

Supporting Information

Carbon Monoxide Bond Cleavage Mediated by an Intramolecular Frustrated Lewis Pair – Access to New N/B Heterocycles via Selective Incorporation of Single Carbon Atoms

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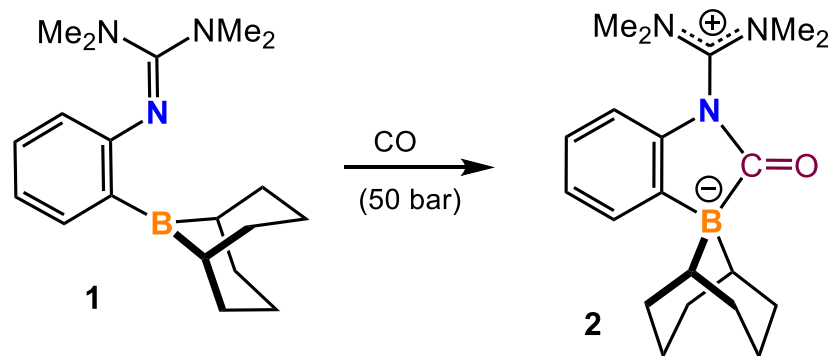
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1. General Remarks

All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk or cannula techniques or in a Vacuum Atmospheres OMNI inert atmosphere dry box containing an atmosphere of purified nitrogen. Toluene, hexanes and benzene were distilled under nitrogen from alkali metals and stored over 4 Å molecular sieves before use. All deuterated solvents were purchased from Cambridge Isotope Labs. C₆D₆ and CD₂Cl₂, DMSO-d₆ were dried and stored over 4 Å molecular sieves before use. TMSOTf (TCI), MeOTf (Matrix Scientifics), HNTf₂ (TCI) were purchased from commercial sources and used without further purification. Compound **1** [1], B(OC₆F₅)₃ [2], Al(C₆F₅)₃ [3], and B(C₆F₅)₃ [4] were prepared according to literature procedures. The ¹H-, ¹³C-, ¹¹B-, ¹⁹F-NMR spectra were obtained from a JOEL ECS 400. All measurements, unless noted otherwise, were carried out at 298 K and NMR chemical shifts were given in ppm. The ¹¹B NMR spectra were referenced to H₃BO₃ in D₂O (δ = 36 ppm), ¹⁹F NMR spectra were referenced to C₆H₅CF₃ in C₆D₆ (δ = 62.3 ppm), The ¹H-NMR spectra were referenced to the residual protonated solvent for ¹H and the ¹³C NMR spectra were referenced to the deuterated solvent peaks. The following abbreviations were used to describe peak multiplicities in the reported NMR spectroscopic data: “s” for singlet, “d” for doublet, “t” for triplet, “q” for quartet, “sept” for septet, “m” for multiplet and “br” for broadened resonances. Elemental analyses were performed using a Perkin Elmer 2400 Series II CHNS/O Analyzer. The IR spectra were obtained from a Nicolet iS 5 FT-IR spectrometer with iD5 ATR accessory.

2. Experimental

2.1. Synthesis of **2**



In the glove box, a 40 mL scintillation vial with magnetic stir bar was charged with **1** (0.5 g, 1.6 mmol) and hexanes (10 mL). The vial was placed in a Parr reactor and the reaction mixture was stirred overnight at room temperature under 50 bar CO pressure. Then the Parr reactor was vented, and the white suspension transferred to a 30 mL Schlenk flask. After centrifugation and decantation of the solvent, the precipitate was washed twice with hexanes and dried under vacuum to give **2** as a colorless solid. Yield 0.46 g (85%). ¹H NMR [400 MHz, CD₂Cl₂]: 7.87 (d, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 7.02-7.10 (m, CH-arom., 2 H), 6.10 (d, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 3.23, 2.96 (2s, CH₃, 2 × 6 H), 1.91-2.16 (m, CH₂-BBN, 6 H), 1.47-1.71 (m, CH₂-BBN, 6 H), 0.68 (s, CH-BBN, 2 H) ppm. ¹³C{H} NMR [125 MHz, CD₂Cl₂]: 209.1 (C=O), 157.1 (C=N), 153.1 (C-B), 143.5 (C-arom.), 134.3, 124.3, 123.3, 110.2 (CH-arom.), 42.0, 41.2 (CH₃), 31.5, 31.4, 26.2, 25.8 (CH₂), 24.2, 24.5 (CH) ppm. ¹¹B NMR [128.4 MHz, CD₂Cl₂]: -15.0 ppm. Anal. Calc. for C₂₀H₃₀BN₃O (339.29): C, 70.80; H, 8.91, N, 12.38, Found: C, 70.68; H, 8.56, 12.07. IR (solid) $\tilde{\nu}_{(C=O)} = 1708 \text{ cm}^{-1}$.

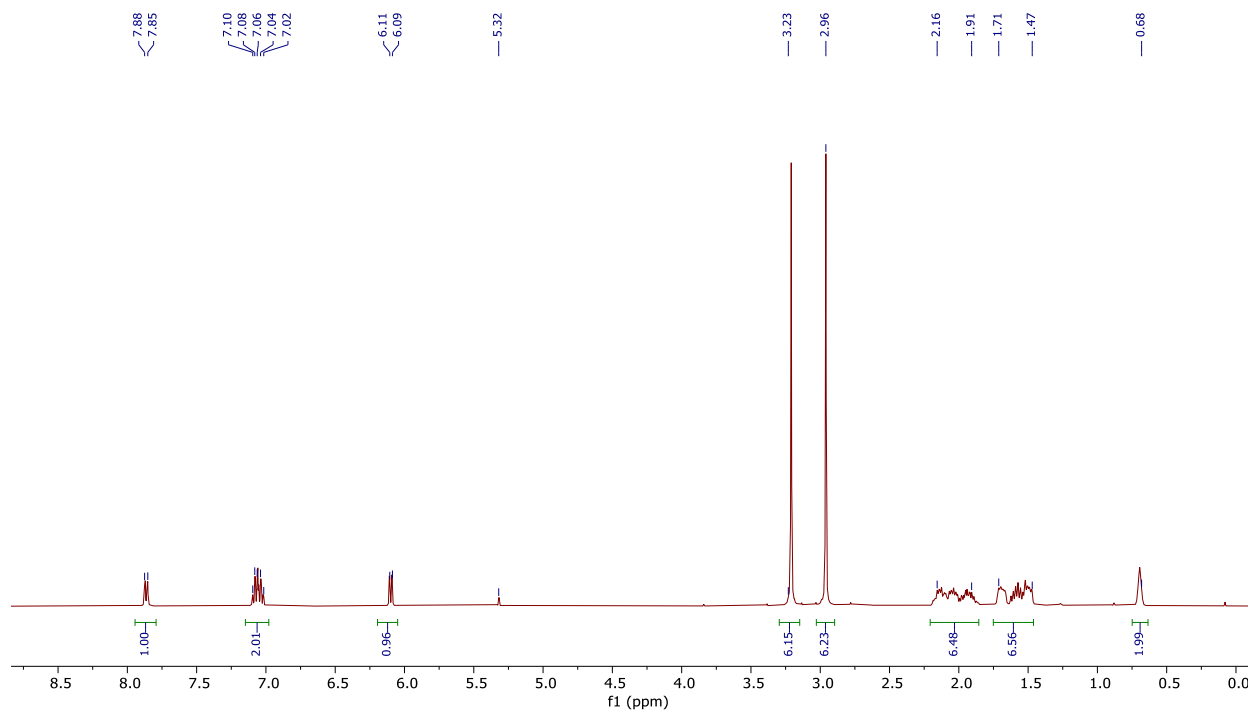


Figure S1. ^1H NMR spectrum of **2** in CD_2Cl_2 .

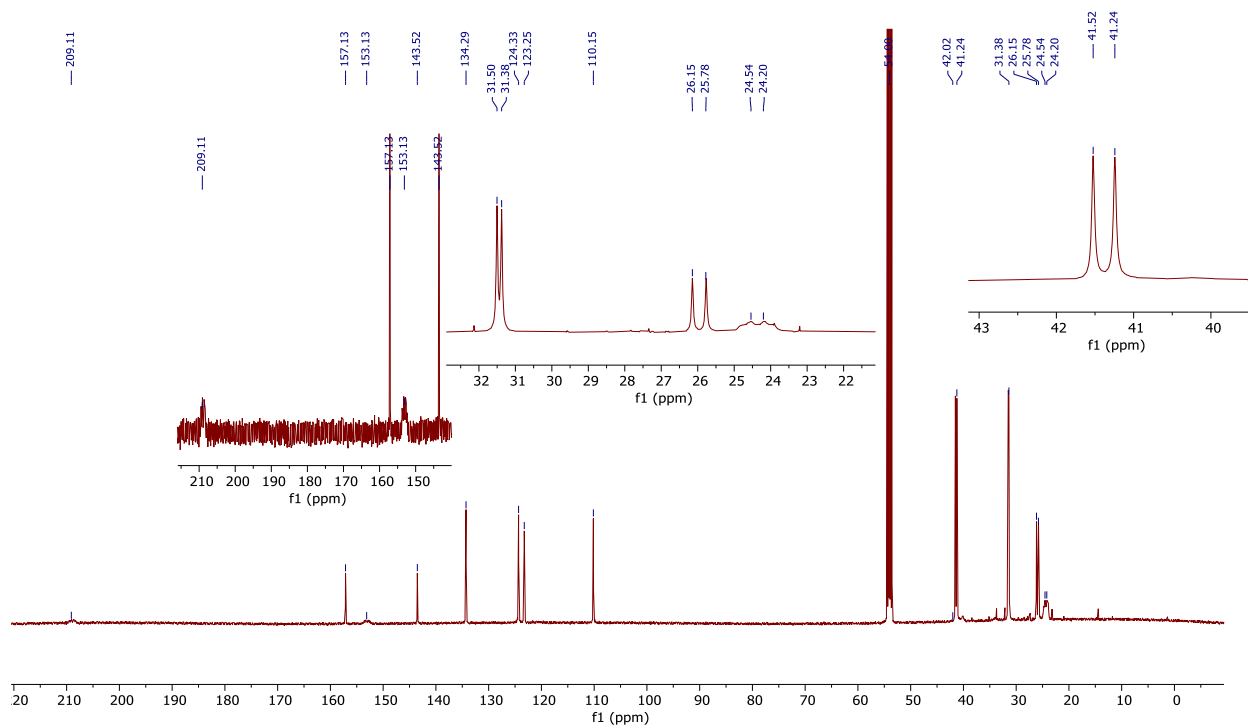


Figure S2. ^{13}C NMR spectrum of **2** in CD_2Cl_2 .

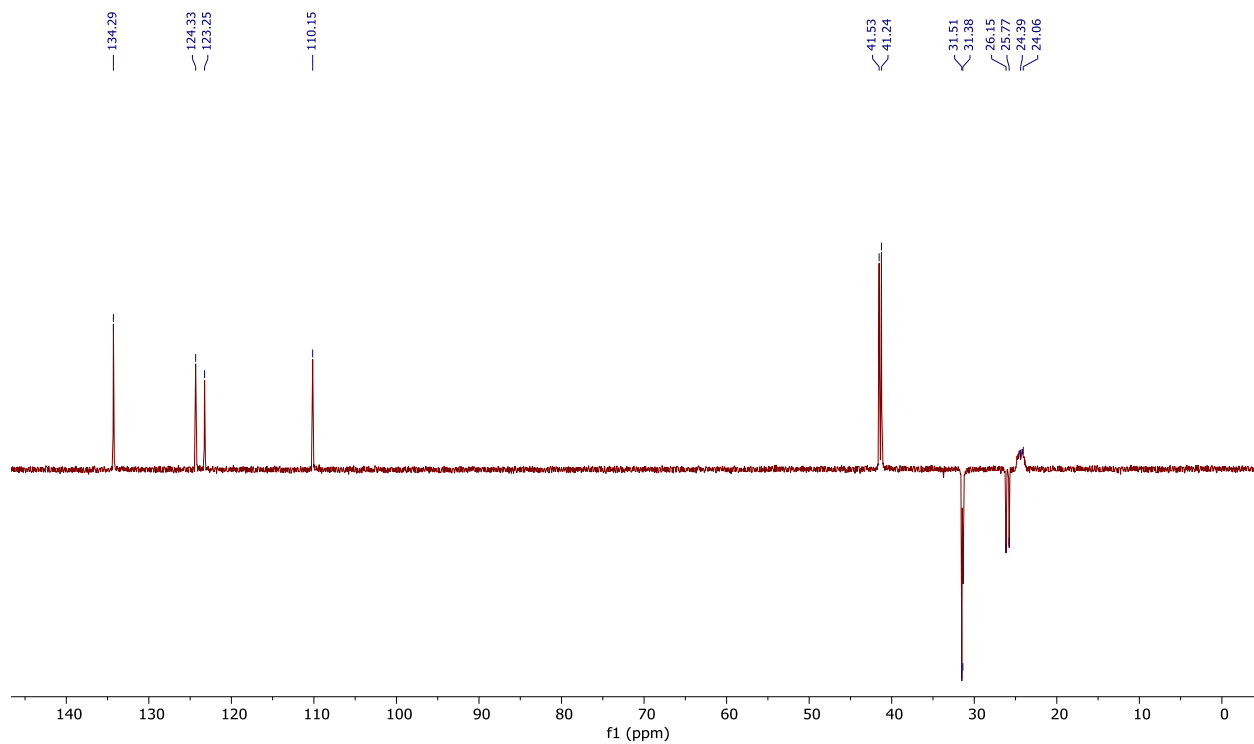


Figure S3. ^{13}C NMR(DEPT) spectrum of **2** in CD_2Cl_2 .

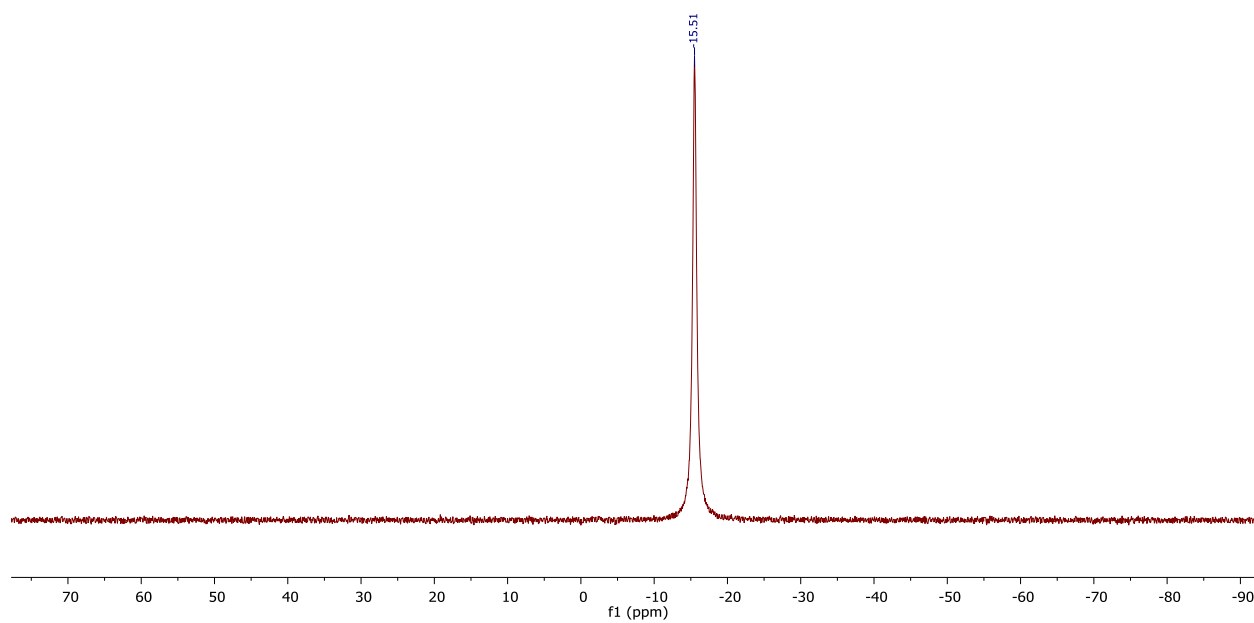
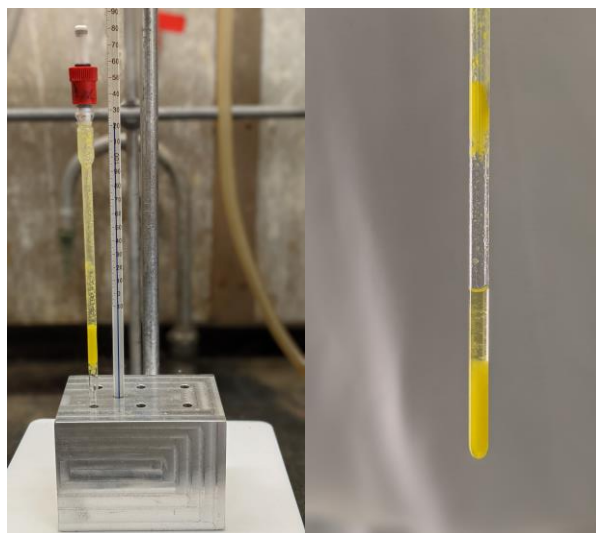
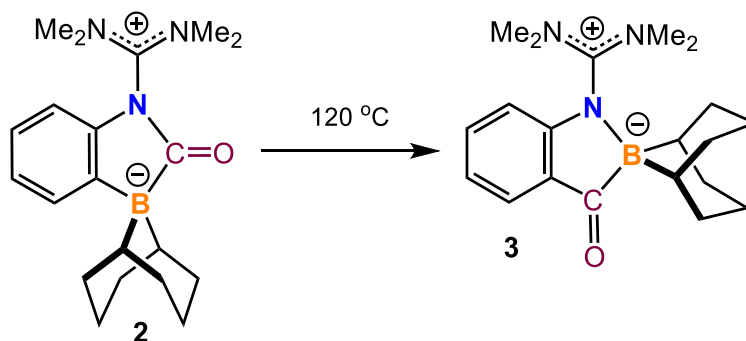


Figure S4. ^{11}B NMR spectrum of **2** in CD_2Cl_2 .

2.2. Synthesis of **3**



In the glove box, a J-Young NMR tube was charged with **2** (100 mg, 2.9 mmol) and C₆D₆ (0.5 mL). Outside the glovebox, the J-Young tube was placed in an aluminum block and heated overnight at 120°C (see picture). The resulting yellow precipitate was washed twice with benzene and dried under vacuum to give 51 mg (50%) of **3**. ¹H NMR [400 MHz, CD₂Cl₂]: 7.47 (d, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 7.34 (t, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 6.92

(t, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 6.40 (d, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 3.08, 2.96 (2s, CH₃, 2 × 6 H), 1.35-2.48 (m, CH₂-BBN, 12 H), 0.75 (s, CH-BBN, 2 H) ppm. ¹³C{H} NMR [125 MHz, CD₂Cl₂]: 165.2 (C=N), 155.9 (C-arom.), 133.2 (CH-arom.), 128.8 (C-arom.), 121.3, 120.8, 113.8 (CH-arom.), 41.2, 41.1 (CH₃), 32.0, 31.6, 25.3, 24.8 (CH₂), 24.4 (CH) ppm. Note: The carbonyl carbon bound to boron could not be detected in the ¹³C{H} NMR. ¹¹B NMR [128.4 MHz, CD₂Cl₂]: 0.3 ppm. Anal. Calc. for C₂₀H₃₀BN₃O (339.25): C, 70.80; H, 8.91, N, 12.38, Found: C, 70.81; H, 8.79, 12.26. IR (solid) $\tilde{\nu}_{(C=O)}$ = 1628 cm⁻¹, 1583 cm⁻¹, 1572 cm⁻¹.

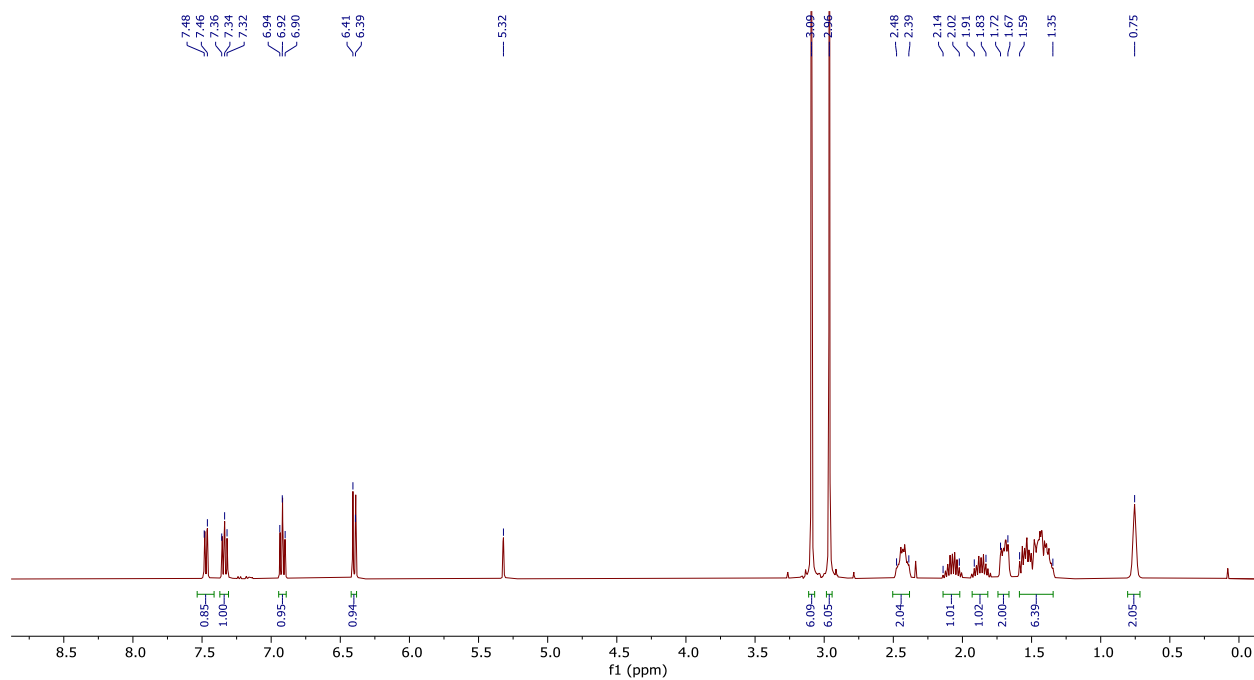


Figure S5. ^1H NMR spectrum of **3** in CD_2Cl_2 .

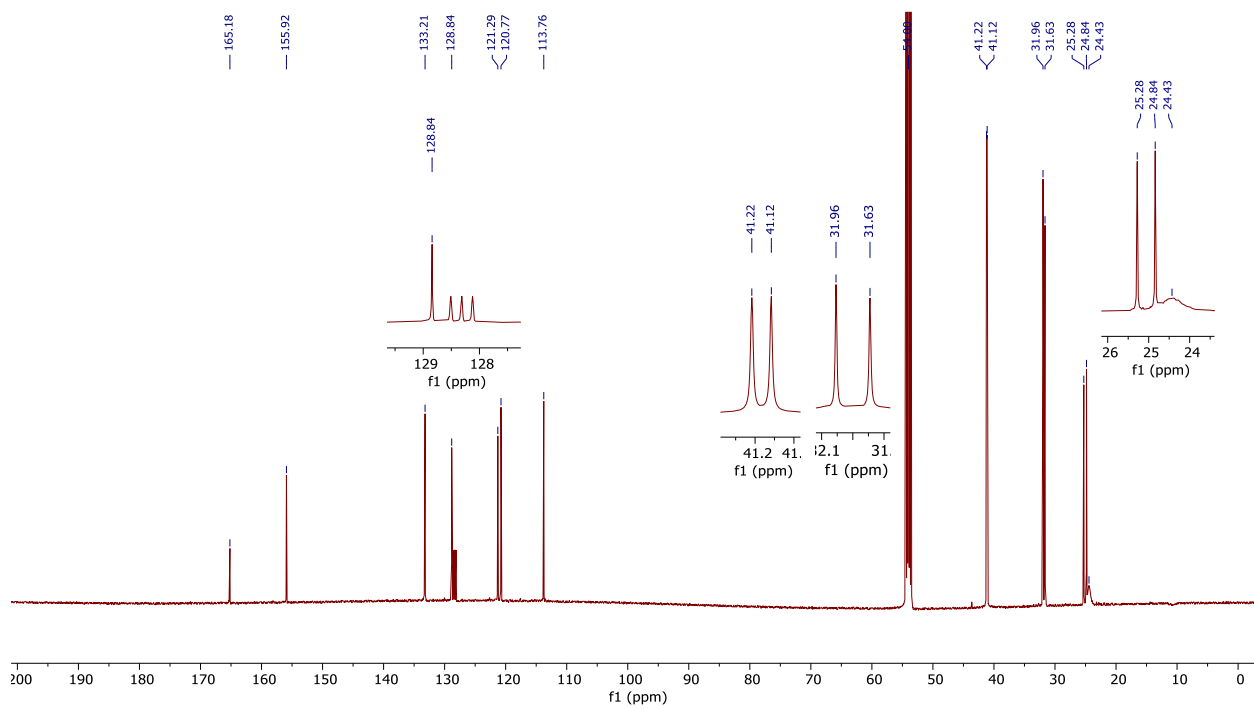


Figure S6. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of **3** in CD_2Cl_2 .

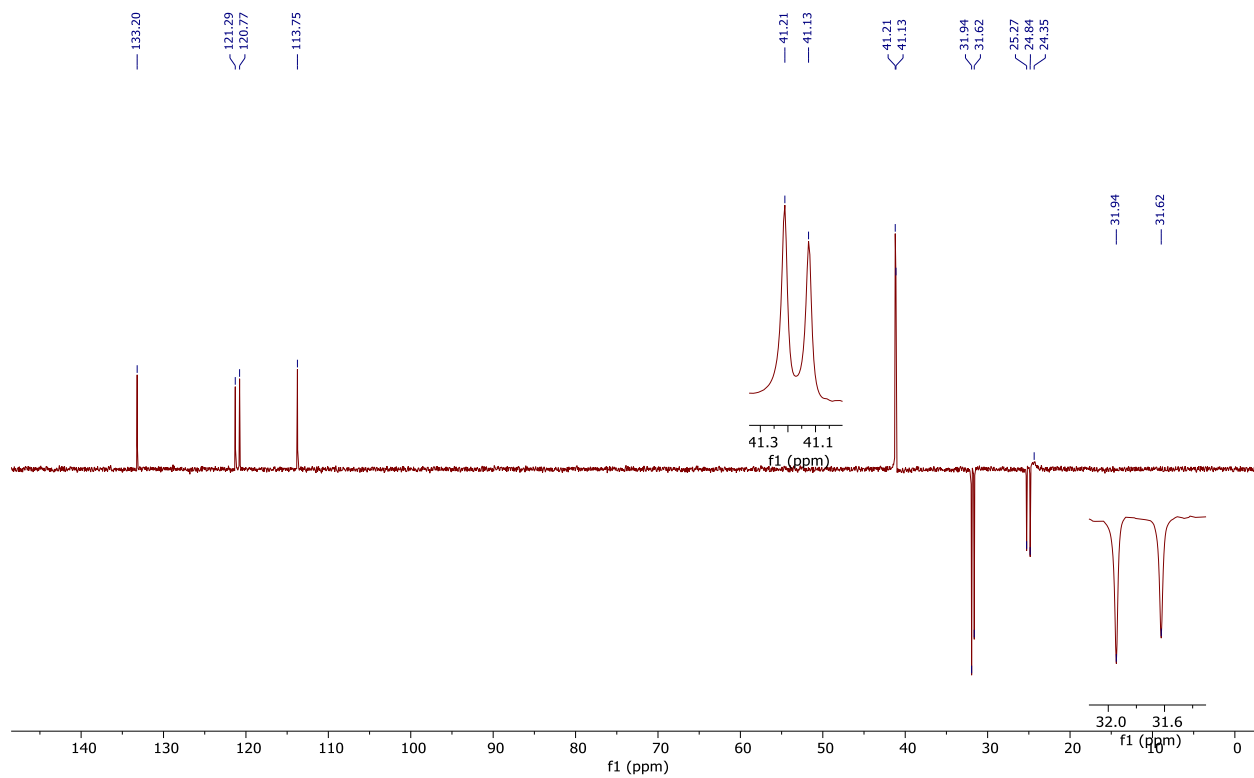


Figure S7. $^{13}\text{C}\{\text{H}\}$ NMR (DEPT) spectrum of **3** in CD_2Cl_2 .

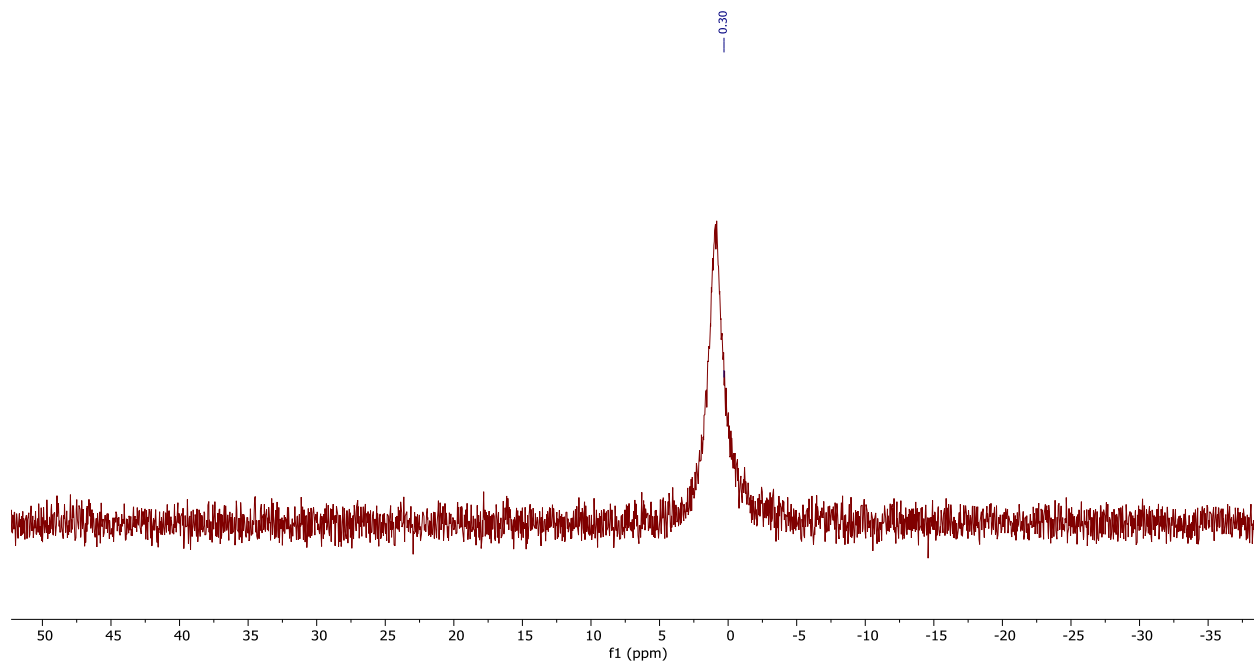
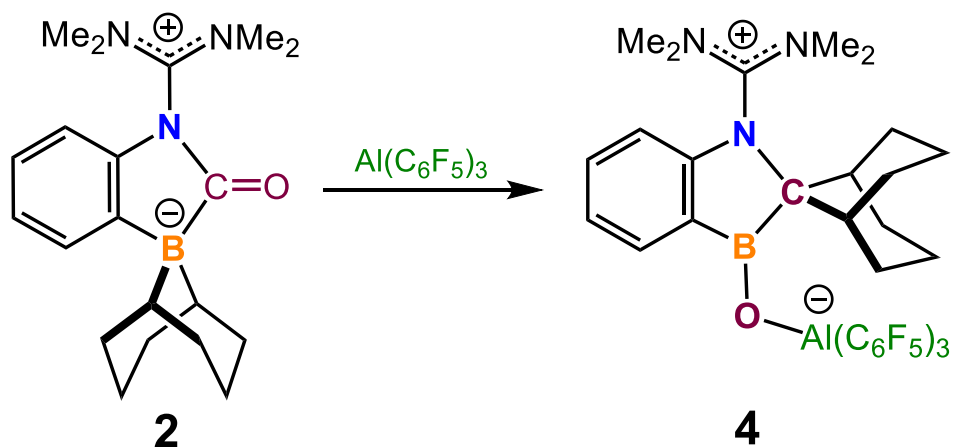


Figure S8. ^{11}B NMR spectrum of **3** in CD_2Cl_2 .

2.3. Synthesis of **4**



In the glove box, a Schlenk flask (30 mL) was charged with **2** (100 mg, 0.3 mmol), $\text{Al}(\text{C}_6\text{F}_5)_3 \cdot \frac{1}{3}\text{toluene}$ (168 mg, 0.3 mmol) and dry benzene (5 mL). The reaction mixture was stirred for one hour, then concentrated to ca. half of the volume and left overnight. The resulting colorless crystals were washed once with benzene and dried under vacuum to give 195 mg (75%) of **4**. ^1H NMR [400 MHz, CD_2Cl_2]: 7.34 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 7.25 (d, $^3J_{\text{H-H}} = 4$ Hz, CH-arom., 1 H), 6.95 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 6.56 (d, $^3J_{\text{H-H}} = 4$ Hz, CH-arom., 1 H), 3.14, 3.10 (2s, CH_3 , 2×6 H), 1.30-2.63 (m, CH-skeleton, 14 H) ppm. $^{13}\text{C}\{\text{H}\}$ NMR [125 MHz, CD_2Cl_2]: 162.9 (C=N), 156.2 (C-arom.), 150.4 (dd, $^1J_{\text{C-F}} = 285$ Hz, $^2J_{\text{C-F}} = 26.3$ Hz ortho-CF), 140.9 (d, $^1J_{\text{C-F}} = 307.5$ Hz, meta-CF), 136.6 (d, $^1J_{\text{C-F}} = 344$ Hz, para-CF), 133.7, 133.1 (CH-arom.), 132.3 (C-arom.), 124.3, 113.5 (CH-arom.), 70.1 (C-quat.) 42.2, 41.6 (CH_3), 33.7 (CH) 30.2, 28.2, 21.4, 21.1 (CH_2) ppm. Note: The ipso carbon bound to boron could not be detected in the $^{13}\text{C}\{\text{H}\}$ NMR. ^{11}B NMR [128.4 MHz, CD_2Cl_2]: 43.0 ppm. ^{19}F NMR [376.3 MHz, CD_2Cl_2]: -123.1, -156.7, -163.4 ppm. Anal. Calc. for $\text{C}_{38}\text{H}_{30}\text{BAIF}_{15}\text{N}_3\text{O}$ (867.45): C, 52.62; H, 3.49, N, 4.84, Found: C, 52.64; H, 3.75, N, 4.26.

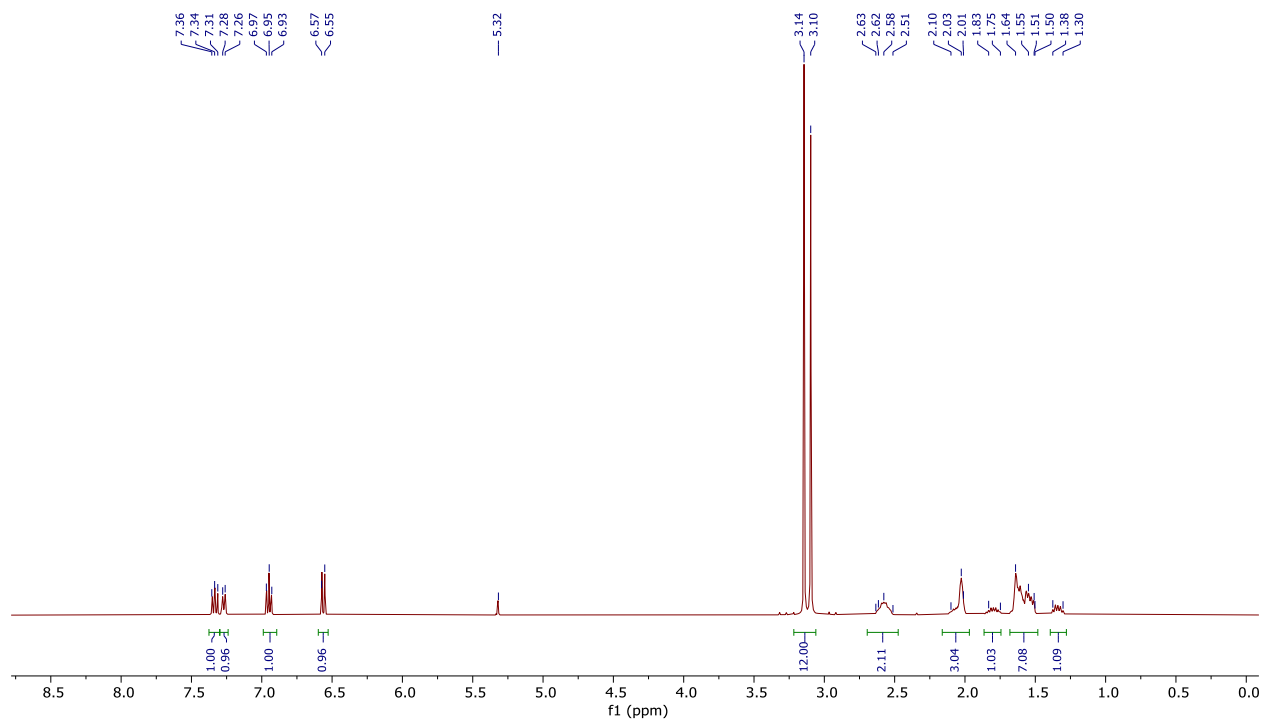


Figure S9. ^1H NMR spectrum of **4** in CD_2Cl_2 .

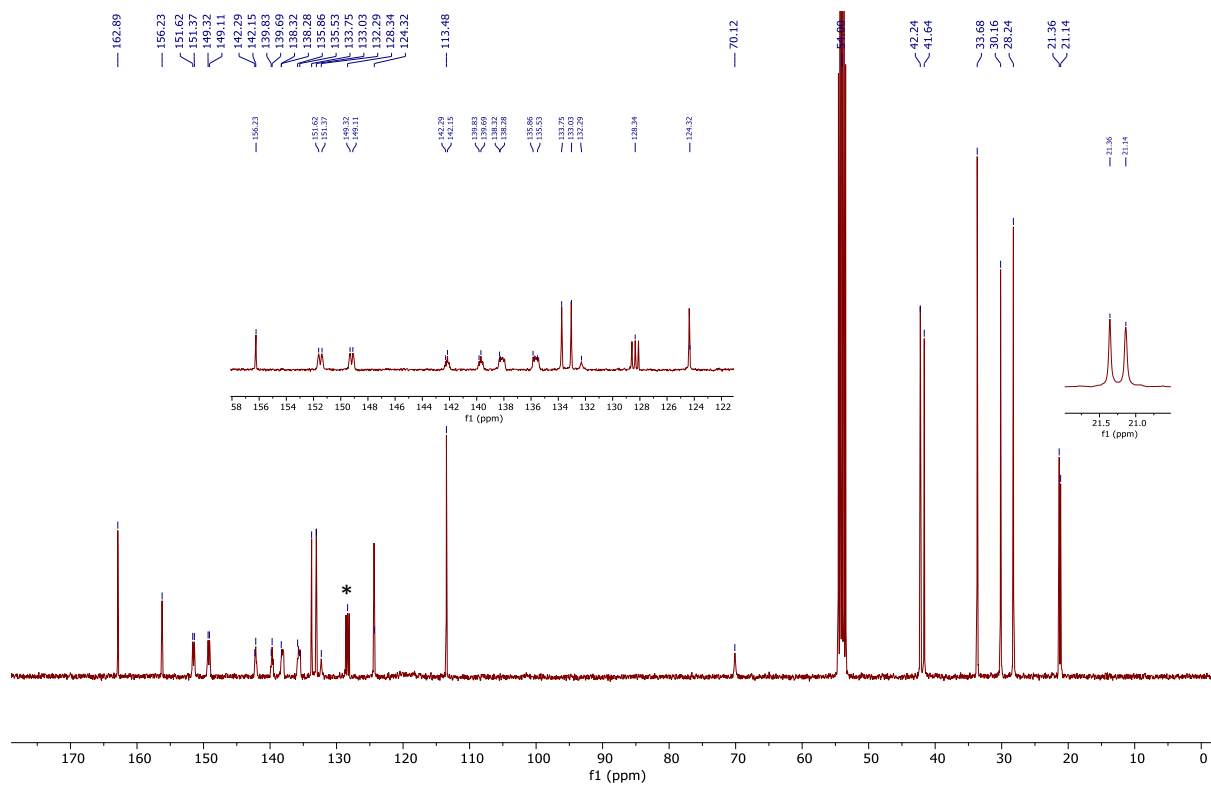


Figure S10. ^{13}C NMR spectrum of **4** in CD_2Cl_2 (* C_6D_6).

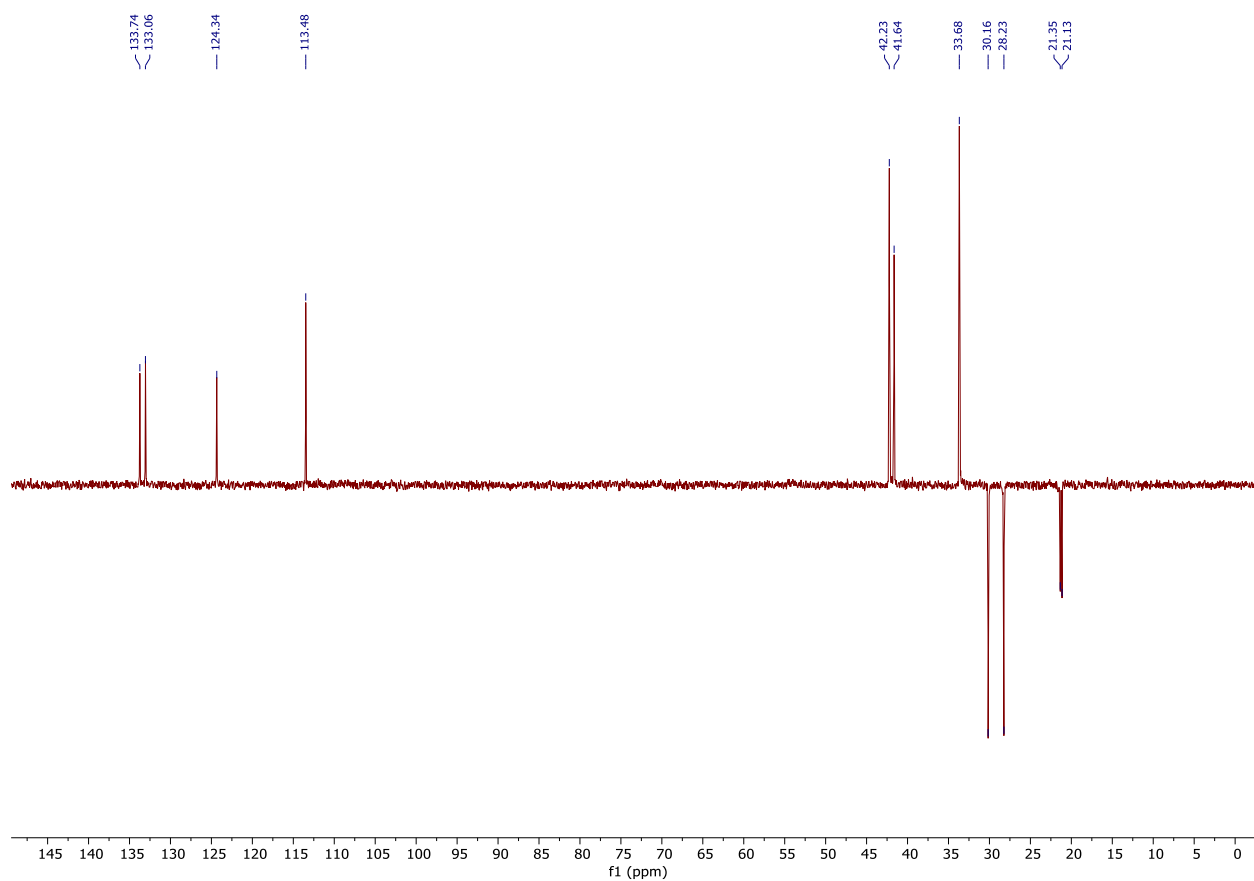


Figure S11. ^{13}C NMR (DEPT) spectrum of **4** in CD_2Cl_2 .

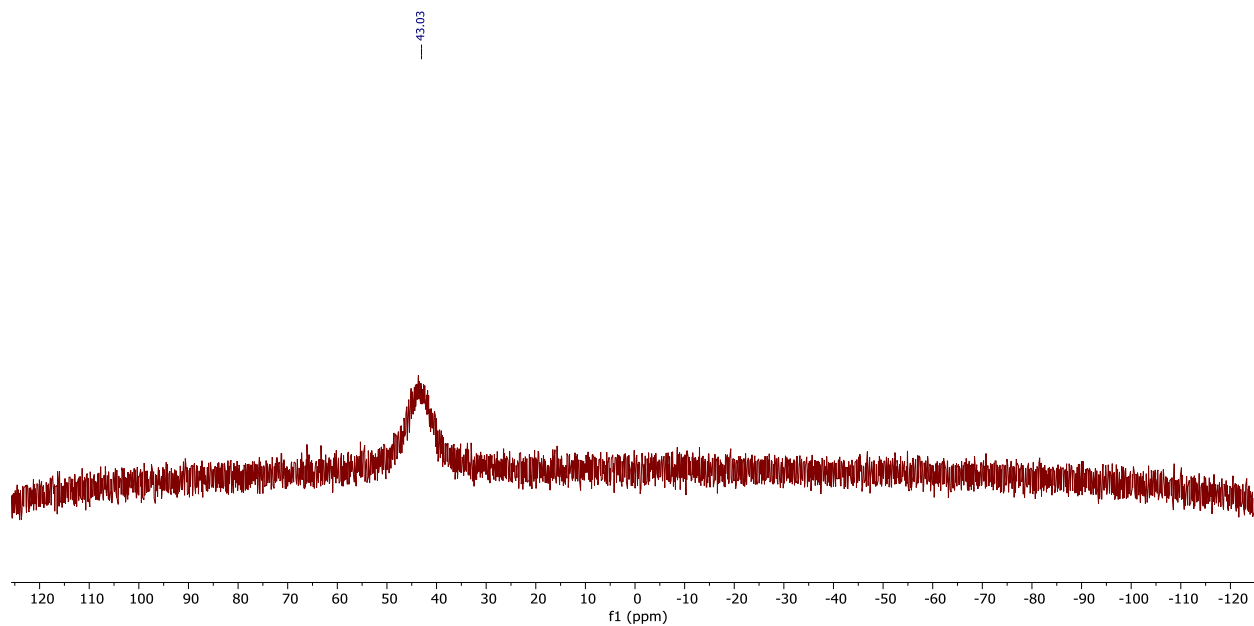


Figure S12. ^{11}B NMR spectrum of **4** in CD_2Cl_2 .

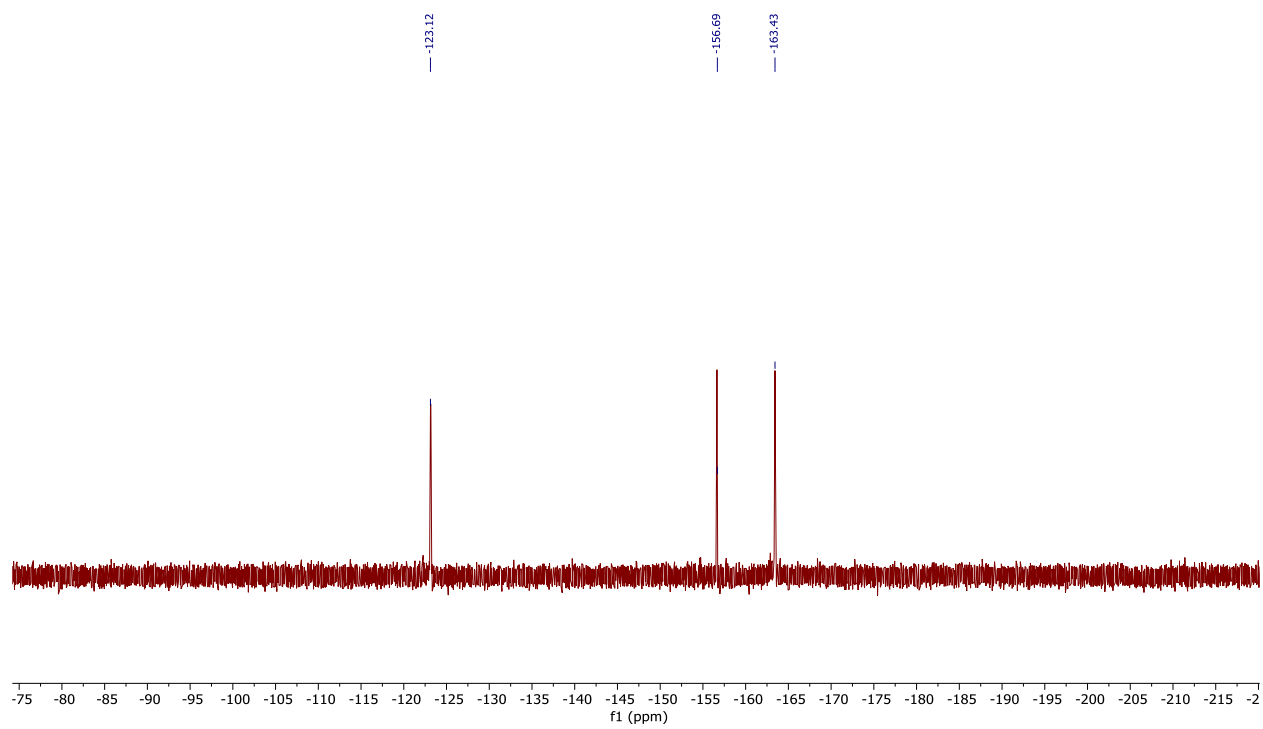
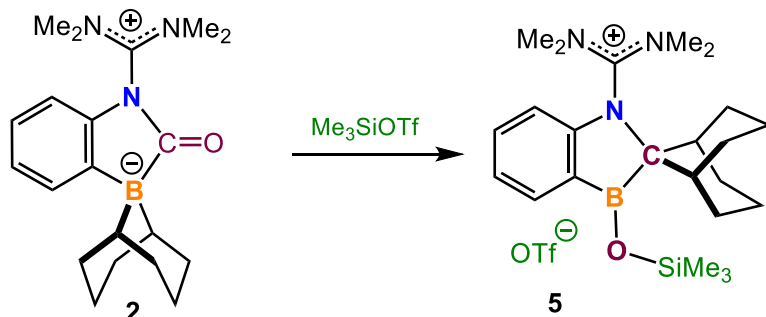


Figure S13. ^{19}F NMR spectrum of **4** in CD_2Cl_2 .

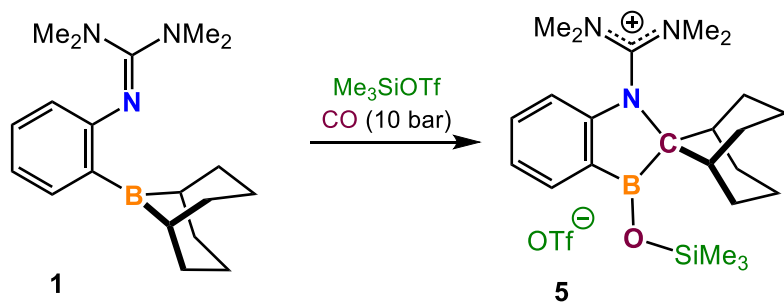
2.4. Synthesis of 5

Method 1: In the glove box, a Schlenk flask (30 mL) was charged with **2** (95 mg, 0.28 mmol), Me₃SiOTf (63 mg, 0.28 mmol) and benzene (5 mL). The reaction mixture was



stirred for 2 hours at room temperature and the resulting colorless crystals were washed once with benzene and dried under vacuum to give 120 mg (76%) of **5**.

Method 2: In the glove box, a 40 mL scintillation vial with a magnetic stir bar was charged with **1** (50 mg, 0.16 mmol), Me₃SiOTf (38 mg, 0.17 mmol) and benzene (5 mL). The vial was placed in a Parr reactor and the reaction mixture was stirred overnight at room temperature under 10 bar CO pressure. After the Parr reactor was vented, the obtained white suspension was transferred to a 30 mL Schlenk flask. After centrifugation and decantation of the solvent, the precipitate was washed twice with benzene and dried under vacuum to give 77 mg (85%) of **5** as a colorless solid.



After centrifugation and decantation of the solvent, the precipitate was washed twice with benzene and dried under vacuum to give 77 mg (85%) of **5** as a colorless solid.

¹H NMR [400 MHz, CD₂Cl₂]:

7.65 (d, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 7.55 (t, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 7.13 (t, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 6.56 (d, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 3.32, 3.08 (2s, CH₃, 2 × 6 H), 2.51-2.58 (m, CH-skeleton, 2 H), 1.99-2.19 (m, CH₂-skeleton, 4 H), 1.49-1.75 (m, CH-skeleton, 8 H) ppm. ¹³C{H} NMR [125 MHz, CD₂Cl₂]: 162.9 (C=N), 158.9 (C-arom.), 136.1, 133.5 (CH-arom.), 124.6 (C-B), 123.5 (CH-arom.), 121.5 (q, ¹J_{C-F} 319 Hz, CF₃), 112.8 (CH-arom.), 72.6 (C-quat.), 43.0, 42.0 (CH₃), 33.3 (CH), 30.9, 28.0, 20.6, 20.0 (CH₂), 1.9 (SiMe₃) ppm. ¹¹B NMR [128.4 MHz, CD₂Cl₂]: 46.0 ppm. ¹⁹F NMR [376.3 MHz, CD₂Cl₂]: -77.7 ppm. ²⁹Si NMR [99.4 MHz, CD₂Cl₂]: 16.1 ppm. Anal. Calc. for C₂₄H₃₉BF₃N₃O₄SSi⁺ (561.54): C, 51.33; H, 7.00, N, 7.48, Found: C, 51.33; H, 6.88, N, 7.44.

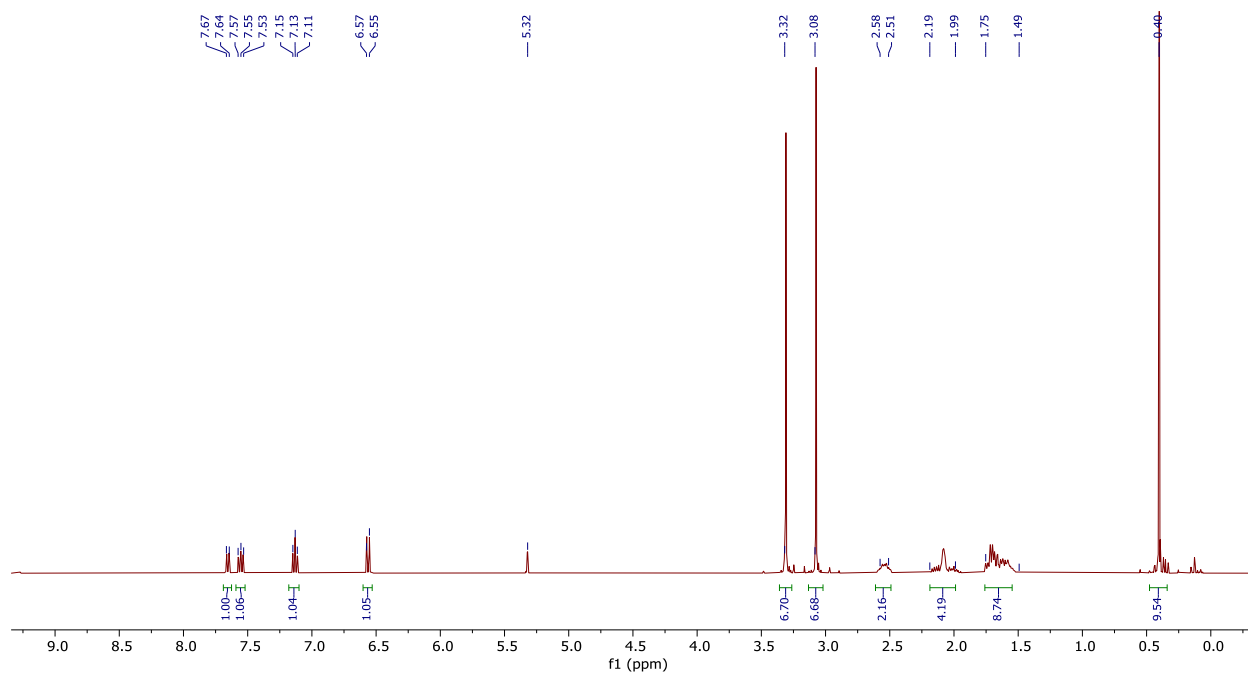


Figure S14. ^1H NMR spectrum of **5** in CD_2Cl_2 .

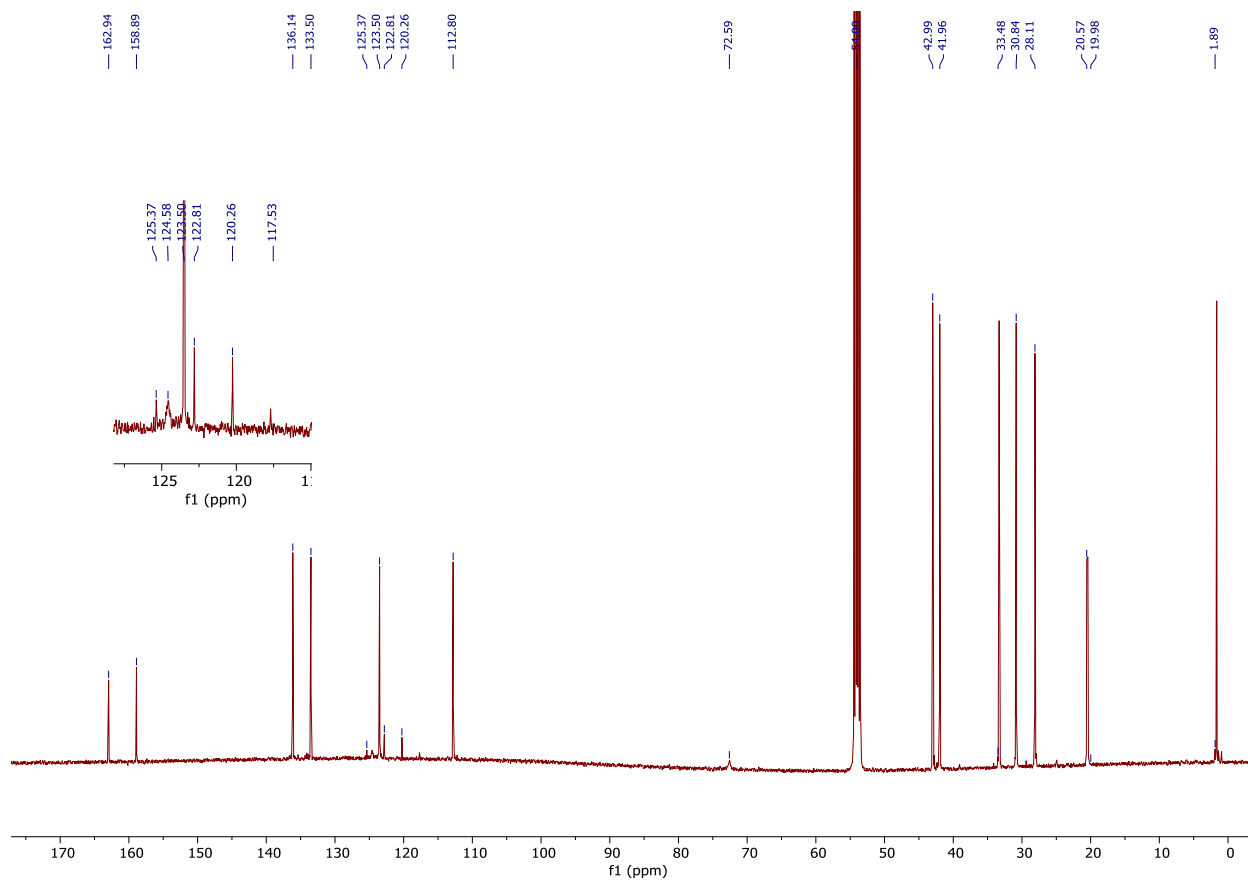


Figure S15. ^{13}C NMR spectrum of **5** in CD_2Cl_2 .

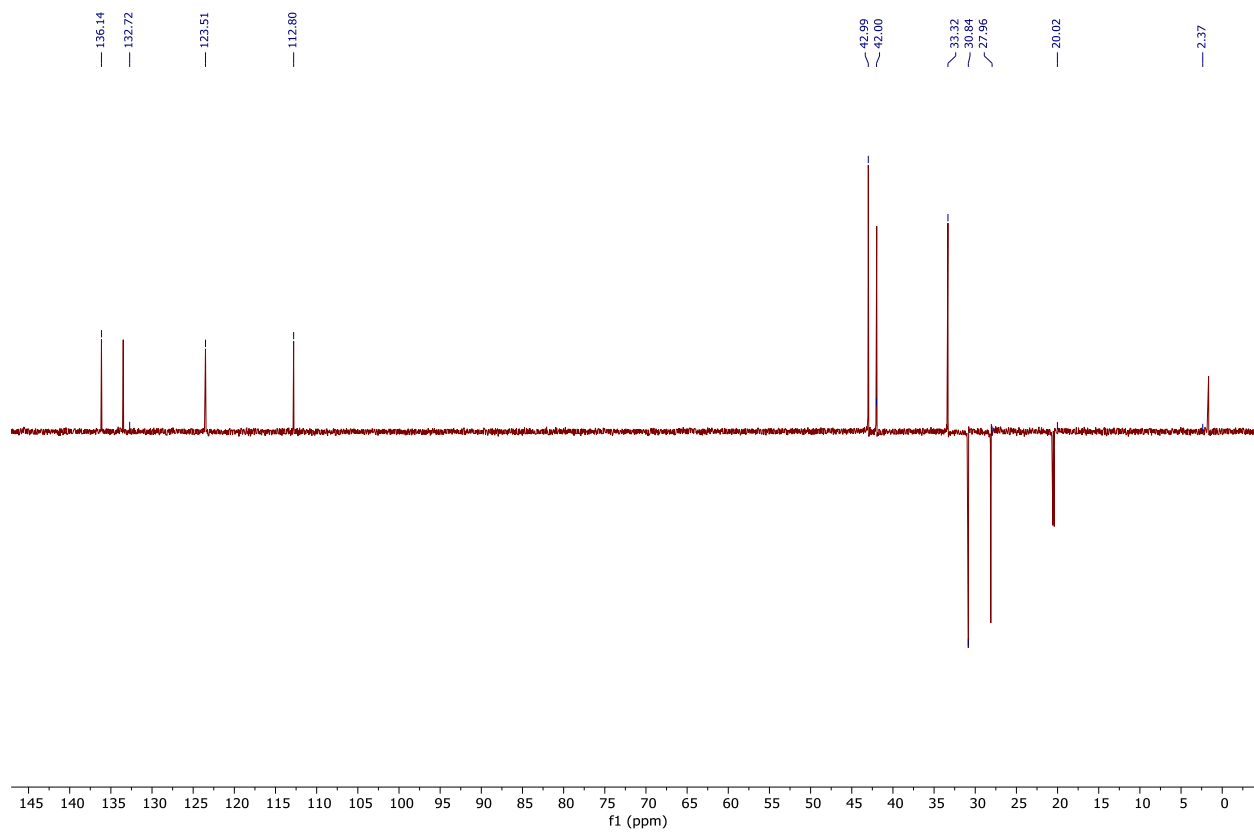


Figure S16. ^{13}C NMR (DEPT) spectrum of **5** in CD_2Cl_2 .

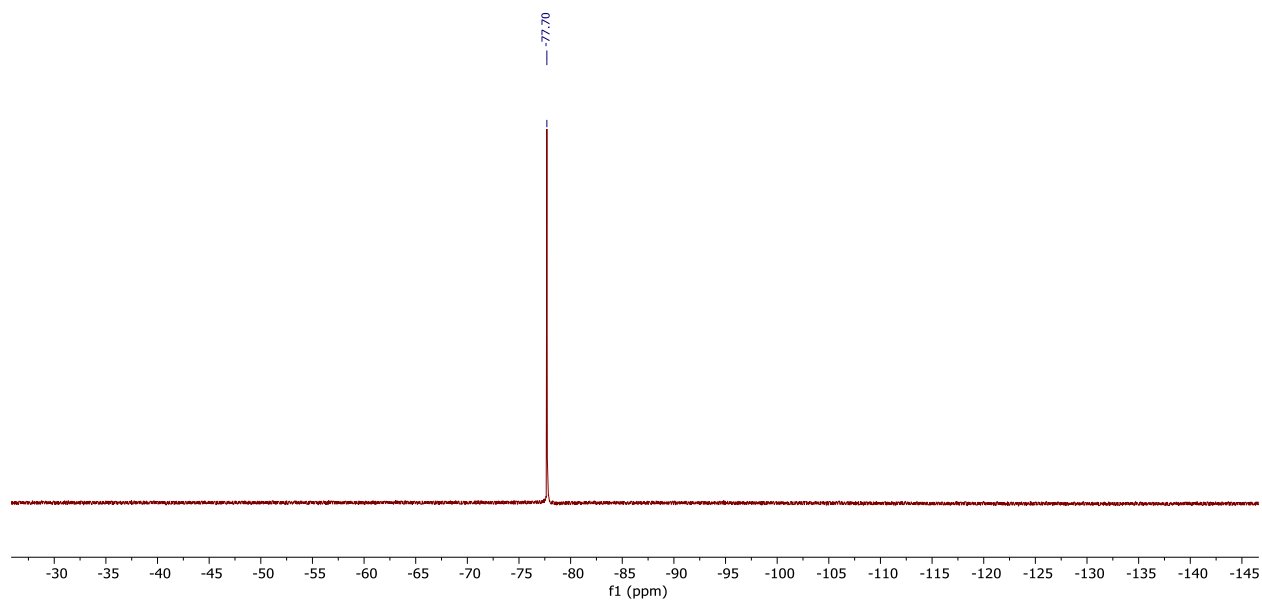


Figure S17. ^{19}F NMR spectrum of **5** in CD_2Cl_2 .

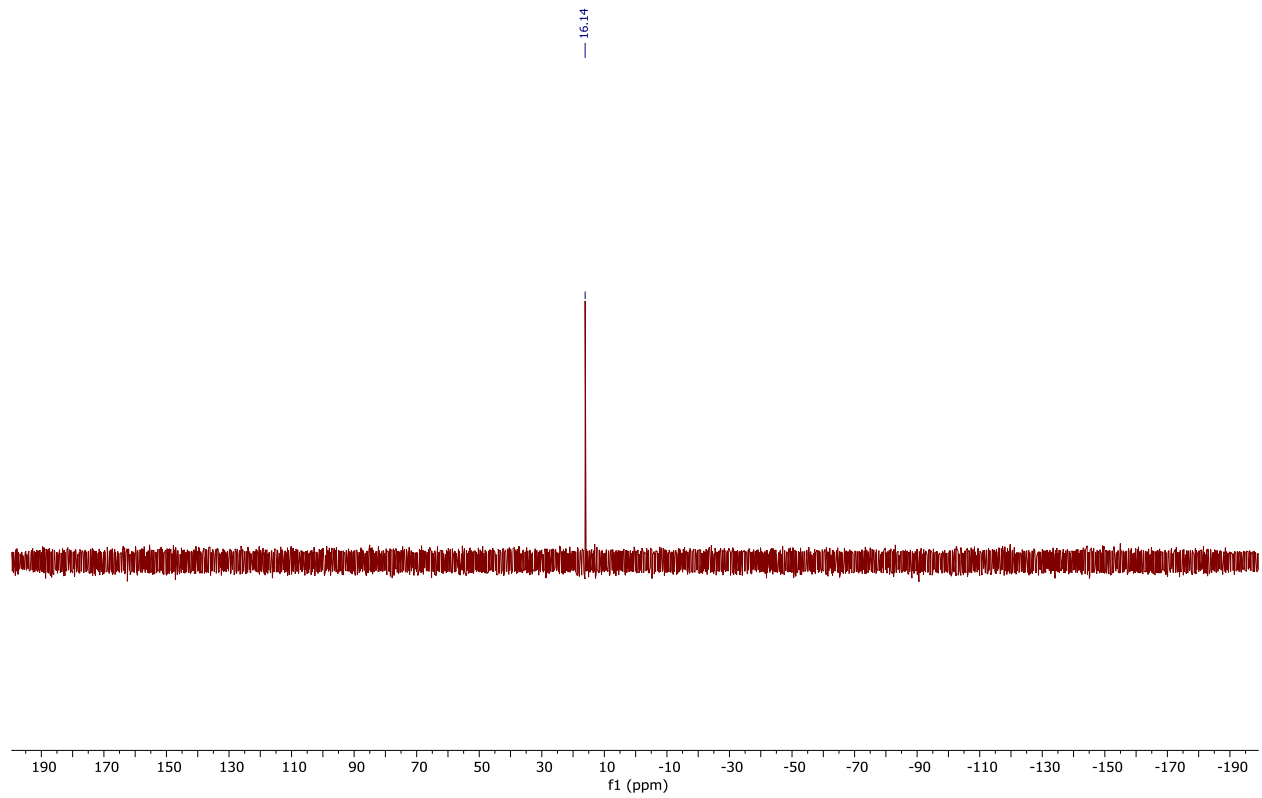


Figure S18. ^{29}Si NMR spectrum of **5** in CD_2Cl_2 .

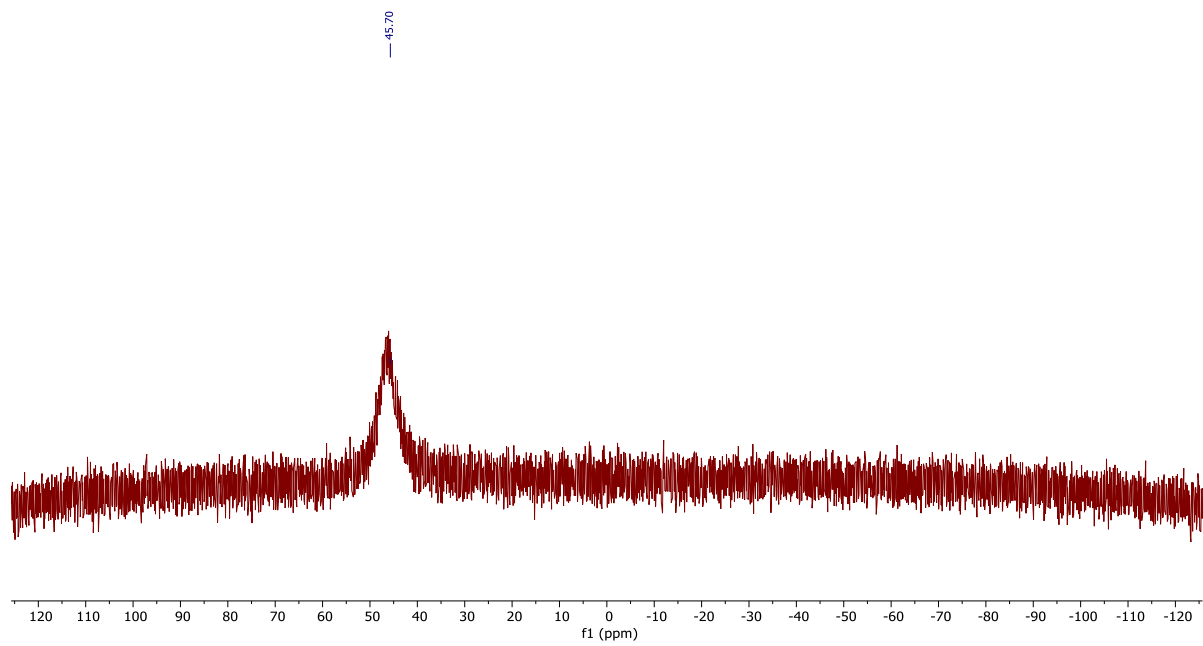
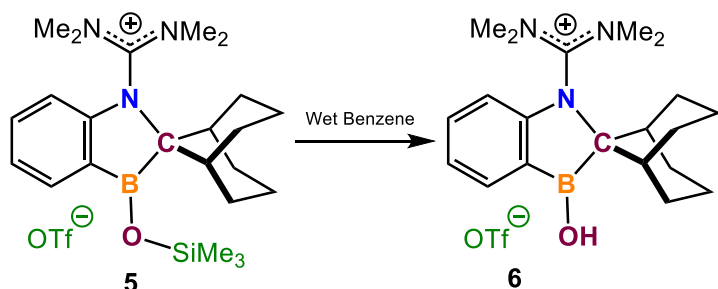


Figure S19. ^{11}B NMR spectrum of **5** in CD_2Cl_2 .

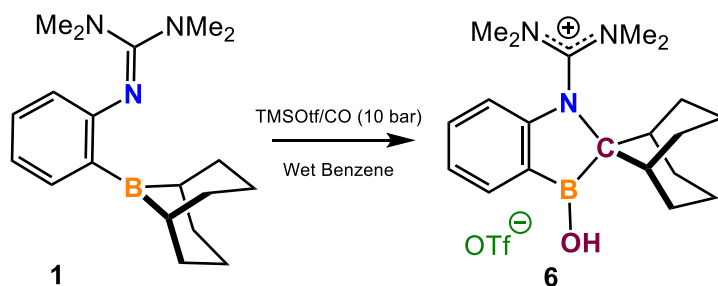
2.5. Synthesis of **6**

Method 1. A scintillation vial was charged with **5** (190 mg, 0.34 mmol), benzene (5 mL) and water (0.05 mL). The reaction mixture was stirred for one hour at room temperature



and the resulting colorless crystals were filtered, washed with benzene and dried under vacuum to give 150 mg (90%) of **6**.

Method 2. In the glove box, a 40 mL scintillation vial with a magnetic stir bar was charged with **1** (50 mg, 0.16 mmol), Me₃SiOTf (38 mg, 0.17 mmol) and benzene (5 mL). The vial was placed in a Parr reactor and the reaction mixture was stirred overnight at room temperature under 10 bar CO pressure. Then the Parr reactor was vented, the white suspension transferred to a 20 mL scintillation vial and a drop of water was added. The reaction mixture was stirred for one



hour and the resulting colorless crystals were filtered, washed with benzene and dried under vacuum to give 68 mg (88%) of **6**.

¹H NMR [400 MHz, DMSO-d₆]: 11.0 (s, B-OH, 1 H), 7.92 (d, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 7.54 (t, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 7.12 (t, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 6.64 (d, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 3.29, 3.02 (2s, CH₃, 2 × 6 H), 2.61-2.76 (m, CH-skeleton, 2 H), 1.92 -2.16 (m, CH₂-skeleton, 4 H), 1.56 -1.71 (m, CH-skeleton, 8 H) ppm. ¹³C{H} NMR [125 MHz, DMSO-d₆]: 160.7 (C=N), 157.3 (C-arom.), 134.6, 132.7 (CH-arom.), 123.8 (C-B), 122.0 (CH-arom.), 120.7 (q, ¹J_{C-F} 319 Hz, CF₃), 111.9 (CH-arom.), 70.2 (C-quat.), 41.5, 40.9 (CH₃), 31.9 (CH), 30.0, 26.8, 20.0, 19.9 (CH₂) ppm. ¹¹B NMR [128.4 MHz, DMSO-d₆]: 19.0 ppm. ¹⁹F NMR [376.3 MHz, DMSO-d₆]: -77.6 ppm. Anal. Calc. for C₂₁H₃₁BF₃N₃O₄⁺ (489.36): C, 51.54; H, 6.39, N, 8.59, Found: C, 51.85; H, 6.15, N, 8.55. IR (solid) $\tilde{\nu}_{\text{(OH)}}$ = 3213 cm⁻¹.

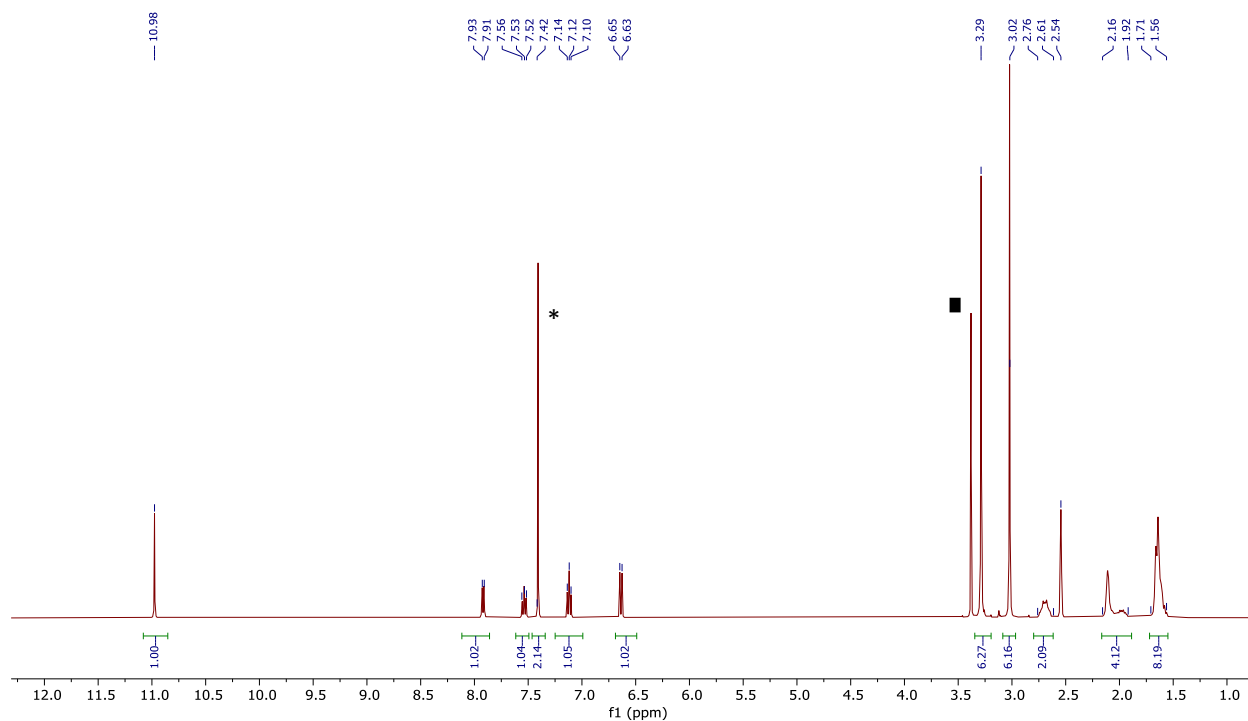


Figure S20. ^1H NMR spectrum of **6** in DMSO-d_6 (* benzene).

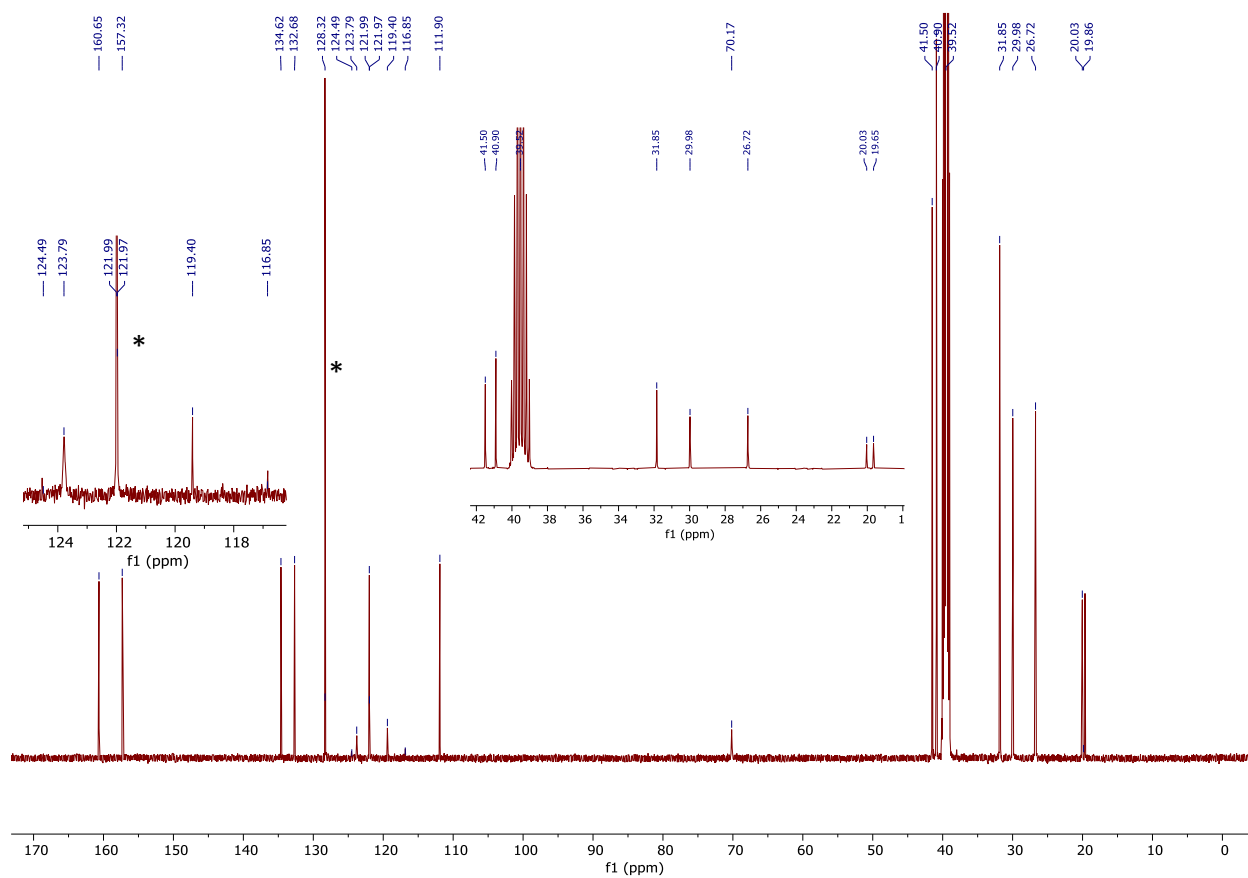


Figure S21. ^{13}C NMR spectrum of **6** in DMSO-d_6 (* benzene).

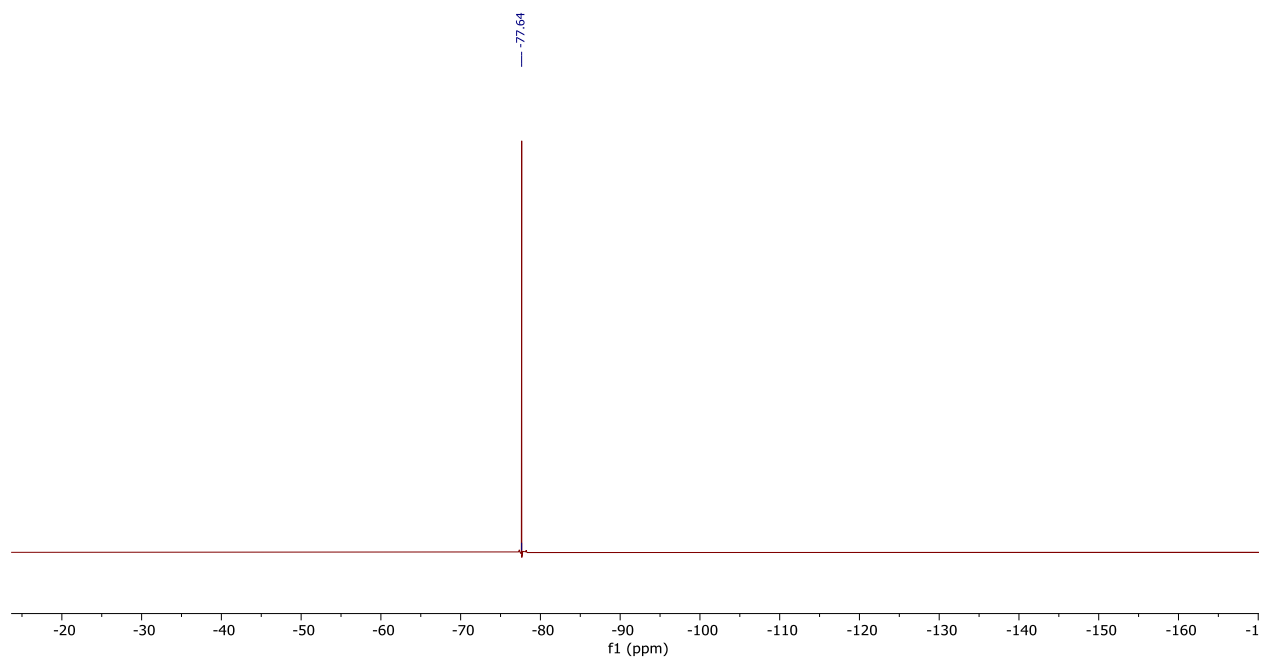


Figure S22. ^{19}F NMR spectrum of **6** in DMSO-d_6 .

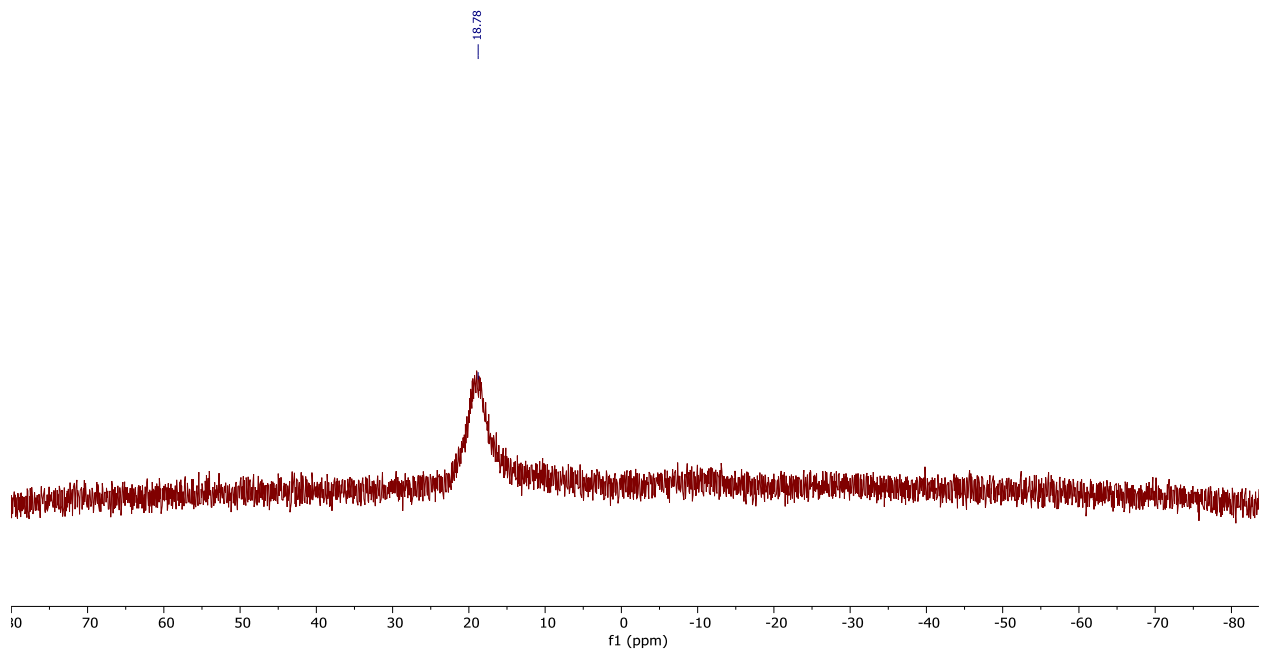
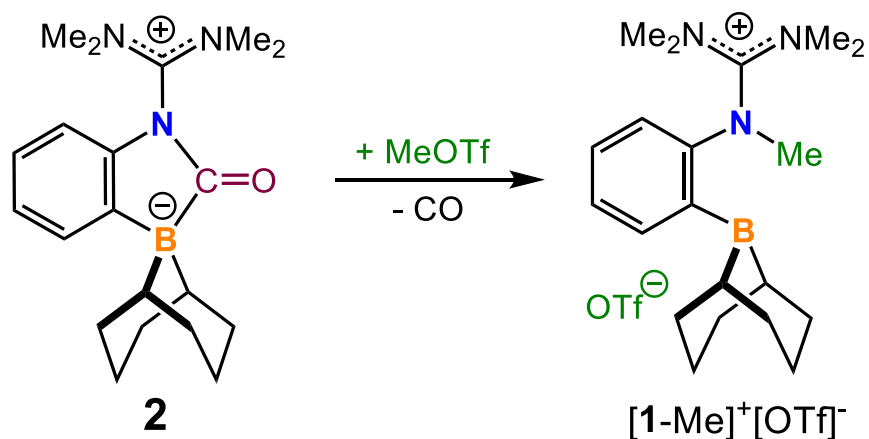


Figure S23. ^{11}B NMR spectrum of **6** in DMSO-d_6 .

2.6. Reaction of **2** with MeOTf - Formation of salt $[1\text{-Me}]^+[\text{OTf}]^-$



In the glove box, a J-Young NMR tube was charged with **2** (10 mg, 0.029 mmol), MeOTf (4.9 mg, 0.029 mmol) and C_6D_6 (0.4 mL). After the reaction mixture was heated at 50°C overnight, the solvent was removed under vacuum. The residue was washed once with hexanes, dried under vacuum and identified by NMR spectroscopy as salt $[1\text{-Me}]^+[\text{OTf}]^-$. ^1H NMR [400 MHz, C_6D_6]: 7.54 (d, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 7.39 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 7.05 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 6.99 (d, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 2.80 (br, CH_3 , 6 H), 2.54 (br, CH_3 , 6 H), 2.88 (s, CH_3 , 3 H), 1.26-2.12 (m, BBN, 14 H) ppm. $^{13}\text{C}\{\text{H}\}$ NMR [100.4 MHz, C_6D_6]: 162.7 (C=N), 147.3 (C-arom.), 135.4 (CH-arom.), 134.4 (C-B), 133.3, 126.6, 125.2 (CH-arom.), 122.4 (q, $^2J_{\text{C-F}} = 322$ Hz, CF_3), 43.9, 41.3, 39.8 (CH_3), 34.9 (CH_2), 32.3 (CH), 23.3 (CH_2) ppm. ^{11}B NMR [128.4 MHz, C_6D_6]: 77.3 ppm. ^{19}F NMR [376.3 MHz, C_6D_6]: -77.9 ppm. Salt $[1\text{-Me}]^+[\text{OTf}]^-$ was independently generated in C_6D_6 by mixing **1** and MeOTf in a J-Young tube. The obtained NMR spectroscopic data were in agreement with the above-reported values.

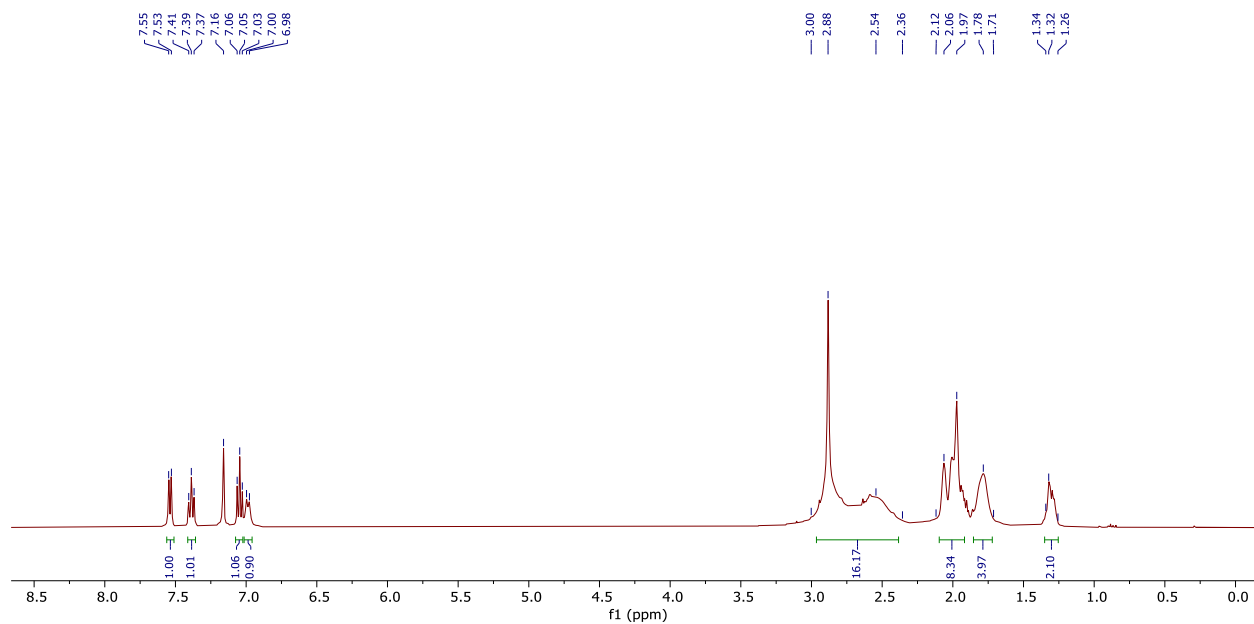


Figure S24. ^1H NMR spectrum of $[\text{1-Me}]^+[\text{OTf}]^-$ in C_6D_6 .

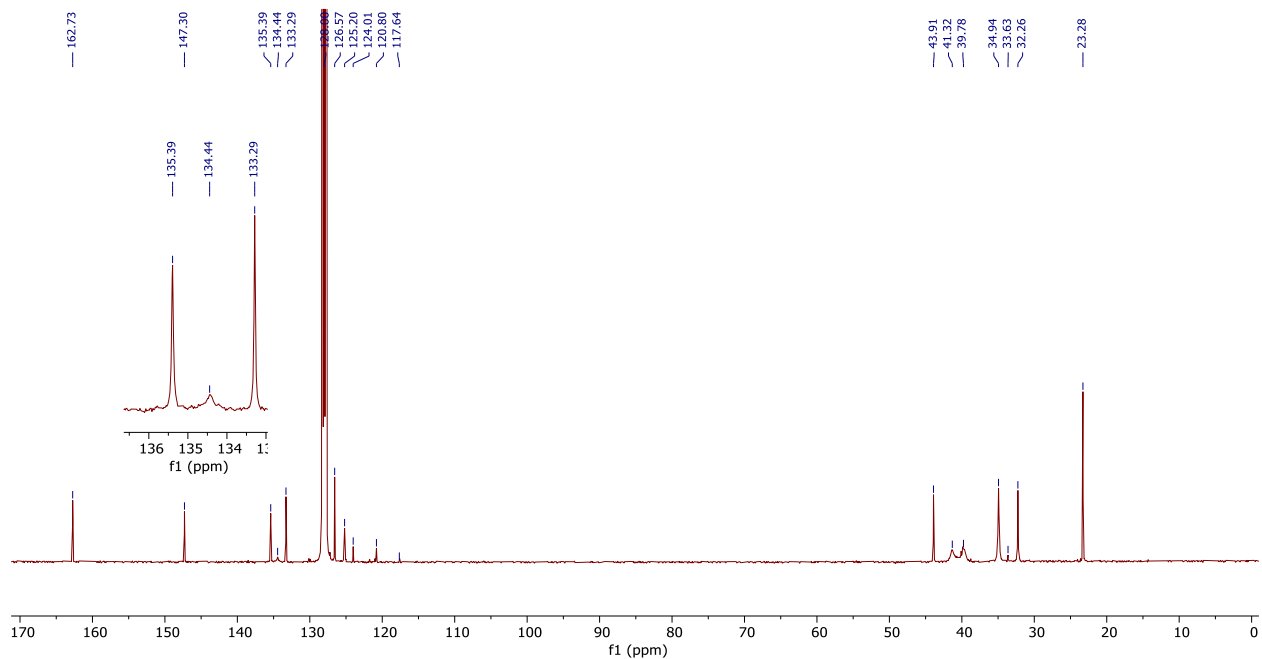


Figure S25. ^{13}C NMR spectrum of $[\text{1-Me}]^+[\text{OTf}]^-$ in C_6D_6 .

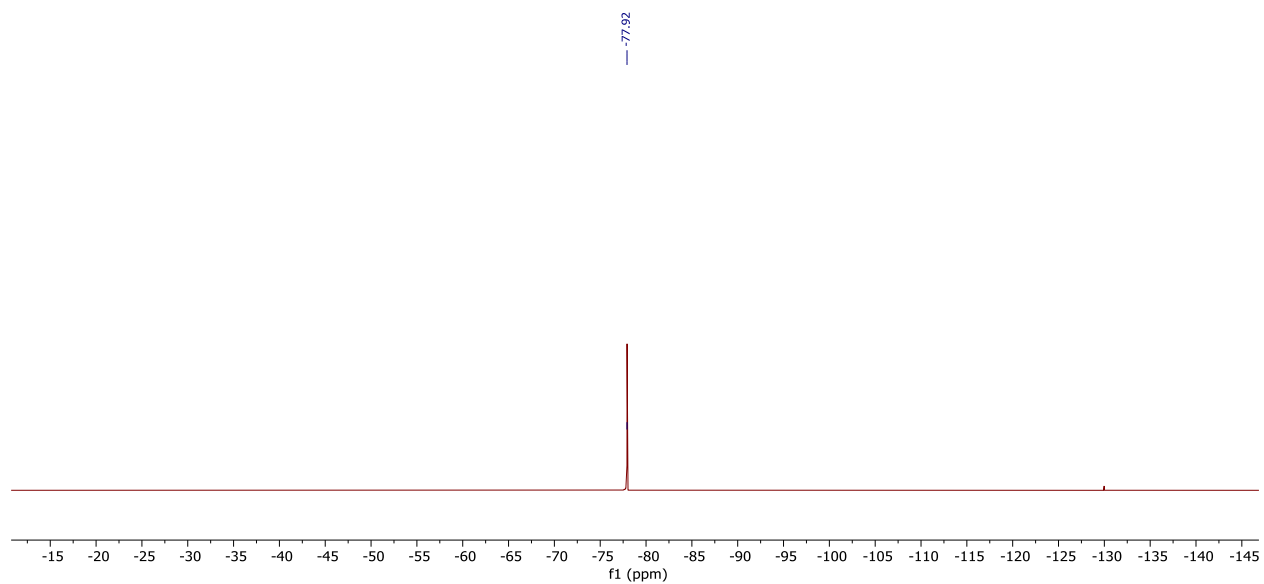


Figure S26. ^{19}F NMR spectrum of $[\mathbf{1}\text{-Me}]^+[\text{OTf}]^-$ in C_6D_6 .

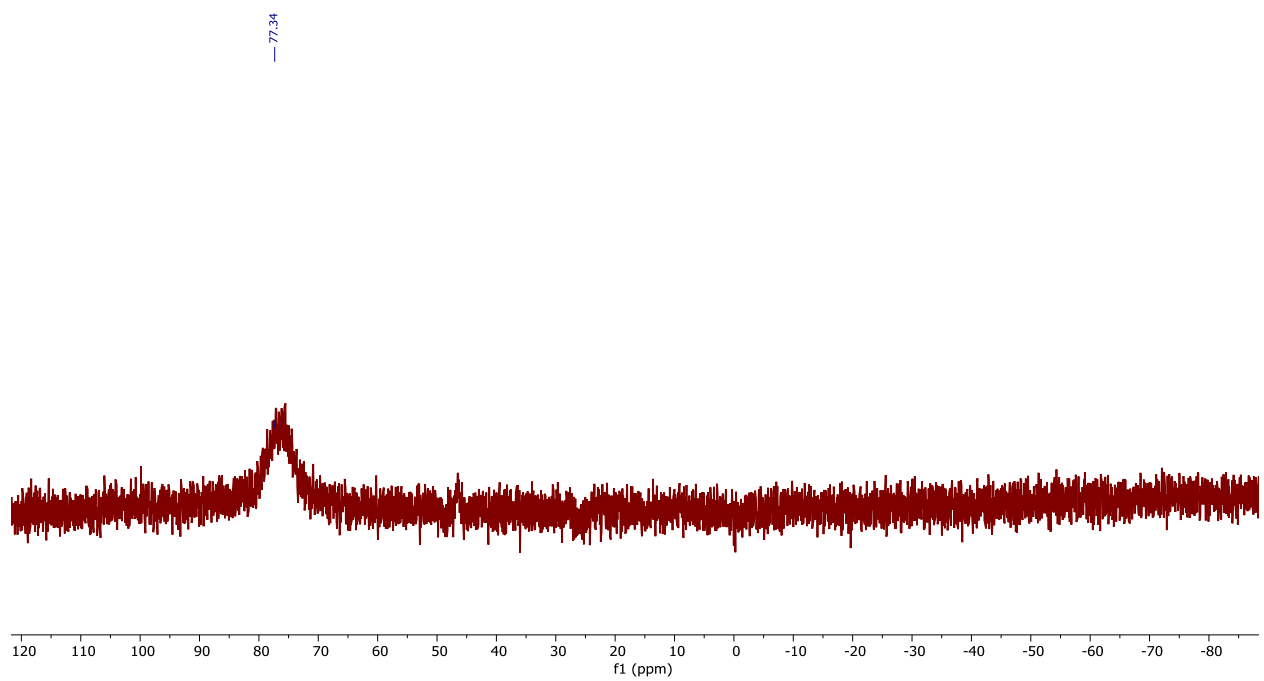
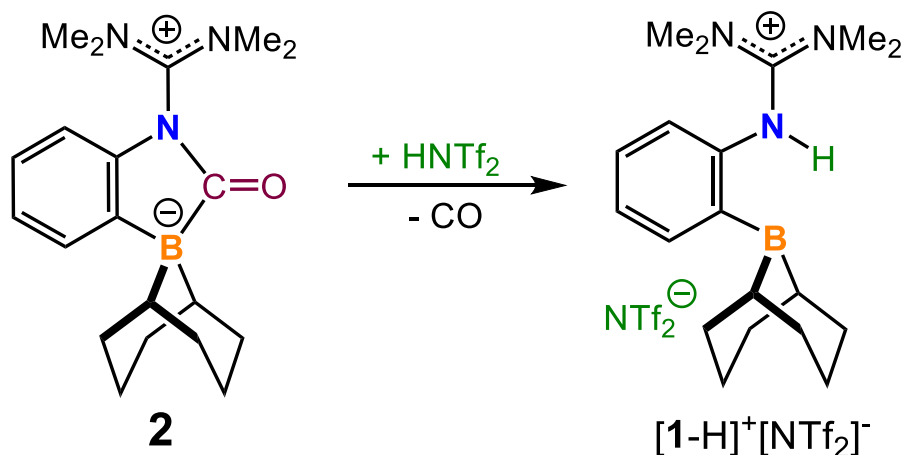


Figure S27. ^{19}F NMR spectrum of $[\mathbf{1}\text{-Me}]^+[\text{OTf}]^-$ in C_6D_6 .

2.7. Reaction of **2** with HNTf₂ - Formation of salt [1-H]⁺[NTf₂]⁻



In the glove box, a J-Young NMR tube was charged with **2** (10 mg, 0.029 mmol), HNTf₂ (8.3 mg, 0.029 mmol) and C₆D₆ (0.4 mL). A single product was formed, which by NMR spectroscopic analysis was identified as salt [1-H]⁺[NTf₂]⁻. ¹H NMR [400 MHz, C₆D₆]: 7.58 (d, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 7.47 (s, NH, 1 H), 7.30 (t, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 7.04 (t, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 6.91 (d, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 2.40 (s, CH₃, 12 H), 1.34-2.06 (m, BBN, 14 H) ppm. ¹³C{H} NMR [100.4 MHz, C₆D₆]: 158.8 (C=N), 141.7 (C-arom.), 135.7 (CH-arom.), 134.3 (C-B), 133.5, 128.2, 122.8 (CH-arom.), 120.6 (q, ²J_{C-F} = 256 Hz, CF₃), 39.9 (CH₃), 34.5 (CH₂), 31.7 (CH), 23.4 (CH₂) ppm. ¹¹B NMR [128.4 MHz, C₆D₆]: 58.0 ppm. ¹⁹F NMR [376.3 MHz, C₆D₆]: -78.2 ppm. IR (solid) $\tilde{\nu}_{(N-H)}$ = 3326 cm⁻¹. Salt [1-H]⁺[NTf₂]⁻ was independently generated in C₆D₆ by mixing **1** and HNTf₂ in a J-Young NMR tube. The obtained NMR spectroscopic data were in agreement with the above values.

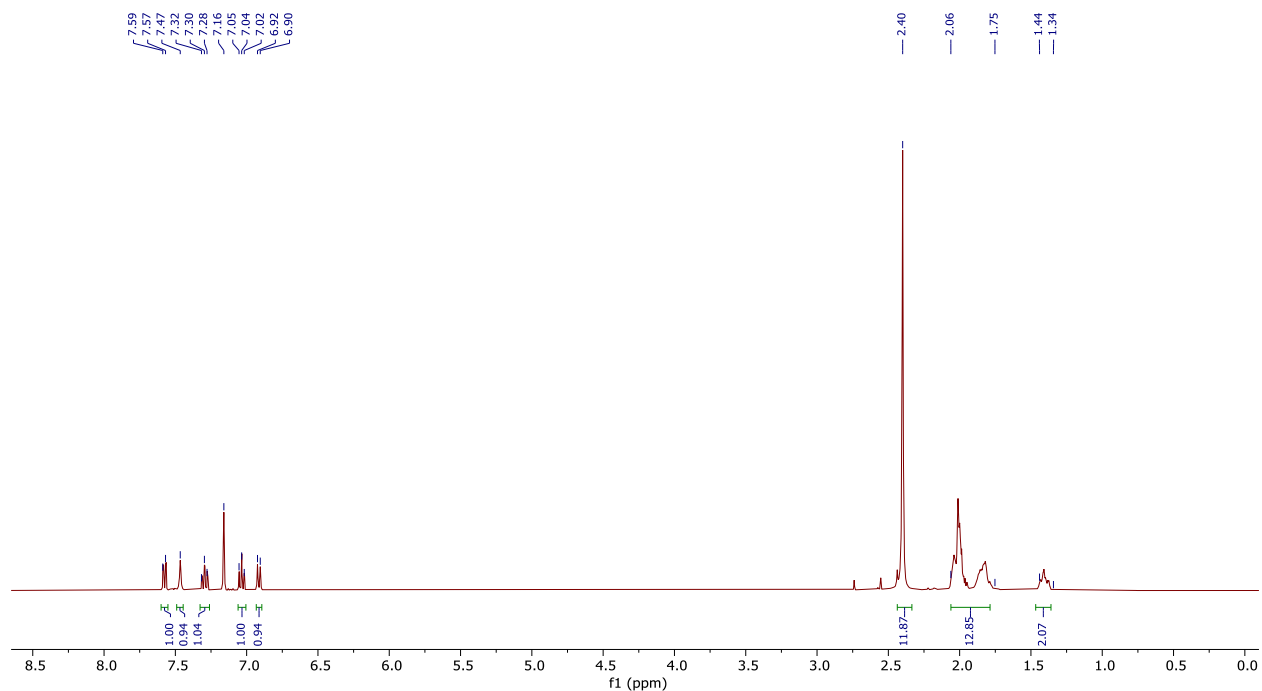


Figure S28. ^1H NMR spectrum of $[\mathbf{1}\text{-H}]^+[\text{NTf}_2]^-$ in C_6D_6 .

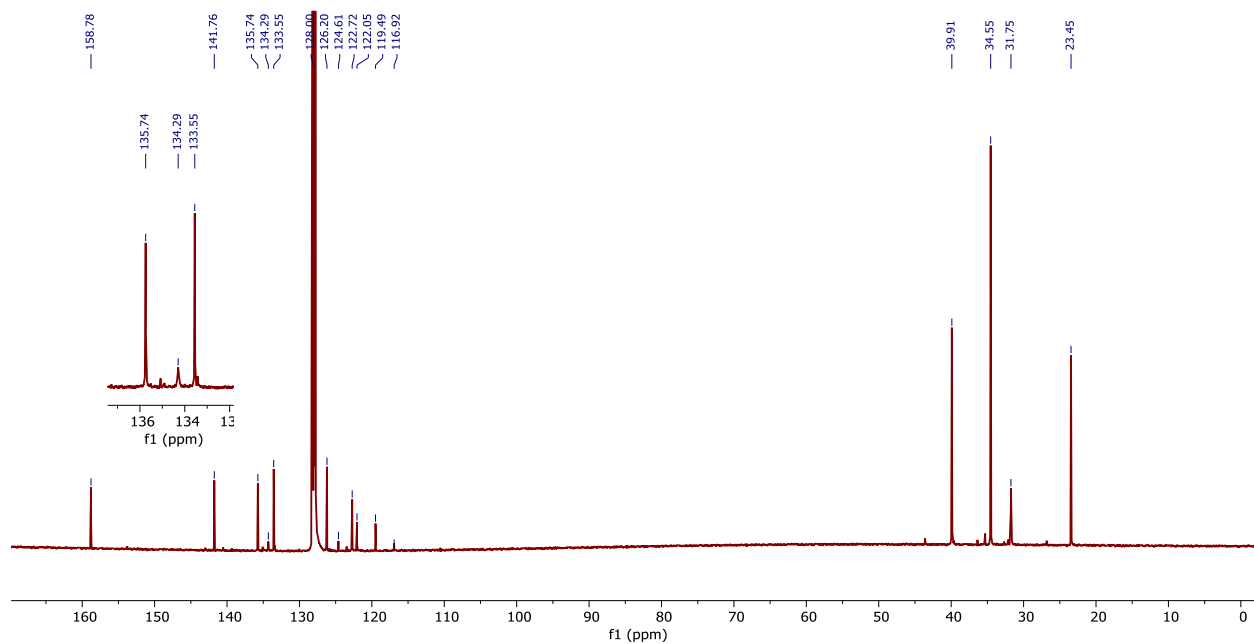


Figure S29. ^{13}C NMR spectrum of $[\mathbf{1}\text{-H}]^+[\text{NTf}_2]^-$ in C_6D_6 .

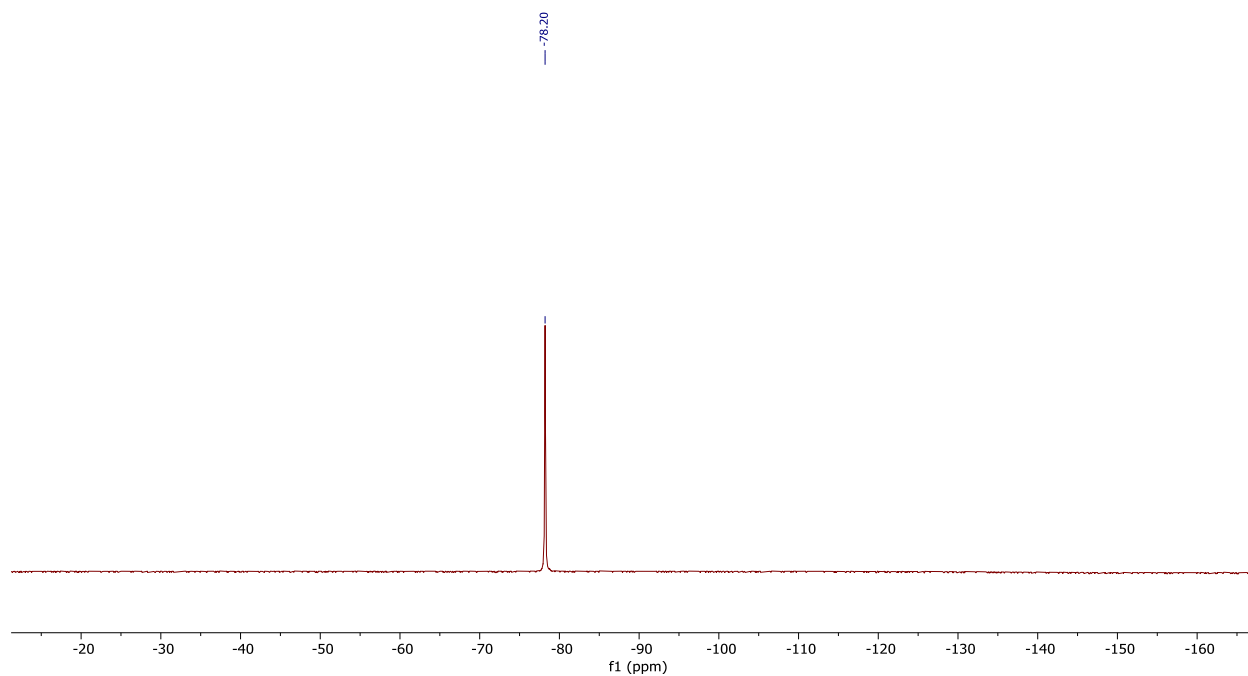


Figure S30. ^{19}F NMR spectrum of $[\text{1-H}]^+[\text{NTf}_2]^-$ in C_6D_6 .

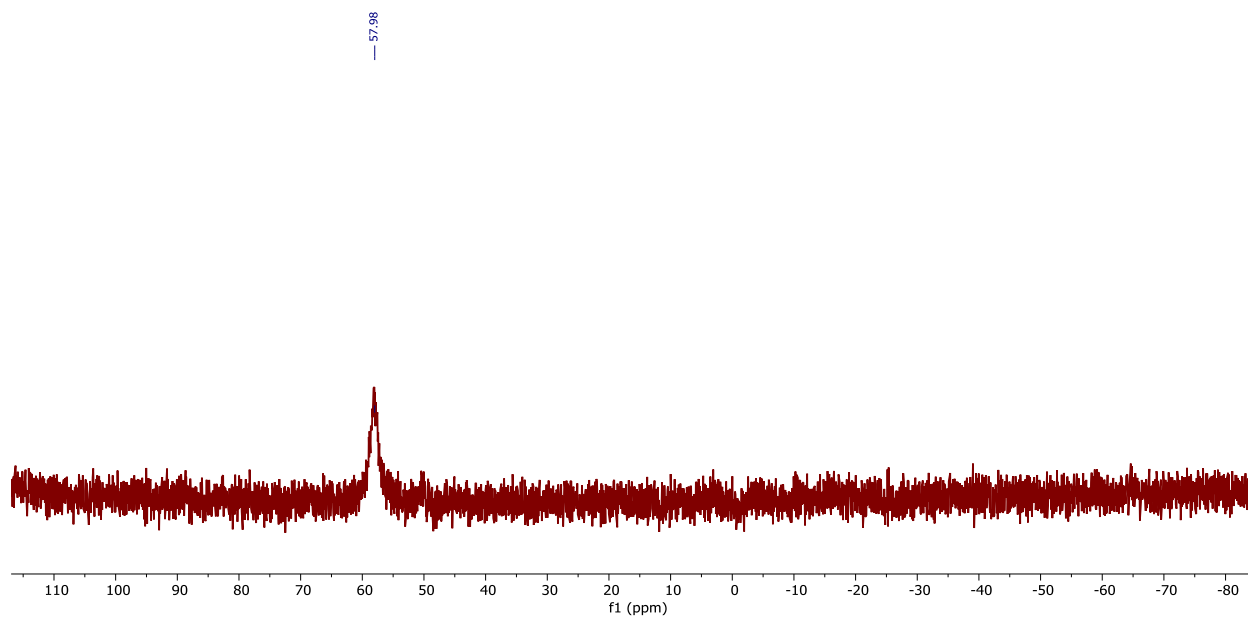


Figure S31. ^{11}B NMR spectrum of $[\text{1-H}]^+[\text{NTf}_2]^-$ in C_6D_6 .

2.8. Reaction of **2** with B(OC₆F₅)₃ – Formation of **7**

In the glove box, a J-Young NMR tube was charged with **2** (15 mg, 0.044 mmol), B(OC₆F₅)₃ (24.7 mg, 0.044 mmol), and C₆D₆ (0.5 mL). The reaction mixture was analyzed by NMR spectroscopy. ¹H NMR [400 MHz, C₆D₆]: 9.04 (d, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 7.13-7.21 (m, CH-arom., 2 H), 6.13 (d, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 2.42, 1.76 (2s, CH₃, 2 × 6 H), 1.03-2.48 (m, CH/CH₂-skeleton, 14 H) ppm. ¹³C{H} NMR [100.4 MHz, C₆D₆]: 163.3 (C=N), 156.2 (C-arom.), 142.9 (d, ¹J_{C-F} = 239 Hz, C-F), 139.7 (C-B), 138.1 (CH-arom.), 138.5 (d, ¹J_{C-F} = 247 Hz, C-F), 135.3 (d, ¹J_{C-F} = 228 Hz, C-F), 132.7 (CH-arom.), 131.5 (C-B), 124.7, 112.8 (CH-arom.), 68.7 (C-quat.), 40.3, 40.1 (CH₃), 33.2 (CH), 29.5, 27.4, 21.3, 20.6 (CH₂) ppm. ¹¹B NMR [128.4 MHz, C₆D₆]: 1.3 [B(OC₆F₅)₃] ppm. ¹⁹F NMR [376.3 MHz, C₆D₆]: -150.7, -167.7, -171.4 ppm.

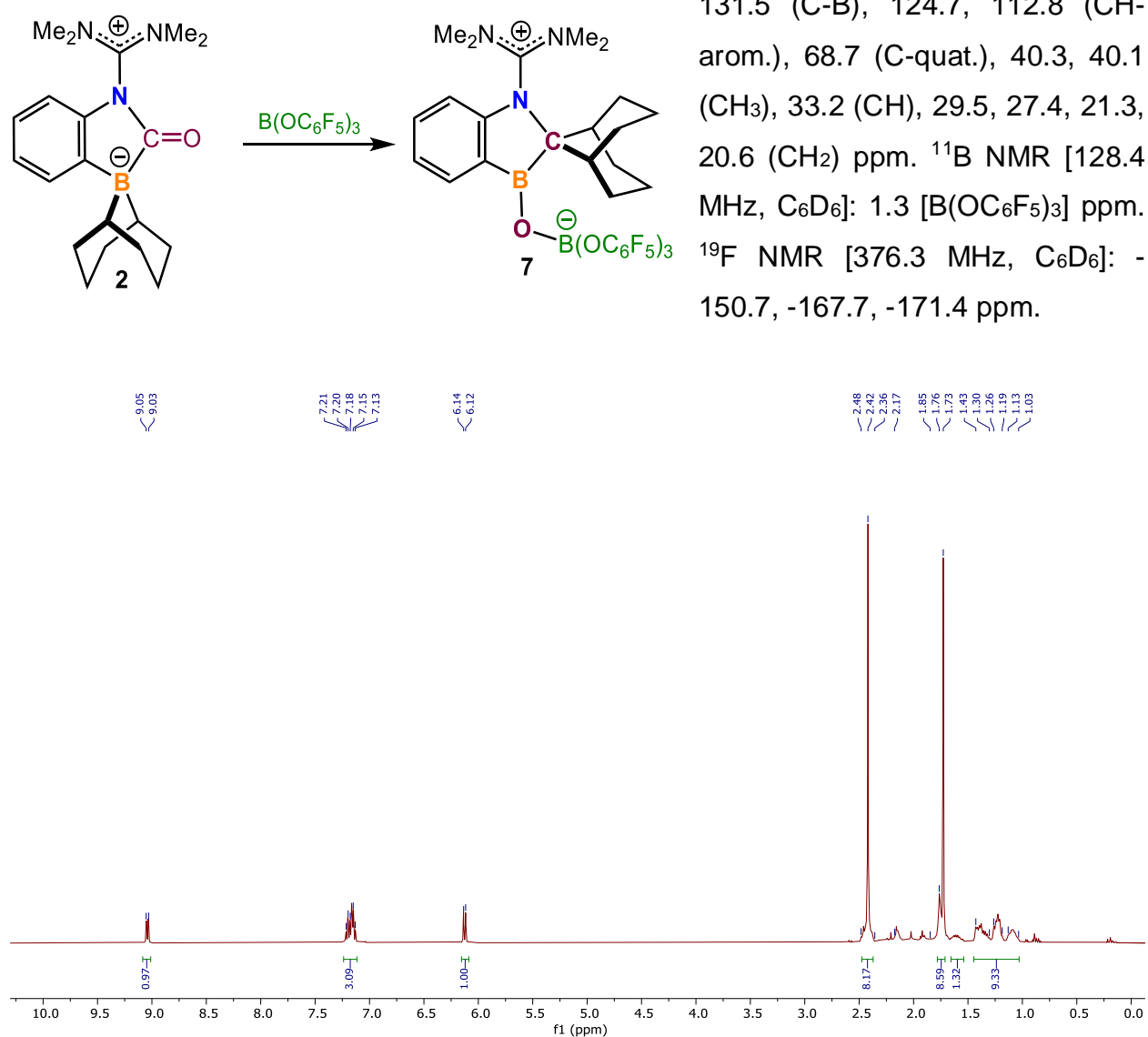


Figure S32. ¹H NMR spectrum of **7** in C₆D₆.

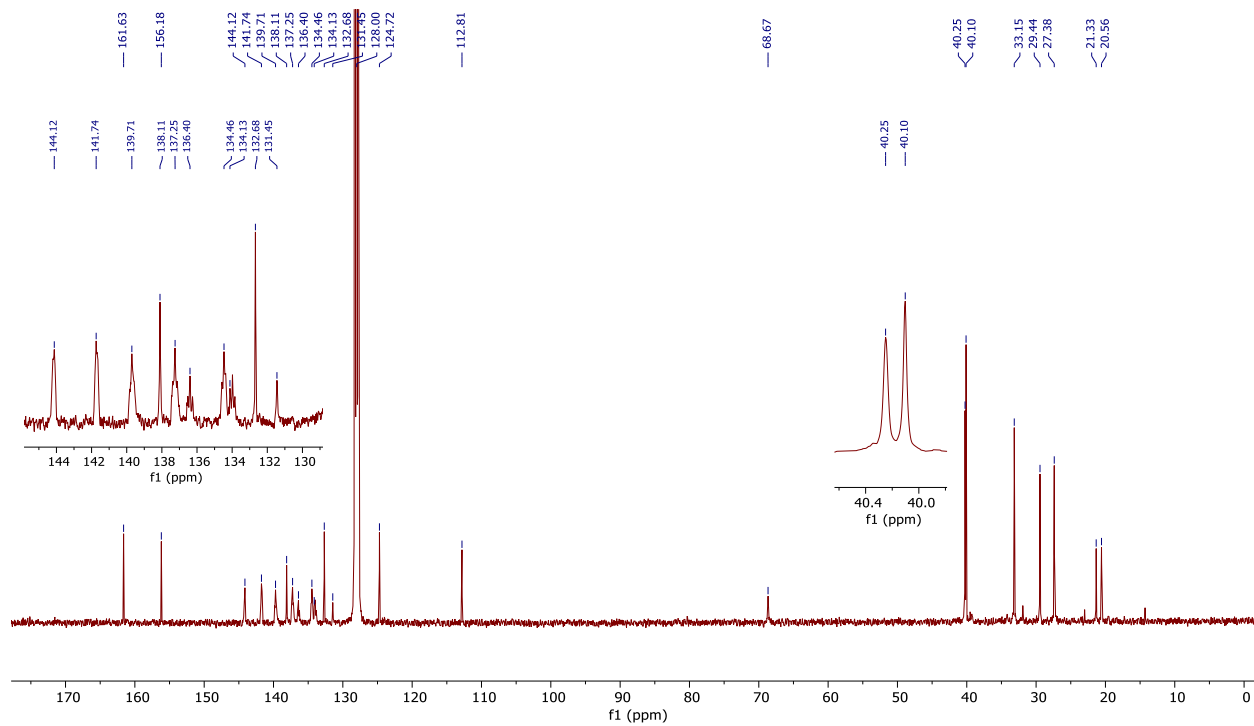


Figure S33. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of **7** in C_6D_6 .

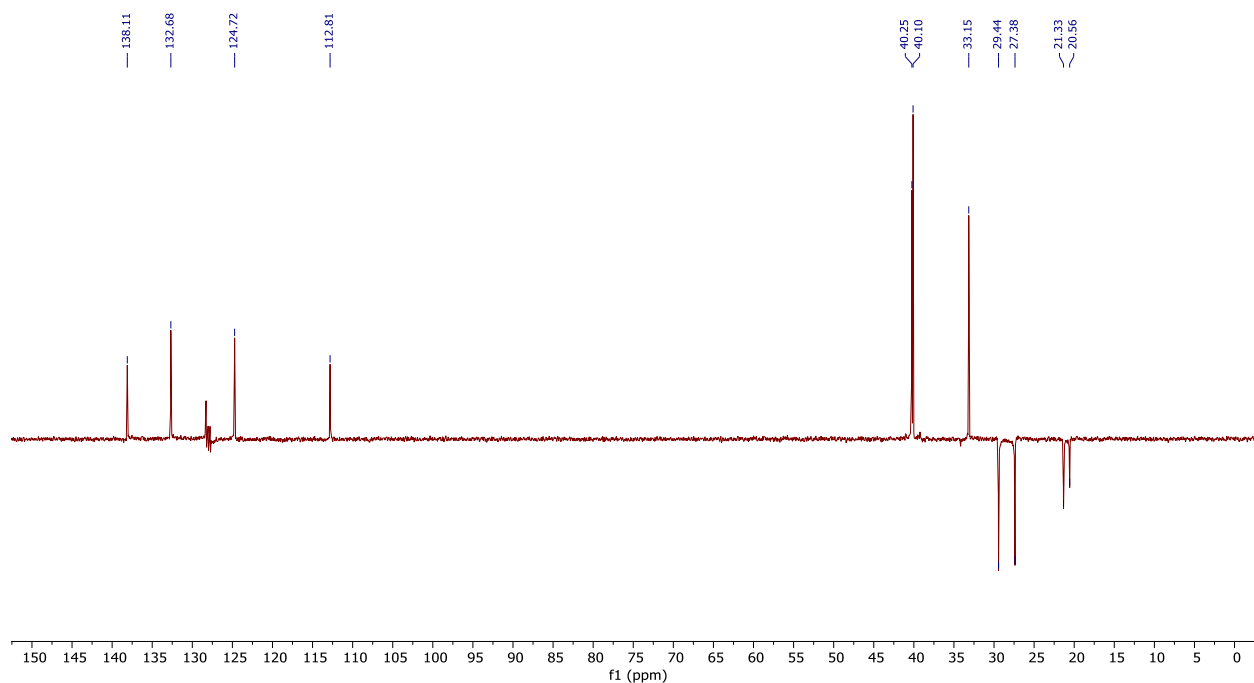


Figure S34. $^{13}\text{C}\{\text{H}\}$ NMR (DEPT) spectrum of **7** in C_6D_6 .

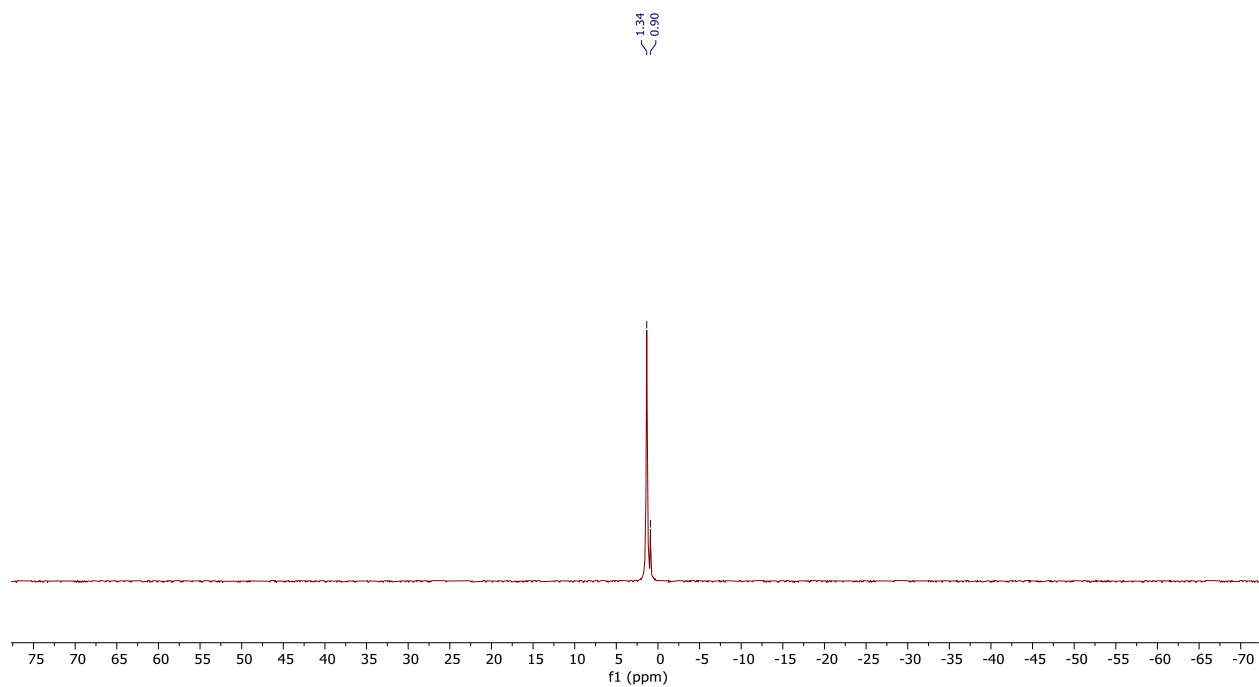


Figure S35. ^{11}B NMR spectrum of **7** in C_6D_6 .

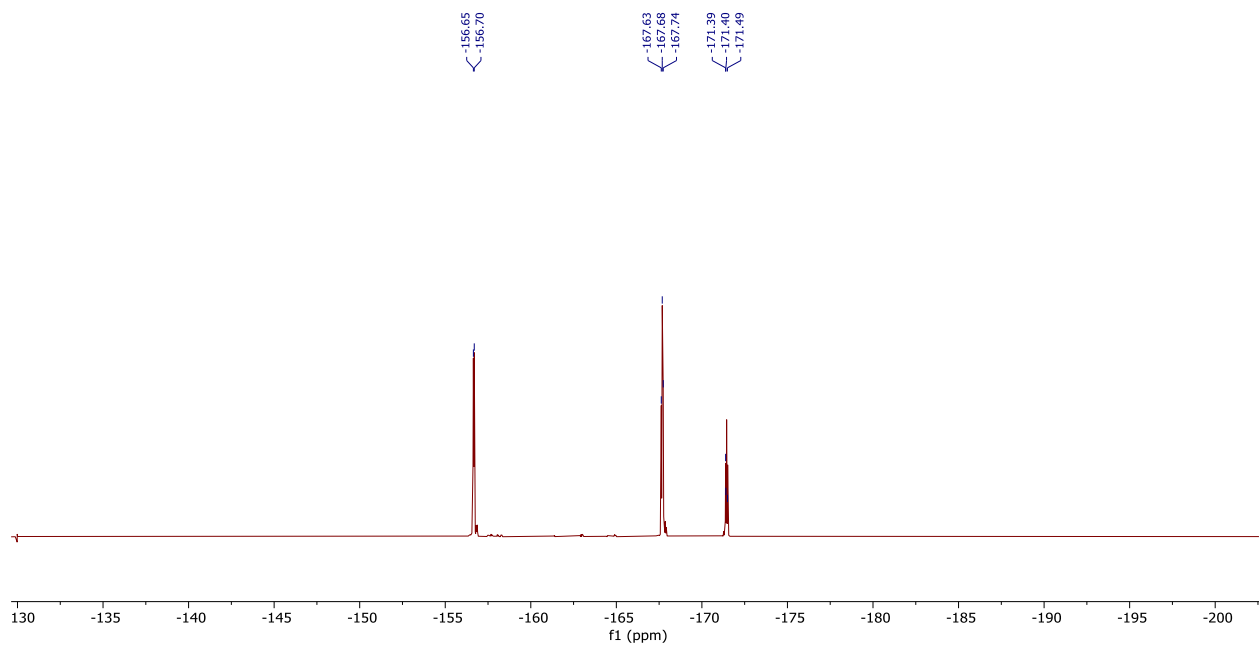
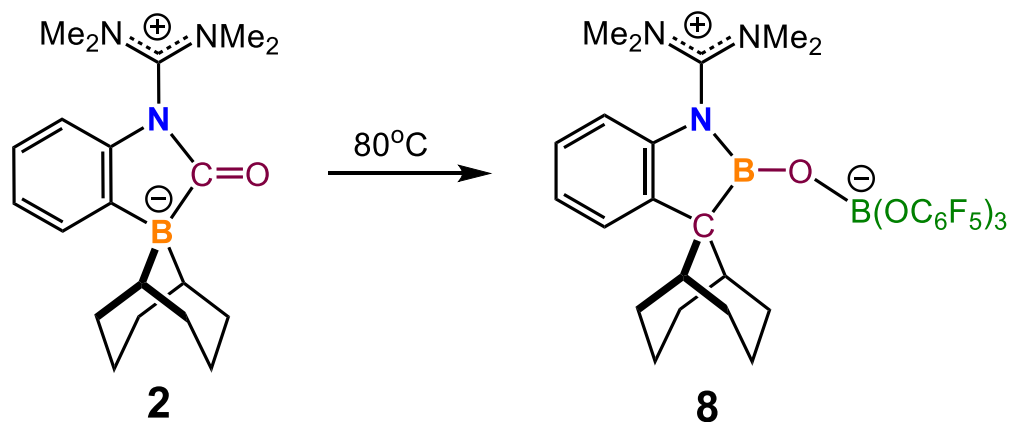


Figure S36. ^{19}F NMR spectrum of **7** in C_6D_6 .

2.9. Synthesis of **8**



In the glove box, a Schlenk flask (30 mL) equipped with a magnetic stir bar was charged with **2** (100 mg, 0.3 mmol), $\text{B}(\text{OC}_6\text{F}_5)_3$ (167 mg, 0.3 mmol) and dry benzene (5 mL). The reaction mixture was stirred for 1 hour at 70°C , concentrated to ca. half of the volume and left overnight. The resulting colorless crystals were washed once with benzene and dried under vacuum to give 215 mg (80%) of **8**. ^1H NMR [400 MHz, CD_2Cl_2]: 7.80 (d, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 7.20 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 7.06 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 6.37 (d, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 3.24, 3.07 (2s, CH_3 , 2×6 H), 0.51-2.36 (m, CH- skeleton, 14 H) ppm. $^{13}\text{C}\{\text{H}\}$ NMR [125 MHz, CD_2Cl_2]: 160.8 (C=N), 143.8 (C-arom.), 142.2 (d, $^1J_{\text{C-F}} = 248$ Hz, C-F), 140.1 (C-arom.), 138.5 (d, $^1J_{\text{C-F}} = 248$ Hz, C-F), 135.3 (d, $^1J_{\text{C-F}} = 248$ Hz, C-F), 133.4 (C-arom.), 131.5, 127.2, 122.7, 110.4 (CH-arom.), 42.4, 41.2 (CH_3), 38.5 (C-quat.), 32.8 (CH), 29.8, 26.6, 21.8, 20.5 (CH_2) ppm. ^{11}B NMR [128.4 MHz, CD_2Cl_2]: 0.2 ($\text{B}(\text{OC}_6\text{F}_5)_3$) ppm. ^{19}F NMR [376.3 MHz, CD_2Cl_2]: -157.7, -167.3, -171.2 ppm. Anal. Calc. for $\text{C}_{38}\text{H}_{30}\text{B}_2\text{F}_{15}\text{N}_3\text{O}_4$ (899.27): C, 50.75; H, 3.36, N, 4.67, Found: C, 50.90; H, 3.23, N, 4.32.

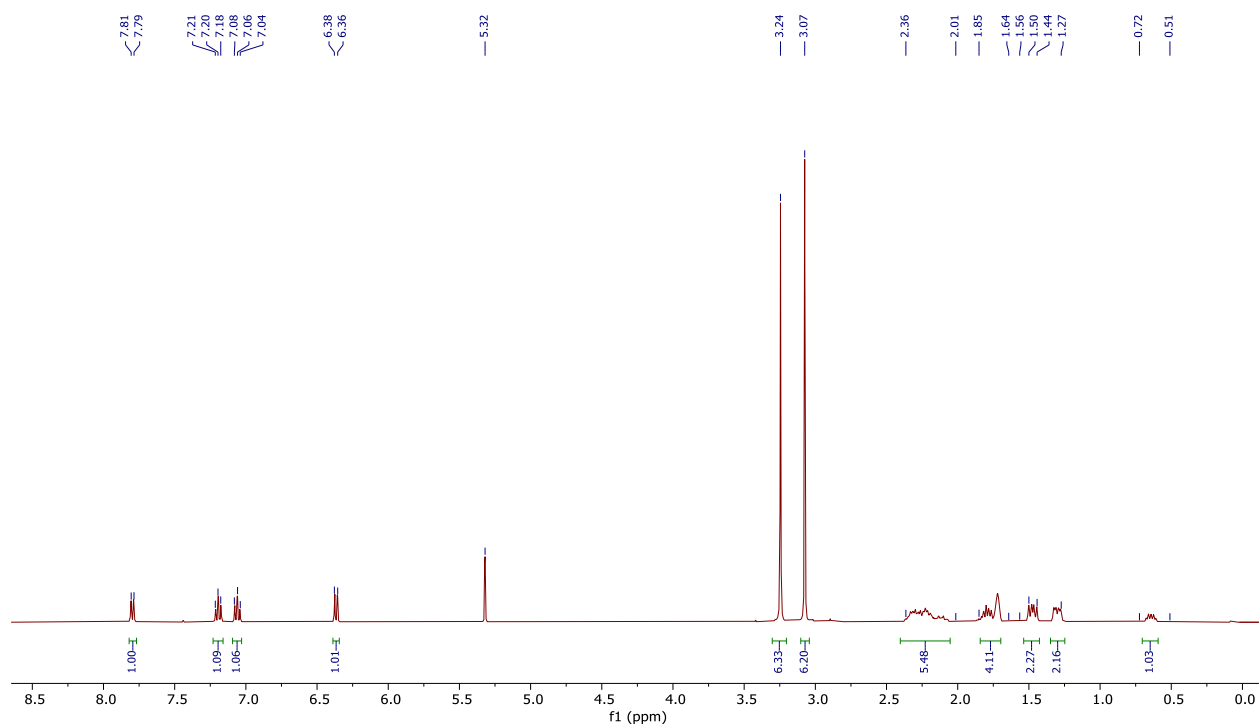


Figure S37. ^1H NMR spectrum of **8** in CD_2Cl_2 .

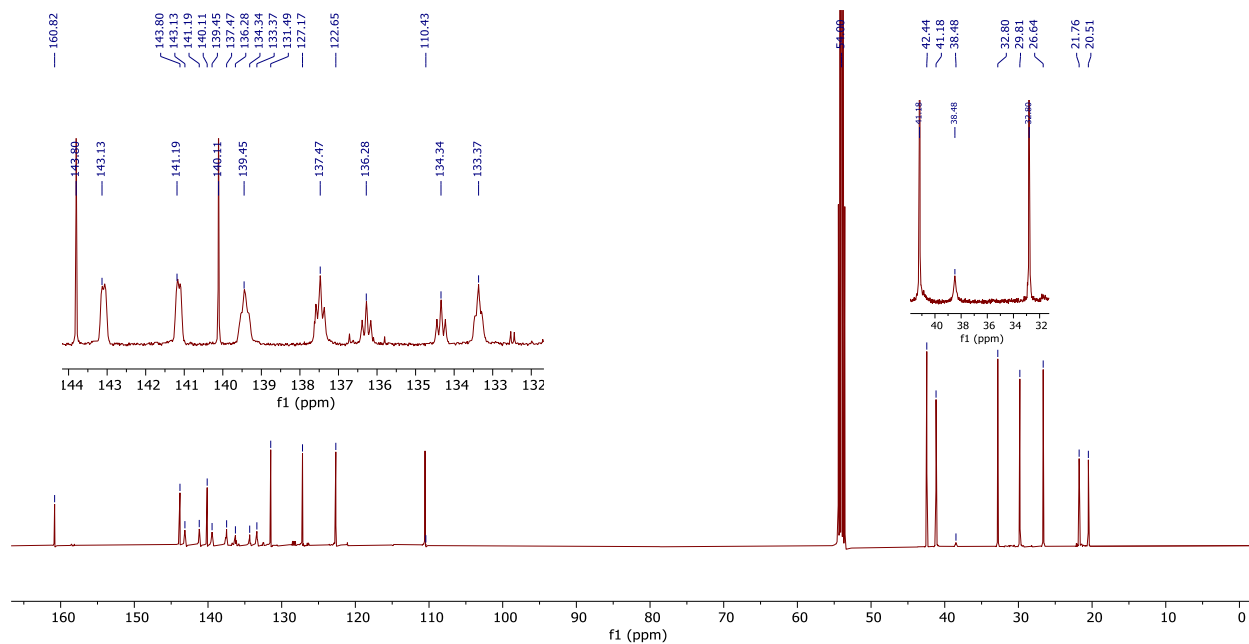


Figure S38. ^{13}C NMR spectrum of **8** in CD_2Cl_2 .

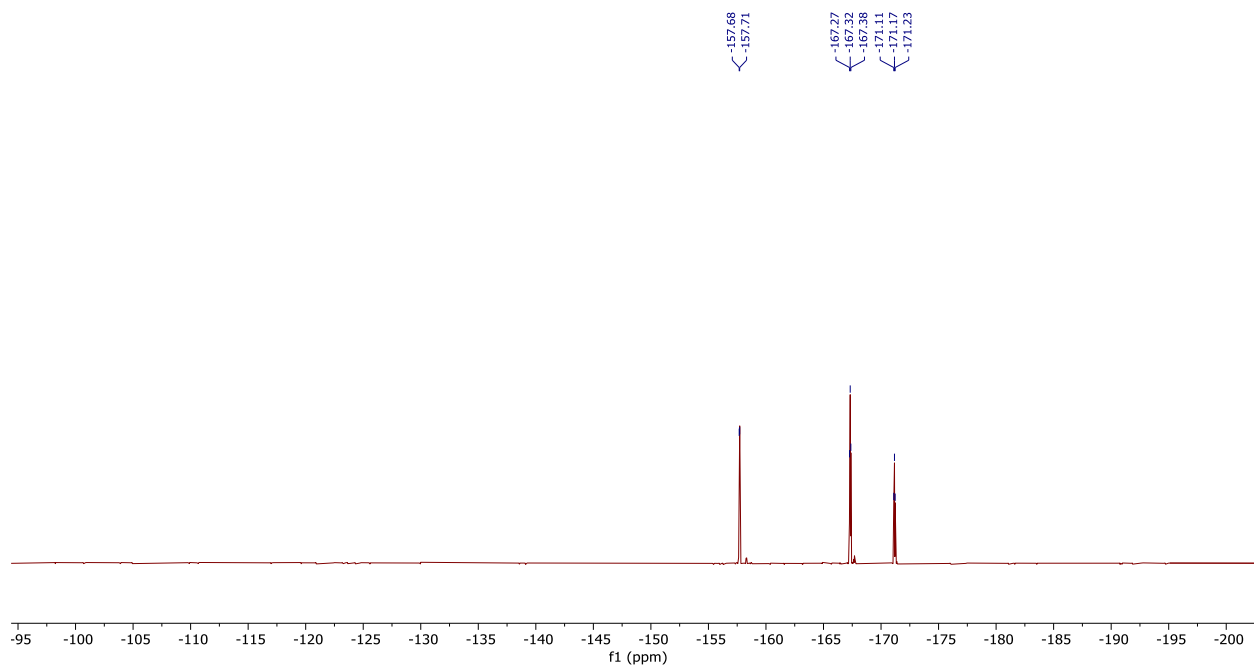


Figure S39. ^{19}F NMR spectrum of **8** in CD_2Cl_2 .

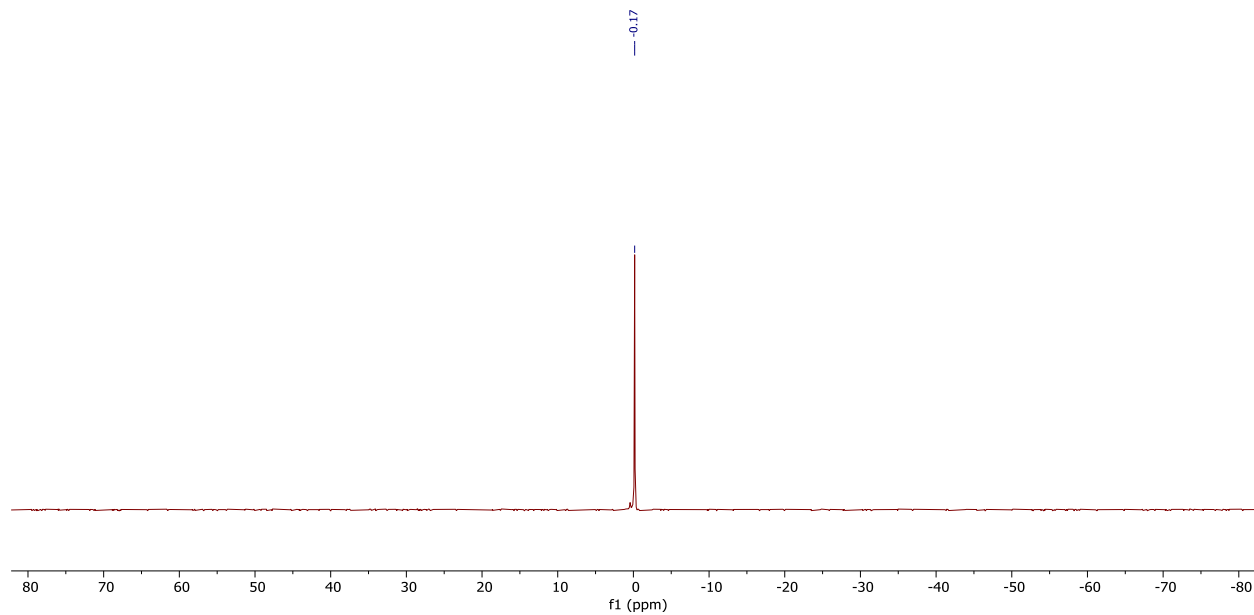
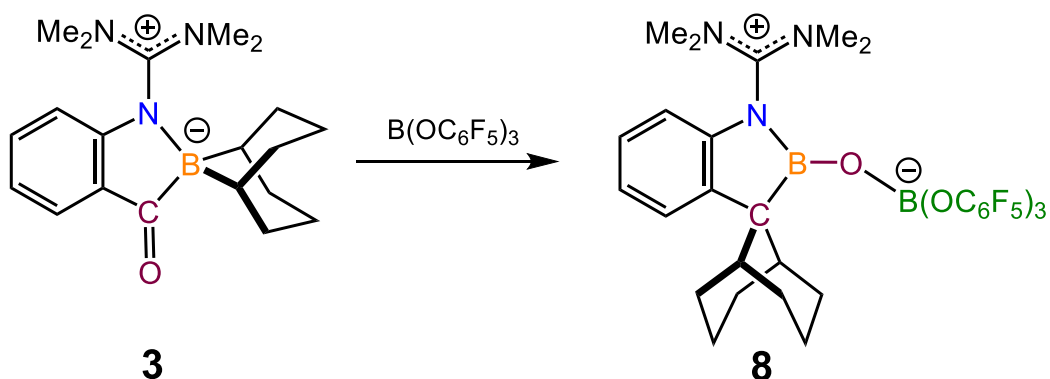


Figure S40. ^{11}B NMR spectrum of **8** in CD_2Cl_2 .

2.10. Reaction of **3** with $B(OC_6F_5)_3$ – Formation of **8**



In the glove box, a J-Young NMR tube was charged with **3** (10 mg, 0.029 mmol), $B(OC_6F_5)_3$ (16.5 mg, 0.029 mmol) and C_6D_6 (0.4 mL). The reaction mixture was analyzed by NMR spectroscopy. NMR data of the compound are in agreement with the above values for **8**.

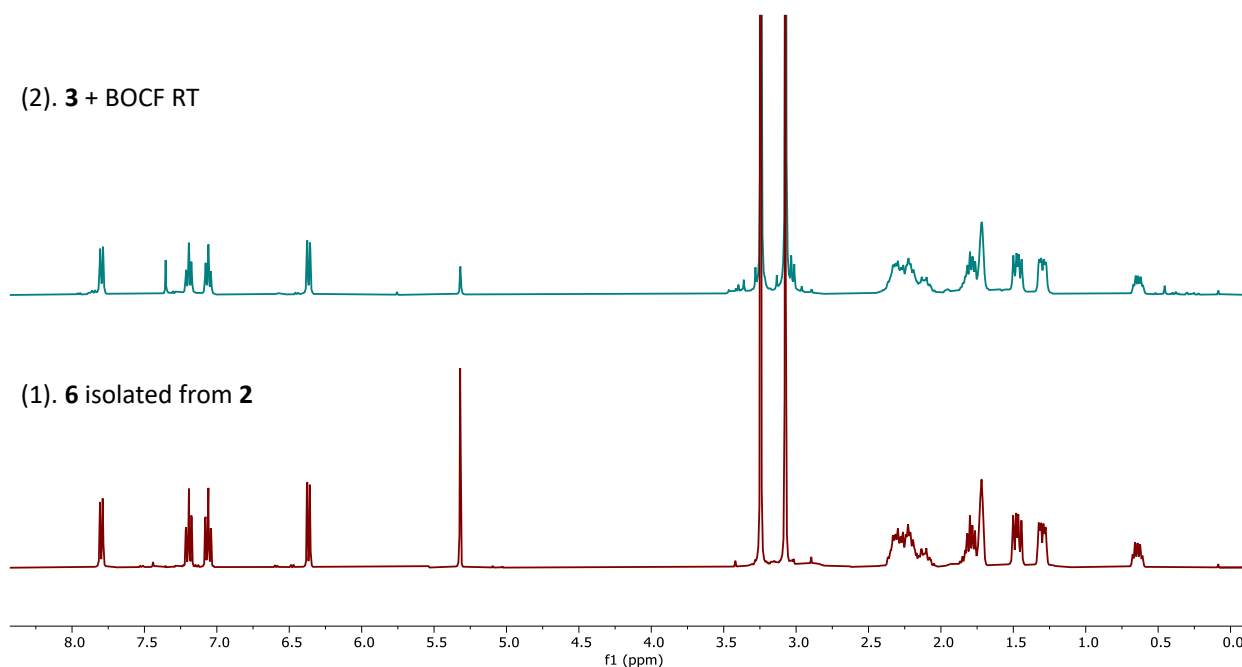
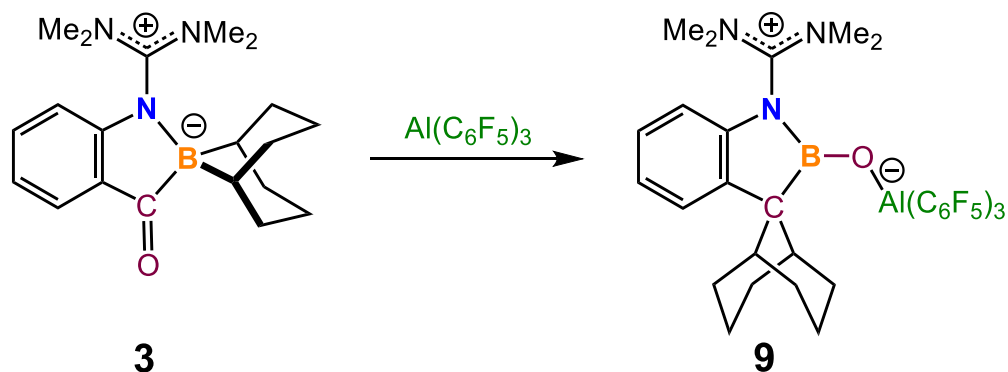


Figure S41. Stack plot of 1H NMR spectra of **8** in CD_2Cl_2 ; bottom: isolated from the reaction of **2** with $B(OC_6F_5)_3$; top: isolated from the reaction of **3** with $B(OC_6F_5)_3$.

2.11. Synthesis of **9**



In the glove box, a Schlenk flask (30 mL) was charged with **3** (30 mg, 0.09 mmol), $\text{Al}(\text{C}_6\text{F}_5)_3 \cdot 1/3\text{Tol}$ (50 mg, 0.09 mmol) and benzene (5 mL). The reaction mixture was stirred for one hour, and all the volatiles were removed. The crude was dissolved in toluene (1 mL) and hexanes added (4 mL). The resulting colorless crystals were washed once with hexanes and dried under vacuum to give 45 mg (58%) of **9**. ^1H NMR [400 MHz, CD_2Cl_2]: 7.81 (d, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 7.21 (t, $^3J_{\text{H-H}} = 8$ Hz, CH- arom., 1 H), 7.07 (t, $^3J_{\text{H-H}} = 8$ Hz, CH- arom., 1 H), 6.40 (t, $^3J_{\text{H-H}} = 8$ Hz, CH- arom., 1 H), 3.05, 2.96 (2s, CH_3 , 2 \times 6 H), 1.30-2.35 (m, CH_2/CH -skeleton, 13 H), 0.58-0.68 (m, CH-skeleton, 1 H) ppm. $^{13}\text{C}\{\text{H}\}$ NMR [125 MHz, CD_2Cl_2]: 159.7 (C=N), 150.3 (dd, $^1J_{\text{C-F}} = 229$ Hz, $^2J_{\text{C-F}} = 21$ Hz, CF), 142.4 (C-arom.), 141.0 (d, $^1J_{\text{C-F}} = 248$ Hz, CF), 140.6 (C-arom.), 136.9 (d, $^1J_{\text{C-F}} = 236$ Hz, CF), 131.4, 127.0, 122.8, 111.2 (CH-arom.), 41.6, 41.2 (CH_3), 38.5 (C-quat.), 32.9 (CH), 30.9, 26.5, 21.5, 20.4 (CH_2) ppm. Note: The ipso carbon bound to aluminum could not be detected. ^{11}B NMR [128.4 MHz, C_6D_6]: 37.0 ppm. ^{19}F NMR [376.3 MHz, CD_2Cl_2]: -122.8, -155.22, -162.27 ppm. Anal. Calc. for $\text{C}_{38}\text{H}_{30}\text{AlBF}_{15}\text{N}_3\text{O}^-$ (867.45): C, 52.62; H, 3.49, N, 4.84, Found: C, 52.25; H, 3.89, N, 4.75.

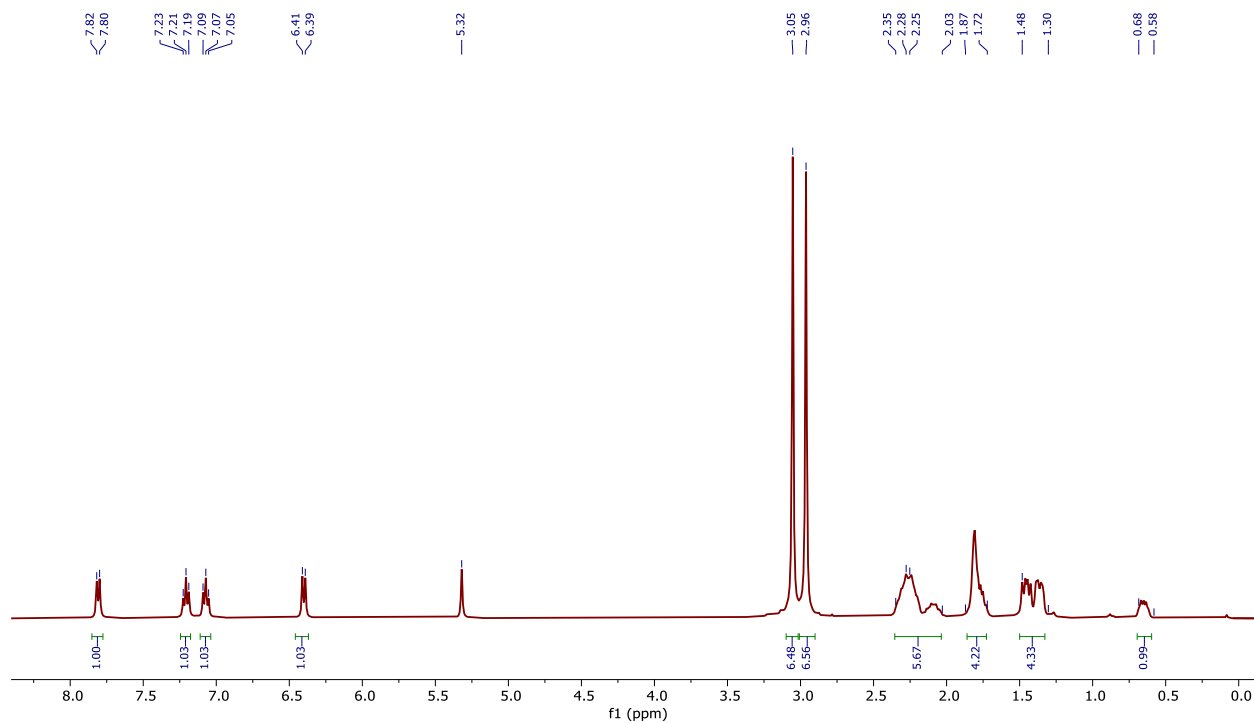


Figure S42. ^1H NMR spectrum of **9** in CD_2Cl_2 .

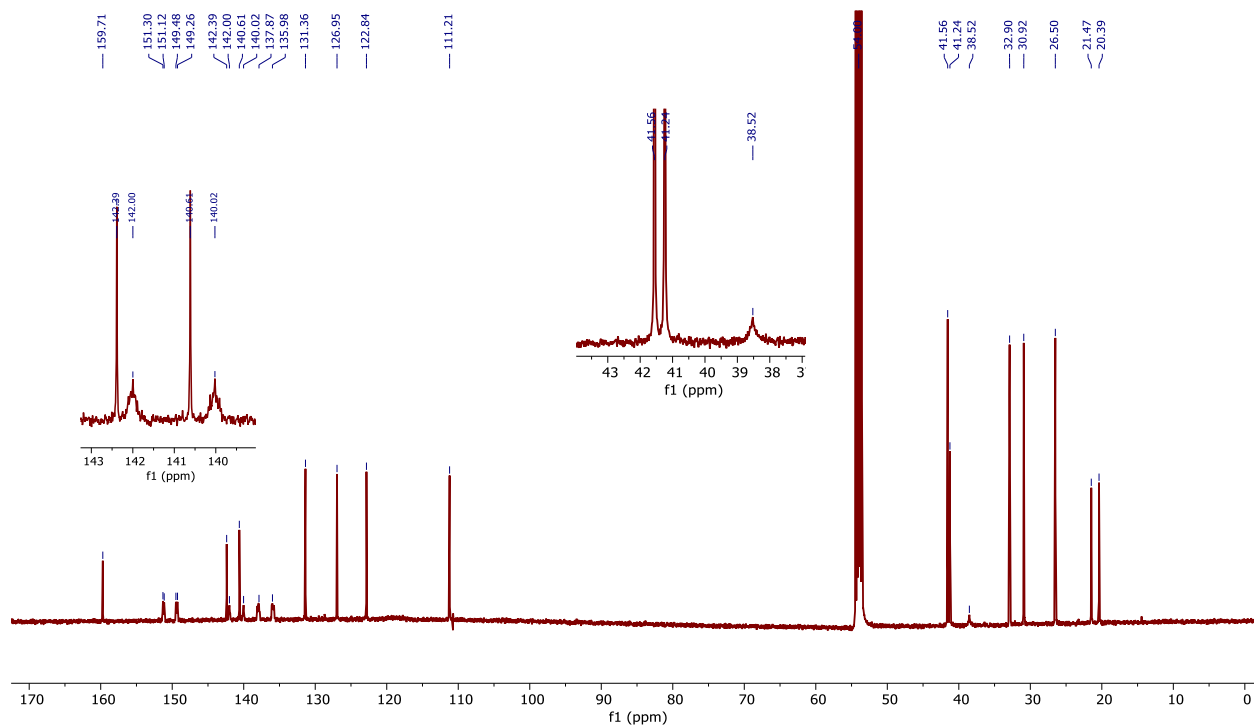


Figure S43. ^{13}C NMR spectrum of **9** in CD_2Cl_2 .

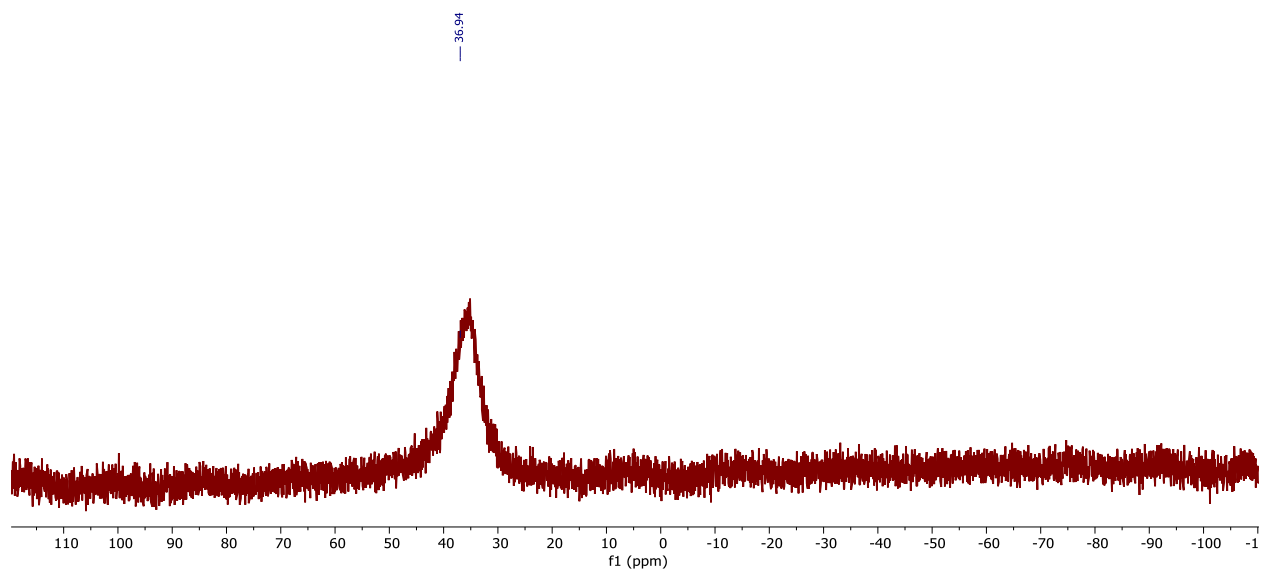


Figure S44. ^{11}B NMR spectrum of **9** in CD_2Cl_2 .

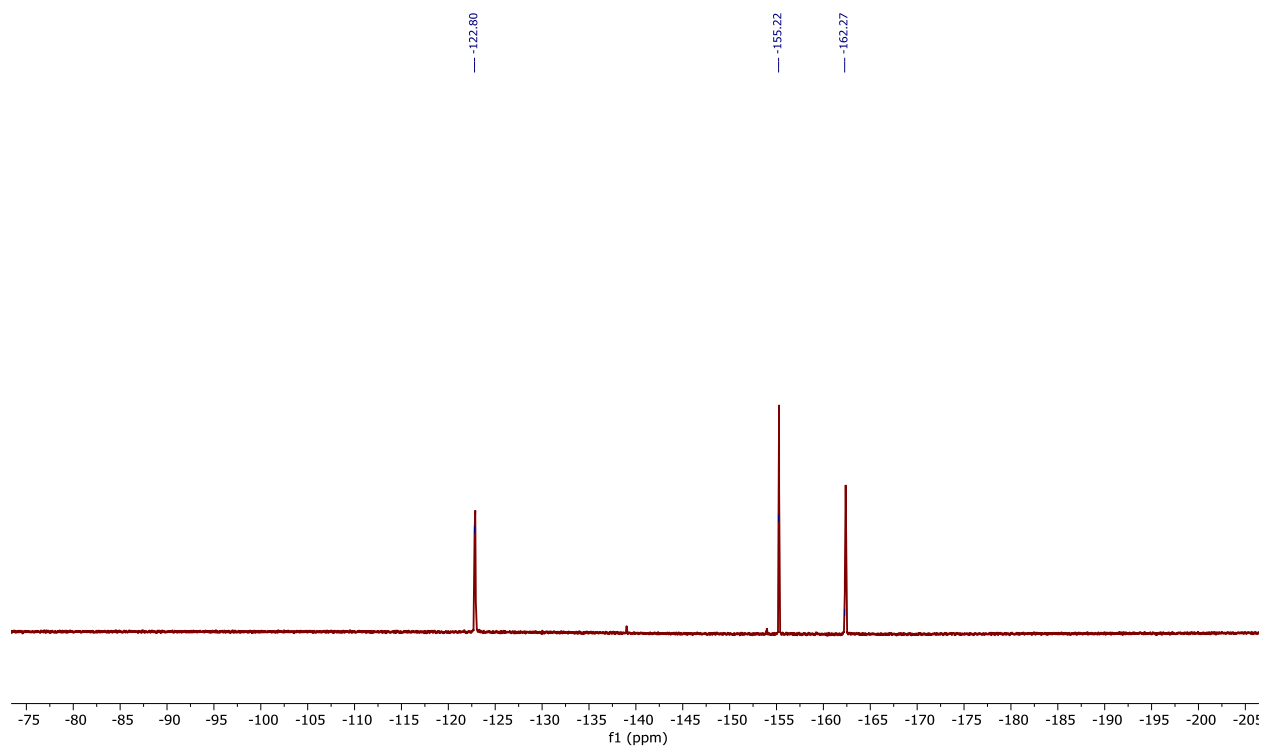
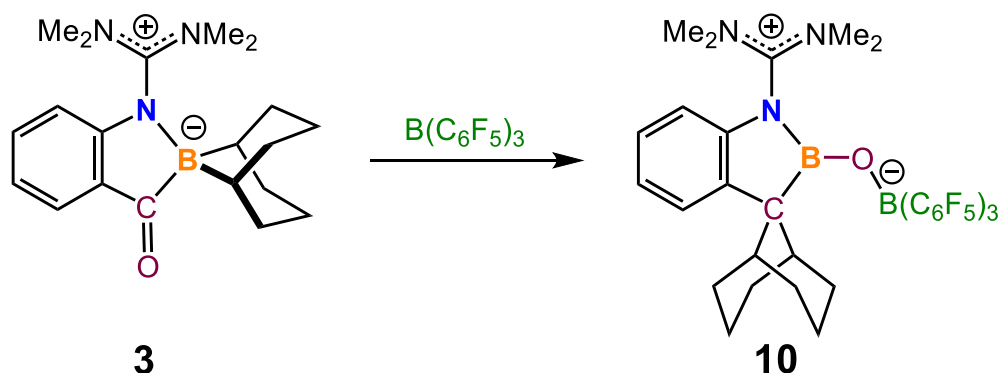


Figure S45. ^{19}F NMR spectrum of **9** in CD_2Cl_2 .

2.12. Synthesis of **10**



A 20 mL scintillation vial equipped with a magnetic stir bar was charged with **3** (50 mg, 0.15 mmol), $\text{B}(\text{C}_6\text{F}_5)_3$ (77 mg, 0.15 mmol) and benzene (5 mL). The reaction mixture was stirred for one hour, concentrated to ca. half of the volume and left overnight. The resulting colorless crystals were washed once with benzene and dried under vacuum to give 105 mg (82%) of **10**. ^1H NMR [400 MHz, CD_2Cl_2]: 7.80 (d, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 7.19 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 7.05 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 7.36 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 3.06, 2.90 (2s, CH_3 , 2 x 6 H), 1.24-2.29 (m, CH_2/CH -skeleton, 13 H), 0.27-0.36 (m, CH-skeleton, 1 H) ppm. $^{13}\text{C}\{\text{H}\}$ NMR [125 MHz, CD_2Cl_2]: 160.1 (C=N), 148.9 (d, $^1J_{\text{C-F}} = 236$ Hz, CF), 141.7, 140.8 (C-arom.), 140.2 (C-B), 137.9 (d, $^1J_{\text{C-F}} = 239$ Hz, CF), 136.9 (d, $^1J_{\text{C-F}} = 255$ Hz, CF), 130.7, 126.6, 122.5, 111.3 (CH-arom.), 41.4, 41.3 (CH_3), 40.2 (C-quat.), 33.5 (CH), 31.6, 26.5, 21.8, 20.2 (CH_2). ppm. ^{11}B NMR [128.4 MHz, CD_2Cl_2]: -7.0 ppm. Note: the trigonal planar boron couldn't be detected in the ^{11}B NMR spectrum. ^{19}F NMR [376.3 MHz, C_6D_6 (75°C)]: -133.7, -160.1, -165.6 ppm. Anal. Calc. for $\text{C}_{38}\text{H}_{30}\text{B}_2\text{F}_{15}\text{N}_3\text{O}$ (851.27): C, 53.62; H, 3.55, N, 4.94, Found: C, 53.18; H, 3.59, N, 4.96

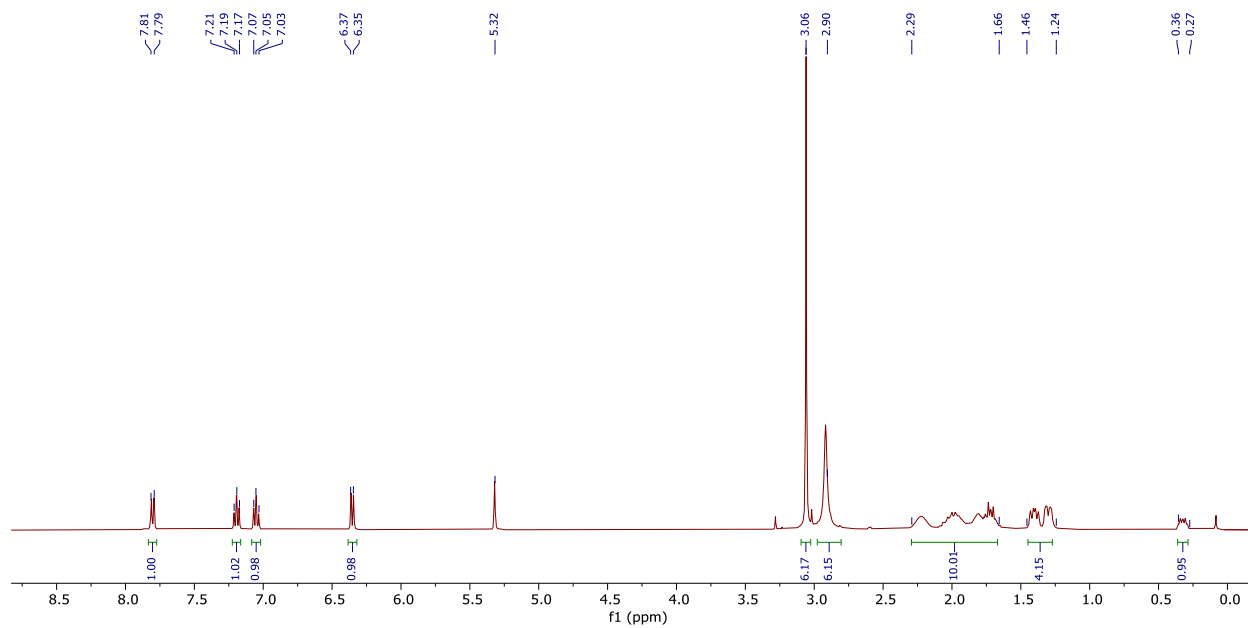


Figure S46. ^1H NMR spectrum of **10** in CD_2Cl_2 .

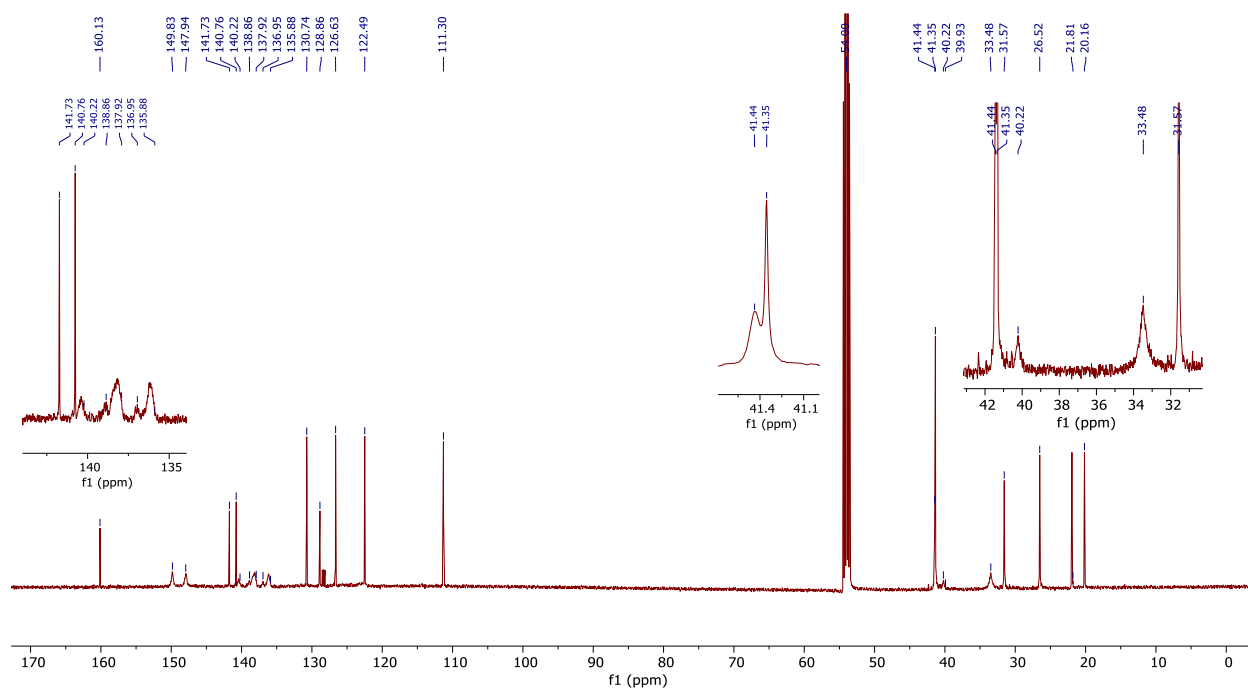


Figure S47. ^{13}C NMR spectrum of **10** in CD_2Cl_2 .

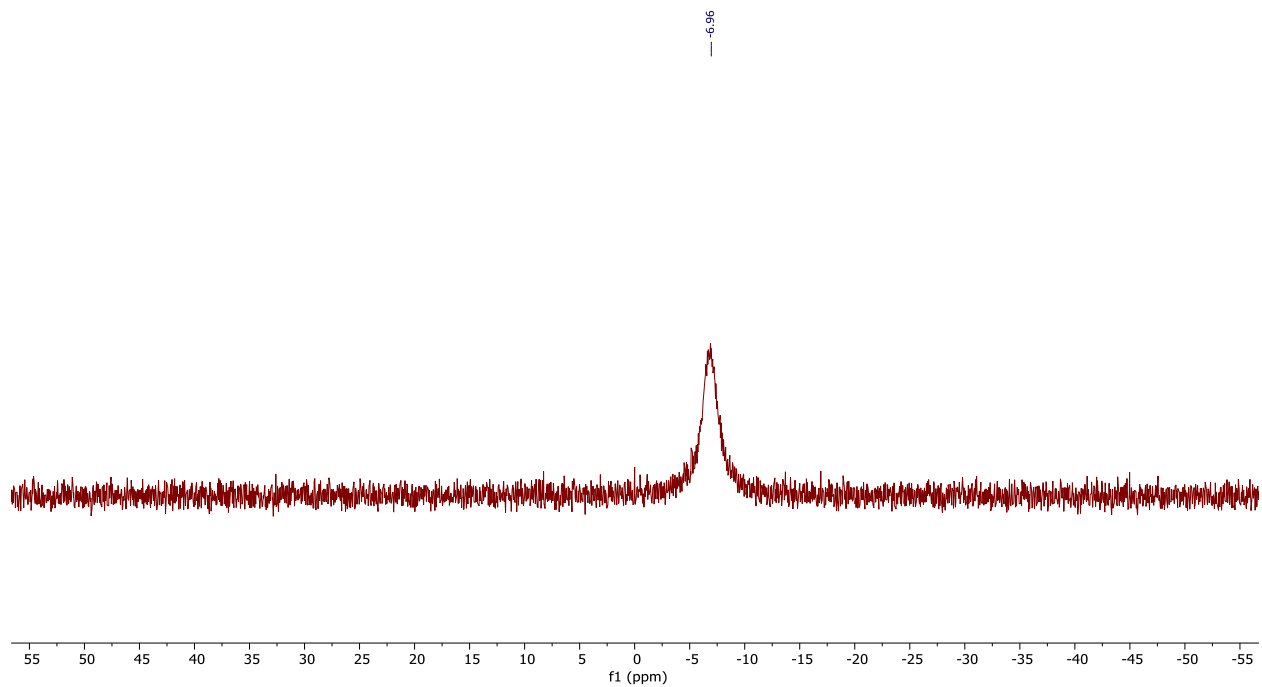


Figure S48. ^{11}B NMR spectrum of **10** in CD_2Cl_2 .

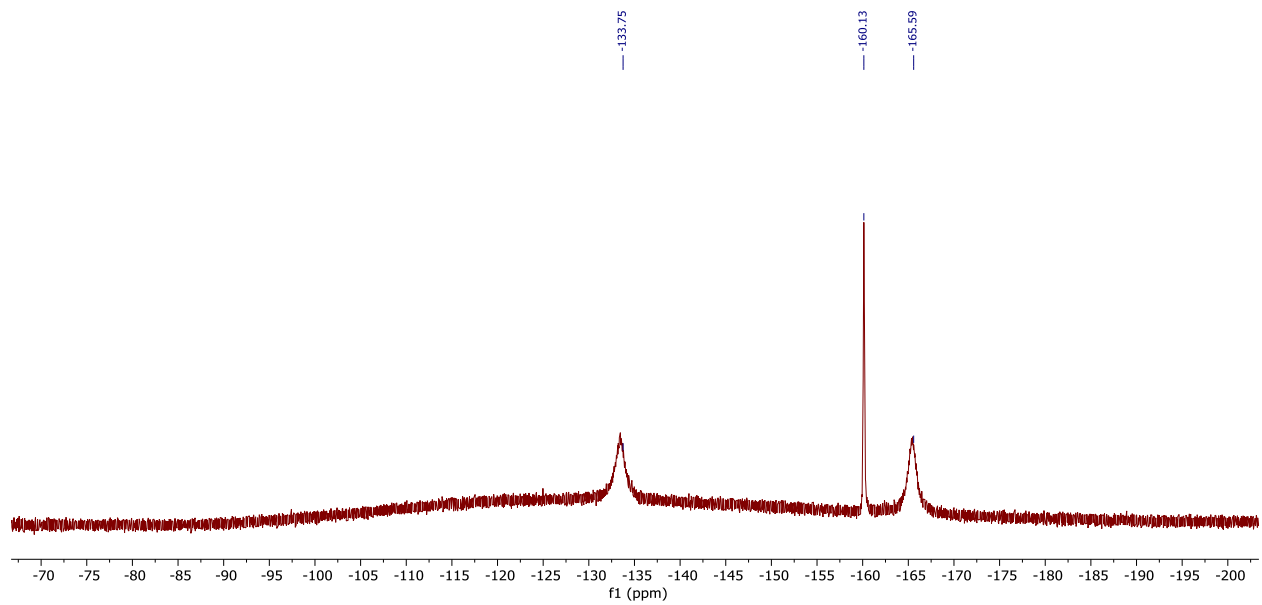


Figure S49. ^{19}F NMR spectrum of **10** in C_6D_6 at $75\text{ }^\circ\text{C}$.

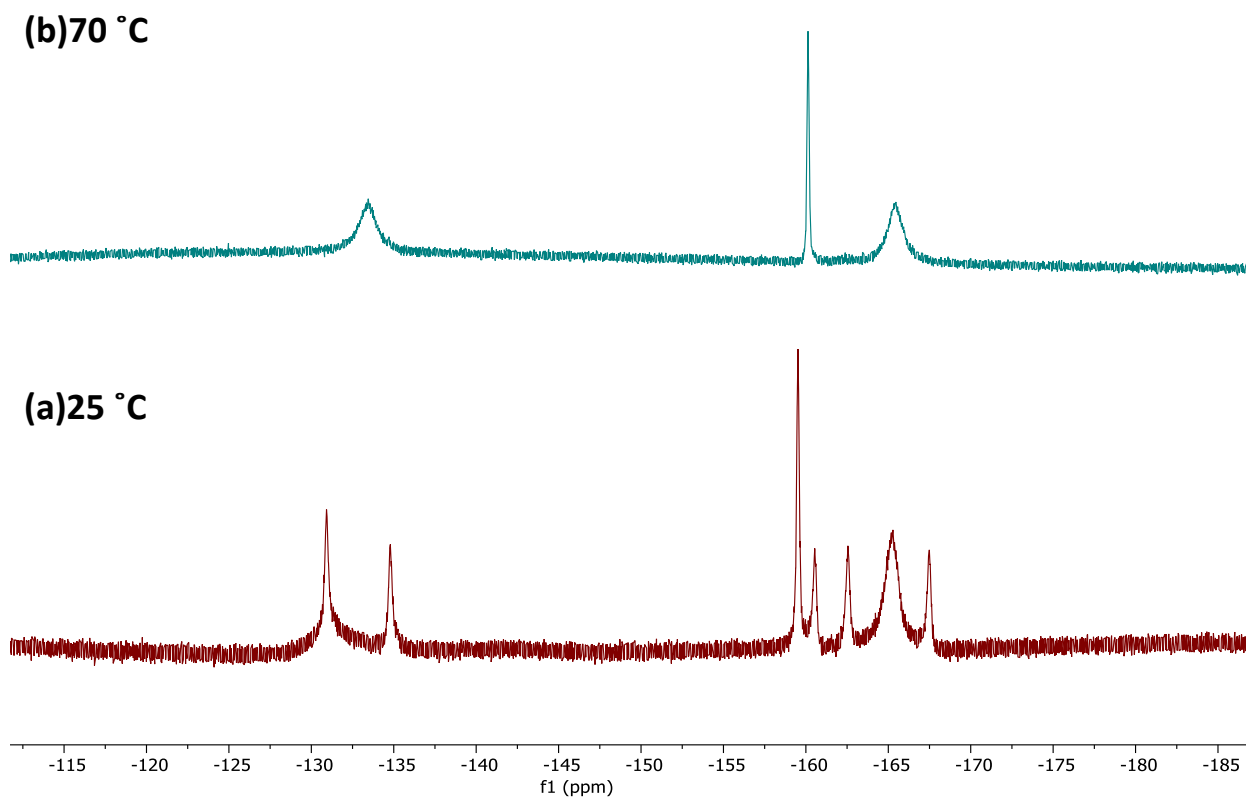
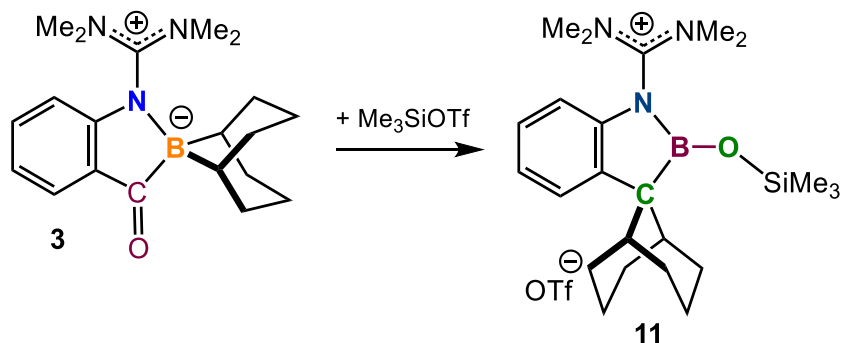


Figure S50. Stack plot of ^{19}F NMR peak variation of **10** in C_6D_6 at a) 25°C and b) 70°C.

2.13. Synthesis of **11**



In the glove box, a Schlenk flask (30 mL) equipped with a magnetic stir bar was charged with **3** (70 mg, 0.20 mmol), Me_3SiOTf (46 mg, 0.21 mmol) and dry benzene (5 mL). After

the reaction mixture was stirred for one hour, all volatiles were removed under vacuum. The residue was dissolved in toluene (2 mL) and left overnight. The resulting colorless crystals were washed once with toluene and dried under vacuum to give 85 mg (75%) of **11**. ^1H NMR [400 MHz, C_6D_6]: 7.63 (d, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 7.31 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 6.94 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 2 H), 3.46, 2.62 (2s, CH_3 , 2×6 H), 1.34 -2.39 (m, CH-skeleton, 14 H), 0.11 (s, SiCH_3 , 9 H) ppm. $^{13}\text{C}\{\text{H}\}$ NMR [125 MHz, C_6D_6]: 157.9 (C=N), 143.1, 138.0 (C-arom.), 130.4, 128.4, 123.0 (CH-arom.), 122.4 (q, $^1J_{\text{C-F}} = 318$ Hz, CF_3), 112.3 (CH-arom.), 42.4, 40.7 (CH_3), 38.2 (C-quat.), 31.9 (CH), 30.0, 26.4, 21.2, 20.3 (CH_2), 1.6 (SiCH_3) ppm. ^{19}F NMR [376.3 MHz, C_6D_6]: -77.5 ppm. ^{29}Si NMR [99.4 MHz, C_6D_6]: 14.1. Anal. Calc. for $\text{C}_{24}\text{H}_{39}\text{BF}_3\text{N}_3\text{O}_4\text{SSi}$ (561.54): C, 51.33; H, 7.00, N, 7.48, Found: C, 51.10; H, 6.96, N, 7.33.

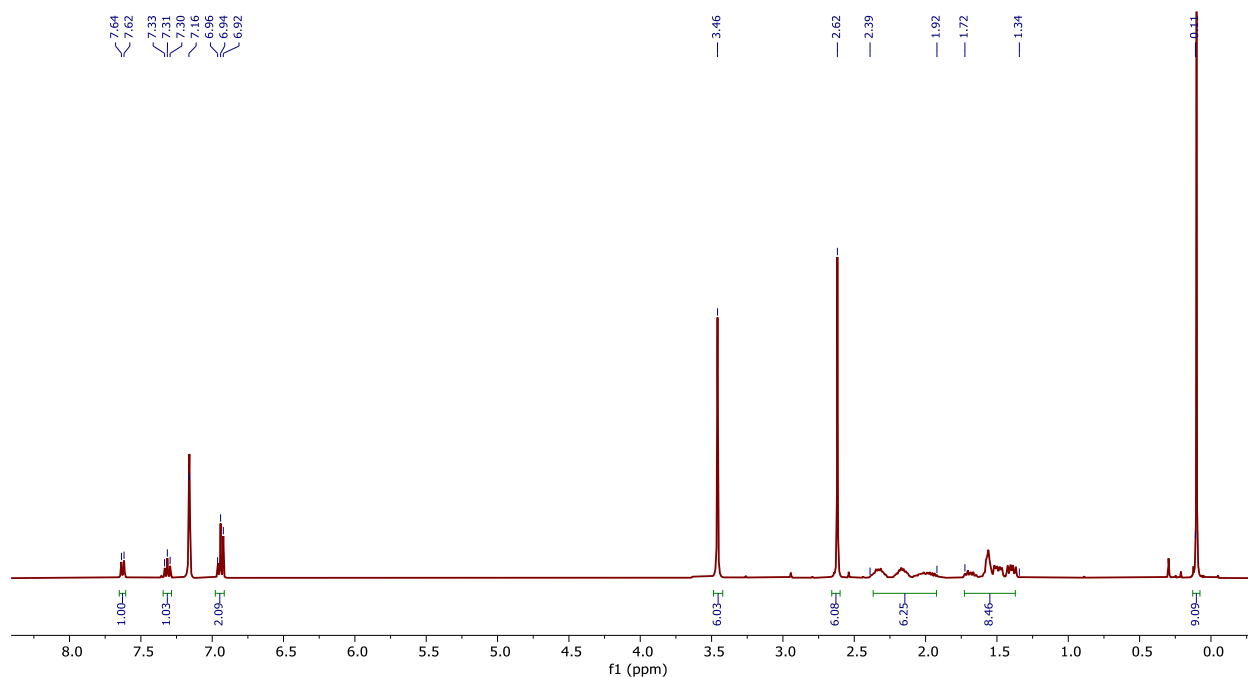


Figure S51. ^1H NMR spectrum of **11** in C_6D_6 .

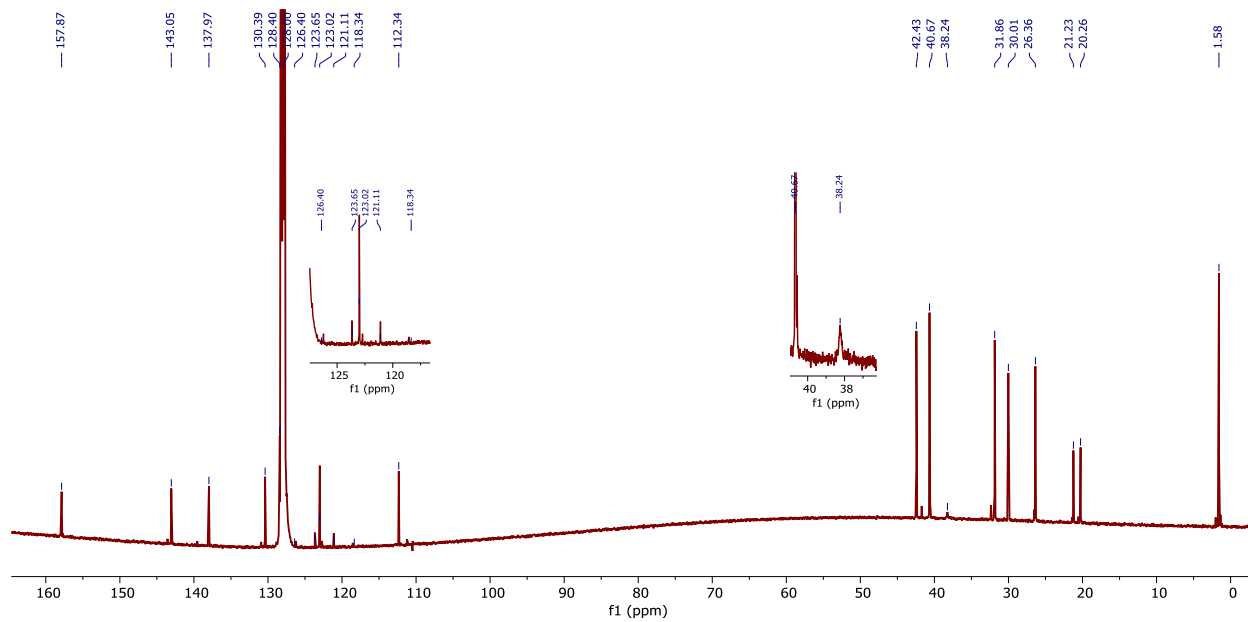


Figure S52. ^{13}C NMR spectrum of **11** in C_6D_6 .

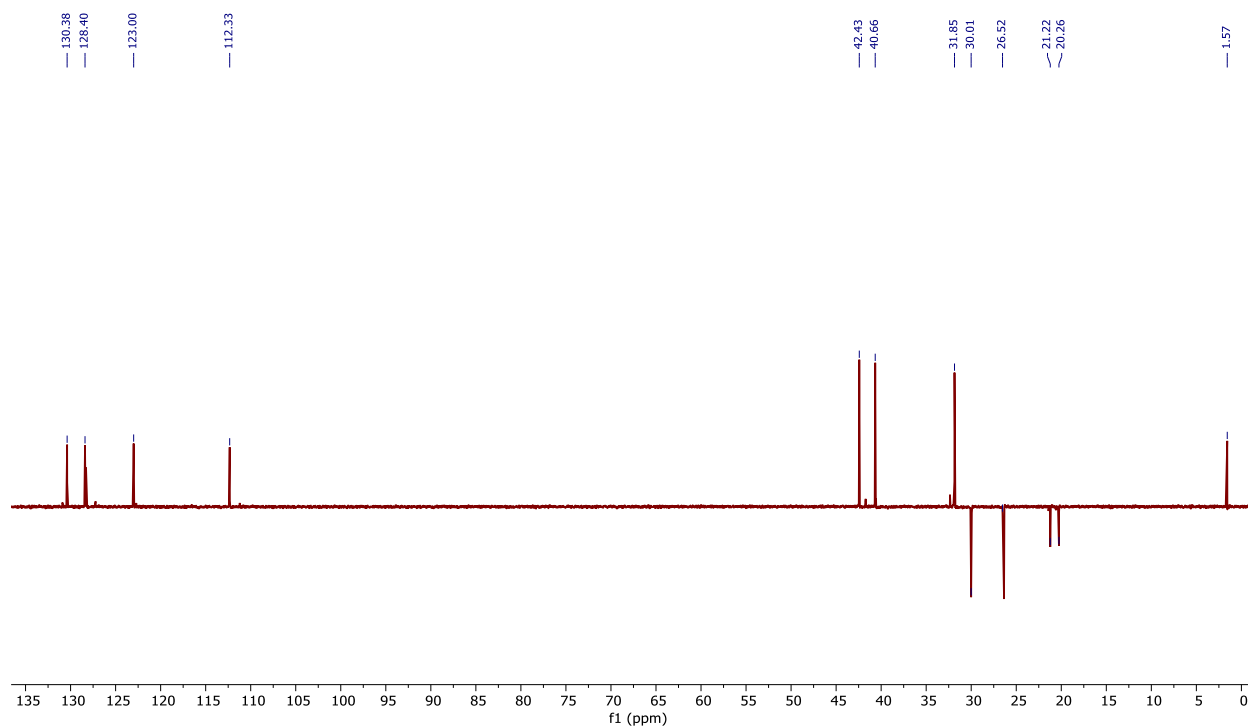


Figure S53. ^{13}C (DEPT) NMR spectrum of **11** in C_6D_6 .

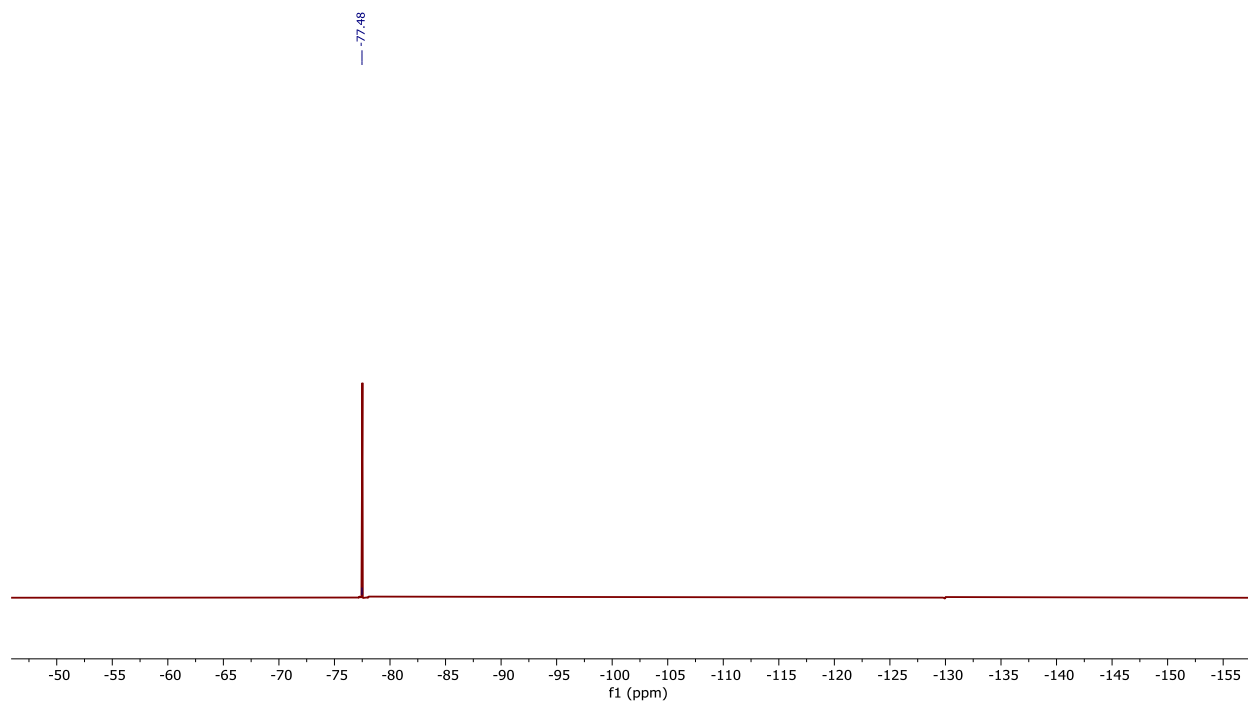


Figure S54. ^{19}F NMR spectrum of **11** in C_6D_6 .

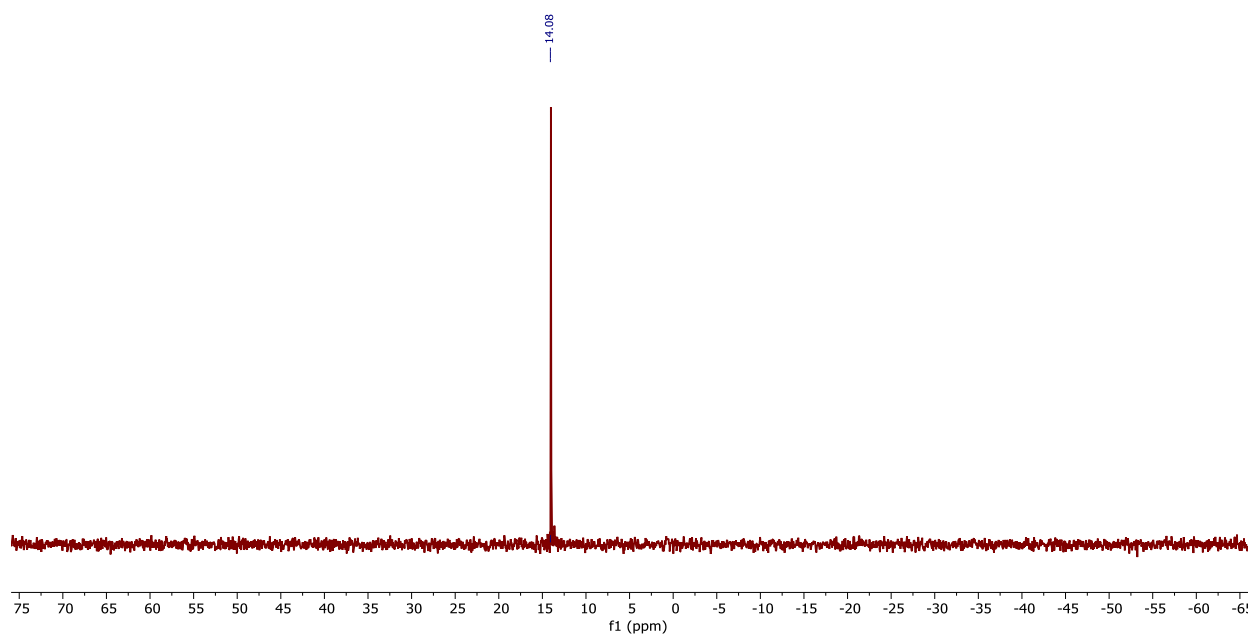
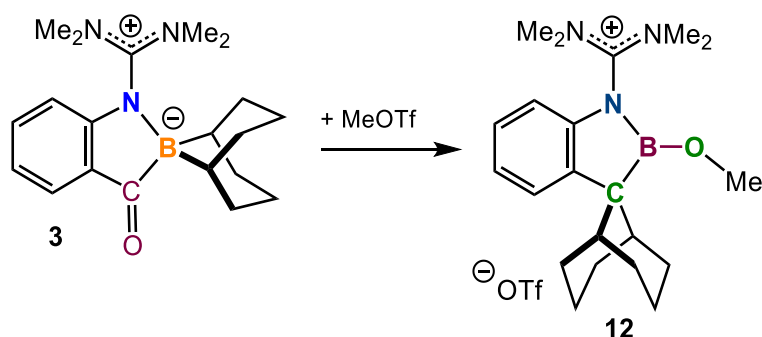


Figure S55. ^{29}Si NMR spectrum of **11** in C_6D_6 .

2.14. Synthesis of **12**



In the glove box, a Schlenk flask (30 mL) equipped with a magnetic stir bar was charged with **3** (51 mg, 0.15 mmol), MeOTf (25 mg, 0.15 mmol) and dry benzene (5 mL). The reaction mixture was stirred at 75°C

overnight. Upon cooling to room temperature colorless crystals formed, which were washed once with benzene and dried under vacuum to give 65 mg (85%) of **12**. ^1H NMR [400 MHz, CD_2Cl_2]: 7.82 (d, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 7.27 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 7.14 (t, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 6.53 (d, $^3J_{\text{H-H}} = 8$ Hz, CH-arom., 1 H), 3.79 (s, OCH_3 , 3 H), 3.48, 3.11 (2s, NCH_3 , 2 \times 6 H), 1.53-2.48 (m, CH/ CH_2 -skeleton, 14 H) ppm. $^{13}\text{C}\{\text{H}\}$ NMR [125 MHz, CD_2Cl_2]: 159.3 (C=N), 143.1, 138.7 (C-arom.), 131.5, 127.9, 123.8 (CH-arom.), 121.4 (q, $^1J_{\text{C-F}} = 319$ Hz, CF_3), 111.3 (CH-arom.), 55.0 (OCH_3), 42.5, 41.6 (NCH_3), 38.8 (C-quat.), 32.7 (CH), 30.2, 26.7, 21.4, 20.5 (CH_2) ppm. ^{11}B NMR [128.4 MHz, CD_2Cl_2]: 39.0 ppm. ^{19}F NMR [376.3 MHz, CD_2Cl_2]: -77.0 ppm. Anal. Calc. for $\text{C}_{22}\text{H}_{33}\text{BF}_3\text{N}_3\text{O}_4\text{S}^-$ (503.39): C, 52.49; H, 6.61, N, 8.35, Found: C, 52.19; H, 6.72, N, 8.24.

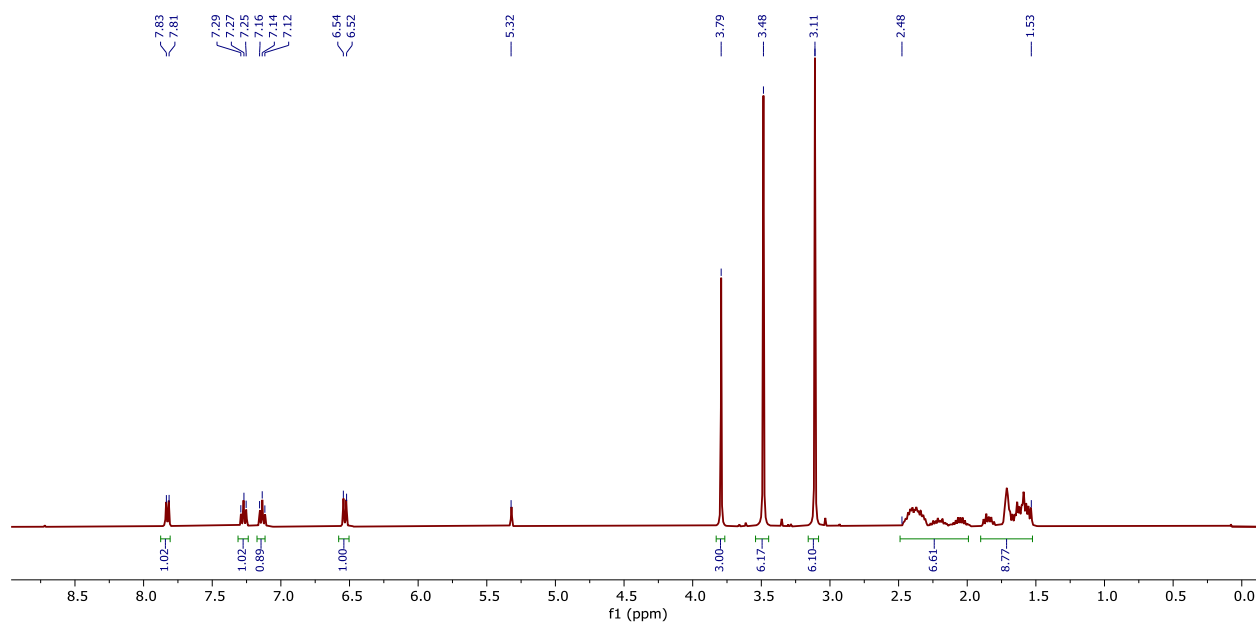


Figure S56. ^1H NMR spectrum of **12** in CD_2Cl_2 .

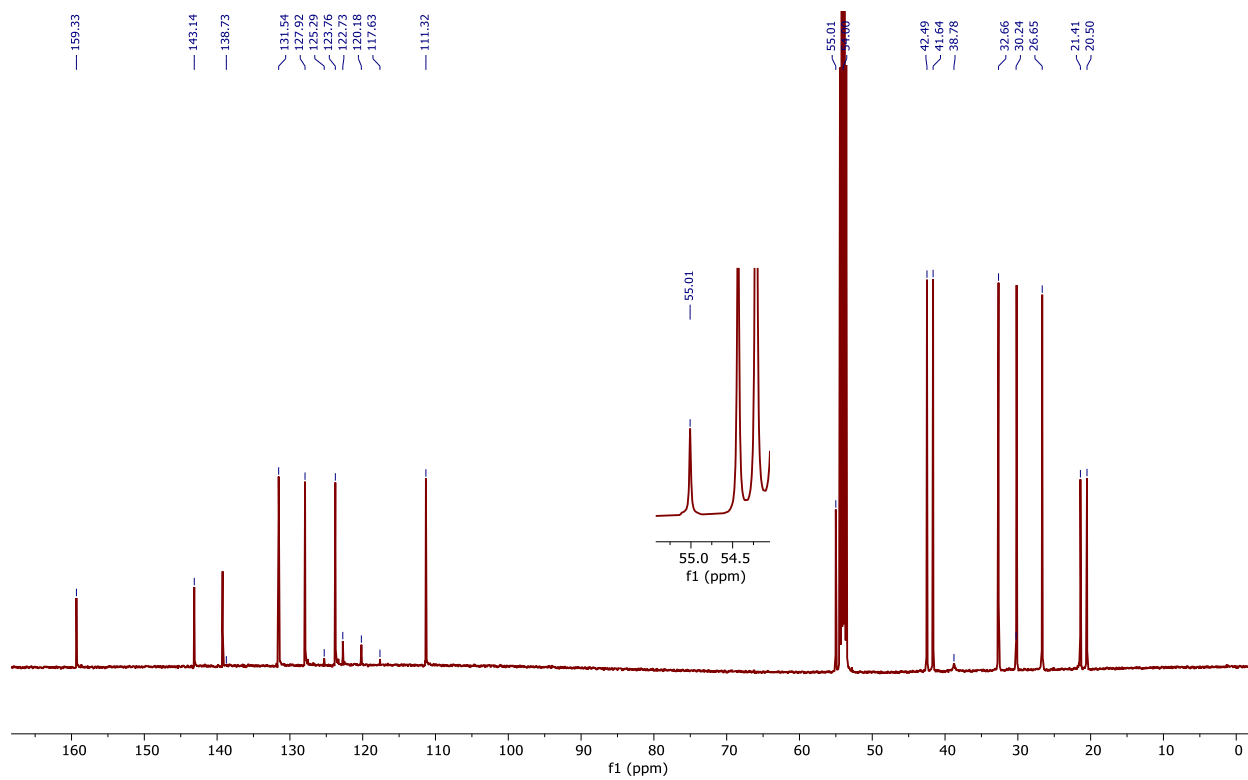


Figure S57. ^{13}C NMR spectrum of **12** in CD_2Cl_2 .

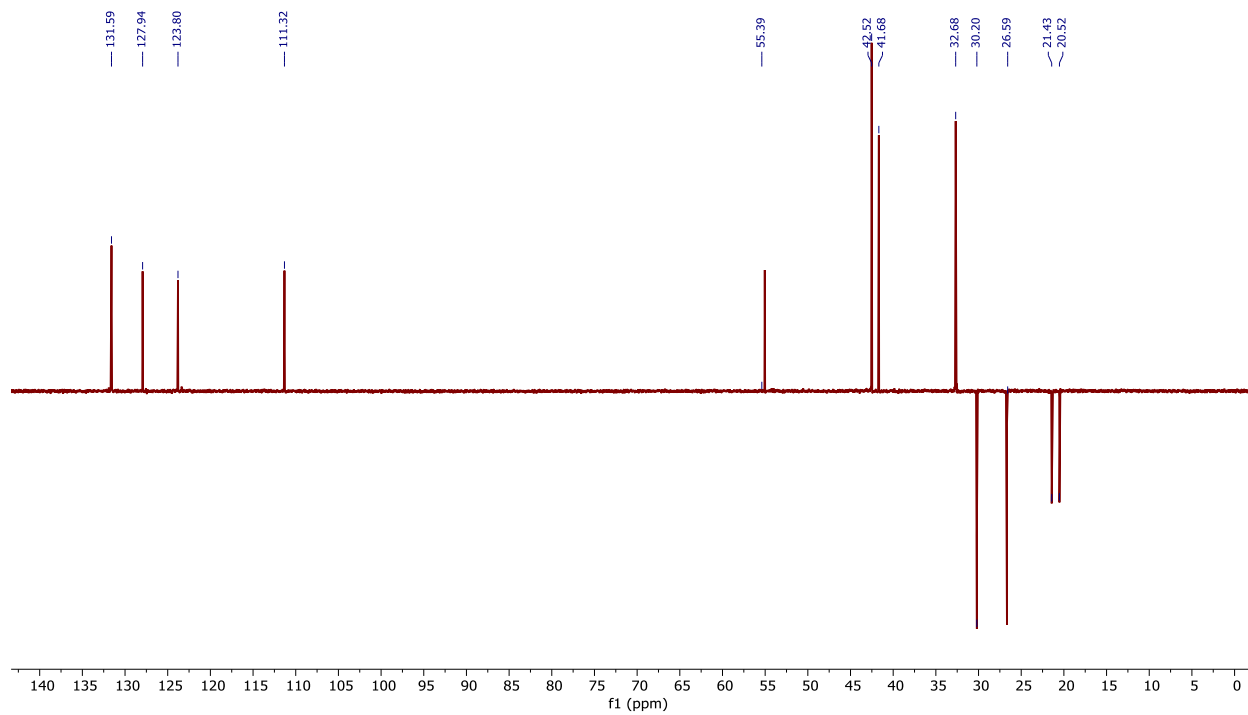


Figure S58. ^{13}C (DEPT) NMR spectrum of **12** in CD_2Cl_2 .

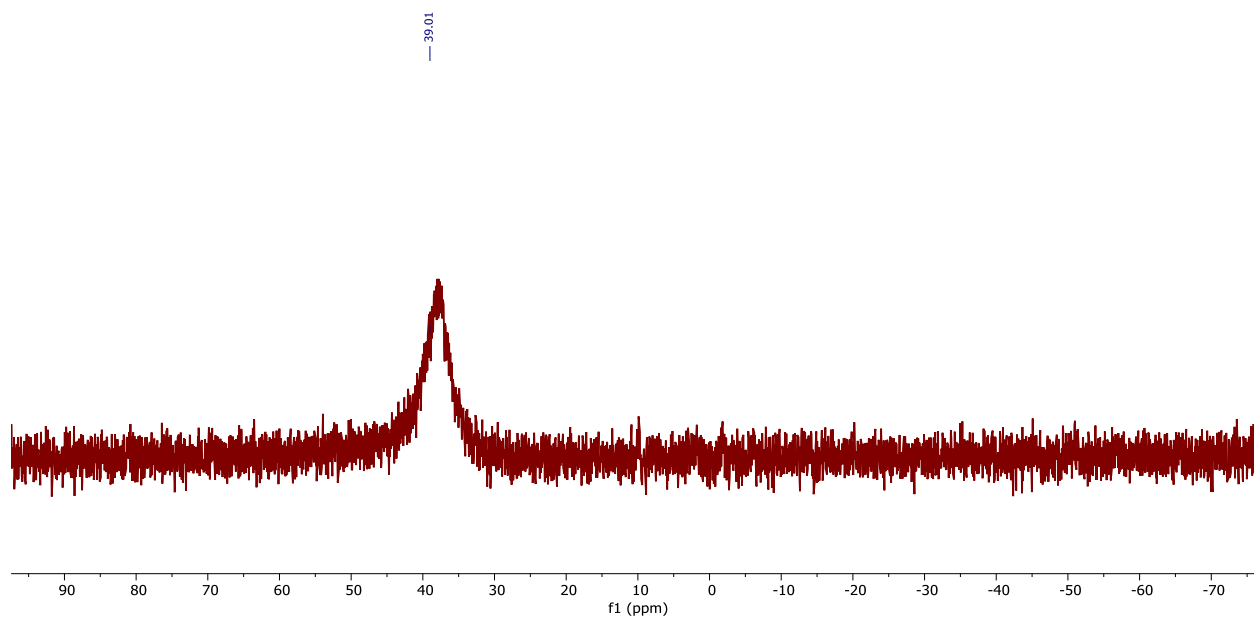


Figure S59. ^{11}B NMR spectrum of **12** in CD_2Cl_2 .

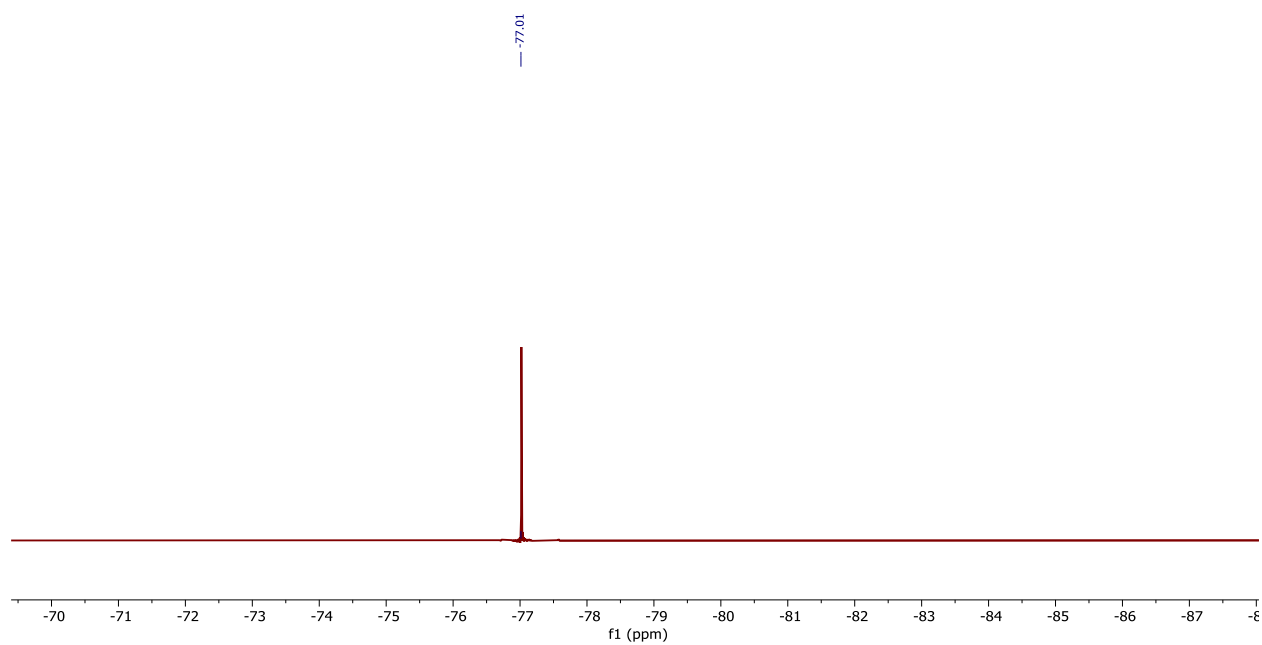
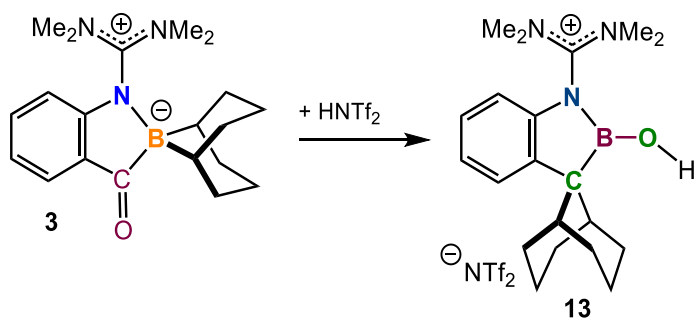


Figure S60. ^{19}F NMR spectrum of **12** in CD_2Cl_2 .

2.15. Synthesis of **13**



In the glove box, a 4 mL scintillation vial equipped with a magnetic stir bar was charged with **3** (50 mg, 0.15 mmol), HNTf₂ (41.5 mg, 0.15 mmol) and dry benzene (5 mL). After stirring the reaction mixture for one hour, all

volatiles were removed under vacuum (10⁻² mbar) to give **13** as a colorless oil. Yield 83 mg (90%). ¹H NMR [400 MHz, C₆D₆]: ¹H NMR [400 MHz, C₆D₆]: 7.72 (br, OH, 1 H), 7.67 (d, ³J_{H-H} = 4 Hz, CH-arom., 1 H), 7.07 (t, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 6.92 (t, ³J_{H-H} = 8 Hz, CH-arom., 1 H), 6.15 (d, ³J_{H-H} = 4 Hz, CH-arom., 1 H), 2.69, 2.34 (2s, CH₃, 2 x 6 H), 1.36-2.57 (m, CH/CH₂-skeleton, 14 H) ppm. ¹³C{H} NMR [125 MHz, C₆D₆]: 157.5 (C=N), 142.8, 139.1 (C-arom.), 131.0, 127.4, 123.3 (CH-arom.), 119.7 (q, ¹J_{C-F} = 318 Hz, CF₃), 111.5 (CH-arom.), 41.2, 40.2 (CH₃), 38.0 (C-quat.), 32.0 (CH), 30.0, 26.2, 20.8, 20.3 (CH₂) ppm. ¹¹B NMR [128.4 MHz, C₆D₆]: 59.0 ppm. ¹⁹F NMR [376.3 MHz, DMSO-d₆]: -76.8 ppm. Anal. Calc. for C₂₂H₃₁BF₃N₄O₅S₂ (620.43): C, 42.59; H, 5.04, N, 9.03, Found: C, 42.49; H, 4.95, N, 9.11. IR (neat) $\tilde{\nu}_{\text{OH}} = 3303 \text{ cm}^{-1}$.

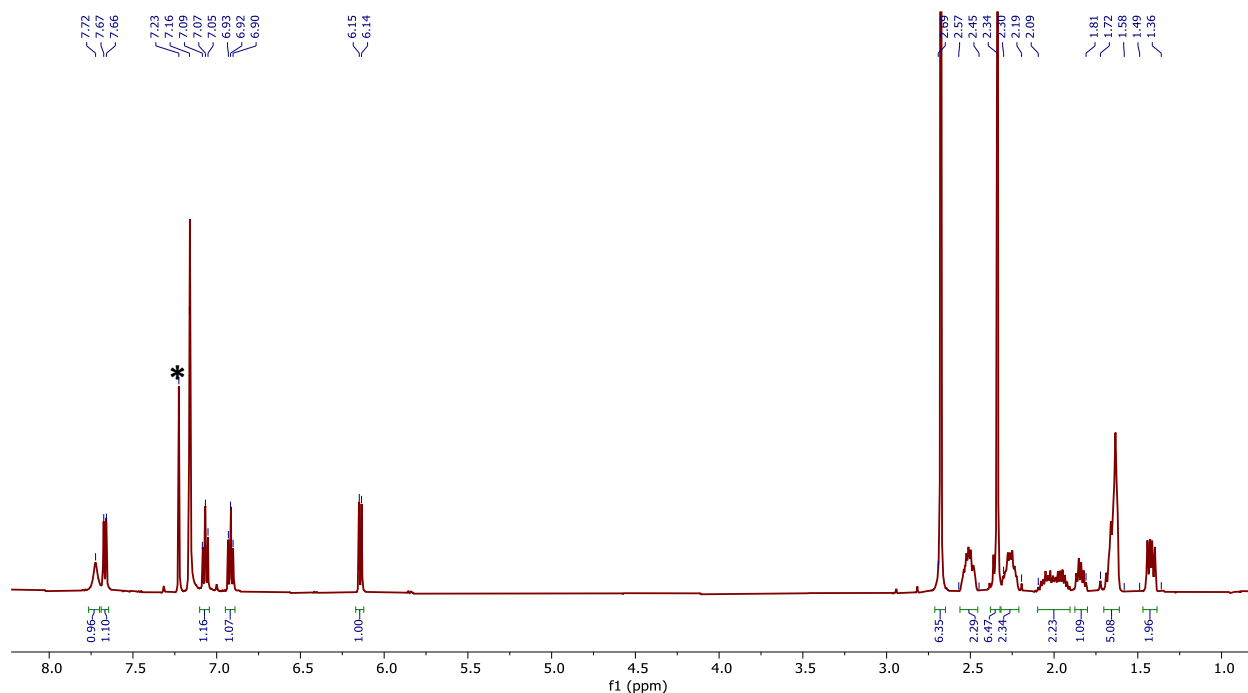


Figure S61. ¹H NMR spectrum of **13** in C₆D₆ (* benzene).

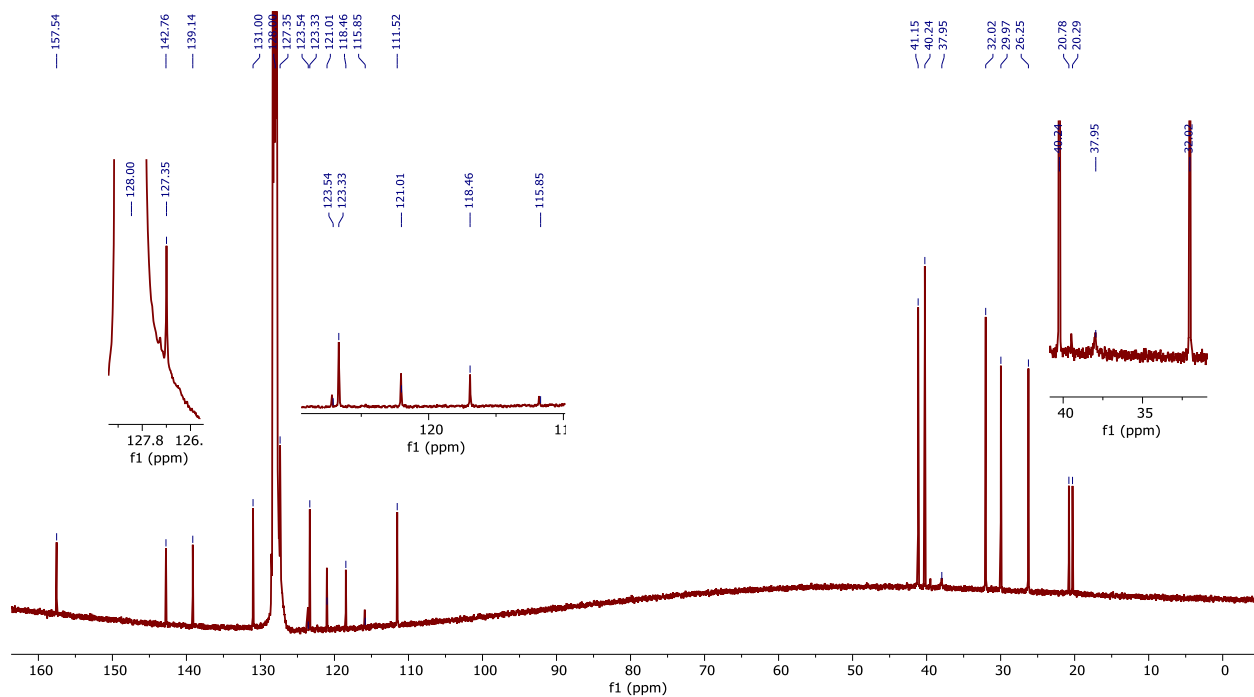


Figure S62. ^{13}C NMR spectrum of **13** in C_6D_6 .

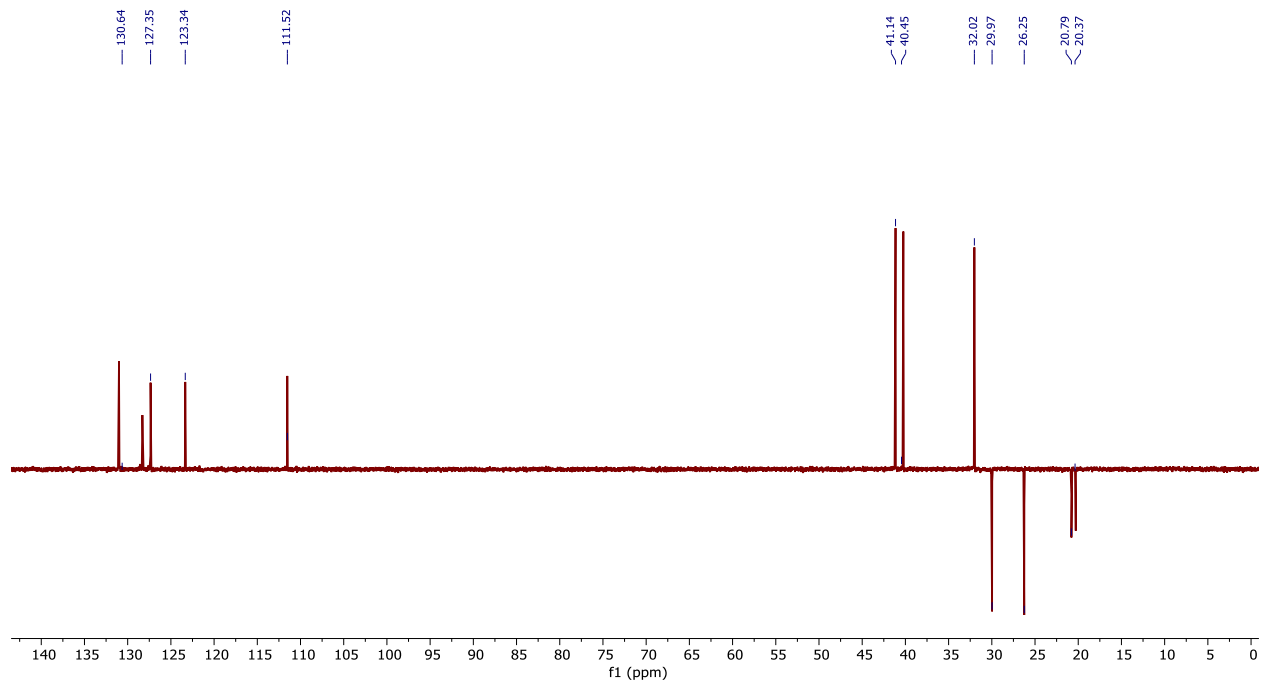


Figure S63. ^{13}C (DEPT) NMR spectrum of **13** in C_6D_6 .

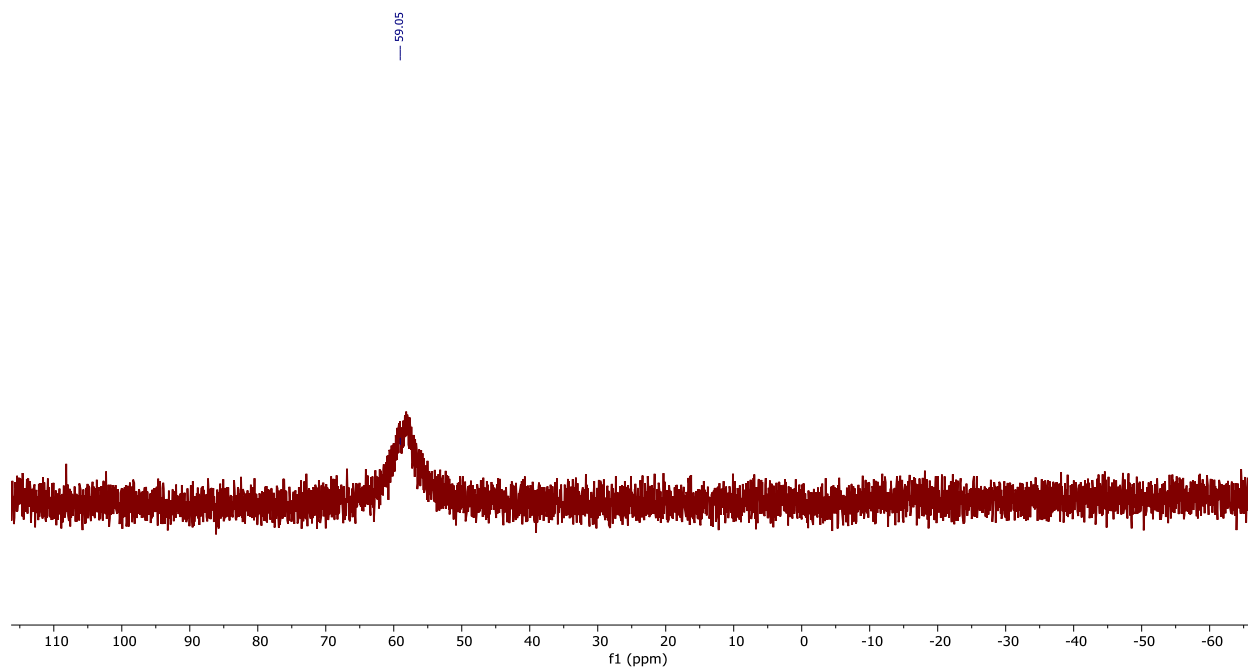


Figure S64. ^{11}B NMR spectrum of **13** in C_6D_6 .

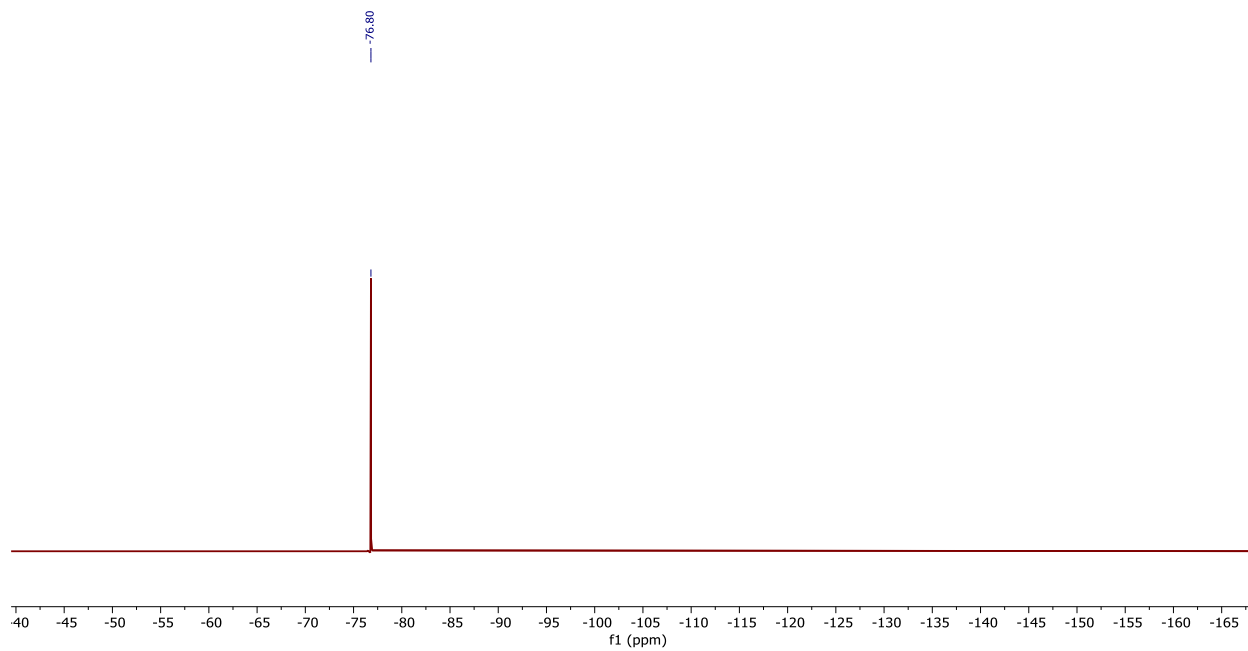


Figure S65. ^{19}F NMR spectrum of **13** in C_6D_6 .

3. X-ray crystallography

CCDC2091784 (2), CCDC2091785 (3), CCDC2091786 (4), CCDC2091787 (5), CCDC2091788 (6), CCDC2097624 (7), CCDC2091789 (8), CCDC2091790 (10), and CCDC2091791 (12) contain the supplementary crystallographic data for this paper.

These data can be obtained from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

General Data Collection

All data sets were collected on a Rigaku XtaLAB Synergy-*i* Kappa diffractometer equipped with a PhotonJet-*i* X-ray source operated at 50 W (50kV, 1 mA) to generate Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) and a HyPix-6000HE HPC detector. Crystals were transferred from the vial and placed on a glass slide with type NVH immersion oil by Cargille. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The crystal and a small amount of the oil were collected on either a MiTiGen MicroLoop or Hampton Research 20 micron nylon CryoLoop of the appropriate size and transferred to the instrument where it was placed under a cold nitrogen stream (Oxford) maintained at 100K throughout the experiment. The samples were optically centered with the aid of a video camera to ensure that no translations were observed as the crystal was rotated through all positions. Then, a unit cell collection was carried out. After it was determined that the unit cell was not present in the CCDC database a data collection strategy was calculated by *CrysAlis^{Pro}* [5]. The crystal was measured for size, morphology, and color.

General Refinement Details

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects using the *CrysAlis^{Pro}* [5]. A numerical absorption correction was applied based on a Gaussian integration over a multifaceted crystal and followed by a semi-empirical correction for adsorption applied using the program *SCALE3 ABSPACK* [6]. The program

SHELXT [7] was used for the initial structure solution and *SHELXL* [8] was used for refinement of the structure. Both of these programs were utilized within the OLEX2 software [9]. Hydrogen atoms bound to carbon and oxygen atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands unless otherwise noted below in the specific refinement details for each structure.

Specific Refinement Details

Compound **3**. To help constrain C-C bond lengths in one of the interstitial benzene molecules (C41 < C46) the AFIX 66 constraint was applied.

Compound **4**. For the interstitial benzene molecule (C42 < C47) the AFIX 66 constraint was applied to maintain reasonable C-C bond distances.

Compound **6**. Within this structure, there was a disordered benzene molecule (C28 < C33) in the interstitial space. The molecule was modeled as split sites (A and B) with refined site occupancies of 0.60 and 0.40, respectively. To help maintain reasonable ADP values for the carbon atoms, a SIMU restraint was applied.

4. References

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