Ru-Catalyzed Isomerization of ω-Alkenylboronates towards Stereoselective Synthesis of Vinylboronates with Subsequent in-situ Functionalization

Guo-Ming Ho, Lucas Segura and Ilan Marek*

Schulich Faculty of Chemistry, Technion—Israel Institute of Technology, Technion City, Haifa, 3200009 (Israel)

Email: chilanm@technion.ac.il

Supporting Information

Table of contents

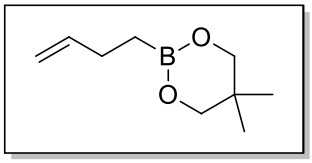
I. General information

Unless stated otherwise, *chemically* based reactions were conducted in flame-dried glassware under a positive pressure of argon. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with phosphomolybdic acid, or potassium permanganate. Column chromatography was performed using Fluka silica gel 60 Å (100-200 mesh) and Fluka Florisil® Adsorbent for Chromatography (40-63 mm, 230-400 mesh). NMR spectra were recorded on Bruker spectrometer (AVIII400) and are reported relative to residual deuterated solvent signals. Chemical shifts are reported in parts per million (ppm) with respect to the residual solvent signal $CDCl_3$ (^{1}H NMR: δ = 7.24; ^{13}C {^{1}H} NMR: δ = 77.00) or C_6D_6 (^{1}H NMR: δ = 7.15; ^{13}C {^{1}H} NMR: δ = 128.00). ^{11}B NMR chemical shifts are reported in ppm with absolute reference relative to ^{1}H. Peak multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, m = multiplet. High-resolution mass spectra (HRMS) were obtained by the mass spectrometry facility of the Technion. Reactions were monitored by gas chromatography spectrometry (GC) using an Agilent Technologies 7820A GC with an Agilent Technologies 19091J-413 (30 m × 0.3 mm) column. Melting points were obtained using a STUART melting point SMP11 with a alcohol thermometer. THF and diethyl ether were dried from Pure-Solv® Purification System (Innovative Technology©). Toluene was distilled over sodium/benzophenone prior to use. All other commercially obtained reagents were used as received.

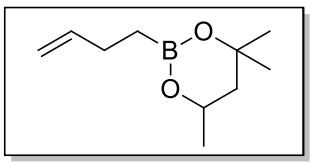
II. Preparation of alkenylboronates

2-(But-3-en-1-yl)-2,3-dihydro-1H-naphtho[1,8-*de*][1,3,2]diazaborinine (**1c**)[1], 2-(3-buten-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1d**)[2], (±)-2-(but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1i**)[3], 2-(but-3-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (**1j**)[1], (±)-2-(hex-1-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1k**)[4], 2-(1-cyclohexylallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1l**)[5], 4,4,5,5-tetramethyl-2-(1-phenyl-3-buten-1-yl)-1,3,2-dioxaborolane (**1m**)[6], 4,4,5,5-tetramethyl-2-[(2*E*)-1-phenyl-2-buten-1-yl]-1,3,2-dioxaborolane (**1n**)[7], (*E*)-methy 5-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-enoate (**1p**)[8] were prepared according to the literature procedures. *cis*-Crotylboronic acid pinacol ester (**1e**, CAS# 69611-01-4), *trans*-crotylboronic acid

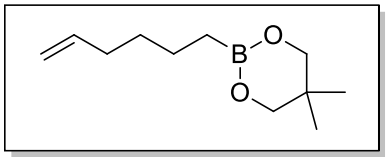
pinacol ester (**1f**, CAS# 69611-02-5) and allylboronic acid pinacol ester (**1g**, CAS# 72824-04-5) were purchased from Sigma-Aldrich and used as received.



2-(But-3-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane (1a). 2,2-Dimethylpropane-1,3-diol (1.435 g, 13.8 mmol, 1.15 equiv), 3-butenylboronic acid (CAS# 379669-72-4, 1.2 g, 12.0 mmol, 1.0 equiv) and $MgSO_4$ (1.73 g, 14.4 mmol, 1.2 equiv) were dissolved in anhydrous diethyl ether (24 mL). The mixture was stirred at room temperature for 16 h. The suspension was filtered and washed with copious amounts of diethyl ether, and then concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/diethyl ether = 20:1 to 10:1) to provide the title compound **1a** as a clear oil (1.82 g, 90%). Rf 0.36 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91–5.81 (m, 1H), 4.99–4.84 (m, 2H), 3.55 (s, 4H), 2.09 (dt, *J* = 7.8, 6.5 Hz, 2H), 0.92 (s, 6H), 0.78 (t, *J* = 7.8 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.3, 112.7, 72.0, 31.6, 28.0, 21.8 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR ($CDCl_3$, 128 MHz) δ 30.27 ppm; HRMS (APCI): *m/z* calcd for $C_9H_{18}BO_2$ ([M + H]$^+$): 169.1394, found 169.1404.

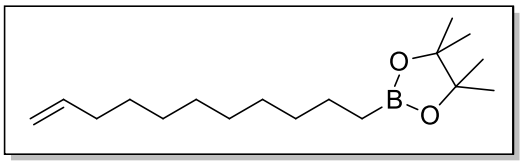


2-(But-3-en-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (1b). The above general procedure was followed using hexylene glycol (CAS# 107-41-5, 1.76 mL, 13.8 mmol, 1.15 equiv), 3-butenylboronic acid (1.2 g, 12.0 mmol, 1.0 equiv) and $MgSO_4$ (1.73 g, 14.4 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography on silica gel (petroleum ether/diethyl ether = 20:1 to 10:1) to give the title compound **1b** as a clear oil (1.92 g, 88%). Rf 0.38 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, C_6D_6) δ 6.08–5.98 (m, 1H), 5.13 (dd, *J* = 17.1, 1.7 Hz 1H), 4.98 (dd, *J* = 10.2, 0.8 Hz, 1H), 3.89–3.80 (m, 1H), 2.36 (dd, *J* = 14.5, 7.3 Hz, 2H), 1.17 (dd, *J* = 13.8 , 3.4 Hz, 1H), 1.12 (d, *J* = 11.5 Hz, 1H), 1.09 (s, 3H), 1.04 (d, *J* = 6.2 Hz, 3H), 1.01 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, C_6D_6) δ 141.8, 113.0, 70.2, 64.4, 45.9, 31.3, 28.9, 28.1, 23.3 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR (C_6D_6, 128 MHz) δ 33.31 ppm; HRMS (APCI): *m/z* calcd for $C_{10}H_{20}BO_2$ ([M + H]$^+$): 183.1551, found 183.1555.

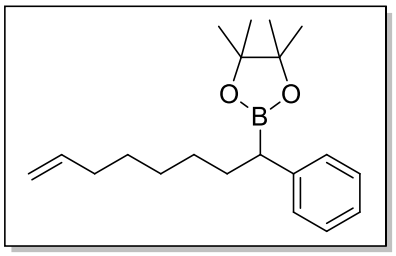


2-(Hex-5-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane (1g). The above general procedure was followed using 2,2-dimethylpropane-1,3-diol (0.93 g, 8.98 mmol, 1.15 equiv), 5-hexenylboronic acid (CAS# 1072952-16-

9, 1.0 g, 7.81 mmol, 1.0 equiv) and $MgSO_4$ (1.12 g, 9.37 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography on silica gel (petroleum ether/diethyl ether = 20:1 to 10:1) to give the title compound **1g** as a clear oil (1.4 g, 91%). Rf 0.38 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84–5.74 (m, 1H), 4.98–4.87 (m, 2H), 3.56 (s, 4H), 2.04–2.00 (m, 2H), 1.37–1.33 (m, 4H), 0.92 (s, 6H), 0.69 (t, *J* = 7.8 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.3, 113.9, 71.9, 33.7, 31.8, 31.6, 23.7, 21.8 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR ($CDCl_3$, 128 MHz) δ 30.41 ppm; HRMS (APCI): *m/z* calcd for $C_{11}H_{22}BO_2$ ([M + H]$^+$): 197.1707, found 197.1721.

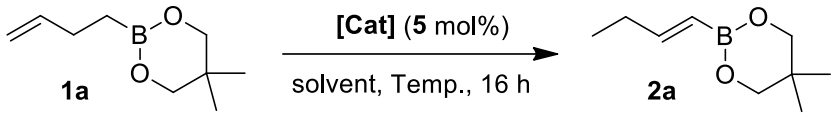


4,4,5,5-Tetramethyl-2-(undec-10-en-1-yl)-1,3,2-dioxaborolane (1h). 11-Bromo-1-undecene (2.15 mL, 9.8 mmol, 1.0 equiv) was dissolved in THF (98 mL) and Mg turnings (0.287 g, 11.8 mmol, 1.2 equiv) were added. The mixture was heated to reflux for 12 h, and then cooled to −78 °C. Trimethylborate (3.35 mL, 29.5 mmol, 3.0 equiv) was added dropwise and the temperature maintained at −78 °C for additional 2 h. Thereafter, reaction mixture was warmed to room temperature and stirred overnight. It was then quenched with 1 M HCl (50 mL) and concentrated to remove THF. The crude mixture was extracted with ethyl acetate (50 mL × 3). The organic extracts were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was dissolved in Et_2O (30 mL), pinacol (1.21 g, 10.3 mmol, 1.05 equiv) and $MgSO_4$ (1.41 g, 11.8 mmol, 1.2 equiv) were added. The mixture was stirred at room temperature for 16 h. The suspension was filtered and washed with copious amounts of diethyl ether, and then concentrated. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/diethyl ether = 20:1 to 10:1) to give the title compound **1h** as a clear oil (1.81 g, 66%). Rf 0.4 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83–5.73 (m, 1H), 4.99–4.88 (m, 2H), 1.99 (dt, *J* = 7.9, 6.6 Hz, 2H), 1.37–1.24 (m, 14H), 1.21 (s, 12H), 0.74 (t, *J* = 7.7 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.3, 114.1, 82.6 (C × 2), 33.9, 32.4, 29.5 (CH_2 × 2), 29.4, 29.2, 29.0, 24.8 (CH_3 × 4), 24.0 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR ($CDCl_3$, 128 MHz) δ 33.96 ppm; HRMS (APCI): *m/z* calcd for $C_{17}H_{34}BO_2$ ([M + H]$^+$): 281.2646, found 281.2660.

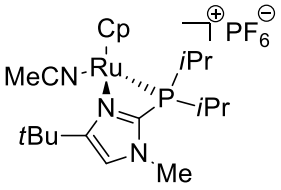


4,4,5,5-Tetramethyl-2-(1-phenylhept-6-en-1-yl)-1,3, 2-dioxaborolane (1o). Based on a literature procedure.[6] (1-Bromooct-7-en-1-yl)benzene (1.2 g, 4.5 mmol, 1.0 equiv) was added to a suspension of Mg turnings (131 mg , 5.4 mmol, 1.2 equiv), pinacolborane (0.66 mL, 4.5 mmol, 1.0 equiv) and triethylamine (0.63 mL, 4.5 mmol, 1.0 equiv) in dry THF (14 mL) at room temperature. The reaction mixture was stirred overnight at 65 °C. It was then quenched with 0.1 M HCl (30 mL), and extracted with diethyl ether (25 mL × 3). The organic extracts were combined, washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/diethyl ether 20:1 to 10:1) to give the title compound **1o** as a pale-yellow oil (0.79 g, 2.51 mmol, 56%). Rf 0.55 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, C_6D_6) δ 7.39 (d, *J* = 7.3 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 7.4 Hz, 1H), 5.78–5.68 (m, 1H), 5.01–4.94 (m, 2H), 2.49 (t, *J* = 7.9 Hz, 1H), 2.10–2.01 (m, 1H), 1.93–1.92 (m, 2H), 1.86–1.77 (m, 1H), 1.37–1.35 (m, 6H), 0.99 (s, 6H), 0.98 (s, 6H); ^{13}C {^{1}H} NMR (100 MHz, C_6D_6) δ 144.1, 139.2, 128.8, 128.6, 125.5, 114.4, 83.1, 34.1, 33.0, 29.6, 29.5, 29.2, 24.6 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR (C_6D_6, 128 MHz) δ 33.79 ppm; HRMS (APCI): *m/z* calcd for $C_{20}H_{32}BO_2$ ([M + H]$^+$): 315.2490, found 315.2502.

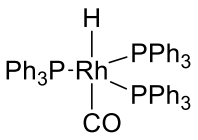
III. Reaction optimization of metal-catalyzed isomerization of alkenylboronate



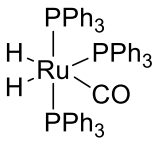
Entry	[M] (x mol%)	solvent	*T*(°C)	yield (%)	*E*/*Z*
1	Grotjahn's catalyst (5 mol%)	Dichloroethane	40	62	>95:5
2	$RhH(CO)(PPh_3)_3$ (5 mol%)	Toluene	100	29	93:7
3	$RuH_2(CO)(PPh_3)_3$ (5 mol%)	Toluene	100	58	91:9
4	$RuHCl(CO)(PPh_3)_3$ (5 mol%)	Toluene	100	64	93:7
5	$RuHCl(CO)(PPh_3)_3$ (5 mol%)	Dichloroethane	60	38	93:7
6	$RuHCl(CO)(PPh_3)_3$ (5 mol%)	Pinacolone	60	11	95:5
7	***$RuHCl(CO)(PPh_3)_3$ (5 mol%)***	***THF***	***60***	***76***	***94:6***
8	$RuHCl(CO)(PPh_3)_3$ (2.5 mol%)	THF	60	72	94:6



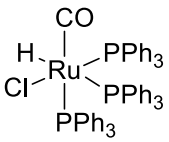
Cat_1:Grotjahn's catalyst



Cat_2

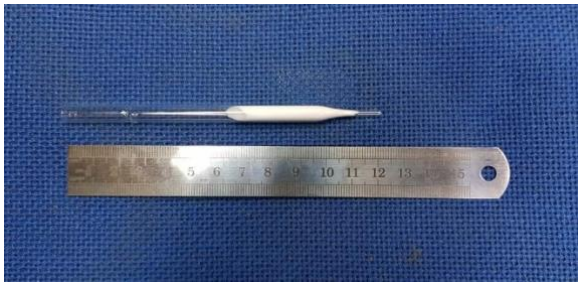


Cat_3

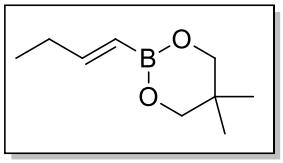


Cat_4

General procedure for isomerization of homoallylboronate 1a. Under argon atmosphere, a flame-dried Schlenk tube was charged with the specified transition-metal catalyst (Grotjahn's catalyst **Cat_1,** $RhH(CO)(PPh_3)_3$ **Cat_2**, $RuH_2(CO)(PPh_3)_3$ **Cat_3** or $RuHCl(CO)(PPh_3)_3$ **Cat_4**, 2.5-5 mol%). The tube was put under vacuum and backfilled with argon (3 times), and then a solution of **1a** (50 mg, 0.297 mmol, 1.0 equiv) in the specified anhydrous solvent (1,2-dichloroethane, toluene, pinacolone or THF, 1.5 mL) was added under an inert atmosphere of argon by a syringe. The reaction mixture was then heated at the indicated temperature and allowed to stir for the specified time. After the reaction had reached to the specified time, the resulting mixture was cooled to room temperature and quenched by evaporation of the solvent. The crude residue was purified by pouring into pentane (ca. 3 mL) to precipitate catalyst, followed by filtering through a short pad of silica gel (see below apparatus) with copious washings by pentane/diethyl ether (20:1) and concentrated. Repeating the described purification procedure until no more precipitate forms (2 to 3 times) to provide the vinylboronate product **2a** along with partial inseparable *E*- and *Z*-allyl isomers as a clear oil.

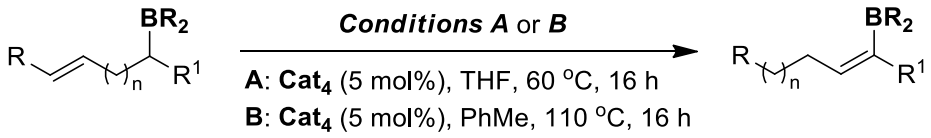


Glass dropper with a short pad of silica gel



(*E*)-2-(But-1-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane (2a). The representative example for the synthesis of vinylboronate **2a** was prepared according to the general procedure described in entry 7 of table 1. Using **Cat$_4$** (14 mg, 0.015 mmol), homoallylboronate **1a** (50 mg, 0.297 mmol) and anhydrous THF (1.5 mL). The reaction mixture was stirred for 16 h at 60 °C. Standard work-up and purification afforded a mixture of the desired product **2a** and the corresponding allyl isomers as a clear oil (49 mg, 0.292 mmol, 98% yield). Using ^{1}H NMR spectroscopic analysis for a mixture of purified products, formation of the title compound **2a** was observed in 76% yield with *E*/*Z* = 94:6, the corresponding allyl isomers were observed in 22% yield. ***E*-2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (dt, *J* = 17.8, 6.0 Hz, 1H), 5.32 (d, *J* = 17.8 Hz, 1H), 3.61 (s, 4H), 2.15–2.08 (m, 2H), 0.98 (t, *J* = 7.8 Hz, 3H), 0.94 (s, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.2, 72.0, 31.7, 28.3, 21.8, 12.6 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR ($CDCl_3$, 128 MHz) δ 26.04 ppm; HRMS (APCI): *m/z* calcd for $C_9H_{18}BO_2$ ([M + H]$^+$): 169.1394, found 169.1381. Isomer ***Z*-2a** was inseparable from isomer ***E*-2a**. ^{1}H NMR signals specific to the isomer ***Z*-2a** are as follows: 6.33–6.26 (m, 1H), 5.18 (d, *J* = 13.6 Hz, 1H), 2.39–2.31 (m, 2H).

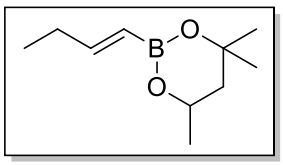
IV. Substrate scope for the Ru-catalyzed isomerization of ω-alkenylboronates



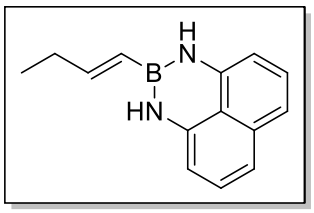
General procedure A for Ru-catalyzed isomerization of ω-alkenylboronates. Under argon atmosphere, $RuHCl(CO)(PPh_3)_3$ (5 mol%) was added to a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was put under vacuum and backfilled with argon (3 times). A solution of alkenylboronate (1.0 equiv) in THF (0.18 M) was

added by syringe and stirred at 60 °C. After 16 h, the resulting mixture was cooled to room temperature and quenched by evaporation of the solvent. The crude residue was purified by pouring into pentane to precipitate catalyst, followed by filtering through a short pad of silica gel with copious washings by pentane/diethyl ether (20:1) and concentrated. Repeating the described purification procedure until no more precipitate forms (2 to 3 times) to provide the vinylboronate product.

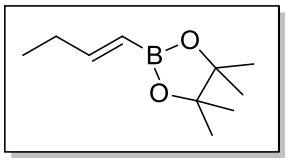
General procedure B for Ru-catalyzed isomerization of ω-alkenylboronates. Under argon atmosphere, $RuHCl(CO)(PPh_3)_3$ (5 mol%) was added to a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was put under vacuum and backfilled with argon (3 times). A solution of alkenylboronate (1.0 equiv) in toluene (0.18 M) were added by syringe and stirred at 110 °C. After 16 h, the resulting mixture was cooled to room temperature and quenched by evaporation of the solvent. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1) to give the vinylboronate product.



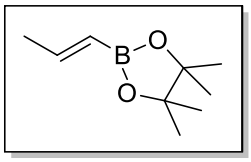
(*E*)-2-(But-1-en-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2b). Synthesized according to the general procedure A, using **Cat$_4$** (14 mg, 0.015 mmol), homoallylboronate **1b** (54 mg, 0.297 mmol) and anhydrous THF (1.5 mL). The reaction mixture was stirred for 16 h at 60 °C. Standard work-up and purification afforded a mixture of the desired product **2b** and the corresponding allyl isomers as a clear oil (53 mg, 0.291 mmol, 98% yield). Using ^{1}H NMR spectroscopic spectroscopic analysis for a mixture of purified products, formation of the title compound **2b** was observed in 70% yield with *E*/*Z* = 94:6, the corresponding allyl isomers were observed in 28% yield. ***E*-2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (dt, *J* = 17.7, 5.8 Hz, 1H), 5.30 (d, *J* = 17.7 Hz, 1H), 4.21–4.13 (m, 1H), 2.13–2.06 (m, 2H), 1.73 (dd, *J* = 13.9, 2.9 Hz, 1H), 1.46 (dd, *J* = 13.9, 11.8 Hz, 1H), 1.26 (s, 6H), 1.23 (d, *J* = 6.2, 3H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.4, 70.5, 64.5, 45.9, 31.2, 28.1, 28.0, 23.1, 12.4 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR ($CDCl_3$, 128 MHz) δ 26.07 ppm; HRMS (APCI): *m/z* calcd for $C_{10}H_{20}BO_2$ ($[M + H]^+$): 183.1551, found 183.1542. Isomer ***Z*-2b** was inseparable from isomer ***E*-2b**. ^{1}H NMR signals specific to the isomer ***Z*-2b** are as follows: 6.30–6.23 (m, 1H), 5.17 (d, *J* = 13.6 Hz, 1H), 2.39–2.32 (m, 2H).



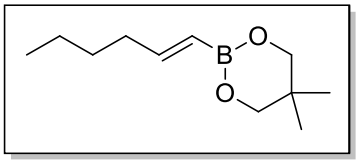
(*E*)-2-(But-1-en-1-yl)-2,3-dihydro-1*H*-naphtho [1,8-*de*] [1,3, 2] diazaborinine (2c). Synthesized according to a modified general procedure A, using **Cat₄** (14 mg, 0.015 mmol), homoallylboronate **1c** (66 mg, 0.297 mmol) and anhydrous THF (1.5 mL). The reaction mixture was stirred for 16 h at 60 °C. Standard work-up and purification by flash column chromatography on Florisil® (petroleum ether/diethyl ether = 20:1 to 10:1) afforded a mixture of the desired product **2c** and the corresponding allyl isomers as a green oil (65 mg, 0.293 mmol, 98% yield). Using ^{1}H NMR spectroscopic analysis, formation of the desired product **2c** was observed in 81% yield with *E*/*Z* **=** 95:5, the corresponding allyl isomers were observed in 17% yield. ***E*-2c**: Rf 0.38 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.8 Hz, 2 H), 7.01 (d, *J* = 8.3 Hz, 2 H), 6.41 (dt, *J* = 18.1, 5.9 Hz, 1 H), 6.31 (d, *J* = 7.3 Hz, 2 H), 5.69 (br, 2 H), 5.55 (dt, *J* = 19.1, 1.6 Hz, 1 H), 2.25–2.18 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.4, 141.3, 136.3, 127.5, 119.7, 117.3, 105.5, 28.6, 12.8 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR ($CDCl_3$, 128 MHz) δ 27.77 ppm; HRMS (APCI): *m/z* calcd for $C_{14}H_{16}BN_2$ ([M + H]$^{+}$): 223.1401, found 223.1427. Isomer ***Z*-2c** was inseparable from isomer ***E*-2c**. ^{1}H NMR signals specific to the isomer ***Z*-2c** are as follows: 5.37 (dt, *J* = 18.0, 1.7 Hz, 1 H), 2.39–2.35 (m, 2H).



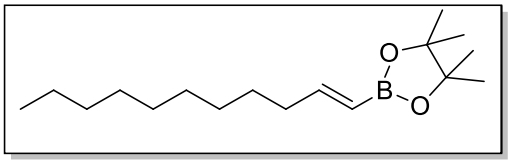
2-(*E*)-But-1-enyl-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (2d). Synthesized according to the general procedure A, using **Cat₄** (14 mg, 0.015 mmol), homoallylboronate **1d** (54 mg, 0.297 mmol) and anhydrous THF (1.5 mL). The reaction mixture was stirred for 16 h at 60 °C. Standard work-up and purification afforded a mixture of the desired product **2d** and the corresponding allyl isomers as a clear oil (53 mg, 0.291 mmol, 98% yield). Using ^{1}H NMR spectroscopic analysis, formation of the desired product **2d** was observed in 72% yield with *E*/*Z* **=** 92:8, the corresponding allyl isomers were observed in 26% yield. The title compound **2d** could also be prepared from starting materials ***Z*-** and ***E*-1e**, giving product **2d** in 74% yield with *E*/*Z* **=** 91:9, respectively. ***E*-2d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (dt, *J* = 18.0, 6.0 Hz, 1H), 5.41 (d, *J* = 18.0 Hz, 1H), 2.18–2.11 (m, 2H), 1.24 (s, 12H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.0, 83.0, 28.5, 24.8, 12.3 (the boron-bound carbon was not observed due to quadrupolar relaxation). The NMR spectral data of ***E*-2d** matched reported literature values.[9] Isomer ***Z*-2d** was inseparable from isomer ***E*-2d**. ^{1}H NMR signals specific to the isomer ***Z*-2d** are as follows: 6.44–6.35 (m, 1H), 5.27 (d, *J* = 13.5 Hz, 1H), 2.41–2.33 (m, 2H).



(*E*)-4,4,5,5-Tetramethyl-2-(prop-1-en-1-yl)-1,3,2-dioxaborolane (2e). Synthesized according to the general procedure A, using **Cat$_4$** (14 mg, 0.015 mmol), alkenylboronate **1f** (50 mg, 0.297 mmol) and anhydrous THF (1.5 mL). The reaction mixture was stirred for 16 h at 60 °C. Standard work-up and purification afforded the desired product **2e** in 92% yield with *E*/*Z* = 90:10 as a clear oil (46 mg, 0.274 mmol). ***E*-2e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66–6.58 (m, 1H), 5.43 (dd, *J* = 17.8, 1.6 Hz, 1H), 1.82 (dd, *J* = 6.4, 1.6 Hz, 3H), 1.24 (s, 12H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.6, 82.7, 24.9, 21.6 (the boron-bound carbon was not observed due to quadrupolar relaxation). ***Z*-2e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53–6.48 (m, 1H), 5.33 (dd, *J* = 13.6, 1.5 Hz, 1H), 1.95 (dd, *J* = 6.9, 1.4 Hz, 3H), 1.25 (s, 12H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.8, 82.8, 24.9, 18.6 (the boron-bound carbon was not observed due to quadrupolar relaxation). The NMR spectral data for both isomers matched reported literature values.[10]

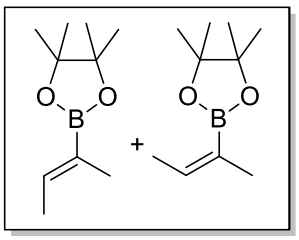


(*E*)-2-(Hex-1-enyl)-5,5-dimethyl-1,3,2-dioxaborinane (2f). Synthesized according to the general procedure A, using **Cat$_4$** (14 mg, 0.015 mmol), alkenylboronate **1g** (58 mg, 0.296 mmol) and anhydrous THF (1.5 mL). The reaction mixture was stirred for 16 h at 60 °C. Standard work-up and purification afforded a mixture of the desired product **2f** and other internal regioisomers as a clear oil (57 mg, 0.290 mmol, 98% yield). Using ^{1}H NMR spectroscopic analysis, formation of the desired product **2b** was observed in 55% yield with *E*/*Z* = 95:5, other internal regioisomers were observed in 43% yield. ***E*-2f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (dt, *J* = 17.9, 6.0 Hz, 1H), 5.33 (d, *J* = 17.9 Hz, 1H), 3.60 (s, 4H), 2.13–2.08 (m, 2H), 1.40–1.25 (m, 4H), 0.94 (s, 6H), 0.86 (t, *J* = 7.6 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.0, 72.0, 35.2, 31.8, 30.6, 22.2, 21.8, 13.9 (the boron-bound carbon was not observed due to quadrupolar relaxation). The NMR spectral data of ***E*-2f** matched reported literature values.[11] Isomer ***Z*-2f** was inseparable from isomer ***E*-2f**. ^{1}H NMR signals specific to the isomer ***Z*-2f** are as follows: 6.31–6.27 (m, 1H), 5.17 (d, *J* = 13.5 Hz, 1H), 2.38–2.32 (m, 2H).

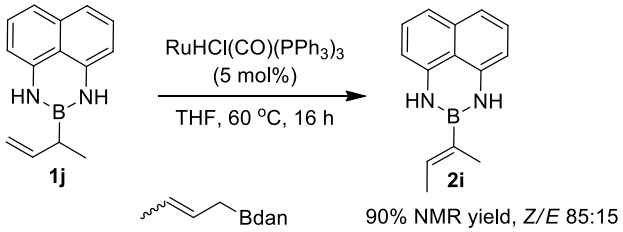


2-(*E*)-Undec-1-enyl-4,4,5,5-tetramethyl-[1, 3,2]-dioxaborolane (2g). Synthesized according to the general procedure A, using **Cat$_4$** (14 mg, 0.015 mmol), alkenylboronate **1h** (83 mg, 0.296 mmol) and anhydrous THF (1.5 mL). The reaction mixture was stirred for 16 h at 60 °C. Standard work-up and purification afforded a mixture of the desired product **2g** and other internal regioisomers as a clear oil (81 mg, 0.289 mmol, 97%

yield). Using ^{1}H NMR spectroscopic analysis, formation of the desired product **2g** was observed in 30% yield with *E*/*Z* = 90:10, other internal regioisomers were observed in 67% yield. ***E*-2g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (dt, *J* = 18.0, 6.2 Hz, 1H), 5.41 (d, *J* = 18.0 Hz, 1H), 2.18–2.11 (m, 2H), 1.40–1.33 (m, 2H), 1.30–1.24 (m, 12H), 1.23 (s, 12H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.0, 83.0, 35.9, 32.0, 29.7, 29.6, 29.4, 29.3, 28.3, 24.8, 22.8, 14.3 (the boron-bound carbon was not observed due to quadrupolar relaxation). The NMR spectral data of **2g** matched reported literature values.[12] Isomer ***Z*-2g** was inseparable from isomer ***E*-2g**. ^{1}H NMR signals specific to the isomer ***Z*-2g** are as follows: 6.45–6.35 (m, 1H), 2.40–2.31 (m, 2H).

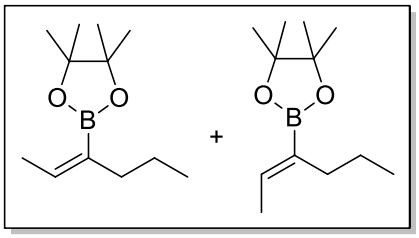


(*Z*)- and (*E*)-2-(But-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h). Synthesized according to the general procedure A, using **Cat$_4$** (14 mg, 0.015 mmol), allylboronate **1i** (54 mg, 0.297 mmol) and anhydrous THF (1.5 mL). The reaction mixture was stirred for 16 h at 60 °C. Standard work-up and purification afforded the desired product **2h** in 92% yield with *E*/*Z* = 32:68 as a clear oil (50 mg, 0.273 mmol). ***Z*-2h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.41 (q, *J* = 7.2 Hz, 1H), 1.68 (dd, *J* = 6.8, 1.0 Hz, 3H), 1.66 (s, 3H), 1.25 (s, 12H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.2, 83.0, 24.9, 14.3, 13.7 (the boron-bound carbon was not observed due to quadrupolar relaxation). ***E*-2h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (q, *J* = 7.2 Hz, 1H), 1.86 (dd, *J* = 6.9, 1.5 Hz, 3H), 1.72 (s, 3H), 1.23 (s, 12H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.7, 82.7, 24.9, 22.9, 17.5 (the boron-bound carbon was not observed due to quadrupolar relaxation). The NMR spectral data for both isomers matched reported literature values.[13,14]

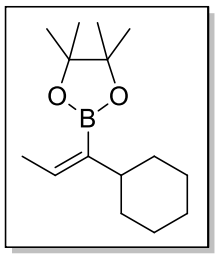


(*Z*)-2-(But-2-en-2-yl)naphtho[1,8-*de*][1,3,2]dioxaborinine (2i). Synthesized according to a modified general procedure A, using **Cat$_4$** (21 mg, 0.022mmol), allylboronate **1j** (contained ca. 15 % of crotylboronate **S1**, 98.2 mg, 0.379 mmol) and anhydrous THF (3.0 mL). The reaction mixture was stirred for 16 h at 60 °C. Standard work-up and purification by flash column chromatography on Florisil® (petroleum ether/diethyl ether = 20:1 to 10:1) afforded the desired product **2i** (90 %, *Z*/*E* = 85:15) along with an inseparable vinylboronate **2c** (which comes from crotylboronate **S1**) as a brown solid (mp 45–50°C). Yield of **2i** was determined by ^{1}H NMR spectroscopic analysis of purified

products using 2-naphthaldehyde as an internal standard. ***Z*-2i**: Rf 0.33 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.8 Hz, 2 H), 7.00 (d, *J* = 8.2 Hz, 2 H), 6.32 (d, *J* = 7.3 Hz, 2 H), 6.14 (q, *J* = 6.3 Hz, 1 H), 5.72 (br, 2 H), 1.77 (d, *J* = 6.3 Hz, 3H), 1.76 (s, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.4, 141.2, 134.1, 127.5, 119.7, 117.3, 105.6, 14.3, 13.6 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR ($CDCl_3$, 128 MHz) δ 28.23 ppm; HRMS (APCI): *m/z* calcd for $C_{14}H_{16}BN_2$ ([M + H]$^+$): 223.1401, found 223.1428. Isomer ***E*-2i** was inseparable from isomer ***Z*-2i**. ^{1}H NMR signals specific to the isomer ***E*-2i** are as follows: 5.96–5.89 (m, 1H), 1.82 (s, 3H). Relative configuration of ***Z*-2i** was comfirmed by transforming the allylBdan compound **1j** to vinylBpin **2h** in two steps, described on page S16.

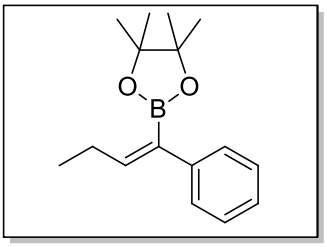


(*E*)- and (*Z*)-2-(Hex-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j). Synthesized according to the general procedure A, using **Cat$_4$** (14 mg, 0.015 mmol), allylboronate **1k** (58 mg, 0.298 mmol) and anhydrous THF (1.5 mL). The reaction mixture was stirred for 16 h at 60 °C. Standard work-up and purification afforded the desired product **2j** in 95% yield with *E*/*Z* = 50:50 as a clear oil (55 mg, 0.284 mmol). ***E*-2j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (q, *J* = 6.2 Hz, 1H), 2.03 (t, *J* = 7.5 Hz, 2H), 1.86 (d, *J* = 6.2 Hz, 1H), 1.43–1.29 (m, 2H), 1.23 (12H, s), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.4, 82.8, 30.9, 24.8, 23.4, 17.2, 13.9 (the boron-bound carbon was not observed due to quadrupolar relaxation). ***Z*-2j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.41 (q, *J* = 6.8 Hz, 1H), 2.10 (t, *J* = 7.5 Hz, 2H), 1.69 (d, *J* = 6.8 Hz, 1H), 1.43–1.29 (m, 2H), 1.25 (12H, s), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.2, 82.9, 30.1, 24.7, 23.0, 14.2, 14.0 (the boron-bound carbon was not observed due to quadrupolar relaxation). Relative configuration of ***E*-2j** was assigned by correlation with ***Z*-2j**. The NMR spectral data of ***Z*-2j** are already described in the literature.[15]

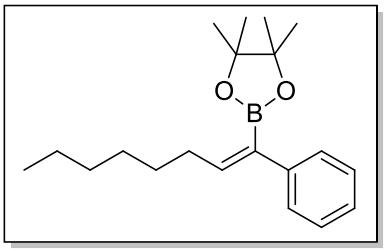


(*E*)-2-(1-Cyclohexylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k). Synthesized according to the general procedure A, using **Cat$_4$** (14 mg, 0.015 mmol), allylboronate **1l** (74 mg, 0.296 mmol) and anhydrous THF (1.5 mL). The reaction mixture was stirred for 16 h at 60 °C. Standard work-up and purification afforded the desired product **2l** in 96% yield with *E*/*Z* = 90:10 as a clear oil (71 mg, 0.284 mmol). ***E*-2k**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.19 (q, *J* = 6.7 Hz, 1H), 2.35 (t, *J* = 11.6 Hz, 1H), 2.09 (dd, *J* = 6.7, 0.6 Hz, 3H), 1.93–1.90 (m, 2H), 1.80–1.77 (m, 2H), 1.68–1.66 (m, 1H), 1.49–1.46 (m, 2H), 1.40–1.33 (m, 2H), 1.25–1.18 (m, 1H), 1.08

(s, 12H); ^{13}C {^{1}H} NMR (100 MHz, C_6D_6) δ 138.0, 82.6, 45.4, 33.7, 27.4, 26.8, 24.9, 17.6 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR (C_6D_6, 128 MHz) δ 31.15 ppm; HRMS (APCI): *m/z* calcd for $C_{15}H_{28}BO_2$ ([M + H]$^+$): 251.2177, found 251.2155. Isomer ***Z*-2k** was inseparable from isomer ***E*-2k**. ^{1}H NMR signals specific to the isomer ***Z*-2k** are as follows: 6.75 (q, *J* = 6.6 Hz, 1H), 2.63–2.52 (m, 1H). Relative configuration of ***E*-2k** was assigned by the nOe experiment, described on page S15.

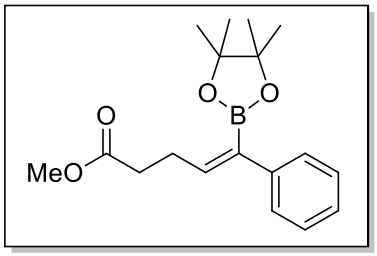


(*E*)-4,4,5,5-Tetramethyl-2-(1-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane (2l). Synthesized according to general procedure B, using **Cat$_4$** (18 mg, 0.019 mmol), homoallylboronate **1m** (100 mg, 0.387 mmol) and anhydrous toluene (2.0 mL). The reaction mixture was stirred for 16 h at 110 °C. Standard work-up and purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) afforded product **2l** in 82% yield with *E*/*Z* = 90:10 as a pale-yellow oil (82 mg, 0.319 mmol). The title compound **2l** could also be prepared from allylboronate **1n,** giving product **2l** in 80% yield with *E*/*Z* = 90:10. ***E*-2l**: Rf 0.37 (petroleum ether/ ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.23 (m, 4H), 7.16 (t, *J* = 7.1 Hz, 1H), 6.37 (t, *J* = 7.5 Hz, 1H), 2.42 (p, *J* = 7.5 Hz, 2H), 1.31 (s, 12H), 1.06 (t, *J* = 7.5 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.0, 143.1, 128.1, 127.1, 126.1, 83.4, 25.3, 24.8, 24.7, 14.4 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR ($CDCl_3$, 128 MHz) δ 31.05 ppm. Relative configuration of ***E*-2l** was assigned by correlation with ***Z*-2l**. The NMR spectral data of ***Z*-2l** are already described in the literature.[16]



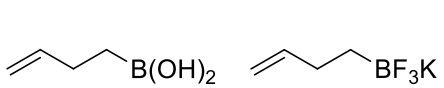
(*E*)-4,4,5,5-Tetramethyl-2-(1-phenylhept-1-en-1-yl)-1,3,2-dioxaborolane (2m). Synthesized according to general procedure B, using **Cat$_4$** (15 mg, 0.016 mmol), alkenylboronate **1o** (100 mg, 0.318 mmol) and anhydrous toluene (1.6 mL). The reaction mixture was stirred for 16 h at 110 °C. Standard work-up and purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) afforded the title compound **2m** in 70% yield with *E*/*Z* = 85:15 as a pale-yellow oil (70 mg, 0.222 mmol). ***E*-2m**: Rf 0.39 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.23 (m, 4H), 7.16 (t, *J* = 7.1 Hz, 1H), 6.37 (t, *J* = 7.5 Hz, 1H), 2.41 (q, *J* = 7.5 Hz, 2H), 1.47–1.41 (m, 2H), 1.31 (s, 12H), 1.29–1.23 (m, 2H), 1.18 (d, *J* = 7.8 Hz, 2H), 0.87 (t, *J* = 6.7 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.6,

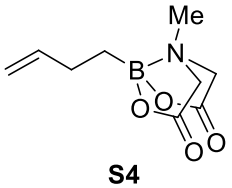
143.2, 128.1, 127.1, 126.0, 83.4, 31.9, 31.7, 29.8, 29.0, 24.8, 22.6, 14.1 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR ($CDCl_3$, 128 MHz) δ 30.73 ppm; HRMS (APCI): *m/z* calcd for $C_{20}H_{32}BO_2$ ([M + H]$^+$): 315.2490, found 315.2502. Relative configuration of ***E*-2m** was assigned by correlation with ***Z*-2m**. The NMR spectral data of ***Z*-2m** are already described in the literature.[17]



(*E*)-Methyl 5-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (2n). Synthesized according to general procedure B, using **Cat$_4$** (15 mg, 0.016 mmol), homoallylboronate **1p** (100 mg, 0.316 mmol) and anhydrous toluene (1.6 mL). The reaction mixture was stirred for 16 h at 110 °C. Standard work-up and purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1) afforded the title compound **2n** in 86% yield with *E*/*Z* = 92:8 as a pale-yellow oil (86 mg, 0.271 mmol). ***E*-2n**: Rf 0.22 (petroleum ether/ ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.25 (m, 4H), 7.20–7.16 (m, 1H), 6.35 (t, *J* = 7.6 Hz, 1H), 3.67 (s, 3H), 2.74 (q, *J* = 7.6 Hz, 2H), 2.47 (t, *J* = 7.6 Hz, 3H), 1.31 (s, 12H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.5, 144.7, 142.7, 128.1, 127.2, 126.4, 83.6, 51.5, 32.3, 29.7, 27.3, 24.8, 24.7 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR ($CDCl_3$, 128 MHz) δ 30.75 ppm; HRMS (APCI): *m/z* calcd for $C_{18}H_{26}BO_4$ ([M + H]$^+$): 317.1919, found 317.1916. ***Z*-2n** was inseparable from isomer ***E*-2n**. ^{1}H NMR signals specific to the isomer ***Z*-2n** are as follows: 6.75 (t, *J* = 7.5 Hz, 1H), 3.62 (s, 3H).

Unsuccessful Substrates

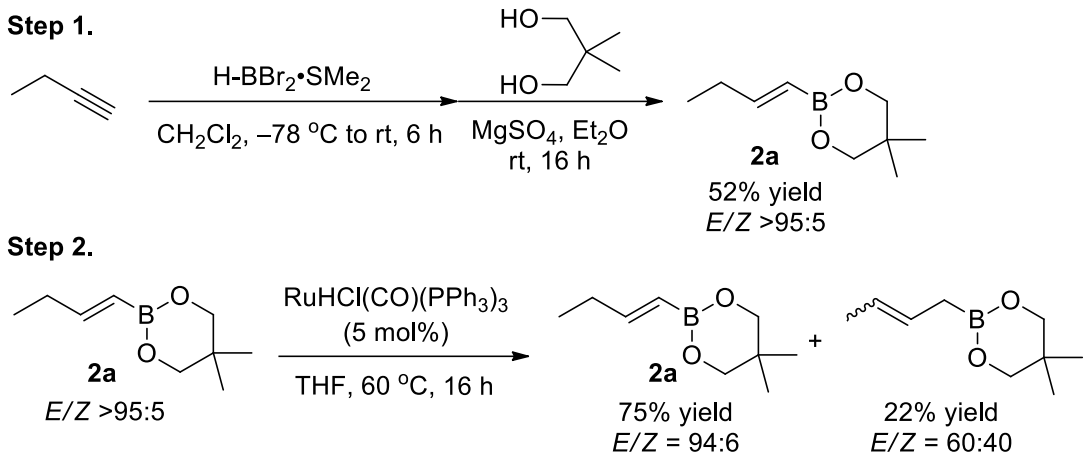




Compound	**S2**	**S3**	**S4**
Condition	A	A	A
Result	complex mixture	decomposed	only allyl isomers were observed

V. Experiments on reverse isomerization of vinylboronates

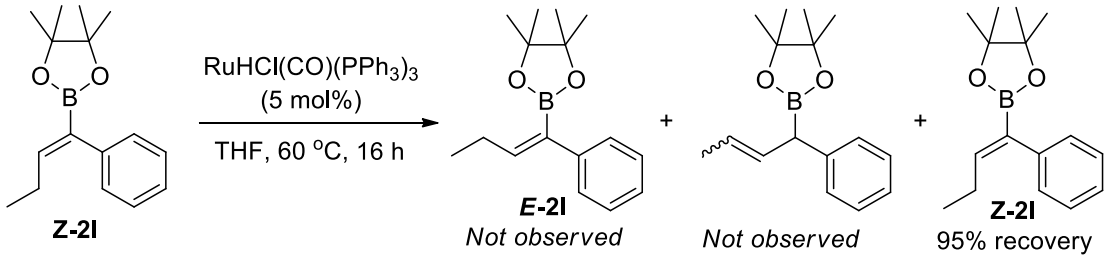
1. The examination of reverse isomerization of vinylboronate 2a



Step 1: Preparation of vinylboronate 2a from hydroboration. Based on a literature procedure.[11] A solution of condensed 1-butyne (7 mL, 87 mmol, 1.75 equiv) in CH_2Cl_2 (5 mL) was added to a CH_2Cl_2 solution of dibromoborane dimethylsulfide complex (1M in CH_2Cl_2, 50 mL, 50 mmol, 1.0 equiv) at −78°C. The mixture was allowed to warm to room temperature during 6 h. The mixture was quenched with 2M NaOH (63 mL, 125 mmol, 2.5 equiv) in an ice bath and extracted with EtOAc (2 × 50 mL). The organic extracts were combined, dried over Na_2SO_4, filtered, and concentrated. The residue was dissolved in anhydrous diethyl ether (70 mL), 2,2-dimethylpropane-1,3-diol (5.7g, 55 mmol, 1.1 equiv) and $MgSO_4$ (7.2 g, 60 mmol, 1.2 equiv) were added. The mixture was stirred for 16 h at room temperature. The suspension was filtered and washed with copious amounts of diethyl ether, and then concentrated. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/diethyl ether = 100:0 to 10:1) to give the vinylboronate **2a** as a clear oil (4.36 g, 52%). The NMR spectra data are already described on page S6.

Step 2: Ru-catalyzed Isomerization of vinylboronate 2a. Under argon atmosphere, $RuHCl(CO)(PPh_3)_3$ (14 mg, 0.015 mmol, 5 mol%) was added to a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was put under vacuum and backfilled with argon (3 times). A solution of **2a** (50 mg, 0.297 mmol, 1.0 equiv) in THF (1.5 mL) was added by syringe and stirred at 60 °C. After 16 h, the mixture was cooled to room temperature and quenched by evaporation of the solvent. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/diethyl ether = 20:0 to 10:1) to give compound **2a** along with partial inseparable *E*- and *Z*-allyl isomers as a clear oil (48 mg, 0.286 mmol, 96% yield). Using ^{1}H NMR spectroscopic analysis for a mixture of purified products, compound **2a** was observed in 74% yield with *E*/*Z* = 94:6, the corresponding allyl isomers were observed in 22% yield.

2. The examination of reverse isomerization of vinylboronate *Z*-2l

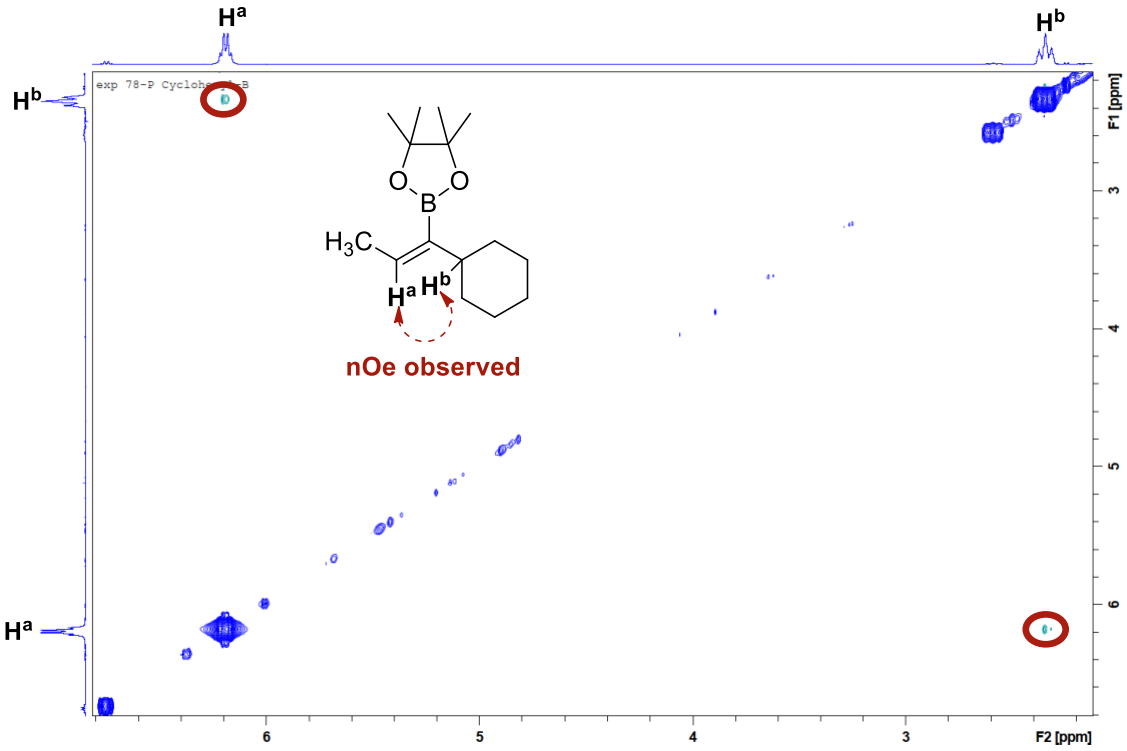


Ru-catalyzed Isomerization of vinylboronate *Z*-2l. According to a modified procedure as described above in **Step 2**. Using $RuHCl(CO)(PPh_3)_3$ (18 mg, 0.019 mmol), vinylboronate ***Z*-2l**[16] (100 mg, 0.387 mmol) and anhydrous THF (1.6 mL). After work-up, the formation of ***E*-2l** and the corresponding ally isomers was not observed in the ^1H NMR spectroscopic analysis of crude residue. Purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) recovered starting material ***Z*-2l** in 95% yield with *E*/*Z* > 95:5 as a pale-yellow oil (95 mg, 0.368 mmol).

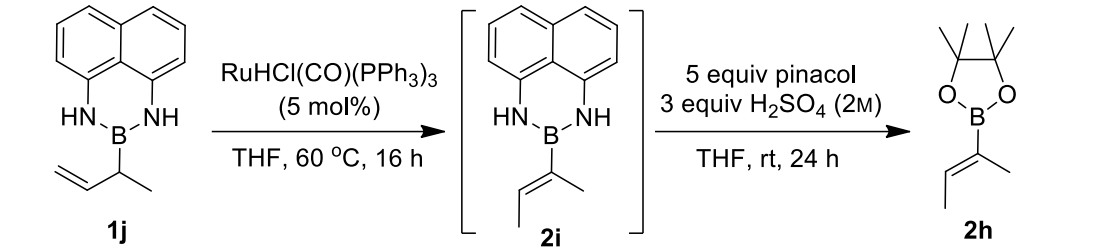
VI. Structure elucidation of *E*-2k and *Z*-2i

1. Determination of relative configuration of *E*-2k

Analysis of the nOe spectrum of **2k** shows a clear through space interaction between the vinyl H (**H^a**) and a CH (**H^b**), supporting the assignment as the *E*-isomer.



2. Determination of relative configuration of *Z*-2i-Bdan



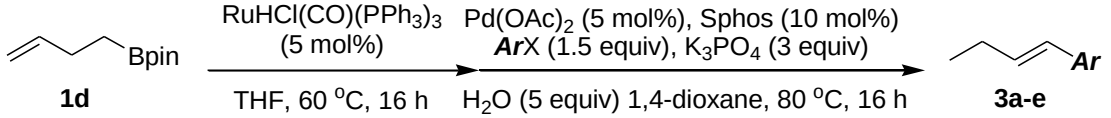
contained ca. 15 % of crotylBdan **S1**

Z/*E* 85:15

42% yield, *Z*/*E* 84:16 based on ^{1}H NMR

Transformation of allylBdan compound 1j to vinylBpin *Z*-2h. Under argon atmosphere, $RuHCl(CO)(PPh_3)_3$ (21 mg, 0.022 mmol, 5 mol%) was added to a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was put under vacuum and backfilled with argon (3 times). A solution of allylBdan **1j** (contained ca. 15 % of crotylBdan **S1**, 98.2 mg, 0.379 mmol, 1.0 equiv) in THF (3.0 mL) was added by syringe and stirred at 60 °C. After 16 h, H_2SO_4 (2 M, 0.67 mL, 1.3 mmol, 3.0 equiv) and pinacol (265 mg, 2.25 mmol, 5.0 equiv) were sequentially added to a stirred solution of containing vinylBdan intermediate **2i**. The mixture was stirred for 24 h at room temperature and quenched by water (5 mL). The mixture was extracted by diethyl ether, dried over Na_2SO_4, filtered, and concentrated. 2-Naphthaldehyde was then added as an internal standard for ^{1}H NMR spectroscopic analysis, formation of the vinylBpin compound **2h** was observed in 42 % yield with *Z*/*E* = 84:16.

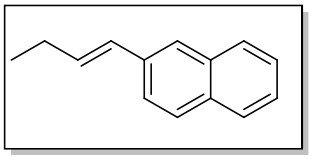
VII. Combined [Ru]-catalyzed isomerization with subsequent functionalization



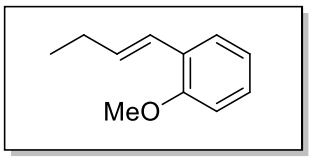
1d **3a-e**

General procedure for preparation of styrenes 3a-e. Under argon atmosphere, $RuHCl(CO)(PPh_3)_3$ (26 mg, 0.027 mmol, 5 mol%) was added to a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was put under vacuum and backfilled with argon (3 times). A solution of **1d** (100 mg, 0.549 mmol, 1.0 equiv) in THF (3.0 mL) was added by syringe and stirred at 60 °C. After 16 h, a second flame-dried Schlenk tube was charged with $Pd(OAc)_2$ (6 mg, 0.027 mmol, 5 mol%), Sphos (22 mg, 0.054 mmol, 10 mol%) and K_3PO_4 (349 mg, 1.648 mmol, 3.0 equiv). The tube was purged with argon, and then a solution of **Ar-X** (0.824 mmol, 1.5 equiv) in 1,4-dioxane (2.2 mL) was added *via* syringe under argon. After stirring for 5 min, the solution containing

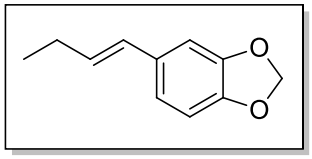
vinylboronate intermediate **2d** and H_2O (49 µL, 2.75 mmol, 5.0 equiv) were added into the one containing the Pd-complex *via* syringe under argon. The second Schlenk tube was sealed with a new septum, and then the reaction mixture was stirred at 80 °C for 16 h. The reaction was cooled to room temperature, quenched with water and extracted with diethyl ether (3 mL × 3). The combined organic phase was filtered through a pad of silica gel with copious washings by diethyl ether and concentrated. The crude residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100:0 to 10:1) to provide styrenyl products **3a-e**.



(*E*)-2-(But-1-en-1-yl)naphthalene (3a). Synthesized according to the general procedure using 2-bromonaphthalene (CAS# 580-13-2, 170 mg, 0.824 mmol). Standard work-up and purification afforded product **3a** as a pale-yellow solid (68 mg, 0.373 mmol, 68%, *E*/*Z* **=** 92:8). Rf 0.44 (petroleum ether/toluene = 20:1); mp 35-36 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.72 (m, 3H), 7.66 (s, 1H), 7.57 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.46–7.37 (m, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.42 (dt, *J* = 15.9, 6.3 Hz, 1H), 2.34–2.27 (m, 2H), 1.15 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.4, 133.7, 133.1, 132.6, 128.9, 128.0, 127.8, 127.6, 126.1, 125.4, 125.3, 123.6, 26.2, 13.7. The NMR spectral data matched reported literature values.[18]

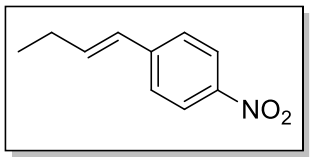


(*E*)-1-(But-1-en-1-yl)-2-methoxybenzene (3b). Synthesized according to the general procedure using 2-bromoanisole (CAS# 578-57-4, 154 mg, 0.824 mmol). Standard work-up and purification afforded product **3b** as a pale-yellow oil (54 mg, 0.333 mmol, 61%, *E*/*Z* **=** 92:8). Rf 0.38 (petroleum ether/ toulene = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.16 (ddd, *J* = 8.2, 7.8, 1.7 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.83 (dd, *J* = 8.2, 0.7 Hz, 1H), 6.69 (d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 15.9, 7.0 Hz, 1H), 3.82 (s, 3H), 2.29–2.21 (m, 2H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.2, 131.9, 127.7, 127.0, 126.3, 124.2, 120.6, 110.8, 55.5, 26.2, 13.9. The NMR spectral data matched reported literature values.[19]

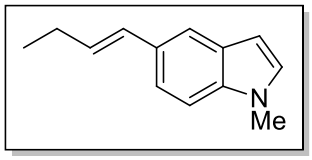


(*E*)-5-(But-1-en-1-yl)benzo[*d*][1,3]dioxole (3c). Synthesized according to the general procedure using 5-bromo-1,3-benzodioxole (CAS# 2635-13-4, 173 mg, 0.824 mmol). Standard work-up and purification afforded product **3c** as a pale-yellow oil (58 mg, 0.329 mmol, 60%, *E*/*Z* **=** 92:8). Rf 0.51 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 1.3 Hz, 1H), 6.75–6.70 (m, 2H), 6.26 (d, *J* = 15.7 Hz, 1H), 6.05 (dt, *J* = 15.7, 6.9 Hz, 1H), 5.91 (s, 2H), 2.22–2.15 (m, 2H),

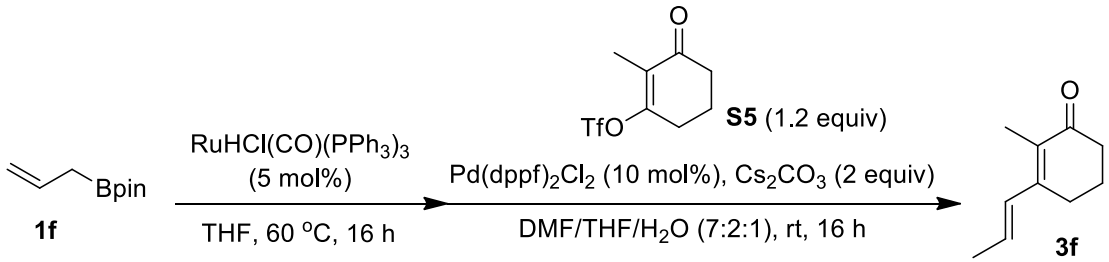
1.06 (t, *J* = 7.2 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.9 , 146.5 , 132.5 , 130.1 , 129.2 , 120.1, 108.2, 105.4, 100.9, 26.2, 13.9. The NMR spectral data matched reported literature values.[20]



(*E*)-1-(But-1-en-1-yl)-4-nitrobenzene (3d). Synthesized according to the general procedure using 1-bromo-4-nitrobenzene (CAS# 586-78-7, 166 mg, 0.824 mmol). Standard work-up and purification afforded product **3d** as a pale-yellow oil (64 mg, 0.363 mmol, 66%, *E*/*Z* = 92:8). Rf 0.47 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 6.51–6.43 (m, 2H), 2.35–2.24 (m, 2H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.4, 144.5, 138.0, 127.2, 126.3, 123.9, 26.2, 13.2. The NMR spectral data matched reported literature values.[21]

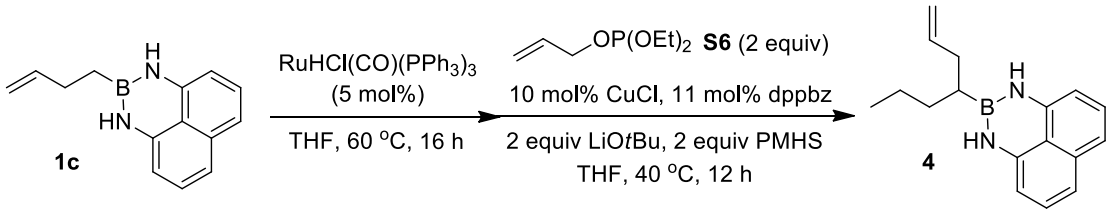


(*E*)-5-(But-1-en-1-yl)-1-methyl-1*H*-indole (3e). Synthesized according to the general procedure using 5-bromo-1-methyl-1*H*-indole (CAS# 10075-52-2, 173 mg, 0.824 mmol). Standard work-up and purification afforded product **3e** as a pale-yellow oil (57 mg, 0.308 mmol, 56%, *E*/*Z* = 91:9). Rf 0.38 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.28 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 3.0 Hz, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.43 (d, *J* = 3.0 Hz, 1H), 6.20 (dt, *J* = 15.8, 6.7 Hz, 1H), 3.76 (s, 3H), 2.28–2.21 (m, 2H), 1.10 (t, *J* = 6.7 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.1, 129.7 (CH × 2), 129.6, 129.1, 128.7, 119.8, 118.5, 109.2, 101.0, 32.8, 26.1, 13.9; HRMS (APCI): *m/z* calcd for $C_{13}H_{16}N$ ([M + H]$^{+}$): 186.1277, found 186.1270.



(*E*)-2-Methyl-3-(prop-1-en-1-yl)cyclohex-2-enone (3f). Under argon atmosphere, $RuHCl(CO)(PPh_3)_3$ (28 mg, 0.029 mmol, 5 mol%) was added to a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was put under vacuum and backfilled with argon (3 times). A solution of **1f** (100 mg, 0.595 mmol, 1.0 equiv) in THF (3.0 mL) was added by syringe and stirred at 60 °C. After 16 h, a second flame-dried Schlenk tube was charged with $Pd(dppf)_2Cl_2$ (43 mg, 0.059 mmol, 10 mol%) and Cs_2CO_3 (388

mg, 1.19 mmol, 2.0 equiv). The flask was purged with argon, and then a solution of vinyl triflate **S5** (184 mg, 0.714 mmol, 1.2 equiv) in the co-solvent DMF/THF/H_2O (4.2/1.2/0.6 mL) was added *via* syringe under argon. After stirring for 5 min, the solution containing vinylboronate intermediate **2e** was added into the one containing the Pd-complex *via* syringe under argon. The second Schlenk tube was sealed with a new septum, and then the reaction mixture was stirred at room temperature for 16 h. The reaction was quenched with water and extracted with diethyl ether (3 mL × 3). The combined organic phase was filtered through a pad of silica gel with copious washings by diethyl ether and concentrated. The crude residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) to give product **3f** as a pale-yellow oil (73 mg, 0.488 mmol, 82%, *E*/*Z* = 91:9). Rf 0.25 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (d, *J* = 15.6 Hz, 1H), 6.16 (dq, *J* = 15.6, 6.7 Hz, 1H), 2.44 (t, *J* = 6.0 Hz, 2H), 2.41–2.37 (m, 2H), 1.96–1.91 (m, 2H), 1.89 (d, *J* = 6.9 Hz, 1H), 1.85 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.0, 149.9, 132.9, 130.3, 129.9, 37.8, 26.1, 22.1, 19.3, 10.4. The NMR spectral data matched reported literature values.[22]



2-(Hept-1-en-4-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4). Under argon atmosphere, $RuHCl(CO)(PPh_3)_3$ (21 mg, 0.022 mmol, 5 mol%) was added to a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was put under vacuum and backfilled with argon (3 times). A solution of **1c** (100 mg, 0.450 mmol, 1.0 equiv) in THF (2.2 mL) was added by syringe and stirred at 60 °C. After 16 h, a mixture of CuCl (4 mg, 0.045 mmol, 10 mol%), dppbz (22 mg, 0.049 mmol, 11 mol%) and LiO*t*Bu (72 mg, 0.900 mmol, 2.0 equiv) in THF (2.2 mL) were stirred for 5 min in a second flame-dried Schlenk tube under argon. The second reaction mixture was added PMHS (54 mg, 0.900 mmol, 2.0 equiv) and stirred at room temperature. After 15 min, the solution containing vinylboronate intermediate **2c** and diethyl allyl phosphate **S6** (CAS# 3066-75-9, 0.16 mL, 0.900 mmol, 2.0 equiv) were added into the one containing the Cu-complex *via* syringe under argon. The second Schlenk tube was sealed with a new septum, and the reaction mixture was stirred at 60 °C. After 12 h, the reaction mixture was quenched with hydrochloric acid (0.5 M in methanol, 10 mL), and extracted with diethyl ether (5 mL × 3). The organic extracts were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was

purified by flash column chromatography on Florisil® (petroleum ether/diethyl ether 20:1 to 10:1) to give product **4** as a clear oil (81 mg, 0.306 mmol, 68%). Rf 0.41 (petroleum ether/ethyl acetate = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 8.2, 7.3 Hz, 2H), 6.98 (dd, *J* = 8.2, 0.7 Hz, 2H), 6.28 (dd, *J* = 7.3, 0.7 Hz, 2H), 5.85–5.78 (m, 1H), 5.59 (br, 2H), 5.03 (dd, *J* = 17.0, 3.4, 1.5 Hz, 1H), 4.96 (ddt, *J* = 10.1, 2.0, 1.0 Hz, 1H), 2.17 (t, *J* = 7.2 Hz, 2H), 1.42–1.28 (m, 4H), 1.09–1.01 (m, 1H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.1, 138.4, 136.3, 127.5, 119.6, 117.4, 115.3, 105.5, 36.4, 34.1, 22.2, 14.1 (the boron-bound carbon was not observed due to quadrupolar relaxation); ^{11}B NMR ($CDCl_3$, 128 MHz) δ 32.98 ppm; HRMS (APCI): *m/z* calcd for $C_{17}H_{22}BN_2$ ($[M + H]^+$): 265.1871, found 265.1864.

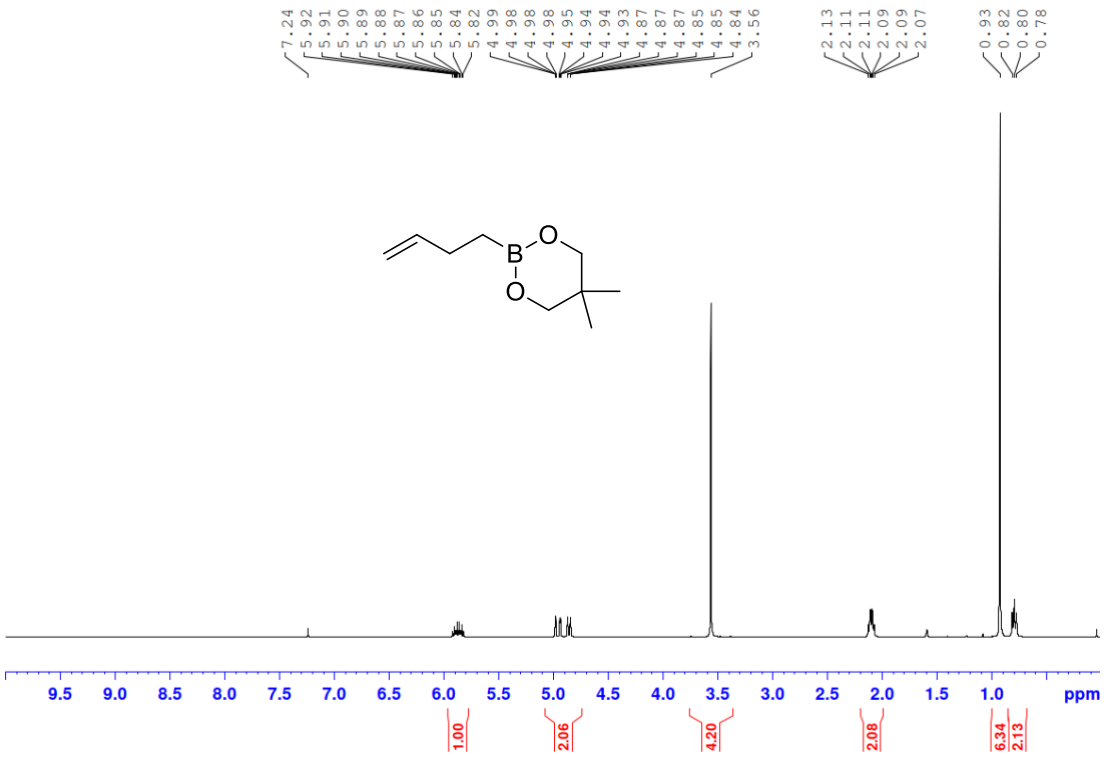
VIII. References

1. H. Yoshida, Y. Takemoto, S. Kamio, I. Osaka, K. Takaki, *Org. Chem. Front.* **2017**, *4*, 1215.
2. P. Sušnik, G. Hilt, *Organometallics*, **2014**, *33*, 5907.
3. A. Millán, J, R. Smith, J. L.-Y. Chen, V. K. Aggarwal, *Angew. Chem. Int. Ed.* **2016**, *55*, 2498.
4. C. A. Incerti–Pradillos, M. A. Kabeshov, A. V. Malkov, *Angew. Chem. Int. Ed.* **2013**, *52*, 5338.
5. P. J. Unsworth, D. Leonori, V. K. Aggarwal, *Angew. Chem. Int. Ed.* **2014**, *53*, 9846.
6. F. Weber, M. Ballmann, C. Kohlmeyer, G. Hilt, *Org. Lett.* **2016**, *18*, 548.
7. L. Chausset-Boissarie, K. Ghozati, E. LaBine, J. L.-Y. Chen, V. K. Aggarwal, C. M. Crudden, *Chem. Eur. J.* **2013**, *19*, 17698.
8. I. Ibrahem, P. Breistein, A. Crdóva, *Angew. Chem. Int. Ed.* **2011**, *50*, 12036.
9. H. Burghart-Stoll, R. Brückner, *Org. Lett.* **2011**, *13*, 2730.
10. T. Hatakeyama, M. Nakamura, E. Nakamura, *J. Am. Chem. Soc.* **2009**, *130,* 15688.
11. M. Althaus, A. Mahmood, J. R. Suárez, S. P. Thomas, V. K. Aggarwal, *J. Am. Chem. Soc.* **2010**, *132,* 4025.
12. Z.-J. Yao, S. Hong, W. Zhang, M. Liu, W. Deng, *Tetrahedron Lett.* **2016**, *57*, 910.
13. J. L.-Y. Chen, H. K. Scott, M. J. Hesse, C. L. Willis, V. K. Aggarwal, *J. Am. Chem. Soc.* **2013**, *135*, 5316.
14. R. J. Armstrong, C. Sandford, C. García-Ruiza, V. K. Aggarwal, *Chem. Commun.* **2017**, *53*, 4922.
15. E. Nieto-Sepulveda, A. D. Bage, L. A. Evans, T. A. Hunt, A. G. Leach, S. P. Thomas, G. C. Lloyd-Jones, *J. Am. Chem. Soc.* **2019**, *141*, 18600.
16. Y. Hu, W. Sun, T. Zhang, N. Xu, J. Xu, Y. Lan, C. Liu, *Angew. Chem. Int. Ed.* **2019**, *58*, 15813.

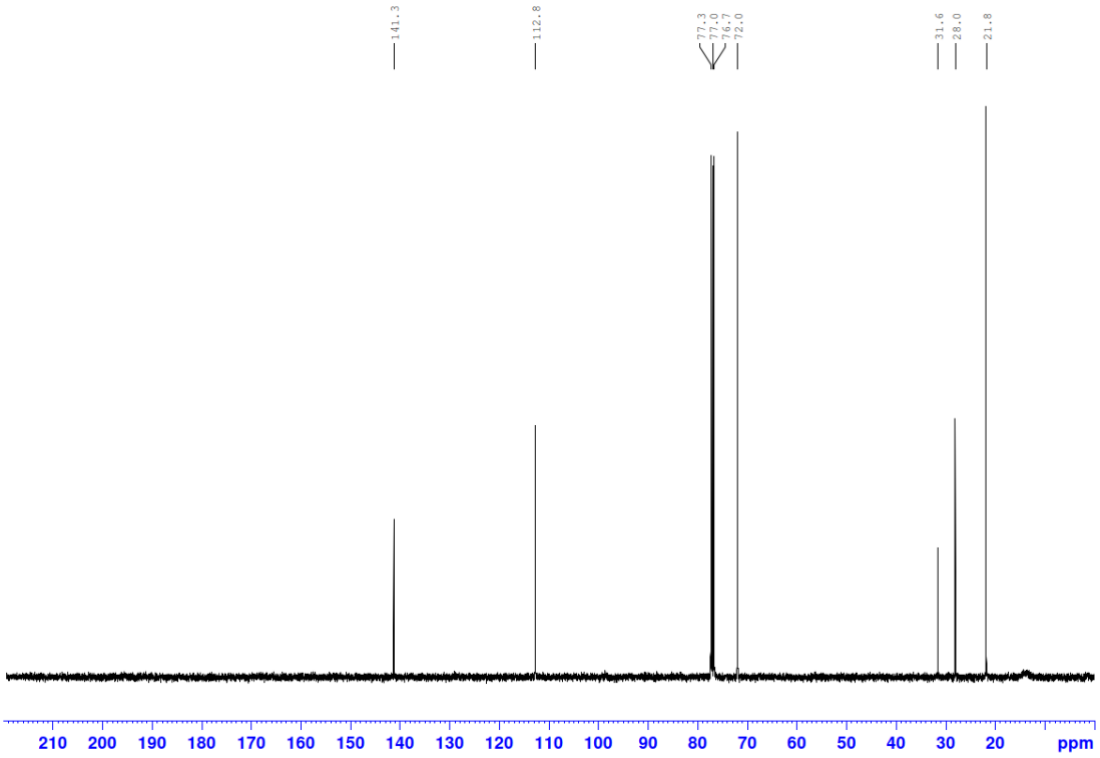
17. S. Xu, .C-T. Lee, H. Rao, E.-i. Negishi, *Adv. Synth. Catal.* **2011**, *353*, 2981.
18. B. Górski, A. Talko, T. Basak, M. Barbasiewicz, *Org. Lett.* **2017**, *19*, 1756.
19. Y. Hu, J. Yu, S. Yang, J.-X. Wang, Y. Yin, *Synth. Commun.* **1999**, *29*, 1157.
20. T. Wang, Y. Hua, S. Zhang, *Org. Biomol. Chem.* **2010**, *8*, 2312.
21. B. Gutmann, P. Elsner, T. Glasnov, D. M. Roberge, C. O. Kappe, *Angew. Chem. Int. Ed.* **2014**, *53*, 11557.
22. M. Cheng, M. Hulce, *J. Org. Chem.* **1990**, *55,* 964.

IX. NMR spectra

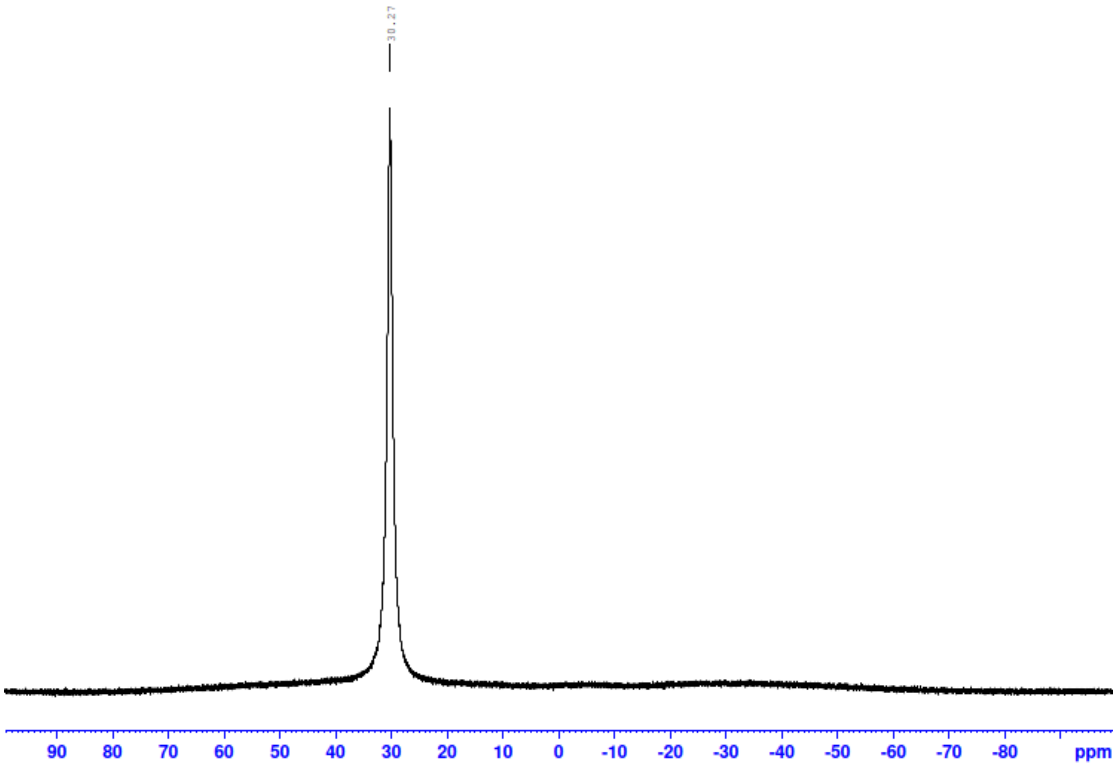
^{1}H NMR Spectrum of **1a**, 400 MHz, $CDCl_3$



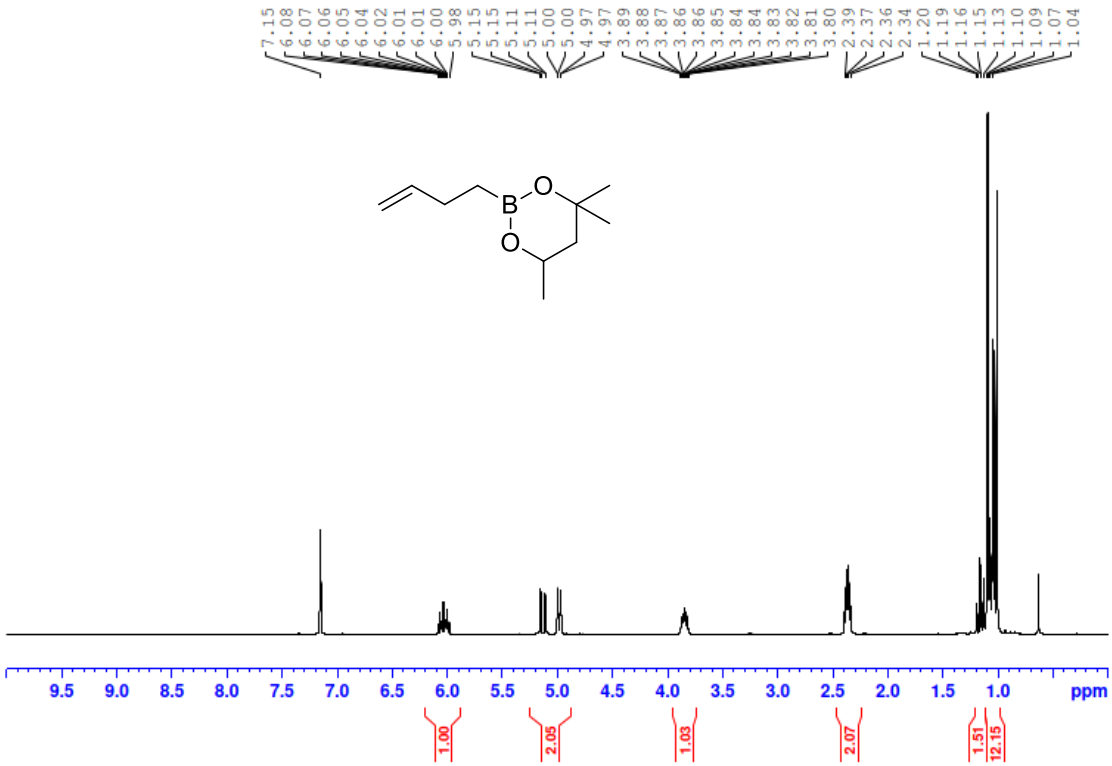
^{13}C {^{1}H} NMR Spectrum of **1a**, 100 MHz, $CDCl_3$



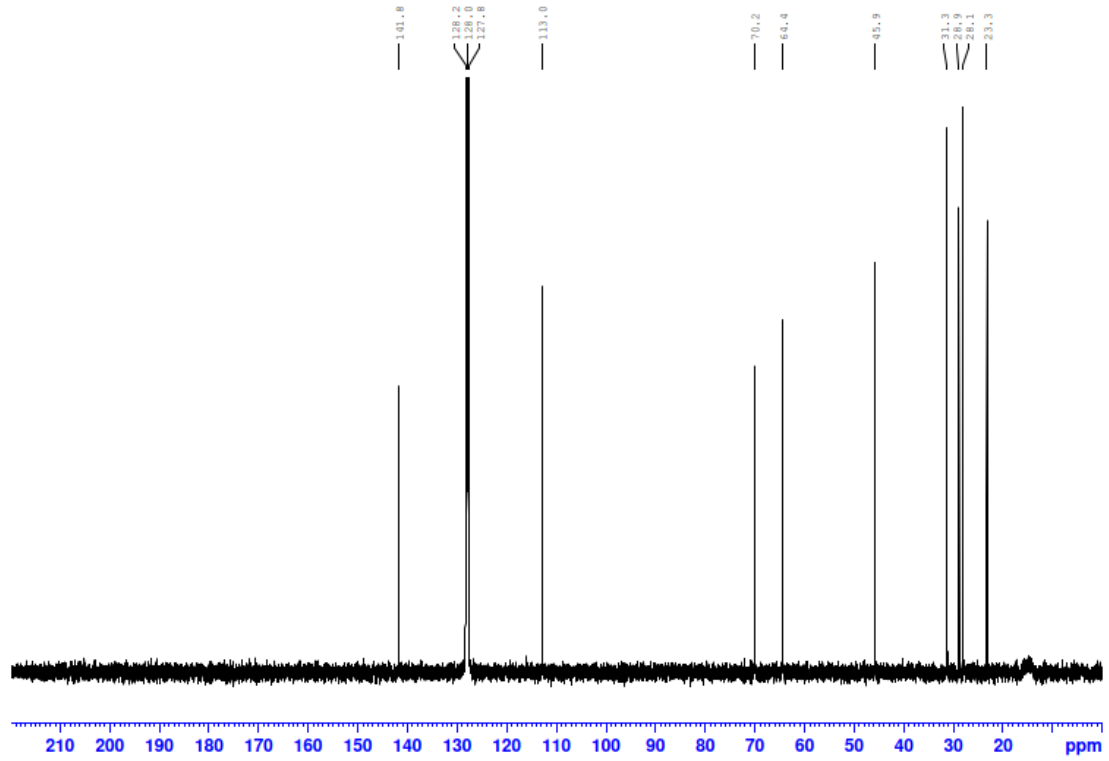
^{11}B NMR Spectrum of **1a**, 128 MHz, $CDCl_3$



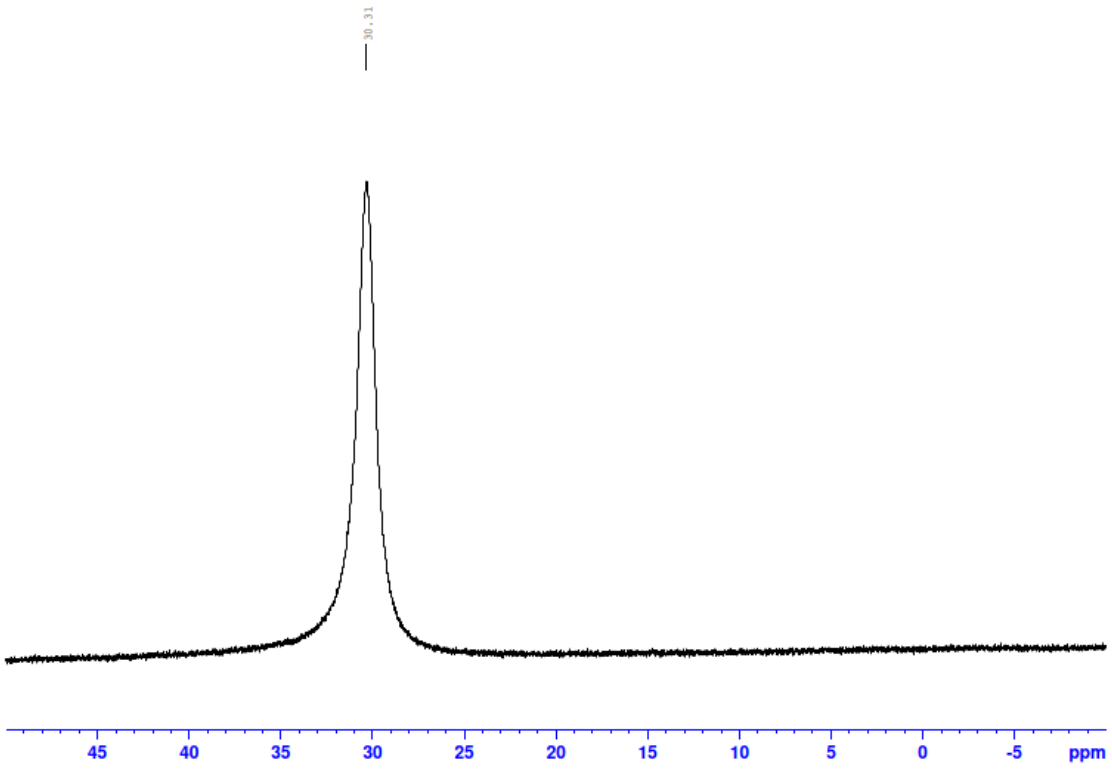
^{1}H NMR Spectrum of **1b**, 400 MHz, C_6D_6



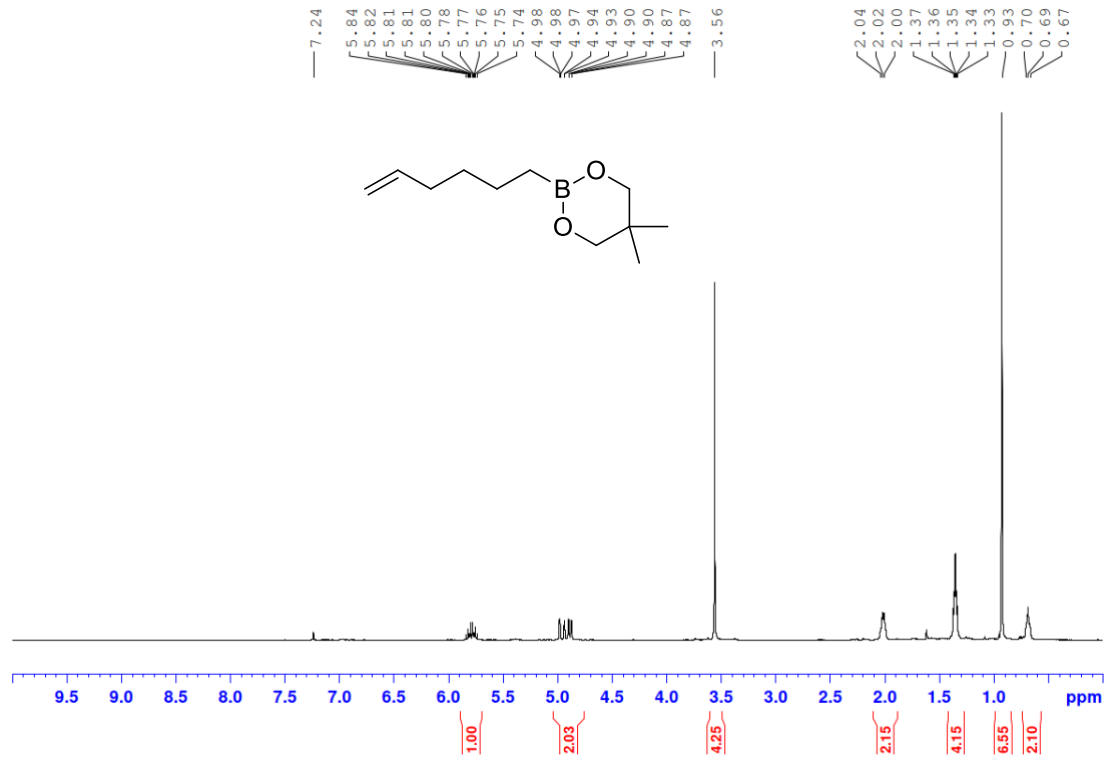
^{13}C {^{1}H} NMR Spectrum of **1b**, 100 MHz, C_6D_6



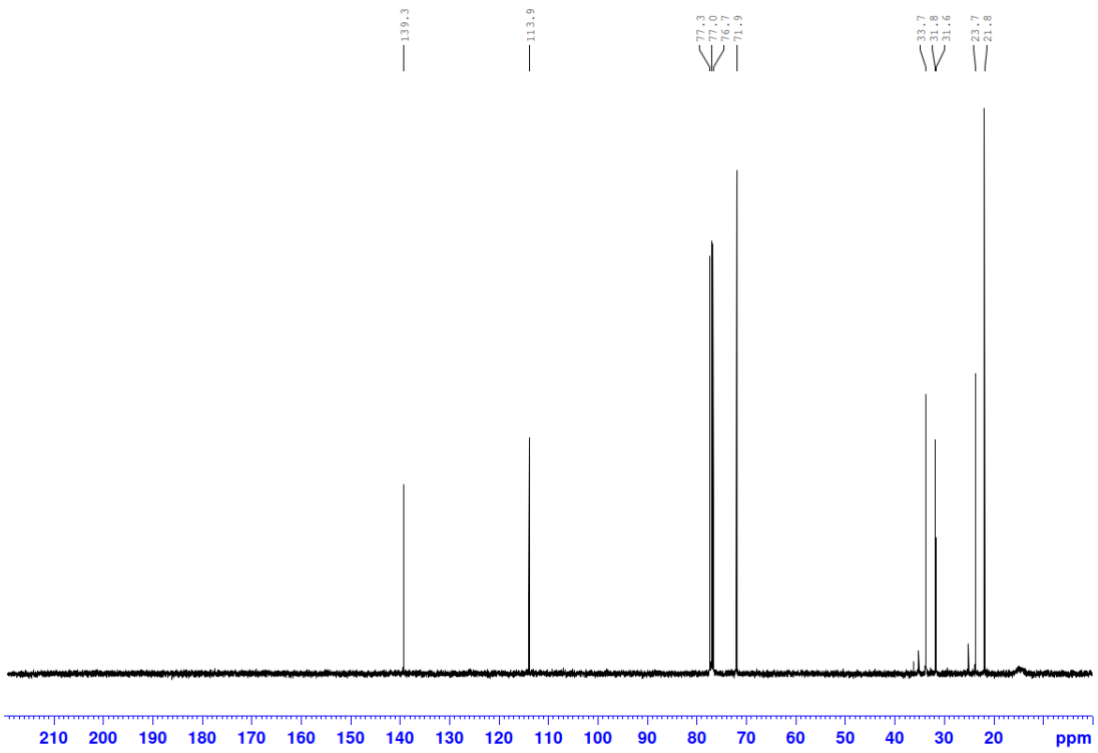
^{11}B NMR Spectrum of **1b**, 128 MHz, C_6D_6



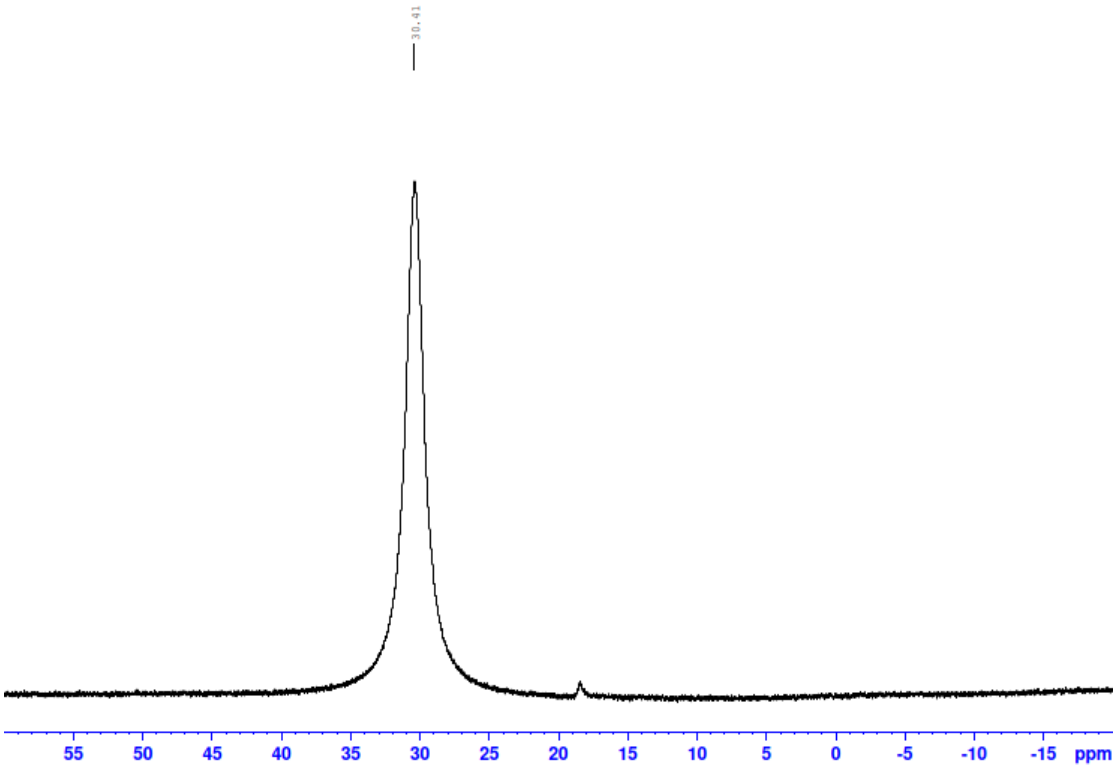
^{1}H NMR Spectrum of **1g**, 400 MHz, $CDCl_3$



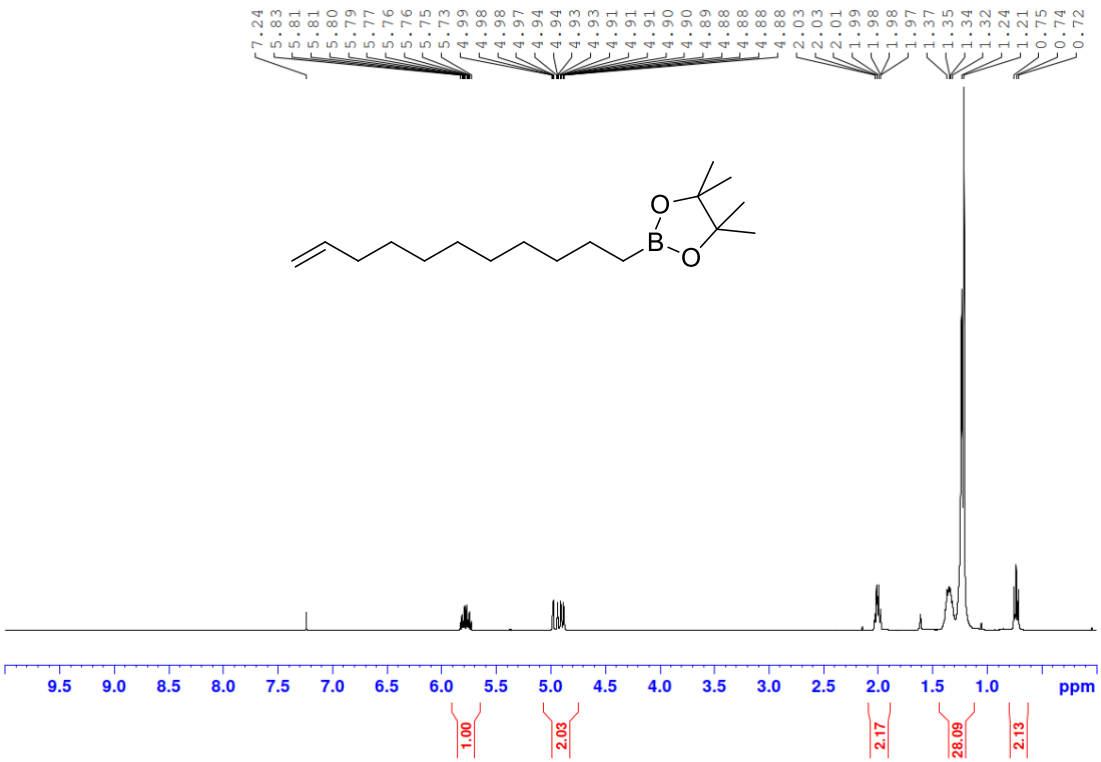
^{13}C {^{1}H} NMR Spectrum of **1g**, 100 MHz, $CDCl_3$



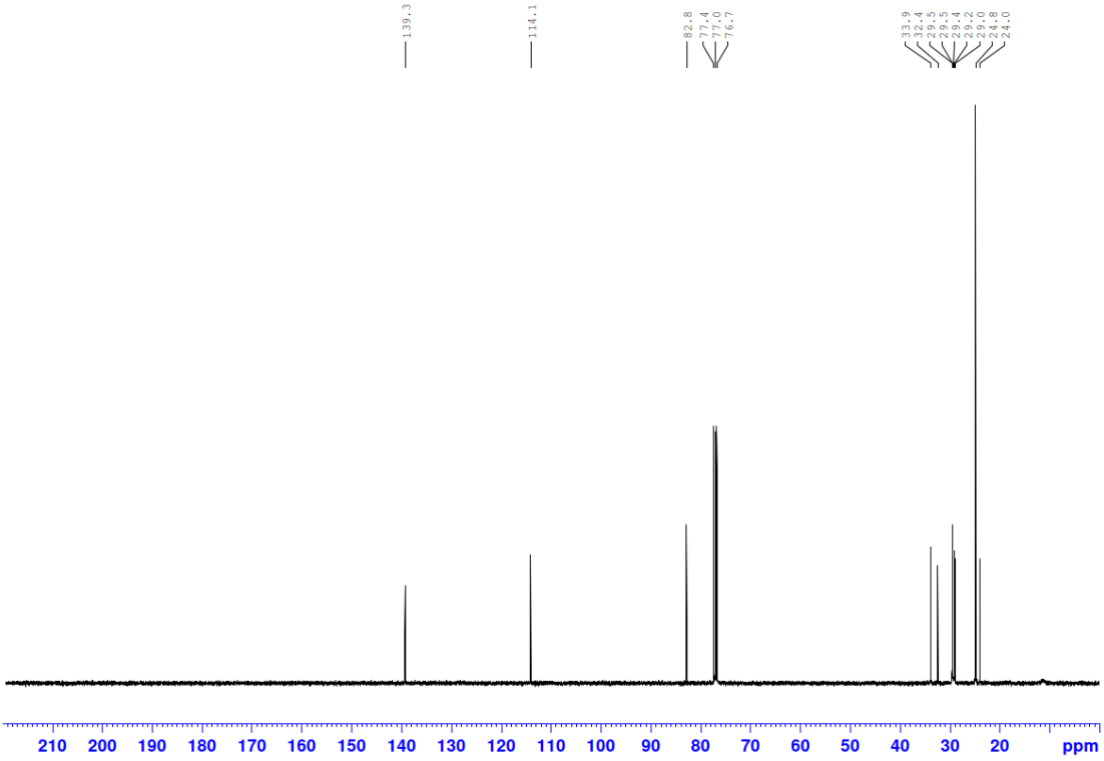
^{11}B NMR Spectrum of **1g**, 128 MHz, $CDCl_3$



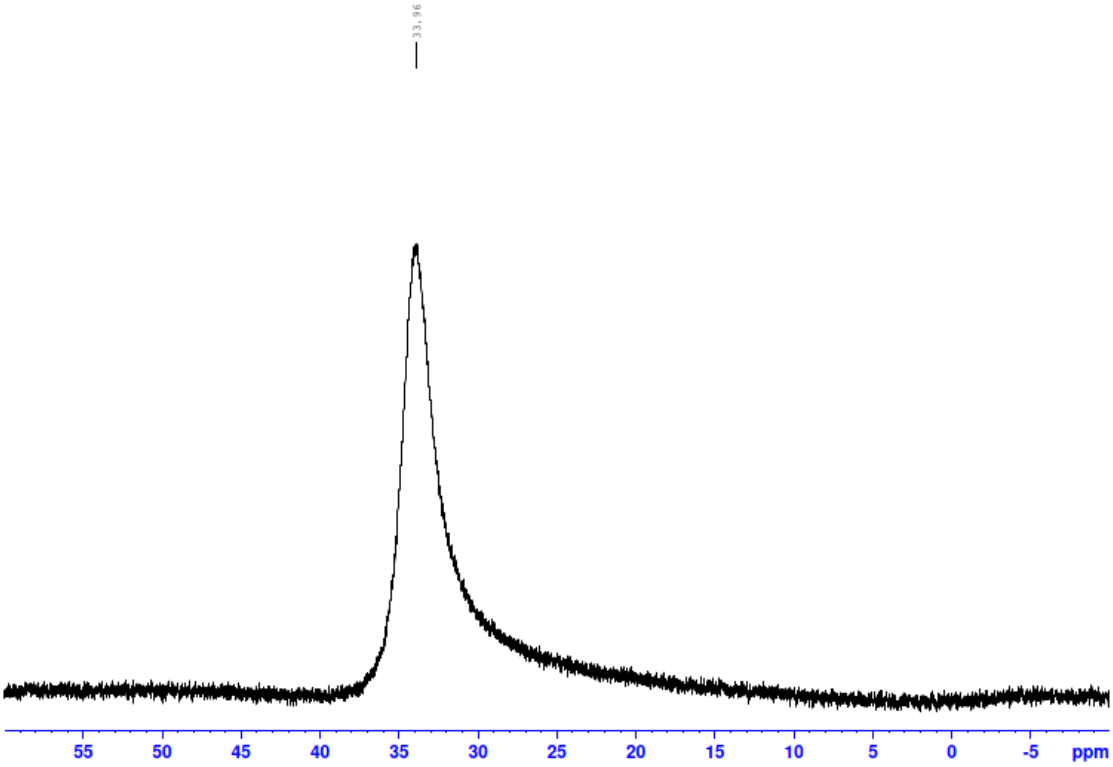
^{1}H NMR Spectrum of **1h**, 400 MHz, $CDCl_3$



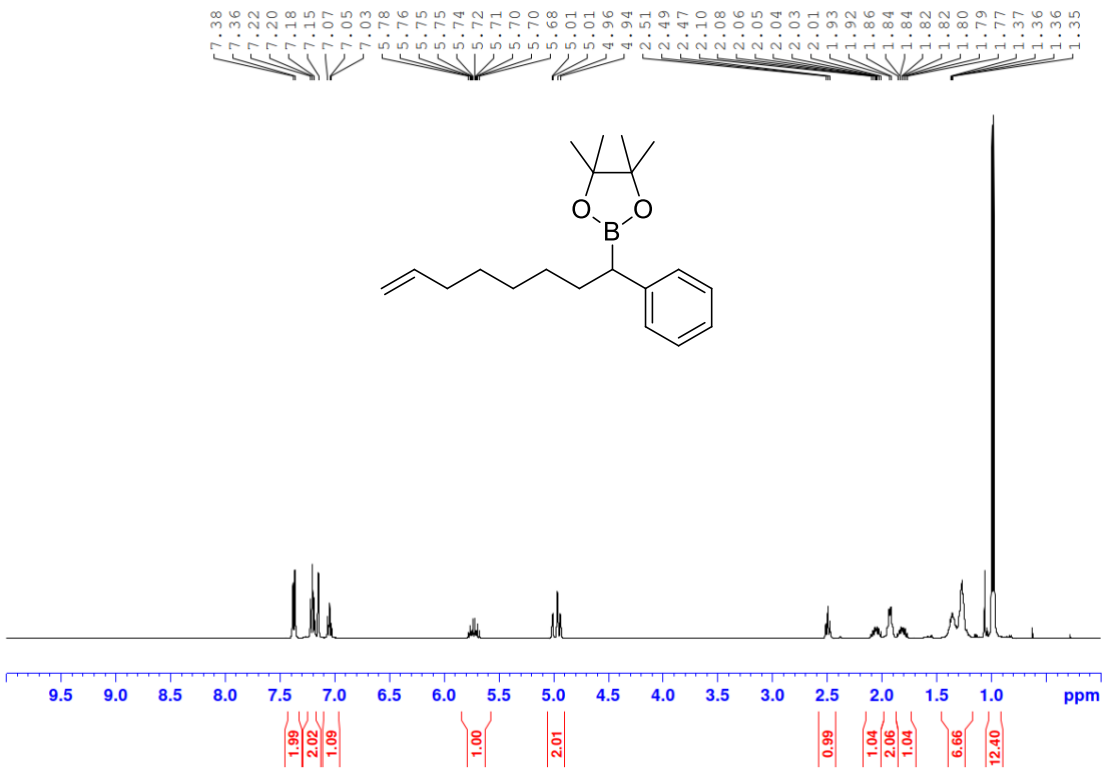
^{13}C {^{1}H} NMR Spectrum of **1h**, 100 MHz, $CDCl_3$



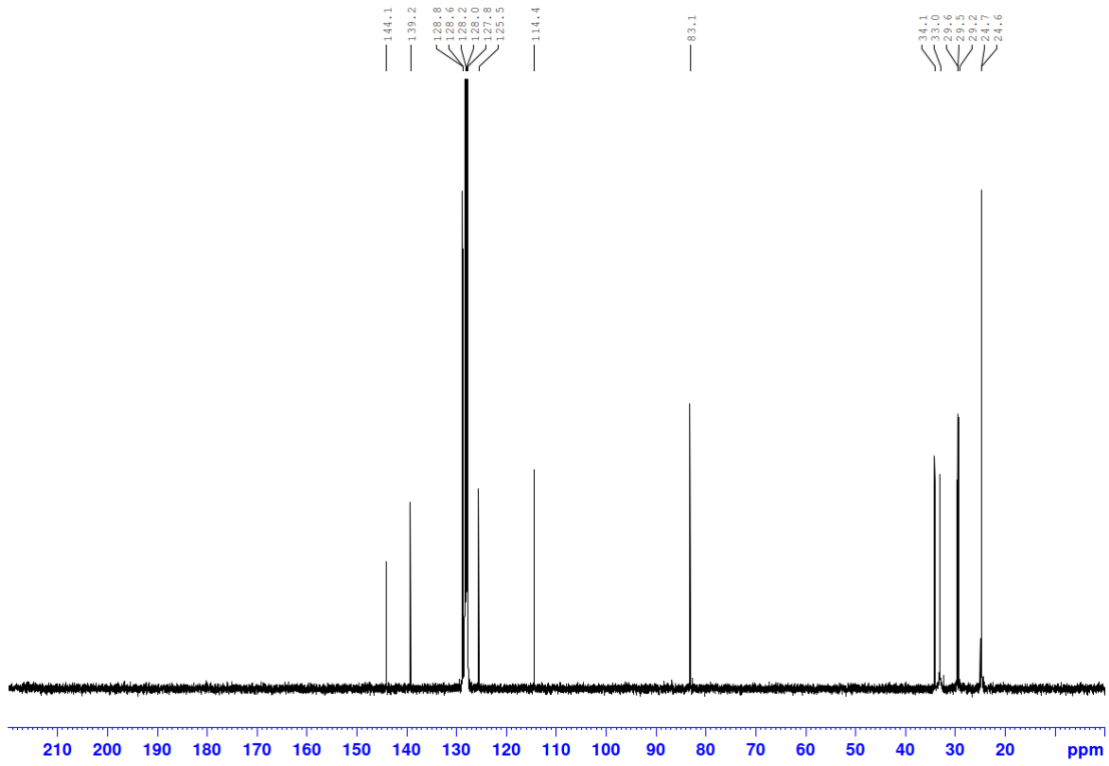
^{11}B NMR Spectrum of **1h**, 128 MHz, $CDCl_3$



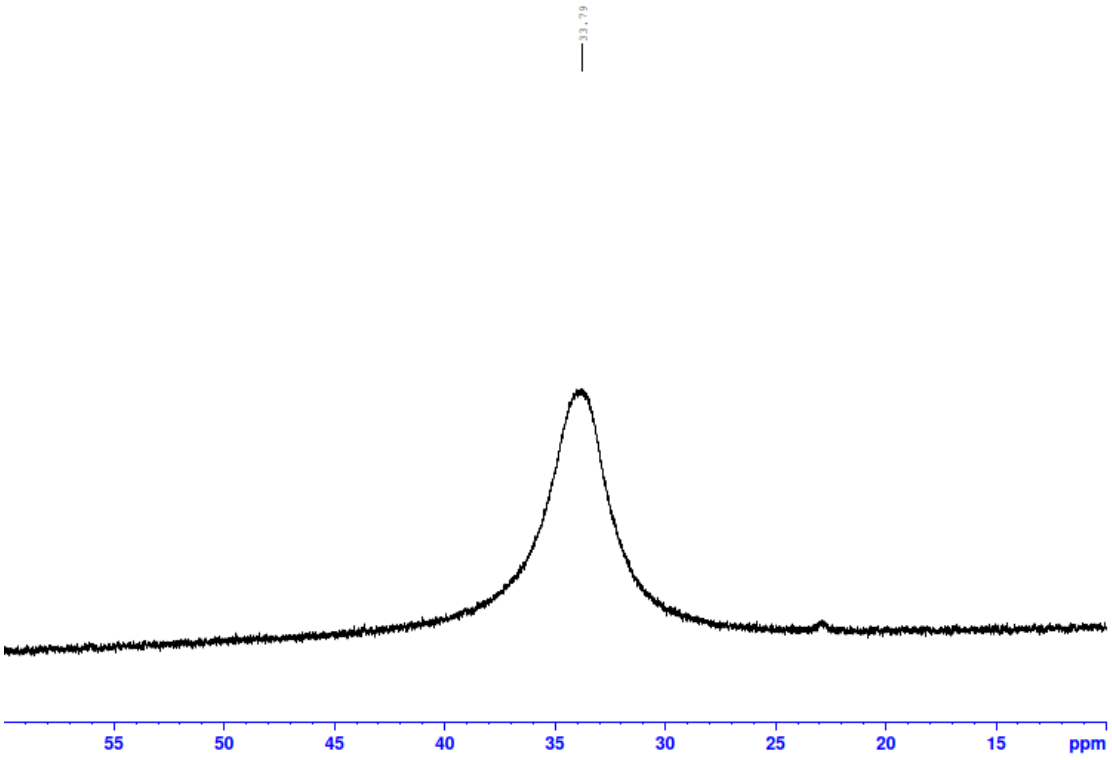
^{1}H NMR Spectrum of **1o**, 400 MHz, C_6D_6



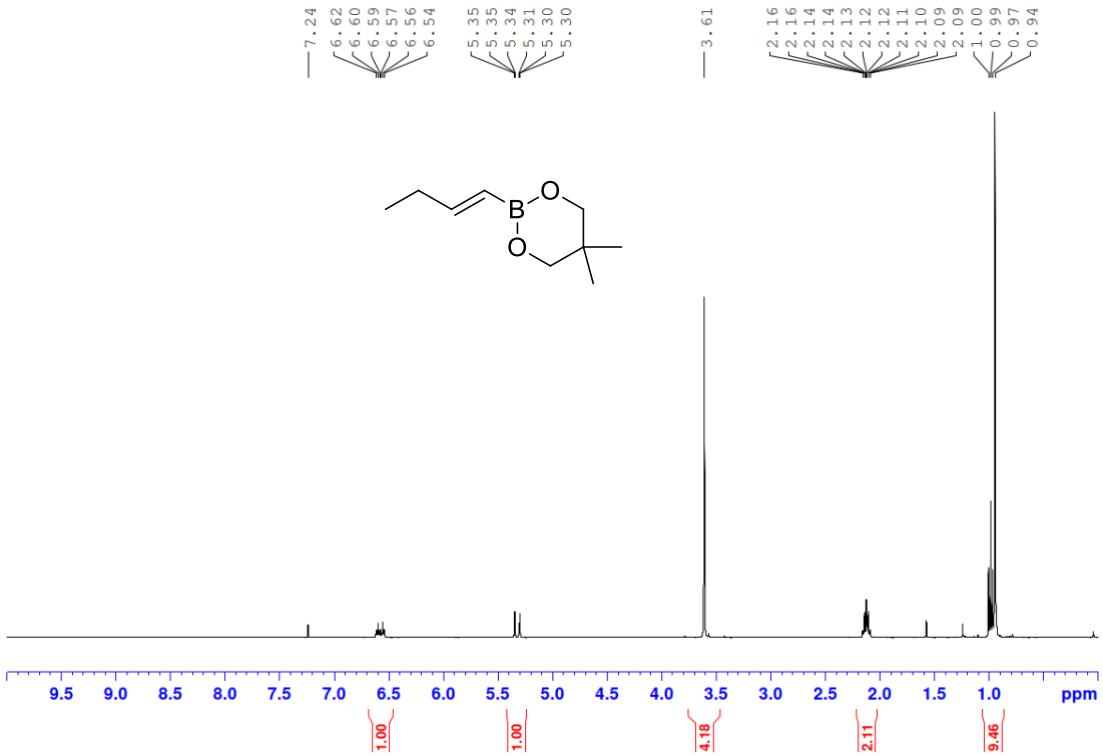
^{13}C {^{1}H} NMR Spectrum of **1o**, 100 MHz, C_6D_6



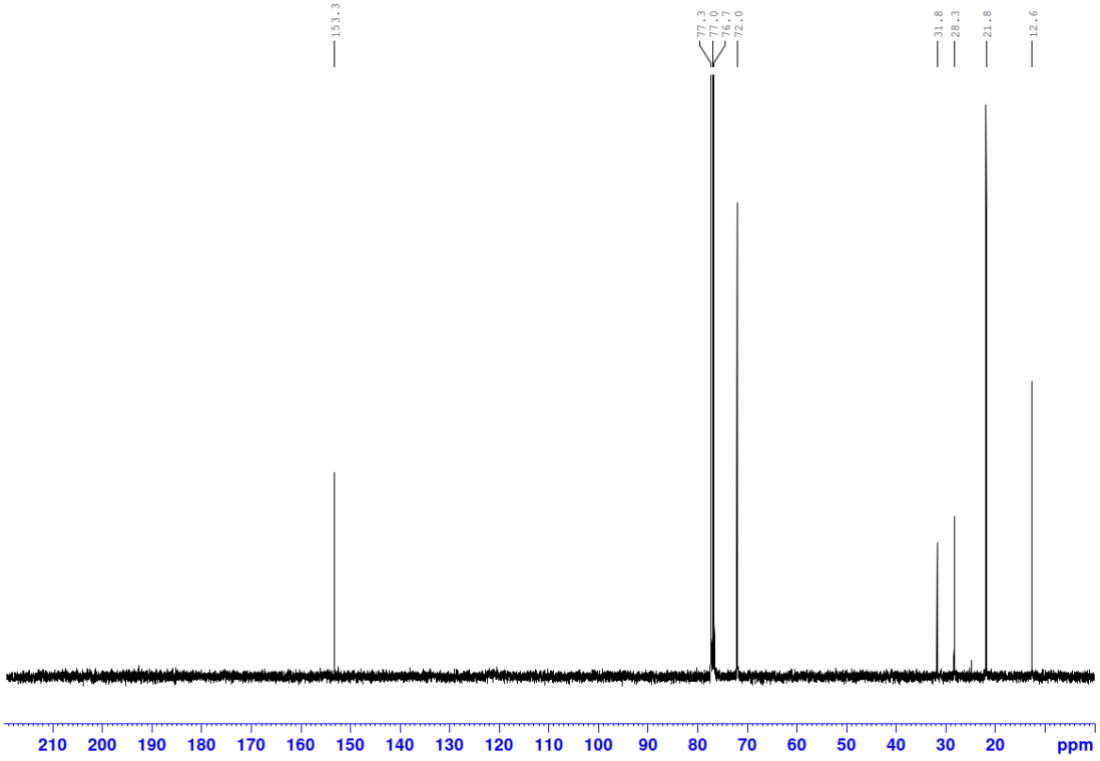
^{11}B NMR Spectrum of **1o**, 128 MHz, C_6D_6



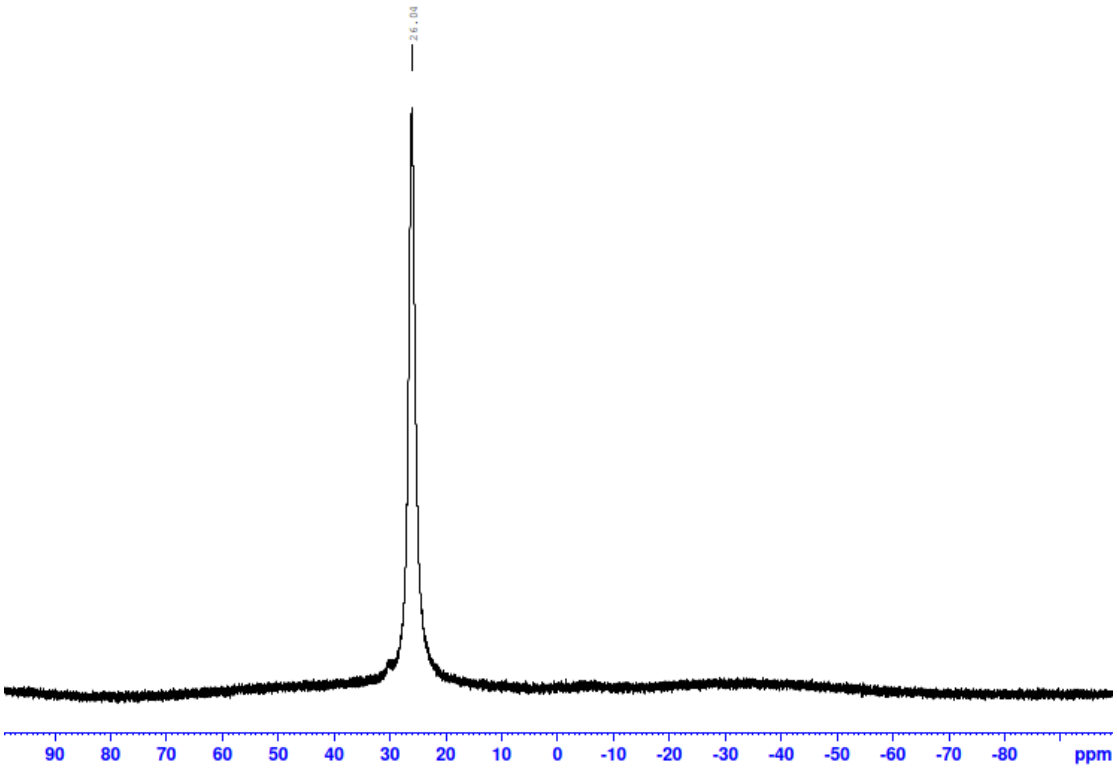
^{1}H NMR Spectrum of **2a**, 400 MHz, $CDCl_3$



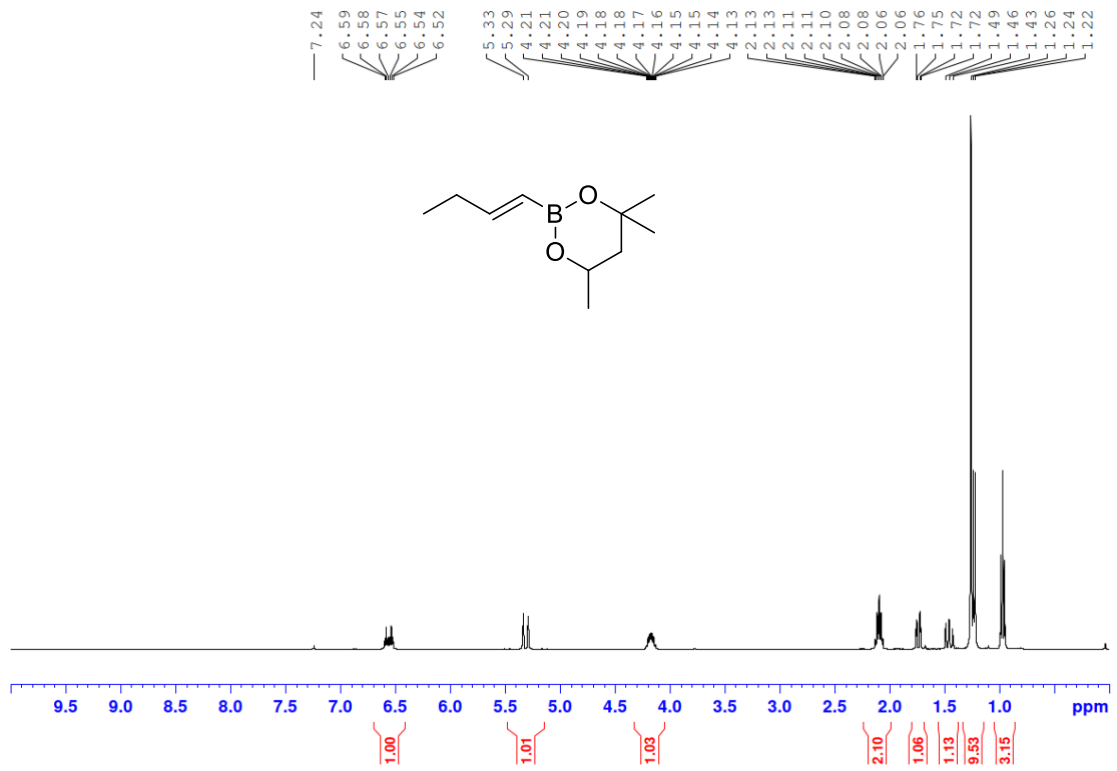
^{13}C {^{1}H} NMR Spectrum of **2a**, 100 MHz, $CDCl_3$



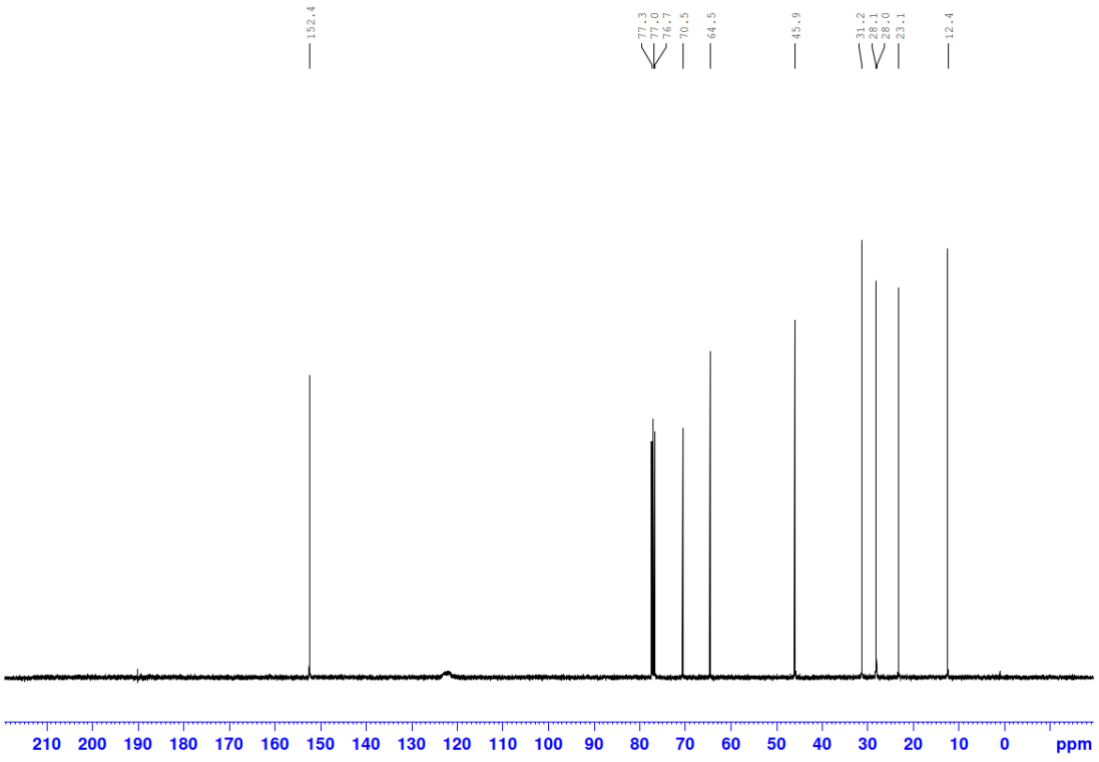
^{11}B NMR Spectrum of **2a**, 128 MHz, $CDCl_3$



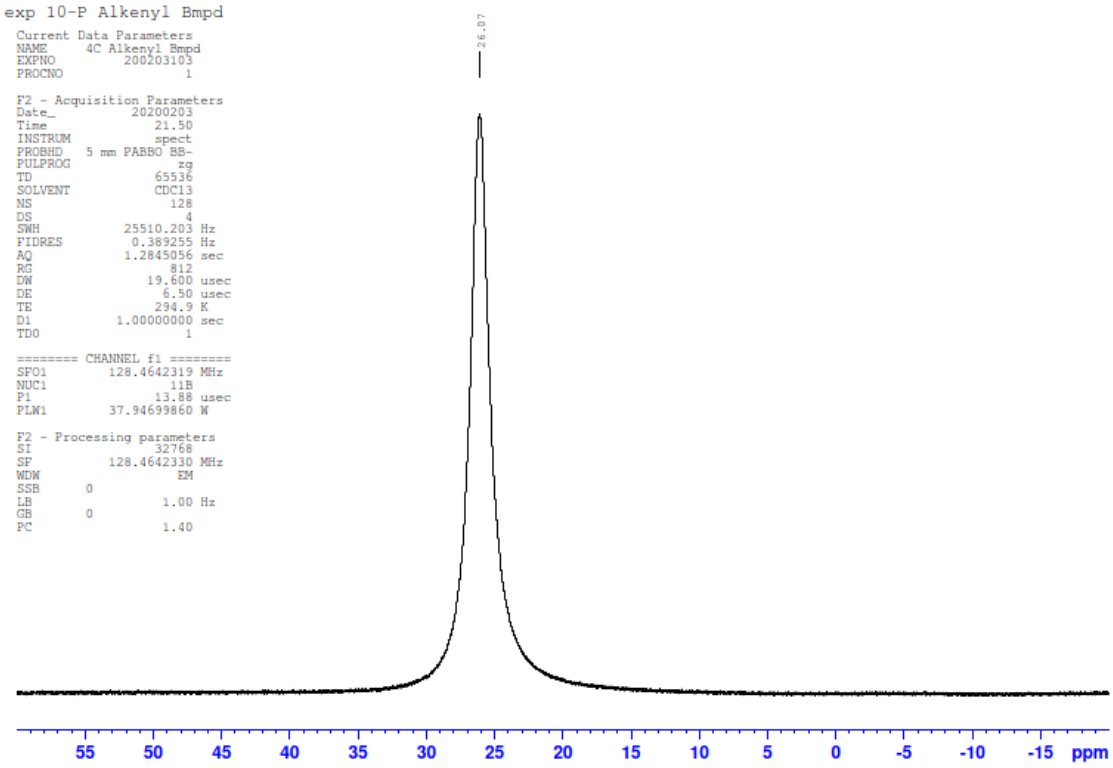
^{1}H NMR Spectrum of **2b**, 400 MHz, $CDCl_3$



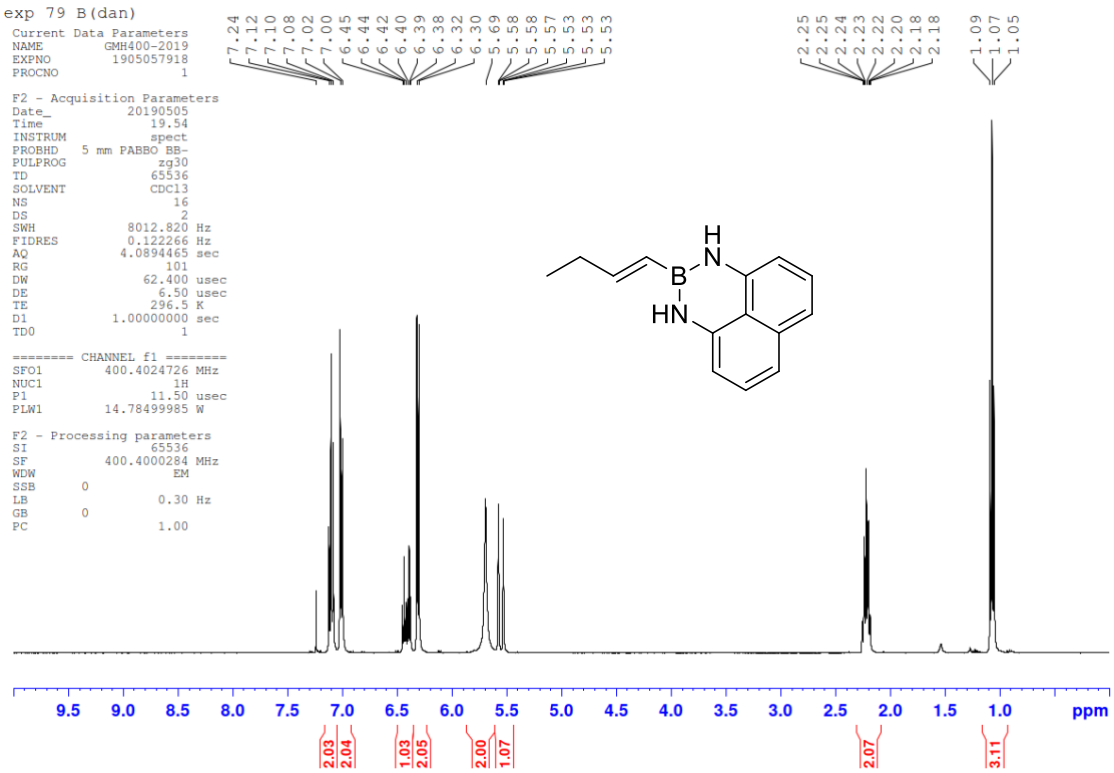
^{13}C {^{1}H} NMR Spectrum of **2b**, 100 MHz, $CDCl_3$



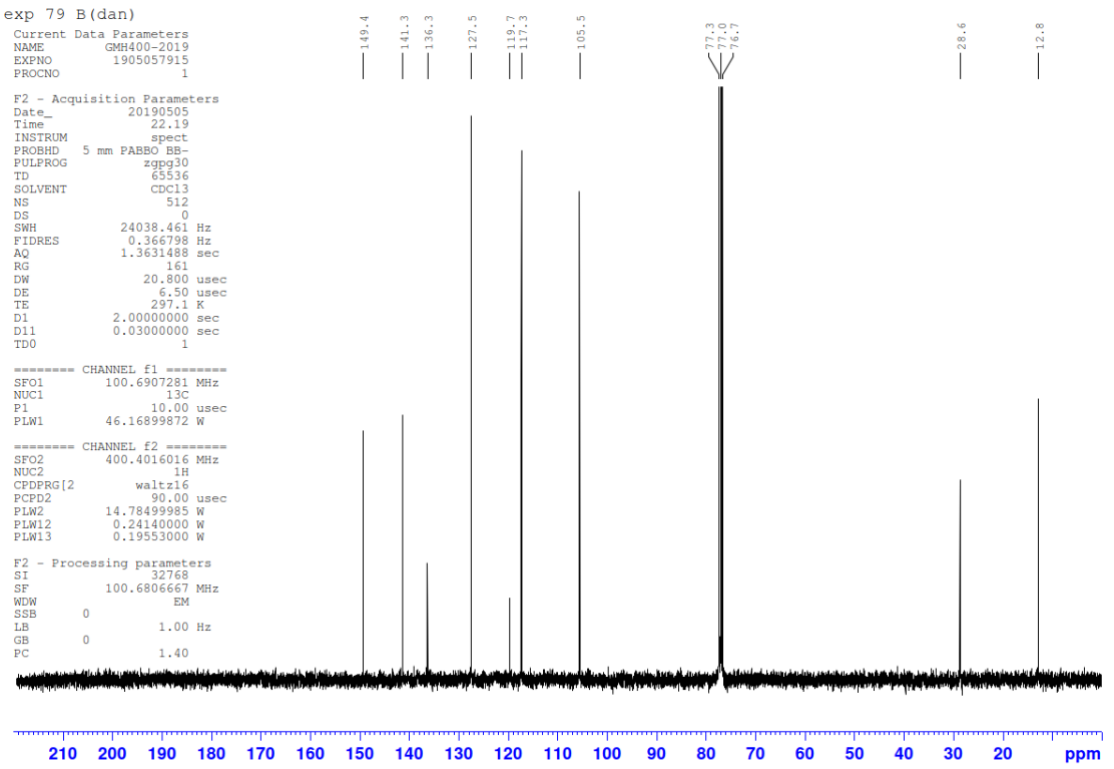
^{11}B NMR Spectrum of **2b**, 128 MHz, $CDCl_3$



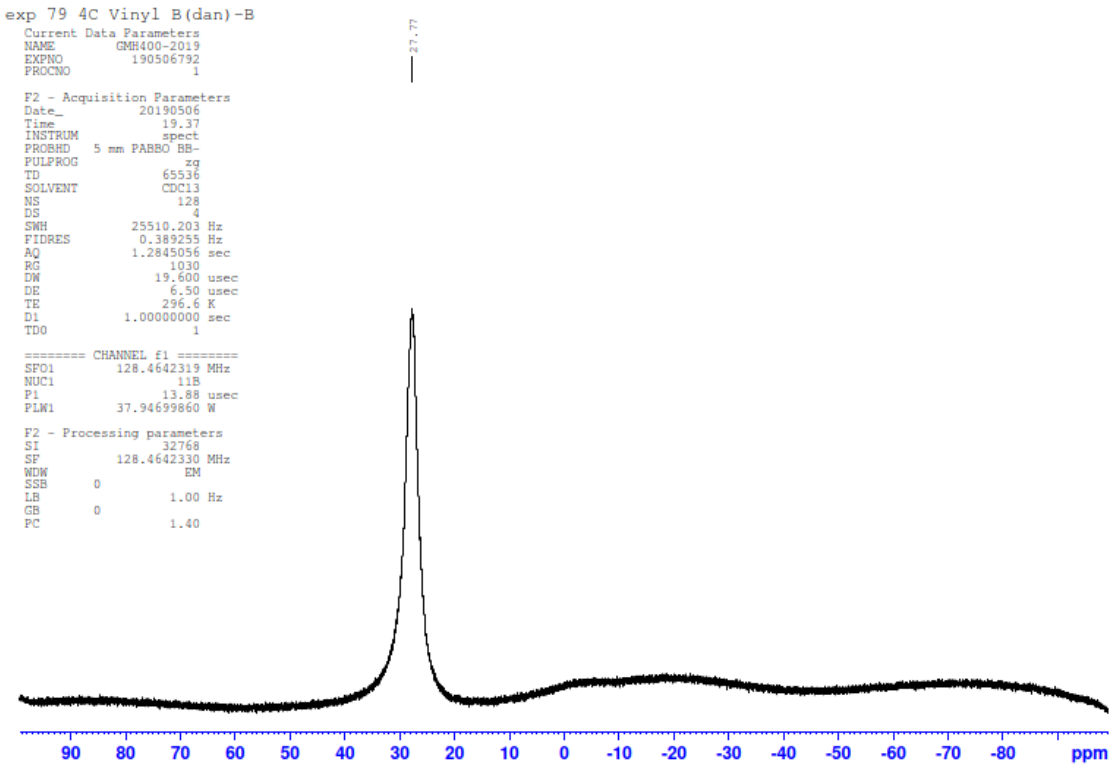
^{1}H NMR Spectrum of **2c**, 400 MHz, $CDCl_3$



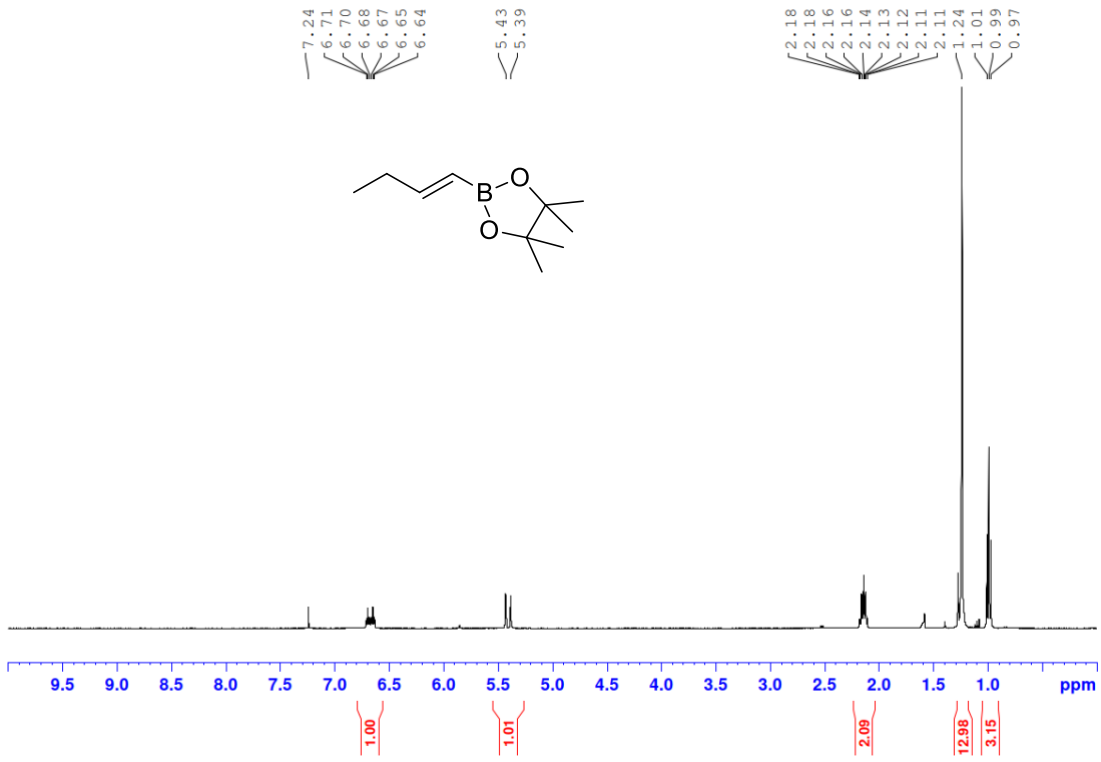
^{13}C {^{1}H} NMR Spectrum of **2c**, 100 MHz, $CDCl_3$



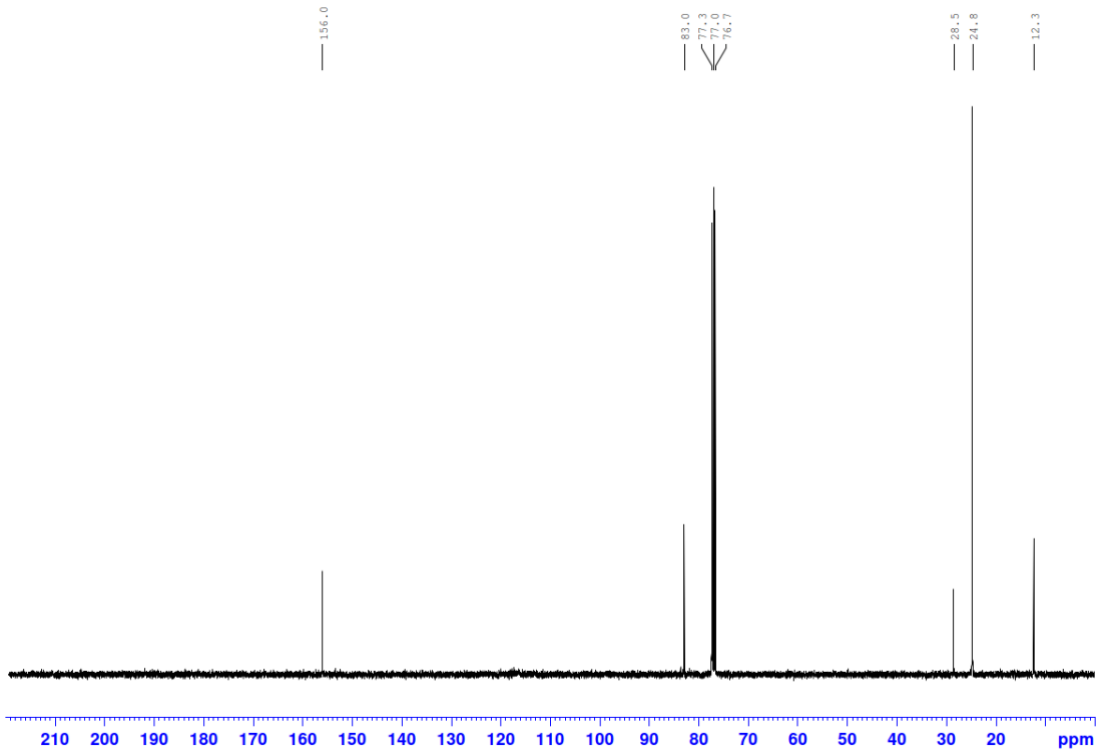
^{11}B NMR Spectrum of **2c**, 128 MHz, $CDCl_3$



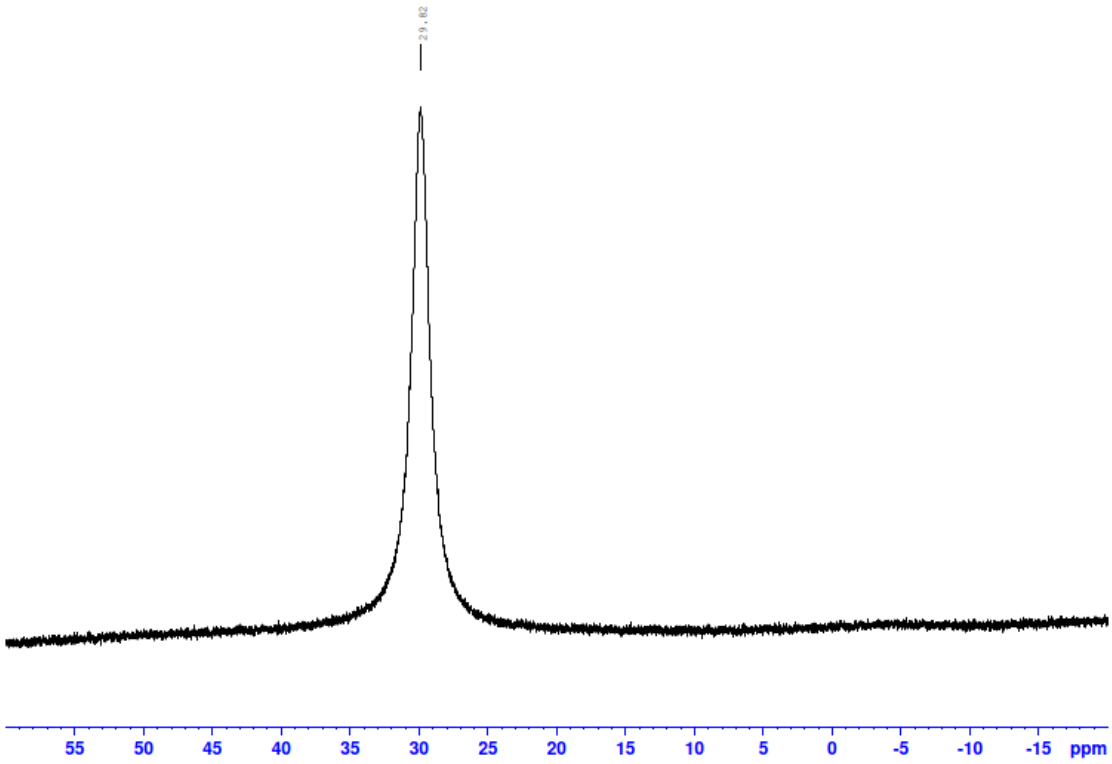
^{1}H NMR Spectrum of **2d**, 400 MHz, $CDCl_3$



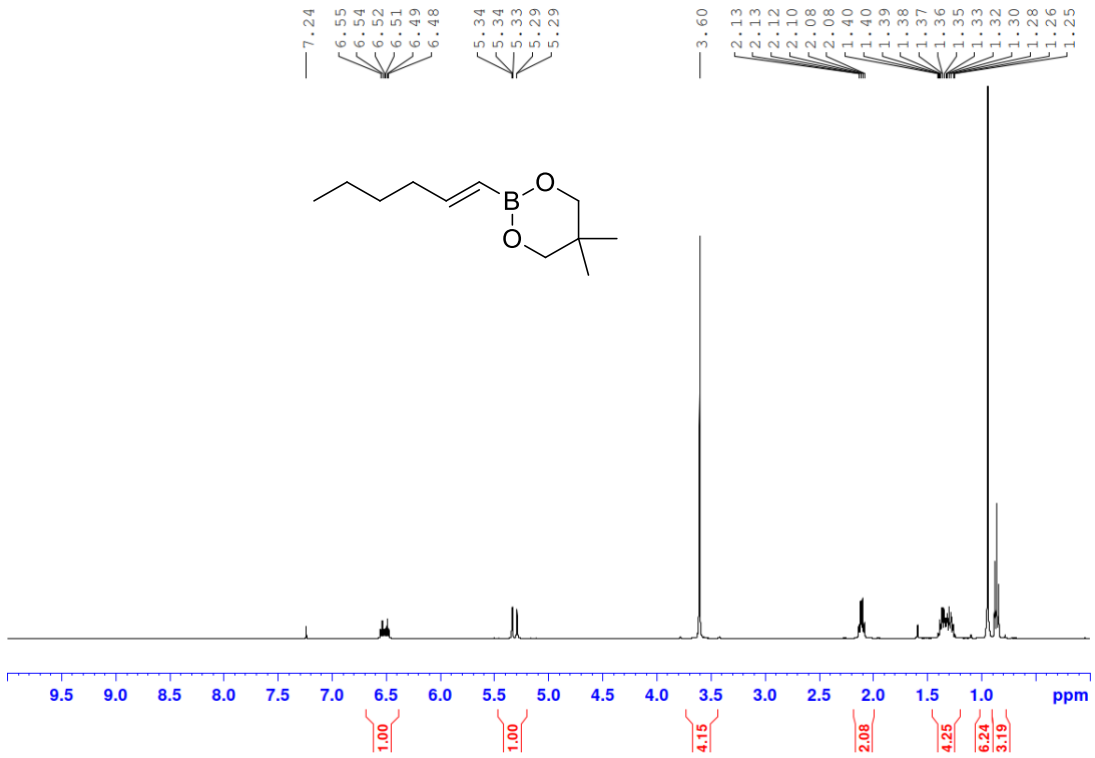
^{13}C {^{1}H} NMR Spectrum of **2d**, 100 MHz, $CDCl_3$



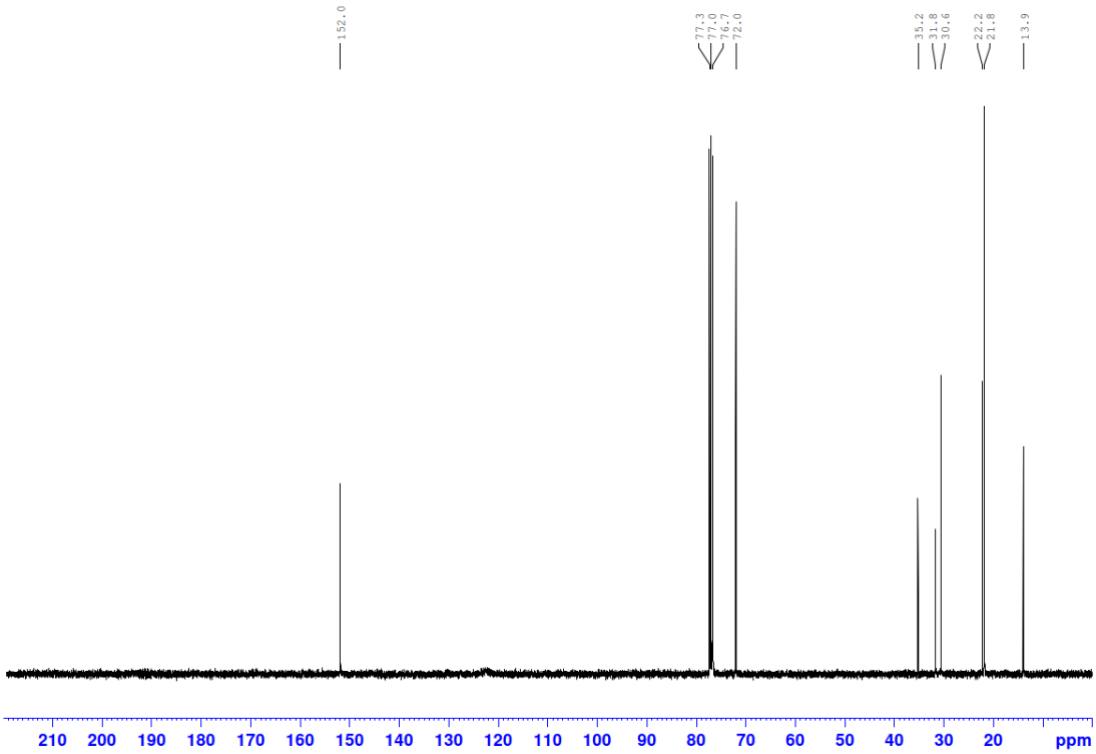
^{11}B NMR Spectrum of **2d**, 128 MHz, $CDCl_3$



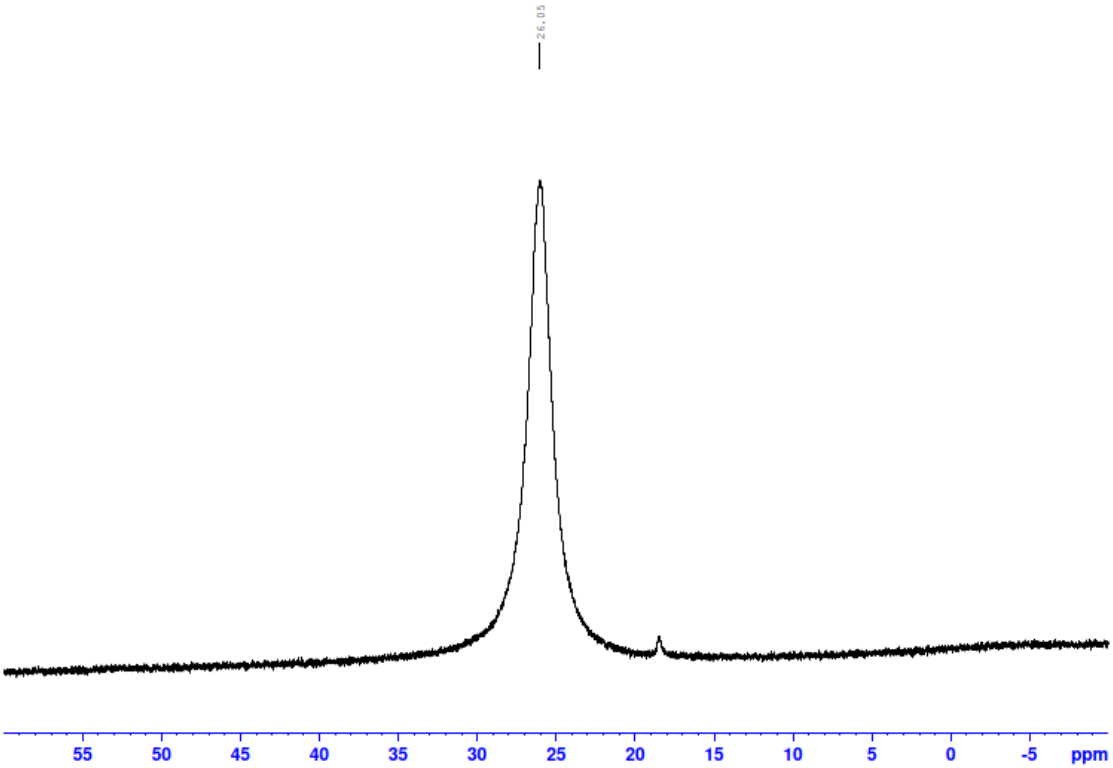
^{1}H NMR Spectrum of **2f**, 400 MHz, $CDCl_3$



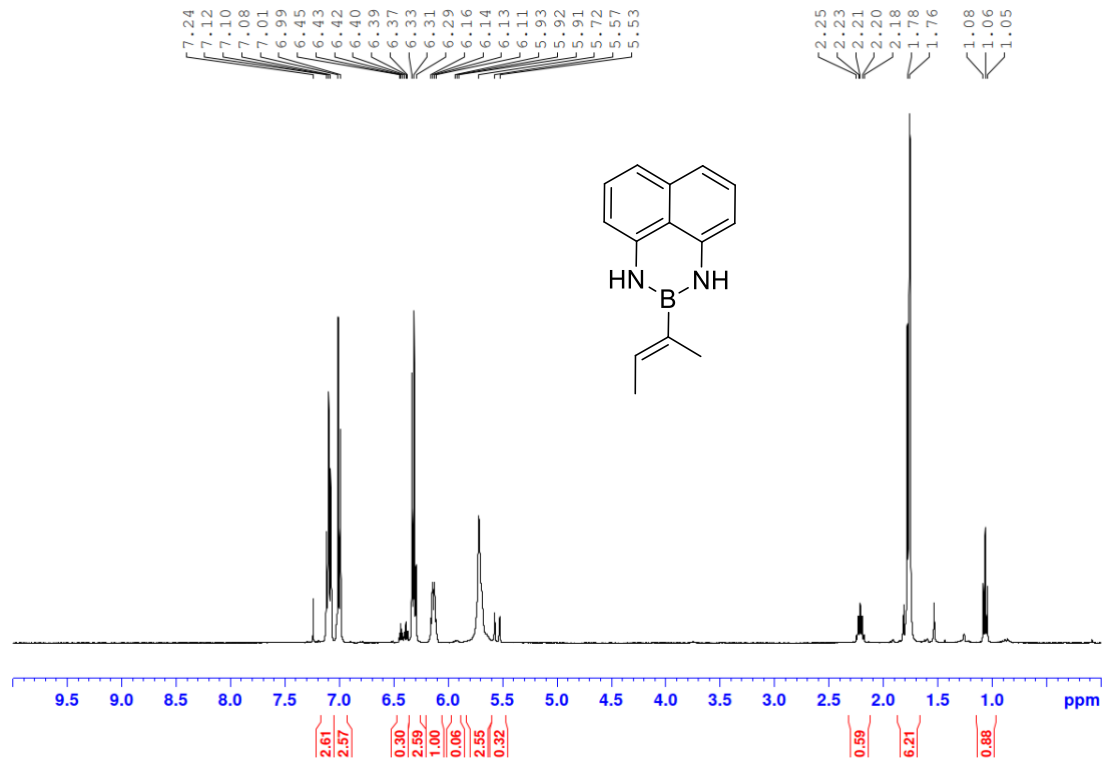
^{13}C {^{1}H} NMR Spectrum of **2f**, 100 MHz, $CDCl_3$



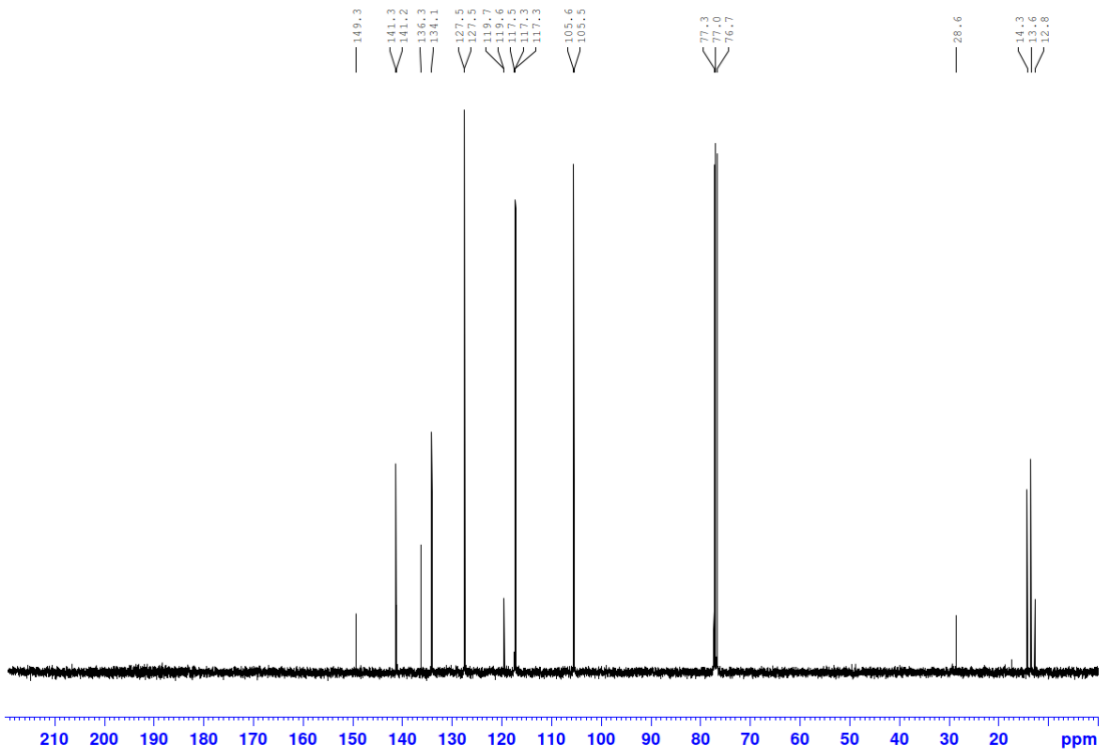
^{11}B NMR Spectrum of **2f**, 128 MHz, $CDCl_3$



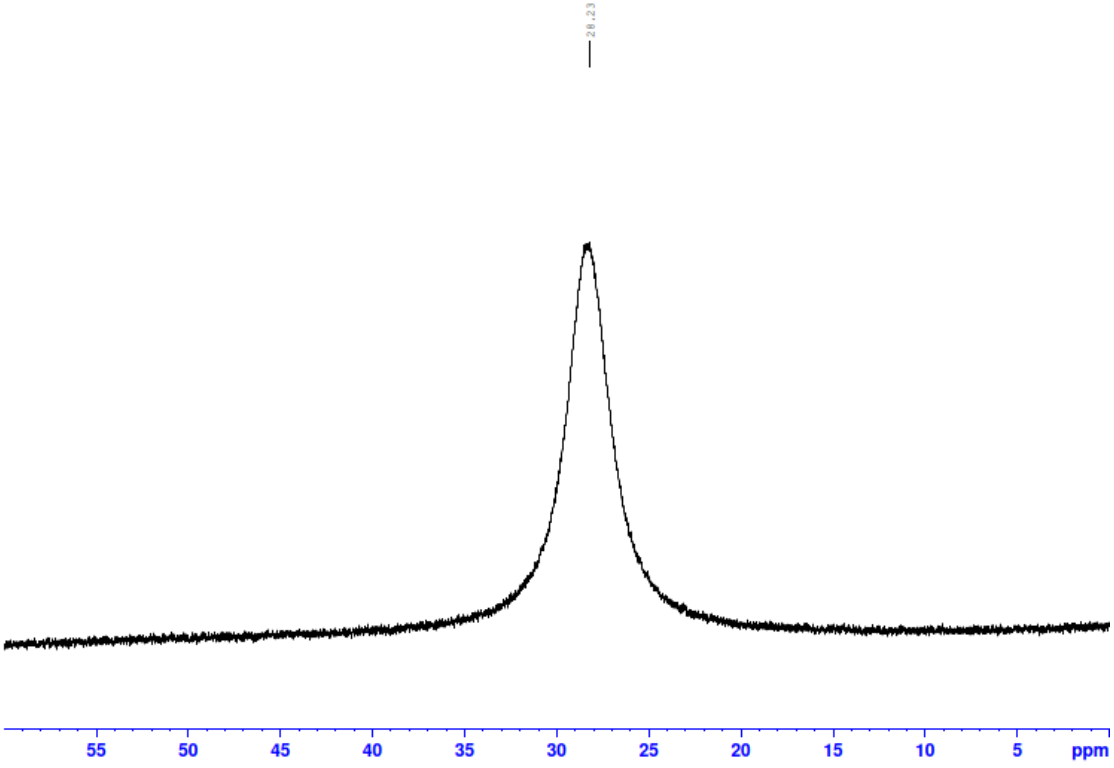
^{1}H NMR Spectrum of **2i**, 400 MHz, $CDCl_3$



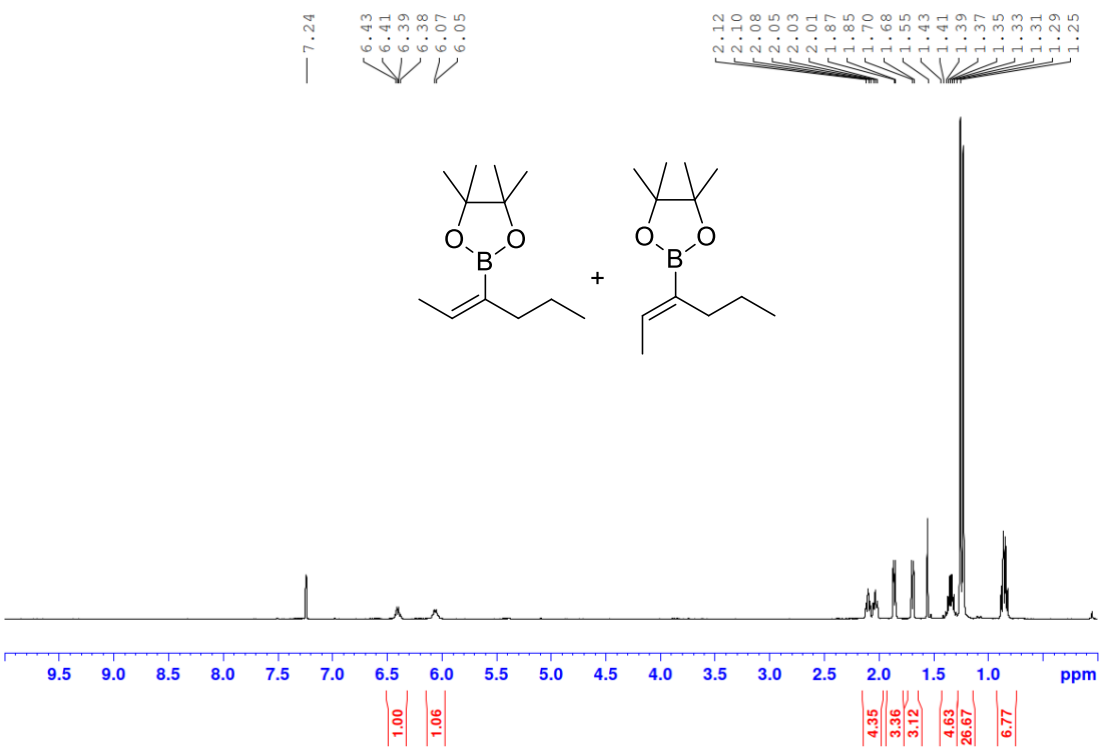
^{13}C {^{1}H} NMR Spectrum of **2i**, 100 MHz, $CDCl_3$



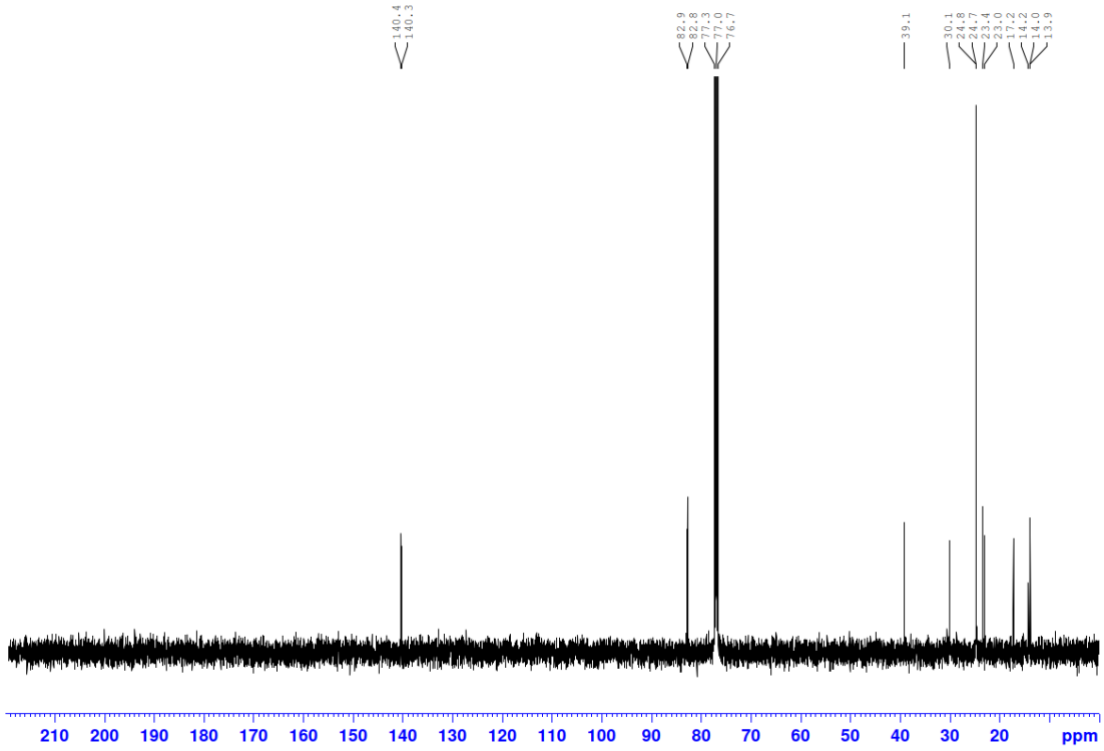
^{11}B NMR Spectrum of **2i**, 128 MHz, $CDCl_3$



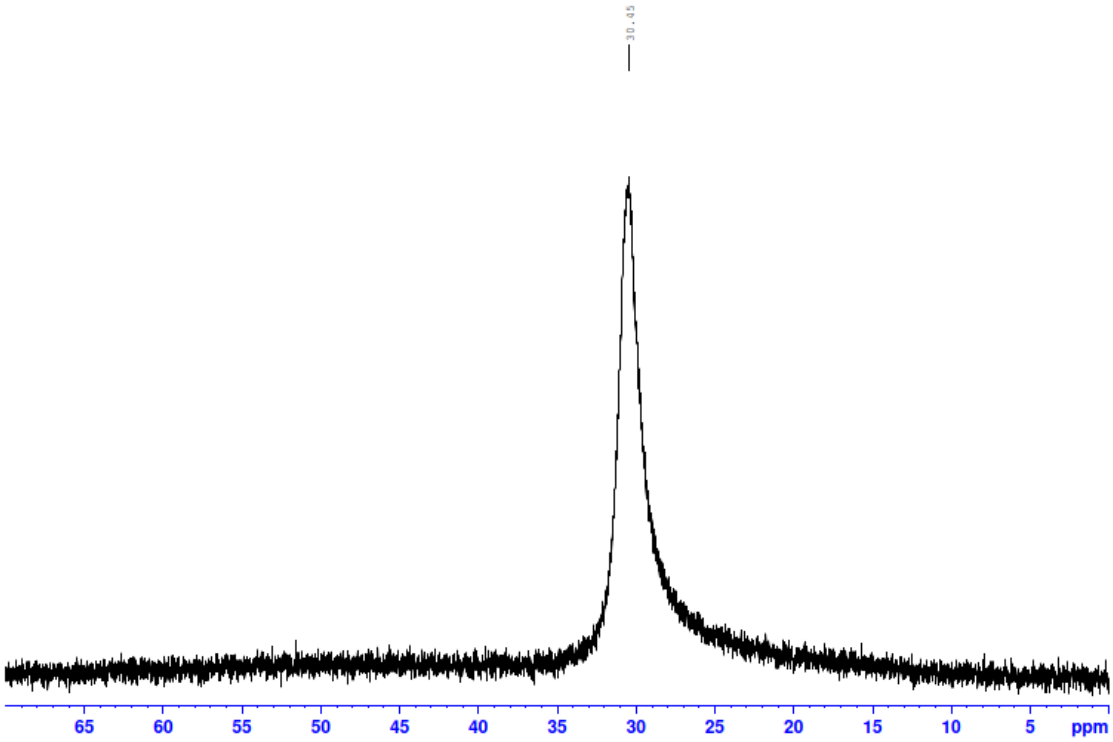
^{1}H NMR Spectrum of **2j**, 400 MHz, $CDCl_3$



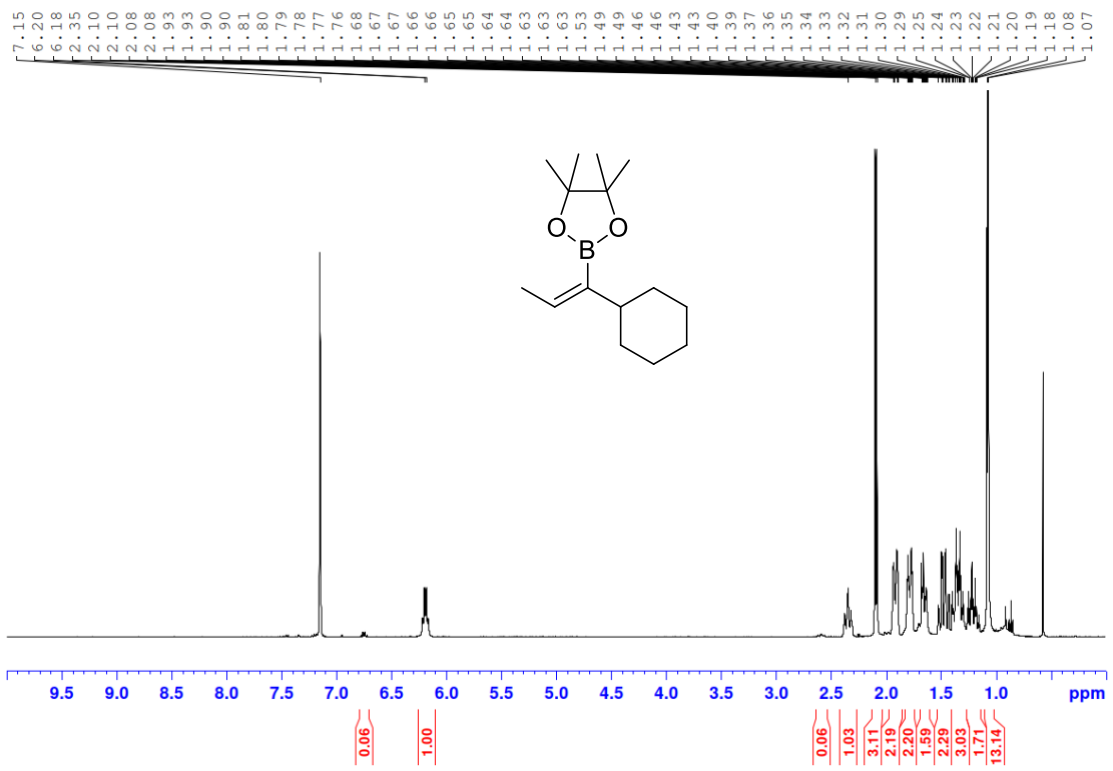
^{13}C {^{1}H} NMR Spectrum of **2j**, 100 MHz, $CDCl_3$



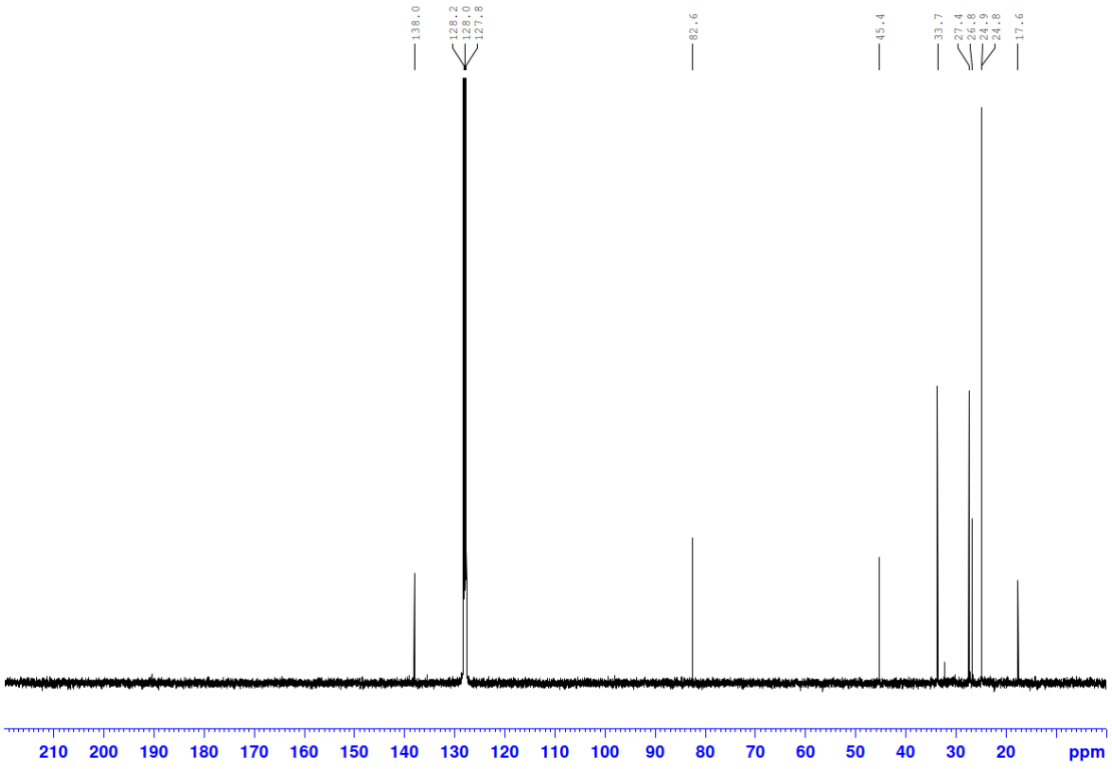
^{11}B NMR Spectrum of **2j**, 128 MHz, $CDCl_3$



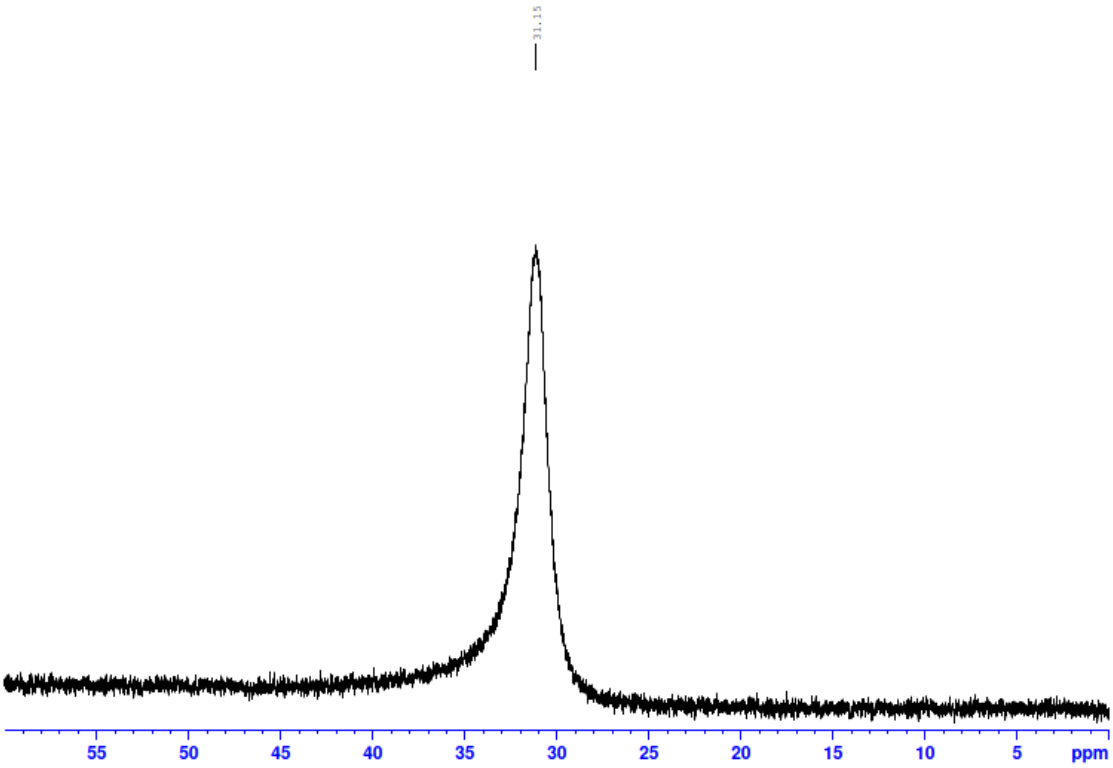
^{1}H NMR Spectrum of **2k**, 400 MHz, C_6D_6



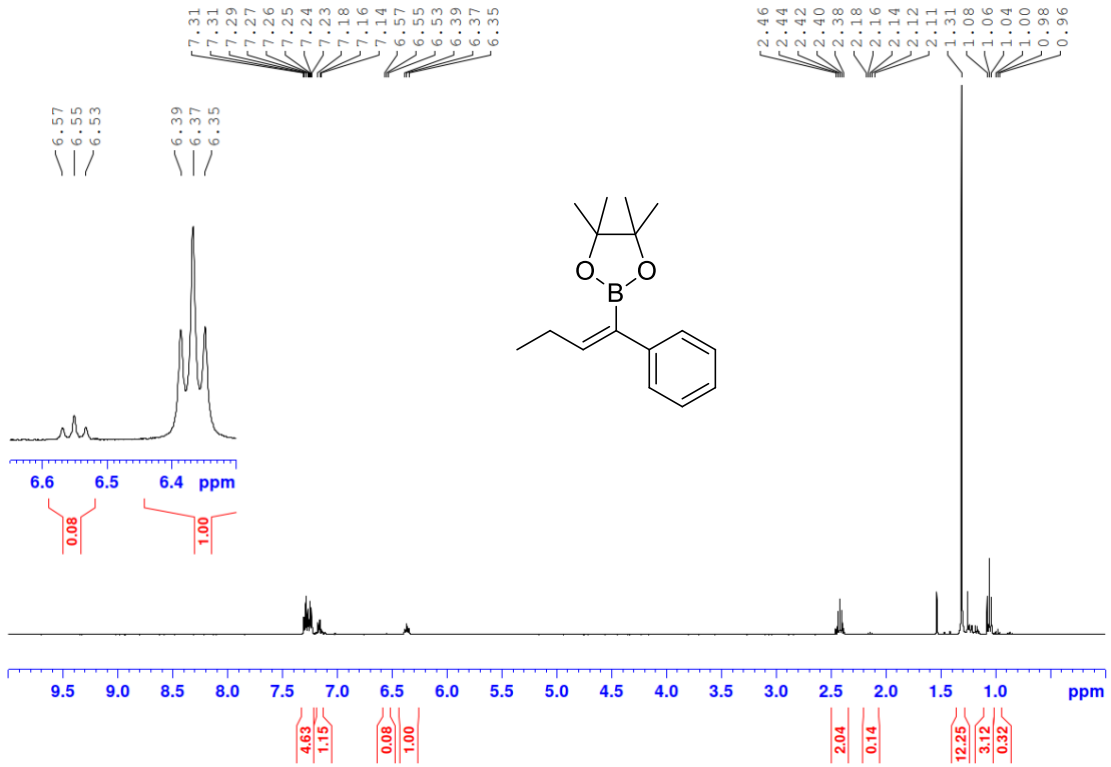
^{13}C {^{1}H} NMR Spectrum of **2k**, 100 MHz, C_6D_6



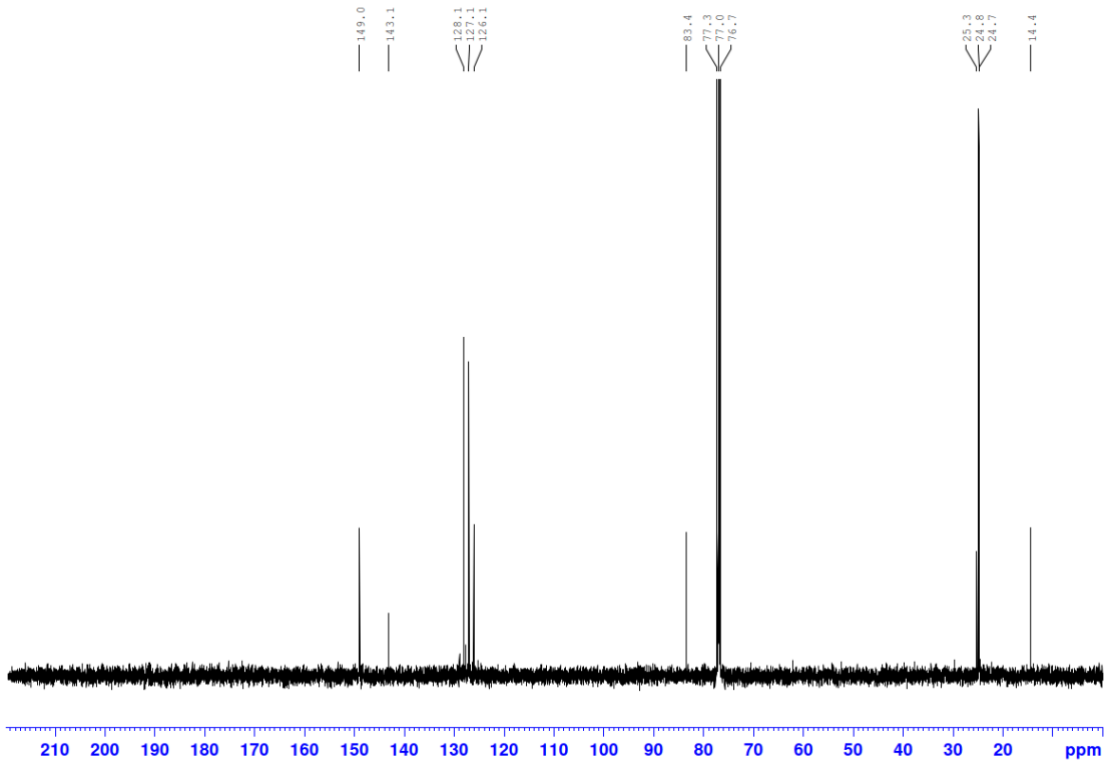
^{11}B NMR Spectrum of **2k**, 128 MHz, C_6D_6



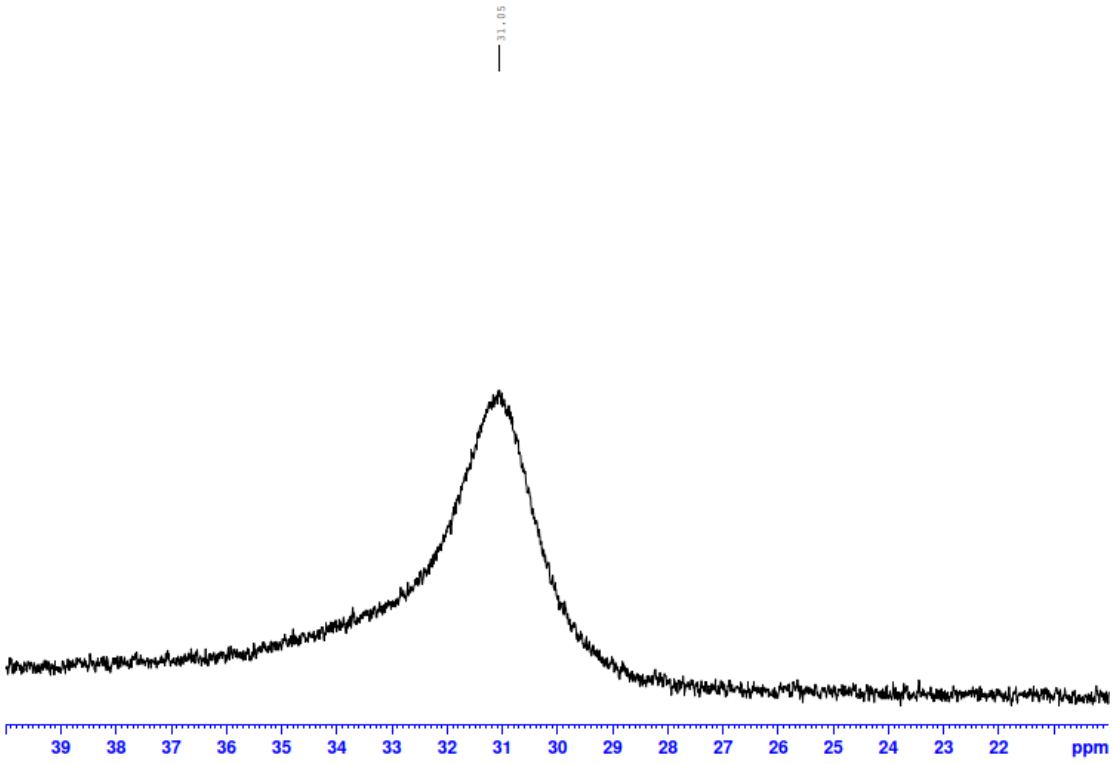
^{1}H NMR Spectrum of **2l**, 400 MHz, $CDCl_3$



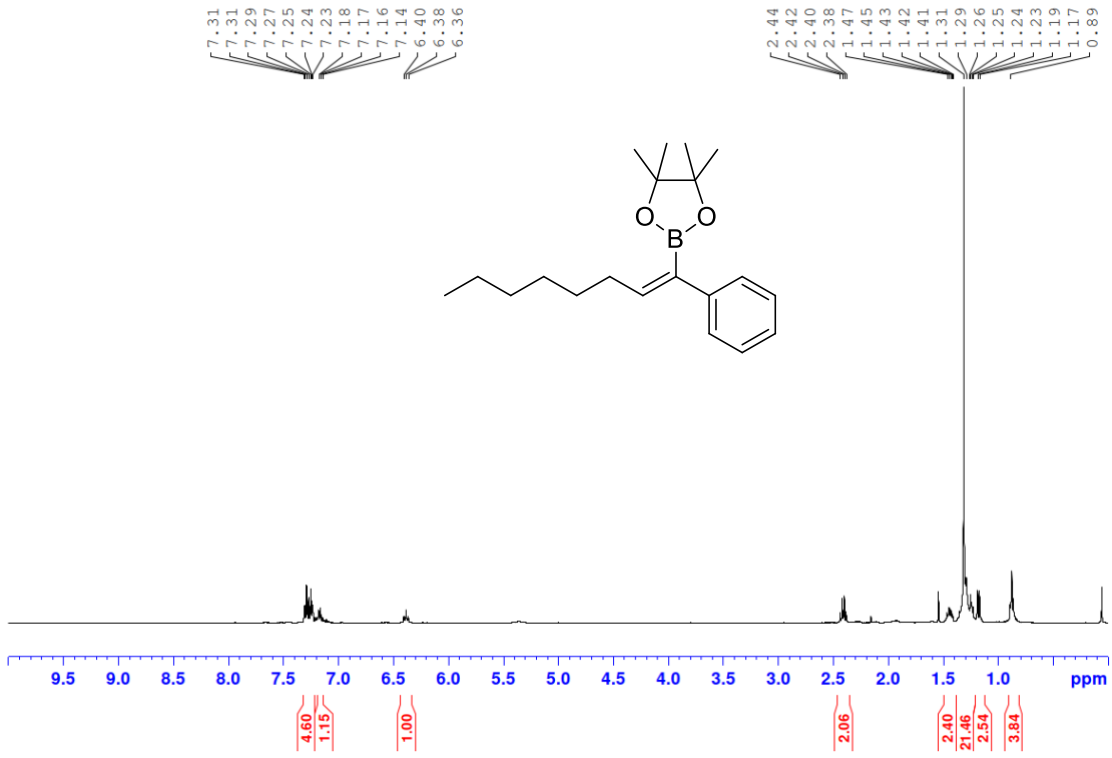
^{13}C {^{1}H} NMR Spectrum of **2l**, 100 MHz, $CDCl_3$



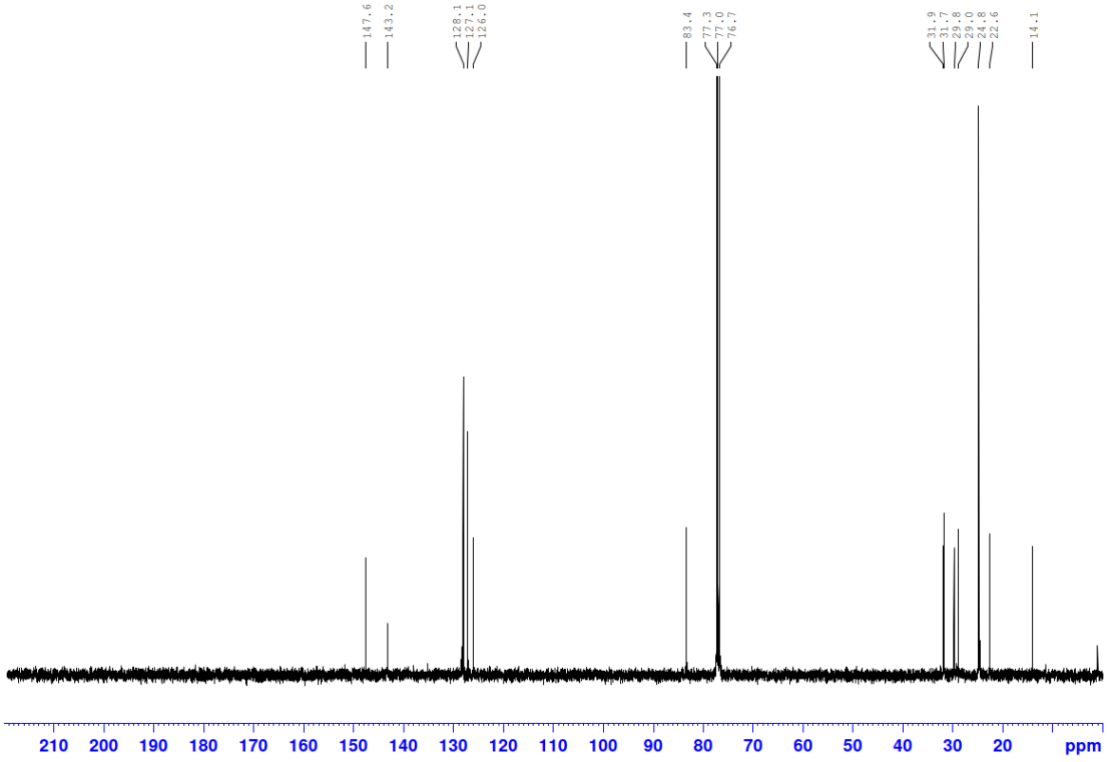
^{11}B NMR Spectrum of **2l**, 128 MHz, $CDCl_3$



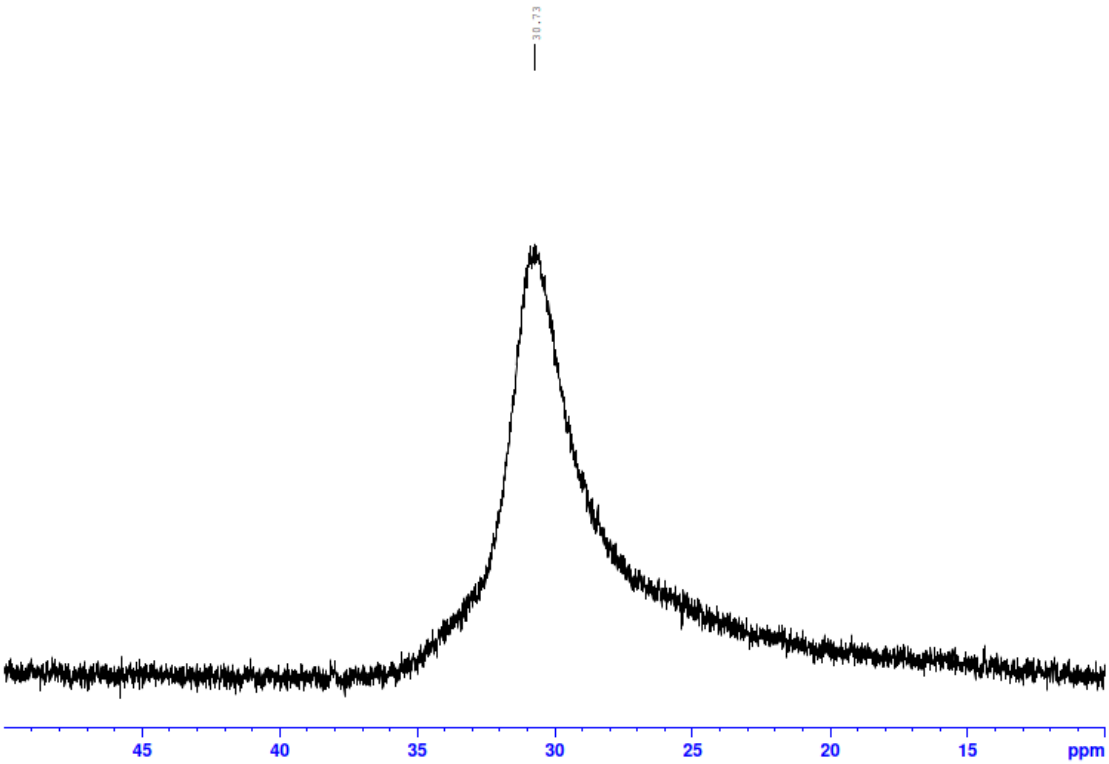
^{1}H NMR Spectrum of **2m**, 400 MHz, $CDCl_3$



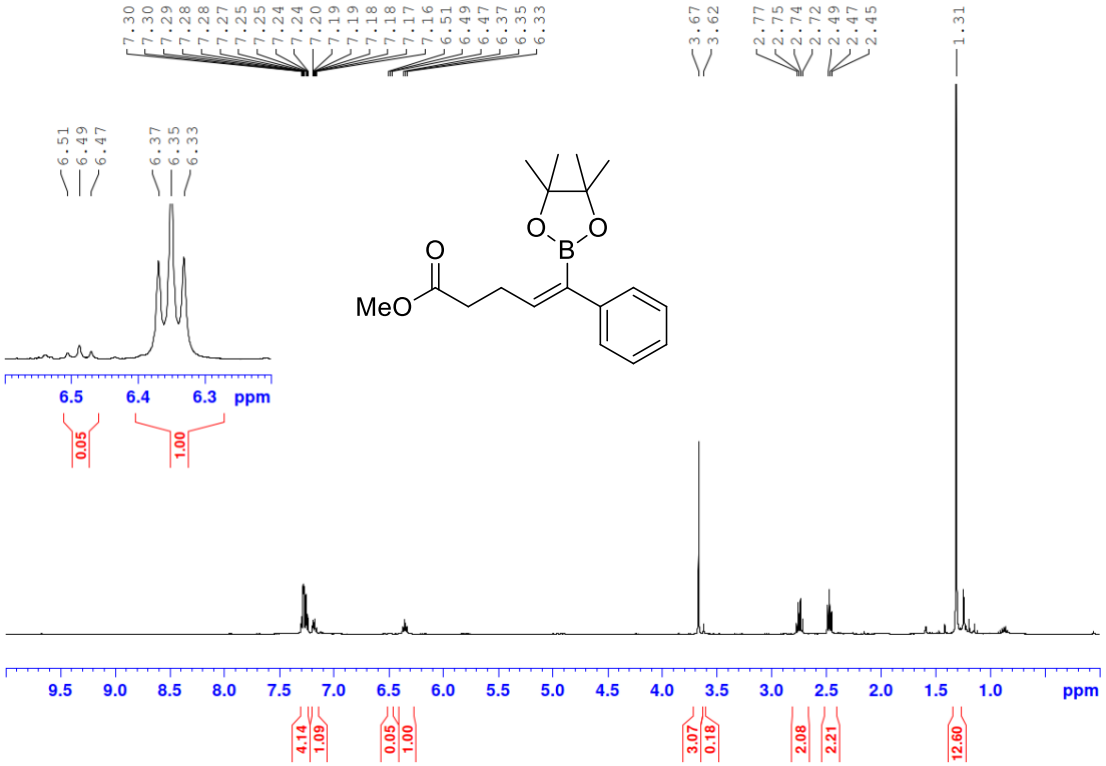
^{13}C {^{1}H} NMR Spectrum of **2m**, 100 MHz, $CDCl_3$



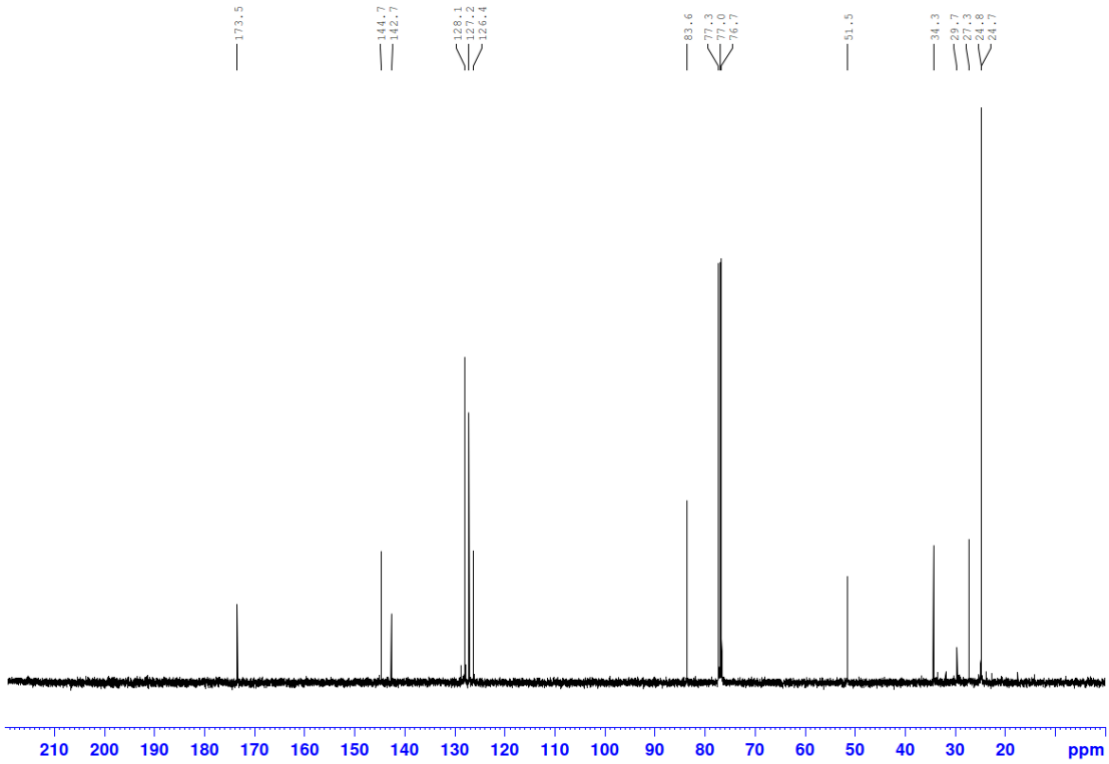
^{11}B NMR Spectrum of **2m**, 128 MHz, $CDCl_3$



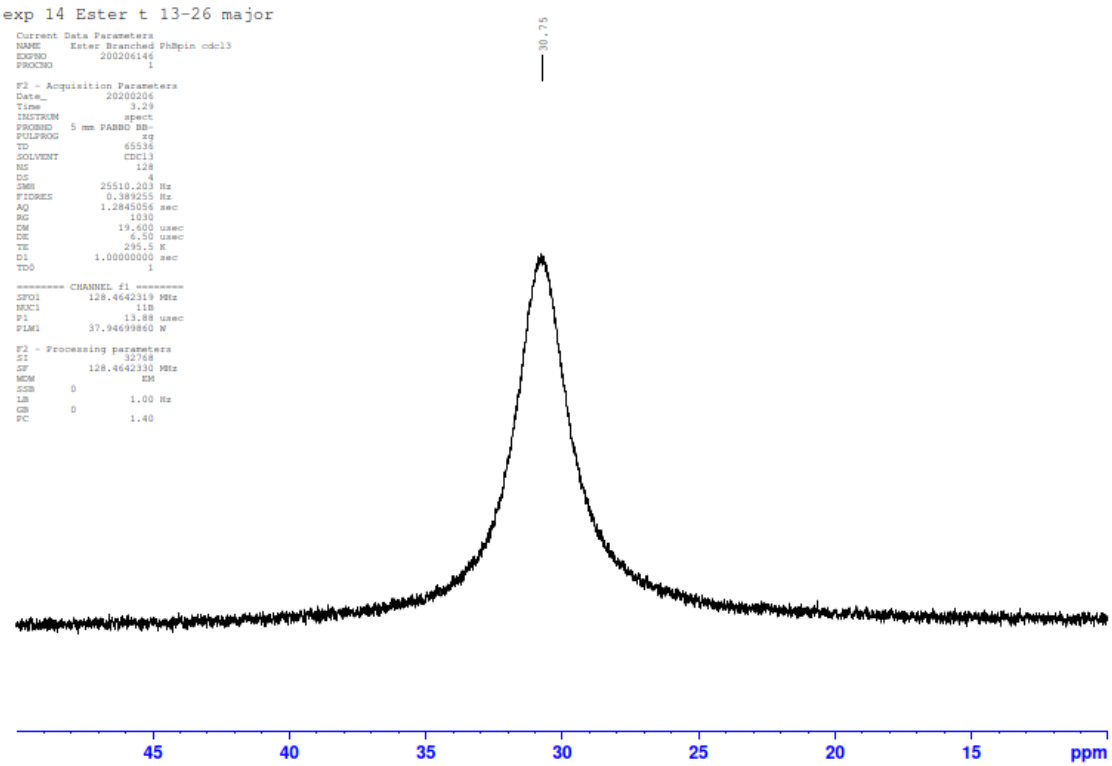
^{1}H NMR Spectrum of **2n**, 400 MHz, $CDCl_3$



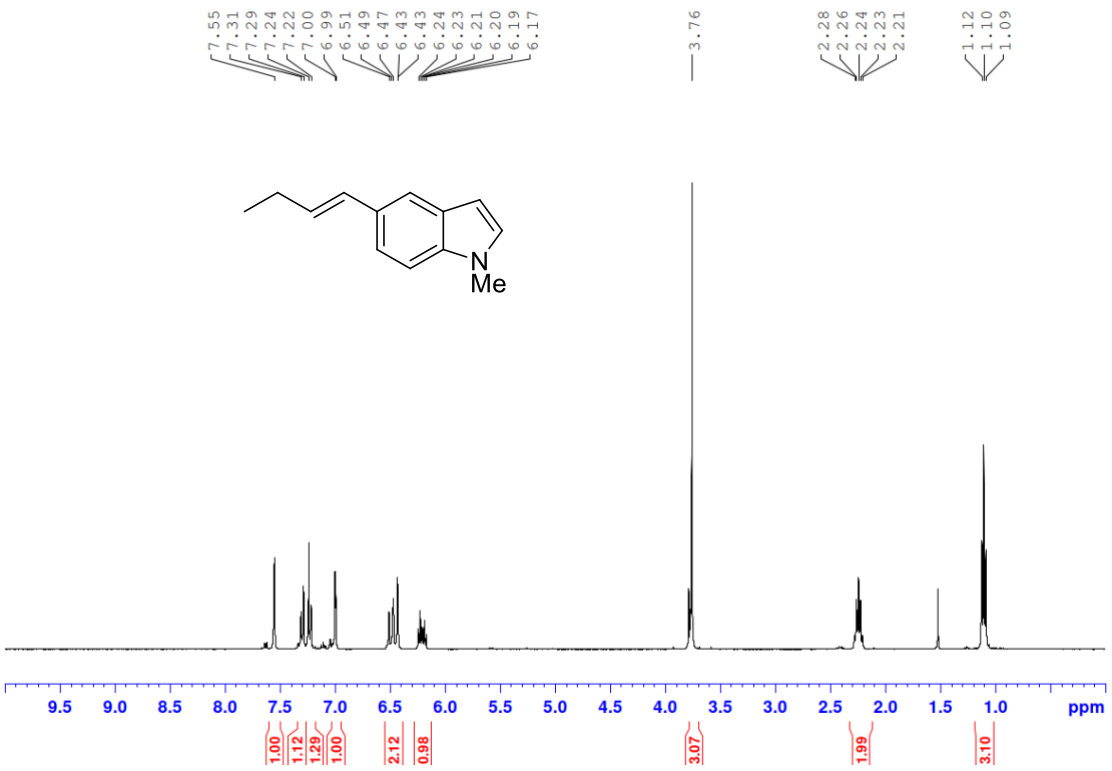
^{13}C {^{1}H} NMR Spectrum of **2n**, 100 MHz, $CDCl_3$



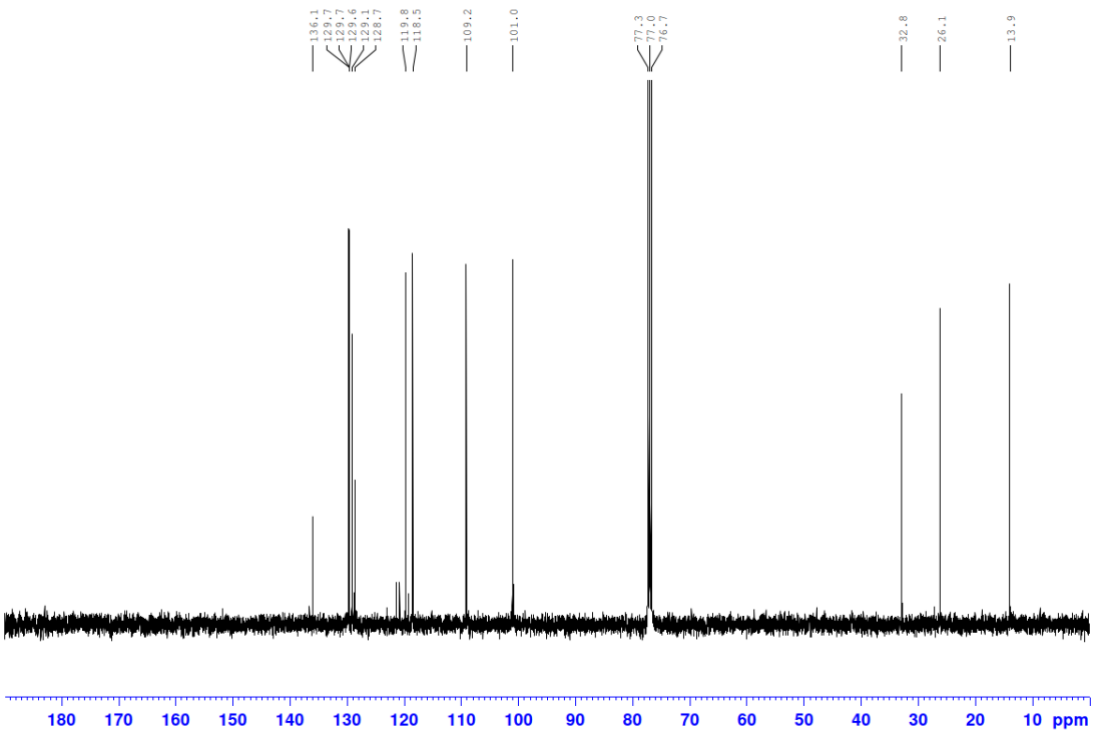
^{11}B NMR Spectrum of **2n**, 128 MHz, $CDCl_3$



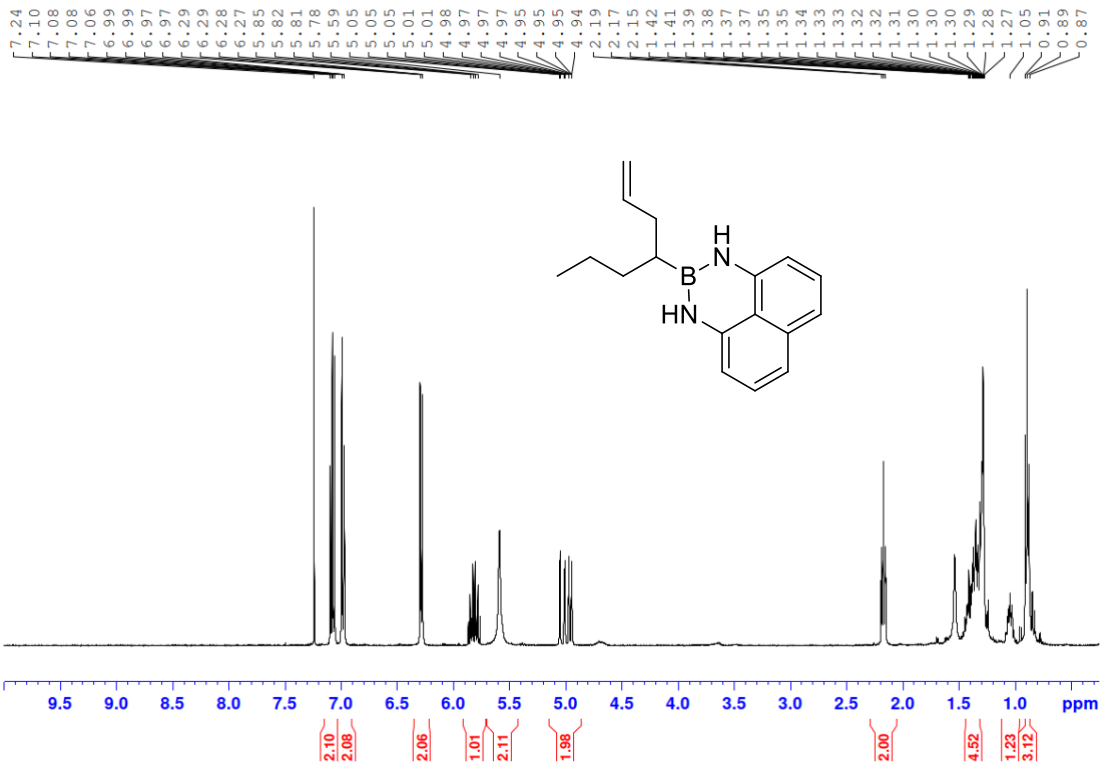
^{1}H NMR Spectrum of **3e**, 400 MHz, $CDCl_3$



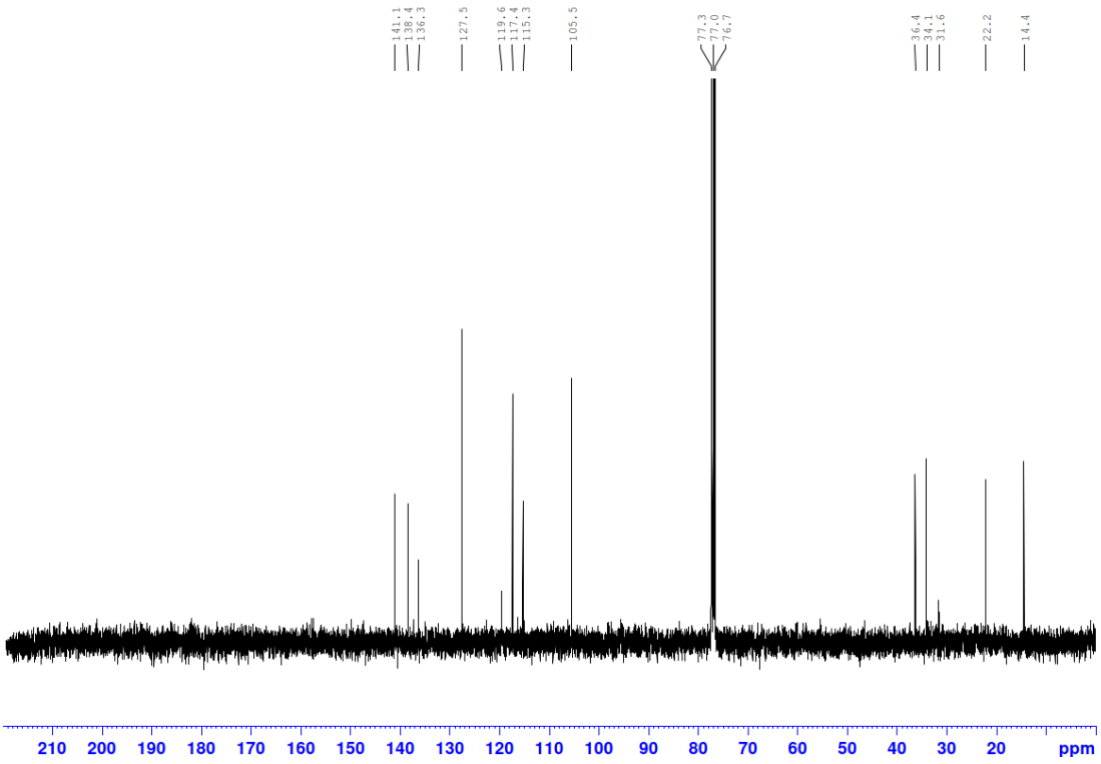
^{13}C {^{1}H} NMR Spectrum of **3e**, 100 MHz, $CDCl_3$



^{1}H NMR Spectrum of **4**, 400 MHz, $CDCl_3$



^{13}C {^{1}H} NMR Spectrum of **4**, 100 MHz, $CDCl_3$



^{11}B NMR Spectrum of **4**, 128 MHz, $CDCl_3$