Electronic Supplementary Material (ESI) for Chemical Communications

Chemo-, Regio- and Stereoselective Iron-Catalysed Hydroboration of Alkenes and Alkynes

Mark D. Greenhalgh and Stephen P. Thomas*

School of Chemistry, University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh EH9 3JJ, U.K.

email: stephen.thomas@ed.ac.uk

Supplementary Information

Table of Contents

General Experimental

All air- and moisture sensitive manipulations were carried out using standard vacuum line and Schlenk techniques, or in a drybox containing a purified nitrogen atmosphere. Solvents for air and moisture sensitive manipulations were obtained from an Anhydrous Engineering Solvent Purification System. All glassware was cleaned using base (KOH, iPrOH) then acid (HCl_{aq}) baths, and dried in an oven.

Iron(II) chloride was purchased from Strem Chemicals Inc. (UK); anhydrous iron chloride, 98% (product number 93-2631. Lot 19226800, 44.00000% Fe, expect 44.059%). All olefins used were purchased from Sigma Aldrich, Alfa Aesar, Acros organics, Tokyo Chemical Industries UK, and Apollo Scientific or synthesised within the laboratory. Pinacol borane and triethylgermanium hydride were purchased from Sigma Aldrich and Apollo Scientific. Grignard reagents and *n*-butyllithium were purchased from Sigma Aldrich (UK).

^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on Bruker Avance III 400 and 500MHz, and Bruker AV I 400MHz spectrometers. All spectra were obtained at ambient temperature. The chemical shifts (δ) were recorded in parts per million (ppm) and the coupling constants (*J*) in Hertz (Hz). ^{1}H and ^{13}C NMR multiplicity and coupling constants are reported where applicable. ^{1}H and ^{13}C spectra were referenced to the residual deuterated solvent peak ($CHCl_3$ 7.27ppm, 77.00ppm).

Aqueous sulphate buffer was prepared by dissolving Na_2SO_4 (1.5 mol) H_2SO_4 (0.5 mol) and adding water to give a total volume of 2000 cm^3. Flash chromatography was performed on silica gel (Merck Kielselgel 60). Analytical thin layer chromatography was performed on aluminium backed silica plates (60 F_{254}).

Infra-red spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Melting points were determined using a Stuart Scientific SMP10 and were uncorrected. High resolution mass spectra were recorded on a Thermo/Finnigan MAT 900 mass spectrometer.

General Procedures

General Procedure A: Catalyst optimisation

4-Phenylbutene (105 µL, 0.7 mmol) was added to a solution of 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine iron(II) chloride [**1**-$FeCl_2$] in anhydrous tetrahydrofuran (3 mL) at room temperature under an atmosphere of nitrogen. An activating agent was added, followed by pinacol borane (110 µL, 0.77 mmol), and the reaction stirred at room temperature for 1 hour. Water (10 mL) was added and the aqueous phase extracted with diethyl ether (3 x 20mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. Trimethoxybenzene (23.5 mg, 0.14 mmol) was added as an internal standard, and a yield for the reaction determined by ^{1}H NMR.

Known compounds were identified by ^{1}H NMR, and characterised by comparison with authentic samples of spectral data.

General Procedure B: Hydroboration: Functional group compatibility

An olefin (0.7 mmol) was added to a solution of iron(II) chloride (0.9 mg, 0.007 mmol) and 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) in anhydrous tetrahydrofuran (3 mL) at room temperature under an atmosphere of nitrogen. Ethylmagnesium bromide (1.4M in Et_2O, 15 µL, 3 drops, 0.021 mmol) was added, followed by pinacol borane, or triethylgermanium hydride (0.77 mmol) and the reaction stirred at room temperature for 1 hour. Water (10 mL) was added and the aqueous phase extracted with diethyl ether (3 x 20mL). The combined organic extracts were washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. Trimethoxybenzene (23.5 mg, 0.14 mmol) was added as an internal standard, and a yield for the reaction determined by ^{1}H NMR.

Known compounds were identified by ^{1}H NMR, and characterised by comparison with authentic samples of spectral data.

In order to determine isolated yields the products were purified by flash silica chromatography.

General Procedure C: Hydroboration: 'solvent-free' conditions

An olefin was added to 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine iron(II) chloride [**1**-$FeCl_2$] (3.9 mg, 0.007 mmol) [in the absence of solvent, or as a suspension in anhydrous toluene (3 mL)], at room temperature under an atmosphere of nitrogen. *n*-Butyllithium (1.1M in hexane, 20 µL, 4 drops, 0.021 mmol) was added, followed by pinacol borane (1.1 equiv. wrt alkene) and the reaction stirred at room temperature for 1 hour. Water (10 mL) was added and the aqueous phase extracted with diethyl ether (3 x 20mL). The combined organic extracts were washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. Trimethoxybenzene (23.5 mg, 0.14 mmol) was added as an internal standard, and a yield for the reaction determined by ^{1}H NMR.

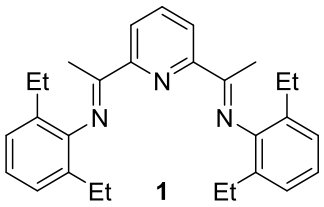
Known compounds were identified by ^{1}H NMR, and characterised by comparison with authentic samples of spectral data.

In order to determine isolated yields the products were purified by flash silica chromatography.

Ligand and catalyst preparation

Bis(imino)pyridine ligand **1**[1] was prepared according to a slight modification upon a literature procedure (see below). Complex [**1**-$FeCl_2$][2] was prepared according to a literature procedure.

2,6-Bis-[1-(2,6-diethylphenylimino)ethyl]pyridine 1



1

2,6-Diethylaniline (4.66 mL, 28.3 mmol) was added to a stirred suspension of 2,6-diacetylpyridine (2.1 g, 13 mmol) and *p*-toluene sulfonic acid (0.15 g, 0.75 mmol) in anhydrous toluene (60 mL) and heated at reflux under Dean-Stark conditions for 16 hours. The solvent was removed *in vacuo* and the yellow solid recrystallised from dichloromethane to give 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (4.9 g, 11.5 mmol, 89%) as yellow needles.

m.p. 185-186 °C (CH_2Cl_2). δ_H (500 MHz, $CDCl_3$) 8.51 (d, *J*= 7.8 Hz, 2H), 7.95 (t, *J*= 7.8 Hz, 1H), 7.17-7.13 (m, 4H), 7.09-7.05 (m, 2H), 2.50-2.34 (m, 8H), 2.28 (s, 6H), 1.18 (t, *J*= 7.6 Hz, 12H). δ_C (126 MHz, $CDCl_3$) 167.0, 155.1, 147.7, 136.9, 131.2, 125.9, 123.3, 122.2, 24.6, 16.8, 13.7. ν_{max} cm^{-1} 2970, 2930, 2874, 1638, 1587, 1568, 1452, 1366, 1242, 1198, 1121, 1101, 1076.

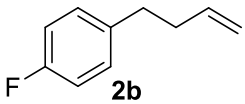
Data were in accordance with those previously reported in the literature.[1]

Synthesis of substrates

General Procedure D

Allylmagnesium bromide (1M in tetrahydrofuran, 1.2 equiv.) was added to 4-halobenzyl bromide (1 equiv.) in anhydrous diethyl ether (0.7 M) at 0 °C under an atmosphere of nitrogen. The reaction was allowed to warm to room temperature over 2 hours. Aqueous sulphate buffer solution (10 mL) was added slowly and the aqueous phase extracted with diethyl ether (3 x 20 mL). The combined organic extracts were washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*.

1-Fluoro-4-(3-butenyl)-benzene 2b

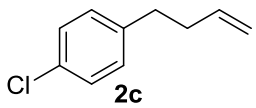


2b

According to general procedure **D**, allylmagnesium bromide (9 mL, 1M in tetrahydrofuran, 9 mmol) and 4-fluorobenzyl bromide (1.32 g, 7 mmol) were reacted in anhydrous diethyl ether (10 mL) to give 1-fluoro-4-(3-butenyl)-benzene **2b** as a colourless oil (933 mg, 6.22 mmol, 89%), which was used without further purification.

δ_H (400 MHz, $CDCl_3$) 7.18-7.12 (m, 2H), 7.01-6.94 (m, 2H), 5.85 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.08-4.97 (m, 2H), 2.73-2.67 (m, 2H), 2.40-2.32 (m, 2H). δ_C (101 MHz, $CDCl_3$) 161.2 (d, *J*= 243 Hz), 137.8, 137.4 (d, *J*= 3 Hz), 129.7 (d, *J*= 8 Hz), 115.1 (d, *J*= 6 Hz), 114.9, 35.6, 34.5. δ_F (376 MHz, $CDCl_3$) -117.8. HRMS (EI) calculated for $C_{10}H_{11}F$ 150.08393. Found 150.08373.

1-Chloro-4-(3-butenyl)-benzene 2c

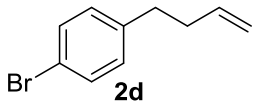


2c

According to general procedure **D**, allylmagnesium bromide (9 mL, 1M in tetrahydrofuran, 9 mmol) and 4-chlorobenzyl bromide (1.44 g, 7 mmol) were reacted in anhydrous diethyl ether (10 mL) to give 1-chloro-4-(3-butenyl)-benzene **2c** as a colourless oil (1.10 g, 6.63 mmol, 95%), which was used without further purification.

δ_H (400 MHz, $CDCl_3$) 7.28-7.23 (m, 2H), 7.14-7.10 (m, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.07-4.97 (m, 2H), 2.72-2.66 (m, 2H), 2.40-2.32 (m, 2H). δ_C (101 MHz, $CDCl_3$) 140.2, 137.6, 131.5, 129.8, 128.3, 115.3, 35.3, 34.7. HRMS (EI) calculated for $C_{10}H_{11}Cl$ 166.0530. Found 166.05438.

1-Bromo-4-(3-butenyl)-benzene 2d



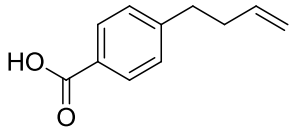
2d

According to general procedure **D**, allylmagnesium bromide (30 mL, 1M in tetrahydrofuran, 30 mmol) and 4-bromobenzyl bromide (6.32 g, 25 mmol) were reacted in anhydrous diethyl ether (20 mL) to give 1-bromo-4-(3-butenyl)-benzene **2d** as a colourless oil (5.10 g, 24.2 mmol, 97%), which was used without further purification.

δ_H (400 MHz, $CDCl_3$) 7.43-7.38 (m, 2H), 7.10-7.04 (m, 2H), 5.85 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.07-4.96 (m, 2H), 2.71-2.64 (m, 2H), 2.40-2.32 (m, 2H). δ_C (101 MHz, $CDCl_3$) 140.7, 137.6, 131.3, 130.2, 119.5, 115.3, 35.3, 34.7.

Data were in accordance with those previously reported in the literature.[3]

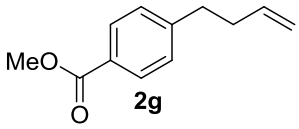
4-(3-Butenyl)-benzoic acid



1-Bromo-4-(3-butenyl)-benzene **2d** (0.21 g, 1 mmol) was added to magnesium turnings (413 mg, 17 mmol) in anhydrous tetrahydrofuran (15 mL) in a flask equipped with a reflux condenser, at room temperature and under a nitrogen atmosphere. A single iodine crystal was added to initiate the reaction. Within 1 minute the iodine colour disappeared and the reaction began to warm. The reaction was periodically cooled in ice and the remaining 1-bromo-4-(3-butenyl)-benzene (1.8 g, 8.7 mmol) was added in portions over 30 minutes at a rate to prevent a high reaction temperature. The reaction was stirred for a further 30 minutes at 0 °C, and then allowed to settle at room temperature for 1 hour. Carbon dioxide was bubbled through the solution, resulting in rapid heating at reflux. After 5 minutes no more heat was produced and so no more carbon dioxide was added. The reaction was quenched with saturated sodium hydrogen carbonate solution and the aqueous phase washed with hexane (2 x 20 mL). The aqueous phase was acidified to pH1 with conc. HCl and extracted with diethyl ether (3 x 20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo* to give 4-(3-butenyl)-benzoic acid as a colourless amorphous solid (1.48 g, 8.41 mmol, 87%).

δ_H (400 MHz, $CDCl_3$) 12.16 (br. s, 1H), 8.07-8.02 (m, 2H), 7.33-7.28 (m, 2H), 5.85 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.09-4.98 (m, 2H), 2.84-2.77 (m, 2H), 2.46-2.38 (m, 2H). δ_C (101 MHz, $CDCl_3$) 171.8, 148.4, 137.4, 130.3, 128.6, 126.9, 115.4, 35.4, 35.0. HRMS (EI) calculated for $C_{11}H_{12}O_2$ 176.08318. Found 176.08294.

4-(3-Butenyl)-benzoic acid methyl ester 2g

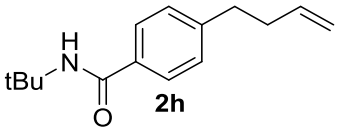


2g

4-(3-Butenyl)-benzoic acid (528 mg, 3 mmol) was dissolved in anhydrous methanol (30 mL) and sulfuric acid (conc., 15 drops), and the reaction heated at reflux for 16 hours. The solution was cooled, saturated sodium hydrogen carbonate solution (30 mL) was added, and the aqueous phase was extracted with diethyl ether (3 x 20 mL). The combined organic extracts were washed with H_2O and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 4-(3-butenyl)-benzoic acid methyl ester **2g** as a pale yellow oil (522 mg, 2.75 mmol, 92%).

δ_H (400 MHz, $CDCl_3$) 7.99-7.94 (m, 2H), 7.29-7.24 (m, 2H), 5.84 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.08-4.97 (m, 2H), 3.91 (s, 3H), 2.81-2.74 (m, 2H), 2.44-2.36 (m, 2H). δ_C (101 MHz, $CDCl_3$) 167.1, 147.3, 137.5, 129.7, 128.5, 127.9, 115.3, 52.0, 35.4, 35.0. HRMS (EI) calculated for $C_{12}H_{14}O_2$ 190.09883. Found 190.09903.

_N_-(_tert_-Butyl)-4-(3-butenyl)-benzamide 2h

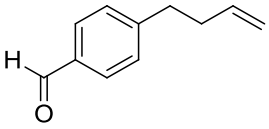


2h

Triphenylphosphine (865 mg, 3.3 mmol) and iodine (838 mg, 3.3 mmol) were added to anhydrous dichloromethane at 0 °C and stirred for 5 minutes under an atmosphere of nitrogen. 4-(3-Butenyl)-benzoic acid (528 mg, 3 mmol) was added followed by the concurrent dropwise addition of both diisopropylethylamine (0.78 mL, 4.5 mmol) and *tert*-butylamine (0.35 mL, 3.3 mmol) over 5 minutes. The reaction was stirred under an atmosphere of nitrogen and allowed to warm to room temperature overnight. Water was added and extracted with dichloromethane (3 x 20 mL). The organic phase was washed sequentially with saturated aqueous sodium thiosulfate solution and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The crude reaction mixture was purified by flash chromatography (7% EtOAc/Hexane) to give *N*-(*tert*-butyl)-4-(3-butenyl)-benzamide **2h** as a colourless solid (622 mg, 2.69 mmol, 90%).

δ_H (400 MHz, $CDCl_3$) 7.67-7.62 (m, 2H), 7.25-7.20 (m, 2H), 5.93 (br s, 1H), 5.83 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.06-4.96 (m, 2H), 2.78-2.72 (m, 2H), 2.42-2.34 (m, 2H), 1.47 (s, 9H). δ_C (101 MHz, $CDCl_3$) 166.8, 145.2, 137.5, 133.5, 128.5, 126.7, 115.3, 51.5, 35.2, 35.1, 28.9. HRMS (EI) calculated for $C_{15}H_{21}NO$ 231.16177. Found 231.16145.

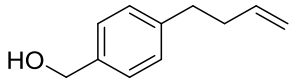
4-(3-Butenyl)-benzaldehyde



1-Bromo-4-(3-butenyl)-benzene **2d** (0.4 g, 2 mmol) was added to magnesium turnings (1.05 g, 43 mmol) in anhydrous tetrahydrofuran (21 mL) in a flask equipped with a reflux condenser, at room temperature and under a nitrogen atmosphere. A single iodine crystal was added to initiate the reaction. Within 1 minute the iodine colour disappeared and the reaction began to warm. The reaction was periodically cooled in ice and the remaining 1-bromo-4-(3-butenyl)-benzene (3.9 g, 19 mmol) was added in portions over 30 minutes at a rate to prevent a high reaction temperature. The reaction was stirred for a further 30 minutes at 0 °C, and then allowed to settle at room temperature for 1 hour. The reaction was cooled to 0 °C, and *N,N*-dimethylformamide (1.53 g, 21 mmol in 10 mL Et_2O) was added dropwise over 2 minutes. The reaction was allowed to warm to room temperature over 1 hour. Aqueous sulfate buffer (10 mL) was added and the aqueous phase extracted with diethyl ether (3 x 20mL). The combined organic extracts were washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 4-(3-butenyl)-benzaldehyde as a yellow oil (3.08 g, 19.3 mmol, 92%).

δ_H (400 MHz, $CDCl_3$) 9.99 (s, 1H), 7.84-7.79 (m, 2H), 7.38-7.23 (m, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.09-4.98 (m, 2H), 2.84-2.77 (m, 2H), 2.46-2.38 (m, 2H). δ_C (101 MHz, $CDCl_3$) 192.0, 149.3, 137.2, 134.5, 129.9, 129.1, 115.5, 35.5, 35.0.

4-(3-Butenyl)-benzyl alcohol 2f

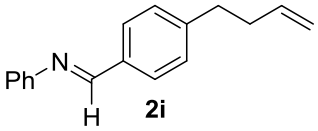


2f

Sodium borohydride (230 mg, 6 mmol) was added to anhydrous ethanol (10 mL) under a nitrogen atmosphere and cooled to 0° C. 4-(3-Butenyl)-benzaldehyde (480 mg, 3 mmol) was added and the reaction was allowed to warm to room temperature over 2 hours. Ethanol was removed under vacuum, and saturated aqueous sodium hydrogen carbonate was added. The aqueous phase was extracted with dichloromethane (3 x 25 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give a colourless oil, which was purified by flash silica chromatography (20% EtOAC/Hexane) to give 4-(3-butenyl)-benzyl alcohol **2f** as a colourless oil (462 mg, 2.85 mmol, 95%).

δ_H (400 MHz, $CDCl_3$) 7.38-7.28 (m, 2H), 7.23-7.18 (m, 2H), 5.87 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H), 5.09-4.97 (m, 2H), 4.67 (d, *J*= 5.5 Hz, 2H), 2.76-2.70 (m, 2H), 2.42-2.35 (m, 2H), 1.65 (t, *J*= 5.5 Hz, 1H). δ_C (101 MHz, $CDCl_3$) 141.4, 138.4, 138.0, 128.6, 127.1, 115.0, 65.3, 35.5, 35.0. HRMS (EI) calculated for $C_{11}H_{14}O$ 162.10392. Found 162.10392.

***N*-Phenyl-4-(3-butenyl)-benzaldimine 2i**

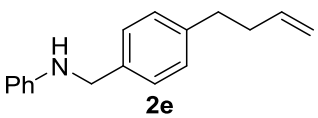


2i

4-(3-Butenyl)-benzaldehyde (2.4 g, 15 mmol), aniline (1.45 mL, 16 mmol) and *para*-toluenesulfonic acid (20 mg) were added to toluene (45 mL) and heated at reflux for 6 hours under Dean-Stark conditions. The cooled mixture was filtered through a plug of silica (3 x 7 cm, petrol ether / ethyl acetate/triethylamine (90:10:1)) and evaporated to give *N*-phenyl-4-(3-butenyl)-benzaldimine **2i** as a yellow oil (3.32 g, 14.1 mmol, 94%). The product was used without further purification.

δ_H (400 MHz, $CDCl_3$) 8.45 (s, 1H), 7.87-7.82 (m, 2H), 7.44-7.38 (m, 2H), 7.34-7.29 (m, 2H), 7.27-7.20 (m, 3H), 5.88 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.11-4.99 (m, 2H), 2.83-2.77 (m, 2H), 2.47-2.39 (m, 2H). δ_C (101 MHz, $CDCl_3$) 160.3, 152.3, 145.7, 137.6, 134.1, 129.1, 128.9, 128.8, 125.7, 120.8, 115.3, 35.4, 35.2. HRMS (EI) calculated for $C_{17}H_{17}N$ 235.13555. Found 235.13607.

***N*-Phenyl-4-(3-butenyl)-benzylamine 2e**



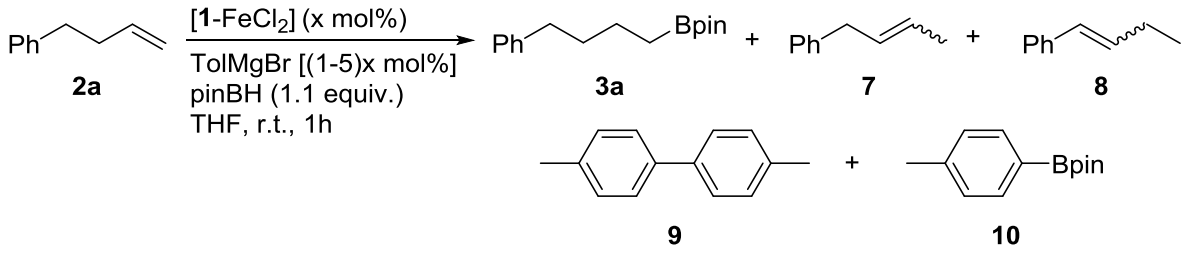
2e

Sodium borohydride (210 mg, 5.5 mmol) was added to anhydrous ethanol (10 mL) under a nitrogen atmosphere and cooled to 0° C. *N*-phenyl-4-(3-butenyl)-benzaldimine **2i** (1 g, 4.25 mmol) was added and the reaction stirred overnight. Ethanol was removed under vacuum, and saturated aqueous

sodium hydrogen carbonate was added. The aqueous phase was extracted with diethyl ether (3 x 25 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow oil, which was purified by flash silica chromatography (4% EtOAC/Hexane) to give *N*-phenyl-4-(3-butenyl)-benzylamine **2e** as a pale yellow oil (719 mg, 3.03 mmol, 71%).

δ_H (400 MHz, $CDCl_3$) 7.34-7.29 (m, 2H), 7.23-7.16 (m, 4H), 6.77-6.71 (m, 1H), 6.69-6.64 (m, 2H), 5.89 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H), 5.11-4.99 (m, 2H), 4.31 (s, 2H), 4.01 (br. s, 1H), 2.77-2.70 (m, 2H), 2.44-2.36 (m, 2H). δ_C (101 MHz, $CDCl_3$) 148.2, 140.9, 138.0, 136.8, 129.2, 128.7, 127.6, 117.5, 114.9, 112.8, 48.1, 35.5, 34.0. HRMS (EI) calculated for $C_{17}H_{19}N$ 237.15120. Found 237.15074.

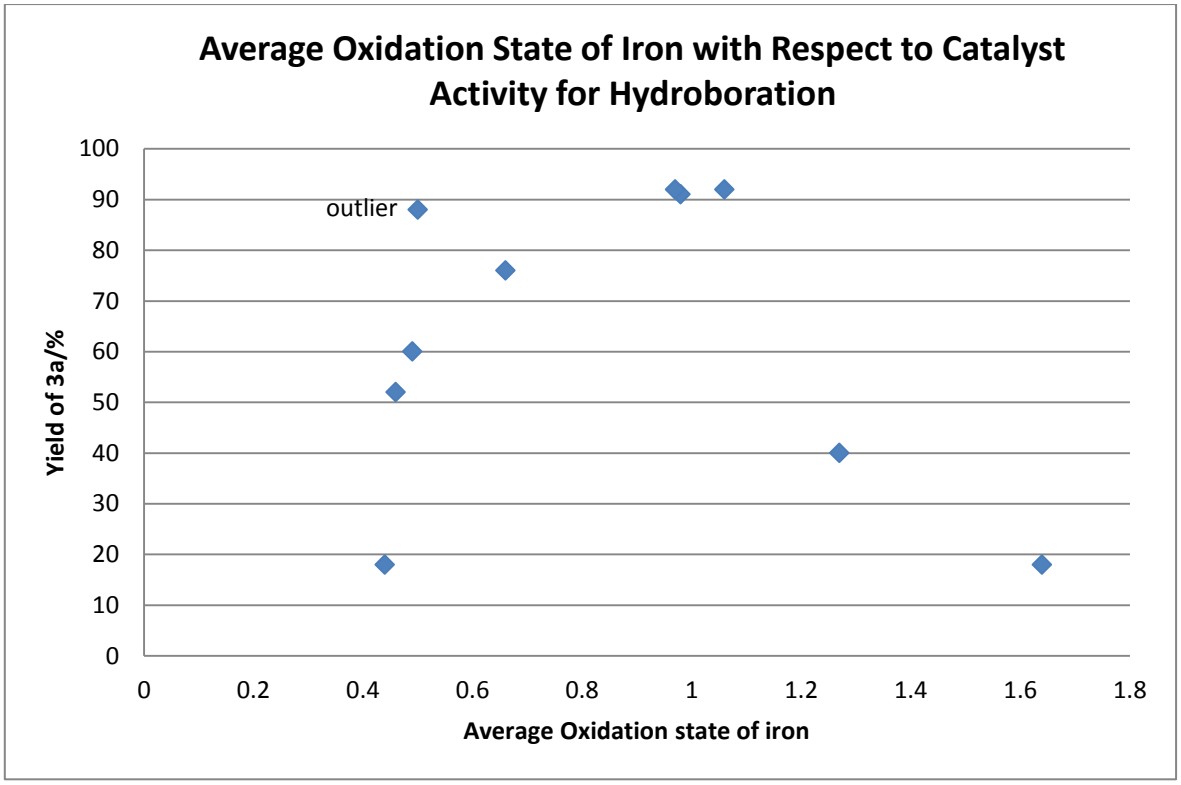
Table S1. Iron oxidation state experiments.



According to general procedure **A**, 4-phenylbutene (105 µL, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine iron(II) chloride [**1**-$FeCl_2$] (19.3/38.6 mg, 0.035/0.07 mmol, 5/10 mol%), and tolylmagnesium bromide (0.035-0.35 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction products. Trimethoxybenzene (23.5 mg, 0.14 mmol) was added as an internal standard, and a yield for each reaction product determined by ^{1}H NMR.

Known compounds were identified by ^{1}H NMR, and characterised by comparison with authentic samples of spectral data.

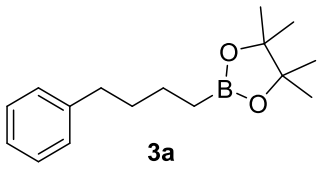
entry	[1-$FeCl_2$]/mol%	TolMgBr/mol%	Yield (%)					Average Fe Oxidation State
			3a	7	8	9	10	
1	5	5	18	-	-	0.9	-	1.64
2	5	10	92	-	6	2.35	2	1.06
3	5	15	91	-	6	2.55	5	0.98
4	5	20	88	7	7	3.75	13	0.50
5	5	25	52	34	8	3.85	22	0.46
6	10	10	40	4	-	3.65	-	1.27
7	10	20	92	-	5	5.15	9	0.97
8	10	30	76	5	10	6.7	17	0.66
9	10	40	60	22	12	7.55	28	0.49
10	10	50	18	58	12	7.8	36	0.44



At both 5 and 10 mol% catalyst loading, maximum catalytic activity was recorded when around 0.5 equivalents (with respect to iron) of bitolyl was produced. If each equivalent of bitolyl formed is the product of a two electron reduction of iron, then this corresponds to an average oxidation state of iron(I). The reduction of iron(II) to iron(I) by reaction with Grignard reagents in iron-catalysed cross-coupling is reported to be both kinetically and thermodynamically feasible, compared to reduction to lower oxidation states.[4]

Hydroboration Products

2-(4-Phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3a

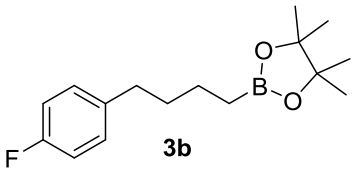


3a

According to General Procedure **B**, 4-phenylbutene (105 µL, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), iron(II) chloride (0.9 mg, 0.007 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) and ethylmagnesium bromide (3 drops, 0.021 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction product, which was purified by flash column chromatography (SiO_2, 2% EtOAc/Hexane) to give 2-(4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3a** as a colourless oil (159 mg, 0.61 mmol, 87%).

δ_H (400 MHz, $CDCl_3$) 7.30-7.24 (m, 2H), 7.21-7.14 (m, 3H), 2.65-2.59 (m, 2H), 1.69-1.60 (m, 2H), 1.53-1.44 (m, 2H) 1.25 (s, 12H), 0.86-0.79 (m, 2H). δ_C (101 MHz, $CDCl_3$) 142.9, 128.4, 128.2, 125.5, 82.9, 35.8, 34.2, 24.8, 23.8. δ_B (128 MHz, $CDCl_3$) 34.4. HRMS (EI) calculated for $C_{16}H_{25}BO_2$ 260.19421. Found 260.19430.

2-(4-(4-Fluorophenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3b

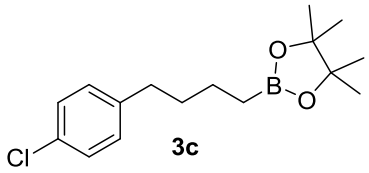


3b

According to General Procedure **B**, 1-fluoro-4-(3-butenyl)-benzene **2b** (105 mg, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), iron(II) chloride (0.9 mg, 0.007 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) and ethylmagnesium bromide (3 drops, 0.021 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction product, which was purified by flash column chromatography (SiO_2, 2% EtOAc/Hexane) to give 2-(4-(4-fluorophenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3b** as a colourless oil (173 mg, 0.62 mmol, 89%).

δ_H (400 MHz, $CDCl_3$) 7.16-7.08 (m, 2H), 6.99-6.90 (m, 2H), 2.62-2.54 (m, 2H), 1.66-1.55 (m, 2H), 1.51-1.41 (m, 2H) 1.25 (s, 12H), 0.85-0.76 (m, 2H). δ_C (101 MHz, $CDCl_3$) 161.1 (d, *J*= 243 Hz), 138.4 (d, *J*= 3 Hz), 129.6 (d, *J*= 8 Hz), 114.8 (d, *J*= 21 Hz), 82.9, 34.9, 34.2, 24.8, 23.6. δ_B (128 MHz, $CDCl_3$) 34.3. δ_F (376 MHz, $CDCl_3$) -118.4. HRMS (EI) calculated for $C_{16}H_{24}BO_2F$ 278.18479. Found 278.18485.

2-(4-(4-Chlorophenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3c

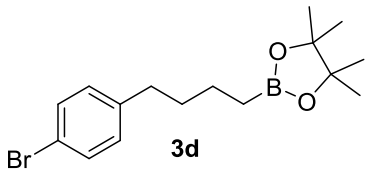


3c

According to General Procedure **B**, 1-chloro-4-(3-butenyl)-benzene **2c** (116 mg, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), iron(II) chloride (0.9 mg, 0.007 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) and ethylmagnesium bromide (3 drops, 0.021 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction product, which was purified by flash column chromatography (SiO_2, 2% EtOAc/Hexane) to give 2-(4-(4-chlorophenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3c** as a colourless oil (169 mg, 0.57 mmol, 82%).

δ_H (400 MHz, $CDCl_3$) 7.26-7.20 (m, 2H), 7.13-7.07 (m, 2H), 2.62-2.54 (m, 2H), 1.66-1.56 (m, 2H), 1.51-1.41 (m, 2H) 1.25 (s, 12H), 0.85-0.77 (m, 2H). δ_C (101 MHz, $CDCl_3$) 141.3, 131.2, 129.7, 128.2, 82.9, 35.0, 34.0, 24.8, 23.6. δ_B (128 MHz, $CDCl_3$) 34.4. HRMS (EI) calculated for $C_{16}H_{24}BO_2Cl$ 294.15524. Found 294.15534.

2-(4-(4-Bromophenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3d

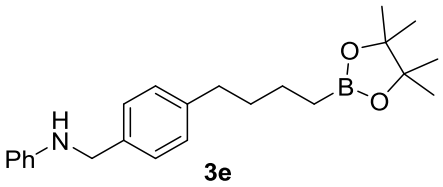


3d

According to General Procedure **B**, 1-bromo-4-(3-butenyl)-benzene **2d** (148 mg, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), iron(II) chloride (0.9 mg, 0.007 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) and ethylmagnesium bromide (3 drops, 0.021 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction product, which was purified by flash column chromatography (SiO_2, 2% EtOAc/Hexane) to give 2-(4-(4-bromophenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3d** as a colourless oil (216 mg, 0.64 mmol, 91%).

δ_H (400 MHz, $CDCl_3$) 7.41-7.35 (m, 2H), 7.08-7.03 (m, 2H), 2.59-2.53 (m, 2H), 1.66-1.56 (m, 2H), 1.50-1.40 (m, 2H) 1.25 (s, 12H), 0.85-0.77 (m, 2H). δ_C (101 MHz, $CDCl_3$) 141.8, 131.2, 130.2, 119.2, 82.9, 35.1, 33.9, 24.8, 23.6. δ_B (128 MHz, $CDCl_3$) 34.3. HRMS (EI) calculated for $C_{16}H_{24}BO_2Br$ 338.10472. Found 338.10550.

2-(4-(*N*-Phenylbenzylamine)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3e

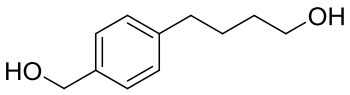


3e

According to General Procedure **B**, *N*-phenyl-4-(3-butenyl)-benzylamine **2e** (166 mg, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), iron(II) chloride (0.9 mg, 0.007 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) and ethylmagnesium bromide (3 drops, 0.021 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction product, which was purified by flash silica chromatography (5% EtOAc/Hexane) to give 2-(4-(*N*-phenylbenzaldimine)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3e** as a bright yellow oil (236 mg, 0.65 mmol, 92%).

δ_H (400 MHz, $CDCl_3$) 7.30-7.26 (m, 2H), 7.22-7.14 (m, 4H), 6.75-6.69 (m, 1H), 6.68-6.63 (m, 2H), 4.29 (s, 2H), 3.98 (br. s, 1H), 2.64-2.58 (m, 2H), 1.68-1.58 (m, 2H), 1.53-1.43 (m, 2H), 1.25 (s, 1H), 0.86-0.80 (m, 2H). δ_C (101 MHz, $CDCl_3$) 148.3, 142.0, 136.5, 129.2, 128.6, 127.5, 117.4, 112.8, 82.9, 48.1, 35.4, 34.2, 24.8, 23.7. δ_B (128 MHz, $CDCl_3$) 34.4. HRMS (EI) calculated for $C_{23}H_{32}BNO_2$ 365.25206. Found 365.25212.

4-(4-Hydroxymethylphenyl)butan-1-ol 3f'



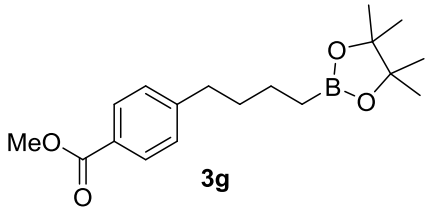
According to a modification of General Procedure **B**, 4-(3-butenyl)-benzyl alcohol **2f** (113 mg, 0.7 mmol), pinacol borane (220 µL, 1.54 mmol), iron(II) chloride (0.9 mg, 0.007 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) and tolylmagnesium bromide (1M in tetrahydrofuran, 0.75 mL, 0.75 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction product, which was purified by flash silica chromatography (15% EtOAc/Hexane) to give 2-(4-(4-Hydroxymethylphenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3f** along with remaining starting material as a colourless oil. The mixture was dissolved in tetrahydrofuran (5 mL) and cooled to 0 °C. 3M Aqueous sodium hydroxide (3M) and 30% hydrogen peroxide [0.5 mL, 1:1 volume ratio, with $1gL^{-1}$ ethylenediaminetetraacetic acid (EDTA)] was added and the mixture stirred for 20 minutes at room temperature. Water (10 mL) was added, and the product extracted with diethylether (3 x 25 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give a colourless oil, which was purified by flash silica chromatography (4% methanol/dichloromethane) to give 4-(4-hydroxymethylphenyl)buan-1-ol **3f'** as a colourless oil (71 mg, 0.39 mmol, 56%).

δ_H (500 MHz, $CDCl_3$) 7.31-7.27 (m, 2H), 7.21-7.17 (m, 2H), 4.66 (s, 2H), 3.66 (t, *J*= 6.5 Hz, 2H), 2.65 (t, *J*= 7.5 Hz, 2H), 1.76 (br. s., 1H), 1.74-1.66 (m, 2H), 1.65-1.57 (m, 2H), 1.38 (br. s., 1H). δ_C (126 MHz,

$CDCl_3$) 141.8, 138.3, 128.6, 127.1, 65.2, 62.8, 35.3, 32.3, 27.5. HRMS (EI) calculated for $C_{11}H_{16}O_2$ 180.11448. Found 180.11494.

Data were in accordance with those previously reported in the literature.[5]

2-(4-(4-Methylbenzoate)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3g

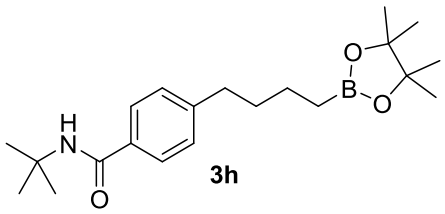


3g

According to General Procedure **B**, 4-(3-butenyl)-benzoic acid methyl ester **2g** (133 mg, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), iron(II) chloride (0.9 mg, 0.007 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) and ethylmagnesium bromide (3 drops, 0.021 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction product, which was purified by flash column chromatography (SiO_2, 7% EtOAc/Hexane) to give 2-(4-(4-methylbenzoate)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3g** as a colourless oil (187 mg, 0.59 mmol, 84%).

δ_H (400 MHz, $CDCl_3$) 7.96-7.91 (m, 2H), 7.26-7.21 (m, 2H), 3.89 (s, 3H), 2.69-2.62 (m, 2H), 1.69-1.59 (m, 2H), 1.52-1.42 (m, 2H), 1.24 (s, 12H), 0.85-0.78 (m, 2H). δ_C (101 MHz, $CDCl_3$) 167.2, 48.5, 129.6, 128.4, 127.5, 82.9, 51.9, 35.8, 33.7, 24.8, 23.6. δ_B (128 MHz, $CDCl_3$) 34.4. ν_{max} cm^{-1} 2978, 2936, 2862, 1721, 1611, 1435, 1371, 1317, 1275, 1179, 1144, 1107. HRMS (EI) calculated for $C_{18}H_{27}BO_4$ 318.19969. Found 318.19941.

2-(4-(4-*N*-*tert*-Butylbenzamide)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3h

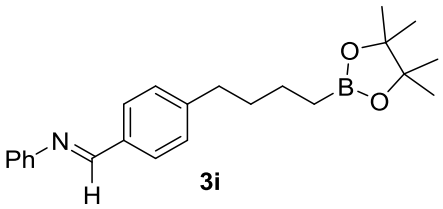


3h

According to General Procedure **B**, *N*-(*tert*-butyl)-4-(3-butenyl)-benzamide **2h** (162 mg, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), iron(II) chloride (2.6 mg, 0.035 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (8.9 mg, 0.035 mmol) and ethylmagnesium bromide (15 drops, 0.105 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction product, which was purified by flash column chromatography (SiO_2, 7% EtOAc/Hexane) to give 2-(4-(4-*N*-*tert*-butylbenzamide)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3h** as a colourless solid (89 mg, 0.25 mmol, 35%).

m.p. 99-101 °C. δ_H (400 MHz, $CDCl_3$) 7.66-7.59 (m, 2H), 7.24-7.18 (m, 2H), 5.91 (br s, 1H), 2.68-2.60 (m, 2H), 1.67-1.58 (m, 2H), 1.51-1.41 (m, 2H), 1.47 (s, 9H), 1.24 (s, 12H), 0.84-0.78 (m, 2H). δ_C (101 MHz, $CDCl_3$) 166.9, 146.4, 133.2, 128.5, 126.7, 82.9, 51.5, 35.5, 33.9, 28.9, 24.8, 23.6. δ_B (128 MHz, $CDCl_3$) 34.5. ν_{max} cm^{-1} 3364, 2965, 2928, 2829, 1634, 1611, 1535, 1504, 1456, 1364, 1304, 1219, 1144. HRMS (EI) calculated for $C_{21}H_{34}BNO_3$ 359.26263. Found 359.26257.

2-(4-(*N*-Phenylbenzaldimine)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3i

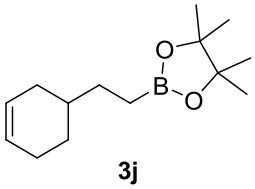


3i

According to General Procedure **B**, *N*-phenyl-4-(3-butenyl)-benzaldimine **2i** (164 mg, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), iron(II) chloride (0.9 mg, 0.007 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) and ethylmagnesium bromide (3 drops, 0.021 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give 2-(4-(*N*-phenylbenzaldimine)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3i** as a yellow oil. Purification of the product by flash silica chromatography resulted mostly in hydrolysis of the product to the aldehyde. A small amount of spectroscopically pure material was obtained however.

δ_H (500 MHz, $CDCl_3$) 8.43 (s, 1H), 7.84-7.79 (m, 2H), 7.42-7.37 (m, 2H), 7.31-7.27 (m, 2H), 7.25-7.19 (m, 3H), 2.71-2.65 (m, 2H), 1.71-1.63 (m, 2H), 1.53-1.45 (m, 2H), 1.26 (s, 1H), 0.86-0.81 (m, 2H). δ_C (126 MHz, $CDCl_3$) 160.4, 152.3, 146.9, 133.8, 129.1, 128.9, 128.8, 125.7, 120.9, 82.9, 35.8, 33.9, 24.8, 23.7. δ_B (128 MHz, $CDCl_3$) 34.5. ν_{max} cm^{-1} 2976, 2928, 2855, 1701, 1626, 1607, 1589, 1570. 1485, 1462, 1450, 1371. 1317, 1167, 1144. HRMS (EI) calculated for $C_{23}H_{30}BNO_2$ 363.23641. Found 363.23688.

2-(2-(Cyclohex-3-en-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3j



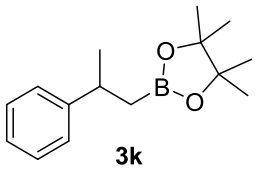
3j

According to General Procedure **B**, 4-vinylcyclohexene (91 µL, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), iron(II) chloride (0.9 mg, 0.007 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) and ethylmagnesium bromide (3 drops, 0.021 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction product, which was purified by flash column chromatography (SiO_2, 2% EtOAc/Hexane) to give 2-(2-(Cyclohex-3-en-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3j** as a colourless oil (144 mg, 0.61 mmol, 87%).

δ_H (400 MHz, $CDCl_3$) 5.67-5.59 (m, 2H), 2.13- 2.04 (m, 1H), 2.04-1.97 (m, 2H), 1.78-1.69 (m, 1H), 1.66-1.55 (m, 1H), 1.50-1.31 (m, 3H), 1.23 (s, 12H), 1.20-1.11 (m, 1H), 0.82-0.75 (m, 2H). δ_C (101 MHz, $CDCl_3$) 126.9, 126.7, 82.8, 35.7, 31.6, 30.6, 28.5, 25.3, 24.8. δ_B (128 MHz, $CDCl_3$) 34.0.

Data were in accordance with those previously reported in the literature.[6]

2-(2-Phenyl-propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3k



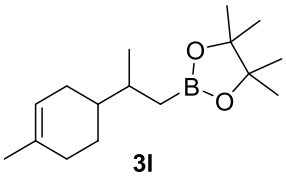
3k

According to General Procedure **C**, α-methylstyrene (91 µL, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine iron(II) chloride [**1**-$FeCl_2$] (3.9 mg, 0.007 mmol) and *n*-BuLi (4 drops, 0.021 mmol) were reacted to give the crude reaction product, which was purified by flash column chromatography (SiO_2, 2% EtOAc/Hexane) to give 2-(2-phenyl-propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3k** as a colourless oil (150 mg, 0.61 mmol, 87%).

δ_H (500 MHz, $CDCl_3$) 7.31-7.25 (m, 4H), 7.20-7.15 (m, 1H), 3.06 (app. sextet, *J*= 7.0 Hz, 1H), 1.31 (d, *J*= 7.0 Hz, 3H), 1.24-1.13 (m, 2H), 1.19 (s, 12H). δ_C (126 MHz, $CDCl_3$) 149.2, 128.1, 126.6, 125.6, 83.0, 35.8, 24.9, 24.8, 24.7, (21.2). δ_B (128 MHz, $CDCl_3$) 33.1.

Data were in accordance with those previously reported in the literature.[6]

2-(2-((*R*)-4-Methylcyclohex-3-en-1-yl)-propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3l (1:1 mixture of diastereoisomers)



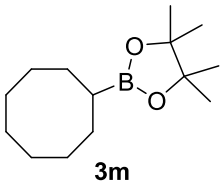
3l

According to General Procedure **C**, (*R*)-limonene (113 µL, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine iron(II) chloride [**1**-$FeCl_2$] (3.9 mg, 0.007 mmol) and *n*-BuLi (4 drops, 0.021 mmol) were reacted to give the crude reaction product, which was purified by flash column chromatography (SiO_2, 2% EtOAc/Hexane) to give 2-(2-((*R*)-4-Methylcyclohex-3-en-1-yl)-propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3l** (1:1 mixture of diastereoisomers) as a colourless oil (127 mg, 0.48 mmol, 69%).

δ_H (500 MHz, $CDCl_3$) 5.39-5.35 (m, 1H), 2.03-1.88 (m, 3H), 1.78-1.63 (m, 3H), 1.64 (s, 3H), 1.36-1.26 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.24-1.14 (m, 1H), 0.93-0.87 (m, 4H), 0.65 (dd, *J*= 15.3, 9.9 Hz, 1H). δ_C (126 MHz, $CDCl_3$) 133.88, 133.85, 121.10, 121.07, 82.8, 40.63, 40.55, 33.9, 33.7, 31.0, 30.9, 29.2, 28.4, 26.8, 25.9, 24.92, 24.90, 24.71, 24.71, 23.5, 19.3, 19.0, (16.6). δ_B (128 MHz, $CDCl_3$) 33.7.

Data were in accordance with those previously reported in the literature.[6]

2-Cyclooctyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3m



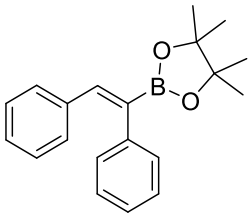
3m

According to General Procedure **C**, cyclooctene (91 µL, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine iron(II) chloride [**1**-$FeCl_2$] (3.9 mg, 0.007 mmol) and *n*-BuLi (4 drops, 0.021 mmol) were reacted to give the crude reaction product, which was purified by flash column chromatography (SiO_2, 2% EtOAc/Hexane) to give 2-cyclooctyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3m** as a colourless oil (147 mg, 0.62 mmol, 88%).

δ_H (500 MHz, $CDCl_3$) 1.77-1.69 (m, 2H), 1.68-1.61 (m, 2H), 1.60-1.43 (m, 10H), 1.24 (s, 12H), 1.15-1.09 (m, 1H). δ_C (126 MHz, $CDCl_3$) 82.7, 27.6, 27.0, 26.8, 26.6, 24.7, (21.3). δ_B (128 MHz, $CDCl_3$) 34.1.

Data were in accordance with those previously reported in the literature.[7]

(*Z*)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5a



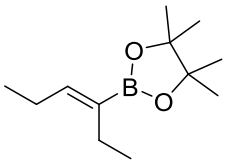
5a

According to General Procedure **B**, diphenylacetylene (125 mg, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), iron(II) chloride (0.9 mg, 0.007 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) and ethylmagnesium bromide (3 drops, 0.021 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction product, which was purified by flash column chromatography (SiO_2, 2% EtOAc/Hexane) to give (*Z*)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **5a** as a colourless solid (167 mg, 0.55 mmol, 78%).

δ_H (400 MHz, $CDCl_3$) 7.39 (br s, 1H), 7.31-7.26 (m, 2H), 7.25-7.17 (m, 3H), 7.16-7.11 (m, 3H), 7.10-7.06 (m, 2H), 1.33 (s, 12H). δ_C (101 MHz, $CDCl_3$) 143.1, 140.4, 137.0, 129.9, 128.8, 128.2, 127.8, 127.6, 126.2, 83.8, 24.8. δ_B (128 MHz, $CDCl_3$) 30.8.

Data were in accordance with those previously reported in the literature.[8]

(*Z*)-2-(1-Ethyl-1-buten-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5b



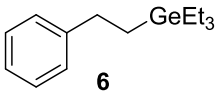
5b

According to General Procedure **B**, 3-hexyne (79 µL,, 0.7 mmol), pinacol borane (110 µL, 0.77 mmol), iron(II) chloride (0.9 mg, 0.007 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) and ethylmagnesium bromide (3 drops, 0.021 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction product, which was purified by flash column chromatography (SiO_2, 2% EtOAc/Hexane) to give (*Z*)-2-(1-ethyl-1-buten-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **5b** as a colourless oil (112 mg, 0.53 mmol, 76%).

δ_H (400 MHz, $CDCl_3$) 6.26 (t, *J*= 7.1 Hz, 1H), 2.19-2.10 (m, 4H), 1.27 (s, 12H), 1.01 (t, *J*= 7.5 Hz, 3H), 0.95 (t, *J*= 7.5 Hz, 3H). δ_C (101 MHz, $CDCl_3$) 146.9, 82.9, 24.7, 21.6, 21.4, 14.8, 13.8. δ_B (128 MHz, $CDCl_3$) 30.8.

Data were in accordance with those previously reported in the literature.[9]

1-Phenyl-2-(triethylgermyl)ethane 6

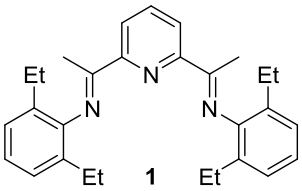


6

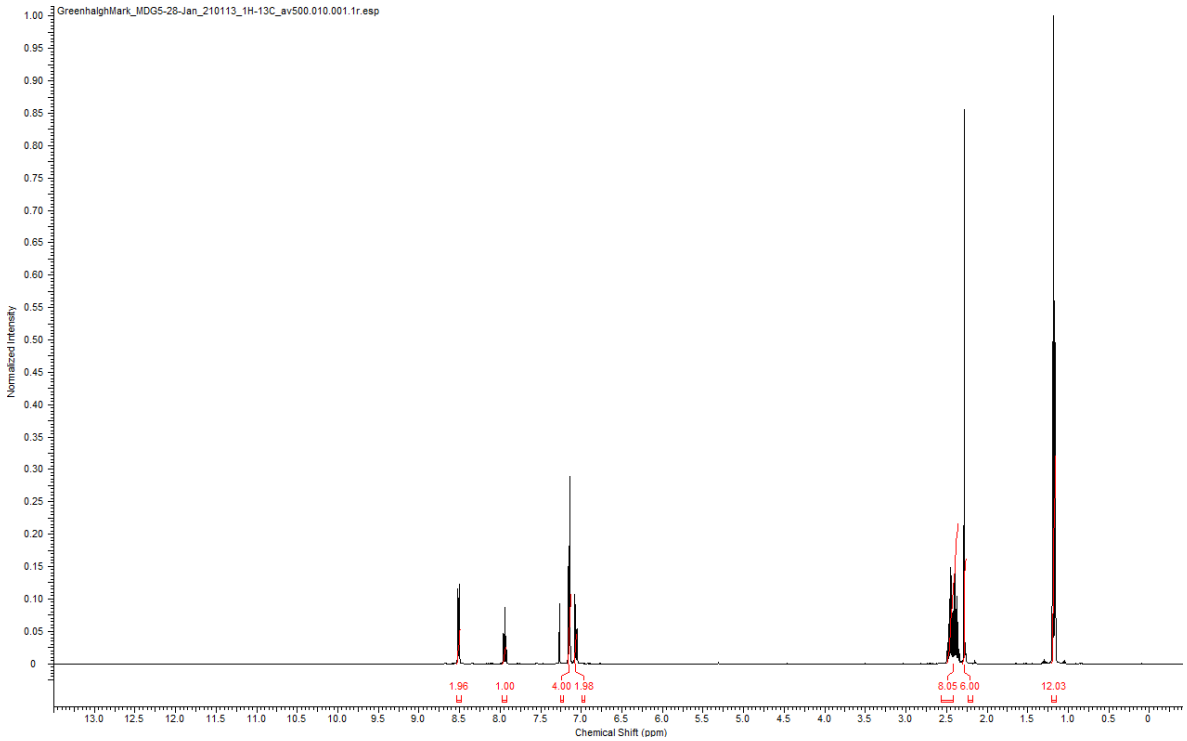
According to General Procedure **B**, styrene (80 µL,, 0.7 mmol), triethylgermanium hydride (120 µL, 0.75 mmol), iron(II) chloride (0.9 mg, 0.007 mmol), 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine **1** (3.0 mg, 0.007 mmol) and ethylmagnesium bromide (3 drops, 0.021 mmol) were reacted in anhydrous tetrahydrofuran (3 mL) to give the crude reaction product, which was purified by filtration through a plug of silica using 0.5% ethyl acetate/petroleum ether to give 1-phenyl-2-(triethylgermyl)ethane **6** as a colourless oil (160 mg, 0.60 mmol, 86%).

δ_H (400 MHz, $CDCl_3$) 7.34-7.28 (m, 2H), 7.26-7.17 (m, 3H), 2.74-2.67 (m, 2H), 1.13-1.06 (m, 2H), 1.06 (t, *J*= 8.0 Hz, 9H), 0.78 (q, *J*= 7.9 Hz, 4H). δ_C (101 MHz, $CDCl_3$) 145.5, 128.3, 127.7, 125.5, 31.3, 13.5, 9.0, 3.9. HRMS (EI) calculated for $C_{14}H_{24}Ge$ 266.10843. Found 266.10812.

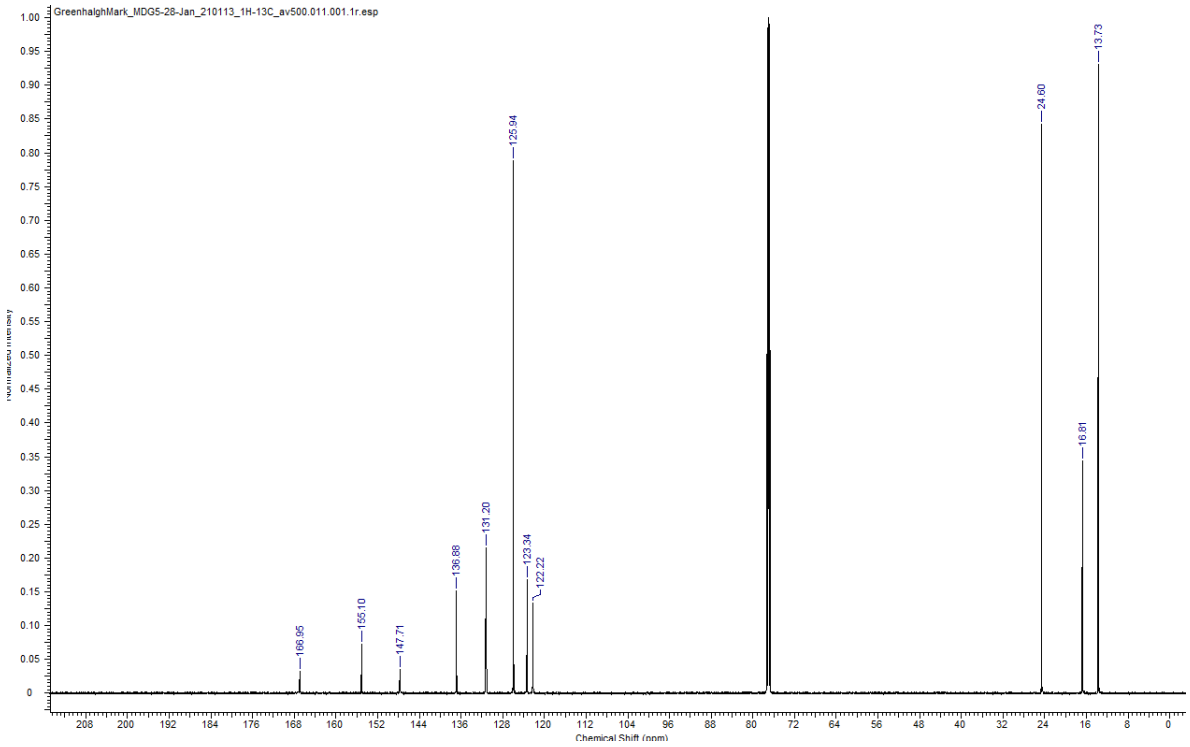
2,6-Bis-[1-(2,6-diethylphenylimino)ethyl]pyridine 1



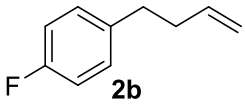
500 MHz



126 MHz

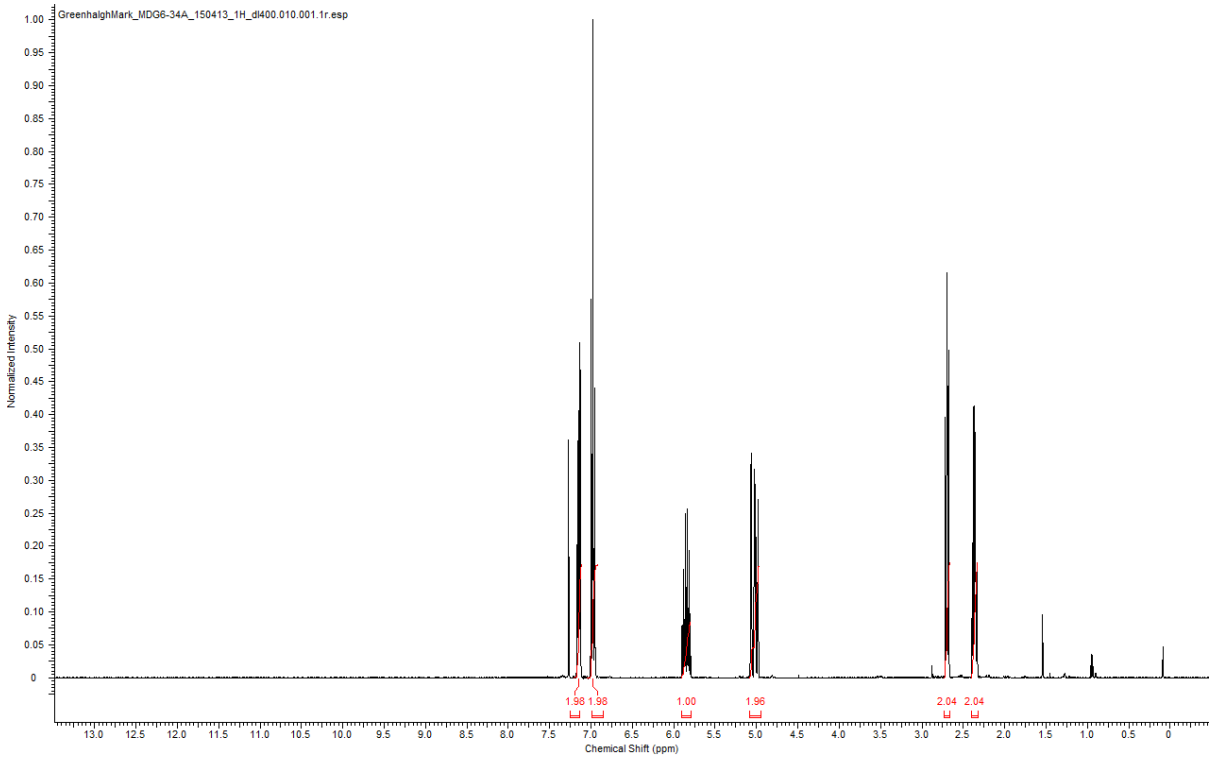


1-Fluoro-4-(3-butenyl)-benzene 2b

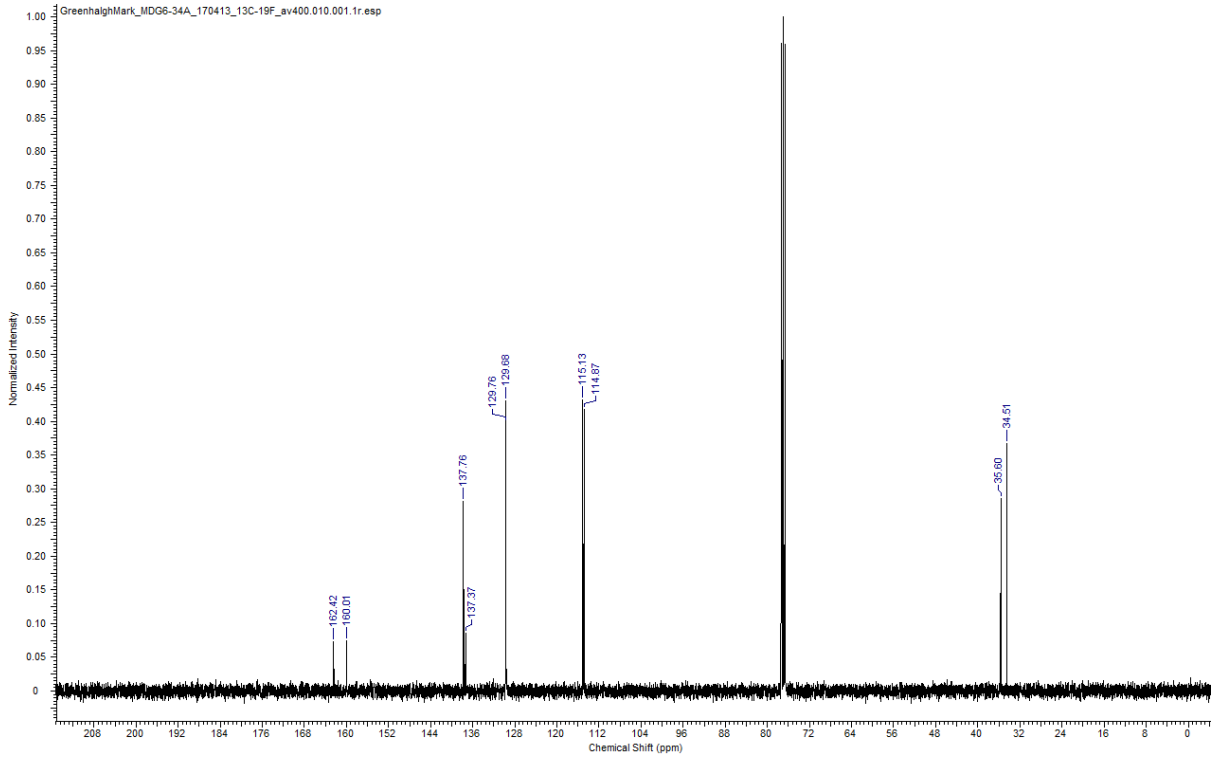


2b

400 MHz

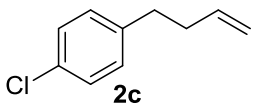


101 MHz



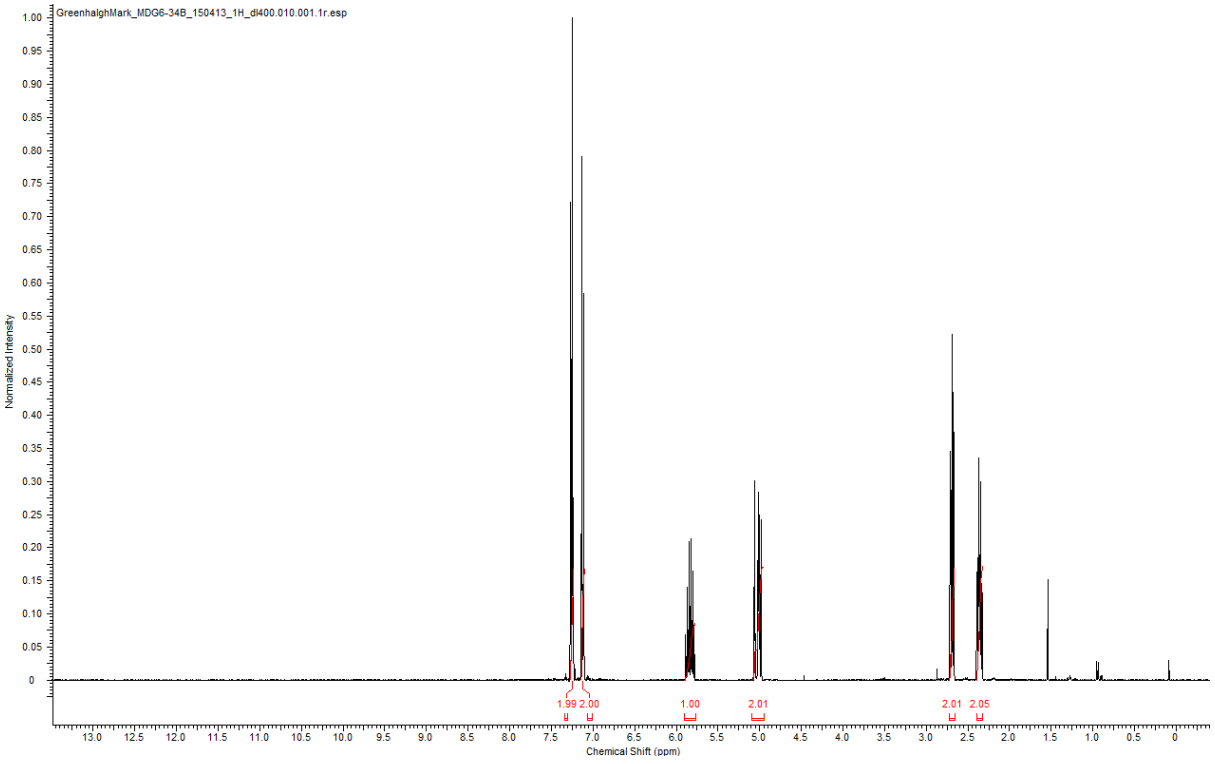
376 MHz

1-Chloro-4-(3-butenyl)-benzene 2c

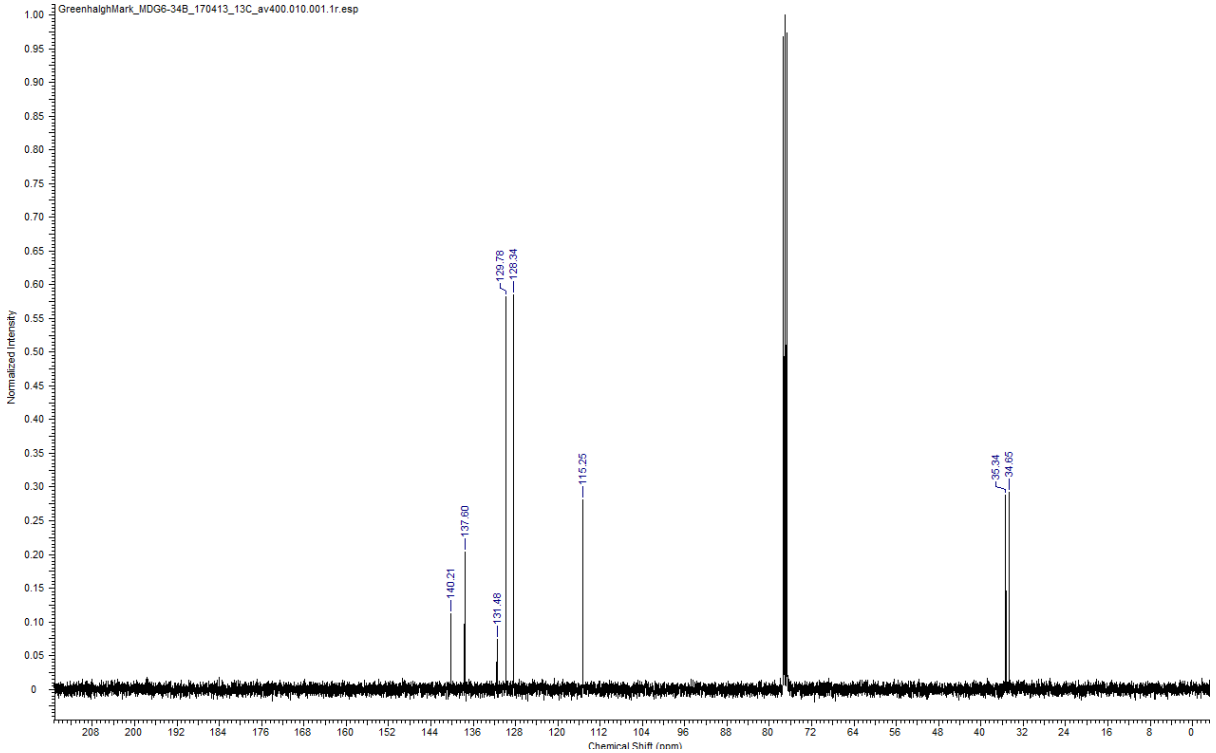


2c

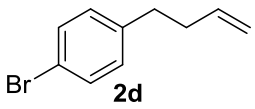
400 MHz



101 MHz

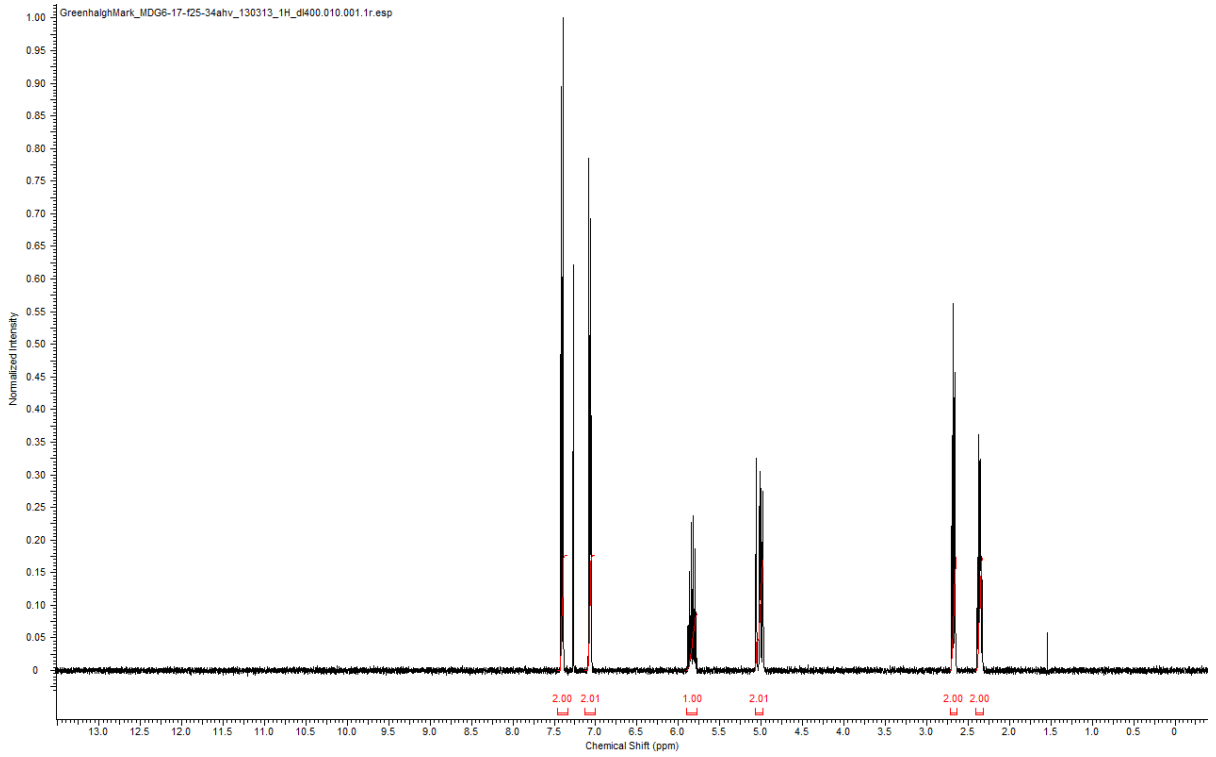


1-Bromo-4-(3-butenyl)-benzene 2d

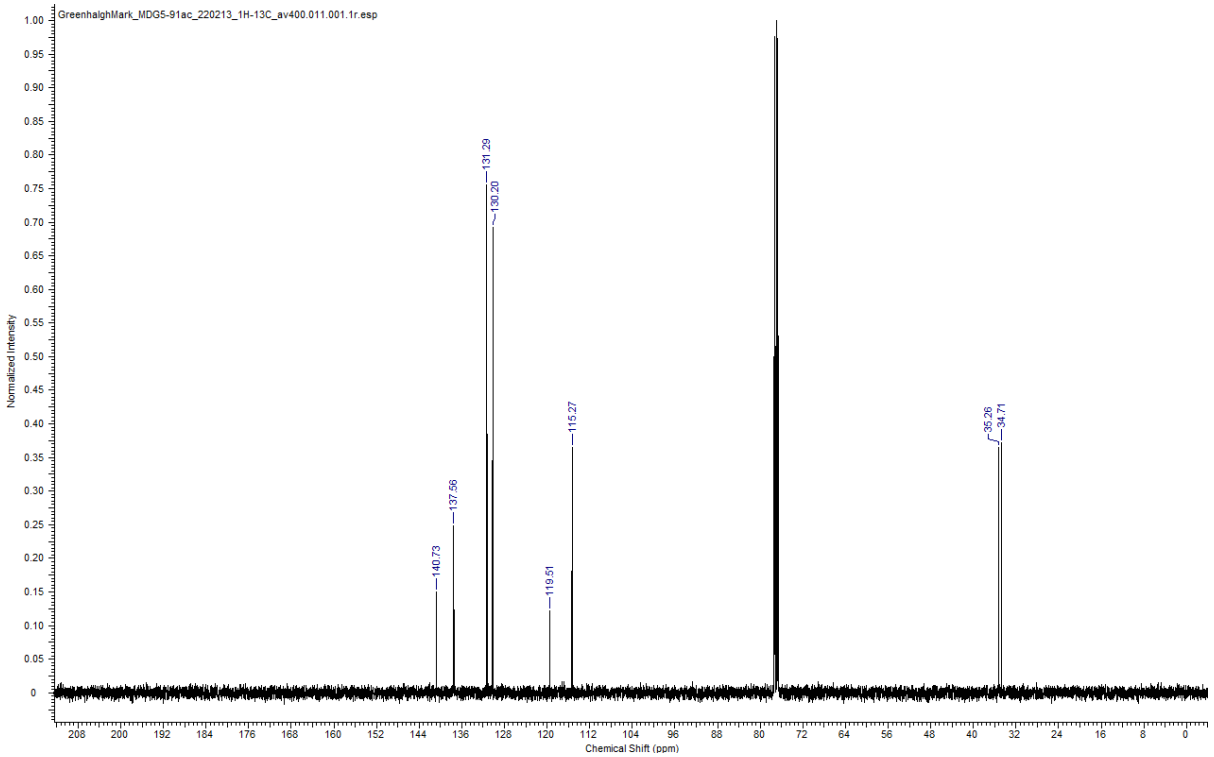


2d

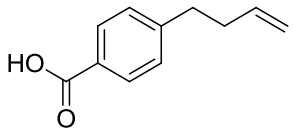
400 MHz



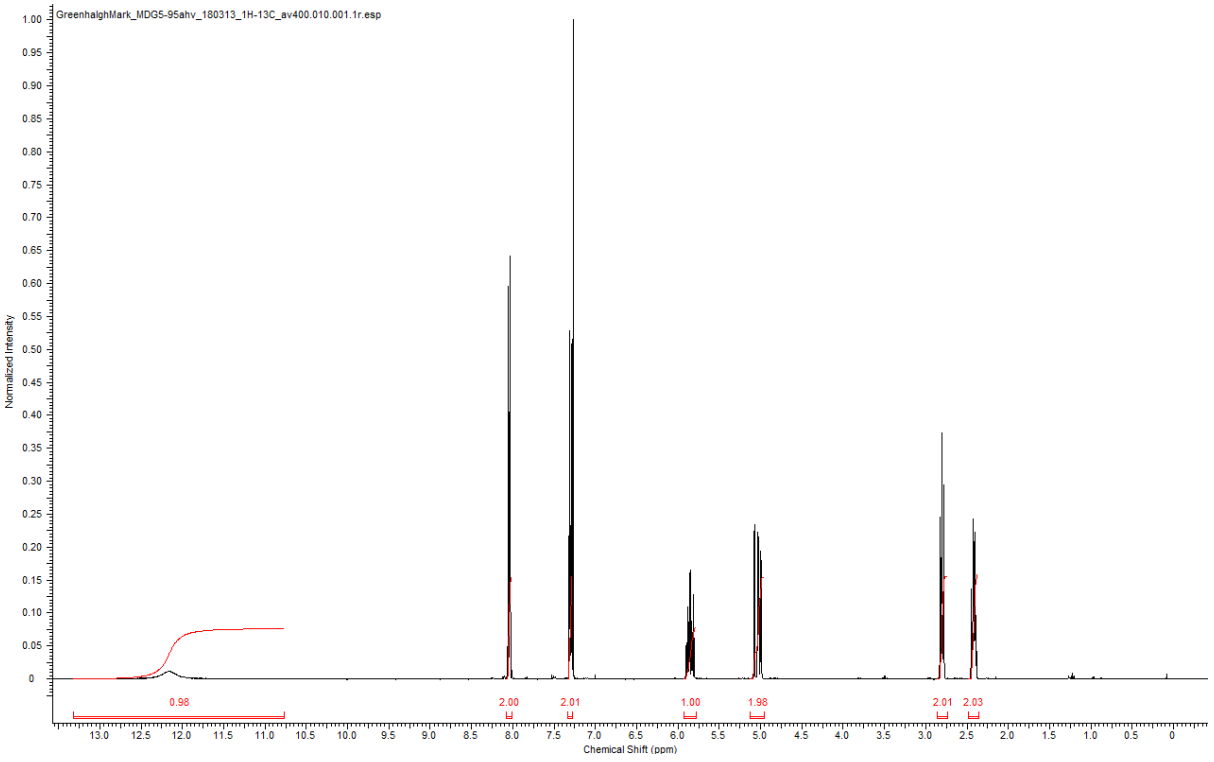
101 MHz



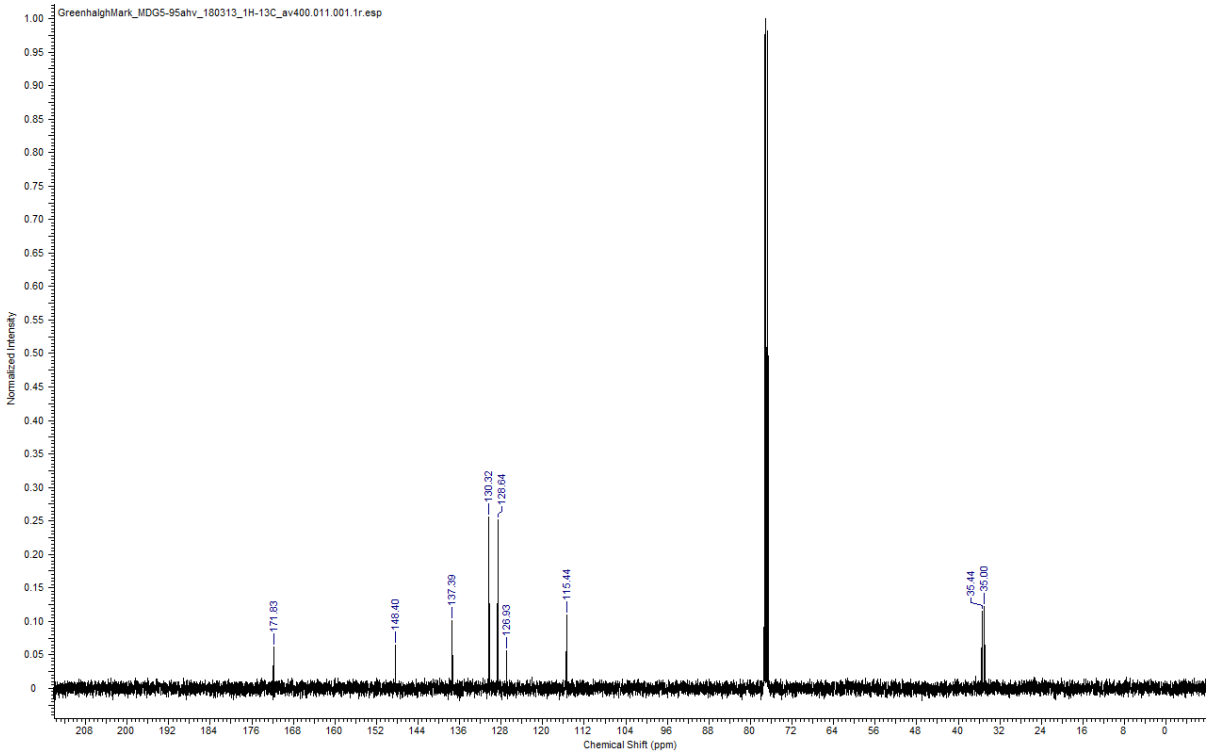
4-(3-Butenyl)-benzoic acid



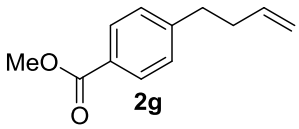
400 MHz



101 MHz

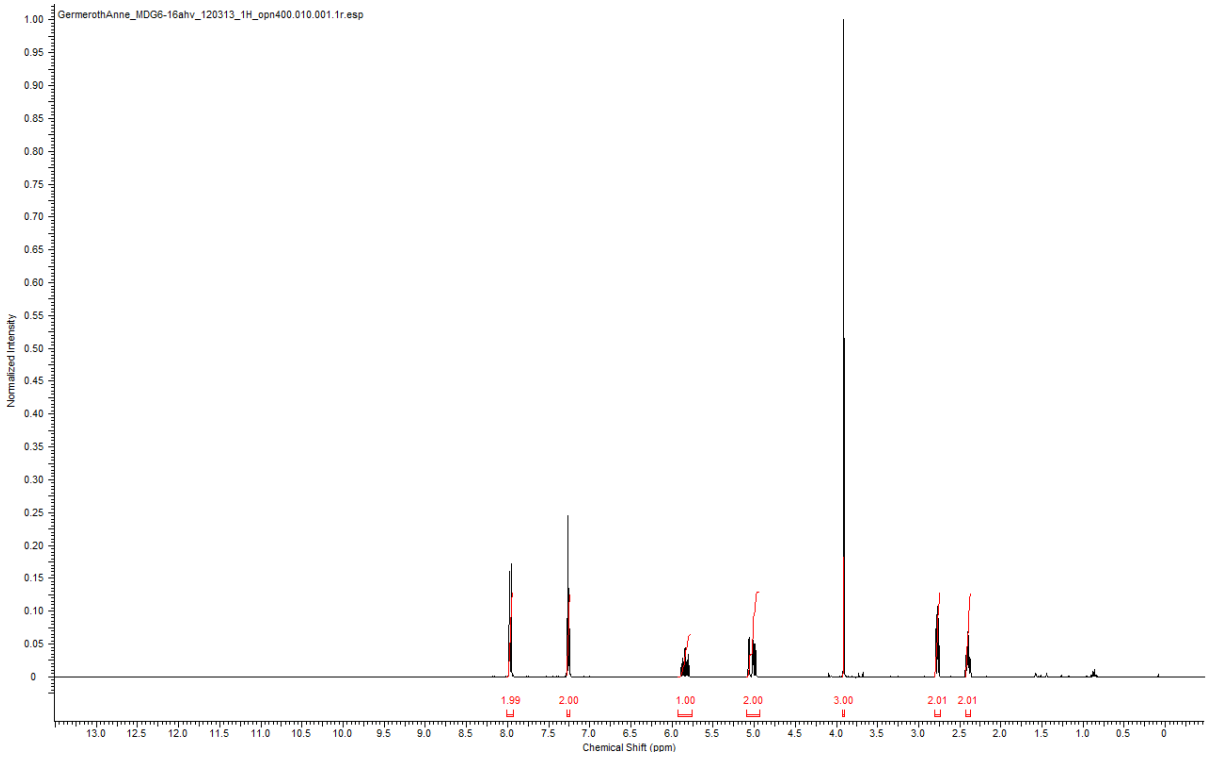


4-(3-Butenyl)-benzoic acid methyl ester 2g

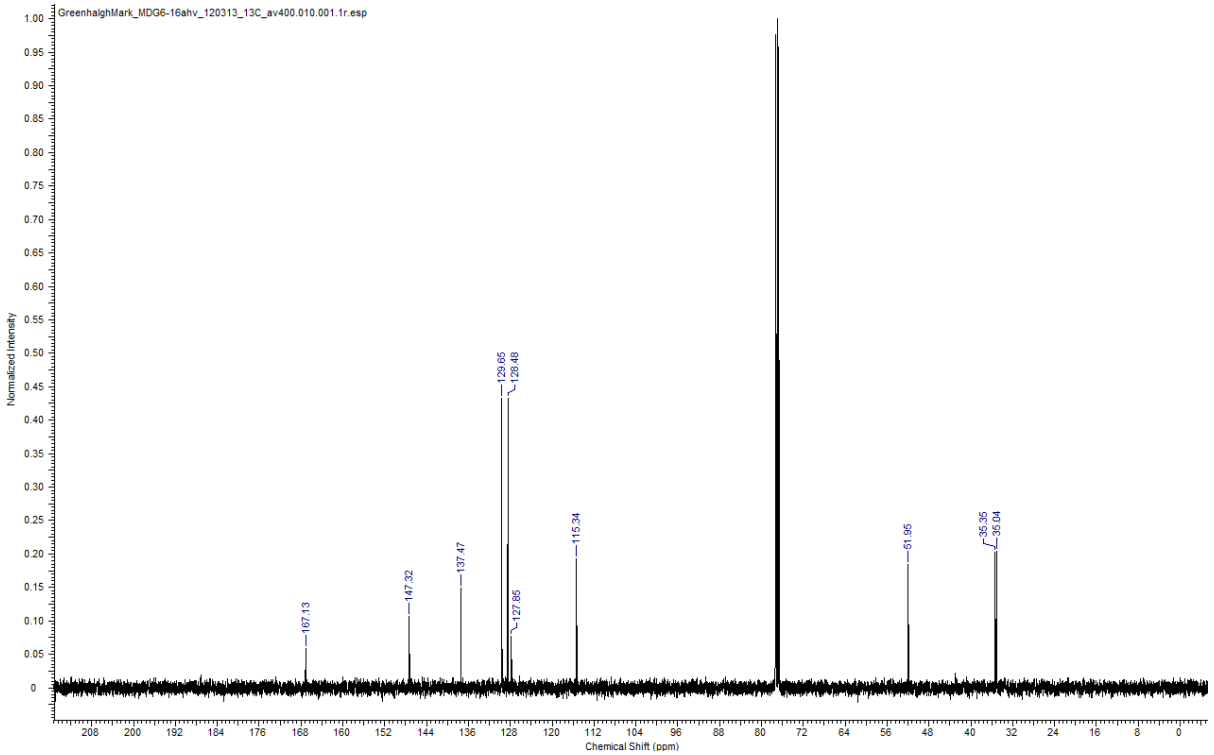


2g

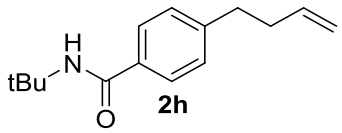
400 MHz



101 MHz

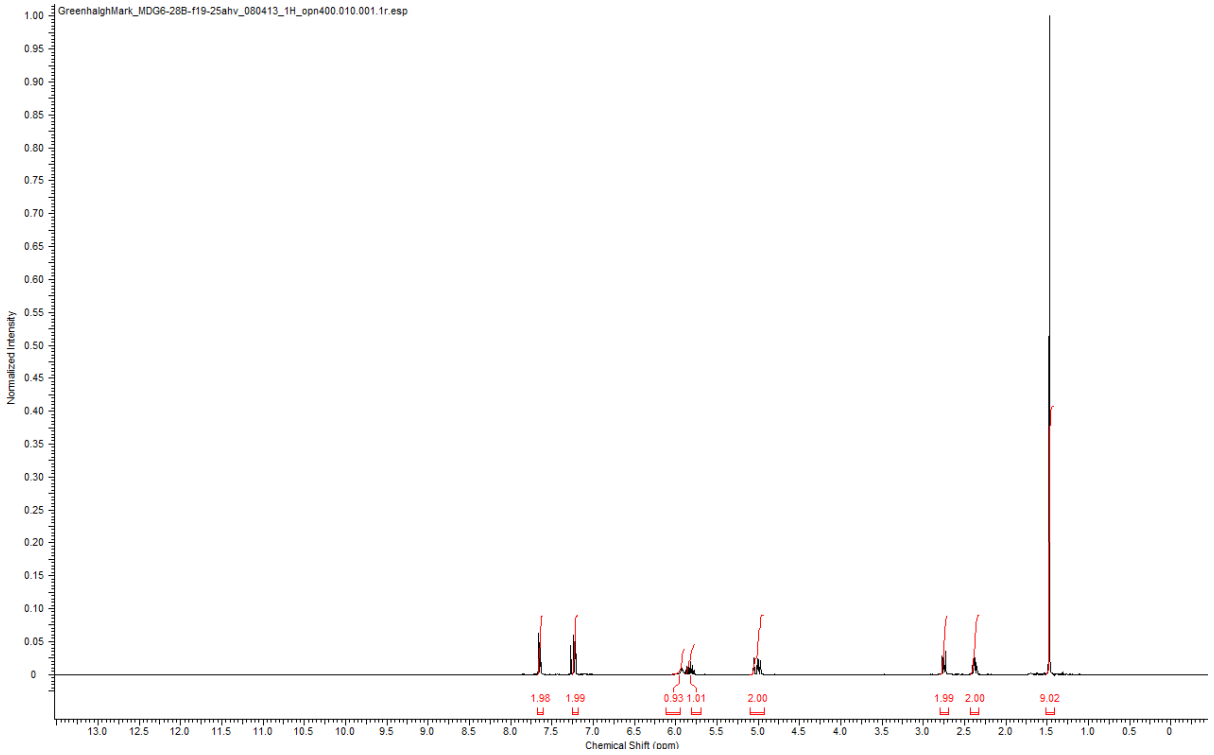


_N_-(_tert_-Butyl)-4-(3-butenyl)-benzamide 2h

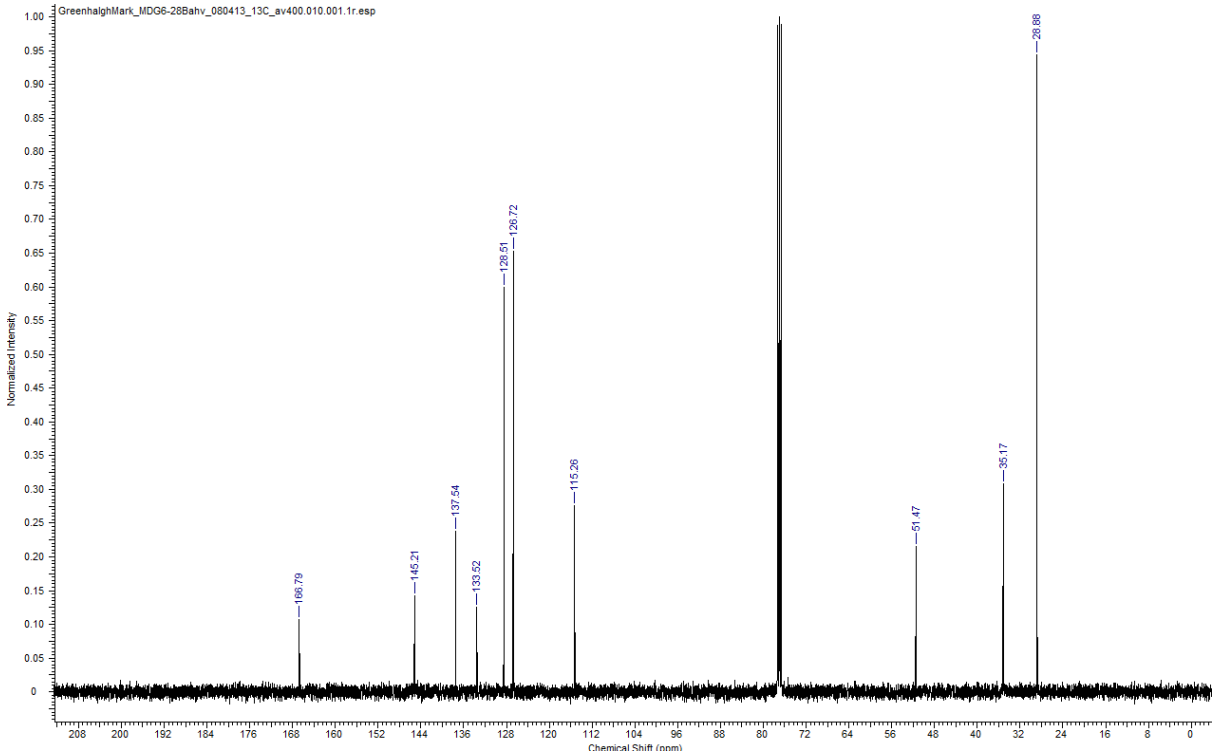


2h

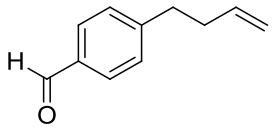
400 MHz



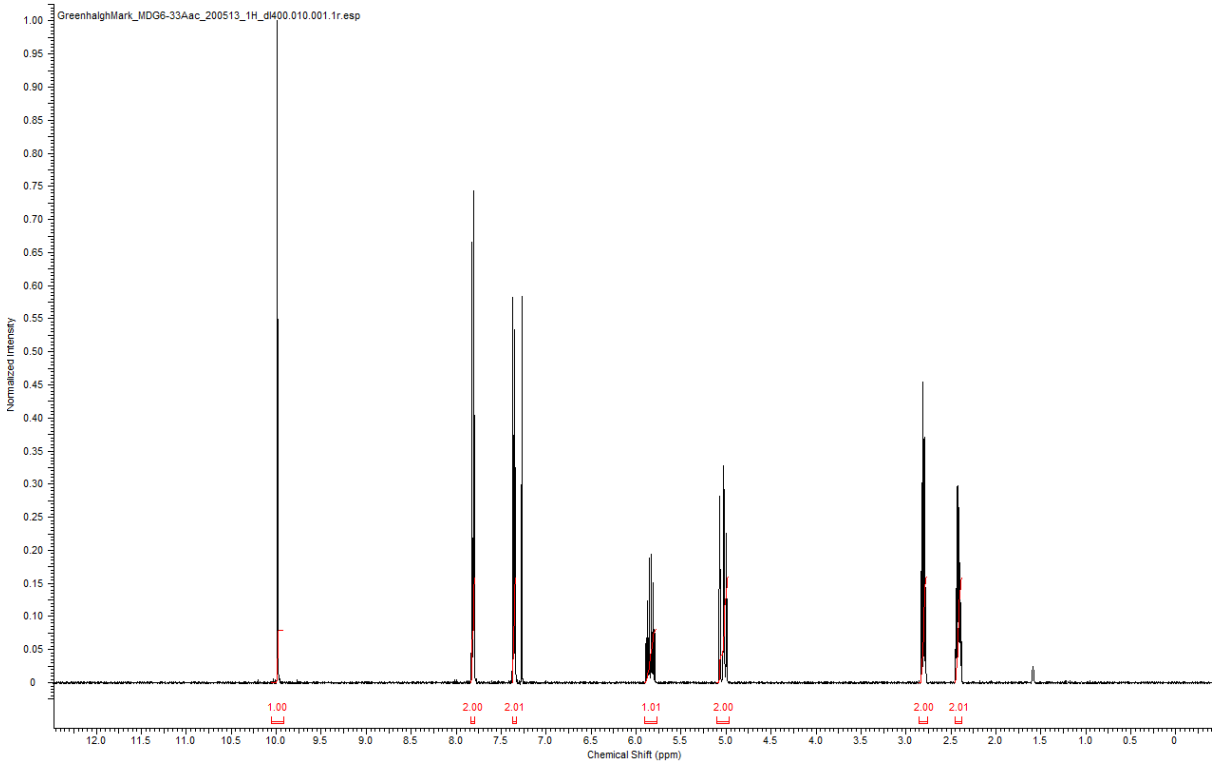
101 MHz



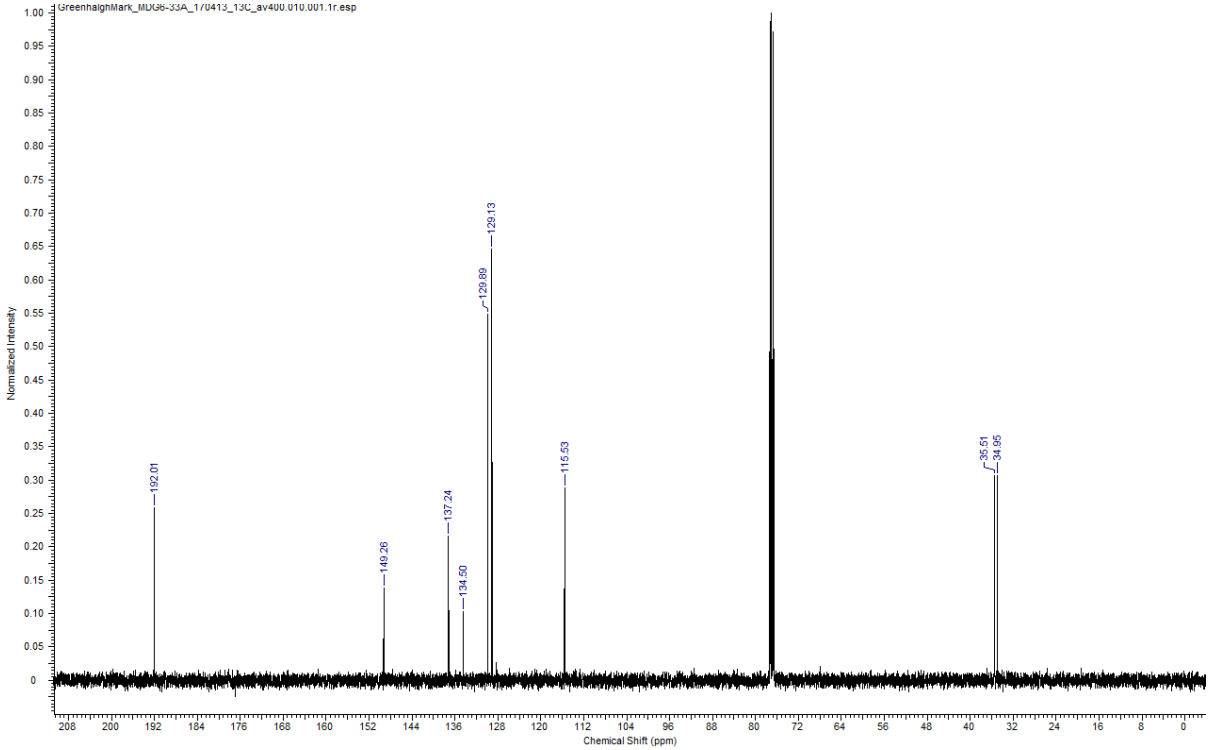
4-(3-Butenyl)-benzaldehyde



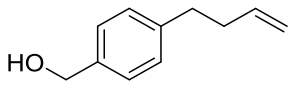
400 MHz



101 MHz

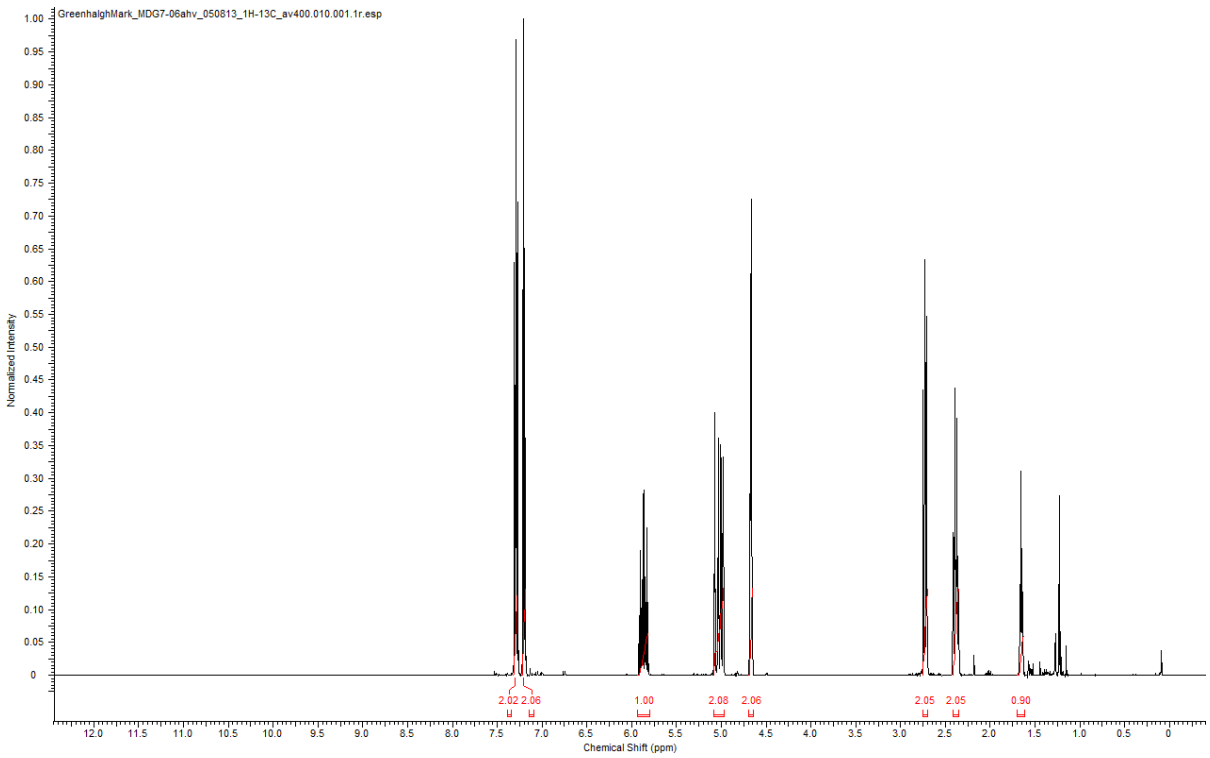


4-(3-Butenyl)-benzyl alcohol 2f

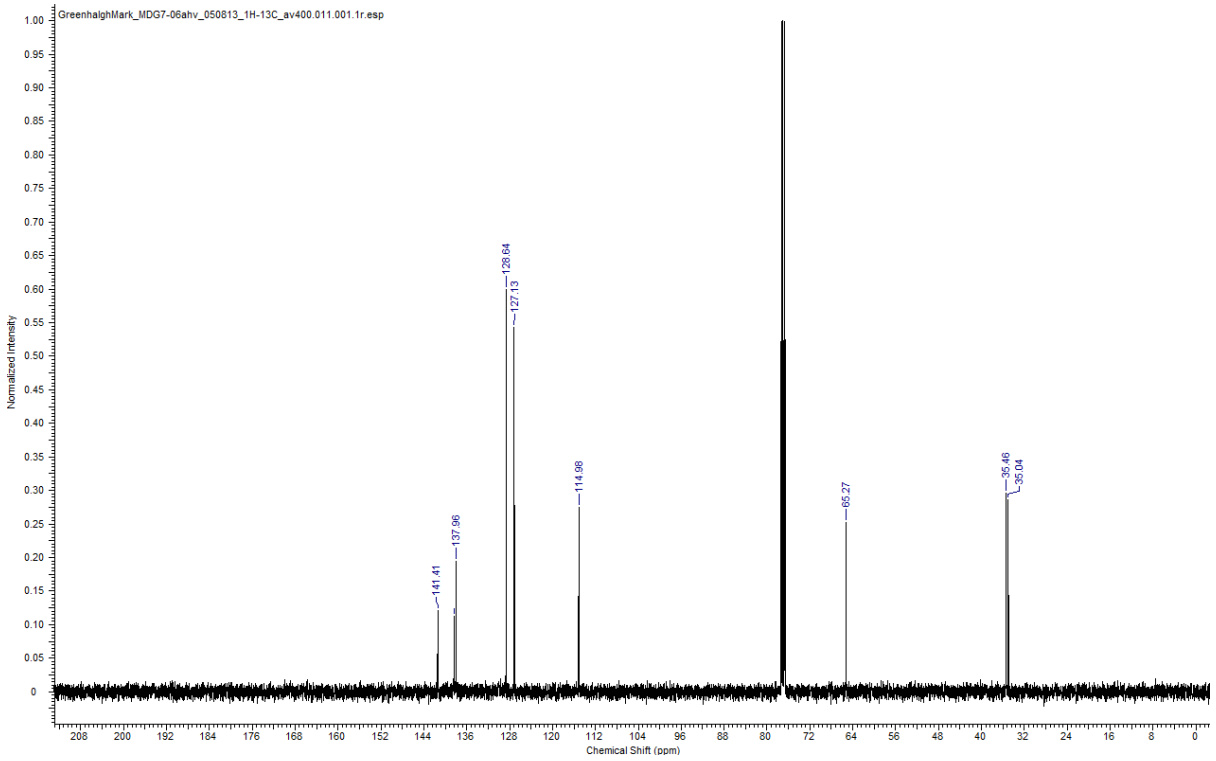


2f

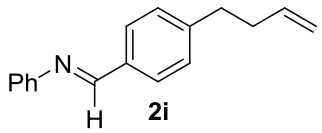
400 MHz



101 MHz

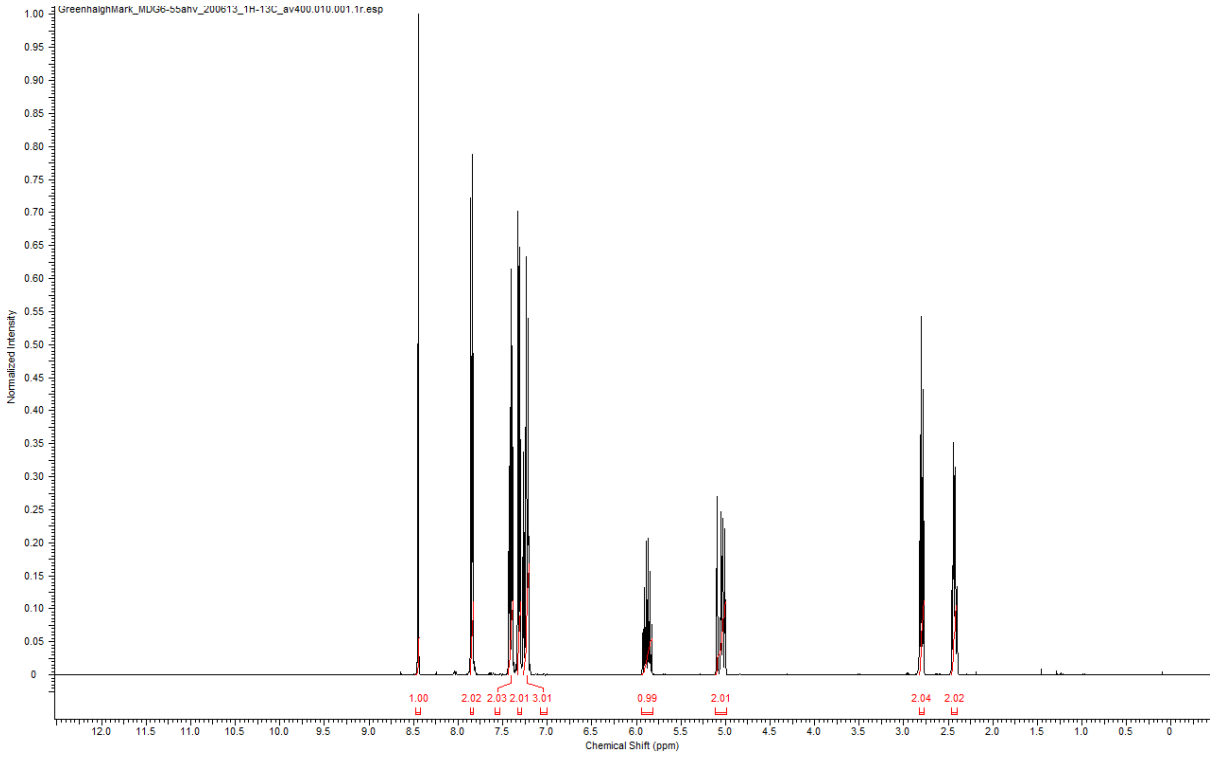


_N_-Phenyl-4-(3-butenyl)-benzaldimine 2i

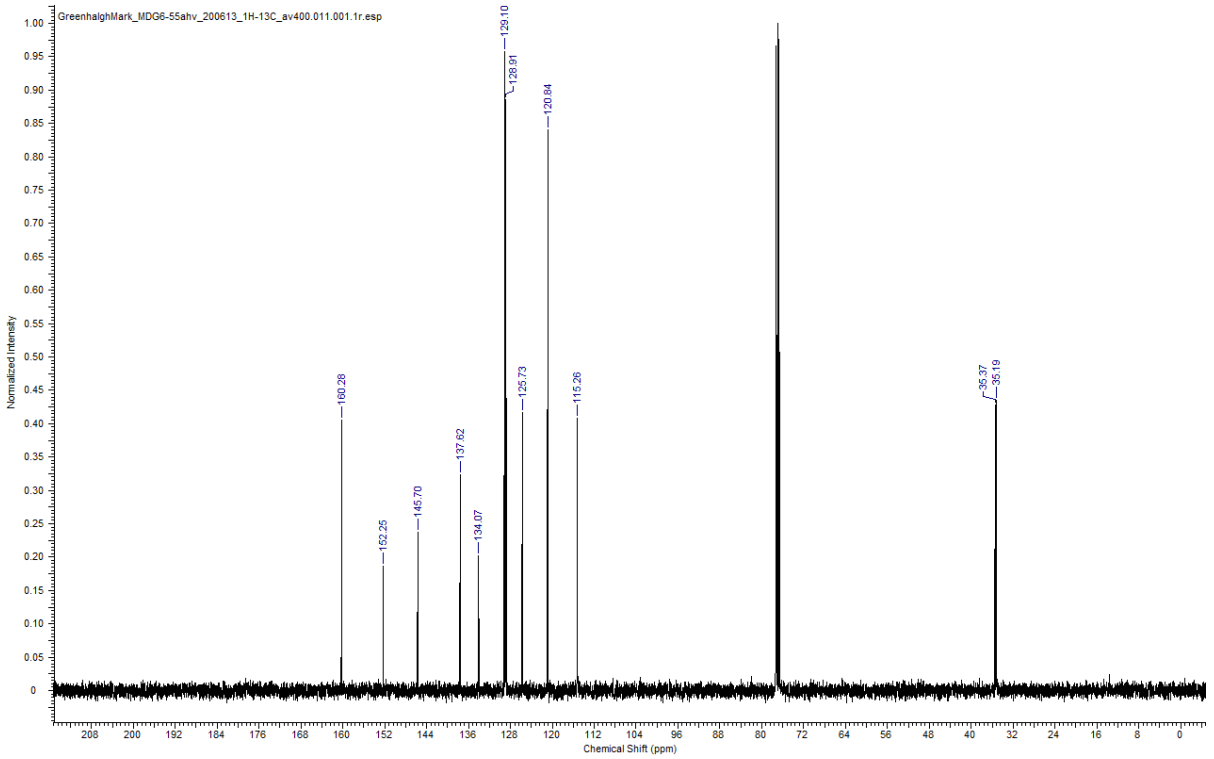


2i

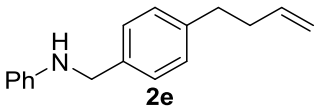
400 MHz



101 MHz

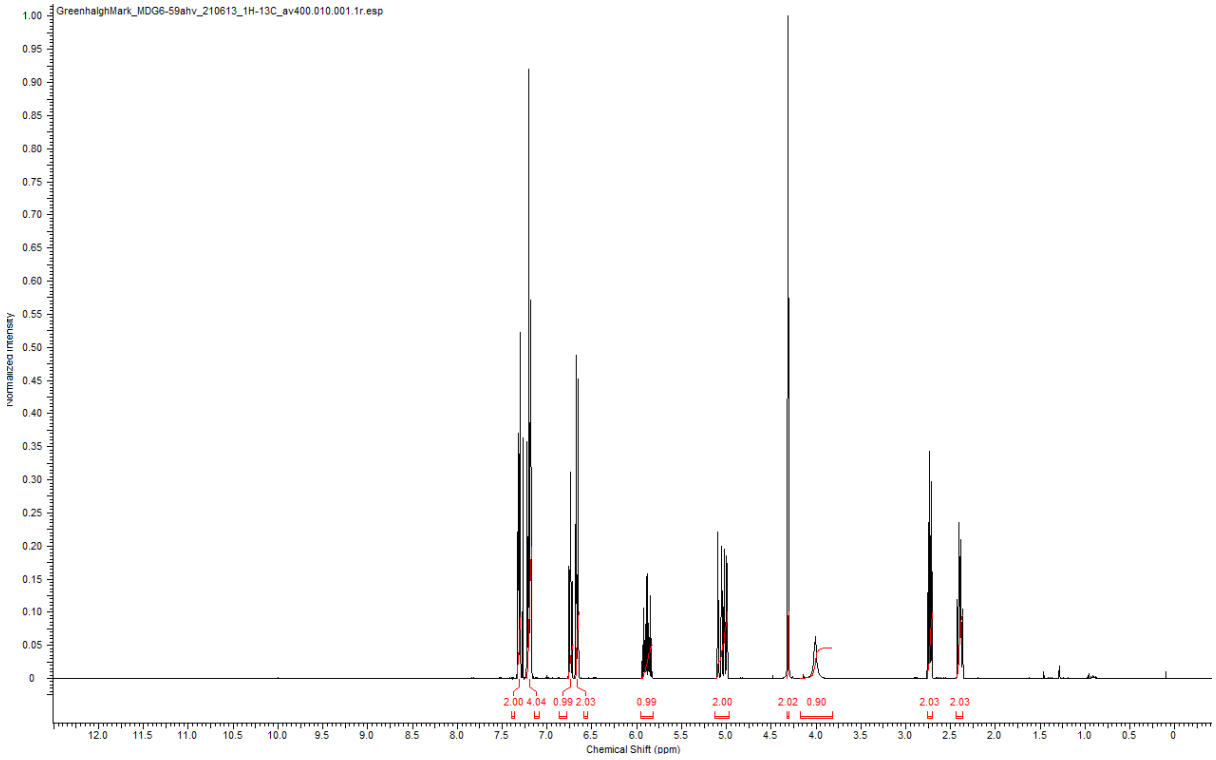


_N_-Phenyl-4-(3-butenyl)-benzylamine 2e

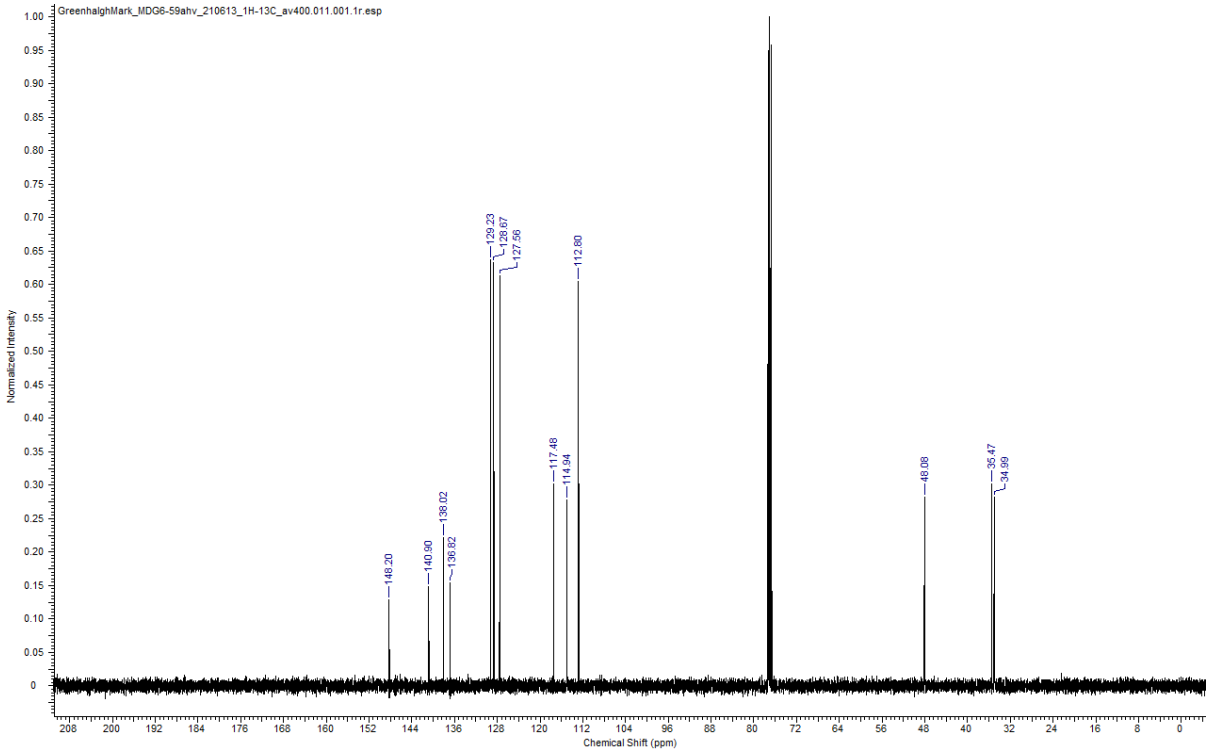


2e

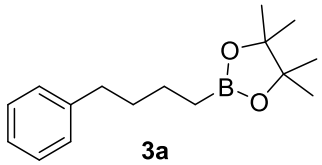
400 MHz



101 MHz

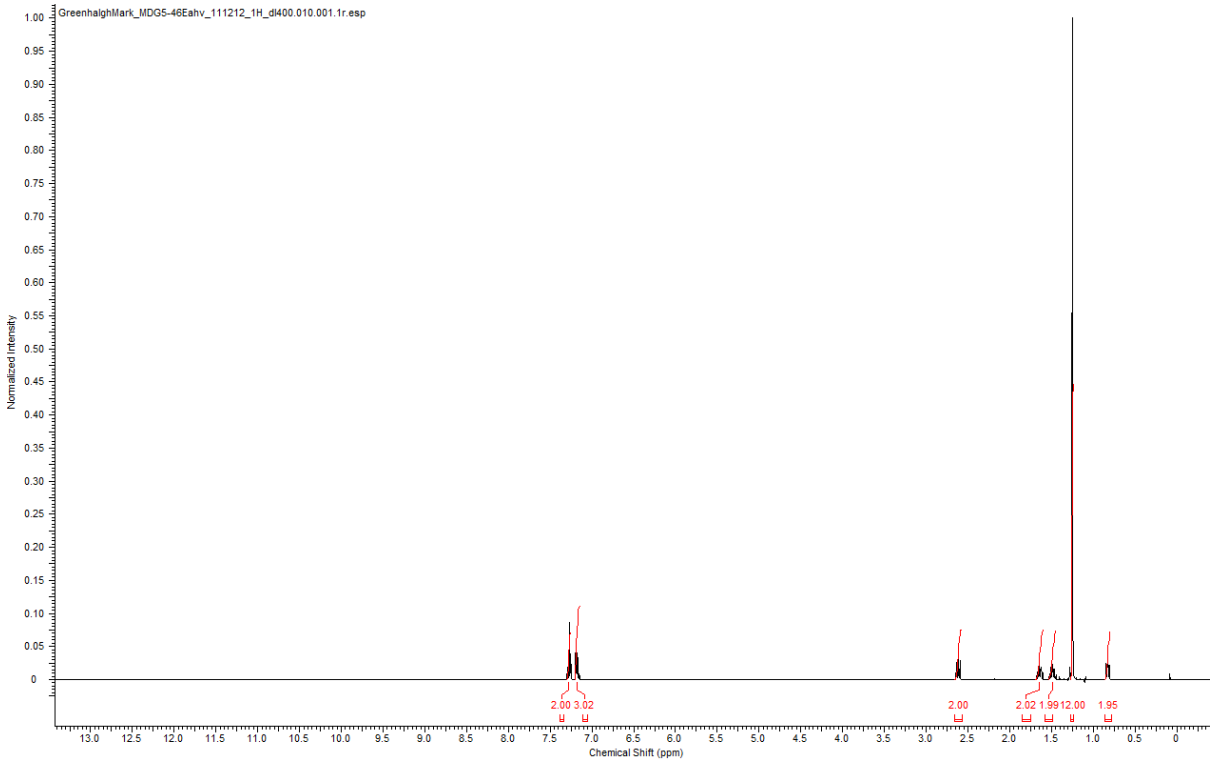

GreenhalghMark_MDG6-59ahv_210613_1H-13C_av400.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
148.20
140.90
138.62
136.82
129.23
128.67
127.56
117.48
114.94
112.80
48.08
35.47
34.99

2-(4-Phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3a

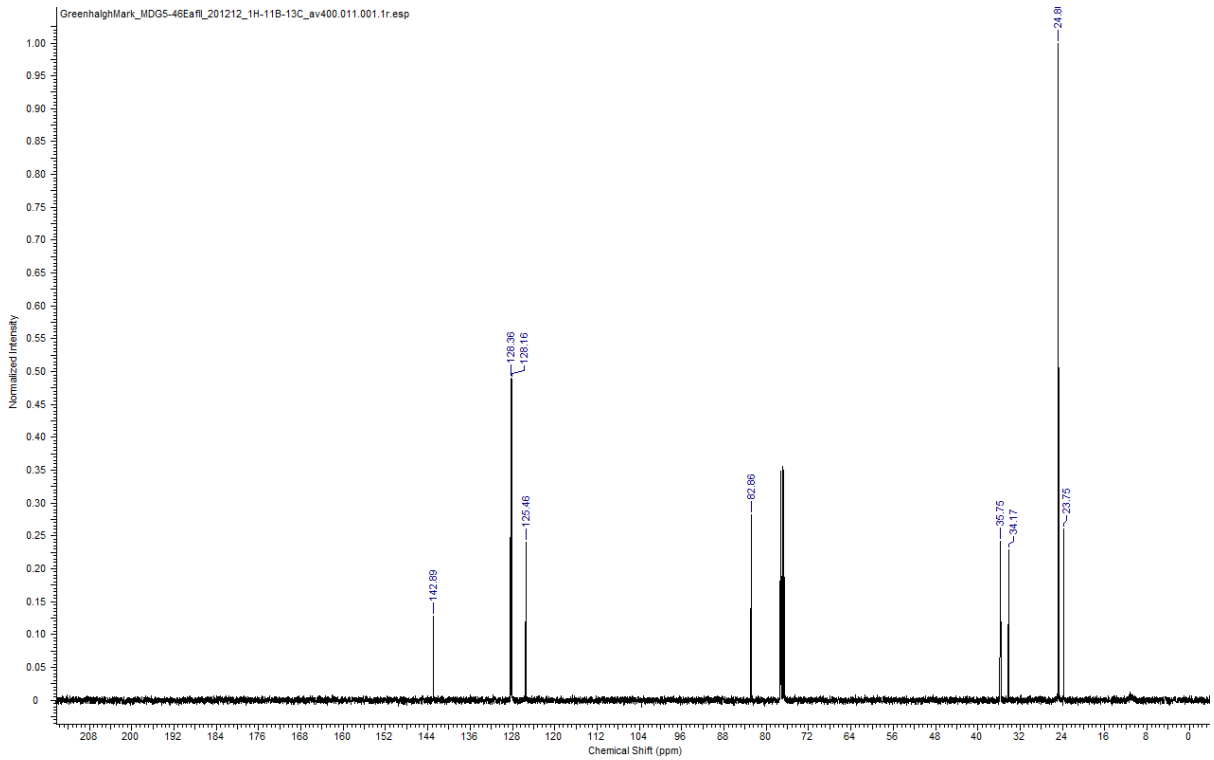


3a

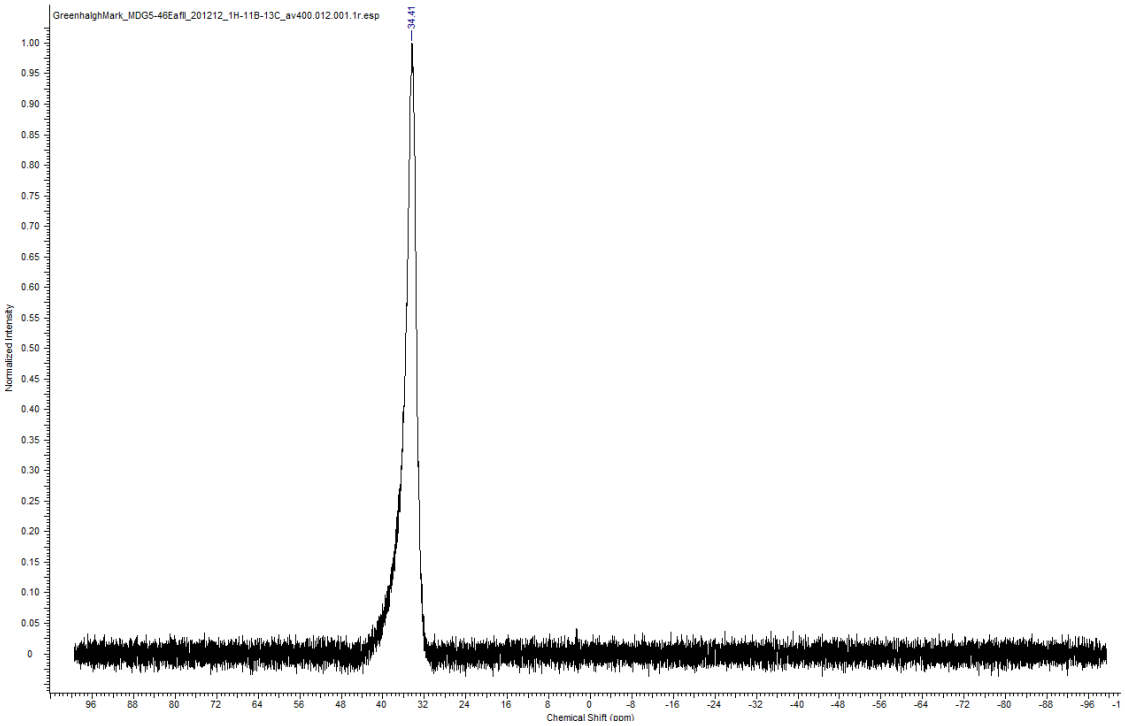
400 MHz



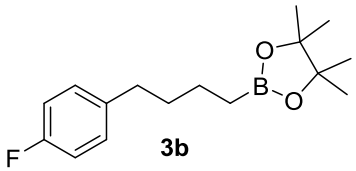
101 MHz



128 MHz

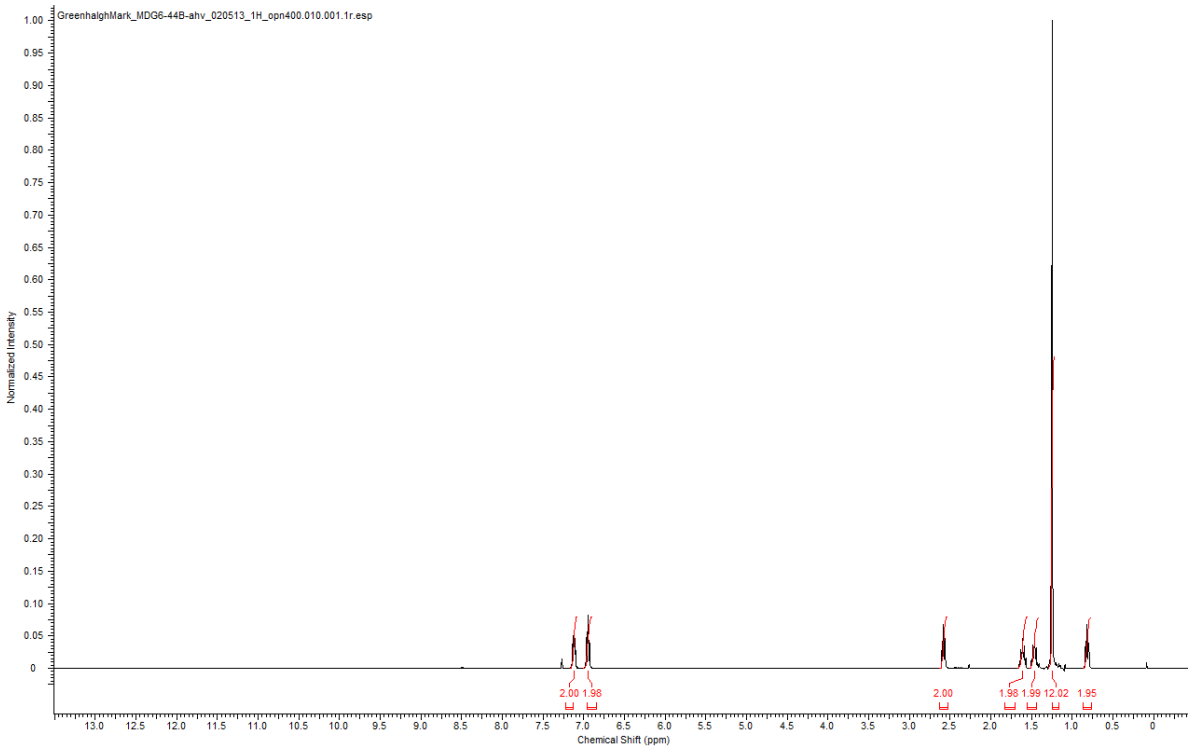


2-(4-(4-Fluorophenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3b

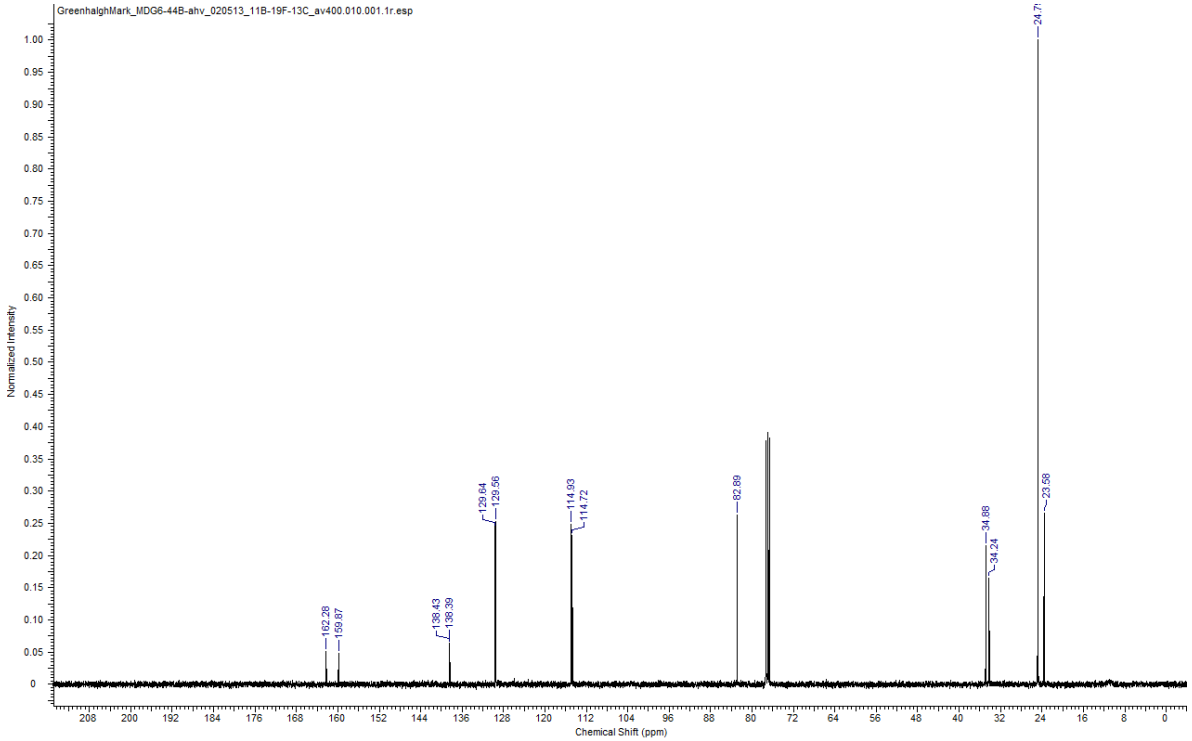


3b

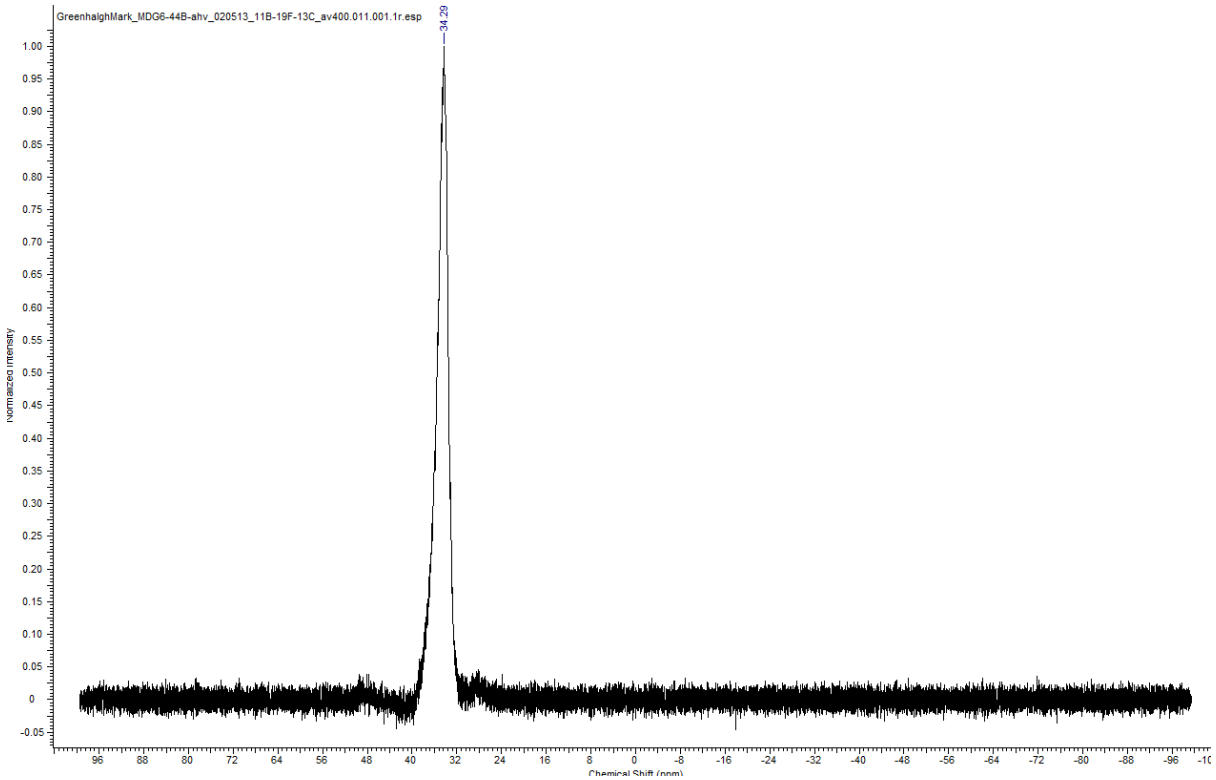
400 MHz



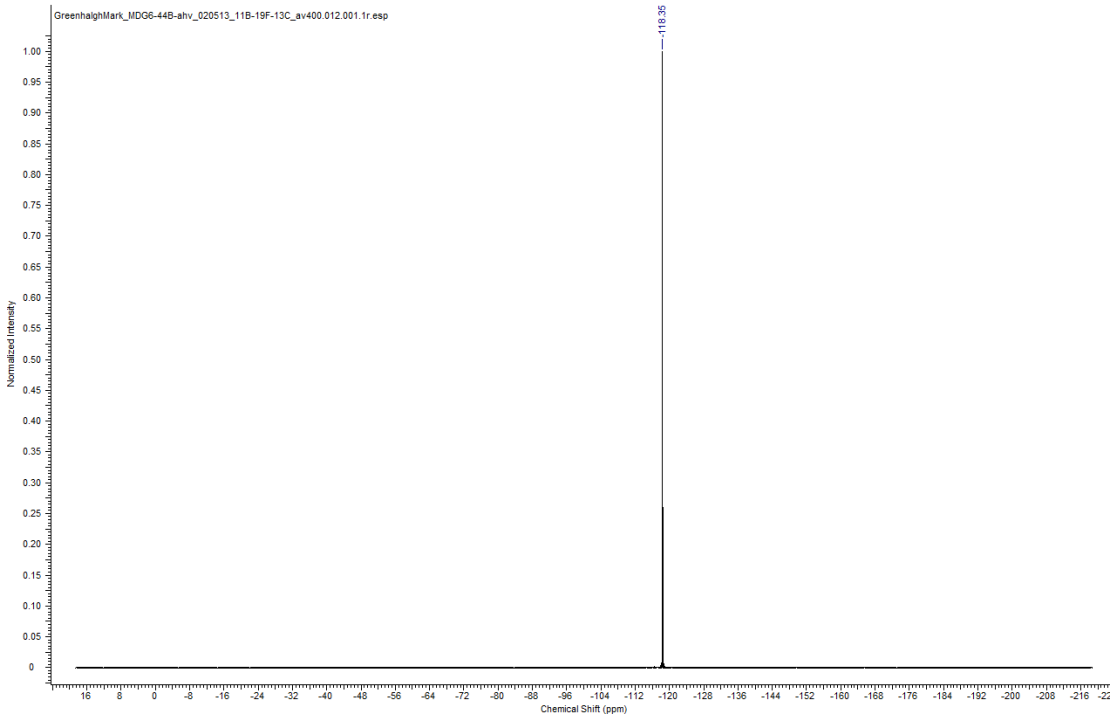
101 MHz



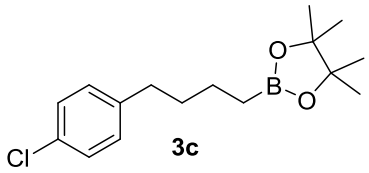
128 MHz



376 MHz

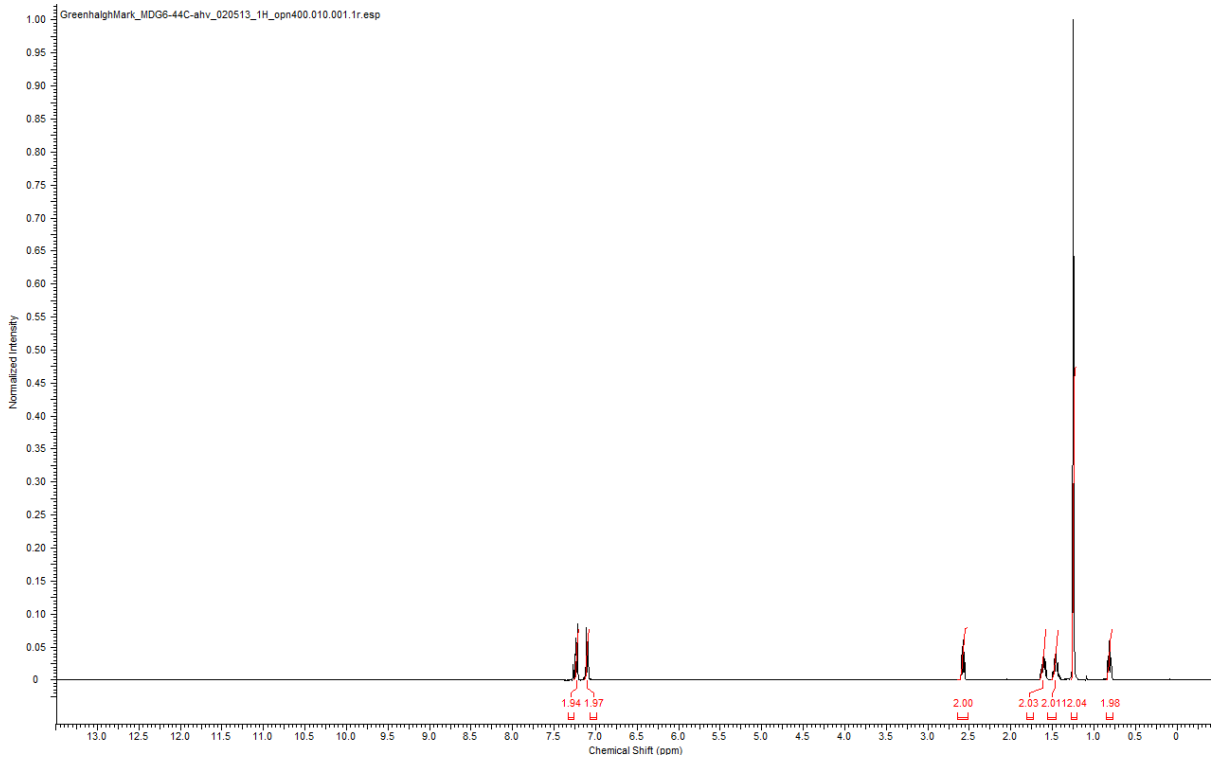


2-(4-(4-Chlorophenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3c

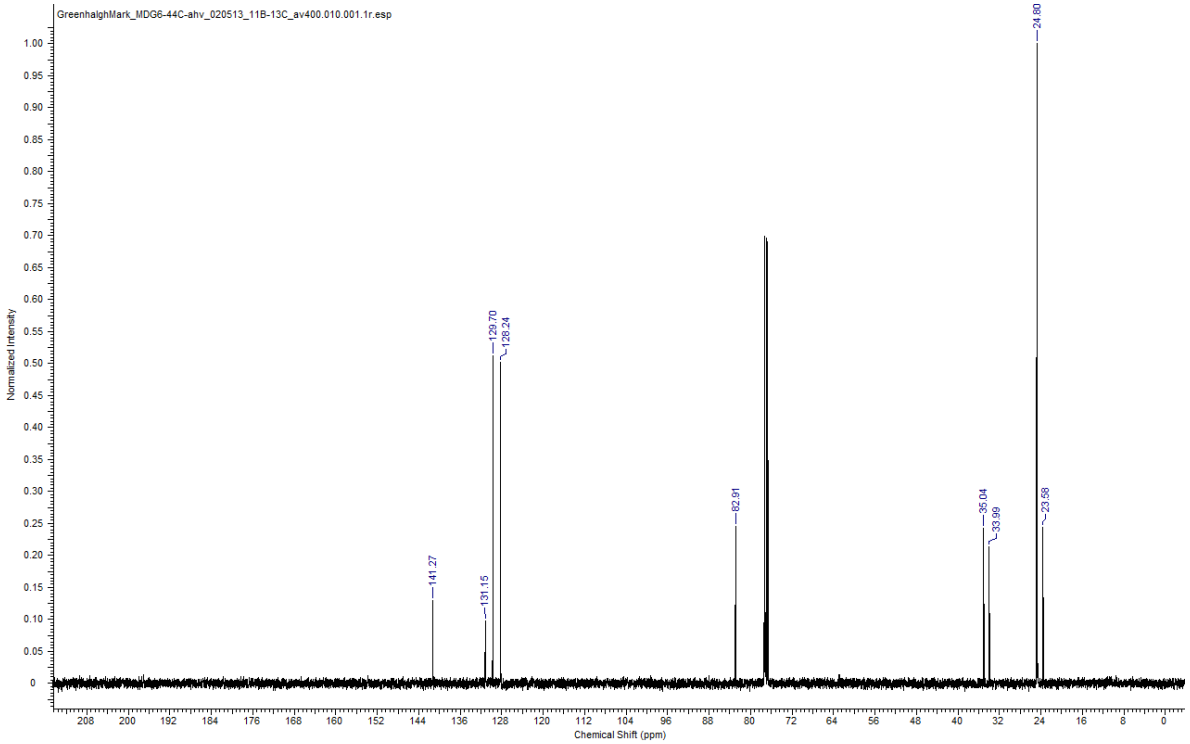


3c

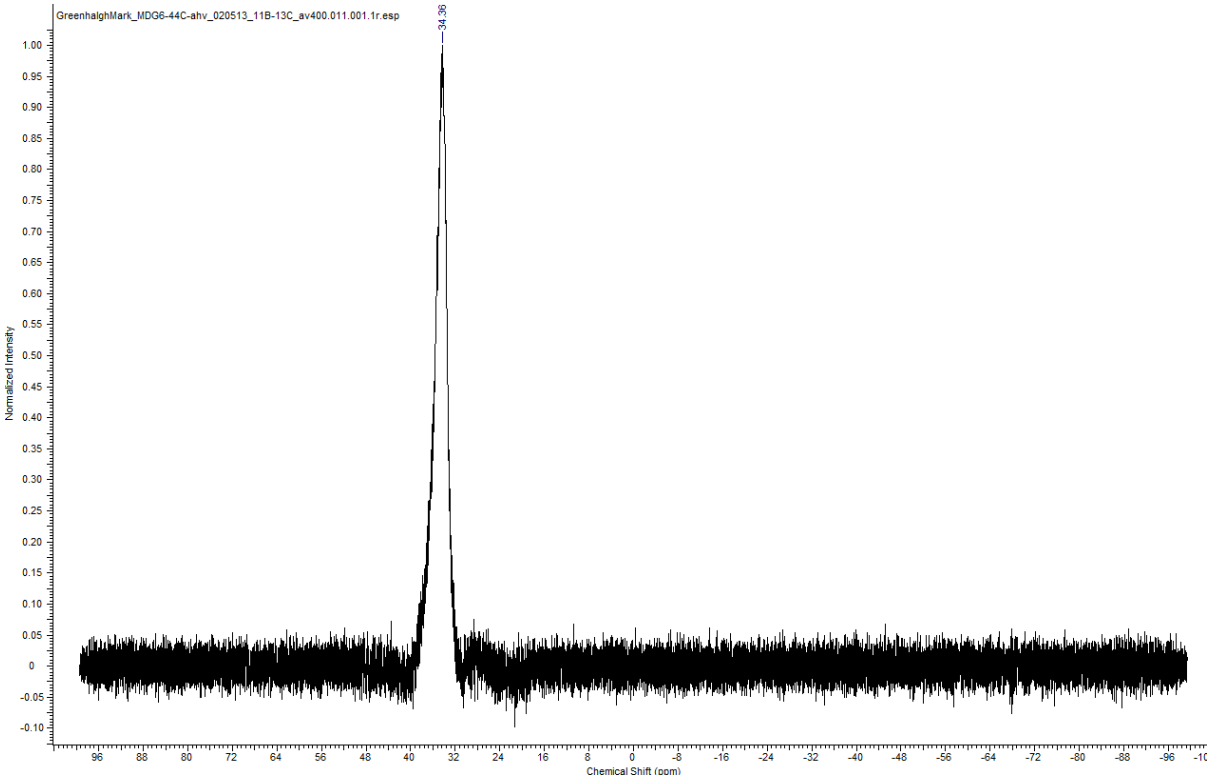
400 MHz



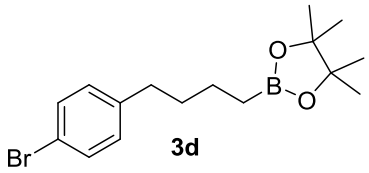
101 MHz



128 MHz

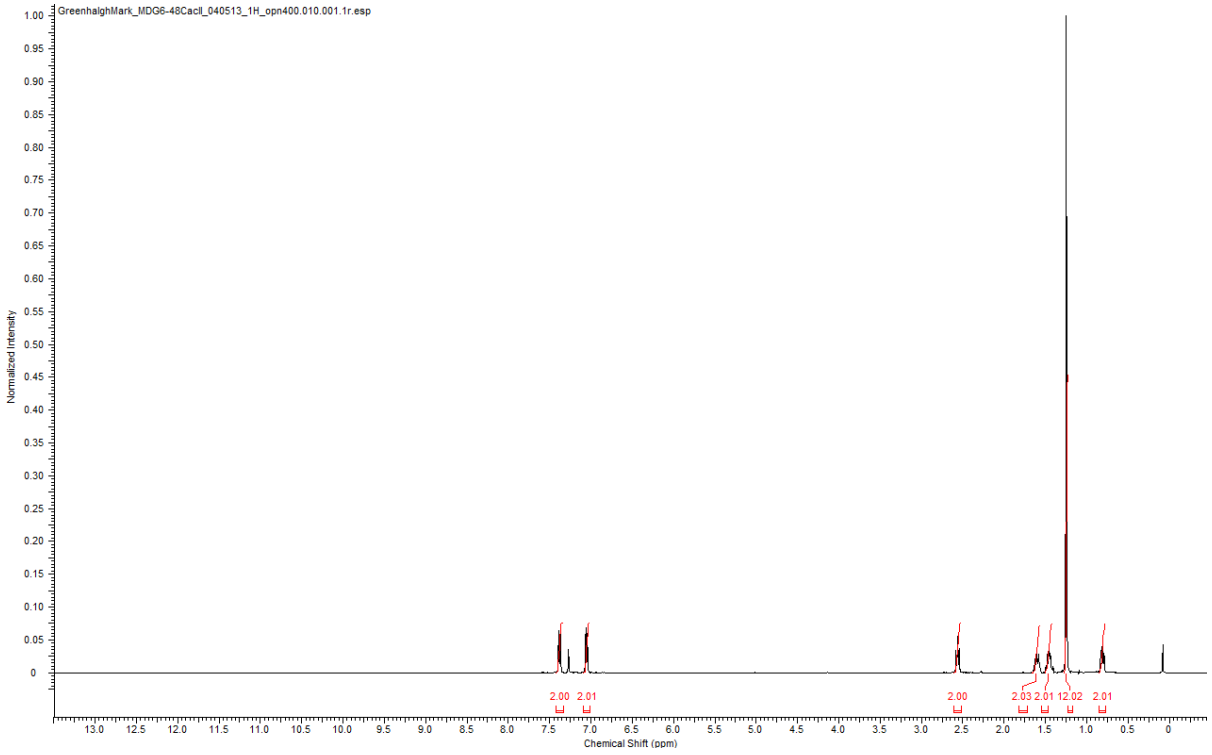


2-(4-(4-Bromophenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3d

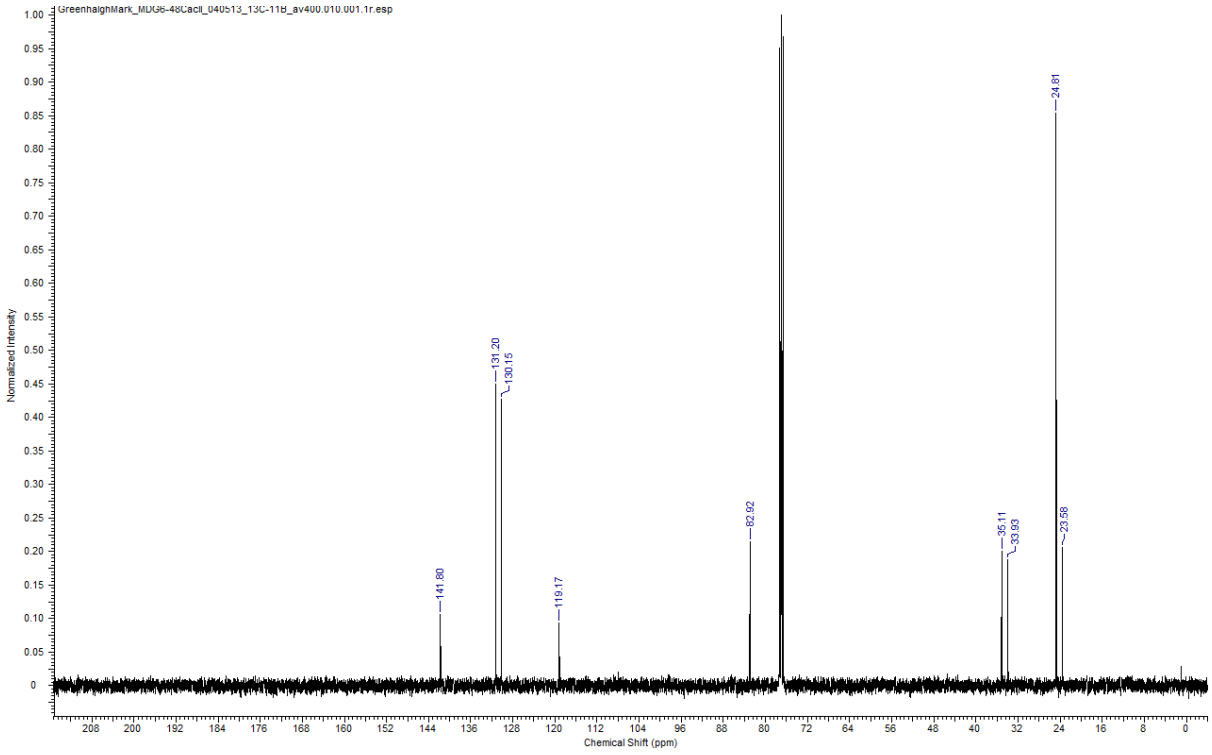


3d

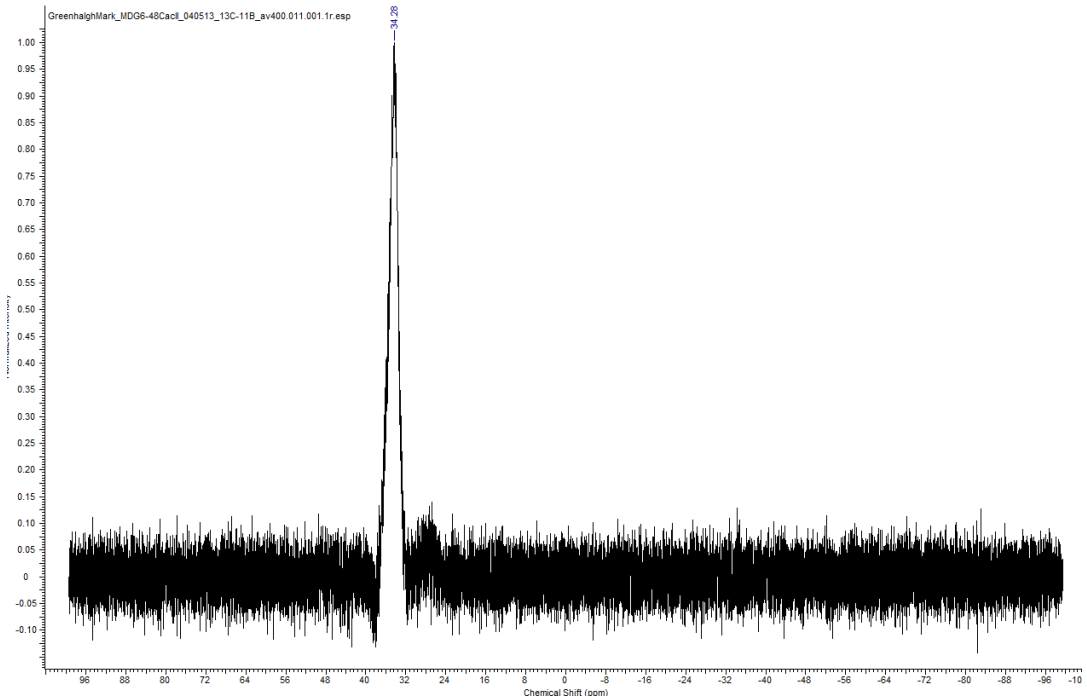
400 MHz



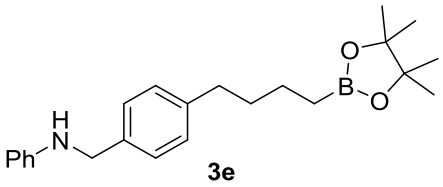
101 MHz



128 MHz

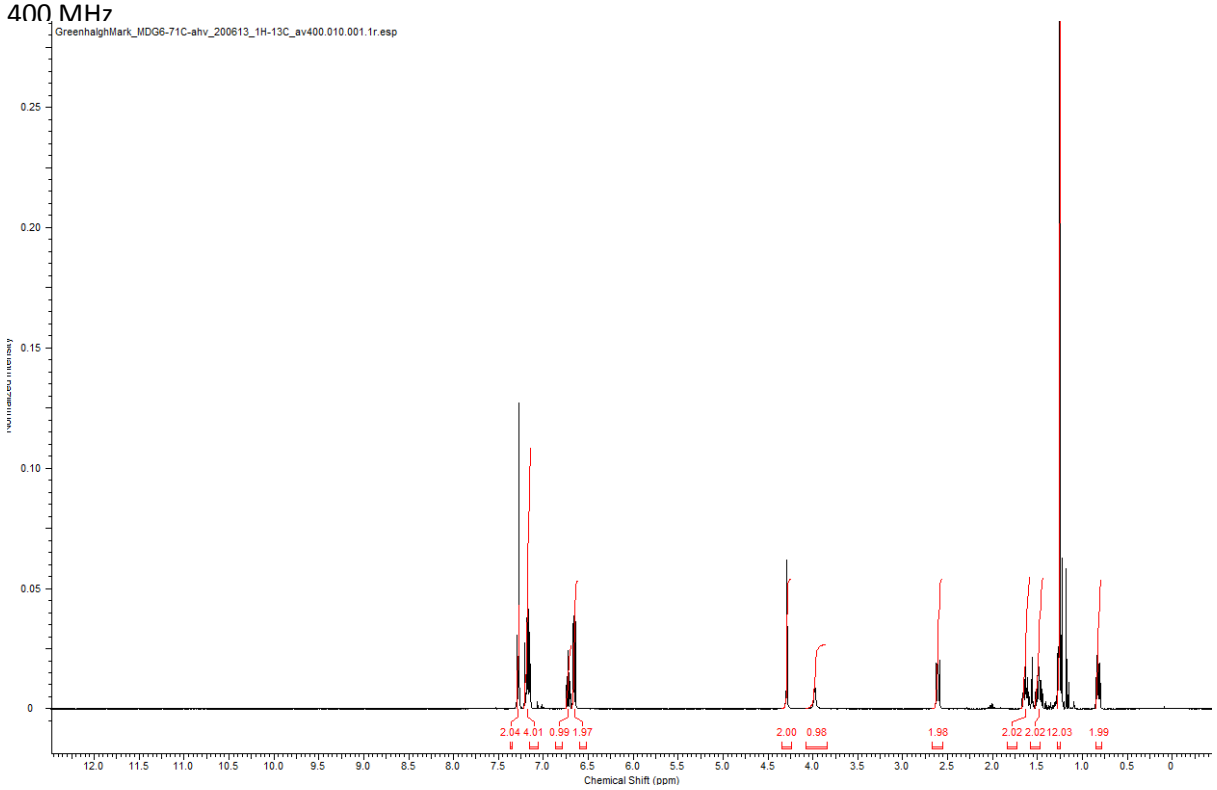


2-(4-(*N*-Phenylbenzylamine)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3e

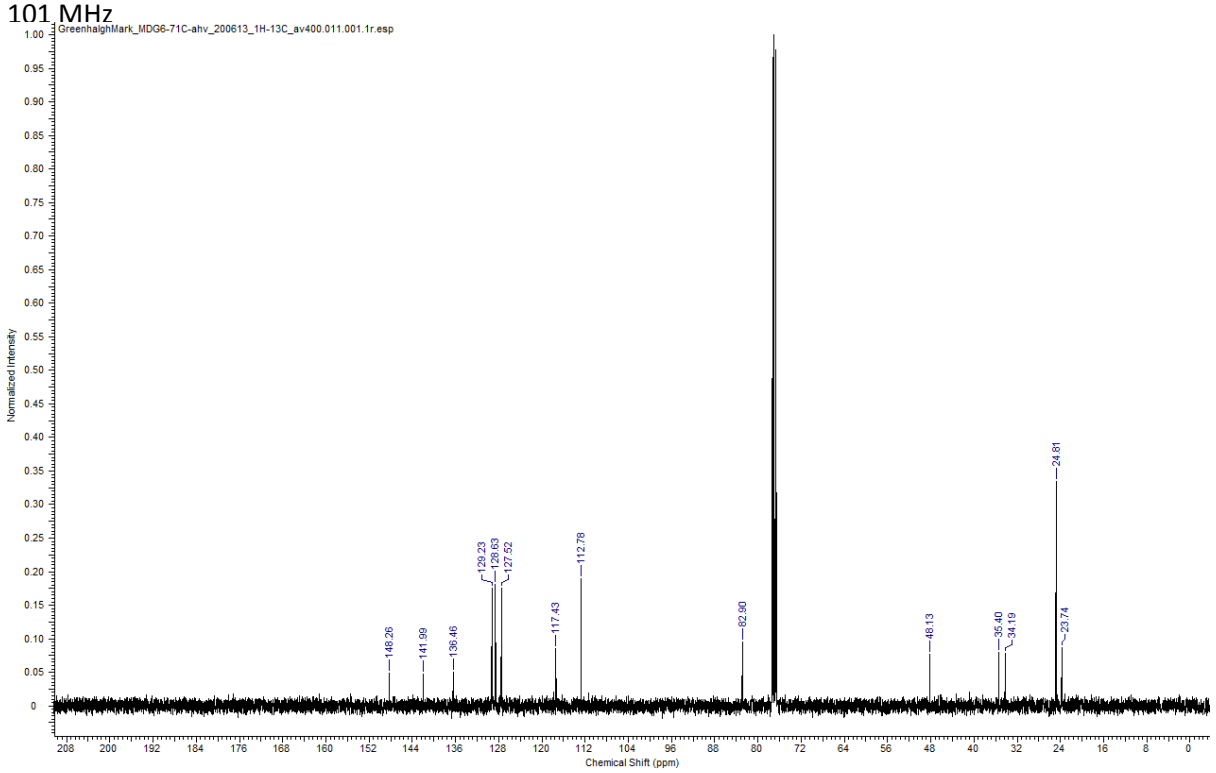


3e

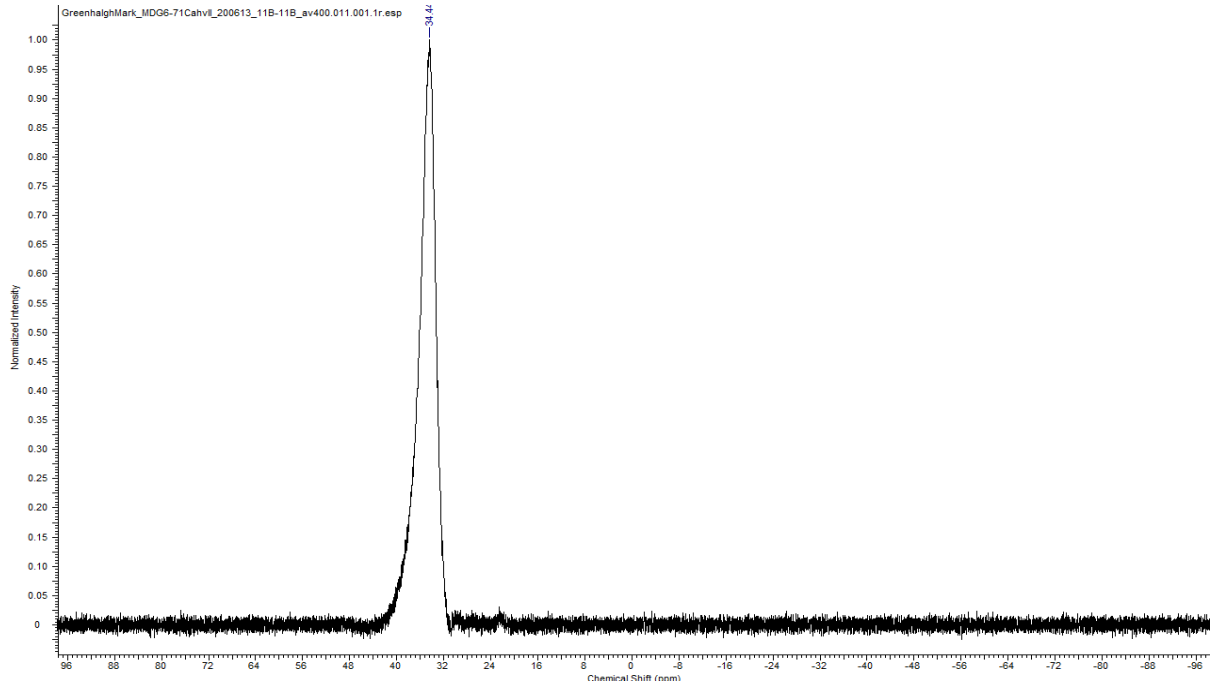
400 MHz



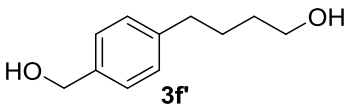
101 MHz



128 MHz

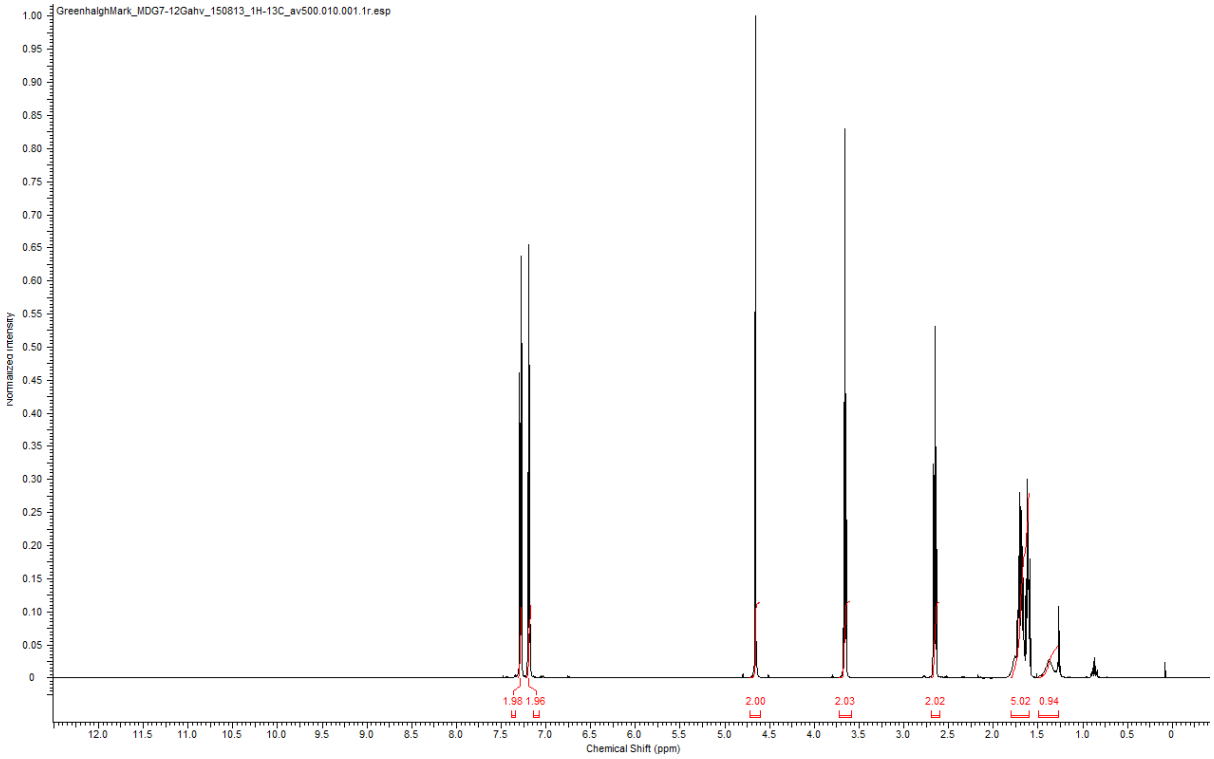


4-(4-Hydroxymethylphenyl)butan-1-ol 3f'

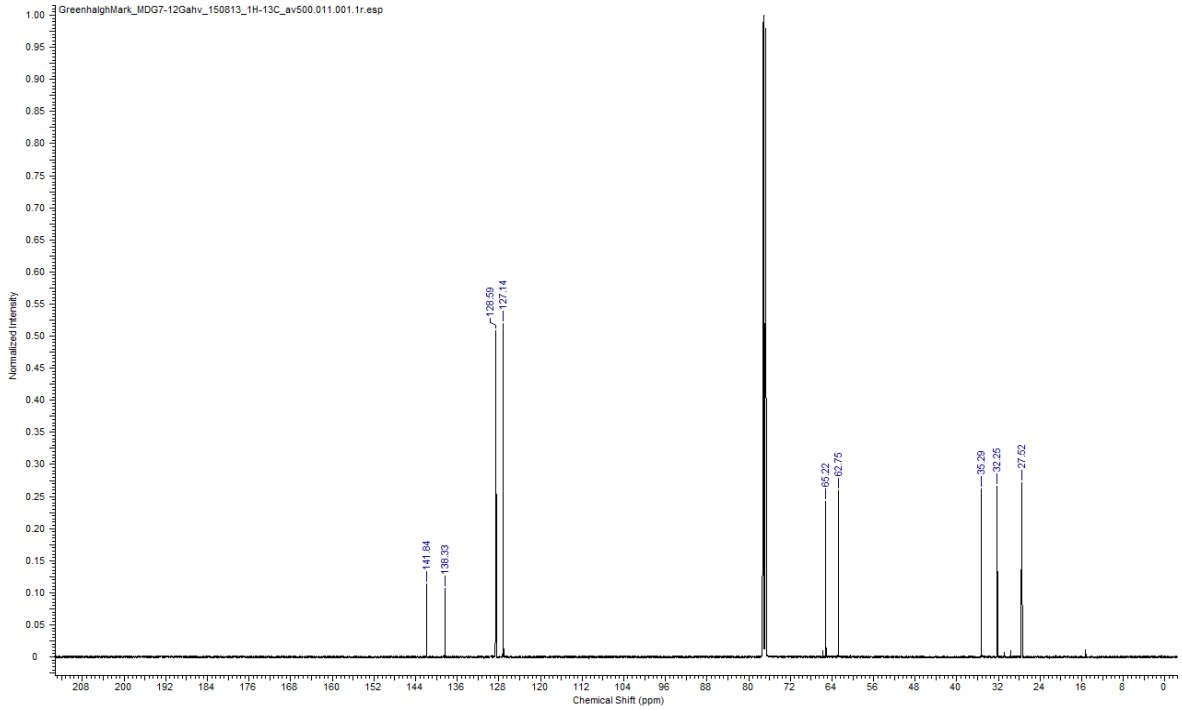


3f'

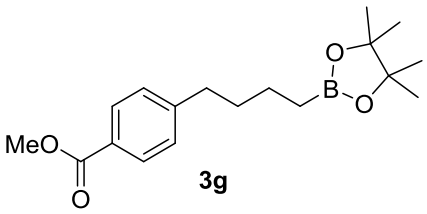
500 MHz



126 MHz

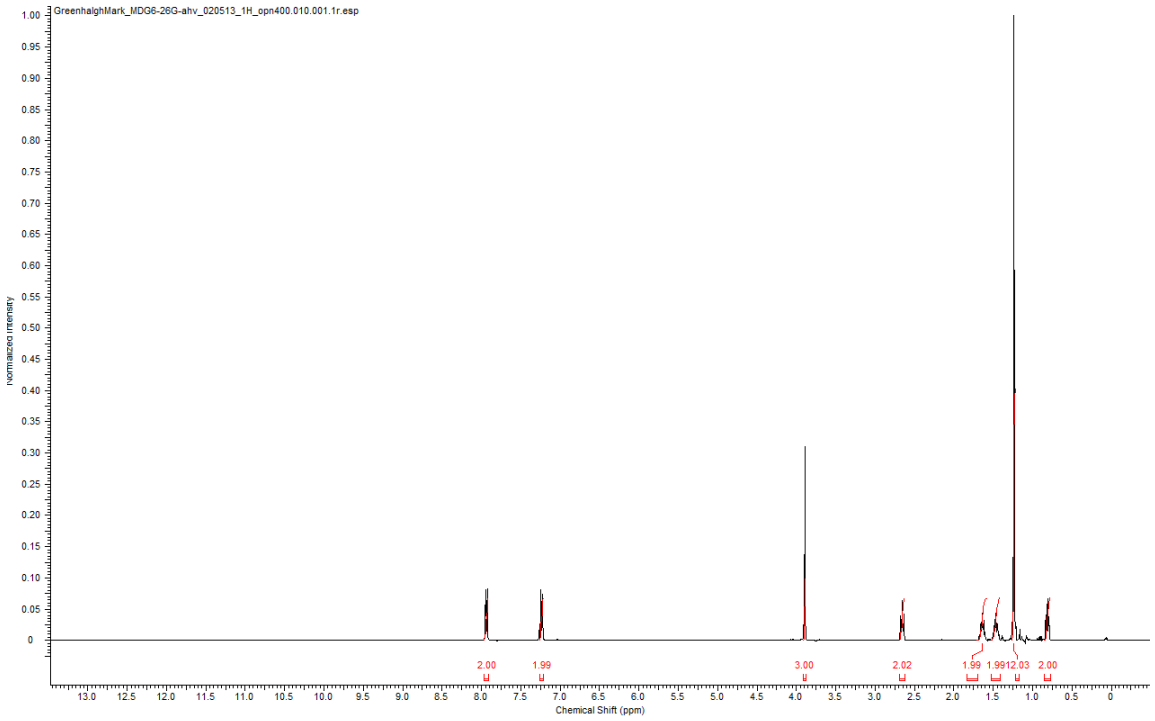


2-(4-(4-Methylbenzoate)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3g

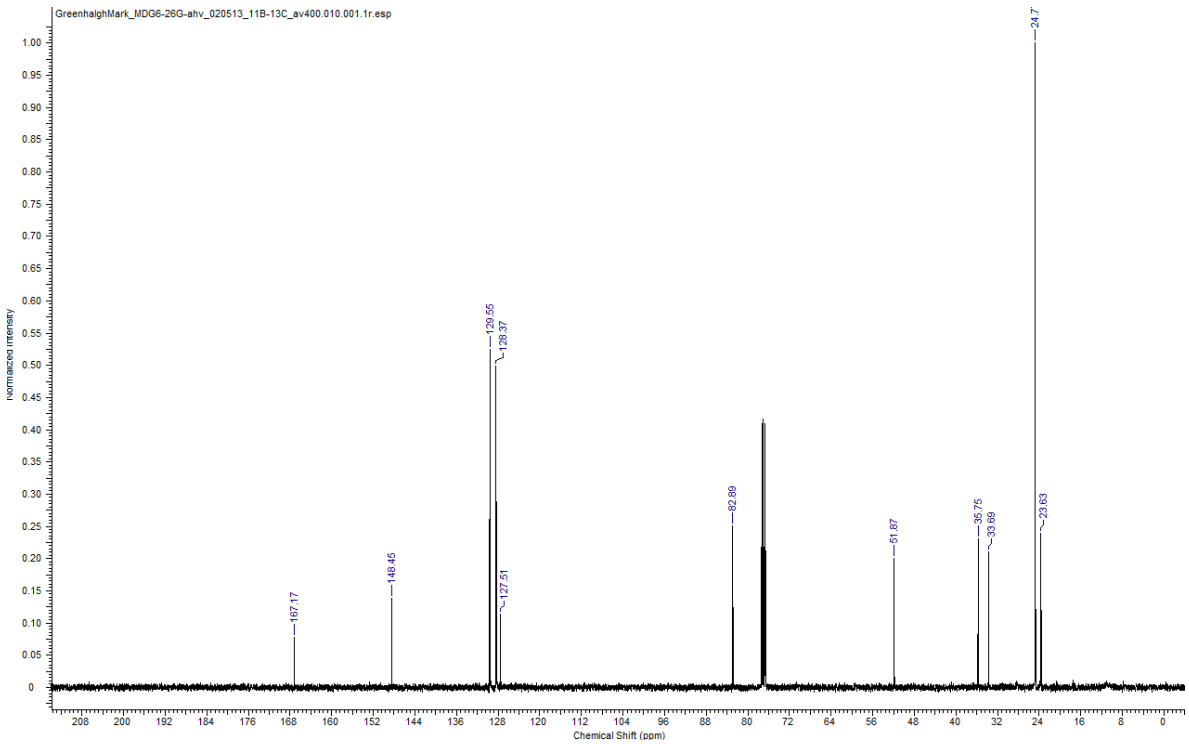


3g

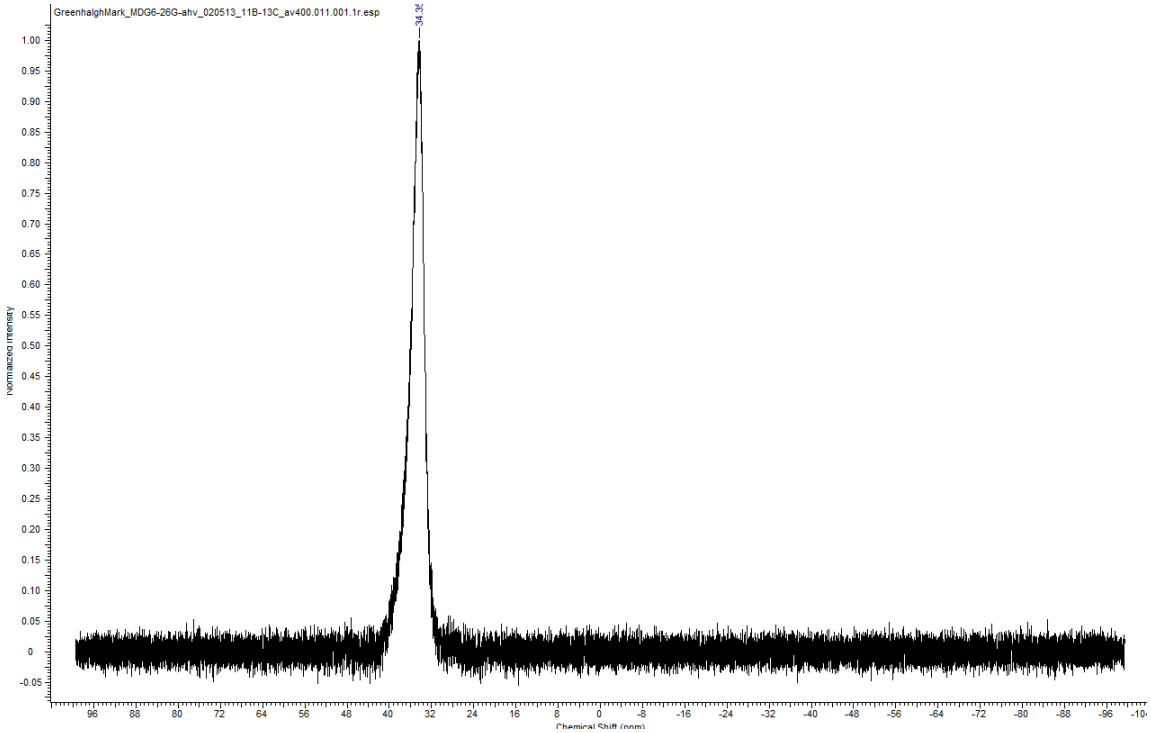
400 MHz



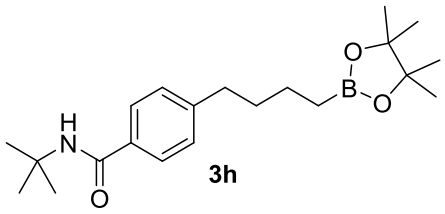
101 MHz



128 MHz

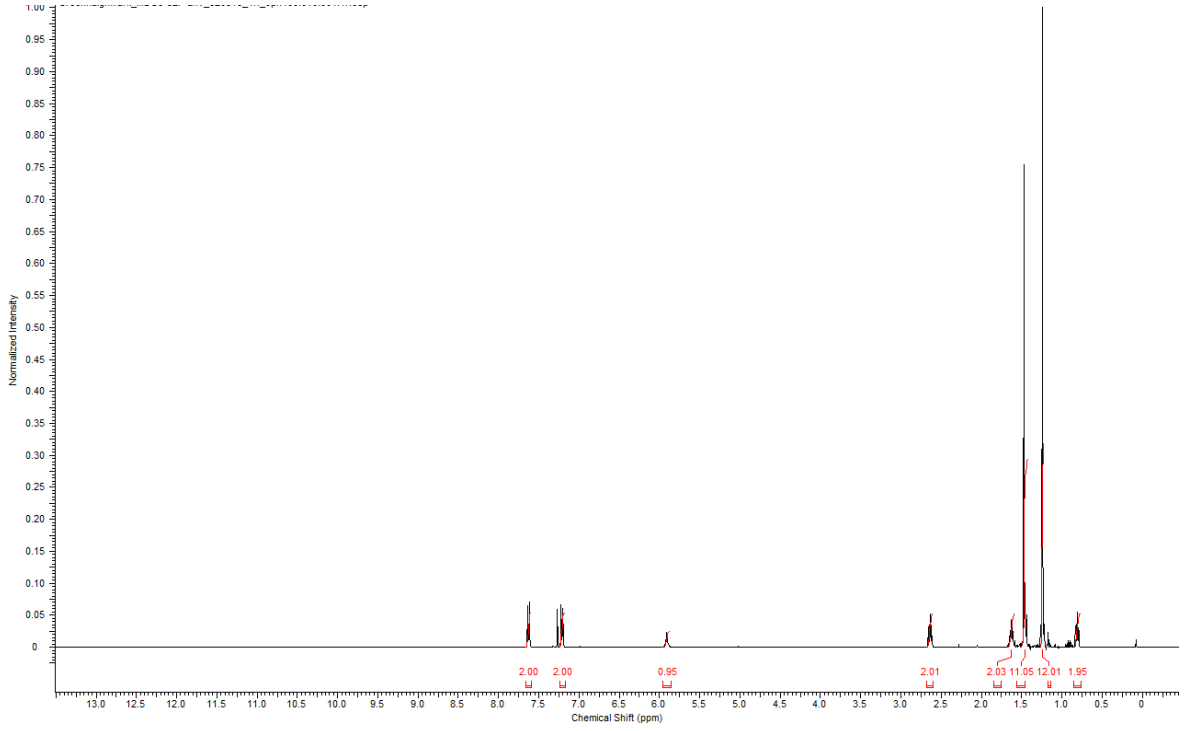


2-(4-(4-*N*-*tert*-Butylbenzamide)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3h

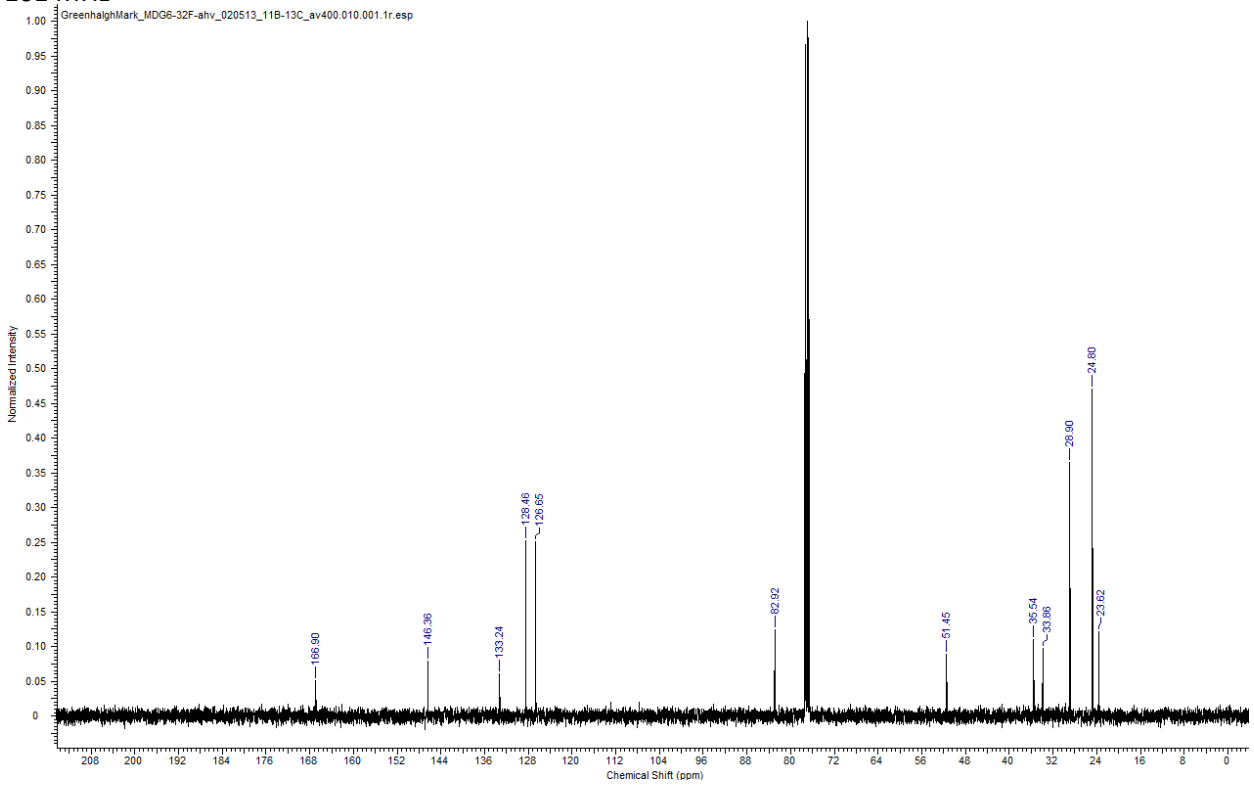


3h

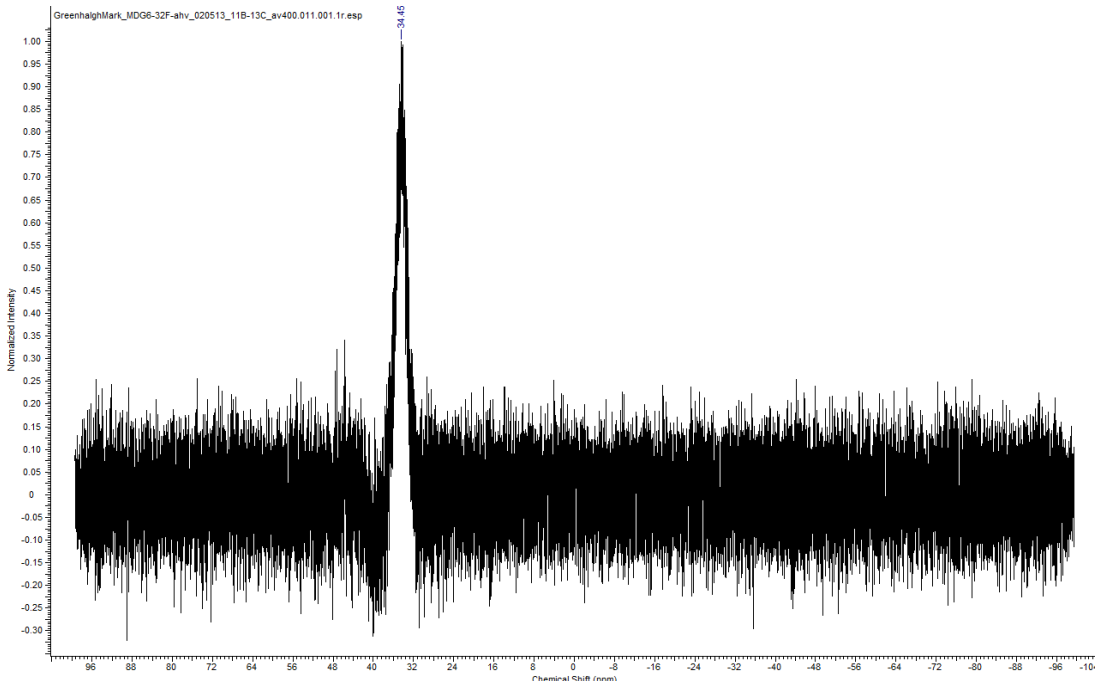
400 MHz



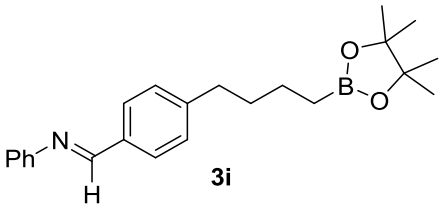
101 MHz



128 MHz

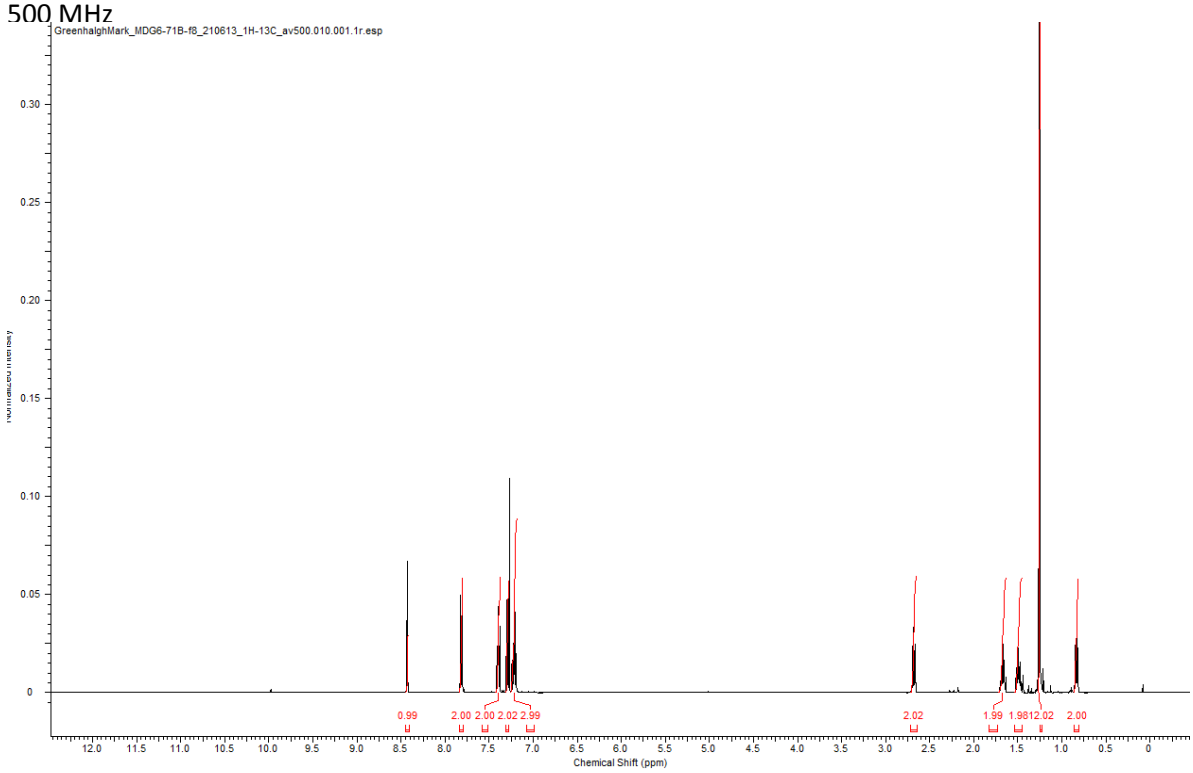


2-(4-(*N*-Phenylbenzaldimine)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3i

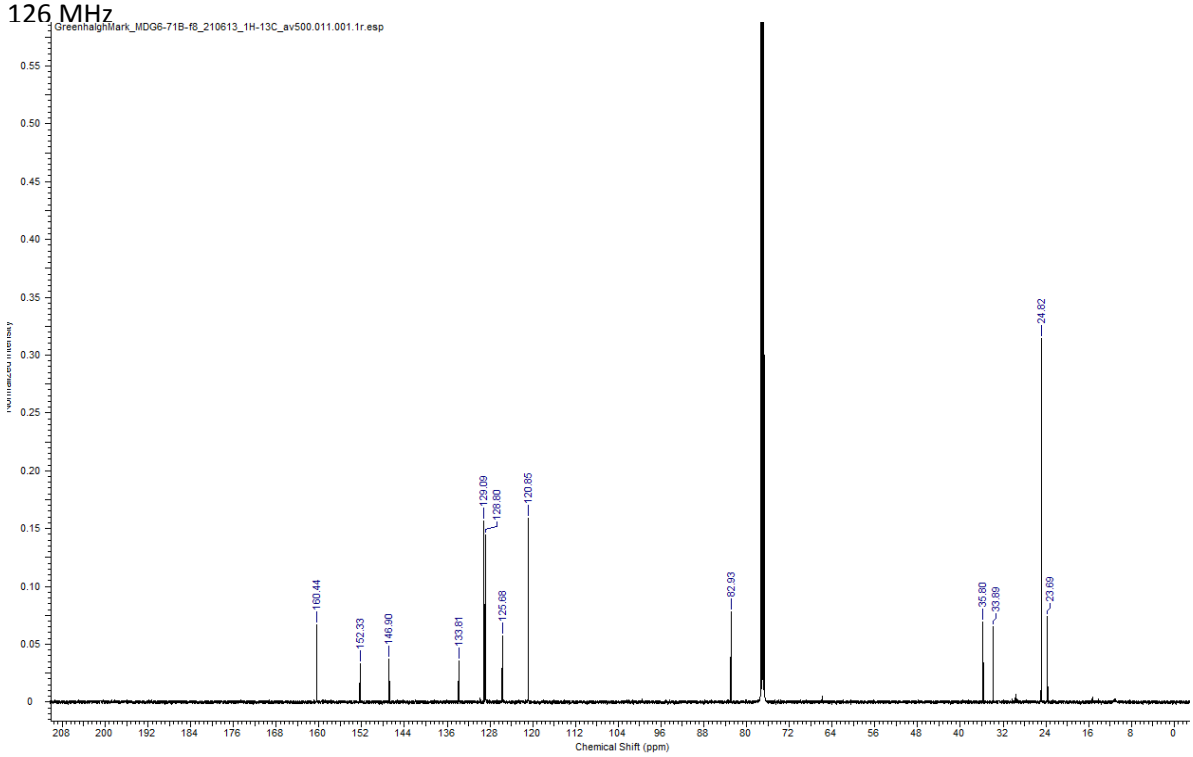


3i

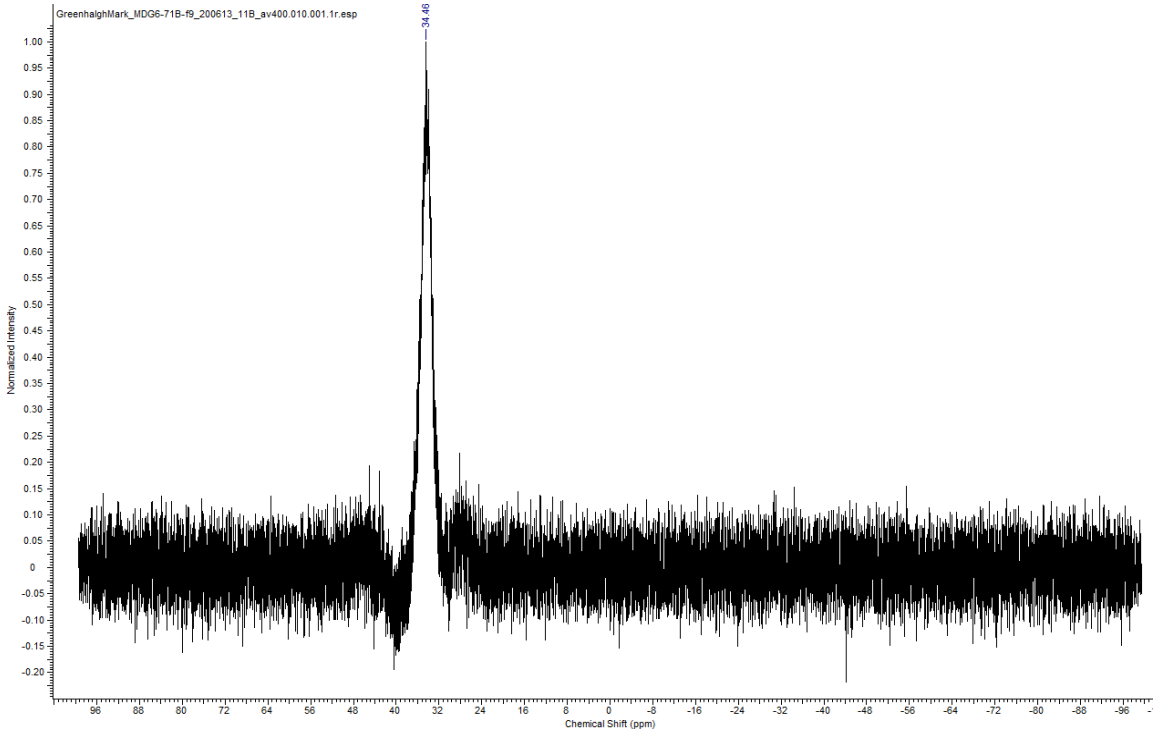
500 MHz



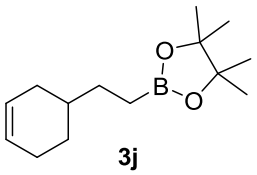
126 MHz



128 MHz

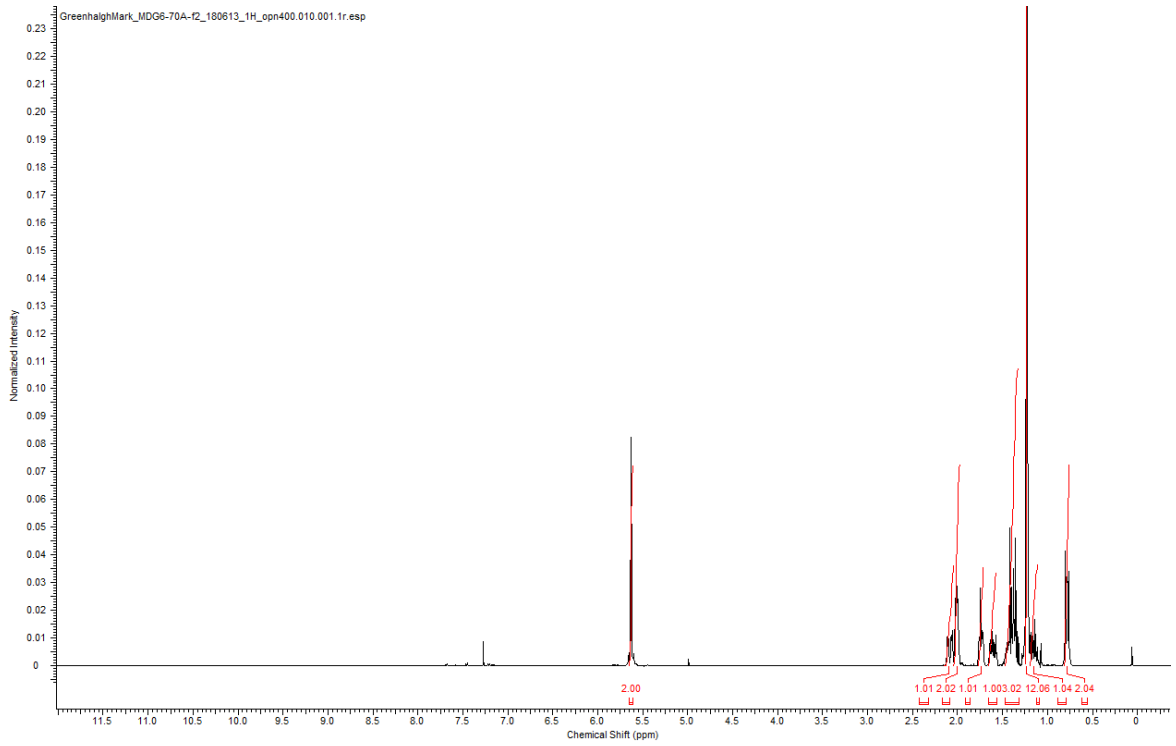


2-(2-(Cyclohex-3-en-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3j

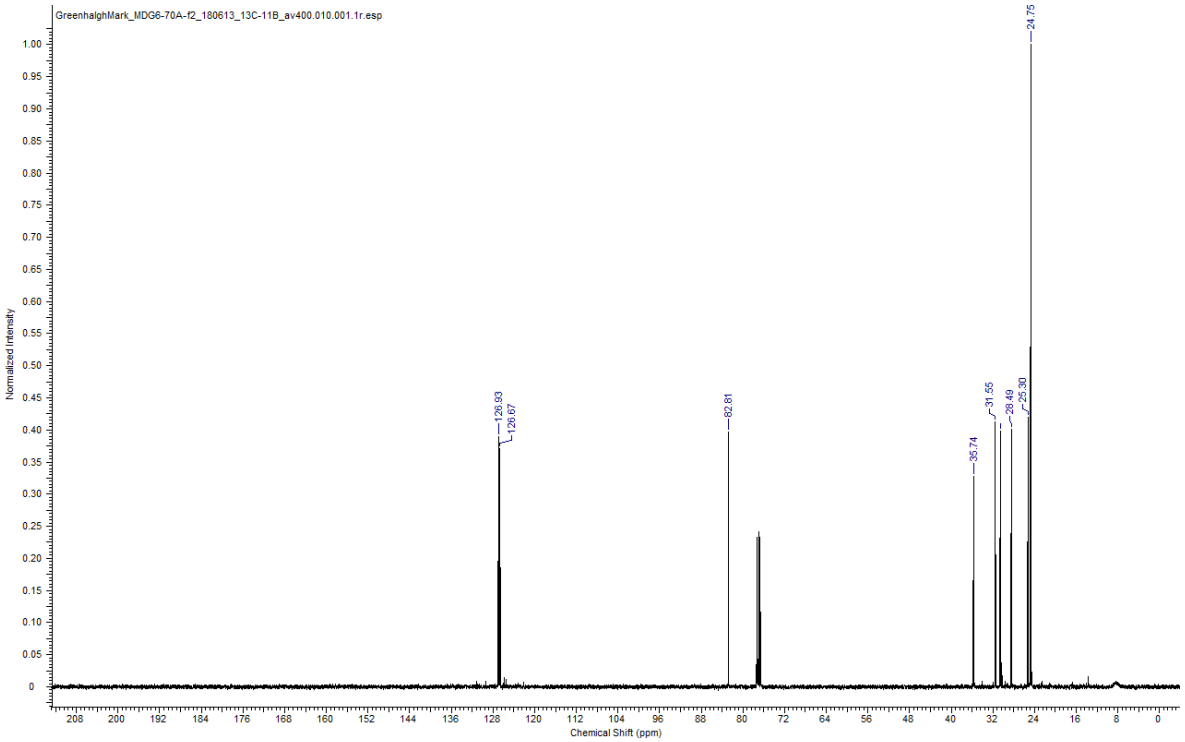


3j

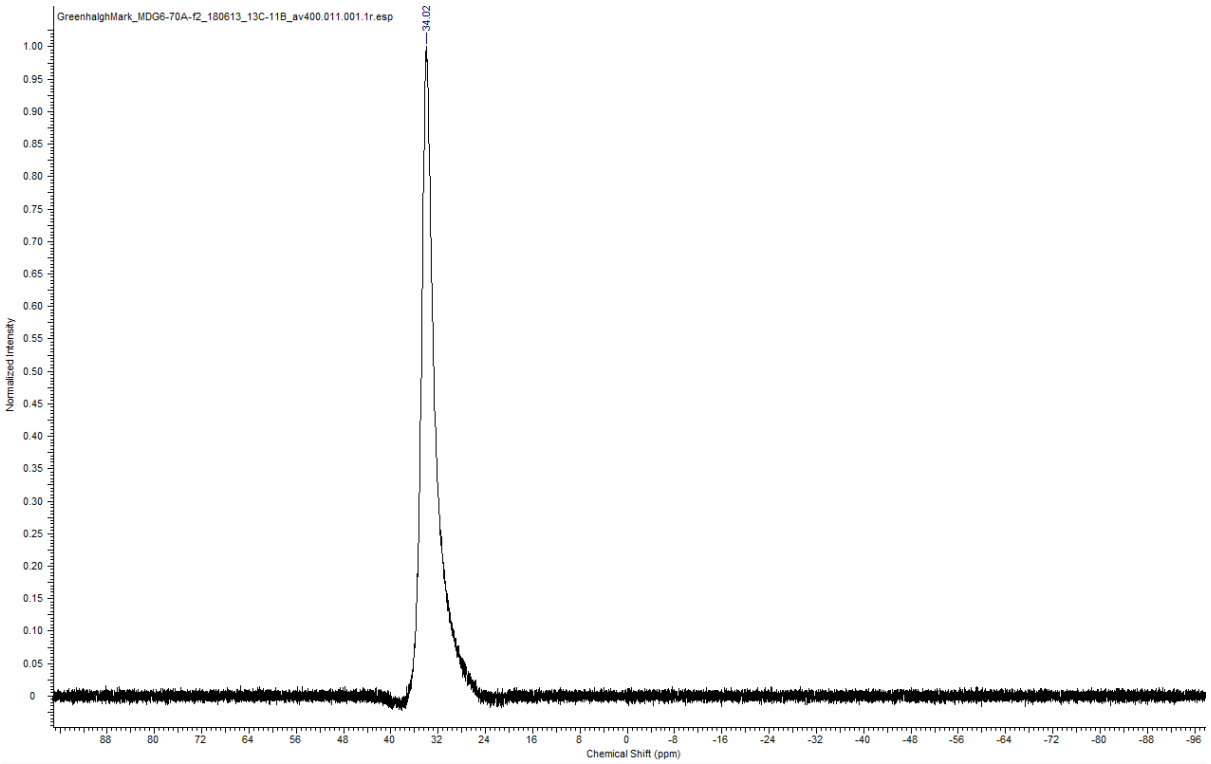
400 MHz



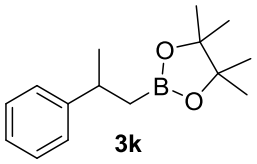
101 MHz



128 MHz

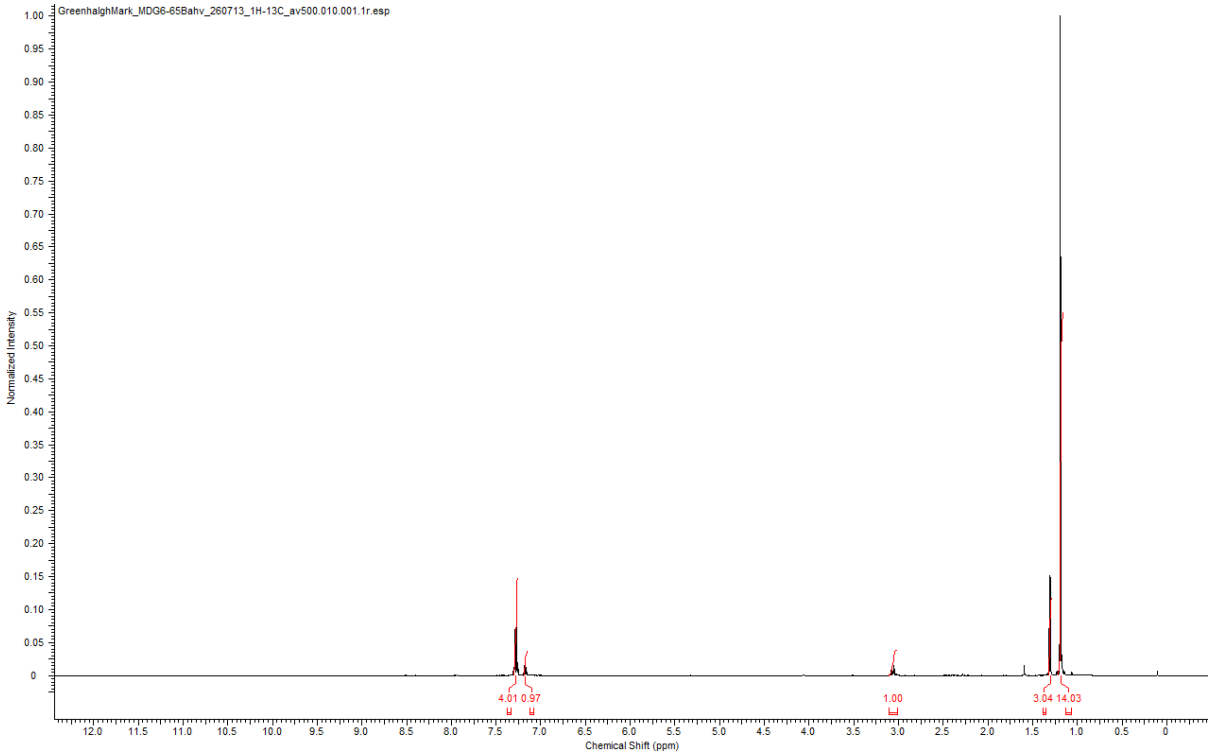


2-(2-Phenyl-2-methylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3k

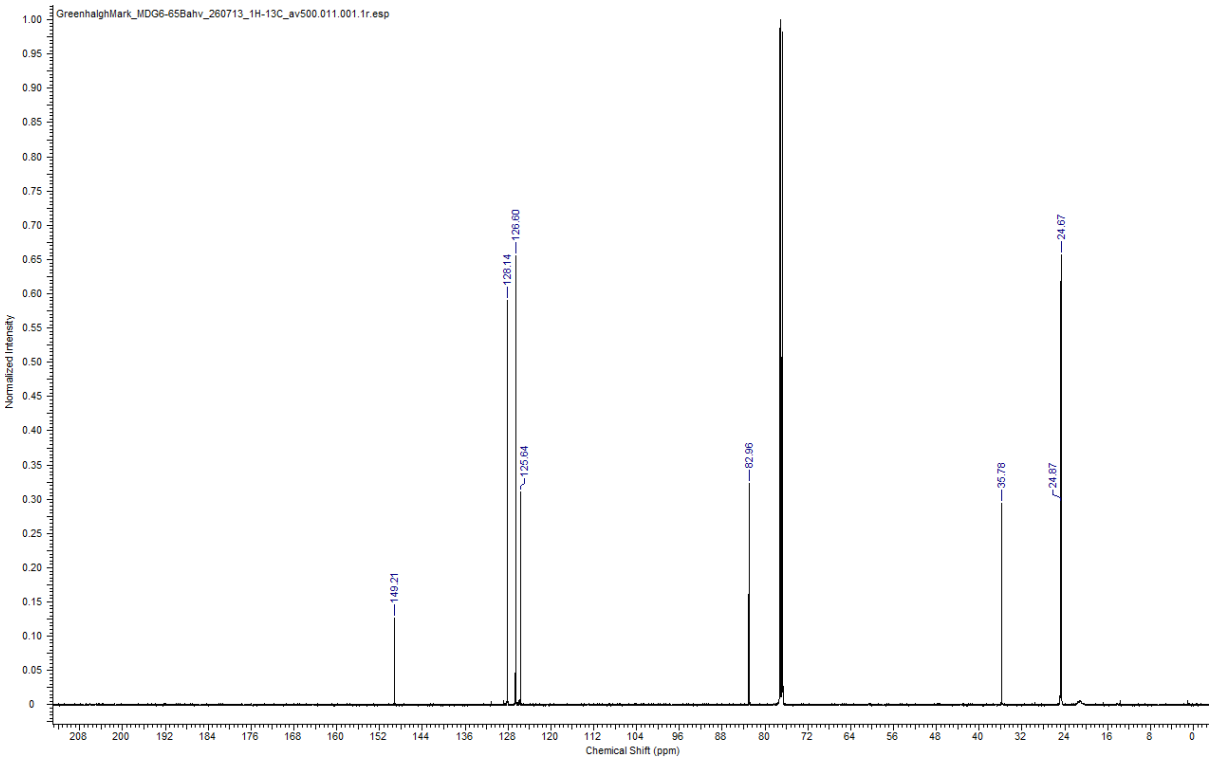


3k

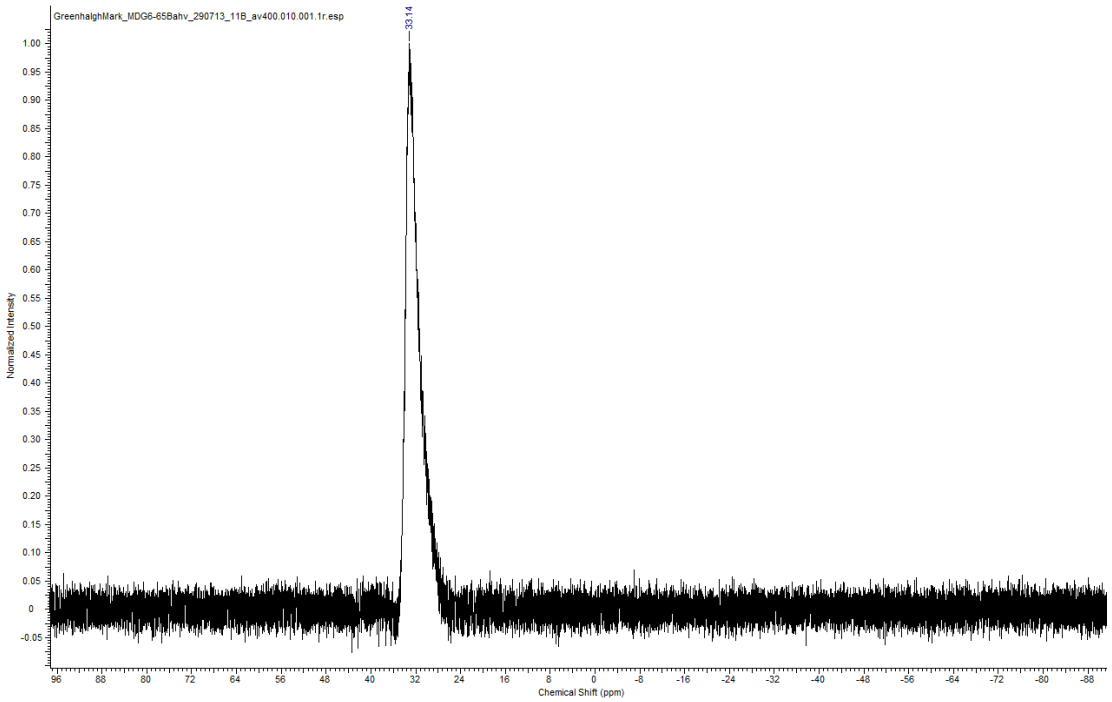
500 MHz



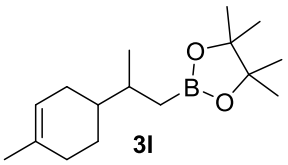
126 MHz



128 MHz

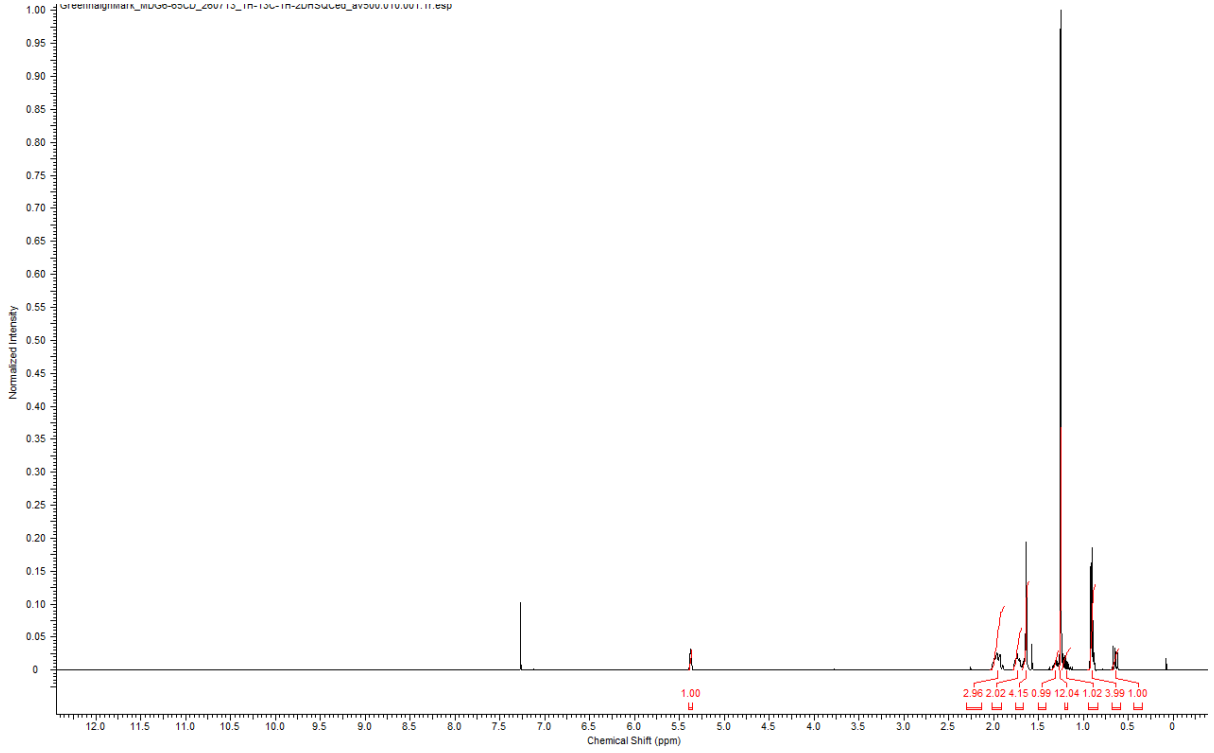


2-(2-((*R*)-4-Methylcyclohex-3-en-1-yl)-propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3l (1:1 mixture of diastereoisomers)

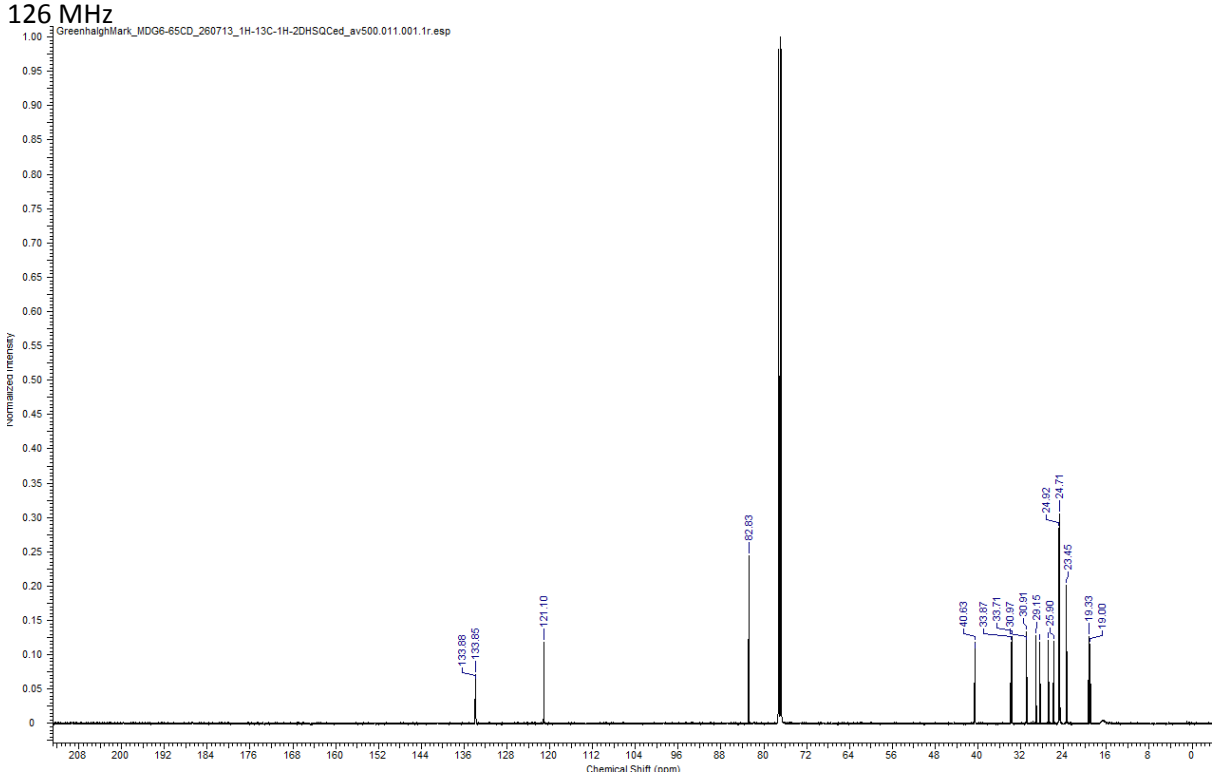


3l

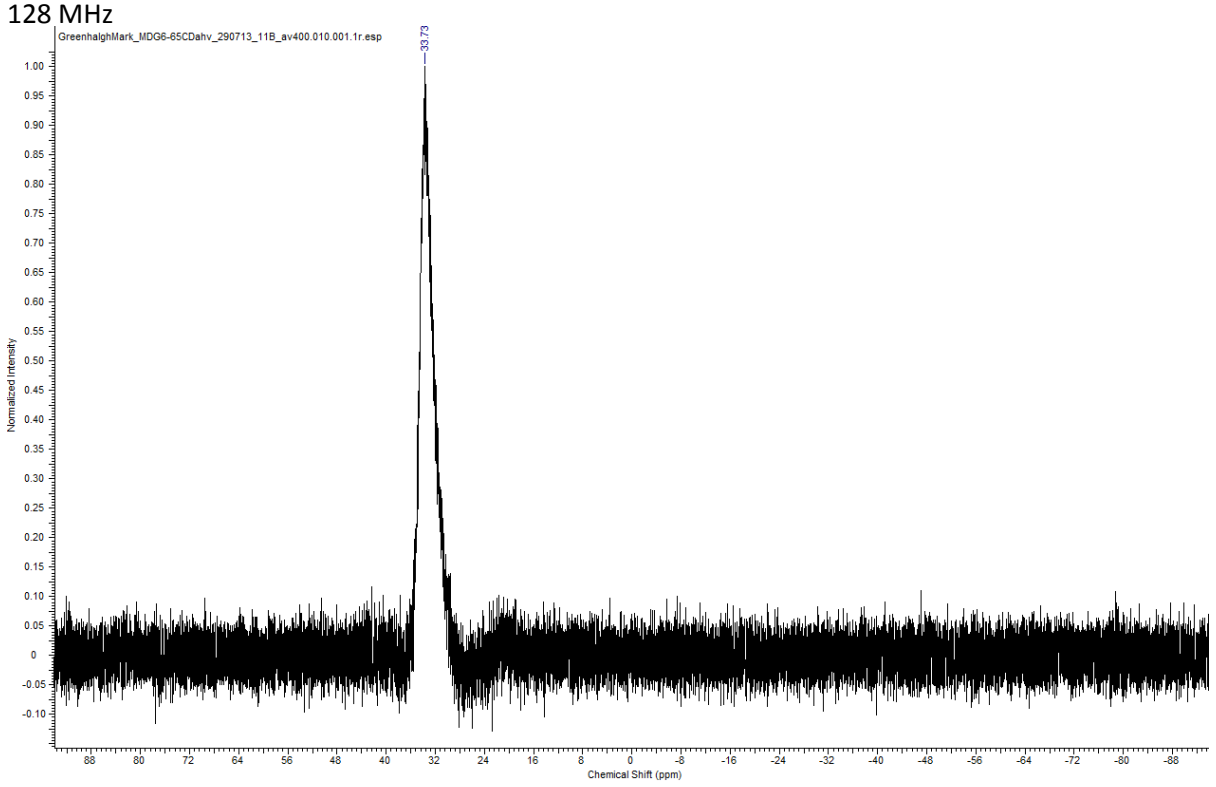
500 MHz



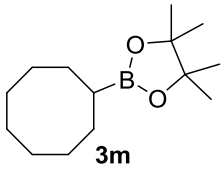
126 MHz



128 MHz

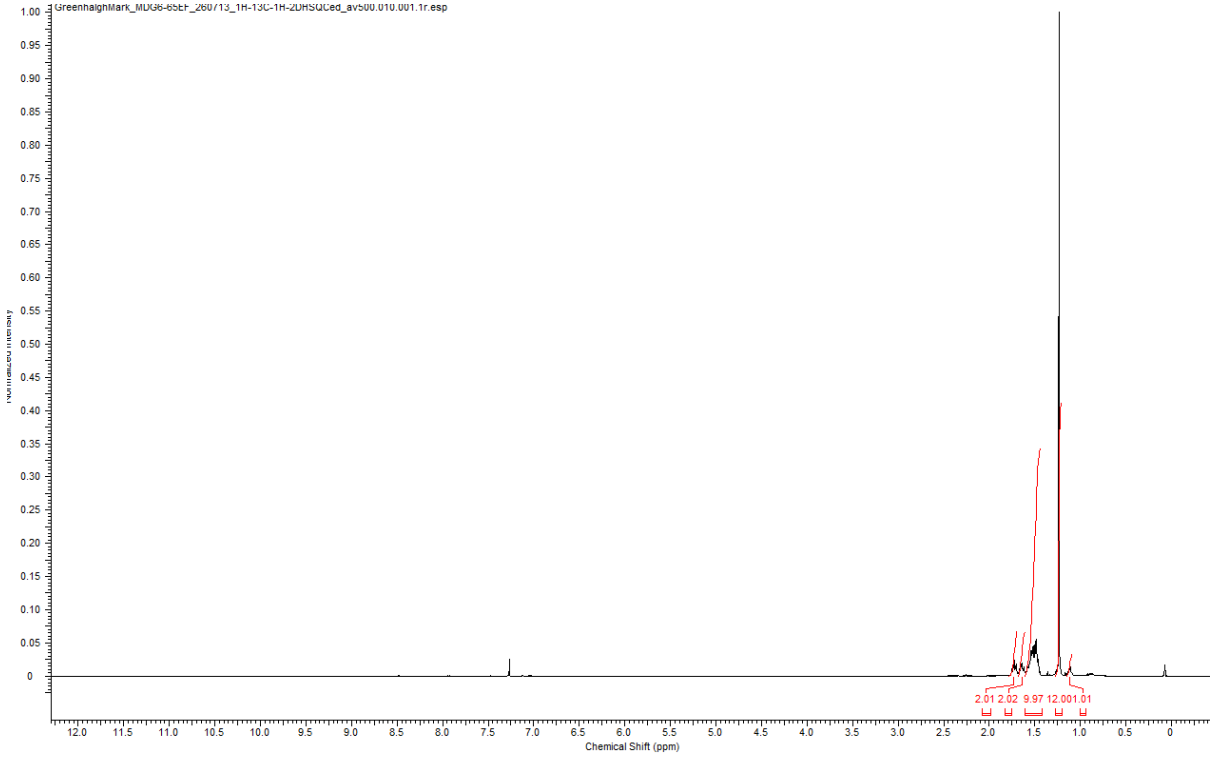


2-Cyclooctyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3m

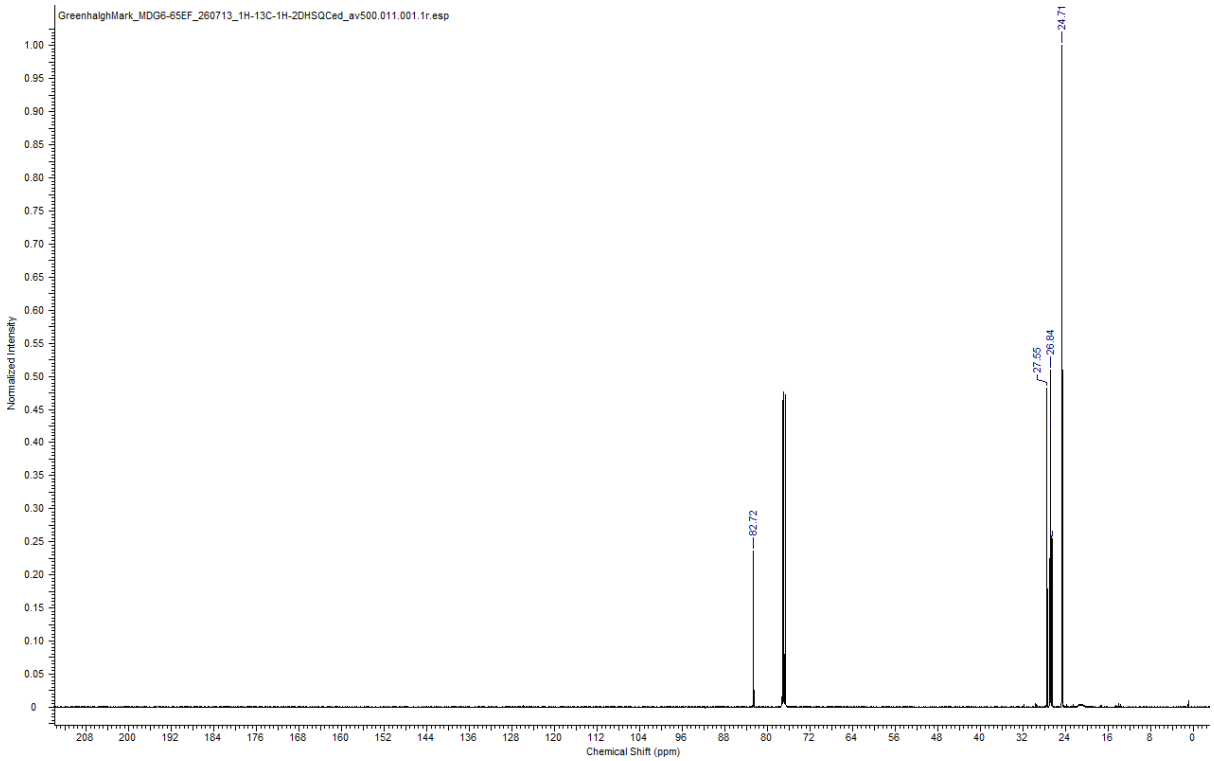


3m

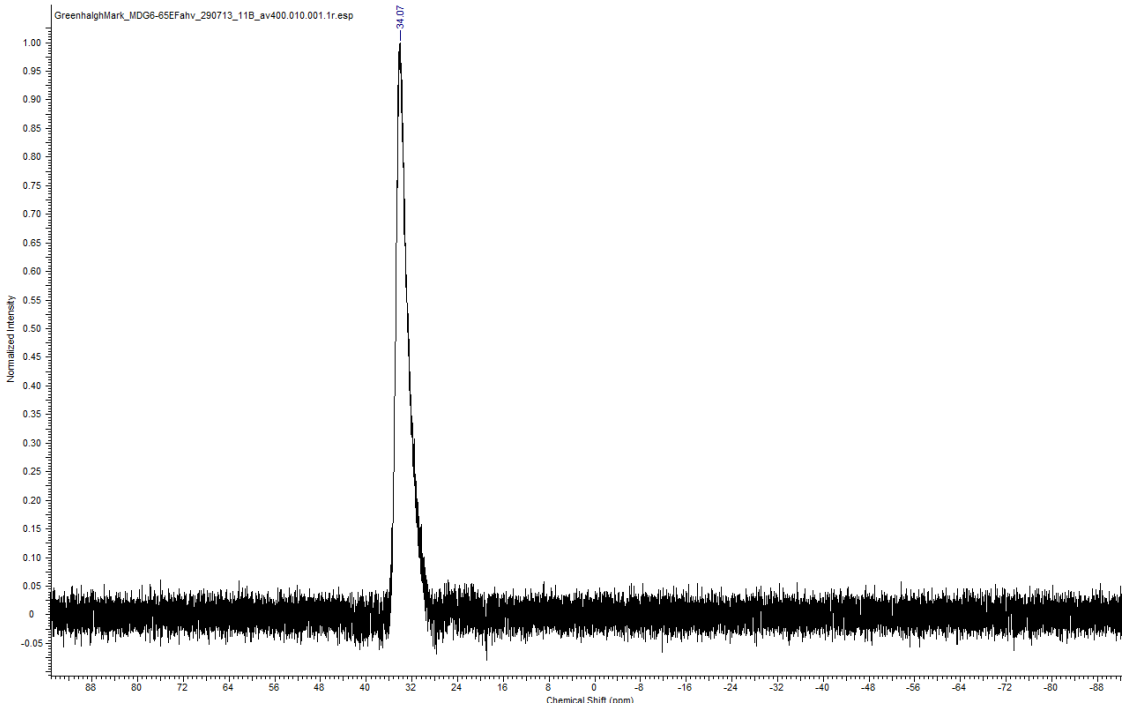
500 MHz



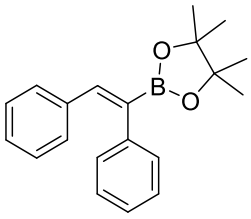
126 MHz



128 MHz

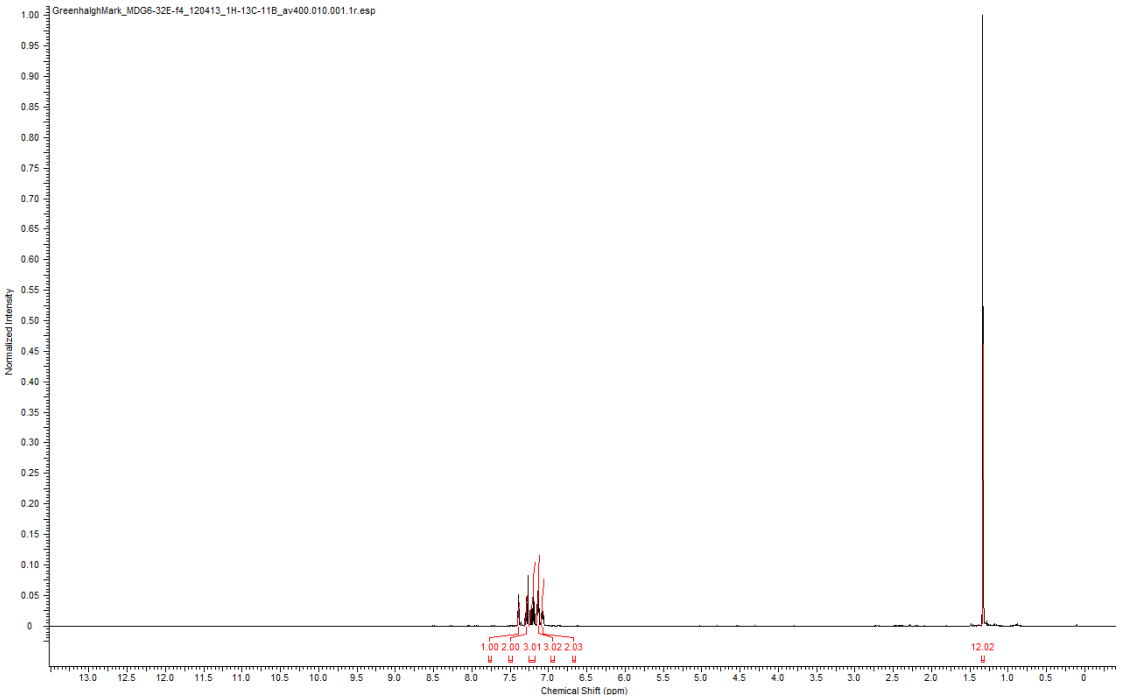


(*Z*)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5a

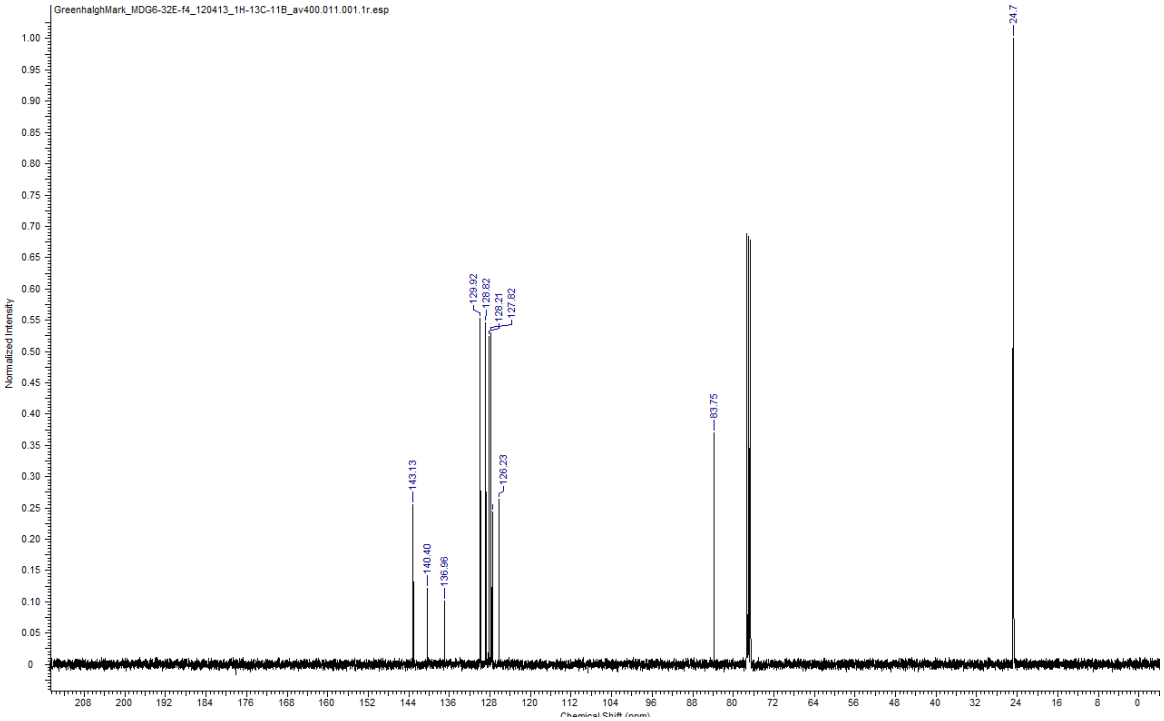


5a

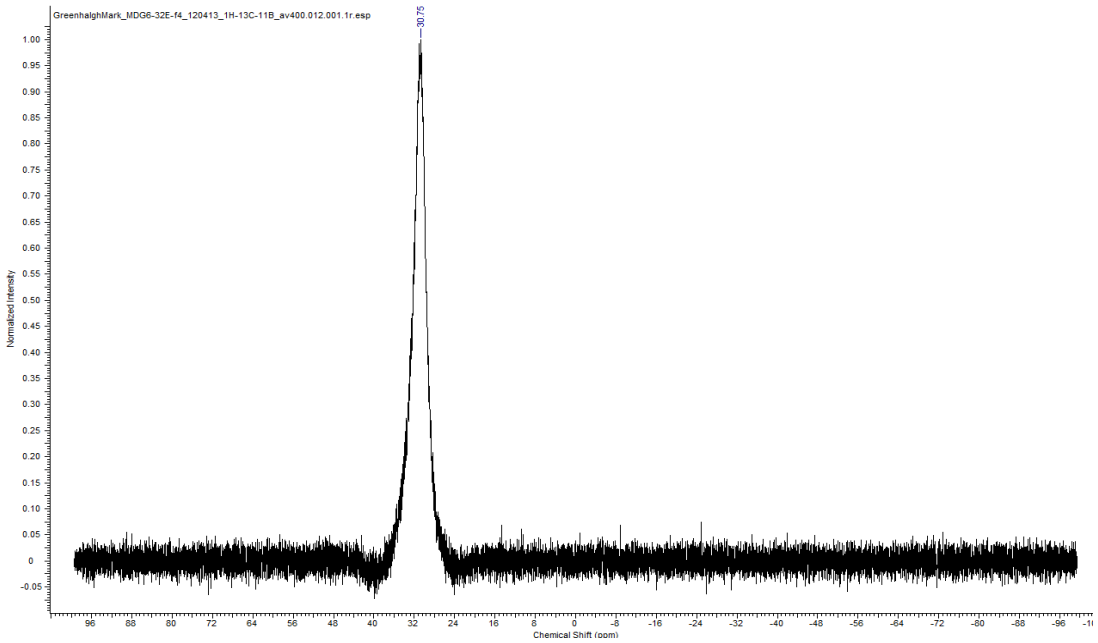
400 MHz



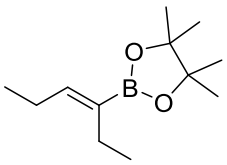
101 MHz



128 MHz

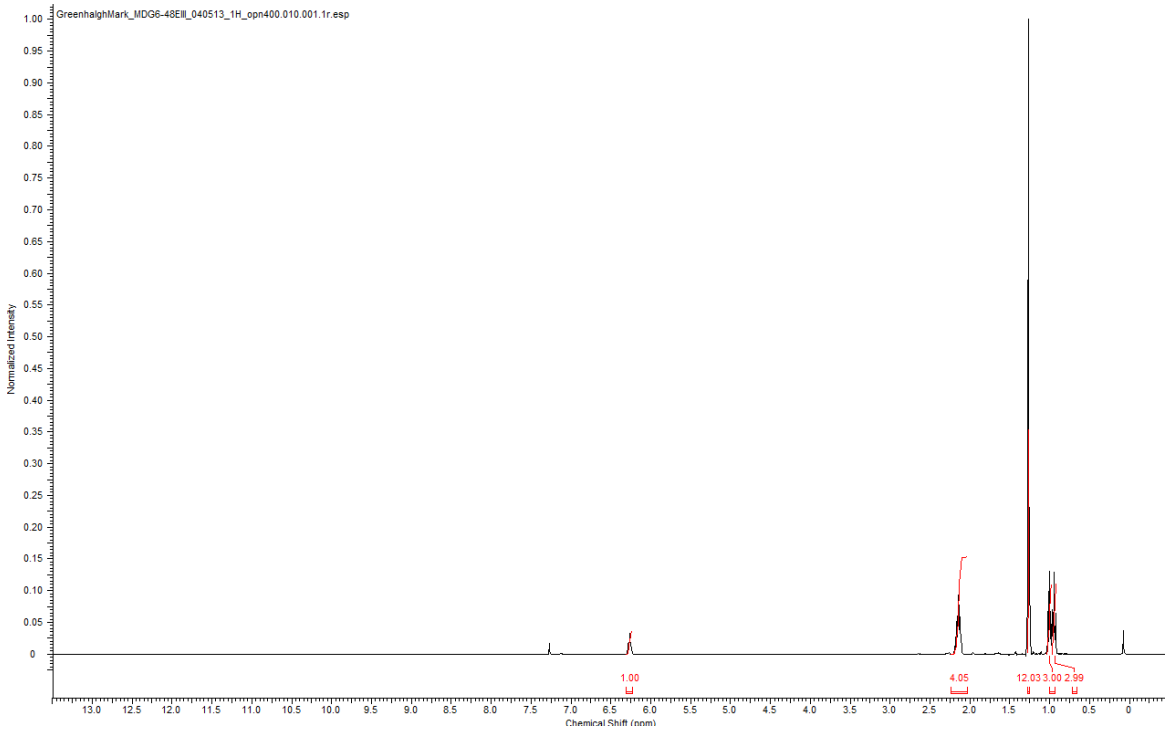


(*Z*)-2-(1-Ethyl-1-buten-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5b

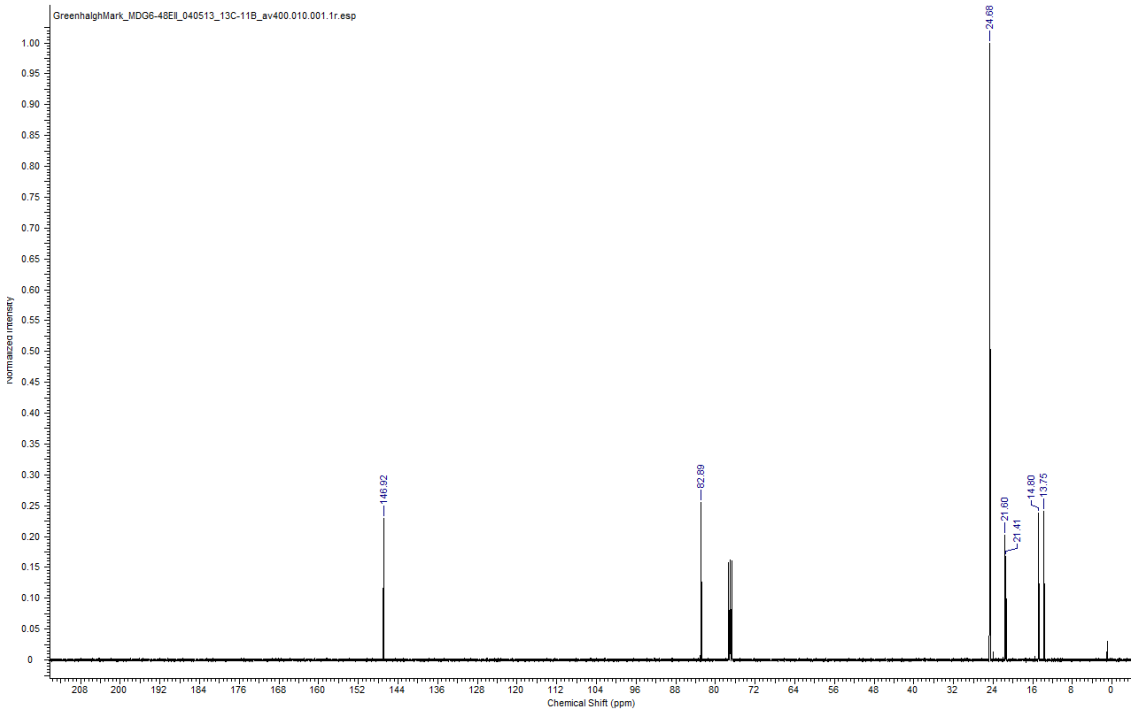


5b

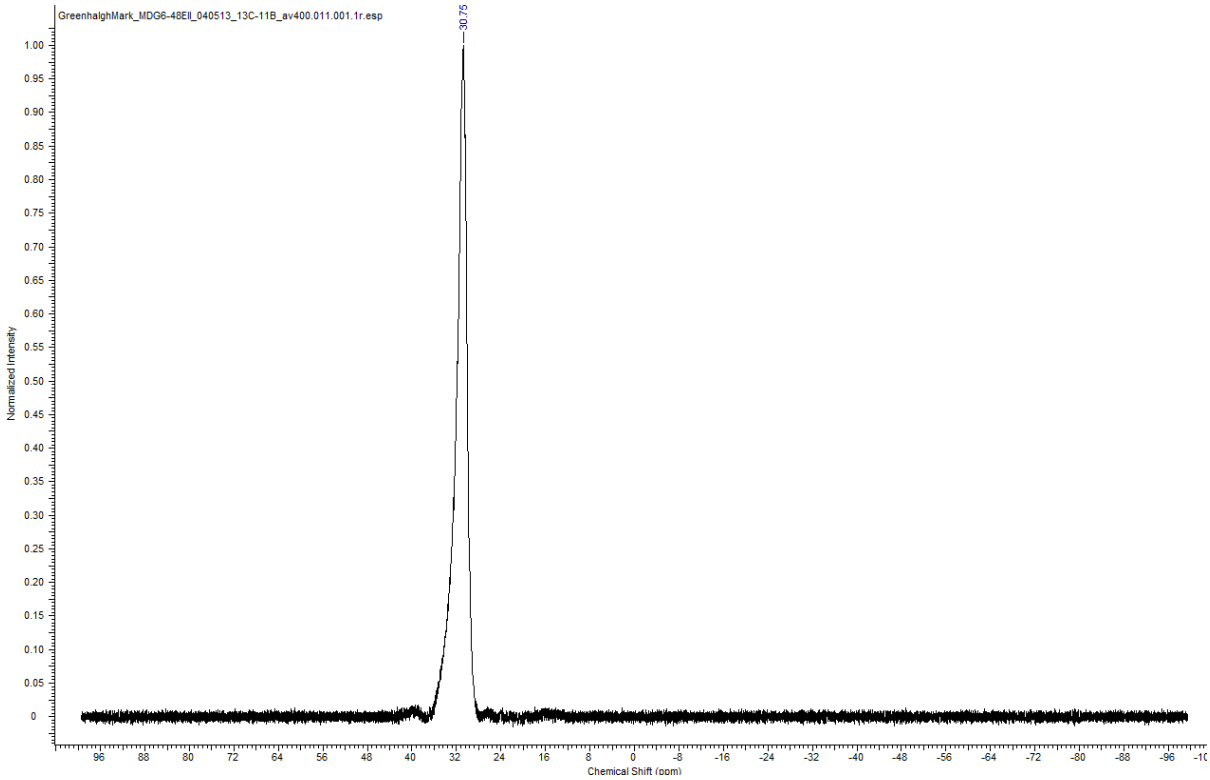
400 MHz



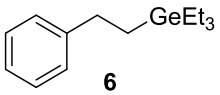
101 MHz



128 MHz

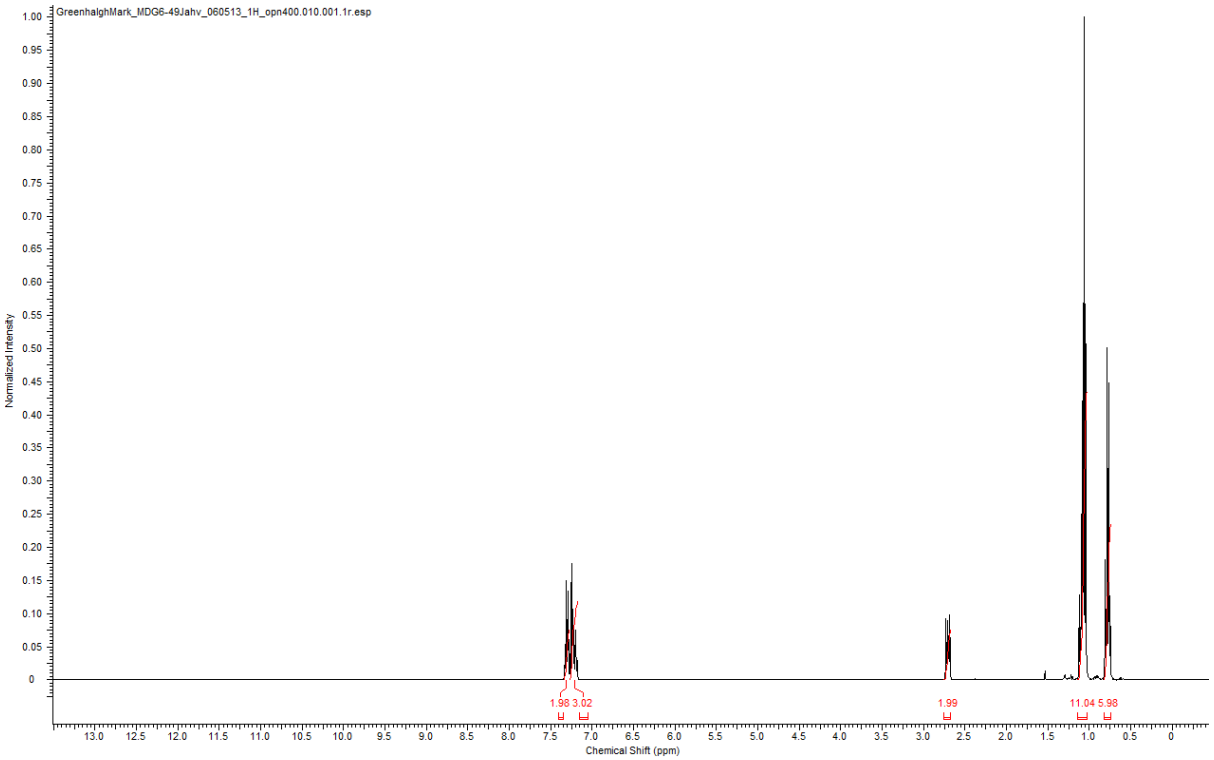


1-Phenyl-2-(triethylgermyl)ethane 6

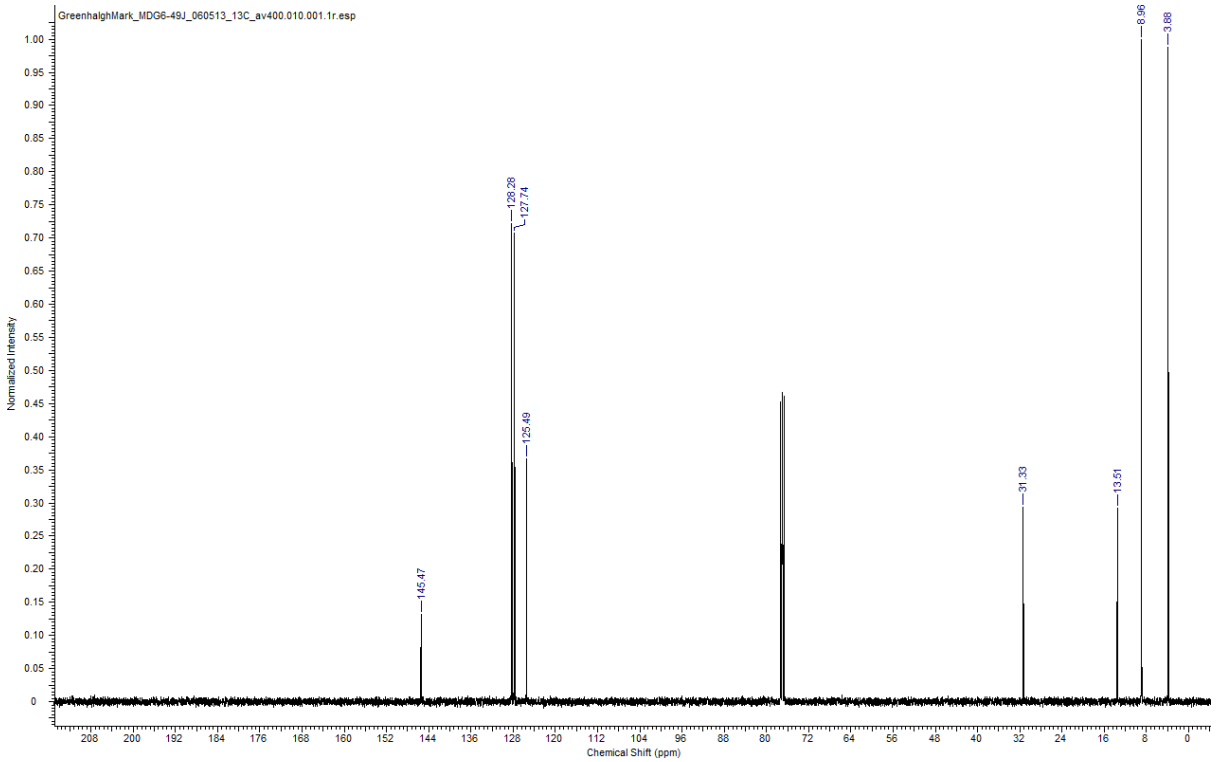


6

400 MHz



101 MHz



References

1. M. A. Esteruelas, A. M. López, L. Méndez, M. Oliván and E. Onate, *Organometallics,* 2003, **22**, 395-406.
2. B. L. Small, M. Brookhart and A. M. A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049-4050.
3. G. A. Molander and D. L. Sandrock, *J. Am. Chem. Soc.* 2008, **130**, 15792-15793.
4. (a) J. Kleimark, A. Hedström, P.-F. Larsson, C. Johansson and P.-O. Norrby, *ChemCatChem,* 2009, 1, 152. (b) J. Kleimark, P.-F. Larsson, P. Emany, A. Hedström and P.-O. Norrby, *Adv. Synth. Catal.,* 2011, 354, 448.
5. H. Radeke *et al. J. Med. Chem.*, 2007, **50**, 4304-4315.
6. L. Zhang, D. Peng, X. Leng and Z. Huang, *Angew. Chem. Int. Ed.*, 2013, **52**, 3676.
7. A. Caballero and S. Sabo-Etienne, *Organometallics*, 2007, **26**, 1191-1195.
8. H. R. Kim and J. Yun, *Chem. Commun.*, 2011, **47**, 2943-2945.
9. S. Pereira and M. Srebnik, *Organometallics*, 1995, **14**, 3127-3128.