Copper Catalyzed Heck-Like Cyclizations of Oxime Esters

Adele Faulkner[a], Nicholas J. Race[a], James S. Scott[b] and John F. Bower[a]*

[a] School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK.
[b] AstraZeneca, Alderley Park, Macclesfield, Cheshire, SK10 4TG, UK.

Electronic Supplementary Information

Table of Contents

General Experimental Details

All reactions involving air-sensitive reagents were performed under a dry nitrogen atmosphere under Schlenk techniques. Anhydrous DMF was purchased from Sigma Aldrich or obtained by distillation from CaH_2. Anhydrous CH_2Cl_2 and THF were obtained by passage through a column of anhydrous alumina. Removal of solvents *in vacuo* was achieved using a Büchi rotary evaporator with bath temperatures up to 50 ºC. Flash column chromatography (FCC) was carried out using Fluorochem 60 silica: 230-400 mesh (40-63 µm). Reactions were monitored by thin layer chromatography (TLC) analysis using Merck Kieselgel $60F_{254}$ aluminium backed plates. Spots were visualized by UV light (λ_{max} = 254nm) and were stained with $KMnO_4$, vanillin or anisaldehyde solutions as required.

^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz JEOL Eclipse 400, Varian 400-MR and Varian 500-MR spectrometer in $CDCl_3$ and referenced to $CDCl_3$ (7.26/77.0 ppm). Chemical shifts are quoted in parts per million (ppm) and coupling constants (*J)* are quoted to the nearest 0.5 Hz. Splittings are recorded as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), heptet (hept) and broad singlet (br. s). Assignments were based upon DEPT, COSY, HMBC and HSQC experiments. Where mixtures of isomers (*e.g.* diastereomers) are characterized together, integrals are normalized to the major isomer. nOe experiments (performed using a Varian VNMR S500b spectrometer) were used where appropriate. Signal assignments for each compound are indicated using an arbitrary numbering system which does not correspond to the IUPAC name.

Infrared spectroscopy was performed on a Perkin Elmer Spectrum RX/FT-IR System Spectrometer and recorded in the range 4000-600 cm^{-1} as a thin film. IR absorbances are quoted in wavenumbers (cm^{-1}).

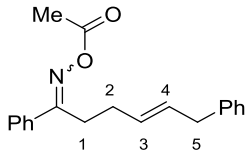
Mass spectra were recorded using either electrospray ionization (ESI^+), performed on a Bruker Daltonics 7.0 Telsa Apex 4 Fourier Transform Ion Cyclotron Resonance (FT-ICR) or chemical ionization (CI^+), performed on a Perkin Elmer Turbo Mass Gold Quadrupole.

Experimental Procedures and Data

General Procedure A for oxime ester formation: Part A: $H_2NOH.HCl$ (120 mol%) and NaOAc (120 mol%) were added to a solution of the appropriate ketone (100 mol%) in MeOH (3 mL/mmol). The mixture was heated at 75 °C until consumption of starting material as shown by TLC analysis. After cooling to room temperature, the mixture was diluted with EtOAc (10 mL/mmol), washed with brine (10 mL/mmol), dried (Na_2SO_4) and concentrated *in vacuo*. The 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_2Cl_2 (3 mL/mmol) at 0 °C was added, *via* syringe, Et_3N (200 mol%) and then ClC(O)*t*Bu (120 mol%). The mixture was then warmed to room temperature and stirred until starting material was consumed (TLC). MeOH (0.5 mL/mmol) and then EtOAc (15 mL/mmol) were added. The mixture was then washed with saturated aq. Na_2CO_3 (2 × 15 mL/mmol) and brine (15 mL/mmol), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by FCC, under the conditions noted, to afford the corresponding oxime ester.

General Procedure B for copper catalysed heck-type cyclizations: An oven-dried reaction tube, fitted with magnetic stirrer, was charged with Cu(II)(2-ethylhexanoate)$_2$ (10 mol%) and oxime ester substrate (100 mol%). The tube was fitted with a rubber septum and purged with argon. Anhydrous benzonitrile (7.5 mL/mmol) was added *via* syringe. The mixture was then placed in a preheated oil bath (100 °C) until complete consumption of starting material was observed (TLC analysis). The mixture was then cooled to room temperature and concentrated *in vacuo* (40 °C, *ca.* 1.0 mmHg). The residue was purified by FCC, under the conditions noted, to afford the target heterocycle.

Oxime ester **5** was synthesized according to a literature procedure.[1]



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

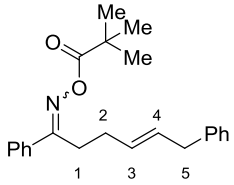
To a solution of (4*E*)-1,6-diphenylhex-4-en-1-one oxime[1] (0.30 g, 1.13 mmol) in pyridine (3 mL) was added 4-dimethylaminopyridine (5 mg, 0.04 mmol) and acetic anhydride (0.25 mL, 2.26 mmol). The reaction was stirred for 16 hours and then 1M HCl (5 mL) was added. The organic extract was washed with saturated aq. Na_2CO_3 (5 mL). H_2O and pyridine were removed by azeotroping with toluene (2 × 5 mL). FCC (10:1 (hexane-EtOAc)) afforded oxime ester **6** (0.30 g, 86%, 1:0.1 mixture of oxime isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *Signals for the major isomer:* 7.72-7.66 (2H, m, ArC<u>H</u>), 7.46-7.37 (3H, m, ArC<u>H</u>), 7.32-7.28 (2H, m, ArC<u>H</u>), 7.24-7.11 (3H, m, ArC<u>H</u>), 5.62 (1H, dt, *J* = 15.0, 7.0, <u>H</u>4), 5.48 (1H, dt, *J* = 15.0, 7.0, <u>H</u>3), 3.31 (2H, d, *J* = 7.0, <u>H</u>5), 2.94 (2H, t, *J* = 7.5, <u>H</u>1), 2.31 (2H, dt, *J* = 7.0, 7.0, <u>H</u>2), 2.26 (3H, s, COC<u>H</u>$_3$).
Characteristic signals for the minor isomer: 2.79 (0.2H, t, *J* = 7.5, <u>H</u>1'), 2.03 (0.3H, s, COC<u>H</u>$_3$').

^{13}C NMR (100 MHz, $CDCl_3$) *Signals for the major isomer only:* 169.0 (<u>C</u>O), 165.7 (<u>C</u>N), 140.4, 134.0 (2 × Ar<u>C</u>), 130.8 (<u>C</u>4), 130.5 (Ar<u>C</u>H), 129.4 (<u>C</u>3), 128.7, 128.4 (2C), 127.4, 126.1 (5 × Ar<u>C</u>H), 38.9 (<u>C</u>5), 29.6 (<u>C</u>2), 28.2 (<u>C</u>1), 19.9 (CO<u>C</u>H$_3$).

FTIR 1768, 1609, 1492, 1452, 1363 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 330.1464, $C_{20}H_{21}NO_2Na$ requires 330.1465.



(4*E*)-1,6-Diphenylhex-4-en-1-one *O*-pivaloyl oxime 7a

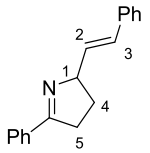
General Procedure A: Part A: (4*E*)-1,6-Diphenylhex-4-en-1-one[1] (4.90 g, 19.6 mmol) was employed and afforded the corresponding oxime (5.19 g, 100%) as a colorless oil. Part B: (4*E*)-1,6-The corresponding oxime (5.00 g, 18.9 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded oxime ester **7a** (6.10 g, 92%, 1:0.1 mixture of oxime isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *Signals for the major isomer:* 7.73-7.70 (2H, m, ArCH), 7.46-7.37 (3H, m, ArCH), 7.31-7.26 (2H, m, ArCH), 7.23-7.18 (1H, m, ArCH), 7.15-7.12 (2H, m, ArCH), 5.66-5.58 (1H, m, H4), 5.54-5.46 (1H, m, H3), 3.31 (2H, d, *J* = 7.0, H5), 2.94-2.90 (2H, m, H1), 2.36-2.30 (2H, m, H2), 1.33 (9H, s, $C(CH_3)_3$).
Characteristic signals for the minor isomer: 2.82-2.77 (0.2H, m, H1'), 2.26-2.20 (0.2H, m, H2'), 1.06 (0.9H, m, $C(CH_3)_3$').

^{13}C NMR (100 MHz, $CDCl_3$) *Signals for the major isomer only:* 175.0 (CN), 166.3 (CO), 140.3, 134.0 (2 × ArC), 130.7 (C4), 130.5 (ArCH), 129.4 (C3), 128.6, 128.4 (2C), 127.3, 126.0 (5 × ArCH), 38.8 (C5), 38.8 ($C(CH_3)_3$), 29.7 (C2), 28.5 (C1), 27.3 ($C(CH_3)_3$).

FTIR 2972, 1756, 1606, 1269, 1106, 1025 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 372.1927, $C_{23}H_{27}O_2NNa$ requires 372.1934.



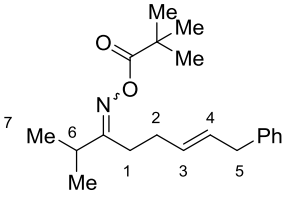
(*E*)-5-phenyl-2-styryl-3,4-dihydro-2*H*-pyrrole 8a

General Procedure B**:** Oxime ester **7a** (40 mg, 0.11 mmol) was employed. FCC (20:1 – 5:1 (hexane-EtOAc)) afforded imine **8a** (23 mg, 81%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 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, H3), 6.37 (1H, dd, *J* = 16.0, 7.0, H2), 4.95-4.89 (1H, m, H1), 3.12 (1H, dddd, *J* = 17.0, 10.0, 5.0, 2.0, H5), 2.97 (1H, dddd, *J* = 17.0, 9.5, 7.5, 2.0, H5'), 2.39 (1H, dddd, *J* = 13.0, 9.5, 8.0, 5.0, H4), 1.89 (1H, dddd, *J* = 13.0, 10.0, 7.5, 7.0, H4').

^{13}C NMR (100 MHz, $CDCl_3$) 173.4 (CN), 137.2, 134.4 (2 × ArC), 131.8 (C2), 130.5 (ArCH), 129.9 (C3), 128.4 (2C), 127.8, 127.2, 126.4, (5 × ArCH), 74.3 (C1), 35.1 (C5), 29.7 (C4).

The spectroscopic properties of this compound were consistent with the data available in the literature.[1]



(6*E*)-2-Methyl-8-phenyloct-6-en-3-one *O*-pivaloyl oxime 7b

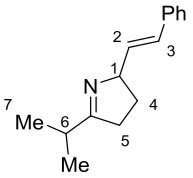
General Procedure A: Part B: (6*E*)-2-Methyl-8-phenyloct-6-en-3-one oxime[1] (400 mg, 1.73 mmol) was employed. FCC (10:1 – 5:1 (hexane-EtOAc)) afforded oxime ester **7b** (477 mg, 83%, 1:0.2 mixture of oxime isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *Signals for the major isomer only:* 7.32-7.26 (2H, m, ArCH), 7.22-7.16 (3H, m, ArCH), 5.69-5.61 (1H, m, H4), 5.55-5.47 (1H, m, H3), 3.35 (2H, d, *J* = 6.5, H5), 2.71 (1H, sep, *J* = 7.0, H6), 2.41-2.36 (2H, m, H1), 2.32-2.25 (2H, m, H2), 1.28 (9H, s, $C(CH_3)_3$), 1.17 (6H, d, *J* = 7.0, H7).
Diagnostic signals for the minor isomer: 3.23 (0.2H, hept, *J* = 7.0, H6'), 1.29 (1.8H, s, $C(CH_3)_3$)', 1.12 (1.2H, d, *J* = 7.0, H7').

^{13}C NMR (100 MHz, $CDCl_3$) *Signals for the major isomer only:* 175.1 (CO), 173.2 (CN), 140.3 (ArC), 130.3 (C4), 129.8 (C3), 128.4, 128.3, 126.0 (3 × ArCH), 38.8 (C5), 38.6 ($C(CH_3)_3$), 34.1 (C6), 29.6 (C2), 27.8 (C1), 27.2 ($C(CH_3)_3$), 19.7 (C7).

FTIR 2970, 2933, 1755, 1454, 1271, 1110 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 338.2085, $C_{20}H_{29}NO_2Na$ requires 338.2091.



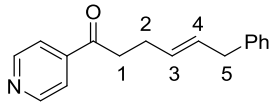
(*E*)-5-Isopropyl-2-styryl-3,4-dihydro-2*H*-pyrrole 8b

General Procedure B**:** Oxime ester **7b** (60 mg, 0.18 mmol) was employed. FCC (15:1 – 2:1 (hexane-EtOAc)) afforded imine **8b** (25 mg, 65%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.39-7.36 (2H, m, ArCH), 7.31-7.27 (2H, m, ArCH), 7.22-7.18 (1H, m, ArCH), 6.54 (1H, dd, *J* = 16.0, 1.5, H3), 6.26 (1H, dd, *J* = 16.0, 7.0, H2), 4.65 (1H, dddd, *J* = 8.0, 7.0, 5.0, 1.5, H1), 2.70 (1H, sep. *J* = 7.0, H6), 2.65-2.58 (1H, m, H5), 2.55-2.46 (1H, m, H5'), 2.20 (1H, dddd, *J* = 13.0, 9.5, 8.0, 5.0, H4), 1.69 (1H, dddd, *J* = 13.0, 9.5, 7.5, 7.0, H4'), 1.19 (6H, d, *J* = 7.0, H7).

^{13}C NMR (100 MHz, $CDCl_3$) 183.6 (CN), 137.3 (ArC), 132.1 (C2), 129.5 (C3), 128.4, 127.1, 126.3 (3 × ArCH), 73.3 (C1), 34.6 (C5), 32.7 (C6), 29.5 (C4), 20.2 (2C, C7).

The spectroscopic properties of this compound were consistent with the data available in the literature.[1]



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

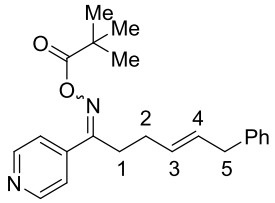
To a solution of 4-(1-(2,2-dimethylhydrazono)ethyl)pyridine[2] (776 mg, 4.76 mmol) in anhydrous THF (24 mL) at -78 °C was added freshly prepared LDA (5.24 mmol) in THF (10 mL) *via* syringe over 5 minutes. After stirring at this temperature for 20 minutes (*E*)-(4-bromobut-2-en-1-yl)benzene[1] (1.5 g, 7.14 mmol) was added *via* syringe over 5 minutes. The reaction mixture was warmed to room temperature over 2 hours after which time 1M HCl (50 mL) was added and the resulting mixture was stirred until complete hydrolysis of the intermediate hydrazone was observed (TLC). The layers were separated and the aqueous layer was extracted with EtOAc (2 × 75 mL). The organic layers were combined and washed with brine (50 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (100% EtOAc) afforded the title compound (352 mg, 29%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.81-8.80 (2H, m, ArC<u>H</u>), 7.72-7.71 (2H, m, ArC<u>H</u>), 7.31-7.27 (2H, m, ArC<u>H</u>), 7.22-7.16 (3H, m, ArC<u>H</u>), 5.71-5.65 (1H, m, <u>H</u>4), 5.61-5.54 (1H, m, <u>H</u>3), 3.34 (2H, d, *J* = 6.5, <u>H</u>5), 3.06 (2H, t, *J* = 7.5, <u>H</u>1), 2.49 (2H, dtd, *J* = 8.0, 6.5, 1.0, <u>H</u>2).

^{13}C NMR (100 MHz, $CDCl_3$) 198.9 (<u>C</u>O), 158.9 (Ar<u>C</u>H), 142.6, 140.4 (2 × Ar<u>C</u>), 130.5 (<u>C</u>4), 129.4 (<u>C</u>3), 128.4, 128.3, 125.9, 120.9 (4 × Ar<u>C</u>H), 38.9 (<u>C</u>5), 38.5 (<u>C</u>1), 26.6 (<u>C</u>2).

FTIR 3027, 2901, 1695, 1556, 1493, 1406, 1367, 1203 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 252.1384, $C_{17}H_{18}NO$ requires 252.1383.



(4*E*)-6-Phenyl-1-(pyridin-4-yl)hex-4-en-1-one *O*-pivaloyl oxime 7c

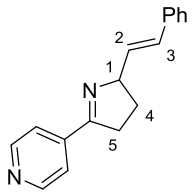
<u>General Procedure A:</u> <u>Part A</u>: (*E*)-6-Phenyl-1-(pyridin-4-yl)hex-4-en-1-one (350 mg, 1.39 mmol) was employed and afforded the corresponding oxime (371 mg, 100%) as a colorless oil. <u>Part B</u>: The corresponding oxime (370 mg, 1.39 mmol) was employed. FCC (1:1 – 0:1 (hexane-EtOAc)) afforded oxime ester **7c** (444 mg, 91%) as a colorless oil. **7c** was obtained as a single oxime isomer but the geometry was not determined.

^{1}H NMR (400 MHz, $CDCl_3$) 8.67-8.65 (2H, m, ArC<u>H</u>), 7.58-7.56 (2H, m, ArC<u>H</u>), 7.30-7.26 (2H, m, ArC<u>H</u>), 7.21-7.17 (1H, m, ArC<u>H</u>), 7.11-7.09 (2H, m, ArC<u>H</u>), 5.61 (1H, dtt, *J* = 15.0, 7.0, 1.0, <u>H</u>4), 5.45 (1H, dtt, *J* = 15.0, 7.0, 1.5, <u>H</u>3), 3.29 (2H, d, *J* = 7.0, <u>H</u>5), 2.92 (2H, t, *J* = 7.5, <u>H</u>1), 2.35-2.29 (2H, m, <u>H</u>2), 1.33 (9H, s, $C(C\underline{H}_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$) 174.6 (<u>C</u>O), 164.2 (<u>C</u>N), 150.3 (Ar<u>C</u>H), 141.6 (Ar<u>C</u>), 140.0 (Ar<u>C</u>), 131.3 (<u>C</u>4), 128.6 (<u>C</u>3), 128.4 (2C), 126.1, 121.3 (4 × Ar<u>C</u>H), 38.8 (2C, $\underline{C}(CH_3)_3$ & <u>C</u>5), 29.4 (<u>C</u>2), 27.9 (<u>C</u>1), 27.2 ($C(\underline{C}H_3)_3$).

FTIR 2973, 1761, 1595, 1453, 1269, 1101, 897 cm^{-1}.

MS (ESI^+) Found $[M+H]^+$: 351.2068, $C_{22}H_{27}O_2N_2$ requires 351.2067.



(*E*)-4-(2-styryl-3,4-dihydro-2*H*-pyrrol-5-yl)pyridine 8c

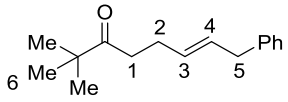
General Procedure B**:** Oxime ester **7c** (50 mg, 0.14 mmol) was employed. In a modification to the general procedure the reaction mixture was heated at 120 °C. FCC (100% EtOAc + 1% Et_3N) afforded imine **8c** (23 mg, 65%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.71 (2H, d, *J* = 5.5, ArCH), 7.74-7.72 (2H, m, ArCH), 7.41-7.38 (2H, m, ArCH), 7.33-7.29 (2H, m, ArCH), 7.25-7.20 (1H, m, ArCH), 6.64 (1H, dd, *J* = 16.0, 1.0, H3), 6.33 (1H, dd, *J* = 16.0, 7.0, H2), 4.98-4.91 (1H, m, H1), 3.10 (1H, dddd, *J* = 14.5, 10.0, 5.0, 2.5, H5), 3.00-2.91 (1H, m, H5'), 2.42 (1H, dddd, *J* = 13.0, 9.5, 8.0, 5.0, H4), 1.92 (1H, dddd, *J* = 13.0, 10.0, 7.5, 7.0, H4').

^{13}C NMR (100 MHz, $CDCl_3$) 172.0 (CN), 150.3 (ArCH), 141.2 (ArC), 137.0 (ArC), 130.9 (C2), 130.4 (C3), 128.5, 127.5, 126.4, 121.7 (4 × ArCH), 74.8 (C1), 35.0 (C5), 29.6 (C4).

FTIR 3027, 2969, 1597, 1548, 1407, 1342 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 249.1392, $C_{17}H_{17}N_2$ requires 249.1392.



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

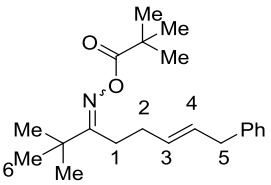
To a solution of NaH (80 mg, 2.00 mmol, 60% dispersion in mineral oil) in anhydrous THF (10 mL) at 0 °C was added ethyl pivaloylacetate (353 µL, 2.0 mmol) dropwise *via* syringe over 1 minute. The mixture was stirred at room temperature until gas evolution stopped (*ca.* 15 minutes). (*E*)-(4-Bromobut-2-en-1-yl)benzene[1] (500 mg, 2.38 mmol) was then added and the mixture was heated at 80 ^oC for 16 hours. The mixture was cooled to room temperature and MeOH (2 mL), water (5 mL) and KOH (500 mg, 9.0 mmol) were added. The mixture was then heated at 75 ^oC until complete consumption of intermediate ester was observed by TLC. After cooling to room temperature, the mixture was acidified with 1M HCl (20 mL) and extracted with EtOAc (2 x 100 mL). The organic extracts were washed with brine (50 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC (60:1 (hexane-EtOAc)) afforded the title compound (318 mg, 69%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.31-7.26 (2H, m, ArCH), 7.21-7.15 (3H, m, ArCH), 5.65-5.57 (1H, m, H4), 5.53-5.45 (1H, m, H3), 3.32 (2H, d, *J* = 6.5, H5), 2.58-2.54 (2H, m, H1), 2.31-2.25 (2H, m, H2), 1.13 (9H, s, H6).

^{13}C NMR (100 MHz, $CDCl_3$) 215.2 (CO), 140.7 (ArC), 130.4 (C3), 129.7 (C4), 128.5, 128.3, 125.9 (3 × ArCH), 44.0 ($C(CH_3)_3$), 39.0 (C5), 36.3 (C1), 26.8 (C2), 26.4 (C6).

FTIR 3027, 2967, 1704, 1494, 1453, 1365, 969 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 253.1566, $C_{16}H_{22}ONa$ requires 253.1563.



(6*E*)-2,2-Dimethyl-8-phenyloct-6-en-3-one *O*-pivaloyl oxime 7d

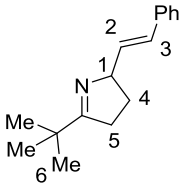
General Procedure A: Part A: (*E*)-2,2-Dimethyl-8-phenyloct-6-en-3-one (310 mg, 1.35 mmol) was employed and afforded the corresponding oxime (297 mg, 94%) as a colorless oil. Part B: The corresponding oxime (295 mg, 1.20 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded oxime ester **7d** (345 mg, 87%) as a colorless oil. **7d** was obtained as a single oxime isomer but the geometry was not determined.

^{1}H NMR (400 MHz, $CDCl_3$) 7.32-7.27 (2H, m, ArCH), 7.23-7.16 (3H, m, ArCH), 5.68-5.61 (1H, m, H4), 5.56-5.49 (1H, m, H3), 3.35 (2H, d, *J* = 6.5, H5), 2.40-2.36 (2H, m, H1), 2.29-2.24 (2H, m, H2), 1.27 (9H, s, $COC(CH_3)_3$), 1.21 (9H, s, H6).

^{13}C NMR (100 MHz, $CDCl_3$) 175.2 (CO), 174.8 (CN), 140.5 (ArC), 130.2 (C3), 130.0 (C4), 128.4 (2C), 126.0 (3 × ArCH), 38.9 (C5), 38.7 ($COC(CH_3)_3$), 38.4 ($C(CH_3)_3$), 30.0 (C2), 27.5 (C1), 27.5 (C6), 27.3 ($COC(CH_3)_3$).

FTIR 2970, 2908, 1756, 1495, 1269, 1129, 1102 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 352.2247, $C_{21}H_{31}NO_2Na$ requires 352.2247.



(*E*)-5-(*tert*-Butyl)-2-styryl-3,4-dihydro-2*H*-pyrrole 8d

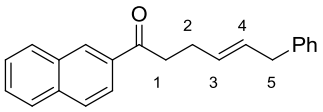
General Procedure B**:** Oxime ester **7d** (80 mg, 0.24 mmol) was employed. FCC (10:1 – 5:1 (hexane-EtOAc)) afforded imine **8d** (38 mg, 69%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.39-7.35 (2H, m, ArCH), 7.31-7.26 (2H, m, ArCH), 7.22-7.17 (1H, m, ArCH) 6.52 (1H, dd, *J* = 16.0, 1.0, H3), 6.26 (1H, dd, *J* = 16.0, 7.0, H2), 4.69-4.63 (1H, m, H1), 2.71-2.63 (1H, m, H5), 2.58-2.49 (1H, m, H5'), 2.18 (1H, dddd, *J* = 12.5, 9.5, 8.0, 5.0, H4), 1.68 (1H, dddd, *J* = 12.5, 9.5, 7.5, 6.5, H4'), 1.21 (9H, s, H6).

^{13}C NMR (100 MHz, $CDCl_3$) 185.5 (CN), 137.3 (ArC), 132.2 (C2), 129.3 (C3), 128.4, 127.1, 126.3 (3 × ArCH), 73.4 (C1), 36.0 ($C(CH_3)_3$), 33.4 (C5), 29.9 (C4), 28.2 (C6).

FTIR 2963, 1626, 1476, 1362, 963, 746 cm^{-1}.

MS (EI^+) Found $[M]^+$: 227.1683, $C_{16}H_{21}N$ requires 227.1674.



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

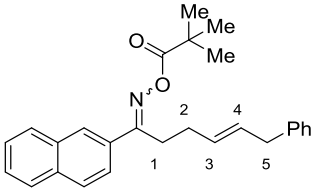
To a solution of 1,1-dimethyl-2-(1-(naphthalen-2-yl)ethylidene)hydrazine[2] (382 mg, 1.80 mmol) in anhydrous THF (9 mL) at -78 °C was added ^{n}BuLi (1.22 mL, 1.55M, 1.90 mmol) dropwise *via* syringe over 5 minutes. After stirring at this temperature for 25 minutes (*E*)-(4-bromobut-2-en-1-yl)benzene[1] (416 mg, 1.98 mmol) was added *via* syringe over 1 minute. The reaction mixture was stirred at this temperature for a further 30 minutes after which time it was warmed to room temperature. After 10 minutes, 1M HCl (20 mL) was added the reaction mixture was stirred until complete hydrolysis of the intermediate hydrazone (TLC). The aqueous layer was extracted with EtOAc (100 mL). The organic layer was then washed with brine (100 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (50:1 – 40:1 (hexane-EtOAc)) afforded the title compound (326 mg, 60%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.48 (1H, d, *J* = 1.5, ArCH), 8.04 (1H, dd, *J* = 8.5, 1.5, ArCH), 7.98-7.95 (1H, m, ArCH), 7.91-7.87 (2H, m, ArCH), 7.63-7.54 (2H, m, ArCH), 7.31-7.26 (2H, m, ArCH), 7.22-7.17 (3H, m, ArCH), 5.74-5.60 (2H, m, H3 & H4), 3.36 (2H, d, *J* = 6.0, H5), 3.22-3.18 (2H, m, H1), 2.58-2.52 (2H, m, H2).

^{13}C NMR (100 MHz, $CDCl_3$) 199.6 (CO), 140.7, 135.5, 134.3, 132.5 (4 × ArC), 130.2 (C3), 130.0 (C4), 129.7, 129.5, 128.5, 128.4 (3C), 127.7, 126.7, 125.9, 123.9 (10 × ArCH), 39.0 (C5), 38.4 (C1), 27.3 (C2).

FTIR 3059, 2899, 1678, 1276, 1180, 1123, 966 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 323.1406, $C_{22}H_{20}ONa$ requires 323.1406.



(4*E*)-1-(Naphthalen-2-yl)-6-phenylhex-4-en-1-one *O*-pivaloyl oxime 7e

General Procedure A: Part A: (*E*)-1-(Naphthalen-2-yl)-6-phenylhex-4-en-1-one (315 mg, 1.05 mmol) was employed and afforded the corresponding oxime (330 mg, 100%) as a colorless oil. Part B: The corresponding oxime (315 mg, 1.00 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded oxime ester **7e** (259 mg, 65%) as a colorless oil. **7e** was obtained as a single oxime isomer but the geometry was not determined.

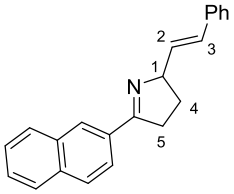
^{1}H NMR (400 MHz, $CDCl_3$) 8.15-8.14 (1H, m, ArCH), 7.94 (1H, dd, *J* = 8.5, 1.5, ArCH), 7.89-7.83 (3H, m, ArCH), 7.56-7.49 (2H, m, ArCH), 7.28-7.24 (2H, m, ArCH), 7.21-7.17 (1H, m, ArCH), 7.13-

7.10 (2H, m, ArCH), 5.69-5.61 (1H, m, H4), 5.58-5.50 (1H, m, H3), 3.32 (2H, d, *J* = 6.5, H5), 3.06-3.02 (2H, m, H1), 2.43-2.37 (2H, m, H2), 1.37 (9H, s, $C(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$) 175.0 (CO), 166.1 (CN), 140.2, 134.2, 132.8, 131.3 (4 × ArC), 130.7 (C4), 129.3 (C3), 128.7, 128.4, 128.3, 127.6 (2C), 127.2, 126.4, 126.0, 124.1 (9 × ArCH), *1 × ArCH not observed due to overlapping signals*, 38.8 (2C) (C5 & $C(CH_3)_3$), 29.8 (C2), 28.2 (C1), 27.3 ($C(CH_3)_3$).

FTIR 2973, 1755, 1604, 1478, 1316, 1104 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 422.2083, $C_{27}H_{29}NO_2Na$ requires 422.2090.



(*E*)-5-(Napthalen-2-yl)-2-styryl-3,4-dihydro-2*H*-pyrrole 8e

General Procedure B**:** Oxime ester **7e** (60 mg, 0.15 mmol) was employed. FCC (10:1 – 5:1 (hexane-EtOAc)) afforded imine **8e** (32 mg, 67%) as a yellow solid.

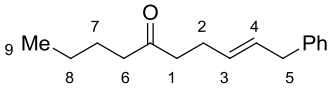
M. p. 121-123 ˚C (CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$) 8.25-8.24 (1H, m, ArCH), 8.17 (1H, dd, *J* = 8.5, 1.5, ArCH), 7.93-7.84 (3H, m, ArCH), 7.56-7.50 (2H, m, ArCH), 7.44-7.40 (2H, m, ArCH), 7.33-7.28 (2H, m, ArCH), 7.25-7.20 (1H, m, ArCH), 6.68 (1H, dd, *J* = 16.0, 1.0, H3), 6.40 (1H, dd, *J* = 16.0, 7.0, H2), 5.01-4.94 (1H, m, H1), 3.26 (1H, dddd, *J* = 17.0, 10.0, 5.0, 2.0, H5), 3.10 (1H, dddd, *J* = 17.0, 9.5, 7.5, 2.0, H5'), 2.44 (1H, dddd, *J* = 13.0, 9.5, 8.0, 5.0, H4), 1.99-1.89 (1H, m, H4').

^{13}C NMR (100 MHz, $CDCl_3$) 173.5 (CN), 137.2, 134.5, 133.0 (3 × ArC), 131.8 (2C, C2 & ArC), 130.1 (C3), 128.7, 128.4, 128.1, 127.8, 127.3, 127.2, 126.4 (3C), 124.7 (10 × ArCH), 74.5 (C1), 35.2 (C5), 29.8 (C4).

FTIR 3021, 2993, 1606, 1592, 1571, 1448 1367, 1255 cm^{-1}.

MS (ESI^+) Found $[M+H]^+$: 298.1587, $C_{22}H_{20}N$ requires 298.1590.



(*E*)-10-Phenyldec-8-en-5-one

To a solution of NaH (139 mg, 3.46 mmol, 60% dispersion in mineral oil) in anhydrous THF (17 mL) at 0 °C was added methyl 3-oxoheptanoate (550 μL, 3.46 mmol) dropwise *via* syringe over 1 minute. The mixture was stirred at room temperature until gas evolution stopped (*ca.* 15 minutes). (*E*)-(4-Bromobut-2-en-1-yl)benzene[1] (800 mg, 3.81 mmol) was then added and the mixture was heated at 80 ^oC for 16 hours. The mixture was cooled to room temperature and MeOH (3.5 mL), water (9 mL) and KOH (872 mg, 15.5 mmol) were added. The mixture was then heated at 75 ^oC until complete consumption of intermediate ester was observed by TLC. After cooling to room temperature, the

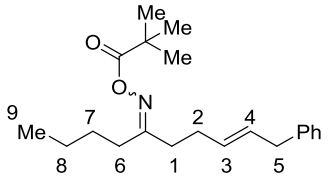
mixture was acidified with 1M HCl (35 mL) and extracted with EtOAc (2 x 200 mL). The organic extracts were washed with brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC (30:1 (hexane-EtOAc)) afforded the title compound (564 mg, 71%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.31-7.26 (2H, m, ArCH), 7.21-7.15 (3H, m, ArCH), 5.65-5.57 (1H, m, H4), 5.53-5.45 (1H, m, H3), 3.32 (2H, d, *J* = 6.5, H5), 2.50-2.46 (2H, m, H1), 2.39 (2H, t, *J* = 7.5, H6), 2.34-2.28 (2H, m, H2), 1.59-1.51 (2H, m, H7), 1.35-1.25 (2H, m, H8), 0.90 (3H, t, *J* = 7.5, H9).

^{13}C NMR (100 MHz, $CDCl_3$) 210.7 (CO), 140.7 (ArC), 130.1 (C3), 129.8 (C4), 128.4, 128.3, 125.9 (3 × ArCH), 42.6 (C6), 42.3 (C1), 38.9 (C5), 26.7 (C2), 25.9 (C7), 22.3 (C8), 13.8 (C9).

FTIR 3027, 2957, 1712, 1494, 1453, 968, 744 cm^{-1}.

MS (EI^+) Found $[M-H]^+$: 229.1587, $C_{16}H_{21}O$ requires 229.1592.



(8*E*)-10-Phenyldec-8-en-5-one *O*-pivaloyl oxime 7f

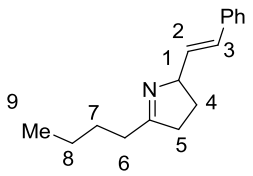
General Procedure A: Part A: (*E*)-10-Phenyldec-8-en-5-one (537 mg, 2.33 mmol) was employed and afforded the corresponding oxime (570 mg, 100%) as a colorless oil. Part B: The corresponding oxime (560 mg, 2.29 mmol) was employed. FCC (30:1 (hexane-EtOAc)) afforded oxime ester **7f** (575 mg, 76%, 1:1 mixture of oxime isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.31-7.26 (2H, m, ArCH), 7.22-7.15 (3H, m, ArCH), 5.68-5.60 (1H, m, H4), 5.56-5.44 (1H, m, H3), 3.33 (2H, d, *J* = 6.5, H5), 2.46-2.40 (2H, m, H1), 2.37-2.23 (4H, m, H6 & H2), 1.59-1.45 (2H, m, H7), 1.42-1.31 (2H, m, H8), 1.28 (4.5H, s, $C(CH_3)_3$), 1.27 (4.5H, s, $C(CH_3)_3$), 0.92 (3H, app. td, *J* = 7.5, 3.5, H9).

^{13}C NMR (100 MHz, $CDCl_3$) 175.2 (CO), 175.1 (CO), 169.8 (2C) (CN), 140.6 (ArC), 140.3 (ArC), 130.5 (C4), 130.2 (C4), 129.8 (C3), 129.5 (C3), 128.4 (3C), 128.3, 126.0, 125.9 (6 × ArCH), 38.9 (2C) (C5), 38.7 (2C, $C(CH_3)_3$), 34.3 (C6), 34.2 (C1), 29.4 (C1), 29.3 (C6), 29.3 (C2), 29.0 (C2), 28.4 (C7), 28.1 (C7), 27.3 (2C, $C(CH_3)_3$), 22.9 (C8), 22.5 (C8), 13.8 (C9), 13.7 (C9).

FTIR 2959, 2932, 1754, 1633, 1453, 1272, 1113, 748 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 352.2241, $C_{21}H_{31}NO_2Na$ requires 352.2247.



(*E*)-5-Butyl-2-styryl-3,4-dihydro-2*H*-pyrrole 8f

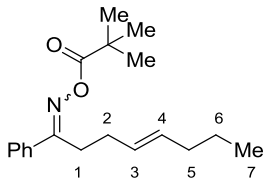
General Procedure B**:** Oxime ester **7f** (100 mg, 0.304 mmol) was employed. FCC (5:1 (hexane-EtOAc + 1% Et_3N) afforded imine **8f** (37 mg, 54%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.39-7.35 (2H, m, ArCH). 7.31-7.26 (2H, m, ArCH), 7.22-7.17 (1H, m, ArCH), 6.54 (1H, dd, *J* = 16.0, 1.0, H3), 6.26 (1H, dd, *J* = 16.0, 7.0, H2), 4.68-4.61 (1H, m, H1), 2.64-2.45 (2H, m, H5), 2.41-2.37 (2H, m, H6), 2.25-2.16 (1H, m, H4), 1.74-1.58 (3H, m, H4' & H7), 1.42-1.33 (2H, m, H8), 0.94 (3H, t, *J* = 7.5, H9).

^{13}C NMR (100 MHz, $CDCl_3$) 179.1 (CN), 137.3 (ArC), 132.2 (C2), 129.4 (C3), 128.4, 127.1, 126.3 (3 × ArCH), 73.6 (C1), 37.3 (C5), 33.7 (C6), 29.6 (C4), 28.6 (C7), 22.6 (C8), 13.9 (C9).

FTIR 2973, 2902, 1741, 1493, 1268, 1124, 1099 cm^{-1}.

MS (EI^+) Found $[M]^+$: 227.1673, $C_{16}H_{21}N$ requires 227.1674.



(4*E*)-1-Phenyloct-4-en-1-one *O*-pivaloyl oxime 7g

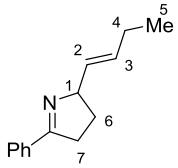
General Procedure A: Part B: (4*E*)-1-Phenyloct-4-en-1-one oxime[1] (400 mg, 1.84 mmol) was employed. FCC (40:1 (hexane-EtOAc)) afforded oxime ester **7g** (441 mg, 80%) as a colorless oil. **7g** was obtained as a single oxime isomer but the geometry was not determined.

^{1}H NMR (400 MHz, $CDCl_3$) 7.74-7.70 (2H, m, ArCH), 7.46-7.37 (3H, m, ArCH), 5.49-5.36 (2H, m, H3 & H4), 2.91-2.86 (2H, m, H1), 2.30-2.24 (2H, m, H2), 1.96-1.91 (2H, m, H5), 1.37-1.31 (11H, m, H6 & C(H_3)$_3$), 0.87 (3H, t, *J* = 7.5, H7).

^{13}C NMR (100 MHz, $CDCl_3$) 175.0 (CO), 166.4 (CN), 134.1 (ArC), 132.0 (C4), 130.4, 128.5 (2 × ArCH), 128.0 (C3), 127.3 (ArCH), 38.8 (C$(CH_3)_3$), 34.5 (C5), 29.8 (C2), 28.7 (C1), 27.3 (C(CH_3)$_3$), 22.5 (C6), 13.6 (C7).

FTIR 2959, 1758, 1479, 1106, 1026 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 324.1930, $C_{19}H_{27}NO_2Na$ requires 324.1934.



(*E*)-2-(But-1-en-1-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrole 8g

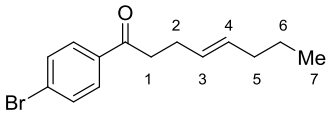
General Procedure B**:** Oxime ester **7g** (60 mg, 0.20 mmol) was employed. FCC (5:1 (hexane-EtOAc)) afforded imine **8g** (28 mg, 70%, 95:5 *E*:*Z*) as a colorless oil.

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

^{13}C NMR (100 MHz, $CDCl_3$) 172.8 (CN), 134.5 (ArC), 133.0 (C3), 130.8 (C2), 130.4, 128.3, 127.8 (3 × ArCH), 74.6 (C1), 35.1 (C7), 29.8 (C6), 25.4 (C4), 13.4 (C5).

The spectroscopic properties of this compound were consistent with the data available in the literature.[1]



(*E*)-1-(4-Bromophenyl)oct-4-en-1-one

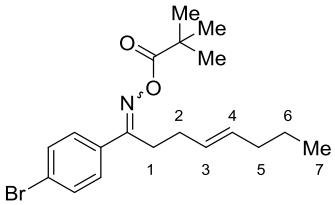
To a solution of (*E*)-2-(1-(4-bromophenyl)ethylidene)-1,1-dimethylhydrazine[2] (1.00 g, 4.15 mmol) in anhydrous THF (28 mL) at –78 °C was added freshly prepared LDA (4.57 mmol) in THF (5 mL) dropwise *via* syringe over 5 minutes. After stirring for 30 minutes (*E*)-(4-bromobut-2-en-1-yl)benzene[1] (740 mg, 4.57 mmol) was added *via* syringe over 1 minute. After stirring at this temperature for 30 minutes the reaction mixture was warmed to room temperature and stirred until complete hydrolysis of the intermediate hydrazine was observed (TLC). 1M HCl (42 mL) was added and the reaction mixture was stirred vigorously for 2 hours. The mixture was extracted with Et_2O (2 × 150 mL) and the combined organic phases were washed with brine (50 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (60:1 (hexane-EtOAc)) afforded the title compound (906 mg, 78%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.83-7.80 (2H, m, ArCH), 7.61-7.58 (2H, m, ArCH), 5.51-5.42 (2H, m, H3 & H4), 2.99 (2H, t, *J* = 7.5, H1), 2.43-2.39 (2H, m, H2), 1.98-1.93 (2H, m, H5), 1.35 (2H, tq, *J* = 7.5, 7.5, H6), 0.86 (3H, t, *J* = 7.5, H7).

^{13}C NMR (100 MHz, $CDCl_3$) 198.7 (CO), 135.7 (ArC), 131.8 (ArCH), 131.6 (C4), 129.6 (ArCH), 128.4 (C3), 128.0 (ArC), 38.6 (C1), 34.6 (C5), 27.2 (C2), 22.5 (C6), 13.6 (C7).

FTIR 2955, 2871, 1675, 1584, 1397, 1201 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 281.0544, $C_{14}H_{18}O^{79}Br$ requires 281.0541.



(4*E*)-1-(4Bromophenyl)oct-4-en-1-one *O*-pivaloyl oxime 7h

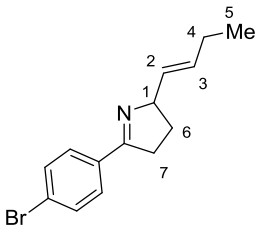
General Procedure A: Part A: (*E*)-1-(4-Bromophenyl)oct-4-en-1-one (887 mg, 3.17 mmol) was employed and afforded the corresponding oxime (902 mg, 97%) as a colorless oil. Part B: The corresponding oxime (890 mg, 3.02 mmol) was employed. FCC (30:1 (hexane-EtOAc)) afforded oxime ester **7h** (863 mg, 75%, 1:0.14 mixture of oxime isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.62-7.59 (1.75H, m, ArCH), 7.55-7.51 (2H, m, ArCH), 7.17-7.14 (0.25H, m, ArCH), 5.47-5.33 (2H, m, H3 & H4), 2.87-2.83 (1.75H, m, H1), 2.76-2.72 (0.25H, m, H1'), 2.27-2.22 (1.75H, m, H2), 2.18-2.13 (0.25H, m, H2'), 1.96-1.90 (2H, m, H5), 1.36-1.30 (10H, m, H6 & $C(CH_3)_3$), 1.07 (1H, s, $C(CH_3)_3$), 0.86 (3H, t, J = 7.5, H7).

^{13}C NMR (100 MHz, $CDCl_3$) *Signals for the major isomer only:* 174.9 (CO), 165.4 (CN), 133.0 (ArC), 132.2 (C4), 131.8 (ArCH), 128.8 (ArCH), 127.7 (C3), 125.0 (ArC), 38.8 ($C(CH_3)_3$), 34.5 (C5), 29.7 (C2), 28.4 (C1), 27.3 ($C(CH_3)_3$), 22.5 (C6), 13.6 (C7).

FTIR 2959, 2930, 1757, 1588, 1480, 1102 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 402.1033, $C_{19}H_{26}NO_2{}^{79}BrNa$ requires 402.1039.



(*E*)-5-(4-Bromophenyl)-2-(but-1-en-1-yl)-3,4-dihydro-2*H*-pyrrole 8h

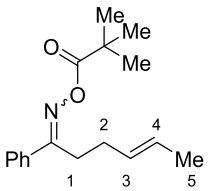
General Procedure B**:** Oxime ester **7h** (100 mg, 0.264 mmol) was employed. FCC (20:1 – 5:1 (hexane-EtOAc)) afforded imine **8h** (47 mg, 64%, 95:5 *E*:*Z*) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *Signals for the E isomer only:* 7.74-7.71 (2H, m, ArCH), 7.53-7.50 (2H, m, ArCH), 5.74 (1H, dtd, J = 15.5, 7.5, 1.5, H3), 5.52 (1H, ddt, J = 15.5, 7.5, 1.5, H2), 4.68-4.62 (1H, m, H1), 3.00 (1H, dddd, J = 17.0, 10.0, 4.5, 2.0, H7), 2.88-2.80 (1H, m, H7'), 2.27 (1H, dddd, J = 12.5, 9.5, 8.0, 4.5, H6), 2.10-2.04 (2H, m, H4), 1.74 (1H, dddd, J = 13.0, 10.0, 8.0, 7.0, H6'), 1.00 (3H, t, J = 7.5, H5).
Diagnostic signals for the Z isomer: 5.35 (0.05H, ddt, J = 10.5, 9.0, 1.5, H2'), 5.00-4.94 (0.05H, m, H1').

^{13}C NMR (100 MHz, $CDCl_3$) *Signals for the E isomer only:* 171.7 (CN), 133.4 (ArC), 133.2 (C3), 131.5 (ArCH), 130.5 (C2), 129.3 (ArCH), 124.9 (ArC), 74.6 (C1), 35.0 (C7), 29.8 (C6), 25.3 (C4), 13.4 (C5).

FTIR 2961, 2871, 1611, 1589, 1485, 1397, 1330, 1069 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 278.0548, $C_{14}H_{17}N^{79}Br$ requires 278.0544.



(4*E*)-1-Phenylhex-4-en-1-one *O*-pivaloyl oxime 7i

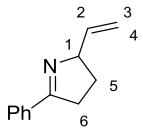
General Procedure A: Part B: (4*E*)-1-Phenylhex-4-en-1-one oxime[3] (272 mg, 1.44 mmol) was employed. FCC (6:1 (hexane-EtOAc)) afforded oxime ester **7i** (365 mg, 93%, 1:0.075 mixture of oxime isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *Data for the major isomer only:* 7.75-7.71 (2H, m, ArCH), 7.46-7.38 (3H, m, ArCH), 5.52-5.37 (2H, m, H3 & H4), 2.90-2.86 (2H, m, H1), 2.29-2.23 (2H, m, H2), 1.64-1.62 (3H, m, H5), 1.34 (9H, s, $C(CH_3)_3$).
Characteristic signals for the minor isomer: 2.77-2.73 (0.15H, m, H1'), 2.36-2.31 (0.15H, m, H2'), 1.57-1.54 (0.15H, m, H5'), 1.06 (0.7H, s, $C(CH_3)_3$').

^{13}C NMR (100 MHz, $CDCl_3$) *Data for the major isomer only:* 175.0 (CO), 166.4 (CN), 134.1 (ArC), 130.4 (ArCH), 129.1 (C4), 128.6 (ArCH), 127.3 (ArCH), 126.5 (C3), 38.8 ($C(CH_3)_3$), 29.7 (C2), 28.7 (C1), 27.3 ($C(CH_3)_3$), 17.8 (C5).

FTIR 2972, 2873, 1757, 1479, 1270, 1104 cm^{-1}.

MS Found $[M+Na]^+$: 296.1623, $C_{17}H_{23}NO_2Na$ requires 296.1621.

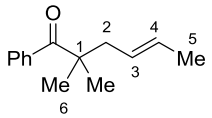


5-Phenyl-2-vinyl-3,4-dihydro-2*H*-pyrrole 8i
General Procedure B: Oxime ester **7i** (35 mg, 0.13 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded imine **8i** (14 mg, 64%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.93-7.84 (2H, m, ArCH), 7.49-7.38 (3H, m, ArCH), 6.01 (1H, ddd, *J* = 17.0, 10.5, 6.5, H2), 5.13 (1H, ddd, *J* = 17.0, 1.0, 1.0, H4), 5.02 (1H, ddd, *J* = 10.5, 1.0, 1.0, H3), 4.75 (1H, dddd, *J* = 6.5, 6.5, 6.5, 1.0, H1), 3.13-3.01 (1H, m, H6), 2.99-2.87 (1H, m, H6'), 2.37-2.24 (1H, m, H5), 1.88-1.74 (1H, m, H5').

^{13}C NMR (100 MHz, $CDCl_3$) 173.3 (CN), 140.1 (C2), 134.4 (ArC), 130.5, 128.4, 127.8 (3 × ArCH), 114.6 (C3), 74.8 (C1), 35.0 (C6), 29.2 (C5).

The spectroscopic properties of this compound were consistent with the data available in the literature.[4]



(*E*)-2,2-dimethyl-1-phenylhex-4-en-1-one
To a suspension of KO^{t}Bu (525 mg, 4.59 mmol) in *t*-BuOH (5 mL) was added isobutyrophenone (500 µL, 3.34 mmol) *via* syringe in one portion. After stirring for 5 minutes, crotonyl bromide (600 µL, 4.96 mmol) was added *via* syringe in one portion and the resulting mixture was heated at reflux for 16 hours. The mixture was cooled to room temperature and quenched by addition of brine (25 mL). The mixture was extracted with Et_2O (50 mL) and the organic phase was dried (Na_2SO_4), filtered and

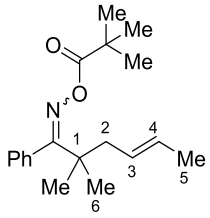
concentrated *in vacuo* to afford a yellow oil. Purification of the residue by FCC (7:2 toluene-hexane)) afforded the title compound (509 mg, 75%, 5:1 mixture of alkene isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.66-7.63 (2H, m, ArCH), 7.48-7.37 (3H, m, ArCH), 5.60-5.51 (0.2H, m, H3' & H4'), 5.45-5.28 (1.8H, m, H3 & H4), 2.50-2.47 (0.4H, m, H2'), 2.43-2.40 (1.6H, m, H2), 1.62 (2.4H, ddt, *J* = 6.0, 1.5, 1.0, H5), 1.55 (0.6H, ddt, *J* = 7.0, 2.0, 1.0, H5'), 1.33 (1H, s, H6'), 1.29 (5H, s, H6).

^{13}C NMR (100 MHz, $CDCl_3$) 209.1 (CO), 139.2 (ArC), 130.7, 128.7, 128.0, 127.6, 126.3 (3 × ArCH, C3 & C4), 47.9 (C1), 43.7 (C2), 25.7 (C6), 18.0 (C5).

FTIR 2970, 1717, 1673, 1446, 965, 712, 699 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 225.1259, $C_{14}H_{18}ONa$ requires 225.1250.



(4*E*)-2,2-dimethyl-1-phenylhex-4-en-1-one *O*-pivaloyl oxime 7j

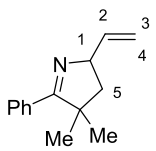
General Procedure A: Part A: (E)-2,2-dimethyl-1-phenylhex-4-en-1-one (496 mg, 2.46 mmol) was employed. In a modification to the general procedure 300 mol% of both $NH_2OH.HCl$ and NaOAc were employed to afford the corresponding oxime (505 mg, 95%). Part B: The corresponding oxime (490 mg, 2.26 mmol) was employed. FCC (6:1 (hexane-EtOAc)) afforded oxime ester **7j** (574 mg, 84%, 5:1 mixture of alkene isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.39-7.33 (3H, m, ArCH), 7.04-7.01 (2H, m, ArCH), 5.68-5.43 (2H, m, H3, H4, H3' & H4'), 2.30-2.27 (0.4H, m, H2'), 2.25-2.23 (1.6H, m, H2), 1.70-1.68 (2.4H, m, H5), 1.59-1.57 (0.6H, m, H5'), 1.26 (1.2H, s, H6'), 1.20 (4.8H, s, H6), 0.89 (9H, s, $C(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$) 175.9 (C), 175.1 (C), 133.4 (ArC), 128.7 (C4), 128.0, 127.7, 126.6 (3 × ArCH), 126.4 (C3), 42.9 (C2), 41.4 (C1), 38.3 ($C(CH_3)_3$), 26.7 ($C(CH_3)_3$), 25.4 (C6), 18.1 (C5).

FTIR 2971, 1756, 1741, 1480, 1444, 1114, 884 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 324.1933, $C_{19}H_{28}NO_2Na$ required 324.1934.



4,4-Dimethyl-5-phenyl-2-vinyl-3,4-dihydro-2*H*-pyrrole 8j

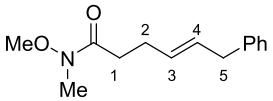
General Procedure B**:** Oxime ester **7j** (45 mg, 0.15 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded imine **8j** (24.5 mg, 82%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) 7.77-7.71 (2H, m, ArCH), 7.43-7.35 (3H, m, ArCH), 6.06 (1H, ddd, *J* = 17.0, 10.5, 6.5, H2), 5.31 (1H, ddd, *J* = 17.0, 1.0, 1.0, H4), 5.15 (1H, ddd, *J* = 10.5, 1.0, 1.0, H3), 4.58 (1H, m, H1), 2.17 (1H, dd, *J* = 12.5, 7.0, H5), 1.75 (1H, dd, *J* = 12.5, 8.5, H5'), 1.38 (3H, s, CH_3), 1.37 (3H, s, CH_3').

^{13}C NMR (125 MHz, $CDCl_3$) 180.1 (CN), 140.5 (C2), 134.6 (ArC), 129.5, 128.1, 128.0 (3 × ArCH), 114.8 (C3), 69.9 (C1), 50.5 ($C(CH_3)_2$), 48.0 (C5), 27.2, 25.8 (2 × CH_3).

FTIR 2959, 2870, 1600, 1570, 1464, 1445 cm^{-1}.

MS (ESI^+) Found $[M+H]^+$: 200.1425, $C_{14}H_{18}N$ requires 200.1434.



(*E*)-*N*-Methoxy-*N*-methyl-6-phenylhex-4-enamide

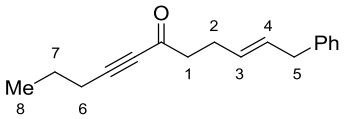
To a solution of ethyl (*E*)-6-phenylhex-4-enoate[5] (1.2 g, 5.50 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride in THF (12 mL) at -20 °C was added *iso*propylmagnesium chloride (2M in THF, 8.5 mL, 17.0 mmol) dropwise over 2 minutes. The reaction mixture was then warmed to -10 °C. The reaction was maintained at this temperature for 80 minutes after which time it was quenched by addition of 1M HCl (40 mL). The mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with brine (50 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (10:1 – 2:1 (hexane-EtOAc)) afforded the title compound (782 mg, 61%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.31-7.26 (2H, m, ArCH), 7.21-7.16 (3H, m, ArCH), 5.69-5.61 (1H, m, H4), 5.50-5.51 (1H, m, H3), 3.66 (3H, s, OCH_3), 3.33 (2H, d, *J* = 6.5, H5), 3.17 (3H, s, NCH_3), 2.51 (2H, t, *J* = 7.5, H1), 2.40-2.34 (2H, m, H2).

^{13}C NMR (100 MHz, $CDCl_3$) 174.0 (CO), 140.7 (ArC), 130.3 (C3), 129.8 (C4), 128.4, 128.3, 125.9 (3 × ArCH), 61.4 (OCH_3), 38.9 (C5), 32.1 (NCH_3), 31.7 (C1), 27.4 (C2).

FTIR 3027, 1659, 1494, 1453, 138, 1177, 969 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 256.1306, $C_{14}H_{19}O_2NNa$ requires 256.1308.



(*E*)-1-Phenylundec-2-en-7-yn-6-one

To a solution of pentyne (630 µL, 6.44 mmol) in THF (10 mL) at -78 °C was added ^{n}BuLi (2.38M in hexane, 2.7 mL, 6.44 mmol). After stirring at this temperature (*E*)-*N*-Methoxy-*N*-methyl-6-phenylhex-4-enamide (1.00 g, 4.29 mmol) in THF (5 mL) was added *via* syringe over 5 minutes. The reaction mixture was stirred at this temperature for 30 minutes and then warmed to room temperature. The reaction was quenched with saturated aq. $NaHCO_3$ (2.5 mL). The mixture was diluted with EtOAc (15 mL) and washed with brine (2 × 30 mL). The aqueous layers were then extracted with EtOAc (2 ×20 mL). The combined organic layers were combined, dried (Na_2SO_4), filtered, and

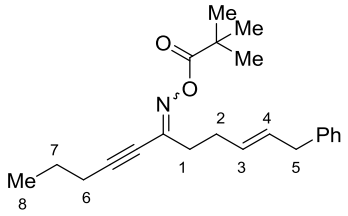
concentrated *in vacuo*. Purification of the residue by FCC (20:1 (hexane-EtOAc)) afforded the title compound (876 mg, 85%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.31-7.27 (2H, m, ArCH), 7.22-7.16 (3H, m, ArCH), 5.64 (1H, dtt, *J* = 15.0, 6.5, 1.5, H3), 5.51 (1H, dtt, *J* = 15.0, 6.5, 1.5, H4), 3.33 (2H, d, *J* = 6.5, H5), 2.65-2.61 (2H, m, H1), 2.44-2.37 (2H, m, H2), 2.34 (2H, t, *J* = 7.0, H6), 1.61 (2H, app. hept, *J* = 7.5, H7), 1.02 (3H, t, *J* = 7.5, H8).

^{13}C NMR (100 MHz, $CDCl_3$) 187.5 (CO), 140.5 (ArC), 130.2 (C3), 129.3 (C4), 128.4, 128.3, 125.9 (3 × ArCH), 94.4 (C≡CCO), 80.9 (C≡CCO), 45.1 (C1), 38.9 (C5), 26.9 (C2), 21.2 (C7), 20.8 (C6), 13.4 (C8).

FTIR 2964, 2210, 1669, 1405, 1243 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 263.1405, $C_{17}H_{20}ONa$ requires 263.1406.



(2*E*)-1-Phenylundec-2-en-7-yn-6-one *O*-pivaloyl oxime 7k

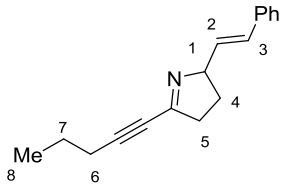
General Procedure A: Part A: (*E*)-1-Phenylundec-2-en-7-yn-6-one (837 mg, 3.49 mmol) was employed. In a modification to the general procedure 100 mol% $NH_2OH.HCl$ was employed, pyridine (130 mol%) was employed as base, ethanol was employed as solvent and the reaction was heated at 50 °C. The corresponding oxime (711 mg, 80%) was obtained as a colorless oil after purification by FCC (10:1 – 5:1 (hexane-EtOAc)). Part B: The corresponding oxime (710 mg, 2.78 mmol) was employed. FCC (15:1 (hexane-EtOAc)) afforded oxime ester **7k** (739 mg, 78%, 1:1 mixture of oxime isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.30-7.25 (2H, m, ArCH), 7.22-7.15 (3H, m, ArCH), 5.70-5.61 (1H, m, H4), 5.56-5.46 (1H, m, H3), 3.33 (2H, d, *J* = 7.0, H5), 2.60-2.52 (2H, m, H2), 2.42-2.31 (4H, m, H1 & H6), 1.60 (2H, app. dhept, *J* = 9.5, 7.5, H7), 1.30 (4H, s, $C(CH_3)_3$), 1.27 (4.5H, s, $C(CH_3)_3$), 1.01 (3H, app. dt, *J* = 10.0, 7.5, H8).

^{13}C NMR (100 MHz, $CDCl_3$) 175.1 (CO), 151.0 (CN), 140.6 (ArC), 130.5 (C4), 129.4 (C3), 128.4, 128.3, 125.9 (3 × ArCH), 105.0 (C≡CCN), 71.9 (C≡CCN), 38.9 (C5), 38.5 ($C(CH_3)_3$), 34.5 (C2), 29.7 (C1), 27.1 ($C(CH_3)_3$), 21.6 (C7), 21.5 (C6), 13.5 (C8).

FTIR 2967, 2874, 2222, 1758, 1593, 1480, 1103 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 362.2092, $C_{22}H_{29}NO_2Na$ requires 362.2090.



(*E*)-5-(Pent-1-yn-1-yl)-2-styryl-3,4-dihydro-2*H*-pyrrole 8k

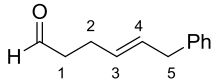
General Procedure B**:** Oxime ester **7k** (80 mg, 0236 mmol) was employed. In a modification to the general procedure $NaHCO_3$ (20 mg, 0.236 mmol) was employed as an additive. FCC (5:1 (hexane-EtOAc)) afforded imine **8k** (14.5 mg, 26%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.38-7.36 (2H, m, ArCH), 7.31-7.26 (2H, m, ArCH), 7.23-7.18 (1H, m, ArCH), 6.57 (1H, d, *J* = 16.0, H3), 6.27 (1H, dd, *J* = 16.0, 6.5, H2), 4.79-4.72 (1H, m, H1), 2.79-2.59 (2H, m, H5), 2.36 (2H, t, *J* = 7.0, H6), 2.29-2.21 (1H, m, H4), 1.78-1.68 (1H, m, H4'), 1.66-1.57 (2H, m, H7), 1.02 (3H, t, *J* = 7.5, H8).

^{13}C NMR (100 MHz, $CDCl_3$) 160.2 (CN), 137.1 (ArC), 131.1 (C2), 129.9 (C3), 128.4, 127.3, 126.3 (3 × ArCH), 95.6 (C≡CCN), 76.7 (C≡CCN, *signal inferred by HMBC from H6*), 74.1 (C1), 40.2 (C5), 29.4 (C4), 21.6 (C7), 21.3 (C6), 13.5 (C8).

FTIR 2967, 2934, 2222, 1758, 1593, 1480, 1103, 1026, 892 cm^{-1}.

MS (ESI^+) Found $[M+H]^+$: 238.1587, $C_{17}H_{20}N$ requires 238.1590.



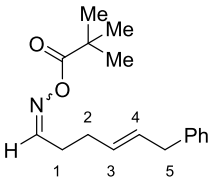
(*E*)-6-Phenylhex-4-enal

To a solution of (*E*)-*N*-methoxy-*N*-methyl-6-phenylhex-4-enamide (815 mg, 3.50 mmol) in CH_2Cl_2 (35 mL) at -78 °C was added DIBAL-H (1M in CH_2Cl_2, 3.7 mL, 3.67 mmol) dropwise *via* syringe over 10 minutes. The reaction was stirred at this temperature for 2 hours followed by quenching with saturated aq. Rochelle salt (30 mL) and warming to room temperature. The mixture was extracted with EtOAc (2 × 60 mL). The combined organic layers were washed with saturated aq. Rochelle salt (60 mL), H_2O (60 mL), brine (60 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue (10:1 (hexane-EtOAc)) afforded the title compound (330 mg, 54%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 9.77 (1H, t, *J* = 1.5, CHO), 7.32-7.27 (2H, m, ArCH), 7.22-7.15 (3H, m, ArCH), 5.65 (1H, dtt, *J* = 15.0, 6.5, 1.5, H4), 5.51 (1H, dtt, *J* = 15.0, 6.5, 1.5, H3), 3.34 (2H, d, *J* = 6.5, H5), 2.55-2.51 (2H, m, H1), 2.41-2.35 (2H, m, H2).

^{13}C NMR (100 MHz, $CDCl_3$) 202.1 (CHO), 140.4 (ArC), 130.4 (C4), 129.3 (C3), 128.4 (2C), 126.0 (3 × ArCH), 43.3 (C1), 38.9 (C5), 25.0 (C2).

The spectroscopic properties of this compound were consistent with the data available in the literature.[6]



(*E*)-6-Phenylhex-4-enal *O*-pivaloyl oxime 7l

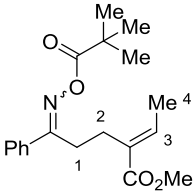
General Procedure A: Part A: (*E*)-6-Phenylhex-4-enal (330 mg, 1.90 mmol) was used. In a modification to the general procedure 300 mol% of $NH_2OH.HCl$ was employed, pyridine replaced NaOAc as base (300 mol%) and EtOH was employed as solvent. The reaction was heated at 80 °C for 16 hours and afforded the corresponding oxime (335 mg, 93%). Part B: The corresponding oxime (335 mg, 1.77 mmol) was employed. FCC (6:1 – 3:1 (hexane-EtOAc)) afforded oxime ester **7l** (334 mg, 69%, 1:0.5 mixture of oxime isomers) as a colorless oil. The two isomers of **7l** are separable by FCC and were characterized individually. Determination of the oxime ester geometry of the two isomers was not carried out. *Caution: product undergoes Beckmann rearrangement if heated too strongly during work-up or concentration after FCC.*

^{1}H NMR (400 MHz, $CDCl_3$) *Data for isomer A:* 7.70 (1H, t, *J* = 6.0, HCN), 7.31-7.26 (2H, m, ArCH), 7.21-7.15 (3H, m, ArCH), 5.66 (1H, dtt, *J* = 15.0, 6.5, 1.5, H4), 5.52 (1H, dtt, *J* = 15.0, 6.5, 1.5, H3), 3.35 (2H, d, *J* = 6.5, H5), 2.50-2.45 (2H, m, H1), 2.34-2.28 (2H, m, H2), 1.27 (9H, s, $C(CH_3)_3$). *Data for isomer B:* 7.31-7.26 (2H, m, ArCH), 7.22-7.15 (4H, m, ArCH and HCHO), 5.67 (1H, m, dtt, *J* = 15.5, 7.0, 1.5, H4), 5.48 (1H, dtt, *J* = 15.5, 6.5, 1.5, H3), 3.35 (2H, d, *J* = 6.5, H5), 2.52 (2H, td, *J* = 7.5, 5.5, H1), 2.30-2.25 (2H, m, H2), 1.28 (9H, s, $C(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$) *Data for isomer A:* 175.4 (CO), 158.8 (HCN), 140.4 (ArC), 130.9 (C4), 129.1 (C3), 128.4 (2C), 126.0 (3 × ArCH), 38.8 (C5), 38.2 ($C(CH_3)_3$), 29.3 (C1), 29.1 (C2), 27.1 ($C(CH_3)_3$). *Data for isomer B:* 175.0 (CO), 158.7 (HCN), 140.2 (ArC), 131.2 (C4), 128.9 (C3), 128.4, 126.0 (2C) (3 × ArCH), 38.9 (C5), 38.7 ($C(CH)_3$)$_3$, 28.6 (C2), 27.2 ($C(CH_3)_3$), 26.4 (C1).

FTIR 3028, 1752, 1494, 1453, 1120, 968 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 296.1624, $C_{17}H_{23}NO_2Na$ requires 296.1621.



(2*E*)-Methyl 2-ethylidene-5-((pivaloyloxy)imino)pentanoate 7m

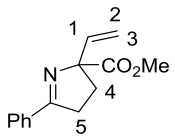
General Procedure A: Part A: Methyl (*E*)-2-ethylidene-5-oxo-5-phenylpentanoate[7] (0.25 g, 1.08 mmol) was used. In a modification to the general procedure, the reaction was stirred at 25 ^oC for 16 hours to afford the corresponding oxime (0.24 g, 90%) as a colorless oil. Part B: The corresponding oxime (0.17 g, 0.69 mmol) was employed. The reaction was stirred for 16 hours and FCC (10:1 (hexane-EtOAc)) afforded oxime ester **7m** (200 mg, 88%, 1:0.1 mixture of oxime isomers) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) *Data for the major isomer:* 7.83-7.77 (2H, m, ArC<u>H</u>), 7.43-7.33 (3H, m, ArC<u>H</u>), 6.86 (1H, q, *J* = 7.5, <u>H</u>3), 3.70 (3H, s, ($CO_2C\underline{H}_3$), 3.01-2.92 (2H, m, <u>H</u>1), 2.60-2.53 (2H, m, <u>H</u>2), 1.71 (3H, d, *J* = 7.5, <u>H</u>4), 1.31 (9H, s, $C(C\underline{H}_3)_3$).
Characteristic signals for the minor isomer: 3.66 (0.3H, s, ($CO_2C\underline{H}_3$'), 2.81-2.76 (0.2H, m, <u>H</u>1', 2.52-2.46 (0.2H, m, <u>H</u>2'), 1.95 (0.3H, d, *J* = 7.5, <u>H</u>4), 1.05 (0.9H, s, $C(C\underline{H}_3)_3$').

^{13}C NMR (100 MHz, $CDCl_3$) *Data for the major isomer:* 175.2 ($\underline{C}OC(CH_3)_3$), 167.6 ($\underline{C}O_2CH_3$), 165.7 (<u>C</u>N), 139.3 (<u>C</u>3), 133.9 (Ar<u>C</u>), 131.3 (<u>C</u>=C3), 130.7, 128.7, 127.4 (3 × Ar<u>C</u>H), 51.7 ($CO_2\underline{C}H_3$), 38.9 ($\underline{C}(CH_3)_3$), 27.4 ($C(\underline{C}H_3)_3$), 27.0 (<u>C</u>1), 23.7 (<u>C</u>2), 14.5 (<u>C</u>4).

FTIR 2974, 1759, 1709, 1268, 1108 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 354.1679, $C_{19}H_{25}NO_4Na$ requires 354.1676.

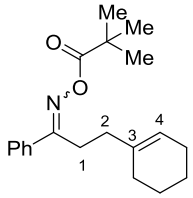


2-Vinyl-3,4-dihydro-2*H*-pyrrole-2-carboxylate 8m
<u>General Procedure B:</u> Oxime ester **7m** (70 mg, 0.21 mmol) was employed. FCC (5:1 (hexane-EtOAc)) afforded imine **8m** (37 mg, 76%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) 7.95-7.92 (2H, m, ArC<u>H</u>), 7.50-7.39 (3H, m, ArC<u>H</u>), 6.30 (1H, dd, *J* = 17.5, 10.5, <u>H</u>1), 5.26 (1H, dd, *J* = 17.5, 1.0, <u>H</u>3), 5.19 (1H, dd, *J* = 10.5, 1.0, <u>H</u>2), 3.78 (3H, s, $CO_2C\underline{H}_3$) 3.17-2.91 (2H, m, <u>H</u>5), 2.63-2.53 (1H, m, <u>H</u>4), 2.24-2.14 (1H, m, <u>H</u>4').

^{13}C NMR (125 MHz, $CDCl_3$) 175.3 (<u>C</u>N), 173.7 ($\underline{C}O_2CH_3$), 138.5 (<u>C</u>2), 133.9 (Ar<u>C</u>), 131.0, 128.4, 128.1 (3 × Ar<u>C</u>H), 114.5 (<u>C</u>2), 83.8 ($N\underline{C}CO_2CH_3$), 52.7 ($CO_2\underline{C}H_3$), 34.8 (<u>C</u>5), 33.0 (<u>C</u>4).

The spectroscopic properties of this compound were consistent with the data available in the literature.[7]



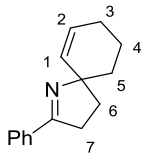
3-(Cyclohex-1-en-1-yl)-1-phenylpropan-1-one *O*-pivaloyl oxime 7n
<u>General Procedure A:</u> <u>Part B</u>: 3-(Cyclohex-1-en-1-yl)-1-phenylpropan-1-one oxime[7] (0.13 g, 0.567 mmol) was employed. The reaction was stirred for 16 hours and FCC (10:1 (hexane-EtOAc)) afforded oxime ester **7n** (165 mg, 93%, 1:0.1 mixture of oxime isomers) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) *Data for the major isomer:* 7.73-7.70 (2H, m, ArC<u>H</u>), 7.45-7.37 (3H, m, ArC<u>H</u>), 5.45-5.42 (1H, m, <u>H</u>4), 2.94-2.90 (2H, m, <u>H</u>1), 2.22-2.17 (2H, m, <u>H</u>2), 1.99-1.92 (4H, m, 2 × $C\underline{H}_2$), 1.61-1.48 (4H, m, 2 × $C\underline{H}_2$), 1.35 (9H, s, $C(C\underline{H}_3)_3$).
Characteristic signals for the minor isomer: 5.36-5.34 (0.1H, m, <u>H</u>4'), 2.82-2.78 (0.2H, m, <u>H</u>1'), 2.14-2.10 (0.2H, m, <u>H</u>2').

^{13}C NMR (100 MHz, $CDCl_3$) 175.1 (CO), 166.9 (CN), 136.0 (C3), 134.3 (ArC), 130.4, 128.5, 127.3 (3 × ArCH), 122.5 (C4), 38.8 ($C(CH_3)_3$), 34.8 (C2), 28.1 (C1), 27.5 (CH_2), 27.3 ($C(CH_3)_3$), 25.2, 22.8, 22.3 (3 × CH_2).

FTIR 2928, 2857, 1759, 1609, 1269, 1108 cm^{-1}.

MS (CI^+) Found $[M+H]^+$: 314.2124, $C_{20}H_{28}NO_2$ requires 314.2120.



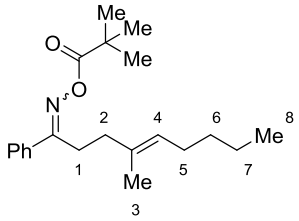
2-Phenyl-1-azaspiro[4.5]deca-1,6-diene 8n

General Procedure B: Oxime ester **7n** (35 mg, 0.11 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded imine **8n** (17 mg, 72%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.90-7.82 (2H, m, ArCH), 7.44-7.34 (3H, m, ArCH), 5.83 (1H, dt, *J* = 10.0, 3.5, H2), 5.54 (dt, *J* = 10.0, 1.0, H1), 3.07-2.91 (2H, m, H7), 2.21-1.53 (8H, m, H3, H4, H5 & H6).

^{13}C NMR (100 MHz, $CDCl_3$) 171.1 (CN), 132.7 (C1), 130.3 (ArCH), 128.3 (ArC), 127.9 (ArCH), 127.9 (C2), 127.8 (ArCH), 75.2 (NCC6), 35.7, 34.8 (2 × CH_2), 34.5 (C7), 25.0, 20.4 (2 × CH_2).

The spectroscopic properties of this compound were consistent with the data available in the literature.[7]



(4*E*)-4-Methyl-1-phenylnon-4-en-1one *O*-pivaloyl oxime 7o

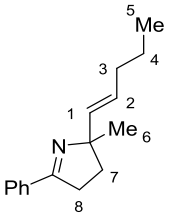
General Procedure A: Part A: (*E*)-4-Methyl-1-phenylnon-4-en-1-one[7] (0.78 g, 3.39 mmol) was used. The reaction was heated at 75°C for 2 hours to afford the corresponding oxime (0.73 g, 88%) as a colorless oil. Part B: The corresponding oxime (0.36 g, 1.50 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded oxime ester **7o** (0.41 g, 85%, 1:0.15 mixture of oxime isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *Signals for the major isomer:* 7.76-7.70 (2H, m, ArCH), 7.48-7.35 (3H, m, ArCH), 5.17 (1H, ttq, *J* = 7.0, 1.0, 1.0, H4), 2.97-2.89 (2H, m, H1), 2.25 (2H, tm, *J* = 8.0, H2), 2.02-1.91 (2H, m, H5), 1.65 (3H, d, *J* = 1.0, H3), 1.35 (9H, s, $C(CH_3)_3$), 1.32-1.25 (4H, m, H6 & H7), 0.93-0.86 (3H, m, H8).
Characteristic signals only for the minor isomer: 5.11-5.06 (0.15H, m, H4'), 2.84-2.97 (0.3H, m, H1'), 2.16 (0.3H, t, *J* = 8.0, H2'), 1.59 (0.45H, d, *J* = 1.0, H3'), 1.07 (1.35H, s, $C(CH_3)_3$').

^{13}C NMR (100 MHz, $CDCl_3$) *Signals for the major isomer only:* 175.1 (CO), 166.8 (CN), 134.2 (ArC), 133.1 (C=C4), 130.4, 128.6, 127.3 (3 × ArCH), 126.4 (C4), 38.8 ($C(CH_3)_3$), 36.5 (C2), 31.8 (C6), 27.8 (C1), 27.6 (C5), 27.3 ($C(CH_3)_3$), 22.3 (C7), 15.9 (C3), 14.0 (C8).

FTIR 2958, 2930, 1759, 1479, 1457, 1444, 1269, 1105 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 352.2253, $C_{21}H_{31}NO_2Na$ requires 352.2247.



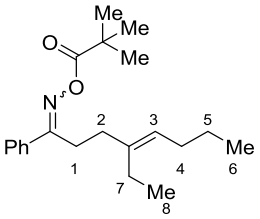
(*E*)-2-Methyl-2-(pent-1-en-1-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrole 8o

General Procedure B: Oxime ester **7o** (50 mg, 0.15 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded imine **8o** (31 mg, 90%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.91-7.83 (2H, m, ArCH), 7.47-7.37 (3H, m, ArCH), 5.67 (1H, dt, *J* = 15.5, 1.0, H1), 5.53 (1H, dt, *J* = 15.5, 6.5, H2), 3.08-2.90 (2H, m, H8), 2.11-1.96 (3H, m, H3 & H7), 1.93-1.81 (1H, m, H7'), 1.46-1.33 (2H, m, H4), 1.42 (3H, s, H6), 0.89 (3H, t, *J* = 7.5, H5).

^{13}C NMR (100 MHz, $CDCl_3$) 170.7 (CN), 136.3 (C1), 134.8 (ArC), 130.3, 128.3, 127.7 (3 × ArCH), 127.2 (C2), 76.1 (NCC6), 36.0 (C7), 34.9 (C8), 34.6 (C3), 27.4 (C6), 22.5 (C4), 13.7 (C5).

The spectroscopic properties of this compound were consistent with the data available in the literature.[7]



(4*E*)-4-Ethyl-1-phenyloct-4-en-1-one *O*-pivaloyl oxime 7p

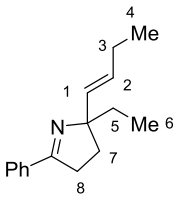
General Procedure A: Part A: (*E*)-4-Ethyl-1-phenyloct-4-en-1-one[7] (0.48 g, 2.08 mmol) was used. The reaction was heated at 75 ^oC for 2 hours to afford the corresponding oxime (0.49 g, 96%) as a colorless oil. Part B: The corresponding oxime (0.24 g, 0.98 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded oxime ester **7p** (0.28 g, 87%, 1:0.1 mixture of oxime isomers and 1:0.1 *E*:*Z* mixture of olefin isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *Signals for major oxime isomer of the major olefin isomer:* 7.76-7.70 (2H, m, ArCH), 7.47-7.36 (3H, m, ArCH), 5.14 (1H, t, *J* = 7.5, H3), 2.96-2.90 (2H, m, H1), 2.25 (2H, t, *J* = 7.5, H2), 2.07 (2H, q, *J* = 7.5, H7), 1.98 (2H, dt, *J* = 7.5, 7.5, H4), 1.38-1.31 (2H, m, H5), 1.35 (9H, s, $C(CH_3)_3$), 0.96 (3H, t, *J* = 7.5, H8), 0.90 (3H, t, *J* = 7.5, H6).
Characteristic signals for the minor isomers: 5.18 (0.1H, t, *J* = 7.0, H3'), 5.06 (0.1H, t, *J* = 7.0, H3'), 2.90-2.86 (0.2H, m, H1'), 2.84-2.70 (0.2H, m, H1'), 2.20-2.15 (0.2H, m, H2'), 1.37 (0.9H, s, $C(CH_3)_3$'), 1.07 (0.9H, s, $C(CH_3)_3$').

^{13}C NMR (100 MHz, $CDCl_3$) *Signals for major oxime isomer of the major olefin isomer only:* 175.1 (CO), 166.8 (CN), 139.4 (C=C3), 134.2 (ArC), 130.4, 128.6, 127.3 (3 × ArCH), 125.5 (C3), 38.8 ($C(CH_3)_3$), 33.2 (C2), 29.6 (C4), 27.9 (C1), 27.3 ($C(CH_3)_3$), 23.1 (2C) (C5 & C7), 13.8 (C6), 13.2 (C8).

FTIR 2962, 2932, 1759, 1479, 1458, 1444, 1104 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 352.2257, $C_{21}H_{31}NO_2Na$ requires 352.2247.



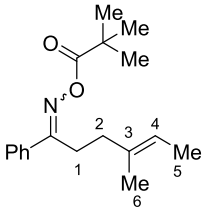
***(E)*-2-(But-1-en-1-yl)-2-ethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole 8p**

General Procedure B: Oxime ester **7p** (50 mg, 0.15 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded imine **8p** (29.5 mg, 86%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.93-7.83 (2H, m, ArCH), 7.47-7.34 (3H, m, ArCH), 5.66 (1H, dt, *J* = 15.5, 1.0, H1), 5.52 (1H, dt, *J* = 15.5, 6.5, H2), 3.02-2.87 (2H, m, H8), 2.09-1.85 (4H, m, H3 & H7), 1.83-1.67 (2H, m, H5), 0.98 (3H, t, *J* = 7.5, H4), 0.92 (3H, t, *J* = 7.5, H6).

^{13}C NMR (100 MHz, $CDCl_3$) 170.8 (CN), 135.1 (ArC), 134.2 (C1), 130.3 (ArCH), 129.6 (C2), 128.4, 127.9 (2 × ArCH), 80.0 (NCC5), 35.1 (C5), 33.9 (C8), 32.4 (C7), 25.7 (C3), 14.0 (C4), 9.0 (C6).

The spectroscopic properties of this compound were consistent with the data available in the literature.[7]



(4*E*)-4-Methyl-1-phenylhex-4-en-1-one *O*-pivaloyl oxime 7q

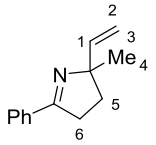
General Procedure A: Part A**:** (*E*)-4-Methyl-1-phenylhex-4-en-1-one[7] (0.19 g, 1.01 mmol) was used. The reaction was heated at 75 ^oC for 2 hours to afford the corresponding oxime (0.20 g, 98%) as a colorless solid. Part B: The corresponding oxime (0.20 g, 1.00 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded oxime ester **7q** (0.25 g, 87%, 1:0.1 mixture of oxime isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *Signals for the major isomer:* 7.76-7.68 (m, 2H, ArCH), 7.48-7.36 (m, 3H, ArCH), 5.26 (1H, qqt, *J* = 6.5, 1.0, 1.0, H4), 2.97-2.89 (2H, m, H1), 2.24 (2H, t, *J* = 8.0, H2), 1.67-1.64 (3H, m, H6), 1.57 (3H, dqt, *J* = 6.5, 1.0, 1.0, 3H, H5), 1.35 (9H, s, 9H, $C(CH_3)_3$). *Characteristic signals only for the minor isomer:* 5.20-5.13 (0.1H, m, H4'), 2.83-2.79 (0.2H, m, H1'), 2.19-2.15 (0.2H, m, H2'), 1.07 (0.9H, s, $C(CH_3)_3$').

^{13}C NMR (100 MHz, $CDCl_3$) *Signals for the major isomer only:* 175.2 (CO), 166.8 (CN), 134.3 (C3), 134.1 (ArC), 130.5, 128.7, 127.4 (3 × ArCH) 120.1 (C4), 38.9 ($C(CH_3)_3$), 36.5 (C2), 27.9 (C1), 27.4 ($C(CH_3)_3$), 15.7 (C6), 13.5 (C5).
Characteristic signals of the minor isomer: 27.1 ($C(CH_3)_3$').

FTIR 2973, 2933, 1757, 1479, 1444, 1269, 1106 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 310.1771, $C_{18}H_{25}NO_2Na$ requires 310.1778.

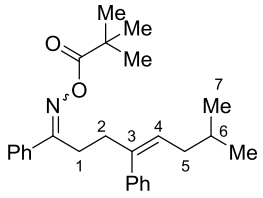


2-Methyl-5-phenyl-2-vinyl-3,4-dihydro-2*H*-pyrrole 8q
General Procedure B: Oxime ester **7q** (45 mg, 0.16 mmol) was employed. FCC (10:1 (toluene-EtOAc)) afforded imine **8q** (28 mg, 96%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.91-7.85 (2H, m, ArCH), 7.47-7.37 (3H, m, ArCH), 6.05 (1H, dd, *J* = 17.5, 10.5, H1), 5.13 (1H, dd, *J* = 17.5, 1.0, H3), 5.02 (1H, dd, *J* = 10.5, 1.0, H2), 3.11-2.91 (2H, m, H6), 2.15-1.84 (2H, m, H5), 1.45 (3H, d, *J* = 1.0, H4).

^{13}C NMR (100 MHz, $CDCl_3$) 171.4 (CN), 144.3 (C1), 134.6 (ArC), 130.4, 128.4, 127.8 (3 × ArCH), 111.3 (C2), 77.0 (NCC4), 35.3 (C5), 34.9 (C6), 26.9 (C4).

The spectroscopic properties of this compound were consistent with the data available in the literature.[7]



(4*Z*)-7-Methyl-1,4-diphenyloct-4-en-1-one *O*-pivaloyl oxime 7r
General Procedure A: Part A: (*Z*)-7-Methyl-1,4-diphenyloct-4-en-1-one[7] (0.52 g, 1.78 mmol) was employed and afforded the corresponding oxime (0.54 g, 99%) as a colorless oil. Part B: The corresponding oxime (0.15 g, 0.49 mmol) was employed. FCC (8:1 (hexane-EtOAc)) afforded oxime ester **7r** (0.16 g, 84%, 1:0.1 mixture of oxime isomers and 1:0.05 *Z*:*E* mixture of olefin isomers) as a colorless oil.

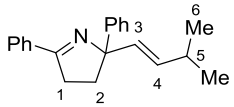
^{1}H NMR (400 MHz, $CDCl_3$) *Signals for the major oxime isomer of the major olefin isomer*: 7.67-7.61(2H, m, ArCH), 7.46-7.18 (6H, m, ArCH), 7.12-7.05 (2H, m, ArCH), 5.52 (1H, t, *J* = 7.5, H4), 2.89-2.80 (2H, m, H1), 2.65-2.58 (2H, m, H2), 1.82 (2H, dd, *J* = 7.0, 7.0, H5), 1.63-1.52 (1H, m, H6), 1.26 (9H, s, $C(CH_3)_3$), 0.83 (6H, d, *J* = 6.5, H7).
Characteristic signals only for minor isomers: 5.67 (0.05H, t, *J* = 7.5, H4 *olefin isomer*), 5.47 (0.1H, t, *J* = 7.5, H4 *oxime* isomer), 2.79-2.72 (0.3H, m, H1 *oxime and olefin isomers*), 2.58-2.51 (0.2H, m,

H2 *oxime isomers*), 2.02 (0.1H, dd, *J* = 7.5, 7.5, H5 *olefin isomer*), 1.29 (0.45H, s, C(CH$_3$)$_3$ *olefin isomer*), 1.07 (0.9H, s, C(CH$_3$)$_3$ *oxime isomer*), 0.92 (0.3H, d, *J* = 6.5, H7 *olefin isomer*).

^{13}C NMR (125 MHz, $CDCl_3$) *Signals for the major isomer only:* 175.0 (CO), 166.5 (CN), 140.2 (C3), 139.9, 134.0 (2 × ArC), 130.4 (ArCH), 128.6, 128.5 (ArCH & C4), 128.2, 127.7, 127.3, 126.8 (4 × ArCH), 38.7 (C(CH$_3$)$_3$), 37.8 (C5), 36.5 (C2), 28.8 (C6), 28.0 (C1), 27.2 (C(CH$_3$)$_3$), 22.3 (C7). *Characteristic signal for the minor isomer*: 27.0 (C(CH$_3$)$_3$').

FTIR 1759, 1460, 1269, 1105 cm^{-1}.

MS (ESI$^+$) Found [M+Na]$^+$: 414.2414 , $C_{26}H_{33}NO_2Na$ requires 414.2404.



(*E*)-2-(3-Methylbut-1-en-1-yl)-2,5-diphenyl-3,4-dihydro-2*H*-pyrrole 8r

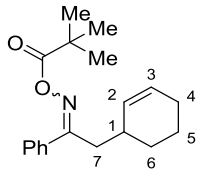
General Procedure B: Oxime ester **7r** (75 mg, 0.19 mmol) was employed. FCC (× 2: 1st column 30:1 (hexane-EtOAc); 2nd column 150:1 (toluene-EtOAc)) afforded imine **8r** (19 mg, 35%) as a pale yellow oil and the corresponding ketone (*Z*)-7-methyl-1,4-diphenyloct-4-en-1-one[7] (19.5 mg, 35%) as a colorless oil.

*Data for **8r**:*

^{1}H NMR (400 MHz, $CDCl_3$) 8.04-7.94 (2H, m, ArCH), 7.57-7.42 (5H, m, ArCH), 7.38-7.31 (2H, m, ArCH), 7.26-7.20 (1H, m, ArCH), 5.84 (1H, dd, *J* = 15.5, 1.0, H3), 5.54 (1H, dd, *J* = 15.5, 6.5, H4), 3.03 (2H, dd, *J* = 8.5, 6.5, H1), 2.58-2.49 (1H, m, H2), 2.38-2.28 (1H, m, H5), 2.26-2.16 (1H, m, H2'), 1.00 (6H, d, *J* = 6.5, H6).

^{13}C NMR (100 MHz, $CDCl_3$) 171.9 (CN), 147.5 (ArC), 135.2 (C4), 131.9 (C3), 130.5, 128.4 (2 × ArCH), 128.1, (ArC), 127.9 (2C), 126.3, 126.1 (4 × ArCH), 81.7 (NCPh), 36.8 (C2), 35.0 (C1), 30.9 (C5), 22.5, 22.4 (2 × C6).

The spectroscopic properties of this compound were consistent with the data available in the literature.[7]



2-(Cyclohex-2-en-1-yl)-1-phenylethan-1-one *O*-pivaloyl oxime 7s

General Procedure A: Part B: 2-(Cyclohex-2-en-1-yl)-1-phenylethan-1-one oxime[2] (320 mg, 1.49 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded oxime ester **7s** (383 mg, 86%, 1:0.2 mixture of oxime isomers) as a colorless oil.

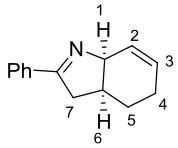
^{1}H NMR (400 MHz, $CDCl_3$) *Data for the major isomer:* 7.76-7.21 (2H, m, ArCH), 7.47-7.36 (3H, m, ArCH), 5.74-5.66 (1H, m, H3), 5.54-5.47 (1H, m, H2), 2.94-2.80 (2H, m, H7), 2.48-2.37 (1H, m, H1), 2.00-1.91 (2H, m, H4), 1.80-1.66 (2H, m, H5 & H6), 1.53-1.43 (1H, m, H5'), 1.37-1.25 (10H, m, H6' & C(CH$_3$)$_3$).

Characteristic signals for the minor isomer: 5.57 (0.2H, m, H2'), 2.72-2.65 (0.4H, m, H1'), 2.27-2.23 (0.1H, m, H7').

^{13}C NMR (100 MHz, $CDCl_3$) *Data for the major isomer only:* 175.2 (CO), 166.0 (CN), 134.5 (ArC), 130.6 (ArCH), 130.0 (C2), 128.7 (ArCH), 128.4 (C3), 127.6 (ArCH), 38.9 ($C(CH_3)_3$), 34.5 (C7), 33.6 (C1), 29.2 (C6), 27.4 ($C(CH_3)_3$), 25.1 (C4), 21.1 (C5).

FTIR 2977, 2921, 1756, 1448, 1270, 1108 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 322.1783, $C_{19}H_{25}NO_2Na$ requires 322.1777.



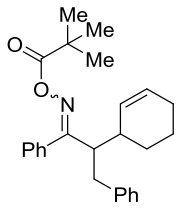
(3a*S,7a*R**)-2-Phenyl-3a,4,5,7a-tetrahydro-3*H*-indole 8s**

General Procedure B**:** Oxime ester **7s** (45 mg, 0.15 mmol) was employed. FCC (5:1 (hexane-EtOAc)) afforded imine **8s** (28 mg, 95%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.76-7.65 (2H, m, ArCH), 7.31-7.21 (3H, m, ArCH), 6.17 (1H, dddd, *J* = 10.0, 2.0, 2.0, 2.0, H2), 5.94-5.87 (1H, m, H3), 4.38-4.31 (1H, m, H1), 3.05 (1H, ddd, *J* = 16.5, 8.5, 2.5, H7), 2.76 (1H, ddd, *J* = 16.5, 2.5, 2.5, H7'), 2.55-2.44 (1H, m, H6), 2.00-1.83 (2H, m, H4), 1.64-1.56 (1H, m, H5), 1.24-1.14 (1H, m, H5').

^{13}C NMR (100 MHz, $CDCl_3$) 171.4 (CN), 134.9 (ArC), 130.4 (ArCH), 129.9 (C3), 128.3, 127.6 (2 × ArCH), 127.4 (C2), 70.1 (C1), 42.0 (C7), 35.2 (C6), 25.5 (C5), 23.3 (C4).

The spectroscopic properties of this compound were consistent with the data in the literature.[2]



2-(Cyclohex-2-en-1-yl)-1,3-diphenylpropan-1-one *O*-pivaloyl oxime 7t

General Procedure A: Part B: 2-(Cyclohex-2-en-1-yl)-1,3-diphenylpropan-1-one oxime[2] (196 mg, 0.643 mmol) was employed. In a modification to the general procedure 300 mol% Et_3N and 200 mol% pivaloyl chloride were employed. FCC (18:1 (hexane-EtOAc)) afforded oxime ester **16** (205 mg, 82%, 1:1 d.r. and 1:0.6 mixture of oxime isomers) as a colorless oil.

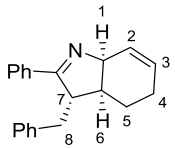
^{1}H NMR (400 MHz, $CDCl_3$) 7.33-7.02 (9H, m, ArCH), 6.90-6.82 (1H, m, ArCH), 5.95-5.56 (2H, m, =CH), 3.26-2.79 (3.6H, m), 2.56-2.49 (0.4H, m), 2.14-1.42 (6H, m), 1.37 (5.5H, m, $C(CH_3)_3$), 1.02 (3.5H, m, $C(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$) 174.8 (2C), 169.2, 169.1, 167.7 (5 × C), 140.8, 140.6, 139.5, 139.3, 136.3, 134.8, 134.5 (7 × ArC), *1 × ArC missing due to overlapping signals*, 129.9, 129.5 (2C), 129.4, 129.3, 129.1, 129.0, 128.9 (2C), 128.8 (2C), 128.7, 128.6 (2C), 128.4 (2C), 128.3 (2C), 128.2, 128.1,

128.0 (2C), 127.8, 127.7, 126.9, 126.7, 126.4, 126.3, 126.0, 125.9 (30 × CH), 53.8, 53.3 (2 × C), 38.6, 38.4 (2 × CH), 38.1, 37.9 (2 × C), 37.3, 37.1 (2 × CH), 36.0 (CH_2), 35.8 (C), 35.2, 34.2, 28.1, 27.6 (4 × CH), 27.4 (CH), 27.1 (CH_2), 26.9 (CH), 25.5, 25.3, 25.2, 25.1 (2C) (5 × CH_2). *Not all ^{13}C alkyl signals can be accurately observed due to complicated overlapping signals in the ^{13}C spectrum.*

FTIR 3027, 2932, 1699, 1267, 1028 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 412.2246, $C_{26}H_{31}NO_2Na$ requires 412.2247.



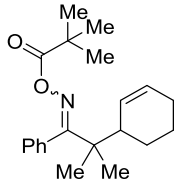
(3*S,3a*S**,7a*S**)-3-Benzyl-2-phenyl-3a,4,5,7a-tetrahydro-3*H*-indole 8t**

General Procedure B**:** Oxime ester **7t** (50 mg, 0.13 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded imine **8t** (20 mg, 55%, 1:0.1 d.r.) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.98-7.88 (2H, m, ArCH), 7.49-7.41 (3H, m, ArCH), 7.37-7.13 (5H, m, ArCH), 6.28-6.19 (1H, m, H2), 6.02-5.93 (1H, m, H3), 4.22-4.13 (1H, m, H1), 3.43 (1H, dd, *J* = 10.0, 3.5, H7), 3.02 (1H, dd, *J* = 14.0, 3.5, H8), 2.70 (1H, dd, *J* = 14.0, 10.0, H8'), 2.29 (ddd, *J* = 13.0, 5.0, 5.0, H6), 1.95-1.86 (2H, m, CH_2), 1.56-1.48 (1H, m, CH_2), 1.16 (1H, m, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) 173.5 (CN), 139.7, 133.8 (2 × ArC) 130.4 (2C) (ArCH & C3), 128.8, 128.6, 128.5, 128.0 (4 × ArCH), 127.0 (C2), 126.3 (ArCH), 67.9 (C1), 56.7 (C7), 40.6 (C6), 36.5 (C8), 25.8 (CH_2), 23.8 (CH_2).

The spectroscopic properties of this compound were consistent with the data in the literature.[2]



2-(Cyclohex-2-en-1-yl)-2-methyl-1-phenylpropan-1-one *O*-pivaloyl oxime 7u

General Procedure A: Part B: 2-(cyclohex-2-en-1-yl)-2-methyl-1-phenylpropan-1-one oxime[2] (303 mg, 1.25 mmol) was employed. In a modification to the general procedure 300 mol% Et_3N and 200 mol% pivaloyl chloride were employed. FCC (10:1 (hexane-EtOAc)) afforded oxime ester **16** (371 mg, 91%, 1:0.3 mixture of oxime isomers) as a colorless oil.

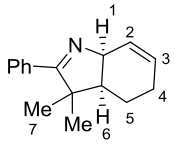
^{1}H NMR (400 MHz, $CDCl_3$) 7.37-7.30 (3.75H, m, ArCH), 7.03-6.98 (2.5H, m, ArCH), 5.83-5.78 (1.25H, m, =CH), 5.76-5.72 (1H, m, =CH), 2.42-2.37 (1H, m, CH), 1.99-1.93 (2H, m, CH), 1.85-1.74 (3.5H, m, CH), 1.67-1.62 (0.5H, m, CH), 1.54-1.29 (2.75H, m, CH), 1.20 (3H, s, CH_3), 1.16 (4.5H, s, CH_3), 0.87 (11.25H, 2 × s, $C(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$) 176.6, 176.3, 175.0 (3 × C), 133.4, 133.3 (2 × ArC), 129.3, 128.0, 127.9, 127.7 (3C), 126.5, 126.4 (8 × CH), *2 × CH not observed due to overlapping signals*, 44.7, 44.4

(2 × C), 43.1, 40.6 (2 × CH), 38.2 (C) 27.6, 26.7 (2 × CH_2), 26.6 (CH_3), 26.5 (CH_2), 26.4 (CH_3), 25.1, 23.7 (2 × CH_2), 23.4 (CH), 22.4 (CH_2), 22.3, 21.0 (2 × CH).

FTIR 2973, 2932, 1739, 1479, 1115 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 350.2087, $C_{21}H_{29}NO_2Na$ requires 350.2091.



(3a*S,7a*S**)-3,3-Dimethyl-2-phenyl-3a,4,5,7a-tetrahydro-3*H*-indole 8u**

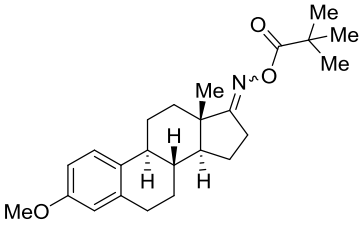
General Procedure B**:** Oxime ester **7u** (35 mg, 0.11 mmol) was employed. FCC (5:1 (hexane-EtOAc)) afforded imine **8u** (18 mg, 75%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.68-7.59 (2H, m, ArCH), 7.40-7.32 (3H, m, ArCH), 6.28 (1H, dddd, *J* = 10.0, 4.0, 3.0, 1.0, H2), 6.04-5.98 (1H, m, H3), 4.43-4.38 (1H, m, H1), 2.21-2.01 (2H, m, H6 & H4), 1.98-1.87 (1H, m, H4'), 1.68-1.60 (1H, m, H5), 1.40 (3H, s, H7), 1.23 (3H, s, H7'), 1.13 (1H, ddd, *J* = 25.0, 12.5, 4.5,H5').

^{13}C NMR (100 MHz, $CDCl_3$) 178.5 (CN), 135.3 (ArC), 130.1 (C3), 129.3 (C2), 128.1, 127.8, 127.5 (3 × ArCH), 65.8 (C1), 53.0 (CC7), 49.6 (C6), 25.7 (C7), 24.2 (C4), 21.4 (C5), 20.7 (C7').

The spectroscopic properties of this compound were consistent with the data in the literature.[2]

Estrone Mechanistic Experiment



Estrone 3-methyl ether *O*-pivaloyl oxime 16

General Procedure A: Part A: Estrone 3-methyl ether (803 mg, 2.83 mmol) was employed and afforded the corresponding oxime (500 mg, 59%) as a colorless solid. Part B: The corresponding oxime (500 mg, 1.67 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded oxime ester **16** (620 mg, 97%) as a colorless solid.

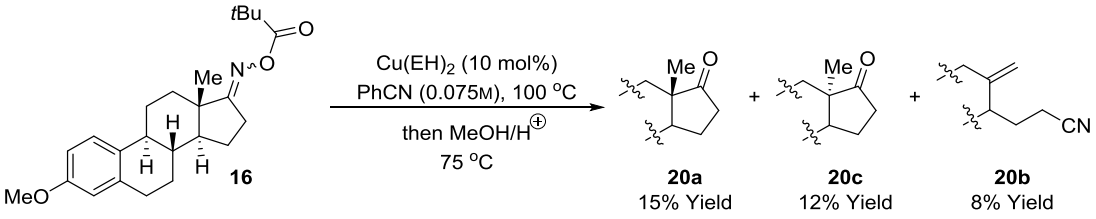
M. p. 144-145 °C (EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) 7.22 (1H, d, *J* = 8.5, ArCH), 6.72 (1H, dd, *J* = 8.5, 3.0, ArCH), 6.64 (1H, d, *J* = 3.0, ArCH), 3.78 (3H, s, OCH_3), 2.94-2.83 (2H, m, H7), 2.71-2.65 (1H, m, H10), 2.61-2.54 (1H, m, H10'), 2.41 (1H, dtd, *J* = 13.5, 4.5, 3.0, H1), 2.31-2.23 (2H, m, H2 & H6), 1.98-1.91 (2H, m, H8 & H9), 1.77 (1H, td, *J* = 13.5, 4.0, H2'), 1.60-1.39 (5H, m, H1', H4, H5, H8' & H9'), 1.28 (9H, s, $C(CH_3)_3$), 1.04 (3H, s, H11).

^{13}C NMR (100 MHz, $CDCl_3$) 179.1 (CN), 175.3 (CO), 157.6, 137.6, 132.0 (3 × ArC), 126.3, 113.9, 111.5 (3 × ArCH), 55.2 (OCH_3), 52.7 (C4), 45.4 (C3), 43.8 (C6), 38.8 ($C(CH_3)_3$), 33.7 (C2), 29.6 (C7), 27.3 ($C(CH_3)_3$), 27.2 (C9), 27.0 (C10), 26.1 (C1), 22.8 (C8), 17.0 (C11).

FTIR 2933, 2870, 1746, 1610, 1501, 1273, 1118 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 406.2345, $C_{24}H_{33}NO_3Na$ requires 406.2353.



Estrone-3-methylether 20a
3-Methoxy-13,17-secoestra-1,3,5-(10)13(18)-tetraenoic nitrile 20b
13*α*-Estrone-3-methylether 20c

General Procedure B**:** Oxime ester **16** (80 mg, 0.21 mmol) was employed and the reaction. In a modification to the general procedure, after concentration, the residue was redissolved in MeOH (7 mL) and 2M HCl (2 mL) was added. The mixture was heated at 75 °C in a sealed tube for 2 hours. After cooling to room temperature the mixture was diluted with Et_2O (10 mL) and washed with Na_2CO_3 (10 mL), brine (10 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue (10:1 – 8:1 (hexane-EtOAc)) afforded **20a-c** (20.6 mg, approx.. 35% combined yield) as a 0.44:0.34:0.22 mixture.

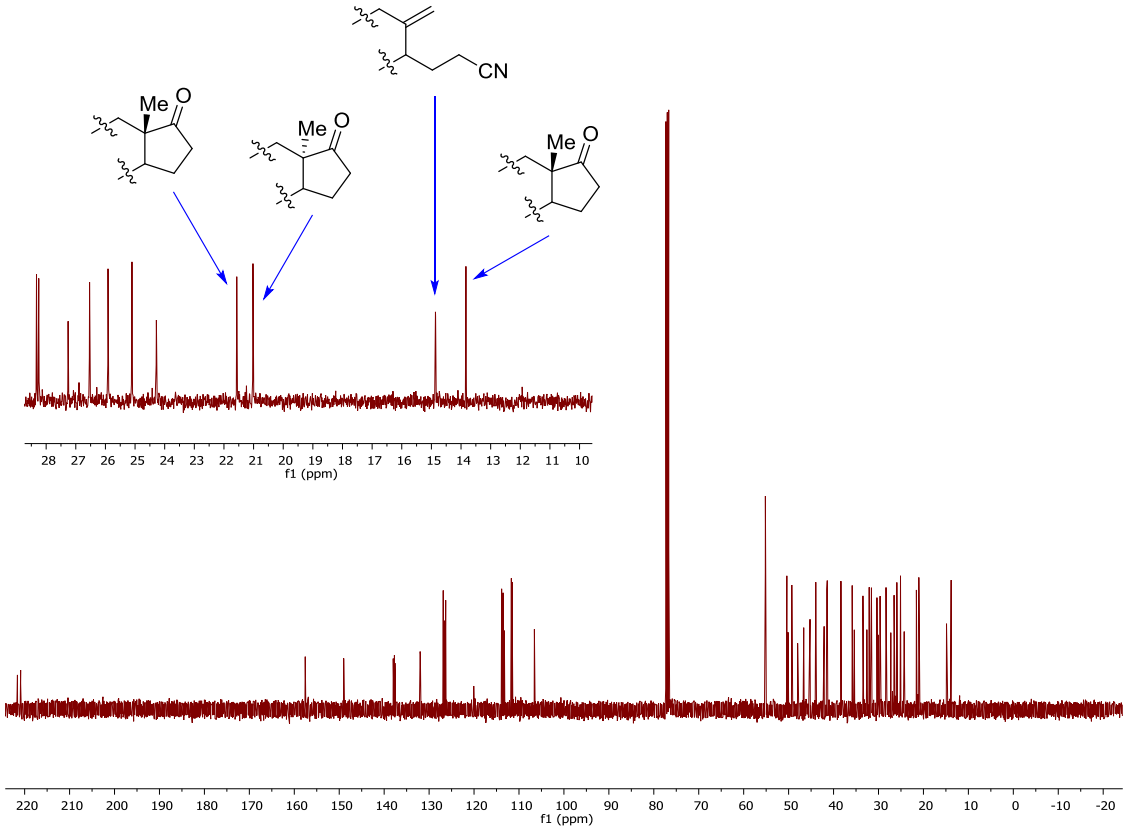
Diagnostic signals for each compound are listed below.

^{1}H NMR (400 MHz, $CDCl_3$)
*Diagnostic signals for **20a**: 0.91 (1.20H, s, CH_3).*
*Diagnostic signals for **20b**: 4.89 (0.22H, s, $=CH_AH_B$), 4.59 (0.22H, s, $=CH_AH_B$).*
*Diagnostic signals for **20c**:1.06 (1.02H, s, CH_3).*

^{13}C NMR (100 MHz, $CDCl_3$)
*Diagnostic signals for **20a**: 21.6, 13.8.*
*Diagnostic signals for **20b**: 14.9.*
*Diagnostic signals for **20c**: 21.0.*

*The spectroscopic properties of these compounds were consistent with the data available in the literature: **20a**[8], **20b**[9] and **20c**[8].*

The most diagnostic method for characterizing the mixture was ^{13}C NMR (shown below).



Cuproin Experiments

An oven-dried reaction tube, fitted with magnetic stirrer, was charged with the specified copper source (10 mol%) and cuproin (10 mol%). The tube was fitted with a rubber septum and purged with argon. Anhydrous benzonitrile (10 mL/mmol) was added *via* syringe. The mixture was then placed in a preheated oil bath (100 ^{o}C) and the appearance of the reactions were observed and monitored photographically. The reaction was also performed in the absence of cuproin.

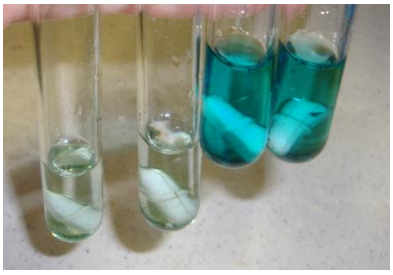
Reaction 1 – Cu(I)OAc was employed in the absence of cuproin

Reaction 2 – Cu(I)OAc was employed in the presence of cuproin

Reaction 3 – Cu(II)(2-ethylhexanoate)$_2$ was employed in the absence of cuproin

Reaction 4 – Cu(II)(2-ethylhexanoate)$_2$ was employed in the presence of cuproin

Addition of reagents



1 2 3 4

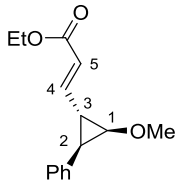
Reaction after 30 minutes

1 2 3 4

Reaction after 15 hours

1 2 3 4

Cyclopropane Substrate Synthesis and Mechanistic Studies



(*E*)-Ethyl 3-((1*S,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)acrylate**

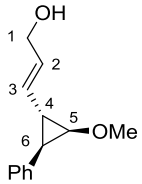
To a solution of (1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropanecarbaldehyde[10] (1.34 g, 7.61 mmol) in CH_2Cl_2 (12 mL) was added ethyl (triphenylphosphoranylidene)acetate (3.17 g, 9.11 mmol) as a solution in CH_2Cl_2 (10 mL) dropwise over 5 minutes. After being stirred for 2 hours, the solution was poured into saturated aq. NaCl (30 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (50 mL). The organic phases were combined, dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (20:1-10:1 (hexane-EtOAc)) afforded the title compound (1.36 g, 73%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.32-7.20 (5H, m, ArC<u>H</u>), 6.71 (1H, dd, *J* = 15.5, 9.5, <u>H</u>4), 5.89 (1H, dd, *J* = 15.5, 0.5, <u>H</u>5), 4.19 (2H, q, *J* = 7.0, C<u>H</u>$_2$CH$_3$), 3.61 (1H, dd, *J* = 7.0, 3.0, <u>H</u>1), 3.27 (3H, s, OC<u>H</u>$_3$), 2.32 (1H, app. t, *J* = 6.5, <u>H</u>2), 2.14 (1H, dddd, *J* = 9.5, 6.0, 3.0, 0.5, <u>H</u>3), 1.29 (3H, t, *J* = 7.0, CH$_2$C<u>H</u>$_3$);

^{13}C NMR (100 MHz, $CDCl_3$) 166.5 (<u>C</u>O), 148.5 (<u>C</u>4), 135.7 (Ar<u>C</u>), 128.1, 128.0, 126.3 (3 × Ar<u>C</u>H), 119.4 (<u>C</u>5), 67.6 (<u>C</u>1), 60.2 (<u>C</u>H$_2$CH$_3$), 58.4 (O<u>C</u>H$_3$), 33.5 (<u>C</u>2), 30.0 (<u>C</u>3), 14.3 (CH$_2$<u>C</u>H$_3$);

FTIR 2982, 1709, 1642, 1498, 1248 cm^{-1}.

MS (ESI$^+$) Found [M+Na]$^+$: 269.1139, $C_{15}H_{18}O_3Na$ requires 269.1148.



(*E*)-3-((1*S,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)prop-2-en-1-ol**

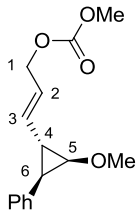
To a solution of (*E*)-ethyl 3-((1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)acrylate (1.25 g, 5.08 mmol) in CH_2Cl_2 (14 mL) at -78 ˚C was added DIBAL-H (1M in CH_2Cl_2, 10.7 mL, 10.7 mmol) over 5 minutes. The reaction was stirred at this temperature for 15 minutes after which time EtOAc (50 mL) and saturated aq. sodium potassium tartrate (50 mL) were added and the mixture was warmed to room temperature with vigorous stirring. After 1 hour the layers were separated and the aqueous layer extracted with EtOAc (3 × 100 mL). The organic layers were combined, washed with saturated aq. sodium potassium tartrate (50 mL), H_2O (50 mL), brine (50 mL), dried (Na_2SO_4) and filtered. Concentration *in vacuo* afforded the title compound (974 mg, 94%) as a yellow oil that was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) 7.30-7.23 (4H, m, ArC<u>H</u>), 7.21-7.17 (1H, m, ArC<u>H</u>), 5.74 (1H, dtd, *J* = 15.5, 6.0, 0.5, <u>H</u>2), 5.52 (1H, ddt, *J* = 15.5, 8.0, 1.5, <u>H</u>3), 4.12-4.09 (2H, m, <u>H</u>1), 3.44 (1H, dd, *J* = 6.5, 3.5, <u>H</u>5), 3.20 (3H, s, OC<u>H</u>$_3$), 2.09 (1H, app. t, *J* = 6.5, <u>H</u>6), 2.05-2.01 (1H, m, <u>H</u>4).

^{13}C NMR (100 MHz, $CDCl_3$) 136.8 (Ar<u>C</u>), 131.8 (<u>C</u>3), 128.4 (<u>C</u>2), 128.0, 127.9, 125.8 (3 × Ar<u>C</u>H), 66.7 (<u>C</u>5), 63.4 (<u>C</u>1), 58.2 (O<u>C</u>H$_3$), 31.9 (<u>C</u>6), 29.1 (<u>C</u>4).

FTIR 3380, 2934, 1701, 1602, 1498, 1354 cm^{-1}.

MS (ESI$^+$) Found $[M+Na]^+$: 227.1043, $C_{13}H_{16}O_2Na$ requires 227.1043.



(*E*)-3-((1*S,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)allyl methyl carbonate**

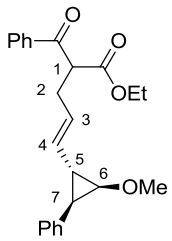
To a solution of (*E*)-3-((1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)prop-2-en-1-ol (800 mg, 3.92 mmol) in THF (6.4 mL) at 0 ˚C was added ^{n}BuLi (1.53 M, 2.85 mL, 4.36 mmol) dropwise over 3 minutes. After stirring at this temperature for 5 minutes methyl chloroformate (0.45 mL, 5.88 mmol) was added dropwise over 30 seconds. After stirring for 30 minutes the reaction mixture was diluted with Et_2O (50 mL), washed with 1M HCl (2 × 40 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (15:1 – 10:1 (hexane-EtOAc)) afforded the title compound (781 mg, 76%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.30-7.17 (5H, m, ArC<u>H</u>), 5.73-5.60 (2H, m, <u>H</u>2 & <u>H</u>3), 4.59 (2H, d, *J* = 6.0, <u>H</u>1), 3.78 (3H, s, $CO_2C\underline{H}_3$), 3.46 (1H, dd, *J* = 6.5, 3.0, <u>H</u>5), 3.21 (3H, s, $OC\underline{H}_3$), 2.12 (1H, t, *J* = 6.5, <u>H</u>6), 2.03 (1H, ddd, *J* = 7.0, 6.5, 3.0, <u>H</u>4).

^{13}C NMR (100 MHz, $CDCl_3$) 155.6 (<u>C</u>O), 136.5 (Ar<u>C</u>), 136.0 (<u>C</u>3), 128.0, 127.9, 125.9 (3 × Ar<u>C</u>H), 122.5 (<u>C</u>2), 68.2 (<u>C</u>1), 66.6 (<u>C</u>5), 58.2 (O<u>C</u>H$_3$), 54.7 ($CO_2\underline{C}H_3$), 32.0 (<u>C</u>6), 29.1 (<u>C</u>4).

FTIR 2957, 1744, 1498, 1443, 1255, 933 cm^{-1}.

MS (ESI$^+$) Found $[M+Na]^+$: 285.1093, $C_{15}H_{18}O_4Na$ requires 285.1097.



(*E*)-Ethyl 2-benzoyl-5-(1*S,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)pent-4-enoate**

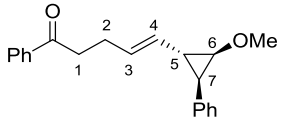
A flame-dried Schlenk tube was charged with Pd_2dba_3 (132 mg, 0.144 mmol) and PPh_3 (227 mg, 0.867 mmol). The flask was evacuated and back-filled with nitrogen three times. Argon-sparged THF (9 mL) was added and the mixture was stirred at room temperature for 15 minutes. After this time (*E*)-3-((1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)allyl methyl carbonate (757 mg, 2.89 mmol) and ethyl benzoylacetate (550 μL, 3.18 mmol) were added as a combined solution in THF (6 mL). The reaction mixture was stirred at room temperature for 18 hours after which time it was concentrated *in vacuo*. Purification of the residue by FCC (12:1 – 10:1 (hexane-EtOAc)) afforded the title compound (1.02 g, 87%, 1:1 d.r.) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.00-7.96 (2H, m, ArCH), 7.61-7.56 (1H, m, ArCH), 7.50-7.44 (2H, m, ArCH), 7.28-7.15 (5H, m, ArCH), 5.52 (1H, dt, *J* = 15.5, 7.0, H3), 5.36 (1H, dd, *J* = 15.5, 7.5, H4), 4.18-4.11 (2H, m, CH_2CH_3), 3.34 (1H, dt, *J* = 7.0, 3.5, H6), 3.15 (3H, app. d, *J* = 2.5, OCH_3), 2.77-2.63 (2H, m, H2), 2.00-1.91 (2H, m, H5 & H7), 1.17 (3H, app. td, *J* = 7.0, 4.0, CH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) 194.6 (2C) (CO), 169.4 (CO_2Et), 136.9 (2C, ArC), 136.3 (ArC), 133.5 (ArCH), 132.4 (2C × C4), 128.7 (2C), 128.6, 127.9 (2C), 127.8, 125.7, 125.6 (8 × ArCH), 125.6 (2C) (C3), *1 × ArC and 3 × ArCH not accurately observable due to signal overlap*, 69.6 (2C × C6), 61.4 (CH_2CH_3), 58.1 (OCH_3), 54.4 (C1), 31.9 (C2), 31.6 (C7), 29.2 (C5), 14.0 (CH_2CH_3).

FTIR 2984 (w), 2935 (w), 1732 (s), 1684 (s), 1597 (m), 1448 (m), 1267 (m) cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 401.1726, $C_{24}H_{26}O_4Na$ requires 401.1723.



(*E*)-5-((1*S,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)-1-phenylpent-4-en-1-one**

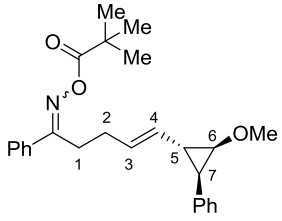
To a solution of (*E*)-ethyl 2-benzoyl-5-((1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)pent-4-enoate (1.00 g, 2.65 mmol) in THF (12 mL) was added KOH (600 mg, 11.9 mmol), MeOH (2.6 mL) and H_2O (6.6 mL). The reaction mixture was heated at reflux for 2 hours after which time the heat was removed and 1M HCl (35 mL) was added. The mixture was stirred for 10 minutes followed by extraction with EtOAc (2 × 120 mL). The combined organic layers were washed with brine (60 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (10:1 (hexane-EtOAc)) afforded the title compound (616 mg, 76%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.97-7.94 (2H, m, ArCH), 7.58-7.54 (1H, m, ArCH), 7.48-7.44 (2H, m, ArCH), 7.29-7.22 (4H, m, ArCH), 7.20-7.16 (1H, m, ArCH), 5.62 (1H, dtd, *J* = 15.5, 7.0, 1.0, H3), 5.35 (1H, ddt, *J* = 15.5, 7.5, 1.5, H4), 3.39 (1H, dd, *J* = 6.5, 3.5, H6), 3.18 (3H, s, OCH_3), 3.06-3.02 (2H, m, H1), 2.49-2.43 (2H, m, H2), 2.04-1.96 (2H, m, H7 & H5).

^{13}C NMR (100 MHz, $CDCl_3$) 199.5 (CO), 137.1, 136.9 (2 × ArC), 133.0 (ArCH), 130.2 (C2), 128.6 (2C) (C3 & ArCH), 128.0, 127.9, 127.8, 125.7 (4 × ArCH), 66.6 (C6), 58.2 (OCH_3), 38.4 (C1), 31.6 (C7), 29.3 (C5), 27.0 (C2).

FTIR 2933, 1685, 1599, 1497, 1450, 1356, 1199 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 329.1507, $C_{21}H_{22}O_2Na$ requires 329.1512.



(4*E*)-5-((1*S,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)-1-phenylpent-4-en-1-one *O*-pivaloyl oxime 21a**

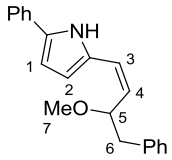
General Procedure A: Part A: (*E*)-5-((1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)-1-phenylpent-4-en-1-one (610 mg, 1.99 mmol) was used. The reaction was heated at 75 ^{o}C for 4 hours to afford the corresponding oxime (568 mg, 89%) as a colorless oil. Part B: The corresponding oxime (565 mg, 1.46 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded oxime ester **21a** (536 mg, 76%, >1:0.05 mixture of oxime isomers) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.73-7.71 (2H, m, ArC<u>H</u>), 7.46-7.37 (3H, m, ArC<u>H</u>), 7.29-7.16 (5H, m, ArC<u>H</u>), 5.52 (1H, dt, *J* = 15.5, 7.0, <u>H</u>3), 5.29 (1H, ddt, *J* = 15.5, 7.0, 1.5, <u>H</u>4), 3.33 (1H, dd, *J* = 6.5, 3.5, <u>H</u>6), 3.16 (3H, s, OC<u>H</u>$_3$), 2.91-2.87 (2H, m, <u>H</u>1), 2.33-2.27 (2H, m, <u>H</u>2), 1.99-1.92 (2H, m , <u>H</u>5 & <u>H</u>7), 1.33 (9H, s, C(C<u>H</u>$_3$)$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) *Signals for the major isomer only:* 175.0 (<u>C</u>O), 166.2 (<u>C</u>N), 137.0, 134.1 (2 × Ar<u>C</u>H), 130.8 (<u>C</u>4), 130.5, 128.6, 128.0 (3 × Ar<u>C</u>H), 127.8 (2C, Ar<u>C</u>H & <u>C</u>3), 127.3, 125.8 (2 × Ar<u>C</u>H), 66.6 (<u>C</u>6), 58.2 (O<u>C</u>H$_3$), 38.8 (<u>C</u>(CH$_3$)$_3$), 31.6 (<u>C</u>7), 29.6 (<u>C</u>2), 29.2 (<u>C</u>5), 28.6 (<u>C</u>1), 27.3 (C(<u>C</u>H$_3$)$_3$).

FTIR 2973, 1755, 1604, 1497, 1445, 1108 cm^{-1}.

MS (ESI^{+}) Found [M+Na]$^{+}$: 428.2190, $C_{26}H_{31}NO_3Na$ requires 428.2196.

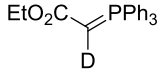


(*Z*)-2-(3-Methoxy-4-phenylbut-1-en-1-yl)-5-phenyl-1*H*-pyrrole 22a

General Procedure B**:** Oxime ester **21a** (100 mg, 0.247 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded pyrrole **22a** (12.5 mg, 17%) as a colorless oil. *N.B. This compound is very unstable and therefore required immediate characterization by NMR. Due to the very high instability only characterization by ^{1}H and ^{13}C NMR could be obtained.*

^{1}H NMR (400 MHz, $CDCl_3$) 10.70 (1H, br. s, N<u>H</u>), 7.51-7.48 (2H, m, ArC<u>H</u>), 7.39-7.35 (3H, m, ArC<u>H</u>), 7.31-7.18 (5H, m, ArC<u>H</u>), 6.52 (1H, dd, *J* = 3.5, 2.5, <u>H</u>1), 6.46 (1H, d, *J* = 12.5, <u>H</u>3), 6.26 (1H, dd, *J* = 3.5, 2.5, <u>H</u>2), 5.30 (1H, dd, *J* = 12.5, 6.0, <u>H</u>4), 4.42-4.37 (1H, m, <u>H</u>5), 3.41 (3H, s, <u>H</u>7), 3.16 (1H, dd, *J* = 13.5, 7.0, <u>H</u>6), 2.99 (1H, dd, *J* = 13.5, 7.0, <u>H</u>6').

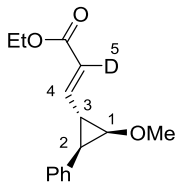
^{13}C NMR (100 MHz, $CDCl_3$) 138.0, 134.0, 132.5, 130.2 (4 × Ar<u>C</u>), 129.4, 128.9, 128.4, 126.4, 126.2, 123.6 (6 × Ar<u>C</u>H), 123.4 (<u>C</u>3), 121.8 (<u>C</u>4), 113.7 (<u>C</u>2), 106.9 (<u>C</u>1), 79.4 (<u>C</u>5), 54.9 (<u>C</u>7), 40.4 (<u>C</u>6).



Ethyl (triphenylphosphoranylidene)acetate-d[11]

To a solution of ethyl (triphenylphosphoranylidene)acetate (5.00 g, 14.4 mmol) in CH_2Cl_2 (20 mL) was added D_2O (1.3 mL). The mixture was stirred vigorously for 2 hours after which time the aqueous layer was syringed off. This process was repeated twice more. H-D exchange was confirmed

by loss of C<u>H</u> signal in the ^{1}H NMR. The title compound was used as a stock solution without further purification.



Ethyl (*E*)-3-((1*S,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)acrylate-2-*d***

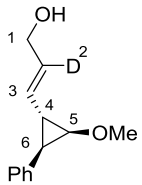
To a solution of (1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropanecarbaldehyde[10] (2.07 g, 11.8 mmol) in CH_2Cl_2 (20 mL) was added freshly prepared ethyl (triphenylphosphoranylidene)acetate-*d* (4.92 g, 14.1 mmol) as a solution in CH_2Cl_2 (20 mL) dropwise over 5 minutes. After being stirred for 2 hours the reaction with quenched by addition of saturated aq. NaCl (50 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (100 mL). The organic phases were combined, dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (10:1 (hexane-EtOAc)) afforded the title compound (2.10 g, 72%) as a colorless oil. *95% D incorporation as determined by ^{1}H NMR.*

<u>^{1}H NMR</u> (500 MHz, $CDCl_3$) 7.35-7.24 (5H, m, ArC<u>H</u>), 6.76-6.72 (1H, m, <u>H</u>4), 5.93 (0.05H, dd, *J* = 15.5, 0.5, <u>H</u>5), 4.23 (2H, q, *J* = 7.0, C<u>H</u>$_2$CH$_3$), 3.65 (1H, dd, *J* = 7.0, 3.0, <u>H</u>1), 3.31 (3H, s, OC<u>H</u>$_3$), 2.36 (1H, app. t, *J* = 6.5, <u>H</u>2), 2.18 (1H, ddd, *J* = 9.5, 6.0, 3.0, <u>H</u>3), 1.33 (3H, t, *J* = 7.0, CH$_2$C<u>H</u>$_3$).

<u>^{13}C NMR</u> (125 MHz, $CDCl_3$) 166.4 (<u>C</u>O), 148.3 (<u>C</u>4), 135.7 (Ar<u>C</u>), 128.1, 128.0, 126.3 (3 × Ar<u>C</u>H), 119.4 (very weak intensity, <u>C</u>5), 119.1 (t, *J* = 25.0, <u>C</u>D), 67.6 (<u>C</u>1), 60.2 (<u>C</u>H$_2$CH$_3$), 58.4 (O<u>C</u>H$_3$), 33.5 (<u>C</u>2), 30.0 (<u>C</u>3), 14.3 (CH$_2$<u>C</u>H$_3$).

<u>FTIR</u> 2983, 2936, 1705, 1631, 1603, 1499, 1235 cm^{-1}.

<u>MS</u> (ESI^{+}) Found [M+Na]$^{+}$: 270.1214, $C_{15}H_{17}DO_3Na$ requires 270.1211.



(*E*)-3-((1*S,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)prop-2-en-2-*d*-1-ol**

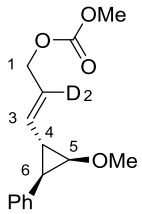
To a solution of ethyl (*E*)-3-((1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)acrylate-2-*d* (2.00 g, 8.10 mmol) in CH_2Cl_2 (23 mL) at -78 ˚C was added DIBAL-H (1M in CH_2Cl_2, 17.0 mL, 17.0 mmol) over 5 minutes. The reaction was stirred at this temperature for 15 minutes after which time EtOAc (70 mL) and saturated aq. sodium potassium tartrate (70 mL) were added and the mixture was warmed to room temperature with vigorous stirring. After 1 hour the layers were separated and the aqueous layer extracted with EtOAc (3 × 120 mL). The organic layers were combined, washed with saturated aq. sodium potassium tartrate (100 mL), H_2O (100 mL), brine (100 mL), dried (Na_2SO_4) and filtered. Concentration *in vacuo* afforded the title compound (1.54 mg, 93%) as a yellow oil that was used without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) 7.32-7.25 (3H, m, ArC<u>H</u>), 7.22-7.19 (2H, m, ArC<u>H</u>), 5.75 (0.05H, dtd, *J* = 15.5, 6.0, 1.0, <u>H</u>5), 5.55-5.51 (1H, m, <u>H</u>4), 4.11 (2H, m, <u>H</u>6), 3.45 (1H, dd, *J* = 6.5, 3.5, <u>H</u>1), 3.22 (3H, s, OC<u>H</u>$_3$), 2.10 (1H, app. t, *J* = 6.5, <u>H</u>2), 2.06-2.03 (1H, m, <u>H</u>3).

^{13}C NMR (125 MHz, $CDCl_3$) 136.8 (Ar<u>C</u>), 131.6 (<u>C</u>4), 128.0, 127.8, 125.8 (3 × Ar<u>C</u>H), 66.7 (<u>C</u>1), 63.2 (<u>C</u>6), 58.2 (O<u>C</u>H$_3$), 31.8 (<u>C</u>2), 29.0 (<u>C</u>3); *<u>C</u>H/D not observed due to anticipated weak intensity.*

FTIR 3403, 2933, 1699, 1602, 1497, 1218 cm^{-1}.

MS (ESI$^+$) Found $[M+Na]^+$: 228.1095, $C_{13}H_{15}DO_2Na$ requires 228.1105.



(*E*)-3-((1*S,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)allyl-2-*d* methyl carbonate**

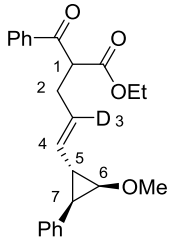
To a solution of (*E*)-3-((1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)prop-2-en-2-*d*-1-ol (1.52 g, 7.41 mmol) in THF (12 mL) at 0 ˚C was added ^{n}BuLi (2.33 M, 3.5 mL, 8.24 mmol) dropwise over 3 minutes. After stirring at this temperature for 10 minutes, methyl chloroformate (0.86 mL, 11.1 mmol) was added dropwise over 30 seconds. After stirring for 30 minutes the reaction mixture was diluted with Et_2O (160 mL) and warmed to room temperature. The mixture was washed with 1M HCl (2 × 80 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (15:1 – 10:1 (hexane-EtOAc)) afforded the title compound (1.21 g, 62%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) 7.30-7.24 (4H, m, ArC<u>H</u>), 7.21-7.18 (1H, m, ArC<u>H</u>), 5.70 (0.05H, dt, *J* = 15.5, 6.0, <u>H</u>5), 5.65-5.62 (1H, m, <u>H</u>4), 4.59 (2H, d, *J* = 1.0, <u>H</u>6), 3.78 (3H, s, OCO$_2$C<u>H</u>$_3$), 3.46 (1H, dd, *J* = 6.5, 3.0, <u>H</u>1), 3.21 (3H, s, OC<u>H</u>$_3$), 2.12 (1H, app. t, *J* = 6.5, <u>H</u>2), 2.03 (1H, ddd, *J* = 8.0, 6.5, 3.0, <u>H</u>3).

^{13}C NMR (125 MHz, $CDCl_3$) 155.6 (O<u>C</u>O$_2$Me), 136.5 (Ar<u>C</u>), 135.9 (<u>C</u>4), 128.0, 127.9, 125.9 (3 × Ar<u>C</u>H), 122.5 (<u>C</u>5), 122.2 (t, *J* = 24.0, <u>C</u>D), 68.1 (<u>C</u>6), 66.6 (<u>C</u>1), 58.2 (O<u>C</u>H$_3$), 54.7 (OCO$_2$<u>C</u>H$_3$), 31.9 (<u>C</u>2), 29.0 (<u>C</u>3).

FTIR 2956, 2826, 1744, 1443, 1258 cm^{-1}.

MS (ESI$^+$) Found $[M+Na]^+$: 286.1154, $C_{15}H_{17}DO_4Na$ requires 286.1160.



Ethyl (*E*)-2-benzoyl-5-((1*S,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)pent-4-enoate-4-*d***

A flame-dried Schlenk tube was charged with Pd_2dba_3 (201 mg, 0.219 mmol) and PPh_3 (343 mg, 1.31 mmol). The flask was evacuated and back-filled with nitrogen three times. Argon-sparged THF (16

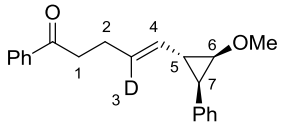
mL) was added and the mixture stirred at room temperature for 15 minutes. After this time (*E*)-3-((1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)allyl-2-*d* methyl carbonate (1.16 g, 4.41 mmol) and ethyl benzoylacetate (840 μL, 4.84 mmol) were added as a combined solution in THF (7 mL). The reaction mixture was stirred at room temperature for 18 hours after which time it was concentrated *in vacuo*. Purification of the residue by FCC (15:1 – 5:1 (hexane-EtOAc)) afforded the title compound (1.39 g, 83%, 1:1 d.r.) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) 7.99-7.97 (2H, m, ArC**H**), 7.60-7.56 (1H, m, ArC**H**), 7.50-7.45 (2H, m, ArC**H**), 7.28-7.24 (2H, m, ArC**H**), 7.22-7.15 (3H, m, ArC**H**), 5.53 (0.05H, dtd, *J*= 15.5, 7.0, 1.0, **H**3), 5.37 (1H, d, *J* = 7.5, **H**4), 4.35 (1H, dd, *J* = 7.5, 7.0, **H**1), 4.20-4.10 (2H, m, C**H**$_2$CH$_3$), 3.34 (1H, app. ddd, *J* = 6.5, 4.5, 3.5, **H**6), 3.15 (3H, app. d, *J* = 3.0, OC**H**$_3$), 2.71 (2H, m, **H**2), 1.99-1.96 (1H, m, **H**7), 1.96-1.92 (1H, m, **H**5), 1.17 (3H, app. td, *J* = 7.0, 5.0, CH$_2$C**H**$_3$).

^{13}C NMR (125 MHz, $CDCl_3$) 194.7 (**C**O$_A$), 194.6 (**C**O$_B$), 169.4 (**C**O$_2$Et), 137.0, 136.3 (2 × Ar**C**), 133.5 (Ar**C**H), 132.3 (**C**4), 128.7, 128.6, 128.0, 127.9, 125.7 (5 × Ar**C**H), 125.6 (**C**3-H), 125.3 (t, *J* = 23.5, **C**3-D), 66.6 (2C) (**C**6), 61.4 (**C**H$_2$CH$_3$), 58.2 (O**C**H$_3$), 54.4 (**C**1), 31.8 (**C**2), 31.6 (**C**7), 29.2 (**C**5), 14.1 (CH$_2$**C**H$_3$).

FTIR 2983, 2935, 1732, 1683, 1597, 1448, 1203 cm^{-1}.

MS (ESI$^+$) Found [M+Na]$^+$: 402.1782, $C_{24}H_{25}DO_4Na$ requires 402.1786.



(*E*)-5-((1*S,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)-1-phenylpent-4-en-1-one-4-*d***

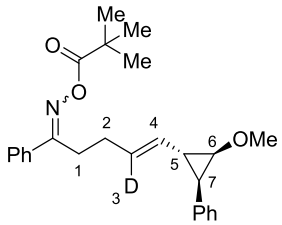
To a solution of (*E*)-ethyl 2-benzoyl-5-((1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)pent-4-enoate (1.37 g, 3.61 mmol) in THF (18 mL) was added KOH (910 mg, 16.2 mmol), MeOH (3.6 mL) and H_2O (9.0 mL). The reaction mixture was heated at reflux for 2 hours after which time the heat was removed and 1M HCl (36 mL) was added. The mixture was stirred for 10 minutes followed by extraction with EtOAc (2 × 140 mL). The combined organic layers were washed with brine (60 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (10:1 (hexane-EtOAc)) afforded the title compound (810 mg, 73%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) 7.97-7.95 (2H, m, ArC**H**), 7.58-7.54 (1H, m, ArC**H**), 7.49-7.45 (2H, m, ArC**H**), 7.29-7.23 (4H, m, ArC**H**), 7.20-7.16 (1H, m, ArC**H**), 5.62 (0.05H, dtd, *J* = 15.5, 7.0, 1.0, **H**3), 5.36-5.33 (1H, m, **H**4), 3.39 (1H, dd, *J* = 6.5, 3.5, **H**6), 3.18 (3H, s, OC**H**$_3$), 3.06-3.03 (2H, m, **H**1), 2.48-2.44 (2H, m, **H**2), 2.03 (1H, app. t, *J* = 6.5, **H**7), 2.00-1.97 (1H, m, **H**5).

^{13}C NMR (125 MHz, $CDCl_3$) 199.5 (**C**O), 137.1, 136.9 (2 × Ar**C**), 132.9 (Ar**C**H), 130.0 (**C**4), 128.5, 128.0, 127.9, 127.8, 125.6 (5 × Ar**C**H), 66.6 (**C**6), 58.1 (O**C**H$_3$), 38.3 (**C**1), 31.5 (**C**7). *C3-H/D not observed due to anticipated weak intensity.*

FTIR 2994, 1685, 1599, 1497, 1202 cm^{-1}.

MS (ESI$^+$) Found [M+Na]$^+$: 330.1577, $C_{21}H_{21}DO_2Na$ requires 330.1575.



(4*E*)-5-((1*S,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)-1-phenylpent-4-en-1-one-4-*d* *O*-pivaloyl oxime-4-*d* 21b**

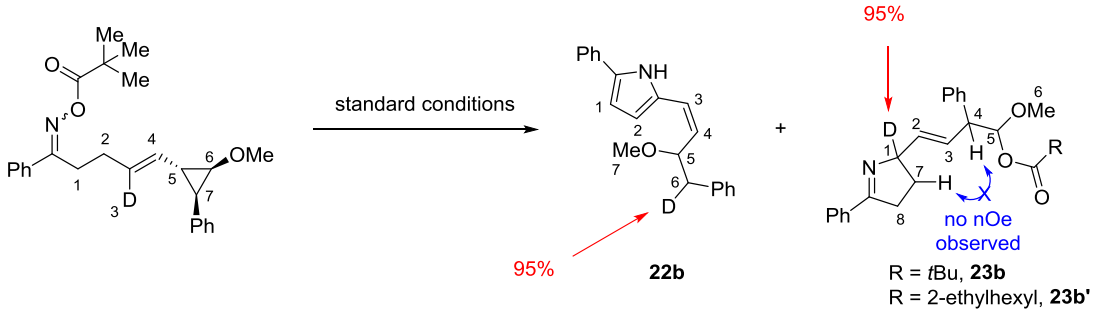
General Procedure A: Part A: (*E*)-5-((1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)-1-phenylpent-4-en-1-one-4-*d* (790 mg, 2.57 mmol) was employed and afforded the corresponding oxime (828 mg, 100%) as a colorless oil. Part B: The corresponding oxime (820 mg, 2.55 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded oxime ester **21b** (847 mg, 81%, 1:0.10 mixture of oxime isomers) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) 7.74-7.71 (2H, m, ArCH), 7.45-7.38 (3H, m, ArCH), 7.29-7.16 (5H, m, ArCH), 5.55-5.49 (0.05H, m, H3), 5.31-5.28 (0.90H, m, H4), 5.23 (0.10H, d, *J* = 7.5, H4'), 3.37-3.32 (1H, m, H6), 3.18 (0.3H, s, OCH_3), 3.17 (1.7H, s, OCH_3), 2.91-2.88 (1.8H, m, H1), 2.79-2.75 (0.2H, m, H1'), 2.32-2.29 (1.8H, m, H2), 2.24-2.21 (0.2H, m, H2'), 2.00-1.93 (2H, m, H5 & H7), 1.33 (8.1H, s, $C(CH_3)_3$), 1.07 (0.9H, s, $C(CH_3)_3$).

^{13}C NMR (125 MHz, $CDCl_3$) *Signals for the major isomer only* 174.9 (CO), 166.2 (CN), 136.9, 134.1 (2 × ArC), 130.7 (C4), 130.5, 128.6, 127.9, 127.8, 127.3, 125.7 (6 × ArCH), 66.6 (C6), 58.1 (OCH_3), 38.8 ($C(CH_3)_3$), 31.6 (C7), 29.5 (C2), 29.1 (C5), 28.5 (C1), 27.3 ($C(CH_3)_3$). *C3-H/D not observed due to anticipated weak intensity.*

FTIR 2972, 2934, 1755, 1603, 1497, 1108 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 429.2256, $C_{26}H_{30}NO_3DNa$ requires 429.2259.



(*Z*)-2-(3-Methoxy-4-phenylbut-1-en-1-yl)-5-phenyl-1*H*-pyrrole 22b
(*E*)-1-Methoxy-2-phenyl-4-(5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl-*d*)but-3-en-1-yl pivalate 23b
(*E*)-1-Methoxy-2-phenyl-4-(5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl-2-*d*)but-3-en-1-yl 2-ethylhexanoate 23b'

General Procedure B**:** Oxime ester **21a** (100 mg, 0.246 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded pyrrole **22b (**6 mg, 8%, approx. 80% pure) as a brown oil. Continued elution afforded **23b** and **23b'** (approx. 1:0.7 mixture of **23b**:**23b'**, 12 mg, approx. 12%) and a yellow oil.
*Data for **22b**:* This compound is very unstable and therefore required immediate characterization by NMR. Due to the very high instability and low quantity of material only characterization by ^{1}H could

be obtained. ^{1}H NMR data for this compound was identical to that of **22a** except for 4.38 (1H, app. t, *J* = 6.5, H5), 3.14 (1H, d, *J* = 7.5, H6), 3.01 (0.05H, dd, *J* = 13.5, 7.0, H6').

*Data for **23b** and **23b':*** Analysis was complicated as both **23b** and **23b'** were each formed as a mixture of 4 diastereomers. ^{1}H and ^{13}C NMR analysis was pursued on the mixture and assignments were made, where possible, with the aid of 2D NMR experiments.

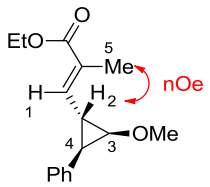
^{1}H NMR (400 MHz, $CDCl_3$) 7.87-7.83 (2H, m, ArCH), 7.45-7.37 (3H, m, ArCH), 7.32-7.18 (5H, m, ArCH), 6.05-5.88 (2H, m, H2 & H5), 5.75-5.56 (1H, m, H3), 3.71-3.65 (1H, m, H4), 3.44-3.31 (3H, m, H6), 3.08-2.86 (2H, m, H8), 2.32-2.22 (1.6H, m, H7 and CH_2), 1.80-1.27 (7.4H, m, H7' & CH_2), 1.18-1.01 (8.4H, 4 × s, $C(CH_3)_3$), 0.96-0.88 (3.4H, m, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) 180.4 (CO-***23b***), 178.2 (CO), 173.7 (CN, *signal inferred by HMBC from H8*), 139.2-139.1 (ArC), 135.2-134.6 (C3), 130.8 (ArCH), 129.0-126.8 (ArCH & C2), 100.2-99.9 (C5), 73.8-75.3 (C1-D), 57.1-57.0 (C8), 53.3-53.0 (C4), 46.8 (CH-***23b'***), 39.1-38.9 ($C(CH_3)_3$-***23b***), 35.2-35.0 (C8), 31.5 (CH_2-***23b'***), 29.8-29.0 (C7, CH_2-***23b'***), 27.1-26.8 ($C(CH_3)_3$-***23b***), 25.2, 22.7 (2 × CH_2-***23b'***), 13.9, 11.8 (2 × CH_3-***23b'***).

FTIR 3057, 2930, 1727, 1606, 1448, 1346, 1156 cm^{-1}.

MS (ESI^+) For R = *t*-Bu: Found $[M+H]^+$: 407.2441, $C_{26}H_{31}DNO_3$ requires 407.2439.
For R = 2-ethylhexyl: Found $[M+H]^+$: 449.2904, $C_{29}H_{37}DNO_3$ requires 449.2909.

*The alkene geometry of **23b**/**23b'** was tentatively assigned as trans because no nOe was observed between H7 and H4 as shown on the molecule.*



(*E*)-Ethyl 3-((1*S,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)-2-methylacrylate**

To a solution of NaH (434 mg, 11.8 mmol, 60% dispersion in mineral oil) in THF (24 mL) at 0 °C was added triethyl phosphonoacetate (2.50 mL, 11.6 mmol) dropwise *via* syringe over 2 minutes. Stirring was continued for a further 15 minutes after which time the reaction mixture was warmed to room temperature and (1*S*,2*S*,3*R*)-2-methoxy-3-phenylcyclopropanecarbaldehyde[10] (2.04 g, 11.6 mmol) in THF (4 mL) was added *via* syringe over 5 minutes. The reaction mixture was stirred for 15 minutes and then quenched by addition of H_2O (5 mL). The mixture was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with brine (50 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (10:1 (hexane-EtOAc)) afforded the title compound (2.70 g, 90%) as a yellow oil.

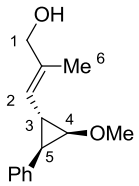
^{1}H NMR (400 MHz, $CDCl_3$) 7.30-7.17 (5H, m, ArCH), 6.28 (1H, dq, *J* = 10.5, 1.5, H1), 4.17 (2H, q, *J* = 7.0, CH_2CH_3), 3.59 (1H, dd, *J* = 7.0, 3.0, H3), 3.23 (3H, s, OCH_3), 2.25 (1H, app. t, *J* = 6.5, H4), 2.16 (1H, ddd, *J* = 10.5, 6.0, 3.0, H2), 1.94 (3H, d, *J* = 1.5, H5), 1.27 (3H, t, *J* = 7.0, CH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) 167.9 (CO), 141.2 (C1), 136.1 (ArC), 128.1, 128.0 (2 × ArCH), 127.0 (C=CH), 126.2 (ArCH), 67.6 (C1), 60.5 (CH_2CH_3), 58.4 (OCH_3), 33.3 (C4), 28.0 (C2), 14.3 (C5), 12.7 (CH_2CH_3).

FTIR 3012, 2909, 1701, 1641, 1498, 1367, 1240, 1174, 1095 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 283.1308, $C_{16}H_{20}O_3Na$ requires 283.1305.

The alkene geometry of the above ester was determined to be E by a nOe between H2 and H6 as shown on the structure.



(*E*)-3-((1*S,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)-2-methylprop-2-en-1-ol**

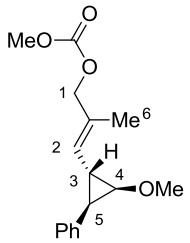
To a solution of (*E*)-Ethyl 3-((1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)-2-methylacrylate (2.70 g, 10.4 mmol) in CH_2Cl_2 (29 mL) at -78 °C was added DIBAL-H (1M in CH_2Cl_2, 22 mL, 22.0 mmol). The reaction mixture was stirred at this temperature for 90 minutes followed by quenching with EtOAc (100 mL) and saturated aq. Rochelle salt (60 mL). The mixture was warmed to room temperature and stirred vigorously for 1 hour. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 150 mL). The combined organic layers were washed with saturated aq. Rochelle salt (100 mL), H_2O (100 mL), brine (100 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo* to afford the title compound (2.15 g, 95%) which was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) 7.31-7.27 (4H, m, ArCH), 7.21-7.17 (1H, m, ArCH), 5.05 (1H, dq, *J* = 9.0, 1.5, H2), 4.02-401 (2H, m, H1), 3.43 (1H, dd, *J* = 6.5, 3.5, H4), 3.20 (3H, s, OCH_3), 2.11 (1H, ddd, *J* = 9.0, 6.5, 3.5, H3), 2.02 (1H, app. t, *J* = 6.5, H5), 1.79 (2H, d, *J* = 1.5, H6).

^{13}C NMR (100 MHz, $CDCl_3$) 137.1 (ArC), 135.7 (C=CH), 128.0, 127.8, 125.7 (3 × ArCH), 125.3 (C2), 68.3 (C1), 67.2 (C4), 58.2 (OCH_3), 32.3 (C5), 26.4 (C3), 14.3 (C6).

FTIR 3402, 2934, 1722, 1702, 1602, 1497 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 241.1202, $C_{14}H_{18}O_2Na$ requires 241.1199.



(*E*)-3-((1*S,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)-2-methylallyl methyl carbonate**

To a solution of (*E*)-3-((1*S**,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)-2-methylprop-2-en-1-ol (2.15 g, 9.86 mmol) in THF (16 mL) at 0 °C was added ^{n}BuLi (1.56M, 7.1 mL, 11.0 mmol) over 5 minutes. The reaction was stirred for 15 minutes followed by addition of methyl chloroformate (1.14

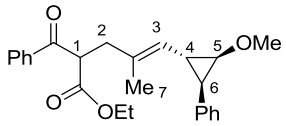
mL, 14.8 mmol) *via* syringe over 1 minute. The reaction mixture was stirred for a further 10 minutes and then diluted with Et_2O (200 mL) and washed with 1M HCl (2 × 100 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (10:1 (hexane-EtOAc)) afforded the title compound (1.68 g, 62%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.30-7.25 (4H, m, ArC<u>H</u>), 7.22-7.17 (1H, m, ArC<u>H</u>), 5.14-5.10 (1H, m, <u>H</u>6), 4.53-4.52 (2H, m, <u>H</u>1), 3.79 (3H, s, $CO_2C\underline{H}_3$), 3.44 (1H, dd, *J* = 6.5, 3.5, <u>H</u>4), 3.20 (3H, s, $OC\underline{H}_3$), 2.12-2.03 (2H, m, <u>H</u>3 & <u>H</u>5), 1.81 (3H, d, *J* = 1.5, <u>H</u>6).

^{13}C NMR (100 MHz, $CDCl_3$) 155.7 (<u>C</u>O), 136.8 (Ar<u>C</u>), 130.2 (<u>C</u>=CH), 129.6 (<u>C</u>2), 128.0, 127.9, 125.8 (3 × Ar<u>C</u>H), 71.1 (<u>C</u>1), 67.1 (<u>C</u>4), 58.3 ($O\underline{C}H_3$), 54.7 ($CO_2\underline{C}H_3$), 32.3 (<u>C</u>5), 26.4 (<u>C</u>3), 14.5 (<u>C</u>6).

FTIR 2957, 1745, 1443, 1256, 927 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 299.1263, $C_{16}H_{20}O_4Na$ requires 299.1254.



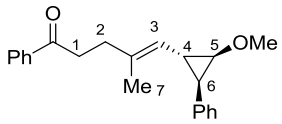
(*E*)-Ethyl 2-benzoyl-5-(1*S,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)-4-methylpent-4-enoate**
A flame-dried Schlenk tube was charged with Pd_2dba_3 (277 mg, 0.303 mmol) and PPh_3 (472 mg, 1.82 mmol). The flask was evacuated and back-filled with nitrogen three times. Argon-sparged THF (22 mL) was added and the mixture stirred at room temperature for 15 minutes. After this (*E*)-3-((1*S**,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)-2-methylallyl methyl carbonate (1.68 g, 6.09 mmol) and ethyl benzoylacetate (1.15 mL, 6.67 mmol) were added as a combined solution in THF (10 mL). The reaction mixture was stirred at room temperature for 18 hours after which time it was concentrated *in vacuo*. Purification of the residue by FCC (15:1 – 5:1 (hexane-EtOAc)) afforded the title compound (2.13 g, 89%, 1:1 d.r.) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.00-7.96 (2H, m, ArC<u>H</u>), 7.61-7.55 (2H, m, ArC<u>H</u>), 7.50-7.44 (2H, m, ArC<u>H</u>), 7.28-7.15 (5H, m, ArC<u>H</u>), 4.85-4.82 (1H, m, <u>H</u>4), 4.51-4.47 (1H, m, <u>H</u>1), 4.17-4.09 (2H, m, $C\underline{H}_2CH_3$), 3.29 (1H, app. ddd, *J* = 7.5, 6.5, 3.5, <u>H</u>6), 3.14 (3H, app. d, *J* = 6.0, $C\underline{H}_3$), 2.76-2.64 (2H, m, <u>H</u>2), 2.01-1.97 (1H, m, <u>H</u>5), 1.87 (1H, app. dt, *J* = 16.5, 6.5, <u>H</u>7), 1.77 (3H, app. dt, *J* = 2.5, 1.5, <u>H</u>3), 1.17 (3H, app. dt, *J* = 14.5, 7.0, $CH_2\underline{H}_3$).

^{13}C NMR (100 MHz, $CDCl_3$) 194.9, 194.8 (2 × <u>C</u>O), 169.5 ($\underline{C}O_2Et$), 137.2 (2C, 2 × Ar<u>C</u>), 136.4 (2C, 2 × Ar<u>C</u>), 133.4 (2C, 2 × Ar<u>C</u>H), 132.6, 132.5 (2 × <u>C</u>=CH), 128.7 (2C, 2 × Ar<u>C</u>H), 128.5 (2C, 2 × Ar<u>C</u>H), 127.9 (2C, 2 × Ar<u>C</u>H), 127.8 (Ar<u>C</u>H), 127.1 (2C, 2 × <u>C</u>4), 125.7, 125.6 (2 × Ar<u>C</u>H), 67.1 (2C, 2 × <u>C</u>6), 61.4 ($\underline{C}H_2CH_3$), 58.2 ($O\underline{C}H_3$), 52.9, 52.8 (2 × <u>C</u>1), 38.4 (2C, 2 × <u>C</u>2), 32.3, 32.2 (2 × <u>C</u>7), 26.6 (2C, 2 × <u>C</u>5), 16.8 (2C, 2 × <u>C</u>3), 14.1, 14.0 (2 × $CH_2\underline{C}H_3$).

FTIR 2986, 2935, 1733, 1685, 1598, 1447, 1228 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 415.1882, $C_{25}H_{28}O_4Na$ requires 415.1880.



(*E*)-5-(1*S,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)-4-methyl-1-phenylpent-4-en-1-one**

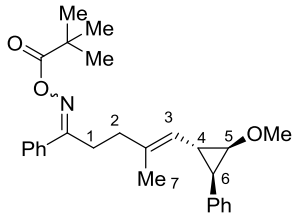
To a solution of (*E*)-ethyl 2-benzoyl-5-(1*S**,2*R**,3*R**)-2-methoxy-3-phenylcyclopropyl)-4-methylpent-4-enoate (2.13 g, 5.43 mmol) in THF (25 mL) was added KOH (1.37 g, 24.5 mmol), MeOH (5.4 mL) and H_2O (13.6 mL). The reaction mixture was heated at reflux for 2 hours after which time the heat was removed and 1M HCl (55 mL) was added. The mixture was stirred for 10 minutes followed by extraction with EtOAc (2 × 200 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification of the residue by FCC (10:1 (hexane-EtOAc)) afforded the title compound (1.46 g, 84%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.97-7.94 (2H, m, ArC<u>H</u>), 7.59-7.54 (1H, m, ArC<u>H</u>), 7.49-7.44 (2H, m, ArC<u>H</u>), 7.28-7.25 (4H, m, ArC<u>H</u>), 7.21-7.16 (1H, m, ArC<u>H</u>), 4.86-4.83 (1H, m, <u>H</u>3), 3.37 (1H, dd, *J* = 6.5, 3.5, <u>H</u>5), 3.18 (3H, s, OC<u>H</u>$_3$), 3.09-3.05 (2H, m, <u>H</u>1), 2.43 (2H, t, *J* = 7.5, <u>H</u>2), 2.10-2.05 (1H, m, <u>H</u>4), 1.95 (1H, app. t, *J* = 6.5, <u>H</u>6), 1.80 (3H, d, *J* = 1.0, <u>H</u>7).

^{13}C NMR (100 MHz, $CDCl_3$) 199.9 (<u>C</u>O), 137.4, 137.0 (2 × Ar<u>C</u>), 135.4 (<u>C</u>=CH), 133.0, 128.6, 128.0, 127.9, 127.8, 125.6 (6 × Ar<u>C</u>H), 124.6 (<u>C</u>3), 67.3 (<u>C</u>5), 58.2 (O<u>C</u>H$_3$), 37.2 (<u>C</u>1), 33.7 (<u>C</u>2), 32.3 (<u>C</u>6), 26.6 (<u>C</u>4), 16.9 (<u>C</u>7).

FTIR 2945, 1683, 1598, 1497, 1448, 1356, 1203 cm^{-1}.

MS (ESI$^+$) Found $[M+Na]^+$: 343.1665, $C_{22}H_{24}O_2Na$ requires 343.1669.



(*E*)-5-(1*S,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)-4-methyl-1-phenylpent-4-en-1-one *O*-pivaloyl oxime 21c**

<u>General Procedure A</u>: <u>Part A</u>: (*E*)-5-(1*S**,2*R**,3*R**)-2-Methoxy-3-phenylcyclopropyl)-4-methyl-1-phenylpent-4-en-1-one (1.46 g, 4.56 mmol) was employed and afforded the corresponding oxime (1.37 g, 90%) as a colorless oil. <u>Part B</u>: The corresponding oxime (790 mg, 2.36 mmol) was employed. FCC (10:1 (hexane-EtOAc)) afforded oxime ester **21c** (969 mg, 98%, 1:0.17 mixture of oxime isomers) as a colorless oil.

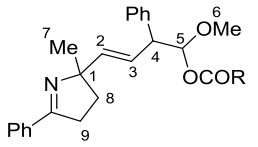
^{1}H NMR (400 MHz, $CDCl_3$) 7.72-7.69 (1.7H, m, ArC<u>H</u>), 7.46-7.36 (3.1H, m, ArC<u>H</u>), 7.30-7.23 (4.1H, m, ArC<u>H</u>), 7.21-7.16 (1.1H, m, ArC<u>H</u>), 4.79 (0.85H, dq, *J* = 8.5, 1.0, <u>H</u>4$_A$), 4.75-4.71 (0.15H, dd, *J* = 8.5, 1.5, <u>H</u>4$_B$), 3.34 (1H, dd, *J* = 6.5, 3.5, <u>H</u>6), 3.17 (3H, s, OC<u>H</u>$_3$), 2.95-2.91 (1.7H, m, <u>H</u>1$_A$), 2.83-2.79 (0.3H, m, <u>H</u>1$_B$), 2.26 (1.7H, t, *J* = 8.0, <u>H</u>2$_A$), 2.18 (0.3H, t, *J* = 8.0, <u>H</u>2$_B$), 2.03 (1H, ddd, *J* = 8.5, 6.5, 3.5, <u>H</u>5), 1.94-1.90 (1H, m, <u>H</u>7), 1.77 (2.55H, d, *J* = 1.0, C<u>H</u>$_{3A}$), 1.71 (0.45H, d, *J* = 1.0, C<u>H</u>$_{3B}$), 1.34 (7.65H, s, C(C<u>H</u>$_3$)$_{3A}$), 1.06 (1.35H, s, C(C<u>H</u>$_3$)$_{3B}$).

^{13}C NMR (100 MHz, $CDCl_3$) *Signals for the major isomer only* 175.0 (<u>C</u>O), 166.5 (<u>C</u>N), 137.2 (Ar<u>C</u>), 134.8 (<u>C</u>=CH), 134.1 (Ar<u>C</u>), 130.4, 128.6, 127.9, 127.8, 127.3, 125.7 (6 × Ar<u>C</u>H), 125.5 (<u>C</u>4),

67.2 (C6), 58.2 (OCH_3), 38.8 ($C(CH_3)_3$), 36.1 (C2), 32.3 (C7), 27.5 (C1), 27.3 ($C(CH_3)_3$), 26.5 (C5), 16.7 (C3).

FTIR 2973, 1756, 1497, 1445, 1105 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 442.2360, $C_{27}H_{33}NO_3Na$ requires 442.2353.



R = *t*-Bu, **23c**
R = 2-ethylhexyl, **23c'**

(*E*)-1-Methoxy-4-(2-methyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-2-phenylbut-3-en-1-yl pivalate 23c

(*E*)-1-methoxy-4-(2-methyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-2-phenylbut-3-en-1-yl 2-ethylhexanoate 23c'

General Procedure B: Oxime ester **21c** (150 mg, 0.358 mmol) was employed. FCC afforded the title compound (26 mg, 18%, 1:0.23 **23c**:**23c'**, approx. 1:1:1:1 mixture of diastereomers) as a yellow oil.

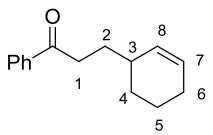
*Data for **23c** and **23c':*** Analysis was complicated as both **23c** and **23c'** were formed as a mixture of 4 diastereomers each. ^1H and ^{13}C NMR analysis was pursued on the mixture and assignments were made, where possible, with the aid of 2D NMR experiments.

^{1}H NMR (400 MHz, $CDCl_3$) 7.85-7.81 (2H, m, ArCH), 7.32-7.37 (3H, m, ArCH), 7.31-7.18 (5H, m, ArCH), 5.94-5.92 (1H, m, H5), 5.88-5.69 (2H, m, H2 & H3), 3.66-3.61 (1H, m, H4), 3.41 (0.1H, s, H6), 3.38 (1.3H, m, H6), 3.30 (0.7H, s, H6), 3.29 (0.9H, s, H6), 3.06-2.87 (2H, m, H9), 2.06-1.97 (1H, m, H8), 1.90-1.81 (1H, m, H8'), 1.40-1.37 (3H, m, H7), 1.17 (1.7H, s, $C(CH_3)_3$), 1.13 (2.1H, s, $C(CH_3)_3$), 1.01 (3.1H, m, $C(CH_3)_3$).
*Characteristic signals for **23c':*** 2.30-2.25 (0.23H, m, CH), 1.66-1.45 (0.92H, m, CH_2), 1.34-1.28 (1.15H, m, CH_2), 0.95-0.78 (1.38H, m, CH_3)

^{13}C NMR (100 MHz, $CDCl_3$) 178.2-178.1 (CO), 171.2-171.1 (CN), 139.6-139.4 (C2), 134.7-134.6 (ArC), 130.4 (ArCH), 128.9-128.7 (ArCH), 128.3-128.2 (ArCH), 127.8 (ArCH), 127.0-126.7 (ArCH), 125.0-124.5 (C3), 100.3-100.1 (C5), 76.3-76.2 (C1), 57.1-57.0 (C6), 53.2-53.1 (C4), 39.1-38.9 ($C(CH_3)_3$), 35.7-35.3 (C8), 34.9-34.8 (C9), 27.4-27.2 (C7), 27.1-26.8 ($C(CH_3)_3$).
*Diagnostic signals for **23c':***46.8 (CH), 31.6, 29.6, 25.3, 22.6 ($4 \times CH_2$), 13.9, 11.8 ($2 \times CH_3$).

FTIR 2962, 2933, 1727, 1614, 1575, 1448, 1282, 1155, 1119 cm^{-1}.

MS (ESI^+) Found $[M+H]^+$: 420.2523, $C_{27}H_{34}NO_3$ requires 420.2533.



3-(Cyclohex-2-en-1-yl)phenylpropan-1-one

To ethyl benzoylacetate (1.00 mL, 5.77 mmol) and NaH (0.23 g, 5.77 mmol) at 0 °C was added DMF (45 mL). The reaction was stirred at room temperature until gas evolution stopped (*ca.* 15 minutes).

Then 3-(iodomethyl)cyclohex-1-ene (1.40 g, 6.30 mmol) was added *via* syringe and the mixture was heated at 60 ^{o}C for 16 hours. The mixture was cooled to room temperature and the solvent removed by concentration *in vacuo* to afford the alkylated product as an orange oil which was used without further purification. To the residue in THF (35 mL), MeOH (15 mL), water (15 mL) and KOH (1.91 g, 28.9 mmol) were added. The mixture was then heated at 75 ^{o}C for 4 hours. After cooling to room temperature, the mixture was acidified with aq. 1 M HCl (25 mL) and extracted with Et_2O (2 × 50 mL). The organic extracts were concentrated *in vacuo*. Purification of the residue by FCC (60:1 (hexane-EtOAc)) afforded the title compound (0.32 g, 26%) as a colourless oil.

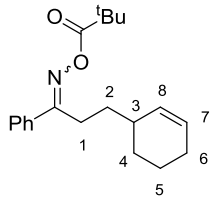
^{1}H NMR (400 MHz, $CDCl_3$) 8.01-7.94 (2H, m, ArCH), 7.60-7.53 (1H, m, ArCH), 7.50-7.44 (2H, m, ArCH), 5.75-5.69 (1H, m, H7), 5.64-5.58 (1H, m, H8), 3.02 (2H, t, *J* = 7.5, H1), 2.24-2.21 (1H, m, H3), 2.03-1.95 (2H, m, H6), 1.88-1.67 (4H, m, H2 & H4 & H5), 1.58-1.47 (1H, m, H5), 1.34-1.22 (1H, m, H4).

^{13}C NMR (100 MHz, $CDCl_3$) 200.5 (CO), 137.0 (ArC), 123.9 (ArCH), 131.2 (C8), 128.5, 128.0 (2 × ArCH), 127.6 (C7), 36.0 (C1), 34.8 (C3), 30.6 (C2), 28.9 (C4), 25.3 (C6), 21.4 (C5).

FTIR 3016, 2924, 2859, 1682, 1597, 1448 cm^{-1}.

MS (ESI^{+}) Found $[M+Na]^{+}$: 237.1260, $C_{15}H_{18}ONa$ requires 237.1250.

The spectroscopic properties of this compound were consistent with data reported in the literature with the exception of the C=O ^{13}C NMR signal.[12] Consequently, this compound has been characterized fully and full data are presented.



3-(Cyclohex-2-en-1-yl)-1-phenylpropan-1-one *O*-pivaloyl oxime 30

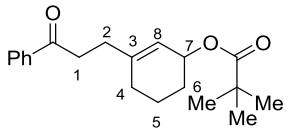
General Procedure A: Part A: 3-(Cyclohex-2-en-1-yl)phenylpropan-1-one (0.28 g, 1.31 mmol) was used and the reaction was heated at 75 ^{o}C for 2 hours to afford the intermediate oxime (0.29 g, 97%, 1:0.1 mixture of oxime isomers) as a colourless solid. General Procedure A**:** Part B: The corresponding oxime (0.10 g, 0.43 mmol) was employed and FCC (6:1 (hexane-EtOAc)) afforded oxime ester **30** (0.12 g, 88%, 1:0.1 mixture of oxime isomers) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$) *Signals for the major isomer*: 7.77-7.71 (2H, m, ArCH), 7.47-7.37 (3H, m, ArCH), 5.73 (1H, ddd, *J* = 10.0, 3.0 & 3.0, H7), 5.58 (1H, dd, *J* = 10.0 & 2.0, H8), 2.88 (2H, t, *J* = 7.5, H1), 2.22-2.11 (1H, m, H3), 2.02-1.95 (2H, m, H6), 1.88-1.79 (1H, m, H4), 1.78-1.69 (1H, m, H5), 1.69-1.47 (3H, m, H2 & H5), 1.35 (s, 9H, $C(CH_3)_3$), 1.35-1.24 (1H, m, H4). *Characteristic signal for the minor isomer:* 1.27 (s, 0.9H, , $C(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$) *Signals for the major isomer only*: 175.1 (CO)), 167.0 (CN), 134.2 (ArC), 130.6, 130.4 (ArCH & C8), 128.6 (ArCH), 128.0 (C7), 127.2 (ArCH), 38.8 ($C(CH_3)_3$), 35.5 (C3), 33.0 (C2), 28.7 (C4), 26.2 (C1), 25.2 (C6), 21.3 (C5).

FTIR 2928, 1757, 1479, 1268, 1106 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 336.1943, $C_{20}H_{27}NO_4Na$ requires 336.1934.



3-(3-Oxo-3-phenylpropyl)cyclohex-2-en-1-yl pivalate 34

General Procedure B: Oxime ester **30** (35 mg, 0.11 mmol) was employed. In a modification to the general procedure 100 wt/mol% 4Å molecular sieves were added. FCC (10:1 (hexane-EtOAc)) afforded imine **8n** (11 mg, 46%) as a colorless oil and ketone **34** (11 mg, 31%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.00-7.95 (2H, m, ArCH), 7.61-7.54 (1H, m, ArCH), 7.51-7.45 (2H, m, ArCH), 5.52-5.47 (1H, m, H8), 5.26-5.18 (1H, m, H7), 3.15-3.08 (2H, m, H1), 2.45 (2H, t, J = 7.5 H2), 2.12-1.94 (2H, m, H4), 1.84-1.71 (2H, m, H6), 1.71-1.61 (2H, m, H5), 1.19 (s, 9H, $C(CH_3)_3$).

^{13}C NMR (125 MHz, $CDCl_3$) 199.6 (Ar(CO)), 178.3 ((CO)$C(CH_3)_3$), 142.9 (C3), 136.9 (ArC), 133.0, 128.6, 128.0 (3 × ArCH), 120.2 (C8), 68.2 (C7), 38.7 ($C(CH_3)_3$), 36.6 (C1), 31.7 (C2), 28.7 (C4), 28.1 (C6), 27.2 ($C(CH_3)_3$), 19.2 (C5).

FTIR 2932, 1720, 1687, 1449, 1281, 1155 cm^{-1}.

MS (ESI^+) Found $[M+Na]^+$: 337.1778, $C_{20}H_{26}O_3Na$ requires 337.1774.

*The data for imine **8n** are presented earlier.*

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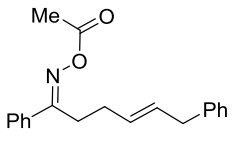
Spectra of Novel Compounds



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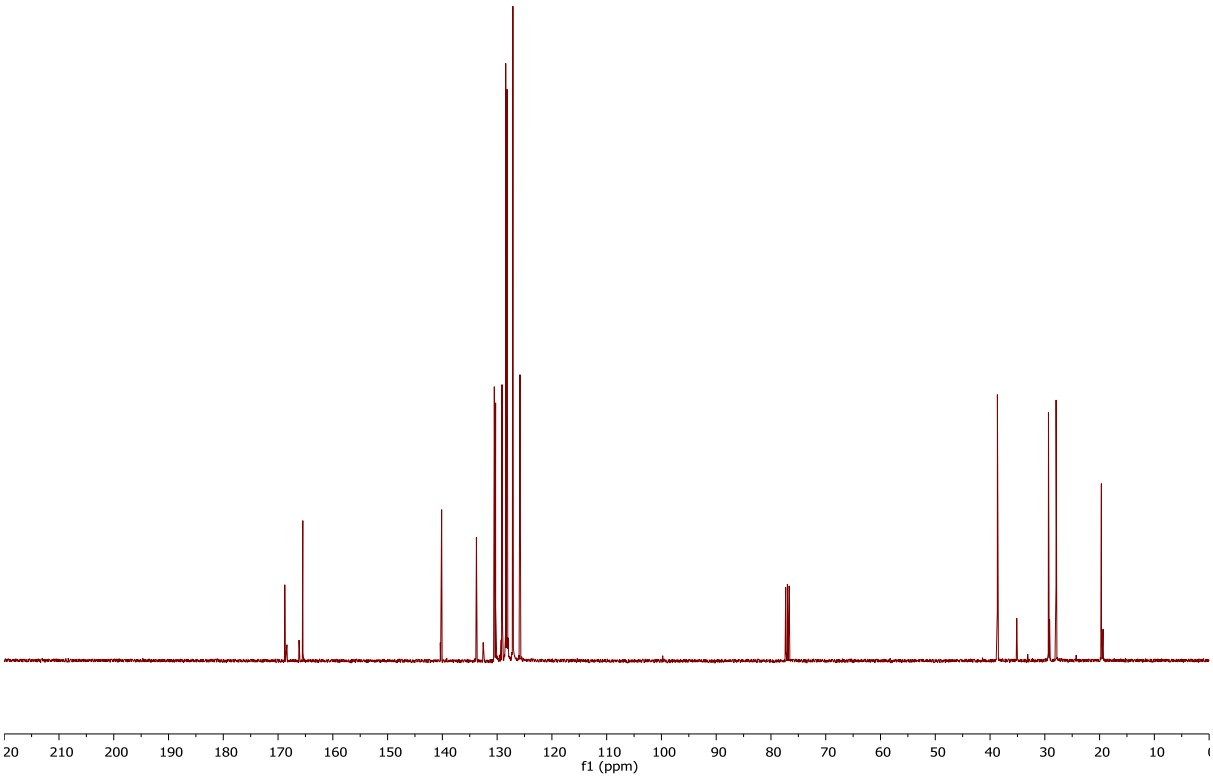

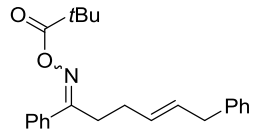
O
tBu
O
N
Ph
Ph

7a

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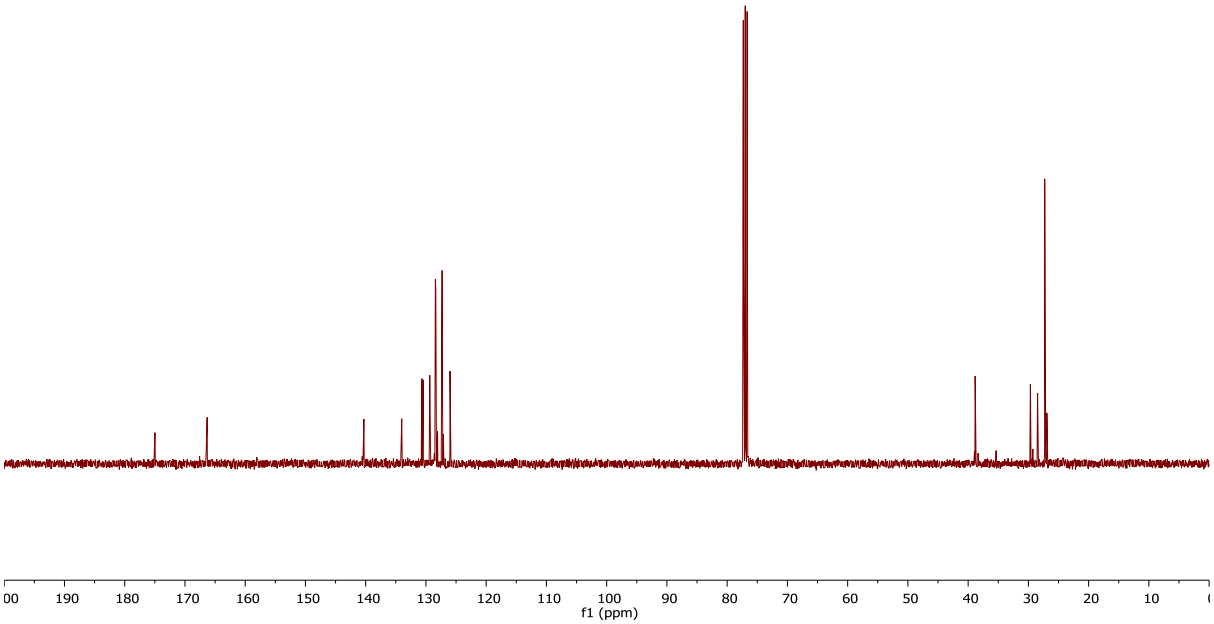
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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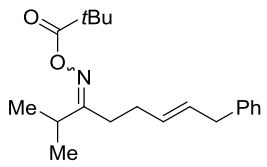
f1 (ppm)


O
tBu
O
N
Me
Ph
Me

7b

.0
8.5
8.0
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7.0
6.5
6.0
5.5
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3.5
3.0
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1.5
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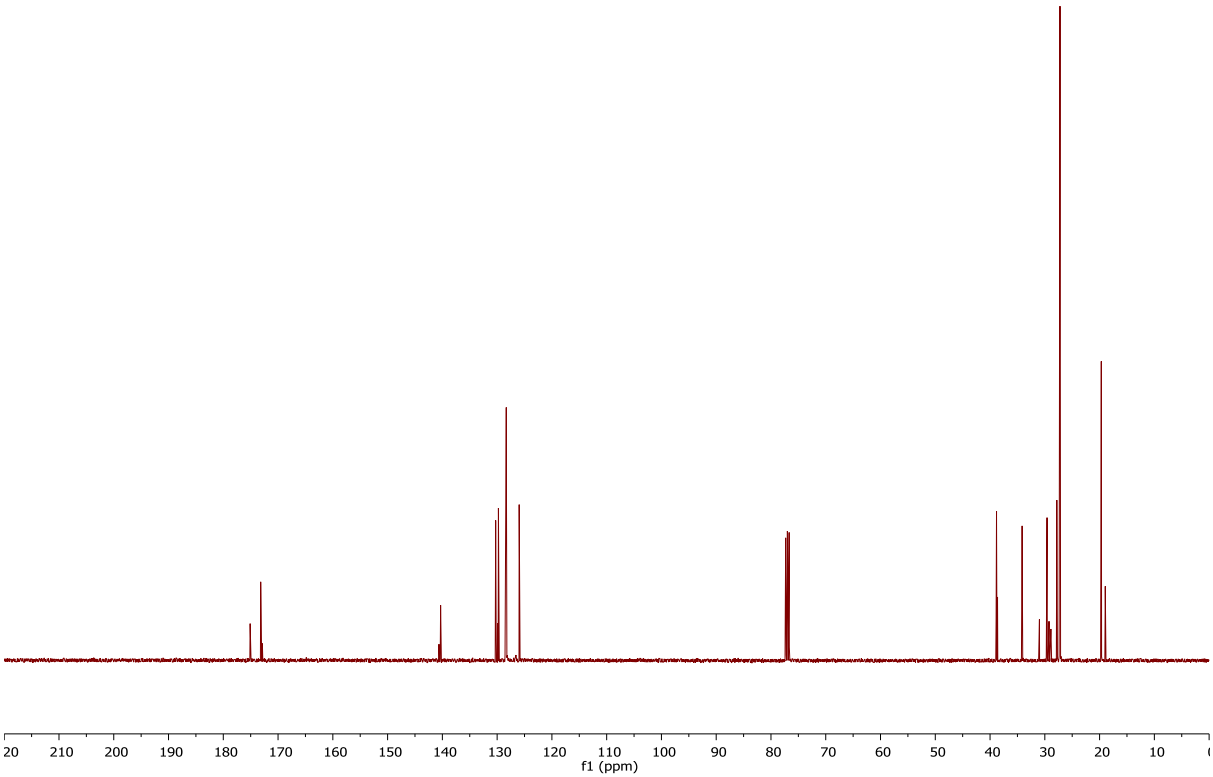
0
f1 (ppm)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20
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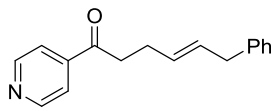
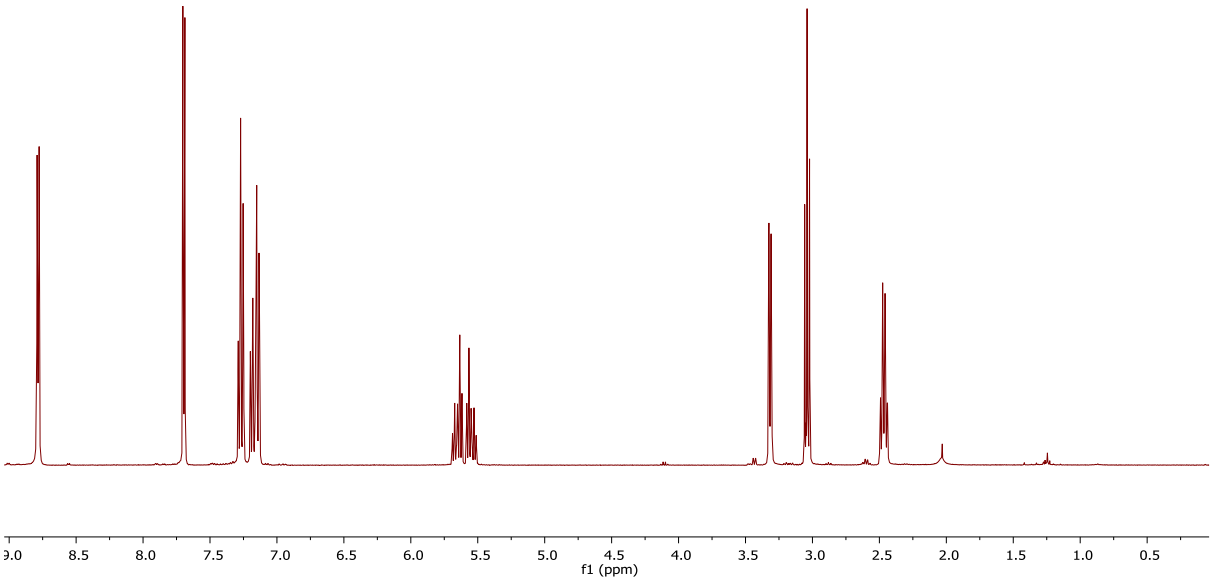
f1 (ppm)


O
Ph
N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6.0
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4.0
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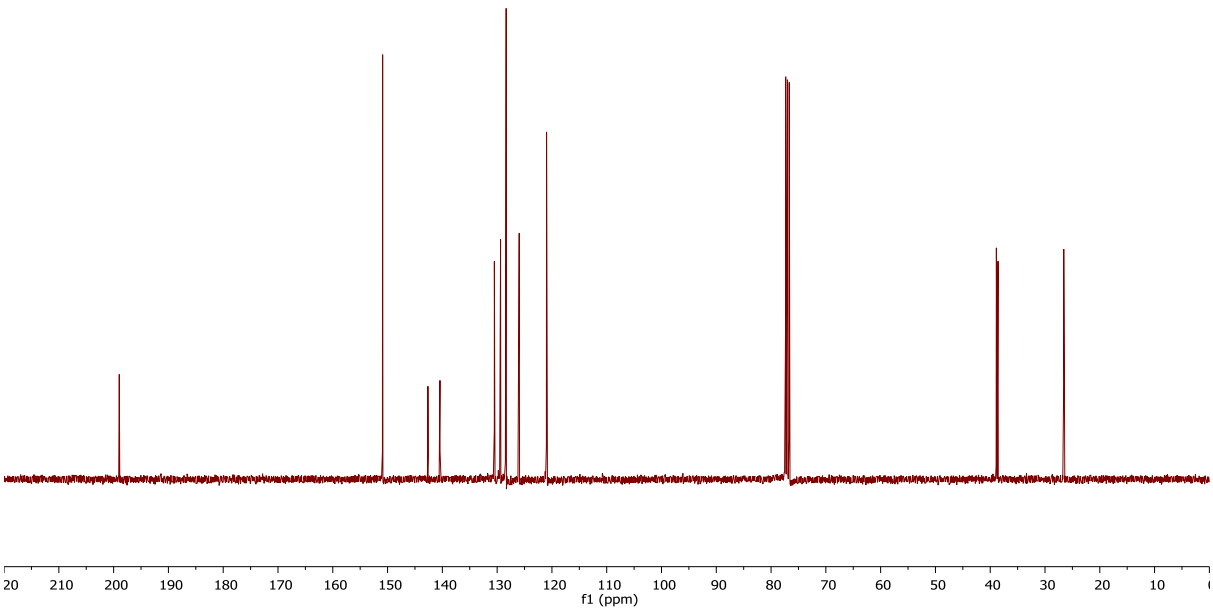
2.0
1.5
1.0
0.5
f1 (ppm)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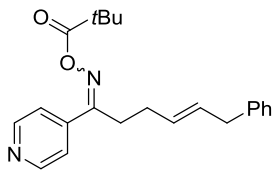
f1 (ppm)


O
tBu
O
N
Ph
N

7c

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8.5
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7.5
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6.5
6.0
5.5
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4.0
3.5
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2.0
1.5
1.0
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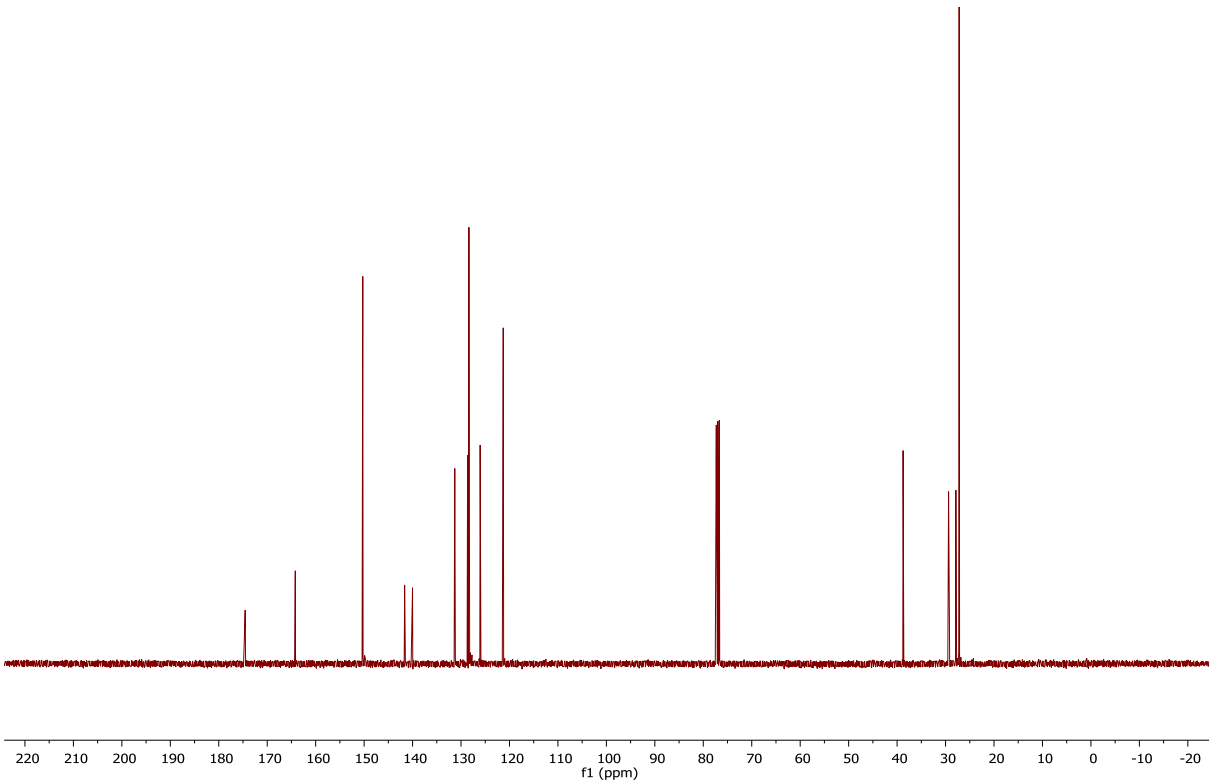
f1 (ppm)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60
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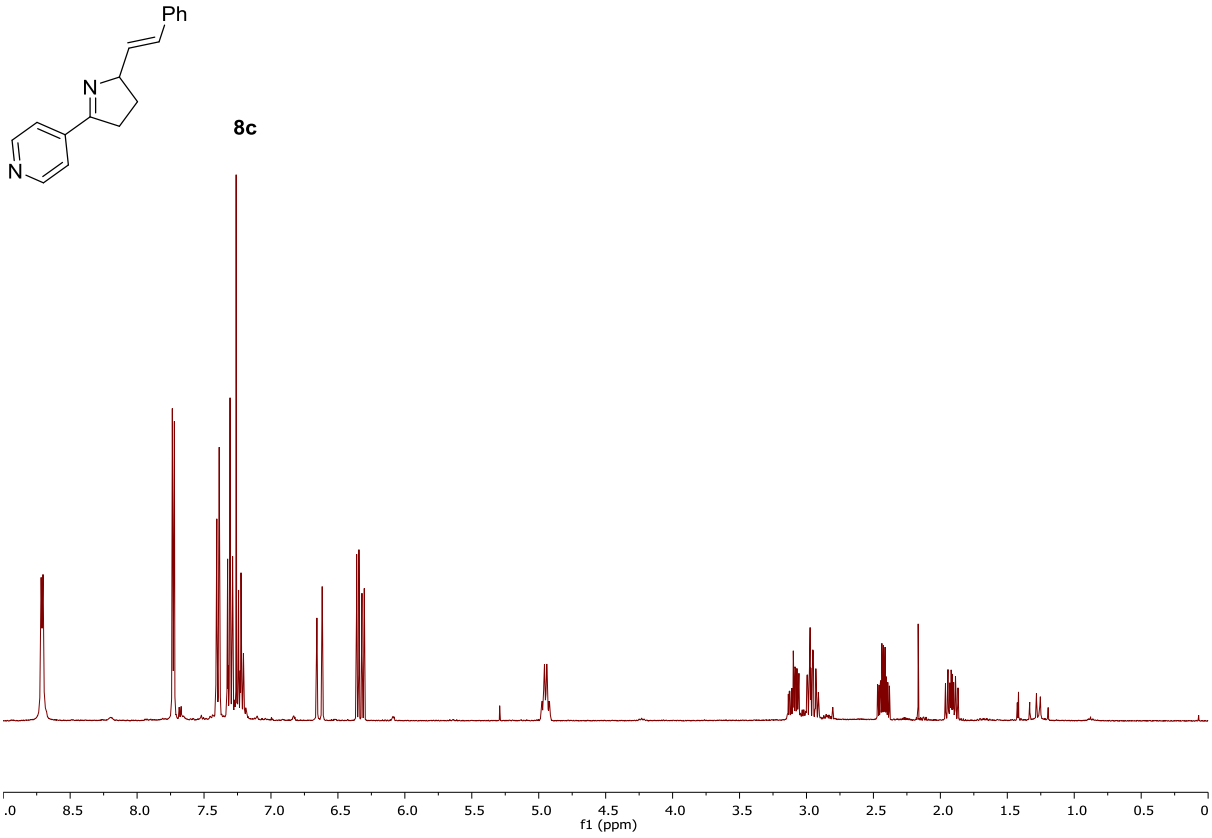
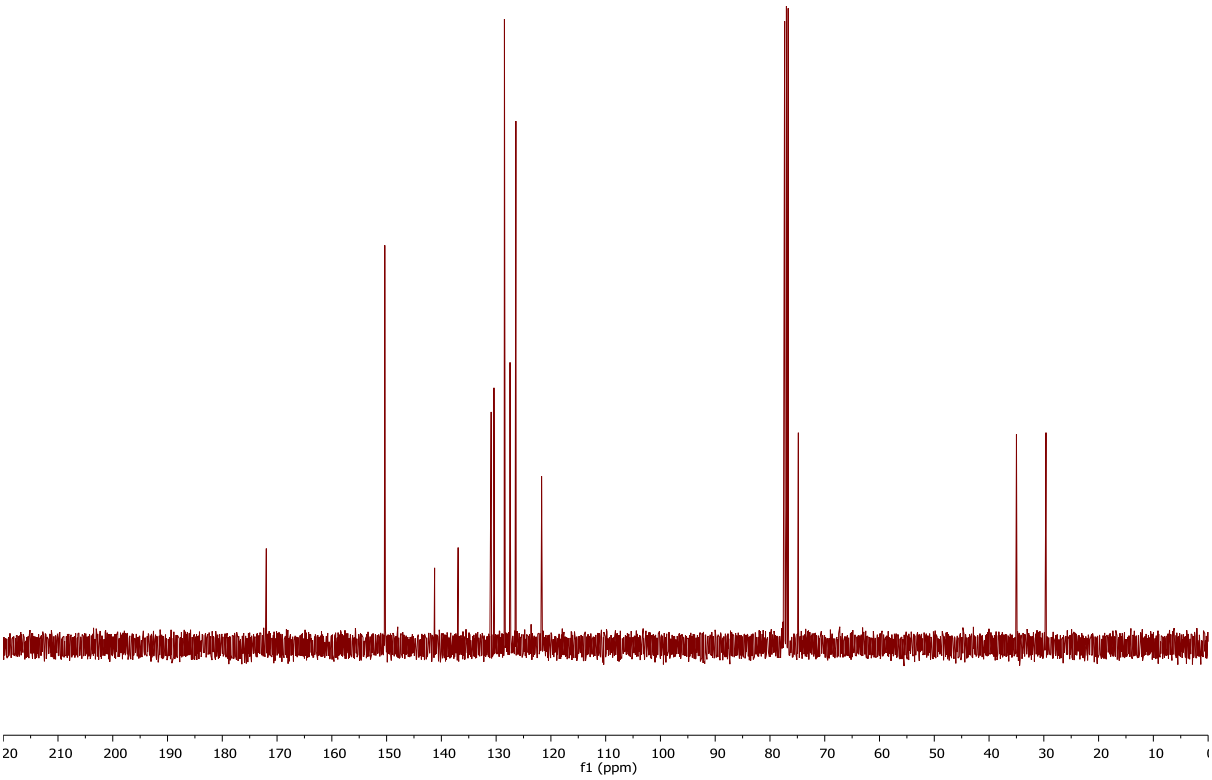
-10
-20
f1 (ppm)


Ph
N
N
8c
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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100
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60
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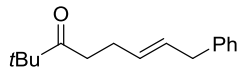
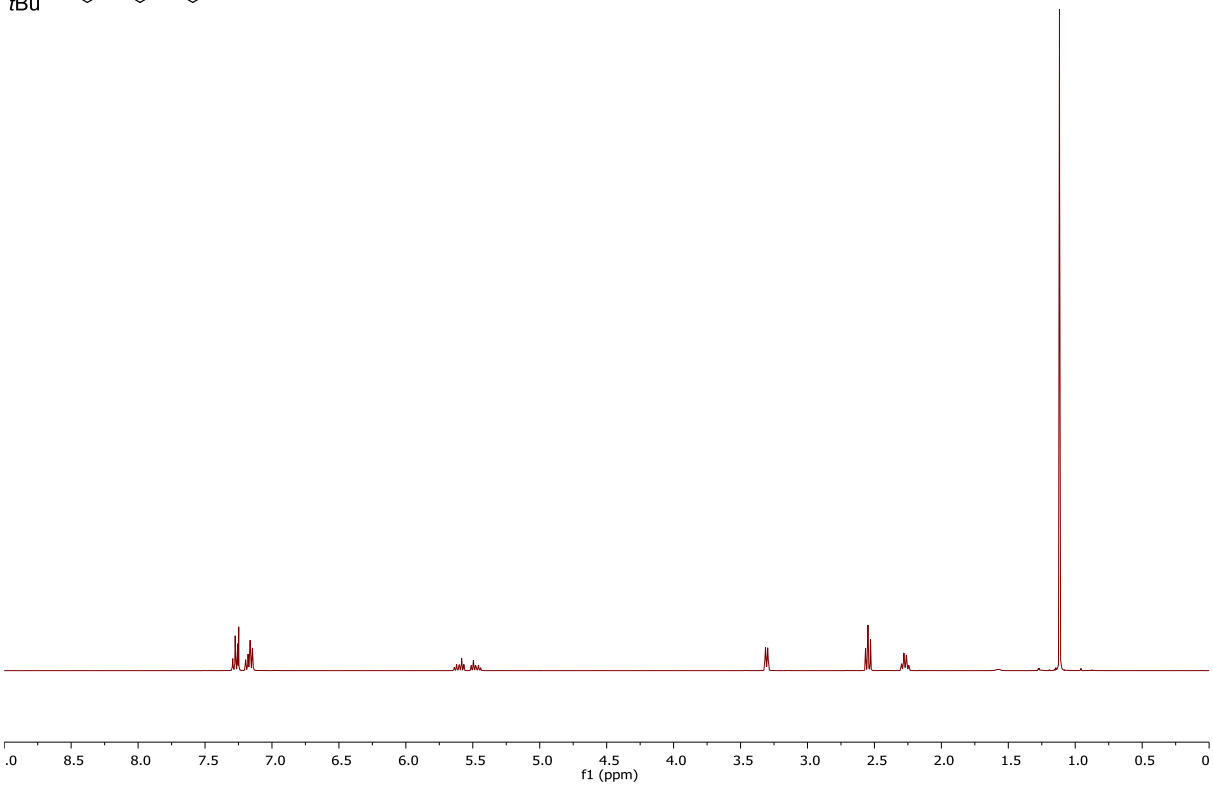
30
20
10
f1 (ppm)


O
tBu
Ph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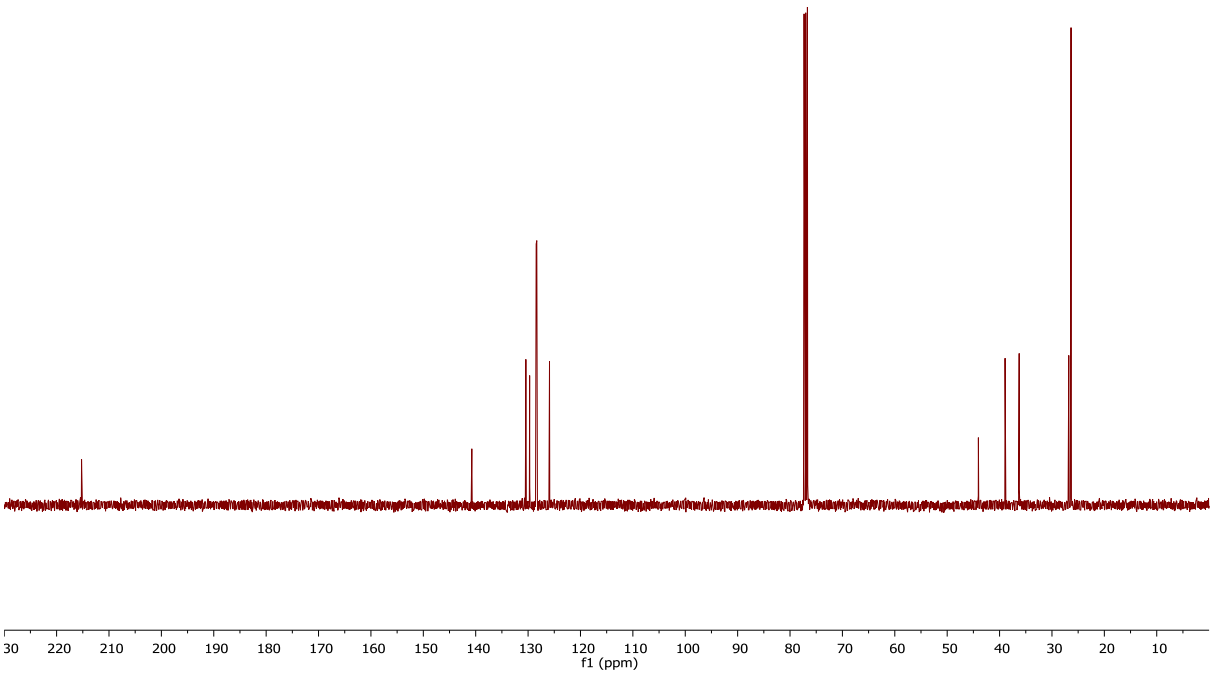
f1 (ppm)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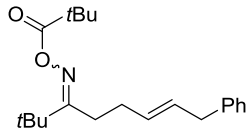
f1 (ppm)


O
tBu
O
N
tBu
Ph

7d

.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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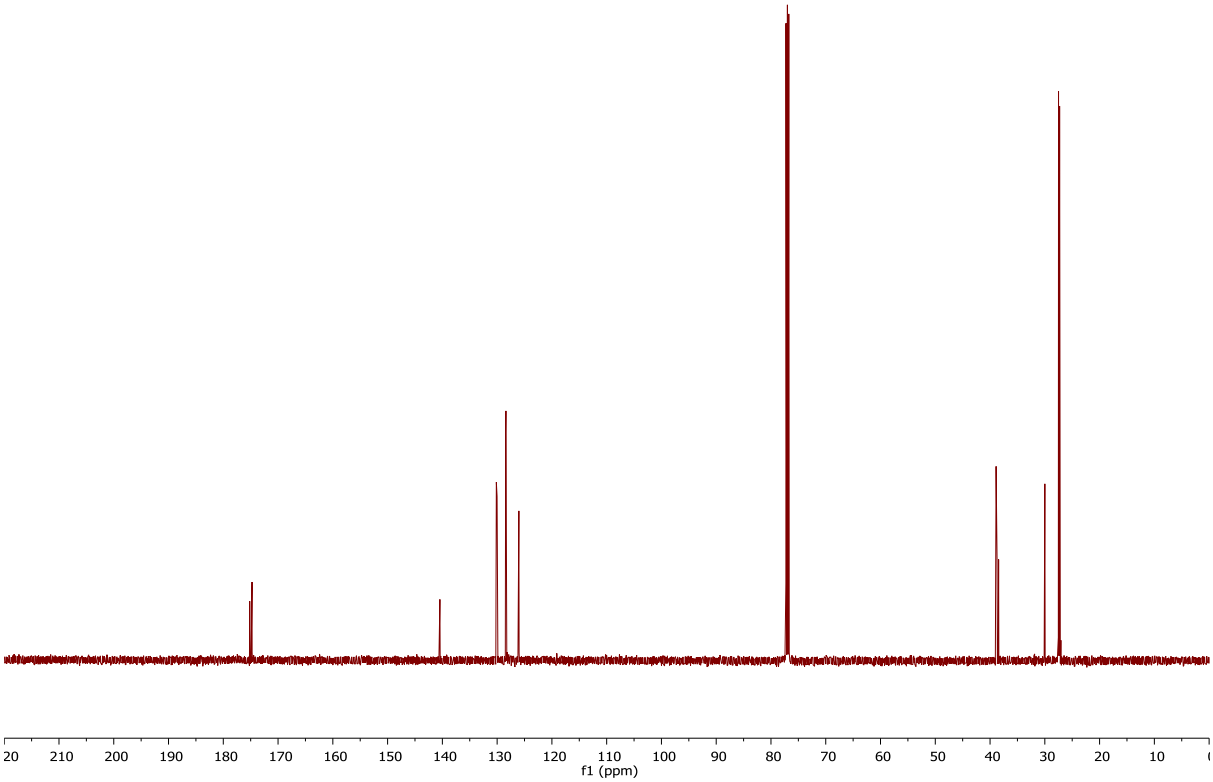
f1 (ppm)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20
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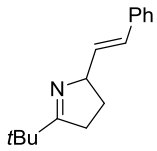
f1 (ppm)


Ph
N
tBu

8d

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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.5
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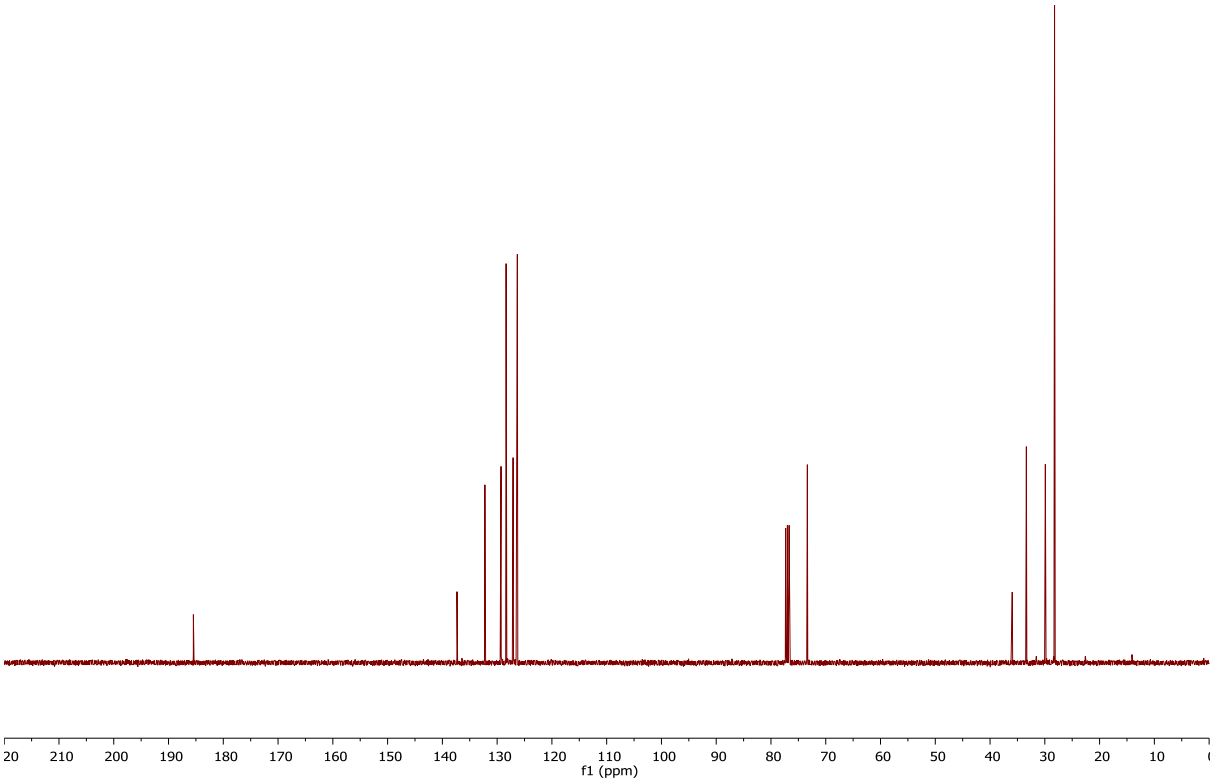
f1 (ppm)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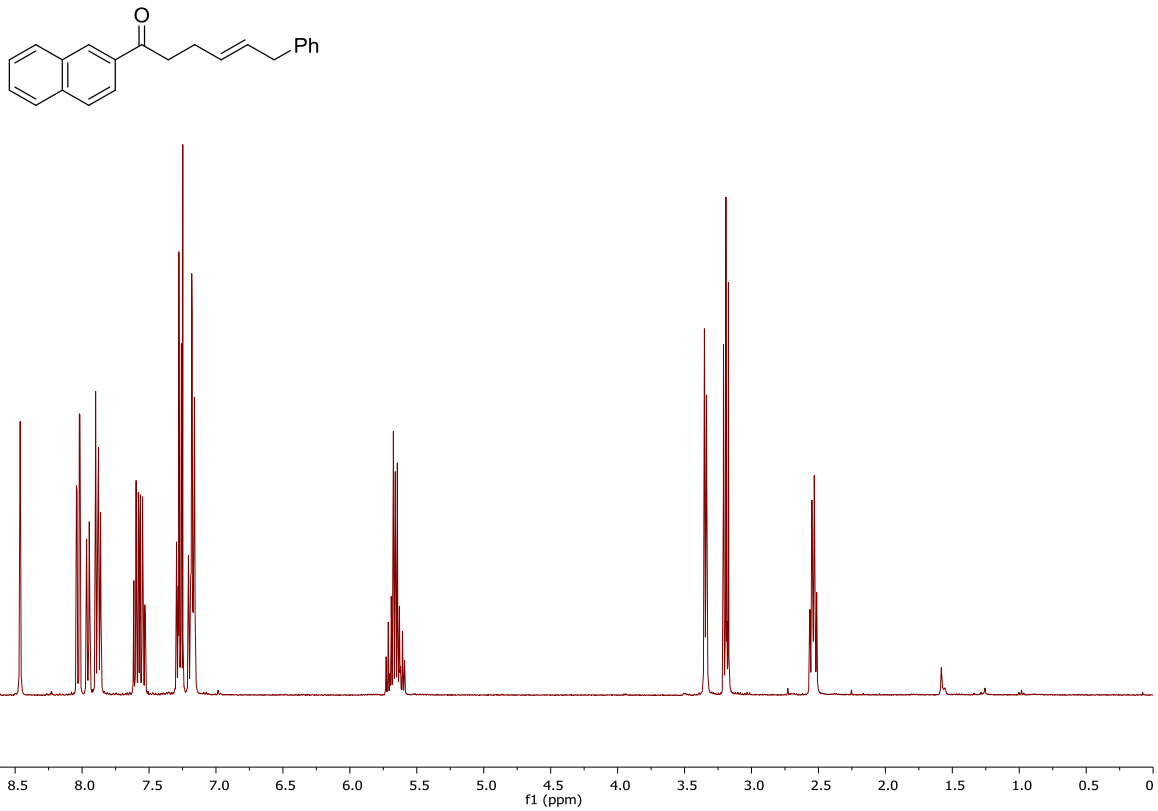
f1 (ppm)


O
Ph
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.5
1.0
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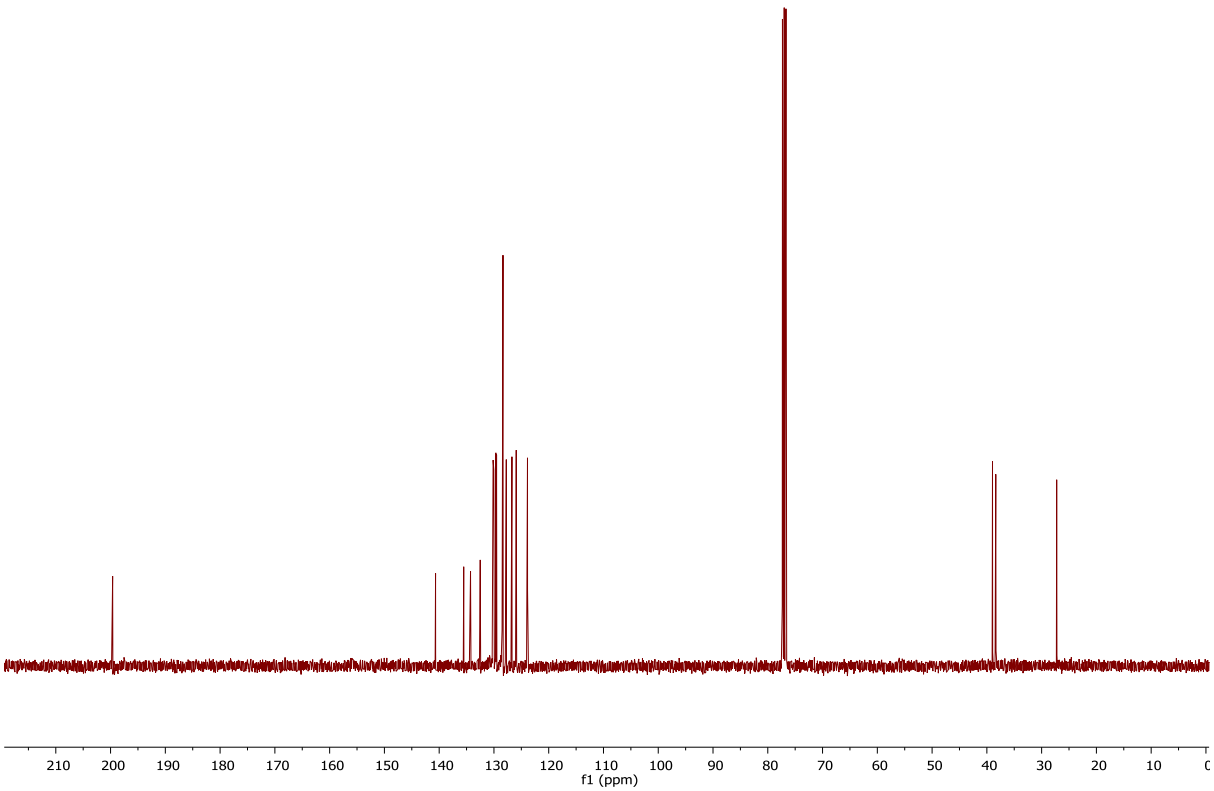
0
f1 (ppm)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200
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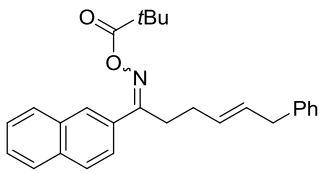
10
f1 (ppm)


O
tBu
O
N
Ph

7e

.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.0
1.5
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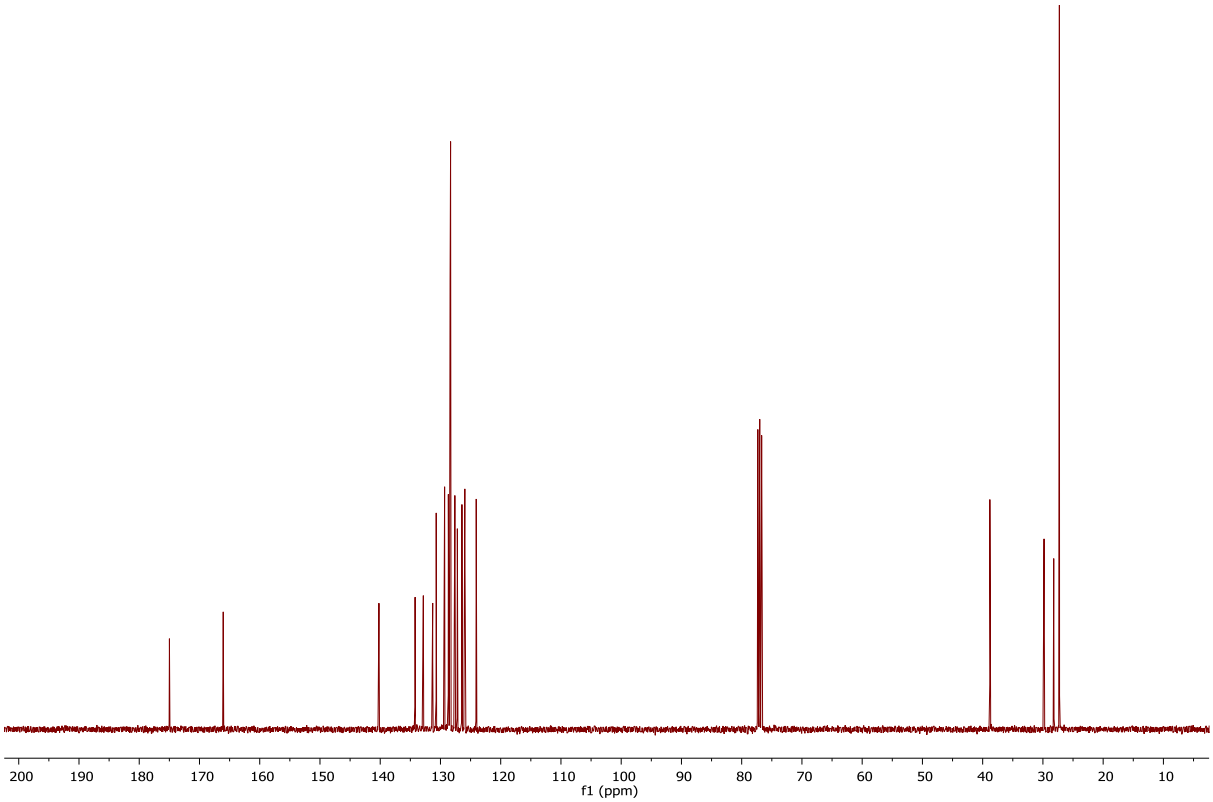
0
f1 (ppm)


200
190
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170
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50
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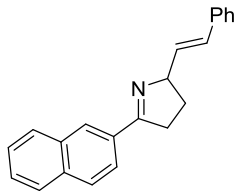
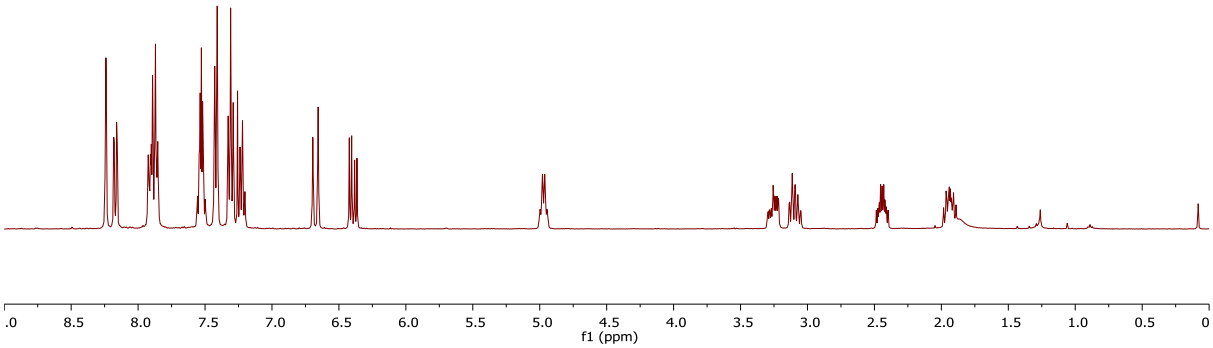
20
10
f1 (ppm)


Ph
N

8e


.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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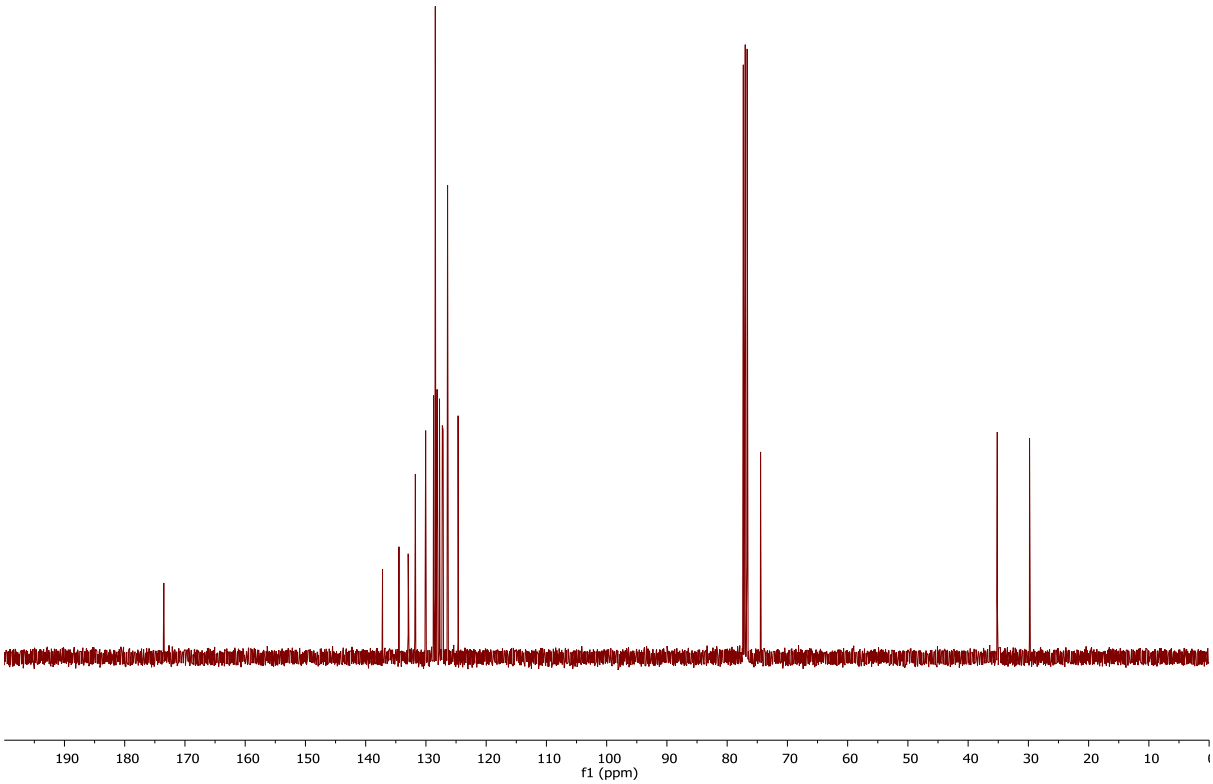
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


190
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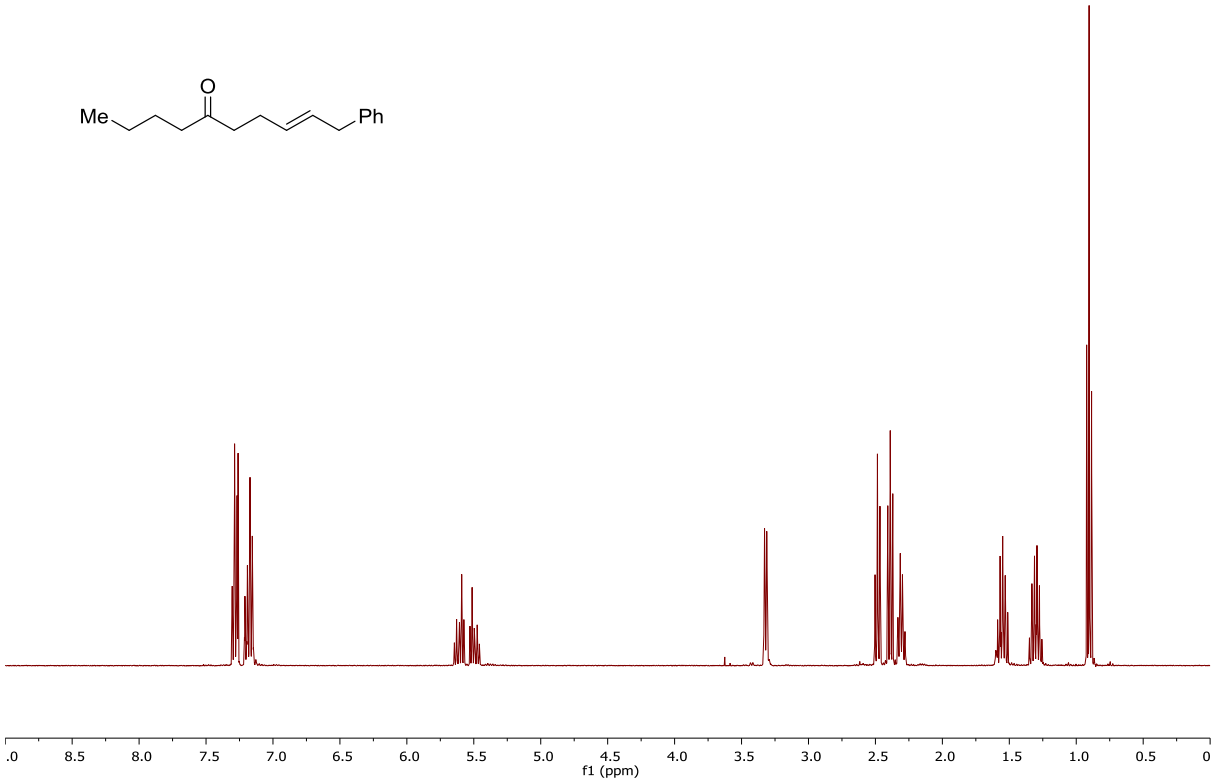
10
f1 (ppm)


O
Me
Ph
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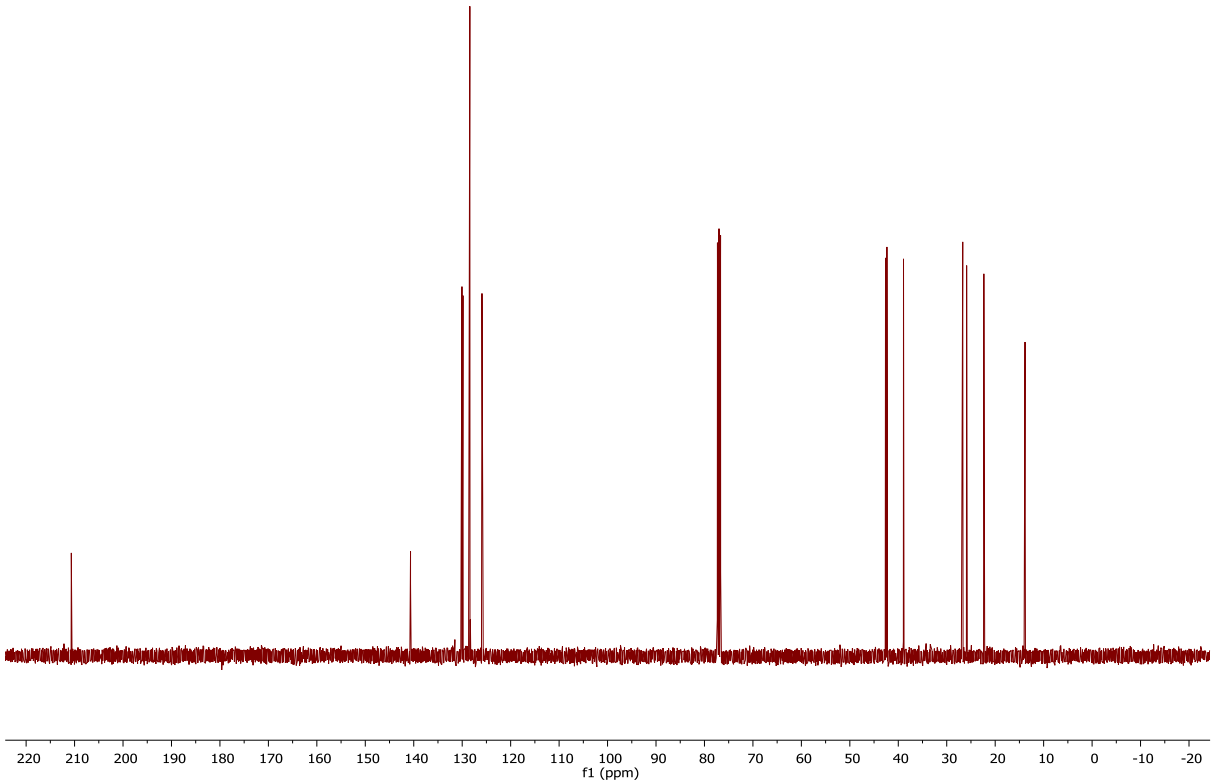
f1 (ppm)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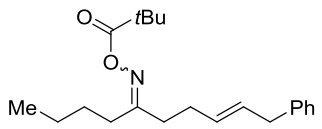
f1 (ppm)


O
tBu
O
N
Me
Ph

7f

.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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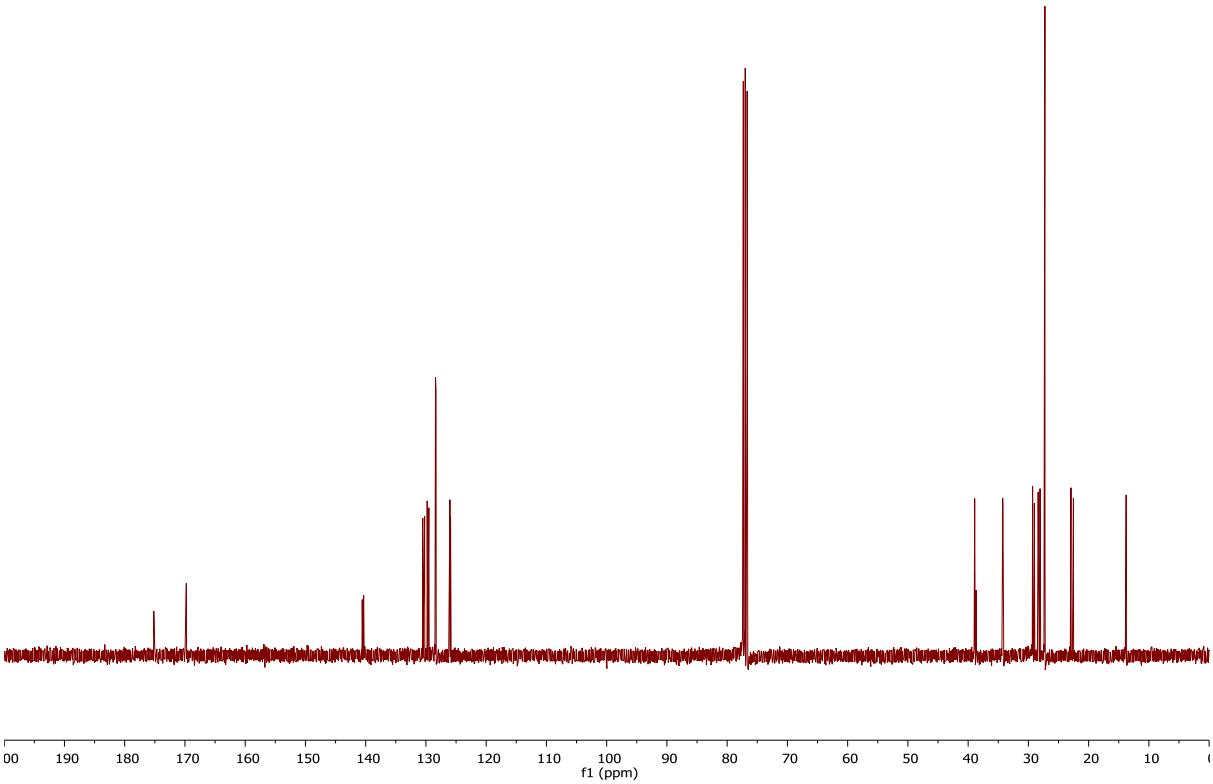
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


00
190
180
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140
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100
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80
70
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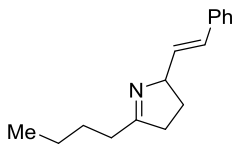
50
40
30
20
10
f1 (ppm)


Ph
N
Me

8f

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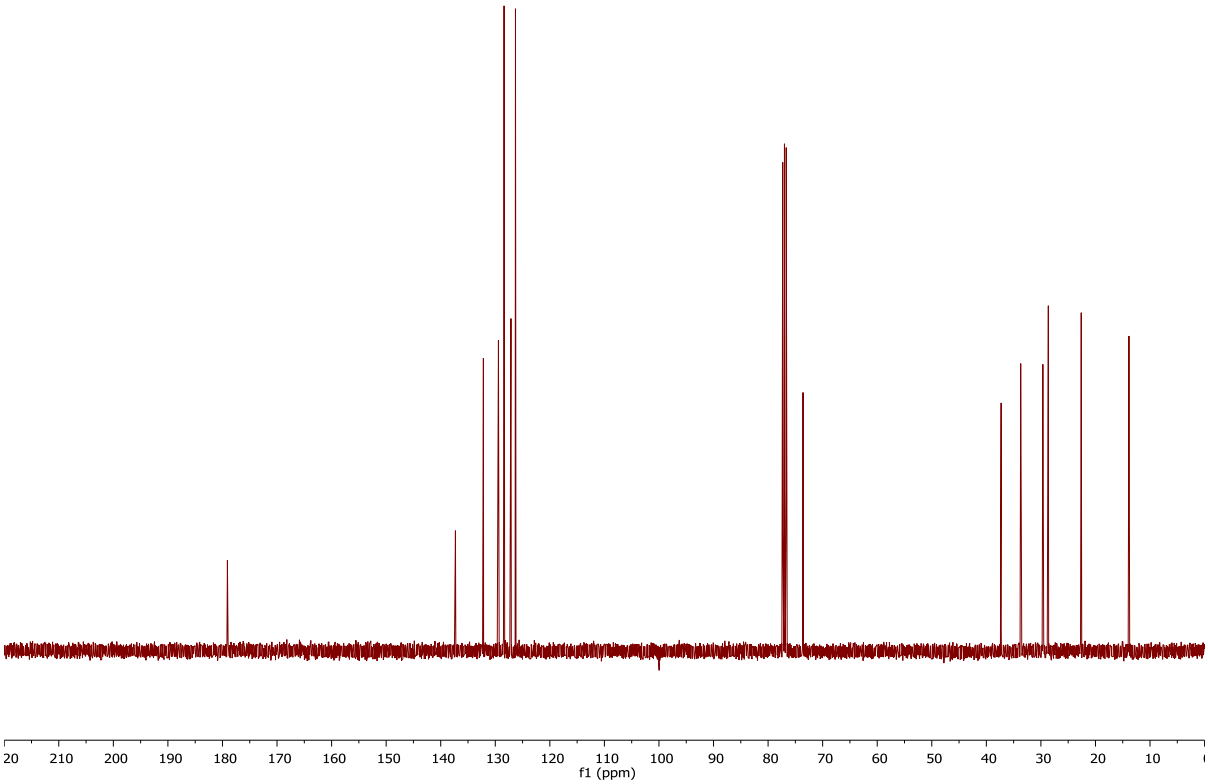
f1 (ppm)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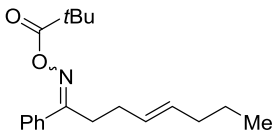
f1 (ppm)


O
tBu
O
N
Ph
Me

7g

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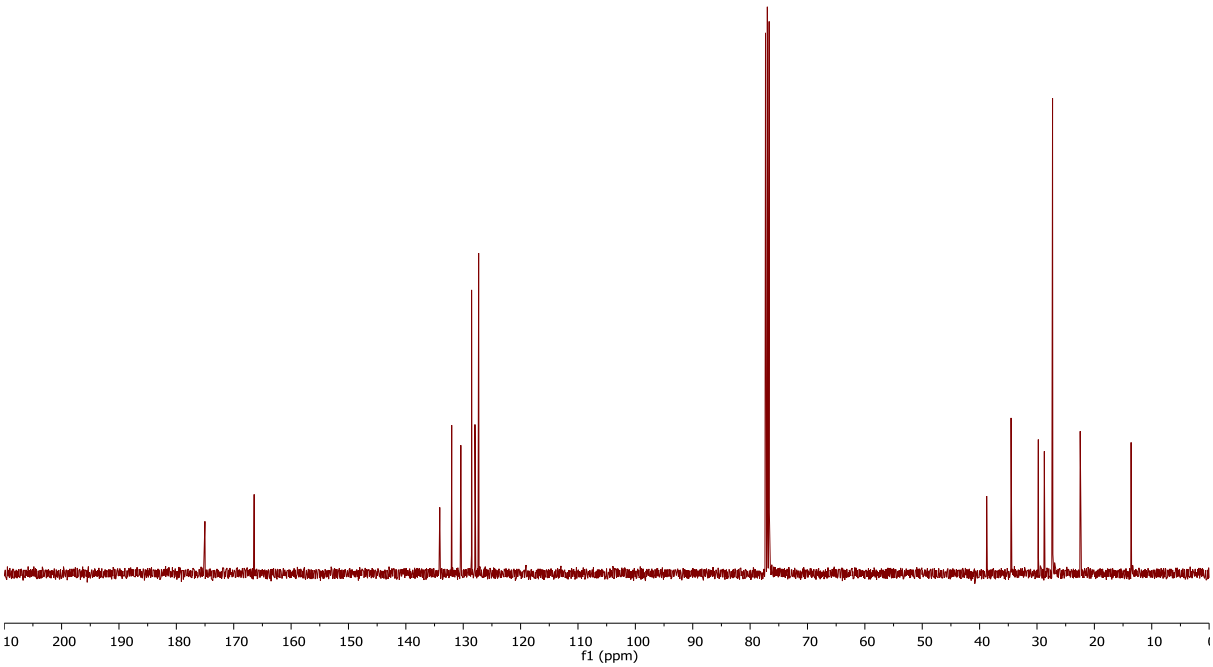
0
f1 (ppm)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80
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50
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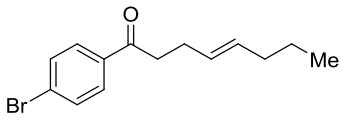
30
20
10
f1 (ppm)


O
Br
Me

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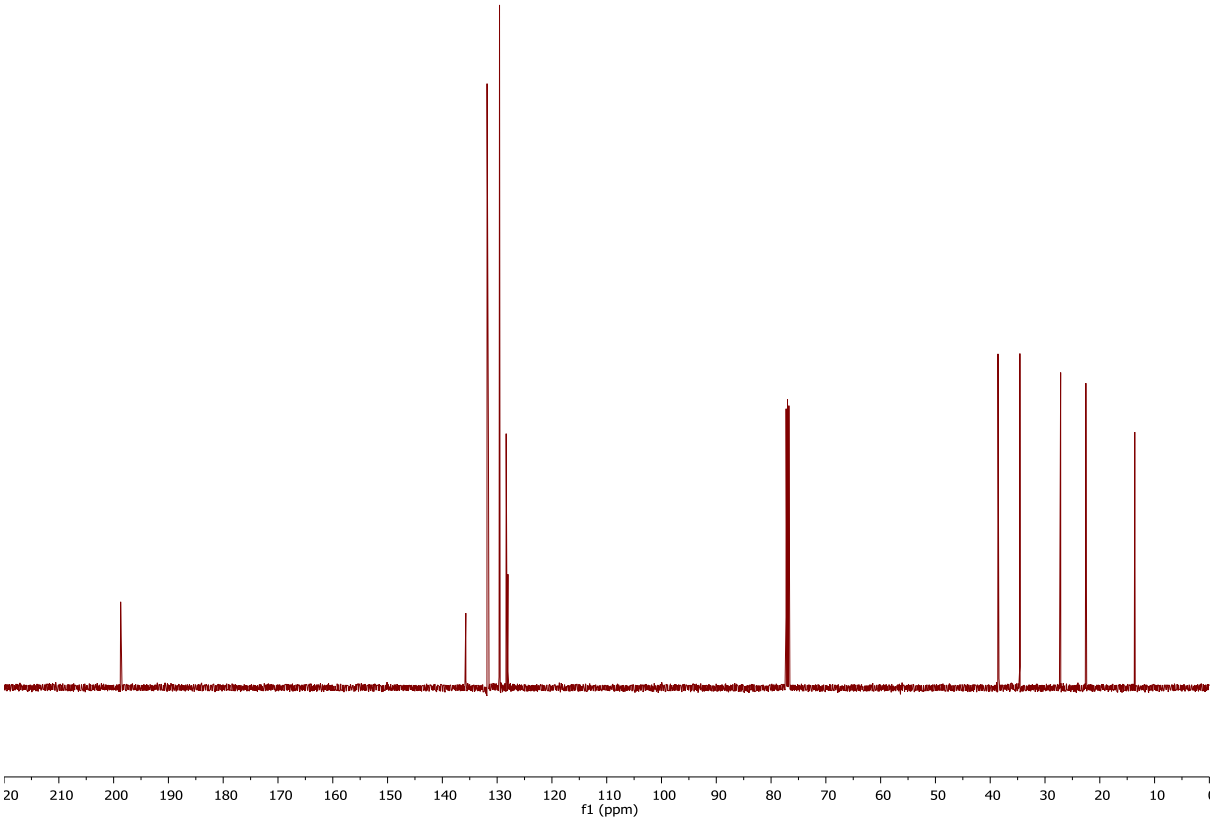
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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100
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60
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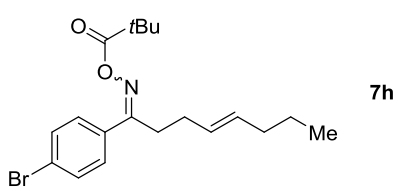
40
30
20
10
f1 (ppm)


O
tBu
O
N
Me
Br

7h

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7.5
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6.5
6.0
5.5
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4.5
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2.0
1.5
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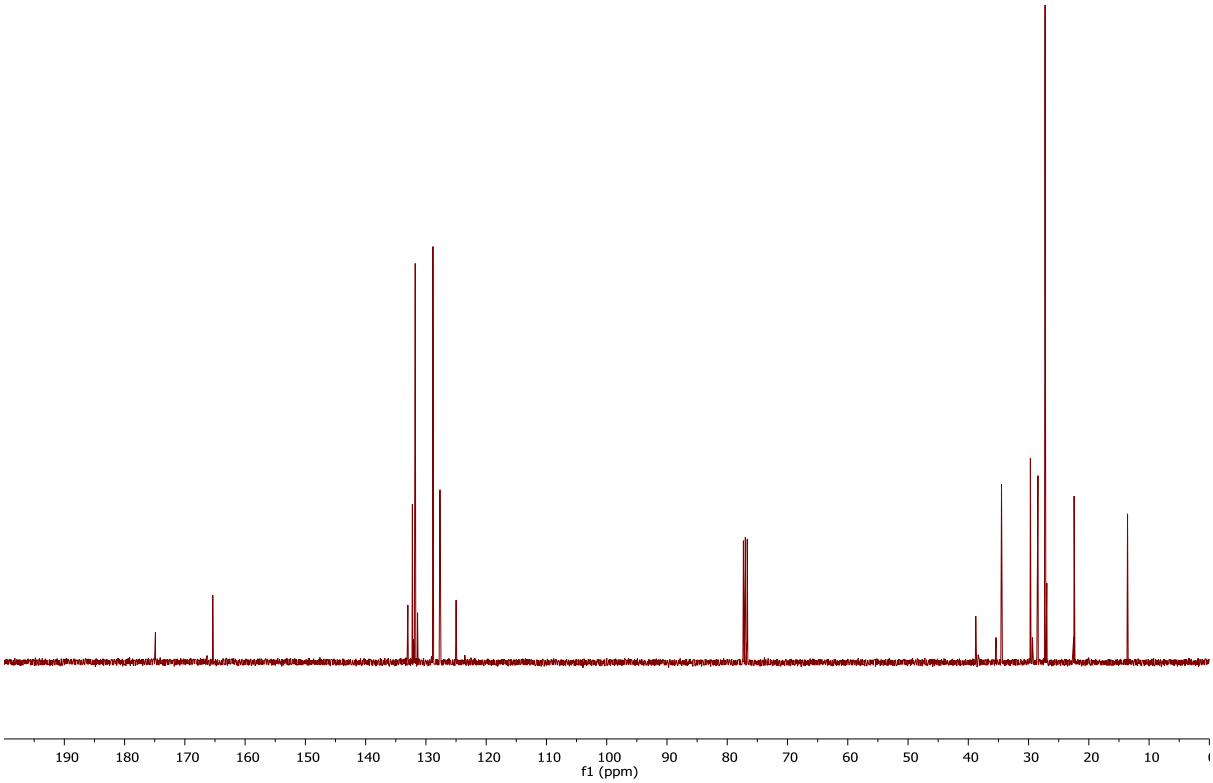
0
f1 (ppm)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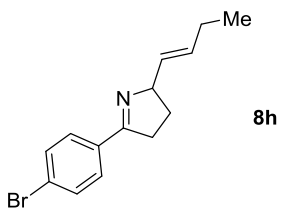
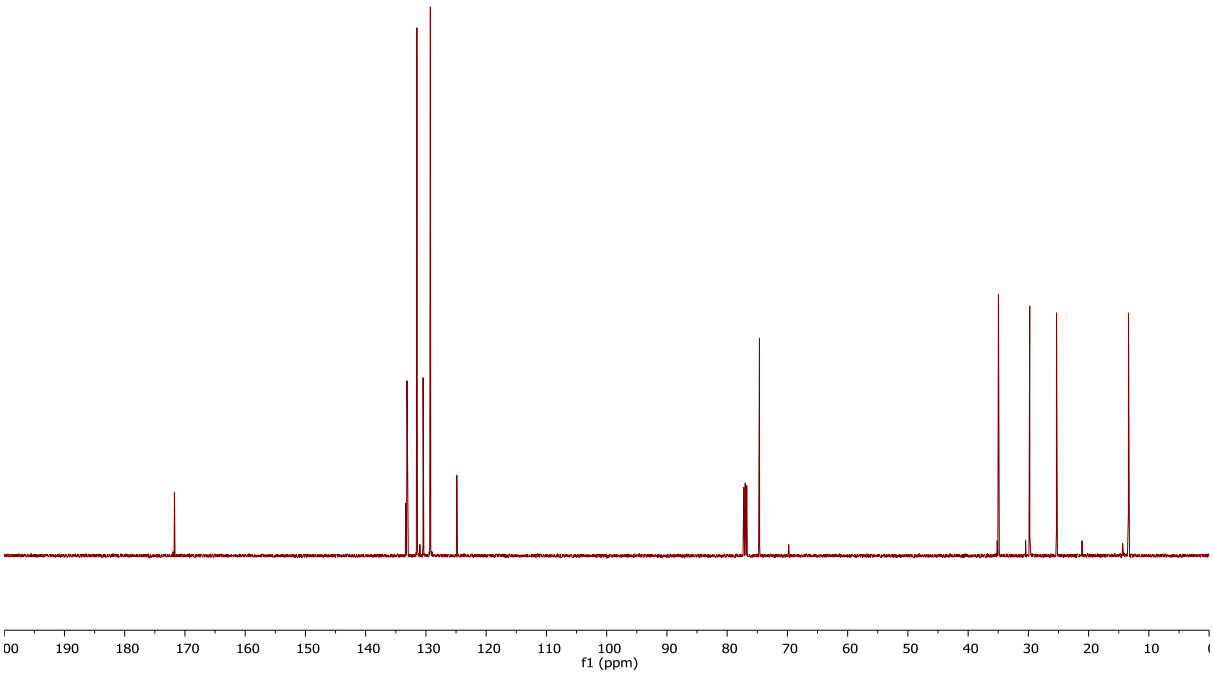
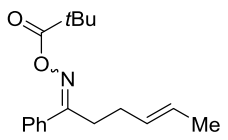
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
N
Br

8h

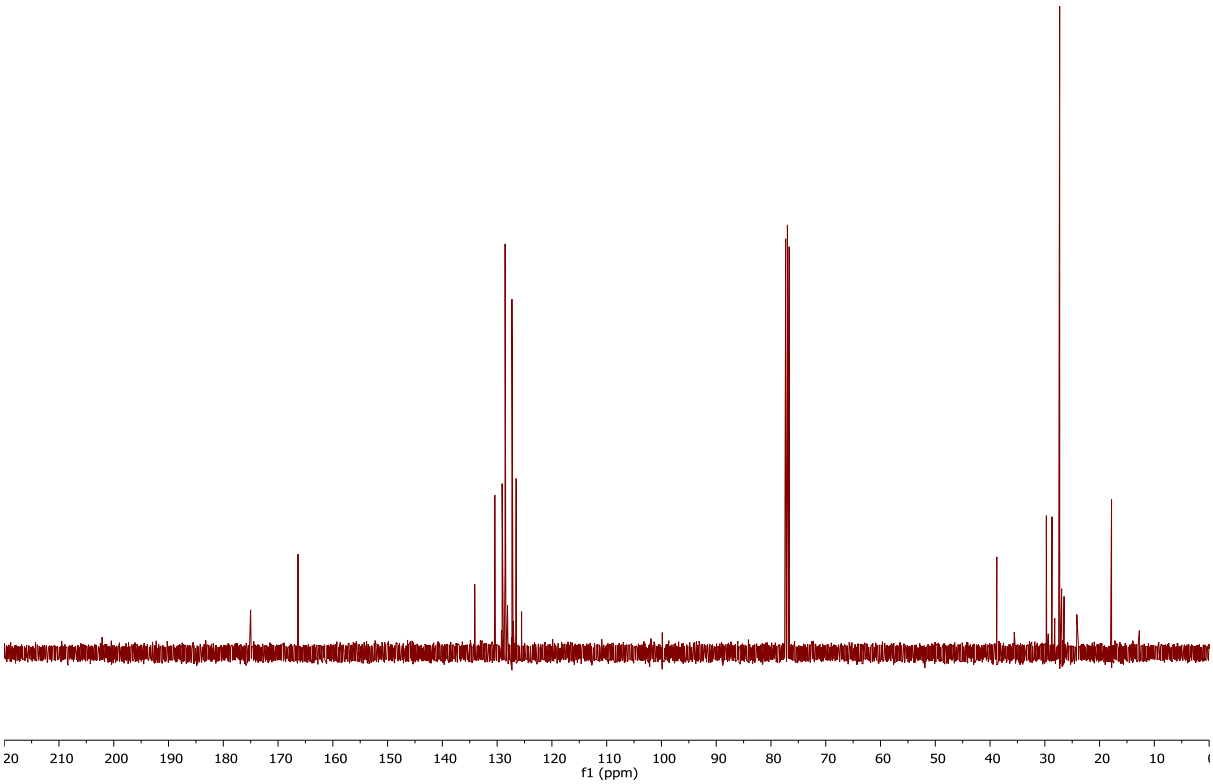
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

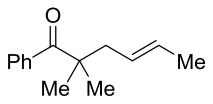

00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
tBu
O
N
Ph
Me

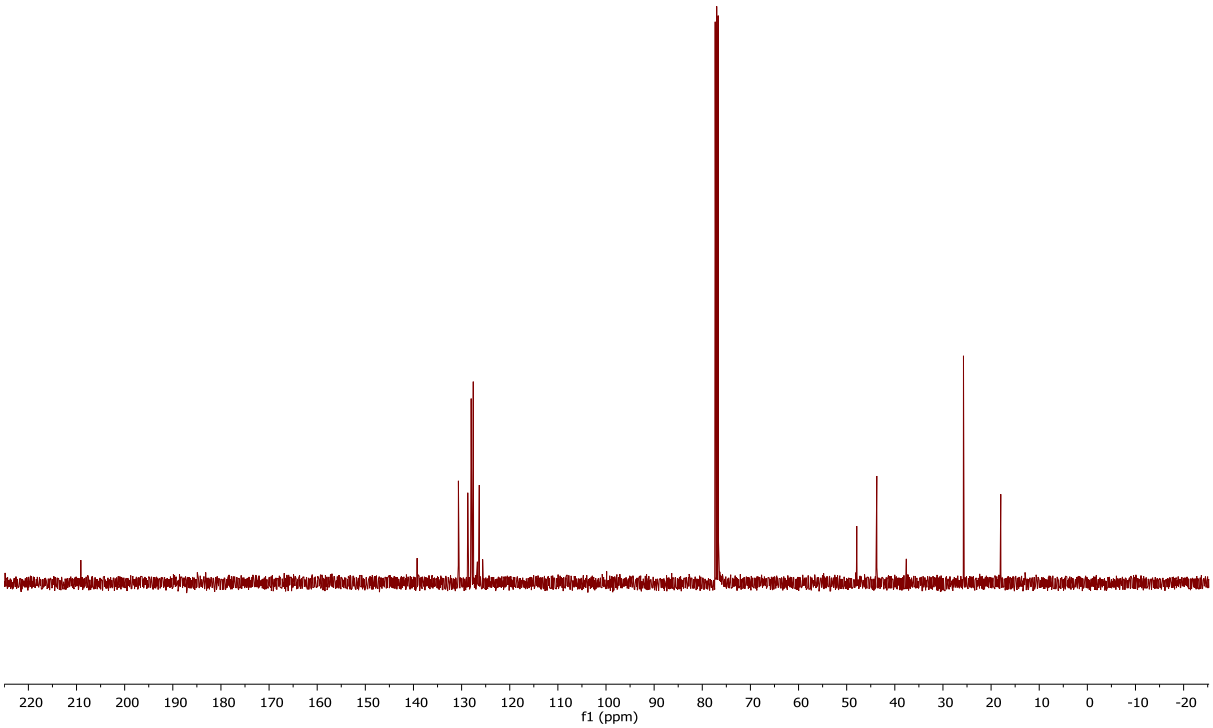
7i

.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
Ph
Me
Me
Me

.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


220
210
200
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180
170
160
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130
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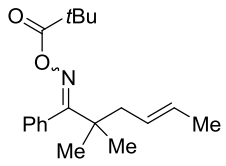
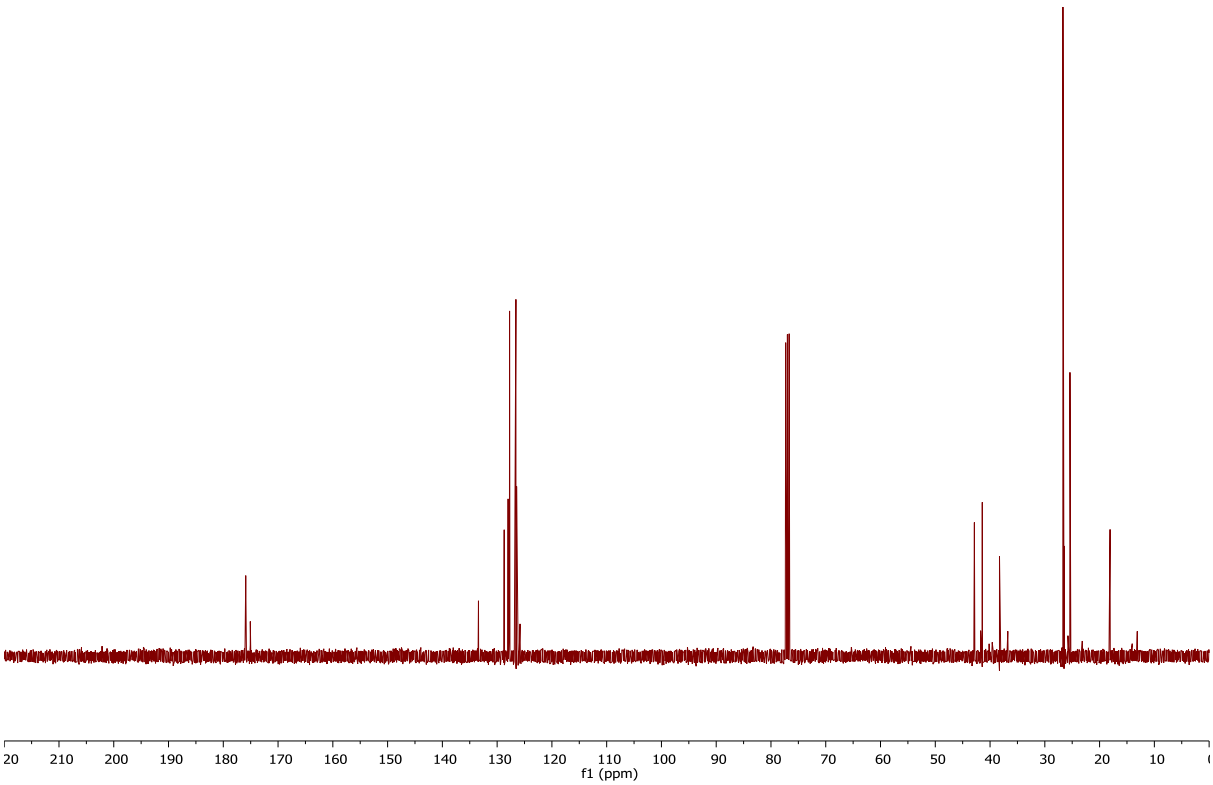
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


O
tBu
O
N
Ph
Me
Me
Me

7j

.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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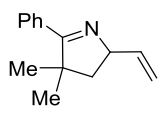
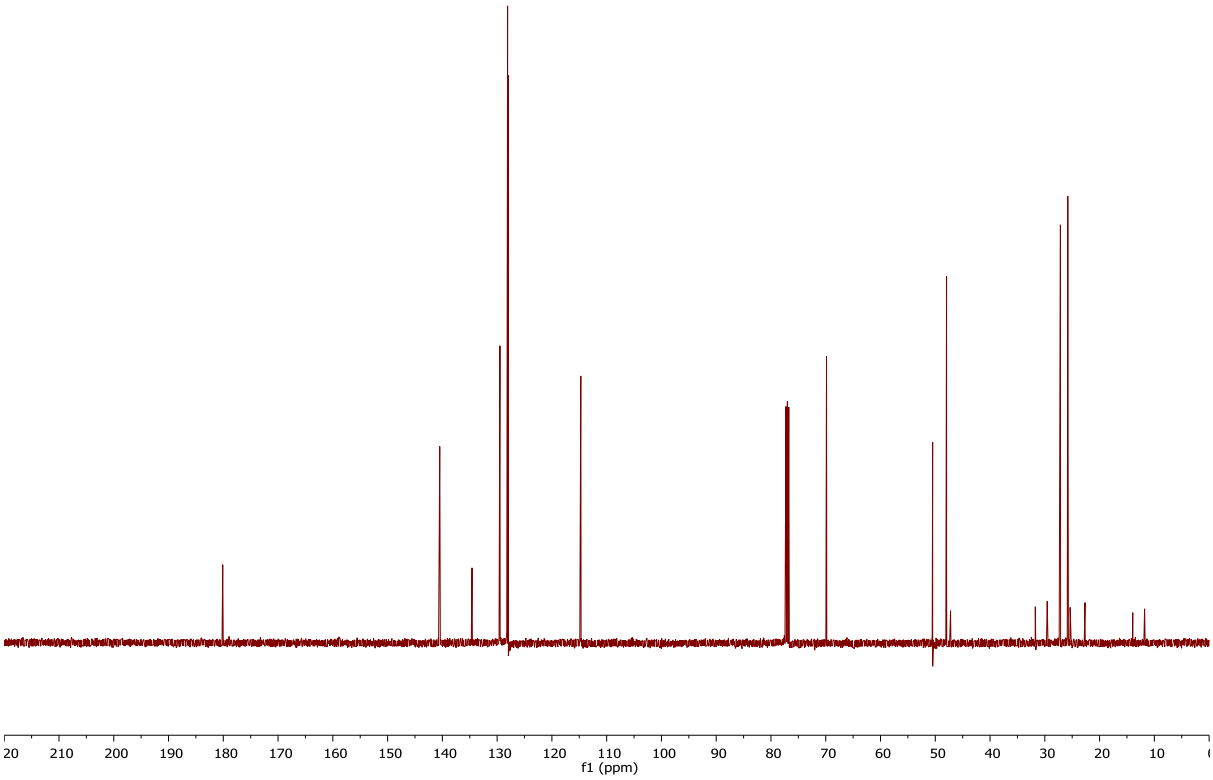
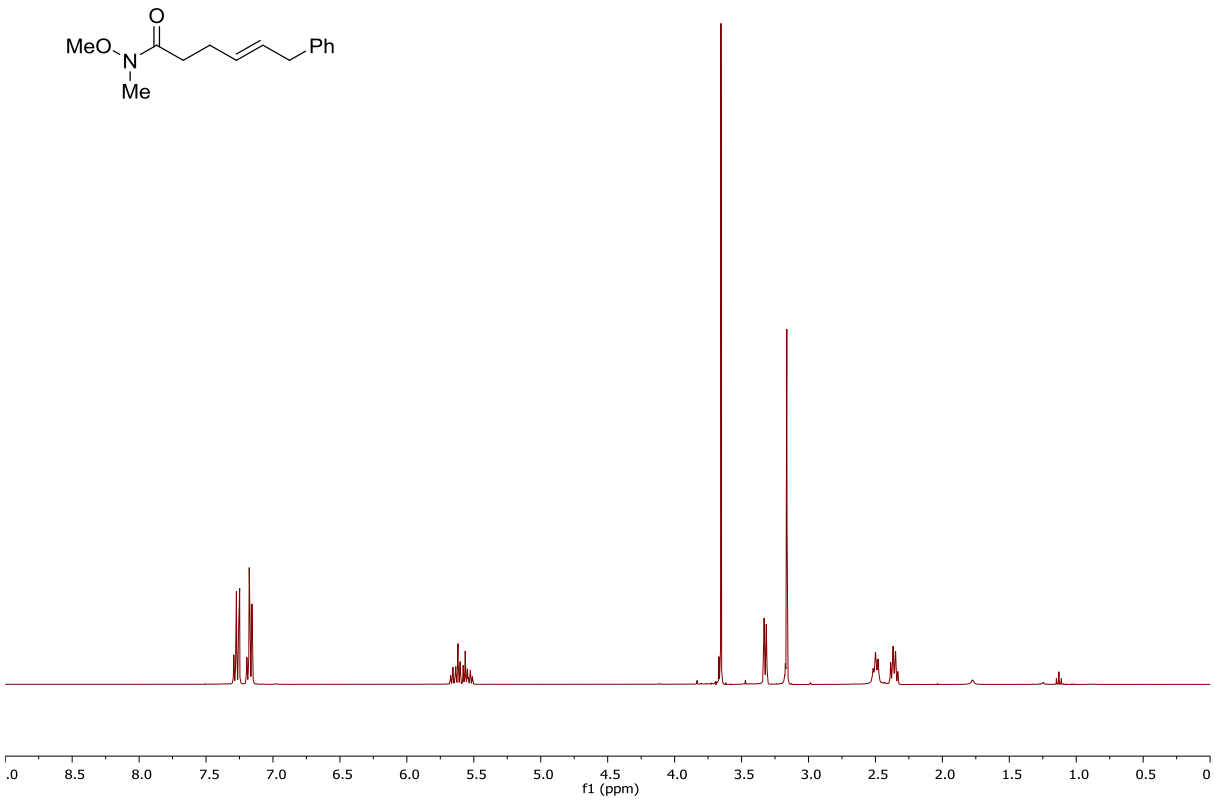
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

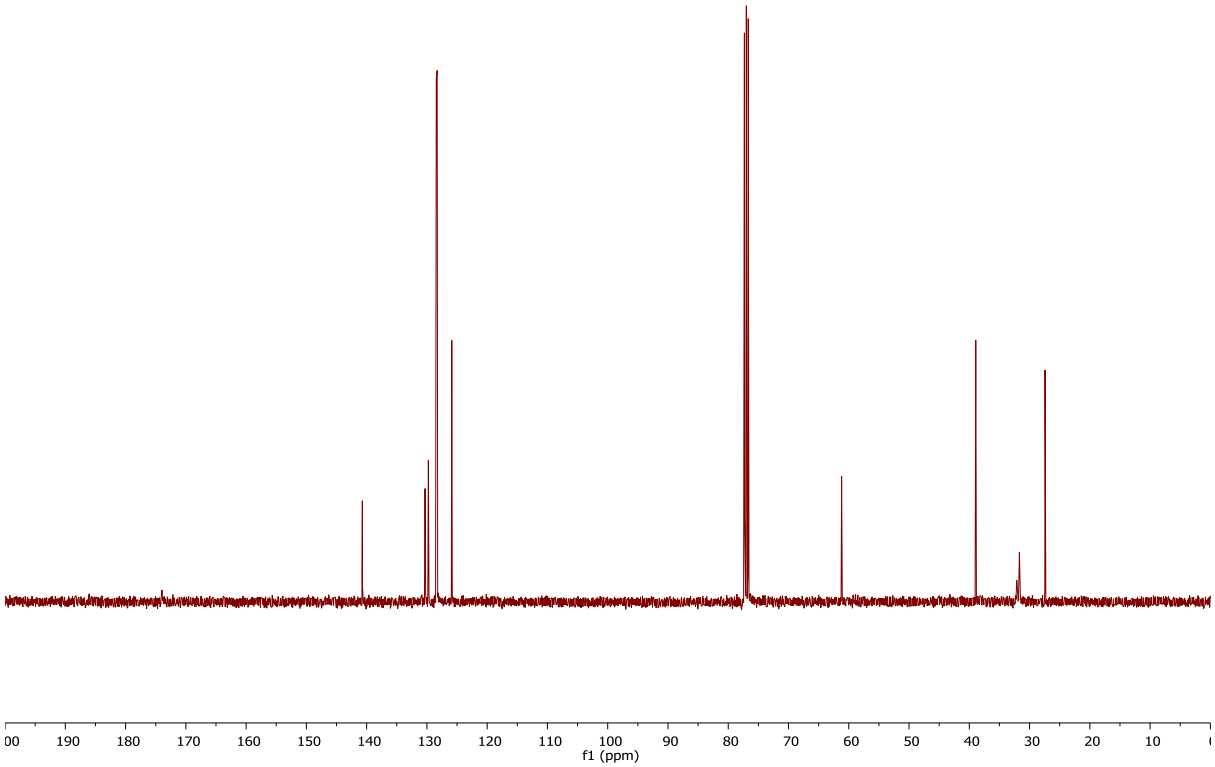

Ph
N
Me
Me

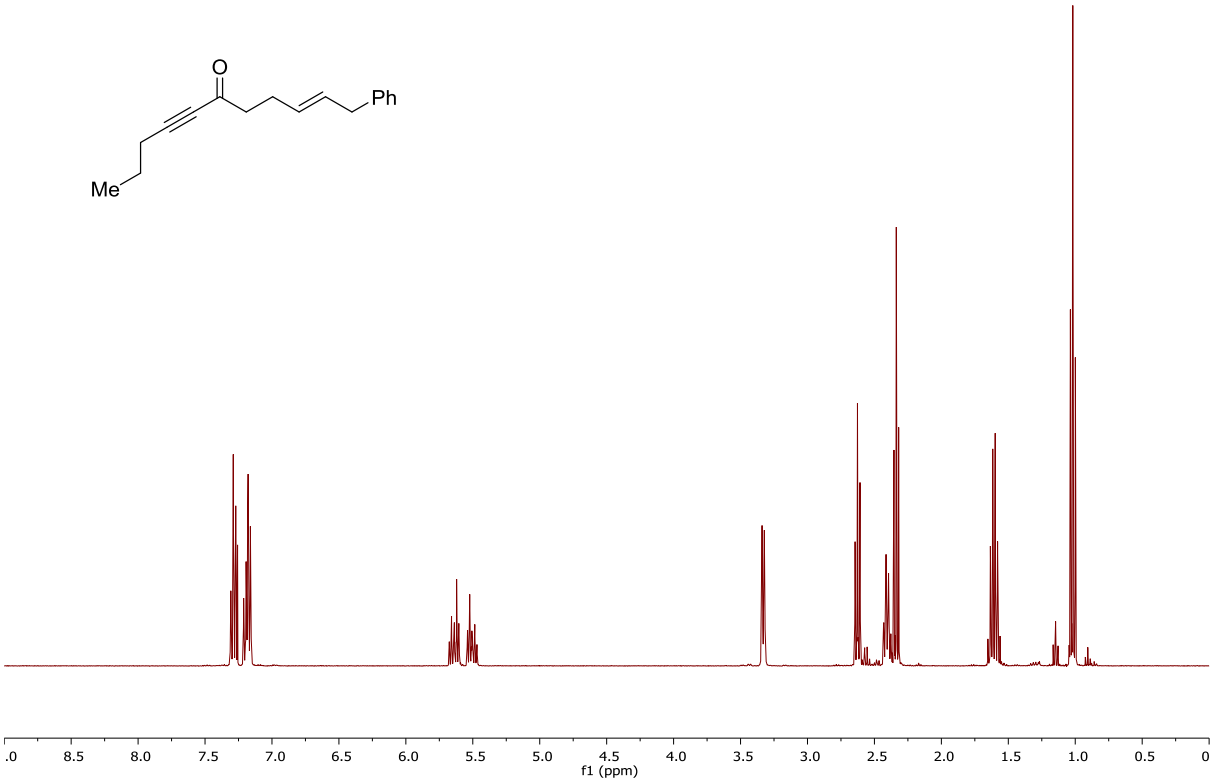
8j

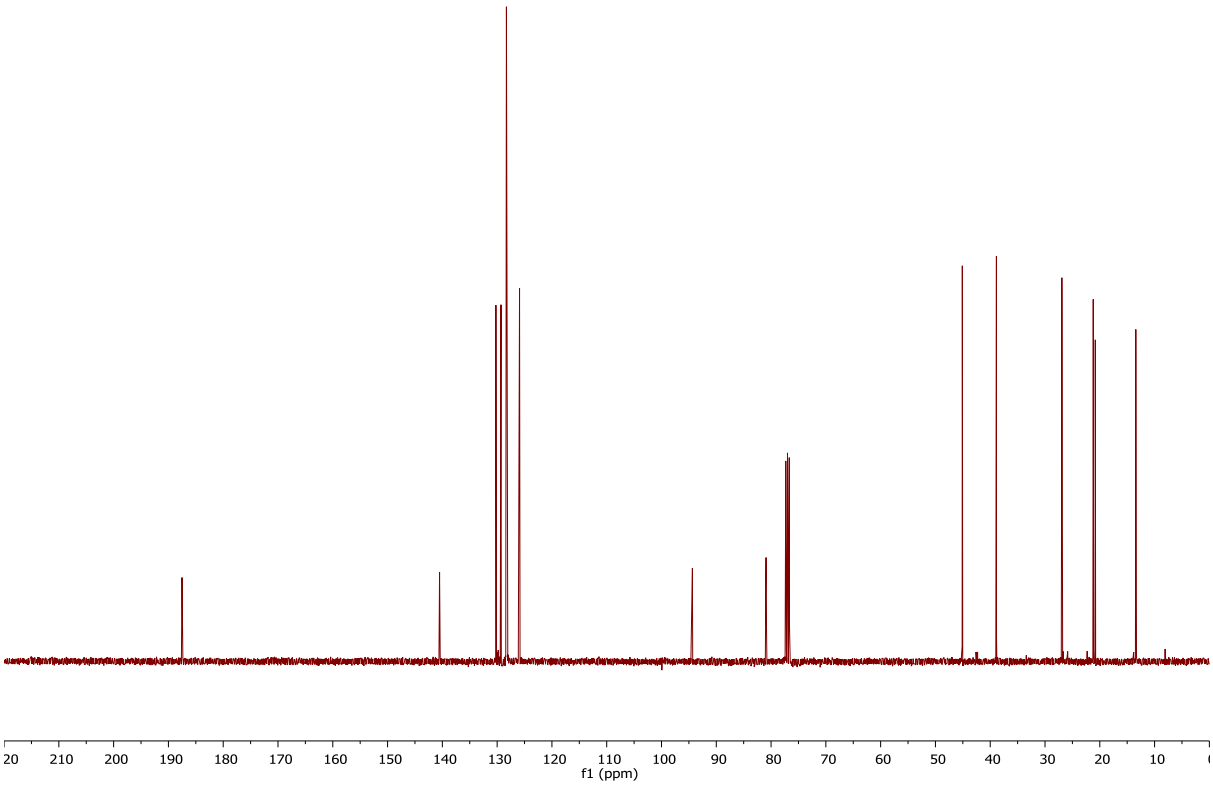
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

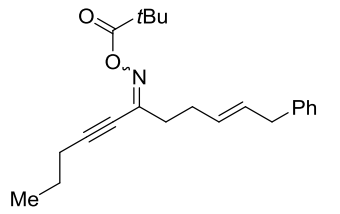

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


MeO
N
Me
O
Ph
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

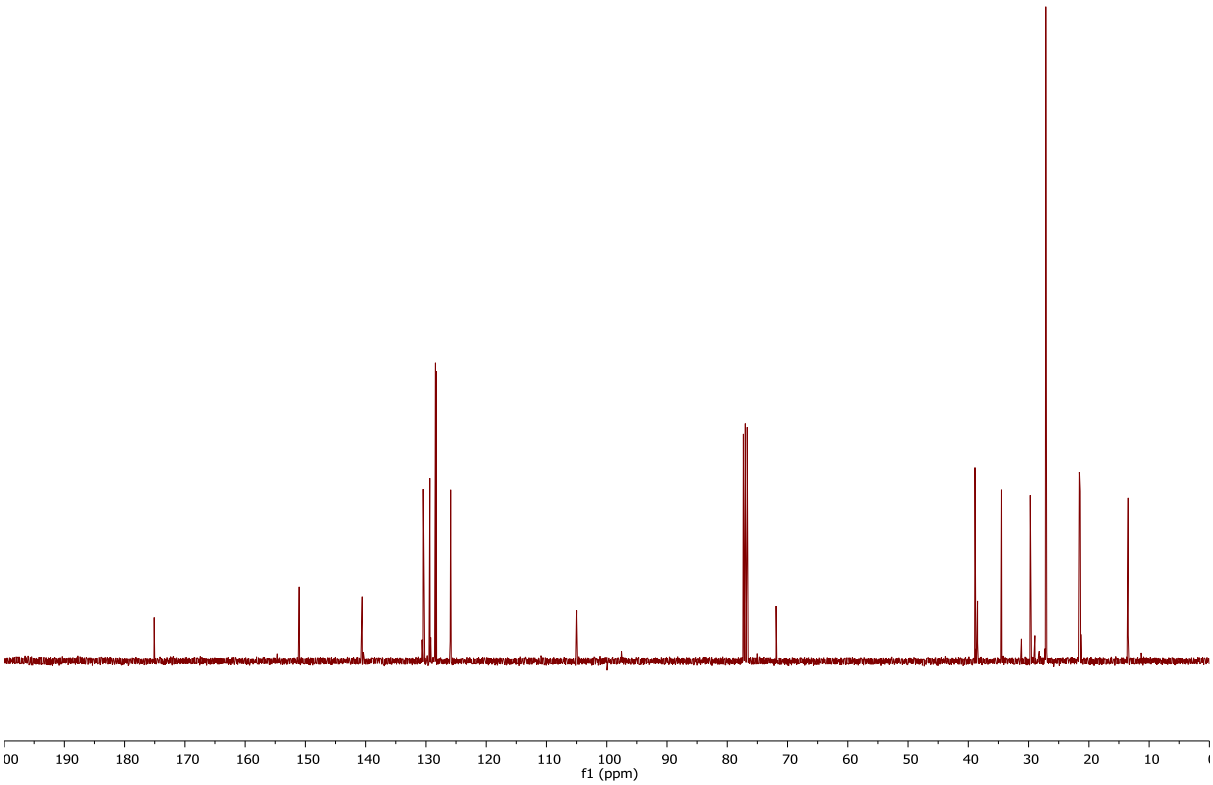

O
Ph
Me
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

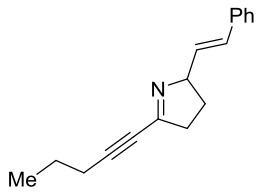

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


O
tBu
O
N
Ph
Me

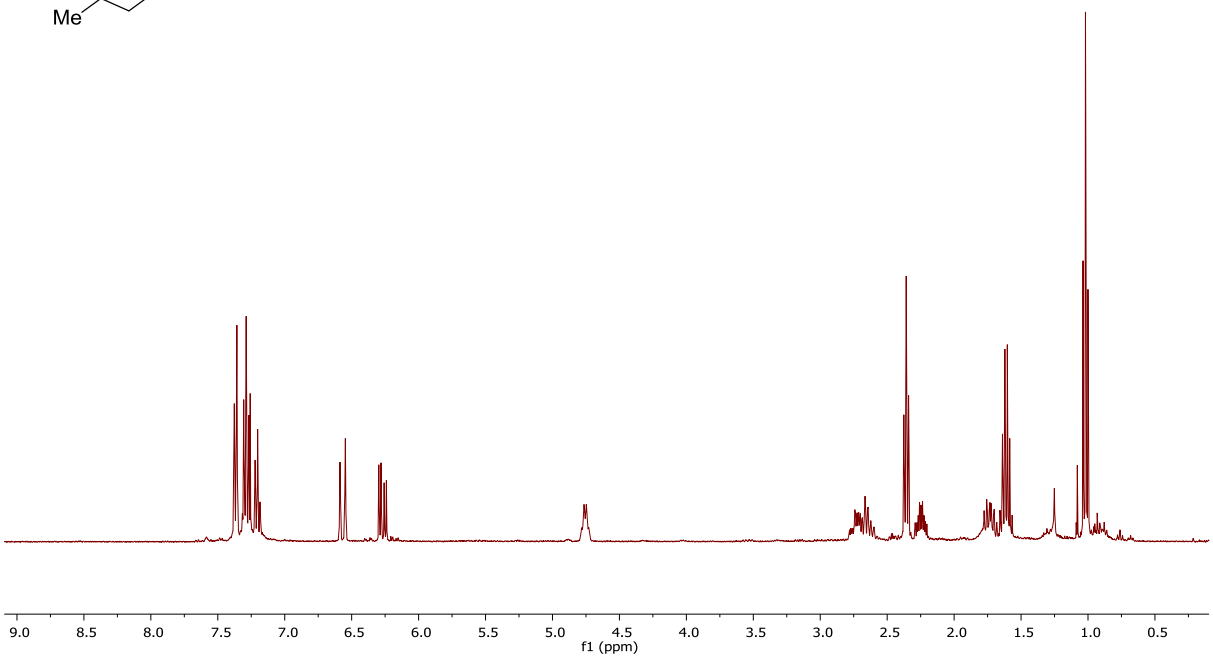
7k

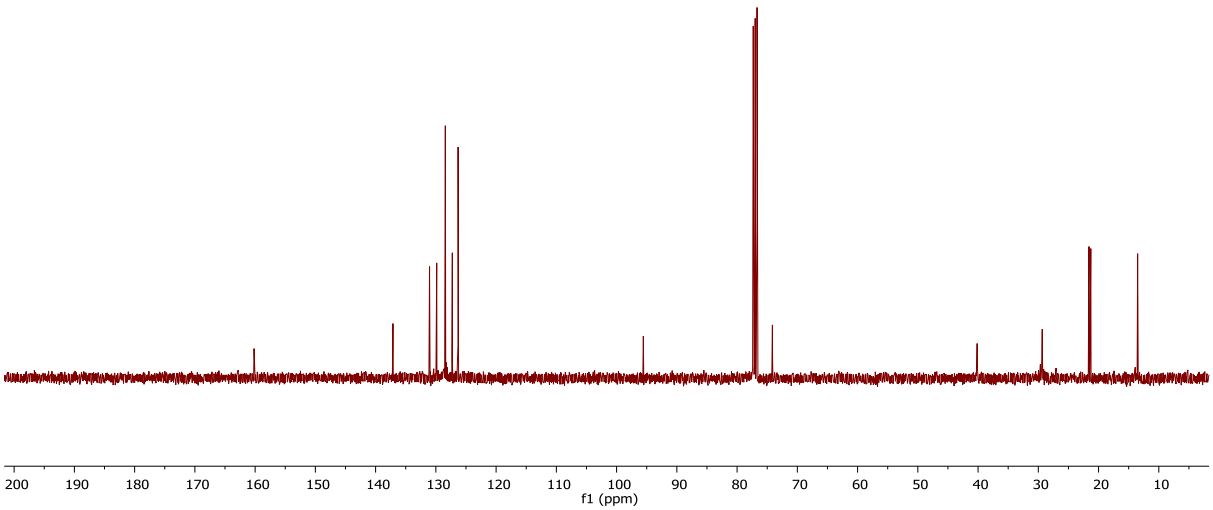
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

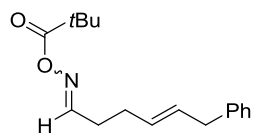

00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Ph
N
Me

8k

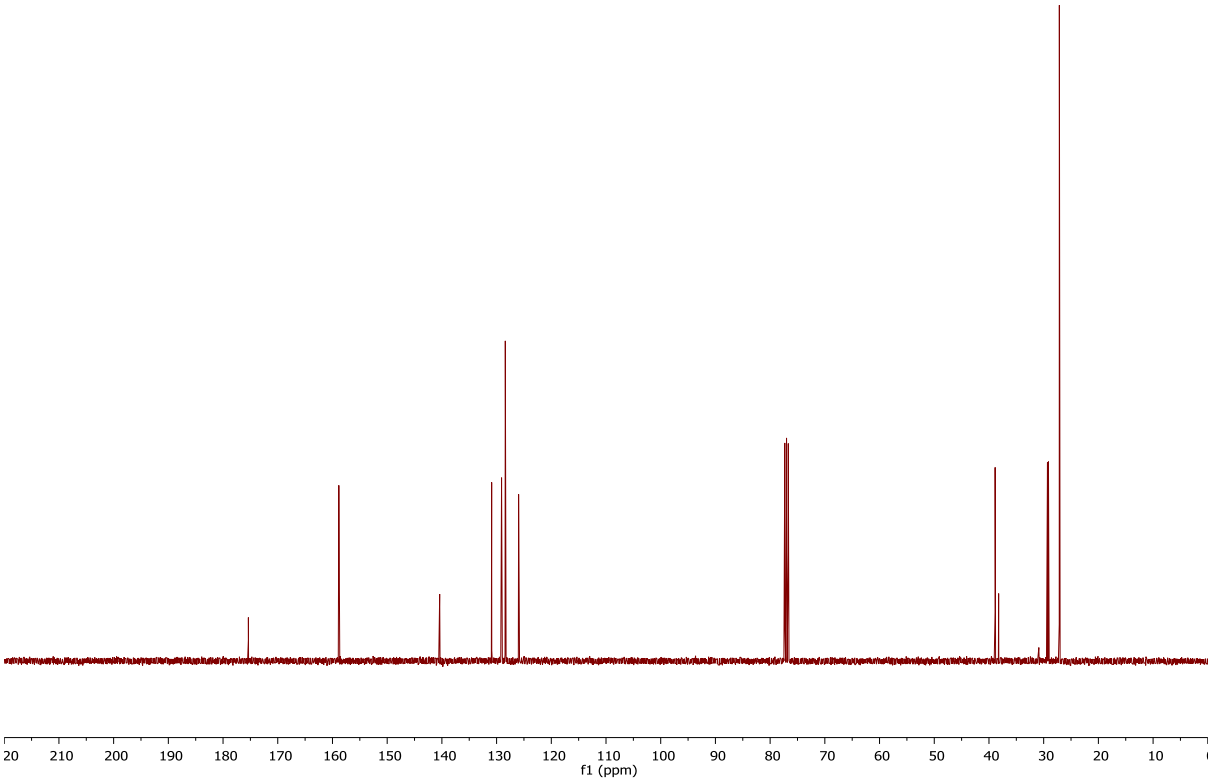

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
tBu
O
N
H
Ph

7l, isomer A

.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


220
210
200
190
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140
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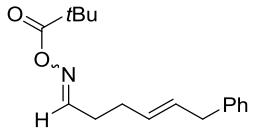
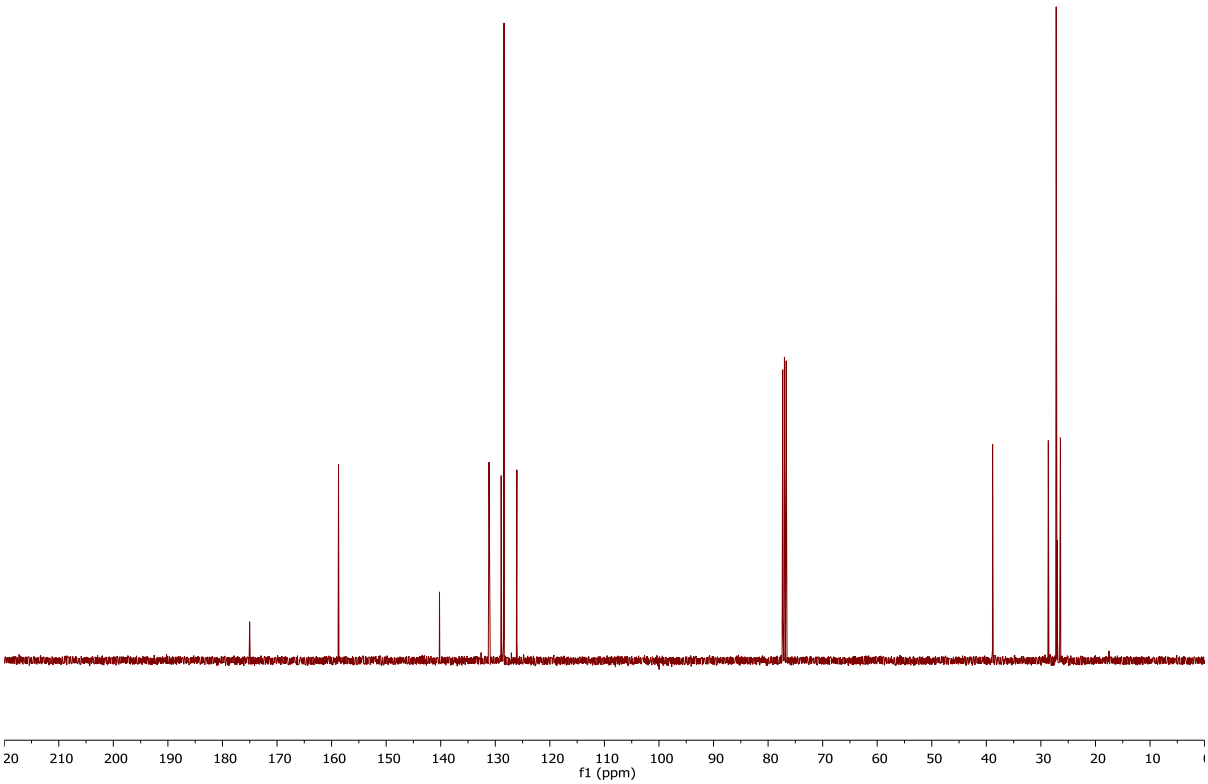
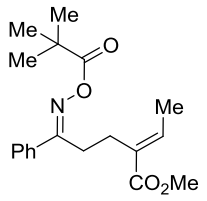
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
tBu
O
N
H
Ph

7l, isomer B

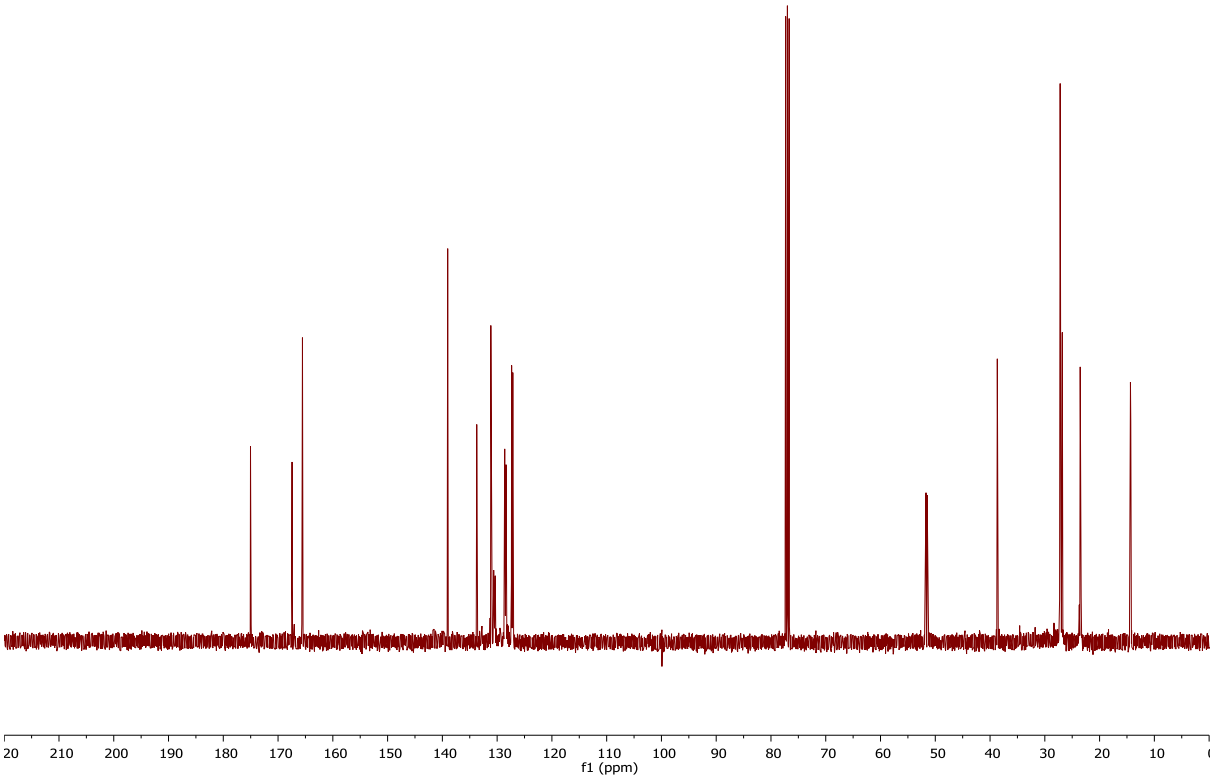
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

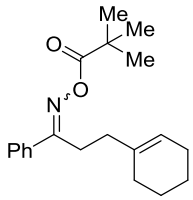

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
Me
Me
O
O
N
Ph
Me
CO2Me

7m

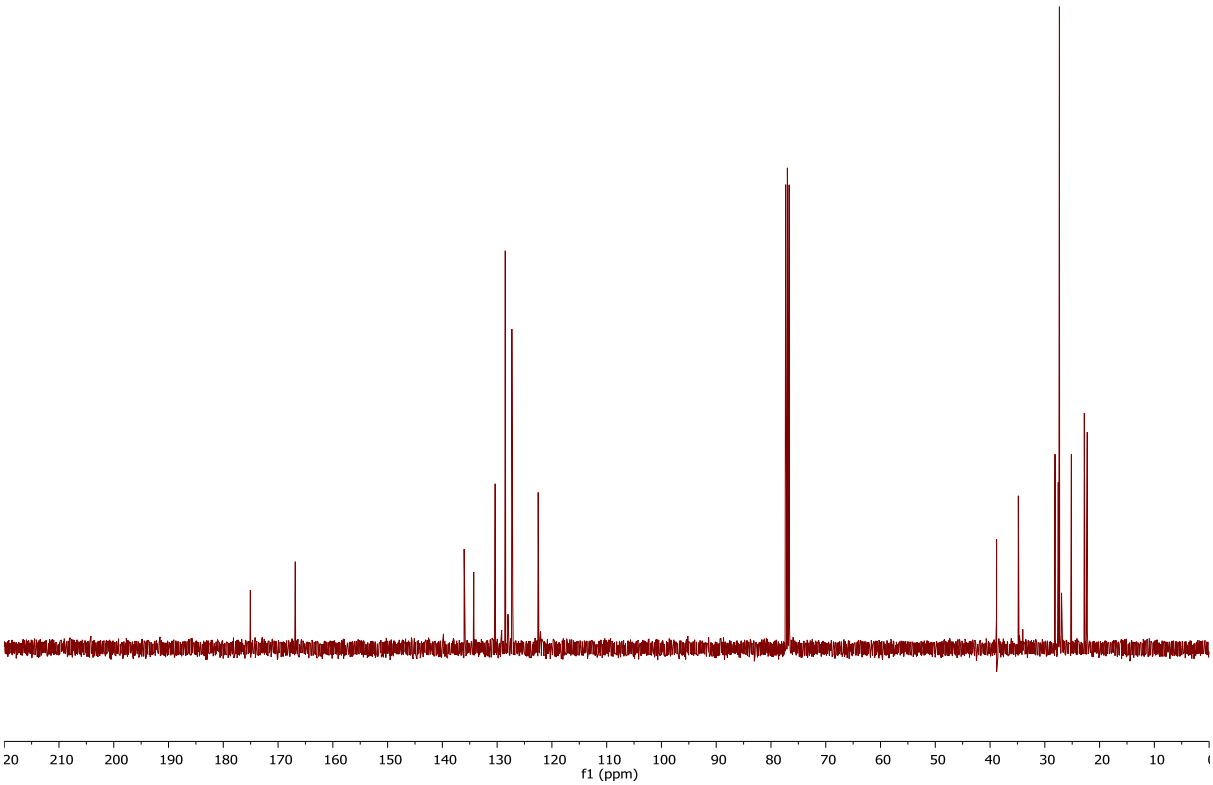
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

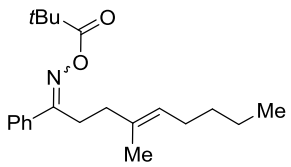

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
Me
Me
O
O
N
Ph

7n

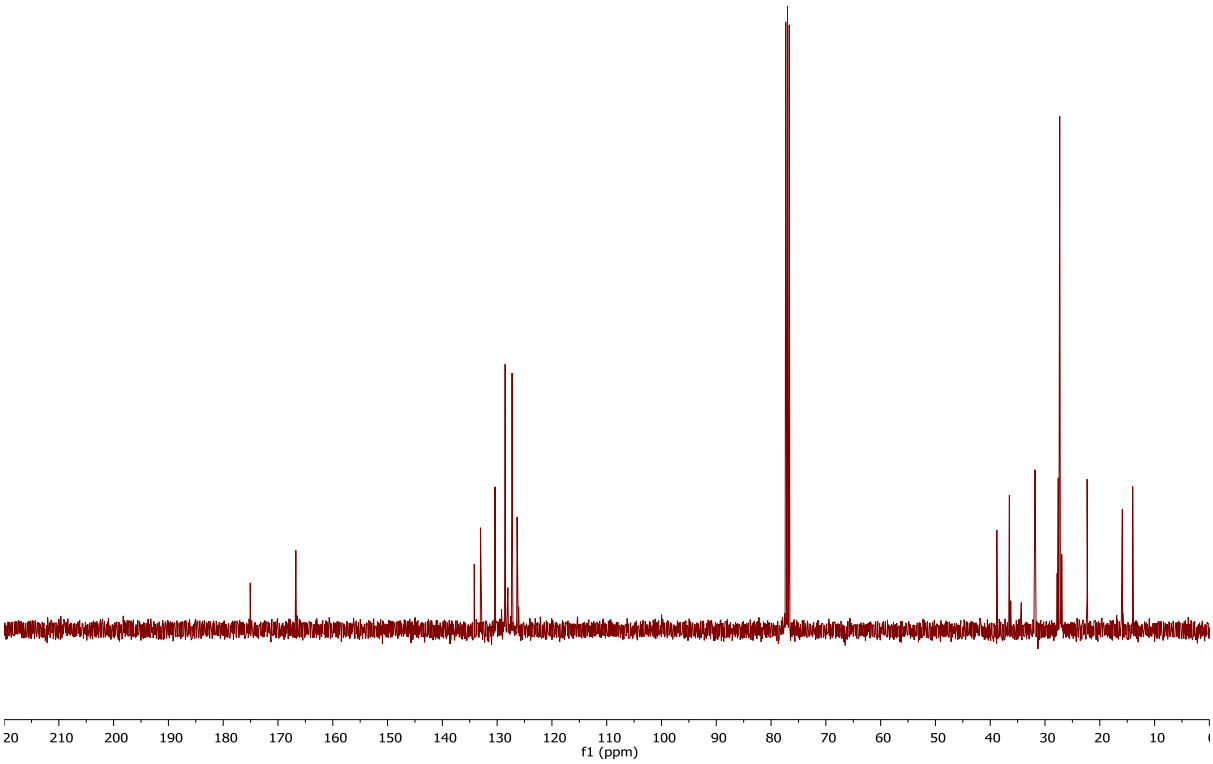
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

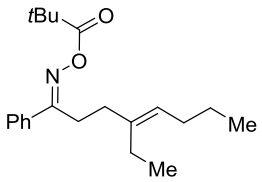

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


tBu
O
O
N
Ph
Me
Me

7o

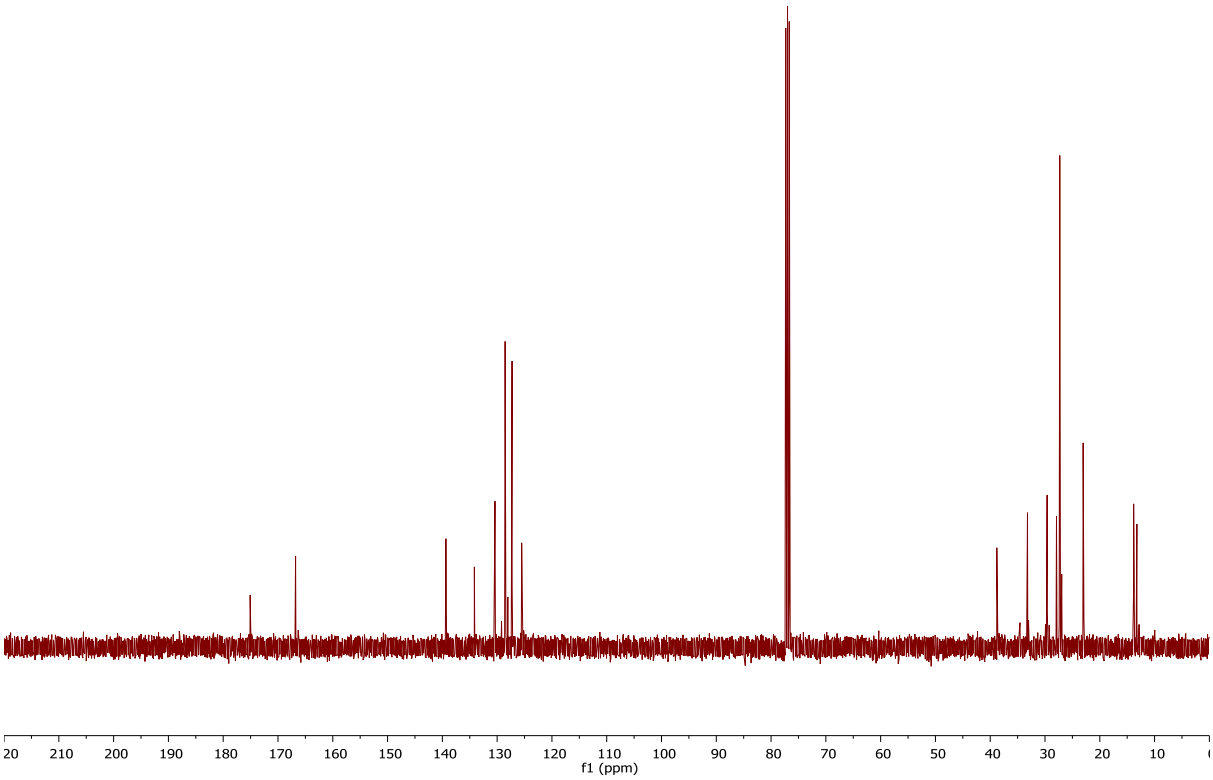
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

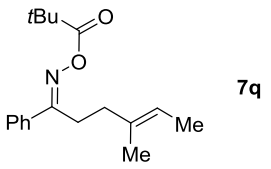

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


tBu
O
N
O
Ph
Me
Me

7p

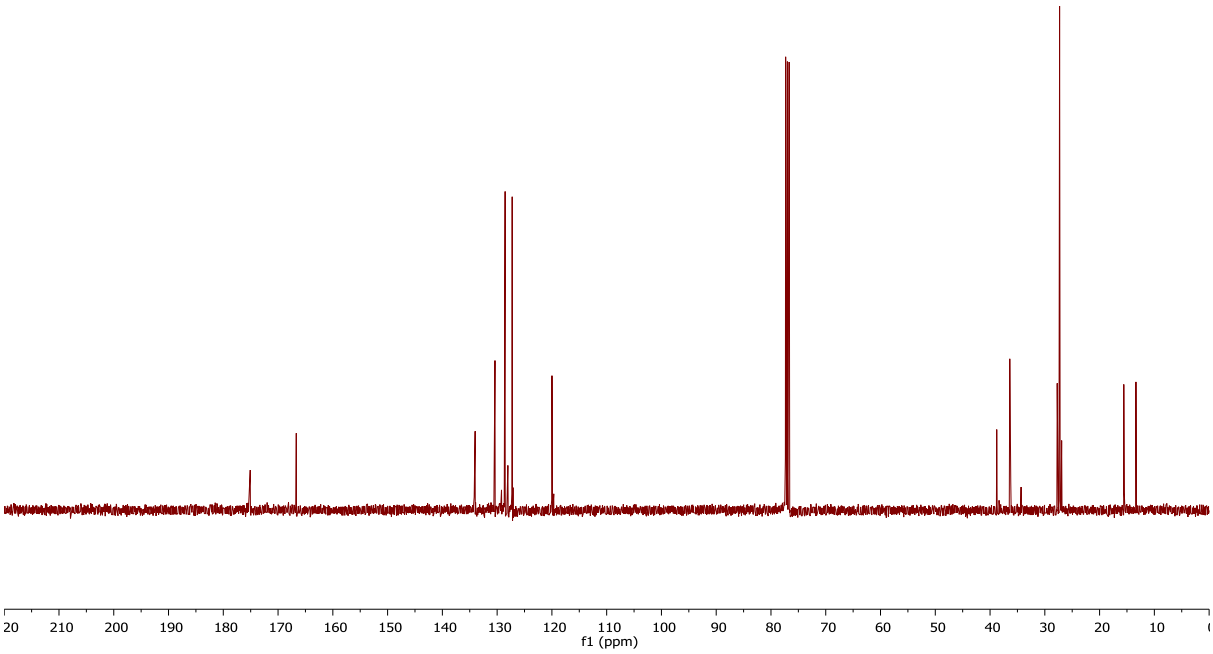
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

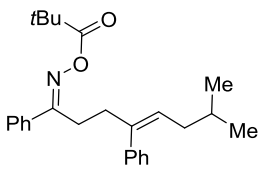

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


tBu
O
O
N
Ph
Me
Me

7q

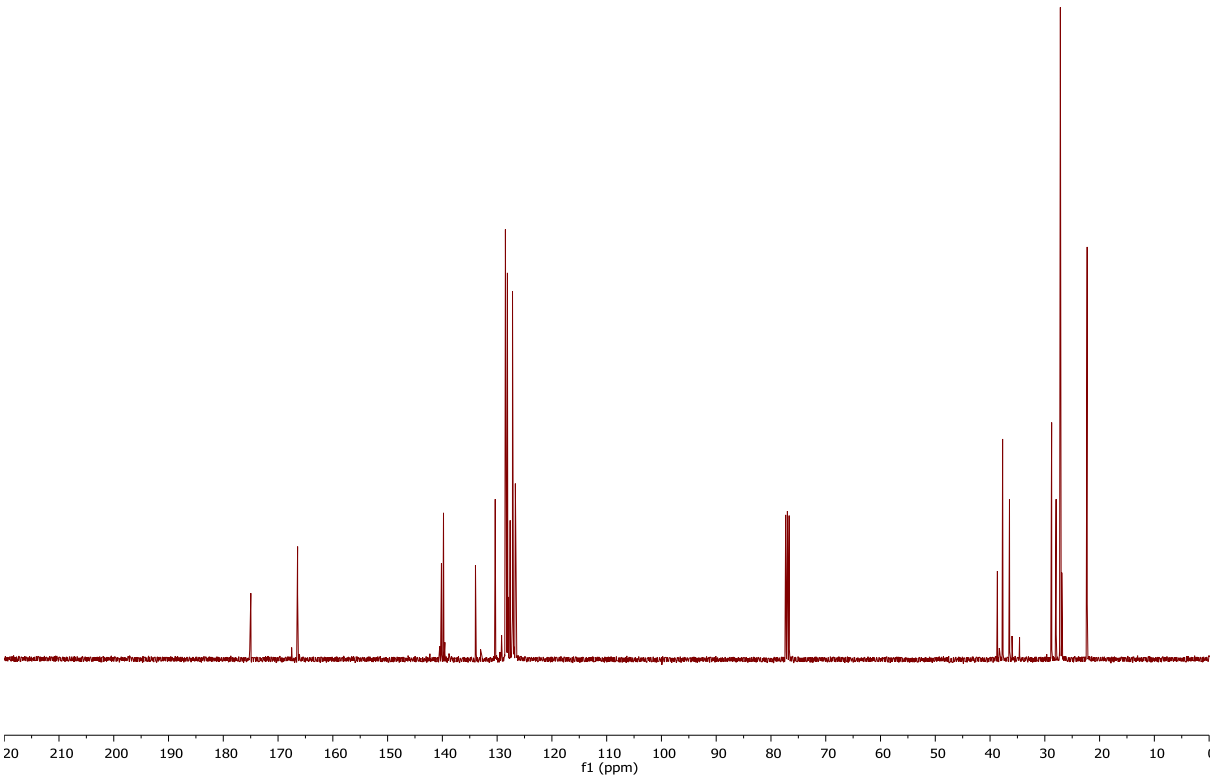
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

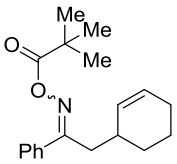

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


tBu
O
N
O
Ph
Me
Me
Ph

7r

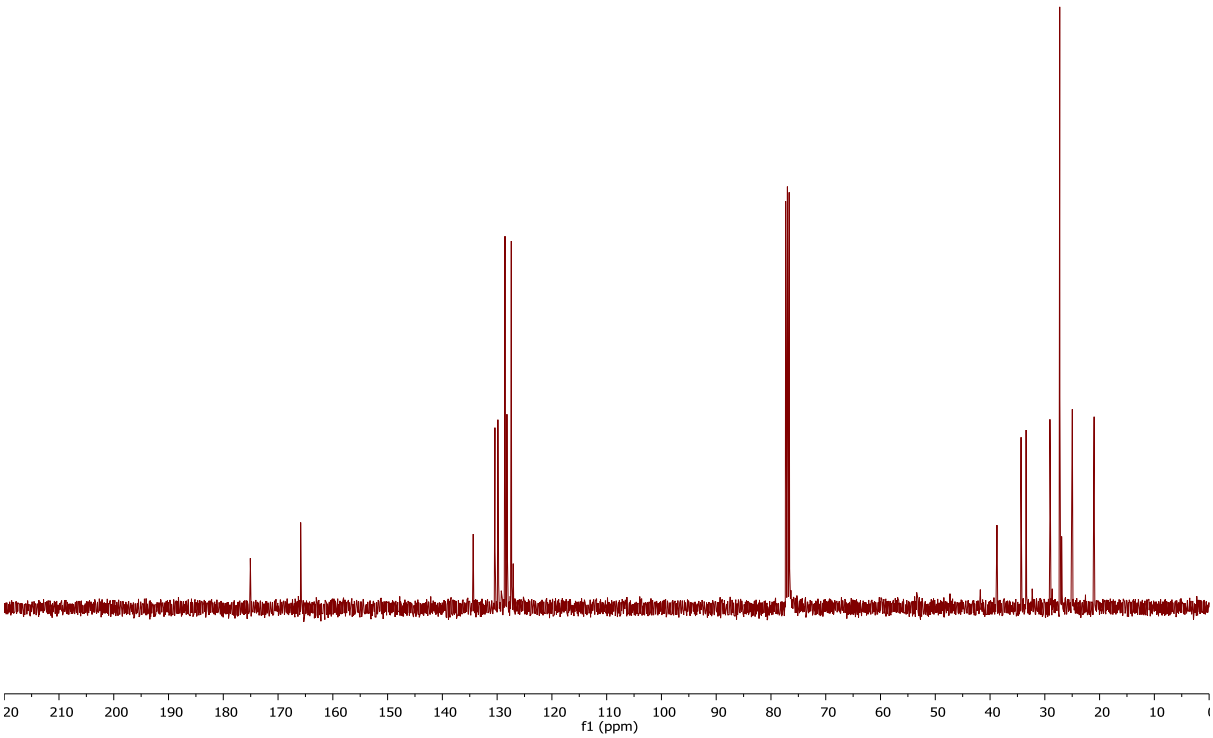
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

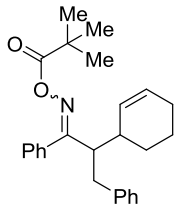

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
Me
Me
O
O
N
Ph

7s

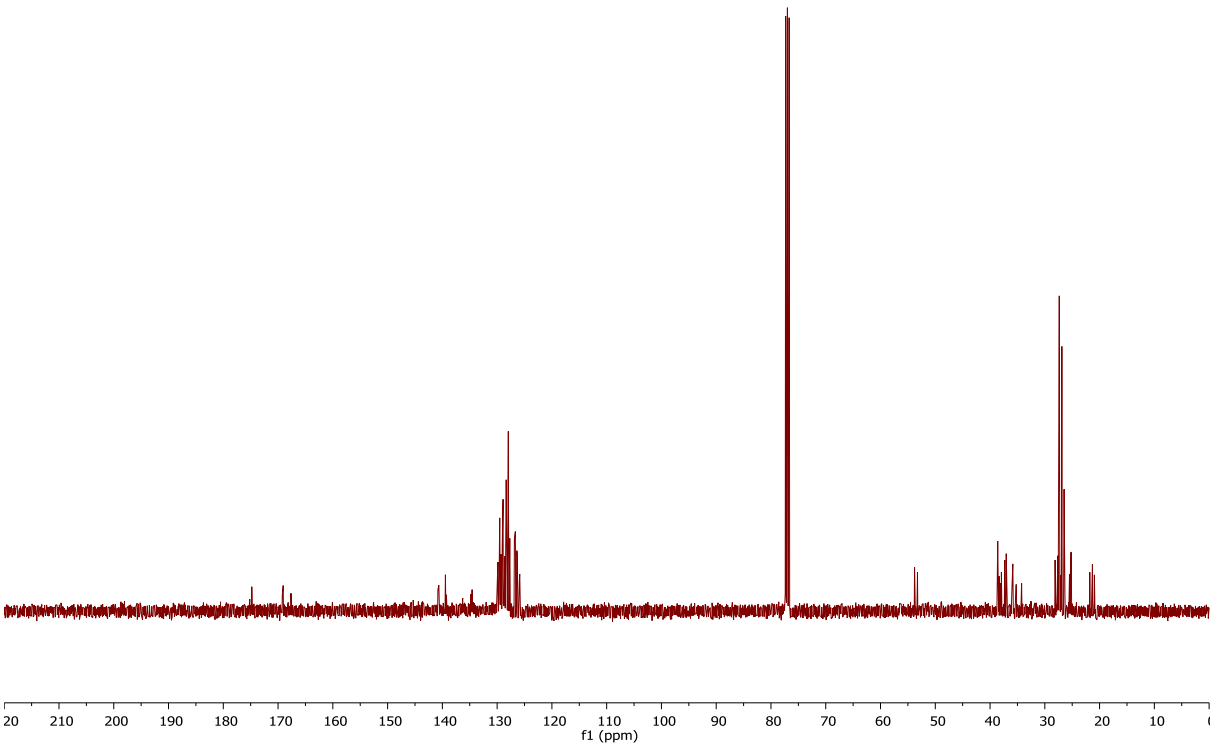
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

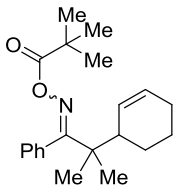

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
Me
Me
O
O
N
Ph
Ph

7t

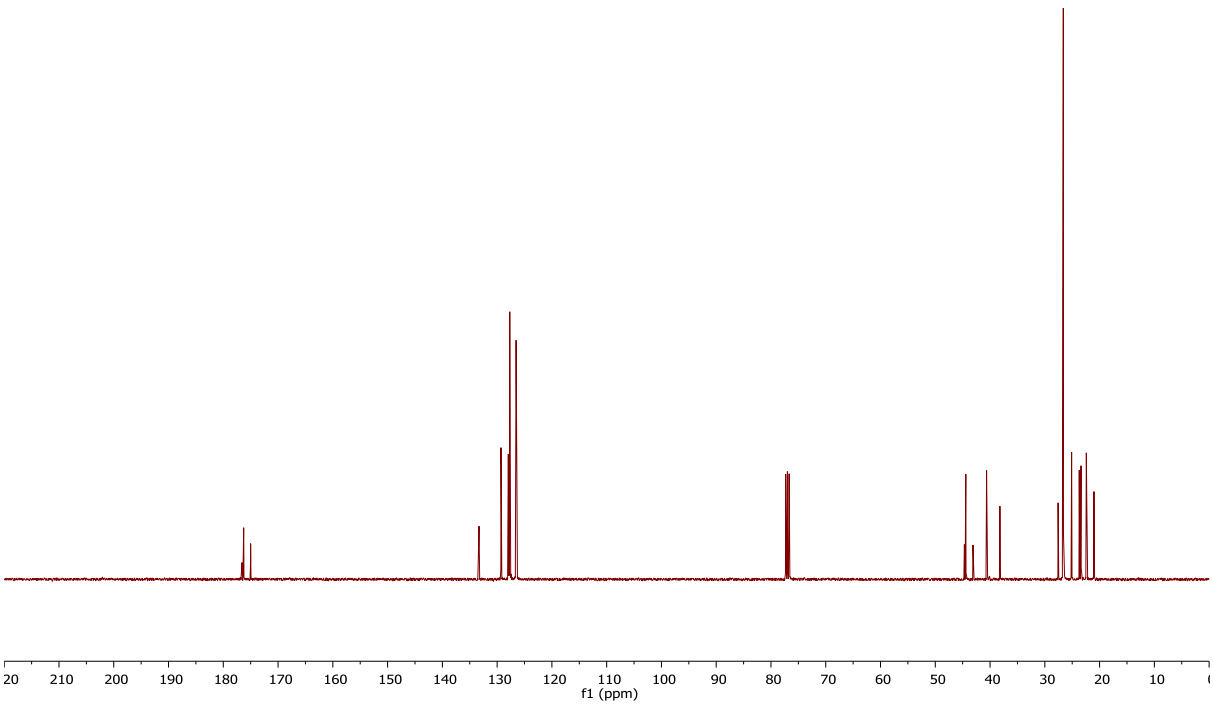
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

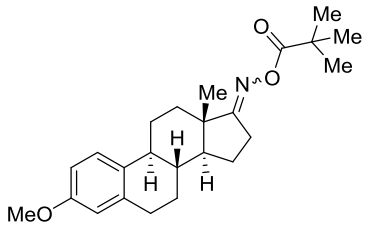

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
Me
Me
O
O
N
Ph
Me
Me

7u

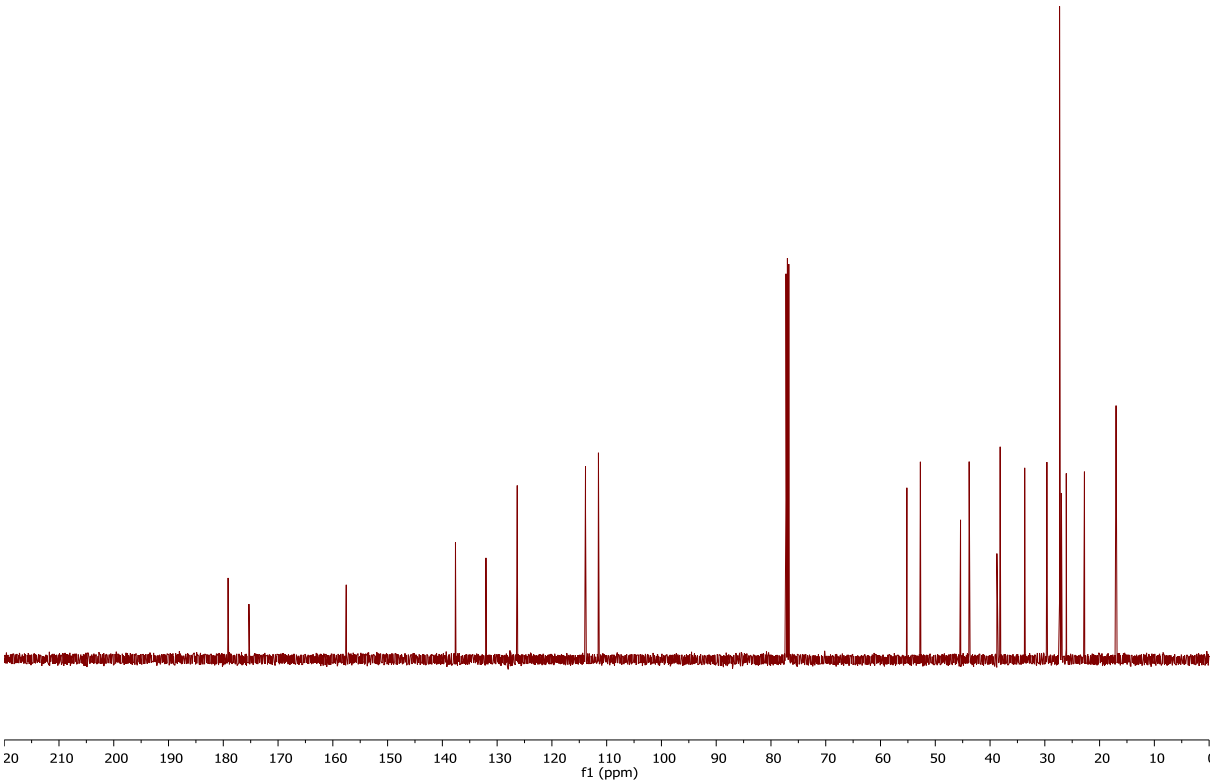
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

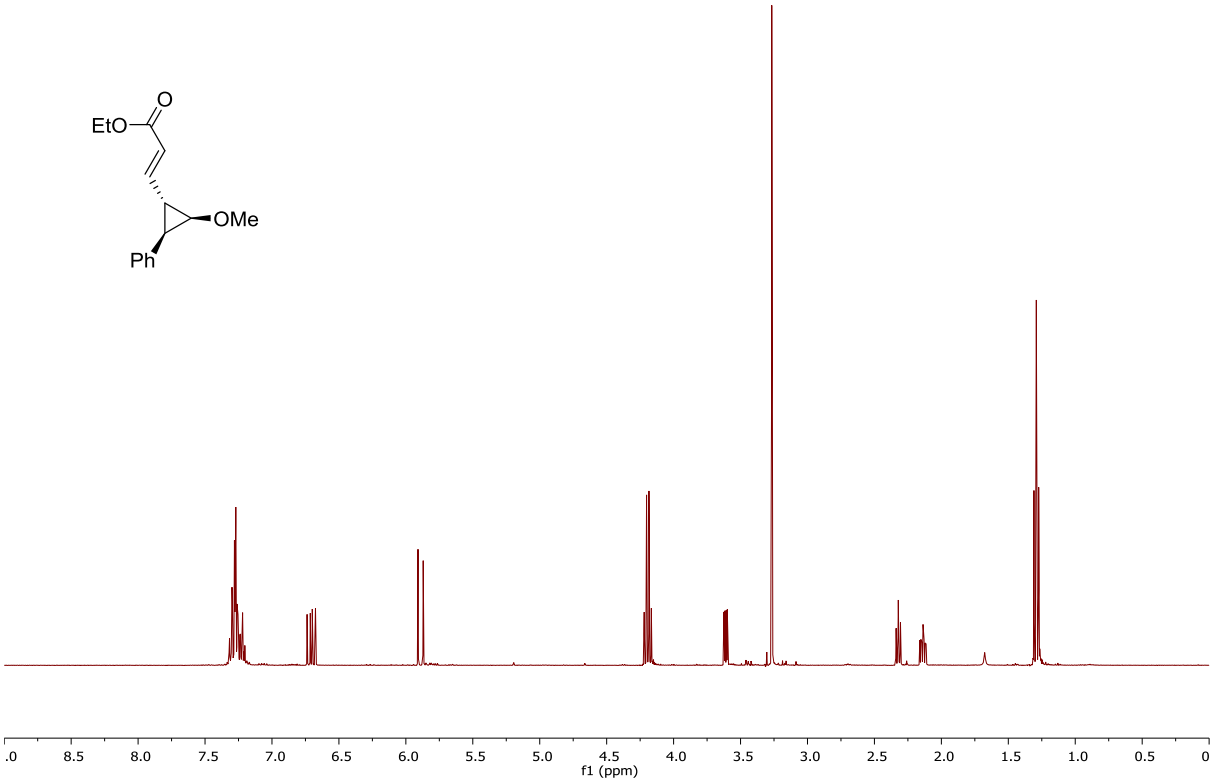

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

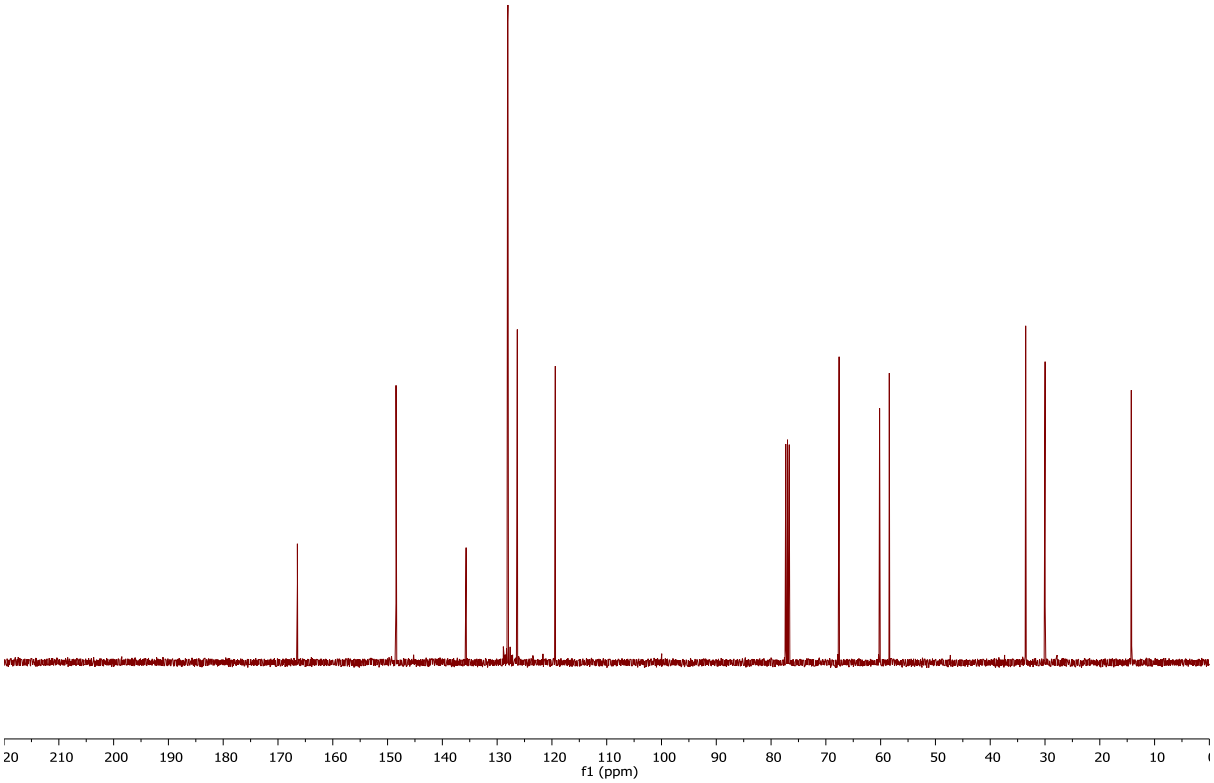

Me
O
Me
Me
N
O
Me
H
H
H
MeO

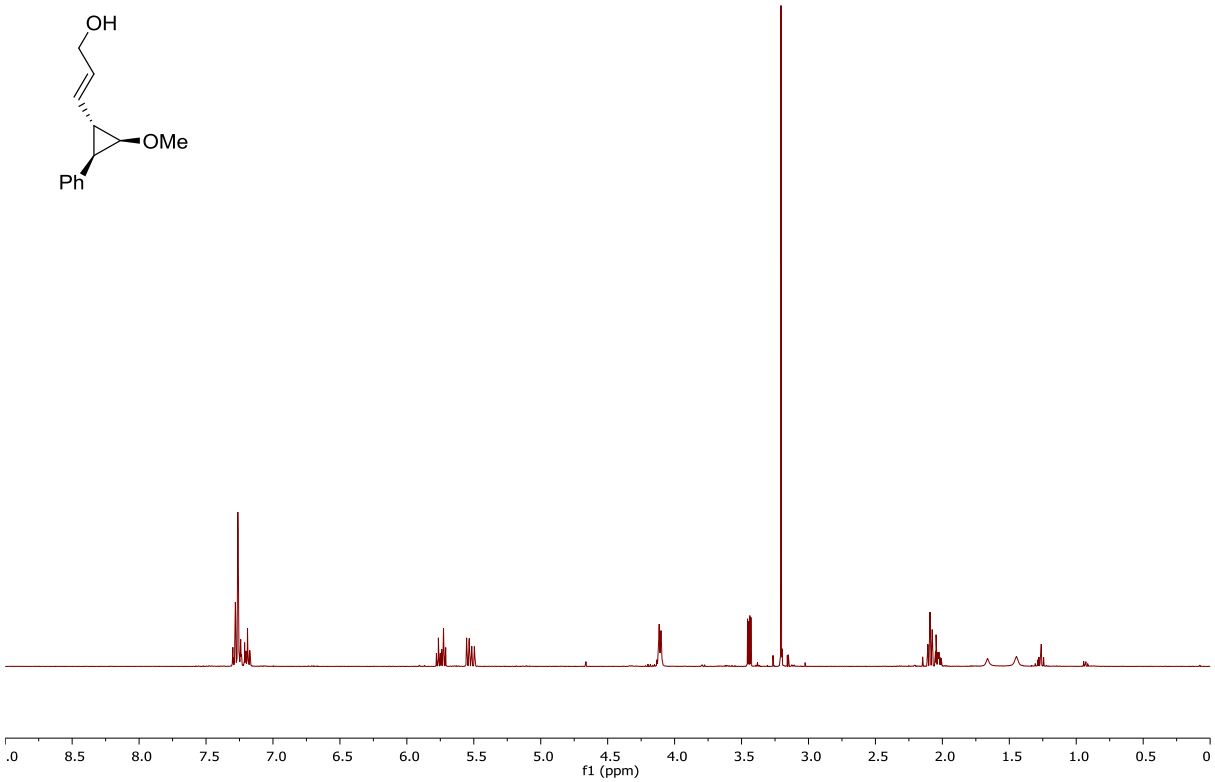
16

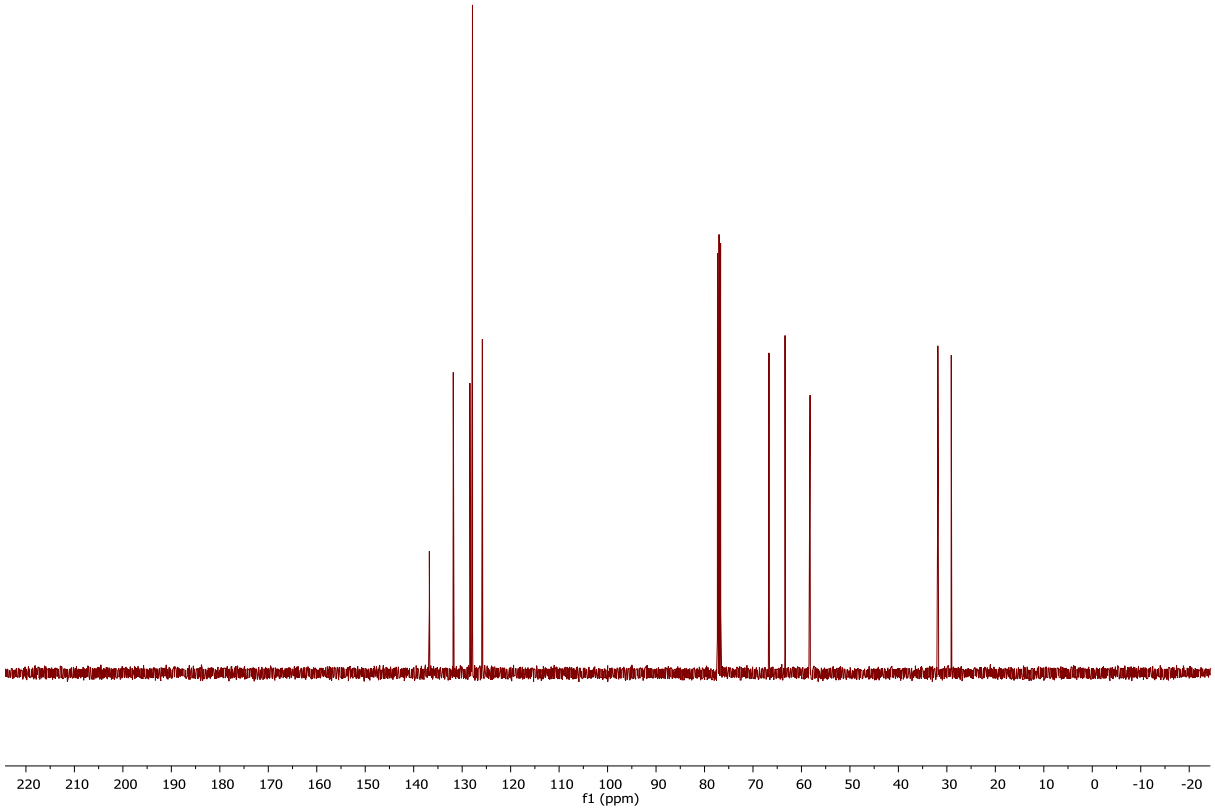
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

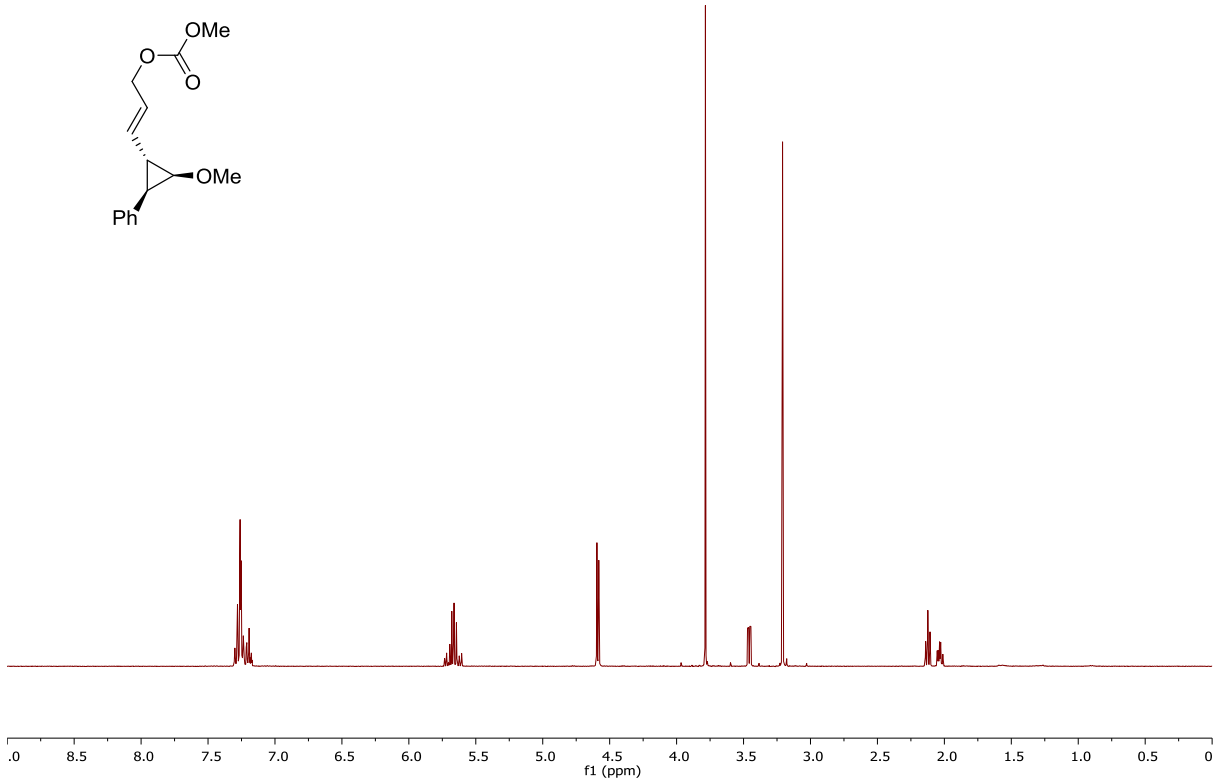

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

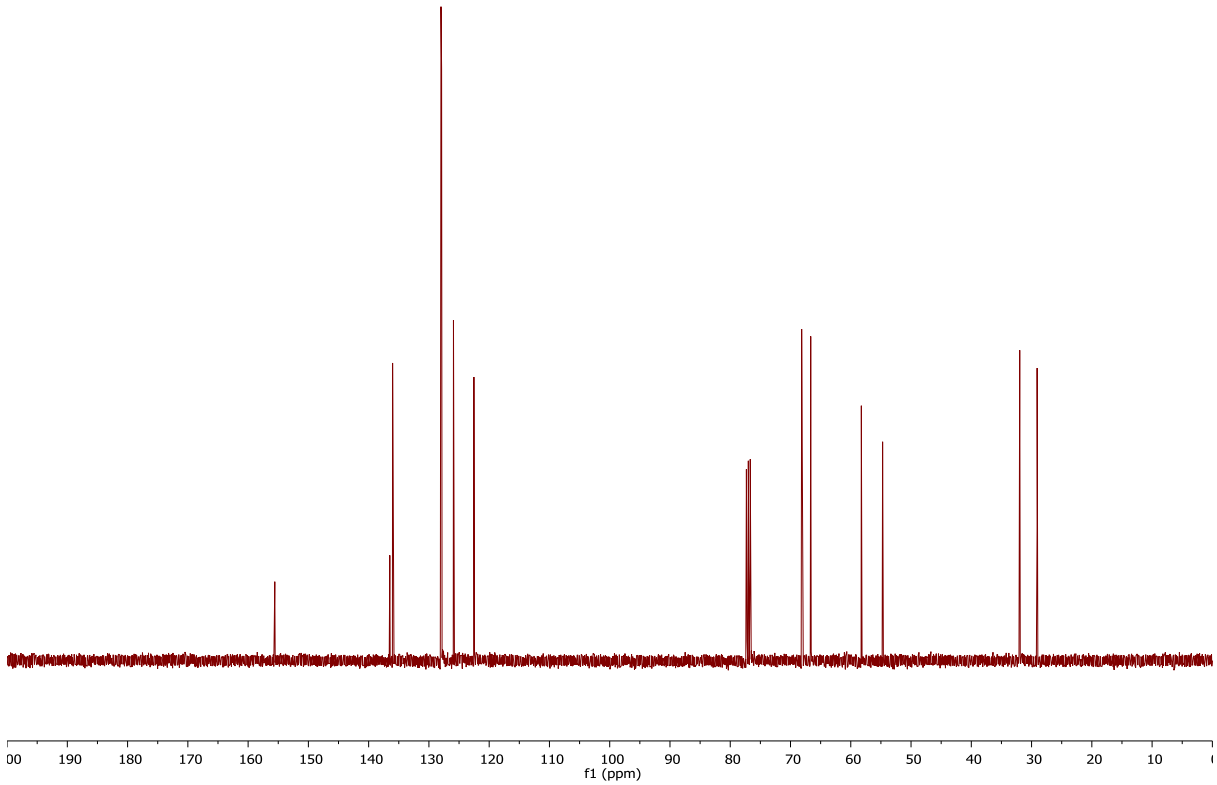

EtO
O
OMe
Ph
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

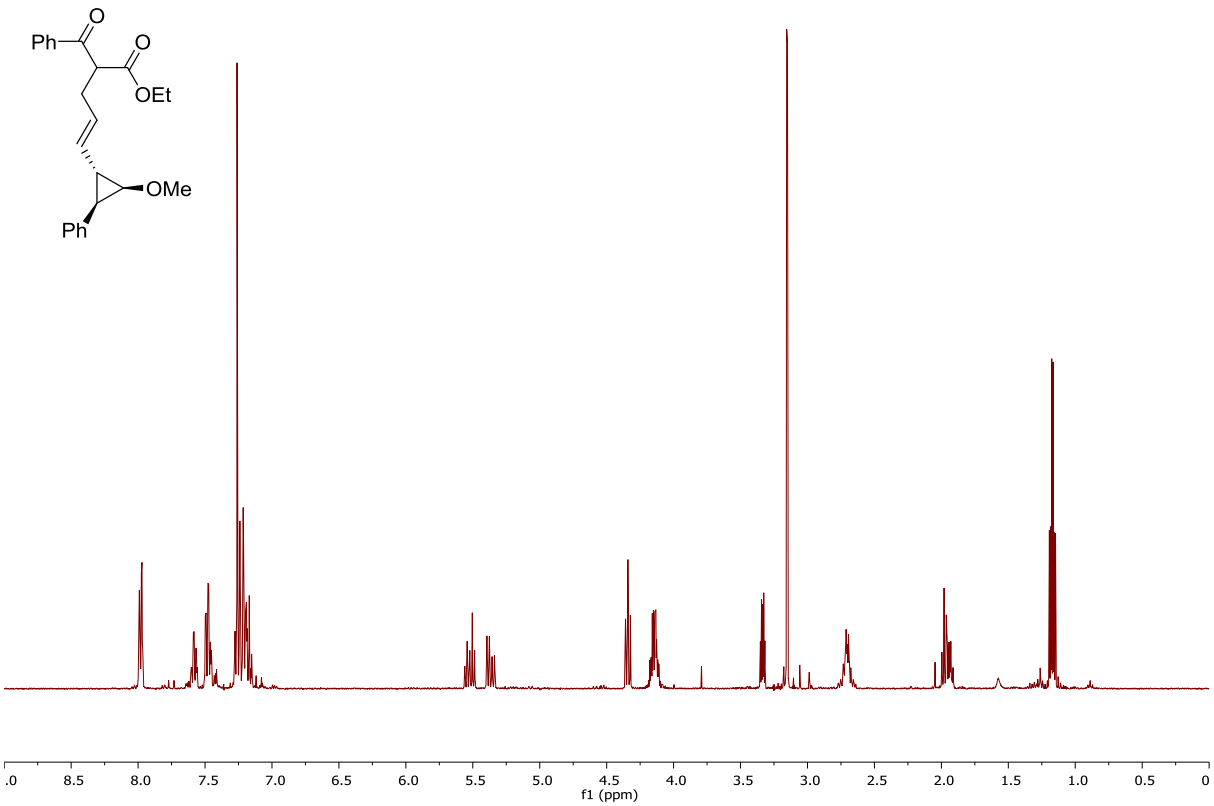

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

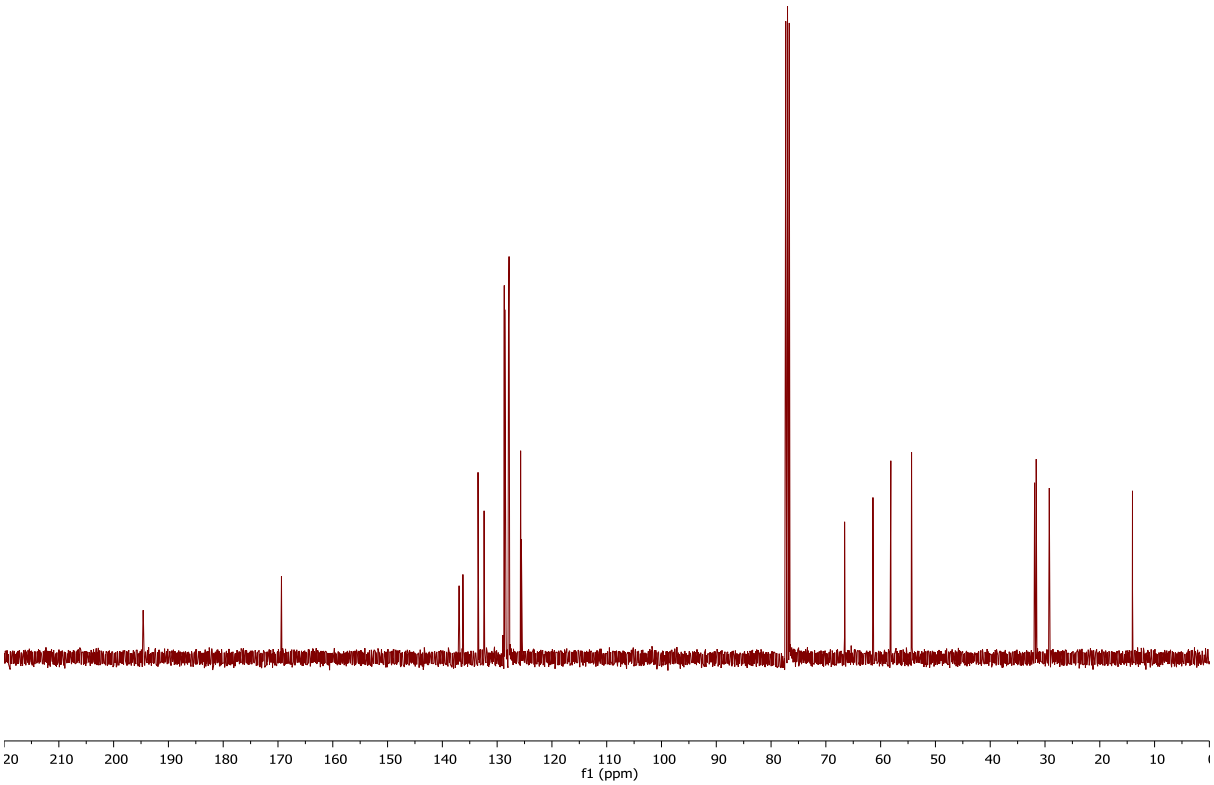

OH
OMe
Ph
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

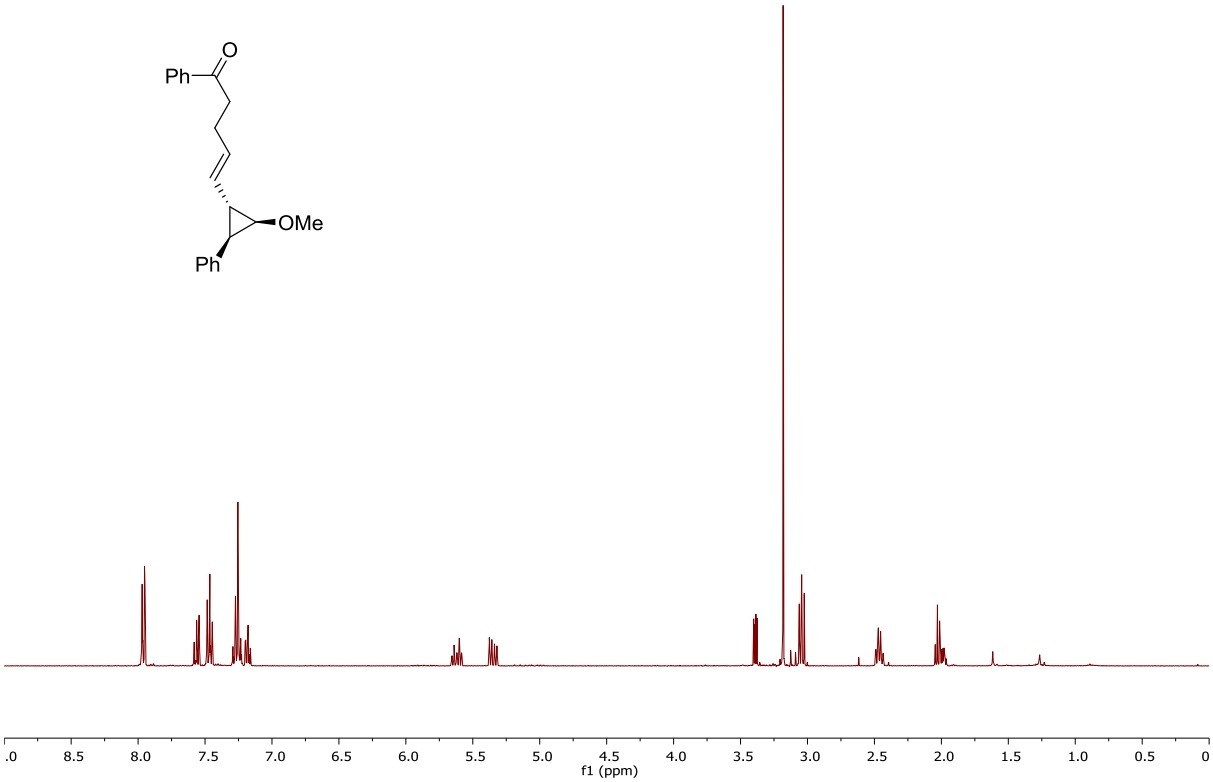

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

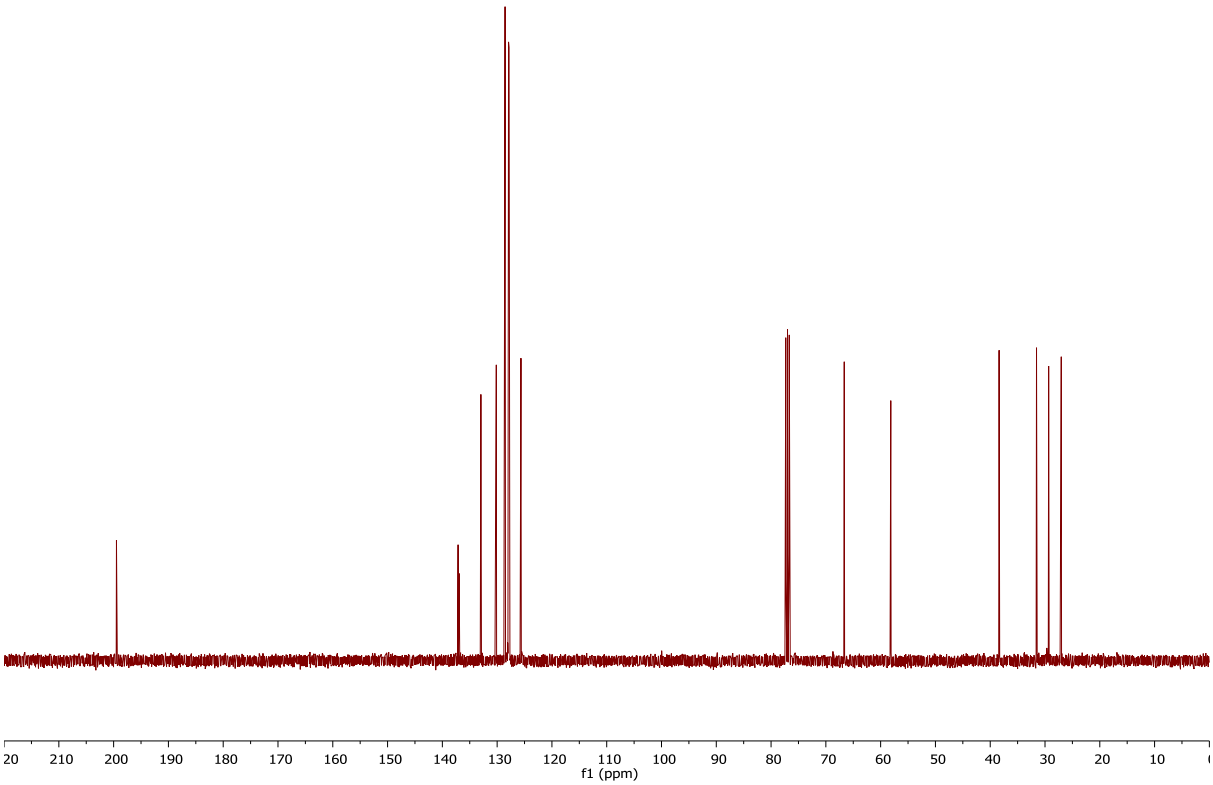

OMe
O
O
OMe
Ph
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

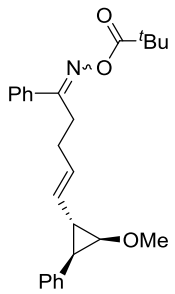

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


O
Ph
O
OEt
OMe
Ph
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

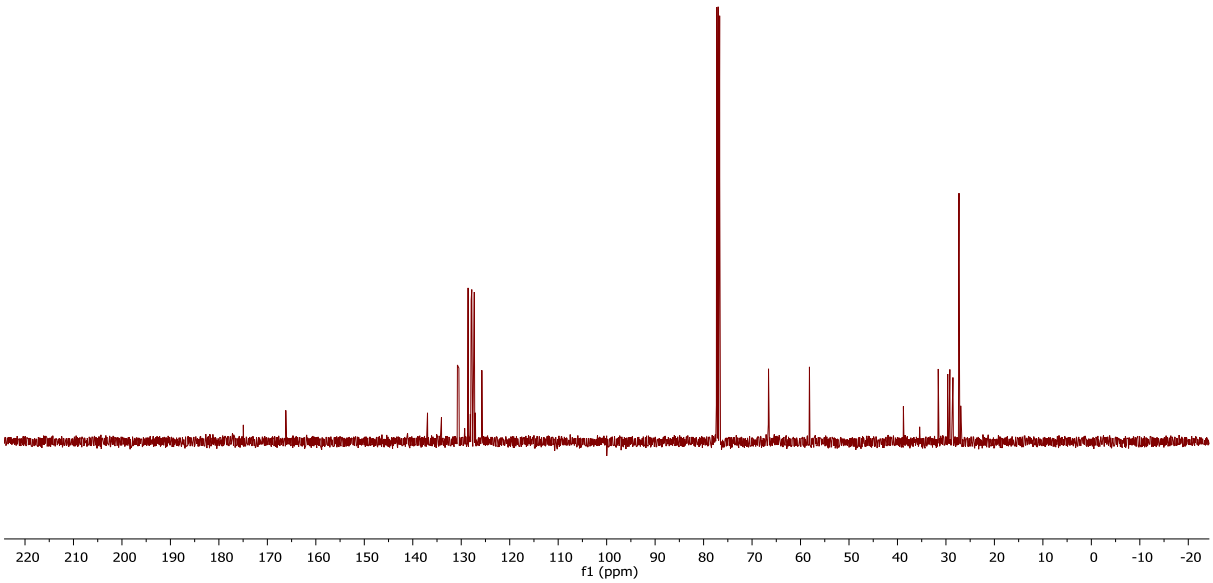

O
Ph
OMe
Ph
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

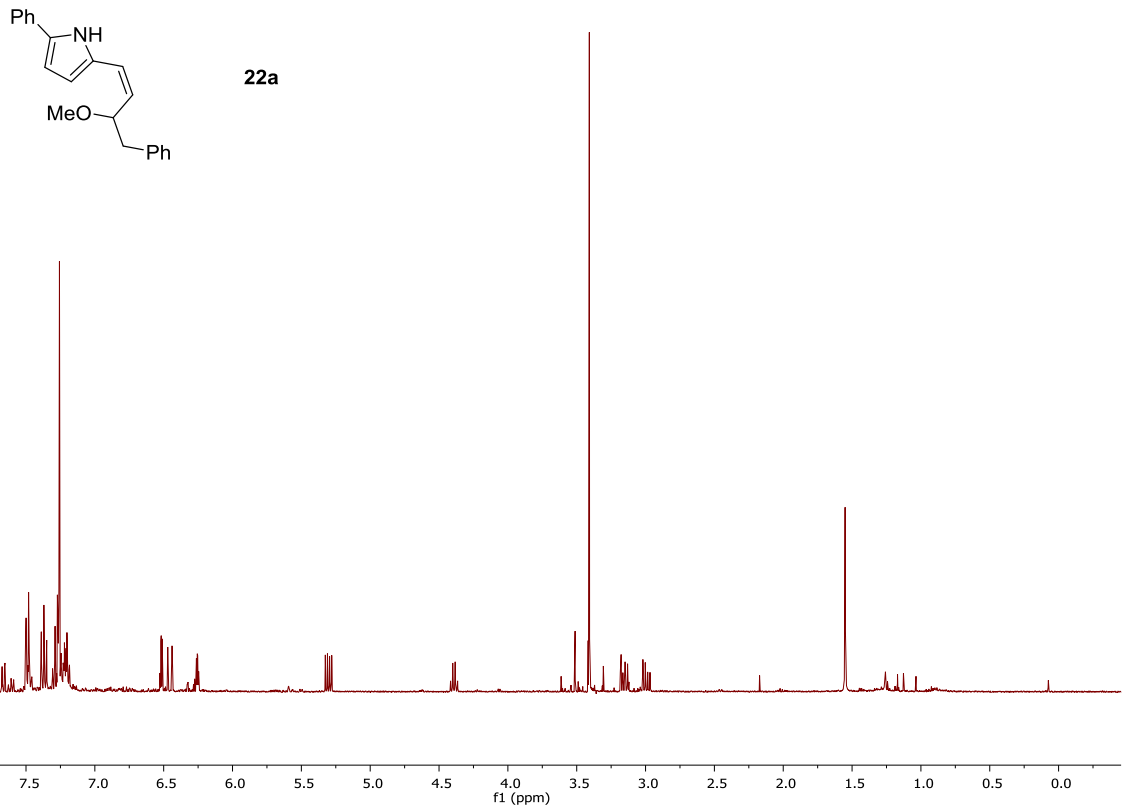

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

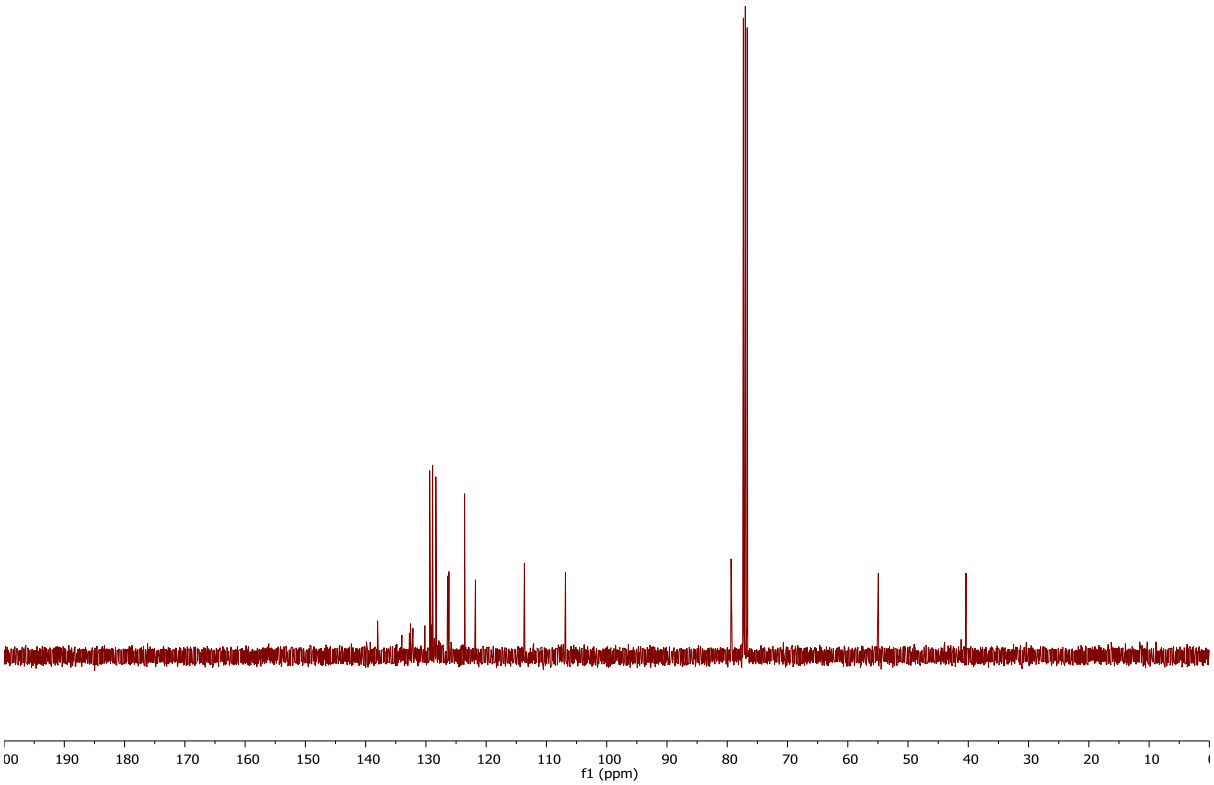

O
tBu
N
O
Ph
OMe
Ph

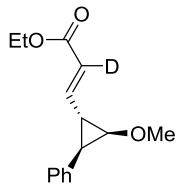
21a

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

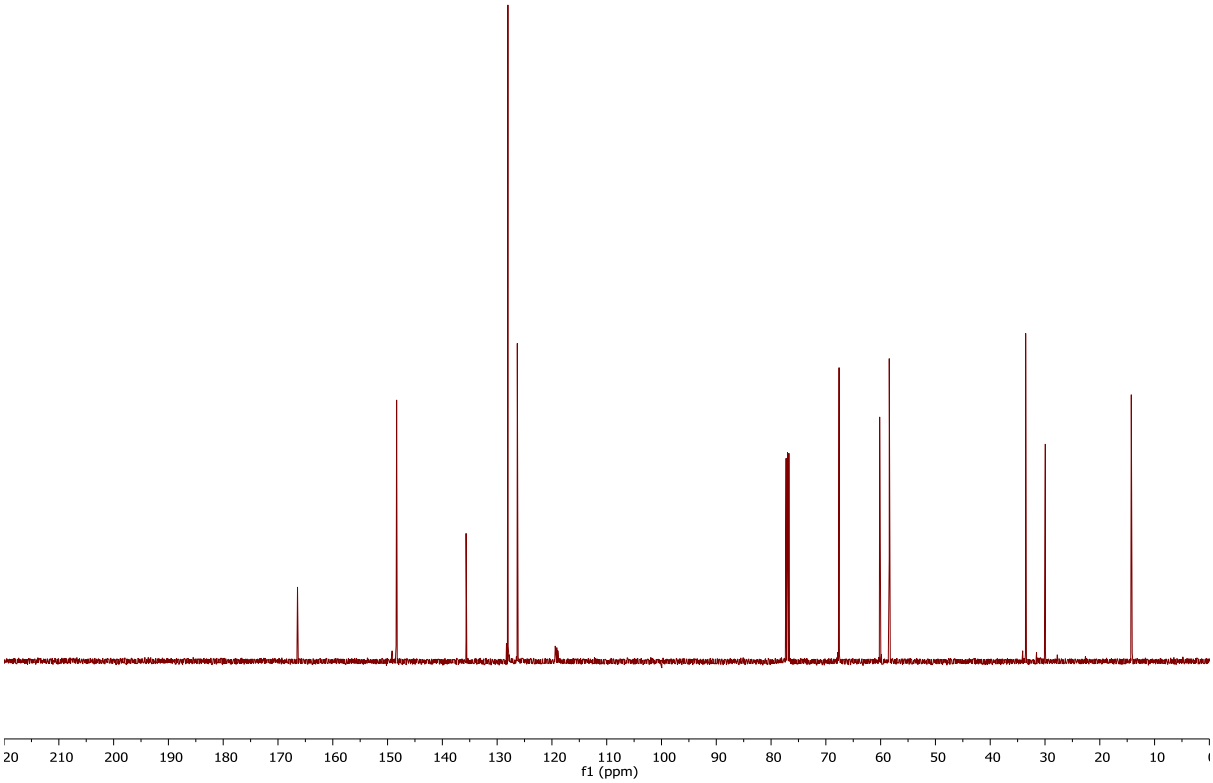

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

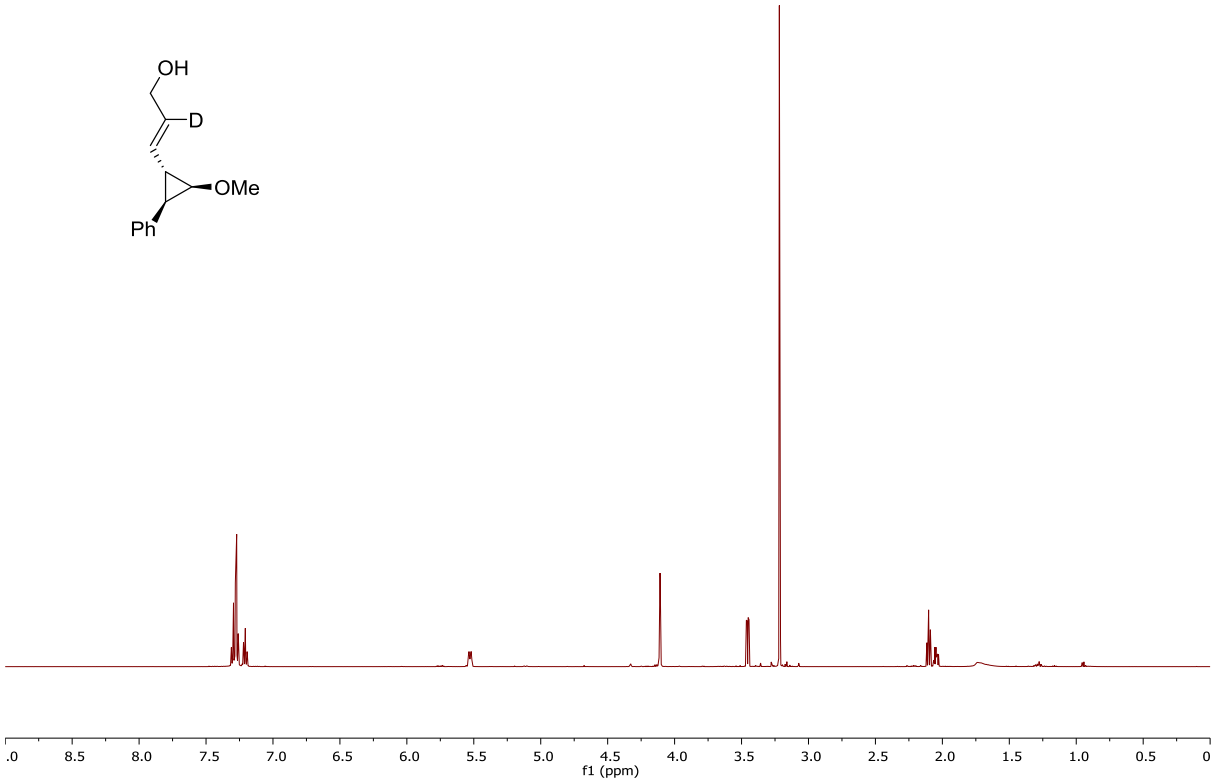

Ph
NH
MeO
Ph
22a
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

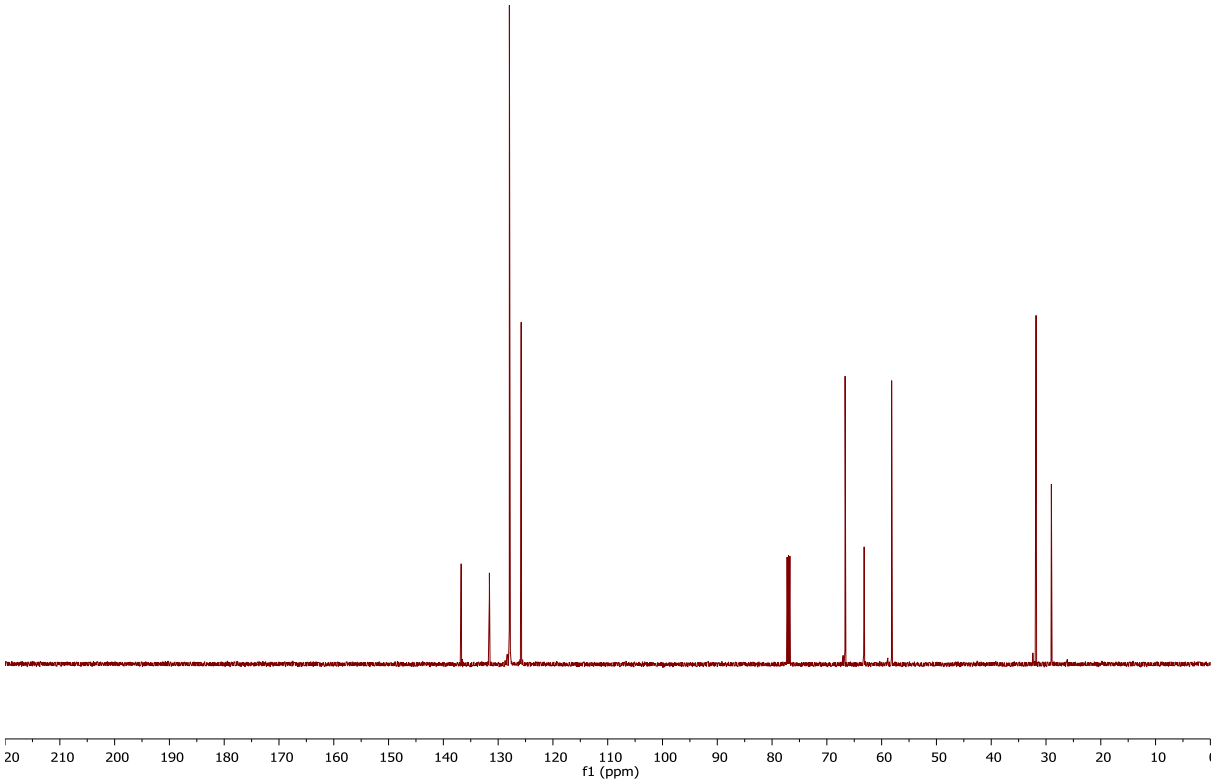

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

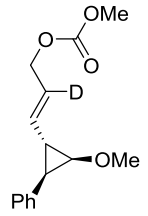

O
EtO
D
OMe
Ph

.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

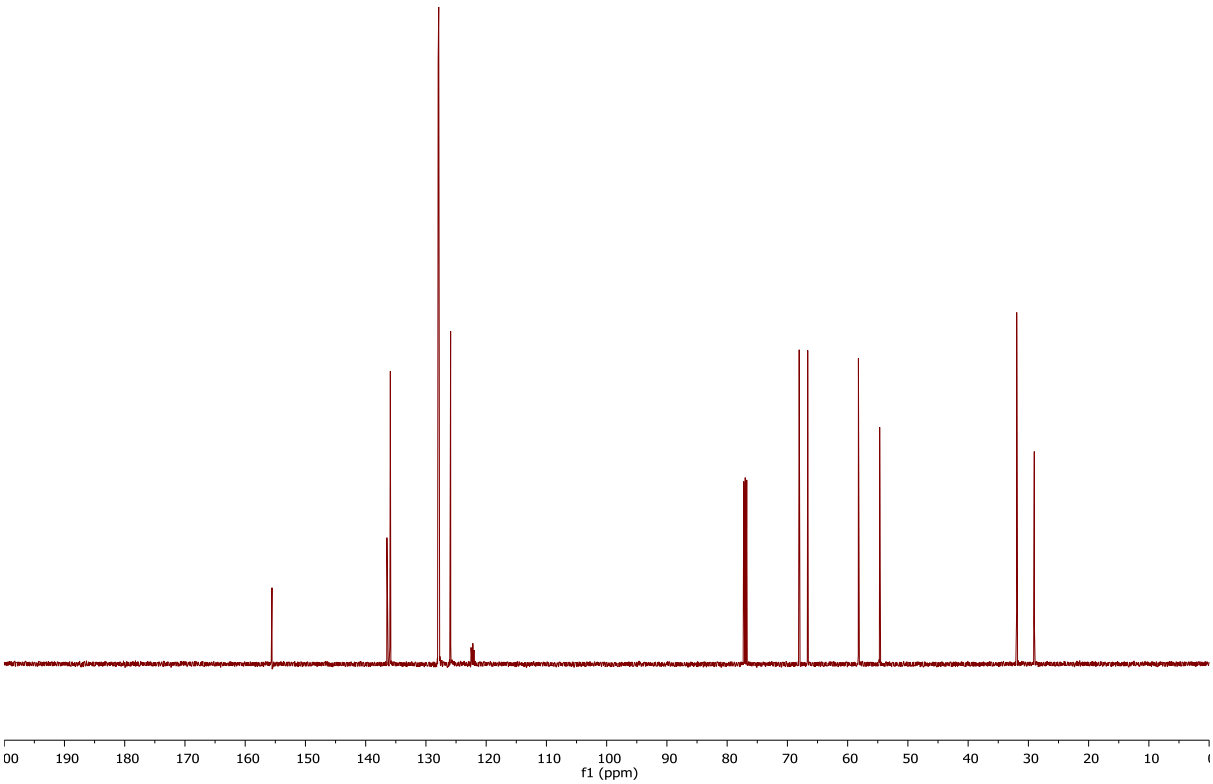

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

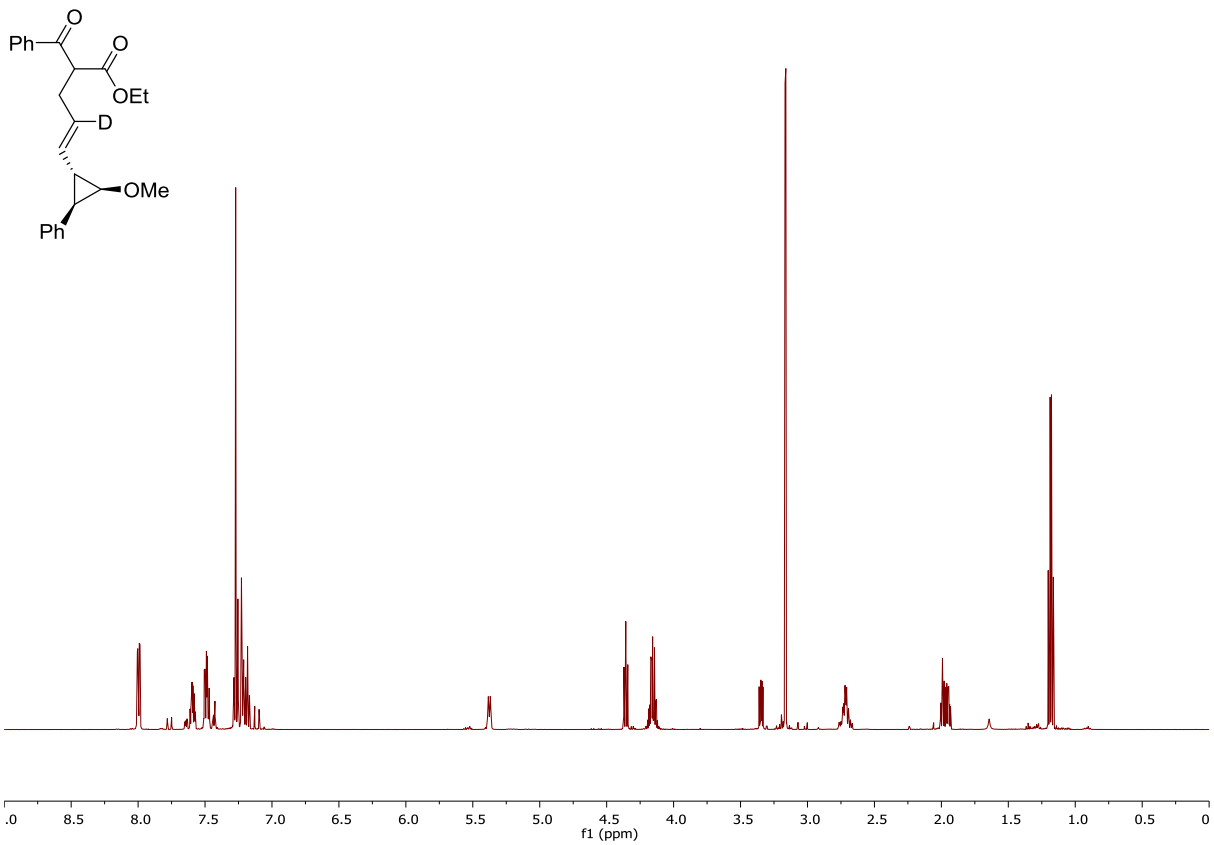

OH
D
OMe
Ph
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

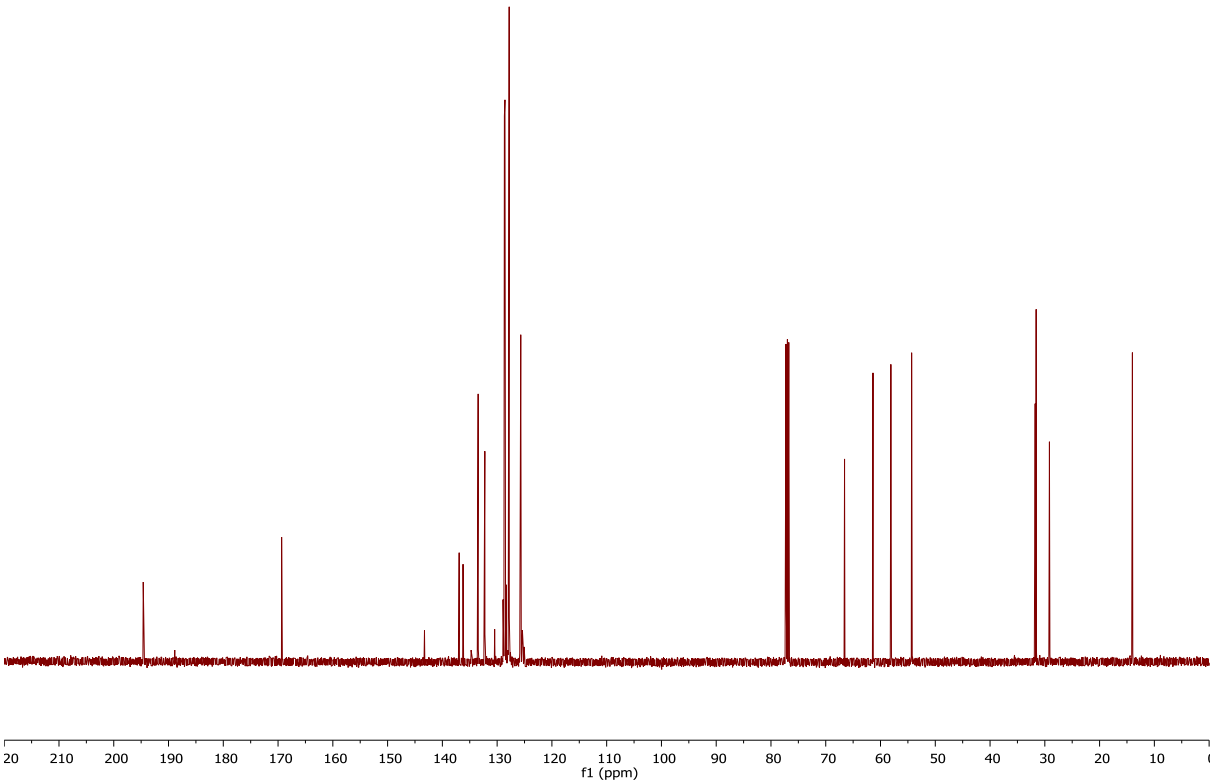

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

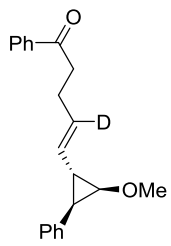

OMe
O
O
D
OMe
Ph

.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

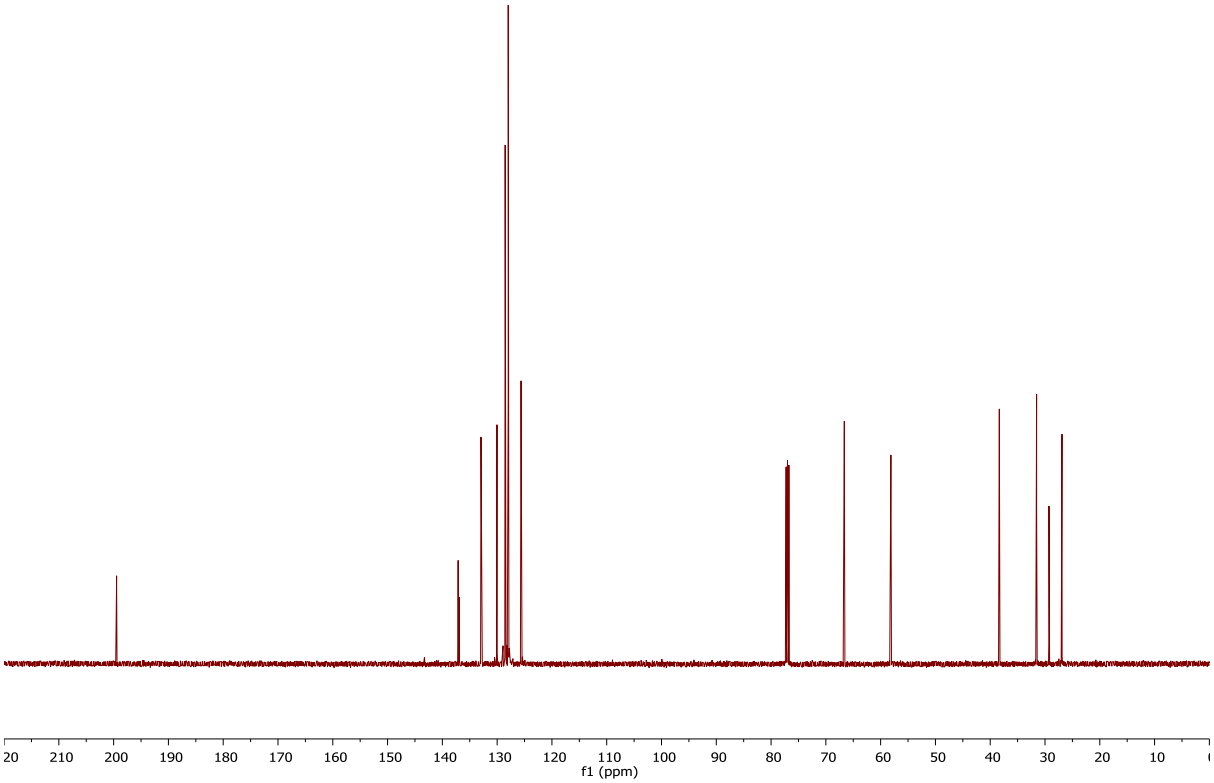

00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

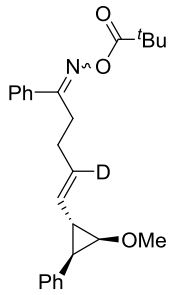

Ph
O
O
OEt
D
OMe
Ph
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


O
Ph
D
OMe
Ph

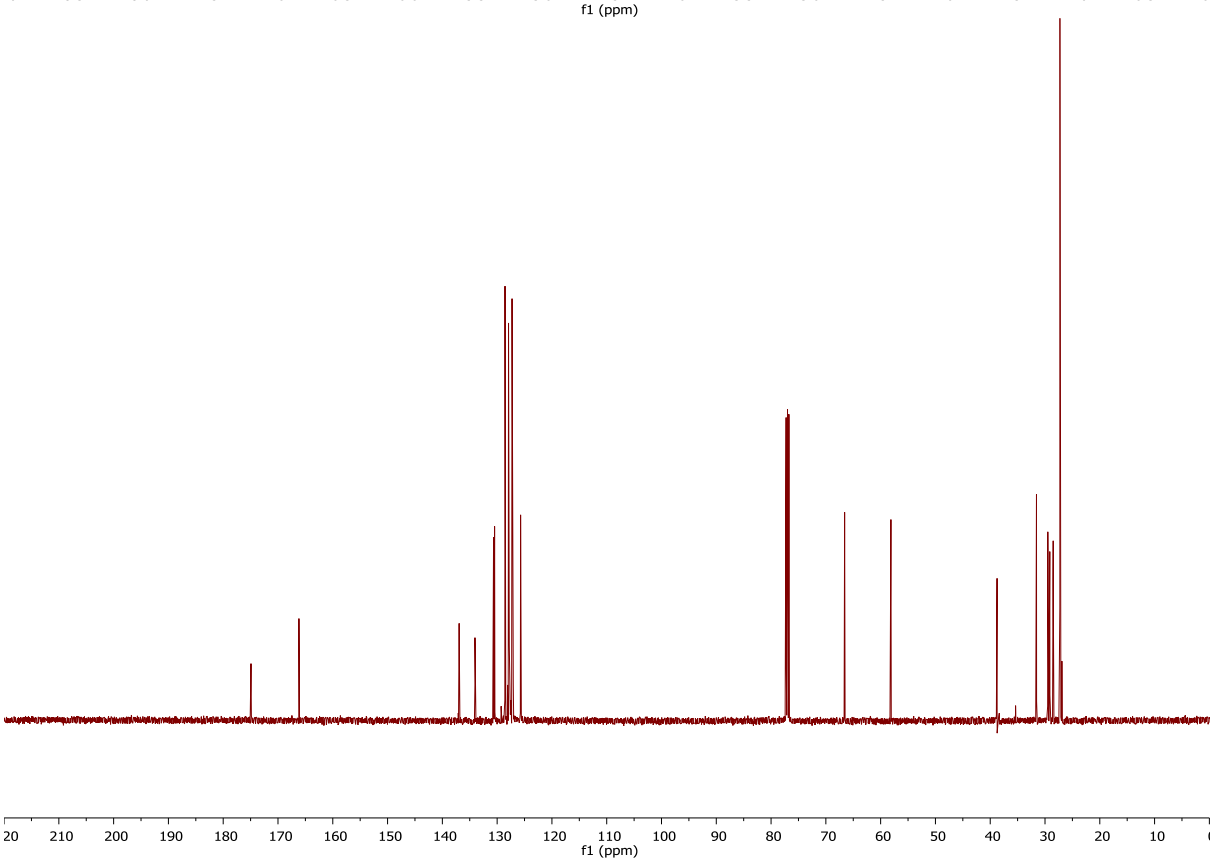
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

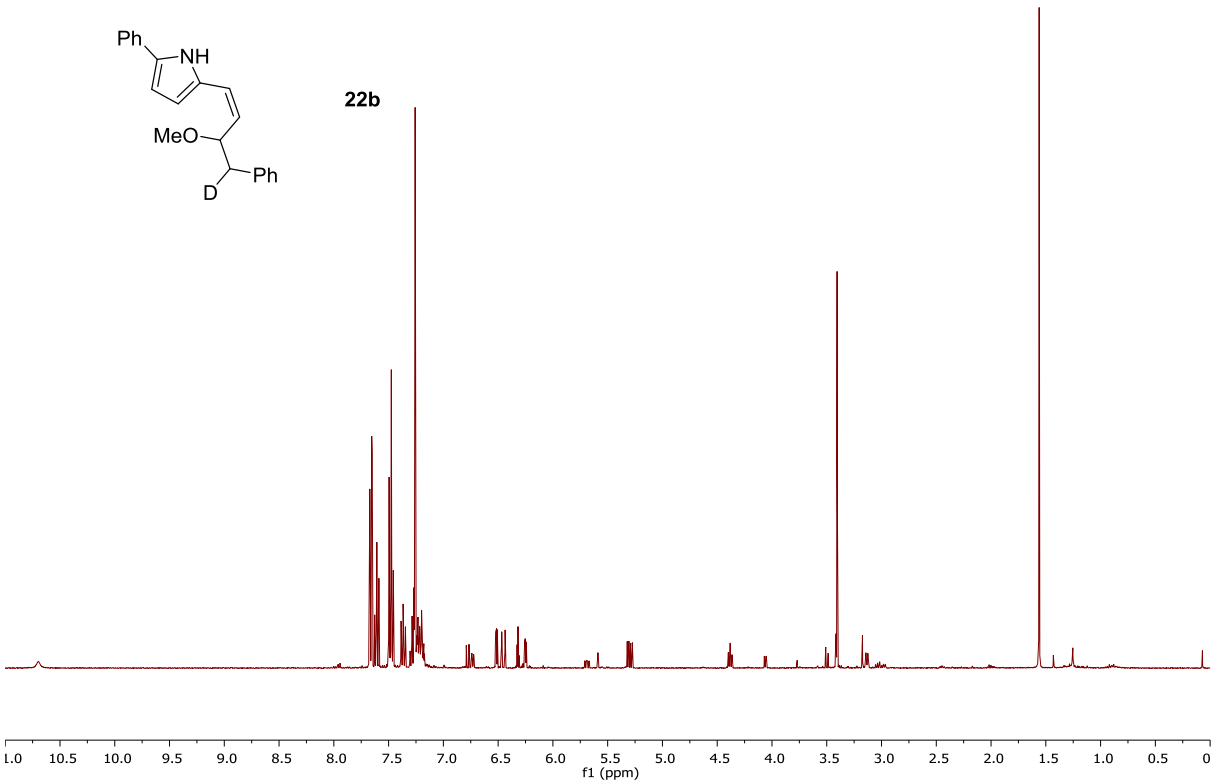

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

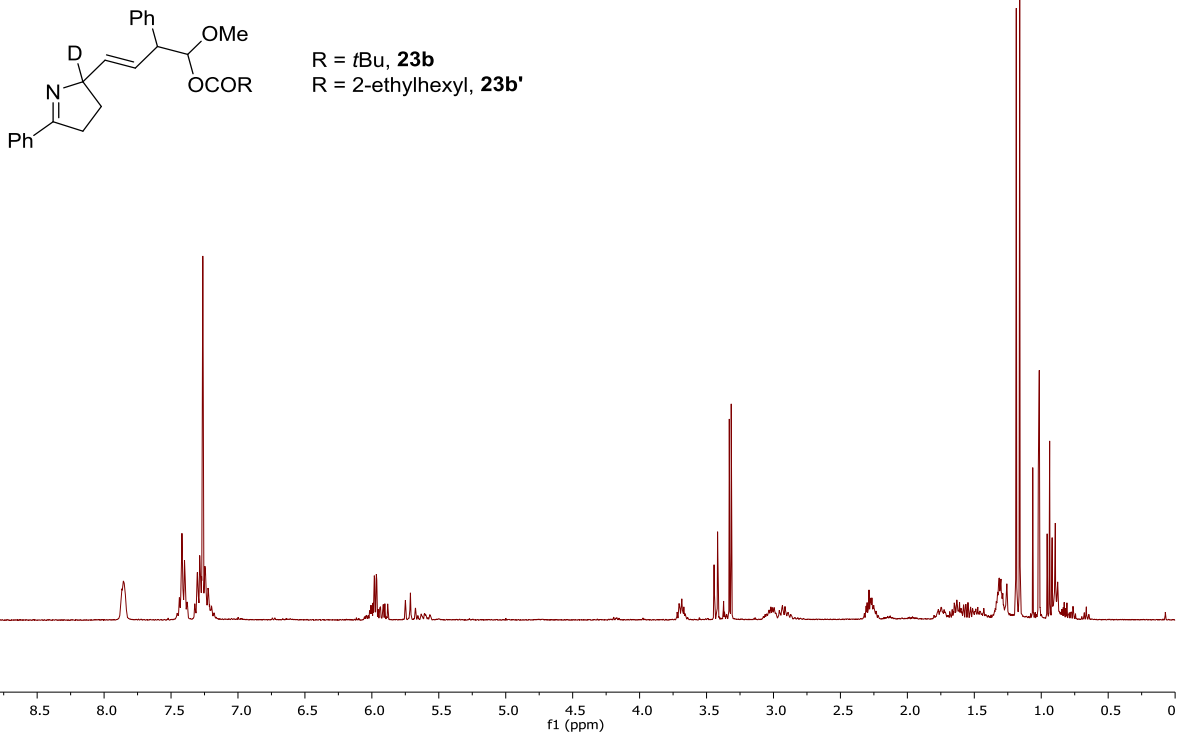

O
tBu
N
O
Ph
D
OMe
Ph

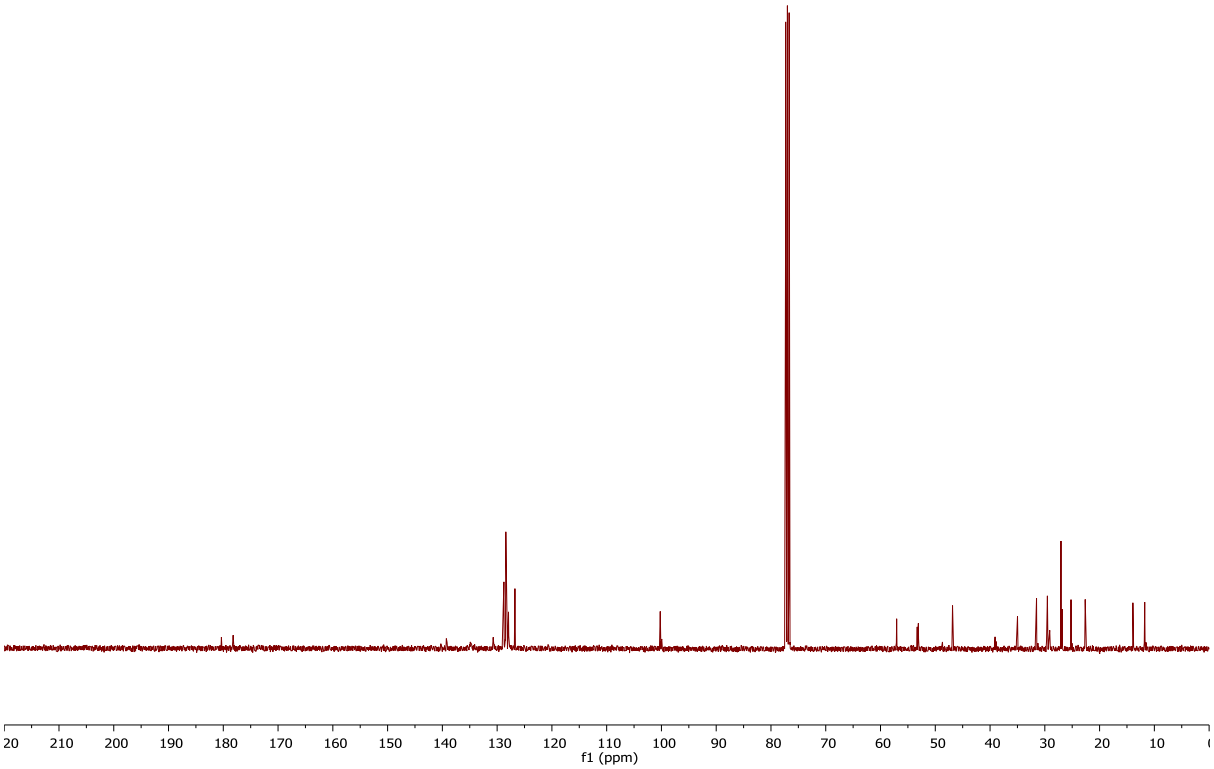
21b

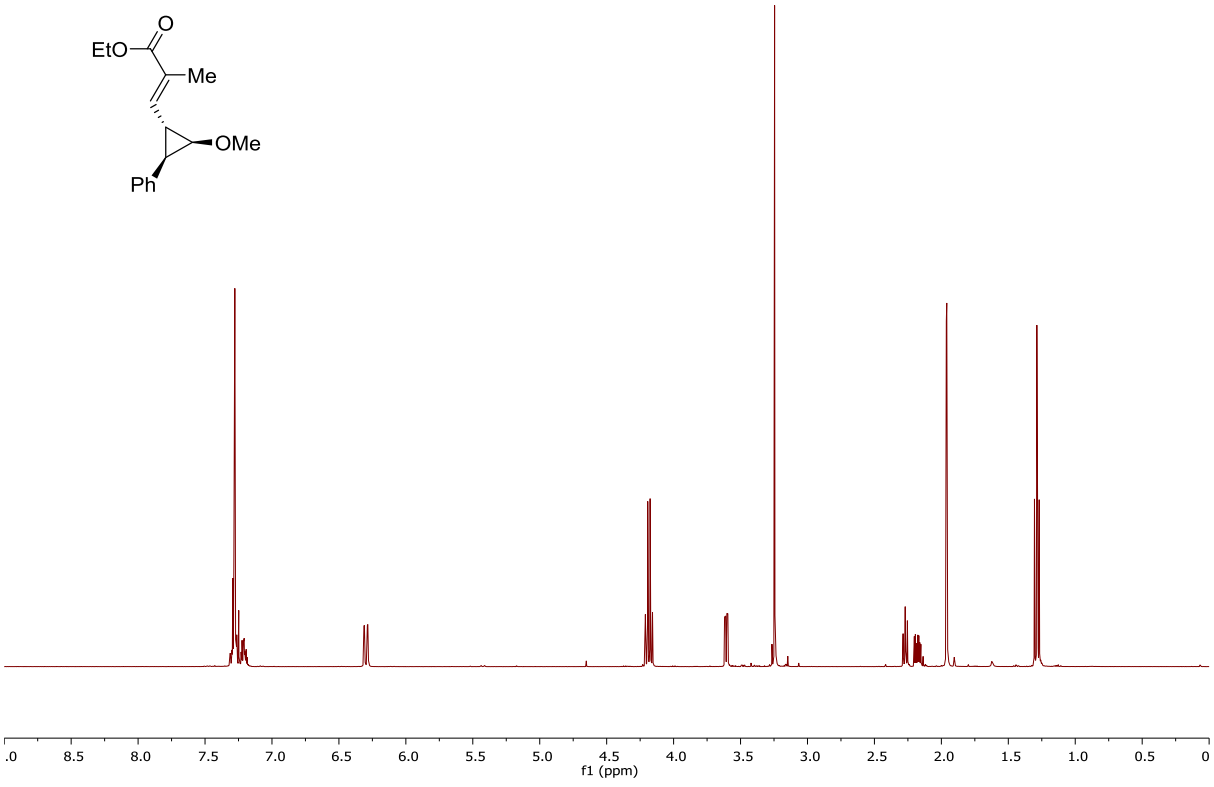
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

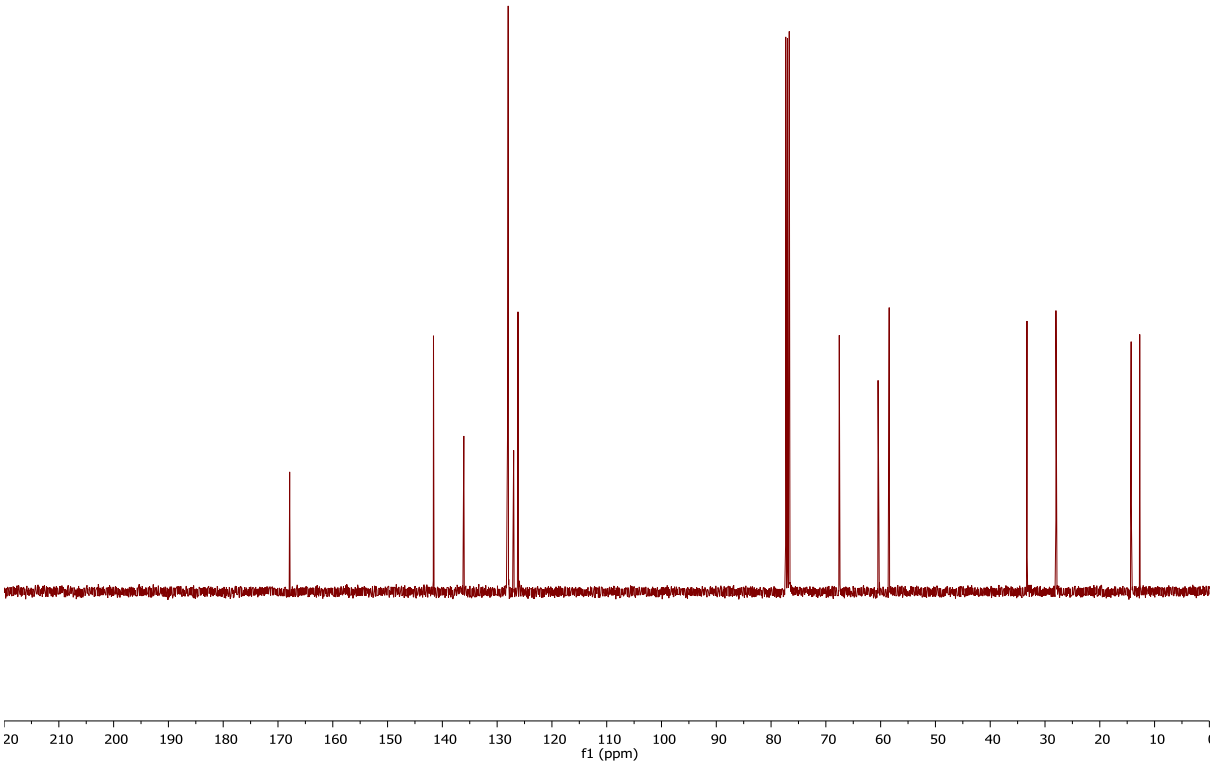

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

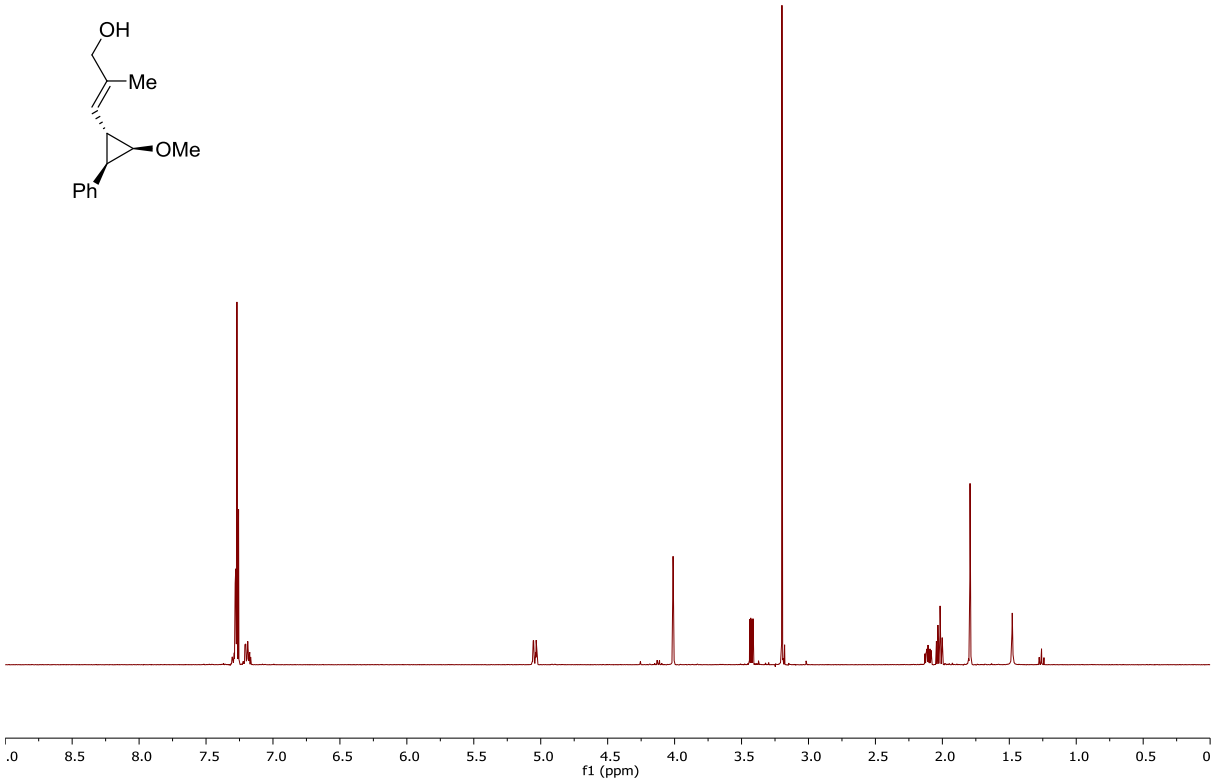

Ph
NH
MeO
D
Ph
22b
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

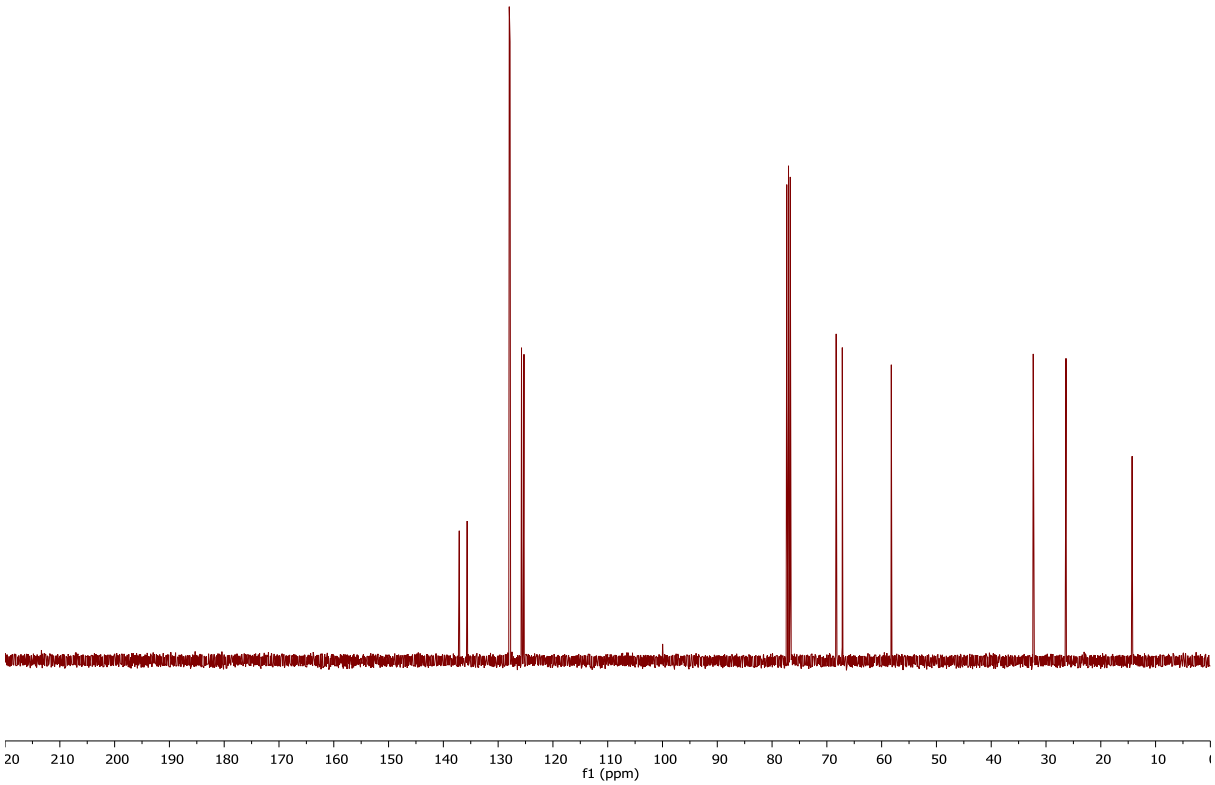

Ph
OMe
D
N
OCOR
Ph
R = tBu, 23b
R = 2-ethylhexyl, 23b'
f1 (ppm)

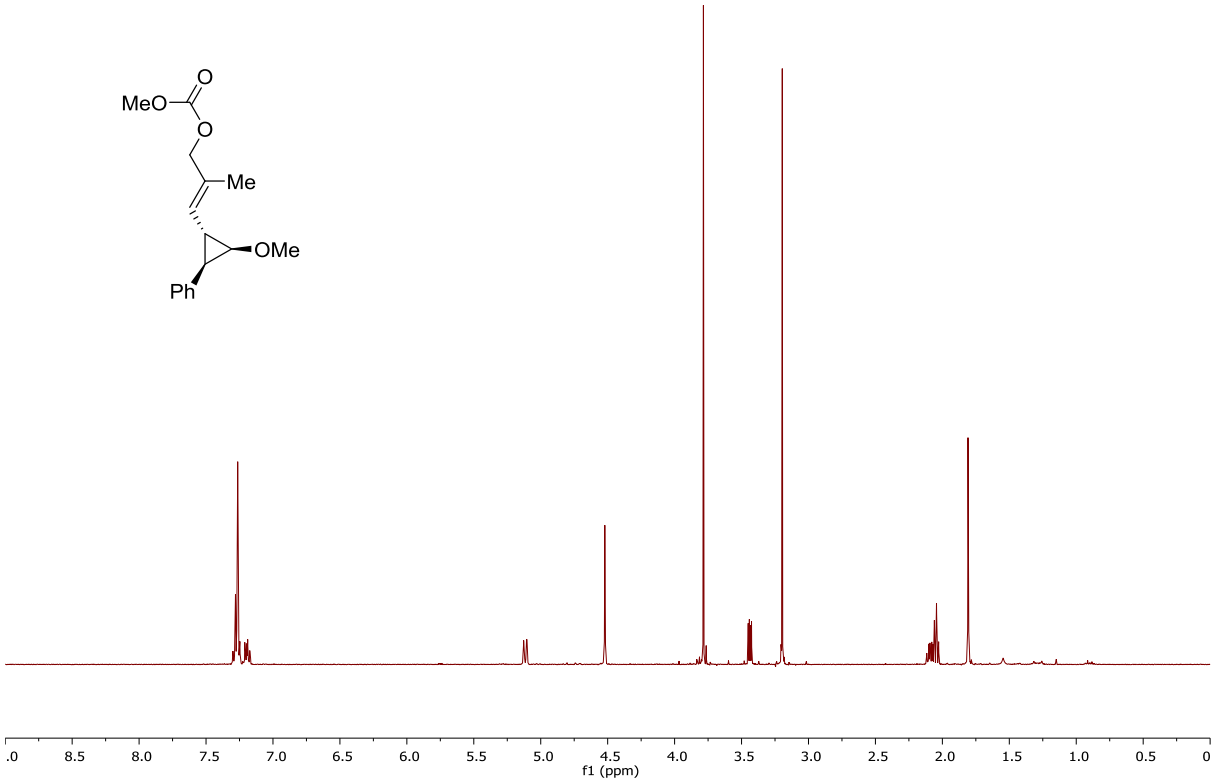

f1 (ppm)

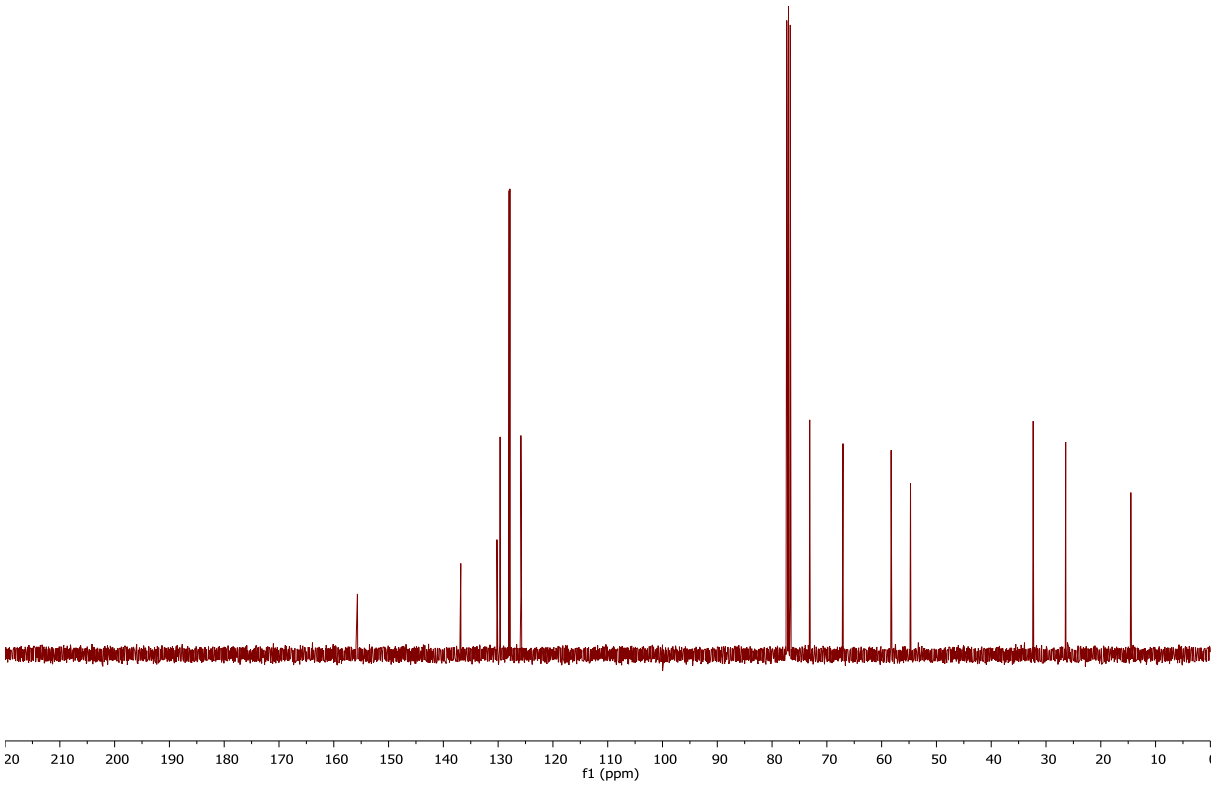

EtO
O
Me
OMe
Ph
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

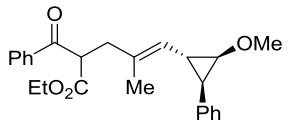

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


OH
Me
OMe
Ph
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

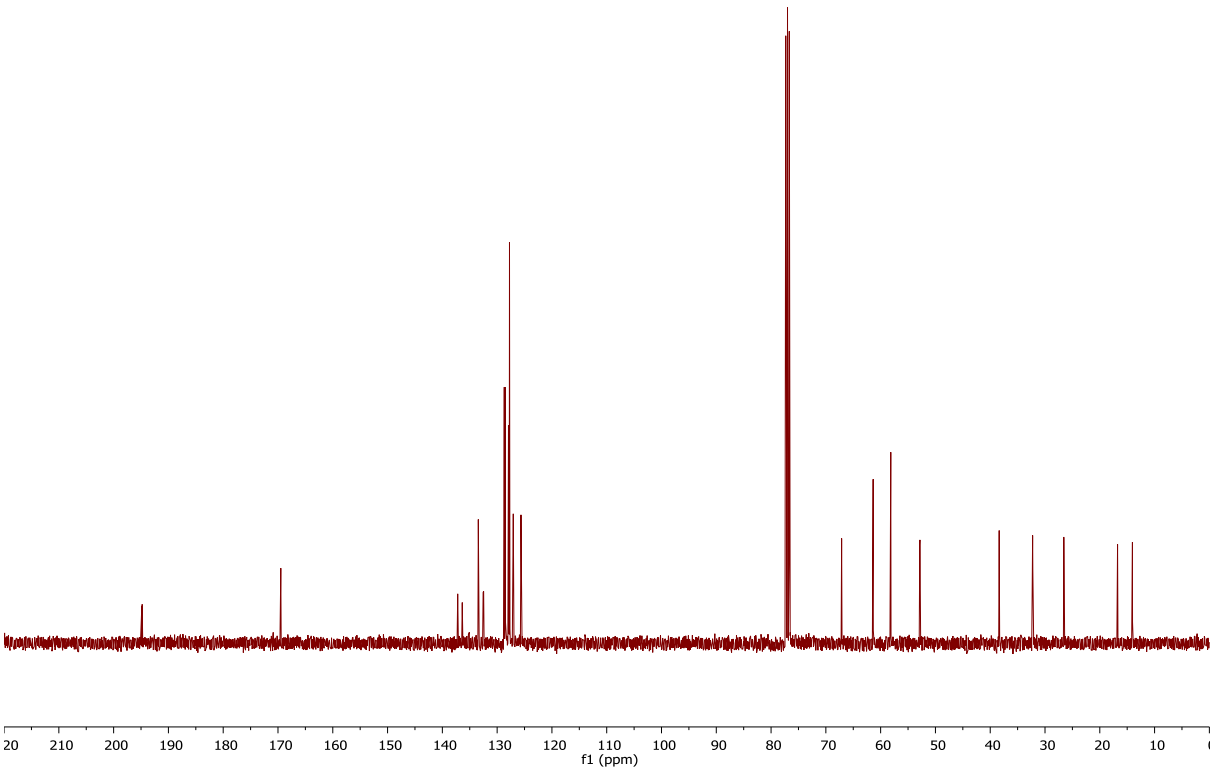

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

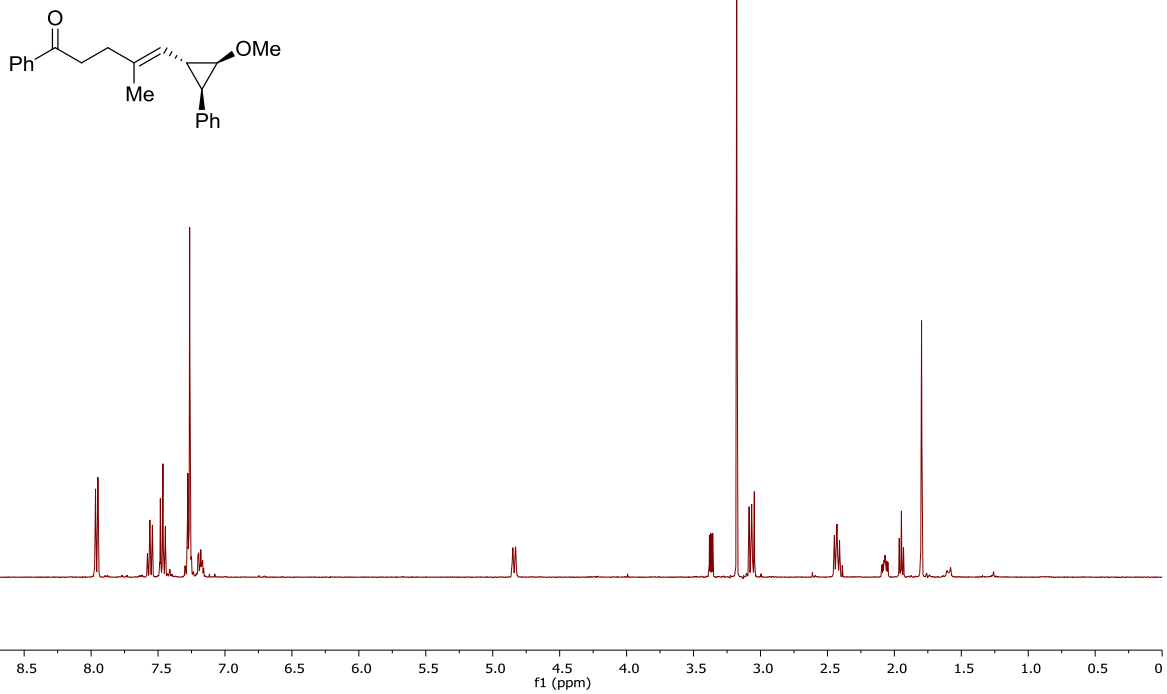

MeO
O
O
Me
OMe
Ph
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

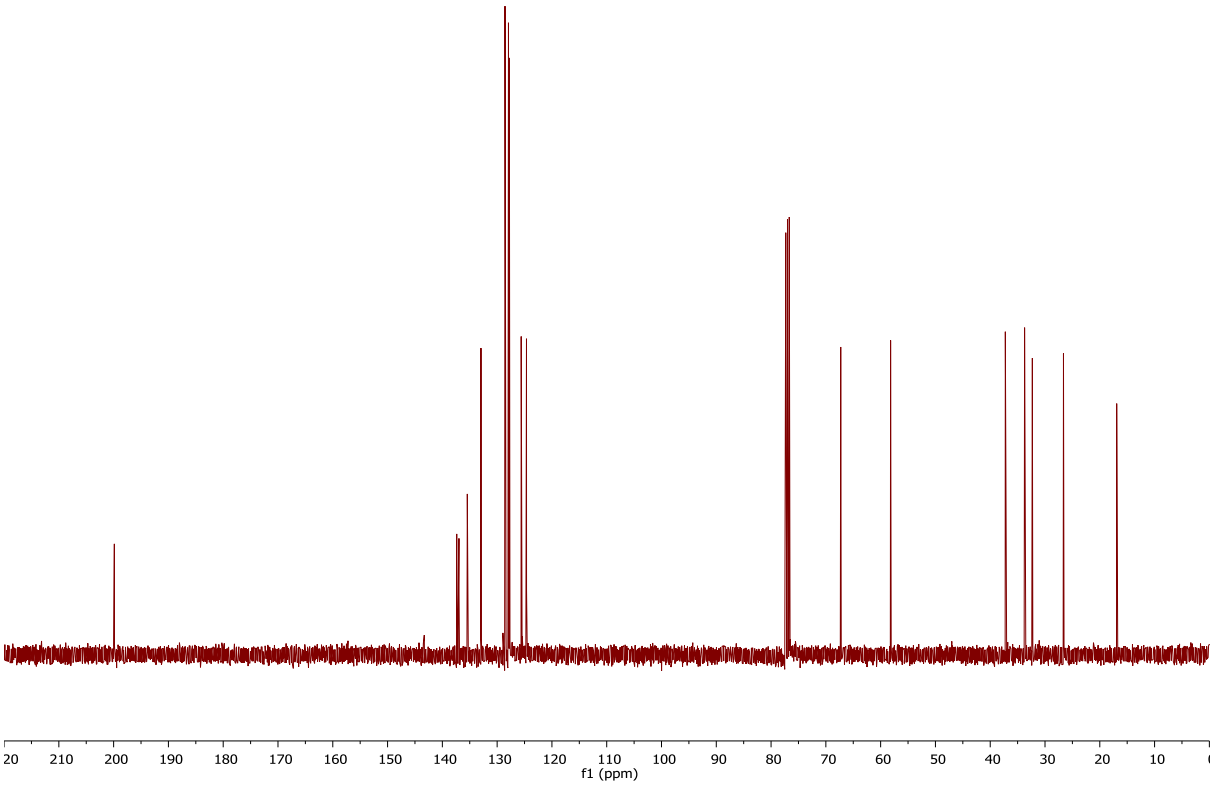

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

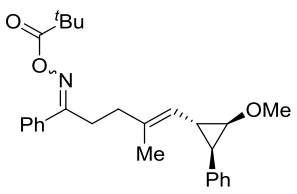

O
Ph
EtO2C
Me
OMe
Ph

.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

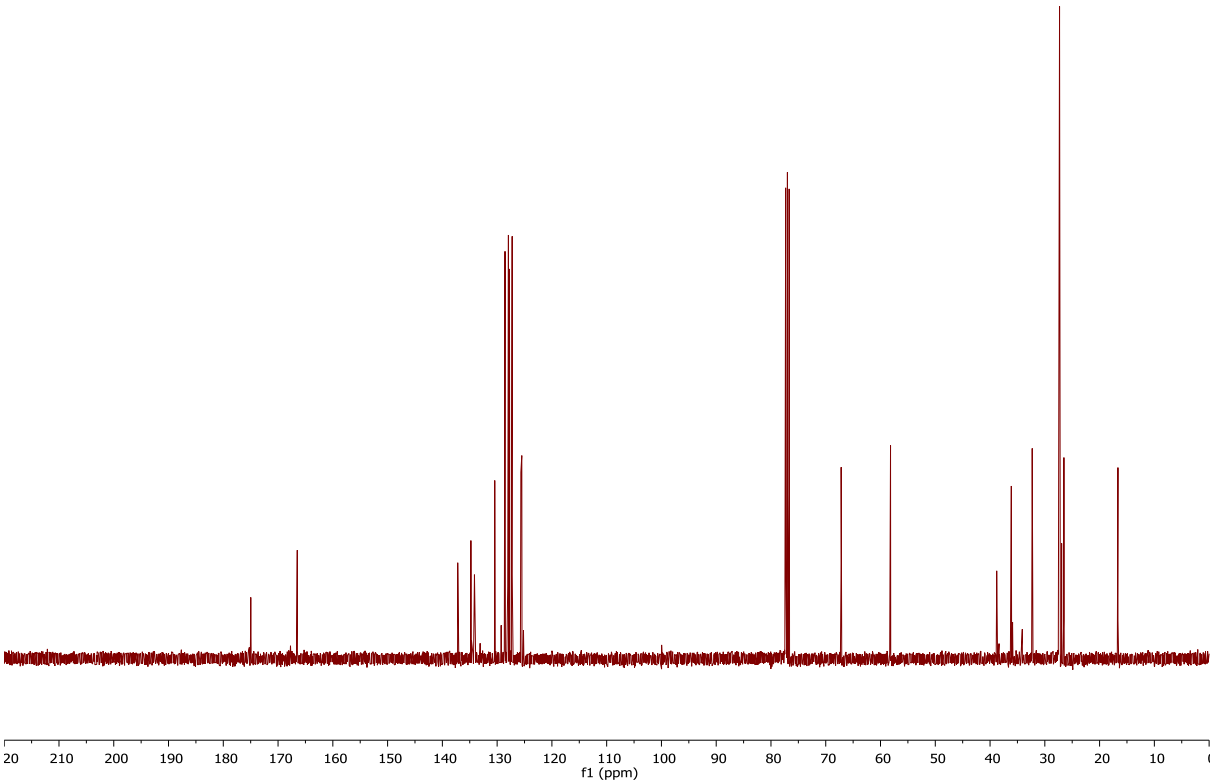

O
Ph
Me
OMe
Ph
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

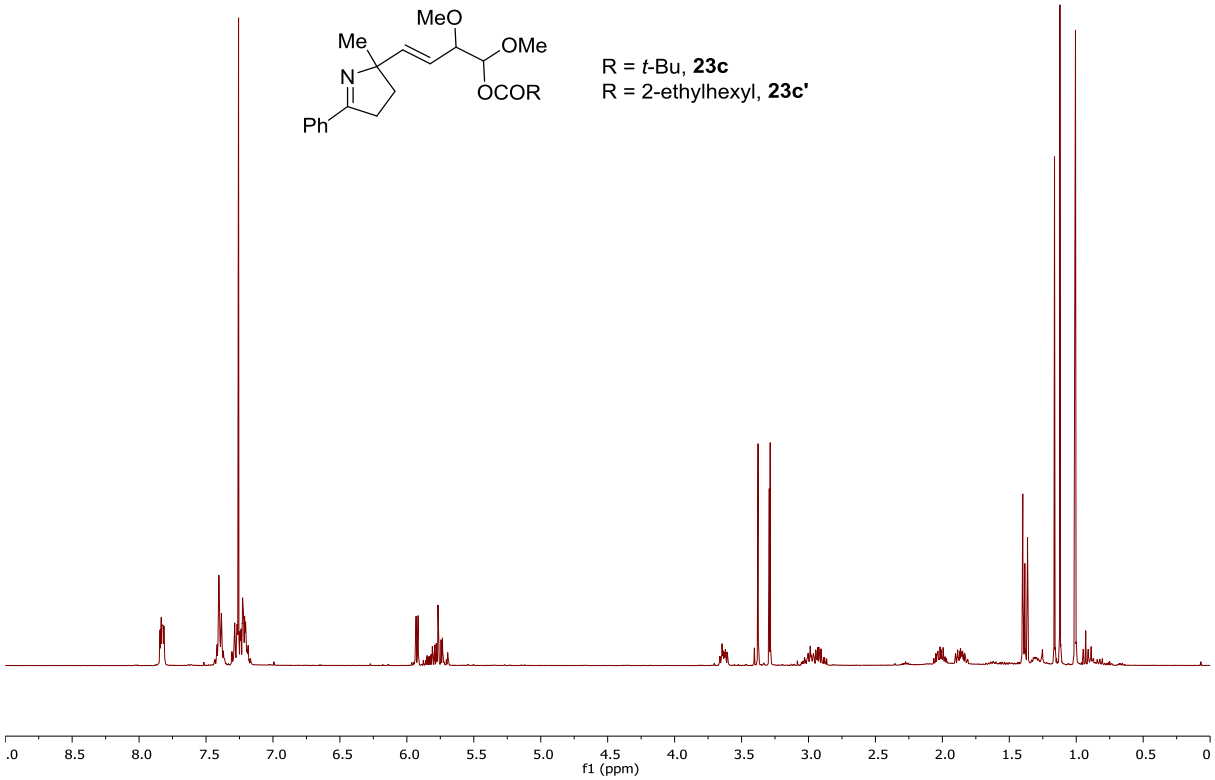

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

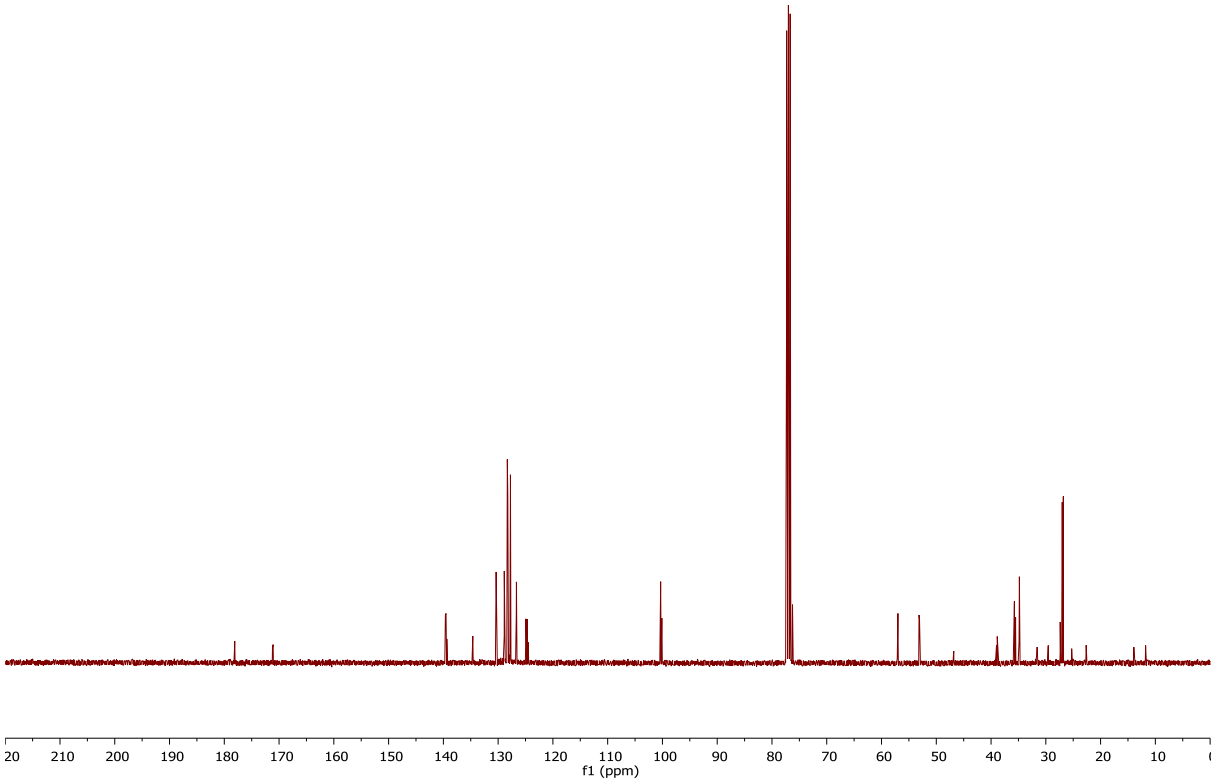

O
tBu
O
N
Ph
Me
OMe
Ph

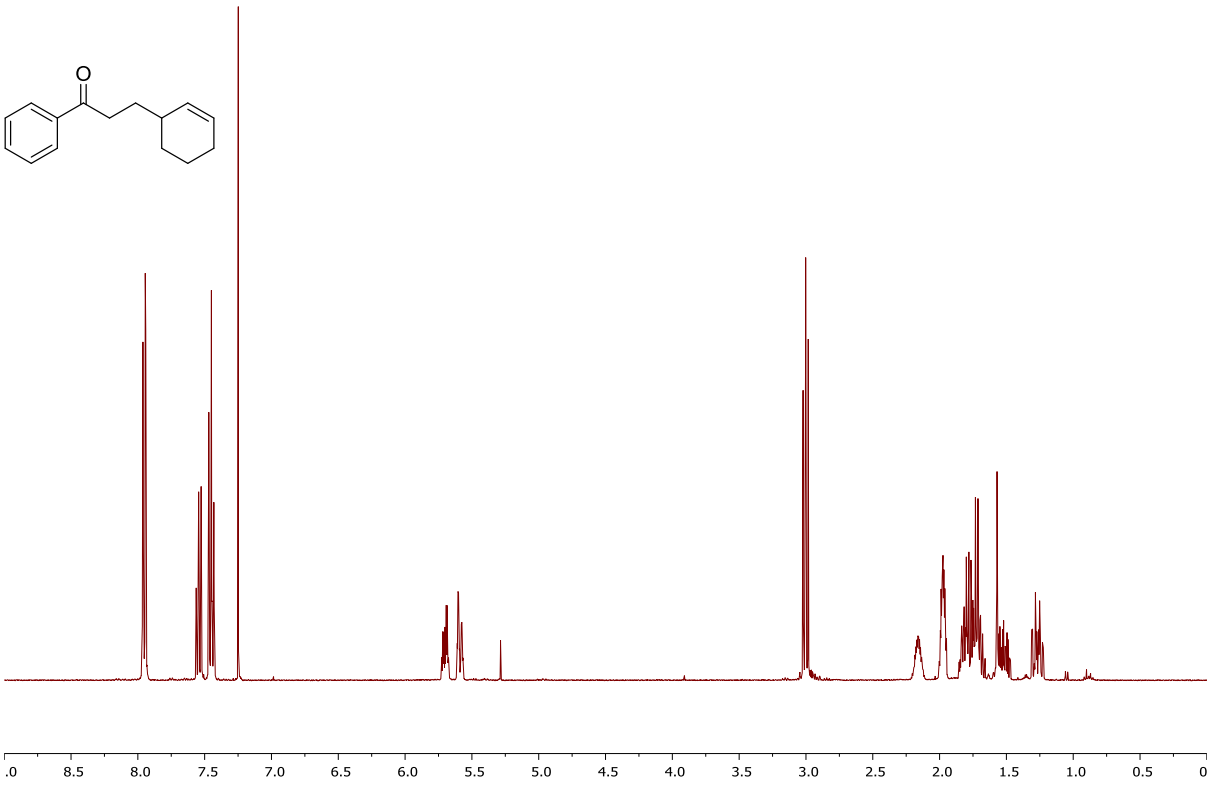
21c

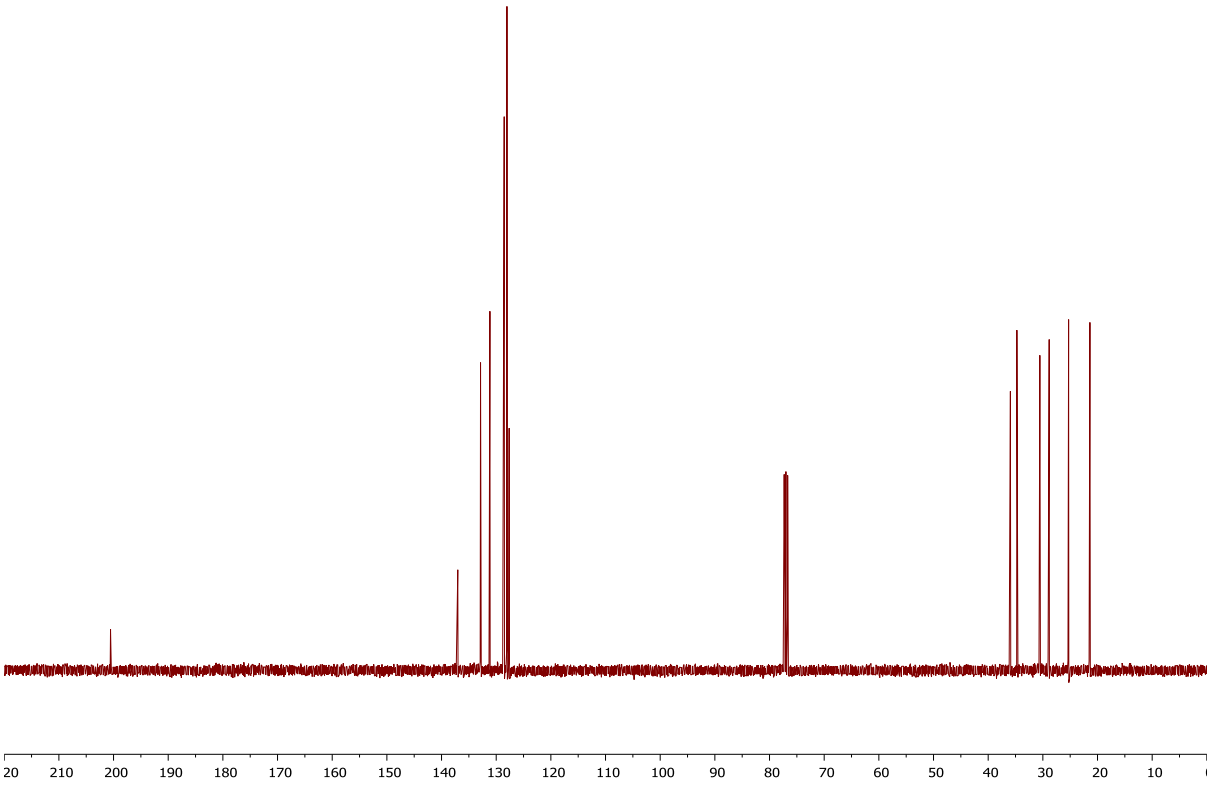
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

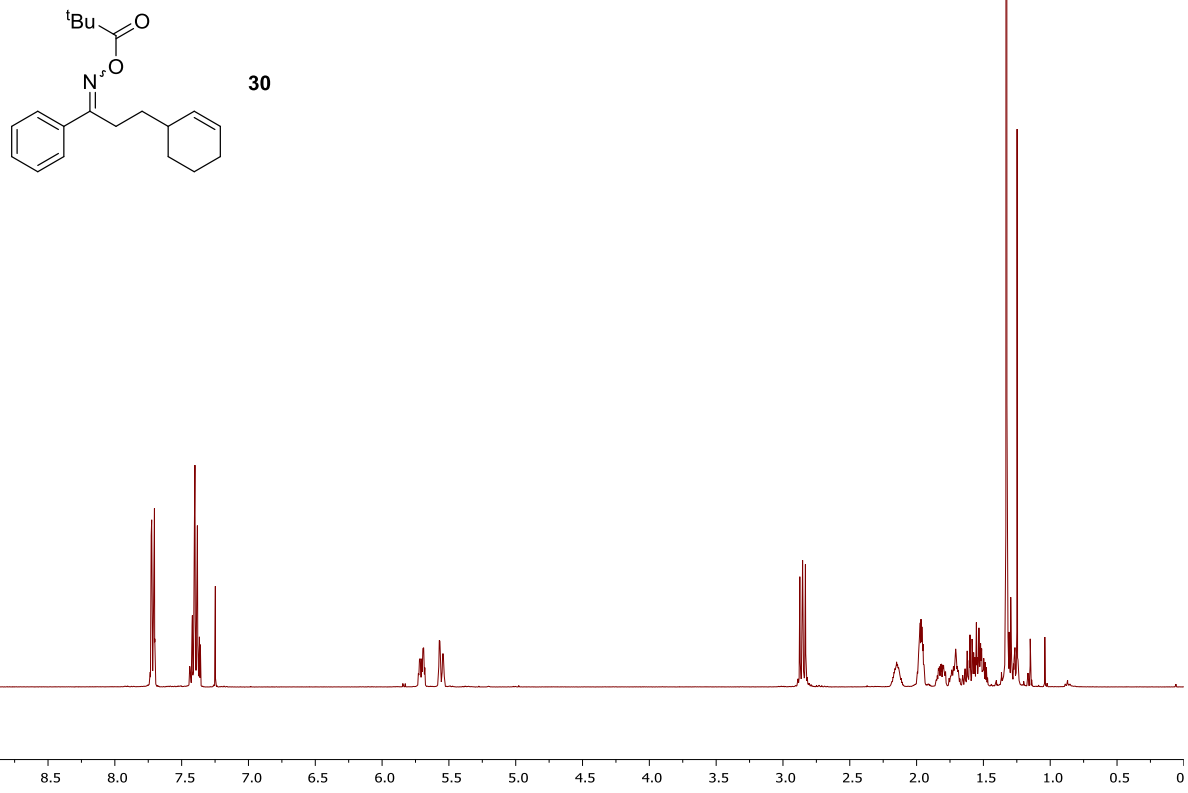

20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


MeO
Me
OMe
N
OCOR
Ph
R = t-Bu, 23c
R = 2-ethylhexyl, 23c'
f1 (ppm)


f1 (ppm)

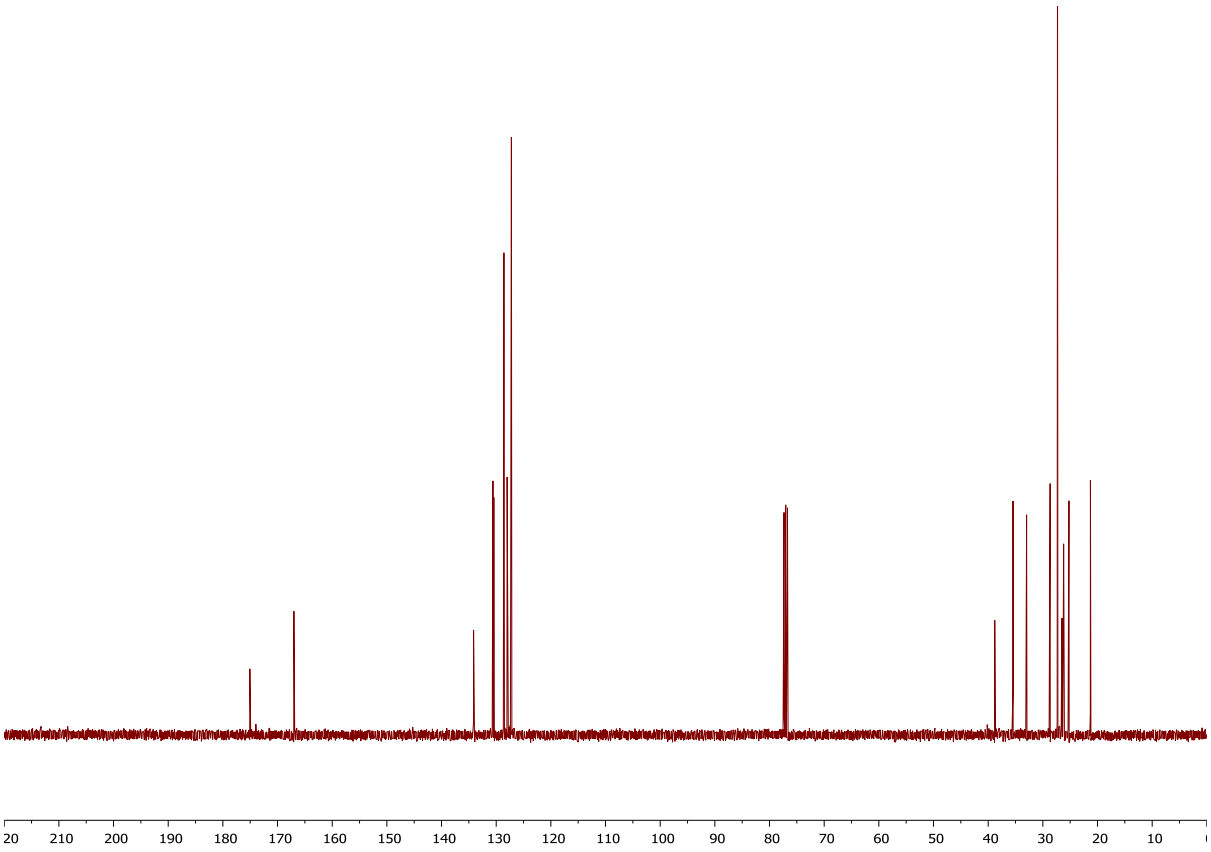

O
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0

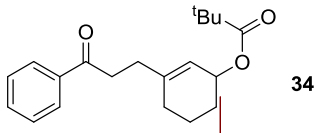

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


tBu
O
O
N
O

30

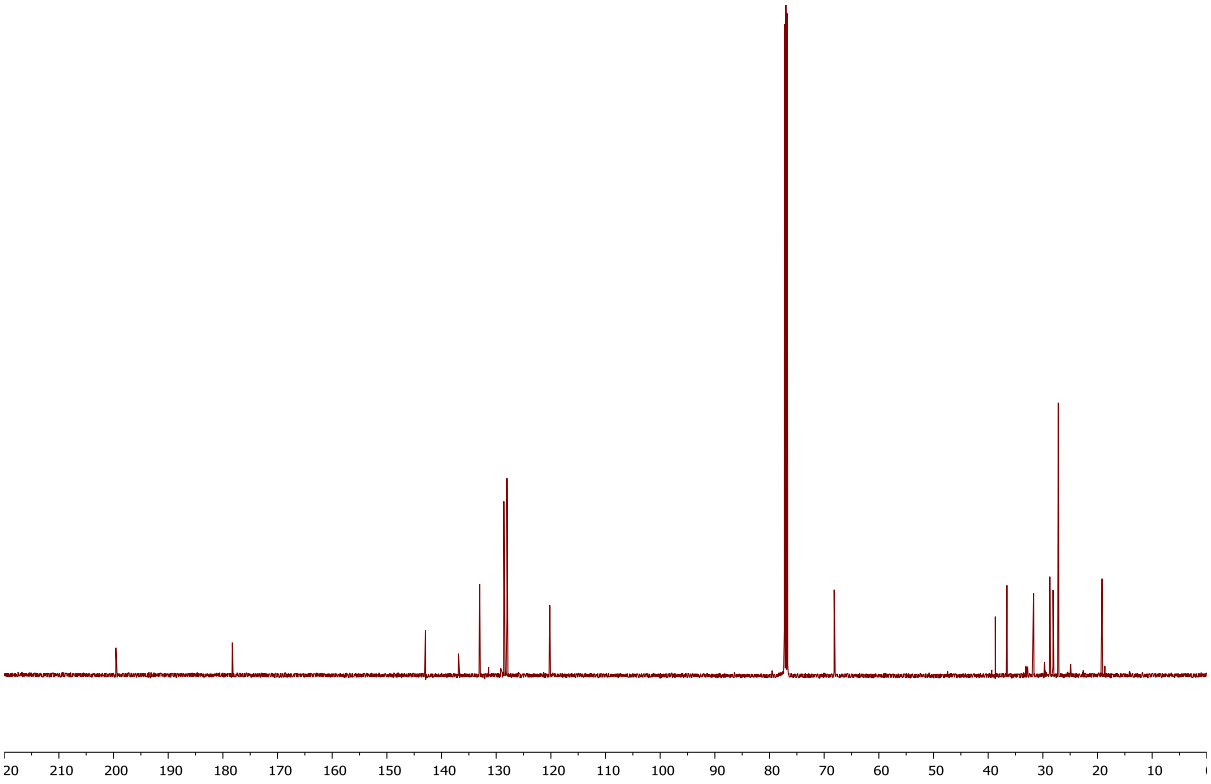
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


tBu
O
O
O

34

.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0


20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10