Sequential Conia-Ene-Type Cyclizations and Negishi Coupling by Cooperative Functions of $B(C_6F_5)_3$, ZnI_2, $Pd(PPh_3)_4$ and an Amine

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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 (λ_{ex} = 254 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. Substrates **1b**–**1g** and **1h** were synthesized according to the literature procedures.[1]

1.3 Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra and proton-decoupled carbon nuclear magnetic resonance (^{13}C {^{1}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 ^{1}H 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).

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.

1.4 Abbreviations Used

DART = direct analysis in real time, H_2O = water, HR = high-resolution, MS = mass spectrometry, NA = not applicable, PMP = 1,2,2,6,6-pentamethylpiperidine, TOF = time-of-flight.

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2. Experimental Section

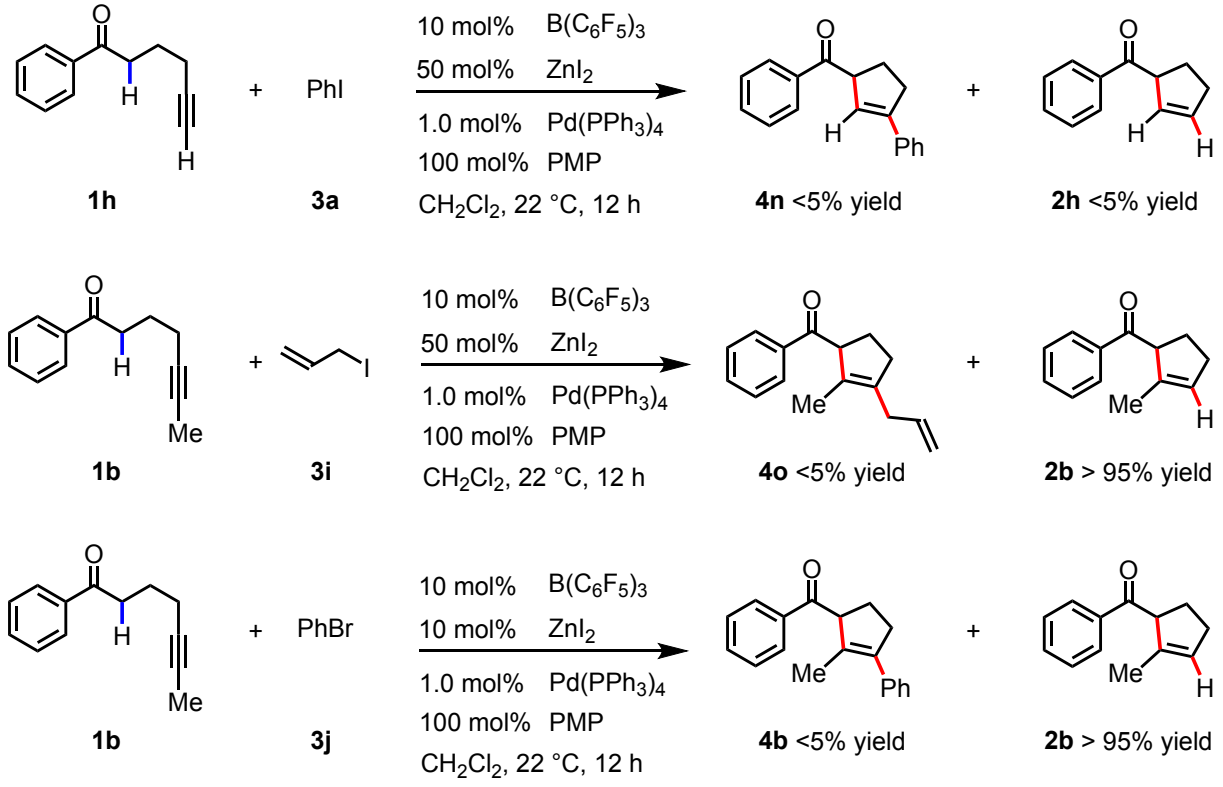
2.1 Optimization Studies

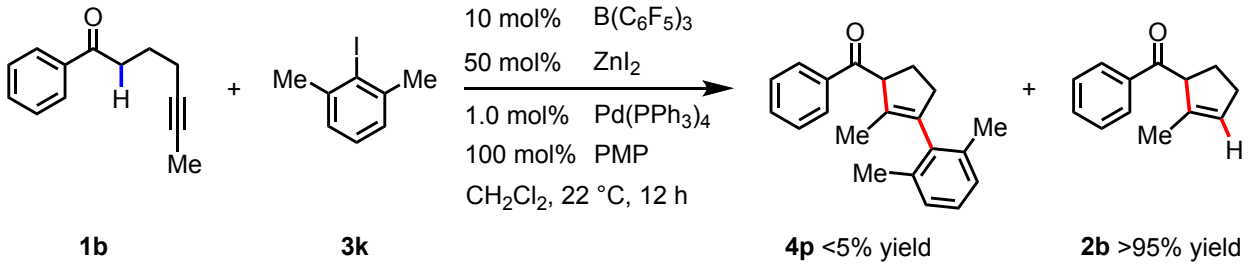
Experimental Procedure for Optimization of Reaction Parameters (see Tables 1 in the manuscript)

To a 7.0 mL oven-dried vial was added, 1-phenylhept-5-yn-1-one **1b** (18.6 mg, 0.10 mmol), $B(C_6F_5)_3$, PMP, ZnI_2, $Pd(PPh_3)_4$ and CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. The resulting mixture was allowed to stir at 22 °C for 12 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2, 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.

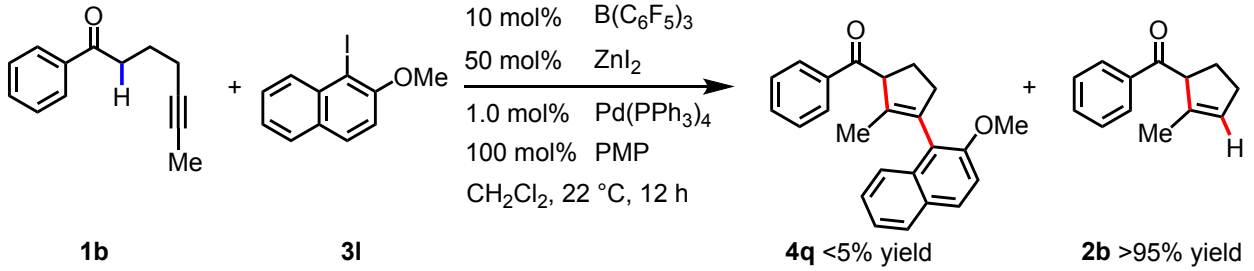
Experiments for Evaluation of Substrate Structure

When alkynyl ketone substrate containing a terminal alkyne unit (**1h**) was used, the transformation was inefficient (<5% of **4n** and **2h** were obtained). In addition, when allyl iodide was used under the standard reaction condition, we only obtained the Conia-ene-type product **2b**. The use of bromobenzene resulted in the formation of Conia-ene-type product **2b**. With more bulky aromatic iodides such as 2,6-dimethyliodebenzene **3k** and 1-iode-2-methoxynaphthalele **3l**, we only obtained the Conia-ene-type product **2b**.



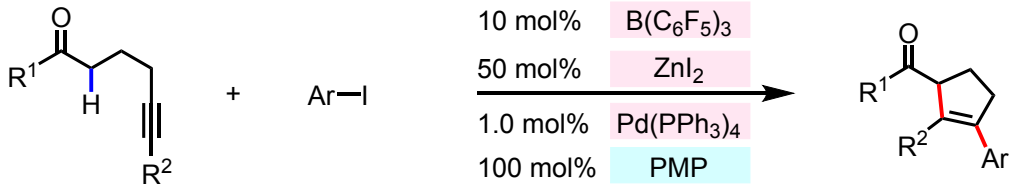


1b **3k** **4p** <5% yield **2b** >95% yield



1b **3l** **4q** <5% yield **2b** >95% yield

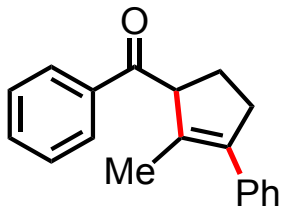
2.2 General Procedures for the Sequential Conia-Ene-Type Cyclization and Negishi Coupling (See Table 2 in the manuscript)



1 **3** **4b–4m**

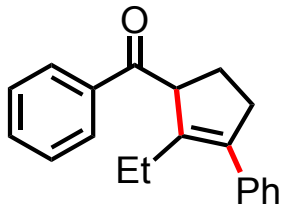
To a 7.0 mL oven-dried vial was added substrate **1** (0.10 mmol), $B(C_6F_5)_3$ (10 mol%), PMP (100 mol%), ZnI_2 (50 mol%), $Pd(PPh_3)_4$ (1.0 mol%) and CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. The resulting mixture was allowed to stir at 22 °C for 12 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2, concentrated *in vacuo* and purified by silica gel column chromatography.

3. Analytical Data



(2-methyl-3-phenylcyclopent-2-en-1-yl)(phenyl)methanone (4b)

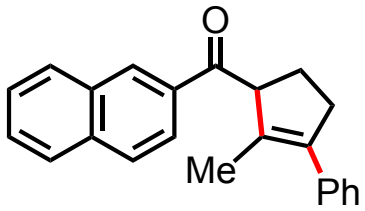
According to the General Procedure, 1-phenylnon-5-yn-1-one **1b** (18.6 mg, 0.10 mmol) reacted with iodobenzene **3a** (24.5 mg, 0.12 mmol**)** following the general procedure. After purification by column chromatography (Hexane:Ethyl acetate = 40:1), **4b** was obtained as a colorless liquid (24.9 mg, 95%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.28 – 7.21 (m, 1H), 4.63 – 4.56 (m, 1H), 2.86 (t, *J* = 6.4 Hz, 2H), 2.45 – 2.33 (m, 1H), 2.16 – 2.03 (m, 1H), 1.80 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) 202.2, 139.1, 137.9, 137.2, 133.1, 133.0, 128.7, 128.6, 128.1, 127.9, 126.7, 77.3, 77.0, 76.8, 58.9, 36.4, 27.7, 14.9; **IR** (neat) 1717, 1674, 1176, 1157, 850, 760, 695 cm^{-1}; HRMS (DART) m/z Calcd for $C_{19}H_{19}O$ (MH^+): 263.1430; found: 263.1439.



(2-ethyl-3-phenylcyclopent-2-en-1-yl)(phenyl)methanone (4c)

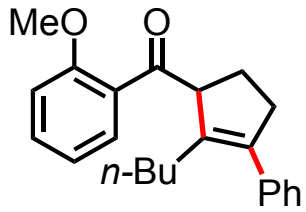
According to the General Procedure, 1-phenyloct-5-yn-1-one **1c** (20.0 mg, 0.10 mmol) reacted with iodobenzene **3a** (24.5 mg, 0.12 mmol**)** following the general procedure. After purification by column chromatography (Hexane:Ethyl acetate = 40:1), **4c** was obtained as a colorless liquid (27.5 mg, 98%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.49 (t, *J* = 6.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.21 (m, 4H), 7.16 (t, *J* = 6.9 Hz, 1H), 4.67 – 4.58 (m, 1H), 2.85 – 2.77 (m, 1H), 2.71 (dd, *J* = 16.7, 7.2 Hz, 1H), 2.43 – 2.23 (m, 3H), 2.09 – 1.90 (m, 2H), 0.84 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.33, 139.04, 139.01, 138.06, 137.07, 132.94, 128.64, 128.45, 128.06, 127.82, 126.65, 55.45, 36.73, 28.12, 21.21, 12.87; **IR** (neat) 2961, 1677, 1595,

1208, 1177, 761, 698 cm^{-1}; HRMS (DART) m/z Calcd for $C_{20}H_{21}O$ (MH^+): 277.1587; found: 277.1586.



(2-methyl-3-phenylcyclopent-2-en-1-yl)(naphthalen-2-yl)methanone (4d)

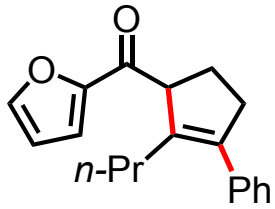
According to the General Procedure, 1-(naphthalen-2-yl)hept-5-yn-1-one **1d** (23.6 mg, 0.10 mmol) reacted with iodobenzene **3a** (24.5 mg, 0.12 mmol**)** following the general procedure. After purification by column chromatography (Hexane:Ethyl acetate = 40:1), **4d** was obtained as a yellow solid (28.5 mg, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.82 (dd, *J* = 13.2, 8.4 Hz, 2H), 7.50 (dt, *J* = 19.7, 7.0 Hz, 2H), 7.28 (d, *J* = 4.4 Hz, 4H), 7.17 (dd, *J* = 7.8, 3.5 Hz, 1H), 4.68 (t, *J* = 7.6 Hz, 1H), 2.90 – 2.72 (m, 2H), 2.47 – 2.28 (m, 1H), 2.10 (dq, *J* = 13.6, 6.9 Hz, 1H), 1.75 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.2, 139.1, 137.8, 135.5, 134.5, 133.2, 132.6, 130.2, 129.6, 128.5, 128.4, 128.1, 127.9, 127.7, 126.7, 126.6, 124.3, 58.9, 36.4, 27.8, 14.9; **IR** (neat) 1669, 1624, 1461, 1438, 1274, 697, 647 cm^{-1}; HRMS (DART) m/z Calcd for $C_{23}H_{21}O$ (MH^+): 313.1587; found: 313.1583.



(2-butyl-3-phenylcyclopent-2-en-1-yl)(2-methoxyphenyl)methanone (4e)

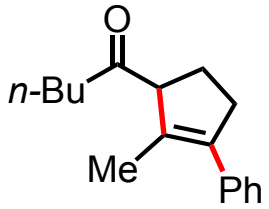
According to the General Procedure, 1-(2-methoxyphenyl)dec-5-yn-1-one **1e** (25.8 mg, 0.10 mmol) reacted with iodobenzene **3a** (24.5 mg, 0.12 mmol**)** following the general procedure. After purification by column chromatography (Hexane:Ethyl acetate = 40:1), **4e** was obtained as a white solid (25.1 mg, 75%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.8 Hz, 1H), 7.44 (t, *J* = 8.5 Hz, 1H), 7.31 (dt, *J* = 14.0, 7.3 Hz, 4H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.07 – 6.89 (m, 2H), 4.76 – 4.61 (m, 1H), 3.90 (s, 3H), 2.87 – 2.75 (m, 1H), 2.75 – 2.62 (m, 1H), 2.42 – 2.16 (m, 2H), 2.09 (dd, *J* = 13.3, 8.5 Hz, 2H), 1.44 – 1.05 (m, 4H), 0.76 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.96, 157.91, 139.21, 138.39, 138.38, 132.78, 129.88, 129.78, 127.96, 127.86, 126.42, 120.67,

111.40, 59.94, 55.46, 36.55, 30.25, 27.87, 27.62, 22.69, 13.81; **IR** (neat) 2953, 1670, 1193, 1179, 906, 754, 727 cm^{-1}; HRMS (DART) m/z Calcd for $C_{23}H_{27}O_2$ (MH^+): 335.2006; found: 335.2012.



furan-2-yl(3-phenyl-2-propylcyclopent-2-en-1-yl)methanone (4f)

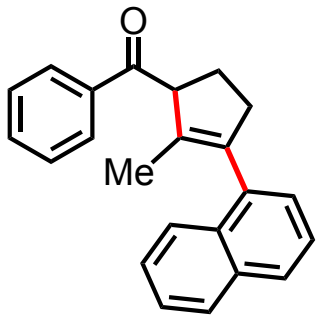
According to the General Procedure, 1-(furan-2-yl)non-5-yn-1-one **1f** (20.4 mg, 0.10 mmol) reacted with iodobenzene **3a** (24.5 mg, 0.12 mmol**)** following the general procedure. After purification by column chromatography (Hexane:Ethyl acetate = 40:1), **4f** was obtained as a colorless liquid (18.3 mg, 65%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.21 (m, 2H), 6.56 (s, 1H), 4.48 (dd, *J* = 9.1, 6.5 Hz, 1H), 2.95 – 2.85 (m, 1H), 2.85 – 2.76 (m, 1H), 2.37 – 2.26 (m, 2H), 2.17 – 2.08 (m, 1H), 2.02 (t, *J* = 9.4 Hz, 1H), 1.53 – 1.37 (m, 1H), 1.34 – 1.21 (m, 1H), 0.79 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.6, 152.7, 146.5, 140.1, 138.1, 137.2, 128.1, 127.8, 126.7, 117.5, 112.2, 56.5, 37.0, 30.1, 27.7, 21.4, 14.1; **IR** (neat) 3118, 1970, 1718, 1491, 1463, 1084, 834, 802 cm^{-1}; HRMS (DART) m/z Calcd for $C_{19}H_{21}O_2$ (MH^+): 281.1536; found: 281.1535.



1-(2-methyl-3-phenylcyclopent-2-en-1-yl)pentan-1-one (4g)

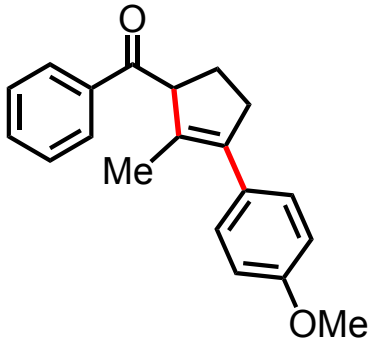
According to the General Procedure, undec-9-yn-5-one **1g** (16.6 mg, 0.10 mmol) reacted with iodobenzene **3a** (24.5 mg, 0.12 mmol**)** following the general procedure. After purification by column chromatography (Hexane:Ethyl acetate = 40:1), **4g** was obtained as a colorless liquid (22.1 mg, 91%). **^{1}H NMR** (500 MHz, $CDCl_3$) 7.35 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.0 Hz, 2H), 7.25 (d, *J* = 7.1 Hz, 1H), 3.72 – 3.59 (m, 1H), 2.91 – 2.72 (m, 2H), 2.47 (td, *J* = 17.0, 16.4, 7.5 Hz, 2H), 2.22 (dd, *J* = 13.3, 6.3 Hz, 1H), 1.99 (dd, *J* = 13.4, 8.5 Hz, 1H), 1.78 (s, 3H), 1.59 (p, *J* = 7.2 Hz, 2H), 1.32 (h, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) 213.1, 139.4, 137.7, 132.7, 128.1, 127.8, 126.8, 64.7, 40.2, 36.5, 26.0, 25.8, 22.4, 14.6, 13.9; **IR** (neat) 2955,

1699, 1621, 1261, 1227, 762 cm^{-1}; HRMS (DART) m/z Calcd for $C_{17}H_{23}O$ (MH^+): 243.1743; found: 243.1739.



(2-methyl-3-(naphthalen-1-yl)cyclopent-2-en-1-yl)(phenyl)methanone (4h)

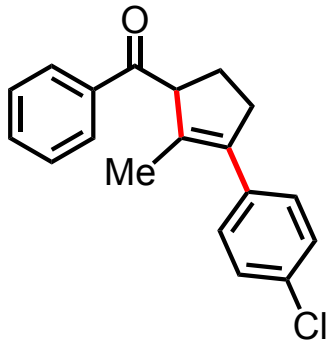
According to the General Procedure, 1-phenylnon-5-yn-1-one **1b** (18.6 mg, 0.10 mmol) reacted with 1-iodonaphthalene **3b** (30.5 mg, 0.12 mmol**)** following the general procedure. After purification by column chromatography (Hexane:Ethyl acetate = 40:1), **4h** was obtained as a bright yellow solid (28.8 mg, 92%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.1 (d, *J* = 8.2 Hz, 3H), 7.9 (d, *J* = 8.1 Hz, 1H), 7.8 (d, *J* = 8.1 Hz, 1H), 7.6 (t, *J* = 7.9 Hz, 1H), 7.6 – 7.4 (m, 5H), 7.3 (d, *J* = 6.8 Hz, 1H), 4.7 (dd, *J* = 10.3, 5.1 Hz, 1H), 2.9 (d, *J* = 9.0 Hz, 1H), 2.8 (s, 1H), 2.6 – 2.5 (m, 1H), 2.3 (dd, *J* = 8.8, 4.7 Hz, 1H), 1.5 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 202.2, 139.1, 137.1, 136.6, 134.9, 133.7, 133.0, 131.4, 128.7, 128.6, 128.2, 127.1, 126.1, 126.0, 125.7, 125.6, 125.4, 57.7, 38.6, 28.4, 14.4; **IR** (neat) 2921, 1676, 1594, 1320, 1252, 801, 777 cm^{-1}; HRMS (DART) m/z Calcd for $C_{23}H_{21}O$ (MH^+): 313.1587; found: 313.1591.



(3-(4-methoxyphenyl)-2-methylcyclopent-2-en-1-yl)(phenyl)methanone (4i)

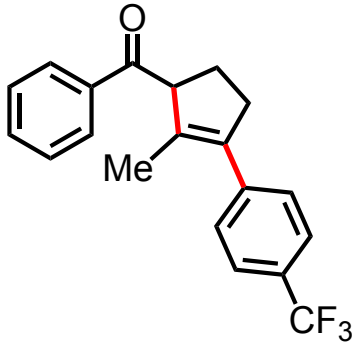
According to the General Procedure, 1-phenylnon-5-yn-1-one **1b** (18.6 mg, 0.10 mmol) reacted with 1-iodo-4-methoxybenzene **3c** (28.1 mg, 0.12 mmol**)** following the general procedure. After purification by column chromatography (Hexane:Ethyl acetate = 40:1), **4i** was obtained as a yellow

solid (27.8 mg, 95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.62 – 4.52 (m, 1H), 3.81 (s, 3H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.44 – 2.29 (m, 1H), 2.14 – 2.01 (m, 1H), 1.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.3, 158.2, 138.4, 137.1, 132.9, 131.7, 130.3, 129.0, 128.6, 128.5, 113.5, 58.9, 55.2, 36.4, 27.6, 14.9; **IR** (neat) 2929, 1675, 1508, 1243, 1208, 1176, 829, 696 cm^{-1}; HRMS (DART) m/z Calcd for $C_{20}H_{21}O_2$ (MH^+): 293.1536; found: 293.1541.



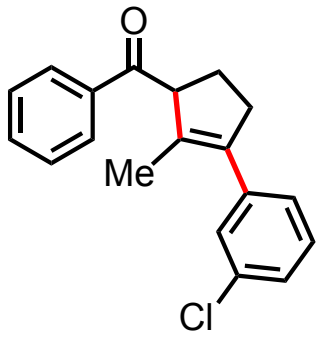
(3-(4-chlorophenyl)-2-methylcyclopent-2-en-1-yl)(phenyl)methanone (4j)

According to the General Procedure, 1-phenylnon-5-yn-1-one **1b** (18.6 mg, 0.10 mmol) reacted with 1-chloro-4-iodobenzene **3d** (28.6 mg, 0.12 mmol**)** following the general procedure. After purification by column chromatography (Hexane:Ethyl acetate = 40:1), **4j** was obtained as a colorless liquid (27.6 mg, 93%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 4.59 (d, *J* = 15.7 Hz, 1H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.47 – 2.31 (m, 1H), 2.10 (dq, *J* = 13.1, 6.3 Hz, 1H), 1.78 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.0, 138.0, 137.0, 136.2, 133.9, 133.1, 132.3, 129.2, 128.7, 128.5, 128.2, 58.7, 36.3, 27.7, 14.9; **IR** (neat) 2933, 1675, 1445, 1341, 1208, 1091, 826 cm^{-1}; HRMS (DART) m/z Calcd for $C_{19}H_{18}O_1Cl$ (MH^+): 297.1041; found: 297.1041.



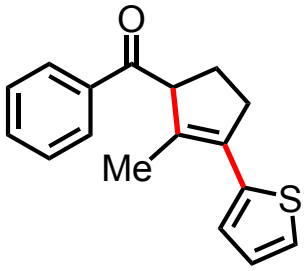
(2-methyl-3-(4-(trifluoromethyl)phenyl)cyclopent-2-en-1-yl)(phenyl)methanone (4k)

According to the General Procedure, 1-phenylnon-5-yn-1-one **1b** (18.6 mg, 0.10 mmol) reacted with 1-iodo-4-(trifluoromethyl)benzene **3e** (32.7 mg, 0.12 mmol**)** following the general procedure. After purification by column chromatography (Hexane:Ethyl acetate = 40:1), **4k** was obtained as a colorless liquid (30.1mg, 91%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.9 Hz, 3H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 4.68 – 4.57 (m, 1H), 2.95 – 2.76 (m, 2H), 2.48 – 2.36 (m, 1H), 2.17 – 2.05 (m, 1H), 1.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$ δ 201.77, 141.47, 141.46, 137.97, 136.94, 135.35, 133.15, 128.71, 128.55, 124.31 (q, *J* = 272.7 Hz), 125.06 (q, *J* = 3.8 Hz), 124.95, 58.71, 36.23, 27.74, 14.88; **^{19}F NMR** (564 MHz, $CDCl_3$) δ –62.44; **IR** (neat) 1677, 1322, 1163, 1067, 886,



(3-(3-chlorophenyl)-2-methylcyclopent-2-en-1-yl)(phenyl)methanone (4l)

According to the General Procedure, 1-phenylnon-5-yn-1-one **1b** (18.6 mg, 0.1 mmol) reacted with 1-chloro-3-iodobenzene **3f** (28.6 mg, 0.12 mmol**)** following the general procedure. After purification by column chromatography (Hexane:Ethyl acetate = 40:1), **4l** was obtained as a colorless liquid (27.3 mg, 92%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.0 (d, *J* = 8.0 Hz, 2H), 7.6 (t, *J* = 6.9 Hz, 1H), 7.5 (t, *J* = 7.7 Hz, 2H), 7.3 (s, 1H), 7.3 – 7.2 (m, 1H), 7.2 (d, *J* = 9.2 Hz, 2H), 4.7 – 4.5 (m, 1H), 2.8 (dd, *J* = 4.2, 2.2 Hz, 2H), 2.4 – 2.3 (m, 1H), 2.2 – 2.0 (m, 1H), 1.8 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.8, 139.6, 137.8, 137.0, 134.5, 133.9, 133.1, 129.3, 128.7, 128.5, 127.9, 126.7, 126.0, 58.7, 36.2, 27.7, 14.8; **IR** (neat) 1672, 1577, 1211, 1177, 786, 750, 711, 694 cm^{-1}; HRMS (DART) m/z Calcd for $C_{19}H_{18}O_1Cl$ (MH^+): 297.1041; found: 297.1047.



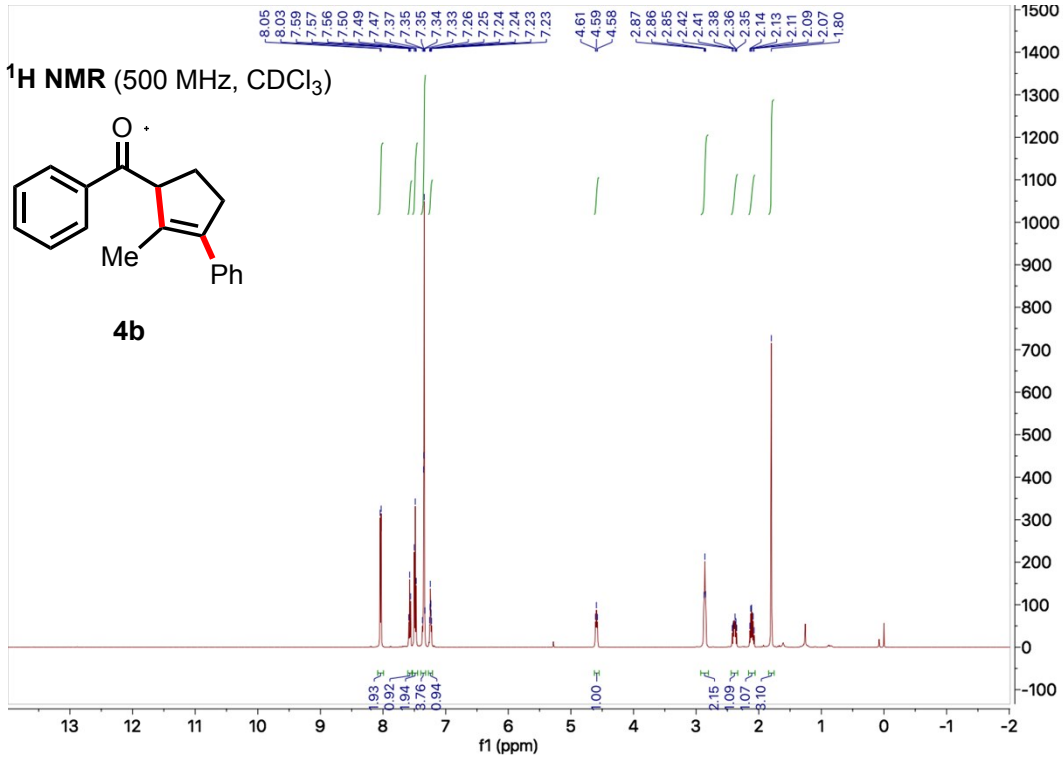
(2-methyl-3-(thiophen-2-yl)cyclopent-2-en-1-yl)(phenyl)methanone (4m)

According to the General Procedure, 1-phenylnon-5-yn-1-one **1b** (18.6 mg, 0.1 mmol) reacted with 2-iodothiophene **3g** (25.2 mg, 0.12 mmol**)** following the general procedure. After purification by column chromatography (Hexane:Ethyl acetate = 40:1), **4m** was obtained as a white solid (22.8 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.1 – 8.0 (m, 2H), 7.6 (t, *J* = 7.4 Hz, 1H), 7.5 (t, *J* = 7.6 Hz, 2H), 7.3 – 7.2 (m, 1H), 7.0 (d, *J* = 4.5 Hz, 2H), 4.7 – 4.5 (m, 1H), 3.1 – 2.8 (m, 2H), 2.5 – 2.3 (m, 1H), 2.2 – 2.0 (m, 1H), 2.0 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.8, 140.0, 136.9, 133.0, 132.8, 132.1, 128.6, 128.5, 126.7, 125.0, 124.4, 59.4, 36.2, 27.6, 15.6; **IR** (neat) 1674, 1594, 1374, 1338, 1177, 1158, 694 cm^{-1}; HRMS (DART) m/z Calcd for $C_{17}H_{17}O_1S$ (MH^+):269.0995; found: 269.0994.

4. References

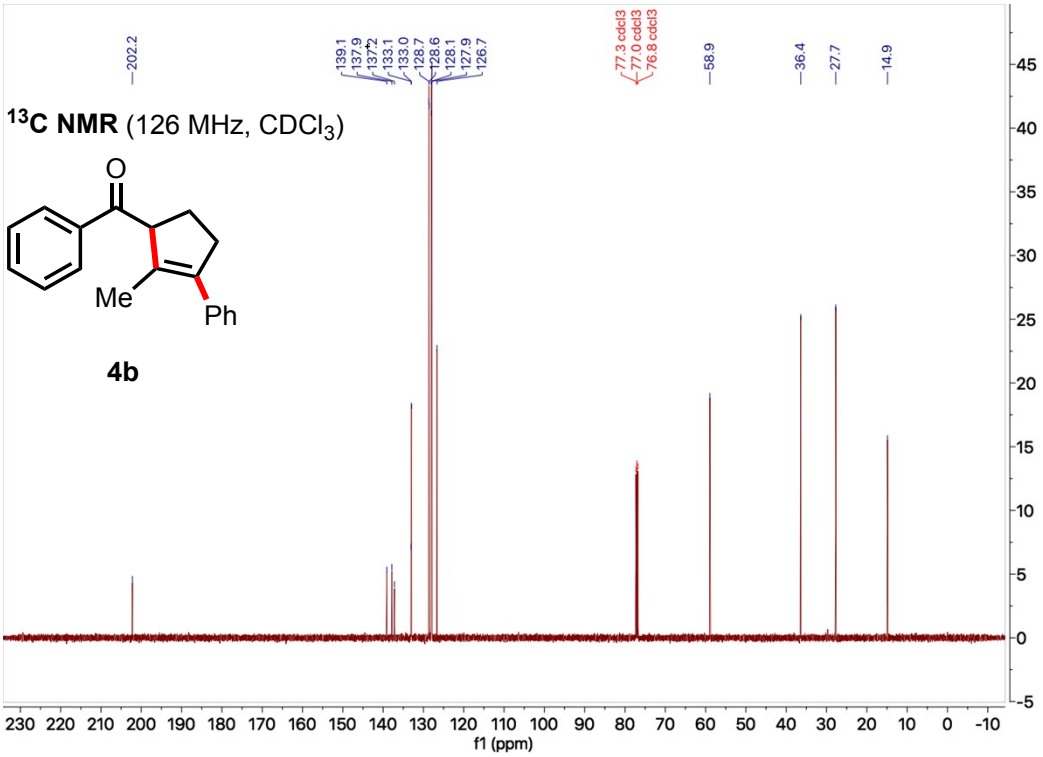
(1) M. Cao, A. Yesilcimen and M. Wasa, *J. Am. Chem. Soc.* 2019, **141**, 4199.

5. NMR Spectra for New Compounds



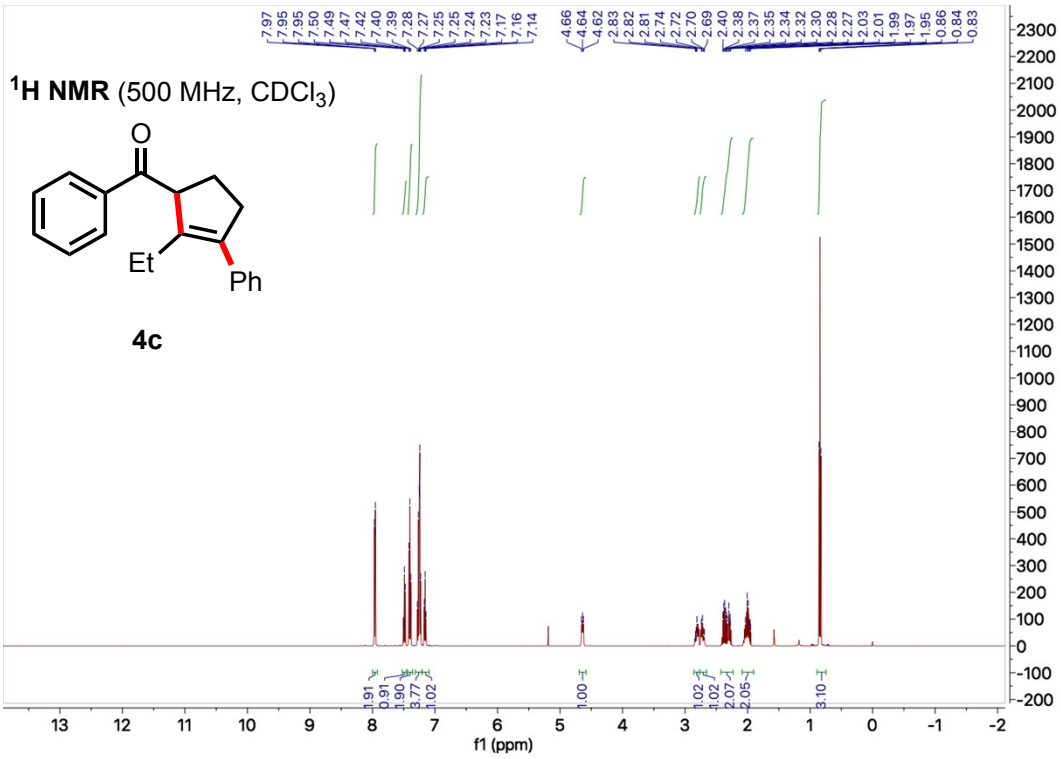
^{1}H NMR (500 MHz, $CDCl_3$)

4b



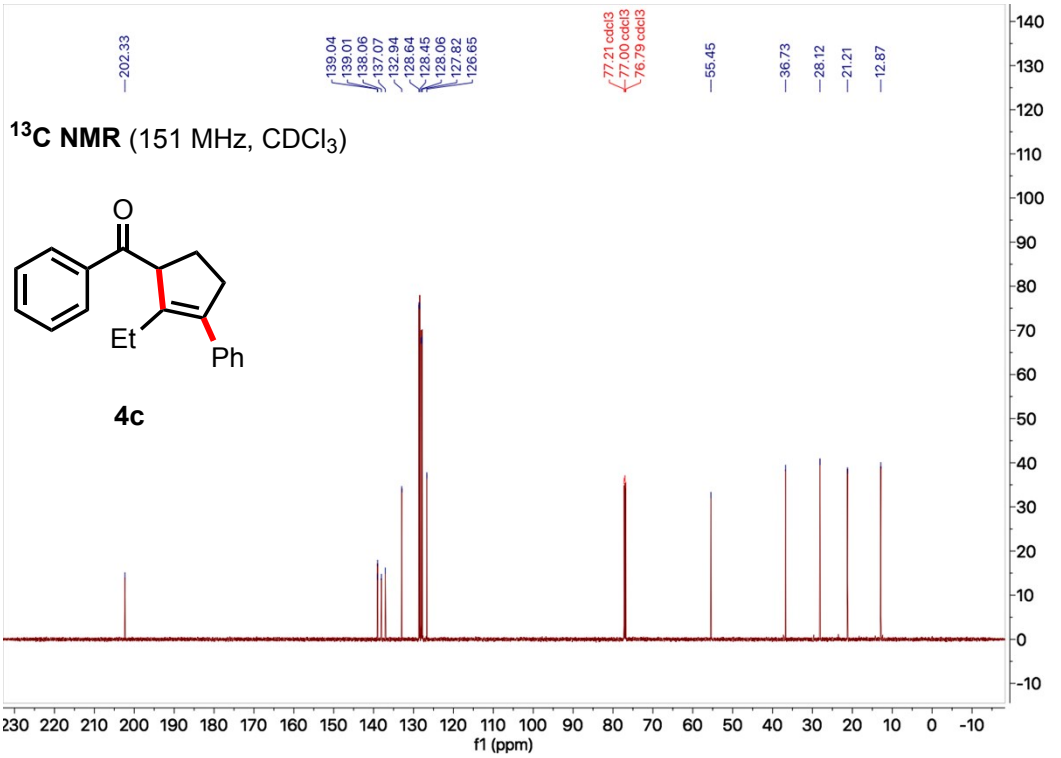
^{13}C NMR (126 MHz, $CDCl_3$)

4b



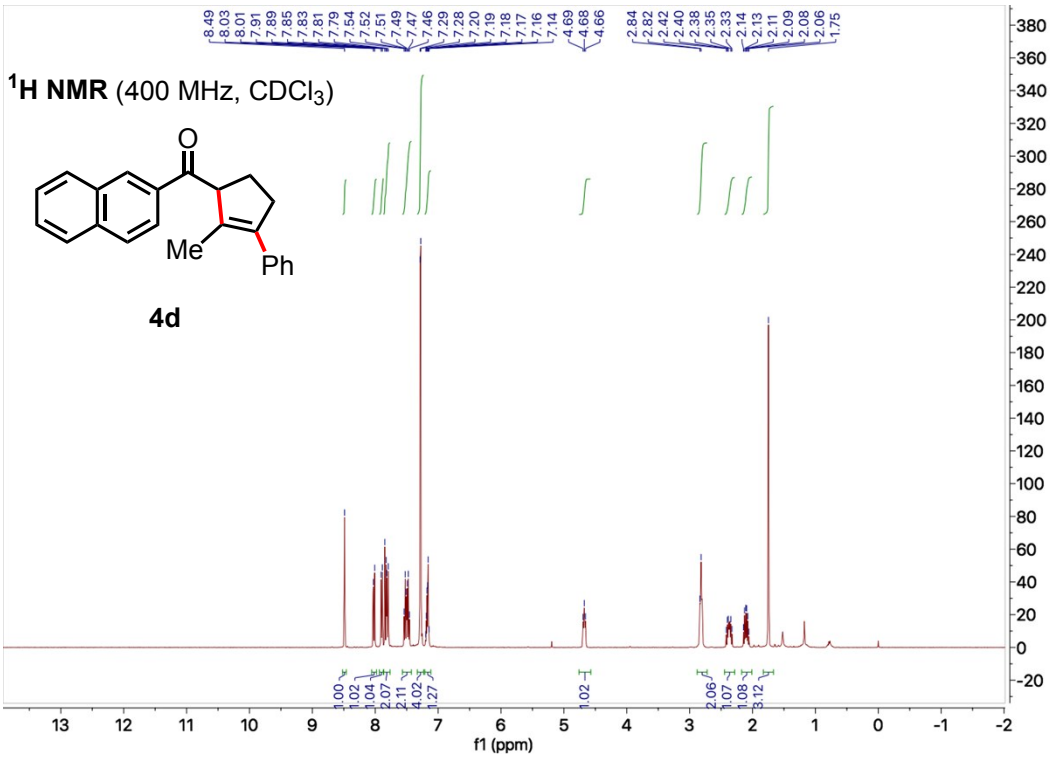
^{1}H NMR (500 MHz, $CDCl_3$)

4c



^{13}C NMR (151 MHz, $CDCl_3$)

4c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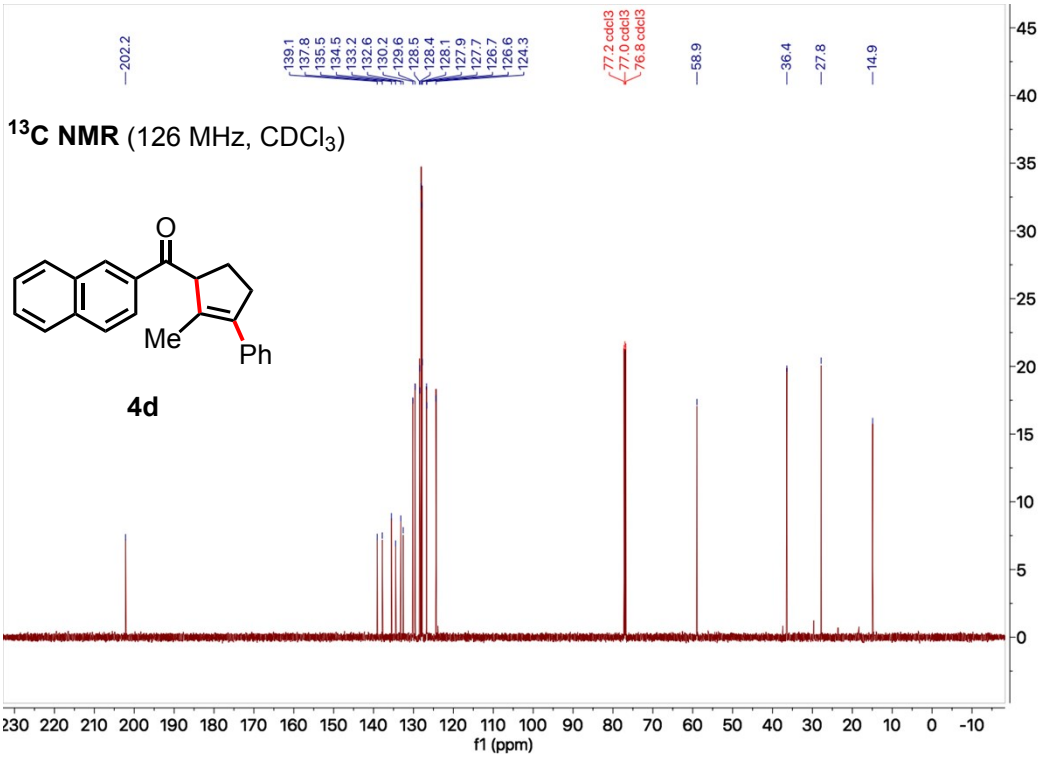
7.52
7.51
7.49
7.47
7.46
7.29
7.28
7.20
7.19
7.18
7.17
7.16
7.14
4.69
4.68
4.66
2.84
2.82
2.42
2.40
2.38
2.35
2.33
2.14
2.13
2.11
2.09
2.08
2.06
1.75
1H NMR (400 MHz, CDCl3)
O
Me
Ph
4d
1.00
1.02
1.04
2.07
2.11
4.02
1.27
1.02
2.06
1.07
1.08
3.12
f1 (ppm)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137.8
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132.6
130.2
129.6
128.5
128.4
128.1
127.9
127.7
126.7
126.6
124.3
77.2 cdcl3
77.0 cdcl3
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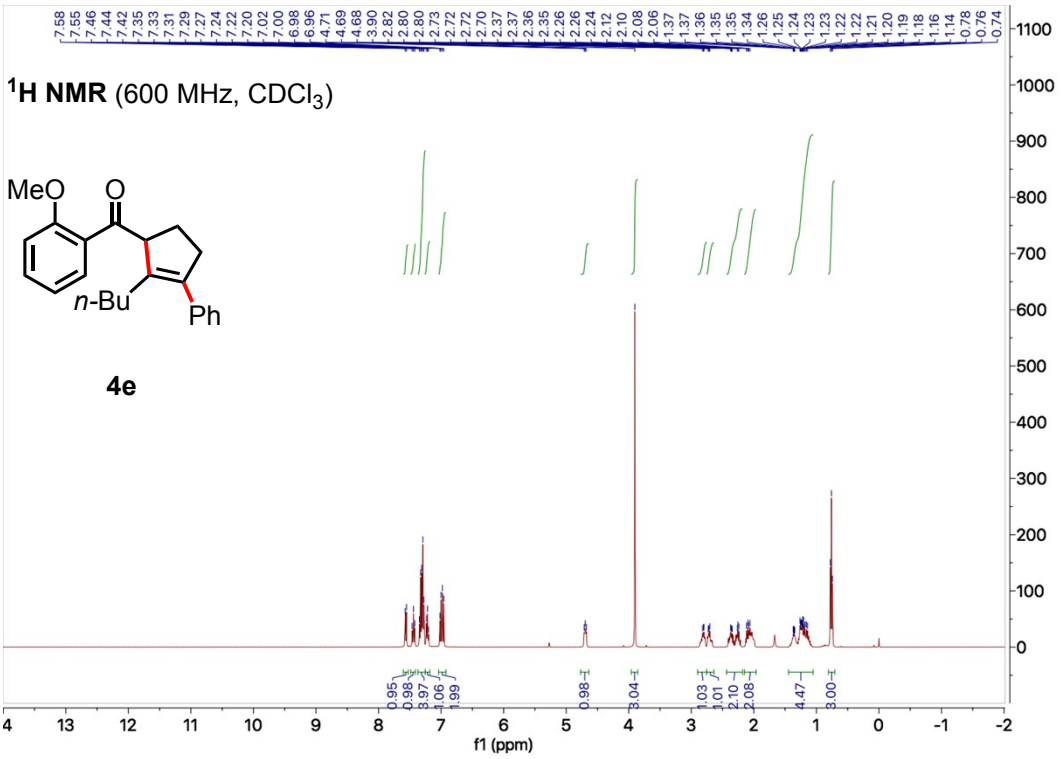
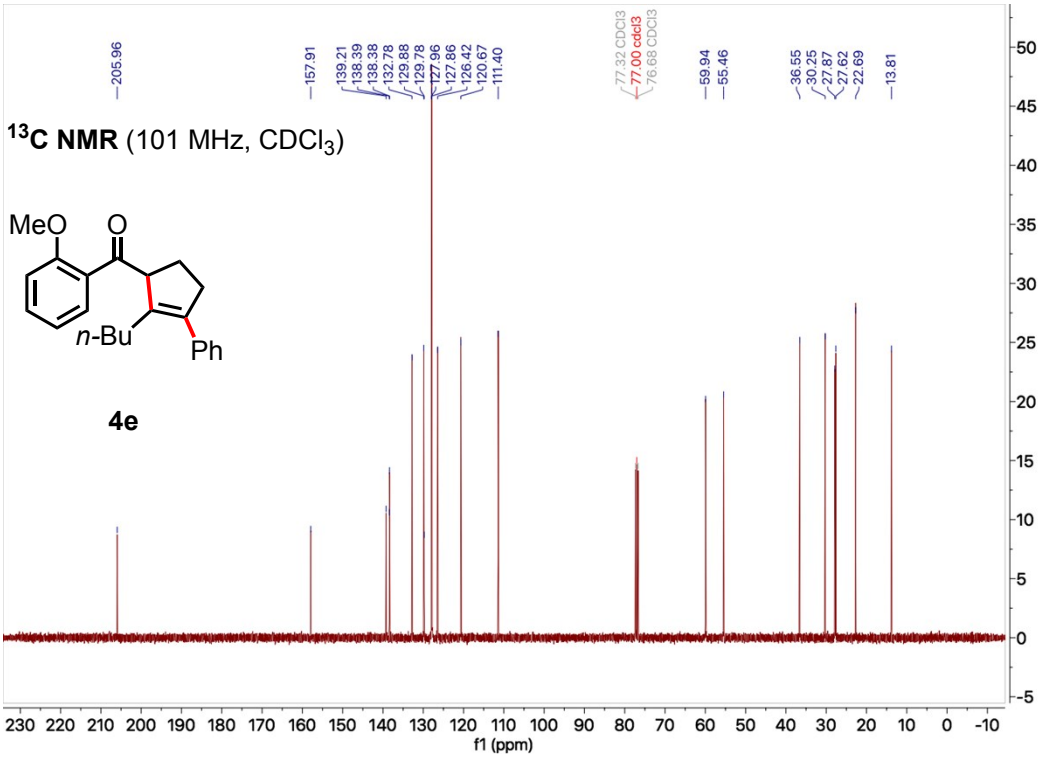
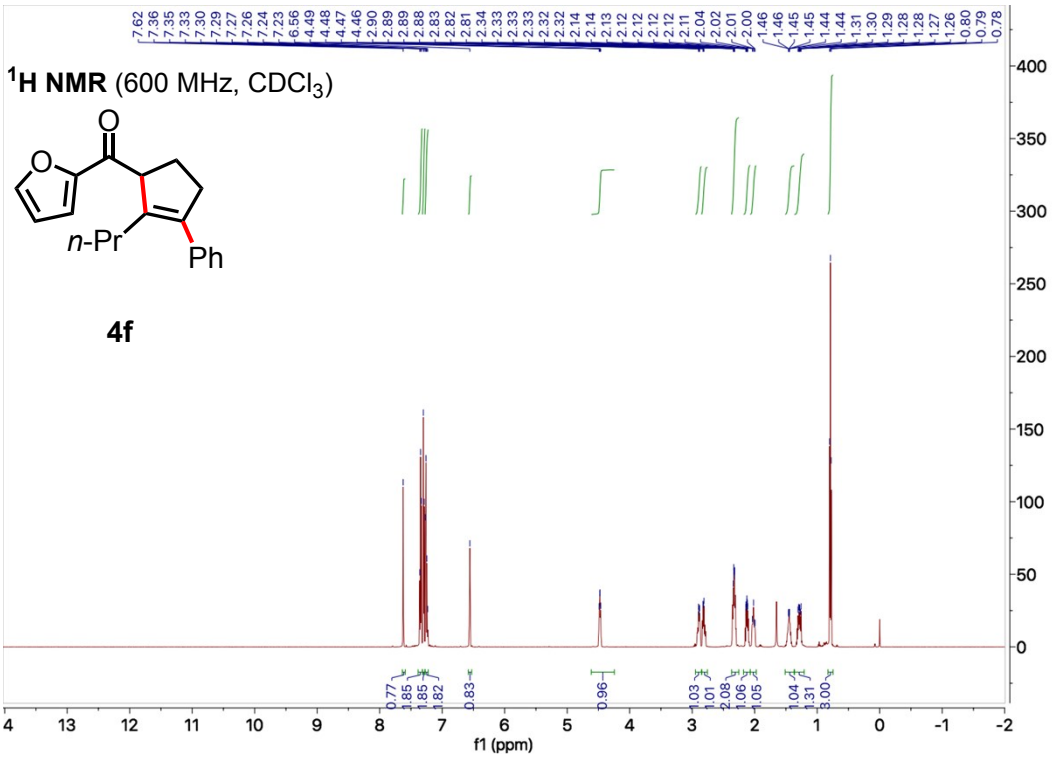
O
Me
Ph
4d
f1 (ppm)


7.58 7.55 7.46 7.44 7.42 7.35 7.33 7.31 7.29 7.27 7.24 7.22 7.20 7.02 7.00 6.98 6.96 4.71 4.69 4.68 3.90 2.82 2.80 2.80 2.73 2.72 2.72 2.70 2.37 2.37 2.36 2.35 2.26 2.26 2.24 2.12 2.10 2.08 2.06 1.37 1.37 1.36 1.35 1.35 1.34 1.26 1.25 1.24 1.23 1.23 1.22 1.22 1.21 1.20 1.19 1.18 1.16 1.14 0.78 0.76 0.74
1H NMR (600 MHz, CDCl3)
MeO
O
n-Bu
Ph
4e
0.95 0.98 0.97 1.06 1.99 0.98 3.04 1.03 1.01 2.10 2.08 4.47 3.00
f1 (ppm)


205.96 157.91 139.21 138.39 138.38 132.78 129.88 129.78 127.96 127.86 126.42 120.67 111.40 77.32 CDCl3 77.00 cdcl3 76.68 CDCl3 59.94 55.46 36.55 30.25 27.87 27.62 22.69 13.81
13C NMR (101 MHz, CDCl3)
MeO
O
n-Bu
Ph
4e
f1 (ppm)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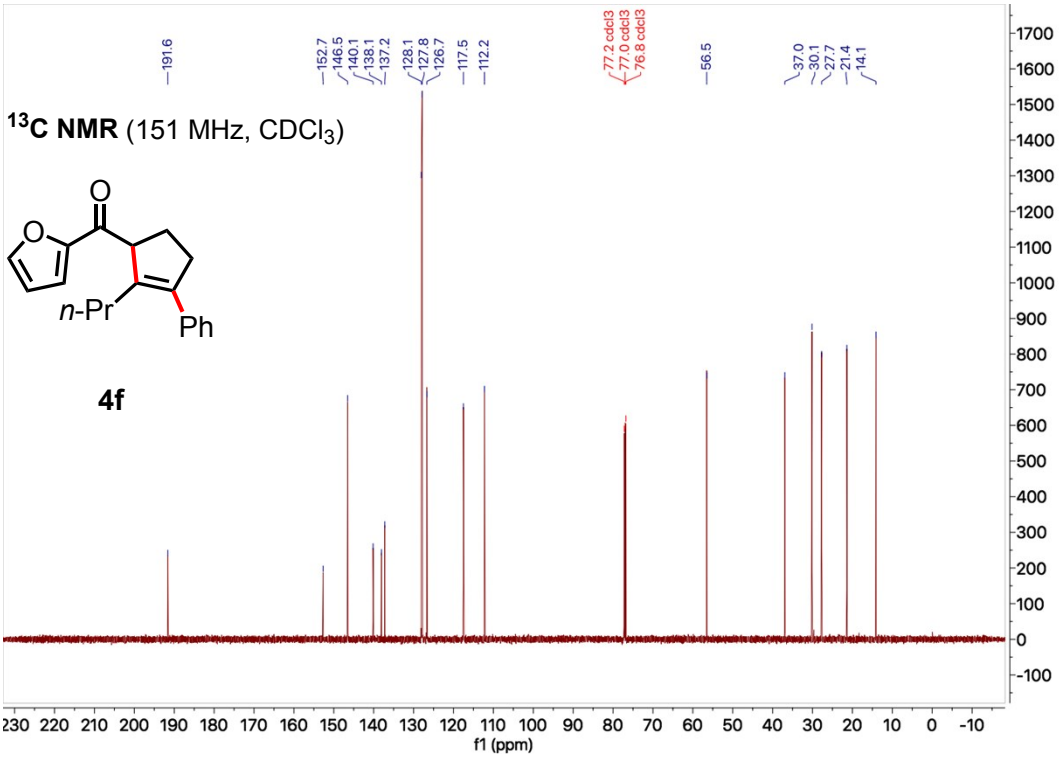
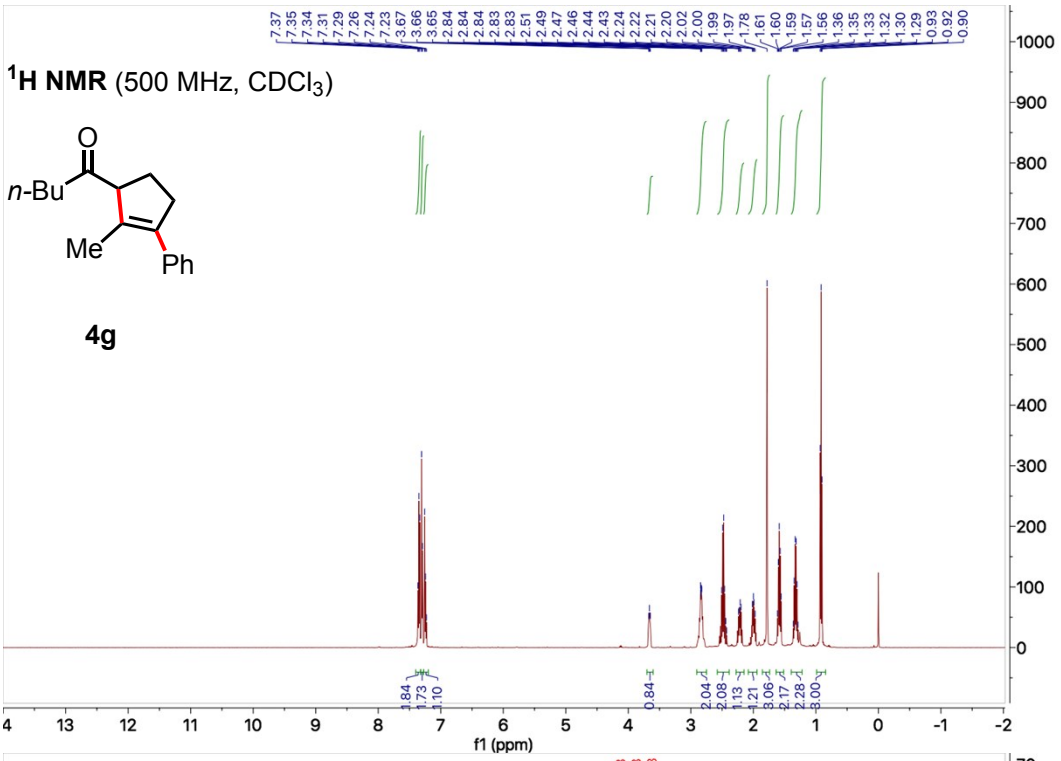
n-Pr
Ph
4f
f1 (ppm)


13C NMR (151 MHz, CDCl3)
n-Pr
Ph
4f
f1 (ppm)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2.84
2.83
2.83
2.51
2.49
2.47
2.46
2.44
2.43
2.24
2.22
2.21
2.20
2.02
2.00
1.99
1.97
1.78
1.61
1.60
1.59
1.57
1.56
1.36
1.35
1.33
1.32
1.30
1.29
0.93
0.92
0.90
1H NMR (500 MHz, CDCl3)
n-Bu
Me
Ph
4g
1.84
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2.17
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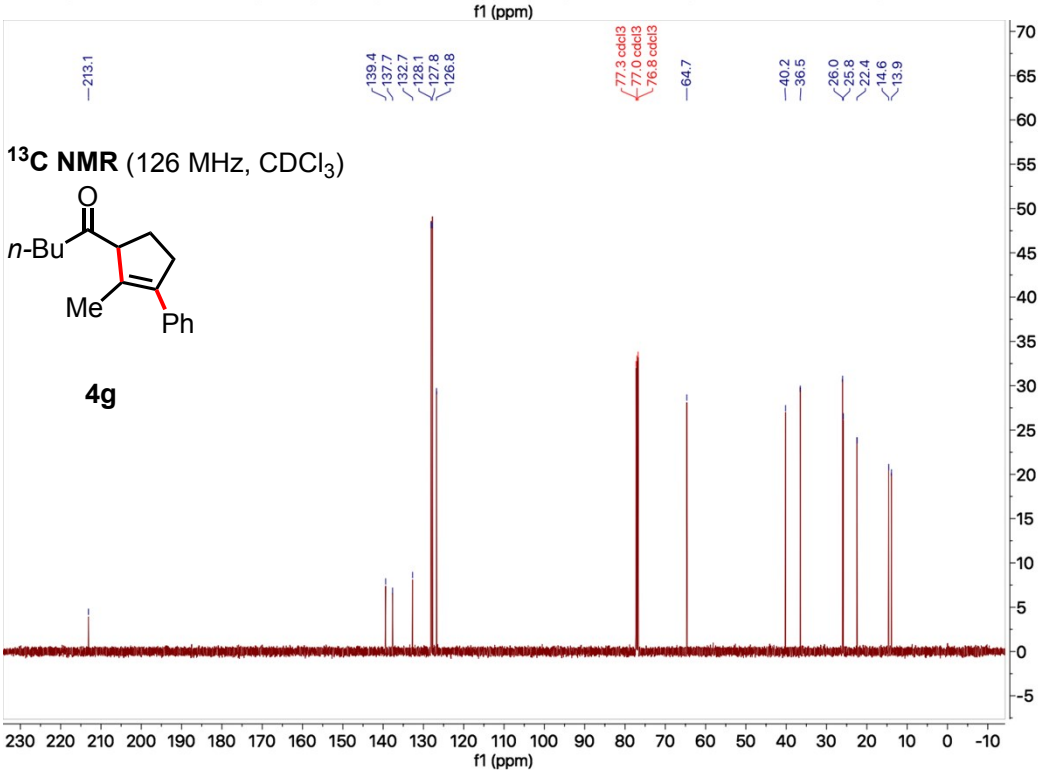
f1 (ppm)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77.3 cdcl3
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76.8 cdcl3
64.7
40.2
36.5
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22.4
14.6
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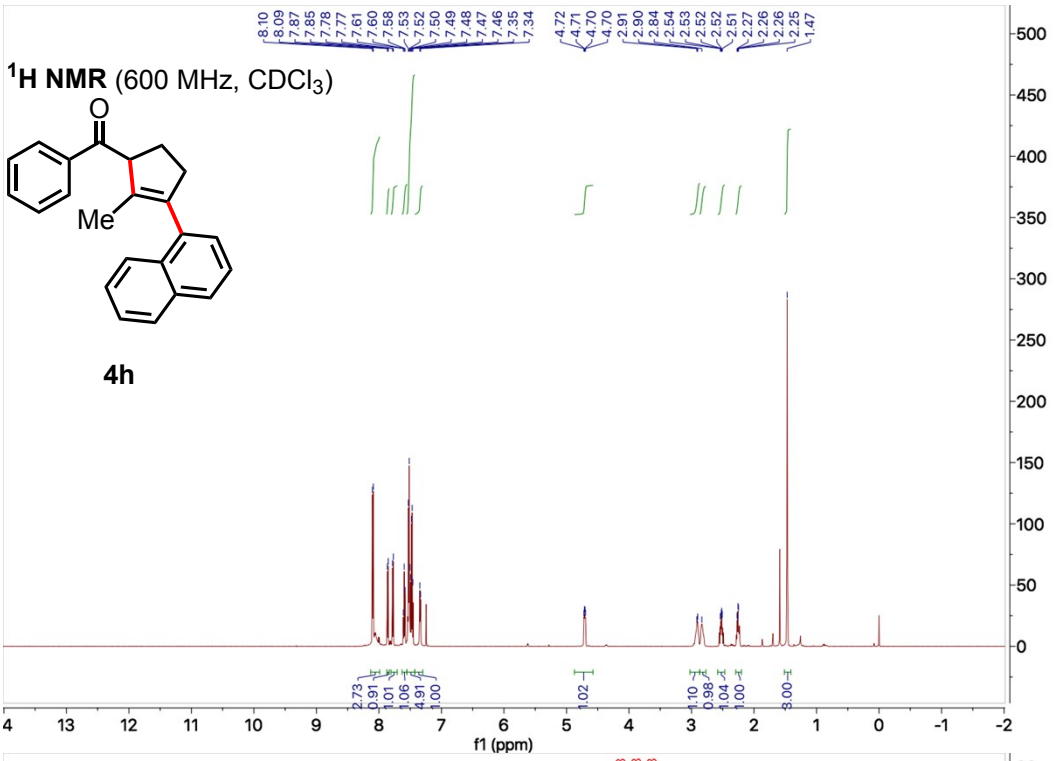
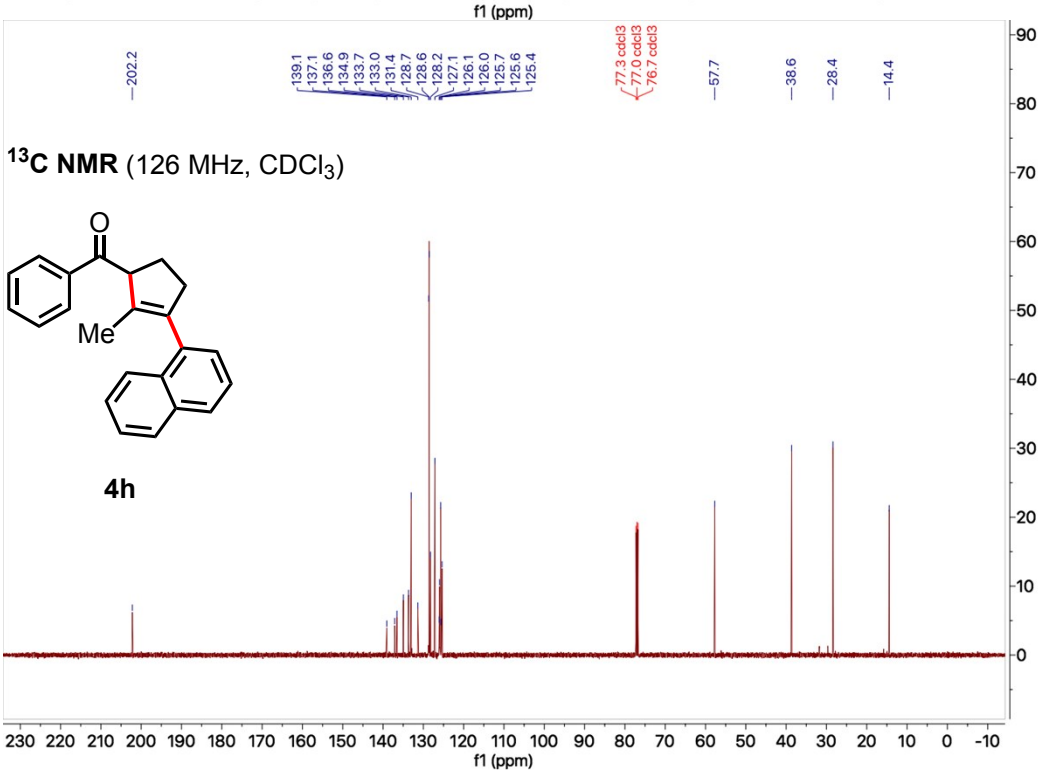
13C NMR (126 MHz, CDCl3)
n-Bu
Me
Ph
4g
f1 (ppm)



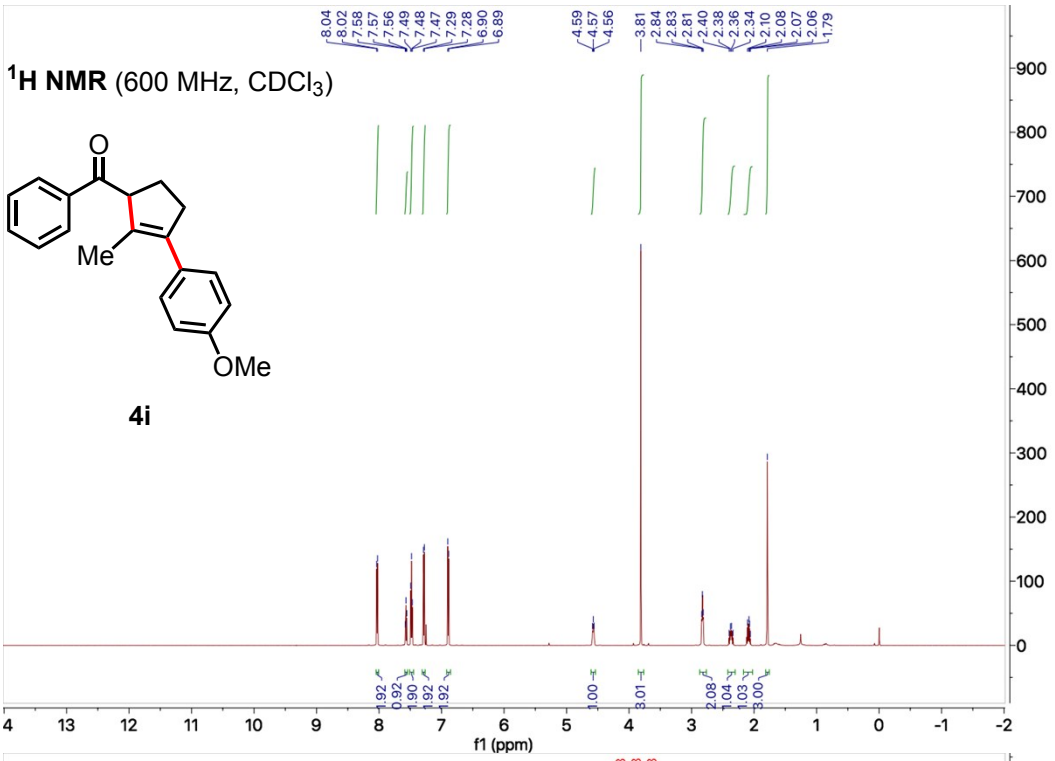
^{1}H NMR (600 MHz, $CDCl_3$)

4h



^{13}C NMR (126 MHz, $CDCl_3$)

4h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2.83
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2.40
2.38
2.36
2.34
2.10
2.08
2.07
2.06
1.79
1H NMR (600 MHz, CDCl3)
O
Me
OMe
4i
1.92
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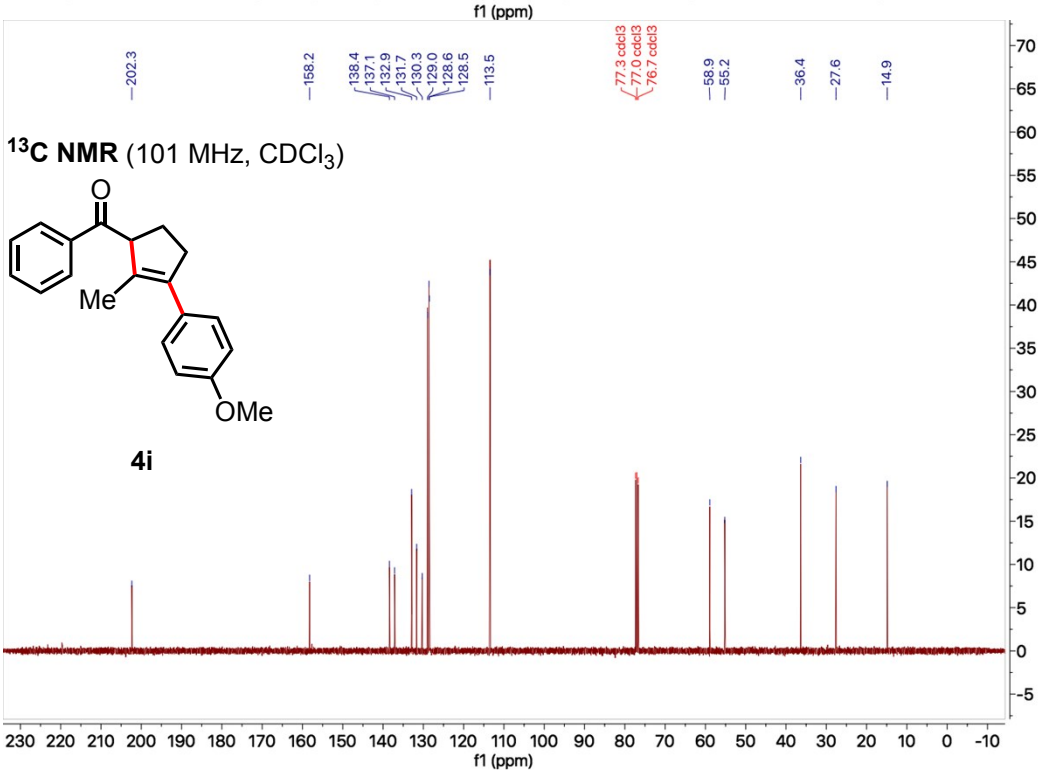
f1 (ppm)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113.5
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77.0 cdcl3
76.7 cdcl3
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27.6
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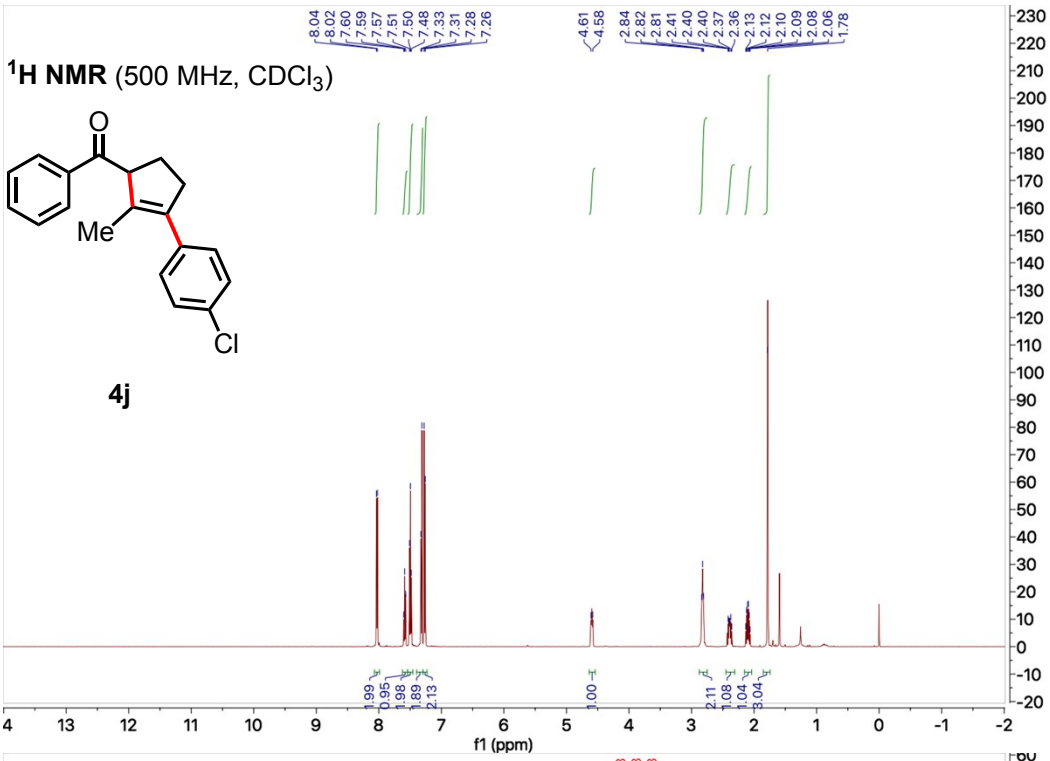
OMe
4i
f1 (ppm)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4.58
2.84
2.82
2.81
2.41
2.40
2.40
2.37
2.36
2.13
2.12
2.10
2.09
2.08
2.06
1.78
1H NMR (500 MHz, CDCl3)
O
Me
Cl
4j
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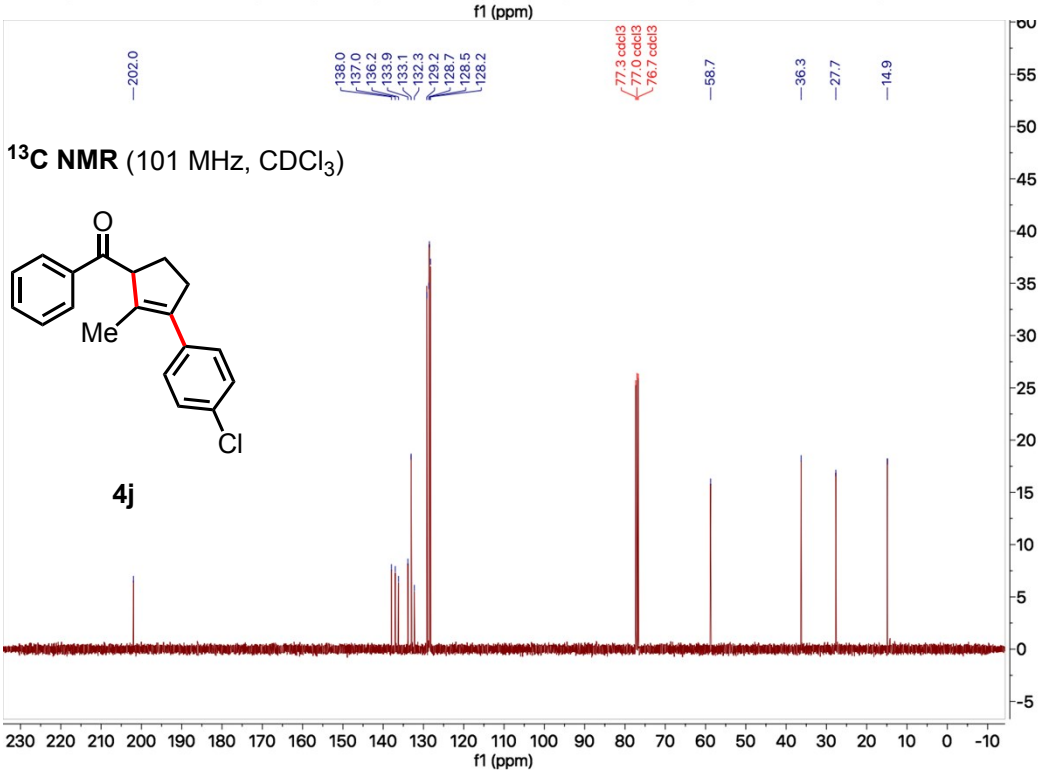
f1 (ppm)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77.0 cdcl3
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58.7
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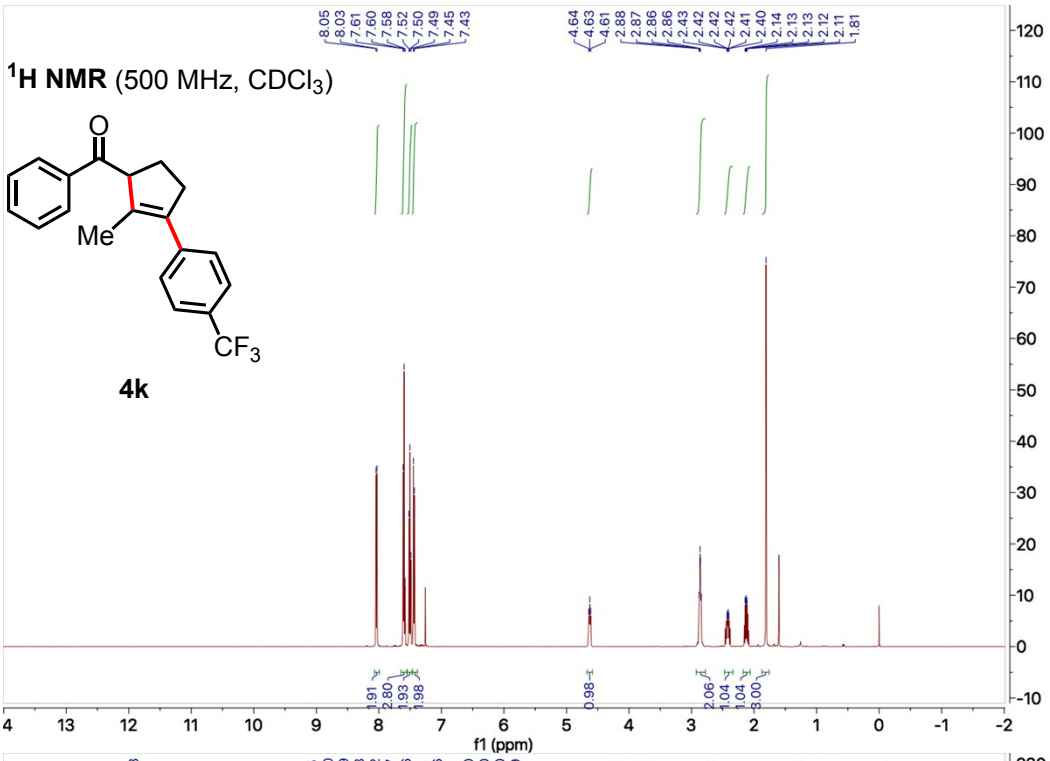
27.7
14.9
13C NMR (101 MHz, CDCl3)
O
Me
Cl
4j
f1 (ppm)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O
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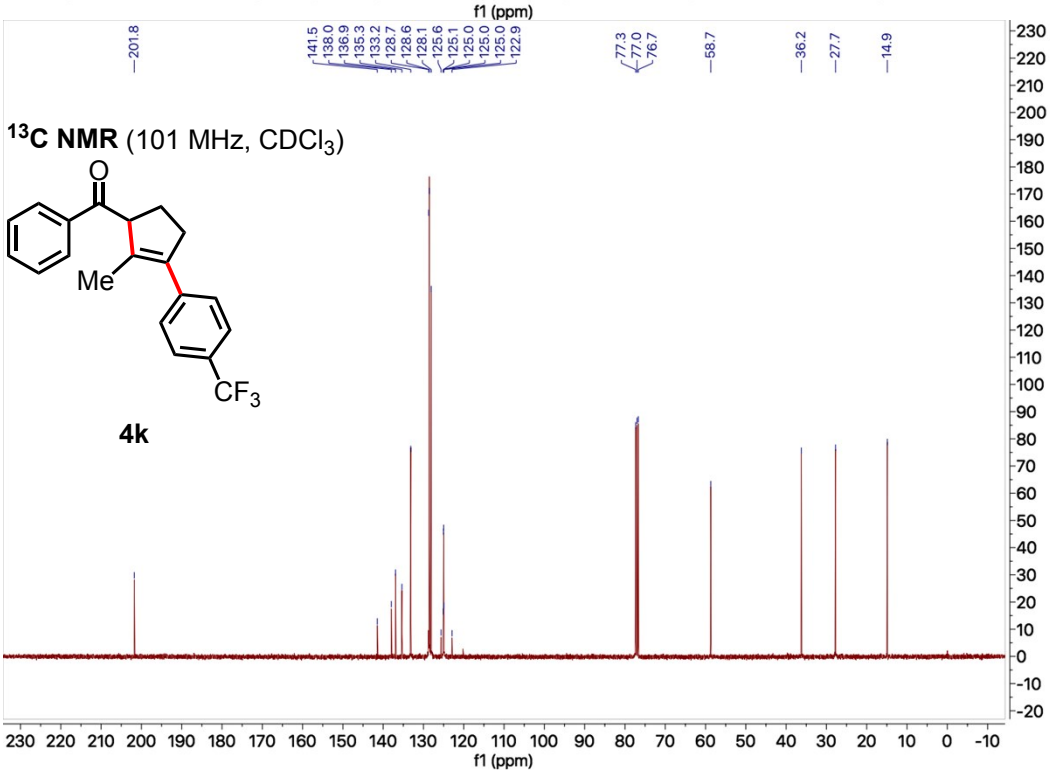
CF3
4k
f1 (ppm)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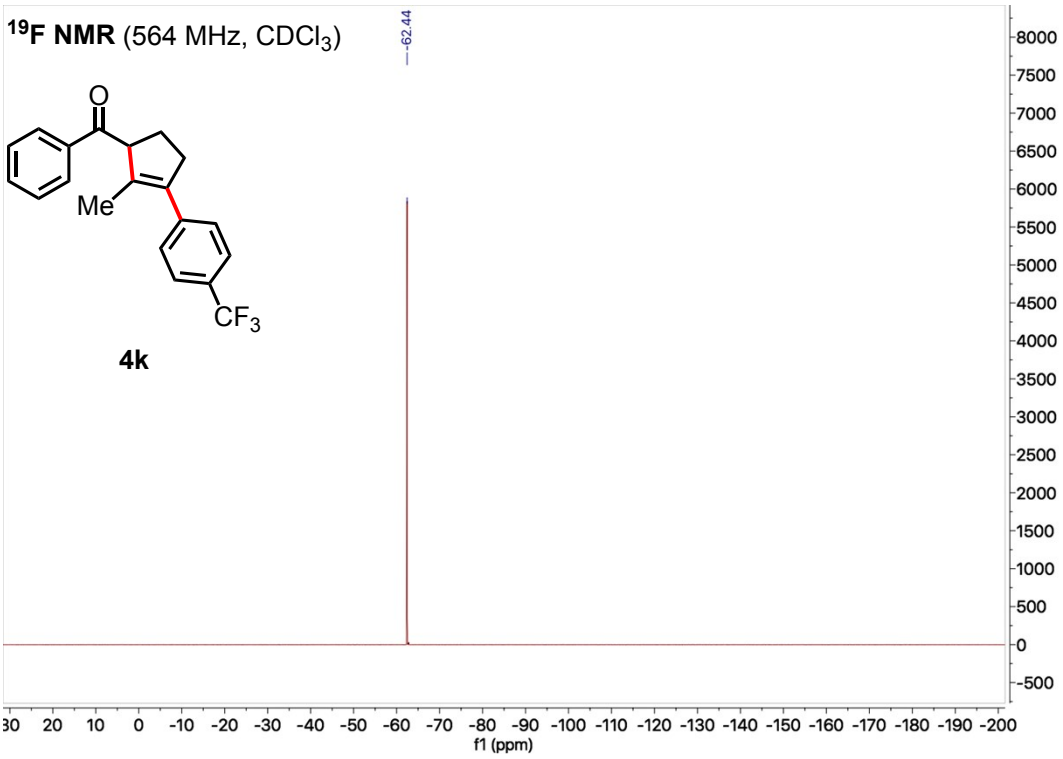
O
Me
CF3
4k
f1 (ppm)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CF3
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4500
4000
3500
3000
2500
2000
1500
1000
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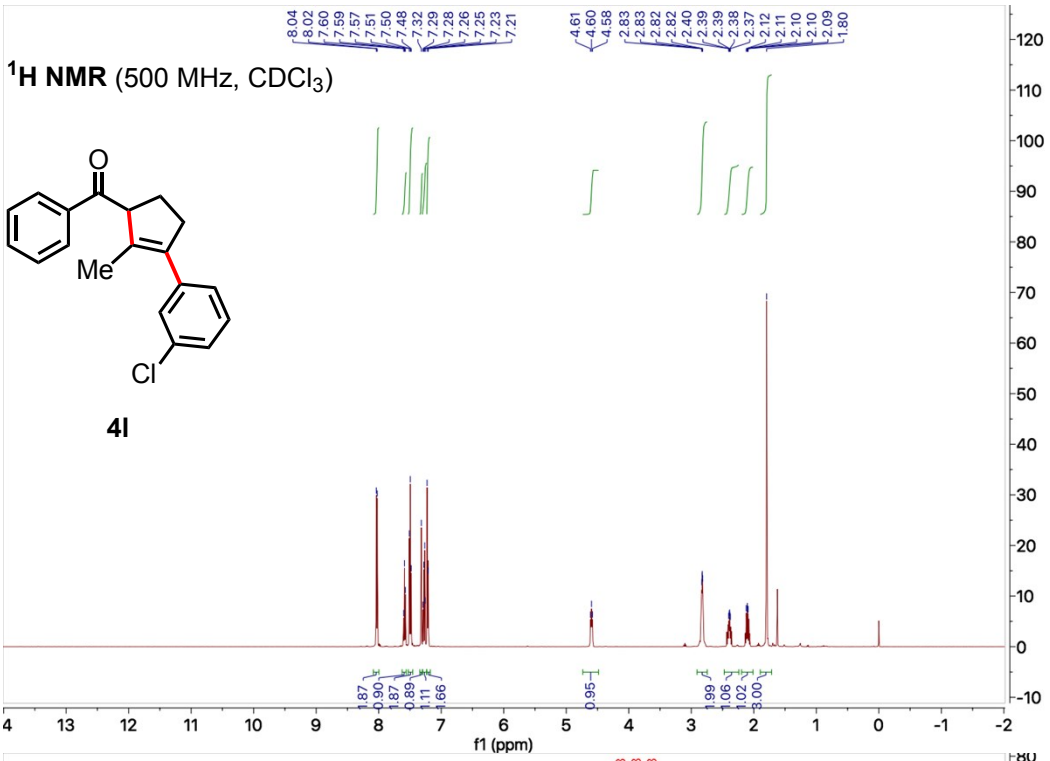
f1 (ppm)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2.83
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2.82
2.82
2.40
2.39
2.39
2.38
2.37
2.12
2.11
2.10
2.10
2.09
1.80
1H NMR (500 MHz, CDCl3)
O
Me
Cl
4l
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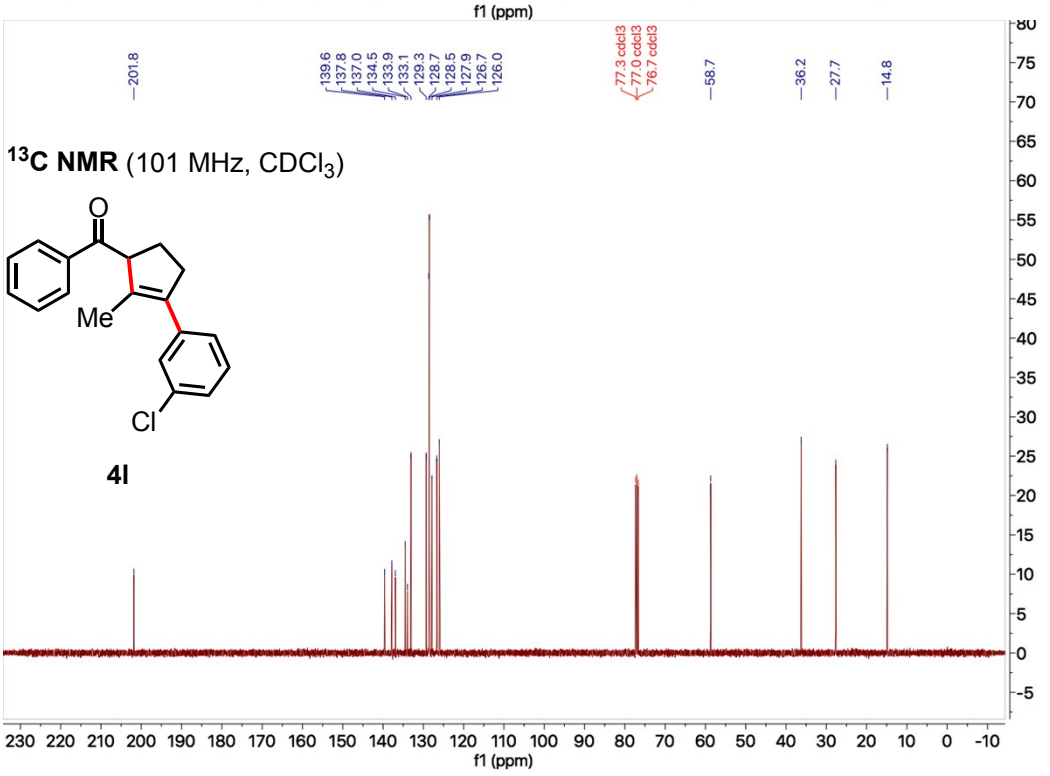
3.00
f1 (ppm)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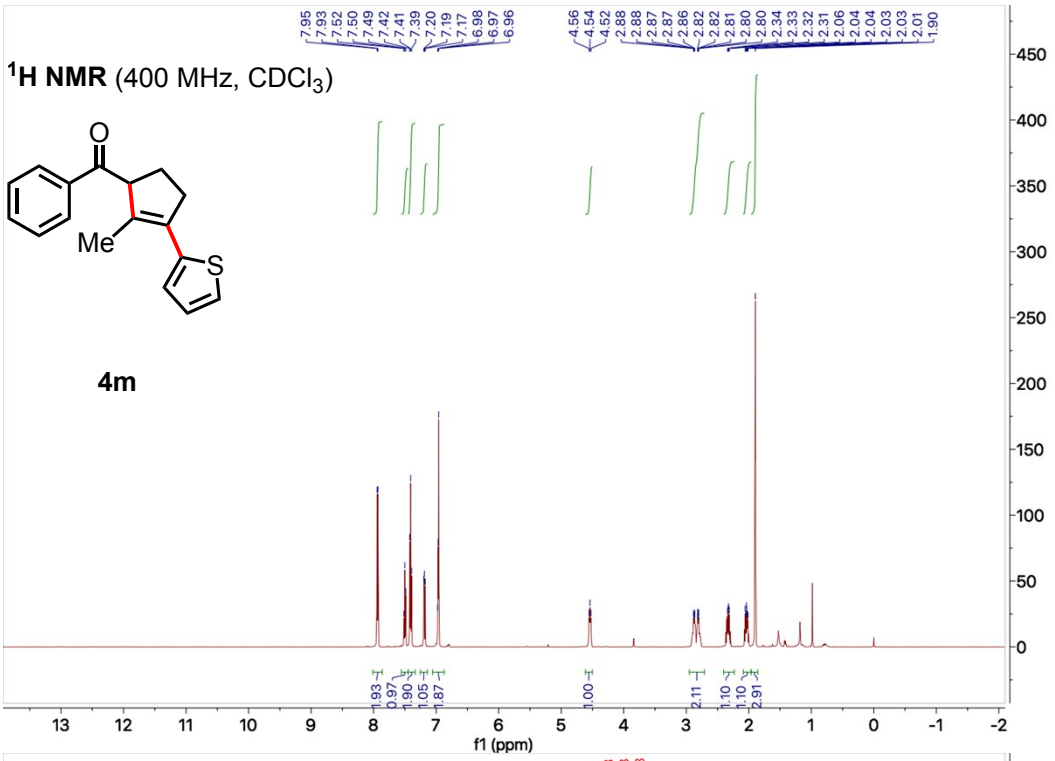
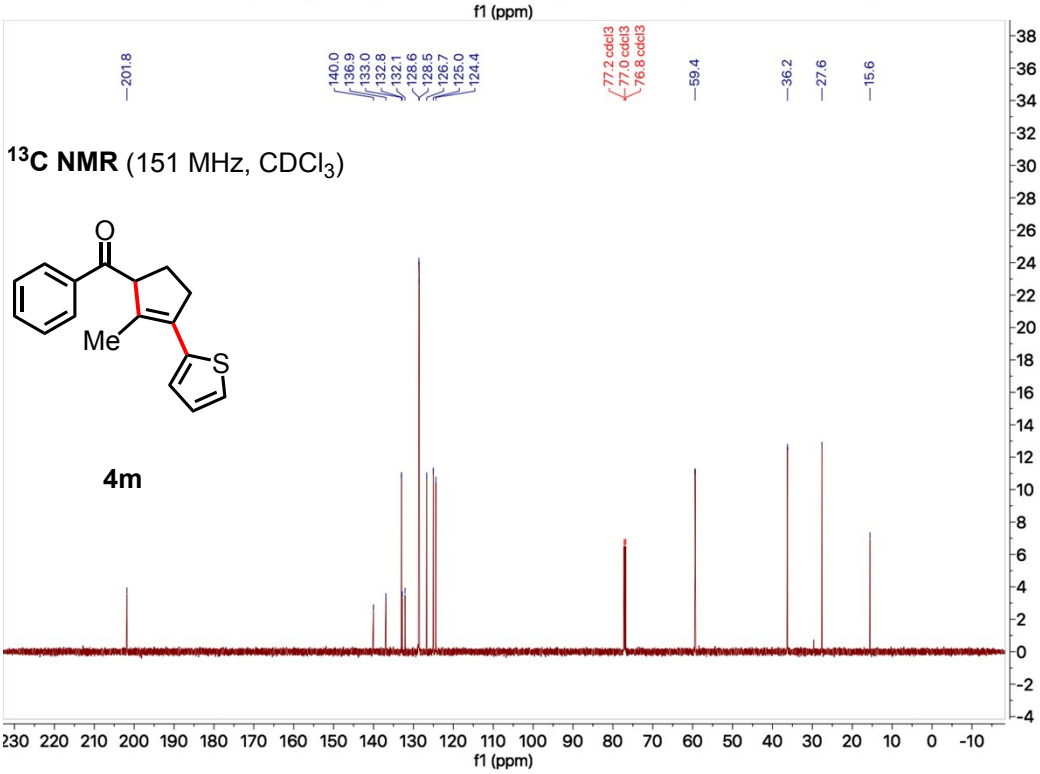
128.5
127.9
126.7
126.0
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
58.7
36.2
27.7
14.8
13C NMR (101 MHz, CDCl3)
O
Me
Cl
4l
f1 (ppm)



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

4m



^{13}C NMR (151 MHz, $CDCl_3$)

4m