

# **Palladium Catalyzed Cyclizations of Oxime Esters with 1,2-Disubstituted Alkenes: Synthesis of Dihydropyrroles**

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## **Supporting Information**

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## General Experimental Details

All solvents and reagents requiring purification were purified using standard laboratory techniques according to methods published by Perrin, Armarego, and Perrin (Pergamon Press, 1966) apart from  $\text{CH}_2\text{Cl}_2$  and THF which were dried by filtration through an activated alumina purification column. Petrol refers to petroleum ether in the boiling range 40–60 °C. Flash column chromatography (FCC) was performed using oven dried Merck Kieselgel 60 (40–63  $\mu\text{m}$ ). Proton nuclear magnetic resonance spectra (NMR) were recorded at 400 MHz.  $^{13}\text{C}$  NMR spectra were recorded at 100 MHz. All assignments of NMR spectra were based on 2D NMR data (COSY, HSQC and HMBC).  $\text{CDCl}_3$  referenced to 7.26 ppm. Coupling constants are quoted to the nearest 0.5 Hz. Where mixtures of isomers (*e.g.* diastereomers) have been characterized together integrals are normalized to the major isomer unless otherwise stated. Mass spectra were recorded using a VG Autospec ( $\text{CI}^+$  mode and  $\text{EI}^+$  mode) and a Brüker Daltonics FT-ICR-MS Apex 4e 7.0T FT-MS ( $\text{ESI}^+$  mode). Infrared spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrometer as a thin films or solids compressed on a diamond plate. Melting points are uncorrected.

## Experimental Procedures and Data

### **General Procedure A** for the preparation of allylic esters via cross metathesis:

To a solution of Grubbs-Hoveyda 2<sup>nd</sup> generation catalyst (1 mol%) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL/mmol allyl benzene derivative) was added allyl benzene derivative (100 mol%) and ethyl acrylate (200 mol%) simultaneously via syringe. The resultant reaction mixture was heated at 40 °C until consumption of starting material occurred as determined by TLC analysis. The reaction mixture was cooled to room temperature, concentrated *in vacuo* and the residue purified by FCC, under the conditions noted, to give the corresponding allylic ester.

### **General Procedure B** for the preparation of allylic alcohols from allylic esters:

To a solution of the corresponding ester (100 mol%) in CH<sub>2</sub>Cl<sub>2</sub> (2.7 mL/mmol ester) at -78 °C was added DIBAL-H (210 mol%, 1 M in CH<sub>2</sub>Cl<sub>2</sub>) dropwise. The solution was stirred at this temperature until consumption of starting material was observed by TLC (*ca.* 15 mins) at which point the reaction was quenched by careful addition of methanol (0.036 mL/mmol DIBAL-H). The reaction was allowed to warm to room temperature whereupon saturated aq. potassium sodium tartrate (2 mL/mmol DIBAL-H) and EtOAc (4 mL/mmol DIBAL-H) were added and the mixture was stirred vigorously for 1 hour. The phases were then separated and the aqueous phase was extracted with EtOAc (2 x 4 mL/mmol DIBAL-H). The organic phases were combined, washed with saturated aq. potassium sodium tartrate (2 mL/mmol DIBAL-H), H<sub>2</sub>O (2 mL/mmol DIBAL-H), brine (2 mL/mmol DIBAL-H), dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. Purification of the residue by FCC, under the conditions noted, afforded the corresponding allylic alcohol.

### **General Procedure C** for the preparation of allylic bromides from allylic alcohols:

To a solution of the corresponding allylic alcohol (100 mol%) in reagent grade Et<sub>2</sub>O (1.1 mL/mmol allylic alcohol) at 0 °C was added phosphorous tribromide (50 mol%) dropwise. The reaction mixture was stirred for 18 hours during which time it was allowed to warm to room temperature. After this time the reaction was quenched by careful pouring into ice-water (2.5 mL/mmol PBr<sub>3</sub>) and extracted with diethyl ether (3 x 2.5 mL/mmol allylic alcohol). The organic layers were combined and washed with water (2.5 mL/mmol allylic alcohol), saturated aq. NaHCO<sub>3</sub> (2.5 mL/mmol allylic alcohol), brine (2.5 mL/mmol allylic alcohol), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The residue was filtered through a short pad of silica to afford the corresponding allylic bromide.

### **General Procedure D** for the preparation of ketone precursors via the corresponding β-keto ester:

To a solution of NaH (100 mol%, 60% dispersion in mineral oil) in anhydrous THF (5 mL/mmol β-keto ester) at 0 °C was added the appropriate β-keto ester (100 mol%) dropwise. The mixture was stirred at this temperature until gas evolution ceased. The appropriate bromide (120 mol%) was then added *via* syringe and the mixture was heated at 50 °C for 18 hours. After consumption of starting material (TLC analysis) MeOH (1 mL/mmol β-keto ester), water (2.5 mL/mmol β-keto ester) and KOH (450 mol%) were added and the mixture was heated at reflux until complete consumption of intermediate ester was observed by TLC (*ca.* 3 hours). After cooling to room temperature, the mixture was acidified with aq. 1 M HCl (8 mL/mmol) and extracted with Et<sub>2</sub>O (20 mL/mmol). The organic extracts were washed with brine (20 mL/mmol), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. Purification of the residue by FCC, under the conditions noted, afforded the corresponding allylated ketone.

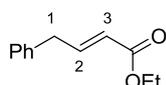
### **General Procedure E** for oxime ester formation:

**Part A:** H<sub>2</sub>NOH.HCl (150 mol%) and NaOAc (150 mol%) were added to a solution of the appropriate ketone (100 mol%) in MeOH (3 mL/mmol) in a round-bottomed flask fitted with a reflux condenser. The mixture was heated at 80 °C until consumption of starting material was observed by TLC. After cooling to room temperature, the mixture was diluted with EtOAc (15 mL/mmol), washed with brine (10 mL/mmol), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. Oxime obtained in this way was used in the next stage without further purification unless otherwise stated.

**Part B:** To a solution of the appropriate oxime (100 mol%) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (3 mL/mmol of oxime) at 0 °C was added Et<sub>3</sub>N (200 mol%) followed by pentafluorobenzoyl chloride (120 mol%) dropwise *via* syringe. The

mixture was then warmed to room temperature and stirred until the reaction was complete as observed by TLC. MeOH (0.5 mL/mmol oxime) was then added and the mixture stirred for a further 10 minutes. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (15 mL/mmol oxime), washed with 1 M HCl (10 mL/mmol oxime), saturated aq. Na<sub>2</sub>CO<sub>3</sub> (10 mL/mmol oxime), brine (15 mL/mmol oxime), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The residue was purified by FCC, under the conditions noted, to afford the corresponding oxime ester. The oxime esters employed in this study were generally bench stable.

**General Procedure F for Narasaka-Heck cyclization:** An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Pd<sub>2</sub>dba<sub>3</sub> (5 mol%), P(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (25 mol%) and oxime ester substrate (100 mol%). The tube was fitted with a rubber septum and purged with argon. Anhydrous Et<sub>3</sub>N (200 mol%) and then anhydrous DMF (10 mL/mmol oxime ester) were added *via* syringe. The mixture was then placed in a preheated oil bath (90 °C) until complete consumption of starting material was observed (TLC). The mixture was then cooled to room temperature and concentrated *in vacuo* (*ca.* 1.0 mmHg). A known amount of 1,3,5-trimethoxybenzene was added as a standard and the product distribution was determined by <sup>1</sup>H NMR of the crude reaction mixture. The residue was purified by FCC, under the conditions noted, to afford the target heterocycle.



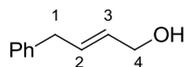
**(E)-Ethyl 4-phenylbut-2-enoate**

General procedure A: Allyl benzene (6.60 mL, 49.9 mmol) and ethyl acrylate (10.9 mL, 99.8 mmol) were employed. FCC (50:1 – 10:1 (hexane-EtOAc)) afforded the title compound (7.96 g, 84%) as a colorless oil.

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.32-7.29 (2H, m, ArCH), 7.25-7.22 (1H, m, ArCH), 7.18-7.16 (2H, m, ArCH), 7.10 (1H, dt, *J* = 15.5, 7.0, H<sub>2</sub>), 5.81 (1H, dt, *J* = 15.5, 1.5, H<sub>3</sub>), 4.17 (2H, q, *J* = 7.0, CH<sub>2</sub>CH<sub>3</sub>), 3.51 (2H, dd, *J* = 7.0, 1.5, H<sub>1</sub>), 1.27 (3H, t, *J* = 7.0, CH<sub>2</sub>CH<sub>3</sub>);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 166.4 (C=O), 147.2 (C<sub>2</sub>), 137.6 (ArC), 128.7, 128.6, 126.6 (3 × ArCH), 122.3 (C<sub>2</sub>), 60.2 (CH<sub>2</sub>CH<sub>3</sub>), 38.4 (C<sub>1</sub>), 14.2 (CH<sub>2</sub>CH<sub>3</sub>).

*The spectroscopic properties of this compound were consistent with the data available in the literature.*<sup>1</sup>



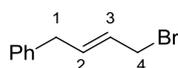
**(E)-4-Phenyl-2-buten-1-ol**

General procedure B: (E)-Ethyl-4-phenylbut-2-enoate (7.80 g, 41.1 mmol) was employed. FCC (7:1 – 3:1 (hexane-EtOAc)) afforded the title compound (5.35 g, 88%) as a colorless oil.

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.32-7.29 (2H, m, ArCH), 7.23-7.18 (3H, m, ArCH), 5.90-5.84 (1H, m, H<sub>2</sub>), 5.74-5.68 (1H, m, H<sub>3</sub>), 4.13 (2H, dd, *J* = 6.0, 1.0, H<sub>4</sub>), 3.40 (2H, d, *J* = 6.5, H<sub>1</sub>), 1.47 (1H, br. s, OH);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 140.0 (ArC), 131.5 (C<sub>2</sub>), 130.3 (C<sub>3</sub>), 128.5, 128.4, 126.1 (3 × ArCH), 63.5 (C<sub>4</sub>), 38.6 (C<sub>1</sub>).

*The spectroscopic properties of this compound were consistent with the data available in the literature.*<sup>2</sup>



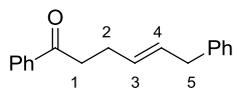
**(E)-(4-Bromobut-2-en-1-yl)benzene**

General procedure C: (E)-4-Phenyl-2-buten-1-ol (5.32 g, 35.9 mmol) was employed to afford the title compound (7.10 g, 94%) as a colorless oil.

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.34-7.30 (2H, m, ArCH), 7.25-7.18 (3H, m, ArCH), 5.98-5.90 (1H, m, H<sub>2</sub>), 5.78 (1H, dtt, *J* = 15.0, 7.5, 1.5, H<sub>3</sub>), 3.97 (2H, dd, *J* = 7.5, 1.0, H<sub>4</sub>), 3.42 (2H, d, *J* = 7.0, H<sub>1</sub>);

$\delta_C$  (100 MHz,  $CDCl_3$ ) 139.3 (ArC), 134.7 (C2), 128.5 (2C, 2  $\times$  ArCH), 127.6 (C3), 126.29 (ArCH), 38.4 (C4), 32.9 (C1).

The spectroscopic properties of this compound were consistent with the data available in the literature.<sup>3</sup>



**(E)-1,6-Diphenylhex-4-en-1-one**

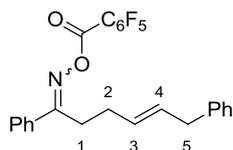
**General Procedure D:** Ethyl benzoylacetate (1.90 mL, 11.0 mmol) and (E)-(4-bromobut-2-en-1-yl)benzene (2.73 g, 13.0 mmol) were employed. FCC (40:1 – 30:1 (hexane-EtOAc)) afforded the title compound (2.15 g, 78%) as a colorless oil.

$\nu_{max}$  /  $cm^{-1}$  (film) 3026 (w), 2901 (w), 1683 (s), 1448 (m), 1202 (m);

$\delta_H$  (400 MHz,  $CDCl_3$ ) 7.99-7.97 (2H, m, ArCH), 7.59-7.55 (1H, m, ArCH), 7.49-7.46 (2H, m, ArCH), 7.32-7.28 (2H, m, ArCH), 7.23-7.18 (3H, m, ArCH), 5.72-5.66 (1H, m, H4), 5.65-5.59 (1H, m, H4), 3.36 (2H, d,  $J = 6.5$ , H5), 3.08 (2H, t,  $J = 7.5$ , H1), 2.53-2.49 (2H, m, H2);

$\delta_C$  (100 MHz,  $CDCl_3$ ) 199.5 (CO), 140.6, 136.9 (2  $\times$  ArC), 132.9 (ArCH), 130.1 (C3), 129.9 (C4), 128.5, 128.4, 128.3, 128.0, 125.9 (5  $\times$  ArCH), 38.9 (C5), 38.3 (C1), 27.1 (C2);

**HRMS** (EI<sup>+</sup>) Found  $[M+H]^+$ : 251.1433,  $C_{18}H_{19}O$  requires 251.1436.



**(4E)-1,6-Diphenylhex-4-en-1-one O-perfluorobenzoyl oxime 9a**

**General procedure E: Part A:** (E)-1,6-Diphenylhex-4-en-1-one (2.00 g, 8.00 mmol) was employed affording the corresponding oxime (2.10 g, 99%) as a colorless solid. **Part B:** The corresponding oxime (2.10 g, 7.92 mmol) was employed. Purification of the residue (50:1 – 30:1 (hexane-EtOAc)) afforded the title compound (2.73 g, 75%, >20:1 mixture of oxime isomers) as a colorless oil that solidified on standing.

$\nu_{max}$  /  $cm^{-1}$  (film) 3028 (w), 2898 (w), 1754 (s), 1653 (m), 1523 (s), 1493 (s), 1321 (s), 1194 (s);

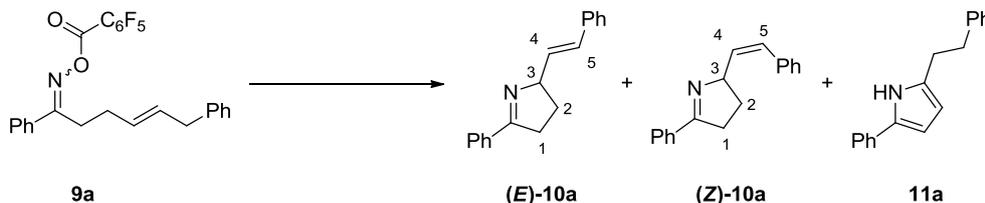
$\delta_H$  (400 MHz,  $CDCl_3$ ) 7.77-7.74 (2H, m, ArCH), 7.53-7.43 (3H, m, ArCH), 7.31-7.27 (2H, m, ArCH), 7.23-7.18 (1H, m, ArCH), 7.16-7.13 (2H, m, ArCH), 5.67-5.60 (1H, m, H4), 5.54-5.46 (1H, m, H3), 3.32 (2H, d,  $J = 6.5$ , H5), 3.03 (2H, t,  $J = 7.5$ , H1), 2.39-2.34 (2H, m, H2);

$\delta_C$  (100 MHz,  $CDCl_3$ ) 168.2 (CN), 156.4 (CO), 140.2, 133.0 (2  $\times$  ArC), 130.9 (2C, ArCH, C4), 128.8 (C3), 128.7, 128.4, 128.3, 127.4, 125.9 (5  $\times$  ArCH), 38.7 (C3), 29.5 (C2), 28.6 (C1).

Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

$\delta_F$  (376 MHz,  $CDCl_3$ ) -137.1 (2F), -147.7 (1F), -159.8 (2F);

**HRMS** (ESI<sup>+</sup>) Found  $[M+Na]^+$ : 482.1150,  $C_{25}H_{18}O_2NF_5Na$  requires 482.1157.



**(E)-5-Phenyl-2-styryl-3,4-dihydro-2H-pyrrole 10a**

**General procedure F:** **9a** (100 mg, 0.22 mmol) was employed. Analysis of the crude reaction mixture revealed a total cyclization yield of 78% and a selectivity of 17:1 (**10a:11a**). *E:Z* ratio of **10a** was 12:1. FCC (15:1 – 5:1 (hexane-EtOAc)) afforded the title compound (34 mg, 64%) as a yellow oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3090 (m), 3027 (w), 1611 (m), 1574 (m), 1494 (m), 1448 (m), 1339 (m), 906 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.93-7.91 (2H, m, ArCH), 7.46-7.40 (5H, m, ArCH), 7.33-7.29 (2H, m, ArCH), 7.24-7.20 (1H, m, ArCH), 6.65 (1H, dd,  $J = 16.0, 1.0$ , H5), 6.37 (1H, dd,  $J = 16.0, 7.0$ , H4), 4.95-4.89 (1H, m, H3), 3.12 (1H, dddd,  $J = 17.0, 10.0, 5.0, 2.0$ , H1), 2.97 (1H, dddd,  $J = 17.0, 9.5, 7.5, 2.0$ , H1'), 2.39 (1H, dddd,  $J = 13.0, 9.5, 8.0, 5.0$ , H2), 1.89 (1H, dddd,  $J = 13.0, 10.0, 7.5, 7.0$ , H2');

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 173.4 (CN), 137.2, 134.4 ( $2 \times$  ArC), 131.8 (C4), 130.5 (ArCH), 129.9 (C5), 128.4 (2C), 127.8, 127.2, 126.4, ( $5 \times$  ArCH), 74.3 (C3), 35.1 (C1), 29.7 (C2);

HRMS ( $\text{EI}^+$ ) Found  $[\text{M}]^+$ : 247.1357,  $\text{C}_{18}\text{H}_{17}\text{N}$  requires 247.1361.

In order to obtain sufficient quantities of **11a** and (**Z**)-**10a** for characterisation the above reaction was repeated on a larger scale. **General procedure F:** **9a** (800 mg, 1.74 mmol) was employed. FCC (25:1 – 5:1 (hexane-EtOAc) + 1%  $\text{Et}_3\text{N}$ ) afforded pyrrole **11a** (13 mg, 3%) and (**Z**)-**10a** (12 mg, 3%) and (**E**)-**10a** (265 mg, 62%) as a colorless oil. Due to the small quantity of (**Z**)-**10a** characterisation was only possible by  $^1\text{H}$  NMR and HRMS. (**Z**)-**10a** was contaminated with significant amounts of dibenzylideneacetone.

Data for (**Z**)-**10a**:

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) Signals for the phenyl ring could not be accurately determined due to dba contaminant, 6.64 (1H, d,  $J = 11.5$ , H5), 5.68 (1H, dd,  $J = 11.5, 9.5$ , H4), 5.24-5.16 (1H, m, H3), 3.20-3.11 (1H, m, H1), 2.95 (1H, dddd,  $J = 17.0, 9.5, 8.0, 2.0$ , H1'), 2.38 (1H, dddd,  $J = 12.5, 9.5, 8.0, 4.5$ , H2), 1.88-1.79 (1H, m, H2');

HRMS ( $\text{EI}^+$ ) Found  $[\text{M}]^+$ : 247.1355,  $\text{C}_{18}\text{H}_{17}\text{N}$  requires 247.1361.

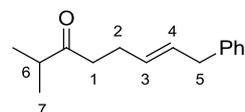
Data for **2-phenyl-5-phenethyl-1H-pyrrole 11a**:

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.92 (1H, br. s, NH), 7.35-7.30 (6H, m, ArCH), 7.27-7.23 (3H, m, ArCH), 7.17-7.14 (1H, m, ArCH), 6.41 (1H, dd,  $J = 3.5, 2.5$ , ArCH), 6.01 (1H, dd,  $J = 3.5, 2.5$ , ArCH), 2.99 (4H, br. s,  $\text{CH}_2\text{CH}_2\text{Ph}$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 133.2, 132.8, 131.0, 130.7 ( $4 \times$  ArC), 128.5 (2C), 126.2, 125.7, 123.3, 107.2, 105.8 ( $8 \times$  ArCH), 36.1 ( $\text{CH}_2$ ), 29.7 ( $\text{CH}_2$ ).

*The spectroscopic properties of this compound were consistent with the data available in the literature.*<sup>4</sup>

The product ratios for the other cyclizations in Schemes 2 and 3 were determined by analogy to the above results. The corresponding pyrroles were not isolated and their identities are inferred by analogy to **11a**.



**(E)-2-Methyl-8-phenyloct-6-en-3-one**

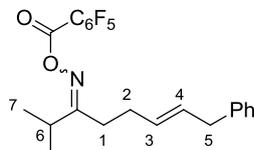
**General Procedure D:** Ethyl isobutyrylacetate (840  $\mu\text{L}$ , 5.20 mmol) and (*E*)-(4-bromobut-2-en-1-yl)benzene (1.31 g, 6.24 mmol) were employed. Purification of the residue by FCC (40:1 – 30:1 (hexane-EtOAc)) afforded the title compound (700 mg, 62%) as a colorless oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3027 (w), 2968 (w), 2931 (w), 1709 (s), 1494 (m), 1453 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.31-7.27 (2H, m, ArCH), 7.22-7.16 (3H, m, ArCH), 5.66-5.58 (1H, m, H4), 5.54-5.46 (1H, m, H3), 3.33 (2H, d,  $J = 7.0$ , H5), 2.59 (1H, sep,  $J = 7.0$ , H6), 2.53 (2H, t,  $J = 7.5$ , H1), 2.33-2.28 (2H, m, H2), 1.09 (6H, d,  $J = 7.0$ , H7);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 214.0 ( $\underline{\text{CO}}$ ), 140.7 ( $\text{Ar}\underline{\text{C}}$ ), 130.2 ( $\underline{\text{C3}}$ ), 129.8 ( $\underline{\text{C4}}$ ), 128.4, 128.3, 125.9 ( $3 \times \text{Ar}\underline{\text{CH}}$ ), 40.8 ( $\underline{\text{C6}}$ ), 40.0 ( $\underline{\text{C1}}$ ), 38.9 ( $\underline{\text{C5}}$ ), 26.6 ( $\underline{\text{C2}}$ ), 18.2 ( $\underline{\text{C7}}$ );

**HRMS** ( $\text{EI}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 217.1585,  $\text{C}_{15}\text{H}_{21}\text{O}$  requires 217.1592.



**(6E)-2-Methyl-8-phenyloct-6-en-3-one O-perfluorobenzoyl oxime 9b**

**General procedure E: Part A:** (*E*)-2-Methyl-8-phenyloct-6-en-3-one (660 mg, 3.06 mmol) was employed affording the corresponding oxime (706 mg, 100%) as a colorless oil. **Part B:** The corresponding oxime (706 mg, 3.06 mmol) was employed. Purification of the residue (20:1 – 10:1 (hexane-EtOAc)) afforded the title compound (1.13 g, 87%, 4:1 mixture of oxime isomers) as a colorless oil.

$\nu_{\text{max}} / \text{cm}^{-1}$  (film) 2972 (w), 1756 (s), 1651 (m), 1523 (m), 1494 (s), 1323 (s), 1192 (s);

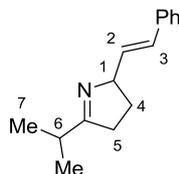
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.31-7.26 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.22-7.14 (3H, m,  $\text{Ar}\underline{\text{CH}}$ ), 5.72-5.54 (1.2H, m,  $\underline{\text{H4}}$ ,  $\underline{\text{H4'}}$  &  $\underline{\text{H3'}}$ ), 5.52-5.44 (0.8H, m,  $\underline{\text{H3}}$ ), 3.36-3.32 (2.2H, m,  $\underline{\text{H5}}$ ,  $\underline{\text{H5'}}$  &  $\underline{\text{H6'}}$ ), 2.74 (0.8H, hep,  $J = 7.0$ ,  $\underline{\text{H6}}$ ), 2.49-2.40 (2.4H, m,  $\underline{\text{H1}}$ ,  $\underline{\text{H1'}}$  &  $\underline{\text{H2'}}$ ), 2.33-2.27 (1.6H, m,  $\underline{\text{H2}}$ ), 1.21 (4.8H, d,  $J = 7.0$ ,  $\underline{\text{H7}}$ ), 1.13 (1.2H, d,  $J = 7.0$ ,  $\underline{\text{H7'}}$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 175.2 ( $\underline{\text{CN}}$ ), 174.9 ( $\underline{\text{CN'}}$ ), 156.7 ( $\underline{\text{CO}}$ ), 140.6 ( $\text{Ar}\underline{\text{C'}}$ ), 140.3 ( $\text{Ar}\underline{\text{C}}$ ), 130.7 ( $\underline{\text{C4}}$ ), 130.4 ( $\underline{\text{C4'}}$ ), 129.8 ( $\underline{\text{C3'}}$ ), 129.3 ( $\underline{\text{C3}}$ ), 128.5 ( $\text{Ar}\underline{\text{CH'}}$ ), 128.4 ( $\underline{\text{2C}}$ ) ( $2 \times \text{Ar}\underline{\text{CH}}$ ), 128.4 ( $\text{Ar}\underline{\text{CH'}}$ ), 126.0 ( $\text{Ar}\underline{\text{CH}}$ ), 126.0 ( $\text{Ar}\underline{\text{CH'}}$ ), 39.0 ( $\underline{\text{C5'}}$ ), 38.8 ( $\underline{\text{C5}}$ ), 34.2 ( $\underline{\text{C6}}$ ), 30.5 ( $\underline{\text{C1'}}$ ), 29.4 ( $\underline{\text{C2}}$ ), 29.1 ( $\underline{\text{C2'}}$ ), 28.9 ( $\underline{\text{C6'}}$ ), 28.4 ( $\underline{\text{C1}}$ ), 19.7 ( $\underline{\text{C7}}$ ), 19.0 ( $\underline{\text{C7'}}$ );

Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -137.5 (2F), -148.2 (1F), -160.0 (2F);

**HRMS** ( $\text{CI}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 426.1490,  $\text{C}_{22}\text{H}_{21}\text{NO}_2\text{F}_5$  requires 426.1492.



**(E)-5-Isopropyl-2-styryl-3,4-dihydro-2H-pyrrole 10b**

**General procedure F: 9b** (80 mg, 0.19 mmol) was employed. In a modification to the general procedure the reaction was heated at 100 °C. Analysis of the crude reaction mixture revealed a total cyclization yield of 72% and a selectivity of 6.5:1 (**10b**:**11b**). *E*:*Z* ratio of **10b** was 14:1. FCC (5:1 – 3:1 (hexane-EtOAc)) afforded the title compound (22 mg, 56%) as a yellow oil.

$\nu_{\text{max}} / \text{cm}^{-1}$  (film) 3027 (w), 2966 (w), 1633 (m), 1493 (m), 1450 (m), 1279 (m);

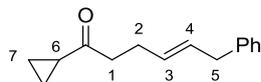
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.39-7.36 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.31-7.27 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.22-7.18 (1H, m,  $\text{Ar}\underline{\text{CH}}$ ), 6.54 (1H, dd,  $J = 16.0$ , 1.5,  $\underline{\text{H3}}$ ), 6.26 (1H, dd,  $J = 16.0$ , 7.0,  $\underline{\text{H2}}$ ), 4.65 (1H, dddd,  $J = 8.0$ , 7.0, 5.0, 1.5,  $\underline{\text{H1}}$ ), 2.70 (1H, sep,  $J = 7.0$ ,  $\underline{\text{H6}}$ ), 2.65-2.58 (1H, m,  $\underline{\text{H5}}$ ), 2.55-2.46 (1H, m,  $\underline{\text{H5'}}$ ), 2.20 (1H, dddd,  $J = 13.0$ , 9.5, 8.0, 5.0,  $\underline{\text{H4}}$ ), 1.69 (1H, dddd,  $J = 13.0$ , 9.5, 7.5, 7.0,  $\underline{\text{H4'}}$ ), 1.19 (6H, d,  $J = 7.0$ ,  $\underline{\text{H7}}$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 183.6 ( $\underline{\text{CN}}$ ), 137.3 ( $\text{Ar}\underline{\text{C}}$ ), 132.1 ( $\underline{\text{C3}}$ ), 129.5 ( $\underline{\text{C3}}$ ), 128.4, 127.1, 126.3 ( $3 \times \text{Ar}\underline{\text{CH}}$ ), 73.3 ( $\underline{\text{C1}}$ ), 34.6 ( $\underline{\text{C5}}$ ), 32.7 ( $\underline{\text{C6}}$ ), 29.5 ( $\underline{\text{C4}}$ ), 20.2 (2C,  $\underline{\text{C7}}$ );

**HRMS** ( $\text{EI}^+$ ) Found  $[\text{M}]^+$ : 213.1519,  $\text{C}_{15}\text{H}_{19}\text{N}$  requires 213.1517.

Diagnostic signals for **9b**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 5.84-5.82 (0.17H, m), 5.79-5.77 (0.17H, m).

Dianostic signals for (**Z**)-**9b**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 5.59 (0.06H, dd,  $J = 11.5, 9.5$ , H2), 4.99-4.91 (0.06H, m, H1).



**(E)-1-Cyclopropyl-6-phenylhex-4-en-1-one**

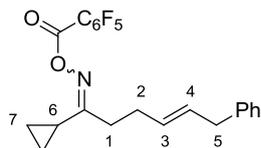
**General Procedure D:** Methyl cyclopropylacetate<sup>5</sup> (500 mg, 3.52 mmol) and (*E*)-(4-bromobut-2-en-1-yl)benzene (887 mg, 4.23 mmol) were employed. In a modification to the general procedure the intermediate ester was purified by FCC (20:1 – 5:1 (hexane-EtOAc)) prior to decarboxylation. FCC of the ketone residue (20:1 (hexane-EtOAc)) afforded the title compound (161 mg, 21%) as a colorless oil.

$\nu_{\text{max}} / \text{cm}^{-1}$  (film) 3027 (w), 2843 (w), 1696 (s), 1494 (m), 1385 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.31 (2H, m, ArCH), 7.22-7.16 (3H, m, ArCH), 5.67-5.59 (1H, m, H4), 5.56-5.48 (1H, m, H3), 3.33 (2H, d,  $J = 6.5$ , H5), 2.64 (2H, t,  $J = 7.5$ , H1), 2.38-2.32 (2H, m, H2), 1.92 (1H, tt,  $J = 8.0, 4.5$ , H6), 1.01 (2H, ddd,  $J = 6.5, 4.5, 3.5$ , H7), 0.87-0.82 (2H, m, H7');

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 210.4 (C=O), 140.7 (ArC), 130.1 (C3), 129.8 (C4), 128.4, 128.3, 125.9 (3  $\times$  ArCH), 43.1 (C1), 38.9 (C5), 26.8 (C2), 20.4 (C6), 10.6 (C7);

**HRMS** ( $\text{CI}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 215.1428,  $\text{C}_{15}\text{H}_{19}\text{O}$  requires 215.1436.



**(4E)-1-Cyclopropyl-6-phenylhex-4-en-1-one O-perfluorobenzoyl oxime 9c**

**General procedure E: Part A:** (*E*)-1-Cyclopropyl-6-phenylhex-4-en-1-one (160 mg, 0.748 mmol) was employed affording the corresponding oxime (169 mg, 99%) as a colorless oil. **Part B:** The corresponding oxime (169 mg, 0.74 mmol) was employed. Purification of the residue (30:1 (hexane-EtOAc)) afforded the title compound (235 mg, 75%, 1.6:1 mixture of oxime isomers) as a colorless oil that solidified on standing.

$\nu_{\text{max}} / \text{cm}^{-1}$  (film) 3030 (w), 2894 (w), 1755 (s), 1655 (m), 1523 (m), 1494 (s), 1322 (s), 1195 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) *Data for the major isomer* 7.30-7.27 (2H, m, ArCH), 7.21-7.14 (3H, m, ArCH), 5.68-5.61 (1H, m, H4), 5.55-5.44 (1H, m, H3), 3.35-3.32 (2H, m, H5), 2.39-2.29 (4H, m, H1 & H2), 1.68 (1H, tt,  $J = 7.5, 5.5$ , H6), 0.96-0.89 (4H, m, H7);

*Diagnostic signals for the minor isomer* 2.26 (0.6H, tt,  $J = 8.5, 5.5$ , H6'), 2.07-2.04 (1.2H, m, H1'), 1.02-0.98 (1.2H, m, H7') and 0.87-0.83 (1.2H, m, H7');

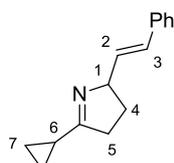
$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) *Data for the major isomer* 172.8 (C=N), 156.5 (C=O), 140.3 (ArC), 130.8 (C4), 129.2 (C3), 128.4 (2C), 126.0 (3  $\times$  ArCH), 38.8 (C5), 29.3 (C2), 29.1 (C1), 14.3 (C6), 6.9 (C7);

*Data for the minor isomer* 171.5 (C=N), 156.5 (C=O), 140.5 (ArC), 130.5 (C4), 129.5 (C3), 128.5, 128.3, 126.0 (3  $\times$  ArCH), 38.9 (C5), 29.7 (C2), 28.8 (C1), 10.3 (C6), 6.5 (C7);

*Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -137.4 (3.2F), -148.0 (1F), -148.3 (0.6F), -160.0 (2F), -160.1 (1.2F);

**HRMS** ( $\text{ESI}^+$ ) Found  $[\text{M}+\text{Na}]^+$ : 446.1150,  $\text{C}_{22}\text{H}_{18}\text{O}_2\text{NF}_5\text{Na}$  requires 446.1148.



### (E)-5-Cyclopropyl-2-styryl-3,4-dihydro-2H-pyrrole 10c

**General procedure F:** **9c** (70 mg, 0.17 mmol) was employed. Analysis of the crude reaction mixture revealed a total cyclization yield of 70% and a selectivity of 14:1 (**10c:11c**). *E:Z* ratio of **10c** was 16:1. FCC (5:1 – 3:1 (hexane-EtOAc)) afforded the title compound (21 mg, 61%) as a yellow oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3025 (w), 2926 (w), 1626 (m), 1449 (m), 964 (m);

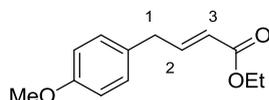
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.39-7.36 (2H, m, ArCH), 7.31-7.27 (2H, m, ArCH), 7.22-7.18 (1H, m, ArCH), 6.55 (1H, dd,  $J = 16.0, 1.5$ , H3), 6.24 (1H, dd,  $J = 16.0, 7.0$ , H2), 4.68-4.61 (1H, m, H1), 2.53-2.35 (2H, m, H5), 2.25-2.17 (1H, m, H4), 1.91 (1H, tt,  $J = 8.0, 5.5$ , H6), 1.74-1.64 (1H, m, H4'), 0.96-0.89 (4H, m, H7);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 180.9 (C=O), 137.2, 131.7 (ArC), 131.7 (C2), 129.8 (C3), 128.4, 127.2, 126.4 (3 × ArCH), 73.1 (C1), 34.7 (C5), 29.4 (C4), 14.3 (C6), 7.9 (C7), 7.8 (C7');

**HRMS** ( $\text{CI}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 212.1434,  $\text{C}_{15}\text{H}_{18}\text{N}$  requires 212.1439.

Diagnostic signals for **11c**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 5.96-5.94 (0.07H, m), 5.86-5.84 (0.07H, m).

Diagnostic signals for (**Z**)-**10c**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 5.55 (0.06H, dd,  $J = 11.5, 9.5$ , H2), 4.94-4.86 (0.06H, m, H1).



### (E)-Ethyl 4-(4-methoxyphenyl)but-2-enoate

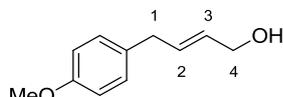
**General procedure A:** 4-Allylanisole (2.00 mL, 13.0 mmol) and ethyl acrylate (2.84 mL, 26.1 mmol) were employed. FCC (50:1 – 30:1 (hexane-EtOAc)) afforded the title compound (2.40 g, 84%) as a colorless oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2982 (w), 2836 (w), 1714 (s), 1642 (m), 1510 (s), 1464 (m), 1244 (s), 1159 (s), 1034 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.11-7.04 (3H, m, 2 × ArCH, H2), 6.87-6.83 (2H, m, ArCH), 5.77 (1H, dt,  $J = 15.5, 1.5$ , H3), 4.19 (2H, q,  $J = 7.0$ ,  $\text{CH}_2\text{CH}_3$ ), 3.79 (3H, s,  $\text{OCH}_3$ ), 3.46 (2H, dd,  $J = 6.5, 1.5$ , H1), 1.27 (3H, t,  $J = 7.0$ ,  $\text{CH}_2\text{CH}_3$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 166.5 (C=O), 158.3 ( $\text{MeOC}_6\text{H}_4$ ), 147.7 (C2), 129.7 (ArCH), 129.6 (ArC), 122.0 (C3), 114.0 (ArCH), 60.2 (C4), 55.2 ( $\text{OCH}_3$ ), 37.5 (C1), 14.2 (C5);

**HRMS** ( $\text{CI}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 221.1179,  $\text{C}_{13}\text{H}_{17}\text{O}_3$  requires 221.1178.



### (E)-4-(4-Methoxyphenyl)but-2-en-1-ol

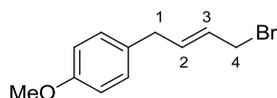
**General procedure B:** (*E*)-Ethyl 4-(4-methoxyphenyl)but-2-enoate (2.40 g, 10.9 mmol) was employed. FCC (4:1 – 2:1 (hexane-EtOAc)) afforded the title compound (1.77 g, 91%) as a colorless oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3332 (br), 2903 (w), 2835 (w), 1610 (m), 1509 (s), 1299 (m), 1241 (s), 1175 (m), 1033 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.10 (2H, d,  $J = 8.5$ , ArCH), 6.84 (2H, d,  $J = 8.5$ , ArCH), 5.86-5.80 (1H, m, H2), 5.70-5.64 (1H, m, H3), 4.11 (2H, dd,  $J = 6.0, 1.0$ , H4), 3.79 (3H, s,  $\text{OCH}_3$ ), 3.33 (2H, d,  $J = 6.5$ , H1), 1.74 (1H, s, OH);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 157.9 ( $\text{MeOC}_6\text{H}_4$ ), 132.0 (2C, ArC, C2), 129.9 (C3), 129.4, 113.8 (2 × ArCH), 63.4 (C4), 55.2 ( $\text{OCH}_3$ ), 37.7 (C1);

**HRMS** ( $\text{ESI}^+$ ) Found  $[\text{M}+\text{Na}]^+$ : 201.0886,  $\text{C}_{11}\text{H}_{14}\text{O}_2\text{Na}$  requires 201.0894.



**(E)-1-(4-Bromobut-2-en-1-yl)-4-methoxybenzene**

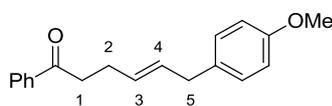
**General procedure C:** (*E*)-4-(4-Methoxyphenyl)but-2-en-1-ol (1.80 g, 10.1 mmol) was employed to afford the title compound (1.82 g, 75%) as a colorless oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3002 (w), 2904 (w), 2834 (w), 1609 (m), 1509 (s), 1300 (m), 1242 (s), 583 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.12-7.09 (2H, m, ArCH), 6.88-6.85 (2H, m, ArCH), 5.95-5.89 (1H, m, H<sub>2</sub>), 5.75 (1H, dtt,  $J = 15.0, 7.5, 1.5$ , H<sub>3</sub>), 3.99-3.97 (2H, m, H<sub>4</sub>), 3.80 (3H, s, OCH<sub>3</sub>), 3.36 (2H, d,  $J = 7.0$ , H<sub>1</sub>);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 158.1 (ArCOMe), 135.2 (C<sub>2</sub>), 131.2 (ArC), 129.5 (ArCH), 127.2 (C<sub>3</sub>), 113.9 (ArCH), 55.2 (OCH<sub>3</sub>), 37.4 (C<sub>1</sub>), 33.0 (C<sub>4</sub>);

**HRMS** ( $\text{Cl}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 241.0229,  $\text{C}_{11}\text{H}_{14}\text{OBr}$  requires 241.0228.



**(E)-6-(4-Methoxyphenyl)-1-phenylhex-4-en-1-one**

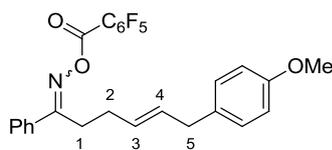
**General Procedure D:** Ethyl benzoylacetate (332  $\mu\text{L}$ , 1.92 mmol) and (*E*)-1-(4-bromobut-2-en-1-yl)-4-methoxybenzene (547 mg, 2.28 mmol) were employed. FCC (35:1 (hexane-EtOAc)) afforded the title compound (308 mg, 58%) as a colorless oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2904 (w), 2835 (w), 1683 (m), 1509 (s), 1448 (m), 1242 (s), 1175 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.96 (2H, d,  $J = 7.5$ , ArCH), 7.56 (1H, t,  $J = 7.5$ , ArCH), 7.46 (2H, t,  $J = 8.0$ , ArCH), 7.08 (2H, d,  $J = 8.5$ , ArCH), 6.83 (2H, d,  $J = 8.5$ , ArCH), 5.67-5.61 (1H, m, H<sub>4</sub>), 5.60-5.54 (1H, m, H<sub>3</sub>), 3.79 (3H, s, OCH<sub>3</sub>), 3.27 (2H, d,  $J = 6.5$ , H<sub>5</sub>), 3.06 (2H, t,  $J = 7.5$ , H<sub>1</sub>), 2.50-2.46 (2H, m, H<sub>2</sub>);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 199.7 (CO), 157.9 (ArCOMe), 137.0 (ArC), 132.9 (ArCH), 132.7 (ArC), 130.4 (C<sub>4</sub>), 129.8 (C<sub>3</sub>), 129.4, 128.5, 128.0, 113.8 (4  $\times$  ArCH), 55.2 (OCH<sub>3</sub>), 38.4 (C<sub>1</sub>), 38.0 (C<sub>5</sub>), 27.1 (C<sub>2</sub>);

**HRMS** ( $\text{Cl}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 281.1547,  $\text{C}_{19}\text{H}_{21}\text{O}_2$  requires 281.1542.



**(4E)-6-(4-Methoxyphenyl)-1-phenylhex-4-en-1-one O-perfluorobenzoyl oxime 9d**

**General procedure E: Part A:** (*E*)-6-(4-Methoxyphenyl)-1-phenylhex-4-en-1-one (292 mg, 1.04 mmol) was employed affording the corresponding oxime (250 mg, 81%) after purification by FCC (8:1 – 3:1 (hexane-EtOAc)) as a colorless oil. **Part B:** The corresponding oxime (250 mg, 0.85 mmol) was employed. Purification of the residue (30:1 – 10:1 (hexane-EtOAc)) afforded the title compound (328 mg, 79%, 10:1 mixture of oxime isomers) as a colorless oil that solidified on standing.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2937 (w), 1765 (s), 1655 (m), 1523 (m), 1499 (s), 1325 (m), 1188 (s);

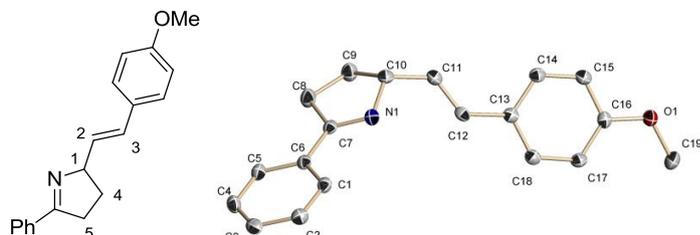
*Data for the major isomer only:*

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.73-7.71 (2H, m, ArCH), 7.50-7.47 (1H, m, ArCH), 7.45-7.42 (2H, m, ArCH), 7.03-7.01 (2H, m, ArCH), 6.81-6.79 (2H, m, ArCH), 5.61-5.55 (1H, m, H<sub>4</sub>), 5.46-5.40 (1H, m, H<sub>3</sub>), 3.78 (3H, s, OCH<sub>3</sub>), 3.23 (2H, d,  $J = 6.5$ , H<sub>5</sub>), 2.98 (2H, t,  $J = 7.5$ , H<sub>1</sub>), 2.34-2.30 (2H, m, H<sub>2</sub>);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 168.3 ( $\underline{\text{CN}}$ ), 157.9 ( $\text{Ar}\underline{\text{COMe}}$ ), 156.5 ( $\underline{\text{CO}}$ ), 133.1, 132.3 ( $2 \times \text{Ar}\underline{\text{C}}$ ), 131.4 ( $\underline{\text{C4}}$ ), 131.0, 129.3, 128.8 ( $3 \times \text{Ar}\underline{\text{CH}}$ ), 128.5 ( $\underline{\text{C3}}$ ), 127.5, 113.7 ( $2 \times \text{Ar}\underline{\text{CH}}$ ), 55.2 ( $\text{O}\underline{\text{CH}_3}$ ), 37.9 ( $\underline{\text{C5}}$ ), 29.5 ( $\underline{\text{C2}}$ ), 28.7 ( $\underline{\text{C1}}$ ); Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -137.1 (2F), -147.6 (1F), -159.8 (2F);

**HRMS** ( $\text{CI}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 490.1434,  $\text{C}_{26}\text{H}_{21}\text{NO}_3\text{F}_5$  requires 490.1442.



**(E)-2-(4-Methoxystyryl)-5-phenyl-3,4-dihydro-2H-pyrrole 10d**

**General procedure F:** **9d** (50 mg, 0.10 mmol) was employed. Analysis of the crude reaction mixture revealed a total cyclization yield of 73% and a selectivity of 15:1 (**10d**:**11d**). *E*:*Z* ratio of **10d** was 15:1. FCC (5:1 – 3:1 (hexane-EtOAc)) afforded the title compound (18 mg, 64%) as a yellow solid. Recrystallisation ( $\text{CH}_2\text{Cl}_2$  layered with hexane) gave crystals suitable for X-ray analysis.

**Mp** 120-121 °C (hexane/ $\text{CH}_2\text{Cl}_2$ )

$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 3029 (w), 1602 (s), 1574 (m), 1508 (s), 1452 (m), 1332 (m) 1240 (s), 1031 (s);

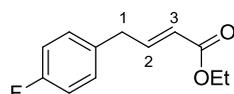
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.95-7.93 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.48-7.42 (3H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.37-7.34 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 6.89-6.85 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 6.61 (1H, d,  $J = 16.0$ ,  $\underline{\text{H3}}$ ), 6.23 (1H, dd,  $J = 16.0$ , 7.5,  $\underline{\text{H2}}$ ), 4.95-4.88 (1H, m,  $\underline{\text{H1}}$ ), 3.83 (3H, s,  $\text{O}\underline{\text{CH}_3}$ ), 3.19-3.11 (1H, m,  $\underline{\text{H5}}$ ), 3.03-2.94 (1H, m,  $\underline{\text{H5}}$ '), 2.45-2.36 (1H, m,  $\underline{\text{H4}}$ ), 1.94-1.85 (1H, m,  $\underline{\text{H4}}$ ');

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 173.4 ( $\underline{\text{CN}}$ ), 159.0 ( $\text{Ar}\underline{\text{COMe}}$ ), 134.4 ( $\text{Ar}\underline{\text{C}}$ ), 130.6 ( $\text{Ar}\underline{\text{CH}}$ ), 130.0 ( $\text{Ar}\underline{\text{C}}$ ), 129.6 ( $\underline{\text{C2}}$ ), 129.5 ( $\underline{\text{C3}}$ ), 128.4, 127.8, 127.5, 113.9 ( $4 \times \text{Ar}\underline{\text{CH}}$ ), 74.4 ( $\underline{\text{C1}}$ ), 55.2 ( $\text{O}\underline{\text{CH}_3}$ ), 35.1 ( $\underline{\text{C5}}$ ), 29.8 ( $\underline{\text{C4}}$ );

**HRMS** ( $\text{EI}^+$ ) Found  $[\text{M}]^+$ : 277.1461,  $\text{C}_{19}\text{H}_{19}\text{NO}$  requires 277.1467.

Diagnostic signals for **11d**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 6.40 (0.07H, dd,  $J = 3.5$ , 2.5), 5.99 (0.07H, dd,  $J = 3.5$ , 2.5).

Diagnostic signals for (*Z*)-**10d**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 5.58 (0.07H, dd,  $J = 11.5$ , 9.5,  $\underline{\text{H2}}$ ), 5.21-5.14 (0.07H, m,  $\underline{\text{H1}}$ ).



**(E)-Ethyl-4-(4-fluorophenyl)but-2-enoate**

**General procedure A:** 1-Allyl-4-fluorobenzene (1.60 mL, 11.9 mmol) and ethyl acrylate (2.57 mL, 23.7 mmol) were employed. FCC (50:1 – 30:1 (hexane-EtOAc)) afforded the title compound (2.18 g, 88%) as a colorless oil.

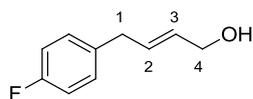
$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 2984 (w), 1714 (s), 1653 (m), 1508 (s), 1267 (s), 1220 (s), 1155 (s), 1038 (m), 822 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.14-7.11 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.06 (1H, dt,  $J = 15.5$ , 7.0,  $\underline{\text{H2}}$ ), 7.02-6.97 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 5.78 (1H, dt,  $J = 15.5$ , 1.5,  $\underline{\text{H3}}$ ), 4.18 (2H, q,  $J = 7.0$ ,  $\text{CH}_2\underline{\text{CH}_3}$ ), 3.49 (2H, d,  $J = 7.0$ ,  $\underline{\text{H1}}$ ), 1.27 (3H, t,  $J = 7.0$ ,  $\text{CH}_2\underline{\text{CH}_3}$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 166.3 ( $\underline{\text{CO}}$ ), 161.7 (d,  $J = 244.0$ ,  $\text{Ar}\underline{\text{CF}}$ ), 146.9 ( $\underline{\text{C2}}$ ), 133.3 (d,  $J = 3.0$ ,  $\text{Ar}\underline{\text{C}}$ ), 130.2 (d,  $J = 8.0$ ,  $\text{Ar}\underline{\text{CH}}$ ), 122.5 ( $\underline{\text{C3}}$ ), 115.4 (d,  $J = 21.5$ ,  $\text{Ar}\underline{\text{CH}}$ ), 60.3 ( $\underline{\text{CH}_2\underline{\text{CH}_3}$ ), 37.5 ( $\underline{\text{C1}}$ ), 14.2 ( $\text{CH}_2\underline{\text{CH}_3}$ );

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -116.4;

**HRMS** ( $\text{Cl}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 209.0971,  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{F}$  requires 209.0978.



**(E)-4-(4-Fluorophenyl)but-2-en-1-ol**

**General procedure B:** (*E*)-Ethyl-4-(4-fluorophenyl)but-2-enoate (2.10 g, 10.1 mmol) was employed. FCC (4:1 – 2:1 (hexane-EtOAc)) afforded the title compound (1.37 g, 82%) as a colorless oil.

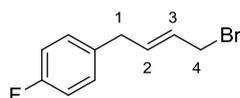
$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 3324 (br), 2905 (w), 1507 (s), 1218 (s), 1156 (m), 970 (m), 821 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.13 (2H, dd,  $J = 8.5, 5.5$ , ArCH), 6.97 (2H, t,  $J = 8.5$ , ArCH), 5.85-5.79 (1H, m, H2), 5.70-5.64 (1H, m, H3), 4.12-4.10 (2H, m, H4), 3.35 (2H, d,  $J = 7.0$ , H1), 1.85 (1H, s, OH);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 161.4 (d,  $J = 243.0$ , ArCF), 135.5 (d,  $J = 3.5$ , ArC), 131.2 (C2), 130.4 (C3), 129.9 (d,  $J = 8.0$ , ArCH), 115.1 (d,  $J = 21.0$ , ArCH), 63.3 (C4), 37.7 (C1);

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -117.3 (m);

**HRMS** ( $\text{ESI}^+$ ) Found  $[\text{M}+\text{Na}]^+$ : 189.0686,  $\text{C}_{10}\text{H}_{11}\text{OFNa}$  requires 189.0692.



**(E)-1-(4-Bromobut-2-en-1-yl)-4-fluorobenzene**

**General procedure C:** (*E*)-4-(4-fluorophenyl)but-2-en-1-ol (800 mg, 4.82 mmol) was employed to afford the title compound (857 mg, 78%) as a colorless oil.

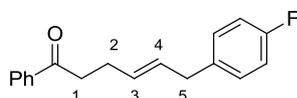
$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 3037 (w), 2904 (w), 1507 (s), 1219 (m), 1156 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.14-7.10 (2H, m, ArCH), 7.02-6.96 (2H, m, ArCH), 5.93-5.86 (1H, m, H2), 5.79-5.70 (1H, m, H3), 3.97 (2H, d,  $J = 7.5$ , H4), 3.38 (2H, d,  $J = 6.0$ , H1);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 161.5 (d,  $J = 244.0$ , ArCF), 134.9 (d,  $J = 3.0$ , ArC), 134.5 (C2), 130.0 (d,  $J = 7.5$ , ArCH), 127.8 (C3), 115.3 (d,  $J = 21.0$ , ArCH), 37.5 (C1), 32.7 (C4);

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) - 117.0;

**HRMS** ( $\text{Cl}^+$ ) Found  $[\text{M}]^+$ : 227.9952,  $\text{C}_{10}\text{H}_{10}\text{FBr}$  requires 227.9950.



**(E)-6-(4-Fluorophenyl)-1-phenylhex-4-en-1-one**

**General Procedure D:** Ethyl benzoylacetate (490  $\mu\text{L}$ , 2.83 mmol) and (*E*)-1-(4-bromobut-2-en-1-yl)-4-fluorobenzene (775 mg, 3.40 mmol) were employed. FCC (60:1 (hexane-EtOAc)) afforded the title compound (441 mg, 58%) as a colorless oil.

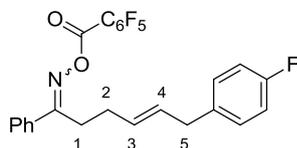
$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 3041 (w), 2905 (w), 1675 (s), 1596 (m), 1506 (s), 1225 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.97-7.95 (2H, m, ArCH), 7.58-7.54 (1H, m, ArCH), 7.48-7.44 (2H, m, ArCH), 7.12-7.08 (2H, m, ArCH), 6.98-6.93 (2H, m, ArCH), 5.66-5.54 (2H, m, H3 and H4), 3.29 (2H, d,  $J = 6.0$ , H5), 3.06 (2H, t,  $J = 7.5$ , H1), 2.51-2.46 (2H, m, H2);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 199.6 ( $\underline{\text{CO}}$ ), 161.3 (d,  $J = 244.0$ ,  $\text{Ar}\underline{\text{CF}}$ ), 137.0 ( $\text{Ar}\underline{\text{C}}$ ), 136.2 (d,  $J = 3.5$ ,  $\text{Ar}\underline{\text{C}}$ ), 133.0 ( $\text{Ar}\underline{\text{CH}}$ ), 130.3 ( $\underline{\text{C3}}$ ), 129.9 ( $\underline{\text{C4}}$ ), 129.8 (d,  $J = 8.0$ ,  $\text{Ar}\underline{\text{CH}}$ ), 128.6, 128.0 ( $2 \times \text{Ar}\underline{\text{CH}}$ ), 115.0 (d,  $J = 21.5$ ,  $\text{Ar}\underline{\text{CH}}$ ), 38.3 ( $\underline{\text{C1}}$ ), 38.1 ( $\underline{\text{C5}}$ ), 27.1 ( $\underline{\text{C2}}$ );

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) - 117.7;

**HRMS** ( $\text{EI}^+$ ) Found  $[\text{M}]^+$ : 268.1266,  $\text{C}_{18}\text{H}_{17}\text{OF}$  requires 268.1263.



**(4E)-6-(4-Fluorophenyl)-1-phenylhex-4-en-1-one O-perfluorobenzoyl oxime 9e**

**General procedure E:** **Part A:** (*E*)-6-(4-Fluorophenyl)-1-phenylhex-4-en-1-one (425 mg, 1.59 mmol) was employed affording the corresponding oxime (440 mg, 98%) as a colorless oil. **Part B:** The corresponding oxime (440 mg, 1.55 mmol) was employed. Purification of the residue (30:1 – 10:1 (hexane-EtOAc)) afforded the title compound (582 mg, 78%, 10:1 mixture of oxime isomers) as a colorless oil that solidified on standing.

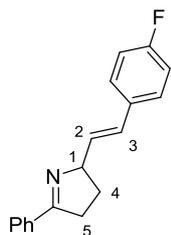
$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 3052 (w), 2897 (w), 1759 (s), 1651 (m), 1524 (m), 1505 (s), 1492 (s), 1323 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) *Signals for the major isomer only* 7.73-7.71 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.51-7.47 (1H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.45-7.42 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.07-7.04 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 6.96-6.92 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 5.60-5.53 (1H, m,  $\underline{\text{H4}}$ ), 5.47-5.40 (1H, m,  $\underline{\text{H3}}$ ), 3.26 (2H, d,  $J = 6.5$ ,  $\underline{\text{H5}}$ ), 3.00 (2H, t,  $J = 7.5$ ,  $\underline{\text{H1}}$ ), 2.36-2.31 (2H, m,  $\underline{\text{H2}}$ ); *Characteristic signals for the minor isomer* 3.29 (0.2H, d,  $J = 6.5$ ), 2.85 (0.2H, t,  $J = 7.5$ ), 2.28-2.24 (0.2H, m);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) *Signals for the major isomer only* 168.2 ( $\underline{\text{CN}}$ ), 161.3 (d,  $J = 243.5$ ,  $\text{Ar}\underline{\text{CF}}$ ), 156.5 ( $\underline{\text{CO}}$ ), 135.8 (d,  $J = 3.0$ ,  $\text{Ar}\underline{\text{C}}$ ), 133.0 ( $\text{Ar}\underline{\text{C}}$ ), 131.0 ( $\text{Ar}\underline{\text{CH}}$ ), 130.9 ( $\underline{\text{C4}}$ ), 129.8 (d,  $J = 8.0$ ,  $\text{Ar}\underline{\text{CH}}$ ), 129.0 ( $\underline{\text{C3}}$ ), 128.8, 127.5 ( $2 \times \text{Ar}\underline{\text{CH}}$ ), 115.0 (d,  $J = 21.0$ ,  $\text{Ar}\underline{\text{CH}}$ ), 37.9 ( $\underline{\text{C5}}$ ), 29.5 ( $\underline{\text{C2}}$ ), 28.6 ( $\underline{\text{C1}}$ ); *Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -117.5 (1F), -137.1 (2F), -147.5 (1F), -159.8 (2F);

**HRMS** ( $\text{ESI}^+$ ) Found  $[\text{M}+\text{Na}]^+$ : 500.1056,  $\text{C}_{25}\text{H}_{17}\text{O}_2\text{NF}_6\text{Na}$  requires 500.1068.



**(E)-2-(4-Fluorostyryl)-5-phenyl-3,4-dihydro-2H-pyrrole 10e**

**General procedure F:** **9e** (80 mg, 0.17 mmol) was employed. Analysis of the crude reaction mixture revealed a total cyclization yield of 67% and a selectivity of 18:1 (**10e**:**11e**). *E:Z* ratio of **10e** was 14:1. FCC (10:1 – 3:1 (hexane-EtOAc)) afforded the title compound (27 mg, 60%) as a yellow oil.

$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 2963 (w), 1610 (m), 1507 (s), 1226 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.93-7.90 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.47-7.42 (3H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.38-7.35 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.02-6.98 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 6.61 (1H, dd,  $J = 16.0, 1.5$ ,  $\underline{\text{H3}}$ ), 6.28 (1H, dd,  $J = 16.0, 7.0$ ,  $\underline{\text{H2}}$ ), 4.93-4.88 (1H, m,  $\underline{\text{H1}}$ ), 3.16-3.09 (1H, m,  $\underline{\text{H5}}$ ), 2.98 (1H, dddd,  $J = 17.0, 9.5, 7.5, 2.0$ ,  $\underline{\text{H5'}}$ ), 2.39 (1H, dddd,  $J = 13.0, 9.5, 8.0, 5.0$ ,  $\underline{\text{H4}}$ ), 1.91-1.84 (1H, m,  $\underline{\text{H4'}}$ );

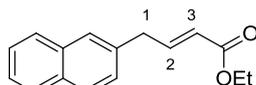
$\delta_C$  (100 MHz,  $CDCl_3$ ) 173.5 ( $\underline{C}N$ ), 162.1 (d,  $J = 247.0$ ,  $Ar\underline{C}F$ ), 134.4 ( $Ar\underline{C}$ ), 133.4 (d,  $J = 3.5$ ,  $Ar\underline{C}$ ), 131.6 ( $\underline{C}2$ ), 130.6 ( $Ar\underline{C}H$ ), 128.8 ( $\underline{C}3$ ), 128.4 ( $Ar\underline{C}H$ ), 127.8 (d,  $J = 8.0$ ,  $Ar\underline{C}H$ ), 127.7 ( $Ar\underline{C}H$ ), 115.3 (d,  $J = 21.5$ ,  $Ar\underline{C}H$ ), 74.3 ( $\underline{C}1$ ), 35.2 ( $\underline{C}5$ ), 29.7 ( $\underline{C}4$ );

$\delta_F$  (376 MHz,  $CDCl_3$ ) -115.1;

**HRMS** ( $EI^+$ ) Found  $[M]^+$ : 265.1261,  $C_{18}H_{16}NF$  requires 265.1267.

Diagnostic signals for **11e**:  $\delta_H$  (400 MHz,  $CDCl_3$ ) 6.41 (0.06H, app. t,  $J = 3.0$ ), 5.98 (0.06H, app. t,  $J = 3.0$ ).

Diagnostic signals for (**Z**)-**10e**:  $\delta_H$  (400 MHz,  $CDCl_3$ ) 5.65 (0.07H, dd,  $J = 11.5, 9.5$ ,  $\underline{H}2$ ), 5.14-5.07 (0.07H, m,  $\underline{H}1$ ).



**(E)-Ethyl 4-(naphthalen-2-yl)but-2-enoate**

To a solution of 2-naphthylacetonitrile (2.50 g, 15.0 mmol) in  $CH_2Cl_2$  (121 mL) was added DIBAL-H (1 M in hexane, 16.5 mL, 16.5 mmol). The reaction mixture was stirred for 2.5 hours at room temperature after which time 1 M HCl (120 mL) was added. The resultant mixture was stirred for 1.5 hours after which time the phases were separated and the aqueous phase extracted with EtOAc (3  $\times$  160 mL). The organic layers were combined, washed with brine (160 mL), dried ( $Na_2SO_4$ ) and concentrated *in vacuo* to give crude aldehyde (2.63 g) which was used directly without any purification.

$\delta_H$  (400 MHz,  $CDCl_3$ ) 9.83 (1H, t,  $J = 2.5$ ,  $\underline{C}HO$ ), 7.87-7.80 (3H, m,  $Ar\underline{C}H$ ), 7.71-7.69 (1H, m,  $Ar\underline{C}H$ ), 7.51-7.47 (3H, m,  $Ar\underline{C}H$ ), 7.33 (1H, dd,  $J = 8.5, 2.0$ ,  $Ar\underline{C}H$ ), 3.86 (2H, d,  $J = 2.5$ ,  $\underline{C}H_2\underline{C}HO$ ).

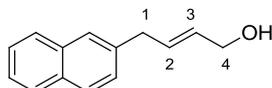
To a solution of crude aldehyde (2.60 g, 15.3 mmol) in  $CH_2Cl_2$  (22 mL) was added (triphenylphosphoranylidene)acetate (5.86 g, 16.8 mmol) as a solution in  $CH_2Cl_2$  (15 mL). The reaction mixture was stirred for 12 hours followed by the addition of brine (30 mL). The layers were separated and the aqueous layer extracted with  $CH_2Cl_2$  (60 mL). The organic layers were combined and dried ( $Na_2SO_4$ ). Purification of the residue by FCC (50:1 – 30:1 (hexane-EtOAc)) afforded the title compound (990 mg, 28% over two steps) as a yellow oil.

$\nu_{max}$  /  $cm^{-1}$  (film) 3053 (w), 2903 (w), 1713 (s), 1651 (m), 1367 (m), 1266 (m), 1159 (m);

$\delta_H$  (400 MHz,  $CDCl_3$ ) 7.84-7.78 (3H, m,  $Ar\underline{C}H$ ), 7.64-7.62 (1H, m,  $Ar\underline{C}H$ ), 7.50-7.43 (2H, m,  $Ar\underline{C}H$ ), 7.31 (1H, dd,  $J = 8.5, 2.0$ ,  $Ar\underline{C}H$ ), 7.19 (1H, dt,  $J = 15.5, 6.5$ ,  $\underline{H}2$ ), 5.86 (1H, dt,  $J = 15.5, 1.5$ ,  $\underline{H}3$ ), 4.19 (2H, q,  $J = 7.0$ ,  $\underline{C}H_2\underline{C}H_3$ ), 3.69 (2H, dd,  $J = 6.5, 1.5$ ,  $\underline{H}1$ ), 1.28 (3H, t,  $J = 7.0$ ,  $\underline{C}H_2\underline{C}H_3$ );

$\delta_C$  (100 MHz,  $CDCl_3$ ) 166.5 ( $\underline{C}O$ ), 147.1 ( $\underline{C}2$ ), 135.2, 133.6, 132.3 (3  $\times$   $Ar\underline{C}$ ), 128.3, 127.6, 127.5, 127.2 (2C), 126.1, 125.6 (7  $\times$   $Ar\underline{C}H$ ), 122.6 ( $\underline{C}3$ ), 60.3 ( $\underline{C}H_2\underline{C}H_3$ ), 38.5 ( $\underline{C}1$ ), 14.2 ( $\underline{C}H_2\underline{C}H_3$ );

**HRMS** ( $EI^+$ ) Found  $[M]^+$ : 240.1155,  $C_{16}H_{16}O_2$  requires 240.1150.



**(E)-4-(Naphthalen-2-yl)but-2-en-1-ol**

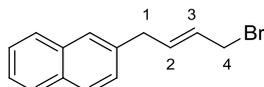
**General procedure B:** (*E*)-Ethyl 4-(naphthalen-2-yl)but-2-enoate (725 mg, 3.02 mmol) was employed. FCC (4:1 – 2:1 (hexane-EtOAc)) afforded the title compound (539 mg, 90%) as a colorless oil.

$\nu_{max}$  /  $cm^{-1}$  (film) 3322 (br), 2865 (w), 1600 (w), 1507 (w), 1089 (w);

$\delta_H$  (400 MHz,  $CDCl_3$ ) 7.83-7.77 (3H, m,  $Ar\underline{C}H$ ), 7.64-7.62 (1H, m,  $Ar\underline{C}H$ ), 7.49-7.41 (2H, m,  $Ar\underline{C}H$ ), 7.33 (1H, dd,  $J = 8.5, 1.5$ ,  $Ar\underline{C}H$ ), 5.98-5.90 (1H, m,  $\underline{H}2$ ), 5.79-5.72 (1H, m,  $\underline{H}3$ ), 4.16-4.14 (2H, m,  $\underline{H}4$ ), 3.55 (2H, d,  $J = 5.5$ ,  $\underline{H}1$ );

$\delta_C$  (100 MHz,  $CDCl_3$ ) 137.5, 133.6, 132.1 (3  $\times$   $Ar\underline{C}$ ), 131.4 ( $\underline{C}2$ ), 130.6 ( $\underline{C}3$ ), 128.0, 127.6, 127.4, 127.3, 126.6, 126.0, 125.3 (7  $\times$   $Ar\underline{C}H$ ), 63.5 ( $\underline{C}4$ ), 38.7 ( $\underline{C}1$ );

**HRMS** (EI<sup>+</sup>) Found [M]<sup>+</sup>: 198.1042, C<sub>14</sub>H<sub>14</sub>O requires 198.1045.



**(E)-2-(4-Bromobut-2-en-1-yl)naphthalene**

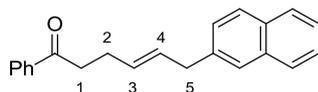
**General procedure C:** (*E*)-4-(Naphthalen-2-yl)but-2-en-1-ol (525 mg, 2.65 mmol) was employed to afford the title compound (600 g, 87%) as a yellow oil.

$\nu_{\max}$  / cm<sup>-1</sup> (film) 3051 (w), 2963 (w), 1599 (m), 1202 (m), 965 (m);

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.84-7.78 (3H, m, ArCH), 7.63-7.61 (1H, m, ArCH), 7.50-7.43 (2H, m, ArCH), 7.32 (1H, dd, *J* = 8.5, 1.5, ArCH), 6.05-5.97 (1H, m, H<sub>2</sub>), 5.82 (1H, dtt, *J* = 15.0, 7.5, 1.5, H<sub>3</sub>), 4.00 (2H, dd, *J* = 7.5, 1.0, H<sub>4</sub>), 3.58 (2H, d, *J* = 6.5, H<sub>1</sub>);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 136.8 (ArC), 134.6 (C<sub>2</sub>), 133.6 (ArC), 132.2 (ArC), 128.1 (C<sub>3</sub>), 127.9, 127.6, 127.5, 127.2, 126.7, 126.0, 125.4 (7 × ArCH), 38.5 (C<sub>1</sub>), 32.9 (C<sub>4</sub>);

**HRMS** (EI<sup>+</sup>) Found [M]<sup>+</sup>: 260.0209, C<sub>14</sub>H<sub>13</sub>Br requires 260.0201.



**(E)-6-(Naphthalen-2-yl)-1-phenylhex-4-en-1-one**

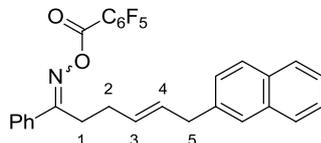
**General Procedure D:** Ethyl benzoylacetate (319  $\mu$ L, 1.85 mmol) and (*E*)-2-(4-bromobut-2-en-1-yl)naphthalene (578 mg, 2.21 mmol) were employed. FCC ( $\times$  2) (30:1 (hexane-EtOAc)) followed by (100:1 (toluene:EtOAc)) afforded the title compound (463 mg, 73%) as a colorless oil.

$\nu_{\max}$  / cm<sup>-1</sup> (film) 3053 (w), 2933 (w), 1682 (s), 1448 (m), 1364 (m), 1272 (m), 1202 (m), 967 (m);

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.99-7.96 (2H, m, ArCH), 7.83-7.78 (3H, m, ArCH), 7.63-7.62 (1H, m, ArCH), 7.58-7.55 (1H, m, ArCH), 7.49-7.43 (4H, m, ArCH), 7.33 (1H, dd, *J* = 8.5, 1.5, ArCH), 5.79-5.73 (1H, m, H<sub>4</sub>), 5.69-5.64 (1H, m, H<sub>3</sub>), 3.52 (2H, d, *J* = 6.5, H<sub>5</sub>), 3.08 (2H, t, *J* = 7.5, H<sub>1</sub>), 2.56-2.51 (2H, m, H<sub>2</sub>);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 199.6 (CO), 138.1, 136.9, 133.6 (3 × ArC), 132.9 (ArCH), 132.0 (ArC), 130.4 (C<sub>3</sub>), 129.8 (C<sub>4</sub>), 128.5, 128.0, 127.8, 127.6, 127.4, 127.3, 126.4, 125.8, 125.2 (9 × ArCH), 39.1 (C<sub>5</sub>), 28.3 (C<sub>1</sub>), 27.1 (C<sub>2</sub>);

**HRMS** (EI<sup>+</sup>) Found [M]<sup>+</sup>: 300.1523, C<sub>22</sub>H<sub>20</sub>O requires 300.1514.



**(4E)-6-(Naphthalen-2-yl)-1-phenylhex-4-en-1-one O-perfluorobenzoyl oxime 9f**

**General procedure E: Part A:** (*E*)-6-(Naphthalen-2-yl)-1-phenylhex-4-en-1-one (450 mg, 1.50 mmol) was employed affording the corresponding oxime (421 mg, 89%) as a colorless oil that solidified on standing. **Part B:** The corresponding oxime (200 mg, 0.635 mmol) was employed. Purification of the residue (50:1 (hexane-EtOAc)) afforded the title compound (260 mg, 81%, 18:1 mixture of oxime isomers) as a colorless oil that solidified on standing.

$\nu_{\max}$  / cm<sup>-1</sup> (film) 2937 (w), 1765 (s), 1655 (m), 1523 (s), 1500 (s), 1323 (m), 1187 (s);

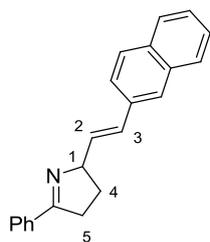
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) Data for the major isomer only: 7.81-7.73 (5H, m, ArCH), 7.58-7.56 (1H, m, ArCH), 7.52-7.40 (5H, m, ArCH), 7.27 (1H, dd,  $J = 8.5, 1.5$ , ArCH), 5.74-5.67 (1H, m, H4), 5.55-5.47 (1H, m, H3), 3.47 (2H, d,  $J = 6.5$ , H5), 3.02 (2H, t,  $J = 7.5$ , H1), 2.41-2.35 (2H, m, H2);  
Diagnostic signal of minor isomer: 2.89 (0.12H, m, H1');

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 168.1 (CN), 156.4 (CO), 137.7, 133.5, 133.0 ( $3 \times \text{ArC}$ ), 131.9 (C4), 130.9 (2C) (ArC & ArCH), 129.0 (C3), 128.7, 127.8, 127.4 (2C), 127.3, 127.2, 126.4, 125.8, 125.2 ( $9 \times \text{ArCH}$ ), 38.8 (C5), 29.5 (C1), 28.5 (C2);

Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -137.0 (2F), -137.3 (0.12F), -147.6 (1F), -148.2 (0.06F), -159.8 (2F), -160.2 (0.12F);

HRMS (ESI<sup>+</sup>) Found  $[\text{M}+\text{Na}]^+$ : 532.1306,  $\text{C}_{29}\text{H}_{20}\text{O}_2\text{NF}_5\text{Na}$  requires 532.1323.



**(E)-2-(2-(Naphthalen-2-yl)vinyl)-5-phenyl-3,4-dihydro-2H-pyrrole 10f**

**General procedure F:** **9f** (52 mg, 0.10 mmol) was employed. Analysis of the crude reaction mixture revealed a total cyclization yield of 69% and a selectivity of >20:1 (**10f**:**11f**). *E*:*Z* ratio of **10f** was 16:1. FCC (10:1 – 3:1 (hexane-EtOAc)) afforded the title compound (19 mg, 64%) as a yellow oil.

$\nu_{\text{max}} / \text{cm}^{-1}$  (film) 3055 (w), 1609 (m), 1572 (m), 1445 (m), 1341 (m);

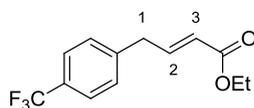
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.96-7.94 (2H, m, ArCH), 7.80-7.75 (4H, m, ArCH), 7.63 (1H, dd,  $J = 8.0, 2.0$ , ArCH), 7.47-7.42 (5H, m, ArCH), 6.81 (1H, d,  $J = 16.0$ , H3), 6.49 (1H, dd,  $J = 16.0, 7.0$ , H2), 5.01-4.96 (1H, m, H1), 3.16 (1H, dddd,  $J = 17.0, 9.5, 5.0, 2.5$ , H5), 3.01 (1H, dddd,  $J = 17.0, 9.5, 7.5, 2.0$ , H5'), 2.43 (1H, dddd,  $J = 13.0, 9.5, 8.0, 5.0$ , H4), 1.94 (1H, dddd,  $J = 13.0, 10.0, 7.0, 7.0$ , H4');

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 173.8 (CN), 134.7, 134.1, 133.6, 132.9 ( $4 \times \text{ArC}$ ), 132.0 (C2), 130.8 (ArCH), 130.2 (C3), 128.5, 128.0 (2C), 127.9, 127.6, 126.3, 126.1, 125.7, 123.7 ( $9 \times \text{ArCH}$ ), 74.3 (C1), 35.2 (C5), 29.7 (C4);

HRMS (CI<sup>+</sup>) Found  $[\text{M}+\text{H}]^+$ : 298.1583,  $\text{C}_{22}\text{H}_{20}\text{N}$  requires 298.1596.

Diagnostic signals for **11f**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 6.42 (0.03H, dd,  $J = 3.5, 2.5$ ), 6.05-6.03 (0.03H, m).

Diagnostic signals for (*Z*)-**10f**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 5.80 (0.06H, dd,  $J = 11.5, 9.5$ , H2), 5.33-5.26 (0.06H, m, H1).



**(E)-Ethyl 4-(4-(trifluoromethyl)phenyl)but-2-enoate**

**General procedure A:** 1-Allyl-4-(trifluoromethyl)benzene (1.67 mL, 10.0 mmol) and ethyl acrylate (2.18 mL, 20.0 mmol) were employed. FCC (30:1 (hexane-EtOAc)) afforded the title compound (1.58 g, 71%) as a colorless oil.

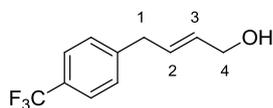
$\nu_{\text{max}} / \text{cm}^{-1}$  (film) 2985 (w), 1716 (m), 1655 (w), 1618 (w), 1321 (s), 1268 (m), 1159 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.57 (2H, d,  $J = 8.0$ , ArCH), 7.29 (2H, d,  $J = 8.0$ , ArCH), 7.07 (1H, dt,  $J = 15.5, 7.0$ , H2), 5.81 (1H, dt,  $J = 15.5, 1.5$ , H3), 4.19 (2H, q,  $J = 7.0$ ,  $\text{CH}_2\text{CH}_3$ ), 3.58 (2H, d,  $J = 7.0$ , H1), 1.28 (3H, t,  $J = 7.0$ ,  $\text{CH}_2\text{CH}_3$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 166.2 ( $\underline{\text{C}}\text{O}$ ), 145.8 ( $\underline{\text{C}}\text{2}$ ), 141.8 (q,  $J = 1.5$ ,  $\text{Ar}\underline{\text{C}}$ ), 129.1 ( $\text{Ar}\underline{\text{C}}\text{H}$ ), 129.1 (q,  $J = 32.0$ ,  $\text{Ar}\underline{\text{C}}\text{CF}_3$ ), 125.6 (q,  $J = 3.8$ ,  $\text{Ar}\underline{\text{C}}\text{H}$ ), 124.1 (q,  $J = 272.0$ ,  $\underline{\text{C}}\text{F}_3$ ), 123.1 ( $\underline{\text{C}}\text{3}$ ), 60.4 ( $\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ ), 38.1 ( $\underline{\text{C}}\text{1}$ ), 14.2 ( $\underline{\text{C}}\text{H}_2\underline{\text{C}}\text{H}_3$ );

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -62.5 (s);

**HRMS** ( $\text{Cl}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 259.0941,  $\text{C}_{13}\text{H}_{14}\text{O}_2\text{F}_3$  requires 259.0946.



**(E)-4-(4-(Trifluoromethyl)phenyl)but-2-en-1-ol**

**General procedure B:** (*E*)-Ethyl 4-(4-trifluoromethyl)phenyl)but-2-enoate (398 mg, 1.54 mmol) was employed. FCC (4:1 – 2:1 (hexane-EtOAc)) afforded the title compound (300 mg, 90%) as a colorless oil.

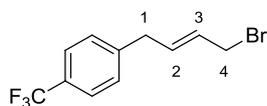
$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 3331 (br), 1321 (s), 1159 (m), 1108 (s), 1064 (s), 969 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.54 (2H, d,  $J = 8.0$ ,  $\text{Ar}\underline{\text{C}}\text{H}$ ), 7.29 (2H, d,  $J = 6.5$ ,  $\text{Ar}\underline{\text{C}}\text{H}$ ), 5.89 – 5.79 (1H, m,  $\underline{\text{H}}\text{3}$ ), 5.75 – 5.67 (1H, m,  $\underline{\text{H}}\text{2}$ ), 4.13 (2H, dd,  $J = 5.5, 1.5$ ,  $\underline{\text{H}}\text{4}$ ), 3.46 (2H, d,  $J = 6.5$ , 2H,  $\underline{\text{H}}\text{1}$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 144.1 ( $\text{Ar}\underline{\text{C}}$ ), 131.2 ( $\underline{\text{C}}\text{2}$ ), 130.2 ( $\underline{\text{C}}\text{3}$ ), 128.9 ( $\text{Ar}\underline{\text{C}}\text{H}$ ), 125.4 (q,  $J = 3.5$ ,  $\text{Ar}\underline{\text{C}}\text{H}$ ), 124.3 (q,  $J = 281.0$ ,  $\underline{\text{C}}\text{F}_3$ ), 63.3 ( $\underline{\text{C}}\text{4}$ ), 38.4 ( $\underline{\text{C}}\text{1}$ );

Signals corresponding to the  $\text{Ar}\underline{\text{C}}\text{CF}_3$  were not observed due to their weak intensity.

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -62.2.



**(E)-1-(4-Bromobut-2-en-1-yl)-4-(trifluoromethyl)benzene**

**General procedure C:** (*E*)-4-(4-(Trifluoromethyl)phenyl)but-2-en-1-ol (265 mg, 1.22 mmol) was employed to afford the title compound (288 mg, 85%) as a colorless oil.

$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 2983 (w), 1618 (m), 1418 (m), 1325 (s), 1163 (m), 1122 (m);

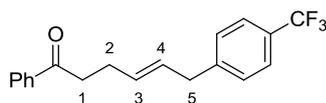
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.56 (2H, d,  $J = 8.0$ ,  $\text{Ar}\underline{\text{C}}\text{H}$ ), 7.29 (2H, d,  $J = 8.0$ ,  $\text{Ar}\underline{\text{C}}\text{H}$ ), 5.94-5.87 (1H, m,  $\underline{\text{H}}\text{2}$ ), 5.78 (1H, dtt,  $J = 15.0, 7.5, 1.5$ ,  $\underline{\text{H}}\text{3}$ ), 3.96 (2H, dd,  $J = 7.5, 1.5$ ,  $\underline{\text{H}}\text{4}$ ), 3.46 (2H, d,  $J = 6.5$ ,  $\underline{\text{H}}\text{1}$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 143.4 ( $\text{Ar}\underline{\text{C}}$ ), 133.5 ( $\underline{\text{C}}\text{2}$ ), 128.9 ( $\text{Ar}\underline{\text{C}}\text{H}$ ), 128.5 ( $\underline{\text{C}}\text{3}$ ), 125.5 (q,  $J = 4.0$ ,  $\text{Ar}\underline{\text{C}}\text{H}$ ), 38.1 ( $\underline{\text{C}}\text{1}$ ), 32.4 ( $\underline{\text{C}}\text{4}$ );

Signals corresponding to the  $\text{Ar}\underline{\text{C}}\text{CF}_3$  and  $\underline{\text{C}}\text{F}_3$  were not observed due to their weak intensity.

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -62.4;

**HRMS** ( $\text{EI}^+$ ) Found  $[\text{M}^+]$ : 277.9912,  $\text{C}_{11}\text{H}_{10}\text{F}_3\text{Br}$  requires 277.9918.



**(E)-1-Phenyl-6-(4-(trifluoromethyl)phenyl)hex-4-en-1-one**

**General Procedure D:** Ethyl benzoylacetate (260  $\mu\text{L}$ , 1.50 mmol) and (*E*)-1-(4-bromobut-2-en-1-yl)-4-(trifluoromethyl)benzene (417 mg, 1.50 mmol) were employed. FCC (30:1 (hexane-EtOAc)) afforded the title compound (310 mg, 65%) as a colorless oil.

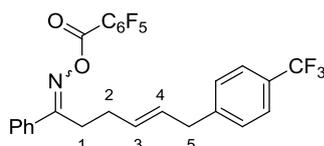
$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2927 (w), 1686 (s), 1617 (m), 1448 (m), 1332 (s), 1277 (m), 1163 (s), 1107 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.97-7.95 (2H, m, ArCH), 7.58-7.52 (3H, m, ArCH), 7.48-7.44 (2H, m, ArCH), 7.28-7.25 (2H, m, ArCH), 5.68-5.58 (2H, m, H3 & H4), 3.39-3.37 (2H, m, H5), 3.07 (2H, t,  $J = 7.5$ , H1), 2.53-2.48 (2H, m, H2);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 199.4 (CO), 144.8 (q,  $J = 1.0$ , ArC), 136.9 (ArC), 133.0 (ArCH), 131.1 (C4), 128.9 (C3), 128.7 (ArCH), 128.5 (ArCH), 128.3 (q,  $J = 32.0$ , ArCF<sub>3</sub>), 128.0 (ArCH), 125.2 (q,  $J = 4.0$ , ArCH), 124.3 (q,  $J = 272.0$ , CF<sub>3</sub>), 38.7 (C5), 38.1 (C1), 27.0 (C2);

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -62.1;

HRMS (EI<sup>+</sup>) Found [M]<sup>+</sup>: 318.1235, C<sub>19</sub>H<sub>17</sub>OF<sub>3</sub> requires 318.1232.



**(4E)-1-Phenyl-6-(4-(trifluoromethyl)phenyl)hex-4-en-1-one O-perfluorobenzoyl oxime 9g**

**General procedure E: Part A:** (E)-1-Phenyl-6-(4-(trifluoromethyl)phenyl)hex-4-en-1-one (221 mg, 0.69 mmol) was employed affording the corresponding oxime (198 mg, 86%) as a colorless oil. **Part B:** The corresponding oxime (198 mg, 0.59 mmol) was employed. Purification of the residue (50:1 (hexane-EtOAc)) afforded the title compound (209 mg, 67%, 20:1 mixture of oxime isomers) as a colorless oil that solidified on standing.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2927 (w), 1767 (m), 1652 (w), 1500 (s), 1449 (m), 1372 (s), 1198 (s), 1150 (s)

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) Data for the major isomer only 7.73-7.71 (2H, m, ArCH), 7.52-7.47 (3H, m, ArCH), 7.45-7.41 (2H, m, ArCH), 7.22 (2H, d,  $J = 8.0$ , ArCH), 5.61-5.55 (1H, m, H4), 5.51-5.44 (1H, m, H3), 3.34 (2H, d,  $J = 6.5$ , H5), 3.01 (2H, t,  $J = 8.0$ , H1), 2.38-2.34 (2H, m, H2);

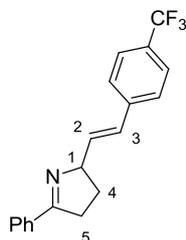
Characteristic signal for the minor isomer: 2.86 (0.05H, t,  $J = 8.0$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) Data for the major isomer only 168.1 (CN), 156.5 (CO), 144.3 (ArC), 133.0 (ArC), 131.0 (ArCH), 130.0 (C4), 128.8, 129.7 (C3), 128.3 (q,  $J = 32.0$ , ArCF<sub>3</sub>), 128.8 (ArCH), 127.4 (ArCH), 125.2 (q,  $J = 4.0$ , ArCH), 124.3 (q,  $J = 272.0$ , CF<sub>3</sub>), 38.5 (C5), 29.5 (C2), 28.5 (C1);  $1 \times \text{ArCH}$  was not observed.

Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -62.4 (3F), -137.2 (2F), -147.5 (1F), -159.9 (2F);

HRMS (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 550.1024, C<sub>26</sub>H<sub>17</sub>NO<sub>2</sub>F<sub>8</sub>Na requires 550.1012.



**(E)-5-Phenyl-2-(4-(trifluoromethyl)styryl)-3,4-dihydro-2H-pyrrole 10g**

**General procedure F:** **9g** (60 mg, 0.114 mmol) was employed. Analysis of the crude reaction mixture revealed a total cyclization yield of 60% and a selectivity of 12:1 (**10g**:**11g**). *E*:*Z* ratio of **10g** was 16:1. FCC (20:1 – 10:1 (hexane-EtOAc)) afforded the title compound (19 mg, 54%) as a yellow oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2964 (w), 1609 (m), 1573 (m), 1323 (s), 1119 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.94-7.92 (2H, m, ArCH), 7.55 (2H, d,  $J = 8.5$ , ArCH), 7.49-7.42 (5H, m, ArCH), 6.67 (1H, d,  $J = 16.0$ , H3), 6.47 (1H, dd,  $J = 16.0, 7.0$ , H2), 4.97-4.92 (1H, m, H1), 3.15 (1H, dddd,  $J = 17.0, 10.0, 5.0, 2.5$ , H5), 3.01 (1H, dddd,  $J = 17.0, 9.5, 7.5, 2.0$ , H5'), 2.42 (1H, dddd,  $J = 13.0, 9.5, 8.0, 5.0$ , H4), 1.90 (1H, dddd,  $J = 13.0, 10.0, 7.5, 7.5$ , H4');

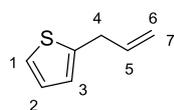
$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 174.1 (CN), 140.7 (ArC), 134.3 (C2), 134.1 (ArC), 130.9 (ArCH), 129.1 (q,  $J = 32.0$ , ArCF<sub>3</sub>), 128.7 (C3), 128.5, 128.0, 126.5 (3 × ArCH), 125.4 (q,  $J = 3.5$ , ArCH), 124.2 (q,  $J = 272.0$ , CF<sub>3</sub>), 73.9 (C1), 35.2 (C5), 29.5 (C4);

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -62.5;

HRMS ( $\text{EI}^+$ ) Found [ $\text{M}^+$ ]: 315.1234,  $\text{C}_{19}\text{H}_{16}\text{NF}_3$  requires 315.1235.

Diagnostic signals for **11g**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 6.41 (0.08H, app. t,  $J = 3.0$ ), 5.99 (0.08H, app. t,  $J = 3.0$ ).

Diagnostic signals for (**Z**)-**10g**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 5.80 (0.07H, dd,  $J = 11.5, 9.5$ , H2), 5.17-5.08 (0.07H, m, H1).

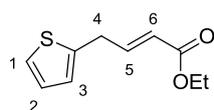


### 2-Allylthiophene<sup>6</sup>

To a solution of thiophene (950  $\mu\text{L}$ , 11.9 mmol) in THF (24 mL) at 0 °C was added *n*-butyl lithium (8.50 mL, 1.54 M, 13.1 mmol) dropwise over 5 minutes. The reaction mixture was stirred at this temperature for 45 minutes after which time it was cooled to -78 °C and CuCN (106 mg, 1.19 mmol) was added. Allyl bromide (1.13 mL, 13.1 mmol) was added and the reaction was stirred for 18 hours during which time it warmed to room temperature. Saturated aq.  $\text{NH}_4\text{Cl}$  (40 mL) was added and the mixture was extracted with  $\text{Et}_2\text{O}$  (2 × 50 mL). The combined organic extracts were washed with brine (30 mL), dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated *in vacuo*. Purification of the residue by Kugelrohr distillation (150 °C) afforded the title compound (640 mg, 43%) as a colorless oil.

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.71 (1H, dd,  $J = 5.0, 1.0$ , H1), 6.96 (1H, dd,  $J = 5.0, 3.5$ , H2), 6.84-6.82 (1H, m, H3), 6.07-5.97 (1H, m, H5), 5.18 (1H, dqd,  $J = 17.0, 1.5, 0.5$ , H6), 5.13 (1H, dqd,  $J = 10.0, 1.5, 0.5$ , H7), 3.60 (2H, dd,  $J = 6.5, 1.5$ , H4).

The spectroscopic properties of this compound were consistent with the data available in the literature.<sup>6</sup>



### (*E*)-Ethyl 4-(thiophen-2-yl)but-2-enoate

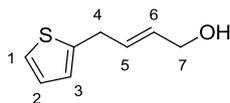
**General procedure A:** 2-Allyl thiophene (630 mg, 5.08 mmol) and ethyl acrylate (1.11 mL, 10.2 mmol) were employed. FCC (50:1 – 30:1 (hexane-EtOAc)) afforded the title compound (705 mg, 70%) as a colorless oil.

$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 2981 (w), 1714 (s), 1654 (m), 1367 (m), 1269 (s), 1164 (s), 1037 (s), 979 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.18 (1H, dd,  $J = 5.0, 1.0$ , H1), 7.08 (1H, dt,  $J = 15.5, 6.5$ , H5), 6.95 (1H, dd,  $J = 5.0, 3.5$ , H2), 6.84-6.83 (1H, m, H3), 5.88 (1H, dt,  $J = 15.5, 1.5$ , H6), 4.19 (2H, q,  $J = 7.0$ ,  $\text{CH}_2\text{CH}_3$ ), 3.71 (2H, ddd,  $J = 6.5, 1.5, 1.0$ , H4), 1.28 (3H, t,  $J = 7.0$ ,  $\text{CH}_2\text{CH}_3$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 166.3 ( $\text{CO}_2\text{Et}$ ), 145.9 (C5), 139.7 (ArC), 127.1 (C2), 125.6 (C3), 124.3 (C1), 122.6 (C6), 60.3 ( $\text{CH}_2\text{CH}_3$ ), 32.2 (C4), 14.2 ( $\text{CH}_2\text{CH}_3$ );

HRMS ( $\text{EI}^+$ ) Found [ $\text{M}^+$ ]: 196.0560,  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}$  requires 196.0558.



**(E)-4-(Thiophen-2-yl)but-2-en-1-ol**

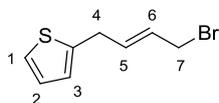
**General procedure B:** (*E*)-Ethyl 4-(thiophen-2-yl)but-2-enoate (700 mg, 3.57 mmol) was employed. FCC (4:1 – 3:1 (hexane-EtOAc)) afforded the title compound (453 g, 82%) as a colorless oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3318 (br), 2865 (w), 1427 (m), 1089 (m), 995 (s), 967 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.15 (1H, dd,  $J = 5.0, 1.0$ , H1), 6.94 (1H, dd,  $J = 5.0, 3.5$ , H2), 6.81-6.79 (1H, m, H3), 5.92-5.85 (1H, m, H5), 5.80-5.74 (1H, m, H6), 4.14 (2H, dd,  $J = 5.5, 1.0$ , H7), 3.58 (2H, d,  $J = 6.5$ , H4);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 142.8 (ArC), 130.7 (C6), 130.4 (C5), 126.9 (C2), 124.6 (C3), 123.6 (C1), 63.3 (C7), 32.6 (C4);

**HRMS** ( $\text{EI}^+$ ) Found  $[\text{M}]^+$ : 154.1450,  $\text{C}_8\text{H}_{10}\text{OS}$  requires 154.0452.



**(E)-2-(4-Bromobut-2-en-1-yl)thiophene**

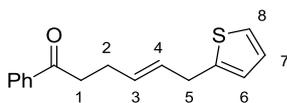
**General procedure C:** (*E*)-4-(Thiophen-2-yl)but-2-en-1-ol (450 mg, 2.92 mmol) was employed to afford the title compound (502 g, 81%) as a yellow oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3034 (w), 2900 (w), 1660 (m), 1415 (m), 1203 (m), 964 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.16 (1H, dd,  $J = 5.0, 1.0$ , H1), 6.94 (1H, dd,  $J = 5.0, 3.5$ , H2), 6.82-6.80 (1H, m, H3), 5.98-5.91 (1H, m, H5), 5.83 (1H, dtt,  $J = 15.0, 7.5, 1.5$ , H6), 3.97 (2H, dd,  $J = 7.5, 1.0$ , H7), 3.60 (2H, d,  $J = 7.0$ , H4);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 142.0 (ArC), 133.7 (C5), 127.9 (C6), 127.0 (C2), 124.9 (C3), 123.9 (C1), 32.5 (C7), 32.4 (C4);

**HRMS** ( $\text{EI}^+$ ) Found  $[\text{M}]^+$ : 215.9611,  $\text{C}_8\text{H}_9\text{BrS}$  requires 215.9608.



**(E)-1-Phenyl-6-(thiophen-2-yl)hex-4-en-1-one**

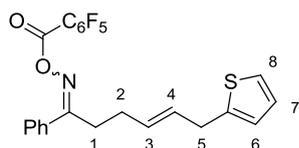
**General Procedure D:** Ethyl benzoylacetate (320  $\mu\text{L}$ , 1.85 mmol) and (*E*)-2-(4-bromobut-2-en-1-yl)thiophene (480 mg, 2.22 mmol) were employed. FCC (60:1 (hexane-EtOAc)) afforded the title compound (248 mg, 52%) as a colorless oil. This material was contaminated with *ca.* 10% of an unknown impurity.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3065 (w), 2897 (w), 1683 (s), 1448 (m), 1203 (m), 966 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.98-7.95 (2H, m, ArCH), 7.59-7.54 (1H, m, ArCH), 7.49-7.44 (2H, m, ArCH), 7.13 (1H, dd,  $J = 5.0, 1.0$ , H8), 6.93 (1H, dd,  $J = 5.0, 3.5$ , H7), 6.80-6.78 (1H, m, H6), 5.74-5.63 (2H, m, H3 & H4), 3.53 (2H, dd,  $J = 5.5, 1.0$ , H5), 3.08 (2H, t,  $J = 7.5$ , H1), 2.53-2.48 (2H, m, H2);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 199.4 (CO), 143.7 (ArC), 136.9 (ArC), 132.9 (ArCH), 130.6 (C4), 129.1 (C3), 128.5, 128.0 (2  $\times$  ArCH), 126.8 (C7), 124.2 (C8), 123.4 (C6), 38.1 (C1), 32.9 (C5), 26.9 (C2);

**HRMS** ( $\text{EI}^+$ ) Found  $[\text{M}]^+$ : 256.0910,  $\text{C}_{16}\text{H}_{16}\text{OS}$  requires 256.0922.



**(4E)-1-Phenyl-6-(thiophen-2-yl)hex-4-en-1-one O-perfluorobenzoyl oxime 9h**

**General procedure E:** **Part A:** (*E*)-1-Phenyl-6-(thiophen-2-yl)hex-4-en-1-one (205 mg, 0.801 mmol) was employed affording the corresponding oxime (176 mg, 81%) as a colorless oil after purification by FCC (15:1 – 5:1 (hexane-EtOAc)). **Part B:** The corresponding oxime (176 mg, 0.649 mmol) was employed. Purification of the residue (50:1 (hexane-EtOAc)) afforded the title compound (221 mg, 73%, 6:1 mixture of oxime isomers) as a colorless oil that solidified on standing.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2899 (w), 1753 (s), 1654 (m), 1522 (m), 1496 (s), 1322 (s), 1196 (s);

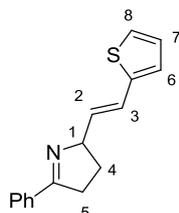
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) Data for the major isomer only 7.76-7.73 (2H, m, ArCH), 7.50-7.41 (3H, m, ArCH), 7.12 (1H, dd,  $J = 5.0, 1.0$ , H8), 6.91 (1H, dd,  $J = 5.0, 3.5$ , H7), 6.75-6.74 (1H, m, H6), 5.68-5.60 (1H, m, H4), 5.58-5.51 (1H, m, H3), 3.49 (2H, d,  $J = 6.5$ , H5), 3.01 (2H, d,  $J = 8.0$ , H1), 2.37-2.32 (2H, m, H2);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 168.2 (CN), 156.4 (CO), 143.2 (ArC), 133.0 (ArC), 131.0 (ArCH), 130.1 (C4), 129.4 (C3), 128.8, 127.5 (2 × ArCH), 126.8 (C7), 124.3 (C6), 123.5 (C8), 32.8 (C5), 29.4 (C2), 28.6 (C1);

Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -136.9 (2F), -137.2 (0.3F), -147.4 (1F), -147.9 (0.15F), -159.6 (2F), -159.9 (0.3F);

**HRMS** (ESI<sup>+</sup>) Found  $[\text{M}+\text{Na}]^+$ : 488.0714,  $\text{C}_{23}\text{H}_{16}\text{O}_2\text{NF}_5\text{SNa}$  requires 488.0731.



**(E)-5-Phenyl-2-(2-(thiophen-2-yl)vinyl)-3,4-dihydro-2H-pyrrole 10h**

**General procedure F:** **9h** (80 mg, 0.17 mmol) was employed. In a modification to the general procedure the reaction was heated at 100 °C. Analysis of the crude reaction mixture revealed a total cyclization yield of 71% and a selectivity of 10:1 (**10h:11h**). *E:Z* ratio of **10h** was 11:1. FCC (10:1 – 3:1 (hexane-EtOAc)) afforded the title compound (26 mg, 60%) as a yellow oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3098 (w), 2938 (w), 1609 (m), 1572 (m), 1492 (m), 1445 (m), 951 (s);

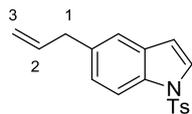
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.92-7.89 (2H, m, ArCH), 7.45-7.42 (3H, m, ArCH), 7.13-7.11 (1H, m, H8), 6.95-6.93 (2H, m, H7 & H6), 6.75 (1H, dd,  $J = 15.5, 1.0$ , H3), 6.20 (1H, dd,  $J = 15.5, 7.0$ , H2), 4.87 (1H, dddd,  $J = 8.5, 7.0, 7.0, 1.0$ , H1), 3.15-3.07 (1H, m, H5), 3.00-2.91 (1H, m, H5'), 2.37 (1H, dddd,  $J = 13.0, 9.5, 8.0, 5.0$ , H4), 1.87 (1H, dddd,  $J = 13.0, 9.5, 7.5, 6.5$ , H4');

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 173.6 (CN), 142.4 (ArC), 134.4 (ArC), 131.6 (C2), 130.6, 128.4, 127.8 (3 × ArCH), 127.2 (C7), 125.3 (C6), 123.8 (C8), 123.1 (ArC), 74.0 (C1), 35.1 (C5), 29.7 (C4);

**HRMS** (EI<sup>+</sup>) Found  $[\text{M}]^+$ : 253.0922,  $\text{C}_{16}\text{H}_{15}\text{NS}$  requires 253.0925.

Diagnostic signals for **11h**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 6.42 (0.09H, app. t,  $J = 3.0$ ), 6.02 (0.09H, app. t,  $J = 3.0$ ).

Diagnostic signals for (**Z**)-**10h**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 5.63 (0.08H, dd,  $J = 11.5, 9.5$ , H2), 5.46-5.39 (0.08H, m, H1).



### 5-Allyl-1-tosyl-1H-indole

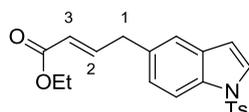
To a solution of 5-bromoindole (1.30 g, 6.63 mmol) in toluene (6 mL) was added *n*-Bu<sub>4</sub>NHSO<sub>4</sub> (158 mg, 0.465 mmol), KOH (8.50 g, 152 mmol) and *p*-TsCl (1.52 g, 7.97 mmol) as a solution in H<sub>2</sub>O (8.5 mL) and toluene (12 mL). The reaction was stirred for 4 hours after which time it was diluted with H<sub>2</sub>O (12 mL). The layers were separated and the organic layer was washed with H<sub>2</sub>O (2 × 10 mL), brine (10 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo* to afford the title compound (2.3 g, 99%) as a pale yellow solid that was used without further purification.  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.86 (1H, dt, *J* = 8.5, 0.5, ArCH), 7.75-7.72 (2H, m, ArCH), 7.65 (1H, dd, *J* = 2.0, 0.5, ArCH), 7.56 (1H, dd, *J* = 3.5, 0.5, ArCH), 7.40 (1H, ddd, *J* = 9.0, 2.0, 0.5, ArCH), 7.24-7.21 (2H, m, ArCH), 6.59 (1H, dd, *J* = 3.5, 1.0, ArCH), 2.35 (3H, s, CH<sub>3</sub>).  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 138.6, 134.5, 131.4, 128.1, 124.3, 123.1, 120.1, 115.0, 110.8, 102.3, 40.4. To a solution of 5-bromo-1-tosyl-1H-indole (890 mg, 2.55 mmol) in degassed DMF (3 mL) in a Schlenk tube was added PdCl<sub>2</sub> (23 mg, 0.13 mmol) triphenylphosphine (134 mg, 0.51 mmol) and allyltributylstannane (0.95 mL, 3.06 mmol). The reaction mixture was heated to 120 °C in a preheated oil bath. After 20 h, the black-green reaction mixture was cooled to rt and diluted with Et<sub>2</sub>O (15 mL) and brine (10 mL). The organic layer was separated, washed with water (10 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. Purification of the residue by FCC (100:0 – 5:1 (hexane:Et<sub>2</sub>O)) afforded the title compound (600 mg, 76%) as a colorless oil.

$\nu_{\text{max}}$  / cm<sup>-1</sup> (film) 3114 (w), 2920 (w), 1367 (s), 1169 (s), 1124 (s);

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.90 (1H, d, *J* = 8.5, ArCH), 7.76-7.74 (2H, m, ArCH), 7.53 (1H, d, *J* = 3.5, ArCH), 7.33-7.32 (1H, m, ArCH), 7.21 (2H, dt, *J* = 8.0, 1.0, ArCH), 7.14 (1H, dd, *J* = 8.5, 1.5, ArCH), 6.59 (1H, dd, *J* = 3.5, 1.0, ArCH), 5.97 (1H, ddt, *J* = 17.0, 10.0, 6.5, H<sub>2</sub>), 5.10-5.04 (2H, m, H<sub>3</sub>), 3.44 (2H, d, *J* = 7.0, H<sub>1</sub>), 2.33 (3H, s, CH<sub>3</sub>);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 144.8 (ArC), 137.6 (C<sub>2</sub>), 135.4, 135.1, 133.5, 131.1 (4 × ArC), 129.8, 126.8, 126.5, 125.5, 120.9 (5 × ArCH), 115.7 (C<sub>3</sub>), 113.4, 108.9 (2 × ArCH), 40.0 (C<sub>1</sub>), 21.5 (CH<sub>3</sub>);

HRMS (EI<sup>+</sup>) Found [M]<sup>+</sup>: 311.0967, C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>S requires 311.0980.



### (E)-Ethyl 4-(1-tosyl-1H-indol-5-yl)but-2-enoate

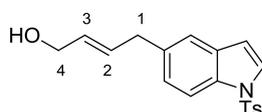
General procedure A: 5-Allyl-1-tosyl-1H-indole (575 mg, 1.84 mmol) and ethyl acrylate (403 μL, 3.70 mmol) were employed. FCC (5:1 – 4:1 (hexane-EtOAc)) afforded the title compound (660 mg, 93%) as a brown oil.

$\nu_{\text{max}}$  / cm<sup>-1</sup> (film) 2981 (w), 1712 (s), 1652 (m), 1596 (m), 1367 (m), 1367 (m);

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.92 (1H, d, *J* = 8.5, ArCH), 7.77-7.75 (2H, m, ArCH), 7.56 (1H, d, *J* = 3.5, ArCH), 7.33-7.32 (1H, m, ArCH), 7.25-7.22 (2H, m, ArCH), 7.13-7.06 (2H, m, ArCH & H<sub>2</sub>), 6.61 (1H, dd, *J* = 3.5, 1.0, ArCH), 5.80 (1H, dt, *J* = 15.5, 1.5, H<sub>3</sub>), 4.18 (2H, q, *J* = 7.0, CH<sub>2</sub>CH<sub>3</sub>), 3.57 (2H, dd, *J* = 7.0, 1.5, H<sub>1</sub>), 2.35 (3H, s, CH<sub>3</sub>), 1.27 (3H, t, *J* = 7.0, CH<sub>2</sub>CH<sub>3</sub>);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 166.5 (CO), 147.4 (C<sub>2</sub>), 144.9, 135.3, 133.7, 132.7, 131.2 (5 × ArC), 129.9, 126.8 (2C), 125.5 (4 × ArCH), 122.2 (C<sub>3</sub>), 121.3, 113.6, 108.8 (3 × ArCH), 60.3 (CH<sub>2</sub>CH<sub>3</sub>), 38.3 (C<sub>1</sub>), 21.6 (CH<sub>3</sub>), 14.2 (CH<sub>2</sub>CH<sub>3</sub>);

HRMS (EI<sup>+</sup>) Found [M]<sup>+</sup>: 383.1194, C<sub>21</sub>H<sub>21</sub>NO<sub>4</sub>S requires 383.1191.



### (E)-4-(1-Tosyl-1H-indol-5-yl)but-2-en-1-ol

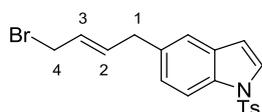
**General procedure B:** (*E*)-Ethyl 4-(1-tosyl-1H-indol-5-yl)but-2-enoate (650 mg, 1.69 mmol) was employed. FCC (4:1 – 2:1 (hexane-EtOAc)) afforded the title compound (432 mg, 75%) as a colorless oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3353 (br), 2920 (w), 1366 (m), 1168 (s), 1123 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.89 (1H, d,  $J = 8.5$ , ArCH), 7.76-7.74 (2H, m, ArCH), 7.53 (1H, d,  $J = 3.5$ , ArCH), 7.32-7.31 (1H, m, ArCH), 7.21 (2H, d,  $J = 8.5$ , ArCH), 7.13 (1H, dd,  $J = 8.5, 1.5$ , ArCH), 6.59 (1H, dd,  $J = 3.5, 1.0$ , ArCH), 5.88-5.82 (1H, m, H<sub>2</sub>), 5.72-5.66 (1H, m, H<sub>3</sub>), 4.12 (2H, dd,  $J = 6.0, 1.0$ , H<sub>4</sub>), 3.43 (2H, d,  $J = 6.5$ , H<sub>1</sub>), 2.33 (3H, s, CH<sub>3</sub>), 1.47 (1H, br. s, OH);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 144.8, 135.3, 135.1, 133.5 (4 × ArC), 131.7 (C<sub>2</sub>), 131.1 (ArC), 130.2 (C<sub>3</sub>), 129.8, 126.8, 126.6, 125.4, 120.9, 113.4, 108.8 (7 × ArCH), 63.5 (C<sub>4</sub>), 38.4 (C<sub>1</sub>), 21.5 (CH<sub>3</sub>);

**HRMS** ( $\text{EI}^+$ ) Found  $[\text{M}]^+$ : 341.1094,  $\text{C}_{19}\text{H}_{19}\text{NO}_3\text{S}$  requires 341.1086.



### (E)-5-(4-Bromobut-2-en-1-yl)-1-tosyl-1H-indole

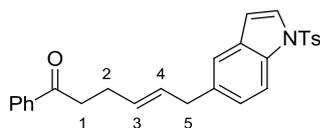
**General procedure C:** (*E*)-4-(1-Tosyl-1H-indol-5-yl)but-2-en-1-ol (425 mg, 1.25 mmol) was employed to afford the title compound (472 mg, 95%) as a colorless oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3030 (w), 2920 (w), 1458 (m), 1169 (s), 1124 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.90 (1H, dd,  $J = 8.5, 1.0$ , ArCH), 7.75 (2H, d,  $J = 8.5$ , ArCH), 7.53 (1H, d,  $J = 3.5$ , ArCH), 7.31-7.30 (1H, m, ArCH), 7.22 (2H, dd,  $J = 8.0, 1.0$ , ArCH), 7.11 (1H, dd,  $J = 8.5, 1.5$ , ArCH), 6.59 (1H, d,  $J = 3.5$ , ArCH), 5.95-5.88 (1H, m, H<sub>2</sub>), 5.78-5.71 (1H, m, H<sub>3</sub>), 3.95 (2H, d,  $J = 7.5$ , H<sub>4</sub>), 3.45 (2H, d,  $J = 6.5$ , H<sub>1</sub>), 2.34 (3H, s, CH<sub>3</sub>);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 144.9, 135.5 (2 × ArC), 134.9 (C<sub>2</sub>), 134.4, 133.5, 131.1 (3 × ArC), 129.9 (ArCH), 127.6 (C<sub>3</sub>), 126.8, 126.6, 125.4, 120.9, 113.5, 108.8 (6 × ArCH), 38.2 (C<sub>1</sub>), 32.9 (C<sub>4</sub>), 21.6 (CH<sub>3</sub>);

**HRMS** ( $\text{EI}^+$ ) Found  $[\text{M}]^+$ : 403.0241,  $\text{C}_{19}\text{H}_{18}\text{NO}_2\text{S}^{79}\text{Br}$  requires 403.0242.



### (E)-1-Phenyl-6-(1-tosyl-1H-indol-5-yl)hex-4-en-1-one

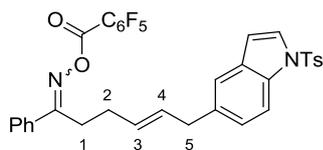
**General Procedure D:** Ethyl benzoylacetate (150  $\mu\text{L}$ , 0.867 mmol) and (*E*)-5-(4-bromobut-2-en-1-yl)-1-tosyl-1H-indole (419 mg, 1.04 mmol) were employed. Careful monitoring of the hydrolysis step is required to prevent deprotection of the indole. FCC (5:1 – 3:1 (hexane-EtOAc)) afforded the title compound (238 mg, 60%) as a colorless oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2141 (w), 2920 (w), 1683 (m), 1367 (m), 1169 (s), 1124 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.96-7.93 (2H, m, ArCH), 7.89 (1H, d,  $J = 8.5$ , ArCH), 7.77-7.74 (2H, m, ArCH), 7.57-7.52 (2H, m, ArCH), 7.47-7.43 (2H, m, ArCH), 7.30-7.29 (1H, m, ArCH), 7.21-7.18 (2H, m, ArCH), 7.12 (1H, dd,  $J = 8.5, 1.5$ , ArCH), 6.59 (1H, dd,  $J = 4.0, 1.0$ , ArCH), 5.68-5.56 (1H, m, H<sub>3</sub>), 5.62-5.56 (1H, m, H<sub>4</sub>), 3.38 (2H, d,  $J = 6.5$ , H<sub>5</sub>), 3.05 (2H, t,  $J = 7.5$ , H<sub>1</sub>), 2.50-2.46 (2H, m, H<sub>2</sub>), 2.32 (3H, s, CH<sub>3</sub>);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 199.6 (CO), 144.8, 136.9, 135.8, 135.3, 133.3 (5 × ArC), 132.9 (ArCH), 131.0 (ArC), 130.1 (2C, C<sub>3</sub> & C<sub>4</sub>), 129.8, 128.5, 128.0, 126.7, 126.4, 125.4, 120.7, 113.3, 108.9 (9 × ArCH), 38.7 (C<sub>5</sub>), 38.3 (C<sub>1</sub>), 27.1 (C<sub>2</sub>), 21.5 (CH<sub>3</sub>);

**HRMS** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 466.1447, C<sub>27</sub>H<sub>25</sub>O<sub>3</sub>NSNa requires 466.1452.



**(4E)-1-Phenyl-6-(1-tosyl-1H-indol-5-yl)hex-4-en-1-one O-perfluorobenzoyl oxime 9i**

**General procedure E: Part A:** (E)-1-Phenyl-6-(1-tosyl-1H-indol-5-yl)hex-4-en-1-one (238 mg, 0.537 mmol) was employed affording the corresponding oxime (220 mg, 89%) as a colorless oil. **Part B:** The corresponding oxime (220 mg, 0.497 mmol) was employed. Purification of the residue (10:1 – 7:1 (hexane-EtOAc)) afforded the title compound (285 mg, 91%, 6:1 mixture of oxime isomers) as a colorless oil that solidified on standing.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2924 (w), 1757 (s), 1652 (m), 1524 (s), 1495 (s), 1370 (s), 1324 (s), 1188 (s), 1170 (s);

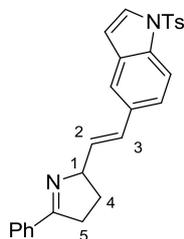
$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.89-7.85 (1H, m, ArCH), 7.77-7.72 (2H, m, ArCH), 7.70-7.66 (2H, m, ArCH), 7.53 (1H, d,  $J = 3.5$ , ArCH), 7.48-7.43 (1H, m, ArCH), 7.41-7.36 (2H, m, ArCH), 7.26-7.18 (3H, m, ArCH), 7.14-7.11 (0.15H, m, ArCH), 7.06 (0.85H, m, dd,  $J = 8.5, 1.5$ , ArCH), 6.59 (1H, dd,  $J = 3.5, 1.0$ , ArCH), 5.62-5.41 (2H, m, H3 & H4), 3.38-3.32 (2H, m, H5), 2.99 (1.7H, t,  $J = 7.5$ , H1), 2.84 (0.3H, t,  $J = 7.5$ , H1'), 2.35-2.22 (5H, m, H2 & CH<sub>3</sub>);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) Data for major isomer only 168.2 (CN), 156.4 (CO), 144.8, 135.3, 135.2, 133.3, 133.0 (5 × ArC), 131.2 (C4), 130.9 (2C, ArCH & ArC), 129.8 (ArCH), 128.7 (C3), 128.7, 127.4, 126.7, 126.4, 125.3, 120.7, 113.2, 108.8 (8 × ArCH), 38.6 (C5), 29.5 (C2), 28.6 (C1), 21.4 (CH<sub>3</sub>);

Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

$\delta_{\text{C}}$  (376 MHz, CDCl<sub>3</sub>) -136.9 (2F), -137.1 (0.3F), -147.2 (1F), -147.7 (0.15F), -159.6 (2F), -159.9 (0.3F);

**HRMS** (ESI<sup>+</sup>) Found [M+Na]<sup>+</sup>: 675.1347, C<sub>34</sub>H<sub>25</sub>O<sub>4</sub>N<sub>2</sub>F<sub>5</sub>SNa requires 675.1339.



**(E)-5-(2-(5-Phenyl-3,4-dihydro-2H-pyrrol-2-yl)vinyl)-1-tosyl-1H-indole 10i**

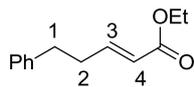
**General procedure F: 9i** (71 mg, 0.11 mmol) was employed. In a modification to the general procedure the reaction mixture was heated at 100 °C. Analysis of the crude reaction mixture was not possible due to overlapping signals. FCC (4:1 – 2:1 (hexane-EtOAc)) afforded the title compound (22 mg, 45%) as a yellow oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2925 (w), 1610 (m), 1456 (m), 1369 (s), 1170 (s);

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.92-7.90 (3H, m, ArCH), 7.75-7.73 (2H, m, ArCH), 7.52-7.50 (2H, m, ArCH), 7.46-7.42 (3H, m, ArCH), 7.39 (1H, dd,  $J = 8.5, 1.5$ , ArCH), 7.22-7.19 (2H, m, ArCH), 6.68 (1H, dd,  $J = 16.0, 1.0$ , H3), 6.61-6.59 (1H, m, ArCH), 6.31 (1H, dd,  $J = 16.0, 7.0$ , H2), 4.94-4.89 (1H, m, H1), 3.15-3.09 (1H, m, H5), 2.97 (1H, dddd,  $J = 17.0, 9.5, 7.5, 2.0$ , H5'), 2.42-2.35 (1H, m, H4), 2.33 (3H, s, CH<sub>3</sub>), 1.87 (1H, dddd,  $J = 13.0, 10.0, 7.5, 7.5$ , H4');

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 173.6 (CN), 144.9, 135.2, 134.2 (2C), 132.8, 131.1 (6 × ArC), 131.1 (C2), 130.7 (ArCH), 129.9 (C3), 129.8, 128.4, 127.9, 126.7 (2C), 123.1, 119.3, 113.5, 109.2 (9 × ArCH), 74.2 (C1), 35.1 (C5), 29.7 (C4), 21.5 (C3);

**HRMS** (EI<sup>+</sup>) Found [M]<sup>+</sup>: 440.1548, C<sub>27</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S requires 440.1559.



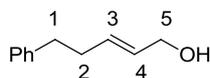
**(E)-Ethyl 5-phenylpent-2-enoate**

To a solution of 3-phenylpropanal (90%, 1.46 mL, 10.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (14 mL) was added ethyl (triphenylphosphoranylidene)acetate (4.21 g, 12.0 mmol) as a solution in  $\text{CH}_2\text{Cl}_2$  (11 mL) dropwise. After being stirred for 2 hours, the solution was poured into saturated aq. NaCl (20 mL). The phases were separated and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (20 mL). The organic phases were combined, dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated *in vacuo*. Purification of the residue by FCC (50:1 (hexane-EtOAc)) afforded the title compound (1.45 g, 71%) as a colorless oil.

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.32-7.28 (2H, m, ArCH), 7.23-7.17 (3H, m, ArCH), 7.01 (1H, dt,  $J = 15.5, 7.0$ , H3), 5.85 (1H, dt,  $J = 15.5, 1.5$ , H4), 4.19 (2H, q,  $J = 7.0$ ,  $\text{CH}_2\text{CH}_3$ ), 2.78 (2H, t,  $J = 8.0$ , H1), 2.56-2.50 (2H, m, H2), 1.29 (3H, t,  $J = 7.0$ ,  $\text{CH}_2\text{CH}_3$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 166.5 (C=O), 148.0 (C3), 140.8 (ArC), 128.4, 128.3, 126.1 (3  $\times$  ArCH), 121.8 (C4), 60.2 ( $\text{CH}_2\text{CH}_3$ ), 34.3 (C1), 33.9 (C2), 14.2 ( $\text{CH}_2\text{CH}_3$ )

*The spectroscopic properties of this compound were consistent with the data available in the literature.*<sup>7</sup>



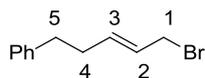
**(E)-6-Phenylpent-2-en-1-ol**

General procedure B: (E)-Ethyl 5-phenylpent-2-enoate (1.45 g, 7.11 mmol) was employed. FCC (4:1 – 2:1 (hexane-EtOAc)) afforded the title compound (982 mg, 85%) as a colorless oil.

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.31-7.27 (2H, m, ArCH), 7.22-7.17 (3H, m, ArCH), 5.78-5.71 (1H, m, H3), 5.70-5.63 (1H, m, H4), 4.08 (2H, dd,  $J = 5.5, 1.0$ , H5), 2.74-2.70 (2H, m, H1), 2.41-2.36 (2H, m, H2), 1.37 (1H, br. s, OH);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 141.7 (ArC), 132.2 (C3), 129.6 (C4), 128.4, 128.3, 125.8 (3  $\times$  ArCH), 63.7 (C5), 35.5 (C1), 33.9 (C2).

*The spectroscopic properties of this compound were consistent with the data available in the literature.*<sup>7</sup>



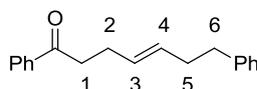
**(E)-(5-Bromopent-3-en-1-yl)benzene**

General procedure C: (E)-6-Phenylpent-2-en-1-ol (970 mg, 5.99 mmol) was employed to afford the title compound (1.26 g, 94%) as a colorless oil.

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.31-7.27 (2H, m, ArCH), 7.22-7.16 (3H, m, ArCH), 5.85-5.78 (1H, m, H3), 5.76-5.69 (1H, m, H2), 3.94 (2H, d,  $J = 7.5$ , H1), 2.71 (2H, t,  $J = 8.0$ , H5), 2.43-2.37 (2H, m, H4);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 141.3 (ArC), 135.4 (C3), 128.4 (2C, 2  $\times$  ArCH), 126.9 (C2), 125.9 (ArCH), 35.2 (C5), 33.8 (C4), 33.3 (C1).

*The spectroscopic properties of this compound were consistent with the data available in the literature.*<sup>8</sup>



**(E)-1,7-Diphenylhept-4-en-1-one**

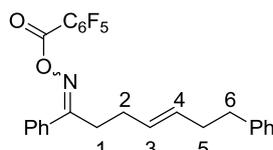
**General Procedure D:** Ethyl benzoylacetate (790  $\mu\text{L}$ , 4.61 mmol) and (*E*)-(5-bromopent-3-en-1-yl)benzene (1.24 g, 5.54 mmol) were employed. FCC (50:1 (hexane-EtOAc)) afforded the title compound (845 mg, 69%) as a colorless oil. This material was contaminated with *ca.* 5% of the bis-alkylated  $\beta$ -keto ester.

$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 3026 (w), 2923 (w), 1683 (s), 1448 (m), 1202 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.98-7.96 (2H, m, ArCH), 7.59-7.55 (1H, m, ArCH), 7.49-7.46 (2H, m, ArCH), 7.29-7.26 (2H, m, ArCH), 7.20-7.16 (3H, m, ArCH), 5.59-5.50 (2H, m, H3 and H4), 3.04-3.01 (2H, m, H1), 2.69-2.66 (2H, m, H6), 2.47-2.43 (2H, m, H2), 2.35-2.30 (2H, m, H5);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 199.6 (CO), 141.9 (ArC), 137.0 (ArC), 132.9 (ArCH), 130.5 (C4), 129.3 (C3), 128.5, 128.4, 128.2, 12.0, 125.7 ( $5 \times$  ArCH), 38.5 (C1), 35.9 (C6), 34.3 (C5), 27.1 (C2);

**HRMS** ( $\text{Cl}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 265.1591,  $\text{C}_{19}\text{H}_{21}\text{O}$  requires 265.1592.



**(4*E*)-1,7-Diphenylhept-4-en-1-one *O*-perfluorobenzoyl oxime 9j**

**General procedure E: Part A:** (*E*)-1,7-Diphenylhept-4-en-1-one (830 mg, 3.14 mmol) was employed affording the corresponding oxime (728 mg, 83%) as a colorless solid. **Part B:** The corresponding oxime (715 mg, 2.56 mmol) was employed. Purification of the residue (50:1 – 20:1 (hexane-EtOAc)) afforded the title compound (984 mg, 80%, 10:1 mixture of oxime isomers) as a yellow oil that solidified on standing.

$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 3027 (w), 2846 (w), 1763 (s), 1652 (m), 1523 (m), 1496 (s), 1322 (m), 1188 (s);

*Data for the major isomer only:*

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.75-7.72 (2H, m, ArCH), 7.51-7.48 (1H, m, ArCH), 7.47-7.42 (2H, m, ArCH), 7.30-7.26 (2H, m, ArCH), 7.20-7.14 (3H, m, ArCH), 5.52-5.46 (1H, m, H4), 5.45-5.39 (1H, m, H3), 2.95 (2H, t,  $J = 7.5$ , H1), 2.63 (2H, t,  $J = 8.0$ , H6), 2.31-2.26 (4H, m, H2 and H5);

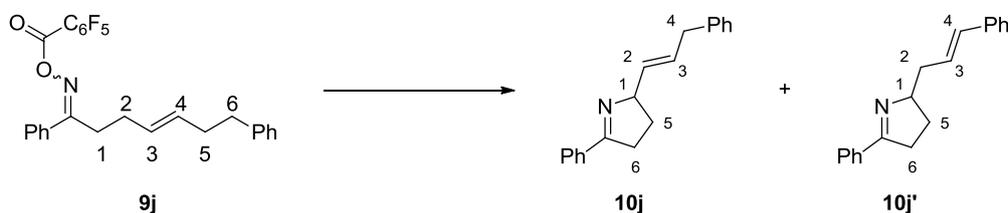
*Characteristic signal for the minor isomer: 2.83-2.80 (0.2H, m, H1')*

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 168.3 (CN), 156.5 (CO), 141.8 (ArC), 133.1 (C4), 131.5, 131.0, 128.7, 128.3, 128.2 ( $5 \times$  ArCH), 128.1 (C3), 127.5 (ArCH), 35.7 (C6), 34.2 (C5), 29.6 (C2), 28.8 (C1);

*Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.*

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -137.1 (2F), -137.4 (0.2F), -147.6 (1F), -148.1 (0.1F), -159.8 (2F), -160.1 (0.2F);

**HRMS** ( $\text{ESI}^+$ ) Found  $[\text{M}+\text{Na}]^+$ : 496.1306,  $\text{C}_{26}\text{H}_{20}\text{NO}_2\text{F}_5\text{Na}$  requires 496.1309.



**(*E*)-5-Phenyl-2-(3-phenylprop-1-en-1-yl)-3,4-dihydro-2*H*-pyrrole 10j**

**General procedure F:** **9j** (60 mg, 0.13 mmol) was employed. In a modification to the general procedure the reaction mixture was heated at 120  $^{\circ}\text{C}$ . Analysis of the crude reaction mixture revealed a total cyclization yield of 76% and a selectivity of 5:1 (**10j**+**10j'**):**11j**). FCC (20:1 – 5:1 (hexane-EtOAc)) afforded the title compound (19 mg, 58%, 6:1 inseparable mixture of alkene regioisomers, **10j**:**10j'**) as a yellow oil.

$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 3027 (w), 2900 (w), 1612 (m), 1574 (m), 1494 (m), 1448 (m), 1338 (m);

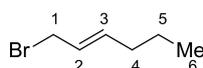
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.89-7.86 (2H, m, ArCH), 7.44-7.38 (3H, m, ArCH), 7.31-7.27 (2H, m, ArCH), 7.23-7.19 (3H, m, ArCH), 5.87 (1H, dtd,  $J = 15.0, 7.0, 1.0$ , H3), 5.67 (1H, dtd,  $J = 15.0, 7.0, 1.5$ , H2), 4.76-4.71 (1H, m, H1), 3.47-3.37 (2H, m, H4), 3.10-3.02 (1H, m, H6), 2.95-2.86 (1H, m, H6'), 2.34-2.25 (1H, m, H5), 1.82-1.73 (1H, m, H5');

**HRMS** (ESI<sup>+</sup>) Found  $[\text{M}+\text{H}]^+$ : 262.1590,  $\text{C}_{19}\text{H}_{20}\text{N}$  requires 262.1581.

*Diagnostic signals for alkene regioisomer 10j*:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 6.50 (0.17H, d,  $J = 15.5$ , H4), 6.30 (0.17H, dt,  $J = 15.5, 7.5$ , H3), 4.42-4.34 (0.17H, m, H1);

*Diagnostic signals for 11j*:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 6.43 (0.2H, app. t,  $J = 3.0$ ), 6.01 (0.2H, dd,  $J = 3.5, 2.5$ ).

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 173.0 (C<sub>N</sub>), 140.4 (ArC), 134.5 (ArC), 133.4 (C2), 130.4 (ArCH), 129.7 (C3), 128.6, 128.4, 128.3, 127.7, 125.9 ( $5 \times$  ArCH), 74.3 (C1), 38.8 (C4), 35.1 (C6), 29.7 (C5);



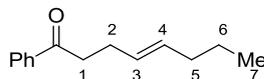
**(E)-1-Bromohex-2-ene**

General procedure C: *trans*-2-Hexen-1-ol (1.0 g, 10 mmol) was employed to afford the title compound (1.2 g, 77%) as a colorless oil.

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 5.80-5.73 (1H, m, H3), 5.72-5.64 (1H, m, H2), 3.95 (2H, d,  $J = 7.0$ , H1), 2.06-2.01 (2H, m, H4), 1.41 (2H, tq,  $J = 7.5, 7.5$ , H5), 0.90 (3H, t,  $J = 7.5$ , H6);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 136.5 (C3), 126.4 (C2), 34.1 (C4), 33.6 (C1), 22.0 (C5), 13.6 (C6);

*The spectroscopic properties of this compound were consistent with the data available in the literature.*<sup>9</sup>



**(E)-1-Phenyloct-4-en-1-one**

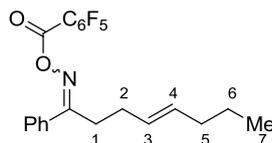
General Procedure D: Ethyl benzoylacetate (1.10 mL, 6.36 mmol) and (*E*)-1-bromohex-2-ene (1.24 g, 7.63 mmol) were employed. FCC (50:1 (hexane-EtOAc)) afforded the title compound (604 mg, 47%) as a colorless oil.

$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 2958 (w), 2872 (w), 1684 (s), 1448 (m), 1201 (m), 967 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.97-7.94 (2H, m, ArCH), 7.57-7.53 (1H, m, ArCH), 7.47-7.43 (2H, m, ArCH), 5.53-5.43 (2H, m, H3 & H4), 3.03 (2H, t,  $J = 7.5$ , H1), 2.46-2.40 (2H, m, H2), 1.99-1.93 (2H, m, H5), 1.36 (2H, tq,  $J = 7.5, 7.5$ , H6), 0.87 (3H, t,  $J = 7.5$ , H7);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 199.8 (C<sub>O</sub>), 137.0 (ArC), 132.9 (ArCH), 131.4 (C4), 128.6 (C3), 128.5, 128.0 ( $2 \times$  ArCH), 38.6 (C1), 34.6 (C5), 27.2 (C2), 22.6 (C6), 13.6 (C7);

**HRMS** (EI<sup>+</sup>) Found  $[\text{M}]^+$ : 202.1363,  $\text{C}_{14}\text{H}_{18}\text{O}$  requires 202.1358.



**(4E)-1-Phenyloct-4-en-1-one O-perfluorobenzoyl oxime 9k**

General procedure E: Part A: (*E*)-1-Phenyloct-4-en-1-one (565 mg, 2.80 mmol) was employed affording the corresponding oxime (589 mg, 97%) as a colorless solid. Part B: The corresponding oxime (300 mg, 1.38 mmol) was employed. Purification of the residue (50:1 – 30:1 (hexane-EtOAc)) afforded the title compound (449 mg, 79%, 20:1 mixture of oxime isomers) as a yellow oil that solidified on standing.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2962 (w), 1762 (s), 1649 (m), 1524 (m), 1493 (s), 1323 (s), 1194 (s);

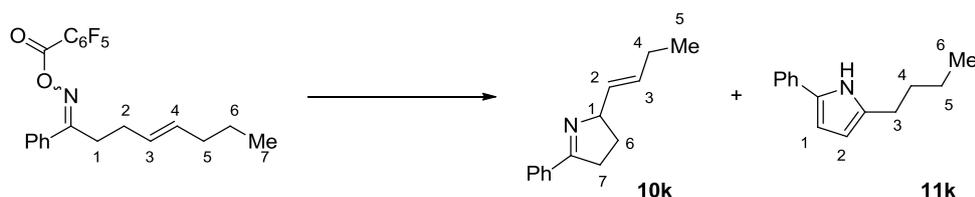
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.75-7.72 (2H, m, ArCH), 7.49-7.41 (3H, m, ArCH), 5.46-5.34 (2H, m, H3 & H4), 2.96 (2H, t,  $J = 8.0$ , H1), 2.30-2.26 (2H, m, H2), 1.94-1.90 (2H, m, H5), 1.32 (2H, tq,  $J = 7.5, 7.5$ , H6), 0.85 (3H, t,  $J = 7.5$ , H7);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 168.4 (CN), 156.5 (CO), 133.1 (ArC), 132.3 (C4), 130.9, 128.7 ( $2 \times$  ArCH), 127.5 (C3), 127.4 (ArCH), 34.4 (C5), 29.7 (C2), 28.9 (C1), 22.4 (C6), 13.5 (C7);

Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -137.2 (2F), -137.5 (0.1F), -147.8 (1F), -148.3 (0.05F), -157.0 (2F), -160.2 (0.1F);

HRMS (ESI<sup>+</sup>) Found  $[\text{M}+\text{Na}]^+$ : 434.1139,  $\text{C}_{21}\text{H}_{18}\text{O}_2\text{NF}_5\text{Na}$  requires 434.1150.



**(E)-2-(But-1-en-1-yl)-5-phenyl-3,4-dihydro-2H-pyrrole 10k**

**General procedure F:** **9k** (100 mg, 0.24 mmol) was employed. In a modification to the general procedure the reaction mixture was heated at 120 °C. Analysis of the crude reaction mixture revealed a total cyclization yield of 87% and a selectivity of 3:1 (**10k**:**11k**). FCC (15:1 – 5:1 (hexane-EtOAc)) afforded pyrrole **11k** (11 mg, 23%) and the title compound (29 mg, 60%, 12:1 mixture of alkene regioisomers) as a yellow oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2961 (w), 1611 (m), 1574 (m), 1448 (m), 1338 (m), 964 (s), 758 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.89-7.86 (2H, m, ArCH), 7.42-7.38 (3H, m, ArCH), 5.75 (1H, dt,  $J = 15.5, 6.5$ , H3), 5.55 (1H, dd,  $J = 15.5, 7.5$ , H2), 4.70-4.66 (1H, m, H1), 3.09-3.02 (1H, m, H7), 2.89 (1H, dddd,  $J = 17.0, 9.5, 7.5, 2.0$ , H7'), 2.27 (1H, dddd,  $J = 13.0, 9.5, 8.0, 5.0$ , H6), 2.11-2.05 (2H, m, H4), 1.75 (1H, dddd,  $J = 13.0, 9.5, 7.5, 7.5$ , H6'), 1.01 (3H, t,  $J = 7.5$ , H5);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 172.8 (CN), 134.5 (ArC), 133.0 (C3), 130.8 (C2), 130.4, 128.3, 127.8 ( $3 \times$  ArCH), 74.6 (C1), 35.1 (C7), 29.8 (C6), 25.4 (C4), 13.4 (C5);

HRMS (EI<sup>+</sup>) Found  $[\text{M}]^+$ : 199.1351,  $\text{C}_{14}\text{H}_{17}\text{N}$  requires 199.1361

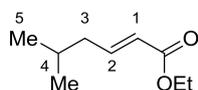
Diagnostic signal for alkene regioisomer (between C3-C4): 4.03-4.22 (0.08H, m, H1);

**2-Phenyl-5-butyl-1H-pyrrole 11k**

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 8.11 (1H, br. s, NH), 7.45-7.42 (2H, m, ArCH), 7.36-7.31 (2H, m, ArCH), 7.18-7.14 (1H, m, ArCH), 6.42 (1H, dd,  $J = 3.5, 2.5$ , H1), 5.99-5.97 (1H, m, H2), 2.65 (2H, t,  $J = 7.5$ , H3), 1.70-1.62 (2H, m, H4), 1.42 (2H, tq,  $J = 7.5, 7.5$ , H5), 0.96 (3H, t,  $J = 7.5$ , H6);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 134.3, 133.0, 130.5 ( $3 \times$  ArC), 128.8, 125.6, 123.3 ( $3 \times$  ArCH), 107.0 (C2), 106.0 (C1), 31.8 (C4), 27.6 (C3), 22.4 (C5), 13.9 (C6).

The spectroscopic properties of this compound were consistent with the data available in the literature.<sup>10</sup>



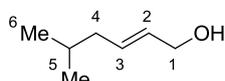
### (E)-Ethyl 5-methylhex-2-enoate

To a solution of NaH (60% dispersion in mineral oil, 880 mg, 22.0 mmol) in THF (100 mL) at 0 °C was added triethyl phosphonoacetate (4.36 mL, 22.0 mmol) dropwise over 10 minutes. After stirring at this temperature for 10 minutes *isovaleraldehyde* (2.46 mL, 23.0 mmol) was added dropwise. After 10 minutes the reaction was warmed to room temperature and quenched with saturated aq. NH<sub>4</sub>Cl (250 mL) and extracted with Et<sub>2</sub>O (3 × 250 mL). The organic layers were combined, washed with H<sub>2</sub>O (250 mL), brine (250 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. Purification of the residue by FCC (30:1 (hexane-EtOAc)) afforded the title compound (2.92 g, 85%) as a colorless oil.

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 6.93 (1H, dt,  $J = 15.5, 7.5$ , H2), 5.80 (1H, dt,  $J = 15.5, 1.5$ , H1), 4.18 (2H, q,  $J = 7.0$ , CH<sub>2</sub>CH<sub>3</sub>), 2.10-2.07 (2H, m, H3), 1.76 (1H, sep,  $J = 6.5$ , H4), 1.28 (3H, t,  $J = 7.0$ , CH<sub>2</sub>CH<sub>3</sub>), 0.92 (6H, d,  $J = 6.5$ , H5);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 166.7 (CO), 148.2 (C2), 122.3 (C1), 60.1 (CH<sub>2</sub>CH<sub>3</sub>), 41.5 (C3), 27.8 (C4), 22.3 (C5), 14.3 (CH<sub>2</sub>CH<sub>3</sub>).

*The spectroscopic properties of this compound were consistent with the data available in the literature.*<sup>11</sup>



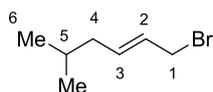
### (E)-5-Methylhex-2-en-1-ol

**General procedure B:** (*E*)-Ethyl 5-methylhex-2-enoate (2.90 g, 18.6 mmol) was employed. FCC (3:1 (hexane-EtOAc)) afforded the title compound (1.46 g, 69%) as a colorless oil.

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 5.71-5.60 (2H, H2 & H3), 4.10-4.09 (2H, m, H1), 1.95-1.92 (2H, m, H4), 1.63 (1H, sep,  $J = 6.5$ , H5), 1.37 (1H, br. s, OH), 0.89 (6H, d,  $J = 6.5$ , H6);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 132.2 (C3), 130.0 (C2), 63.8 (C1), 41.6 (C4), 28.2 (C5), 22.3 (C6).

*The spectroscopic properties of this compound were consistent with the data available in the literature.*<sup>12</sup>



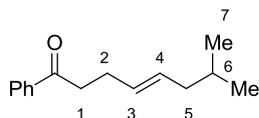
### (E)-1-Bromo-5-methylhex-2-ene

**General procedure C:** (*E*)-5-Methylhex-2-en-1-ol (1.47 g, 12.9 mmol) was employed to afford the title compound (1.44 g, 63%) as a colorless oil.

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 5.79-5.73 (1H, m, H3), 5.71-5.65 (1H, m, H2), 3.96 (2H, d,  $J = 7.5$ , H1), 1.96-1.93 (2H, m, H4), 1.64 (1H, sep,  $J = 6.5$ , H5), 0.89 (6H, d,  $J = 6.5$ , H6);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 135.5 (C3), 127.4 (C2), 41.3 (C4), 33.6 (C1), 28.2 (C5), 22.2 (C6).

*The spectroscopic properties of this compound were consistent with the data available in the literature.*<sup>13</sup>



### (E)-7-Methyl-1-phenyloct-4-en-1-one

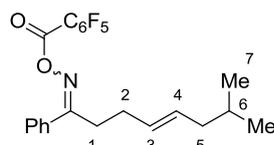
**General Procedure D:** Ethyl benzoylacetate (1.14 mL, 6.60 mmol) and (*E*)-1-bromo-5-methylhex-2-ene (1.39 g, 7.92 mmol) were employed. FCC (50:1 (hexane-EtOAc)) afforded the title compound (642 mg, 45%) as a colorless oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2954 (w), 2968 (w), 1684 (s), 1448 (m), 1201 (m), 968 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.97-7.95 (2H, m, ArCH), 7.57-7.54 (1H, m, ArCH), 7.48-7.44 (2H, m, ArCH), 5.48-5.46 (2H, m, H3 & H4), 3.04 (2H, t,  $J = 7.5$ , H1), 2.46-2.42 (2H, m, H2), 1.88-1.85 (2H, m, H5), 1.57 (1H, sep,  $J = 6.5$ , H6), 0.86 (6H, d,  $J = 6.5$ , H7);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 199.8 (CO), 137.0, (ArC), 132.9 (ArCH), 130.3 (C4), 129.6 (C3), 128.5 (ArCH), 128.0 (ArCH), 41.9 (C5), 38.6 (C1), 28.4 (C6), 27.3 (C2), 22.2 (C7);

HRMS (ESI<sup>+</sup>) Found  $[\text{M}+\text{Na}]^+$ : 239.1406,  $\text{C}_{15}\text{H}_{20}\text{ONa}$  requires 239.1415.



#### (4E)-7-Methyl-1-phenyloct-4-en-1-one O-perfluorobenzoyl oxime 9l

**General procedure E: Part A:** (E)-7-Methyl-1-phenyloct-4-en-1-one (635 mg, 2.94mmol) was employed affording the corresponding oxime (551 mg, 82%) as a colorless solid after purification by FCC (20:1 – 4:1 (hexane-EtOAc)). **Part B:** The corresponding oxime (545 mg, 2.36 mmol) was employed. Purification of the residue (30:1 (hexane-EtOAc)) afforded the title compound (766 mg, 75%, 10:1 mixture of oxime isomers) as a yellow oil that solidified on standing.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2956 (w), 1762 (s), 1651 (m), 1523 (m), 1495 (s), 1324 (s), 1188 (s), 1000 (s);

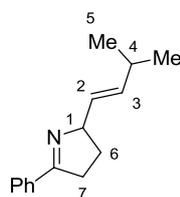
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) Signals for the major isomer only 7.75-7.73 (2H, m, ArCH), 7.50-7.47 (1H, m, ArCH), 7.45-7.41 (2H, m, ArCH), 5.44-5.33 (2H, m, H4 & H3), 2.98-2.95 (2H, m, H1), 2.31-2.26 (2H, m, H2), 1.85-1.82 (2H, m, H5), 1.60-1.49 (1H, m, H6), 0.84 (6H, d,  $J = 6.5$ , H7);

Diagnostic signals for the minor isomer: 2.83-2.80 (0.2H, m, H1'), 2.24-2.20 (0.2H, m, H2');

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) Signals for the major isomer only 168.4 (CN), 156.5 (CO), 133.1 (ArC), 131.2 (C4), 131.0 (ArCH), 128.8 (ArCH), 128.5 (C3), 127.5 (ArCH), 41.8 (C5), 29.8 (C2), 29.0 (C1), 28.3 (C6), 22.2 (C7); Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -137.1 (2F), -137.4 (0.2F), -147.6 (1F), -148.1 (0.1F), -159.8 (2F), -160.1 (0.2F);

HRMS (ESI<sup>+</sup>) Found  $[\text{M}+\text{Na}]^+$ : 448.1306,  $\text{C}_{22}\text{H}_{20}\text{O}_2\text{NF}_5\text{Na}$  requires 448.1316.



#### (E)-2-(3-Methylbut-1-en-1-yl)-5-phenyl-3,4-dihydro-2H-pyrrole 10l

**General procedure F:** 9l (120 mg, 0.282 mmol) was employed. In a modification to the general procedure the reaction mixture was heated at 120 °C. Analysis of the crude reaction mixture revealed a total cyclization yield of 73% and a selectivity of 5:1 (10l:11l). FCC (15:1 – 5:1 (hexane-EtOAc)) afforded the title compound (35 mg, 58%) as a yellow oil.

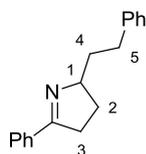
$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2957 (w), 2867 (w), 1612 (w), 1448 (w), 1338 (w), 968 (m), 758 (s), 691 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.89-7.86 (2H, m, ArCH), 7.43-7.38 (3H, m, ArCH), 5.68 (1H, ddd,  $J = 15.5, 6.5, 1.0$ , H3), 5.50 (1H, ddd,  $J = 15.5, 7.0, 1.0$ , H2), 4.70-4.64 (1H, m, H1), 3.05 (1H, dddd,  $J = 14.5, 10.0, 5.0, 2.0$ , H7), 2.93-2.84 (1H, m, H7'), 2.35-2.23 (2H, m, H4 & H6), 1.78-1.69 (1H, m, H6'), 1.01 (6H, dd,  $J = 7.0, 1.5$ , H5);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 172.8 ( $\underline{\text{CN}}$ ), 138.2 ( $\underline{\text{C3}}$ ), 134.5 ( $\text{Ar}\underline{\text{C}}$ ), 130.4 ( $\text{Ar}\underline{\text{CH}}$ ), 128.8 ( $\underline{\text{C2}}$ ), 128.3 ( $\text{Ar}\underline{\text{CH}}$ ), 127.8 ( $\text{Ar}\underline{\text{CH}}$ ), 74.6 ( $\underline{\text{C1}}$ ), 35.1 ( $\underline{\text{C7}}$ ), 30.8 ( $\underline{\text{C4}}$ ), 29.9 ( $\underline{\text{C6}}$ ), 22.4 ( $\underline{\text{C5}}$ ), 22.3 ( $\underline{\text{C5}}'$ );

**HRMS** ( $\text{ESI}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 214.1590,  $\text{C}_{15}\text{H}_{20}\text{N}$  requires 214.1586.

Diagnostic signals for **11**:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 6.41 (0.16H, app. t,  $J = 3.0$ ), 5.97-5.95 (0.16H, m).



### 2-Phenethyl-5-phenyl-3,4-dihydro-2H-pyrrole 13

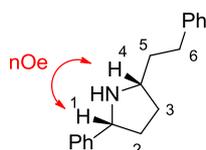
A 3-necked round-bottomed flask was charged with **10a** (40 mg, 0.16 mmol) and EtOAc (2.9 mL). Under an atmosphere of  $\text{N}_2$  was added Pd/C (10%, 5.1 mg, 0.049 mmol).  $\text{H}_2$  gas was bubbled through the reaction mixture for 10 seconds and the reaction was stirred vigorously under a  $\text{H}_2$  atmosphere (balloon) for 1 hour. (NB: Close monitoring of the reaction is required to ensure that over-reduction (of the imine) does not occur). Upon consumption of starting material (TLC) the reaction mixture was filtered through Celite washing with EtOAc (ca. 30 mL). The filtrate was concentrated *in vacuo* and purification of the residue (10:1 (hexane-EtOAc)) afforded the title compound (30 mg, 85%) as a yellow oil.

$\nu_{\text{max}} / \text{cm}^{-1}$  (film) 3003 (w), 2860 (w), 1611 (m), 1574 (m), 1494 (m), 1449 (m), 1024 (m),

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.89-7.86 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.46-7.40 (3H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.31-7.25 (4H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.21-7.17 (1H, m,  $\text{Ar}\underline{\text{CH}}$ ), 4.23 (1H, dddd,  $J = 7.5, 7.5, 6.0, 6.0$ ,  $\underline{\text{H1}}$ ), 3.09-3.02 (1H, m,  $\underline{\text{H3}}$ ), 2.95-2.80 (3H, m,  $\underline{\text{H3}}'$  &  $\underline{\text{H5}}$ ), 2.28-2.21 (1H, m,  $\underline{\text{H2}}$ ), 2.20-2.14 (1H, m,  $\underline{\text{H4}}$ ), 1.86 (1H, dddd,  $J = 13.5, 9.5, 7.5, 6.0$ ,  $\underline{\text{H4}}'$ ), 1.67 (1H, dddd,  $J = 13.0, 10.0, 7.5, 7.0$ ,  $\underline{\text{H2}}'$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 172.1 ( $\underline{\text{CN}}$ ), 142.3 ( $\text{Ar}\underline{\text{C}}$ ), 134.5 ( $\text{Ar}\underline{\text{C}}$ ), 130.4, 128.4 ( $\underline{\text{C2}}$ ), 128.3, 127.7, 125.7 ( $6 \times \text{Ar}\underline{\text{CH}}$ ), 72.6 ( $\underline{\text{C1}}$ ), 38.3 ( $\underline{\text{C4}}$ ), 35.0 ( $\underline{\text{C3}}$ ), 33.1 ( $\underline{\text{C5}}$ ), 28.6 ( $\underline{\text{C2}}$ );

**HRMS** ( $\text{CI}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 250.1600,  $\text{C}_{18}\text{H}_{20}\text{N}$  requires 250.1596.



### 2-Phenethyl-5-phenylpyrrolidine 14

A 3-necked round-bottomed flask was charged with **10a** (20 mg, 0.081 mmol) and EtOAc (1.5 mL). Under an atmosphere of  $\text{N}_2$  was added Pd/C (10% by wt, 2.6 mg, 0.025 mmol).  $\text{H}_2$  gas was bubbled through the reaction mixture for 10 seconds and the reaction was stirred vigorously under a  $\text{H}_2$  atmosphere for 18 hours. The reaction mixture was filtered through Celite® washing with EtOAc (ca. 30 mL). The filtrate was concentrated *in vacuo* to afford the title compound (19 mg, 95%, 10:1 dr) as a yellow oil.

$\nu_{\text{max}} / \text{cm}^{-1}$  (film) 2929 (w), 1494 (m), 1453 (m), 1279 (m);

Data for the major diastereomer only:

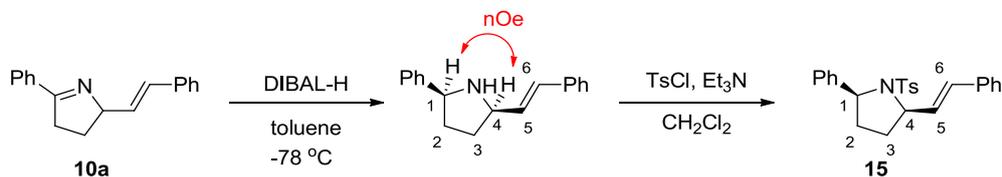
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.43-7.41 (2H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.35-7.29 (4H, m,  $\text{Ar}\underline{\text{CH}}$ ), 7.25-7.19 (4H, m,  $\text{Ar}\underline{\text{CH}}$ ), 4.19 (1H, t,  $J = 8.0$ ,  $\underline{\text{H1}}$ ), 3.24 (1H, tt,  $J = 7.0, 7.0$ ,  $\underline{\text{H4}}$ ), 2.81-2.70 (2H, m,  $\underline{\text{H6}}$ ), 2.40 (1H, br. s,  $\underline{\text{NH}}$ ), 2.22-2.15 (1H, m,  $\underline{\text{H2}}$ ), 2.06-1.99 (1H, m,  $\underline{\text{H3}}$ ), 1.98-1.91 (1H, m,  $\underline{\text{H5}}$ ), 1.89-1.83 (1H, m,  $\underline{\text{H5}}'$ ), 1.80-1.72 (1H, m,  $\underline{\text{H2}}'$ ), 1.62-1.54 (1H, m,  $\underline{\text{H3}}'$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 144.5 ( $\text{Ar}\underline{\text{C}}$ ), 142.3 ( $\text{Ar}\underline{\text{C}}$ ), 128.3 (3C), 126.8, 126.7, 125.7 ( $6 \times \text{Ar}\underline{\text{CH}}$ ), 62.6 ( $\underline{\text{C1}}$ ), 58.7 ( $\underline{\text{C4}}$ ), 38.4 ( $\underline{\text{C5}}$ ), 33.8 ( $\underline{\text{C2}}$ ), 33.6 ( $\underline{\text{C6}}$ ), 31.4 ( $\underline{\text{C3}}$ );

**HRMS** ( $\text{CI}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 252.1754,  $\text{C}_{18}\text{H}_{22}\text{N}$  requires 252.1752.

Diagnostic signals for the minor diastereoisomer:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 4.37 (0.1H, t,  $J = 7.5$ , H1), 3.46 (0.1H, tt,  $J = 7.0$ , H4);

The relative stereochemistry of the major diastereomer was corroborated by *nOe* experiments as indicated on the compound structure.



### (2*S*,5*R*)-2-Phenyl-5-((*E*)-styryl)pyrrolidine

To a solution of imine **10a** (30 mg, 0.12 mmol) in anhydrous toluene (0.7 mL) at -78 °C was added DIBAL-H (1 M in hexane, 0.36 mL, 0.36 mmol) dropwise. After stirring for 90 minutes saturated aq.  $\text{NH}_4\text{Cl}$  (0.4 mL) was added and the reaction mixture was allowed to warm to rt. The mixture was diluted with  $\text{CH}_2\text{Cl}_2$  (20 mL), dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated *in vacuo* to give the title compound (30 mg, quant., >20:1 d.r.) as a yellow oil.

$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 3421 (br), 3025 (w), 1600 (w), 1492 (m), 1449 (m), 963 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.45-7.40 (4H, m, ArCH), 7.35-7.30 (4H, m, ArCH), 7.26-7.22 (2H, m, ArCH), 6.60 (1H, d,  $J = 16.0$ , H6), 6.35 (1H, dd,  $J = 16.0, 7.5$ , H5), 4.27 (1H, t,  $J = 7.5$ , H1), 3.95-3.90 (1H, m, H4), 2.35-2.20 (2H, br. s and m, NH & H2), 2.14-2.07 (1H, m, H3), 1.86-1.75 (2H, m, H2' & H3');

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 144.5 (ArC), 137.1 (ArC), 132.9 (C5), 129.9 (C6), 128.5, 128.3, 127.3, 126.9, 126.7, 126.3 (6  $\times$  ArCH), 62.5 (C1), 61.2 (C4), 33.9 (C2), 32.1 (C3);

HRMS (ESI<sup>+</sup>) Found  $[\text{M}+\text{H}]^+$ : 250.1590,  $\text{C}_{18}\text{H}_{20}\text{N}$  requires 250.1590.

The relative stereochemistry was corroborated by *nOe* experiments as indicated on the compound structure.

### (2*S*,5*R*)-2-Phenyl-5-((*E*)-styryl)-1-tosylpyrrolidine **15**

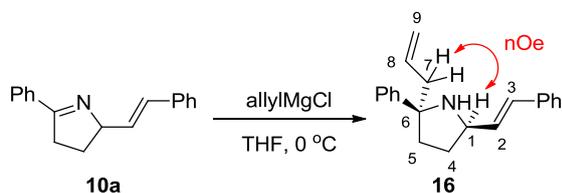
To a solution of the above amine (25 mg, 0.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.2 mL) was added Et<sub>3</sub>N (28  $\mu\text{L}$ , 0.20 mmol) and *p*-TsCl (21 mg, 0.11 mmol). The reaction mixture was stirred for 18 hours after which time it was diluted with Et<sub>2</sub>O (20 mL), washed with saturated aq.  $\text{Na}_2\text{CO}_3$  (2  $\times$  15 mL), dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated *in vacuo*. Purification of the residue by FCC (8:1 – 5:1 (hexane-EtOAc)) afforded the title compound (35 mg, 85%, >20:1 d.r.) as a colorless oil.

$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 3027 (w), 2870 (w), 1345 (m), 1154 (m), 1090 (m),

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.66-7.63 (2H, m, ArCH), 7.41-7.22 (12H, m, ArCH), 6.66 (1H, dd,  $J = 16.0, 1.0$ , H6), 6.27 (1H, dd,  $J = 16.0, 7.5$ , H5), 4.97 (1H, dd,  $J = 7.5, 5.0$ , H1), 4.60-4.55 (1H, m, H4), 2.41 (3H, s, CH<sub>3</sub>), 2.16-2.07 (1H, m, H2), 2.01-1.83 (3H, m, H2', H3, H3');

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 143.2, 142.5, 136.6, 136.0 (4  $\times$  ArC), 131.5 (C6), 130.2 (C5), 129.4, 128.5, 128.3, 127.7, 127.6, 127.1, 126.6, 126.5 (8  $\times$  ArCH), 64.7 (C1), 63.4 (C4), 34.6 (C2), 31.5 (C3), 21.4 (CH<sub>3</sub>);

HRMS (ESI<sup>+</sup>) Found  $[\text{M}+\text{Na}]^+$ : 426.1498,  $\text{C}_{25}\text{H}_{25}\text{NO}_2\text{SNa}$  requires 426.1485.



### (2R,5R)-2-Allyl-2-phenyl-5-((E)-styryl)pyrrolidine 16

To a solution of **10a** (18 mg, 0.073 mmol) in THF (0.73 mL) at 0 °C was added allylmagnesium chloride in THF (0.36 M, 0.11 mmol) dropwise. The reaction mixture was stirred for 18 hours during which time it warmed to room temperature. The reaction was quenched by addition of saturated aq. NH<sub>4</sub>Cl (2 mL) and extracted with Et<sub>2</sub>O (3 × 5 mL). The combined organic phases were washed with brine (2 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo* to afford the title compound (20 mg, 95%, > 20:1 d.r.) as a yellow oil.

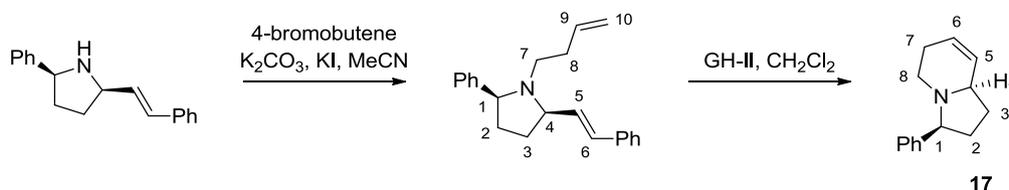
$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3059 (w), 2963 (w), 1637 (w), 1492 (m), 1445 (m), 1278 (w), 1071 (m), 963 (m);

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.53-7.50 (2H, m, ArCH), 7.39-7.28 (6H, m, ArCH), 7.24-7.19 (2H, m, ArCH), 6.56 (1H, d,  $J = 16.0$ , H<sub>3</sub>), 6.24 (1H, dd,  $J = 16.0, 7.5$ , H<sub>2</sub>), 5.48 (1H, dddd,  $J = 16.5, 10.0, 8.5, 6.0$ , H<sub>8</sub>), 5.08-5.02 (2H, m, H<sub>9</sub>), 4.02 (1H, ddd,  $J = 8.5, 7.5, 6.0$ , H<sub>1</sub>), 2.64 (1H, dddd,  $J = 14.0, 6.0, 1.0, 1.0$ , H<sub>7</sub>), 2.53 (1H, dd,  $J = 14.0, 8.0$ , H<sub>7'</sub>), 2.16-1.95 (4H, m, H<sub>4</sub>, H<sub>5</sub>, H<sub>5'</sub>, NH), 1.70-1.61 (1H, m, H<sub>4'</sub>);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 148.4 (ArC), 137.2 (ArC), 134.6 (C<sub>8</sub>), 133.9 (C<sub>2</sub>), 129.3 (C<sub>3</sub>), 128.5, 127.9, 127.1, 126.3, 126.1, 126.0 (6 × ArCH), 118.1 (C<sub>9</sub>), 66.8 (C<sub>6</sub>), 59.8 (C<sub>1</sub>), 46.9 (C<sub>7</sub>), 38.8 (C<sub>5</sub>), 31.9 (C<sub>4</sub>);

HRMS (CI<sup>+</sup>) Found [M+H]<sup>+</sup>: 290.1900, C<sub>21</sub>H<sub>24</sub>N requires 290.1909.

The relative stereochemistry was corroborated by *nOe* experiments as indicated on the compound structure.



### (2S,5R)-1-(But-3-en-1-yl)-2-phenyl-5-((E)-styryl)pyrrolidine

To a solution of K<sub>2</sub>CO<sub>3</sub> (177 mg, 1.28 mmol), KI (5.00 mg, 0.03 mmol) and (2S,5R)-2-phenyl-5-((E)-styryl)pyrrolidine above (160 mg, 0.64 mmol) in MeCN (10 mL) was added 4-bromo-1-butene (260  $\mu$ L, 2.56 mmol). The reaction mixture was refluxed for 18 hours after which time it was cooled to room temperature and concentrated *in vacuo*. Purification of the residue (50:1 (hexane-EtOAc)) afforded the title compound (138 mg, 71%) as a colorless oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3025 (w), 2936 (w), 1492 (m), 1449 (m), 964 (m), 907 (m);

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.44-7.42 (4H, m, ArCH), 7.35-7.31 (4H, m, ArCH), 7.25-7.21 (2H, m, ArCH), 6.59 (1H, d,  $J = 16.0$ , H<sub>6</sub>), 6.29 (1H, dd,  $J = 16.0, 8.0$ , H<sub>5</sub>), 5.67-5.58 (1H, m, H<sub>9</sub>), 4.86-4.82 (2H, m, H<sub>10</sub>), 3.70 (1H, t,  $J = 7.5$ , H<sub>1</sub>), 3.39-3.34 (1H, m, H<sub>4</sub>), 2.66-2.57 (2H, m, H<sub>7</sub>), 2.21-2.14 (1H, m, H<sub>2</sub>), 2.07-1.98 (3H, m, H<sub>8</sub>, H<sub>3</sub>), 1.82-1.69 (2H, m, H<sub>2'</sub>, H<sub>3'</sub>);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 145.5 (ArC), 137.4 (ArC), 137.2 (C<sub>9</sub>), 134.4 (C<sub>5</sub>), 129.9 (C<sub>6</sub>), 128.5, 128.2, 127.3, 127.2, 126.7, 126.3 (6 × ArCH), 115.1 (C<sub>10</sub>), 69.1 (C<sub>1</sub>), 67.7 (C<sub>4</sub>), 52.2 (C<sub>7</sub>), 34.5 (C<sub>2</sub>), 32.0 (C<sub>8</sub>), 31.6 (C<sub>3</sub>);

HRMS (CI<sup>+</sup>) Found [M+H]<sup>+</sup>: 304.2056, C<sub>22</sub>H<sub>26</sub>N requires 304.2065.

### (3S,8aR)-3-Phenyl-1,2,3,5,6,8a-hexahydroindolizine 17

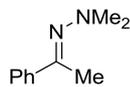
To a stirring solution of Grubbs-Hoveyda 2<sup>nd</sup> generation catalyst (1.0 mg, 1.7 × 10<sup>-3</sup> mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15.5 mL) was added (2S,5R)-1-(but-3-en-1-yl)-2-phenyl-5-((E)-styryl)pyrrolidine (50 mg, 0.17 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and the reaction mixture was stirred for 1 hour at room temperature. When the reaction was complete (TLC) the reaction mixture was concentrated *in vacuo* (CAUTION: product is volatile, concentrate with care). Purification of the residue by FCC (15:1 (hexane-EtOAc) + 1% Et<sub>3</sub>N)) afforded the title compound (23 mg, 70%) as a yellow oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3027 (w), 2789 (w), 1494 (m), 1029 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.40-7.37 (2H, m, ArCH), 7.34-7.30 (2H, m, ArCH), 7.26-7.22 (1H, m, ArCH), 5.87 (1H, ddt,  $J = 10.0, 2.5, 1.5$ , H6), 5.74 (1H, ddt,  $J = 10.0, 5.0, 2.5$ , H5), 3.28 (1H, t,  $J = 8.0$ , H1), 2.85-2.79 (2H, m, H4 & H8), 2.38-2.29 (1H, m, H7), 2.23-2.15 (2H, m, H2 & H8'), 2.06-2.01 (1H, m, H7'), 1.93-1.87 (1H, m, H3), 1.77-1.69 (1H, m, H2'), 1.63 (1H, m, H3');

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 143.3 (ArC), 128.5 (C6), 128.3, 127.6, 126.9 ( $3 \times$  ArCH), 125.9 (C5), 68.2 (C1), 62.5 (C4), 46.6 (C8), 33.0 (C2), 28.2 (C3), 26.9 (C7);

HRMS ( $\text{EI}^+$ ) Found  $[\text{M}]^+$ : 199.1362,  $\text{C}_{14}\text{H}_{17}\text{N}$  requires 199.1361.



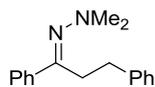
**(E)-1,1-Dimethyl-2-(1-phenylethylidene)hydrazone**

To a solution of acetophenone (10.0 g, 83 mmol) and dimethylhydrazine (7.14 mL, 94 mmol) in benzene (75 mL) was added trifluoroacetic acid (5 drops). The reaction mixture was heated at reflux using Dean-Stark apparatus until all the water had been driven off. Once complete the reaction was concentrated *in vacuo* to afford the title compound (13.5 g, 100%) which was used without further purification.

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.77-7.73 (2H, m, ArCH), 7.39-7.35 (3H, m, ArCH), 2.62 (6H, s,  $\text{N}(\text{CH}_3)_2$ ), 2.36 (3H, s,  $\text{CH}_3$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 161.9 (CN), 138.9 (ArC), 129.1, 128.2, 126.2 ( $3 \times$  ArCH), 47.1 ( $\text{N}(\text{CH}_3)_2$ ), 15.4 ( $\text{CH}_3$ ).

The spectroscopic properties of this compound were consistent with the data available in the literature.<sup>14</sup>



**(E)-2-(1,3-Diphenylpropylidene)-1,1-dimethylhydrazone**

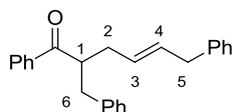
To a solution of the above hydrazone (4.00 g, 25.0 mmol) in THF (120 mL) at  $-78^\circ\text{C}$  was added  $^t\text{BuLi}$  (1.6 M in hexane, 17.0 mL, 27.2 mmol) dropwise over 10 minutes during which time the reaction mixture darkened. Upon completion of addition the reaction was stirred at this temperature for 30 minutes after which time benzyl bromide (pre-filtered through a short pad of  $\text{K}_2\text{CO}_3$ , 2.56 mL, 29.6 mmol) was added dropwise. This resulted in the reaction mixture to become light yellow in colour. After 1 hour the reaction was complete as judged by TLC analysis. Water (70 mL) was added slowly and the reaction was allowed to warm to room temperature. The reaction mixture was transferred to a separatory funnel, the layers were separated and the aqueous was extracted with  $\text{Et}_2\text{O}$  ( $3 \times 150$  mL). The organics were combined and washed with brine (150 mL), dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated *in vacuo*. Purification of the residue by FCC (10:1 (hexane-EtOAc)) afforded the title compound (5.42 g, 86%) as a yellow oil.

$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 2950 (w), 1604 (m), 1495 (s), 1453 (s), 1445 (s), 1305 (m), 1020 (m), 955 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.71-7.69 (2H, m, ArCH), 7.43-7.41 (3H, m, ArCH), 7.33-7.28 (2H, m, ArCH), 7.24-7.20 (3H, m, ArCH), 3.27-3.23 (2H, m,  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 2.81-2.77 (2H, m,  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 2.54 (6H, s,  $\text{NMe}_2$ );

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 168.0 (CN), 141.2, 137.8 ( $2 \times$  ArC), 129.3, 128.4, 128.3, 128.2, 127.0, 126.1 ( $6 \times$  ArCH), 47.7 ( $\text{NMe}_2$ ), 33.1 ( $\text{CH}_2\text{CH}_2\text{Ph}$ ), 30.2 ( $\text{CH}_2\text{CH}_2\text{Ph}$ );

HRMS ( $\text{CI}^+$ ) Found  $[\text{M}+\text{H}]^+$ : 253.1706,  $\text{C}_{17}\text{H}_{21}\text{N}_2$  requires 253.1705.



**(E)-2-Benzyl-1,6-diphenylhex-4-en-1-one**

To a solution of the above hydrazone (4.0 g, 15.9 mmol) in THF (160 mL) at  $0^\circ\text{C}$  was added  $^t\text{BuLi}$  (1.6 M in hexane, 10.9 mL, 17.5 mmol) dropwise over 10 minutes. After stirring at this temperature for 40 minutes and

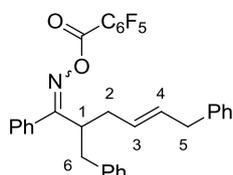
(*E*)-(4-bromobut-2-en-1-yl)benzene (3.60 g, 17.5 mmol) was added *via* syringe over 5 minutes. The reaction was stirred for 18 hours during which time it warmed to room temperature. 1 M HCl (80 mL) was added and the mixture stirred vigorously for 90 minutes until hydrolysis was complete (TLC). The mixture was extracted with EtOAc (2 × 200 mL) and the organic layers were washed with brine (150 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. Purification of the residue by FCC (50:1 (hexane-EtOAc)) afforded the title compound (3.7 g, 70%) as a yellow oil.

$\nu_{\max}$  / cm<sup>-1</sup> (film) 3026 (w), 1677 (s), 1596 (m), 1493 (m), 1447 (m), 1230 (m), 968 (m);

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.88-7.86 (2H, m, ArCH), 7.58-7.53 (1H, m, ArCH), 7.46-7.42 (2H, m, ArCH), 7.29-7.24 (4H, m, ArCH), 7.22-7.18 (4H, m, ArCH), 7.10-7.07 (2H, m, ArCH), 5.66-5.58 (1H, m, H<sub>4</sub>), 5.49-5.41 (1H, m, H<sub>3</sub>), 3.86-3.79 (1H, m, H<sub>1</sub>), 3.29 (2H, d, *J* = 6.5, H<sub>5</sub>), 3.15 (1H, dd, *J* = 13.5, 7.5, H<sub>6</sub>), 2.85 (1H, dd, *J* = 13.5, 6.5, H<sub>6'</sub>), 2.58-2.50 (1H, m, H<sub>2</sub>), 2.36-2.30 (1H, m, H<sub>2'</sub>);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 203.3 (C=O), 140.4, 139.8, 137.3 (3 × ArC), 132.8 (ArCH), 131.9 (C<sub>4</sub>), 129.0, 128.5, 128.4, 128.3 (2C), 128.2 (6 × ArCH), 128.0 (C<sub>3</sub>), 126.2, 125.9 (2 × ArCH), 48.4 (C<sub>1</sub>), 38.9 (C<sub>5</sub>), 37.7 (C<sub>6</sub>), 35.3 (C<sub>2</sub>);

HRMS (EI<sup>+</sup>) Found [M]<sup>+</sup>: 340.1831, C<sub>25</sub>H<sub>24</sub>O requires 340.1827.



**(4*E*)-2-Benzyl-1,6-diphenylhex-4-en-1-one *O*-perfluorobenzoyl oxime 9m**

General procedure E: Part A: (*E*)-2-Benzyl-1,6-diphenylhex-4-en-1-one (3.50 g, 10.3 mmol) was employed affording the corresponding oxime (3.62 g, 99%) as a colorless oil. Part B: The corresponding oxime (3.6 g, 10 mmol) was employed. Purification of the residue (50:1 – 25:1 (hexane-EtOAc)) afforded the title compound (4.75 g, 84%, 1.5:1 mixture of oxime isomers) as a yellow oil.

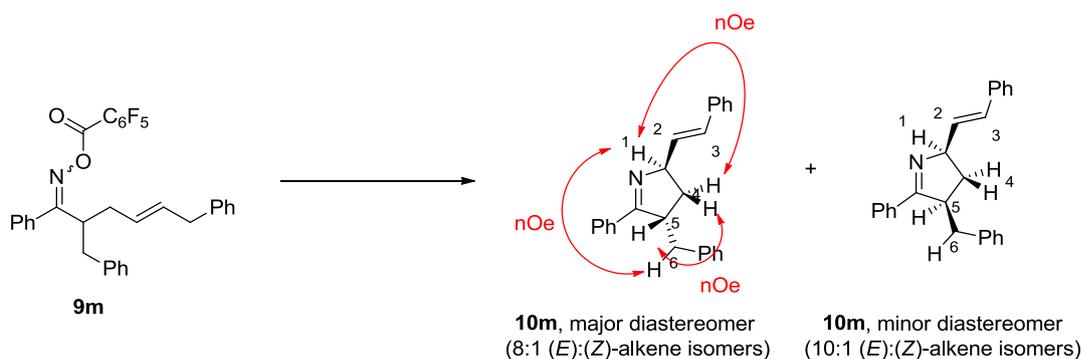
$\nu_{\max}$  / cm<sup>-1</sup> (film) 2971 (w), 1754 (s), 1648 (m), 1522 (m), 1493 (s), 1321 (s), 1190 (s);

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.44-7.16- (19.8H, m, ArCH), 7.12-7.09 (4H, m, ArCH), 7.05-7.03 (1.2H, m, ArCH), 5.70-5.52 (2.2H, m), 5.45-5.39 (1H, m), 3.71-3.65 (1H, m, H<sub>1A</sub>), 3.37 (1.2H, d, *J* = 6.5, H<sub>5B</sub>), 3.30 (2H, d, *J* = 6.5, H<sub>5A</sub>), 3.23-3.05 (2.2H, m), 2.96 (1H, dd, *J* = 14.0, 6.5), 2.88 (0.6H, dd, *J* = 13.5, 7.5), 2.61-2.54 (1H, m), 2.47-2.40 (1.6H, m), 2.33-2.27 (0.6H, m);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 171.3 (CN), 171.2 (C=O), 156.6 (C=O), 156.4 (C=O), 140.4, 140.1, 139.2, 138.8 (4 × ArC), 134.0, 132.8, 132.5, 132.4, 130.0, 129.3, 129.2, 128.8, 128.5 (3C), 128.4 (2C), 128 (2C), 128.2, 128.1, 127.8, 127.7, 126.8, 126.6, 126.4, 126.0 (2C), 48.3, 45.1, 39.1, 38.9, 38.1, 38.0, 35.0, 34.9;

Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

$\delta_{\text{F}}$  (376 MHz, CDCl<sub>3</sub>) -136.8 (2.4F), (-137.1 (2F), -147.4 (1.2 F), -148.0 (1F), -159.5 (2.4F), -160.0 (2F);



**(2*R*,4*S*)-4-Benzyl-5-phenyl-2-((*E*)-styryl)-3,4-dihydro-2*H*-pyrrole 10m**

**General procedure F:** **9m** (500 mg, 0.91 mmol) was employed. In a modification to the general procedure the reaction was heated at 100 °C. Analysis of the <sup>1</sup>H NMR of the crude reaction mixture revealed trace amounts of the corresponding pyrrole. FCC (20:1 – 5:1 (hexane-EtOAc)) followed by (50:1 (toluene-EtOAc)) afforded the title compound (190 mg, 62%, 1.6:1 d.r.) as a yellow oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3082 (w), 2929 (w), 1600 (m), 1574 (m), 1446 (m), 1446 (m);

For the data listed below: A = major diastereomer (E-alkene), B = minor diastereomer (E-alkene), C = major diastereomer (Z-alkene), D = minor diastereomer (Z-alkene)

Ratio of 1.6:1:0.2:0.1, A:B:C:D

Data for (E)-alkene isomers:

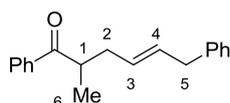
$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 8.05-8.02 (3.5H, m, ArCH), 8.00-7.98 (2H, m, ArCH), 7.54-7.49 (8.5H, m, ArCH), 7.45-7.41 (5.5H, m, ArCH), 7.39-7.19 (23.5H, m, ArCH), 6.69-6.59 (2.8H, m, H<sub>3A</sub> & H<sub>3B</sub> & H<sub>3C</sub> & H<sub>3D</sub>), 6.40 (1.6H, dd,  $J = 16.0, 7.0$ , H<sub>2A</sub>), 6.14 (1H, dd,  $J = 16.0, 7.0$ , H<sub>2B</sub>), 4.99-4.95 (1H, m, H<sub>1B</sub>), 4.67-4.63 (1.6H, m, H<sub>1A</sub>), 3.91-3.80 (2.6H, m, H<sub>5A</sub> & H<sub>5B</sub>), 3.26 (1H, dd,  $J = 14.0, 4.0$ , H<sub>6B</sub>), 3.11 (1.6H, dd,  $J = 14.0, 4.0$ , H<sub>6A</sub>), 2.74-2.66 (2.6H, m, H<sub>6'A</sub> & H<sub>6'B</sub>), 2.49 (1H, ddd,  $J = 13.5, 9.0, 9.0$ , H<sub>4B</sub>), 2.28 (1.6H, ddd,  $J = 13.0, 7.0, 2.0$ , H<sub>4A</sub>), 1.98 (1.6H, ddd,  $J = 13.0, 9.0, 9.0$ , H<sub>4'A</sub>), 1.83 (1H, ddd,  $J = 13.0, 5.0, 5.0$ , H<sub>4'B</sub>);

H<sub>3</sub> for all isomers is listed above due to signal overlap.

Diagnostic signals for (Z)-alkene isomers:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 5.72 (0.2H, dd,  $J = 11.5, 9.5$ , H<sub>2C</sub>), 5.51 (0.1H, dd,  $J = 11.5, 9.5$ , H<sub>2D</sub>), 5.27-5.23 (0.1H, m, H<sub>1D</sub>), 4.89-4.84 (0.2H, m, H<sub>1C</sub>), 3.91-3.80 (0.3H, m, H<sub>5C</sub> & H<sub>5D</sub>), 2.74-2.66 (0.3H, m, H<sub>6'C</sub> & H<sub>6'D</sub>)

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) Data for (E)-alkene isomer only: 175.8 (C<sub>NB</sub>), 175.6 (C<sub>NA</sub>), 139.5 (ArC<sub>B</sub>), 139.4 (ArC<sub>A</sub>), 137.1 (2C, ArC<sub>B</sub> & ArC<sub>A</sub>), 134.0 (ArC<sub>B</sub>), 133.5 (ArC<sub>A</sub>), 132.4 (C<sub>2B</sub>), 131.9 (C<sub>2A</sub>), 130.4 (ArCH), 130.2 (C<sub>3B</sub>), 130.1 (C<sub>3A</sub>), 129.6, 128.9, 128.8, 128.6, 128.5, 128.4 (3C), 128.3 (2C), 128.0 (2C), 127.1 (2C), 126.3 (2C), 126.2 (17 × ArCH), 71.6 (C<sub>1B</sub>), 72.3 (C<sub>1A</sub>), 49.3 (C<sub>5B</sub>), 49.1 (C<sub>5A</sub>), 39.3 (C<sub>6B</sub>), 37.4 (C<sub>6A</sub>), 35.8 (C<sub>4A</sub>), 34.5 (C<sub>4B</sub>).

The relative stereochemistry of the major diastereomer of (E)-**10m** was corroborated by *nOe* experiments as indicated on the compound structure. Signals corresponding to the alkene isomers were assigned in analogy to **10a**.



**(E)-2-Methyl-1,6-diphenylhex-4-en-1-one**

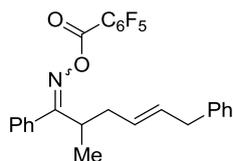
To a solution of NaH (60% dispersion in mineral oil, 162 mg, 4.05 mmol) in THF (4 mL) was added propiophenone (320  $\mu\text{L}$ , 2.41 mmol) dropwise over 5 minutes. The reaction mixture was heated at reflux for 90 minutes after which time (E)-(4-bromobut-2-en-1-yl)benzene (506 mg, 2.41 mmol) was added *via* syringe in one portion. The reaction mixture was heated at reflux for an additional 90 minutes. After this time it was cooled to room temperature, diluted with H<sub>2</sub>O (3 mL) and extracted with Et<sub>2</sub>O (3 × 30 mL). The organic layers were combined, washed with brine (5 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. Purification of the residue by FCC (50:1 (hexane-EtOAc)) followed by (50:1 (toluene:EtOAc)) gave the title compound (451 mg, 71%) as a colorless oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2970 (w), 1679 (s), 1448 (m), 1229 (m), 968 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.96-7.93 (2H, m, ArCH), 7.59-7.54 (1H, m, ArCH), 7.49-7.44 (2H, m, ArCH), 7.28-7.24 (2H, m, ArCH), 7.20-7.16 (1H, m, ArCH), 7.13-7.09 (2H, m, ArCH), 5.66-5.58 (1H, m, H<sub>4</sub>), 5.52-5.44 (1H, m, H<sub>3</sub>), 3.58-3.49 (1H, dt,  $J = 7.0, 7.0$ , H<sub>1</sub>), 3.30 (2H, d,  $J = 6.5$ , H<sub>5</sub>), 2.53 (1H, dddd,  $J = 14.0, 7.0, 6.5, 1.0$ , H<sub>2</sub>), 2.34-2.16 (1H, m, H<sub>2'</sub>), 1.21 (3H, d,  $J = 7.0$ , H<sub>6</sub>);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 203.9 (C=O), 140.6 (ArC), 136.6 (ArC), 132.8 (ArCH), 131.4 (C<sub>4</sub>), 128.6 (C<sub>3</sub>), 128.6, 128.4, 128.3 (2C), 125.9 (5 × ArCH), 40.8 (C<sub>1</sub>), 39.0 (C<sub>5</sub>), 36.5 (C<sub>2</sub>), 17.0 (C<sub>6</sub>);

HRMS (EI<sup>+</sup>) Found [M]<sup>+</sup>: 264.1508, C<sub>19</sub>H<sub>20</sub>O requires 264.1514.



**(4E)-2-Methyl-1,6-diphenylhex-4-en-1-one O-perfluorobenzoyl oxime 9n**

**General procedure E:** **Part A:** (*E*)-2-Methyl-1,6-diphenylhex-4-en-1-one (415 mg, 1.57 mmol) was employed affording the corresponding oxime (379 mg, 80%) as a colorless oil. **Part B:** The corresponding oxime (379 mg, 1.36 mmol) was employed. Purification of the residue (50:1 – 30:1 (hexane-EtOAc)) afforded the title compound (494 mg, 77%, 10:1 mixture of oxime isomers) as a colorless oil.

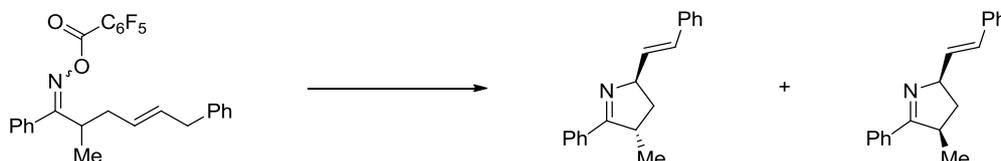
$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 2973 (w), 1760 (s), 1652 (m), 1523 (m), 1494 (s), 1323 (s), 1188 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.50-7.44 (3H, m, ArCH), 7.42-7.38 (5H, m, ArCH), 7.31-7.25 (4H, m, ArCH), 7.21-7.17 (6H, m, ArCH), 7.14-7.12 (2H, m, ArCH), 5.70-5.51 (3H, m, H<sub>4A</sub>, H<sub>4B</sub>, H<sub>3A</sub>), 5.47-5.40 (1H, m, H<sub>3B</sub>), 3.54 (1H, dt,  $J = 7.5, 7.5$ , H<sub>1A</sub>), 3.38 (2H, d,  $J = 6.5$ , H<sub>5A</sub>), 3.32 (2H, d,  $J = 6.5$ , H<sub>5B</sub>), 3.01 (1H, dt,  $J = 7.5, 7.5$ , H<sub>1B</sub>), 2.47-2.41 (2H, m, H<sub>2A</sub>, H<sub>2B</sub>), 2.29-2.23 (1H, m, H<sub>2'B</sub>), 2.21-2.15 (1H, m, H<sub>2'A</sub>), 1.30 (3H, d,  $J = 7.0$ , H<sub>6A</sub>), 1.27 (3H, d,  $J = 7.0$ , H<sub>6B</sub>);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 173.2 (CN), 173.0 (CN), 156.7 (CO), 156.5 (CO), 140.5, 140.2, 133.3, 132.3 (4 × ArC), 132.1 (C<sub>4</sub>), 132.0 (C<sub>4</sub>), 129.9, 129.2, 128.4 (2C), 128.3 (3C), 128.2, 128.1, 126.7, 125.9 (2C) (12 × ArCH), 128.0 (2C) (C<sub>3</sub>), 40.6 (C<sub>1B</sub>), 39.0 (C<sub>5A</sub>), 38.9 (C<sub>5B</sub>), 36.7 (C<sub>2A</sub>), 36.6 (C<sub>2B</sub>), 36.2 (C<sub>1A</sub>), 17.4 (C<sub>6B</sub>), 17.3 (C<sub>6A</sub>); Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

$\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ) -137.2 (2F), 137.5 (2F), -147.8 (1F), -148.4 (1F), -159.8 (2F), -160.3 (2F);

**HRMS** (ESI<sup>+</sup>) Found  $[\text{M}+\text{Na}]^+$ : 496.1306,  $\text{C}_{26}\text{H}_{20}\text{O}_2\text{NF}_5\text{Na}$  requires 496.1325.



**(E)-4-Methyl-5-phenyl-2-styryl-3,4-dihydro-2H-pyrrole 10n**

**General procedure F:** **9n** (50 mg, 0.11 mmol) was employed. Analysis of the <sup>1</sup>H NMR of the crude reaction mixture revealed trace amounts of the corresponding pyrrole. FCC (20:1 – 5:1 (hexane-EtOAc)) afforded the title compound (22 mg, 77%, 3:2 d.r.) as a yellow oil.

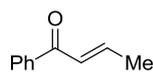
$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3075 (w), 2944 (w), 1610 (m), 1572 (m), 1443 (m);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) *Data for (E)-isomer only:* 7.91-7.89 (1.2H, m, ArCH), 7.86-7.83 (0.8H, m, ArCH), 7.46-7.40 (6H, m, ArCH), 7.34-7.28 (1.2H, m, ArCH), 7.25-7.19 (0.8H, m, ArCH), 6.69-6.61 (1H, m, H<sub>3A</sub> & H<sub>3B</sub>), 6.38 (0.6H, dd,  $J = 16.0, 7.0$ , H<sub>2A</sub>), 6.37 (0.4H, m, dd,  $J = 16.0, 7.0$ , H<sub>2B</sub>), 4.92-4.84 (1H, m, H<sub>1A</sub> & H<sub>1B</sub>), 3.62-3.53 (0.6H, m, H<sub>5B</sub>), 3.52-3.44 (0.4H, m, H<sub>5A</sub>), 2.65 (0.4H, ddd,  $J = 13.0, 9.0, 9.0$ , H<sub>4A</sub>), 2.10-2.04 (1.2H, m, H<sub>4B</sub>), 1.62 (0.4H, ddd,  $J = 13.0, 5.5, 5.5$ , H<sub>4'A</sub>), 1.27 (1.2H, d,  $J = 7.0$ , H<sub>6A</sub>), 1.24 (1.8H, d,  $J = 7.0$ , H<sub>6B</sub>);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 177.6 (CN<sub>A</sub>), 177.5 (CN<sub>B</sub>), 137.3, 137.2, 133.9, 133.4 (4 × ArC), 132.8 (C<sub>2B</sub>), 132.0 (C<sub>2A</sub>), 130.4, 130.2 (2 × ArCH), 130.2 (C<sub>3A</sub>), 129.6 (C<sub>3B</sub>), 129.0, 128.9, 128.5, 128.4 (2C), 128.1 (2C), 127.2, 126.4, 126.3 (10 × ArCH), 72.4 (C<sub>1A</sub>), 72.1 (C<sub>1B</sub>), 42.4 (C<sub>5A</sub>), 42.0 (C<sub>5B</sub>), 39.3 (C<sub>4B</sub>), 38.3 (C<sub>4A</sub>), 20.1 (C<sub>6A</sub>), 18.0 (C<sub>6B</sub>);

**HRMS** (EI<sup>+</sup>) Found 261.1512,  $\text{C}_{19}\text{H}_{19}\text{N}$  requires 261.1517.

*The stereochemistry of the major diastereomer was assigned as cis by analogy with 10m.*

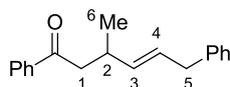


**(E)-1-Phenylbut-2-en-1-one**<sup>15</sup>

To a solution of AlCl<sub>3</sub> (5.45 g, 41.0 mmol) in benzene (20 mL) at 0 °C was added crotonoyl chloride (90%, 3.41 mL, 32.0 mmol) dropwise over 10 minutes. The reaction mixture was stirred for 1 hour after which time it was poured into ice/1 M HCl (200 mL, 1:1). The aqueous was extracted with Et<sub>2</sub>O (2 × 50 mL). The organic layers were combined, washed with 4M NaOH (30 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The residue was purified by distillation (90 °C, *ca.* 1 mmHg) to afford the title compound (2.3 g, 49%) as a colorless oil.

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.91-7.88 (2H, m, ArCH), 7.53-7.48 (1H, m, ArCH), 7.45-7.40 (2H, m, ArCH), 7.04 (1H, dq, *J* = 15.5, 7.0, CH=CHMe), 6.88 (1H, dq, *J* = 15.5, 1.5, CH=CHMe), 1.95 (3H, dd, *J* = 7.0, 1.5, CH<sub>3</sub>).

The spectroscopic properties of this compound were consistent with the data available in the literature.<sup>15</sup>



**(E)-3-Methyl-1,6-diphenylhex-4-en-1-one**<sup>16</sup>

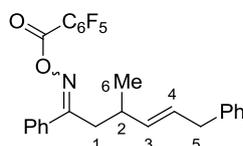
This procedure was conducted under Schlenk-line techniques. To a solution of Schwartz's reagent (1.90 g, 7.36 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (74 mL) was added 3-phenyl-1-propyne (1.03 mL, 8.30 mmol) dropwise *via* syringe. After stirring at room temperature for 20 minutes the solvent was removed *in vacuo*. After removal of the solvent the atmosphere was backfilled with nitrogen and anhydrous dioxane (93 mL), (*E*)-1-phenylbut-2-en-1-one (544 mg, 3.73 mmol) and [Rh(COD)Cl]<sub>2</sub> (35 mg, 0.0745 mmol) were added sequentially. The reaction mixture was then stirred at room temperature for 36 hours after which time saturated aq. NaHCO<sub>3</sub> (150 mL) was added and the aqueous phase was extracted with EtOAc (3 × 150 mL). The organic layers were combined, washed with brine (150 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. Purification of the residue by FCC (50:1 – 40:1 (hexane-EtOAc)) afforded the desired product (658 mg, 67%) as a pale yellow oil.

$\nu_{\text{max}}$  / cm<sup>-1</sup> (film) 3027 (w), 2927 (w), 1682 (s), 1448 (m), 1279 (m), 1211 (m);

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.95-7.93 (2H, m, ArCH), 7.57-7.54 (1H, m, ArCH), 7.48-7.44 (2H, m, ArCH), 7.28-7.25 (2H, m, ArCH), 7.20-7.16 (1H, m, ArCH), 7.14-7.12 (2H, m, ArCH), 5.62-5.50 (2H, m, H<sub>3</sub> & H<sub>4</sub>), 3.31 (2H, d, *J* = 6.3, H<sub>5</sub>), 3.05-2.99 (1H, m, H<sub>1</sub>), 2.93-2.87 (2H, m, H<sub>1</sub>' & H<sub>2</sub>), 1.10 (3H, d, *J* = 6.5, H<sub>6</sub>);

$\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 199.6 (C=O), 140.7 (ArC), 137.4 (ArC), 136.2 (C<sub>3</sub>), 132.9, 128.5 (2C), 128.3, 128.1 (5 × ArCH), 127.7 (C<sub>4</sub>), 125.9 (ArCH), 45.7 (C<sub>1</sub>), 38.9 (C<sub>5</sub>), 33.0 (C<sub>2</sub>), 20.5 (C<sub>6</sub>);

HRMS (EI<sup>+</sup>) Found [M+H]<sup>+</sup>: 264.1519, C<sub>19</sub>H<sub>20</sub>O requires 264.1514.



**(4E)-3-Methyl-1,6-diphenylhex-4-en-1-one O-perfluorobenzoyl oxime 9o**

General procedure E: Part A: (*E*)-3-Methyl-1,6-diphenylhex-4-en-1-one (635 mg, 2.41 mmol) was employed affording the corresponding oxime (551 mg, 82%) as a colorless solid after purification by FCC (20:1 – 4:1 (hexane-EtOAc)). Part B: The corresponding oxime (545 mg, 1.95 mmol) was employed. Purification of the residue (30:1 (hexane-EtOAc)) afforded oxime ester **142** (766 mg, 75%, 10:1 mixture of oxime isomers) as a yellow oil that solidified on standing.

$\nu_{\text{max}}$  / cm<sup>-1</sup> (film) 2965 (w), 2930 (w), 1760 (s), 1651 (m), 1523 (m), 1494 (s), 1324 (s), 1189 (s);

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.68-7.65 (2H, m, ArCH), 7.49-7.45 (1H, m, ArCH), 7.43-7.38 (2H, m, ArCH), 7.27-7.23 (2H, m, ArCH), 7.19-7.15 (1H, m, ArCH), 7.08-7.06 (2H, m, ArCH), 5.47 (1H, dtd, *J* = 15.0, 6.5, 1.0, H<sub>4</sub>), 5.33

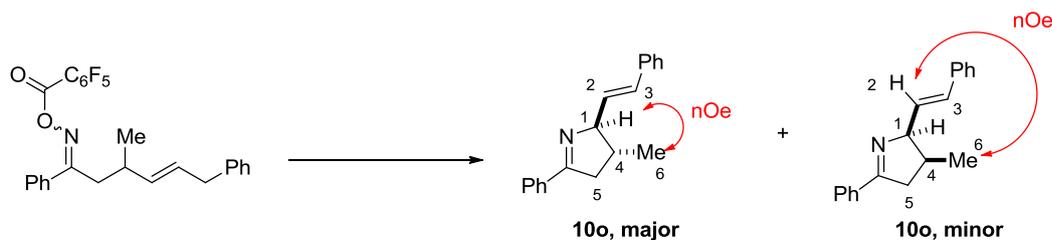
(1H, ddt,  $J = 15.0, 8.0, 1.0$ , H3), 3.24 (2H, dt,  $J = 6.5$ , H5), 2.99-2.89 (2H, m, H1), 2.55-2.44 (1H, m, H2), 1.06 (3H, d,  $J = 6.5$ , H6)'

$\delta_C$  (100 MHz,  $CDCl_3$ ) 168.0 (CN), 156.5 (CO), 140.2 (ArC), 134.8 (C3), 133.4 (ArC), 130.9 (ArCH), 128.9 (C4), 128.7, 128.4, 128.3, 127.6, 125.9 ( $5 \times$  ArCH), 38.7 (C5), 35.6 (C1), 35.2 (C2), 20.6 (C6);

Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

$\delta_F$  (376 MHz,  $CDCl_3$ ) -136.9 (2F), -137.1 (0.2F), -147.5 (1F), 147.9 (0.1F), -159.6 (2F), -160.0 (0.2F);

**HRMS** (ESI<sup>+</sup>) Found  $[M+Na]^+$ : 495.1306,  $C_{26}H_{20}O_2NF_5Na$  requires 496.1307.



**(E)-3-Methyl-5-phenyl-2-styryl-3,4-dihydro-2H-pyrrole 10o**

**General procedure F:** **9o** (60 mg, 0.13 mmol) was employed. In a modification to the general procedure the reaction mixture was heated at 100 °C. Analysis of the <sup>1</sup>H NMR of the crude reaction mixture revealed trace amounts of the corresponding pyrrole. FCC (20:1 – 5:1 (hexane-EtOAc)) afforded the title compound (20 mg, 61%, 2:1 d.r.) as a yellow oil.

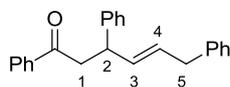
$\nu_{max}$  /  $cm^{-1}$  (film) 3026 (w), 2955 (w), 1608 (m), 1493 (m), 1447 (m), 1340 (m), 964 (m);

$\delta_H$  (400 MHz,  $CDCl_3$ ) 7.93-7.88 (2H, m, ArCH), 7.45-7.39 (5H, m, ArCH), 7.33-7.29 (2H, m, ArCH), 7.24-7.20 (1H, m, ArCH), 6.70-6.63 (1H, m, H3), 6.31 (0.66H, dd,  $J = 16.0, 7.5$ , H2a), 6.26 (0.33H, dd,  $J = 16.0, 7.5$ , H2b), 4.89-4.84 (0.33H, m, H1b), 4.39-4.34 (0.66H, m, H1a), 3.29 (0.66H, m, ddd,  $J = 17.0, 8.5, 2.0$ , H5a), 3.20-3.12 (0.33H, m, H5b), 2.78-2.68 (0.66H, m, H4b & H5b'), 2.62 (0.66H, m, H4a), 2.36-2.25 (0.66H, m, H4a), 1.24 (2H, d,  $J = 7.0$ , H6a), 1.03 (1H, d,  $J = 7.0$ , H6b);

$\delta_C$  (100 MHz,  $CDCl_3$ ) 173.6 (CN), 173.1 (CN), 137.4, 127.2, 134.6, 134.5 ( $4 \times$  ArC), 131.5 (C3b), 130.9 (C2a), 130.6 (2C, C3a, ArCH), 130.4 (ArCH), 128.4 (2C, ArCH), 128.1 (C2b), 127.3, 127.2, 126.4 ( $3 \times$  ArCH), 81.6 (C1a), 76.5 (C1b), 43.2 (C5a), 43.1 (C5b), 39.1 (C4a), 36.3 (C4b), 18.6 (C6a), 16.0 (C6b); Only signals for  $7 \times$  ArCH were resolvable.

**HRMS** (EI<sup>+</sup>) Found  $[M]^+$ : 261.1528,  $C_{19}H_{19}N$  requires 261.1517.

The relative stereochemistry of the two diastereomers was corroborated by *nOe* experiments as indicated on the compound structure. The major diastereomer was determined to be *trans* by these experiments.



**(E)-1,3,6-Triphenylhex-4-en-1-one**<sup>16</sup>

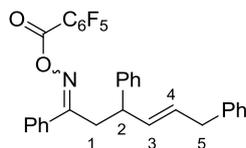
This procedure was conducted under Schlenk-line techniques. To a solution of Schwartz's reagent (1.03 g, 4.0 mmol) in anhydrous  $CH_2Cl_2$  (16 mL) was added 3-phenyl-1-propyne (546  $\mu$ L, 4.4 mmol) dropwise *via* syringe. After stirring at room temperature for 20 minutes the solvent was removed *in vacuo*. After removal of the solvent the atmosphere was backfilled with nitrogen and anhydrous dioxane (20 mL), chalcone (416 mg, 2.0 mmol) and  $[Rh(COD)Cl]_2$  (19.7 mg, 0.04 mmol) were added sequentially. The reaction mixture was then stirred at room temperature for 36 hours after which time saturated aq.  $NaHCO_3$  (50 mL) was added and the aqueous phase was extracted with EtOAc ( $3 \times 100$  mL). The organic layers were combined, washed with brine (50 mL), dried ( $Na_2SO_4$ ), filtered and concentrated *in vacuo*. Purification of the residue by FCC (50:1 – 40:1 (hexane-EtOAc)) afforded the desired product (411 mg, 63%) as a pale yellow oil.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3060 (w), 2896 (w), 1683 (s), 1446 (s), 1257 (s), 1129 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.92-7.80 (2H, m, ArCH), 7.56-7.52 (1H, m, ArCH), 7.45-7.42 (2H, m, ArCH), 7.32-7.23 (6H, m, ArCH), 7.22-7.15 (2H, m, ArCH), 7.11-7.08 (2H, m, ArCH), 5.75 (1H, ddt,  $J = 15.5, 7.5, 1.5$ , H3), 5.60 (1H, dtd,  $J = 15.5, 6.5, 1.0$ , H4), 4.15-4.11 (1H, m, H2), 3.44-3.32 (4H, m, H1 & H5);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 198.5 (CO), 143.7, 140.4, 137.2 ( $3 \times \text{ArC}$ ), 133.9 (C3), 133.0 (ArCH), 129.4 (C4), 128.6 (2C), 128.5, 128.3, 128.1, 127.6, 126.4, 125.9 ( $8 \times \text{ArCH}$ ), 44.6 (C1), 43.9 (C2), 38.9 (C5);

HRMS ( $\text{EI}^+$ ) Found [ $\text{M}^+$ ]: 326.1671,  $\text{C}_{24}\text{H}_{22}\text{O}$  requires 326.1671.



### (4E)-1,3,6-Triphenylhex-4-en-1-one O-perfluorobenzoyl oxime 9p

**General procedure E: Part A:** (E)-1,3,6-Triphenylhex-4-en-1-one (245 mg, 0.75 mmol) was employed affording the corresponding oxime (255 mg, 100%) as a colorless solid. **Part B:** The corresponding oxime (250 mg, 0.73 mmol) was employed. Purification of the residue (50:1 – 20:1 (hexane-EtOAc)) afforded the title compound (300 mg, 77%, 10:1 mixture of oxime isomers) as a colorless oil that solidified on standing.

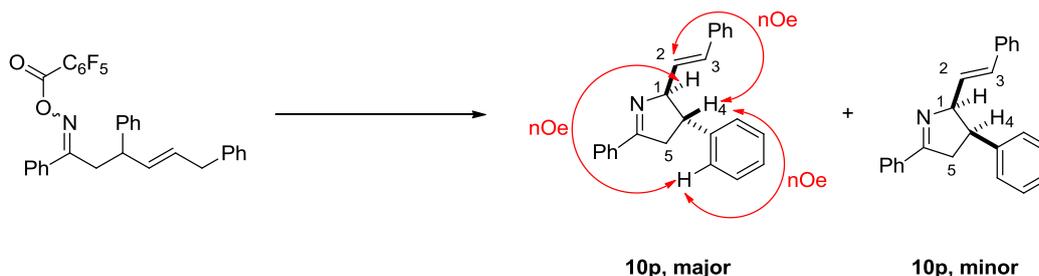
$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3027 (w), 1763 (s), 1651 (m), 1525 (m), 1493 (s), 1324 (s), 1197 (s), 1001 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) Data for major isomer only 7.62-7.59 (2H, m, ArCH), 7.51-7.47 (1H, m, ArCH), 7.43-7.39 (2H, m, ArCH), 7.32-7.25 (4H, m, ArCH), 7.23-7.15 (4H, m, ArCH), 7.12-7.09 (2H, m, ArCH), 5.67 (1H, dd,  $J = 15.5, 7.5$ , H3), 5.57 (1H, dt,  $J = 15.5, 6.5$ , H4), 3.62 (1H, dd,  $J = 15.5, 8.0$ , H2), 3.49-2.32 (1H, m, H1), 3.32-3.24 (3H, m, H1' & H5);

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 167.3 (CN), 156.2 (CO), 142.6, 139.9, 133.2 ( $3 \times \text{ArC}$ ), 132.2 (C3), 130.8 (ArCH), 130.5 (C4), 128.7, 128.5 (2C), 128.3, 127.6, 127.1, 126.8, 126.0 ( $8 \times \text{ArCH}$ ), 46.2 (C2), 38.7 (C5), 35.2 (C1);

Signals corresponding to the perfluorinated benzoyl ester moiety were not resolvable due to their anticipated weak intensity.

HRMS ( $\text{ESI}^+$ ) Found [ $\text{M}+\text{Na}$ ] $^+$ : 558.1463,  $\text{C}_{31}\text{H}_{22}\text{O}_2\text{NF}_5\text{Na}$  requires 558.1478.



### (E)-3,5-Diphenyl-2-styryl-3,4-dihydro-2H-pyrrole 10p

**General procedure F:** 9p (110 mg, 0.206 mmol) was employed. Analysis of the  $^1\text{H}$  NMR of the crude reaction mixture revealed trace amounts of the corresponding pyrrole. FCC (20:1 – 5:1 (hexane-EtOAc)) afforded the title compound (40 mg, 67%, 5:1 d.r.) as a yellow oil. The diastereomers were separable after repeated FCC. Their  $^1\text{H}$  and  $^{13}\text{C}$  NMR data is listed individually and not normalised relative to the major diastereomer.

$\nu_{\max}$  /  $\text{cm}^{-1}$  (film) 3059 (w), 3027 (w), 1612 (m), 1494 (m), 1447 (m), 1339 (m);

Data for major diastereomer:

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.96-7.93 (2H, m, ArCH), 7.49-7.43 (3H, m, ArCH), 7.39-7.19 (10H, m, ArCH), 6.58 (1H, d,  $J = 16.0$ , H3), 6.37 (1H, dd,  $J = 16.0, 7.0$ , H2), 4.93-4.88 (1H, m, H1), 3.61 (1H, ddd,  $J = 17.0, 9.5, 2.0$ , H5), 3.45-3.39 (1H, m, H4), 3.19 (1H, ddd,  $J = 17.0, 8.0, 2.0$ , H5');

$\delta_C$  (100 MHz, CDCl<sub>3</sub>) 172.2 (C<sub>N</sub>), 143.2, 137.1, 134.1 (3 × ArC), 130.9 (ArCH), 130.6 (C<sub>2</sub>), 130.5 (C<sub>3</sub>), 128.8, 128.5, 128.4, 127.9, 127.4, 127.2, 126.7, 126.5 (8 × ArCH), 82.4 (C<sub>1</sub>), 50.5 (C<sub>4</sub>), 44.2 (C<sub>5</sub>);

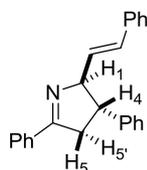
Data for minor diastereomer:

$\delta_H$  (400 MHz, CDCl<sub>3</sub>) 8.02-8.00 (2H, m, ArCH), 7.53-7.46 (3H, m, ArCH), 7.30-7.25 (2H, m, ArCH), 7.22-7.09 (8H, m, ArCH), 6.52 (1H, d,  $J = 16.0$ , H<sub>2</sub>), 5.75 (1H, dd,  $J = 16.0, 7.0$ , H<sub>3</sub>), 5.22-5.17 (1H, m, H<sub>1</sub>), 3.95-3.89 (1H, m, H<sub>4</sub>), 3.45 (1H, ddd,  $J = 17.0, 8.5, 1.5$ , H<sub>5</sub>), 3.37 (1H, ddd,  $J = 17.0, 7.0, 1.5$ , H<sub>5'</sub>);

$\delta_C$  (100 MHz, CDCl<sub>3</sub>) 173.7 (C<sub>N</sub>), 140.5, 137.4, 134.2 (3 × ArC), 130.9 (C<sub>3</sub>), 130.9 (ArCH), 128.8 (C<sub>2</sub>), 128.6, 128.3 (2C), 128.2, 127.9, 127.1, 126.6, 126.4 (8 × ArCH), 77.3 (C<sub>1</sub>), 48.1 (C<sub>4</sub>), 41.4 (C<sub>5</sub>);

HRMS (EI<sup>+</sup>) Found [M]<sup>+</sup>: 323.1672, C<sub>24</sub>H<sub>21</sub>N requires 323.1764.

The relative stereochemistry of the two diastereomers was corroborated by *nOe* experiments as indicated on the compound structure. Additionally, the relative stereochemistry was determined by *nOe* analysis according to the method of Butts *et al.*<sup>17</sup> The *nOe* observed between H(3) and H(3') was used to calibrate calculations as the distance between these protons (1.76 Å) is reliably predicted by molecular modelling. Further interproton distances were then readily calculated from *nOe* strengths according to the published method. Comparison of the calculated distance between the protons indicated with that obtained from DFT calculations for *cis* and *trans* models of compound **10p** shows a closer correlation to the *trans* model. On this basis the stereochemistry was assigned as *trans* by NMR.



*Trans* diastereomer

Protons measured	Relative Distance	<i>nOe</i> distance / Å	Model distance / Å	Error / %
5-5'			1.76	5.11
5-1	1.64	3.04	3.17	4.21
5'-5	0.99	1.82	1.76	3.66
4-1	1.57	2.91	3.03	3.88
1-5	1.69	3.13	3.17	1.31
1-4	1.55	2.86	3.03	5.61

Mean average error = 3.96

Standard deviation = 1.49893

MAE + STD = 5.46

*Cis* diastereomer

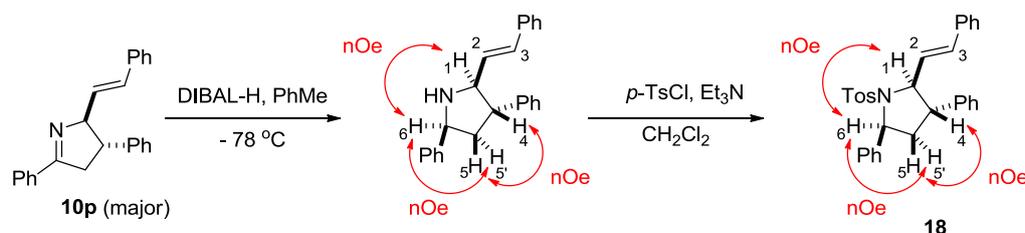
Protons measured	Relative Distance	<i>nOe</i> distance / Å	Model distance / Å	Error / %
5-5'			1.76	6.82
5-1	1.64	3.04	3.18	15.35
5'-5	0.99	1.82	1.76	8.11

4-1	1.57	2.91	2.29	12.75
1-5	1.69	3.13	3.18	12.79
1-4	1.55	2.86	2.29	10.71

Mean average error = 11.09

Standard deviation = 3.196115

MAE + STD = 14.28



### (2S,3S,5S)-3,5-Diphenyl-2-((E)-styryl)pyrrolidine

To a solution of imine **trans-10p** (31 mg, 0.096 mmol) in toluene (0.96 mL) at  $-78\text{ }^{\circ}\text{C}$  was added DIBAL-H (1 M in heptane, 0.30 mL, 0.30 mmol) dropwise. After stirring for 60 minutes saturated aq.  $\text{NH}_4\text{Cl}$  (0.4 mL) was added and the reaction mixture was allowed to warm to rt. The mixture was diluted with  $\text{CH}_2\text{Cl}_2$  (20 mL), dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated *in vacuo* to give the title compound (22 mg, 71%., >20:1 d.r.) as a yellow oil.

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.50-7.47 (2H, m, ArCH), 7.37-7.17 (13H, m, ArCH), 6.43 (1H, d,  $J = 15.5$ , H3), 6.32 (1H, dd,  $J = 15.5$ , 7.0, H2), 4.61 (1H, dd,  $J = 8.5$ , 7.0, H6), 3.95 (1H, dd,  $J = 9.0$ , 7.0, H1), 3.24-3.17 (1H, m, H4), 2.49 (1H, ddd,  $J = 13.0$ , 8.0, 8.0, H5), 2.39-2.32 (1H, m, H5');

$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 144.9, 142.7, 137.0 ( $3 \times \text{ArC}$ ), 130.8 (2C) (C2 & C3), 128.5, 128.4 (2C), 127.8, 127.3, 127.0, 126.7, 126.4 (2C) ( $9 \times \text{ArCH}$ ), 69.6 (C1), 61.4 (C6), 51.1 (C4), 43.1 (C5);

The relative stereochemistry was corroborated by *nOe* experiments as indicated on the compound structure. The spectroscopic properties of this compound were consistent with the data available in the literature.<sup>18</sup>

### (2S,3S,5S)-3,5-Diphenyl-2-((E)-styryl)-1-tosylpyrrolidine 18

To a solution of the above amine (17 mg, 0.052 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.65 mL) was added  $\text{Et}_3\text{N}$  (15  $\mu\text{L}$ , 0.10 mmol) and *p*-TsCl (10 mg, 0.052 mmol). The reaction mixture was stirred for 3 hours after which time it was diluted with  $\text{Et}_2\text{O}$  (10 mL), washed with saturated aq.  $\text{Na}_2\text{CO}_3$  ( $2 \times 10$  mL), dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated *in vacuo*. Purification of the residue by FCC (20:1 – 5:1 (hexane-EtOAc)) afforded the title compound (23 mg, 92%, >20:1 d.r.) as a colorless oil. Crystals suitable for X-ray diffraction were grown from slow evaporation of  $\text{CH}_2\text{Cl}_2$ .

**Mp** 152-153  $^{\circ}\text{C}$  ( $\text{CH}_2\text{Cl}_2$ )

$\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film) 3060 (w), 2927 (w), 1599 (m), 1494 (m), 1449 (m), 1349 (s), 1162 (s);

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.66 (2H, d,  $J = 8.0$ , ArCH), 7.47-7.45 (2H, m, ArCH), 7.38 (2H, t,  $J = 7.5$ , ArCH), 7.32-7.20 (11H, m, ArCH), 7.04 (2H, d,  $J = 7.0$ , ArCH), 6.32 (1H, d,  $J = 16.0$ , H3), 6.16 (1H, dd,  $J = 16.0$ , 8.0, H2), 5.37-5.35 (1H, m, H6), 4.39-4.36 (1H, m, H1), 3.22 (1H, ddd,  $J = 11.5$ , 9.5, 6.5, H4), 2.40 (3H, s, CH<sub>3</sub>), 2.32-2.22 (2H, m, H5);

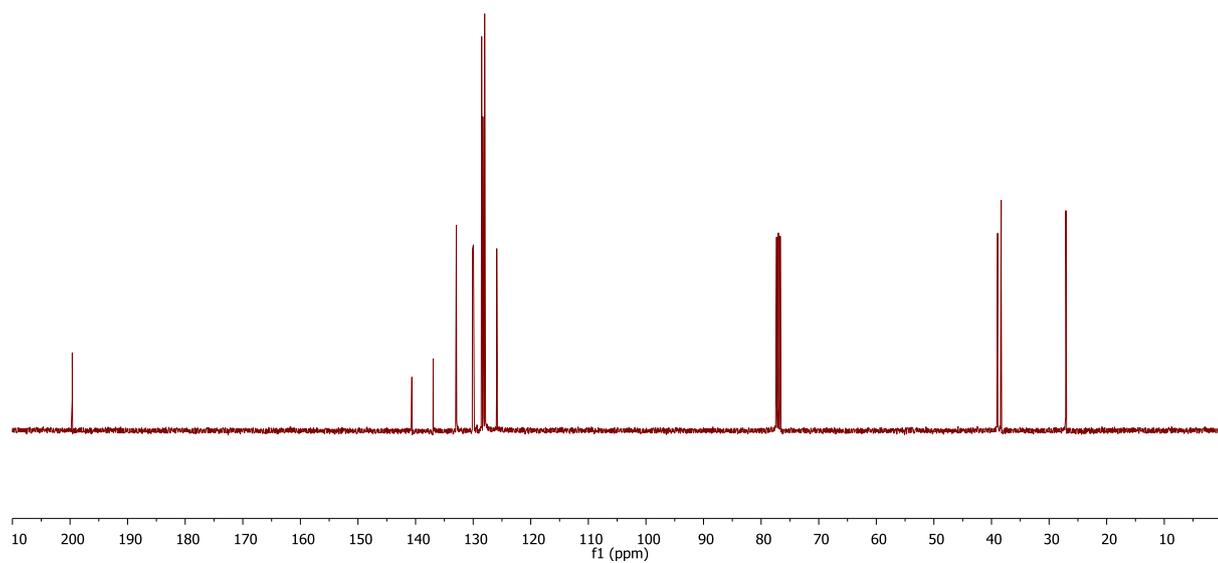
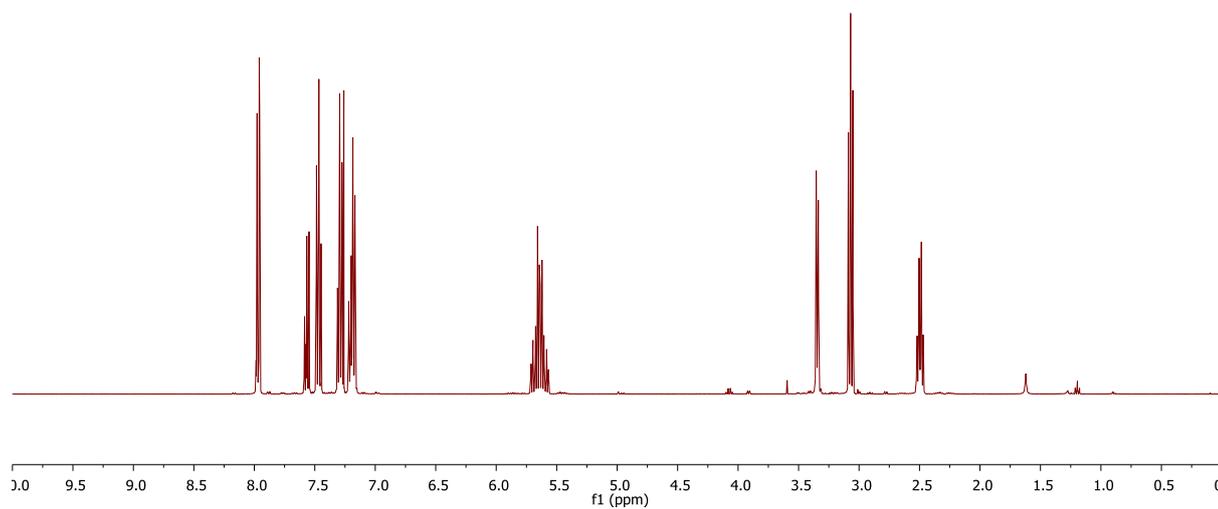
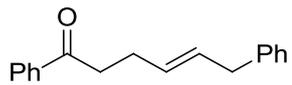
$\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 143.4, 142.4, 138.8, 136.5, 136.3 ( $5 \times \text{ArC}$ ), 132.7 (C3), 129.4 (ArCH), 128.6 (C2), 128.4 (3C), 127.9, 127.6, 127.2, 127.1, 126.5, 126.4 (2C) ( $10 \times \text{ArCH}$ ), 70.2 (C1), 63.3 (C6), 49.7 (C4), 41.2 (C5), 21.5 (C7);

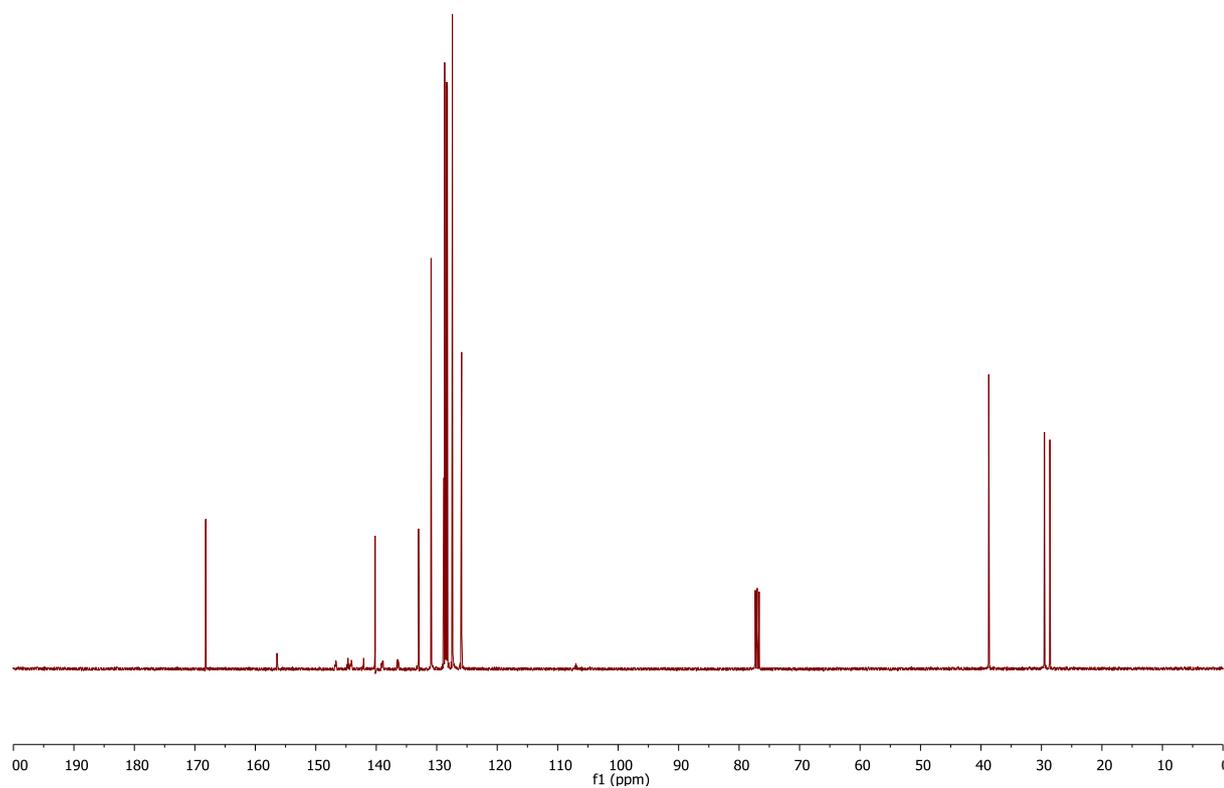
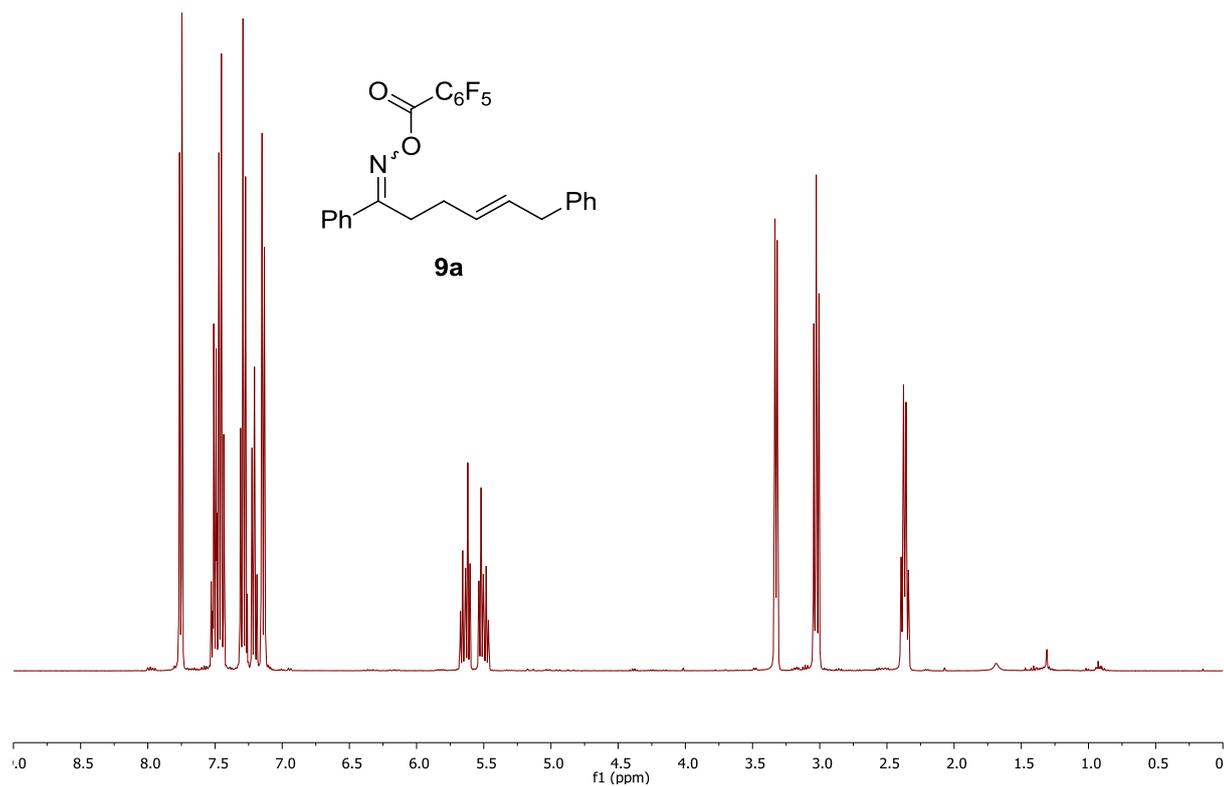
**HRMS** ( $\text{EI}^+$ ) Found  $[\text{M}]^+$ : 479.1921,  $\text{C}_{31}\text{H}_{29}\text{NO}_2\text{S}$  requires 479.1919.

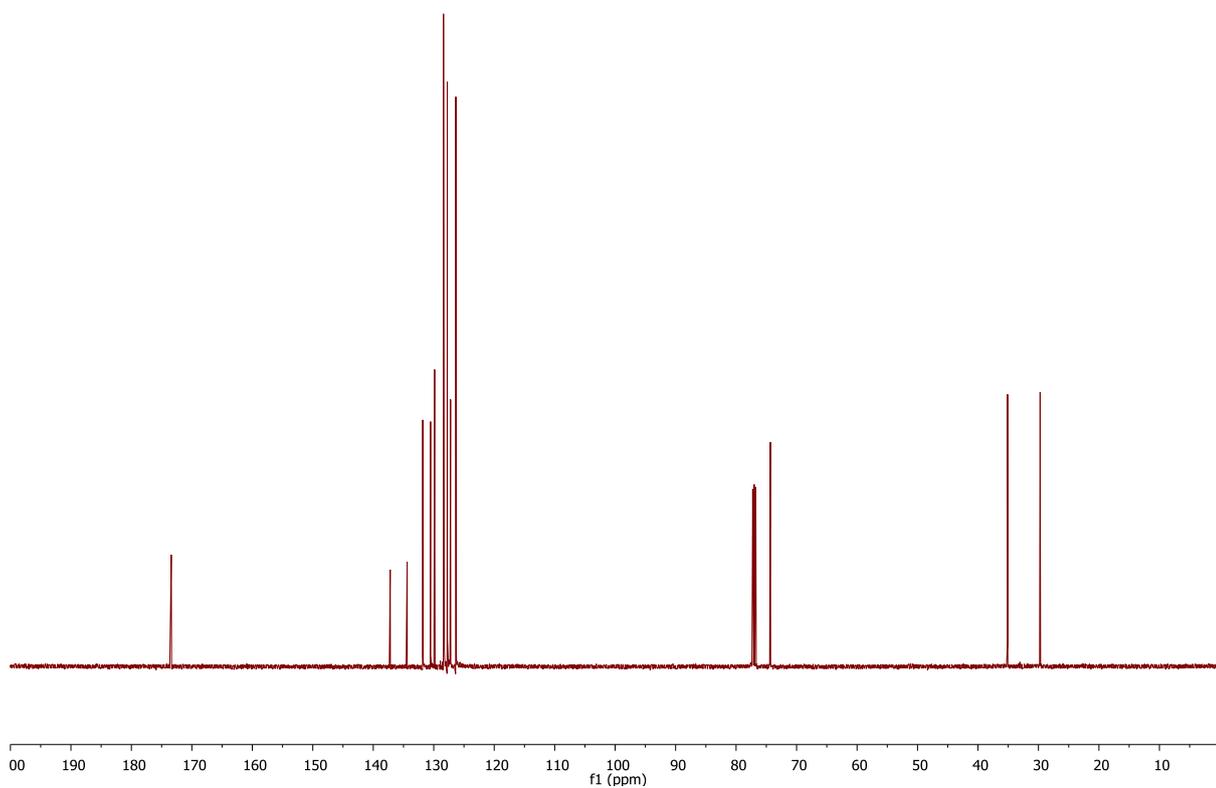
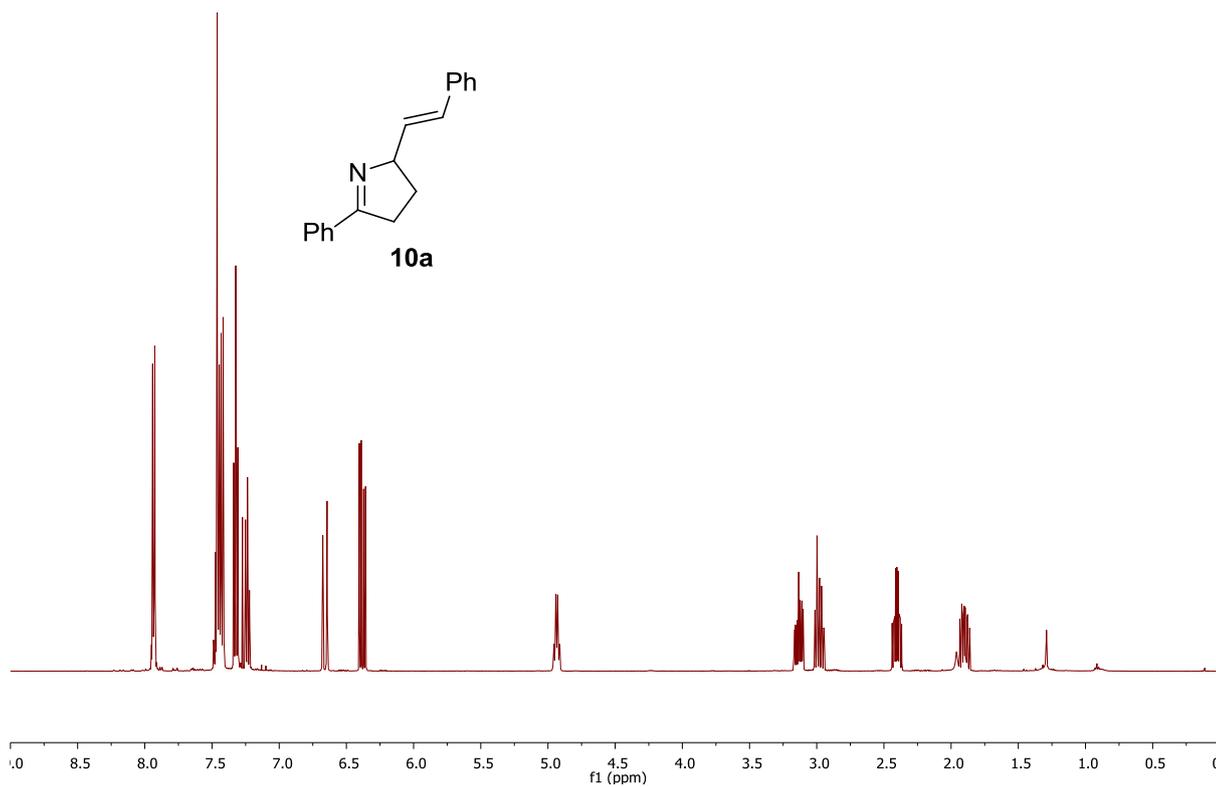
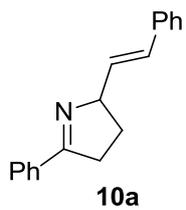
## References

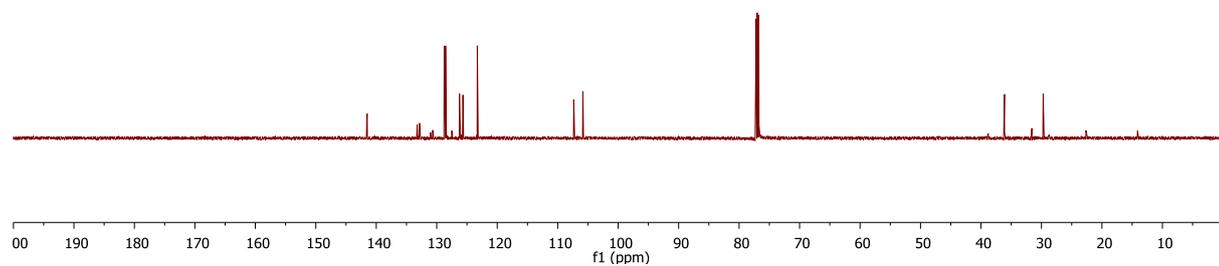
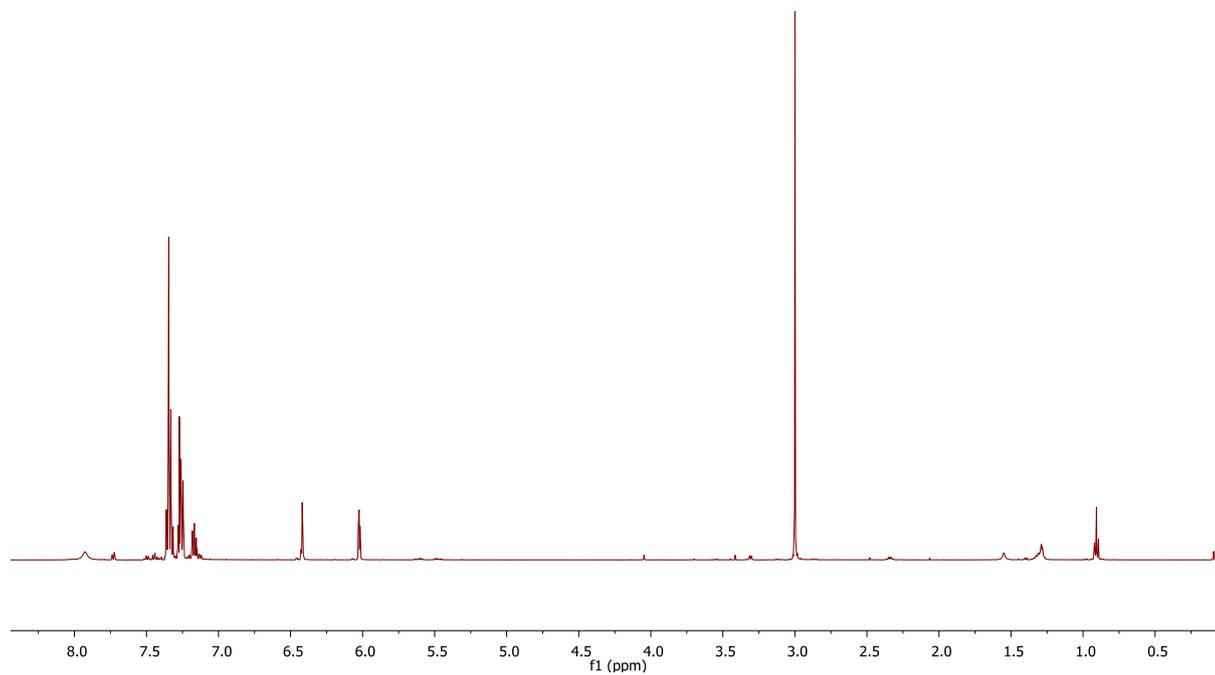
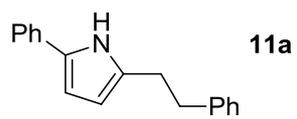
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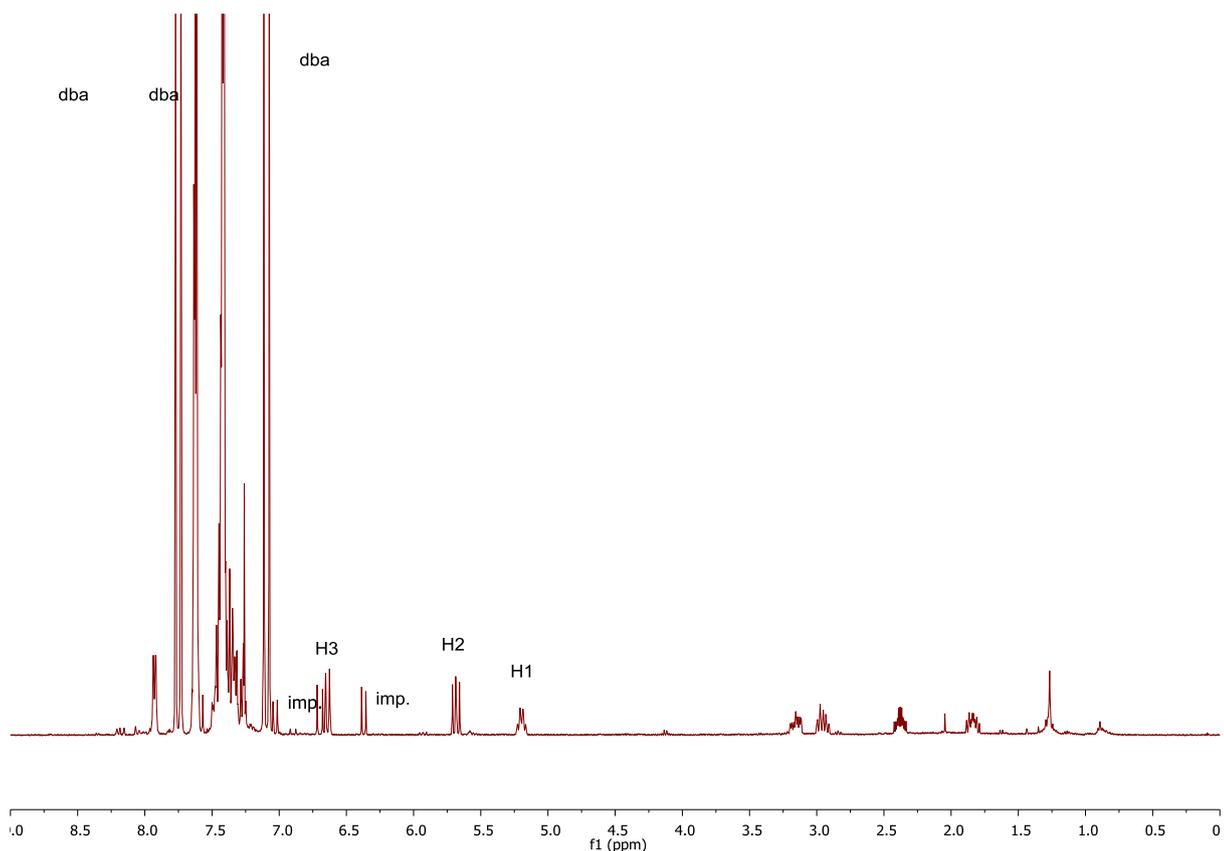
# Spectra of novel compounds



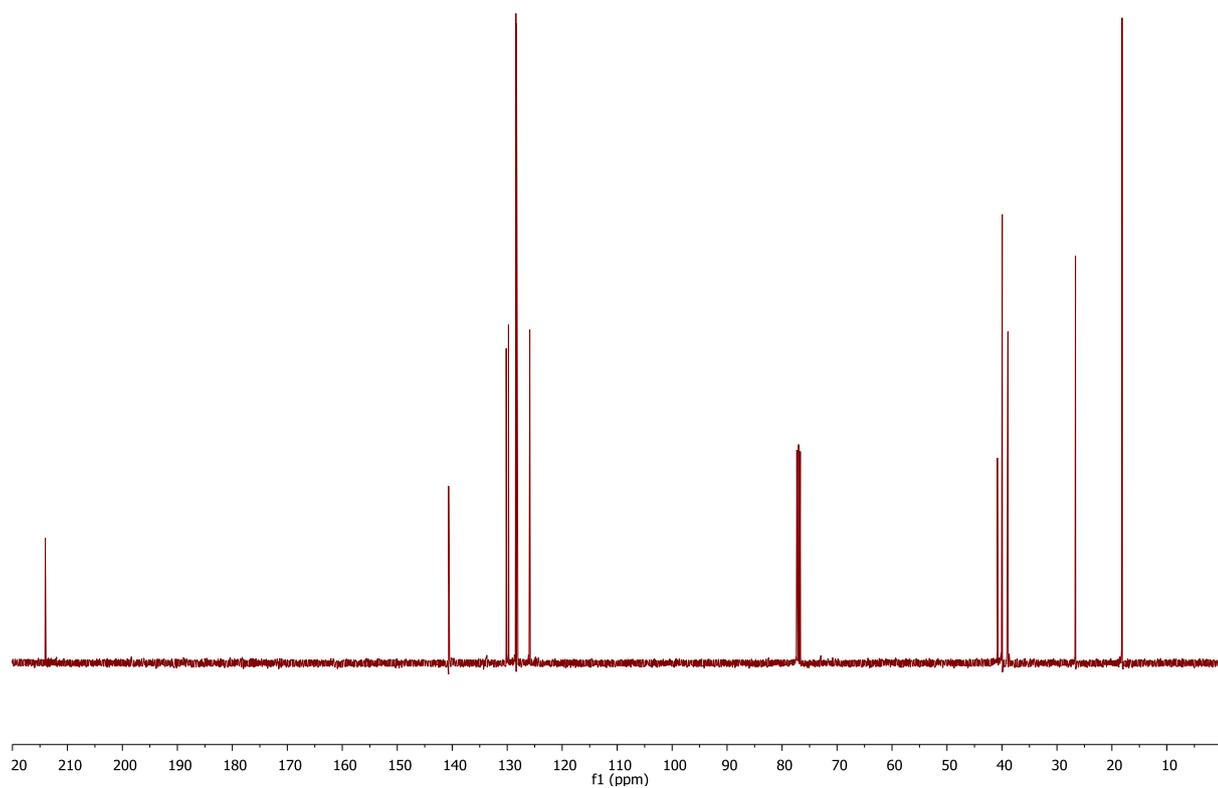
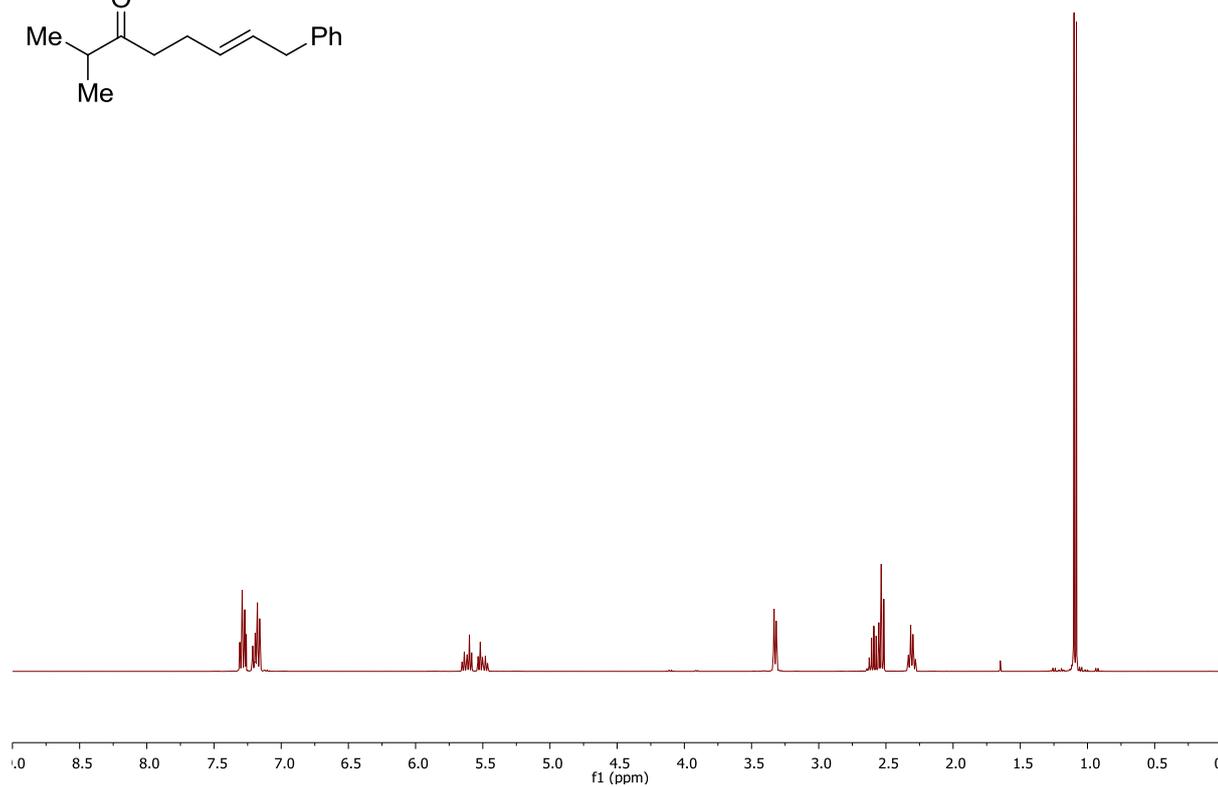
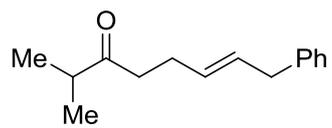




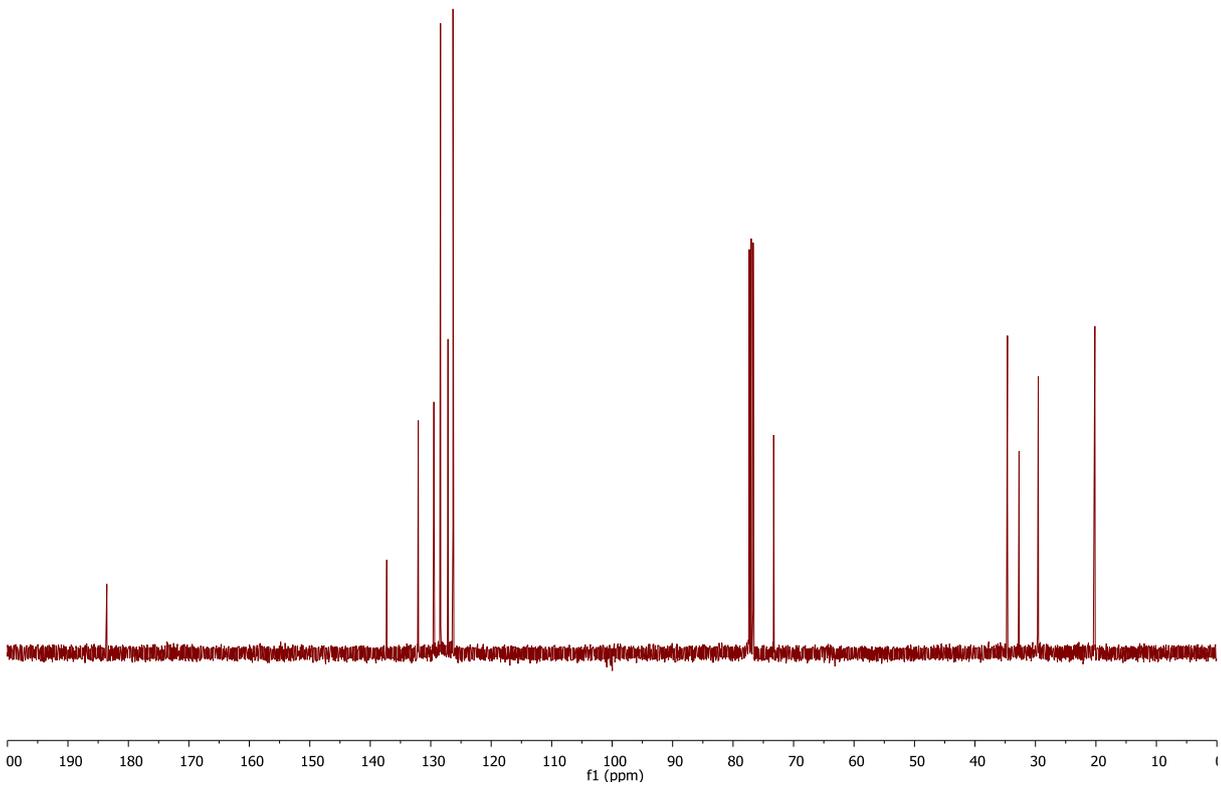
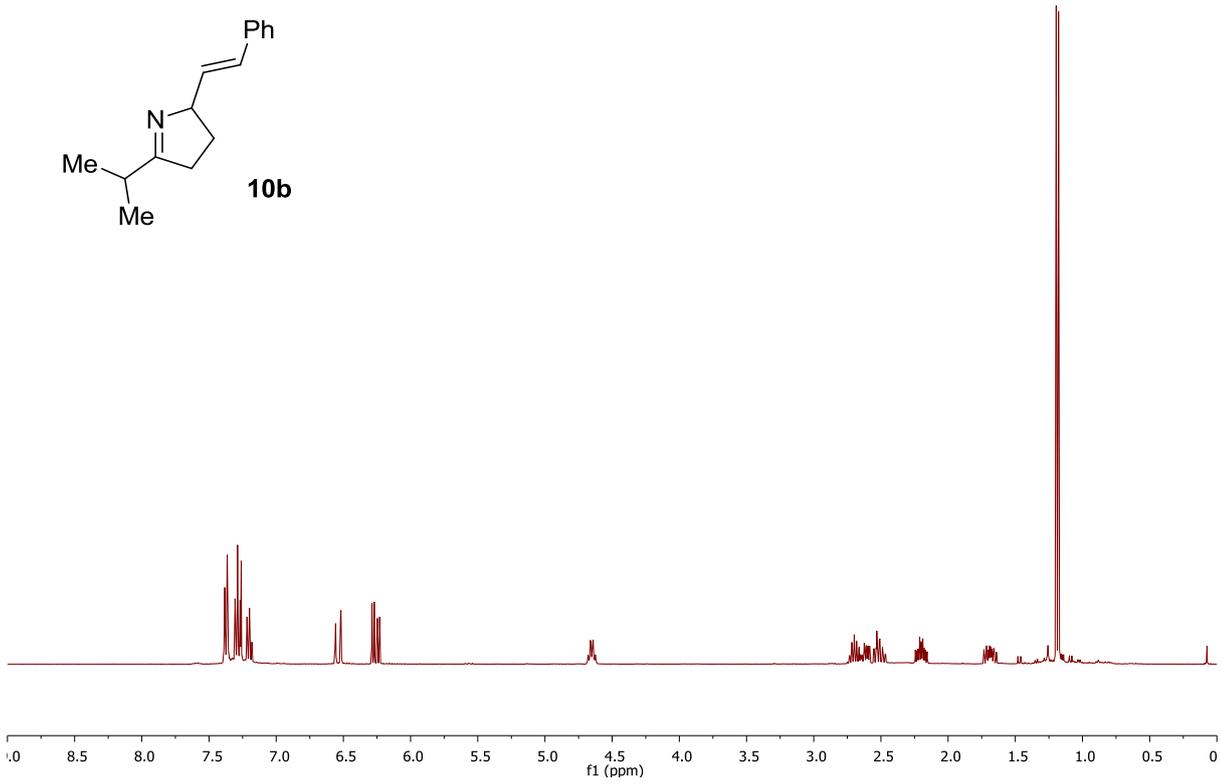
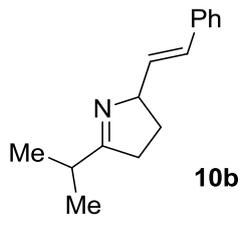


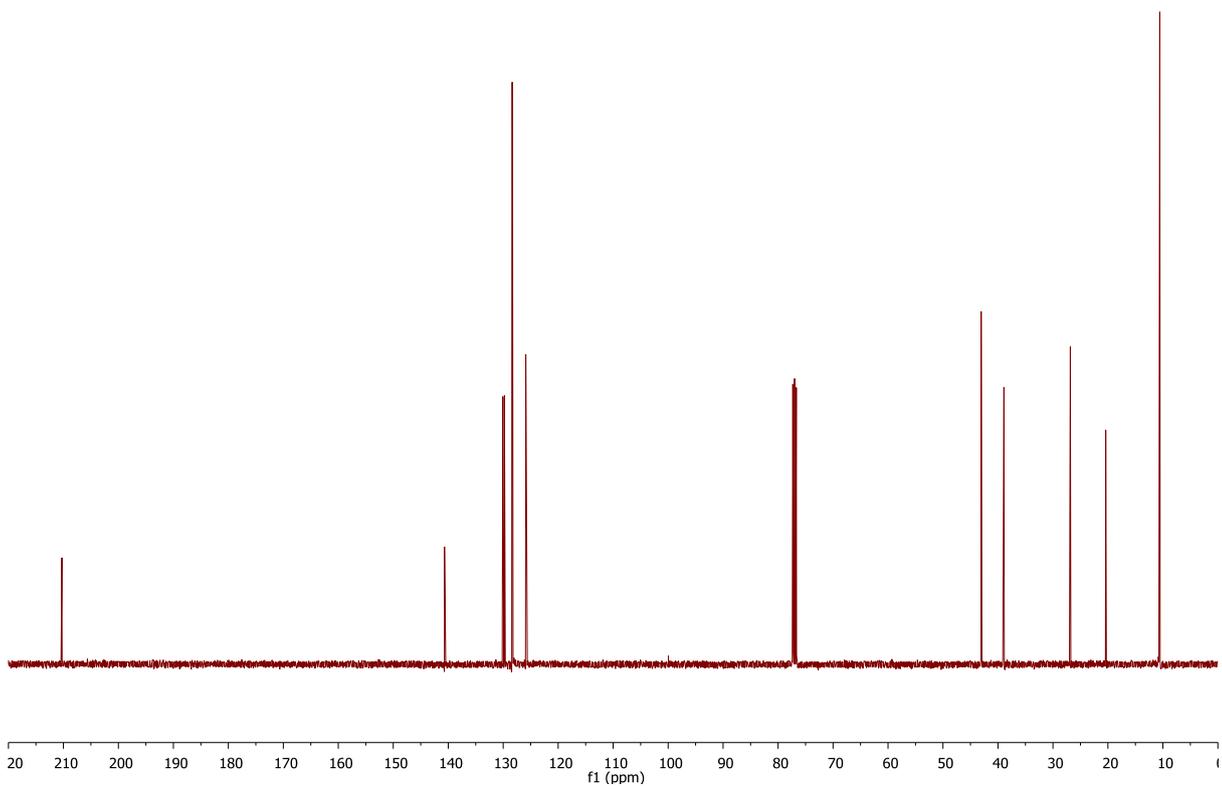
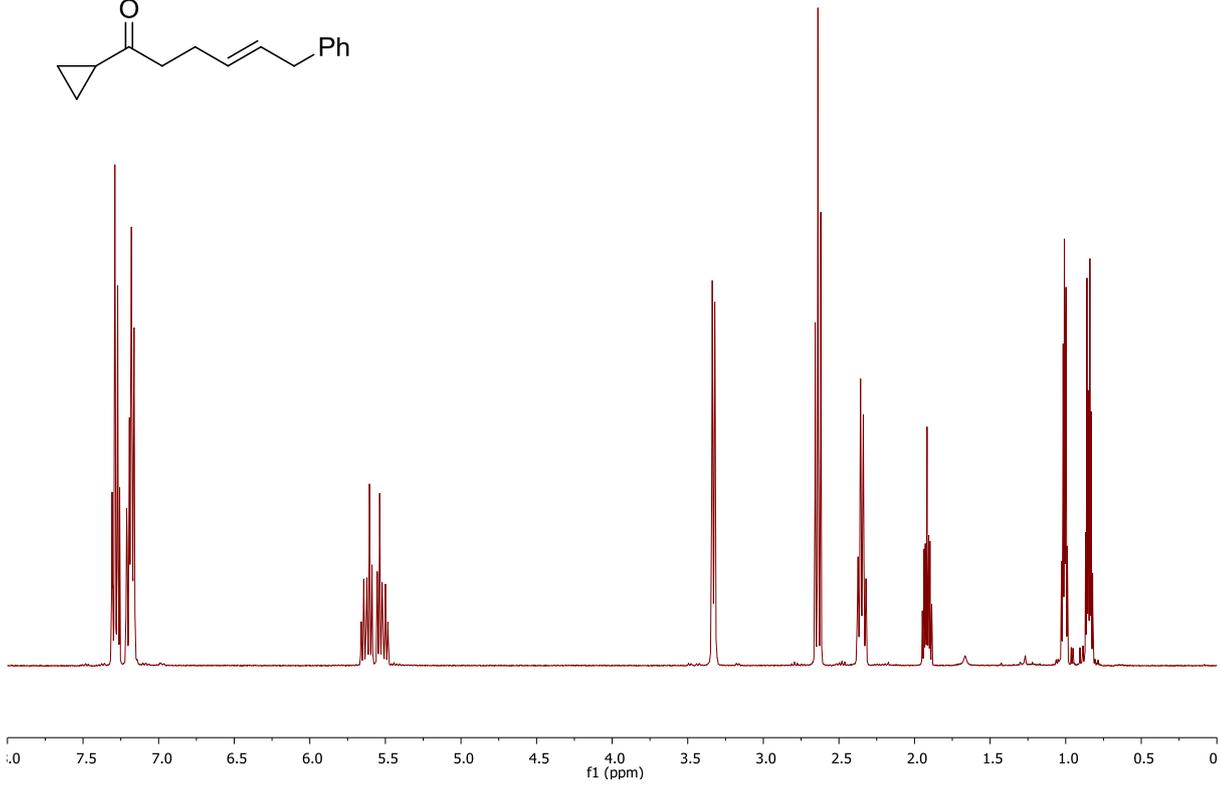
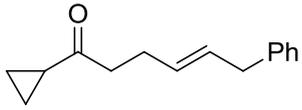


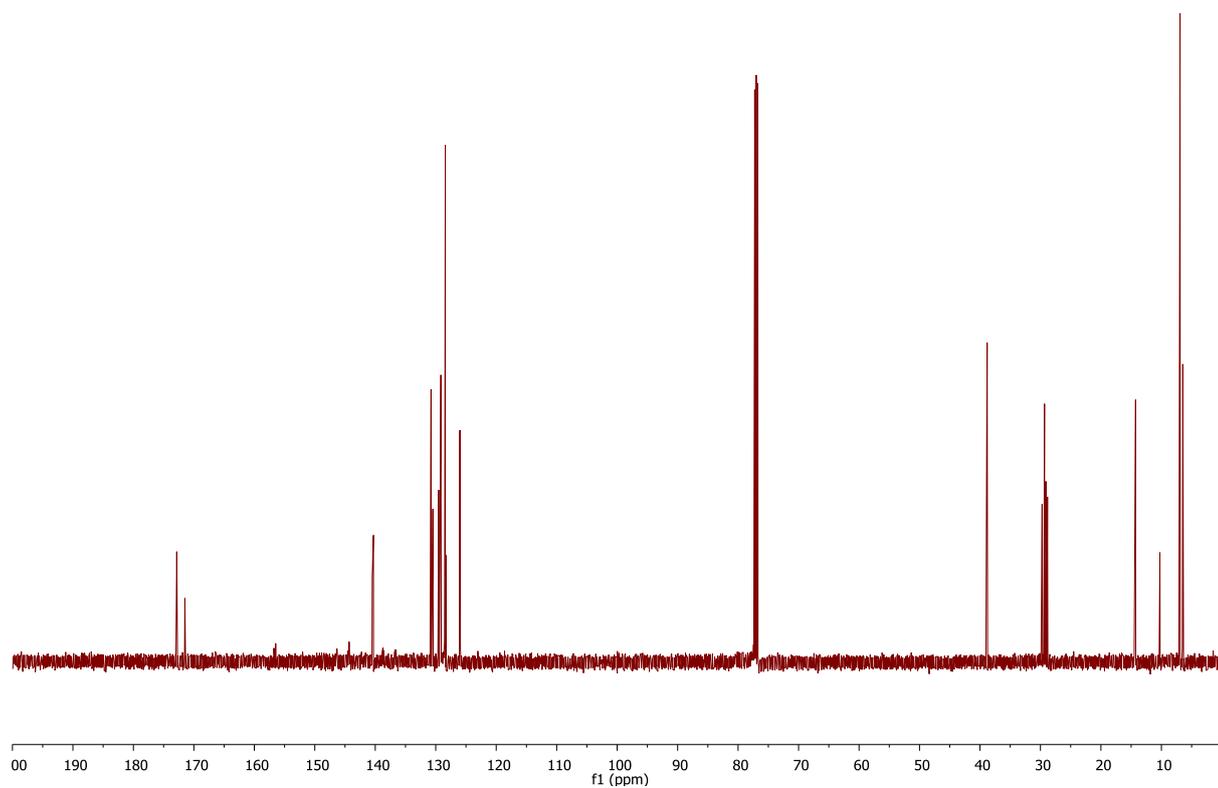
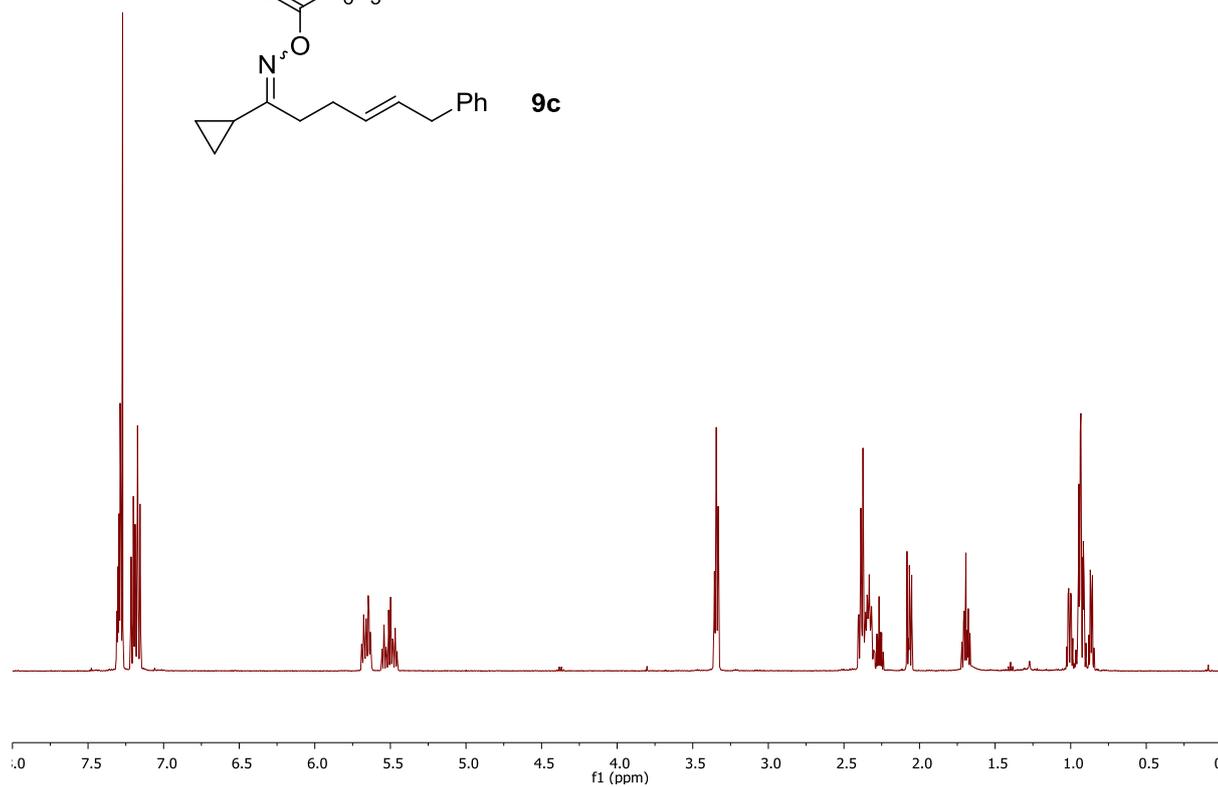
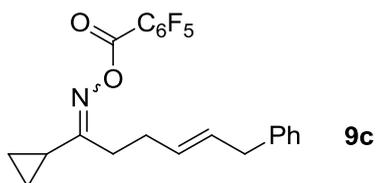
*(Z)-10a* was contaminated with dba and was characterised by  $^1\text{H}$  NMR and HRMS only due to low quantities of material

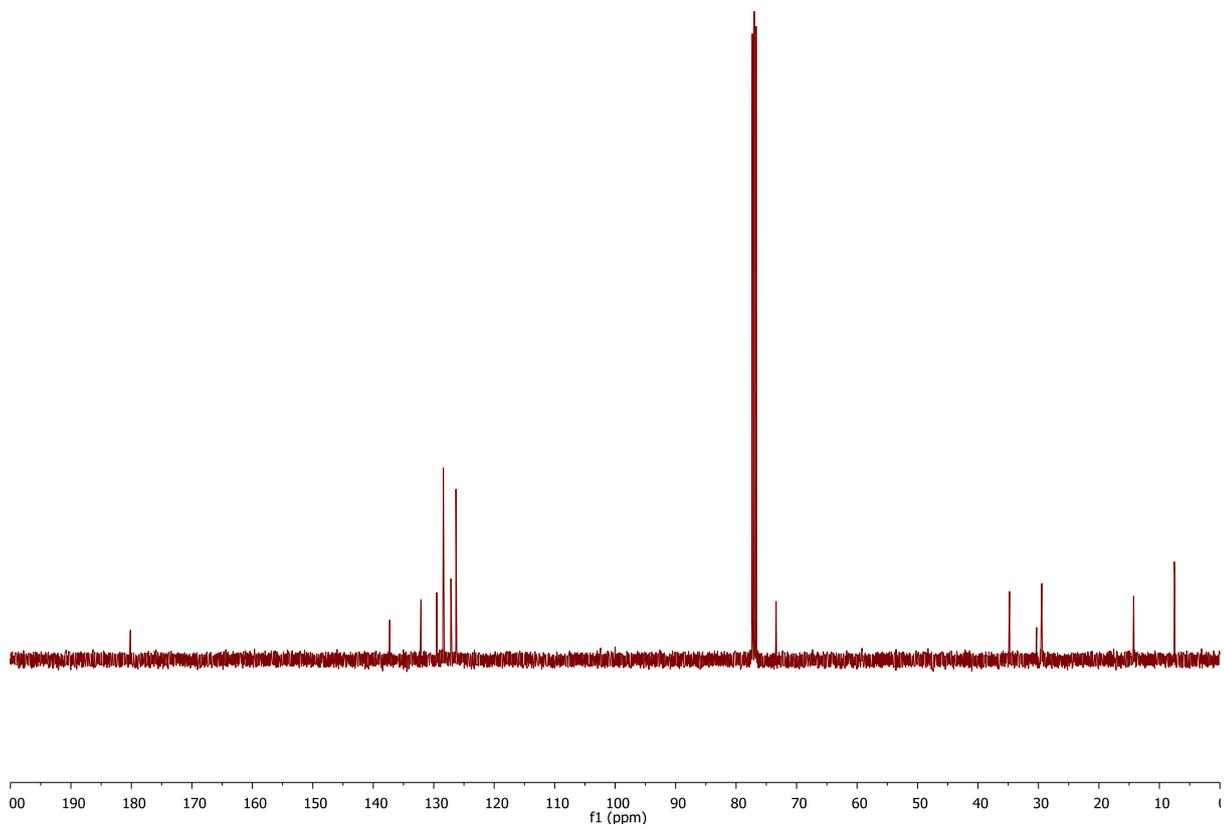
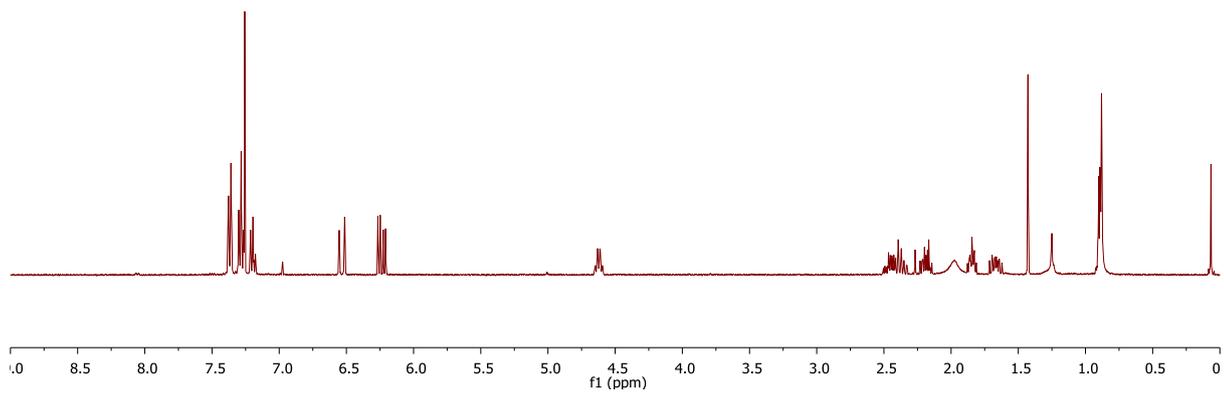
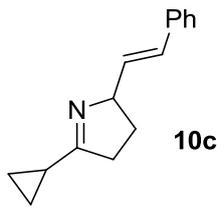


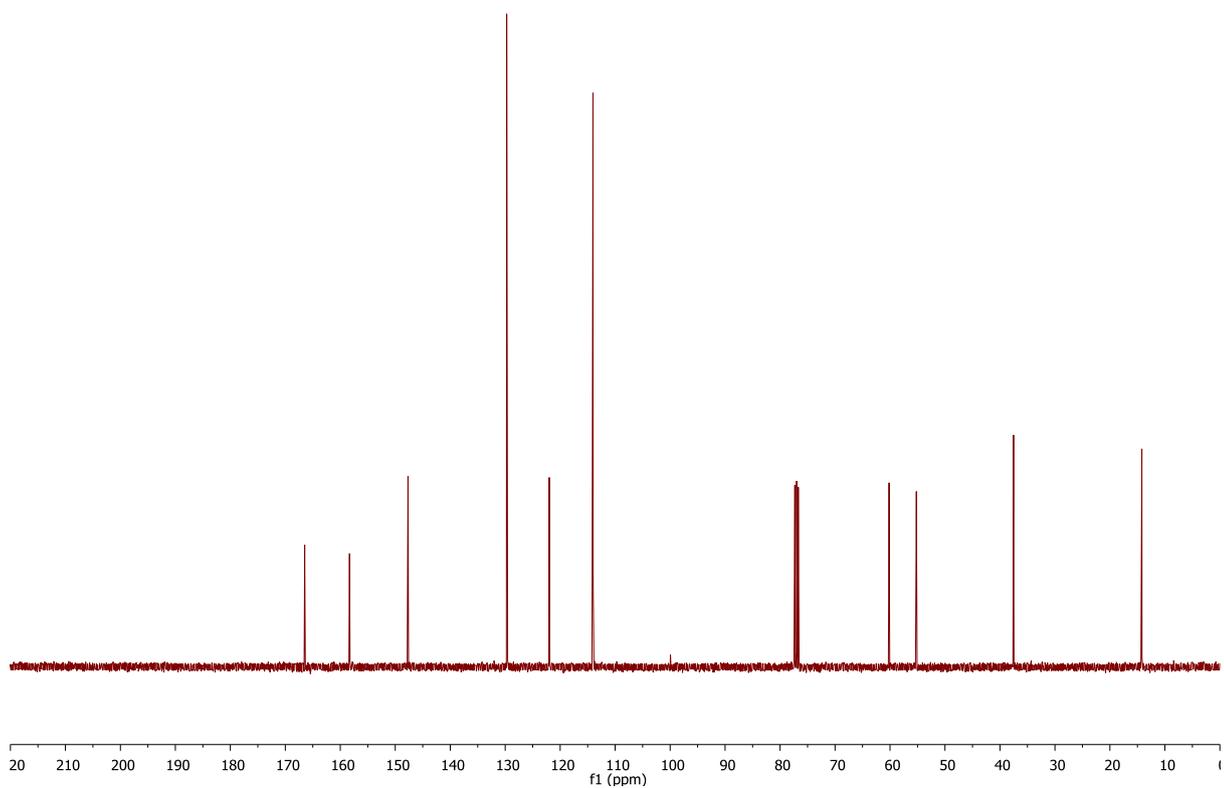
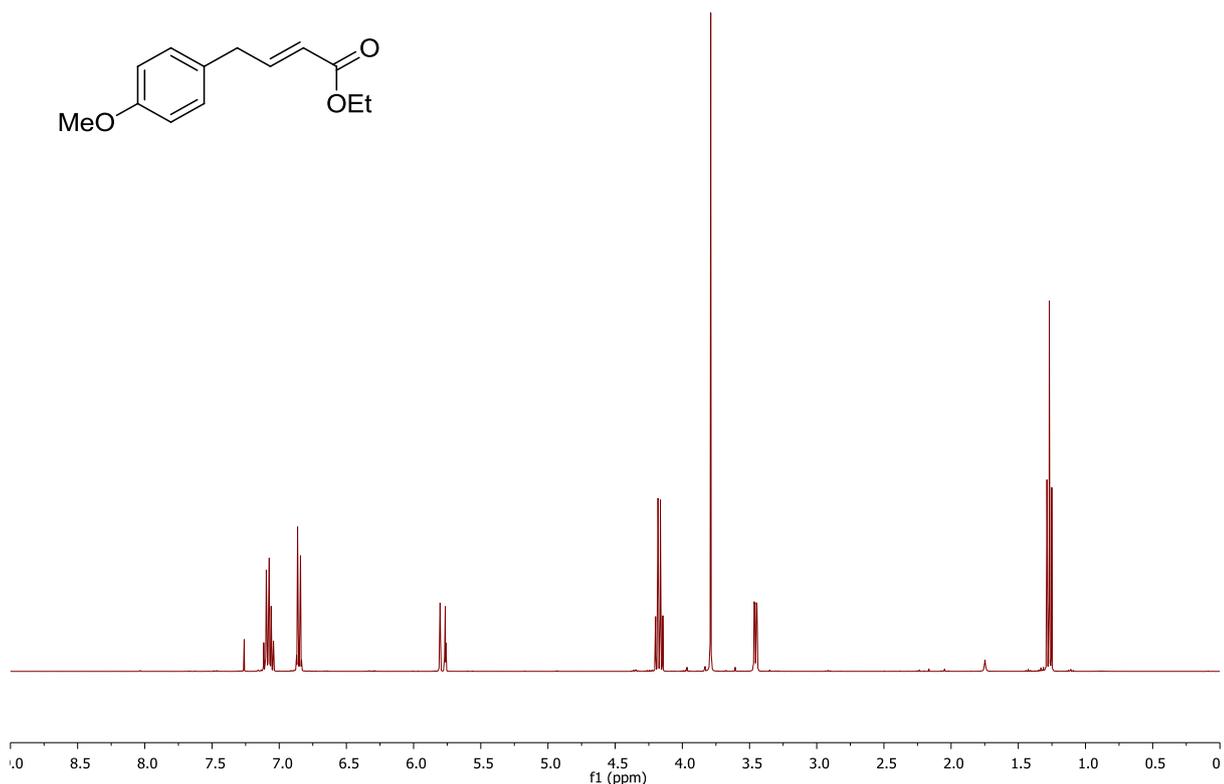
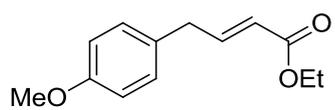


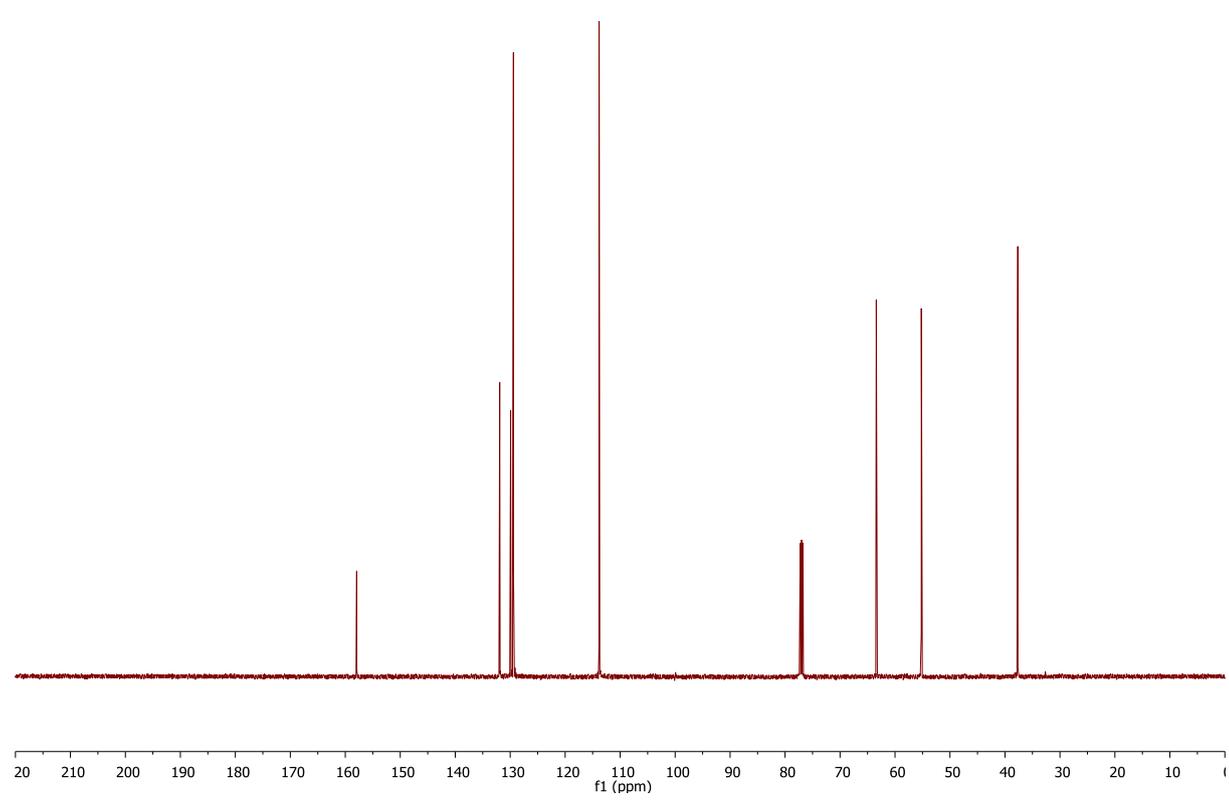
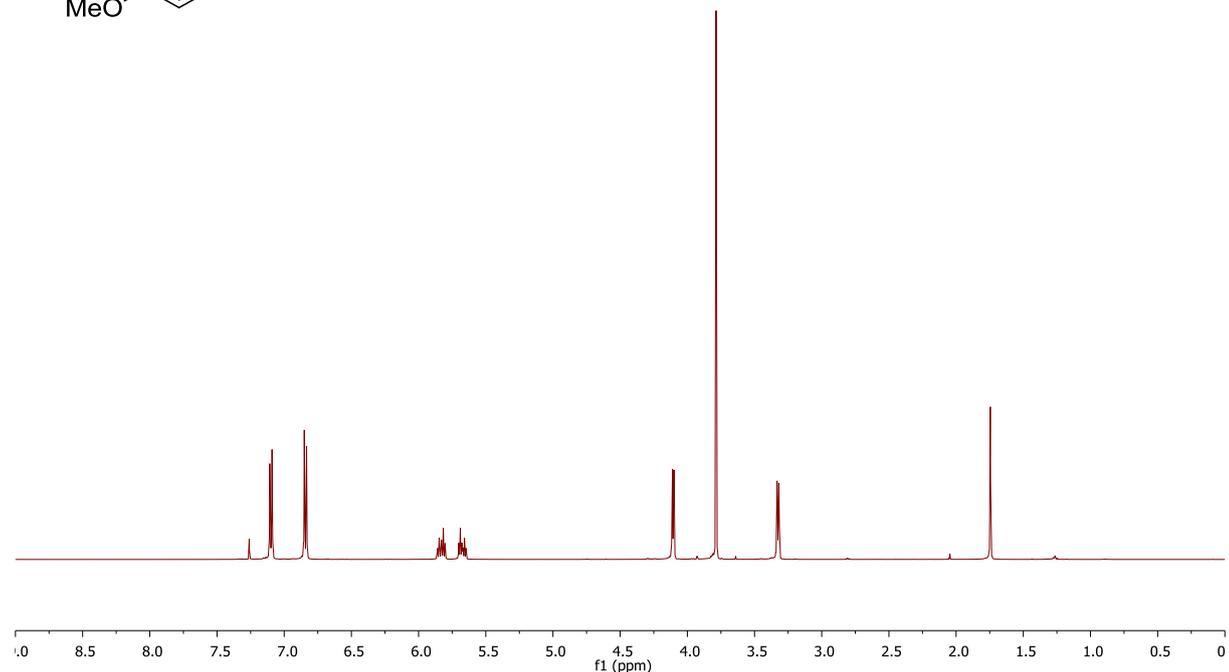
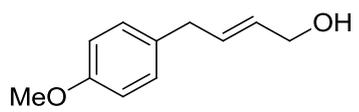


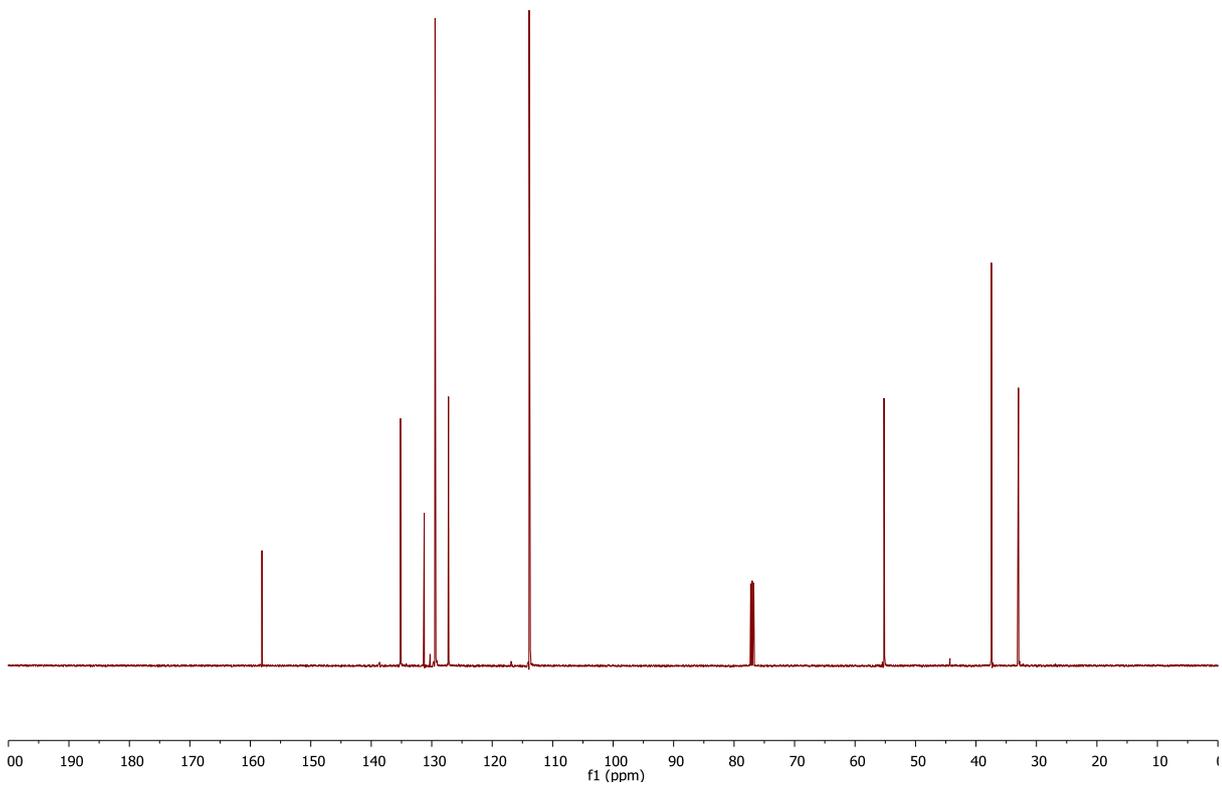
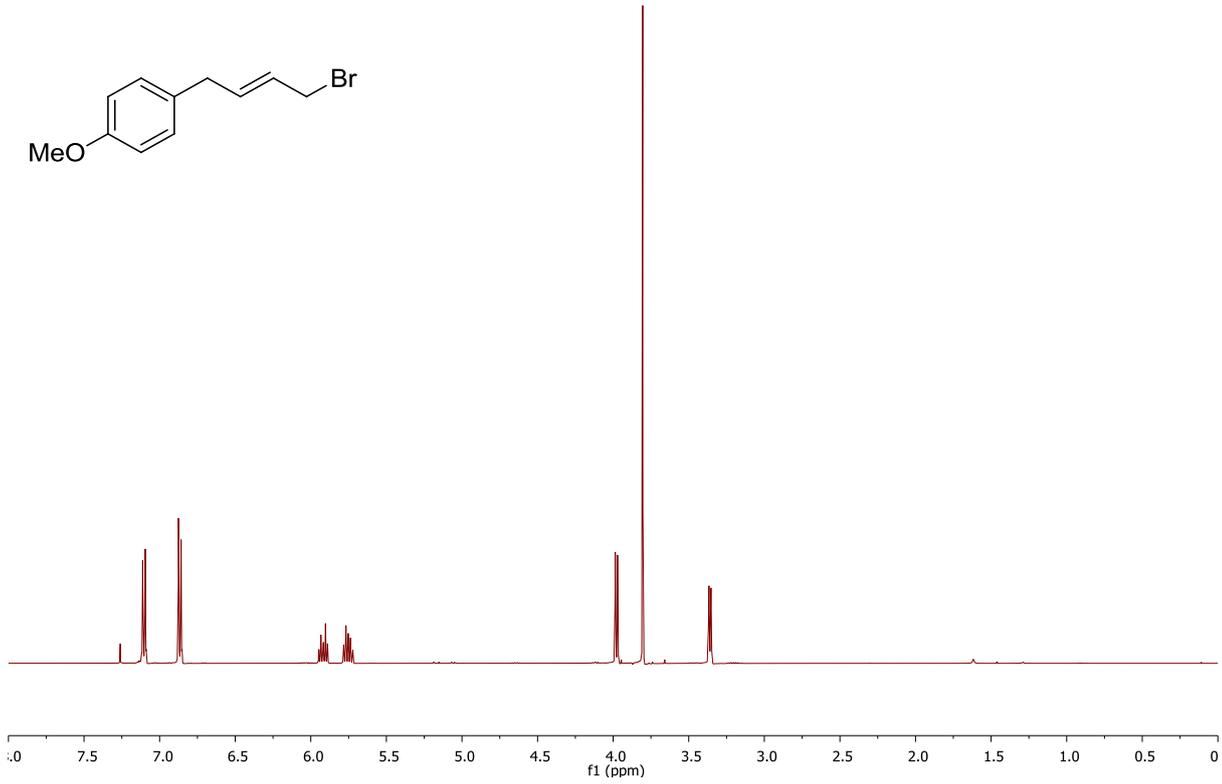
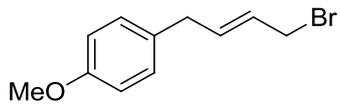


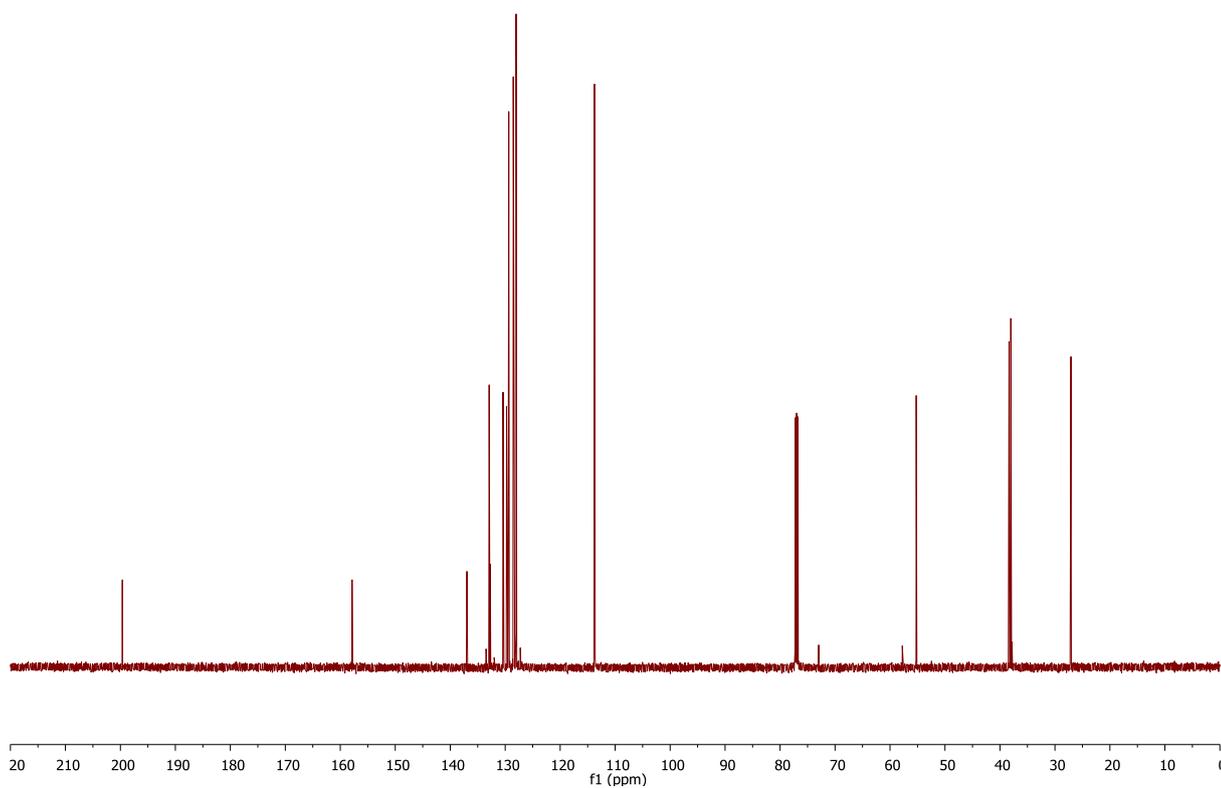
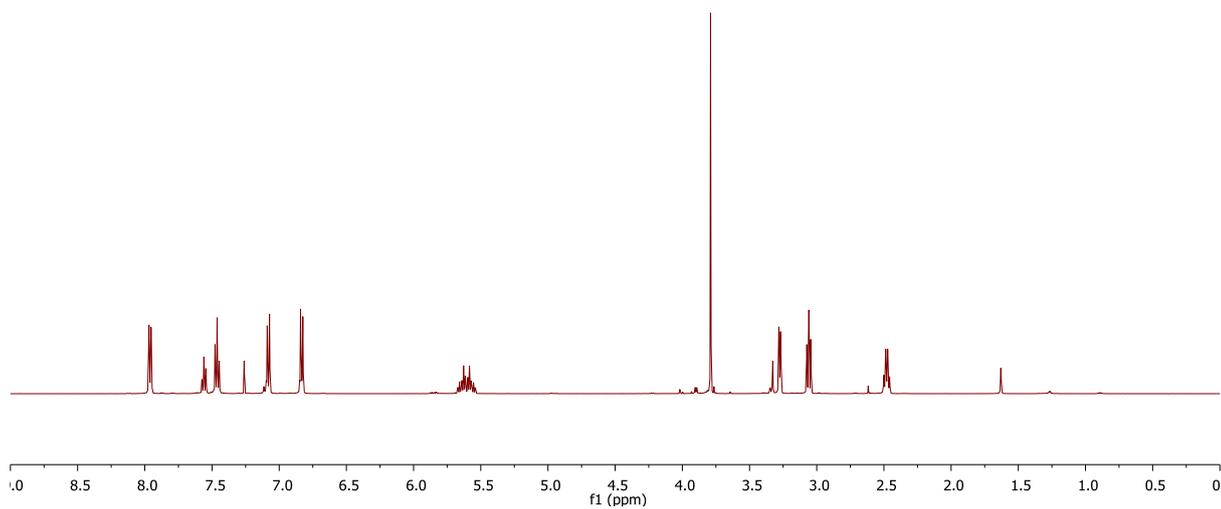
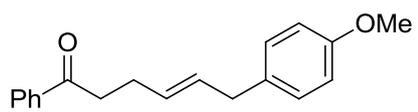


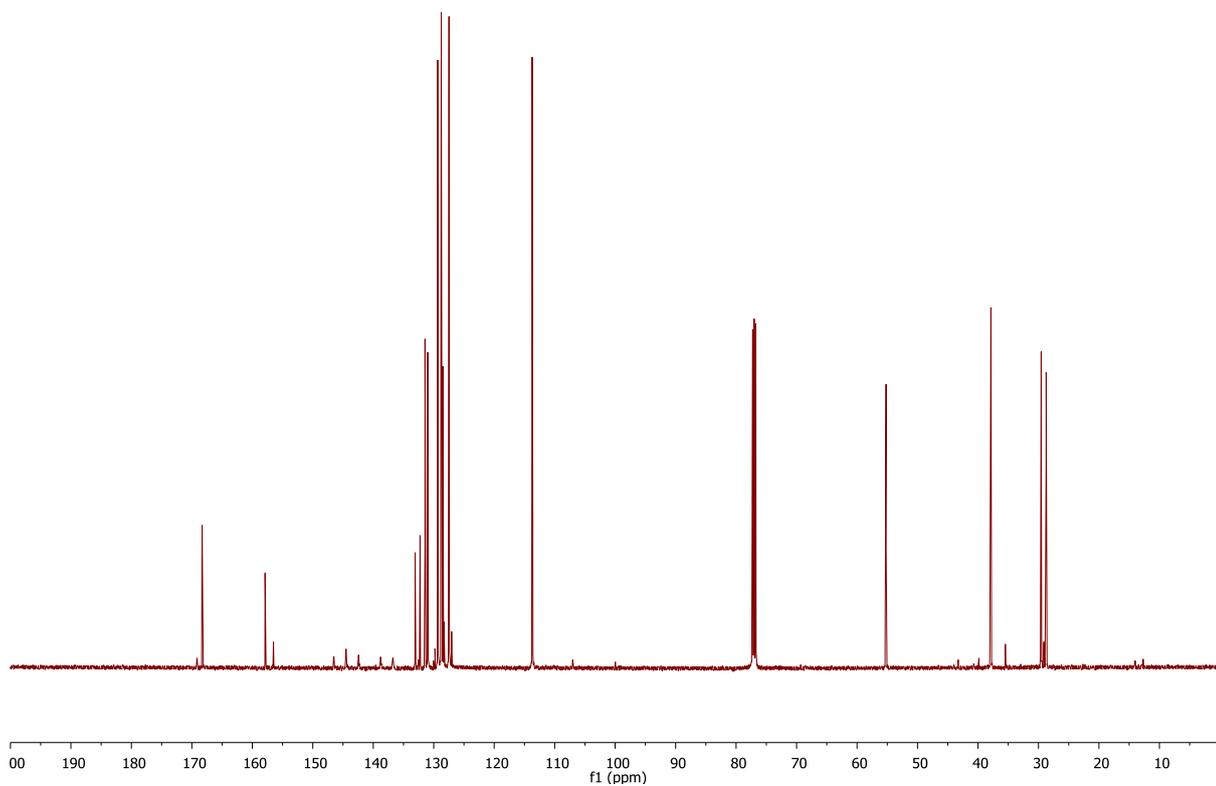
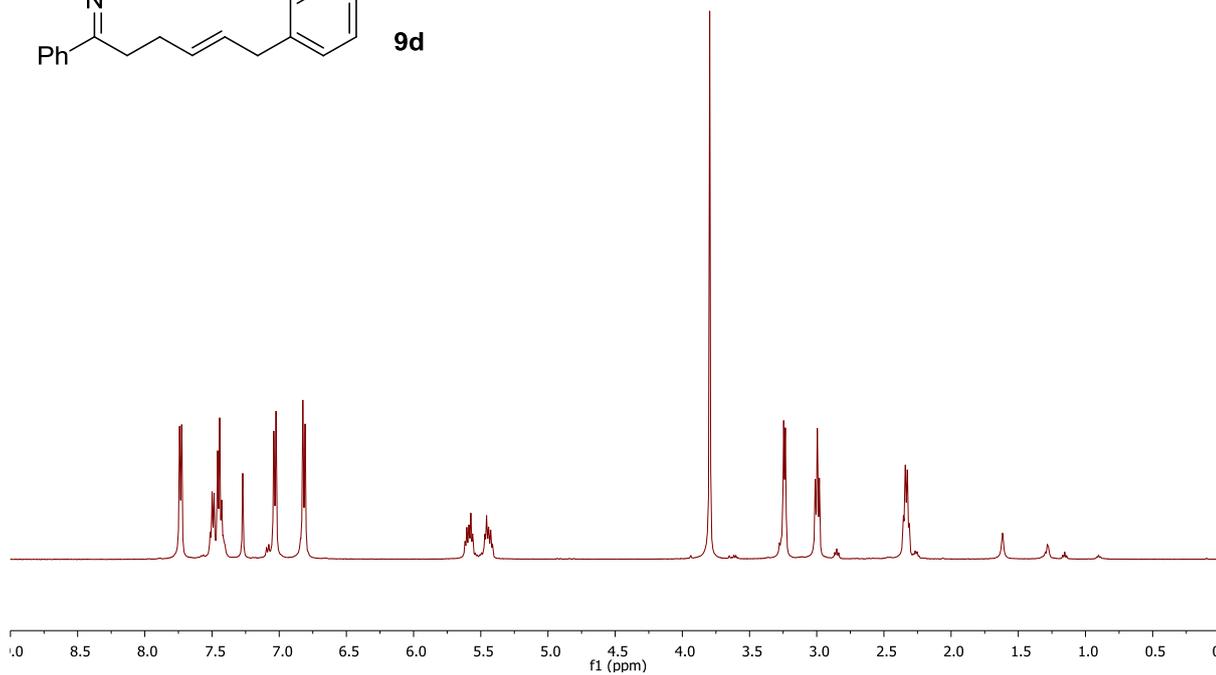
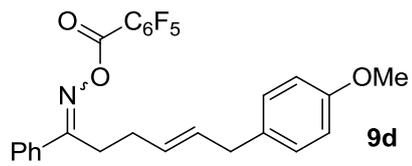


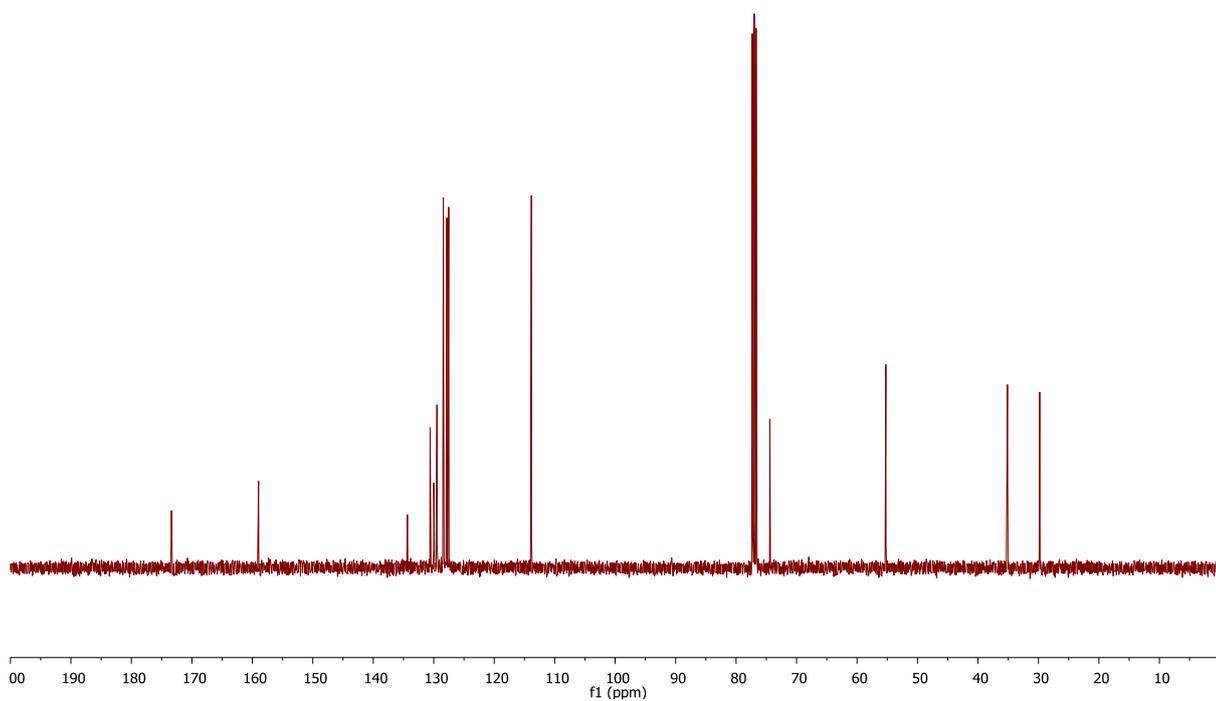
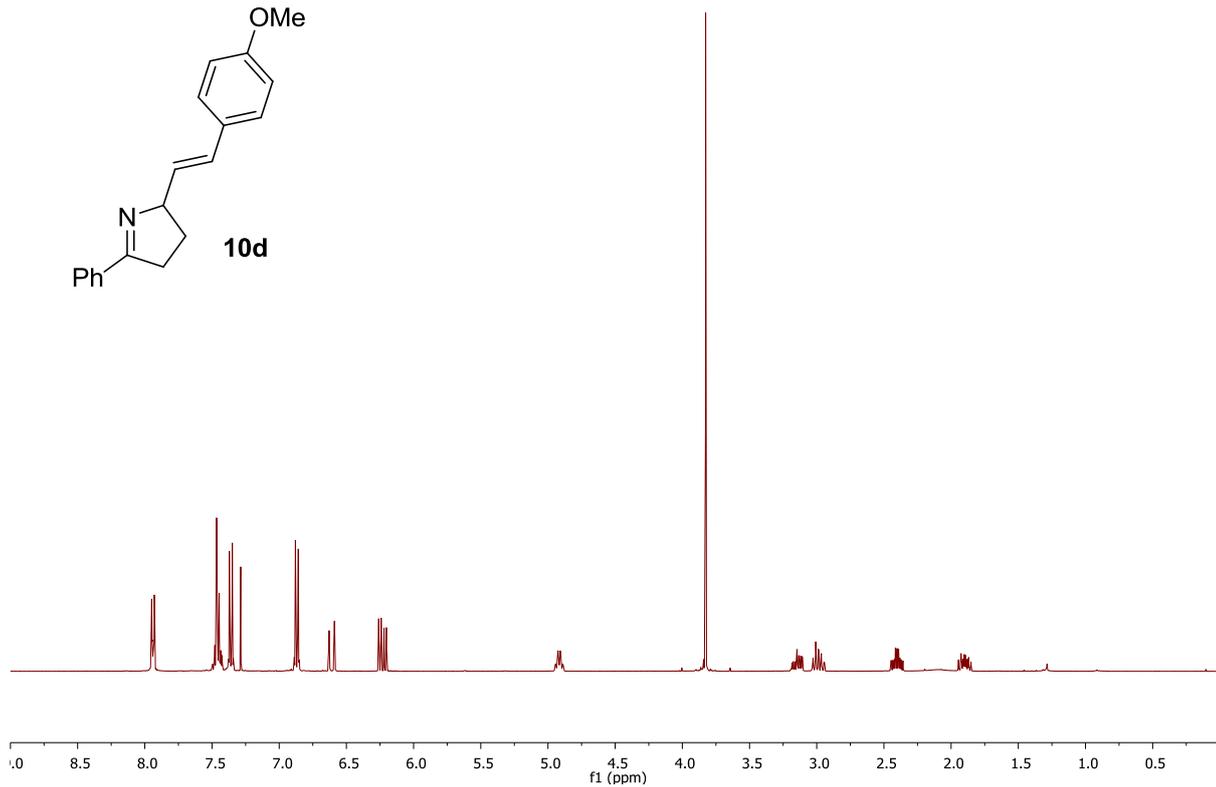
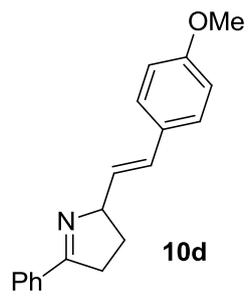


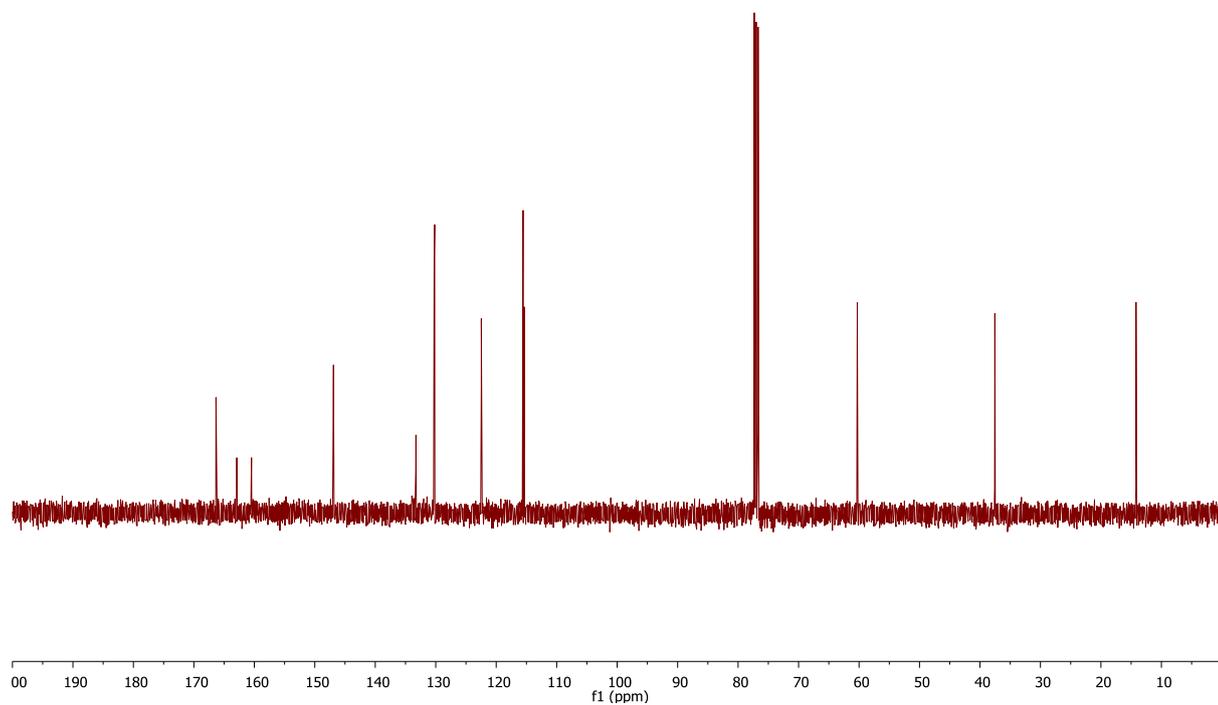
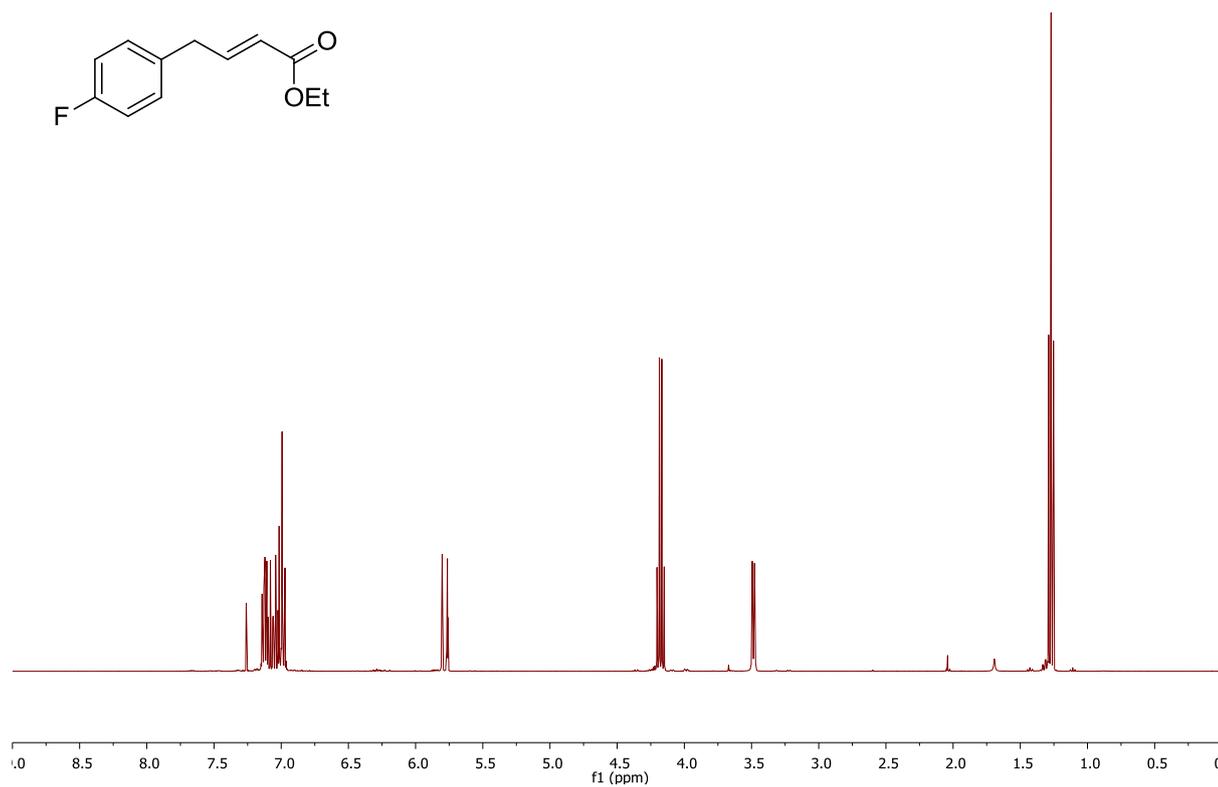
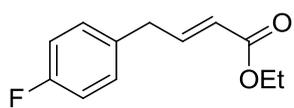


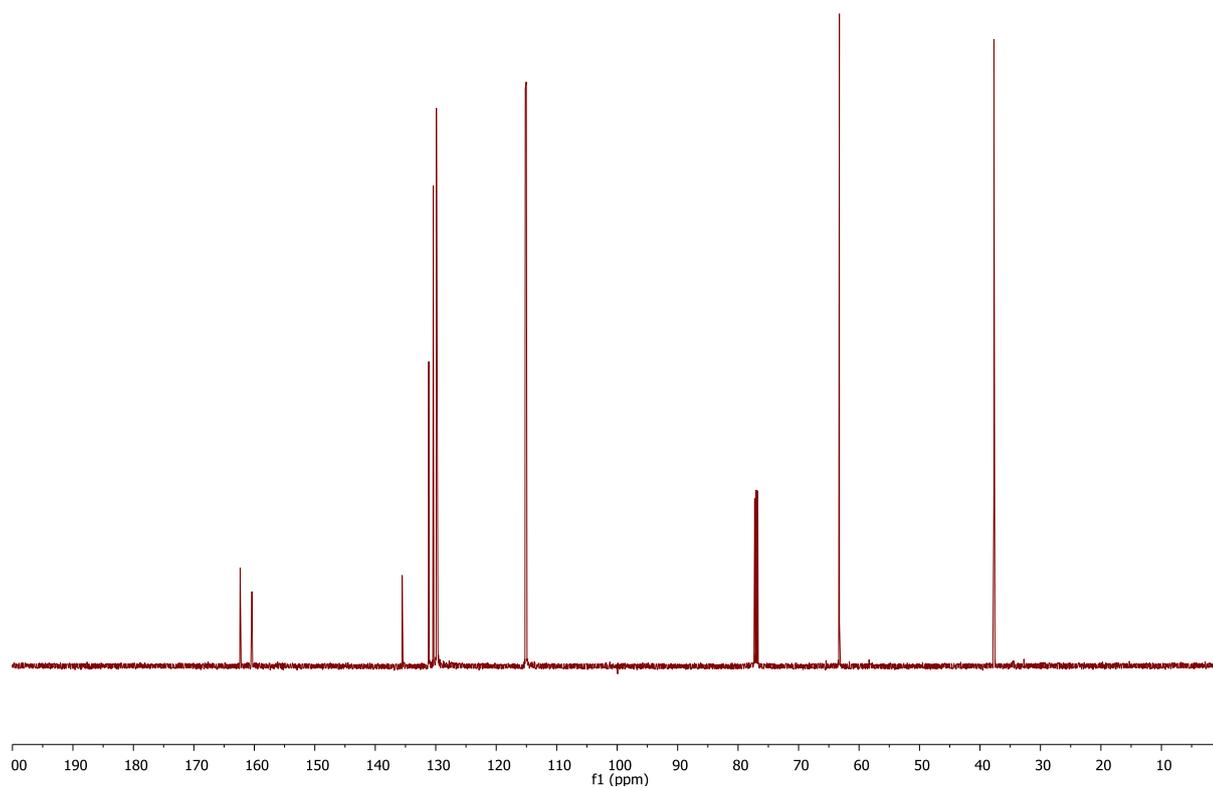
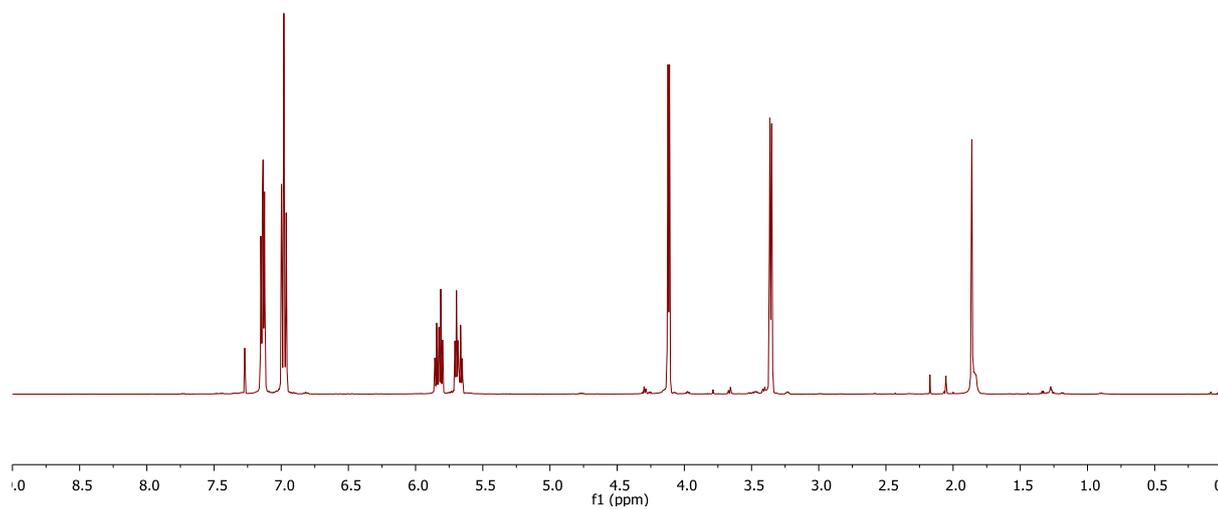
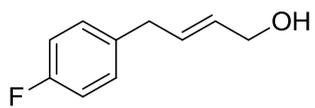


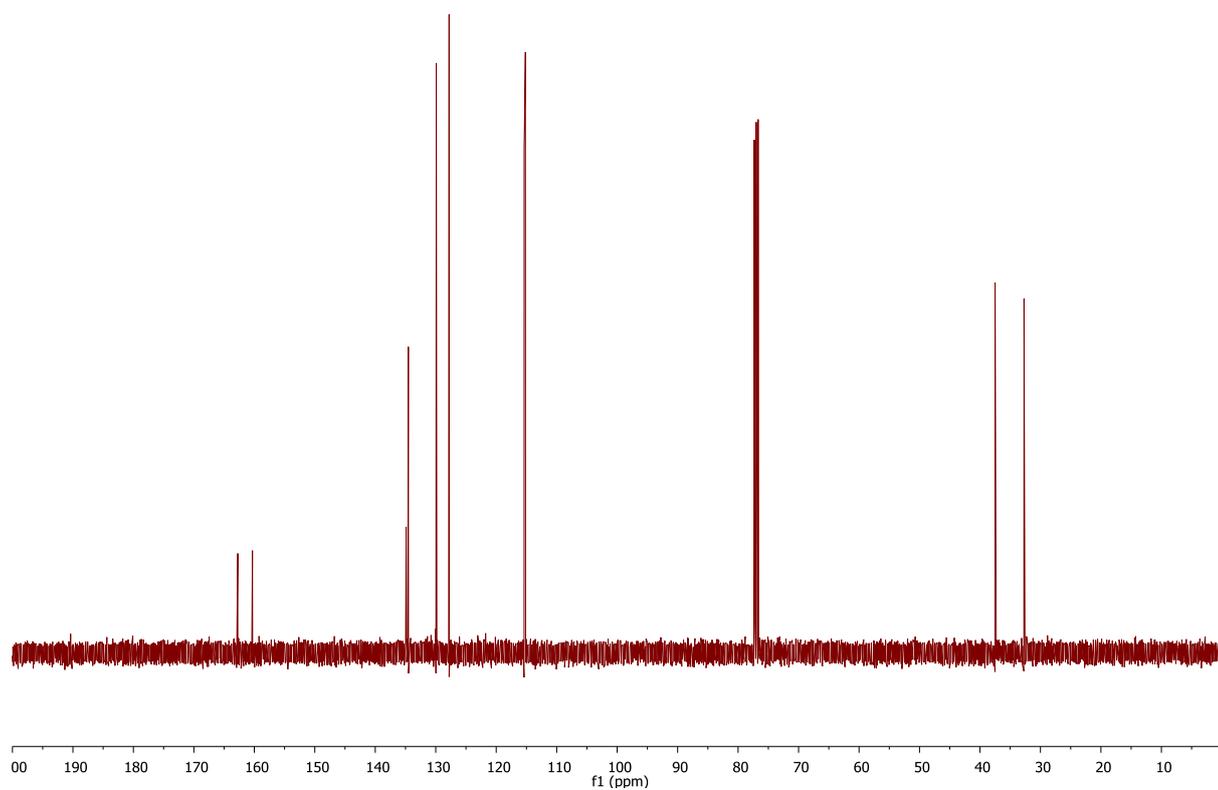
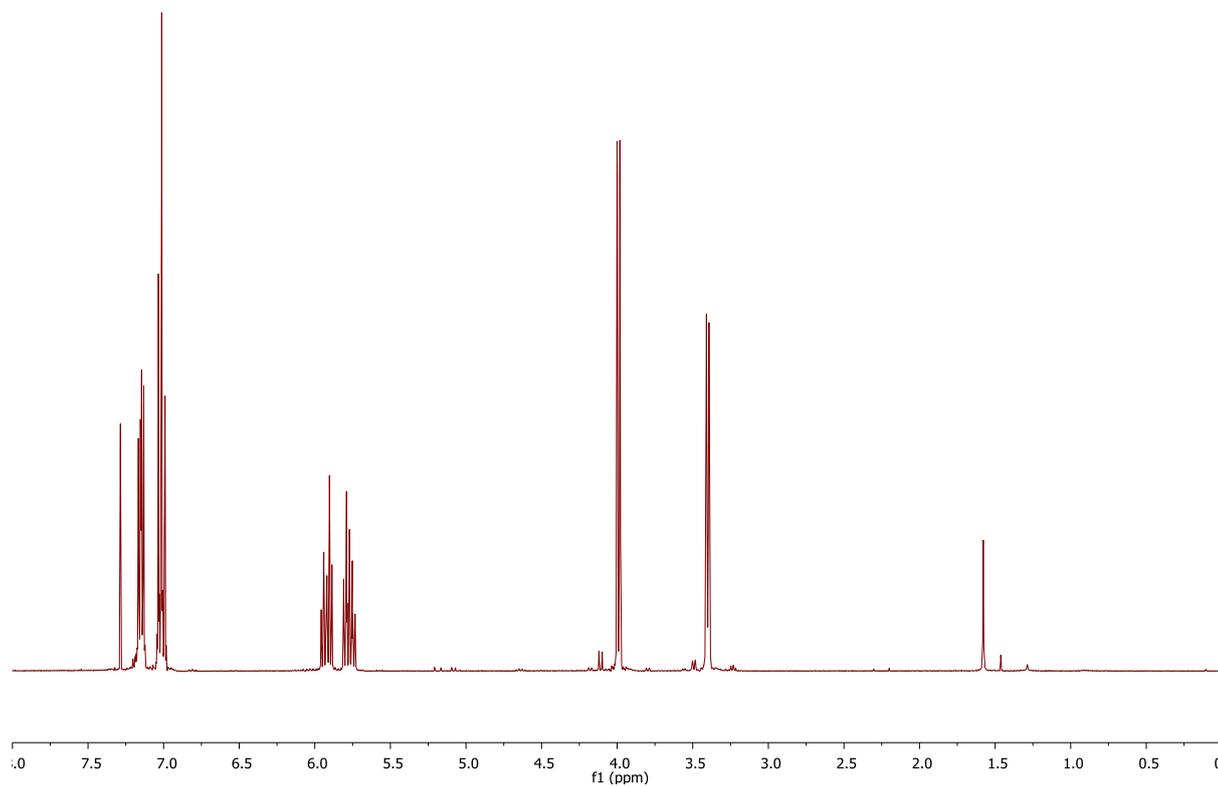
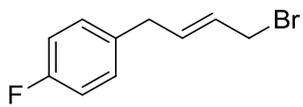


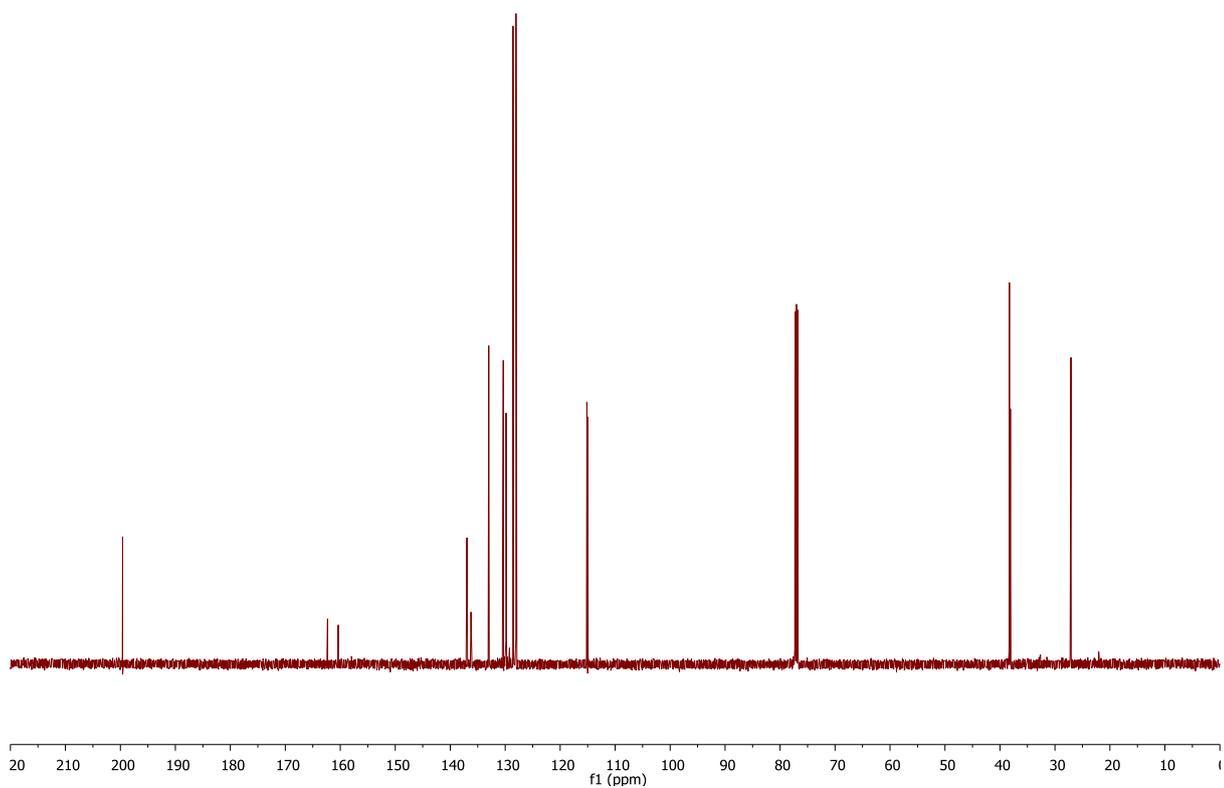
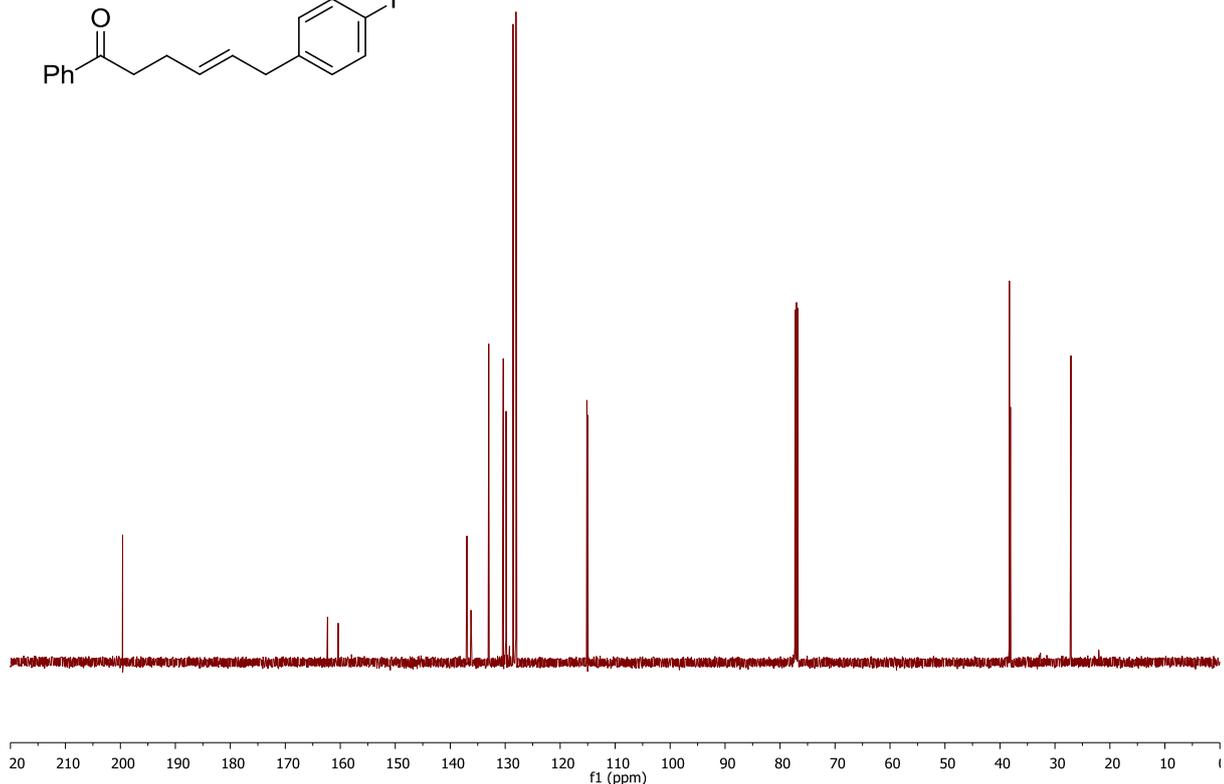
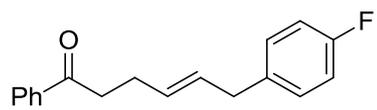


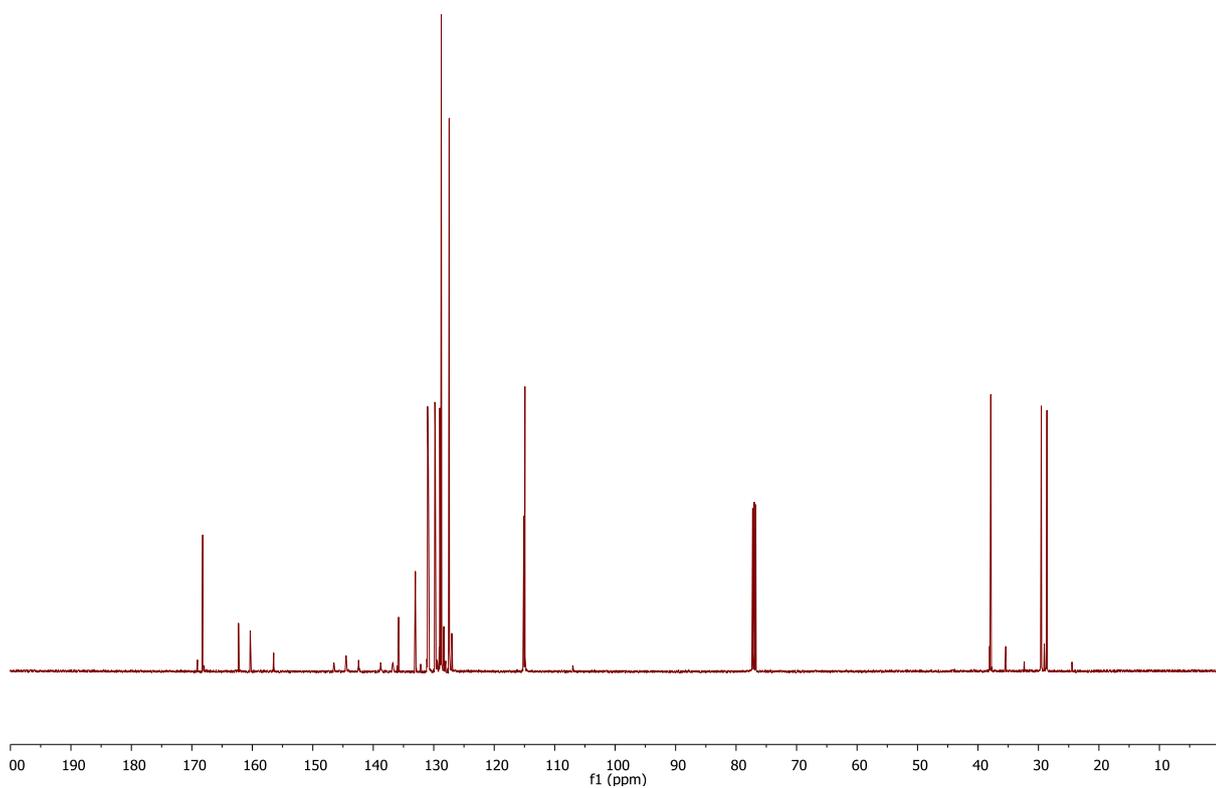
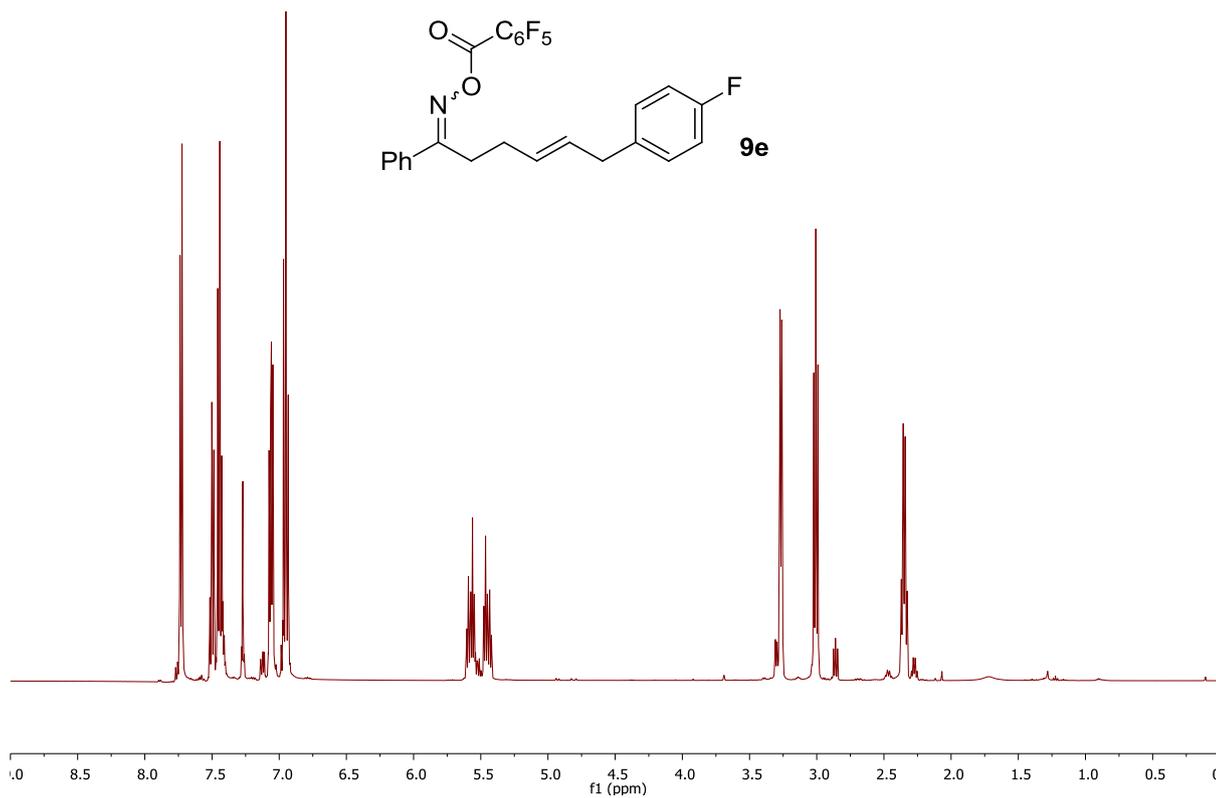
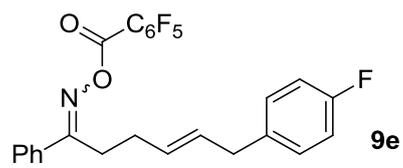


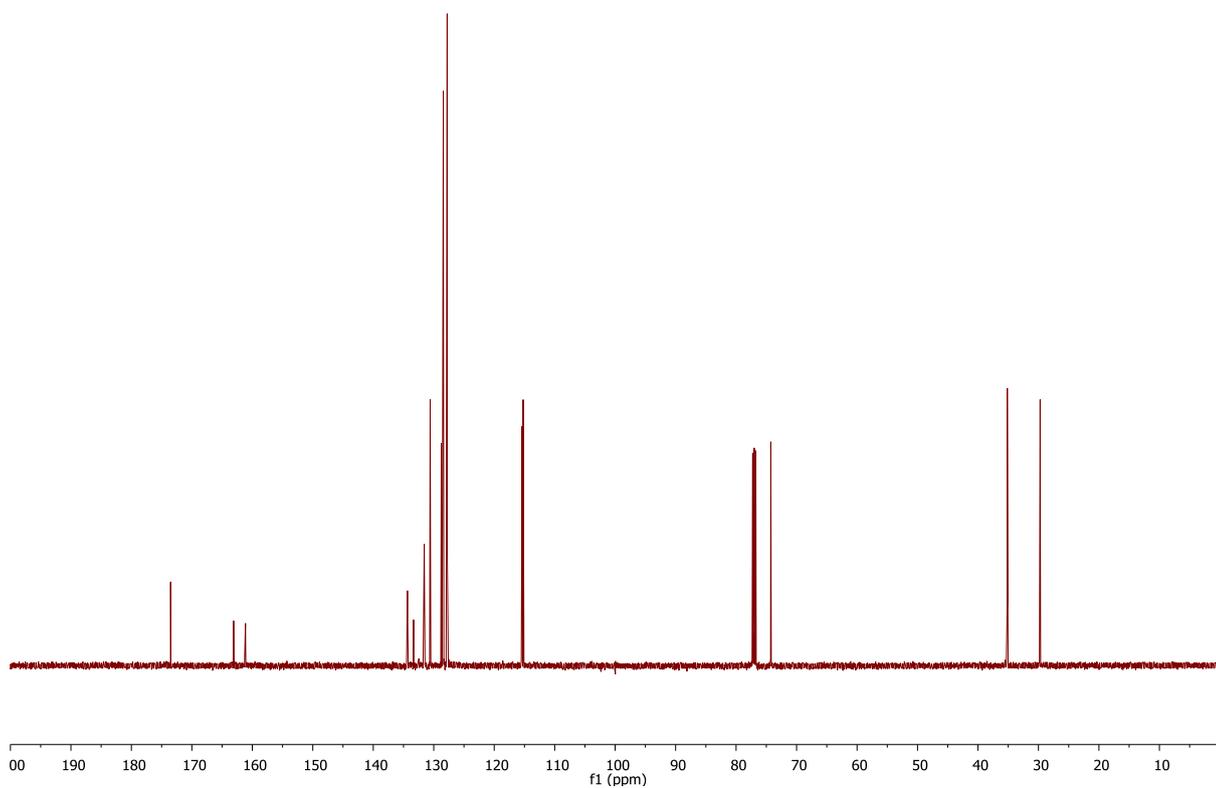
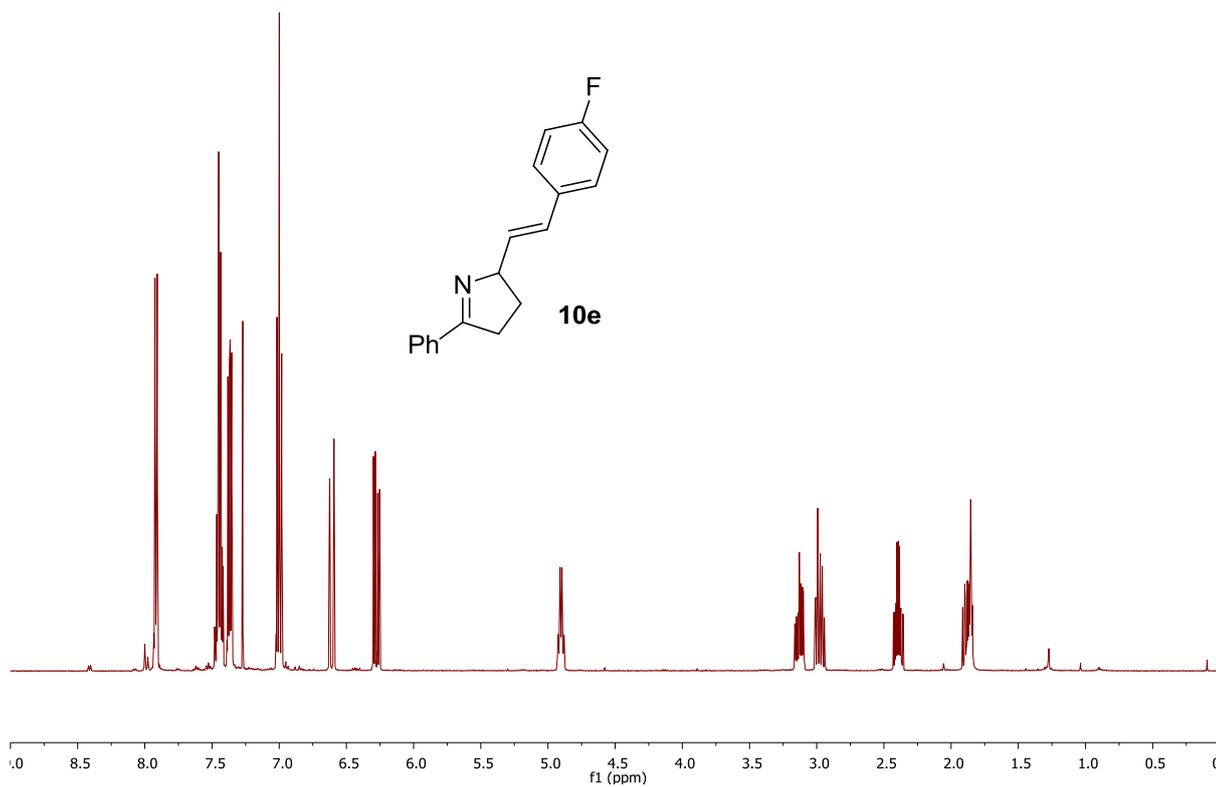
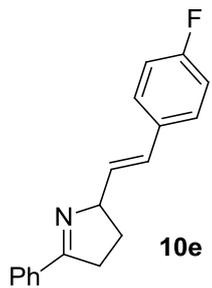


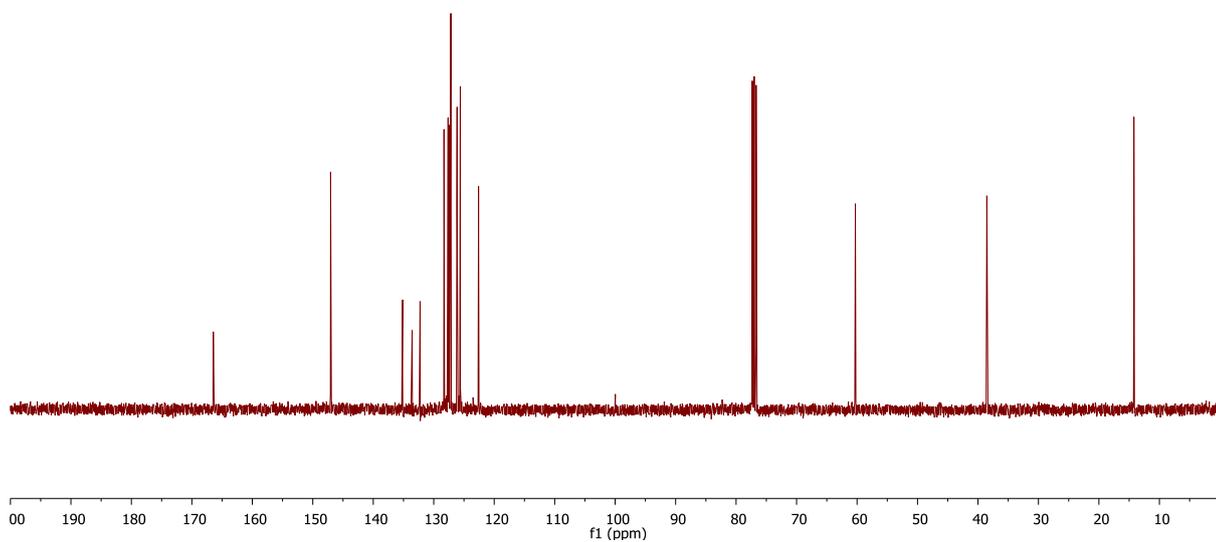
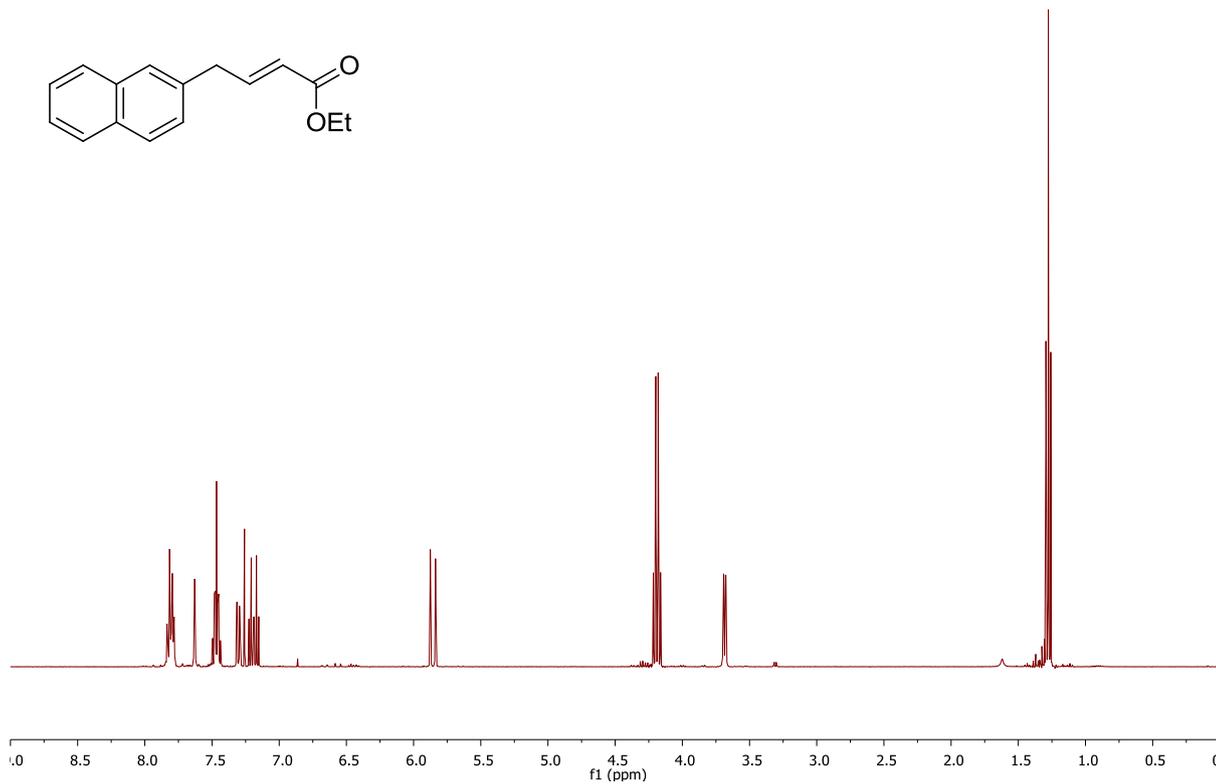
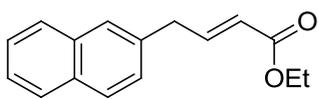


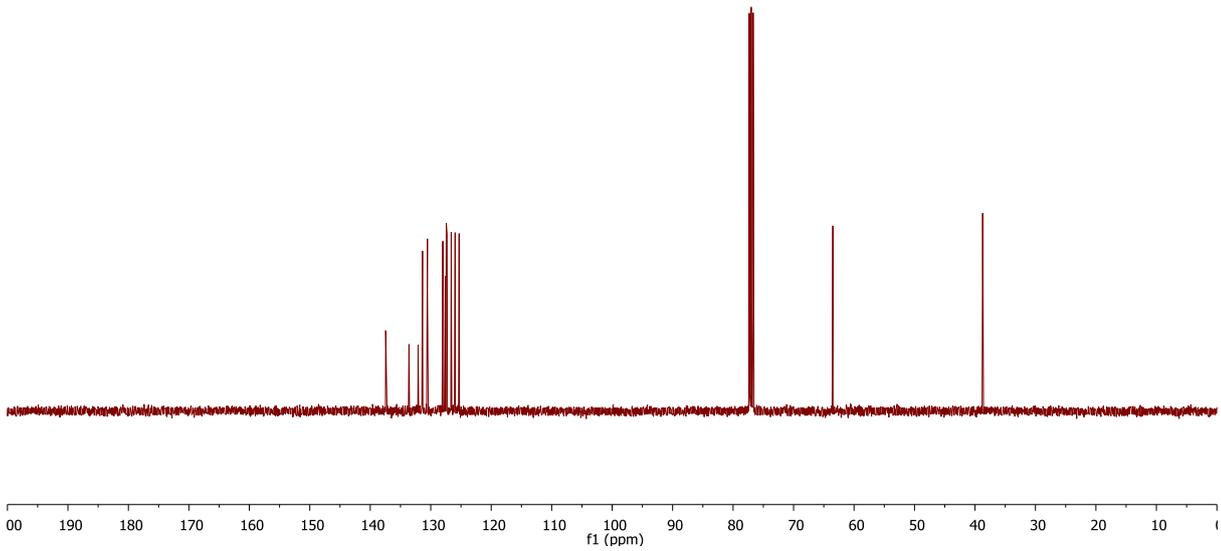
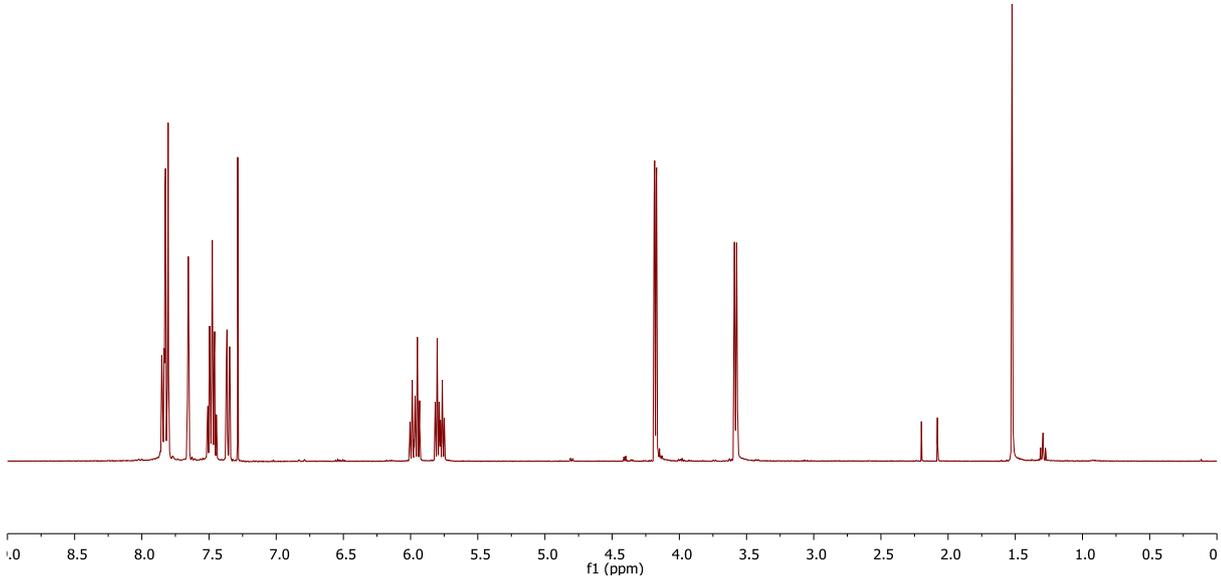
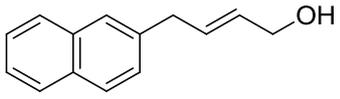


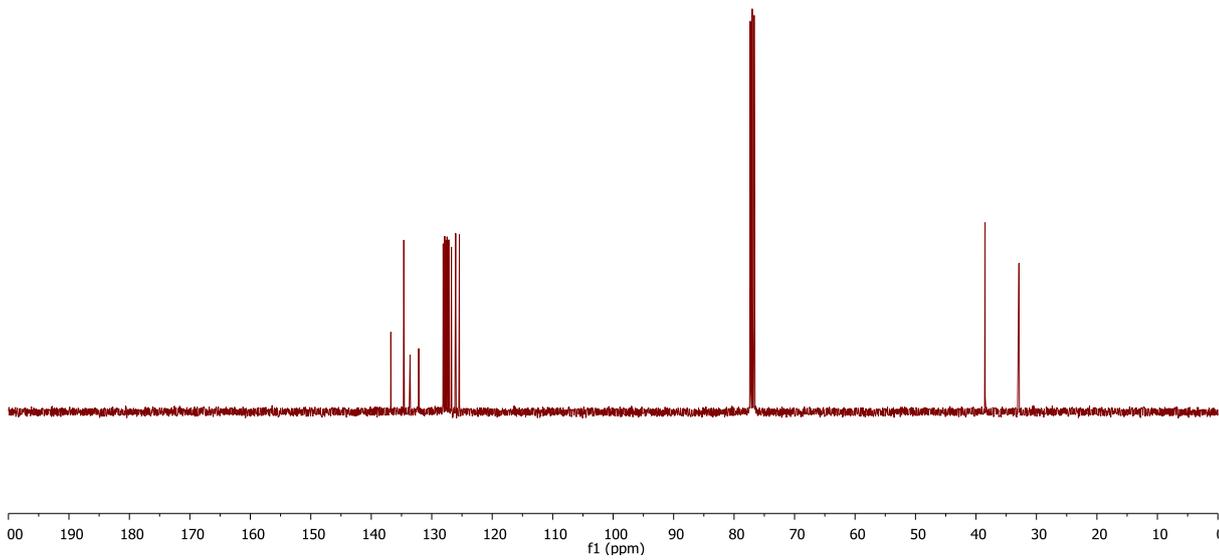
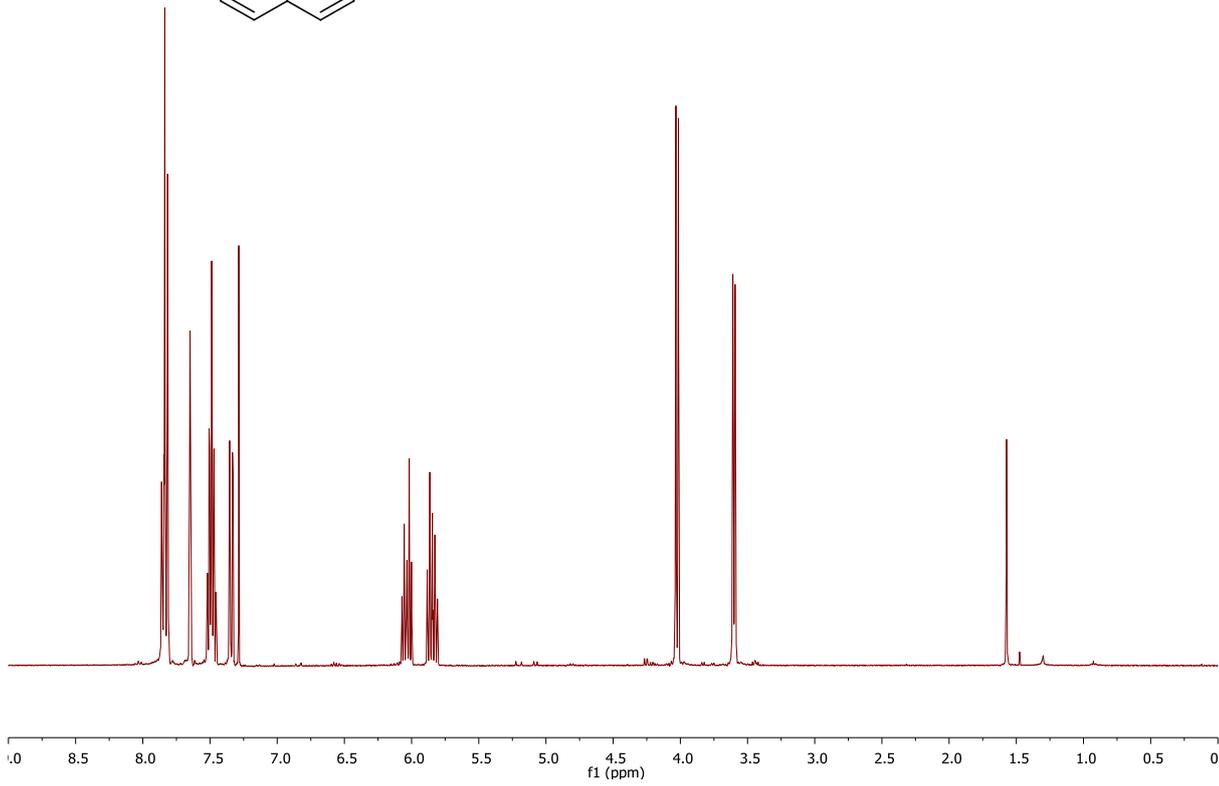
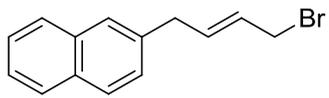


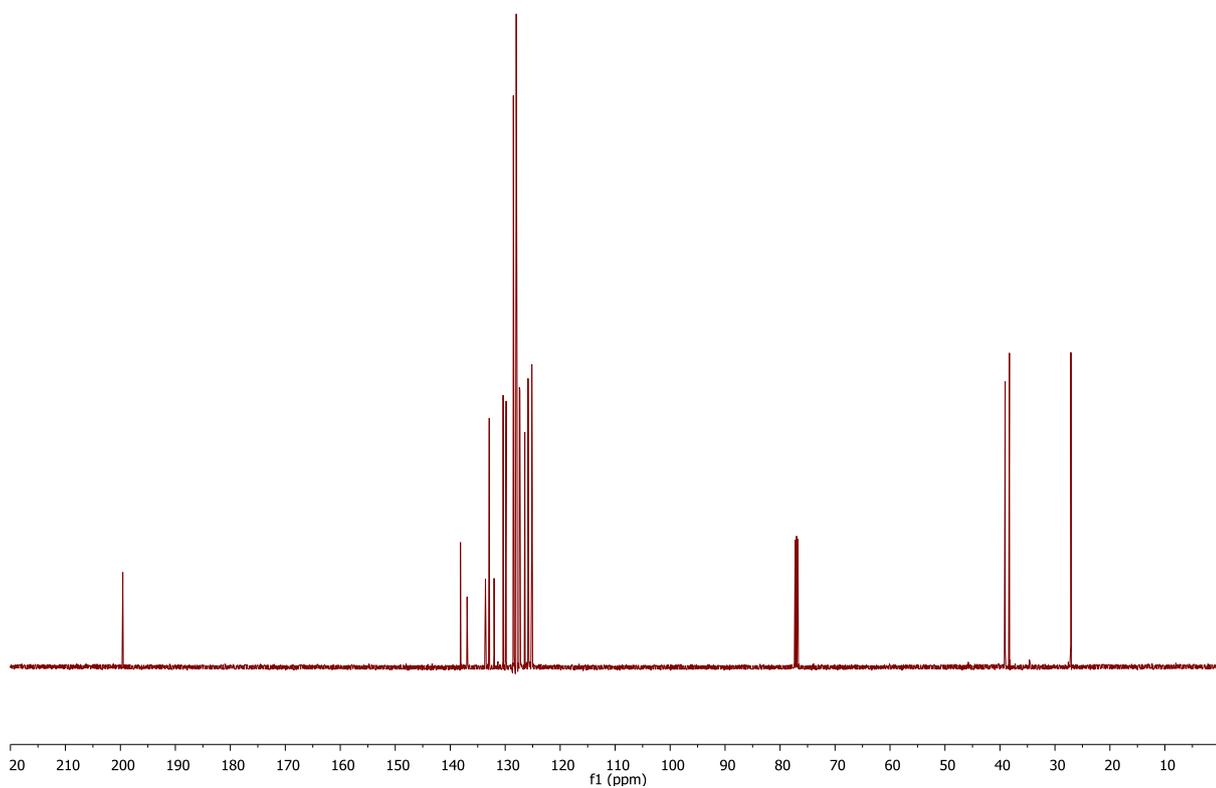
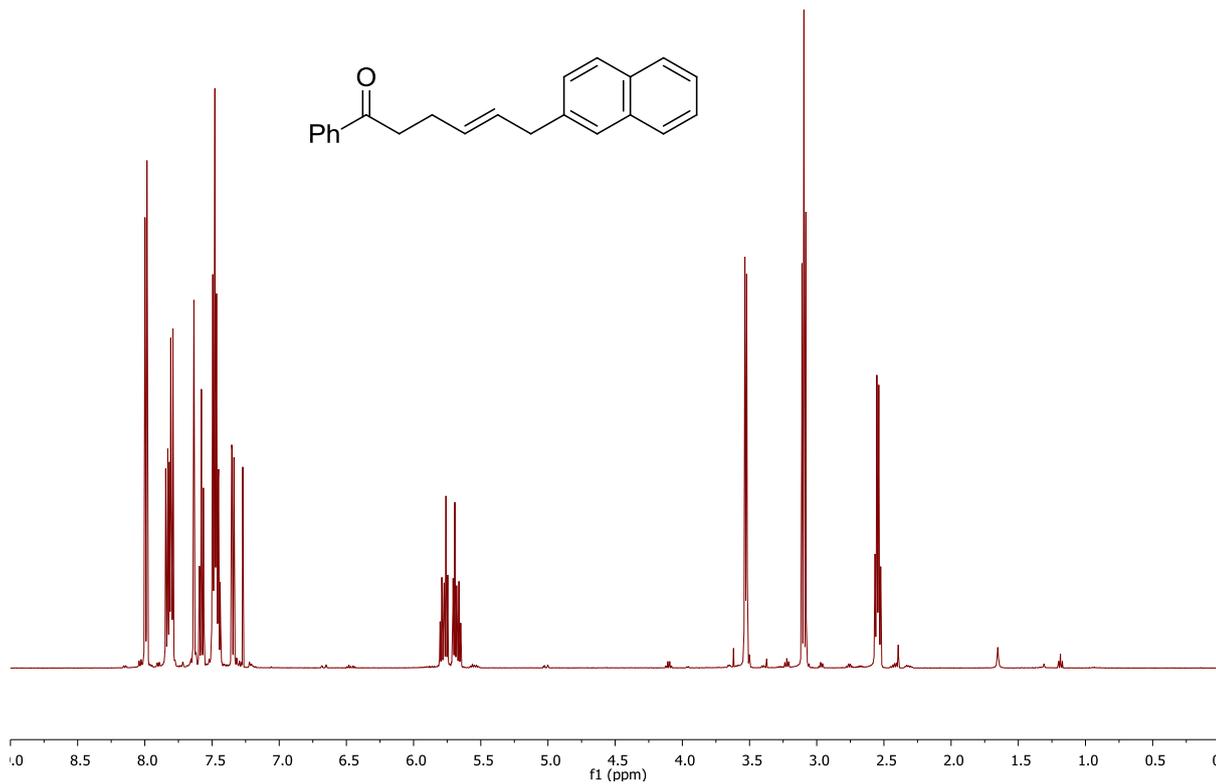
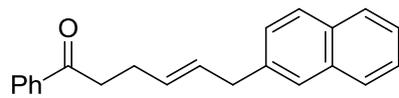


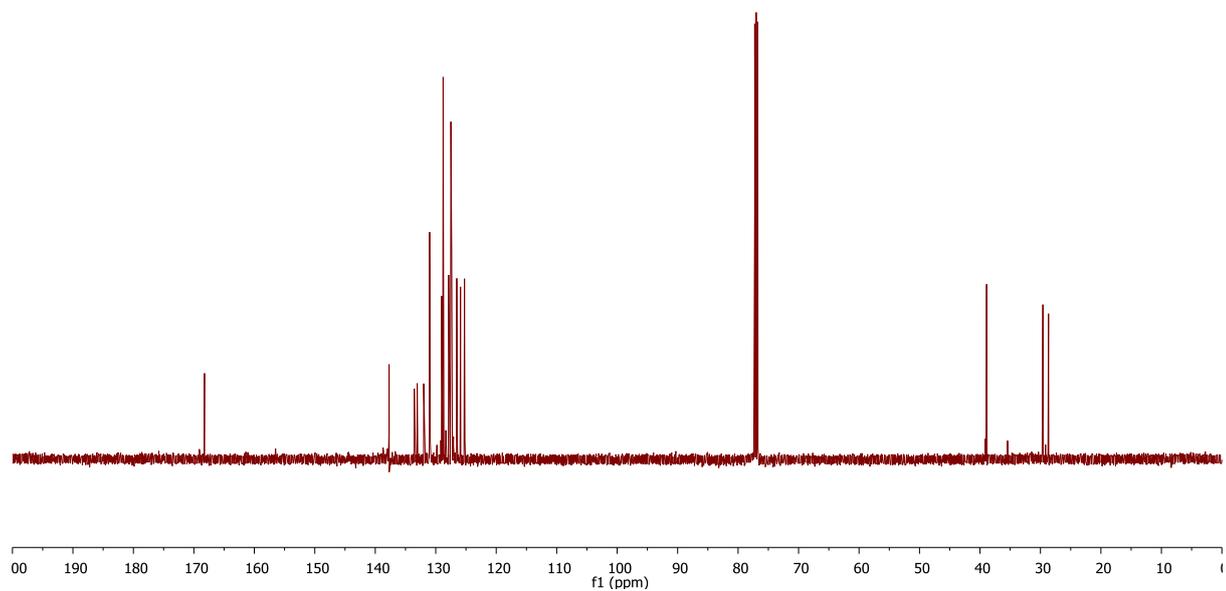
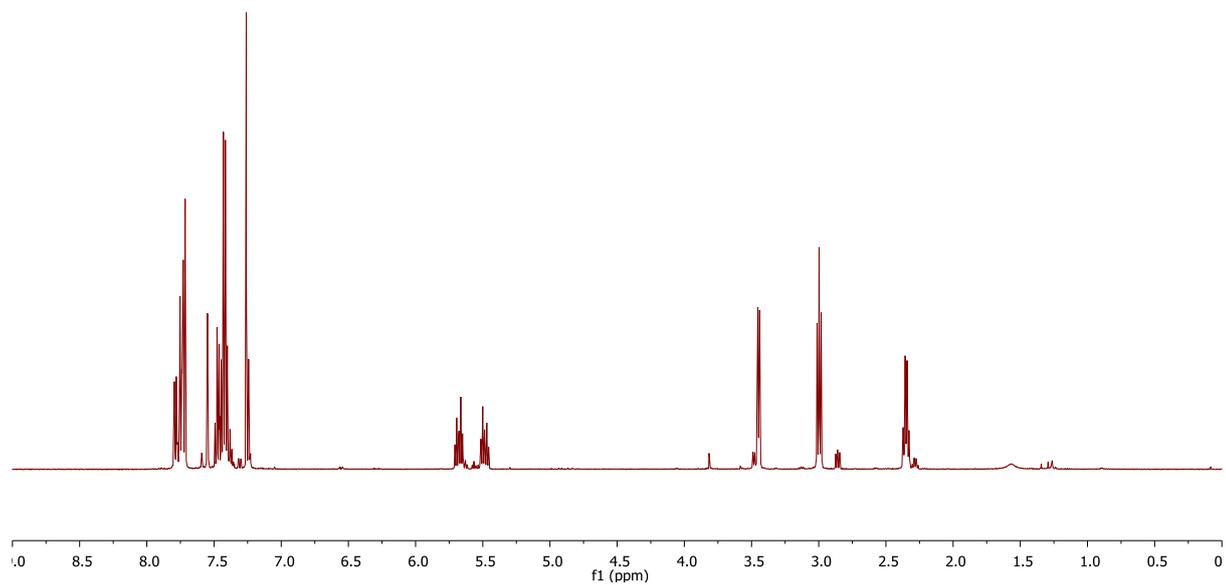
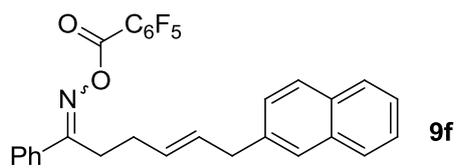


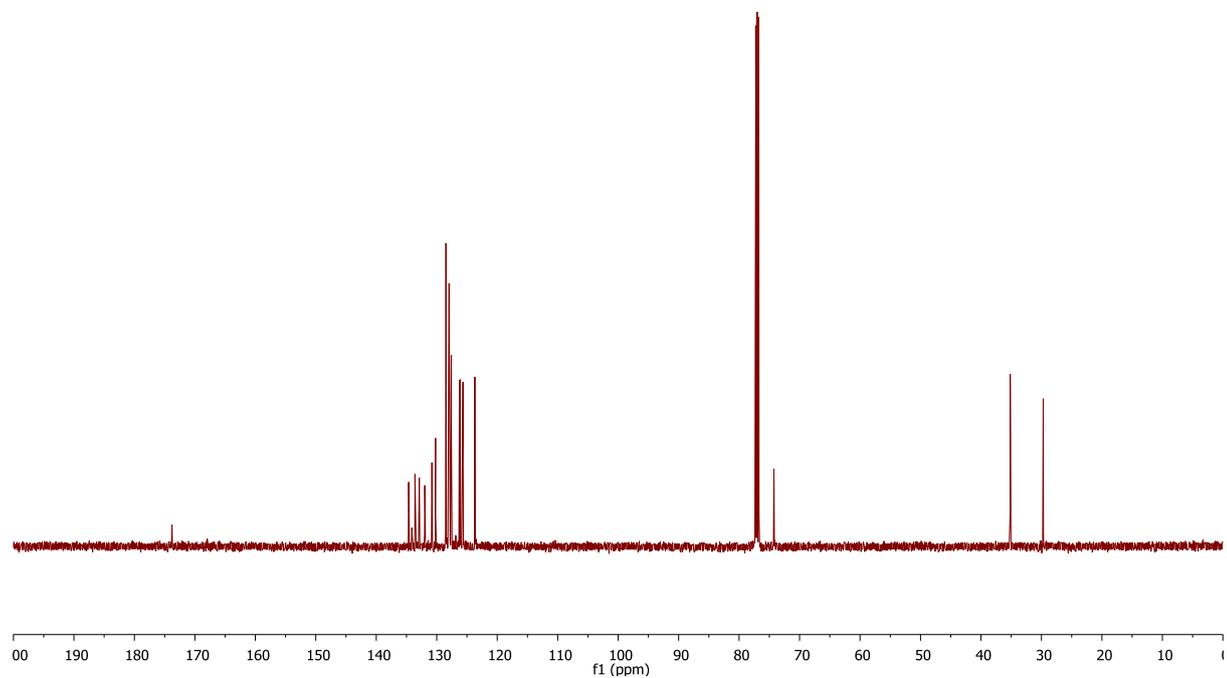
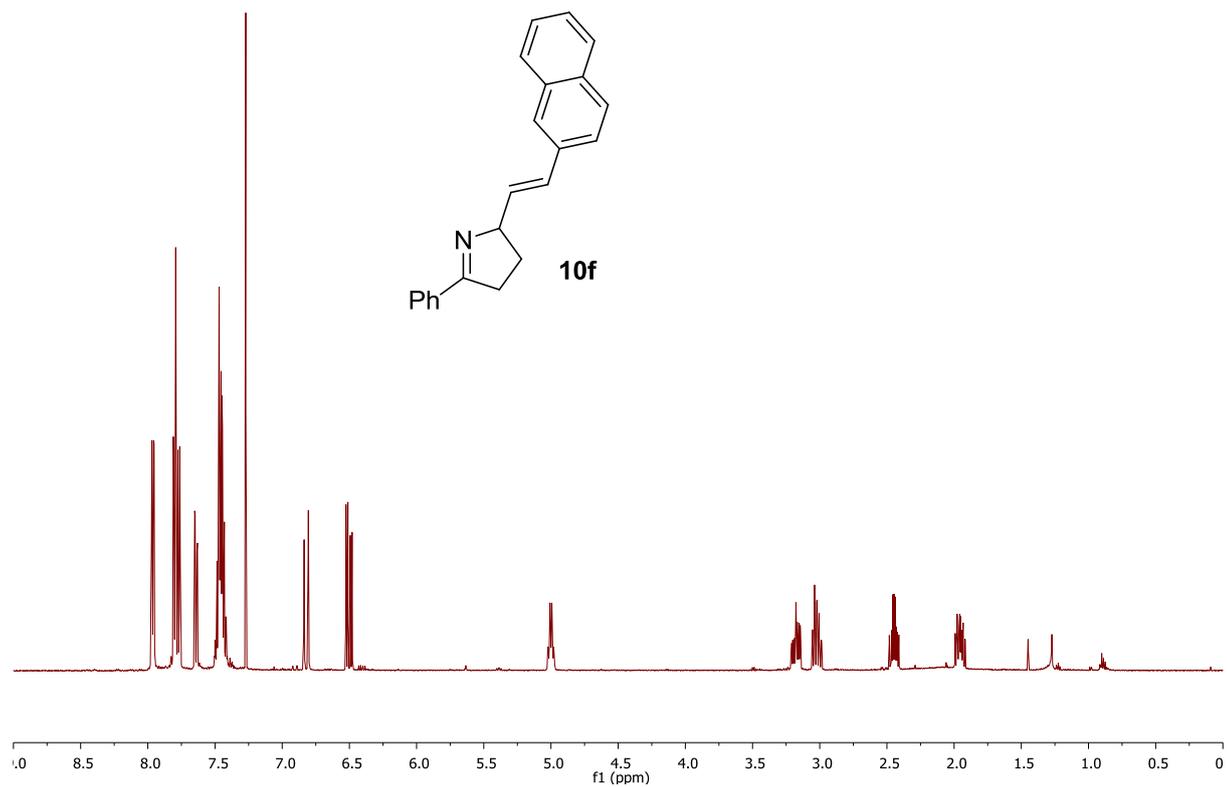
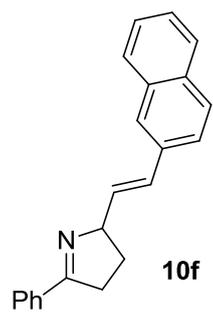


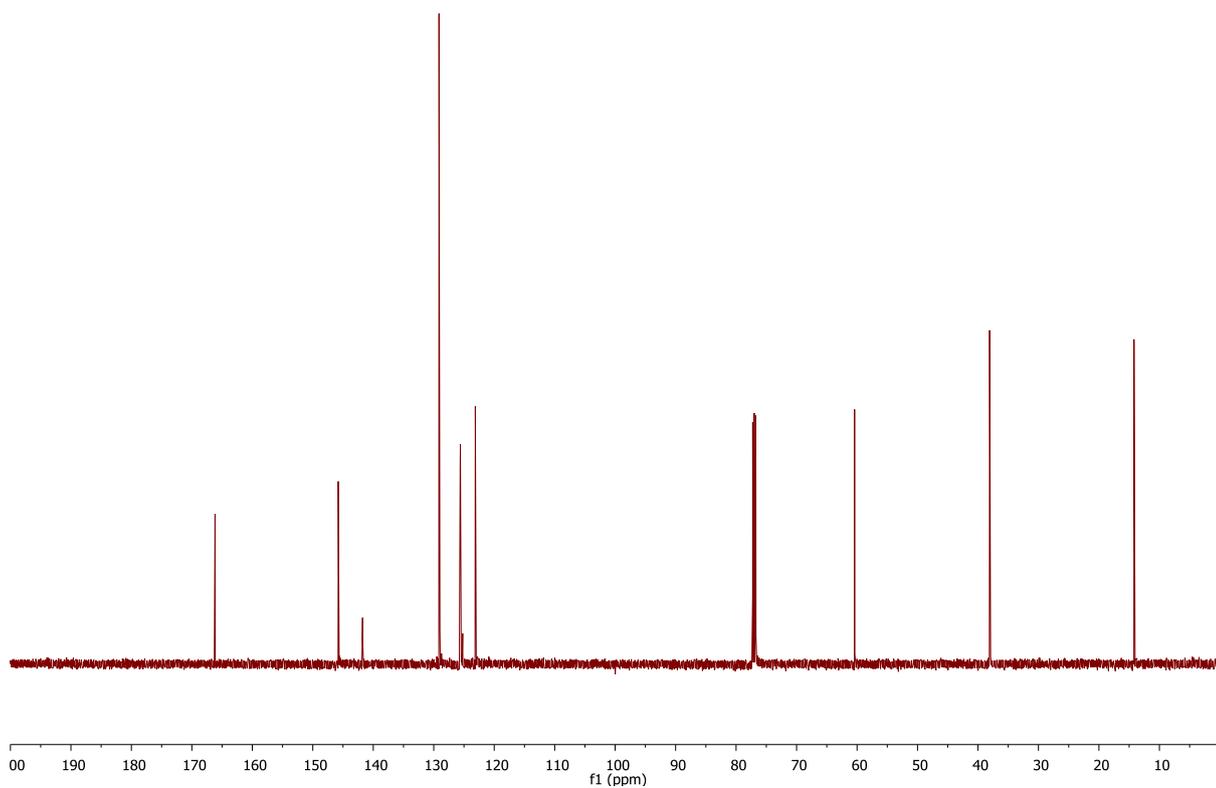
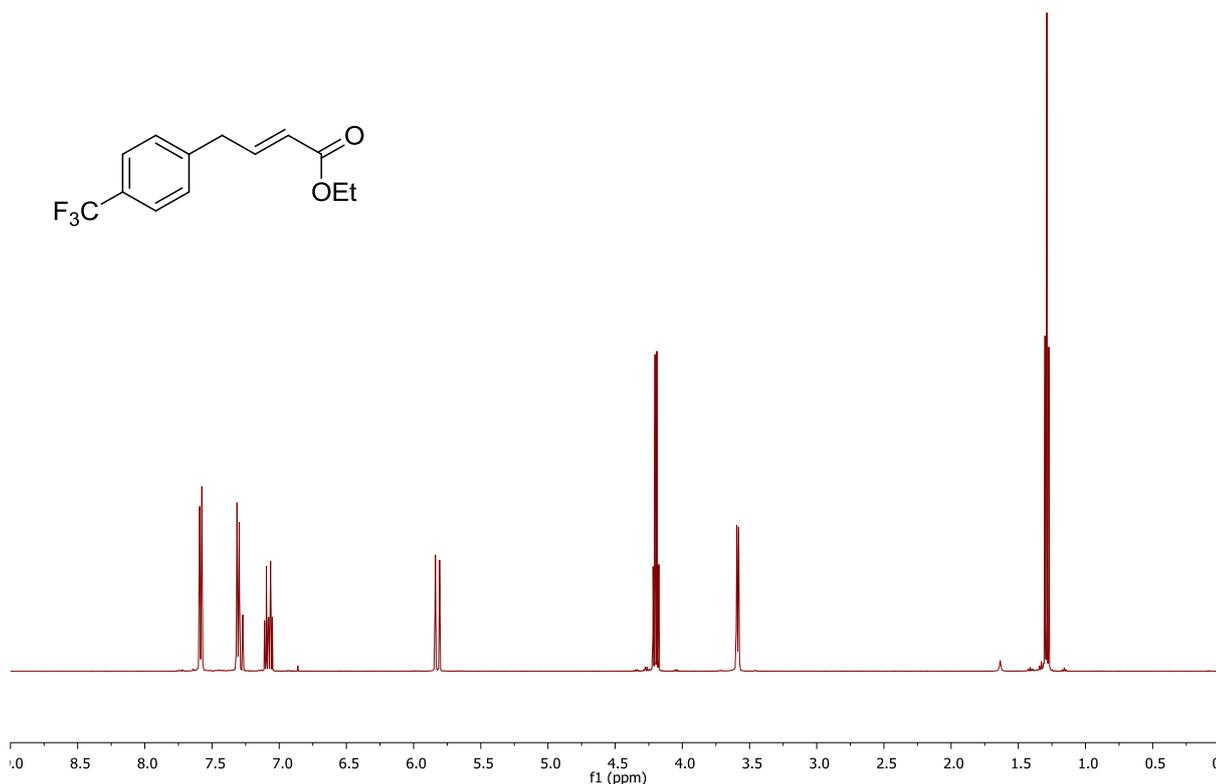
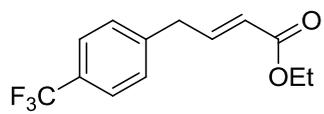


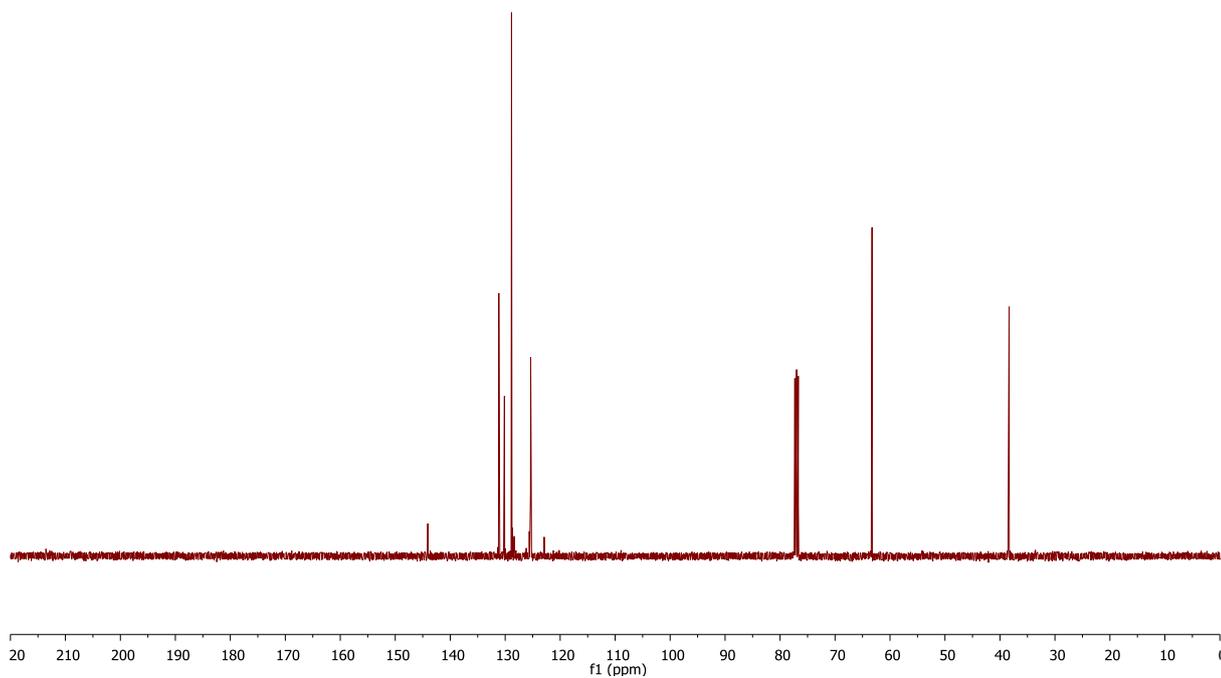
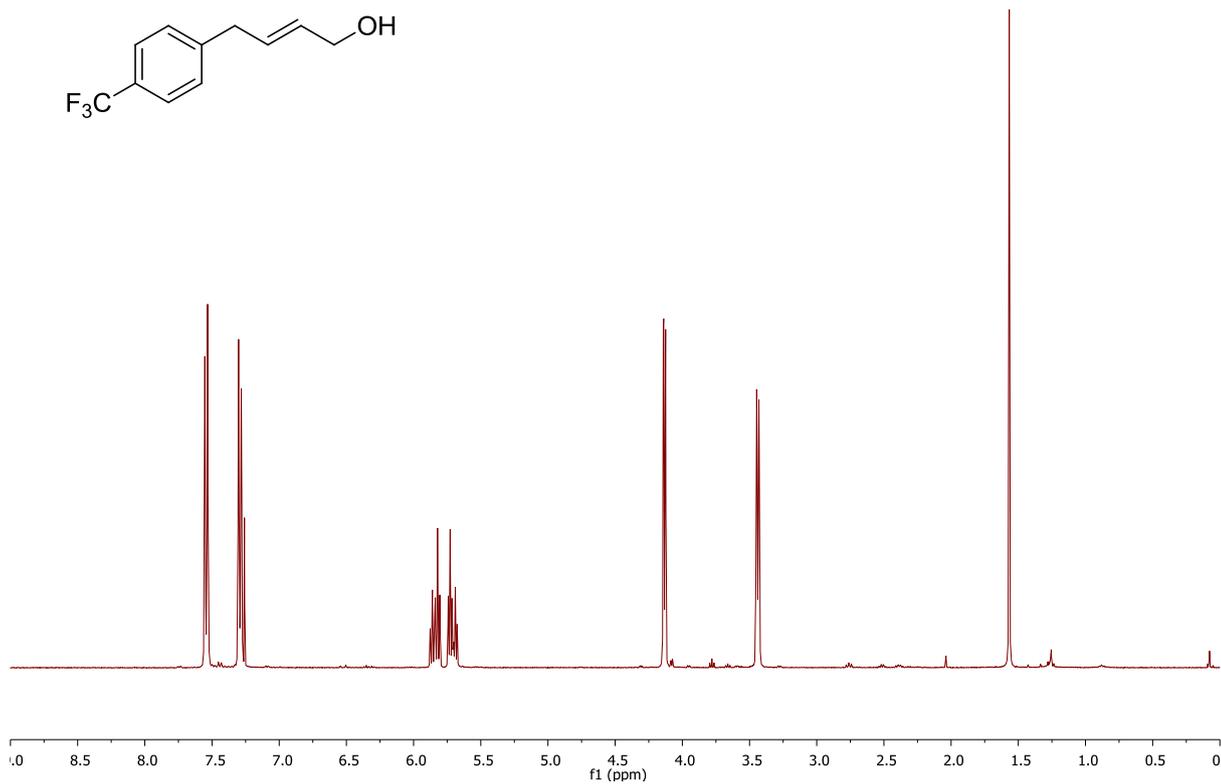
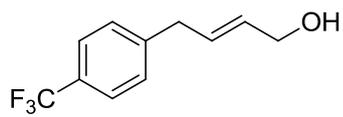


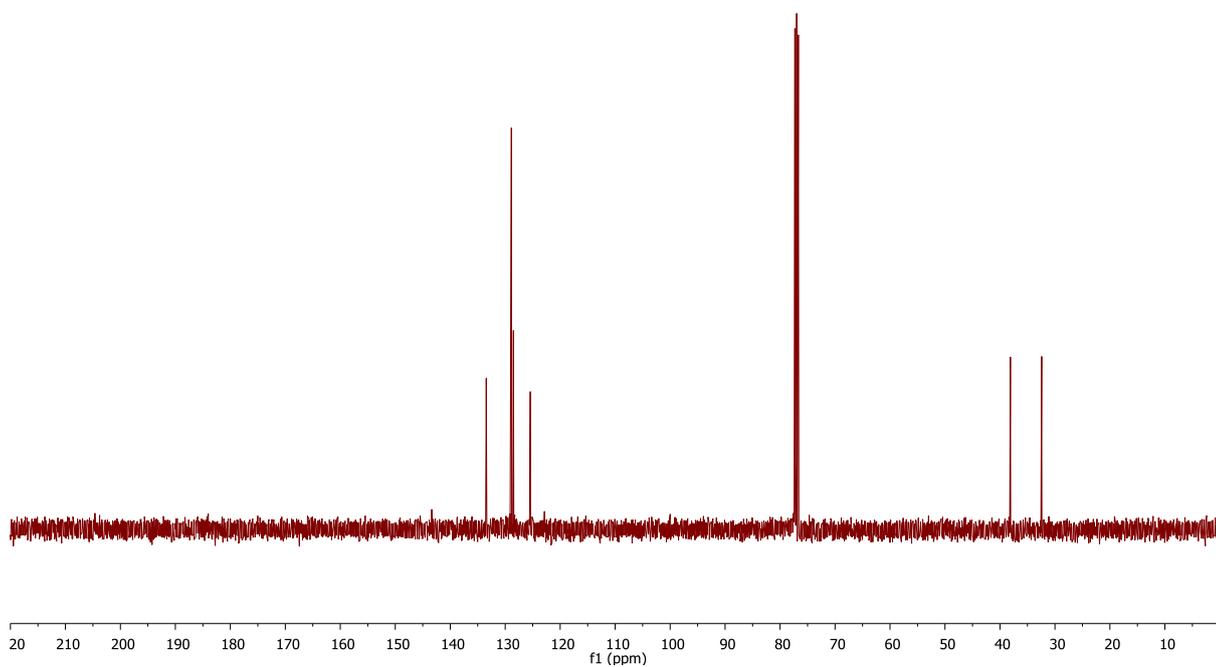
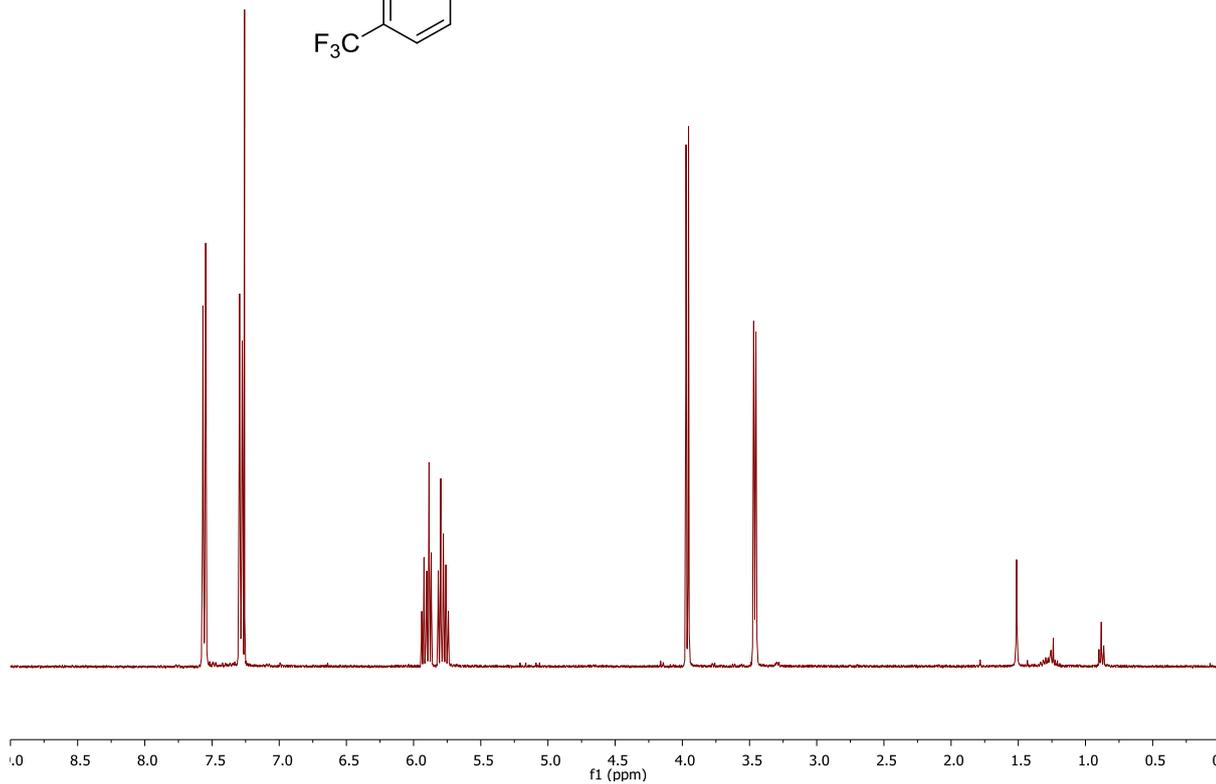
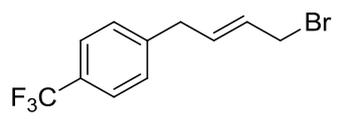


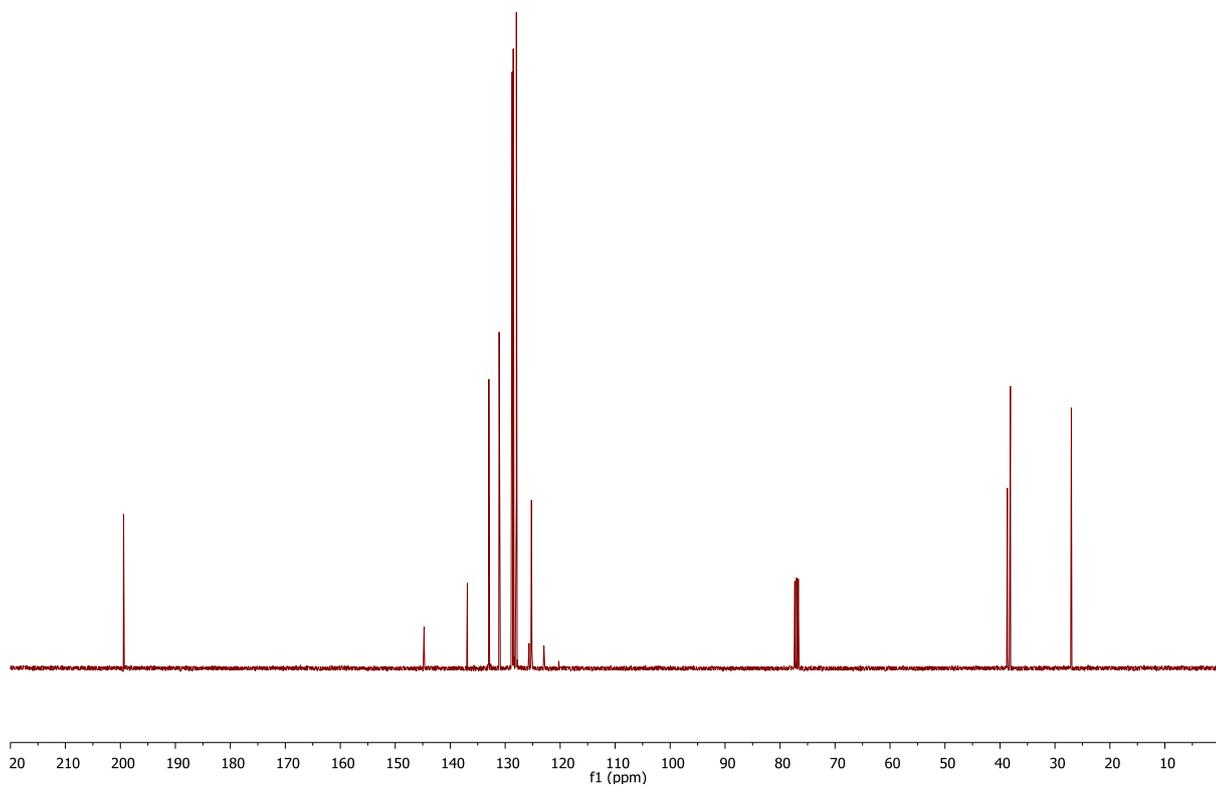
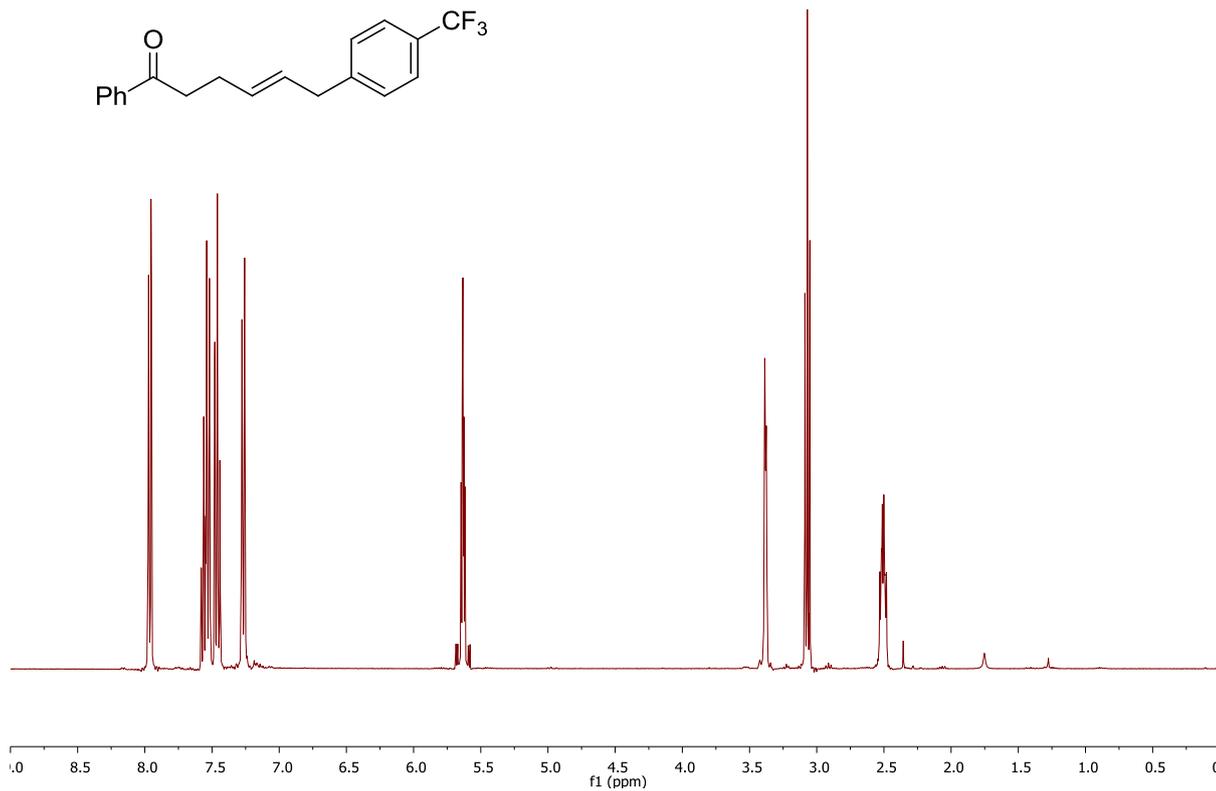
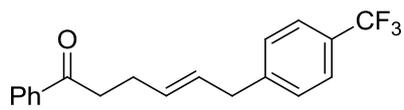


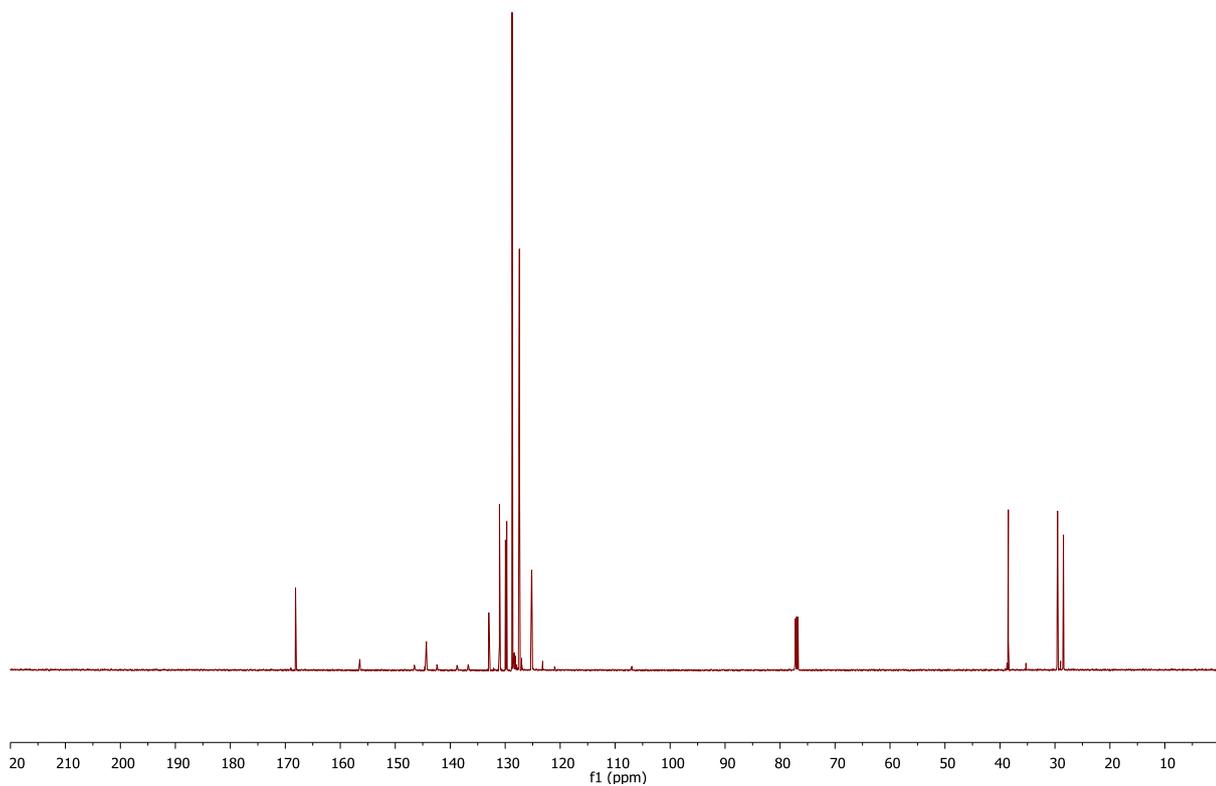
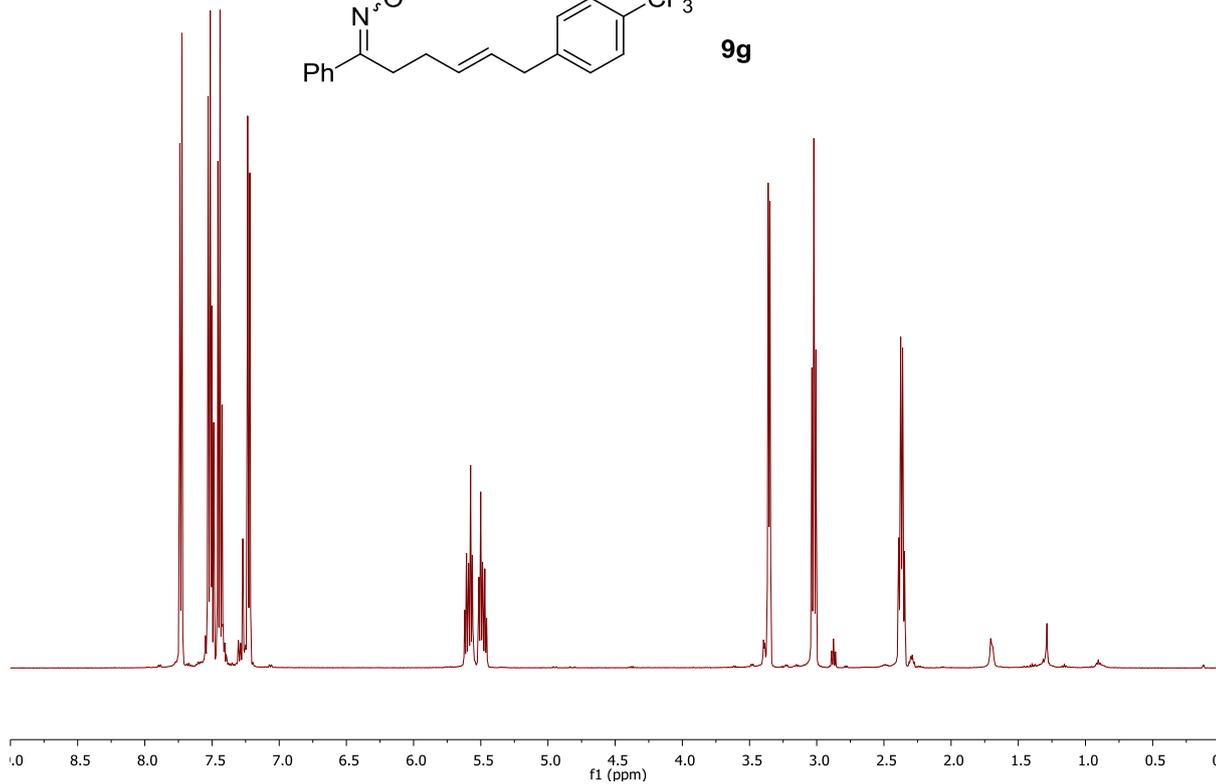
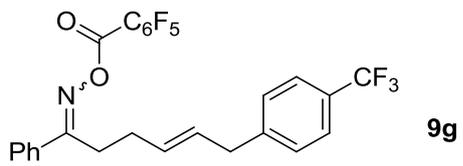


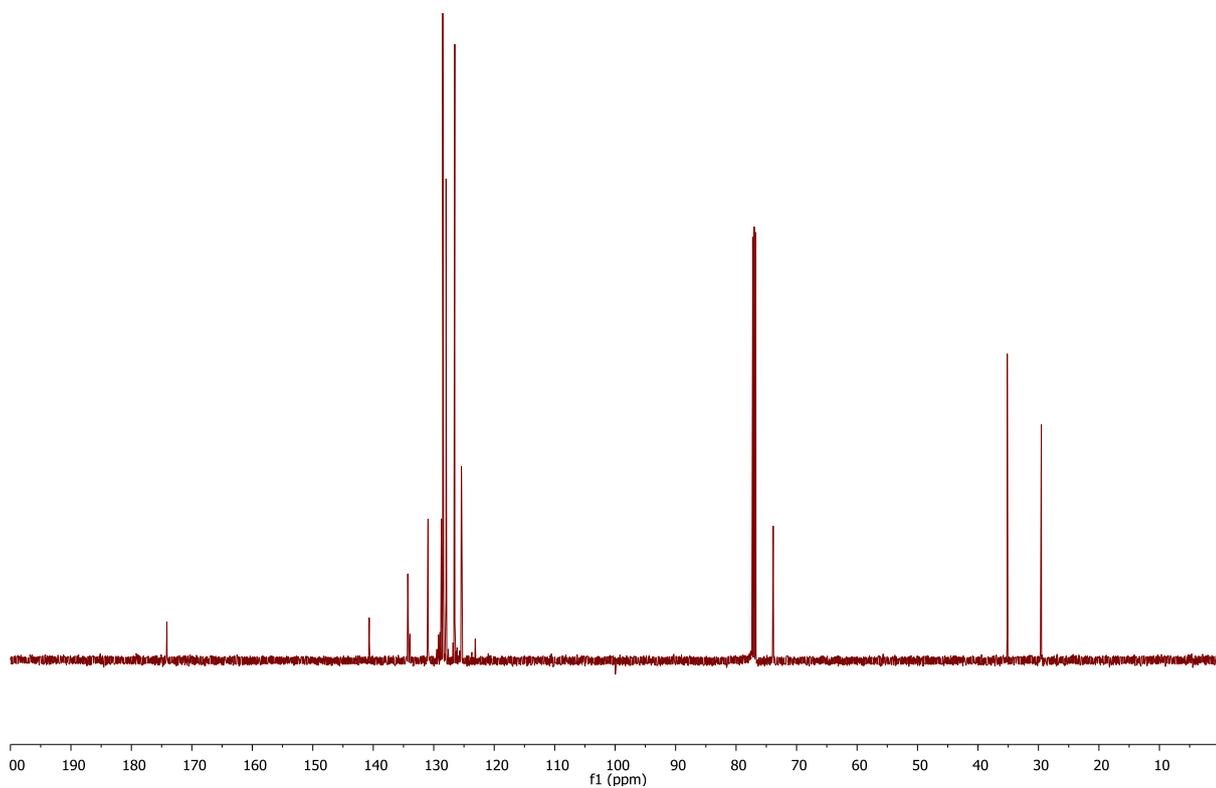
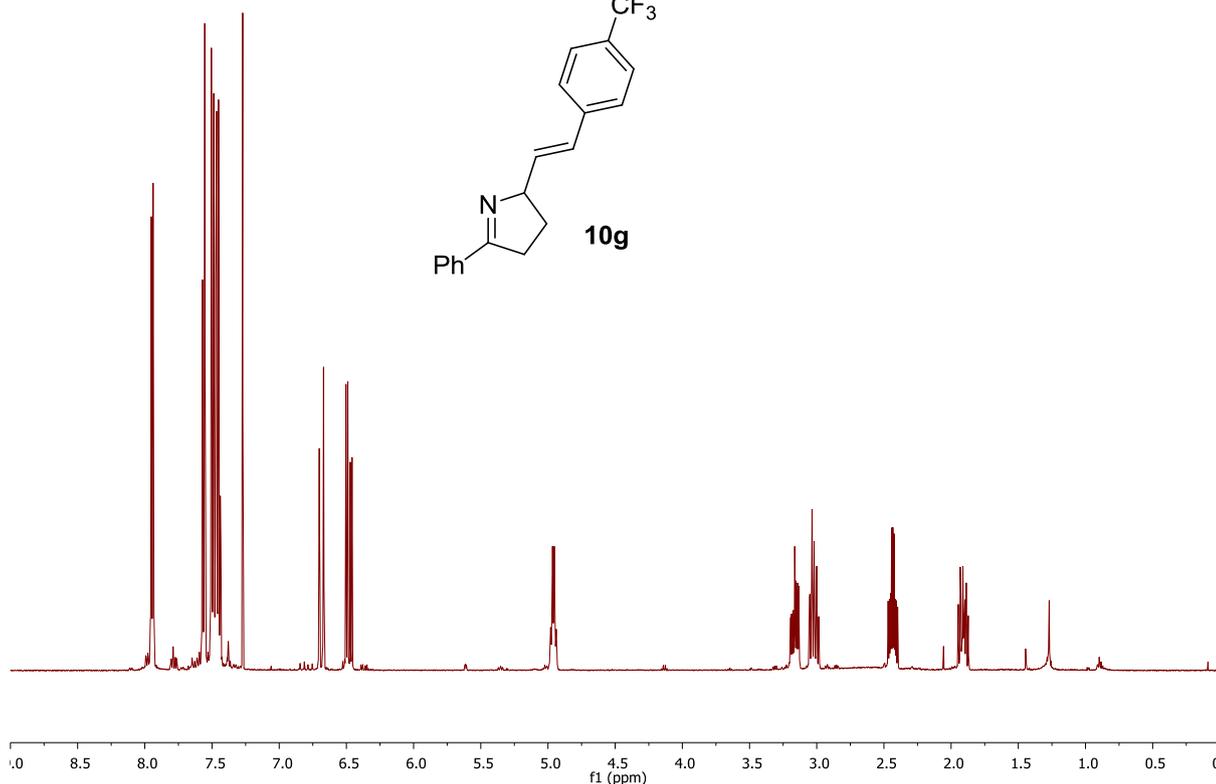
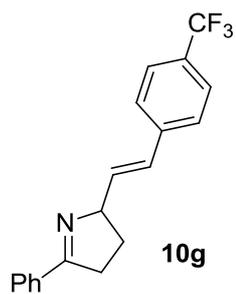


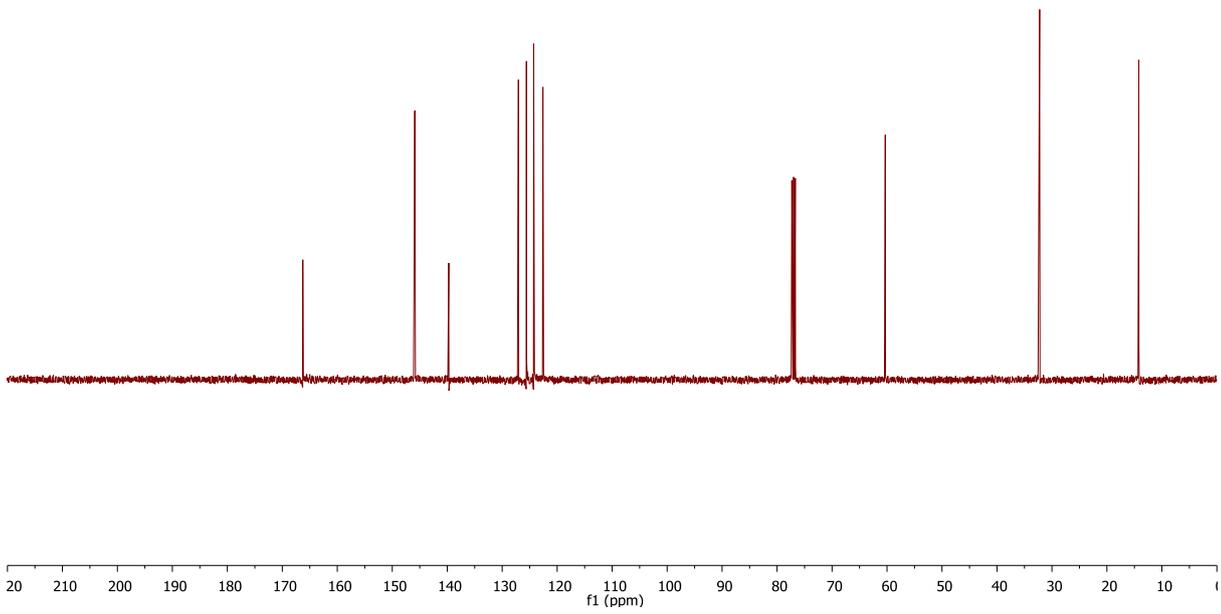
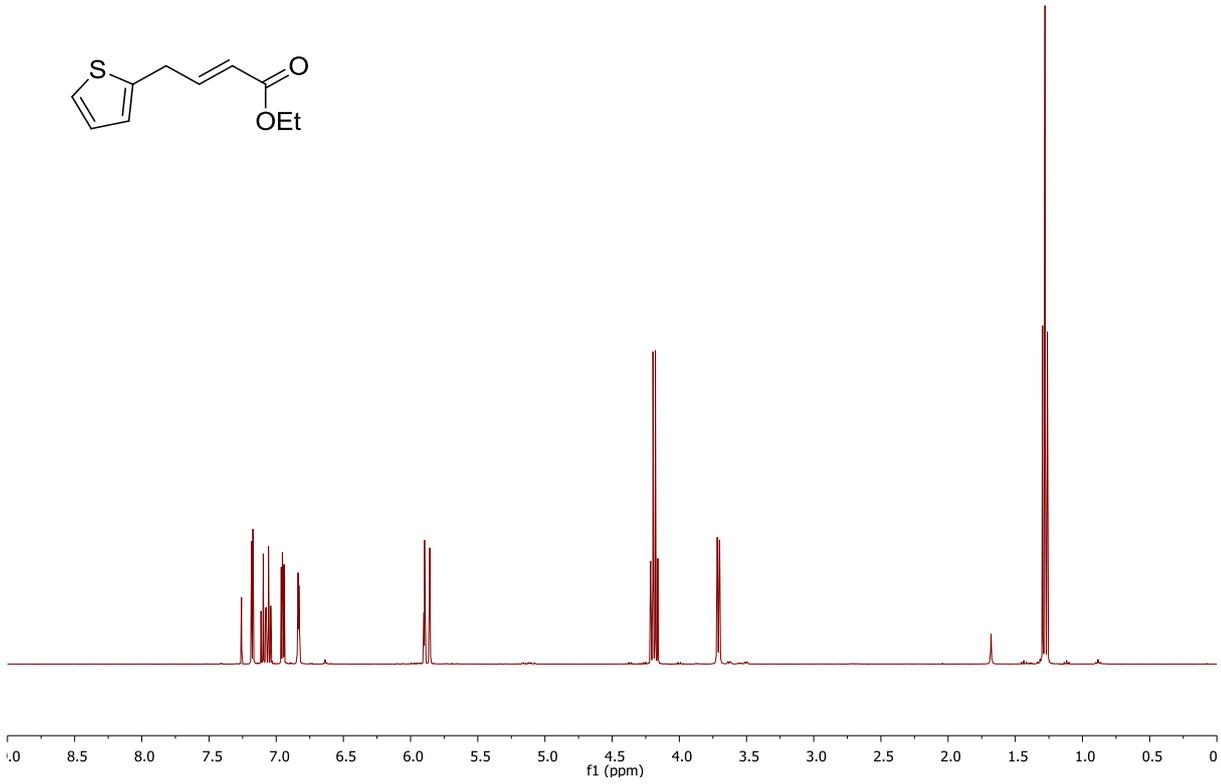
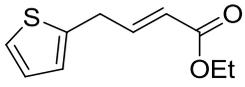


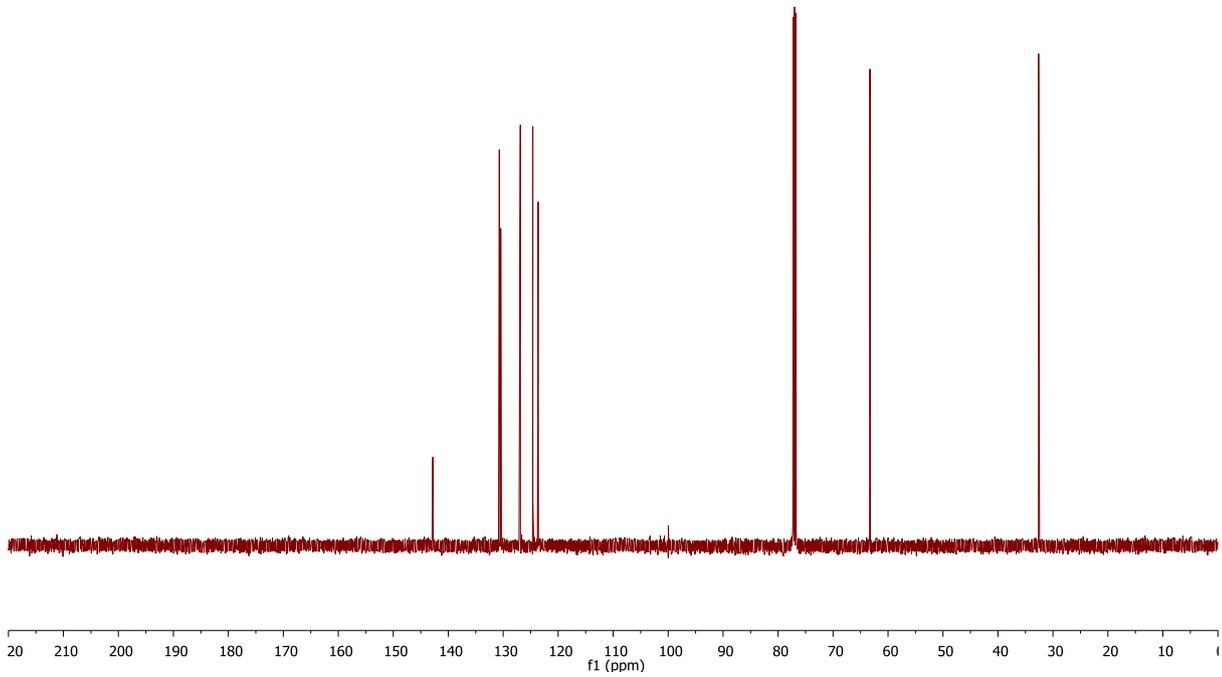
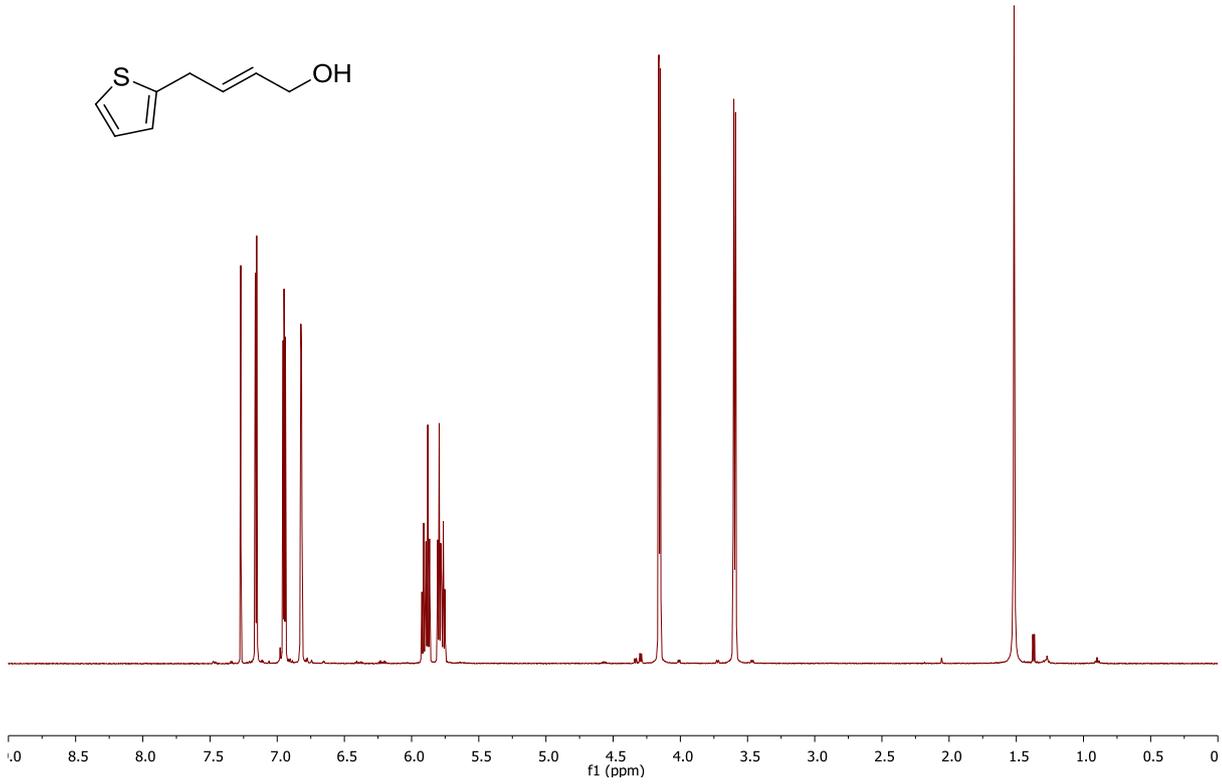
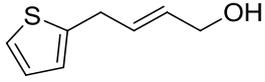


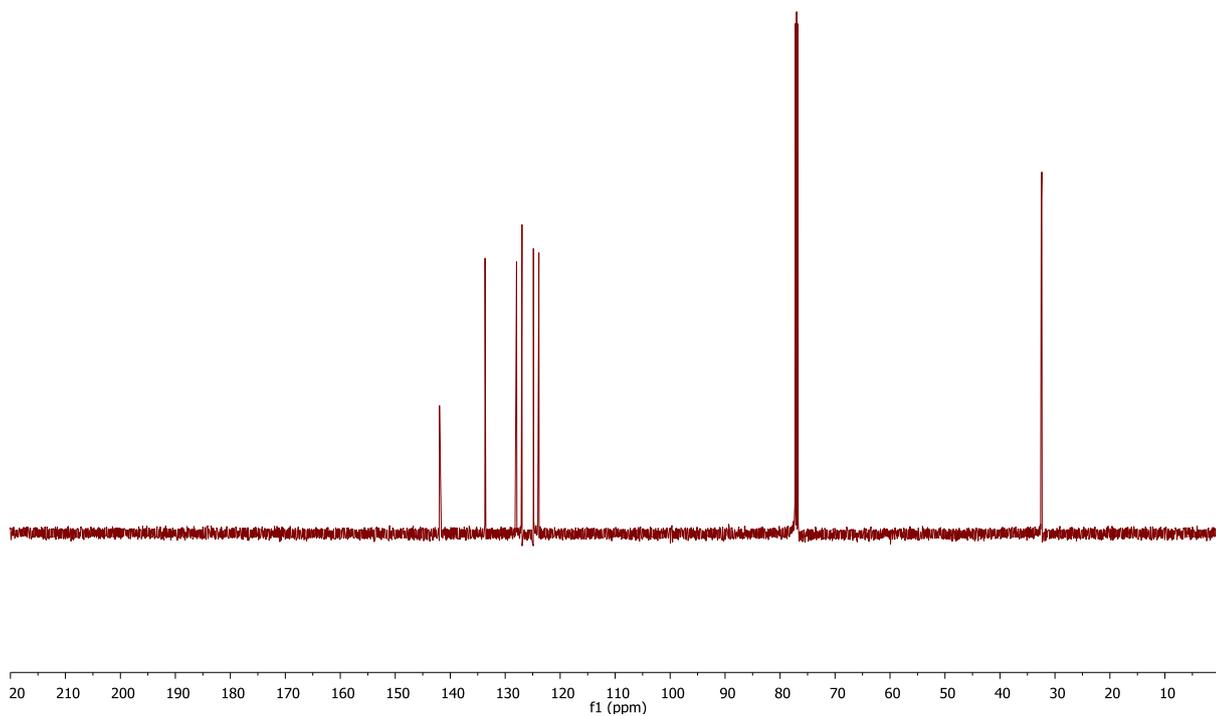
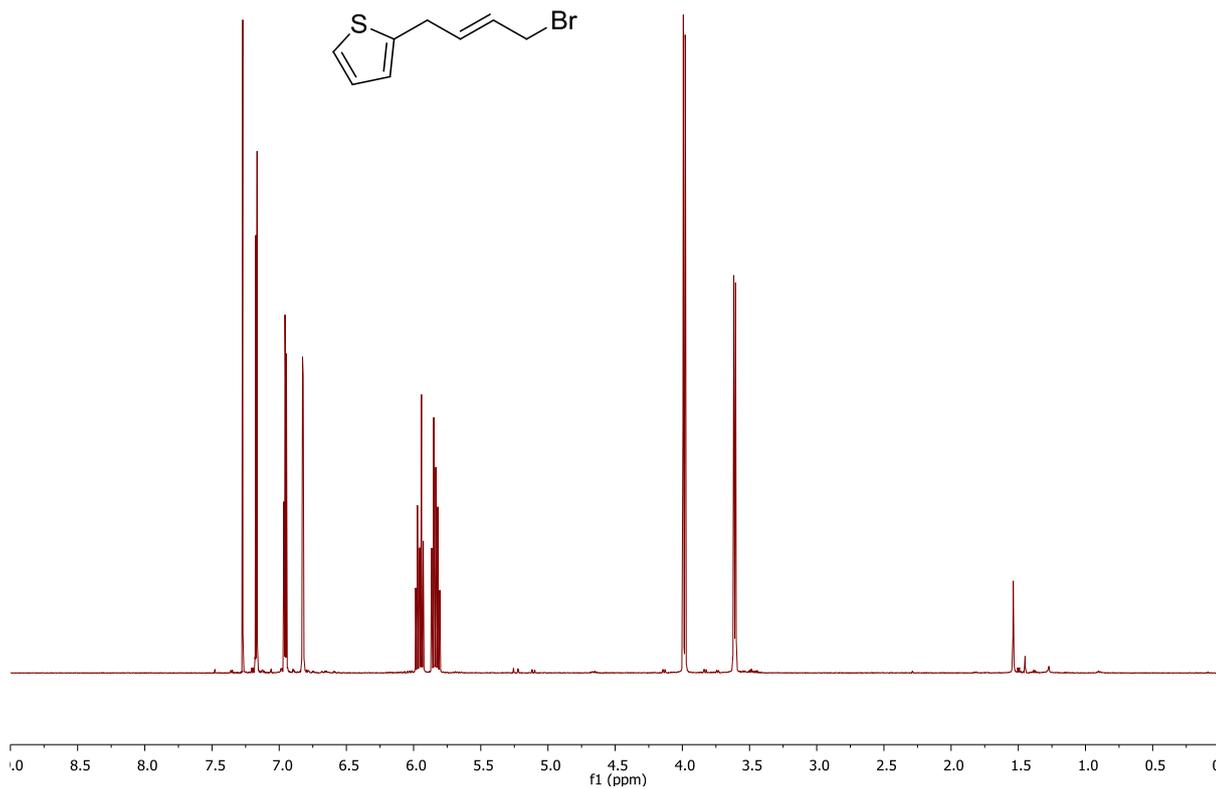
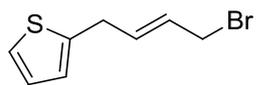


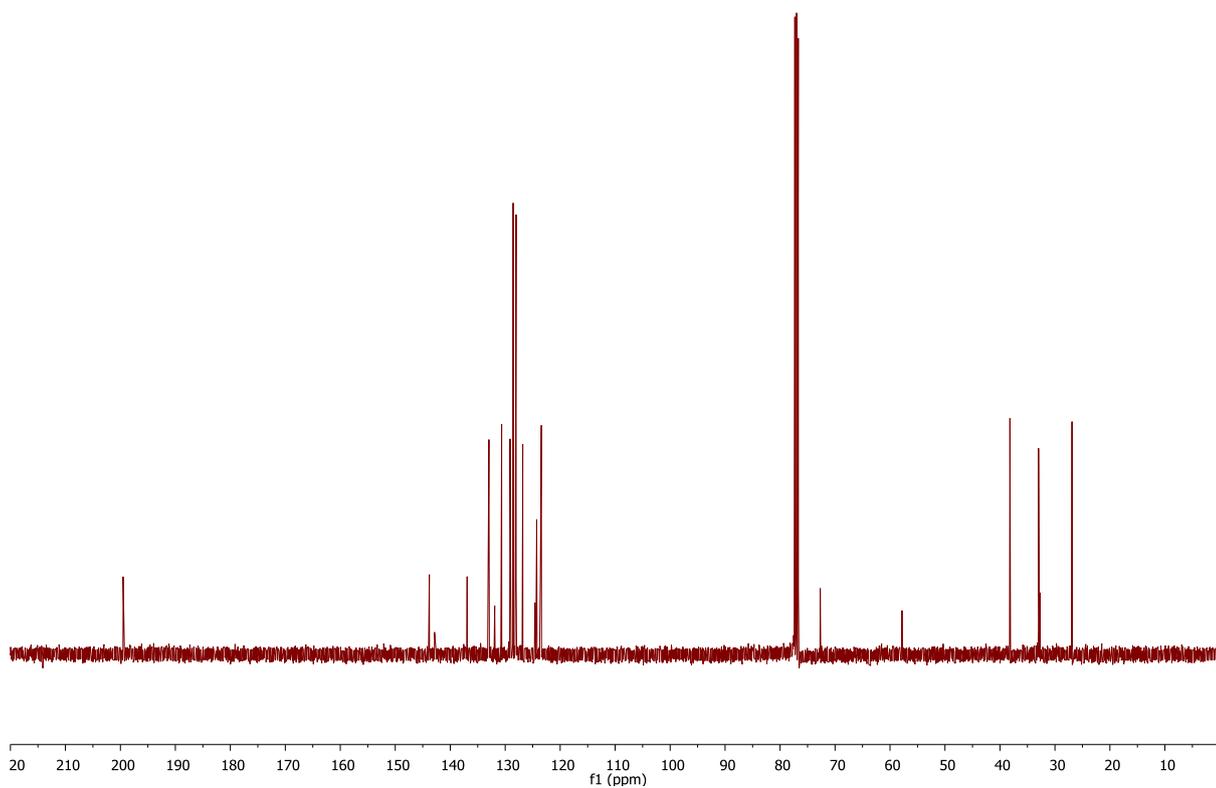
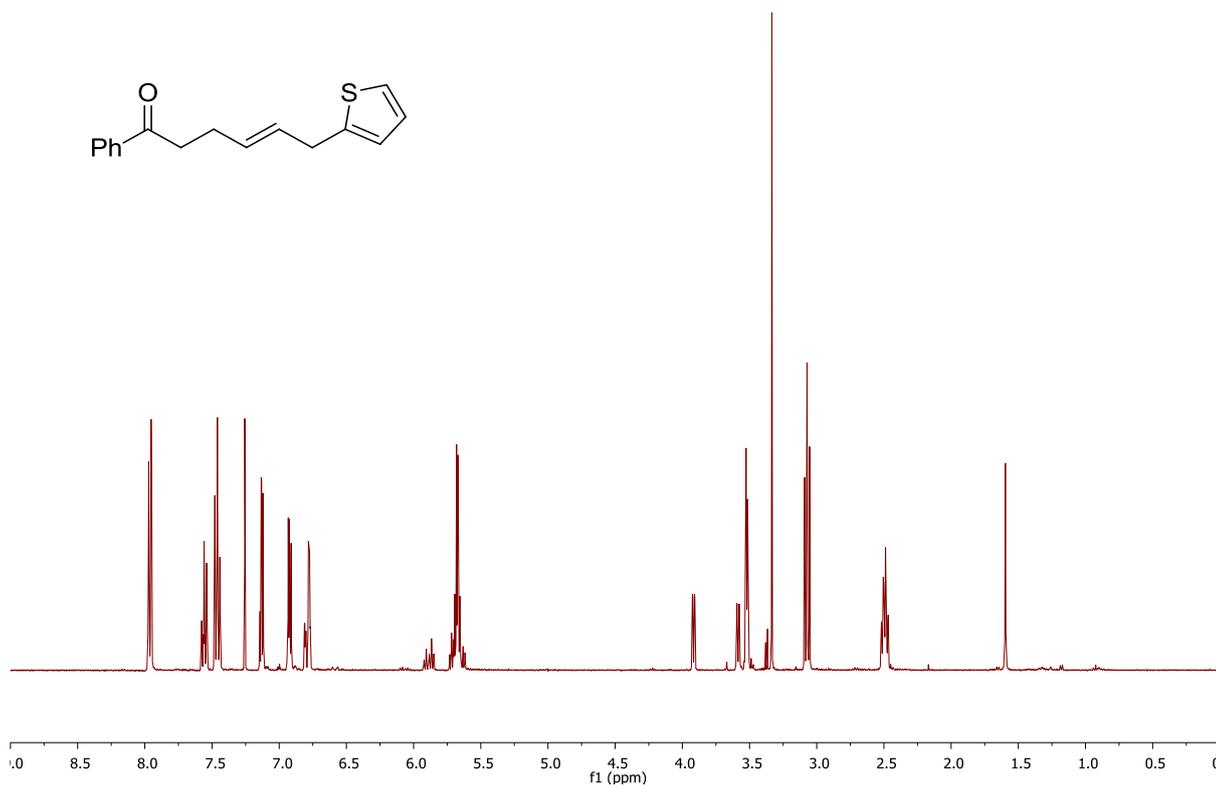
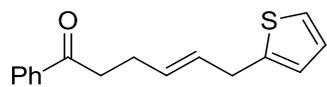


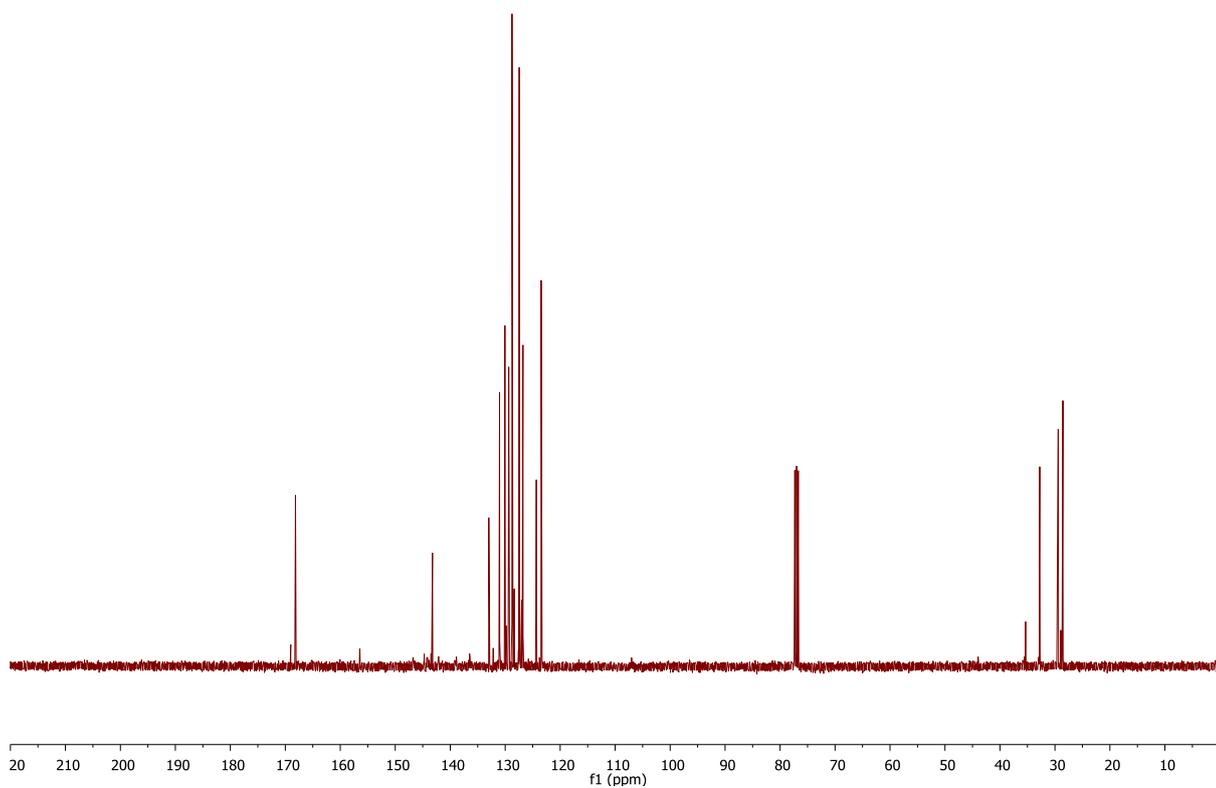
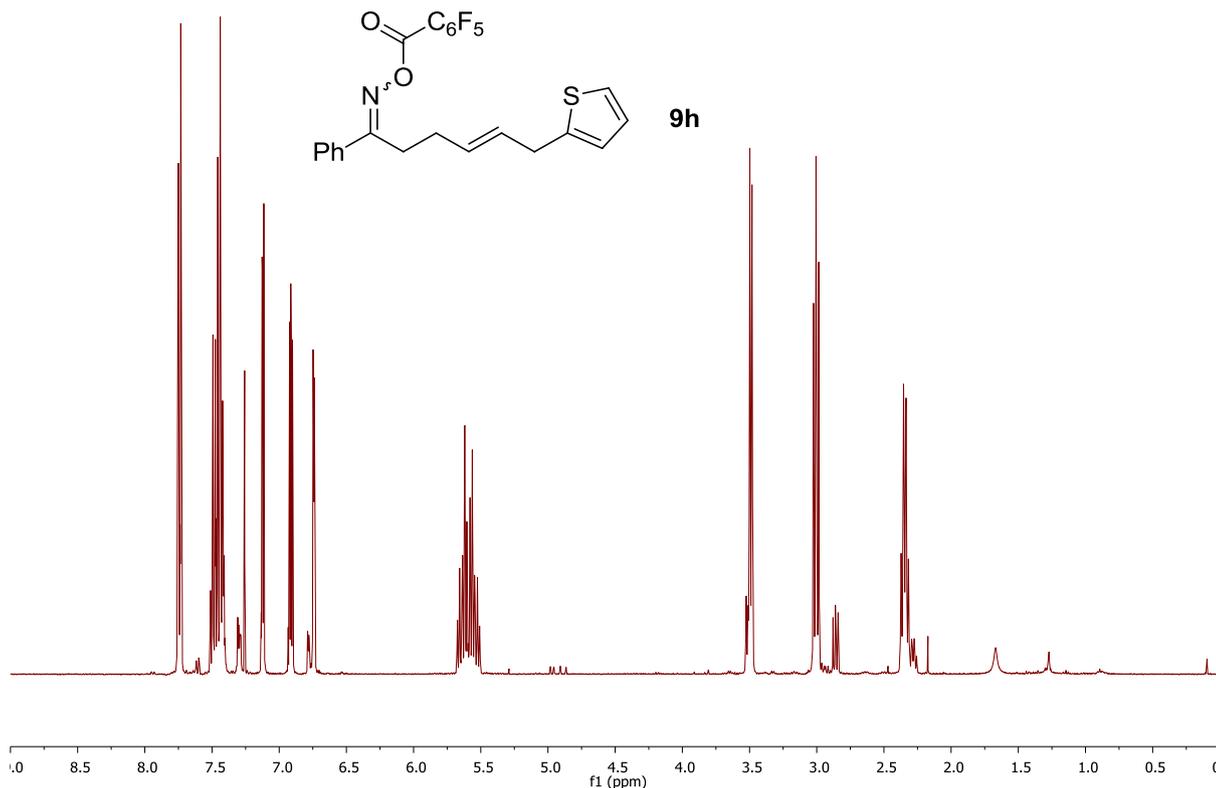
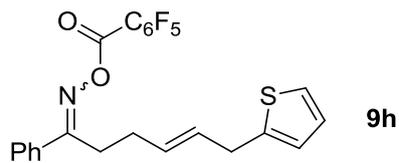


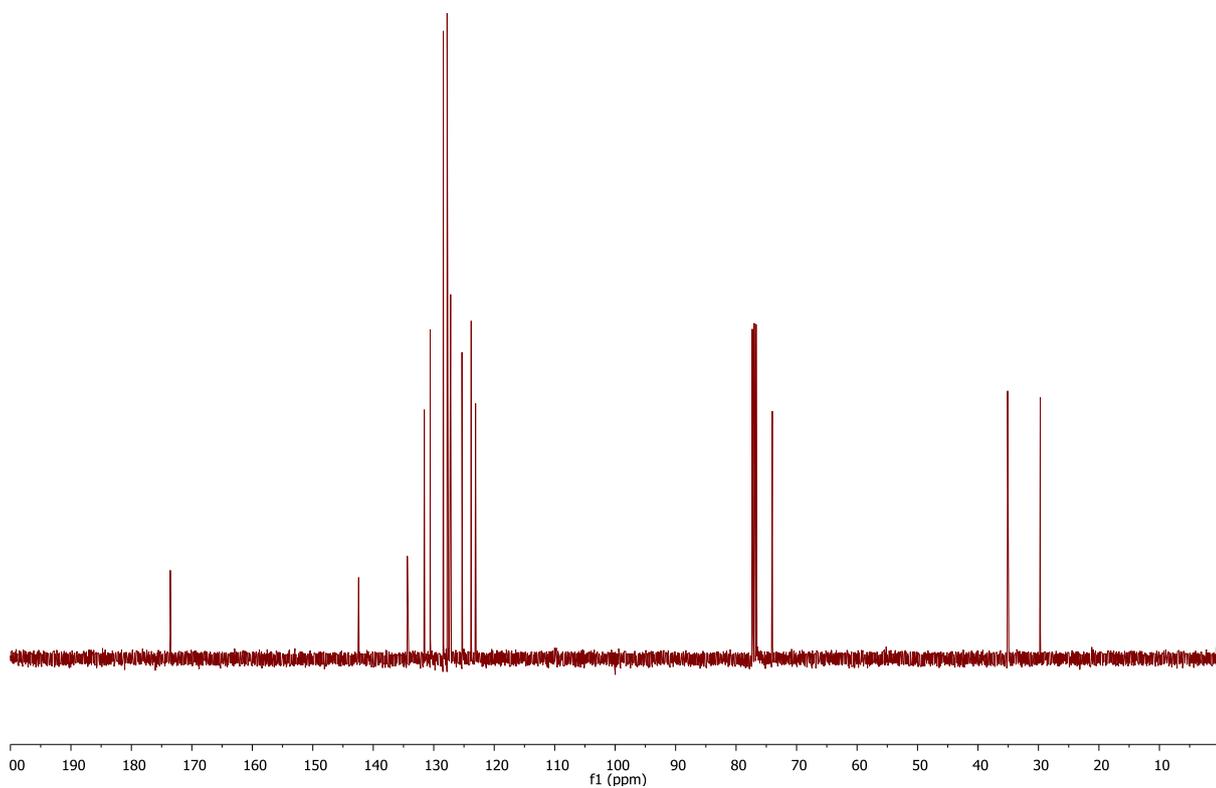
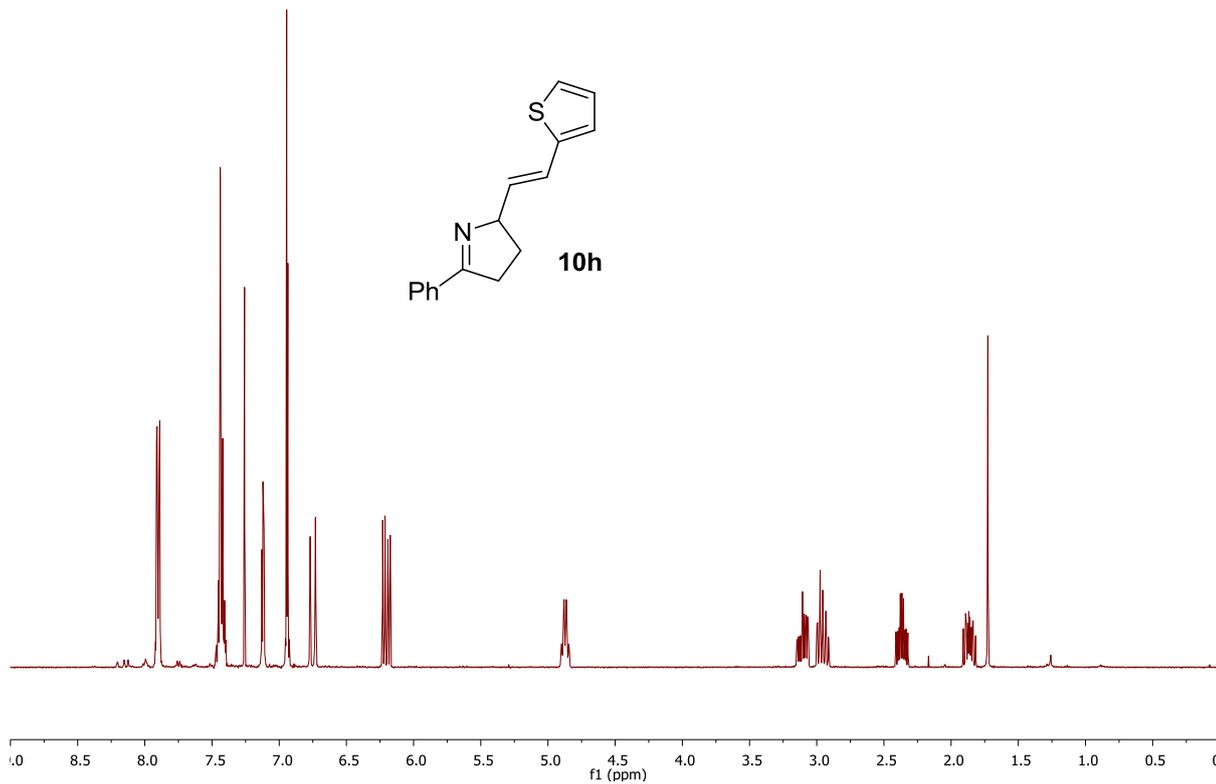
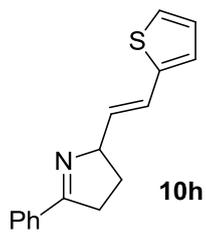


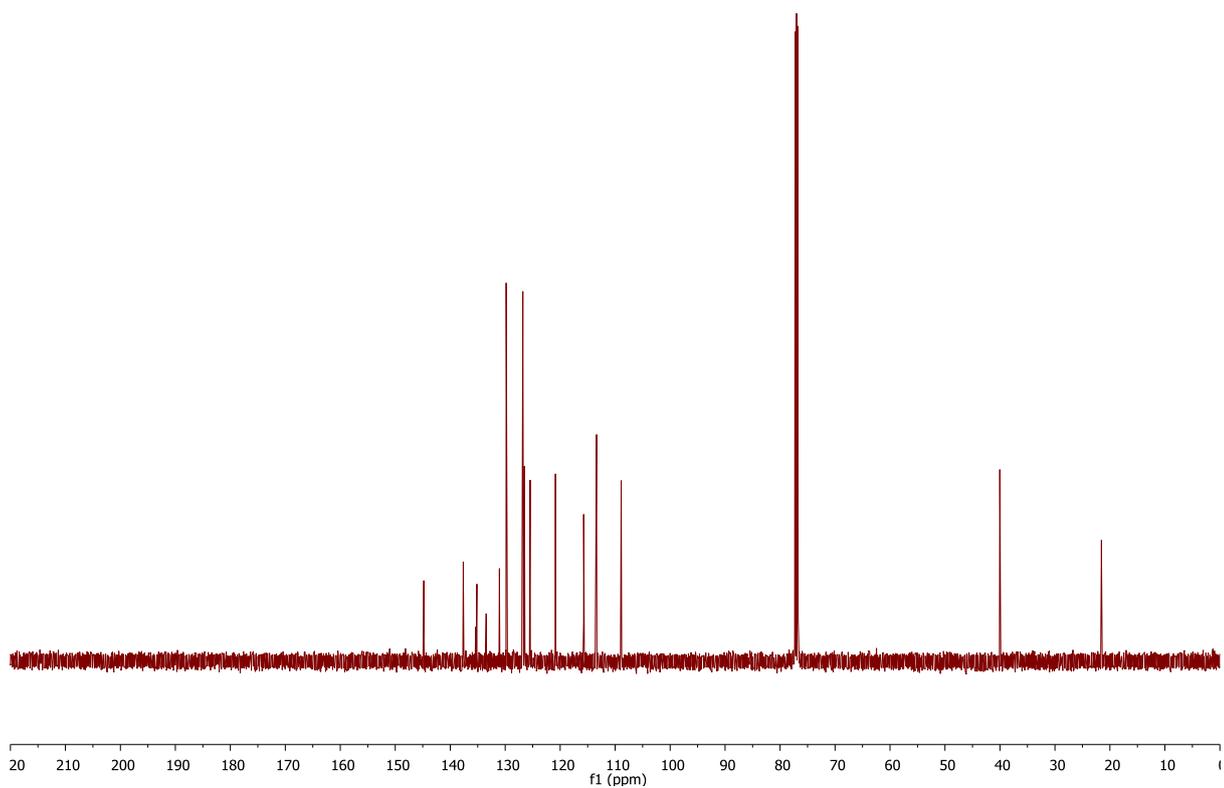
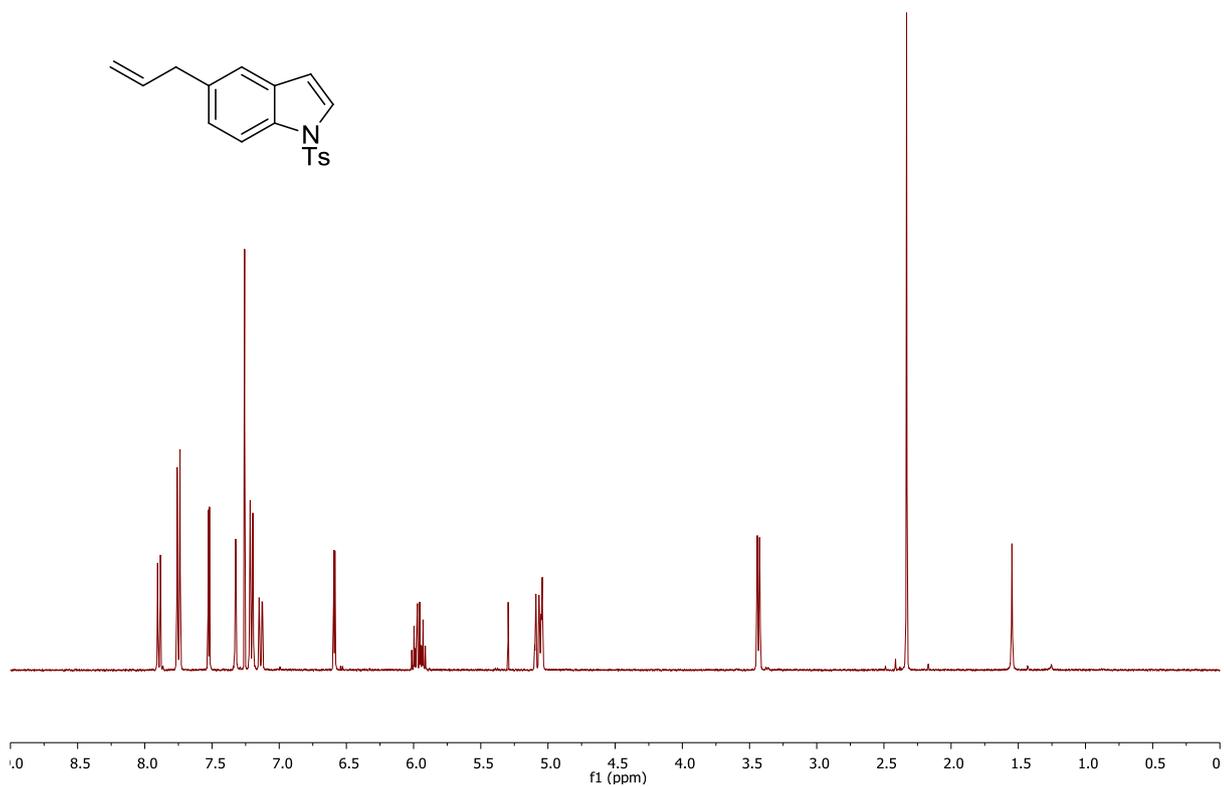
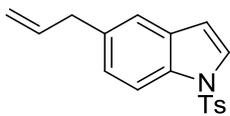


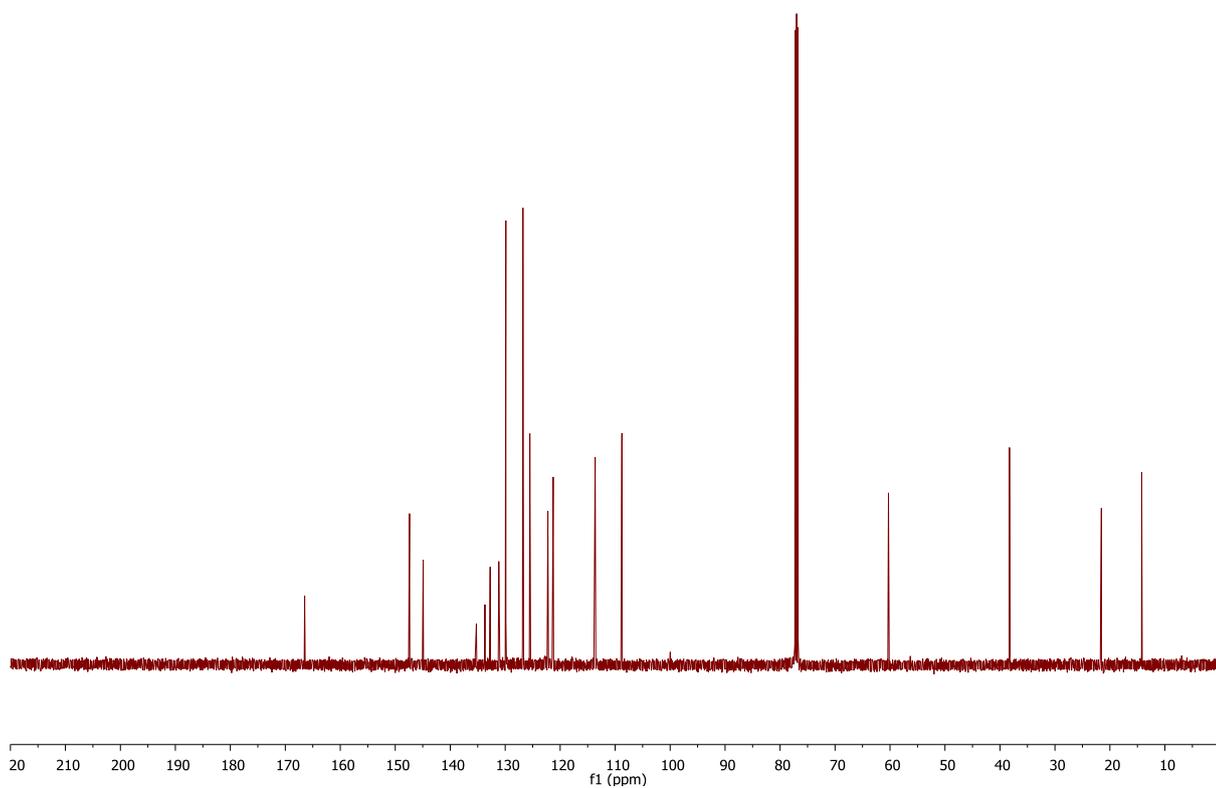
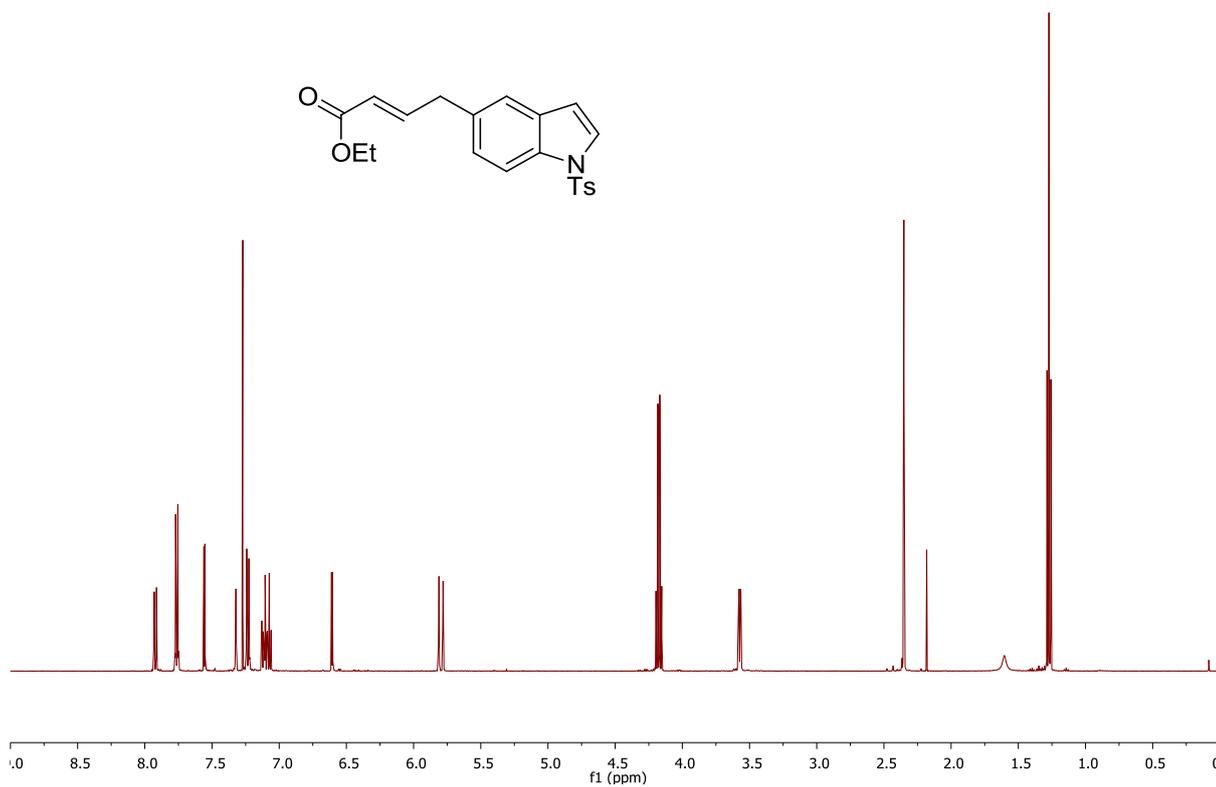
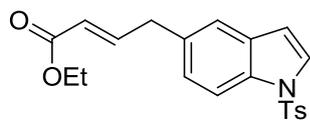


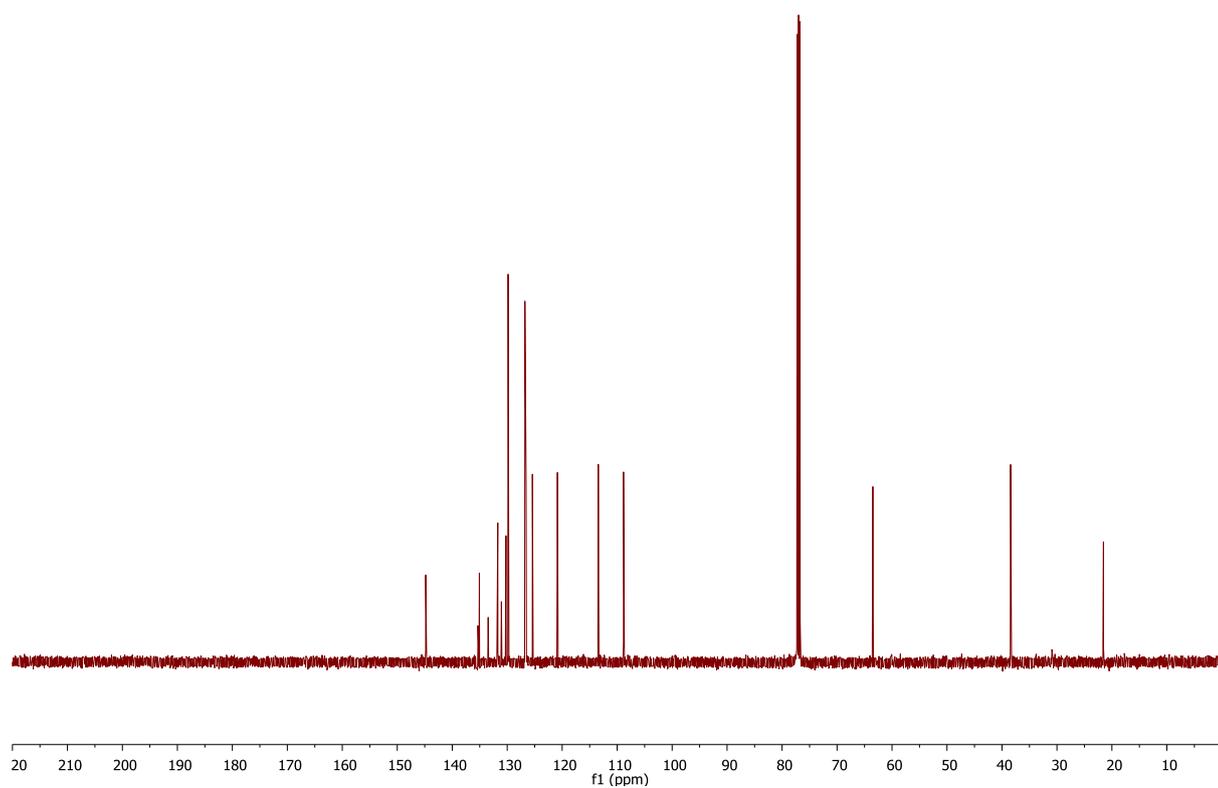
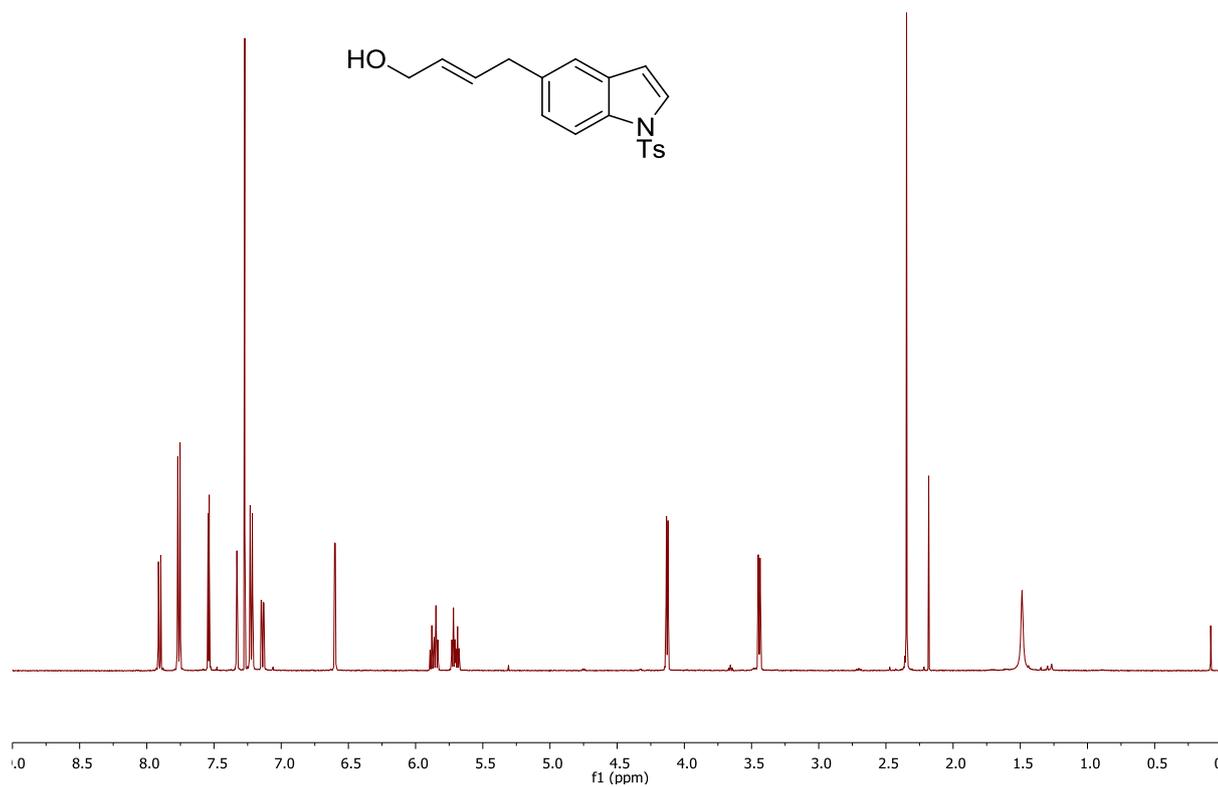
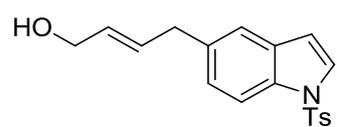


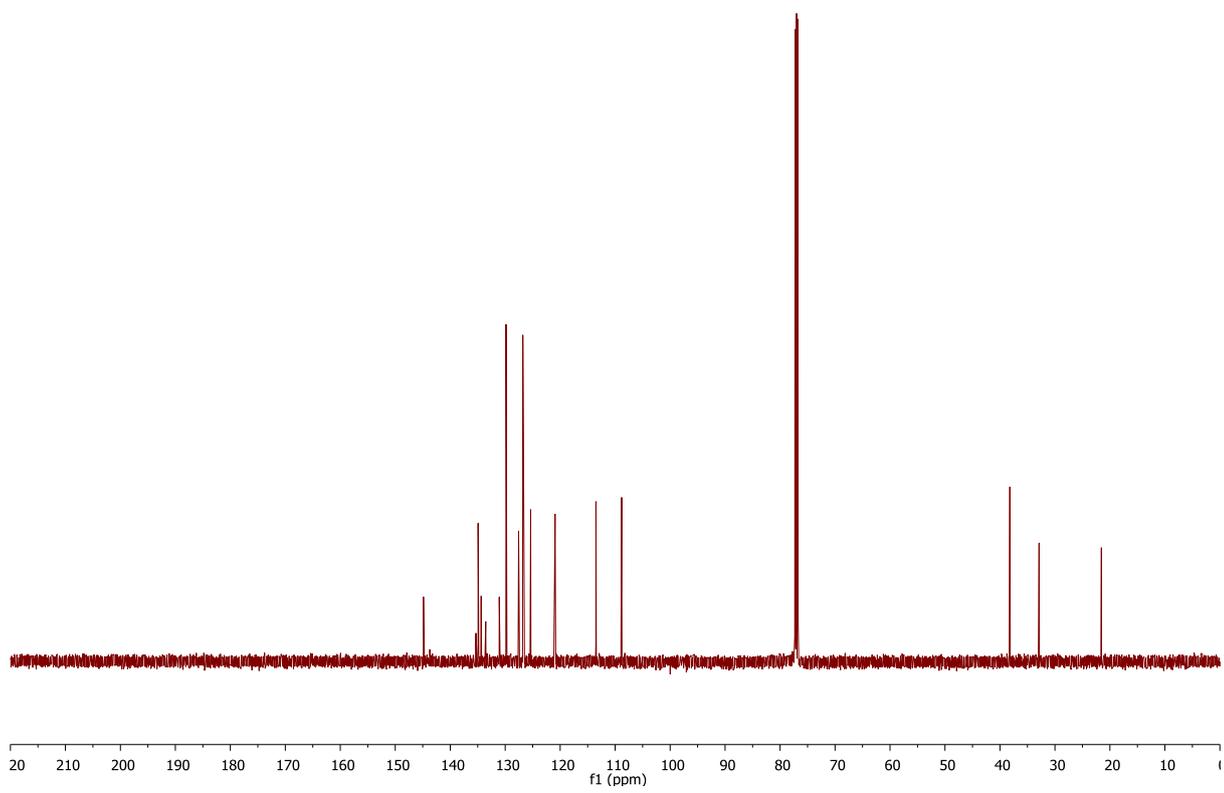
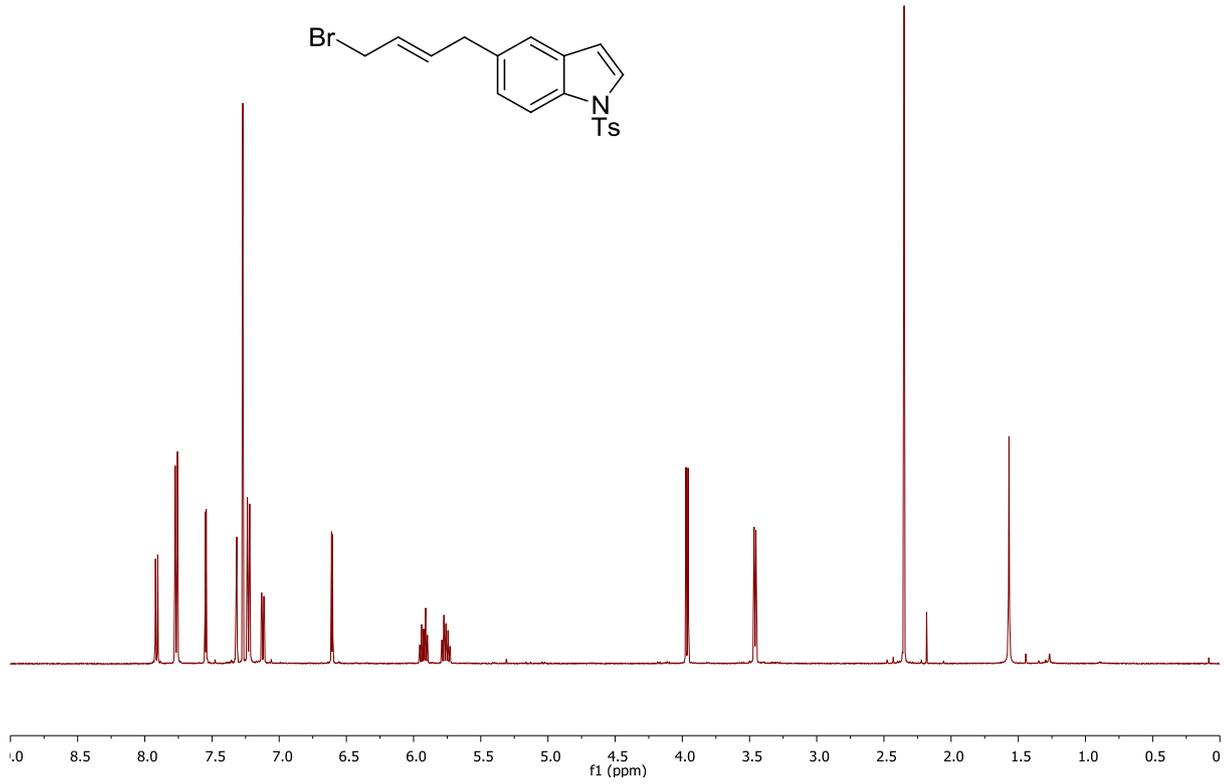
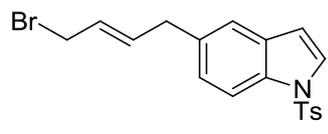


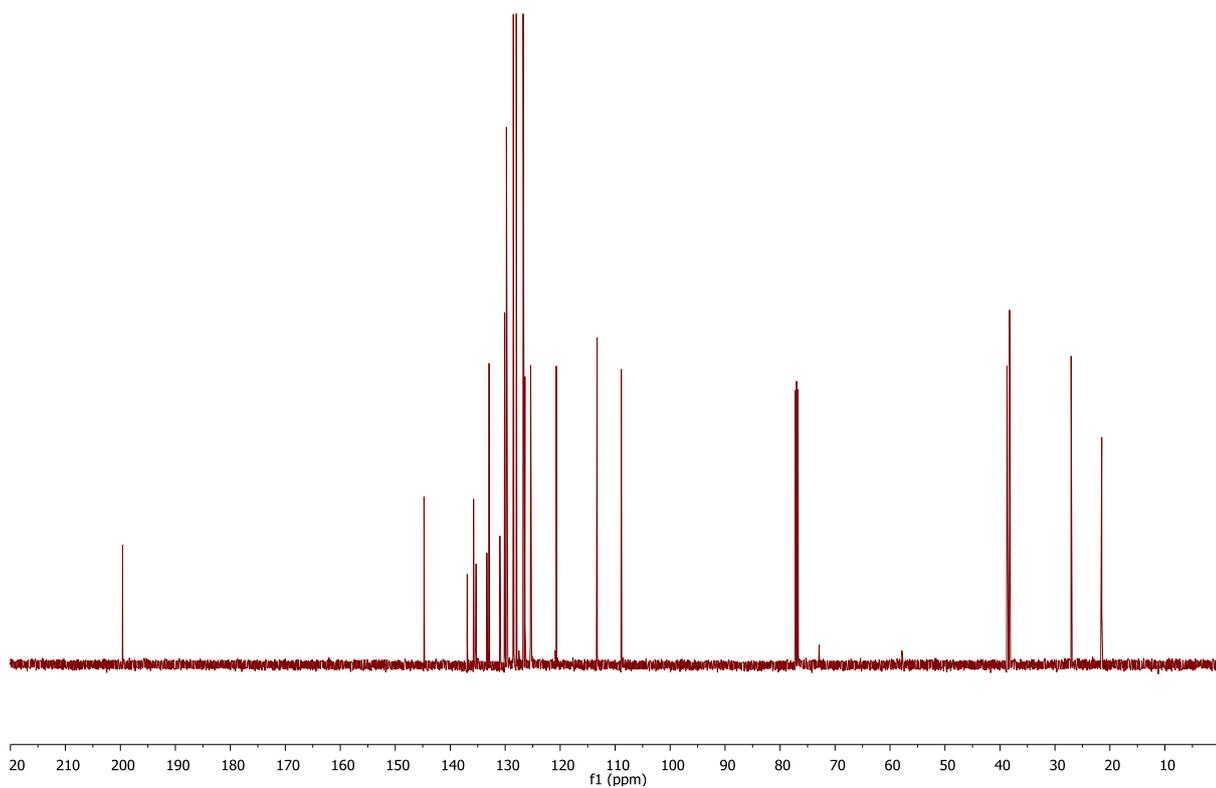
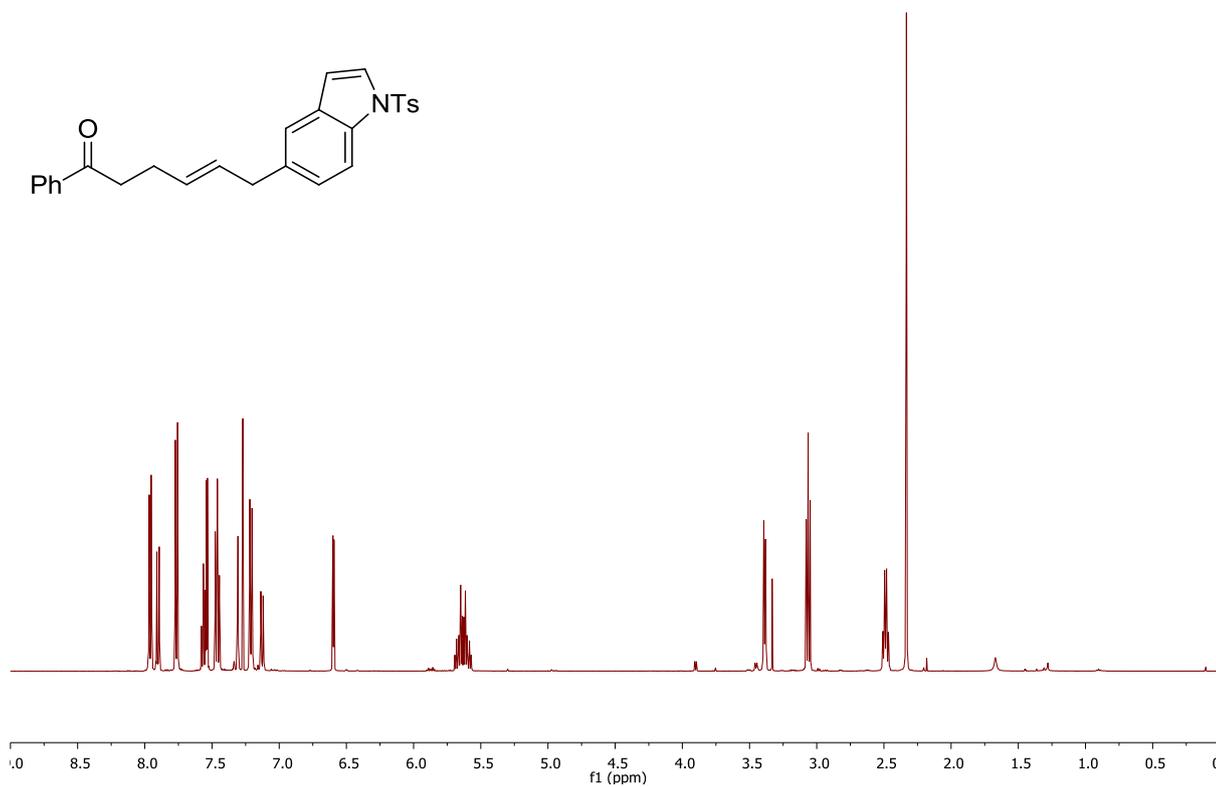
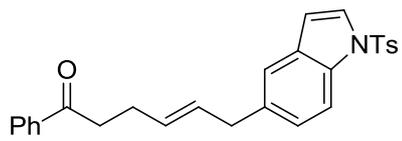


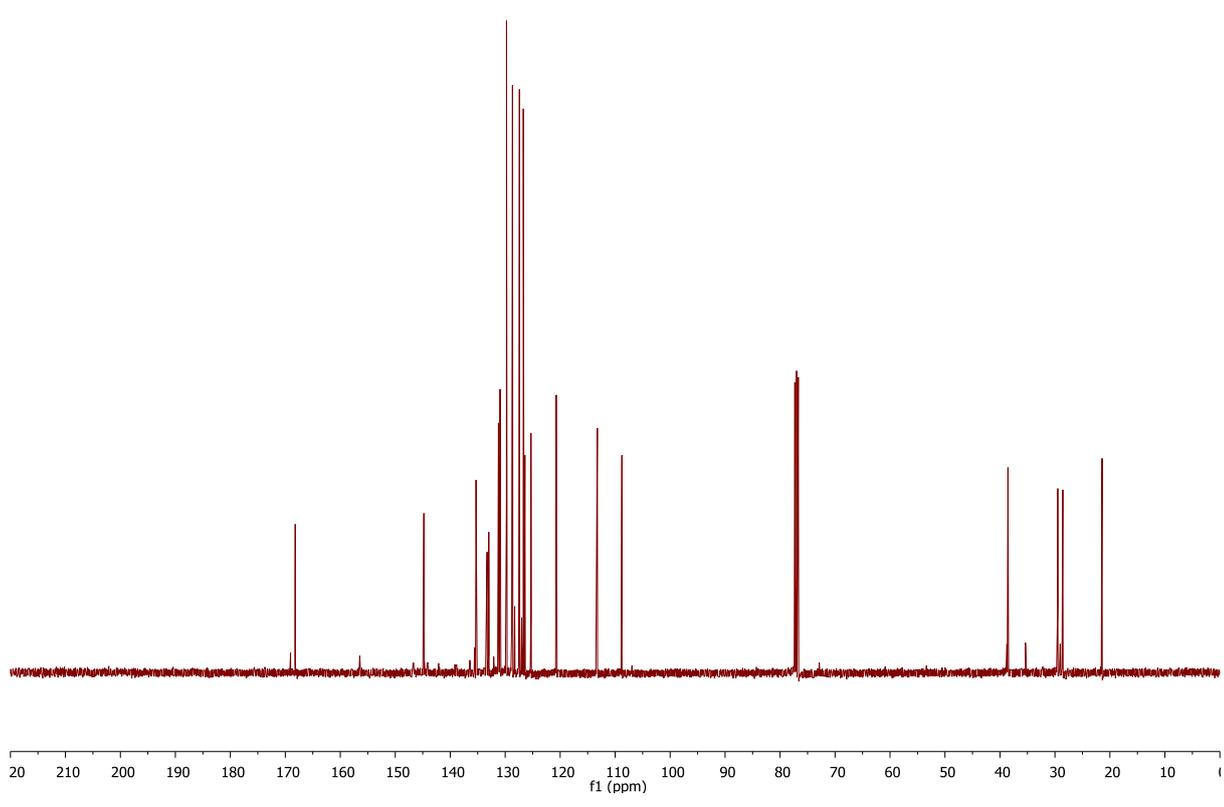
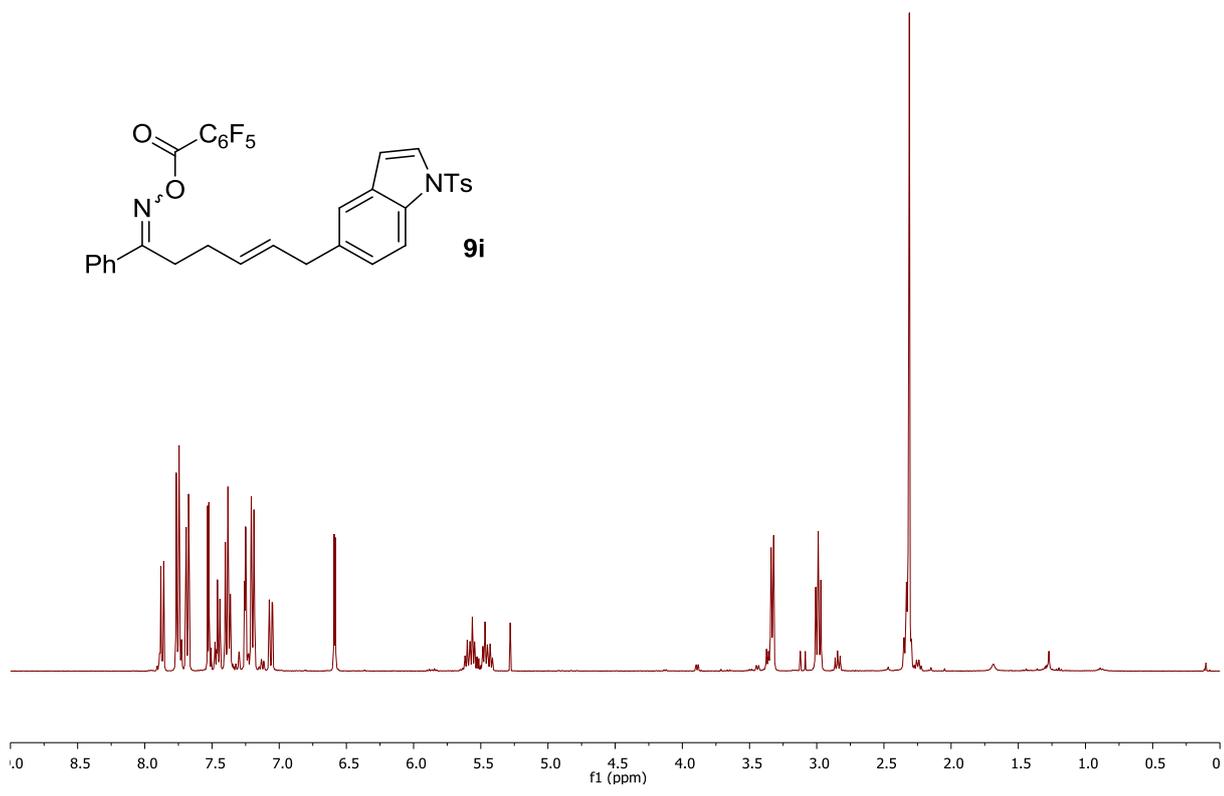
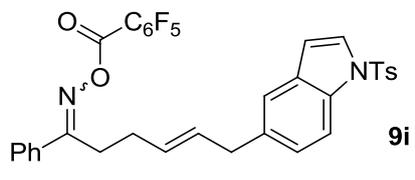


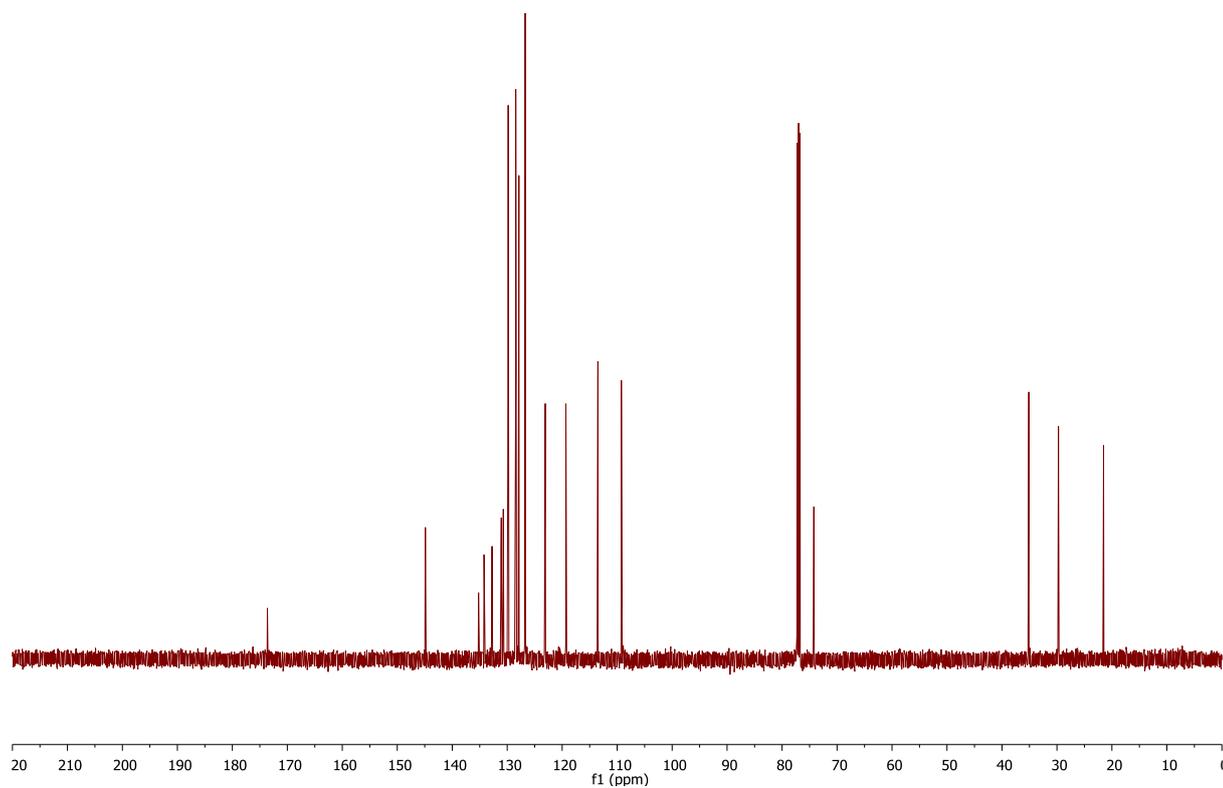
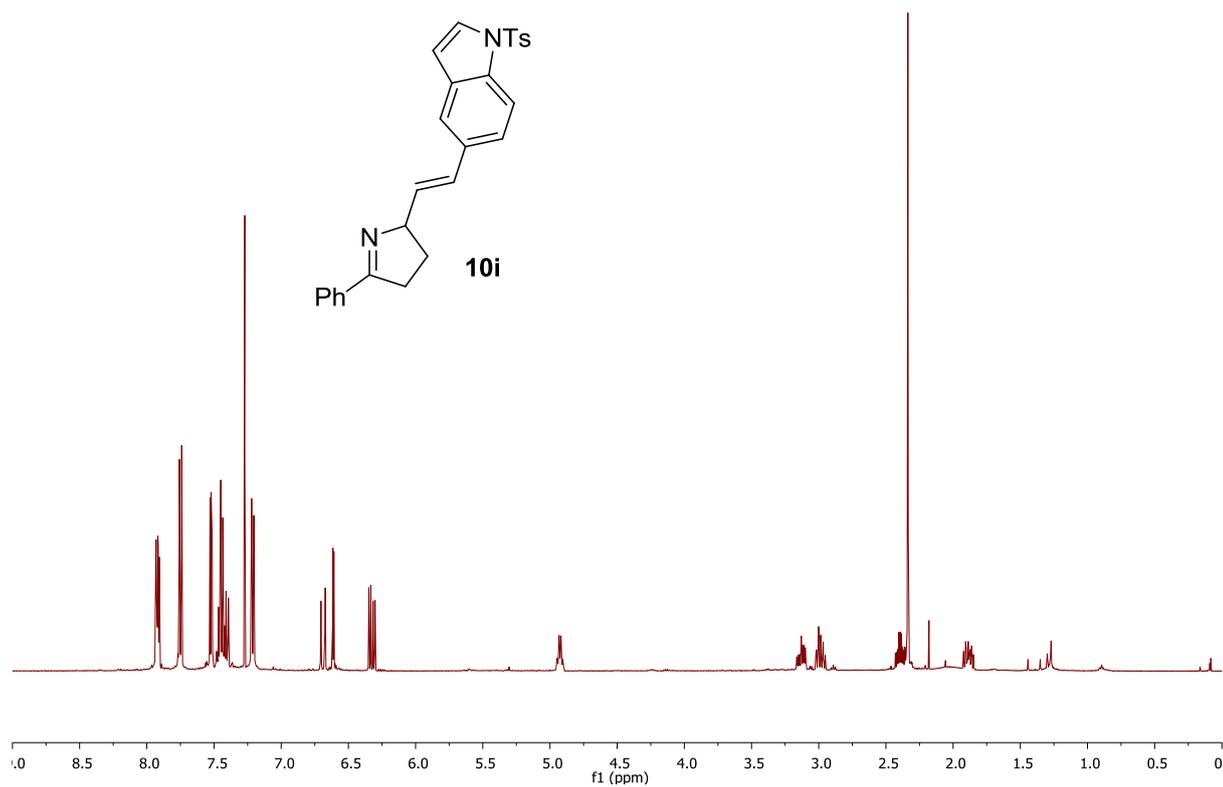
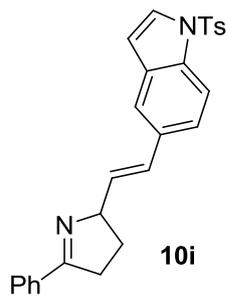


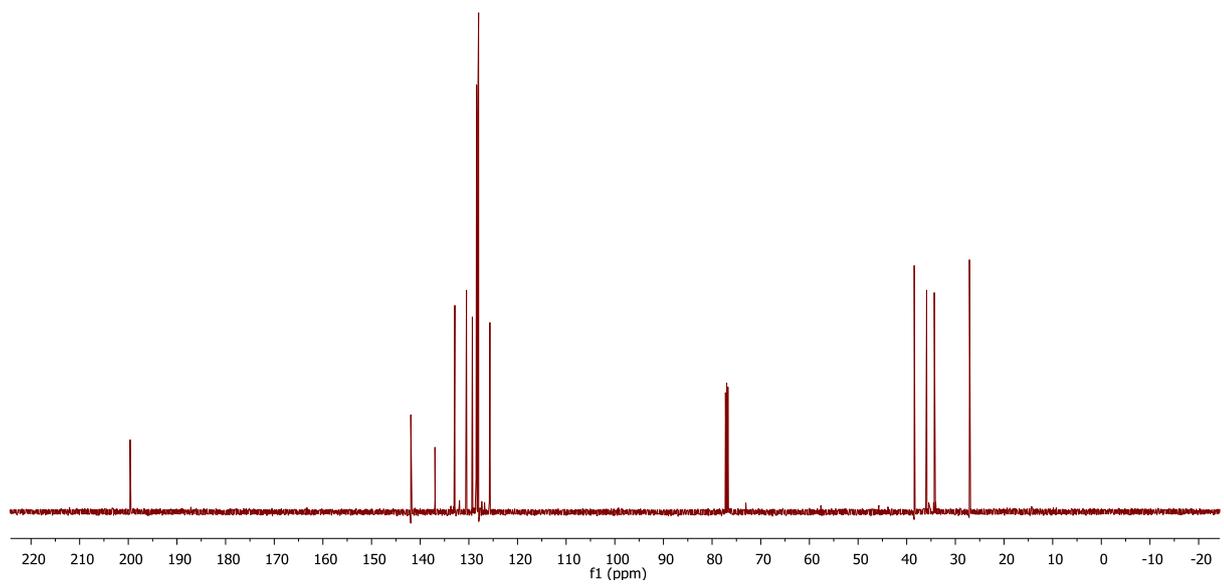
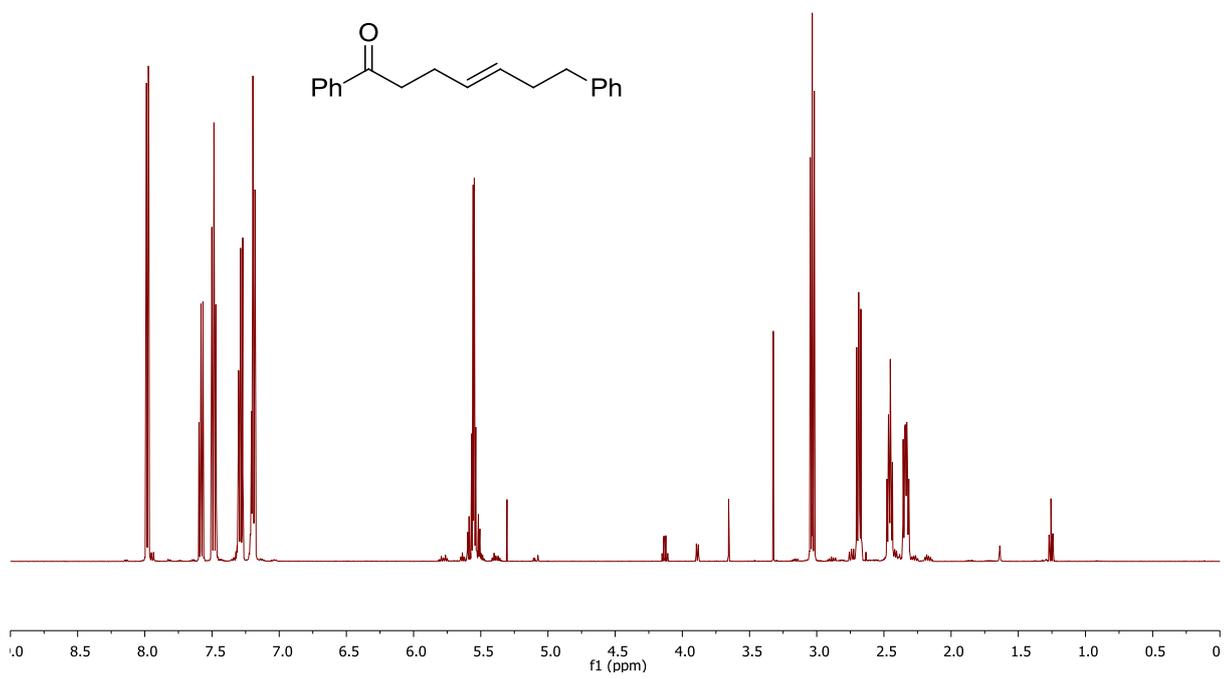


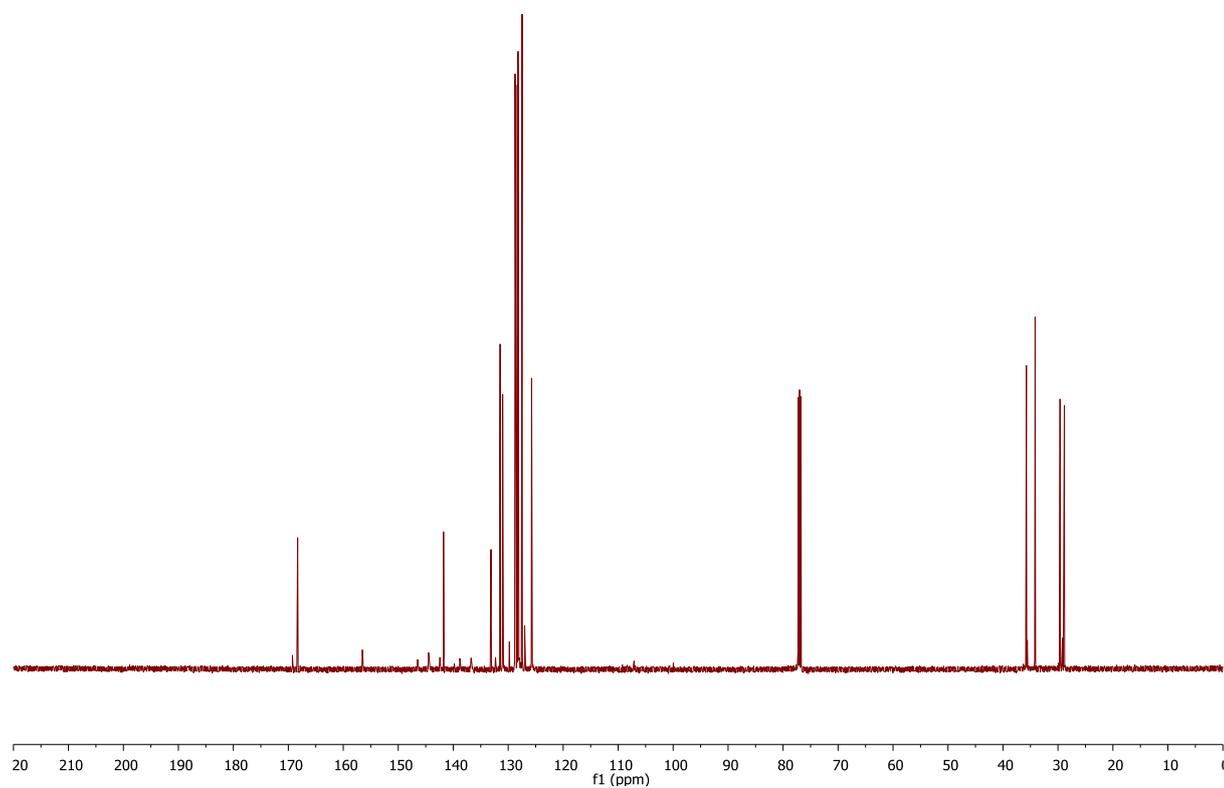
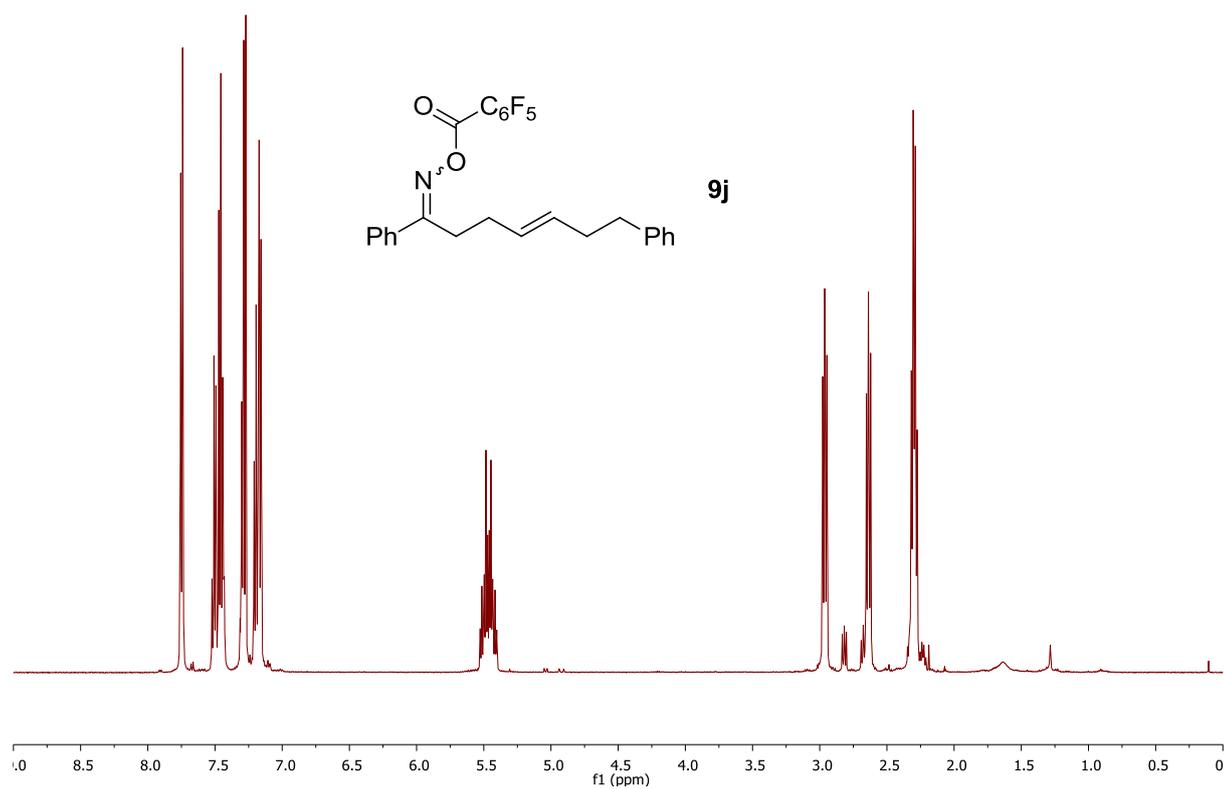


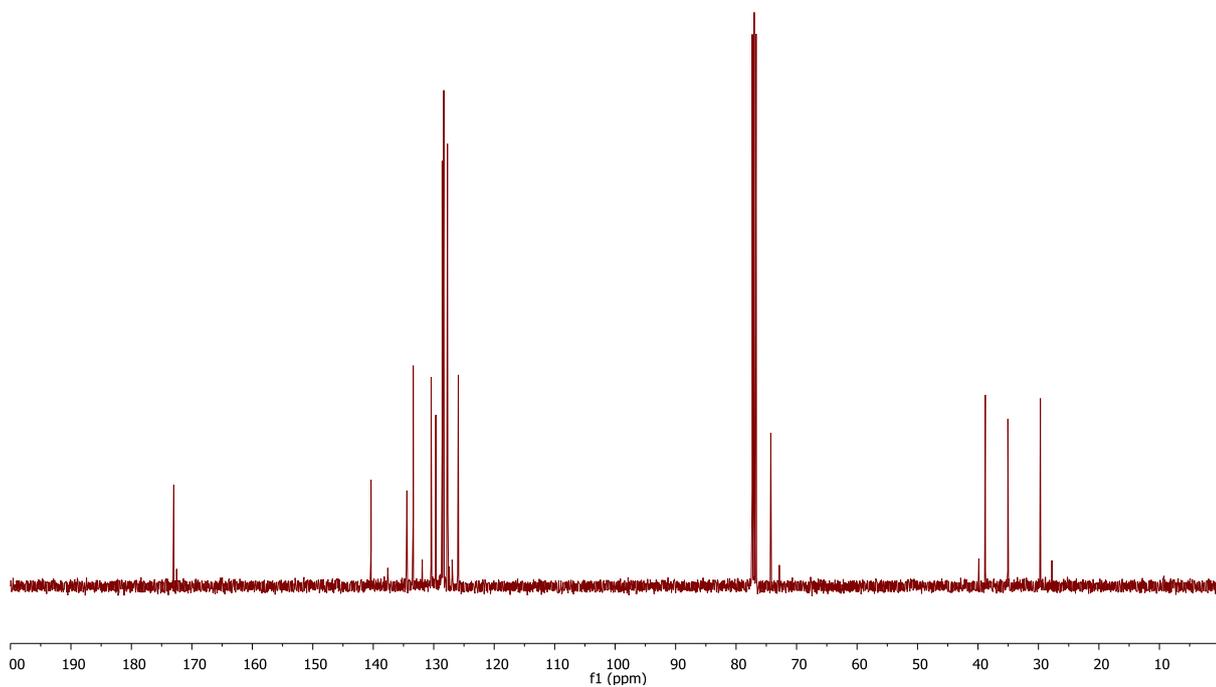
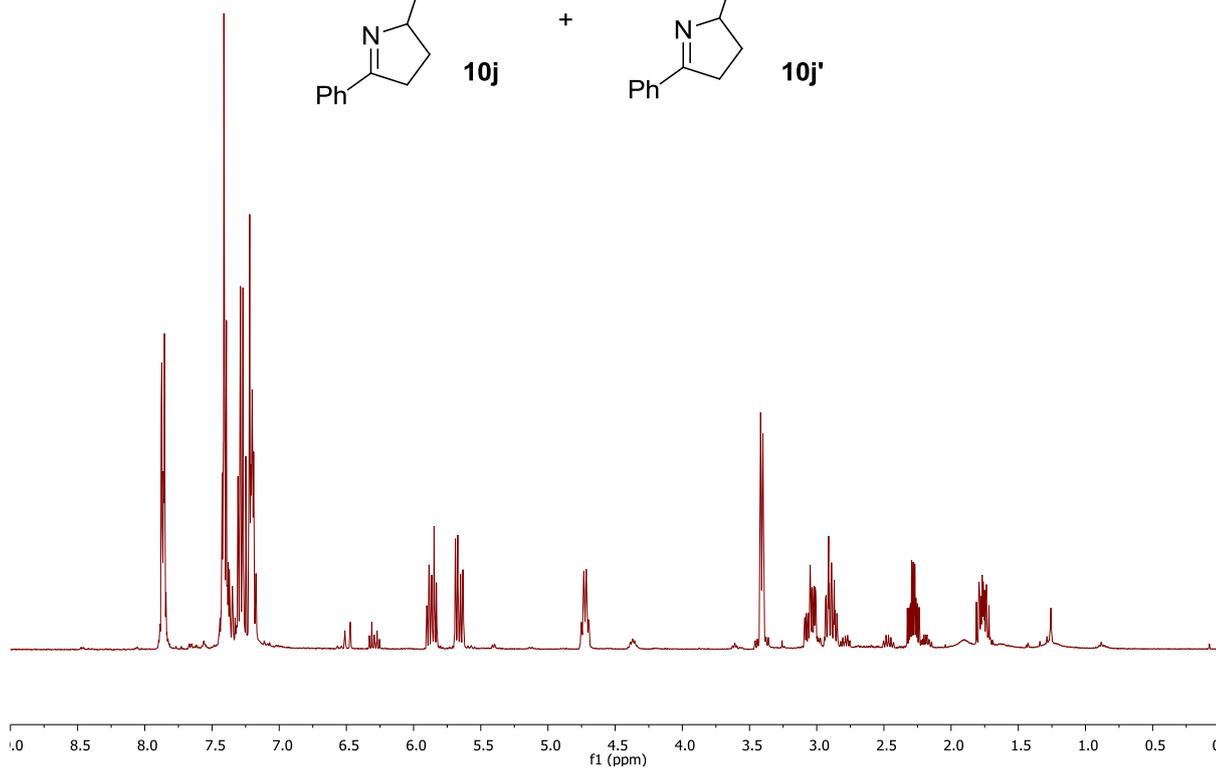
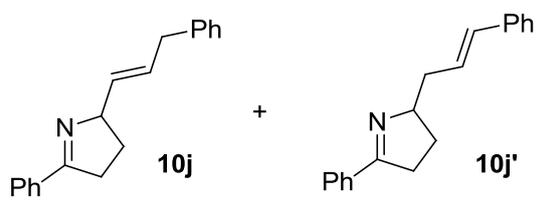


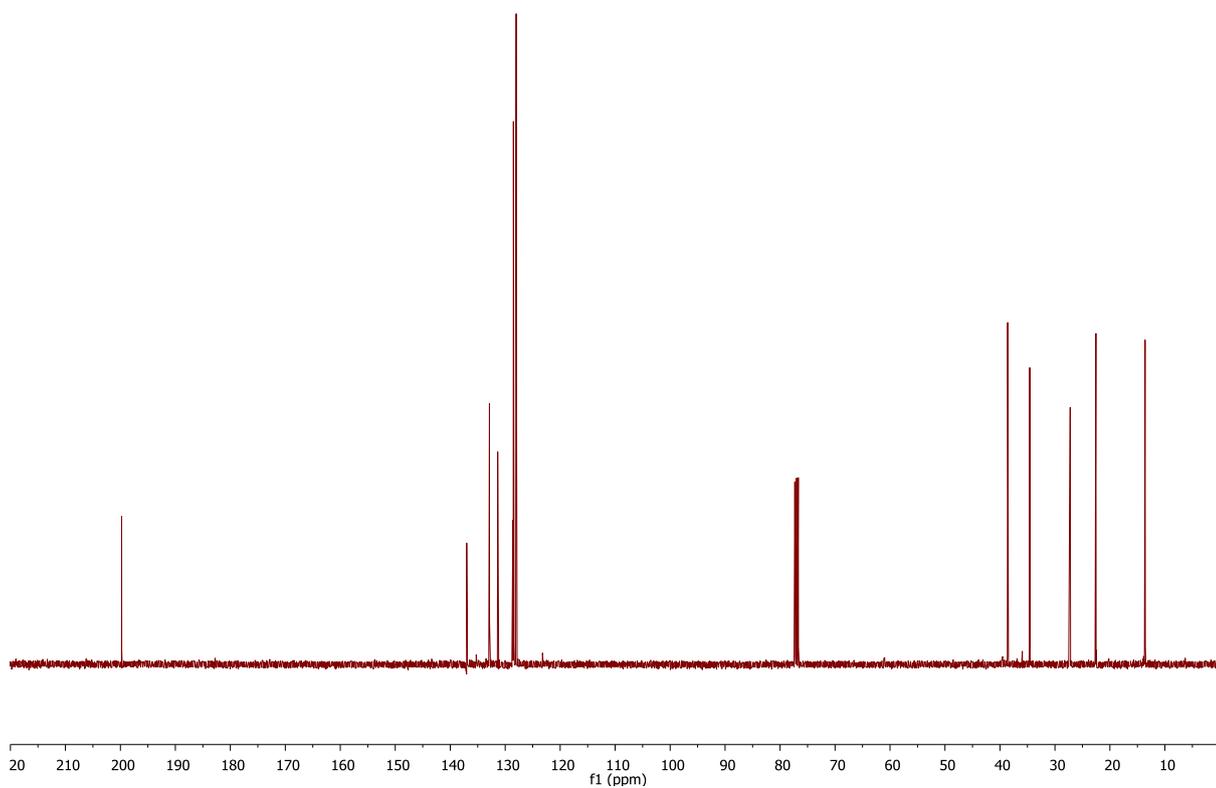
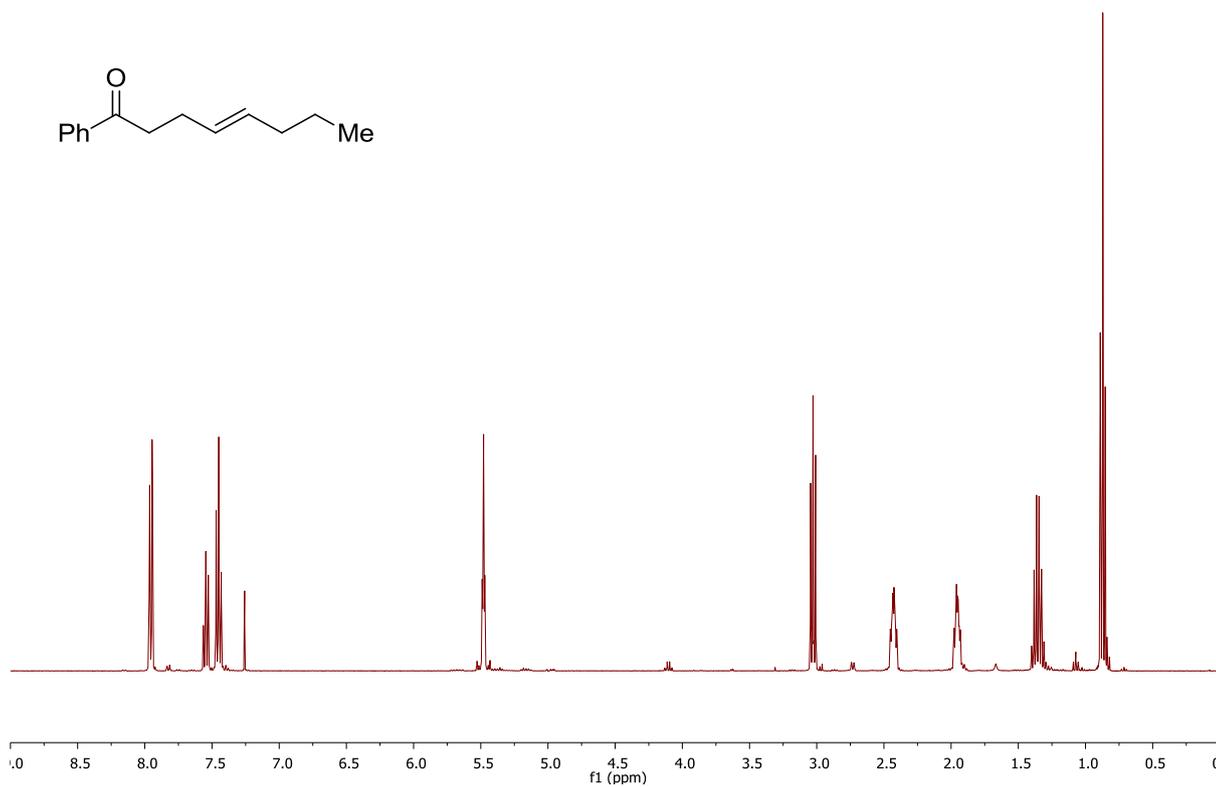
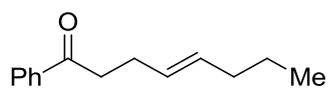


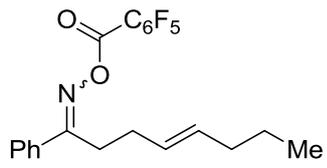




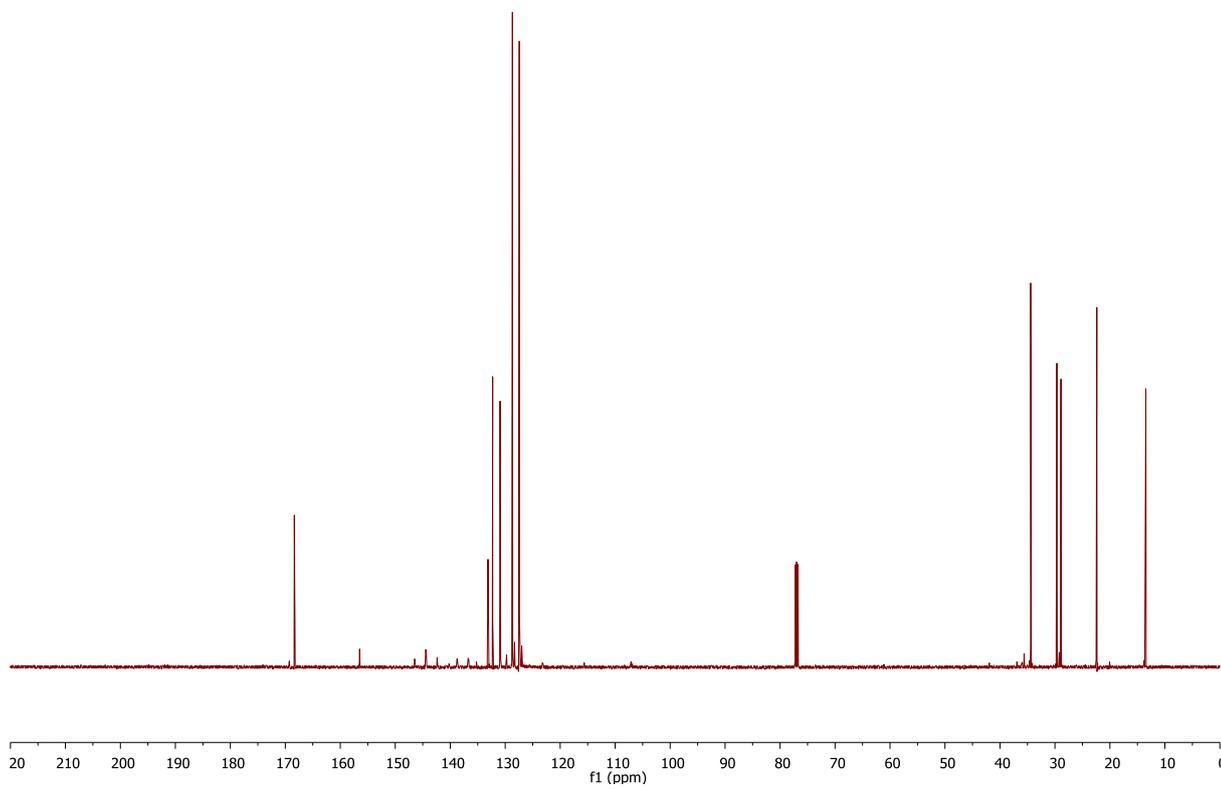
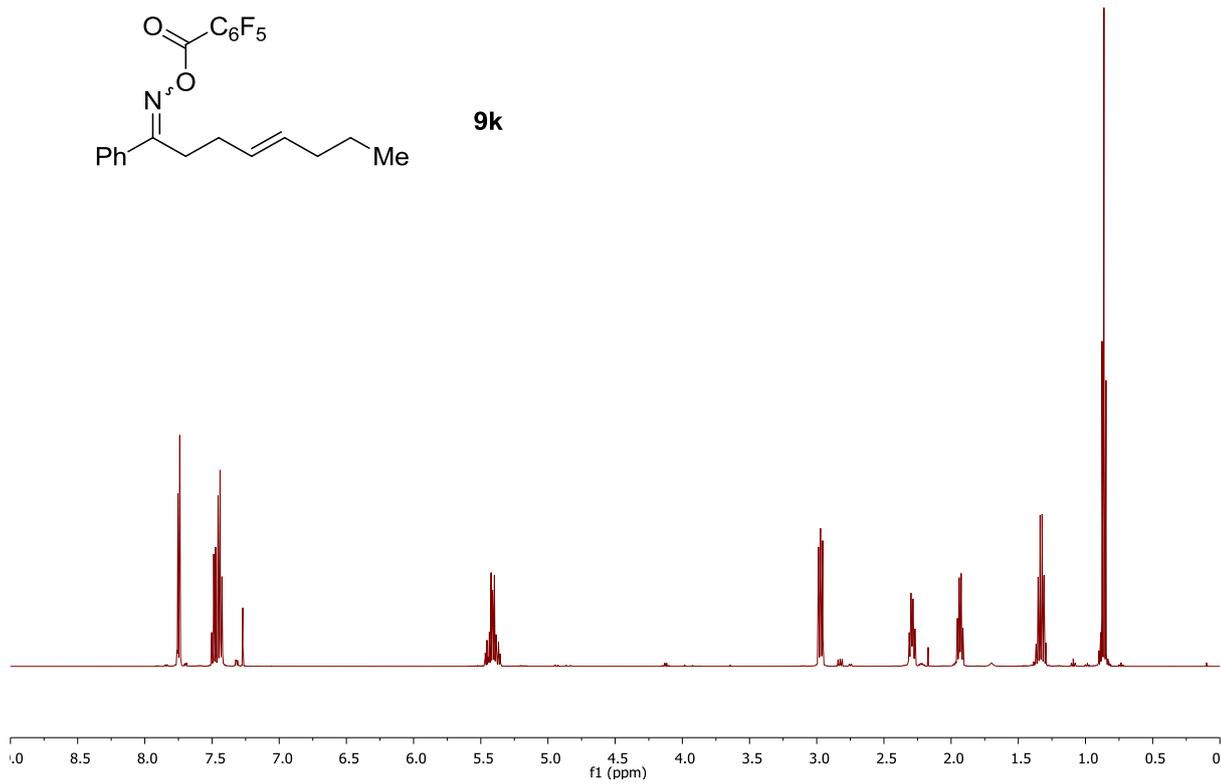


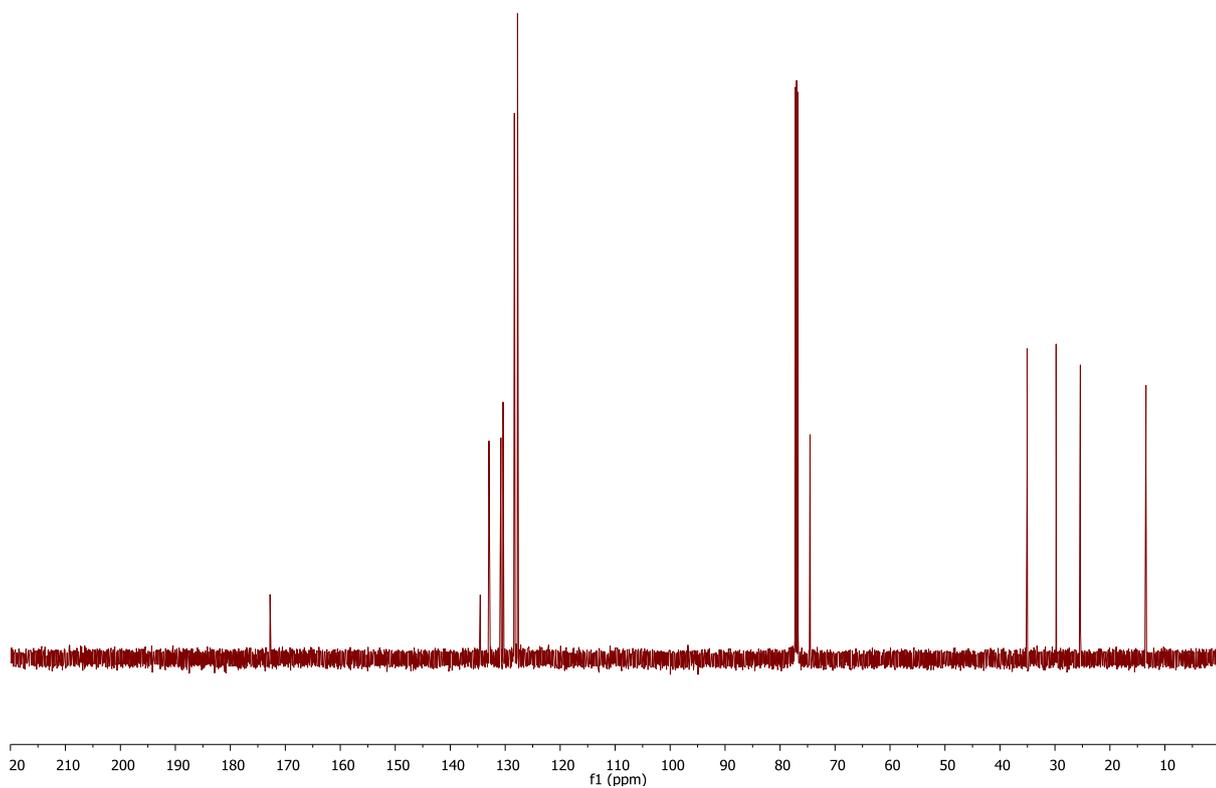
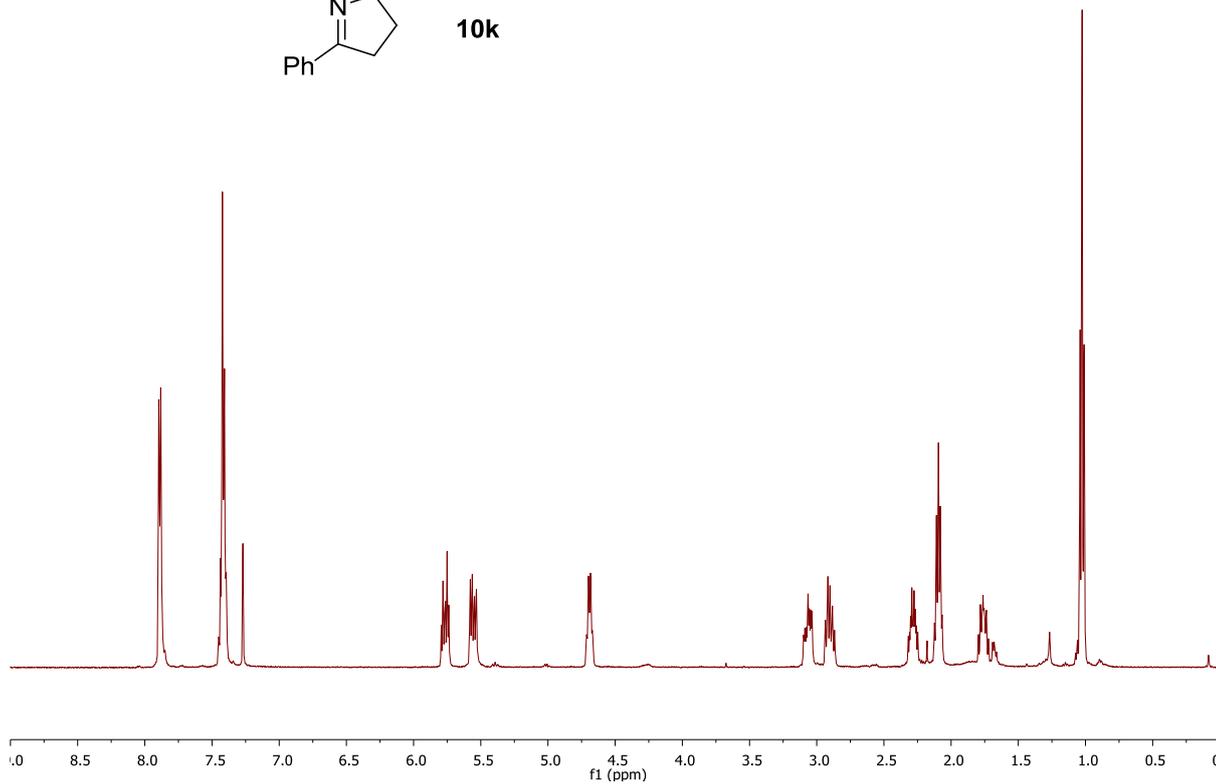
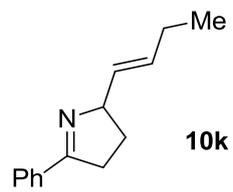


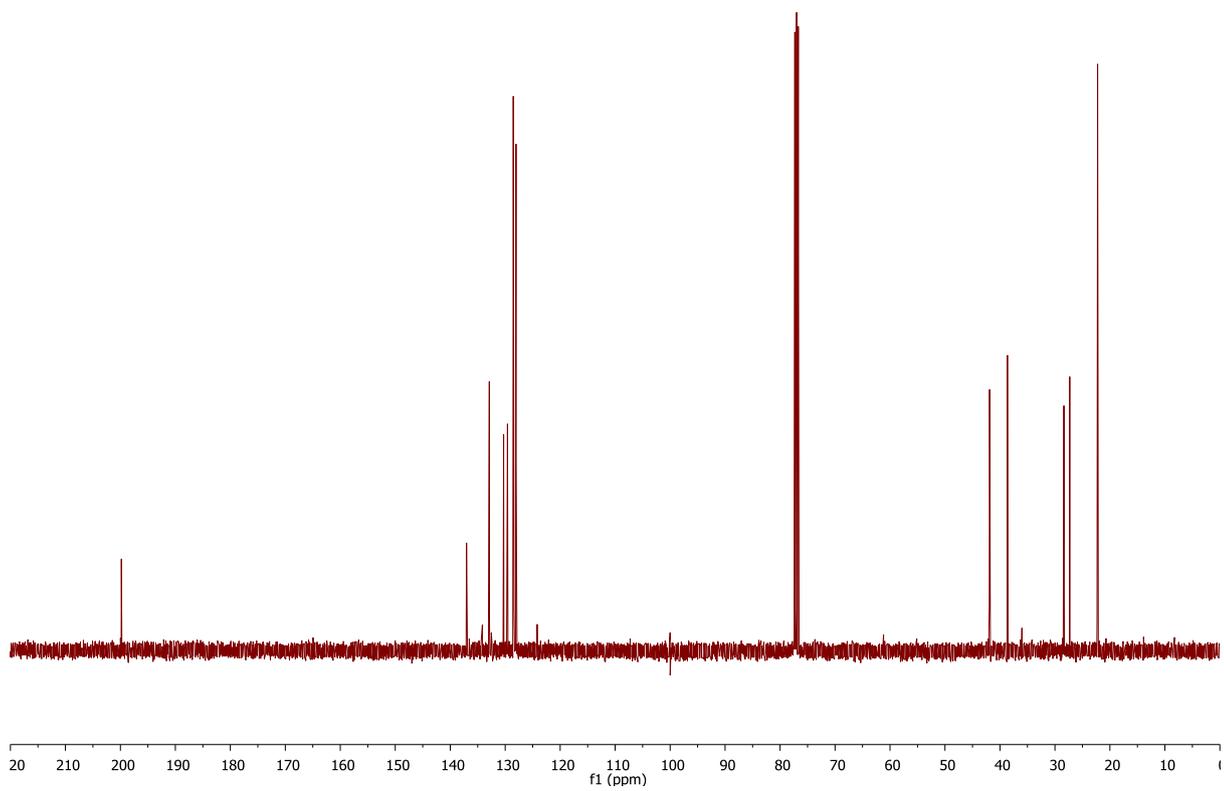
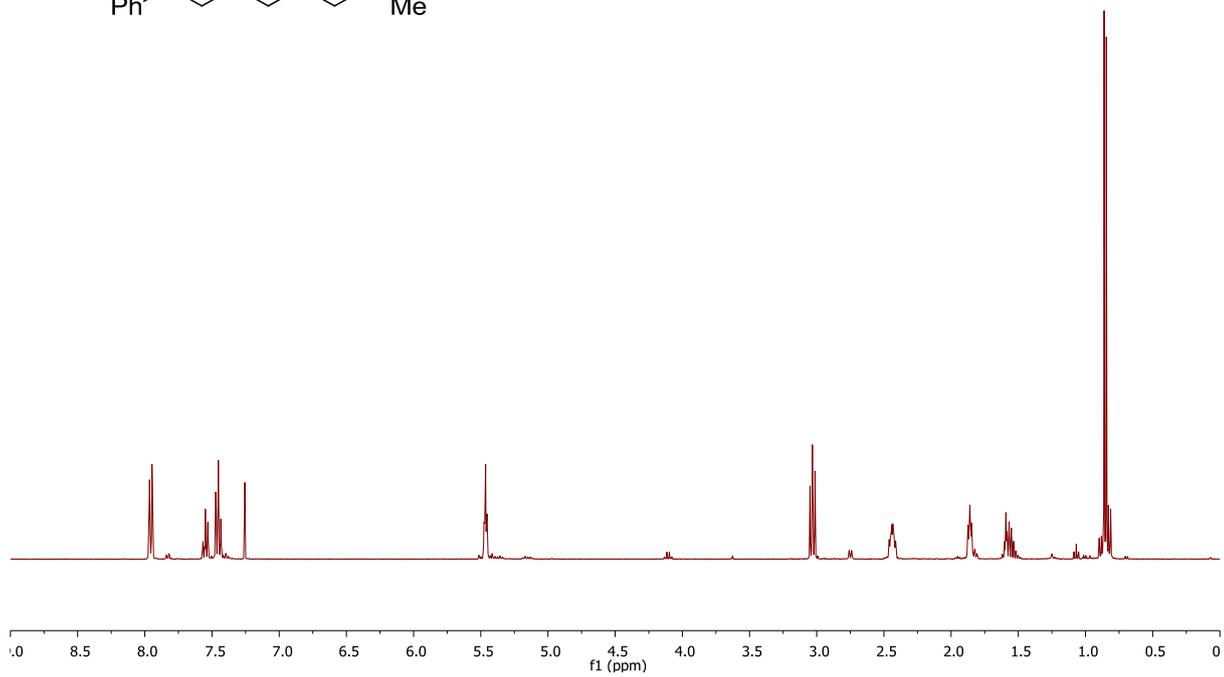
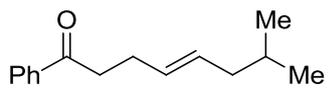


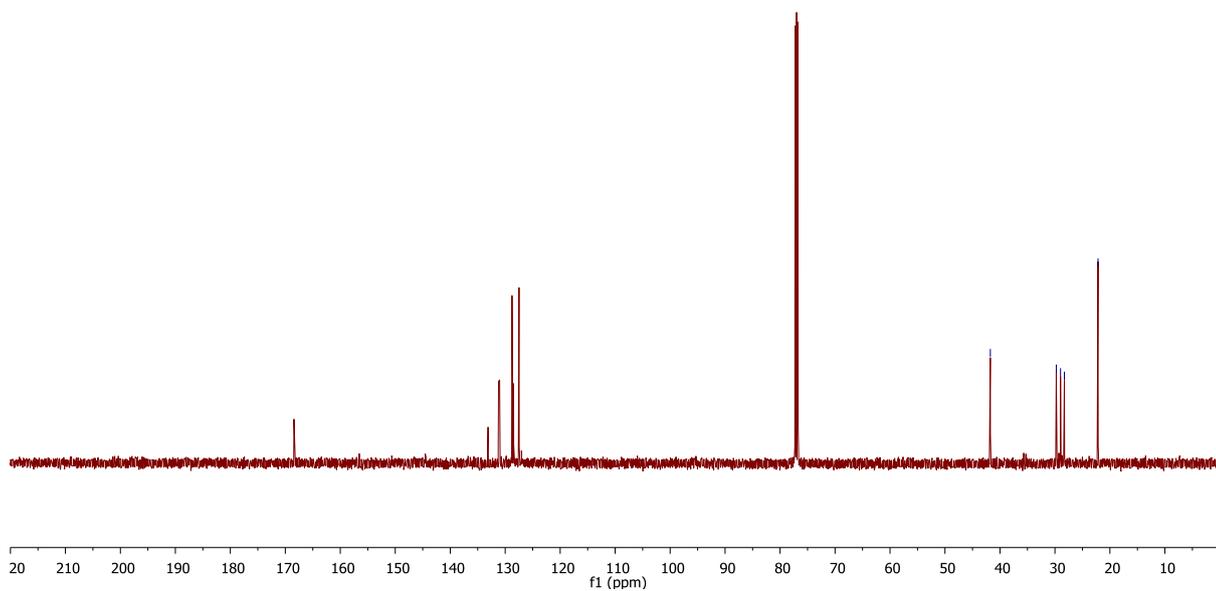
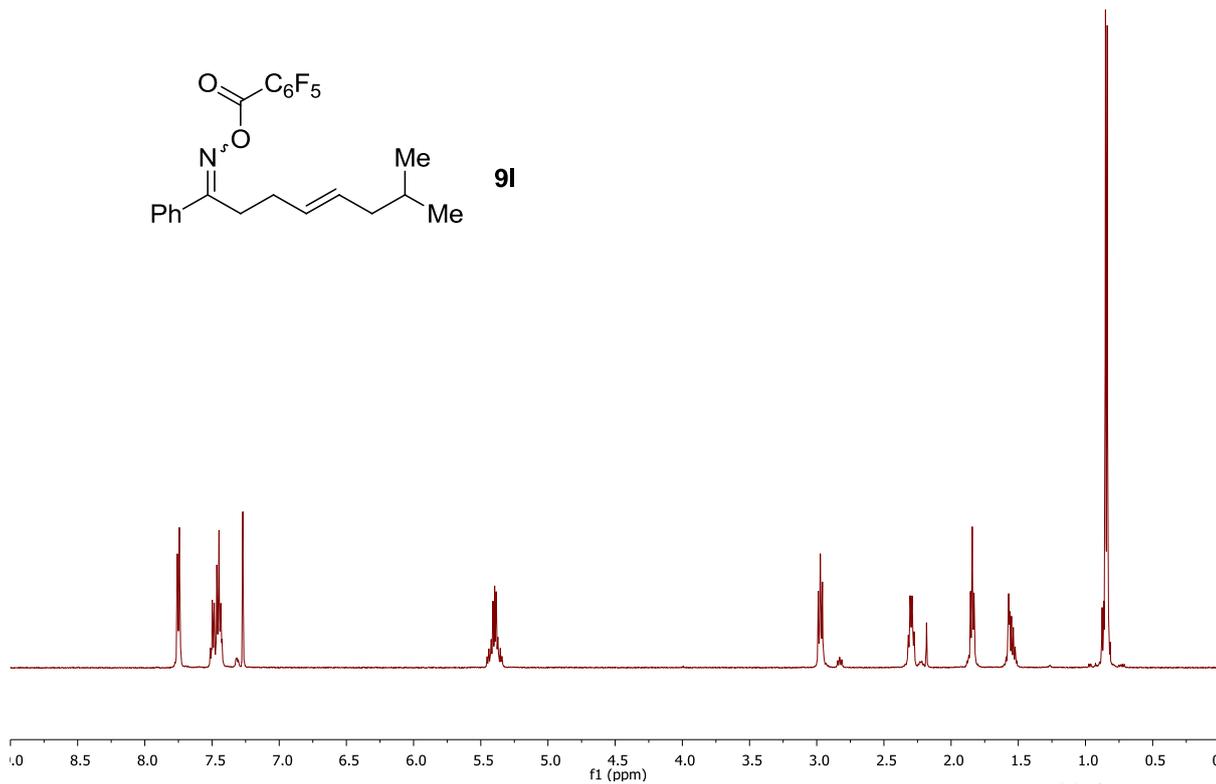
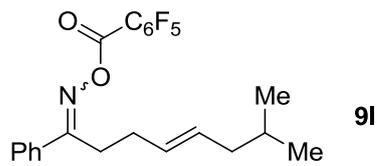


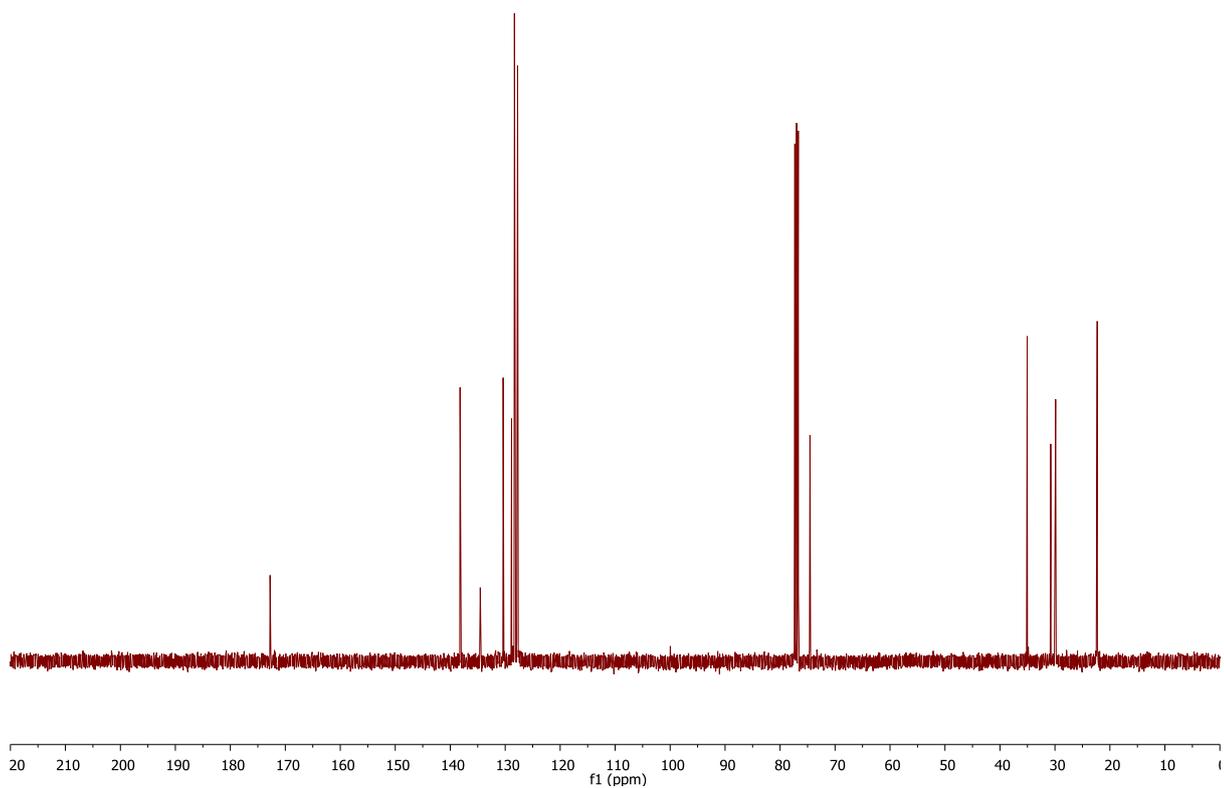
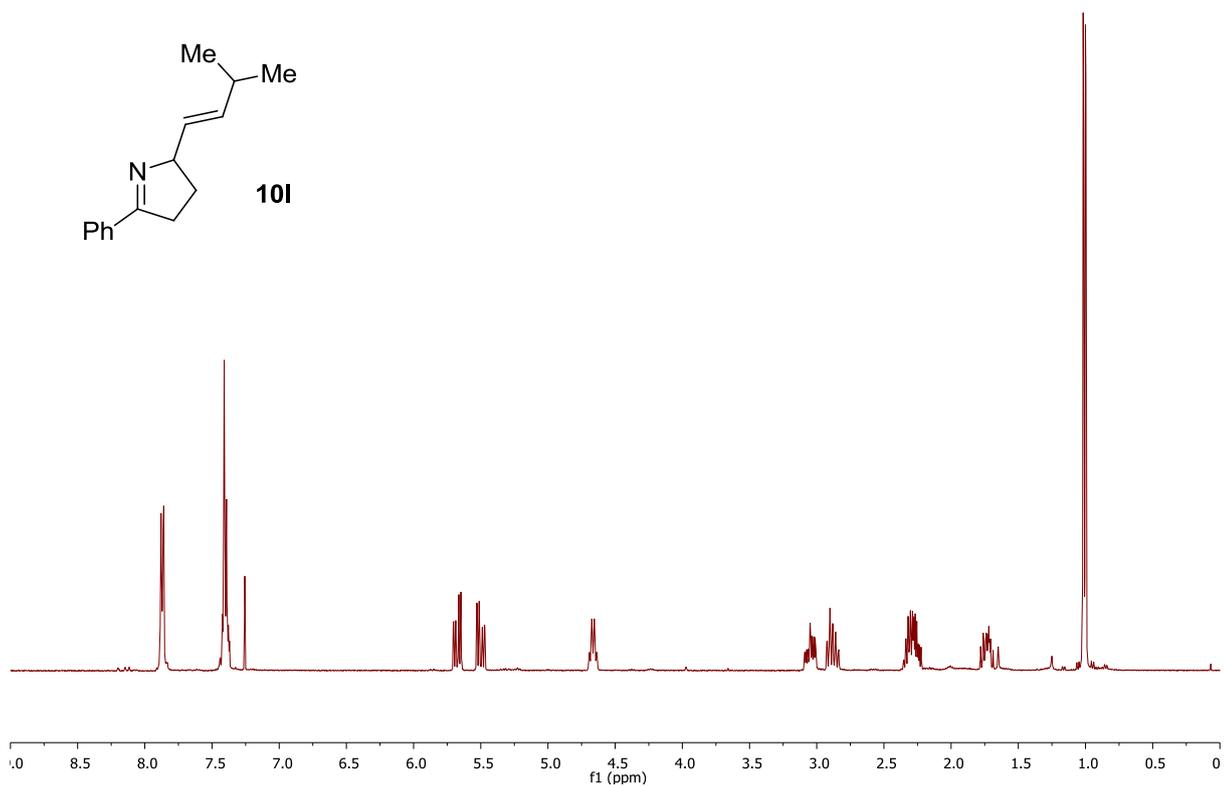
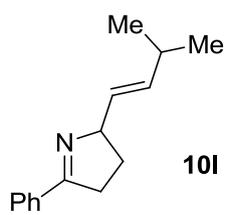
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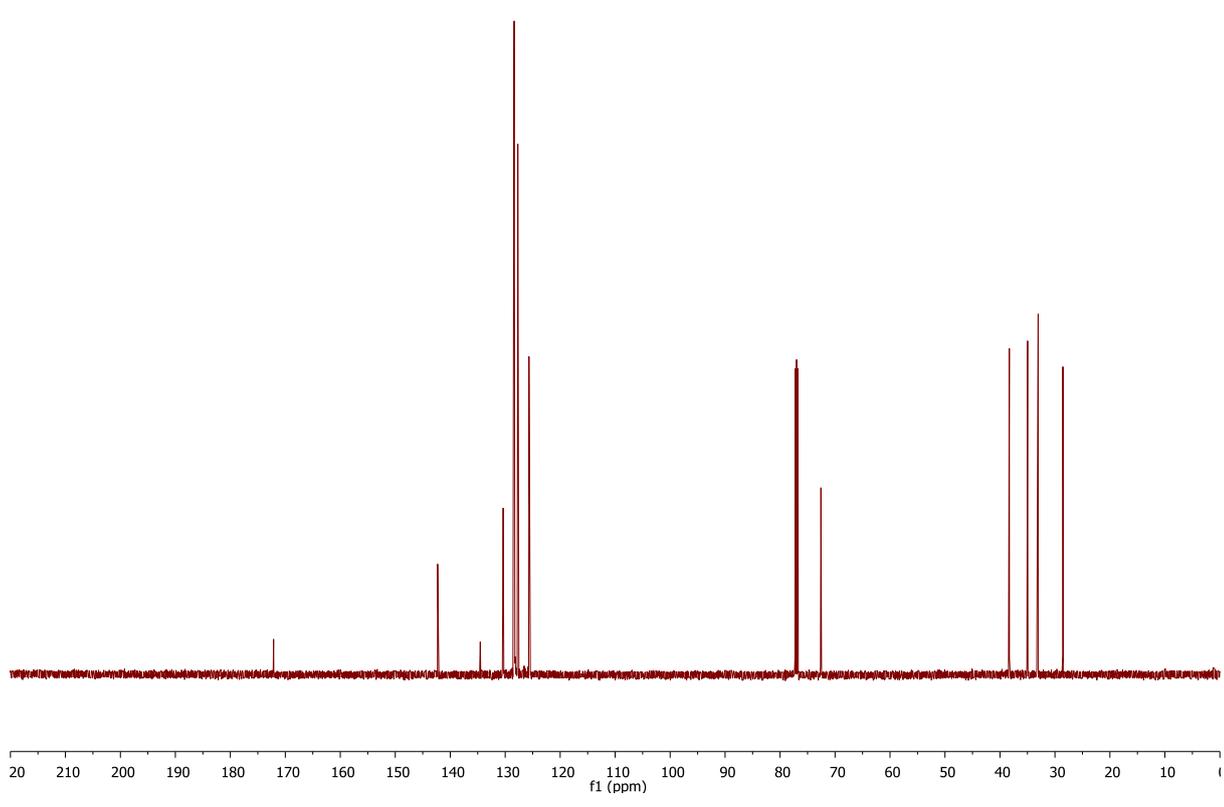
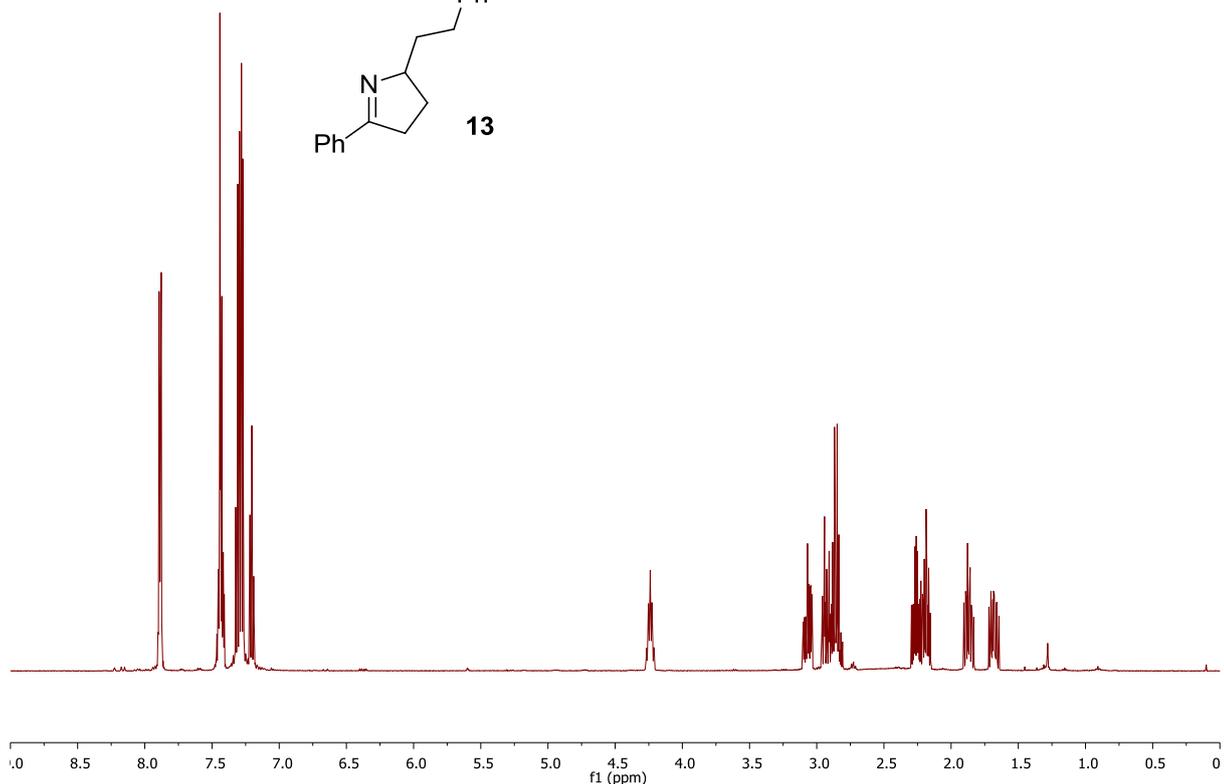
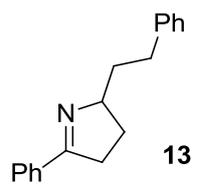


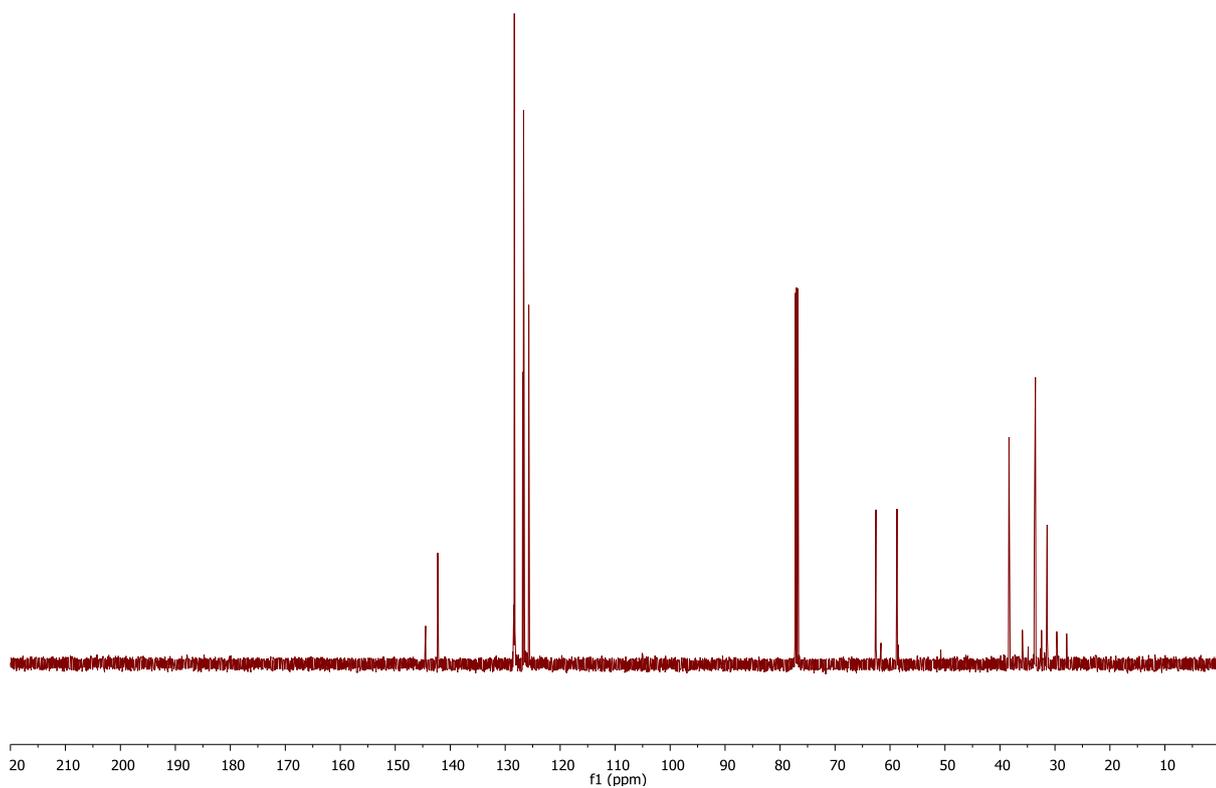
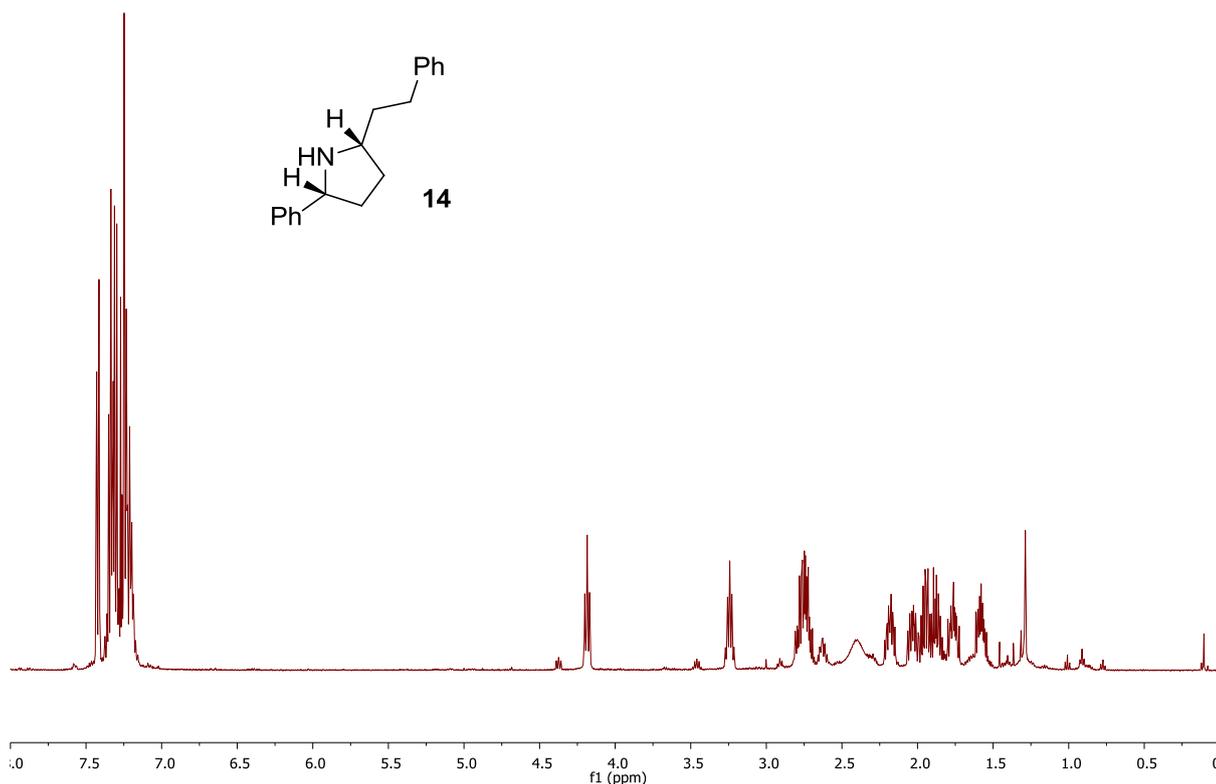
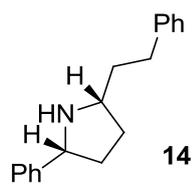


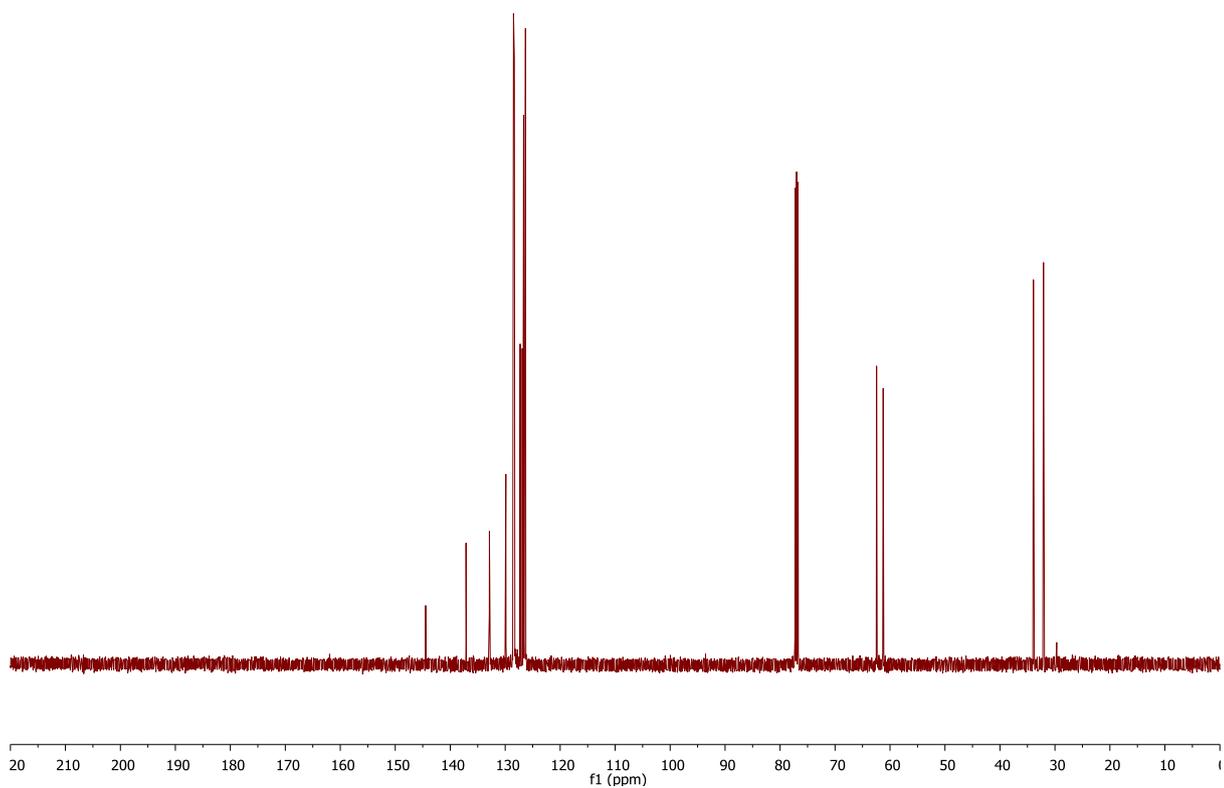
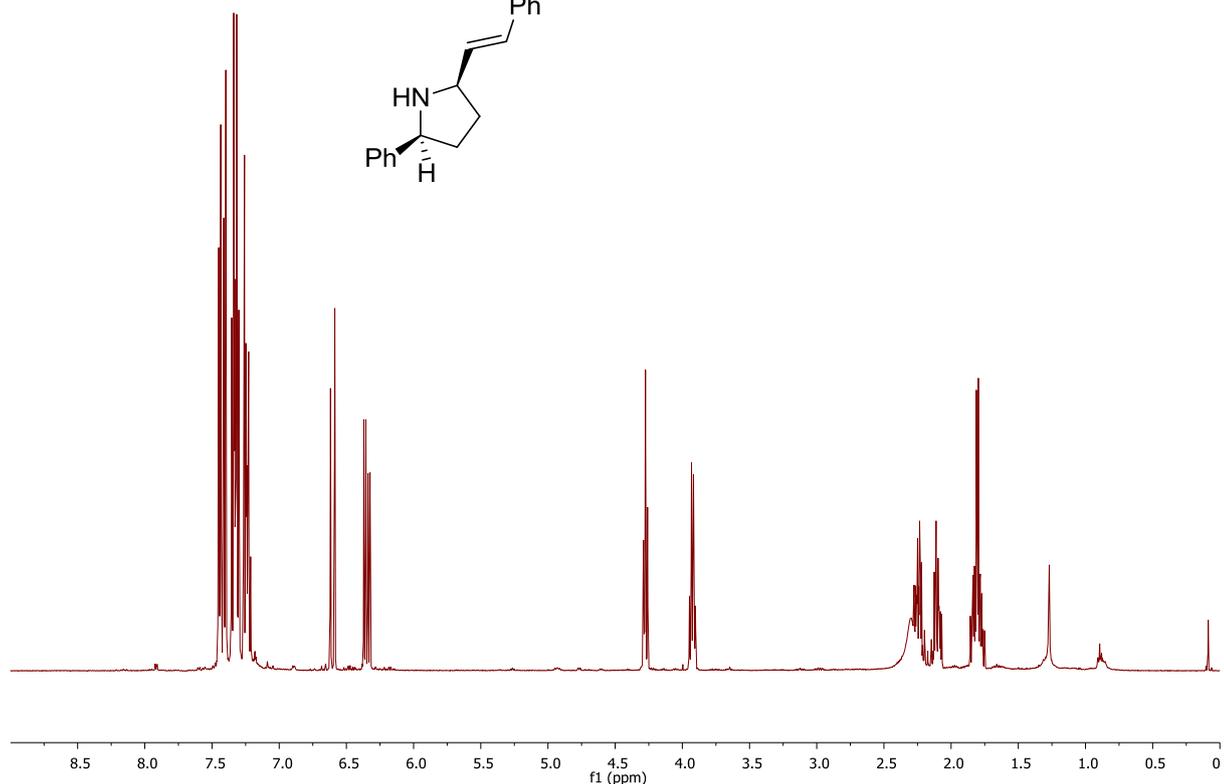
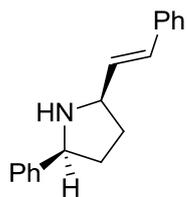


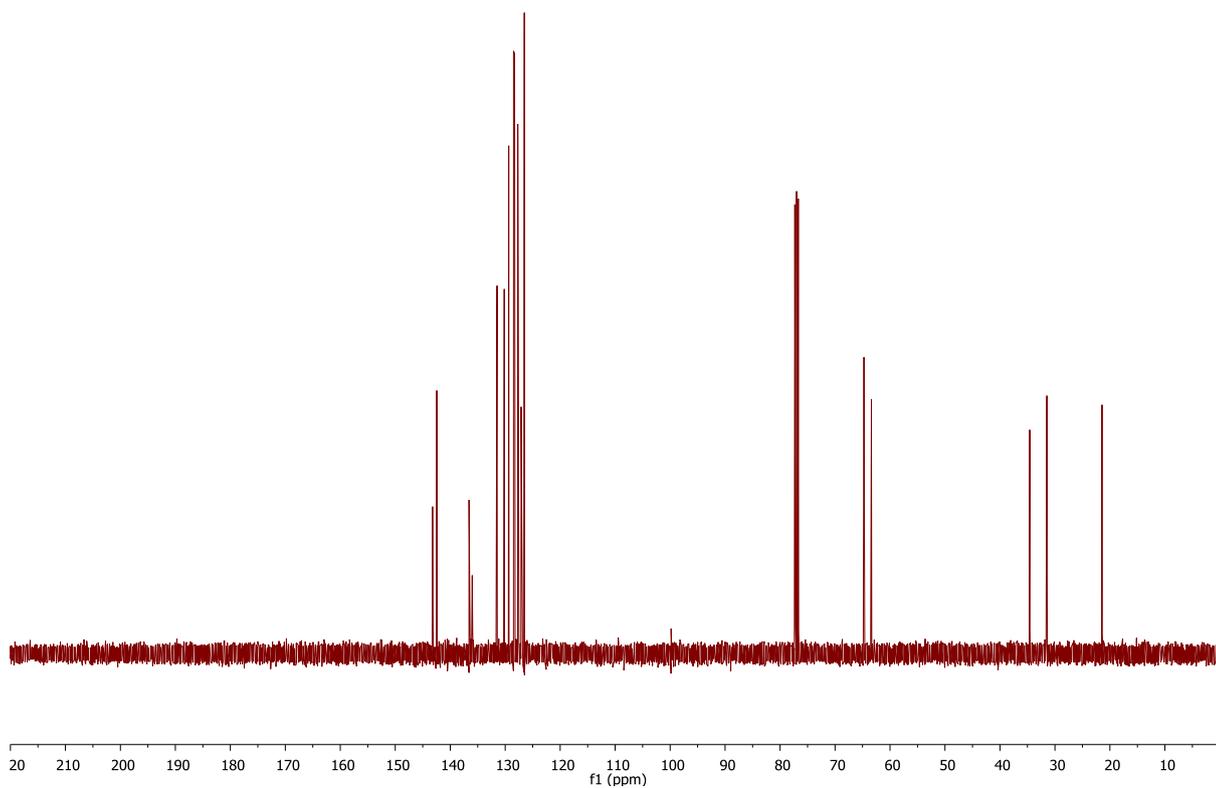
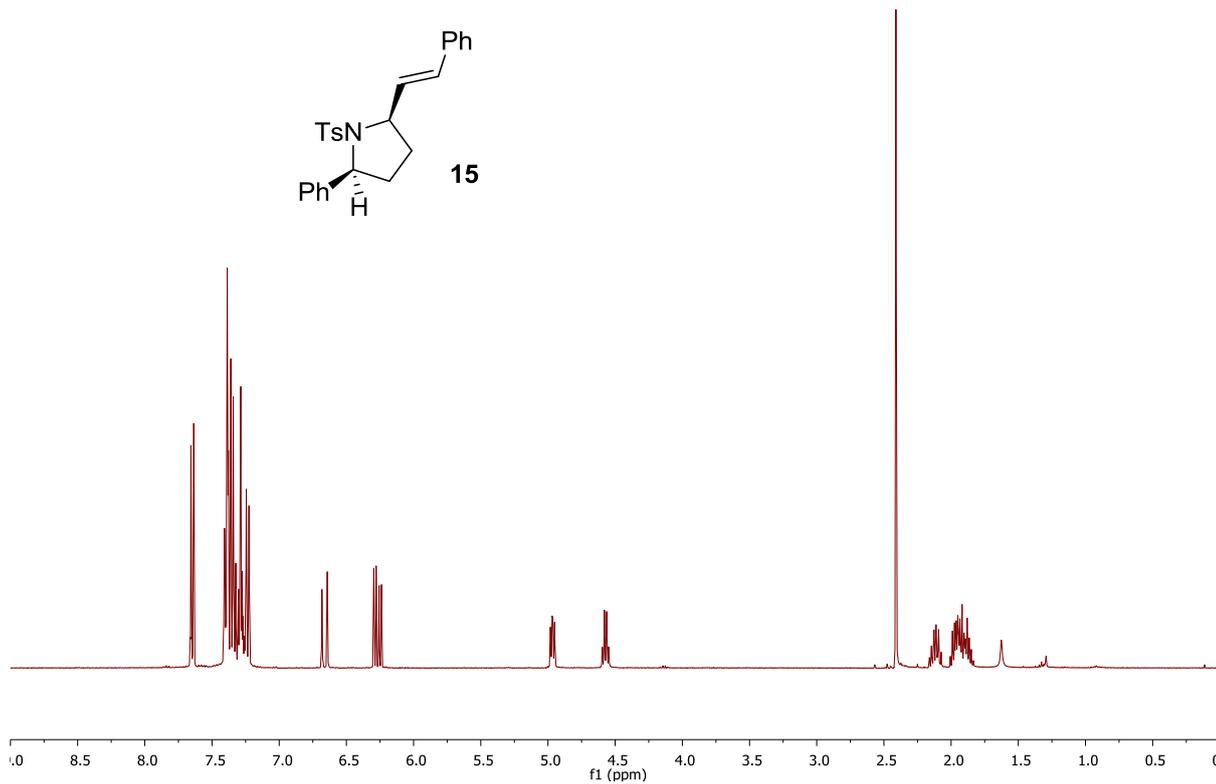
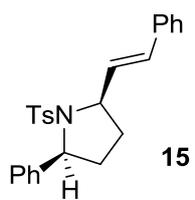


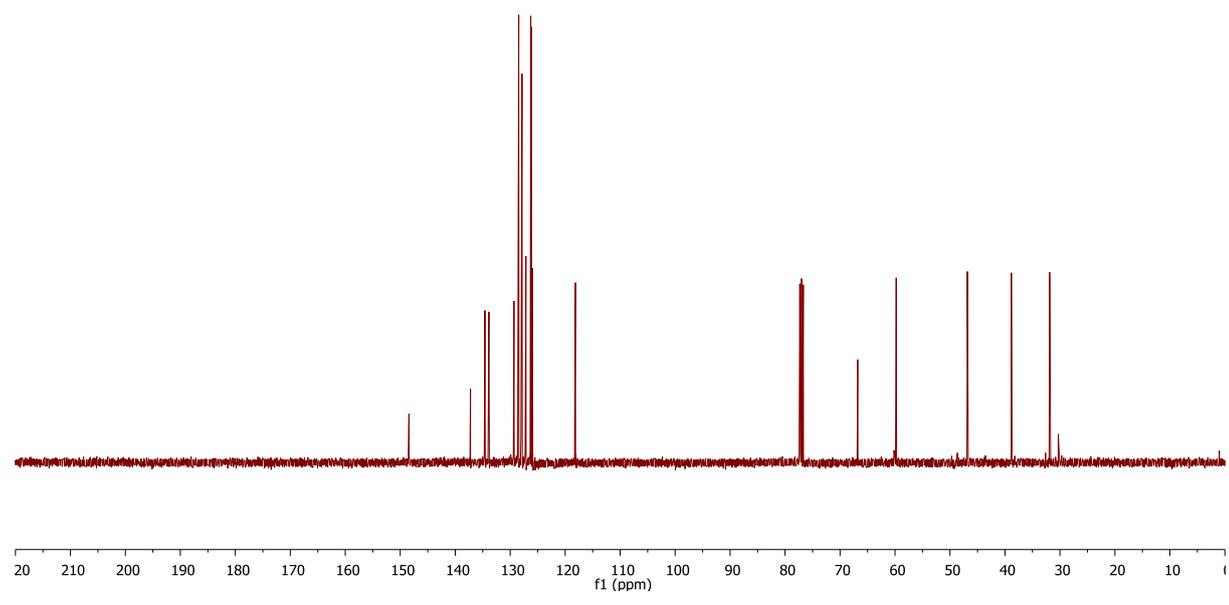
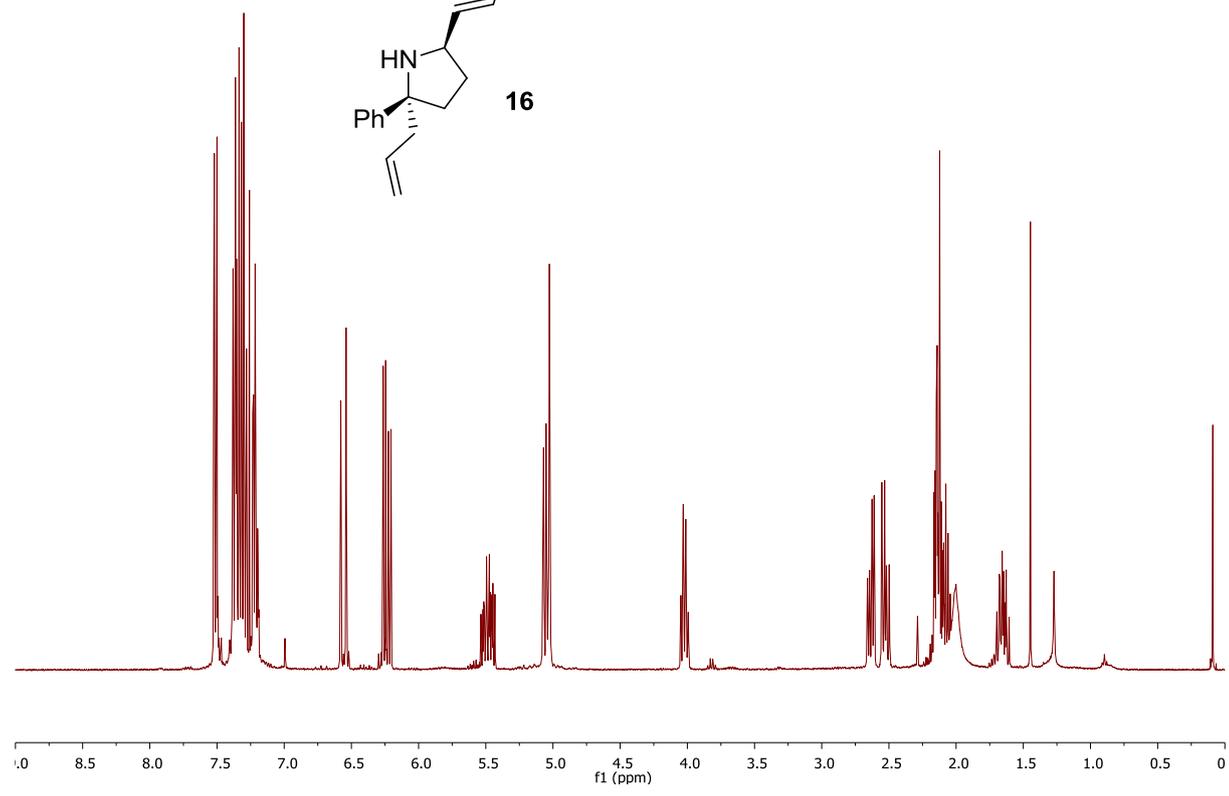
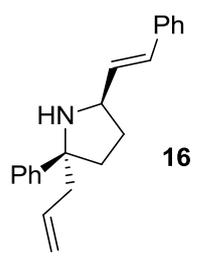


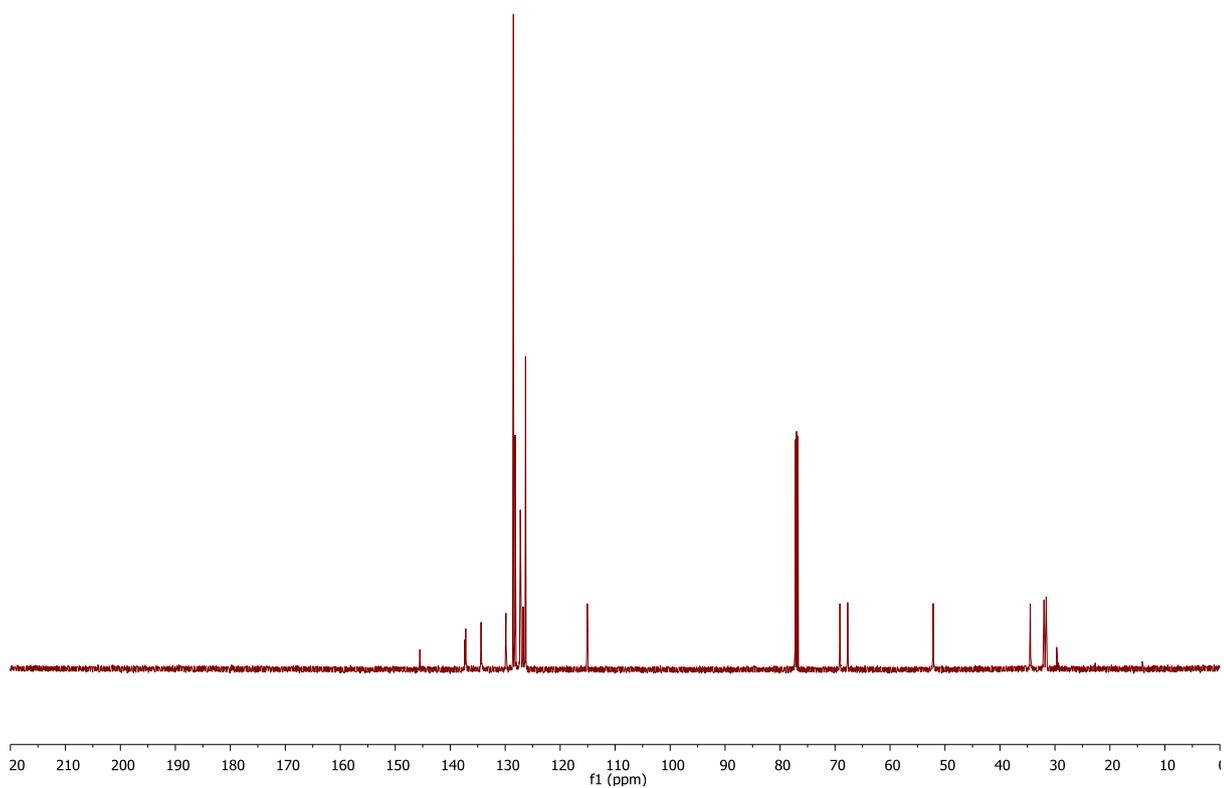
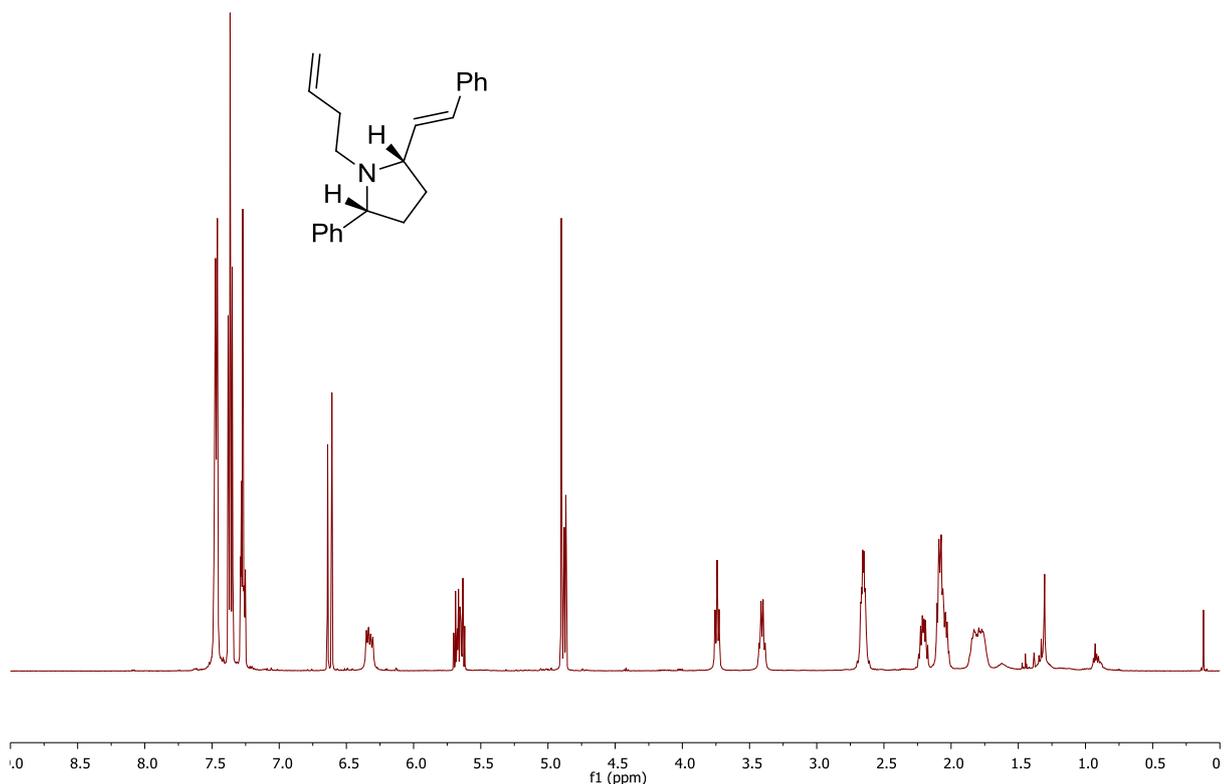


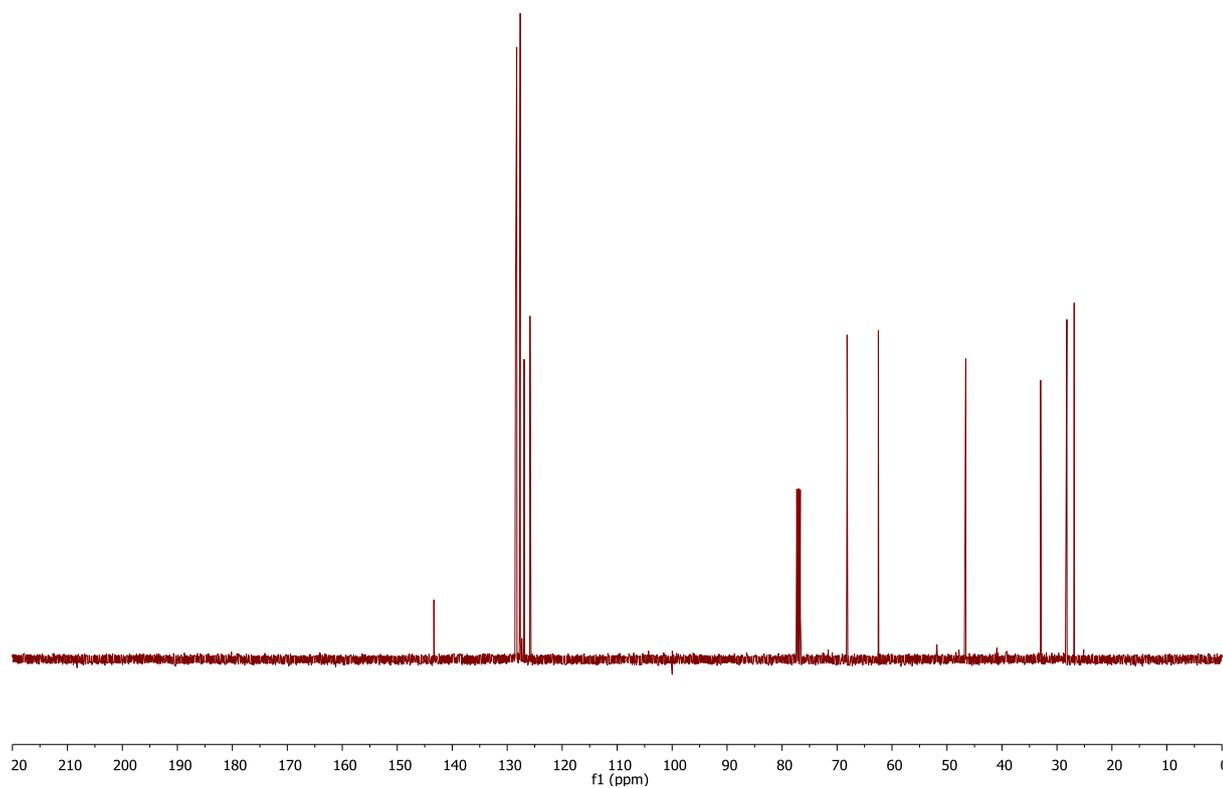
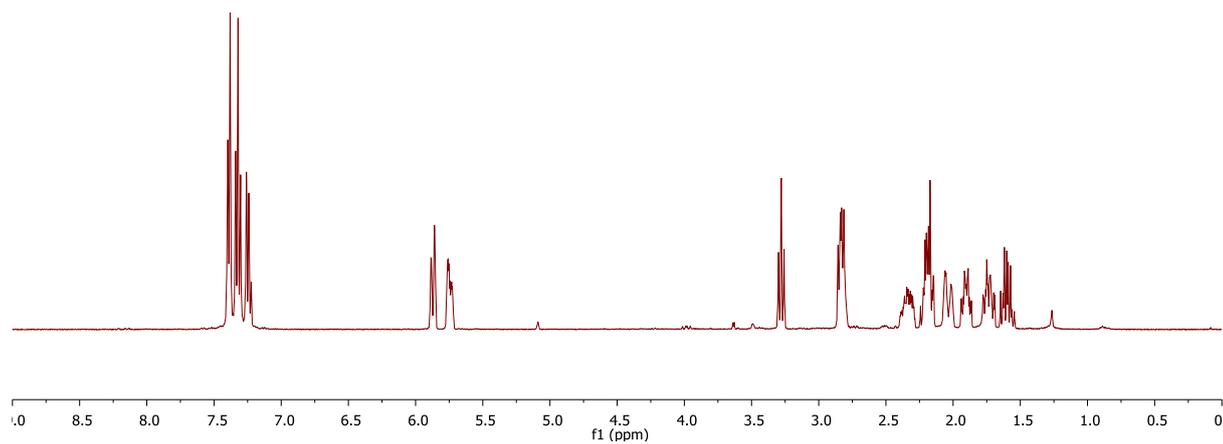
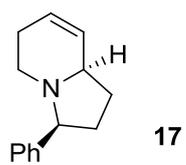


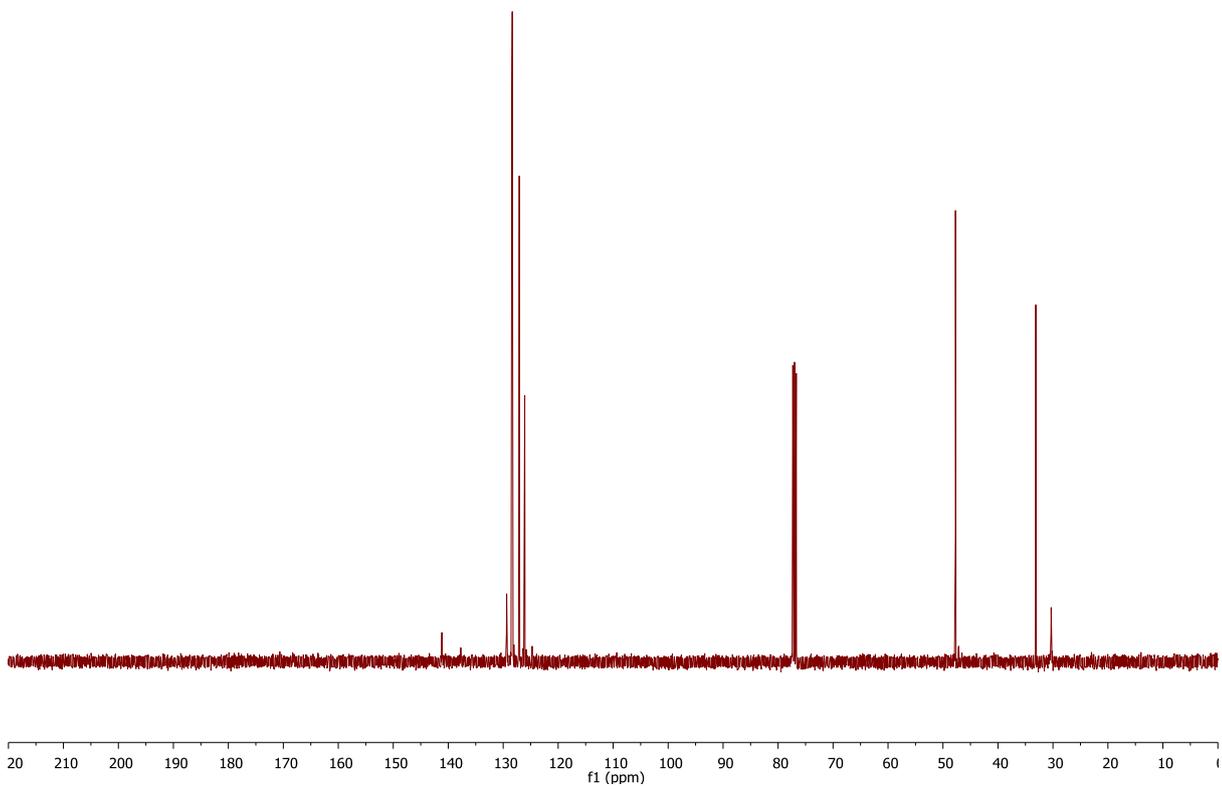
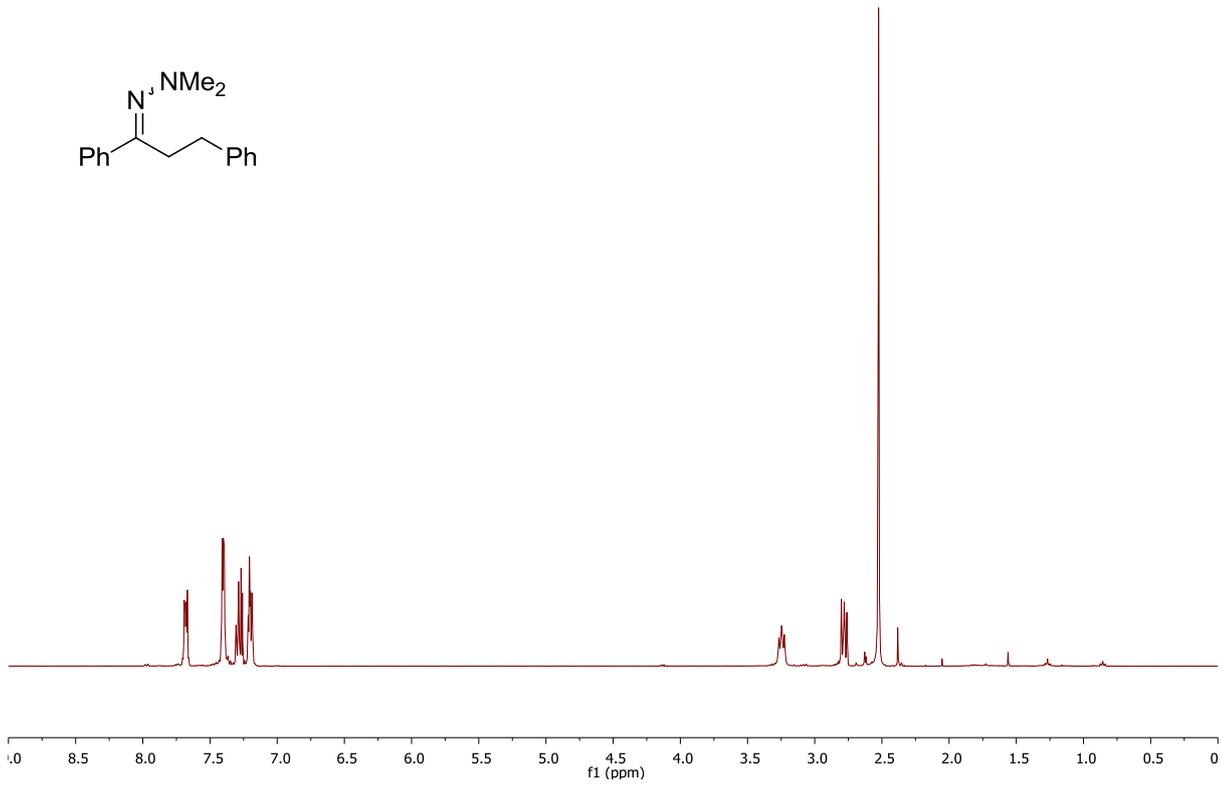
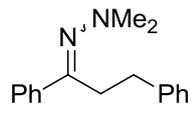


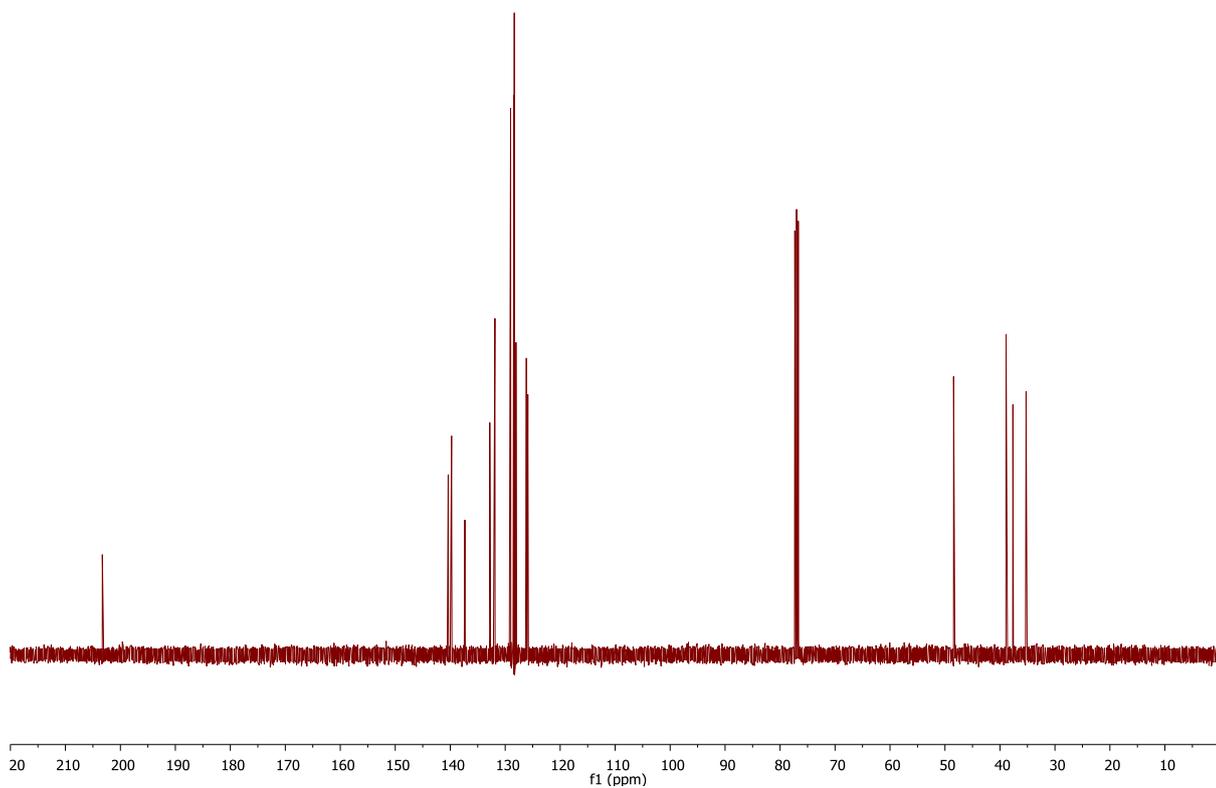
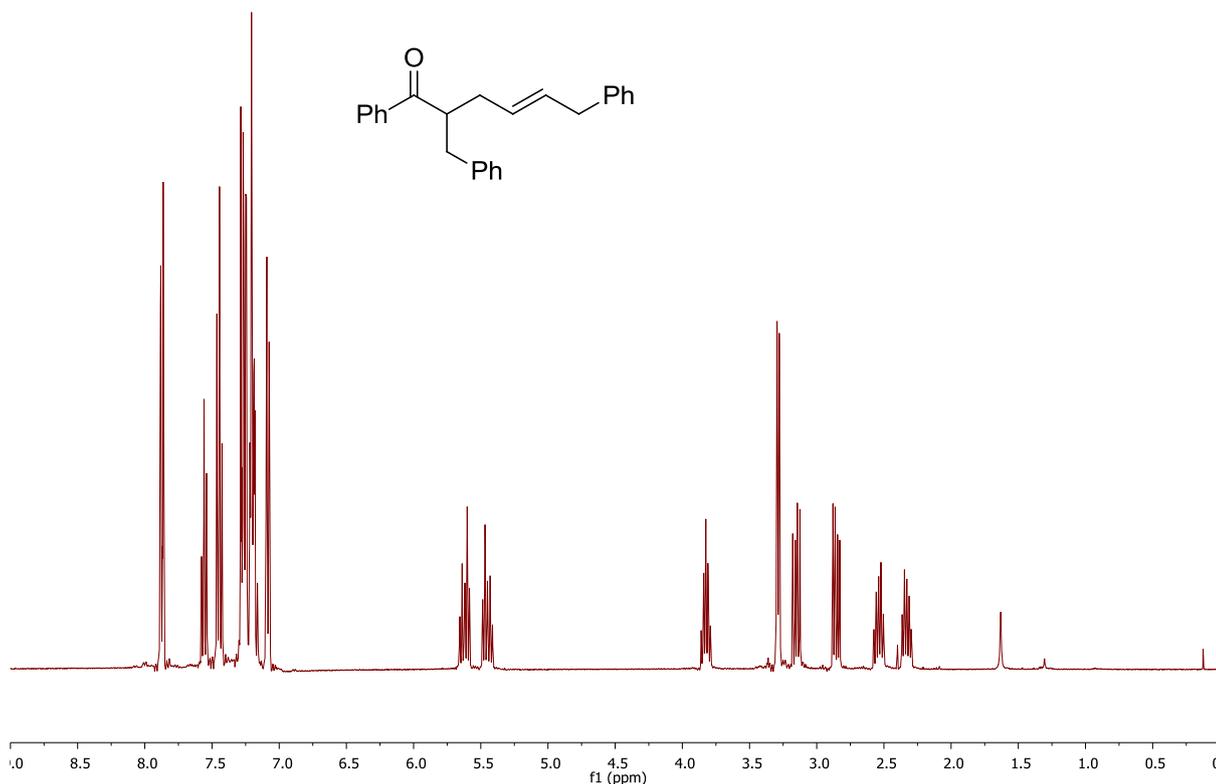
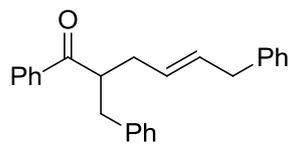


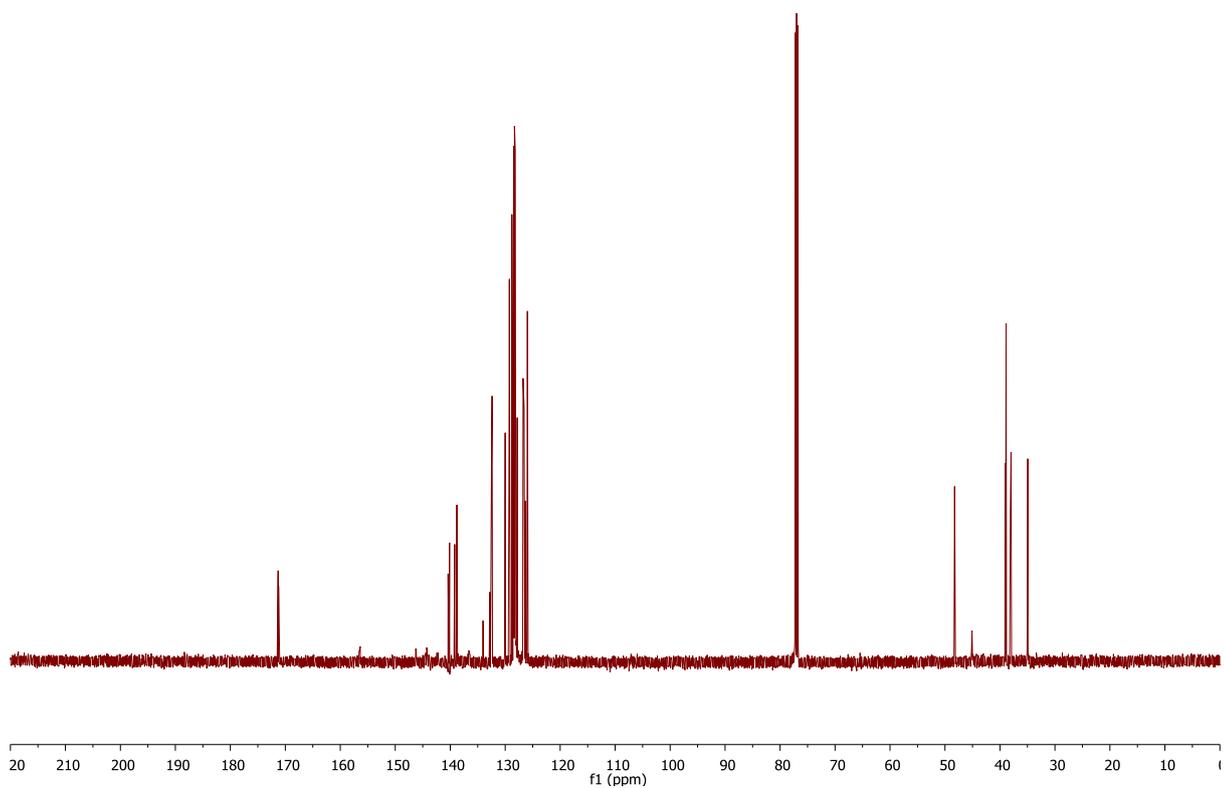
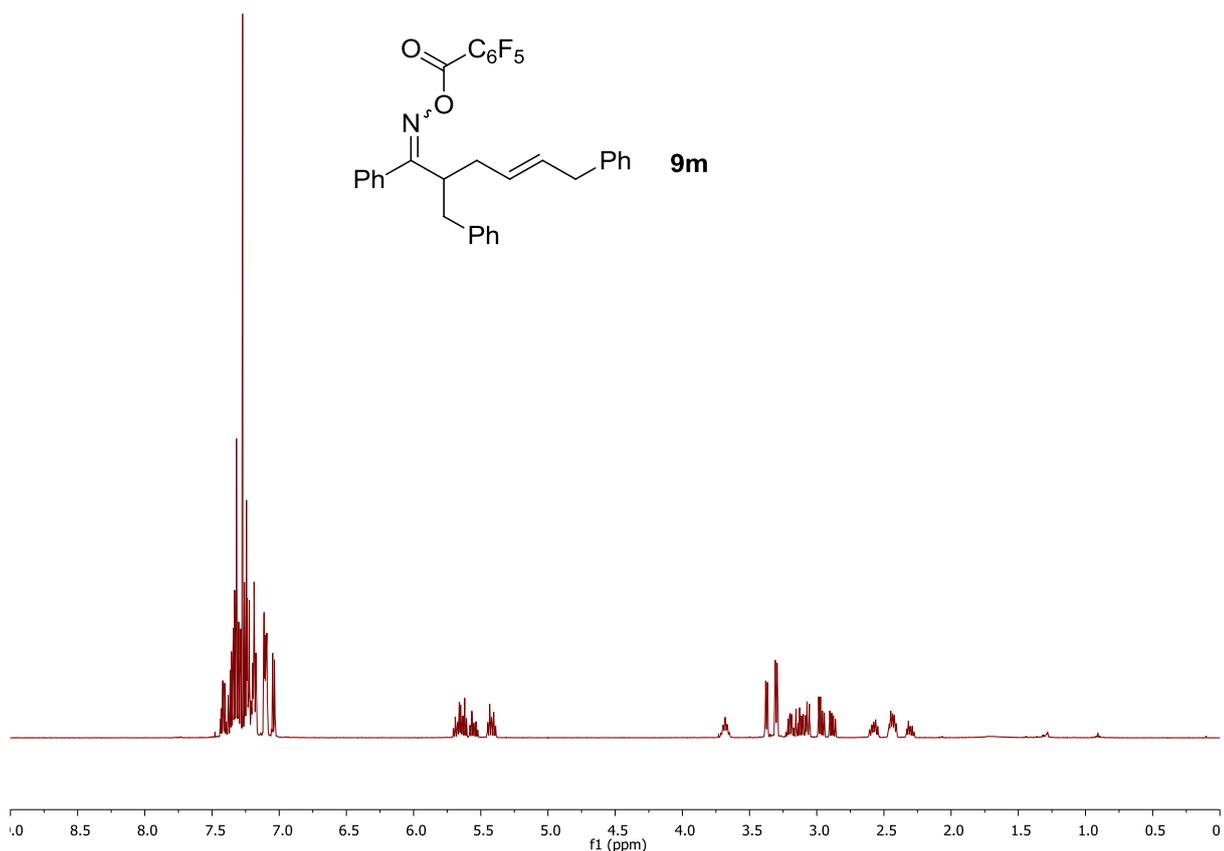
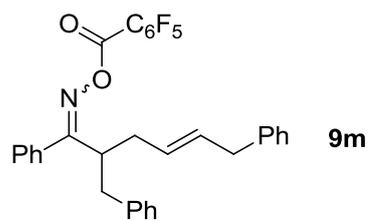


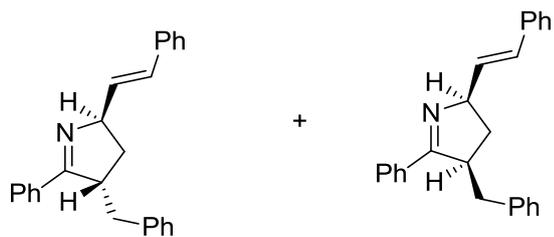












**10m**, major diastereomer (8:1 (*E*):(*Z*)-alkene isomers)      **10m**, minor diastereomer (10:1 (*E*):(*Z*)-alkene isomers)

