

Enantioselective Conia-Ene-Type Cyclizations of Alkynyl Ketones through Cooperative Action of $B(C_6F_5)_3$, *N*-Alkylamine and a Zn-Based Catalyst

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1. Procedures, Materials and Instrumentation

1.1 General Experimental Procedures

All reactions were performed in standard, oven-dried glassware fitted with rubber septa under an inert atmosphere of nitrogen unless otherwise described. Stainless steel syringes or cannulas were used to transfer air- and moisture-sensitive liquids. Reported concentrations refer to solution volumes at room temperature. Evaporation and concentration *in vacuo* were performed using house vacuum (ca. 40 mm Hg). Column chromatography was performed with SiliaFlash® 60 (40–63 micron) silica gel from Silicycle. Thin layer chromatography (TLC) was used for reaction monitoring and product detection using pre-coated glass plates covered with 0.25 mm silica gel with fluorescent indicator; visualization by UV light ($\lambda_{\text{ex}} = 254 \text{ nm}$) or KMnO_4 stain.

1.2 Materials

Reagents were purchased in reagent grade from commercial suppliers and used without further purification, unless otherwise described. H_2O , in synthetic procedures, refers to distilled water. Chiral ligands **L1-L12** were prepared according to the procedures previously reported in the literature.¹⁻⁴ Substrates **1a-1s** and **3a** were also synthesized according to the literature procedures.⁵⁻¹⁴

1.3 Instrumentation

Proton nuclear magnetic resonance (^1H NMR) spectra and proton-decoupled carbon nuclear magnetic resonance (^{13}C { $^1\text{H}}$ } NMR) spectra were recorded at 25°C (unless stated otherwise) on Inova 600 (600 MHz) or Varian Unity/Inova 500 (500 MHz) or Oxford AS400 (400 MHz) spectrometers at the Boston College nuclear magnetic resonance facility. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent. The solvent peak was referenced to 0 ppm for ^1H for tetramethylsilane and 77.0 ppm for ^{13}C for CDCl_3 . Data are represented as follows: chemical

shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sp = septet, m = multiplet), coupling constants in Hertz (Hz).

Optical rotations were measured using a 1 mL cell with a 5 cm path length on a Rudolph Research Analytical Autopol IV Polarimeter. Infrared spectra were recorded on a Bruker FT-IR Alpha (ATR mode) spectrophotometer. Data are represented as follows: frequency of absorption (cm^{-1}). High-resolution mass spectrometry was performed on a JEOL AccuTOF-DART (positive mode) or Agilent 6220 TOF-ESI (positive mode) at the Mass Spectrometry Facility, Boston College. Chiral HPLC analyses were carried using Agilent 1200 series instruments with Daicel CHIRALPAK® columns or Daicel CHIRALCEL® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm).

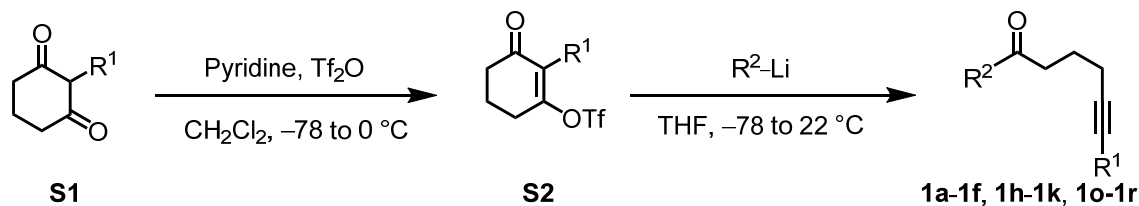
1.4 Abbreviations Used

Bn = benzyl, DART = direct analysis in real time, DCE = 1,2-dichloroethane, DCM = dichloromethane, er = enantiomeric ratio, Et_2O = diethyl ether, EtOAc = ethyl acetate, H_2O = water, HPLC = high pressure liquid chromatography, HR = high-resolution, LC = liquid chromatography, MS = mass spectrometry, NA = not applicable, PMP = 1,2,2,6,6-pentamethylpiperidine, PTFE = Polytetrafluoroethylene, PTLC = preparative thin layer chromatography, Tf = trifluoromethanesulfonate, THF = tetrahydrofuran, TOF = time-of-flight, Ts = 4-toluenesulfonyl.

2. Experimental Section

2.1 Substrate Preparation

General Procedure A:



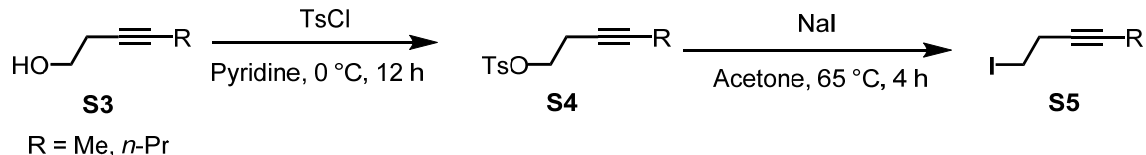
Preparation of S2:

To a solution of cyclohexanedione **S1** (1.0 equiv.) in dichloromethane (0.2 M), pyridine (2.0 equiv.) was added. The mixture was then cooled to $-78 \text{ }^\circ\text{C}$ and trifluoromethane sulfonic anhydride (Tf_2O , 1.2 equiv.) was added slowly at $-78 \text{ }^\circ\text{C}$. The reaction mixture was allowed to stir for 10 min at $-78 \text{ }^\circ\text{C}$ and warmed to $0 \text{ }^\circ\text{C}$. After the starting material (**S1**) was consumed (as determined by TLC), the mixture was acidified with 1N HCl (aq.) and extracted with dichloromethane (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 , and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (pentane:ether = 5:1) to yield **S2**.⁵

Preparation of 1a-1f, 1h-1k, 1o-1r:

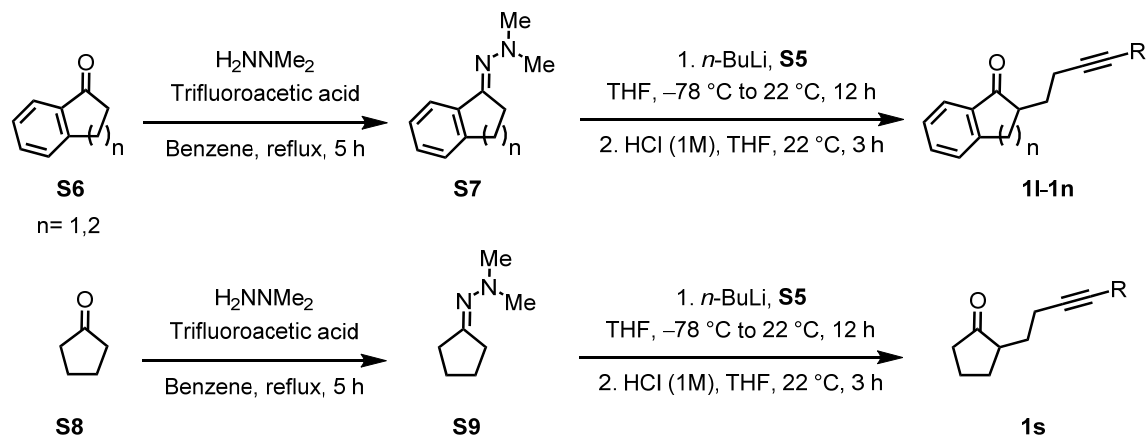
To a solution of **S2** (1.0 equiv.) in THF (0.25 M) at $-78 \text{ }^\circ\text{C}$ under N_2 atmosphere was added $\text{R}^2\text{-Li}$ (0.9 equiv.),⁶⁻⁷ dropwise. The reaction mixture was allowed to stir at $-78 \text{ }^\circ\text{C}$ for 10 minutes, then for 10 minutes at $0 \text{ }^\circ\text{C}$, followed by 30 minutes at room temperature. Upon completion of the reaction, saturated NH_4Cl (aq.) was added to quench the reaction and the mixture was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo*. The resulting mixture was purified by silica gel column chromatography using (hexanes:ethyl acetate = 100:1) to afford **1**.⁵

General Procedure B:



Synthesis of **S5**:

S5 was prepared from **S3** according to the known procedures.¹² To a solution of the alkynol **S3** (1.0 equiv.) in dry pyridine (1.25 M) was added *p*-toluene sulfonyl chloride (1.1 equiv.) and the reaction mixture was allowed to stir at 0 °C for 12 h. Upon completion, the reaction mixture was poured into water and was subsequently extracted with Et₂O (3 x 50 mL). The combined ether layers were washed with saturated CuSO₄ (aq.) and brine, and then dried over anhydrous MgSO₄. The solvent was removed *in vacuo*, and the crude product **S4** was used without further purification. To a solution of **S4** (1.0 equiv.) in acetone (0.4 M) was added sodium iodide (3.0 equiv.). The reaction mixture was allowed to heat at reflux for 4 h. Subsequently, the reaction mixture was concentrated *in vacuo*, and the resulting mixture was poured into water and extracted with pentane (3 x 50 mL). The combined organic layers were washed with water then brine, and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the resulting mixture was purified by silica gel column chromatography (hexanes:ethyl acetate = 50:1) to afford **S5** as a colorless liquid.

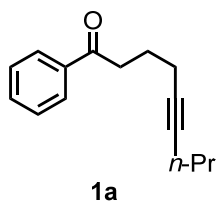


Synthesis of S7 and S9:

To a stirred solution of cycloketone **S6** or **S8** (1.0 equiv.) in benzene (0.6 M) was added *N,N*-dimethylhydrazine (1.2 equiv.) and trifluoroacetic acid (10 drops). The mixture was allowed to stir at reflux for 15 h with a Dean-Stark apparatus. Benzene was removed by distillation at atmospheric pressure. The residue was dissolved in Et₂O (30 mL), and ice water (25 mL) was added. After extraction with Et₂O (3 x 20 mL), the combined organic layers was washed with brine and dried over Na₂SO₄. After filtration and removal of the solvent, the residue was purified by distillation to give the desired compound **S7** or **S9**.¹³

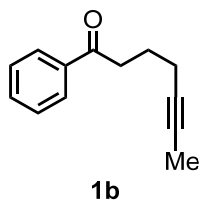
Synthesis of 1l-1n, 1s:

To a solution of *N,N*-dimethylhydrazone **S7** or **S9** (1.0 equiv.) in THF (0.25 M) was added *n*-BuLi (1.2 equiv.), dropwise at -5 °C. The reaction mixture was allowed to stir for 1 h at -5 °C, whereupon a solution of **S5** (1.1 equiv.) in THF (1 M) was added dropwise. The reaction mixture was allowed to stir at room temperature for 12 h, then 2N HCl (aq., 20 mL) was added to the solution. The reaction mixture was allowed to stir at room temperature for 3 h and extracted with ethyl acetate (5 x 10 mL). The combined organic layers was successively washed with aqueous Na₂S₂O₄ solution (2 x 50 mL), brine (2 x 50 mL) and dried over Na₂SO₄. After filtration and removal of the solvent, the residue was purified by silica gel column chromatography to give compound **1**.¹³



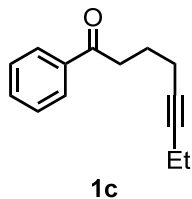
1-Phenylnon-5-yn-1-one (1a)

1-Phenylnon-5-yn-1-one was prepared following the **General Procedure A** starting with 30 mmol of 2-propylcyclohexane-1,3-dione.⁸ The product was obtained as a pale-yellow oil (5.9 g, 92% yield). **¹H NMR** (500 MHz, CDCl₃) δ 7.99 (d, *J* = 9.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 7.3 Hz, 2H), 2.33 – 2.26 (m, 2H), 2.17 – 2.09 (m, 2H), 1.93 (p, *J* = 7.0 Hz, 2H), 1.50 (h, *J* = 7.3 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 202.55, 139.68, 135.59, 131.19, 130.69, 83.78, 81.99, 39.97, 26.20, 25.12, 23.40, 20.97, 16.13; **IR** (neat) 2958, 2930, 2869, 1682, 1596, 1579, 1447, 1366, 1228, 1000, 745, 689 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₅H₁₉O (MH⁺): 215.1430; found: 215.14261.



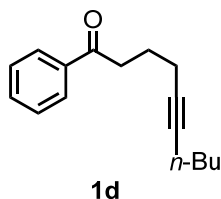
1-Phenylhept-5-yn-1-one (1b)

1-Phenylhept-5-yn-1-one was prepared following the **General Procedure A** starting with 10 mmol of 2-methylcyclohexane-1,3-dione. The product was obtained as a colorless oil (1.7 g, 90% yield). **¹H NMR** (500 MHz, CDCl₃) δ 7.99 (d, *J* = 9.7 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.49 – 7.44 (m, 2H), 3.10 (t, *J* = 7.3 Hz, 2H), 2.31 – 2.23 (m, 2H), 1.92 (p, *J* = 7.0 Hz, 2H), 1.78 (t, *J* = 2.6 Hz, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 202.50, 139.67, 135.59, 131.19, 130.68, 81.04, 79.06, 39.98, 26.06, 20.93, 6.11; **IR** (neat) 2934, 2915, 1681, 1595, 1579, 1446, 1365, 1319, 1228, 1198, 1000, 745, 689 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₃H₁₅O (MH⁺): 187.11174; found: 187.11099.



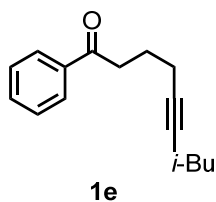
1-Phenyloct-5-yn-1-one (1c)

1-Phenyloct-5-yn-1-one was prepared following the **General Procedure A** starting with 10 mmol of 2-ethylcyclohexane-1,3-dione.⁸ The product was obtained as a yellow oil (1.7 g, 88% yield). **¹H NMR** (500 MHz, CDCl₃) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 7.3 Hz, 2H), 2.29 (t, *J* = 6.7 Hz, 2H), 2.16 (q, *J* = 7.1 Hz, 2H), 1.93 (p, *J* = 7.1 Hz, 2H), 1.11 (t, *J* = 7.9 Hz, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 202.54, 139.68, 135.59, 131.19, 130.69, 85.31, 81.20, 39.95, 26.16, 20.94, 16.96, 15.05; **IR** (neat) 2970, 2934, 1681, 1596, 1579, 1447, 1366, 1318, 1228, 1000, 745, 689 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₄H₁₇O (MH⁺): 201.12739; found: 201.12675.



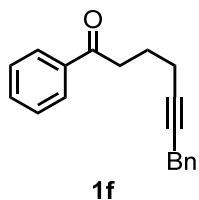
1-Phenyldec-5-yn-1-one (1d)

1-Phenyldec-5-yn-1-one was prepared following the **General Procedure A** starting with 10 mmol of 2-butylcyclohexane-1,3-dione.⁸ The product was obtained as a colorless oil (1.9 g, 85% yield). **¹H NMR** (500 MHz, CDCl₃) δ 7.99 (d, *J* = 7.1 Hz, 2H), 7.56 (t, 1H), 7.47 (t, *J* = 7.9 Hz, 2H), 3.11 (t, *J* = 7.3 Hz, 2H), 2.33 – 2.26 (m, 2H), 2.19 – 2.11 (m, 2H), 1.97 – 1.87 (m, 2H), 1.50 – 1.33 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 202.55, 139.68, 135.58, 131.19, 130.69, 83.92, 81.81, 39.96, 33.82, 26.18, 24.59, 21.07, 20.97, 16.26; **IR** (neat) 2953, 2929, 1683, 1596, 1447, 1366, 1228, 1000, 743, 689 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₆H₂₁O (MH⁺): 229.15869; found: 229.15855.



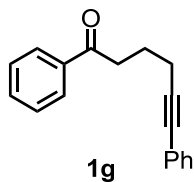
8-Methyl-1-phenylnon-5-yn-1-one (1e)

8-Methyl-1-phenylnon-5-yn-1-one was prepared following the **General Procedure A** starting with 10 mmol of 2-isobutylcyclohexane-1,3-dione.⁹ The product was obtained as a colorless oil (1.8 g, 78% yield). **¹H NMR** (500 MHz, CDCl₃) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.12 (t, *J* = 7.3 Hz, 2H), 2.33 – 2.28 (m, 2H), 2.07 – 2.02 (m, 2H), 1.94 (p, *J* = 7.0 Hz, 2H), 1.81 – 1.71 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 6H); **¹³C NMR** (151 MHz, CDCl₃) δ 202.54, 139.67, 135.59, 131.19, 130.68, 82.79, 82.71, 39.99, 30.87, 30.63, 26.24, 24.60, 20.99; **IR** (neat) 2953, 2903, 1683, 1595, 1579, 1447, 1366, 1228, 1000, 748, 689 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₆H₂₁O (MH⁺): 229.15869; found: 229.15854.



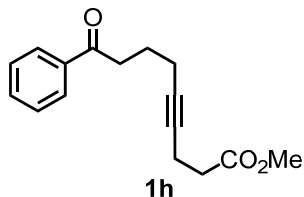
1,7-Diphenylhept-5-yn-1-one (1f)

1,7-Diphenylhept-5-yn-1-one was prepared following the **General Procedure A** starting with 10 mmol of 2-benzylcyclohexane-1,3-dione.⁸ The product was obtained as a yellow oil (2.4 g, 90% yield). **¹H NMR** (500 MHz, CDCl₃) δ 7.96 (d, *J* = 9.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H), 3.58 (s, 2H), 3.13 (t, *J* = 7.3 Hz, 2H), 2.40 – 2.33 (m, 2H), 1.98 (p, *J* = 7.0 Hz, 2H); **¹³C NMR** (151 MHz, CDCl₃) δ 202.45, 140.14, 139.68, 135.65, 131.25, 131.14, 130.73, 130.53, 129.14, 84.38, 81.43, 39.96, 27.85, 26.07, 21.08; **IR** (neat) 3057, 3019, 1679, 1595, 1156, 1000, 728, 688 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₉H₁₉O (MH⁺): 263.14304; found: 263.14192.



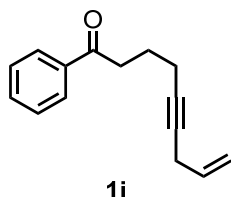
1,6-Diphenylhex-5-yn-1-one (1g)

1,6-Diphenylhex-5-yn-1-one was prepared based on a known procedure with the following modifications.¹⁴ To a solution of iodobenzene (4.3 g, 21 mmol, 2.1 equiv.), 1-phenylhex-5-yn-1-one⁵ (1.7 g, 10 mmol, 1.0 equiv.), triethylamine (20.2 g, 200 mmol, 20 equiv.) in THF (2 M) under N₂ was added Pd(PPh₃)₄ (115 mg, 0.1 mmol, 1 mol%) and CuI (38 mg, 0.2 mmol, 2 mol%). The reaction mixture was allowed to stir at 22 °C for 12 h. The mixture was filtered through a plug of Celite and the filtrate was washed with Et₂O, then concentrated under reduced pressure. The product was purified by column chromatography (hexanes:ethyl acetate = 20:1) to give the desired product as pale-yellow oil (2.4 g, 95% yield). **¹H NMR** (500 MHz, CDCl₃) δ 8.00 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.38 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.31 – 7.26 (m, 3H), 3.19 (t, *J* = 7.2 Hz, 2H), 2.56 (t, *J* = 6.8 Hz, 2H), 2.06 (p, *J* = 7.0 Hz, 2H); **¹³C NMR** (151 MHz, CDCl₃) δ 202.37, 139.63, 135.68, 134.21, 131.25, 130.87, 130.71, 130.31, 126.43, 91.96, 84.13, 39.92, 25.81, 21.61; **IR** (neat) 3055, 2934, 1681, 1595, 1488, 1446, 1228, 755, 689 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₈H₁₇O (MH⁺): 249.12739; found: 249.12754.



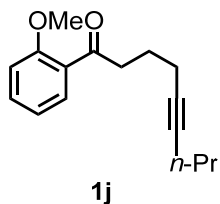
Methyl 9-oxo-9-phenylnon-4-ynoate (1h)

Methyl 9-oxo-9-phenylnon-4-ynoate was prepared following the **General Procedure A** starting with 10 mmol of methyl 3-(2,6-dioxocyclohexyl) propanoate.¹⁰ The product was obtained as a colorless oil (1.7 g, 65% yield). **¹H NMR** (500 MHz, CDCl₃) δ 7.98 (d, *J* = 9.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 3.66 (s, 3H), 3.09 (t, *J* = 7.3 Hz, 2H), 2.52 – 2.44 (m, 4H), 2.30 – 2.25 (m, 2H), 1.91 (p, *J* = 7.0 Hz, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ 199.80, 172.51, 136.99, 132.96, 128.55, 128.03, 80.17, 79.09, 51.65, 37.19, 33.79, 23.27, 18.22, 14.74; **IR** (neat) 2948, 1735, 1682, 1446, 1365, 1229, 1165, 749, 650 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₆H₁₉O₃ (MH⁺): 259.1329; found: 259.13287.



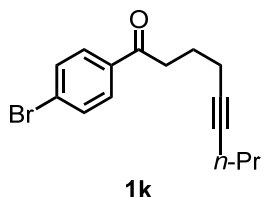
1-Phenylnon-8-en-5-yn-1-one (1i)

1-Phenylnon-8-en-5-yn-1-one was prepared following the **General Procedure A** starting with 10 mmol of 2-allylcyclohexane-1,3-dione.¹¹ The product was obtained as a colorless oil (1.8 g, 87% yield). **¹H NMR** (500 MHz, CDCl₃) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.87 – 5.77 (m, 1H), 5.30 (dd, *J* = 16.9, 1.8 Hz, 1H), 5.09 (dd, *J* = 9.9, 1.7 Hz, 1H), 3.12 (t, *J* = 7.3 Hz, 2H), 2.97 – 2.91 (m, 2H), 2.38 – 2.30 (m, 2H), 1.96 (p, *J* = 7.0 Hz, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ 200.12, 137.34, 133.57, 133.29, 128.89, 128.37, 116.00, 82.17, 77.94, 37.63, 23.76, 23.45, 18.68; **IR** (neat) 2935, 2896, 1682, 1596, 1447, 1367, 1199, 990, 914, 750, 689 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₅H₁₇O (MH⁺): 213.12739; found: 213.12681.



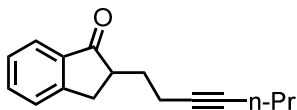
1-(2-Methoxyphenyl)non-5-yn-1-one (1j)

1-(2-Methoxyphenyl)non-5-yn-1-one was prepared following the **General Procedure A** starting with 10 mmol of 2-propylcyclohexane-1,3-dione.⁸ The product was obtained as a colorless oil (1.7 g, 72% yield). **¹H NMR** (500 MHz, CDCl₃) δ 7.67 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.03 – 6.94 (m, 2H), 3.90 (s, 3H), 3.09 (t, *J* = 7.3 Hz, 2H), 2.28 – 2.22 (m, 2H), 2.16 – 2.08 (m, 2H), 1.91 – 1.84 (m, 2H), 1.49 (h, *J* = 7.2 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 202.37, 158.44, 133.19, 130.17, 128.58, 120.59, 111.50, 80.66, 79.67, 55.44, 42.69, 23.81, 22.48, 20.76, 18.43, 13.45; **IR** (neat) 2958, 2931, 1671, 1595, 1483, 1462, 1435, 1282, 1243, 1023, 756 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₆H₂₁O₂ (MH⁺): 245.15361; found: 245.15500.



1-(4-Bromophenyl)non-5-yn-1-one (1k)

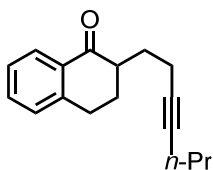
1-(4-Bromophenyl)non-5-yn-1-one was prepared following the **General Procedure A** starting with 10 mmol of 2-propylcyclohexane-1,3-dione.⁸ The product was obtained as a colorless oil (2.2 g, 76% yield). **¹H NMR** (500 MHz, CDCl₃) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 3.07 (t, *J* = 7.3 Hz, 2H), 2.32 – 2.26 (m, 2H), 2.15 – 2.09 (m, 2H), 1.92 (p, *J* = 7.0 Hz, 2H), 1.50 (q, *J* = 7.2 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 198.80, 135.72, 131.84, 129.57, 128.07, 81.25, 79.18, 37.23, 23.41, 22.46, 20.73, 18.25, 13.48; **IR** (neat) 2957, 2930, 1683, 1583, 1394, 1227, 1068, 1009, 991, 809 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₅H₁₈OBr (MH⁺): 293.05355; found: 293.05285.



1l

2-(Hept-3-yn-1-yl)-2,3-dihydro-1H-inden-1-one (1l)

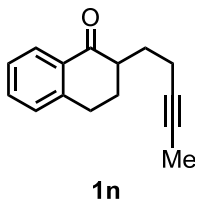
2-(Hept-3-yn-1-yl)-2,3-dihydro-1H-inden-1-one was prepared following the **General Procedure B** starting with 20 mmol of 2,3-dihydro-1H-inden-1-one. The product was obtained as a dark brown oil (2.2 g, 50% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 3.43 – 3.33 (m, 1H), 2.91 – 2.81 (m, 2H), 2.48 – 2.31 (m, 2H), 2.25 – 2.14 (m, 1H), 2.14 – 2.06 (m, 2H), 1.69 – 1.60 (m, 1H), 1.49 (dt, *J* = 14.5, 7.2 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 211.14, 156.17, 139.42, 137.31, 130.01, 129.16, 126.52, 83.94, 81.71, 49.24, 35.35, 33.36, 25.06, 23.39, 19.79, 16.14; IR (neat) 2957, 2927, 1708, 1607, 1462, 1275, 747 cm⁻¹; HRMS (DART) *m/z* Calcd for C₁₆H₁₉O (MH⁺): 227.14304; found: 227.14176.



1m

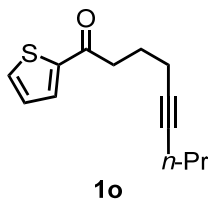
2-(Hept-3-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one (1m)

2-(Hept-3-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one was prepared following the **General Procedure B** starting with 20 mmol of 3,4-dihydronaphthalen-1(2H)-one. The product was obtained as a brown oil (3.0 g, 62% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, *J* = 8.9 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 3.07 – 2.99 (m, 2H), 2.73 – 2.63 (m, 1H), 2.44 – 2.36 (m, 1H), 2.36 – 2.20 (m, 3H), 2.15 – 2.08 (m, 2H), 1.93 – 1.83 (m, 1H), 1.68 – 1.57 (m, 1H), 1.49 (h, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 202.65, 146.53, 135.76, 135.21, 131.30, 130.05, 129.20, 83.54, 82.07, 49.05, 31.64, 31.30, 30.90, 25.12, 23.41, 19.20, 16.13; IR (neat) 2956, 2927, 2863, 2837, 1679, 1598, 1453, 1432, 1226, 909, 773 cm⁻¹; HRMS (DART) *m/z* Calcd for C₁₇H₂₁O (MH⁺): 241.15869; found: 241.15897.



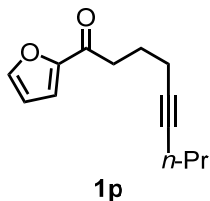
2-(Pent-3-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one (1n)

2-(Pent-3-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one was prepared following the **General Procedure B** starting with 20 mmol of 3,4-dihydronaphthalen-1(2H)-one. The product was obtained as a brown oil (2.8 g, 67% yield). **¹H NMR** (500 MHz, CDCl₃) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 3.10 – 2.96 (m, 2H), 2.70 – 2.62 (m, 1H), 2.44 – 2.32 (m, 1H), 2.32 – 2.16 (m, 3H), 1.93 – 1.82 (m, 1H), 1.76 (s, 3H), 1.67 – 1.54 (m, 1H); **¹³C NMR** (151 MHz, CDCl₃) δ 202.65, 146.51, 135.77, 135.21, 131.30, 130.04, 129.19, 81.13, 78.85, 48.97, 31.61, 31.26, 30.93, 19.15, 6.13; **IR** (neat) 2915, 2856, 1678, 1598, 1452, 1226, 891, 739 cm⁻¹; **HRMS** (DART) Calcd for C₁₅H₁₅O (MH⁺): 213.12739; found: 213.12708.



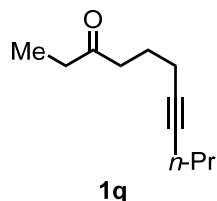
1-(Thiophen-2-yl)non-5-yn-1-one (1o)

1-(Thiophen-2-yl)non-5-yn-1-one was prepared following the **General Procedure A** starting with 10 mmol of 2-propylcyclohexane-1,3-dione.⁸ The product was obtained as a pale-yellow oil (1.8 g, 82% yield). **¹H NMR** (500 MHz, CDCl₃) δ 7.75 (d, *J* = 4.8 Hz, 1H), 7.63 (d, *J* = 6.0 Hz, 1H), 7.15 – 7.12 (m, 1H), 3.04 (t, *J* = 7.3 Hz, 2H), 2.29 (tt, *J* = 6.8, 2.4 Hz, 2H), 2.13 (tt, *J* = 7.1, 2.4 Hz, 2H), 1.93 (p, *J* = 7.0 Hz, 2H), 1.50 (h, *J* = 7.3 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 195.44, 147.04, 136.04, 134.41, 130.69, 83.83, 81.84, 40.63, 26.50, 25.09, 23.36, 20.93, 16.11; **IR** (neat) 2957, 2930, 1657, 1516, 1412, 1336, 1234, 1067, 718 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₃H₁₇OS (MH⁺): 221.09946; found: 221.10027.



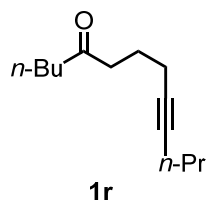
1-(Furan-2-yl)non-5-yn-1-one (1p)

1-(Furan-2-yl)non-5-yn-1-one was prepared following the **General Procedure A** starting with 10 mmol of 2-propylcyclohexane-1,3-dione.⁸ The product was obtained as a pale-yellow oil (1.6 g, 79% yield). **¹H NMR** (500 MHz, CDCl₃) δ 7.58 (d, *J* = 0.9 Hz, 1H), 7.20 (d, *J* = 4.2 Hz, 1H), 6.53 (dd, *J* = 3.5, 1.7 Hz, 1H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.30 – 2.24 (m, 2H), 2.16 – 2.08 (m, 2H), 1.95 – 1.87 (m, 2H), 1.50 (q, *J* = 7.2 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 191.72, 155.41, 148.87, 119.53, 114.74, 83.79, 81.82, 39.86, 26.11, 25.08, 23.36, 20.97, 16.09; **IR** (neat) 2959, 2931, 1675, 1567, 1467, 1393, 1224, 1013, 812, 761 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₃H₁₇O₂ (MH⁺): 205.1223; found: 205.12050.



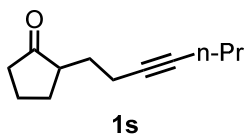
Undec-7-yn-3-one (1q)

Undec-7-yn-3-one was prepared following the **General Procedure A** starting with 10 mmol of 2-propylcyclohexane-1,3-dione.⁸ The product was obtained as a colorless oil (1.0 g, 60% yield). **¹H NMR** (500 MHz, CDCl₃) δ 2.53 (t, *J* = 6.7 Hz, 2H), 2.44 (qd, *J* = 7.3, 1.3 Hz, 2H), 2.19 (t, *J* = 6.8 Hz, 2H), 2.12 (t, *J* = 7.6 Hz, 2H), 1.76 (p, *J* = 7.1 Hz, 2H), 1.50 (h, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.6 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 214.03, 83.79, 82.07, 43.81, 38.86, 25.94, 25.33, 23.57, 21.04, 16.30, 10.66; **IR** (neat) 2958, 2932, 1711, 1456, 1373, 1112 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₁H₁₉O (MH⁺): 167.14304; found: 167.14235.



Tridec-9-yn-5-one (1r)

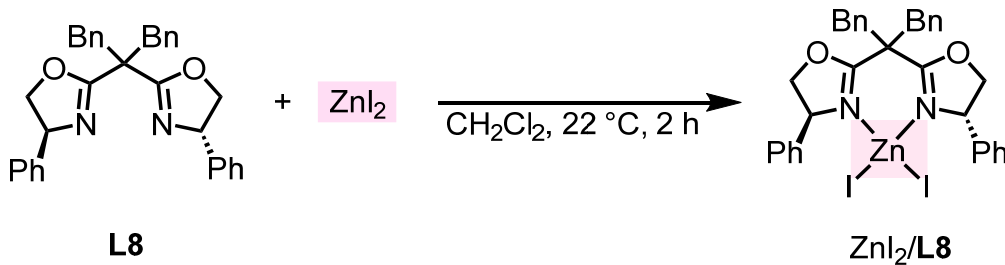
Tridec-9-yn-5-one was prepared following the **General Procedure A** starting with 10 mmol of 2-propylcyclohexane-1,3-dione.⁸ The product was obtained as a colorless oil (1.40g, 72% yield). **¹H NMR** (500 MHz, CDCl₃) δ 2.53 (t, *J* = 7.3 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.23 – 2.16 (m, 2H), 2.16 – 2.10 (m, 2H), 1.75 (p, *J* = 7.1 Hz, 2H), 1.62 – 1.45 (m, 4H), 1.36 – 1.27 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 213.59, 83.58, 81.87, 45.31, 43.96, 28.63, 25.65, 25.11, 24.98, 23.35, 20.80, 16.47, 16.09; **IR** (neat) 2956, 2930, 2869, 1711, 1454, 1370, 1125, 1083 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₃H₂₃O (MH⁺): 195.17434; found: 195.17324.



2-(Hept-3-yn-1-yl)cyclopentan-1-one (1s)

2-(Hept-3-yn-1-yl)cyclopentan-1-one was prepared following the **General Procedure B** starting with 20 mmol of cyclopentanone. The product was obtained as a brown oil (2.8 g, 78% yield). **¹H NMR** (500 MHz, CDCl₃) δ 2.37–2.17 (m, 5H), 2.17 – 2.07 (m, 3H), 2.07 – 1.91 (m, 2H), 1.79 (d, *J* = 9.0 Hz, 1H), 1.58 – 1.38 (m, 4H), 0.96 (t, *J* = 7.8 Hz, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 223.66, 83.51, 81.83, 50.87, 40.73, 32.06, 31.77, 25.08, 23.37, 23.35, 19.67, 16.10; **IR** (neat) 2958, 2930, 2868, 1734, 1452, 1153 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₂H₁₉O (MH⁺): 179.14304; found: 179.14191.

2.2 Preparation Chiral ZnI₂/BOX Complexes



Chiral ZnI₂/BOX complex (ZnI₂/**L8**) was prepared according to a literature procedure.^{2,15} To a 25 mL oven-dried sealed tube was added (4*S*,4'*S*)-2,2'-(1,3-diphenylpropane-2,2-diyl)bis(4-phenyl-4,5-dihydrooxazole) (**L8**, 973 mg, 2.0 mmol), ZnI₂ (766 mg, 2.4 mmol), and CH₂Cl₂ (10 mL) under nitrogen atmosphere. The resulting mixture was allowed to stir at 22 °C for 2 h. Upon completion, the solution was transferred to a syringe fitted with a 0.22 μm PTFE filter and filtered under nitrogen into a Schlenk tube. The solvent was removed *in vacuo* to deliver **ZnI₂/L8** complex as a pale yellow solid (1.5 g, 95% yield).

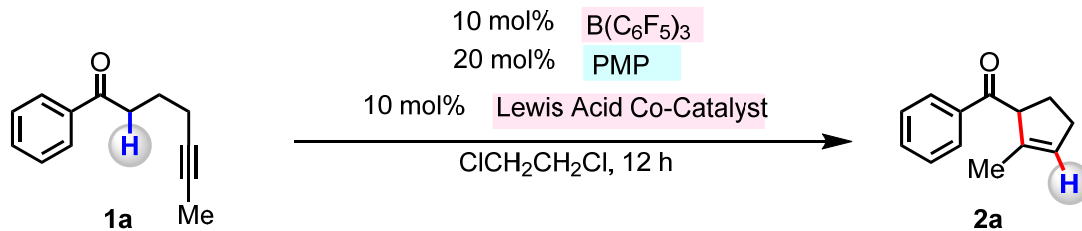
¹H NMR (500 MHz, CDCl₃) δ 7.51 – 7.42 (m, 6H), 7.28 – 7.21 (m, 2H), 7.21 – 7.11 (m, 8H), 6.62 (d, *J* = 7.5 Hz, 4H), 5.69 (t, *J* = 10.5 Hz, 2H), 4.96 (t, *J* = 9.8 Hz, 2H), 4.22 (t, *J* = 9.7 Hz, 2H), 3.91 (d, *J* = 14.2 Hz, 2H), 3.44 (d, *J* = 14.2 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 168.43, 135.45, 133.74, 130.04, 129.21, 128.95, 128.88, 128.39, 128.24, 75.40, 68.43, 51.85, 44.63.

2.3 Optimization Studies

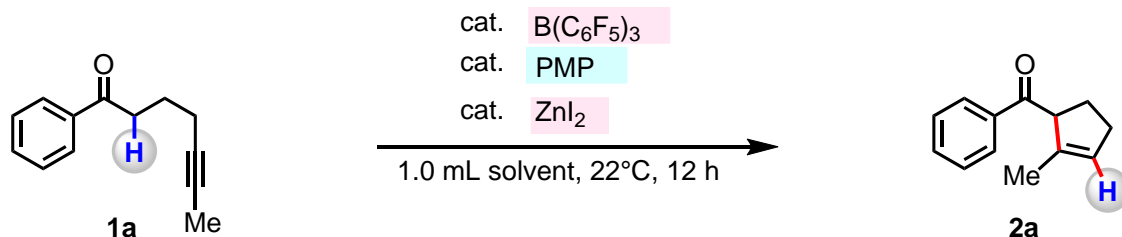
Experimental Procedure for Optimization of Racemic Conia-Ene-Type Reaction

(see Tables SI-1 and SI-2)

To a 7.0 mL oven-dried vial was added Lewis acid Co-catalyst, 1-phenylhept-5-yn-1-one **1a** (37.2 mg, 0.2 mmol), B(C₆F₅)₃, PMP, and solvent (1.0 mL) under nitrogen atmosphere. The resulting mixture was allowed to stir at 22 °C or 80 °C for 12 h. Upon completion, the reaction mixture was diluted with CH₂Cl₂, and concentrated *in vacuo*. The product yield was determined by the ¹H NMR analysis of the unpurified product mixture using mesitylene as the internal standard.

Table SI-1. Evaluation of Lewis Acid Co-Catalyst

entry	Lewis Acid Co-Catalyst	Reaction temperature (°C)	yield of 2a (%)
1	AgOTf	80	16
2	Mg(OTf) ₂	80	0
3	In(OTf) ₃	80	13
4	Yb(OTf) ₃	80	0
5	CuOTf	80	15
6	[Cu(OTf) ₂] ₂ •C ₆ H ₆	80	18
7	AuPPh ₃ Cl/AgOTf	80	40
8	AuPPh ₃ Cl	80	>95
9	Zn(OTf) ₂	80	64
10	ZnCl ₂	80	>95
11	ZnI ₂	80	>95
12	Zn(OAc) ₂	80	>95
13	Zn(NTf ₂) ₂	80	0
14	AuPPh ₃ Cl	22	0
15	ZnCl ₂	22	78
16	ZnI ₂	22	>95
17	Zn(OAc) ₂	22	15

Table SI-2. Evaluation of Reaction Conditions and Control Experiments

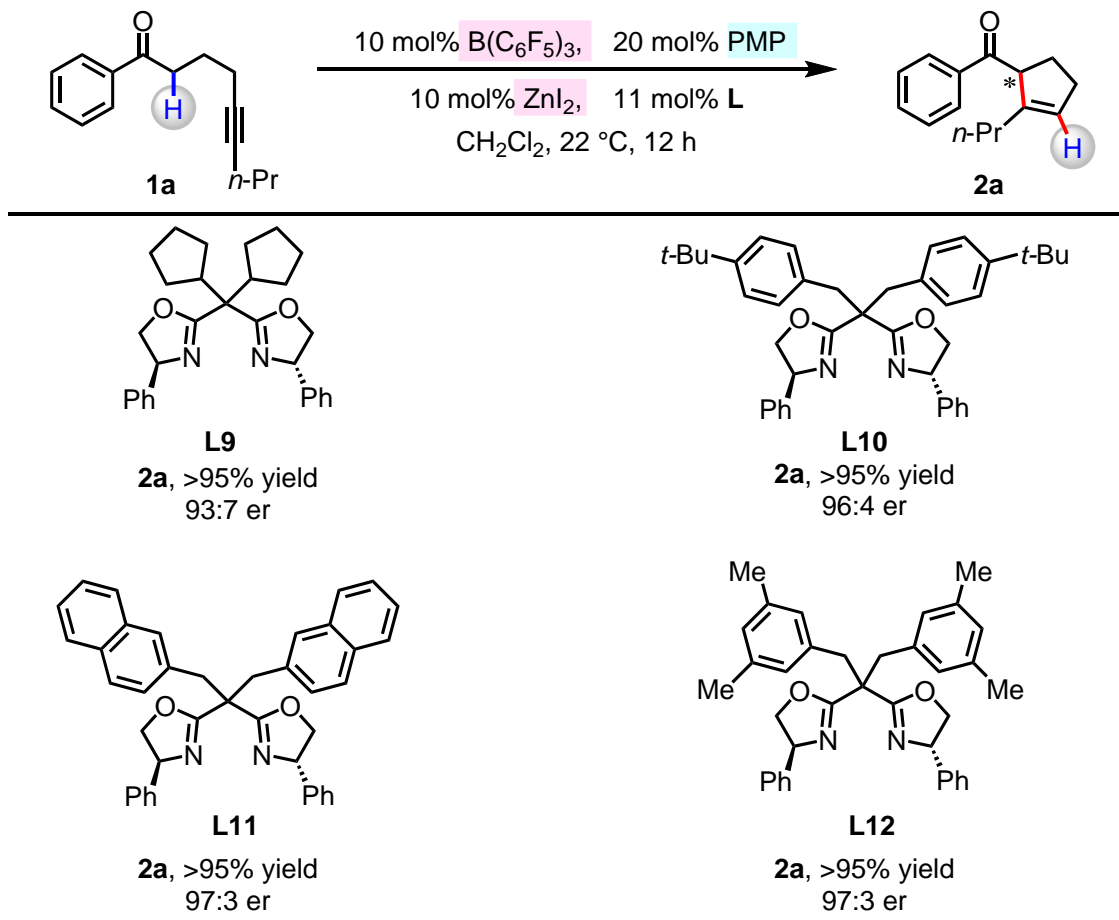
entry	$\text{B}(\text{C}_6\text{F}_5)_3$ (mol%)	PMP (mol%)	ZnI_2 (mol%)	solvent	yield of 2a (%)
1	10	20	10	CH_2Cl_2	>95
2	10	none	10	CH_2Cl_2	<5
3	none	20	10	CH_2Cl_2	0
4	10	20	none	CH_2Cl_2	0
5	5	10	5	CH_2Cl_2	>95
6	10	20	10	$\text{ClCH}_2\text{CH}_2\text{Cl}$	>95
7	10	20	10	THF	5
8	10	20	10	Toluene	80

Experimental Procedure for Optimization of BOX Ligands (See Table SI-3 and Table 2 in the manuscript)

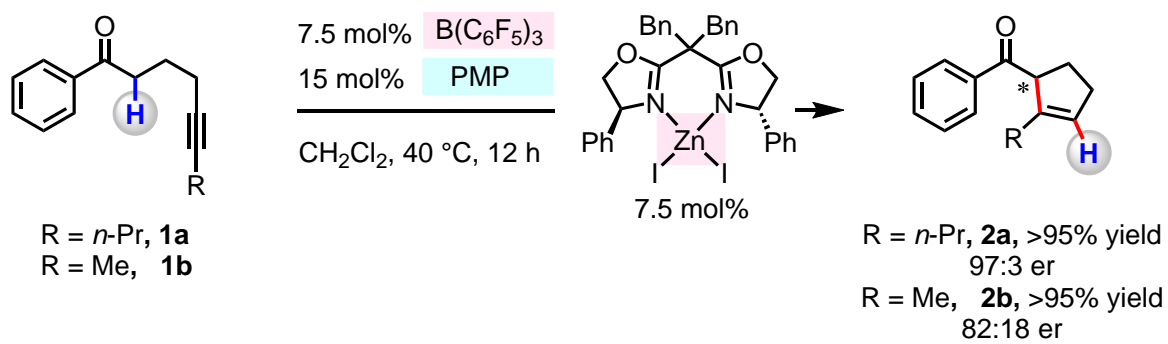
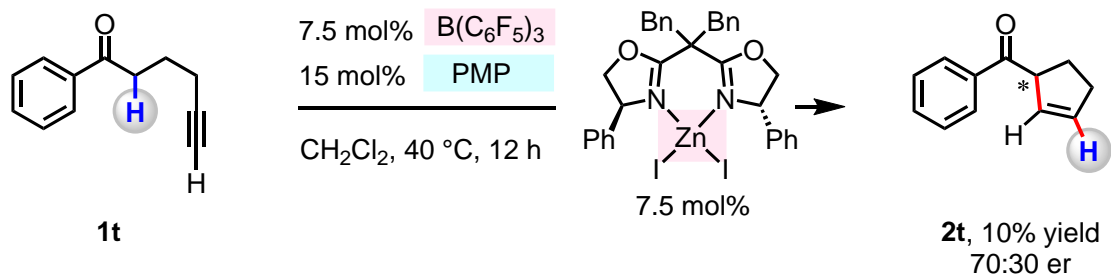
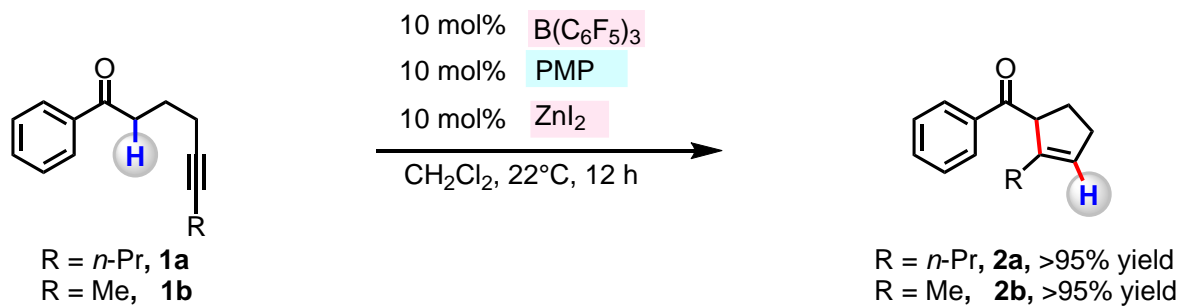
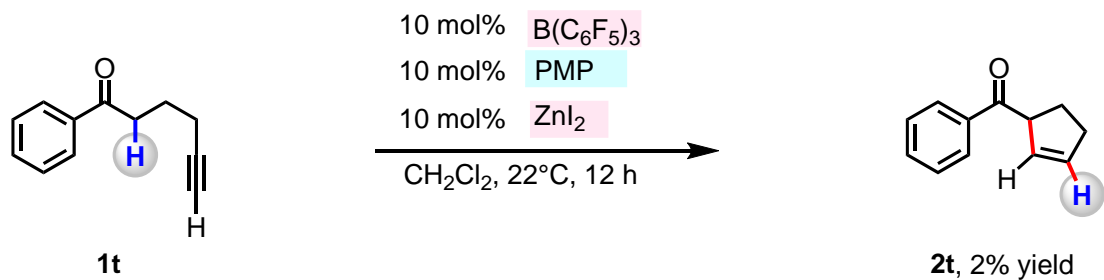
To a 7.0 mL oven-dried vial was added ZnI_2 (0.02 mmol, 10 mol%), ligand (0.022 mmol, 11 mol%), CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. The mixture was allowed to stir for 30 minutes at 22 °C. Subsequently, 1-phenylpent-4-yn-1-one **1a** (0.20 mmol), $\text{B}(\text{C}_6\text{F}_5)_3$ (0.02 mmol), PMP (0.04 mmol), and CH_2Cl_2 (0.5 mL) were added to the vial under nitrogen atmosphere, and the resulting mixture was allowed to stir at 22 °C for 12 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 , concentrated *in vacuo*. The product yield was determined by the ^1H NMR analysis of the unpurified product mixture using mesitylene as the internal standard. The product was purified by preparative TLC (hexanes:EtOAc = 10:1).

The er values of product **2a** was determined by HPLC analysis of the isolated and purified product.

Table SI-3. Evaluation of Chiral Ligands

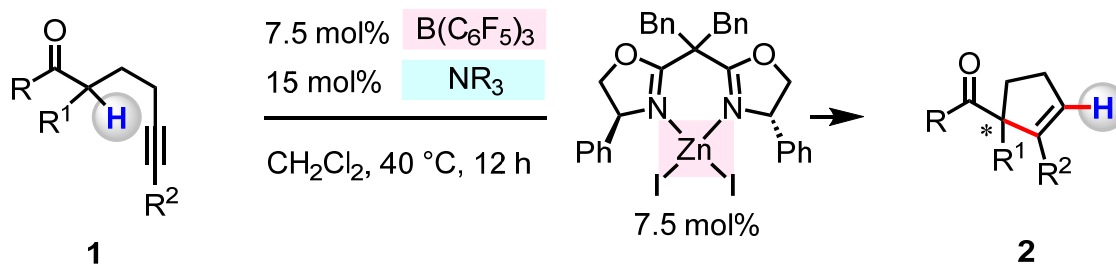


Experiments for Evaluation of Substrate Structure



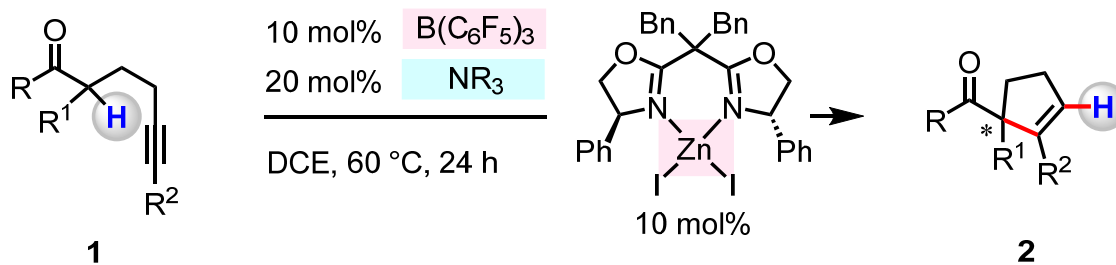
2.4 General Procedures for the Enantioselective Conia-Ene-Type Reaction (See Table 1, Table 3 and Table 4 in the manuscript)

General Procedure C



To a 7.0 mL oven-dried vial was added substrate **1** (0.2 mmol), $ZnI_2/L8$ (7.5 mol%), $B(C_6F_5)_3$ (7.5 mol%), PMP or *N*-methylpiperidine (15 mol%), and CH_2Cl_2 (1.0 mL) under nitrogen atmosphere. The resulting mixture was allowed to stir at 40 °C for 12 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 , concentrated *in vacuo* and purified by silica gel column chromatography.

General Procedure D

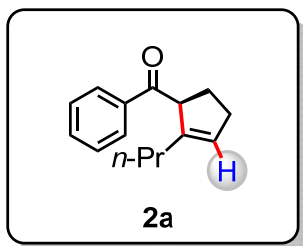


To a 7.0 mL oven-dried vial was added substrate **1** (0.2 mmol), $ZnI_2/L8$ (10 mol%), $B(C_6F_5)_3$ (10 mol%), PMP or *N*-methylpiperidine (20 mol%), and DCE (1.0 mL) under nitrogen atmosphere. The resulting mixture was allowed to stir at 60 °C for 24 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 , concentrated *in vacuo* and purified by silica gel column chromatography.

2.5 Procedure for Large Scale Reaction

To a 25 mL oven-dried sealed tube was added substrate 1-phenylnon-5-yn-1-one **1a** (1.5 g, 7 mmol), ZnI₂/**L8** (141 mg, 0.175 mmol, 2.5 mol%), B(C₆F₅)₃ (179 mg, 0.350 mmol, 5.0 mol%), PMP (109 mg, 0.700 mmol, 10 mol%), and CH₂Cl₂ (10 mL) under nitrogen atmosphere. The resulting mixture was allowed to stir at 40 °C for 24 h. Upon completion, the solvent was removed *in vacuo* and purification by silica gel column chromatography gave the product as a pale yellow oil (1.4 g, 94% yield, 97:3 er). The er value was determined by HPLC analysis of the isolated and purified product.

3. Analytical Data



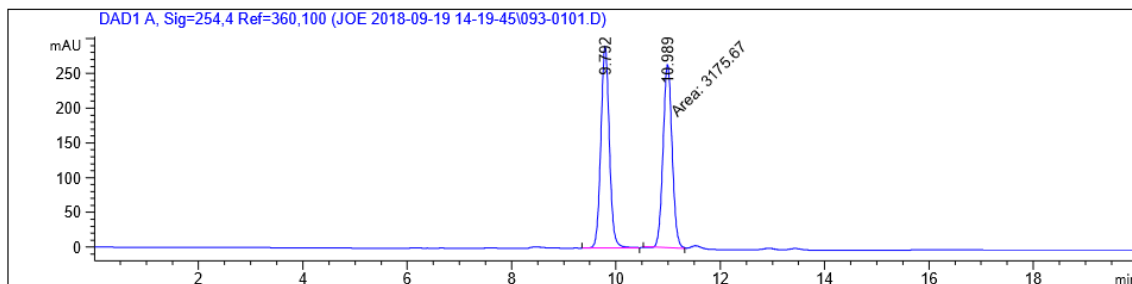
(*S*)-Phenyl(2-propylcyclopent-2-en-1-yl)methanone (**2a**)

According to the General Procedure **C**, 1-phenylnon-5-yn-1-one **1a** (42.9 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2a** (42.0 mg, 98%) as a colorless oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.00 (d, $J = 7.1$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 5.71 – 5.58 (m, 1H), 4.42 (t, $J = 7.6$ Hz, 1H), 2.55 – 2.44 (m, 1H), 2.44 – 2.37 (m, 1H), 2.37 – 2.26 (m, 1H), 2.12 – 2.00 (m, 2H), 2.00 – 1.89 (m, 1H), 1.52 – 1.35 (m, 2H), 0.86 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 202.56, 143.21, 137.18, 132.88, 128.57, 128.48, 127.29, 54.88, 32.12, 31.65, 29.68, 20.89, 13.98; **IR** (neat) 2956, 2929, 2869, 1707, 1676, 1447, 1314, 1258, 1069, 710, 699 cm^{-1} ; **HRMS** (DART) m/z Calcd for $\text{C}_{15}\text{H}_{19}\text{O}$ (MH^+): 215.1430; found: 215.1427; **HPLC** (Chiralcel OD-H; 1%/99% isopropanol/ hexanes, 0.5 mL/min; $t_r = 9.8$ min (major), 10.9 min (minor); 97:3 er). $[\alpha]_D^{25} = -19.6^\circ$ ($c = 1.0$, CH_2Cl_2). For the determination of absolute configuration, see section **SI-4**.

```

Acq. Operator   : SYSTEM                      Seq. Line :    1
Acq. Instrument : Wasa_LC1                    Location  :   93
Injection Date  : 9/19/2018 2:20:51 PM       Inj       :    1
                                                    Inj Volume: 4.000 µl
Method          : C:\Chem32\1\Data\JOE 2018-09-19 14-19-45\column3 1%IPA 99% hexane 20min-0.5mL.M (Sequence Method)
Last changed    : 9/19/2018 2:19:47 PM by SYSTEM
Method Info     : Column3 20min-1% iPrOH 99% hexane-0.5mL

```



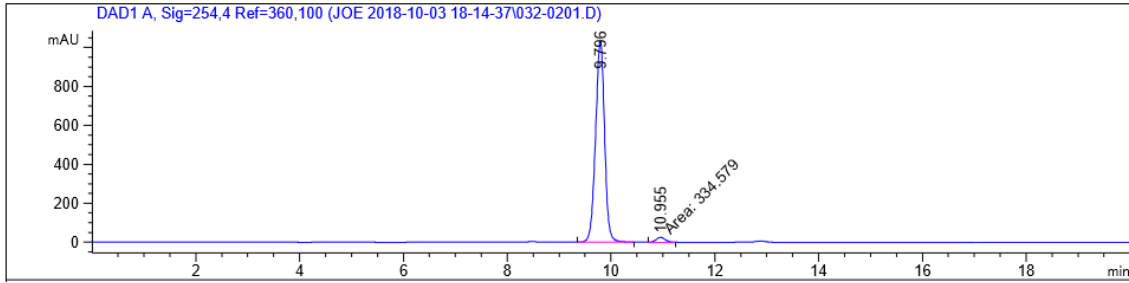
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.792	BB	0.1738	3275.03320	289.89484	50.7702
2	10.989	MM	0.2007	3175.66724	263.68991	49.2298

Totals : 6450.70044 553.58475

```

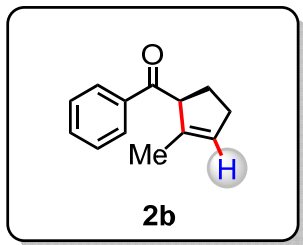
Acq. Operator   : SYSTEM                      Seq. Line :    2
Acq. Instrument : Wasa_LC1                   Location  :   32
Injection Date  : 10/3/2018 6:37:25 PM      Inj       :    1
                                                Inj Volume: 4.000 µl
Method          : C:\Chem32\1\Data\JOE 2018-10-03 18-14-37\column3 1%IPA 99% hexane 20min-0.5mL.M (Sequence Method)
Last changed    : 10/3/2018 6:14:40 PM by SYSTEM
Method Info     : Column3 20min-1% iProH 99% hexane-0.5mL
  
```



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.796	BB	0.1868	1.24999e4	1035.63757	97.3931
2	10.955	MM	0.2156	334.57858	25.86999	2.6069

Totals : 1.28345e4 1061.50756



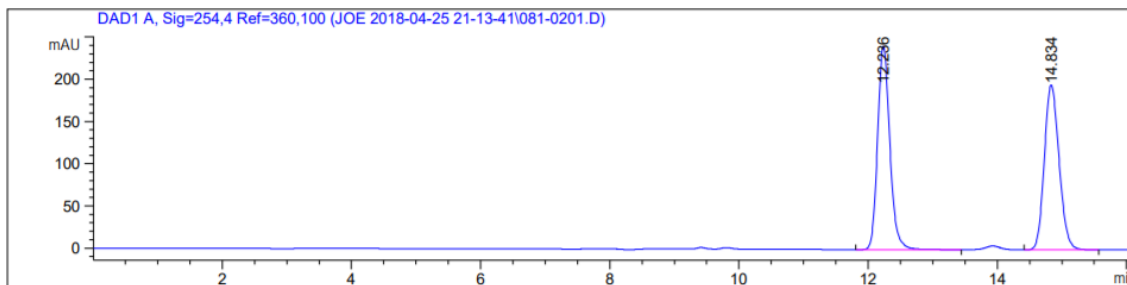
(S)-(2-Methylcyclopent-2-en-1-yl)(phenyl)methanone (2b)

According to the General Procedure C, 1-phenylhept-5-yn-1-one **1b** (37.2 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2b** (35.7 mg, 96%) as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.67 – 5.56 (m, 1H), 4.37 (t, *J* = 7.3 Hz, 1H), 2.53 – 2.43 (m, 1H), 2.43 – 2.30 (m, 2H), 2.14 – 2.05 (m, 1H), 1.70 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 205.48, 141.63, 140.32, 136.09, 131.93, 131.75, 131.70, 59.32, 34.93, 32.87, 18.98; **IR** (neat) 3057, 2928, 1704, 1674, 1578, 1345, 1175, 1111, 1000, 775, 697 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₃H₁₅O (MH⁺): 187.1117; found: 187.1114; **HPLC** (Chiralcel OD-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; *t_r* = 11.5 min (major), 13.6 min (minor); 82:18 er); [*α*]_D²⁵ = -36.7° (*c* = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

```

Acq. Operator   : SYSTEM                      Seq. Line :    2
Acq. Instrument : Wasa_LC1                    Location  :   81
Injection Date  : 4/25/2018 10:15:40 PM      Inj       :    1
                                           Inj Volume: 4.000 µl
Method          : C:\Chem32\1\Data\JOE 2018-04-25 21-13-41\column2 1%IPA 99% hexane 60min-0.5mL.M (Sequence Method)
Last changed    : 4/25/2018 9:13:43 PM by SYSTEM
Method Info     : Column2 60min-1% iPrOH 99% hexane-0.5mL

```

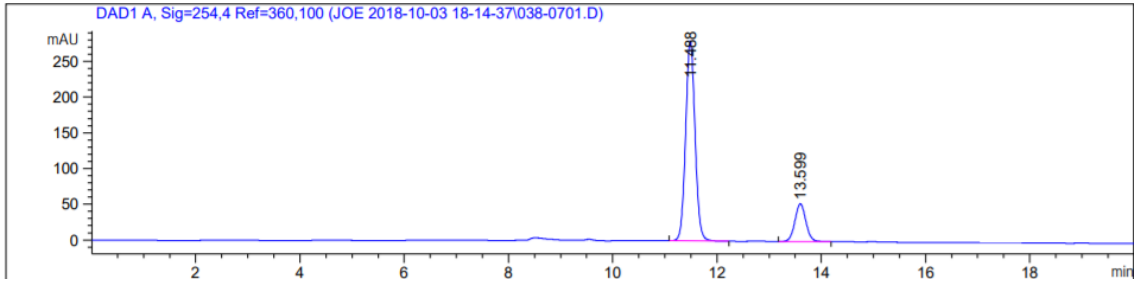


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.236	BB	0.2038	3175.99268	240.84023	50.6041
2	14.834	BB	0.2474	3100.15894	195.06850	49.3959

Totals : 6276.15161 435.90872

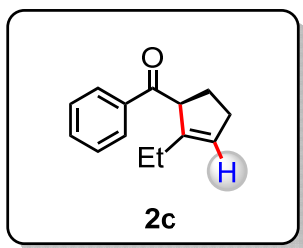
Acq. Operator : SYSTEM
 Acq. Instrument : Wasa_LC1
 Injection Date : 10/3/2018 8:42:17 PM
 Seq. Line : 7
 Location : 38
 Inj : 1
 Inj Volume : 4.000 µl
 Method : C:\Chem32\1\Data\JOE 2018-10-03 18-14-37\column3 1%IPA 99% hexane 20min-0.5mL.M (Sequence Method)
 Last changed : 10/3/2018 6:14:40 PM by SYSTEM
 Method Info : Column3 20min-1% iPrOH 99% hexane-0.5mL
 Additional Info : Peak(s) manually integrated



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

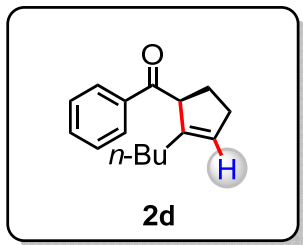
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.488	BB	0.1941	3508.73730	280.17123	81.9336
2	13.599	BB	0.2247	773.67737	52.87839	18.0664

Totals : 4282.41467 333.04962



(S)-(2-Ethylcyclopent-2-en-1-yl)(phenyl)methanone (2c)

According to the General Procedure C, 1-phenyloct-5-yn-1-one **1c** (40.0 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2c** (38.0 mg, 95%) as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 8.00 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.64 (q, *J* = 1.8 Hz, 1H), 4.43 (t, *J* = 7.8 Hz, 1H), 2.57 – 2.45 (m, 1H), 2.44 – 2.26 (m, 2H), 2.16 – 2.03 (m, 2H), 2.01 – 1.88 (m, 1H), 1.03 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 202.57, 144.90, 137.21, 132.88, 128.57, 128.49, 126.31, 55.04, 31.62, 29.66, 23.10, 12.20; **IR** (neat) 2933, 2876, 2850, 1706, 1675, 1446, 1272, 1023, 1001, 700, 647 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₄H₁₇O (MH⁺): 201.1274; found: 201.1264; **HPLC** (Chiralcel OD-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; tr = 10.3 min (major), 12.4 min (minor); 96:4 er); [α]_D²⁵ = -23.1° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

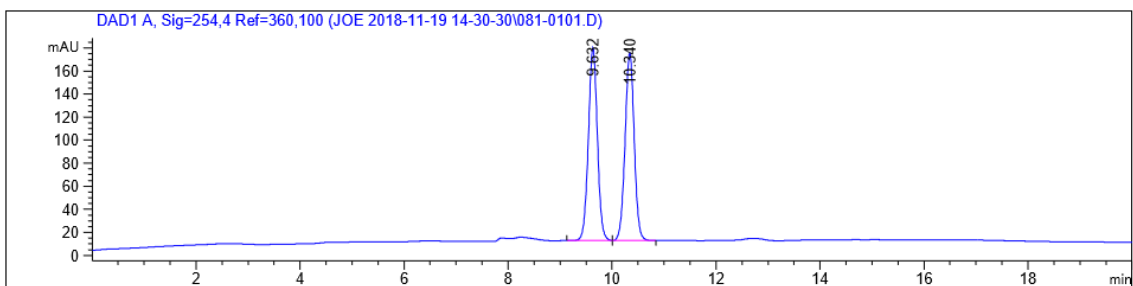


(S)-(2-Butylcyclopent-2-en-1-yl)(phenyl)methanone (2d)

According to the General Procedure C, 1-phenyldec-5-yn-1-one **1d** (45.7 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2d** (45.2 mg, 99%) as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 8.00 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.64 (d, *J* = 1.6 Hz, 1H), 4.42 (t, *J* = 7.9 Hz, 1H), 2.54 – 2.44 (m, 1H), 2.44 – 2.28 (m, 2H), 2.15 – 2.01 (m, 2H), 1.99 – 1.89 (m, 1H), 1.45 – 1.35 (m, 2H), 1.33 – 1.18 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 202.57, 143.40, 137.20, 132.87, 128.56, 128.49, 127.14, 54.94, 31.64, 29.88, 29.66, 22.52, 13.89; **IR** (neat) 2953, 2927, 2857, 1707, 1676, 1342, 1109, 931, 859, 699, 669 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₆H₂₁O (MH⁺): 229.1587; found: 229.1582; **HPLC** (Chiralcel OD-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; tr = 9.7 min (major), 10.3 min (minor); 97:3 er); [α]_D²⁵ = -31.4° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

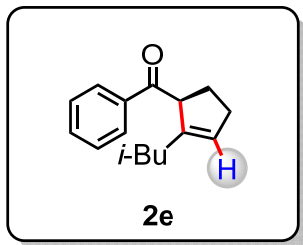
Acq. Operator : SYSTEM
Acq. Instrument : Wasa_LC1
Injection Date : 11/19/2018 2:32:22 PM
Method : C:\Chem32\1\Data\JOE 2018-11-19 14-30-30\column3 1%IPA 99% hexane 20min-0.5mL.M (Sequence Method)
Last changed : 11/19/2018 2:30:33 PM by SYSTEM
Method Info : Column3 20min-1% iPrOH 99% hexane-0.5mL

Seq. Line : 1
Location : 81
Inj : 1
Inj Volume : 4.000 µl



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.632	BB	0.1864	2012.38794	167.17357	50.2800
2	10.340	BB	0.1886	1989.97559	162.84615	49.7200
Totals :				4002.36353	330.01971	



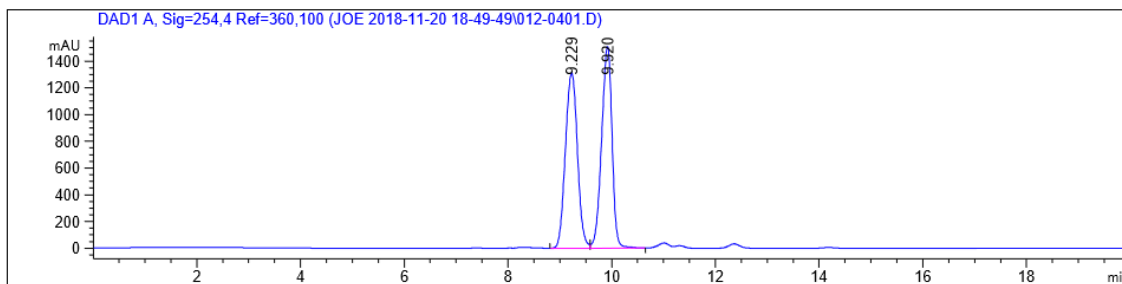
(S)-(2-Isobutylcyclopent-2-en-1-yl)(phenyl)methanone (2e)

According to the General Procedure **D**, 8-methyl-1-phenylnon-5-yn-1-one **1e** (45.7 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2e** (44.4 mg, 97%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 5.86 – 5.45 (m, 1H), 4.40 (t, *J* = 7.5 Hz, 1H), 2.56 – 2.44 (m, 1H), 2.44 – 2.27 (m, 2H), 2.10 – 1.99 (m, 1H), 1.96 – 1.89 (m, 2H), 1.74 – 1.62 (m, 1H), 0.97 – 0.70 (m, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 202.55, 142.17, 137.20, 132.87, 128.67, 128.57, 128.48, 54.68, 39.35, 31.61, 29.75, 26.42, 23.14, 22.06; IR (neat) 2949, 2924, 2864, 1676, 1461, 1445, 1364, 1205, 958, 849, 779 cm⁻¹; HRMS (DART) *m/z* Calcd for C₁₆H₂₁O (MH⁺): 229.1587; found: 229.1576; HPLC (Chiralcel OD-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; tr = 9.2 min (major), 9.9 min (minor); 96:4 er); [α]_D²⁵ = -24.9° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

```

Acq. Operator   : SYSTEM                      Seq. Line :    4
Acq. Instrument : Wasa_LC1                    Location  :   12
Injection Date  : 11/20/2018 9:34:41 PM      Inj       :    1
                                           Inj Volume: 4.000 µl
Method          : C:\Chem32\1\Data\JOE 2018-11-20 18-49-49\column3 1%IPA 99% hexane 20min-0.5mL.M (Sequence Method)
Last changed    : 11/20/2018 6:49:53 PM by SYSTEM
Method Info     : Column3 20min-1% iPrOH 99% hexane-0.5mL

```

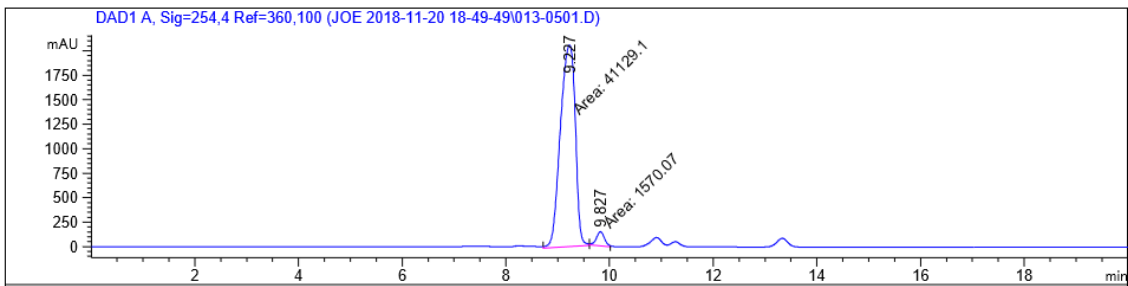


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.229	BV	0.2560	2.11567e4	1313.11548	50.0211
2	9.920	VB	0.2194	2.11388e4	1508.86450	49.9789

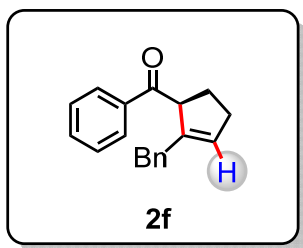
Totals : 4.22955e4 2821.97998

Acq. Operator : SYSTEM Seq. Line : 5
 Acq. Instrument : Wasa_LC1 Location : 13
 Injection Date : 11/20/2018 9:55:37 PM Inj : 1
 Inj Volume : 4.000 µl
 Method : C:\Chem32\1\Data\JOE 2018-11-20 18-49-49\column3 1%IPA 99% hexane 20min-0.5mL.M (Sequence Method)
 Last changed : 11/20/2018 6:49:53 PM by SYSTEM
 Method Info : Column3 20min-1% iPrOH 99% hexane-0.5mL



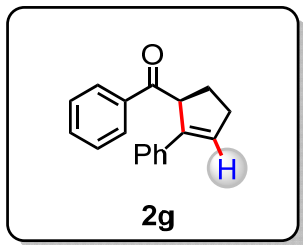
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.227	MM	0.3331	4.11291e4	2058.13403	96.3230
2	9.827	MM	0.1823	1570.07068	143.57298	3.6770
Totals :				4.26992e4	2201.70702	



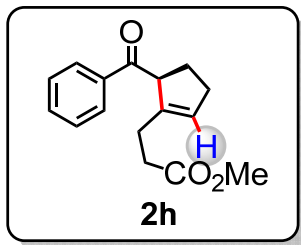
(S)-(2-Benzylcyclopent-2-en-1-yl)(phenyl)methanone (2f)

According to the General Procedure **D**, 1,7-diphenylhept-5-yn-1-one **1f** (52.5 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2f** (43.2 mg, 80%) as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 7.88 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.23 (dd, *J* = 13.4, 6.3 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 5.62 (s, 1H), 4.38 – 4.25 (m, 1H), 3.56 (d, *J* = 15.5 Hz, 1H), 3.23 (d, *J* = 15.4 Hz, 1H), 2.56 – 2.44 (m, 1H), 2.44 – 2.27 (m, 2H), 2.10 – 2.01 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 202.41, 142.36, 139.41, 137.03, 132.92, 129.75, 128.98, 128.53, 128.51, 128.29, 126.03, 53.91, 36.64, 31.59, 29.79; **IR** (neat) 3058, 3024, 2931, 1674, 1594, 1447, 1211, 1072, 1025, 758, 700 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₉H₁₉O (MH⁺): 263.1430; found: 263.1431; **HPLC** (Chiralcel OD-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; tr = 12.1 min (minor) , 13.2 min (major); 98:2 er); [α]_D²⁵ = -14.1° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.



(S)-Phenyl(2-phenylcyclopent-2-en-1-yl)methanone (2g)

According to the General Procedure **D**, 1,6-diphenylhex-5-yn-1-one **1g** (49.6 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % Et₂O in hexanes) to give **2g** (24.8 mg, 50%) as a colorless solid. ¹H NMR (600 MHz, CDCl₃) δ 8.06 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.49 – 6.44 (m, 1H), 4.95 (d, *J* = 11.7 Hz, 1H), 2.73 – 2.50 (m, 3H), 2.17 – 2.10 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 201.11, 141.64, 136.52, 135.57, 133.05, 130.12, 128.69, 128.65, 128.37, 127.07, 125.78, 53.48, 32.39, 30.06; IR (neat) 3052, 3025, 2937, 2843, 1678, 1577, 1445, 1207, 980, 752, 690 cm⁻¹; HRMS (DART) *m/z* Calcd for C₁₈H₁₇O (MH⁺): 249.12739; found: 249.12799; HPLC (Chiralcel OD-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; tr = 20.6 min (minor), 26.6 min (major); 91:9 er); [α]²⁵_D = -34.6° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.



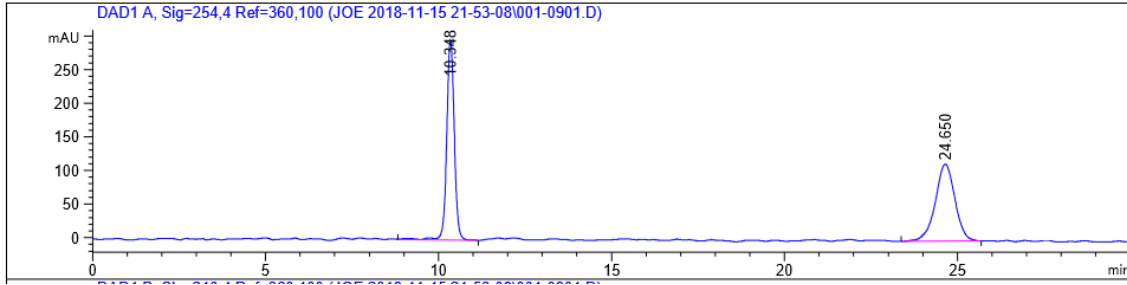
Methyl (*S*)-3-(5-benzoylcyclopent-1-en-1-yl)propanoate (2h)

According to the General Procedure C, methyl 9-oxo-9-phenylnon-4-ynoate **1h** (51.7 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2h** (50.1 mg, 97%) as a colorless oil. **¹H NMR** (600 MHz, CDCl₃) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.66 (s, 1H), 4.45 (d, *J* = 7.1 Hz, 1H), 3.63 (s, 3H), 2.54 – 2.44 (m, 3H), 2.44 – 2.35 (m, 3H), 2.34 – 2.27 (m, 1H), 2.13 – 1.96 (m, 1H); **¹³C NMR** (151 MHz, CDCl₃) δ 204.66, 176.22, 144.01, 139.51, 135.69, 131.29, 131.18, 130.66, 57.68, 54.19, 35.13, 34.31, 32.34, 27.85; **IR** (neat) 2920, 2849, 1734, 1676, 1445, 1342, 1208, 1162, 1000, 701, 670 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₆H₁₉O₃ (MH⁺): 259.1329; found: 259.1335; **HPLC** (Chiralcel OD-H; 5%/ 95% isopropanol/ hexanes, 1.0 mL/min; tr = 10.3 min (minor), 24.6 min (major); 94:6 er); [α]_D²⁵ = +1.7° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

```

Acq. Operator   : SYSTEM                      Seq. Line :    9
Acq. Instrument : Wasa_LC1                    Location  :    1
Injection Date  : 11/16/2018 6:02:44 AM      Inj       :    1
                                                    Inj Volume: 4.000 µl
Acq. Method     : C:\Chem32\1\Data\JOE 2018-11-15 21-53-08\column3 5% IPA 95% hex 60min-1.0ml
                                                    .M
Last changed    : 11/15/2018 9:53:12 PM by SYSTEM
Analysis Method : C:\Chem32\1\Data\JOE 2018-11-15 21-53-08\column3 5% IPA 95% hex 60min-1.0ml
                                                    .M (Sequence Method)

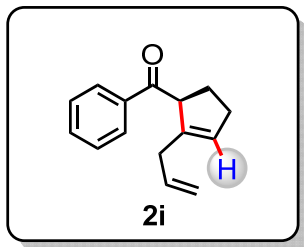
```



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.348	VB R	0.2295	4508.04883	297.70328	49.9701
2	24.650	BB	0.5998	4513.44385	114.50896	50.0299

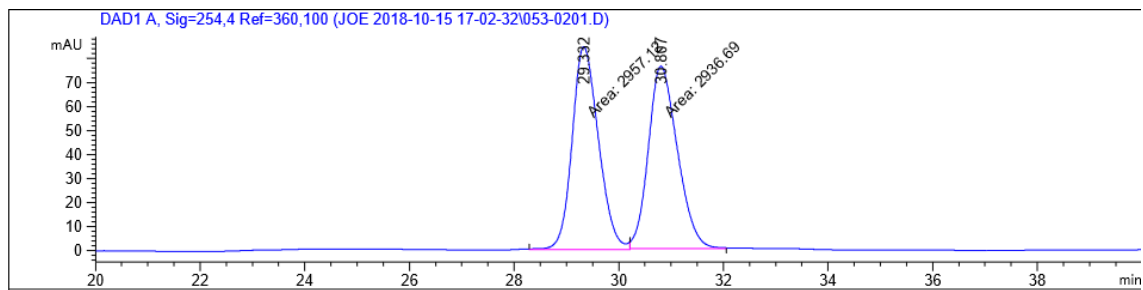
Totals : 9021.49268 412.21224



(S)-(2-Allylcyclopent-2-en-1-yl)(phenyl)methanone (2i)

According to the General Procedure C, 1-phenylnon-8-en-5-yn-1-one **1i** (42.5 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % Et₂O in hexanes) to give **2i** (40.0 mg, 94%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, *J* = 8.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 5.87 – 5.74 (m, 1H), 5.72 – 5.64 (m, 1H), 5.02 – 4.89 (m, 2H), 4.44 (t, *J* = 7.5 Hz, 1H), 2.91 (dd, *J* = 16.3, 6.0 Hz, 1H), 2.70 (dd, *J* = 16.2, 7.5 Hz, 1H), 2.55 – 2.45 (m, 1H), 2.44 – 2.30 (m, 2H), 2.11 – 2.00 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 202.29, 141.28, 137.10, 135.78, 132.95, 128.80, 128.57, 128.52, 116.14, 54.42, 34.61, 31.68, 29.68; IR (neat) 3059, 2936, 1711, 1674, 1578, 1407, 1211, 1177, 1000, 861, 700 cm⁻¹; HRMS (DART) *m/z* Calcd for C₁₅H₁₇O (MH⁺): 213.12739; found: 213.12726; HPLC (Chiralcel OD-H; 0.3%/ 99.7% isopropanol/ hexanes, 0.5 mL/min; tr = 30.4 min (major), 32.2 min (minor); 97:3 er); [α]_D²⁵ = -1.5° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

Acq. Operator : SYSTEM Seq. Line : 2
Acq. Instrument : Wasa_LC1 Location : 53
Injection Date : 10/15/2018 6:05:25 PM Inj : 1
 Inj Volume : 4.000 µl
Acq. Method : C:\Chem32\1\Data\JOE 2018-10-15 17-02-32\column3 0.3% IPA 99.7% hex 60min-0
 .Sml.M
Last changed : 10/15/2018 5:02:35 PM by SYSTEM
Analysis Method : C:\Chem32\1\Data\JOE 2018-10-15 17-02-32\column3 0.3% IPA 99.7% hex 60min-0
 .Sml.M (Sequence Method)



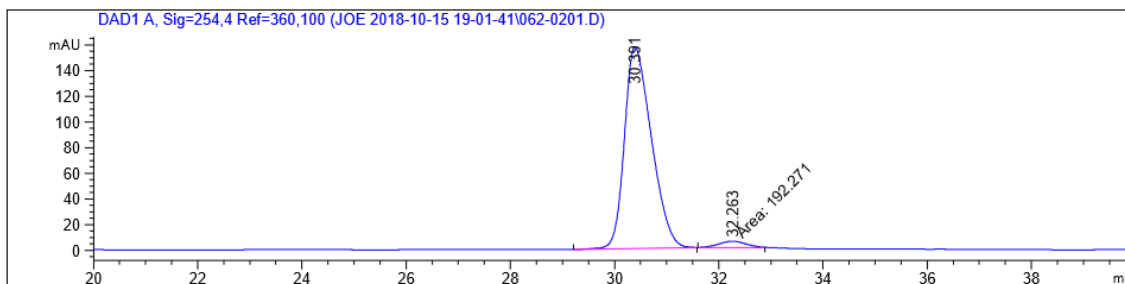
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.332	MM	0.5842	2957.11914	84.36610	50.1733
2	30.807	MM	0.6442	2936.69336	75.97674	49.8267

Totals : 5893.81250 160.34284

```

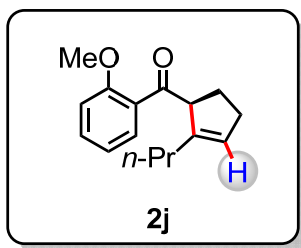
Acq. Operator   : SYSTEM                      Seq. Line :    2
Acq. Instrument : Wasa_LC1                   Location  :   62
Injection Date  : 10/15/2018 7:43:43 PM      Inj       :    1
                                          Inj Volume: 4.000 µl
Acq. Method     : C:\Chem32\1\Data\JOE 2018-10-15 19-01-41\column3 0.3% IPA 99.7% hex 40min-0
                                          .5ml.M
Last changed    : 10/15/2018 7:01:44 PM by SYSTEM
Analysis Method : C:\Chem32\1\Data\JOE 2018-10-15 19-01-41\column3 0.3% IPA 99.7% hex 40min-0
                                          .5ml.M (Sequence Method)
  
```



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

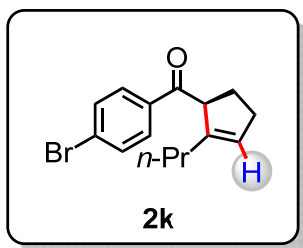
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.391	BB	0.5504	5657.95703	157.00883	96.7134
2	32.263	MM	0.6373	192.27145	5.02845	3.2866

Totals : 5850.22849 162.03728



(S)-(2-Methoxyphenyl)(2-propylcyclopent-2-en-1-yl)methanone (2j)

According to the General Procedure C, 1-(2-methoxyphenyl)non-5-yn-1-one **1j** (48.9 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2j** (46.4 mg, 95%) as a colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.55 (d, $J = 9.1$ Hz, 1H), 7.44 (t, $J = 7.0$ Hz, 1H), 7.00 (t, $J = 7.5$ Hz, 1H), 6.96 (d, $J = 8.3$ Hz, 1H), 5.62 – 5.55 (m, 1H), 4.48 – 4.36 (m, 1H), 3.89 (s, 3H), 2.48 – 2.38 (m, 1H), 2.35 – 2.27 (m, 1H), 2.26 – 2.19 (m, 1H), 2.09 – 2.00 (m, 2H), 1.97 – 1.89 (m, 1H), 1.48 – 1.35 (m, 2H), 0.85 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 206.35, 158.03, 143.88, 132.81, 129.91, 129.87, 127.03, 120.67, 111.44, 59.09, 55.48, 32.16, 31.37, 29.38, 20.84, 14.02; **IR** (neat) 2954, 2928, 2867, 2847, 1671, 1595, 1483, 1462, 1435, 1281, 1243, 1021, 999, 754 cm^{-1} ; **HRMS** (DART) m/z Calcd for $\text{C}_{16}\text{H}_{21}\text{O}_2$ (MH^+): 245.15361; found: 245.15409; **HPLC** (Chiralcel OD-H; 1%/99% isopropanol/ hexanes, 0.5 mL/min; $t_r = 14.6$ min (major), 16.4 min (minor); 93:7 er); $[\alpha]_D^{25} = -45.0^\circ$ ($c = 1.0$, CH_2Cl_2). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

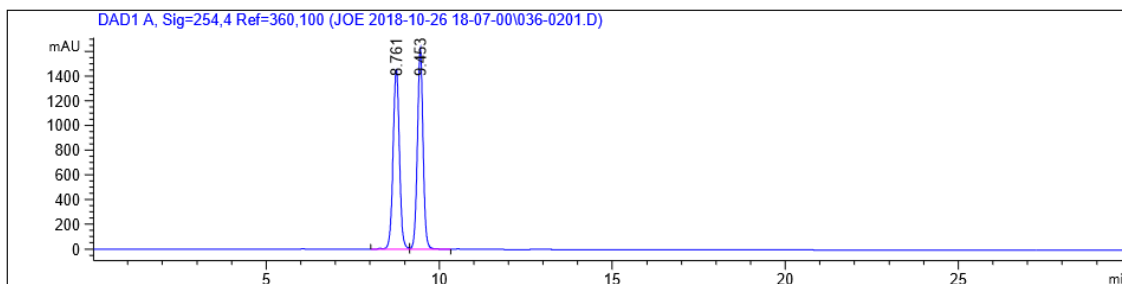


(S)-(4-Bromophenyl)(2-propylcyclopent-2-en-1-yl)methanone (2k)

According to the General Procedure C, 1-(2-methoxyphenyl)non-5-yn-1-one **1k** (58.6 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2j** (56.8 mg, 97%) as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 5.67 – 5.59 (m, 1H), 4.41 – 4.25 (m, 1H), 2.53 – 2.45 (m, 1H), 2.43 – 2.26 (m, 2H), 2.09 – 1.98 (m, 2H), 1.97 – 1.87 (m, 1H), 1.51 – 1.35 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 201.52, 142.93, 135.83, 131.89, 130.03, 128.08, 127.52, 55.00, 32.10, 31.64, 29.55, 20.87, 13.96; **IR** (neat) 2956, 2928, 2869, 1706, 1675, 1581, 1208, 1102, 1068, 839, 756 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₅H₁₈OBr (MH⁺): 293.05355; found: 293.05226; **HPLC** (Chiralcel OD-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; tr = 8.7 min (major), 9.4 min (minor); 97:3 er); [α]_D²⁵ = -27.2° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

Acq. Operator : SYSTEM
 Acq. Instrument : Wasa_LC1
 Injection Date : 10/26/2018 6:39:50 PM
 Method : C:\Chem32\1\Data\JOE 2018-10-26 18-07-00\column3 1% IPA 99% hex 30min-0.5ml.M (Sequence Method)
 Last changed : 10/26/2018 6:07:03 PM by SYSTEM

Seq. Line : 2
 Location : 36
 Inj : 1
 Inj Volume : 4.000 µl



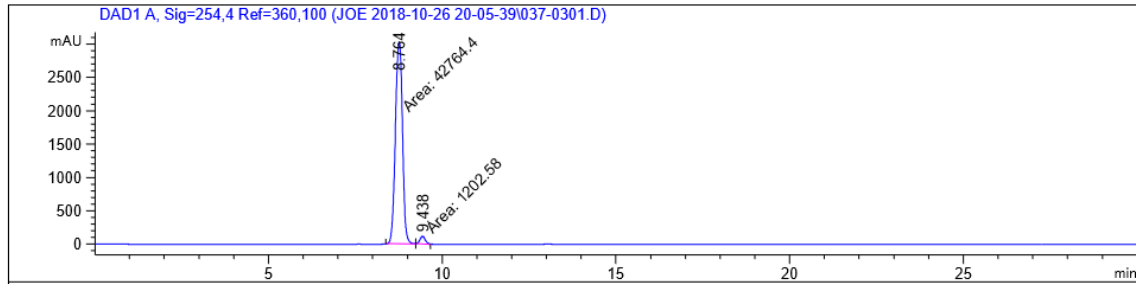
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.761	VV R	0.1948	1.86652e4	1457.95239	49.8964
2	9.453	VB	0.1758	1.87427e4	1634.13538	50.1036

Totals : 3.74079e4 3092.08777

Acq. Operator : SYSTEM
Acq. Instrument : Wasa LC1
Injection Date : 10/26/2018 9:09:24 PM
Method : C:\Chem32\1\Data\JOE 2018-10-26 20-05-39\column3 1% IPA 99% hex 30min-0.5ml.M (Sequence Method)
Last changed : 10/26/2018 8:05:41 PM by SYSTEM

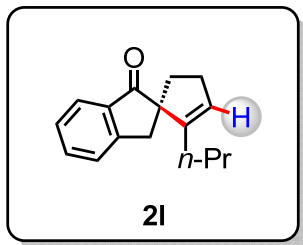
Seq. Line : 3
Location : 37
Inj : 1
Inj Volume : 4.000 µl



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.764	MM	0.2357	4.27644e4	3023.44922	97.2648
2	9.438	MM	0.1751	1202.58374	114.45716	2.7352

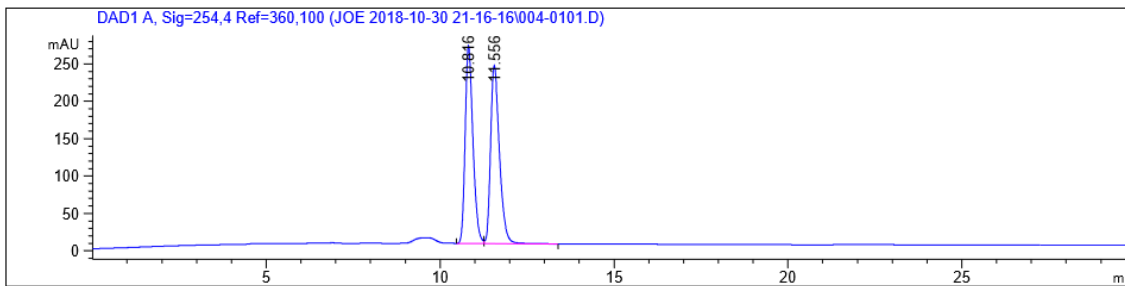
Totals : 4.39669e4 3137.90638



(R)-2-Propylspiro[cyclopentane-1,2'-inden]-2-en-1'(3'H)-one (2I)

According to the General Procedure C, 2-(hept-3-yn-1-yl)-2,3-dihydro-1*H*-inden-1-one **1I** (45.3 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using *N*-methylpiperidine as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2I** (44.4 mg, 98%) as a pale yellow oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 5.70 – 5.63 (m, 1H), 3.24 (d, *J* = 17.4 Hz, 1H), 3.08 (d, *J* = 17.4 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.50 – 2.35 (m, 2H), 1.95 – 1.85 (m, 1H), 1.73 – 1.64 (m, 2H), 1.51 – 1.32 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 213.24, 155.99, 148.63, 139.37, 137.47, 130.05, 129.49, 129.00, 126.73, 67.30, 42.38, 40.60, 33.51, 32.29, 23.50, 16.72; **IR** (neat) 2953, 2926, 2868, 2847, 1704, 1604, 1462, 1275, 909, 780, 729 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₆H₁₉O (MH⁺): 227.1430; found: 227.1429; **HPLC** (Chiralcel OD-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; tr = 10.7 min (minor), 11.5 min (major); 99:1 er); [α]_D²⁵ = -131.7° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

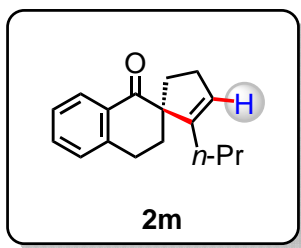
Acq. Operator : SYSTEM Seq. Line : 1
 Acq. Instrument : Wasa_LC1 Location : 4
 Injection Date : 10/30/2018 9:18:10 PM Inj : 1
Inj Volume : 4.000 µl
 Method : C:\Chem32\1\Data\JOE 2018-10-30 21-16-16\column4 1%IPA 99% hexane 30min-0.5mL.M (Sequence Method)
 Last changed : 10/30/2018 9:16:19 PM by SYSTEM
 Method Info : Column4 30min-1% iPrOH 99% hexane-0.5mL



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.816	BV	0.2395	4120.73535	264.92889	49.4271
2	11.556	VB	0.2704	4216.26660	238.31940	50.5729

Totals : 8337.00195 503.24829



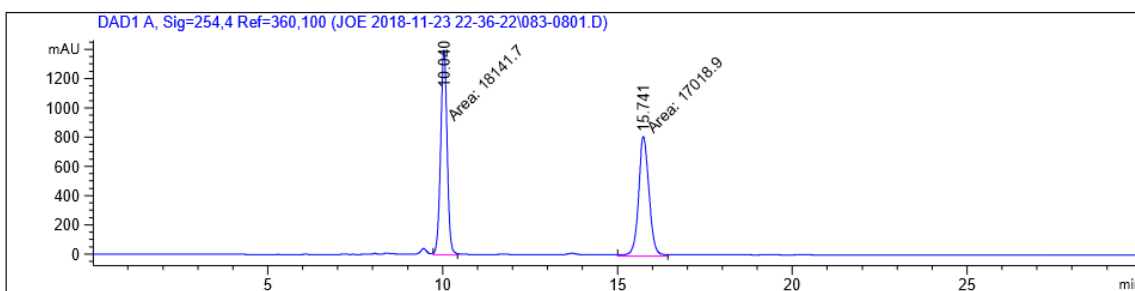
(R)-2-Propyl-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-2-en-1'-one (2m)

According to the General Procedure **D**, 2-(hept-3-yn-1-yl)-3,4-dihydronaphthalen-1(2*H*)-one **1m** (48.1 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using *N*-methylpiperidine as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2m** (9.6 mg, 20%) as a pale yellow oil. **¹H NMR** (600 MHz, CDCl₃) δ 8.06 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 5.65 (s, 1H), 3.24 – 3.08 (m, 1H), 2.98 – 2.86 (m, 1H), 2.45 – 2.36 (m, 1H), 2.35 (dd, *J* = 4.4, 2.4 Hz, 2H), 2.05 (t, *J* = 6.9 Hz, 2H), 1.96 – 1.81 (m, 3H), 1.61 – 1.45 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 203.22, 149.39, 146.32, 135.73, 134.68, 131.15, 130.64, 129.28, 128.58, 64.11, 36.59, 35.00, 32.80, 32.37, 29.02, 23.72, 16.92; **IR** (neat) 2952, 2924, 2867, 2848, 1674, 1597, 1431, 1215, 904, 831, 789 cm⁻¹; HRMS (DART) *m/z* Calcd for C₁₇H₂₁O (MH⁺): 241.15869; found: 241.15884; **HPLC** (Chiralcel OD-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; tr = 10.0 min (major), 15.7 min (minor); 98:2 er); [α]_D²⁵ = -12.3° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

```

Acq. Operator   : SYSTEM                               Seq. Line :    8
Acq. Instrument : Wasa_LC1                             Location  :   83
Injection Date  : 11/24/2018 5:04:10 AM                Inj       :    1
                                                    Inj Volume: 4.000 µl
Method          : C:\Chem32\1\Data\JOE 2018-11-23 22-36-22\column3 1% IPA 99% hex 30min-0.5ml
                                                    .M (Sequence Method)
Last changed    : 11/23/2018 10:36:26 PM by SYSTEM

```



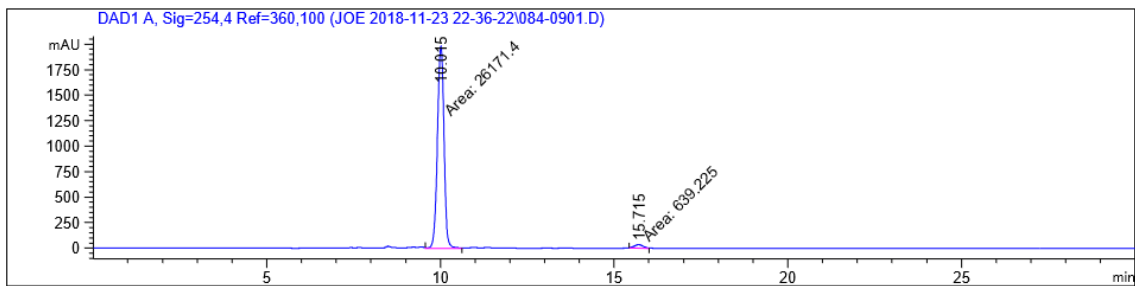
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.040	MM	0.2158	1.81417e4	1400.84106	51.5967
2	15.741	MM	0.3471	1.70189e4	817.21051	48.4033

Totals : 3.51607e4 2218.05157

Acq. Operator : SYSTEM
 Acq. Instrument : Wasa_LC1
 Injection Date : 11/24/2018 5:35:06 AM
 Method : C:\Chem32\1\Data\JOE 2018-11-23 22-36-22\column3 1% IPA 99% hex 30min-0.5ml.M (Sequence Method)
 Last changed : 11/23/2018 10:36:26 PM by SYSTEM
 Additional Info : Peak(s) manually integrated

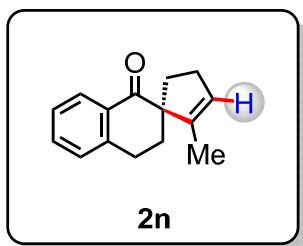
Seq. Line : 9
 Location : 84
 Inj : 1
 Inj Volume : 4.000 µl



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.015	MM	0.2197	2.61714e4	1985.49268	97.6158
2	15.715	MM	0.3074	639.22522	34.66180	2.3842

Totals : 2.68107e4 2020.15448

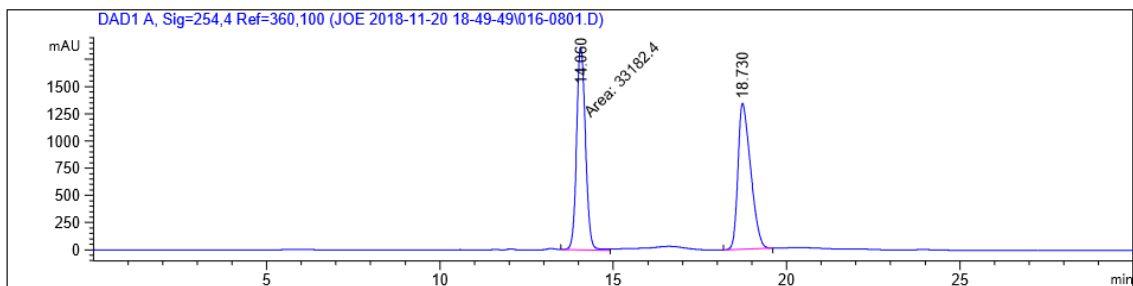


(R)-2-Methyl-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-2-en-1'-one

According to the General Procedure **D**, 2-(pent-3-yn-1-yl)-3,4-dihydronaphthalen-1(2*H*)-one **1n** (42.5 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using *N*-methylpiperidine as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2n** (31.0 mg, 73%) as a pale yellow oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.05 (d, $J = 7.8$ Hz, 1H), 7.45 (t, $J = 7.4$ Hz, 1H), 7.29 (t, $J = 7.5$ Hz, 1H), 7.23 (d, $J = 7.6$ Hz, 1H), 5.65 – 5.60 (m, 1H), 3.19 – 3.09 (m, 1H), 2.96 – 2.87 (m, 1H), 2.40 – 2.34 (m, 1H), 2.34 – 2.29 (m, 1H), 2.11 – 1.99 (m, 2H), 1.91 – 1.80 (m, 1H), 1.65 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 203.14, 146.36, 144.77, 135.78, 134.64, 131.19, 130.64, 130.56, 129.27, 63.82, 36.31, 34.72, 32.34, 28.96, 16.11; **IR** (neat) 2848, 2765, 1674, 1597, 1375, 1216, 1021, 900, 830, 738, 486 cm^{-1} ; HRMS (DART) Calcd for $\text{C}_{15}\text{H}_{15}\text{O}$ (MH^+): 213.12739; found: 213.12669; **HPLC** (Chiralcel OD-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; tr = 14.0 min (major), 18.7 min (minor); 91:9 er); $[\alpha]_{\text{D}}^{25} = -21.1^\circ$ (c = 1.0, CH_2Cl_2). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.


```

Acq. Operator   : SYSTEM                               Seq. Line :    8
Acq. Instrument : Wasa_LC1                             Location  :   16
Injection Date  : 11/20/2018 11:18:28 PM              Inj       :    1
                                                    Inj Volume: 4.000 µl
Method          : C:\Chem32\1\Data\JOE 2018-11-20 18-49-49\column3 1% IPA 99% hex 30min-0.5ml
                .M (Sequence Method)
Last changed    : 11/20/2018 6:49:53 PM by SYSTEM
  
```



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

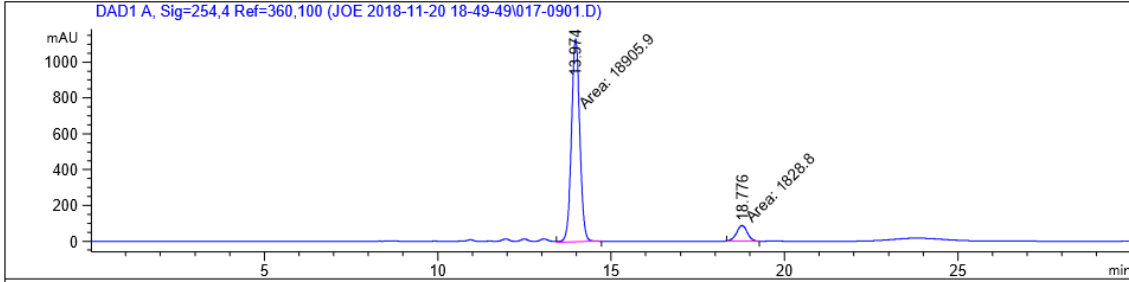
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.060	MM	0.2969	3.31824e4	1862.94519	49.2553
2	18.730	BB	0.3908	3.41858e4	1343.65039	50.7447

Totals : 6.73682e4 3206.59558

```

Acq. Operator   : SYSTEM                      Seq. Line :    9
Acq. Instrument : Wasa_LC1                    Location  :   17
Injection Date  : 11/20/2018 11:49:25 PM     Inj       :    1
                                          Inj Volume: 4.000 µl
Method          : C:\Chem32\1\Data\JOE 2018-11-20 18-49-49\column3 1% IPA 99% hex 30min-0.5ml
                  .M (Sequence Method)
Last changed    : 11/20/2018 6:49:53 PM by SYSTEM

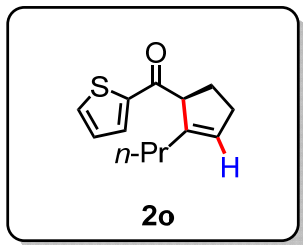
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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.974	MM	0.2783	1.89059e4	1132.41357	91.1800
2	18.776	MM	0.3532	1828.79651	86.29856	8.8200

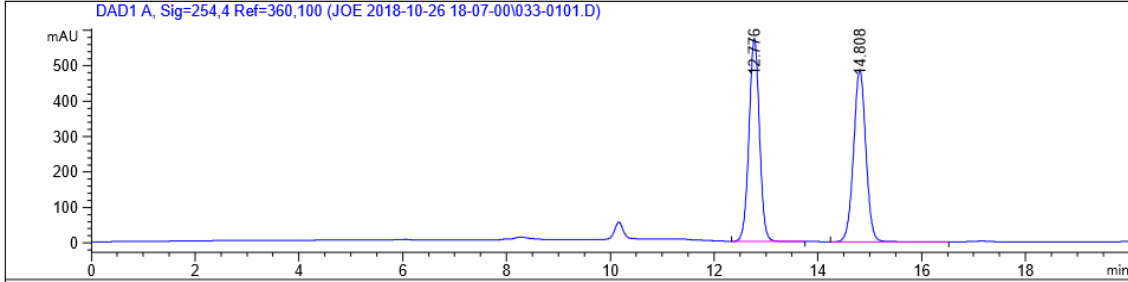
Totals : 2.07347e4 1218.71214



(S)-(2-Propylcyclopent-2-en-1-yl)(thiophen-2-yl)methanone (2o)

According to the General Procedure C, 1-(thiophen-2-yl)non-5-yn-1-one **1o** (44.1 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2o** (43.7 mg, 99%) as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 7.78 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.64 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.14 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.64 (d, *J* = 1.6 Hz, 1H), 4.24 (t, *J* = 6.8 Hz, 1H), 2.58 – 2.47 (m, 1H), 2.45 – 2.36 (m, 1H), 2.36 – 2.27 (m, 1H), 2.18 – 2.09 (m, 1H), 2.09 – 2.00 (m, 1H), 2.00 – 1.91 (m, 1H), 1.54 – 1.36 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 195.69, 144.56, 143.01, 133.68, 131.99, 128.11, 127.68, 56.75, 32.04, 31.79, 29.77, 20.87, 13.96; **IR** (neat) 2953, 2926, 2866, 1652, 1410, 1231, 1207, 1060, 892, 860, 720 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₃H₁₇OS (MH⁺): 221.0995; found: 221.0998; **HPLC** (Chiralcel OD-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; tr = 12.8 min (major), 14.8 min (minor); 98:2 er); [α]_D²⁵ = -89.5° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

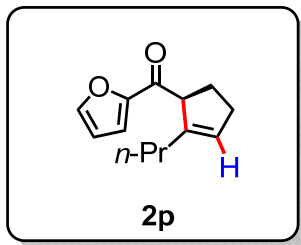
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Acq. Instrument : Wasa_LC1
Injection Date : 10/26/2018 6:08:53 PM
Seq. Line : 1
Location : 33
Inj : 1
Inj Volume : 4.000 µl
Acq. Method : C:\Chem32\1\Data\JOE 2018-10-26 18-07-00\column3 1% IPA 99% hex 30min-0.5ml.M
Last changed : 10/26/2018 6:07:03 PM by SYSTEM
Analysis Method : C:\Chem32\1\Data\JOE 2018-10-26 18-07-00\column3 1% IPA 99% hex 30min-0.5ml.M (Sequence Method)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

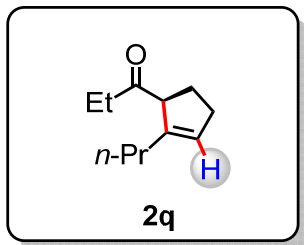
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.776	BB	0.2154	8034.31201	573.58746	50.0399
2	14.808	BB	0.2545	8021.49268	486.06281	49.9601

Totals : 1.60558e4 1059.65027



(S)-Furan-2-yl(2-propylcyclopent-2-en-1-yl)methanone (2p)

According to the General Procedure C, 1-(furan-2-yl)non-5-yn-1-one **1p** (40.9 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **2p** (40.5 mg, 99%) as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 7.61 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.23 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.55 (dd, *J* = 3.6, 1.7 Hz, 1H), 5.63 (d, *J* = 1.7 Hz, 1H), 4.26 – 4.18 (m, 1H), 2.57 – 2.46 (m, 1H), 2.43 – 2.34 (m, 1H), 2.33 – 2.22 (m, 1H), 2.16 – 2.07 (m, 1H), 2.07 – 1.98 (m, 1H), 1.98 – 1.88 (m, 1H), 1.53 – 1.35 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 191.79, 152.78, 146.52, 142.82, 127.68, 117.54, 112.16, 55.47, 31.98, 31.72, 29.18, 20.83, 13.93; **IR** (neat) 2955, 2928, 1662, 1564, 1462, 1390, 1289, 1013, 811, 918, 593 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₃H₁₇O₂ (MH⁺): 205.1223; found: 205.1218; **HPLC** (Chiralcel OD-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; tr = 12.3 min (major), 15.7 min (minor); 97:3 er); [α]_D²⁵ = -103.8° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.



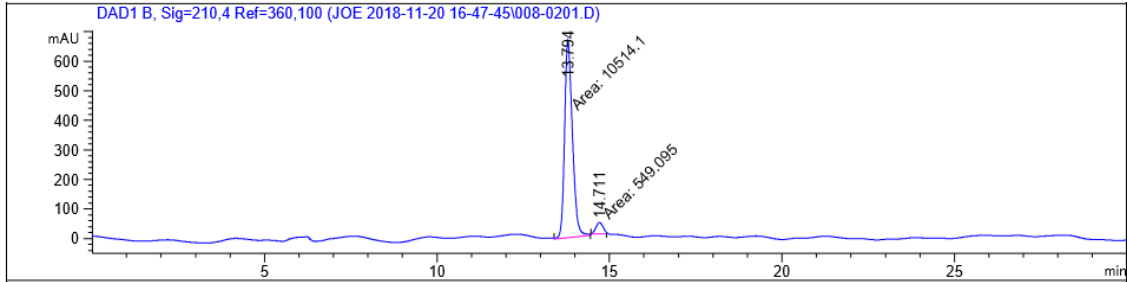
(S)-1-(2-Propylcyclopent-2-en-1-yl)propan-1-one (2q)

According to the General Procedure C, undec-7-yn-3-one **1q** (33.2 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % Et₂O in pentane) to give **2q** (30.2 mg, 91%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 5.58 (s, 1H), 3.51 (t, *J* = 9.0 Hz, 1H), 2.45 (q, *J* = 7.1 Hz, 3H), 2.41 – 2.30 (m, 1H), 2.20 – 2.10 (m, 1H), 2.04 – 1.87 (m, 3H), 1.54 – 1.36 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 216.66, 145.66, 130.17, 63.15, 36.08, 34.70, 34.43, 30.72, 23.45, 16.61, 10.52; IR (neat) 2955, 2924, 2869, 2850, 1704, 1457, 1376, 1181, 1111, 798 cm⁻¹; HRMS (DART) *m/z* Calcd for C₁₁H₁₉O (MH⁺): 167.14304; found: 167.14224; HPLC (Chiralcel OD-H; 0.3%/ 99.7% isopropanol/ hexanes, 0.5 mL/min; *t_r* = 13.9 min (major), 14.7 min (minor); 95:5 er); [α]_D²⁵ = -189.3° (*c* = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.


```

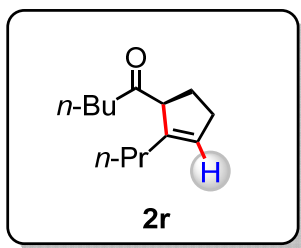
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Acq. Instrument : Wasa_LC1                   Location  :    8
Injection Date  : 11/20/2018 5:19:50 PM     Inj       :    1
                                          Inj Volume: 4.000 µl
Method          : C:\Chem32\1\Data\JOE 2018-11-20 16-47-45\column3 0.3% IPA 99.7% hex 30min-0
                  .5ml.M (Sequence Method)
Last changed    : 11/20/2018 4:47:48 PM by SYSTEM

```



Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.794	MM	0.2625	1.05141e4	667.44690	95.0367
2	14.711	MM	0.2392	549.09467	38.26130	4.9633
Totals :				1.10632e4	705.70820	

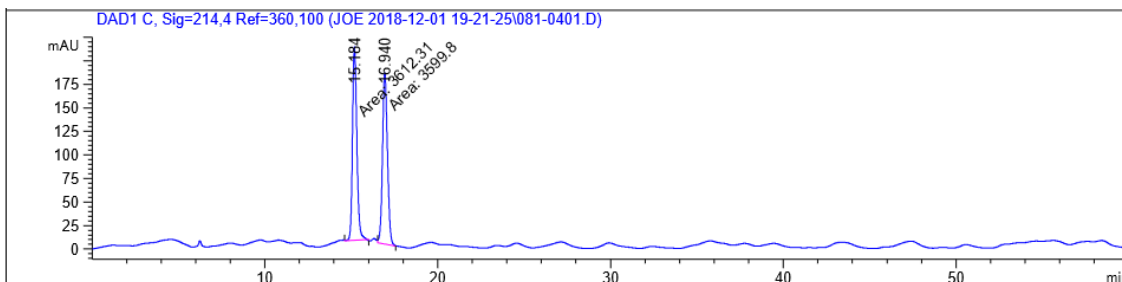


(S)-1-(2-Propylcyclopent-2-en-1-yl)pentan-1-one (2r)

According to the General Procedure C, tridec-9-yn-5-one **1r** (38.9 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using PMP as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % Et₂O in pentane) to give **2r** (30.3 mg, 78%) as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 5.61 – 5.55 (m, 1H), 3.49 (d, *J* = 5.8 Hz, 1H), 2.51 – 2.40 (m, 3H), 2.40 – 2.32 (m, 1H), 2.19 – 2.09 (m, 1H), 2.04 – 1.87 (m, 3H), 1.58 – 1.52 (m, 2H), 1.52 – 1.37 (m, 2H), 1.30 (h, *J* = 7.4 Hz, 2H), 0.95 – 0.84 (m, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 216.22, 145.64, 130.19, 63.33, 42.69, 34.69, 34.43, 30.61, 28.47, 25.06, 23.45, 16.61, 16.54; IR (neat) 2954, 2928, 2869, 1703, 1461, 1405, 1377, 1125, 1060 cm⁻¹; HRMS (DART) *m/z* Calcd for C₁₃H₂₃O (MH⁺): 195.17434; found: 195.17326; HPLC (Chiralcel OD-H; 0.3%/ 99.7% isopropanol/ hexanes, 0.5 mL/min; tr = 14.4 min (major), 16.1 min (minor); 96:4 er); [α]_D²⁵ = -136.9° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

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 Last changed : 12/1/2018 7:21:28 PM by SYSTEM

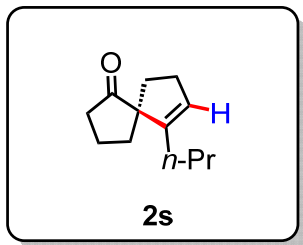
Seq. Line : 4
 Location : 81
 Inj : 1
 Inj Volume : 4.000 µl



Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.184	MM	0.2931	3612.30859	205.42609	50.0867
2	16.940	MM	0.3289	3599.79712	182.43704	49.9133

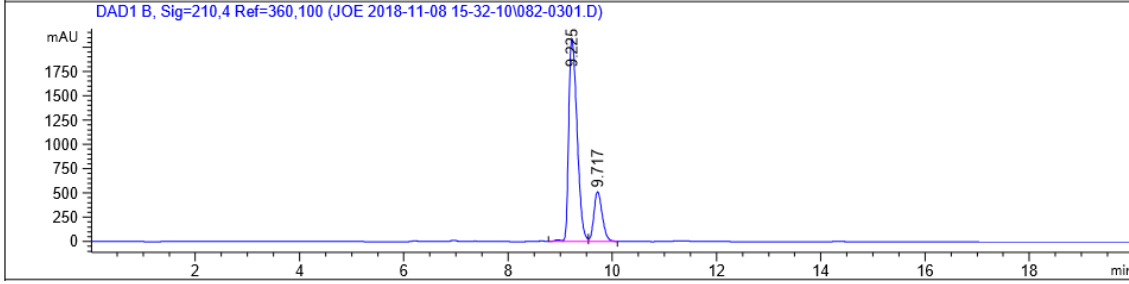
Totals : 7212.10571 387.86313



(S)-6-Propylspiro[4.4]non-6-en-1-one (2s)

According to the General Procedure C, 2-(hept-3-yn-1-yl)cyclopentan-1-one **1s** (35.7 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using *N*-methylpiperidine as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % Et₂O in pentane) to give **2s** (28.4 mg, 82%) as a colorless oil. **¹H NMR** (500 MHz, CDCl₃) δ 5.65 – 5.59 (m, 1H), 2.45 – 2.26 (m, 3H), 2.23 – 2.10 (m, 1H), 2.10 – 2.00 (m, 3H), 1.91 – 1.78 (m, 4H), 1.78 – 1.71 (m, 1H), 1.58 – 1.38 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 222.72, 145.09, 126.90, 64.61, 38.05, 36.91, 34.51, 30.14, 20.93, 20.06, 14.15; **IR** (neat) 2953, 2924, 2867, 1730, 1449, 1121, 1092, 959, 890, 817, 790 cm⁻¹; **HRMS** (DART) *m/z* Calcd for C₁₂H₁₉O (MH⁺): 179.14304; found: 179.14233; HPLC (Chiralcel OJ-H; 0.5%/ 99.5% isopropanol/ hexanes, 0.5 mL/min; tr = 9.2 min (major), 9.7 min (minor); 80:20 er); [α]_D²⁵ = -42.5° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

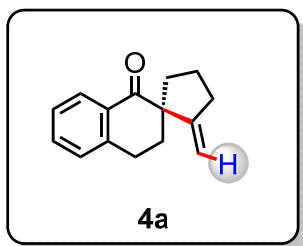
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 Acq. Instrument : Wasa_LC1 Location : 82
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Inj Volume : 4.000 µl
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 -0.5mL.M (Sequence Method)
 Last changed : 11/8/2018 3:32:13 PM by SYSTEM
 Method Info : Column4 20min-0.5% iPROH 99.5% hexane-0.5mL



Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.225	VV R	0.1751	2.32191e4	2087.54468	80.4174
2	9.717	VB	0.1734	5654.11865	509.70819	19.5826

Totals : 2.88732e4 2597.25287

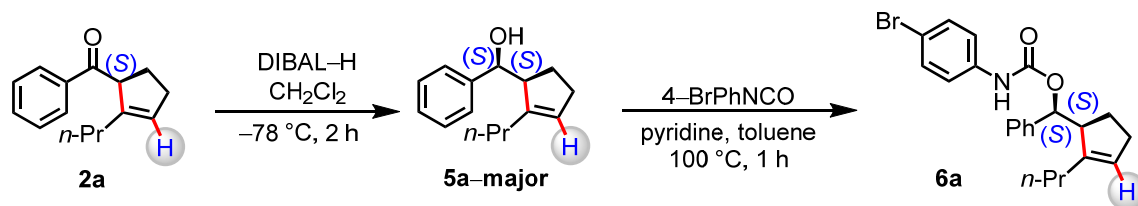


(R)-2-Methylene-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-1'-one (4a)

According to the General Procedure C, 2-(pent-4-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one¹³ **3a** (42.5 mg, 0.2 mmol) was subjected to the Conia-ene-type reaction using *N*-methylpiperidine as the Brønsted base catalyst. The product was purified by silica gel column chromatography (1.0 % EtOAc in hexanes) to give **4a** (41.6 mg, 98%) as a pale yellow oil. ¹H NMR (600 MHz, CDCl₃) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 5.01 (s, 1H), 4.65 (s, 1H), 3.12 – 3.01 (m, 1H), 3.01 – 2.91 (m, 1H), 2.67 – 2.54 (m, 1H), 2.53 – 2.43 (m, 1H), 2.41 – 2.29 (m, 1H), 2.29 – 2.18 (m, 1H), 2.04 – 1.90 (m, 1H), 1.87 – 1.76 (m, 1H), 1.76 – 1.65 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 203.13, 157.96, 146.40, 135.75, 134.78, 131.32, 130.73, 129.27, 109.75, 59.45, 39.27, 36.77, 36.63, 28.87, 25.51; IR (neat) 2829, 2874, 1677, 1598, 1452, 1430, 1317, 1218, 889, 740 cm⁻¹; HRMS (DART) Calcd for C₁₅H₁₇O (MH⁺): 213.12739; found: 213.12739; HPLC (Chiralcel OJ-H; 1%/ 99% isopropanol/ hexanes, 0.5 mL/min; tr = 15.6 min (major), 17.6 min (minor); 68:32 er); [α]_D²⁵ = +4.0° (c = 1.0, CH₂Cl₂). The absolute configuration for this product was assigned in analogy to that determined for product **2a**.

4. Determination of Absolute Configuration

To determine the absolute configuration of **2a**, it was first transformed to **6a** according to a literature procedure.¹⁶⁻¹⁷ **6a** was then recrystallized and its X-ray crystallographic analysis was carried out as described below.



(S)-Phenyl((S)-2-propylcyclopent-2-en-1-yl)methanol (**5a-major**)

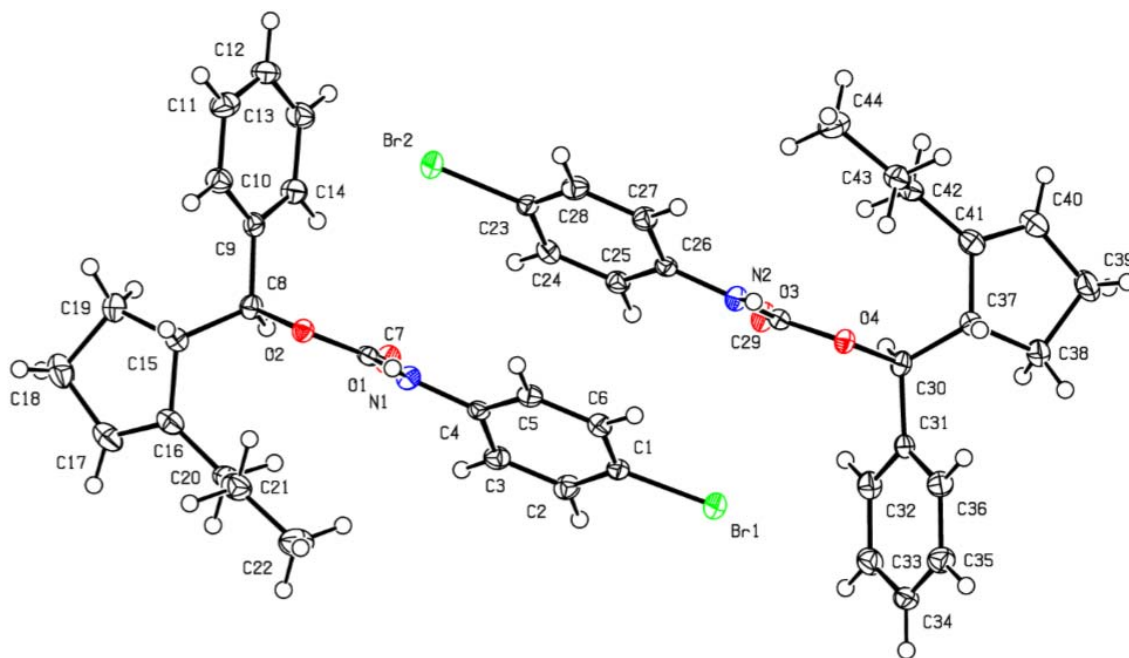
To a solution of (S)-phenyl(2-propylcyclopent-2-en-1-yl)methanone **2a** (642 mg, 3.0 mmol, 1.0 equiv.) in CH₂Cl₂ (0.1 M) was added DIBAL-H (1.7 g, 12 mmol, 4.0 equiv.), dropwise at -78 °C. The reaction mixture was allowed to stir for 2 h at -78 °C. Then, 1N HCl (30 mL) was added to the solution. The reaction mixture was extracted with CH₂Cl₂ (3 x 30 mL). The combined organic layers were washed with brine (2 x 50 mL) and dried over Na₂SO₄. After filtration and removal of the solvent, ¹H NMR analysis of the crude material revealed that **5a-major** and **5a-minor** were obtained in the ratio of 1.2:1.0. The crude material was purified by silica gel column chromatography (1.0 % Et₂O in hexanes) to give compound **5a-major** (314 mg, 48%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 5.45 (s, 1H), 4.73 (t, *J* = 5.1 Hz, 1H), 3.07 – 3.01 (m, 1H), 2.19 – 1.95 (m, 3H), 1.94 – 1.79 (m, 3H), 1.72 (ddd, *J* = 12.7, 8.6, 4.3 Hz, 1H), 1.52 – 1.33 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

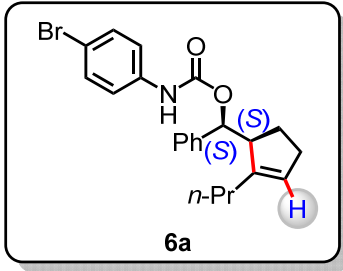
(S)-Phenyl((S)-2-propylcyclopent-2-en-1-yl)methyl (4-bromophenyl)carbamate (**6a**)

To a solution of **5a-major** (151 mg, 0.70 mmol, 1.0 equiv.) in toluene (0.035 M) were added *p*-bromophenyl isocyanate (416 mg, 2.1 mmol, 3.0 equiv.) and pyridine (277 mg, 3.5 mmol, 5.0 equiv.). The resulting heterogeneous solution was allowed to stir at 100 °C for 1 h. The solution was then cooled and filtered through a short plug of Celite using CH₂Cl₂. The filtrate was concentrated and the residue was purified by silica gel column chromatography (10 % EtOAc in hexanes) to give compound **6a** (261 mg, 90%) as a white solid. **6a** was

recrystallized using the vapor-vapor diffusion method, using EtOH to dissolve the product in an inner vial, and pentane as the precipitant placed in the outer vial in order for slow diffusion to occur into the inner vial. The solution was placed at 0 °C, whereupon a crystal was obtained for X-ray crystallographic analysis which revealed that the absolute configuration of **6a** is (*S,S*); see **SI Section 7** for X-ray crystallographic data.

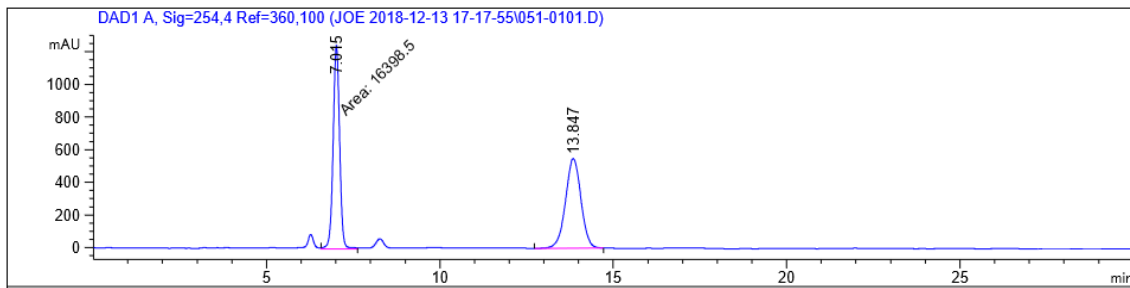
¹H NMR (500 MHz, CDCl₃) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 5.5 Hz, 4H), 7.30 – 7.24 (m, 4H), 6.64 (s, 1H), 5.74 (d, *J* = 6.6 Hz, 1H), 5.43 (s, 1H), 3.19 – 3.10 (m, 1H), 2.23 – 2.07 (m, 2H), 2.07 – 1.96 (m, 1H), 1.84 – 1.73 (m, 2H), 1.73 – 1.63 (m, 1H), 1.63 – 1.53 (m, 1H), 1.53 – 1.43 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 152.55, 144.32, 138.95, 136.99, 131.93, 127.99, 127.71, 127.48, 126.82, 120.21, 115.91, 79.11, 51.32, 32.57, 30.45, 26.88, 21.06, 14.10; **IR** (neat) 3313, 2953, 2926, 1697, 1592, 1530, 1488, 1396, 1305, 1217, 1073, 1045, 822, 698 cm⁻¹; **HRMS** (DART) Calcd for C₂₂H₂₅NO₂Br (MH⁺): 414.10632; found: 414.10436; **HPLC** (Chiralcel OD-H; 5%/ 95% isopropanol/ hexanes, 1.0 mL/min; tr = 13.8 min (major), 7.0 min (minor); 97:3 er); [α]_D²⁵ = -46.0° (c = 1.0, CH₂Cl₂).





Acq. Operator : SYSTEM
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 Method Info : column3 5% IPA 95% hex 30min-1.0ml.M

Seq. Line : 1
 Location : 51
 Inj : 1
 Inj Volume : 4.000 µl



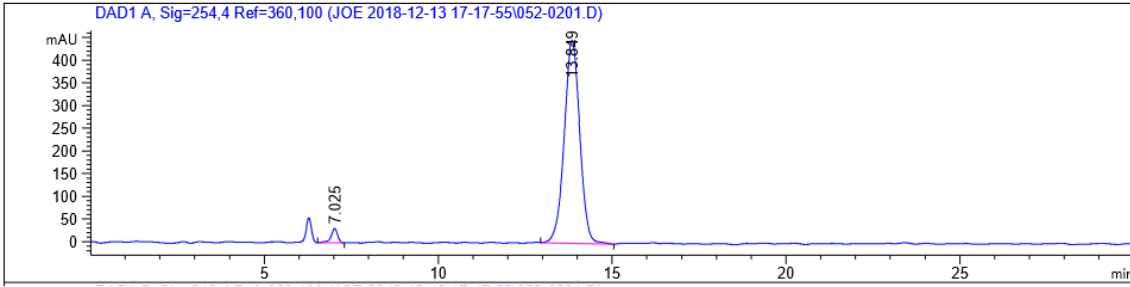
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1	7.015	MM	0.2188	1.63985e4	1248.84399	49.1235
2	13.847	BB	0.4789	1.69836e4	548.99237	50.8765

Totals : 3.33821e4 1797.83636

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Acq. Operator   : SYSTEM                      Seq. Line :    2
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                                           Inj Volume: 4.000 µl
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Last changed    : 12/13/2018 5:17:58 PM by SYSTEM
Method Info     : column3 5% IPA 95% hex 30min-1.0ml.M
  
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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

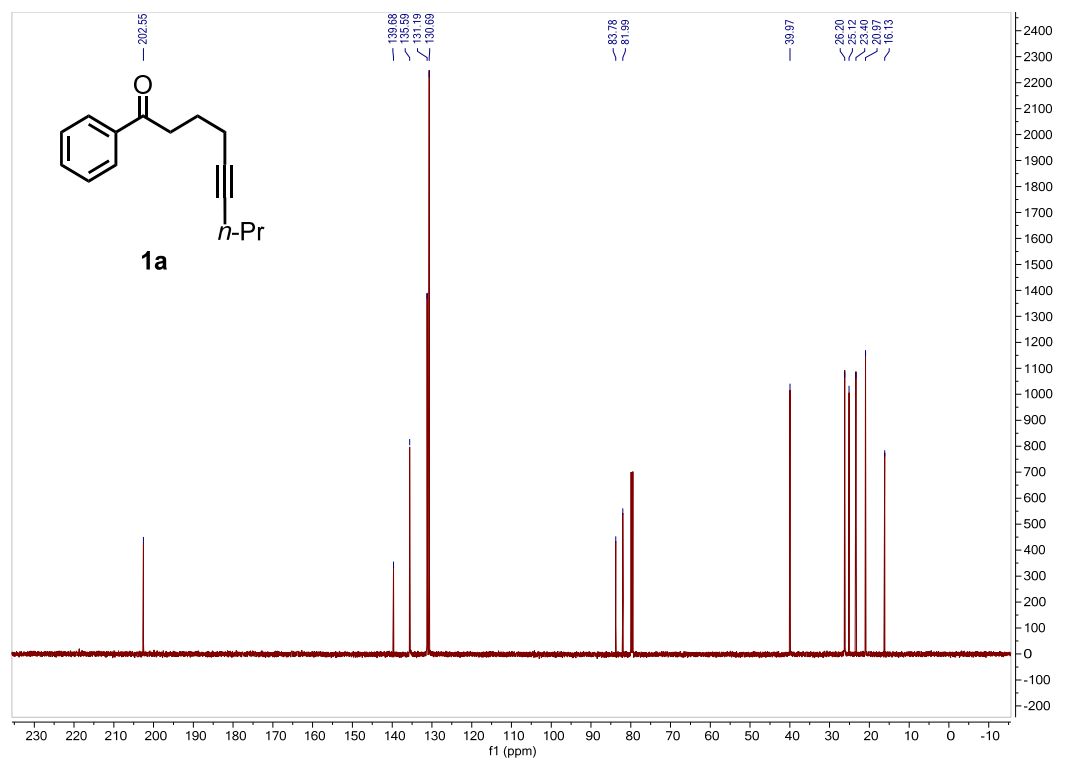
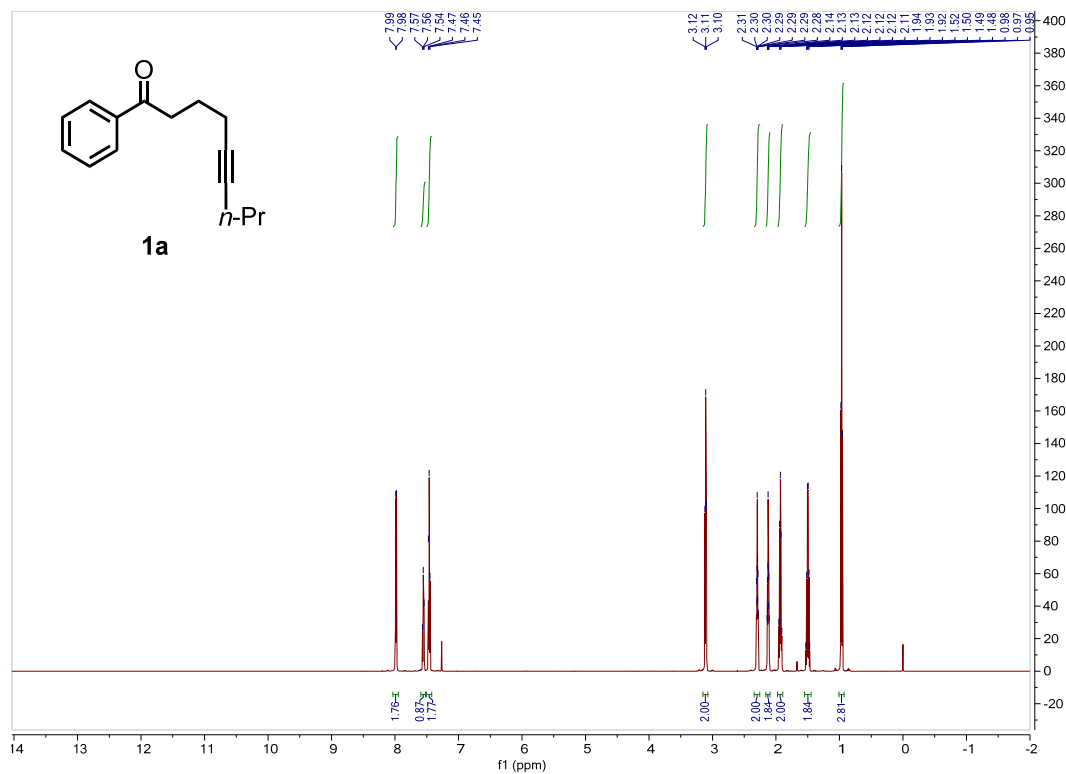
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1	7.025	VB	0.2011	424.25800	31.91942	2.9631
2	13.849	BB	0.4810	1.38937e4	446.47955	97.0369
Totals :				1.43180e4	478.39898	

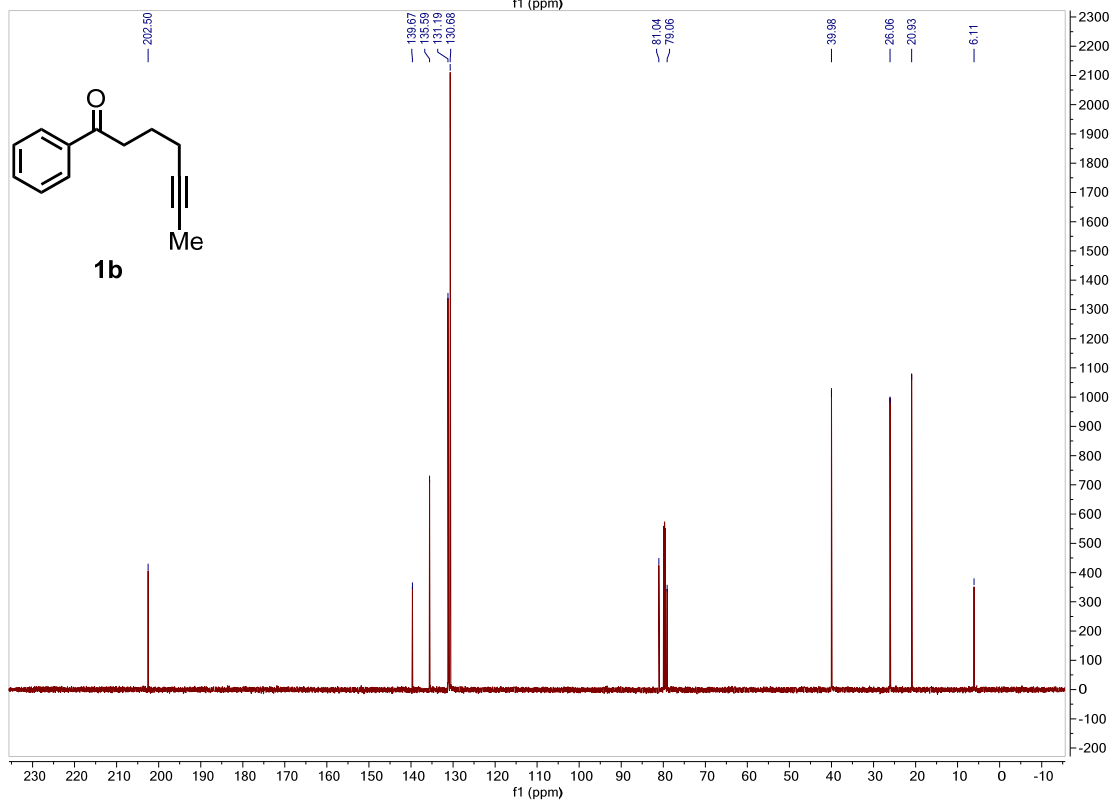
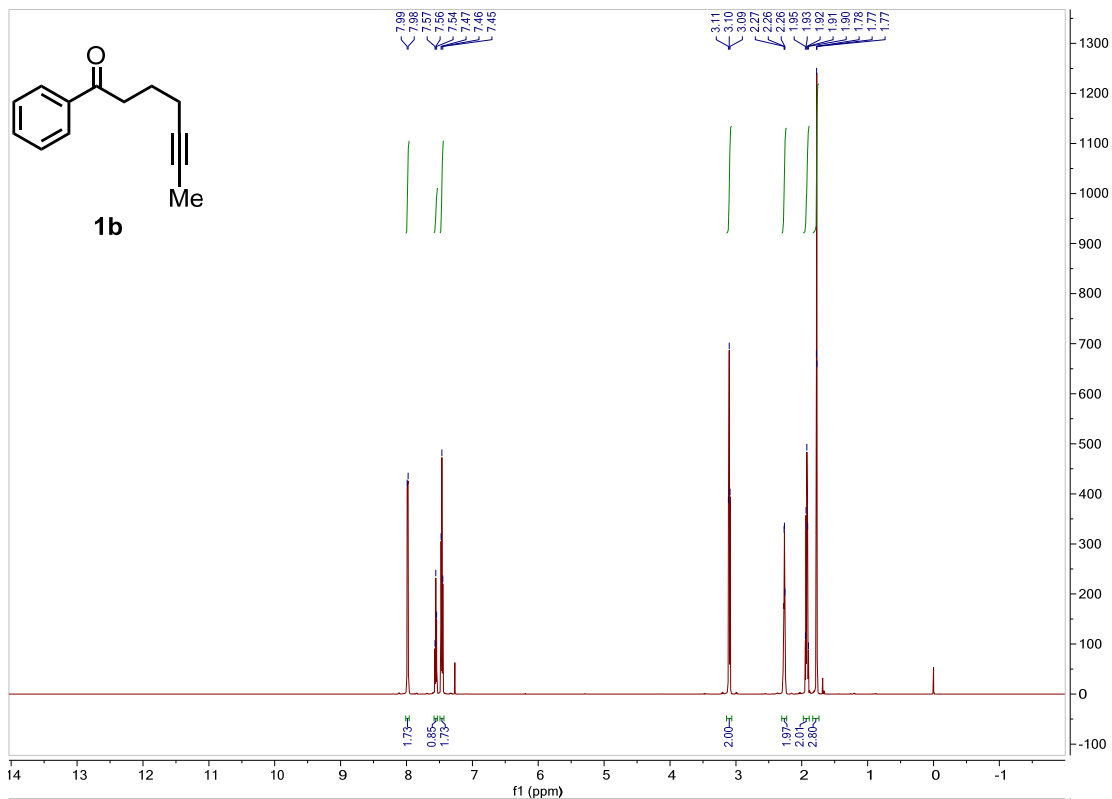
5. References

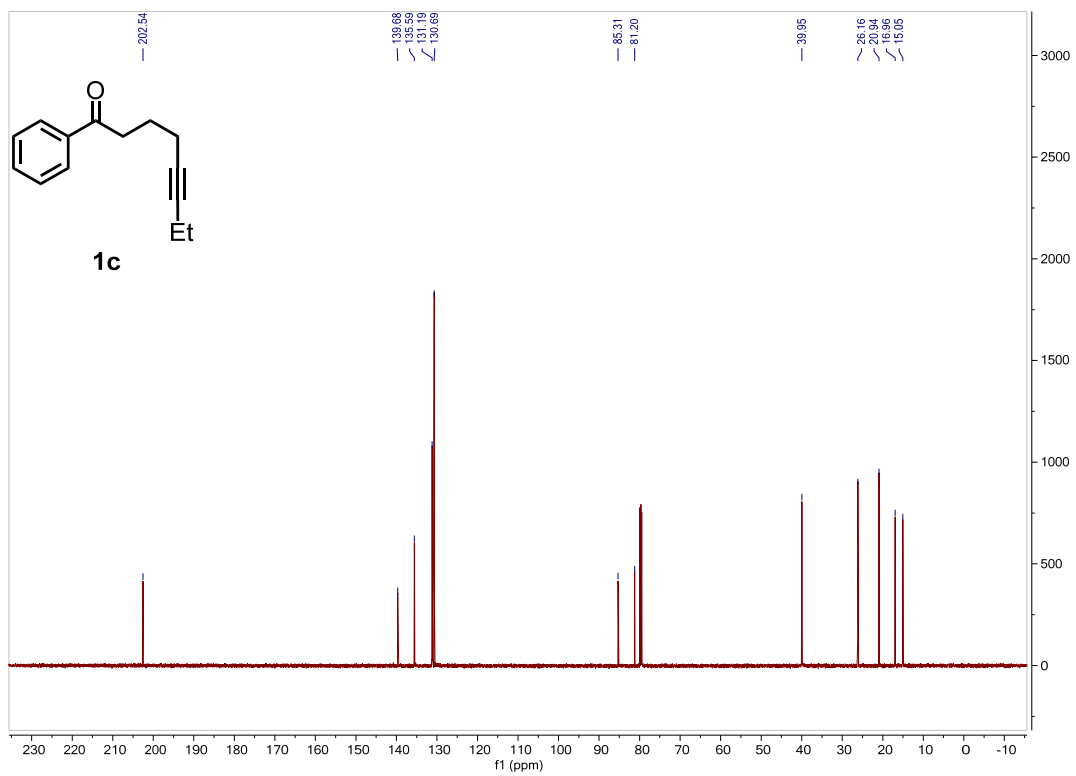
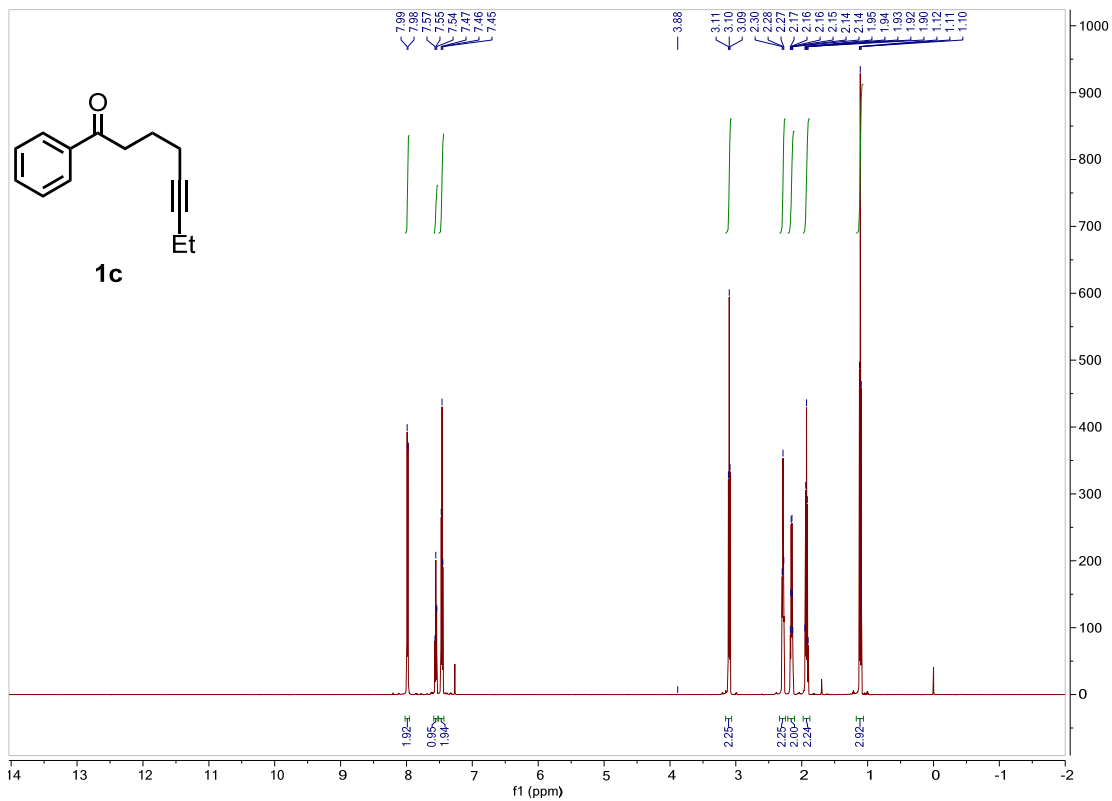
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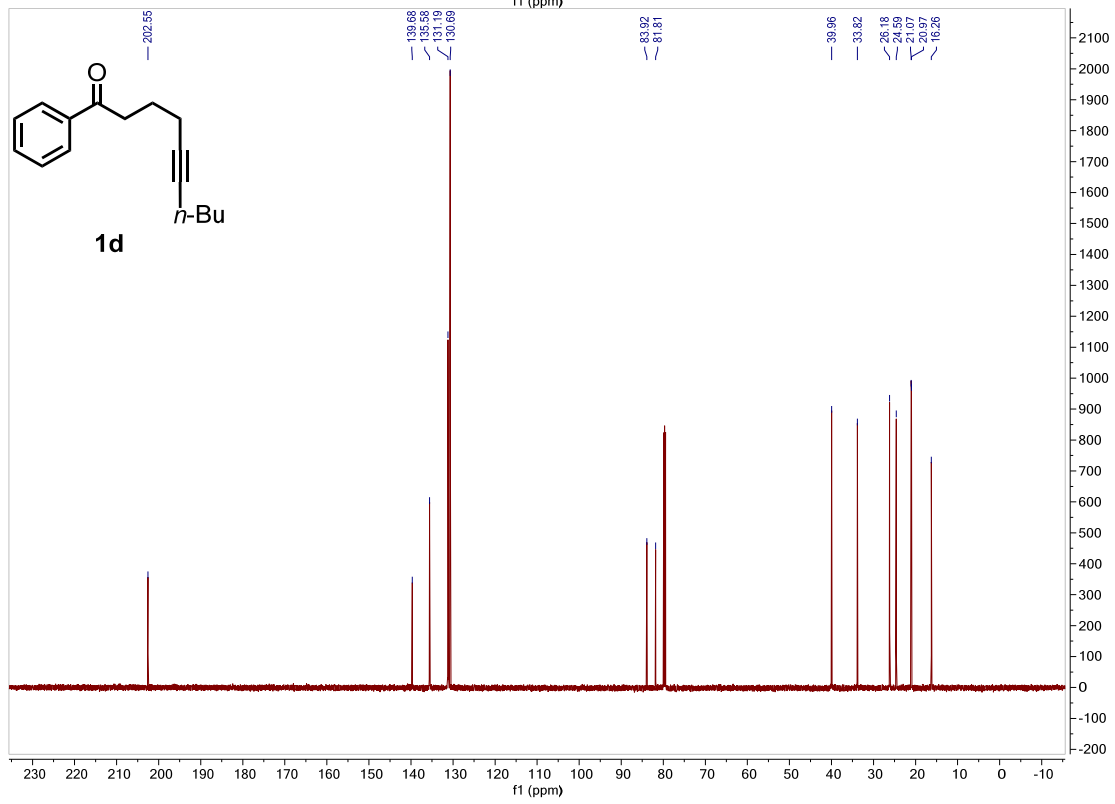
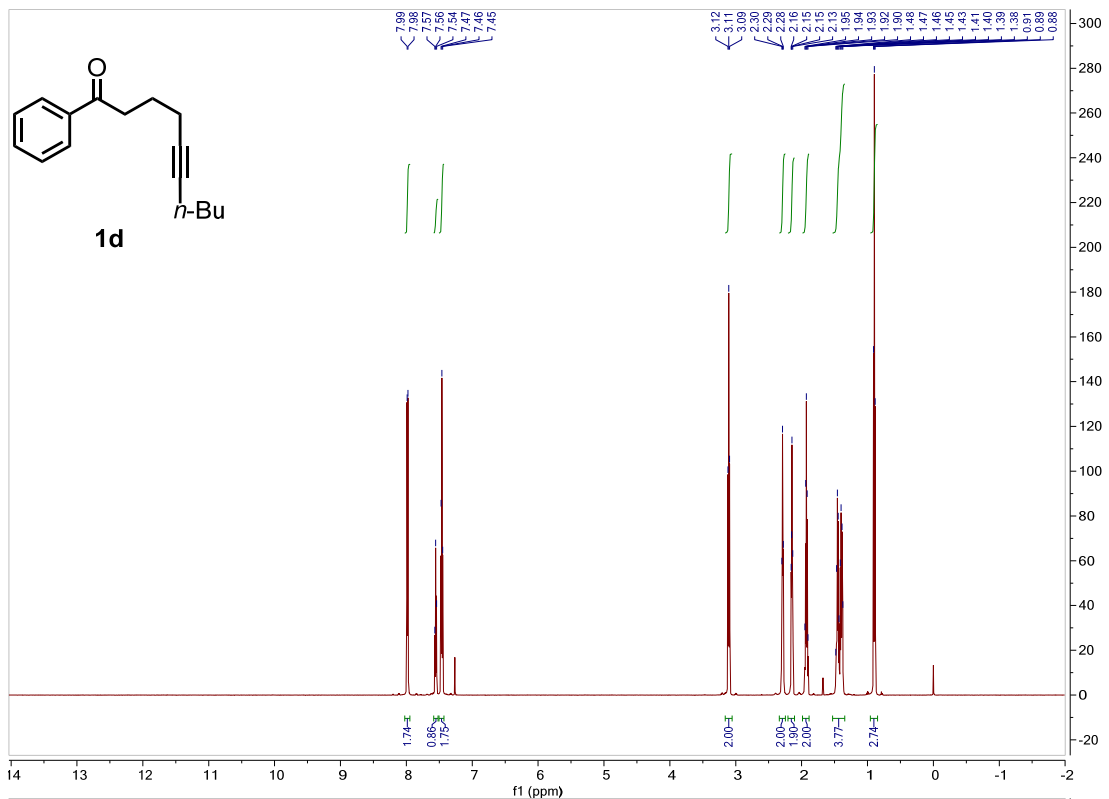
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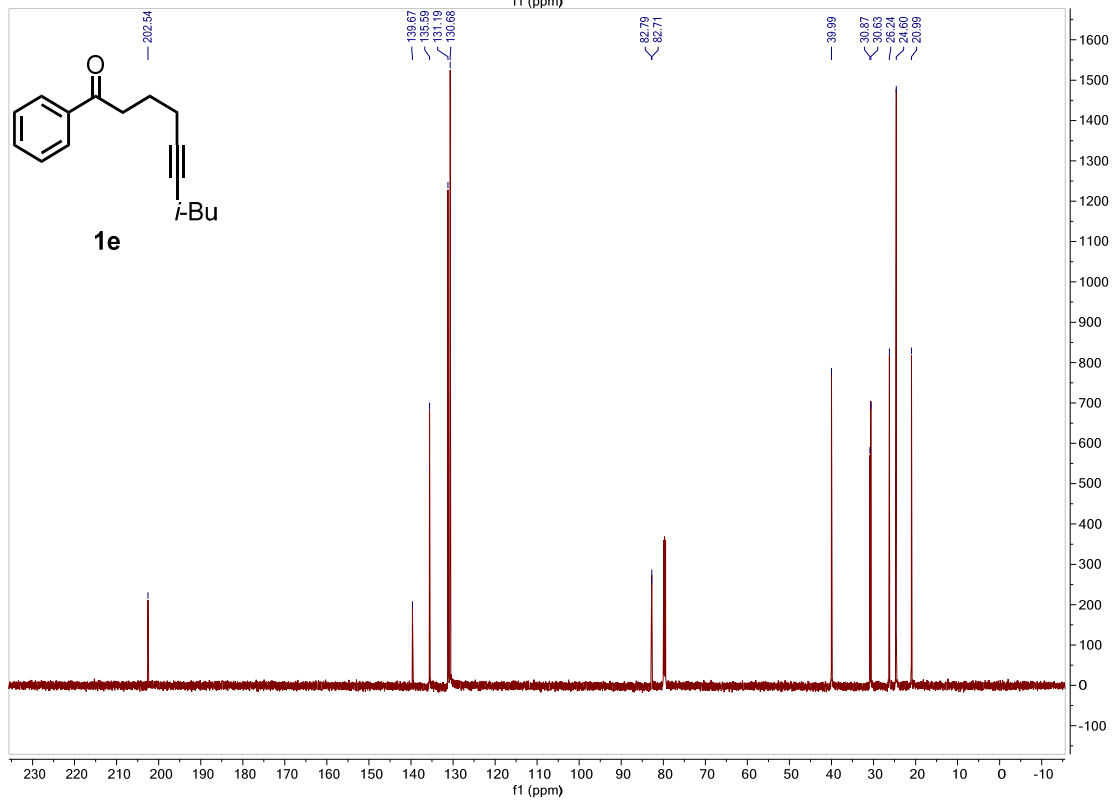
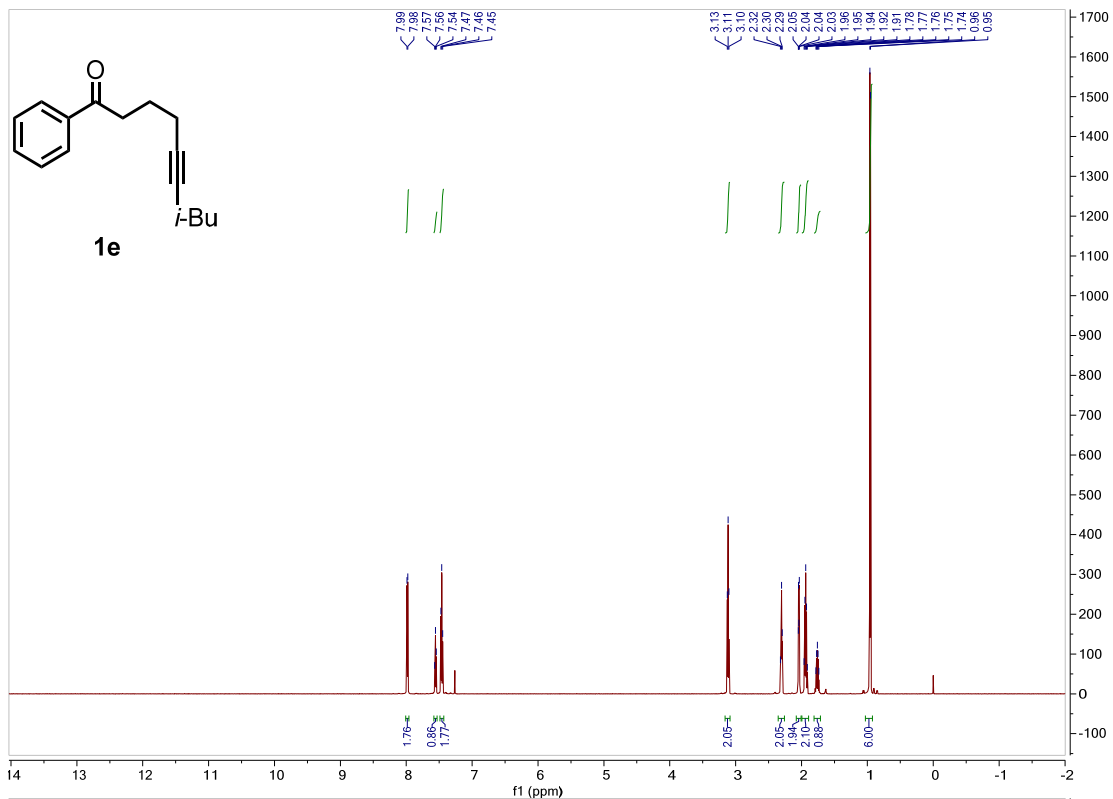
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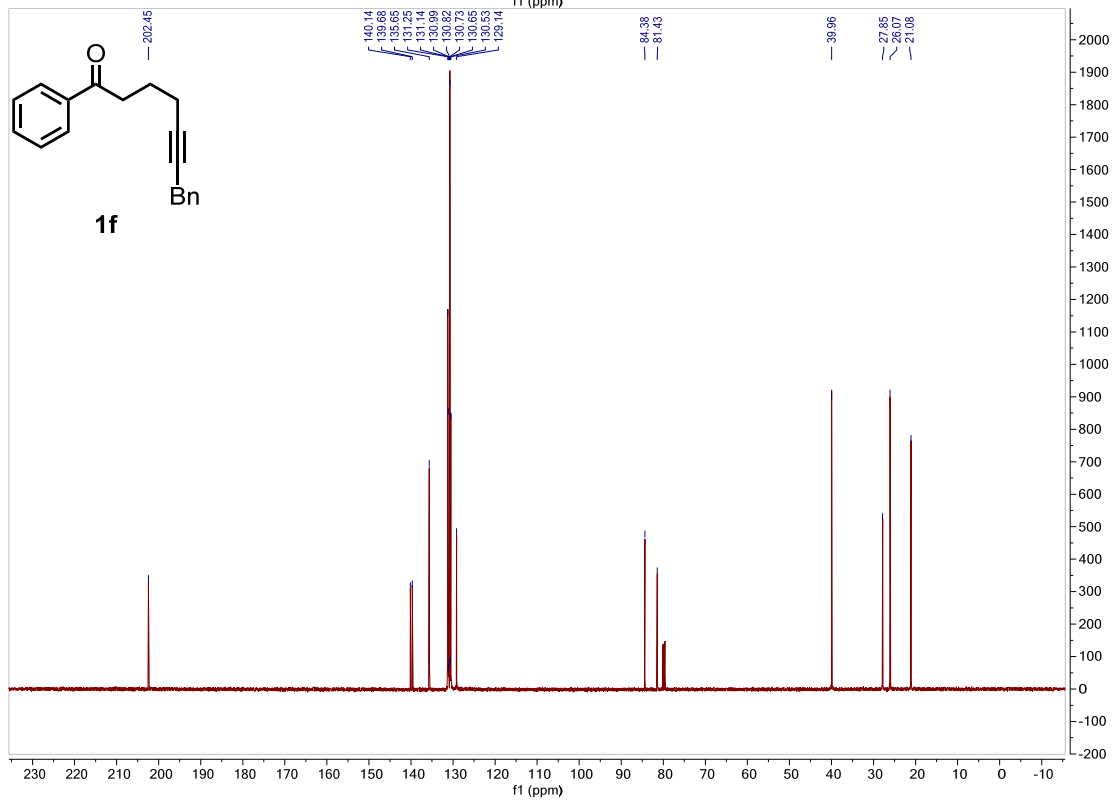
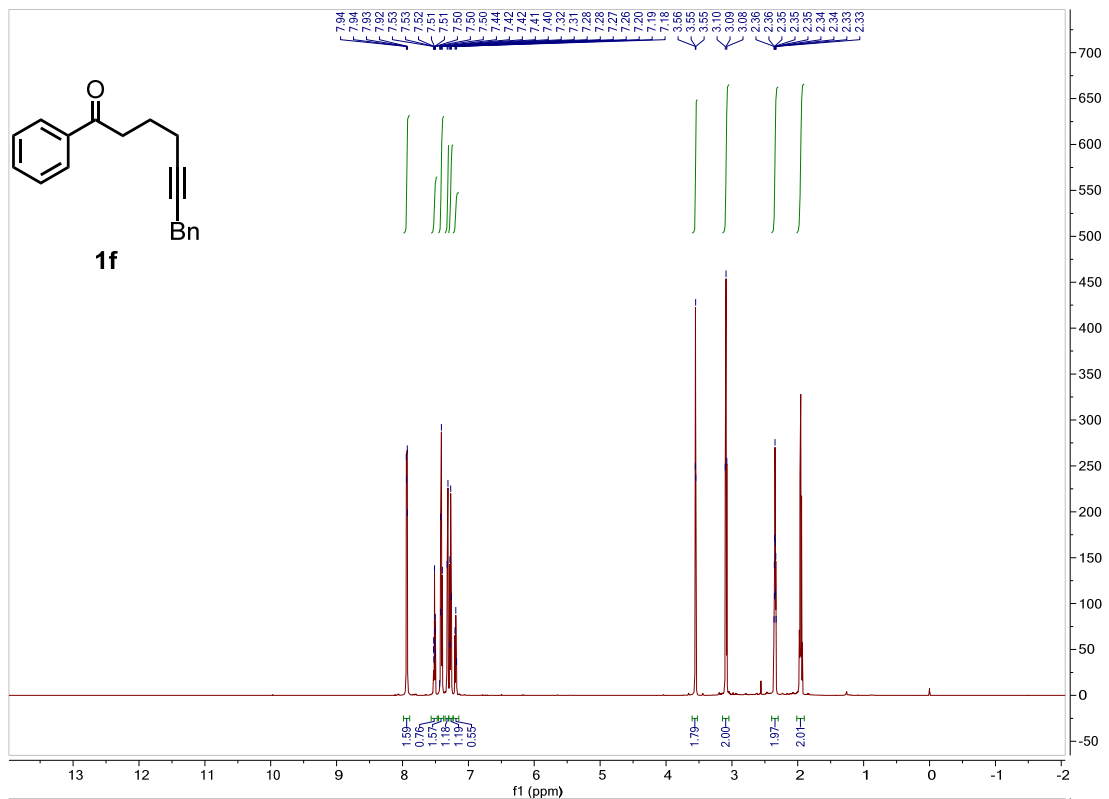


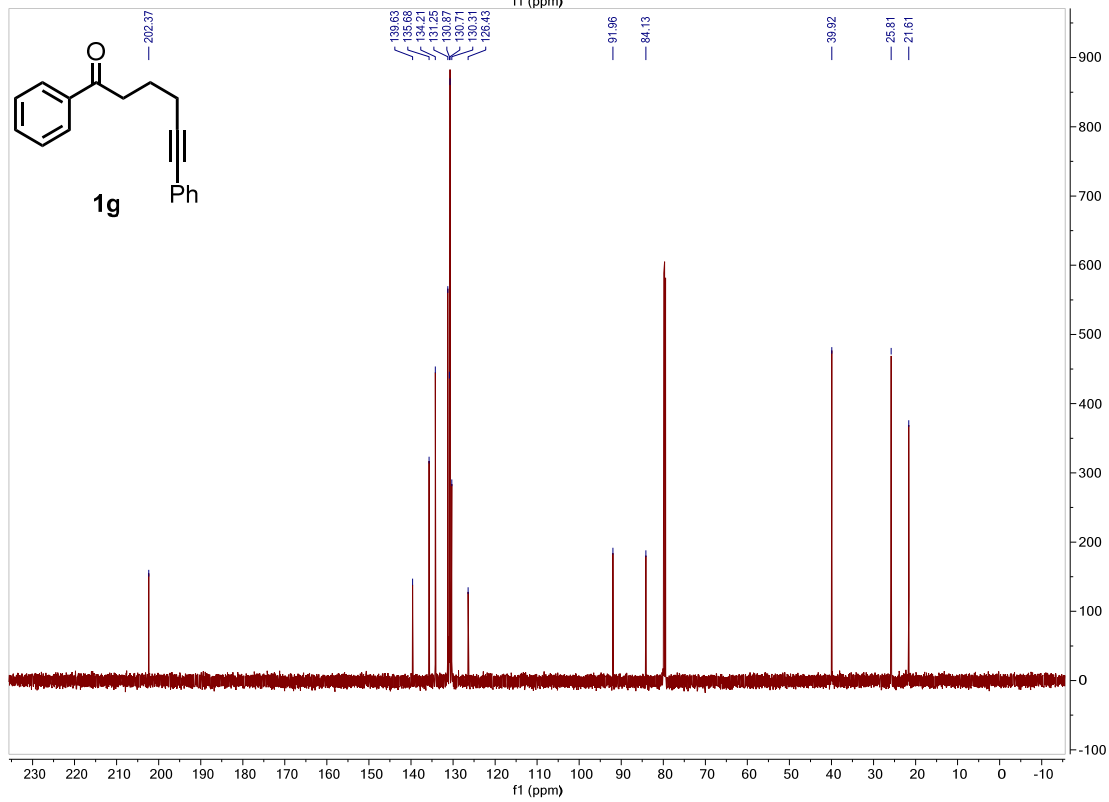
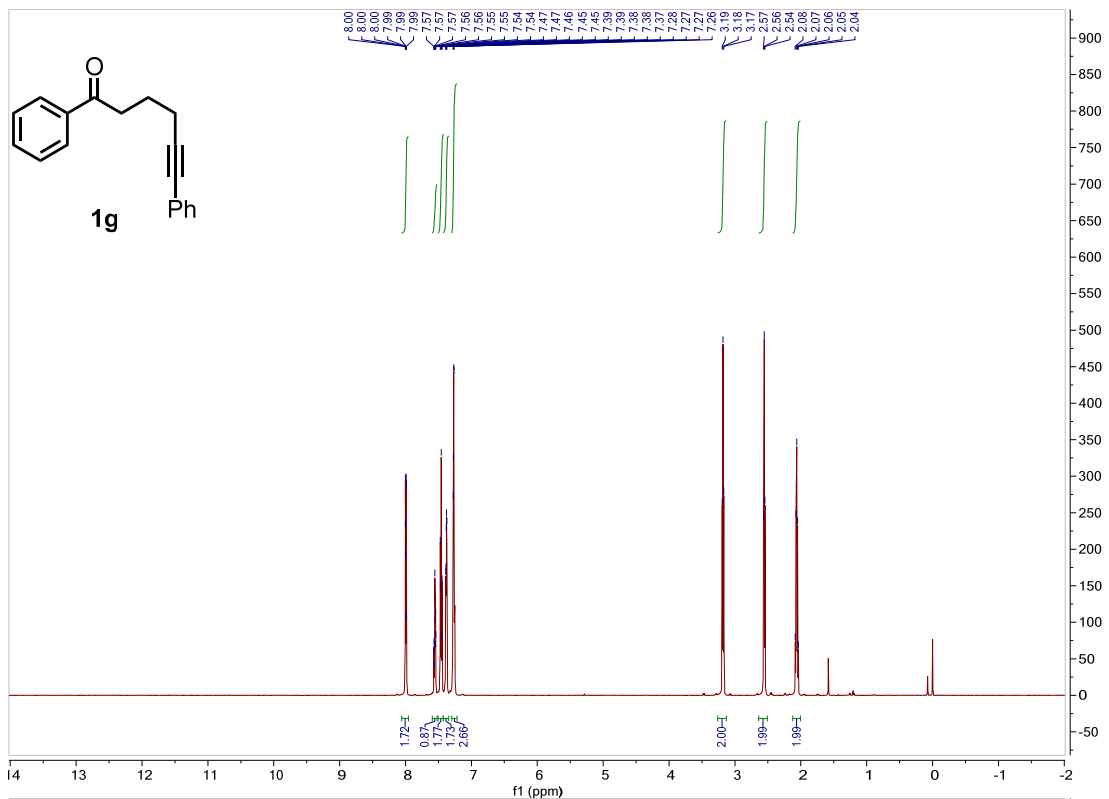


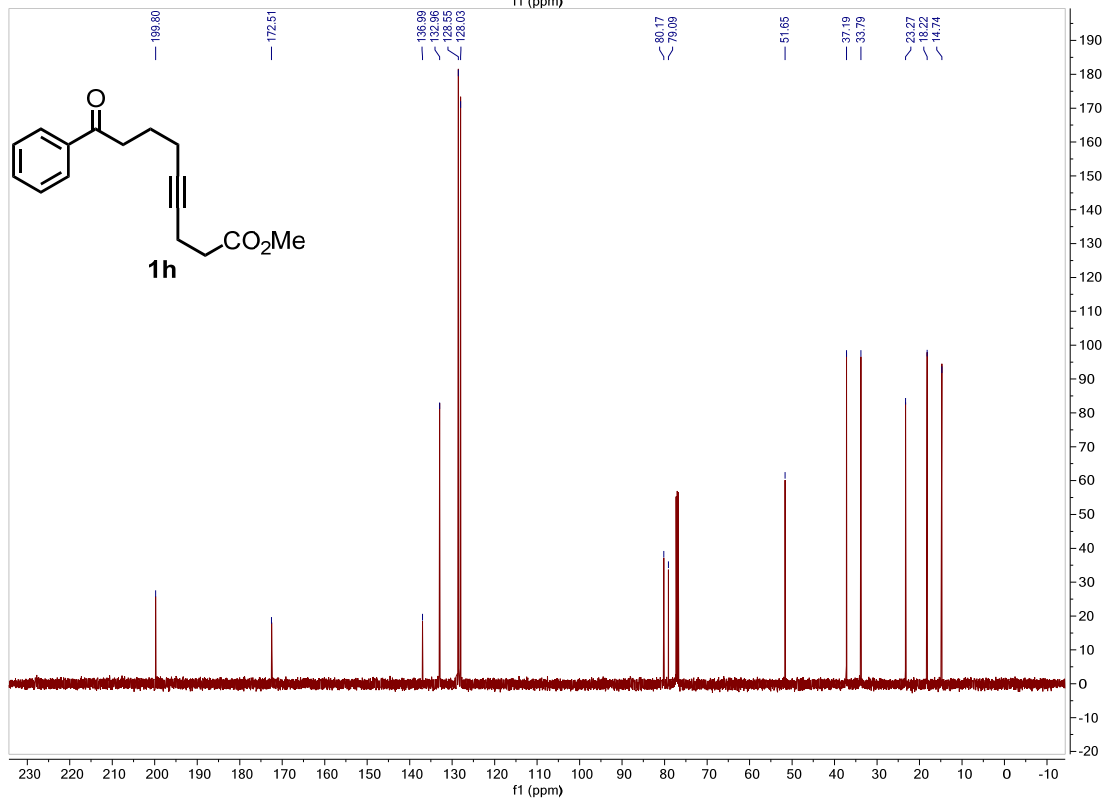
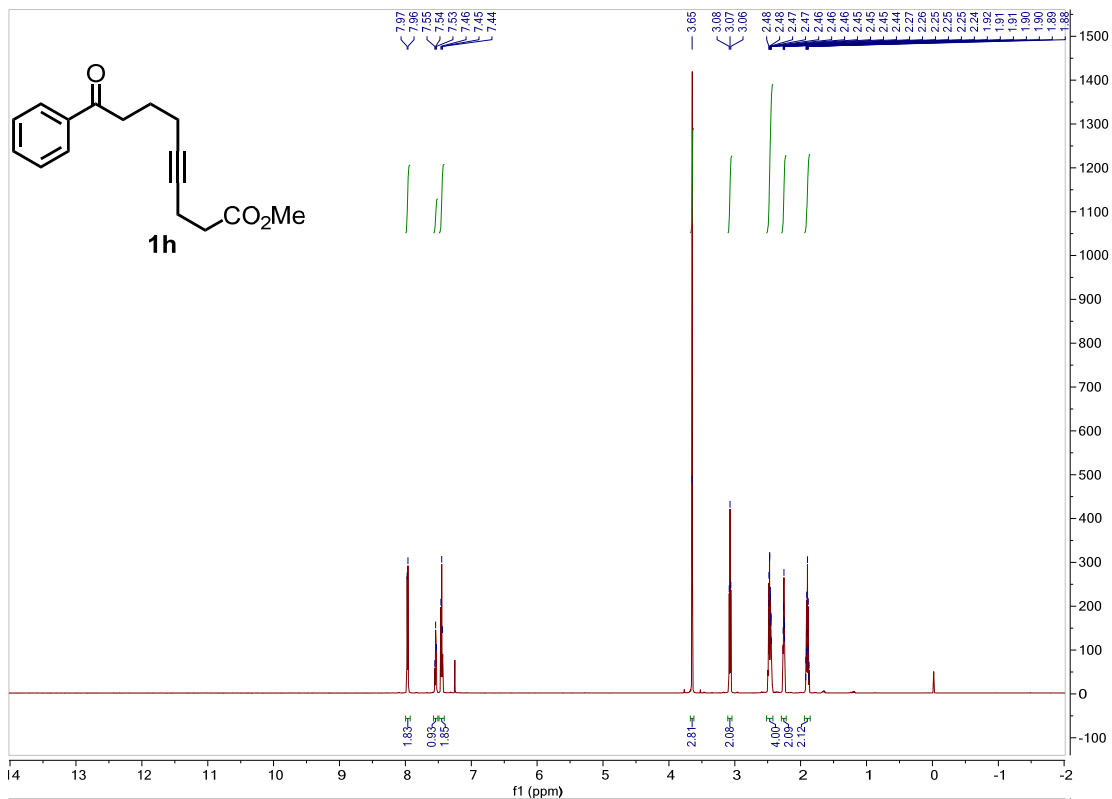


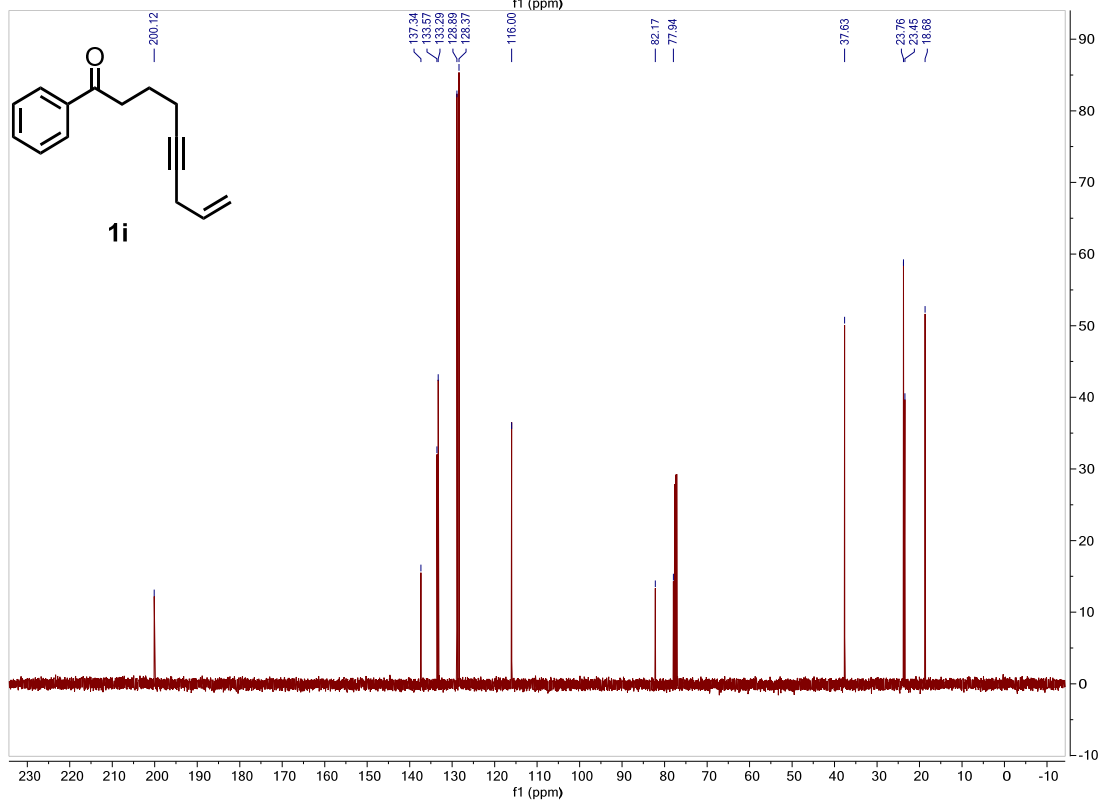
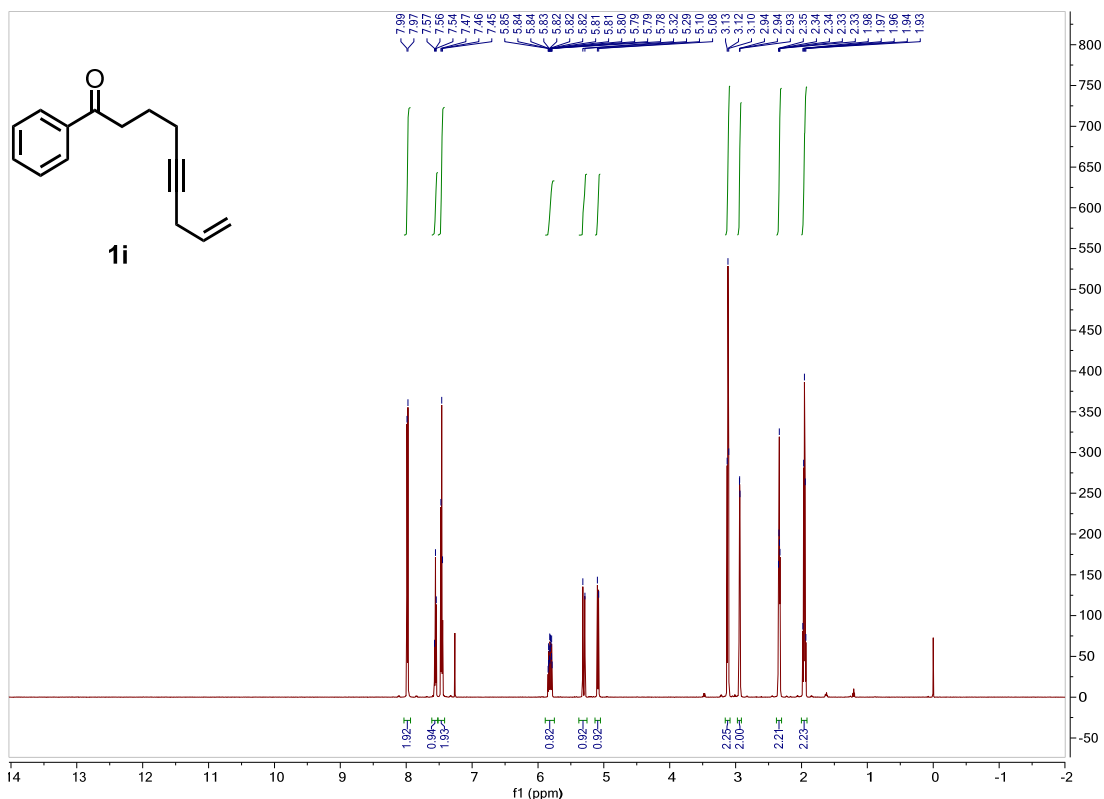


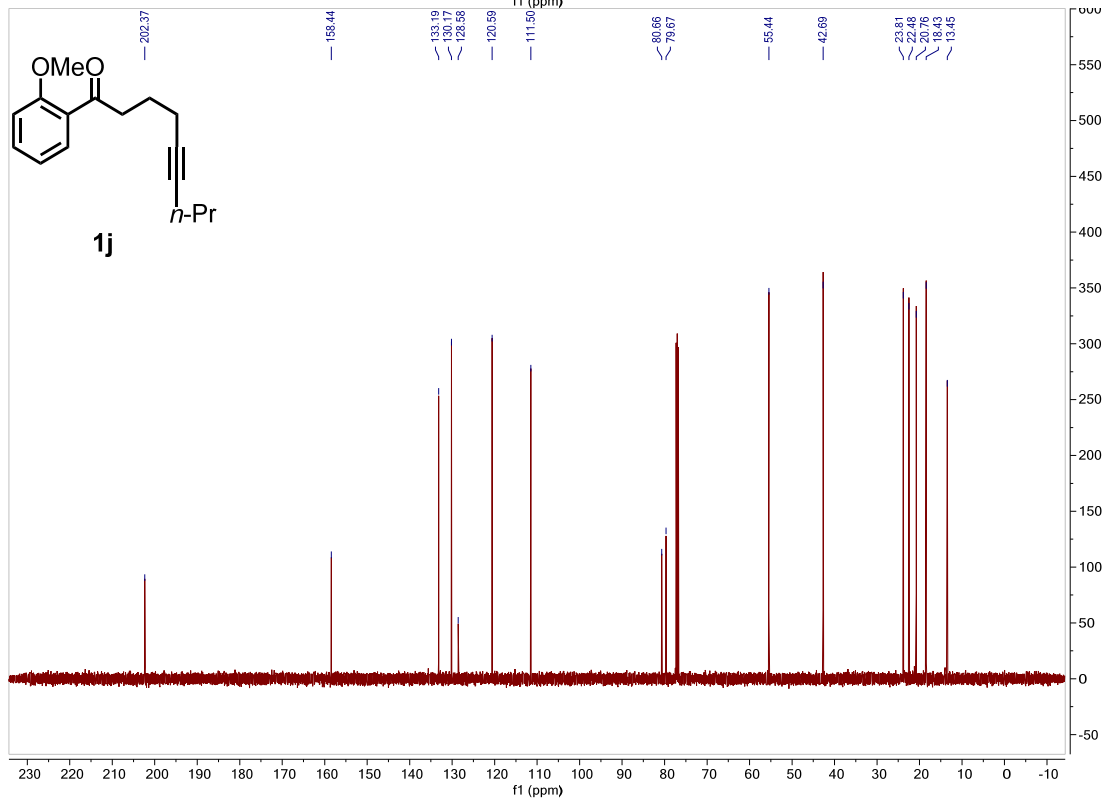
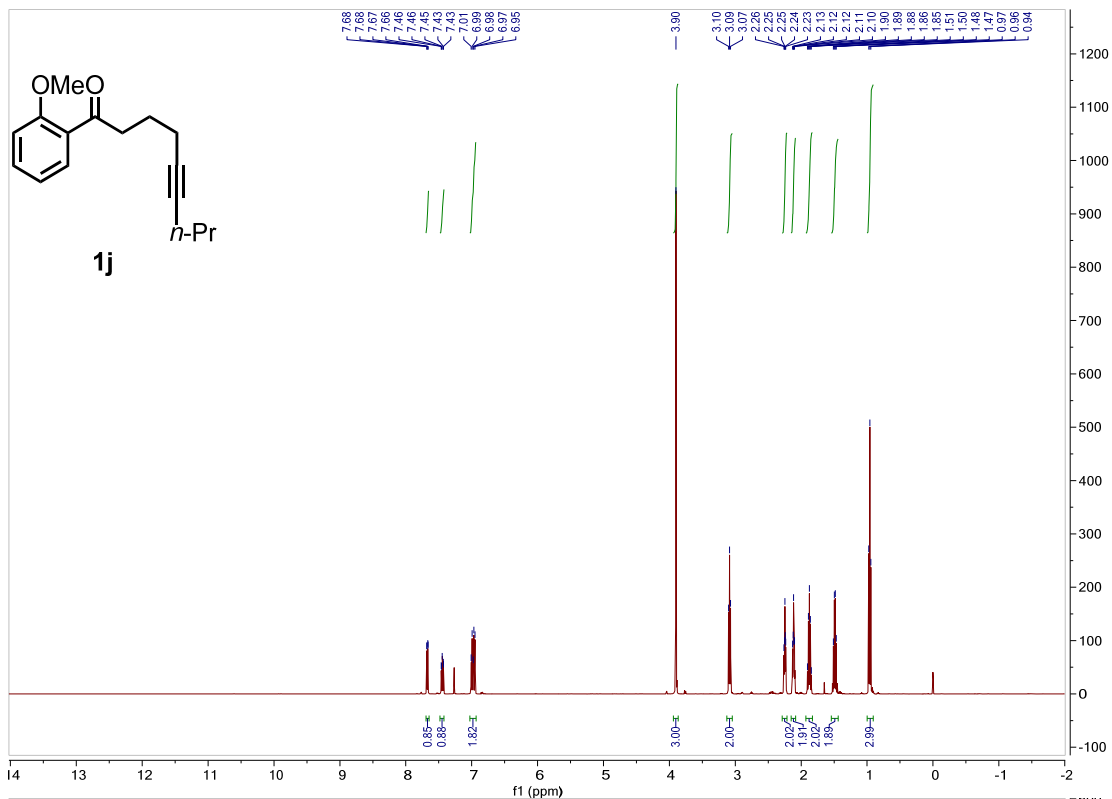


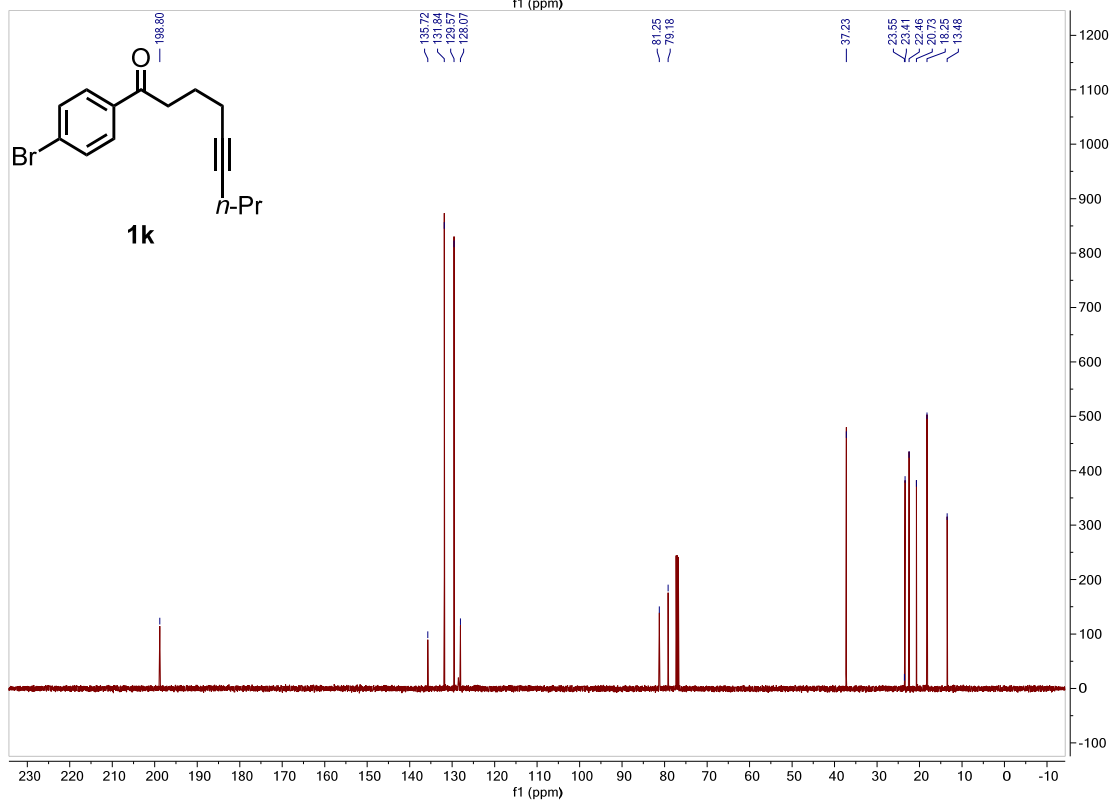
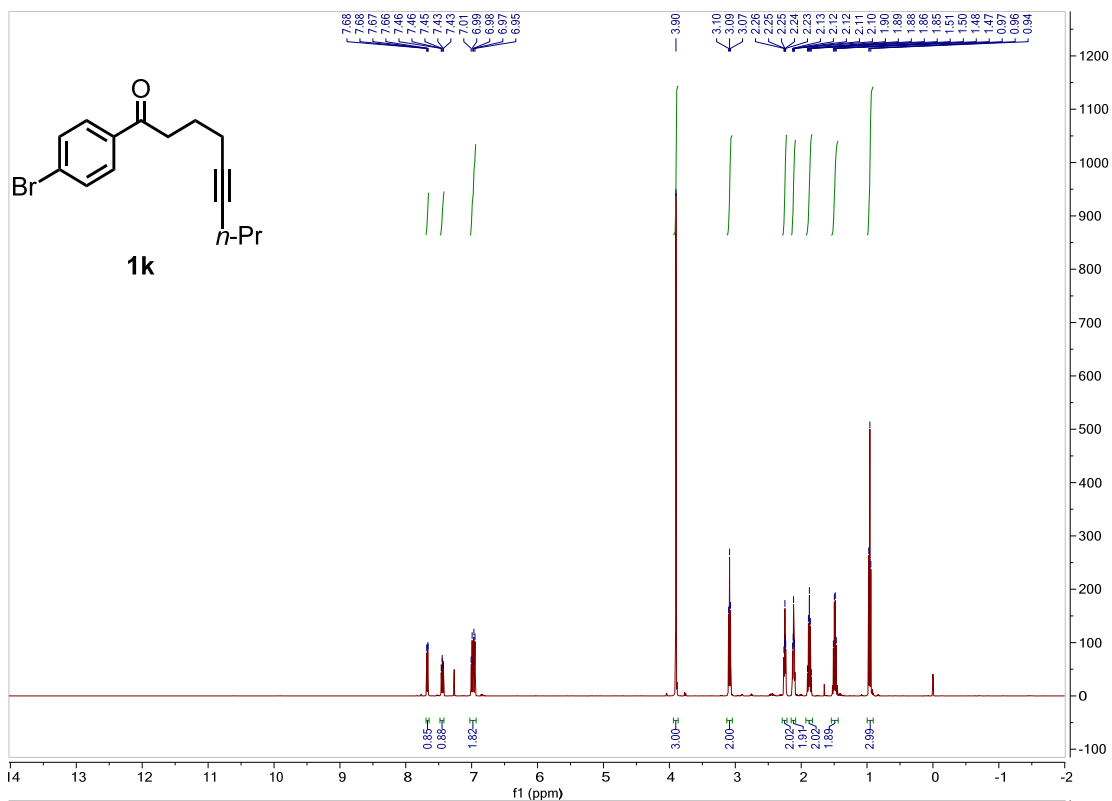


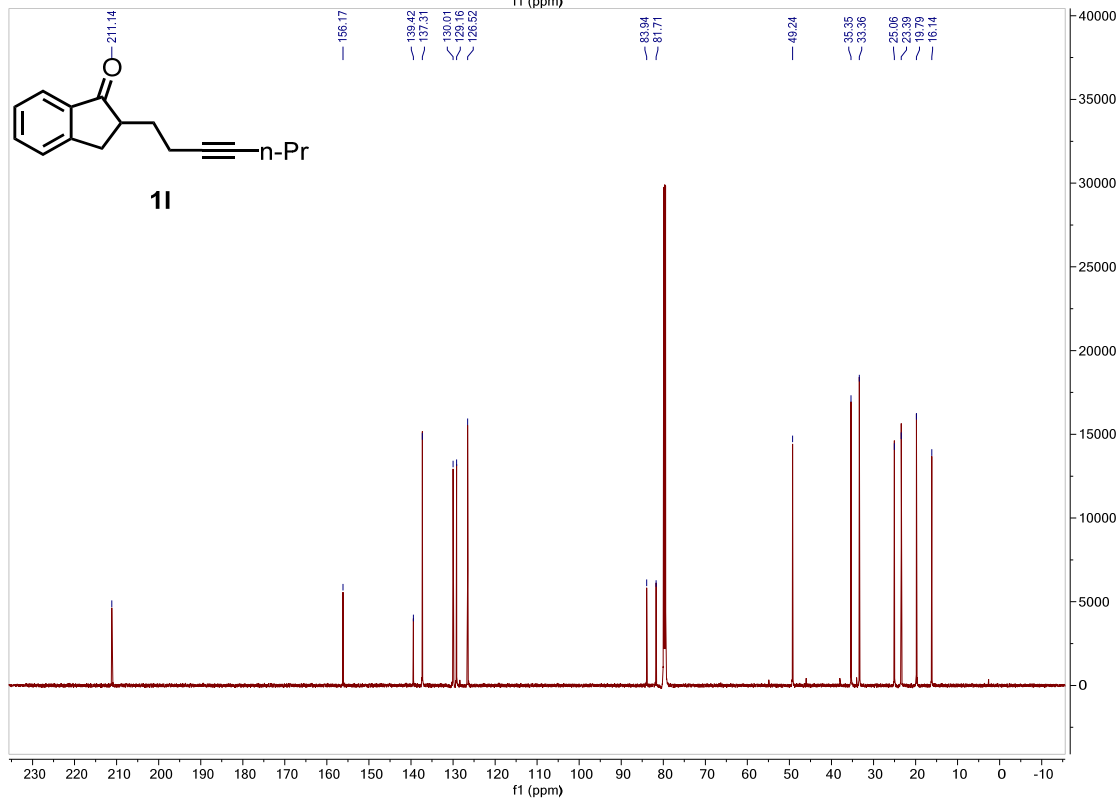
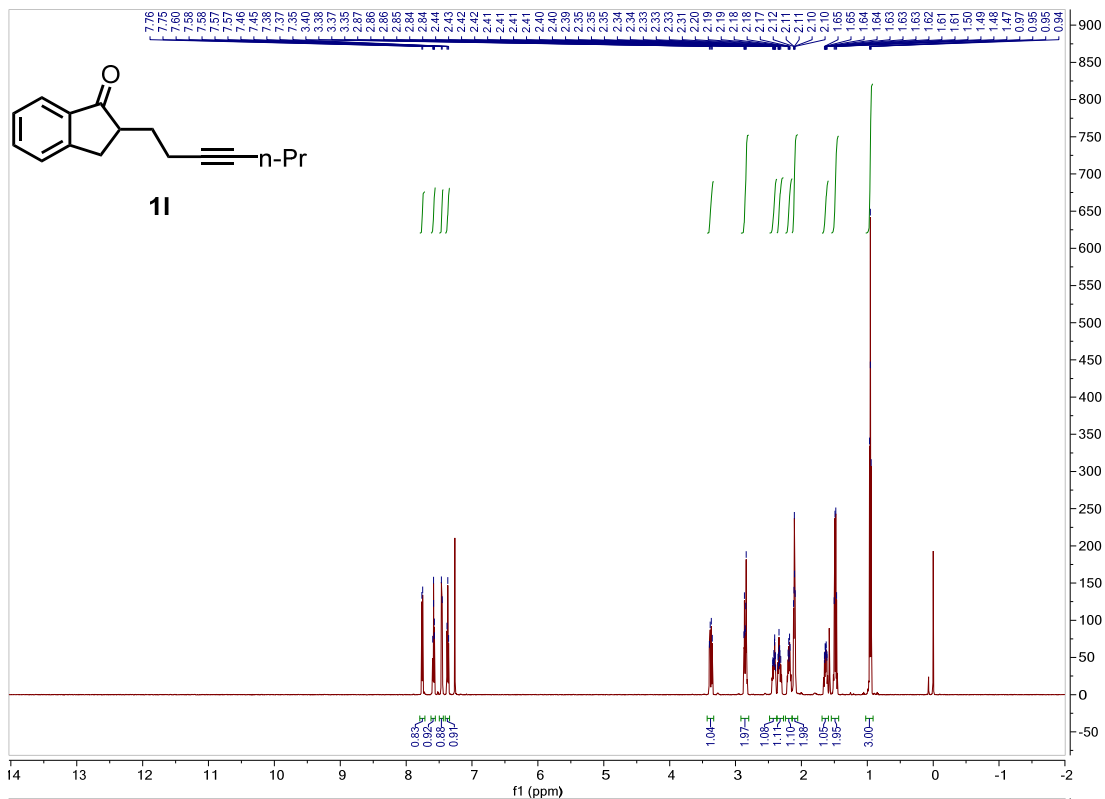


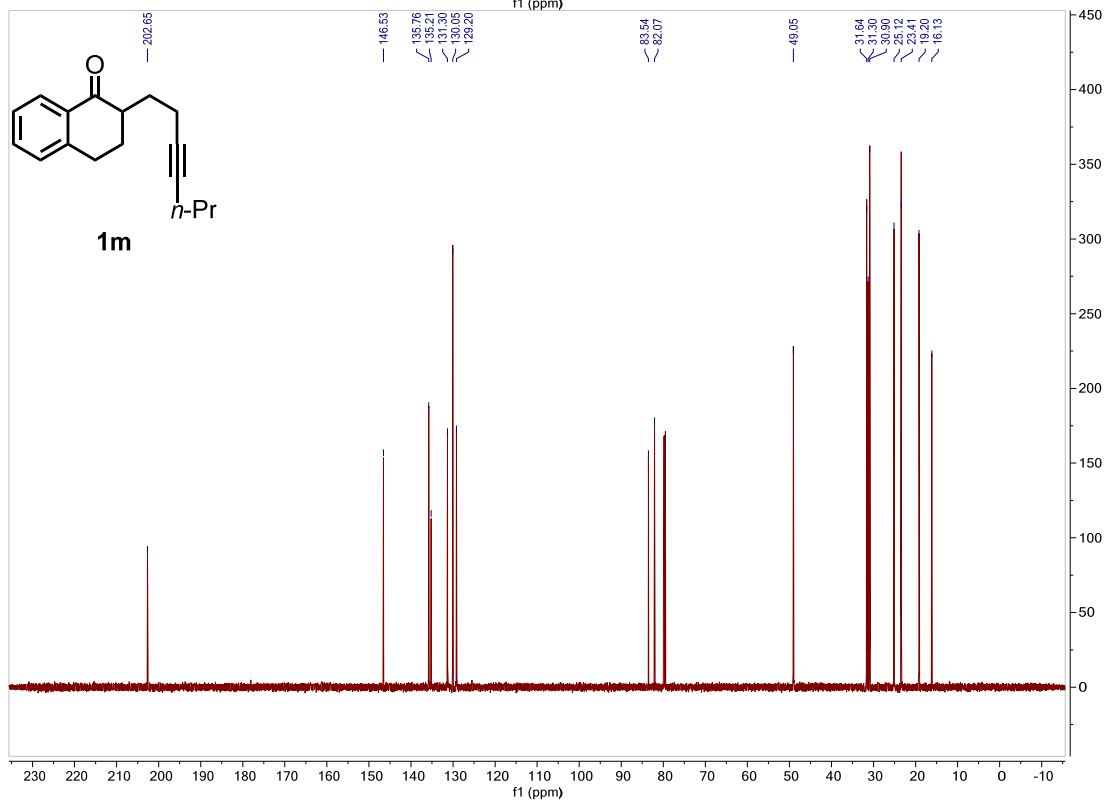
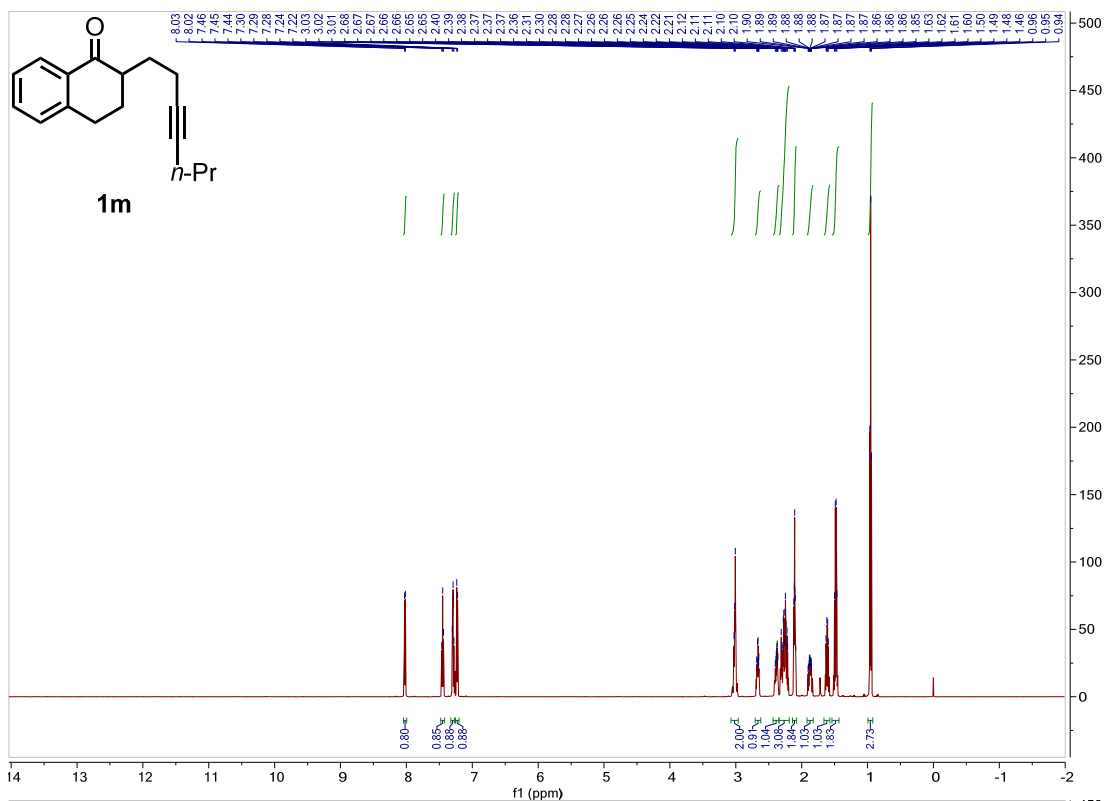


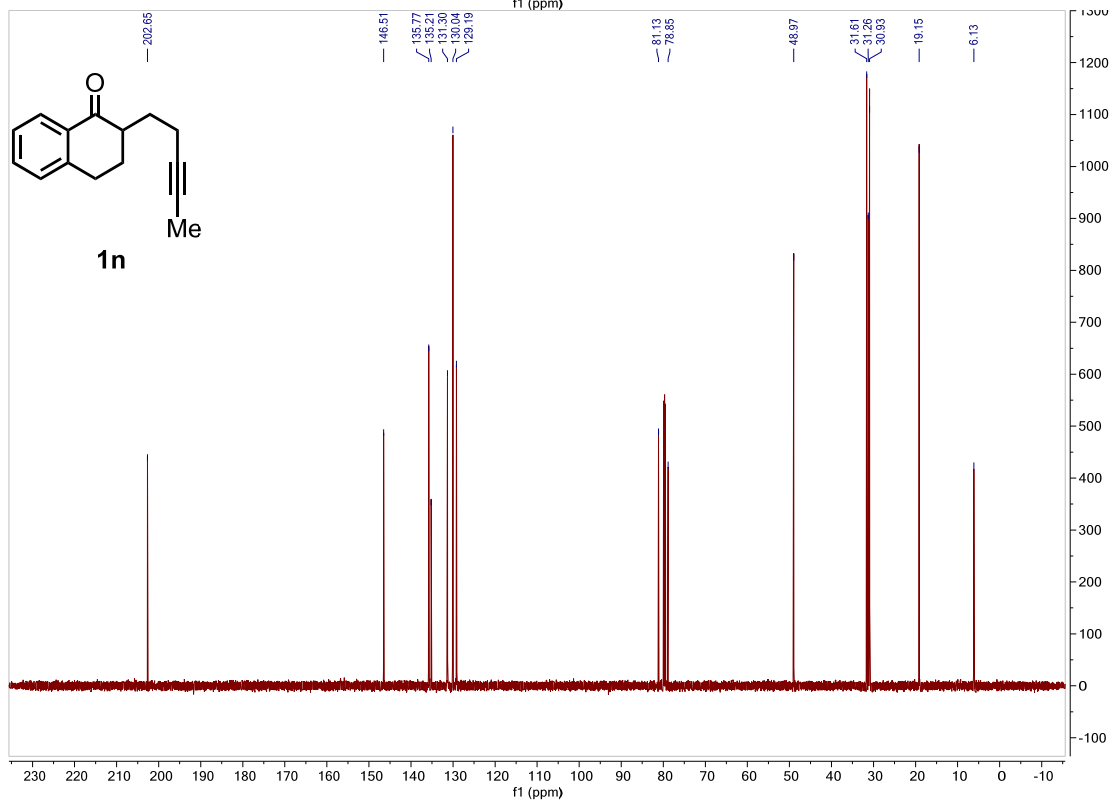
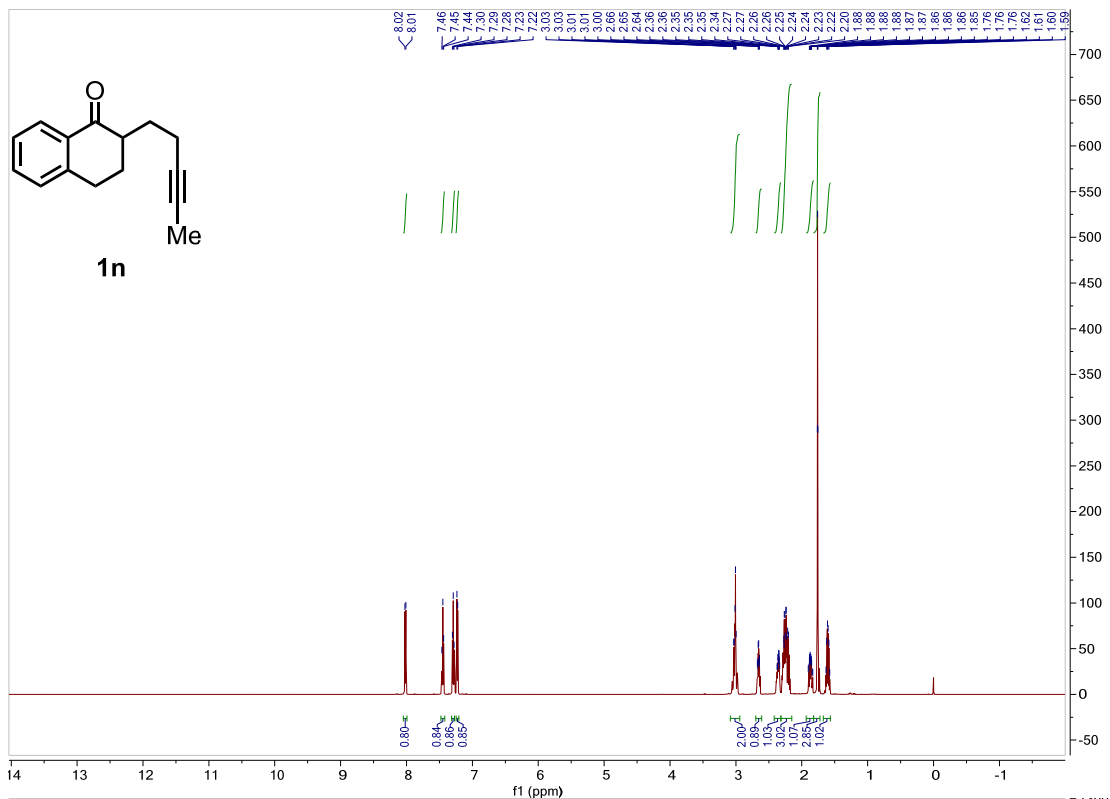


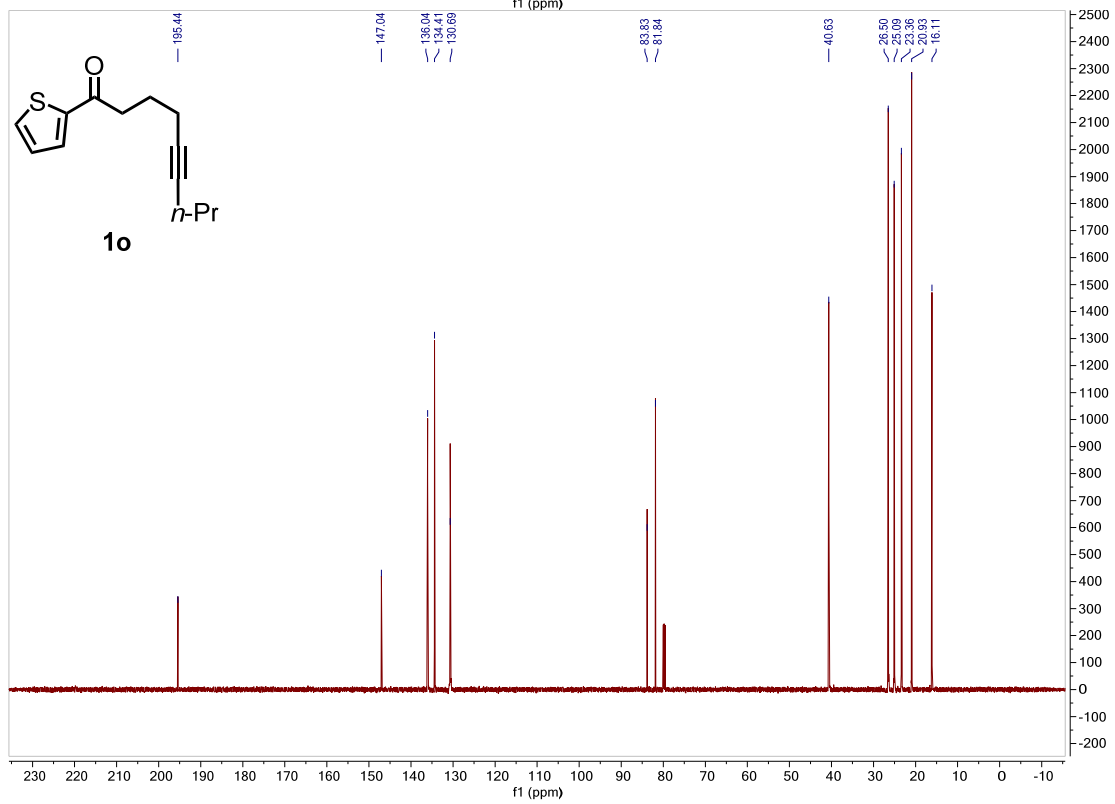
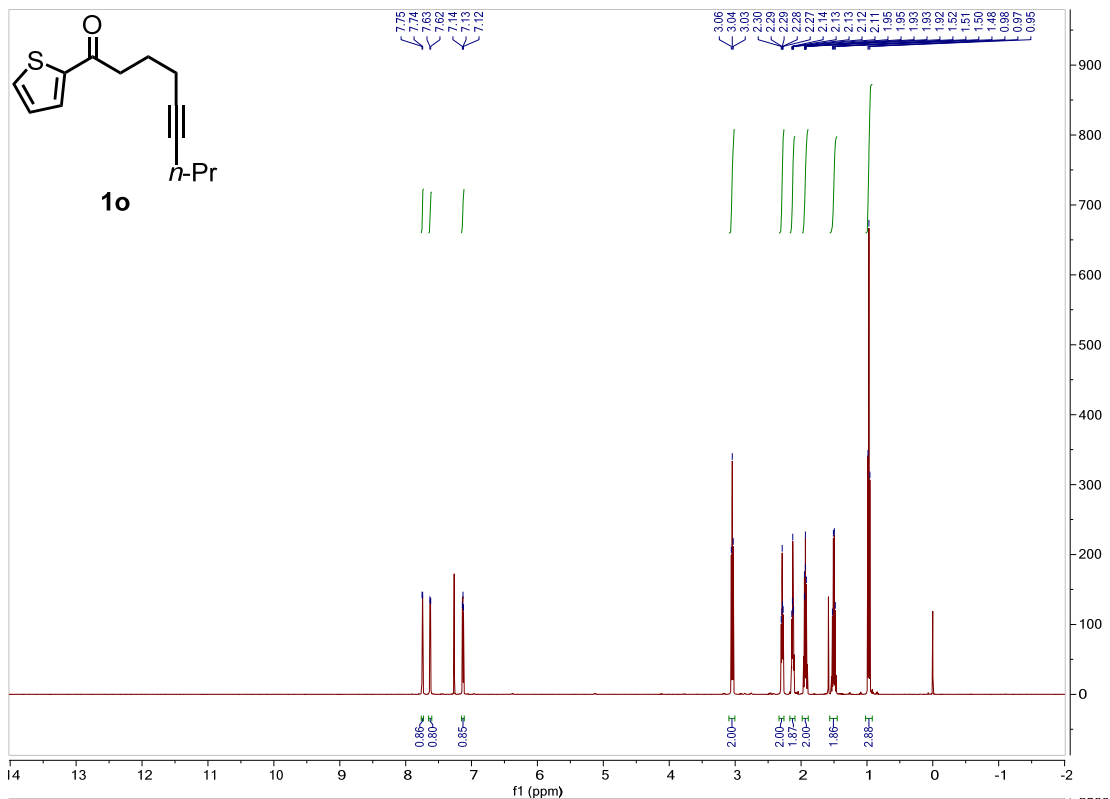


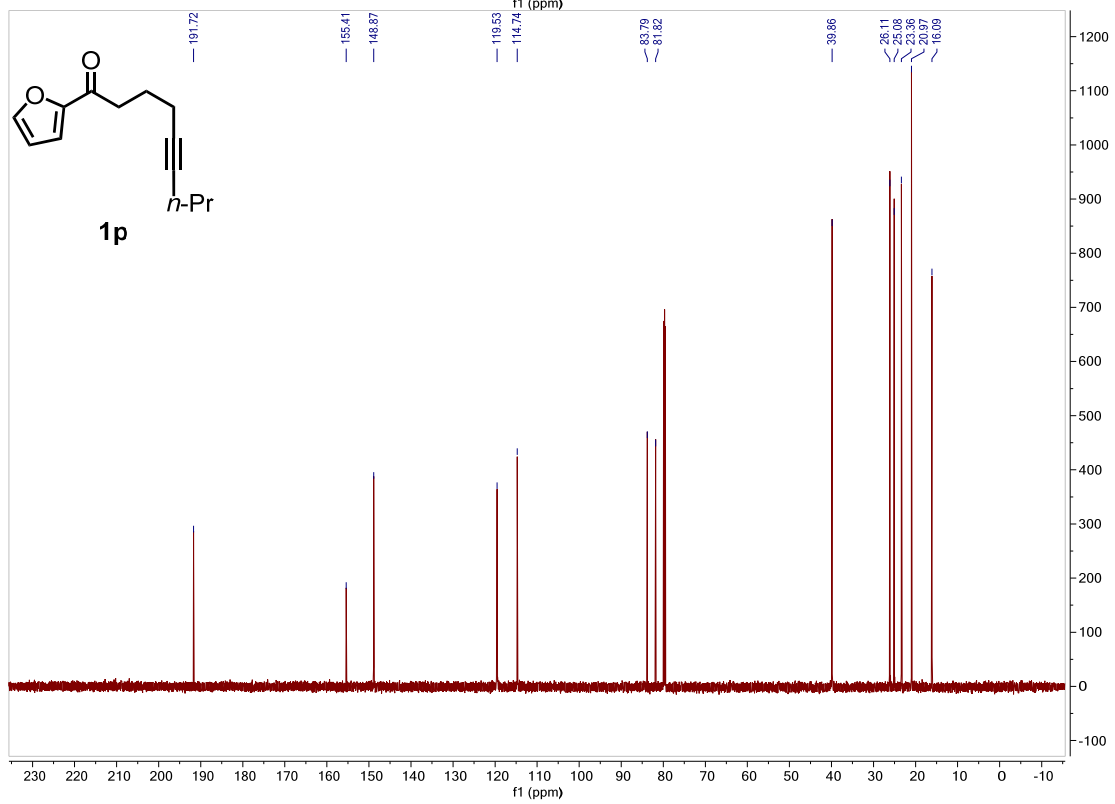
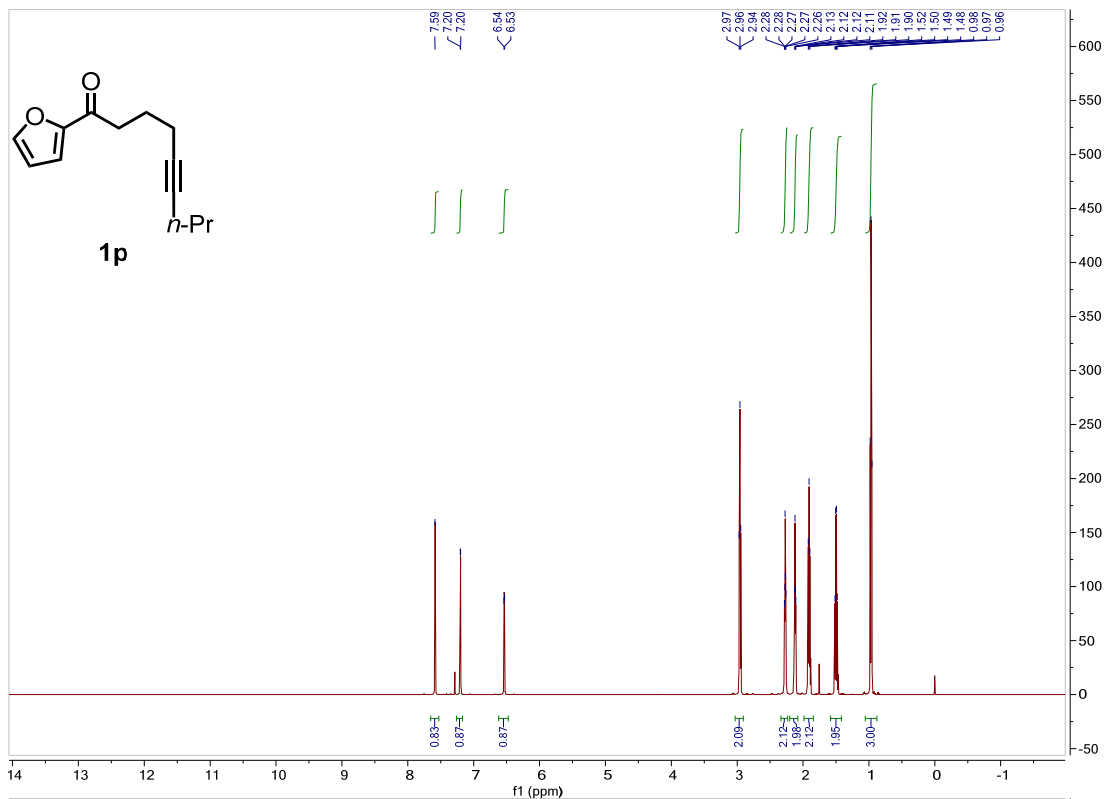


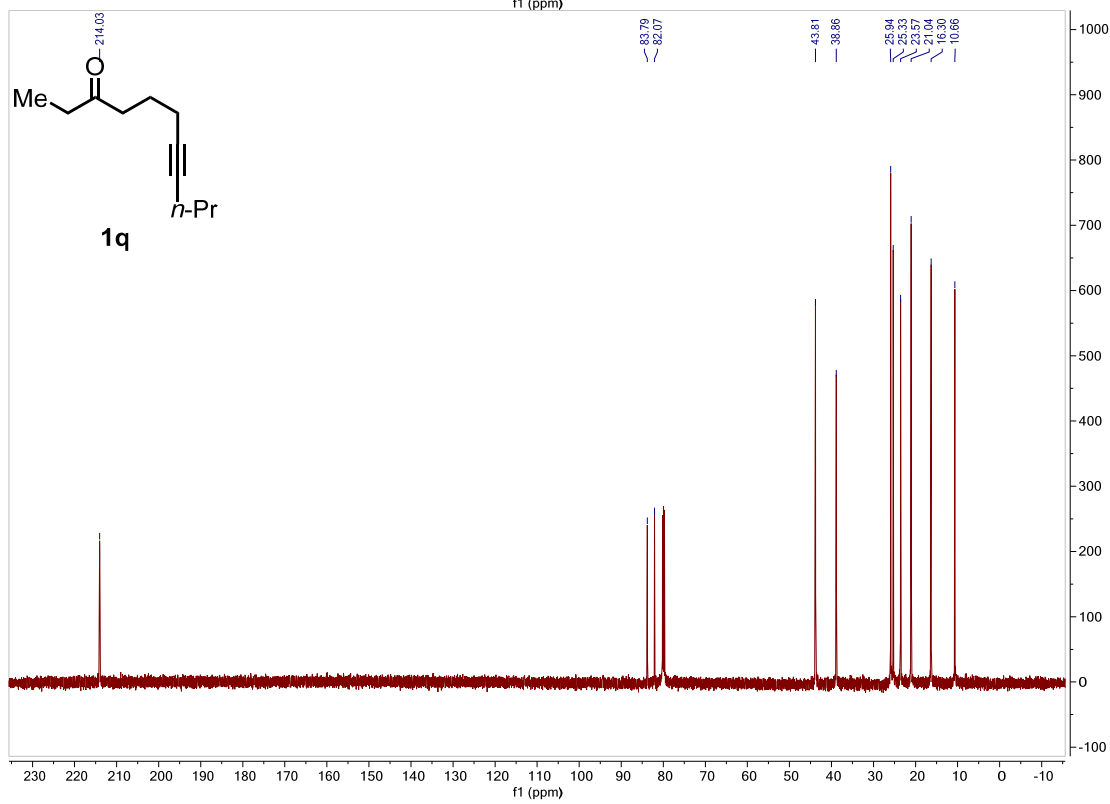
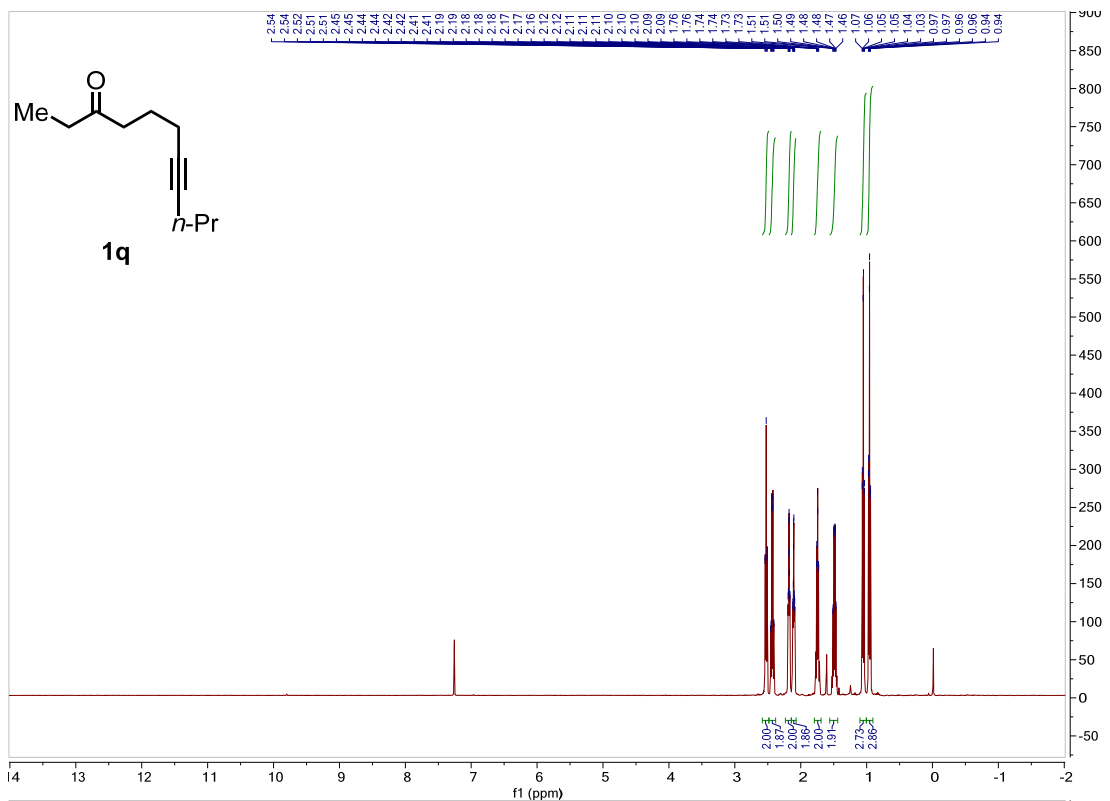


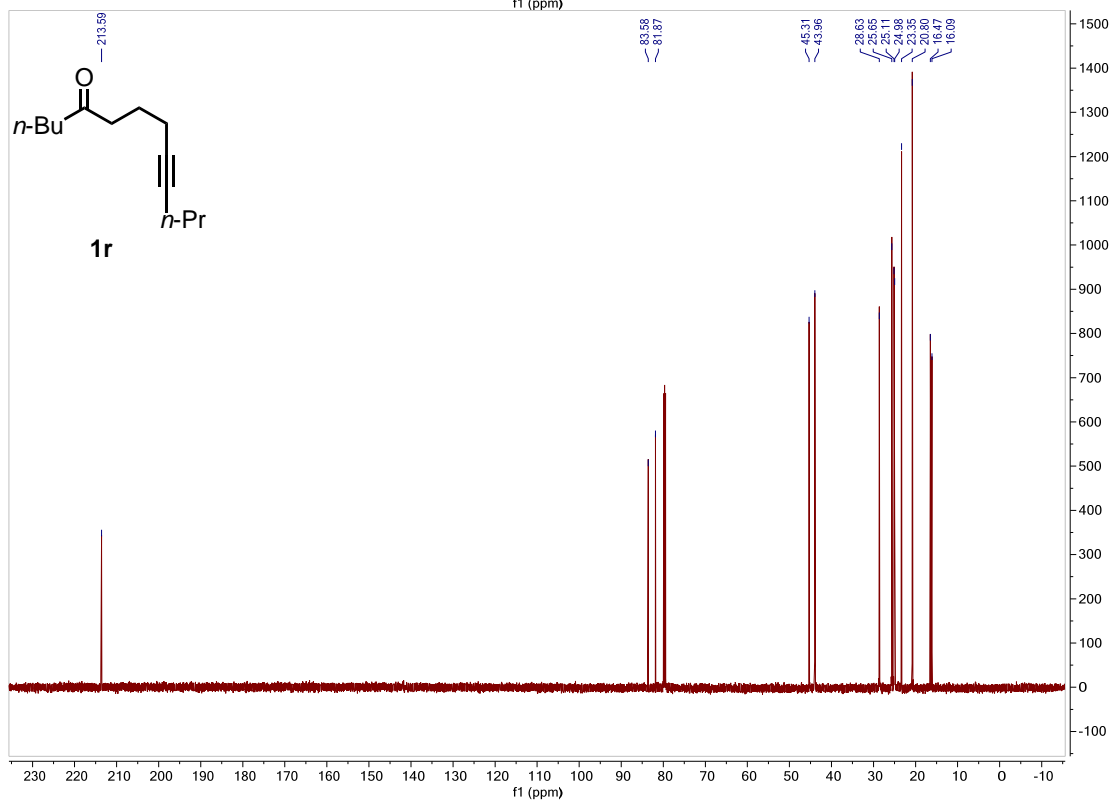
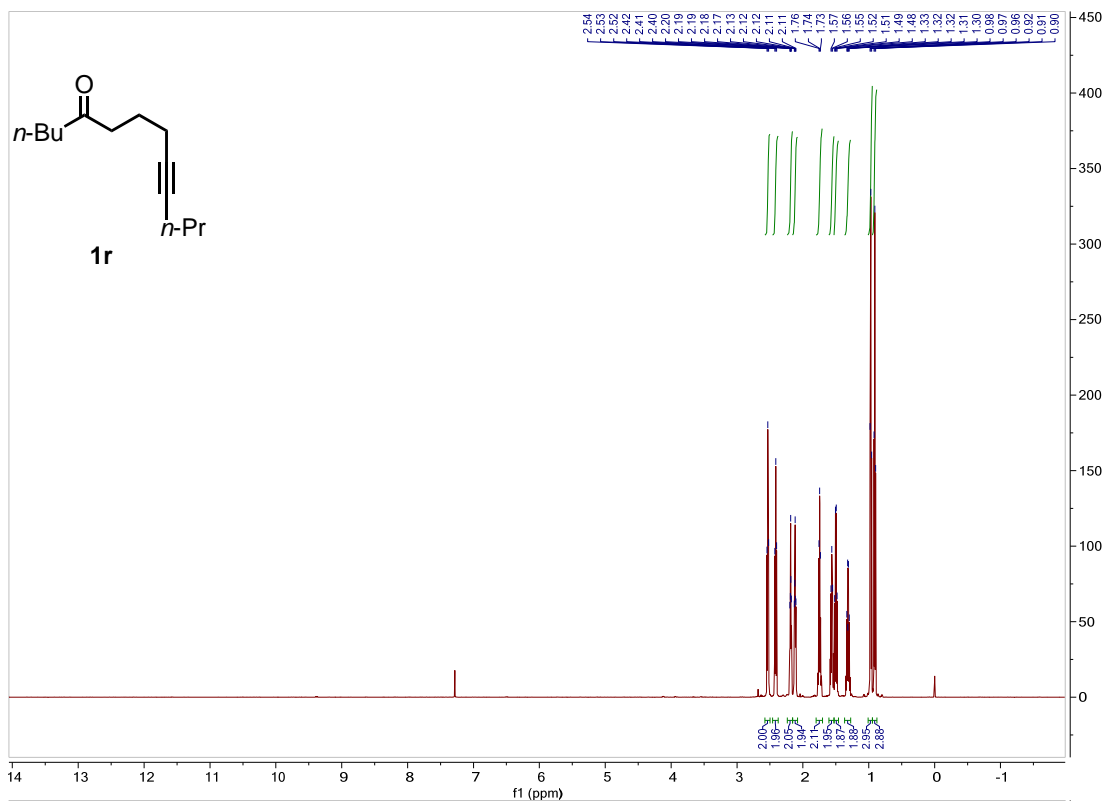


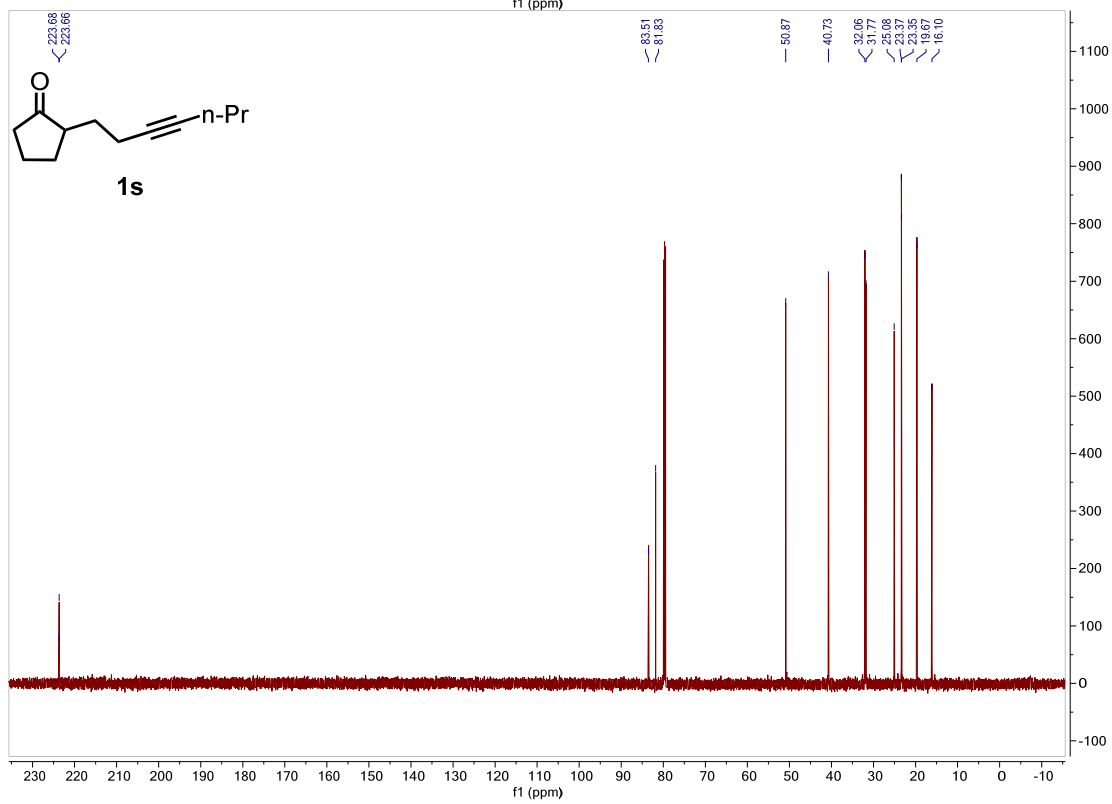
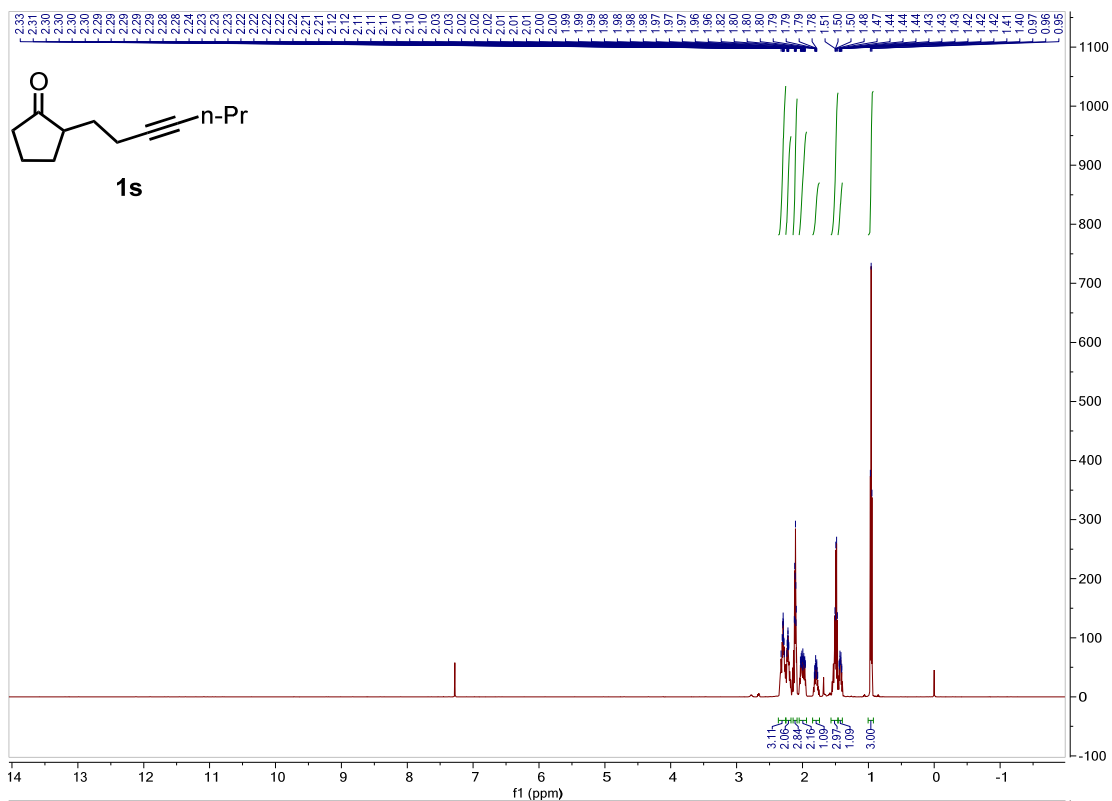


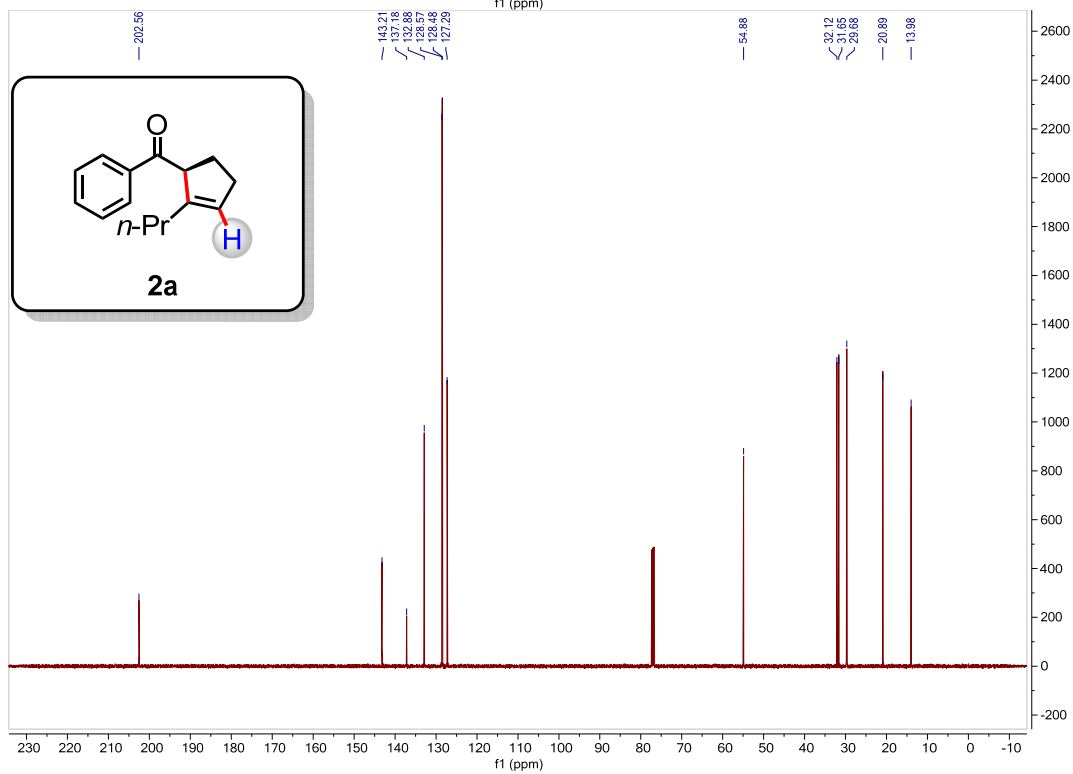
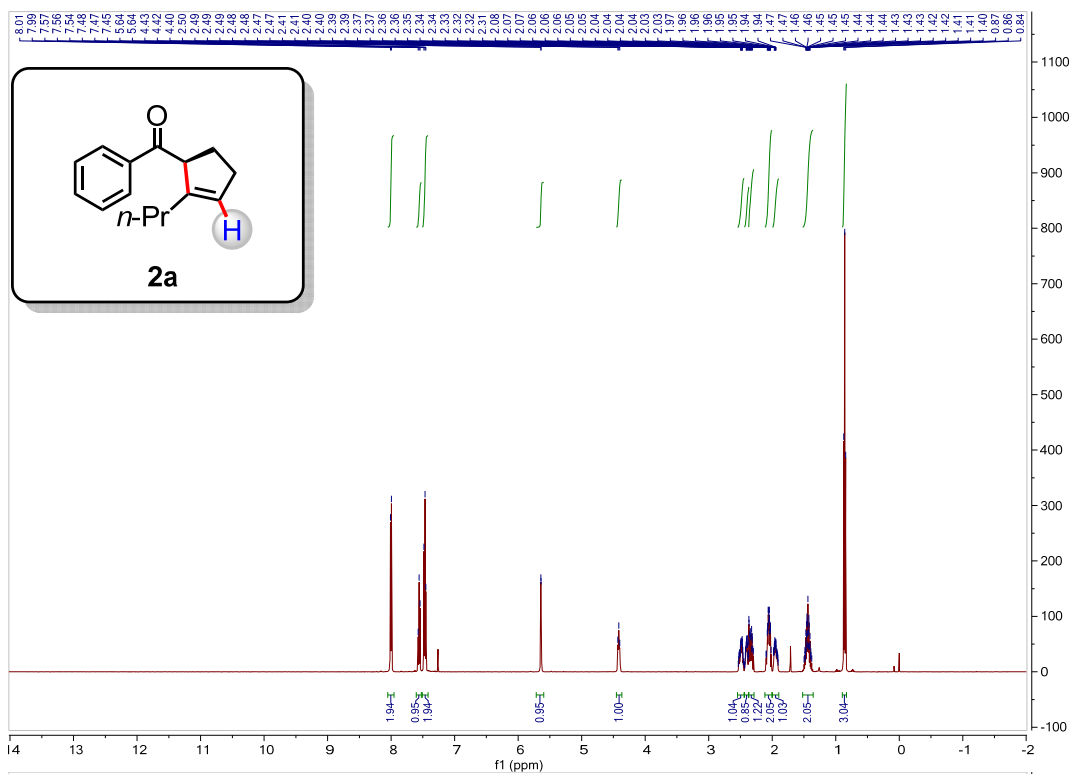


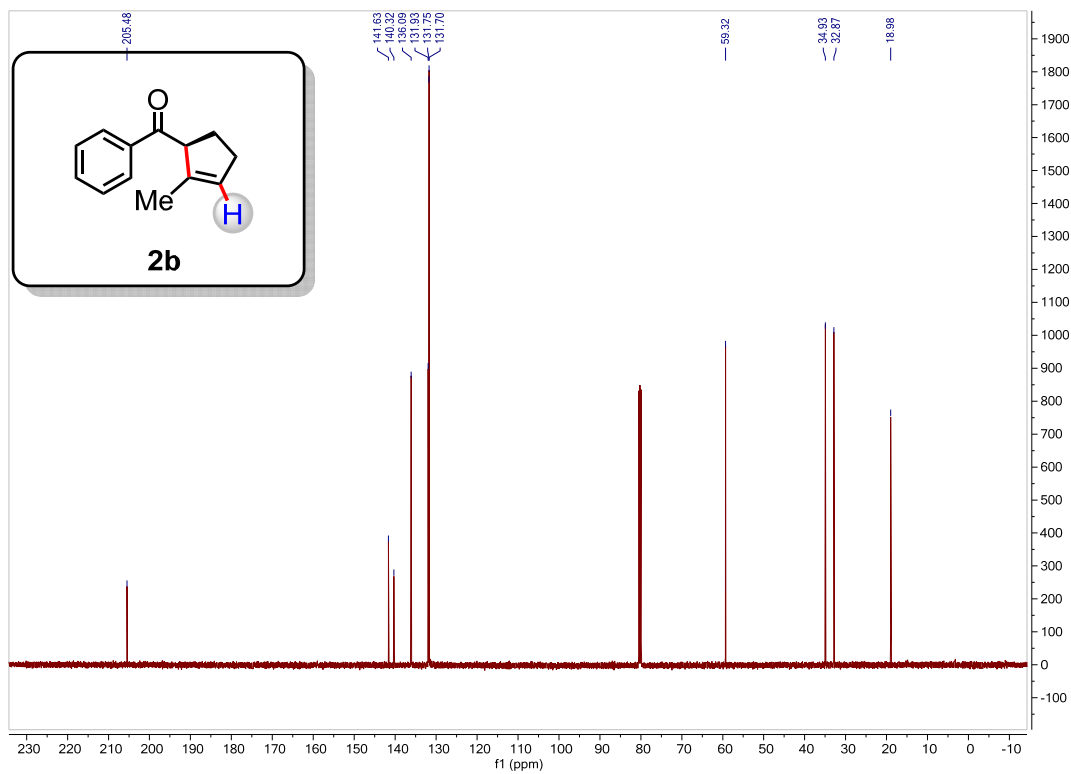
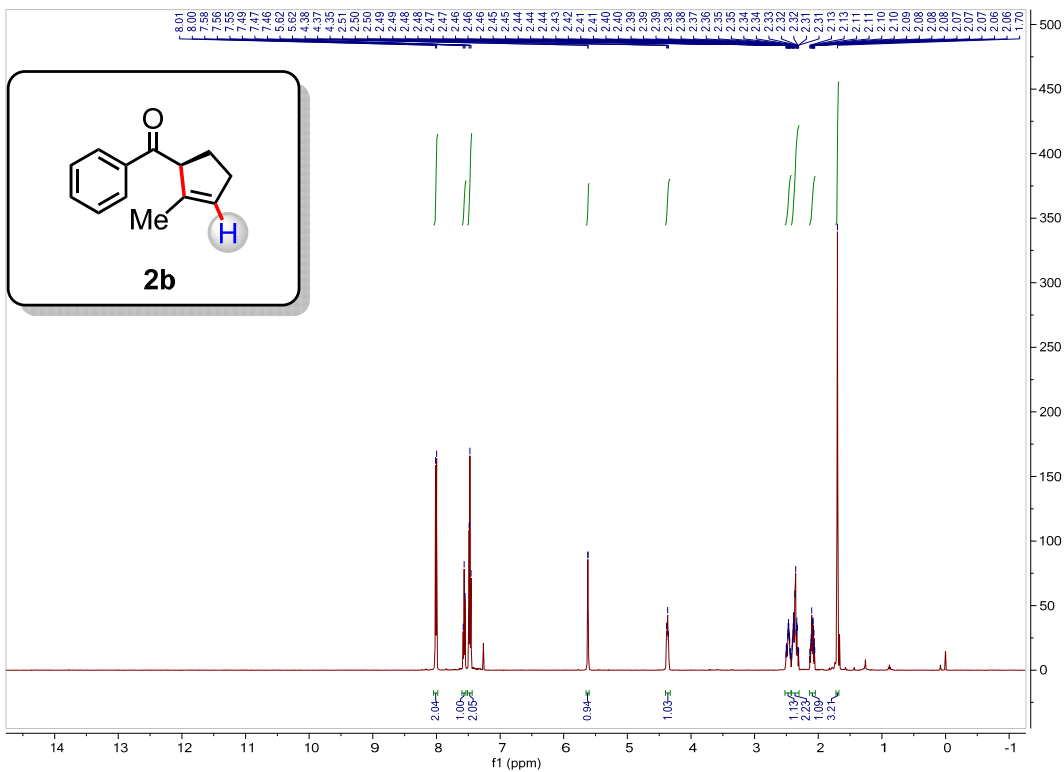


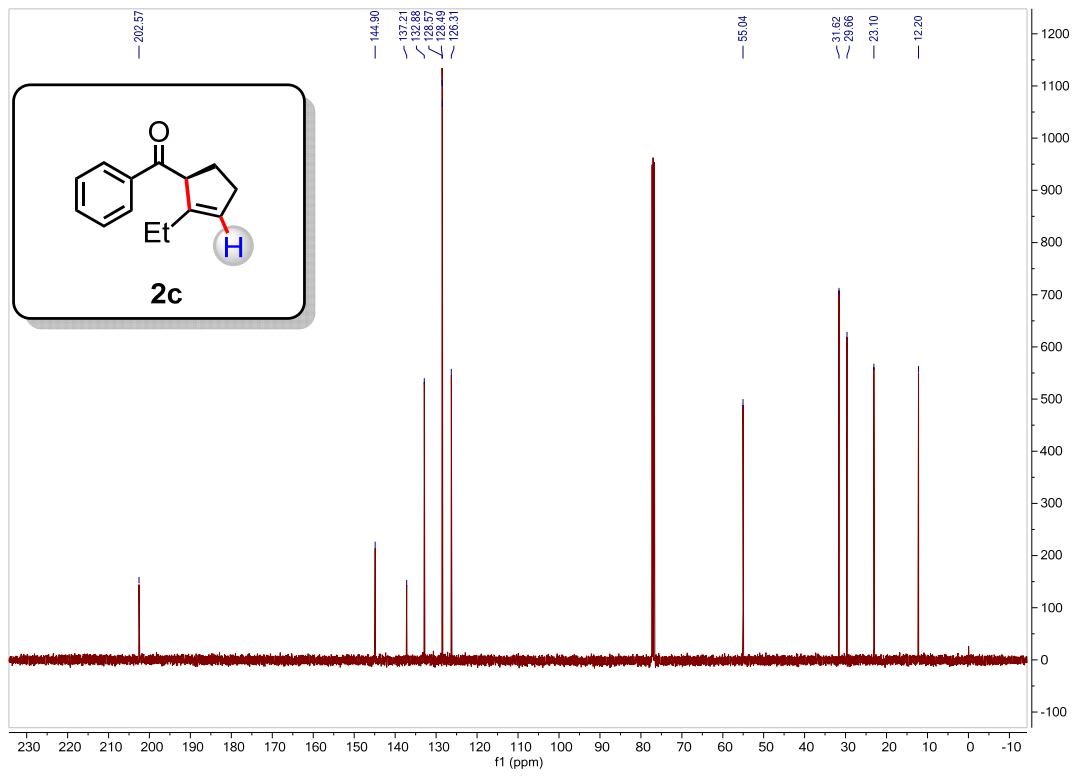
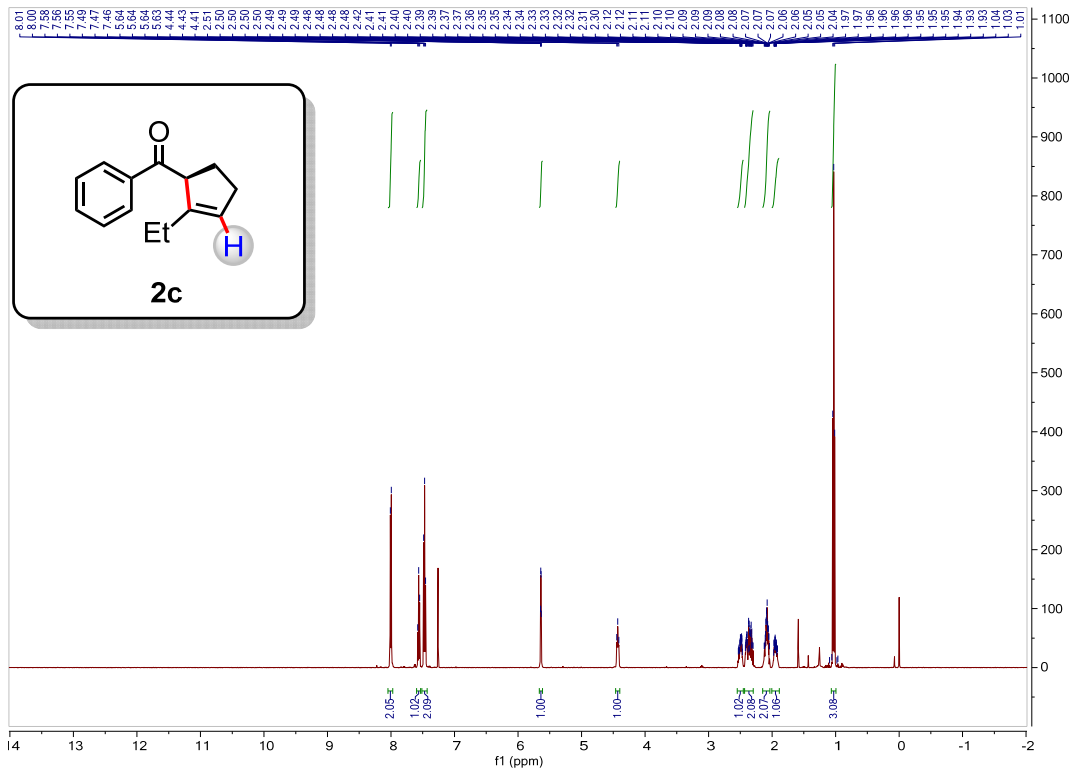


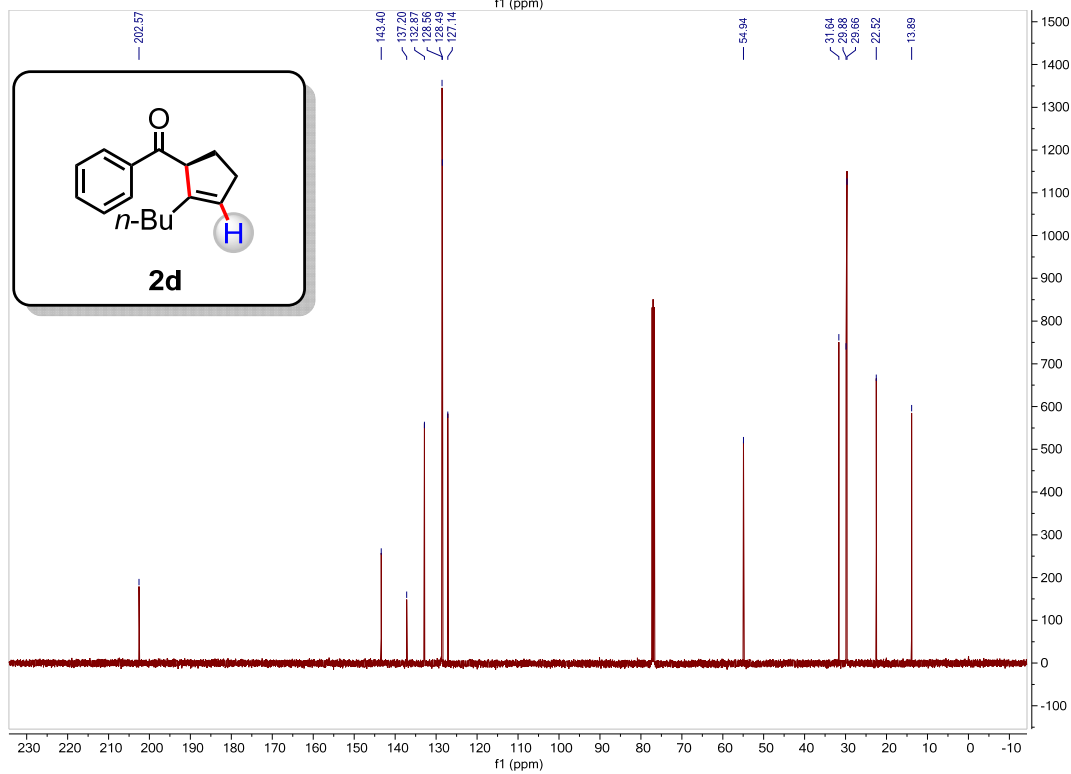
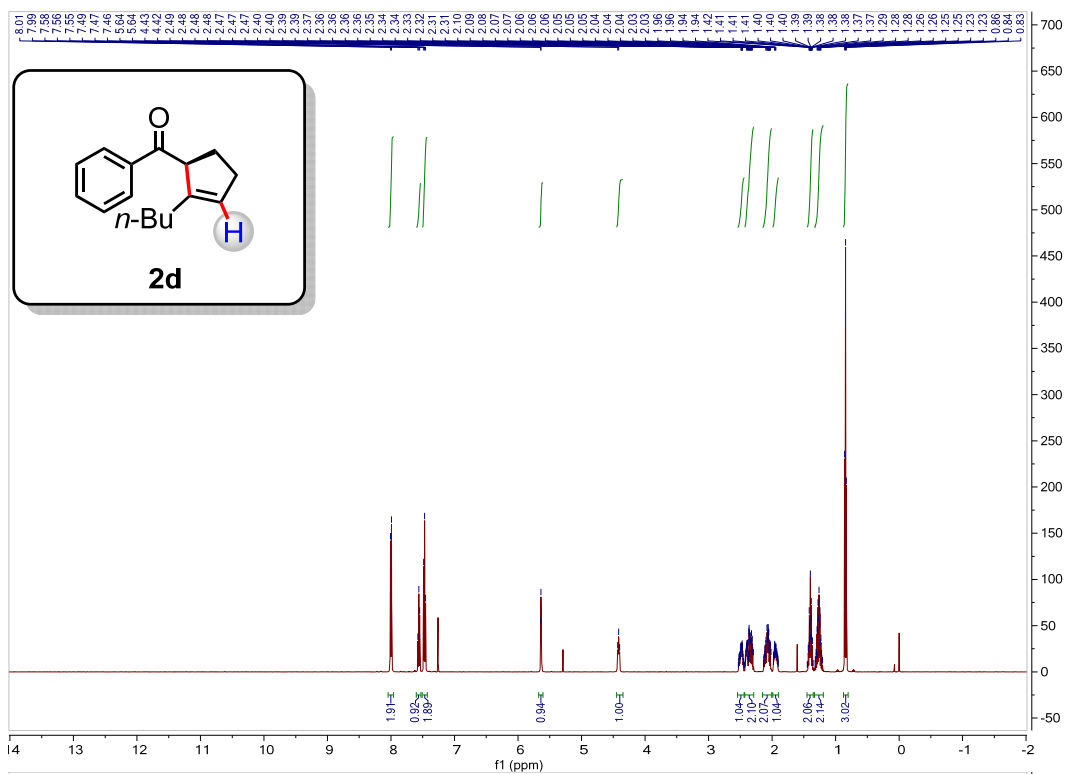


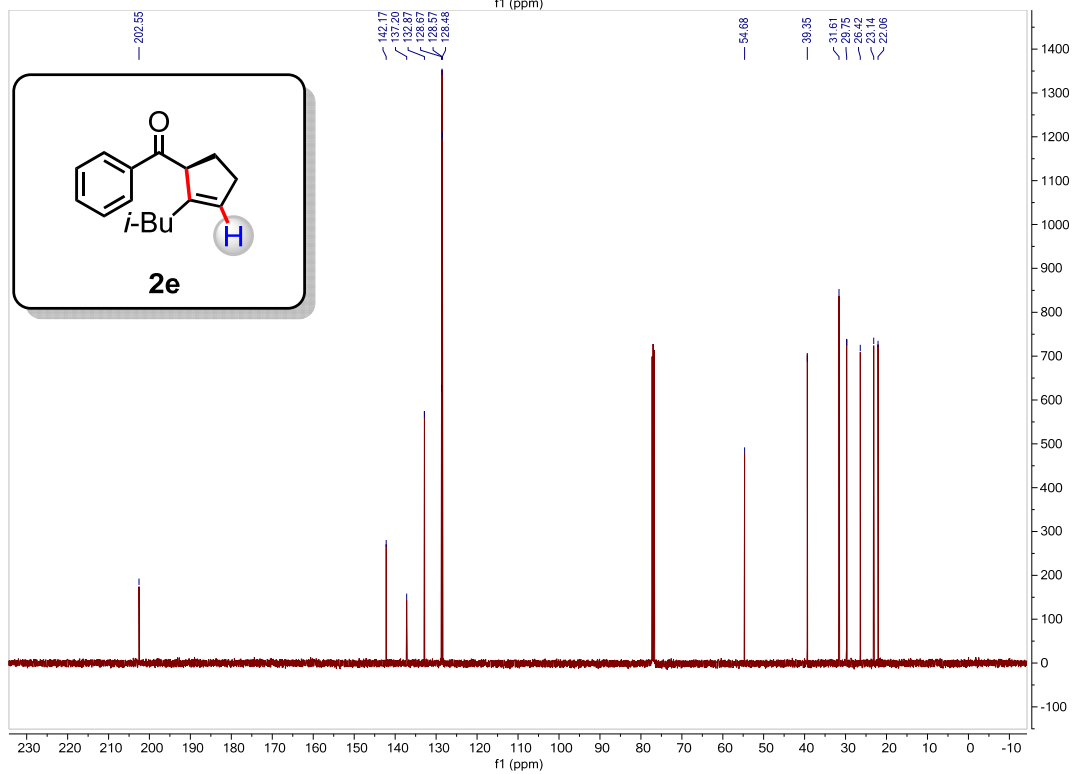
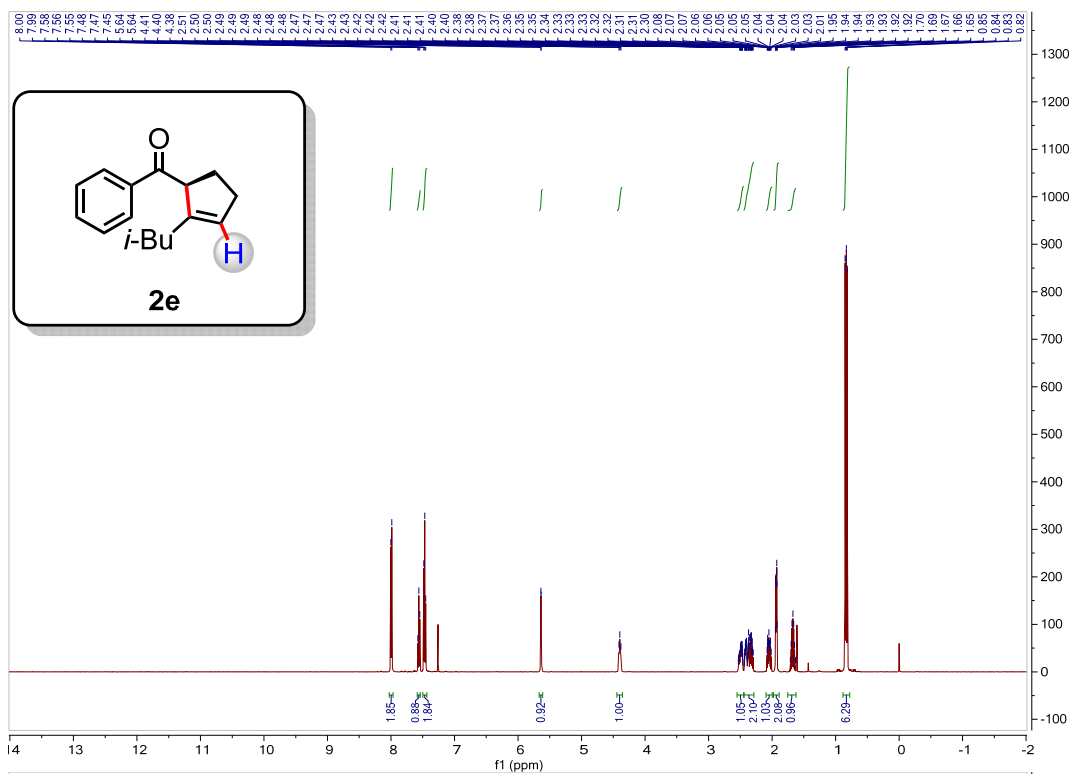


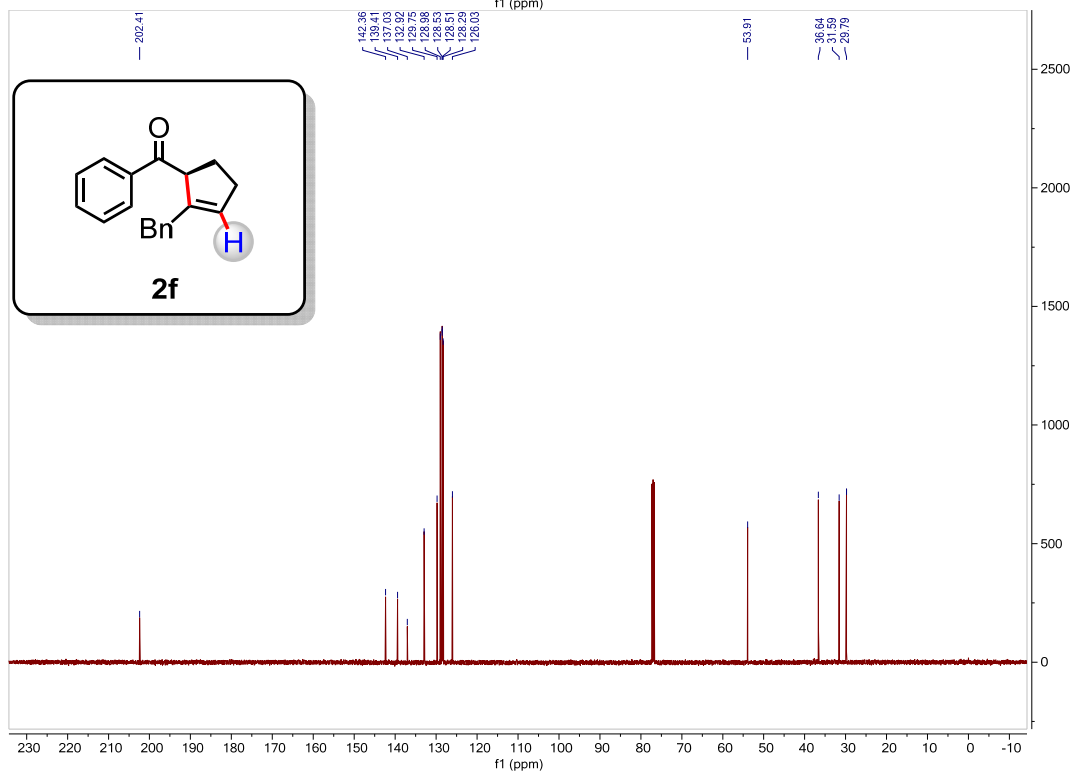
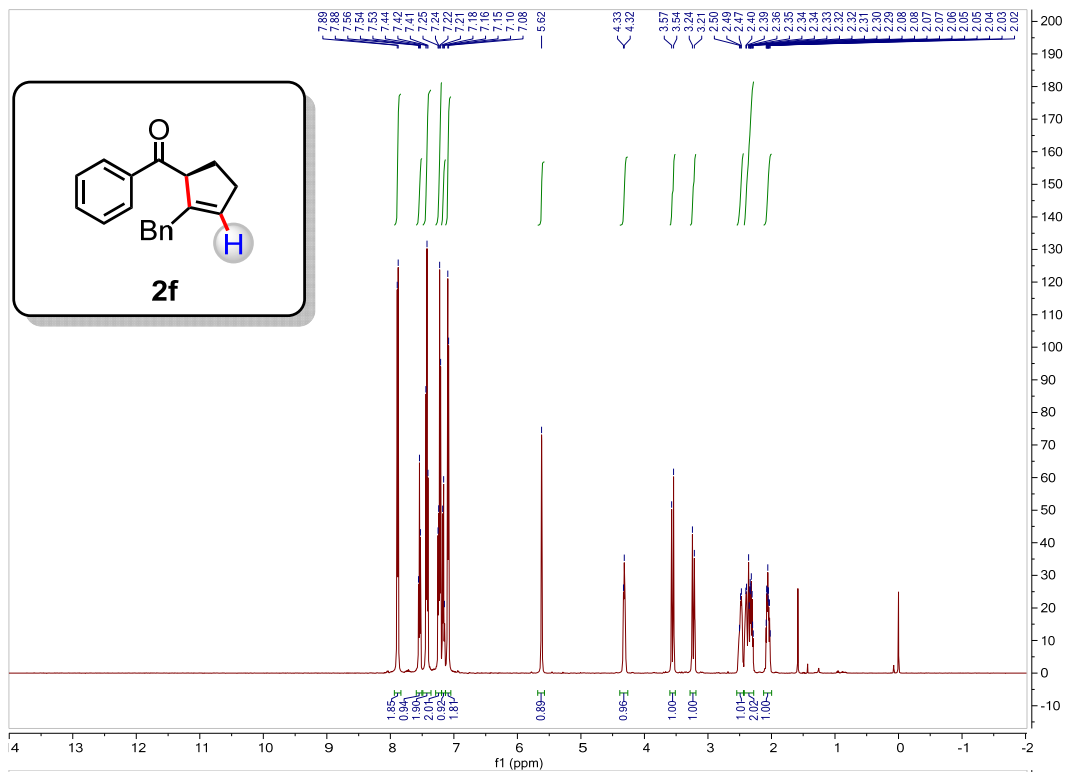


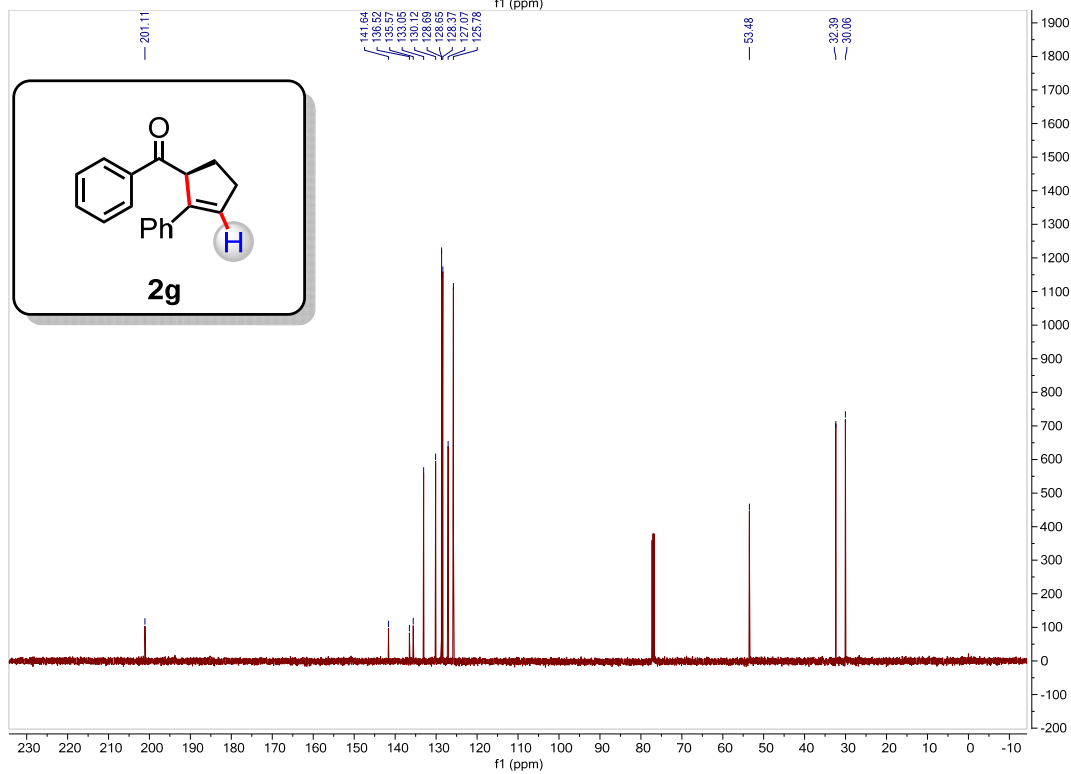
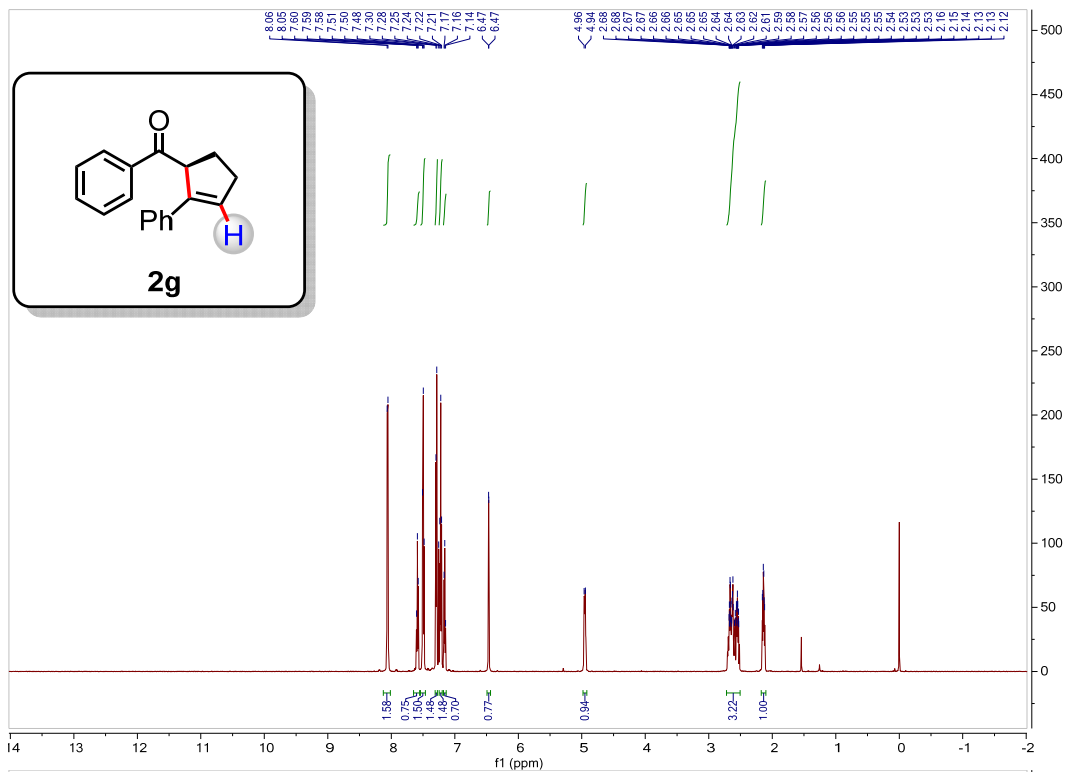


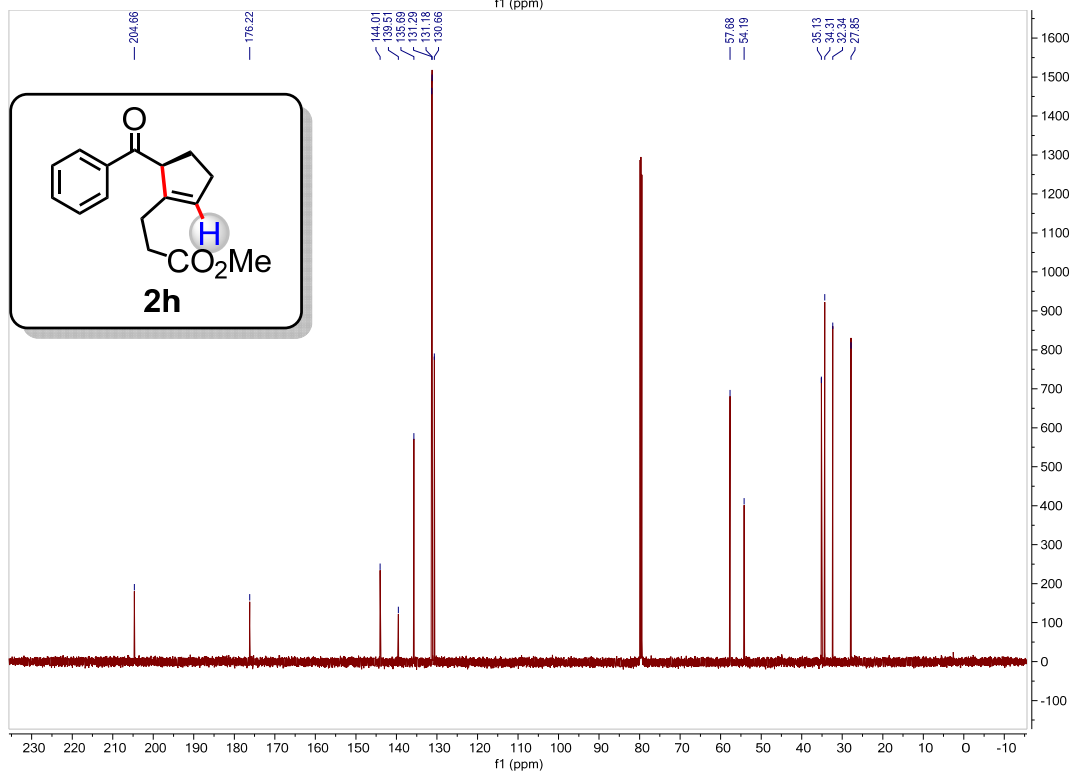
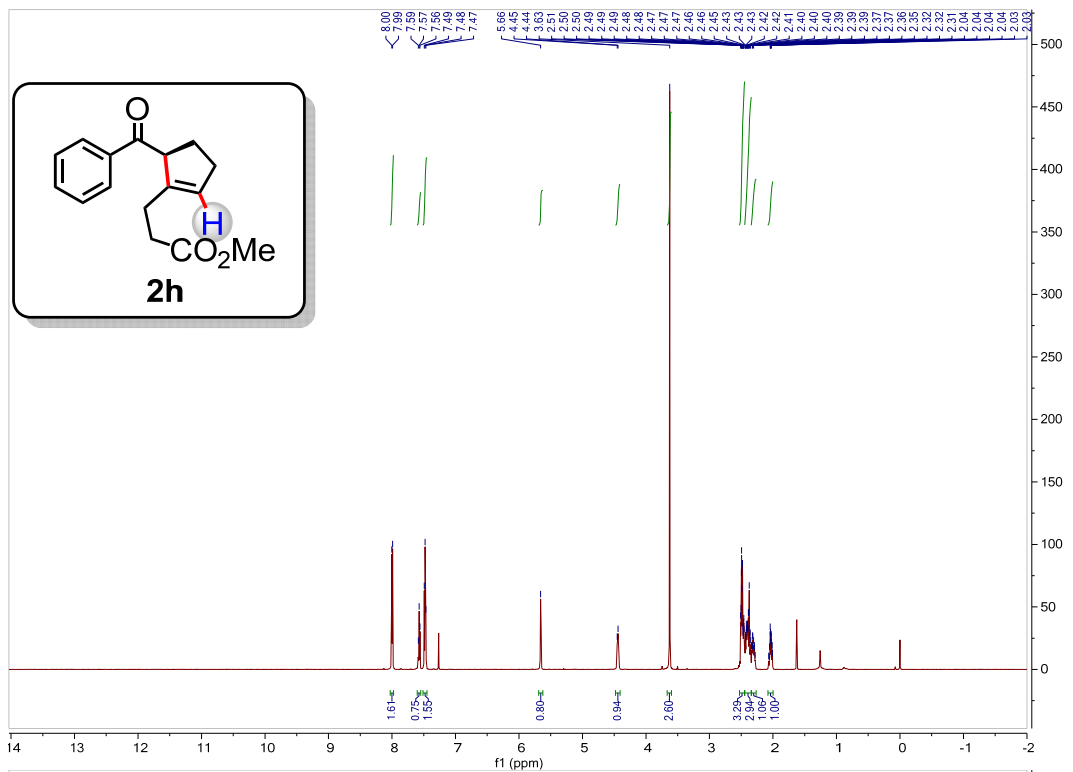


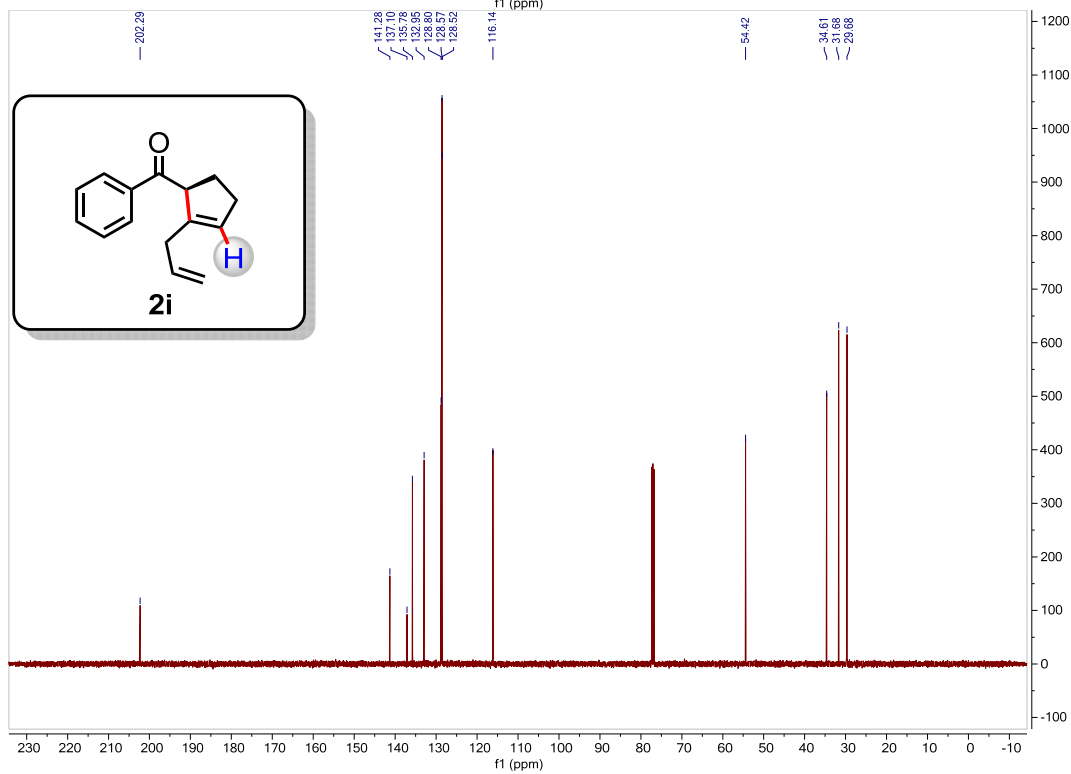
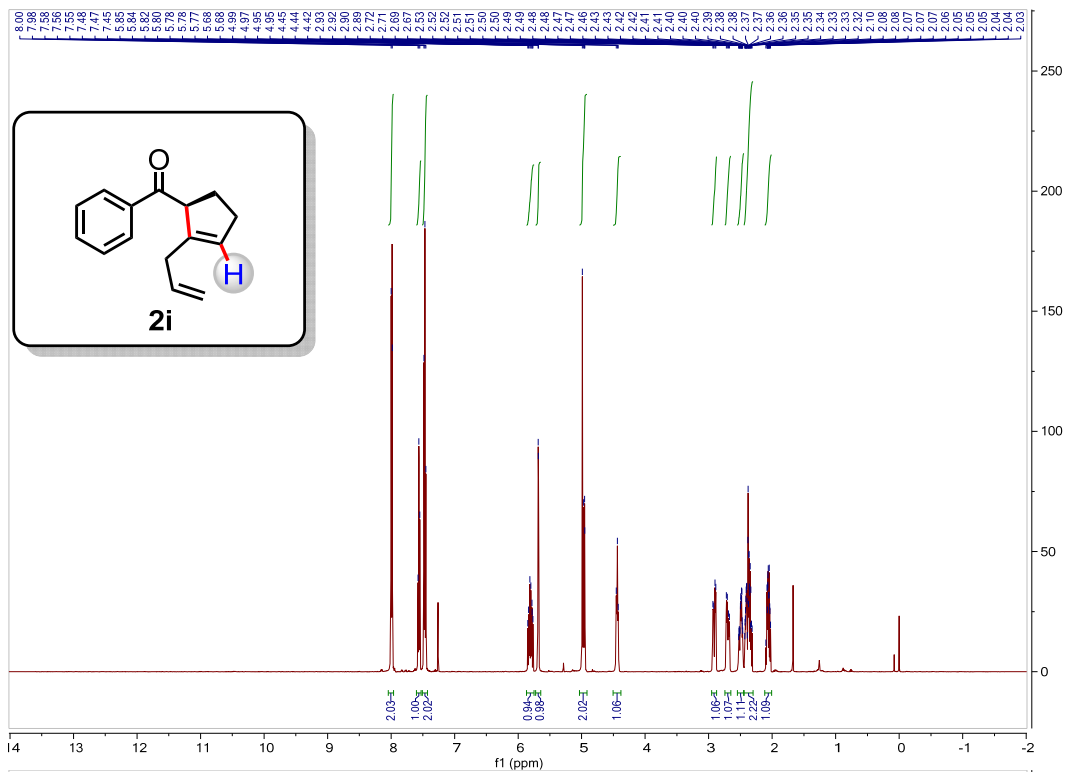


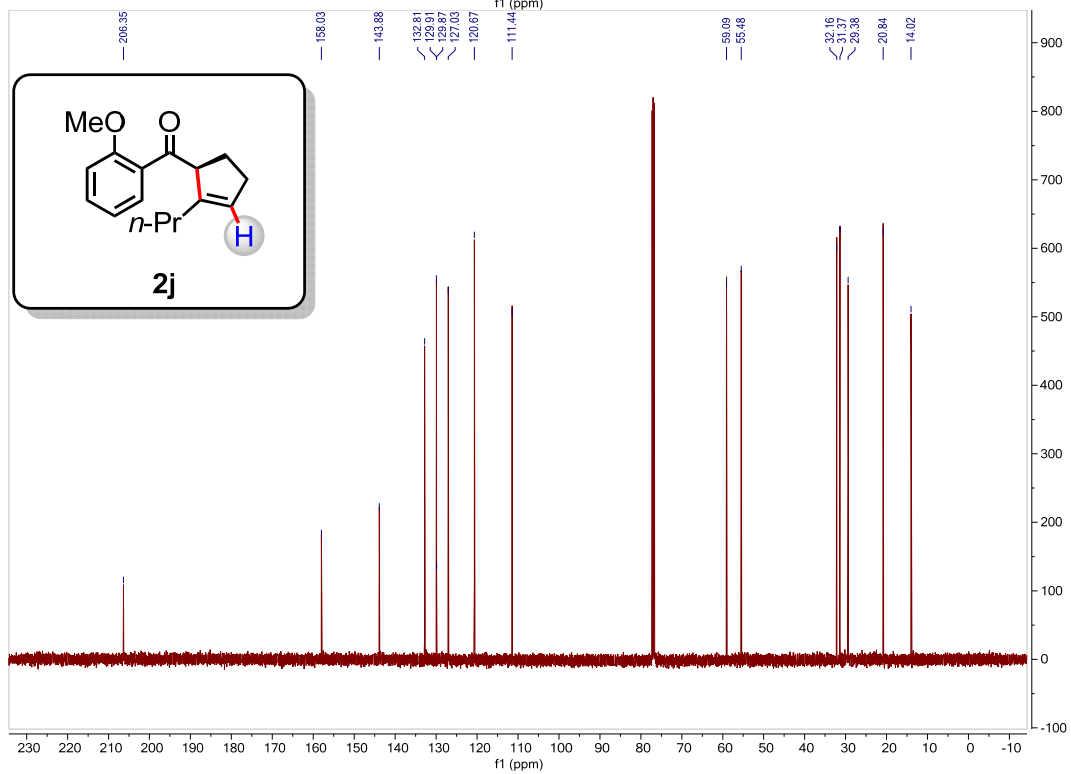
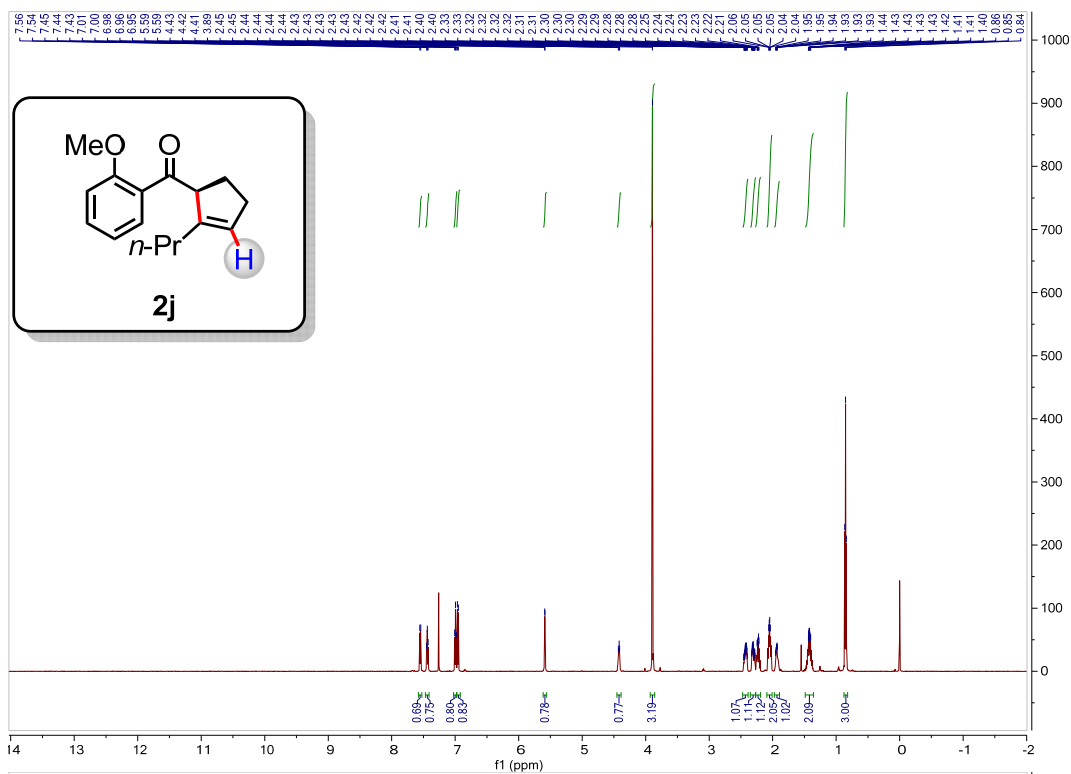


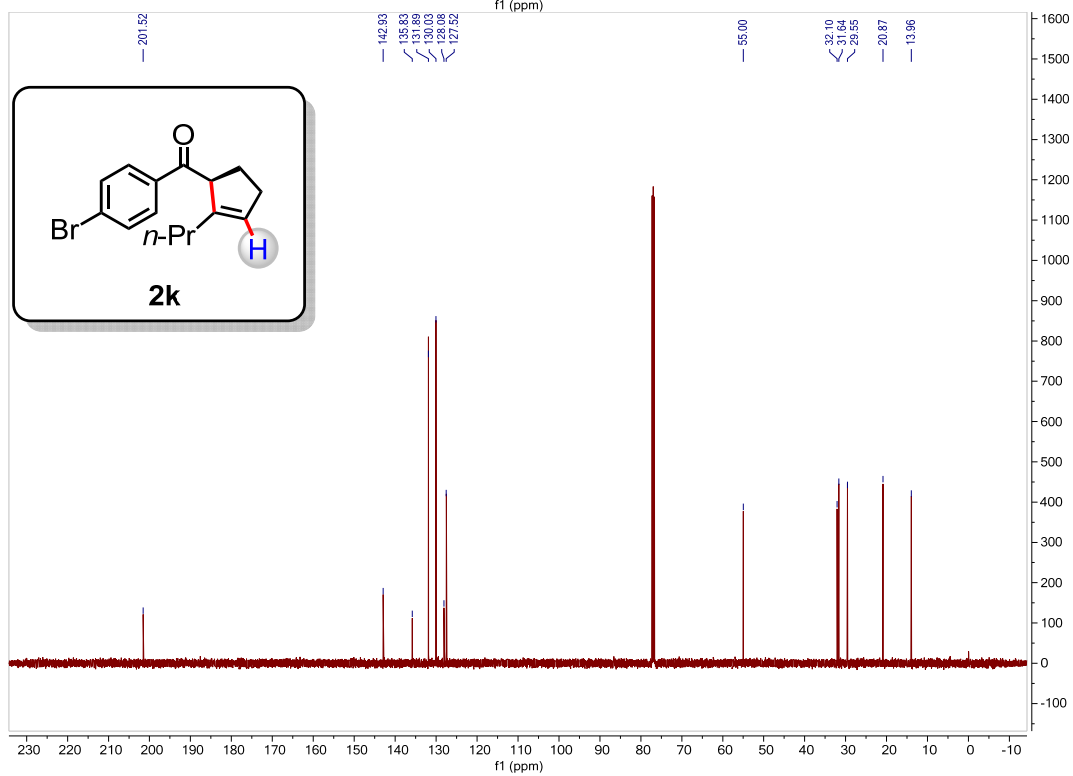
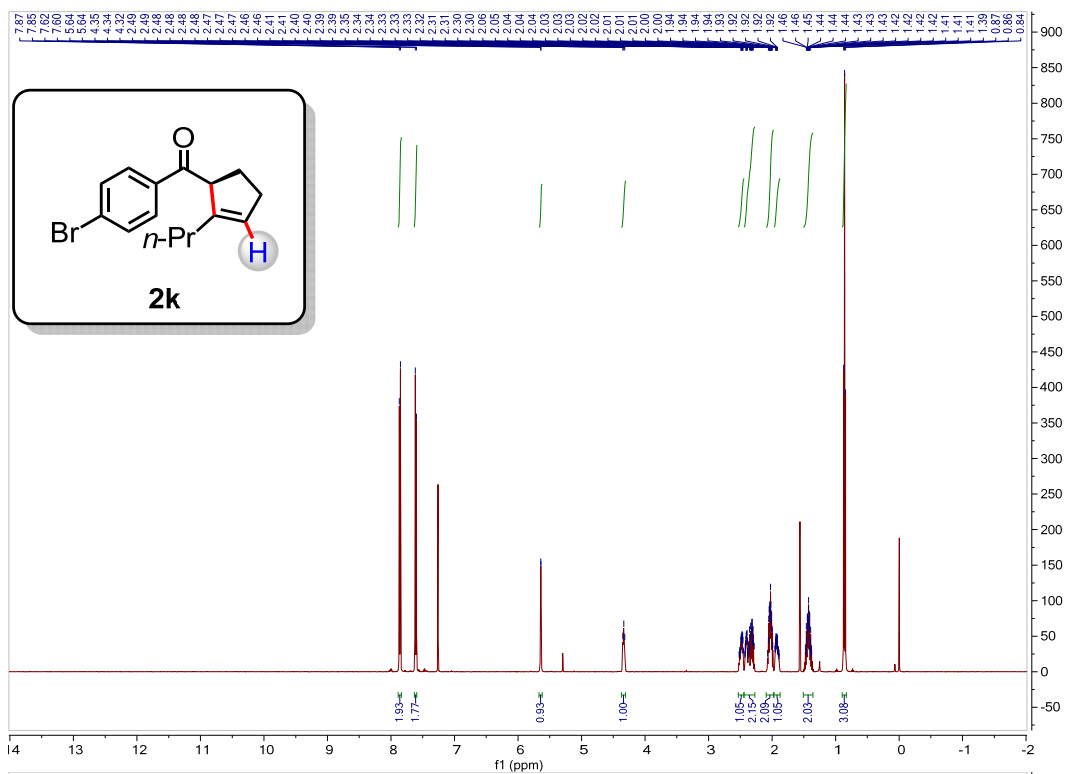


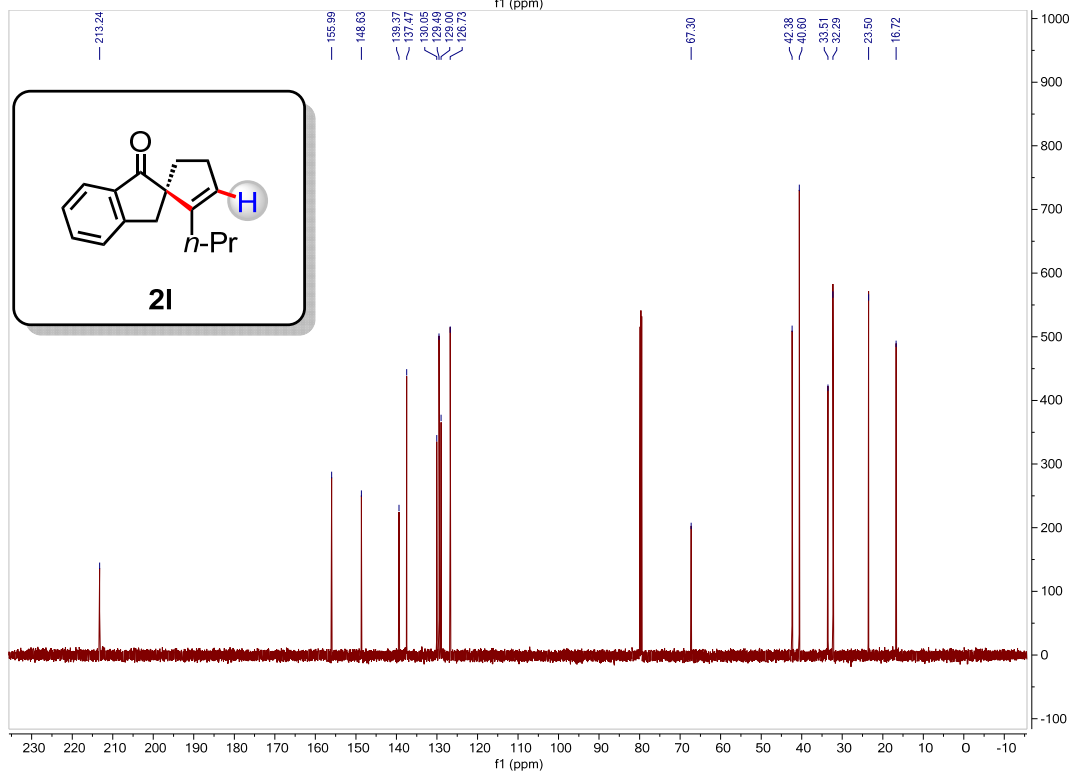
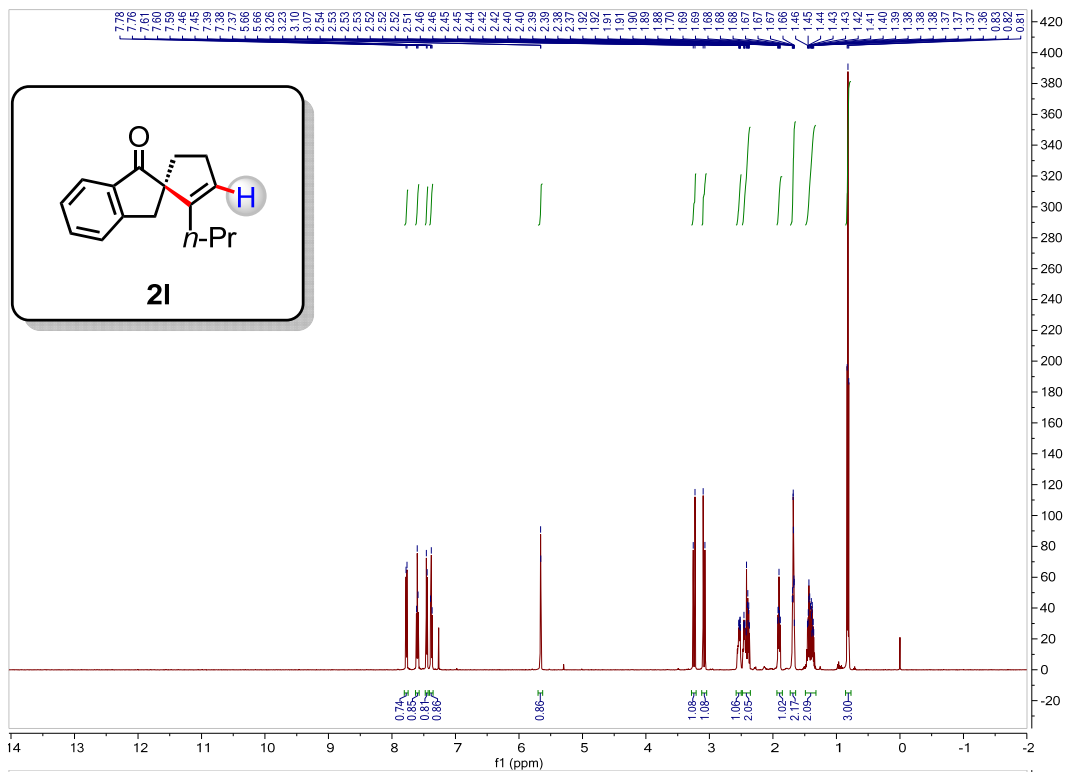


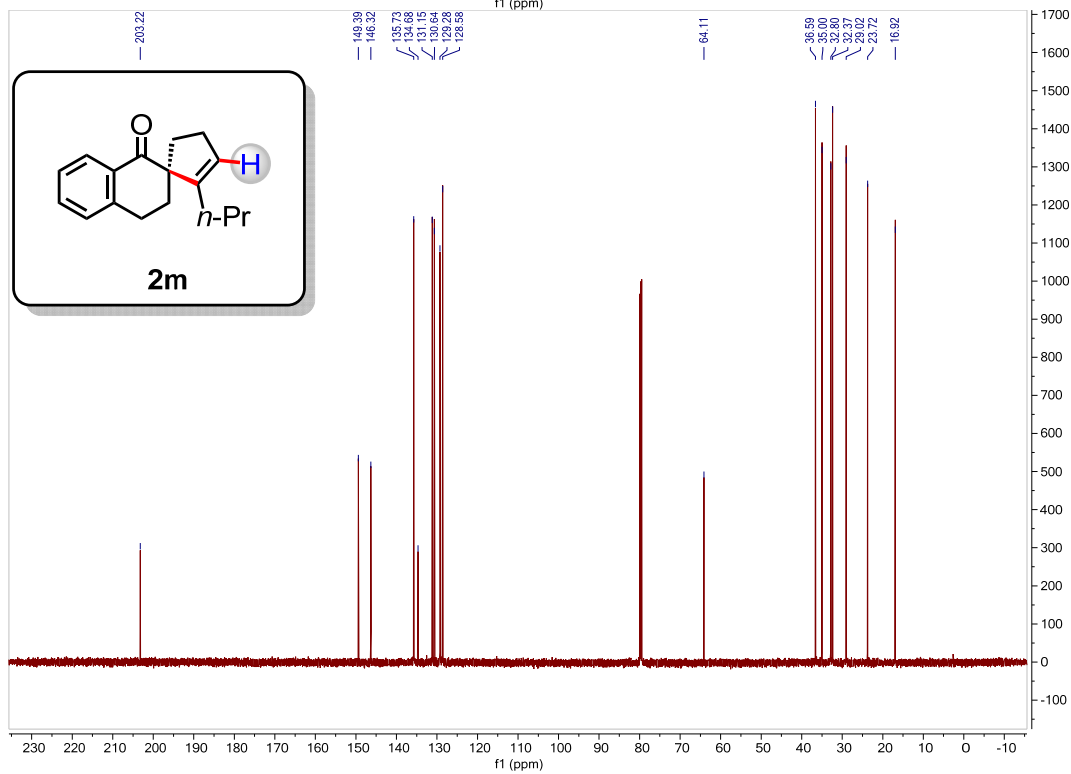
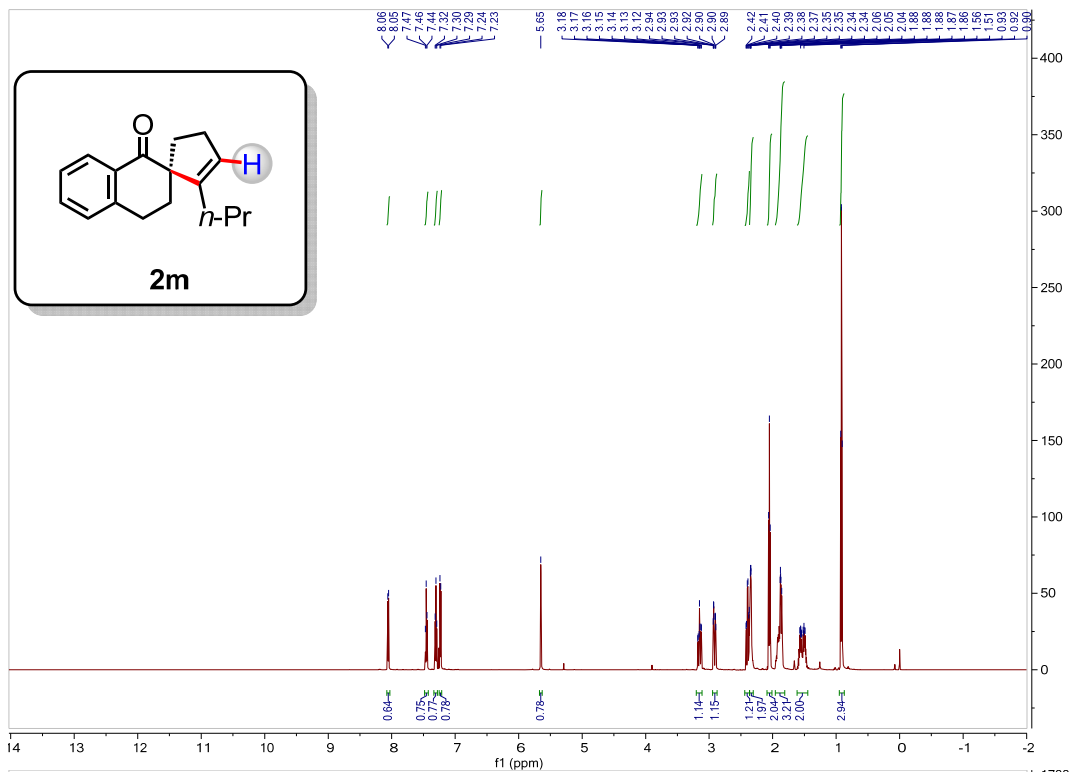


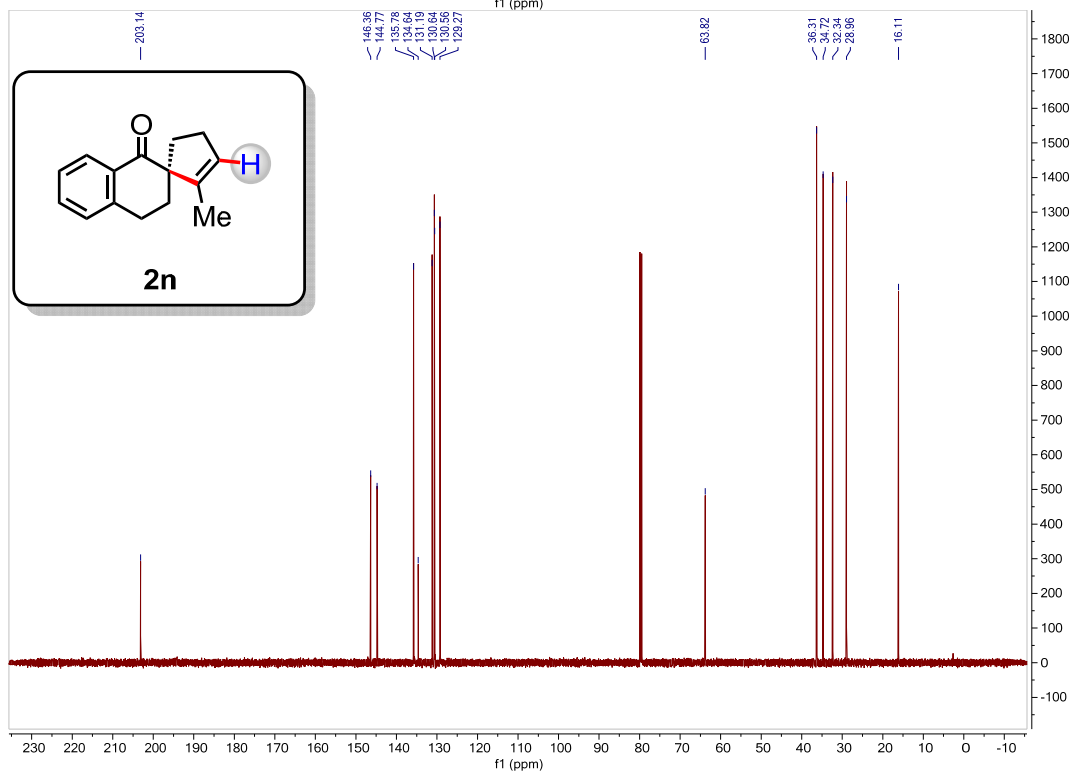
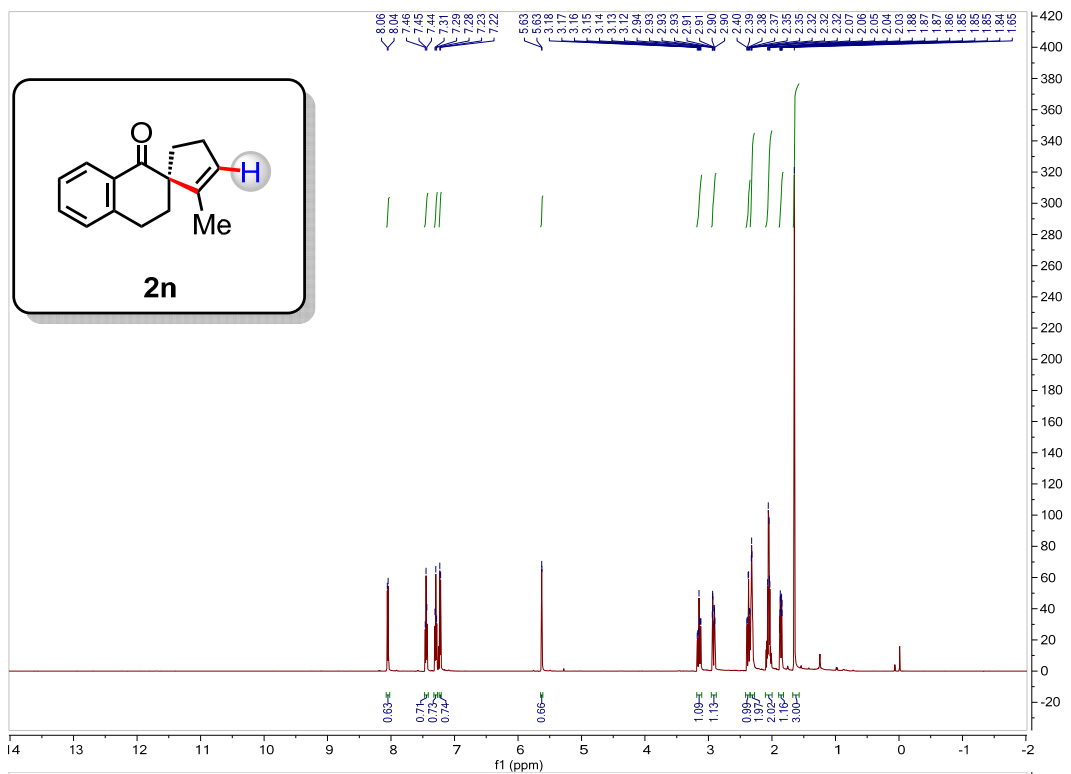


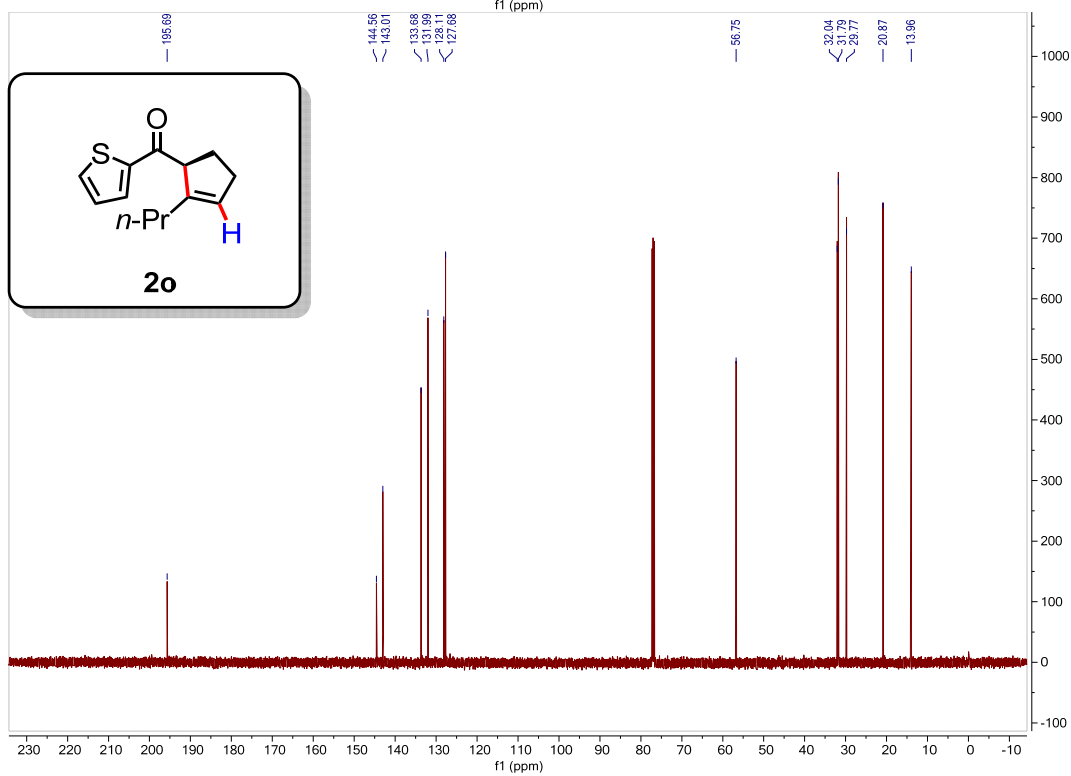
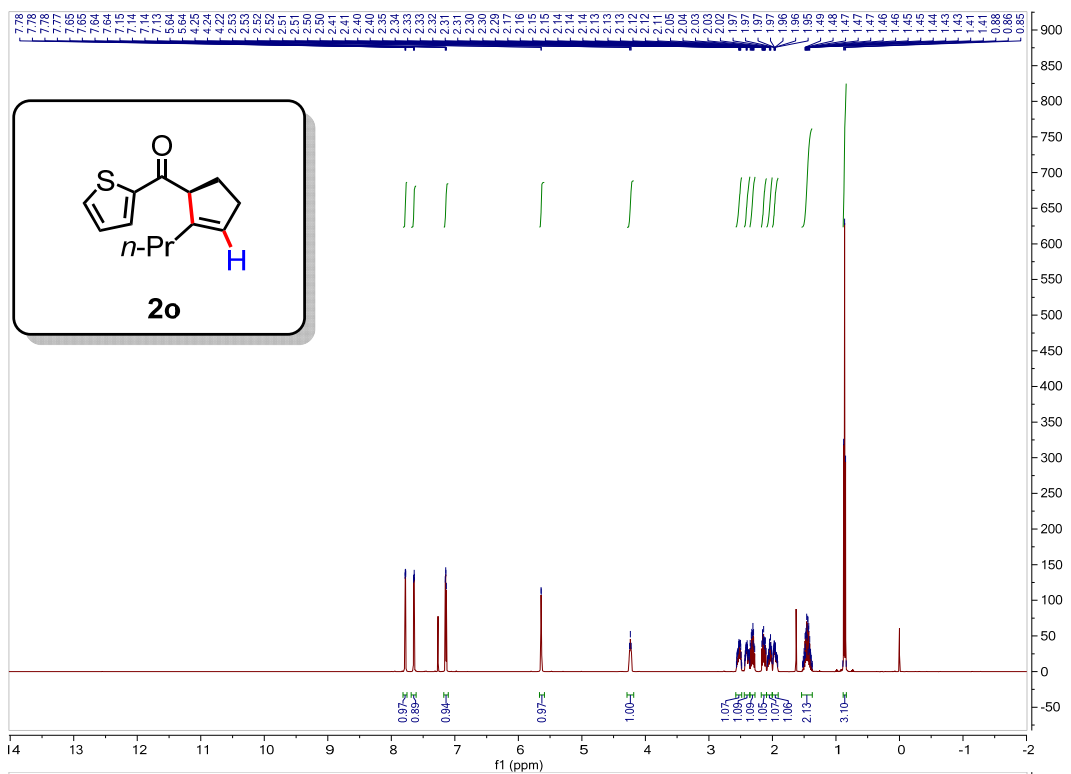


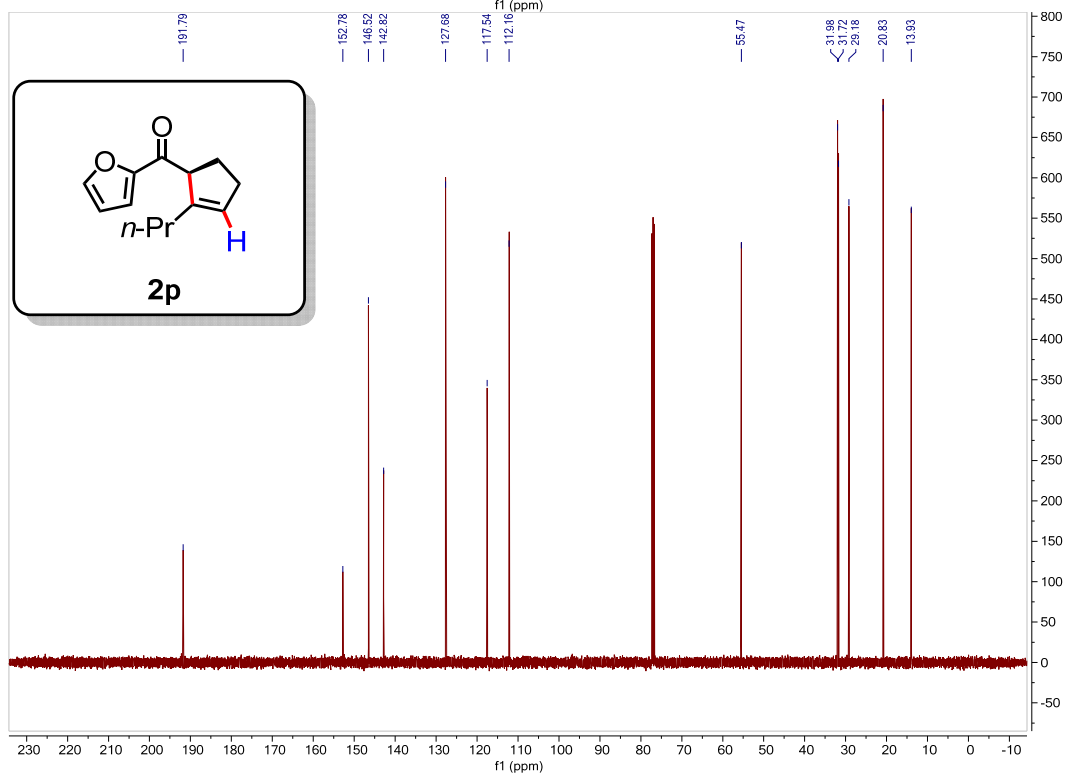
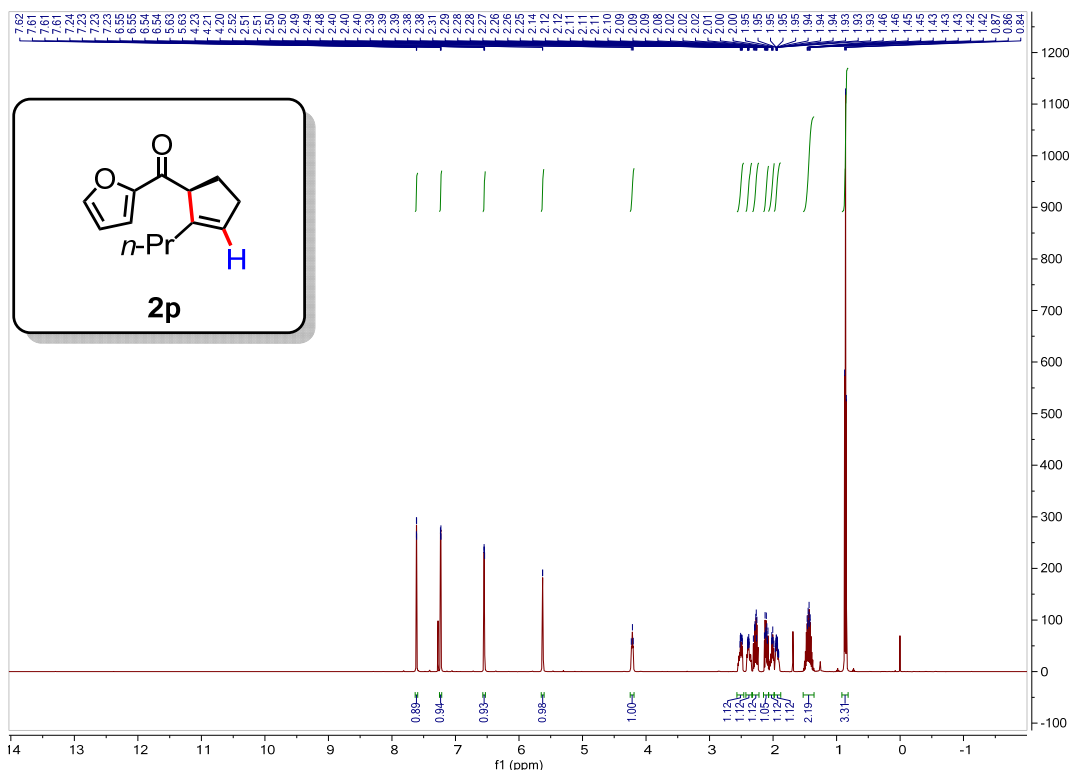


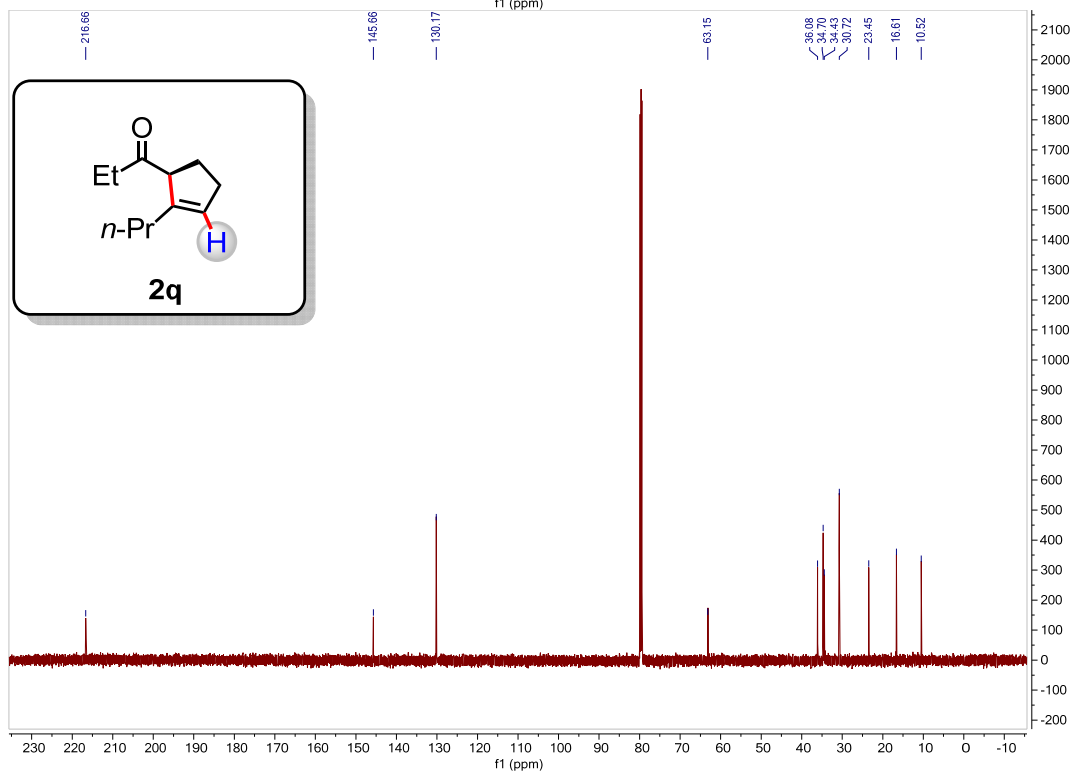
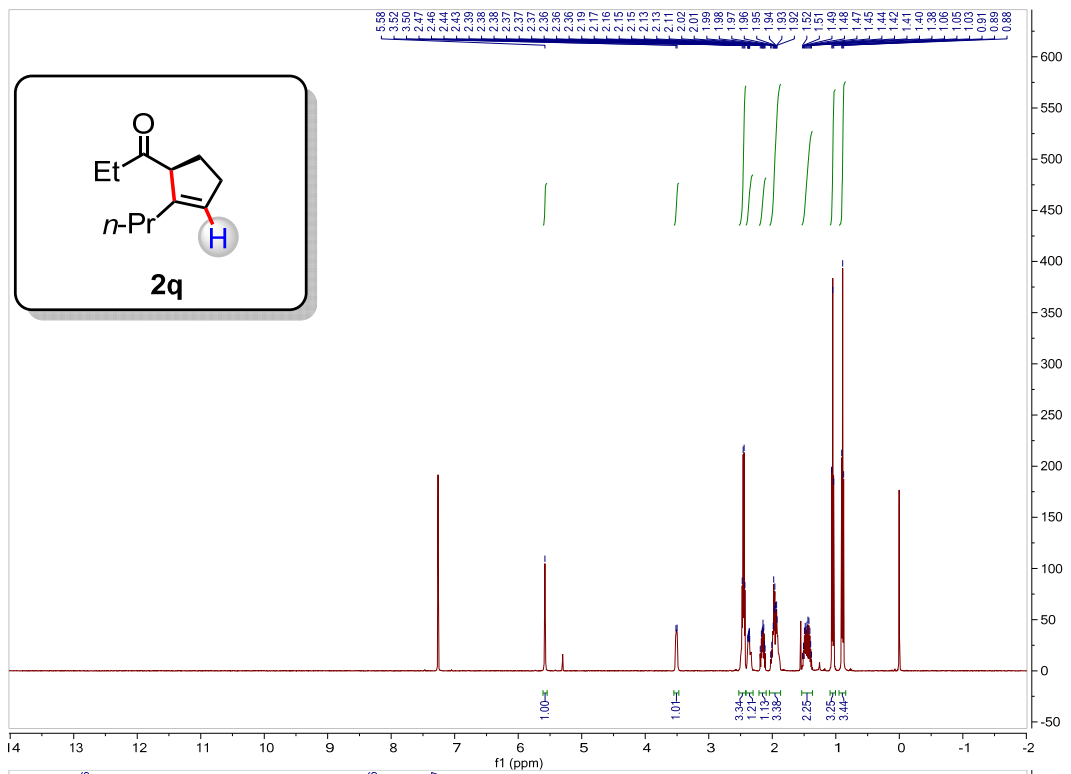


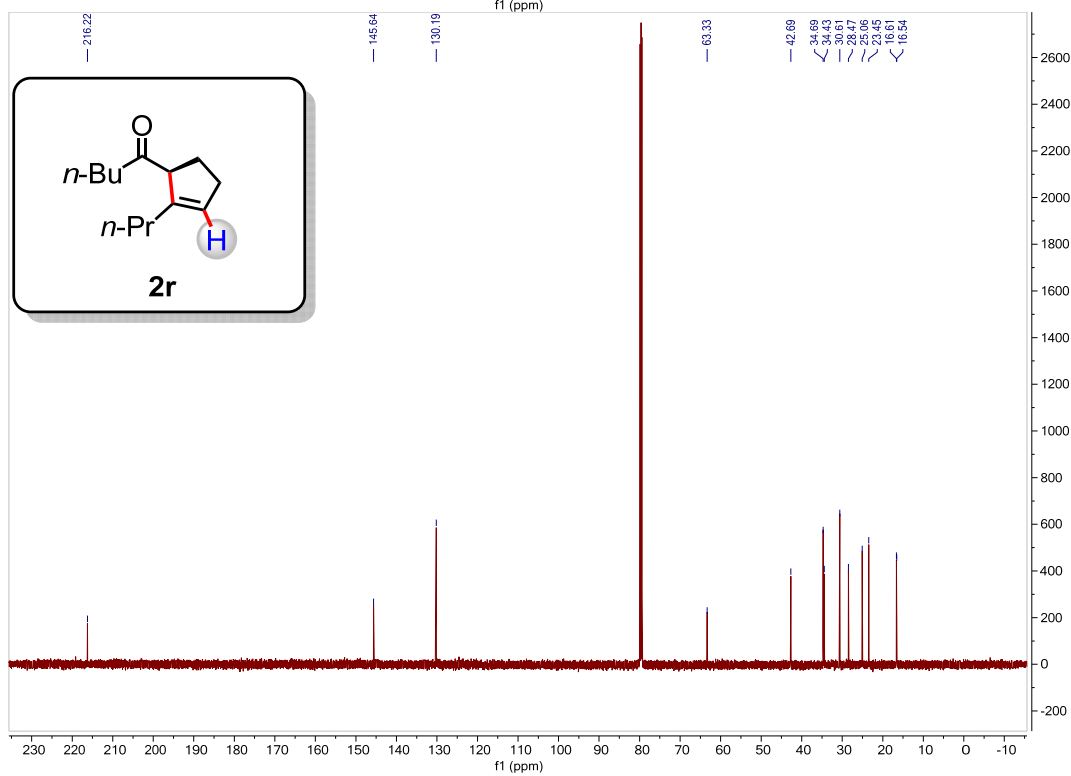
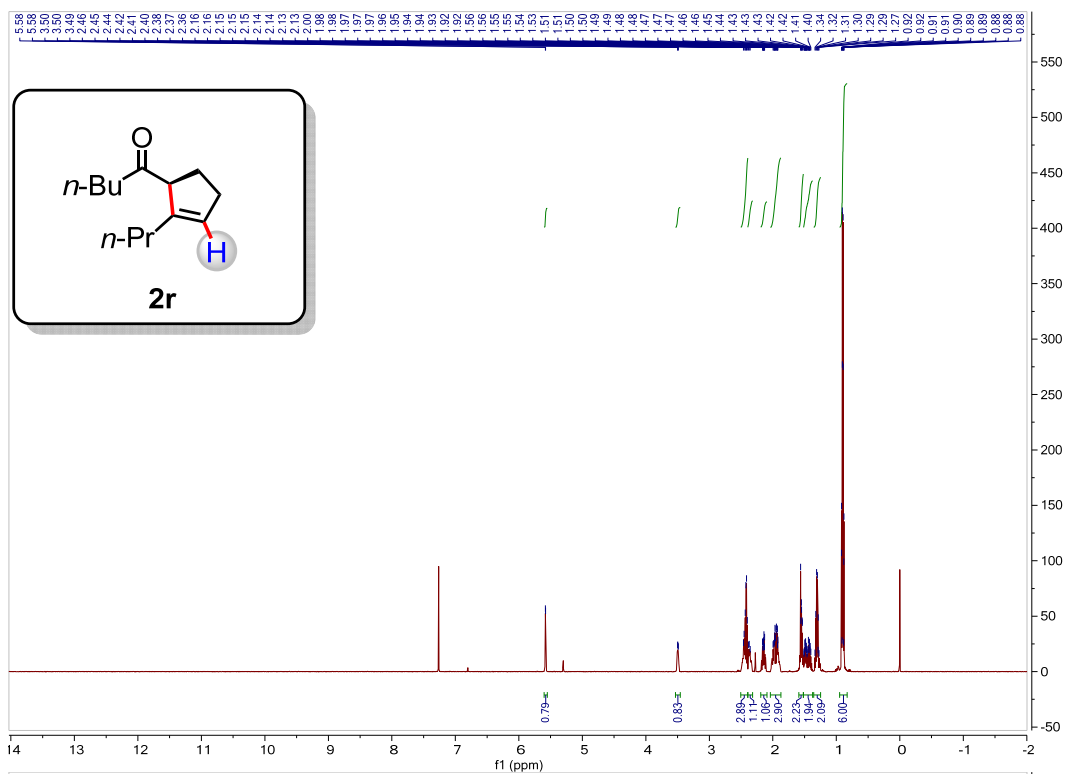


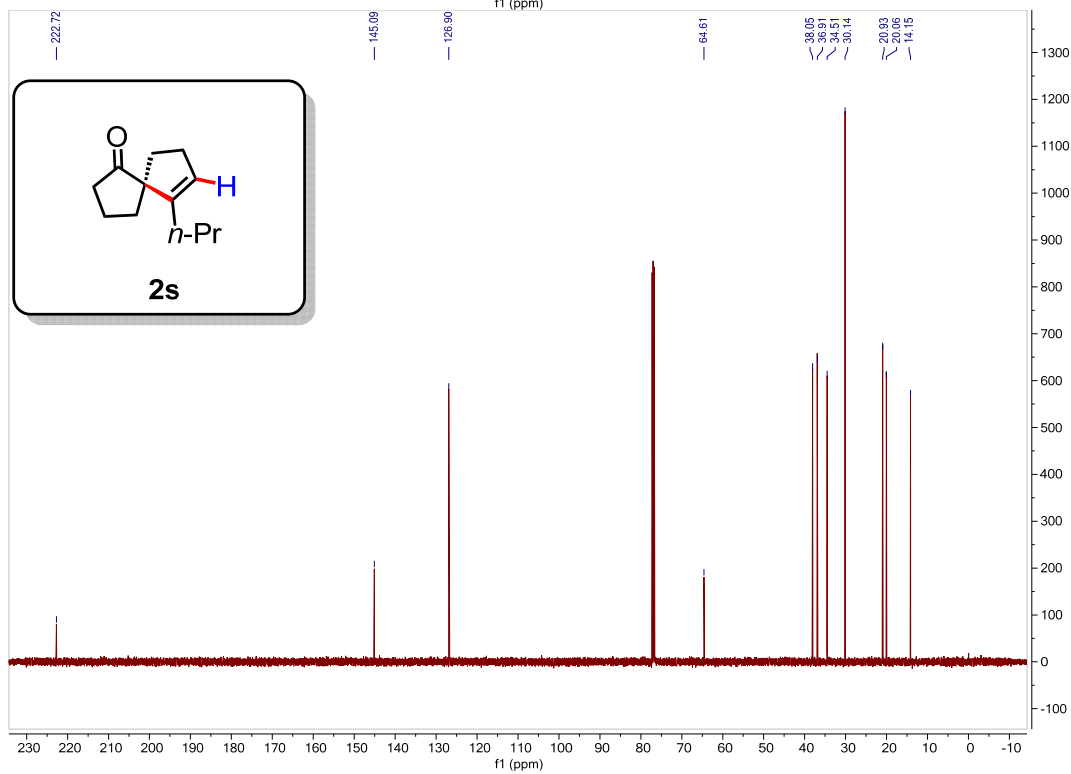
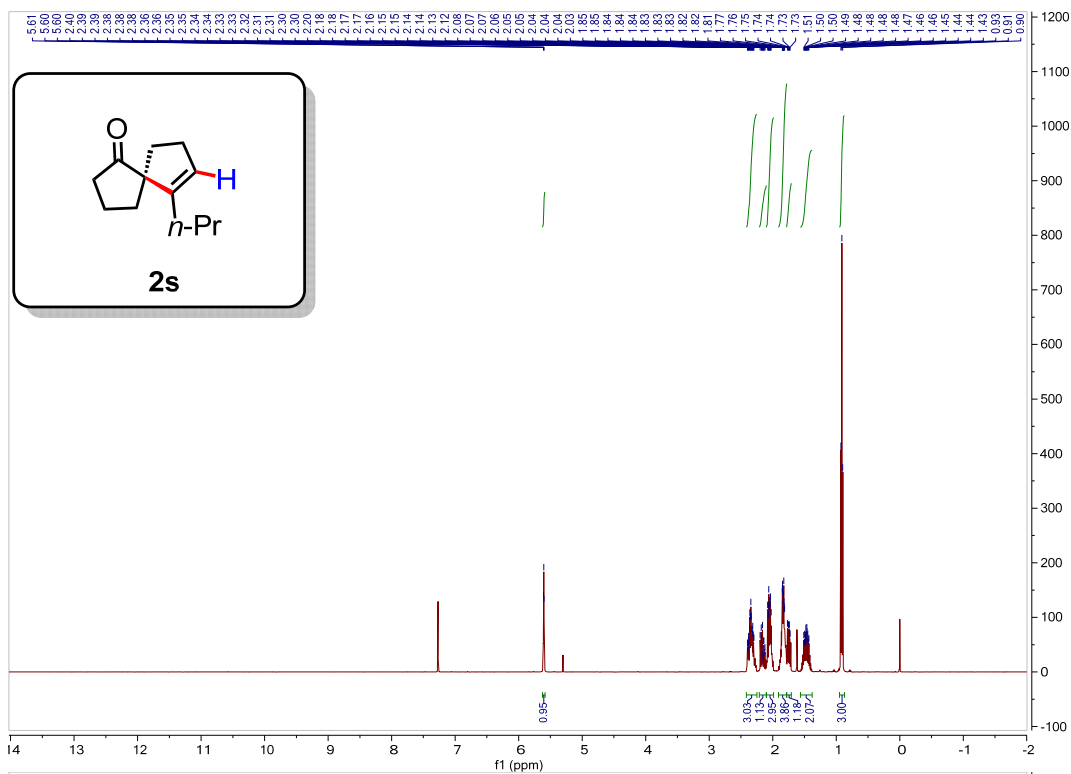


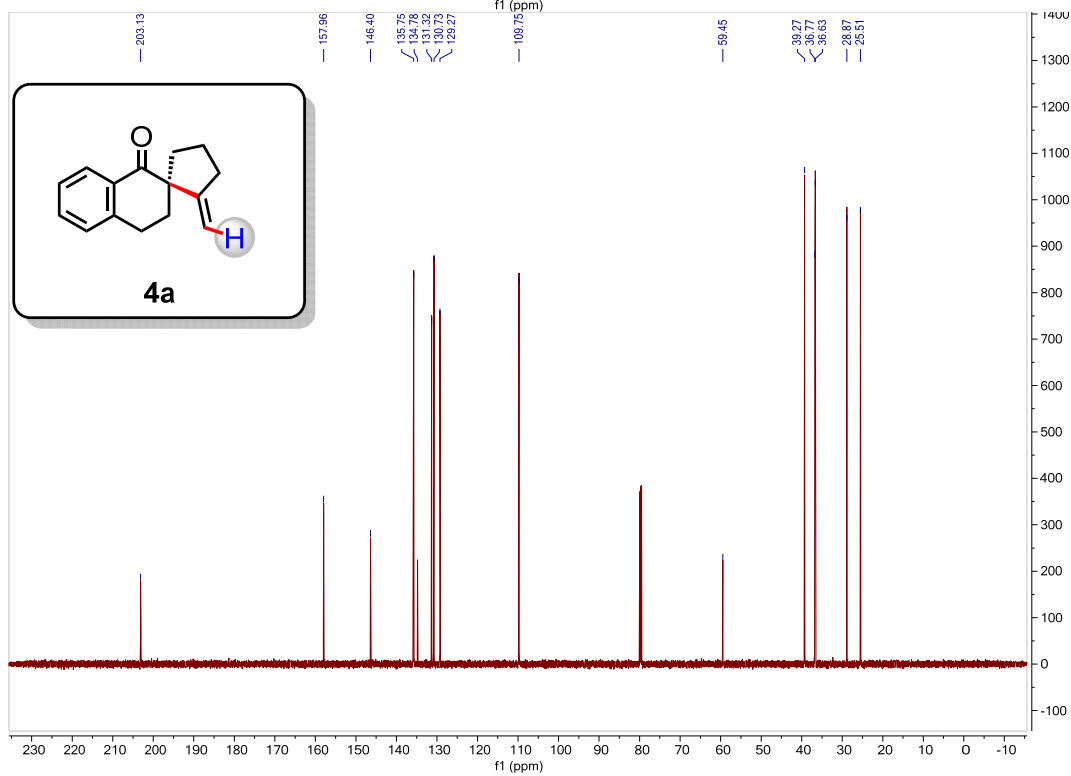
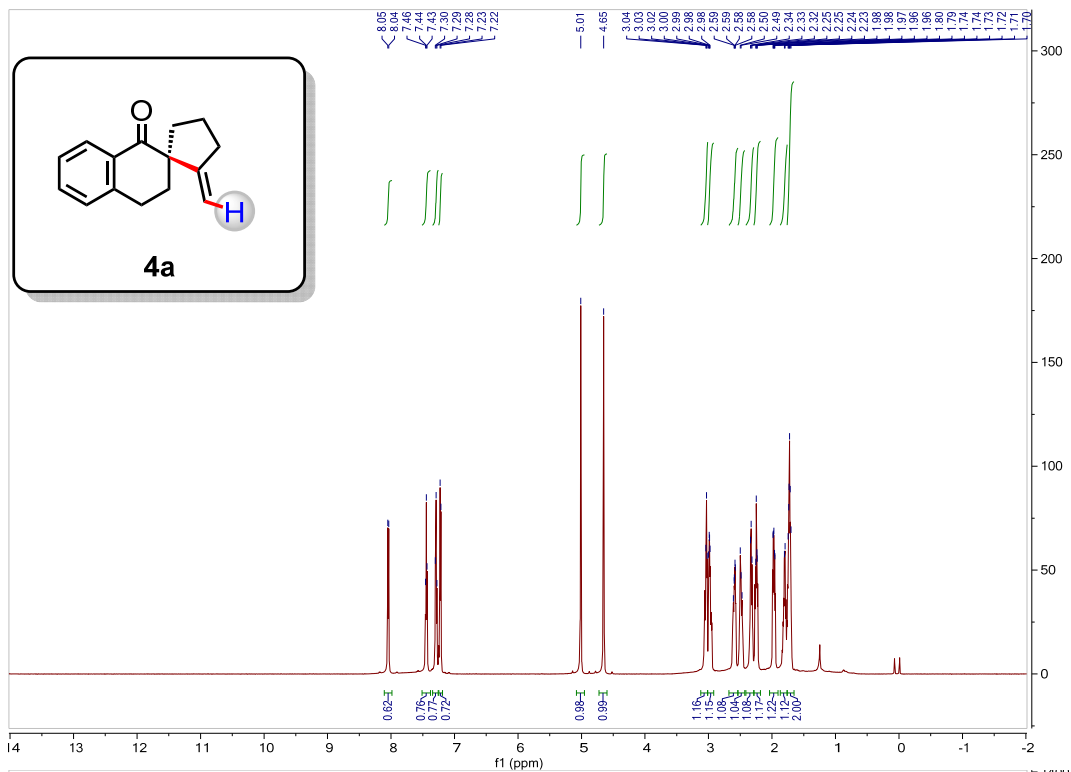


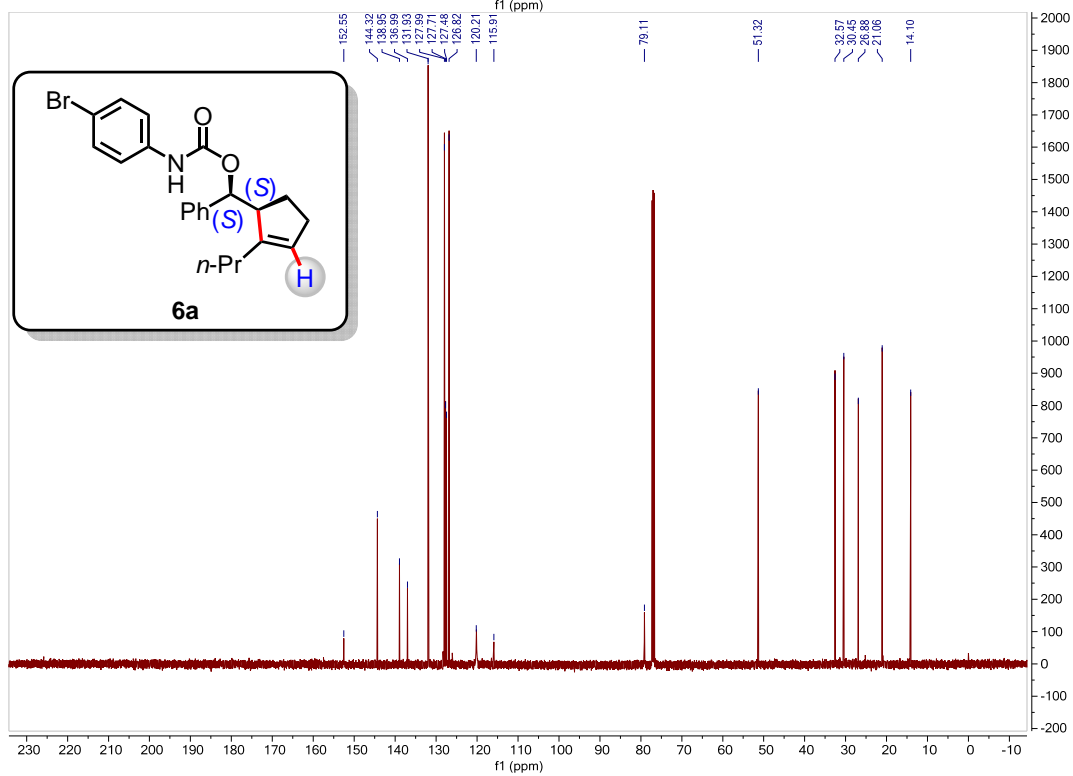
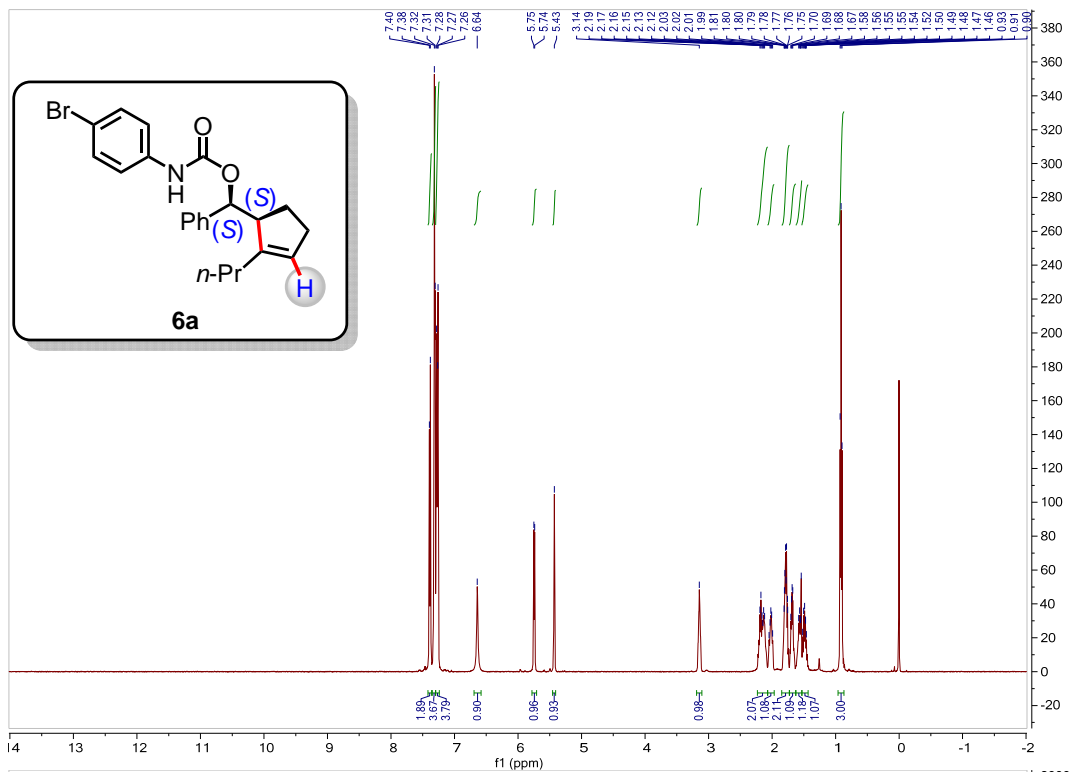












7. X-Ray Crystallography Data of 6a

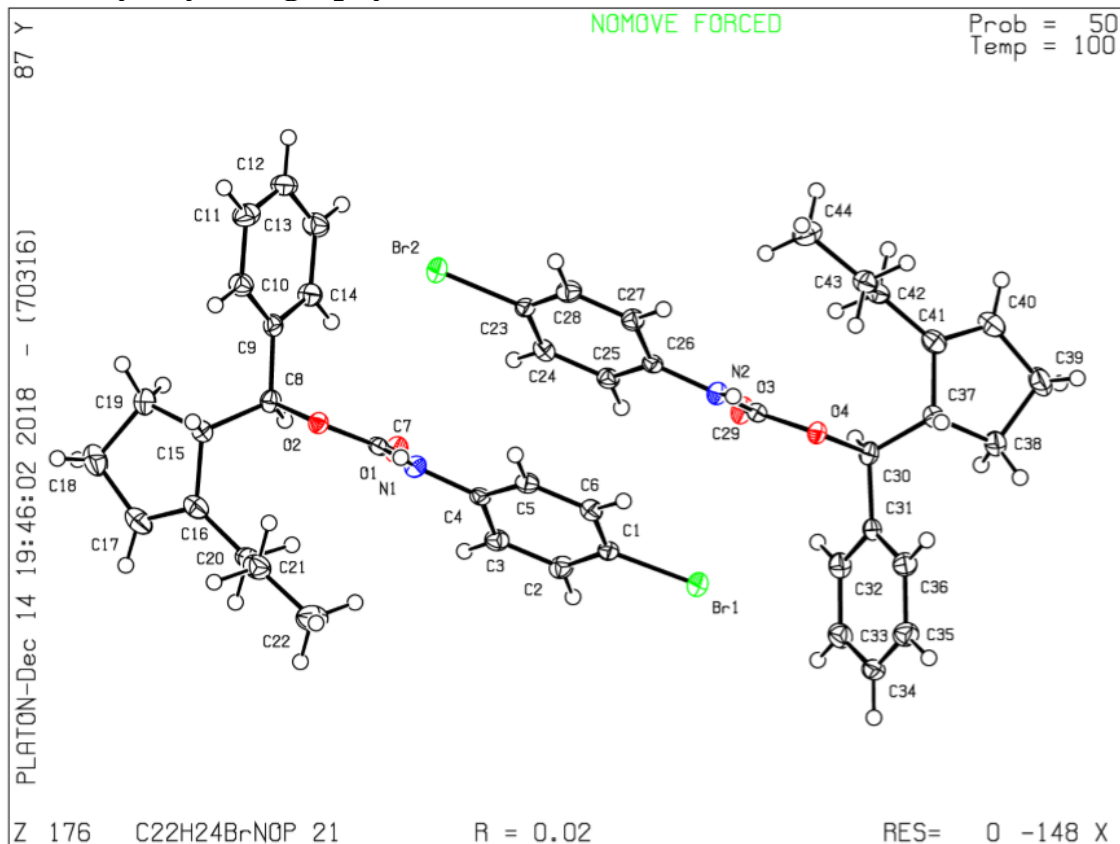


Table SI-4. Crystal data and structure refinement for C₂₂H₂₄BrNO₂.

Identification code	C ₂₂ H ₂₄ BrNO ₂	
Empirical formula	C ₂₂ H ₂₄ Br N O ₂	
Formula weight	414.33	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2 ₁	
Unit cell dimensions	a = 5.1733(7) Å	α = 90°.
	b = 21.213(3) Å	β = 97.186(3)°.
	c = 17.838(2) Å	γ = 90°.
Volume	1942.2(4) Å ³	
Z	4	
Density (calculated)	1.417 Mg/m ³	
Absorption coefficient	3.002 mm ⁻¹	
	S-131	

F(000)	856
Crystal size	0.600 x 0.320 x 0.250 mm ³
Theta range for data collection	2.496 to 66.756°.
Index ranges	-6<=h<=6, -25<=k<=25, -20<=l<=21
Reflections collected	30083
Independent reflections	6781 [R(int) = 0.0411]
Completeness to theta = 66.756°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.4524
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6781 / 3 / 478
Goodness-of-fit on F ²	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0220, wR2 = 0.0569
R indices (all data)	R1 = 0.0221, wR2 = 0.0570
Absolute structure parameter	0.021(12)
Extinction coefficient	n/a
Largest diff. peak and hole	0.369 and -0.319 e.Å ⁻³

Table SI-5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{22}\text{H}_{24}\text{BrNO}_2$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Br(1)	5552(1)	4272(1)	373(1)	27(1)
Br(2)	8026(1)	5755(1)	4587(1)	28(1)
N(1)	8293(4)	4037(1)	3778(1)	18(1)
N(2)	6281(4)	5943(1)	1162(1)	17(1)
O(1)	4149(4)	4070(1)	4106(1)	22(1)
O(2)	7713(4)	3972(1)	4984(1)	17(1)
O(3)	1851(4)	5883(1)	877(1)	21(1)
O(4)	4533(4)	6040(1)	-23(1)	17(1)
C(1)	6504(6)	4167(1)	1432(2)	19(1)
C(2)	4892(6)	3817(1)	1835(2)	22(1)
C(3)	5475(6)	3765(1)	2614(2)	21(1)
C(4)	7673(5)	4067(1)	2983(2)	16(1)
C(5)	9320(5)	4393(1)	2562(2)	19(1)
C(6)	8750(6)	4445(1)	1784(2)	21(1)
C(7)	6491(5)	4034(1)	4275(2)	17(1)
C(8)	6067(5)	3935(1)	5595(2)	18(1)
C(9)	6056(5)	4574(1)	5963(2)	18(1)
C(10)	8155(6)	4783(1)	6472(2)	23(1)
C(11)	8145(6)	5384(2)	6781(2)	27(1)
C(12)	6055(6)	5782(2)	6582(2)	26(1)
C(13)	3961(6)	5578(2)	6083(2)	27(1)
C(14)	3957(6)	4974(1)	5778(2)	23(1)
C(15)	7162(5)	3395(1)	6112(2)	20(1)
C(16)	6529(6)	2736(1)	5786(2)	24(1)
C(17)	5701(7)	2367(2)	6299(2)	31(1)
C(18)	5627(8)	2681(2)	7049(2)	38(1)
C(19)	5897(6)	3381(2)	6853(2)	26(1)
C(20)	6859(6)	2541(2)	4996(2)	26(1)
C(21)	9695(6)	2526(2)	4827(2)	29(1)
C(22)	9871(7)	2342(2)	4009(2)	36(1)

C(23)	7432(5)	5826(1)	3517(2)	18(1)
C(24)	5238(6)	5543(1)	3130(2)	20(1)
C(25)	4809(5)	5585(1)	2349(2)	19(1)
C(26)	6541(5)	5909(1)	1959(2)	16(1)
C(27)	8711(5)	6201(1)	2359(2)	20(1)
C(28)	9153(6)	6160(1)	3142(2)	22(1)
C(29)	4005(5)	5944(1)	689(2)	17(1)
C(30)	2302(5)	6083(1)	-624(2)	18(1)
C(31)	2150(5)	5466(1)	-1050(2)	18(1)
C(32)	341(6)	5017(2)	-893(2)	23(1)
C(33)	224(6)	4438(2)	-1259(2)	27(1)
C(34)	1896(6)	4309(2)	-1788(2)	25(1)
C(35)	3688(6)	4754(2)	-1950(2)	26(1)
C(36)	3833(6)	5330(1)	-1578(2)	23(1)
C(37)	2767(5)	6672(1)	-1085(2)	20(1)
C(38)	830(6)	6705(1)	-1822(2)	26(1)
C(39)	161(8)	7410(2)	-1942(2)	36(1)
C(40)	850(6)	7676(2)	-1166(2)	28(1)
C(41)	2246(5)	7290(1)	-694(2)	22(1)
C(42)	3279(6)	7452(1)	107(2)	23(1)
C(43)	6244(6)	7513(2)	256(2)	25(1)
C(44)	7136(7)	7665(2)	1081(2)	33(1)

Table SI-6. Bond lengths [\AA] and angles [$^\circ$] for $\text{C}_{22}\text{H}_{24}\text{BrNO}_2$.

Br(1)-C(1)	1.904(3)
Br(2)-C(23)	1.901(3)
N(1)-C(7)	1.364(4)
N(1)-C(4)	1.417(4)
N(1)-H(1N)	0.89(2)
N(2)-C(29)	1.360(4)
N(2)-C(26)	1.414(4)
N(2)-H(2N)	0.86(2)
O(1)-C(7)	1.214(4)
O(2)-C(7)	1.347(3)
O(2)-C(8)	1.468(3)
O(3)-C(29)	1.210(3)
O(4)-C(29)	1.348(3)
O(4)-C(30)	1.476(3)
C(1)-C(6)	1.382(4)
C(1)-C(2)	1.384(4)
C(2)-C(3)	1.389(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.395(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.389(4)
C(5)-C(6)	1.387(4)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(8)-C(9)	1.506(4)
C(8)-C(15)	1.534(4)
C(8)-H(8)	1.0000
C(9)-C(14)	1.385(4)
C(9)-C(10)	1.397(4)
C(10)-C(11)	1.388(4)
C(10)-H(10)	0.9500
C(11)-C(12)	1.384(5)
C(11)-H(11)	0.9500

C(12)-C(13)	1.383(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.392(4)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-C(16)	1.532(4)
C(15)-C(19)	1.548(4)
C(15)-H(15)	1.0000
C(16)-C(17)	1.317(5)
C(16)-C(20)	1.499(4)
C(17)-C(18)	1.498(5)
C(17)-H(17)	0.9500
C(18)-C(19)	1.535(5)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(21)	1.535(4)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-C(22)	1.524(5)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-C(28)	1.375(4)
C(23)-C(24)	1.389(4)
C(24)-C(25)	1.387(4)
C(24)-H(24)	0.9500
C(25)-C(26)	1.383(4)
C(25)-H(25)	0.9500
C(26)-C(27)	1.397(4)
C(27)-C(28)	1.388(4)
C(27)-H(27)	0.9500

C(28)-H(28)	0.9500
C(30)-C(31)	1.511(4)
C(30)-C(37)	1.532(4)
C(30)-H(30)	1.0000
C(31)-C(32)	1.387(4)
C(31)-C(36)	1.391(4)
C(32)-C(33)	1.391(5)
C(32)-H(32)	0.9500
C(33)-C(34)	1.384(5)
C(33)-H(33)	0.9500
C(34)-C(35)	1.378(5)
C(34)-H(34)	0.9500
C(35)-C(36)	1.388(4)
C(35)-H(35)	0.9500
C(36)-H(36)	0.9500
C(37)-C(41)	1.525(4)
C(37)-C(38)	1.551(4)
C(37)-H(37)	1.0000
C(38)-C(39)	1.544(4)
C(38)-H(38A)	0.9900
C(38)-H(38B)	0.9900
C(39)-C(40)	1.494(5)
C(39)-H(39A)	0.9900
C(39)-H(39B)	0.9900
C(40)-C(41)	1.322(4)
C(40)-H(40)	0.9500
C(41)-C(42)	1.502(4)
C(42)-C(43)	1.529(4)
C(42)-H(42A)	0.9900
C(42)-H(42B)	0.9900
C(43)-C(44)	1.521(4)
C(43)-H(43A)	0.9900
C(43)-H(43B)	0.9900
C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800

C(44)-H(44C)	0.9800
C(7)-N(1)-C(4)	124.2(2)
C(7)-N(1)-H(1N)	120(2)
C(4)-N(1)-H(1N)	116(2)
C(29)-N(2)-C(26)	126.2(2)
C(29)-N(2)-H(2N)	118(2)
C(26)-N(2)-H(2N)	115(2)
C(7)-O(2)-C(8)	117.0(2)
C(29)-O(4)-C(30)	117.4(2)
C(6)-C(1)-C(2)	121.3(3)
C(6)-C(1)-Br(1)	120.0(2)
C(2)-C(1)-Br(1)	118.7(2)
C(1)-C(2)-C(3)	119.5(3)
C(1)-C(2)-H(2)	120.2
C(3)-C(2)-H(2)	120.2
C(2)-C(3)-C(4)	119.9(3)
C(2)-C(3)-H(3)	120.1
C(4)-C(3)-H(3)	120.1
C(5)-C(4)-C(3)	119.5(3)
C(5)-C(4)-N(1)	119.1(2)
C(3)-C(4)-N(1)	121.4(3)
C(6)-C(5)-C(4)	120.8(3)
C(6)-C(5)-H(5)	119.6
C(4)-C(5)-H(5)	119.6
C(1)-C(6)-C(5)	118.9(3)
C(1)-C(6)-H(6)	120.5
C(5)-C(6)-H(6)	120.5
O(1)-C(7)-O(2)	125.1(3)
O(1)-C(7)-N(1)	125.6(3)
O(2)-C(7)-N(1)	109.3(2)
O(2)-C(8)-C(9)	108.1(2)
O(2)-C(8)-C(15)	106.3(2)
C(9)-C(8)-C(15)	115.6(2)
O(2)-C(8)-H(8)	108.9

C(9)-C(8)-H(8)	108.9
C(15)-C(8)-H(8)	108.9
C(14)-C(9)-C(10)	118.8(3)
C(14)-C(9)-C(8)	119.5(3)
C(10)-C(9)-C(8)	121.6(3)
C(11)-C(10)-C(9)	120.5(3)
C(11)-C(10)-H(10)	119.7
C(9)-C(10)-H(10)	119.7
C(12)-C(11)-C(10)	120.0(3)
C(12)-C(11)-H(11)	120.0
C(10)-C(11)-H(11)	120.0
C(13)-C(12)-C(11)	119.9(3)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(12)-C(13)-C(14)	120.1(3)
C(12)-C(13)-H(13)	119.9
C(14)-C(13)-H(13)	119.9
C(9)-C(14)-C(13)	120.6(3)
C(9)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.7
C(16)-C(15)-C(8)	114.1(2)
C(16)-C(15)-C(19)	102.4(2)
C(8)-C(15)-C(19)	111.3(2)
C(16)-C(15)-H(15)	109.6
C(8)-C(15)-H(15)	109.6
C(19)-C(15)-H(15)	109.6
C(17)-C(16)-C(20)	125.1(3)
C(17)-C(16)-C(15)	110.6(3)
C(20)-C(16)-C(15)	124.3(3)
C(16)-C(17)-C(18)	113.7(3)
C(16)-C(17)-H(17)	123.1
C(18)-C(17)-H(17)	123.1
C(17)-C(18)-C(19)	102.4(3)
C(17)-C(18)-H(18A)	111.3
C(19)-C(18)-H(18A)	111.3

C(17)-C(18)-H(18B)	111.3
C(19)-C(18)-H(18B)	111.3
H(18A)-C(18)-H(18B)	109.2
C(18)-C(19)-C(15)	105.8(3)
C(18)-C(19)-H(19A)	110.6
C(15)-C(19)-H(19A)	110.6
C(18)-C(19)-H(19B)	110.6
C(15)-C(19)-H(19B)	110.6
H(19A)-C(19)-H(19B)	108.7
C(16)-C(20)-C(21)	114.5(3)
C(16)-C(20)-H(20A)	108.6
C(21)-C(20)-H(20A)	108.6
C(16)-C(20)-H(20B)	108.6
C(21)-C(20)-H(20B)	108.6
H(20A)-C(20)-H(20B)	107.6
C(22)-C(21)-C(20)	111.5(3)
C(22)-C(21)-H(21A)	109.3
C(20)-C(21)-H(21A)	109.3
C(22)-C(21)-H(21B)	109.3
C(20)-C(21)-H(21B)	109.3
H(21A)-C(21)-H(21B)	108.0
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(28)-C(23)-C(24)	121.3(3)
C(28)-C(23)-Br(2)	119.8(2)
C(24)-C(23)-Br(2)	118.9(2)
C(25)-C(24)-C(23)	119.3(3)
C(25)-C(24)-H(24)	120.4
C(23)-C(24)-H(24)	120.4
C(26)-C(25)-C(24)	120.3(3)
C(26)-C(25)-H(25)	119.8

C(24)-C(25)-H(25)	119.8
C(25)-C(26)-C(27)	119.5(3)
C(25)-C(26)-N(2)	123.0(2)
C(27)-C(26)-N(2)	117.4(2)
C(28)-C(27)-C(26)	120.5(3)
C(28)-C(27)-H(27)	119.8
C(26)-C(27)-H(27)	119.8
C(23)-C(28)-C(27)	119.1(3)
C(23)-C(28)-H(28)	120.5
C(27)-C(28)-H(28)	120.5
O(3)-C(29)-O(4)	125.4(2)
O(3)-C(29)-N(2)	125.7(3)
O(4)-C(29)-N(2)	108.8(2)
O(4)-C(30)-C(31)	107.3(2)
O(4)-C(30)-C(37)	106.2(2)
C(31)-C(30)-C(37)	116.0(2)
O(4)-C(30)-H(30)	109.0
C(31)-C(30)-H(30)	109.0
C(37)-C(30)-H(30)	109.0
C(32)-C(31)-C(36)	119.3(3)
C(32)-C(31)-C(30)	119.1(3)
C(36)-C(31)-C(30)	121.5(3)
C(31)-C(32)-C(33)	120.2(3)
C(31)-C(32)-H(32)	119.9
C(33)-C(32)-H(32)	119.9
C(34)-C(33)-C(32)	120.0(3)
C(34)-C(33)-H(33)	120.0
C(32)-C(33)-H(33)	120.0
C(35)-C(34)-C(33)	120.2(3)
C(35)-C(34)-H(34)	119.9
C(33)-C(34)-H(34)	119.9
C(34)-C(35)-C(36)	120.0(3)
C(34)-C(35)-H(35)	120.0
C(36)-C(35)-H(35)	120.0
C(35)-C(36)-C(31)	120.3(3)

C(35)-C(36)-H(36)	119.8
C(31)-C(36)-H(36)	119.8
C(41)-C(37)-C(30)	114.0(2)
C(41)-C(37)-C(38)	102.5(2)
C(30)-C(37)-C(38)	111.3(2)
C(41)-C(37)-H(37)	109.6
C(30)-C(37)-H(37)	109.6
C(38)-C(37)-H(37)	109.6
C(39)-C(38)-C(37)	105.7(2)
C(39)-C(38)-H(38A)	110.6
C(37)-C(38)-H(38A)	110.6
C(39)-C(38)-H(38B)	110.6
C(37)-C(38)-H(38B)	110.6
H(38A)-C(38)-H(38B)	108.7
C(40)-C(39)-C(38)	102.3(3)
C(40)-C(39)-H(39A)	111.3
C(38)-C(39)-H(39A)	111.3
C(40)-C(39)-H(39B)	111.3
C(38)-C(39)-H(39B)	111.3
H(39A)-C(39)-H(39B)	109.2
C(41)-C(40)-C(39)	113.9(3)
C(41)-C(40)-H(40)	123.1
C(39)-C(40)-H(40)	123.1
C(40)-C(41)-C(42)	124.5(3)
C(40)-C(41)-C(37)	110.7(3)
C(42)-C(41)-C(37)	124.7(3)
C(41)-C(42)-C(43)	114.5(2)
C(41)-C(42)-H(42A)	108.6
C(43)-C(42)-H(42A)	108.6
C(41)-C(42)-H(42B)	108.6
C(43)-C(42)-H(42B)	108.6
H(42A)-C(42)-H(42B)	107.6
C(44)-C(43)-C(42)	111.2(3)
C(44)-C(43)-H(43A)	109.4
C(42)-C(43)-H(43A)	109.4

C(44)-C(43)-H(43B)	109.4
C(42)-C(43)-H(43B)	109.4
H(43A)-C(43)-H(43B)	108.0
C(43)-C(44)-H(44A)	109.5
C(43)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
C(43)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table SI-7. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{22}\text{H}_{24}\text{BrNO}_2$. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^* 2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Br(1)	37(1)	24(1)	18(1)	1(1)	-3(1)	-1(1)
Br(2)	39(1)	26(1)	16(1)	2(1)	-2(1)	-2(1)
N(1)	15(1)	20(1)	18(1)	-1(1)	1(1)	-1(1)
N(2)	15(1)	21(1)	16(1)	1(1)	4(1)	-1(1)
O(1)	16(1)	29(1)	21(1)	1(1)	1(1)	1(1)
O(2)	16(1)	18(1)	16(1)	1(1)	2(1)	-1(1)
O(3)	16(1)	31(1)	18(1)	2(1)	3(1)	0(1)
O(4)	16(1)	20(1)	14(1)	1(1)	0(1)	-1(1)
C(1)	25(1)	15(1)	17(1)	-2(1)	1(1)	5(1)
C(2)	19(1)	23(2)	21(1)	-2(1)	-2(1)	0(1)
C(3)	20(1)	19(1)	23(2)	-2(1)	5(1)	-2(1)
C(4)	17(1)	12(1)	18(1)	-1(1)	0(1)	4(1)
C(5)	17(1)	18(2)	22(1)	-2(1)	2(1)	-1(1)
C(6)	24(1)	17(1)	21(1)	1(1)	4(1)	-2(1)
C(7)	19(1)	11(1)	19(1)	0(1)	1(1)	0(1)
C(8)	18(1)	21(1)	17(1)	1(1)	4(1)	1(1)
C(9)	20(1)	19(1)	16(1)	2(1)	4(1)	-2(1)
C(10)	22(1)	21(1)	25(2)	-1(1)	1(1)	-1(1)
C(11)	28(2)	26(2)	27(2)	-6(1)	2(1)	-6(1)
C(12)	35(2)	19(1)	27(2)	-4(1)	10(1)	-3(1)
C(13)	29(2)	22(2)	29(2)	0(1)	6(1)	6(1)
C(14)	23(1)	22(2)	24(2)	-1(1)	2(1)	1(1)
C(15)	22(1)	17(1)	20(1)	2(1)	2(1)	0(1)
C(16)	23(1)	18(1)	30(2)	2(1)	1(1)	1(1)
C(17)	33(2)	19(2)	39(2)	6(1)	3(1)	-2(1)
C(18)	51(2)	31(2)	33(2)	11(2)	11(2)	-2(2)
C(19)	32(2)	26(2)	21(2)	4(1)	6(1)	-1(1)
C(20)	29(2)	16(1)	29(2)	-2(1)	-2(1)	0(1)
C(21)	29(2)	23(2)	34(2)	-1(1)	2(1)	6(1)

C(22)	40(2)	30(2)	39(2)	-7(2)	9(2)	2(2)
C(23)	24(1)	16(1)	15(1)	-2(1)	-1(1)	6(1)
C(24)	21(1)	16(1)	23(2)	3(1)	4(1)	0(1)
C(25)	19(1)	16(1)	21(1)	0(1)	-1(1)	-2(1)
C(26)	17(1)	13(1)	18(1)	-1(1)	2(1)	3(1)
C(27)	19(1)	19(1)	21(1)	-1(1)	2(1)	-2(1)
C(28)	18(1)	22(2)	24(2)	-4(1)	0(1)	-1(1)
C(29)	20(1)	13(1)	17(1)	0(1)	2(1)	1(1)
C(30)	16(1)	22(2)	15(1)	2(1)	1(1)	1(1)
C(31)	20(1)	17(1)	16(1)	2(1)	-2(1)	3(1)
C(32)	23(1)	25(2)	22(2)	3(1)	3(1)	2(1)
C(33)	30(2)	22(2)	27(2)	2(1)	-2(1)	-4(1)
C(34)	34(2)	17(1)	23(1)	-2(1)	-5(1)	4(1)
C(35)	28(2)	25(2)	25(2)	-3(1)	3(1)	6(1)
C(36)	22(1)	23(2)	23(2)	-1(1)	3(1)	0(1)
C(37)	22(1)	18(1)	20(1)	2(1)	2(1)	1(1)
C(38)	32(2)	22(2)	22(2)	3(1)	-2(1)	-1(1)
C(39)	48(2)	24(2)	32(2)	9(1)	-10(2)	-1(2)
C(40)	27(2)	19(2)	35(2)	3(1)	0(1)	0(1)
C(41)	19(1)	19(1)	27(2)	2(1)	5(1)	-3(1)
C(42)	28(2)	16(1)	24(2)	-1(1)	6(1)	2(1)
C(43)	29(2)	20(2)	26(2)	-1(1)	5(1)	-2(1)
C(44)	40(2)	30(2)	29(2)	-8(1)	-1(1)	-1(2)

Table SI-8. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{22}\text{H}_{24}\text{BrNO}_2$.

	x	y	z	U(eq)
H(1N)	9980(50)	4058(16)	3953(18)	21
H(2N)	7700(50)	5998(17)	970(19)	21
H(2)	3396	3613	1581	26
H(3)	4380	3526	2895	25
H(5)	10855	4584	2811	23
H(6)	9885	4667	1498	25
H(8)	4249	3827	5374	22
H(10)	9600	4512	6608	27
H(11)	9574	5521	7129	33
H(12)	6059	6195	6787	32
H(13)	2521	5851	5948	32
H(14)	2503	4835	5440	27
H(15)	9092	3443	6232	24
H(17)	5197	1941	6204	37
H(18A)	7088	2539	7422	45
H(18B)	3960	2598	7249	45
H(19A)	7014	3602	7263	32
H(19B)	4168	3588	6781	32
H(20A)	5866	2837	4639	31
H(20B)	6092	2117	4902	31
H(21A)	10491	2946	4928	35
H(21B)	10691	2219	5168	35
H(22A)	9085	1925	3908	54
H(22B)	11703	2329	3922	54
H(22C)	8936	2653	3671	54
H(24)	4045	5323	3398	24
H(25)	3318	5391	2080	23
H(27)	9892	6428	2094	24
H(28)	10625	6360	3414	26
H(30)	667	6141	-386	21

H(32)	-821	5107	-534	28
H(33)	-1003	4129	-1147	32
H(34)	1807	3914	-2040	30
H(35)	4826	4666	-2315	31
H(36)	5087	5634	-1686	27
H(37)	4594	6670	-1214	24
H(38A)	1641	6536	-2254	31
H(38B)	-761	6458	-1769	31
H(39A)	1215	7605	-2306	43
H(39B)	-1711	7470	-2122	43
H(40)	332	8084	-1026	33
H(42A)	2716	7122	444	27
H(42B)	2490	7855	241	27
H(43A)	7056	7114	119	30
H(43B)	6826	7852	-67	30
H(44A)	6292	8053	1221	50
H(44B)	9031	7721	1155	50
H(44C)	6661	7317	1399	50

Table SI-9. Torsion angles [°] for C₂₂H₂₄BrNO₂.

C(6)-C(1)-C(2)-C(3)	2.8(4)
Br(1)-C(1)-C(2)-C(3)	-176.3(2)
C(1)-C(2)-C(3)-C(4)	0.1(4)
C(2)-C(3)-C(4)-C(5)	-2.8(4)
C(2)-C(3)-C(4)-N(1)	178.5(3)
C(7)-N(1)-C(4)-C(5)	145.5(3)
C(7)-N(1)-C(4)-C(3)	-35.8(4)
C(3)-C(4)-C(5)-C(6)	2.6(4)
N(1)-C(4)-C(5)-C(6)	-178.6(2)
C(2)-C(1)-C(6)-C(5)	-3.0(4)
Br(1)-C(1)-C(6)-C(5)	176.1(2)
C(4)-C(5)-C(6)-C(1)	0.2(4)
C(8)-O(2)-C(7)-O(1)	1.0(4)
C(8)-O(2)-C(7)-N(1)	-177.8(2)
C(4)-N(1)-C(7)-O(1)	-1.7(4)
C(4)-N(1)-C(7)-O(2)	177.0(2)
C(7)-O(2)-C(8)-C(9)	-100.4(3)
C(7)-O(2)-C(8)-C(15)	134.9(2)
O(2)-C(8)-C(9)-C(14)	100.3(3)
C(15)-C(8)-C(9)-C(14)	-140.8(3)
O(2)-C(8)-C(9)-C(10)	-77.7(3)
C(15)-C(8)-C(9)-C(10)	41.3(4)
C(14)-C(9)-C(10)-C(11)	-0.6(4)
C(8)-C(9)-C(10)-C(11)	177.4(3)
C(9)-C(10)-C(11)-C(12)	-0.5(5)
C(10)-C(11)-C(12)-C(13)	0.9(5)
C(11)-C(12)-C(13)-C(14)	-0.3(5)
C(10)-C(9)-C(14)-C(13)	1.2(4)
C(8)-C(9)-C(14)-C(13)	-176.9(3)
C(12)-C(13)-C(14)-C(9)	-0.7(5)
O(2)-C(8)-C(15)-C(16)	-74.6(3)
C(9)-C(8)-C(15)-C(16)	165.4(2)
O(2)-C(8)-C(15)-C(19)	170.1(2)

C(9)-C(8)-C(15)-C(19)	50.2(3)
C(8)-C(15)-C(16)-C(17)	-133.8(3)
C(19)-C(15)-C(16)-C(17)	-13.4(3)
C(8)-C(15)-C(16)-C(20)	47.2(4)
C(19)-C(15)-C(16)-C(20)	167.6(3)
C(20)-C(16)-C(17)-C(18)	178.4(3)
C(15)-C(16)-C(17)-C(18)	-0.6(4)
C(16)-C(17)-C(18)-C(19)	14.4(4)
C(17)-C(18)-C(19)-C(15)	-21.7(3)
C(16)-C(15)-C(19)-C(18)	21.5(3)
C(8)-C(15)-C(19)-C(18)	143.7(3)
C(17)-C(16)-C(20)-C(21)	-112.7(4)
C(15)-C(16)-C(20)-C(21)	66.2(4)
C(16)-C(20)-C(21)-C(22)	-178.4(3)
C(28)-C(23)-C(24)-C(25)	1.5(4)
Br(2)-C(23)-C(24)-C(25)	-179.1(2)
C(23)-C(24)-C(25)-C(26)	-0.3(4)
C(24)-C(25)-C(26)-C(27)	-0.9(4)
C(24)-C(25)-C(26)-N(2)	176.8(2)
C(29)-N(2)-C(26)-C(25)	32.0(4)
C(29)-N(2)-C(26)-C(27)	-150.3(3)
C(25)-C(26)-C(27)-C(28)	0.9(4)
N(2)-C(26)-C(27)-C(28)	-176.9(3)
C(24)-C(23)-C(28)-C(27)	-1.5(4)
Br(2)-C(23)-C(28)-C(27)	179.2(2)
C(26)-C(27)-C(28)-C(23)	0.3(4)
C(30)-O(4)-C(29)-O(3)	0.8(4)
C(30)-O(4)-C(29)-N(2)	-177.6(2)
C(26)-N(2)-C(29)-O(3)	-4.0(4)
C(26)-N(2)-C(29)-O(4)	174.4(2)
C(29)-O(4)-C(30)-C(31)	-103.7(3)
C(29)-O(4)-C(30)-C(37)	131.6(2)
O(4)-C(30)-C(31)-C(32)	100.5(3)
C(37)-C(30)-C(31)-C(32)	-140.9(3)
O(4)-C(30)-C(31)-C(36)	-77.5(3)

C(37)-C(30)-C(31)-C(36)	41.0(4)
C(36)-C(31)-C(32)-C(33)	0.3(4)
C(30)-C(31)-C(32)-C(33)	-177.8(3)
C(31)-C(32)-C(33)-C(34)	-0.7(4)
C(32)-C(33)-C(34)-C(35)	0.4(4)
C(33)-C(34)-C(35)-C(36)	0.4(4)
C(34)-C(35)-C(36)-C(31)	-0.9(4)
C(32)-C(31)-C(36)-C(35)	0.5(4)
C(30)-C(31)-C(36)-C(35)	178.6(3)
O(4)-C(30)-C(37)-C(41)	-75.1(3)
C(31)-C(30)-C(37)-C(41)	165.7(2)
O(4)-C(30)-C(37)-C(38)	169.6(2)
C(31)-C(30)-C(37)-C(38)	50.4(3)
C(41)-C(37)-C(38)-C(39)	21.0(3)
C(30)-C(37)-C(38)-C(39)	143.2(3)
C(37)-C(38)-C(39)-C(40)	-20.9(3)
C(38)-C(39)-C(40)-C(41)	13.5(4)
C(39)-C(40)-C(41)-C(42)	177.5(3)
C(39)-C(40)-C(41)-C(37)	0.1(4)
C(30)-C(37)-C(41)-C(40)	-133.9(3)
C(38)-C(37)-C(41)-C(40)	-13.5(3)
C(30)-C(37)-C(41)-C(42)	48.7(4)
C(38)-C(37)-C(41)-C(42)	169.1(3)
C(40)-C(41)-C(42)-C(43)	-111.9(3)
C(37)-C(41)-C(42)-C(43)	65.1(4)
C(41)-C(42)-C(43)-C(44)	-178.9(3)

Symmetry transformations used to generate equivalent atoms:

Table SI-10. Hydrogen bonds for C₂₂H₂₄BrNO₂ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)#1	0.89(2)	2.14(2)	3.013(3)	167(3)
N(2)-H(2N)...O(3)#1	0.86(2)	2.19(3)	2.990(3)	156(3)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z