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ELECTRONIC SUPPLEMENTARY INFORMATION

Rapid, Iterative Syntheses of Unsymmetrical Di- and Triarylboranes from Crystalline Aryldifluoroboranes

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Experimental methods.

General methods. ***Caution! Haloboranes are highly corrosive and fluoroboranes potentially release HF on contact with moisture; appropriate safety precautions should be taken.*** All reactions were conducted under N_2, with rigorously anhydrous conditions, using standard Schlenk and glove box techniques. Solvents were distilled from a solvent purification system onto freshly activated 4-Å molecular sieves and degassed briefly under dynamic vacuum. Benzene-*d*6, Me_3SiCl, Me_2SiHCl, and *N*,*N*-dimethylaniline were stored over freshly activated 4-Å molecular sieves and degassed with three freeze-pump-thaw cycles. Sodium tetrafluoroborate was finely ground, dried *in vacuo* at 120 °C for 16 h, and stored in the glove box. The following reagents were used as received from Sigma-Aldrich (MilliporeSigma) or Oakwood Products: acenaphthene, 1,4-xylene, *N*-bromosuccinimide, Br_2, 2-bromomesitylene (MesBr), bromopentamethylbenzene (Ph*Br), 1-bromonaphthalene (NaphBr), 9-bromoanthracene (AnBr), 1,4-dibromobenzene, benzo[*b*]thiophene, pentafluorobromobenzene, 3,5-bis(trifluoromethyl)-1-bromobenzene (Ar^FBr), 1,4-bromo-*N*,*N*-dimethylaniline, ^{n}BuLi (2.5 M in hexanes), and BBr_3. The following reagents were prepared using literature methods: 1-bromoacenaphthene,[1] 2,5-dibromo-1,4-xylene,[2] all aryltrimethylsilanes (**1**, except for **1b**),[3–5] 1,4-bis(dibromoboryl)benzene (**2f**),[6] mesityllithium (MesLi),[7] 1-naphthyllithium (NaphLi),[8] and 1,1′-dilithioferrocene ($FcLi_2$·tmeda).[9] Solutions of C_6F_5MgBr and Ar^FMgBr were prepared by reacting ArBr and unactivated Mg turnings in Et_2O (*ca*. 0.3 M) in the glove box over 1–2 h and were stored at –35 °C in the glove box.

NMR spectroscopy. Multi-nuclear NMR spectra were collected using Bruker Avance III HD 400 MHz and Varian VNMRS 500 MHz instruments. Spectra were recorded on C_6D_6 solutions in 5-mm-o.d. glass NMR tubes equipped with PTFE valves (J. Young) at 298 K and referenced to internal C_6D_6 (^{1}H: 7.15 ppm, ^{13}C: 128.06 ppm), external $BF_3·OEt_2$ (^{11}B: 0 ppm) and $CFCl_3$ (^{19}F: 0 ppm). Data were processed and graphics were generated using MestReNova (version 14.2.0).[10]

X-ray crystallography. ***Crystal handling and data acquisition for 3 and 4a–b*.** Crystals were submerged in Paratone-N™ oil on microscope slides in a N_2-filled glove box, transported in sealed vials at –78 °C, and selected under a microscope in a N_2-filled glove bag positioned near the diffractometer. The selected crystals were affixed to a Hampton cryo-loop using Paratone-N™ oil, which was sealed under N_2 with a screw cap before being transferred quickly to the cold N_2 stream at the goniometer. Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer with a Metaljet liquid Ga X-ray source (λ = 1.34139 Å) and Photon II CPAD detector. Data were collected at 150 K under a cold N_2 stream maintained by an Oxford Cryostream 800 cooler, which also protected the sensitive crystals from moisture.

Crystal handling and data acquisition for 4d. Crystals were submerged in Paratone-N™ oil on microscope slides in a N_2-filled glove box, transferred to, and selected under a microscope positioned near the diffractometer quickly, but without further precautions (Note: the crystals were observed to decompose appreciably after *ca*. 1 h in air). Single-crystal X-ray diffraction data were collected on a Bruker ApexII diffractometer with a Mo X-ray source (λ = 1.34139 Å) and Photon II CPAD detector. Data were collected at 150 K under a cold N_2 stream maintained by an Oxford Cryostream 1000 cooler, which also protected the sensitive crystals from moisture.

Crystal handling and data acquisition for 5, 6, and $BBr_3 \cdot NMe_2(4\text{-}C_6H_4R)$. Crystals were submerged in Paratone-N™ oil on microscope slides in a N_2-filled glove box, transferred to, and selected under a microscope positioned near the diffractometer without further precautions. The selected crystals were affixed to a MiteGen loop using Paratone-N™ oil and transferred to the goniometer. Data were collected, at 298 K in air, on a Bruker D8 diffractometer with a Cu X-ray source (λ = 1.54178 Å) and Photon CPAD detector.

***Unit cell determination, integration, and scaling*.** Diffraction data were processed using the Bruker APEX3 software suite. Final unit cells were determined using the difference-vectors or fast Fourier-transform methods to index diffraction spots from *ca*. 150 frames of data. In the cases of **3c** and **4a**, which were twinned, the unit cells of each twin component were determined using CELL_NOW; in both cases, the second twin component adopts the same unit cell, rotated *ca*. 180° around a reciprocal axis with respect to the first. Data were integrated using SAINT and scaled using SADABS (TWINABS for **3c** and **4a**).

***Structure solution and refinement*.** Structure solution and refinement was performed using Olex2 (version 1.5).[11] The structures were solved using intrinsic phasing methods (ShelXT)[12] and refined using least-squares (Gauss-Newton) methods (olex2.refine). For **3,** further refinement employed Hirshfeld atom refinement as implemented in NoSpherA2 (Non-Spherical Atoms in Olex2).[13] Non-spherical atomic scattering factors were generated from Hirshfeld partitioning of the electron density, described by the molecular wavefunction calculated at the r^2SCAN/cc-pVTZ level of theory using ORCA (version 5.0.4).[14] Least-squares refinement of the crystallographic data was then performed using those scattering factors. Scattering-factor calculations were iterated between refinements until a converged model was achieved, to a maximum of 10 cycles. "Normal" integration accuracy, SCF threshold, and SCF convergence strategy were used to calculate the wavefunction. In all cases, final refinements were conducted with a $1/\sigma^2(F^2)$ weighting scheme and extinction parameters where appropriate ($x > 3\sigma(x)$).

For **3h**, which exhibited 80/20 rotational disorder about the B–C bond, the atomic displacement parameters (ADPs) of the C2/C2a and B1/B1a pairs were constrained to be equal, and rigid-bond restraints (RIGU) were used for the F1/F1a and F2/F2a pairs. The C–H distances and ADPs of H atoms were refined freely unless stated otherwise. In **3a**, H6a-c were refined isotropically (AFIX 134). In **3b**, 10 of the 15 H atoms were refined using ISOR restraints and the 1,3-distances of H8a-c, H9a-c, and H10a-c were restrained. In **3e**, H1, which exhibited a 50/50 disorder with the BF_2 group, was refined isotropically (AFIX 44). In **3h**, H2 in the minor component had to be refined isotropically with a fixed distance (AFIX 43). In **6**·0.5C_6H_5F, the solvent was disordered such that the F atom could not be located and a solvent mask was applied (as implemented in Olex2), which found 104 electrons across 2 voids per unit cell with a total volume of 392 Å^3. This is consistent with 2 molecules of C_6H_5F per unit cell (100 electrons), or 0.5 per asymmetric unit.

Data were deposited in the Cambridge Crystallographic Data Centre, deposition numbers 2292569–2292582 and 2305672. Intermolecular interactions were measured using Mercury (version 2020.3.0)[15] and graphics were generated using Ortep3 (version 2020.1).[16]

Computational details. Calculations were performed using the PW6B95 functional with empirical dispersion (D3) and Becke-Johnson damping, denoted PW6B95-D3(BJ), as implemented in Gaussian 16 (revision C.01).[17] Geometry optimisations, vibrational frequency calculations, and isotropic NMR shielding tensor calculations were performed using the def2-TZVP basis set in C_6H_6 using the SMD implicit solvent model. Chemical shifts were referenced to shielding tensors calculated at the same level for $BF_3{\cdot}OEt_2$ (^{11}B: 0 ppm) and $CFCl_3$ (^{19}F: –164.9 ppm).

Syntheses.

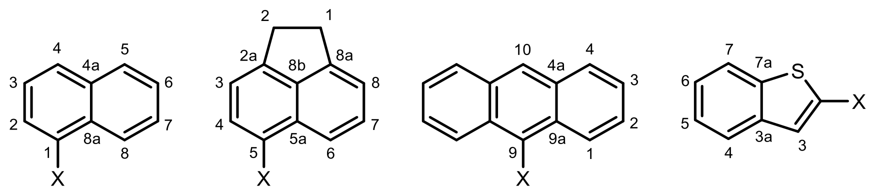
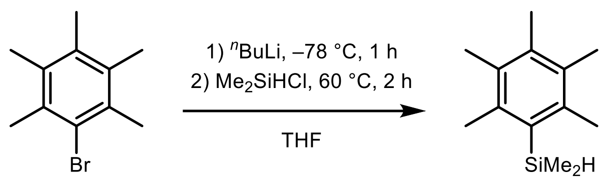


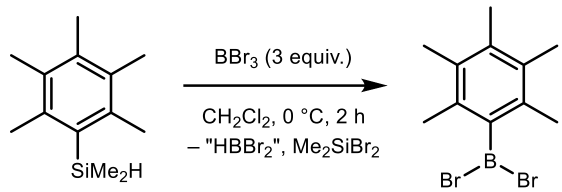
Figure S1. Standard numbering schemes for (hetero)aryl groups.

Synthesis of 1b.



In a 100-mL round-bottom Schlenk flask, Ph*Br (4.54 g, 20.0 mmol) was dissolved in THF (20 mL) and cooled to –78 °C. Subsequently, ^{n}BuLi (9.6 mL, 1.2 equiv.) was added dropwise to the solution and the reaction mixture was held at –78 °C for 1 h. Chlorodimethylsilane (4.4 mL, 2.0 equiv.) was added in a single portion, the suspension was allowed to warm to ambient temperature, and was then heated to 60 °C for 2 h, during which a white precipitate formed. The volatiles were removed *in vacuo* and the residue was extracted with Et_2O (20 mL), washed with H_2O (2 x 20 mL), dried over $MgSO_4$, and evaporated, yielding **1b** (4.04 g, 97.9% w.r.t. Ph*Br) as a white powder that was used without further purification. The ^{1}H NMR spectrum agreed with previously reported data.

Synthesis of 2b.



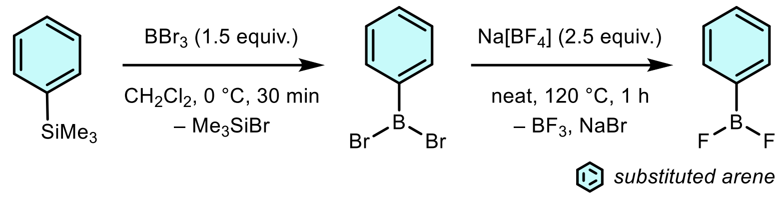
In a 25-mL Schlenk tube, **1b** (2.06 g, 10.0 mmol) was dissolved in CH_2Cl_2 (10 mL), cooled to 0 °C, and BBr_3 (2.8 mL, 30 mmol, 3.0 equiv.) was added dropwise with stirring. After 2 h at 0 °C, volatile materials were removed under dynamic vacuum, yielding **2b** (2.98 g, 93.9% w.r.t. **1b**) as colourless plates.

^{1}H NMR (400 MHz, C_6D_6): δ 1.82 (s, 6H, *m*-Me), 1.96 (s, 3H, *p*-Me), 2.09 (s, 5H, *o*-Me).

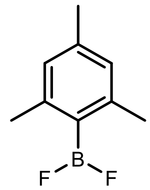
^{13}C NMR (126 MHz, C_6D_6): δ 14.9 (*m*-Me), 16.2 (*p*-Me), 20.4 (*o*-Me), 130.0 (C_m), 132.5 (C_o), 136.4 (C_p), 140.7 (C_i, observed by ^{1}H-^{13}C HMBC).

^{11}B NMR (128 MHz, C_6D_6): δ 62.

Synthesis of 3.



In a 25-mL Schlenk tube, arylsilane **1** (10 mmol) was dissolved in CH_2Cl_2 (10 mL; 1,2-$C_2H_4Cl_2$ for **1g**), cooled to 0 °C, and BBr_3 (15 mmol, 1.5 equiv. per B atom) was added dropwise with stirring. After 30 min at 0 °C (2 h for **1b**, 2 h at 70°C in 1,2-dichloroethane for **1g**, 30 min at –78 °C for **1h**), volatile materials were removed under dynamic vacuum, yielding intermediate **2**, and solid Na[BF_4] (2.5 equiv. per B atom, 8.0 equiv. for **2h**) was added under a positive pressure of N_2. The Schlenk tube was equipped with a septum and cannula that was fed into a saturated aqueous Na[HCO_3] bath, and an air stream was pointed half-way up the tube to prevent sublimation into the cannula. The tube was then heated with stirring to 120 °C, resulting in melting and evolution of BF_3, evidenced by bubbling and fuming in the Na[HCO_3] bath, as well as slow deposition of crystals on the tube walls. Heating was continued for 1 h or until fuming had ceased. The tube was cooled to 0 °C, traces of BF_3 were removed under dynamic vacuum, and the crude mixture was sublimed under vacuum and/or extracted with pentane to afford **3**.



3a (84% yield, colourless needles, purified by recrystallisation from pentane). Crystals suitable for X-ray crystallography were obtained via sublimation during the reaction.

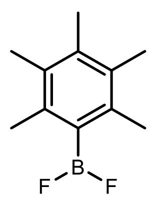
^{1}H NMR (500 MHz, C_6D_6): δ 1.96 (s, 3H, *p*-Me), 2.27 (t, J_{HF} = 3.0 Hz, 6H, *o*-Me), 6.56 (dec, $^4J_{HH}$ = 0.7 Hz, 2H, H_m).

^{13}C NMR (126 MHz, C_6D_6): δ 20.9 (*p*-Me), 22.4 (t, J_{CF} = 3.1 Hz, *o*-Me), 120.3 (C_i, observed by ^{1}H-^{13}C HMBC), 129.0 (C_m), 142.6 (C_p), 146.7 (t, J_{CF} = 2.6 Hz, C_o).

^{11}B NMR (128 MHz, C_6D_6): δ 25.9 (t, $^1J_{BF}$ = 75 Hz).

^{19}F NMR (377 MHz, C_6D_6): δ –70.1 (m).

HRMS data could not be obtained due to immediate decomposition of the solid on contact with moist air.



3b (89% yield, colourless plates, purified by recrystallisation from pentane). Crystals suitable for X-ray crystallography were obtained upon storing a saturated pentane solution at –35 °C for 16 h.

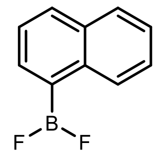
^{1}H NMR (500 MHz, C_6D_6): δ 1.84 (s, 6H, *m*-Me), 1.92 (s, 3H, *p*-Me), 2.09 (s, 5H, *o*-Me).

^{13}C NMR (126 MHz, C_6D_6): δ 15.4 (*m*-Me), 16.3 (*p*-Me), 20.4 (*o*-Me), 125.6 (C_i, observed by ^{1}H-^{13}C HMBC), 132.2 (C_m), 136.2 (C_o), 137.7 (C_p).

^{11}B NMR (128 MHz, C_6D_6): δ 27.3 (t, $^1J_{BF}$ = 75 Hz).

^{19}F NMR (377 MHz, C_6D_6): δ –63.5 (m).

HRMS (APCI): m/z calcd. for $[C_{11}H_{15}BF_2]^+$ 196.1229; found 196.1232.



3c (81% yield, colourless needles, purified by recrystallisation from pentane). Crystals suitable for X-ray crystallography were obtained via sublimation during the reaction.

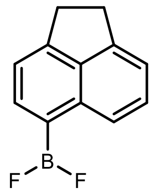
^{1}H NMR (400 MHz, C_6D_6): δ 7.03 (dd, *J* = 8.2, 6.9 Hz, 1H, H3), 7.20 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H, H7), 7.28 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H, H6), 7.51 (dt, *J* = 8.1, 1.1 Hz, 1H, H5), 7.60 (dt, *J* = 8.2, 1.1 Hz, 1H, H4), 7.90 (dd, *J* = 6.9, 1.4 Hz, 1H, H2), 8.42 (d, *J* = 8.5 Hz, 1H, H8).

^{13}C NMR (126 MHz, C_6D_6): δ 120.9 (C1, observed by ^{1}H-^{13}C HMBC), 124.5 (C3), 125.9 (C7), 126.8 (t, J_{CF} = 4.0 Hz, C8), 127.4 (obscured by C_6D_6, C6), 128.7 (C5), 133.3 (C8a), 134.7 (C4), 137.1 (C4a), 138.7 (t, J_{CF} = 6.0 Hz, C2).

^{11}B NMR (128 MHz, C_6D_6): δ 25.3 (t, $^{1}J_{BF}$ = *ca*. 75 Hz).

^{19}F NMR (377 MHz, C_6D_6): δ –82.7 (m).

HRMS data could not be obtained due to immediate decomposition of the solid on contact with moist air.



3d (80% yield, colourless needles, purified by recrystallisation from pentane). Crystals suitable for X-ray crystallography were obtained by slow evaporation of a saturated pentane solution at ambient temperature.

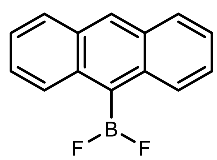
^{1}H NMR (400 MHz, C_6D_6): δ 2.80 (m, 2H, H2), 2.84 (m, 2H, H1), 6.88 (d, J = 7.0 Hz, 1H, H3), 7.04 (d, J = 6.9 Hz, 1H, H8), 7.35 (dd, J = 8.4, 6.9 Hz, 1H, H7), 7.99 (d, J = 7.0 Hz, 1H, H4), 8.19 (d, J = 8.4 Hz, 1H, H6).

^{13}C NMR (101 MHz, C_6D_6): δ 29.73 (C1), 30.31 (C2), 116.3 (C5, observed by ^{1}H-^{13}C HMBC) 118.6 (C3), 119.7 (C8), 122.5 (t, J_{CF} = 3.3 Hz, C6), 129.5 (C7), 135.8 (t, J_{CF} = 2.3 Hz, C5a), 139.0 (C8b), 140.82 (t, J_{CF} = 6.0 Hz, C4), 146.4 (C8a), 154.0 (C2a).

^{11}B NMR (128 MHz, C_6D_6): δ 25.5 (s).

^{19}F NMR (377 MHz, C_6D_6): δ –85.7 (s).

HRMS (APCI): m/z calcd. for $[C_{12}H_9BF_2+H]^+$ 203.0838; found 203.0832.



3e (54% yield, yellow needles, purified by sublimation at 2 × 10^{-2} mbar, 2 h followed by recrystallisation from pentane at –35 °C). Crystals suitable for X-ray crystallography were obtained upon storing a saturated pentane solution at –35 °C for 16 h.

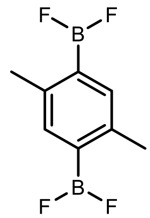
^{1}H NMR (400 MHz, C_6D_6): δ 7.20 (m, 4H, H2/H3), 7.68 (d*, J = 8.2 Hz, 2H, H4), 8.15 (s, 1H, H10), 8.32 (d*, J = 8.8 Hz, 2H, H1). Asterisk (*) denotes unresolved fine structure.

^{13}C NMR (126 MHz, C_6D_6): δ 137.5 (C4a, t, J_{CF} = 1.5 Hz), 133.5 (C10), 131.0 (C9a), 129.1 (C4), 127.4 (C3), 127.2 (C1, t, J_{CF} = 4.5 Hz), 125.0 (C2), n.o. (C9).

^{11}B NMR (128 MHz, C_6D_6): δ 27.0 (t, $^1J_{BF}$ = *ca*. 70 Hz).

^{19}F NMR (377 MHz, C_6D_6): δ –63.9 (d).

HRMS (APCI): m/z calcd. for $[C_{14}H_9BF_2+H]^+$ 227.0838; found 227.0837.



3g (79% yield, colourless needles, purified by recrystallisation from pentane). Crystals suitable for X-ray crystallography were obtained via sublimation during the reaction.

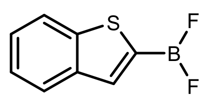
^{1}H NMR (400 MHz, C_6D_6): δ 2.16 (s, 6H, Me), 7.41 (s, 2H, H_{Ar}).

^{13}C NMR (101 MHz, C_6D_6): δ 20.7 (Me), 128.0 (C_{Ar}–B, observed by ^{1}H-^{13}C HMBC) 139.0 (C_{Ar}–H), 142.9 (C_{Ar}–Me).

^{11}B NMR (128 MHz, C_6D_6): δ 24.8 (s).

^{19}F NMR (377 MHz, C_6D_6): δ –80.9 (s).

HRMS data could not be obtained due to immediate decomposition of the solid on contact with moist air.



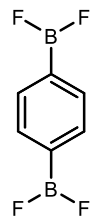
3h (31% yield, pale yellow needles, purified by sublimation at 120 °C under an atmosphere of N_2). Crystals suitable for X-ray crystallography were obtained via sublimation during the reaction. Small amounts of side products co-sublimed with the product and attempts to separate them via crystallisation were unsuccessful.

^{1}H NMR (400 MHz, C_6D_6): δ 7.03 (m, 2H, H5/6), 7.44 (m, 2H, H4/7), 7.62 (s, 1H, H3).

^{11}B NMR (128 MHz, C_6D_6): δ 23.3 (s).

^{19}F NMR (377 MHz, C_6D_6): δ –88.1 (m).

HRMS (APCI): m/z calcd. for $[C_8H_5BF_2S]^+$ 182.0168; found 182.0175.



NMR-scale synthesis of 3f. This reaction is a modification of that given above for **3**. In the glove box, a 5-mm o.d. NMR tube equipped with a J. Young PTFE valve was charged with **2f** (0.0060 g, 0.014 mmol) and Na[BF_4] (0.0181 g, 0.165 mmol, 11 equiv.). The tube was connected to a high-vacuum Schlenk line, cooled to –60 °C, and evacuated. It was then closed and heated to 120 °C for 1 h under static vacuum, during which colourless needles deposited on the reactor walls. The tube was then cooled to –60 °C and evacuated to remove any BF_3 and transferred into the glove box. A small amount of **1f** (0.0024 g, 0.0085 mmol) was added as an internal standard, the solids were suspended in C_6D_6 (while **1–3f** are soluble, residual Na^+ salts are not), and the yield was determined to be *ca*. 90% by ^{1}H NMR spectroscopy.

Small amounts of unreacted **2f** (^{11}B: 58.2 ppm) and an incompletely fluorinated intermediate (^{11}B: 42.4 ppm, ^{19}F: –88.2 ppm (d)) were observed by ^{11}B and ^{19}F NMR spectroscopy. The slightly decreased yield is attributed to **2f** remaining on the reactor walls above the mixture during the reaction, as well as co-sublimation of the intermediate with the product under static vacuum.

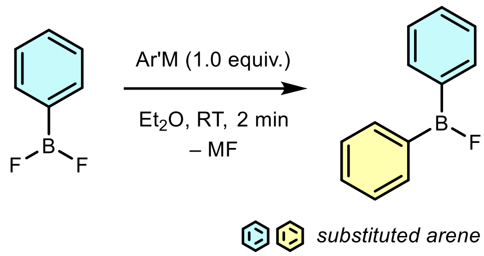
^{1}H NMR (400 MHz, C_6D_6): δ 7.46 (s).

^{13}C NMR (101 MHz, C_6D_6): δ 135.2 (t, J_{CF} = 4.7 Hz, C–H), n.o. (C–B)

^{11}B NMR (128 MHz, C_6D_6): δ 24.5 (s).

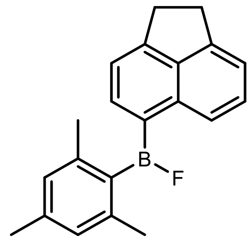
^{19}F NMR (377 MHz, C_6D_6): δ –88.8 (d).

Synthesis of 4.



Using solid MesLi. In the glove box, a vial was charged with solid **3** (0.20 mmol) and MesLi (0.22 mmol, 1.1 equiv.). Diethyl ether (*ca*. 0.5 mL) was added, the vial was shaken for 2 min, and the resulting suspension was filtered through cotton into a new vial. The Et_2O was evaporated, and the solid was extracted and crystallised from benzene by slow evaporation, yielding **4**.

Using ethereal C_6F_5MgBr. In the glove box, a vial was charged with solid **3** (0.20 mmol) and Et_2O (*ca*. 0.5 mL), after which C_6F_5MgBr (0.32 M in Et_2O) was added dropwise. The vial was shaken for 2 min, and the resulting suspension was filtered through Celite into a new vial. The Et_2O was evaporated, and the solid was extracted and crystallised from benzene/pentane by slow evaporation, yielding **4**.



4a (99% yield, colourless needles). Crystals suitable for X-ray crystallography were obtained via slow evaporation of a saturated Et_2O solution at ambient temperature.

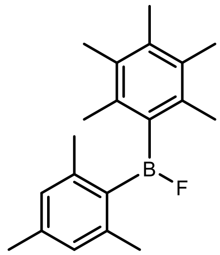
^{1}H NMR (400 MHz, C_6D_6): δ 2.20 (s, 3H, *p*-Me (Mes)), 2.28 (d, J = 1.8 Hz, 6H, *o*-Me (Mes)), 2.86 (m, 2H, H2 (Ace)), 2.92 (m, 2H, H1 (Ace)), 6.79 (s, 2H, H_m (Mes)), 6.99 (d*, J = 7.0 Hz, 1H, H3 (Ace)), 7.09 (d*, J = 6.9 Hz, 1H, H8 (Ace)), 7.40 (dd, J = 8.4, 6.9 Hz, 1H, H7 (Ace)), 8.15 (d, J = 7.0 Hz, 1H, H4 (Ace)), 8.57 (d, J = 8.4 Hz, 1H, H6 (Ace)). Asterisk (*) denotes unresolved fine structure.

^{13}C NMR (101 MHz, C_6D_6): δ 21.0 (*p*-Me (Mes)), 22.0 (*o*-Me (Mes)), 29.9 (C1 (Ace)), 30.4 (C2 (Ace)), 119.1 (C3 (Ace)), 119.8 (C8 (Ace)), 123.2 (d, J_{CF} = 6.6 Hz, C6 (Ace)), 127.6 (C_m (Mes)), 129.5 (C7 (Ace)), 135.3 (C_i (Mes), observed by ^{1}H-^{13}C HMBC), 135.8 (C5a (Ace)), 138.5 (C_p (Mes)), 139.4 (C8b (Ace)), 139.7 (d, J_{CF} = 2.6 Hz, C_o (Mes)), 143.2 (d, J_{CF} = 12.6 Hz, C4 (Ace)), 146.3 (C8a (Ace)), 153.8 (C2a (Ace)), n.o. (C5 (Ace)).

^{11}B NMR (128 MHz, C_6D_6): δ 52 ($\Delta\nu_{½}$ = 750 Hz).

^{19}F NMR (377 MHz, C_6D_6): δ –35.9.

HRMS (APCI): m/z calcd. for $[C_{21}H_{20}BF]^+$ 302.1637; found 302.1635.



4b (97% yield, colourless needles). Crystals suitable for X-ray crystallography were obtained via slow evaporation of a saturated pentane solution at ambient temperature.

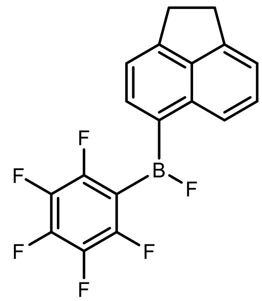
^{1}H NMR (400 MHz, C_6D_6): δ 1.98 (s, 6H, *m*-Me (Ph*)), 2.06 (s, 3H, *p*-Me (Ph*)), 2.08 (s, 3H, *p*-Me (Mes)), 2.22 (d, J_{BF} = 2.2 Hz, 6H, *o*-Me (Ph*)), 2.42 (d, J_{BF} = 3.1 Hz, 6H, *o*-Me (Mes)), 6.73 (s, 2H, H_m (Mes)).

^{13}C NMR (101 MHz, C_6D_6): δ 15.4 (*m*-Me (Ph*)), 16.9 (*p*-Me (Ph*)), 20.2 (*o*-Me (Ph*)), 21.0 (*p*-Me (Mes)), 22.9 (d, *J* = 3.3 Hz, *o*-Me (Mes)), 129.3 (C_m (Mes)), 132.2 (C_m (Ph*)), 134.5 (d, J_{CF} = 2.9 Hz, C_o (Ph*)), 136.0 (d, J_{CF} = 1.8 Hz, C_p (Ph*)), 138.2 (C_p (Mes)), 138.4 (C_i (Ph*)), 141.3 (C_i (Mes)), 144.9 (d, J_{CF} = 4.6 Hz, C_o (Mes)).

^{11}B NMR (128 MHz, C_6D_6): δ 53 ($\Delta\nu_{1/2}$ = 620 Hz).

^{19}F NMR (377 MHz, C_6D_6): δ –13.4.

HRMS (APCI): m/z calcd. for $[C_{20}H_{26}BF]^+$ 296.2106; found 296.2097.



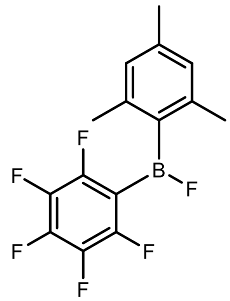
4c (92% yield, colourless needles). Crystals suitable for X-ray crystallography were obtained via slow evaporation of a saturated benzene/pentane (1:2) solution at ambient temperature.

^{1}H NMR (400 MHz, C_6D_6): δ 2.83 (m, 2H, H2), 2.89 (m, 2H, H1), 6.98 (d, J = 7.1 Hz, 1H, H3), 7.10 (d, J = 7.0 Hz, 1H, H8), 7.44 (dd, J = 8.4, 6.9 Hz, 1H, H7), 7.83 (d, J = 7.0 Hz, 1H, H4), 8.51 (d, J = 8.4 Hz, 1H, H6).

^{13}C NMR (101 MHz, C_6D_6): δ 29.8 (C1 (Ace)), 30.5 (C2 (Ace)), 118.9 (C3 (Ace)), 120.3 (C8 (Ace)), 123.0 (d, $^{3}J_{CF}$ = 8.2 Hz, C6 (Ace)), 130.2 (C7 (Ace)), 135.3 (C5a (Ace)), 137.2 (d*, $^{1}J_{CF}$ = 253 Hz, C_m (C_6F_5)), 139.1 (C8b (Ace)), 142.6 (d*, $^{1}J_{CF}$ = 258 Hz, C_p (C_6F_5)), 145.1 (d, $^{2}J_{CF}$ = 13.9 Hz, C4 (Ace)), 146.6 (C8a (Ace)), 147c.6 (d*, $^{1}J_{CF}$ = 248 Hz, C_o (C_6F_5)), 156.0 (C2a (Ace)).

^{11}B NMR (128 MHz, C_6D_6): δ 47 ($\Delta\nu_{1/2}$ = 580 Hz).

^{19}F NMR (377 MHz, C_6D_6): δ –160.9 (m, F_m (C_6F_5)), –149.8 (tt, *J* = 20.6, 3.6 Hz, F_p (C_6F_5)), –130.6 (m, F_o (C_6F_5)), –35.9 (BF).



4d (95% yield, brown oil).

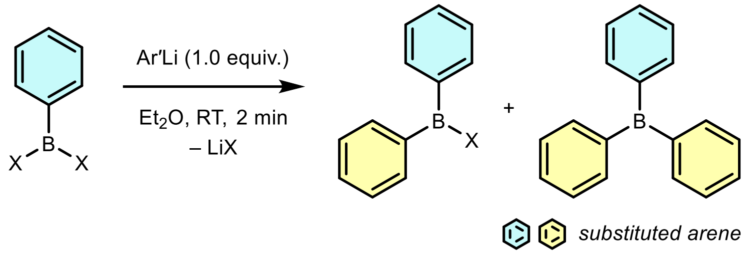
^{1}H NMR (400 MHz, C_6D_6): δ 2.08 (s, 3H, *p*-Me (Mes)), 2.15 (d, J_{HF} = 2.4 Hz, 6H, *o*-Me (Mes)), 6.65 (s, 2H, H_m (Mes)).

^{13}C NMR (101 MHz, C_6D_6): δ 20.9 (*p*-Me (Mes)), 21.7 (*o*-Me (Mes)), 108.6 (C_i (C_6F_5)), 129.0 (C_p (Mes)), 132.2 (C_i (Mes)), 137.2 (d, J = 252.7 Hz, C_m (C_6F_5)), 140.4 (C_m (Mes)), 140.6 (C_o (Mes)), 144.1 (d, J = 258.1 Hz, C_p (C_6F_5)), 149.5 (d, J = 251.7 Hz, C_o (C_6F_5)).

^{11}B NMR (128 MHz, C_6D_6): δ 50 ($\Delta\nu_{½}$ = 520 Hz).

^{19}F NMR (377 MHz, C_6D_6): δ –163.0 (m, F_m (C_6F_5)), –145.9 (ttd, J = 21.0, 6.1, 3.1 Hz, F_p (C_6F_5)), –131.4 (m, F_o (C_6F_5)), –17.1 (BF).

NMR-scale reactions of $ArBX_2$ with Ar′M.



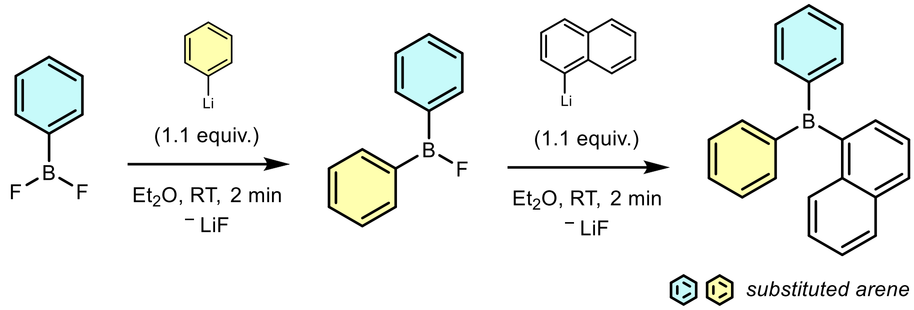
Reactions were generally performed as described for **4** (*vide supra*). The resultant solid mixture was extracted with C_6D_6, filtered into an NMR tube, and the ratio of ArAr′BX to $BAr(Ar')_2$ was measured by ^1H NMR spectroscopy. Assuming quantitative consumption of Ar′M, the relative ratios of the products were ascertained by integrating well separated multiplets in the aromatic region of the ^1H NMR spectra. In all cases, the only resonances in the ^{11}B and ^{19}F NMR spectra could be attributed to ArAr′BX, $BAr(Ar')_2$, and unreacted $ArBX_2$.

Table S1. Optimisation of In Situ Synthesis of ArAr′BX from $ArBX_2$ and Ar′M

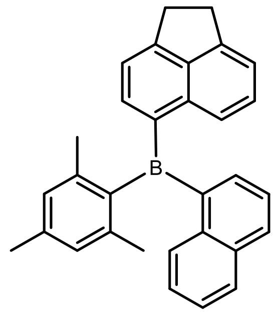
$ArBX_2$	Ar′M	Solvent	T (°C)	ArAr′BX : $BAr(Ar')_2$	NMR yield of ArAr′BX (%)
3b	MesLi	Et_2O	25	>20 : 1	>95
3d	MesLi	Et_2O	25	>20 : 1	>95
3a	C_6F_5MgBr	Et_2O	25	>20 : 1	>95
3d	C_6F_5MgBr	Et_2O	25	>20 : 1	>95
3b	NaphLi	C_5H_{12}	–35[a]	3.3 : 1	60
3b	NaphLi	C_5H_{12}	25	3.1 : 1	60
3b	NaphLi	C_6H_6	25	1.3 : 1	40
3b	NaphLi	Et_2O	25	1 : 3.9	10
3a	NaphLi	C_5H_{12}	25	1.3 : 1	40
3d	NaphLi	C_5H_{12}	25	1 : 2.1	20
3a	Ar^FMgBr	Et_2O	25	6.9 : 1	70
3d	Ar^FMgBr	Et_2O	25	2.5 : 1[b]	--[b]
2b	MesLi	C_5H_{12}	25	--[c]	--[c]
2b	NaphLi	C_5H_{12}	25	1 : 4.1	10

[a] NaphLi suspended in pentane was added dropwise to **3b** in pentane. [b] Accurate assessment of the yields of ArAr′BF or $BArAr'_2$ was not possible due to incomplete solubility of the sample in C_6D_6, which we attribute to the formation of sparingly soluble Et_2O adducts. [c] Complex mixture in the ^1H NMR spectrum; resonances could not be unambiguously identified as ArAr′BBr or $BArAr'_2$, but large amount of unreacted **2b** remained.

Synthesis of 5.



In the glove box, a vial was charged with solid **3** (0.20 mmol) and aryllithium (0.20 mmol, 1.0 equiv. per B atom). Diethyl ether (*ca*. 0.5 mL) was added, resulting in a white suspension, and the vial was shaken for 2 min, during which some of the precipitate had dissolved. Solid NaphLi (0.22 mmol, 1.1 equiv.) was then added, and the vial was again shaken for 2 min, resulting in a pale violet suspension. The Et_2O was evaporated, the solid was extracted with benzene, dried, and then recrystallised from pentane or Et_2O at –35 °C, yielding **5** as colourless crystals.



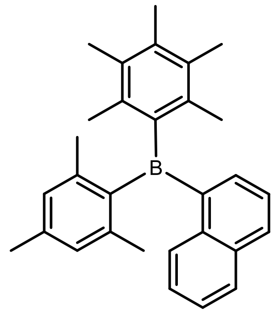
5a (91% yield, white powder). Repeated attempts to grow crystals suitable for X-ray crystallography failed, only returning very small, fragile colourless needles and plates.

^{1}H NMR (400 MHz, C_6D_6): δ 2.15 (s, 3H, *p*-Me (Mes)), 2.19 (s, 3H, *o*-Me (Mes)), 2.23 (s, 3H, *o*-Me (Mes)), 2.91 (s, 4H, H1/2 (Ace)), 6.83 (s, 1H, H_m (Mes)), 6.84 (s, 1H, H_m (Mes)), 6.99 (m, 4H, H3/7/8 (Ace) + H7 (Naph)), 7.15 (m, 1H, H6 (Naph), overlapping with residual solvent signal), 7.27 (dd, *J* = 8.2, 6.9 Hz, 1H, H3 (Naph)), 7.66 (m, 2H, H6 (Ace) + H5 (Naph)), 7.75 (d*, *J* = 8.3 Hz, 1H, H4 (Naph)), 7.82 (dd, *J* = 6.9, 1.3 Hz, 1H, H2 (Naph)), 7.89 (d, *J* = 7.1 Hz, 1H, H4 (Ace)), 8.19 (dq, *J* = 8.4, 0.9 Hz, 1H, H8 (Naph)). Asterisk (*) denotes unresolved fine structure.

^{13}C NMR (101 MHz, C_6D_6): δ 21.0 (*p*-Me (Mes)), 22.8 (*o*-Me (Mes)), 22.9 (*o*-Me (Mes)), 29.9 (C1/2 (Ace)), 30.3 (C1/2 (Ace)), 119.2 (C3 (Ace)), 119.4 (C8 (Ace)), 123.7 (C6 (Ace)), 125.3 (C3 (Naph)), 125.5 (C6 (Naph)), 126.0 (C7 (Naph)), 128.1 (C_m (Mes)), 128.2 (C_m (Mes)), 128.5 (C7 (Ace)), 128.6 (C5 (Naph)), 129.4 (C8 (Naph)), 131.5 (C4 (Naph)), 133.7 (C8a (Naph)), 134.9 (C2 (Naph)), 135.4 (C5a (Ace)), 136.5 (C4a (Naph)), 137.7 (C_p (Mes)), 138.5 (C_o (Mes)), 138.6 (C_o (Mes)), 139.4 (C8b (Ace)), 139.6 (br, C5 (Ace)), 140.3 (C4 (Ace)), 145.8 (br, C1 (Naph) + C_i (Mes)), 146.2 (C8a (Ace)), 151.9 (C2a (Ace)).

^{11}B NMR (128 MHz, C_6D_6): δ 73 ($\Delta\nu_{½}$ = 1340 Hz).

HRMS (APCI): m/z calcd. For $[C_{31}H_{27}B]^+$ 410.2200; found 410.2222.



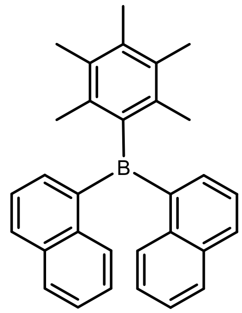
5b (94% yield, white powder). Crystals suitable for X-ray crystallography were obtained via slow evaporation of a saturated pentane solution at ambient temperature.

^{1}H NMR (400 MHz, C_6D_6): δ 2.02 (s, 6H, *m*-Me (Ph*)), 2.13 (s, 3H, *p*-Me (Ph*)), 2.15 (s, 3H, *p*-Me (Mes)), 2.16 (s, 6H, *o*-Me (Mes)), 6.76 (s, 2H, H_m (Mes)), 7.08 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H, H7 (Naph)), 7.19 (m, 2H, H3/H6 (Naph), overlapping with residual solvent signal), 7.63 (m, 1H, H5 (Naph)), 7.71 (m, 2H, H2/H4 (Naph)), 8.28 (dq, *J* = 8.4, 0.9 Hz, 1H, H8 (Naph)), n.o. (*o*-Me (Ph*)).

^{13}C NMR (101 MHz, C_6D_6): δ 15.7 (*m*-Me (Ph*)), 16.6 (*p*-Me (Ph*)), 20.9 (*p*-Me (Mes)), 21.3 (br, *o*-Me (Ph*)) 23.3 (*o*-Me (Mes)), 125.5 (C3 (Naph)), 125.7 (C6 (Naph)), 126.3 (C7 (Naph)), 127.8 (C8 (Naph)), 128.7 (C5 (Naph)), 129.2 (C_m (Mes)), 131.8 (C4 (Naph)), 132.0 (C_m (Ph*)), 133.5 (C8a (Naph)), 134.7 (C2 (Naph)), 135.4 (C_p (Ph*)), 136.2 (C4a (Naph)), 139.2 (C_p (Mes)), 141.1 (C_o (Mes)), 143.7 (C_i (Mes), observed by ^{1}H-^{13}C HMBC), 146.1 (C_i (Ph*), observed by ^{1}H-^{13}C HMBC), 148.5 (C1 (Naph)), n.o. (C_o (Ph*)).

^{11}B NMR (128 MHz, C_6D_6): δ 75 ($\Delta\nu_{½}$ = 1200 Hz).

HRMS (APCI): m/z calcd. for $[C_{30}H_{33}B+H]^+$ 405.2748; found 410.2748.



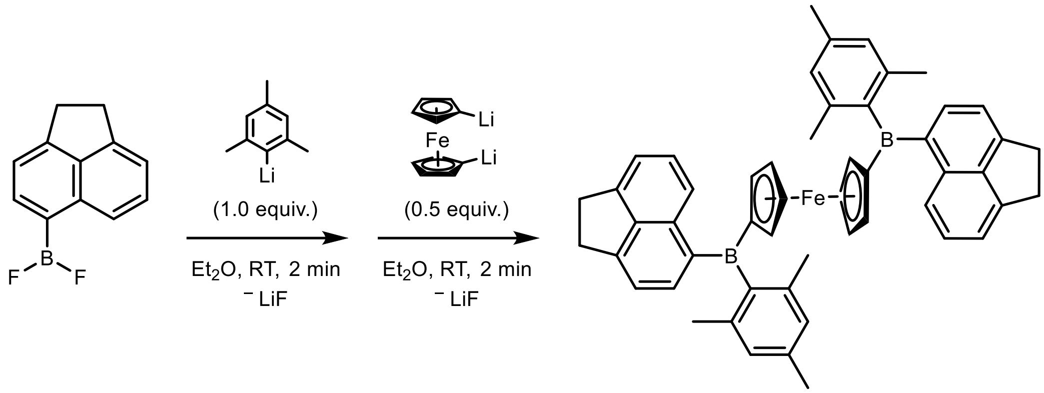
5c (99% yield, white powder). Crystals suitable for X-ray crystallography were obtained via slow evaporation of a saturated Et_2O solution at ambient temperature.

^{1}H NMR (400 MHz, C_6D_6): δ 2.03 (s, 3H, *m*-Me (Ph*)), 2.16 (s, 1H, *p*-Me (Ph*)), 2.19 (s, 3H, *o*-Me (Ph*)), 6.87 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H, H7 (Naph)), 7.08 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H, H6 (Naph)), 7.24 (dd, *J* = 8.2, 6.9 Hz, 1H, H3 (Naph)), 7.61 (d*, *J* = 8.2 Hz, 1H, H5 (Naph)), 7.72 (d*, *J* = 8.3 Hz, 1H, H4 (Naph)), 7.91 (dd, *J* = 6.9, 1.4 Hz, 1H, H2 (Naph)), 8.06 (d*, *J* = 8.6 Hz, 1H, H8 (Naph)).

^{13}C NMR (126 MHz, C_6D_6): δ 15.4 (*m*-Me (Ph*)), 16.4 (*p*-Me (Ph*)), 21.4 (*o*-Me (Ph*)), 125.3 (C3 (Naph)), 125.6 (C6 (Naph)), 126.2 (C7 (Naph)), 128.6 (C5 (Naph)), 128.9 (C8 (Naph)), 132.1 (C4 (Naph)), 132.1 (C_m (Ph*)), 132.9 (C_o (Ph*)), 133.7 (C8a (Naph)), 134.6 (C_p (Ph*)), 136.2 (C4a (Naph)), 136.3 (C2 (Naph)), 144.9 (C1 (Naph), observed by ^{1}H-^{13}C HMBC), 146.7 (C_i (Ph*), observed by ^{1}H-^{13}C HMBC).

^{11}B NMR (128 MHz, C_6D_6): δ 74 ($\Delta\nu_{½}$ = 1200 Hz).

Synthesis of 6.



In the glove box, a vial was charged with **3d** (0.0440 g, 0.218 mmol) and MesLi (0.0298 g, 0.236 mmol). Diethyl ether (*ca*. 0.5 mL) was added, resulting in a white suspension, and the vial was shaken for 2 min, during which most of the precipitate gradually dissolved. A suspension of $FcLi_2$·tmeda (0.0304 g, 0.0968 mmol) in Et_2O (0.5 mL) was added dropwise, resulting in the immediate formation of deep red-violet suspension. The vial was shaken for 2 min, the Et_2O was evaporated, then the red solid was extracted with fluorobenzene (5 mL) and filtered. Volatile materials were removed from the filtrate under dynamic vacuum and the resultant red gel was washed with pentane (5 mL), affording **6** (0.0701 g, 0.0934 mmol, 96.5% w.r.t. $FcLi_2$·tmeda) as a pink powder.

A single crystal of **6**·$0.5C_6H_5F$ was found as a small, partially decomposed red block upon evaporation of a saturated fluorobenzene solution at ambient temperature.

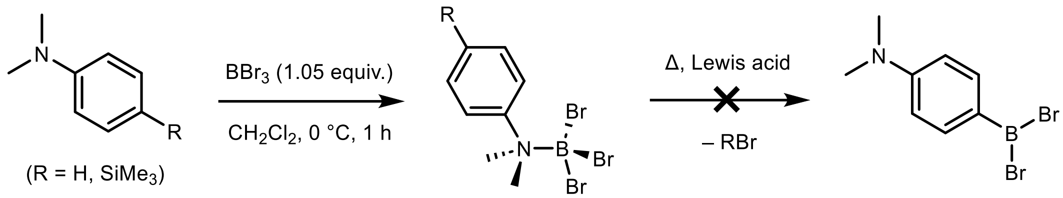
^{1}H NMR (400 MHz, C_6D_6): δ 2.25 (s, 12H, *o*-Me (Mes)), 2.27 (s, 6H, *p*-Me (Mes)), 3.02 (s, 8H, H1/2 (Ace)), 4.71 (t, *J* = 1.9 Hz, 4H, H_{Cp} (Fc)), 4.80 (t, *J* = 1.8 Hz, 4H, H_{Cp} (Fc)), 6.88 (s, 4H, H_m (Mes)), 7.04 (d, *J* = 6.8 Hz, 2H, H8 (Ace)), 7.21 (m, 4H, H3/7 (Ace)), 8.05 (d, *J* = 8.4 Hz, 2H, H6 (Ace)), 8.96 (d, *J* = 7.1 Hz, 2H, H4 (Ace)).

^{13}C NMR (101 MHz, C_6D_6): δ 21.1 (*p*-Me (Mes)), 23.1 (*o*-Me (Mes)), 30.0 (C1 (Ace)), 30.3 (C2 (Ace)), 76.1 (C_{Cp} (Fc)), 79.3 (C_{Cp} (Fc)), 118.9 (C3 (Ace)), 119.3 (C8 (Ace)), 123.6 (C6 (Ace)), 128.2 (C_m (Mes)), 128.3 (C7 (Ace)), 135.8 (C5a (Ace)), 137.0 (C_p (Mes)), 137.5 (C5 (Ace)), 137.8 (C_o (Mes)), 139.2 (C8b (Ace)), 139.7 (C4 (Ace)), 145.2 (C_i (Mes)), 146.1 (C8a (Ace)), 150.9 (C2a (Ace)), n.o. (C_{Cp}–B (Fc)).

^{11}B NMR (128 MHz, C_6D_6): δ 72 ($\Delta\nu_{½}$ ~ 3000 Hz).

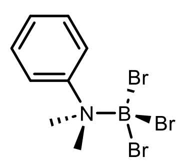
HRMS (APCI): m/z calcd. for $[C_{52}H_{48}B_2Fe]^+$ 750.3286; found 750.3310.

Syntheses of $BBr_3{\cdot}NMe_2(4\text{-}C_6H_4R)$ (R = H, $SiMe_3$).



In a 25 mL Schlenk flask, 1,4-$Me_2NC_6H_4R$ (2.0 mmol) was dissolved in CH_2Cl_2 (3 mL) and cooled to 0 °C. Boron tribromide (2.1 mmol) was added dropwise, resulting in a pale brown (R = H) or yellow (R = $SiMe_3$) solution. The solution was warmed to ambient temperature and stirred for 1 h before volatile materials were removed under dynamic vacuum, affording $BBr_3{\cdot}NMe_2(4\text{-}C_6H_4R)$ as white powders containing traces of [Me_2(4-RC_6H_4)NH][BBr_4], determined by NMR spectroscopy.

No Si/B or H/B exchange was observed during the reaction, or after heating to 80 °C in C_6D_6, with or without catalytic Me_3SiNTf_2 or $AlOTf_3$ (10 mol%, Tf = SO_2CF_3), despite a previous report of spontaneous H/B exchange to form 1,4-$Me_2NC_6H_4BBr_2$ in the presence of a slight excess of BBr_3.[18]

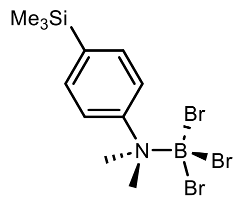


R = H (99% yield, off-white powder). Crystals suitable for X-ray crystallography were grown by vapour diffusion of pentane into a saturated fluorobenzene solution at –35 °C over several days.

^{1}H NMR (400 MHz, C_6D_6): δ 2.80 (q, $^3J_{BH}$, Me, 6H), 6.87 (m, H_o/H_p, 3H), 7.16 (m, H_m, 2H, overlapping with residual solvent signal).

^{13}C NMR (126 MHz, C_6D_6): δ 50.6 (Me), 124.4 (C_m), 127.5 (C_o/C_p), 128.0 (C_o/C_p), 144.5 (C_i).

^{11}B NMR (128 MHz, C_6D_6): δ –2.8.



R = $SiMe_3$ (95% yield, off-white powder). Crystals suitable for X-ray crystallography were grown by vapour diffusion of pentane into a saturated fluorobenzene solution at –35 °C over several days.

^{1}H NMR (500 MHz, C_6D_6): δ 0.09 (s, $SiMe_3$, 9H), 2.83 (q, $^3J_{BH}$ = 3.0 Hz, NMe_2, 6H), 7.21 (d, $^3J_{HH}$ = 8.2 Hz, C_o, 2H), 7.24 (d, C_m, 2H).

^{13}C NMR (126 MHz, C_6D_6): δ –1.77 ($SiMe_3$), 50.59 (NMe_2), 123.75 (C_o), 132.68 (C_m), 140.89 (C_i), 145.24 (C_p).

^{11}B NMR (128 MHz, C_6D_6) δ –2.8.

Experimental and calculated data.

Table S2. Calculated ΔG and ΔH (kcal mol^{-1}) for Reactions of **3** with $[BF_4]^-$ and FIAs (kcal mol^{-1}) of **3**[a]

	ΔG	ΔH	FIA[b]
BF_3	0.0	0.0	345.1[c]
3a	15.0	14.1	331.0
3b	16.9	15.8	329.3
3c	10.3	9.9	335.2
3d	13.8	13.0	332.1
3e	10.7	10.2	334.9
3f	7.5	7.5	337.6
3g	9.2	7.6	337.5
3h	8.5	8.2	336.9

[a] Calculated at the PW6B95-D3(BJ)/def2-TZVP level of theory in C_6H_6 (SMD solvent model) at 298 K. [b] Defined as FIA = –ΔH(A + F^- → AF^-). ***Note:*** FIAs are typically calculated in the gas phase without solvation. However, as these reactions are isodesmic, we believe that the calculated trends in FIA should be accurate. [c] From reference X; calculated in the gas phase.

Table S3. Experimental and Calculated ^{11}B and ^{19}F Chemical Shifts of **3–6**[a]

	δ(^{11}B) (ppm)		δ(^{19}F) (ppm)	
	exptl.	calcd.	exptl.	calcd.
3a	25.9	26.2	–70.1	–65.4
3b	27.3	29.0	–63.5	–51.5
3c	25.3	26.1	–82.7	–79.8
3d	25.5	26.4	–85.7	–83.7
3e	27.0	29.0	–63.9	–54.1
3f	24.5	25.7	–88.8	–85.1
3g	24.8	25.7	–80.9	–75.7
3h	23.3	24.0	–88.1	–84.8
4a	52	55.0	–35.9	–20.8
4b	53	58.5	–13.4	7.1
4c	48	47.9	–35.9	–24.7
4d	50	50.0	–17.1	–6.8
5a	75	78.4		
5b	73	76.0		
5c	74	77.7		
6	72	74.2		

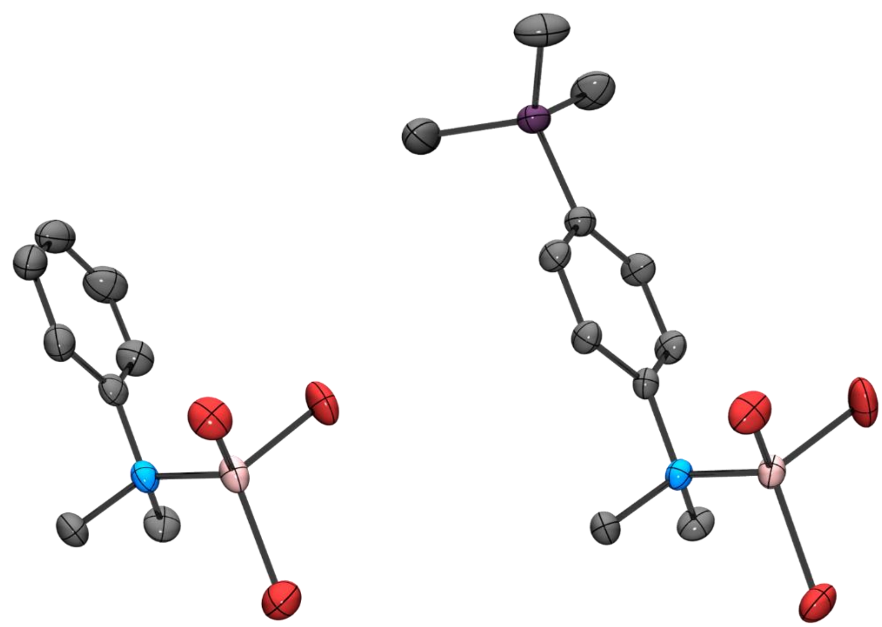
[a] Calculated using the GIAO method at the PW6B95-D3(BJ)/aug-cc-pVTZ level of theory in C_6H_6 (SMD solvent model) at 298 K and averaged for each nuclear environment.

Table S4. Selected Experimental and Calculated[a] Bond Lengths (in Å) and Angles (in °) of **3** and Related Compounds

	B–F		B–C		F–B–F		|F(1)–B–C(1)–C(2)|	
	exptl.	**calcd.**	**exptl.**	**calcd.**	**exptl.**	**calcd.**	**exptl.**	**calcd.**
3a	1.3176(7)	1.328	1.5528(12)	1.540	113.14(8)	113.30	2.92(3)	7.64
3b	1.2965(15) 1.3080(15)	1.327	1.5735(17)	1.548	115.21(11)	114.13	60.58(15)	54.67
3c	1.3210(18) 1.3252(18)	1.325 1.326	1.541(2)	1.544	114.04(12)	114.87	2.05(14)	0.12
3d	1.3261(14) 1.3262(14)	1.327 1.328	1.5396(13)	1.537	113.68(9)	115.13	3.80(12)	0.10
3e	1.3207(17) 1.3210(16)	1.326	1.6769(15)	1.548	112.09(12)	114.22	2.77(13)	41.48
3f		1.321		1.546		116.65		0.38
3g	1.3222(15) 1.3252(16)	1.323 1.325	1.5496(16)	1.544	114.93 (11)	115.32	0.33(14)	0.01
3h	1.330(3) 1.335(3)	1.323	1.527(3)	1.525	115.8(2)	116.62	1.6(5)	0.02
EindBF$_2$[b]	1.3146(15)		1.576(3)		114.78(18)		76.19(7)	
TerBF$_2$[c]	1.307(2)		1.560(2)		115.43(12)		72.27(16)	

[a] Calculated at the PW6B95-D3(BJ)/def2-TZVP level of theory in C_6H_6 (SMD solvent model). [b] From reference 12 of the main text. [c] From reference 13 of the main text.

$BBr_3 \cdot Me_2N(4\text{-}C_6H_4R)$



R = H **R = $SiMe_3$**

Figure S2. Thermal ellipsoid plots (298 K, 30% probability level) of $BBr_3 \cdot NMe_2(4\text{-}C_6H_4R)$. Colours denote brown (Br), violet (Si), blue (N), pink (B), and grey (C), with H atoms omitted for clarity.

Dimerisation Energies (kcal mol⁻¹)

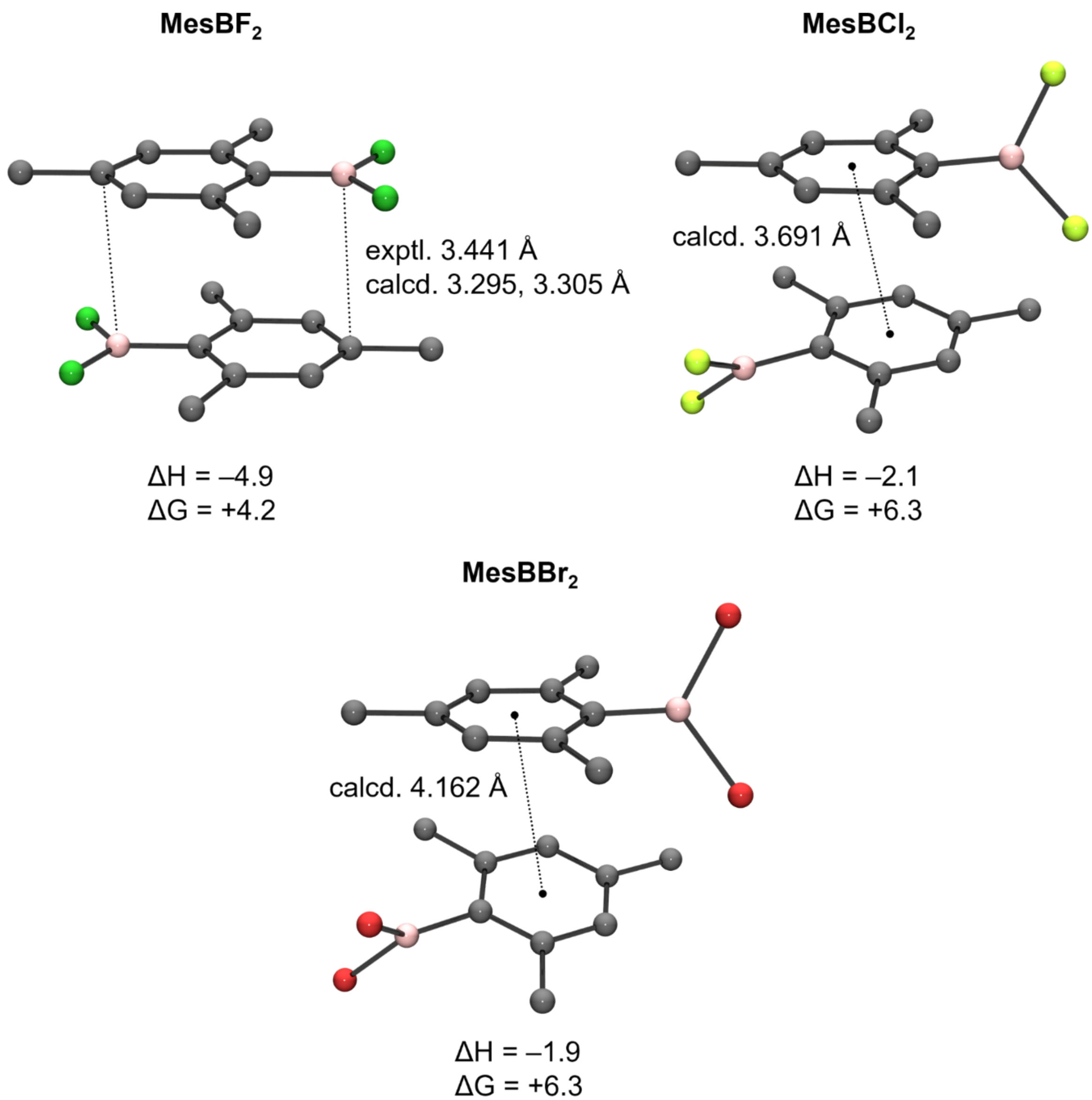


Figure S3. Optimised geometries and thermochemical data for calculated (PW6B95-D3(BJ)/def2-TZVP) $MesBX_2$ dimers. Colours denote brown (Br), yellow-green (Cl), green (F), pink (B), and grey (C), with H atoms omitted for clarity.

Table S5. Selected Experimental and Calculated[a] Bond Lengths (in Å) and Angles (in °) of **4–6**

		B–F		B–C		F–B–C		|F–B–C–C|	
		exptl.	**calcd.**	**exptl.**	**calcd.**	**exptl.**	**calcd.**	**exptl.**	**calcd.**
4a	Ace	1.344(3)	1.346	1.532(4)	1.542	118.8(2)	118.75	9.4(3)	14.08
	Mes			1.577(4)	1.563	114.4(2)	116.50	72.7(3)	60.28
4b	Ph*	1.348(2)	1.346	1.569(3)	1.563	112.83(15)	115.85	56.3(2)	65.09
	Mes			1.566(2)	1.557	121.51(16)	116.86	25.4(2)	38.35
4c	Ace	1.330(3)	1.335	1.543(4)	1.529	120.6(2)	121.07	8.7(3)	12.41
	C_6F_5			1.598(4)	1.578	114.5(2)	114.29	56.8(3)	49.26
4d	Mes		1.334		1.543		118.88		41.15
	C_6F_5				1.571		114.38		33.33
5a	Ace				1.554				
	Mes				1.570				
	Naph				1.560				
5b	Ph*			1.583(3)	1.572				
	Mes			1.583(4)	1.569				
	Naph			1.574(3)	1.565				
5c	Ph*			1.570(4)	1.570				
	Naph			1.577(4)	1.561				
	Naph			1.567(3)	1.560				
6	Ace			1.570(4), 1.569(7)	1.559				
	Mes			1.584(6), 1.582(7)	1.573				
	Fc			1.547(6), 1.529(6)	1.544				

[a] Calculated at the PW6B95-D3(BJ)/def2-TZVP level of theory in C_6H_6 (SMD solvent model).

NMR spectra.

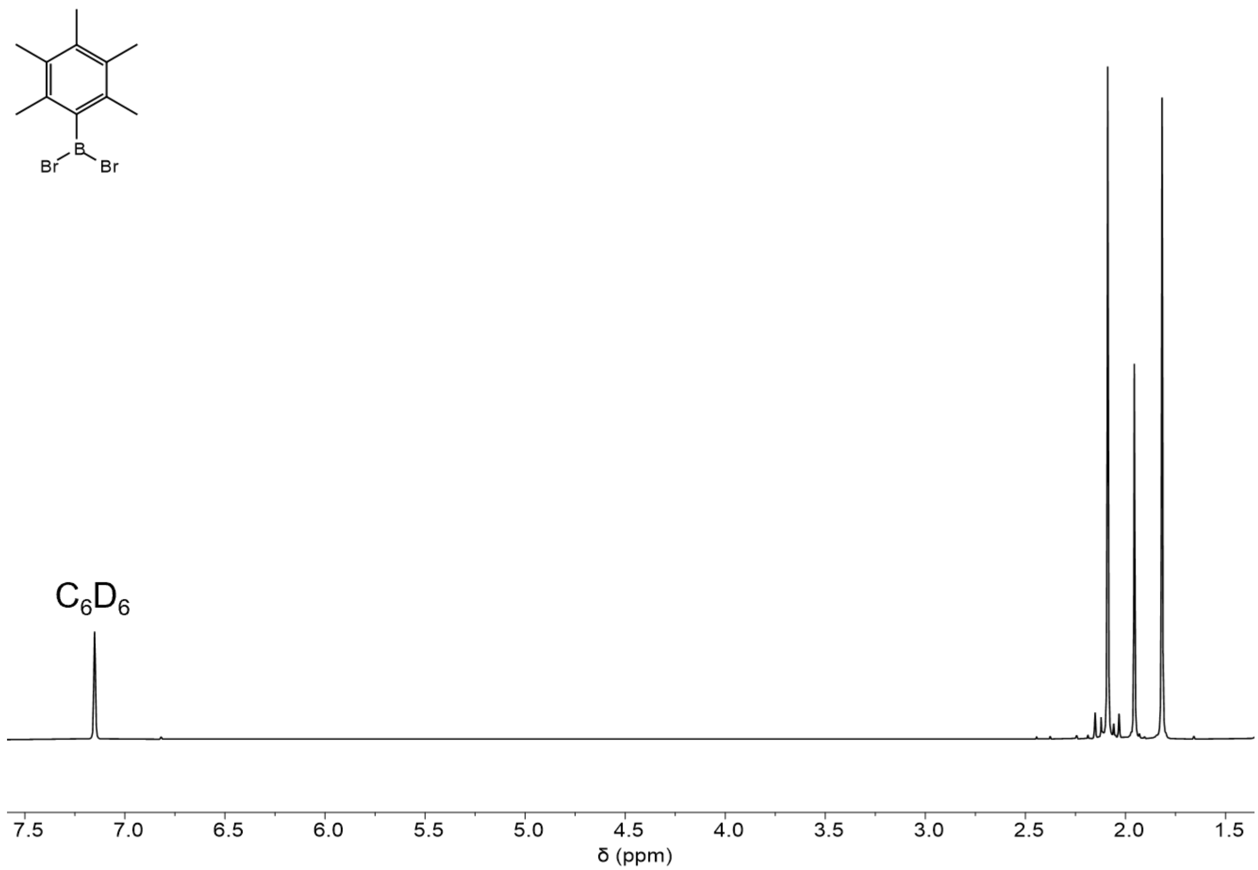


Figure S4. ^{1}H NMR spectrum of **2b**.

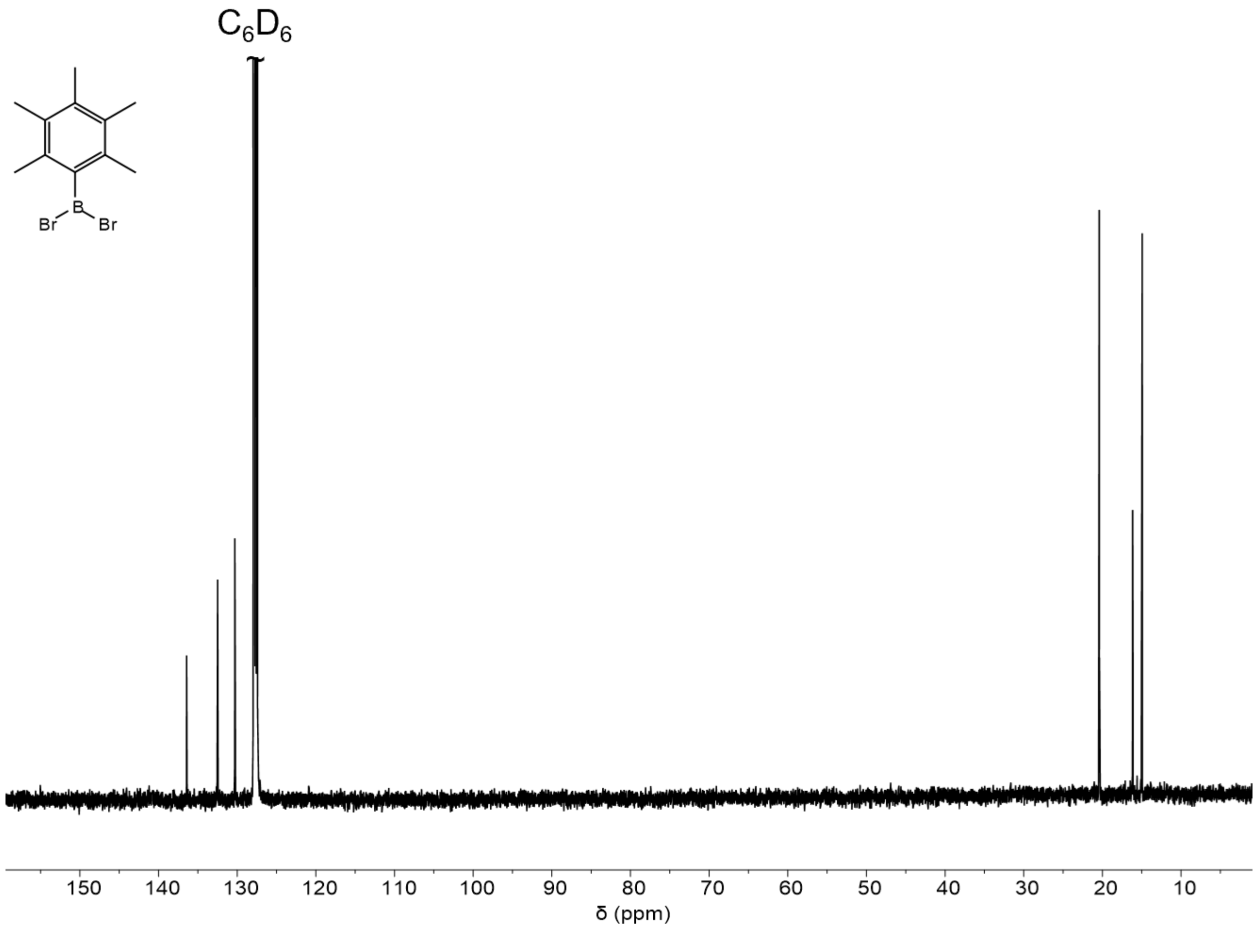


Figure S5. ^{13}C NMR spectrum of **2b**.

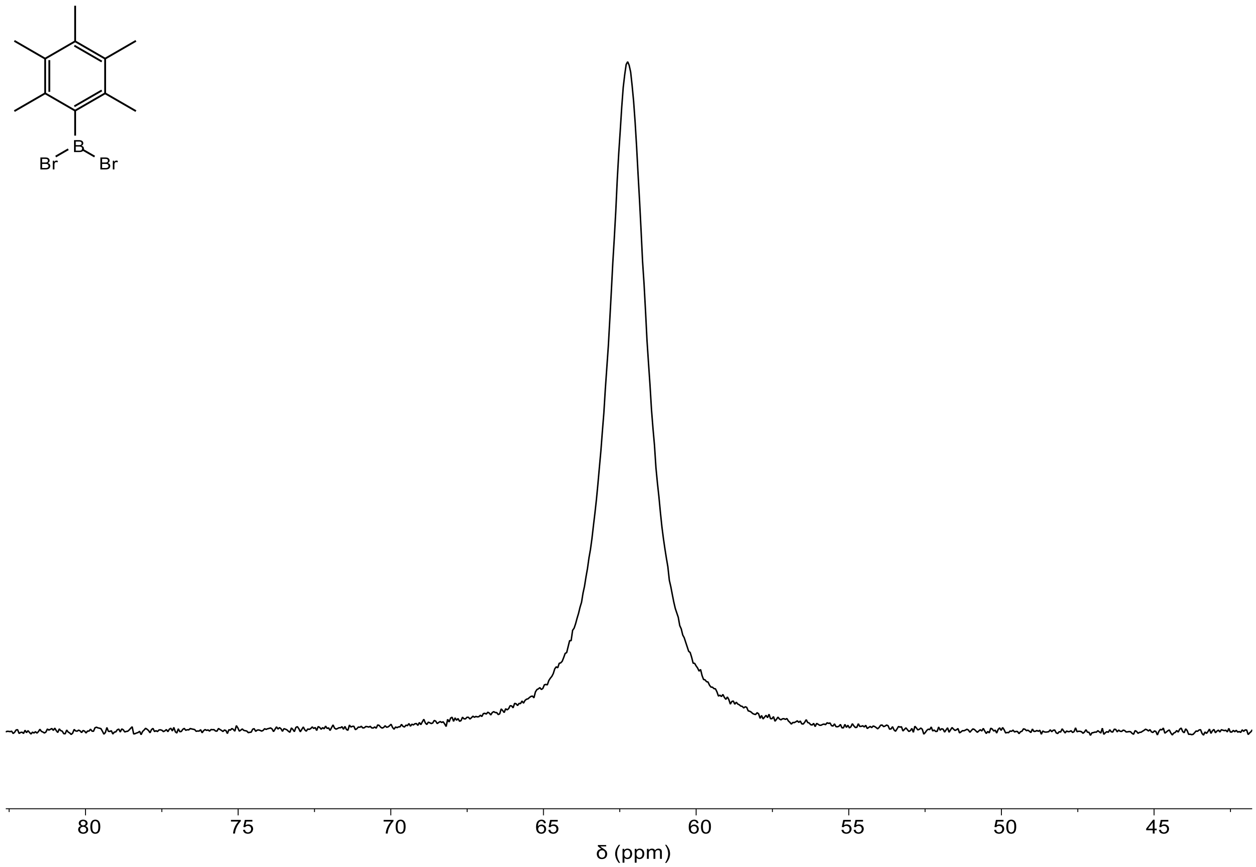


Figure S6. ^{11}B NMR spectrum of **2b**.

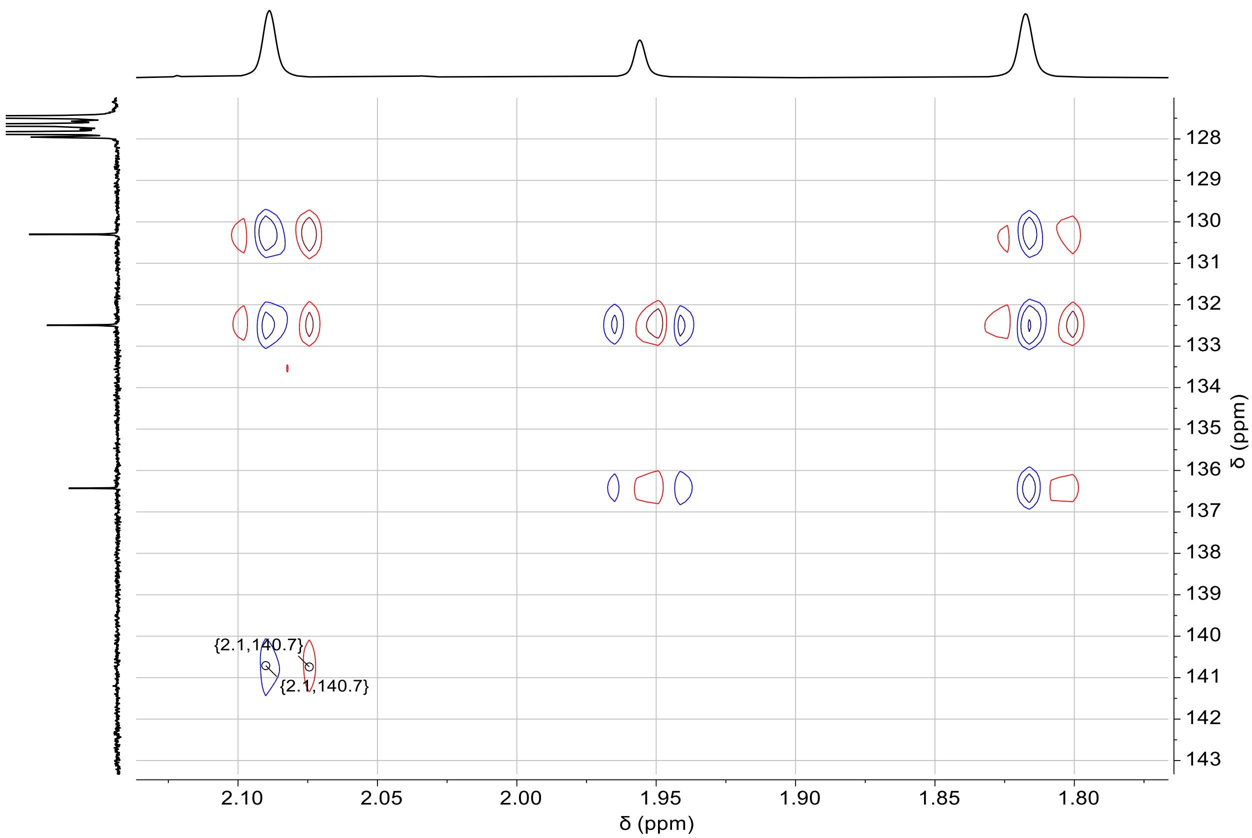


Figure S7. [1]H-[13]C HMBC NMR spectrum of **2b**. Labelled peak correlates to the C_i atom.

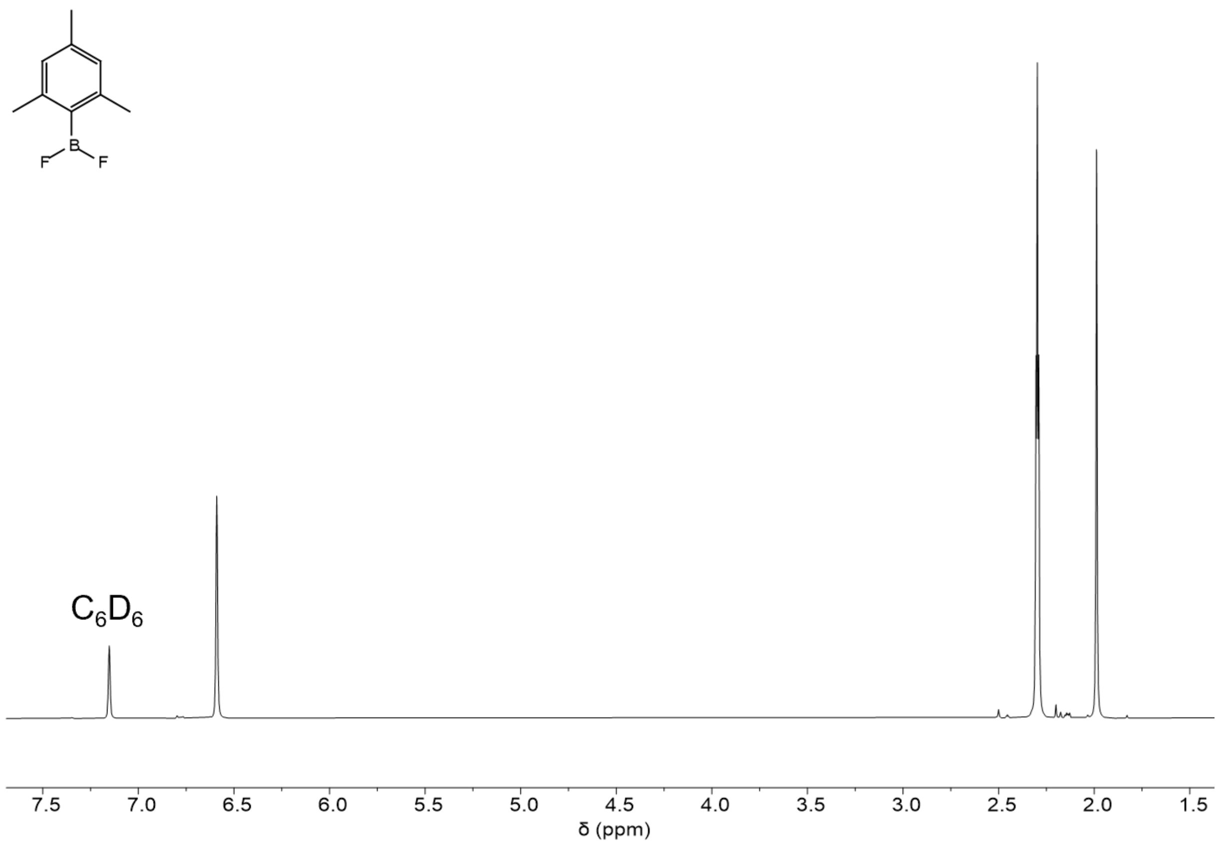


Figure S8. ^{1}H NMR spectrum of **3a**.

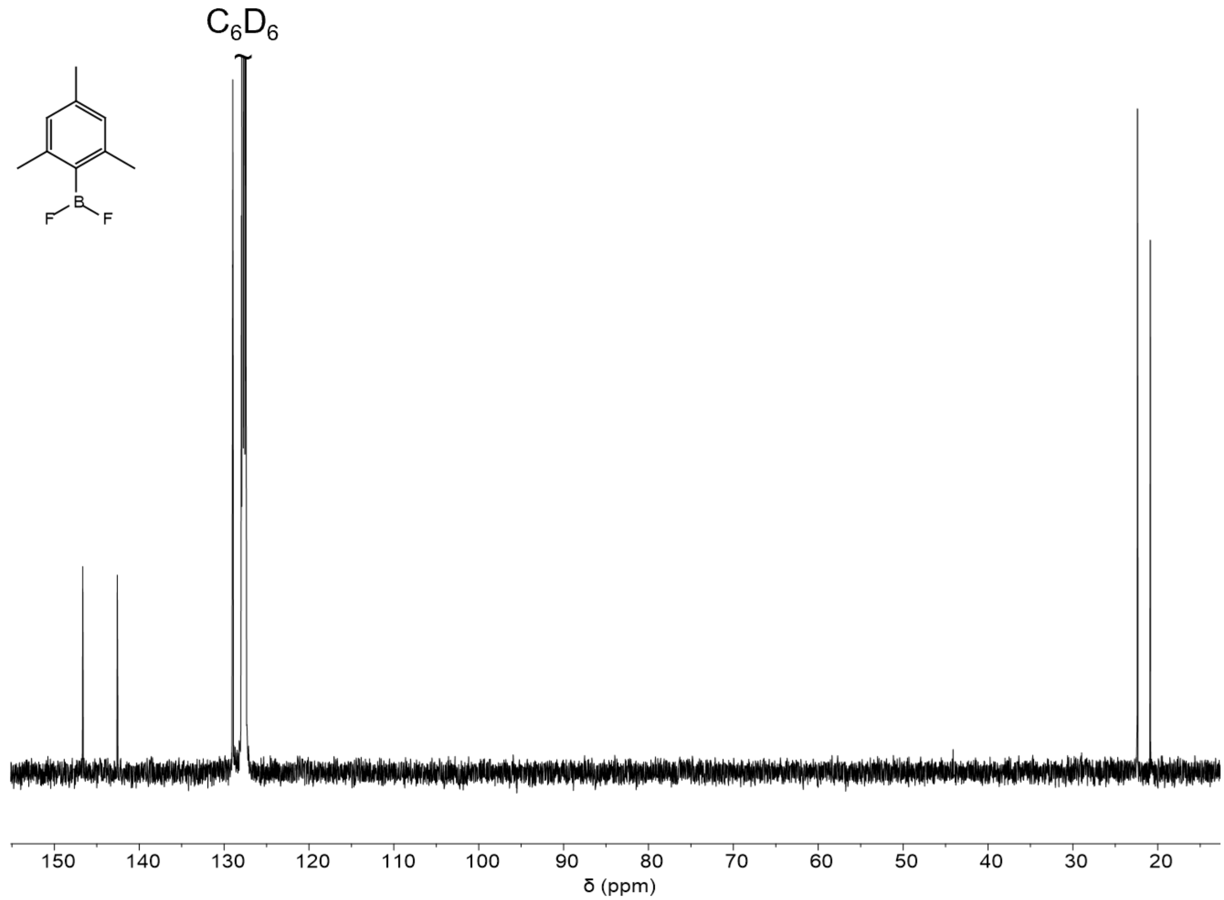


Figure S9. ^{13}C NMR spectrum of **3a**.

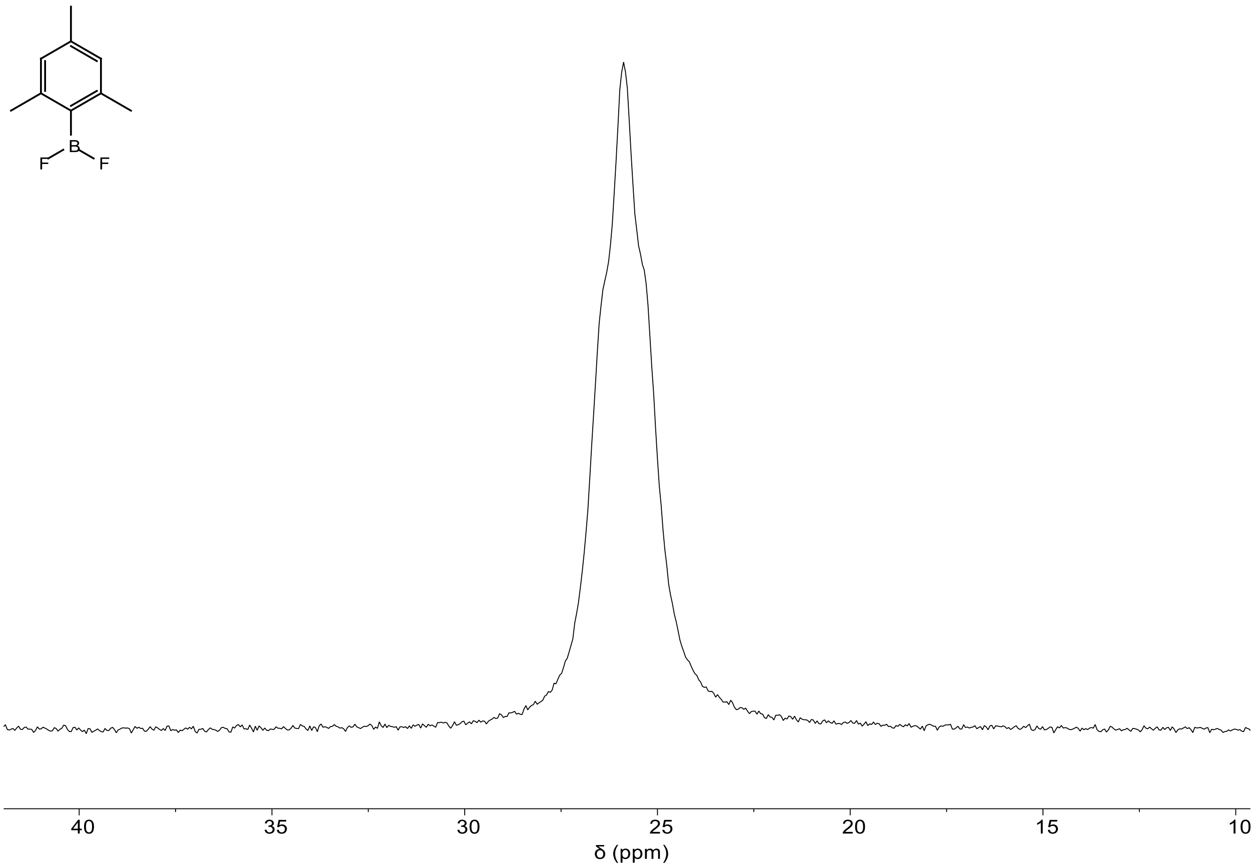


Figure S10. ^{11}B NMR spectrum of **3a**.

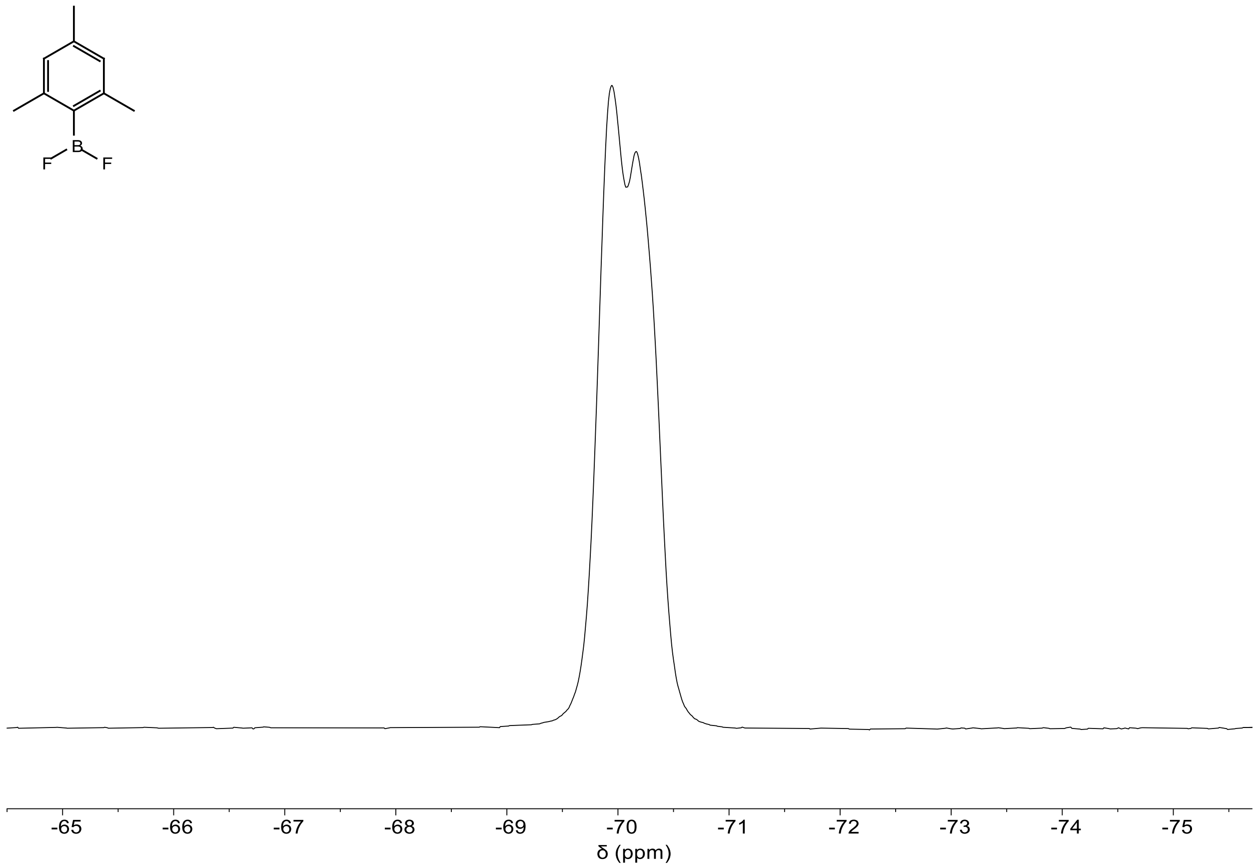


Figure S11. ^{19}F NMR spectrum of **3a**.

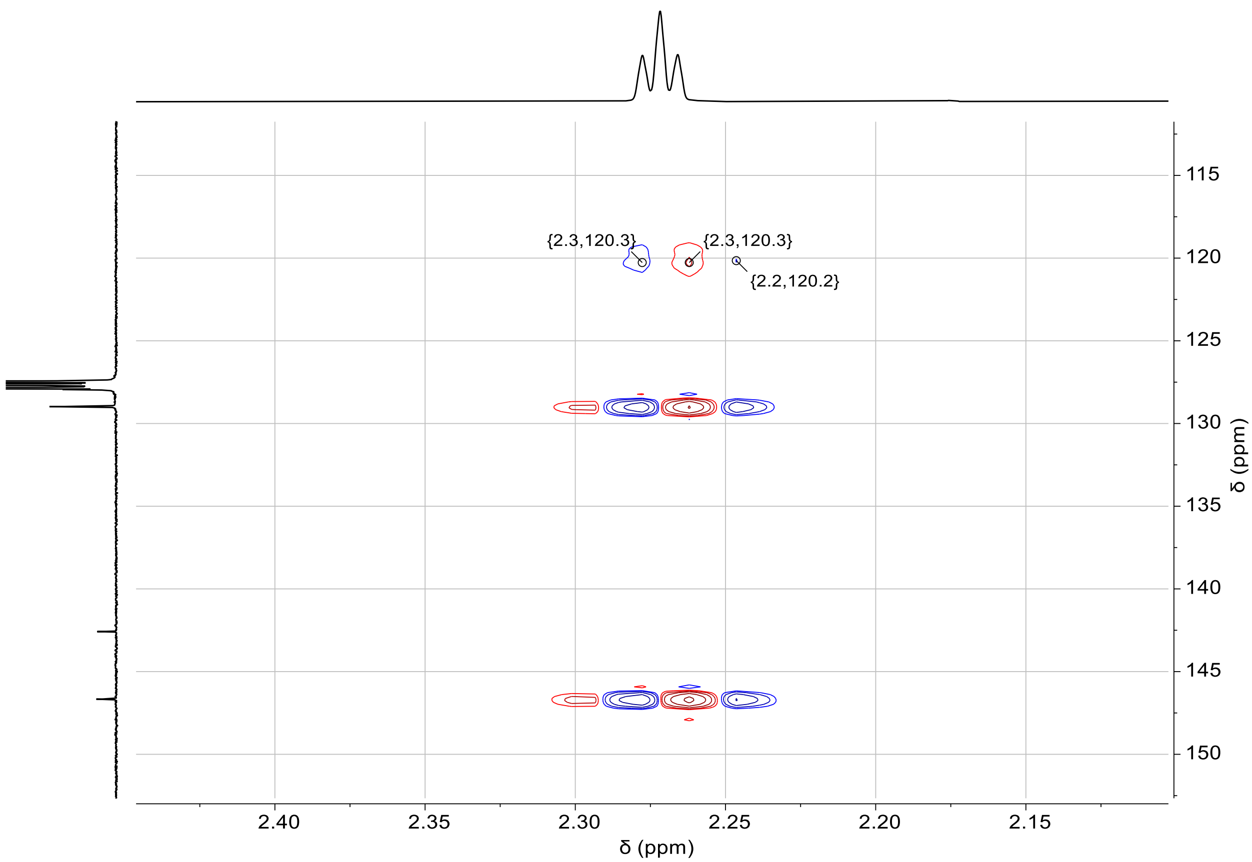


Figure S12. ^{1}H-^{13}C HMBC NMR spectrum of **3a**. Labelled peak correlates to the C_i atom.

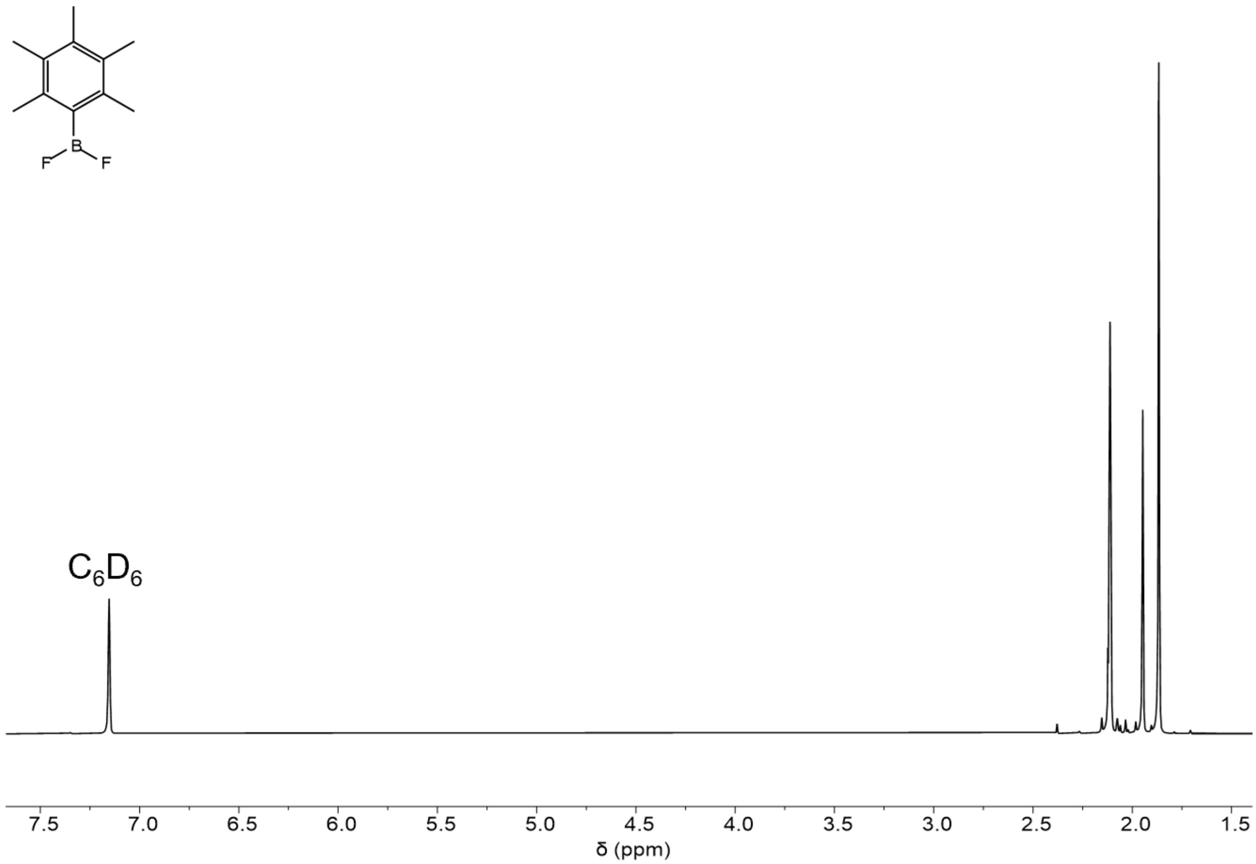


Figure S13. ^{1}H NMR spectrum of **3b**.

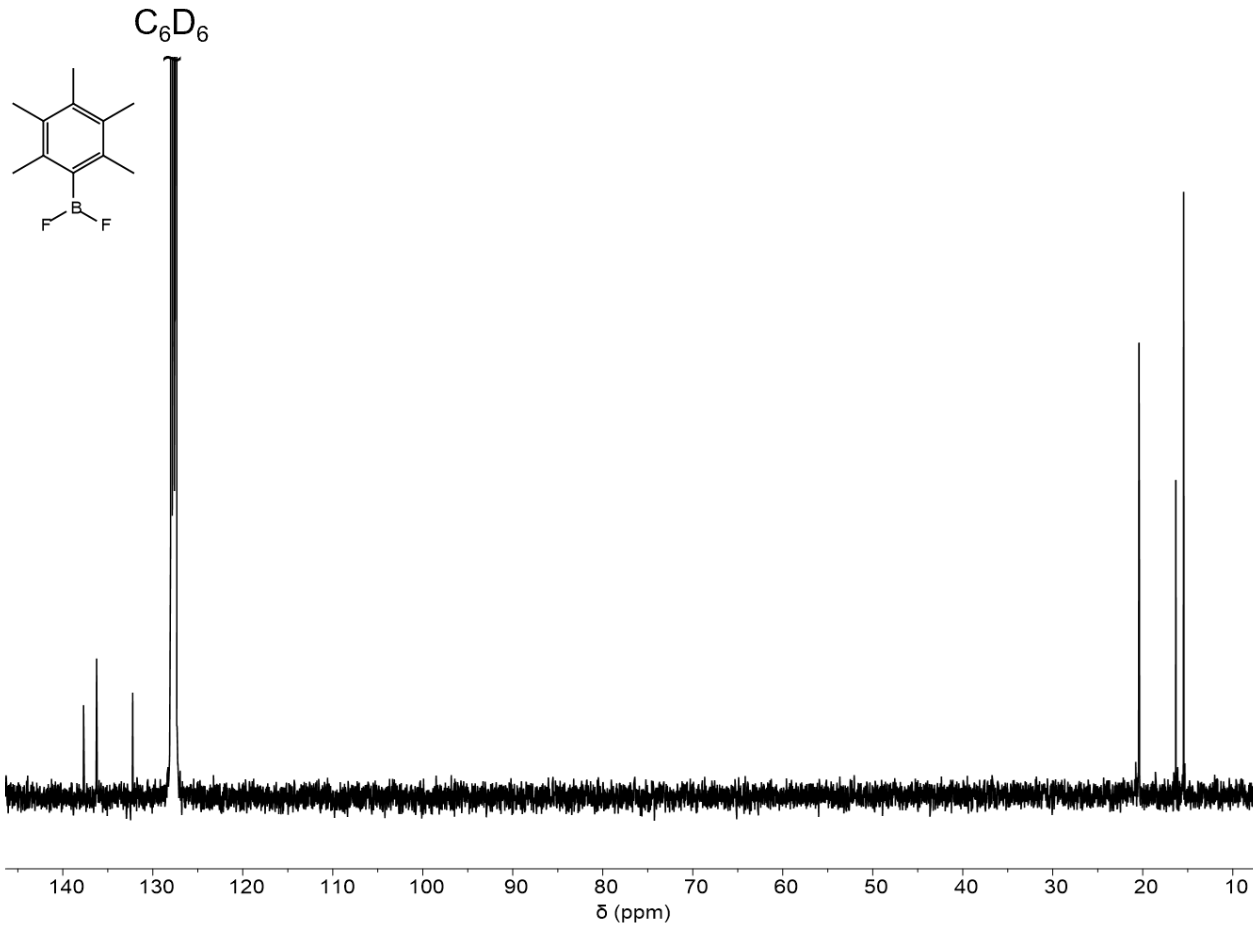


Figure S14. ^{13}C NMR spectrum of **3b**.

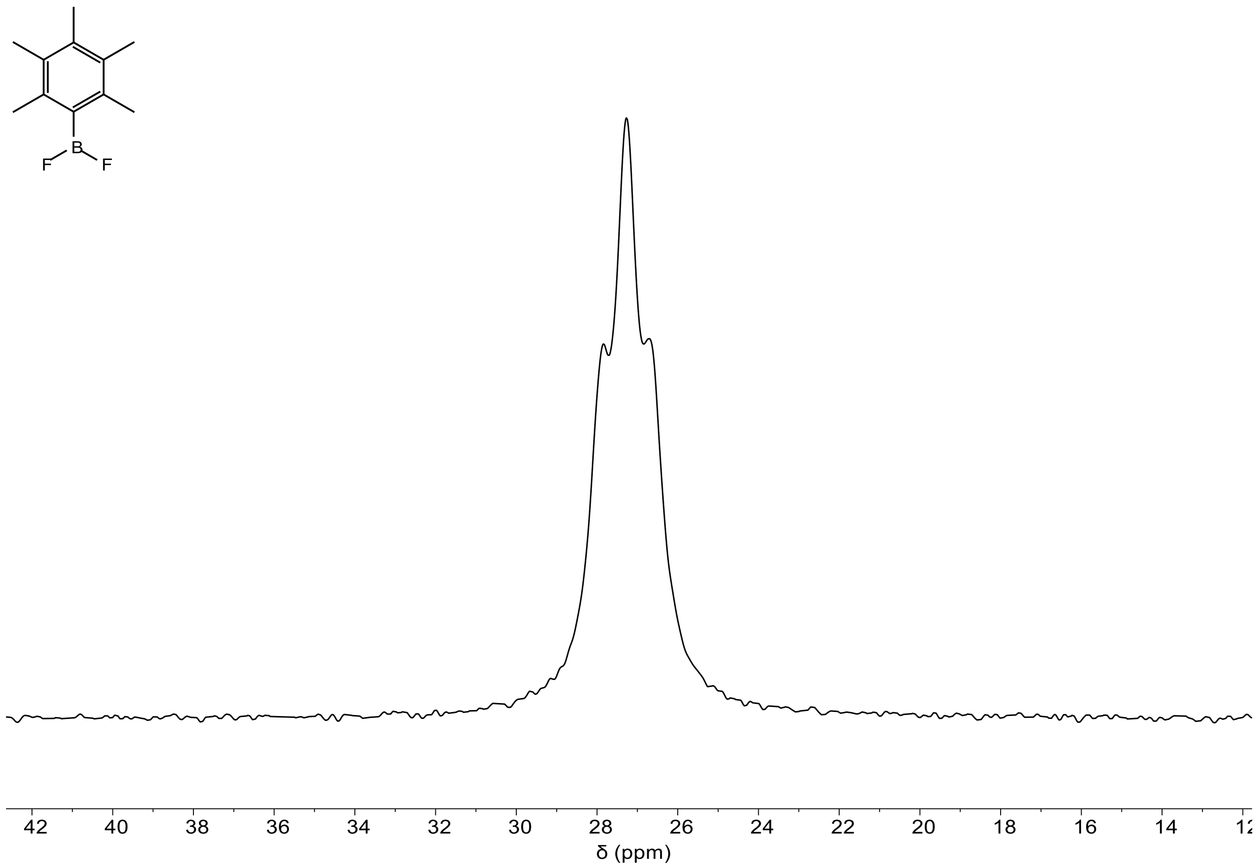


Figure S15. ^{11}B NMR spectrum of **3b**.

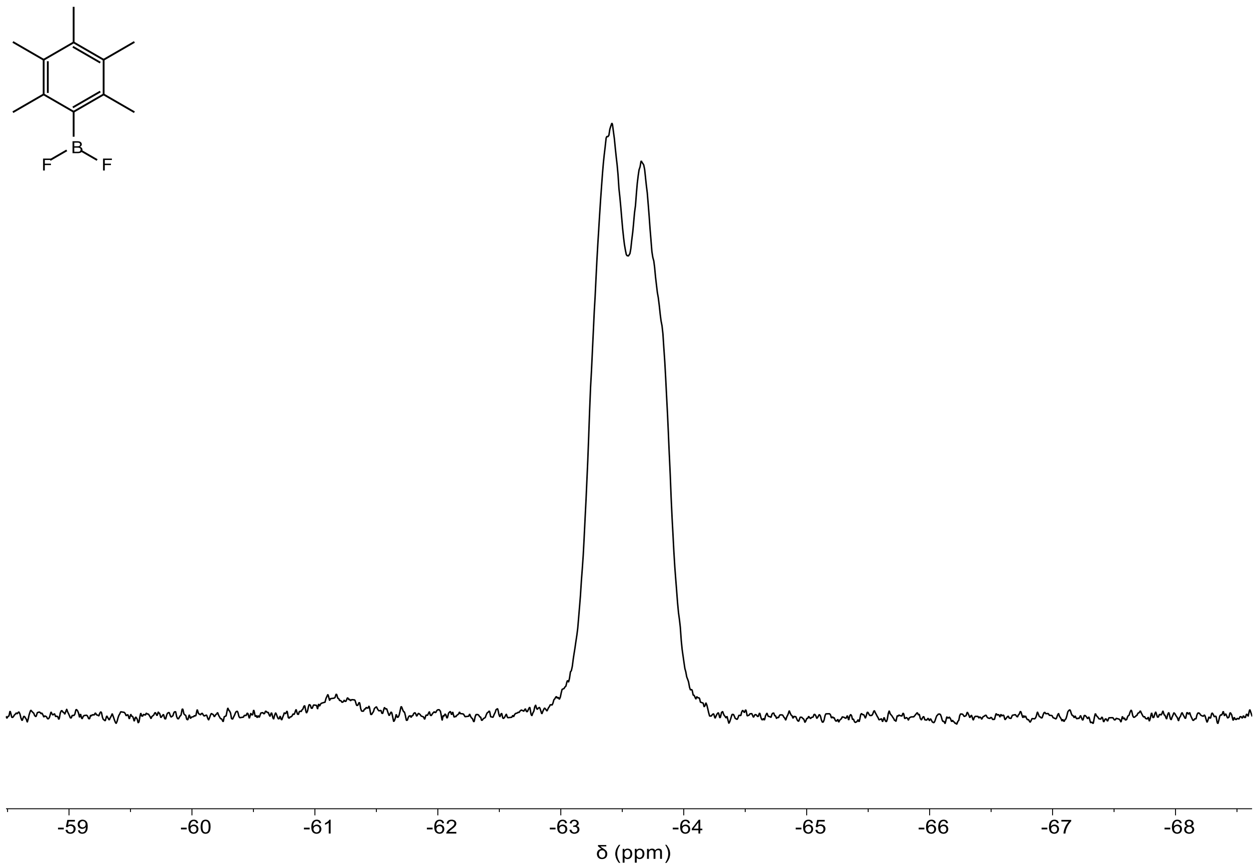


Figure S16. ^{19}F NMR spectrum of **3b**.

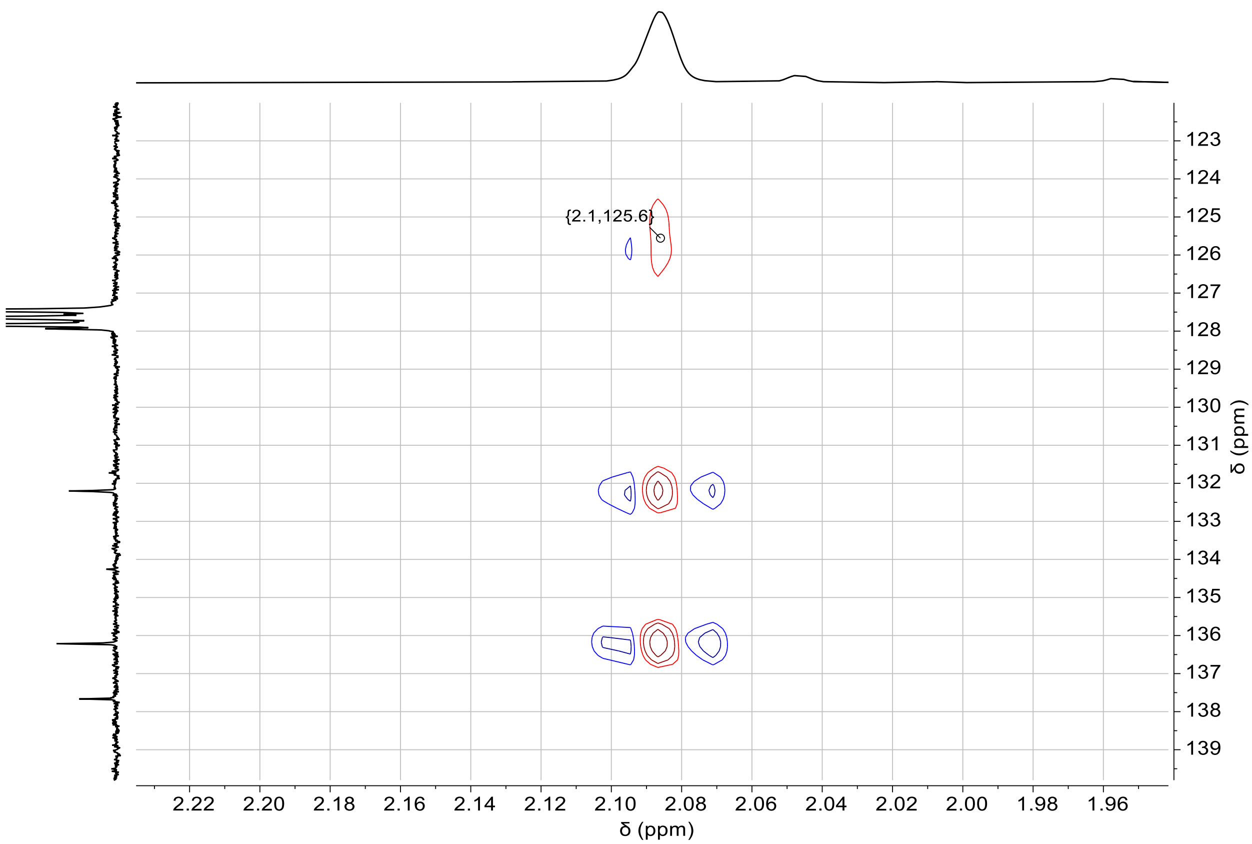


Figure S17. ^{1}H-^{13}C HMBC NMR spectrum of **3b**. Labelled peak correlates to the C_i atom.

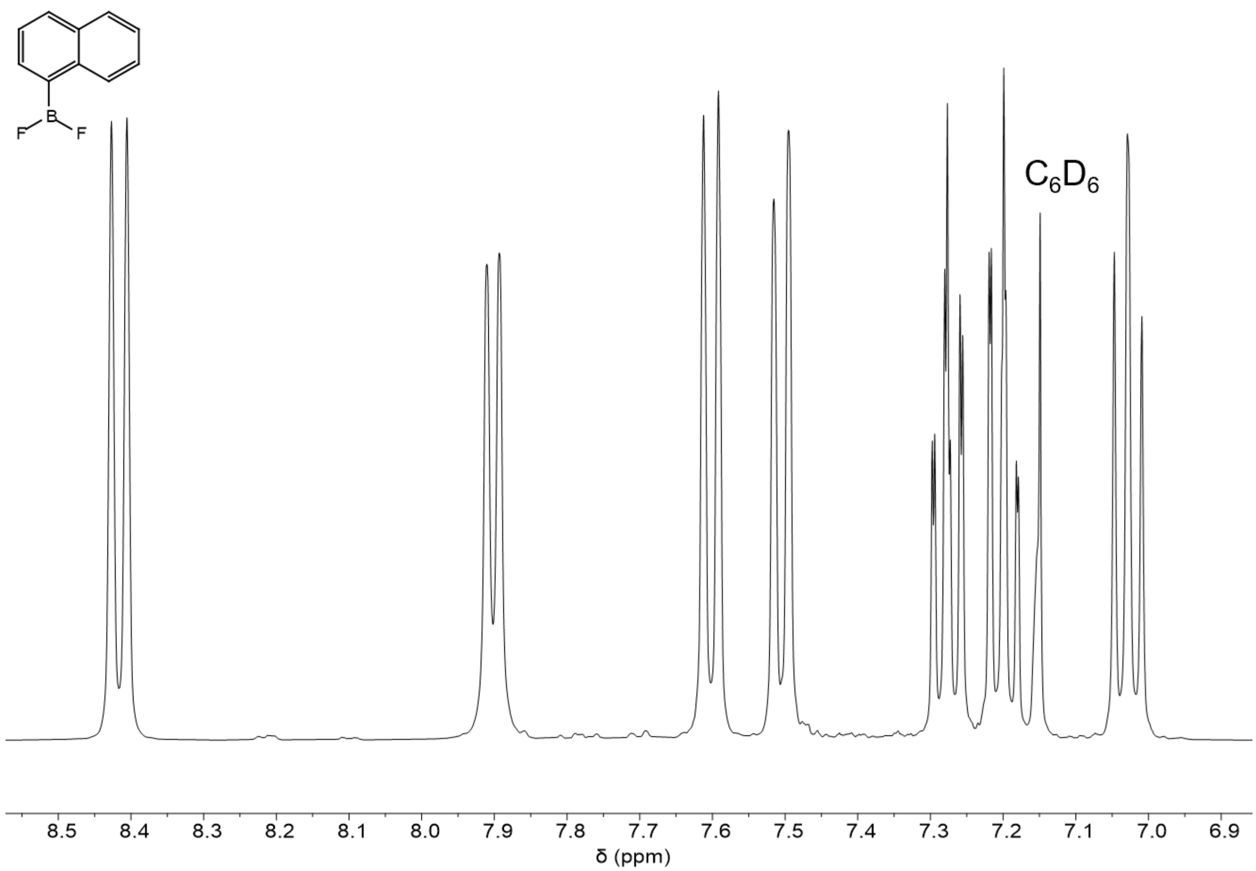


Figure S18. [1]H NMR spectrum of **3c**.

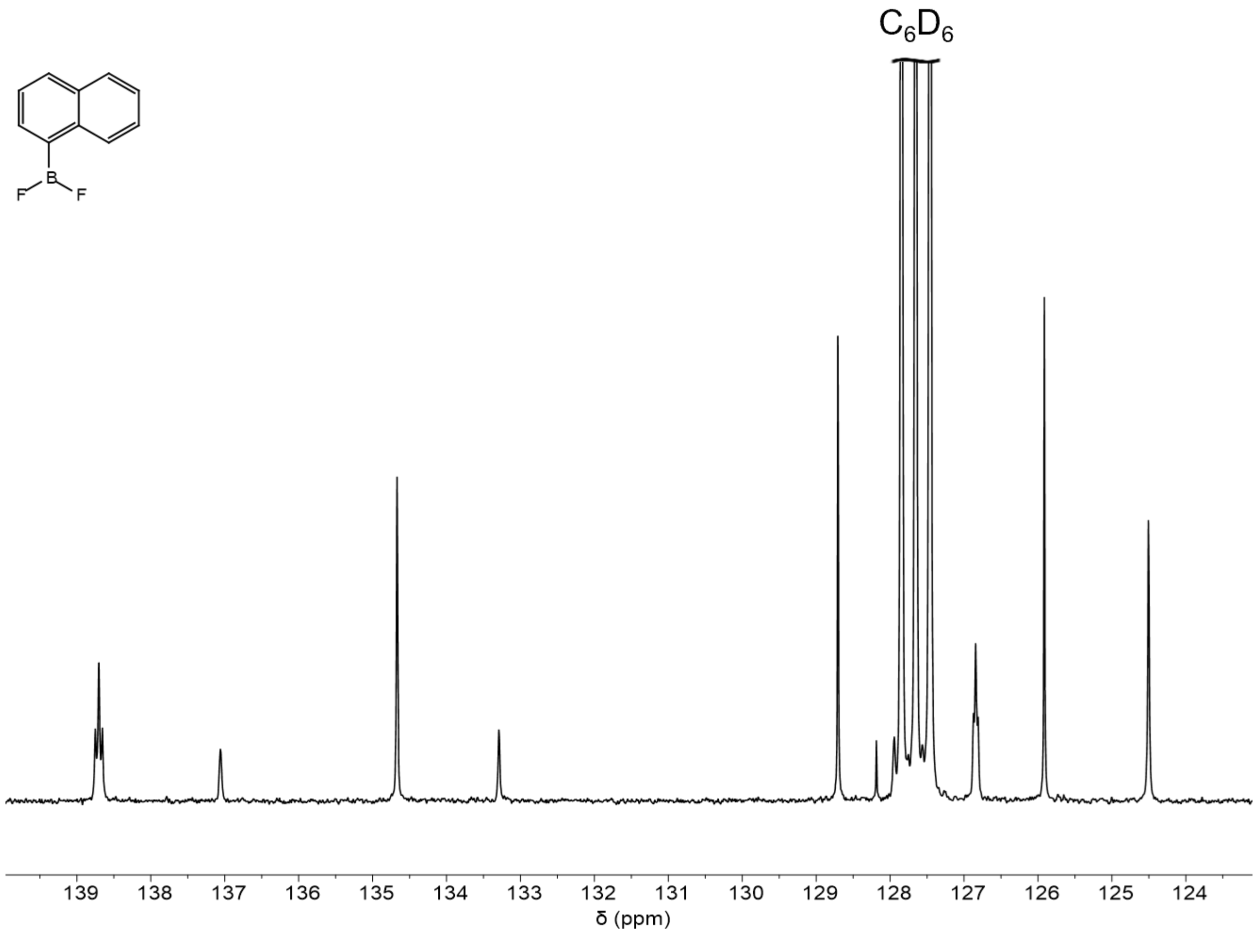


Figure S19. ^{13}C NMR spectrum of **3c**.

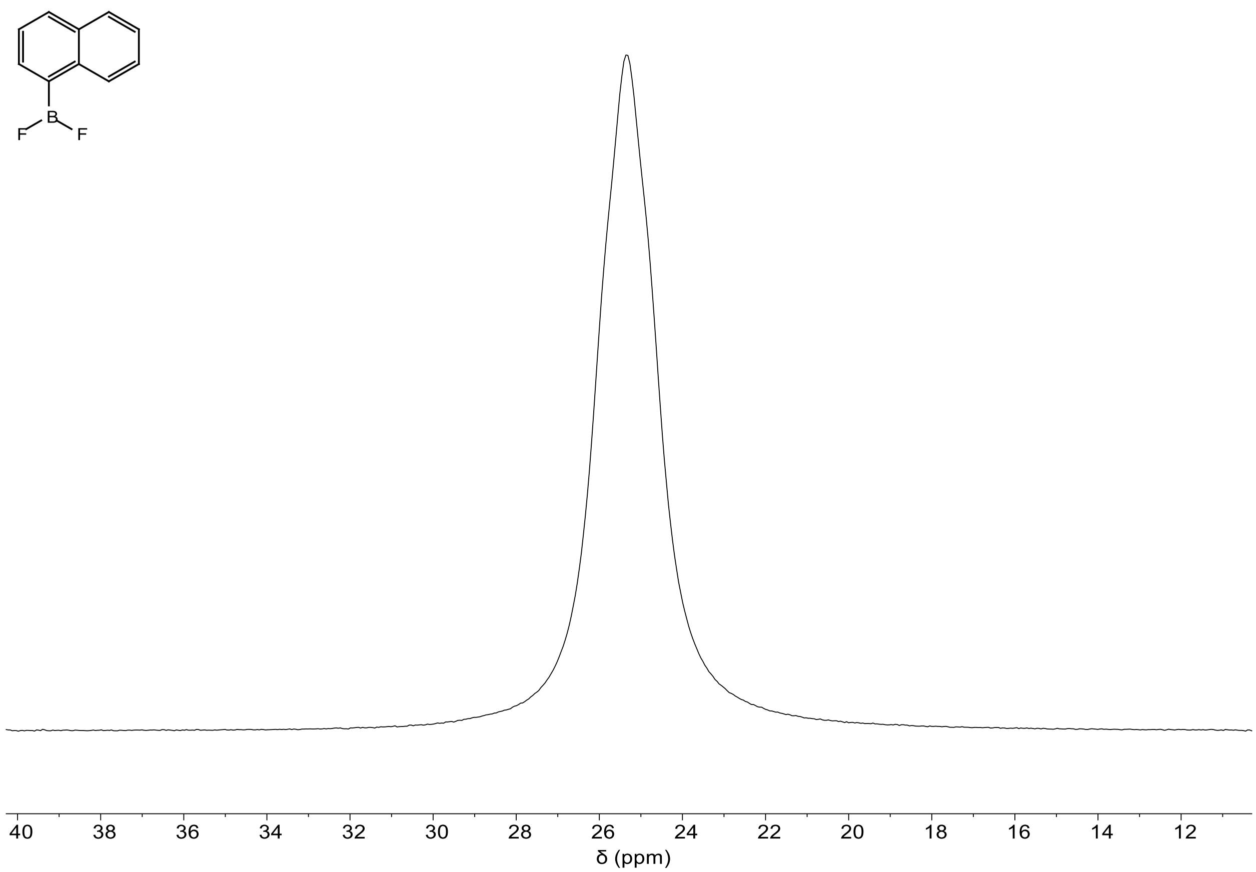


Figure S20. ^{11}B NMR spectrum of **3c**.

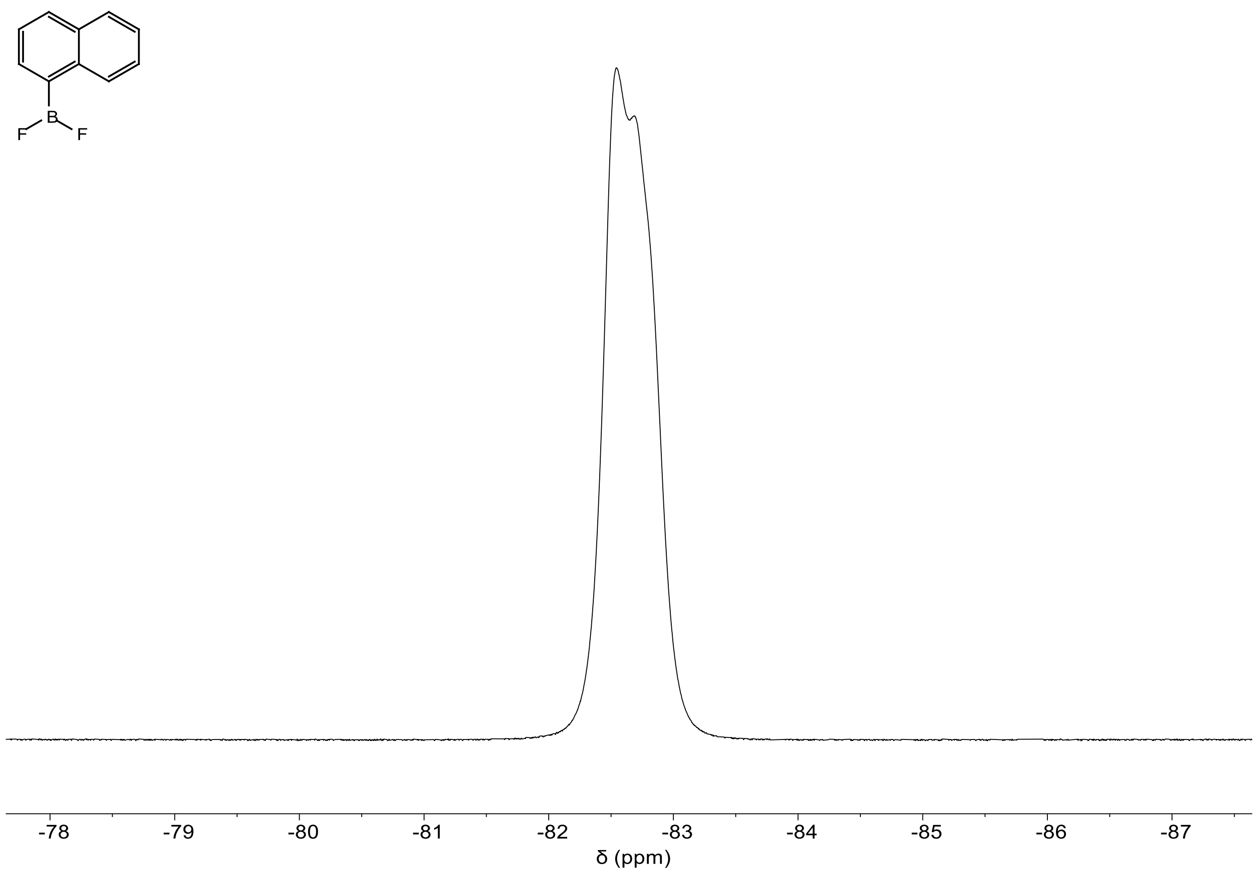


Figure S21. ^{19}F NMR spectrum of **3c**.

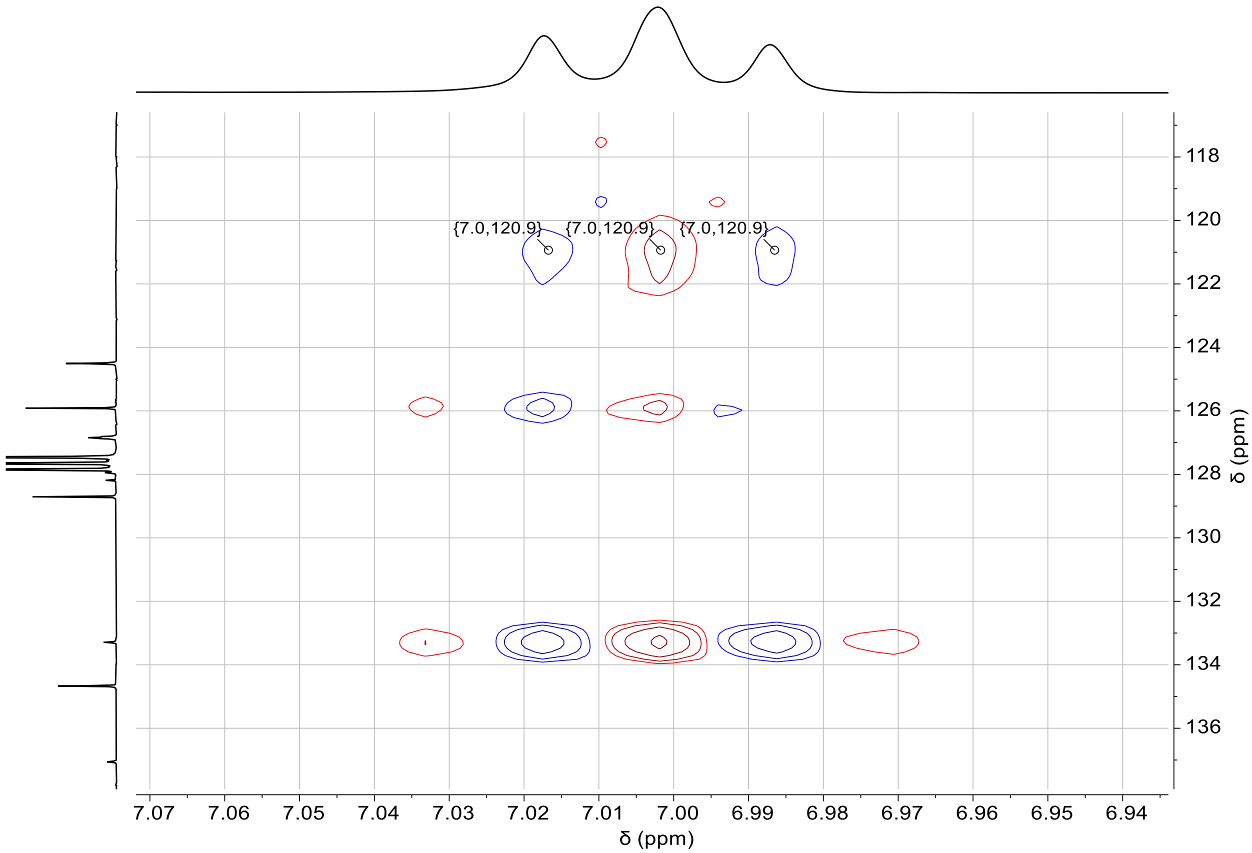


Figure S22. ^{1}H-^{13}C HMBC NMR spectrum of **3c**. Labelled peak correlates to C1.

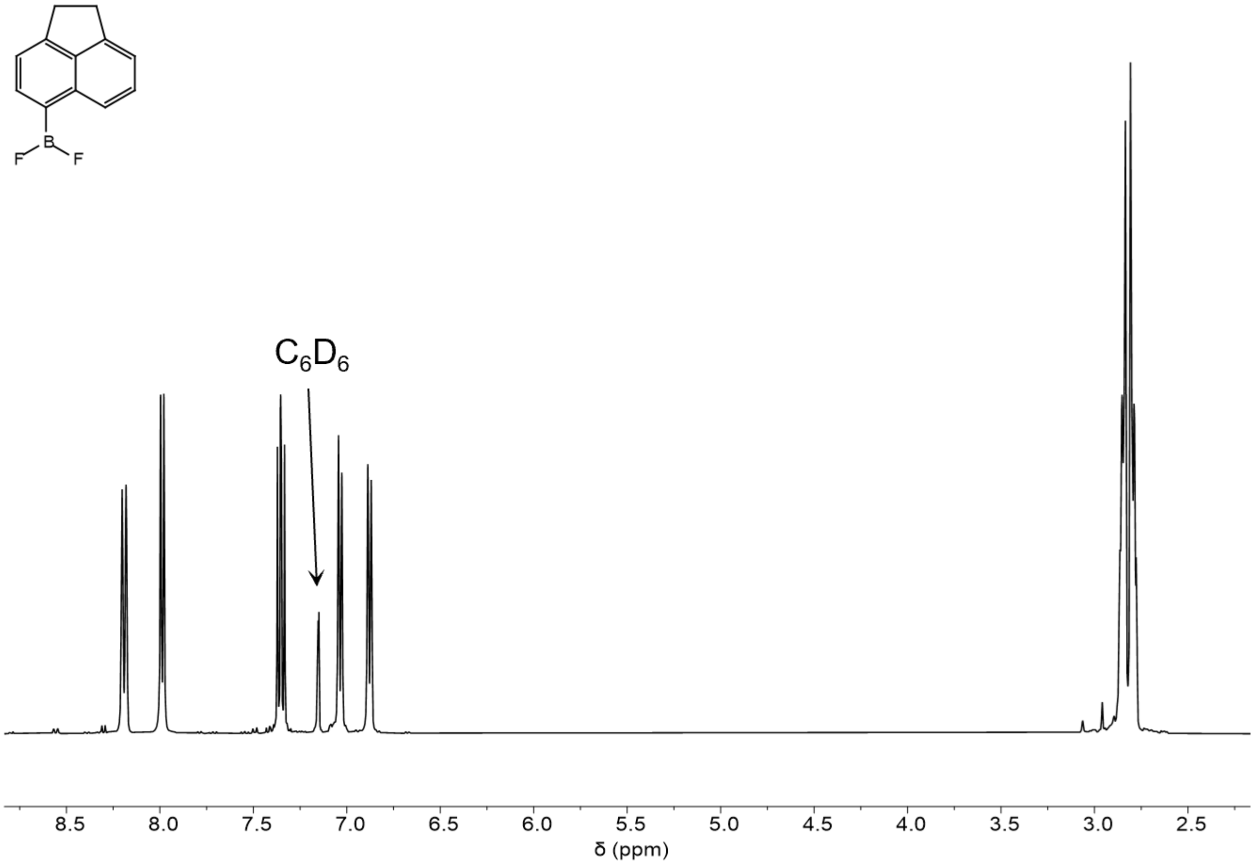


Figure S23. ^{1}H NMR spectrum of **3d**.

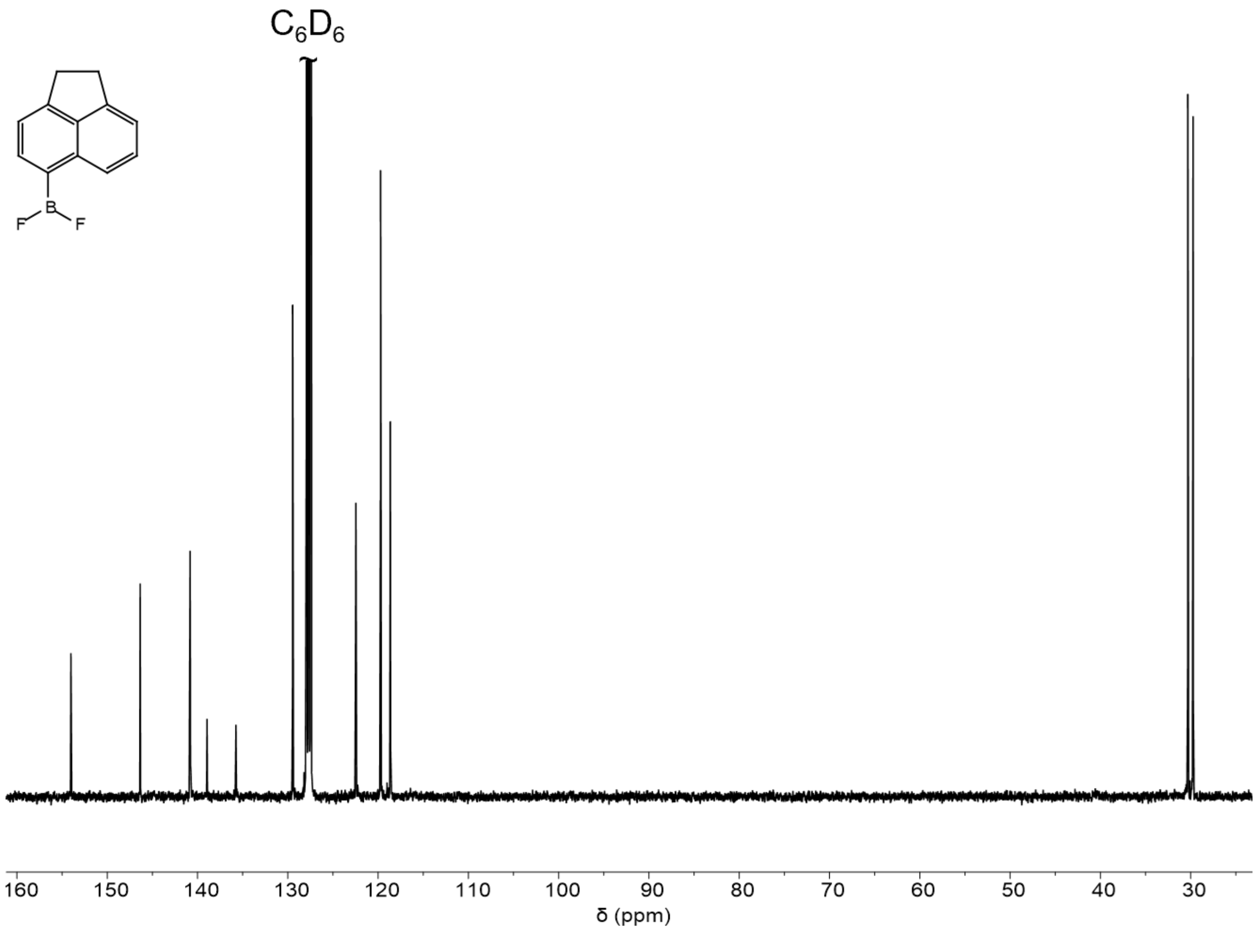


Figure S24. ^{13}C NMR spectrum of **3d**.

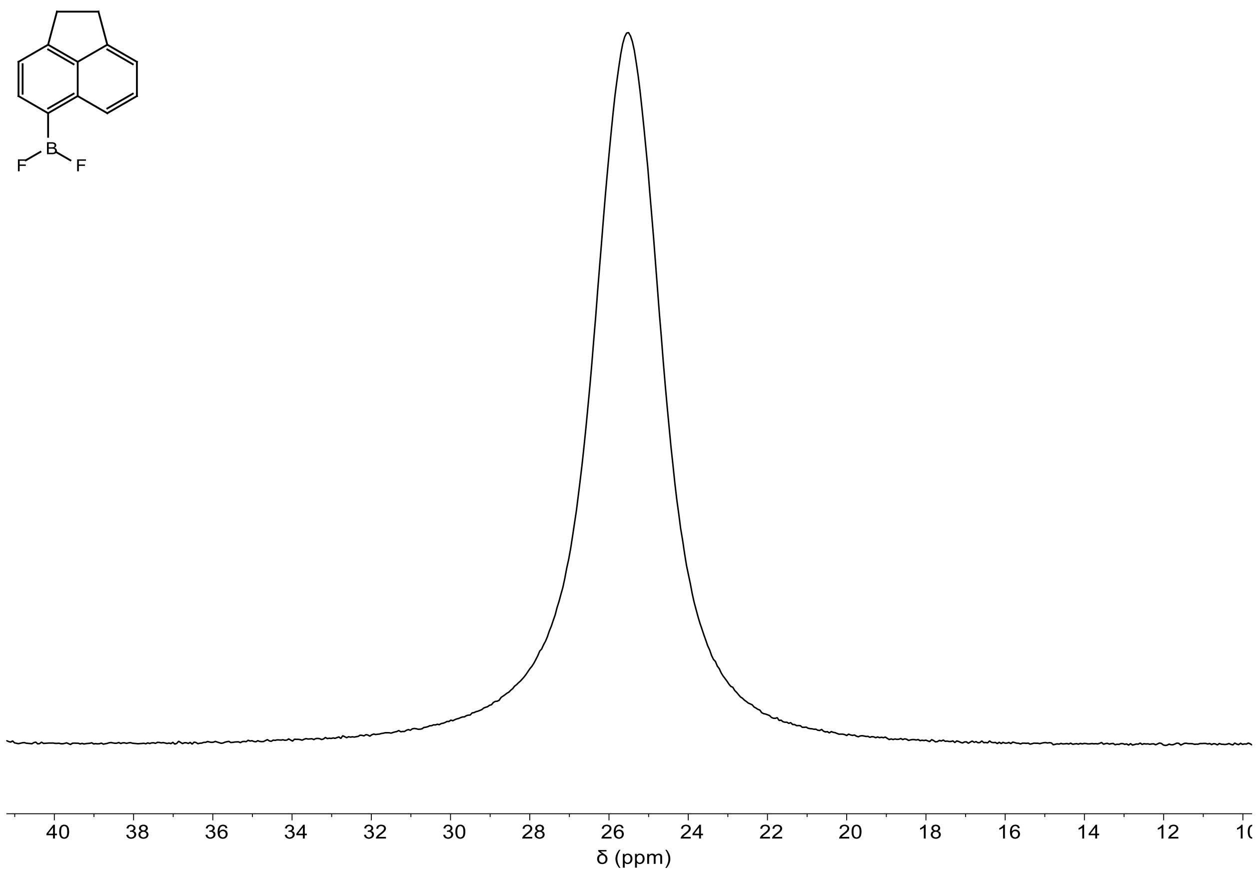


Figure S25. ^{11}B NMR spectrum of **3d**.

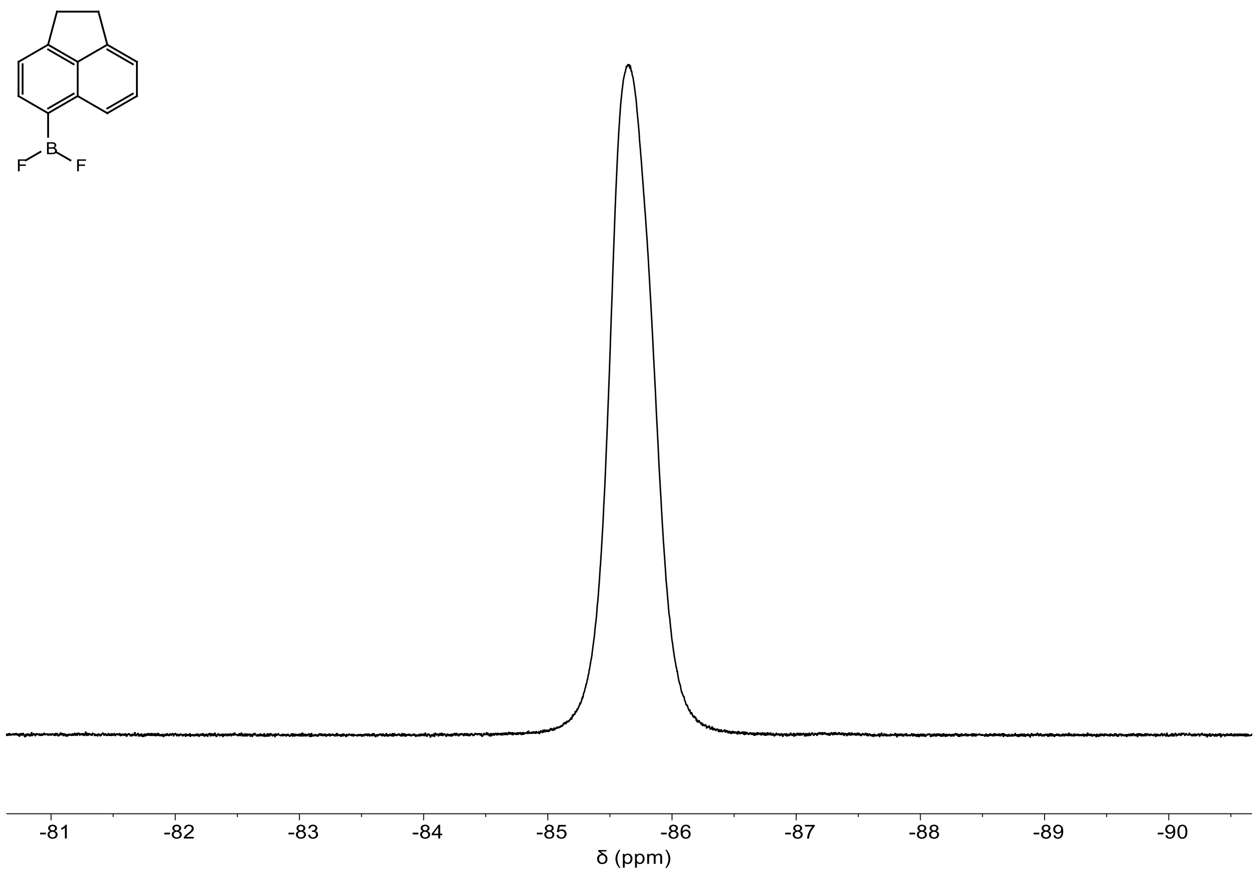


Figure S26. ^{19}F NMR spectrum of **3d**.

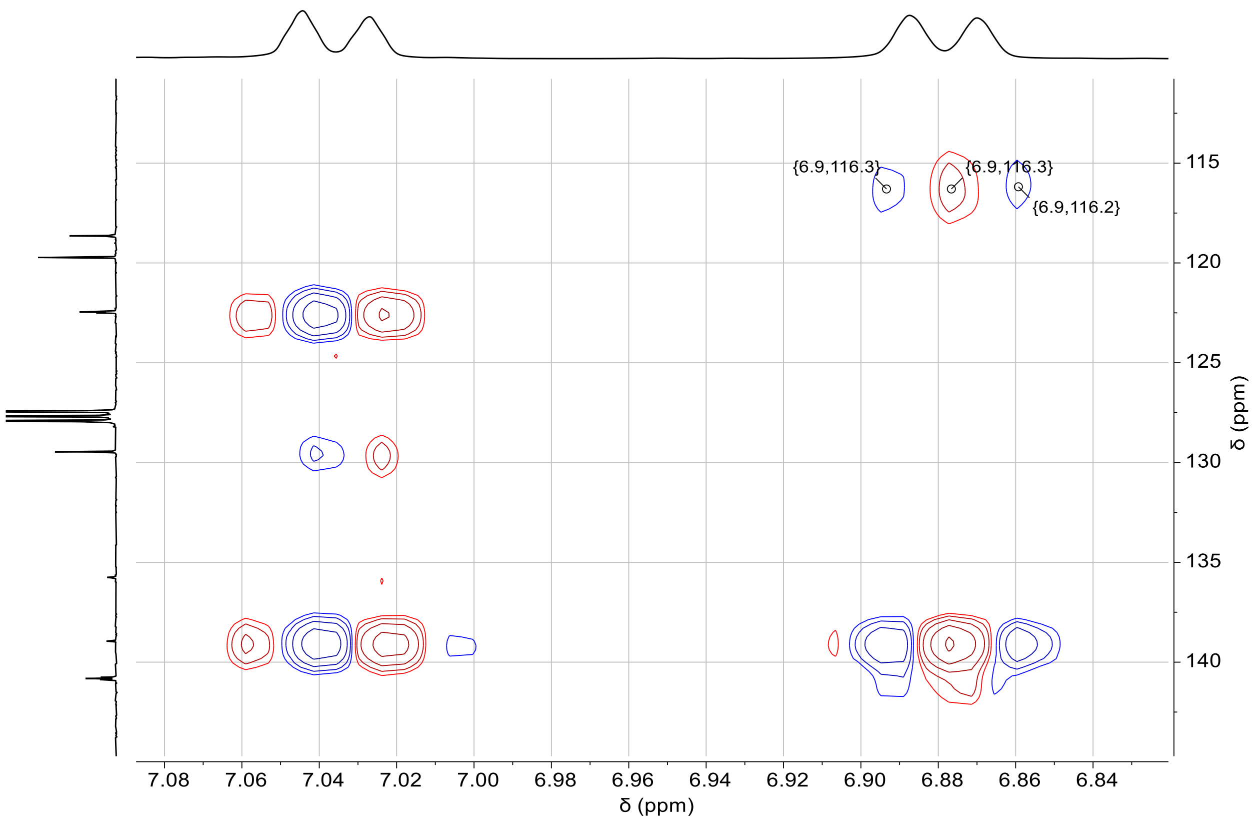


Figure S27. ^{1}H-^{13}C HMBC NMR spectrum of **3d**. Labelled peak correlates to C5.

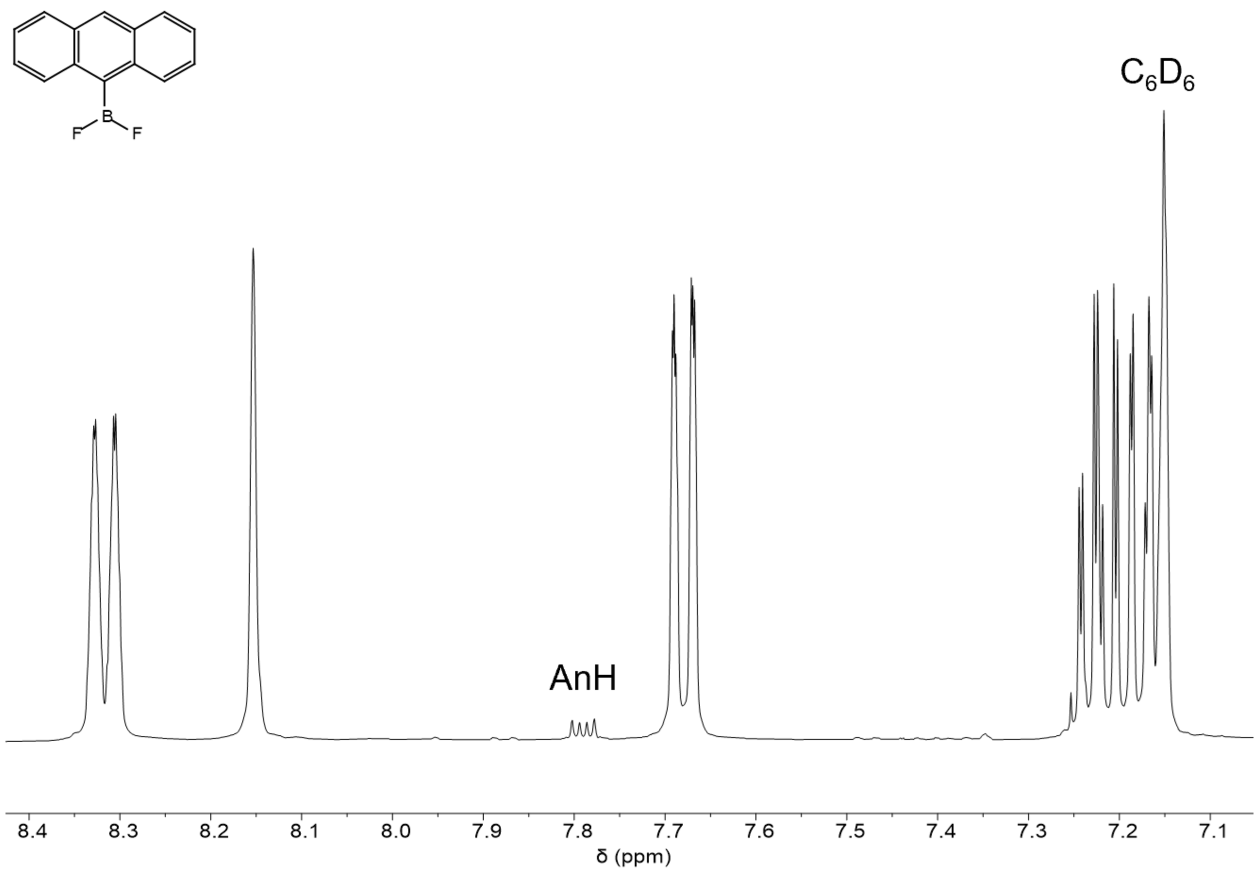


Figure S28. ^{1}H NMR spectrum of **3e**.

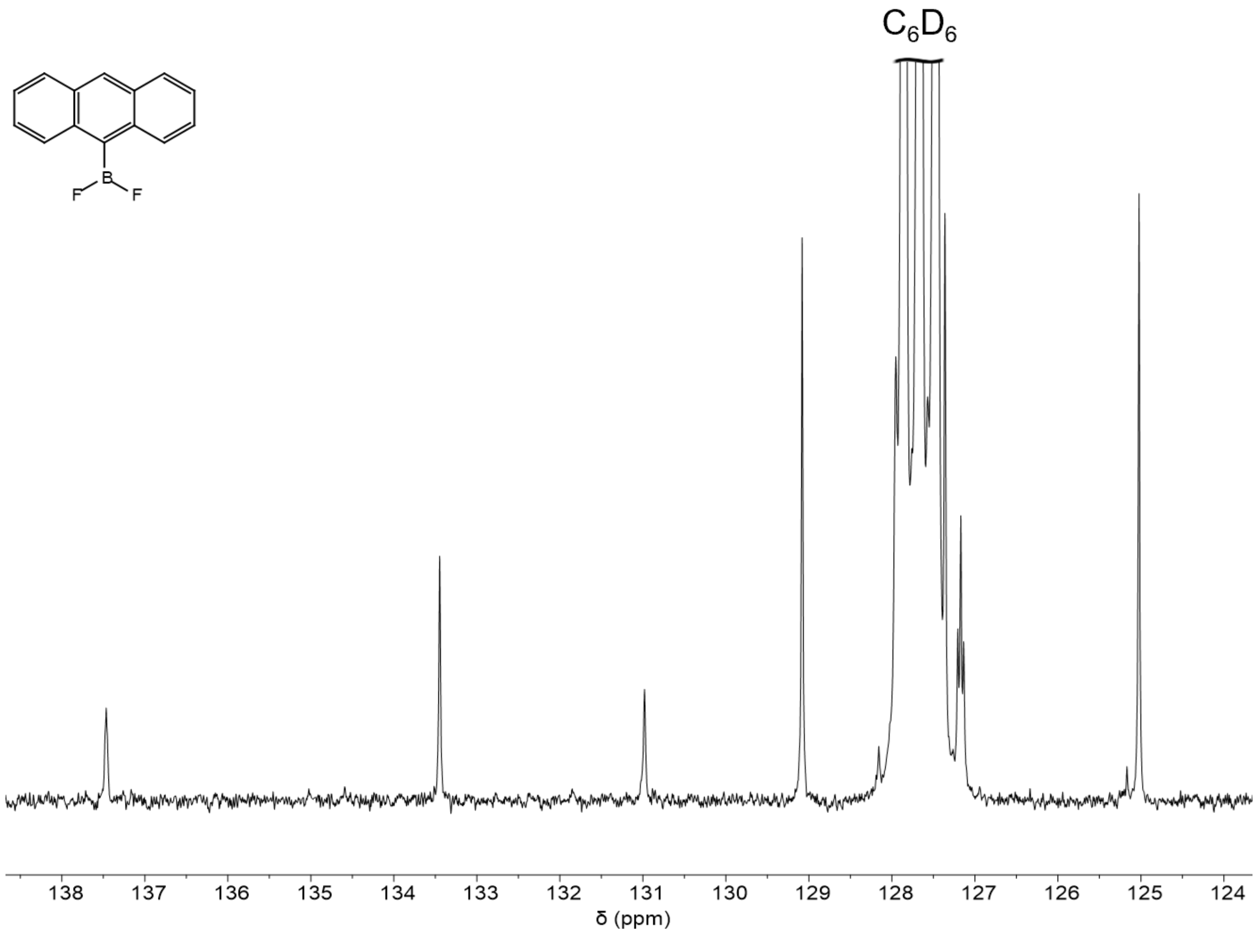


Figure S29. ^{13}C NMR spectrum of **3e**.

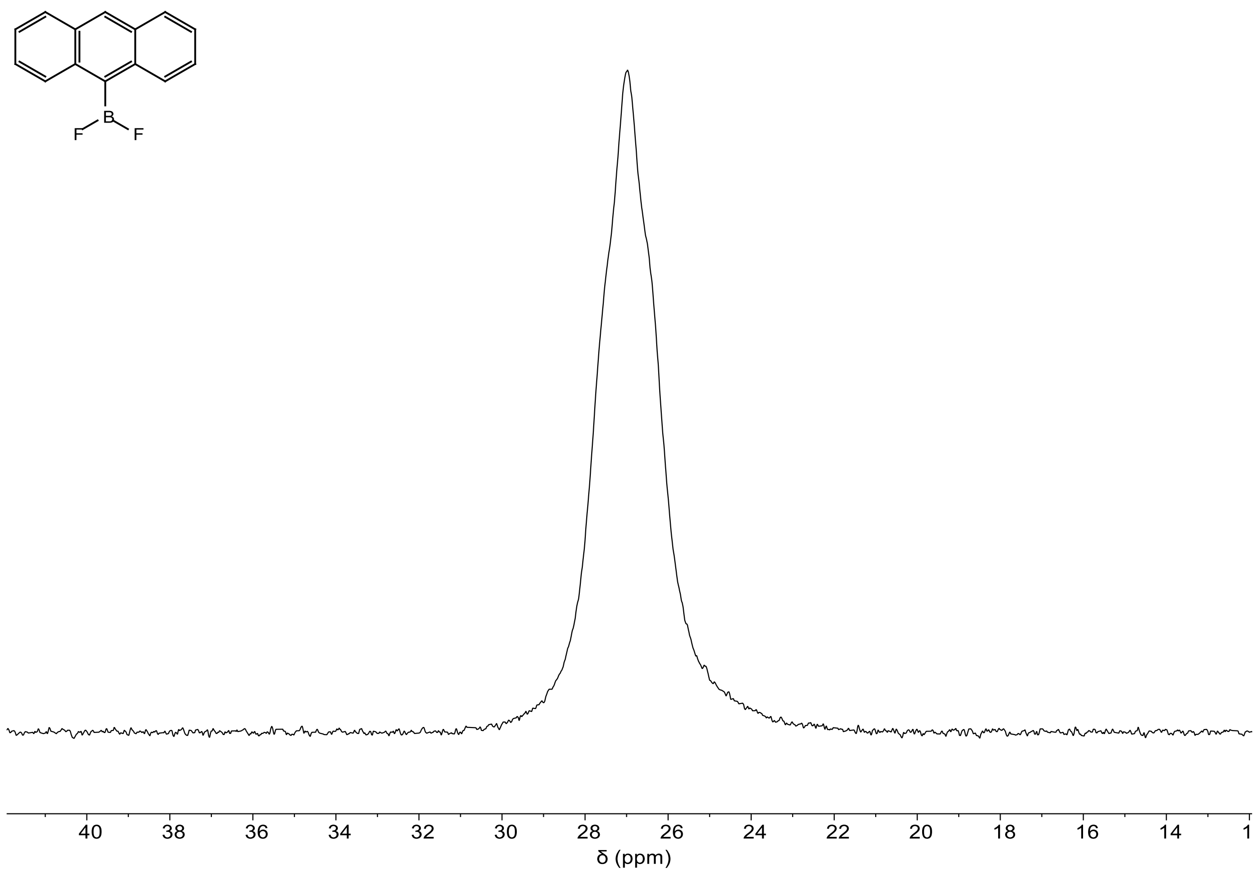


Figure S30. ^{11}B NMR spectrum of **3e**.

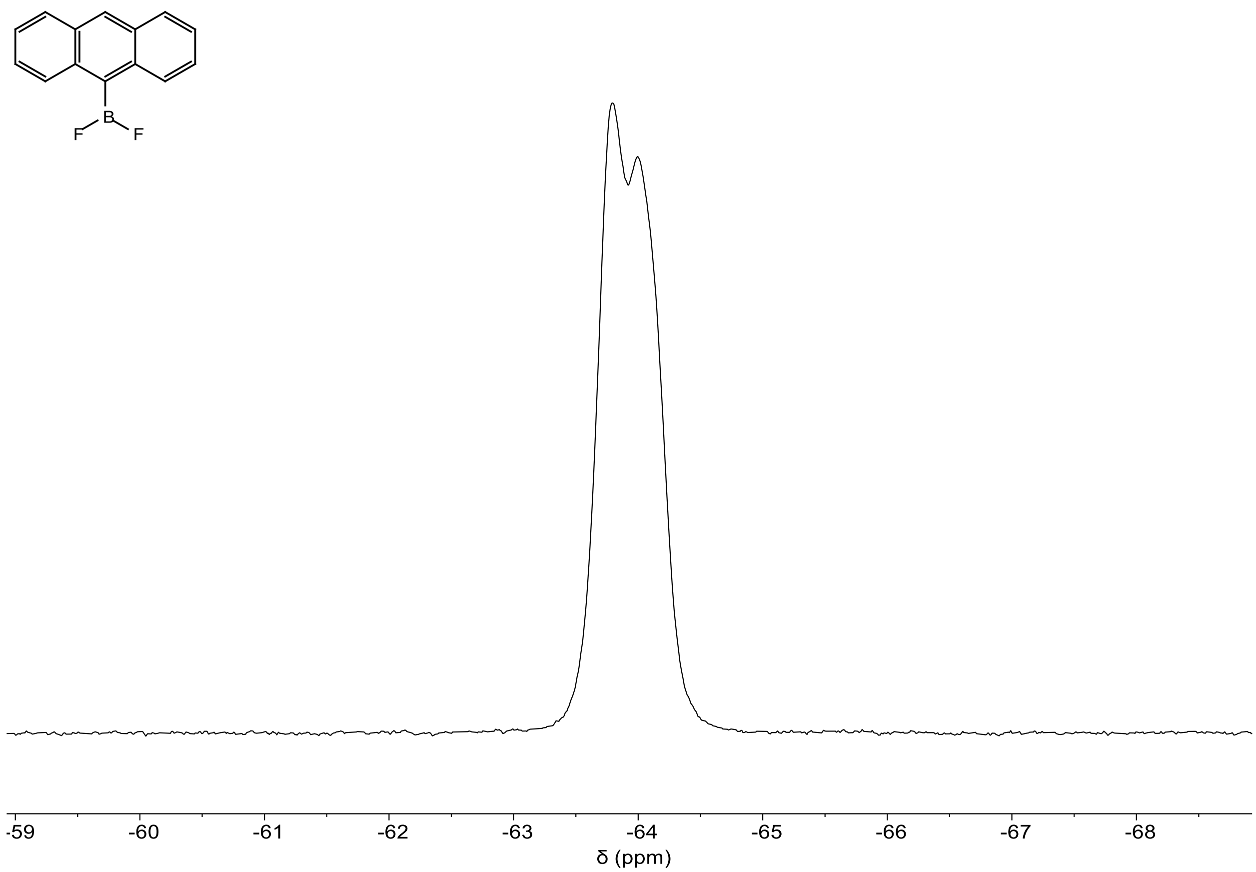


Figure S31. ^{19}F NMR spectrum of **3e**.

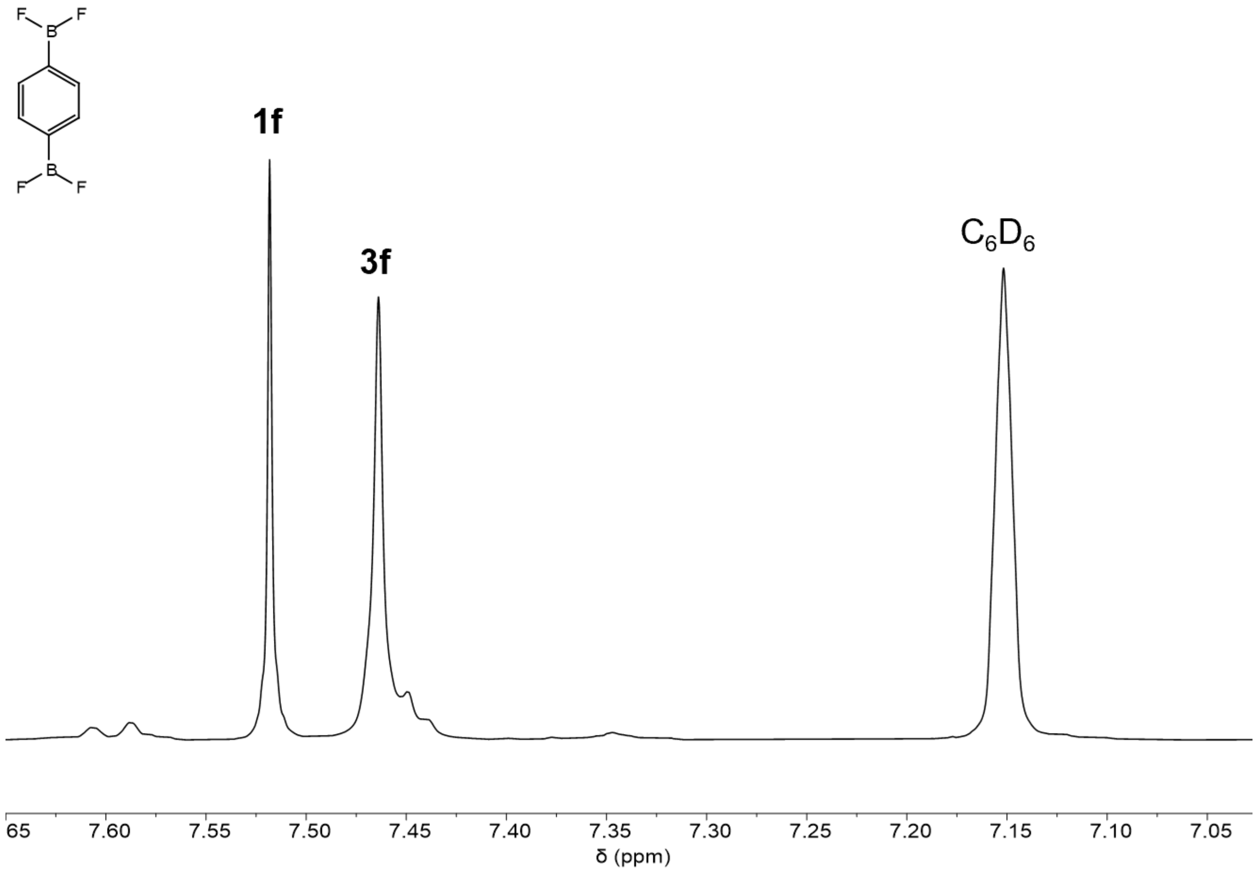


Figure S32. ^{1}H NMR spectrum of **3f**.

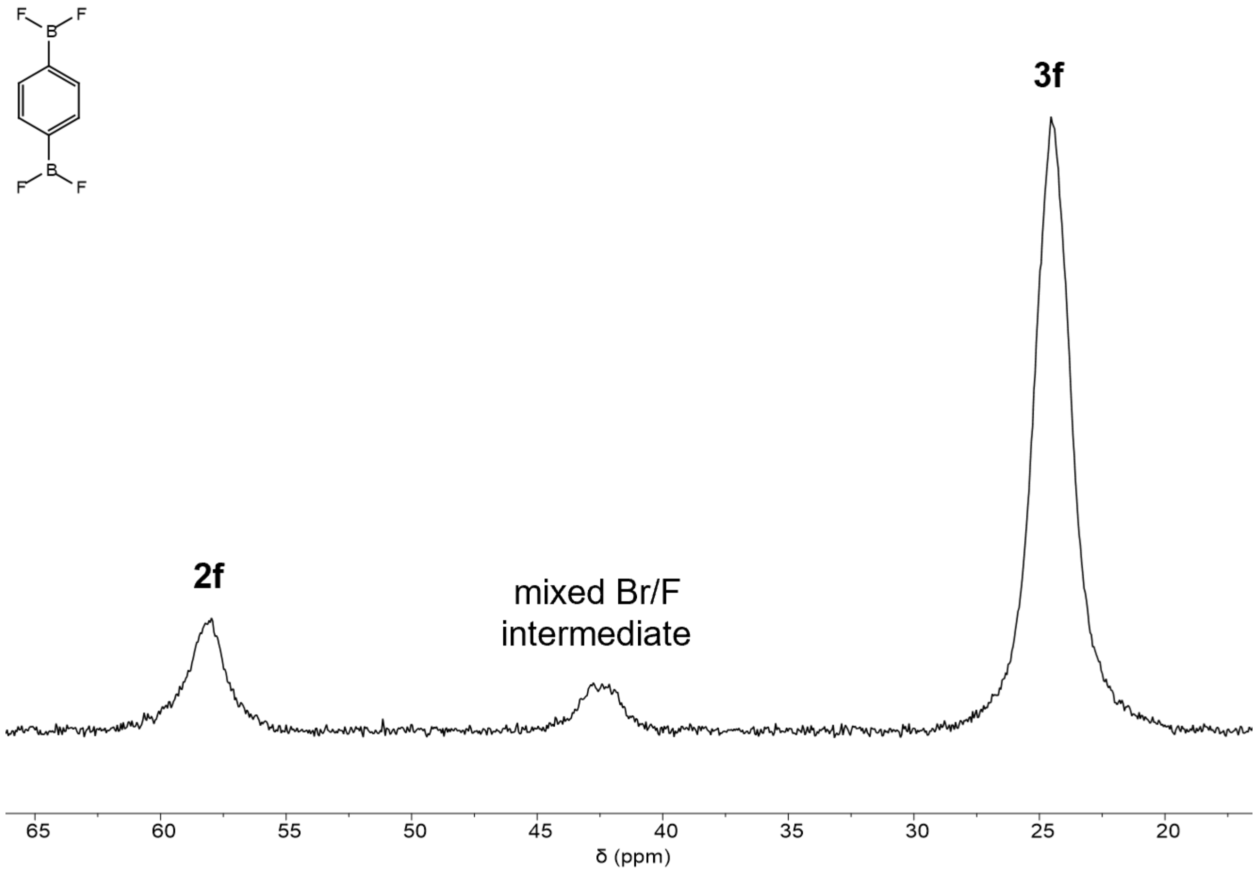


Figure S33. ^{11}B NMR spectrum of **3f**.

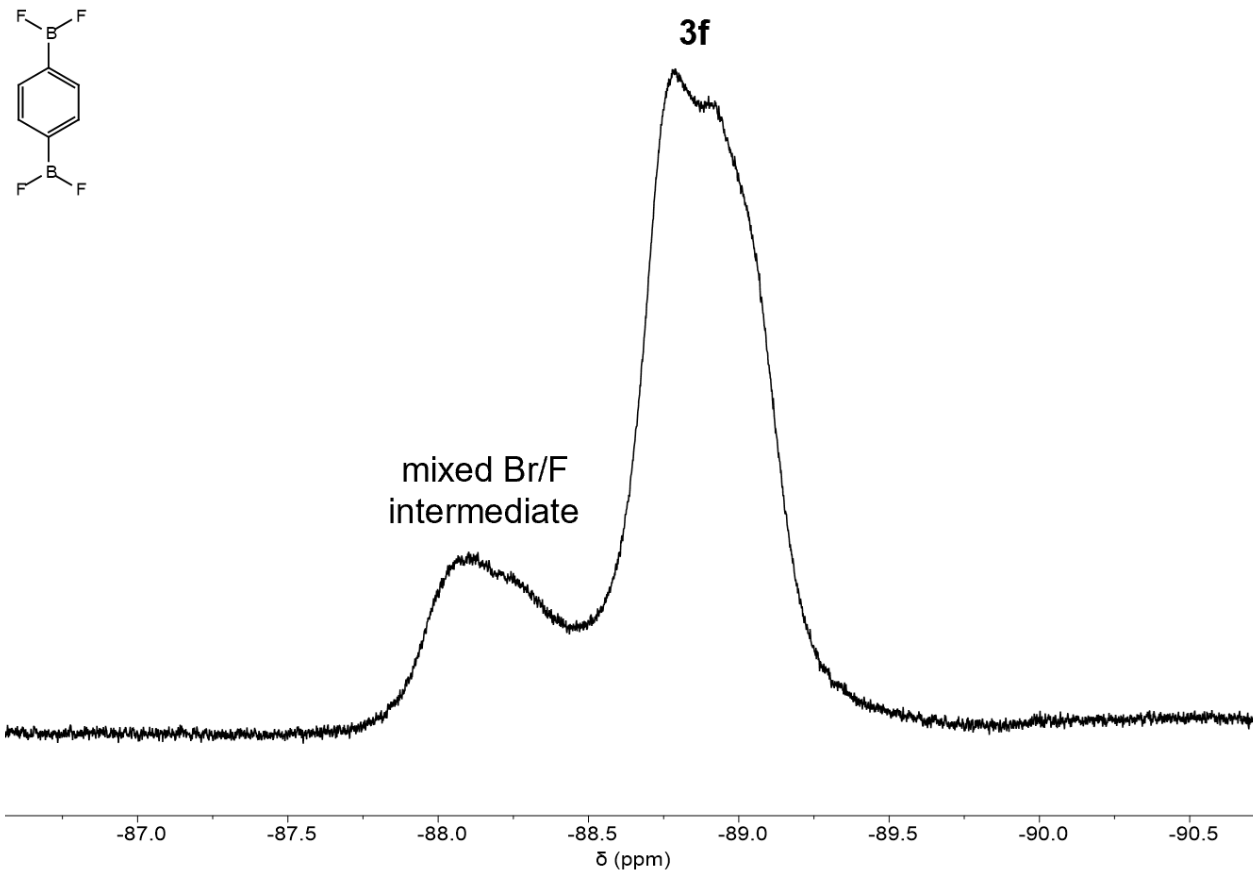


Figure S34. ^{19}F NMR spectrum of **3f**.

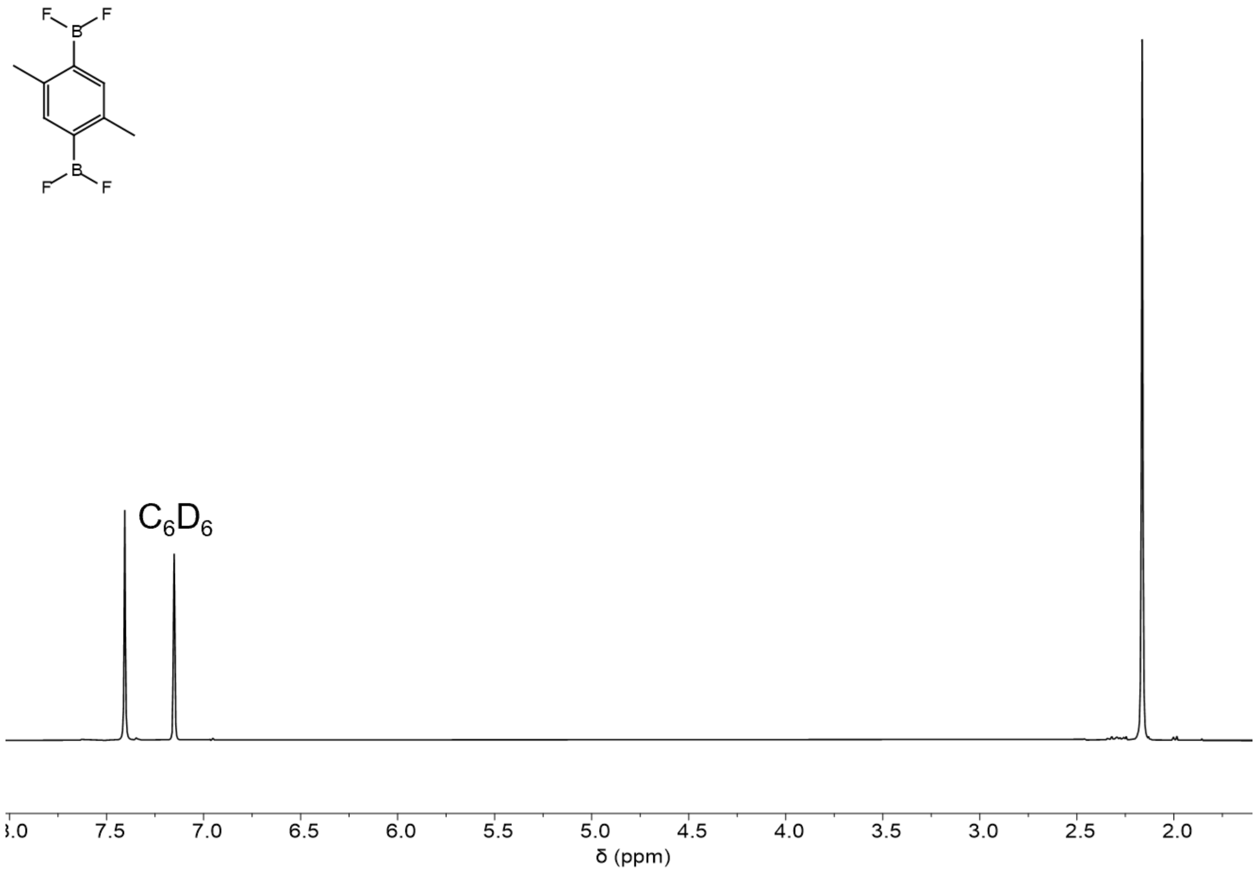


Figure S35. ^{1}H NMR spectrum of **3g**.

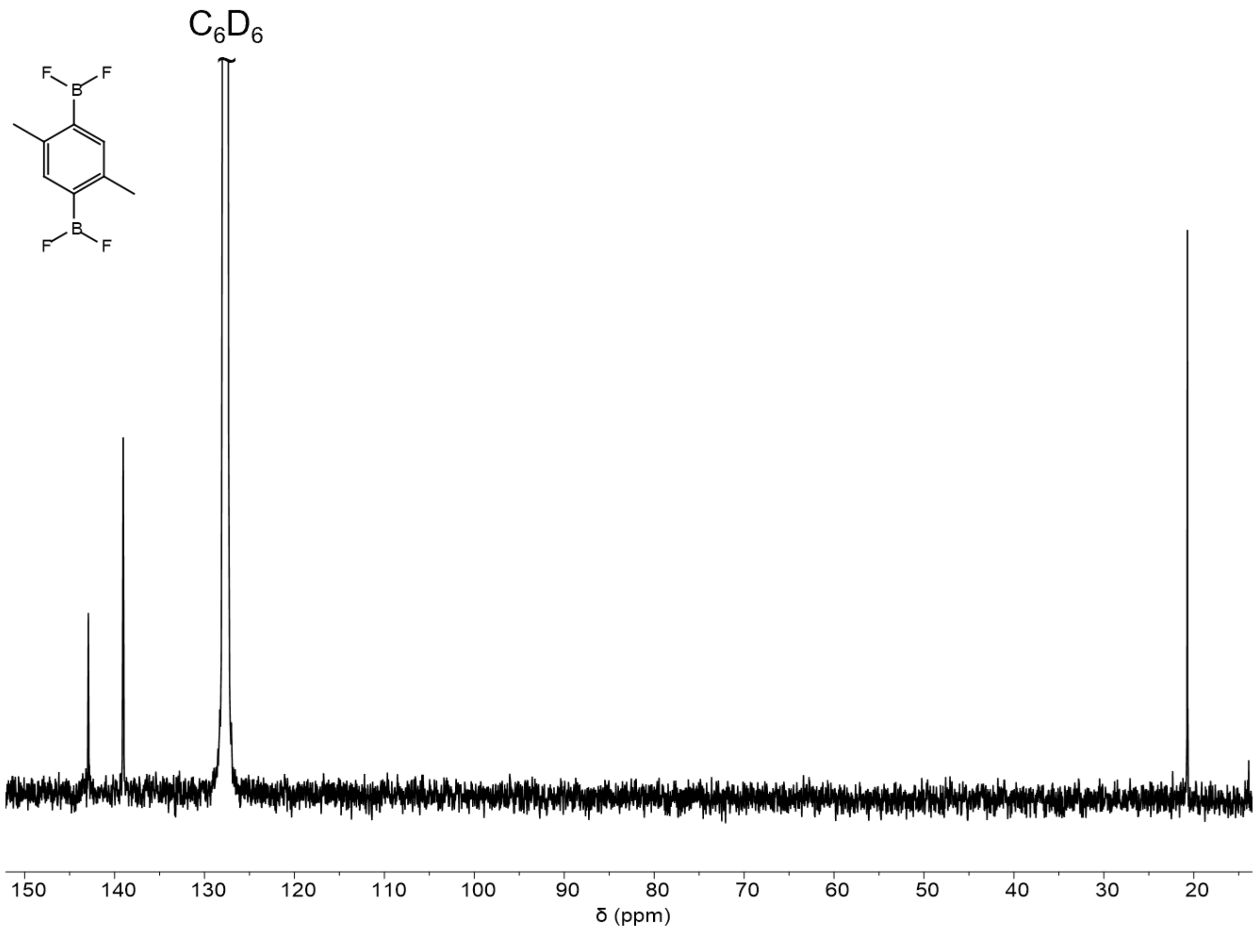


Figure S36. ^{13}C NMR spectrum of **3g**.

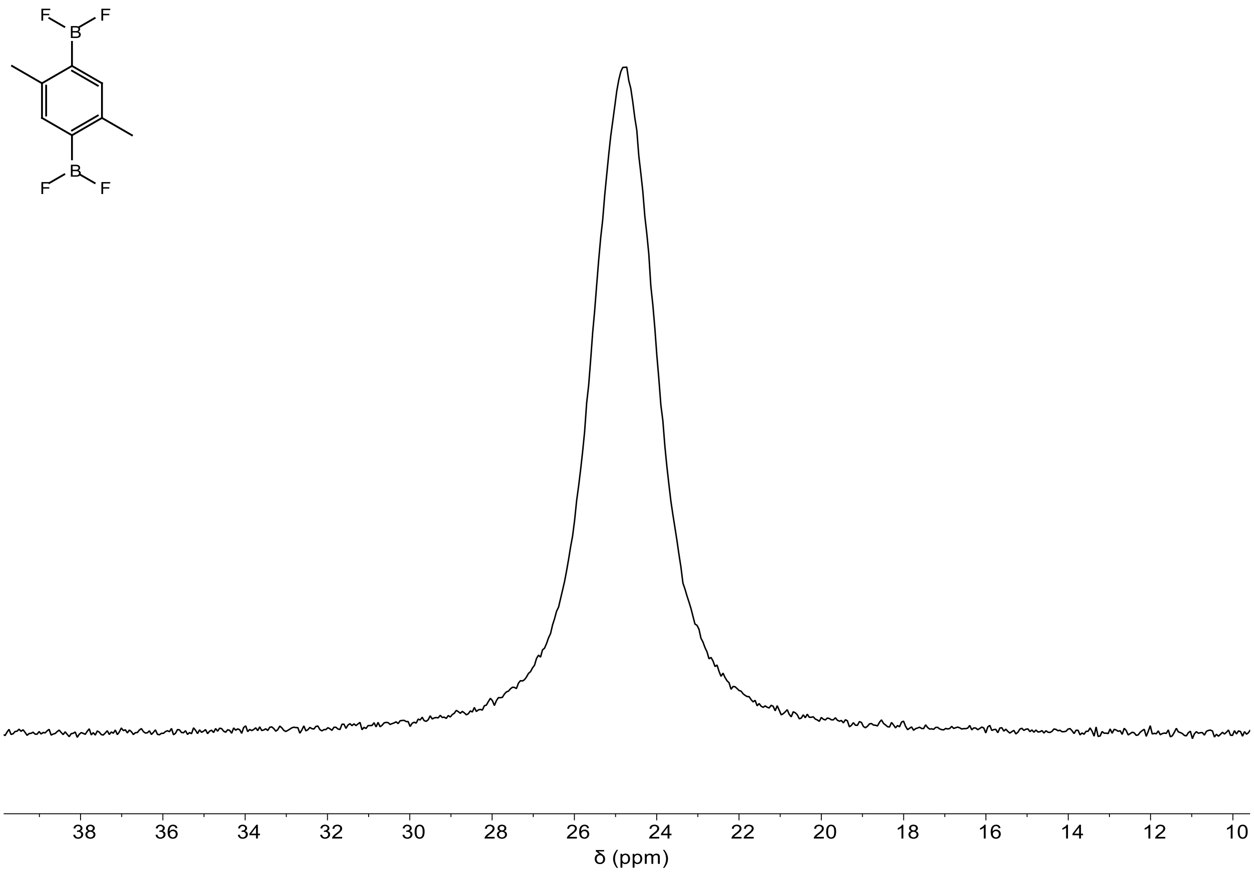


Figure S37. ^{11}B NMR spectrum of **3g**.

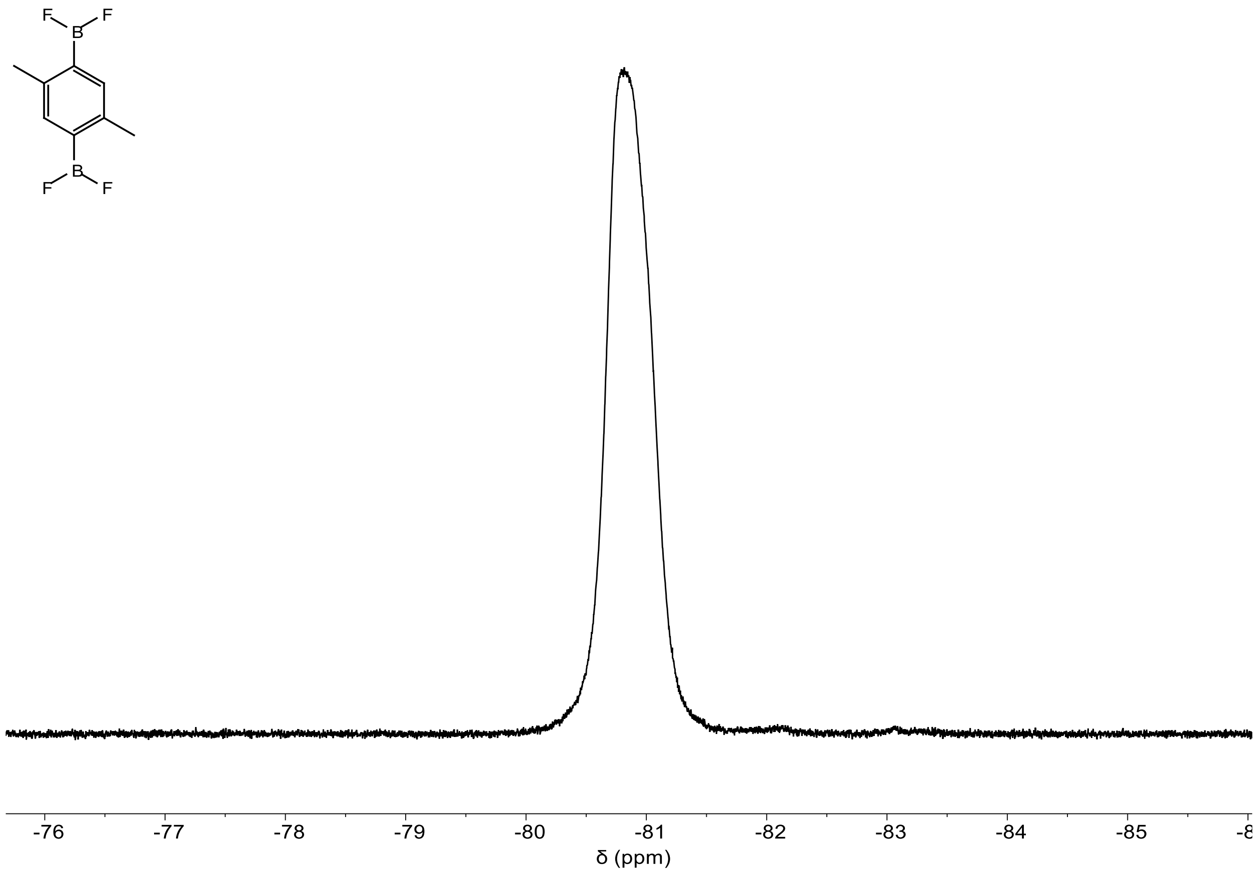


Figure S38. ^{19}F NMR spectrum of **3g**.

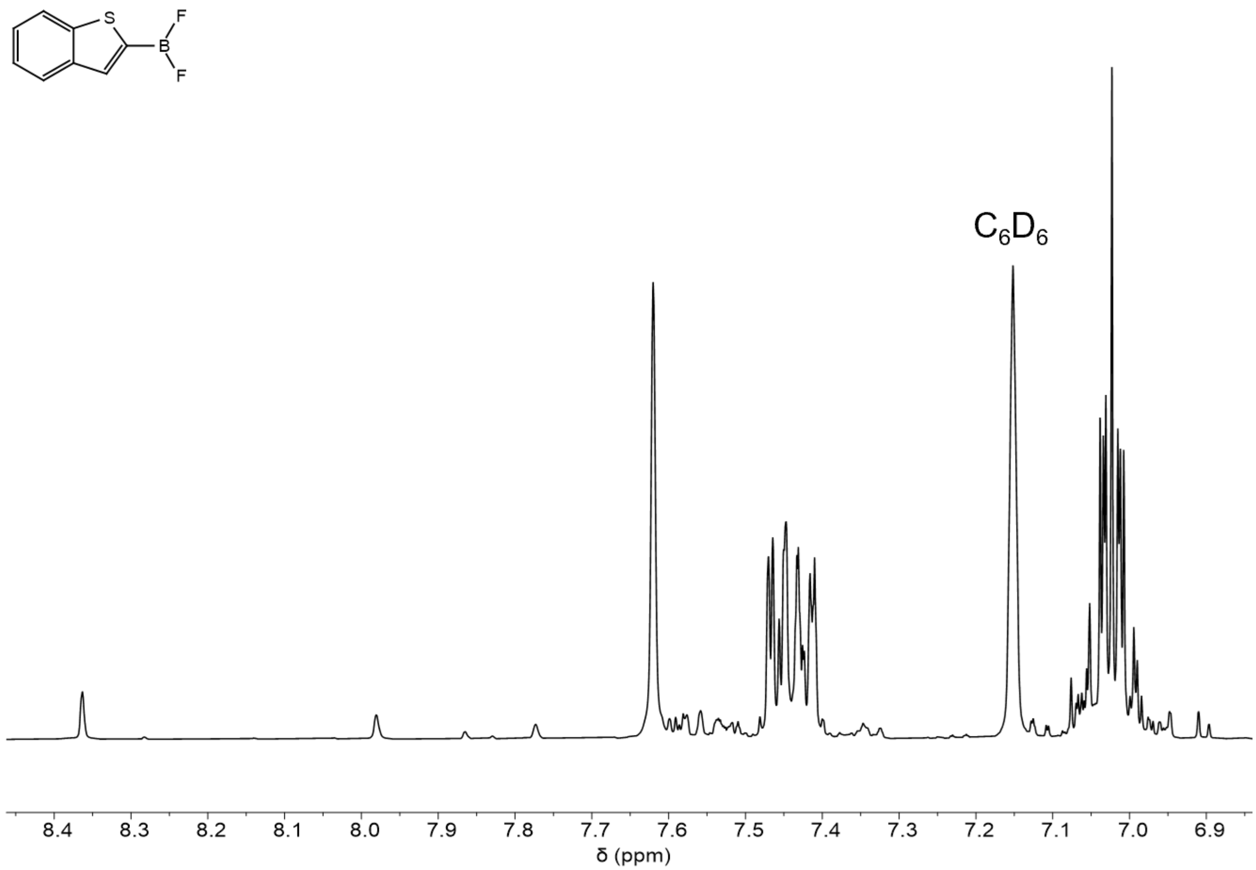
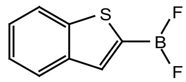


Figure S39. ^{1}H NMR spectrum of **3h**.



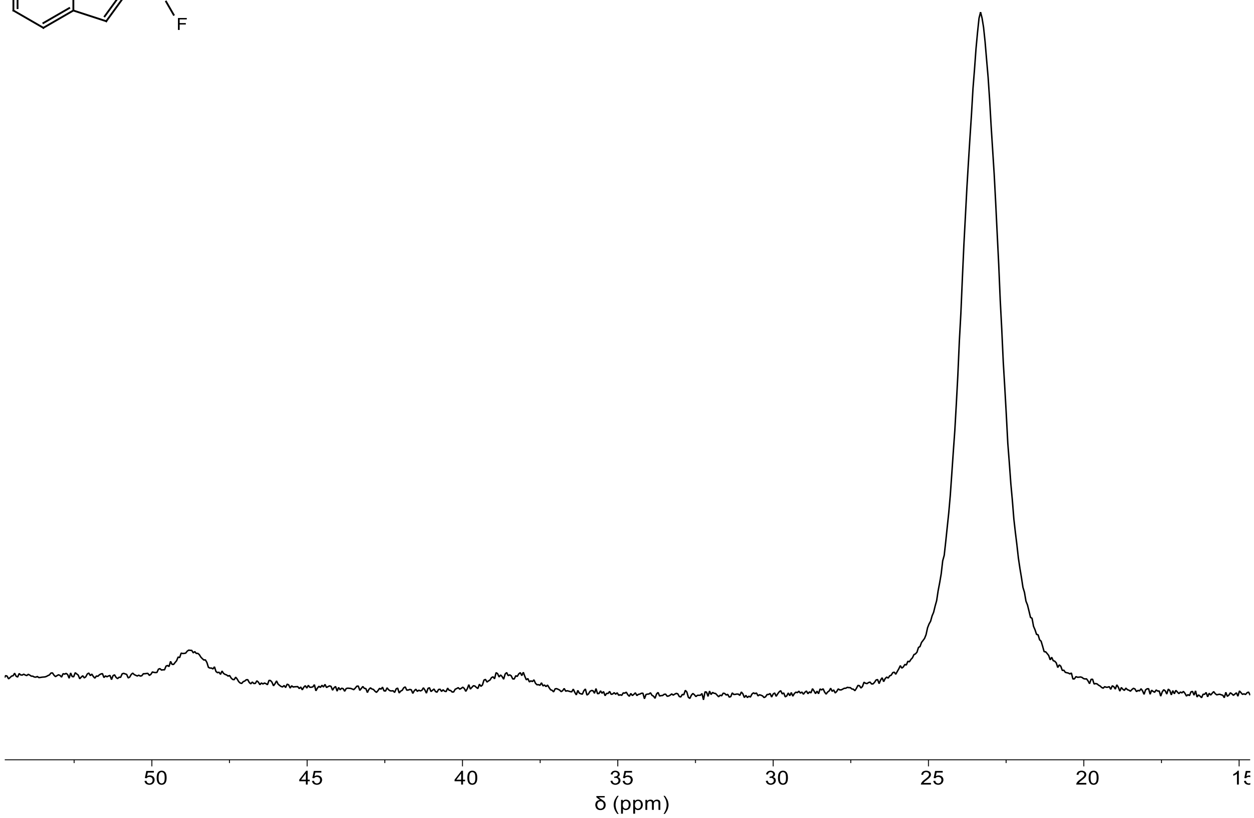


Figure S40. ^{11}B NMR spectrum of **3h**.

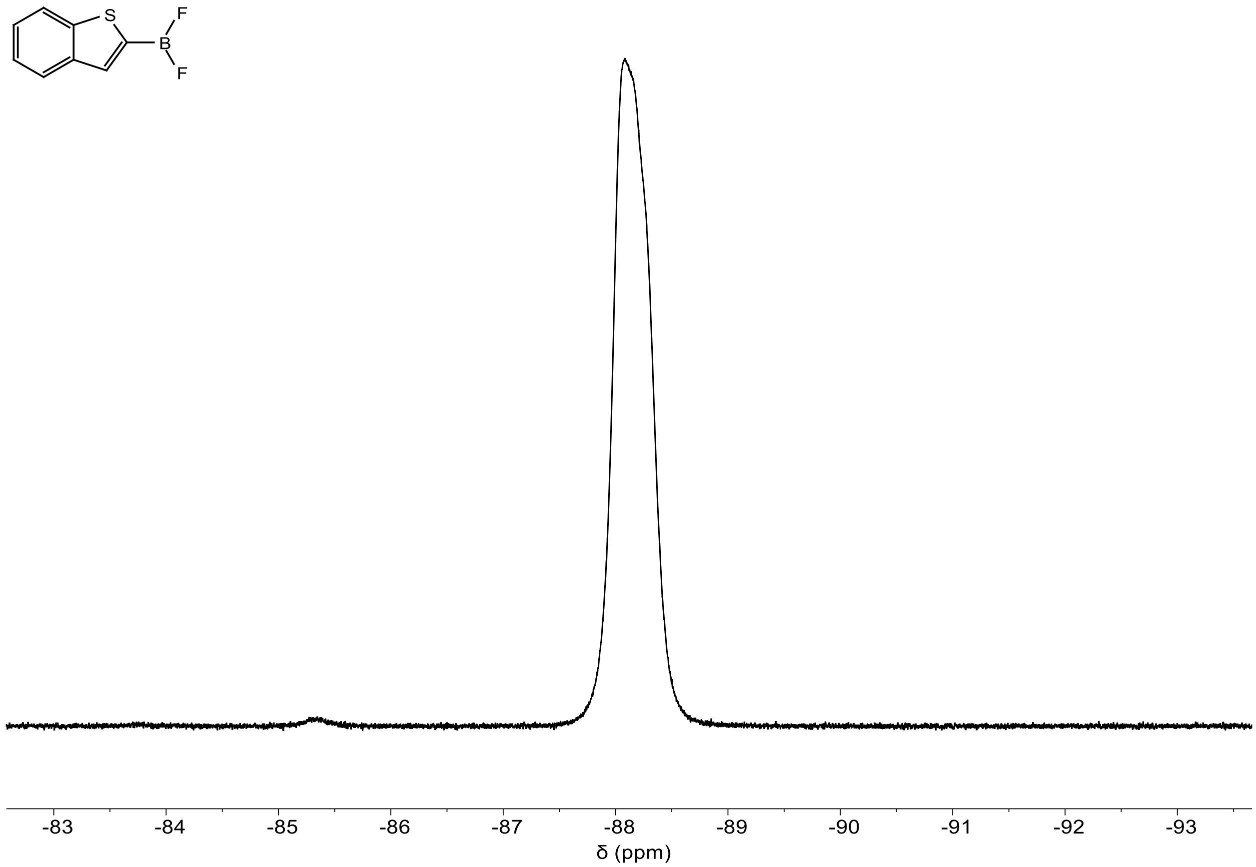


Figure S41. ^{19}F NMR spectrum of **3h**.

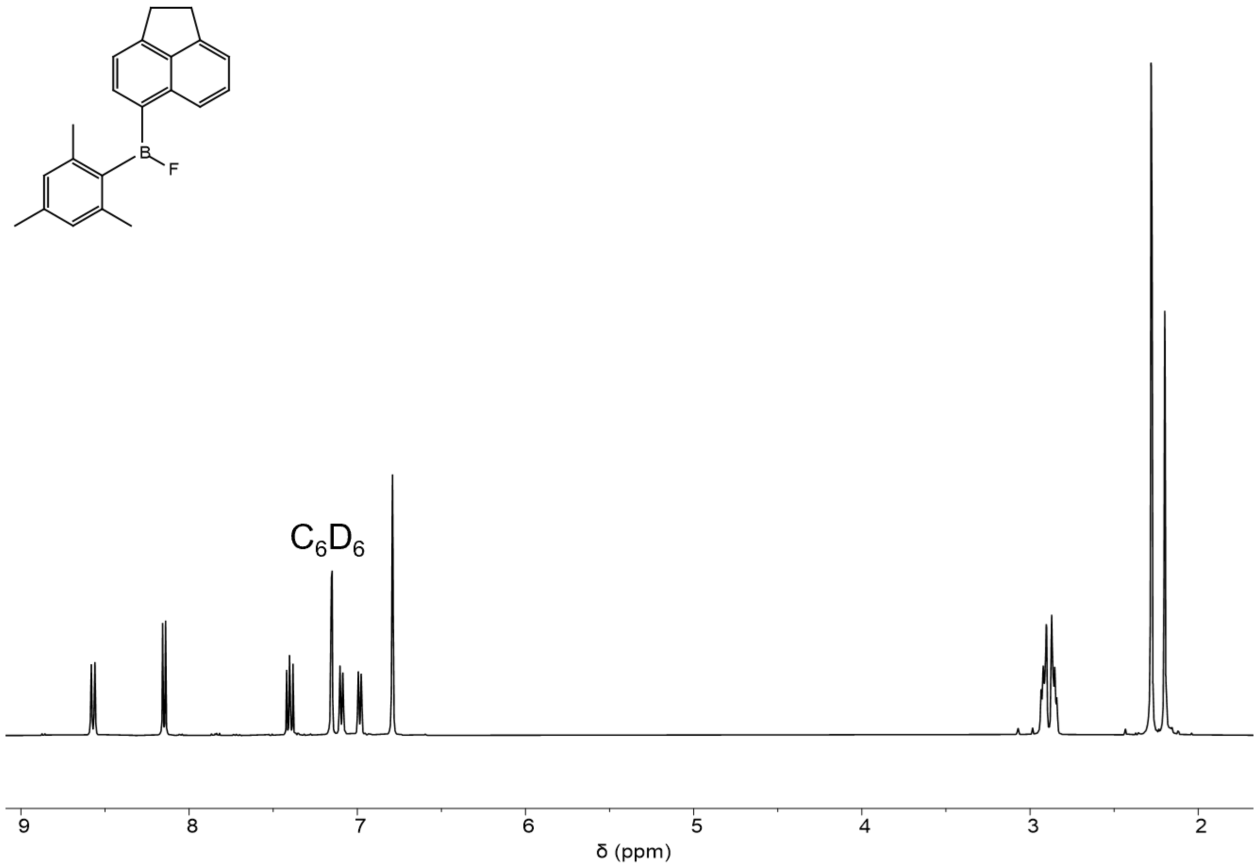


Figure S42. ^{1}H NMR spectrum of **4a**.

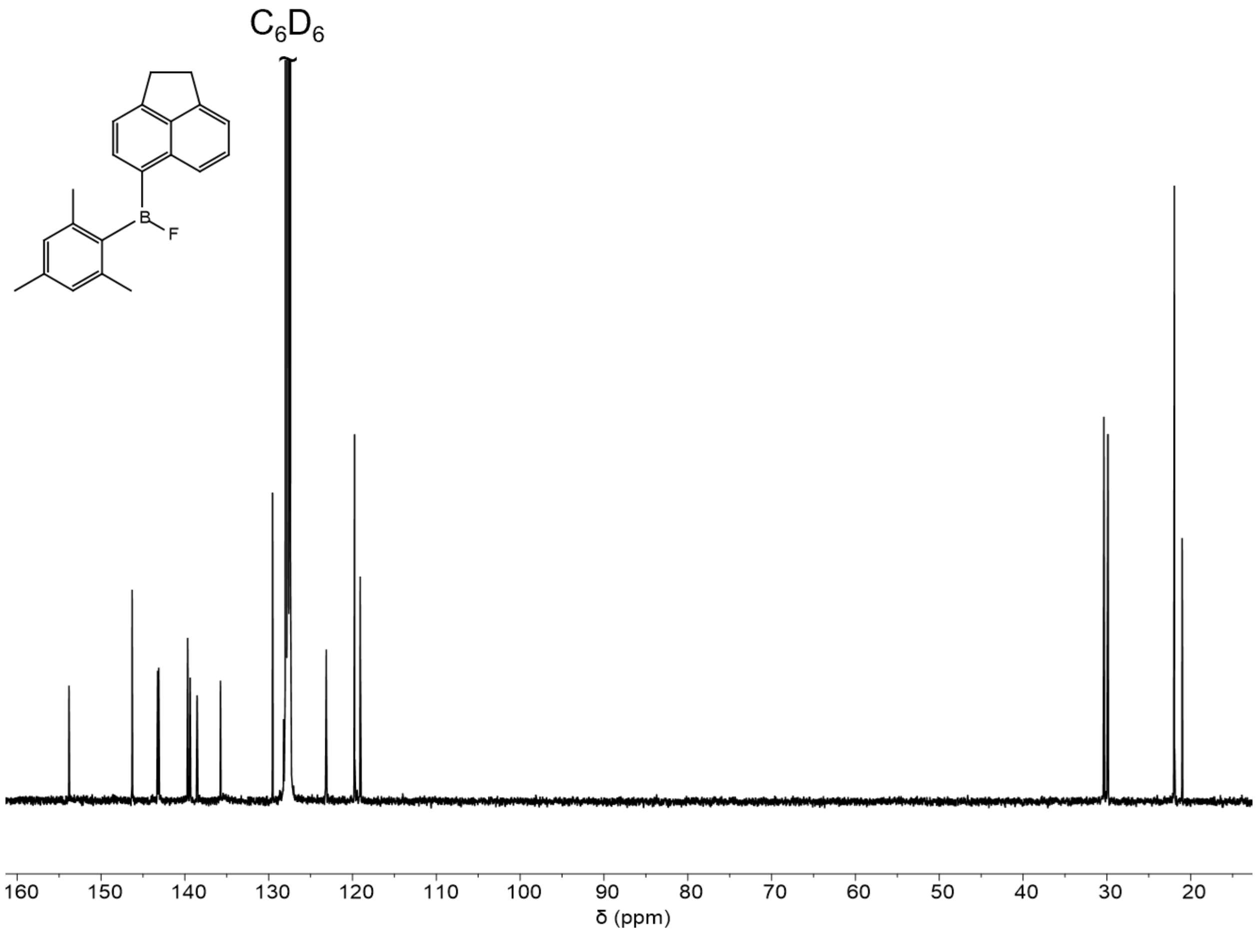


Figure S43. ^{13}C NMR spectrum of **4a**.

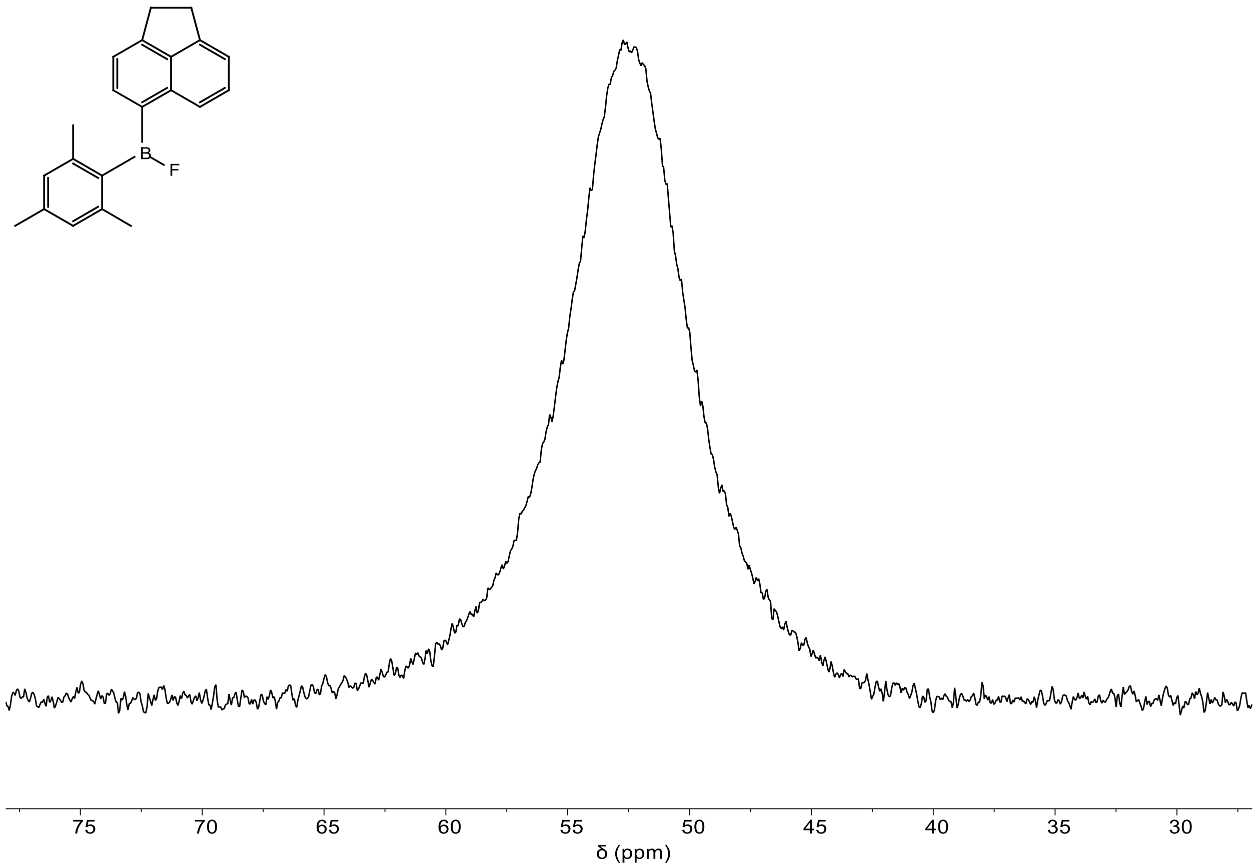


Figure S44. ^{11}B NMR spectrum of **4a**.

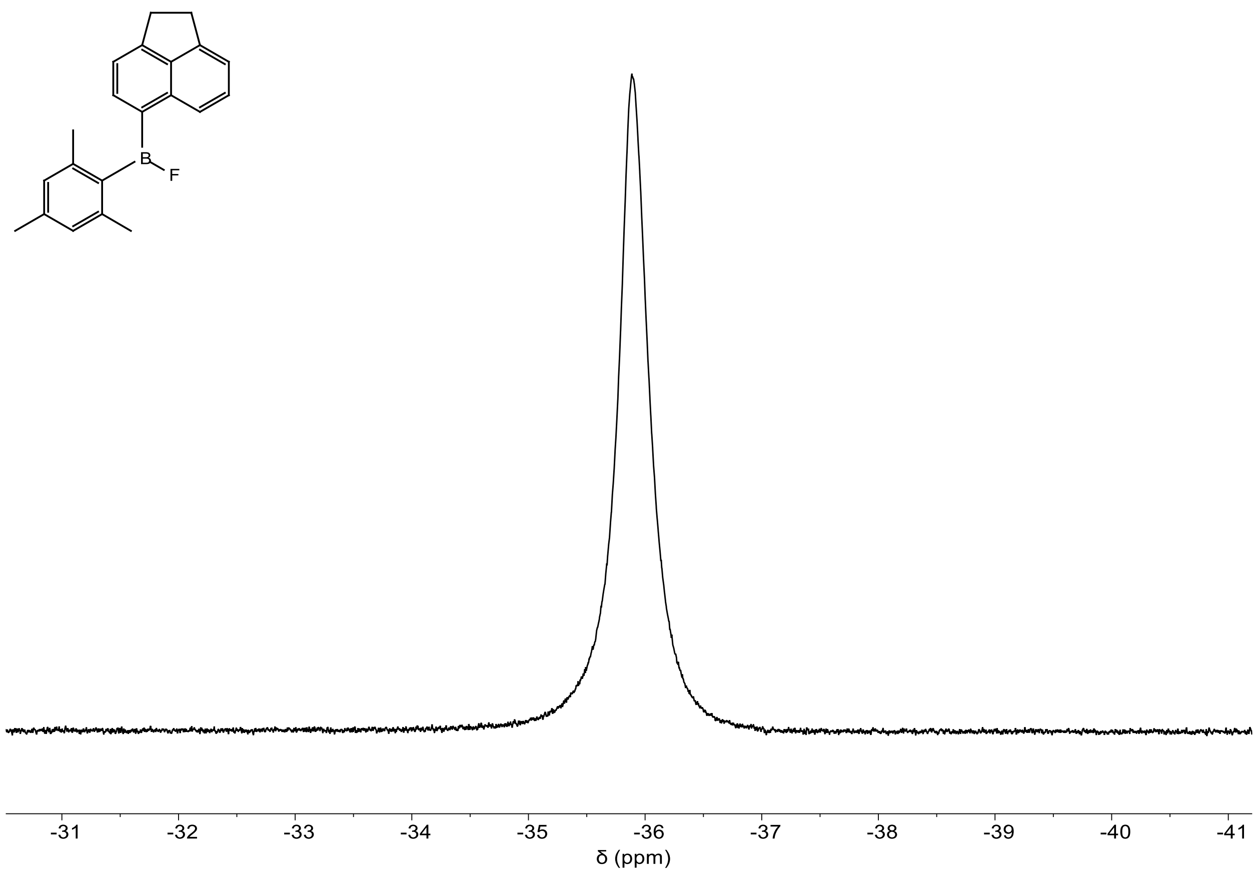


Figure S45. ^{19}F NMR spectrum of **4a**.

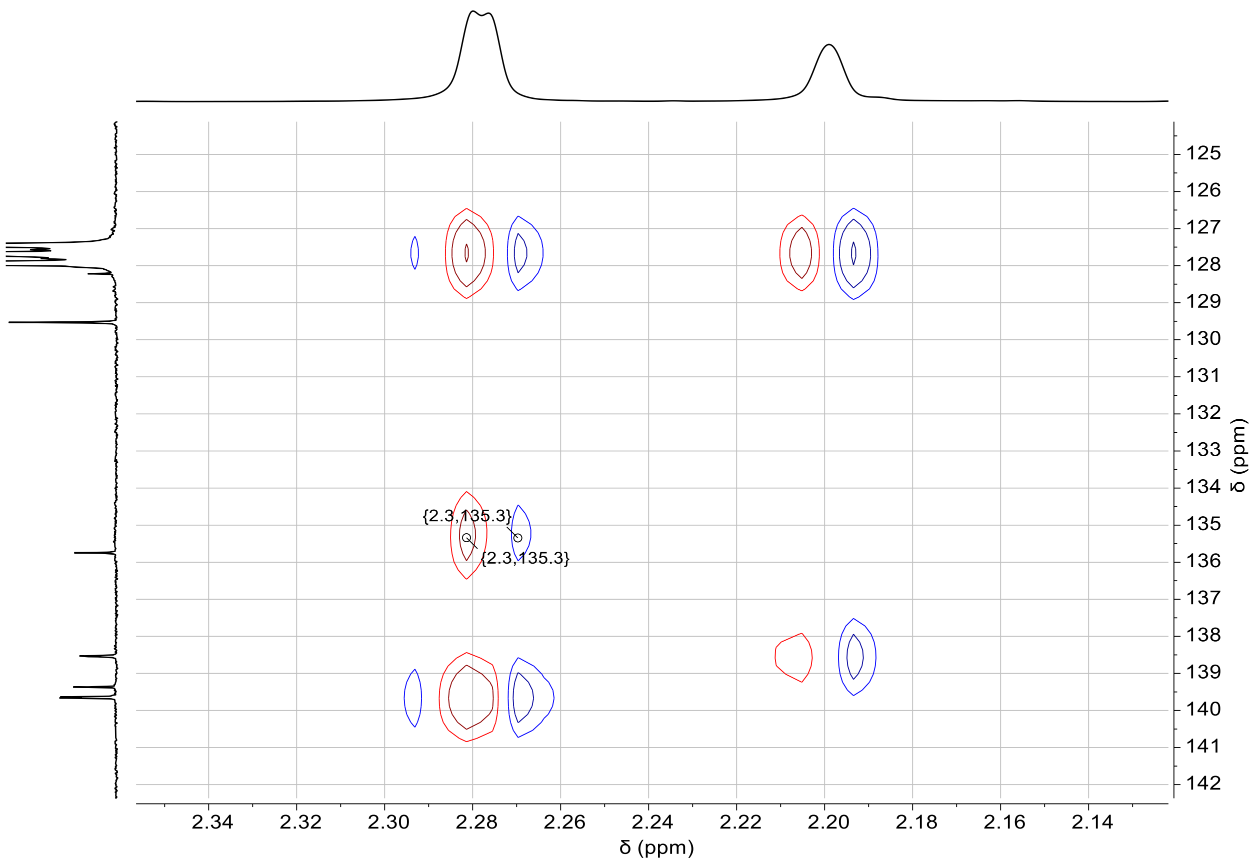


Figure S46. ^{1}H-^{13}C HMBC NMR spectrum of **4a**. Labelled peak correlates to C_i (Mes).

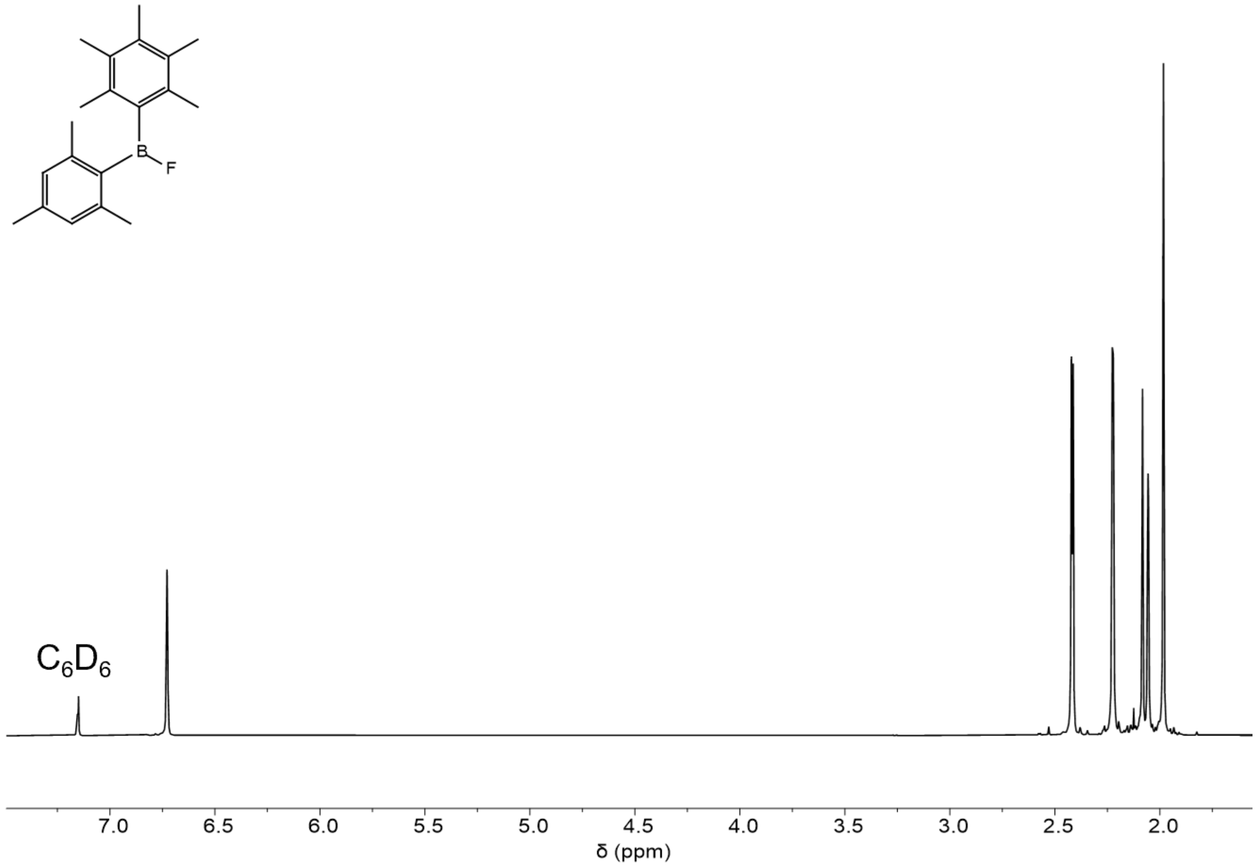


Figure S47. ¹H NMR spectrum of **4b**.

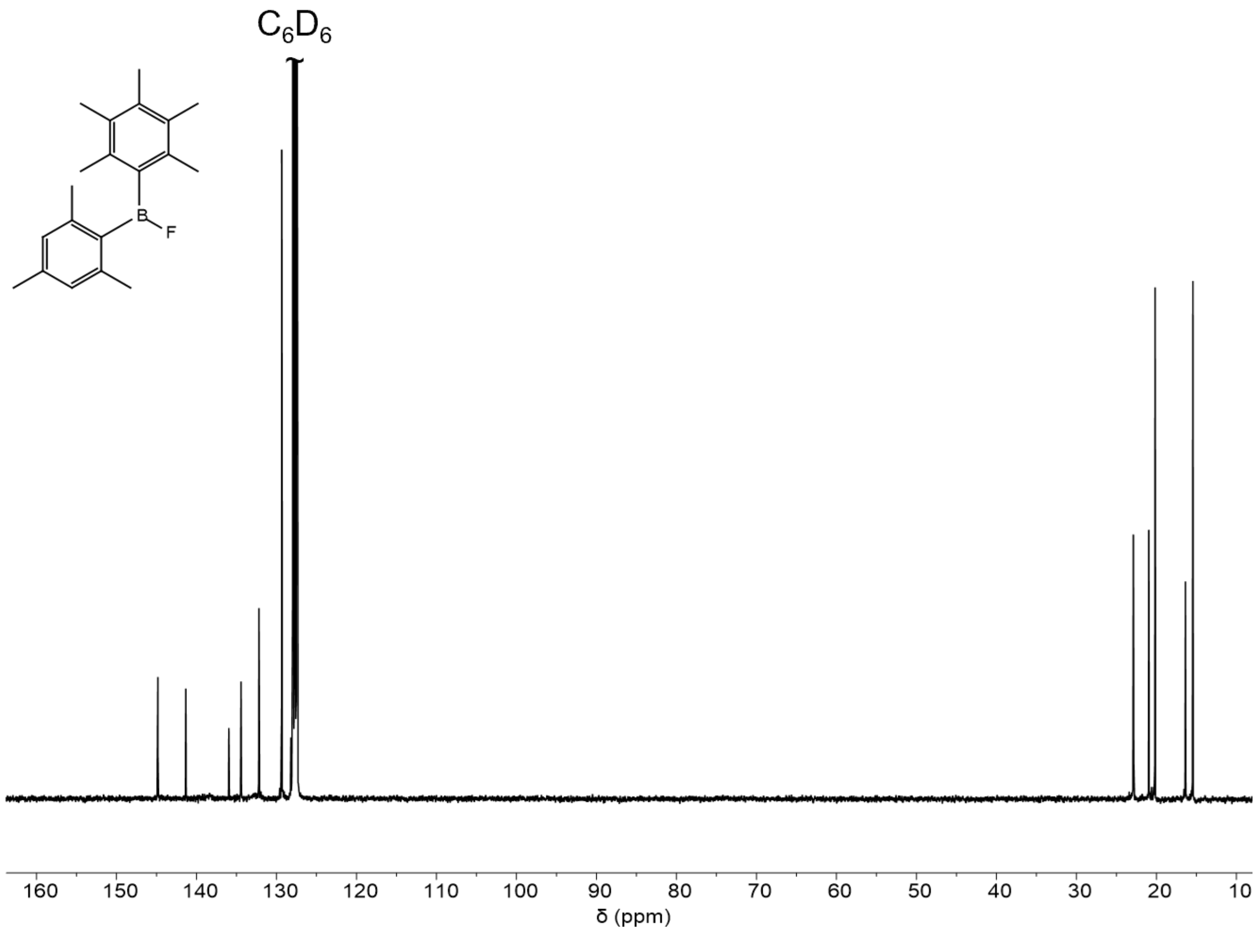


Figure S48. ^{13}C NMR spectrum of **4b**.

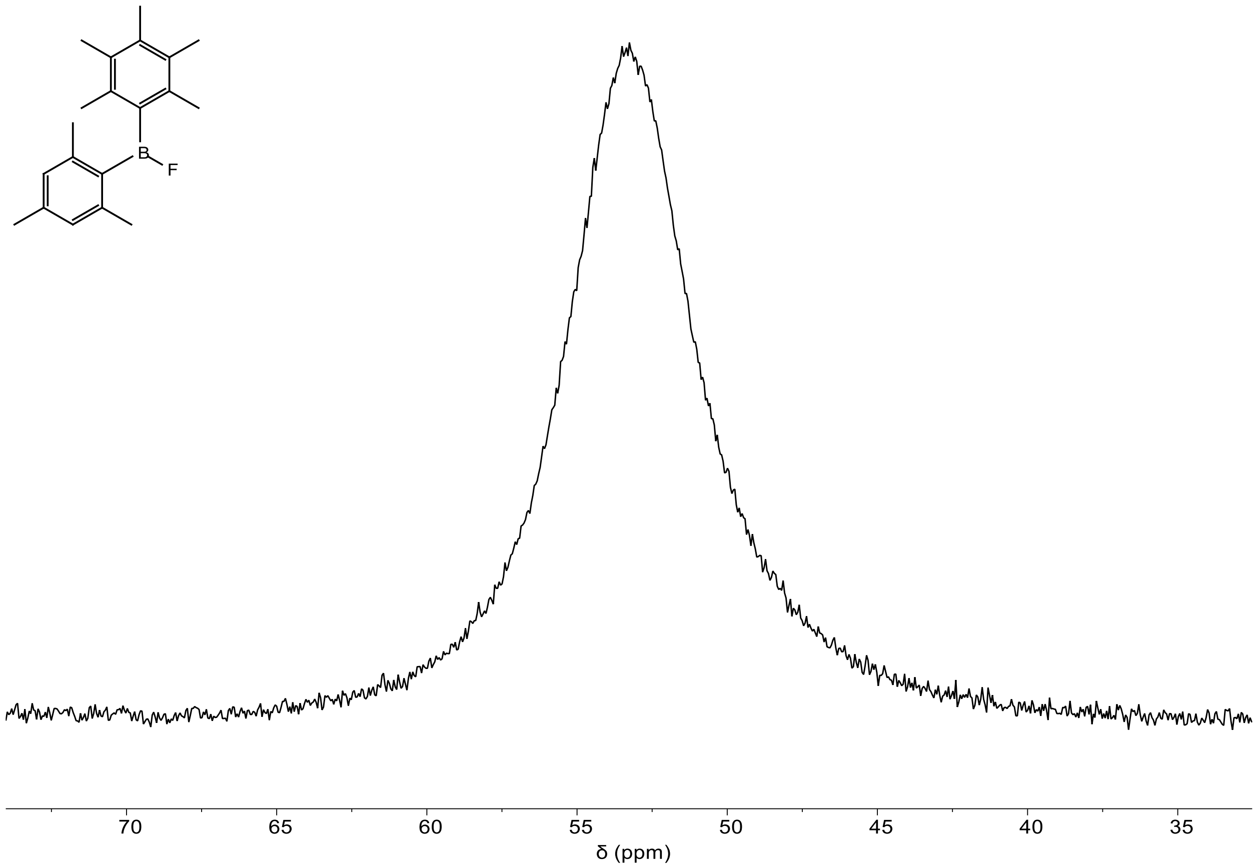


Figure S49. ^{11}B NMR spectrum of **4b**.

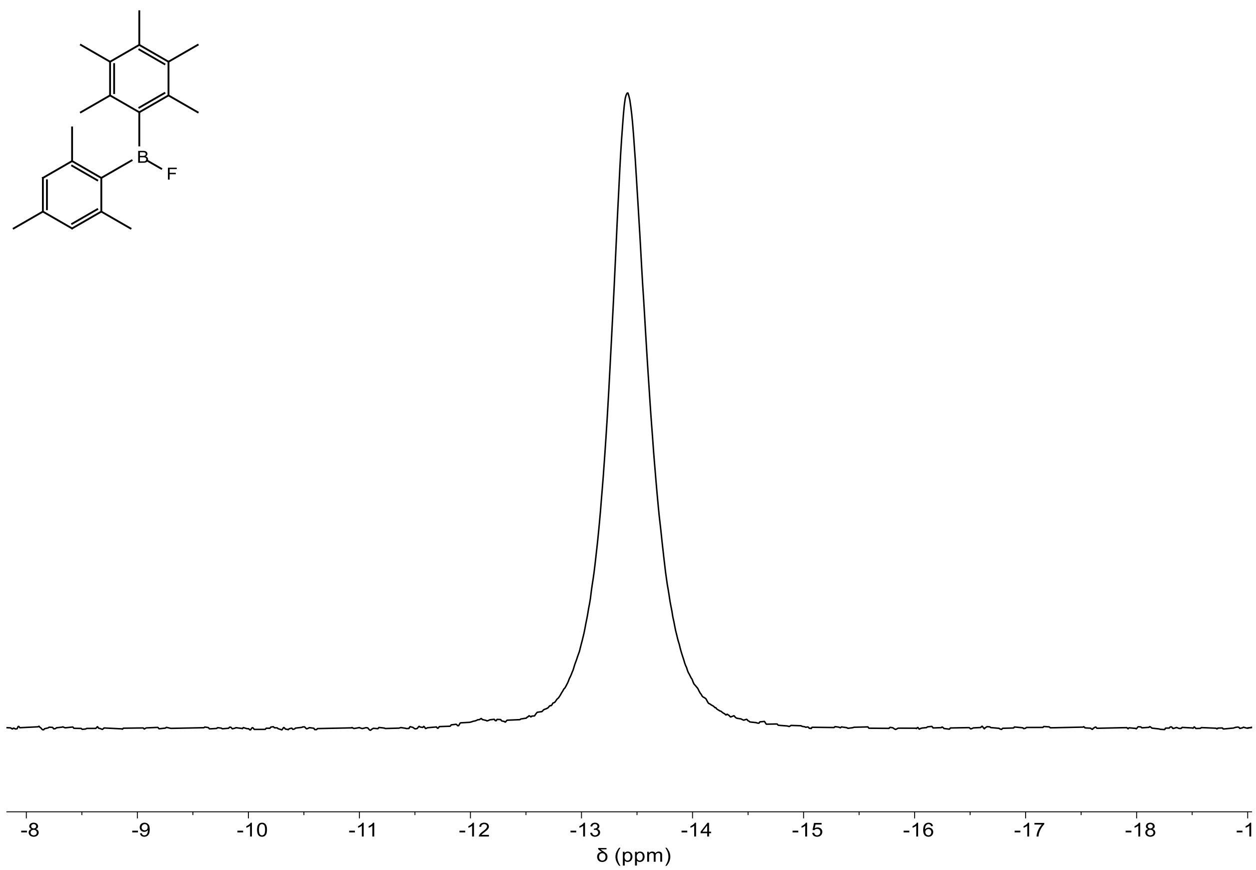


Figure S50. [19]F NMR spectrum of **4b**.

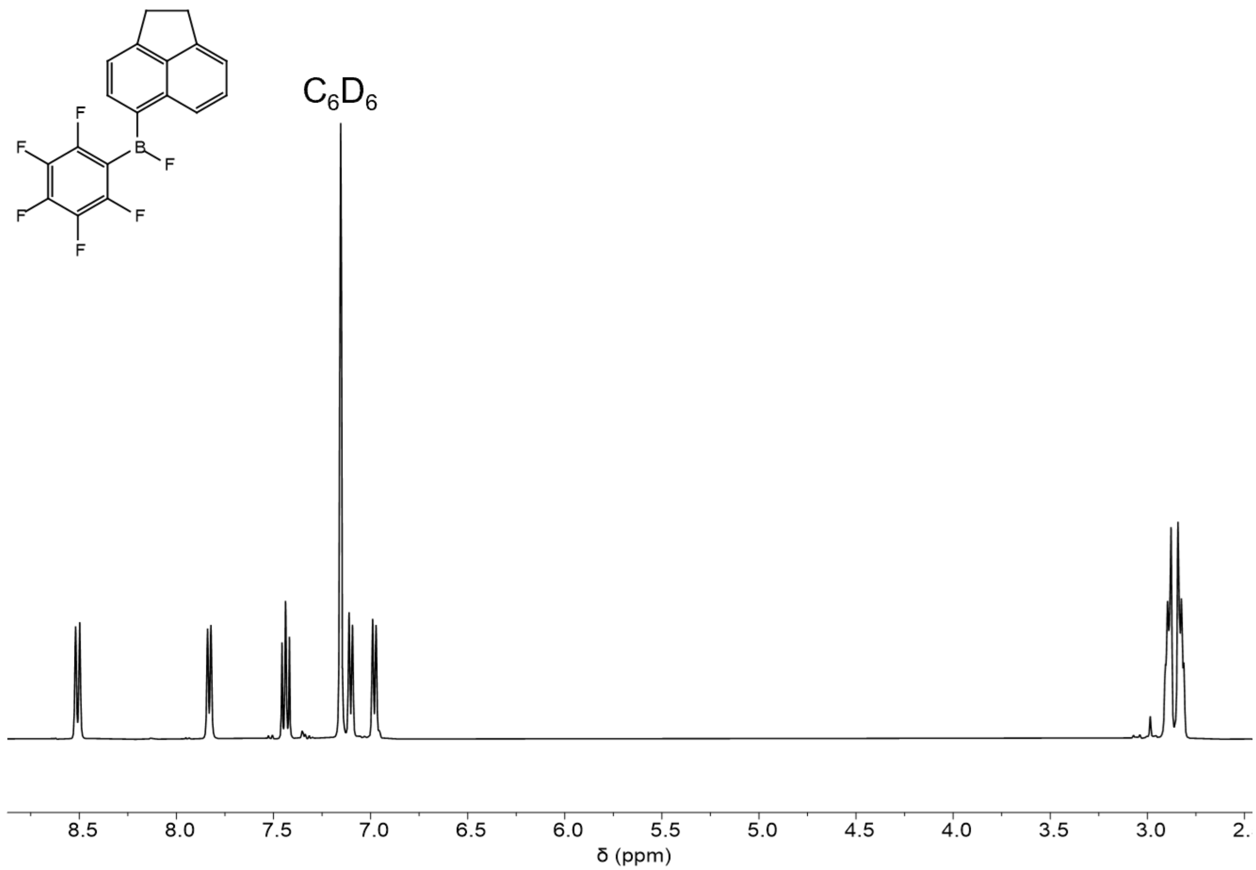


Figure S51. ^{1}H NMR spectrum of **4c**.

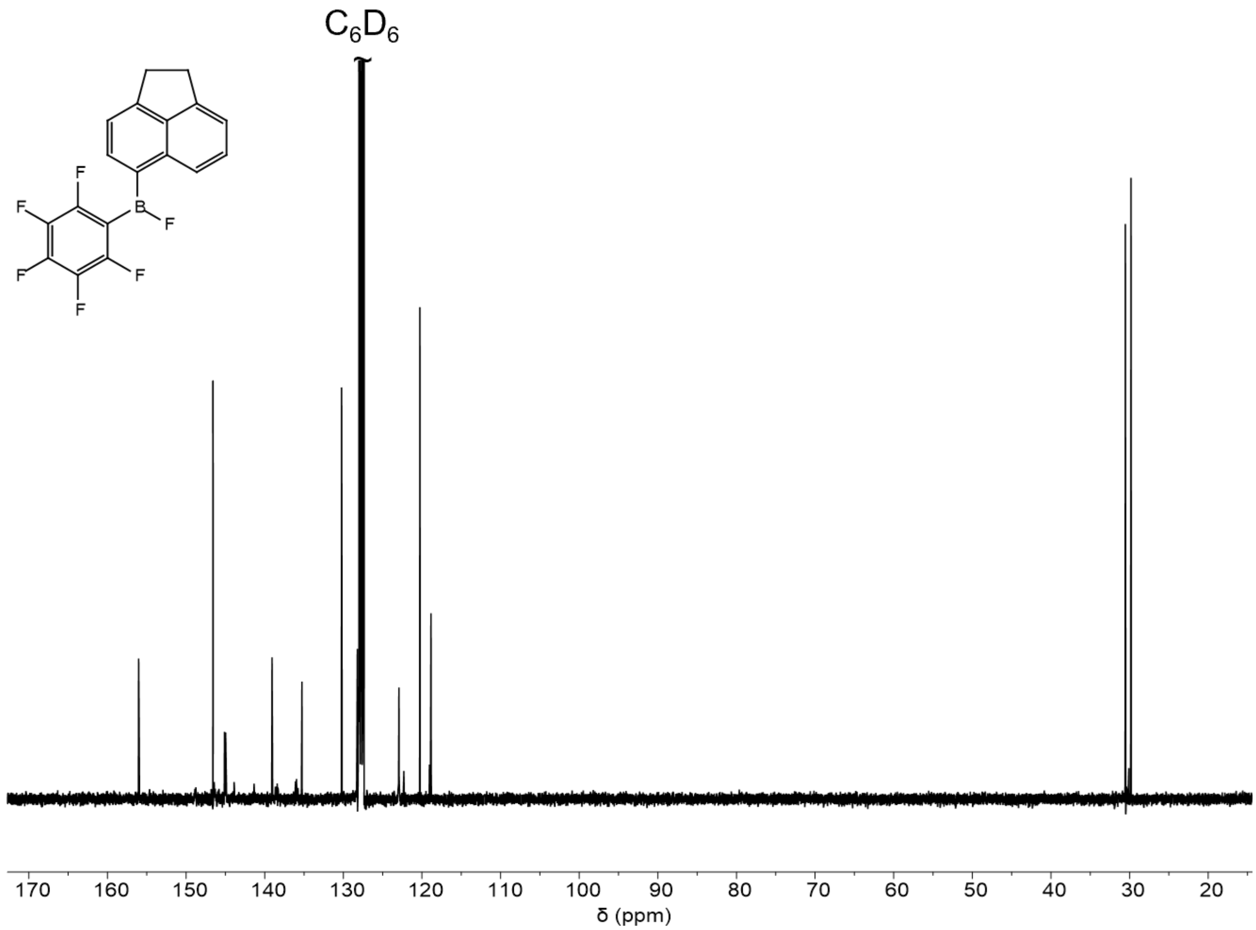


Figure S52. ^{13}C NMR spectrum of **4c**.

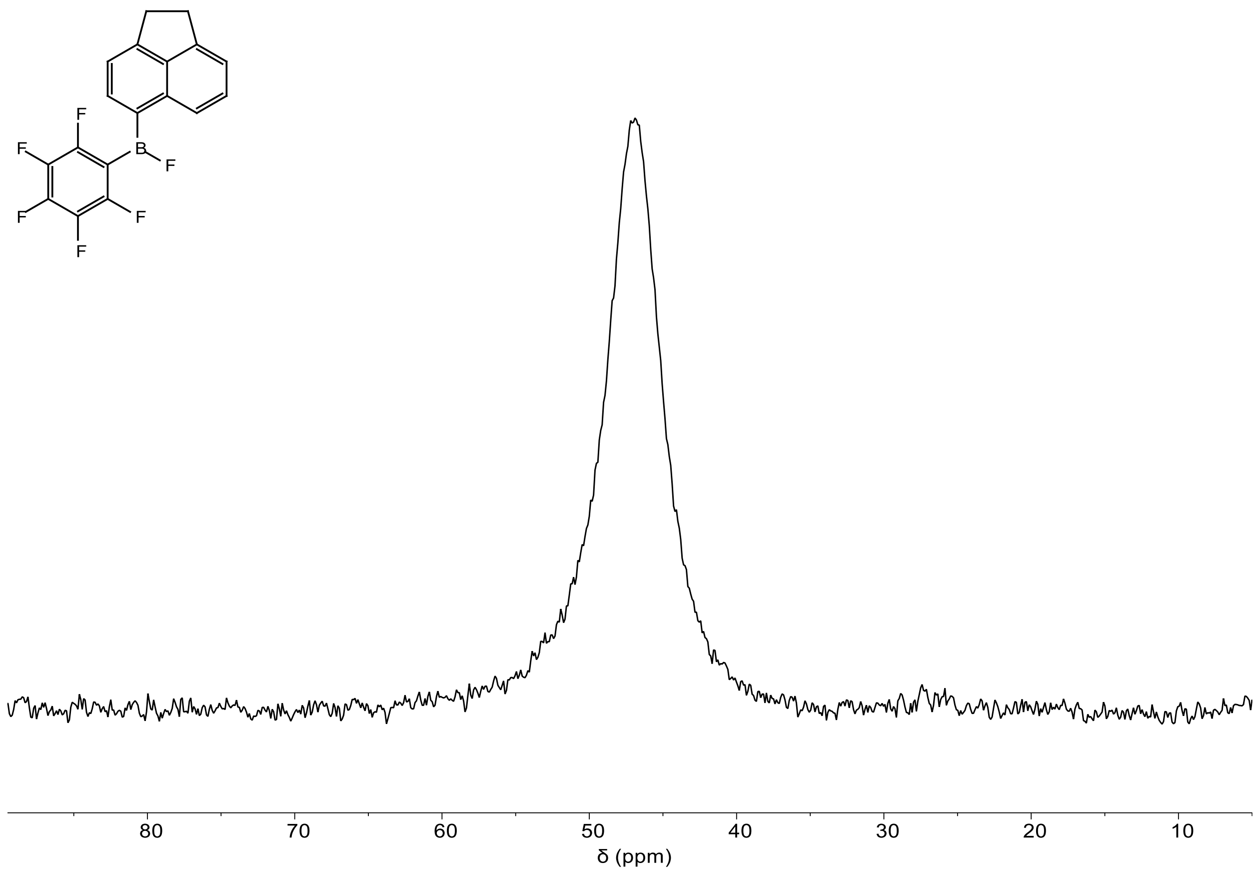


Figure S53. ^{11}B NMR spectrum of **4c**.

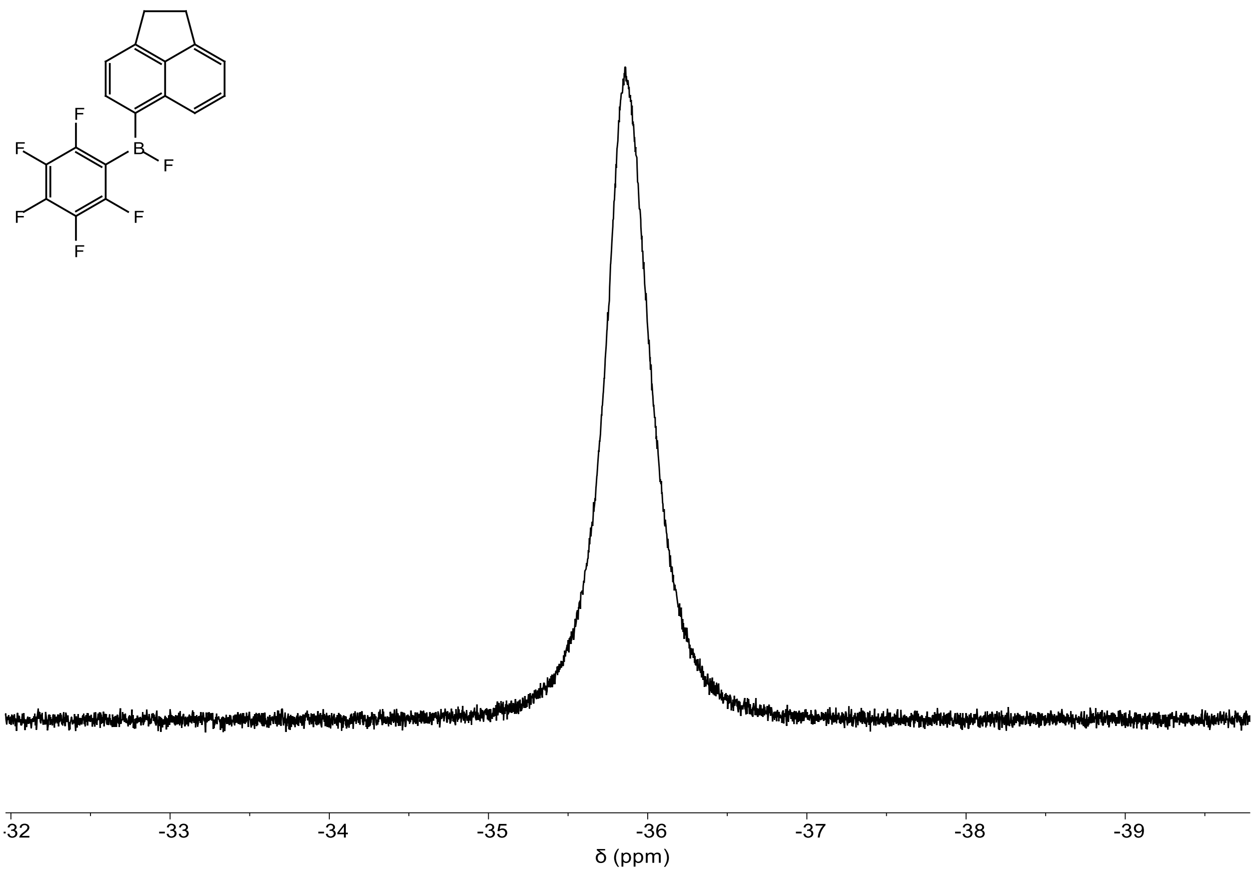


Figure S54. Fluorine-on-boron region in the ^{19}F NMR spectrum of **4c**.

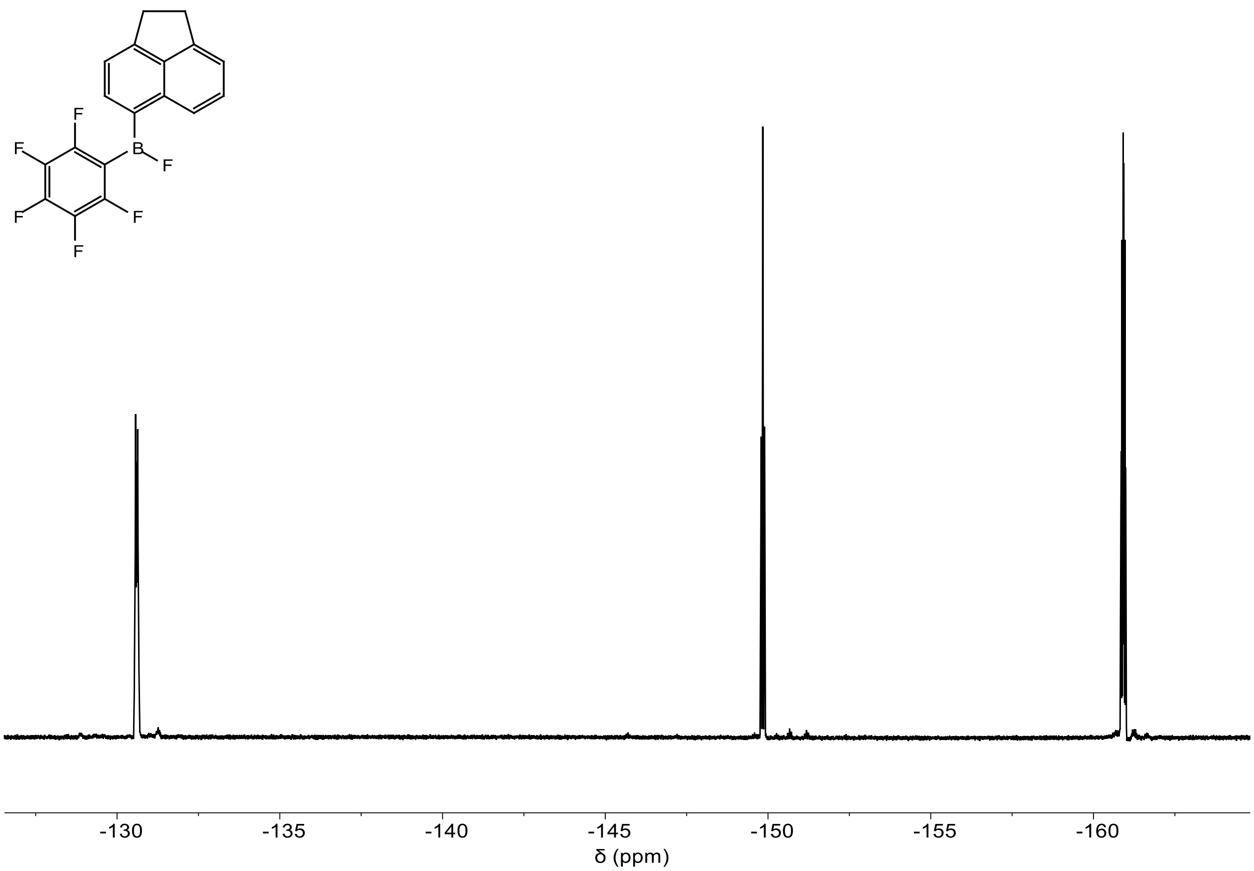


Figure S55. Fluorine-on-carbon region in the ^{19}F NMR spectrum of **4c**.

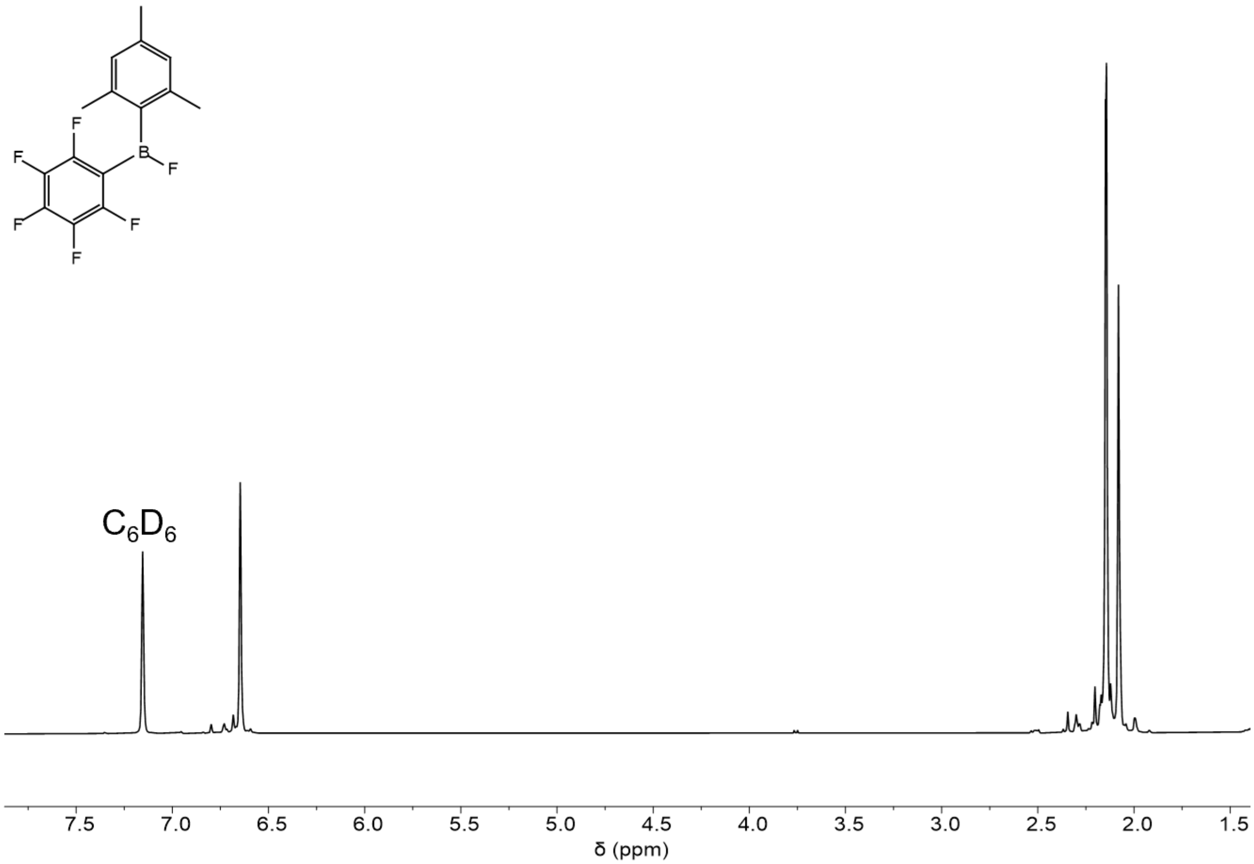


Figure S56. [1]H NMR spectrum of **4d.**

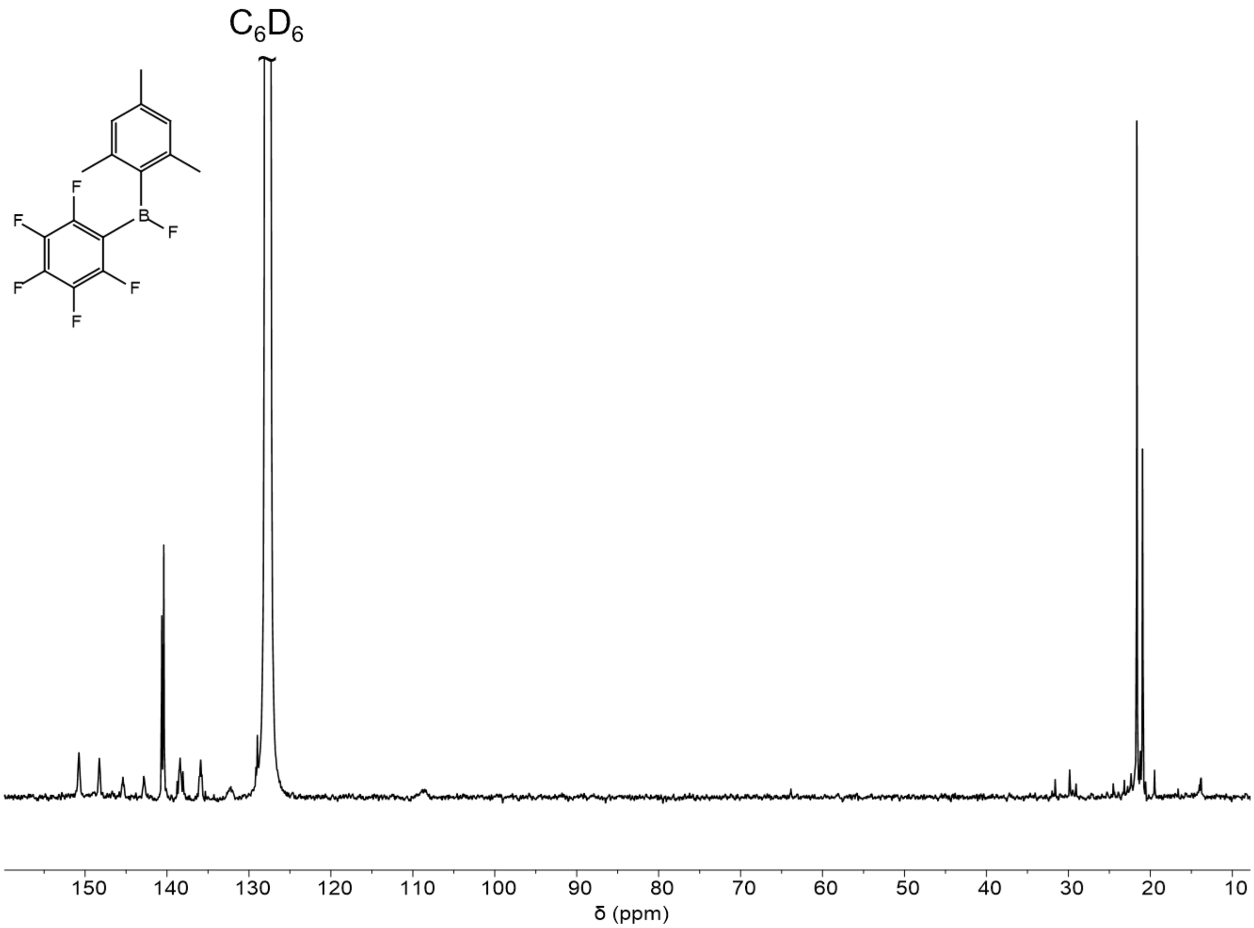


Figure S57. ^{13}C NMR spectrum of **4d.**

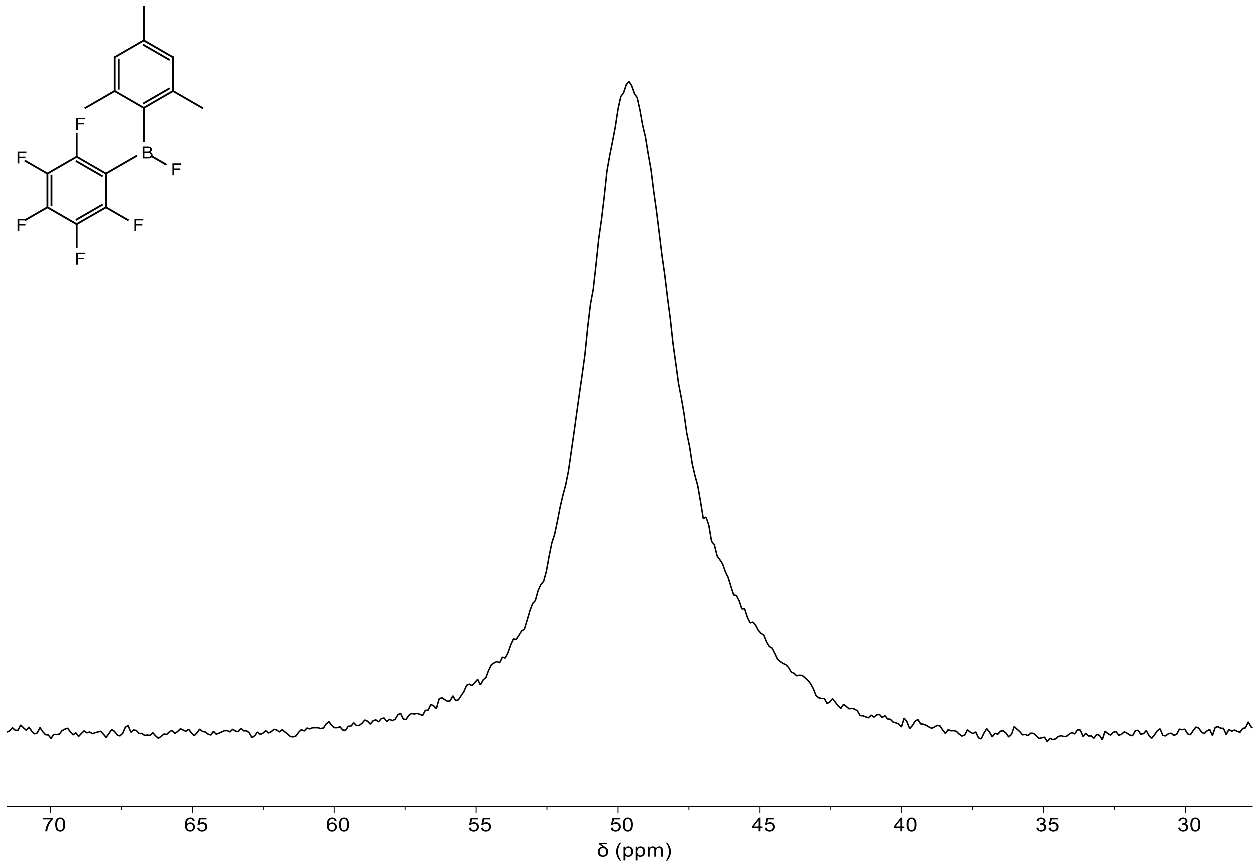


Figure S58. ^{11}B NMR spectrum of **4d.**

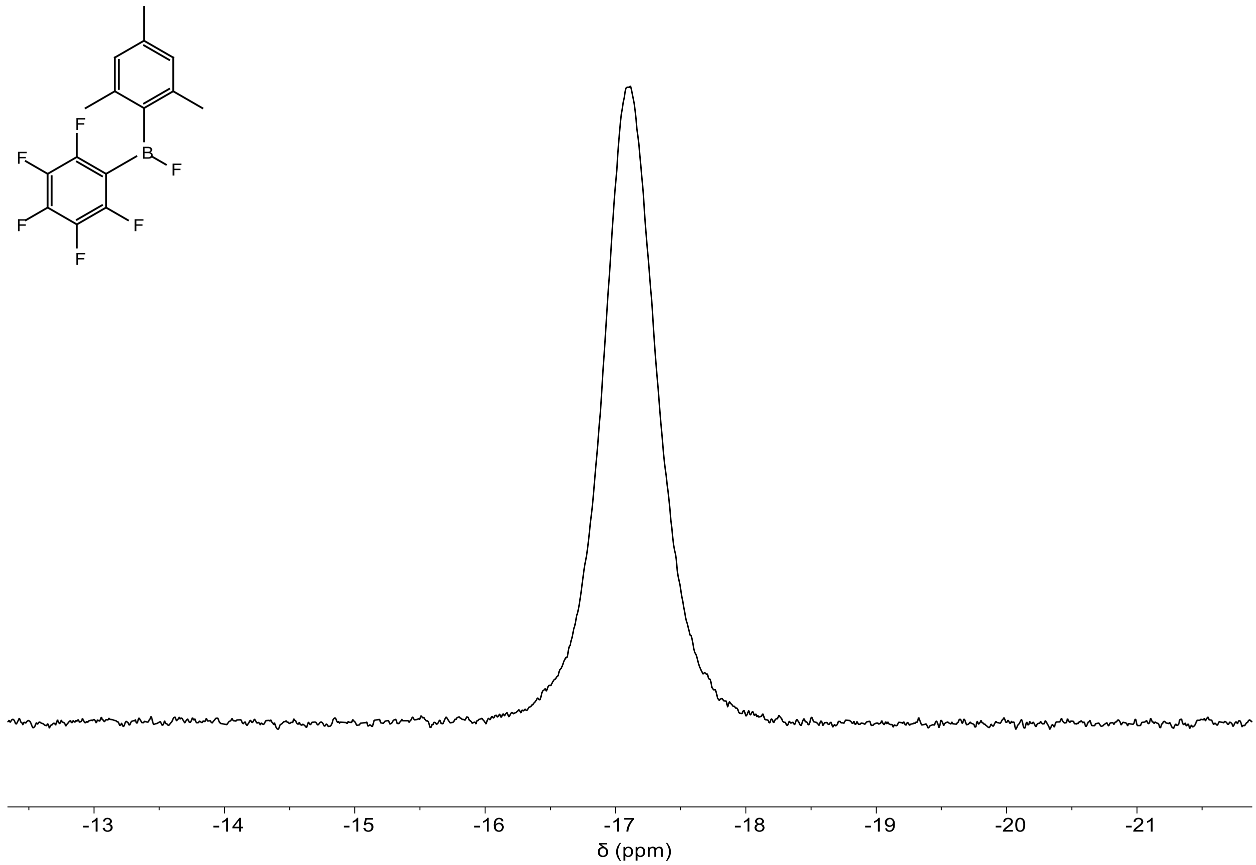


Figure S59. Fluorine-on-boron region in the ^{19}F NMR spectrum of **4d.**

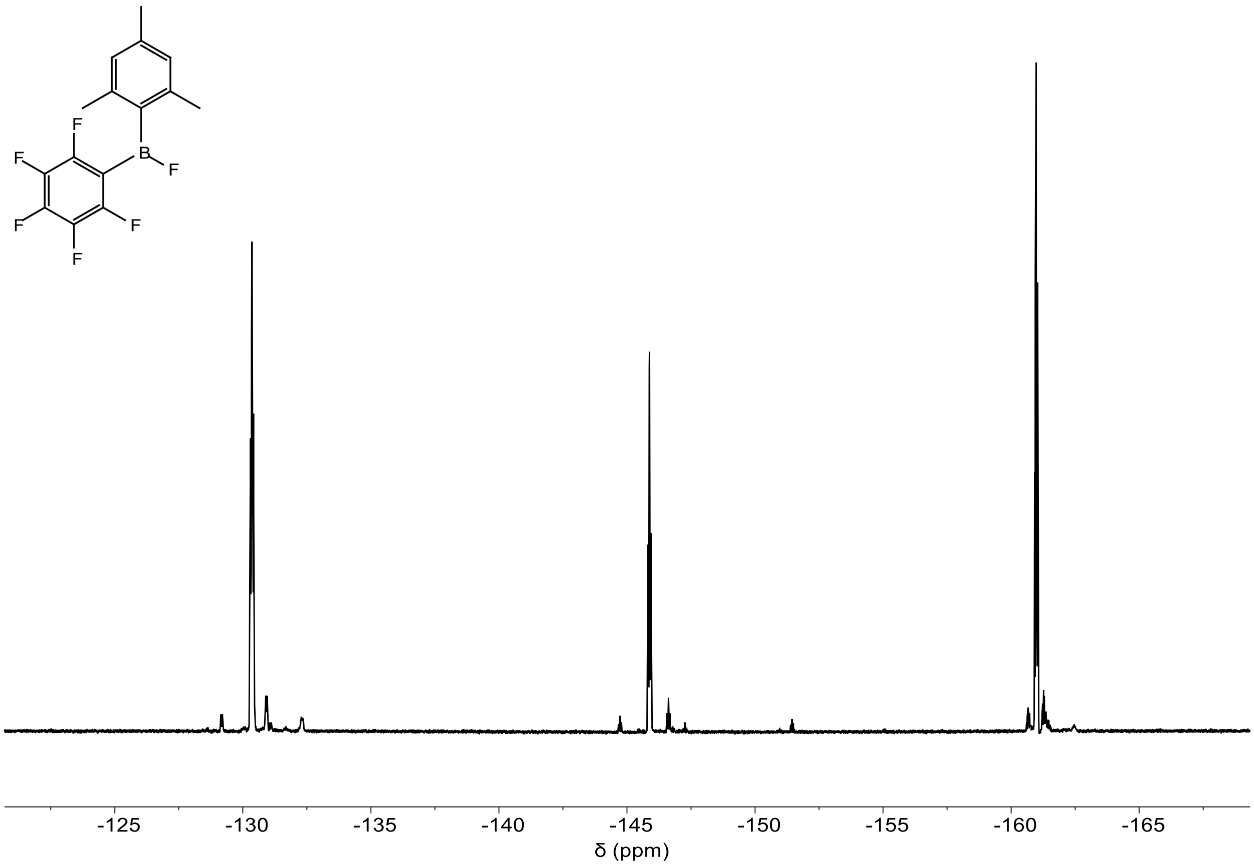


Figure S60. Fluorine-on-carbon region in the ^{19}F NMR spectrum of **4d.**

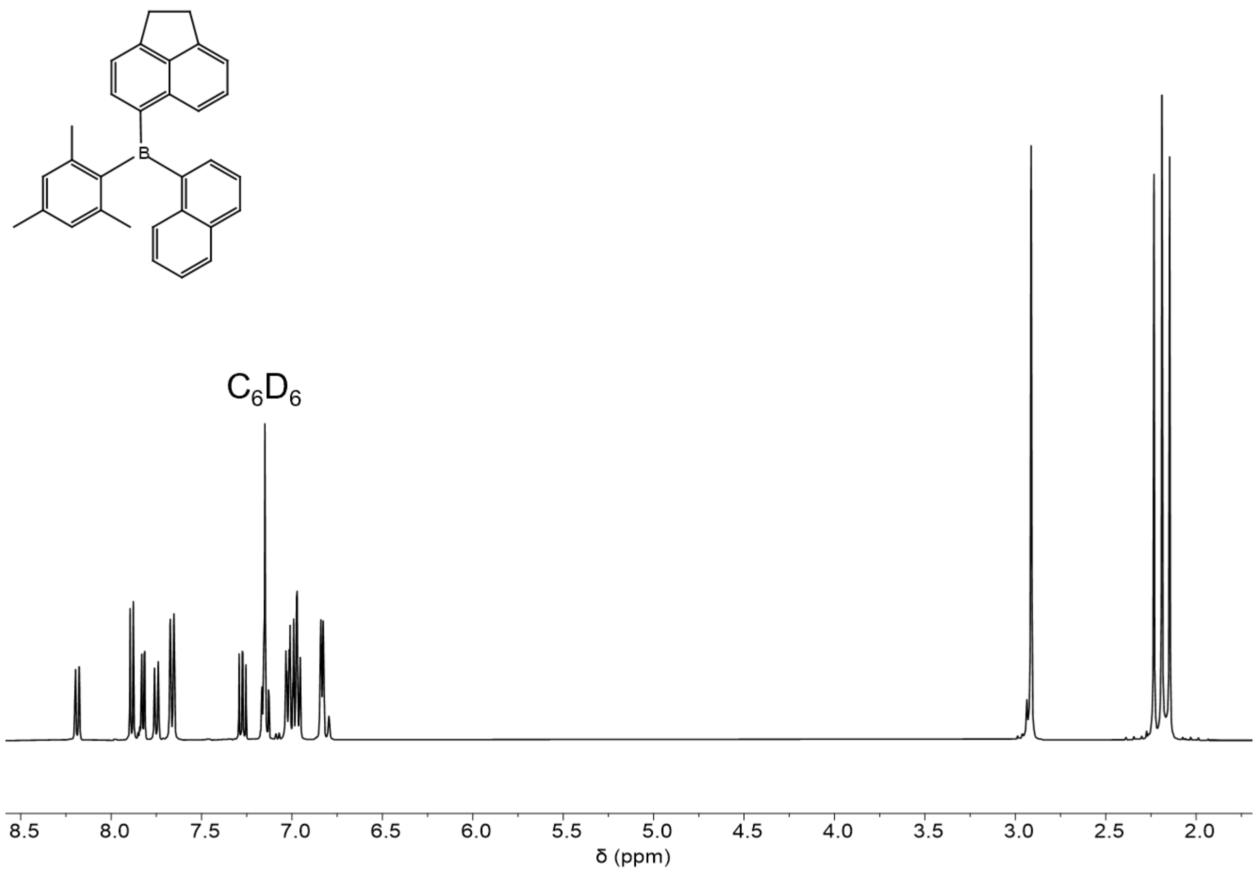


Figure S61. ^{1}H NMR spectrum of **5a**.

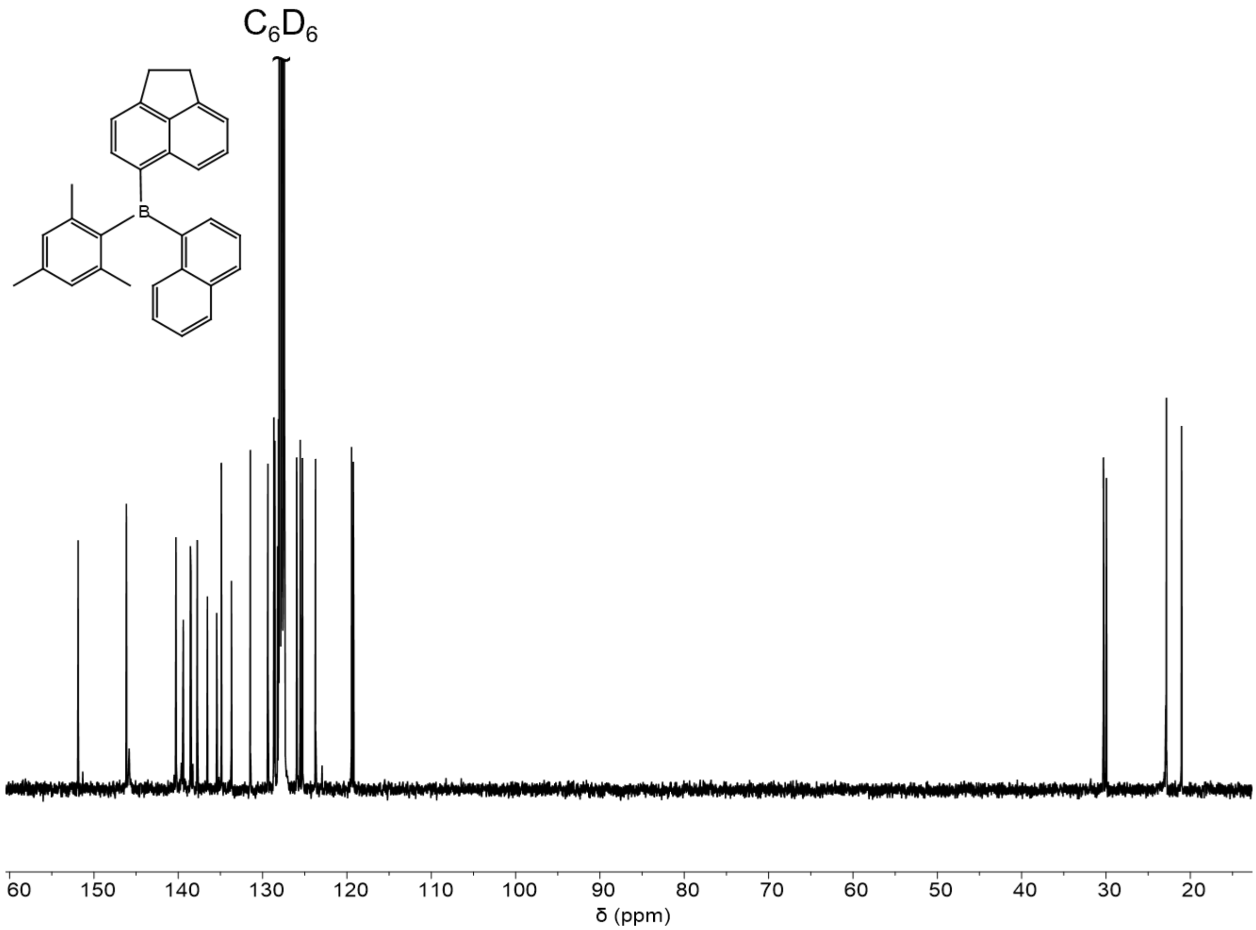


Figure S62. ^{13}C NMR spectrum of **5a**.

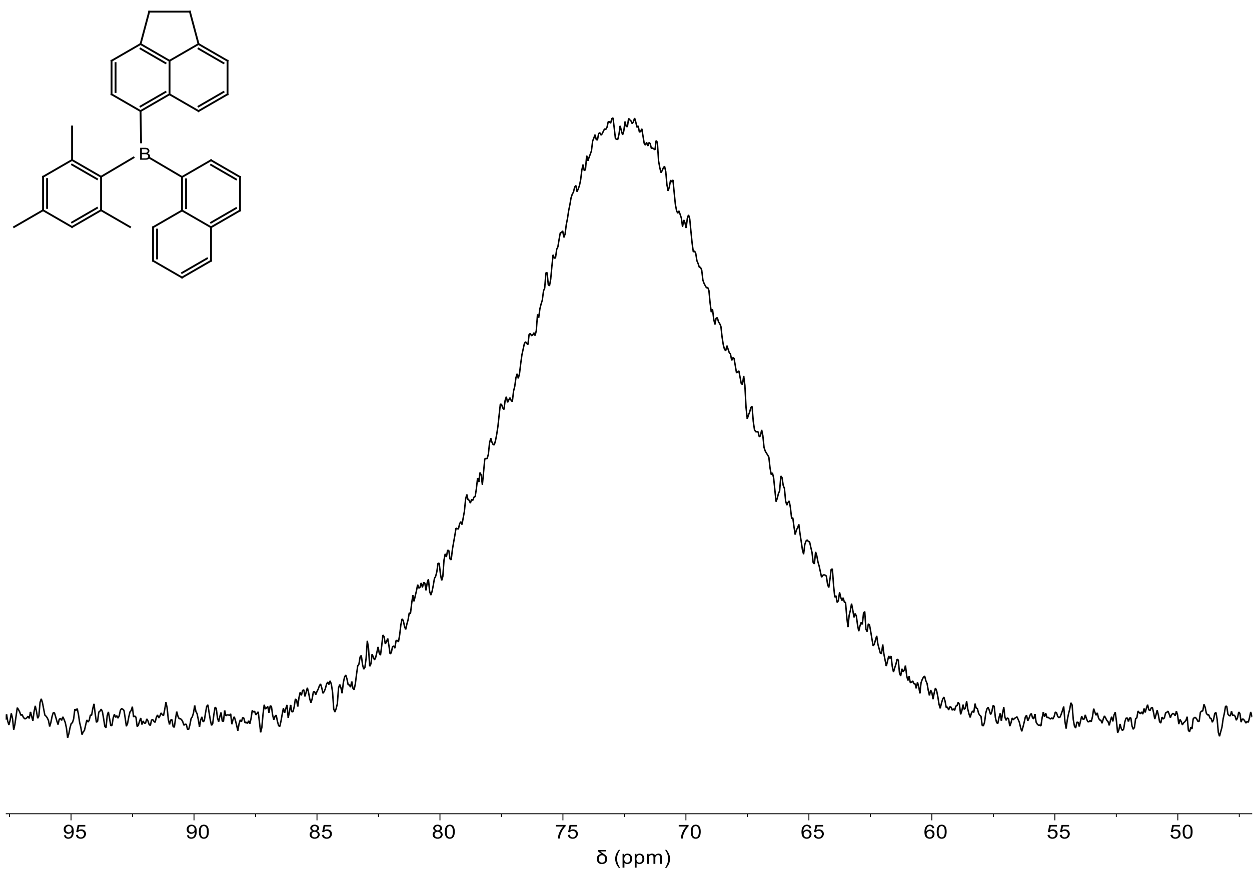


Figure S63. ^{11}B NMR spectrum of **5a**.

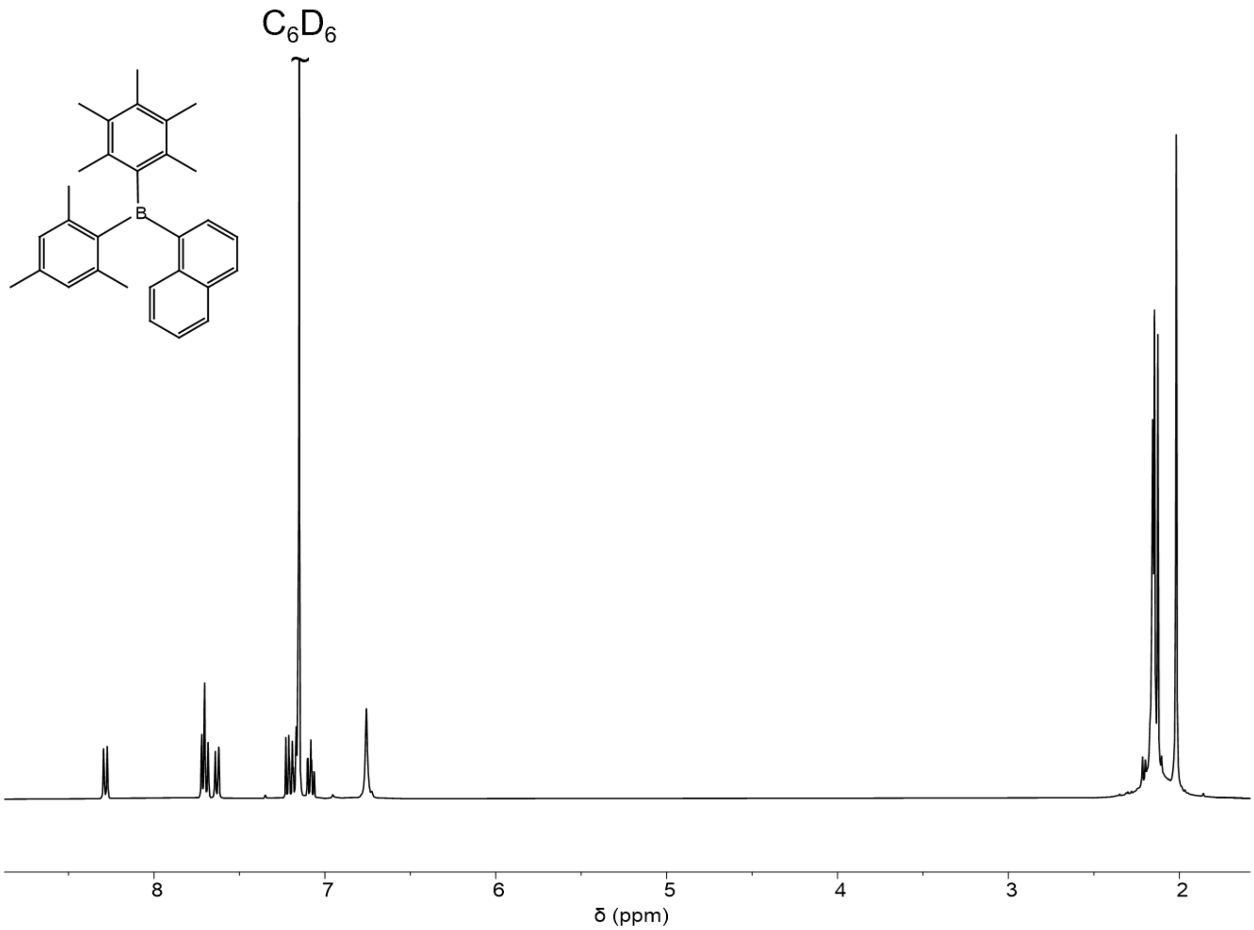


Figure S64. [1]H NMR spectrum of **5b**.

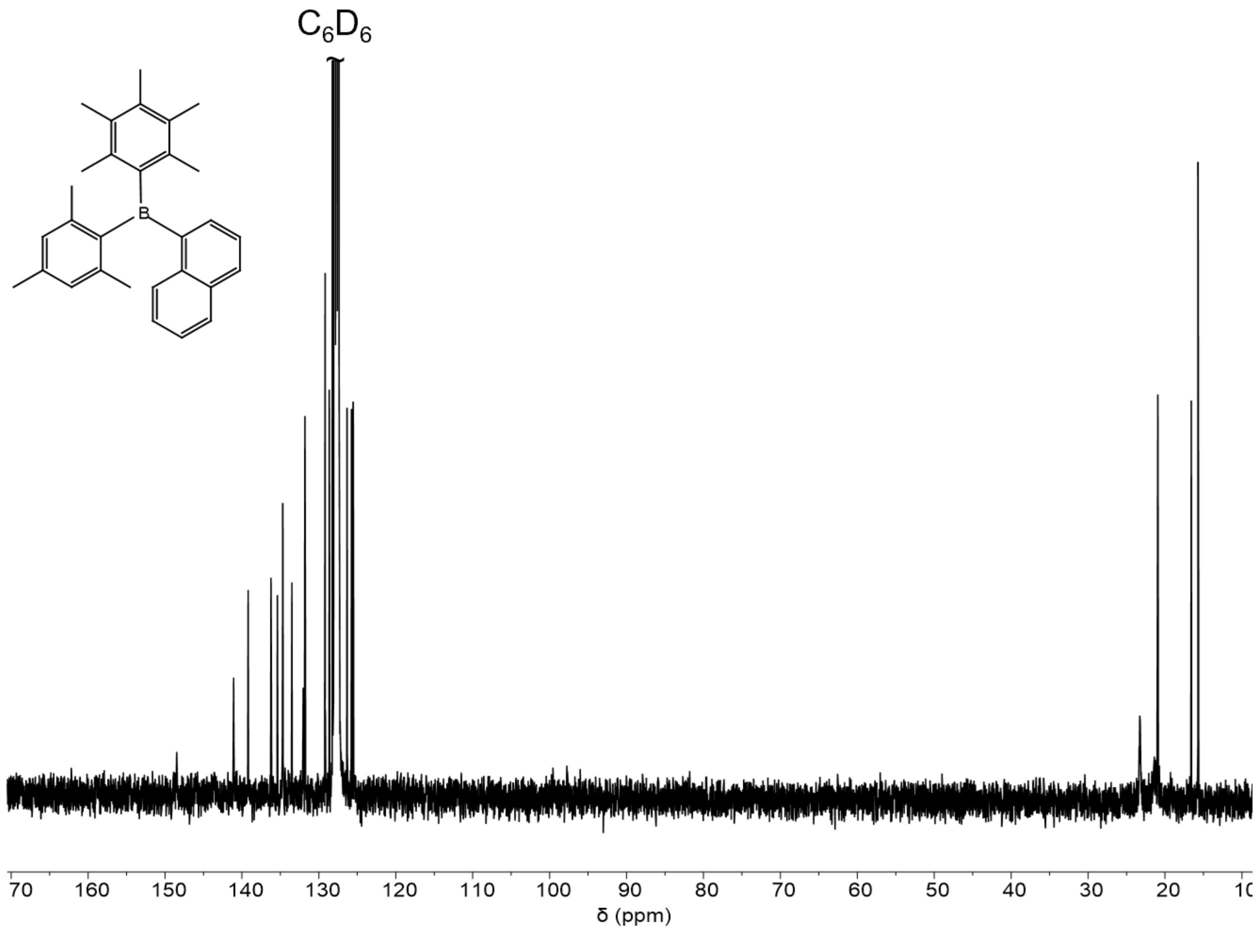


Figure S65. ^{13}C NMR spectrum of **5b**.

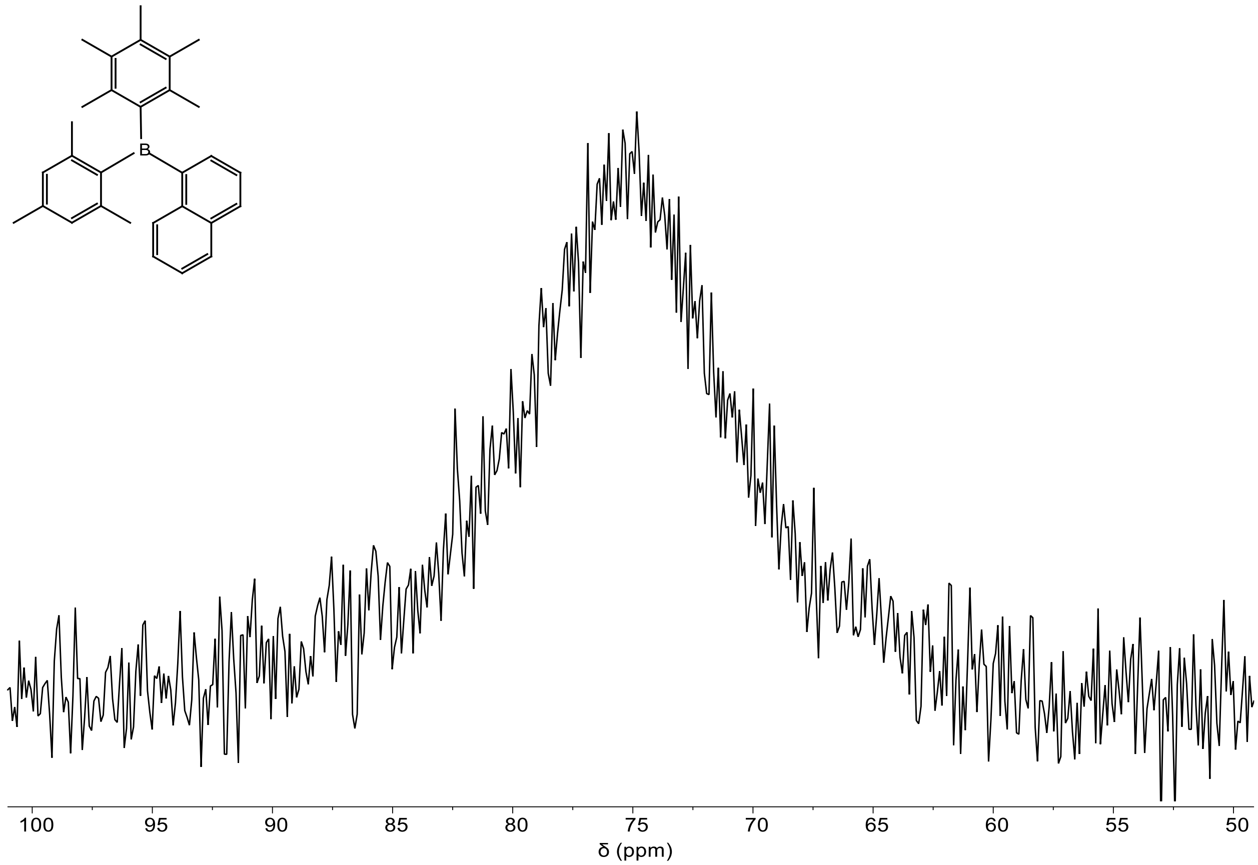


Figure S66. ^{11}B NMR spectrum of **5b**.

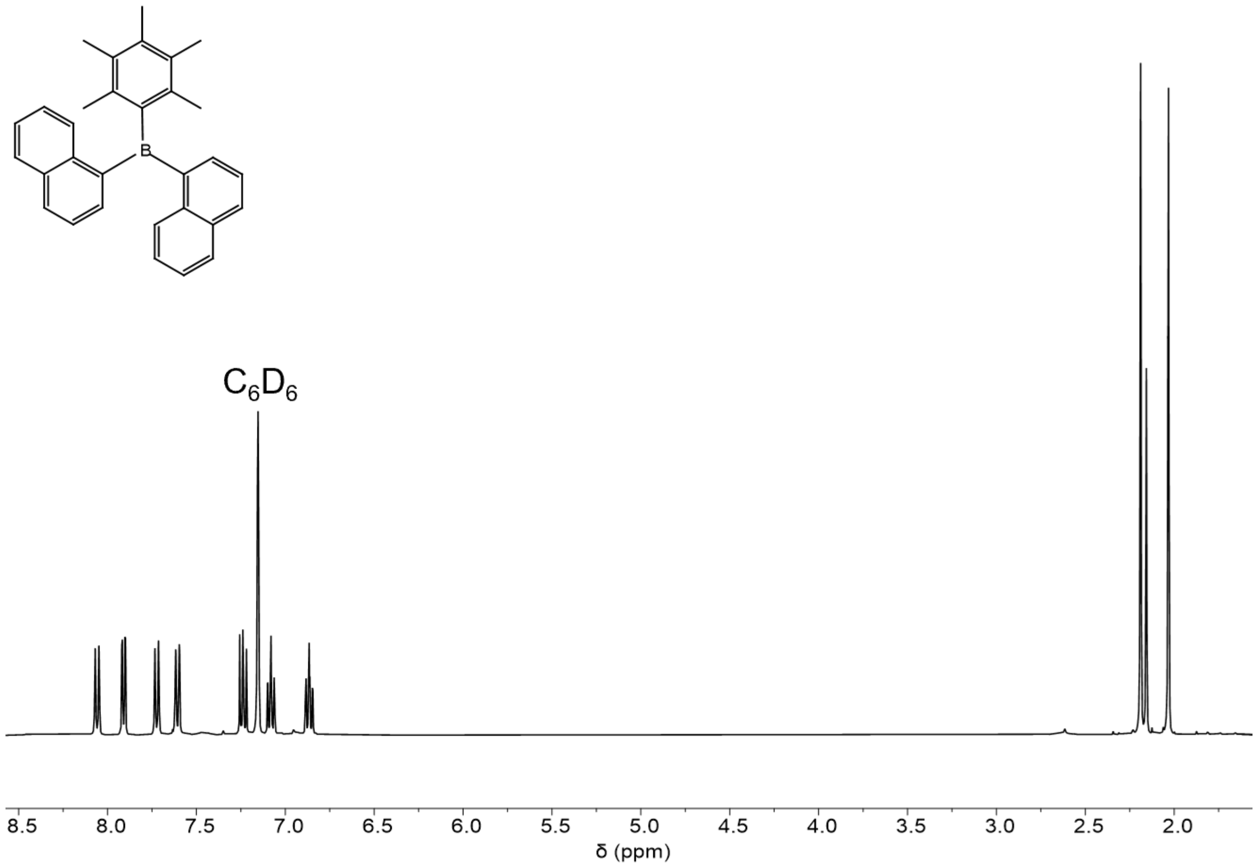


Figure S67. ^{1}H NMR spectrum of **5c**.

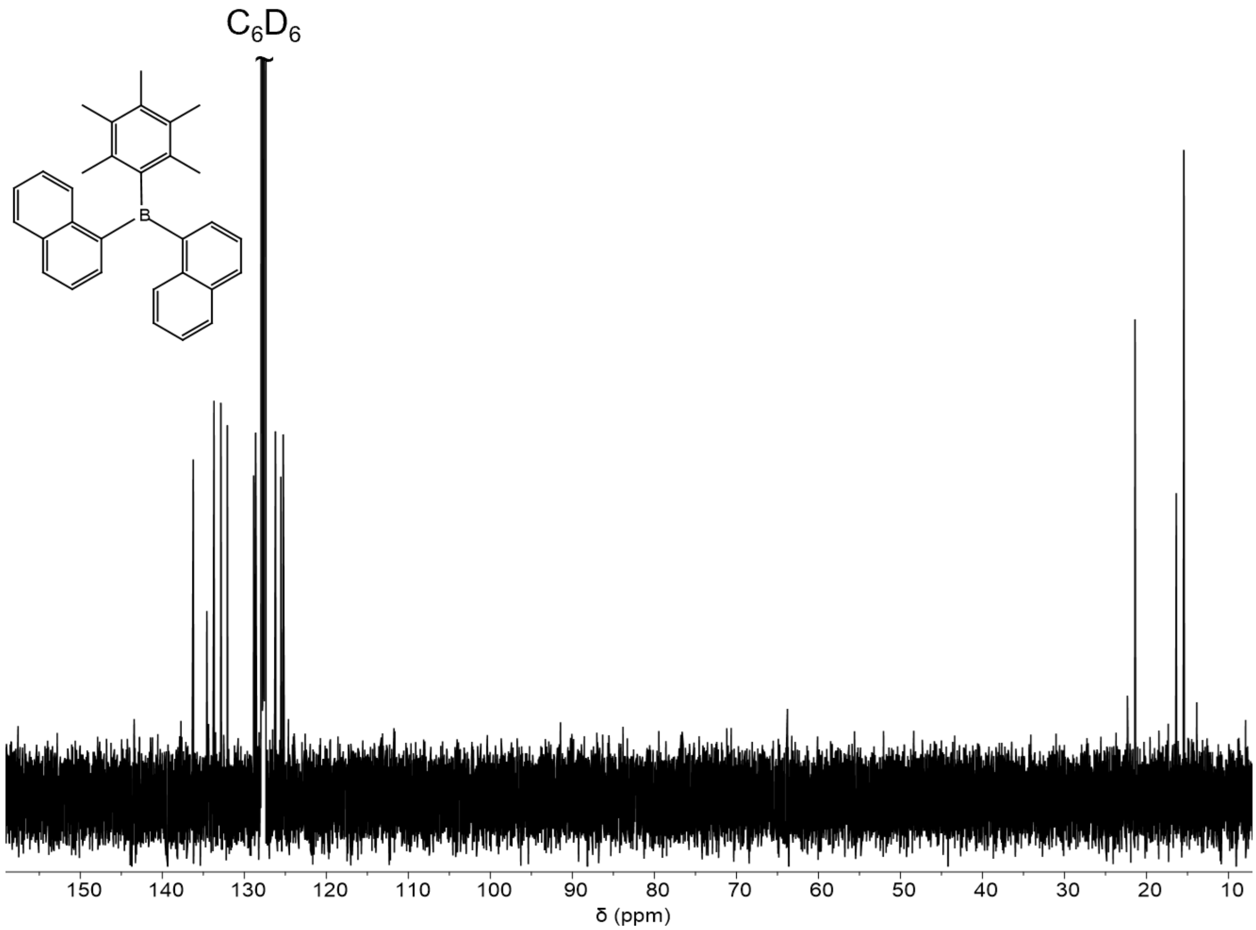


Figure S68. ^{13}C NMR spectrum of **5c**.

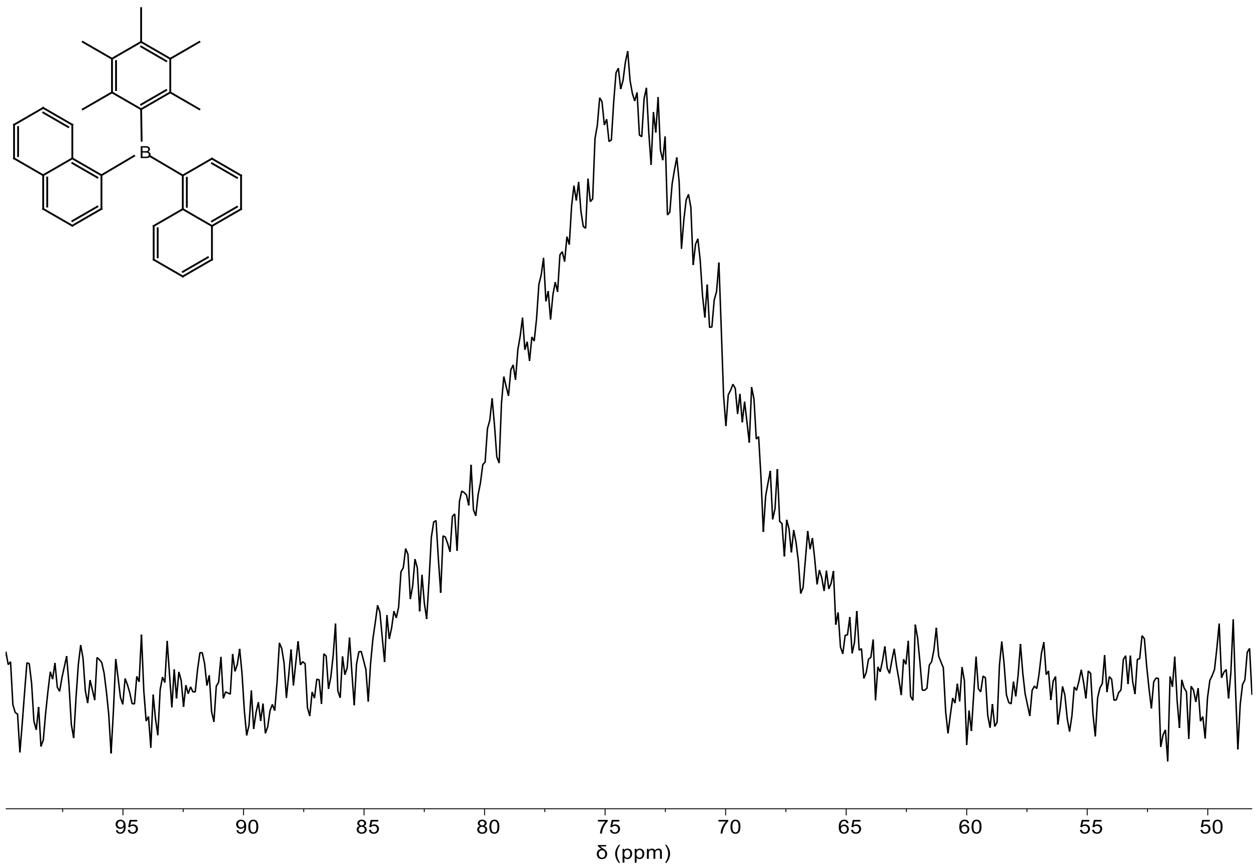


Figure S69. ^{11}B NMR spectrum of **5c**.

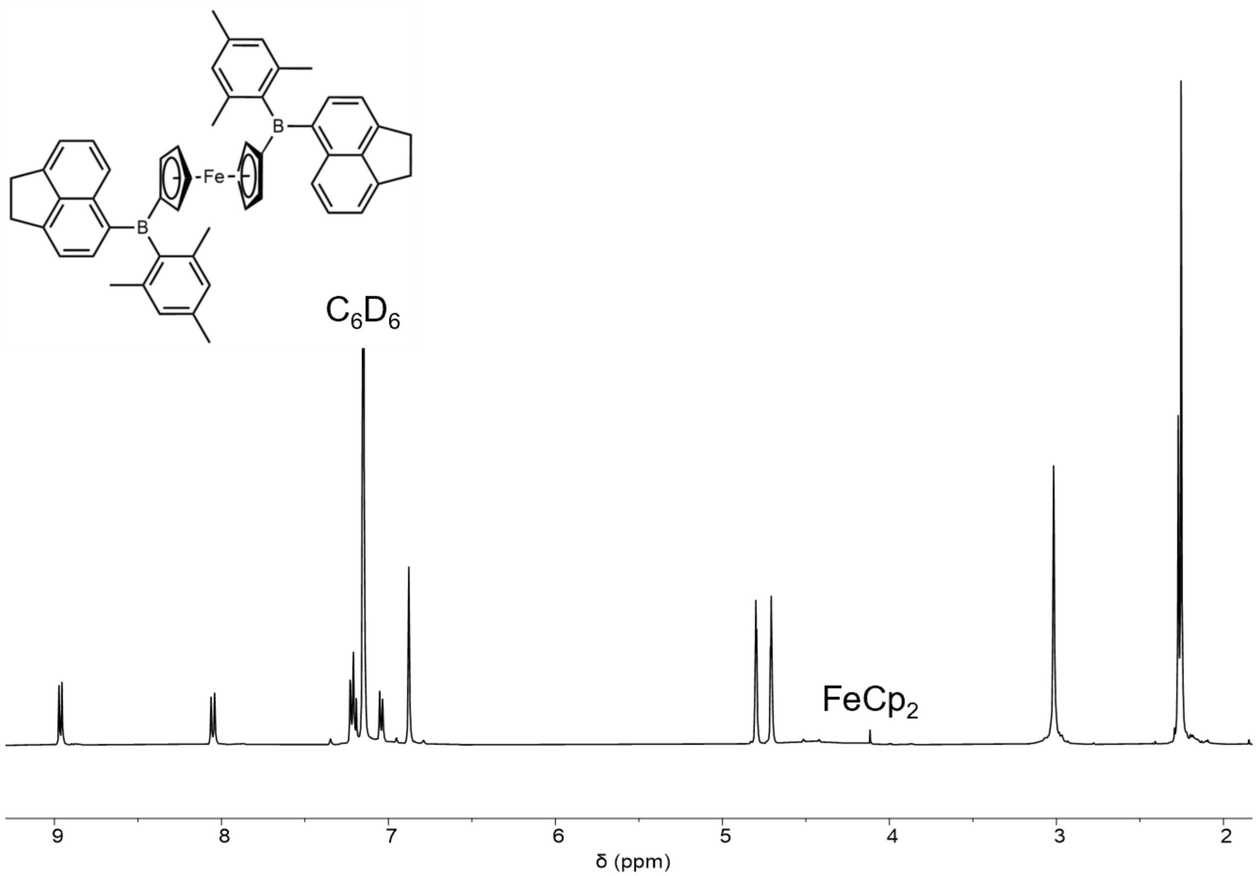


Figure S70. ^{1}H NMR spectrum of **6**.

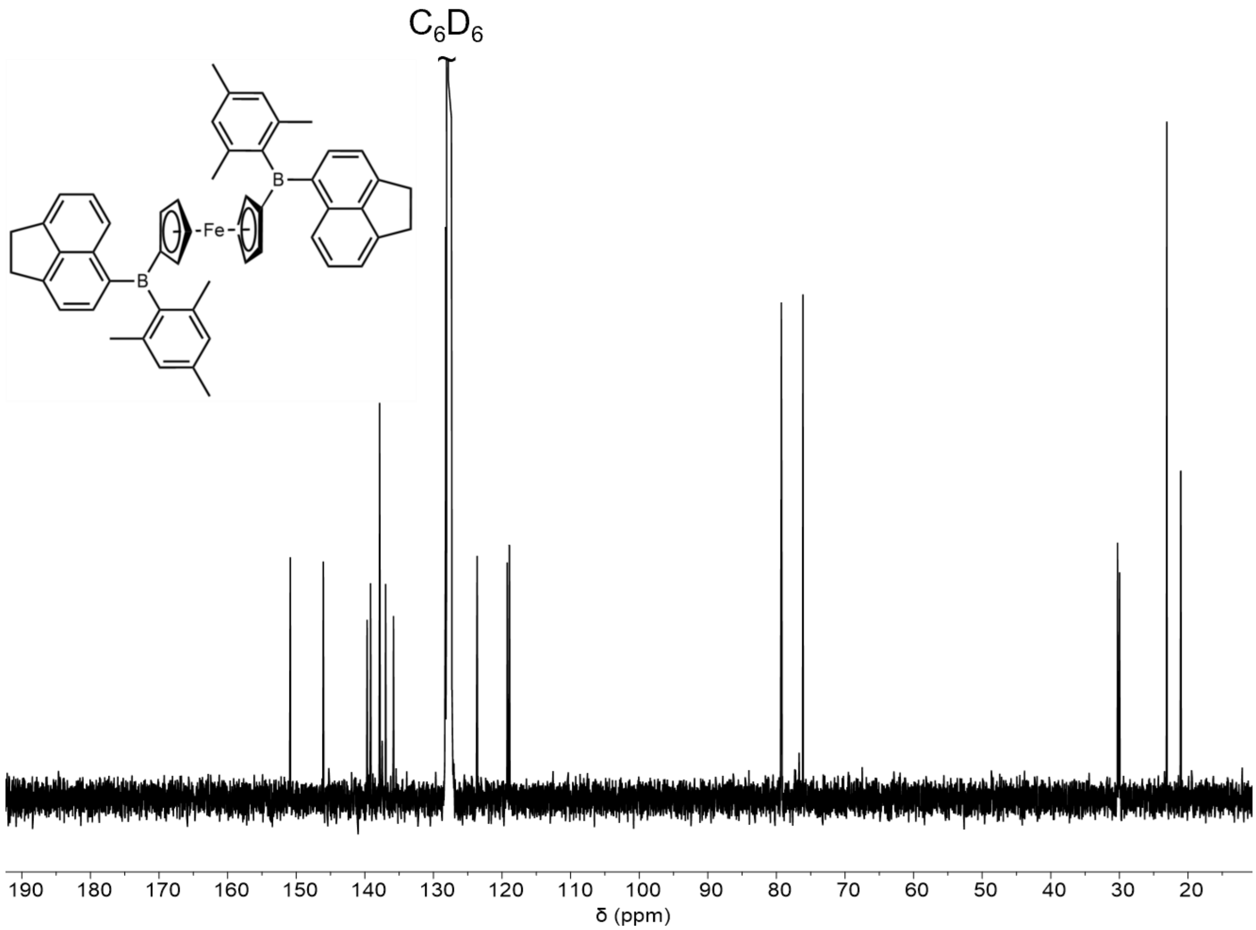


Figure S71. ^{13}C NMR spectrum of **6**.

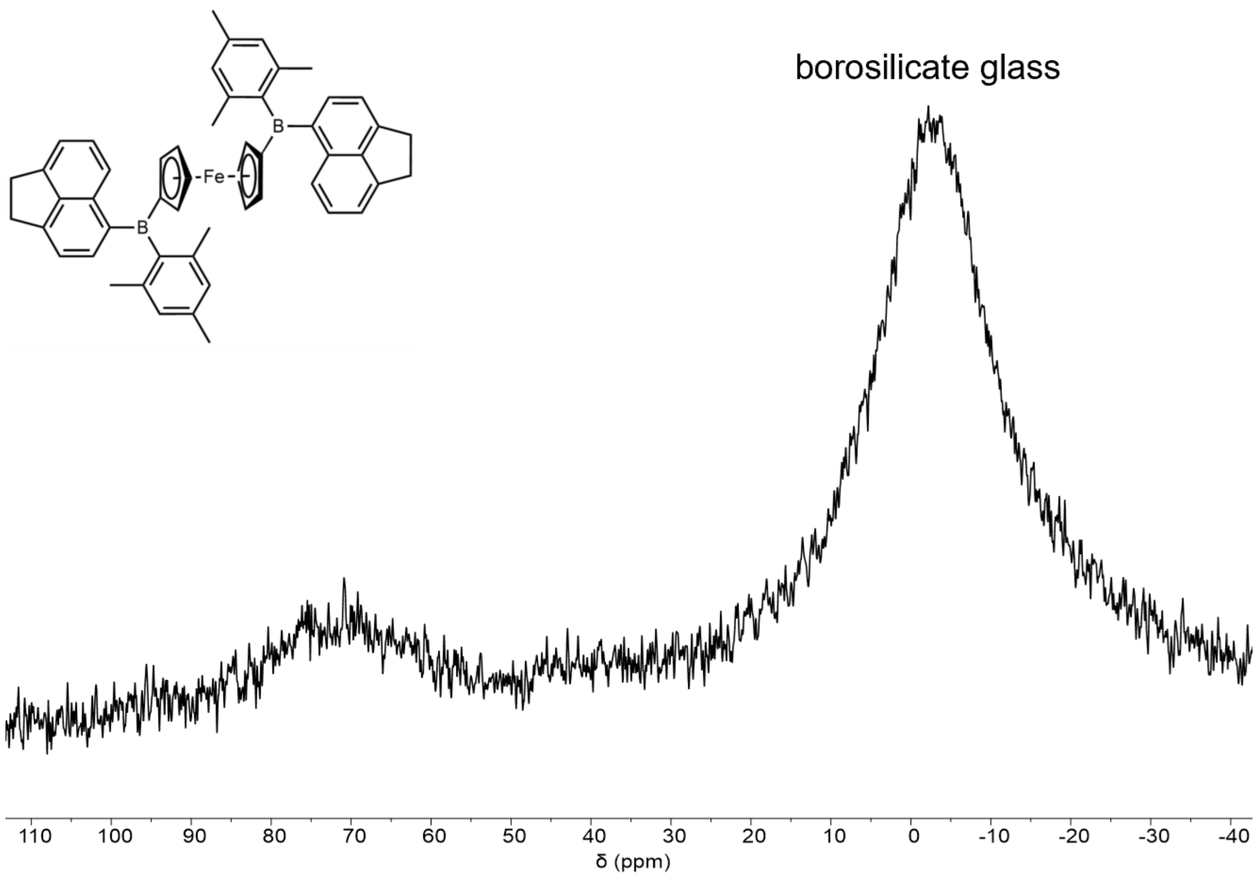


Figure S72. ^{11}B NMR spectrum of **6**.

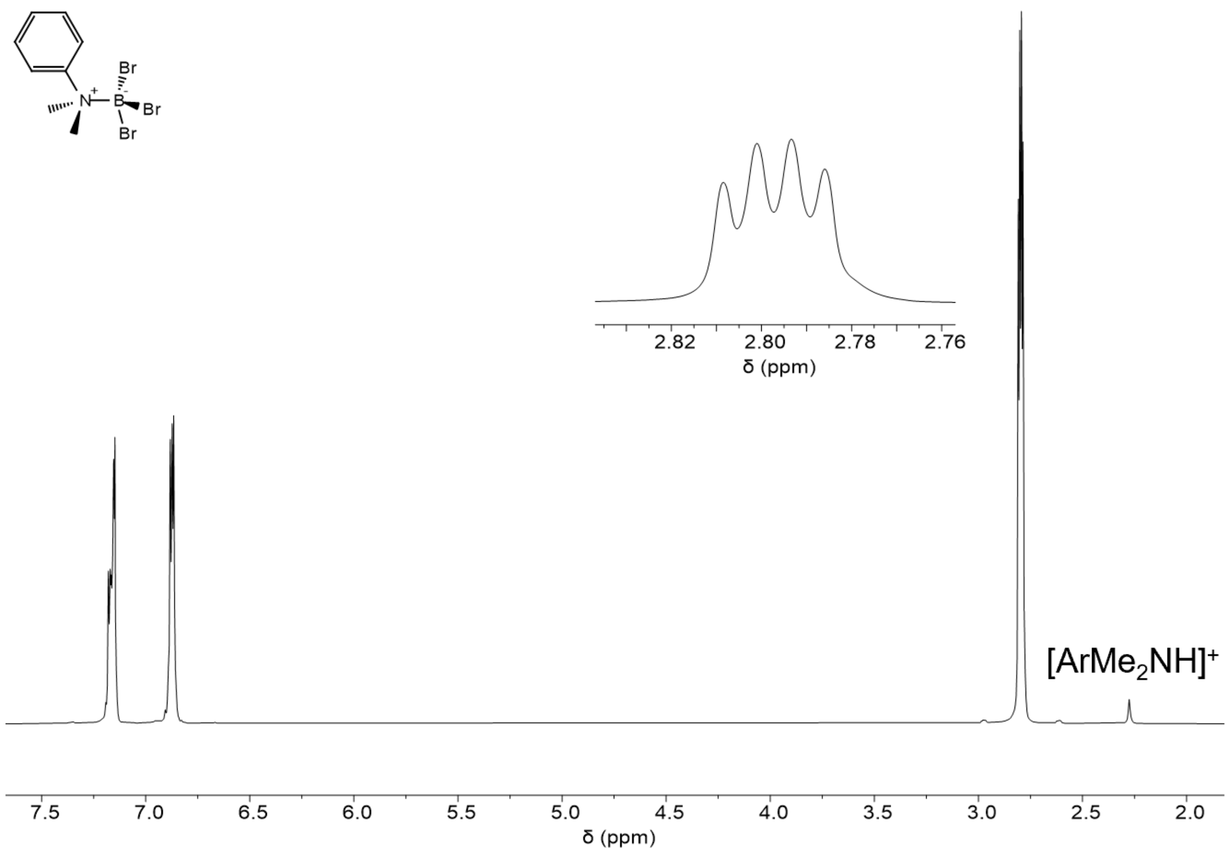


Figure S73. ^{1}H NMR spectrum of $BBr_3 \cdot NMe_2Ph$.

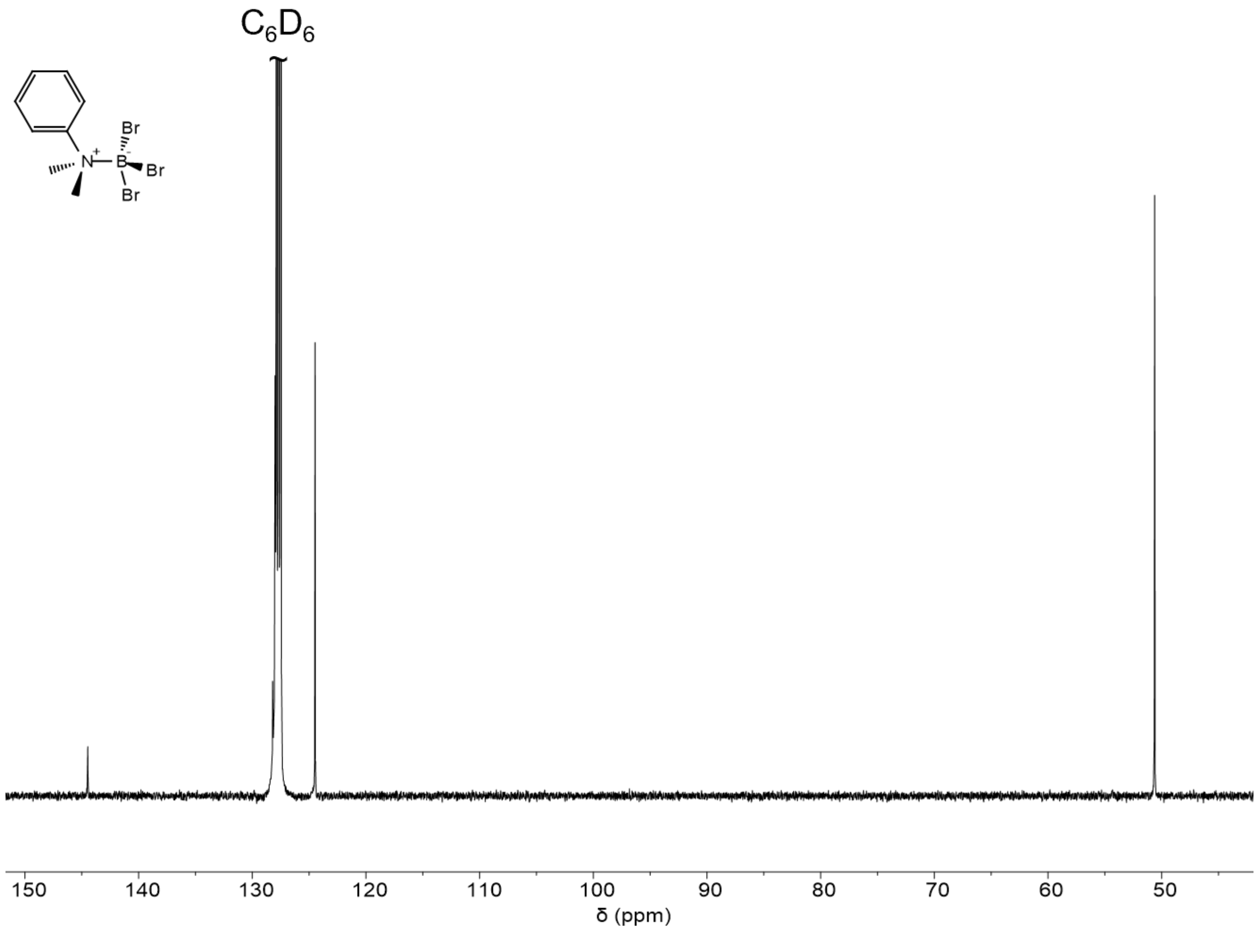


Figure S74. ^{13}C NMR spectrum of $BBr_3 \cdot NMe_2Ph$.

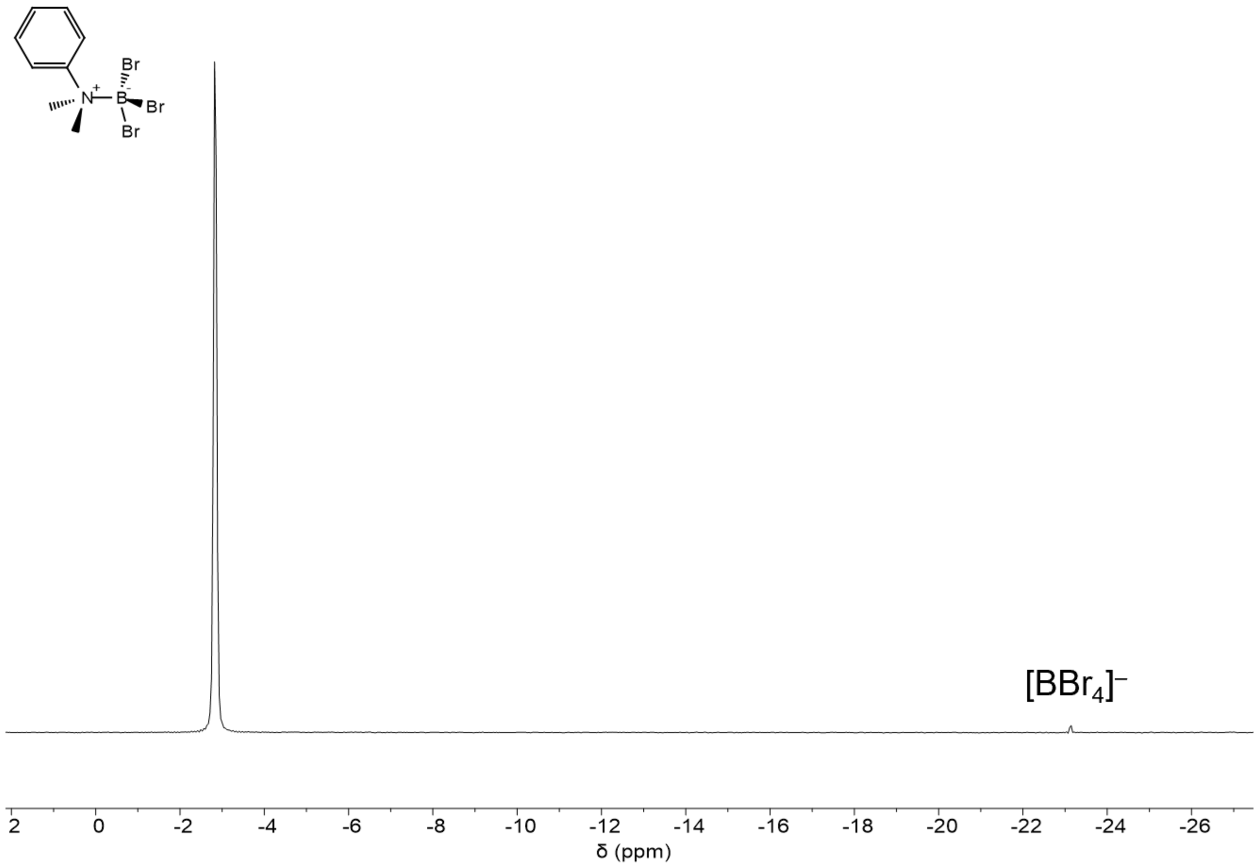


Figure S75. ^{11}B NMR spectrum of $BBr_3{\cdot}NMe_2Ph$.

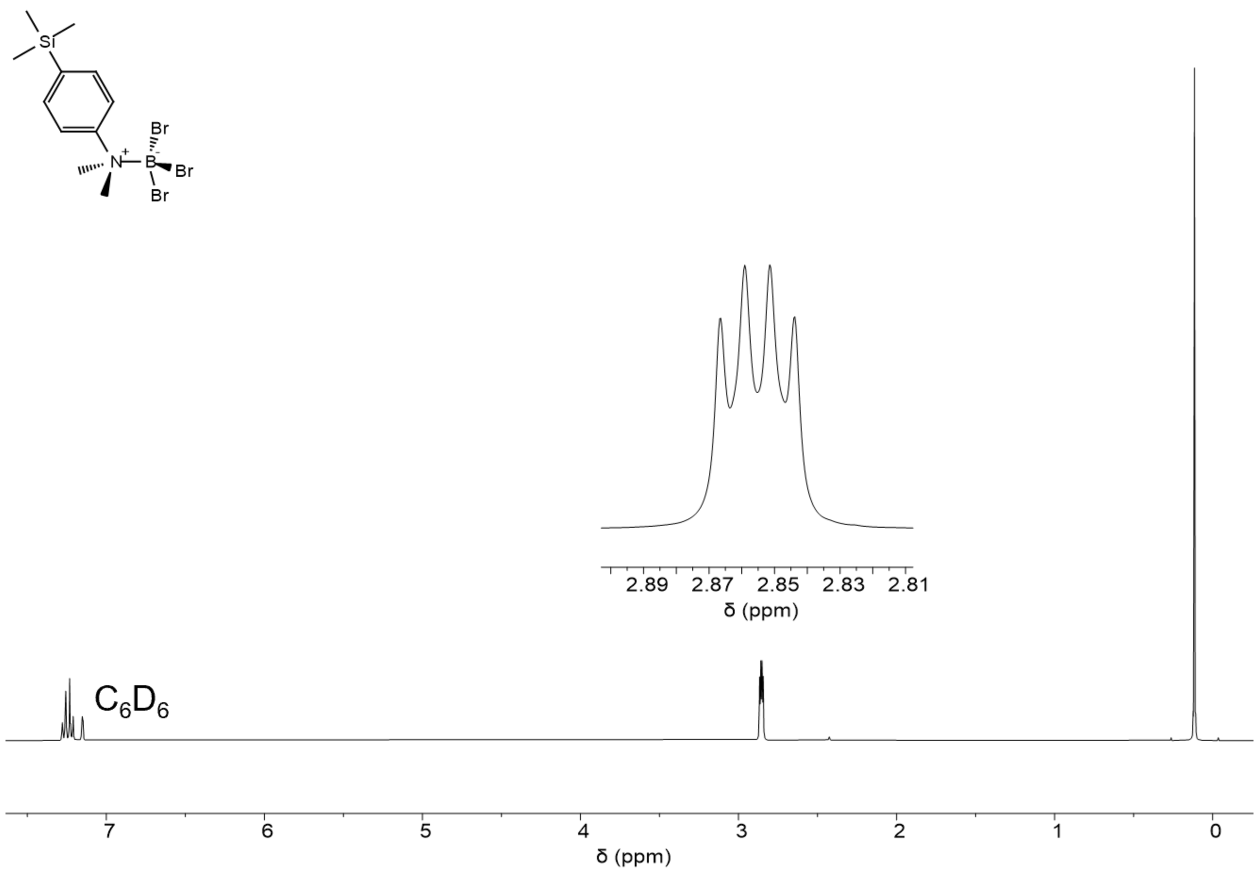


Figure S76. [1]H NMR spectrum of $BBr_3{\cdot}NMe_2(4\text{-}C_6H_4SiMe_3)$.

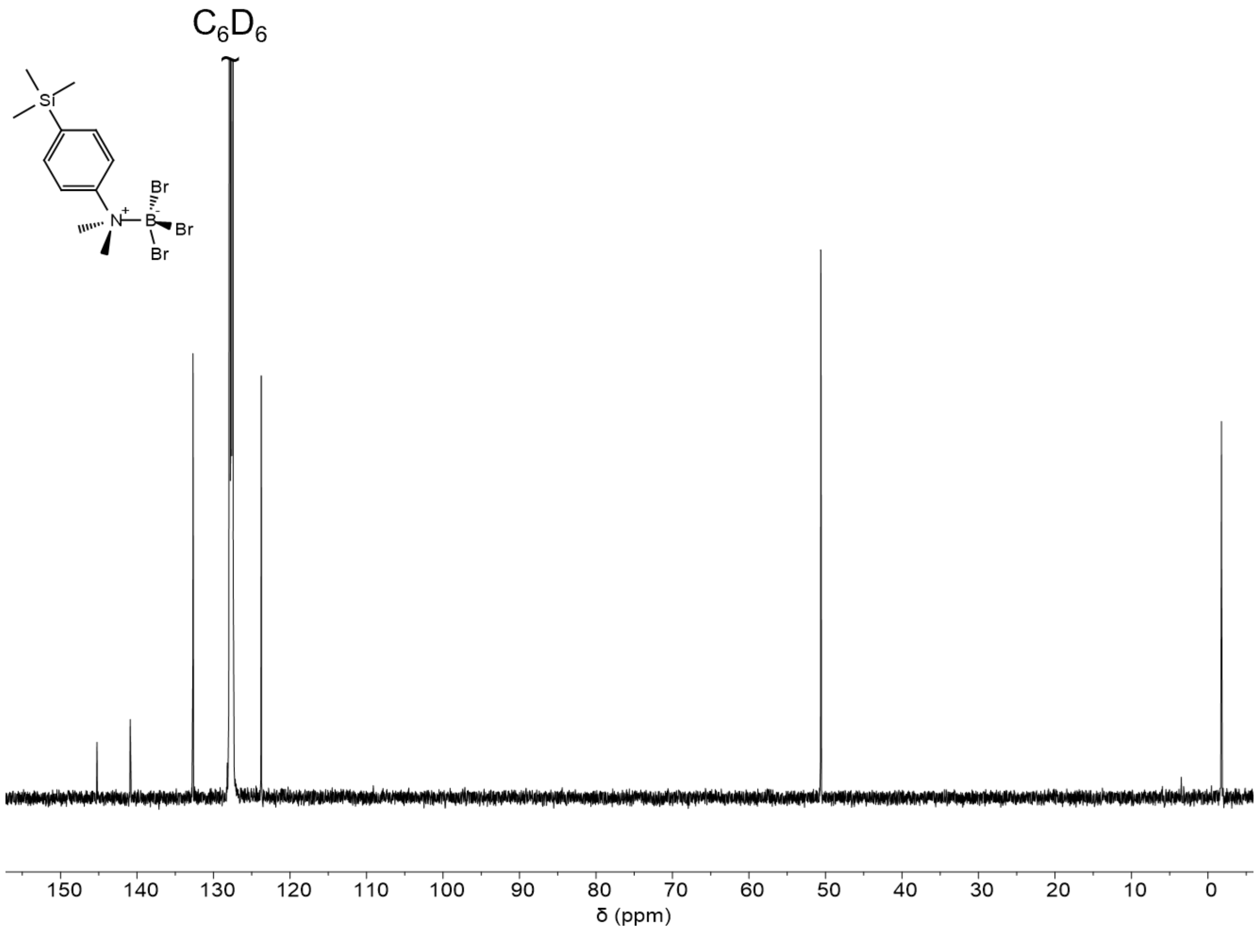


Figure S77. ^{13}C NMR spectrum of $BBr_3 \cdot NMe_2(4\text{-}C_6H_4SiMe_3)$.

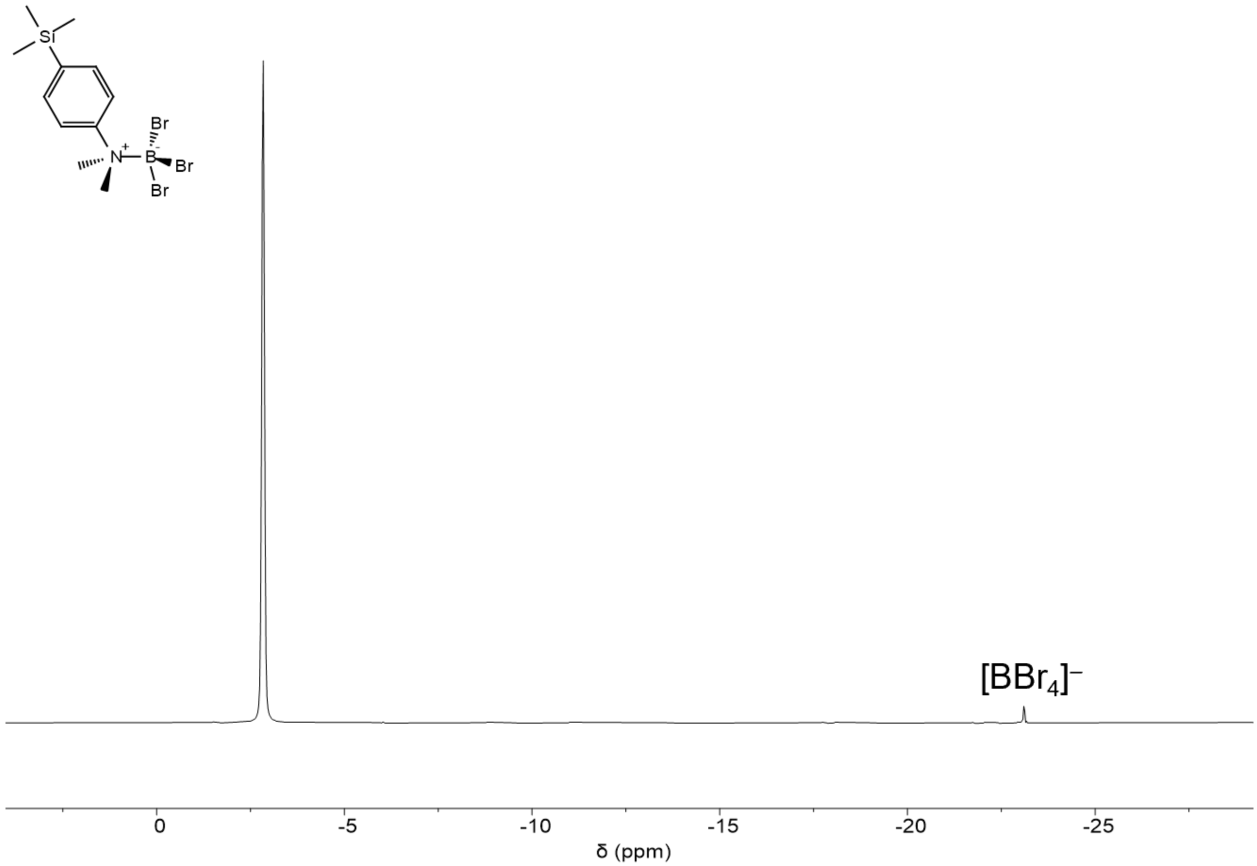


Figure S78. ^{11}B NMR spectrum of $BBr_3{\cdot}NMe_2(4\text{-}C_6H_4SiMe_3)$.

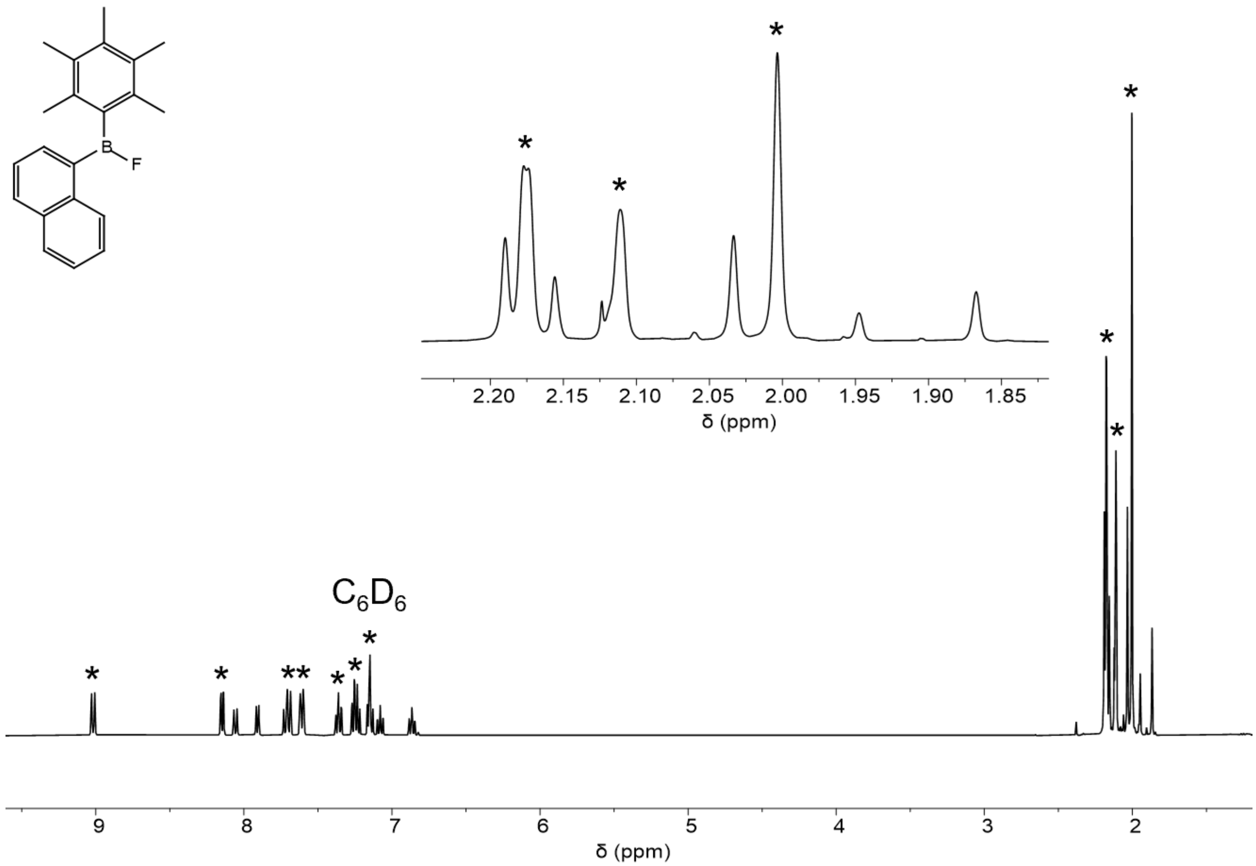


Figure S79. [1]H NMR spectrum of product mixture from reaction of **3b** with NaphLi in pentane at 25°C. Asterisks denote Ph*B(Naph)F.

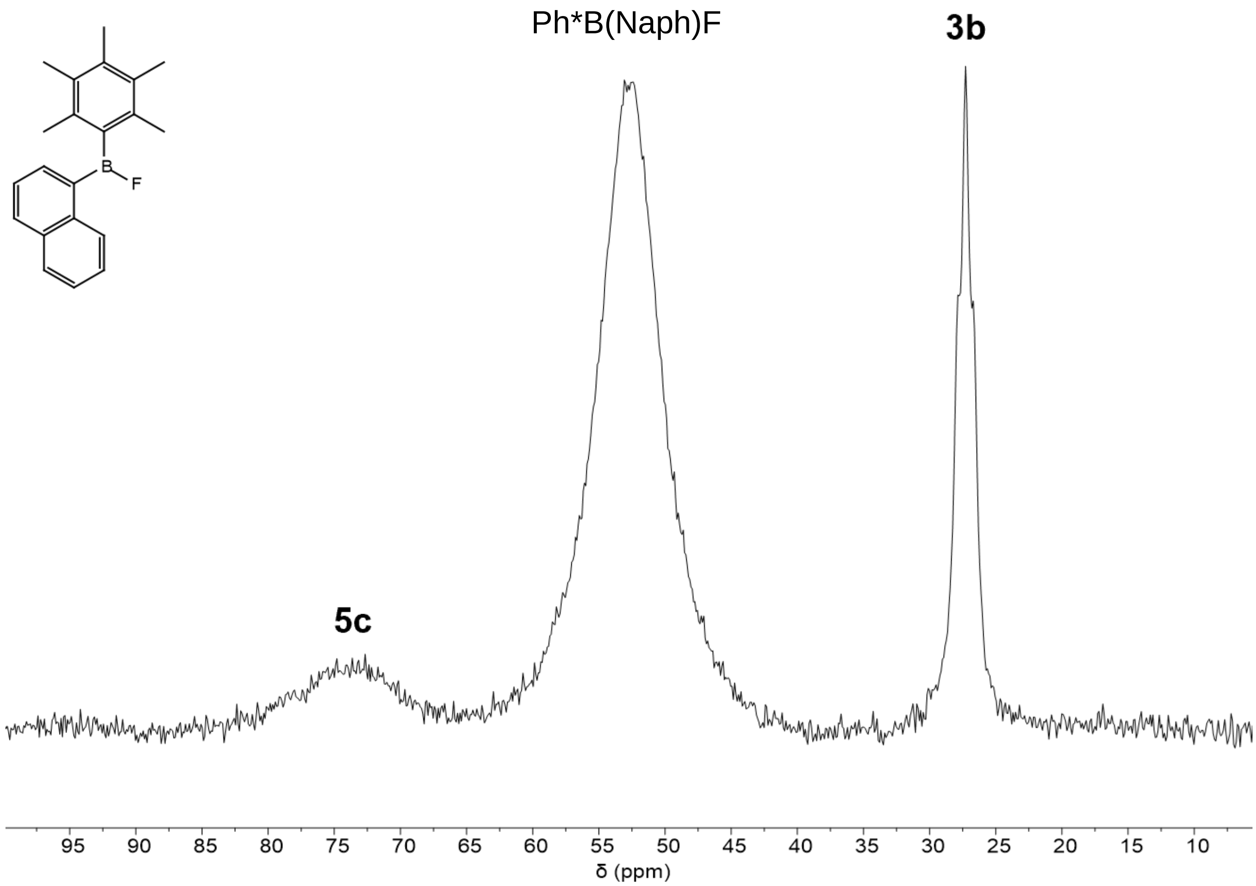


Figure S80. ^{11}B NMR spectrum of product mixture from reaction of **3b** with NaphLi in pentane at 25°C.

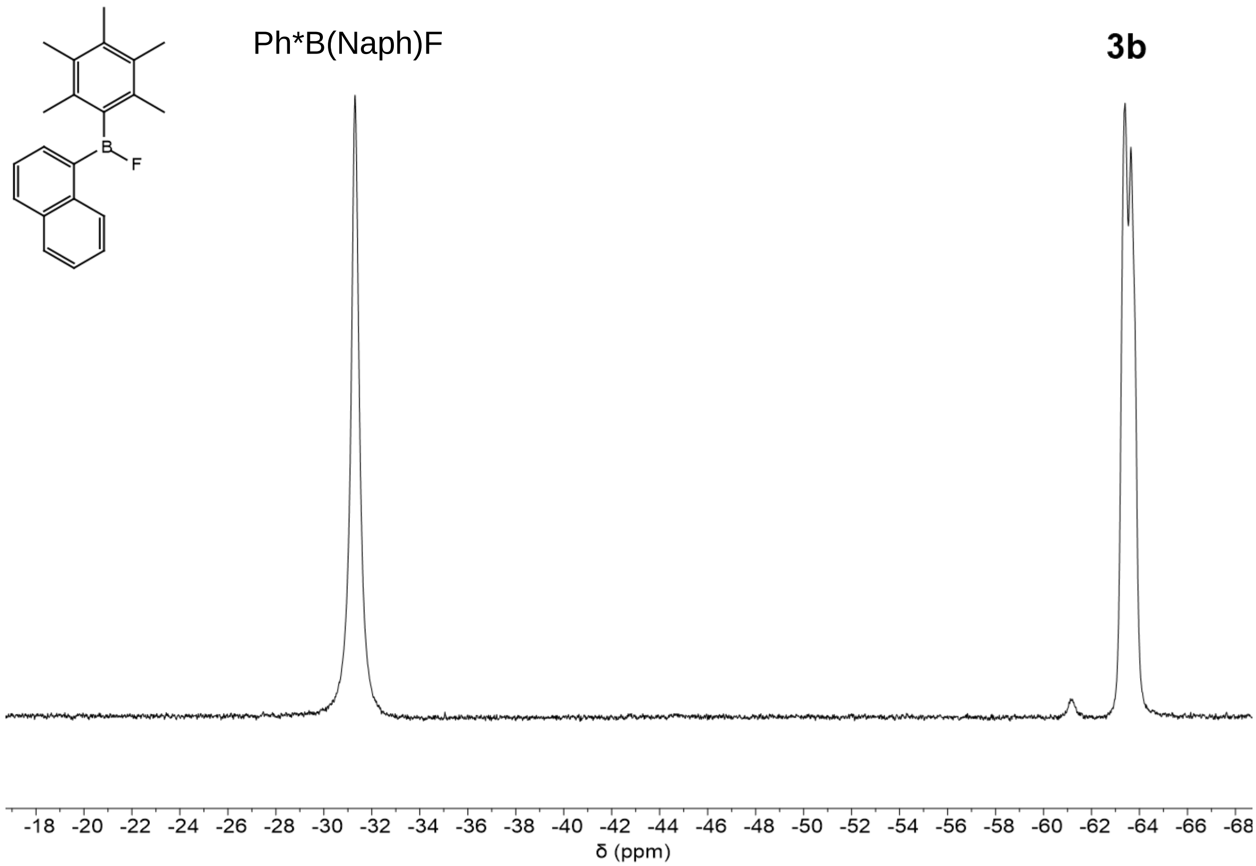


Figure S81. ^{19}F NMR spectrum of product mixture from reaction of **3b** with NaphLi in pentane at 25°C.

Optimised geometries.

MesBF2 (3a)

F	0.9828290000	-0.9079130000	2.9917620000
F	0.3712930000	0.5831780000	1.4661710000
C	0.5834680000	3.2832070000	1.9442590000
C	3.2869490000	4.6502360000	5.8803120000
C	2.5833180000	-0.2018350000	5.1160420000
C	2.6759710000	3.5610800000	5.0601230000
C	2.8584360000	2.2299850000	5.4013910000
C	1.9281550000	3.8479060000	3.9314250000
C	2.3210820000	1.1999380000	4.6502280000
C	1.3748720000	2.8511990000	3.1433760000
C	1.5655560000	1.4988940000	3.4950380000
B	0.9624860000	0.3719350000	2.6368160000
H	0.5226520000	4.3666870000	1.9107390000
H	-0.4290030000	2.8884650000	1.9616920000
H	1.0389220000	2.9426700000	1.0176900000
H	2.8532870000	5.6170490000	5.6425790000
H	4.3591250000	4.7128740000	5.6966780000
H	3.1542280000	4.4648820000	6.9436100000
H	3.2166540000	-0.1873390000	5.9977540000
H	3.0805590000	-0.7960830000	4.3536600000
H	1.6626690000	-0.7210430000	5.3699820000
H	3.4359290000	1.9863400000	6.2819720000
H	1.7686140000	4.8801750000	3.6546250000

Ph*BF2 (3b)

F	-2.2610400000	-1.3604960000	-0.9792760000
F	-3.3399450000	-0.7347370000	0.8672760000
C	0.4980400000	4.6077070000	-0.0605220000
C	-2.3853130000	4.6194940000	0.1208430000
C	-3.8450510000	2.1270010000	-0.0397260000
C	1.9561300000	2.1277820000	0.0090550000
C	0.5201210000	-0.4009130000	0.0053500000
C	-2.3431220000	2.1109950000	0.0066190000
C	-1.6453540000	3.3164090000	0.0386240000
C	-0.2501470000	3.3087520000	-0.0077000000
C	0.4555590000	2.1037640000	-0.0063650000
C	-0.2393660000	0.8949250000	-0.0187670000
C	-1.6387740000	0.9020360000	-0.0252340000
B	-2.4270760000	-0.4301070000	-0.0470870000
H	-0.0728010000	5.3750720000	-0.5732190000
H	1.4435490000	4.5026300000	-0.5817730000
H	0.7207830000	4.9843250000	0.9393730000
H	-1.8534940000	5.3361310000	0.7399750000
H	-3.3722910000	4.4928350000	0.5515290000
H	-2.5157180000	5.0770410000	-0.8612820000
H	-4.2054620000	2.8553640000	-0.7623110000
H	-4.2764460000	2.3909060000	0.9255900000
H	-4.2616330000	1.1665520000	-0.3253570000
H	2.3326950000	2.8563520000	0.7230830000
H	2.3609640000	2.4002220000	-0.9664750000
H	2.3775210000	1.1658970000	0.2737960000
H	1.1945820000	-0.4858710000	-0.8448530000
H	-0.1333240000	-1.2655660000	-0.0161910000
H	1.1284420000	-0.4815090000	0.9048310000

NaphBF2 (3c)

F	-5.9171300000	2.4389880000	0.0796970000
F	-4.1671590000	3.8182210000	-0.0319700000
C	0.5459870000	1.2344930000	-0.1069880000
C	-0.1329790000	2.4619980000	-0.1245860000
C	-1.4973600000	2.5091920000	-0.0785360000
C	-0.1633620000	0.0725190000	-0.0429680000
C	-4.3502440000	0.1052820000	0.1032880000
C	-3.6945980000	1.3168820000	0.0387850000
C	-2.2664660000	1.3277640000	-0.0117370000
C	-1.5719500000	0.0878590000	0.0060180000
C	-2.2999610000	-1.1167750000	0.0726380000
C	-3.6623110000	-1.1132630000	0.1206340000
B	-4.5964550000	2.5656240000	0.0272800000
H	1.6240420000	1.2148300000	-0.1439920000
H	0.4300130000	3.3812700000	-0.1749440000
H	-1.9916350000	3.4642890000	-0.0934200000
H	-5.4286780000	0.0944970000	0.1416470000
H	-1.7522160000	-2.0478490000	0.0850970000
H	-4.2119270000	-2.0398950000	0.1713860000
H	0.3418280000	-0.8818610000	-0.0285670000

AceBF2 (3d)

F	-3.2863330000	4.8032240000	-0.0633220000
F	-1.2020820000	5.5924620000	0.1190310000
C	0.3176690000	-0.8321350000	0.0564800000
C	-1.0102240000	-1.6188600000	-0.0644900000
C	0.6479040000	1.7647670000	0.1519360000
C	-0.0346990000	2.9908760000	0.1352100000
C	-1.4122270000	3.1080320000	0.0368330000
C	-0.0859160000	0.6142220000	0.0662180000
C	-4.1792520000	0.5570830000	-0.2341620000
C	-3.5929810000	1.7961420000	-0.1573640000
C	-2.1907880000	1.9130530000	-0.0524590000
C	-1.4813450000	0.7024560000	-0.0338200000
C	-2.0801160000	-0.5630860000	-0.1126740000
C	-3.4395420000	-0.6411840000	-0.2138980000
B	-1.9915210000	4.5268050000	0.0294150000
H	0.8578590000	-1.0904980000	0.9648240000
H	0.9881800000	-1.0429540000	-0.7739200000
H	-1.1558000000	-2.2886750000	0.7800740000
H	-1.0271950000	-2.2366620000	-0.9596480000
H	1.7241920000	1.7501700000	0.2308230000
H	0.5490070000	3.8970520000	0.2027280000
H	-5.2544860000	0.4979480000	-0.3136540000
H	-4.2126490000	2.6763610000	-0.1775960000
H	-3.9521910000	-1.5891020000	-0.2777450000

AnBF2 (3e)

F	-0.2729730000	0.4080860000	2.2234260000
F	1.6652720000	-0.6841090000	2.3088760000
C	5.4875950000	2.9942300000	2.7787830000
C	-0.6013760000	3.2791570000	6.7023580000
C	4.9428390000	1.9689520000	1.9739220000
C	4.7530420000	3.5139480000	3.7923540000
C	2.6876920000	3.5835810000	5.0878490000
C	0.6513750000	3.7148690000	6.4237340000
C	-1.1686940000	2.2406710000	5.9307630000
C	3.6940450000	1.4869830000	2.2044240000
C	3.4435220000	3.0389360000	4.0621800000
C	1.4017890000	3.1464980000	5.3620470000
C	-0.4810200000	1.6739240000	4.9057420000
C	2.8887390000	1.9899680000	3.2630220000
C	0.8310510000	2.1039380000	4.5654660000
C	1.5826660000	1.5292820000	3.5216520000
B	0.9770400000	0.3916960000	2.6645610000
H	6.4819190000	3.3610650000	2.5780200000
H	-1.1661420000	3.7152030000	7.5113530000
H	5.5277290000	1.5655810000	1.1618280000
H	5.1465240000	4.3047650000	4.4134800000
H	3.1134950000	4.3733750000	5.6908130000
H	1.1075210000	4.5014970000	7.0061970000
H	-2.1630740000	1.8915570000	6.1623770000
H	3.3084250000	0.7102150000	1.5660500000
H	-0.9434340000	0.8809760000	4.3431030000

1,4-C6H4(BF2)2 (3f)

F	1.8133910000	4.7360100000	-0.3144960000
F	-0.0589200000	5.8142080000	0.3010210000
F	-1.8186770000	-1.5673590000	-0.3028490000
F	-3.6909470000	-0.4891610000	0.3127860000
C	-2.2821330000	2.1025040000	0.3382500000
C	-1.5928420000	3.2978790000	0.3351410000
C	-0.2406880000	3.3340470000	-0.0040450000
C	0.4045870000	2.1443290000	-0.3399400000
C	-0.2847040000	0.9489510000	-0.3368280000
C	-1.6368570000	0.9127850000	0.0023550000
B	0.5292210000	4.6705620000	-0.0063290000
B	-2.4067630000	-0.4237330000	0.0046630000
H	-3.3285390000	2.0848350000	0.6020430000
H	-2.1010100000	4.2134820000	0.5966570000
H	1.4509900000	2.1619970000	-0.6037460000
H	0.2234690000	0.0333510000	-0.5983420000

p-Xyl-(BF2)2 (3g)

F	1.8936360000	4.5713840000	-0.2888440000
F	0.1050220000	5.8418010000	0.1490830000
F	-1.9863650000	-1.6023460000	-0.1515990000
F	-3.7750200000	-0.3319050000	0.2860840000
C	0.5557570000	-0.3351250000	-0.4860500000
C	-2.4369850000	4.5745270000	0.4841390000
C	-2.2827740000	2.1026460000	0.2371620000
C	-1.6433130000	3.3305800000	0.2321790000
C	-0.2625790000	3.3420510000	-0.0132450000
C	0.4015430000	2.1367550000	-0.2390780000
C	-0.2379170000	0.9088210000	-0.2340930000
C	-1.6186510000	0.8973490000	0.0113410000
B	0.5913790000	4.6280360000	-0.0497400000
B	-2.4726000000	-0.3886410000	0.0478900000
H	1.6008280000	-0.0893830000	-0.6479440000
H	0.1943320000	-0.8703680000	-1.3609720000
H	0.4960310000	-1.0248900000	0.3525550000
H	-3.4820920000	4.3288030000	0.6458320000
H	-2.3770880000	5.2643910000	-0.3543700000
H	-2.0756930000	5.1096500000	1.3591910000
H	-3.3463220000	2.0777610000	0.4250280000
H	1.4650910000	2.1616410000	-0.4269480000

BtpBF2 (3h)

S	-0.3470060000	-2.9688990000	-0.0006380000
F	0.1954610000	-6.0887800000	-0.0012130000
F	2.4417390000	-5.9321450000	-0.0008780000
C	1.1761060000	-3.7947150000	-0.0006270000
C	2.2221350000	-2.9224480000	-0.0003790000
C	2.6169970000	-0.4054630000	0.0000730000
C	2.0112780000	0.8249270000	0.0002130000
C	0.6155860000	0.9355560000	0.0001010000
C	-0.1874040000	-0.1799990000	-0.0001530000
C	0.4235610000	-1.4302140000	-0.0003000000
C	1.8253260000	-1.5598770000	-0.0001880000
B	1.2701840000	-5.3170080000	-0.0009040000
H	3.2505240000	-3.2466570000	-0.0003370000
H	3.6926070000	-0.4922500000	0.0001580000
H	2.6123090000	1.7205070000	0.0004090000
H	0.1618630000	1.9143280000	0.0002130000
H	-1.2618490000	-0.0879300000	-0.0002400000

AceMesBF (4a)

F	5.8132870000	6.6893150000	2.2118470000
C	5.0774430000	5.3752760000	4.1910400000
C	5.4225020000	4.3149240000	5.0154650000
C	4.8474640000	4.0691350000	6.2726060000
C	3.8740550000	4.9200160000	6.7156490000
C	3.4928370000	5.9975220000	5.9031020000
C	2.4789600000	6.7636040000	6.4958300000
C	1.9962840000	7.8487820000	5.8218170000
C	2.5394960000	8.1463610000	4.5575780000
C	3.5327220000	7.3958930000	3.9782220000
C	4.0585970000	6.2707080000	4.6481050000
C	2.1273600000	6.1688560000	7.8316550000
C	3.0651760000	4.9465520000	7.9805320000
C	6.7835450000	4.4119060000	2.2602970000
C	6.2663350000	3.1789150000	1.8517770000
C	7.1153530000	2.2252190000	1.3053000000
C	8.4737360000	2.4522190000	1.1684730000
C	8.9779210000	3.6781140000	1.5820020000
C	8.1565880000	4.6587730000	2.1093830000
C	4.8059820000	2.8564330000	1.9852480000
C	9.3787550000	1.4140920000	0.5835840000
C	8.7474990000	5.9765430000	2.5174020000
B	5.8667530000	5.5190440000	2.8739240000
H	6.1900630000	3.6376980000	4.6690940000
H	5.1771550000	3.2251810000	6.8593710000
H	1.2162710000	8.4725920000	6.2316660000
H	2.1574770000	9.0017380000	4.0205520000
H	3.9072240000	7.6731080000	3.0083030000
H	2.2762440000	6.8872400000	8.6348460000
H	1.0806240000	5.8744540000	7.8671110000
H	2.5063070000	4.0215880000	8.1060000000
H	3.7108750000	5.0387720000	8.8514880000
H	6.7024560000	1.2811730000	0.9767820000
H	10.0373640000	3.8747320000	1.4859100000
H	4.1763090000	3.7284150000	1.8273440000
H	4.5124900000	2.0971310000	1.2650470000
H	4.5741300000	2.4734260000	2.9782320000
H	8.8357210000	0.5029990000	0.3493050000
H	9.8447180000	1.7718910000	-0.3332580000
H	10.1826160000	1.1600500000	1.2722950000
H	8.5302840000	6.7480620000	1.7806150000
H	8.3464430000	6.3230680000	3.4685000000
H	9.8270720000	5.9058120000	2.6160010000

Ph*MesBF (4b)

F	0.0971040000	8.3344300000	5.1349970000
C	4.0182360000	7.6816890000	6.8674380000
C	2.7556140000	8.0768790000	6.4621840000
C	1.0947400000	11.5842110000	4.3136220000
C	3.6681160000	8.6555750000	4.2985330000
C	0.2152660000	10.1442190000	2.5760440000
C	5.1110680000	7.7374540000	6.0150470000
C	0.7943530000	12.7037880000	3.5385460000
C	0.8088260000	10.3050980000	3.8313180000
C	4.9121760000	8.2228530000	4.7346130000
C	2.5606780000	8.5792630000	5.1597720000
C	-0.1074410000	11.2628950000	1.8093240000
C	1.6949030000	11.7625420000	5.6803770000
C	1.6367000000	7.9846250000	7.4588320000
C	6.4595870000	7.2800060000	6.4710740000
C	0.1658010000	12.5409600000	2.3032730000
C	-0.0389070000	8.7621370000	2.0416440000
C	3.5614190000	9.1742830000	2.8944500000
C	1.1374540000	14.0807190000	4.0274480000
C	-0.2196220000	13.7499710000	1.5025000000
C	-0.7464820000	11.1141180000	0.4592140000
B	1.1497960000	9.0560890000	4.7065620000
H	4.1541770000	7.3184320000	7.8770900000
H	5.7503990000	8.2711040000	4.0535400000
H	2.7349450000	12.0853680000	5.6311060000
H	1.6740420000	10.8420760000	6.2559250000
H	1.1528260000	12.5107690000	6.2549640000
H	0.9724000000	7.1529550000	7.2357030000
H	1.0234660000	8.8830050000	7.4712690000
H	2.0343110000	7.8356990000	8.4586820000
H	6.4585790000	6.2107960000	6.6782930000
H	6.7550170000	7.7830410000	7.3898490000
H	7.2188690000	7.4741440000	5.7191660000
H	0.3043150000	7.9908620000	2.7247610000
H	0.4732600000	8.6009830000	1.0940040000
H	-1.0986710000	8.5836020000	1.8657490000
H	3.3833120000	10.2471350000	2.8771970000
H	2.7446100000	8.7095490000	2.3490370000
H	4.4809160000	8.9779950000	2.3502030000
H	0.2777390000	14.5771420000	4.4809220000
H	1.4788880000	14.7149390000	3.2138850000
H	1.9257920000	14.0576670000	4.7715910000
H	-0.4926180000	14.5817330000	2.1446370000
H	-1.0654580000	13.5491720000	0.8539770000
H	0.6001460000	14.0902910000	0.8671060000
H	-0.7270360000	10.0898330000	0.1080900000
H	-0.2444530000	11.7260160000	-0.2874300000
H	-1.7904590000	11.4289280000	0.4764260000

AceB(C6F5)F (4c)

F	5.9123950000	6.6819610000	2.2872780000
C	8.1375270000	4.6880410000	1.9890700000
C	8.9799470000	3.7584500000	1.4181320000
C	8.4976600000	2.4943720000	1.1434310000
C	7.1892970000	2.1755670000	1.4454510000
C	6.3800820000	3.1284770000	2.0285450000
C	6.8227010000	4.4067880000	2.3193270000
C	2.9346750000	4.9047420000	7.9359370000
C	2.0586680000	6.1729160000	7.7999280000
C	4.0779640000	6.2754780000	4.6724040000
C	3.6179400000	7.4367210000	4.0185090000
C	2.6389370000	8.2117490000	4.5909420000
C	2.0490710000	7.9053410000	5.8310110000
C	2.4686570000	6.7845370000	6.4892830000
C	3.4667760000	5.9933750000	5.9033150000
C	3.7800630000	4.8804860000	6.6963840000
C	4.7317550000	4.0004770000	6.2604650000
C	5.3534730000	4.2540490000	5.0302350000
C	5.0746310000	5.3488560000	4.2230320000
B	5.8990290000	5.5213830000	2.9474040000
H	3.5560330000	4.9362000000	8.8285740000
H	2.3312250000	4.0025280000	8.0106210000
H	0.9987240000	5.9285680000	7.8059950000
H	2.2243110000	6.8629060000	8.6244330000
H	4.0279850000	7.7250520000	3.0663610000
H	2.3069510000	9.0949780000	4.0661160000
H	1.2838490000	8.5501790000	6.2358110000
H	5.0087080000	3.1292900000	6.8338830000
H	6.1078060000	3.5549040000	4.7004400000
F	5.1186430000	2.7799740000	2.2843990000
F	6.7251470000	0.9637170000	1.1682510000
F	9.2882020000	1.5902020000	0.5894340000
F	10.2397900000	4.0601660000	1.1327790000
F	8.6408250000	5.8941730000	2.2491360000

MesB(C6F5)F (4d)

F	0.1840100000	8.0860710000	4.7659560000
C	3.7497320000	9.2753450000	2.9276930000
C	0.1011130000	12.5731110000	2.4230150000
C	6.4556470000	7.4252900000	6.6627850000
C	1.5189860000	7.7468380000	7.2477480000
C	-0.5328130000	11.3843170000	2.1225050000
C	2.6045750000	8.5264520000	5.0802150000
C	4.9968470000	8.3315670000	4.8399130000
C	0.8325970000	10.2168530000	3.7561890000
C	1.0951350000	12.6011700000	3.3803840000
C	5.1169930000	7.8071100000	6.1183810000
C	-0.1667930000	10.2370560000	2.7935210000
C	3.7723500000	8.7047530000	4.3161820000
C	1.4453650000	11.4322210000	4.0210520000
C	2.7145710000	7.9745900000	6.3692320000
C	3.9643450000	7.6428780000	6.8675980000
B	1.2109050000	8.9068920000	4.5372040000
H	4.6327120000	8.9612740000	2.3782040000
H	2.8788130000	8.9626600000	2.3594190000
H	3.7581630000	10.3642450000	2.9486340000
H	6.9126090000	6.6428630000	6.0590740000
H	7.1373690000	8.2738480000	6.6552740000
H	6.3790510000	7.0616620000	7.6830930000
H	1.8322690000	7.5776090000	8.2737280000
H	0.8354760000	8.5923730000	7.2424720000
H	0.9521550000	6.8763600000	6.9246600000
H	5.8839650000	8.4533980000	4.2336590000
H	4.0388130000	7.2402850000	7.8679770000
F	2.4074780000	11.5139000000	4.9373120000
F	1.6980910000	13.7462920000	3.6713720000
F	-0.2433200000	13.6832440000	1.7949310000
F	-1.4810600000	11.3602420000	1.1955550000
F	-0.7959480000	9.1152150000	2.4544730000

AceMesBNaph (5a)

C	4.6743620000	6.9781910000	-2.3001600000
C	5.2133660000	9.2907090000	0.5392620000
C	4.8501860000	8.1308620000	-1.5930340000
C	4.6801290000	5.7430350000	-1.6338210000
C	5.3699200000	9.2539110000	1.8929800000
C	5.0470080000	8.1004800000	-0.1974380000
C	4.8700980000	5.6843790000	-0.2828500000
C	5.3750340000	8.0225120000	2.5624010000
C	5.0723930000	6.8526790000	0.4813670000
C	5.2608710000	6.8202340000	1.8966300000
C	5.0150830000	5.4433860000	4.2089890000
C	5.8577260000	4.8350660000	5.1275500000
C	5.6126470000	4.7736340000	6.5109090000
C	4.4535800000	5.3148490000	6.9903870000
C	3.5585660000	5.9017300000	6.0846600000
C	2.4010050000	6.3703560000	6.7228610000
C	1.4183030000	6.9415130000	5.9662800000
C	1.6087350000	7.0254460000	4.5726480000
C	2.7441660000	6.5695400000	3.9515760000
C	3.7891110000	5.9908240000	4.7037650000
C	2.5108000000	6.1043060000	8.1994820000
C	3.8803760000	5.4034170000	8.3763720000
C	6.3988550000	4.3598530000	2.1856910000
C	5.8685470000	3.0628060000	2.0949070000
C	6.6445780000	2.0288950000	1.6004310000
C	7.9623760000	2.2286970000	1.2129420000
C	8.4824060000	3.5069350000	1.3176350000
C	7.7217740000	4.5729300000	1.7802960000
C	4.4467980000	2.7865170000	2.4903430000
C	8.7897860000	1.0923870000	0.6997380000
C	8.3478910000	5.9350980000	1.8422310000
B	5.5122330000	5.5309370000	2.7390040000
H	4.5236510000	7.0120890000	-3.3681080000
H	5.2036410000	10.2324650000	0.0100310000
H	4.8360500000	9.0891410000	-2.0913280000
H	4.5299880000	4.8328940000	-2.1938730000
H	5.4875670000	10.1683360000	2.4538450000
H	4.8626950000	4.7291130000	0.2145650000
H	5.4976330000	8.0166760000	3.6353740000
H	6.7700050000	4.3899730000	4.7569230000
H	6.3313180000	4.2986280000	7.1618960000
H	0.5062310000	7.3156830000	6.4065900000
H	0.8270730000	7.4628880000	3.9696810000
H	2.8321330000	6.6509570000	2.8811000000
H	2.4590090000	7.0287080000	8.7708250000
H	1.6936570000	5.4765510000	8.5484340000
H	3.7718250000	4.4153140000	8.8185910000
H	4.5378620000	5.9671760000	9.0351420000
H	6.2111970000	1.0411510000	1.5148800000
H	9.5079670000	3.6845650000	1.0236160000
H	3.7678390000	3.5588590000	2.1307000000
H	4.1099640000	1.8345450000	2.0886510000
H	4.3359080000	2.7516680000	3.5725650000
H	8.9218610000	0.3259700000	1.4621750000
H	8.3151600000	0.6138210000	-0.1551520000
H	9.7751780000	1.4298830000	0.3913070000
H	7.9646890000	6.5804360000	1.0532950000
H	8.1432190000	6.4347790000	2.7867990000
H	9.4259940000	5.8698000000	1.7231100000

Ph*MesBNaph (5b)

C	3.9647250000	2.3281680000	4.4177010000
C	3.5033820000	1.0807750000	3.9771120000
C	2.5891140000	0.3571430000	4.7392740000
C	2.1104970000	0.8905830000	5.9373490000
C	2.6027660000	2.1071750000	6.4104870000
C	3.5243340000	2.8281600000	5.6481070000
C	3.9375530000	0.5369260000	2.6437580000
C	2.1136570000	-0.9898580000	4.2772000000
C	1.0649000000	0.1514730000	6.7202530000
C	2.1324860000	2.6268390000	7.7384610000
C	4.0674410000	4.1253970000	6.1770970000
C	4.6507590000	4.5413290000	2.9487340000
C	3.4180580000	4.7950190000	2.3199170000
C	3.1555610000	6.0471910000	1.7815750000
C	4.0588210000	7.0907170000	1.8748170000
C	5.2571180000	6.8488390000	2.5279410000
C	5.5728030000	5.6041980000	3.0455680000
C	2.3565390000	3.7437750000	2.1721000000
C	3.7587930000	8.4354230000	1.2932890000
C	6.9018190000	5.4626530000	3.7300400000
C	6.3798310000	2.4453230000	3.2976910000
C	6.9255540000	1.7801460000	4.3741020000
C	8.2272420000	1.2565780000	4.3516680000
C	8.9811470000	1.3596360000	3.2216780000
C	8.4608410000	1.9765320000	2.0646510000
C	9.2170540000	2.0487900000	0.8776160000
C	8.7035240000	2.6279710000	-0.2455940000
C	7.4018310000	3.1510950000	-0.2272270000
C	6.6480420000	3.0969860000	0.9108880000
C	7.1514280000	2.5248680000	2.0975790000
B	4.9878890000	3.1221160000	3.5273800000
H	4.4682380000	1.2760090000	2.0519210000
H	4.6035700000	-0.3194180000	2.7504070000
H	3.0829440000	0.2082390000	2.0548130000
H	2.8213550000	-1.4534290000	3.5989180000
H	1.9763060000	-1.6694540000	5.1135750000
H	1.1576760000	-0.9272080000	3.7540990000
H	0.4421180000	0.8299220000	7.2940630000
H	0.4089100000	-0.4180220000	6.0693450000
H	1.5087160000	-0.5531150000	7.4262070000
H	2.7779720000	3.4075630000	8.1221380000
H	1.1265380000	3.0441180000	7.6725310000
H	2.0988130000	1.8361140000	8.4843210000
H	4.7443750000	4.5942790000	5.4732210000
H	3.2758190000	4.8421200000	6.3898410000
H	4.6195780000	3.9748180000	7.1045760000
H	2.2109330000	6.2117360000	1.2815970000
H	5.9713700000	7.6540960000	2.6360800000
H	2.7502790000	2.8140330000	1.7707050000
H	1.8959510000	3.5055220000	3.1278860000
H	1.5757700000	4.0905820000	1.5006510000
H	3.8856730000	9.2225410000	2.0341230000
H	4.4315930000	8.6627820000	0.4673640000
H	2.7408380000	8.4853570000	0.9175450000
H	6.8537340000	4.8328160000	4.6135860000
H	7.6434480000	5.0221180000	3.0666500000
H	7.2728330000	6.4384000000	4.0324800000
H	6.3396550000	1.6787180000	5.2757080000
H	8.6234560000	0.7696820000	5.2295560000
H	9.9832510000	0.9574830000	3.1874560000
H	10.2123430000	1.6288850000	0.8734640000
H	9.2900200000	2.6766440000	-1.1500360000
H	6.9917480000	3.5955670000	-1.1210330000
H	5.6468560000	3.4944380000	0.9053320000

Ph*BNaph2 (5c)

C	9.2158500000	2.6690780000	11.2239190000
C	9.1063780000	1.9887780000	10.0107330000
C	7.8739030000	1.9093300000	9.3636820000
C	6.7501560000	2.5031130000	9.9421490000
C	6.8632890000	3.2158360000	11.1374920000
C	8.0972750000	3.2868360000	11.7837610000
C	10.3202360000	1.3162620000	9.4311690000
C	7.7454120000	1.1920400000	8.0516080000
C	5.4137860000	2.3766090000	9.2709430000
C	5.6568600000	3.8967730000	11.7154150000
C	8.2455650000	4.0459250000	13.0729560000
C	11.6502130000	3.7762920000	11.4406730000
C	11.1519750000	4.9996240000	11.0447460000
C	11.9861050000	6.0771470000	10.7122440000
C	13.3391050000	5.9183580000	10.7328520000
C	13.9129480000	4.6752990000	11.0718640000
C	15.3104570000	4.4932690000	11.0552000000
C	15.8622470000	3.2852500000	11.3653190000
C	15.0318540000	2.2039580000	11.6960590000
C	13.6745630000	2.3538200000	11.7228180000
C	13.0677600000	3.5917570000	11.4281680000
C	10.8452890000	1.7712680000	13.1545820000
C	10.3629130000	0.4882160000	13.0076430000
C	10.6421080000	-0.5276090000	13.9337240000
C	11.3764590000	-0.2476570000	15.0468200000
C	11.8499250000	1.0591250000	15.2865110000
C	12.5746050000	1.3657890000	16.4558640000
C	13.0156580000	2.6343340000	16.6930710000
C	12.7386000000	3.6534470000	15.7693350000
C	12.0407610000	3.3832510000	14.6267960000
C	11.5855360000	2.0806390000	14.3371610000
B	10.6024190000	2.7416440000	11.9562360000
H	10.6378190000	1.7798070000	8.4975780000
H	11.1680770000	1.3609910000	10.1117950000
H	10.1374110000	0.2634850000	9.2213200000
H	8.7094020000	1.0319610000	7.5825390000
H	7.2750070000	0.2145280000	8.1696270000
H	7.1328290000	1.7551980000	7.3514570000
H	4.6000630000	2.4143630000	9.9878550000
H	5.2454710000	3.1791750000	8.5502020000
H	5.3264940000	1.4392170000	8.7302750000
H	4.9690320000	3.1806710000	12.1673130000
H	5.9249090000	4.6129070000	12.4834030000
H	5.0986450000	4.4321340000	10.9505660000
H	7.5600650000	3.6881450000	13.8393850000
H	9.2514480000	3.9553880000	13.4775950000
H	8.0519070000	5.1103840000	12.9410910000
H	10.0817570000	5.1414740000	11.0126080000
H	11.5513800000	7.0256370000	10.4367410000
H	13.9948160000	6.7375250000	10.4756710000
H	15.9367970000	5.3307820000	10.7847490000
H	16.9332680000	3.1551980000	11.3492340000
H	15.4696730000	1.2453740000	11.9282290000
H	13.0520480000	1.5091010000	11.9670170000
H	9.7693990000	0.2498030000	12.1371730000
H	10.2685200000	-1.5254700000	13.7627110000
H	11.5955870000	-1.0182010000	15.7715770000
H	12.7683790000	0.5743550000	17.1650320000
H	13.5691790000	2.8595050000	17.5915400000
H	13.0774050000	4.6590840000	15.9652330000
H	11.8257540000	4.1798250000	13.9334470000

Fc_BAceMes_2

Fe	6.6105170000	4.6797190000	7.5104910000
C	6.6072750000	4.9007130000	9.5424390000
C	5.5342070000	5.6257540000	8.9899180000
C	6.0762850000	6.5871750000	8.0989380000
C	7.4776920000	6.4453560000	8.1007340000
C	7.8407290000	5.3897970000	9.0007920000
C	8.7414420000	5.8427630000	12.0437400000
C	9.3506430000	1.3254230000	14.0856220000
C	9.8645670000	1.8579900000	9.1483790000
C	9.0187990000	4.3781360000	11.8631810000
C	9.0540650000	3.5561030000	12.9754740000
C	9.3326740000	2.1994900000	12.8709970000
C	9.5966080000	1.6896630000	11.6132560000
C	9.5869330000	2.4922850000	10.4780130000
C	9.2896920000	3.8531530000	10.5877950000
C	15.0422490000	5.9141220000	7.2888030000
C	14.0257510000	5.9352640000	6.1214690000
C	11.8211640000	5.2586070000	9.0451000000
C	12.2085410000	5.1362170000	10.3973670000
C	13.5264760000	5.2528640000	10.7611380000
C	14.5537180000	5.5020760000	9.8306810000
C	14.2159390000	5.6379280000	8.5150260000
C	12.8678990000	5.5187800000	8.1456090000
C	12.6909780000	5.6923580000	6.7661520000
C	11.4261010000	5.6228830000	6.2565310000
C	10.3598080000	5.3806600000	7.1402160000
C	10.4950880000	5.1800070000	8.5066720000
C	5.3513190000	3.3026900000	6.6752660000
C	6.5070340000	2.6546640000	7.1517250000
C	7.6228240000	3.2077930000	6.4727050000
C	7.1512610000	4.1978060000	5.5886630000
C	5.7238940000	4.2797410000	5.6952070000
C	3.6975280000	2.7848150000	3.7063310000
C	-0.9215190000	3.6192280000	5.4183730000
C	2.7080820000	6.8803030000	6.4856600000
C	2.7576130000	3.6385040000	4.5074310000
C	1.4279640000	3.2705590000	4.6092900000
C	0.5106380000	4.0405580000	5.3128480000
C	0.9628880000	5.2070730000	5.9014450000
C	2.2888450000	5.6135230000	5.8027160000
C	3.2090240000	4.8275900000	5.1049970000
C	5.3335310000	9.9498530000	0.9244580000
C	6.4264600000	10.0109560000	2.0191450000
C	4.5396140000	6.9511220000	2.9897670000
C	3.4198040000	6.3940210000	2.3349700000
C	2.8948170000	6.9901100000	1.2160770000
C	3.4308360000	8.1666200000	0.6581190000
C	4.5213290000	8.7284250000	1.2573580000
C	5.0562000000	8.1168890000	2.4010310000
C	6.1729120000	8.8108430000	2.8865710000
C	6.8150520000	8.3245700000	3.9889130000
C	6.3271350000	7.1483430000	4.5849590000
C	5.2129920000	6.4447690000	4.1496770000
B	9.2310450000	4.8092780000	9.3392570000
B	4.7284380000	5.2158680000	4.9767200000
H	6.5272270000	4.0824250000	10.2353710000

H	4.4893310000	5.4584750000	9.1779100000
H	5.5140700000	7.2767030000	7.4962240000
H	8.1651280000	7.0371800000	7.5245500000
H	8.9154670000	6.1467530000	13.0726120000
H	7.7104240000	6.0881450000	11.7947840000
H	9.3744970000	6.4557270000	11.4031590000
H	10.0036150000	1.7315540000	14.8559010000
H	9.6958930000	0.3238120000	13.8452400000
H	8.3563810000	1.2390980000	14.5221970000
H	10.4816240000	0.9702930000	9.2609770000
H	10.3735750000	2.5411200000	8.4742060000
H	8.9390420000	1.5485950000	8.6634820000
H	8.8703770000	3.9854680000	13.9516320000
H	9.8297110000	0.6385010000	11.5082970000
H	15.8016180000	5.1486660000	7.1442320000
H	15.5686140000	6.8624100000	7.3754180000
H	14.0391360000	6.8858210000	5.5923980000
H	14.2468820000	5.1667440000	5.3834490000
H	11.4696280000	4.9466510000	11.1559470000
H	13.7864120000	5.1505940000	11.8042010000
H	15.5761840000	5.5848480000	10.1675860000
H	11.2287150000	5.7468910000	5.2019330000
H	9.3705320000	5.3124010000	6.7177640000
H	4.3447750000	3.1280120000	7.0106200000
H	6.5445530000	1.9033150000	7.9193220000
H	8.6527920000	2.9467740000	6.6331720000
H	7.7625580000	4.7918300000	4.9341900000
H	3.1503320000	2.1208430000	3.0423260000
H	4.3253370000	2.1702000000	4.3491690000
H	4.3681520000	3.3893230000	3.0961600000
H	-1.0166520000	2.6812320000	5.9637230000
H	-1.3609600000	3.4627450000	4.4347910000
H	-1.5150180000	4.3673810000	5.9362650000
H	1.8652670000	7.5552680000	6.6097650000
H	3.4807690000	7.4015290000	5.9269120000
H	3.1065480000	6.6733460000	7.4784820000
H	1.0942460000	2.3657970000	4.1183510000
H	0.2642020000	5.8293520000	6.4444390000
H	5.7695280000	9.8727590000	-0.0694090000
H	4.7166230000	10.8459160000	0.9249960000
H	6.3636550000	10.9303260000	2.5979160000
H	7.4266330000	9.9816470000	1.5919130000
H	2.9650070000	5.4950560000	2.7117840000
H	2.0360610000	6.5374820000	0.7431450000
H	2.9809050000	8.5973310000	-0.2238530000
H	7.6791510000	8.8178050000	4.4091240000
H	6.8381480000	6.7879540000	5.4631190000

BF3·OEt2

F	-2.7073090000	-0.5619520000	-0.3745790000
F	-1.6388410000	0.4063620000	1.3883600000
F	-0.7188390000	-1.4243240000	0.3553020000
O	-0.6908610000	0.6515120000	-0.7403990000
C	-0.6778920000	-0.7122550000	-2.7857100000
C	-0.3910920000	3.0587080000	-0.7742000000
C	0.1297310000	0.0759710000	-1.7938950000
C	-1.3230650000	1.9195250000	-1.0666310000
B	-1.5069470000	-0.3172760000	0.2388630000
H	-1.4479260000	-0.1049020000	-3.2540500000
H	-1.1473350000	-1.5698180000	-2.3150280000
H	-0.0110790000	-1.0708720000	-3.5667070000
H	0.5195370000	2.9989010000	-1.3647790000
H	-0.1266000000	3.0762340000	0.2787700000
H	-0.8874740000	3.9945100000	-1.0204770000
H	0.6446760000	0.9128310000	-2.2552160000
H	0.8579290000	-0.5406260000	-1.2822240000
H	-2.2167050000	1.9647090000	-0.4562920000
H	-1.6217050000	1.8789020000	-2.1106700000

C6F6

F	1.7433720000	3.9825030000	-0.0015390000
F	3.0960650000	1.6404330000	0.0004220000
F	1.7429790000	-0.7017640000	0.0014910000
F	-0.9598250000	-0.7016170000	0.0005960000
F	-2.3126680000	1.6407160000	-0.0013860000
F	-0.9597230000	3.9826540000	-0.0024250000
C	-0.9888030000	1.6405280000	-0.0009450000
C	-0.2983190000	2.8358630000	-0.0014780000
C	1.0818470000	2.8357960000	-0.0010070000
C	1.7722040000	1.6403840000	-0.0000070000
C	1.0817740000	0.4451440000	0.0005670000
C	-0.2985020000	0.4452090000	0.0000750000

MesBCl2

Cl	-0.2509850000	-0.7086360000	3.2924240000
Cl	1.4503390000	0.1206610000	0.9865590000
C	0.4685850000	3.2270040000	2.0109930000
C	3.2796960000	4.6552210000	5.8890680000
C	2.6685110000	-0.2174000000	4.9885970000
C	2.6861000000	3.5649140000	5.0549810000
C	2.9351090000	2.2323030000	5.3524340000
C	1.8726120000	3.8529250000	3.9721640000
C	2.3835600000	1.2048120000	4.6082390000
C	1.3225790000	2.8524010000	3.1852420000
C	1.5727180000	1.5136560000	3.5063580000
B	0.9630430000	0.3821950000	2.6505880000
H	0.1161240000	4.2503840000	2.1012860000
H	-0.4040700000	2.5831720000	1.9173500000
H	1.0268070000	3.1510180000	1.0791030000
H	3.0370210000	5.6352840000	5.4891060000
H	4.3635520000	4.5677210000	5.9353870000
H	2.9107820000	4.6092420000	6.9125160000
H	3.5370020000	-0.2767100000	5.6380810000
H	2.8614050000	-0.8426360000	4.1185190000
H	1.8268430000	-0.6578000000	5.5208550000
H	3.5746920000	1.9869010000	6.1892590000
H	1.6614850000	4.8849360000	3.7289250000

MesBBr2

Br	-0.5133900000	-0.6539700000	3.3099220000
Br	1.6246190000	-0.0209930000	0.9244370000
C	0.4277030000	3.2232090000	2.0480130000
C	3.3014840000	4.6626560000	5.8814990000
C	2.6989140000	-0.2124950000	4.9626280000
C	2.6998840000	3.5720260000	5.0533370000
C	2.9639630000	2.2396310000	5.3394880000
C	1.8631320000	3.8598480000	3.9881580000
C	2.4072250000	1.2120770000	4.5994750000
C	1.3022880000	2.8591750000	3.2093980000
C	1.5710070000	1.5220890000	3.5181590000
B	0.9541920000	0.3934870000	2.6686130000
H	0.0719790000	4.2457710000	2.1339190000
H	-0.4443560000	2.5751340000	1.9739260000
H	0.9708920000	3.1406820000	1.1074610000
H	3.0558930000	5.6424500000	5.4825910000
H	4.3855840000	4.5747310000	5.9190470000
H	2.9406820000	4.6183560000	6.9079560000
H	3.5658090000	-0.2788390000	5.6134390000
H	2.8968060000	-0.8253980000	4.0842240000
H	1.8573200000	-0.6639890000	5.4863400000
H	3.6197750000	1.9943920000	6.1637220000
H	1.6421050000	4.8915380000	3.7522810000

MesBF2 dimer

F	6.1662700000	2.8505440000	4.5196230000
F	5.2806030000	4.3828290000	3.1829490000
F	1.2818020000	-1.1556440000	3.1612360000
F	0.4713430000	0.3134740000	1.7107680000
C	3.9618120000	3.6942200000	0.8714080000
C	3.1514860000	-1.1440260000	0.1083760000
C	5.8944480000	0.1681900000	4.0325900000
C	3.7834680000	-0.0639210000	0.9242500000
C	4.5308840000	-0.3686780000	2.0518490000
C	3.6390100000	1.2691840000	0.5802750000
C	5.1123680000	0.6146260000	2.8338950000
C	4.1987980000	2.2883280000	1.3344450000
C	4.9377190000	1.9731190000	2.4924010000
C	0.6739510000	3.0243270000	2.1311170000
C	3.3507950000	4.4933040000	6.0463030000
C	2.6381460000	-0.3769400000	5.4102500000
C	2.7436970000	3.3824960000	5.2530850000
C	2.9185150000	2.0601420000	5.6331430000
C	1.9971590000	3.6389920000	4.1161470000
C	2.3800570000	1.0117810000	4.9075530000
C	1.4429050000	2.6222250000	3.3540020000
C	1.6377100000	1.2799950000	3.7369410000
B	5.4712190000	3.0867490000	3.4107780000
B	1.1214100000	0.1287040000	2.8558820000
H	3.4083630000	3.6901820000	-0.0627920000
H	4.8935500000	4.2299120000	0.7097420000
H	3.3922760000	4.2636820000	1.6012030000
H	2.3972760000	-0.7422640000	-0.5616600000
H	2.6823060000	-1.8912590000	0.7438840000
H	3.8982390000	-1.6573170000	-0.4967460000
H	5.9155370000	-0.9163770000	4.0803910000
H	5.4603720000	0.5405890000	4.9569760000
H	6.9204580000	0.5255160000	3.9999780000
H	4.6575010000	-1.4041680000	2.3351690000
H	3.0619110000	1.5251720000	-0.2968980000
H	0.6110170000	4.1067750000	2.0712580000
H	-0.3373000000	2.6266060000	2.1379150000
H	1.1505880000	2.6628160000	1.2227370000
H	3.2605810000	5.4436690000	5.5292030000
H	4.4053480000	4.3069680000	6.2374690000
H	2.8612730000	4.5888680000	7.0147730000
H	3.2161220000	-0.3388200000	6.3286700000
H	3.1898860000	-0.9697120000	4.6852890000
H	1.7132190000	-0.9099610000	5.6150570000
H	3.4981560000	1.8387620000	6.5183810000
H	1.8506040000	4.6636090000	3.8055720000

MesBCl2 dimer

Cl	-0.7215000000	-0.8040930000	3.5604130000
Cl	0.2291780000	0.3583160000	1.0124730000
Cl	7.5754200000	3.5439810000	3.1920680000
Cl	5.0716040000	5.1167710000	3.1520570000
C	3.9961110000	3.6335660000	0.5149480000
C	3.4186360000	-1.3058150000	0.7434500000
C	6.0869510000	0.9161530000	4.2898860000
C	3.9900140000	-0.0490140000	1.3153690000
C	4.7419830000	-0.0819890000	2.4782800000
C	3.7764040000	1.1800350000	0.7153770000
C	5.3082030000	1.0587540000	3.0158290000
C	4.3033110000	2.3530240000	1.2318010000
C	5.1085800000	2.3013220000	2.3847620000
C	0.5334690000	3.2934150000	2.2832640000
C	3.5742020000	3.8066160000	6.1904030000
C	2.2295630000	-0.7770400000	4.8408540000
C	2.7953350000	2.9199170000	5.2737630000
C	2.8296810000	1.5433560000	5.4255100000
C	2.0340980000	3.4399670000	4.2413730000
C	2.0981560000	0.6994490000	4.6110450000
C	1.3043240000	2.6311350000	3.3851100000
C	1.3031520000	1.2377180000	3.5818090000
B	5.8408340000	3.5607740000	2.8883520000
B	0.3650170000	0.3294910000	2.7624820000
H	3.5270690000	3.4250530000	-0.4421040000
H	4.8864630000	4.2292680000	0.3275320000
H	3.3138530000	4.2521130000	1.0943620000
H	2.8914750000	-1.1161530000	-0.1862720000
H	2.7171730000	-1.7701500000	1.4353590000
H	4.2029690000	-2.0350900000	0.5486140000
H	5.7440910000	0.0430040000	4.8391260000
H	5.9809560000	1.7807130000	4.9390950000
H	7.1495620000	0.7842660000	4.0951120000
H	4.8894860000	-1.0254300000	2.9860510000
H	3.1823880000	1.2296340000	-0.1855600000
H	0.5227120000	4.3697570000	2.4267680000
H	-0.4979510000	2.9525110000	2.2329170000
H	0.9864650000	3.0881740000	1.3154230000
H	3.3956890000	4.8555440000	5.9758450000
H	4.6444280000	3.6253580000	6.0999660000
H	3.3080330000	3.6207100000	7.2294030000
H	3.1979910000	-0.9987430000	5.2823120000
H	2.1450950000	-1.3480900000	3.9207390000
H	1.4665390000	-1.1449970000	5.5241740000
H	3.4475270000	1.1116170000	6.2010450000
H	2.0060720000	4.5099130000	4.0951990000

MesBBr2 dimer

Br	-1.2424740000	-0.5754530000	3.5264410000
Br	0.2701810000	0.5099520000	0.8663640000
Br	7.9249550000	3.7263980000	2.6074940000
Br	5.0524100000	5.1596580000	3.1191260000
C	4.3723500000	3.4519260000	0.1386010000
C	3.5980370000	-1.4290410000	0.8442990000
C	6.2315630000	1.1152230000	4.2290990000
C	4.1895750000	-0.1360630000	1.3066110000
C	4.8975430000	-0.0675700000	2.4972220000
C	4.0454210000	1.0243790000	0.5658240000
C	5.4699020000	1.1112830000	2.9380560000
C	4.5818130000	2.2315430000	0.9834140000
C	5.3178800000	2.2790480000	2.1750090000
C	0.1822080000	3.4754180000	2.6604890000
C	3.4551470000	3.6571670000	6.4204300000
C	2.0129840000	-0.7921730000	4.7042210000
C	2.6423680000	2.8537480000	5.4566160000
C	2.6939500000	1.4680400000	5.4694950000
C	1.8136000000	3.4661620000	4.5326230000
C	1.9218110000	0.7015920000	4.6162490000
C	1.0480900000	2.7371280000	3.6367880000
C	1.0841880000	1.3356250000	3.6841920000
B	6.0114780000	3.5864210000	2.6023060000
B	0.1543290000	0.5074450000	2.7775230000
H	4.0434430000	3.1759480000	-0.8589140000
H	5.2799740000	4.0442040000	0.0365060000
H	3.6124680000	4.1012430000	0.5702450000
H	3.1330140000	-1.3250740000	-0.1314040000
H	2.8372520000	-1.7841800000	1.5377800000
H	4.3578840000	-2.2055670000	0.7776780000
H	5.9466630000	0.2671060000	4.8454400000
H	6.0529260000	2.0208710000	4.8058320000
H	7.3045610000	1.0490630000	4.0563150000
H	5.0086570000	-0.9593950000	3.0989510000
H	3.4941200000	0.9927560000	-0.3629720000
H	0.0671990000	4.5126340000	2.9611020000
H	-0.8129500000	3.0422360000	2.5803700000
H	0.6176650000	3.4660840000	1.6629480000
H	3.3292750000	4.7225830000	6.2531590000
H	4.5151980000	3.4257610000	6.3343770000
H	3.1649070000	3.4413310000	7.4475890000
H	2.9415160000	-1.0905240000	5.1829860000
H	1.9764800000	-1.2640640000	3.7246930000
H	1.1941820000	-1.2040970000	5.2916720000
H	3.3484240000	0.9691210000	6.1712210000
H	1.7609770000	4.5451750000	4.5049680000

BF3

F	0.8459750000	0.8122360000	0.0000000000
F	-1.1191770000	-0.3224500000	0.0000000000
F	-1.1191770000	1.9469220000	0.0000000000
B	-0.4641600000	0.8122360000	0.0000000000

[BF4]-

F	-0.4636570000	0.8122360000	1.4015390000
F	0.8574290000	0.8122360000	-0.4666860000
F	-1.1252190000	-0.3317830000	-0.4674060000
F	-1.1252190000	1.9562560000	-0.4674060000
B	-0.4640090000	0.8122360000	-0.0000400000

[MesBF3]-

F	-0.1114311848	-0.3425714570	3.3441708862
F	1.9388791763	-0.7059983646	2.3821128148
F	0.4310307967	0.6514187309	1.3635274518
C	0.5927897751	3.3241938751	1.9587310847
C	3.3334130575	4.6725692901	5.8843589028
C	2.5252760727	-0.1776418593	5.1070325518
C	2.7134239549	3.5859460788	5.0597484674
C	2.8607657707	2.2522492300	5.4033202572
C	1.9702404508	3.8712363123	3.9304141519
C	2.3051694274	1.2349164401	4.6401211068
C	1.3981189034	2.8717650789	3.1461362910
C	1.5669065093	1.5201990375	3.4771150338
B	0.9455400113	0.2779514828	2.6224043585
H	0.5194021395	4.4091811509	1.9475523855
H	-0.4116041251	2.9122675721	1.9755679318
H	1.0382745334	3.0021234390	1.0222609326
H	3.0166553331	5.6542897451	5.5431134766
H	4.4209067230	4.6404234469	5.8316822222
H	3.0627530869	4.5805311704	6.9344962028
H	2.8215630161	-0.1897429927	6.1535074270
H	3.3074607996	-0.6652435755	4.5303304253
H	1.6315196021	-0.7810827048	4.9913242457
H	3.4187662509	1.9940041588	6.2940348797
H	1.8205956875	4.9049506030	3.6484433994

[Ph*BF3]-

F	-0.0838060000	-0.3410710000	3.0651620000
F	2.0968330000	-0.6841250000	2.4393750000
F	0.7842750000	0.6876950000	1.2166980000
C	3.7143050000	1.8945530000	6.6264150000
C	1.8630930000	5.3279490000	3.4701260000
C	0.4605090000	3.2832770000	2.0435670000
C	3.3001020000	4.6786430000	5.9078430000
C	2.3782220000	-0.1805640000	5.1681440000
C	2.7190250000	3.5826620000	5.0568540000
C	2.8780820000	2.2472910000	5.4266060000
C	1.9826000000	3.8955590000	3.9157460000
C	2.2813210000	1.2371100000	4.6678470000
C	1.3759130000	2.8785770000	3.1697350000
C	1.5675240000	1.5295330000	3.4959330000
B	1.0734800000	0.2945500000	2.5423560000
H	4.5254040000	2.6030730000	6.7693640000
H	4.1656160000	0.9135940000	6.5171390000
H	3.1328280000	1.8783660000	7.5512990000
H	2.7355140000	5.9076340000	3.7571440000
H	0.9884480000	5.8286400000	3.8921960000
H	1.7789460000	5.3971930000	2.3899480000
H	-0.0560000000	4.2102930000	2.2832250000
H	-0.2862100000	2.5229310000	1.8598030000
H	0.9934570000	3.4384860000	1.1045260000
H	2.6927980000	5.5779400000	5.8665640000
H	4.3097790000	4.9574080000	5.5975580000
H	3.3555350000	4.3843290000	6.9514660000
H	2.2813830000	-0.2132360000	6.2521380000
H	3.3308220000	-0.6455590000	4.9118860000
H	1.5954490000	-0.7969890000	4.7462530000

[NaphBF3]-

F	-4.2773720000	3.4556470000	1.1335840000
F	-5.9594210000	2.3587670000	0.0389580000
F	-4.3213380000	3.4175450000	-1.1533540000
C	0.5323100000	1.2483780000	-0.0300000000
C	-0.1710190000	2.4646100000	-0.0365220000
C	-1.5364180000	2.4742880000	-0.0220310000
C	-0.1521610000	0.0684780000	-0.0120150000
C	-4.3415320000	0.0612980000	0.0336870000
C	-3.7078000000	1.2786330000	0.0146290000
C	-2.2824930000	1.2736520000	-0.0023980000
C	-1.5629320000	0.0470630000	0.0021670000
C	-2.2773090000	-1.1680160000	0.0207470000
C	-3.6402310000	-1.1573730000	0.0376260000
B	-4.5794730000	2.6509560000	0.0085790000
H	1.6123430000	1.2510220000	-0.0389450000
H	0.3733540000	3.3971060000	-0.0507880000
H	-2.0718570000	3.4092070000	-0.0263030000
H	-5.4218320000	0.0431780000	0.0453620000
H	-1.7267940000	-2.0984210000	0.0236540000
H	-4.1876350000	-2.0892600000	0.0521910000
H	0.3784550000	-0.8736290000	-0.0065920000

[AceBF3]-

F	-2.9345360000	4.7142250000	1.1298710000
F	-2.8603530000	4.7482960000	-1.1561070000
F	-1.1165690000	5.6024060000	0.0566330000
C	0.3307210000	-0.8760430000	0.0341900000
C	-1.0174810000	-1.6405150000	-0.0461030000
C	0.6794860000	1.7330280000	0.0741480000
C	0.0009800000	2.9741970000	0.0619370000
C	-1.3688340000	3.1114370000	0.0114700000
C	-0.0506440000	0.5815920000	0.0308800000
C	-4.1586170000	0.5951130000	-0.1555130000
C	-3.5426700000	1.8190470000	-0.1069970000
C	-2.1322810000	1.9109420000	-0.0403910000
C	-1.4465430000	0.6873390000	-0.0288360000
C	-2.0734700000	-0.5659030000	-0.0768990000
C	-3.4362080000	-0.6190310000	-0.1413520000
B	-2.0766360000	4.5687950000	0.0107580000
H	0.8807870000	-1.1401620000	0.9359550000
H	0.9767840000	-1.1223320000	-0.8067410000
H	-1.1507730000	-2.3026070000	0.8077800000
H	-1.0657420000	-2.2669210000	-0.9353460000
H	1.7600510000	1.7164190000	0.1181570000
H	0.5957560000	3.8765340000	0.0953090000
H	-5.2370700000	0.5536700000	-0.2074540000
H	-4.1281510000	2.7245420000	-0.1213750000
H	-3.9673890000	-1.5593890000	-0.1812930000

[AnBF3]-

F	0.9814090000	0.7600980000	1.2111510000
F	-0.2902460000	-0.1629700000	2.8471960000
F	1.8769160000	-0.7914240000	2.6478950000
C	5.4751800000	2.9749500000	2.7967950000
C	-0.5928860000	3.3272480000	6.7379840000
C	4.9245660000	1.9405930000	2.0070620000
C	4.7414330000	3.5130780000	3.8018300000
C	2.6860660000	3.6099750000	5.1069570000
C	0.6627330000	3.7457280000	6.4475130000
C	-1.1785010000	2.2982040000	5.9666180000
C	3.6680170000	1.4791450000	2.2410790000
C	3.4250790000	3.0553790000	4.0756170000
C	1.4041560000	3.1683110000	5.3814870000
C	-0.5004540000	1.7228120000	4.9392890000
C	2.8513210000	2.0074820000	3.2840210000
C	0.8249860000	2.1188680000	4.5872820000
C	1.5453050000	1.5274810000	3.5295440000
B	1.0008660000	0.3171050000	2.5558220000
H	6.4751870000	3.3306190000	2.5972050000
H	-1.1451980000	3.7732630000	7.5518300000
H	5.5100530000	1.5132640000	1.2067270000
H	5.1437420000	4.3048880000	4.4181250000
H	3.1175780000	4.3993470000	5.7078050000
H	1.1314940000	4.5312240000	7.0236880000
H	-2.1794540000	1.9650220000	6.1974750000
H	3.2721420000	0.6913130000	1.6270800000
H	-0.9657390000	0.9438400000	4.3668030000

[F2B-C6H4-BF3]-

F	-0.2542670000	5.8168790000	0.3579610000
F	1.0999920000	4.9866490000	-1.2930470000
F	1.6526000000	4.6632420000	0.9021900000
F	-1.8005800000	-1.6179250000	-0.1306630000
F	-3.7342190000	-0.5191360000	0.1369800000
C	-2.3328140000	2.0975530000	0.1426890000
C	-1.6423170000	3.2940060000	0.1441110000
C	-0.2566900000	3.3393630000	0.0015280000
C	0.4095640000	2.1210710000	-0.1428380000
C	-0.2673310000	0.9198120000	-0.1456190000
C	-1.6581040000	0.8832710000	-0.0025650000
B	0.5723240000	4.7342900000	-0.0062810000
B	-2.4114460000	-0.4414370000	0.0012740000
H	-3.4079890000	2.0954960000	0.2566090000
H	-2.1818510000	4.2221770000	0.2648030000
H	1.4854720000	2.1239970000	-0.2473760000
H	0.2772000000	-0.0074350000	-0.2574150000

[F2B-Xyl-BF3]-

F	0.1612710000	5.5375200000	-1.1238900000
F	1.9677290000	4.4599410000	-0.2280790000
F	0.4238680000	5.4381490000	1.1494480000
F	-2.0046920000	-1.6370640000	-0.1311780000
F	-3.8012060000	-0.3643140000	0.2379110000
C	0.5527640000	-0.3670500000	-0.4107660000
C	-2.4138270000	4.5644890000	0.4248990000
C	-2.2957010000	2.0847010000	0.1979100000
C	-1.6404440000	3.3009920000	0.1930780000
C	-0.2533950000	3.3274080000	-0.0182700000
C	0.3952470000	2.1113380000	-0.2049250000
C	-0.2480390000	0.8827370000	-0.1976810000
C	-1.6364580000	0.8641320000	0.0077970000
B	0.5922730000	4.7162210000	-0.0546010000
B	-2.4824210000	-0.4044390000	0.0364670000
H	1.6052890000	-0.1226390000	-0.5232460000
H	0.2354550000	-0.9032560000	-1.3033590000
H	0.4536940000	-1.0591890000	0.4230830000
H	-3.4851020000	4.3800960000	0.3839740000
H	-2.1583050000	5.3200170000	-0.3130780000
H	-2.1772370000	4.9902470000	1.3982140000
H	-3.3662680000	2.0703720000	0.3549500000
H	1.4646350000	2.1299720000	-0.3650210000

[BtpBF3]-

S	-0.3100430000	-2.9617620000	0.0055790000
F	1.2025630000	-5.8771760000	-1.3380690000
F	0.1632600000	-5.9460510000	0.6959800000
F	2.4562380000	-5.8707590000	0.5724100000
C	1.2122910000	-3.7905120000	0.0223840000
C	2.2356970000	-2.9018180000	0.0302070000
C	2.6123390000	-0.3701600000	0.0144290000
C	2.0021990000	0.8637960000	-0.0012310000
C	0.6096200000	0.9716120000	-0.0150420000
C	-0.1812720000	-0.1578200000	-0.0150830000
C	0.4324410000	-1.4041420000	-0.0021150000
C	1.8351890000	-1.5317010000	0.0144830000
B	1.2600490000	-5.4118250000	-0.0090430000
H	3.2679590000	-3.2155670000	0.0488340000
H	3.6897830000	-0.4469430000	0.0253190000
H	2.6043970000	1.7598820000	-0.0027840000
H	0.1477430000	1.9472590000	-0.0261610000
H	-1.2576270000	-0.0746990000	-0.0256730000

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