Supplementary Information (SI) for Catalysis Science & Technology.

Uncovering the Role of Boronic Acids and Boroxines in the Catalytic Hydroboration of Alkenes

Ryan Perry[a], Candace Richardson[b], Dustin Kenefake[a], Charles Leist[a], Vani Gupta[b], Daniel Rose[b], Suresh Mummadi[b]* and Clemens Krempner[a]*

[a] Texas Tech University, Lubbock, TX 79409

[b] University of Virginia's College, 1 College Ave, Wise, VA 24293

svm3se@uvawise.edu

clemens.krempner@ttu.edu

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. All deuterated solvents were purchased from Cambridge Isotope Labs. C_6D_6 and $CDCl_3$ were stored over 4 Å molecular sieves prior to use. HBpin (Oakwood), $[MeBO]_3$ (Strem), $B_{10}H_{14}$ (Sigma) and MeBpin (Aaron Chemicals) were purchased from commercial sources and stored in the glove box. The boroxines $[3,4,5\text{-}F_3\text{-}C_6H_2BO]_3$, $[C_6F_5BO]_3$, $[C_6H_5BO]_3$ and $[3,5\text{-}(CF_3)_2\text{-}C_6H_3BO]_3$ were synthesized by dehydration of the corresponding boronic acid with thionylchloride according to a literature procedure [1]. A solution of 9-Me-BBN was prepared according to a literature procedure [2].

The ^1H, ^{13}C and ^{11}B NMR spectra were obtained from a JOEL ECS 400 instrument. All measurements, unless noted otherwise, were carried out at 298 K and the NMR chemical shifts were given in ppm. The ^{11}B NMR spectra were referenced to H_3BO_3 in D_2O (δ = 36 ppm). The ^1H-NMR spectra were referenced to the residual protonated solvent for ^1H, ^{13}C 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.

Table S1. List of purchased boronic acids.

Entry	Boronic acids	Vendor	Purity
1	3,4,5-F_3-$C_6H_2B(OH)_2$	Enamine LLC	95%
2	$C_6F_5B(OH)_2$	Combi-Blocks	97%
3	$C_6H_5B(OH)_2$	Alfa Aesar	98%
4	3,5-$(CF_3)_2$-$C_6H_3B(OH)_2$	Acros Organics	97%
5	3,4,5-Cl_3-$C_6H_2B(OH)_2$	Ark Pharm, Inc.	95%
6	2,4,6-F_3-$C_6H_2B(OH)_2$	Combi-Blocks	98%
7	3-CF_3-$C_6H_4B(OH)_2$	Oakwood Chemical	95%
8	4-MeO-$C_6H_4B(OH)_2$	Oakwood Chemical	98%
9	4-F_3CO-$C_6H_4B(OH)_2$	Oakwood Chemical	97%
10	4-CF_3-$C_6H_4B(OH)_2$	Oakwood Chemical	97%
11	2-CF_3-$C_6H_4B(OH)_2$	Enamine LLC	95%
12	2,6-Cl_2-$C_6H_3B(OH)_2$	AA Blocks LLC	97%
13	2,4,6-Me_3-$C_6H_2B(OH)_2$	TCI	98%
14	$Me(B(OH)_2$	A2B	98%

2. Experimental Procedures

2.1 Catalyst screening

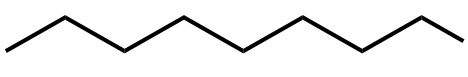
In the glove box, a 4 mL scintillation vial equipped with a magnetic stir bar was charged with the respective catalyst (1 mol% aryl boronic acid or 0.33 mol% aryl boroxine based on 1-octene) and 1 mL of a 20 mL stock solution prepared from combining of 1-octene (6.363 g, 58 mmol, 0.72 g/mL), HBpin (9.073 g, 70 mmol,) and mesitylene (759 mg, 5.8 mmol). Note: For the pre-catalysts $MeB(OH)_2$ and $[MeBO]_3$ the scale of the reaction was increased two-fold. Then, the vial was sealed with a Teflon-lined screw cap, placed in an aluminum block and heated at 80°C for 48 hours with stirring (450 rpm). After cooling to room temperature, an aliquot was taken from the reaction mixture and added to an NMR tube. $CDCl_3$ was added to the NMR tube, and the resulting clear solution was analyzed by ^1H NMR spectroscopy. Conversions were determined by integration of the respective signals against mesitylene as the internal standard.

2.2 Substrate Scope

General procedure

On a benchtop, a 4 mL one-dram scintillation vial equipped with a magnetic stir bar was charged with the catalyst 3,4,5-trifluorophenyl boronic acid (2 mol% based on the alkene). After transferring the vial into a glovebox, HBpin and the respective alkene were added. Then the vial was sealed with a Teflon lined screw cap and subsequently heated in the glovebox for 24 hours at 80°C with stirring at 1000 rpm if not stated otherwise. At room temperature the crude product (except for **9**) was diluted with $CHCl_3$ and subsequently purified using a short plug of silica (3/4") in 15 ml ChemGlass filter frit with $CHCl_3$ as the eluent.

2.2.1 Compound **1**



1-Octene (168 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.65 mmol). Colorless oil. Yield 63%. ^1H NMR (400 MHz, $CDCl_3$) δ = 1.43-1.33 (m, 2 H), 1.31-1.17 (m, 22 H), 0.87 (t, $^3J_{H-H}$ = 6.7 Hz, 3 H), 0.76 (t, $^3J_{H-H}$ = 7.7

Hz, 2 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 82.9, 32.6, 32.1, 29.5, 29.4, 25.0, 24.1, 22.8, 14.3, 11.2 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 34.5 ppm. The spectral data are consistent with previously reported values [3].

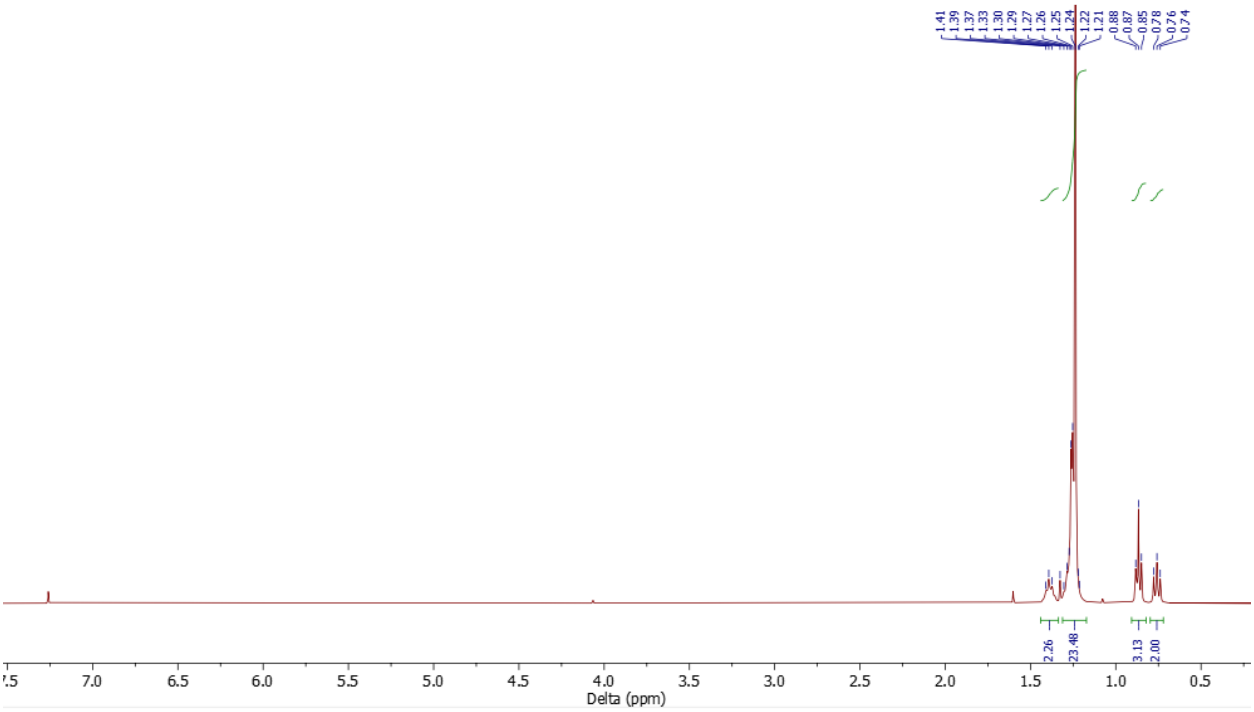


Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

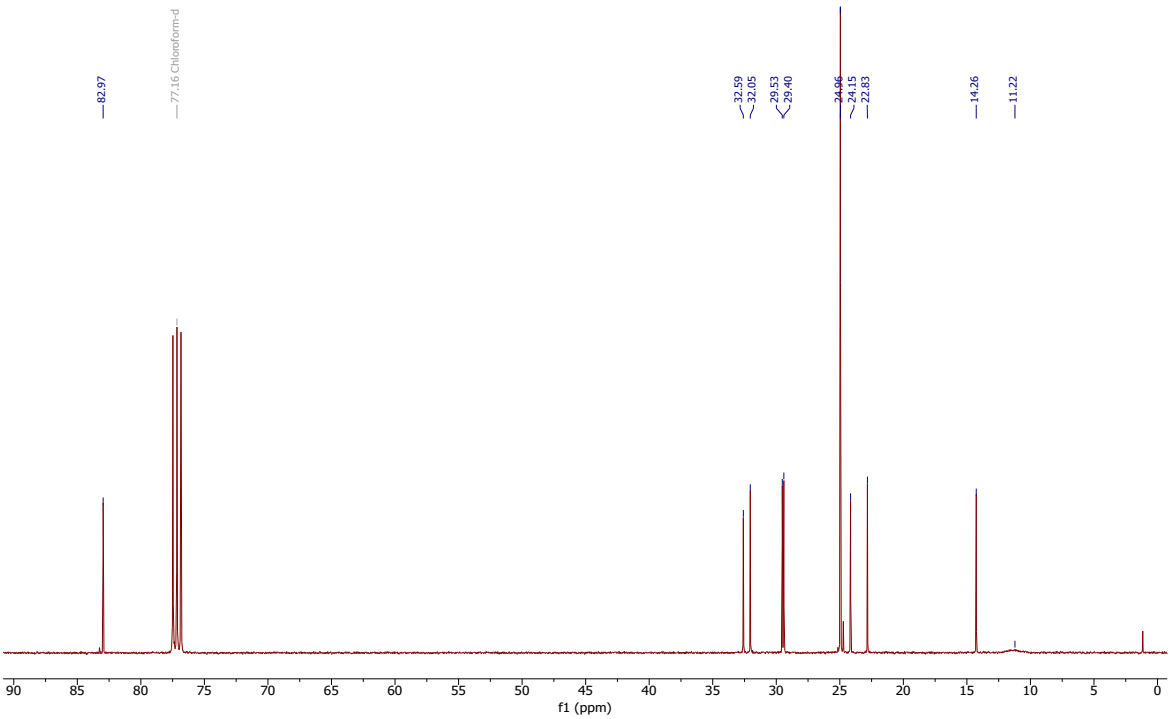


Figure S2. $^{13}C\{H\}$ NMR spectrum of **1** in $CDCl_3$.

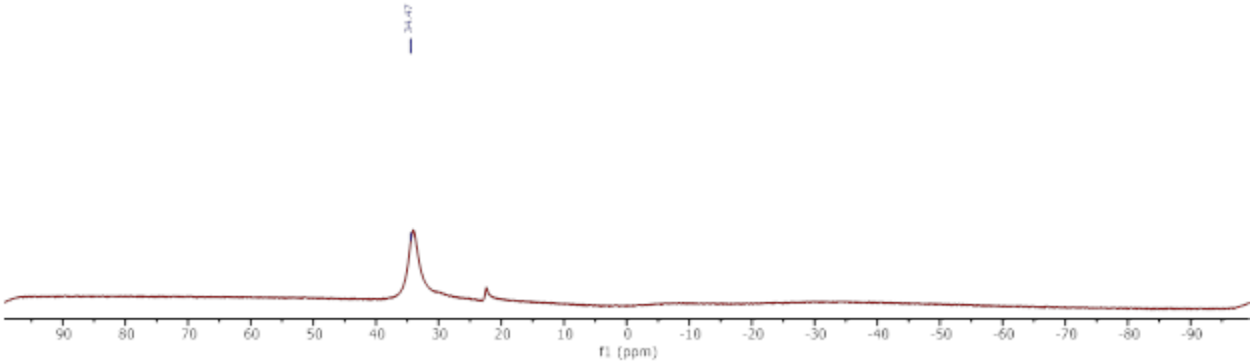
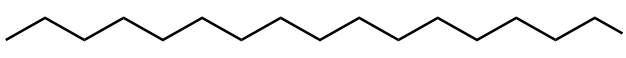


Figure S3. $^{11}B\{H\}$ NMR spectrum of **1** in $CDCl_3$.

2.2.2 Compound **2**



1-Hexadecene (337 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.65 mmol). Colorless oil. Yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.44-1.34 (m, 3 H), 1.31-1.17 (m, 38 H), 0.87 (t, *J* = 6.7 Hz, 3 H), 0.76 (t, *J* = 7.8 Hz, 2 H). $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 83.0, 32.6, 32.1, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 25.0, 24.2, 22.8, 14.8, 11.3 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 34.8 ppm. The spectral data are consistent with previously reported values [4].

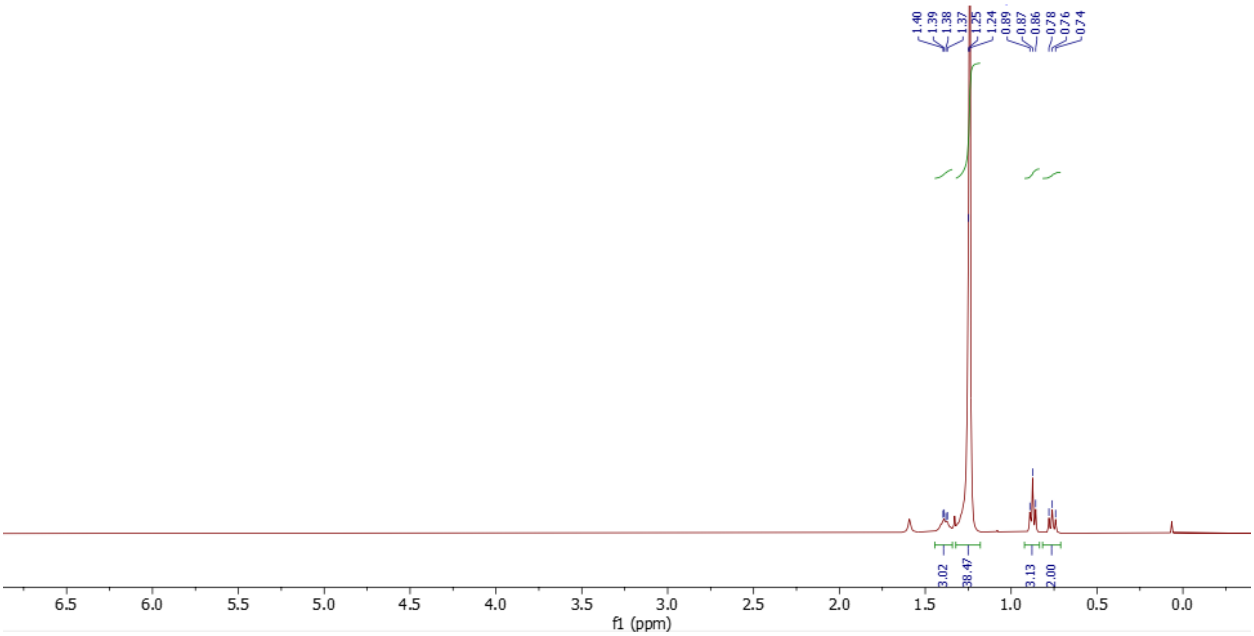


Figure S4. ^{1}H NMR spectrum of **2** in $CDCl_3$.

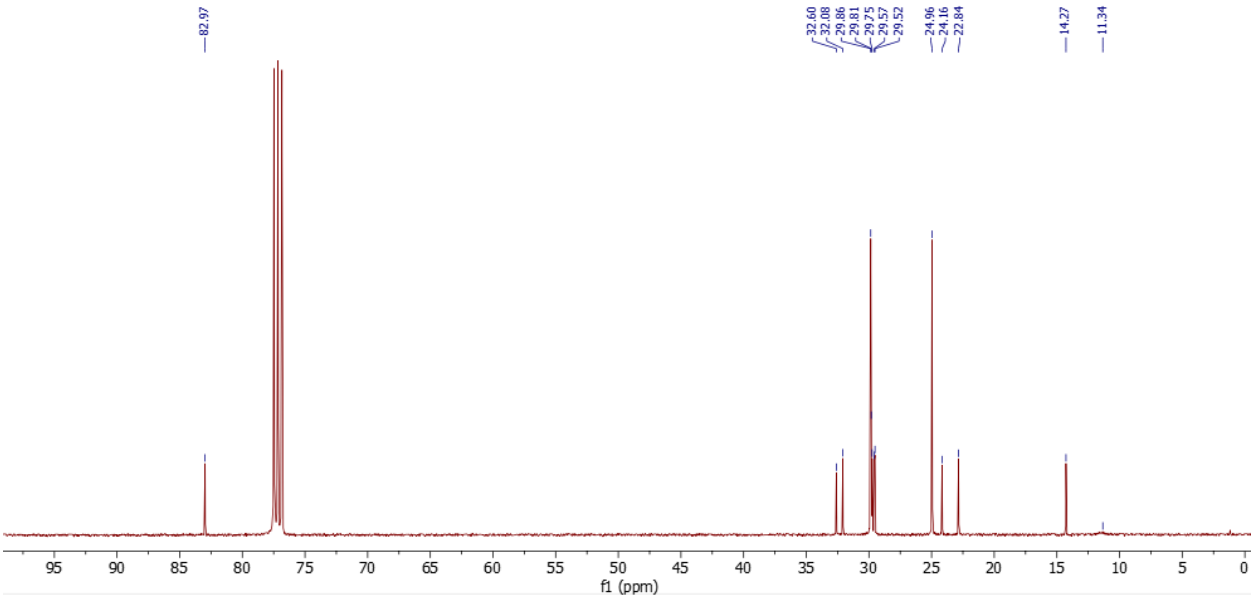


Figure S5. $^{13}C\{H\}$ NMR spectrum of **2** in $CDCl_3$.

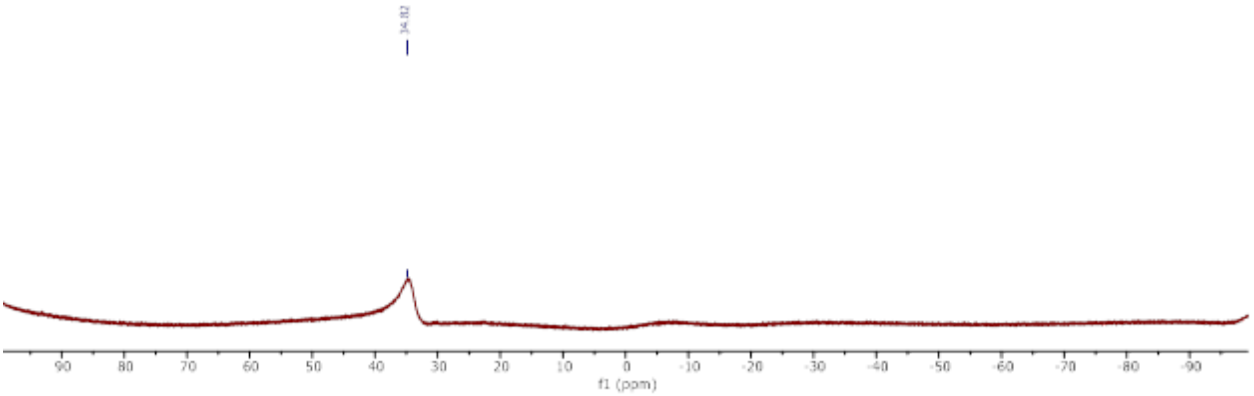
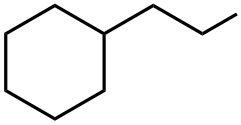


Figure S6. $^{11}B\{H\}$ NMR spectrum of **2** in $CDCl_3$.

2.2.3 Compound **3**



Vinyl cyclohexane (165 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.65 mmol). Colorless oil. Yield 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.75-1.55 (m, 5 H), 1.34-1.24 (m, 3 H), 1.24 (s, 12 H), 1.18-1.05 (m, 4 H), 0.89-0.79 (m, 1 H), 0.78-0.71 (m, 1 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 83.0, 40.1, 33.1, 31.5, 27.0, 26.6, 25.0 ppm. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 34.0 ppm. The spectral data are consistent with previously reported values [3].

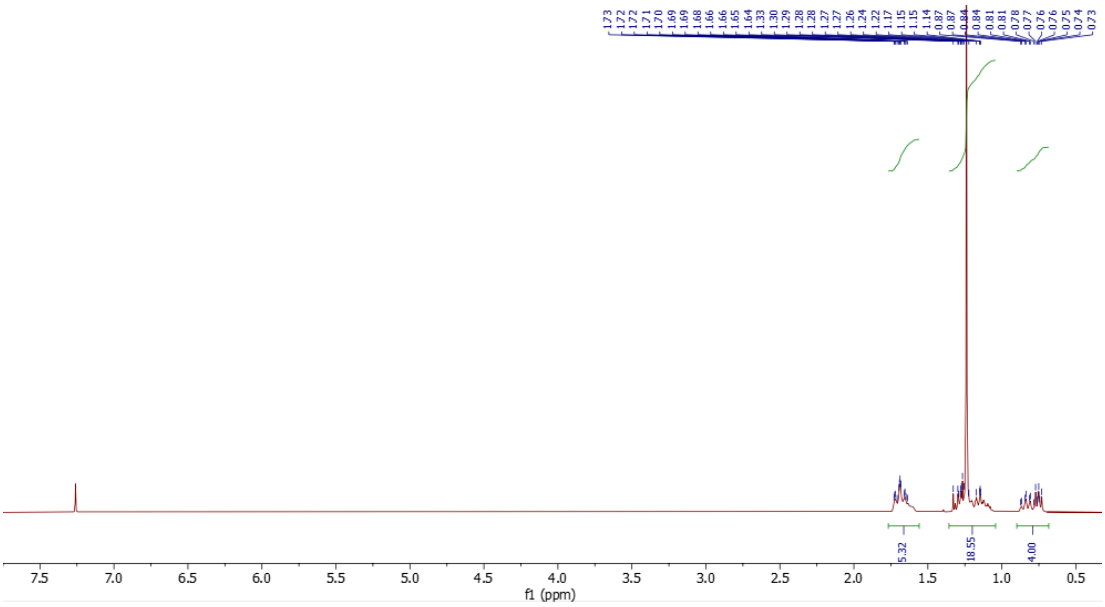


Figure S7. ^{1}H NMR spectrum of **3** in $CDCl_3$.

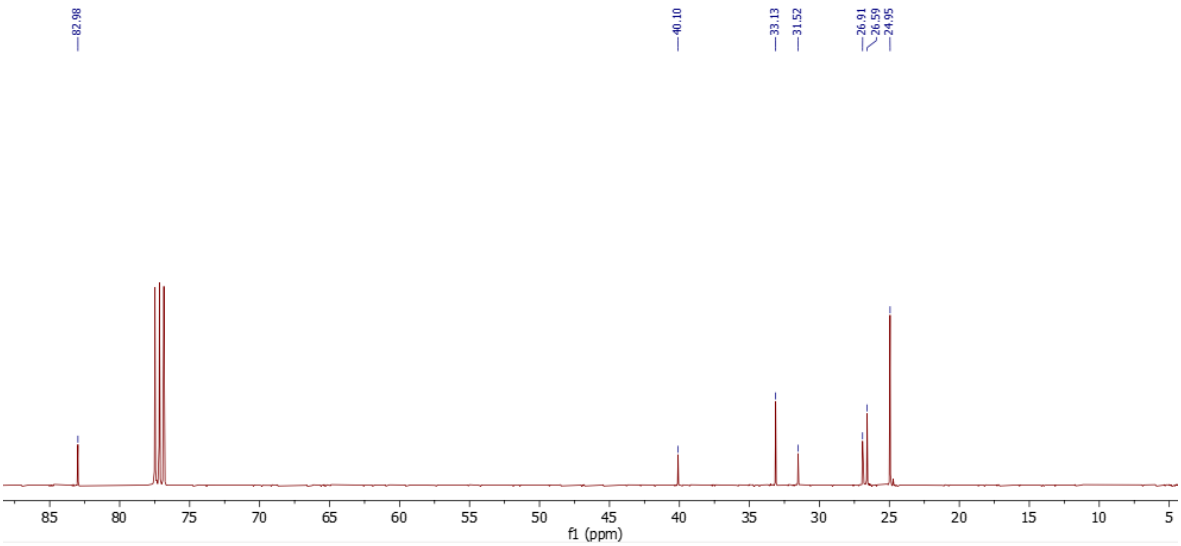


Figure S8. $^{13}C\{H\}$ NMR spectrum of **3** in $CDCl_3$.

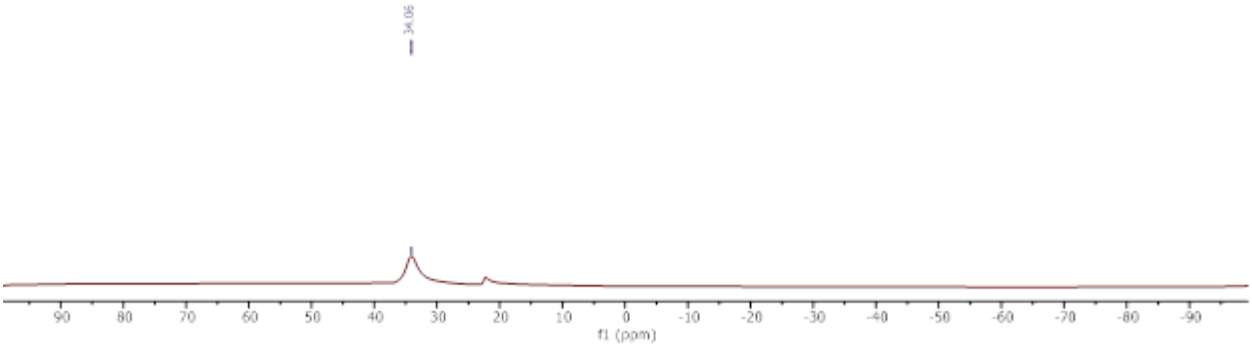
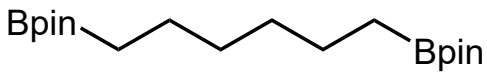


Figure S9. $^{11}B\{H\}$ NMR spectrum of **3** in $CDCl_3$.

2.2.4 Compound **4**



1,5-hexadiene (123 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (10.6 mg, 0.6 mmol) and HBpin (400 mg, 3.1 mmol). Colorless oil. Yield 82%. ^1H NMR (400 MHz, $CDCl_3$) δ = 1.43-1.33 (m, 4 H), 1.31-1.25 (m, 4 H), 1.22 (s, 24 H), 0.74 (t, $^3J_{H-H}$ = 7.8 Hz, 3H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 82.9, 32.4, 24.9, 24.1, 11.3 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.9 ppm. The spectral data are consistent with previously reported values [5].

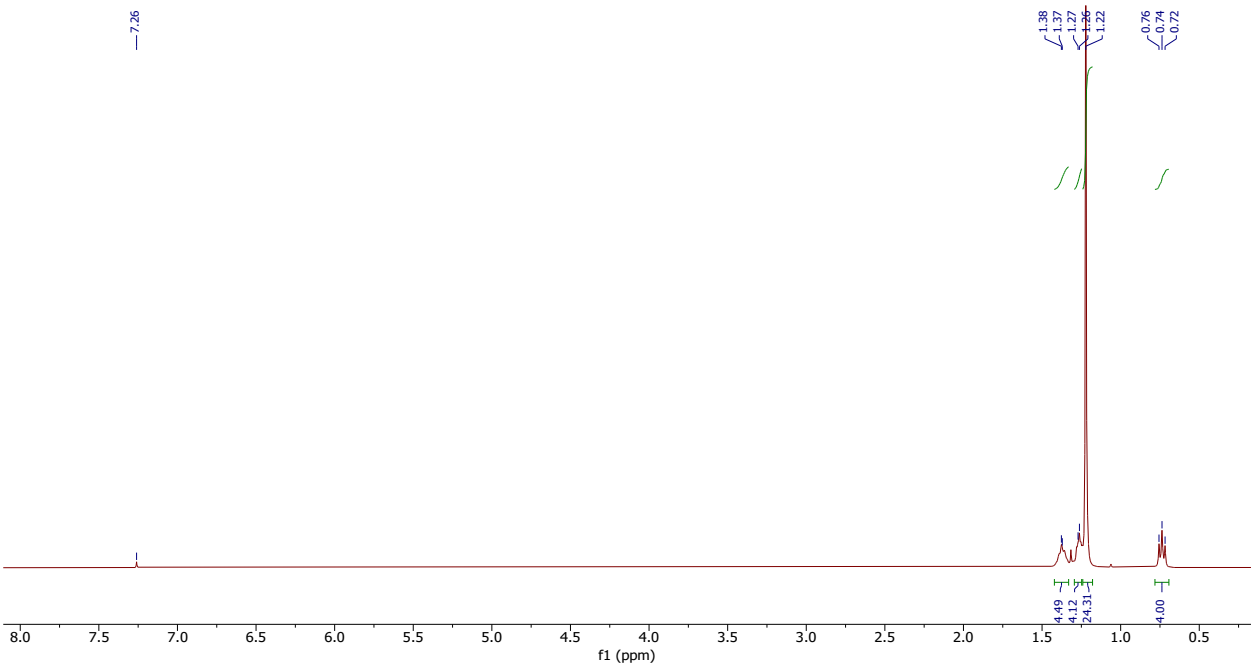


Figure S10. ^{1}H NMR spectrum of **4** in $CDCl_3$.

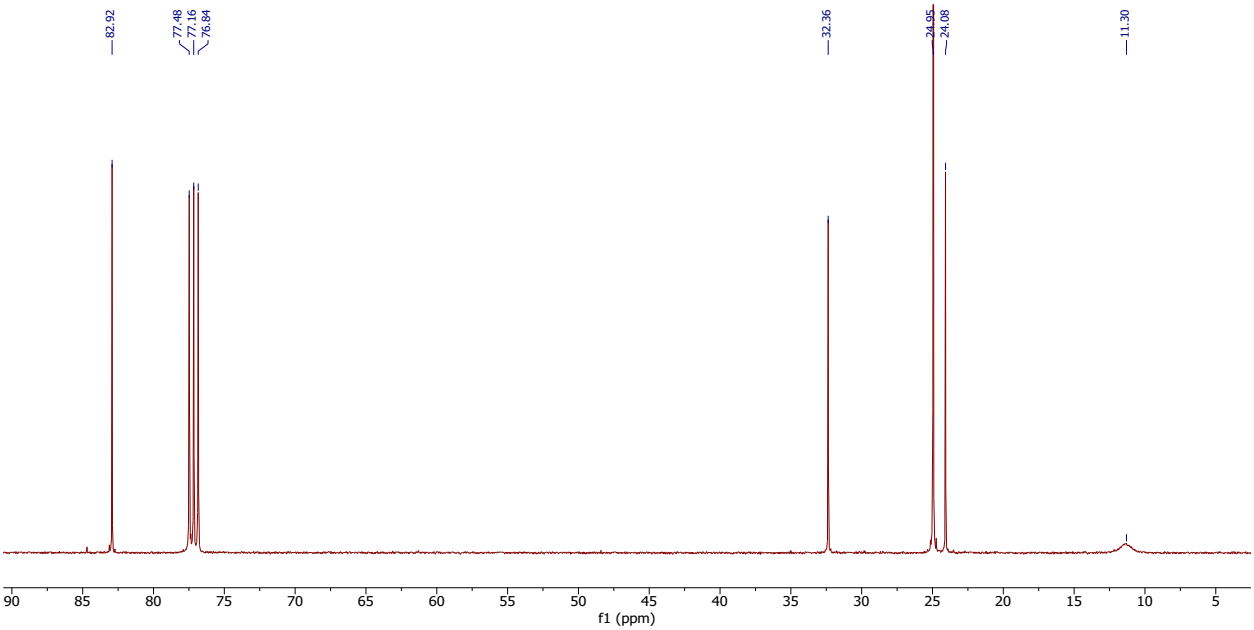


Figure S11. $^{13}C\{H\}$ NMR spectrum of **4** in $CDCl_3$.

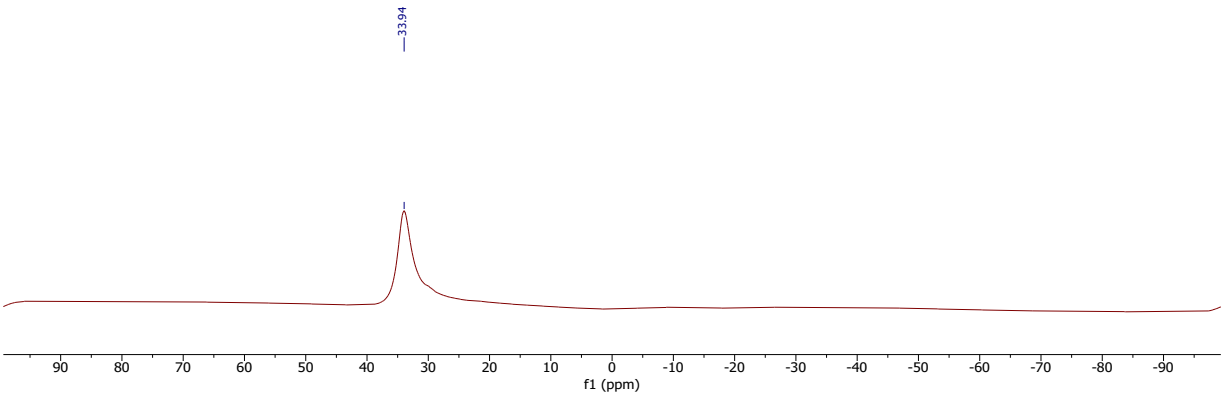
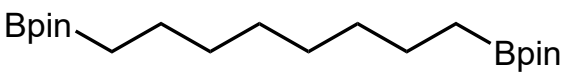


Figure S12. $^{11}B\{H\}$ NMR spectrum of **4** in $CDCl_3$.

2.2.5 Compound **5**



1,7-octadiene (165 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (10.6 mg, 0.6 mmol) and HBpin (400 mg, 3.1 mmol). Colorless oil. Yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48-1.34 (m, 4 H), 1.29-1.19 (m, 8 H), 1.23 (s, 24 H), 0.75 (t, $^{3}J_{H-H}$ = 7.8 Hz, 4 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ 82.6, 32.6, 29.5, 25.0, 24.1 ppm. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.6 ppm. The spectral data are consistent with previously reported values [5].

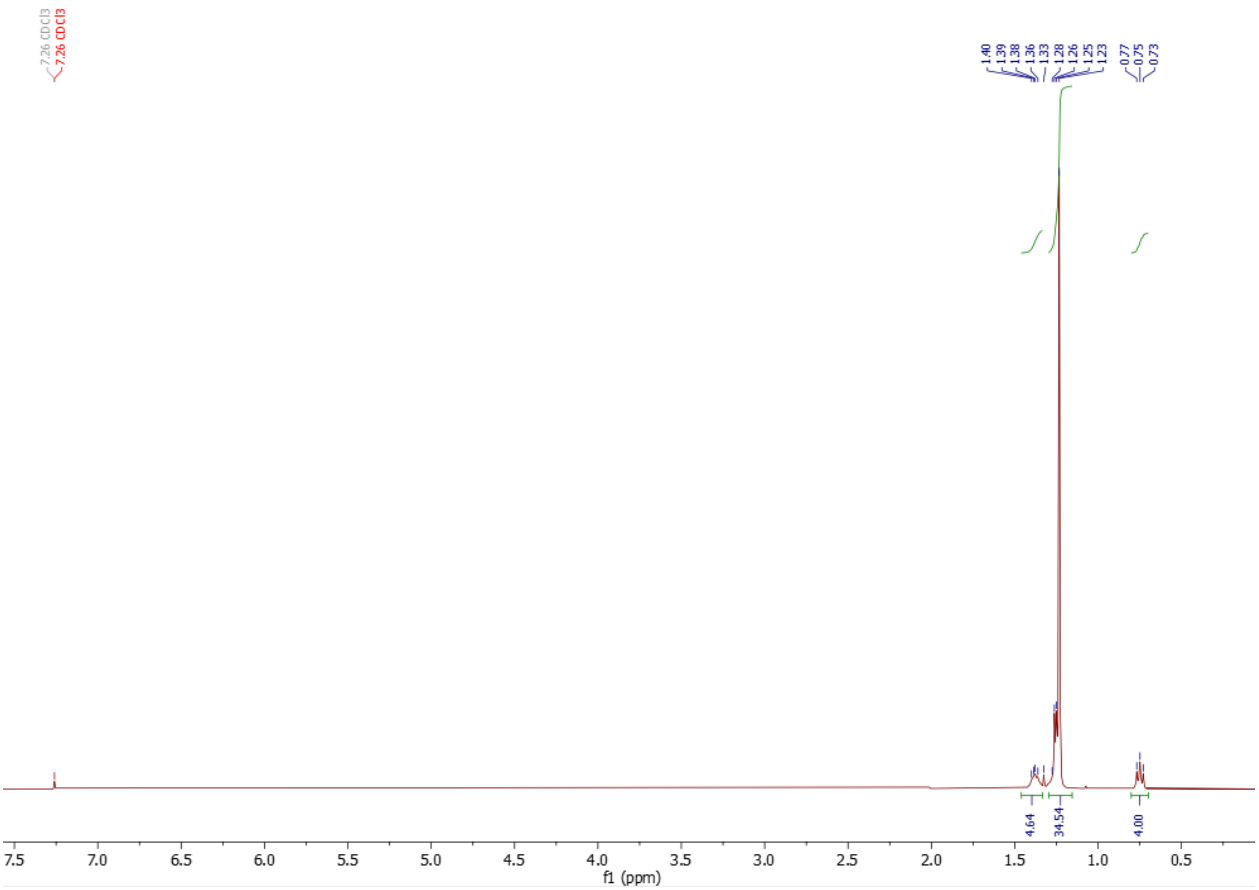


Figure S13. ^{1}H NMR spectrum of **5** in $CDCl_3$.

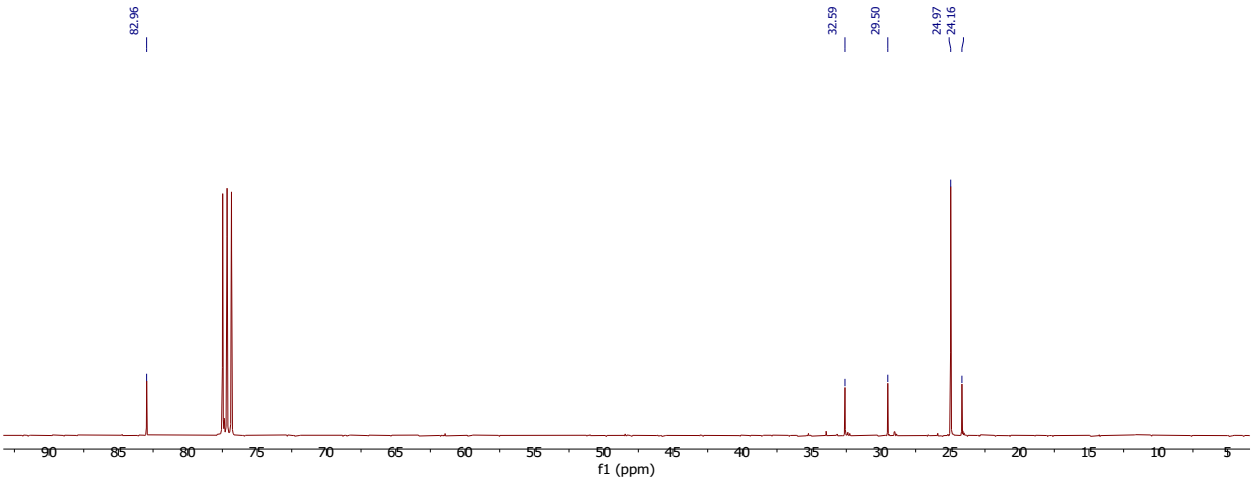


Figure S14. $^{13}C\{H\}$ NMR spectrum of **5** in $CDCl_3$.

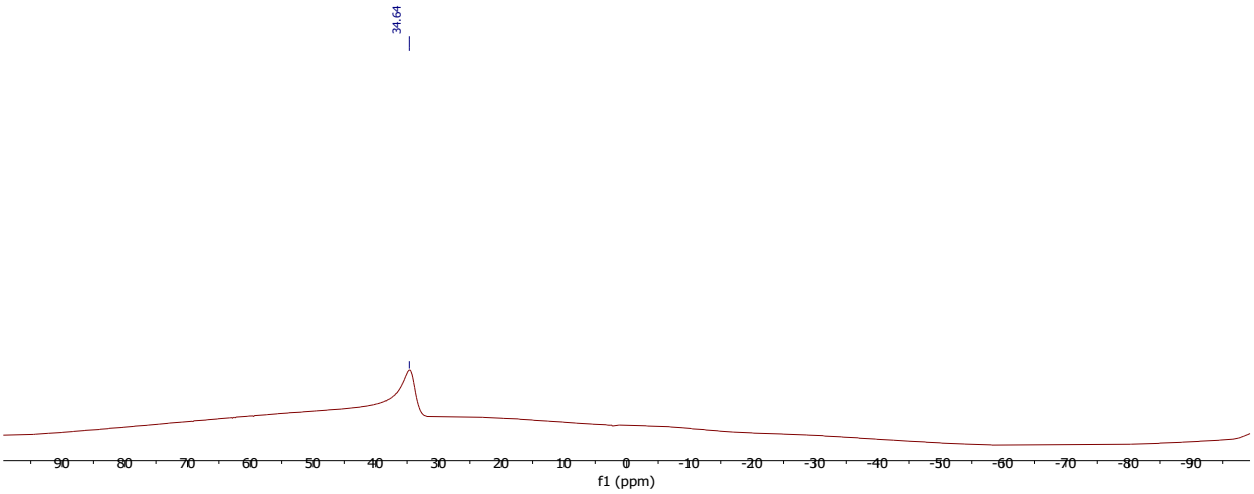
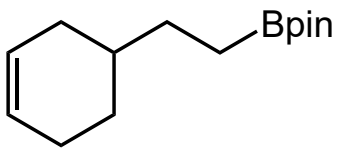


Figure S15. $^{11}B\{H\}$ NMR spectrum of 5 in $CDCl_3$.

2.2.6 Compound **6**



4-Vinylcyclohexene (162 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.65 mmol). Colorless oil. Yield 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.62 (m, 2 H), 2.15-2.01 (m, 2 H), 1.80-1.55 (m, 2 H), 1.47-1.33 (m, 3H), 1.29-1.07 (m, 2 H), 1.21 (s, 12 H), 1.22-1.06 (m, 2 H), 0.79 (t, $^{3}J_{H-H}$ = 7.5 Hz, 2 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 127.1, 126.9, 83.0, 35.9, 31.7, 30.8, 28.6, 25.5, 24.9, 24.7 ppm. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 34.6 ppm. The spectral data are consistent with previously reported values [3].

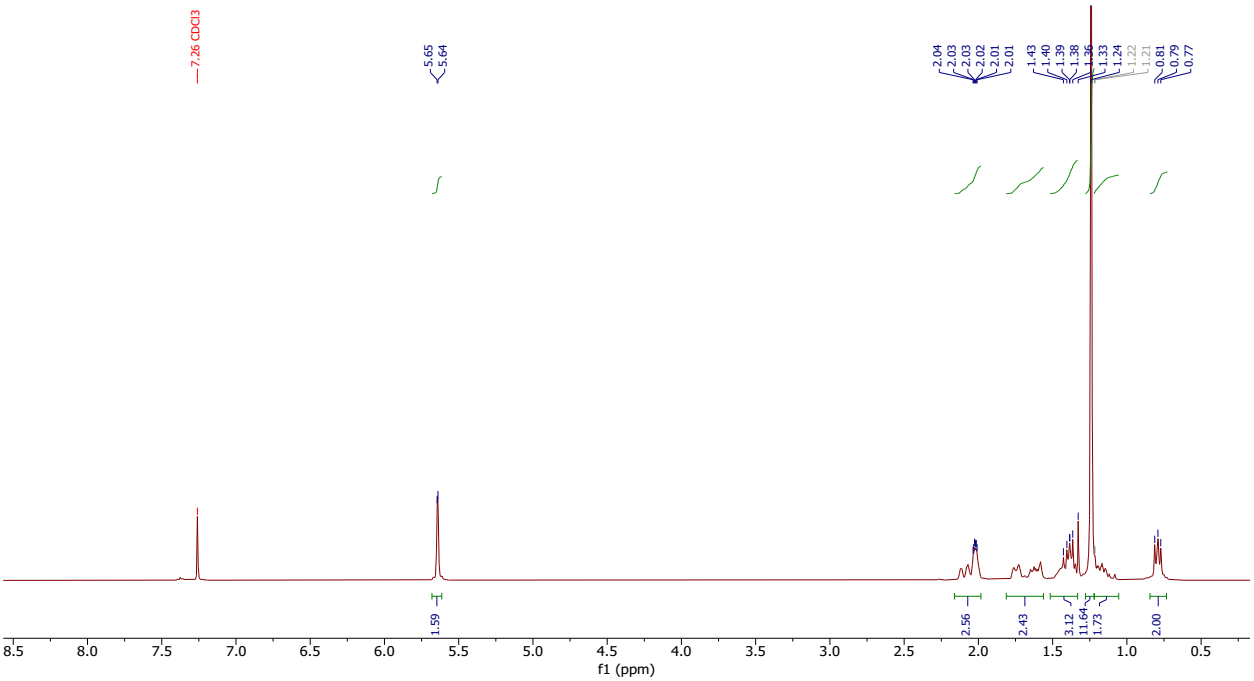


Figure S16. ^{1}H NMR spectrum of **6** in $CDCl_3$.

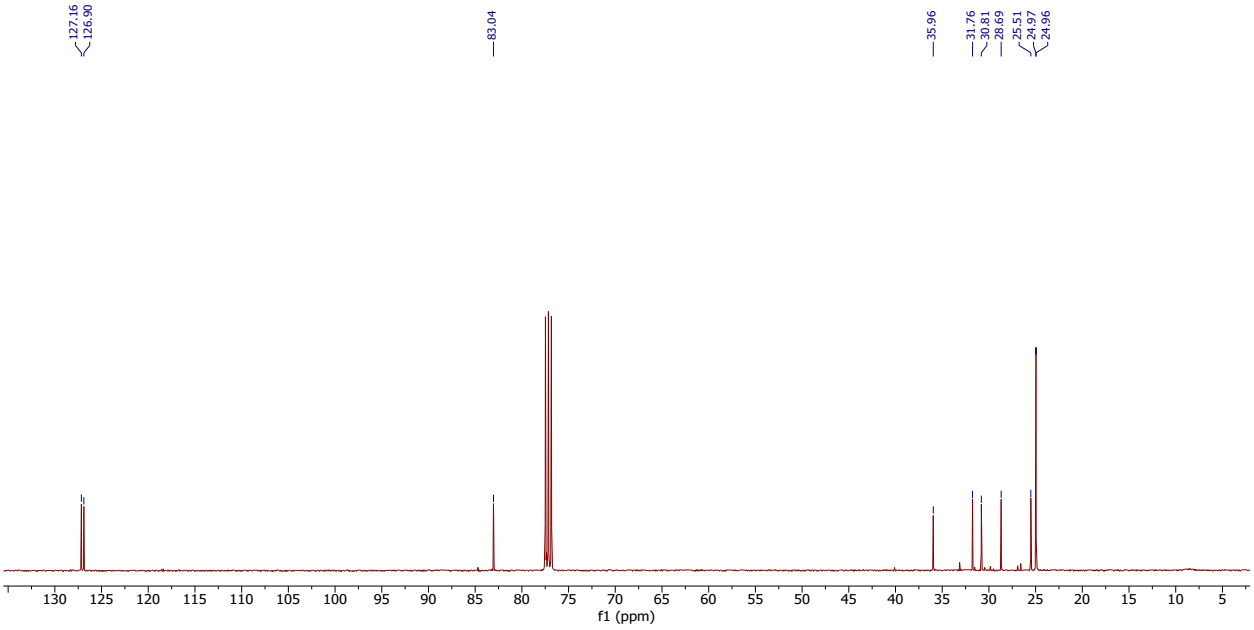


Figure S17. $^{13}C\{H\}$ NMR spectrum of **6** in $CDCl_3$.

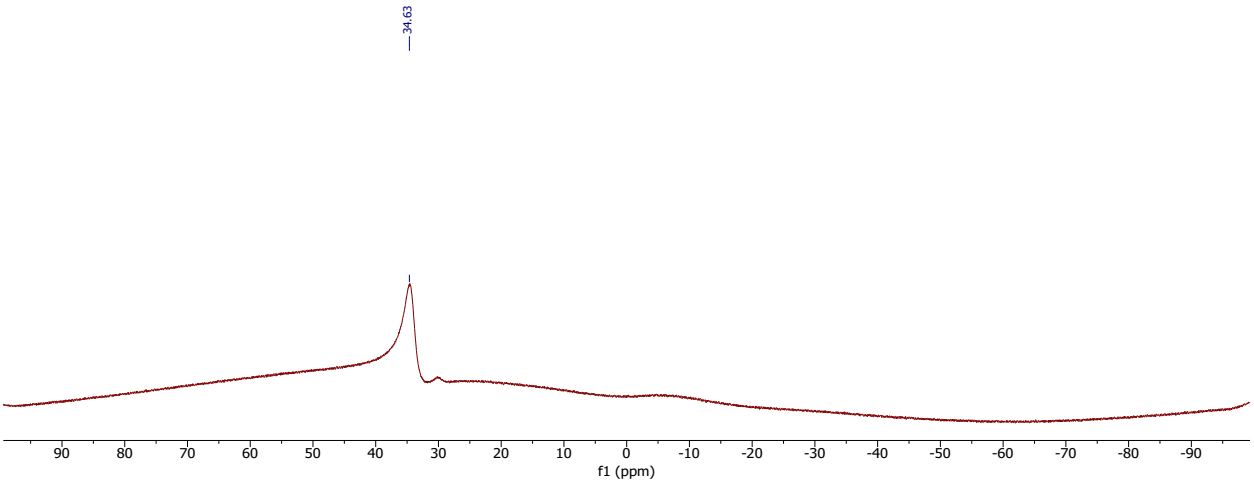
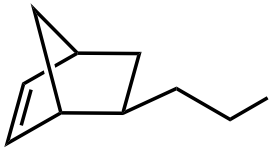


Figure S18. $^{11}B\{H\}$ NMR spectrum of **6** in $CDCl_3$.

2.2.7 Compound **7**



2-Vinyl-5-norbornene (mixture of exo and endo) (180 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (10.6 mg, 0.6 mmol) and HBpin (211 mg, 1.65 mmol). Colorless oil. Yield 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.10-6.05 (m, 1 H), 5.94-5.89 (m, 1 H), 2.83-2.66 (m, 2 H), 1.97-1.87 (m, 1 H), 1.85-1.75 (m, 1 H), 1.38-1.33 (m, 1 H), 1.24 (s, 12 H), 1.22-1.12 (m, 3 H), 0.78-0.69 (m, 2 H), 0.52-0.45 (m, 1 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 137.0, 132.6, 83.0, 49.7, 45.2, 42.7, 41.6, 32.3, 28.9, 25.0 ppm. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.9 ppm. GC-MS: m/z of $[M]^+$ = 248.200.

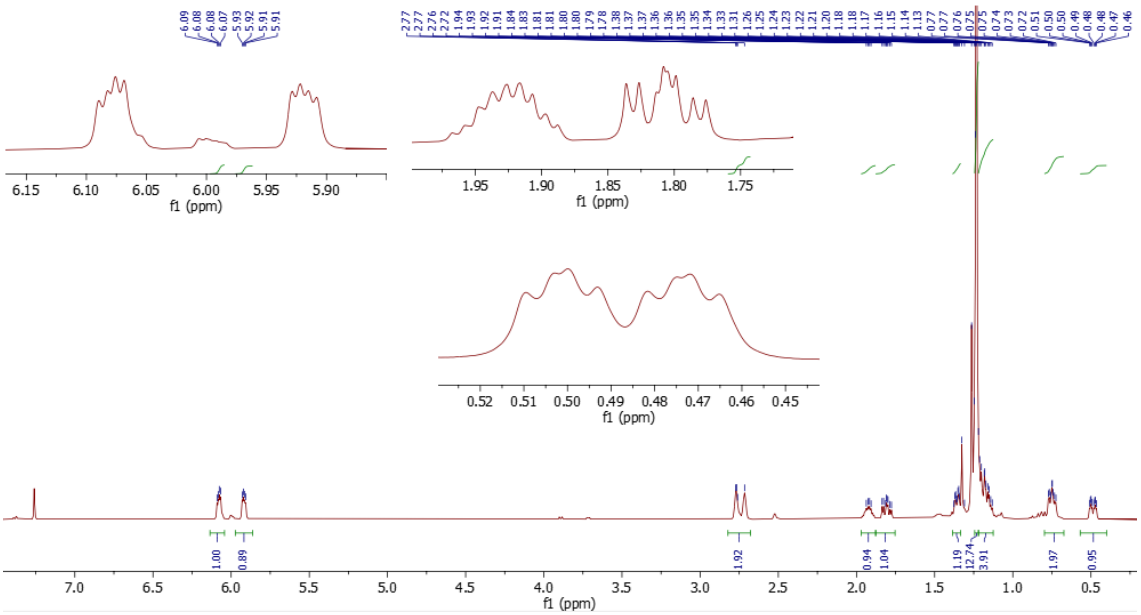


Figure S19. ^{1}H NMR spectrum of **7** in $CDCl_3$.

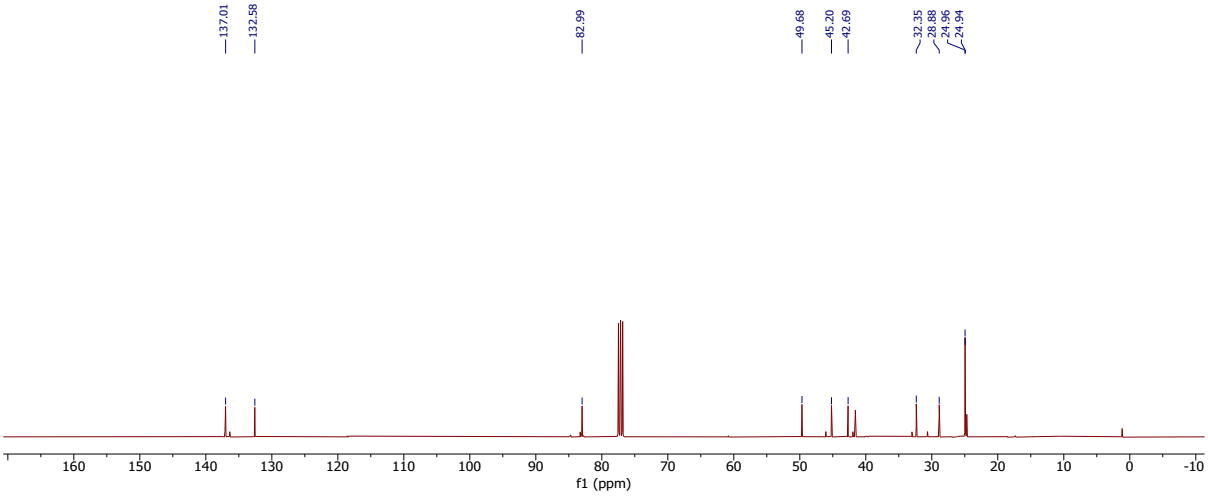


Figure S20. $^{13}C\{H\}$ NMR spectrum of **7** in $CDCl_3$.

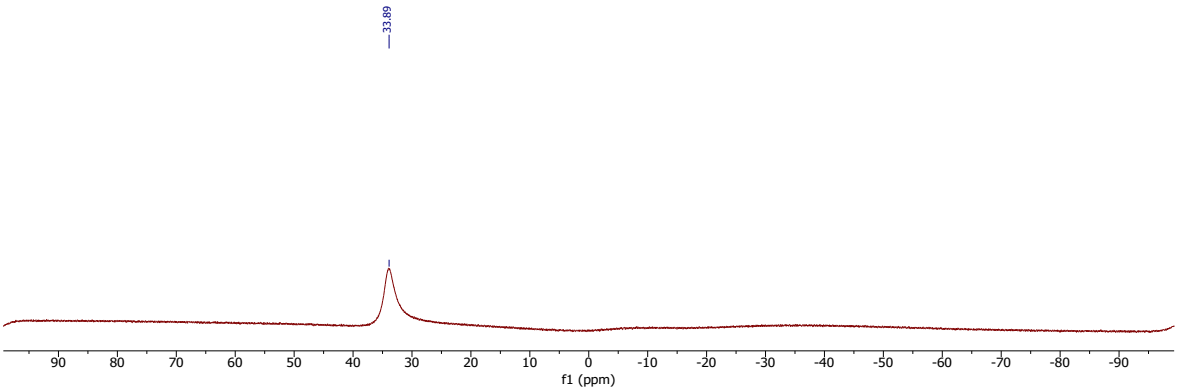
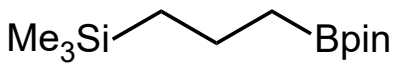


Figure S21. $^{11}B\{H\}$ NMR spectrum of **7** in $CDCl_3$.

2.2.8 Compound **8**



Allyl trimethylsilane (343 mg, 3 mmol), 3,4,5-trifluorophenyl boronic acid (10.6 mg, 0.6 mmol), HBpin (346 mg, 2.7 mmol). Colorless liquid. Yield 517 mg (71%). ^{1}H NMR [400 MHz, $CDCl_3$] δ = 1.43 (pent, $^{3}J_{H\text{-}H}$ = 8.4 Hz, CH_2, 2 H), 1.24 (s, CH_3, 12 H), 0.83 (t, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2 H), 0.52 (t, $^{3}J_{H\text{-}H}$ = 3.6 Hz, CH_2, 2 H), -0.04 (s, CH_3, 9 H) ppm. ^{13}C{H} NMR [101MHz, $CDCl_3$] δ= 82.9, 24.9, 20.2, 18.7, 15.5, -1.50 ppm. ^{11}B{H} NMR [128 MHz, $CDCl_3$] δ = 32.4 ppm. The spectral data are consistent with previously reported values [6].

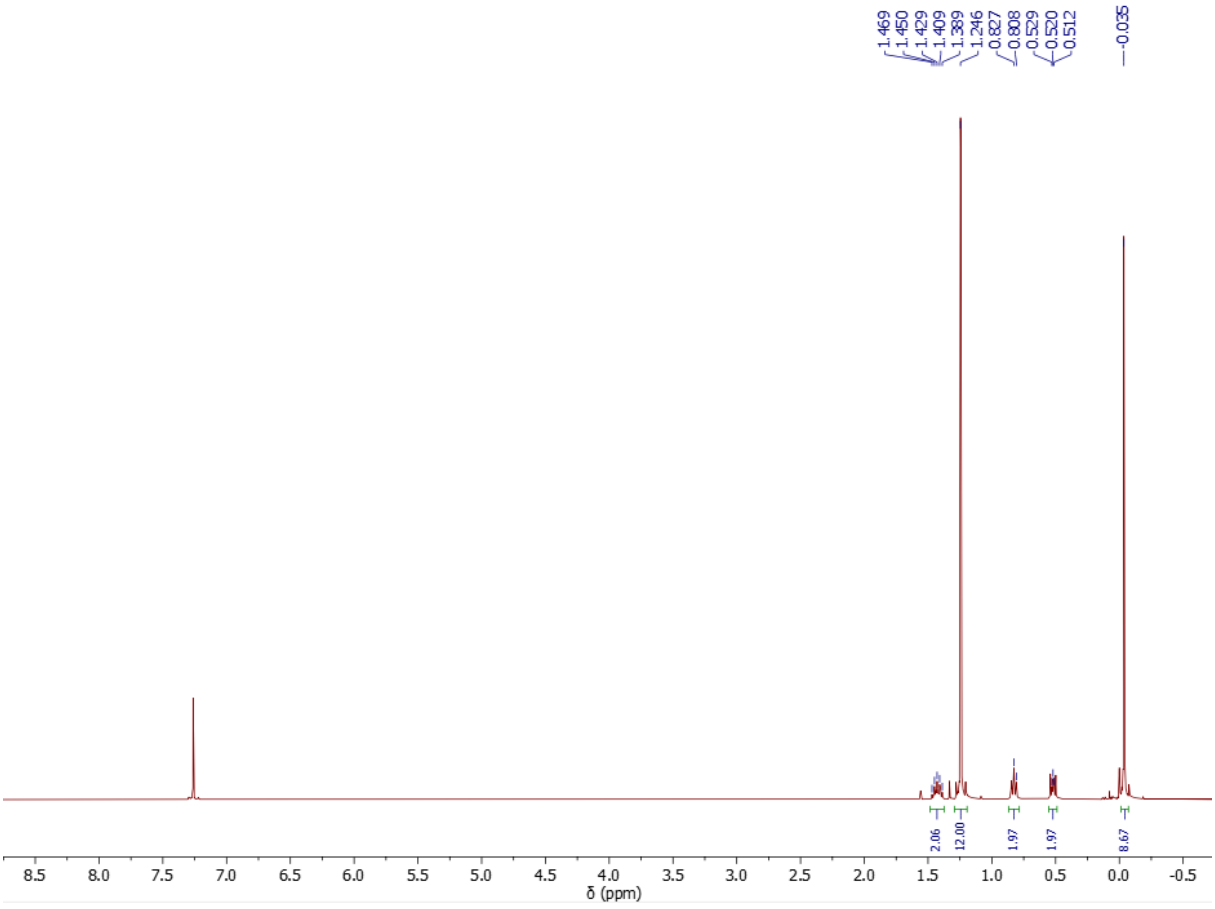


Figure S22. ^{1}H NMR spectrum of **8** in $CDCl_3$.

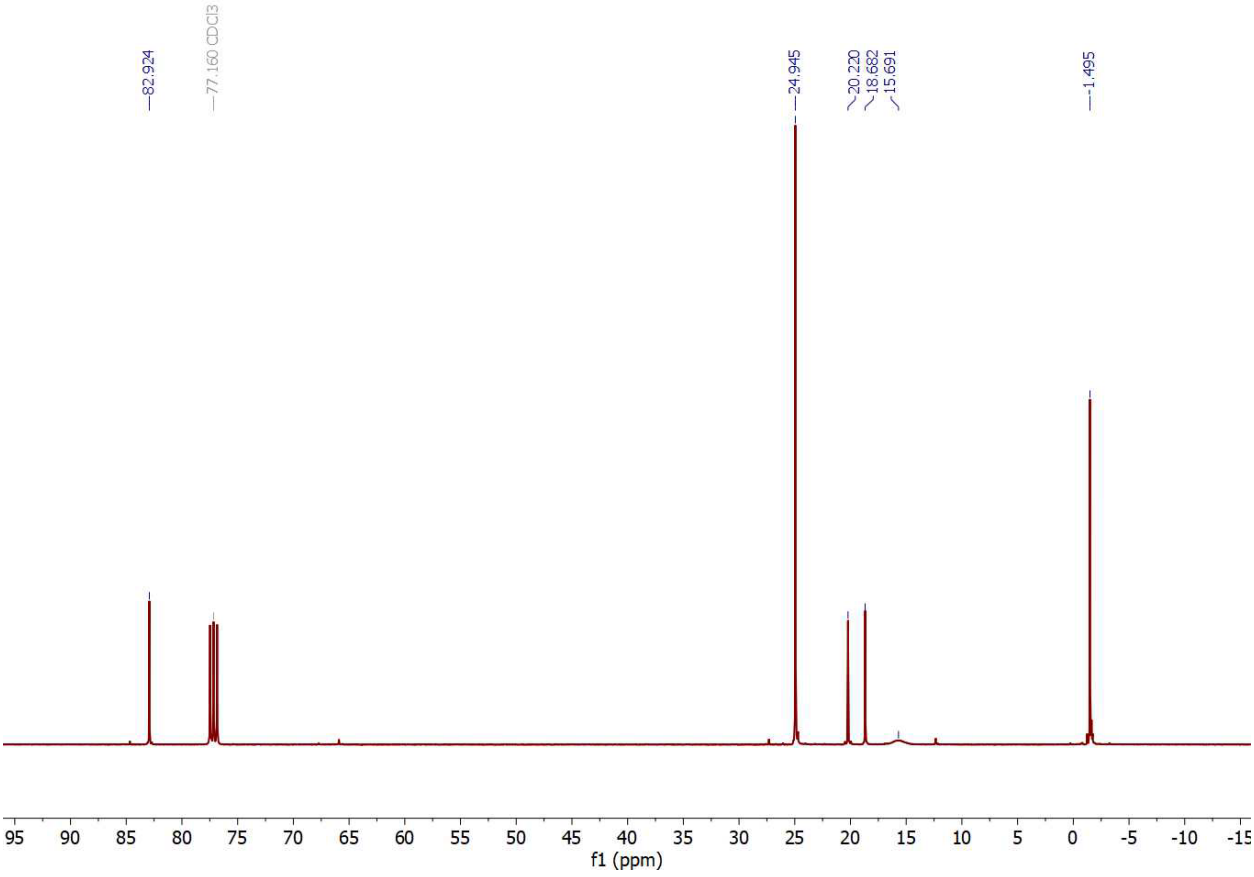


Figure S23. $^{13}C\{H\}$ NMR spectrum of **8** in $CDCl_3$.

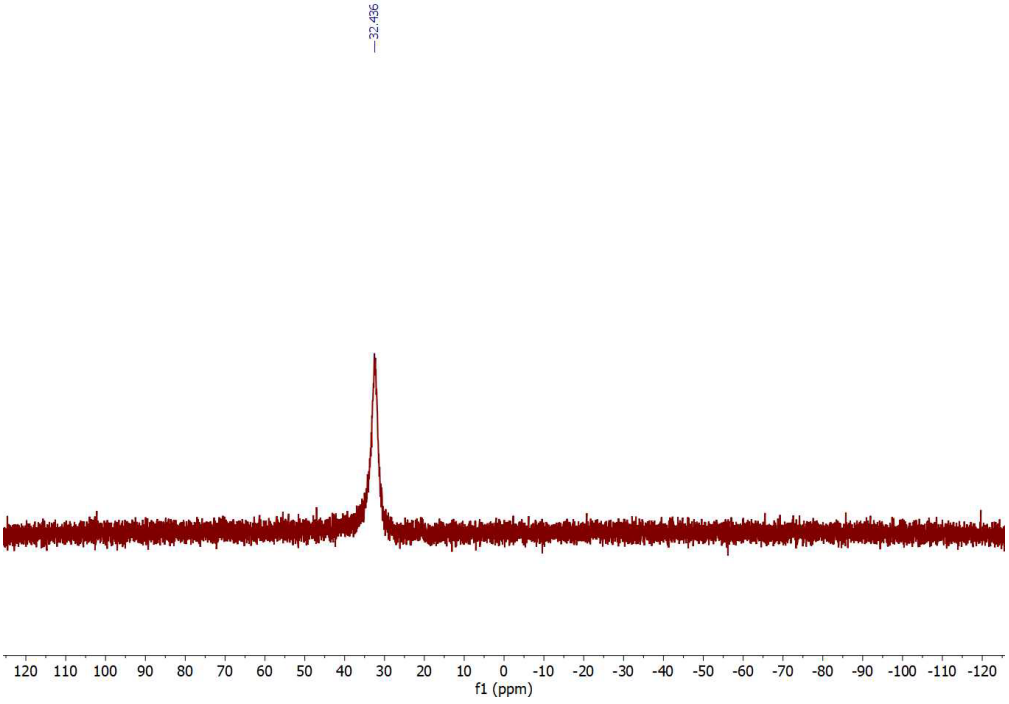
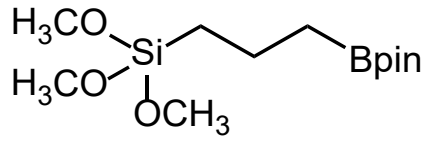


Figure S24. $^{11}B\{H\}$ NMR spectrum of **8** in $CDCl_3$.

2.2.9 Compound **9**



Vinyltrimethoxysilane (243 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.65 mmol). The crude product was purified by Kugelrohr oven distillation (5 mbar, 165 °C) to give **9** as a colorless oil. Yield 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.54 (s, 9 H), 1.59-1.46 (m, 2 H), 1.21 (s, 12 H), 0.83 (t, J = 7.7 Hz, 2 H), 0.72-0.63 (m, 2 H) ppm. ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 83.0, 50.5, 25.0, 17.4, 12.1 ppm. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B{H} NMR [128 MHz, $CDCl_3$] δ = 33.7 ppm. The spectral data are consistent with previously reported values [6].

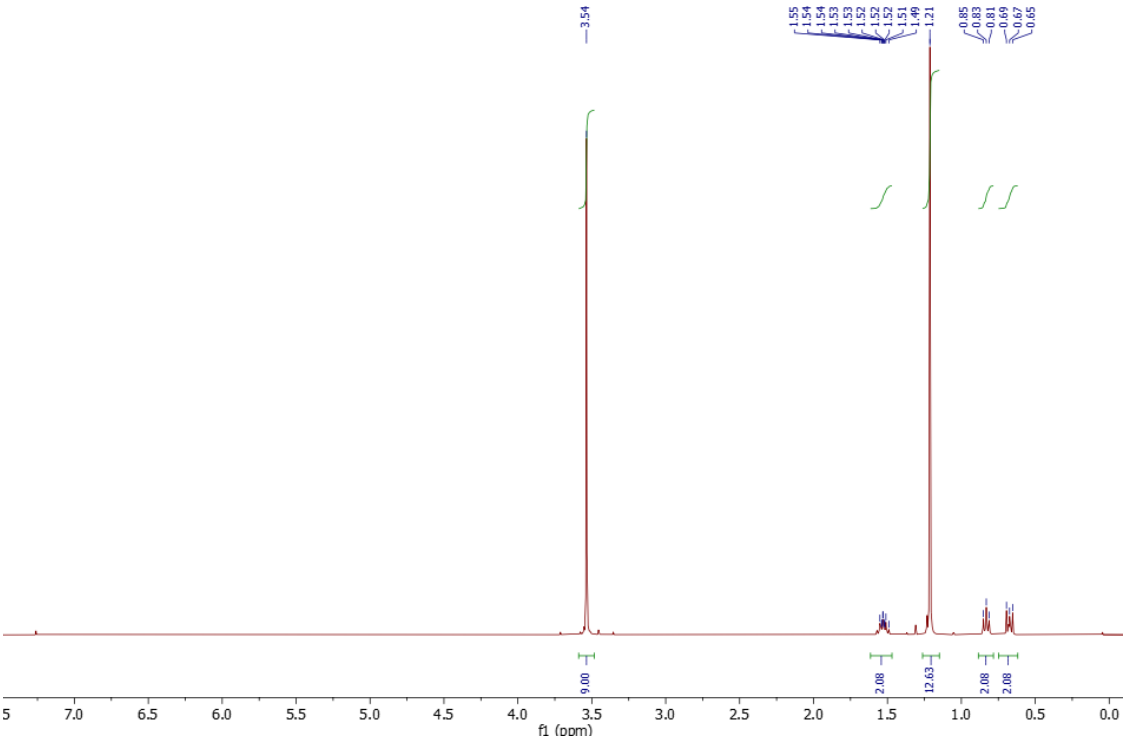


Figure S25. ^{1}H NMR spectrum of **9** in $CDCl_3$.

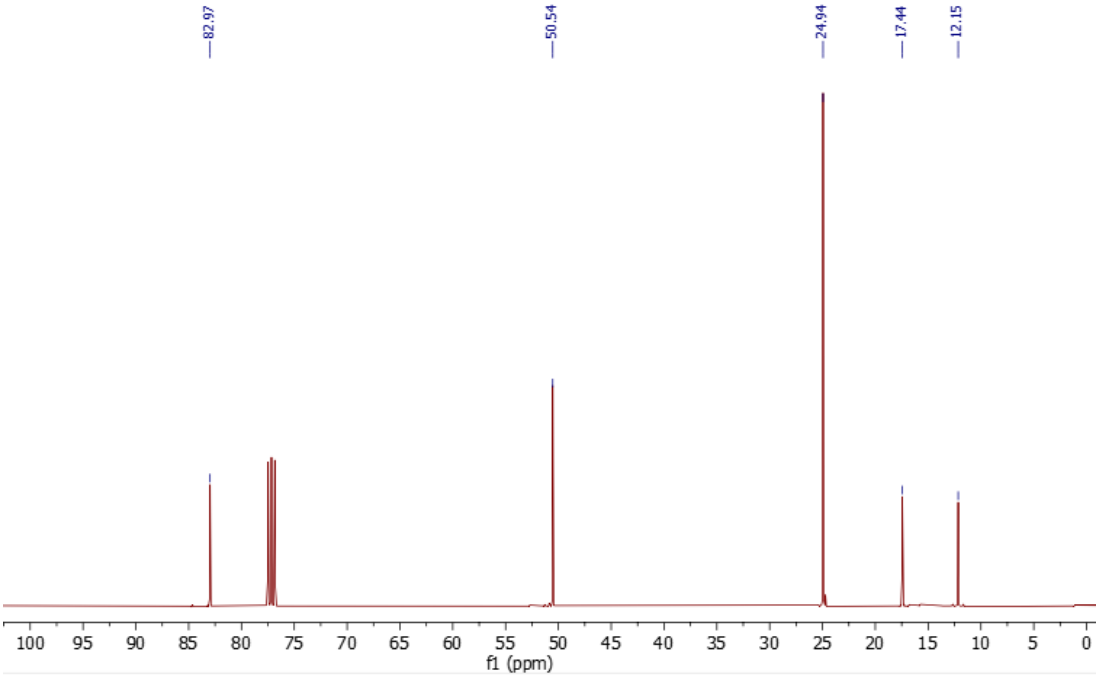


Figure S26. $^{13}C\{H\}$ NMR spectrum of **9** in $CDCl_3$.

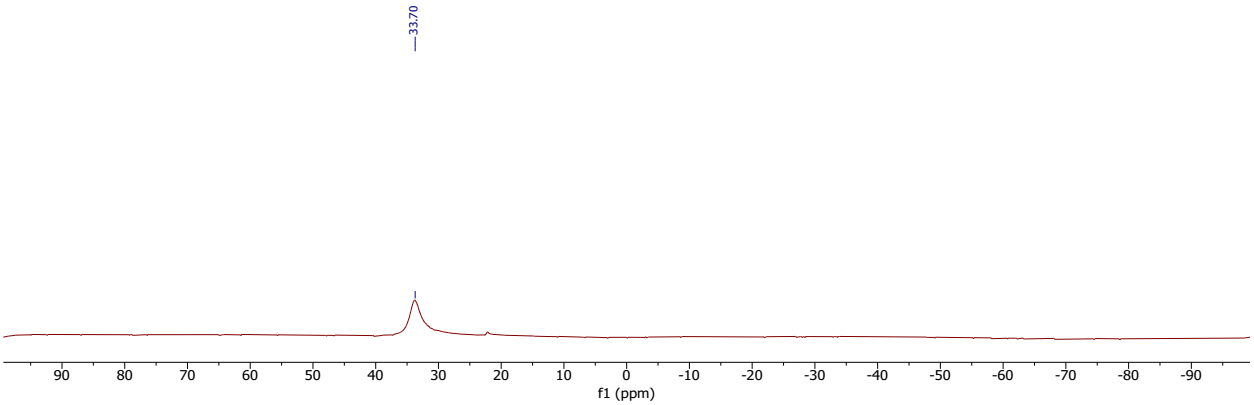
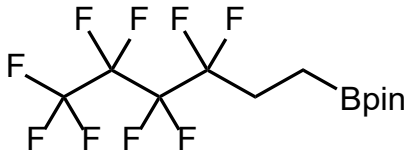


Figure S27. $^{11}B\{H\}$ NMR spectrum of **9** in $CDCl_3$.

2.2.10 Compound **10**



3,3,4,4,5,5,6,6,6-Nonafluoro-1-hexene (369 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.65 mmol). Colorless oil. Yield 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.28-2.09 (m, 2 H), 1.25 (s, 12 H), 1.08-0.99 (m, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -81.1, -116.3, -124.5, -126.1 ppm. ^{11}B NMR (128

MHz, $CDCl_3$) δ = 33.8 ppm. The spectral data are consistent with previously reported values [7].

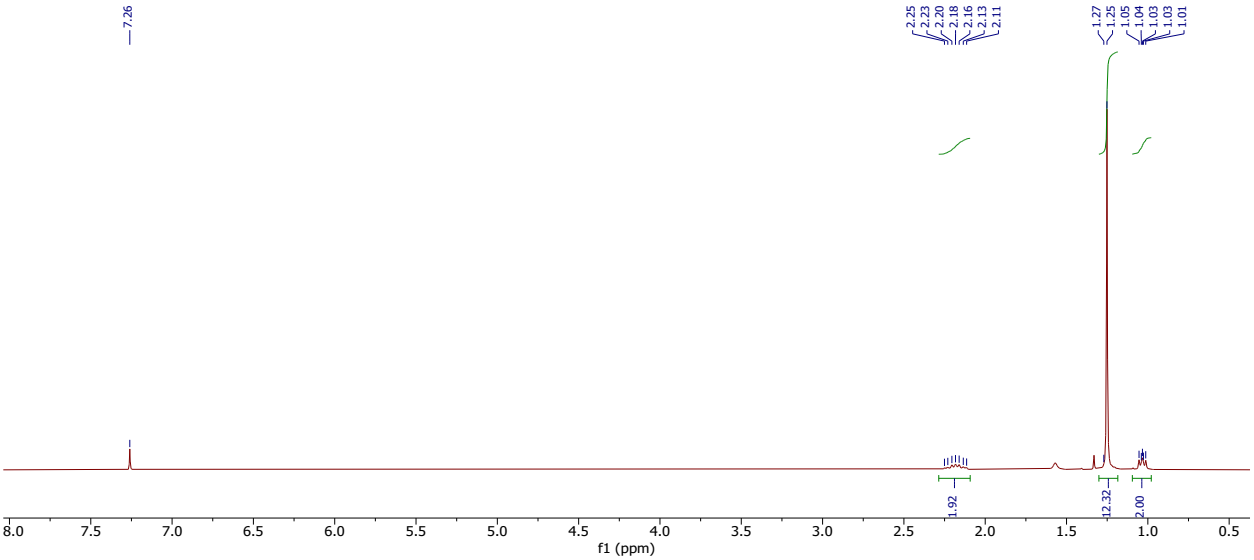


Figure S28. ^{1}H NMR spectrum of **10** in $CDCl_3$.

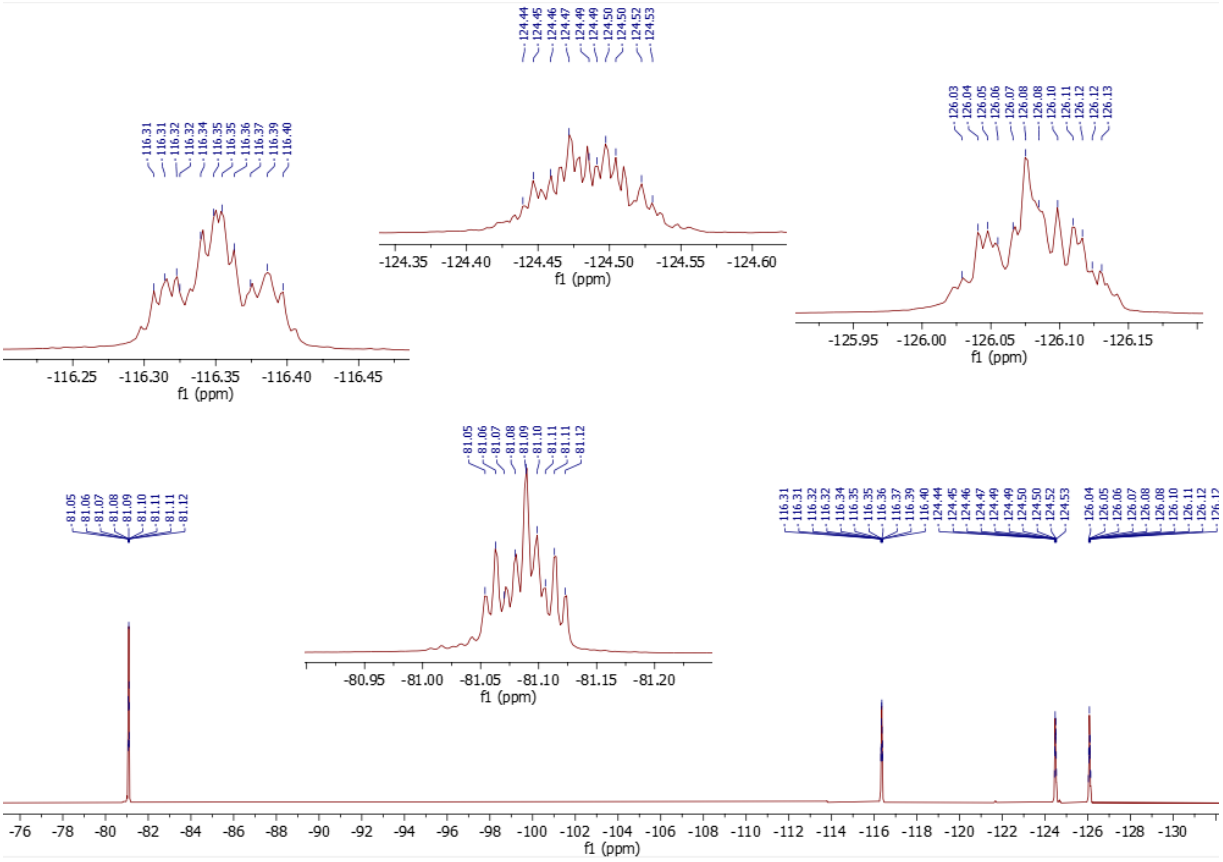


Figure S29. ^{19}F NMR spectrum of **10** in $CDCl_3$.

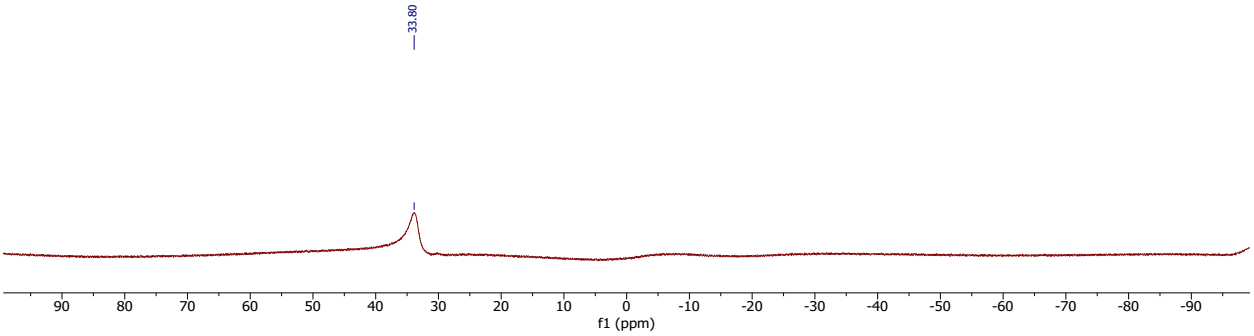
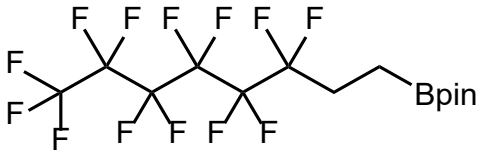


Figure S30. $^{11}B\{H\}$ NMR spectrum of **10** in $CDCl_3$.

2.2.11 Compound **11**



Method A. 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octene (519 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.65 mmol). Colorless oil. Yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.26-2.08 (m, 2 H), 1.24 (s, 12 H), 1.07-0.98 (m, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -80.1, -116.1, -122.1, -122.9, -123.6, -126.2 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.3 ppm. The spectral data are consistent with previously reported values [7].

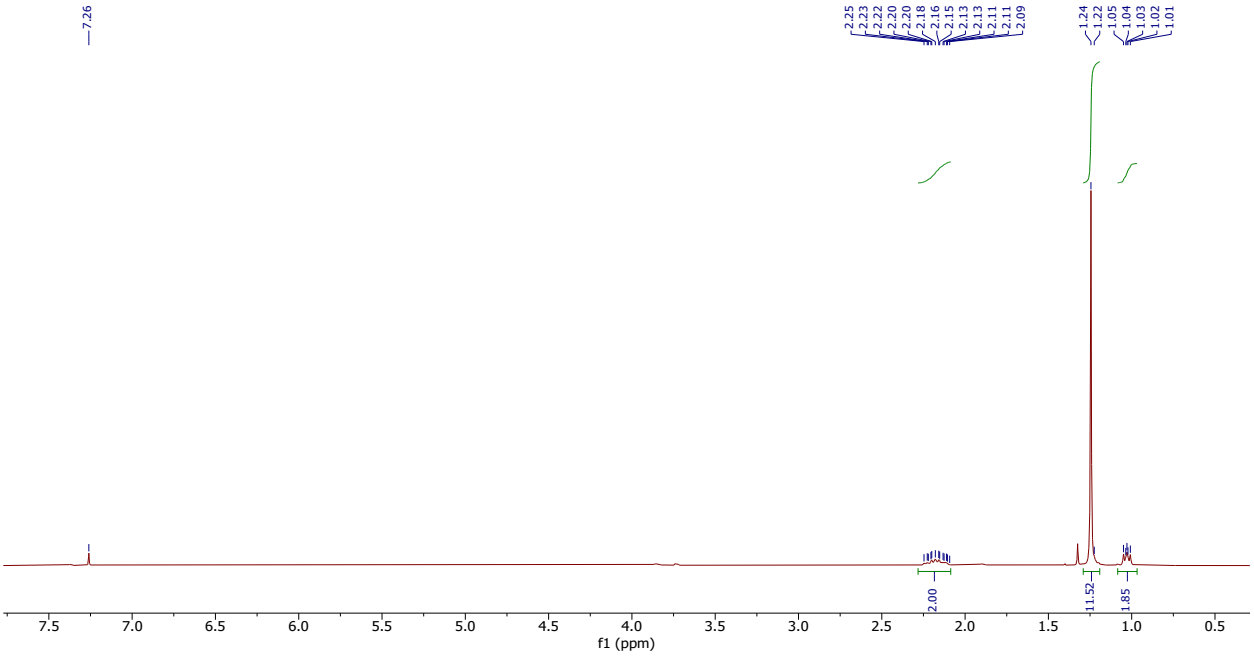


Figure S31. ^{1}H NMR spectrum of **11** in $CDCl_3$.

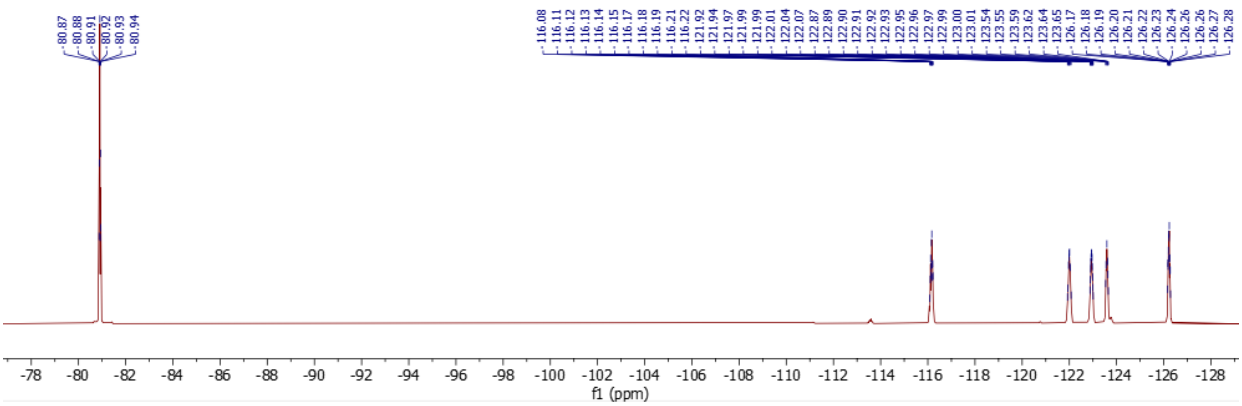


Figure S32. ^{19}F NMR spectrum of **11** in $CDCl_3$.

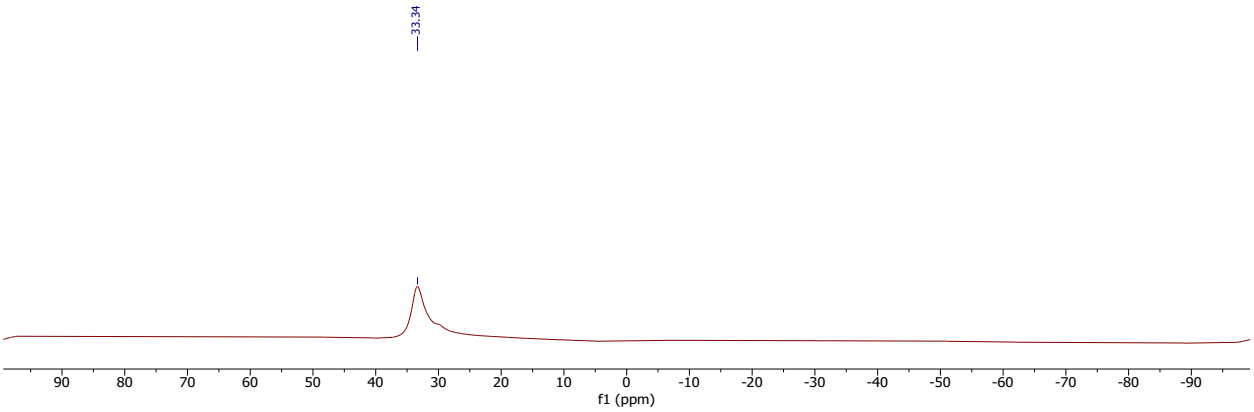
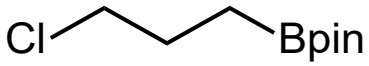


Figure S33. $^{11}B\{H\}$ NMR spectrum of **11** in $CDCl_3$.

2.2.12 Compound **12**



Allyl chloride (230 mg, 3 mmol), 3,4,5-trifluorophenyl boronic acid (10.6 mg, 0.6 mmol), HBpin (346 mg, 2.7 mmol). Colorless liquid. Yield 379 mg (62%). ^1H NMR [400 MHz, $CDCl_3$] δ = 3.52 (t, $^3J_{H-H}$ = 6.8 Hz, $ClCH_2$, 2 H), 1.87 (quint, $^3J_{H-H}$ = 8 Hz, CH_2, 2 H), 1.23 (s, CH_3, 12 H), 0.90 (t, $^3J_{H-H}$ = 7.6 Hz) ppm. $^{13}C\{H\}$ NMR [101MHz, $CDCl_3$] δ= 83.3, 47.3, 27.4, 24.9, 8.6 ppm. $^{11}B\{H\}$ NMR [128 MHz, $CDCl_3$] δ = 32.1 ppm. The spectral data are consistent with previously reported values [4].

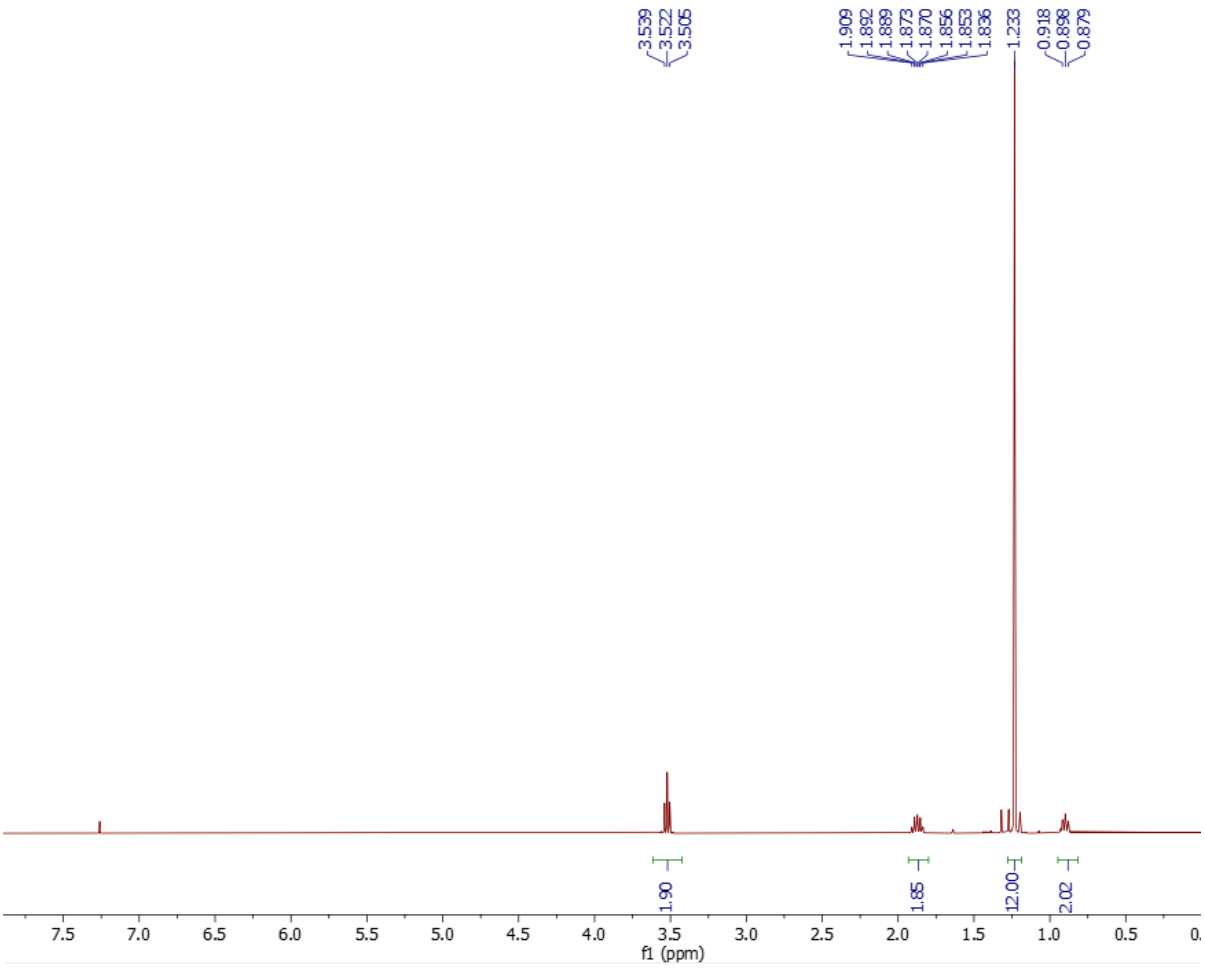


Figure S34. ^{1}H NMR spectrum of **12** in $CDCl_3$.

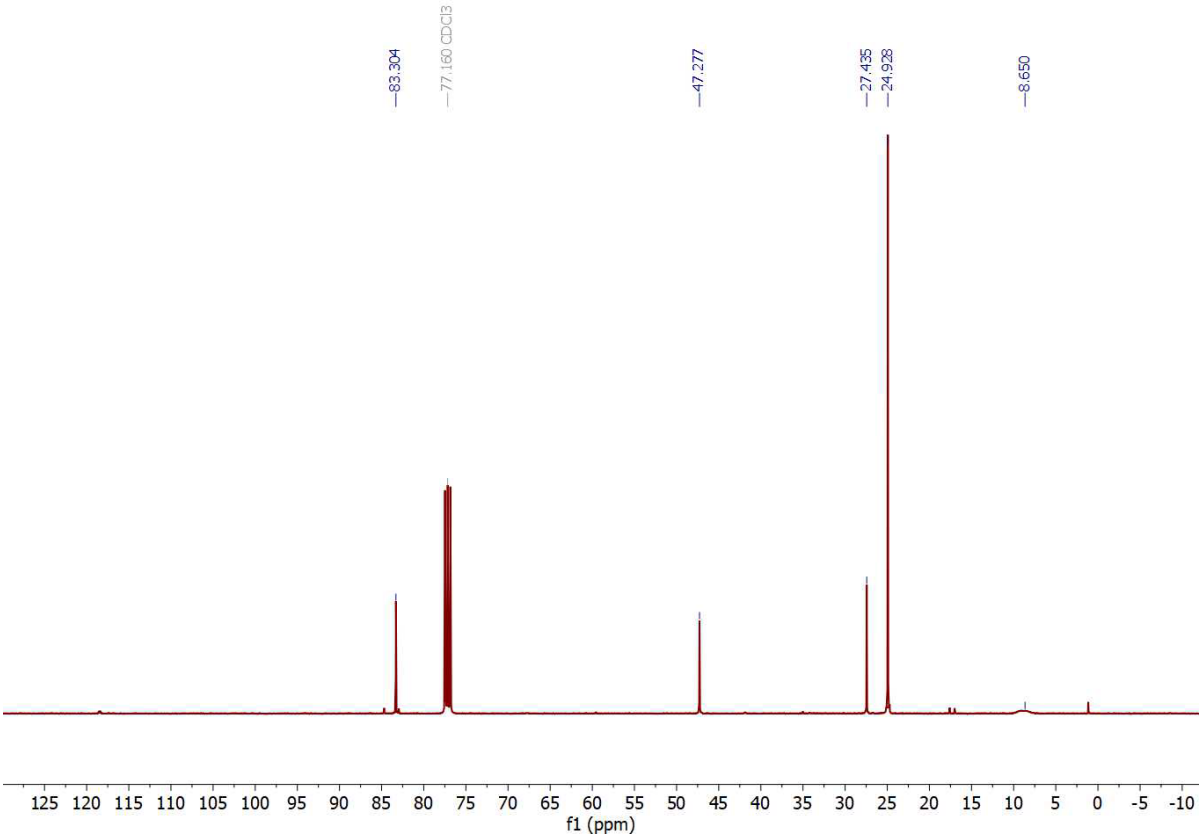


Figure S35. $^{13}C\{H\}$ NMR spectrum of **12** in $CDCl_3$.

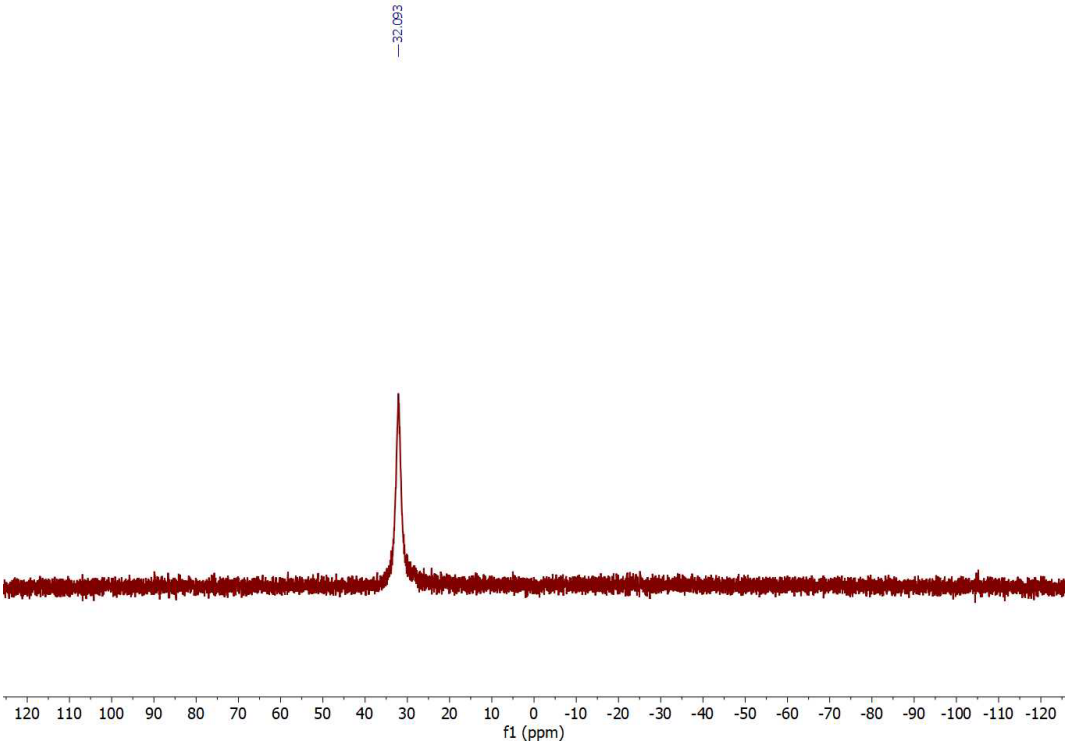
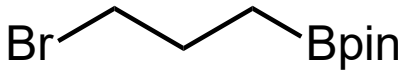


Figure S36. $^{11}B\{H\}$ NMR spectrum of **12** in $CDCl_3$.

2.2.13 Compound **13**



Allyl bromide (363 mg, 3 mmol), 3,4,5-trifluorophenyl boronic acid (10.6 mg, 0.6 mmol), HBpin (346 mg, 2.7 mmol). Colorless liquid. Yield 510 mg (68%). ^{1}H NMR [400 MHz, $CDCl_3$] δ = 3.42 (t, $^{3}J_{H-H}$ = 8 Hz, $BrCH_2$, 2 H), 1.96 (pent, $^{3}J_{H-H}$ = 7.6 Hz, CH_2, 2 H), 1.24 (s, CH_3, 12 H), 0.91 (t, $^{3}J_{H-H}$ = 7.6 Hz) ppm. ^{13}C{H} NMR [101MHz, $CDCl_3$] δ= 83.3, 36.4, 27.6, 24.9, 10.2 ppm. ^{11}B{H} NMR [128 MHz, $CDCl_3$] δ = 32.1 ppm. The spectral data are consistent with previously reported values [8].

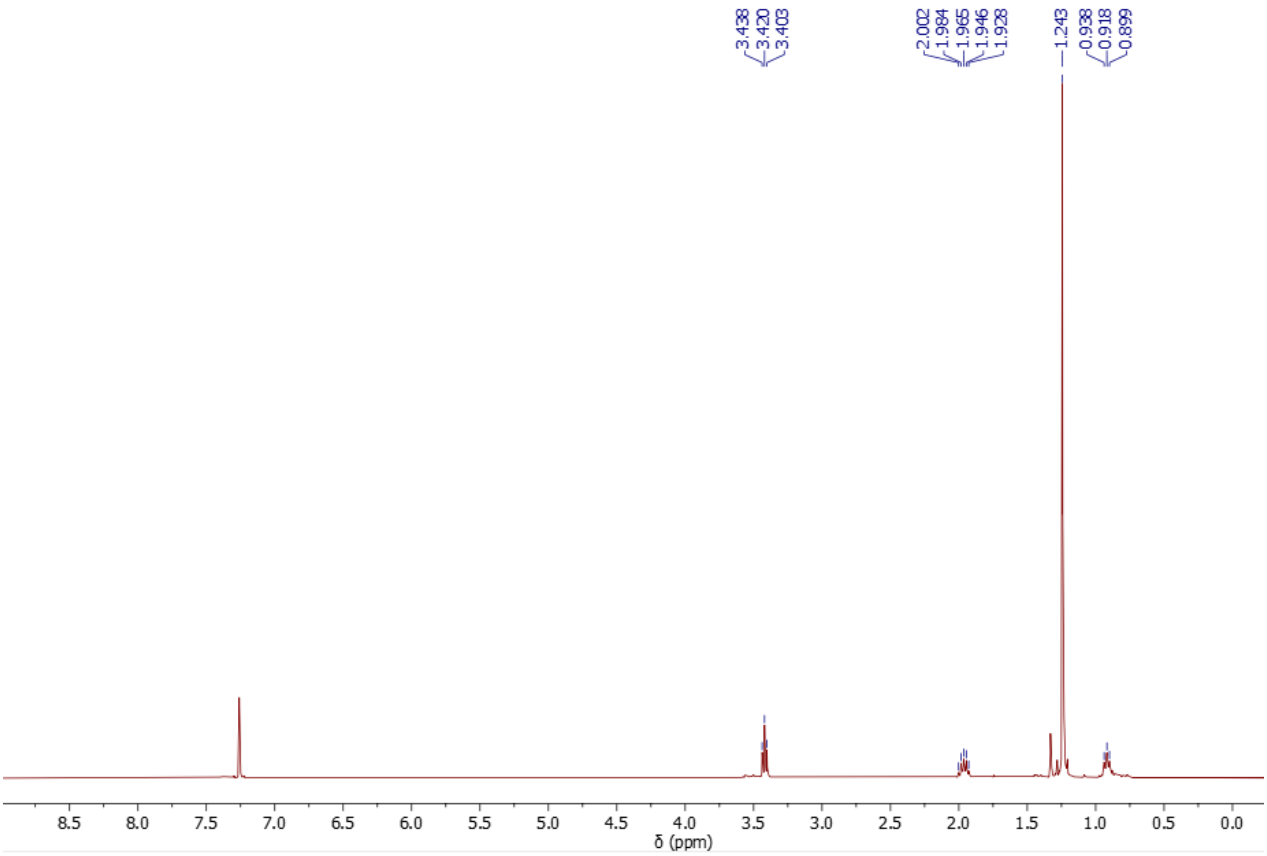


Figure S37. ^{1}H NMR spectrum of **13** in $CDCl_3$.

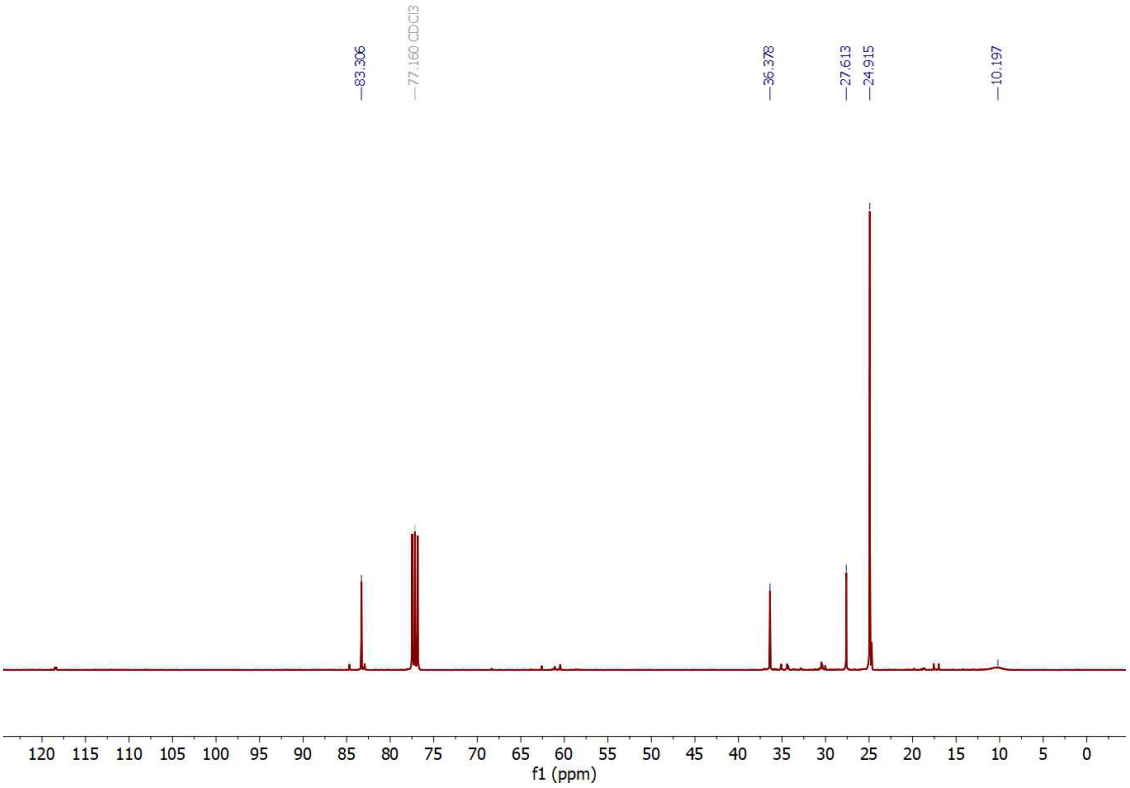


Figure S38. $^{13}C\{H\}$ NMR spectrum of **13** in $CDCl_3$.

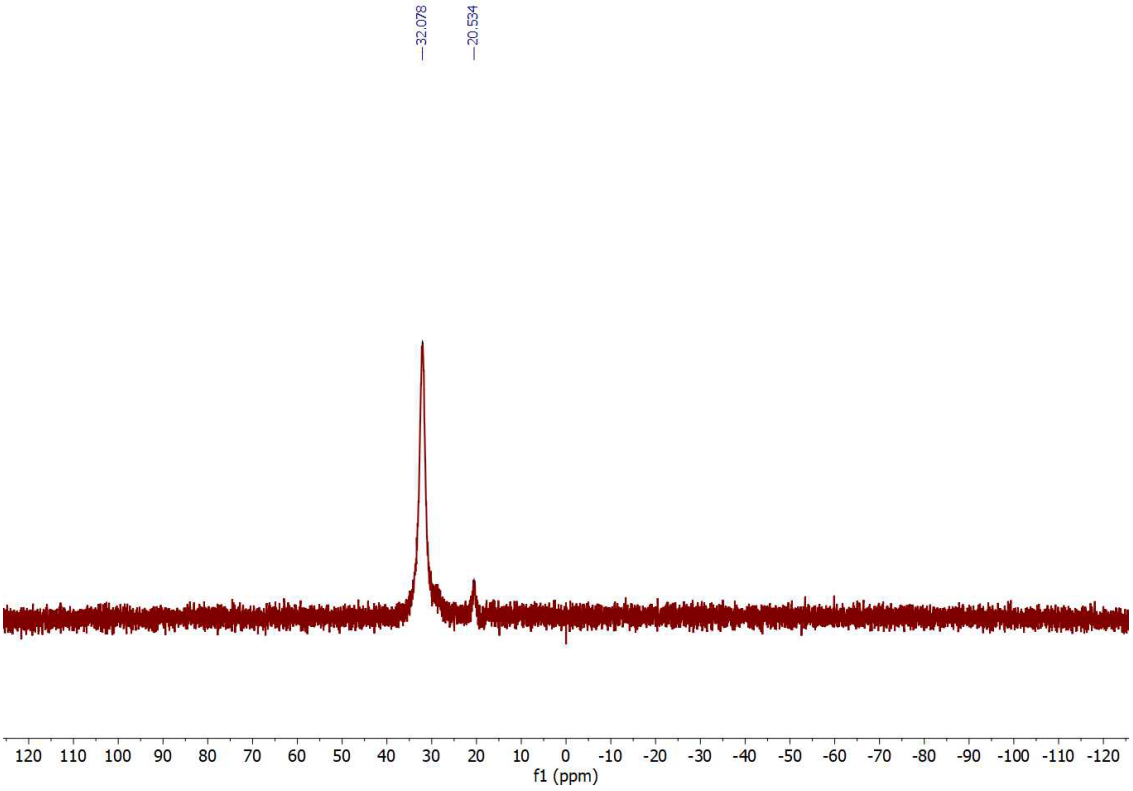
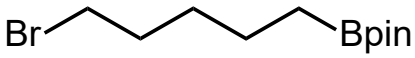


Figure S39. $^{11}B\{H\}$ NMR spectrum of **13** in $CDCl_3$.

2.2.14 Compound **14**



5-Bromopentene (223 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.65 mmol). Colorless oil. Yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.40 (t, $^{3}J_{H-H}$ = 6.9 Hz, 2 H), 1.92-1.79 (m, 2 H), 1.46-1.37 (m, 4 H), 1.24 (s, 12 H), 0.82-0.72 (m, 2 H) ppm. ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 83.1, 34.1, 32.8, 31.0, 25.0, 23.3 ppm. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.9 ppm. The spectral data are consistent with previously reported values [5].

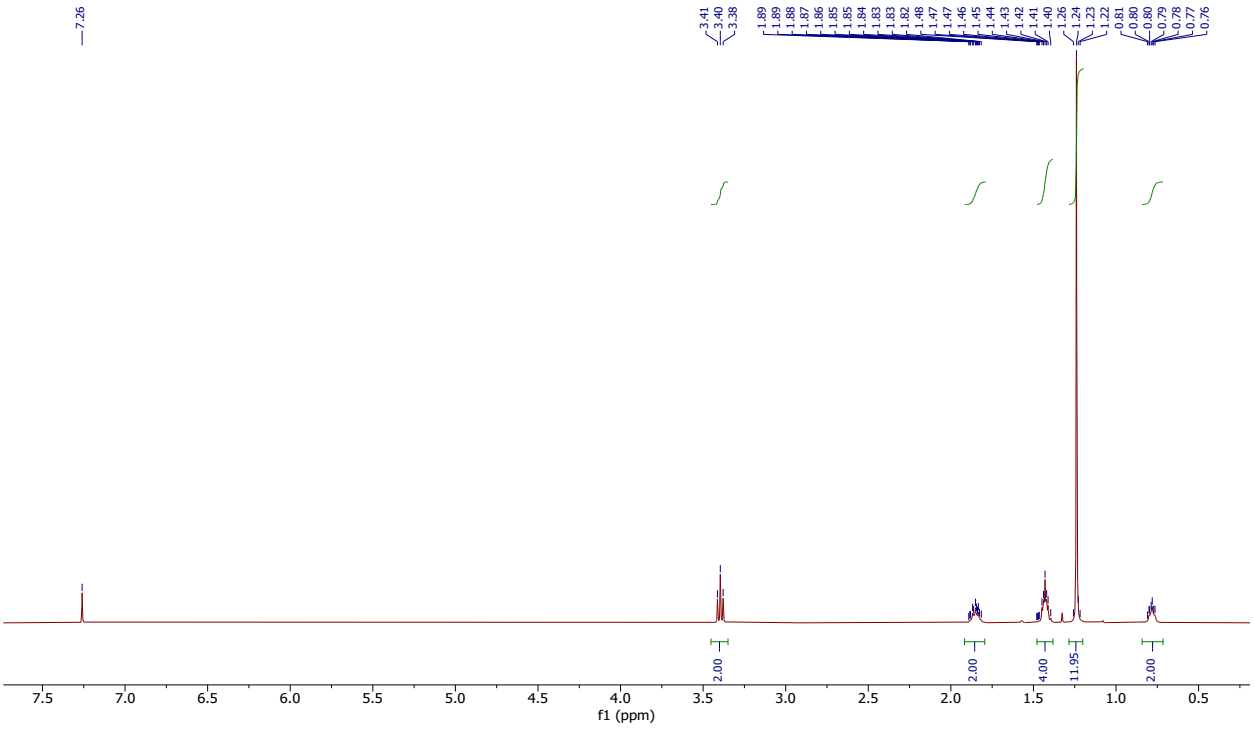


Figure S40. ^{1}H NMR spectrum of **14** in $CDCl_3$.

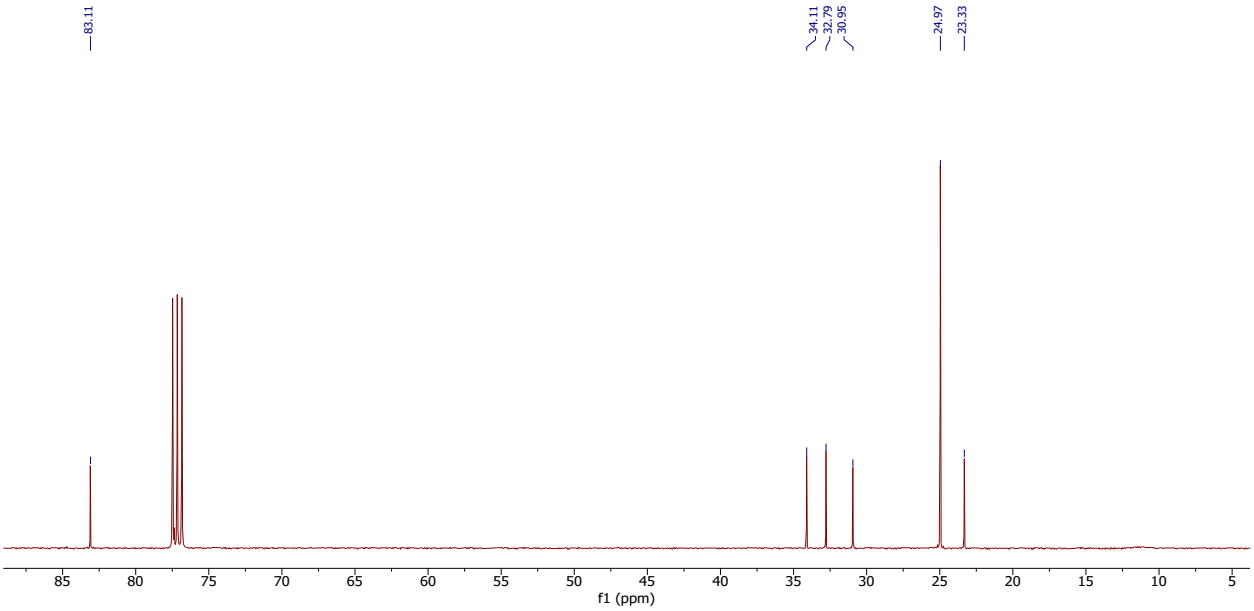


Figure S41. $^{13}C\{H\}$ NMR spectrum of **14** in $CDCl_3$.

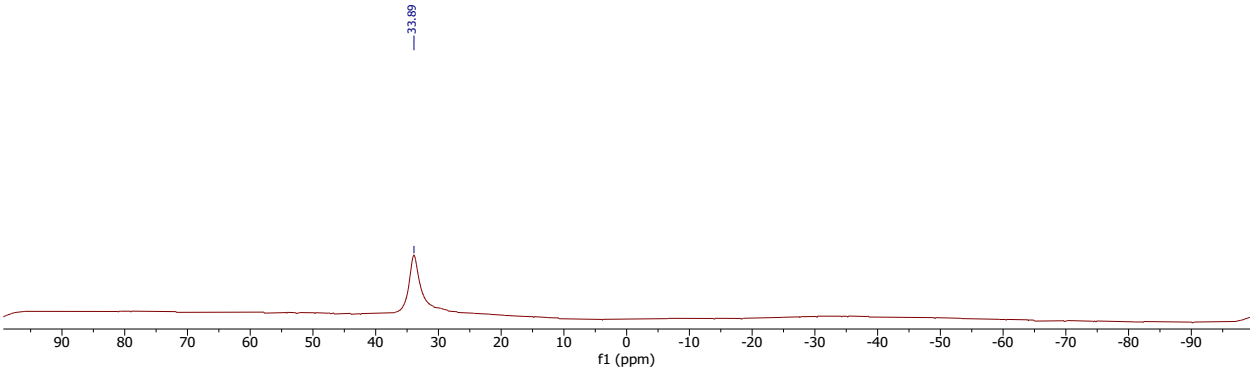
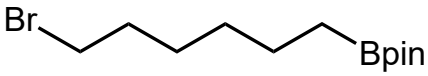


Figure S42. $^{11}B\{H\}$ NMR spectrum of **14** in $CDCl_3$.

2.2.15 Compound **15**



6-Bromohexene (245 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.65 mmol). Colorless oil. Yield 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.39 (t, $^{3}J_{H-H}$ = 6.9 Hz, 2 H), 1.89-1.78 (m, 2 H), 1.47-1.34 (m, 4 H), 1.35-1.27 (m, 2 H), 1.24 (s, 12 H), 0.77 (t, $^{3}J_{H-H}$ = 7.7 Hz, 2 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 83.0, 34.1, 32.9, 31.5, 28.0, 25.0, 24.7, 23.9, 11.2 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.9 ppm. The spectral data are consistent with previously reported values [5].

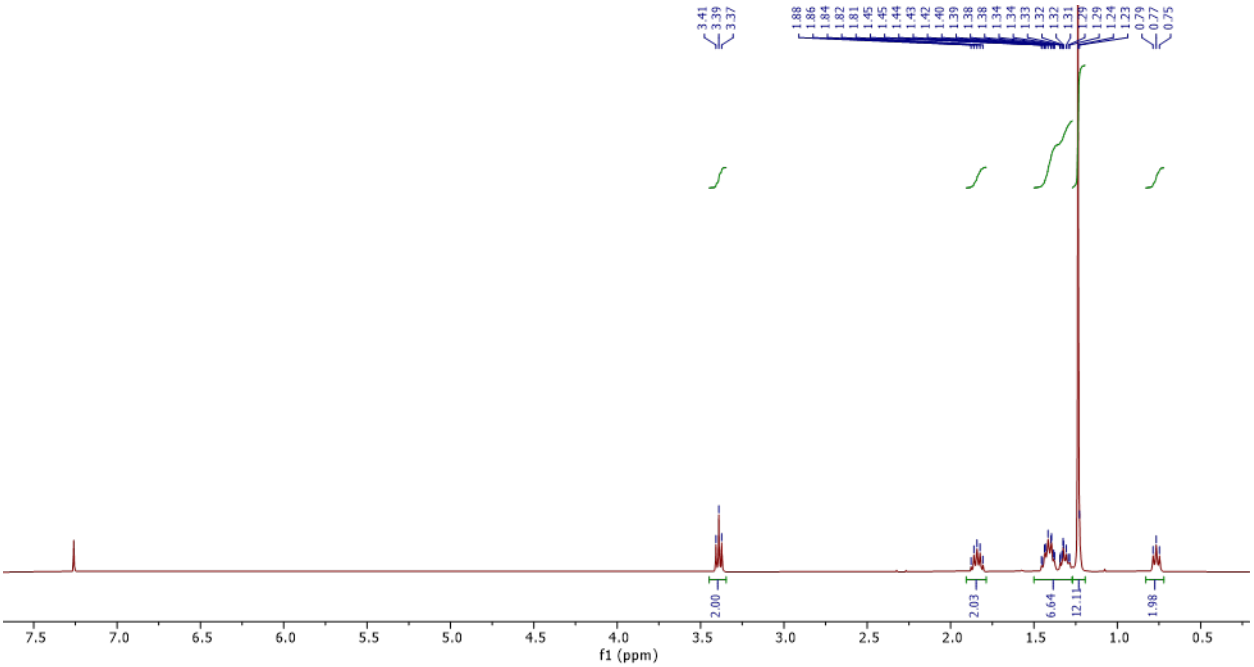


Figure S43. ^{1}H NMR spectrum of **15** in $CDCl_3$.

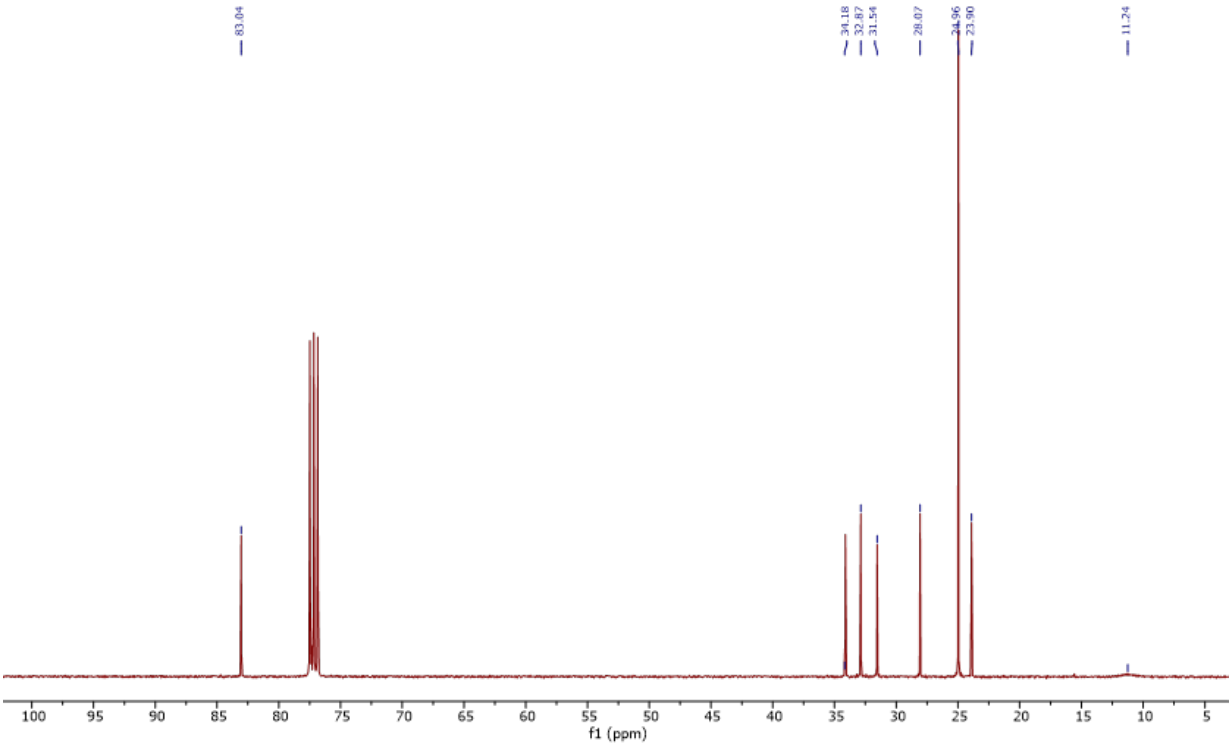


Figure S44. $^{13}C\{H\}$ NMR spectrum of **15** in $CDCl_3$.

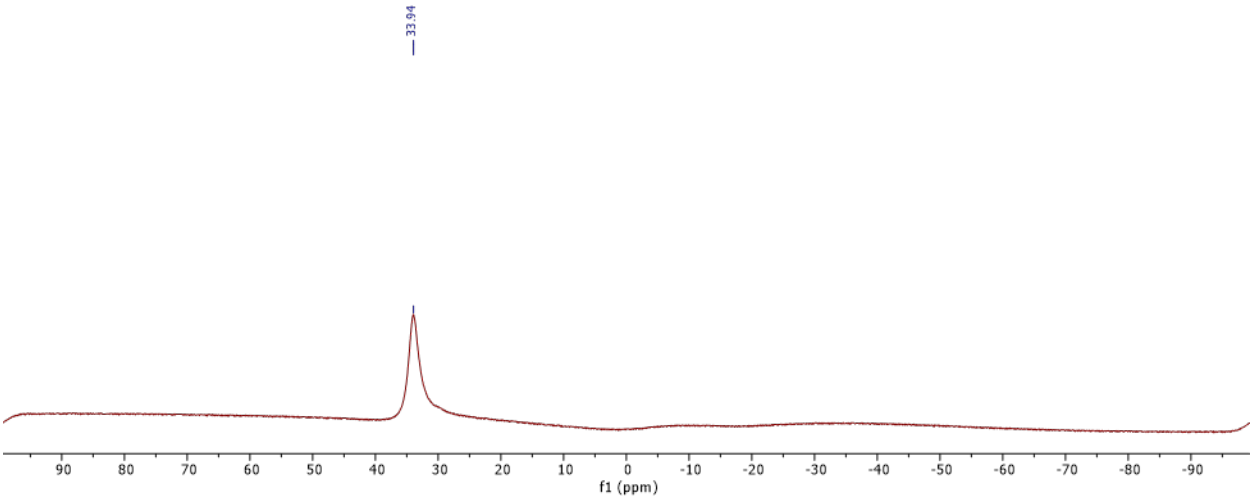
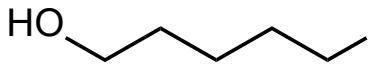


Figure S45. $^{11}B\{H\}$ NMR spectrum of **15** in $CDCl_3$.

2.2.16 Compound **16**



5-Pentenol (129 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (400 mg, 3.1 mmol). After 24 h, the crude dissolved in ca. 8 mL of $CHCl_3$ and 3 to 4 drops of water were stirred for 48 h at room temperature. After treating with dry $MgSO_4$, the resulting $CHCl_3$ solution was filtered through a short plug of silica (3/4") in 15 ml ChemGlass filter frit yields a colorless oil, 68%. ^1H NMR (400 MHz, $CDCl_3$) δ = 3.64 (t, $^3J_{H-H}$ = 6.6 Hz, 2 H), 1.63-1.51 (m, 3 H), 1.48-1.33 (m, 4 H), 1.24 (s, 12 H), 0.79 (t, $^3J_{H-H}$ = 7.5 Hz, 2 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 83.1, 63.1, 32.6, 28.5, 25.0, 23.7 ppm. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 34.3 ppm. The spectral data are consistent with previously reported values [9].

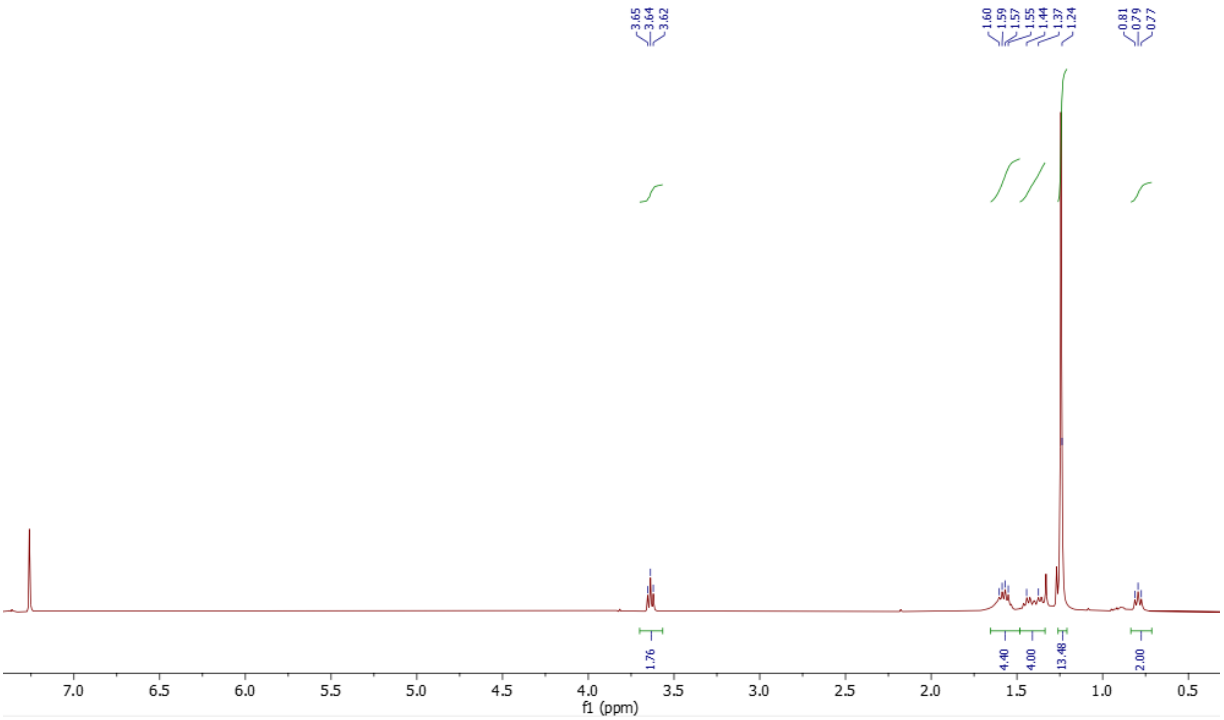


Figure S46. ^{1}H NMR spectrum of **16** in $CDCl_3$.

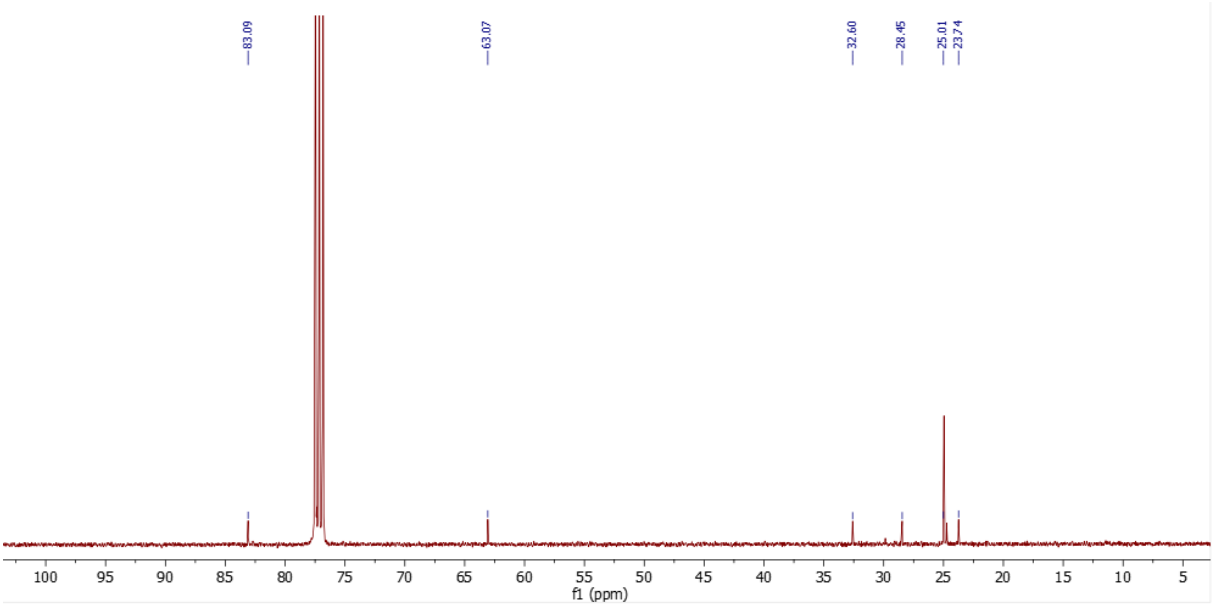


Figure S47. $^{13}C\{H\}$ NMR spectrum of **16** in $CDCl_3$.

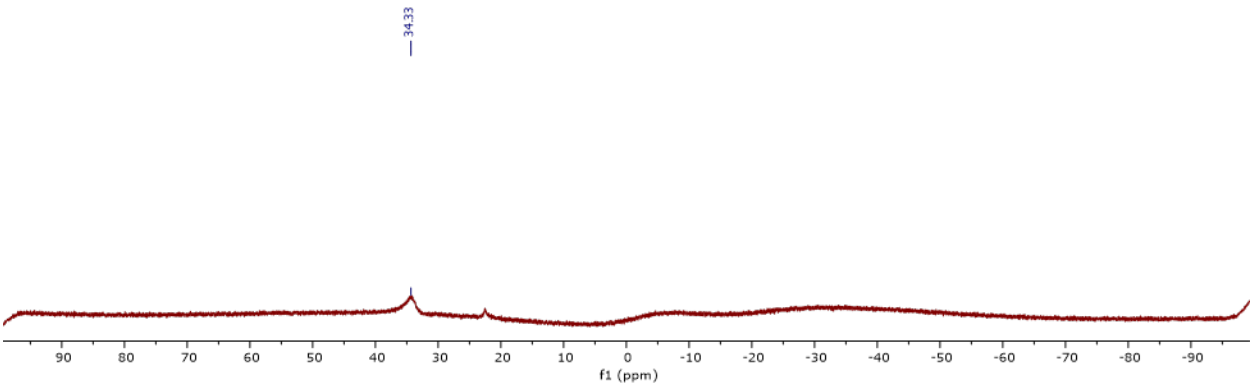
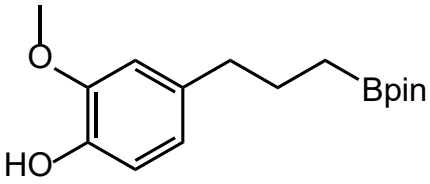


Figure S48. $^{11}B\{H\}$ NMR spectrum of **16** in $CDCl_3$.

2.2.17 Compound **17**



Eugenol (246 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (400 mg, 3.1 mmol). After 24 h, the crude dissolved in ca. 8 mL of $CHCl_3$ and 3 to 4 drops of water were stirred for 48 h at room temperature. After treating with dry $MgSO_4$, the crude was purified via Method B. Colorless oil. Yield 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.72 (d, $^{3}J_{H-H}$ = 7.8 Hz, 1 H), 6.62-6.53 (m, 2 H), 5.51 (s, 1 H), 3.76 (s, 3 H), 2.59-2.37 (m, 2 H), 1.68-1.56 (m, 2 H), 1.16 (s, 12 H), 0.73 (t, $^{3}J_{H-H}$ = 7.9 Hz, 2 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 146.3, 143.6, 134.7, 121.1, 114.2, 111.2, 83.0, 55.9, 38.3, 26.4, 24.9, 11.0 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.8 ppm. The spectral data are consistent with previously reported values [10].

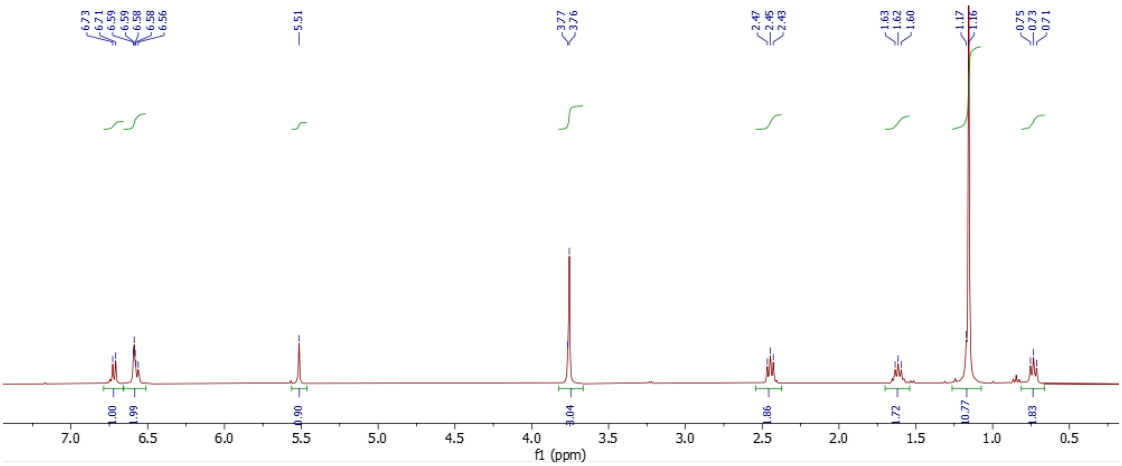


Figure S49. ^{1}H NMR spectrum of **17** in $CDCl_3$.

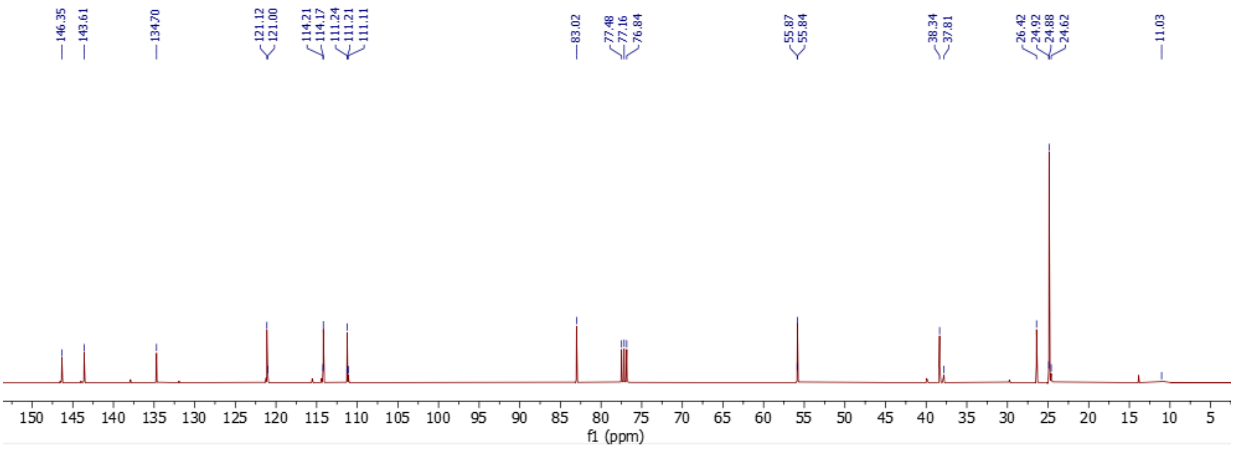


Figure S50. $^{13}C\{H\}$ NMR spectrum of **17** in $CDCl_3$.

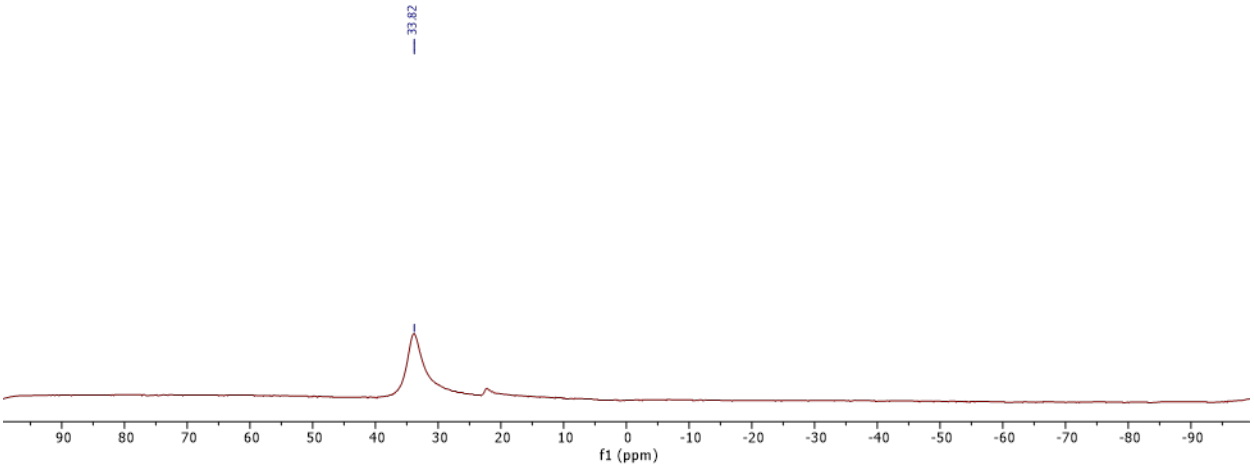
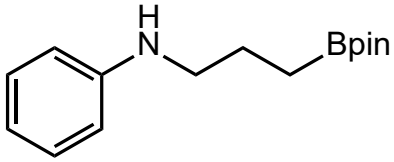


Figure S51. $^{11}B\{H\}$ NMR spectrum of **17** in $CDCl_3$.

2.2.18 Compound **18**



N-allyl aniline (200 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (400 mg, 3.1 mmol). After 24 h, the crude was dissolved in ca. 8 mL of $CHCl_3$ and 3 to 4 drops of water were stirred for 24 h at room temperature. After treating with dry $MgSO_4$, the resulting $CHCl_3$ solution was filtered through a short plug of silica (3/4") in 15 ml ChemGlass filter frit yields a colorless oil, 63%. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.23-7.12 (m, 1 H), 6.73-6.64 (m, 1 H), 6.63-6.58 (m, 1 H), 3.11 (t, $^3J_{H-H}$ = 7.0 Hz, 1 H), 1.75 (p, $^3J_{H-H}$ = 7.4 Hz, 1 H), 1.26 (s, 6 H), 0.88 (t, $^3J_{H-H}$ = 7.6 Hz, 1 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 148.7, 129.3, 117.0, 112.8, 83.2, 46.2, 25.0, 24.0 ppm. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz,

$CDCl_3$) δ = 33.8 ppm. The spectral data are consistent with previously reported values [6].

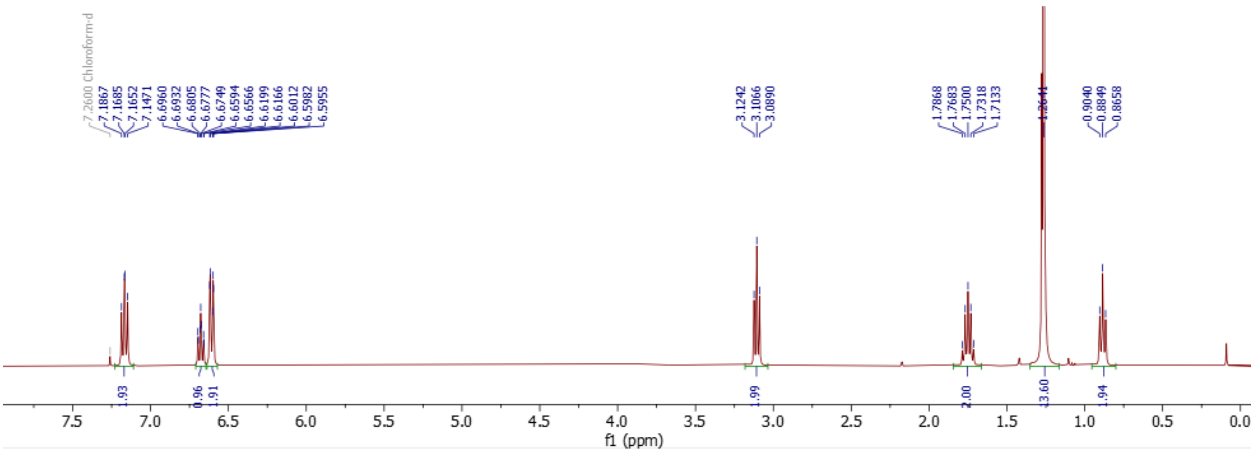


Figure S52. ^{1}H NMR spectrum of **18** in $CDCl_3$.

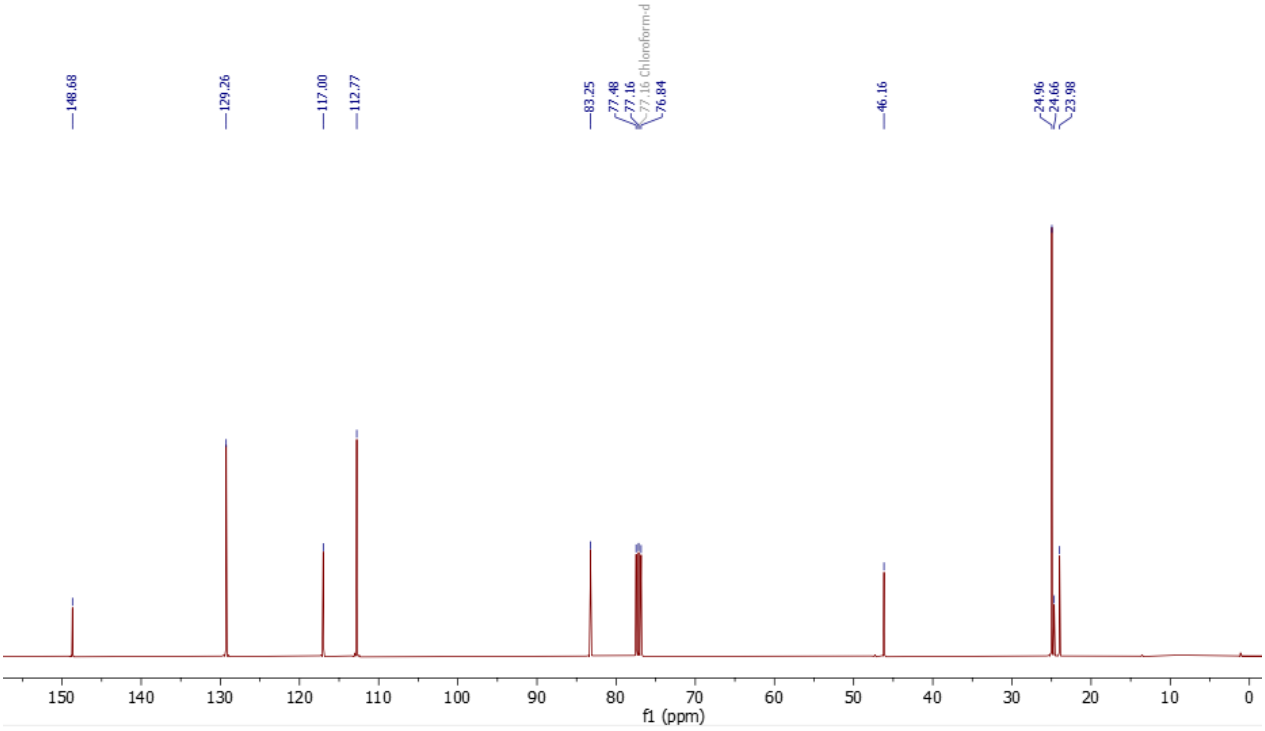


Figure S53. $^{13}C\{H\}$ NMR spectrum of **18** in $CDCl_3$.

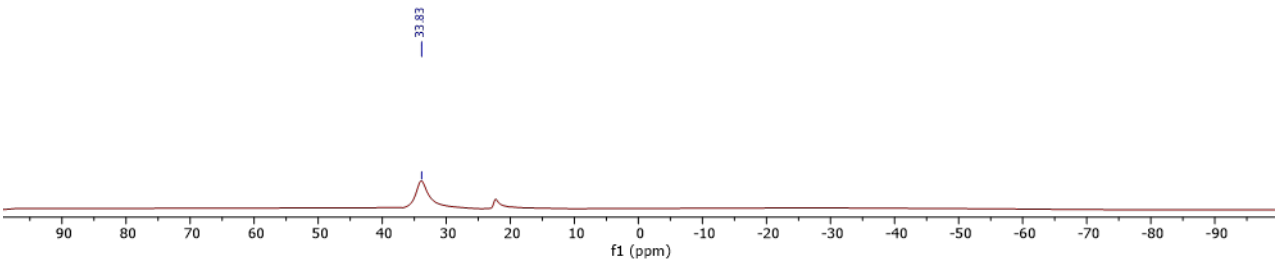
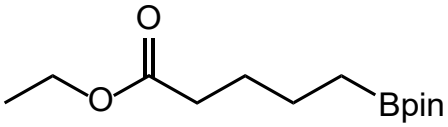


Figure S54. $^{11}B\{H\}$ NMR spectrum of **18** in $CDCl_3$.

2.2.19 Compound **19**



Ethyl-4-pentenoate (192 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (192 mg, 1.5 mmol). Colorless oil. Yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.10 (q, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 2 H), 2.27 (t, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2 H), 1.67-1.53 (m, 1 H), 1.48-1.38 (m, 1 H), 1.26-1.20 (m, 3 H), 1.23 (s, 12 H), 0.78 (t, $^{3}J_{H\text{-}H}$ = 7.9 Hz, 2 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 174.0, 83.1, 60.2, 34.4, 27.7, 25.0, 23.8, 14.4, 11.2 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.8 ppm. The spectral data are consistent with previously reported values [11].

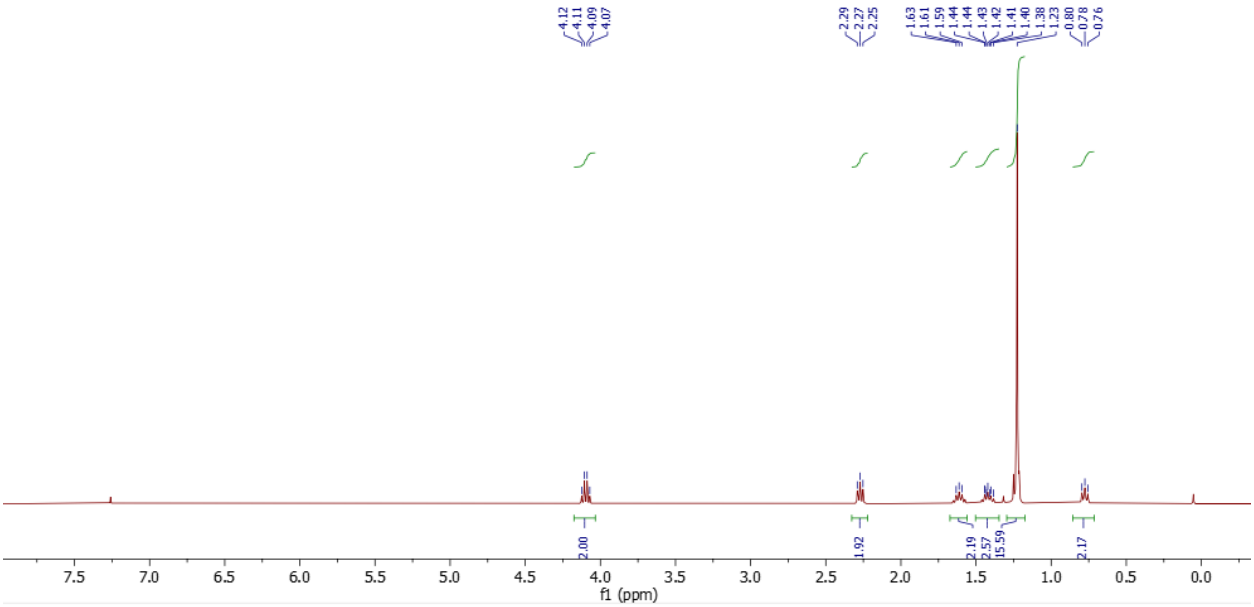


Figure S55. ^{1}H NMR spectrum of **19** in $CDCl_3$.

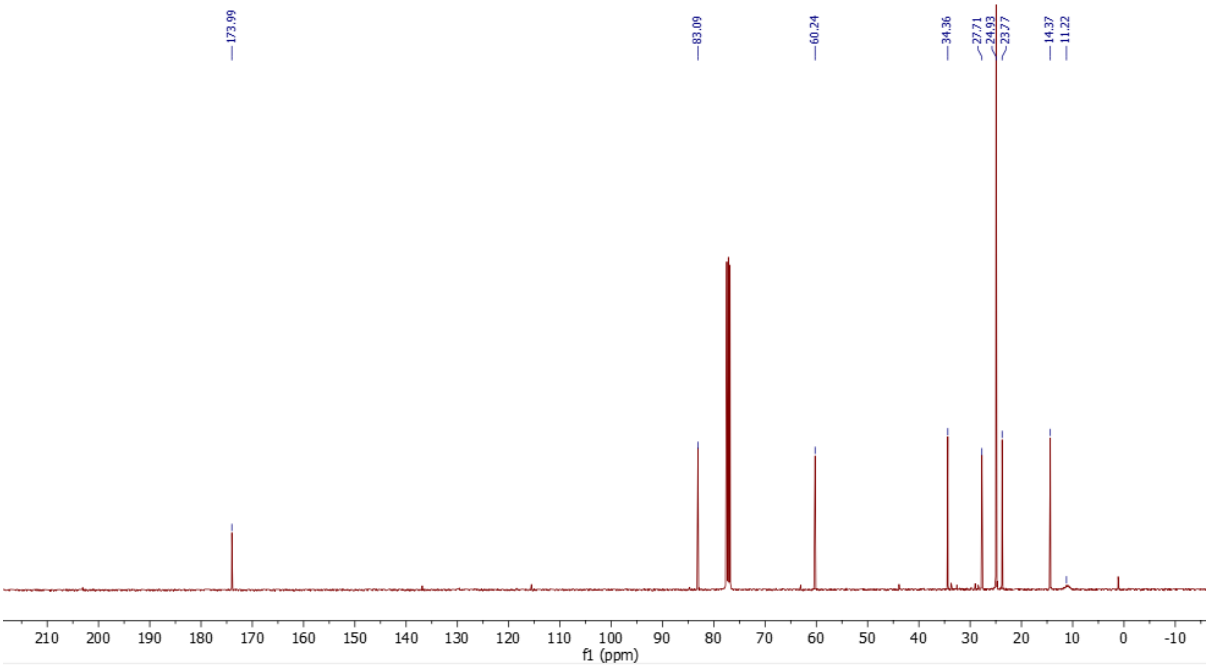


Figure S56. $^{13}C\{H\}$ NMR spectrum of **19** in $CDCl_3$.

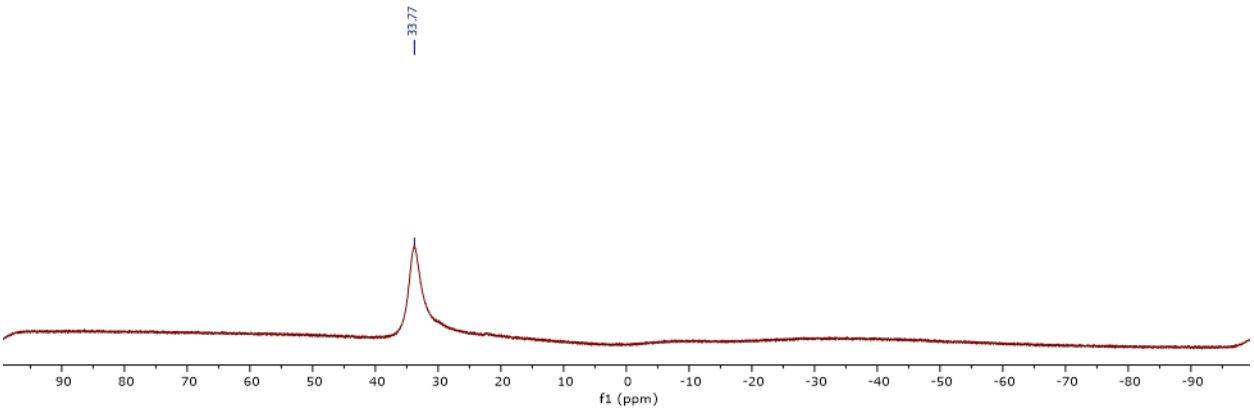
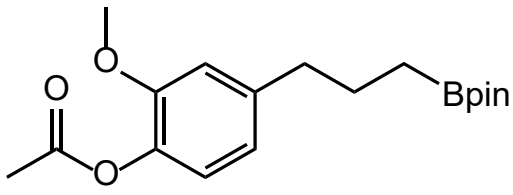


Figure S57. $^{11}B\{H\}$ NMR spectrum of **19** in $CDCl_3$.

2.2.20 Compound **20**



Eugenyl Acetate (309 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (192 mg, 1.5 mmol). Pale yellow crystalline solid. Yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.91-6.80 (m, 1 H), 6.74-6.64 (m, 1 H), 3.74 (s, 3 H), 2.55-2.47 (m, 2 H), 2.23 (s, 3 H), 1.66 (p, $^{3}J_{H-H}$ = 7.9 Hz, 2 H), 1.18 (s, 12 H), 0.76 (t, $^{3}J_{H-H}$ = 7.9 Hz, 2 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 169.4, 150.7, 141.8, 137.7, 122.4, 120.7, 112.8, 83.1, 55.9, 38.7,

26.2, 25.0, 20.9, 11.2 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 34.2 ppm. GC-MS: m/z of $[M]^+$ = 334.199.

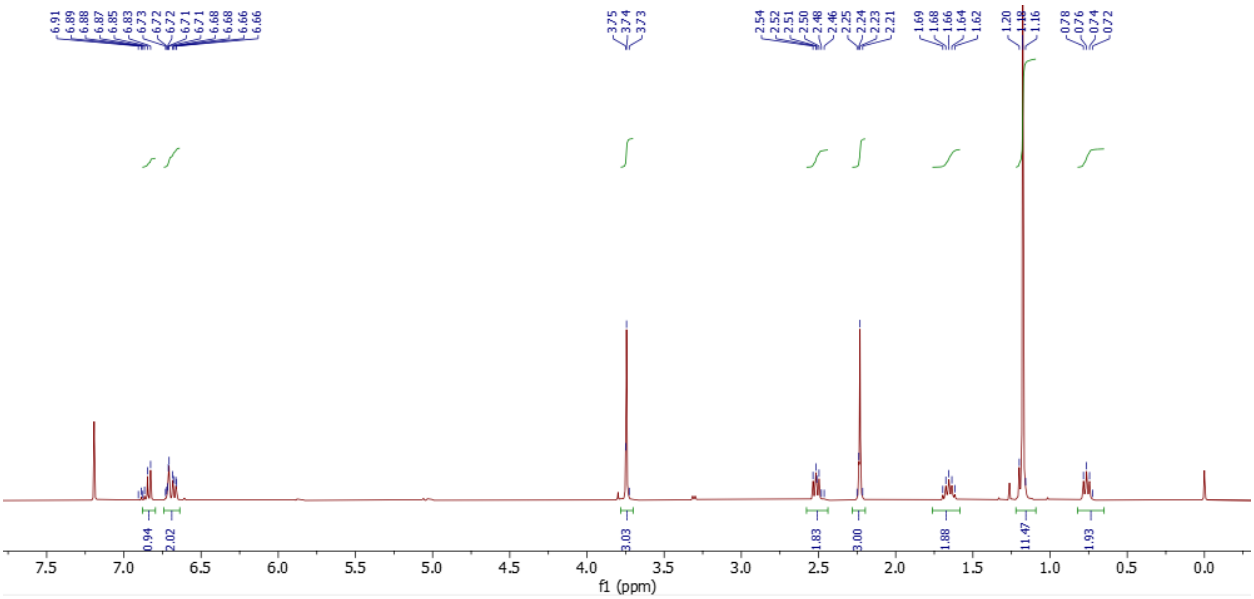


Figure S58. ^{1}H NMR spectrum of **20** in $CDCl_3$.

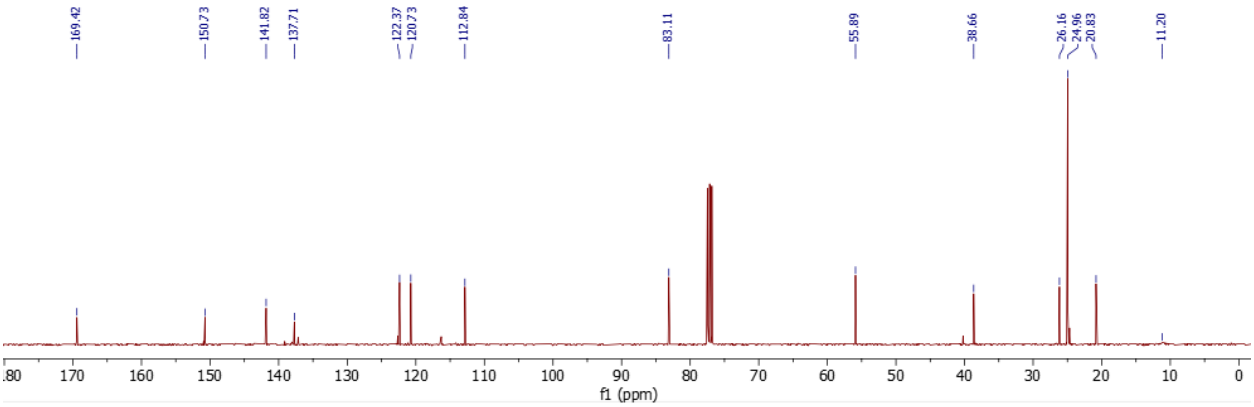


Figure S59. ^{13}C{H} NMR spectrum of **20** in $CDCl_3$.

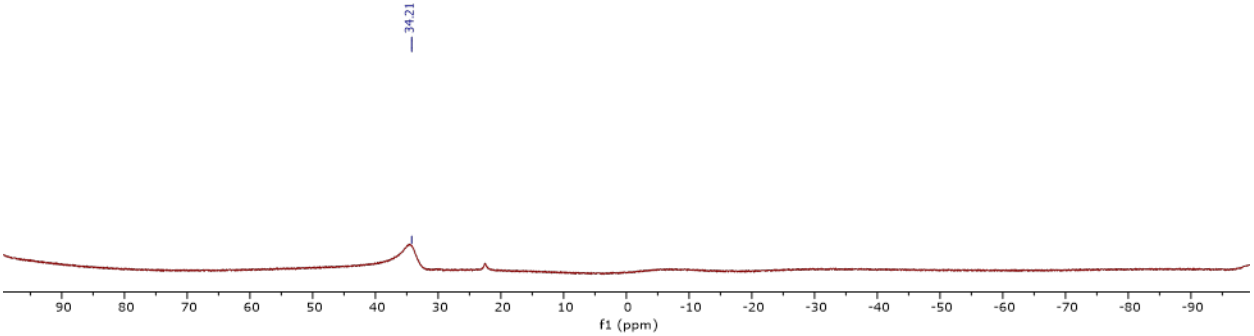
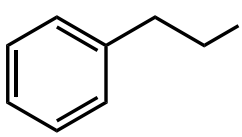


Figure S60. ^{11}B{H} NMR spectrum of **20** in $CDCl_3$.

2.2.21 Compound **21**



Styrene (156 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.65 mmol). Colorless oil. Yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.09 (m, 5 H), 2.74 (t, $^{3}J_{H\text{-}H}$ = 7.9 Hz, 2 H), 1.21 (s, 12 H), 1.14 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 2 H) ppm. ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ = 144.5, 128.3, 128.1, 125.6, 83.2, 30.1, 25.0 ppm. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.9 ppm. The spectral data are consistent with previously reported values [11].

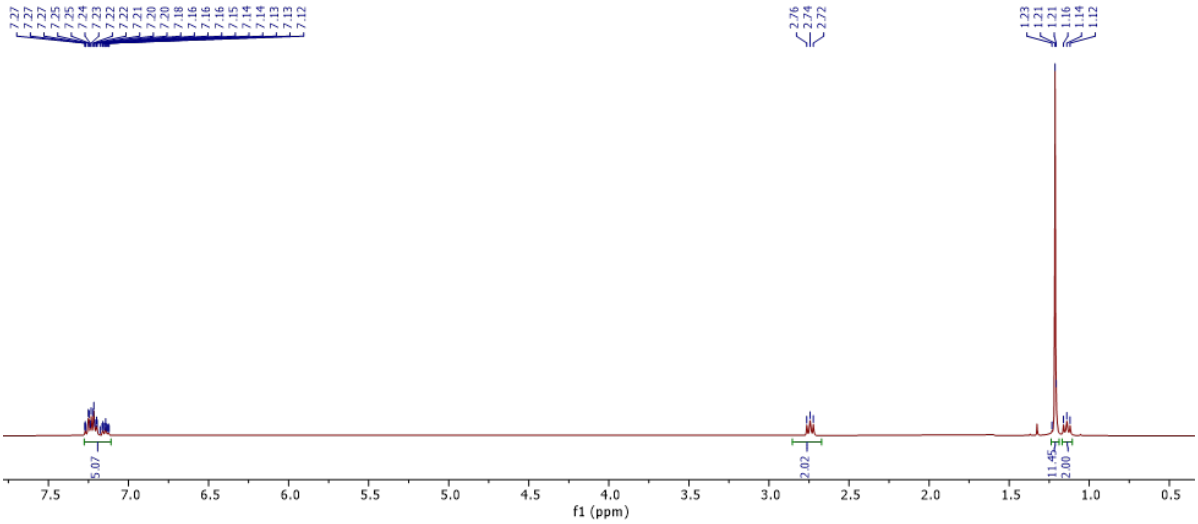


Figure S61. ^{1}H NMR spectrum of **21** in $CDCl_3$.

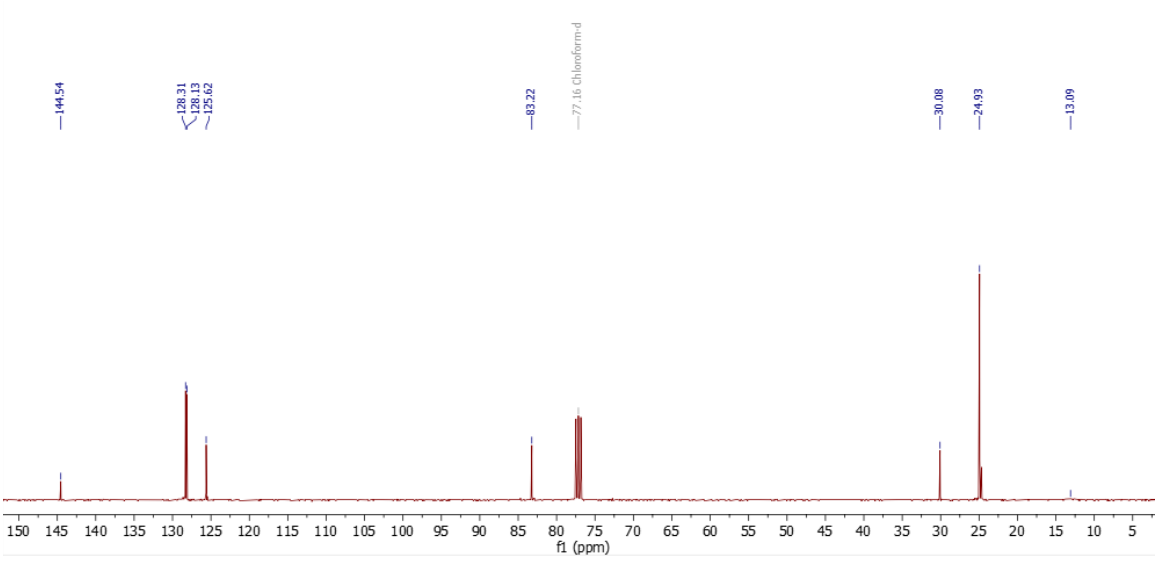


Figure S62. ^{13}C{H} NMR spectrum of **21** in $CDCl_3$.

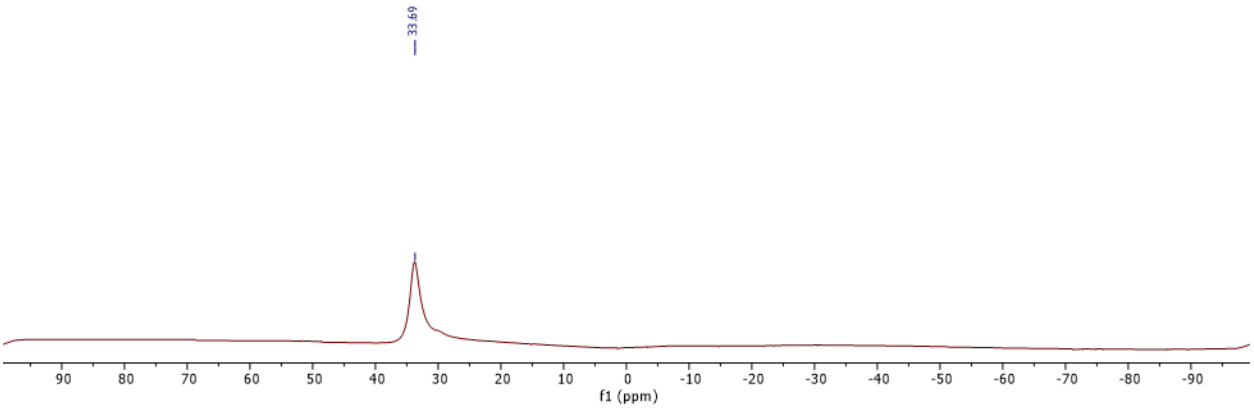
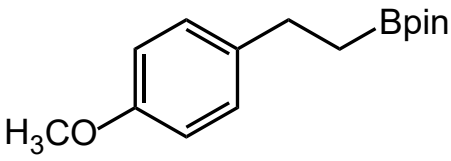


Figure S63. $^{11}B\{H\}$ NMR spectrum of **21** in $CDCl_3$.

2.2.22 Compound **22**



4-Methoxystyrene (403 mg, 3 mmol), 3,4,5-trifluorophenyl boronic acid (10.6 mg, 0.6 mmol) and HBpin (422 mg, 3.3 mmol). Colorless liquid. Yield 783 mg (98*%).* ^{1}H NMR [400 MHz, $CDCl_3$] δ = 7.13 (d, $^{3}J_{H-H}$ = 8.4 Hz, CH-arom., 2 H), 6.81 (d, $^{3}J_{H-H}$ = 8.8 Hz, CH-arom., 2 H), 3.77 (s, CH_3, 3 H), 2.69 (t, $^{3}J_{H-H}$ = 8.4 Hz, CH_2, 2 H), 1.22 (s, CH_3, 12 H), 1.11 (t, $^{3}J_{H-H}$ = 8 Hz, CH_2, 2 H) ppm. $^{13}C\{H\}$ NMR [101MHz, $CDCl_3$] δ= 157.6, 136.7, 129.0, 113.7, 83.2, 55.3, 29.1, 24.9, 13.4 ppm. $^{11}B\{H\}$ NMR [128 MHz, $CDCl_3$] δ = 32.4 ppm. The spectral data are consistent with previously reported values [11].

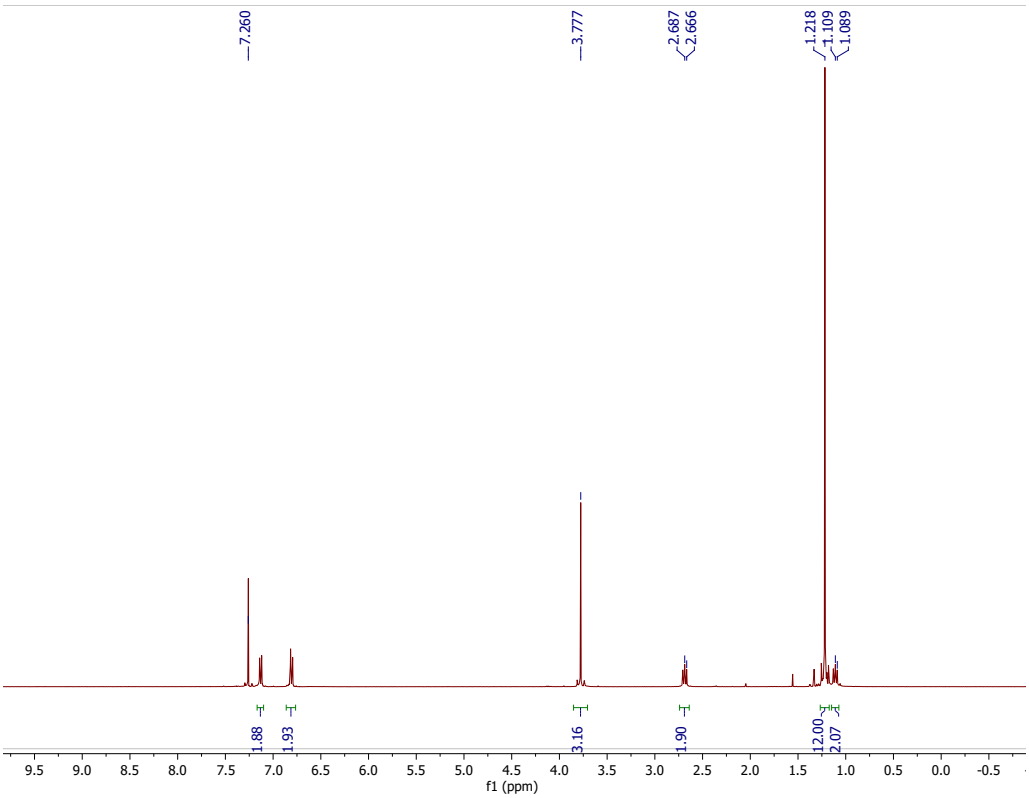


Figure S64. ^{1}H NMR spectrum of **22** in $CDCl_3$.

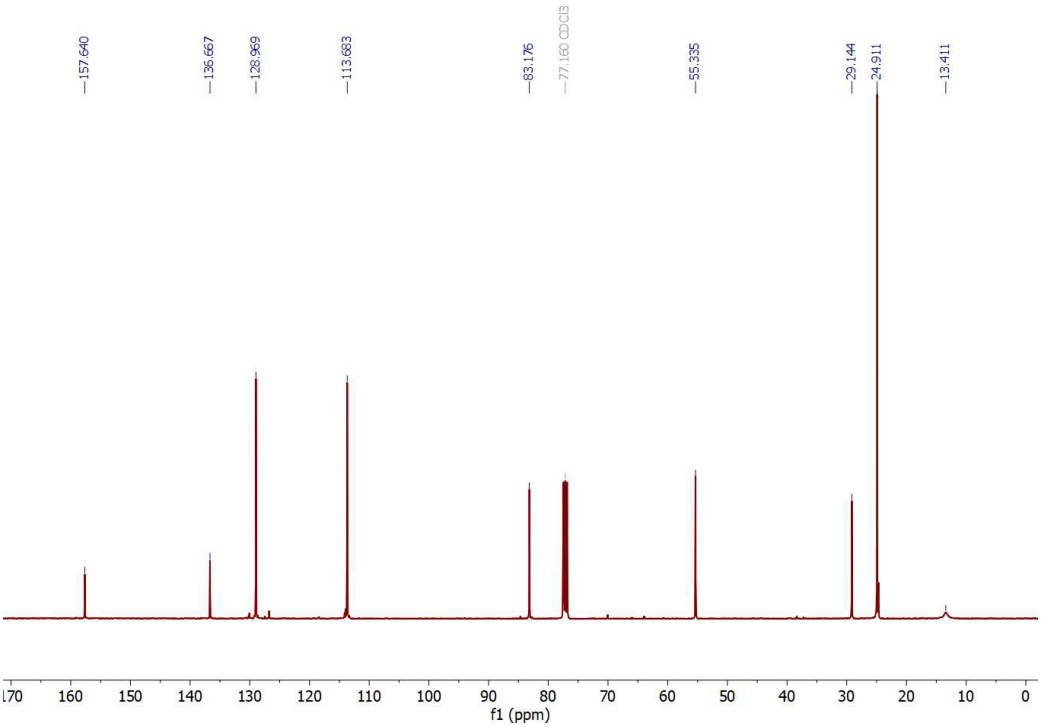


Figure S65. $^{13}C\{H\}$ NMR spectrum of **22** in $CDCl_3$.

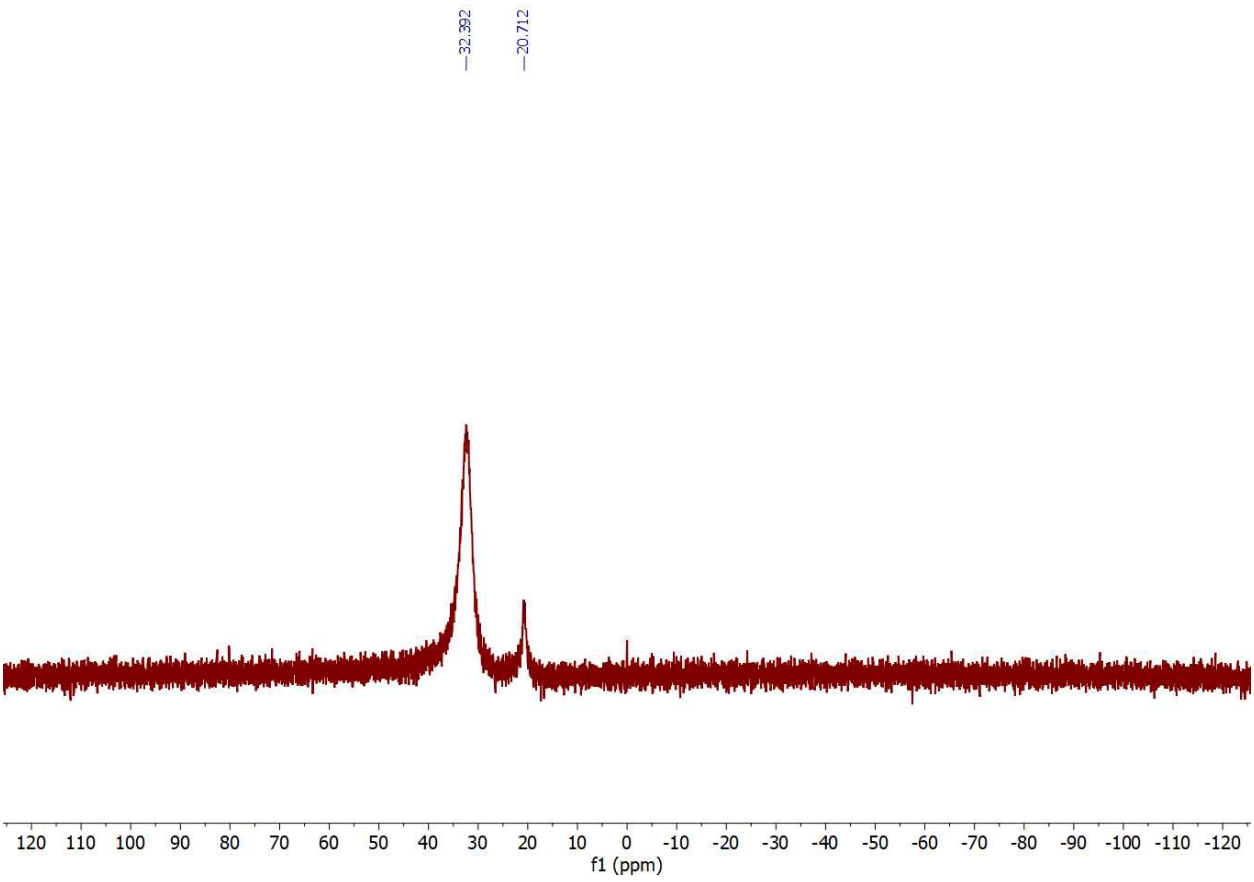
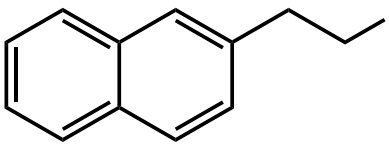


Figure S66. $^{11}B\{H\}$ NMR spectrum of **22** in $CDCl_3$.

2.2.23 Compound **23**



2-Vinyl naphthalene (231 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.65 mmol). Colorless oil. Yield ca. 65% [contaminated with $(Bpin)_2O$]. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81-7.70 (m, 3 H), 7.64 (s, 1 H), 7.46-7.33 (m, 3 H), 2.96-2.86 (m, 2 H), 1.24-1.18 (m, 2 H), 1.22 (s, 12 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, C_6D_6) δ = 142.4, 134.4, 132.6, 126.3, 126.0, 125.2, 83.0, 30.7, 24.9, 13.3 ppm. ^{11}B NMR (128 MHz, C_6D_6) δ = 33.2 ppm. The spectral data are consistent with previously reported values [5].

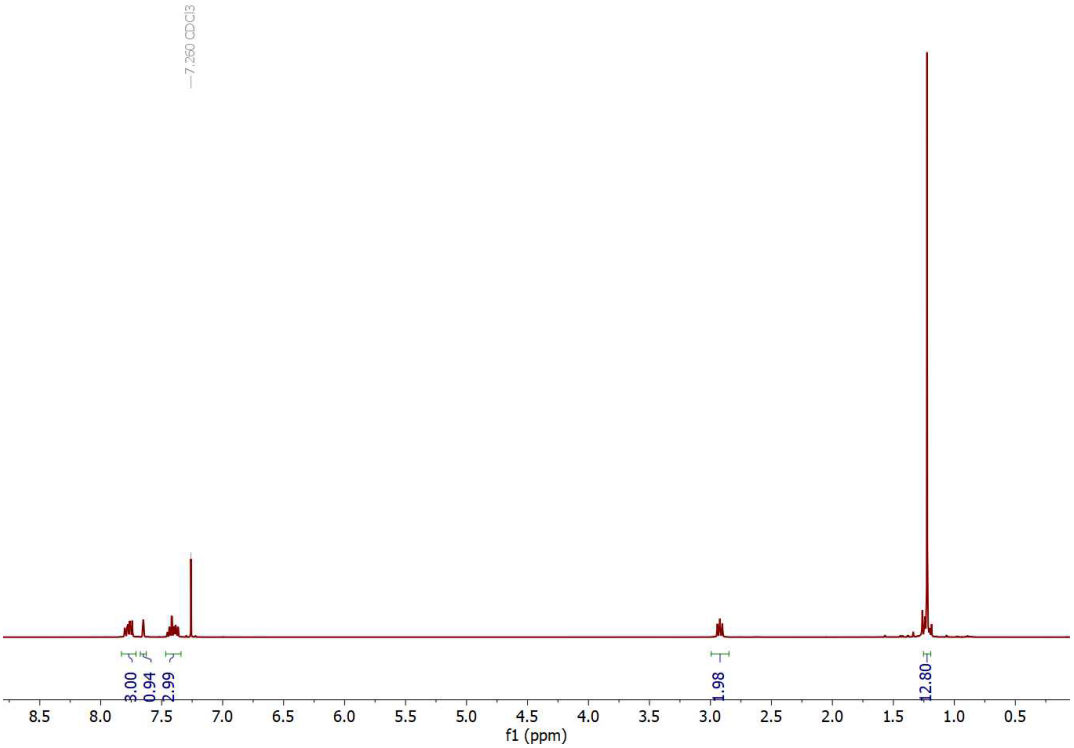


Figure S67. ^{1}H NMR spectrum of **23** in $CDCl_3$.

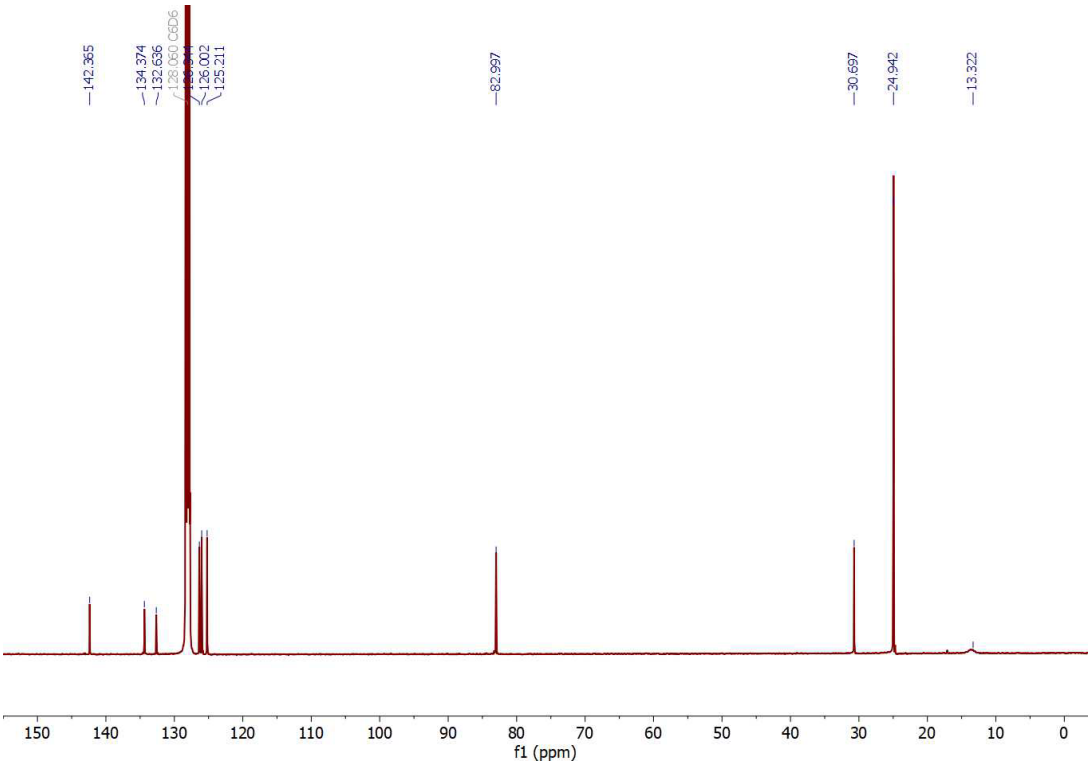


Figure S68. $^{13}C\{H\}$ NMR spectrum of **23** in C_6D_6.

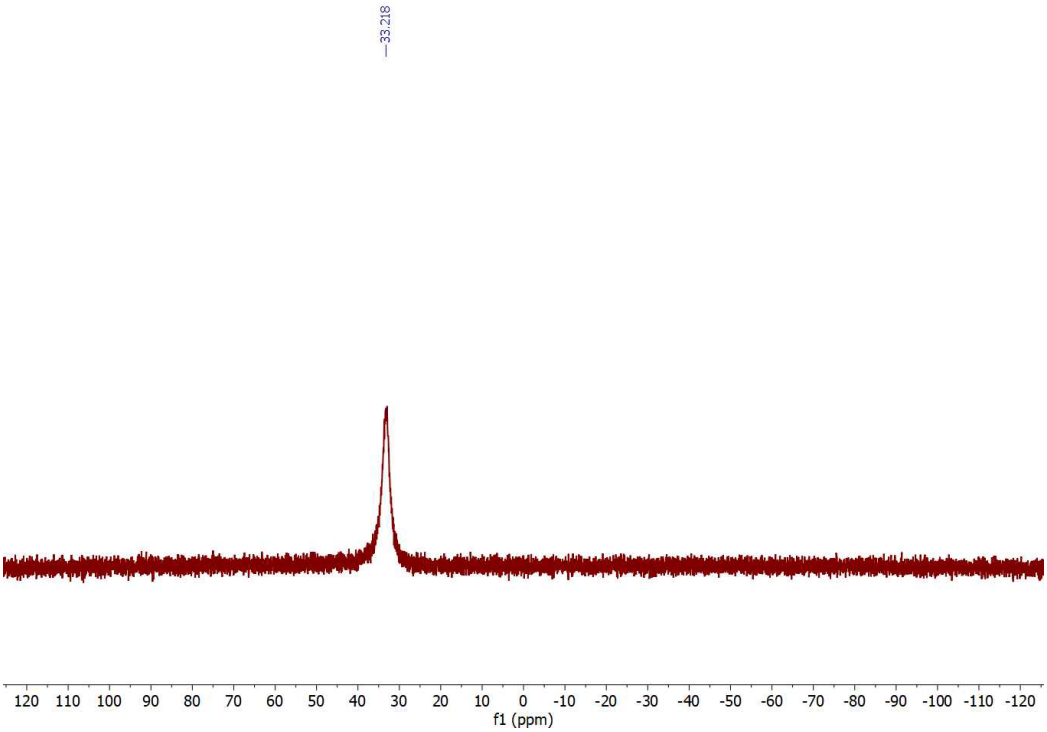
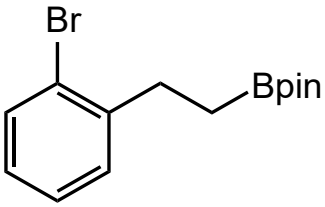


Figure S69. $^{11}B\{H\}$ NMR spectrum of **23** in C_6D_6.

2.2.24 Compound **24**



2-Bromostyrene (274 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.65 mmol). Colorless oil. Yield 32%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52-7.47 (m, 1 H), 7.30-7.16 (m, 2 H), 7.05-6.98 (m, 1 H), 2.88-2.80 (m, 2 H), 1.24 (s, 12 H), 1.18-1.08 (m, 2 H) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ = 143.6, 132.8, 129.9, 127.4, 127.4, 125.0, 83.3, 83.3, 30.6, 25.0, 24.7, 11.5 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.6 ppm. The spectral data are consistent with previously reported values [5].

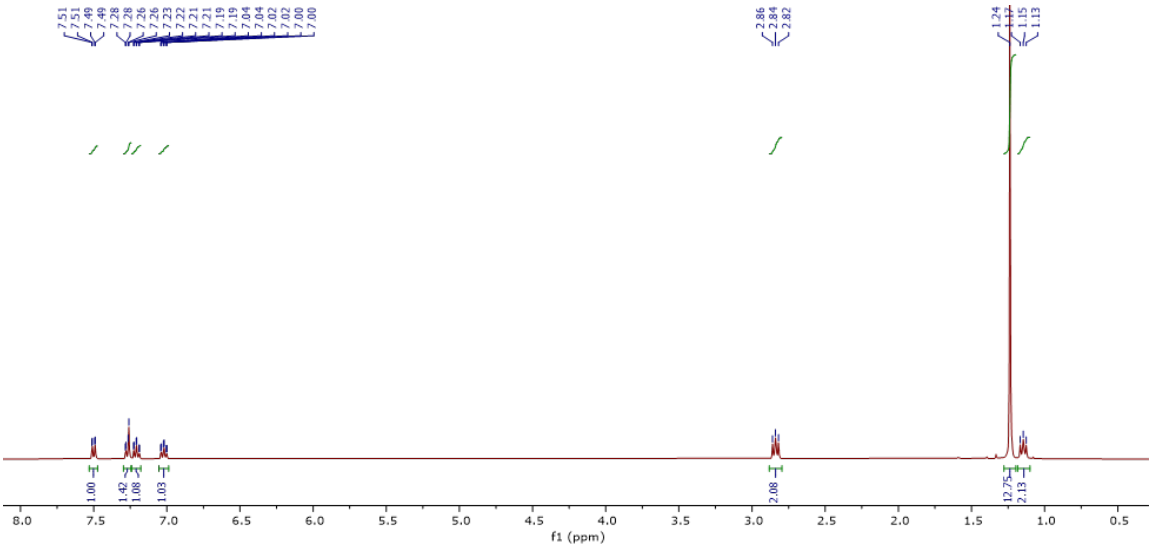


Figure S70. ^{1}H NMR spectrum of **24** in $CDCl_3$.

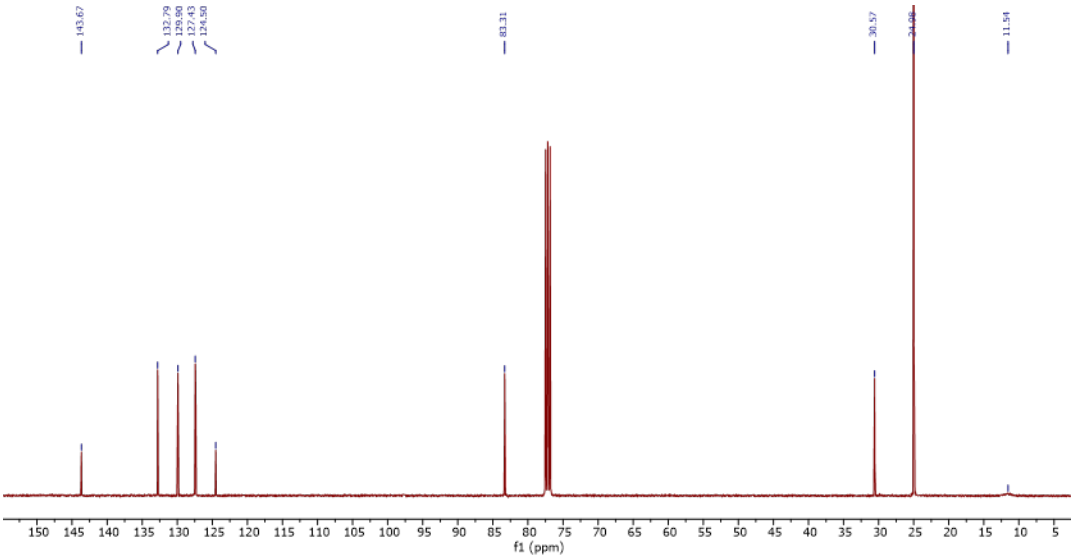


Figure S71. $^{13}C\{H\}$ NMR spectrum of **24** in $CDCl_3$.

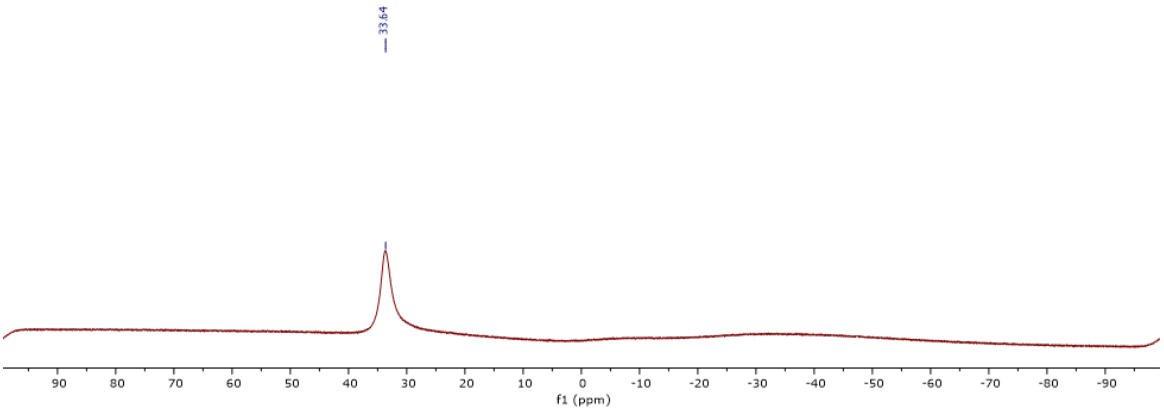
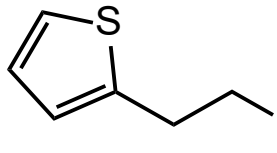


Figure S72. $^{11}B\{H\}$ NMR spectrum of **24** in $CDCl_3$.

2.2.25 Compound **25**



2-Vinylthiophene (165 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (211 mg, 1.7 mmol). Pale yellow liquid. Yield 306 mg (86%). ^{1}H NMR [400 MHz, C_6D_6] δ = 6.82 (m, CH, 1 H), 6.74 (d, 3.6 Hz, CH, 2 H), 3.02 (t, $^{3}J_{H\text{-}H}$ = 8 Hz, CH_2, 2 H), 1.31 (t, $^{3}J_{H\text{-}H}$ = 8 Hz, CH_2, 2 H), 1.02 (s, CH_3, 12 H) ppm. ^{13}C{H} NMR [101 MHz, $CDCl_3$] δ = 147.9, 126.6, 123.5, 122.7, 83.3, 24.9, 24.5, 13.7 ppm. ^{11}B{^{1}H} NMR [128 MHz, $CDCl_3$] δ = 32.4 ppm. The spectral data are consistent with previously reported values [5].

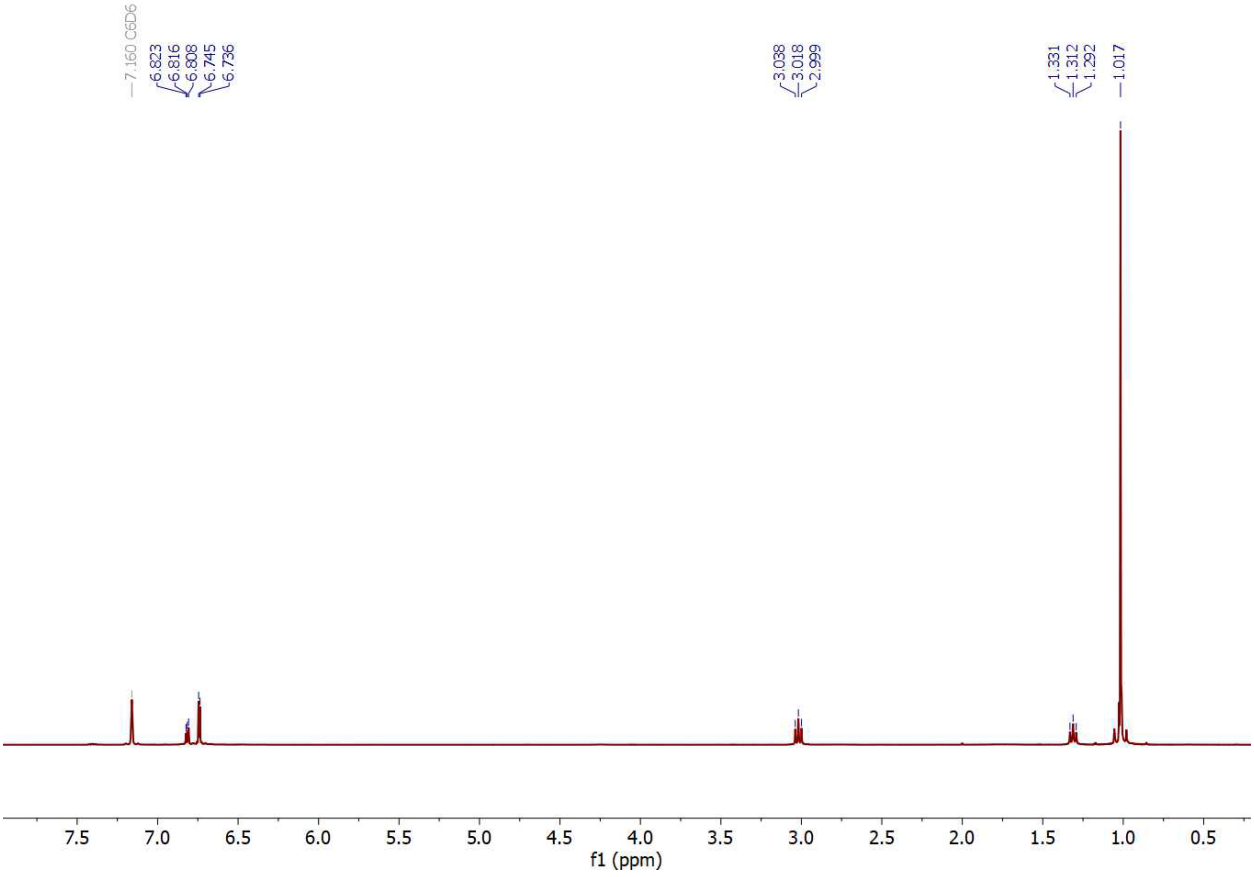


Figure S73. ^{1}H NMR spectrum of **25** in C_6D_6.

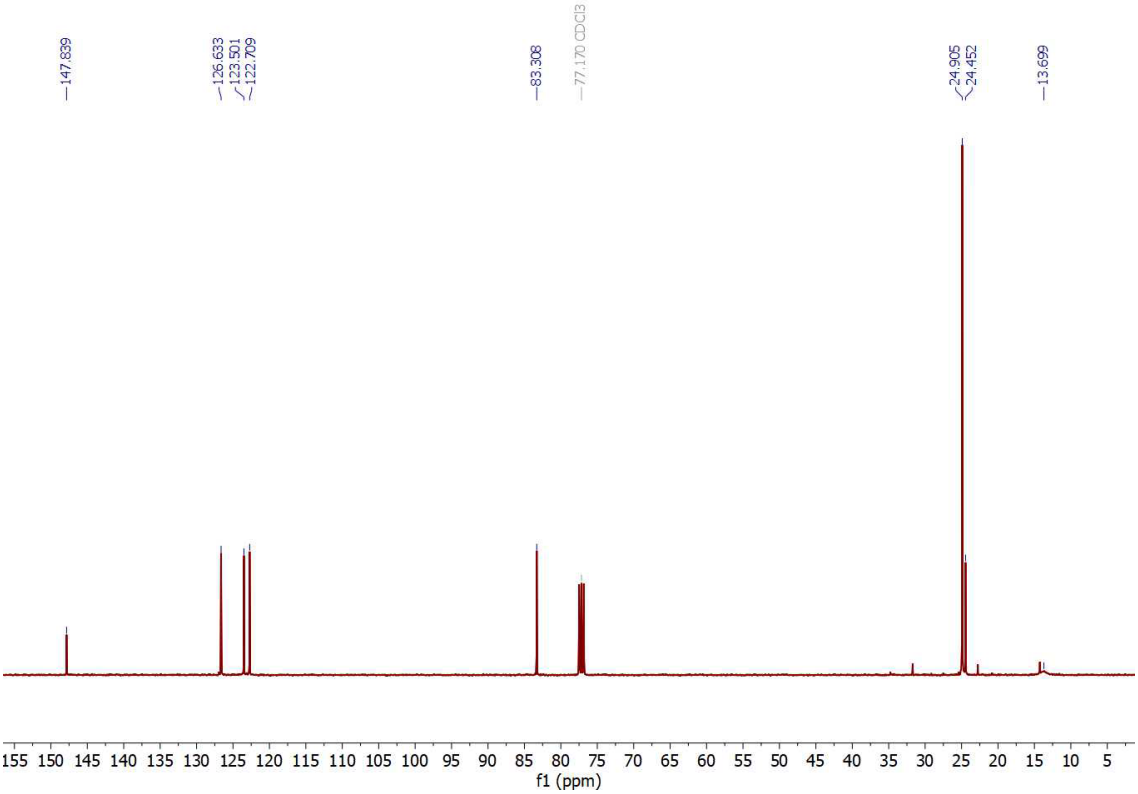


Figure S74. $^{13}C\{H\}$ NMR spectrum of **25** in $CDCl_3$.

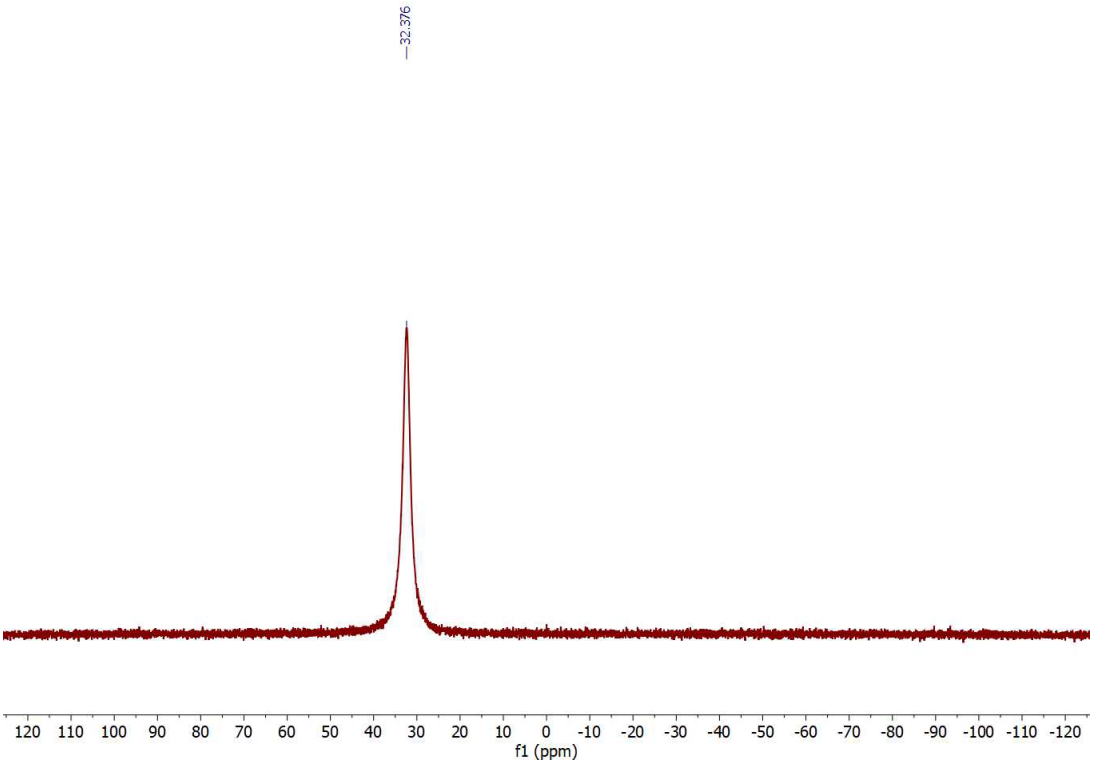
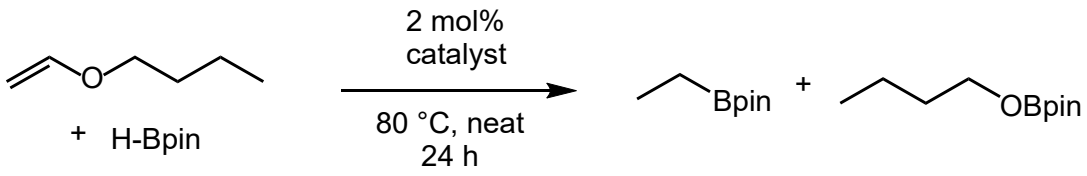


Figure S75. $^{11}B\{H\}$ NMR spectrum of **1** in $CDCl_3$.

2.2.26 Hydroboration of vinyl butyl ether

Vinyl butyl ether (150 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (5.3 mg, 0.3 mmol) and HBpin (400 mg, 3.1 mmol). Upon vacuum distillation at 100°C of the crude product, a mixture of Et-Bpin and BuO-Bpin was obtained as an oil (Figure S76 and S77). Subsequent vacuum distillation of the oily mixture allowed for the separation of both compounds (Figure S78 to S81).



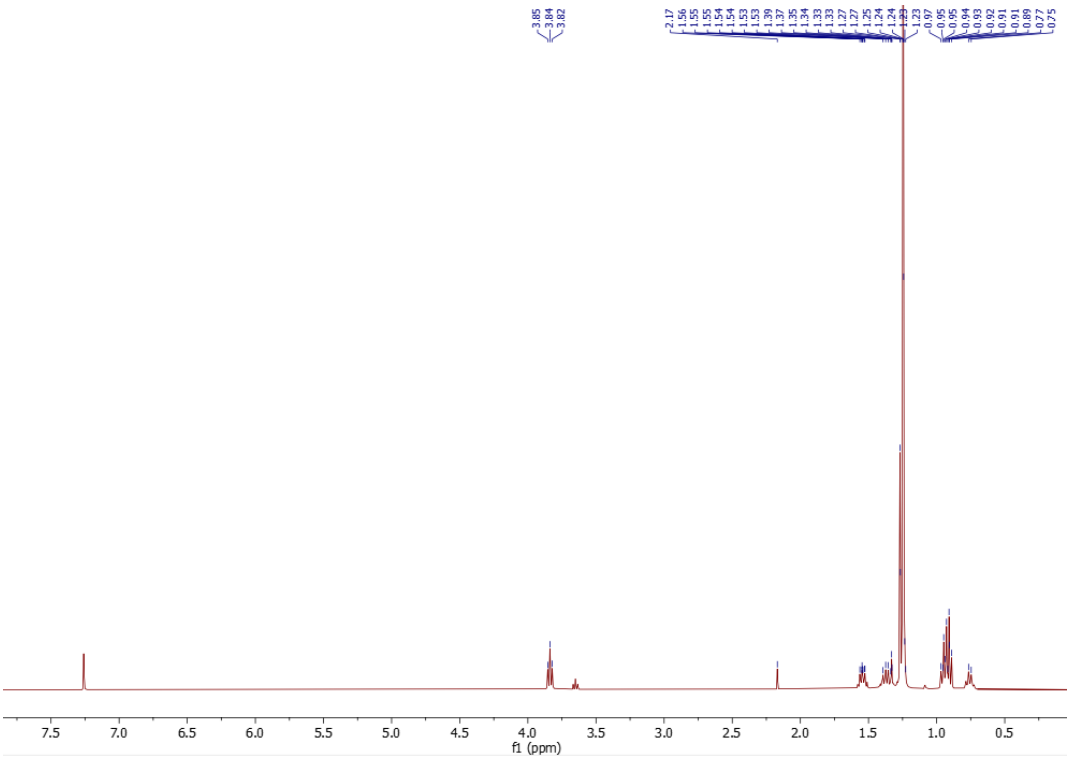


Figure S76. ^{1}H NMR spectrum of the crude reaction mixture in $CDCl_3$.

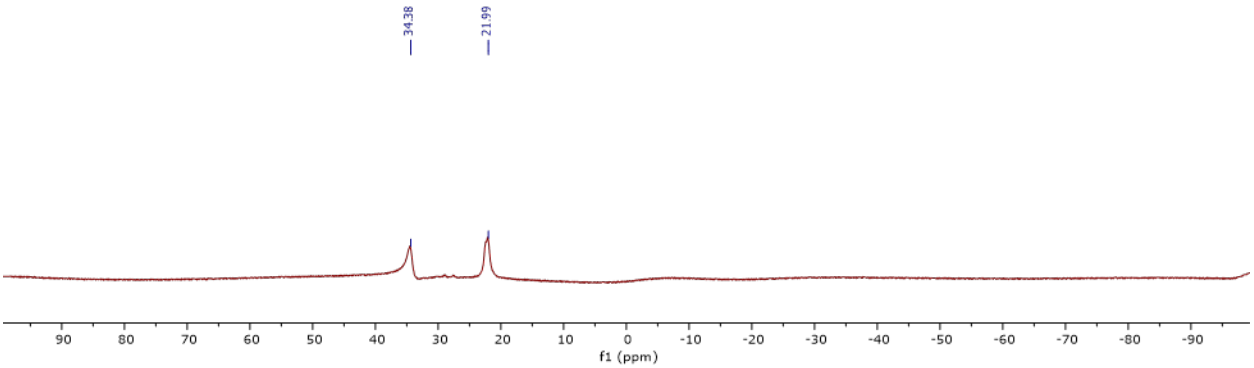


Figure S77. $^{11}B\{H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$.

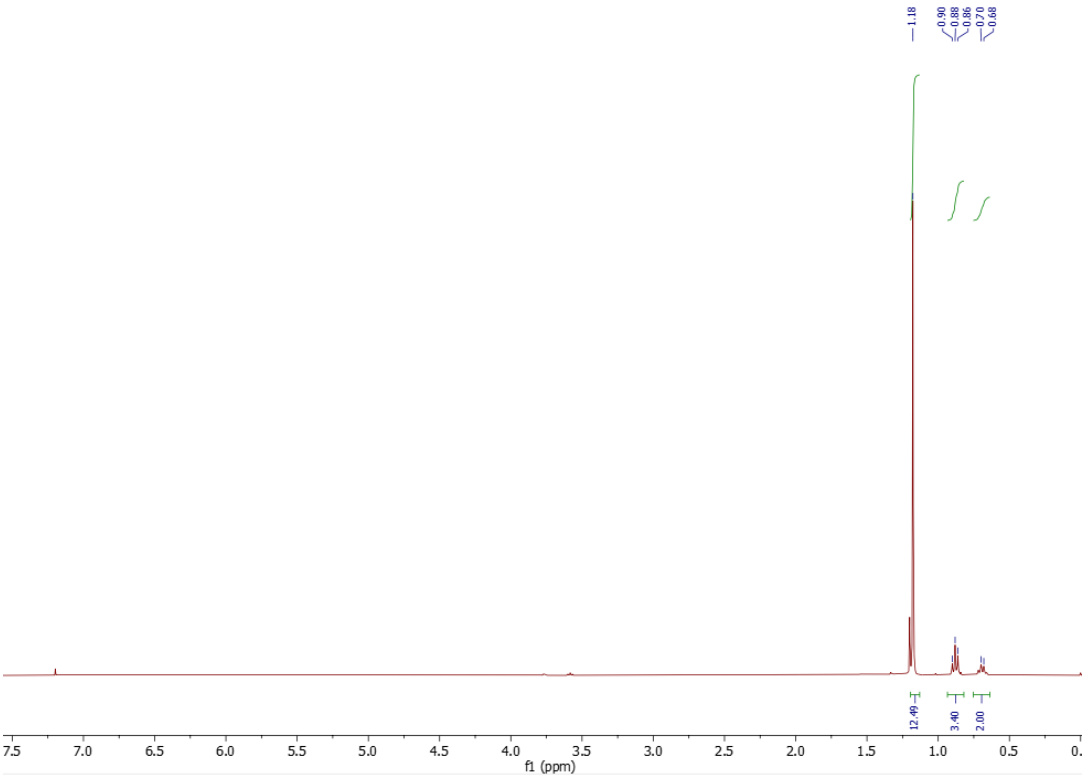


Figure S78. ^{1}H NMR spectrum of EtBpin in $CDCl_3$.

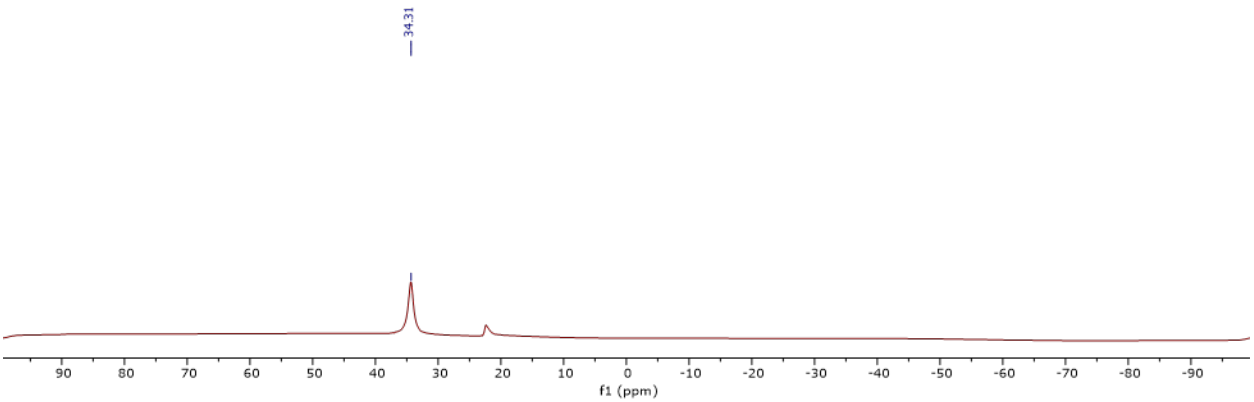


Figure S79. $^{11}B\{H\}$ NMR spectrum of crude EtBpin in $CDCl_3$.

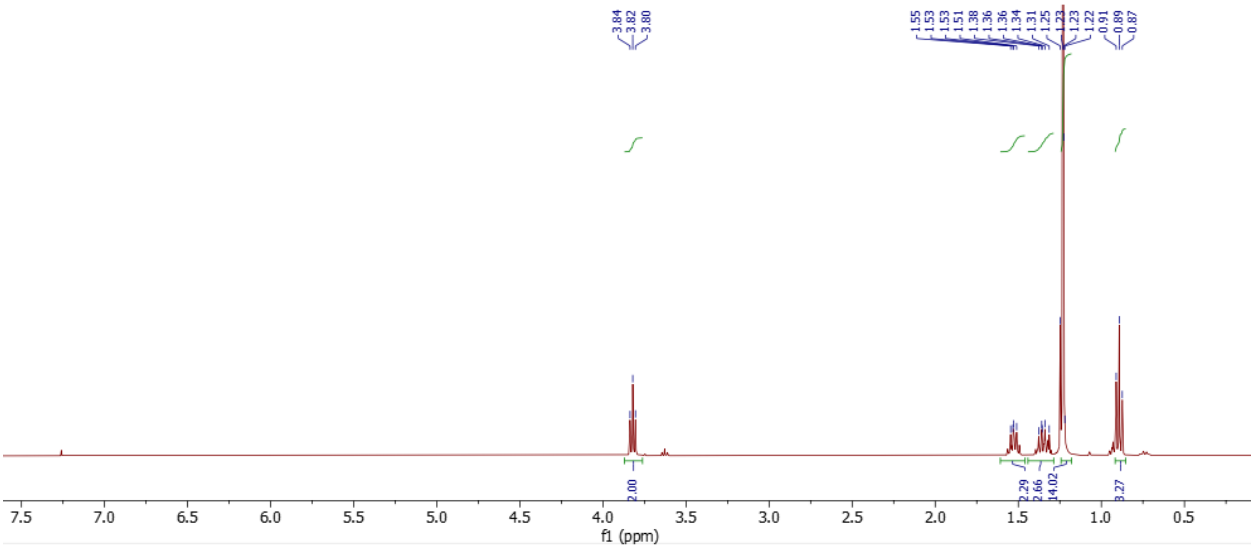


Figure S80. ^{1}H NMR spectrum of Bu^{n}OBpin in $CDCl_3$.

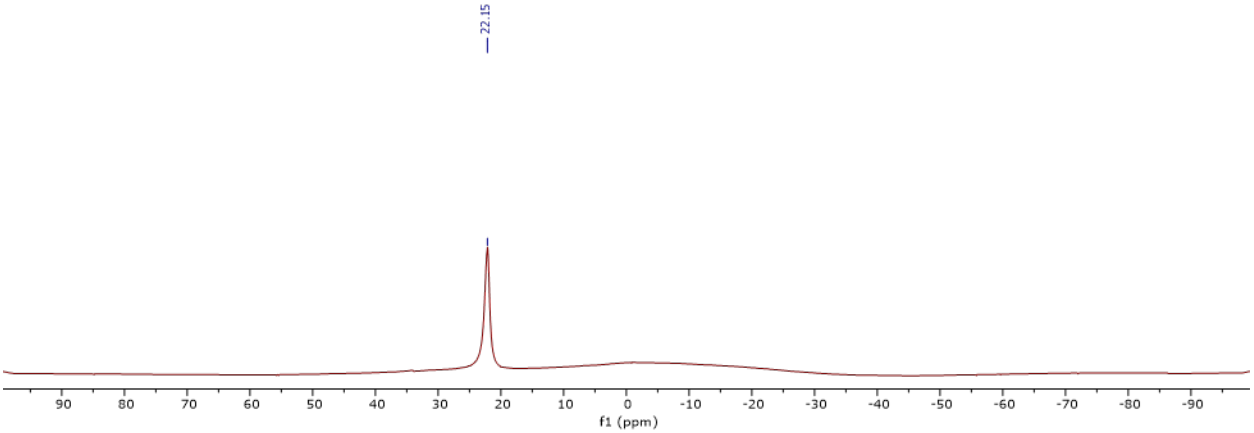
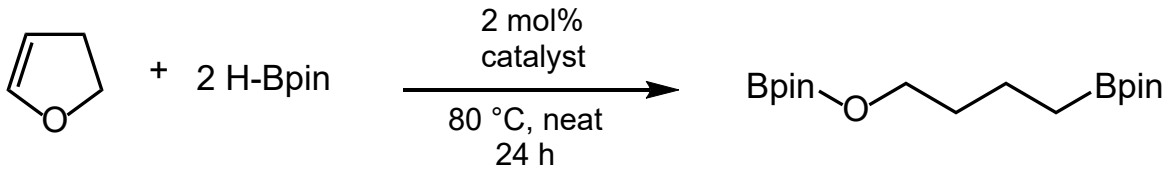


Figure S81. $^{11}B\{H\}$ NMR spectrum of Bu^{n}OBpin in $CDCl_3$.

2.2.27 Hydroboration of 2,3-dihydrofuran

Method A. 2,3-dihydrofuran (105 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (10.6 mg, 0.6 mmol) and HBpin (400 mg, 3.1 mmol). The product was isolated as a colorless oily material upon vacuum distillation (5 mbar, 190°C).



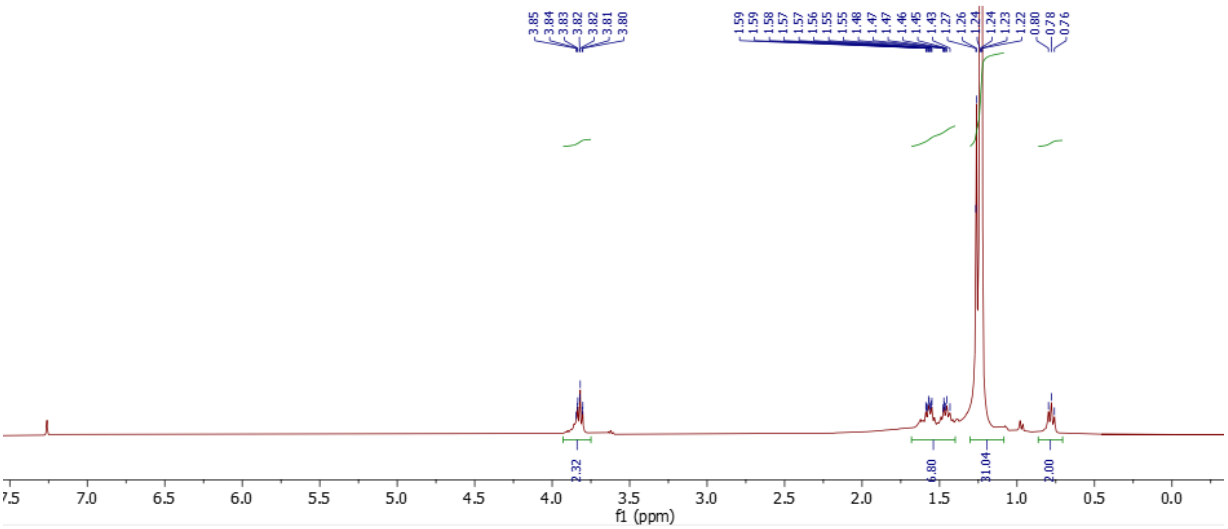


Figure S82. ^{1}H NMR spectrum of crude pinBO$(CH_2)_4$Bpin in $CDCl_3$.

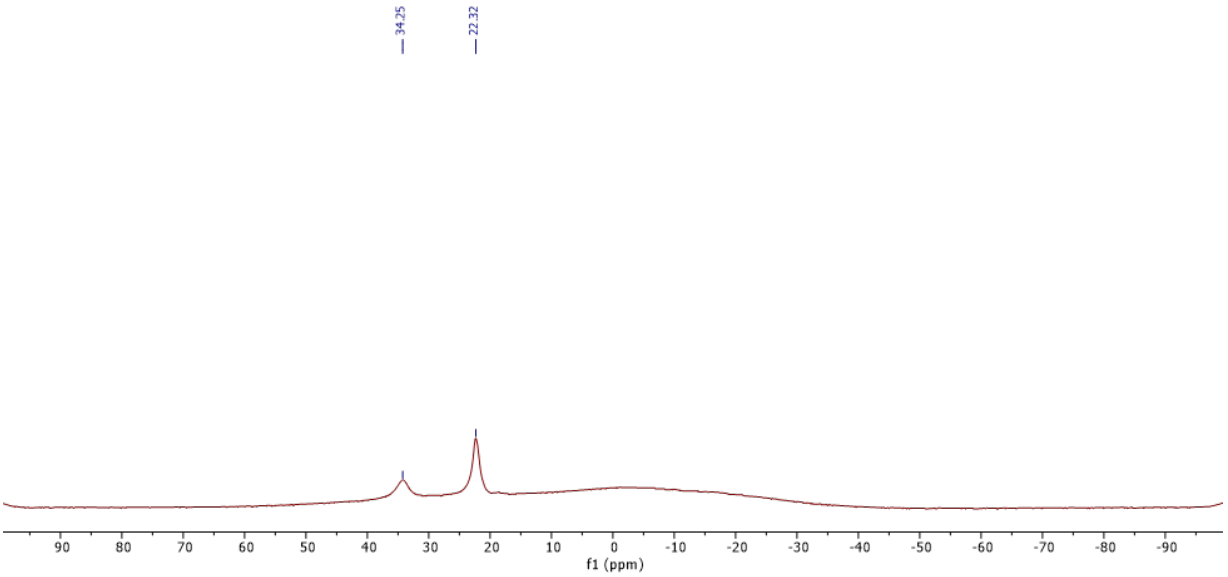
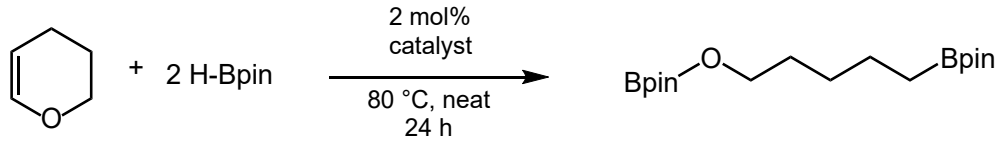


Figure S83. $^{11}B\{H\}$ NMR spectrum of crude pinBO$(CH_2)_4$Bpin in $CDCl_3$.

Hydroboration of 3,4-dihydro-*2H*-pyran

Method A. 3,4-dihydro-*2H*-pyran (126 mg, 1.5 mmol), 3,4,5-trifluorophenyl boronic acid (10.6 mg, 0.6 mmol) and HBpin (400 mg, 3.1 mmol). The product was isolated as a colorless oil upon vacuum distillation (5 mbar, 200°C).



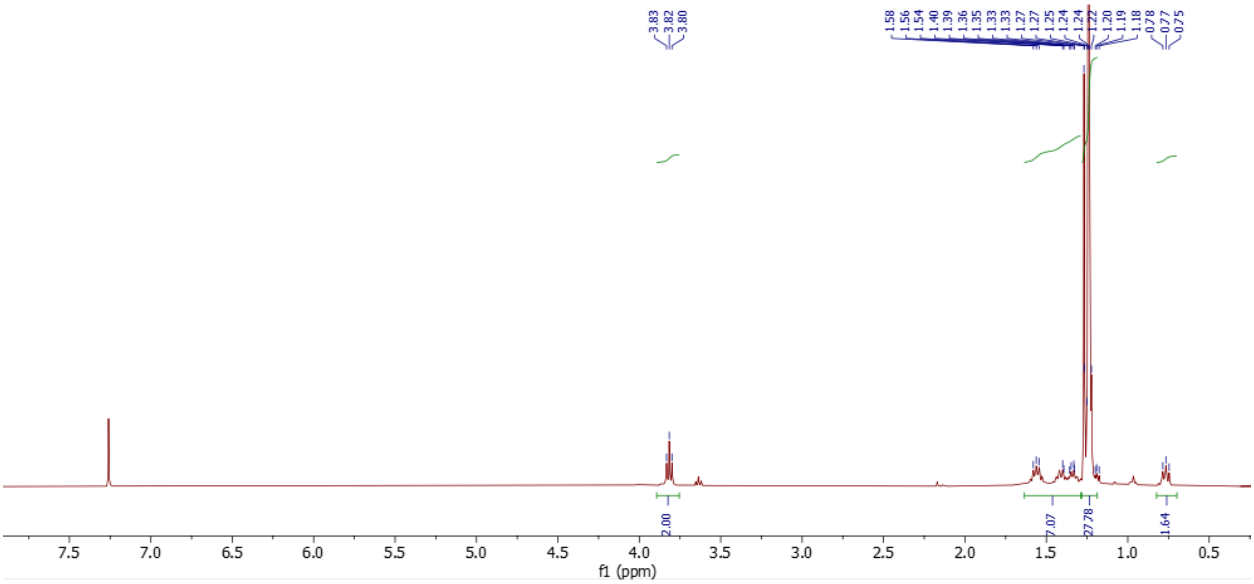


Figure S84. ^{1}H NMR spectrum of crude pinBO$(CH_2)_5$Bpin in $CDCl_3$.

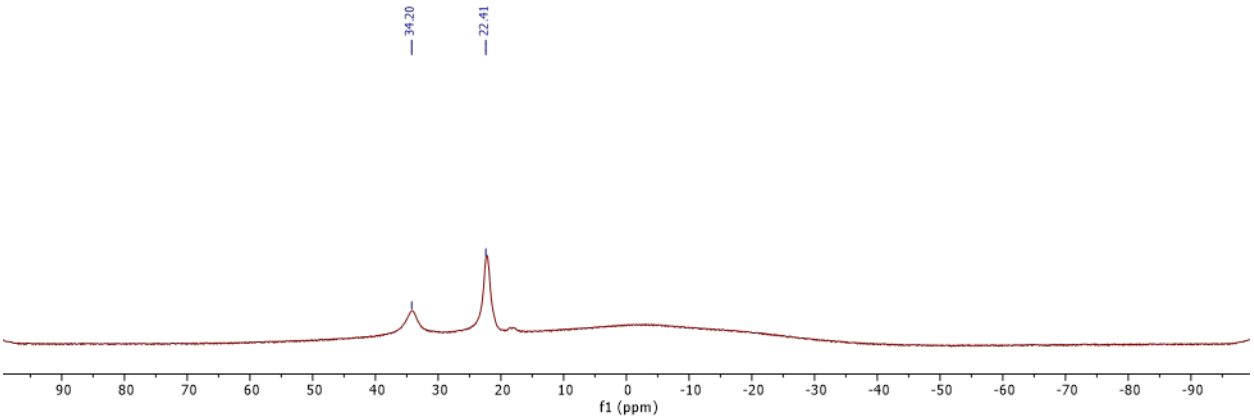


Figure S85. $^{11}B\{H\}$ NMR spectrum of crude pinBO$(CH_2)_5$Bpin in $CDCl_3$.

2.3 Stoichiometric experiments

2.3.1 Reaction of $[MeBO]_3$ with one equivalent of HBPin

In the glove box, a J-Young NMR tube was charged with $[MeBO]_3$ (20 mg, 0.16 mmol), HBPin (20 mg, 0.16 mmol) and ca. 0.5 mL C_6D_6. The mixture was heated at 40°C for 24 hours and subsequently analyzed by ^{11}B NMR spectroscopy.

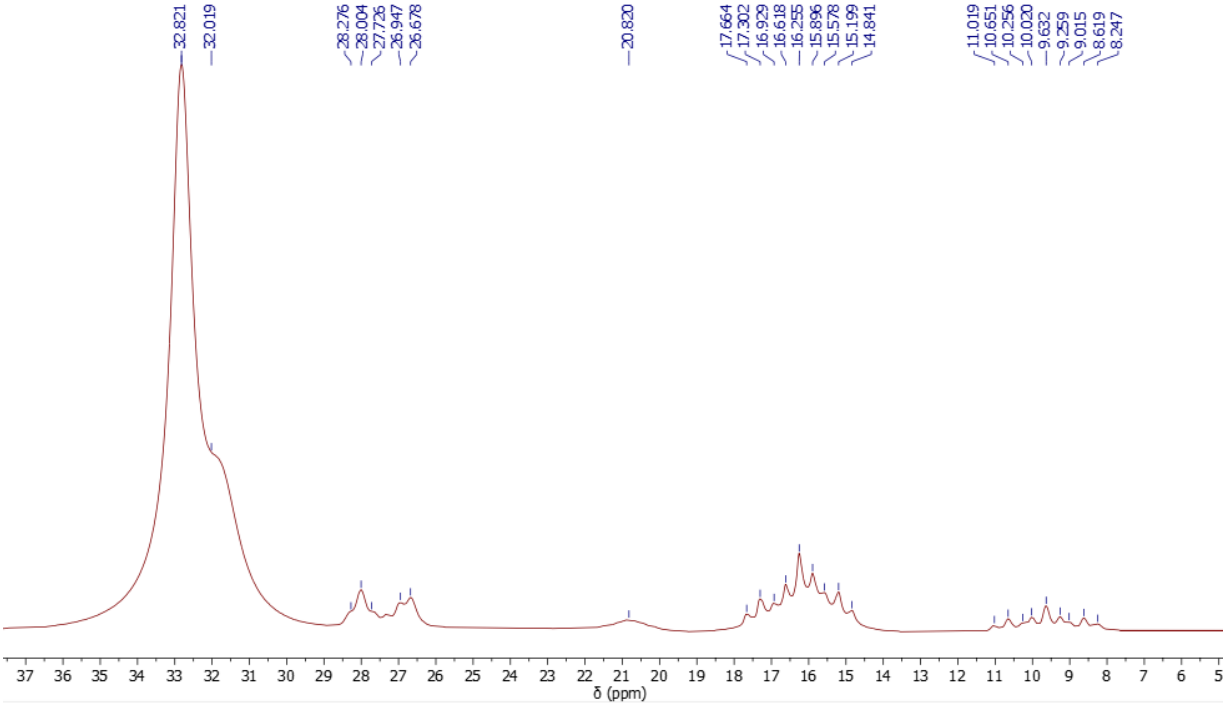


Figure S86. ^{11}B NMR spectrum of the reaction of $[MeBO]_3$ with one equivalent of HBPin after 24 hours at 40°C (C_6D_6).

2.3.2 Reaction of $[MeBO]_3$ with 6 equivalents of HBPin

In the glove box, a J-Young NMR tube was charged with $[MeBO]_3$ (20 mg, 0.16 mmol), HBPin (133 mg, 0.96 mmol) and ca. 0.4 mL C_6D_6. The mixture was heated at 40°C for 24 hours and subsequently analyzed by ^{11}B NMR spectroscopy.

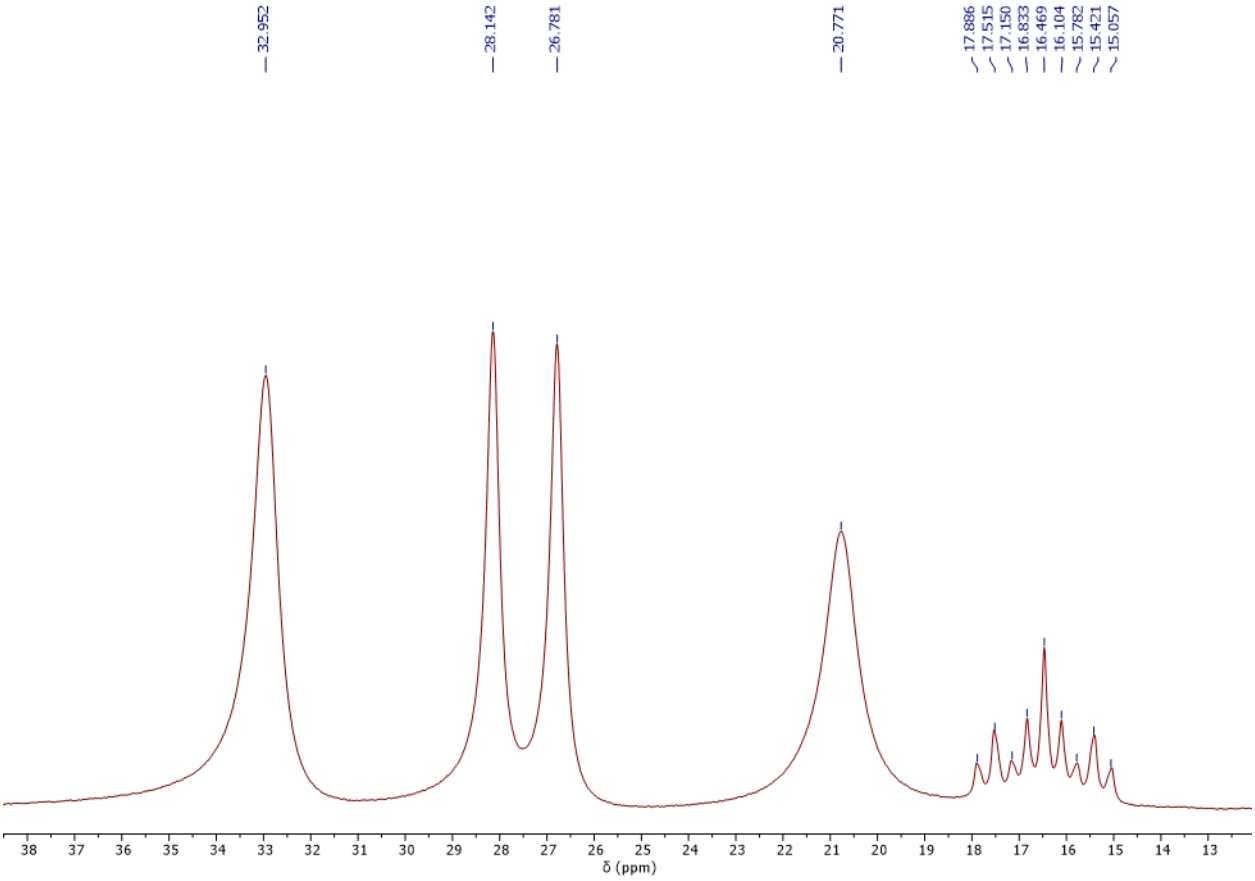


Figure S87. ^{11}B NMR spectrum of the reaction of $[MeBO]_3$ with six equivalents of HBPin after 24 hours at 40°C (C_6D_6).

2.3.3 Reaction of $[MeBO]_3$ with 10 equivalents of HBPin

In the glove box, a J-Young NMR tube was charged with $[MeBO]_3$ (22 mg, 0.18 mmol), HBPin (228 mg, 1.8 mmol) and ca. 0.3 mL C_6D_6. The mixture was heated at 40°C for 24 hours and subsequently analyzed by ^{11}B NMR spectroscopy.

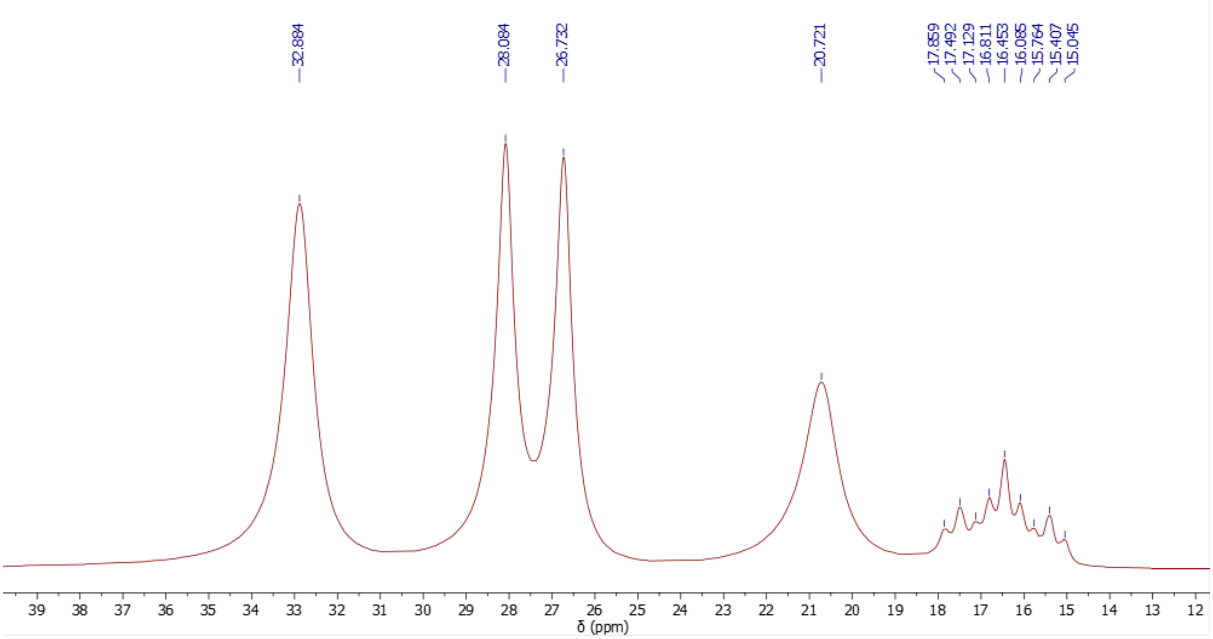


Figure S88. ^{11}B NMR spectrum of the reaction of $[MeBO]_3$ with ten equivalents of HBPin after 24 hours at 40°C (C_6D_6).

2.3.4 Reaction of $MeB(OH)_2$ with 5 equivalents of HBPin

In the glove box, a J-Young NMR tube was charged with $MeB(OH)_2$ (30 mg, 0.5 mmol), and ca. 0.4 mL C_6D_6. The solution was sonicated and gently heated to solubilize. This was then frozen at -20 °C for 30 minutes before adding HBPin (320 mg, 2.5 mmol) cooled to -20 °C. After 30 minutes the J-Young is removed from the freezer. This was allowed to warm to RT over 24 hours and subsequently analyzed by ^{11}B NMR spectroscopy.

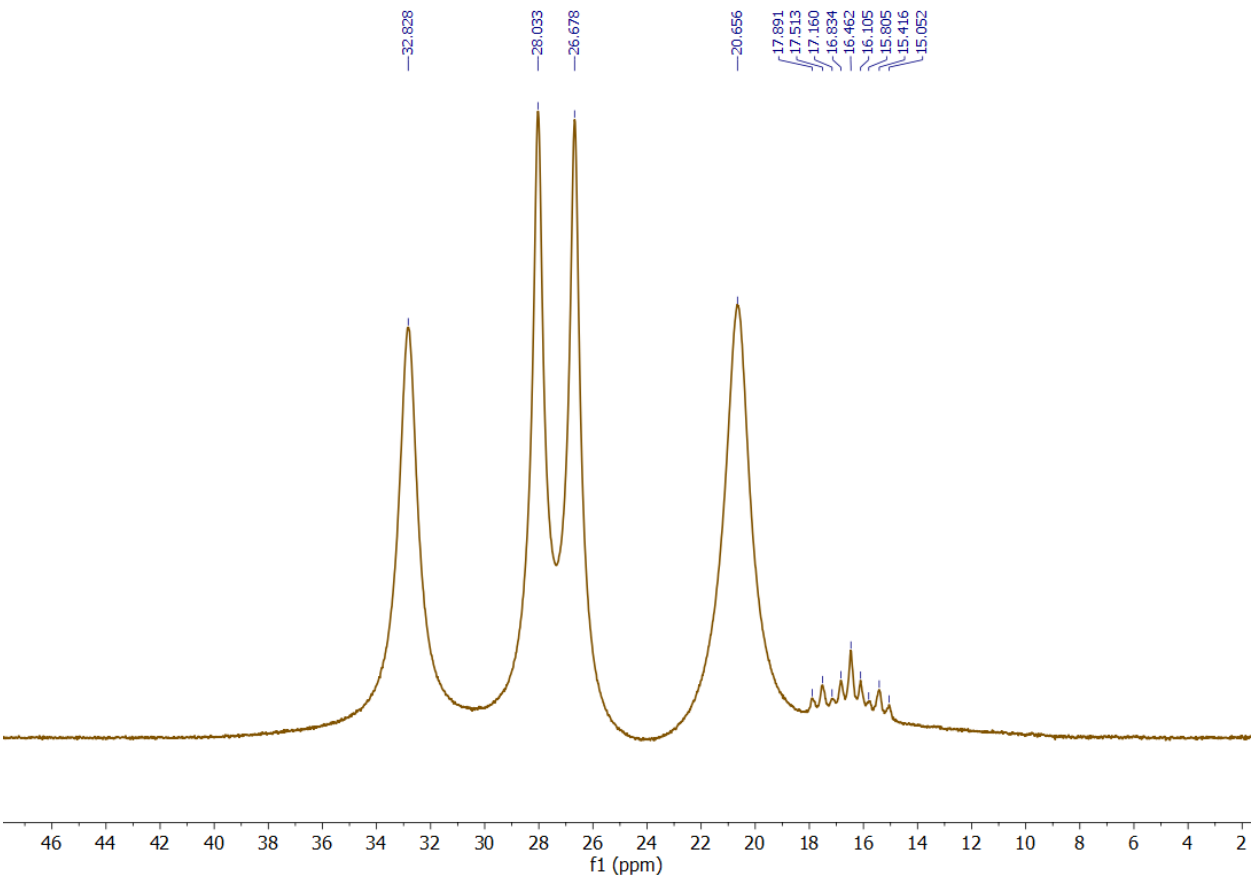


Figure S89. ^{11}B NMR spectrum of the reaction of $MeB(OH)_2$ with 5 equivalents of HBPin after 24 hours at RT (C_6D_6).

2.3.5 Monitoring the reaction of $(MeBO)_3$ with 9 equivalents of HBPin

In the glove box, a J-Young NMR tube was charged with $(MeBO)_3$ (20 mg, 0.16 mmol), HBPin (183 mg, 1.4 mmol), and ca. 0.4 mL C_6D_6. Over the course of 12 hours forty-seven ^{11}B NMR spectra were collected with the first spectrum collected ca. 10 mins after initial mixing.

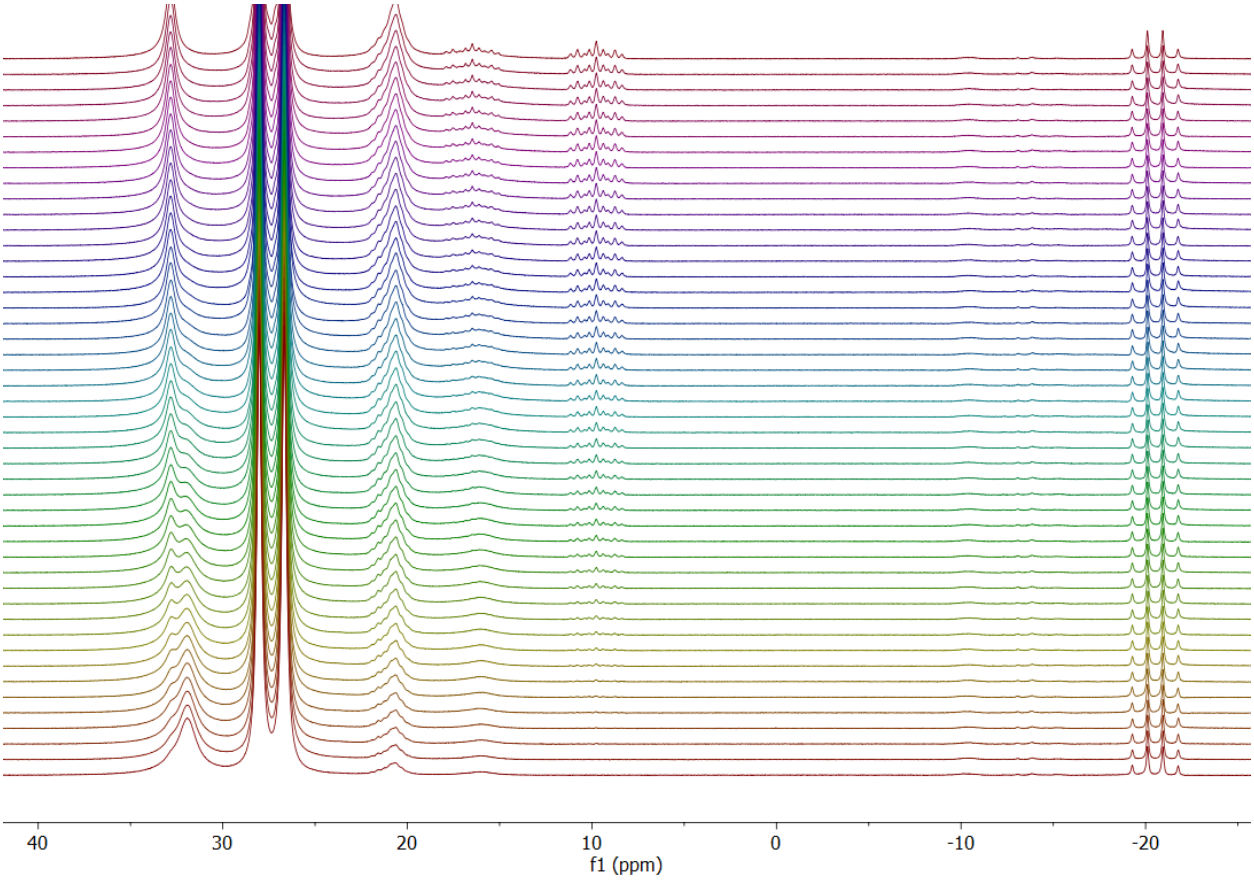


Figure S90. ^{11}B NMR spectra taken every ~15 minutes over 12 h at room temperature, C_6D_6.

2.3.6 HBPin Control Experiment

In the glove box, a J-Young NMR tube was charged with HBPin and ca. 0.5 mL C_6D_6. This was then heated at 80°C for 24 h and subsequently a ^{11}B NMR spectrum recorded.

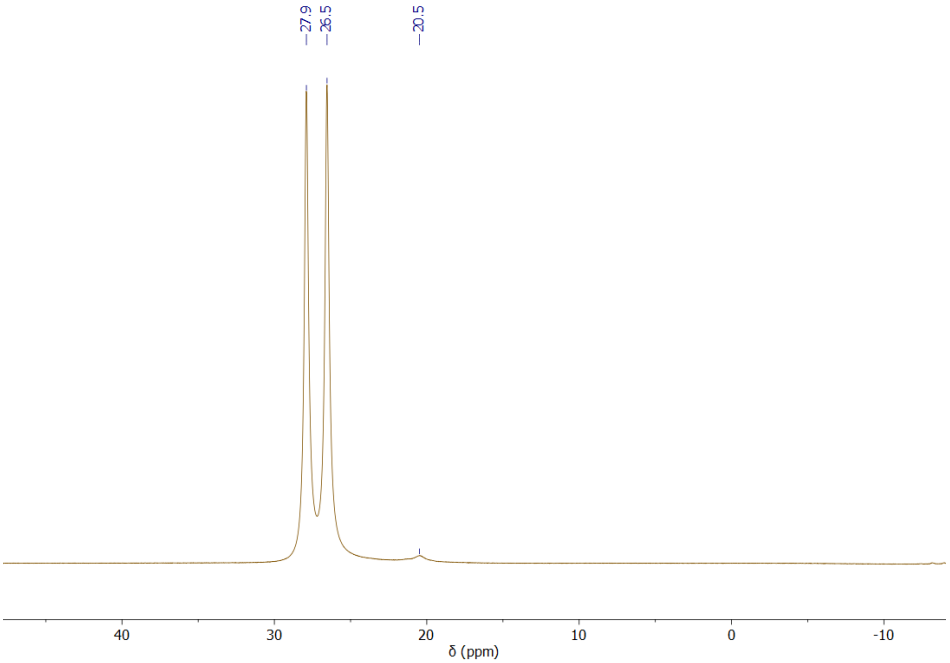


Figure S91. ^{11}B NMR spectrum of HBpin after heating at 80°C for 24 h (C_6D_6).

2.3.7 HBPin Control Experiment

In the glove box, a J-Young NMR tube was charged with decaborane (19 mg, 0.16 mmol), HBPin (204 mg, 1.6 mmol), and ca. 0.4 mL C_6D_6. This was then heated at 80°C for 24 h and subsequently analyzed via ^{11}B NMR spectroscopy.

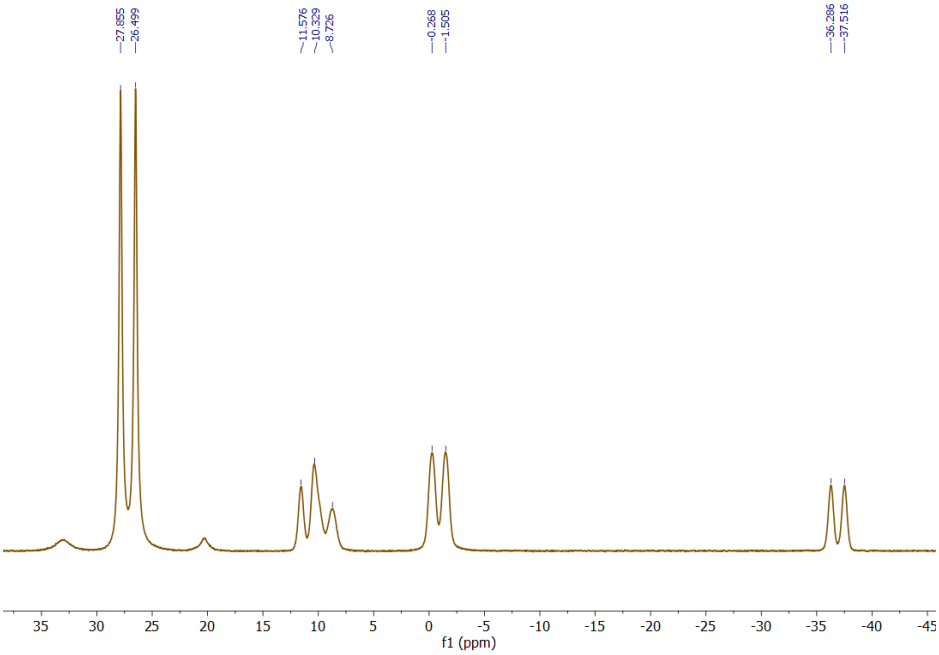


Figure S92. ^{11}B NMR spectrum of the reaction after heating at 80°C for 24 h (C_6D_6).

2.4 Reference Compounds

2.4.1 Methyl boronic acid, $MeB(OH)_2$

^1H NMR [400 MHz, $CDCl_3$] δ = 4.22 (s, OH, 2 H), 1.60 (s, H_2O, 2 H), 0.44 (s, CH_3, 3 H), 0.32 (s, CH_3, 3 H), $^{11}B\{^1H\}$ NMR [128 MHz, $CDCl_3$] δ = 32.8 ppm.

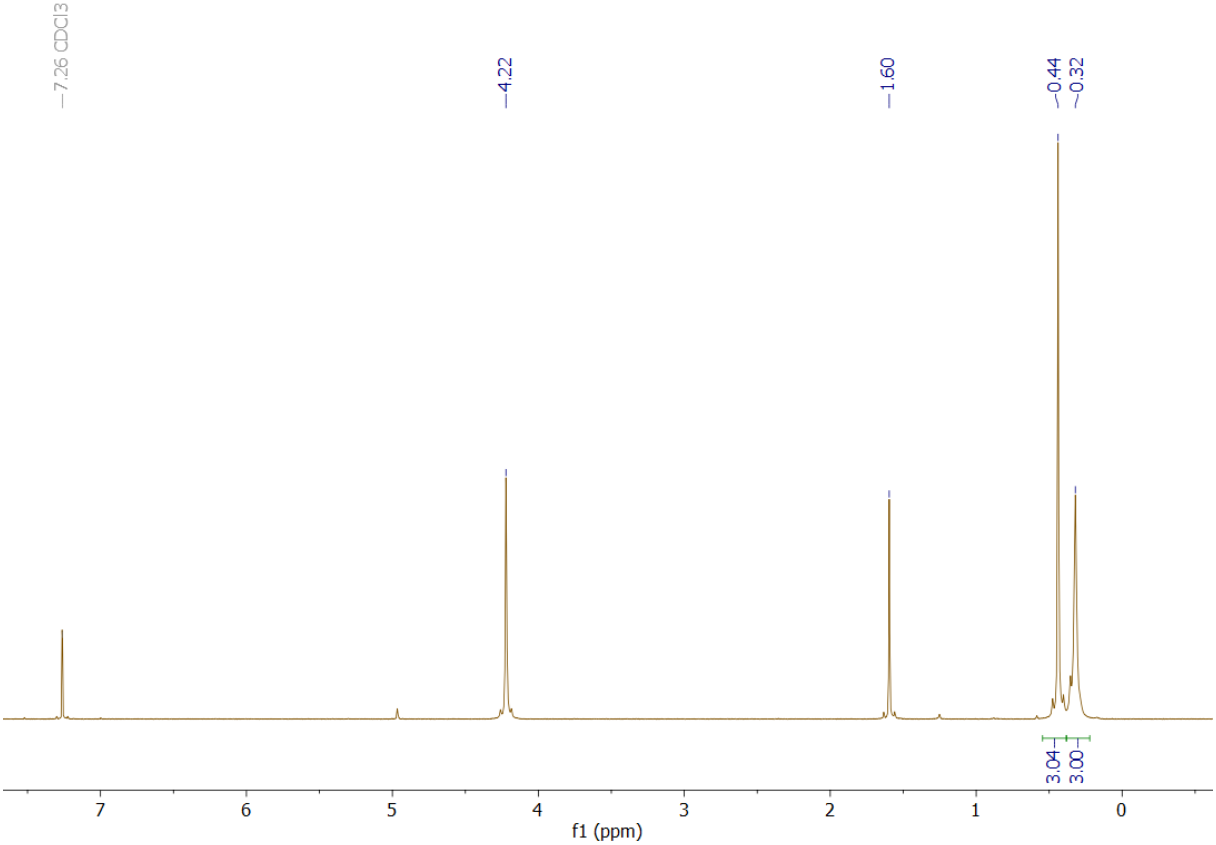


Figure S93. ^1H NMR spectrum of a commercial sample of $MeB(OH)_2$ in $CDCl_3$ displaying a natural equilibrium with $(MeBO)_3$ in a 3:1 ratio, respectively.

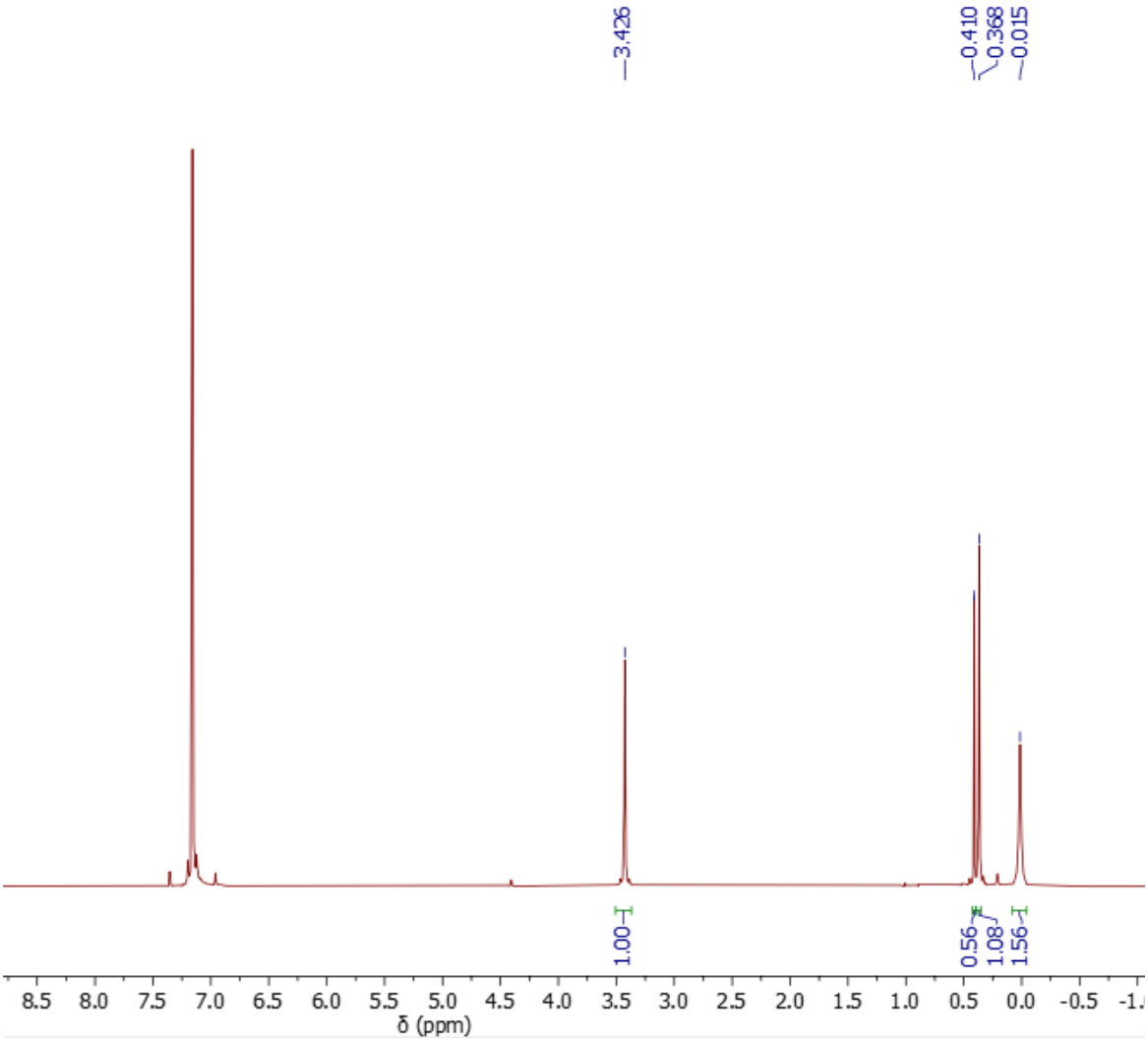


Figure S94. ^{1}H NMR spectrum of a commercial sample of $MeB(OH)_2$ in C_6D_6.

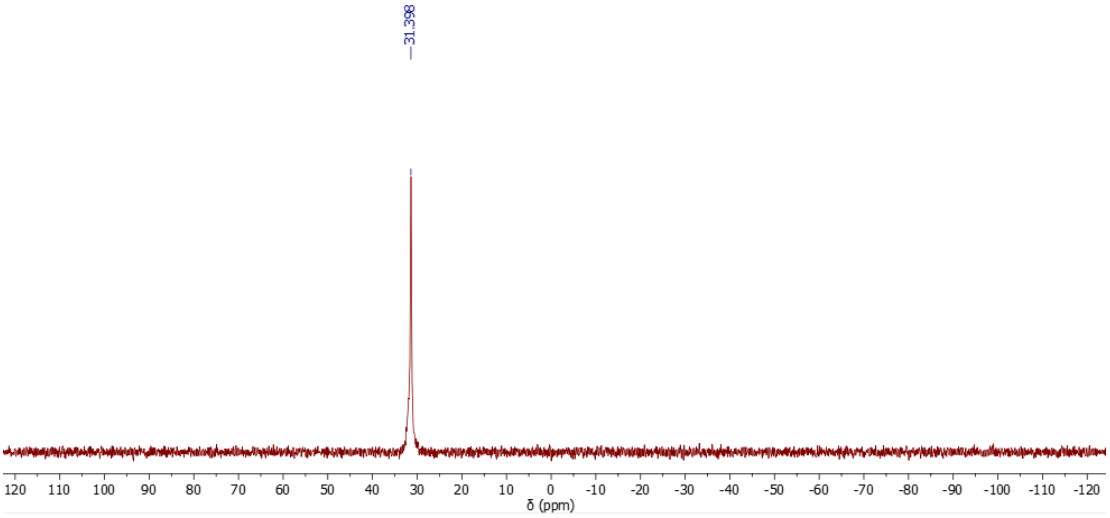


Figure S95. ^{11}B{H} NMR spectrum of a commercial sample of $MeB(OH)_2$ in C_6D_6.

2.4.2 Methylboroxine $(MeBO)_3$

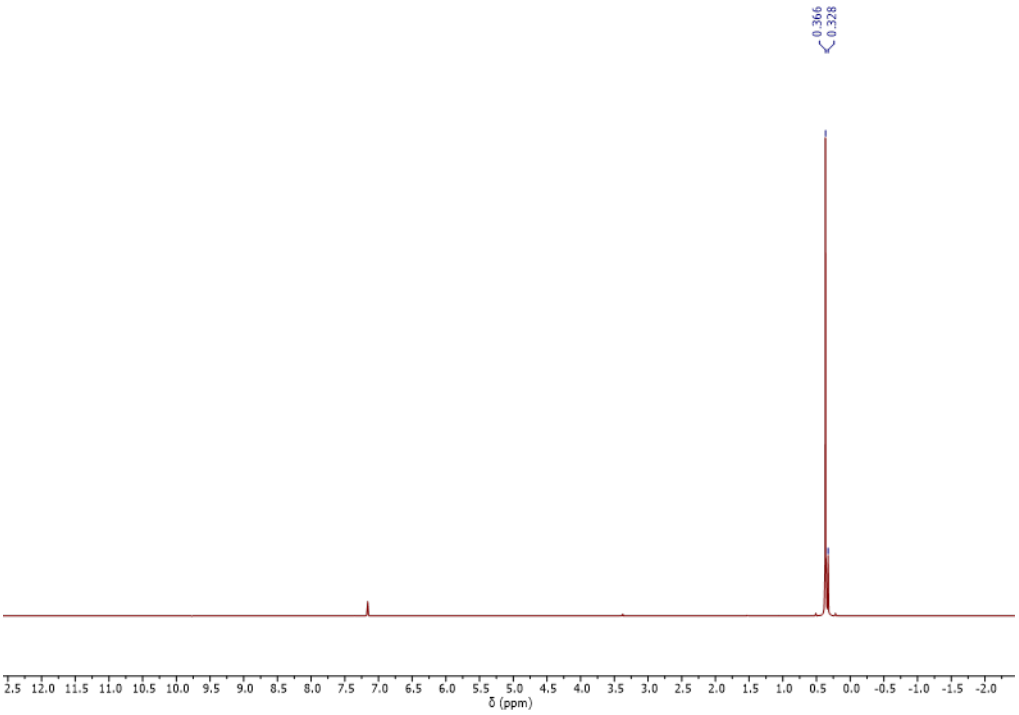


Figure S96. ^{1}H NMR spectrum of a commercial sample of $[MeBO]_3$ in C_6D_6.

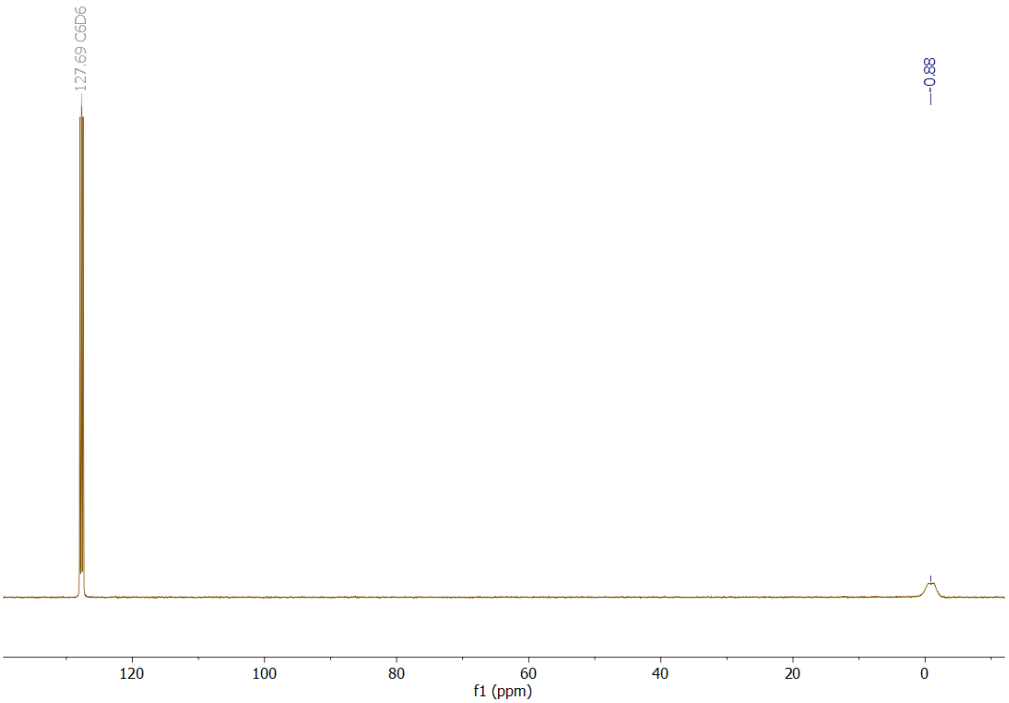


Figure S97. $^{13}C\{H\}$ NMR spectrum of a commercial sample of $[MeBO]_3$ in C_6D_6.

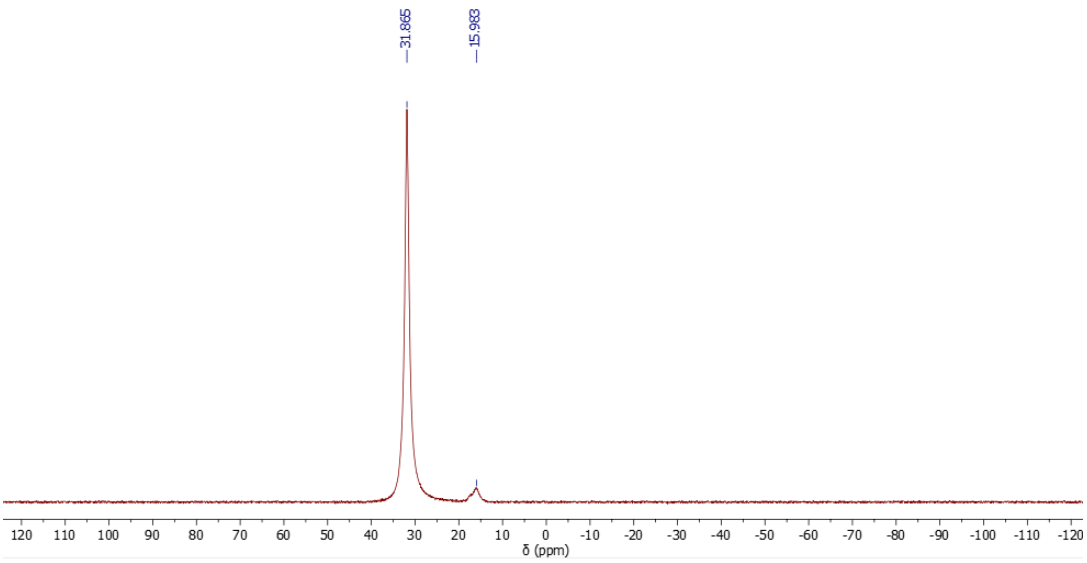


Figure S98. $^{11}B\{H\}$ NMR spectrum of a commercial sample of $[MeBO]_3$ in C_6D_6.

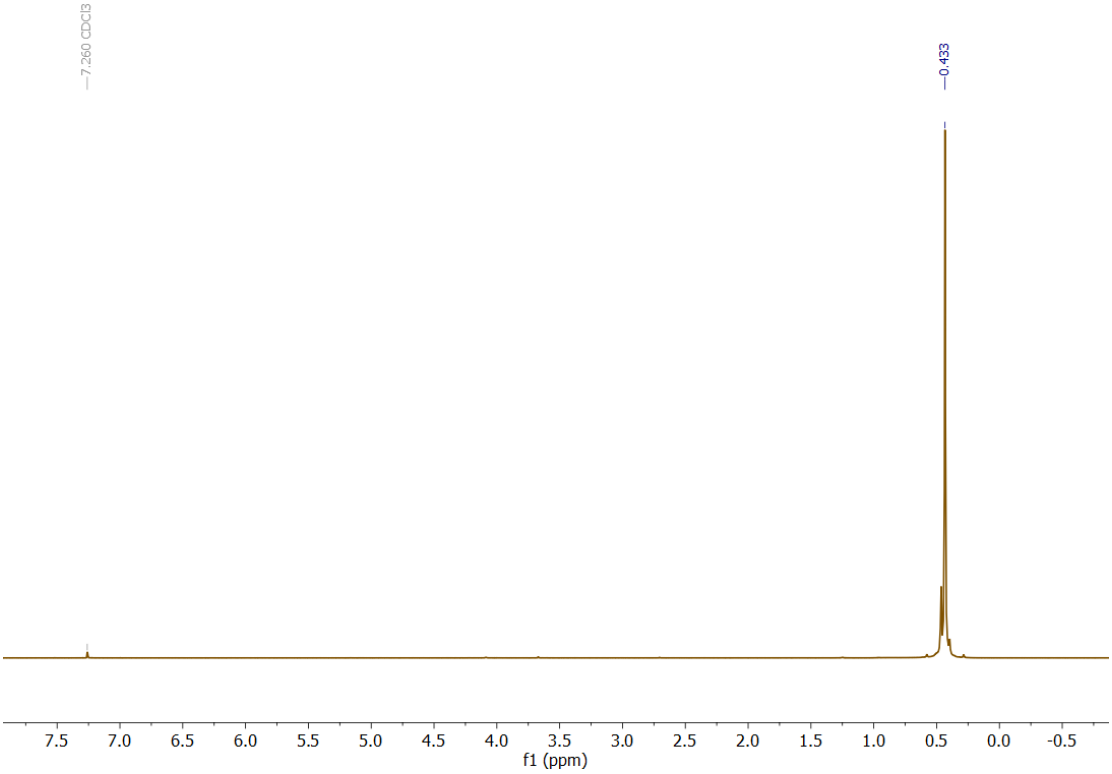


Figure S99. ^{1}H NMR spectrum of a commercial sample of $[MeBO]_3$ in $CDCl_3$.

2.4.3 Me-Bpin

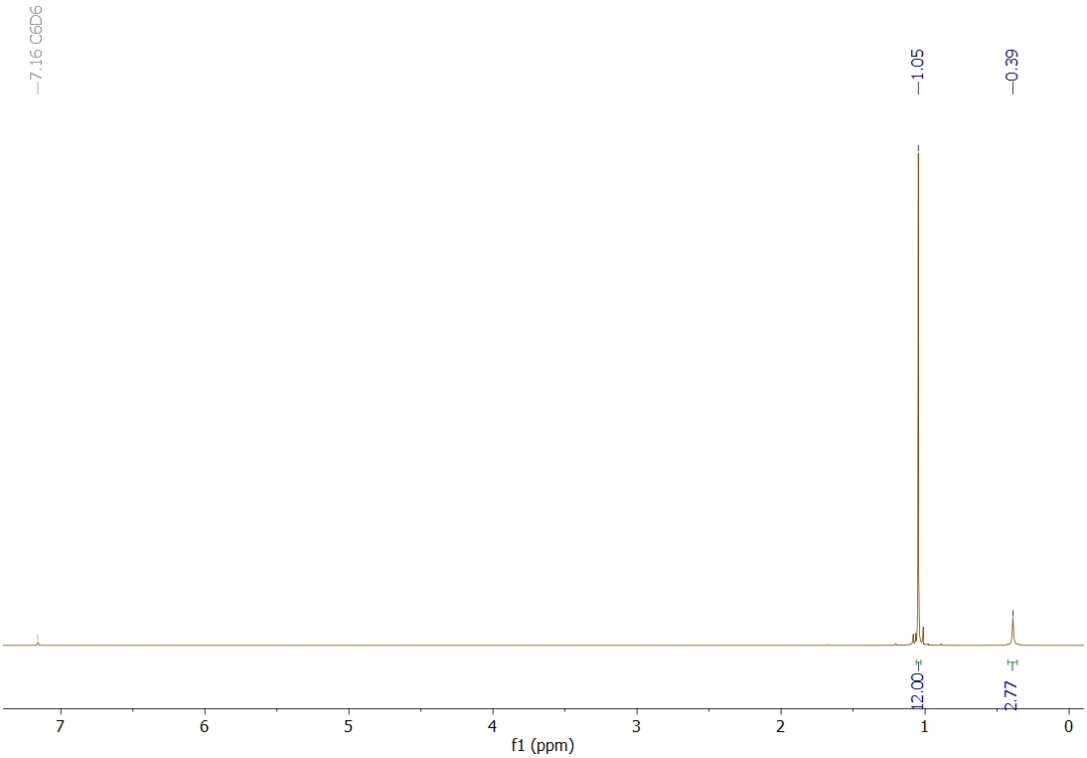


Figure S100. ^{1}H NMR spectrum of a commercial sample of MeBpin in C_6D_6.

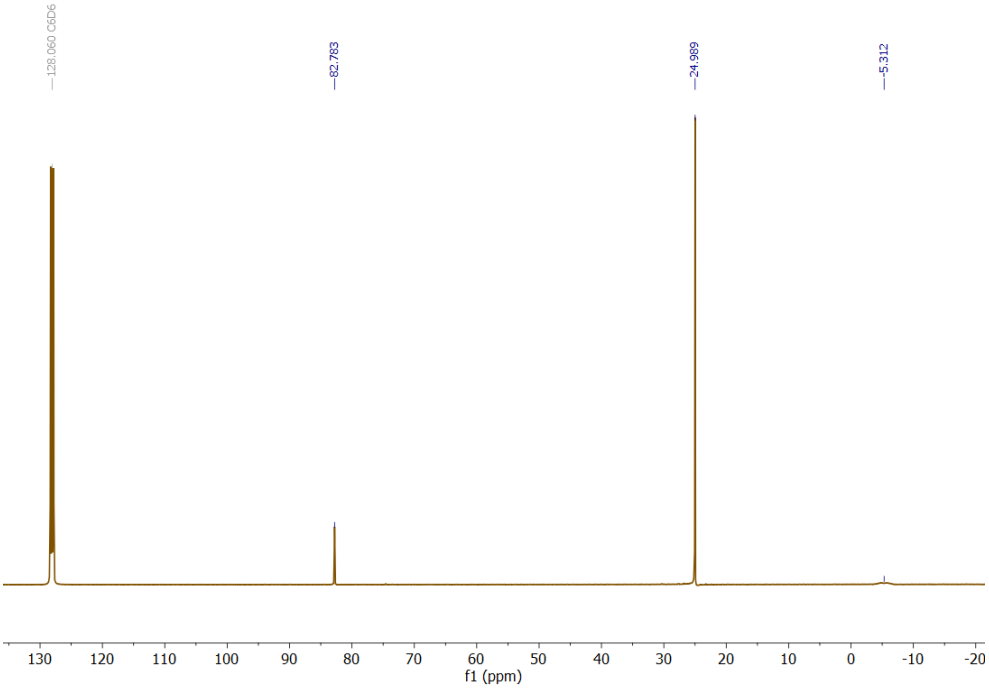


Figure S101. $^{13}C\{H\}$ NMR spectrum of a commercial sample of MeBpin in C_6D_6.

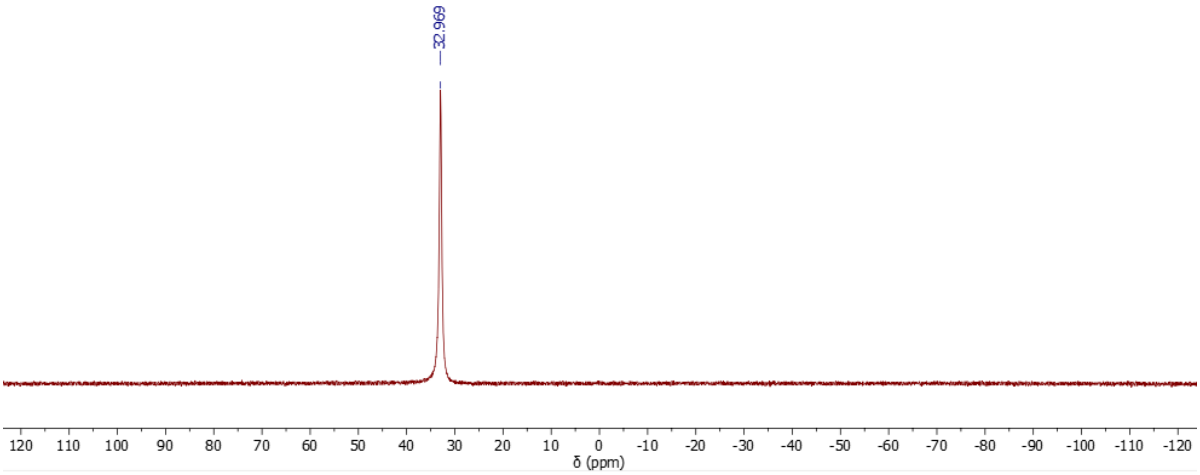


Figure S102. $^{11}B\{H\}$ NMR spectrum of a commercial sample of MeBpin in C_6D_6.

2.4.4 pinBOBpin ($C_{12}H_{24}B_2O_5$)

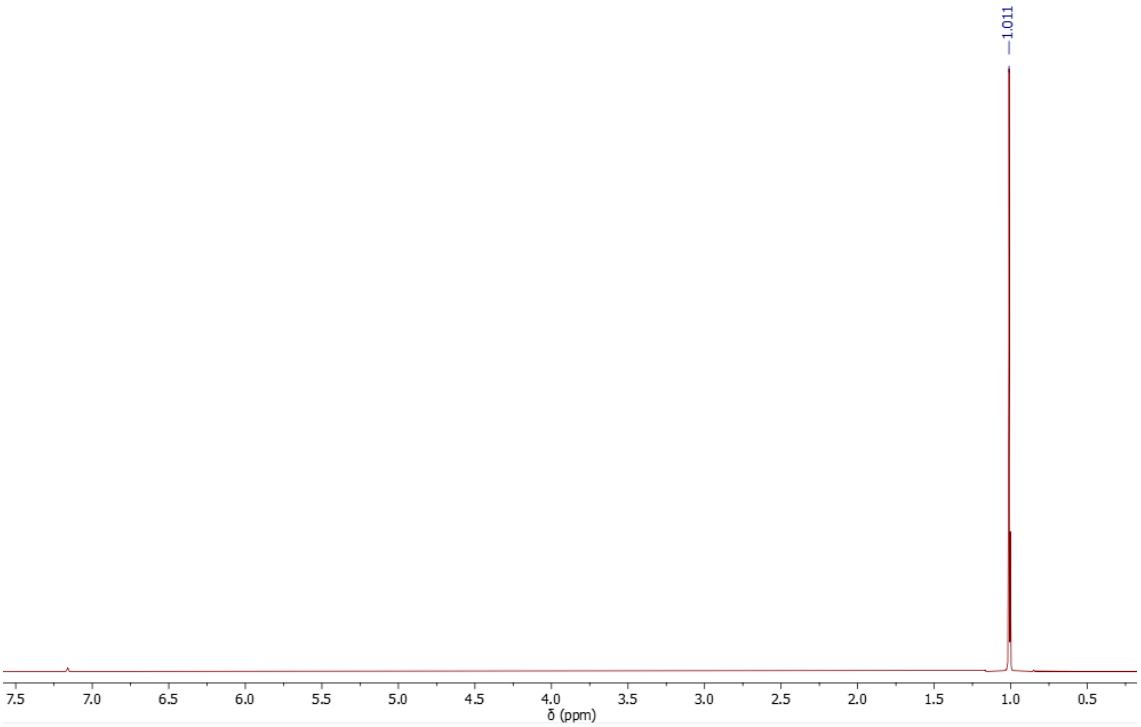


Figure S103. ^{1}H NMR spectrum of pinBOBpin in C_6D_6.

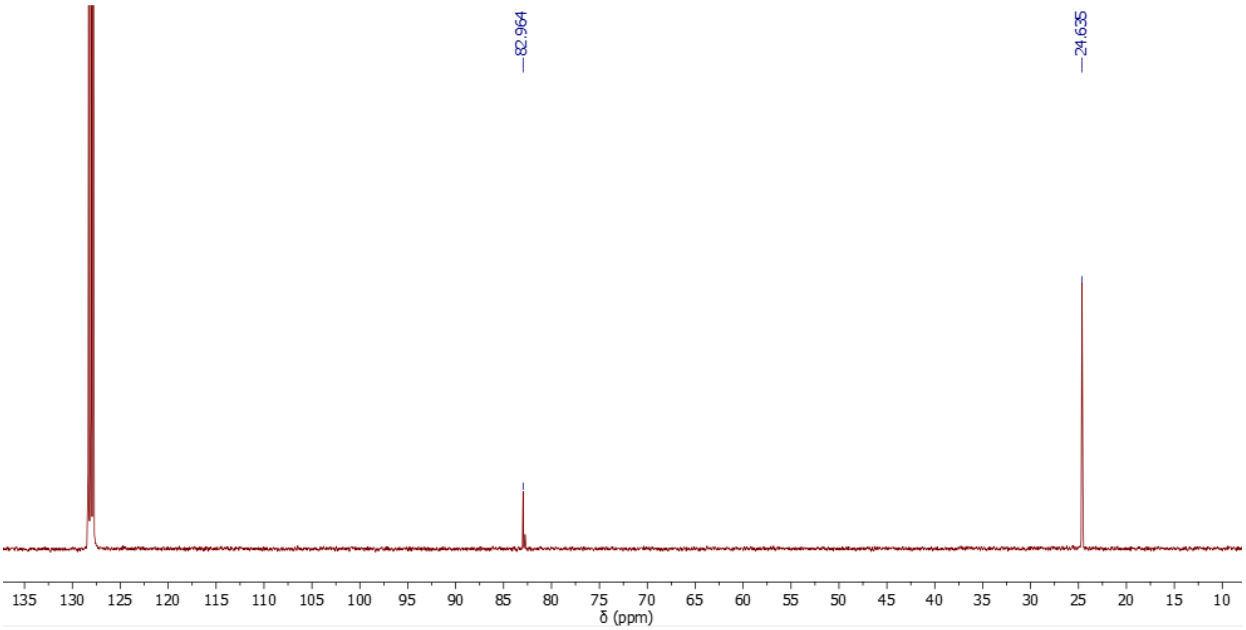


Figure S104. $^{13}C\{H\}$ NMR spectrum of pinBOBpin in C_6D_6.

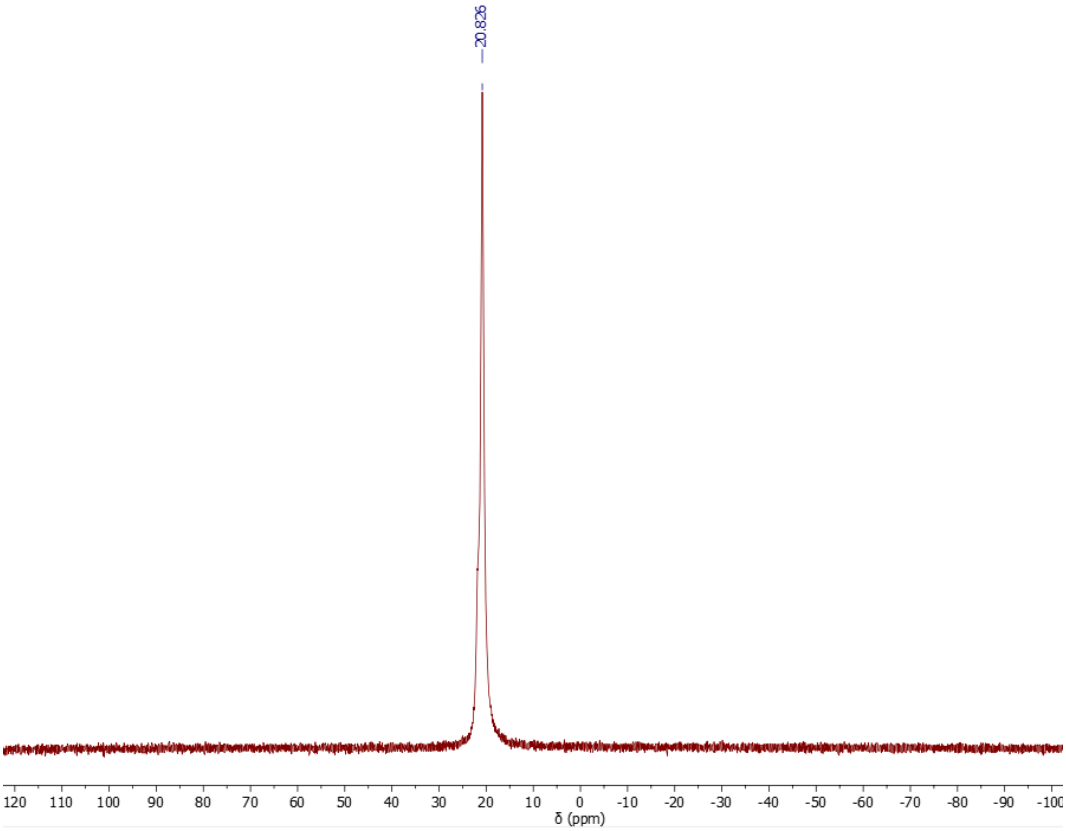


Figure S105. $^{11}B\{H\}$ NMR spectrum of pinBOBpin in C_6D_6.

2.4.5 Decaborane ($B_{10}H_{14}$)

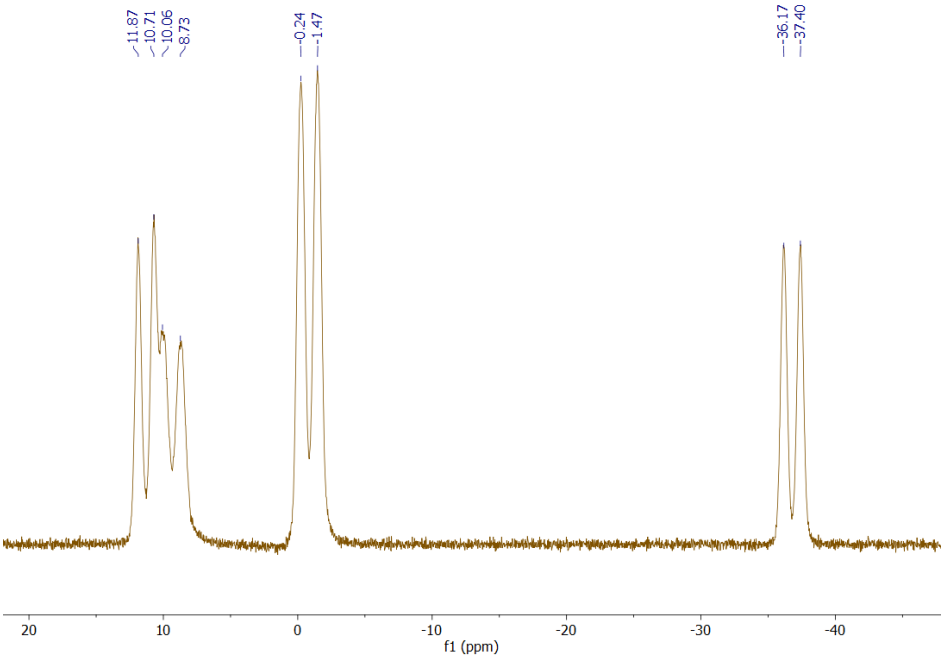


Figure S106. ^{11}B NMR spectrum of a commercial sample of $B_{10}H_{14}$ in C_6D_6

2.4.6 9-Me-BBN

In the glove box, a J-Young NMR tube was charged with 9-BBN (37 mg, 0.3 mmol), 0.6 M trimethyl aluminum (0.5 ml, 0.3 mmol), and ca. 0.2 mL C_6D_6. This was allowed to react at room temperature for 1 h and then analyzed by ^{11}B NMR spectroscopy.

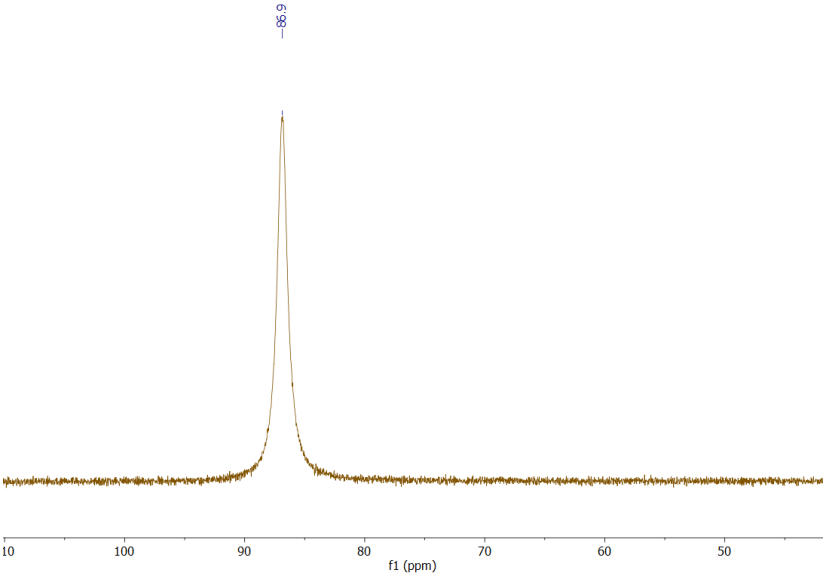


Figure S107. $^{11}B\{H\}$ NMR spectrum of MeBBN in C_6D_6.

2.4.7 9-Octenyl-BBN

In the glove box, a J-Young NMR tube was charged with 9-BBN (24.4 mg, 0.2 mmol), cyclooctadiene (110 mg, 1.0 mmol), and ca. 0.5 mL C_6D_6. This was allowed to react at room temperature for 1 h and then analyzed by ^{11}B NMR spectroscopy.

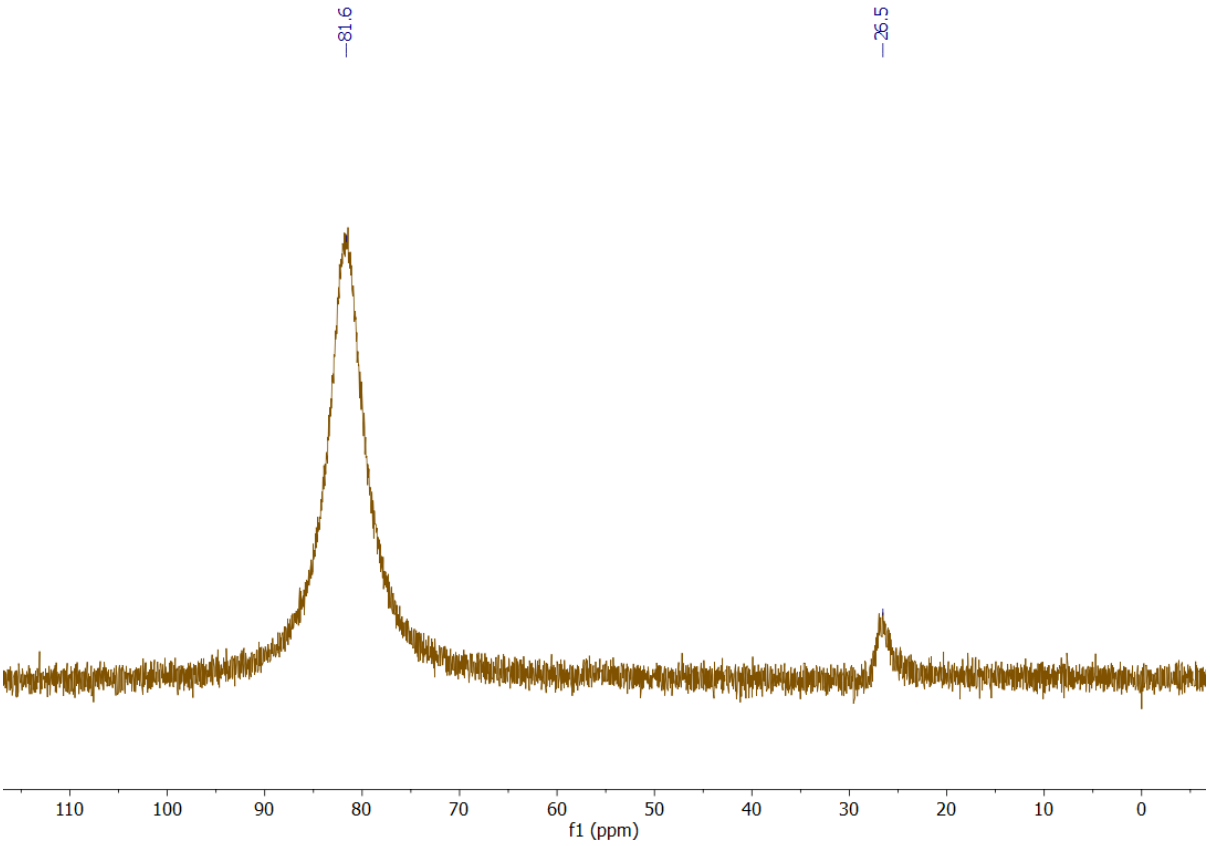


Figure S108. $^{11}B\{H\}$ NMR spectrum of 9-octenyl-BBN in C_6D_6

2.4.8 Trioctylborane [$B(oct)_3$]

In the glove box, an oven dried Schlenk flask was charged with BH_3xSMe_2 (327 mg, 4.3 mmol) and 1-octene (1.689 g, 15.05 mmol). This was allowed to react at room temperature for 12 h before vacuum distillation and analysis by ^1H and ^{11}B NMR spectroscopy.

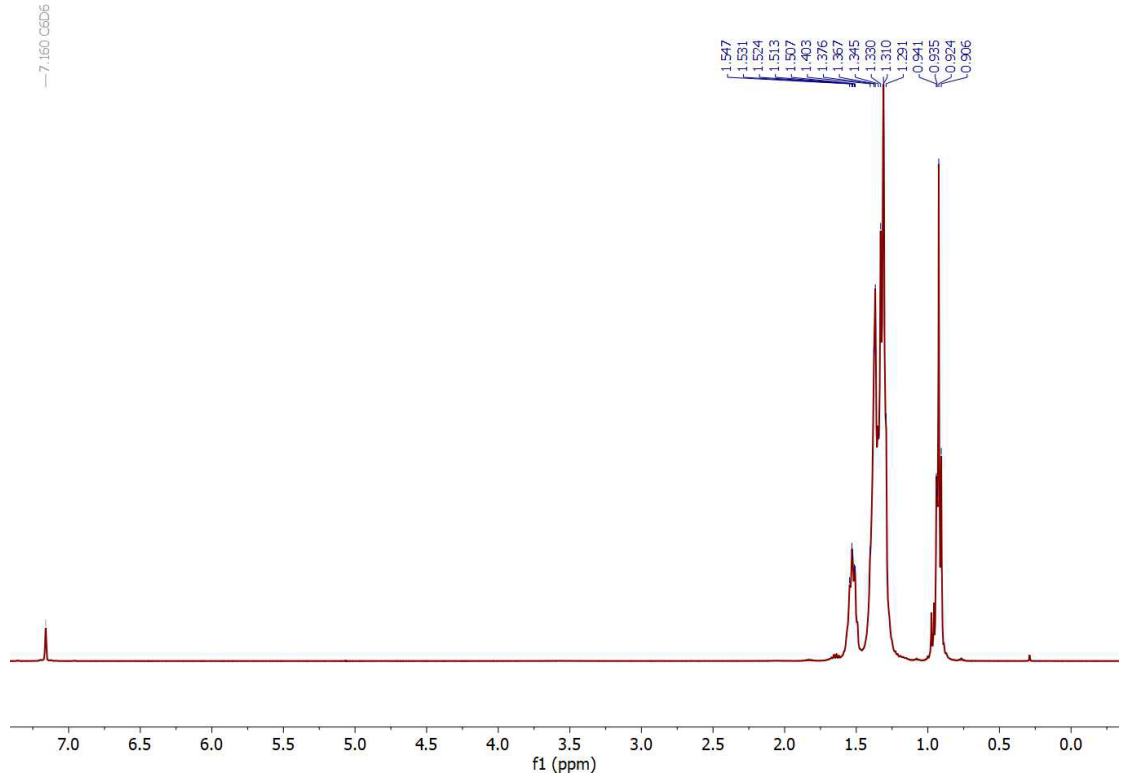


Figure S109. ^{1}H NMR spectrum of trioctylborane C_6D_6.

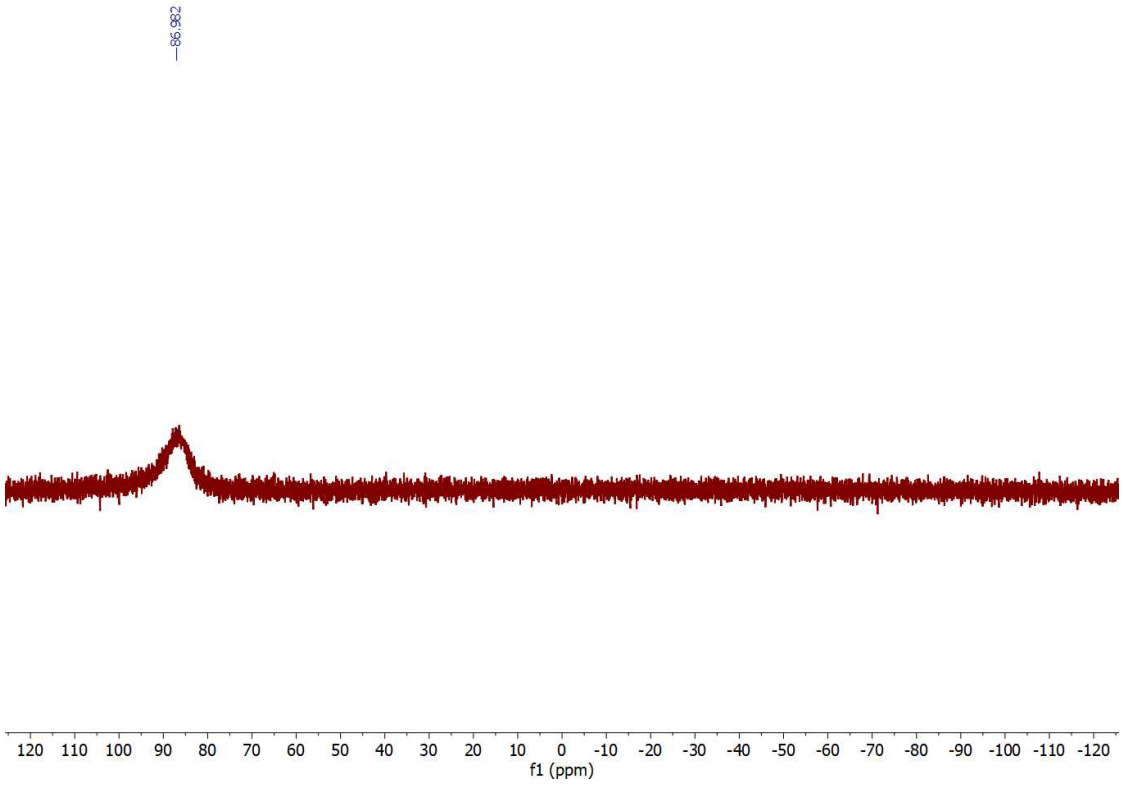


Figure S110. $^{11}B\{H\}$ NMR spectrum of trioctylborane C_6D_6.

2.5. Kinetic Experiments

2.5.1 Hydroboration of 1-octene with MeB(OH) as the pre-catalyst

In the glove box, a J-Young NMR tube was charged with $MeB(OH)_2$ (10.4 mg, 0.174 mmol), HBPin (445 mg, 3.5 mmol), 1-octene (325.5 mg, 2.9 mmol), mesitylene (34.9 mg, 0.29 mmol), and ca. 0.4 mL C_6D_6. The NMR tube was immediately placed in a 400 MHz NMR spectrometer, and ^1H NMR spectra were recorded at regular intervals over a 12 h period. The spectra were subsequently analyzed by integrating the vinylic proton signals of 1-octene relative to mesitylene.

2.5.2 Hydroboration of 1-octene with $(MeBO)_3$ as the pre-catalyst

In the glove box, a J-Young NMR tube was charged with $(MeBO)_3$ (7.3 mg, 0.058 mmol), HBPin (445 mg, 3.5 mmol), 1-octene (325.5 mg, 2.9 mmol), mesitylene (34.9 mg, 0.29 mmol), and ca. 0.4 mL C_6D_6. The NMR tube was immediately placed in a 400 MHz NMR spectrometer, and ^1H NMR spectra were recorded at regular intervals over a 12 h period. The spectra were subsequently analyzed by integrating the vinylic proton signals of 1-octene relative to mesitylene.

3. References

1. Frohn, H.-J.; Adonin, N. Y.; Bardin, V. V.; Starichenko, V. F. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2827-2833.
2. Lin, W.; Dong, J.; Chung, T. C. M. *Macromolecules* **2008**, *41*, 8452-8457.
3. N. Slesarchuk, G. Doerksen, P. Vasko, T. Repo, *Chem. Commun.* **2025**, *61*, 6372–6375.
4. H. Shu, X. Tao, S. Ni, J. Liu, J. Xu, Y. Pan, Y. Wang, *Chem. Sci.* **2025**, *16,* 2682–2689.
5. S. Li, C. Hu, X. Cui, J. Zhang, L. L. Liu, L. Wu, *Angew. Chem. Int. Ed.* **2021**, *60,* 26238–26245.
6. J. Liu, J. Du, F. Yu, L. Gan, G. Liu, Z. Huang, *ACS Catal.* **2023**, *13,* 7995–8003.
7. R. Dong, Y. Huang, L. Wei, L. Xie, Z. Weng, *J. Org. Chem.*, **2025** *90,* 7567–7573.
8. S. Shil, B. P. Patra, T. Begam, S. Bera, *J. Am. Chem. Soc.* **2025**, *147,* 26486–26495.
9. J. H. Kim and Y. K. Chung, *RSC Adv.* **2014**, *4,* 39755–39758.
10. P. Huninik, J. Szyling, A. Czapik, J. Walkowiak, *Green Chem.* **2023**, *25,* 3715–3722.
11. A. Prakash, S. Basappa, D. K. Jangid, R. S. Dhayal, S. K. Bose, *Inorg. Chem.* **2025,** *64,* 15951–15960.