

# Heck-Mizoroki Coupling of Vinyl iodide and Applications in The Synthesis of Dienes and Trienes

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## SUPPORTING INFORMATION

1. General Experimental Details
2. Experimental Procedures
3. <sup>1</sup>H, <sup>13</sup>C and 2D NMR Spectra

### 1. General Experimental Details

All reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring unless otherwise stated. All chemicals were purchased from commercial suppliers and used without further purification. Anhydrous acetonitrile was obtained by distillation of HPLC grade acetonitrile over calcium hydride. Anhydrous THF was obtained by distillation of HPLC grade THF over sodium metal, with a benzophenone indicator. Screening of conditions were undertaken on a Radley's Carousel, using Radley's reaction tubes. Monitoring of reactions was achieved using any of TLC, <sup>1</sup>H NMR and GC. GC data was obtained by removing 0.01 mL samples from the reaction mixture and diluting into 1 mL acetonitrile. GC experiments were run on a Hewlett Packard 5890 Series II Gas Chromatograph fitted with a Hewlett Packard 6890 series injector, using a FactorFour™ capillary column VF-5 ms, 30 m, 0.25 mm, 0.25 μm. The experiment conditions were an initial temperature of 30 °C, held for 5 minutes, followed by a gradient of 20 °C/minute to 150 °C, with a hold time of 11 minutes. Where a reference was used, naphthalene or 1,3,5-trimethoxybenzene were used as a reference for conversion calculations. Celite/silica filtration used Celite® S and technical grade silica gel: pore size 60 Å, 230-400 mesh particle size, 40-63 μm particle size. The term 'evaporated' refers to the removal of solvent in vacuo. TLC was performed using silica plates. The silica plates were polyester-backed silica TLC plates with 0.2 mm silica gel and fluorescent indicator. Spots were visualised using an ultraviolet (UV) lamp and KMnO<sub>4</sub> dip. Unless stated otherwise, the term 'column chromatography' refers to silica gel flash chromatography. Silica gel chromatography used technical grade silica gel: pore size 60 Å, 230-400 mesh particle size, 40-63 μm particle size. Where silver nitrate-impregnated silica gel was used, this was prepared according to Li and coworkers.<sup>1</sup> HMR experiments were carried out on either a Bruker Avance-400 or a Varian VNMRS-700 spectrometer in deuterated chloroform (CDCl<sub>3</sub>). Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) reference. Experiments undertaken included <sup>1</sup>H, <sup>11</sup>B, <sup>19</sup>F, <sup>13</sup>C, COSY, PSYCHE, HSQC and HMBC NMR. Electrospray ionisation (ESI) mass spectroscopy was undertaken using a LTQ FT (ThermoFinnigan) high resolution, accurate mass LC ES MS/MS or a Thermo Scientific LTQ Orbitrap XL. Samples were made up as 1 mg per mL solutions in acetonitrile. GC/MS EI was undertaken using a Waters GCT Premier. Atmospheric solids analysis probe (ASAP) mass spectroscopy was undertaken using LCT Premier XE (Waters) high resolution, accurate mass ultra performance liquid chromatography (UPLC) ASAP or a Thermo Scientific LTQ Orbitrap XL. Samples were either made up as 1 mg per mL solutions in acetonitrile or run as solids. Infra-red (IR) spectroscopy were undertaken using either a Perkin Elmer-1600 FTIR or UATR Two FTIR spectrometers, using both liquid and solid samples. Melting point measurements were undertaken using a Gallenkamp melting point apparatus. Where products were susceptible to polymerisation, these were stored with approximately 20 ppm BHT under argon at either 4 °C or -18 °C.



## 2. Experimental Procedures

**Table 3** Determining optimal reaction conditions for formation of diene **6a**.

Entry	Base	Ligand	Approx. conversion/ %
1	-	-	4
2	-	PPh <sub>3</sub>	2
3	-	P(O-tol) <sub>3</sub>	1
4	-	dppf	<1
5	AgOA <sub>c</sub>	-	42
6	AgOA <sub>c</sub>	PPh <sub>3</sub>	30 <sup>a</sup>
7	AgOA <sub>c</sub>	P(O-tol) <sub>3</sub>	52
8	AgOA <sub>c</sub>	dppf	20 <sup>a</sup>
9	Et <sub>3</sub> N	-	-
10	Et <sub>3</sub> N	PPh <sub>3</sub>	-
11	Et <sub>3</sub> N	P(O-tol) <sub>3</sub>	- <sup>b</sup>
12	Et <sub>3</sub> N	dppf	- <sup>c</sup>

<sup>a</sup> Complex <sup>1</sup>H NMR spectra may have rendered these estimates less accurate due to overlapping peaks.

<sup>b</sup> <sup>1</sup>H NMR too complex to accurately estimate product conversion.

<sup>c</sup> <sup>1</sup>H NMR highly complex, but no product signals present.

Product formation monitored by <sup>1</sup>H NMR. Conversions and reagent proportions estimated using integrals from crude <sup>1</sup>H NMR spectra, using signals for naphthalene as a reference.

General conditions used for base and ligand screen detailed in **Table 3**

$\text{Pd}(\text{OAc})_2$  (0.0650 mmol) monodentate ligand (0.130 mmol) or bidentate ligand (0.0650 mmol) and base (0.780 mmol) were added to reaction tubes under argon. MeCN (4.5 mL), previously degassed by the freeze-pump-thaw method (4x cycles) was added to each tube together with vinyl iodide **17** (0.650 mmol) and vinyl boronate **15** (0.780 mmol). The reaction tubes were then evacuated and filled with argon, and the reaction tubes stirred at 50 °C for 3 days. An internal reference compound of naphthalene (0.0650 mmol) was used. Reaction products and conversions were identified by  $^1\text{H}$  NMR.

**Table 4** Determining optimal starting material ratios for formation of diene **6a**.

Entry	Equivalents <b>2</b> added wrt vinyl iodide	Approx. conversion / %
1	0.8	44
2	1	43
3	1.1	50
4	1.2	69

Product formation monitored by  $^1\text{H}$  NMR. Ratios estimated using integrals from crude  $^1\text{H}$  NMR spectra.

General conditions used for equivalents screen detailed in **Table 4**

$\text{Pd}(\text{OAc})_2$  (0.0650 mmol),  $\text{P}(o\text{-tol})_3$  (0.130 mmol) and  $\text{AgOAc}$  (0.780 mmol) were added to reaction tubes under argon. MeCN (4.5 mL), previously degassed by the freeze-pump-thaw method (4x cycles) was added to each tube together with vinyl iodide **17** (0.650 mmol) and vinyl boronate **15**. The reaction tubes were then evacuated and filled with argon, and the reaction tubes stirred at 50 °C for 36 h. Reaction products and conversions were identified by  $^1\text{H}$  NMR

**Table 5** Results of catalyst screen for formation of diene **6a**.

Entry	Catalyst used	Conversion after 17 h/ %
1	Pd(OAc) <sub>2</sub>	55
2	Pd(dba) <sub>2</sub>	35
3	Pd(dppf)Cl <sub>2</sub>	47
4	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	25
5	PdCl <sub>2</sub>	50
6	PdBr <sub>2</sub>	50
7	PdI <sub>2</sub>	40

Product formation monitored by GC, using naphthalene as internal standard.

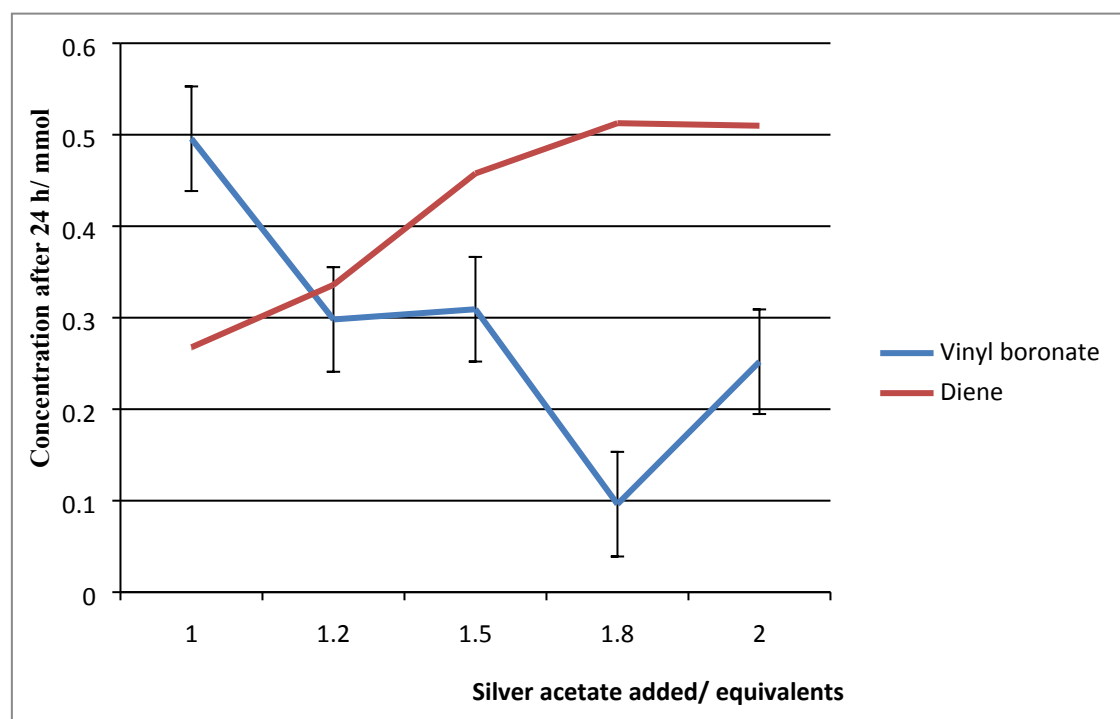
*General conditions used for catalyst screen detailed in Table 5*

To oven dried reaction tubes under argon were added catalyst (0.0325 mmol), P(*o*-tol)<sub>3</sub> (19.8 mg, 0.0650 mmol), AgOAc (0.130 g, 0.780 mmol) and naphthalene (9.00 mg, 0.0650 mmol). MeCN (2 mL), previously degassed by a bubbling argon needle, was added to each tube together with vinyl iodide (0.100 g, 0.650 mmol) and 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane (0.100 g, 0.650 mmol). The reaction tubes were then heated to 50 °C for 17 h with vigorous stirring, after which a portion was taken and analysed by GC and <sup>1</sup>H NMR. Reaction products and conversions were identified relative to naphthalene internal standard.

**Table 6** The effect of silver acetate loading on the formation of diene **6a**.

Entry	Equivalents silver acetate used	Diene <b>6a</b> concentration after 24 h/ mmol	Vinyl boronate <b>2</b> concentration after 24 h/ mmol
1	1	0.268	0.496
2	1.2	0.336	0.298
3	1.5	0.458	0.309
4	1.8	0.513	0.096
5	2	0.510	0.252

Product formation monitored by GC, using naphthalene as internal standard. Insoluble suspension caused stirring problems.

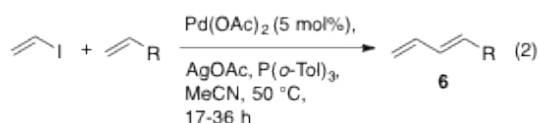
**Figure 1** Graph showing the effect of silver acetate loading on the concentration of vinyl boronate **4a** and diene **6a**.

General conditions used for silver acetate equivalent screen detailed in **Table 6**

To oven dried reaction tubes under argon were added Pd(OAc)<sub>2</sub> (7.30 mg, 0.0325 mmol), P(*o*-tol)<sub>3</sub> (19.8 mg,

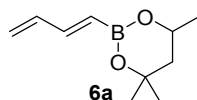
0.0650 mmol), AgOAc and naphthalene (9.00 mg, 0.0650 mmol). MeCN (2 mL), previously degassed by a bubbling argon needle, was added to each tube together with vinyl iodide (0.100 g, 0.650 mmol) and 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane (0.100 g, 0.650 mmol). The reaction tubes were then heated to 50 °C for 22 h with vigorous stirring, after which a portion was taken and analysed by GC and <sup>1</sup>H NMR. Reaction products and conversions were identified relative to naphthalene internal standard.

General conditions used for chain extension using vinyl iodide detailed in **Table 1**



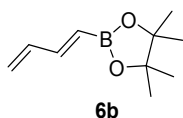
Pd(OAc)<sub>2</sub> (0.0975 mmol), P(o-tol)<sub>3</sub> (0.195 mmol) and AgOAc (2.34 mmol) were added to a dry round-bottomed flask under Ar in the absence of light. MeCN (6 mL) (previously degassed by sparging with Ar), was added, followed by alkene (3.9 mmol) and then vinyl iodide (1.95 mmol) under a positive pressure of Ar. The flask was purged with Ar for 2 minutes and stirred at 50 °C for between 17 hours and 3 days. Conversion was determined by <sup>1</sup>H NMR. The reaction mixture was diluted with EtOAc (60 mL, containing approximately 3 ppm BHT) and passed through a short Celite/silica plug. Concentration *in vacuo* gave crude product which was analysed by <sup>1</sup>H NMR. Where purification was undertaken, this was achieved using silica gel chromatography.

Synthesis of (*E*)-2-(buta-1,3-dienyl)-4,4,6-trimethyl-1,3,2-dioxaborinane **6a**



To an oven dried round bottomed flask was added Pd(OAc)<sub>2</sub> (146 mg, 0.650 mmol), P(o-tol)<sub>3</sub> (395 mg, 1.30 mmol) and AgOAc (2.60 g 15.6 mmol), MeCN (24 mL, previously degassed by sparging with Ar), was added together with vinyl iodide (2.00 g, 13.0 mmol) and 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane (2.00 g, 13.0 mmol). The reaction mixture was heated at 50 °C for 48 h with vigorous stirring. The reaction mixture was allowed to cool, diluted with Et<sub>2</sub>O (250 mL) and passed through a short Celite/silica plug. The organic extracts were washed with H<sub>2</sub>O (100 mL) and brine (100 mL), dried over MgSO<sub>4</sub>, filtered and evaporated to yield the crude product as an orange oil (2.60 g), which was purified by silica gel chromatography (eluent 0-4% EtOAc in petroleum ether). Pure fractions were evaporated to yield (*E*)-2-(buta-1,3-dienyl)-4,4,6-trimethyl-1,3,2-dioxaborinane as a pale yellow oil (1.71 g, 73%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.33-1.26 (9H, m), 1.50 (1H, dd, J = 13.9, 11.7 Hz), 1.81-1.76 (1H, m), 4.22 (1H, dqd, J = 12.2, 6.3, 2.7 Hz), 5.18 (1H, dd, J = 9.8, 1.7 Hz), 5.32 (1H, dd, J = 17.1, 1.7 Hz), 5.51 (1H, d, J=17.5), 6.39 (1H, dt, J = 17.1, 10.2 Hz), 6.91 (1H, dd, J = 17.6, 10.5 Hz); <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>): δ 26.2; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 23.1, 28.0, 31.2, 46.0, 64.7, 70.7, 119.5, 139.1, 147.2; IR (ν<sub>max</sub>, cm<sup>-1</sup>) *inter alia* 29734, 1591; LRMS (ASAP) 181.2; HRMS (ASAP) calculated [C<sub>10</sub>H<sub>17</sub><sup>10</sup>BO<sub>2</sub>+H]<sup>+</sup> 180.1431, found 180.1428. This compound stored with ~20 ppm BHT under Ar in the refrigerator in order to prevent polymerisation.

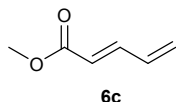
Synthesis of 2-[(*1E*)-buta-1,3,-dienyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **6b**<sup>2</sup>



To a dry Schlenk flask was added Pd(OAc)<sub>2</sub> (29.0 mg, 0.125 mmol), P(o-tol)<sub>3</sub> (76.0 mg, 0.250 mmol) and AgOAc (0.500 g, 3.00 mmol), followed by dry MeCN (4.5 mL, previously degassed by sparging with Ar). Vinylboronic acid pinacol ester (0.424 mL, 2.50 mmol) was added, followed by vinyl iodide (0.185 mL, 2.50

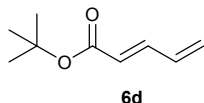
mmol). The reaction mixture was then heated to 55 °C with vigorous stirring for 2 days. The mixture was allowed to cool, diluted with Et<sub>2</sub>O (280 mL) and passed through a short Celite/silica gel plug. The organic extracts were washed with 5% HCl (40 mL), H<sub>2</sub>O (80 mL) and brine (80 mL), dried over MgSO<sub>4</sub> and evaporated to yield the crude product as an orange oil (980 mg) which was purified by silica gel chromatography (elution solvent 9:1 hexane:EtOAc) to give 2-[(*IE*)-buta-1,3,-dienyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as a an orange oil (0.318 g, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.30 (12H, s), 5.28 (1H, ddt, J = 10.0, 1.5, 0.7), 5.40 (1H, ddt, J = 17.1, 1.6, 0.8 Hz), 5.60 (1H, dq, J = 17.7, 0.7 Hz), 6.44 (1H, dddd, J = 16.9, 10.5, 9.9, 0.8 Hz), 7.03 (1H, dd, J = 17.8, 10.4 Hz); <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 29.8; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 24.7, 121.0, 138.8, 150.1; IR (ν<sub>max</sub>, cm<sup>-1</sup>) *inter alia* 2978; LRMS (ASAP) 181.1; HRMS (ASAP) calculated [C<sub>10</sub>H<sub>17</sub><sup>11</sup>BO<sub>2</sub>+H]<sup>+</sup> 181.1402, found 181.1434 .

#### Synthesis of methyl (2*E*)-penta-2,4-dienoate **6c**<sup>3</sup>



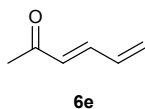
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.76 (3H, s), 5.50 (1H, ddt, J = 10.0, 1.4, 0.7 Hz), 5.61 (1H, ddt, J = 16.9, 1.5, 0.8 Hz), 5.92 (1H, dq, J = 15.4, 0.7 Hz), 6.46 (1H, dddd, J = 16.9, 10.9, 10.0, 0.7 Hz), 7.22-7.32 (1H, m, plus CHCl<sub>3</sub>); LCMS (EI) 112.1; HRMS (EI) calculated [C<sub>6</sub>H<sub>7</sub>O<sub>2</sub>+H] 112.0516, found 112.0519.

#### Synthesis of tert-butyl (2*E*)-penta-2,4-dienoate **6d**



Product obtained as a yellow oil (84 mg, 28%), following silica gel chromatography, eluent 10% EtOAc in hexane. <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 1.49 (9H, s), 5.44 (1H, ddd, J = 10.0, 1.5, 0.8 Hz), 5.57 (1H, ddt, J = 17.0, 1.6, 0.8 Hz), 5.84 (1H, dd, J = 15.4, 0.8 Hz), 6.43 (1H, dddd, J = 16.9, 10.9, 10.0, 0.8 Hz), 7.16 (1H, ddt, J = 15.4, 11.0, 0.8 Hz); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ 28.1, 124.2, 124.7, 134.8, 143.5, 166.1; IR (ν<sub>max</sub>, cm<sup>-1</sup>) *inter alia* 3008, 2981, 2936, 1708; LCMS (ESI) 326.2; HRMS (ASAP) calculated [C<sub>18</sub>H<sub>32</sub>O<sub>4</sub> (2M)+NH<sub>4</sub>] 326.2326, found 326.2326.

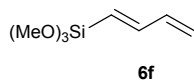
#### Synthesis of (3*E*)-hexa-3,5-dien-2-one **6e**<sup>4</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.29 (3H, s), 5.48-5.57 (1H, m), 5.61-5.71 (1H, m), 6.16 (1H, d, J = 15.7 Hz), 6.47 (1H, dddd, J = 16.9, 10.8, 9.9, 0.7 Hz), 7.10 (1H, ddt, J = 15.8, 10.8, 0.8 Hz); LCMS (EI) 96.1; HRMS (EI) calculated [C<sub>6</sub>H<sub>8</sub>O] 96.0577, found 96.0575.

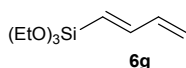


Synthesis of (*E*)-buta-1,3-dien-1-yltrimethoxysilane **6f**



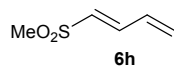
<sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 3.58 (9H, s), 5.25 (1H, ddt, J = 10.0, 1.5, 0.7 Hz), 5.36 (1H, ddt, J = 17.0, 1.5, 0.7 Hz), 5.55 (1H, dq, J = 18.6, 0.7 Hz), 6.38 (1H, dtd, J = 17.0, 10.0, 0.8 Hz), 6.82 (1H, ddt, J = 18.6, 10.2, 0.8 Hz); LCMS (EI) 174.1; HRMS (EI) calculated [C<sub>7</sub>H<sub>14</sub>O<sub>3</sub>Si] 174.0703, found 174.0707.

Synthesis of (*E*)-buta-1,3-dien-1-yltriethoxysilane **6g**



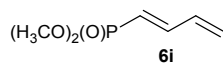
<sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 1.23 (9H, t, J = 7.0 Hz), 3.83 (6H, q, J = 7.0 Hz), 5.23 (1H, ddt, J = 10.0, 1.5, 0.7 Hz), 5.33 (1H, ddt, J = 17.0, 1.5, 0.7 Hz), 5.58 (1H, dq, J = 18.5, 0.7 Hz), 6.37 (1H, dtd, J = 17.0, 10.1, 0.9 Hz), 6.81 (1H, ddt, J = 18.6, 10.2, 0.8 Hz); LCMS (EI) 216.1; HRMS (EI) calculated [C<sub>10</sub>H<sub>20</sub>O<sub>3</sub>Si] 216.1175, found 216.1177.

Synthesis of (*3E*)-4-methanesulfonylbuta-1,3-diene **6h**<sup>5</sup>



<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 2.94 (3H, s), 5.61-5.65 (m, 1H), 5.72 (1H, dt, J = 16.8, 0.9 Hz), 6.11 (1H), 6.43 (1H), 7.13-7.20 (m, 1H); LCMS (EI) 132.0; HRMS (EI) calculated [C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>S] 132.0247, found 132.0245.

Synthesis of dimethyl [(*E*)-buta-1,3-dien-1-yl]phosphonate **6i**



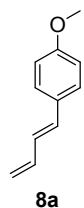
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 2.04 (6H, s), 5.44-5.49 (1H, m), 5.52-5.60 (1H, m), 5.64-5.68 (1H, m), 6.41 (1H, dtd, J = 17.0, 10.3, 1.9 Hz), 7.04-7.13 (1H, m); LRMS (ASAP) 163.1; HRMS (ASAP) calculated [C<sub>6</sub>H<sub>11</sub>O<sub>3</sub>P+H] 163.0515, found 163.0519.

General conditions used for SM couplings on boronate diene **6a**

To a completely cooled, oven dried round bottomed flask was added (*E*)-2-(buta-1,3-dienyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (183 mg, 1.01 mmol), followed by BHT (20 ppm, 0.014 mL of a 1x10<sup>-3</sup> M solution in THF), 1,3,5-trimethoxybenzene (0.675 mL of a 1 M solution in THF, 0.675 mmol), aryl or vinyl halide (0.675 mmol), *t*-BuOK (91.0 mg, 0.810 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (39.0 mg, 0.0338 mmol). After purging with Ar for 2 minutes, degassed THF (6 mL) under Ar and the reaction mixture further degassed by sparging with Ar for 2 minutes. The reaction mixture was heated to 60 °C. After the reaction was complete, the mixture was allowed to cool, diluted with EtOAc (containing approximately 3 ppm BHT, 80 mL) and passed through a short Celite/silica gel plug and the organic extracts were evaporated to yield crude product. A small portion of the crude product was used for

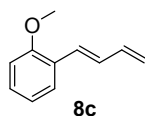
GC and  $^1\text{H}$  NMR analysis to determine crude yield. The crude product was purified by silica gel chromatography to yield the desired polyene.

*1-[(1E)-Buta-1,3-dien-1-yl]-4-methoxybenzene 8a<sup>6</sup>*



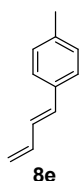
After a 4.5 hour reaction time, the product was obtained as a colourless oil (1.06:1 reference:product, 75 mg, 69%) following silica gel chromatography on silver nitrate impregnated silica (eluent 5% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.81 (3H, s), 5.11 (1H, ddt,  $J = 10.7, 1.5, 0.7$  Hz), 5.28 (1H, ddt,  $J = 16.9, 1.6, 0.8$  Hz), 6.44-6.54 (2H, m), 6.67 (1H, ddt,  $J = 15.5, 10.5, 0.8$  Hz), 6.83-6.87 (2H, m), 7.32-7.38 (2H, m);  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ )  $\delta$  55.7, 114.4, 116.8, 127.67, 127.99 (2 coincident peaks), 130.3, 132.7, 137.7, 159.6. IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ) *inter alia* 2957, 2921, 2852, 1678, 1659, 1649, 1641; GCMS 160.100; HRMS (ASAP) calculated [ $\text{C}_{11}\text{H}_{12}\text{O}$ ] 160.088, found 160.0885.

*1-[(1E)-Buta-1,3-dien-1-yl]-2-methoxybenzene 8c*

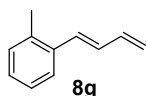


After a 25 h reaction, the product was obtained as a colourless oil (containing 0.87:1 reference:product, 25 mg, 23%), following silica gel chromatography on silver nitrate impregnated silica (eluent 5% EtOAc in hexane);  $^1\text{H}$  NMR: (700 MHz,  $\text{CDCl}_3$ )  $\delta$  3.86 (3H, s), 5.15 (1H, ddt,  $J = 10.0, 1.5, 0.7$  Hz), 5.31 (1H, ddt,  $J = 16.9, 1.6, 0.8$  Hz), 6.55 (1H, dtd,  $J = 17.0, 10.2, 0.7$  Hz), 6.79-6.85 (1H, m), 6.87 (1H, dd,  $J = 8.3, 1.1$  Hz), 6.90-6.95 (2H, m), 7.22 (1H, ddd,  $J = 8.2, 7.3, 1.7$  Hz), 7.48 (1H, dd,  $J = 7.6, 1.7$  Hz);  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ )  $\delta$  55.4, 85.9, 110.9, 116.9, 120.6, 126.5, 127.6, 128.6, 130.2, 137.9, 156.8. IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ) *inter alia* 2348, 2293, 2162, 1972; LRMS (ASAP) 161.1; HRMS (ASAP) calculated [ $\text{C}_{11}\text{H}_{13}\text{O}$ ] 161.0966, found 161.0967.

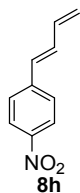
*1-[(1E)-Buta-1,3-dien-1-yl]-4-methylbenzene 8e<sup>6</sup>*



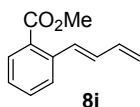
After a 6 h reaction, the product was obtained as a yellow oil (containing 0.135:1 unreacted aryl:product, 87 mg, 89%), following silica gel chromatography (eluent 1% EtOAc in hexane);  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$  2.34 (3H, s), 5.15 (1H, ddt,  $J = 10.0, 1.6, 0.8$  Hz), 5.32 (1H, ddt,  $J = 17.1, 1.8, 0.9$  Hz), 6.47-6.59 (2H, m), 6.75 (1H, m), 7.14 (2H, d,  $J = 7.9$  Hz), 7.31-7.33 (2H, m);  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ )  $\delta$  21.1, 117.0, 126.3, 128.7, 129.3, 132.8, 134.3, 137.3, 137.5; IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ) *inter alia* 2348, 2168, 2002; LRMS (ASAP) 145.1; HRMS (ASAP) calculated [ $\text{C}_{11}\text{H}_{12}+\text{H}$ ] 145.1017, found 145.1012.

*1-[(1E)-Buta-1,3-dien-1-yl]-2-methylbenzene 8g*<sup>6</sup>

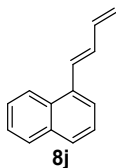
After a 25 h reaction, the product was obtained as a colourless oil (containing 0.45:1 reference:product, 39 mg, 40%), following silica gel impregnated with silver nitrate chromatography (eluent 1% EtOAc in hexane); <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 2.81 (3H,s), 5.18 (1H, ddd, J = 10.0, 1.6, 0.8 Hz), 5.34 (1H, ddd, J = 17.0, 1.7, 0.8 Hz), 6.56 (1H, dt, J = 16.9, 10.1 Hz), 6.70 (1H, ddd, J = 15.5, 10.3, 0.8 Hz), 6.80 (1H, d, J = 15.5 Hz), 7.14-7.20 (3H, m), 7.47-7.52 (1H, m); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 19.8, 117.4, 125.2, 126.1, 127.5, 126.1, 127.5, 130.4, 130.5, 130.7, 135.6, 136.0, 137.5; IR (ν<sub>max</sub>, cm<sup>-1</sup>) *inter alia* 2348, 2320, 2158, 2014, 1980; LRMS (ASAP) 145.1; HRMS (ASAP) calculated [C<sub>11</sub>H<sub>12</sub>+H] 145.1017, found 145.1006.

*1-[(1E)-Buta-1,3-dien-1-yl]-4-nitrobenzene 8h*<sup>7</sup>

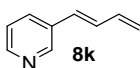
After a 6 h reaction, product was obtained as a yellow solid (78 mg, 66%), following silica gel impregnated with silver nitrate chromatography (eluent 1% EtOAc in hexane); mp 66.0-69.9 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.35 (1H, d, J = 10.0 Hz), 5.48 (1H, d, J = 16.9 Hz), 6.52 (1H, dt, J = 16.9, 10.3 Hz), 6.60 (1H, d, J = 15.7 Hz), 6.93 (1H, dd, J = 15.7, 10.5 Hz), 7.50 (2H, d, J = 8.7 Hz), 8.16 (2H, d, J = 14.0 Hz); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ 120.9, 124.1, 126.8, 130.4, 134.0, 136.4; IR (ν<sub>max</sub>, cm<sup>-1</sup>) *inter alia* 1602, 1588, 1510 (s); LRMS (ASAP) 175.1; HRMS (ASAP) calculated [C<sub>10</sub>H<sub>9</sub>NO<sub>2</sub>], 175.0633, found 175.0624.

*(E)-Methyl-2-(buta-1,3-dienyl) benzoate 8i*

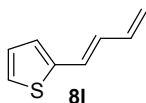
After a 23 h reaction, product was obtained as a colourless oil (containing 1:1:0.33 reference:unreacted aryl:product, 29 mg, 24%), following silica gel impregnated with silver nitrate chromatography (eluent 1% EtOAc in hexane); <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 3.90 (3H, s), 5.21 (1H, ddt, J = 10.0, 1.5, 0.8 Hz), 5.36 (1H, ddt, J = 16.8, 1.5, 0.8 Hz), 6.58 (1H, dtd, J = 16.9, 10.3, 0.8 Hz), 6.71 (1H, ddt, J = 15.6, 10.5, 0.9 Hz), 7.28 (1H, td, J = 7.6, 1.2 Hz), 7.40 (1H, m), 7.46 (1H, tdd, J = 7.9, 1.5, 0.7 Hz), 7.59-7.69 (1H, m), 7.84-7.89 (1H, m); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 52.1, 118.4, 126.7, 127.1, 130.5, 131.1, 131.9, 132.3, 137.4, 138.7, 166.9, 167.8; IR (ν<sub>max</sub>, cm<sup>-1</sup>) *inter alia* 2388, 2350, 2338, 2026, 1968; LRMS (ASAP) 188.1; HRMS (ASAP) calculated [C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>], 189.0916, found 189.0923.

2-[(1E)-Buta-1,3-dien-1-yl]-naphthalene **8j**<sup>6</sup>

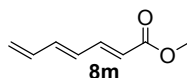
After a 22 h reaction, the product was obtained as a colourless oil (containing 2.09:1 reference:product, 82 mg, 68%), following silica gel impregnated with silver nitrate chromatography (eluent 1% EtOAc in hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.25 (1H, ddt, J = 9.9, 1.4, 0.7 Hz), 5.40 (1H, ddt, J = 16.8, 1.6, 0.8 Hz), 6.67 (1H, ddt, J = 16.8, 10.3 Hz), 6.86 (1H, ddt, J = 15.3, 10.6, 0.9 Hz), 7.36 (1H, d, J = 15.3 Hz), 7.45-7.55 (3H, m), 7.68 (1H, dt, J = 7.3, 1.0 Hz), 7.76-7.83 (1H, m), 7.84-7.89 (1H, m), 8.15 (1H, dq, J = 8.1, 0.9 Hz); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 117.9, 123.4, 123.6, 125.6, 125.7, 126.0, 128.0, 128.6, 129.6, 131.2, 132.5, 133.7, 134.5, 137.4. IR (ν<sub>max</sub>, cm<sup>-1</sup>) *inter alia* 2374, 2348, 2156, 2030, 1974; LRMS (ASAP) 180.1; HRMS (ASAP) calculated [C<sub>12</sub>H<sub>14</sub>], 180.0939, found 180.0941.

3-[(1E)-Buta-1,3-dien-1-yl]-pyridine **8k**<sup>8</sup>

After a 24 h reaction, the product was obtained as a yellow oil (containing 1.03 borate by-product:product, 78 mg, 88%), following silica gel chromatography (eluent 10-50% EtOAc in hexane); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.20-5.28 (1H, m), 5.39 (1H, dd, J = 17.0, 1.4 Hz), 6.45-6.56 (2H, m), 6.83 (1H, dd, J = 15.7 Hz, 10.5 Hz), 7.18-7.25 (1H, m), 7.66-7.77 (1H, m), 8.45 (1H, d, J = 4.8 Hz), 8.61 (1H, s); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ 119.1, 123.5, 128.9, 131.6, 132.6, 136.6, 148.4, 148.5. IR (ν<sub>max</sub>, cm<sup>-1</sup>) *inter alia* 2364, 2334, 2168, 2030, 1968, 1678, 1659, 1641; LRMS (ASAP) 131.1; HRMS (ASAP) calculated [C<sub>9</sub>H<sub>10</sub>N], 132.0813, found 132.0817.

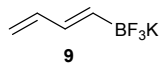
2-[(1E)-Buta-1,3-dien-1-yl]-thiophene **8l**<sup>9</sup>

After a 23 h reaction time, product was obtained as a colourless oil (containing 0.14:1 reference:product, 42 mg, 46%), following silica gel impregnated with silver nitrate chromatography (eluent 1% EtOAc in hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.15 (1H, ddt, J = 10.1, 1.5, 0.7 Hz), 5.31 (1H, ddt, J = 16.9, 1.6, 0.7 Hz), 6.44 (1H, dt, J = 16.8, 10.0 Hz), 6.57-6.75 (2H, m), 6.94-6.99 (2H, m), 7.14-7.19 (1H, m); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ 117.6, 124.6, 125.8, 127.7, 129.5, 136.8, 142.6; IR (ν<sub>max</sub>, cm<sup>-1</sup>) *inter alia* 2389, 2162, 2020, 1974, 1678, 1659, 1649, 1641; LRMS (ASAP) 136.0; HRMS (ASAP) calculated [C<sub>8</sub>H<sub>8</sub>S-H], 135.0267, found 135.0268.

Methyl (3E,5E)-octa-3,5,7-trienoate **8m**<sup>10</sup>

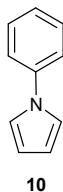
After a 4 h reaction time, product was obtained as a colourless oil (49 mg, 53%), following silica gel impregnated with silver nitrate chromatography (eluent 0-10% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.75 (3H, s), 5.32 (1H, dd,  $J = 9.9, 1.3$  Hz), 5.42 (1H, dd,  $J = 16.7, 1.3$  Hz), 5.91 (1H, d,  $J = 15.3$  Hz), 6.27-6.49 (2H, m), 6.56 (1H, ddt,  $J = 14.8, 10.7, 0.7$  Hz), 7.31 (1H, ddd,  $J = 15.3, 11.3, 0.7$  Hz);  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ )  $\delta$  51.4, 120.9, 121.5, 130.2, 136.0, 140.8, 144.2, 167.2; IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ) *inter alia* 2360, 2334, 2158, 1974, 1678, 1659, 1649, 1641; LRMS (ASAP) 138.1; HRMS (ASAP) calculated [ $\text{C}_8\text{H}_{10}\text{O}_2$ ], 139.0752, found 139.0759.

Potassium (*E*)-buta-1,3-dien-1-yltrifluoroborane **9**



(*E*)-2-(Buta-1,3-dienyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (0.10 g, 0.56 mmol) was dissolved in MeOH (1.1 mL), then MeCN (1.1 mL) was added. KF (0.13 g, 2.21 mmol) in  $\text{H}_2\text{O}$  (0.4 mL) was added dropwise at RT, followed by (+)-tartaric acid (0.17g, 1.13 mmol) in THF (1.7 mL) dropwise. The resulting white suspension was stirred for 1 min, then sonicated for 1 min, then stirred for 5 minutes. MeCN (1.7 mL) was added, the reaction was stirred for 2 min, then MeCN (0.5 mL) was added and the reaction stirred for a further 2 min. The suspension was filtered, the white solid was washed with MeCN (3 x 3 mL) and the filtrate concentrated *in vacuo* to give desired product as a white solid (90 mg, 100%); m.p. 126.6 °C (decomp);  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ )  $\delta$  4.74 (1H, dd,  $J = 9.1, 2.5$  Hz) 4.89 (1H, dd,  $J = 16.3, 2.2$  Hz), 5.63-5.73 (1H, m), 6.18-6.34 (2H, m);  $^{11}\text{B}$  NMR (128 MHz, acetone- $d_6$ )  $\delta$  2.7 (q,  $J=56.0$  Hz);  $^{19}\text{F}$  NMR (376 MHz, acetone- $d_6$ )  $\delta$  -142.0 (dd,  $J = 105.8, 48.7$  Hz);  $^{13}\text{C}$  NMR (151 MHz, acetone- $d_6$ )  $\delta$  112.0, 136.1, 143.0; IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ) *inter alia* 3186, 1592; LRMS (ESI -ve) 120.0; HRMS (ESI -ve) calculated [ $\text{C}_4\text{H}_5^{10}\text{BF}_3\text{K-K}$ ], 120.0478, found 120.0481.

*N*-Phenyl pyrrole **10**<sup>11</sup>



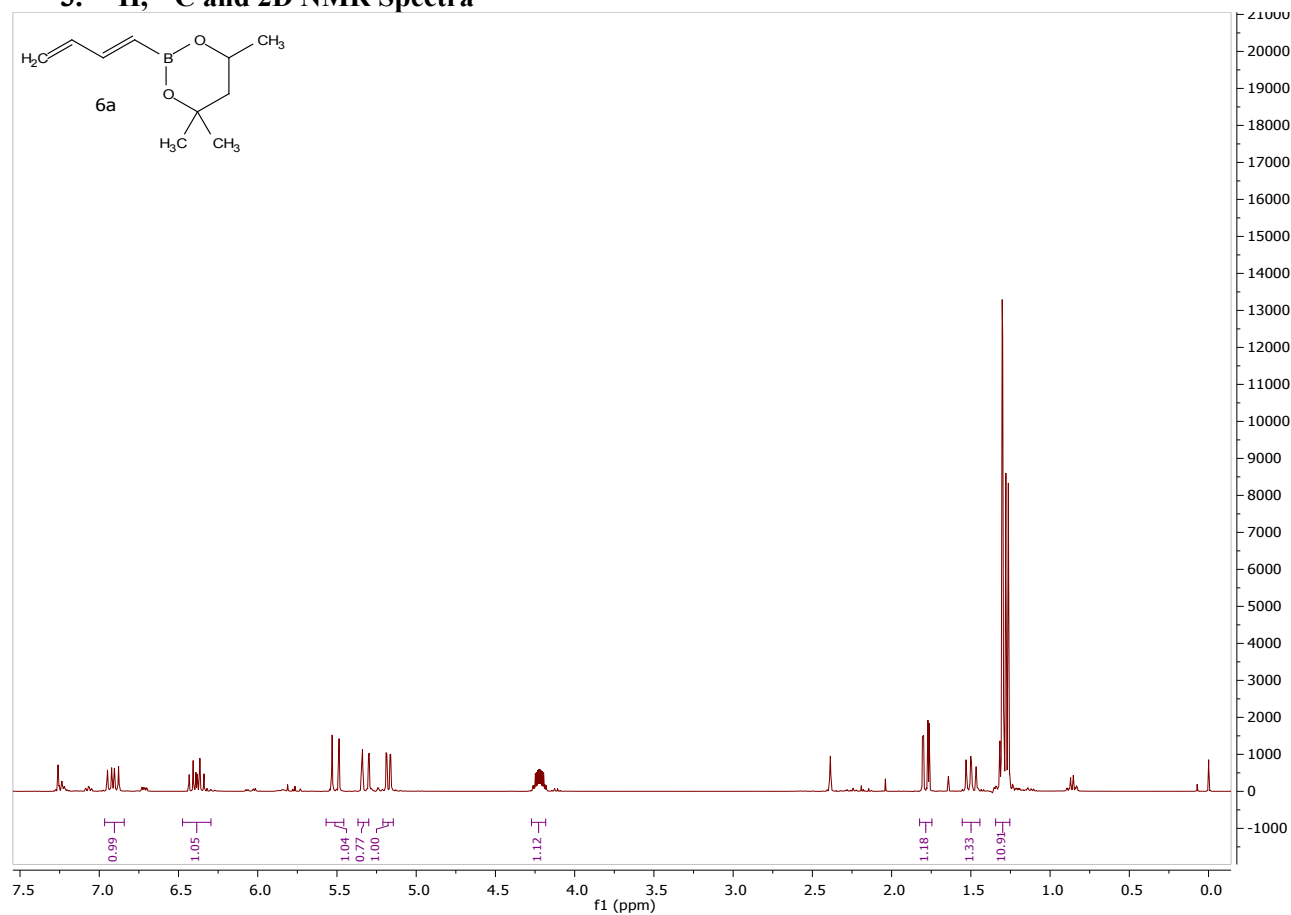
$\text{Pd}(\text{OAc})_2$  (48 mg, 0.195 mmol),  $\text{P}(\text{o-tol})_3$  (0.119 g, 0.39 mmol) and  $\text{AgOAc}$  (0.78 g, 4.68 mmol) were added to a dry round-bottomed flask under Ar in the absence of light. MeCN (6 mL) (previously degassed by sparging with Ar), was added, followed by vinyl iodide (0.288 mL, 3.9 mmol) and then 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane (0.672 mL, 1.95 mmol) under a positive pressure of Ar. The flask was purged with Ar for 5 minutes and stirred at 50 °C for 6 h. Nitrosobenzene (0.379 g, 3.51 mmol) was then added and the reaction stirred at the same temperature overnight. A further 0.3 equivalents of nitrosobenzene was added (0.126 mg, 1.17 mmol) and the reaction stirred for a further 2.5 hours. 0.2 equivalents of nitrosobenzene was then added (84 mg, 0.78 mmol) and the reaction stirred overnight. The reaction was allowed to cool, then diluted with dichloromethane (120 mL) and passed through a short Celite/silica plug. Concentration *in vacuo* gave 1.1 g of a dark brown oil. The crude product was purified by silica gel chromatography, elution gradient 2-10% toluene in hexane to give desired product as a white solid (267 mg, 48%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.35 (2H, t,  $J=2.2$  Hz), 7.10 (2H, t, 2.2 Hz), 7.21-7.29 (1H, m), 7.36-7.46 (4H, m);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  110.4, 119.3, 120.6, 125.6, 129.5, 140.8. Spectra are consistent with the literature.

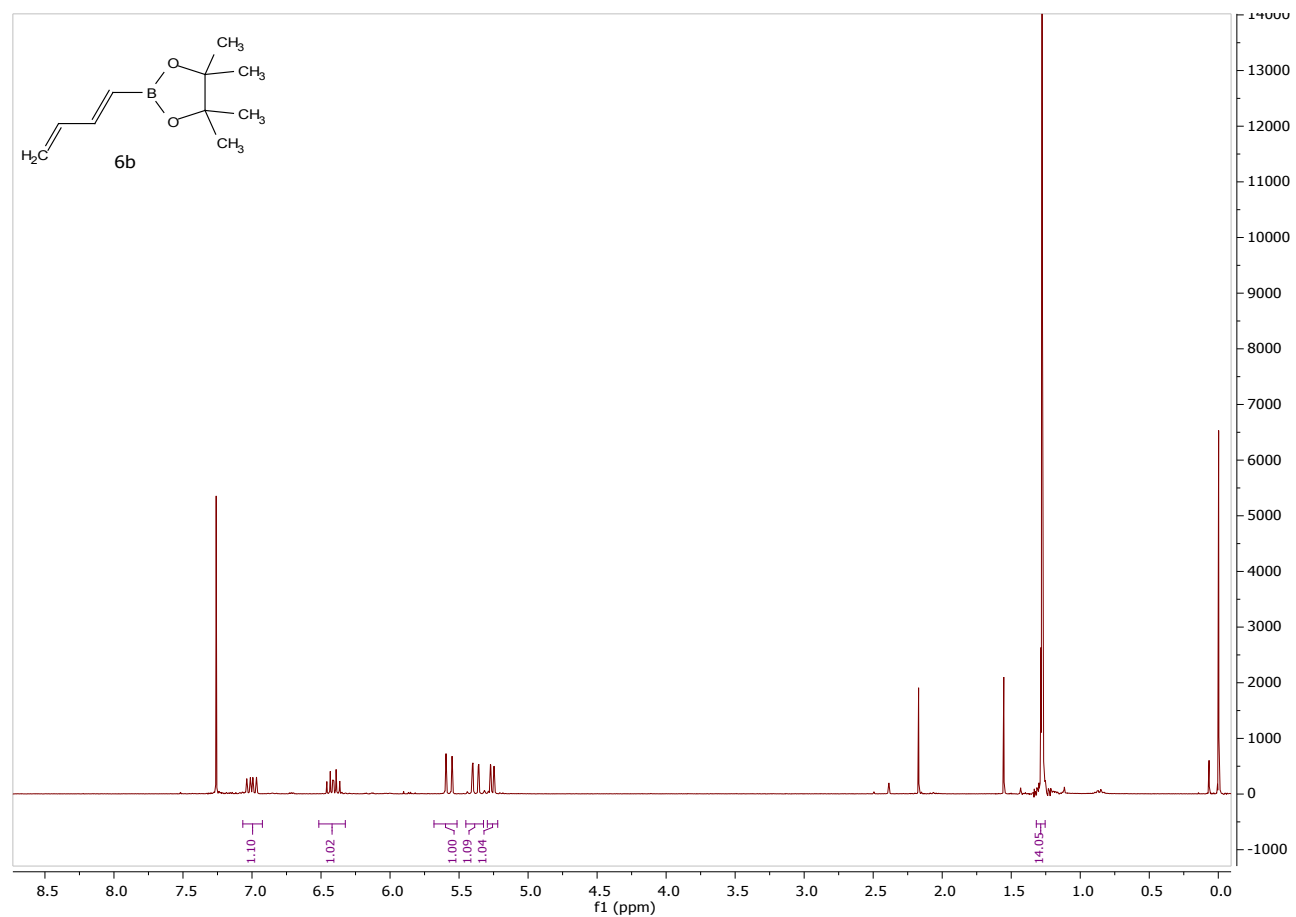
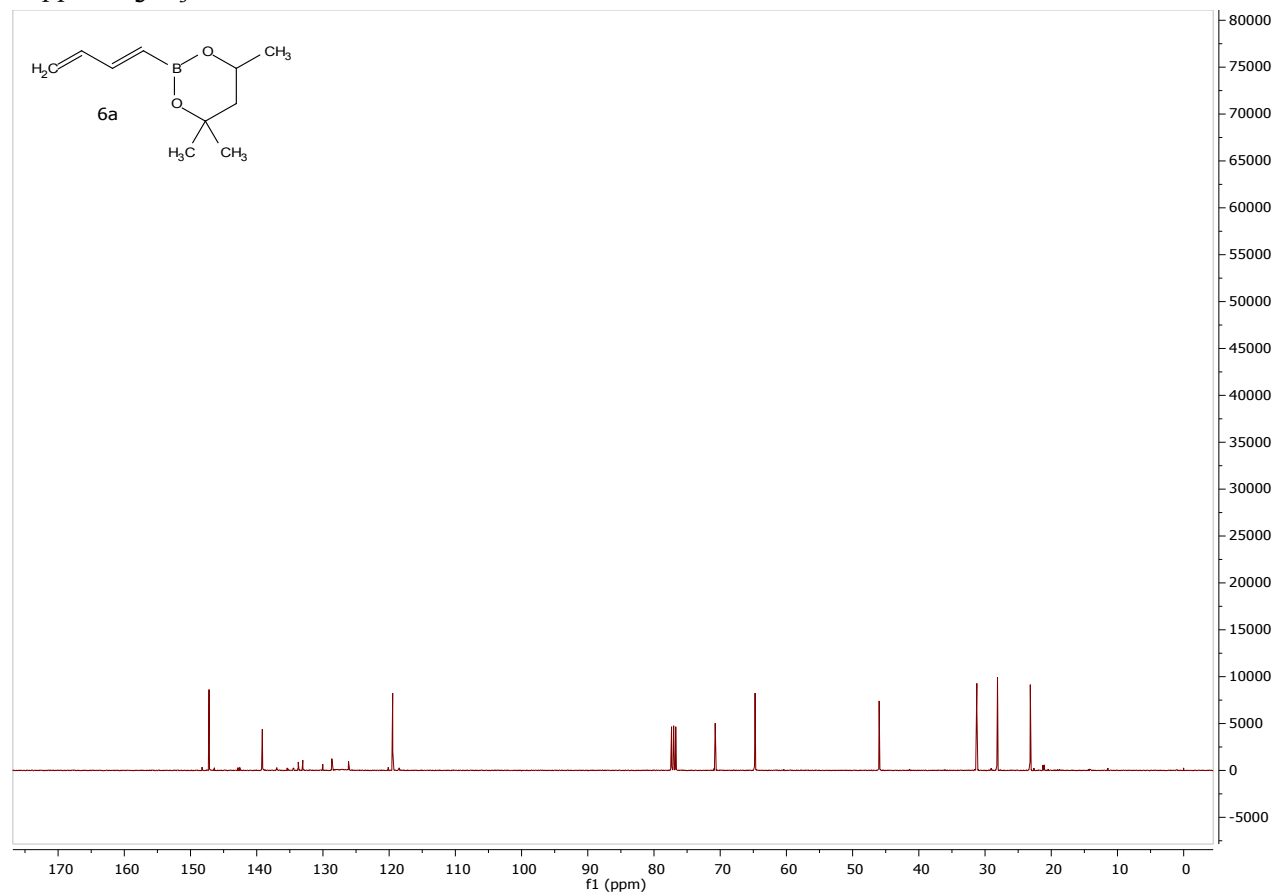
References

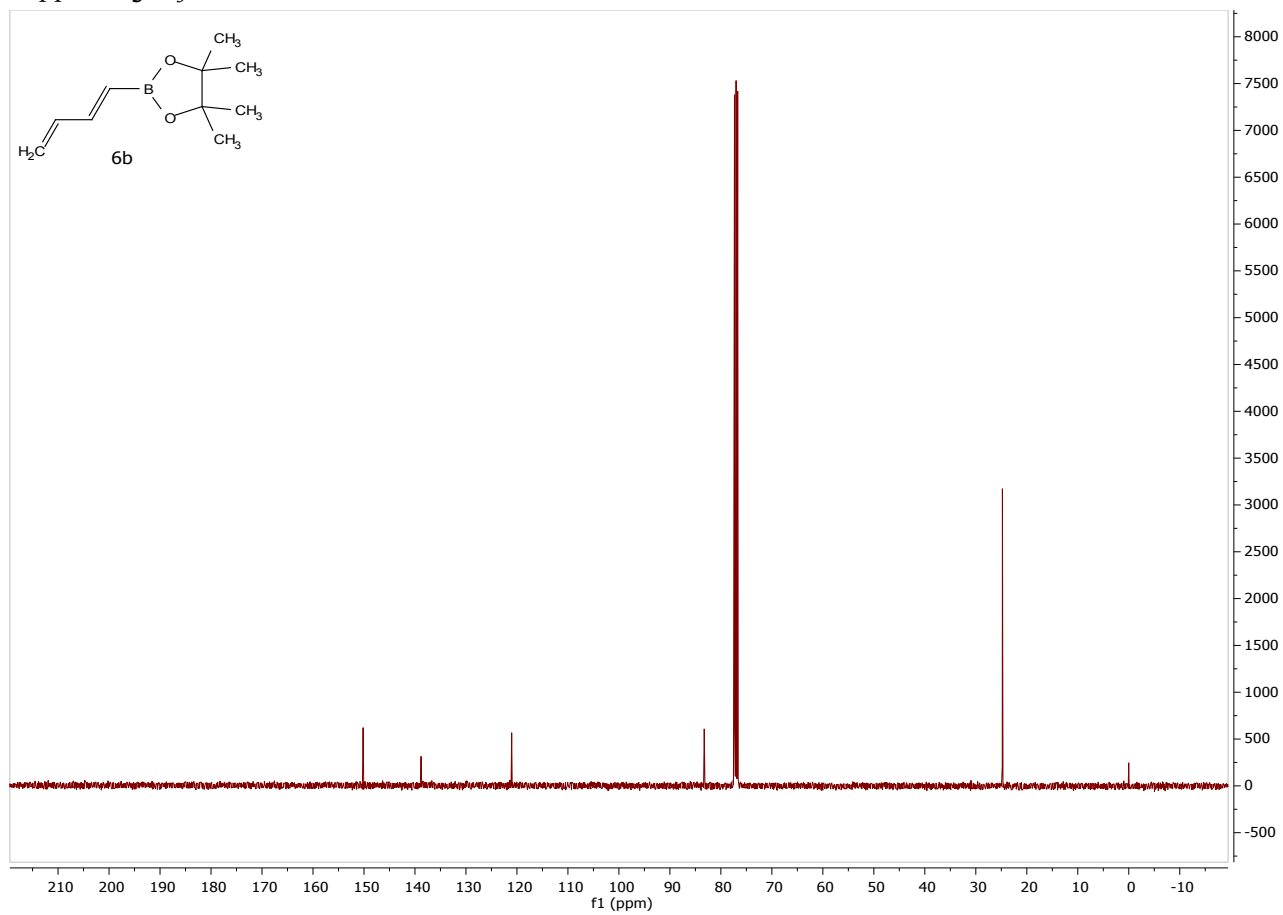
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- 2) Coombs, J. R.; Zhang, L.; Morken, J. P., *Org. Lett.*, **2015**, *17*, 1708-1711.
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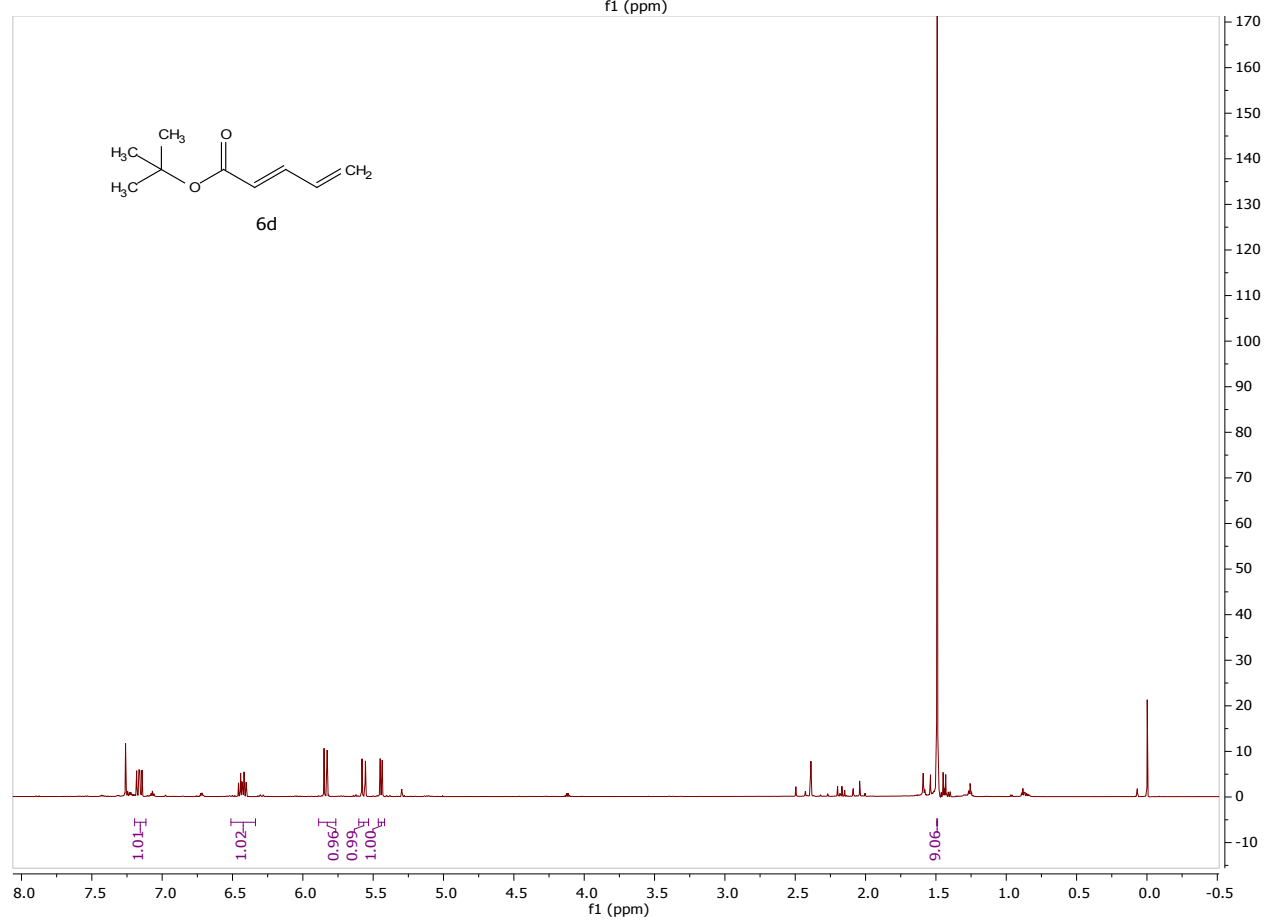
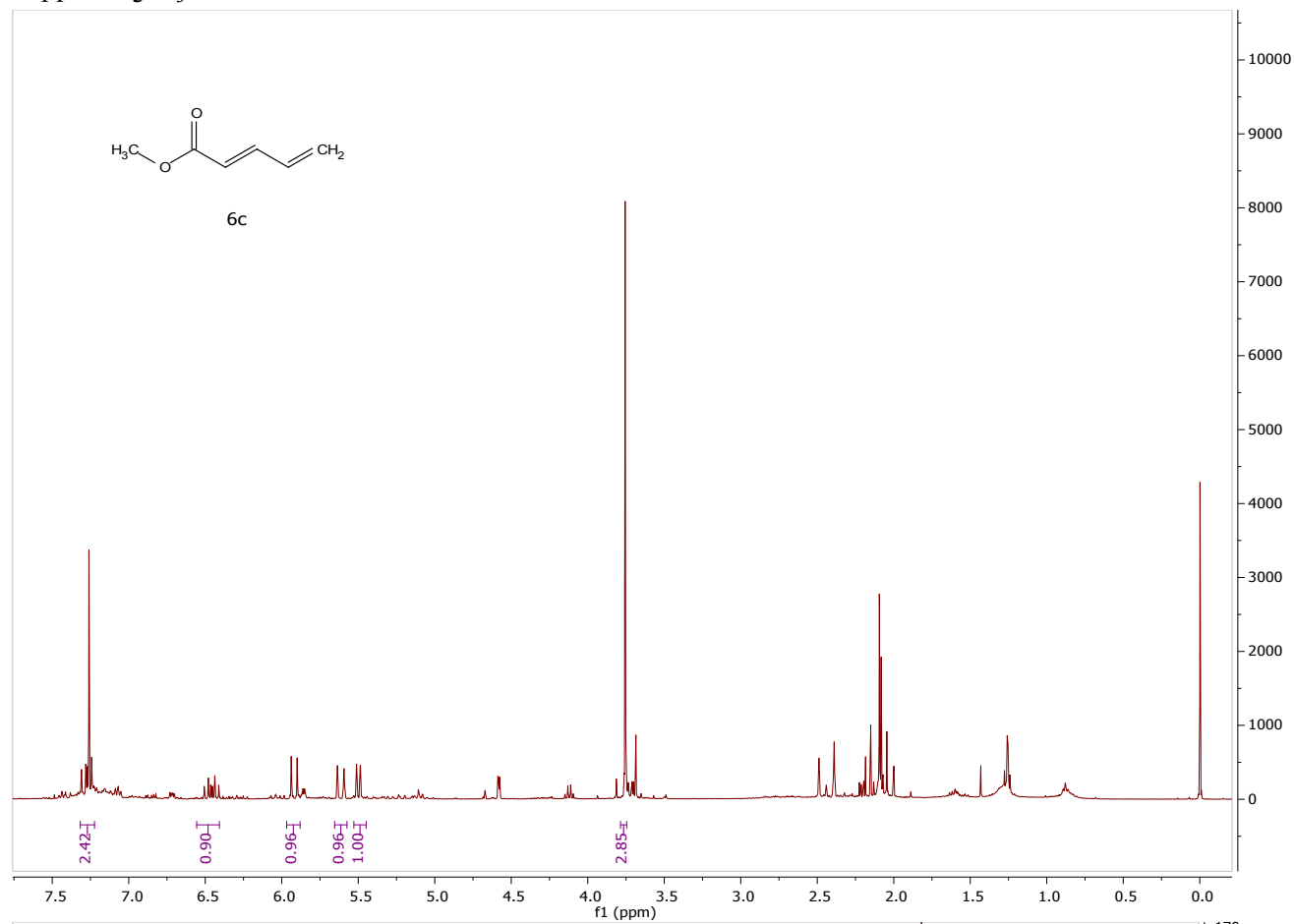
### 3. $^1\text{H}$ , $^{13}\text{C}$ and 2D NMR Spectra

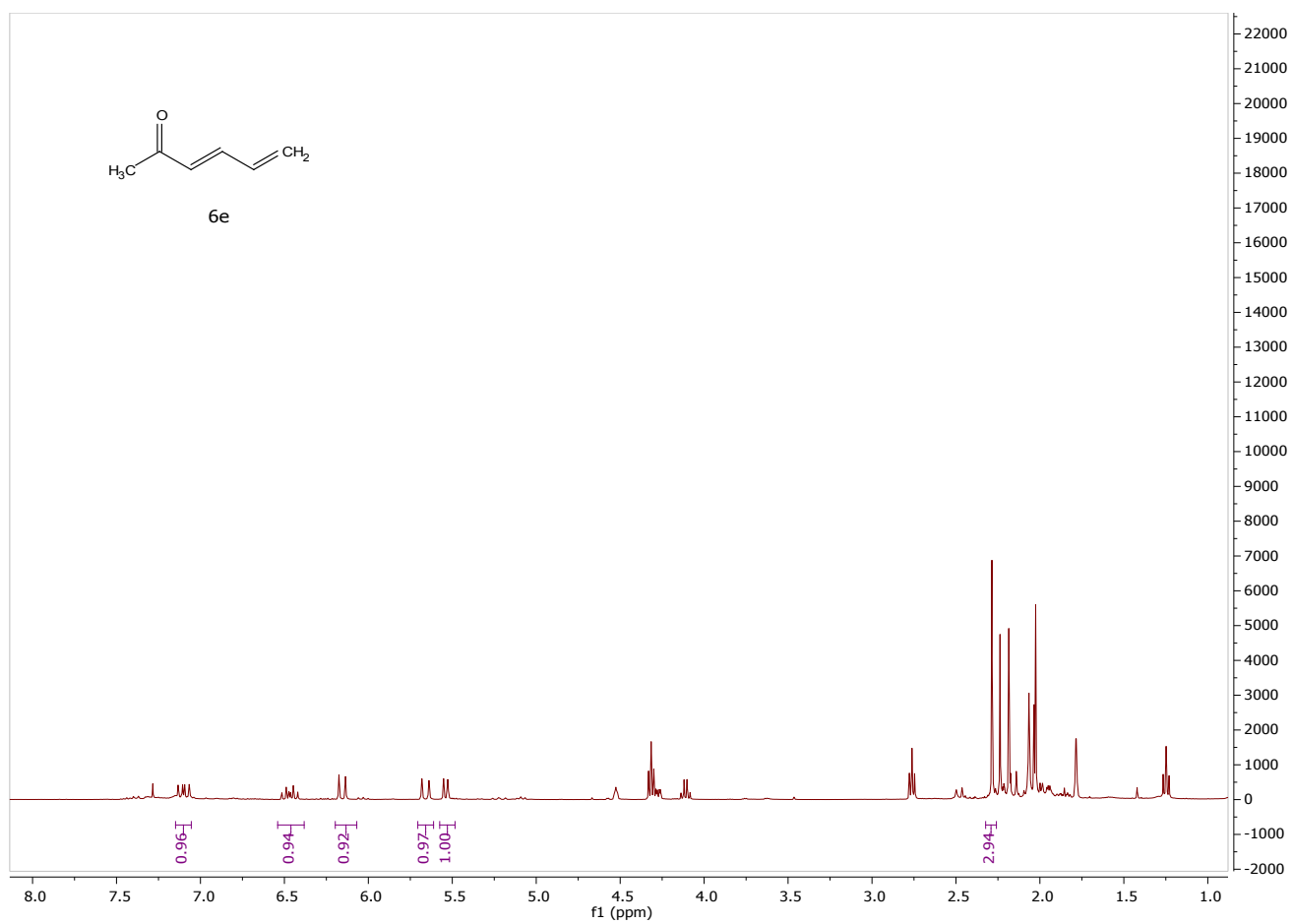
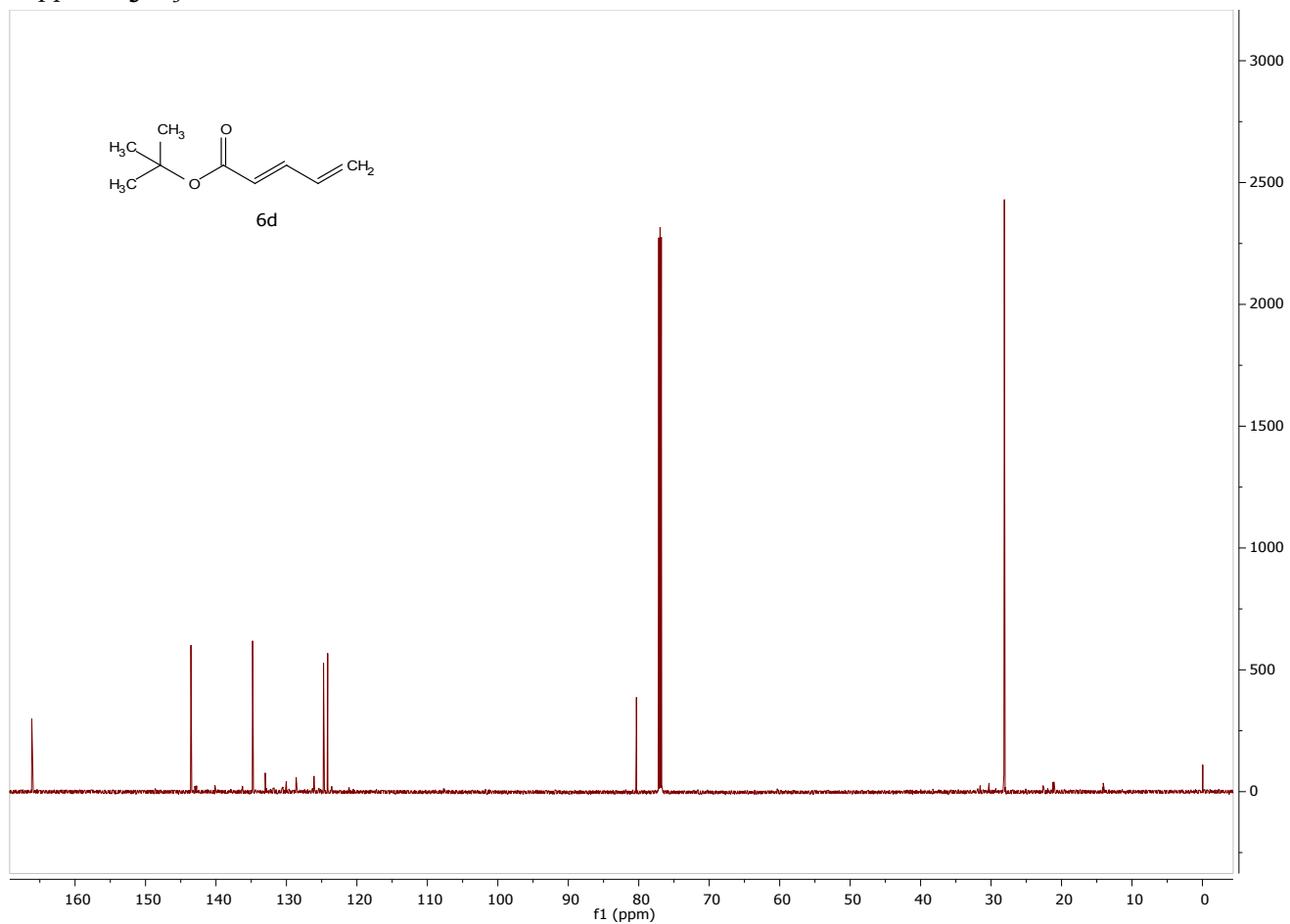


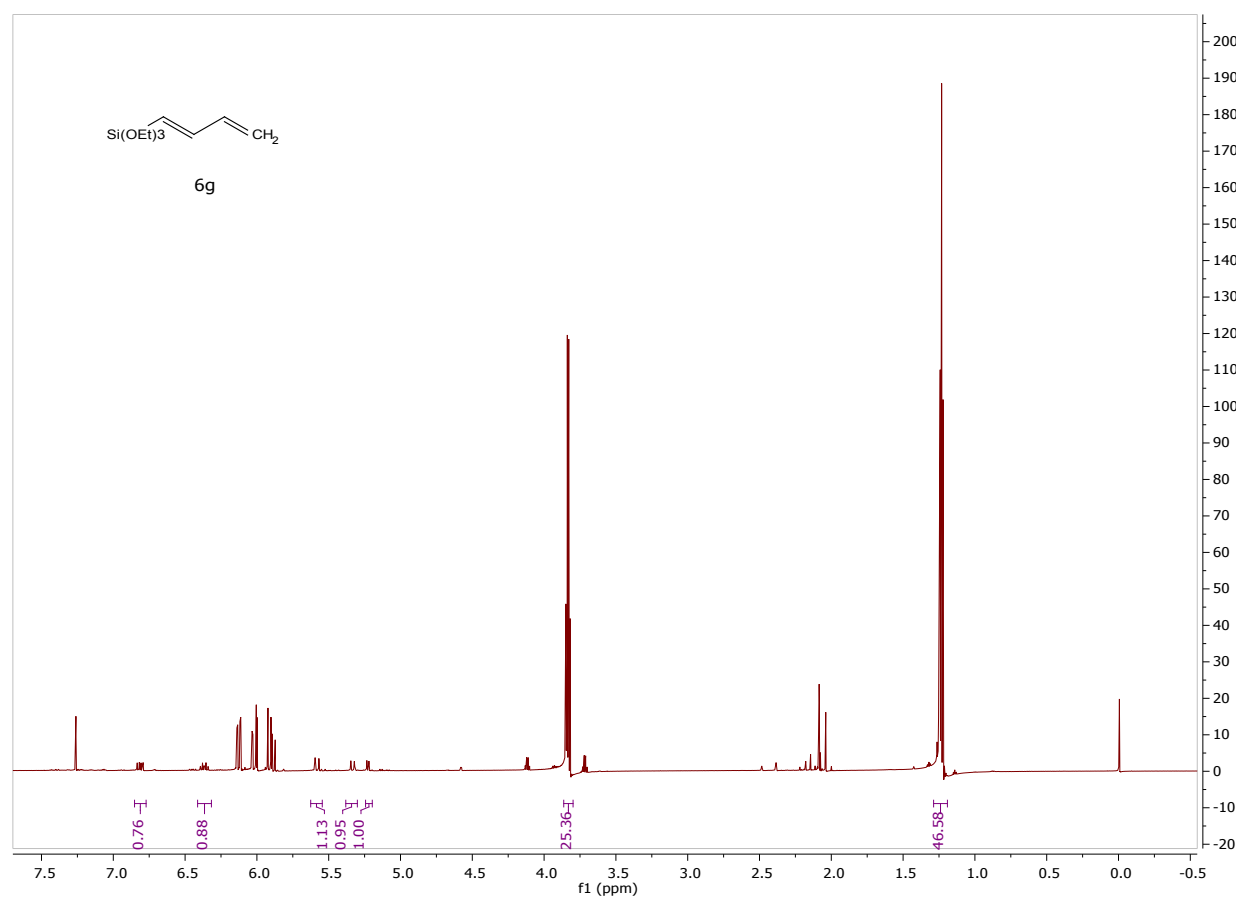
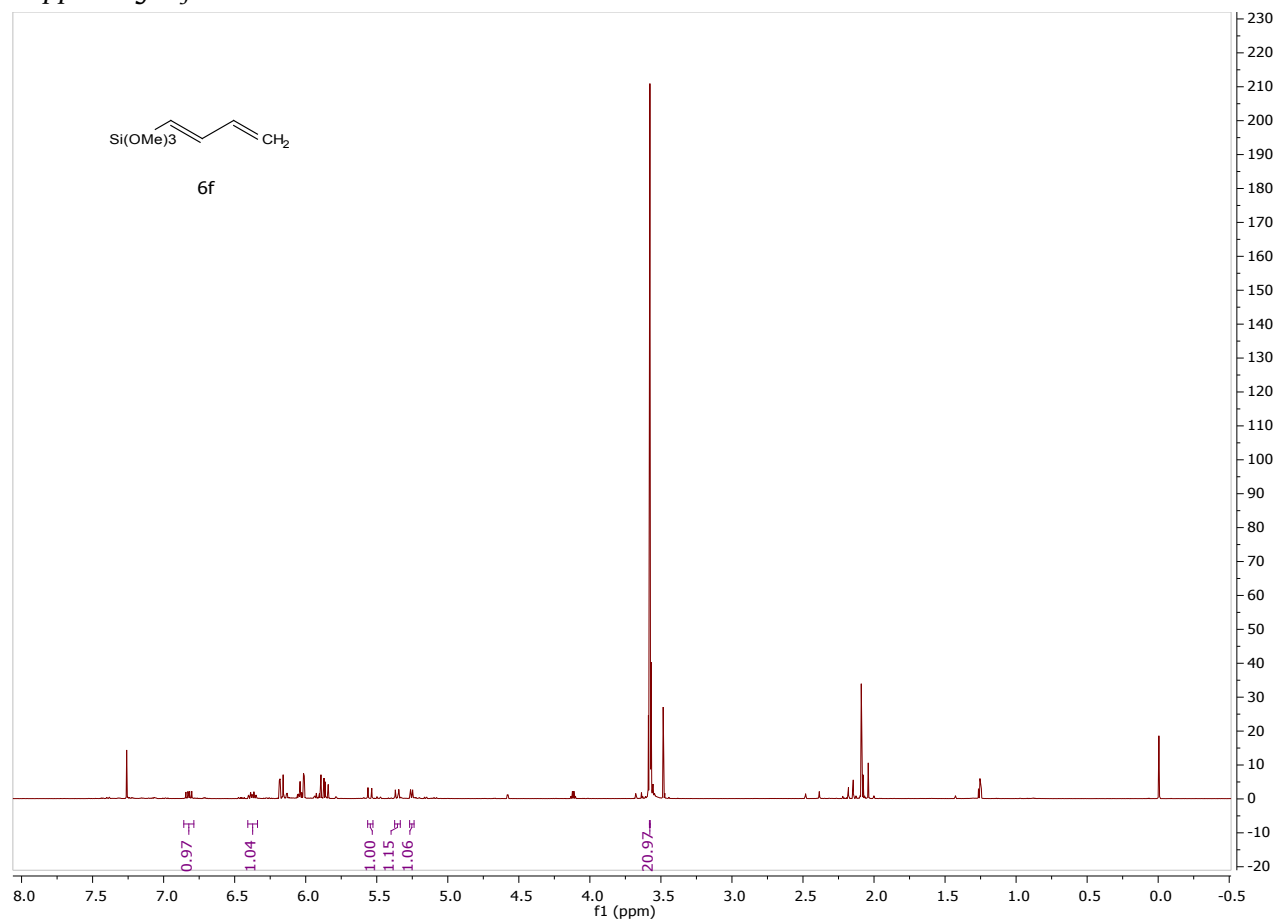


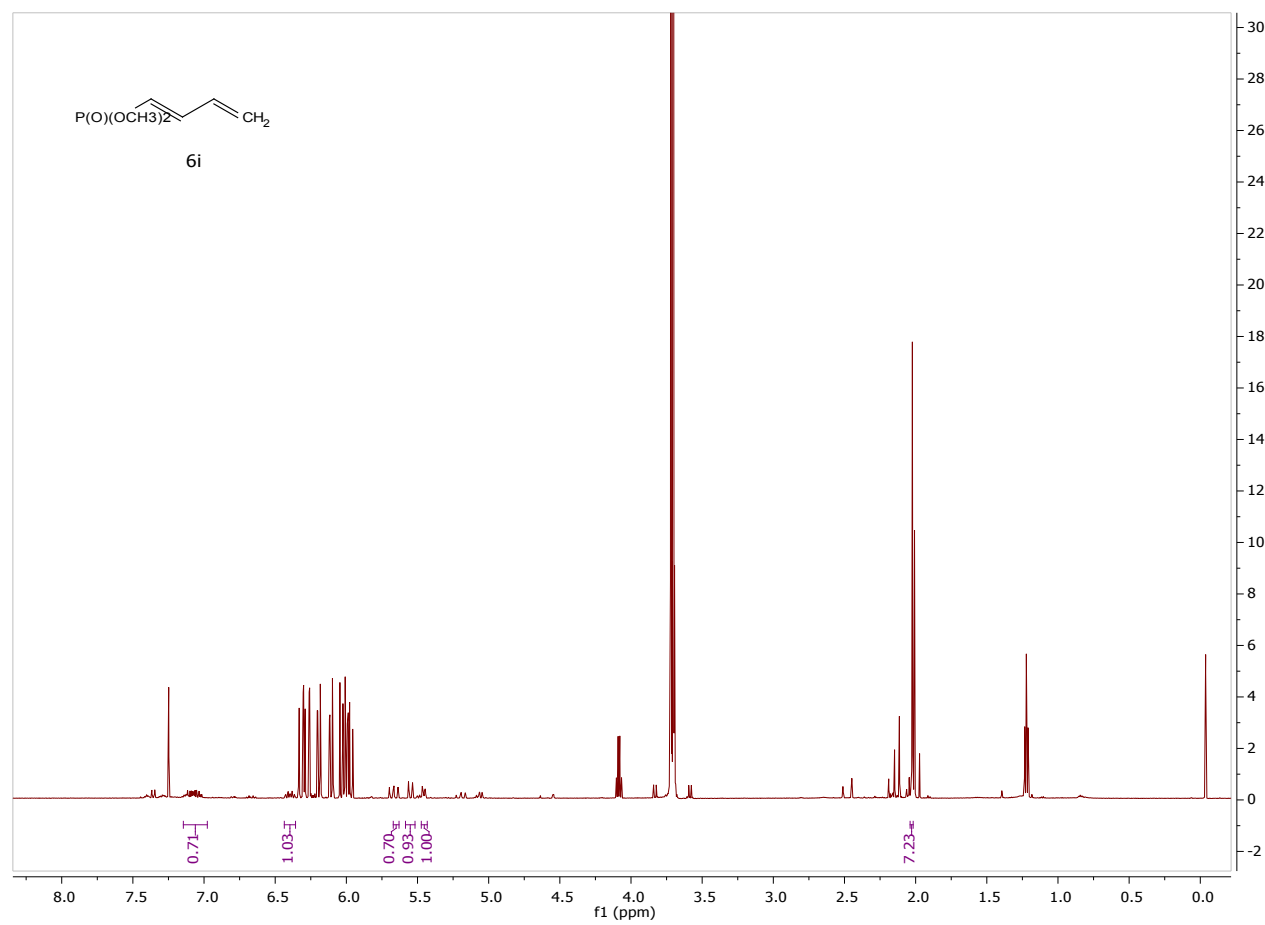
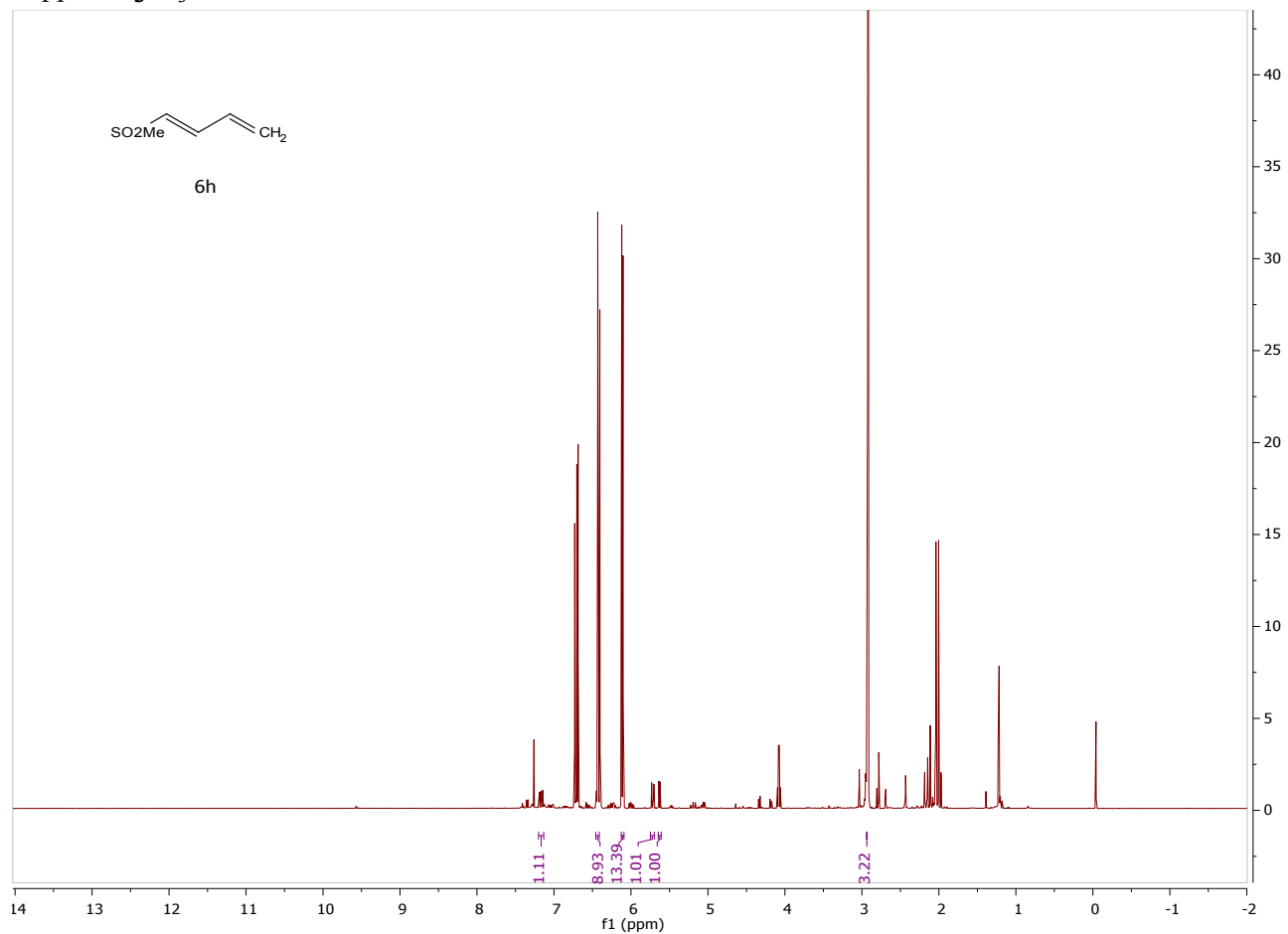


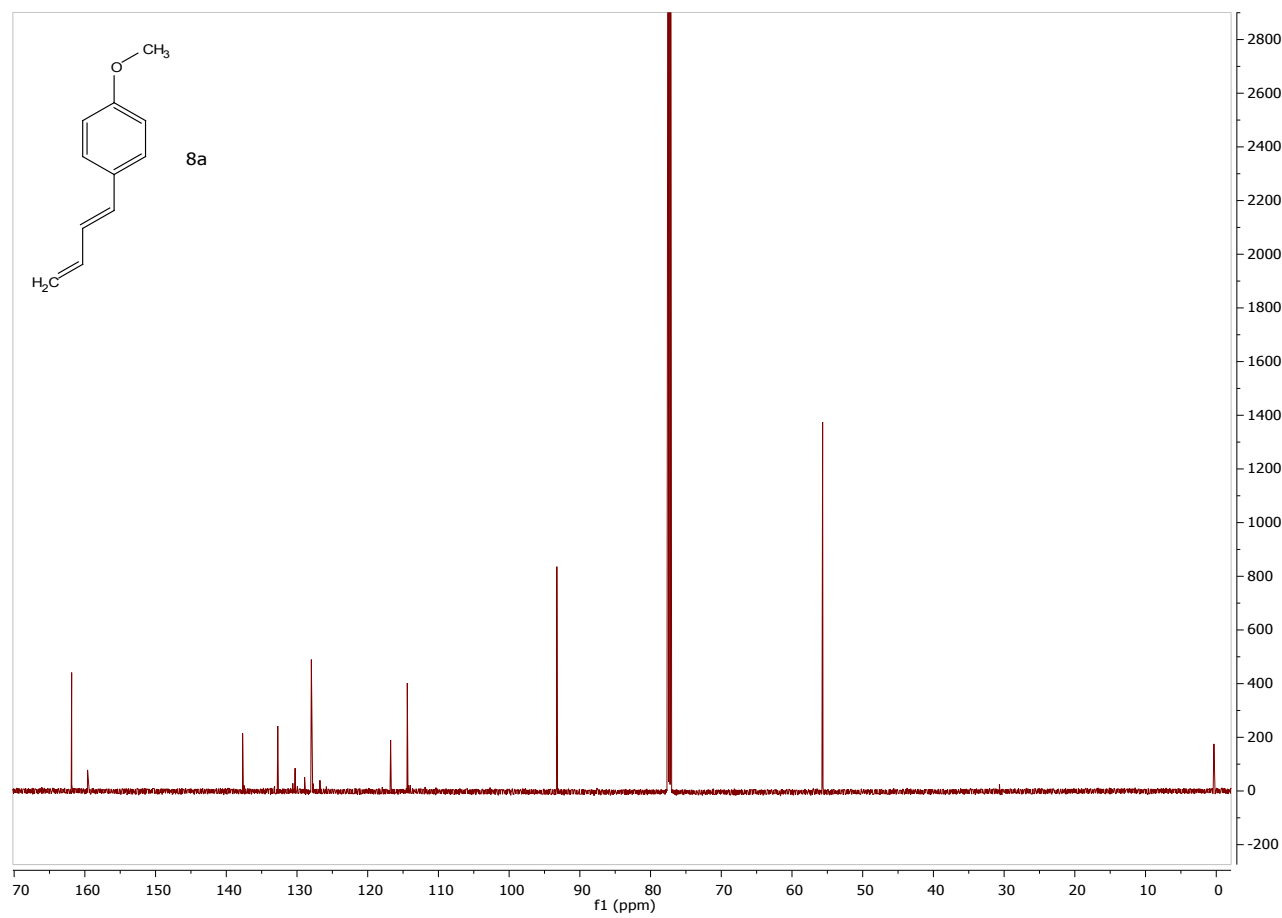
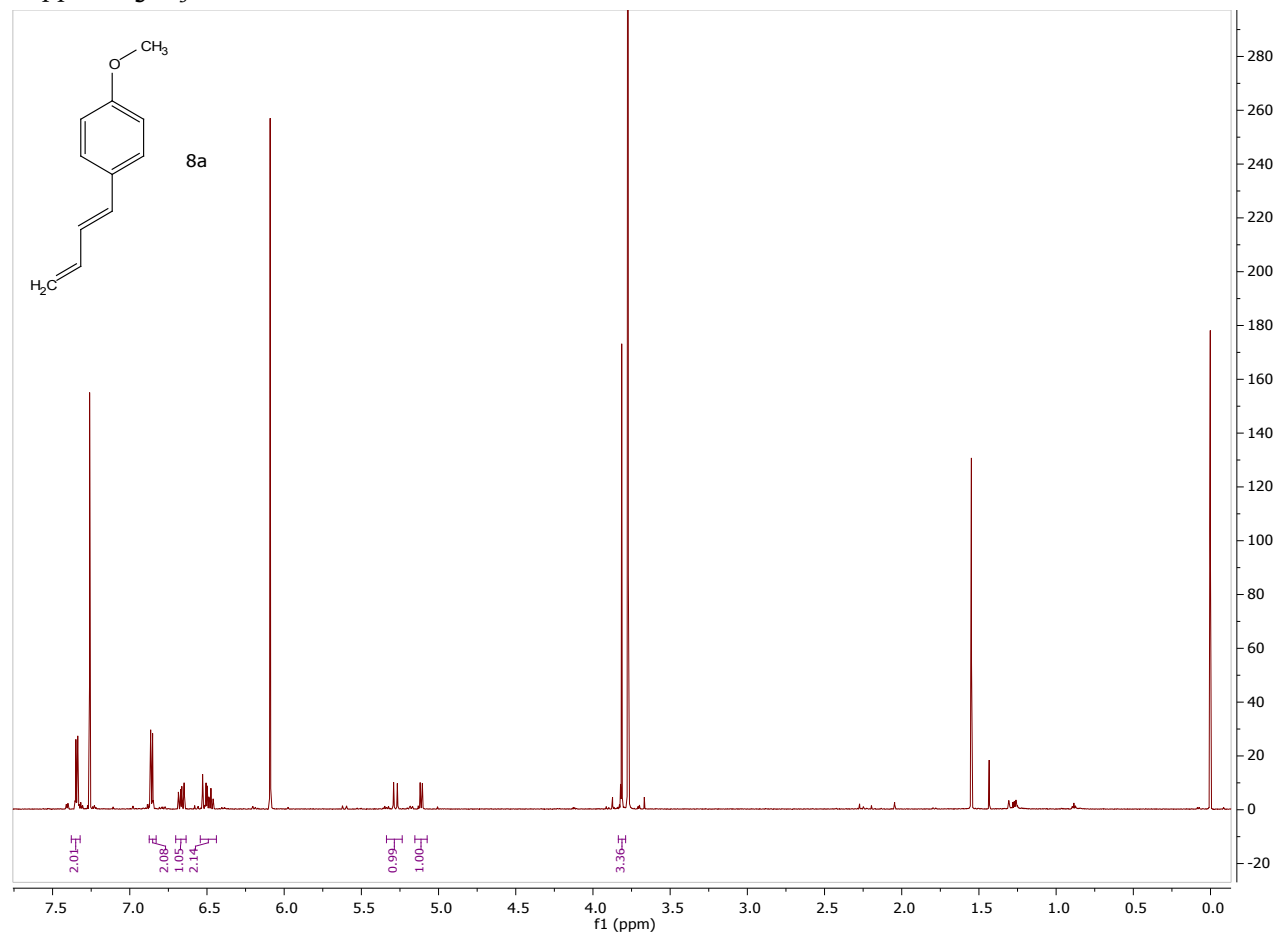


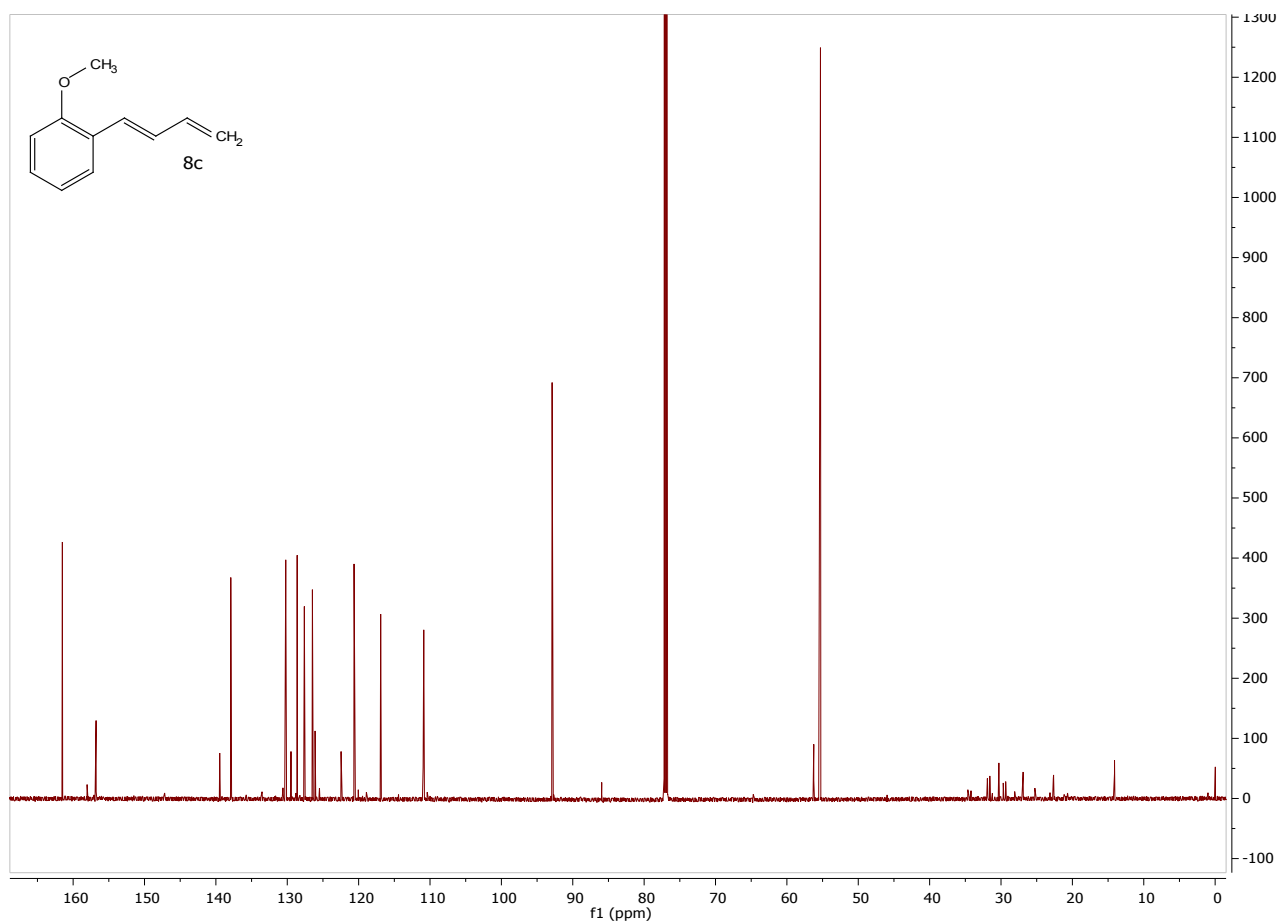
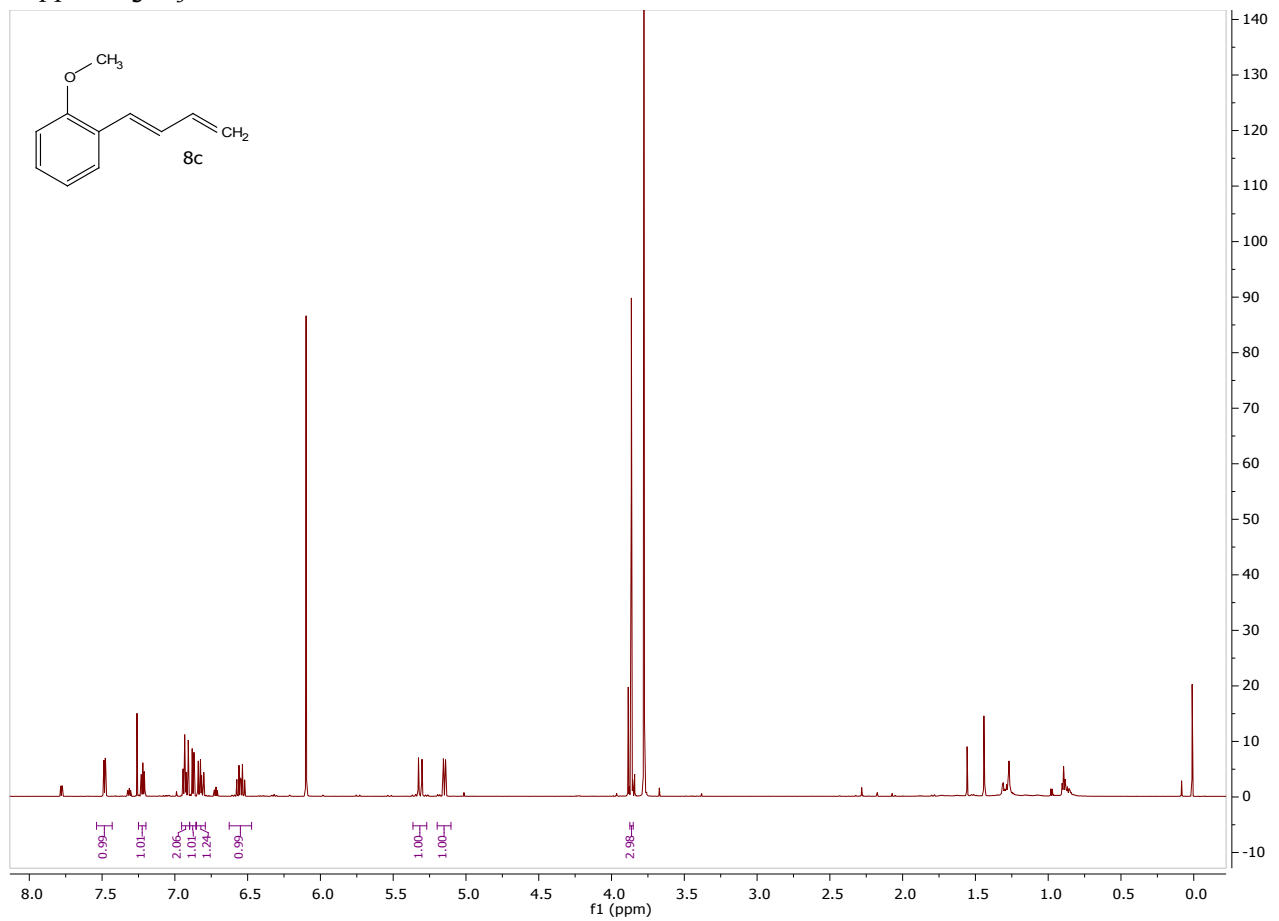


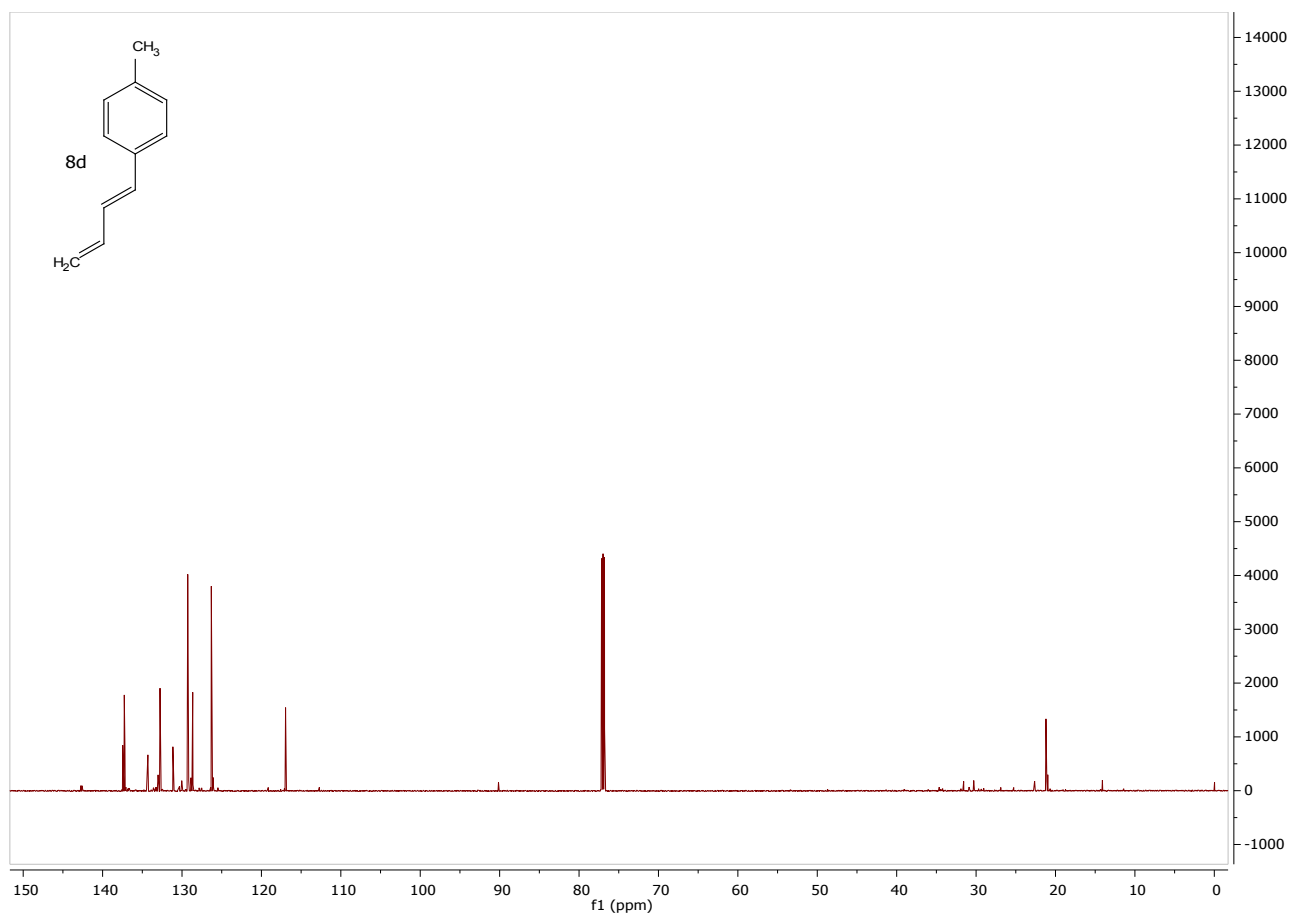
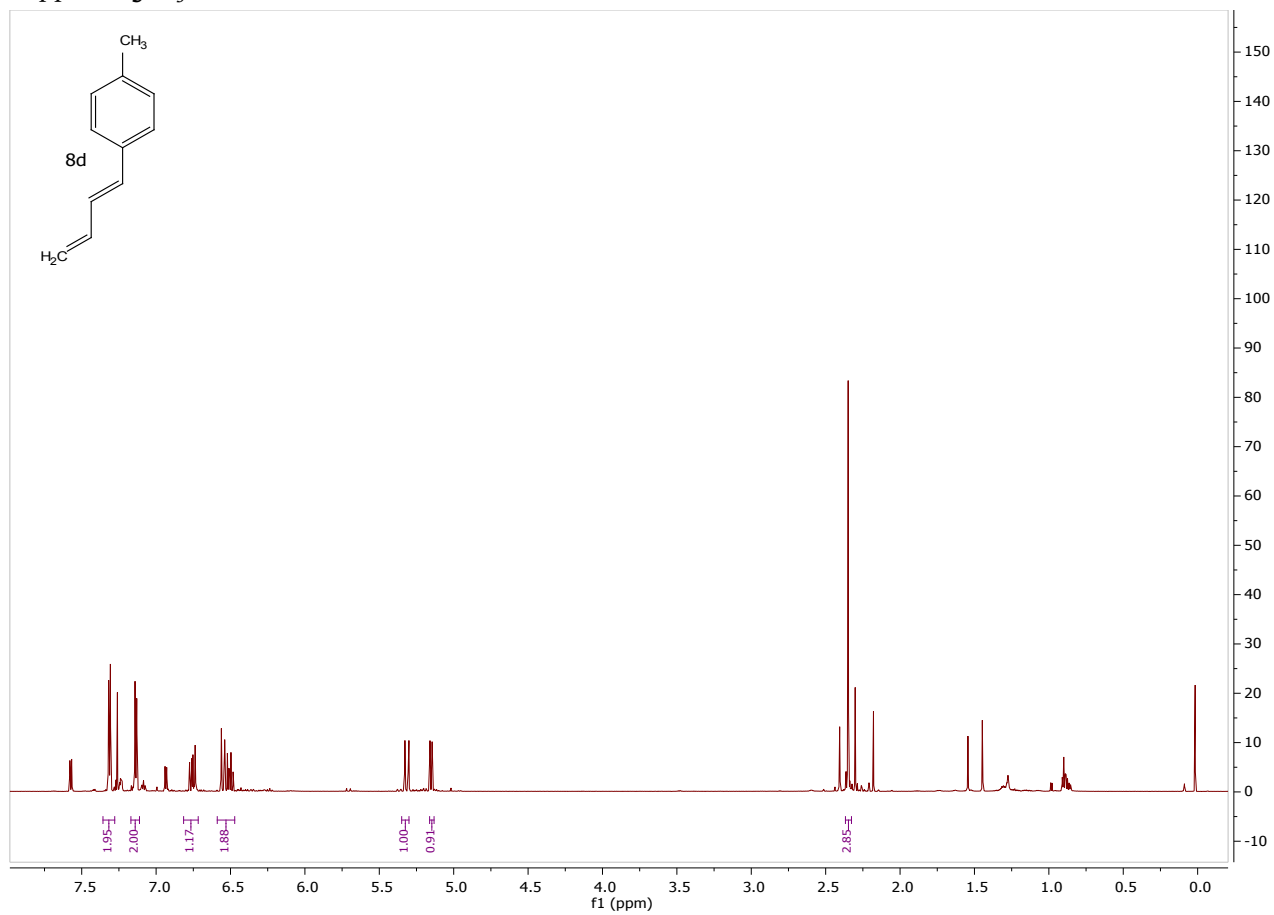


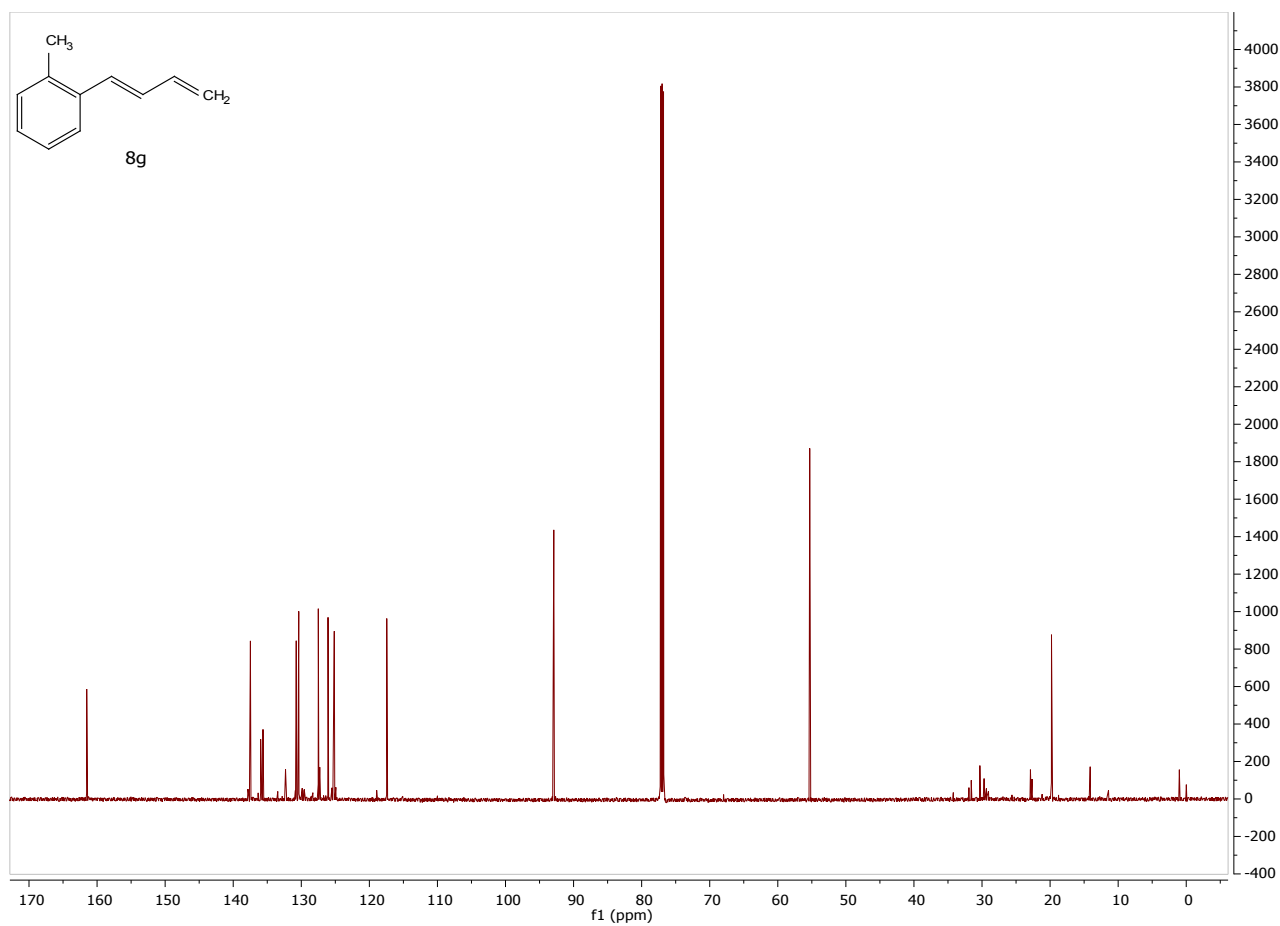
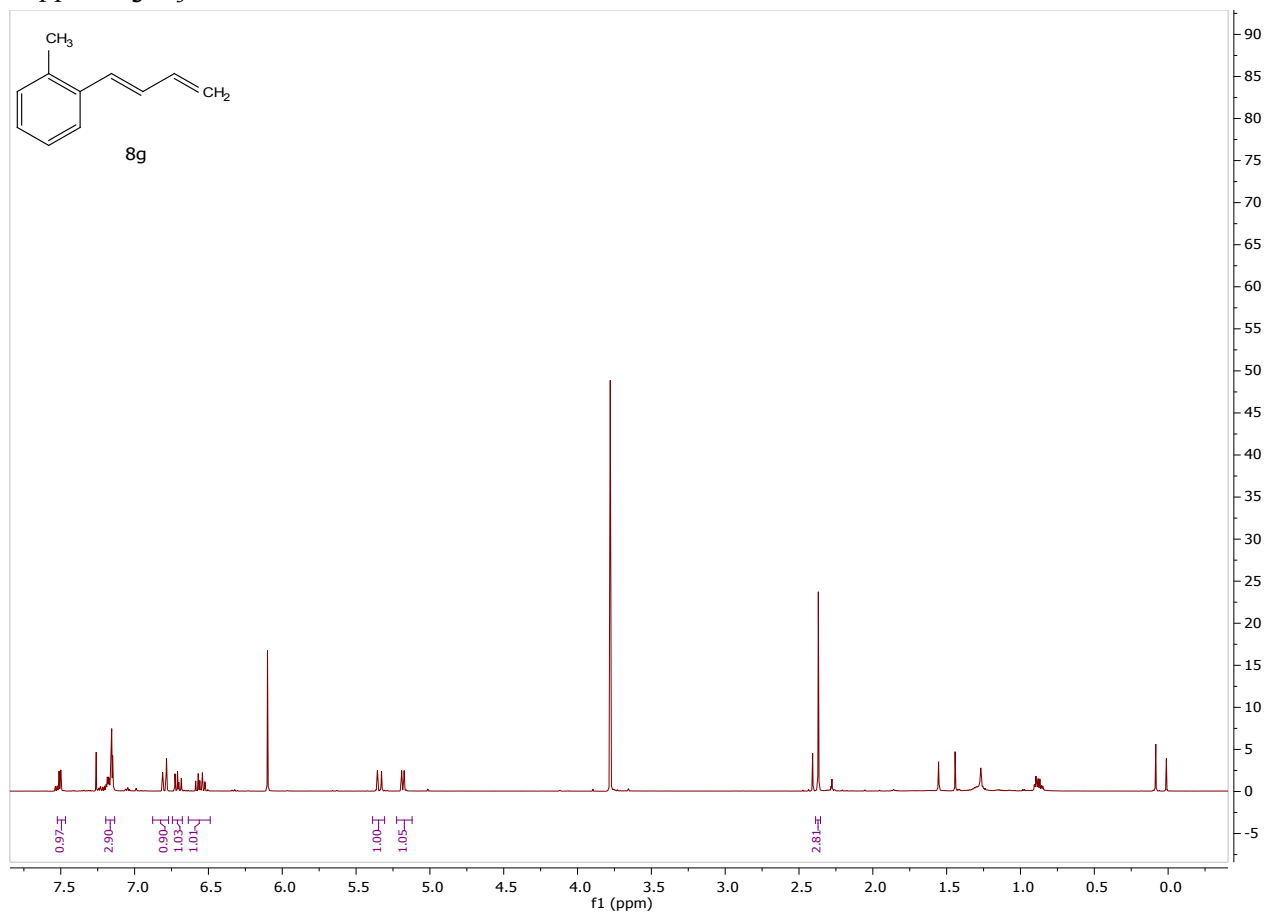




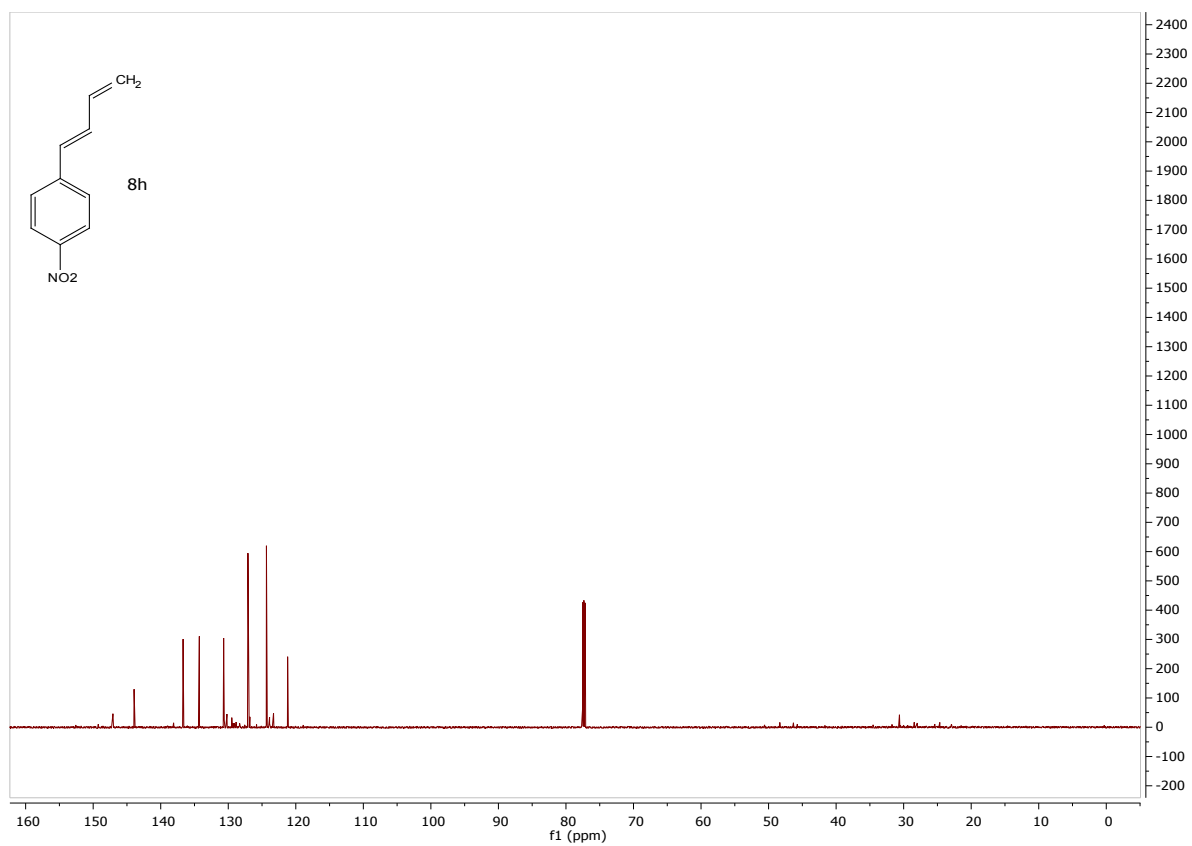
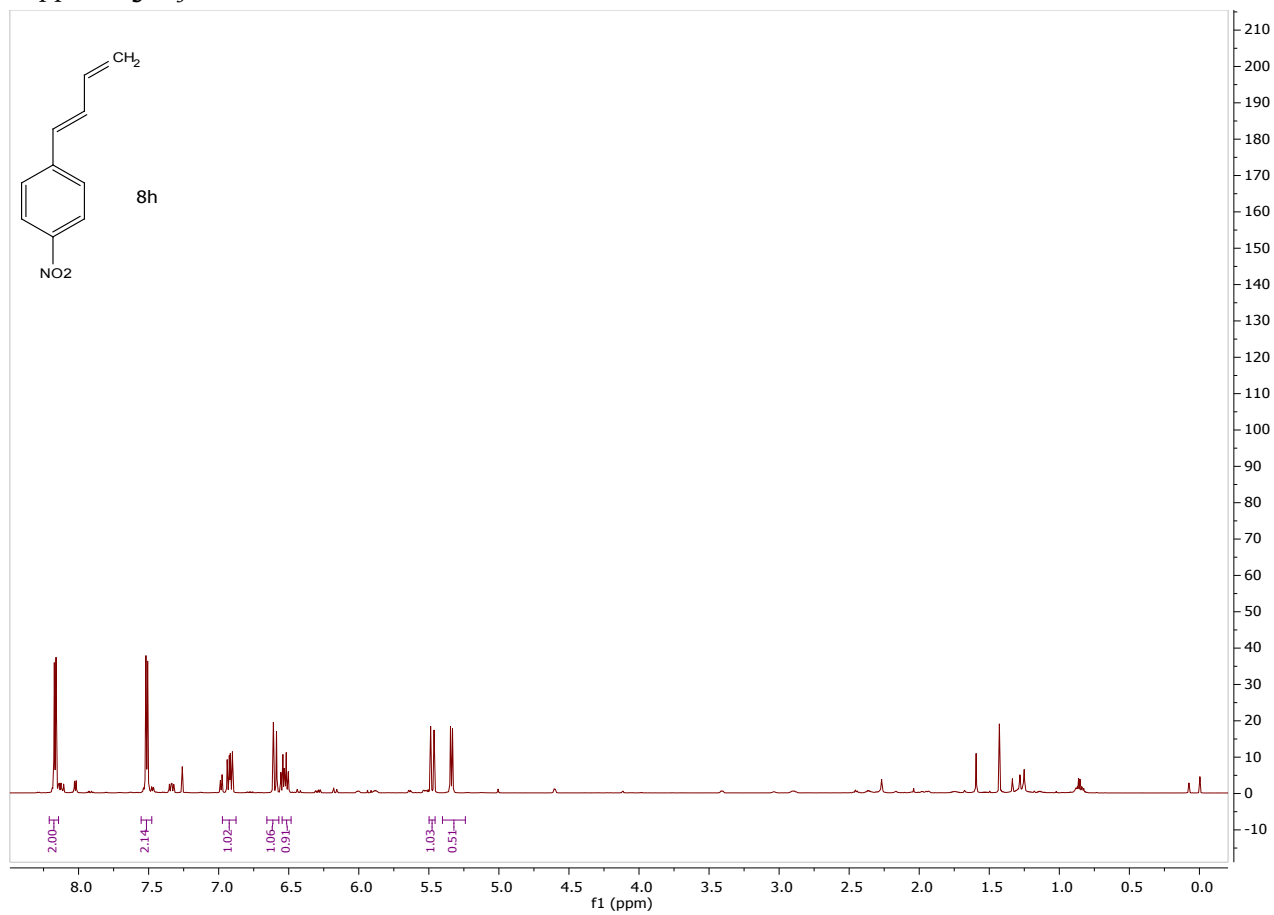


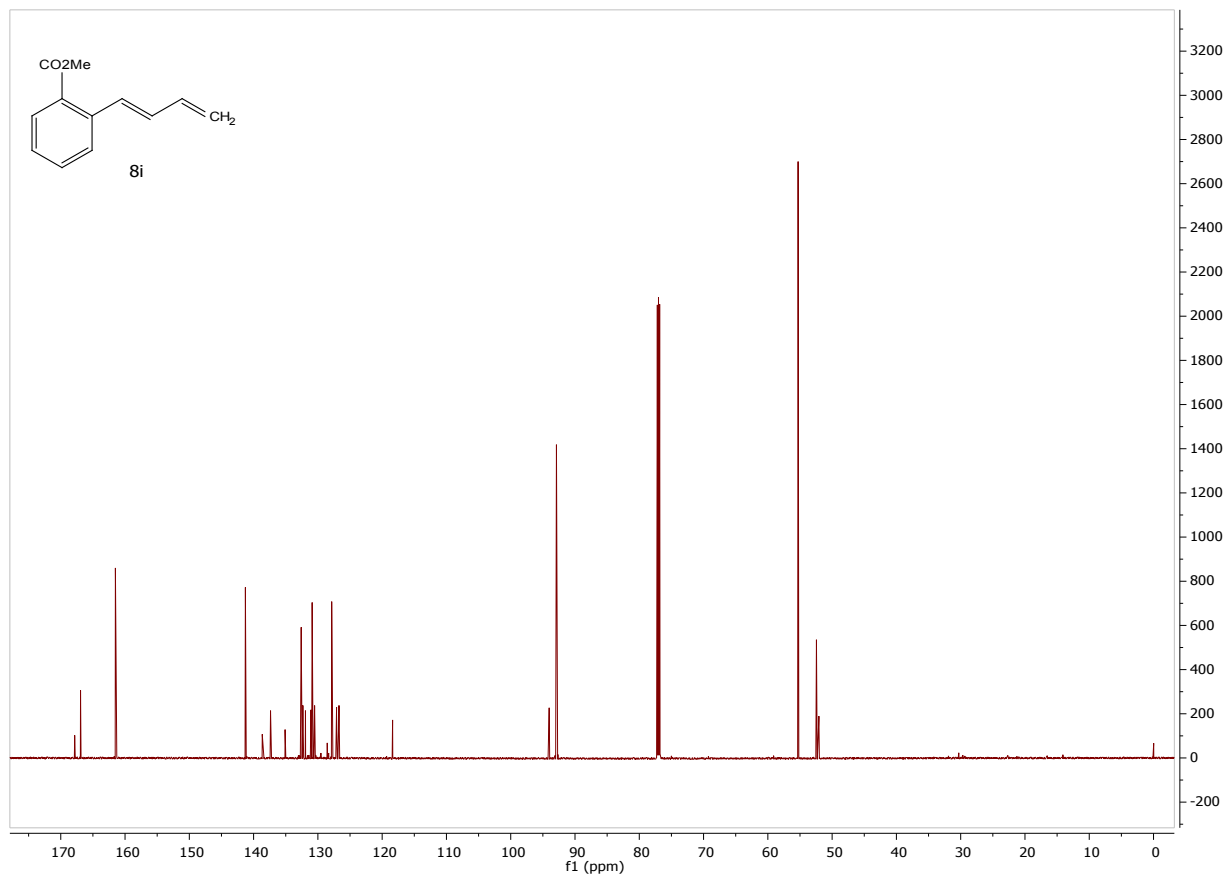
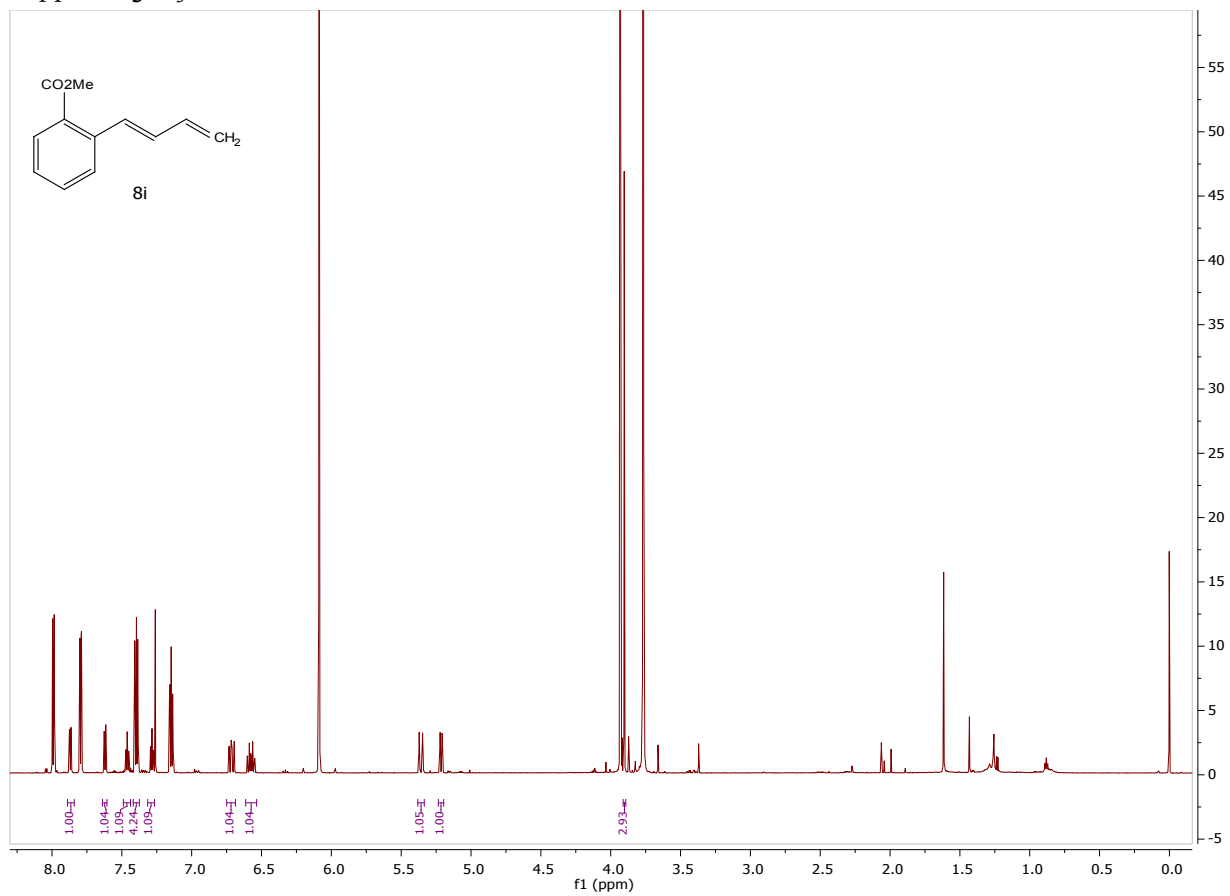


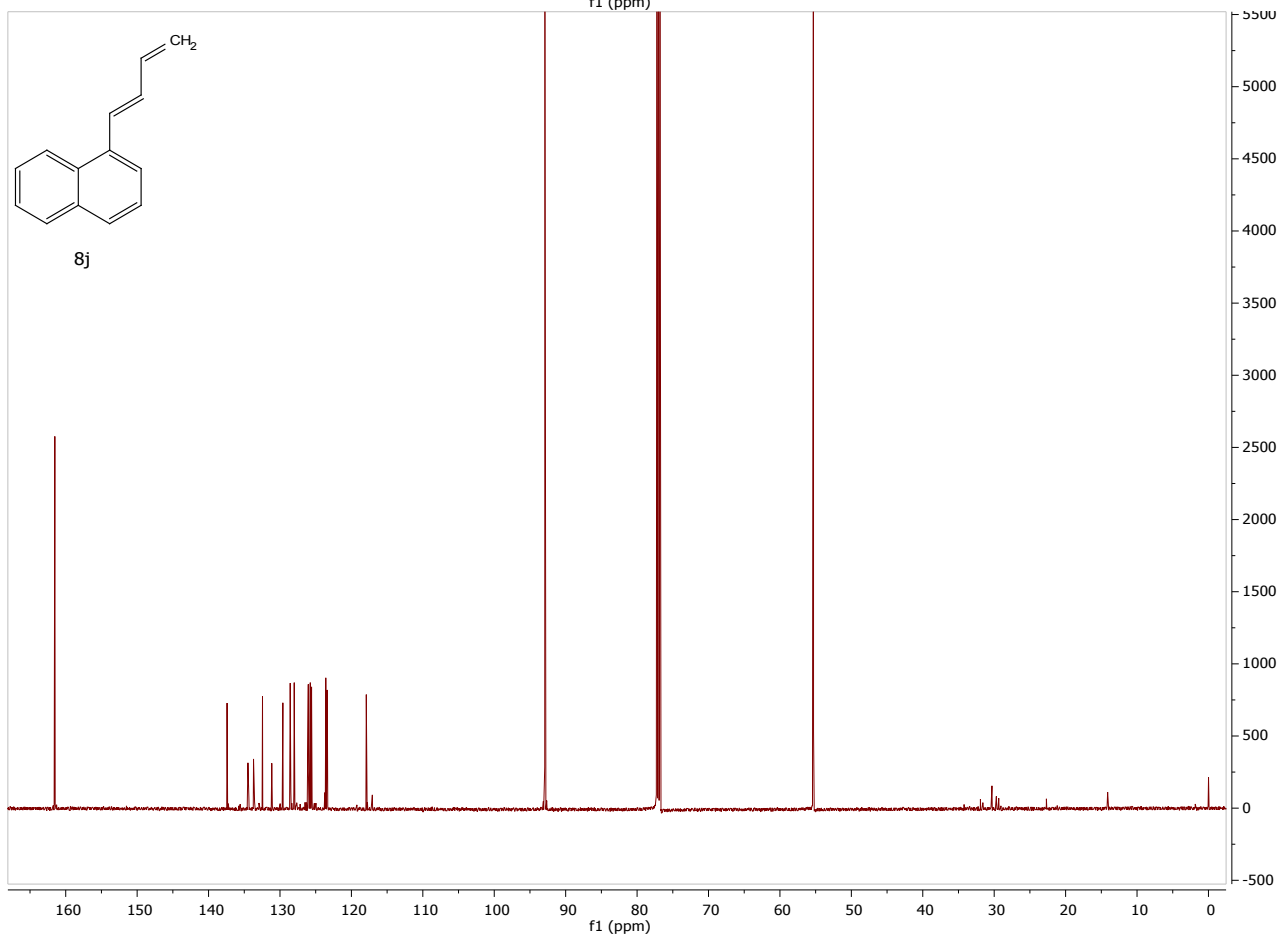
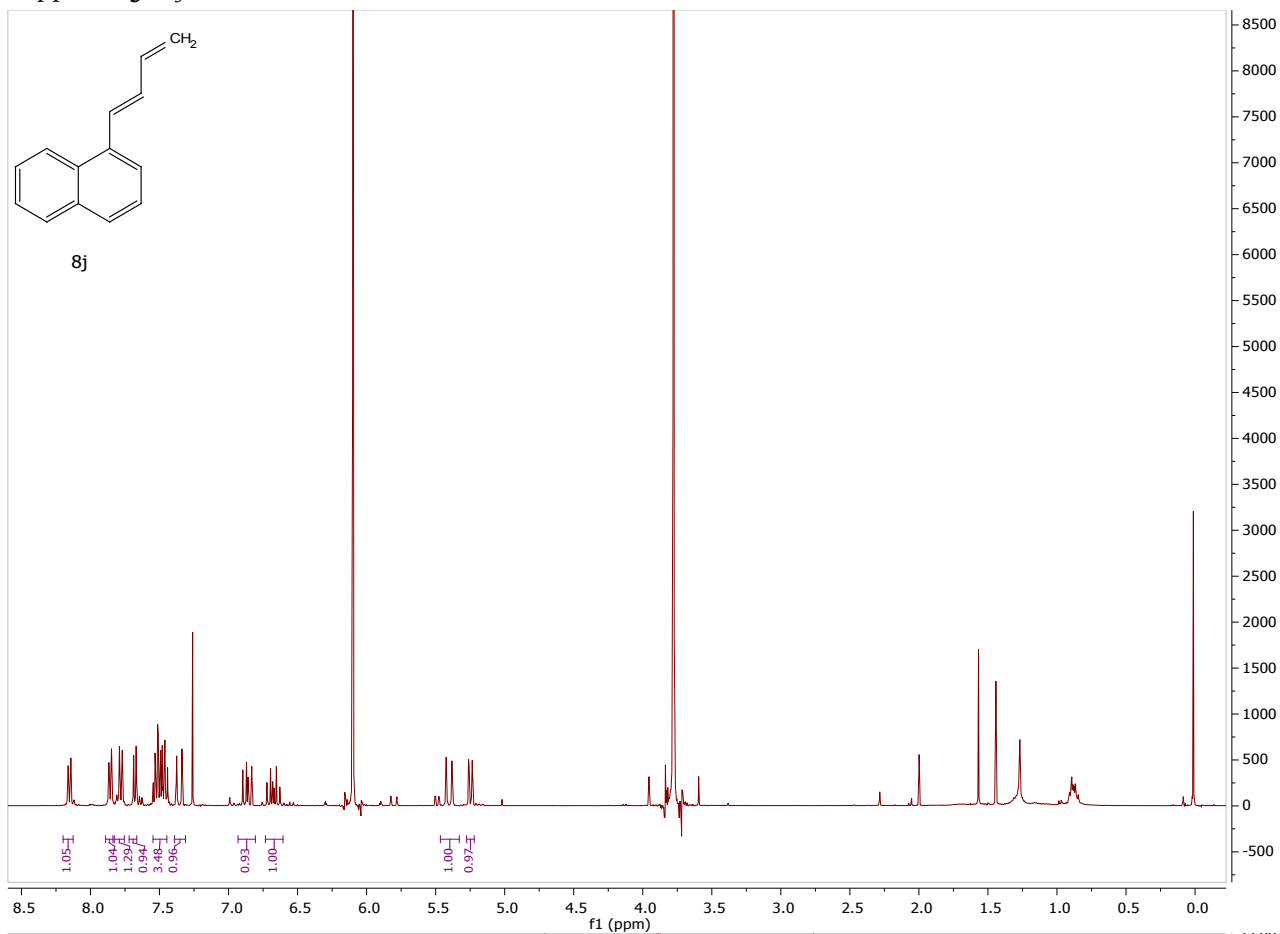


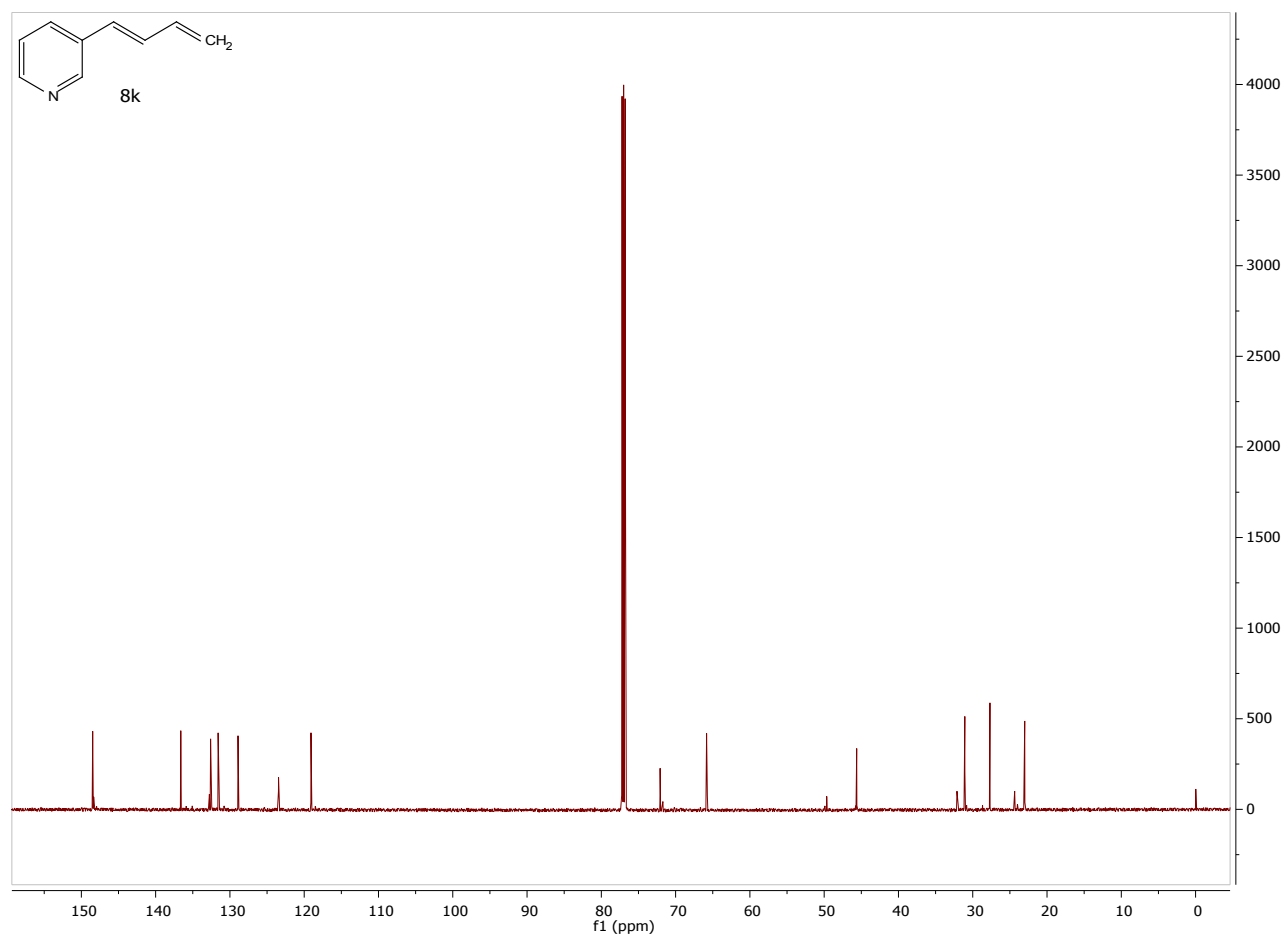
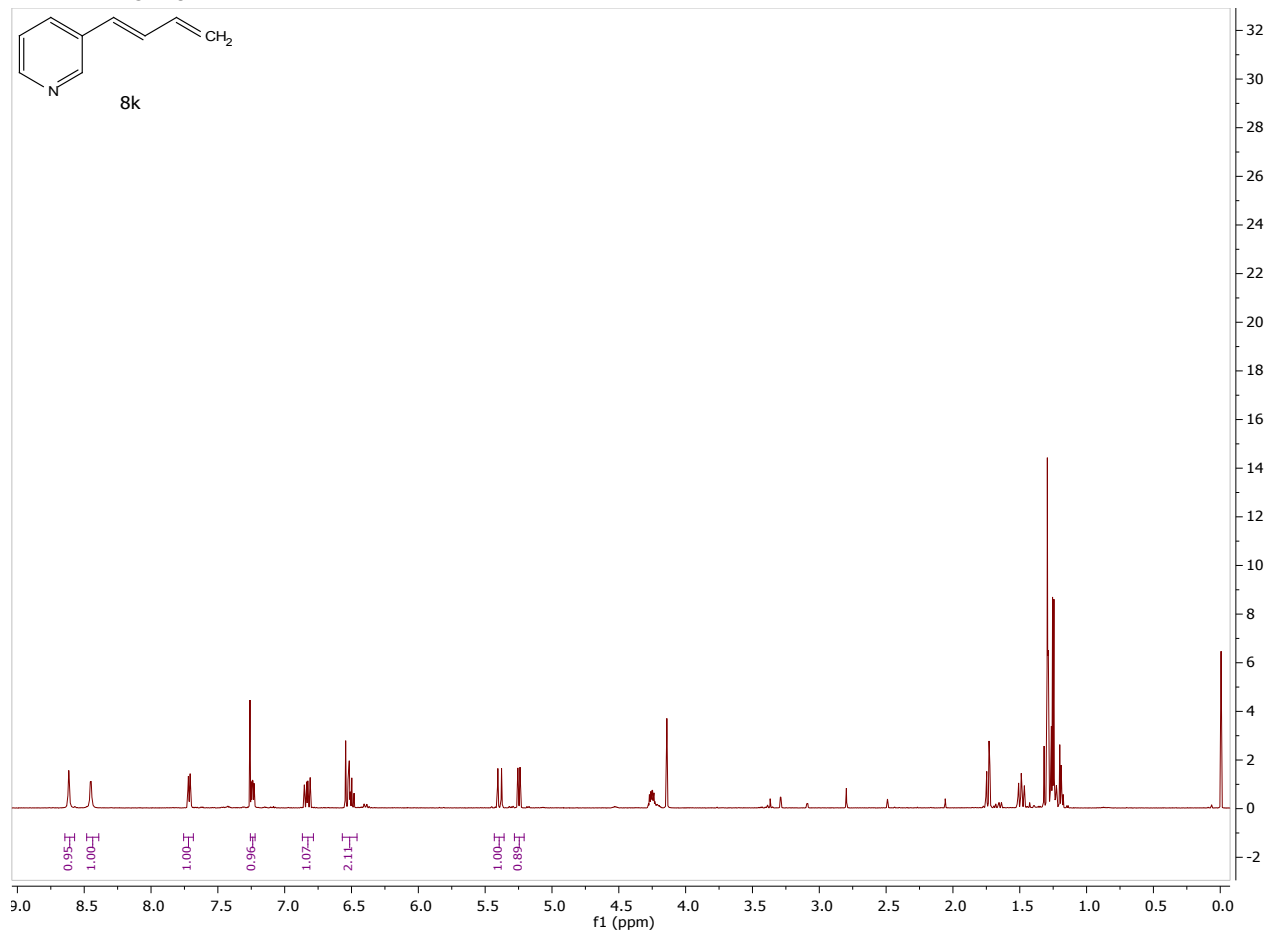


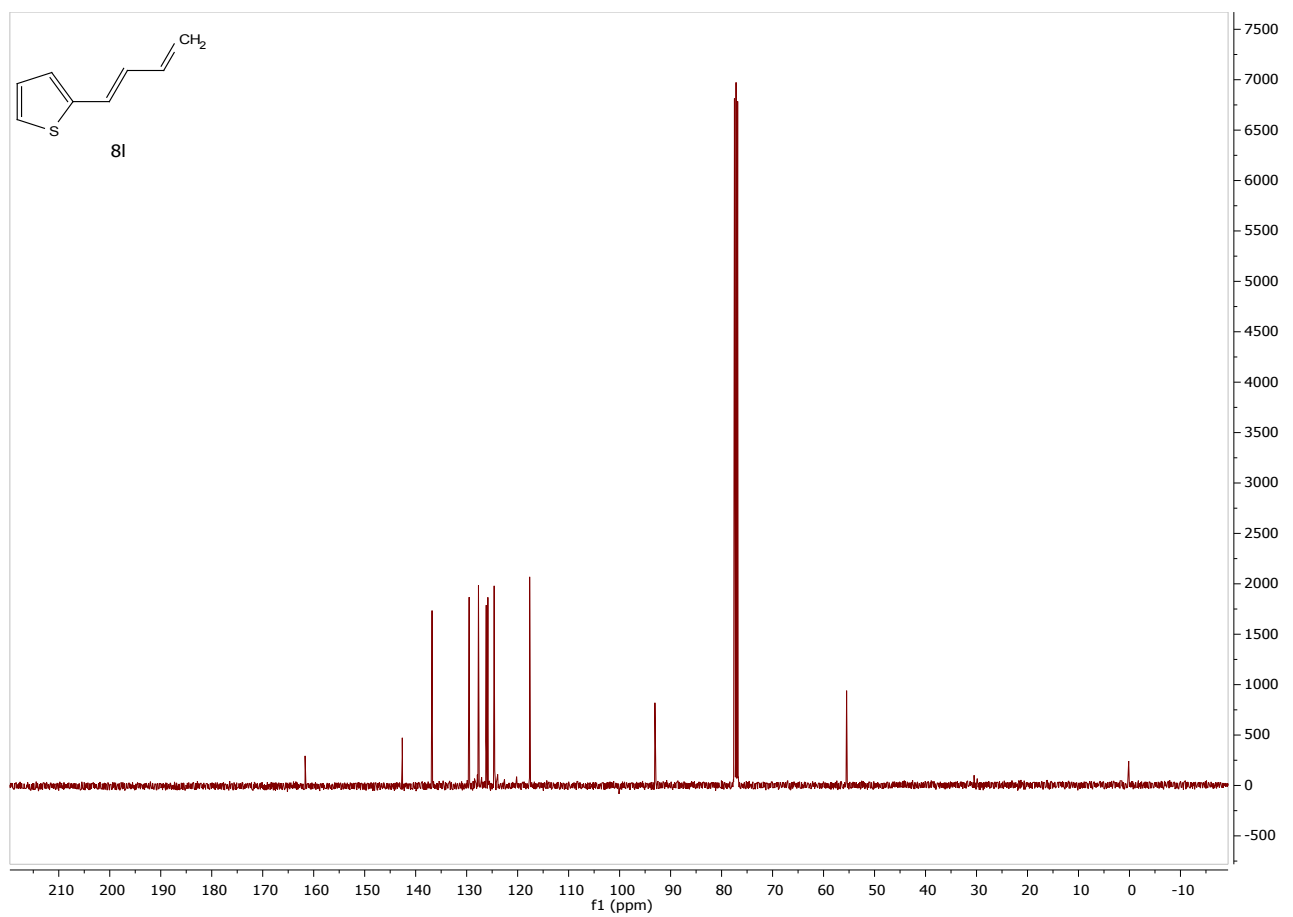
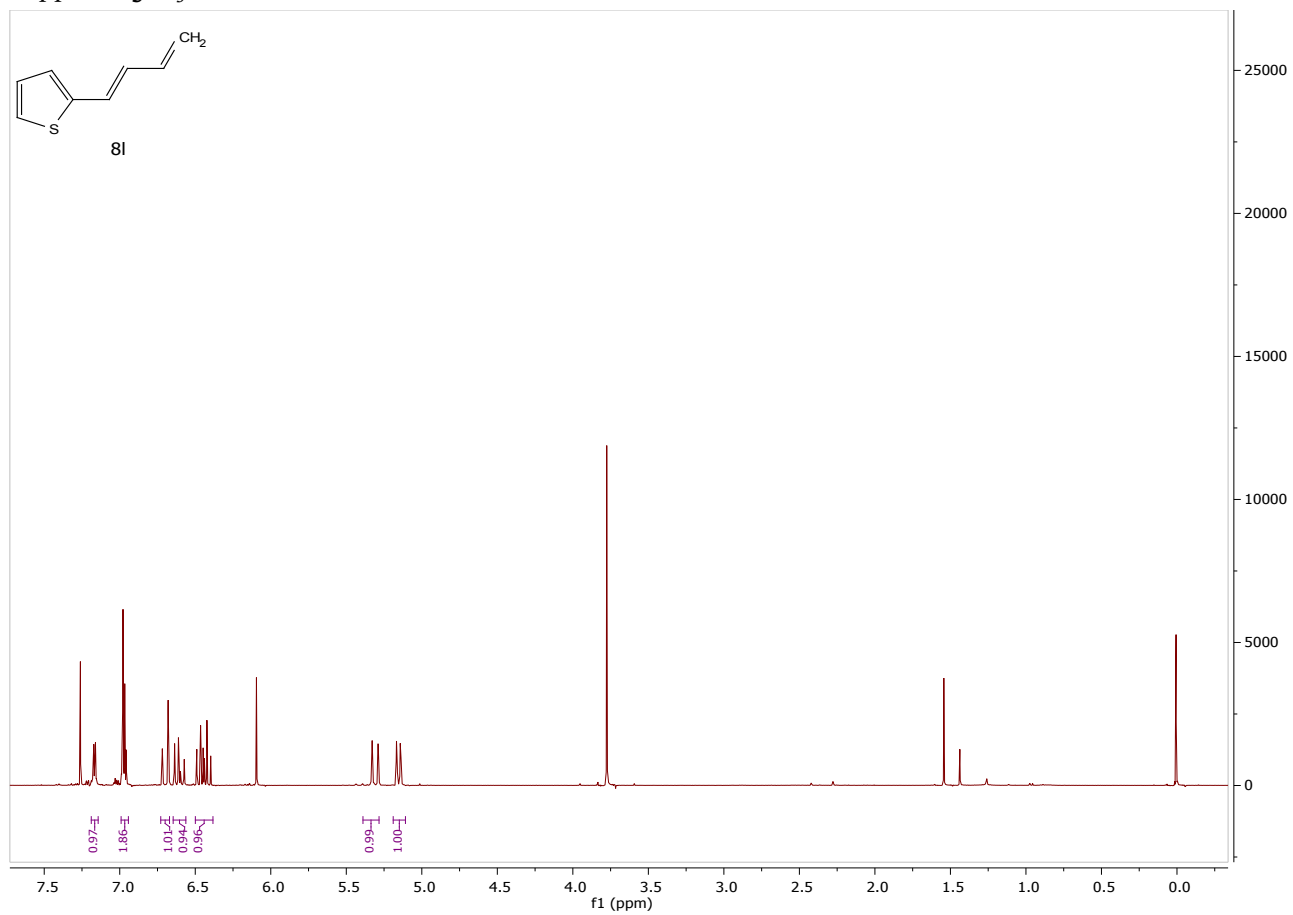


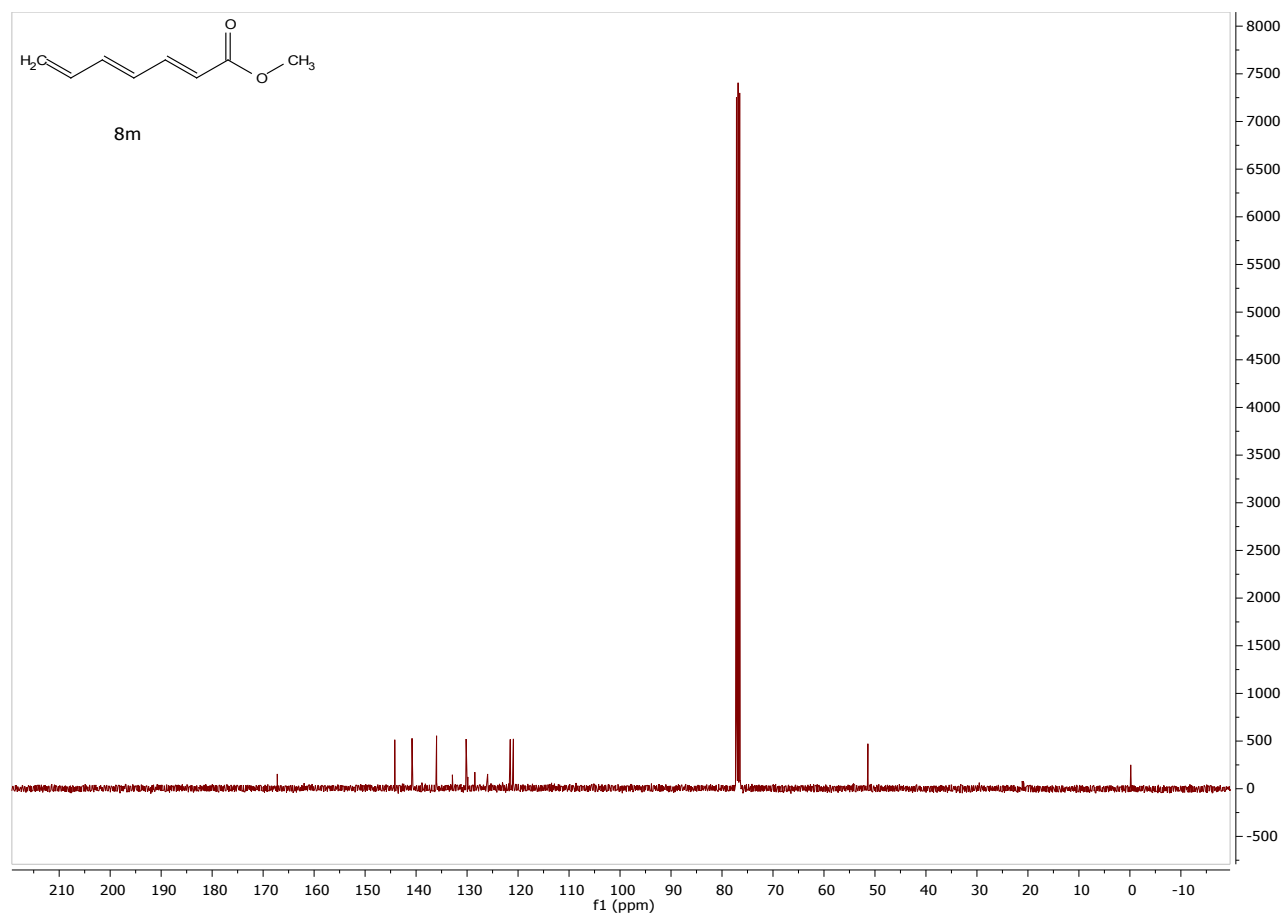
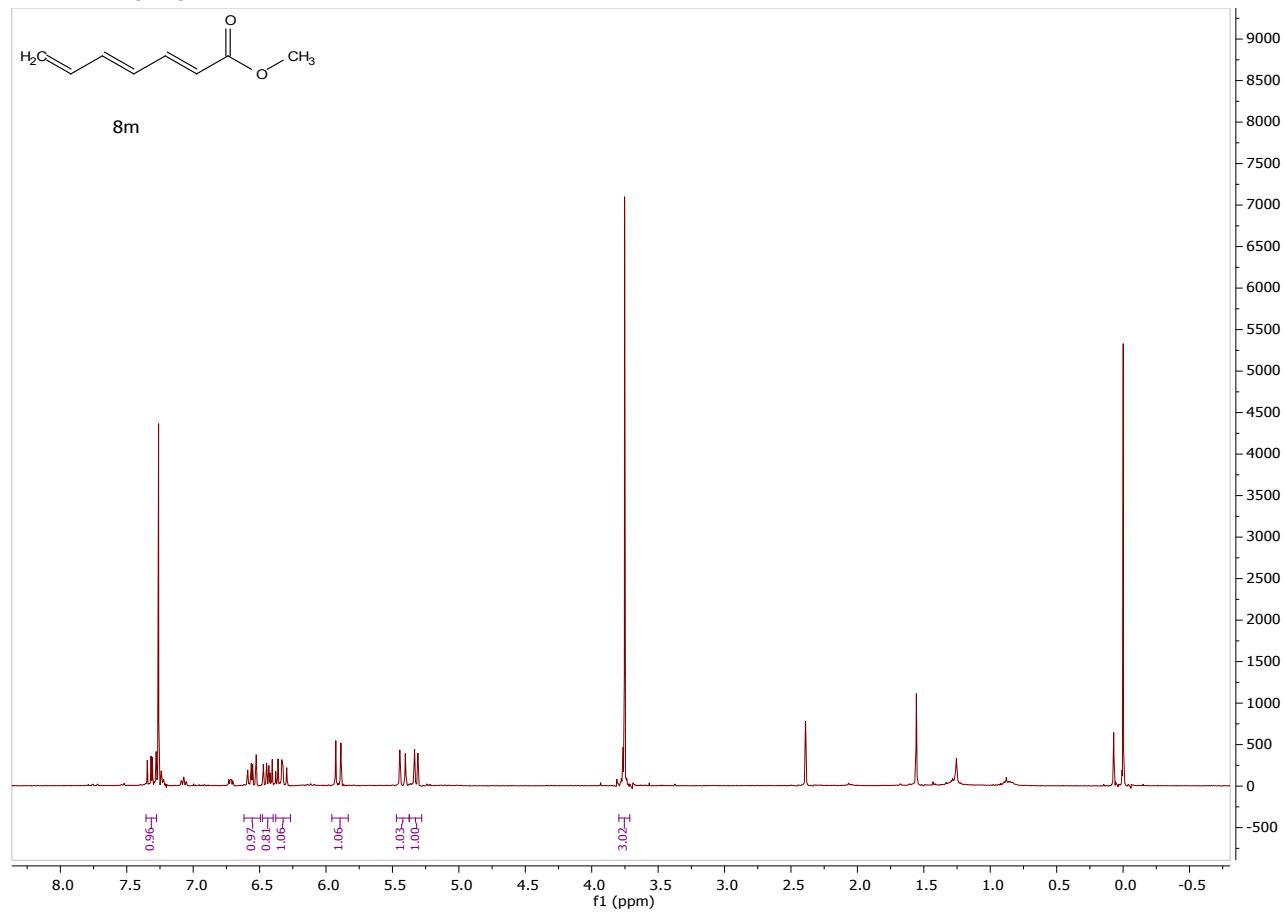




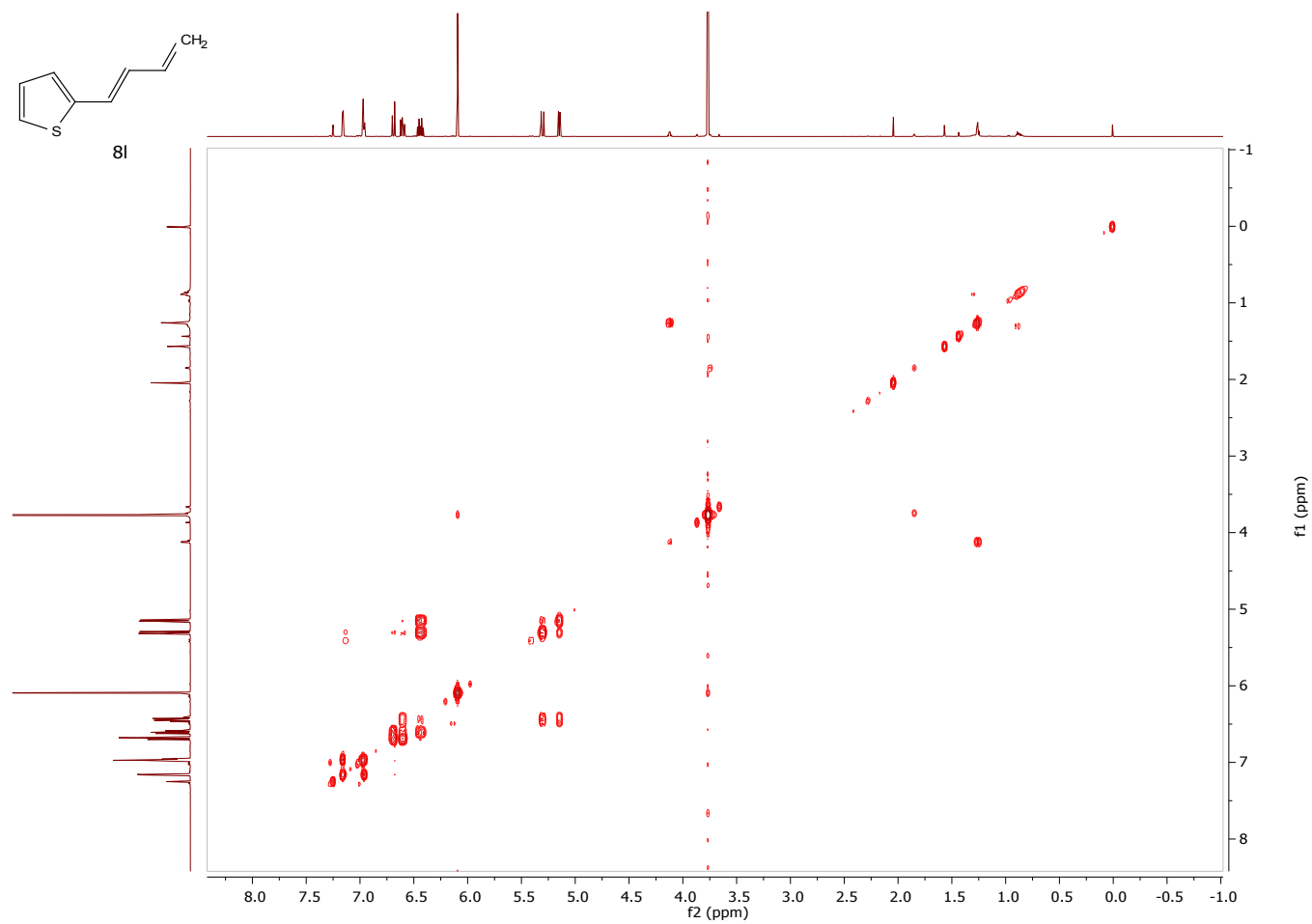


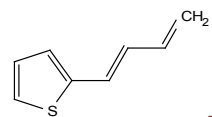






Peaks were assigned using COSY, HSQC and HMBC spectra, example below.





8I

