

Supplementary Data for:

Stoichiometric Reductions of Alkyl-Substituted Ketones and Aldehydes to Borinic Esters

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Materials and Methods

General Considerations: All reactions and work-up procedures were performed under an inert atmosphere of dry N₂ using standard Schlenk techniques or a glovebox (MBraun glovebox equipped with a -35 °C freezer). Pentane and toluene (Aldrich) were dried using an Innovative Technologies solvent system. Deuterated solvents (CD₂Cl₂, d₈-toluene, C₆D₅Br) were purchased from Cambridge Isotope Laboratories, Inc. and stored over activated 4Å molecular sieves prior to use. Ketones and aldehydes were purchased from either Sigma-Aldrich or Alfa Aesar, B(C₆F₅)₃ was purchased from Boulder Scientific, BPh₃ was purchased from Strem, and C₁₀H₆(PPh₂)₂ was prepared from a known literature procedure.¹ All were used without further purification. Hydrogen gas (Grade 5.0) was obtained from Linde and purified through a Matheson Model 450B or Matheson Nanochem WeldAssure™ gas purifier.

NMR spectra were obtained on a Bruker Avance III 400 MHz, Varian Mercury 300 MHz, Agilent DD2 600 MHz, or Agilent DD2 500 MHz spectrometer. Spectra were referenced to residual solvent of d₈-toluene (¹H = 2.08 for methyl; ¹³C = 20.40 for CH₃), CD₂Cl₂ (¹H = 5.32, ¹³C = 54.0), or C₆D₅Br (¹H = 7.28 ppm for meta proton; ¹³C = 122.4 ppm for ipso carbon). Chemical shifts are listed in ppm and coupling constants are listed in Hz. NMR assignments are supported by additional 2D experiments. High-resolution mass spectrometry (HRMS) was performed in house.

Syntheses and Characterizations

*In general, borinic esters and boron enolates synthesized for this communication were highly prone to decomposition upon isolation. Boron enolates have been characterized in solution, and attempts to isolate borinic ester **5b** cleanly were unsuccessful (see below). These materials are stable in their crude reaction mixture for days; for those products which were isolated successfully, they were stored in a -35 °C freezer.*

General Synthesis – Ketone Hydrogenation (NMR scale): The ketone (0.05 mmol), B(C₆F₅)₃ (0.05 mmol), and 1,3,5-tri-*tert*-butylbenzene (internal standard, 0.02-0.03 mmol) were combined in 0.4 mL of d₈-tol or C₆D₅Br and transferred to a J-Young tube. The tube was degassed by three freeze-pump-thaw cycles on a vacuum/H₂ Schlenk line and filled with H₂ (4 atm) at -196 °C. The tube was then heated to 110 °C until the reaction was complete, as evidenced by ¹H, ¹⁹F, and ¹¹B NMR. NMR yields were calculated using ¹H integration and a known amount of internal standard (1,3,5-tri-*tert*-butylbenzene). For isolation, the reaction was repeated without internal standard and, once the reaction was complete, the solvent was removed *in vacuo*, the resulting material was dissolved in

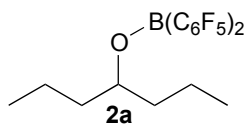
pentane and filtered over celite. The filtrate was concentrated yielding the borinic ester product.

*These products are sensitive to air and moisture, and were unstable in dichloromethane (with the exception of **2a**). Once isolated, the materials were stored in a -35 °C freezer under a N₂ atmosphere.*

General Synthesis – Ketone Hydrogenation (large scale): The ketone (0.5 mmol) was quantitatively transferred to a vial containing B(C₆F₅)₃ (0.5 mmol) with 1 mL toluene. The resulting solution was quantitatively transferred to a 50 mL Schlenk bomb equipped with a magnetic stir bar using 3 mL toluene. The reaction vessel was degassed by three freeze-pump-thaw cycles on a vacuum/H₂ Schlenk line and filled with H₂ (4 atm) at -196 °C. The reaction was heated to 110 °C for the required reaction time, after which the volatiles were removed *in vacuo* and the resulting material was dissolved in minimal pentane and filtered over celite. The solution was concentrated, yielding the desired products as clear or faint yellow oils.

General Synthesis – Boron Enolate Synthesis: The aldehyde (0.05 mmol) and borane (0.05 mmol) were combined in 0.5 mL of d₈-tol or C₆D₅Br and heated to 110 °C until the reaction was complete, as evidenced by ¹H, ¹⁹F (where applicable), and ¹¹B NMR. Isolation attempts were unsuccessful, as the materials decompose upon concentration. They are therefore characterized from the crude reaction mixtures.

General Synthesis – Boron Enolate Hydrogenation: A crude reaction mixture containing **4a** or **4b** was added to a vial containing B(C₆F₅)₃ (0.01 mmol). The resulting solution was combined with phosphine (0.01 mmol) and the reaction was transferred to a J-Young tube. The tube was degassed by three freeze-pump-thaw cycles on a vacuum/H₂ Schlenk line and filled with H₂ (4 atm) at -196 °C. The tube was then heated to 110 °C until the reaction was complete, as evidenced by ¹H, ¹⁹F, ³¹P, and ¹¹B NMR. NMR yields were calculated using ¹H integration and a known amount of internal standard (1,3,5-tri-*tert*-butylbenzene). The reaction was repeated without internal standard, and the reactions (upon completion) were concentrated, dissolved in minimal pentane and filtered to remove the phosphine. Successive washings with cold pentane yielded the pure product **5a** or **5b**.



2a: Reaction time: 24 h. Isolated as a faint yellow oil (228 mg, 99%).

¹H NMR (400 MHz, 298 K, CD₂Cl₂): δ 4.21 (quintet, ³J_{H-H} = 6.0 Hz, 1H, OCH), 1.70-1.55 (m, 4H, 2xCH₂), 1.47-1.36 (m, 2H, CH₂), 1.33-1.22 (m, 2H, CH₂), 0.88 (t, ³J_{H-H} = 7.3 Hz, 6H, CH₃).

¹⁹F NMR (377 MHz, 298 K, CD₂Cl₂): δ -132.3 (dd, ³J_{F-F} = 23.2 Hz, ⁴J_{F-F} = 9.5 Hz, 2F, *o*-C₆F₅), -150.8 (t, ³J_{F-F} = 20.1 Hz, 1F, *p*-C₆F₅), -161.8 - -162.0 (m, 2F, *m*-C₆F₅).

¹¹B NMR (128 MHz, 298 K, CD₂Cl₂): δ 39.3 (br s).

¹³C{¹H} NMR (101 MHz, 298 K, CD₂Cl₂): δ 148.0 (dm, ¹J_{C-F} ~ 249 Hz, C₆F₅), 138.0 (dm, ¹J_{C-F} ~ 254 Hz, C₆F₅), 82.5 (s, OCH), 38.6 (s, CH₂), 18.7 (s, CH₂), 14.3 (s, CH₃).

HRMS (EI) calcd for C₁₉H₁₅BF₁₀O 460.1056, found 460.1067.

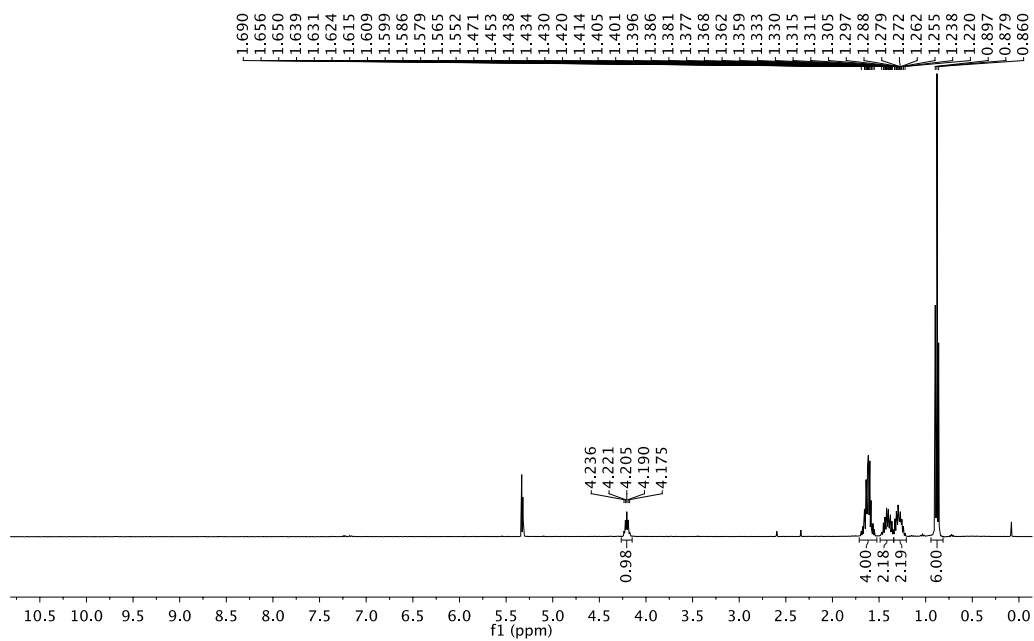


Figure S1: ¹H NMR spectrum of **2a**.

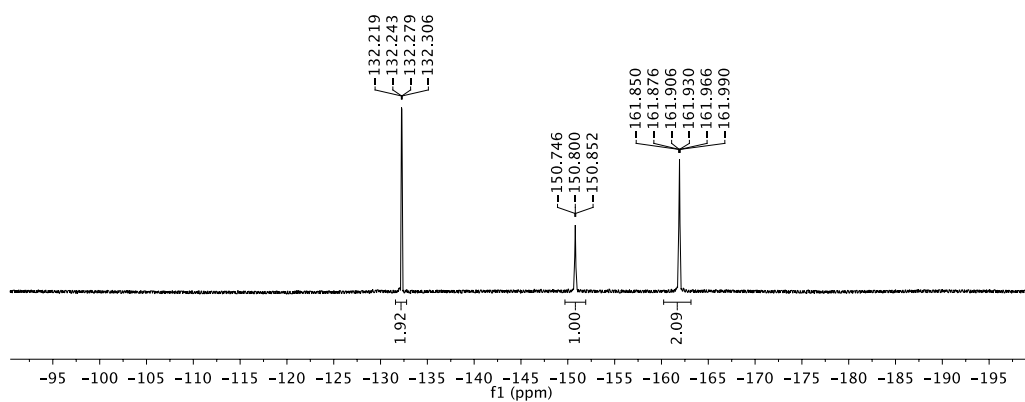


Figure S2: ¹⁹F NMR spectrum of **2a**.

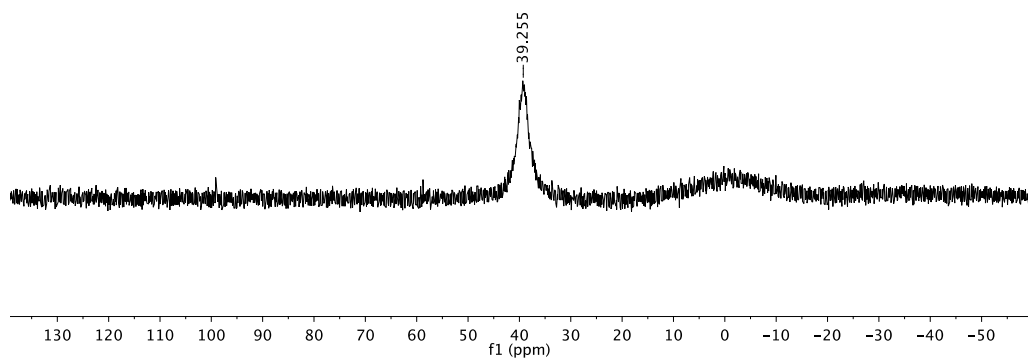


Figure S3: ^{11}B NMR spectrum of **2a**.

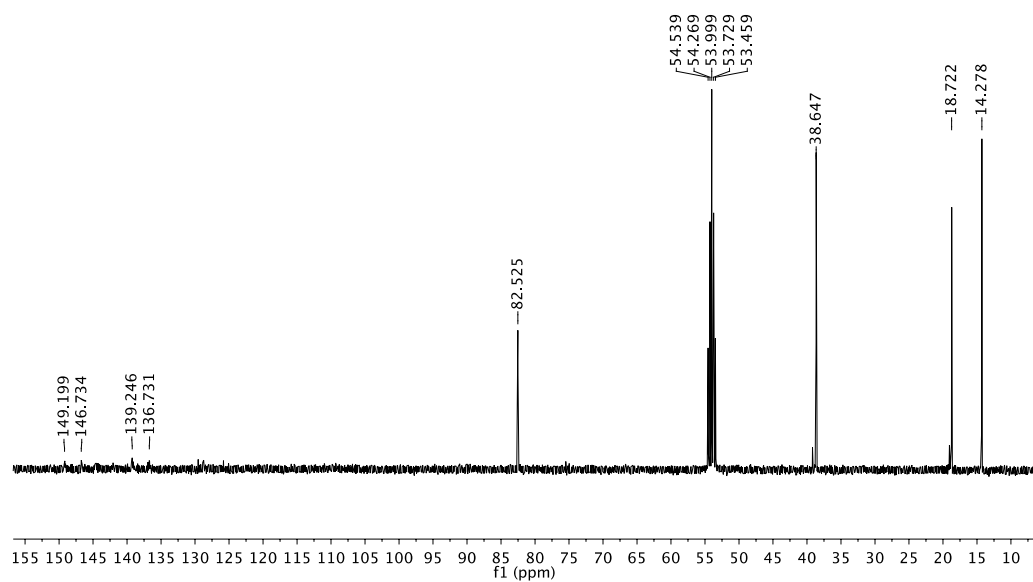
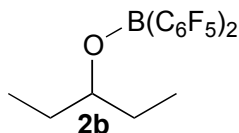


Figure S4: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2a**.



2b: Reaction time: 24 h. Isolated as a clear oil (213 mg, 99%). Unidentified impurities in the ^{19}F NMR spectrum were recurrent but minor (Figure S6).

^1H NMR (300 MHz, 298 K, $\text{C}_6\text{D}_5\text{Br}$): δ 3.97-3.89 (m, 1H, OCH), 1.64-1.42 (m, 4H, 2x CH_2), 0.83 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 6H, 2x CH_3).

^{19}F NMR (282 MHz, 298 K, $\text{C}_6\text{D}_5\text{Br}$): δ -131.4 (dd, $^3J_{\text{F-F}} = 24.4$ Hz, $^4J_{\text{F-F}} = 9.7$ Hz, 2F, *o*- C_6F_5), -149.0 (t, $^3J_{\text{F-F}} = 20.9$ Hz, 1F, *p*- C_6F_5), -160.1 - -160.3 (m, 2F, *m*- C_6F_5).

^{11}B NMR (128 MHz, 298 K, $\text{C}_6\text{D}_5\text{Br}$): δ 39.2 (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 298 K, $\text{d}_8\text{-tol}$), partial: δ 147.7 (dm, $^1J_{\text{C-F}} \sim 245$ Hz, C_6F_5), 143.0 (dm, $^1J_{\text{C-F}} \sim 256$ Hz, C_6F_5), 137.6 (dm, $^1J_{\text{C-F}} \sim 255$ Hz, C_6F_5), 84.5 (s, OCH), 28.7 (s, CH_2), 9.3 (s, CH_3).

HRMS (EI) calcd for $\text{C}_{17}\text{H}_{11}\text{BF}_{10}\text{O}$ 432.0743, found 432.0727.

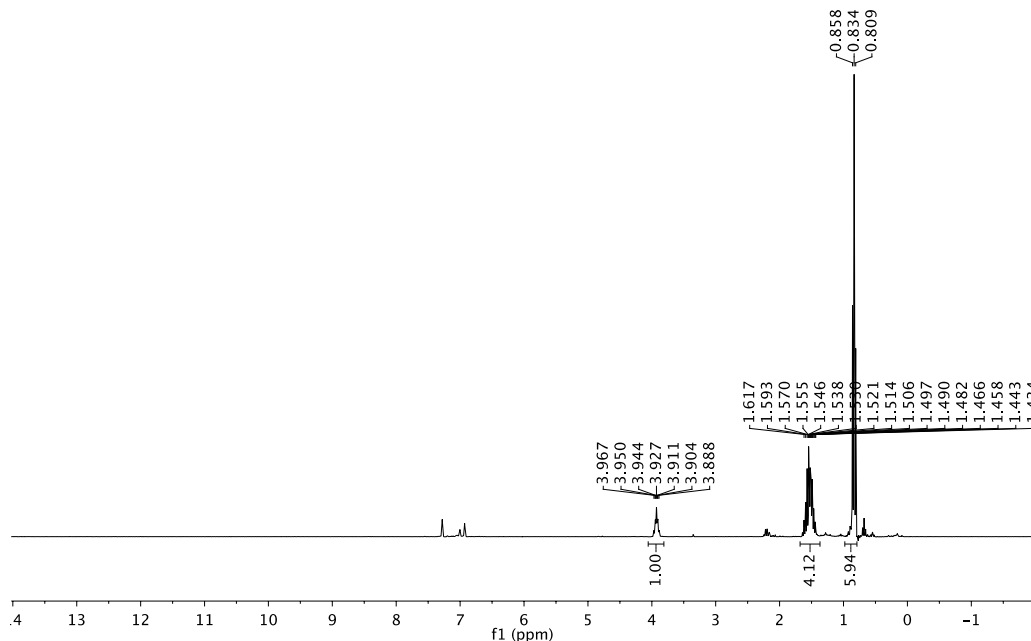


Figure S5: ^1H NMR spectrum of **2b**.

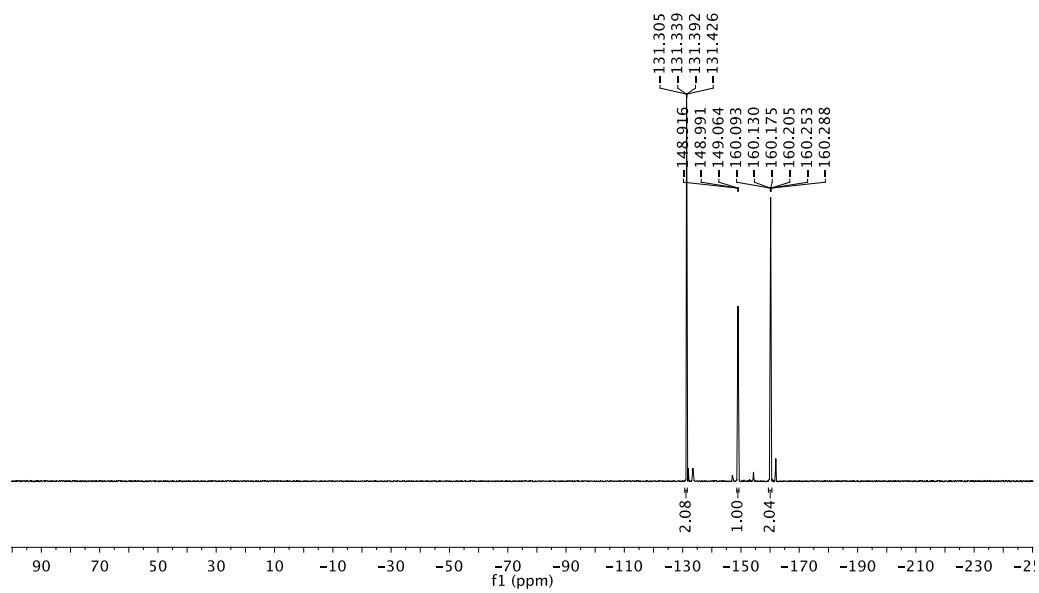


Figure S6: ^{19}F NMR spectrum of **2b**.

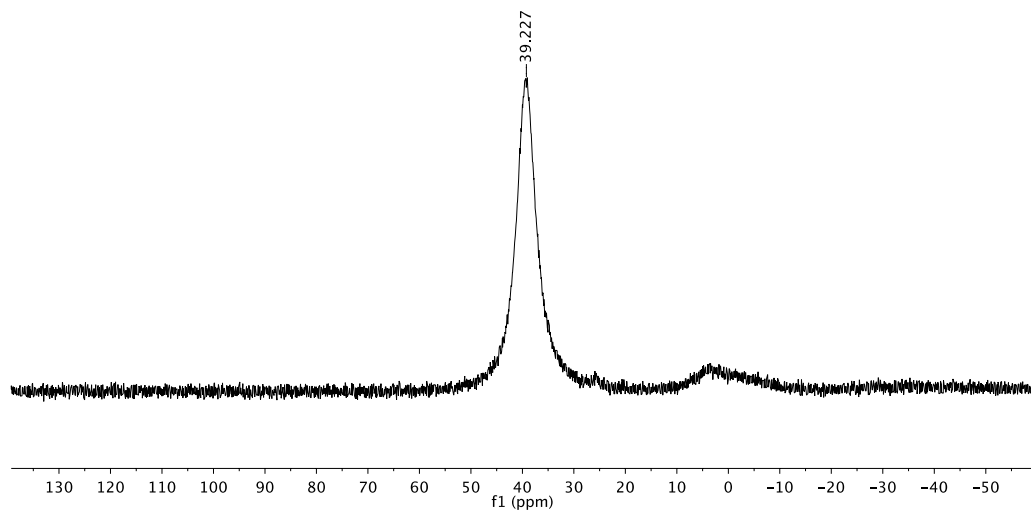


Figure S7: ^{11}B NMR spectrum of **2b**.

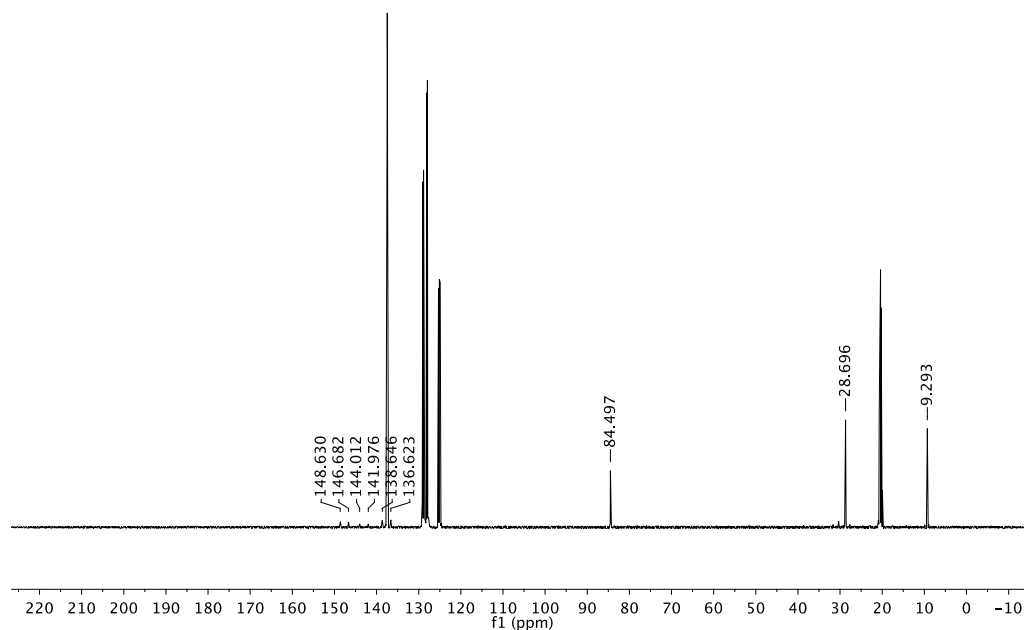
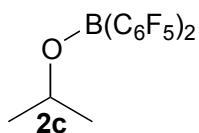


Figure S8: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2b**.



2c: Reaction time: 21 h. Isolated as a clear oil (168 mg, 83%). Unidentified impurities in the ^{19}F NMR were recurrent but minor (Figure S10).

^1H NMR (400 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 4.17 (septet, $^3J_{\text{H-H}} = 6.0$ Hz, 1H, OCH), 1.09 (d, $^3J_{\text{H-H}} = 6.0$ Hz, 6H, 2xCH₃).

^{19}F NMR (377 MHz, 298 K, $\text{d}_8\text{-tol}$): δ -133.0 (dd, $^3J_{\text{F-F}} = 23.5$ Hz, $^4J_{\text{F-F}} = 9.3$ Hz, 2F, *o*-C₆F₅), -149.4 (br t, $^3J_{\text{F-F}} = 20.5$ Hz, 1F, *p*-C₆F₅), -161.1 (br s, 2F, *m*-C₆F₅).

^{11}B NMR (128 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 39.3 (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 298 K, $\text{d}_8\text{-tol}$), partial: δ 74.6 (s, OCH), 24.1 (s, 2xCH₃).

HRMS (EI) calcd for C₁₅H₇BF₁₀O 404.0430, found 404.0438.

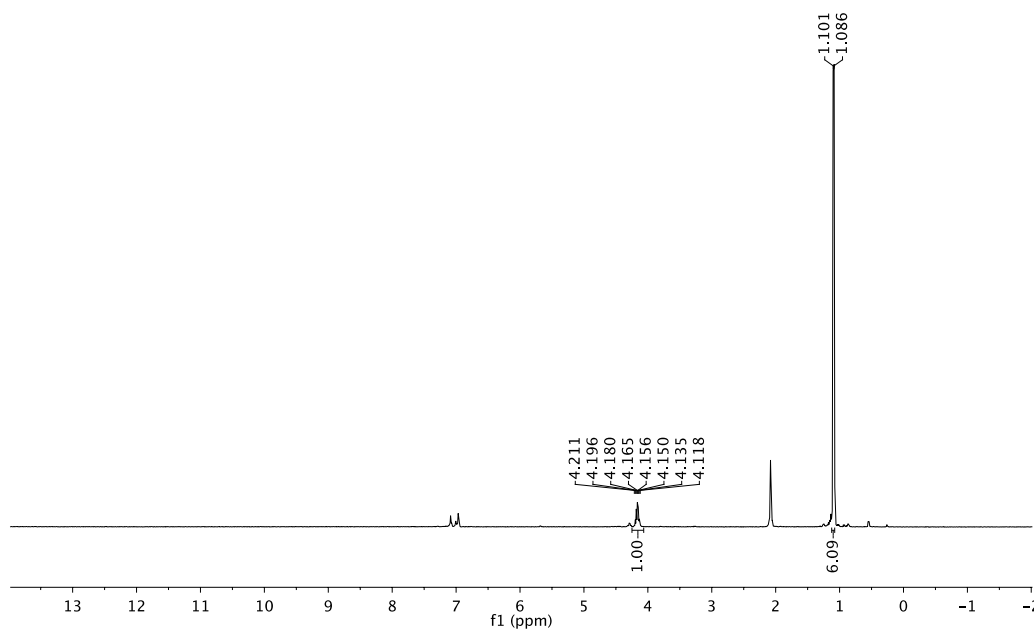


Figure S9: ¹H NMR spectrum of **2c**.

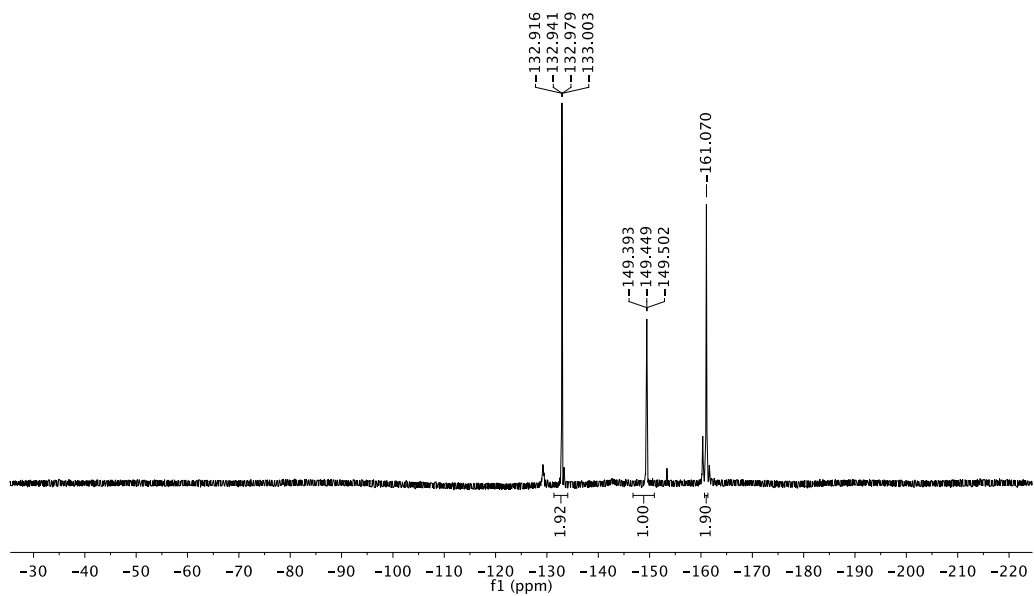


Figure S10: ¹⁹F NMR spectrum of **2c**.

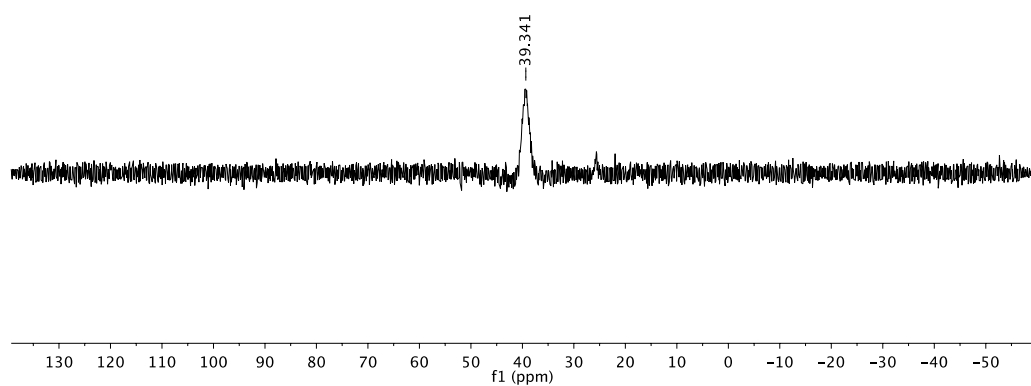


Figure S11: ^{11}B NMR spectrum of **2c**.

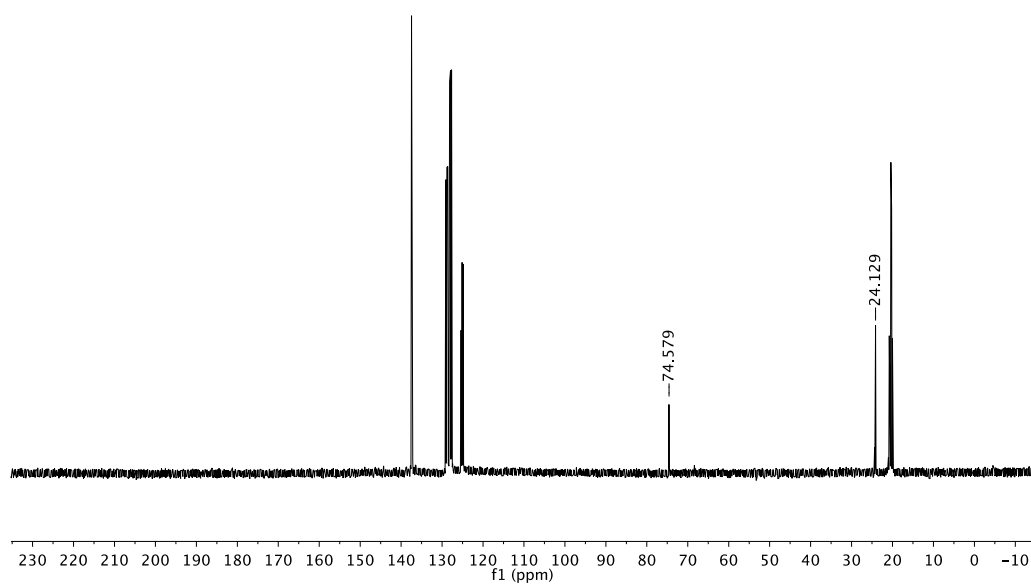
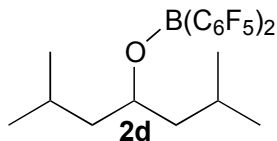


Figure S12: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2c**.



2d: Reaction time: 120 h. NMR yield 94%.

^1H NMR (400 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 4.26 (pentet, $^3J_{\text{H-H}} = 6.2$ Hz, 1H, OCH), 1.68-1.51 (m, 4H, $2\times\text{CH}_2$), 1.38-1.31 (m, 2H, $2\times\text{CH}$), 0.79 (d, $^3J_{\text{H-H}} = 6.5$ Hz, 6H, $2\times\text{CH}_3$), 0.72 (d, $^3J_{\text{H-H}} = 6.4$ Hz, 6H, $2\times\text{CH}_3$).

^{19}F NMR (377 MHz, 298 K, $\text{d}_8\text{-tol}$): δ -132.2 (br s, 2F, *o*- C_6F_5), -149.3 (br s, 1F, *p*- C_6F_5), -161.1 (br s, 2F, *m*- C_6F_5).

^{11}B NMR (128 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 39.3 (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 298 K, $\text{d}_8\text{-tol}$), partial: δ 147.8 (dm, $^1J_{\text{C-F}} \sim 240$ Hz, C_6F_5), 143.1 (dm, $^1J_{\text{C-F}} \sim 259$ Hz, C_6F_5), 137.7 (dm, $^1J_{\text{C-F}} \sim 255$ Hz, C_6F_5), 79.2 (s, OCH), 45.7 (s, CH_2), 24.5 (s, CH), 22.8 (s, CH_3), 22.4 (s, CH_3).

HRMS (EI) calcd for $\text{C}_{21}\text{H}_{19}\text{BF}_{10}\text{O}$ 488.1369, found 488.1364

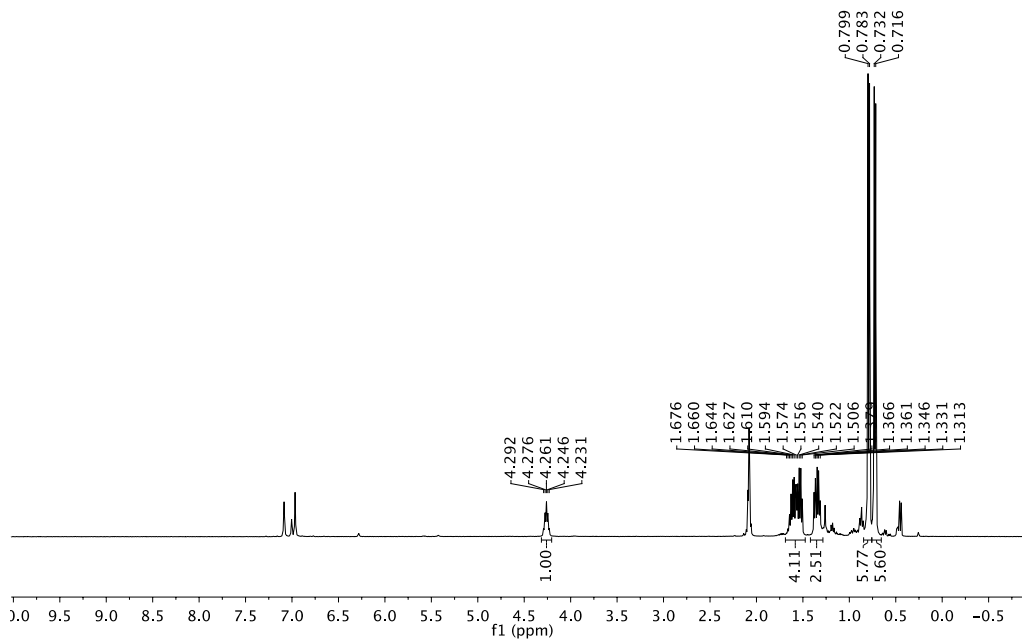


Figure S13: ^1H NMR spectrum of **2d**.

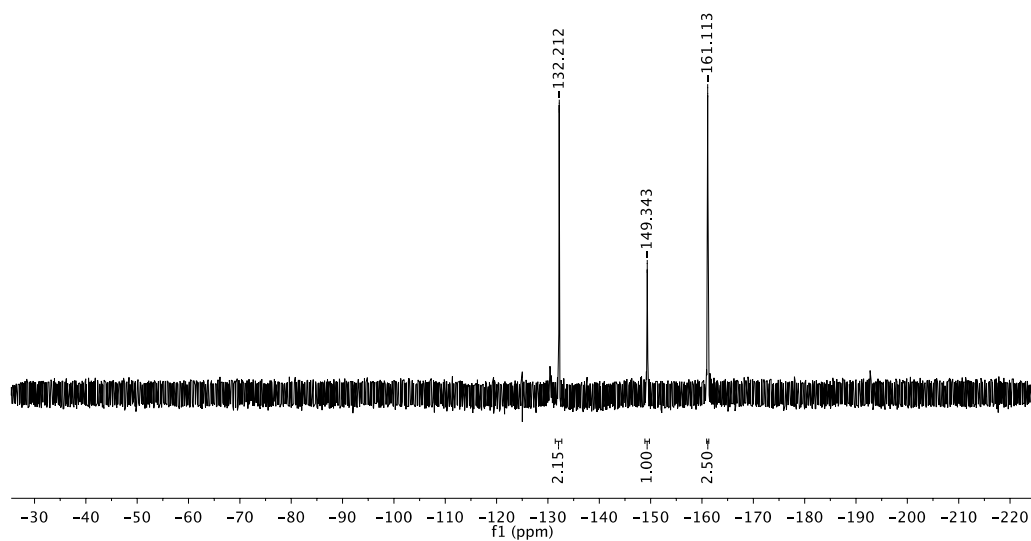


Figure S14: ^{19}F NMR spectrum of **2d**.

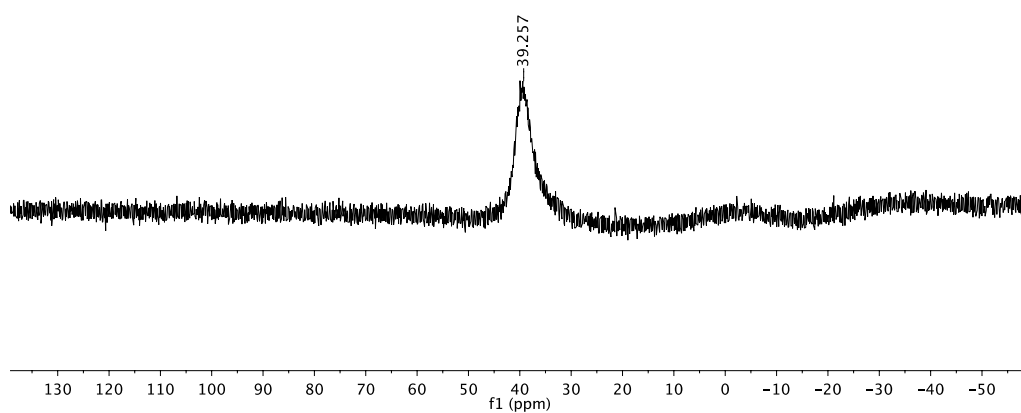


Figure S15: ^{11}B NMR spectrum of **2d**.

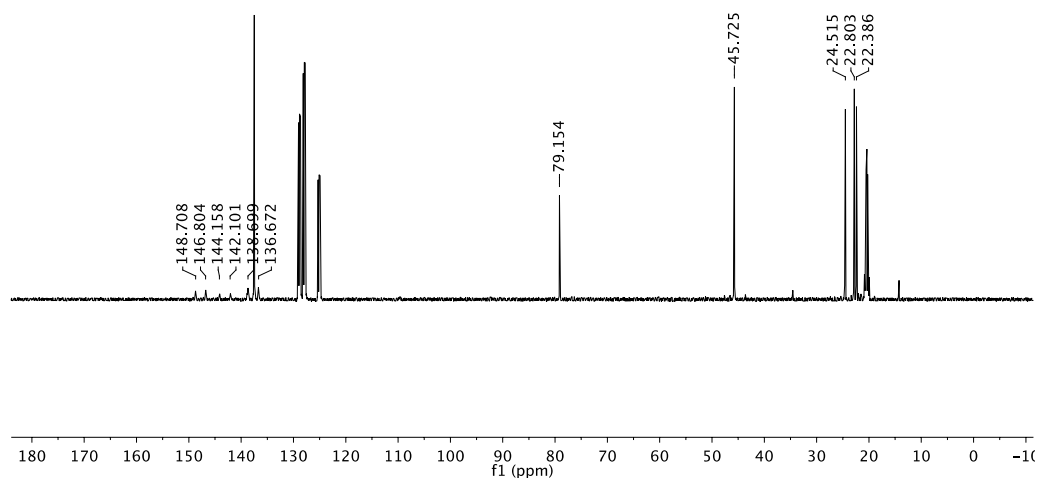
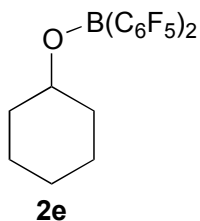


Figure S16: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2d**.



2e: Reaction time: 24 h. NMR yield: 97%. Isolated as a faint yellow oil (from cyclohexanone: 201 mg, 91%; from cyclohexenone: 208 mg, 94%).

^1H NMR (400 MHz, 298 K, $\text{C}_6\text{D}_5\text{Br}$): δ 4.26 (br, 1H, OCH), 1.77-1.58 (m, 6H, Cy), 1.33-1.21 (m, 4H, Cy).

^{19}F NMR (377 MHz, 298 K, $\text{C}_6\text{D}_5\text{Br}$): δ -131.9 (dd, $^3J_{\text{F-F}} = 23.8$ Hz, $^4J_{\text{F-F}} = 9.7$ Hz, 2F, *o*- C_6F_5), -149.5 (br s, 1F, *p*- C_6F_5), -160.7 (br s, 2F, *m*- C_6F_5).

^{11}B NMR (128 MHz, 298 K, $\text{C}_6\text{D}_5\text{Br}$): δ 39.1 ppm (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 298 K, $\text{C}_6\text{D}_5\text{Br}$), partial: δ 79.1 (s, OCH), 34.1 (s, CH_2), 25.3 (s, CH_2), 23.0 (s, CH_2).

HRMS (EI) calcd for $\text{C}_{18}\text{H}_{11}\text{BF}_{10}\text{O}$ 444.0743, found 444.0739.

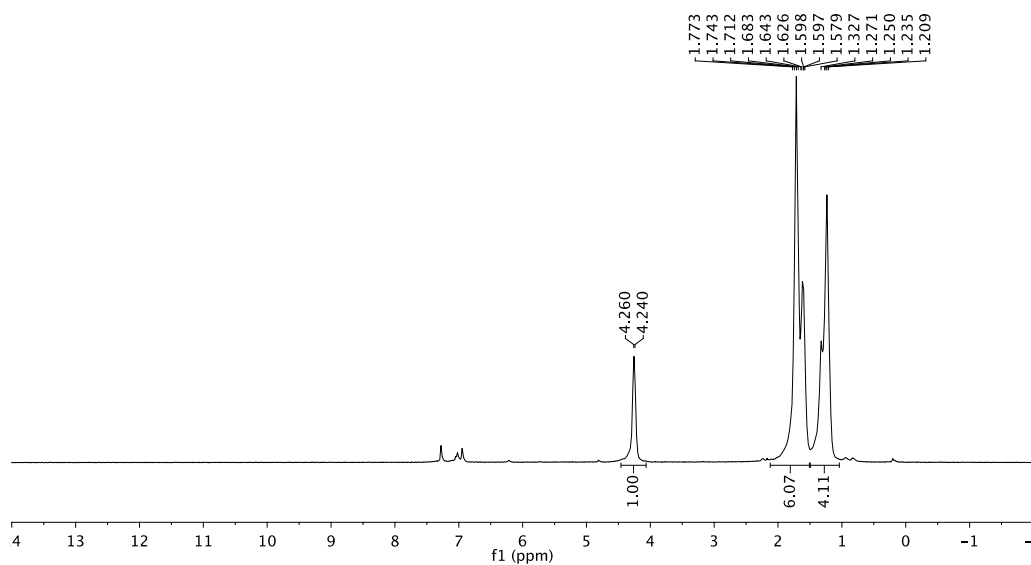


Figure S17: ^1H NMR spectrum of **2e**.

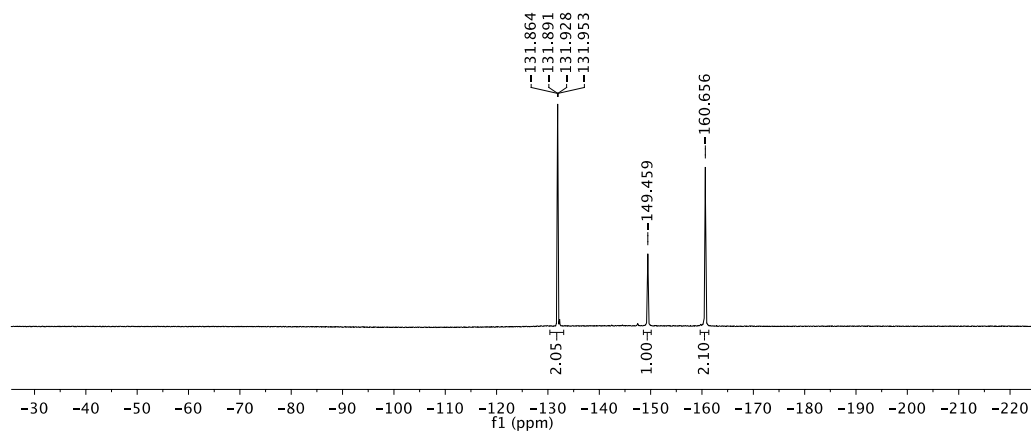


Figure S18: ^{19}F NMR spectrum of **2e**.

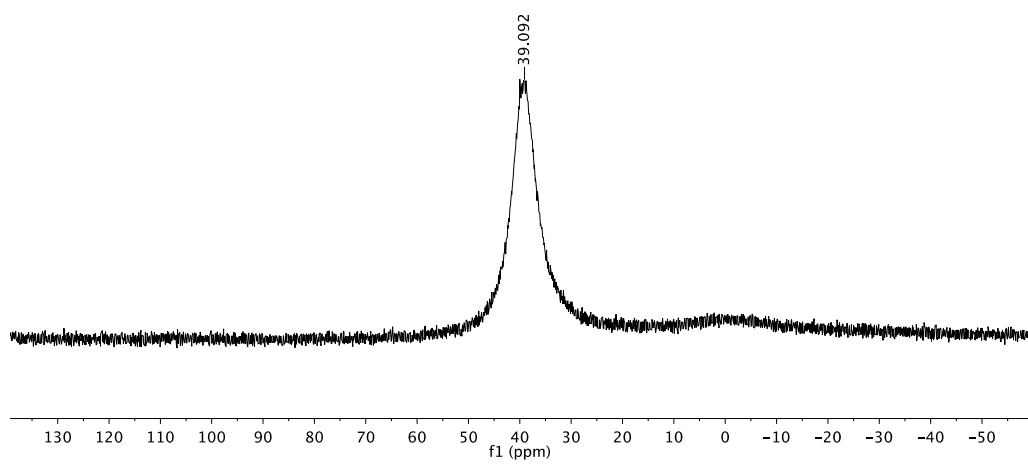


Figure S19: ^{11}B NMR spectrum of **2e**.

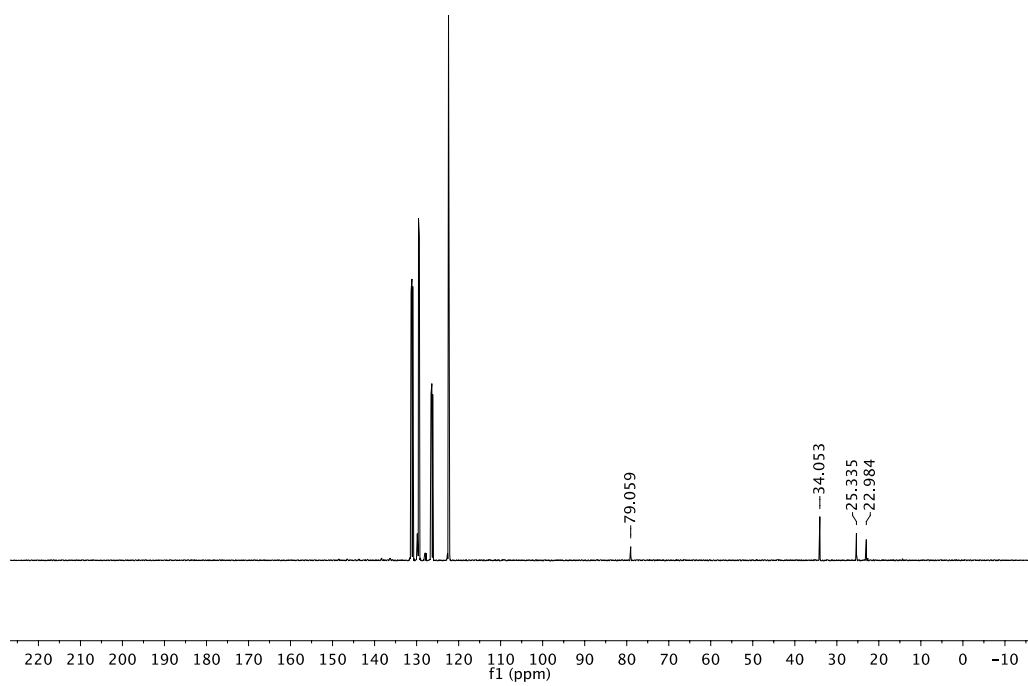
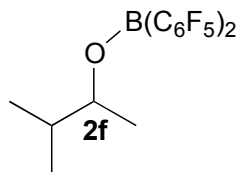


Figure S20: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2e**.



2f: Reaction time: 65 h. NMR yield: 85%.

^1H NMR (400 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 3.92-3.86 (m, 1H, OCH), 1.58-1.47 (m, 1H, *i*Pr CH), 1.12 (d, $^3J_{\text{H-H}} = 6.3$ Hz, 3H, OCH-CH₃), 0.88 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 3H, *i*Pr CH₃), 0.78 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, *i*Pr CH₃).

^{19}F NMR (377 MHz, 298 K, $\text{d}_8\text{-tol}$): δ -132.6 (dd, $^3J_{\text{F-F}} = 23.5$ Hz, $^4J_{\text{F-F}} = 9.3$ Hz, 2F, *o*-C₆F₅), -149.4 (br s, 1F, *p*-C₆F₅), -161.1 (br s, 2F, *m*-C₆F₅).

^{11}B NMR (128 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 39.4 (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 298 K, $\text{d}_8\text{-tol}$), partial: δ 147.8 (dm, $^1J_{\text{C-F}} \sim 248$ Hz, C₆F₅), 137.7 (dm, $^1J_{\text{C-F}} \sim 256$ Hz, C₆F₅), 82.9 (s, OCH), 34.3 (s, *i*Pr CH), 19.8 (s, OCH-CH₃), 18.4 (s, *i*Pr CH₃), 16.7 (s, *i*Pr CH₃).

HRMS (EI) calcd for C₁₇H₁₁BF₁₀O 432.0743, found 432.0750.

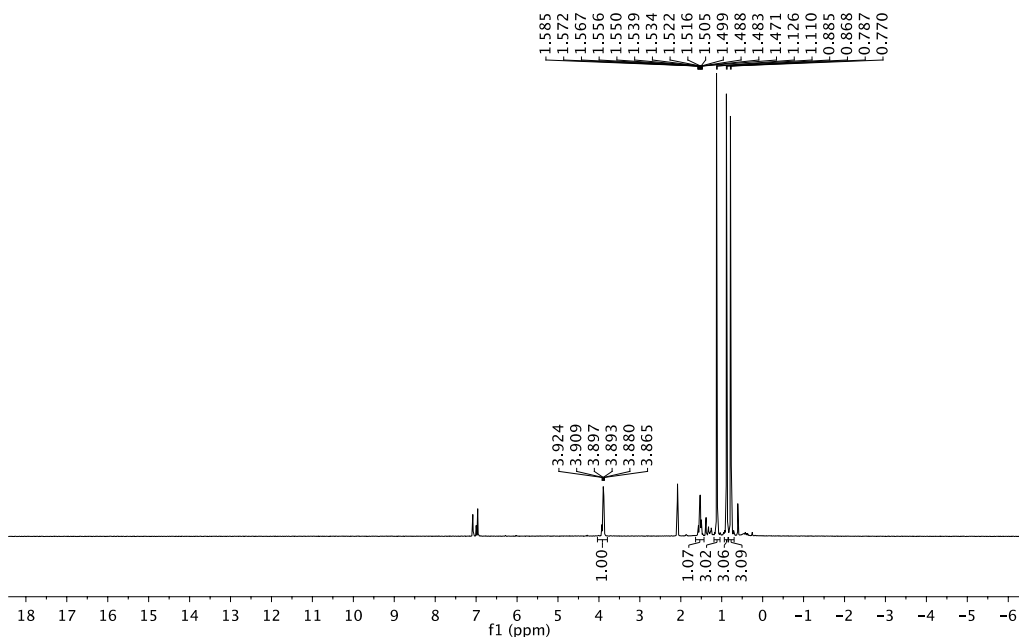


Figure S21: ^1H NMR spectrum of **2f**.

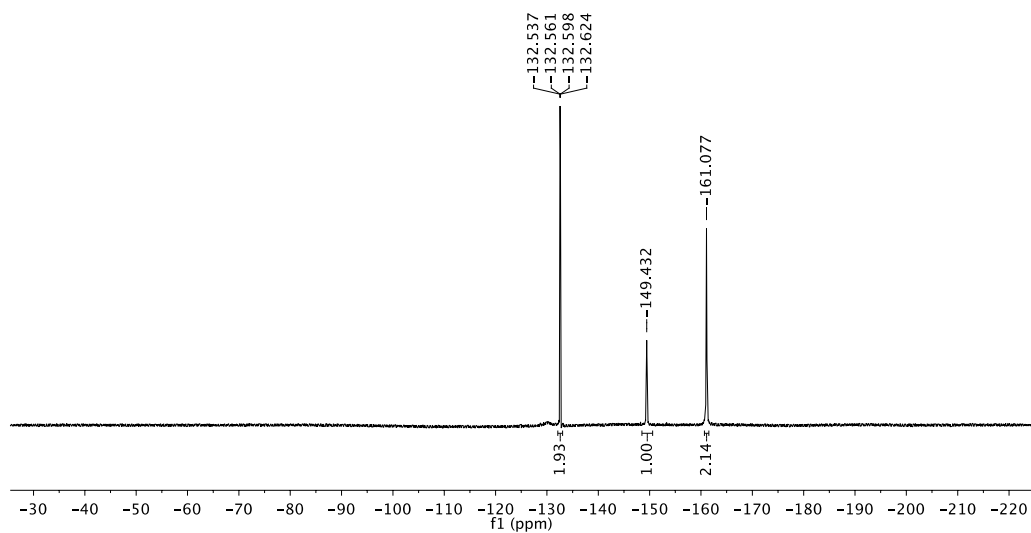


Figure S22: ^{19}F NMR spectrum of **2f**.

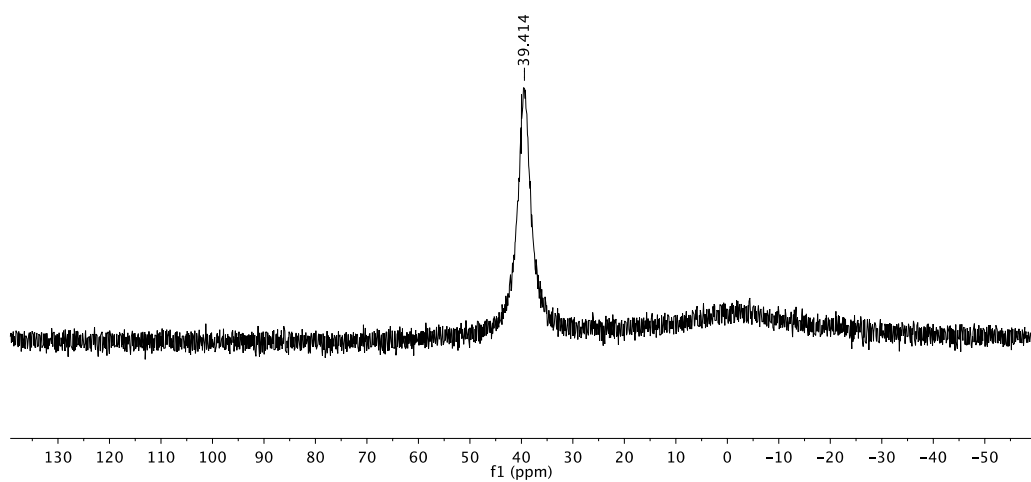


Figure S23: ^{11}B NMR spectrum of **2f**.

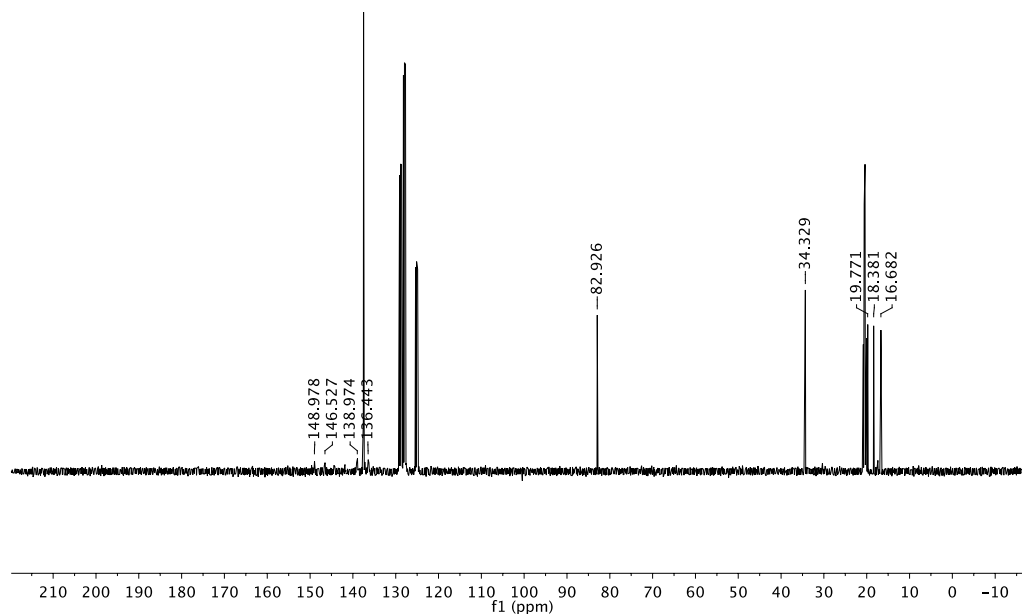
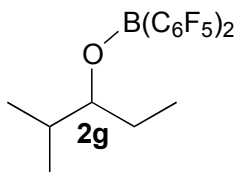


Figure S24: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2f**.



2g: Reaction time: 68 h. NMR yield: >99%.

^1H NMR (300 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 3.74 (dt, $^3J_{\text{H-H}} = 8.4, 4.7$ Hz, 1H, OCH), 1.74-1.34 (m, 3H, CH_2 and *i*Pr CH), 0.86 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CH_3), 0.82-0.77 (m, 6H, $2\times\text{CH}_3$).

^{19}F NMR (377 MHz, 298 K, CD_2Cl_2): δ -132.0 (dd, $^3J_{\text{F-F}} = 23.5$ Hz, $^4J_{\text{F-F}} = 9.3$ Hz, 2F, *o*- C_6F_5), -150.9 (t, $^3J_{\text{F-F}} = 20.6$ Hz, 1F, *p*- C_6F_5), -161.9 - -162.1 (m, 2F, *m*- C_6F_5).

^{11}B NMR (96 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 39.5 (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 298 K, $\text{d}_8\text{-tol}$), partial: δ 87.9 (s, OCH), 32.2 (s, *i*-Pr CH), 26.0 (s, CH_2), 18.3 (s, CH_3), 16.8 (s, CH_3), 9.5 (s, CH_3).

HRMS (EI) calcd for $\text{C}_{18}\text{H}_{13}\text{BF}_{10}\text{O}$ 446.0900, found 446.0903.

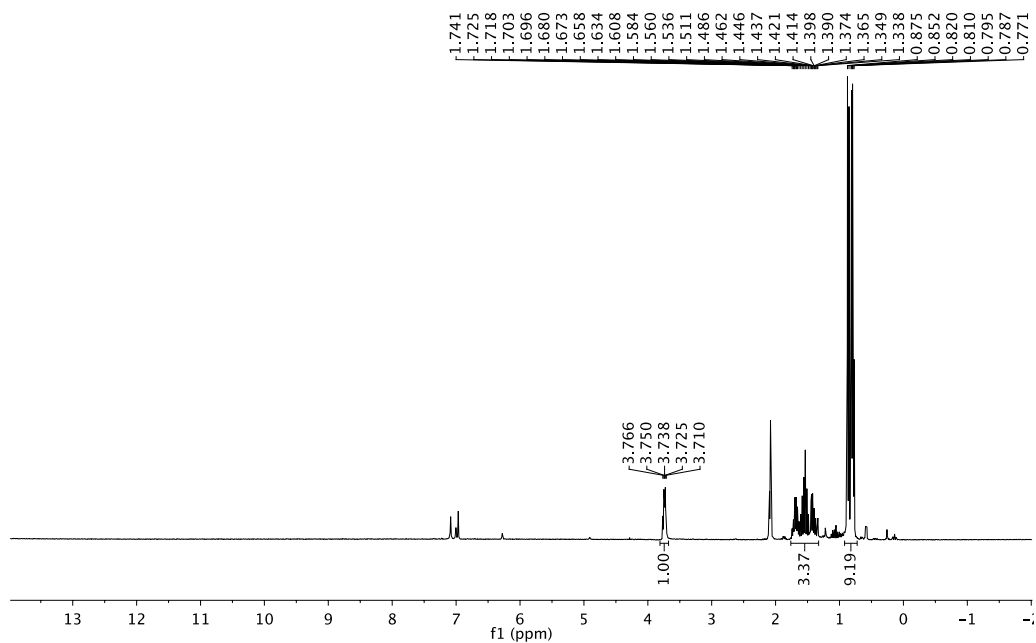


Figure S25: ^1H NMR spectrum of **2g**.

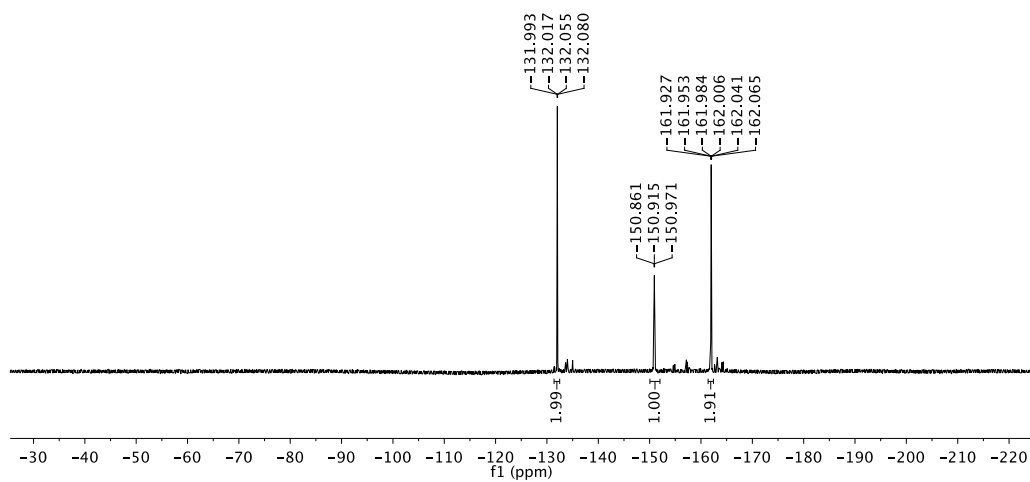


Figure S26: ^{19}F NMR spectrum of **2g**.

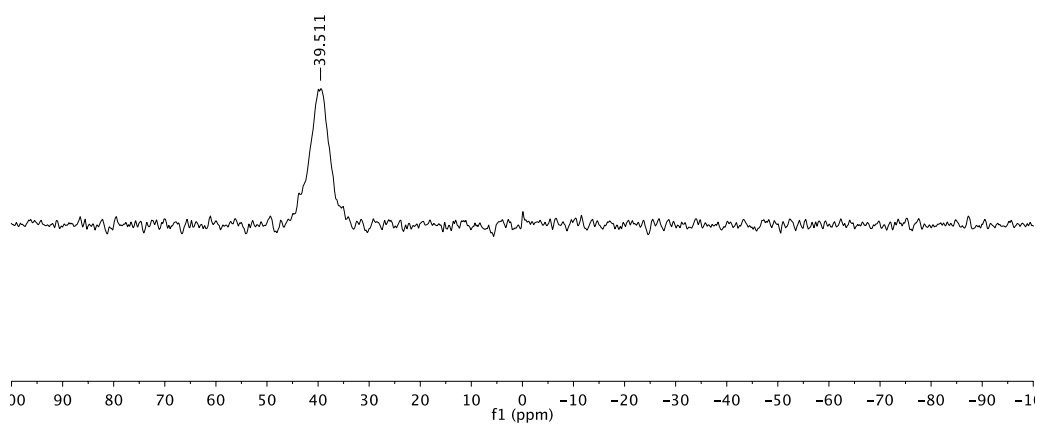


Figure S27: ^{11}B NMR spectrum of **2g**.

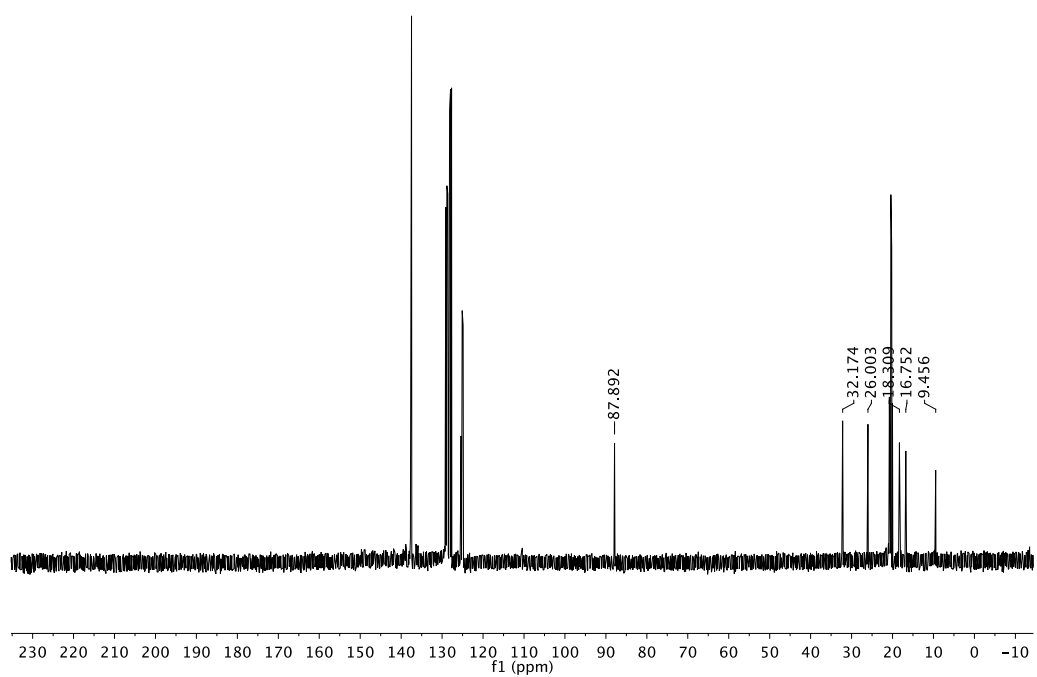
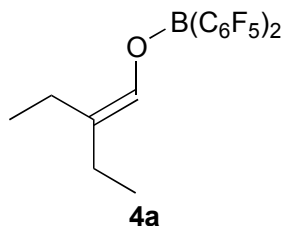


Figure S28: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2g**.



4a: Reaction time: 24 h. Characterized from the crude reaction mixture with HC_6F_5 .

^1H NMR (400 MHz, 298 K, d_8 -tol): δ 6.37 (s, 1H, alkene CH), 2.29 (q, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, CH_2), 1.77 (qd, $^3J_{\text{H-H}} = 7.5$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz, 2H, CH_2), 1.02 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 3H, CH_3), 0.82 (t, $^3J_{\text{H-H}} = 7.5$ Hz, 3H, CH_3). HC_6F_5 : δ 5.86-5.77 (m, 1H).

^{19}F NMR (376 MHz, 298 K, d_8 -tol): δ -131.9 (d, $^3J_{\text{F-F}} = 22.7$ Hz, 2F, *o*- C_6F_5), -148.1 (t, $^3J_{\text{F-F}} = 21.0$ Hz, 1F, *p*- C_6F_5), -160.9 - -161.0 (m, 2F, *m*- C_6F_5). HC_6F_5 : δ -139.2 - -139.3 (m, 2F), -154.3 (t, $^3J_{\text{F-F}} = 19.9$ Hz, 1F), -162.4 - -162.6 (m, 2F).

^{11}B NMR (128 MHz, 298 K, d_8 -tol): δ 39.8 (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 298 K, d_8 -tol), partial: δ 148.3 (dm, $^1J_{\text{C-F}} \sim 245$ Hz, C_6F_5), 143.6 (dm, $^1J_{\text{C-F}} \sim 254$ Hz, C_6F_5), 133.6 (dm, $^1J_{\text{C-F}} \sim 251$ Hz, C_6F_5), 133.5 (s, alkene CH), 133.5 (s, quat. C), 24.3 (s, CH_2), 20.9 (s, CH_2), 12.7 (s, CH_3), 12.4 (s, CH_3). HC_6F_5 , partial: δ 100.5 (td, $^2J_{\text{C-F}} = 23.1$ Hz, $^3J_{\text{C-F}} = 3.5$ Hz, CH).

HRMS (EI) calcd for $\text{C}_{18}\text{H}_{11}\text{BF}_{10}\text{O}$ 444.0743, found 444.0730.

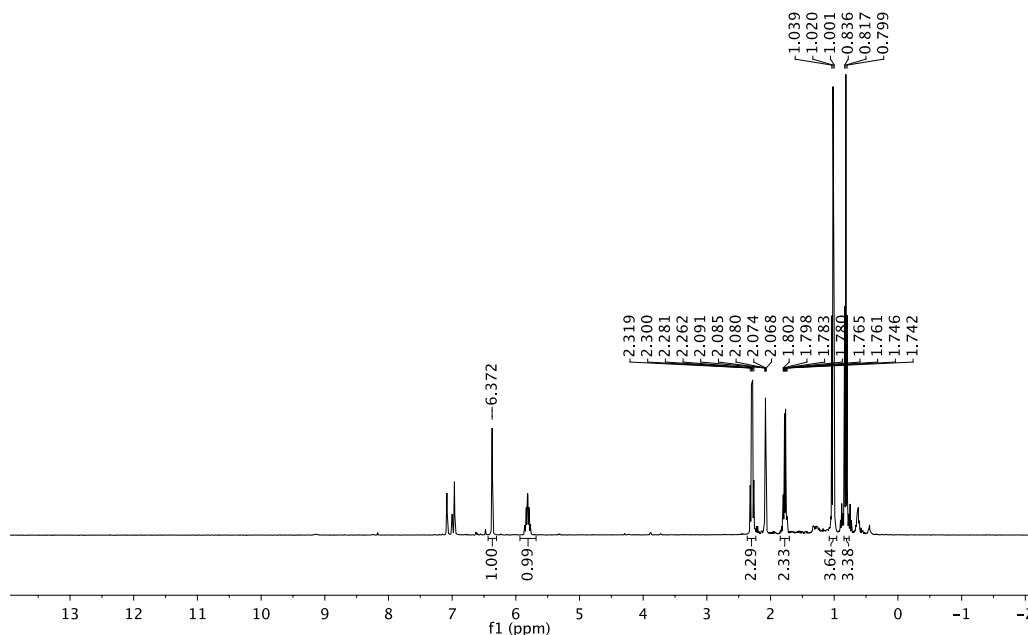


Figure S29: ^1H NMR spectrum of **4a**.

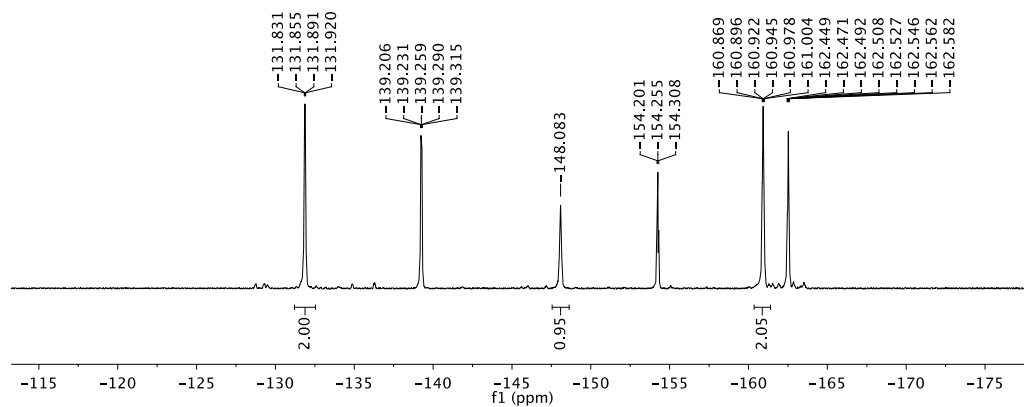


Figure S30: ¹⁹F NMR spectrum of **4a** with HC₆F₅.

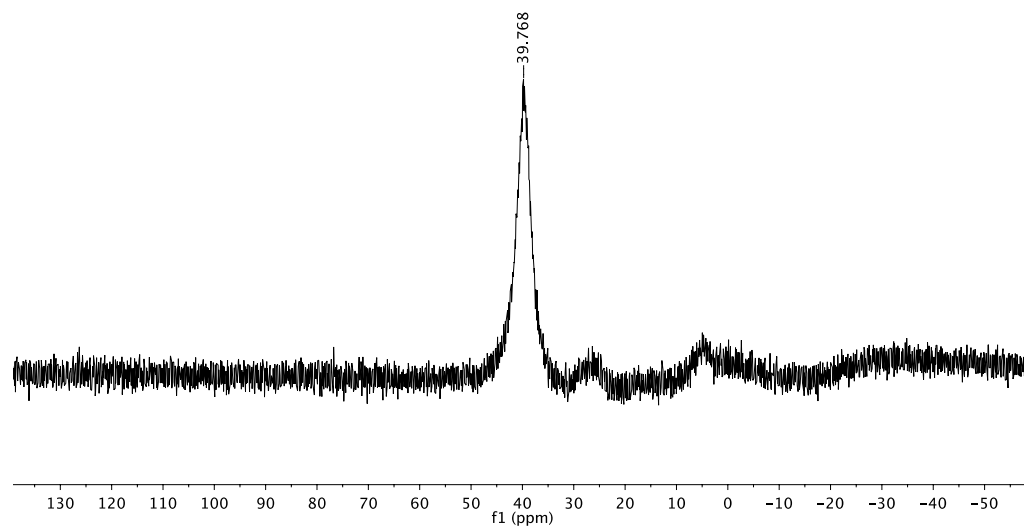


Figure S31: ¹¹B NMR spectrum of **4a**.

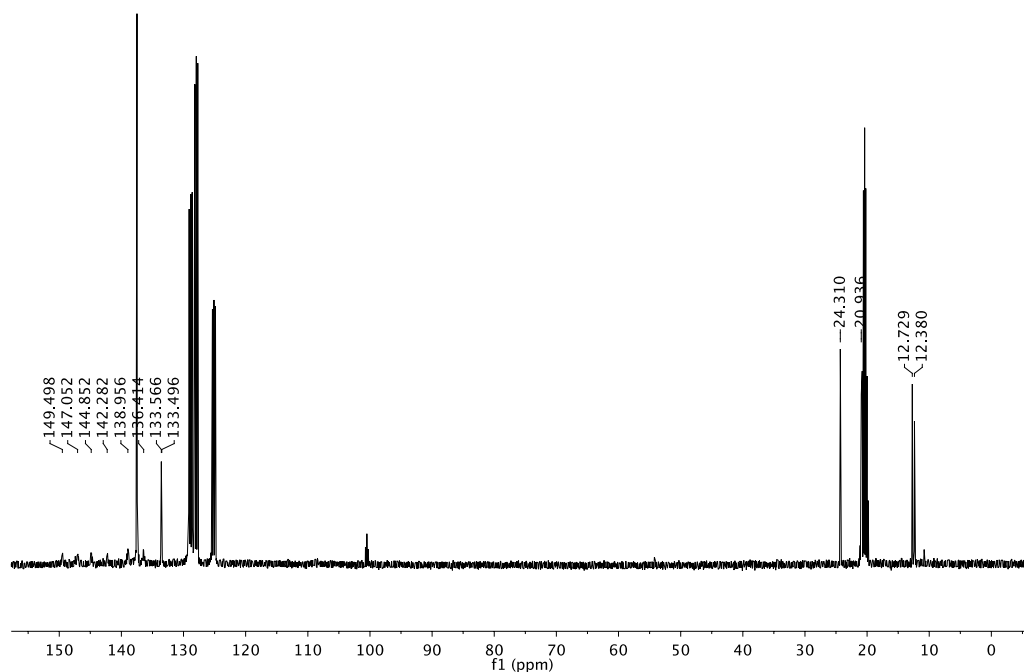
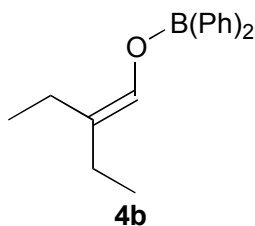


Figure S32: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4a**.



4b: Reaction time: 24 h. Characterized from the crude reaction mixture with C_6H_6 .

^1H NMR (400 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 7.73-7.71 (m, 4H, *o*-CH), 7.24-7.19 (m, 6H, *m*-CH + *p*-CH), 6.61 (br t, $^4J_{\text{H-H}} = 1.2$ Hz, 1H, alkene CH), 2.41 (q, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, CH_2), 1.80 (qd, $^3J_{\text{H-H}} = 7.4$ Hz, $^4J_{\text{H-H}} = 1.2$ Hz, 2H, CH_2), 1.10 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 3H, CH_3), 0.87 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 3H, CH_3). C_6H_6 : δ 7.12 (s).

^{11}B NMR (128 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 45.2 (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 135.8 (s, alkene CH), 135.3 (s, *o*-CH), 130.8 (s, *p*-CH), 127.9 (s, *m*-CH), 127.8 (s, quat. C), 24.5 (s, CH_2), 21.0 (s, CH_2), 13.1 (s, CH_3), 12.7 (s, CH_3). C_6H_6 : δ 128.5.

HRMS (EI) calcd for $\text{C}_{18}\text{H}_{21}\text{BO}$ 264.1685, found 264.1686.

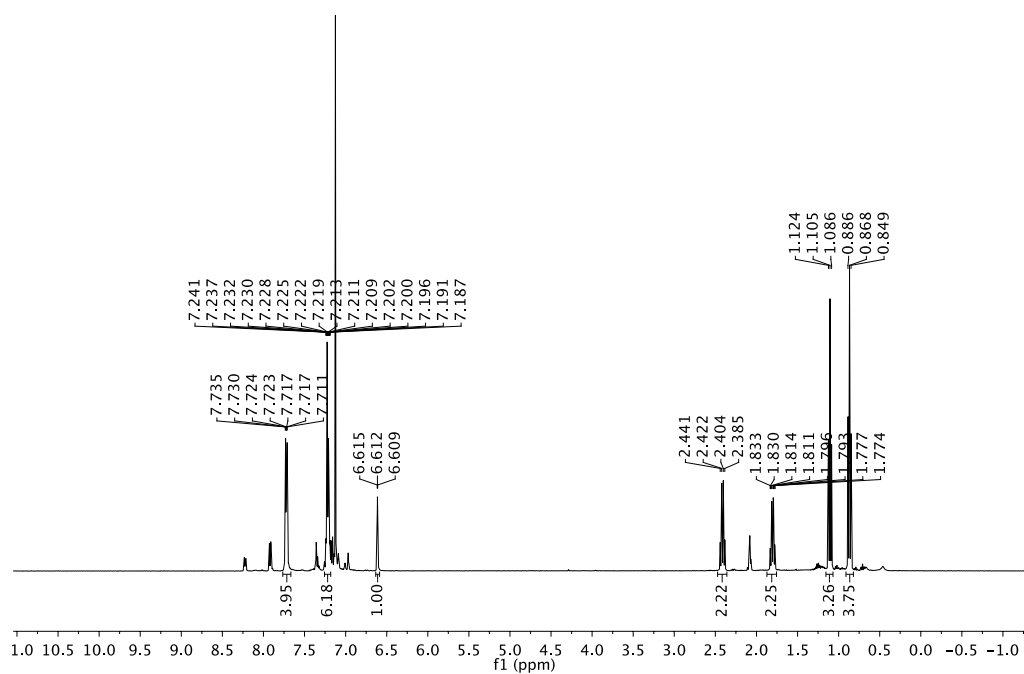


Figure S33: ¹H NMR spectrum of **4b**.

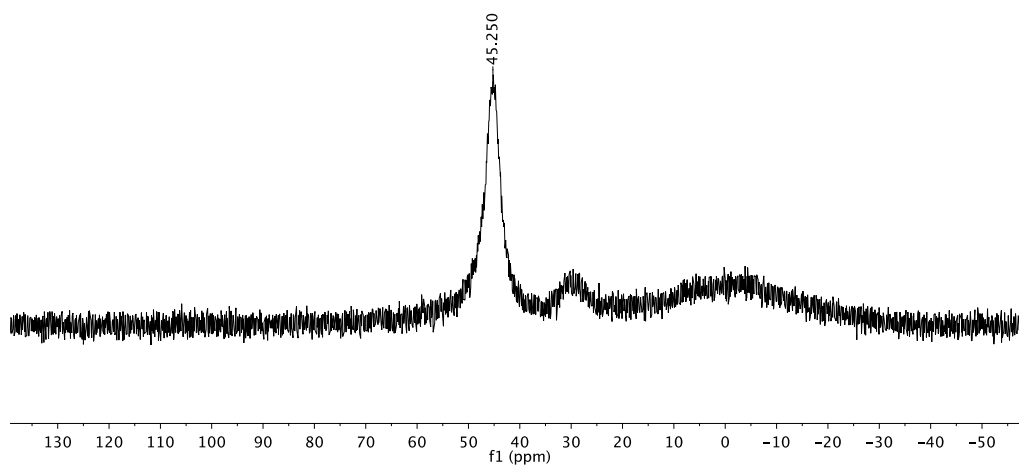


Figure S34: ¹¹B NMR spectrum of **4b**.

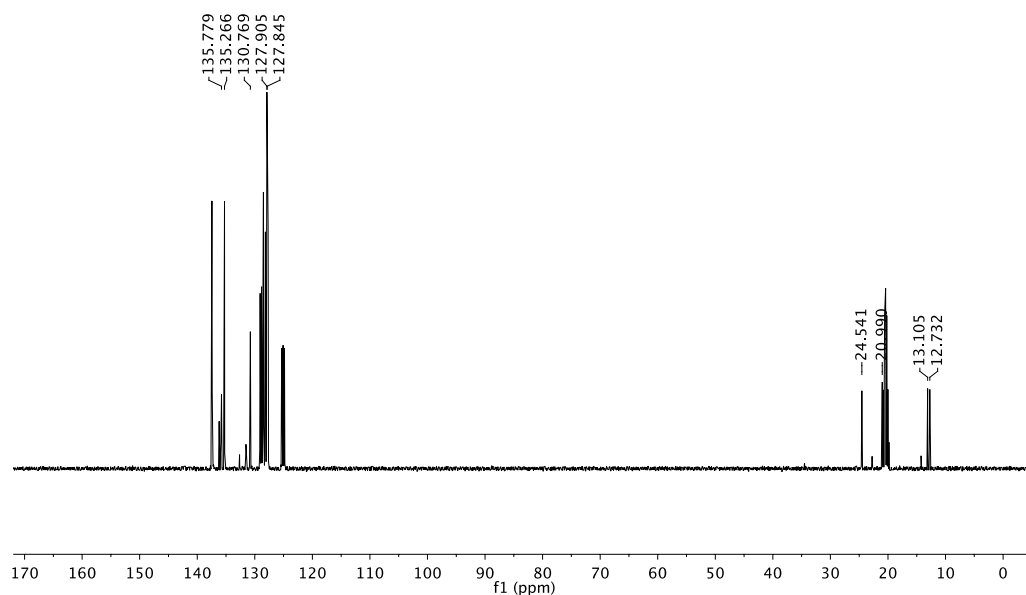
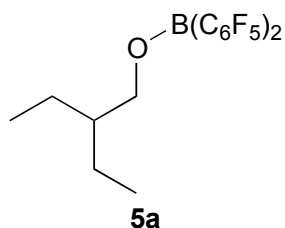


Figure S35: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4b**.



5a: Reaction time: 24 h. NMR yield: 79%.

^1H NMR (600 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 3.88 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 1H, OCH_2), 1.38-1.23 (m, 5H, CH + 2x CH_2), 0.77 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 6H, 2x CH_3).

^{19}F NMR (377 MHz, 298 K, $\text{d}_8\text{-tol}$): δ -132.5 - -132.6 (m, 2F, *o*- C_6F_5), -148.9 (br s, 1F, *p*- C_6F_5), -160.9 (br s, 2F, *m*- C_6F_5).

^{11}B NMR (128 MHz, 298 K, $\text{d}_8\text{-tol}$): δ 40.0 (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 298 K, $\text{d}_8\text{-tol}$), partial: δ 72.0 (s, OCH_2), 42.6 (s, CH), 23.2 (s, 2x CH_2), 11.1 (s, 2x CH_3).

HRMS (EI) calcd for $\text{C}_{18}\text{H}_{13}\text{BF}_{10}\text{O}$ 446.0900, found 446.0891.

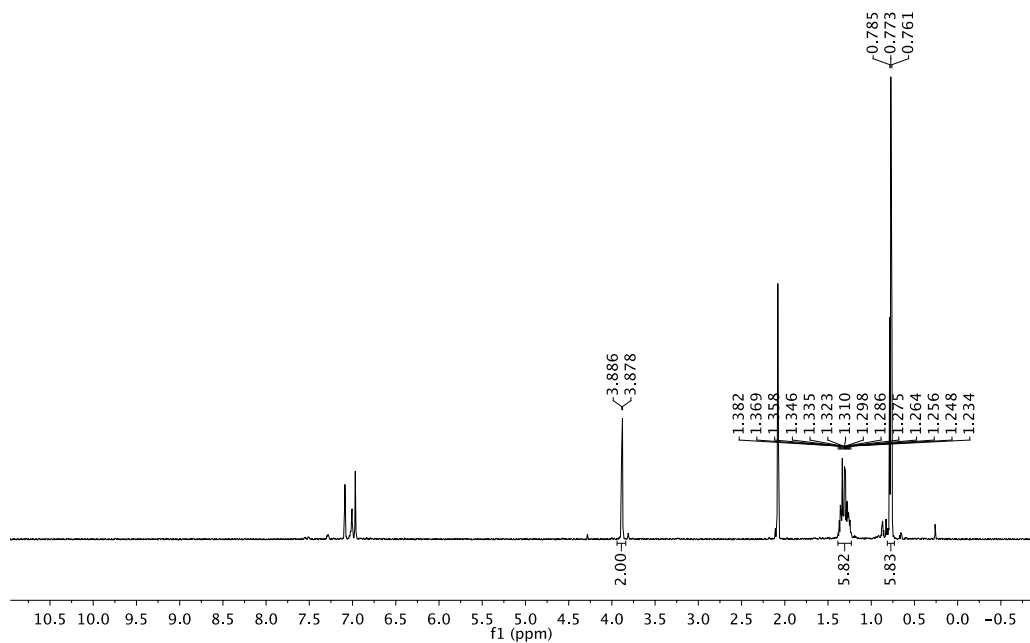


Figure S36: ¹H NMR spectrum of **5a**.

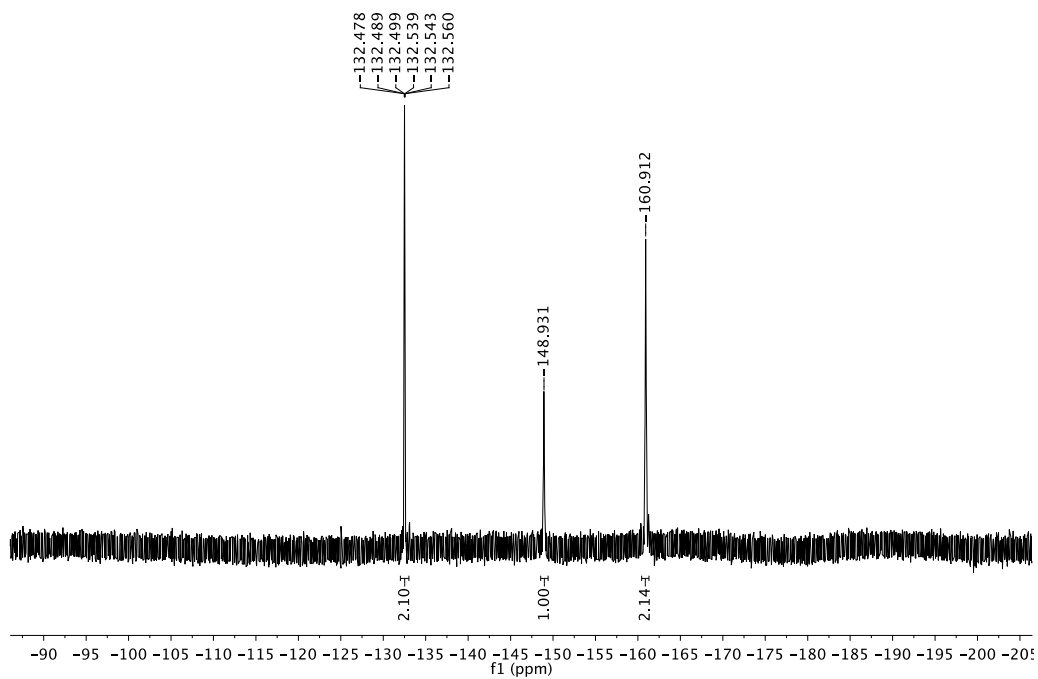


Figure S37: ¹⁹F NMR spectrum of **5a**.

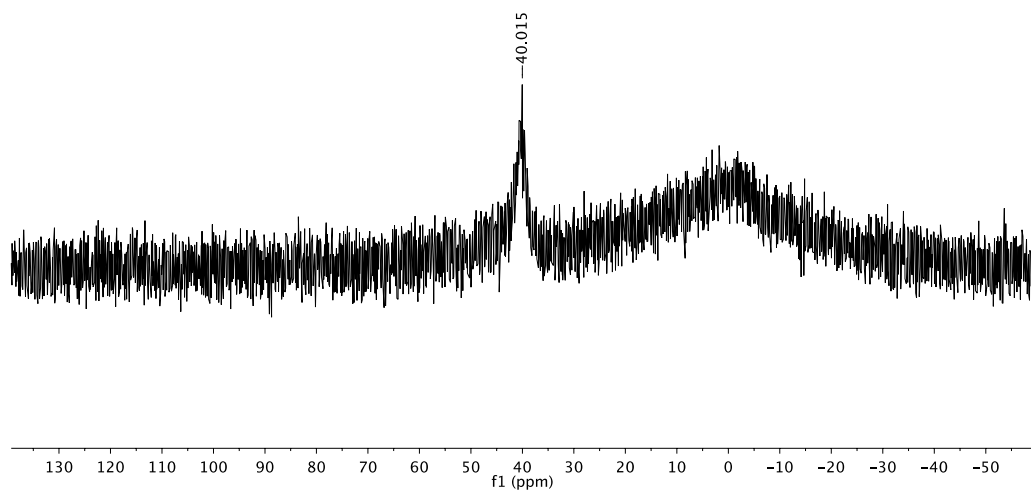


Figure S38: ^{11}B NMR spectrum of **5a**.

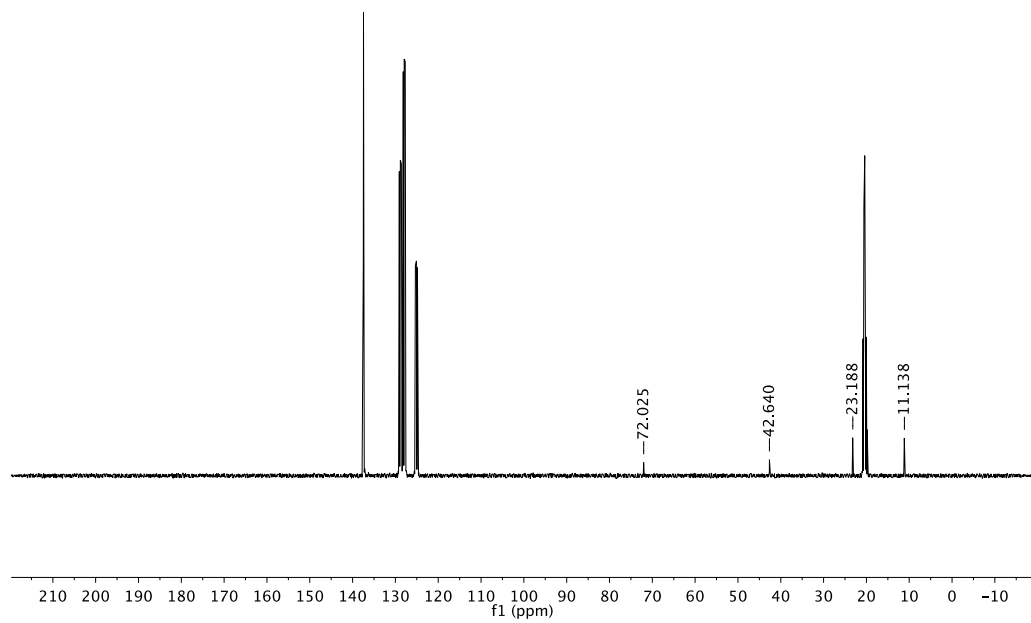
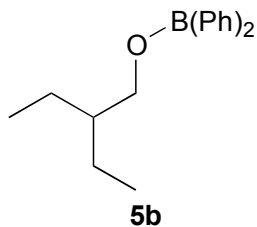


Figure S39: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5a**.



5b: Reaction time: 24 h. NMR yield: 70%.

NMR spectra contain residual pentane from washes. Attempts to remove the solvent resulted in decomposition.

^1H NMR (400 MHz, 298 K, d_8 -tol): δ 7.67-7.64 (m, 4H, *o*-CH), 7.25-7.21 (m, 6H, *m*-CH and *p*-CH), 3.95 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 2H, OCH_2), 1.43-1.31 (m, 5H, CH and $2\times\text{CH}_2$), 0.79 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 6H, $2\times\text{CH}_3$).

^{11}B NMR (128 MHz, 298 K, d_8 -tol): δ 45.7 (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 298 K, d_8 -tol), partial: δ 134.6 (s, *o*-CH), 130.2 (s, *p*-CH), 127.9 (s, *m*-CH), 69.6 (s, OCH_2), 43.4 (s, CH), 23.6 (s, $2\times\text{CH}_2$), 11.4 (s, $2\times\text{CH}_3$).

HRMS (EI) calcd for $\text{C}_{18}\text{H}_{23}\text{BO}$ 266.1842, found 266.1846.

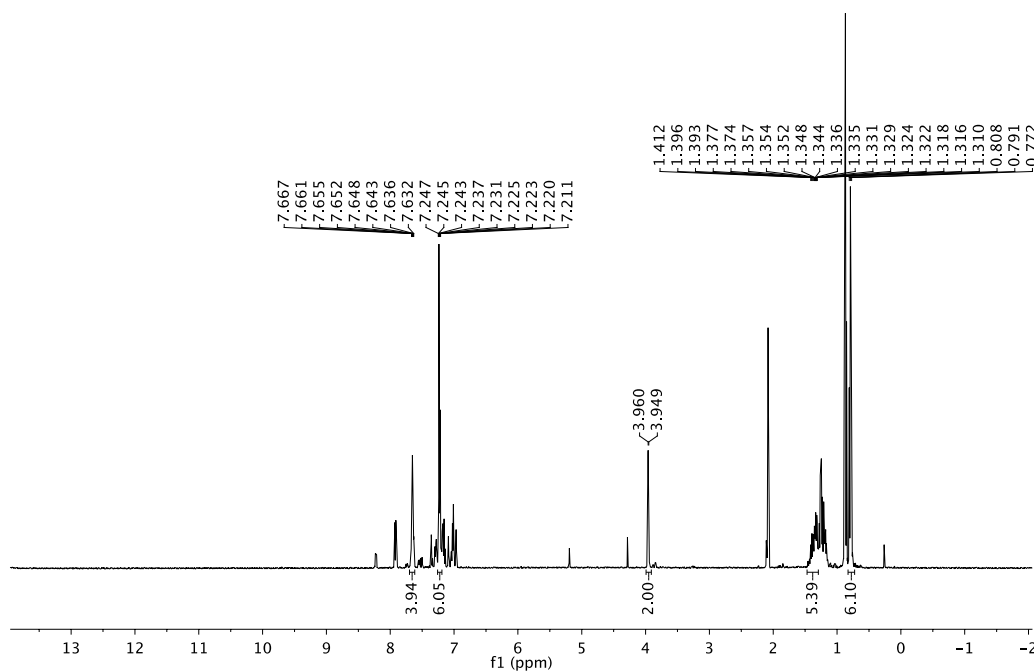


Figure S40: ^1H NMR spectrum of **5b** (contains residual pentane).

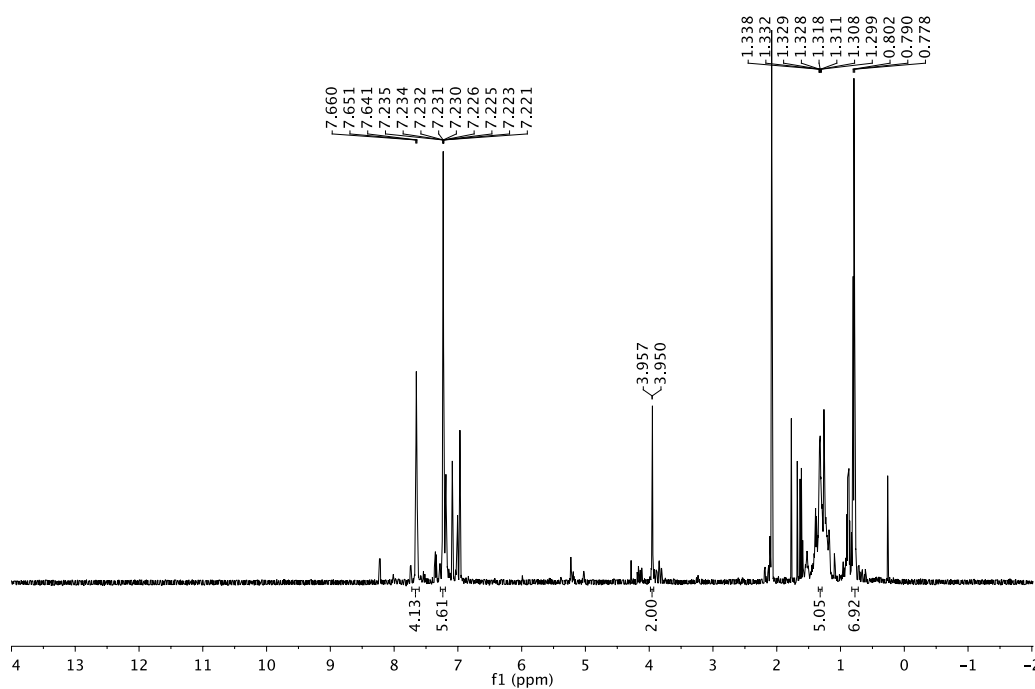


Figure S41: ¹H NMR spectrum of **5b** after attempts to remove residual pentane.

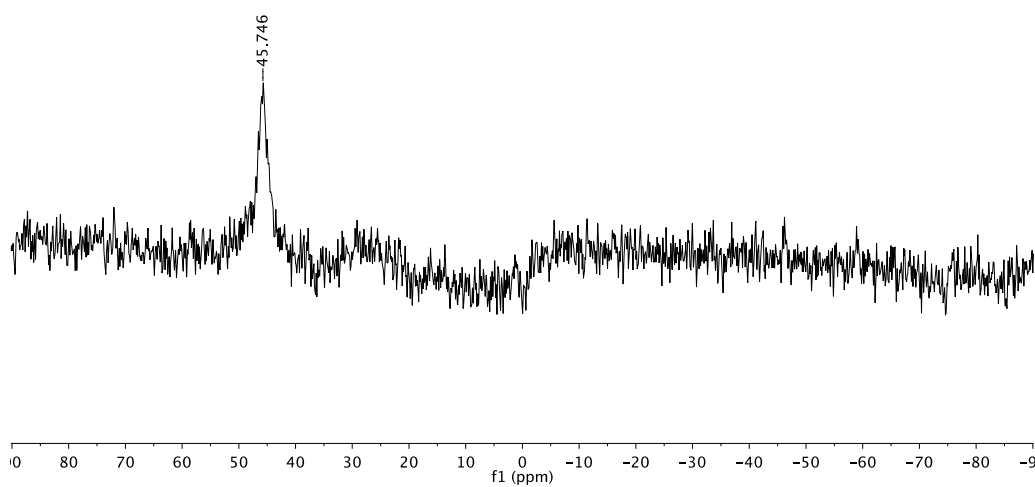


Figure S42: ¹¹B NMR spectrum of **5b**.

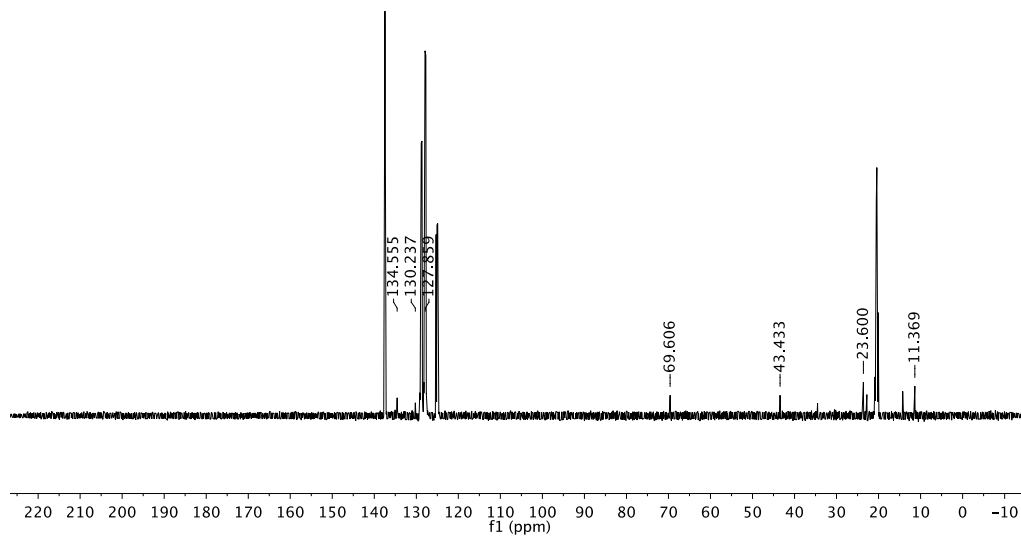


Figure S43: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5b** (contains residual pentane).

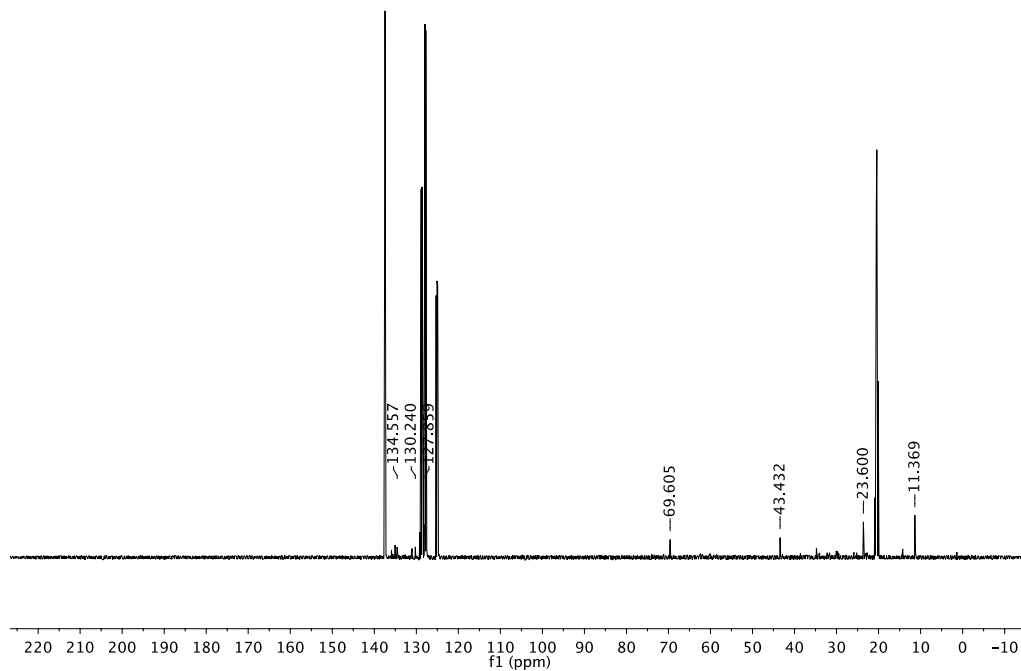


Figure S44: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5b** after attempts to remove residual pentane.

1. R. D. Jackson, S. James, A. G. Orpen, and P. G. Pringle, *J. Organomet. Chem.*, 1993, **458**, C3–C4.

