the planar structure did not reproduce the experimental absorptions in any way, suggesting that the non-planar form of **2a** is prevalent in solution.

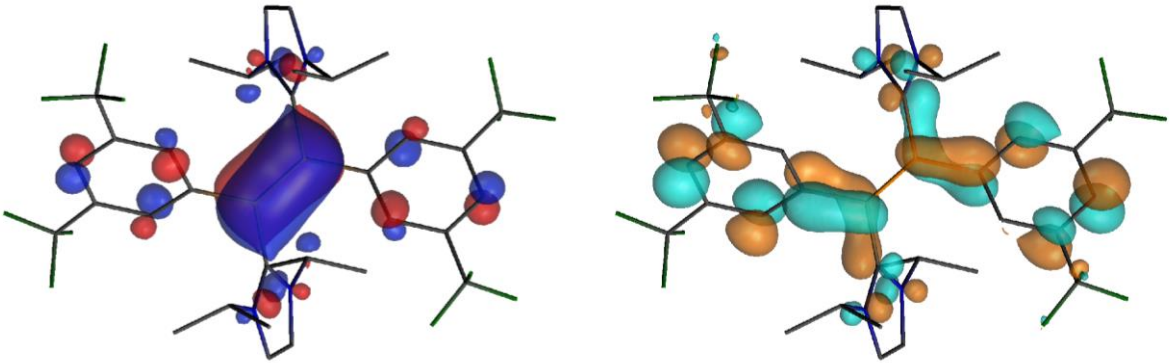


Figure S53. Plots of the HOMO (left) and LUMO (right) of **2a** calculated at the OLYP/ZORA/TZ2P level of theory in the gas phase.

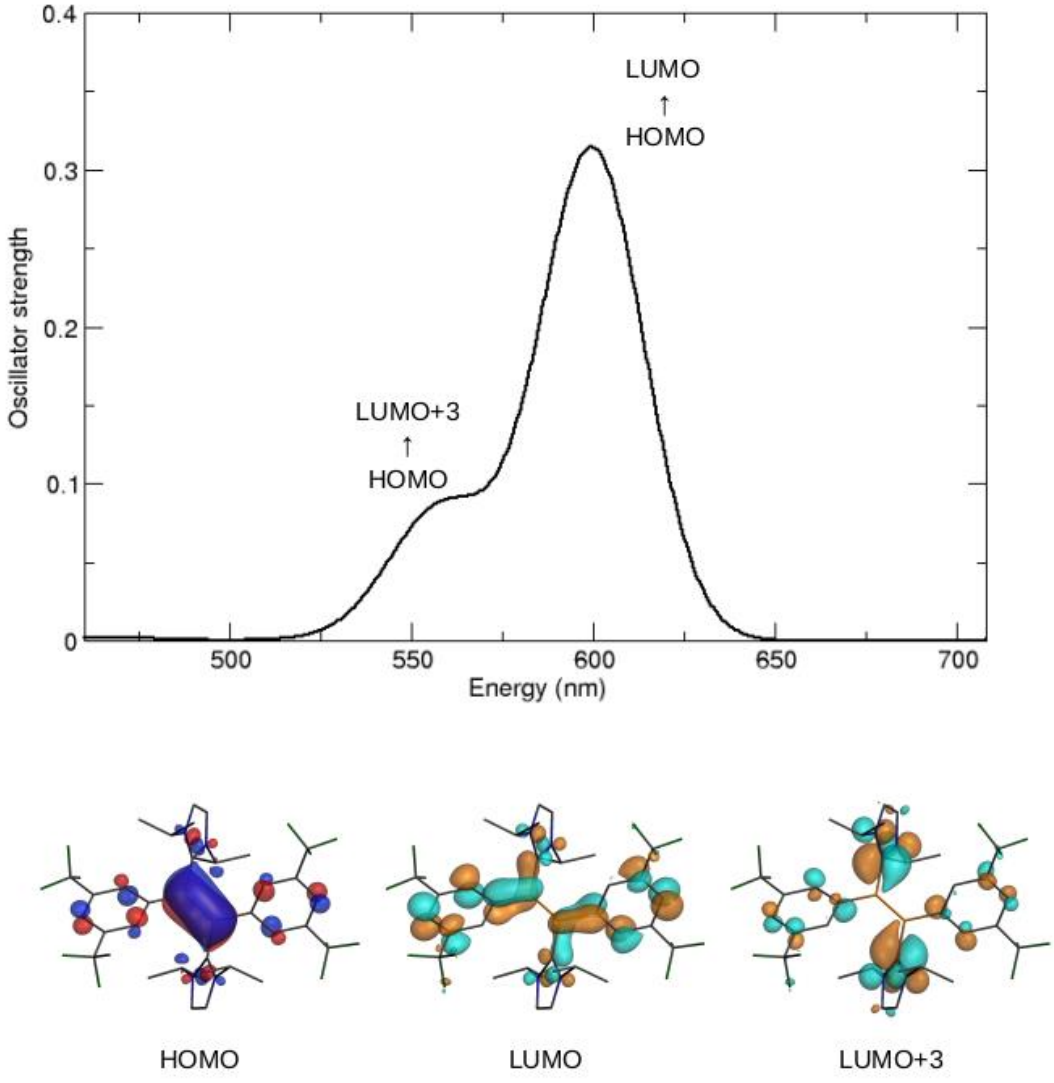


Figure S54. Calculated UV-vis spectrum of **2a** at the OLYP/ZORA/TZ2P level of theory with the relevant frontier MOs involved in the transitions.

Geometry optimizations of 2a in the gas phase at the ω-B97XD/6-31G(d) level of theory

Gas-phase geometry optimizations were performed with the Gaussian09 program,[17] using the hybrid, range-separated density-functional ω-B97XD,[18] which considers dispersion interaction through a range separation (22% for short-range and 100% Hartree-Fock for long-range). The electronic configuration of **2a** was described with a Pople's split-valence basis set of double-ζ quality with one polarization function (for heavy atoms), 6-31G(d), for all the atoms.

At this level of theory, the optimized geometry of **2a** is in accordance with that of the X-ray crystallographically-derived structure. Despite the differences in geometry, the plot of the HOMO looks near-identical to that obtained at the OLYP/ZORA/TZ2P level of theory (compare Fig. S53 and S55). Due to the planarity, however, the LUMO extends over B-C_{aryl} π-bonding interactions in conjugation with the C_{ortho}-C_{meta} aryl π bonds and shows a strong B-B antibonding component, without any contribution from the perpendicular NHC ligands.

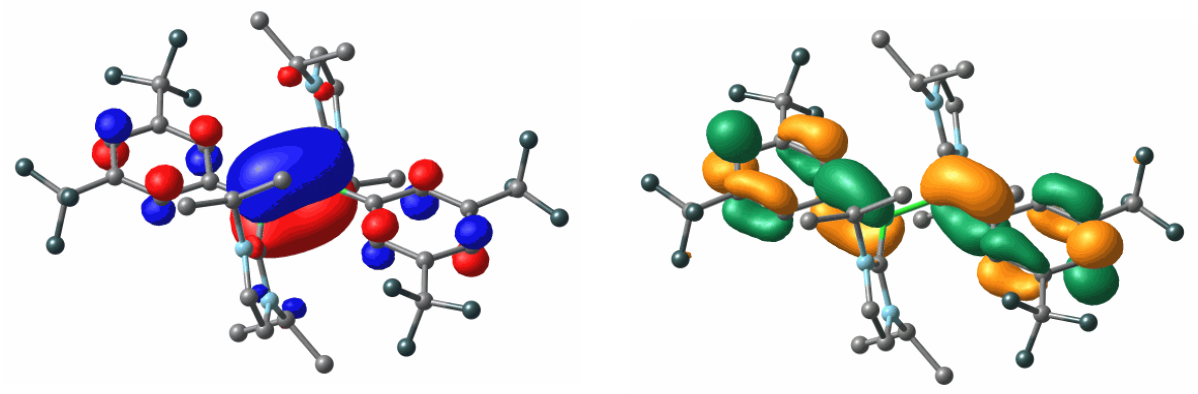


Figure S55. Plots of the HOMO (left) and LUMO (right) of **2a** calculated at the ω-B97XD/6-31G(d) level of theory in the gas phase.

Mechanistic analyses of the reduction of borane 1 to diborene 2

Geometry optimizations at the ω-B97XD/6-31G(d) level of theory were carried out without symmetry constraints, and the stationary points were characterized by analytical frequency calculations, i.e. energy minima (reactants, intermediates and products) must exhibit only positive harmonic frequencies whereas each energy maximum (transition state) exhibits one and only one negative frequency. From these last calculations, zero-point energy (ZPE) and thermal and entropy corrections were obtained, which were added to the electronic energy in order to express the calculated values as Gibbs free energies.

Calculations were also performed to include the solvent effect through the PCM model using the SMD parameters according to Truhlar's model[19-23] with benzene as solvent (ε = 2.2706). In order to improve the numerical results, single-point calculations were carried out on the gas-phase optimized geometries using a mixed basis set of triple-ζ quality with one polarization function, 6-311G(d,p), for all the atoms except Br: this much heavier atom was treated with the LANL08d relativistic pseudopotential.[24-26] These energies were added to the gas-phase calculations reported as the final energy values. As a result the composite level of theory is the following: (SMD:benzene)ω-B97XD/(6-311G(d,p),LANL08d)//ω-B97XD/6-31G(d).

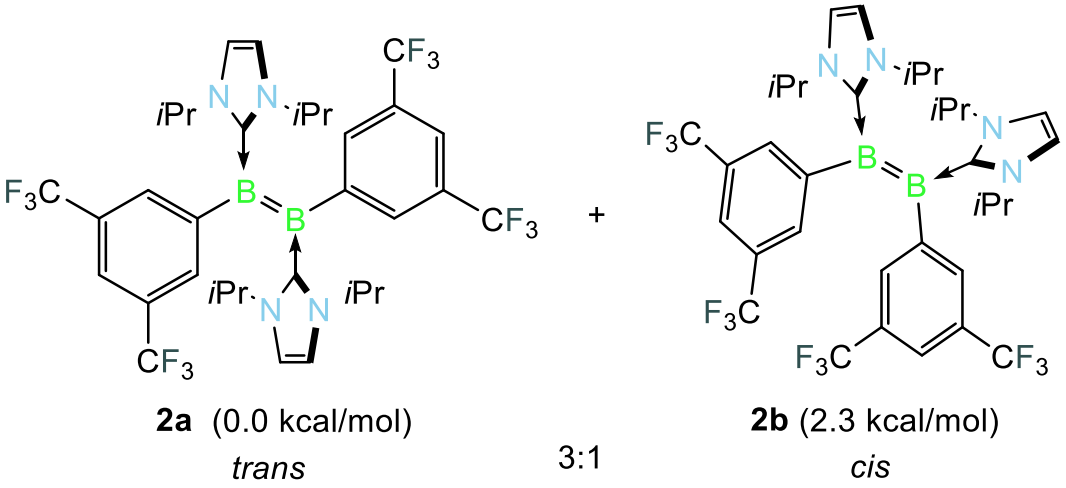


Figure S56. Relative Gibbs free energy of both isomers of **2** calculated at the (SMD:benzene)ω-B97XD/(6-311G(d,p),LANL08d) level.

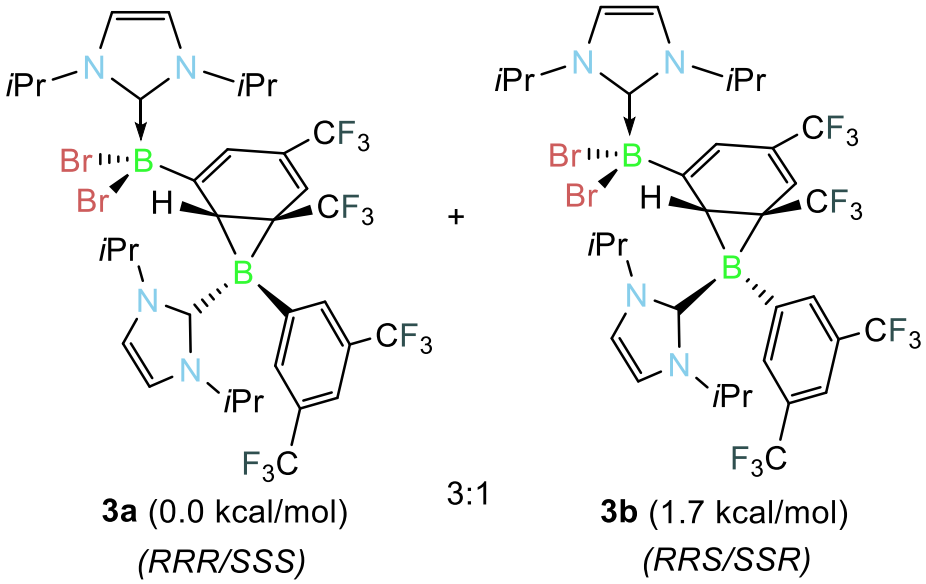


Figure S57. Relative Gibbs free energy of both diastereomers of **3** calculated at the (SMD:benzene)ω-B97XD/(6-311G(d,p),LANL08d) level.

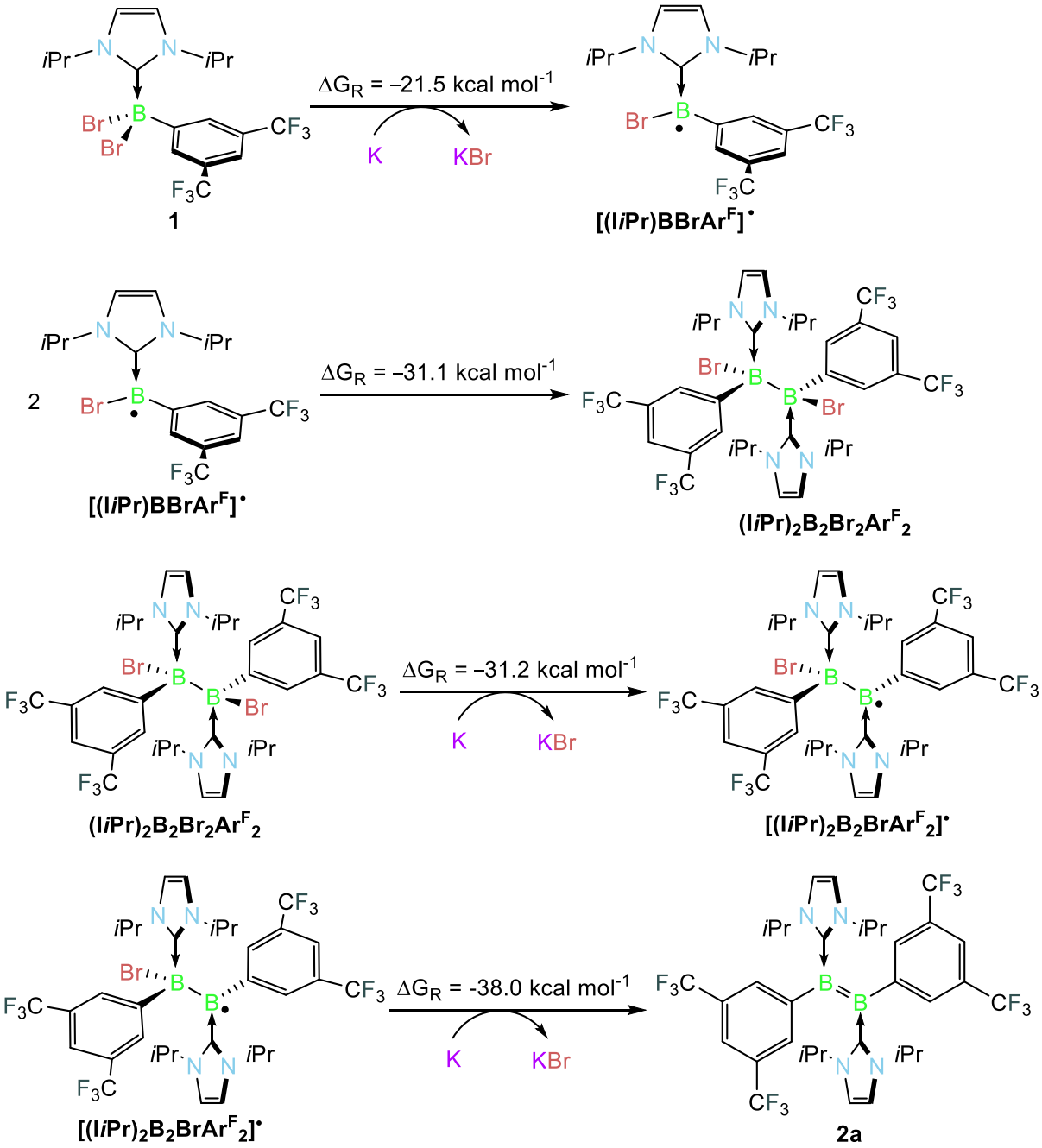


Figure S58. Radical reaction mechanism via homocoupling of boryl radicals to diborene **2a** calculated at the (SMD:benzene)ω-B97XD/(6-311G(d,p),LANL08d) level.

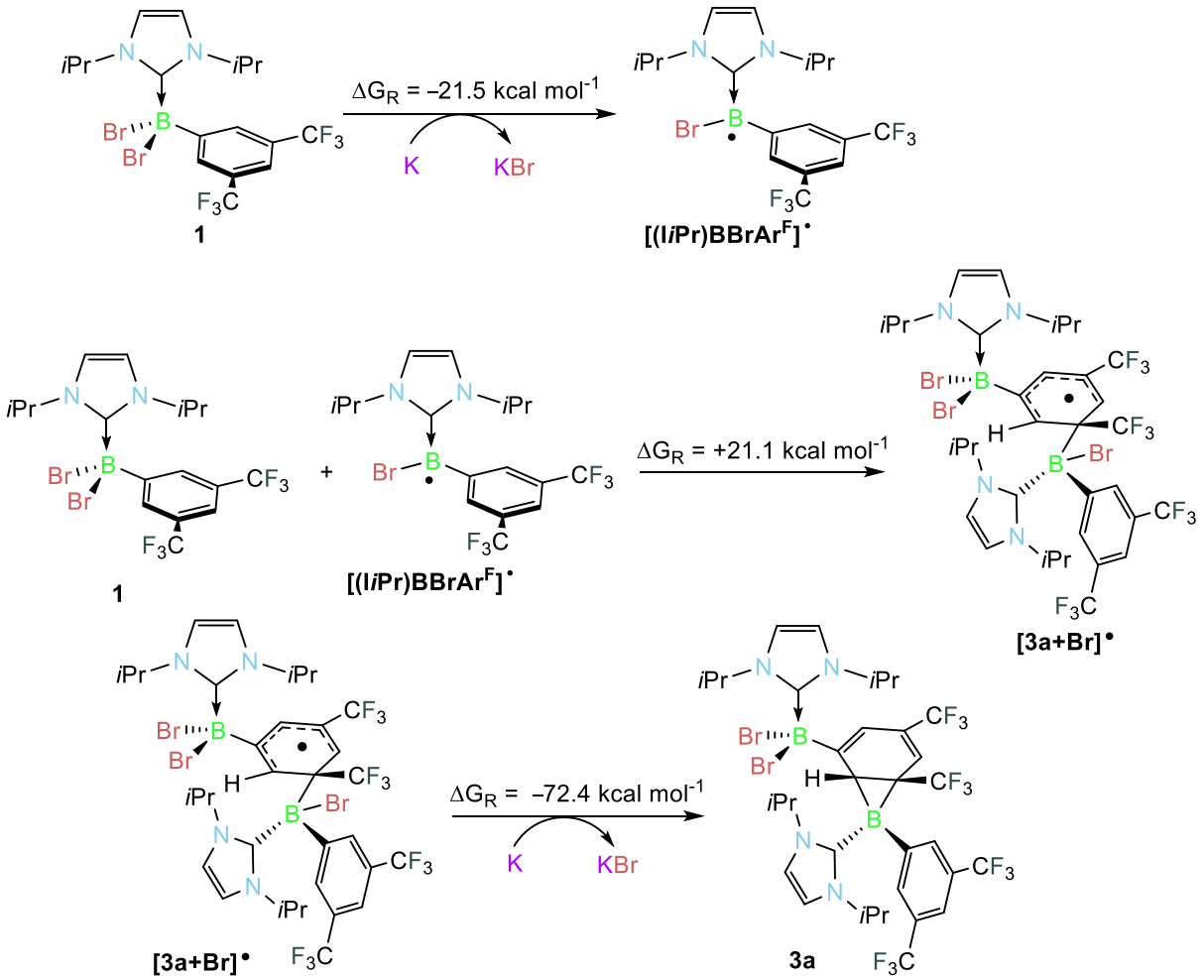


Figure S59. Boryl-radical-based reaction mechanism of the conversion from **1** to borirane-borane **3a** calculated at the (SMD:benzene)ω-B97XD/(6-311G(d,p),LANL08d) level.

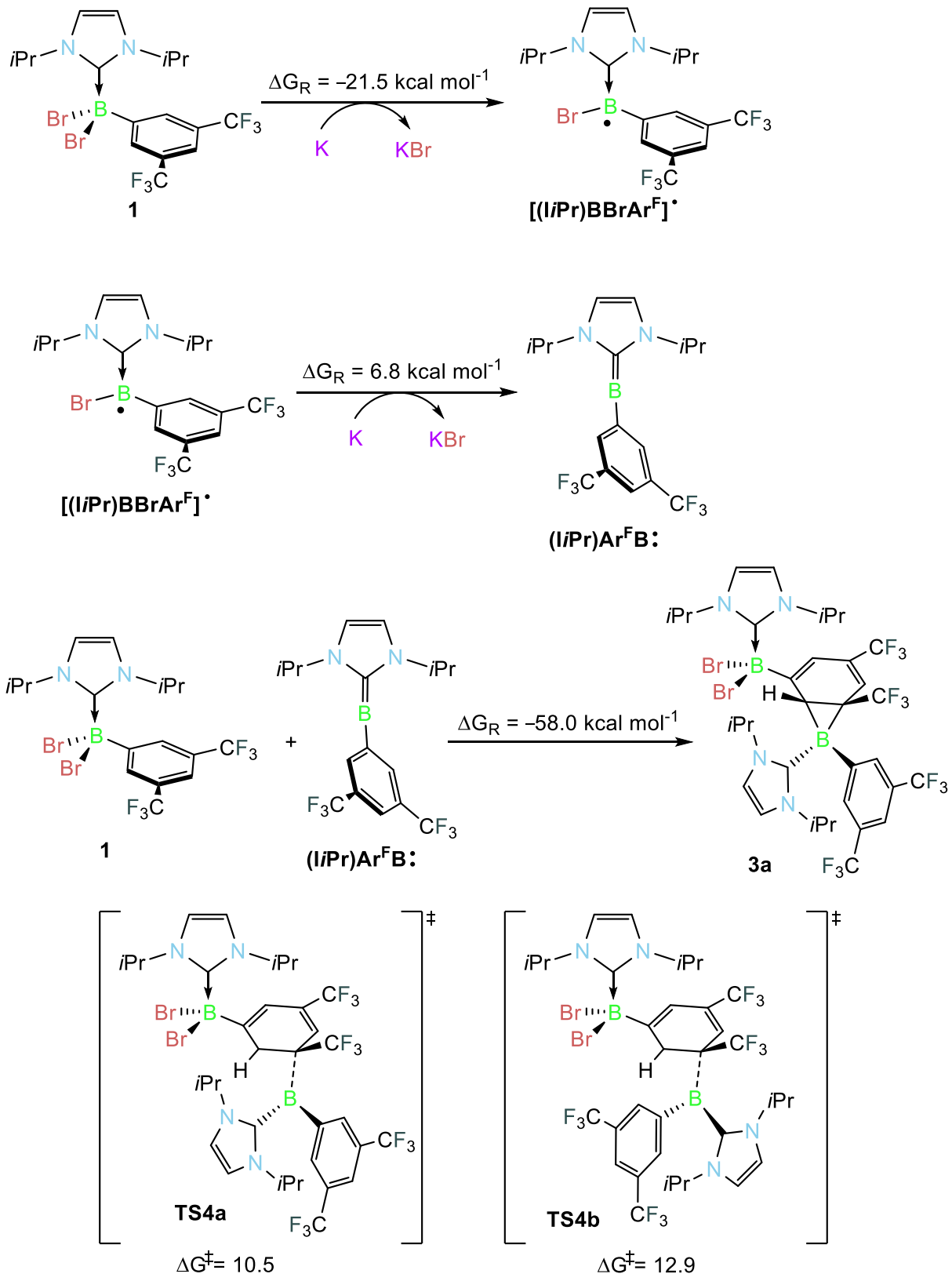


Figure S60. Borylene-based reaction mechanism of the conversion from **1** to borirane-borane **3a** calculated at the (SMD:benzene)ω-B97XD/(6-311G(d,p),LANL08d) level.

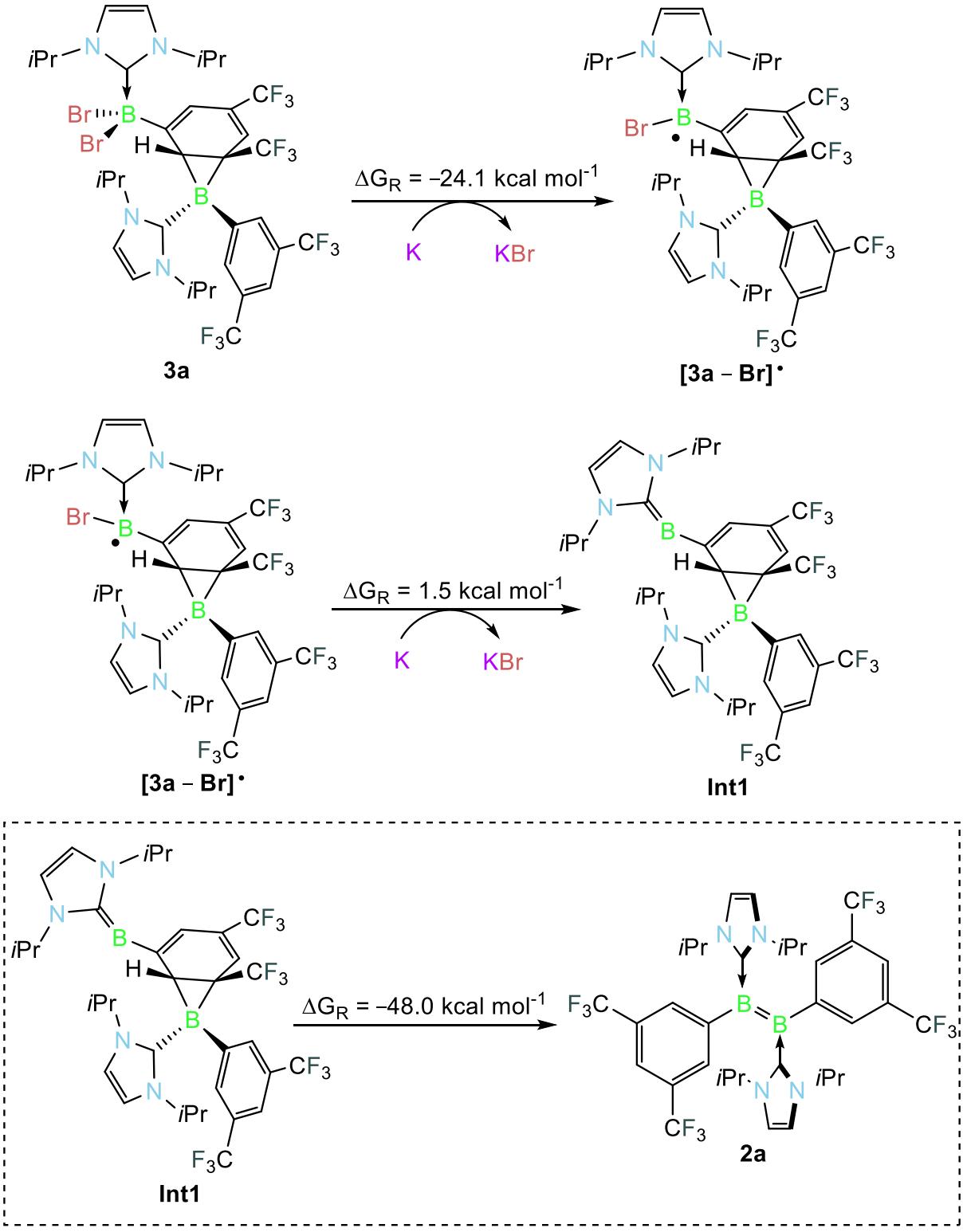


Figure S61. Reaction mechanism of the conversion of **3a** to **2a** via generation of dicoordinate borylene **Int1** calculated at the (SMD:benzene)ω-B97XD/(6-311G(d,p),LANL08d) level. See the complete reaction mechanism of the route from **Int1** to **2a** in Figure 3 in the manuscript.

Table S1. Cartesian coordinates (x-y-z format) of the optimized geometry of **2a** calculated at the OLYP/ZORA/TZ2P level.

N 2.308692 5.345798 6.607220
N 1.143979 5.800032 4.828538
N 2.686704 -0.186254 3.802662
N 4.598650 0.659105 4.399921
C 3.540741 4.073188 3.293552
C 3.565274 3.308327 2.100949
C 4.323112 3.668019 0.985453
C 5.113950 4.823166 0.995202
C 5.107763 5.607481 2.152250
C 4.336835 5.245474 3.259479
C 4.315577 2.770572 -0.229428
C 5.914015 6.883147 2.215561
C 2.054660 4.898138 5.331326
C 1.575405 6.486185 6.878191
C 0.846330 6.768655 5.767796
C 3.317886 4.766385 7.528076
C 4.559032 5.664300 7.618057
C 2.717512 4.458755 8.902961
C 0.504962 5.703715 3.492827
C -1.007720 5.479014 3.611010
C 0.852547 6.915349 2.620981
C 1.526140 1.684933 6.302983
C 0.276068 2.299858 6.560452
C -0.546522 1.926641 7.624440
C -0.171672 0.898562 8.497334
C 1.050493 0.259643 8.266250
C 1.868176 0.642247 7.200912
C -1.892176 2.593517 7.785268
C 1.529807 -0.819977 9.207603
C 3.244578 0.899150 4.440040
C 3.668460 -1.062596 3.381243
C 4.862619 -0.535409 3.755829

C 1.237452 -0.360837 3.534951

C 0.687728 -1.605332 4.240805

C 0.941808 -0.360906 2.029884

C 5.631329 1.494646 5.062012

C 6.760333 1.869548 4.097570

C 6.151343 0.817526 6.337209

B 2.684408 3.647259 4.567031

B 2.467712 2.128075 5.098237

H 2.948255 2.419261 2.045695

H 5.701911 5.106307 0.131295

H 4.366227 5.891827 4.132380

H 1.617850 7.003071 7.824145

H 0.142523 7.566875 5.589774

H 3.589973 3.826658 7.040015

H 5.313538 5.178372 8.245707

H 4.330027 6.636279 8.068403

H 5.001229 5.837527 6.633581

H 3.446791 3.894295 9.492796

H 1.813623 3.853908 8.817984

H 2.478756 5.368388 9.465231

H 0.953854 4.809852 3.054255

H -1.423791 5.313732 2.611880

H -1.521878 6.343645 4.043719

H -1.238198 4.602510 4.220977

H 0.466057 6.755128 1.609278

H 1.932407 7.059853 2.550583

H 0.402167 7.837945 3.003740

H -0.063035 3.080321 5.889472

H -0.811352 0.601561 9.319089

H 2.808825 0.115664 7.067572

H 3.455157 -1.974043 2.844594

H 5.860823 -0.916100 3.605913

H 0.782700 0.528573 3.976585

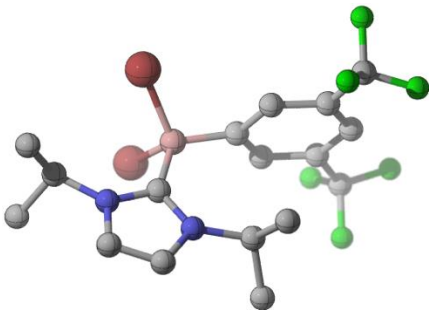
H -0.400212 -1.636647 4.122745

H 1.092697 -2.529862 3.814405

H 0.910830 -1.589269 5.309322
H -0.142040 -0.394209 1.878734
H 1.321829 0.540710 1.544188
H 1.372082 -1.231581 1.523849
H 5.081696 2.399178 5.335811
H 7.409318 2.608097 4.579002
H 7.386001 1.009294 3.834908
H 6.371739 2.310867 3.178814
H 6.857121 1.486391 6.841044
H 5.338867 0.598642 7.034855
H 6.679054 -0.117287 6.118994
F 5.123614 1.670626 -0.054954
F 3.067918 2.281533 -0.510826
F 4.755001 3.393428 -1.359068
F 5.108257 7.996631 2.229265
F 6.676486 6.955814 3.353132
F 6.766006 7.035084 1.164442
F -2.829969 2.064625 6.930870
F -1.846606 3.935165 7.513776
F -2.402982 2.467445 9.043210
F 2.472406 -0.345828 10.089091
F 2.122478 -1.862612 8.545637
F 0.529983 -1.354837 9.963195

Table S2. Cartesian coordinates (x-y-z format) of the optimized geometries for all the species involved in the reaction mechanisms calculated at the ω-B97XD/6-31G(d) level.

1 **Boryl radical [(I*i*Pr)BBrAr^{F}]$^{\bullet}$**



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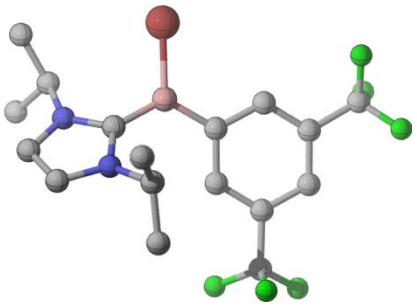
C	0.573682	-0.121318	-0.604477
Br	-1.703385	1.243632	-1.938107
N	-3.106761	0.261249	0.981957
C	1.365359	-1.266236	-0.473057
H	0.892185	-2.242860	-0.494776
C	2.742357	-1.177768	-0.282171
C	3.374609	0.058005	-0.232517
H	4.443126	0.127156	-0.068016
C	2.606885	1.204689	-0.403795
C	1.233599	1.113893	-0.601906
H	0.656629	2.024014	-0.735990
C	3.521907	-2.438457	-0.027192
C	3.254414	2.562054	-0.393394
C	-1.769472	0.132195	0.810372
C	-2.217579	0.592049	2.957191
H	-2.002915	0.784131	3.995225
C	-3.392481	0.550353	2.295607
H	-4.400547	0.698028	2.646574
C	0.190633	0.228055	2.459750
H	0.734893	-0.146247	1.602359
C	0.728891	1.607619	2.821883
H	1.788912	1.524725	3.078902
H	0.202238	2.033760	3.683163
H	0.641049	2.297822	1.979180
C	0.340009	-0.796033	3.582151



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B	-1.012768	0.755274	0.105117
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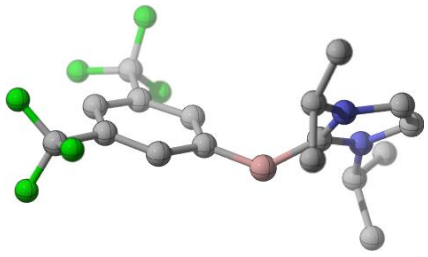
C	0.480710	0.421594	-0.070116
Br	-1.557307	2.632087	0.335997
N	-3.346912	-0.289937	-0.476849
C	0.894453	-0.857415	-0.500238
H	0.145359	-1.600793	-0.755164
C	2.233541	-1.198079	-0.621846
C	3.231697	-0.263330	-0.363083
H	4.278560	-0.524339	-0.461986
C	2.848262	1.022549	0.017018
C	1.510706	1.359379	0.163726
H	1.246319	2.365991	0.470993
C	2.598173	-2.615340	-0.959984
C	3.909134	2.070690	0.218139
C	-2.126026	-0.316486	0.136460
C	-3.277048	-2.189641	0.629760
H	-3.465771	-3.148634	1.084308
C	-4.059117	-1.430038	-0.166775
H	-5.049050	-1.612633	-0.551782
C	-1.109378	-1.871201	1.851363
H	-0.289075	-1.163720	1.737289
C	-1.728661	-1.676720	3.234790
H	-0.973796	-1.857233	4.005818
H	-2.558286	-2.372584	3.402339
H	-2.101113	-0.654355	3.347842
C	-0.577874	-3.284579	1.634138
H	0.202373	-3.493392	2.371260

H	1.404943	-0.961846	3.767726
H	-0.109646	-1.751696	3.298301
H	-0.113306	-0.458127	4.520281
C	-4.179269	0.072870	-0.023490
H	-3.681248	-0.159575	-0.960357
C	-5.039657	-1.123027	0.369990
H	-5.795318	-1.290747	-0.402850
H	-5.559752	-0.966075	1.321555
H	-4.417646	-2.019464	0.443005
C	-4.952169	1.374506	-0.199467
H	-5.701709	1.245180	-0.985459
H	-4.268252	2.171377	-0.503239
H	-5.473693	1.674614	0.716405
F	3.339887	-2.867409	1.239204
F	3.136542	-3.436950	-0.834677
F	4.842353	-2.263777	-0.196090
F	2.501823	3.457798	0.276793
F	3.423178	3.046996	-1.632914
F	4.462277	2.539589	0.194843
H	-0.138604	-3.403986	0.641031
H	-1.364326	-4.037136	1.761976
C	-3.820214	0.742370	-1.412840
H	-2.948370	1.363061	-1.623788
C	-4.293994	0.107854	-2.718588
H	-4.499366	0.897212	-3.447320
H	-5.218804	-0.464216	-2.585653
H	-3.528682	-0.553999	-3.134156
C	-4.887885	1.604984	-0.745910
H	-5.208910	2.394642	-1.431883
H	-4.480814	2.072030	0.154107
H	-5.767360	1.008868	-0.475918
F	2.658325	-3.382963	0.149969
F	1.690058	-3.192692	-1.769379
F	3.792926	-2.708666	-1.562752
F	3.524507	3.021572	1.084556
F	4.214573	2.691017	-0.936509
F	5.052909	1.539264	0.688015

Borylene (I*i*Pr)Ar^{F}B:



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C	-0.314901	-0.115469	-0.515052
N	3.348130	0.780095	-0.172083
C	-0.759660	1.123330	-0.009234
H	-0.039974	1.913248	0.188733
C	-2.104169	1.358698	0.247765
C	-3.048220	0.349980	0.083946

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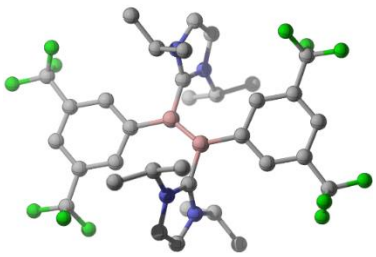

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N	0.234019	-3.007167	-0.612781
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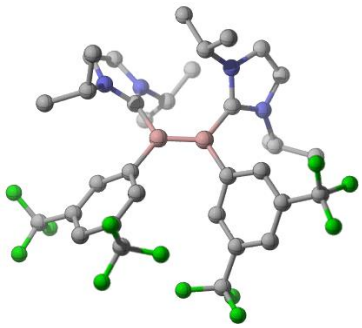
B	0.589733	-0.511478	0.144258
N	-0.419740	-2.597909	1.396959
C	2.729842	1.029970	0.285630
H	2.094953	1.901826	0.379895
C	4.101479	1.241026	0.269378
C	4.995696	0.176410	0.192360

H	-4.092668	0.526585	0.311103	H	6.065743	0.339534	0.175349
C	-2.622915	-0.891476	-0.382643	C	4.460053	-1.105812	0.152953
C	-1.293146	-1.111084	-0.714412	C	3.084487	-1.310121	0.171018
H	-0.999289	-2.066814	-1.136674	H	2.725743	-2.336615	0.148016
C	-2.520380	2.689608	0.812745	C	4.596465	2.658212	0.290727
C	-3.645668	-1.969410	-0.619397	C	5.358144	-2.309942	0.129827
C	2.405349	-0.216169	-0.069430	C	0.177903	-2.032376	0.324199
C	4.295662	-0.842374	0.997278	C	-0.353926	-4.164401	-0.140276
H	4.935045	-1.462769	1.603165	H	-0.436808	-5.061433	-0.731581
C	4.524007	0.366075	0.450809	C	-0.757994	-3.907656	1.126008
H	5.400610	0.991797	0.493191	H	-1.264608	-4.537972	1.837630
C	2.312857	-2.461397	0.990026	C	0.702066	-2.774872	-1.988367
H	1.250969	-2.216458	1.120347	H	1.319684	-1.876050	-1.919496
C	2.464700	-3.404341	-0.206177	C	1.567670	-3.933551	-2.468989
H	1.882705	-4.317880	-0.050694	H	1.984996	-3.687935	-3.449622
H	3.516789	-3.679300	-0.340154	H	0.993799	-4.860261	-2.580374
H	2.113920	-2.916866	-1.122951	H	2.399808	-4.111727	-1.781723
C	2.815500	-3.082480	2.288608	C	-0.491102	-2.471890	-2.891215
H	2.202419	-3.953897	2.535055	H	-0.152076	-2.318781	-3.920757
H	2.755589	-2.370885	3.117358	H	-0.989444	-1.560365	-2.547083
H	3.850548	-3.428936	2.192399	H	-1.215951	-3.293225	-2.883904
C	3.232709	1.862445	-1.150246	C	-0.669901	-1.867590	2.650457
H	2.157152	2.031827	-1.275394	H	-0.805352	-0.831660	2.326247
C	3.849068	3.151397	-0.617031	C	-1.943409	-2.360293	3.325064
H	3.657764	3.967723	-1.319440	H	-2.199887	-1.677926	4.140390
H	4.935524	3.061186	-0.508012	H	-1.818265	-3.357798	3.762769
H	3.421974	3.417489	0.354133	H	-2.779022	-2.382996	2.620616
C	3.818109	1.424031	-2.492922	C	0.563177	-1.947722	3.545867
H	3.658794	2.196149	-3.252032	H	0.396883	-1.376756	4.464915
H	3.331960	0.500934	-2.823183	H	1.434447	-1.530865	3.031197
H	4.895428	1.246995	-2.399511	H	0.780428	-2.986294	3.820227
F	-2.289672	2.758813	2.137393	F	4.403846	3.271949	-0.900990
F	-1.840122	3.704111	0.248981	F	3.946879	3.406293	1.203685
F	-3.828256	2.931209	0.628313	F	5.907600	2.746389	0.561733
F	-3.100531	-3.197535	-0.584005	F	5.350250	-2.959999	1.309069

F	-4.238460	-1.836677	-1.819602	F	4.964996	-3.207099	-0.800022
F	-4.623553	-1.937753	0.303113	F	6.635565	-1.996338	-0.140169
				N	-0.234032	3.007194	0.612661
				C	-2.149271	0.253997	-0.209371
				B	-0.589675	0.511453	-0.144235
				N	0.419726	2.597850	-1.397059
				C	-2.729781	-1.030018	-0.285425
				H	-2.094898	-1.901889	-0.379622
				C	-4.101425	-1.241054	-0.269134
				C	-4.995630	-0.176422	-0.192224
				H	-6.065678	-0.339535	-0.175180
				C	-4.459975	1.105800	-0.152936
				C	-3.084411	1.310091	-0.171037
				H	-2.725652	2.336583	-0.148125
				C	-4.596414	-2.658238	-0.290425
				C	-5.358051	2.309942	-0.129908
				C	-0.177871	2.032347	-0.324259
				C	0.353801	4.164445	0.140063
				H	0.436658	5.061513	0.731315
				C	0.757874	3.907646	-1.126209
				H	1.264461	4.537941	-1.837870
				C	-0.702098	2.774960	1.988256
				H	-1.319398	1.875912	1.919492
				C	-1.568159	3.933405	2.468621
				H	-1.985457	3.687801	3.449269
				H	-0.994643	4.860350	2.579886
				H	-2.400319	4.111149	1.781267
				C	0.491110	2.472544	2.891239
				H	0.152072	2.319473	3.920783
				H	0.989786	1.561139	2.547273
				H	1.215669	3.294133	2.883847
				C	0.669860	1.867494	-2.650535
				H	0.805354	0.831580	-2.326284
				C	1.943322	2.360206	-3.325227
				H	2.199809	1.677786	-4.140505

H	1.818109	3.357669	-3.763010
H	2.778964	2.383019	-2.620817
C	-0.563255	1.947562	-3.545901
H	-0.396957	1.376632	-4.464970
H	-1.434484	1.530645	-3.031210
H	-0.780579	2.986128	-3.820229
F	-4.403401	-3.272068	0.901184
F	-3.947112	-3.406240	-1.203648
F	-5.907633	-2.746410	-0.561013
F	-5.350213	2.959851	-1.309232
F	-4.964838	3.207208	0.799806
F	-6.635460	1.996383	0.140198

Diborene 2b



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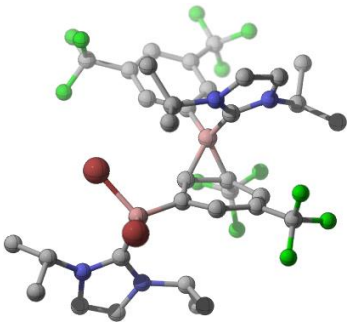
B	0.795535	0.929083	-0.053037
N	2.681534	2.518316	-0.967375
C	1.267628	-1.534000	-0.848217
H	0.343896	-1.485787	-1.416518
C	1.998822	-2.715434	-0.846195
C	3.199384	-2.812456	-0.148267
H	3.772058	-3.731484	-0.152187
C	3.636815	-1.699017	0.557928
C	2.880783	-0.529280	0.580407
H	3.246718	0.311462	1.166860

Borirane-borane 3a



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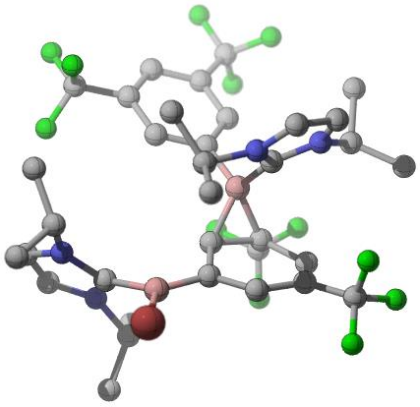
Br	-4.048745	0.054670	-1.633794
F	1.543023	-4.751083	0.066741
B	1.266571	0.524433	-0.027948
N	2.334498	2.359406	-1.623180
C	2.363737	-0.617020	0.230201
Br	-1.714071	-2.246359	-0.906638
F	3.638703	-5.228189	-0.202110
B	-2.602825	-0.477505	-0.292153
N	1.061295	0.954204	-2.638154
C	2.081068	-1.943032	-0.113498
H	1.074009	-2.204348	-0.429257
F	2.500714	-4.365466	-1.829033

C	1.494636	-3.875910	-1.657741	N	-4.294445	-1.868778	1.229737
C	4.961040	-1.711868	1.262709	C	3.050102	-2.940239	-0.037567
C	1.693336	2.226354	-0.072288	F	5.944073	-0.722891	2.640975
C	2.673844	4.192085	0.452402	N	-3.464210	-0.150252	2.243177
H	2.848767	5.093413	1.017378	C	4.334676	-2.649517	0.405240
C	3.287469	3.717032	-0.653164	H	5.091585	-3.422031	0.457130
H	4.092205	4.130271	-1.239772	F	6.883559	-1.957501	1.132726
C	0.918534	3.345725	2.039964	C	4.622826	-1.345099	0.788947
H	0.241748	2.488874	1.973621	C	3.650891	-0.351489	0.706198
C	1.839572	3.156670	3.243284	H	3.902092	0.650065	1.042344
H	1.249101	3.143715	4.164916	F	6.461962	0.128443	0.726714
H	2.574522	3.965582	3.324299	F	0.313162	1.817245	3.484209
H	2.374820	2.205629	3.166134	C	2.687403	-4.325486	-0.493971
C	0.118401	4.642656	2.098913	F	1.372712	0.018923	2.930467
H	-0.499846	4.657963	3.001400	C	5.979746	-0.982944	1.322651
H	-0.540661	4.738454	1.231853	C	1.527630	1.292759	-1.420005
H	0.773507	5.521198	2.137351	F	2.328178	1.957713	2.722561
C	3.037728	1.700167	-2.136874	C	2.358274	2.689970	-2.960705
H	2.384813	0.829047	-2.082585	H	2.933372	3.518490	-3.340379
C	2.737528	2.456085	-3.429121	F	-2.467912	4.662990	-0.221623
H	2.999504	1.831493	-4.288199	C	1.558150	1.805068	-3.598129
H	3.314241	3.385345	-3.499854	H	1.298598	1.710252	-4.639747
H	1.673733	2.699854	-3.498205	F	-0.449269	5.331650	0.182888
C	4.489642	1.239340	-2.045637	C	3.156195	3.033702	-0.604682
H	4.709635	0.559606	-2.874000	H	2.839574	2.607889	0.347490
H	4.674691	0.704214	-1.111402	F	-0.971906	4.577065	-1.777519
H	5.185718	2.083887	-2.111877	C	0.208600	-0.210778	-2.915634
F	0.174502	-4.064096	-1.495247	H	-0.127915	-0.540106	-1.938356
F	1.694675	-3.676232	-2.977545	C	2.880987	4.534991	-0.596631
F	2.107874	-5.028516	-1.340027	H	3.257471	5.017364	-1.505570
F	5.889494	-1.009455	0.571358	H	3.395773	4.990349	0.254539
F	4.891416	-1.142804	2.480584	H	1.813869	4.745291	-0.507629
F	5.453378	-2.949120	1.425673	C	4.632460	2.716789	-0.838257
N	-2.646997	2.558958	0.970568	H	4.988664	3.168554	-1.770893
C	-1.680874	-0.376730	0.111703	H	4.806585	1.639368	-0.885911

B	-0.789486	0.942361	0.046646	H	5.230640	3.122461	-0.016967
N	-1.645734	3.313074	-0.786434	C	-1.010492	0.177052	-3.741448
C	-1.300175	-1.507570	0.857137	H	-1.725557	-0.649534	-3.709916
H	-0.378344	-1.467103	1.429220	H	-0.752253	0.373490	-4.788879
C	-2.047885	-2.678115	0.862591	H	-1.504283	1.053964	-3.316512
C	-3.246337	-2.764735	0.158668	C	0.644973	1.426633	1.163042
H	-3.832934	-3.674717	0.168600	C	1.025097	-1.334153	-3.545562
C	-3.663475	-1.652292	-0.559854	H	0.398074	-2.228373	-3.612336
C	-2.890780	-0.492948	-0.589114	H	1.897716	-1.580763	-2.933844
H	-3.242703	0.347848	-1.184603	H	1.362928	-1.071599	-4.554953
C	-1.564623	-3.837925	1.687608	C	0.172266	2.775592	0.852897
C	-4.966950	-1.656027	-1.302521	H	0.643749	3.613602	1.357903
C	-1.664291	2.254597	0.073072	C	-0.803450	2.995370	-0.051720
C	-3.228114	3.772534	0.667034	C	-1.644939	1.921875	-0.557492
H	-4.024437	4.196809	1.257226	H	-2.527965	2.199011	-1.123660
C	-2.604385	4.244964	-0.433840	C	-1.467098	0.643949	-0.151609
H	-2.760631	5.154838	-0.990537	C	-0.207634	0.270437	0.527204
C	-3.020680	1.738473	2.132709	H	-0.269450	-0.620345	1.151587
H	-2.382020	0.857258	2.074564	C	1.156292	1.286925	2.559192
C	-4.479547	1.302013	2.032084	C	-1.168427	4.386393	-0.456413
H	-4.713300	0.616901	2.852219	C	-3.437733	-0.832411	1.071984
H	-5.161943	2.157121	2.105240	C	-4.832135	-1.848139	2.495162
H	-4.669467	0.780886	1.090847	H	-5.528894	-2.595743	2.836595
C	-2.713150	2.479790	3.431626	C	-4.319096	-0.771696	3.127466
H	-2.986522	1.852166	4.284930	H	-4.485421	-0.405182	4.125368
H	-1.646035	2.707345	3.505377	C	-4.757706	-2.835461	0.207467
H	-3.276342	3.416781	3.508562	H	-4.233869	-2.585069	-0.710269
C	-0.868924	3.377354	-2.030486	C	-6.250257	-2.633871	-0.035696
H	-0.212878	2.503714	-1.975552	H	-6.438417	-1.600413	-0.339688
C	-0.038435	4.655662	-2.076428	H	-6.852856	-2.865645	0.849471
H	0.577030	4.667852	-2.980867	H	-6.573078	-3.295866	-0.844423
H	-0.672751	5.549844	-2.101541	C	-4.374147	-4.251243	0.618865
H	0.625541	4.725197	-1.210751	H	-4.869091	-4.557576	1.547373
C	-1.796580	3.225735	-3.234142	H	-3.291077	-4.321388	0.749831
H	-1.208339	3.210483	-4.157152	H	-4.672758	-4.950619	-0.167273

H	-2.354581	2.286988	-3.168248
H	-2.511948	4.053083	-3.303050
F	-1.775686	-3.626922	3.004039
F	-0.244992	-4.040960	1.539586
F	-2.186826	-4.986250	1.371934
F	-4.813518	-1.295349	-2.590278
F	-5.838546	-0.769859	-0.765771
F	-5.571620	-2.853275	-1.291367
C	-2.920087	1.209684	2.484874
H	-1.955729	1.248173	1.987829
C	-3.866711	2.231687	1.859776
H	-4.804842	2.283985	2.424434
H	-4.096641	1.966647	0.824328
H	-3.397636	3.218868	1.859762
C	-2.687208	1.460293	3.968843
H	-3.624456	1.545081	4.529363
H	-2.159638	2.410880	4.070234
H	-2.061516	0.683577	4.416516

Borirane-boryl radical [3a – Br]•



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Br	-4.671672	-0.084552	0.602611
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B	0.822357	-0.736226	-0.017111
N	1.636078	-2.620511	1.651221
C	1.893092	0.457610	0.001191
F	2.800997	5.089181	0.926223
B	-2.925841	0.230915	-0.262131
N	0.119223	-1.331522	2.466969
C	1.487554	1.738341	0.386963
H	0.432101	1.916203	0.584738
F	1.435434	4.058644	2.253087
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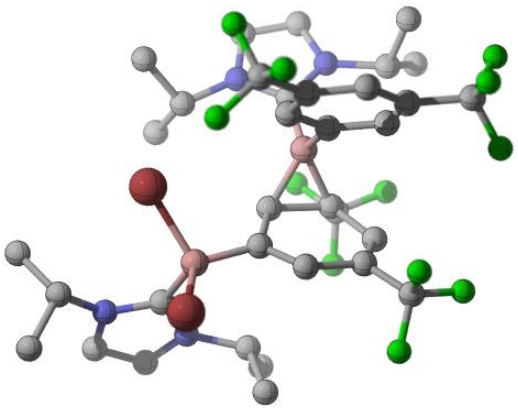
C	2.389845	2.792426	0.509807

Borirane-borane 3b



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Br	-2.936195	-2.588844	-0.762861
F	1.928606	-3.031703	3.799777
B	1.115429	1.112291	0.349186
N	2.618260	2.908840	1.556283
C	1.971924	-0.234672	0.497651
Br	-2.093789	-0.871035	1.944526
F	2.330550	-4.626714	2.393596
B	-2.320998	-0.753916	-0.109783
N	0.733059	2.591963	2.541045
C	1.533506	-1.237455	1.368414
H	0.578983	-1.121021	1.872551
F	0.407826	-3.628292	2.388892
N	-4.812749	0.181408	0.159062

F	5.769593	0.867678	-1.826886	C	2.247592	-2.418055	1.546921
N	-2.345167	2.013357	-2.058866	F	6.068235	-0.932980	-0.449684
C	3.739762	2.601457	0.241322	N	-3.726795	1.091056	-1.473794
H	4.448187	3.414192	0.344004	C	3.429899	-2.642844	0.850962
F	6.400453	2.105138	-0.167287	H	3.984444	-3.563914	0.981500
C	4.159393	1.341884	-0.171490	F	5.688516	-3.055201	-0.652882
C	3.249337	0.295609	-0.295893	C	3.869341	-1.669291	-0.036299
H	3.604911	-0.665495	-0.656727	C	3.147557	-0.491071	-0.209480
F	6.061427	-0.015431	0.120989	H	3.508775	0.231741	-0.936002
F	0.394544	-1.681656	-3.726199	F	4.937636	-1.665325	-2.135842
C	1.875062	4.122273	0.975823	F	-0.197581	3.398836	-2.440216
F	1.529576	-0.075069	-2.838851	C	1.726933	-3.432681	2.526388
C	5.600459	1.083035	-0.511485	F	0.233251	3.849312	-0.374600
C	0.836161	-1.573849	1.350537	C	5.137737	-1.843340	-0.819036
F	2.268079	-2.111833	-2.729146	C	1.461892	2.211440	1.470982
C	1.410625	-3.038569	2.944060	F	1.848287	3.648213	-1.809965
H	1.933130	-3.872840	3.382433	C	2.608348	3.720451	2.669291
F	-2.810672	-4.951552	-0.387448	H	3.436711	4.359371	2.927606
C	0.458478	-2.227794	3.457297	F	0.283210	-1.535850	-4.495216
H	-0.009112	-2.220889	4.427950	C	1.420226	3.526228	3.284459
F	-0.758892	-5.537864	-0.750628	H	1.009575	3.964591	4.179347
C	2.653058	-3.208183	0.764072	F	2.210880	-0.555645	-4.370252
H	2.481744	-2.746064	-0.208765	C	3.757207	2.790832	0.630087
F	-1.350352	-4.814699	1.199512	H	3.352999	2.272668	-0.239183
C	-0.863712	-0.249162	2.643046	F	1.824909	-2.347991	-3.218567
H	-1.040204	0.138454	1.639283	C	-0.607505	2.097527	2.878743
C	2.451533	-4.716421	0.643391	H	-0.799998	1.293326	2.175806
H	2.707351	-5.231861	1.576103	C	4.865314	1.957077	1.267568
H	3.109250	-5.105772	-0.139086	H	5.322920	2.492892	2.107145
H	1.419541	-4.959275	0.384028	H	5.643104	1.744322	0.529081
C	4.050355	-2.845841	1.264238	H	4.475947	1.002608	1.629173
H	4.254588	-3.316827	2.232500	C	4.234012	4.170605	0.186860
H	4.169074	-1.764942	1.373226	H	4.705730	4.722201	1.007577
H	4.800102	-3.201247	0.551064	H	3.405434	4.759244	-0.211750
C	-2.173910	-0.813968	3.181837	H	4.983249	4.052237	-0.601005

H	-2.959115	-0.056592	3.115977	C	-0.629927	1.498501	4.279457
H	-2.082879	-1.118258	4.231091	H	-1.595615	1.009313	4.435197
H	-2.492332	-1.668397	2.580100	H	-0.501442	2.256955	5.060363
C	0.432695	-1.573527	-1.355312	H	0.152030	0.741088	4.387193
C	-0.278645	0.849346	3.526846	C	0.766352	1.657883	-1.142154
H	-1.012820	1.653104	3.641561	C	-1.649331	3.190893	2.668462
H	0.629284	1.274293	3.088844	H	-2.648375	2.757119	2.775476
H	-0.040135	0.469949	4.526981	H	-1.560017	3.620244	1.666468
C	-0.047466	-2.951476	-1.173301	H	-1.546753	3.997898	3.403575
H	0.564750	-3.763899	-1.550937	C	1.185571	0.881188	-2.312822
C	-1.204069	-3.214153	-0.511819	H	1.871088	1.341333	-3.017730
C	-2.148135	-2.195167	-0.150783	C	0.762969	-0.380122	-2.501582
H	-3.119634	-2.497427	0.228529	C	-0.301469	-0.965352	-1.701831
C	-1.905934	-0.858390	-0.428111	H	-0.674357	-1.938904	-2.000623
C	-0.521049	-0.481259	-0.830386	C	-0.932870	-0.268983	-0.733133
H	-0.442593	0.446647	-1.393135	C	-0.359775	1.022274	-0.259208
C	1.142161	-1.353793	-2.646725	H	-1.102219	1.745484	0.084516
C	-1.533351	-4.623001	-0.130524	C	0.659684	3.116743	-1.428151
C	-2.677799	1.683616	-0.784067	C	1.278104	-1.195982	-3.643988
C	-2.433265	3.906751	-0.946993	C	-3.607763	0.200109	-0.456538
H	-2.396807	4.929017	-0.608652	C	-5.666005	1.076486	-0.443693
C	-2.193136	3.378160	-2.169118	H	-6.673952	1.234086	-0.096827
H	-1.921606	3.857538	-3.095073	C	-4.991391	1.639715	-1.467999
C	-3.044506	2.985716	1.327500	H	-5.303030	2.381167	-2.182654
H	-2.960552	1.970630	1.724506	C	-5.283843	-0.762418	1.197939
C	-4.483050	3.465786	1.497405	H	-4.466355	-1.455935	1.371453
H	-5.170689	2.758170	1.028358	C	-6.459706	-1.569876	0.656912
H	-4.620912	4.456510	1.049658	H	-6.161380	-2.081000	-0.262874
H	-4.727291	3.534943	2.561793	H	-7.343282	-0.953494	0.458531
C	-2.031238	3.880116	2.033366	H	-6.738683	-2.327142	1.395082
H	-2.098211	4.920572	1.698353	C	-5.572562	-0.010756	2.490324
H	-1.007646	3.535729	1.875706	H	-6.359694	0.741203	2.362499
H	-2.235770	3.871292	3.108258	H	-4.658543	0.478182	2.838450
C	-2.379143	1.072561	-3.198094	H	-5.898944	-0.717363	3.258771
H	-2.225128	0.085219	-2.762027	C	-2.786130	1.265713	-2.612689

C	-3.764517	1.116112	-3.838513
H	-3.973463	2.105559	-4.260858
H	-4.533244	0.877111	-3.097150
H	-3.821504	0.378858	-4.644706
C	-1.248628	1.356072	-4.178505
H	-1.392280	2.304424	-4.708714
H	-1.222503	0.559011	-4.925635
H	-0.279453	1.368402	-3.675087
H	-1.787017	1.250115	-2.189429
C	-2.946840	0.096577	-3.581458
H	-3.902044	0.165863	-4.114877
H	-2.910754	-0.858749	-3.052234
H	-2.131383	0.110260	-4.309731
C	-2.986558	2.614951	-3.290138
H	-3.932617	2.669344	-3.839842
H	-2.180959	2.750375	-4.014756
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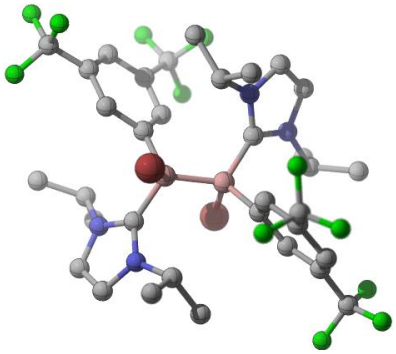
Diborane ($I\mathit{i}Pr)_2B_2Br_2Ar^F{}_2$



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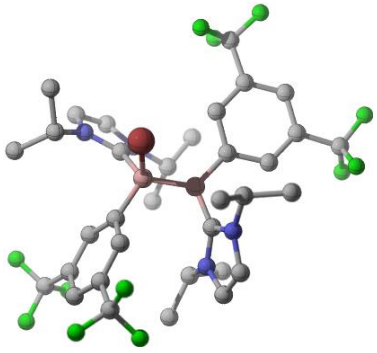
C	2.183262	0.143762	0.115533
B	0.604378	0.415856	-0.173420
N	0.631155	3.024368	0.591846
C	3.228140	0.616598	-0.682525
H	2.998942	1.108605	-1.622818
C	4.564970	0.448085	-0.329933
C	4.916364	-0.227840	0.829518
H	5.955651	-0.366228	1.100680
C	3.893961	-0.730557	1.627021
C	2.560356	-0.541333	1.280956
H	1.794117	-1.003783	1.894263
C	5.612426	0.978836	-1.265595
C	4.213718	-1.554304	2.842706
C	0.268724	1.729341	0.801369

Diboranyl radical $[(I\mathit{i}Pr)_2B_2BrAr^F{}_2]^\bullet$



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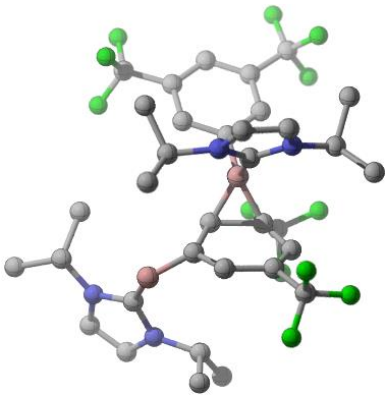
B	-0.447930	-0.709571	-0.490642
N	-0.741143	-3.372516	-0.575717
C	-2.559701	0.784216	-1.009090
H	-1.947536	1.322912	-1.724319
C	-3.849749	1.224060	-0.754340
C	-4.671285	0.553146	0.153162
H	-5.680455	0.896442	0.348303
C	-4.154388	-0.552209	0.806664
C	-2.847703	-0.976271	0.560007
H	-2.480728	-1.840819	1.109248
C	-4.340230	2.507519	-1.360499
C	-4.946640	-1.293077	1.842231
C	-0.251326	-2.252937	0.010514

C	-0.424990	3.019868	2.509651	C	0.278474	-4.054767	1.241157
H	-0.902299	3.240587	3.449712	H	0.714846	-4.598792	2.062482
C	0.190465	3.824599	1.622852	C	-0.403875	-4.487346	0.159050
H	0.355231	4.889282	1.635177	H	-0.673545	-5.484578	-0.147939
C	-0.813562	0.598119	2.821140	C	0.872283	-1.842107	2.241894
H	-0.780254	-0.275074	2.180392	H	0.943301	-0.840000	1.814049
C	0.155027	0.370947	3.979547	C	-0.136826	-1.821595	3.388167
H	-0.133398	-0.541938	4.508982	H	0.224553	-1.154510	4.176802
H	0.131135	1.202921	4.692799	H	-0.272868	-2.817764	3.824886
H	1.181308	0.245768	3.627387	H	-1.114022	-1.458168	3.052991
C	-2.247951	0.806054	3.300561	C	2.258206	-2.299688	2.680782
H	-2.653079	-0.149234	3.645544	H	2.687210	-1.542535	3.343529
H	-2.885799	1.174365	2.494769	H	2.926065	-2.416571	1.824970
H	-2.299951	1.512827	4.137035	H	2.223976	-3.244289	3.236946
C	1.488583	3.588207	-0.471132	C	-1.610304	-3.443515	-1.769431
H	1.762823	2.759793	-1.110560	H	-1.795453	-2.412772	-2.063654
C	0.696075	4.581854	-1.311884	C	-0.877094	-4.145000	-2.906805
H	1.328679	4.956726	-2.121872	H	-1.506417	-4.143484	-3.801696
H	0.356006	5.441049	-0.723233	H	-0.643525	-5.186689	-2.658063
H	-0.172755	4.086998	-1.754078	H	0.047717	-3.610154	-3.136036
C	2.763982	4.162072	0.139480	C	-2.939638	-4.100641	-1.405457
H	3.448384	4.448061	-0.664066	H	-3.608897	-4.050415	-2.269339
H	3.264841	3.410434	0.756693	H	-3.423214	-3.585356	-0.570548
H	2.570689	5.050272	0.751033	H	-2.818188	-5.157537	-1.142976
F	5.599858	0.319763	-2.439850	F	-4.179709	3.535687	-0.494826
F	5.403430	2.279051	-1.553054	F	-3.681044	2.835975	-2.480323
F	6.852609	0.875811	-0.763543	F	-5.649705	2.459952	-1.657169
F	3.418975	-1.238478	3.882576	F	-5.039282	-2.606590	1.554401
F	4.036678	-2.866879	2.604475	F	-4.350828	-1.211521	3.052585
F	5.484237	-1.393272	3.248295	F	-6.193552	-0.823426	1.981242
N	-1.509070	-1.985873	-2.584960	N	0.348165	2.976066	-0.718713
C	-2.130799	-0.339482	0.041710	C	2.197485	0.346931	0.064915
B	-0.618064	-0.894725	-0.247484	B	0.657455	0.496937	0.054988
N	0.447759	-2.642197	-1.982085	N	-0.790672	2.459505	1.041251
C	-2.483530	0.981383	-0.275435	C	2.849541	-0.800425	-0.453009

H	-1.761588	1.619030	-0.772000	H	2.262022	-1.547098	-0.977553
C	-3.754129	1.490216	-0.038406	C	4.221048	-0.976614	-0.352818
C	-4.753033	0.685252	0.499590	C	5.036709	-0.010482	0.236969
H	-5.748507	1.074324	0.676175	H	6.108026	-0.149046	0.305331
C	-4.433034	-0.630337	0.804897	C	4.426999	1.144074	0.723494
C	-3.145456	-1.123569	0.599585	C	3.051207	1.310336	0.649988
H	-2.921842	-2.146068	0.887969	H	2.615294	2.214841	1.070480
C	-3.995523	2.950624	-0.287469	C	4.821607	-2.268929	-0.825581
C	-5.454747	-1.550944	1.409068	C	5.238402	2.230830	1.367087
C	-0.557485	-1.804991	-1.630834	C	0.104635	1.961273	0.150484
C	-1.101198	-2.937850	-3.497018	C	-0.389828	4.089449	-0.371388
H	-1.714126	-3.232519	-4.332627	H	-0.358090	5.004815	-0.939802
C	0.124877	-3.346711	-3.118505	C	-1.101772	3.767284	0.732656
H	0.794078	-4.069291	-3.555658	H	-1.806516	4.347667	1.304137
C	-2.731158	-1.198312	-2.840306	C	1.190909	2.875375	-1.923824
H	-2.777724	-0.453062	-2.058915	H	1.570534	1.852056	-1.917637
C	-3.970685	-2.081309	-2.749055	C	2.357429	3.854634	-1.837042
H	-4.863598	-1.467663	-2.901215	H	3.003968	3.727498	-2.710168
H	-3.969495	-2.865900	-3.514027	H	2.009637	4.894490	-1.827202
H	-4.045906	-2.551972	-1.765012	H	2.958876	3.676421	-0.942198
C	-2.598708	-0.456351	-4.168454	C	0.343130	3.058349	-3.179527
H	-3.452270	0.217151	-4.290850	H	0.983682	2.969692	-4.061967
H	-1.682810	0.140645	-4.163038	H	-0.418848	2.277328	-3.242103
H	-2.579822	-1.136443	-5.026950	H	-0.141431	4.040560	-3.209916
C	1.788032	-2.727729	-1.377887	C	-1.214054	1.731496	2.245109
H	1.751038	-2.094870	-0.499088	H	-1.256695	0.685143	1.939691
C	2.802089	-2.156548	-2.365113	C	-2.605152	2.165129	2.692124
H	3.775115	-2.041105	-1.880170	H	-2.998538	1.430817	3.400425
H	2.927962	-2.811031	-3.235468	H	-2.584993	3.139151	3.194259
H	2.465183	-1.174215	-2.708821	H	-3.292454	2.218519	1.844389
C	2.095919	-4.147053	-0.919223	C	-0.161042	1.887703	3.340127
H	3.050814	-4.146544	-0.385057	H	-0.466975	1.336764	4.235328
H	1.318208	-4.490789	-0.233028	H	0.804207	1.496996	3.000953
H	2.177363	-4.848066	-1.757651	H	-0.035730	2.941909	3.610477
F	-3.376751	3.381996	-1.400683	F	4.212231	-2.747673	-1.921991

F	-3.519682	3.697625	0.730892	F	4.713866	-3.231703	0.122150
F	-5.300497	3.241121	-0.412550	F	6.130101	-2.156654	-1.108677
F	-5.149294	-1.852096	2.684722	F	4.946099	2.365554	2.676375
F	-5.521266	-2.718364	0.740946	F	4.994026	3.433653	0.802260
F	-6.688049	-1.020035	1.409581	F	6.559882	2.015234	1.277532
Br	-0.316943	-2.451049	1.187889	Br	0.021383	-0.677431	-2.583070
Br	0.393464	1.075149	-2.200257				

Int1



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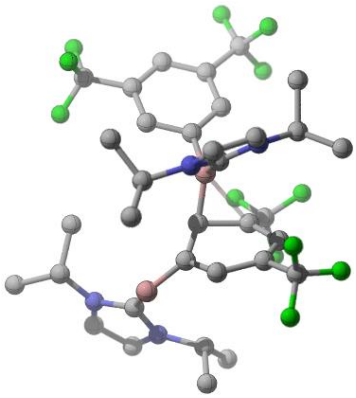
N	-0.988534	-2.811184	-1.466105
C	-1.884245	0.145854	0.217124
F	-4.715261	3.970258	-0.477135
B	2.948698	1.301655	-0.986757
N	-0.415813	-1.141120	-2.697974
C	-2.129020	1.419624	-0.302143
H	-1.339081	1.928621	-0.847977
F	-3.448512	3.338293	-2.116184
N	3.167758	3.594118	0.157166
C	-3.353474	2.061012	-0.140806
F	-4.874290	-0.756792	3.139988
N	4.072022	1.946831	1.268146
C	-4.384910	1.444799	0.556925
H	-5.343371	1.933762	0.678562

TS1



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ν_{min} = –91.9 cm^{-1}

F	3.105988	3.883755	1.103740
B	0.461081	-0.507302	0.319234
N	0.608124	-2.940553	1.375783
C	1.897016	0.032387	-0.060323
F	5.195525	3.425568	0.757686
B	-2.880679	1.528862	0.862065
N	0.010131	-1.370930	2.728007
C	2.344155	1.182119	0.597705
H	1.680428	1.696005	1.287824
F	4.172082	2.613603	2.484980
N	-2.570085	3.908744	-0.065582
C	3.619472	1.697861	0.388950
F	4.406094	-0.852589	-3.367478
N	-3.657714	2.552830	-1.388920
C	4.491172	1.079896	-0.498741

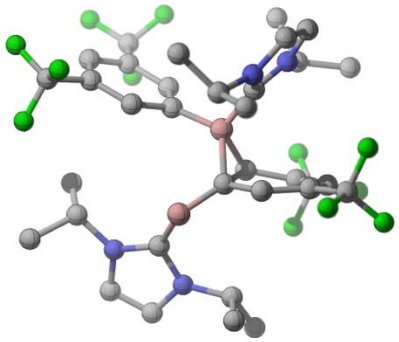
F	-6.390391	0.143097	1.883536	H	5.486306	1.474169	-0.663142
C	-4.154928	0.186328	1.101538	F	6.149784	-0.176777	-2.274818
C	-2.923730	-0.444648	0.940734	C	4.053516	-0.050223	-1.180369
H	-2.768008	-1.413531	1.407419	C	2.776404	-0.562574	-0.968403
F	-5.484730	-1.742548	1.319734	H	2.455011	-1.428433	-1.539782
F	1.345836	-0.870290	3.245427	F	5.179105	-2.037722	-1.737919
C	-3.532061	3.412232	-0.771236	F	-1.460021	-0.580600	-3.490491
F	-0.423829	0.255738	2.736265	C	4.032045	2.908821	1.177216
C	-5.231474	-0.533648	1.864337	F	0.412344	0.203296	-2.751551
C	-0.610493	-1.516471	-1.417246	C	4.954138	-0.771657	-2.145062
F	-0.533256	-1.901916	2.948471	C	0.354648	-1.619838	1.450198
C	-1.016035	-3.249676	-2.772162	F	0.179191	-1.930981	-3.092486
H	-1.278724	-4.260702	-3.036804	C	0.407979	-3.523508	2.605829
F	4.431069	-3.277771	-0.458026	H	0.527045	-4.581529	2.769514
C	-0.656833	-2.199531	-3.545813	F	-4.578112	-3.156972	0.851875
H	-0.545232	-2.118309	-4.614486	C	0.037200	-2.537313	3.457134
F	2.851578	-4.498496	0.380519	H	-0.218355	-2.572140	4.503247
C	-1.405014	-3.623625	-0.310449	F	-3.219733	-4.338835	-0.358065
H	-1.133250	-3.031795	0.564714	C	1.081276	-3.646397	0.170060
F	2.834917	-3.998457	-1.723479	H	0.844419	-2.971647	-0.655207
C	-0.075849	0.221056	-3.148691	F	-2.750335	-3.917520	1.709897
H	0.216295	0.749500	-2.242333	C	-0.269610	-0.028570	3.271589
C	-0.639190	-4.942678	-0.275987	H	-0.477314	0.590675	2.396575
H	-0.944918	-5.608477	-1.090985	C	0.314205	-4.948756	-0.031212
H	-0.851485	-5.457041	0.665748	H	0.591263	-5.702875	0.714110
H	0.437472	-4.778096	-0.343888	H	0.560091	-5.356432	-1.015652
C	-2.919245	-3.824118	-0.338706	H	-0.763975	-4.786545	0.016889
H	-3.221173	-4.422755	-1.205627	C	2.590888	-3.857888	0.259916
H	-3.446544	-2.867444	-0.376607	H	2.842051	-4.536807	1.082706
H	-3.237492	-4.353067	0.564638	H	3.114752	-2.911107	0.416086
C	1.120771	0.196050	-4.091778	H	2.959273	-4.299534	-0.670752
H	1.455122	1.221471	-4.269545	C	-1.523224	-0.041895	4.135960
H	0.869867	-0.254117	-5.059475	H	-1.819842	0.989769	4.341785
H	1.950904	-0.348170	-3.637384	H	-1.355915	-0.548002	5.093777
C	0.545098	-1.080756	1.023280	H	-2.345742	-0.523748	3.604100

C	-1.308729	0.884956	-3.757568	C	-0.920328	-1.005042	-1.223055
H	-1.078475	1.924174	-4.011341	C	0.960573	0.500226	4.005468
H	-2.145798	0.885944	-3.054183	H	0.776044	1.527159	4.335375
H	-1.621500	0.373046	-4.674714	H	1.843469	0.501073	3.359059
C	1.415309	-2.232726	0.793483	H	1.182079	-0.105222	4.891599
H	1.327702	-3.079015	1.468091	C	-1.739147	-2.116937	-0.927162
C	2.309407	-2.266281	-0.222007	H	-1.729575	-2.965831	-1.605601
C	2.616932	-1.098175	-1.013432	C	-2.555908	-2.130930	0.179292
H	3.429018	-1.151656	-1.731901	C	-2.799512	-0.923419	0.913944
C	2.067217	0.123106	-0.688125	H	-3.644595	-0.897827	1.596694
C	0.855132	0.189431	0.154987	C	-2.146442	0.254931	0.612078
H	0.746547	1.120939	0.711347	C	-0.868527	0.178387	-0.201483
C	0.232317	-0.884263	2.472057	H	-0.673949	1.121918	-0.718458
C	3.102416	-3.503453	-0.493983	C	-0.448151	-0.821533	-2.613075
C	3.347485	2.237804	0.141730	C	-3.275243	-3.366774	0.579423
C	3.793473	4.137976	1.267341	C	-2.990964	2.609850	-0.190571
H	3.775136	5.192887	1.484511	C	-2.997219	4.648778	-1.157909
C	4.375522	3.120000	1.938874	H	-2.775247	5.696665	-1.272983
H	4.960826	3.134634	2.843089	C	-3.691649	3.814497	-1.961756
C	2.441840	4.268365	-0.913772	H	-4.186635	4.010971	-2.898181
H	2.811971	3.783842	-1.833227	C	-1.820869	4.339268	1.105818
C	2.751481	5.759456	-0.945487	H	-2.323040	3.827070	1.945702
H	3.828770	5.944058	-0.996745	C	-1.893671	5.848962	1.295906
H	2.343550	6.273558	-0.067637	H	-2.929872	6.199987	1.313059
H	2.287851	6.203749	-1.830421	H	-1.352503	6.380604	0.504595
C	0.939749	3.994417	-0.813724	H	-1.426351	6.115320	2.247982
H	0.528891	4.364957	0.131321	C	-0.376315	3.836680	1.048312
H	0.745242	2.918431	-0.872674	H	0.155410	4.255894	0.187503
H	0.406945	4.480763	-1.637505	H	-0.358105	2.745575	0.958907
C	4.380921	0.569109	1.673965	H	0.164868	4.117188	1.958407
H	3.473051	-0.003798	1.461095	C	-4.191032	1.299249	-1.932474
C	5.527987	0.006181	0.836447	H	-3.438430	0.538803	-1.698022
H	6.471395	0.503211	1.088895	C	-5.497185	0.928021	-1.231776
H	5.331755	0.150059	-0.230898	H	-6.278199	1.662732	-1.457756
H	5.632564	-1.067842	1.014630	H	-5.351497	0.892898	-0.146756

C	4.648920	0.476342	3.170356
H	5.576598	0.986627	3.453709
H	4.757493	-0.577622	3.439756
H	3.817907	0.889193	3.749292

H	-5.835949	-0.058786	-1.562014
C	-4.333383	1.366665	-3.447386
H	-5.117351	2.068156	-3.755000
H	-4.611060	0.376832	-3.819365
H	-3.389260	1.650458	-3.920915

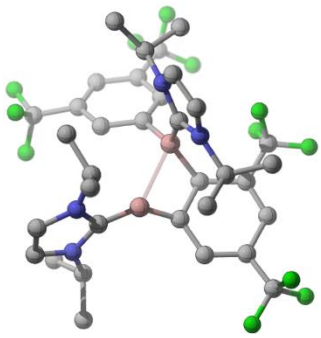
Int2



E(scf) = −2784.54745438 a.u.

F	4.577657	-1.047629	-2.330992
B	-0.254322	0.582073	-0.072107
N	-1.271473	3.003521	0.226832
C	1.343574	0.632934	0.044685
F	5.630033	0.826469	-2.091898
B	-0.217016	-1.963852	-1.153330
N	-0.968958	2.441703	-1.828761
C	2.184415	0.392943	-1.048175
H	1.751970	0.028909	-1.977508
F	3.840232	0.731038	-3.308129
N	1.445952	-3.699935	-0.095414
C	3.560294	0.592816	-0.971239
F	3.722028	0.779952	3.591351
N	-0.667515	-3.944115	0.389635
C	4.147940	1.030405	0.210526
H	5.216457	1.196863	0.270016
F	5.229435	1.937377	2.554285
C	3.334202	1.242812	1.316230
C	1.957977	1.040100	1.232799

TS2



E(scf) = −2784.54817214 a.u.

ν_{min} = −48.8 cm^{-1}

F	3.719795	2.933950	-1.942947
B	0.131686	-0.589868	0.210281
N	0.763575	-0.848808	2.776178
C	1.647899	-0.484533	-0.301152
F	5.563388	2.187082	-1.092204
B	-1.075748	1.376690	-0.285516
N	-1.369734	-0.878845	2.411031
C	2.306909	0.747089	-0.386997
H	1.762505	1.640917	-0.096794
F	3.996372	2.945609	0.197868
N	-0.932900	3.878345	-0.925339
C	3.622780	0.856262	-0.827568
F	3.690096	-3.617096	-2.223240
N	-0.817850	3.477623	1.200976
C	4.334604	-0.273299	-1.212207
H	5.362314	-0.197140	-1.545818
F	5.557096	-2.518943	-2.211951
C	3.687890	-1.504085	-1.171749

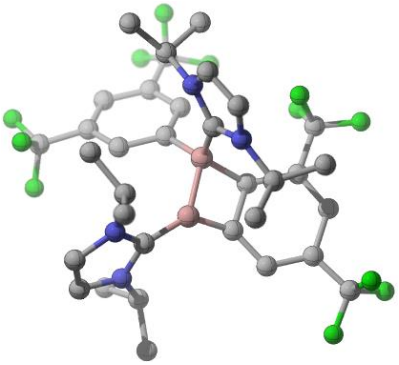
H	1.346356	1.204914	2.116877	C	2.365136	-1.604248	-0.746766
F	3.320774	2.832104	3.053329	H	1.884642	-2.577871	-0.754501
F	-2.437810	-1.543981	3.264529	F	4.813857	-3.416518	-0.389312
C	4.406257	0.283160	-2.173263	F	-0.105254	-3.736773	-1.517025
F	-1.733570	0.467055	3.606158	C	4.233824	2.223797	-0.916066
C	3.911400	1.697361	2.627509	F	-0.647049	-3.542794	0.563963
C	-0.846408	1.994638	-0.561049	C	4.437584	-2.762100	-1.509821
F	-3.846333	0.102988	3.315052	C	-0.163953	-0.816491	1.762512
C	-1.674113	4.073178	-0.543260	F	-1.970401	-4.573422	-0.801875
H	-2.061892	4.981548	-0.112204	C	0.137353	-0.909744	4.007429
F	-4.474274	-0.108967	-2.907284	H	0.683964	-0.946887	4.934078
C	-1.485798	3.718610	-1.834788	F	-5.815034	0.215292	-2.129008
H	-1.679899	4.257773	-2.747368	C	-1.188539	-0.922940	3.777111
F	-5.712789	-0.073070	-1.128586	H	-2.019253	-0.968705	4.462320
C	-1.206141	3.019548	1.697771	F	-5.695449	-1.903397	-2.581621
H	-0.961091	1.996470	1.976207	C	2.211345	-1.092422	2.627250
F	-4.692608	1.717817	-1.771435	H	2.522223	-0.547977	1.741918
C	-0.536724	1.721146	-3.039484	F	-5.912383	-1.250343	-0.536666
H	-0.335774	0.699988	-2.710093	C	-2.718186	-0.937424	1.824224
C	-2.561217	3.376758	2.297924	H	-2.572430	-0.897703	0.757077
H	-2.828517	4.422529	2.108560	C	2.460806	-2.584829	2.416508
H	-2.520686	3.230160	3.380383	H	2.266814	-3.142175	3.340210
H	-3.342188	2.728067	1.894497	H	3.497166	-2.756283	2.111317
C	-0.085399	3.949350	2.157109	H	1.805744	-2.979157	1.636147
H	-0.301163	4.992438	1.899116	C	3.006021	-0.533604	3.803121
H	0.870575	3.669534	1.705823	H	2.844286	-1.096762	4.728585
H	0.020752	3.884653	3.244042	H	2.773756	0.520525	3.982009
C	-1.651792	1.696695	-4.080585	H	4.070527	-0.608953	3.564298
H	-1.369155	1.016737	-4.889222	C	-3.395070	-2.260480	2.165144
H	-1.813708	2.686166	-4.523233	H	-4.324114	-2.333574	1.592376
H	-2.592250	1.348397	-3.650493	H	-3.640386	-2.339407	3.230958
C	-2.434079	-0.084285	1.416360	H	-2.751926	-3.098763	1.887841
C	0.749750	2.344779	-3.577279	C	-1.821700	-2.209205	-1.000144
H	1.126240	1.748381	-4.413295	C	-3.556115	0.276662	2.207807
H	1.525055	2.378145	-2.807940	H	-4.541093	0.175243	1.742758

H	0.571156	3.363923	-3.938562	H	-3.099068	1.191959	1.820323
C	-3.494969	0.163472	0.617248	H	-3.694034	0.372583	3.291162
H	-4.474018	0.351588	1.043613	C	-3.129639	-2.165893	-1.310600
C	-3.371253	0.020361	-0.814676	H	-3.716200	-3.079159	-1.335610
C	-2.243177	-0.488007	-1.378030	C	-3.813722	-0.905654	-1.562948
H	-2.255552	-0.772097	-2.426439	C	-3.153293	0.284058	-1.429710
C	-1.011488	-0.758388	-0.651934	H	-3.713235	1.215610	-1.498746
C	-1.080837	-0.318395	0.907725	C	-1.784043	0.327258	-1.035627
H	-0.479934	-0.972354	1.541093	C	-0.962797	-0.965273	-1.004671
C	-2.626820	-0.260414	2.886291	H	-0.352021	-1.024178	-1.921564
C	-4.552577	0.373450	-1.650802	C	-1.159493	-3.508077	-0.700234
C	0.223820	-3.099562	-0.242379	C	-5.289934	-0.952382	-1.714576
C	1.308845	-4.910393	0.565794	C	-1.013913	2.879837	-0.006210
H	2.153792	-5.536652	0.801256	C	-0.673462	5.080369	-0.297843
C	-0.001327	-5.077509	0.834399	H	-0.567175	6.005267	-0.841528
H	-0.509632	-5.887306	1.330593	C	-0.605020	4.830653	1.030238
C	2.685977	-3.122337	-0.595504	H	-0.430586	5.497223	1.859476
H	2.361672	-2.358349	-1.313981	C	-1.036045	3.675239	-2.377162
C	3.513660	-4.162211	-1.347203	H	-1.209288	2.601336	-2.490970
H	2.911736	-4.654235	-2.116342	C	0.283152	4.041929	-3.052540
H	3.915120	-4.926437	-0.671952	H	1.115624	3.482644	-2.617372
H	4.361476	-3.669020	-1.829801	H	0.496705	5.112951	-2.957829
C	3.469754	-2.464908	0.537848	H	0.227593	3.805368	-4.119061
H	3.766510	-3.214439	1.280787	C	-2.232283	4.439278	-2.936250
H	2.864933	-1.703144	1.037968	H	-2.103437	5.522299	-2.826250
H	4.373986	-1.991436	0.147247	H	-3.154167	4.145412	-2.426088
C	-2.120833	-3.743521	0.379758	H	-2.344325	4.221680	-4.002288
H	-2.271820	-2.670191	0.509914	C	-0.695756	2.741234	2.463742
C	-2.709302	-4.167024	-0.966254	H	-0.989541	1.720648	2.215436
H	-2.601254	-5.248230	-1.109580	C	0.758647	2.719890	2.925984
H	-2.191658	-3.653886	-1.785039	H	1.130030	3.729659	3.133739
H	-3.772068	-3.910182	-1.013092	H	1.395494	2.261705	2.163374
C	-2.784496	-4.449117	1.556211	H	0.836491	2.128831	3.843590
H	-2.767356	-5.538966	1.441855	C	-1.652847	3.292262	3.514211
H	-3.832558	-4.141432	1.607668	H	-1.370988	4.302560	3.832526

H	-2.304622	-4.179194	2.500649

H	-1.630558	2.644359	4.395978
H	-2.677520	3.320972	3.132698

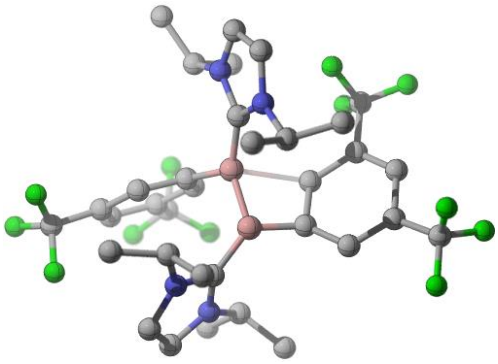
Int3



E(scf) = −2784.58431338 a.u.

F	4.190601	2.593643	-1.629858
B	-0.064757	-0.325344	0.210644
N	0.524734	-1.137832	2.710569
C	1.465173	-0.490054	-0.303865
F	5.846684	1.396611	-0.915194
B	-0.735187	1.249320	-0.193342
N	-1.553795	-0.639444	2.414362
C	2.365152	0.582140	-0.284849
H	2.034434	1.541733	0.102317
F	4.469385	2.309415	0.487165
N	-0.082429	3.672224	-0.899202
C	3.676245	0.468033	-0.740447
F	2.765240	-3.888783	-2.374119
N	0.094623	3.287700	1.218638
C	4.142116	-0.734973	-1.255394
H	5.162514	-0.834868	-1.609251
F	4.773364	-3.015917	-2.699660
C	3.255701	-1.810487	-1.325423
C	1.942998	-1.682647	-0.879235
H	1.271168	-2.526741	-0.968461
F	4.248985	-3.883101	-0.733767
F	-0.811415	-3.721852	-1.250537

TS3



E(scf) = −2784.56597541 a.u.

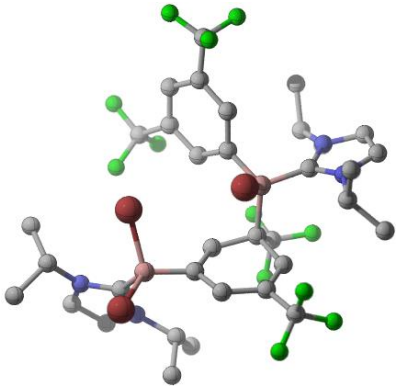
ν_{min} = −288.7 cm^{-1}

F	4.746979	1.971863	1.144367
B	-0.072555	-0.418601	0.541359
N	-0.462069	-2.445569	2.178047
C	1.459746	-0.739560	0.203020
F	6.049562	0.247594	1.225305
B	-0.368045	1.120411	-0.067830
N	-1.906677	-0.854013	2.408885
C	2.465039	-0.143161	0.987254
H	2.186020	0.330711	1.924982
F	4.529577	0.538820	2.742919
N	1.386513	2.574453	-1.336279
C	3.796748	-0.114984	0.593196
F	2.786992	-1.674494	-3.664616
N	1.253522	3.010751	0.769559
C	4.200452	-0.717280	-0.595704
H	5.238686	-0.702115	-0.903612
F	4.859913	-1.751256	-3.042115
C	3.230538	-1.336717	-1.374323
C	1.891651	-1.342557	-0.986976
H	1.164936	-1.813705	-1.642757
F	3.510981	-3.367210	-2.536742

C	4.552725	1.679934	-0.703856	F	-2.205729	-3.340009	-1.684285
F	-1.398517	-3.320863	0.786026	C	4.785745	0.649588	1.424511
C	3.754915	-3.145102	-1.795725	F	-2.833966	-3.105420	0.371337
C	-0.368324	-0.758144	1.745612	C	3.604920	-2.030775	-2.653709
F	-2.828935	-4.162208	-0.601534	C	-0.809795	-1.216337	1.685053
C	-0.098021	-1.245618	3.940656	F	-4.307474	-3.138859	-1.206769
H	0.422033	-1.547067	4.832500	C	-1.350119	-2.839636	3.158061
F	-5.683037	1.209237	-2.214704	H	-1.276188	-3.787966	3.661387
C	-1.393404	-0.932116	3.752956	F	-5.014865	3.059844	-1.767143
H	-2.215201	-0.898783	4.449379	C	-2.244585	-1.843449	3.306505
F	-5.910236	-0.896449	-2.692275	H	-3.093147	-1.756967	3.964733
C	1.901359	-1.625230	2.492403	F	-6.064979	1.260507	-2.372577
H	2.291027	-1.053330	1.654214	C	0.621238	-3.306987	1.670541
F	-6.101613	-0.228074	-0.647373	H	1.449914	-2.638672	1.445301
C	-2.881888	-0.301564	1.864236	F	-5.941796	1.783552	-0.285441
H	-2.751130	-0.250189	0.798608	C	-2.621404	0.429725	2.358778
C	1.868837	-3.106789	2.115107	H	-2.232093	0.940938	1.480185
H	1.593195	-3.720052	2.982759	C	0.192627	-4.014561	0.390454
H	2.846956	-3.424342	1.755197	H	-0.626842	-4.712760	0.585614
H	1.131411	-3.286613	1.331634	H	1.040153	-4.567189	-0.027436
C	2.797325	-1.344483	3.693605	H	-0.153117	-3.296141	-0.353606
H	2.547225	-1.972255	4.560667	C	1.100179	-4.288323	2.736412
H	2.750446	-0.291593	3.992754	H	0.368186	-5.080046	2.929460
H	3.830284	-1.572085	3.415787	H	1.333838	-3.781527	3.677892
C	-3.888067	-1.404668	2.175712	H	2.011756	-4.772110	2.374947
H	-4.787262	-1.223905	1.578545	C	-4.121312	0.208025	2.188145
H	-4.182209	-1.421340	3.233331	H	-4.604920	1.149223	1.916756
H	-3.486175	-2.381172	1.900039	H	-4.585786	-0.159219	3.111393
C	-2.231446	-1.878563	-0.899743	H	-4.309571	-0.509150	1.387661
C	-3.341393	1.073578	2.332804	C	-2.946270	-1.201631	-1.028385
H	-4.346398	1.260395	1.940693	C	-2.298744	1.246942	3.609138
H	-2.683851	1.851163	1.937890	H	-2.766051	2.233802	3.535147
H	-3.376110	1.158209	3.425480	H	-1.218295	1.379502	3.724284
C	-3.505957	-1.595606	-1.235873	H	-2.679880	0.760167	4.514148
H	-4.260839	-2.375608	-1.218966	C	-4.059647	-0.428133	-1.185745

C	-3.933451	-0.245939	-1.577866	H	-5.040023	-0.892456	-1.220917
C	-3.064065	0.807350	-1.475942	C	-3.966781	0.990948	-1.324890
H	-3.448068	1.825864	-1.580018	C	-2.750027	1.619197	-1.169028
C	-1.725937	0.589438	-1.050733	H	-2.706343	2.707065	-1.137380
C	-1.163909	-0.824165	-0.984539	C	-1.591797	0.869441	-0.887612
H	-0.560262	-1.048681	-1.880919	C	-1.620869	-0.599282	-1.006375
C	-1.840210	-3.257269	-0.508348	H	-0.899351	-1.067202	-1.675564
C	-5.383820	-0.036783	-1.794147	C	-3.083520	-2.679192	-0.894448
C	-0.315724	2.733054	0.050697	C	-5.228767	1.770077	-1.443963
C	0.475189	4.799703	-0.333371	C	0.706245	2.257947	-0.211948
H	0.750080	5.665810	-0.910827	C	2.335077	3.538117	-1.063450
C	0.584023	4.559956	0.994599	H	3.001211	3.926726	-1.815538
H	0.961081	5.186407	1.793908	C	2.248853	3.815895	0.258147
C	-0.298048	3.476869	-2.341809	H	2.825272	4.489989	0.869081
H	-0.717325	2.468325	-2.416452	C	1.173499	1.924449	-2.642727
C	1.037683	3.526831	-3.078478	H	0.704310	0.967907	-2.401940
H	1.738906	2.807133	-2.655513	C	2.506880	1.664859	-3.335871
H	1.490017	4.524096	-3.029232	H	3.212446	1.174813	-2.659005
H	0.877369	3.281463	-4.132986	H	2.958279	2.588571	-3.715500
C	-1.317303	4.481696	-2.868437	H	2.342494	1.001750	-4.188449
H	-0.948471	5.511062	-2.783568	C	0.208066	2.747244	-3.488355
H	-2.259914	4.405303	-2.318753	H	0.605581	3.752246	-3.670721
H	-1.518234	4.284619	-3.924428	H	-0.759663	2.830090	-2.986550
C	0.046464	2.620501	2.527008	H	0.052638	2.258096	-4.454641
H	-0.474817	1.682542	2.335209	C	0.764012	2.995154	2.154019
C	1.451876	2.297779	3.024362	H	0.358289	1.986901	2.281147
H	2.042936	3.204783	3.188411	C	1.900628	3.211066	3.145994
H	1.987711	1.660092	2.316531	H	2.274972	4.240568	3.118189
H	1.378573	1.767871	3.979154	H	2.736151	2.532214	2.956034
C	-0.756332	3.449636	3.521388	H	1.528811	3.028024	4.158250
H	-0.246144	4.385156	3.776851	C	-0.368185	4.006238	2.314380
H	-0.890536	2.879223	4.445196	H	-0.013601	5.022598	2.110366
H	-1.744102	3.696241	3.119342	H	-0.759558	3.975608	3.335725
				H	-1.184206	3.772832	1.623044

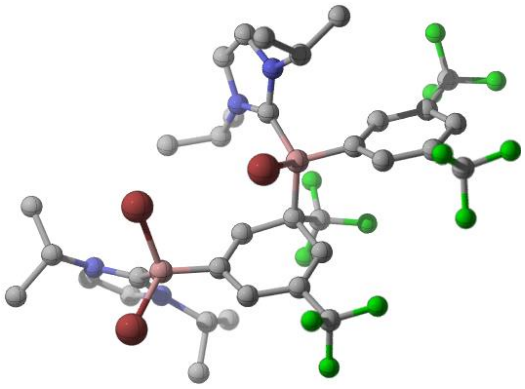
[4a+Br]•



E(scf) = -10499.9803636 a.u.

Br	-4.090676	1.143090	-1.993739
F	3.609207	-3.154144	-3.192982
B	1.785819	0.438422	0.067594
N	4.193771	0.385848	1.252819
C	1.750690	-1.199683	0.040981
Br	-1.860578	-1.348609	-1.535035
F	3.288335	-5.105204	-2.308380
B	-2.814093	0.248208	-0.672710
N	3.959534	2.077883	-0.065204
C	2.574165	-1.841420	-0.898762
H	3.213362	-1.240449	-1.539123
F	4.815731	-3.789987	-1.519779
N	-4.662711	-1.319783	0.433124
C	2.578099	-3.218850	-1.069274
F	-1.330274	-3.828607	1.247800
N	-4.016874	0.280747	1.733438
C	1.725822	-4.029851	-0.326279
H	1.706763	-5.102347	-0.474512
F	0.003207	-5.534808	1.179541
C	0.901931	-3.420435	0.604372
C	0.932613	-2.039847	0.796484
H	0.306203	-1.638899	1.579393
F	0.192269	-4.061288	2.756245
F	-0.113780	1.795311	3.219269

[4b+Br]•



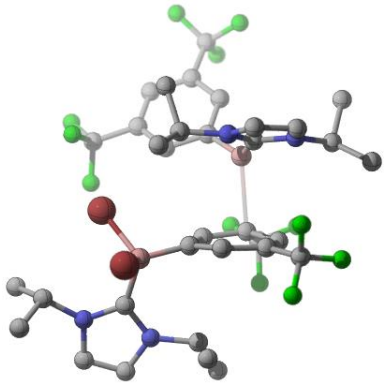
E(scf) = -10499.9727390 a.u.

Br	-4.629298	2.056172	-0.978784
F	5.232796	2.701270	-2.120430
B	1.332971	-0.458167	-0.299564
N	0.460386	-3.128484	-0.163515
C	2.900533	-0.129266	-0.036671
Br	-2.923087	-0.624960	-2.027970
F	6.735427	2.711400	-0.560606
B	-3.363570	0.562582	-0.406664
N	1.993102	-2.646078	-1.598612
C	3.516061	1.020245	-0.541958
H	2.946380	1.678268	-1.192153
F	4.824485	3.677529	-0.238505
N	-5.268282	-1.125372	0.396563
C	4.841621	1.325465	-0.249341
F	6.165163	-2.731233	1.039176
N	-4.167948	-0.234440	2.030842
C	5.609970	0.476138	0.537256
H	6.646693	0.704655	0.751403
F	6.967943	-1.157340	2.289378
C	5.017970	-0.676764	1.037904
C	3.684113	-0.964878	0.763482
H	3.249825	-1.865685	1.188739
F	5.141396	-2.174994	2.856908
F	-0.174585	0.257180	3.208683

C	3.562557	-3.821277	-2.030206	C	5.415588	2.605964	-0.791801
F	0.999196	-0.034625	2.986027	F	1.030842	-1.368560	2.461799
C	-0.055400	-4.219883	1.439828	C	5.826420	-1.675918	1.813702
C	3.310358	0.984453	0.410304	C	1.212466	-2.093899	-0.625613
F	2.013495	1.868838	2.851819	F	1.907834	0.568563	2.742430
C	5.381675	1.079252	1.273588	C	0.755453	-4.287253	-0.851488
H	6.221187	0.765227	1.871394	H	0.259574	-5.220496	-0.644535
F	-1.275216	5.300992	-0.909855	F	-0.432544	4.973161	0.973660
C	5.235663	2.135386	0.448457	C	1.714764	-3.983174	-1.744138
H	5.926918	2.917091	0.181379	H	2.220401	-4.600360	-2.467992
F	0.611640	5.423060	0.145352	F	1.563611	4.373399	0.386115
C	3.991184	-0.796356	2.120323	C	-0.556236	-3.174754	0.905180
H	2.950973	-1.078797	2.002325	H	-0.525275	-2.211932	1.388649
F	0.554737	4.688277	-1.885103	F	0.021713	4.631404	-1.109756
C	3.484048	3.116293	-1.012339	C	2.978497	-1.999581	-2.500542
H	2.417634	2.957676	-1.132257	H	3.003868	-0.950307	-2.230222
C	4.223758	-0.428993	3.584244	C	-0.175901	-4.211960	1.959506
H	5.276063	-0.202432	3.787706	H	-0.238436	-5.236016	1.577105
H	3.942789	-1.281898	4.208913	H	-0.871445	-4.131428	2.800085
H	3.613165	0.426868	3.874917	H	0.835526	-4.035865	2.334049
C	4.879904	-1.948606	1.662261	C	-1.941021	-3.405095	0.306816
H	5.940970	-1.718693	1.812300	H	-2.022928	-4.399990	-0.145345
H	4.718719	-2.185633	0.609096	H	-2.166994	-2.655360	-0.456974
H	4.643974	-2.840360	2.250449	H	-2.695464	-3.332954	1.098258
C	3.711096	4.508981	-0.431338	C	4.362591	-2.604157	-2.286524
H	3.179312	5.232826	-1.053256	H	5.086076	-2.053801	-2.894972
H	4.770277	4.788885	-0.419075	H	4.403436	-3.655800	-2.592513
H	3.317627	4.589506	0.585837	H	4.672392	-2.531888	-1.241039
C	0.611119	1.286222	1.006370	C	0.396561	0.364093	0.880288
C	4.150029	2.920082	-2.368847	C	2.490777	-2.094261	-3.943299
H	3.760283	3.662506	-3.071346	H	3.171428	-1.528640	-4.586201
H	3.914613	1.926403	-2.756322	H	1.494612	-1.653464	-4.024979
H	5.237636	3.042073	-2.307578	H	2.465010	-3.127626	-4.306792
C	0.622710	2.739484	0.633827	C	0.724718	1.831239	0.755129
H	1.418849	3.360168	1.027695	H	1.722073	2.148213	1.027549

C	-0.298134	3.262988	-0.215030	C	-0.156513	2.741192	0.278872
C	-1.391335	2.503284	-0.708948	C	-1.485695	2.398439	-0.087536
H	-2.073117	2.930433	-1.434389	H	-2.148583	3.146751	-0.506043
C	-1.612817	1.206990	-0.205583	C	-1.930024	1.079268	0.096858
C	-0.720174	0.680131	0.695922	C	-1.065993	0.145701	0.623822
H	-0.936786	-0.292337	1.120048	H	-1.457218	-0.852554	0.763839
C	0.875093	1.222175	2.504206	C	0.793835	-0.037109	2.312641
C	-0.109841	4.668449	-0.708246	C	0.259628	4.178256	0.132703
C	-3.811685	-0.273101	0.511374	C	-4.249238	-0.281230	0.676654
C	-5.375047	-1.439476	1.603781	C	-5.798258	-1.629644	1.562208
H	-6.097544	-2.223627	1.759447	H	-6.612894	-2.335123	1.565586
C	-4.978431	-0.435783	2.414907	C	-5.116595	-1.068924	2.583787
H	-5.291071	-0.180749	3.412884	H	-5.226970	-1.194350	3.647097
C	-4.966957	-2.145422	-0.757971	C	-5.926098	-1.338532	-0.913451
H	-4.329367	-1.772866	-1.554678	H	-5.356495	-0.761101	-1.635282
C	-6.417869	-1.916749	-1.169509	C	-7.339831	-0.767874	-0.860595
H	-6.584516	-0.851033	-1.351167	H	-7.294810	0.293251	-0.598966
H	-7.130187	-2.271328	-0.416168	H	-7.978617	-1.292713	-0.141647
H	-6.614345	-2.458080	-2.099487	H	-7.799545	-0.858680	-1.848996
C	-4.602975	-3.599540	-0.489556	C	-5.848078	-2.807477	-1.305560
H	-5.196679	-4.028521	0.325974	H	-6.366544	-3.456338	-0.590413
H	-3.541765	-3.677526	-0.240566	H	-4.801335	-3.115623	-1.379000
H	-4.790741	-4.190603	-1.390691	H	-6.314760	-2.946500	-2.284945
C	-3.537251	1.608479	2.188661	C	-3.427674	0.771542	2.836144
H	-2.532842	1.715992	1.792679	H	-2.485517	0.934371	2.322659
C	-4.430718	2.690974	1.588077	C	-4.224627	2.073286	2.855238
H	-5.446128	2.630392	1.996979	H	-5.182738	1.937656	3.370494
H	-4.484328	2.583057	0.500391	H	-4.420296	2.419823	1.836347
H	-4.019479	3.678121	1.819106	H	-3.653378	2.844680	3.379949
C	-3.442418	1.675101	3.707416	C	-3.115703	0.239289	4.228617
H	-4.424429	1.696747	4.192623	H	-4.006633	0.169321	4.862506
H	-2.926233	2.600495	3.975683	H	-2.425654	0.934920	4.711992
H	-2.859776	0.839855	4.106859	H	-2.624232	-0.736949	4.183274
Br	1.345587	0.842513	-1.905444	Br	0.689827	0.359702	-2.078268

TS4a

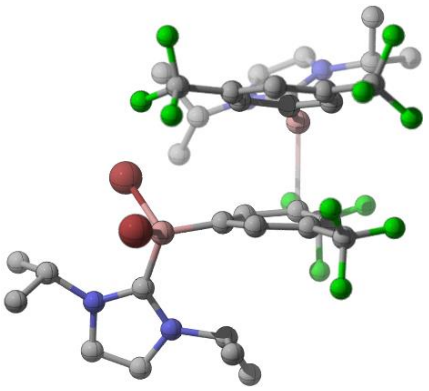


E(scf) = −7928.13001685 a.u.

ν_{min} = −293.20 cm^{-1}

Br	3.671450	-0.215138	2.045610
F	-1.440640	-4.203738	0.969122
B	-2.182721	1.001203	-0.283121
N	-2.220394	3.178645	1.062159
C	-2.854006	-0.379204	-0.298923
Br	1.210178	-2.210744	0.972966
F	-1.051553	-4.098327	-1.152041
B	2.434168	-0.644065	0.471769
N	-1.342301	1.531924	2.163261
C	-2.171769	-1.607457	-0.304536
H	-1.090760	-1.629173	-0.255368
F	-2.775683	-5.185790	-0.422290
N	4.172260	-2.292392	-0.698780
C	-2.852102	-2.819986	-0.314922
F	-6.866012	-1.825814	-1.681944
N	3.844456	-0.476971	-1.825160
C	-4.238160	-2.870307	-0.328623
H	-4.764853	-3.816427	-0.325690
F	-6.954822	-2.710210	0.285942
C	-4.934386	-1.660654	-0.336189
C	-4.265763	-0.447104	-0.326274
H	-4.850811	0.467991	-0.341276
F	-6.989297	-0.555926	0.062445
F	0.237976	1.462800	-3.782835

TS4b



E(scf) = −7928.12331334 a.u.

ν_{min} = −275.32 cm^{-1}

Br	2.952379	-1.975529	-0.884132
F	0.754884	-1.255900	-3.340411
B	-2.340534	1.213913	-0.061058
N	-3.890784	3.140968	-0.503966
C	-2.289548	-0.174395	-0.725723
Br	2.175589	1.161030	-1.751591
F	-0.727035	-2.460130	-4.353952
B	2.371196	-0.158154	-0.179156
N	-1.840135	3.589773	-1.097370
C	-1.330042	-0.525620	-1.697281
H	-0.624411	0.215315	-2.059252
F	0.485528	-3.338042	-2.799567
N	4.870618	0.658471	0.250839
C	-1.200901	-1.834512	-2.134793
F	-5.194375	-3.436031	-0.905608
N	3.724001	0.473926	2.073462
C	-2.064474	-2.826970	-1.673331
H	-1.959989	-3.849390	-2.017924
F	-3.563060	-4.777624	-0.441636
C	-3.043308	-2.491377	-0.750632
C	-3.132339	-1.192184	-0.257401
H	-3.847879	-0.971748	0.529680
F	-4.282699	-3.380112	1.049553
F	-0.423637	2.301011	3.628305

C	-2.034964	-4.080335	-0.235824	C	-0.159678	-2.214007	-3.153009
F	-1.317931	0.141476	-3.084206	F	-1.030226	3.326030	1.829416
C	-6.435742	-1.686031	-0.414711	C	-4.014185	-3.527605	-0.258757
C	-1.971170	1.844801	1.000446	C	-2.636757	2.592200	-0.614399
F	-1.665350	2.285419	-3.184834	F	-2.478872	2.192435	2.979573
C	-1.767776	3.688044	2.253855	C	-3.860036	4.463921	-0.917549
H	-1.857430	4.729663	2.512424	H	-4.736203	5.090666	-0.907019
F	2.874549	4.515436	0.255753	F	-0.206100	-3.227654	3.386336
C	-1.194440	2.659878	2.929963	C	-2.590666	4.742062	-1.277771
H	-0.685197	2.651908	3.879125	H	-2.151264	5.655783	-1.644030
F	0.995234	5.336177	-0.426674	F	-2.282700	-2.690377	3.110474
C	-2.902927	3.900099	-0.018902	C	-5.004146	2.388513	0.061225
H	-2.614478	3.340300	-0.921358	H	-4.522493	1.745596	0.821311
F	1.194290	4.621493	1.606203	F	-1.203769	-3.711061	1.533565
C	-0.974683	0.157706	2.561761	C	-0.476306	3.384657	-1.578702
H	-0.661497	-0.343055	1.647393	H	-0.194357	2.391440	-1.227552
C	-2.427496	5.344268	-0.106917	C	-5.661769	1.496394	-0.992154
H	-2.795694	5.945354	0.732729	H	-6.138308	2.105410	-1.768473
H	-2.822847	5.790981	-1.023427	H	-6.427138	0.865829	-0.528037
H	-1.338026	5.408429	-0.136574	H	-4.926936	0.841441	-1.469161
C	-4.417513	3.801735	0.152984	C	-6.006924	3.305160	0.752015
H	-4.738678	4.292203	1.078705	H	-6.560540	3.917536	0.030991
H	-4.740458	2.756979	0.186411	H	-5.510687	3.962880	1.471503
H	-4.920338	4.287551	-0.688682	H	-6.737365	2.695682	1.291054
C	0.213456	0.151168	3.512204	C	-0.439199	3.372337	-3.105404
H	0.565837	-0.878636	3.609600	H	0.564269	3.101945	-3.447034
H	-0.055204	0.517959	4.509712	H	-0.693363	4.354714	-3.519306
H	1.048228	0.735393	3.117391	H	-1.145521	2.634412	-3.498064
C	-0.199657	1.501436	-1.483913	C	-0.850048	0.950508	1.764793
C	-2.191928	-0.561668	3.135562	C	0.497656	4.386886	-0.968836
H	-1.934647	-1.609214	3.319290	H	1.518465	4.059747	-1.187423
H	-3.028403	-0.538697	2.432158	H	0.371336	4.434571	0.115405
H	-2.506941	-0.105307	4.080821	H	0.359057	5.391952	-1.384091
C	0.221809	2.816924	-1.124942	C	-1.251877	-0.284118	2.337937
H	-0.194866	3.672592	-1.643098	H	-2.073132	-0.303911	3.044221

C	1.115566	2.984926	-0.095328	C	-0.659643	-1.446660	1.913824
C	1.732079	1.890749	0.536585	C	0.422105	-1.432881	1.016910
H	2.472653	2.062406	1.309434	H	0.861860	-2.369652	0.696449
C	1.502295	0.599684	0.063269	C	0.964915	-0.225318	0.592390
C	0.543068	0.419081	-0.942748	C	0.324398	0.964906	0.981381
H	0.393452	-0.568337	-1.368550	H	0.760384	1.920424	0.704745
C	-0.765478	1.338985	-2.868871	C	-1.216092	2.192952	2.531041
C	1.538789	4.360864	0.329806	C	-1.100106	-2.766187	2.481770
C	3.467612	-1.137233	-0.700690	C	3.642885	0.343075	0.725464
C	4.960295	-2.368139	-1.823171	C	5.704818	1.003419	1.288396
H	5.587641	-3.219324	-2.030384	H	6.727446	1.303221	1.128791
C	4.762010	-1.231268	-2.523505	C	4.992003	0.882052	2.428377
H	5.190285	-0.902385	-3.454537	H	5.276290	1.054468	3.452150
C	4.246039	-3.311239	0.373625	C	5.365311	0.533193	-1.139380
H	3.617532	-2.949060	1.181963	H	4.529129	0.167109	-1.727911
C	5.675786	-3.392122	0.899184	C	6.468003	-0.519433	-1.191910
H	5.994667	-2.408386	1.255845	H	6.087801	-1.469229	-0.805434
H	6.383668	-3.748737	0.143064	H	7.356196	-0.225344	-0.621742
H	5.705717	-4.090088	1.740833	H	6.769573	-0.668075	-2.232733
C	3.679936	-4.632702	-0.130779	C	5.775552	1.900285	-1.671160
H	4.260666	-5.033829	-0.969067	H	6.608489	2.330958	-1.103910
H	2.642068	-4.494047	-0.445622	H	4.923210	2.583927	-1.633340
H	3.699014	-5.369762	0.677094	H	6.092697	1.802193	-2.713377
C	3.574821	0.945446	-2.157289	C	2.739313	-0.012331	3.072843
H	2.555600	1.139794	-1.844555	H	1.760545	0.180429	2.648935
C	4.536650	1.825642	-1.363535	C	2.929572	-1.515486	3.257428
H	5.563163	1.707231	-1.730246	H	3.873905	-1.728727	3.771870
H	4.512699	1.564279	-0.301421	H	2.937640	-2.021681	2.287432
H	4.244981	2.874528	-1.461737	H	2.103292	-1.924682	3.844225
C	3.631662	1.189973	-3.659551	C	2.826205	0.774952	4.373855
H	4.649092	1.138075	-4.062333	H	3.736992	0.558835	4.943043
H	3.255258	2.198555	-3.848717	H	1.975844	0.487704	4.997985
H	2.988216	0.491299	-4.201478	H	2.757465	1.851752	4.193468

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