Supporting information for

Stereo- and Regiocontrolled Methylboration of Terminal Alkynes

Oleksandr Zhurakovskyi, Rafael M. P. Dias, Adam Noble, Varinder K. Aggarwal

School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK

Contents

General Experimental

Unless indicated otherwise, reactions were performed in non-dried glassware under an atmosphere of nitrogen. Reactions were monitored by gas chromatography (GCMS) or thin-layer chromatography (TLC) where appropriate. Purifications were performed using standard[1] flash chromatography on silica gel or distillation. The products were analyzed using GCMS, NMR, and HRMS where appropriate. Crude regioisomeric ratios were estimated by GCMS and then reconfirmed by ^{1}H NMR.

CH_2Cl_2 (500 ppm water, as stated by the vendor) was used as received from Fisher. $AlMe_3$ (2M solution in toluene, Sigma-Aldrich SKU 198048-100ML) and modified methylaluminoxane (MMAO-12, 7 wt% aluminum in toluene, Sigma-Aldrich SKU 404594-4X25ML) were stored at 23 °C in dark and used as received. Zirconocene dichloride (≥98%, Sigma Aldrich SKU 196215-100G) was stored at 23 °C in dark under nitrogen, and used as received. *i*-PrOBpin (98%, Sigma-Aldrich SKU 417149-100ML) has been distilled under reduced pressure, discarding the forerun 5 vol%, and stored in a Schlenk tube at 23 °C under nitrogen. Commercially available alkynes were purchased from Sigma-Aldrich or Alfa Aesar and used as received. Alkynes **1l**, **1n**, and **1m** were prepared following literature procedures, as described below, and stored at −20 °C.

Analytical Chromatography

GCMS was performed on an Agilent 6890 Series GC system with a 5973 MS detector, HP-5MS UI column (15 m x 0.25 mm x 0.25 μm) and using a 50→250 °C ramp over 15 min.

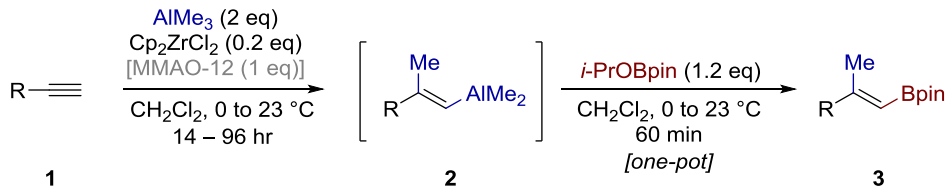
NMR Spectrometry

Routine NMR spectra were recorded on Varian, Bruker and JEOL spectrometers at 400 MHz for ^{1}H and 100 MHz for ^{13}C spectra. High-resolution spectra were run on Bruker Cryocarbon 500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C). Signals are reported relative to the residual signal of the non-deuterated solvent ($CDCl_3$: δ = 7.26 ppm for ^{1}H spectra; and $CDCl_3$: δ = 77.16 ppm for ^{13}C spectra). ^{1}H NMR data are reported as follows: integration, chemical shift (parts per million, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad, app = apparent), coupling constant (Hz) and description. ^{13}C NMR assignments, where possible, were made on the basis of chemical shifts and phase-edited HSQC spectra.

Mass Spectrometry

High-resolution mass spectra (HRMS) were recorded by the University of Bristol Spectrometry Services Laboratory using electrospray (ESI; Bruker micrOTOF II) or MALDI ionization.

General Procedure, Small Scale



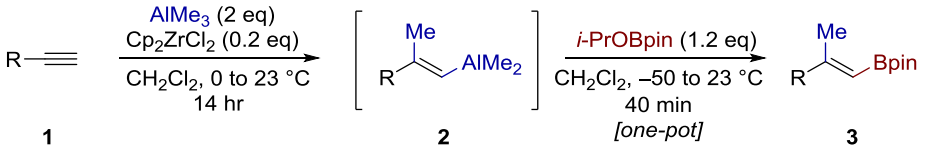
Zirconocene dichloride (29 mg, 0.1 mmol, 0.2 eq) was placed into a non-dry 25 mL pear-shaped flask and the atmosphere was exchanged with nitrogen 3 times. Reagent-grade CH_2Cl_2 (500 ppm water, as stated by the vendor) was added (1.1 mL) to give a clear colorless solution, which was then cooled to 0 °C. *If necessary, modified methylaluminoxane (MMAO-12, 7wt% in toluene, 0.22 mL, 0.50 mmol, 1 eq) was added at 0 °C at this point (see the main text for the discussion).* $AlMe_3$ (2 M in toluene, 0.50 mL, 1.0 mmol, 2 eq) was added dropwise at 0 °C and the resulting clear yellowish solution was stirred for 5–10 min. Neat starting alkyne **1** (0.50 mmol) was then added with a syringe, the ice bath was removed, and the mixture was stirred at 23 °C overnight (14 hr). If GCMS analysis indicated incomplete consumption of the starting material, the reaction mixture was stirred further (in some cases, the carboalumination took up to 96 hr, as reported below). The reaction typically turned clear yellow by this point.

Neat *i*-PrOBpin (0.12 mL, 0.6 mmol, 1.2 eq) was then added at 0 °C in one portion, the ice bath was removed, and the mixture was stirred at 23 °C for 60 min. The Al–B exchange is fast (typically <5 min) and exothermic. In the absence of cooling, 10-30% of proto-demetallated side-product was observed.

The reaction mixture was then cooled to 0 °C and diluted with 5 mL of reagent-grade CH_2Cl_2. A solution of HCl (1 M in H_2O, 1 mL) was added dropwise (caution: gas evolution!) and the mixture was stirred at 0 °C for 10 min, until gas evolution ceased. The mixture was then diluted with 1 M HCl (10 mL) and extracted with CH_2Cl_2 (4×3 mL). The combined organic layer was washed with brine (4 mL) and dried over Na_2SO_4. The solution was passed through a plug of silica (w×h 1×2 cm), washing the plug with 10 mL of CH_2Cl_2, then concentrated. A 3-5 mg aliquot was submitted for NMR analysis to measure regioselectivity. Purification of the crude sample by silica chromatography then provided the target vinyl boronate (2% diethyl ether—pentane with a gradient to 10 or 20% of diethyl ether—pentane, as appropriate, over 10 column volumes).

Acid-sensitive substrates (silyl ethers) were worked up similarly, using pure water instead of HCl. Hard-to-separate suspensions were observed in these cases.

General Procedure, Gram Scale



1 **2** **3**

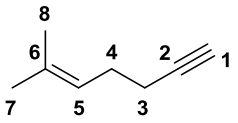
Zirconocene dichloride (350 mg, 1.2 mmol, 0.2 eq) was placed into a non-dry 100 mL round-bottom flask and the atmosphere has been exchanged for nitrogen 3 times. Reagent-grade CH_2Cl_2 (13 mL; 500 ppm water, as stated by the vendor) was added to give a clear colorless solution. $AlMe_3$ (2 M in toluene, 6.0 mL, 12.0 mmol, 2 eq) was added dropwise at 0 °C and the resulting clear yellowish solution was stirred for 5-10 min. Neat starting alkyne **1** (6.0 mmol) was then added with a syringe over ca. 30 sec, the ice bath was removed and the mixture was stirred at 23 °C for 14 hr, until GCMS analysis indicated complete consumption of the starting material. The reaction turned clear yellow by this point.

The reaction mixture was then cooled to −50 °C (dry ice bath), and neat *i*-PrOBpin (1.48 mL, 7.2 mmol, 1.2 eq) was added to the rapidly stirred reaction mixture in one portion over ca. 5 sec **(CAUTION: strong exotherm!)** After 10 min, the ice bath was removed, and the mixture was stirred at 23 °C for 30-60 min. *Note: in the absence of cooling, 30–40% of proto-demetallated side-product was observed; conversely, an attempt to control the exotherm by the slow addition of* i-*PrOBpin at 0 °C also resulted in diminished yields – this reagent should be added in one portion, presumably to avoid side reactions with the excess of vinyl aluminum species.*

The reaction mixture was then cooled to 0 °C and diluted with 25 mL of reagent-grade CH_2Cl_2 (~5 reaction volumes). Water (1 mL) was slowly added in 0.2 mL portions to quench reactive aluminum species, while avoiding thermal runaway (CAUTION: gas liberation). After 10 min, another 1 mL of water was added, and the mixture was stirred at 0 °C for 10 min, until bubbling ceased.

The reaction mixture was then diluted either with 1 M HCl (15 mL, for acid-stable products; allows to avoid [Al] precipitation) or water (15 mL, for acid-labile products), and extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4, filtered, and concentrated. A 5 mg aliquot was submitted for ^1H NMR analysis to measure regioselectivity. Purification of the crude sample by silica chromatography then provided the target vinyl boronate (2% diethyl ether—pentane with a gradient to 10 or 20% of diethyl ether—pentane, as appropriate, over 10 column volumes).

Compound Data



6-Methylhept-5-en-1-yne (1l)[2,3]

Following the procedure from Spring[2] and Beumel, Jr,[3] 1-bromo-4-methyl-3-pentene (1.60 mL, 1.96 g, 12 mmol) was added dropwise over 30 min to a cold solution (10 °C ice bath) of lithium acetylide diethylamine complex (90%, 1.29 g, 12.6 mmol, 1.05 eq) in anhydrous DMSO (7 mL). When the addition was finished, the reaction mixture was allowed to warm to 23 °C and stirred for 1 hr.

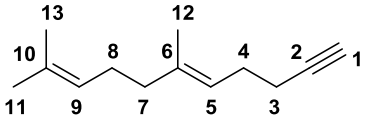
The reaction mixture was then placed into ice bath (0 °C) and the unreacted materials were carefully quenched with water (10 mL; CAUTION: intense gas liberation). The product was then extracted with pentane (4×8 mL), washed with brine (5 mL), dried over Na_2SO_4 and carefully concentrated (200 Torr, 25 °C). Careful fractional distillation in Kugelrohr (80 °C/300 Torr to remove impurities, then 80→100 °C/225 Torr to distill the product) then afforded the product as a clear colorless, volatile, oil.

Yield: 850 mg (31%).

Clear colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.21 – 5.13 (m, 1H, H-5), 2.27 – 2.16 (m, 4H, H-3,4), 1.94 (t, *J* = 2.4 Hz, 1H, H-1), 1.71 (s, 3H, CH_3), 1.63 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.34 (C-6), 122.69 (C-5), 84.72 (C-2), 68.24 (C-1), 27.41 (CH_2), 25.84 (CH_3), 19.08 (CH_2), 17.95 (CH_3).



(*E*)-6,10-Dimethylundeca-5,9-dien-1-yne (1m)[4]

Prepared following a literature procedure by Gibbs[4] from 2.0 mL of geranyl bromide (10 mmol), 1.8 mL of TMS-propyne (12 mmol, 1.2 eq), 9.0 mL of *n*-BuLi (1.6M in hexane, 14.4 mmol, 1.4 eq), and 15 mL of TBAF (1M in THF, 15 mmol, 1.5 eq).

Clear colorless oil.

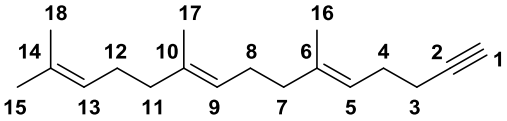
Yield: 1.01 g (57 %).

R_f 0.28 (100% pentane)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.22 – 5.14 (m, 1H, =C–H), 5.14 – 5.05 (m, 1H, =C–H), 2.29 – 2.14 (m, 4H, 2×CH_2), 2.14 – 1.95 (m, 4H, 2×CH_2), 1.94 (t, *J*=2.4, 1H, H-1), 1.68 (q, *J*=1.4, 3H, CH_3), 1.62 (d, *J*=1.3, 3H, CH_3), 1.60 (d, *J*=1.2, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ 136.87 (C_q), 131.53 (C_q), 124.37 (=C–H), 122.60 (=C–H), 84.70 (C-2), 68.22 (C-1), 39.80 (CH_2), 27.34 (CH_2), 26.79 (CH_2), 25.83 (CH_3), 19.07 (CH_2), 17.84 (CH_3), 16.26 (CH_3).

IR (neat): 3310 (m), 2119 (w), 1669 (w), 1441 (m), 1376 (m), 834 (m), 626 (s).



(5E,9*E*)-6,10,14-Trimethylpentadeca-5,9,13-trien-1-yne (1n)[4]

Prepared following a literature procedure by Gibbs[4] from 856 mg of farnesyl bromide (3.0 mmol), 0.53 mL of TMS-propyne (3.6 mmol, 1.2 eq), 2.7 mL of *n*-BuLi (1.6M in hexane, 4.3 mmol, 1.4 eq), and 4.5 mL of TBAF (1M in THF, 4.5 mmol, 1.5 eq).

Yield: 290 mg (40%).

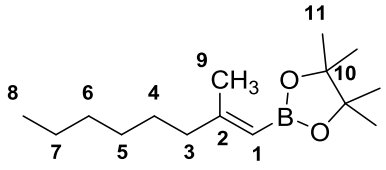
Clear colorless oil.

Rf 0.67 (4% ether-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.22 – 5.14 (m, 1H), 5.14 – 5.05 (m, 2H), 2.28 – 2.15 (m, 4H), 2.13 – 1.95 (m, 8H), 1.94 (t, *J*=2.4, 1H, H-1), 1.68 (d, *J*=1.3, 3H, CH_3), 1.63 (d, *J*=0.8, 3H, CH_3), 1.60 (s, 6H, 2×CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ 136.90, 135.18, 131.42, 124.53, 124.21, 122.59, 84.71, 68.23, 39.87, 39.79, 27.34, 26.91, 26.67, 25.85, 19.08, 17.84, 16.28, 16.17.

IR (neat): 3311 (m), 2119 (w), 1668 (w), 1442 (m), 1381 (m), 627 (s).



(*E*)-4,4,5,5-Tetramethyl-2-(2-methyloct-1-en-1-yl)-1,3,2-dioxaborolane (3a)[5,6]

Clear colorless oil.

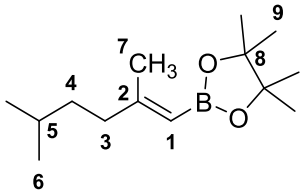
Yield: 100 mg (82%), rr 98:2.

R_f 0.20 (1% ether–pentane)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.12 – 5.09 (m, H-1), 2.12 – 2.04 (m, 2H, H-3), 1.97 (d, *J*=1.0, 3H, H-9), 1.49 – 1.38 (m, 2H, H-4), 1.34 – 1.20 (m, 18H, H-5,6,7,11), 0.95 – 0.81 (m, 3H, H-8).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.49 (C-2), 82.70 (C-10), 42.35 (C-3), 31.93 (CH_2), 29.20 (CH_2), 27.77 (C-4), 25.02 (C-11), 22.75 (CH_2), 21.31 (C-9), 14.24 (C-8). *Note:* C-1 not seen due to relaxation on B.

IR (neat): 1638 (m), 1441 (w), 1369 (m), 1319 (s), 1263 (m), 1142 (s).



(*E*)-2-(2,5-Dimethylhex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)[7]

Clear colorless oil.

Yield: 94 mg (79%), rr 98:2.

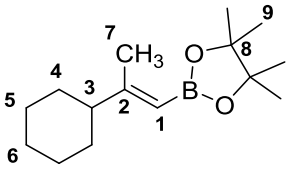
Gram-scale yield: 1.17 g (82%), rr 97:3.

R_f 0.57 (10% ether–pentane)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.11 (h, *J*=1.1, 1H, H-1), 2.12 – 2.05 (m, 2H, H-3), 1.97 (d, *J*=1.0, 3H, H-7), 1.60 – 1.45 (m, 1H, H-5), 1.37 – 1.28 (m, 2H, H-4), 1.26 (s, 12H, H-9), 0.87 (d, *J*=6.6, 6H, H-6).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.68 (C-2), 112.62 (br.s, C-1), 82.69 (C-8), 40.14 (C-3), 37.08 (C-4), 27.85 (C-5), 25.01 (C-9), 22.69 (C-6), 21.34 (C-7).

IR (neat): 1637 (m), 1367 (m), 1316 (s), 1263 (m), 1141 (s), 970 (m), 852 (m).



(*E*)-2-(2-Cyclohexylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)[5,6]

Clear colorless oil.

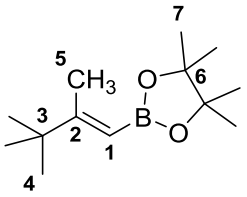
Yield: 97 mg (78%), rr >98:2.

R_f 0.38 (3% ether–pentane)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.10 (p, *J*=1.0, 1H, H-1), 1.96 (d, *J*=1.0, 3H, H-7), 1.94 – 1.84 (m, 1H, H-3), 1.80 – 1.61 (m, 5H, H-alk), 1.26 (s, 13H, H-9 + ½×H-alk), 1.23 – 1.09 (m, 4H, H-alk).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.00 (C-2), 110.59 (br, C-1), 82.70 (C-8), 49.61 (C-3), 31.98 (CH_2), 26.84 (CH_2), 26.51 (CH_2), 25.02 (C-9), 19.88 (C-7).

IR (neat): 1633 (m), 1445 (m), 1387 (m), 1370 (m), 1345 (m), 1316 (s), 1258 (m), 1142 (s), 967 (m), 849 (m).



(*E*)-4,4,5,5-Tetramethyl-2-(2,3,3-trimethylbut-1-en-1-yl)-1,3,2-dioxaborolane (3d)[5]

Clear colorless oil.

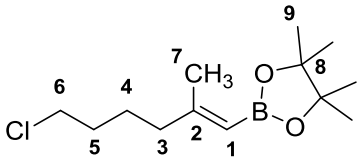
Yield: 68 mg (61%), rr >98:2.

R_f 0.31 (3% ether–pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.21 (q, *J*=0.9, 1H, H-1), 2.00 (d, *J*=0.9, 3H, H-5), 1.27 (s, 12H, H-7), 1.06 (s, 9H, H-4).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.21 (C-2), 109.62 (br, C-1), 82.78 (C-6), 38.31 (C-3), 29.21 (C-4), 25.04 (C-7), 17.63 (C-5).

IR (neat): 1627 (m), 1369 (m), 1346 (s), 1319 (m), 1281 (m), 1145 (s).



(*E*)-2-(6-Chloro-2-methylhex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)

Clear colorless oil.

Yield: 103 mg (79%), rr >98:2.

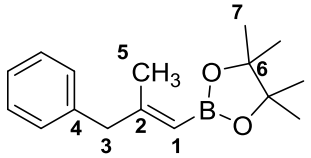
R_f 0.18 (3% ether–pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.11 (dq, *J*=2.2, 1.2, 1H, H-1), 3.52 (t, *J*=6.6, 2H, H-6), 2.12 (td, *J*=7.5, 1.1, 2H, H-3), 1.97 (d, *J*=1.0, 3H, H-7), 1.80 – 1.70 (m, 2H, H-5), 1.65 – 1.54 (m, 2H, H-4), 1.26 (d, *J*=6.0, 12H, H-9).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.04 (C-2), 113.59 (br, C-1), 82.79 (C-8), 45.08 (C-6), 41.29 (C-3), 32.22 (C-5), 25.00 (C-9), 24.86 (C-4), 21.15 (C-7).

IR (neat): 1638 (m), 1370 (m), 1317 (s), 1263 (s), 1142 (s).

HRMS (TOF ESI$^+$), m/z: calcd for $C_{13}H_{26}BClO_2$ $[M+H]^+$ 259.1633, found 259.1625.



(*E*)-4,4,5,5-Tetramethyl-2-(2-methyl-3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (3f)[8]

Clear colorless oil.

Yield: 105 mg (81%), rr 97:3.

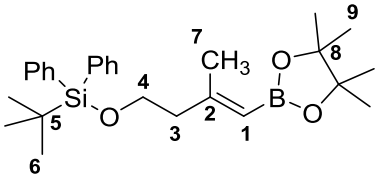
Gram-scale yield: 1.22 g (79%), rr 97:3.

R_f 0.17 (4% ether–pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.25 (m, 2H, H-Ph), 7.23 – 7.13 (m, 3H, H-Ph), 5.13 (h, *J*=1.1, 1H, H-1), 3.45 – 3.37 (m, 2H, H-3), 1.97 (d, *J*=1.0, 3H, H-5), 1.26 (s, 12H, H-7).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.41 (C-2), 139.38 (C-4), 129.40 (C-Ph), 128.42 (C-Ph), 126.26 (C-Ph), 115.23 (br.s, C-1), 82.84 (C-6), 48.90 (C-3), 25.01 (C-7), 21.13 (C-5).

IR (neat): 3062 (w), 3027 (w), 1638 (m), 1385 (m), 1367 (s), 1318 (s), 1251 (m), 1141 (s), 670 (m), 852 (m), 699 (m).



(*E*)-*tert*-Butyl((3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)oxy)diphenylsilane (3g)

MMAO-12 assisted carboalumination. Non-acidic workup.

Clear colorless oil.

Yield: 165 mg (73%), rr 93:7.

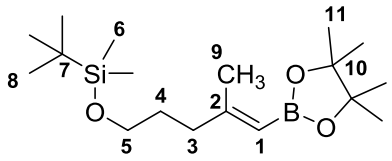
R_f 0.20 (10% ether-pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.63 (m, 4H, H-Ph), 7.45 – 7.33 (m, 6H, H-Ph), 5.12 – 5.08 (m, 1H, H-1), 3.78 (t, *J*=7.1, 2H, H-4), 2.38 (td, *J*=7.1, 1.0, 2H, H-3), 1.95 (d, *J*=1.0, 3H, H-7), 1.26 (s, 12H, H-9), 1.05 (s, 9H, H-6).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.79 (C-2), 135.73 (C-Ph), 134.10 (C-Ph), 129.67 (C-Ph), 127.74 (C-Ph), 115.31 (br.s, C-1), 82.75 (C-8), 62.93 (C-4), 45.23 (C-3), 27.01 (C-6), 24.99 (C-9), 21.74 (C-7), 19.36 (C-5).

IR (neat): 3020 (w), 1640 (m), 1365 (m), 1317 (m), 1262 (m), 1142 (s), 1106 (s), 1072 (m), 701 (s).

HRMS (TOF ESI$^+$), m/z: calcd for $C_{27}H_{39}BO_3SiNa^+$ $[M+Na]^+$ 473.2659, found 473.2642.



(*E*)-*tert*-Butyldimethyl((4-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)oxy)silane (3h)

Prepared by general procedure, performing the carboalumination for 24 hr. Non-acidic workup.

Clear colorless oil.

Yield: 128 mg (75%), rr 96:4.

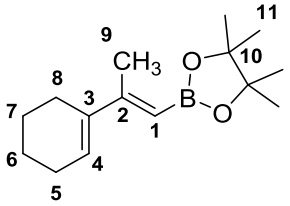
R_f 0.26 (4% ether-pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.12 (h, *J*=1.1, 1H, H-1), 3.60 (t, *J*=6.5, 2H, H-5), 2.13 (td, *J*=7.9, 1.2, 2H, H-3), 1.98 (d, *J*=1.0, 3H, H-9), 1.71 – 1.62 (m, 2H, H-4), 1.26 (s, 12H, H-11), 0.88 (s, 9H, H-8), 0.03 (s, 6H, H-6).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.80 (C-2), 113.18 (br.s, C-1), 82.73 (C-10), 63.02 (C-5), 38.51 (C-3), 31.05 (C-4), 26.10 (C-8), 25.01 (C-11), 21.40 (C-9), 18.46 (C-7), −5.12 (C-6).

IR (neat): 1638 (m), 1369 (m), 1317 (s), 1257 (s), 1142 (s), 1102 (s), 833 (s), 773 (s).

HRMS (TOF ESI$^+$), m/z: calcd for $C_{18}H_{37}BO_3SiNa^+$ $[M+Na]^+$ 363.2501, found 363.2507.



(*E*)-2-(2-(Cyclohex-1-en-1-yl)prop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)

Prepared according to the general procedure, with the alumination step taking 20 hr.

Clear yellow oil.

Yield: 91 mg (73%), rr 97:3.

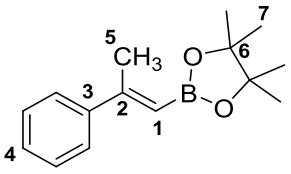
R_f 0.35 (5% ether-pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.09 (tt, *J*=4.1, 1.4, 1H, H-4), 5.36 (s, 1H, H-1), 2.24 – 2.15 (m, 4H, H-5,8), 2.14 (s, 3H, H-9), 1.74 – 1.60 (m, 2H, H-6/7), 1.59 – 1.50 (m, 2H, H-7/6), 1.27 (s, 12H, H-11).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.91 (C-2), 138.88 (C-3), 127.63 (C-4), 110.96 (br.s, C-1), 82.82 (C-10), 26.36 (C-5/8), 25.87 (C-8/5), 24.99 (C-11), 23.20 (C-6/7), 22.23 (C-7/6), 18.21 (C-9).

IR (neat): 1601 (m), 1449 (w), 1370 (m), 1332 (s), 1321 (s), 1305 (m), 1261 (m), 1142 (s).

HRMS (TOF ESI$^+$), m/z: calcd for $C_{15}H_{26}BO_2^+$ $[M+H]^+$ 249.2023, found 249.2033.



(*E*)-4,4,5,5-Tetramethyl-2-(2-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (3j)[5,8–10]

Prepared by general procedure, performing the carboalumination for 96 hr.

Clear yellow oil.

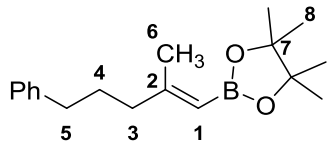
Yield: 83 mg (45%), rr 97:3.

R_f 0.32 (5% ether-pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.39 (m, 2H, H-Ph), 7.27 – 7.16 (m, 3H, H-Ph), 5.68 (q, *J*=1.0, 1H, H-1), 2.33 (d, *J*=1.0, 3H, H-5), 1.24 (s, 12H, H-7).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.91 (C-2), 143.97 (C-3), 128.27 (C-Ph), 128.03 (C-4), 125.95 (C-Ph), 115.42 (br.s, C-1), 83.07 (C-6), 25.04 (C-7), 20.23 (C-5).

IR (neat): 1618 (m), 1446 (m), 1379 (m), 1353 (s), 1320 (s), 1207 (m), 1142 (s), 979 (m), 759 (s).



(*E*)-4,4,5,5-Tetramethyl-2-(2-methyl-5-phenylpent-1-en-1-yl)-1,3,2-dioxaborolane (3k)

Clear colorless oil.

Yield: 115 mg (80%), rr >98:2.

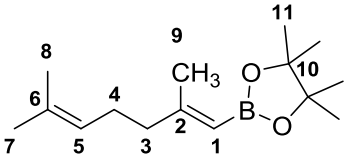
R_f 0.23 (3% ether–pentane)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.23 (m, 2H, H-Ph), 7.23 – 7.11 (m, 3H, H-Ph), 5.16 (q, *J*=1.0, 1H, H-1), 2.61 (t, *J*=7.7, 2H, H-5), 2.20 – 2.09 (m, 2H, H-3), 1.99 (d, *J*=1.0, 3H, H-6), 1.86 – 1.74 (m, 2H, H-4), 1.28 (s, 12H, H-8).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.66 (C-2), 142.56 (Cq), 128.54 (C-Ph), 128.37 (C-Ph), 125.78 (C-Ph), 113.22 (br, C-1), 82.74 (C-7), 41.75 (C-3), 35.60 (C-5), 29.37 (C-4), 25.01 (C-8), 21.28 (C-6).

IR (neat): 3026 (w), 1637 (m), 1369 (m), 1316 (s), 1251 (m), 1140 (s), 970 (m).

HRMS (TOF ESI$^+$), m/z: calcd for $C_{18}H_{28}BO_2$ $[M+H]^+$ 287.2180, found 287.2174.



(*E*)-2-(2,6-Dimethylhepta-1,5-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)[2]

Clear colorless oil.

Yield: 106 mg (85%), rr 95:5.

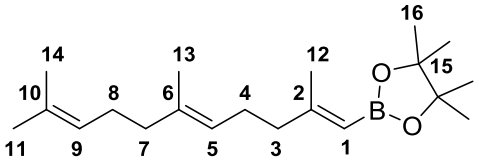
Gram-scale yield: 756 mg (50%), rr 95:5.

R_f 0.18 (3% ether-pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.16 – 5.12 (m, 1H, H-1), 5.14 – 5.08 (m, 1H, H-5), 2.17 – 2.06 (m, 4H, H-3,4), 1.98 (d, J=1.0, 3H, H-9), 1.67 (s, 3H, H-7/8), 1.59 (d, J=0.7, 3H, H-8/7), 1.27 (s, 12H, H-11).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.95 (C-2), 131.84 (C-6), 124.13 (C-5), 82.76 (C-10), 42.25 (C-3), 26.55 (C-4), 25.82 (C-8/7), 25.03 (C-11), 21.42 (C-9), 17.80 (C-7/8). *Note: C-1 not observed due to broadening on B.*

IR (neat): 1638 (m), 1368 (m), 1316 (s), 1263 (m), 1142 (s), 970 (m), 852 (m).



4,4,5,5-Tetramethyl-2-((1*E*,5*E*)-2,6,10-trimethylundeca-1,5,9-trien-1-yl)-1,3,2-dioxaborolane (3m)

Non-acidic workup.

Clear colorless oil.

Yield: 124 mg (78 %), rr 95:5.

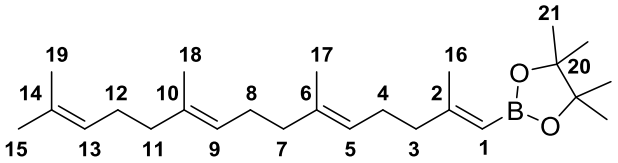
R_f 0.31 (4% ether–pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.20 – 5.05 (m, 3H, H-1,5,9), 2.18 – 1.92 (m, 11H, H-3,4,7,8,12), 1.70 – 1.66 (m, 3H, CH_3), 1.59 (app.t, *J*=1.8, 6H, 2×CH_3), 1.26 (s, 12H, H-16).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.95 (C-2), 135.45 (C_q), 131.41 (C_q), 124.51 (CH), 123.99 (CH), 112.82 (br.s, C-1), 82.72 (C-15), 42.26 (CH_2), 39.84 (CH_2), 26.90 (CH_2), 26.46 (CH_2), 25.83 (CH_3), 25.01 (C-16), 21.41 (C-12), 17.83 (CH_3), 16.12 (CH_3).

IR (neat): 1637 (m), 1368 (m), 1316 (s), 1263 (m), 1141 (s), 970 (m), 851 (m).

HRMS (TOF ESI$^+$), m/z: calcd for $C_{20}H_{36}BO_2^+$ $[M+H]^+$ 319.2807, found 319.2809.



4,4,5,5-Tetramethyl-2-((1*E*,5*E*,9*E*)-2,6,10,14-tetramethylpentadeca-1,5,9,13-tetraen-1-yl)-1,3,2-dioxaborolane (3n)

Non-acidic workup.

Clear colorless oil.

Yield: 155 mg (80 %), rr 95:5.

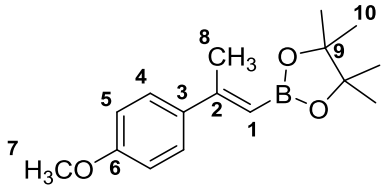
R_f 0.33 (4% ether-pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.19 – 5.04 (m, 4H, H-1,5,9,13), 2.18 – 2.10 (m, 4H), 2.10 – 2.02 (m, 4H), 2.01 – 1.94 (m, 6H), 1.68 (d, *J*=1.3, 3H, CH_3), 1.63 – 1.55 (m, 9H, 3×CH_3), 1.27 (s, 12H, H-21).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.81 (C-2), 135.33 (C_q), 134.90 (C_q), 131.20 (C_q), 124.42 (=C–H), 124.24 (=C–H), 123.85 (=C–H), 112.74 (C-1), 82.57 (C-20), 42.13 (CH_2), 39.72 (CH_2), 39.70 (CH_2), 26.77 (CH_2), 26.67 (CH_2), 26.34 (CH_2), 25.69 (CH_3), 24.86 (C-21), 21.28 (CH_3), 17.68 (CH_3), 16.00 (CH_3), 15.98 (CH_3).

IR (neat): 1638 (m), 1368 (s), 1316 (s), 1263 (s), 1142 (s), 970 (m), 851 (m).

HRMS (TOF ESI$^+$), m/z: calcd for $C_{25}H_{44}BO_2^+$ $[M+H]^+$ 387.3433, found 387.3434.



(*E*)-2-(2-(4-Methoxyphenyl)prop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)[10]

MMAO-12 assisted carboalumination. Non-acidic workup – the product is acid-sensitive.

Clear colorless oil that turns into white wax after ageing at −20 °C for 14 hr.

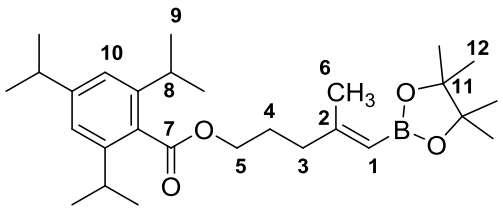
Yield: 120 mg (88%), rr 98:2.

R_f 0.20 (10% ether-pentane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J*=8.8, 2H, H-4), 6.85 (d, *J*=8.8, 2H, H-5), 5.73 – 5.68 (m, 1H, H-1), 3.81 (s, 3H, H-7), 2.39 (d, *J*=1.0, 3H, H-8), 1.31 (s, 12H, H-10).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.69 (C_q), 157.20 (C_q), 136.23 (C-3), 127.19 (C-4), 113.58 (C-5), 82.98 (C-9), 55.41 (C-7), 25.04 (C-10), 20.11 (C-8). *Note: C-1 not observed due to broadening on B.*

IR (neat): 1615 (m), 1602 (s), 151 (s), 1352 (s), 1250 (s), 1236 (s), 1141 (s), 1031 (m), 827 (s), 805 (m).



(*E*)-4-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 2,4,6-triisopropylbenzoate (3p)

MMAO-12 assisted carboalumination.

Clear colorless oil.

Yield: 155 mg (69%), rr 95:5 → >99:1 after chromatographic separation.

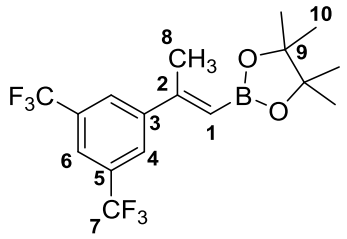
R_f 0.22 (10% ether–pentane)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (s, 2H, H-10), 5.14 (q, *J*=1.1, 1H, H-1), 4.30 (t, *J*=6.6, 2H, H-5), 2.95 – 2.77 (m, 3H, H-8), 2.27 – 2.17 (m, 2H, H-3), 1.99 (d, *J*=1.0, 3H, H-6), 1.94 – 1.84 (m, 2H, H-4), 1.35 – 1.17 (m, 30H, H-12, 9).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.09 (C-7), 161.22 (C-2), 150.19 (C-Ph), 144.89 (C-Ph), 130.75 (C_q), 120.98 (C-10), 113.49 (br.s, C-1), 82.86 (C-11), 64.83 (C-5), 38.51 (C-3), 34.58 (C-8), 31.65 (C-8), 26.81 (C-4), 25.02 (C-12), 24.32 (C-9), 24.10 (C-9), 21.30 (C-6).

IR (neat): 1725 (s), 1639 (m), 1369 (m), 1319 (m), 1251 (s), 1139 (s), 1074 (m), 971 (m).

HRMS (TOF ESI$^+$), m/z: calcd for $C_{28}H_{45}BO_4Na^+$ $[M+Na]^+$ 479.3308, found 479.3305.



(*E*)-2-(2-(3,5-*bis*(Trifluoromethyl)phenyl)prop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3q)

MMAO-assisted carboalumination. Non-acidic workup – the product is acid-sensitive.

Yield: 63 mg (33%), rr >98:2.

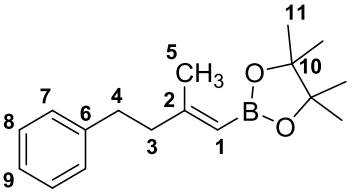
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.88 (m, 2H, H-4), 7.81 – 7.76 (m, 1H, H-6), 5.85 (q, *J*=1.0, 1H, H-1), 2.43 (d, *J*=1.0, 3H, H-8), 1.33 (s, 12H, H-10).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.40 (C_q), 145.98 (C_q), 131.71 (q, *J*=33.1, C-5), 126.07 (m, C-4), 123.53 (q, *J*=252, C-7), 122.18 (C_q), 121.54 (q, *J*=3.8, C-6), 83.57 (C-9), 25.04 (C-10), 19.99 (C-8). *Note: C-1 is not observed due to broadening on B.*

^{19}F NMR (377 MHz, $CDCl_3$): δ −62.94.

IR (neat): 1627 (w), 1376 (m), 1355 (m), 1278 (s), 1179 (m), 1135 (s).

HRMS (MALDI), m/z: calcd for $C_{17}H_{19}BF_6O_2^+$ [M^+] 403.1278, found 403.1285.



(*E*)-4,4,5,5-Tetramethyl-2-(2-methyl-4-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane (3t)[5,11]

Prepared according to the general procedure on gram scale.

Clear colorless oil.

Yield: 1.27 g (78%), rr 93:7 → 98:2 (after chromatographic separation).

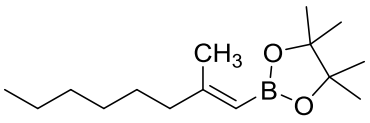
R_f 0.26 (5% ether-pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.23 (m, 2H, H-Ph), 7.23 – 7.15 (m, 3H, H-Ph), 5.22 (q, *J*=1.0, 1H, H-1), 2.82 – 2.73 (m, 2H, H-4), 2.45 – 2.37 (m, 2H, H-3), 2.05 (d, *J*=1.0, 3H, H-5), 1.28 (s, 12H, H-11).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.23 (C-2), 142.28 (C-6), 128.46 (C-Ar), 128.41 (C-Ar), 125.91 (C-Ar), 113.46 (br.s, C-1), 82.81 (C-10), 44.04 (C-3), 34.43 (C-4), 25.01 (C-11), 21.53 (C-5).

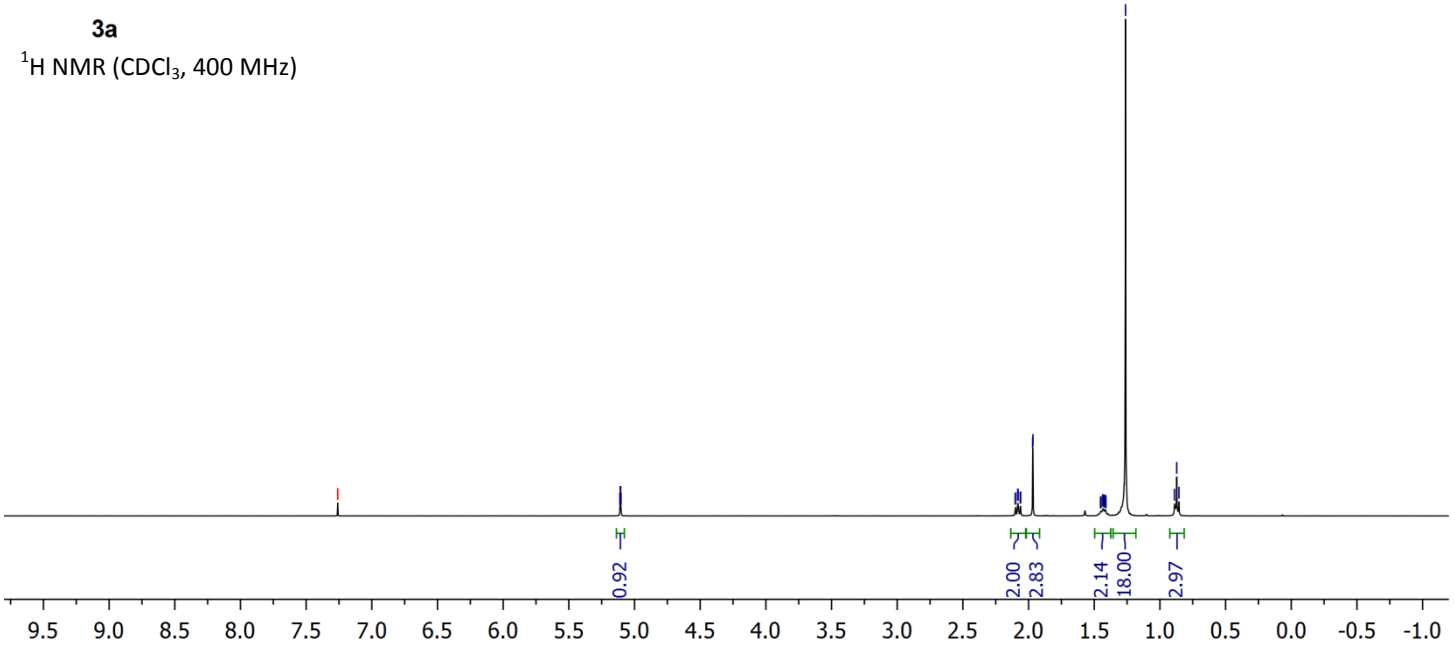
IR (neat): 3063 (w), 3027 (w), 1638 (m), 1379 (m), 1368 (s), 1317 (s), 1264 (s), 1140 (s), 969 (m), 851 (m).

NMR Spectra

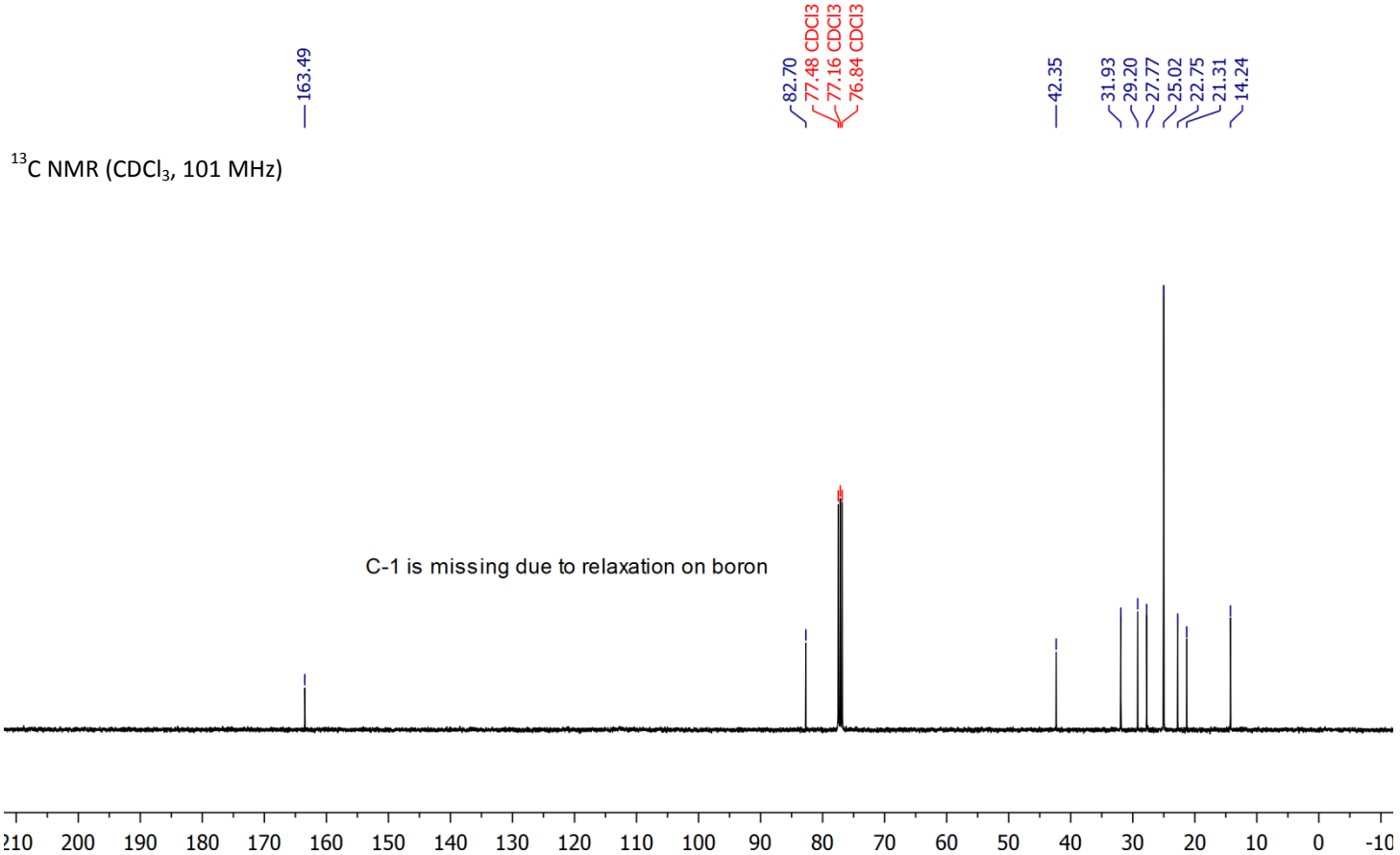


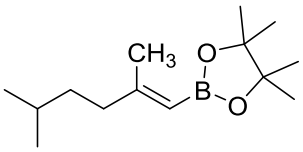
3a

^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

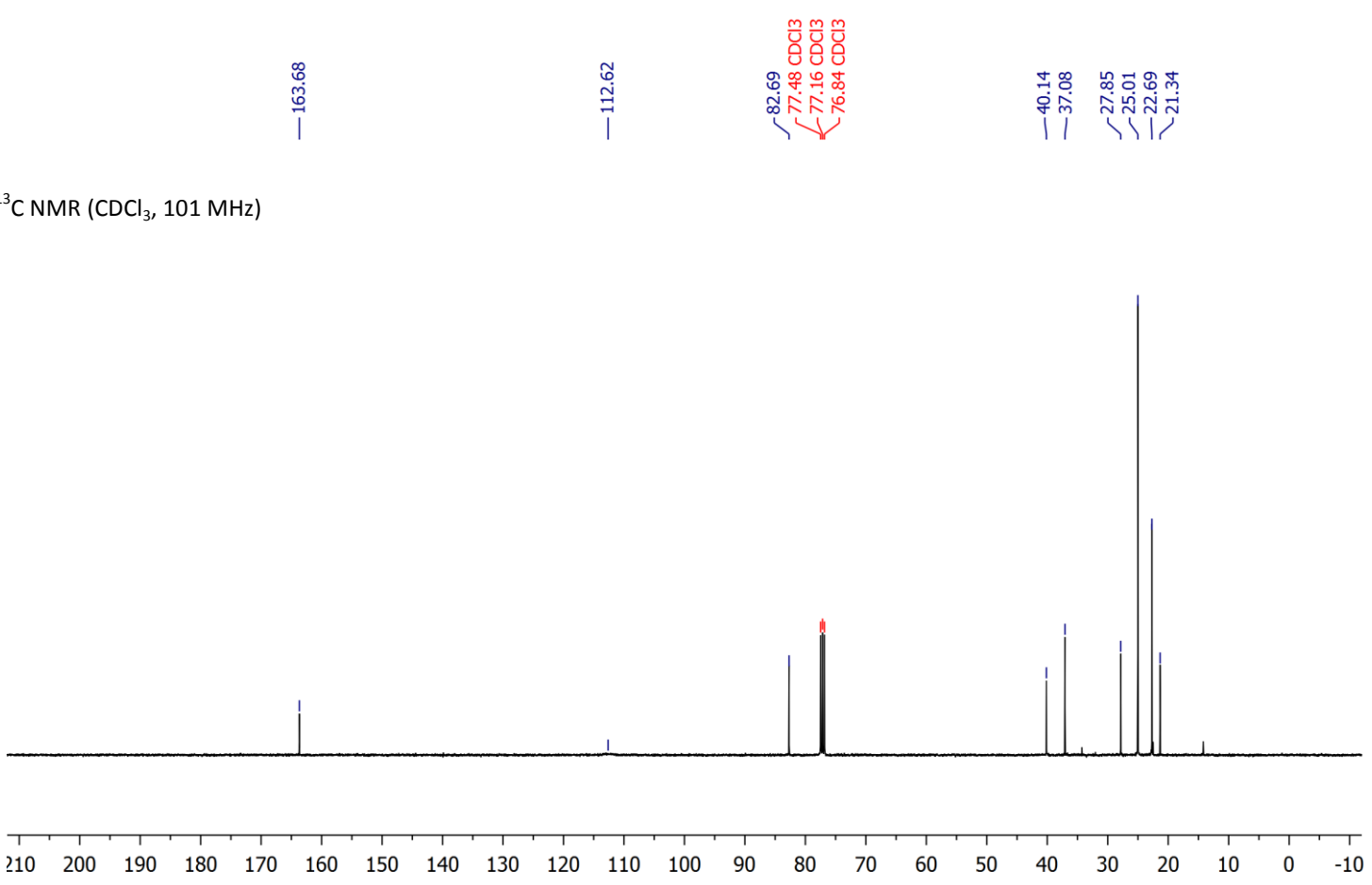


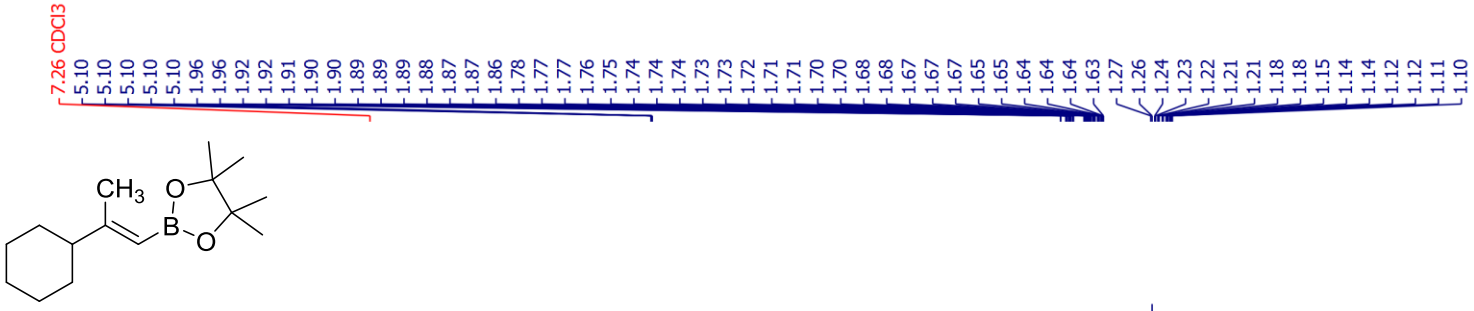


3b

^{1}H NMR ($CDCl_3$, 400 MHz)

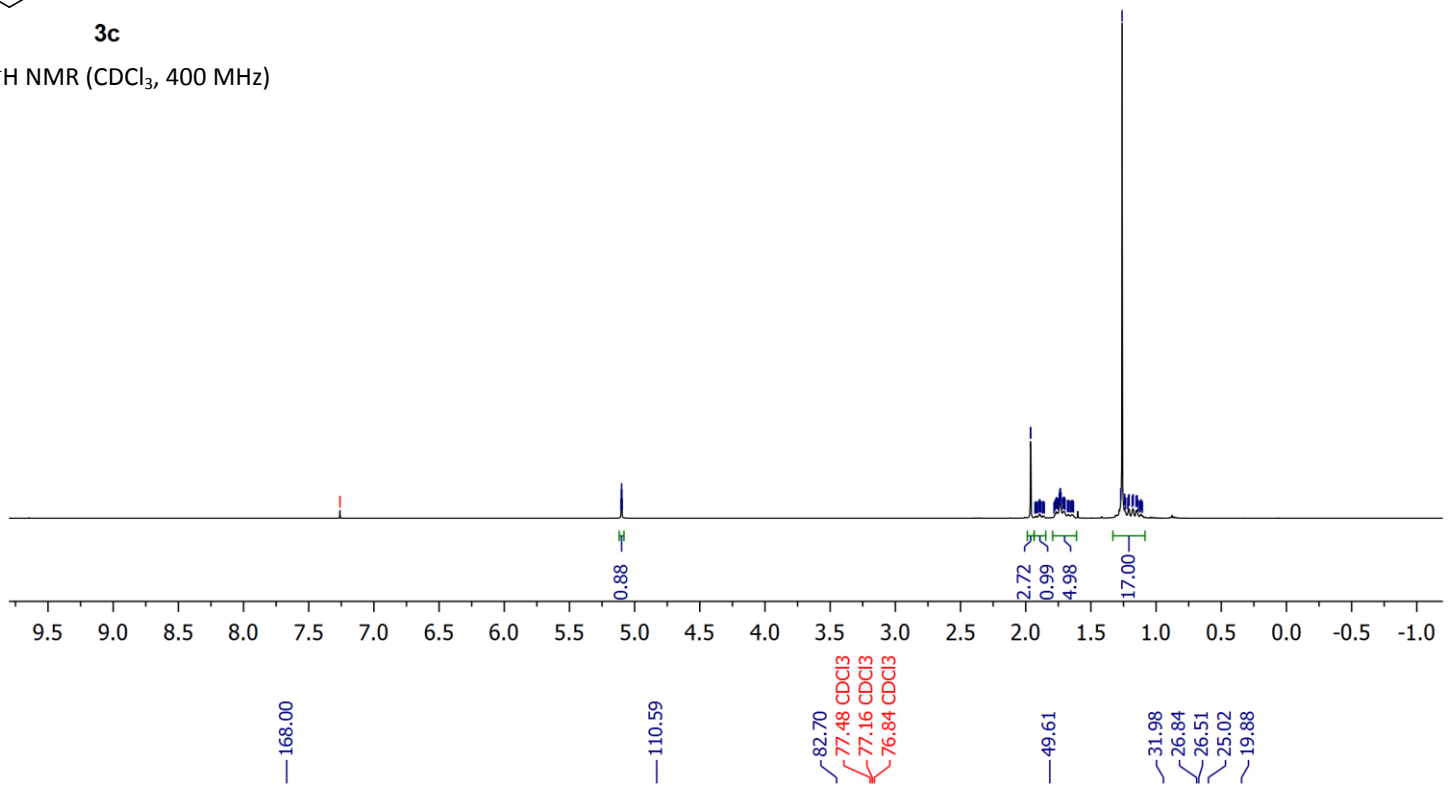
^{13}C NMR ($CDCl_3$, 101 MHz)



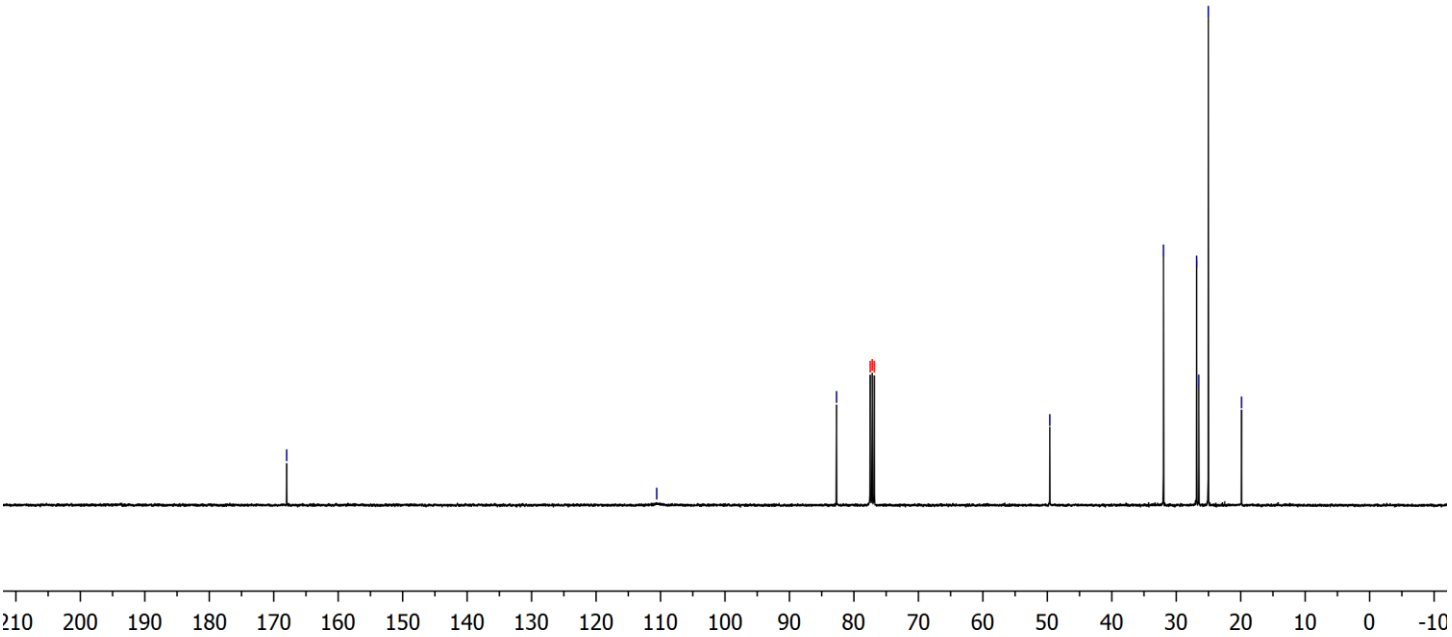


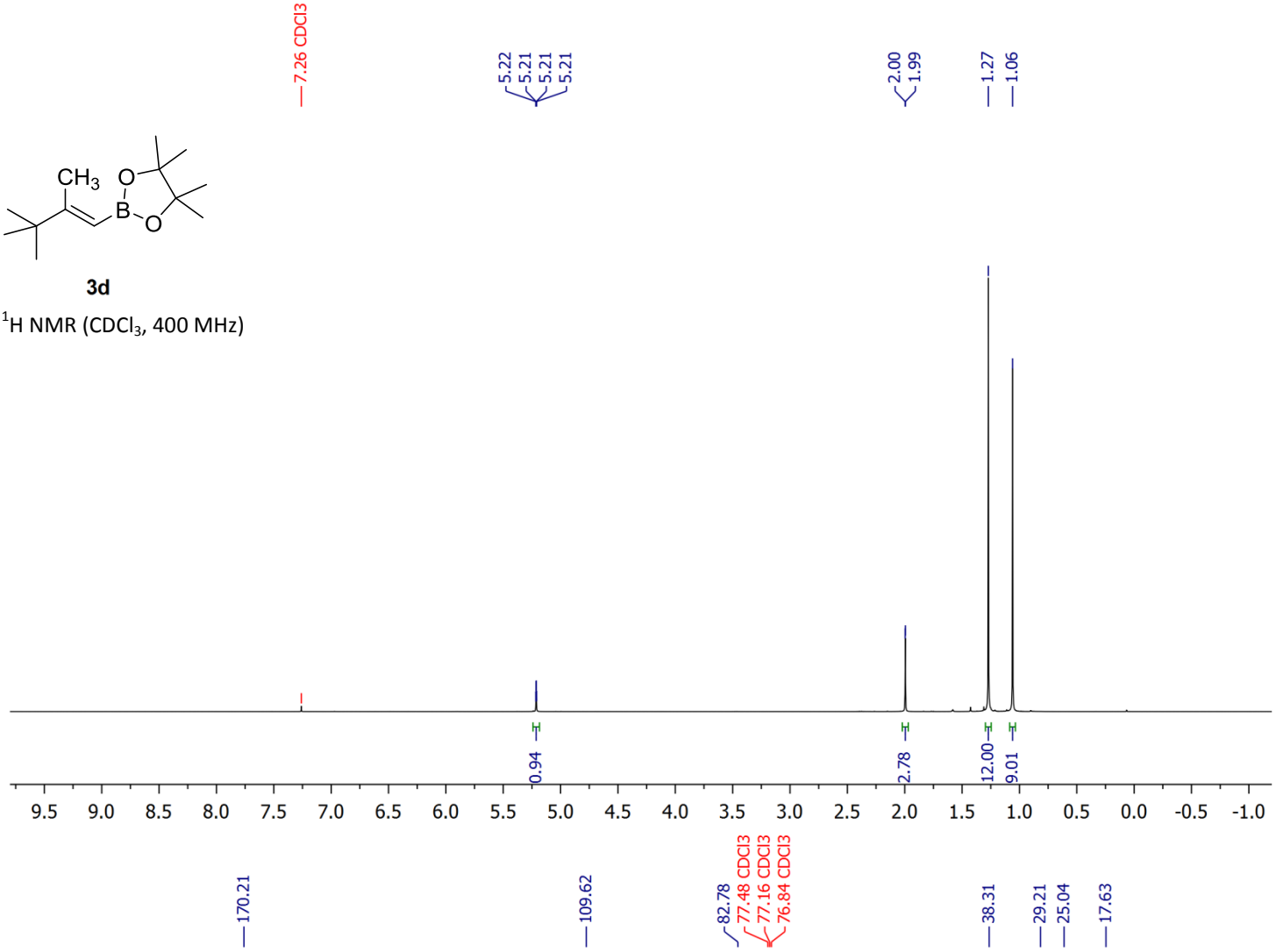
3c

^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

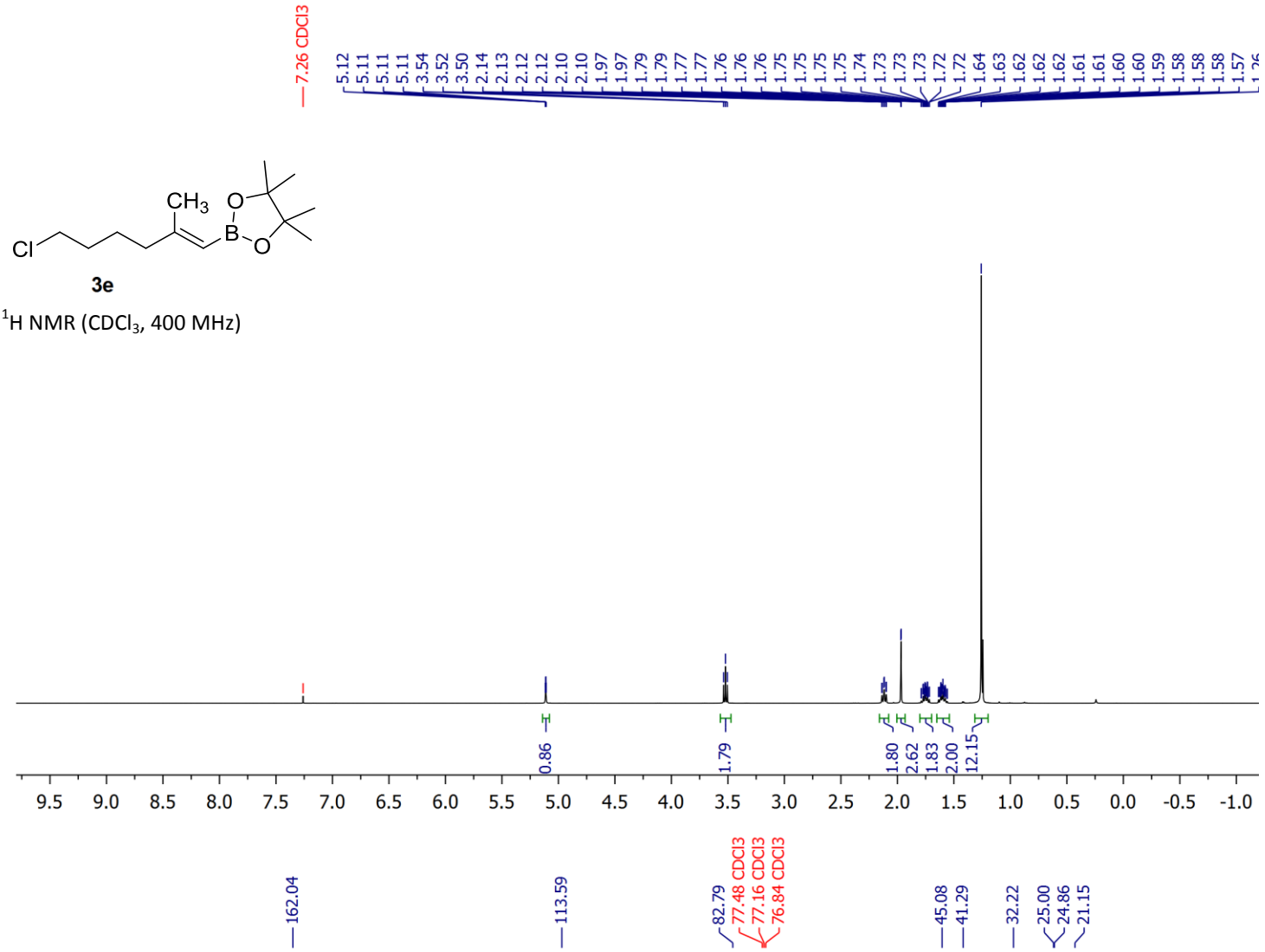




3d

^{1}H NMR ($CDCl_3$, 400 MHz)

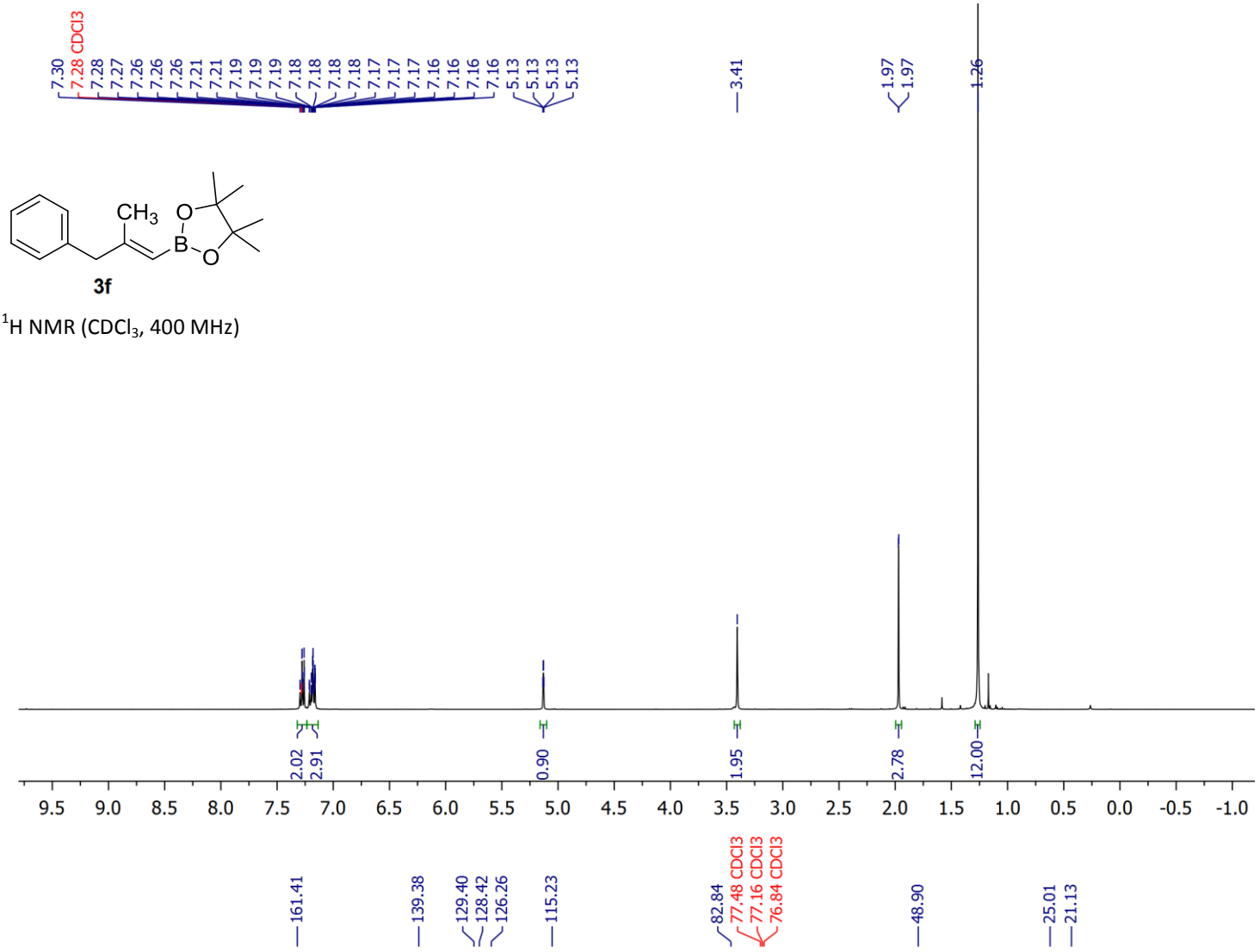
^{13}C NMR ($CDCl_3$, 101 MHz)



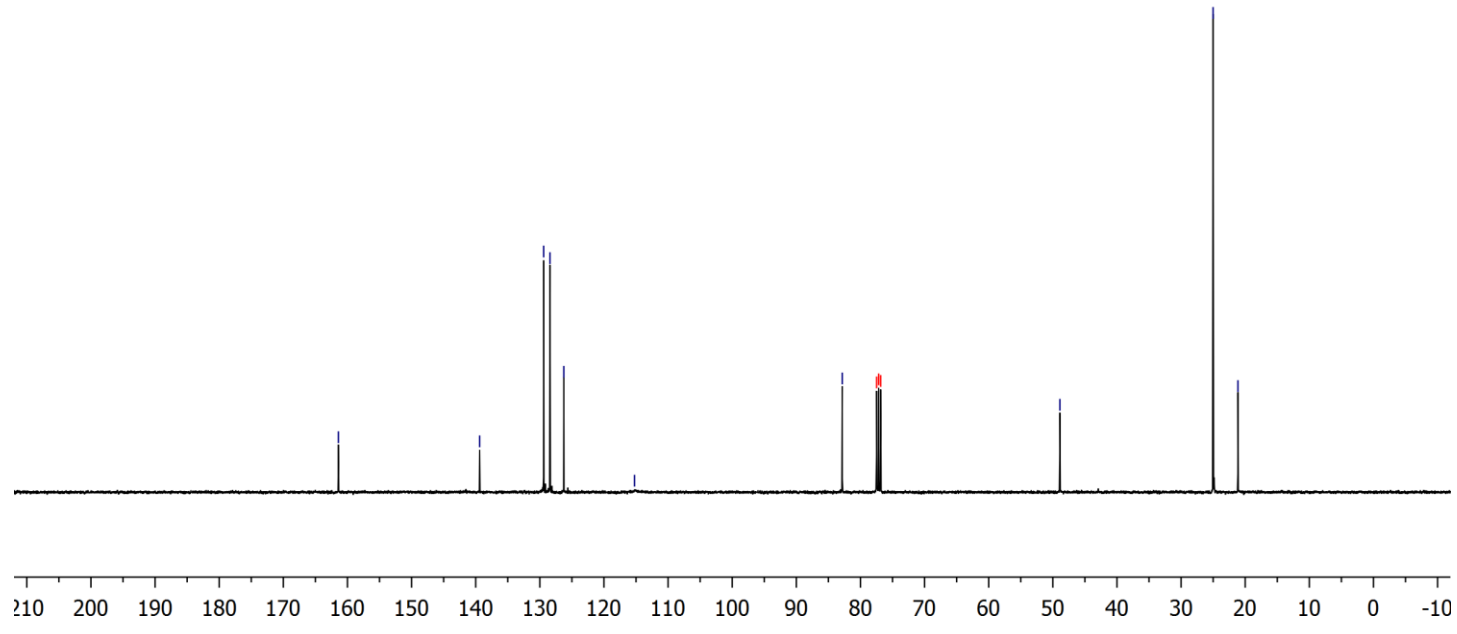
3e

^{1}H NMR ($CDCl_3$, 400 MHz)

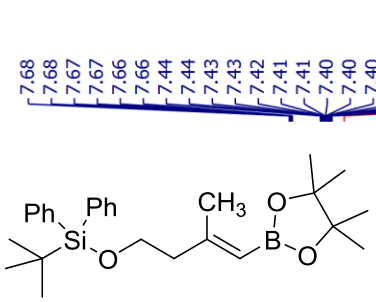
^{13}C NMR ($CDCl_3$, 101 MHz)



^{1}H NMR ($CDCl_3$, 400 MHz)

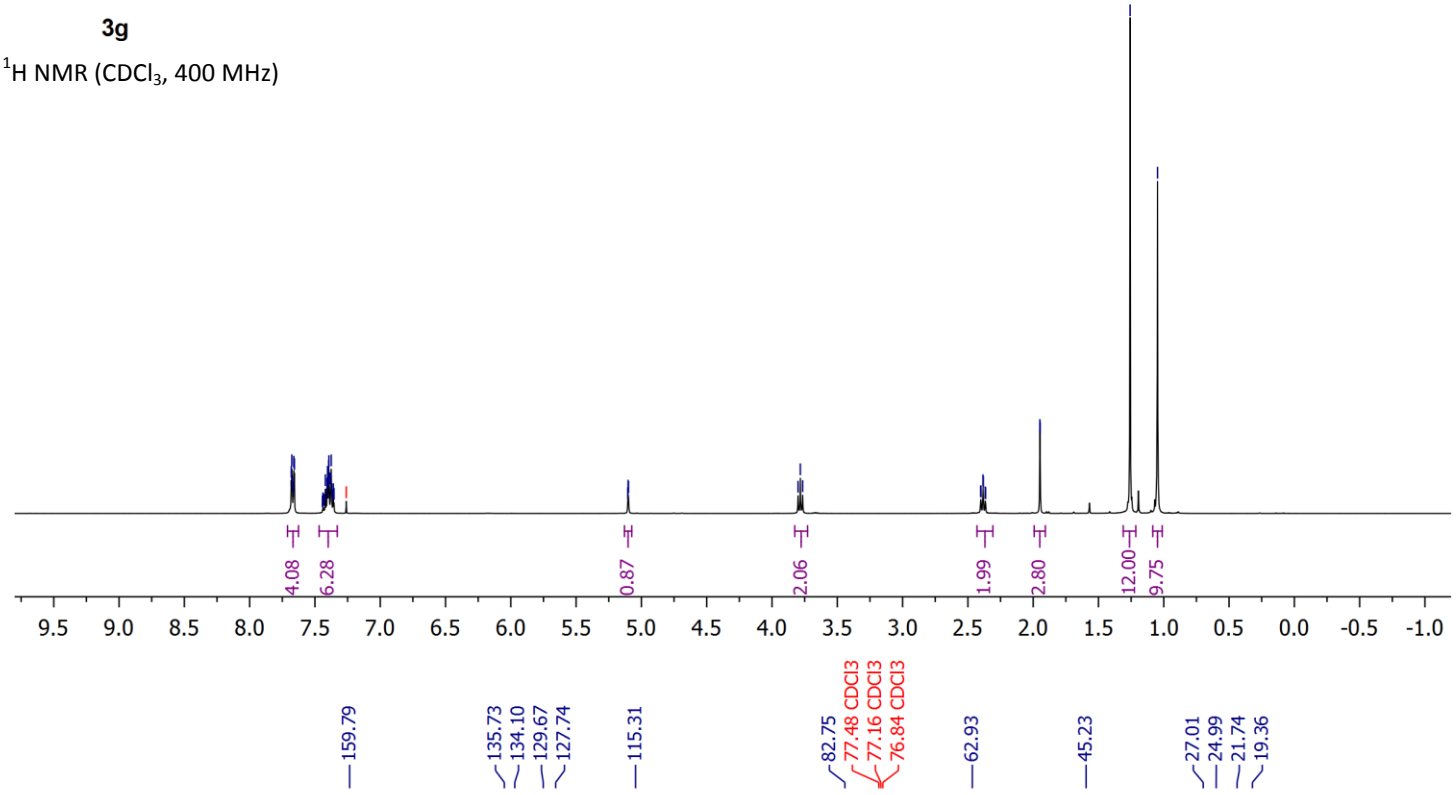


^{13}C NMR ($CDCl_3$, 101 MHz)

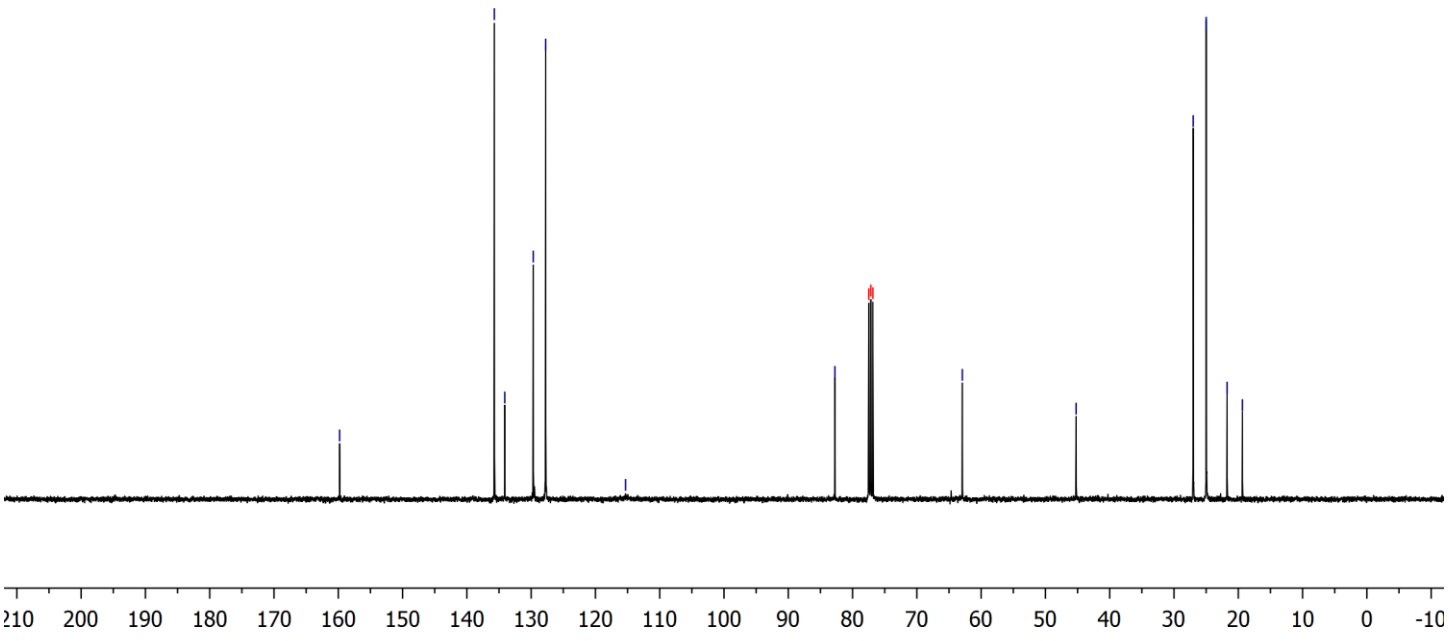


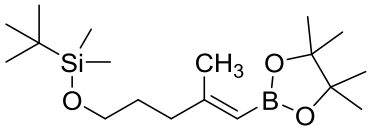
3g

^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

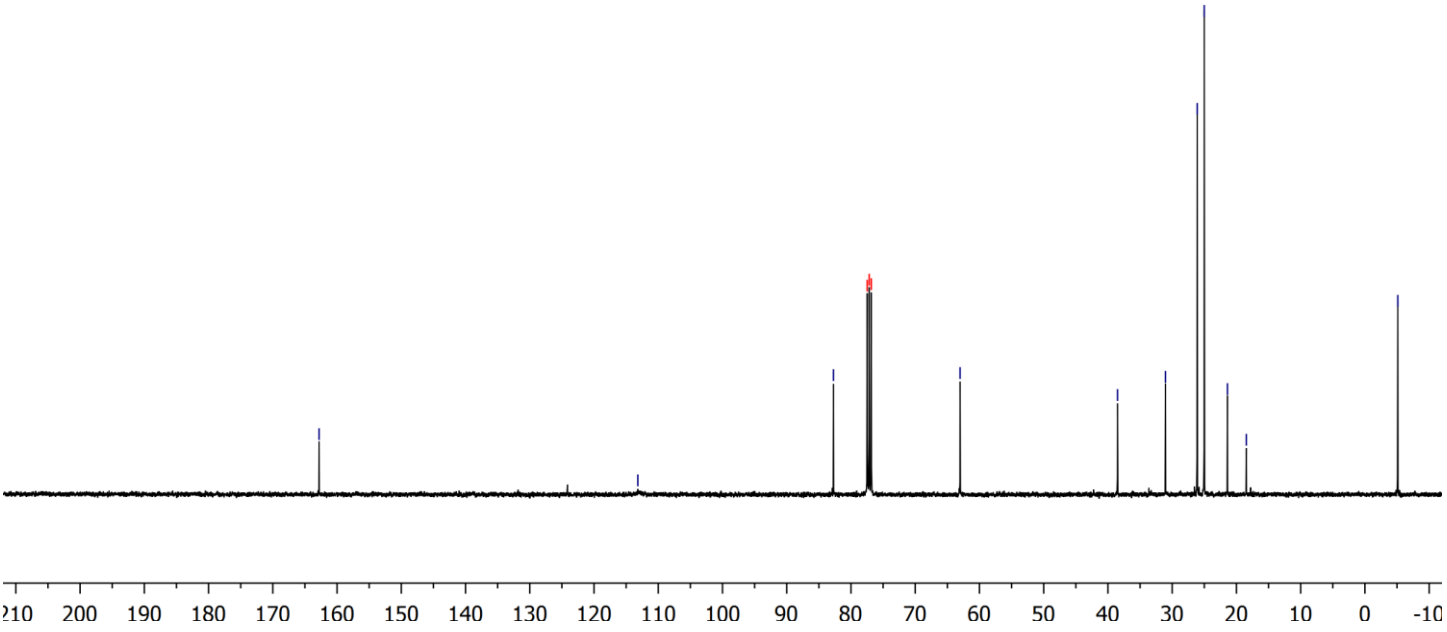


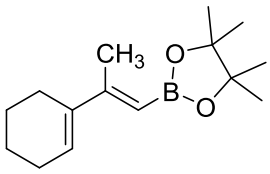


3h

^{1}H NMR ($CDCl_3$, 400 MHz)

^{13}C NMR ($CDCl_3$, 101 MHz)

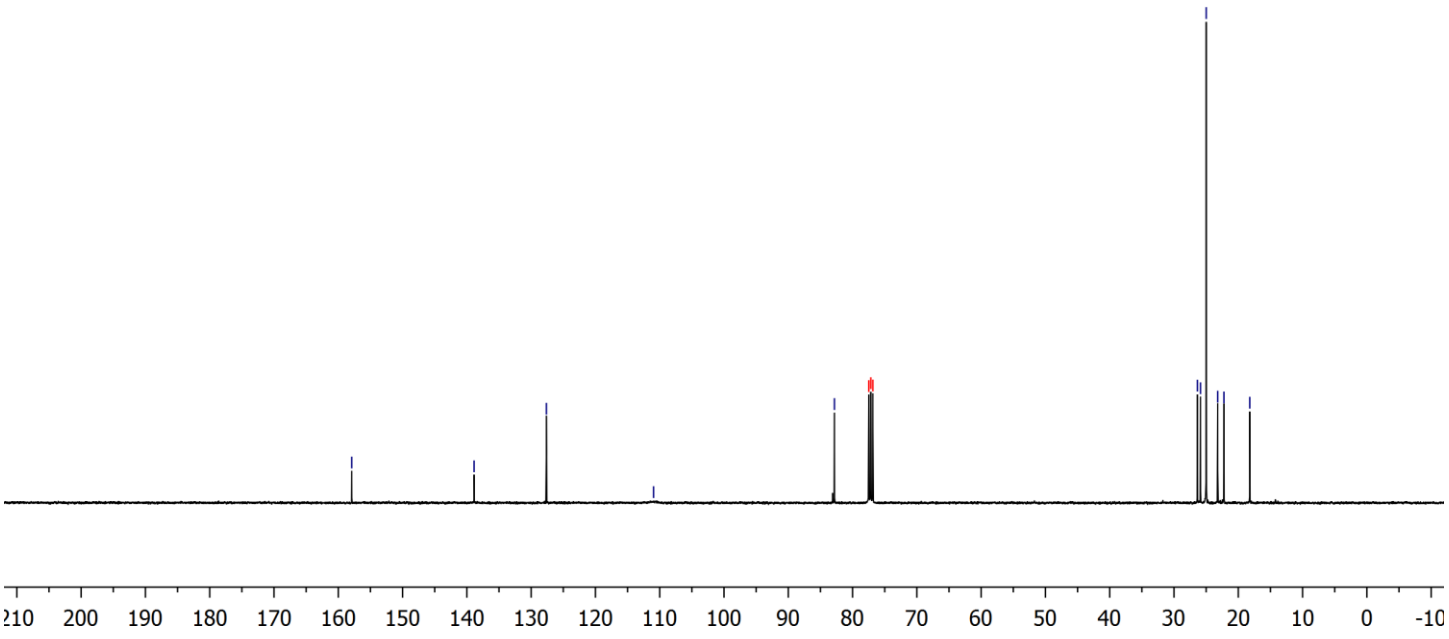


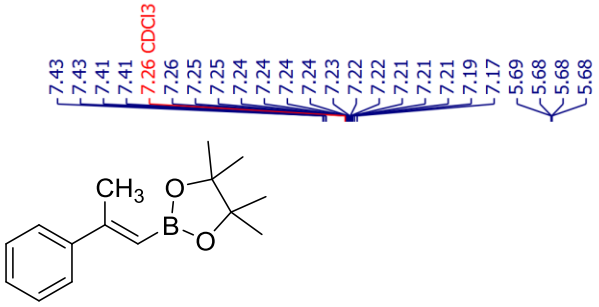


3i

^{1}H NMR ($CDCl_3$, 400 MHz)

^{13}C NMR ($CDCl_3$, 101 MHz)

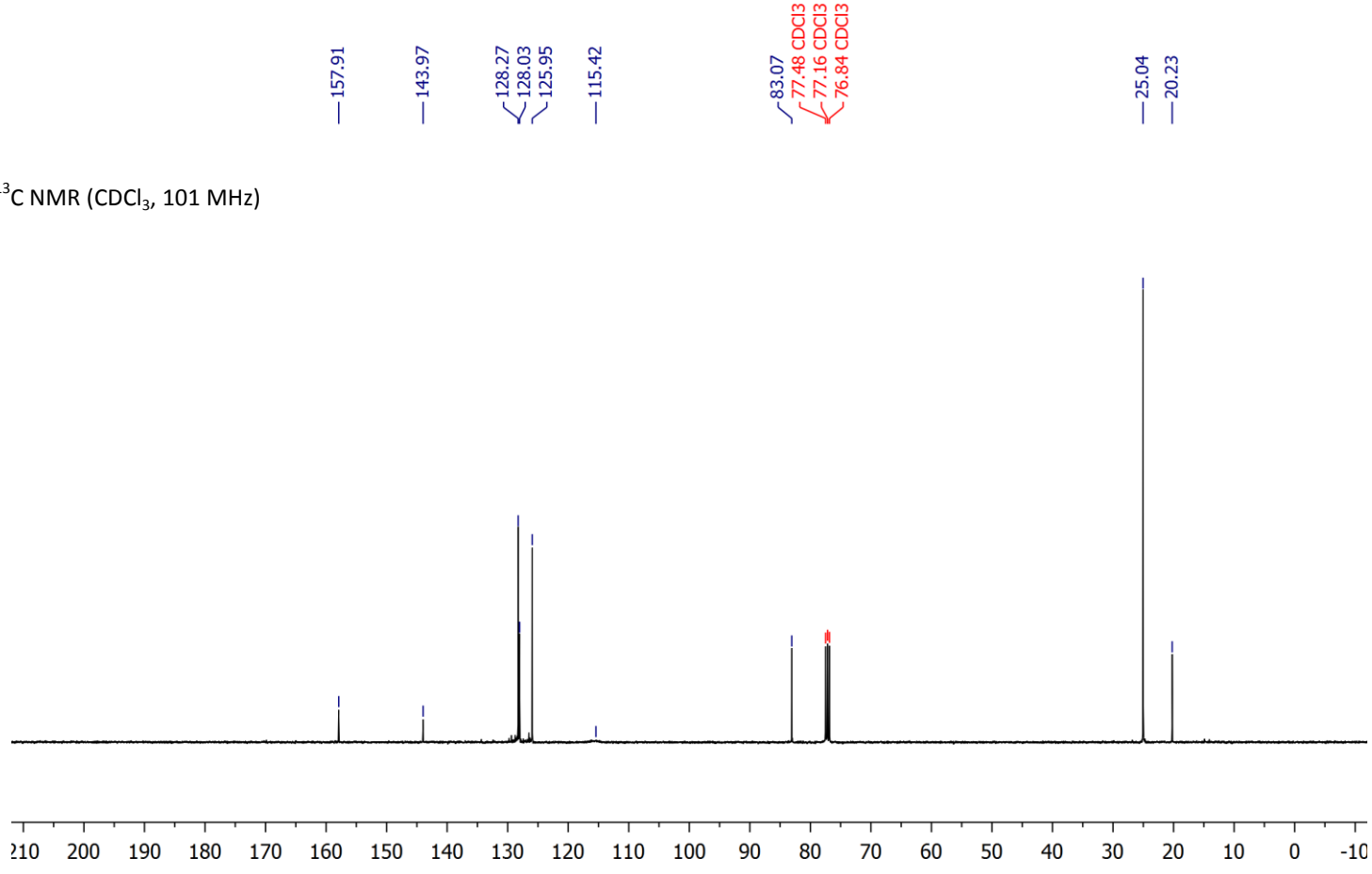


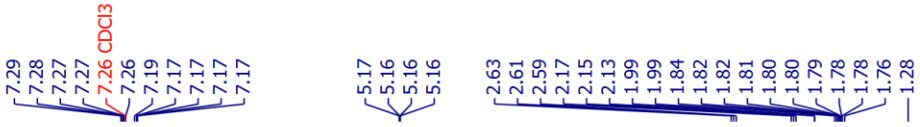


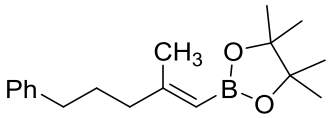
3j

^{1}H NMR ($CDCl_3$, 400 MHz)

^{13}C NMR ($CDCl_3$, 101 MHz)

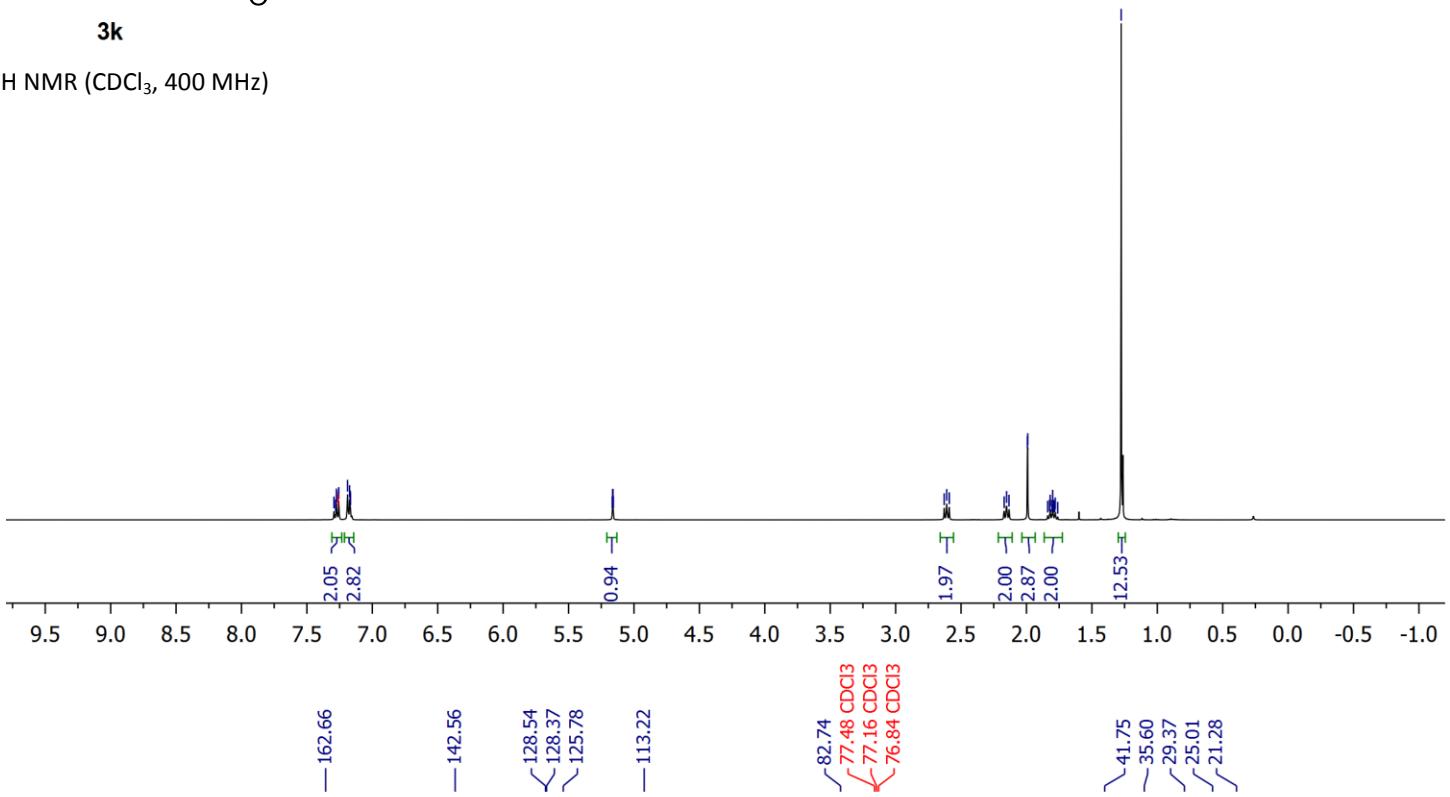




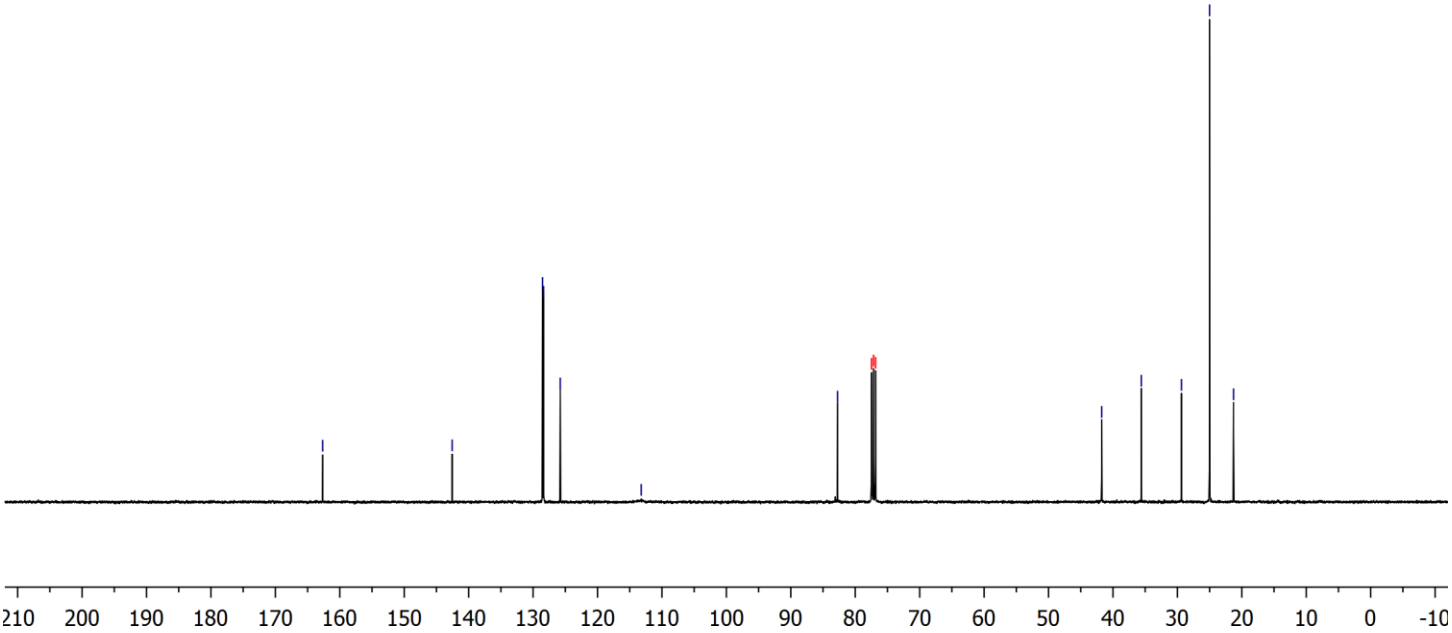


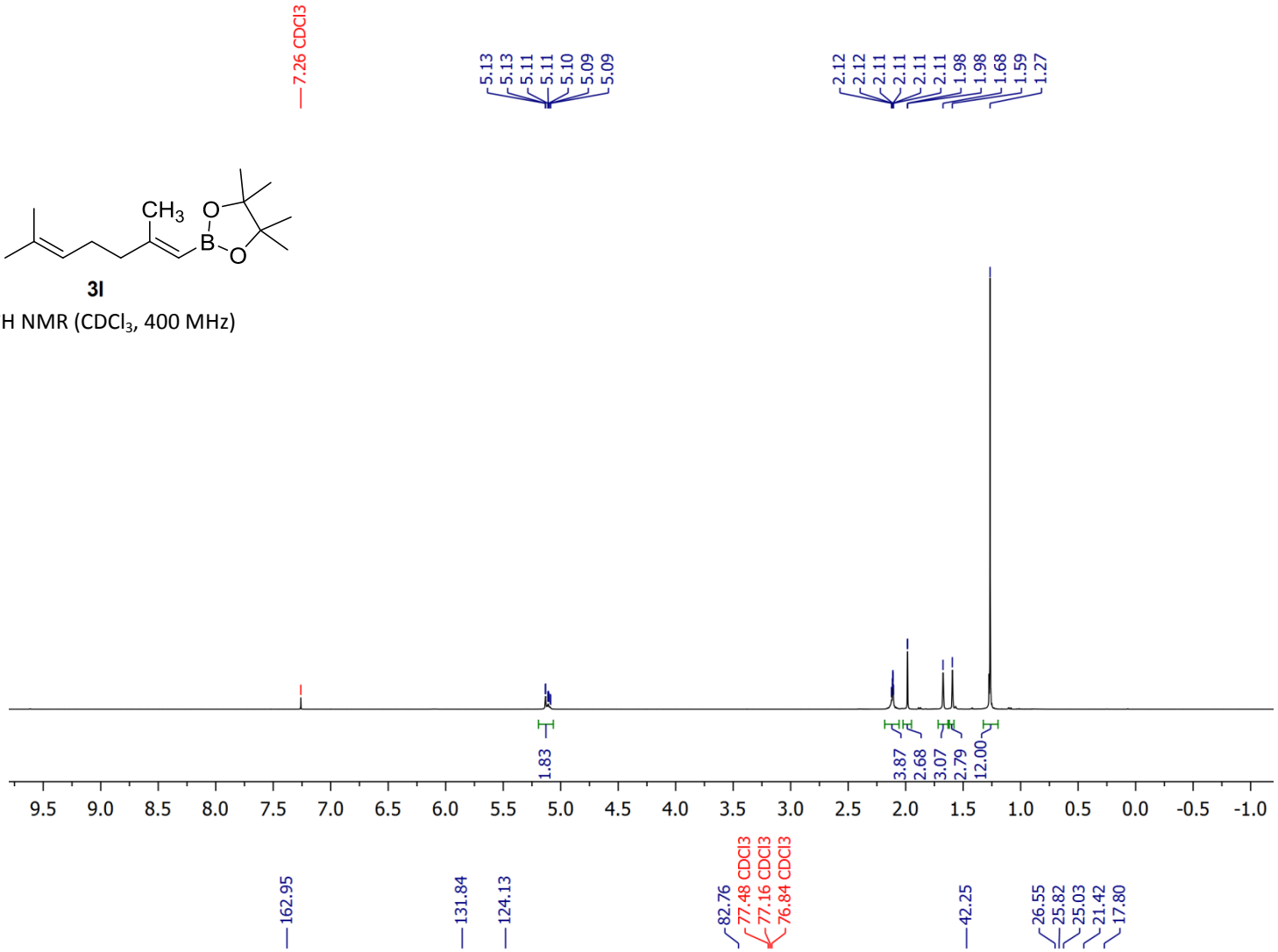
3k

^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

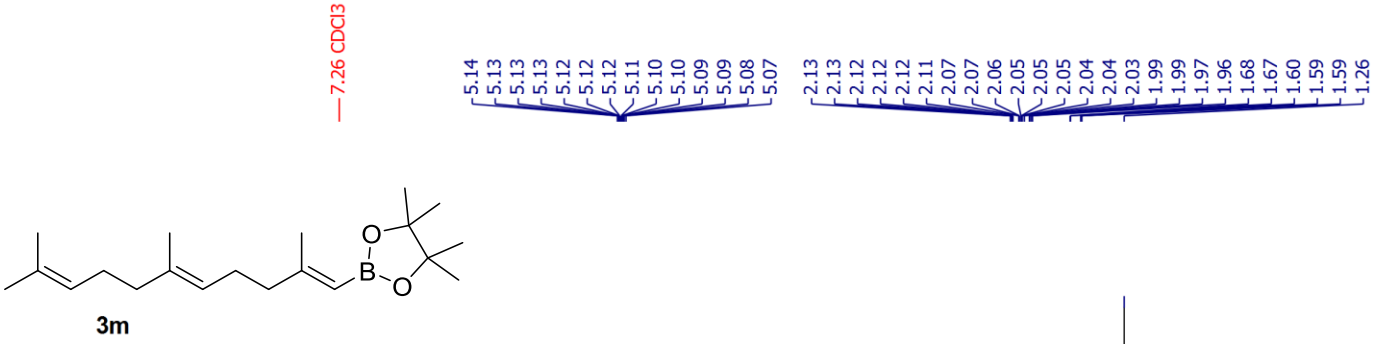




3l

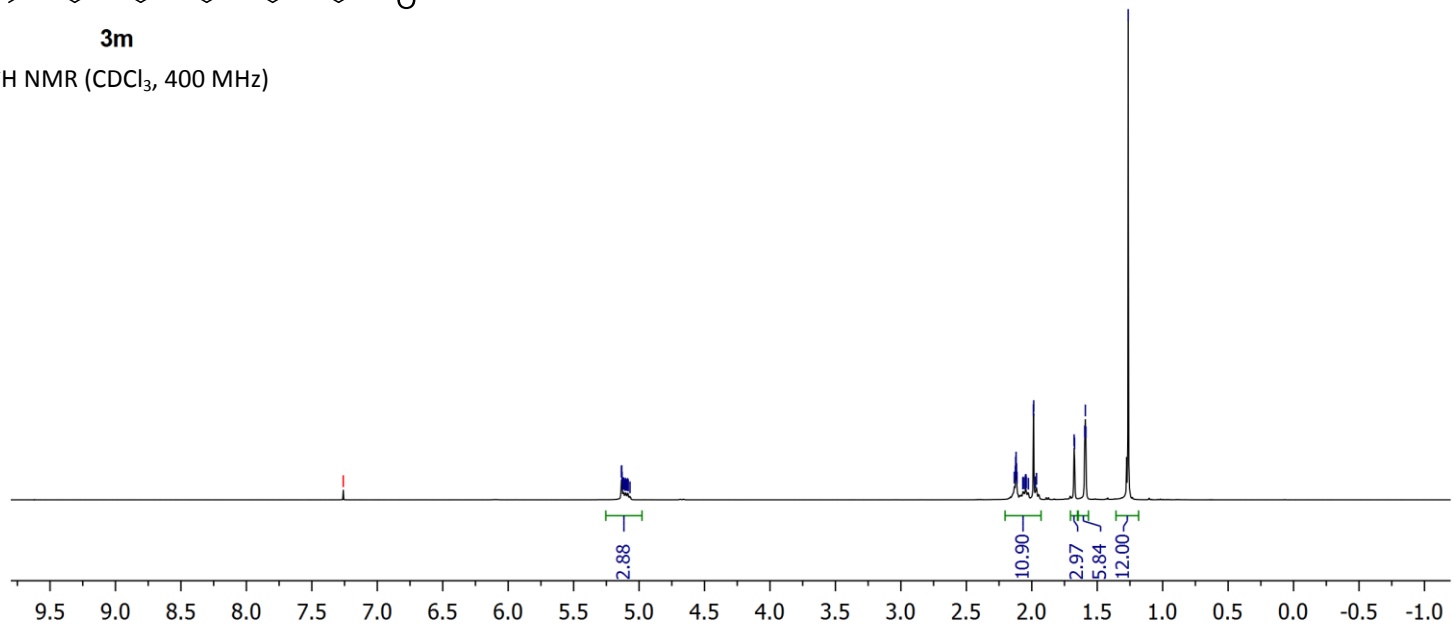
^{1}H NMR ($CDCl_3$, 400 MHz)

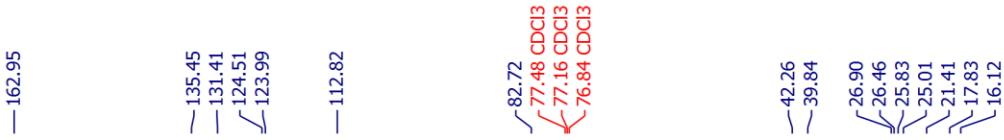
^{13}C NMR ($CDCl_3$, 101 MHz)



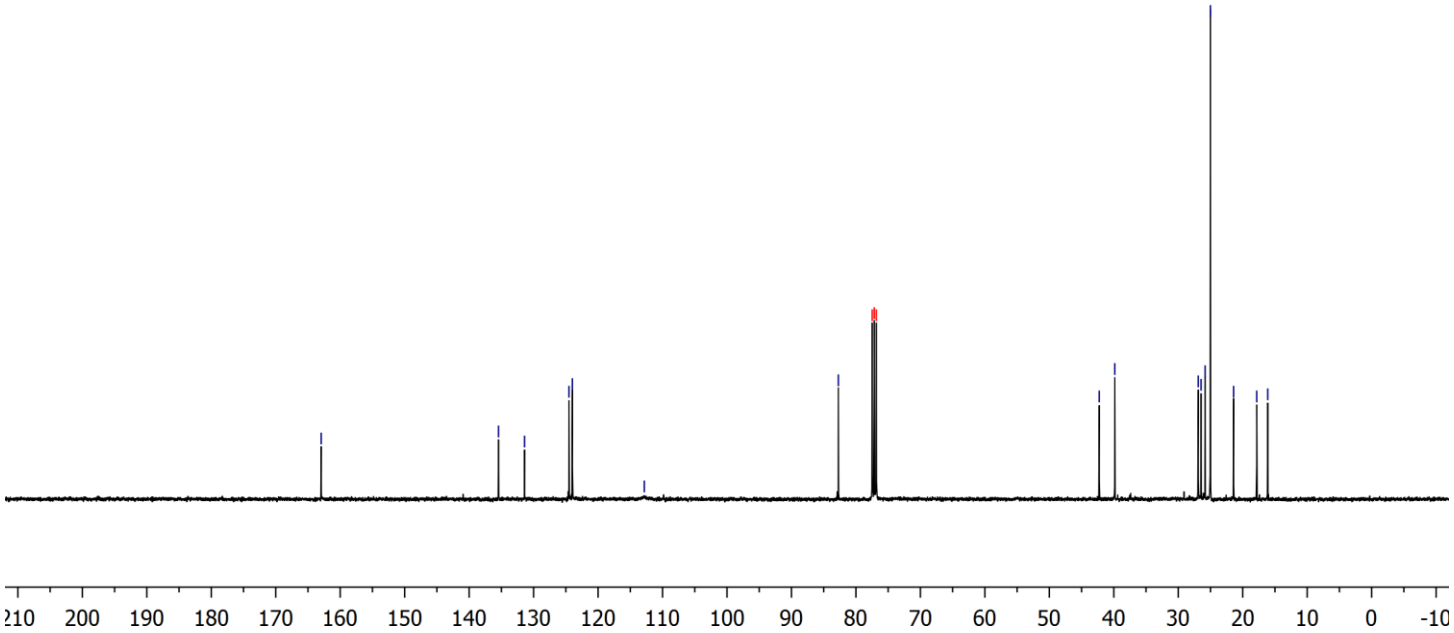
3m

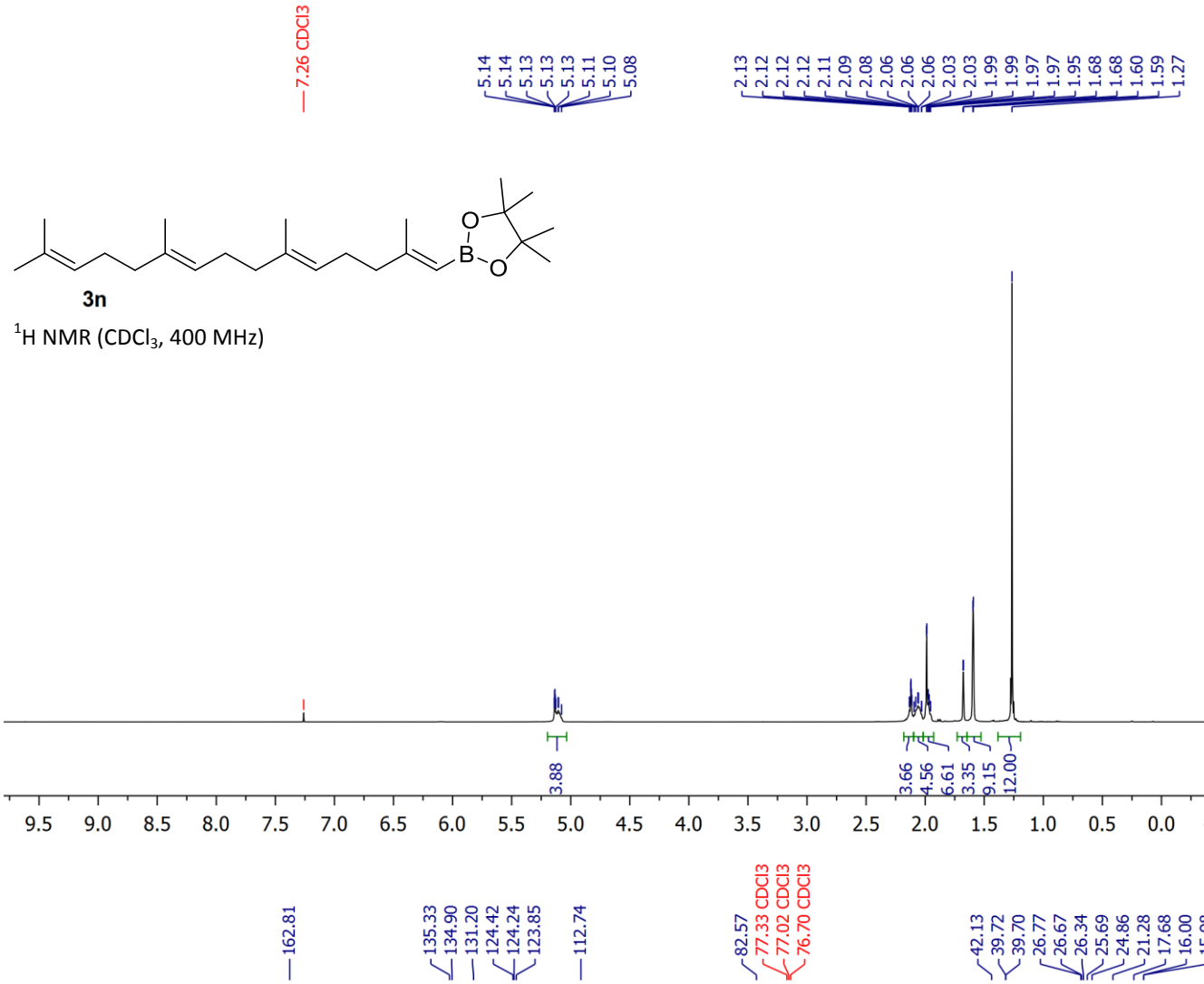
^{1}H NMR ($CDCl_3$, 400 MHz)



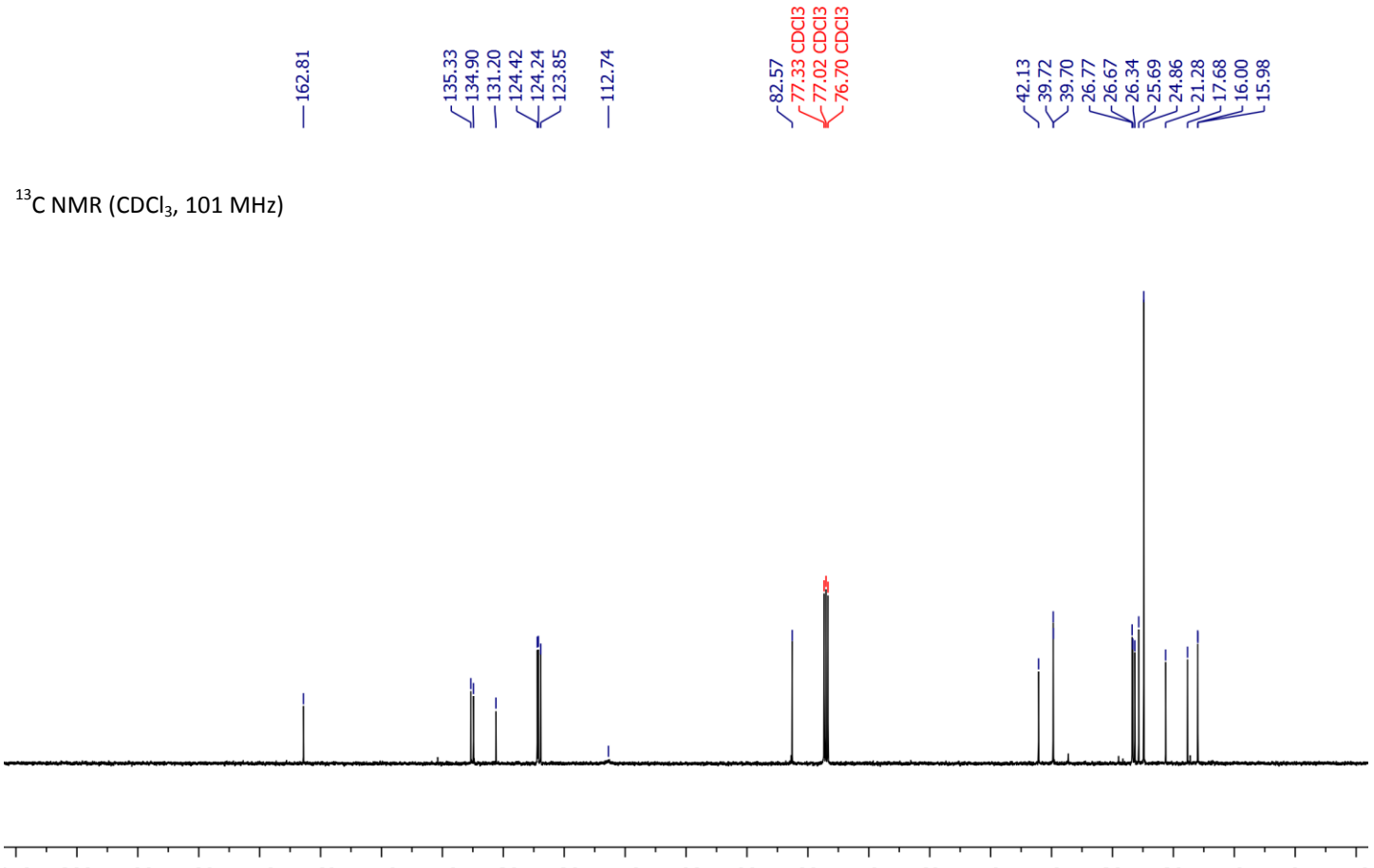


^{13}C NMR ($CDCl_3$, 101 MHz)

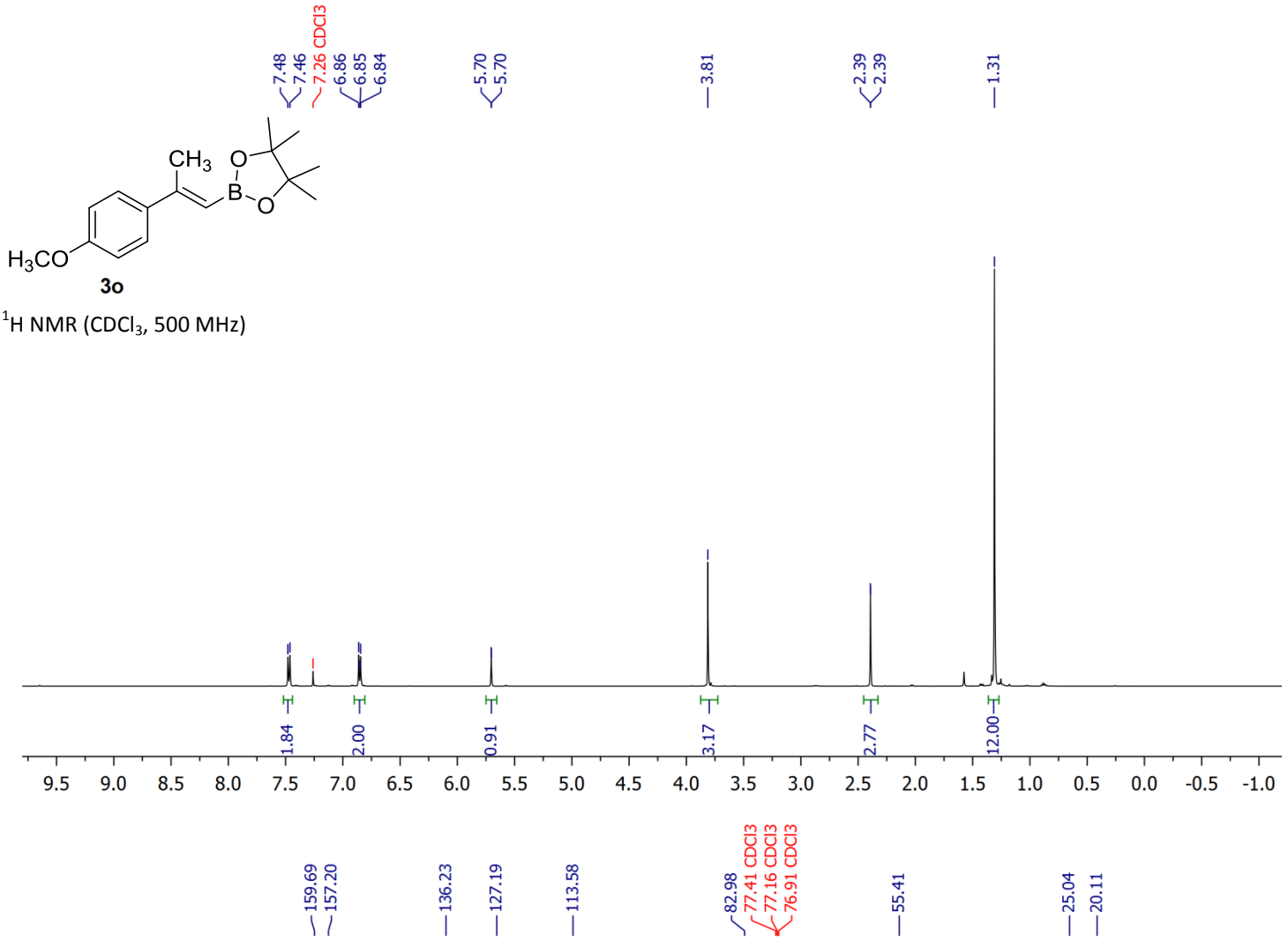




^{1}H NMR ($CDCl_3$, 400 MHz)



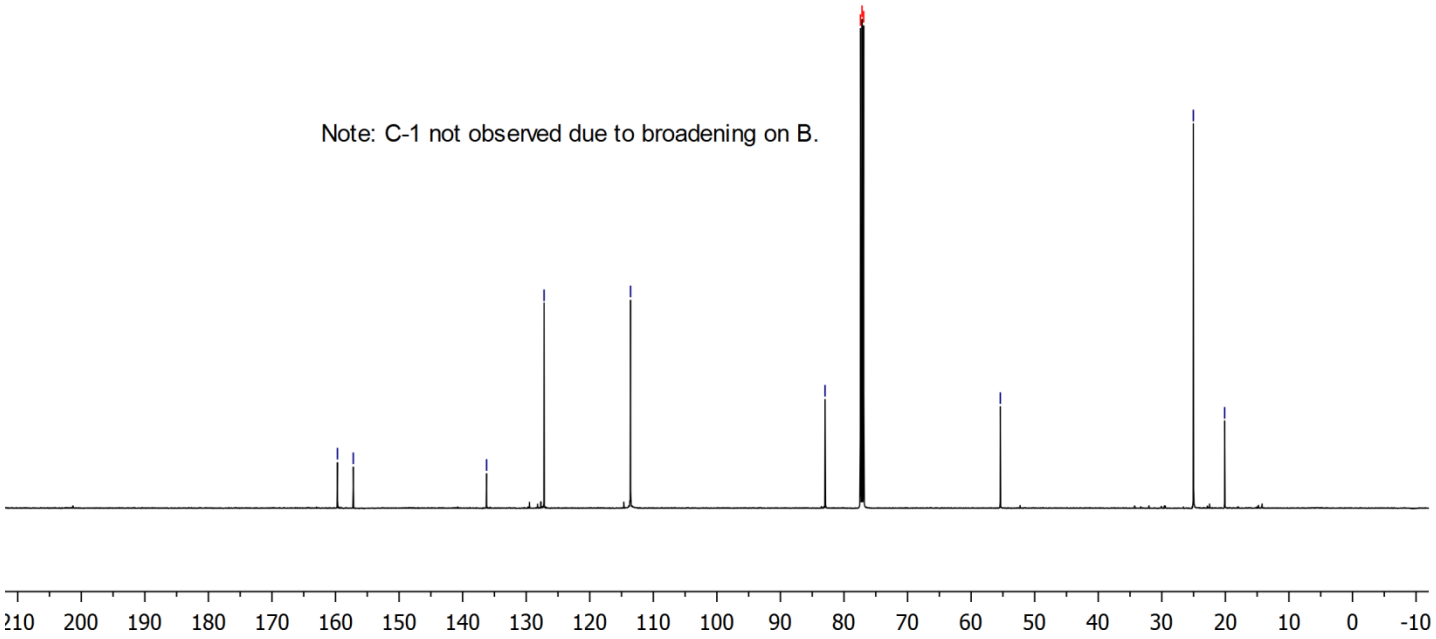
^{13}C NMR ($CDCl_3$, 101 MHz)

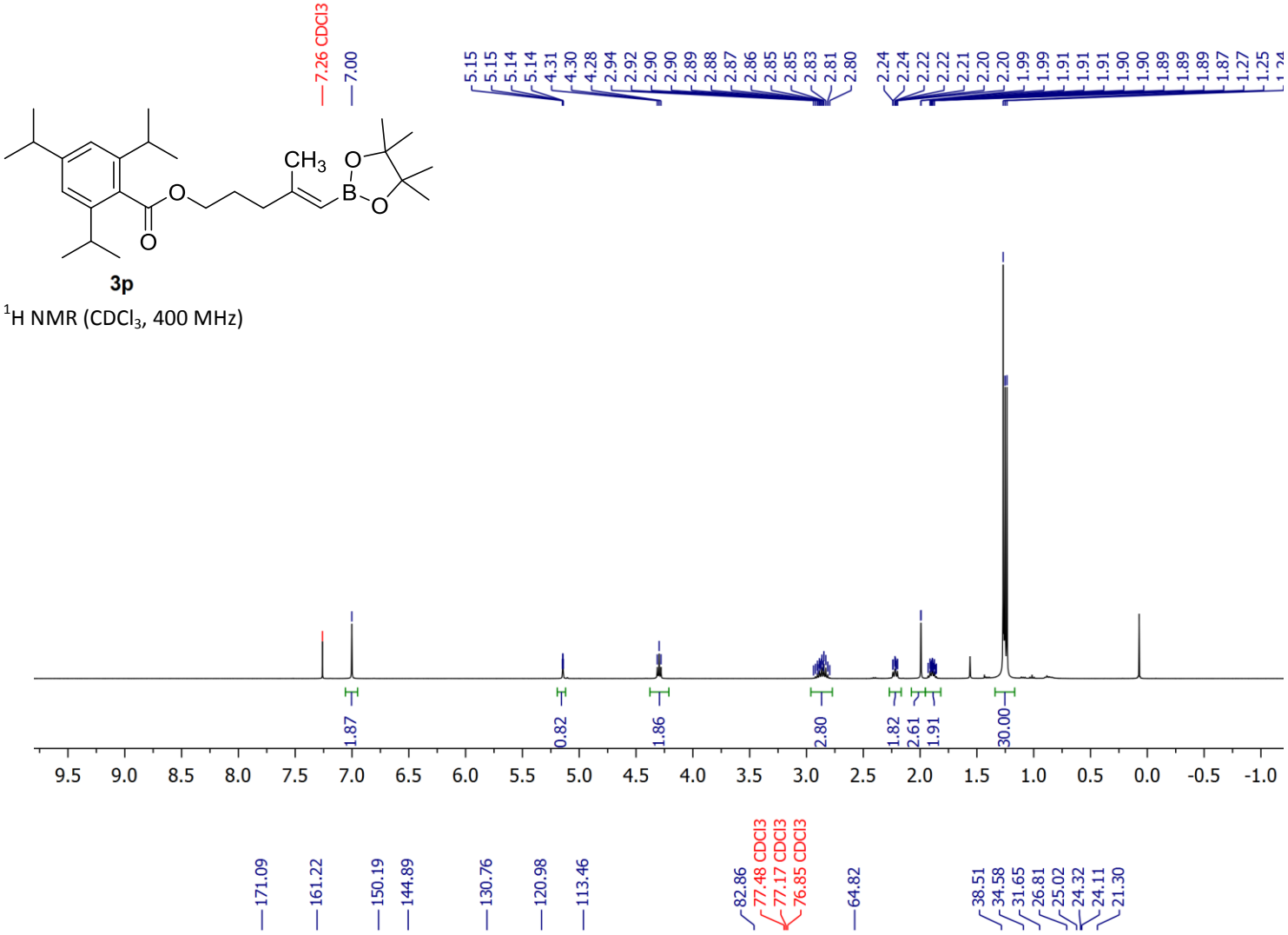


3o

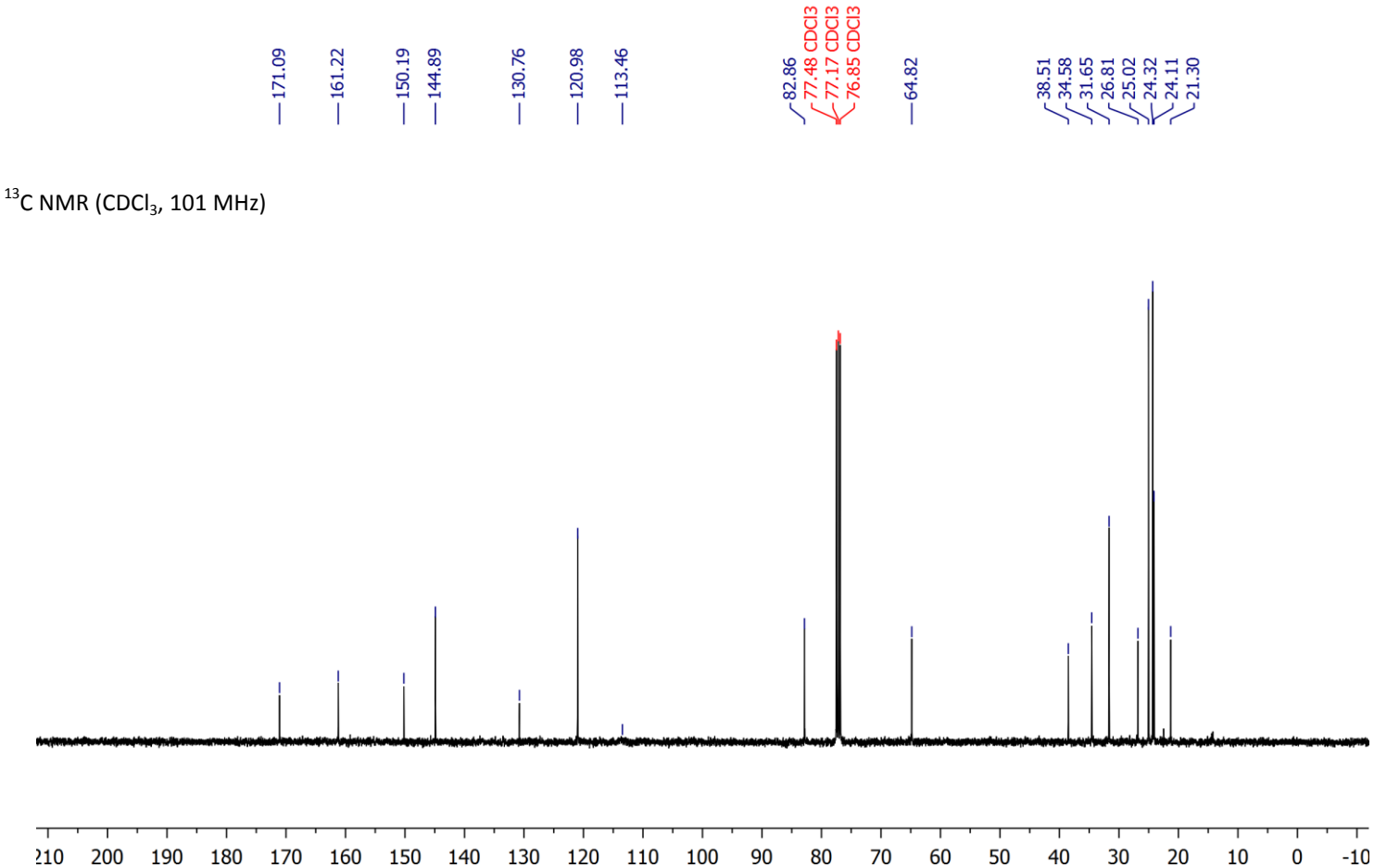
^{1}H NMR ($CDCl_3$, 500 MHz)

^{13}C NMR ($CDCl_3$, 126 MHz)





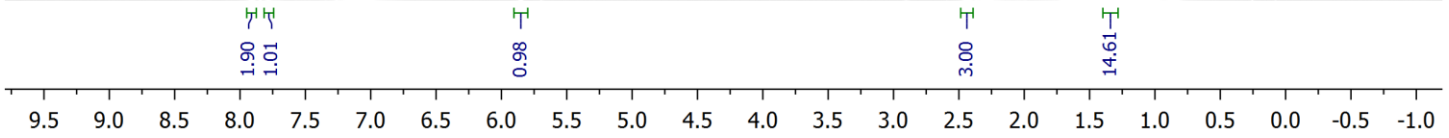
^{1}H NMR ($CDCl_3$, 400 MHz)



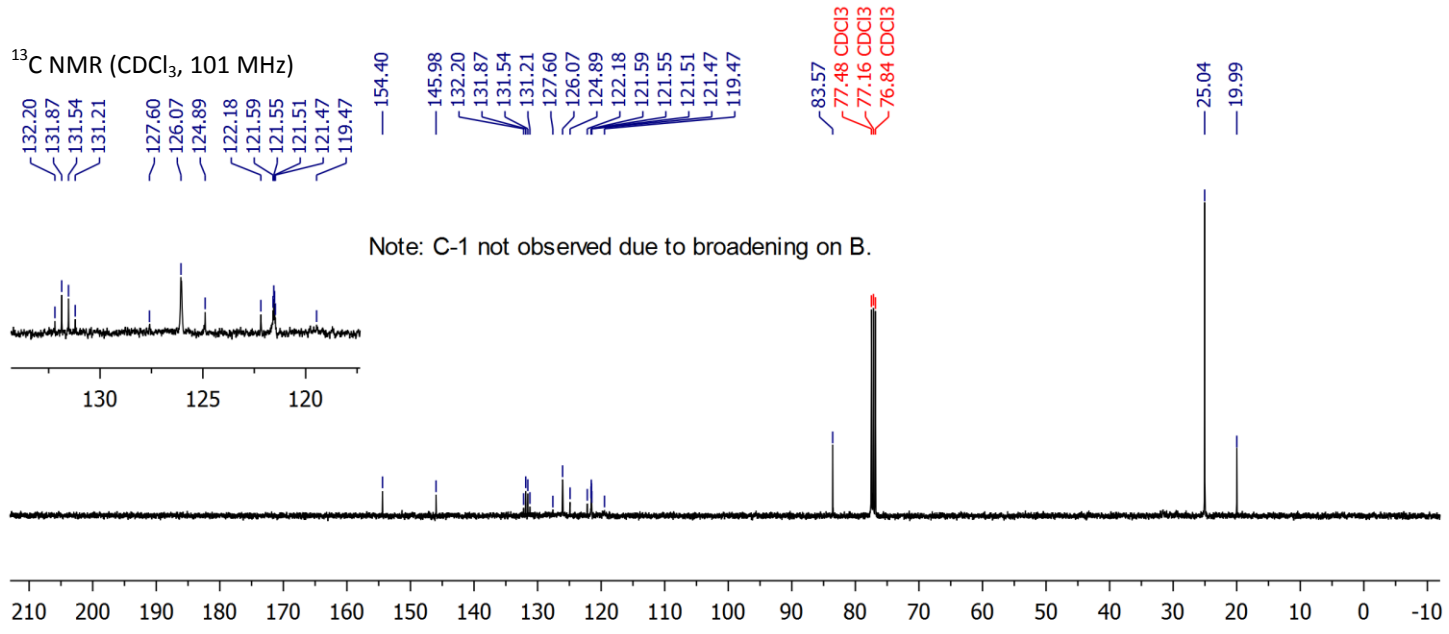
^{13}C NMR ($CDCl_3$, 101 MHz)

3q

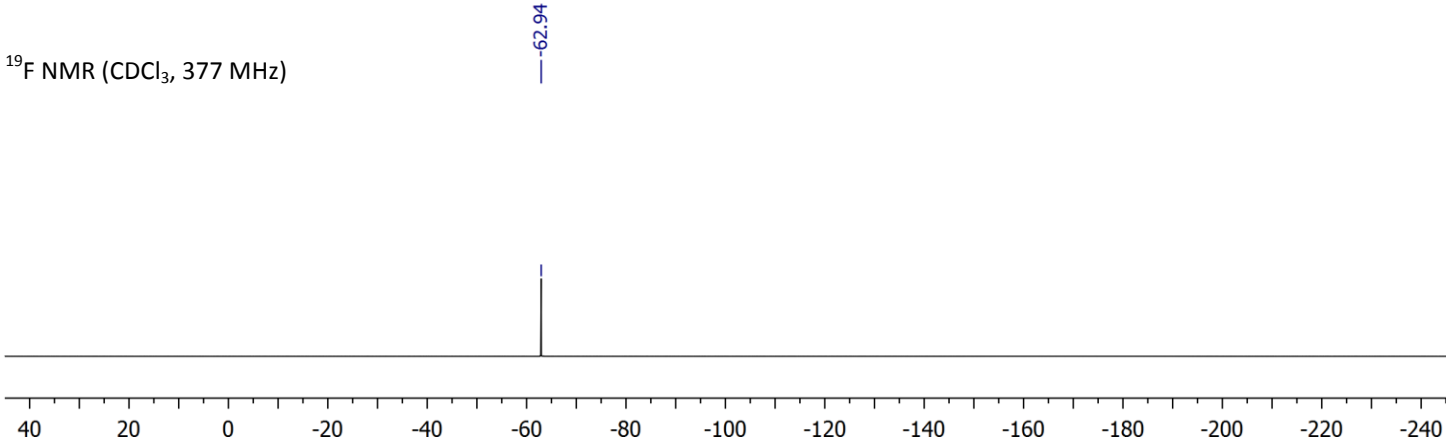
^{1}H NMR ($CDCl_3$, 400 MHz)

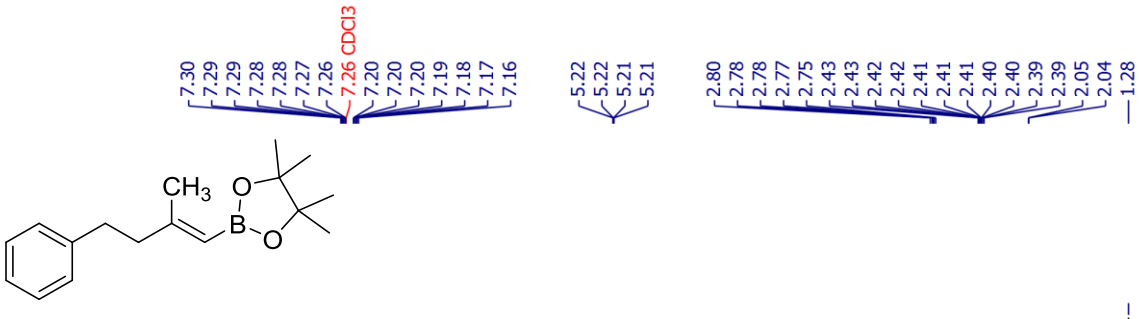


^{13}C NMR ($CDCl_3$, 101 MHz)



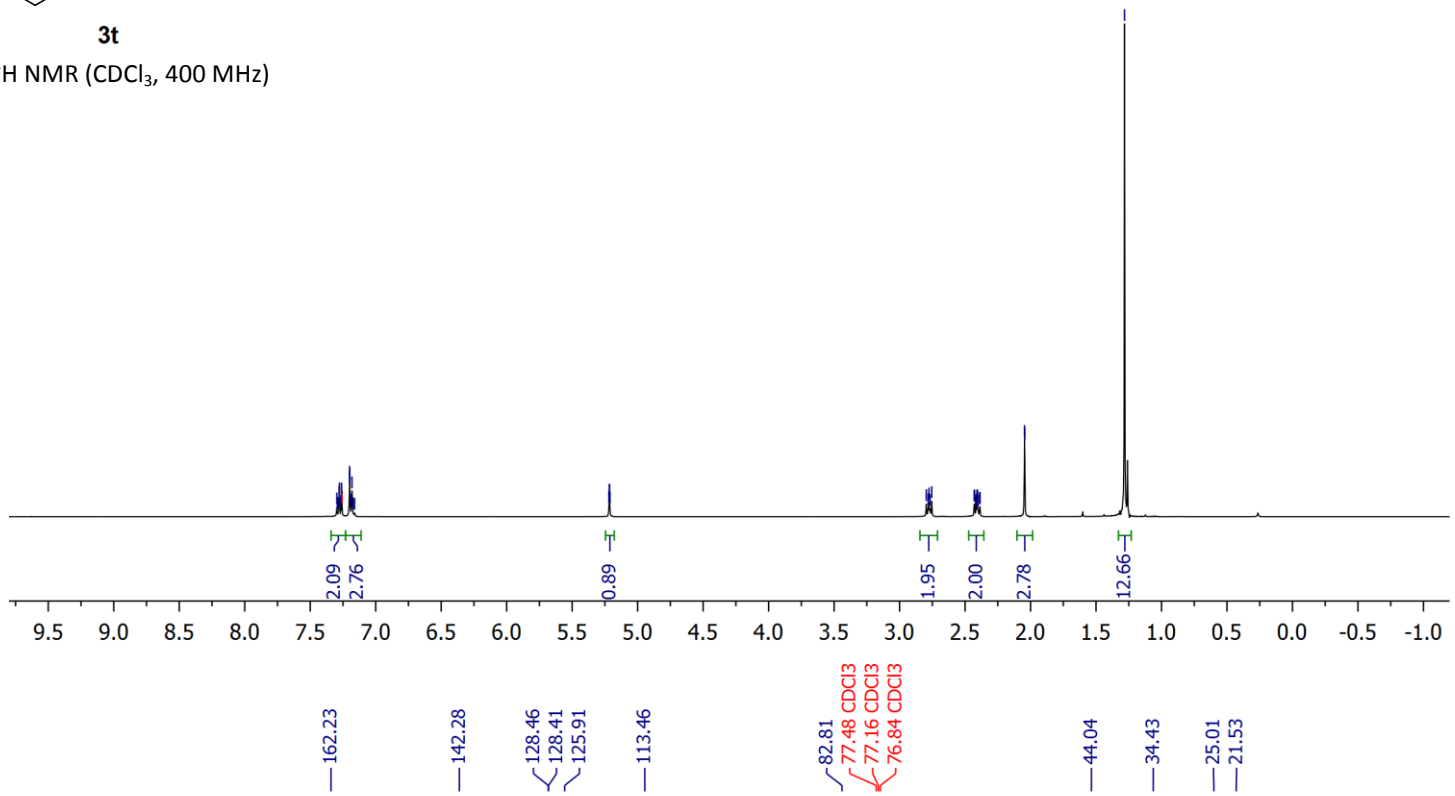
^{19}F NMR ($CDCl_3$, 377 MHz)



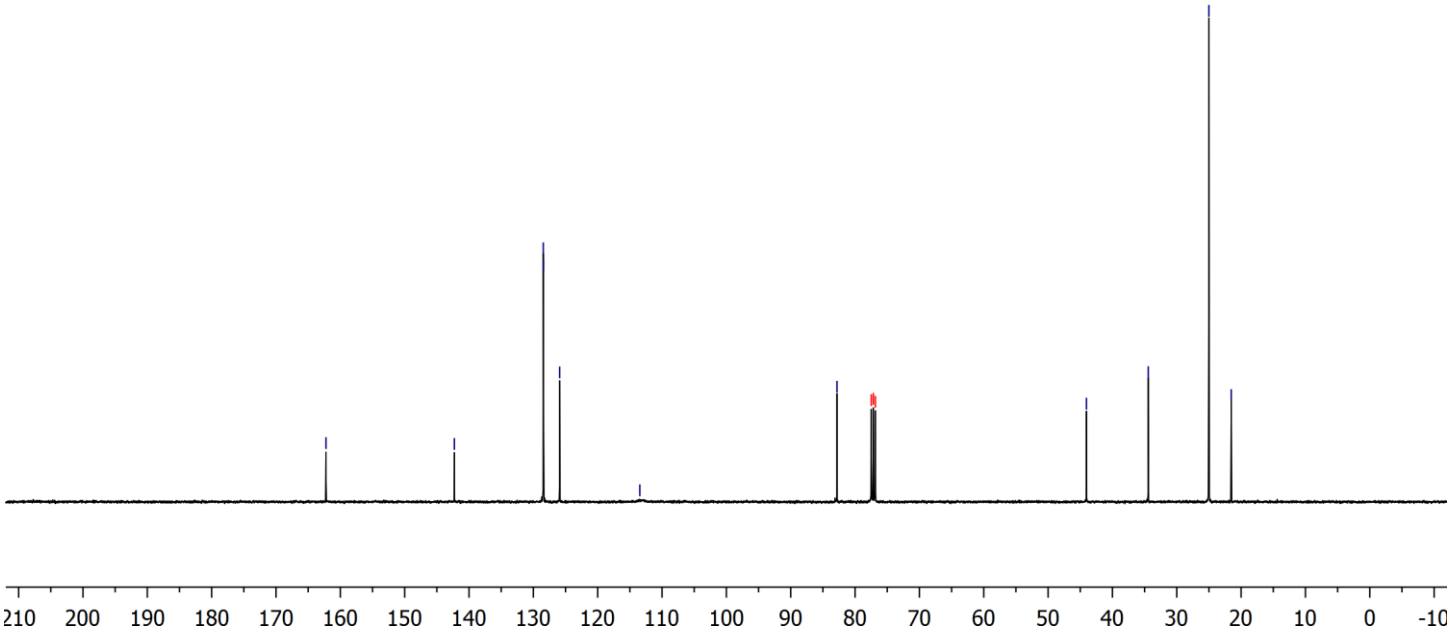


3t

^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)



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