Palladium(II)-catalyzed intramolecular carboxypalladation-olefin insertion cascade: direct access to indeno[1,2-*b*]furan-2-ones

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Supporting Information

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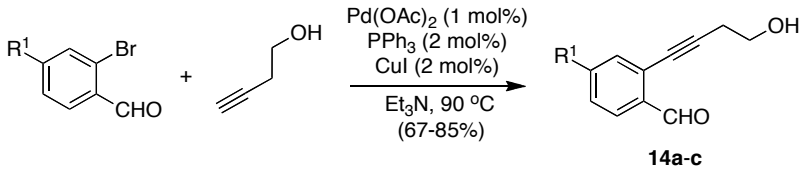
1. General:

All reagents and solvents were purchased from commercial suppliers (Avra, Alfa Aesar, Sigma-Aldrich, CDH) and used without further purification. All reactions were carried out in oven-dried glassware under nitrogen atmosphere. The reactions were monitored by thin-layer chromatography using Merck silica gel 60 F_{254} and visualized by UV detection or using *p*-anisaldehyde stain or molecular iodine. Silica gel (230-400 mesh) was used for flash column chromatography. Melting points were recorded on a Royal melting point apparatus in capillaries and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ at room temperature on a Bruker Avance 300 spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Chemical shifts (δ) are expressed in ppm using TMS as internal standard and coupling constants (*J*) are given in Hz. Infrared (IR) spectra were obtained in an Agilent Cary630 FTIR spectrometer with a diamond ATR accessory for solid and liquid samples, requiring no sample preparation and the major frequencies were reported in cm^{-1}. Elemental analyses were determined at the CAI de Microanálisis Elemental, Universidad Complutense, by using a Leco 932 CHNS combustion microanalyzer. ESI-MS spectra were obtained with a JMS-T100LC (JEOL) instrument. HPLC analyses were performed using a JASCO HPLC system (a JASCO PU 980 pump and a UV-975 UV/Vis detector) using a mixture of hexane and *i*-PrOH as eluents.

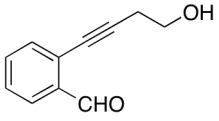
2. General procedure for the Sonogashira coupling: Synthesis of compounds 14a-c.



14a-c

To a solution of 2-bromoarylaldehyde (27 mmol, 1 equiv) and 3-butyn-1-ol (29.7 mmol, 1.1 equiv) in Et_3N (50 mL) was added $Pd(OAc)_2$ (0.27 mmol, 1 mol%), PPh_3 (0.54 mmol, 2 mol%) and CuI (0.54 mmol, 2 mol%). The resulting mixture was degassed with nitrogen and heated with stirring at 90 °C for 3 h. After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature and filtered through a pad of celite. The celite bed was washed well with ethyl acetate (2 x 50 mL) and the filtrate was washed with water, brine and dried over anhyd. Na_2SO_4. The solvent was evaporated to dryness under reduced pressure and the crude mixture was chromatographed over silica using petroleum ether and ethyl acetate (75: 25, v/v) as eluent to obtain compounds **14a-c**.

2-(4-Hydroxybut-1-ynyl)benzaldehyde (14a)[1]:

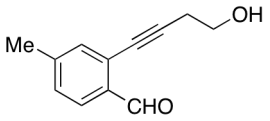


14a

Yellow viscous liquid; yield: 85%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.76 (t, *J* = 6.0 Hz, 2H), 3.87 (t, *J* = 6.0 Hz, 2H), 7.40-7.46 (m, 1H), 7.51-7.54 (m, 2H), 7.86 (d, *J* = 7.8 Hz, 1H), 10.44 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.9, 60.9, 78.2, 94.5, 126.7, 128.1, 128.2, 133.4, 133.8, 135.9, 192.3.

[1] Dell'Acqua, M.; Castano, B.; Cecchini, C.; Pedrazzini, T.; Pirovano, V.; Rossi, E.; Caselli, A.; Abbiati, G. *J. Org. Chem*. **2014**, *79*, 3494.

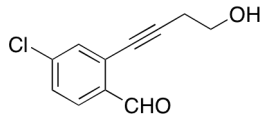
2-(4-Hydroxybut-1-ynyl)-4-methylbenzaldehyde (14b):



14b

Orange viscous liquid; yield: 78%; IR (neat) 3382, 2881, 2227, 1686, 1597, 1390, 1253, 1205, 1040 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.75 (t, *J* = 6.3Hz, 2H), 3.87 (t, *J* = 6.3 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.35 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 10.37 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 24.0, 60.9, 78.6, 93.8, 126.5, 128.5, 129.2, 133.8, 133.9, 144.9, 191.8. Anal Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.27; H, 6.65.

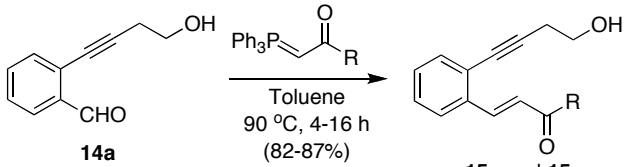
4-Chloro-2-(4-hydroxybut-1-ynyl)benzaldehyde (14c):



14c

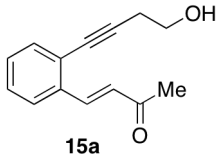
Yellow viscous liquid; yield: 73%; IR (neat) 3370, 2911, 2236, 1690, 1601, 1399, 1230, 1018 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.1 (brs, 1H), 2.77 (t, *J* = 6.3Hz, 2H), 3.87 (t, *J* = 6.3 Hz, 2H), 7.40 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 10.39 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.0, 60.8, 76.6, 95.9, 128.0, 128.8, 129.5, 133.2, 134.4, 140.2, 190.8. Anal Calcd for $C_{11}H_9ClO_2$: C, 63.32; H, 4.35. Found: C, 63.04; H, 4.39.

3. General procedure for the synthesis of compounds 15a and 15o.



A mixture of compound **14a** (3 mmol, 1 equiv) and Wittig ylide (3.6 mmol, 1.2 equiv) in toluene was heated at 90 °C for 4 h for **15a** and 16 h for **15q**. After cooling, the solvent was evaporated to dryness and the residue was treated with ether. The solidified $OPPh_3$ was removed by filtration and the filtrate was concentrated to afford the crude products. The crude was purified by flash column chromatography eluting with petroleum ether and ethyl acetate mixture (80:20, v/v).

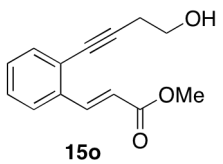
(*E*)-4-(2-(4-Hydroxybut-1-ynyl)phenyl)but-3-en-2-one (15a):



15a

Off-white solid; mp 49-50 °C, yield: 87%; IR (neat) 3412, 3018, 2318, 1680, 1572, 1218, 1053 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.21 (brs, 1H), 2.41 (s, 3H), 2.78 (t, *J* = 6.0 Hz, 2H), 3.90 (q, *J* = 6.0 Hz, 2H), 6.78 (d, *J* = 16.5 Hz, 1H), 7.31-7.35 (m, 2H), 7.46-7.49 (m, 1H), 7.61-7.64 (m, 1H), 8.06 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.4, 28.8, 62.5, 81.2, 95.2, 126.1, 127.5, 129.6, 129.7, 131.4, 134.3, 137.2, 143.3, 200.5. Anal Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.17; H, 6.41.

(*E*)-Methyl 3-(2-(4-hydroxybut-1-ynyl)phenyl)acrylate (15o):

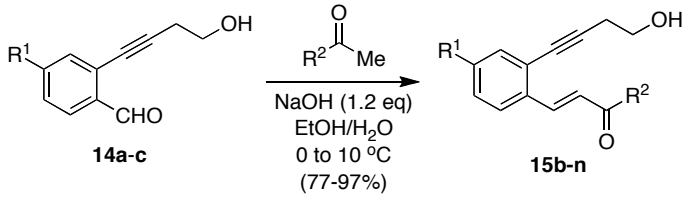


15o

Pale yellow viscous liquid; yield: 82%; IR (neat) 3419, 2948, 2228, 1700, 1631, 1476, 1434, 1318, 1268, 1193 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.0

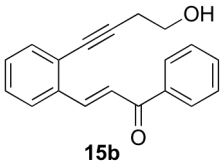
(brs, 1H), 2.70 (t, J = 6.0 Hz, 2H), 3.59 (s, 3H), 3.82 (t, J = 6.0 Hz, 2H), 6.44 (d, J = 16.2 Hz, 1H), 7.20-7.25 (m, 2H), 7.37-7.40 (m, 1H), 7.51-7.55 (m, 1H), 8.16 (d, J = 16.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.0, 51.9, 61.1, 79.7, 93.8, 118.8, 124.5, 126.0, 128.1, 129.8, 132.7, 135.6, 143.2, 167.7. Anal Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.87; H, 6.21.

4. General procedure for the synthesis of compounds 15b-n.



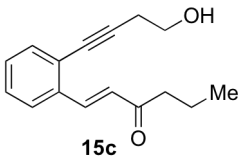
To a solution of methyl ketone (4 mmol, 1 equiv) in 3:1 EtOH/H_2O mixture was added NaOH (4.8 mmol, 1.2 equiv) at 0 °C. After 10 minutes stirring, aldehyde **14** (4.4 mmol, 1.1 equiv) was added and the stirring was continued at 10 °C for 4-5 h. After completion of the reaction, as monitored by TLC, the reaction mixture was poured into ice water then acidified with 1.5N HCl. The aqueous suspension was extracted with CH_2Cl_2 (2 x 30 mL), washed with water and brine. The organic layer was dried over anhyd. Na_2SO_4 and then concentrated under reduced pressure. The crude product was purified by flash column chromatography using petroleum ether and ethyl acetate mixture as eluent (70:30, v/v).

(*E*)-3-(2-(4-Hydroxybut-1-ynyl)phenyl)-1-phenylprop-2-en-1-one (15b):



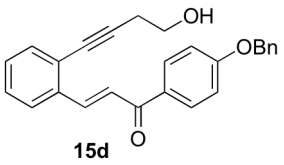
Yellow viscous liquid; yield: 81%; IR (neat) 3413, 2885, 2349, 1660, 1592, 1215, 1047 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (brs, 1H), 2.69 (t, J = 6.3Hz, 2H), 3.81 (t, J = 6.3 Hz, 2H), 7.26-7.29 (m, 2H), 7.40-7.55 (m, 5H), 7.66-7.69 (m, 1H), 7.94-7.97 (m, 2H), 8.28 (d, J = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 24.1, 61.1, 79.9, 94.2, 123.3, 125.1, 126.1, 128.2, 128.6, 130.0, 132.8, 132.9, 136.2, 138.1, 143.4, 191.1. HRMS (ESI): calcd for $C_{19}H_{16}NaO_2$, m/z 299.1048 ([M+Na]$^+$); found, m/z 299.1042. *one aromatic carbon is merged with others.

(*E*)-1-(2-(4-Hydroxybut-1-ynyl)phenyl)hex-1-en-3-one (15c):



Colorless viscous liquid; yield: 83%; IR (neat) 3401, 3012, 2320, 1668, 1582, 1221, 1032 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J = 7.5 Hz, 3H), 1.65 (sextet, 2H, J = 7.5 Hz), 2.60 (t, J = 7.5 Hz, 2H), 2.70 (t, J = 6.3 Hz, 2H), 3.82 (t, J = 6.3 Hz, 2H), 6.72 (d, J = 16.2 Hz, 1H), 7.20-7.26 (m, 2H), 7.37-7.40 (m, 1H), 7.54-7.57 (m, 1H), 8.03 (d, J = 16.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0, 20.0, 26.1, 44.9, 63.1, 81.8, 96.0, 126.9, 128.1, 129.3, 130.3, 131.9, 134.9, 137.9, 142.9, 203.4. Anal Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.01; H, 7.32.

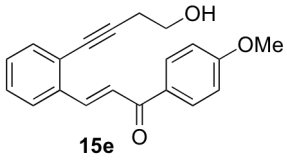
(*E*)-1-(4-(Benzyloxy)phenyl)-3-(2-(4-hydroxybut-1-ynyl)phenyl)prop-2-en-1-one (15d):



15d

Pale yellow solid; mp 91-92 ^{o}C, yield: 86%; IR (neat) 3371, 2950, 2881, 2309, 1655, 1597, 1338, 1263, 1173, 1031 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.9 (brs, 1H), 2.69 (t, *J* = 6.0 Hz, 2H), 3.83 (t, *J* = 6.0 Hz, 2H), 5.09 (s, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 7.25-7.42 (m, 8H), 7.51 (d, *J* = 15.6 Hz, 1H), 7.66-7.69 (m, 1H), 7.98 (d, *J* = 8.7 Hz, 2H), 8.28 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.1, 61.1, 70.2, 80.0, 94.3, 114.7, 123.0, 125.0, 126.1, 127.5, 128.1, 128.3, 128.7, 129.8, 131.0, 131.1, 132.7, 136.2, 136.5, 142.5, 162.7, 189.1. HRMS (ESI): calcd for $C_{26}H_{22}NaO_3$, m/z 405.1467 ([M+Na]$^+$); found, m/z 405.1458.

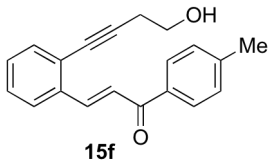
(*E*)-3-(2-(4-Hydroxybut-1-ynyl)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (15e):



15e

Off-white solid; mp 87-88 ^{o}C, yield: 88%; IR (neat) 3486, 3056, 2936, 2230, 1655, 1609, 1512, 1475, 1339, 1166, 1022 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.1 (brs, 1H), 2.70 (t, *J* = 6.0 Hz, 2H), 3.83 (s, 3H), 3.84 (t, *J* = 6.0 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 7.25-7.28 (m, 2H), 7.39-7.42 (m, 1H), 7.52 (d, *J* = 15.9 Hz, 1H), 7.66-7.69 (m, 1H), 7.99 (d, *J* = 8.7 Hz, 2H), 8.29 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.1, 55.5, 61.1, 79.9, 94.3, 113.9, 123.0, 125.0, 126.1, 128.1, 129.8, 130.9, 131.0, 132.7, 136.4, 142.5, 163.6, 189.1. HRMS (ESI): calcd for $C_{20}H_{18}NaO_3$, m/z 329.1154 ([M+Na]$^+$); found, m/z 329.1146.

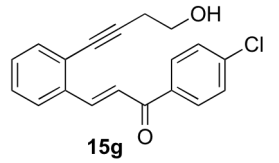
(*E*)-3-(2-(4-Hydroxybut-1-ynyl)phenyl)-1-p-tolylprop-2-en-1-one (15f):



15f

Pale yellow solid; mp 91-92 ^{o}C, yield: 78%; IR (neat) 3485, 2927, 2878, 2349, 1657, 1604, 1479, 1315, 1219, 1088 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.8 (brs, 1H), 2.37(s, 3H), 2.69 (t, *J* = 6.0 Hz, 2H), 3.83 (t, *J* = 6.0 Hz, 2H), 7.19-7.28 (m, 4H), 7.39-7.42 (m, 1H), 7.52 (d, *J* = 15.9 Hz, 1H), 7.66-7.70 (m, 1H), 7.88 (d, *J* = 8.1 Hz, 2H), 8.29 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 22.7, 59.7, 78.5, 92.9, 121.3, 123.7, 124.8, 126.8, 127.6, 128.6, 128.8, 131.5, 134.7, 135.0, 137.9, 142.4, 188.2. HRMS (ESI): calcd for $C_{20}H_{18}NaO_2$, m/z 313.1204 ([M+Na]$^+$); found, m/z 313.1194. *One aromatic carbon is merged with others.

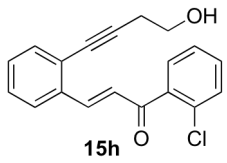
(*E*)-1-(4-Chlorophenyl)-3-(2-(4-hydroxybut-1-ynyl)phenyl)prop-2-en-1-one (15g):



15g

Pale yellow solid; mp 112-113 ^{o}C, yield: 77%; IR (neat) 3471, 3066, 2945, 2309, 1656, 1591, 1316, 1186, 1060 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.70 (t, *J* = 6.3Hz, 2H), 3.82 (t, *J* = 6.3 Hz, 2H), 7.27-7.30 (m, 2H), 7.40-7.43 (m, 3H), 7.47 (d, *J* = 15.6 Hz, 1H), 7.66-7.69 (m, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 8.29 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 24.1, 61.1, 79.8, 94.3, 122.6, 125.2, 126.2, 128.2, 129.0, 130.0, 130.2, 132.9, 136.0, 136.3, 139.3, 143.8, 189.0. HRMS (ESI): calcd for $C_{19}H_{15}ClNaO_2$, m/z 333.0658 ([M+Na]$^+$); found, m/z 333.0647.

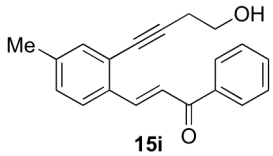
(*E*)-1-(2-Chlorophenyl)-3-(2-(4-hydroxybut-1-ynyl)phenyl)prop-2-en-1-one (15h):



15h

Yellow viscous liquid; yield: 90%; IR (neat) 3389, 3059, 2230, 1642, 1589, 1472, 1431, 1300, 1252, 1038 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.90 (brs, 1H), 2.65 (t, *J* = 6.3 Hz, 2H), 3.74-3.76 (m, 2H), 7.17 (d, *J* = 16.2 Hz, 1H), 7.31-7.51 (m, 7H), 7.68-7.71 (m, 1H), 7.98 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 23.9, 61.0, 79.6, 93.8, 125.0, 126.3, 126.8, 127.3, 128.3, 129.4, 130.2, 130.4, 131.4, 132.8, 135.7, 139.0, 145.1, 194.5. Anal Calcd for $C_{19}H_{15}ClO_2$: C, 73.43; H, 4.86. Found: C, 73.10; H, 5.07. *One aromatic carbon is merged with others.

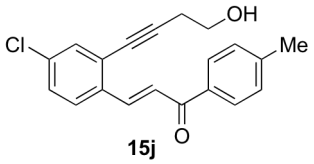
(*E*)-3-(2-(4-Hydroxybut-1-ynyl)-4-methylphenyl)-1-phenylprop-2-en-1-one (15i):



15i

Yellow viscous liquid; yield: 92%; IR (neat) 3390, 3022, 2261, 1655, 1577, 1455, 1322, 1242, 1030 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 1H), 2.75 (t, *J* = 6.0 Hz, 2H), 3.89 (t, *J* = 6.0 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.31 (s, 1H), 7.48-7.62 (m, 4H), 7.66 (d, *J* = 8.1 Hz, 1H), 8.01-8.04 (m, 2H), 8.33 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 21.3, 24.1, 61.1, 80.0, 93.7, 122.3, 125.1, 126.1, 128.6, 129.2, 132.8, 133.3, 133.5, 138.2, 140.6, 143.4, 191.2. Anal Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.43; H, 6.13. *one aromatic carbon is merged with others.

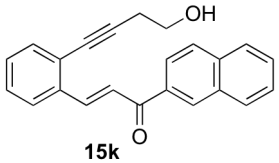
(*E*)-3-(4-Chloro-2-(4-hydroxybut-1-ynyl)phenyl)-1-p-tolylprop-2-en-1-one (15j):



15j

Pale yellow gummy solid; yield: 96%; IR (neat) 3360, 3048, 2223, 1620, 1556, 1431, 1249, 1032 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.44(s, 3H), 2.50 (brs, 1H), 2.76 (t, *J* = 6.3 Hz, 2H), 3.90 (t, *J* = 6.3 Hz, 2H), 7.29-7.33 (m, 3H), 7.46 (d, *J* = 2.1 Hz, 1H), 7.56 (d, *J* = 15.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 8.28 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 24.1, 61.0, 78.8, 95.7, 123.4, 126.5, 127.3, 128.5, 128.8, 129.4, 132.4, 134.9, 135.3, 135.7, 141.6, 144.0, 190.1. Anal Calcd for $C_{20}H_{17}ClO_2$: C, 73.96; H, 5.28. Found: C, 73.66; H, 5.17.

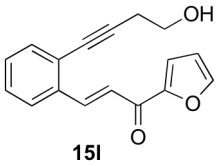
(*E*)-3-(2-(4-Hydroxybut-1-ynyl)phenyl)-1-(naphthylen-2-yl)prop-2-en-1-one (15k):



15k

Pale brown solid; mp 113-114 ^oC, yield: 81%; IR (neat) 3439, 3053, 2950, 2227, 1647, 1582, 1476, 1275, 1185, 1054 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.73 (t, *J* = 6.3Hz, 2H), 2.77 (brs, 1H), 3.85 (t, *J* = 6.3 Hz, 2H), 7.30-7.34 (m, 2H), 7.45-7.48 (m, 1H), 7.52-7.62 (m, 2H), 7.71 (d, *J* = 15.6 Hz, 1H), 7.75-7.78 (m, 1H), 7.86-7.98 (m, 3H), 8.08 (dd, *J* = 8.4, 1.5 Hz, 1H), 8.39 (d, *J* = 15.6 Hz, 1H), 8.51 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.1, 60.1, 78.9, 93.3, 122.2, 123.6, 124.2, 125.3, 125.9, 126.9, 127.2, 127.5, 127.6, 128.6, 129.0, 129.2, 131.6, 131.9, 134.5, 134.6, 135.3, 142.3, 189.8. Anal Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.33; H, 5.52.

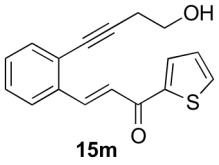
(*E*)-1-(Furan-2-yl)-3-(2-(4-hydroxybut-1-ynyl)phenyl)prop-2-en-1-one (15l):



15l

Pale yellow solid; mp 71-72 °C, yield: 93%; IR (neat) 3415, 3124, 2957, 2220, 1648, 1589, 1460, 1383, 1092 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.70 (t, *J* = 6.0 Hz, 2H), 3.85 (t, *J* = 6.0 Hz, 2H), 6.52 (dd, *J* = 3.6, 1.8 Hz, 1H), 7.20-7.28 (m, 3H), 7.38-7.45 (m, 2H), 7.58- 7.59 (m, 1H), 7.65-7.68 (m, 1H), 8.34 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.1, 61.1, 79.9, 94.4, 112.7, 117.9, 122.3, 125.2, 126.3, 128.1, 130.1, 132.7, 136.0, 142.5, 146.7, 153.7, 178.4. HRMS (ESI): calcd for $C_{17}H_{14}NaO_3$, m/z 289.0841 ($[M+Na]^+$); found, m/z 289.0833.

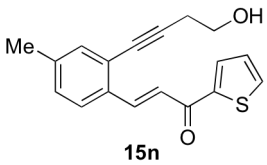
(*E*)-3-(2-(4-Hydroxybut-1-ynyl)phenyl)-1-(thiophen-2-yl)prop-2-en-1-one (15m):



15m

Pale brown solid; mp 78-79 °C, yield: 89%; IR (neat) 3483, 3071, 2921, 2225, 1640, 1579, 1515, 1409, 1335, 1221, 1059 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.54 (brs, 1H), 2.78 (t, *J* = 6.0 Hz, 2H), 3.92 (t, *J* = 6.0 Hz, 2H), 7.20 (dd, *J* = 4.8, 3.9 Hz, 1H), 7.33-7.38 (m, 2H), 7.45-7.50 (m, 2H), 7.71 (d, *J* = 4.8 Hz, 1H), 7.73-7.76 (m, 1H), 7.89 (d, *J* = 3.9 Hz, 1H), 8.41 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.6, 59.6, 78.4, 93.0, 121.3, 123.7, 124.7, 126.6, 126.8, 128.6, 130.6, 131.3, 132.7, 134.6, 141.1, 143.9, 181.0. Anal Calcd for $C_{17}H_{14}O_2S$: C, 72.31; H, 5.00; S, 11.36. Found: C, 72.15; H, 5.24; S, 11.11.

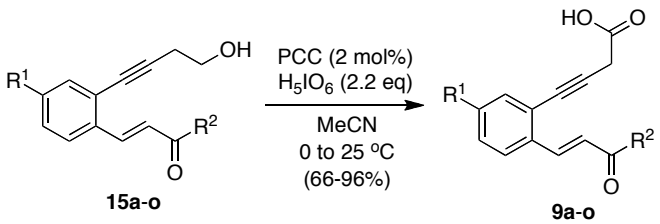
(*E*)-3-(2-(4-Hydroxybut-1-ynyl)-4-methylphenyl)-1-(thiophen-2-yl)prop-2-en-1-one (15n):



15n

Brown solid; mp 85-86 °C, yield: 97%; IR (neat) 3367, 3089, 2925, 2220, 1635, 1565, 1515, 1410, 1355, 1229, 1055 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.50 (brs, 1H), 2.77 (t, *J* = 6.0 Hz, 2H), 3.91 (t, *J* = 6.0 Hz, 2H), 7.15-7.31 (m, 3H), 7.45 (d, *J* = 15.6 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.69 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.88 (dd, *J* = 3.9, 0.9 Hz, 1H), 8.38 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 24.1, 61.1, 80.0, 94.0, 121.7, 125.2, 126.2, 128.3, 129.2, 132.0, 133.3, 133.4, 134.0, 140.6, 142.6, 145.5, 182.5. Anal Calcd for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44; S, 10.82. Found: C, 72.65; H, 5.55; S, 10.66.

5. General procedure for the periodic acid oxidation of alcohols 15: Synthesis of compounds 9a-o.[2]

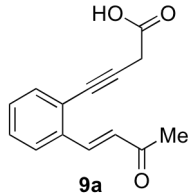


To a stirred suspension of periodic acid (4.4 mmol, 2.2 equiv) in acetonitrile (15 mL) was added alcohol **15** (2 mmol, 1 equiv) and PCC (0.04 mmol, 2 mol%) at 0 °C. The

[2] Hunsen, M. *Synthesis* **2005**, 2487

temperature was gradually raised to 25 ^{o}C and stirring was continued for further 6 h. After disappearance of the alcohol in TLC, the reaction mixture was diluted with ethyl acetate and washed once with water followed by brine and dried over anhyd. Na_2SO_4. The solvent was evaporated and the crude was purified through silica column chromatography using CH_2Cl_2 and methanol as eluent (97:3, v/v).

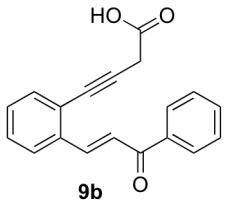
4-(2-((*E*)-3-Oxobut-1-enyl)phenyl)but-3-ynoic acid (9a):



9a

Pale yellow solid; yield: 87%; IR (neat) 3452, 2945, 2322, 1719, 1630, 1362, 1201, 1052 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.68 (s, 2H), 6.75 (d, *J* = 16.5 Hz, 1H), 7.31- 7.38 (m, 2H), 7.48-7.51 (m, 1H), 7.64-7.67 (m, 1H), 8.14 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.0, 27.1, 82.0, 87.3, 124.2, 126.3, 129.0, 129.1, 130.3, 133.2, 136.4, 142.5, 173.3, 200.3. Anal Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.35; H, 5.21.

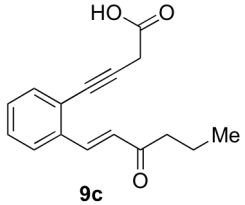
4-(2-((*E*)-3-Oxo-3-phenylprop-1-enyl)phenyl)but-3-ynoic acid (9b):



9b

Pale brown solid; mp 81-82 ^{o}C, yield: 86%; IR (neat) 3491, 2931, 2349, 1724, 1648, 1341, 1218, 1018 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.64 (s, 2H), 4.25 (brs, 1H), 7.35-7.37 (m, 2H), 7.47-7.62 (m, 5H), 7.74-7.77 (m, 1H), 7.99-8.02 (m, 2H), 8.31 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 25.3, 80.2, 85.2, 122.3, 122.7, 124.9, 127.1, 127.2, 128.5, 131.4, 131.8, 135.0, 136.6, 141.7, 171.1, 189.8. HRMS (ESI): calcd for $C_{19}H_{14}NaO_3$, m/z 313.0841 ([M+Na]$^{+}$); found, m/z 313.0832. *one aromatic carbon is merged with others.

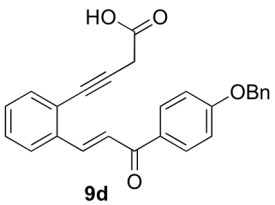
4-(2-((*E*)-3-Oxohex-1-enyl)phenyl)but-3-ynoic acid (9c):



9c

Brown viscous liquid; yield: 66%; IR (neat) 3450, 2965, 1716, 1631, 1478, 1315, 1187 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.2 Hz, 1H), 1.70 (sextet, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 3.65 (s, 2H), 6.78 (d, *J* = 16.2 Hz, 1H), 7.31-7.34 (m, 2H), 7.47-7.50 (m, 1H), 7.63-7.66 (m, 1H), 8.12 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 18.0, 26.8, 42.2, 81.5, 87.3, 124.0, 126.0, 127.8, 128.6, 129.9, 133.0, 136.2, 141.0, 172.5, 202.0. HRMS (ESI): calcd for $C_{16}H_{16}NaO_3$, m/z 279.0997 ([M+Na]$^{+}$); found, m/z 279.0989.

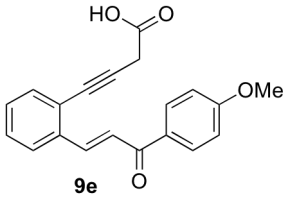
4-(2-((*E*)-3-(4-(Benzyloxy)phenyl)-3-oxoprop-1-enyl)phenyl)but-3-ynoic acid (9d):



9d

Pale yellow solid; mp 129-130 ^{o}C, yield: 90%; IR (neat) 3031, 2231, 1743, 1604, 1320, 1257, 1172 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (s, 2H), 5.07 (s, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 7.25-7.38 (m, 7H), 7.43-7.46 (m, 1H), 7.53 (d, *J* = 15.6 Hz, 1H), 7.65-7.68 (m, 1H), 7.96 (d, *J* = 8.7 Hz, 2H), 8.23 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.9, 70.3, 81.8, 87.4, 114.8, 123.7, 124.1, 126.5, 127.5, 128.3, 128.6, 128.9, 129.8, 131.3, 133.3, 136.3, 136.8, 142.4, 162.8, 172.5, 189.5. HRMS (ESI): calcd for $C_{26}H_{20}NaO_4$, m/z 419.1259 ([M+Na]$^{+}$); found, m/z 419.1248.

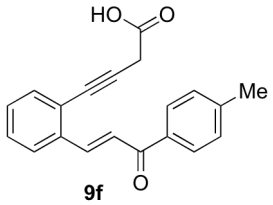
4-(2-((*E*)-3-(4-Methoxyphenyl)-3-oxoprop-1-enyl)phenyl)but-3-ynoic acid (9e):



9e

Off-white solid; mp 105-106 ^{o}C, yield: 84%; IR (neat) 3251, 2955, 2349, 1740, 1648, 1508, 1456, 1172, 1024 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.64 (s, 2H), 3.88 (s, 3H), 6.98 (d, *J* = 9.0 Hz, 2H), 7.35-7.40 (m, 2H), 7.51-7.53 (m, 1H), 7.61 (d, *J* = 15.6 Hz, 1H), 7.74-7.77 (m, 1H), 8.03 (d, *J* = 9.0 Hz, 2H), 8.31 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.8, 55.5, 81.6, 87.5, 113.9, 123.5, 124.2, 126.3, 128.5, 129.8, 130.9, 131.1, 133.2, 136.7, 142.4, 163.6, 171.9, 189.5. HRMS (ESI): calcd for $C_{20}H_{16}NaO_4$, m/z 343.0946 ([M+Na]$^{+}$); found, m/z 343.0934.

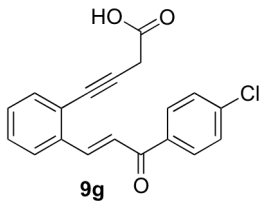
4-(2-((*E*)-3-Oxo-3-p-tolylprop-1-enyl)phenyl)but-3-ynoic acid (9f):



9f

Off-white solid; mp 129-130 ^{o}C, yield: 82%; IR (neat) 3036, 2345, 1724, 1657, 1609, 1481, 1340, 1225, 1033 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 1H), 3.70 (s, 2H), 7.28-7.77 (m, 7H), 7.95 (d, *J* = 7.5 Hz, 1H), 8.32 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 26.8, 81.7, 87.4, 123.7, 124.1, 126.4, 128.6, 128.9, 129.3, 129.9, 133.2, 135.4, 136.6, 142.7, 143.9, 172.5, 190.7. HRMS (ESI): calcd for $C_{20}H_{16}NaO_3$, m/z 327.0997 ([M+Na]$^{+}$); found, m/z 327.0986.

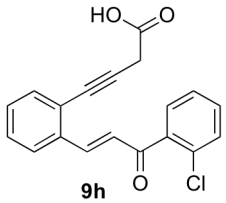
4-(2-((*E*)-3-(4-Chlorophenyl)-3-oxoprop-1-enyl)phenyl)but-3-ynoic acid (9g):



9g

Colorless solid; mp 85-86 ^{o}C, yield: 85%; IR (neat) 3504, 2928, 2351, 1731, 1653, 1592, 1339, 1223, 1093, 1011 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.66 (s, 2H), 7.37-7.54 (m, 5H), 7.58 (d, *J* = 15.9 Hz, 1H), 7.74-7.77 (m, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 8.33 (d, *J* = 15.9Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.8, 81.6, 87.5, 123.2, 124.3, 126.5, 128.6, 128.9, 130.0, 130.1, 133.3, 136.3, 136.4, 139.4, 143.6, 172.3, 189.8. HRMS (ESI): calcd for $C_{19}H_{13}ClNaO_3$, m/z 347.0451 ([M+Na]$^{+}$); found, m/z 347.0441.

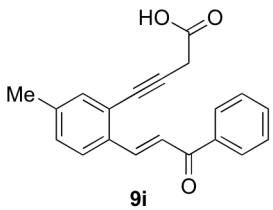
4-(2-((*E*)-3-(2-Chlorophenyl)-3-oxoprop-1-enyl)phenyl)but-3-ynoic acid (9h):



9h

Brown viscous liquid; yield: 80%; IR (neat) 3066, 2925, 2344, 1716, 1649, 1592, 1433, 1301, 1212 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.53 (s, 2H), 7.19 (d, *J* = 16.2 Hz, 1H), 7.33- 7.51 (m, 7H), 7.68-7.71 (m, 1H), 8.00 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.0, 81.4, 87.2, 124.2, 126.4, 126.8, 127.0, 127.5, 128.7, 129.5, 130.2, 130.3, 131.4, 133.0, 136.1, 139.0, 144.7, 172.0, 195.0. HRMS (ESI): calcd for $C_{19}H_{13}ClNaO_3$, m/z 347.0451 ([M+Na]$^{+}$); found, m/z 347.0439.

4-(5-Methyl-2-((*E*)-3-oxo-3-phenylprop-1-enyl)phenyl)but-3-ynoic acid (9i):

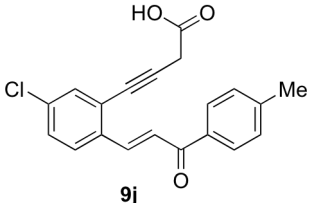


9i

Brown solid; mp 125-126 ^{o}C, yield: 96%; IR (neat) 3445, 3012, 2159, 1731, 1641, 1468, 1340, 1252, 1145 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.65 (s, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.35 (s,

1H), 7.47-7.60 (m, 4H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.99-8.02 (m, 2H), 8.30 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 21.2, 26.8, 81.8, 86.9, 122.8, 124.2, 126.4, 128.6, 128.7, 129.7, 132.8, 133.7, 138.2, 140.5, 143.3, 172.7, 191.4. Anal Calcd for $C_{20}H_{16}O_2$: C, 78.93; H, 5.30. Found: C, 78.61; H, 5.18. *one aromatic carbon is merged with others.

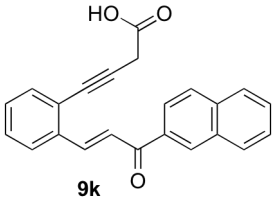
4-(2-((*E*)-3-Oxo-3-p-tolylprop-1-enyl)phenyl)but-3-ynoic acid (9j):



9i

Colorless solid; mp 135-136 ^{o}C, yield: 80%; IR (neat) 3472, 3051, 2131, 1718, 1665, 1608, 1488, 1332, 1262, 1131 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43(s, 3H), 3.64 (s, 2H), 7.28-7.35 (m, 3H), 7.50 (d, *J* = 2.1 Hz, 1H), 7.58 (d, *J* = 15.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 8.25 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6, 25.6, 79.5, 87.5, 122.8, 124.5, 126.4, 127.7, 127.8, 128.3, 131.7, 134.1, 134.2, 134.6, 140.2, 142.9, 170.9, 189.2. Anal Calcd for $C_{20}H_{15}ClO_3$: C, 70.90; H, 4.46; Cl. Found: C, 70.61; H, 4.35

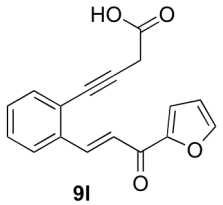
4-(2-((*E*)-3-(Naphthalene-2-yl)-3-oxoprop-1-enyl)phenyl)but-3-ynoic acid (9k):



9k

Brown solid; mp 74-75 ^{o}C, yield: 91%; IR (neat) 3502, 3032, 2113, 1729, 1657, 1625, 1601, 1474, 1357, 1266, 1173 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60 (s, 2H), 7.32-7.40 (m, 2H), 7.51-7.62 (m, 3H), 7.73 (d, *J* = 15.9 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.85-7.91 (m, 2H), 7.97 (d, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 15.9 Hz, 1H), 8.51 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.0, 80.7, 86.9, 122.6, 123.4, 123.6, 125.5, 125.9, 126.9, 127.5, 127.6, 127.7, 128.6, 129.0, 129.4, 131.6, 132.3, 134.4, 134.6, 135.6, 142.3, 172.0, 190.0. Anal Calcd for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74. Found: C, 80.85; H, 4.65.

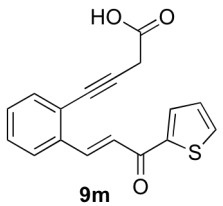
4-(2-((*E*)-3-(Furan-2-yl)-3-oxoprop-1-enyl)phenyl)but-3-ynoic acid (9l):



9l

Brown gummy solid; yield: 78%; IR (neat) 3450, 2928, 2340, 1716, 1648, 1597, 1460, 1334, 1087 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.66 (s, 2H), 6.60 (dd, *J* = 3.3, 1.5 Hz, 1H), 7.32-7.39 (m, 3H), 7.50-7.56 (m, 2H), 7.65- 7.66 (m, 1H), 7.75-7.77 (m, 1H), 8.41 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.7, 82.0, 87.7, 112.7, 118.0, 122.8, 124.5, 126.4, 128.5, 130.0, 133.1, 136.4, 142.3, 146.8, 153.7, 171.3, 178.7. HRMS (ESI): calcd for $C_{17}H_{12}NaO_4$, m/z 303.0633 ($[M+Na]^+$); found, m/z 303.0624.

4-(2-((*E*)-3-Oxo-3-(thiophen-2-yl)prop-1-enyl)phenyl)but-3-ynoic acid (9m):

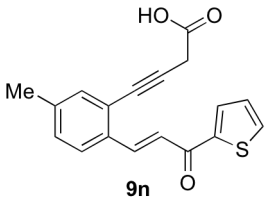


9m

Brown solid; mp 179-180 ^{o}C, yield: 93%; IR (neat) 3394, 3079, 2341, 1724, 1696, 1642, 1478, 1411, 1294, 1213, 1063 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.59 (s, 2H), 7.20 (dd, *J* = 4.5, 3.9 Hz, 1H), 7.31-7.39 (m, 2H), 7.52-7.57 (m, 2H), 7.69-7.74 (m, 2H), 7.90 (d, *J* = 3.9 Hz, 1H), 8.30 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.9, 81.1, 88.6, 123.3,

124.3, 124.6, 128.3, 128.4, 129.9, 132.1, 133.4, 133.9, 136.1, 142.1, 145.4, 170.0, 181.3. Anal Calcd for $C_{17}H_{12}O_3S$: C, 68.90; H, 4.08; S, 10.82. Found: C, 68.61; H, 4.00; S, 10.58.

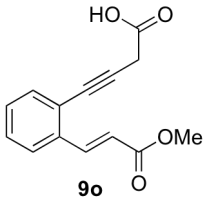
4-(5-Methyl-2-((*E*)-3-oxo-3-(thiophen-2-yl)prop-1-enyl)phenyl)but-3-ynoic acid (9n):



9n

Brown solid; mp 179-180 ^{o}C, yield: 77%; IR (neat) 2900, 2678, 1732, 1629, 1545, 1409, 1354, 1273, 1179 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.58 (s, 2H), 7.16-7.22 (m, 3H), 7.37 (s, 1H), 7.54 (d, *J* = 15.6 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.70 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.89 (dd, *J* = 3.9, 0.9 Hz, 1H), 8.27 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 26.9, 81.1, 88.2, 122.3, 124.2, 126.6, 128.3, 129.4, 132.0, 133.2, 133.8, 133.9, 140.3, 142.0, 145.5, 169.9, 182.3. Anal Calcd for $C_{18}H_{14}O_3S$: C, 69.66; H, 4.55; S, 10.33. Found: C, 69.39; H, 4.49; S, 10.11.

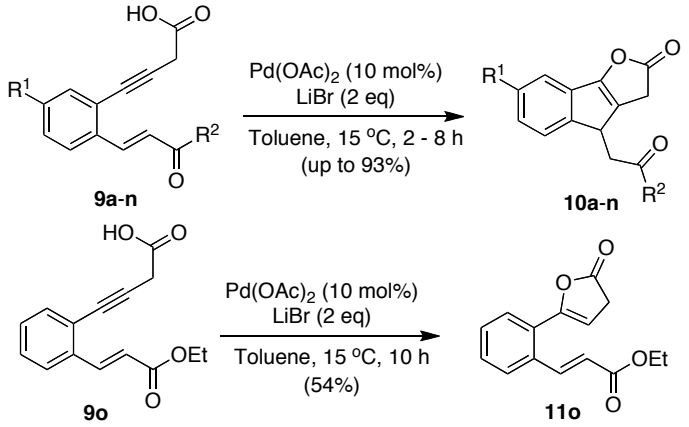
4-(2-((*E*)-2-(4-Methoxycarbonyl)vinyl)phenyl)but-3-ynoic acid (9o):



9o

Brown solid; 113-114 ^{o}C, yield: 94%; IR (neat) 2950, 2106, 1704, 1637, 1432, 1320, 1267, 1169, 1016 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.69 (s, 2H), 3.83 (s, 3H), 6.57 (d, *J* = 15.9 Hz, 1H), 7.33-7.36 (m, 2H), 7.50-7.52 (m, 1H), 7.62-7.64 (m, 1H), 8.23 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.8, 51.9, 81.7, 86.9, 119.4, 123.6, 126.3, 128.6, 129.7, 133.1, 130.0, 142.8, 167.7, 173.2. Anal Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.63; H, 4.91.

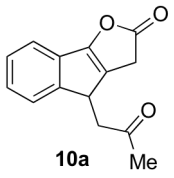
6. General procedure for the palladium-catalyzed intramolecular carboxypalladation-olefin insertion cascade: Synthesis of compounds 10a-n and 11o



To a stirred solution of acid **9** (0.5 mmol, 1 equiv) in toluene (3 mL) at 0 ^{o}C under nitrogen atmosphere were added $Pd(OAc)_2$ (0.05 mmol, 10 mol%) and LiBr (1 mmol, 2 equiv). The reaction mixture was stirred at 15 ^{o}C for 2-8 h. After completion of the reaction, as indicated by TLC, the reaction mixture was directly poured onto silica

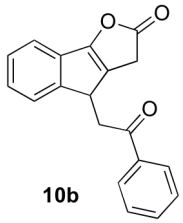
column and purified using petroleum ether-ethyl acetate mixture (95:5, v/v) as eluent to afford the pure products.

4-(2-Oxopropyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10a):



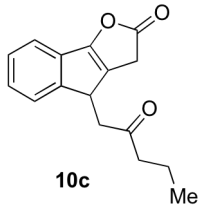
Colorless solid; mp 104 ^{o}C, yield: 93%; IR (neat) 3066, 2910, 1801, 1640, 1596, 1421, 1230, 1061 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.21 (s, 3H), 2.50 (dd, *J* = 18.3, 9.6 Hz, 1H), 3.12 (dd, *J* = 18.3, 4.8 Hz, 1H), 3.41 (d, *J* = 24.6 Hz, 1H), 3.63 (dd, *J* = 24.6, 1.5 Hz, 1H), 3.91 (dd, *J* = 9.6, 4.8 Hz, 1H), 7.27- 7.41 (m, 4H); ^{13}C NMR (75MHz, $CDCl_3$): δ 30.1, 35.1, 39.7, 44.8, 117.9, 122.1, 123.7, 126.3, 127.3, 132.2, 147.6, 157.2, 177.8, 206.5 Anal Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.39; H, 5.21.

4-(2-Oxo-2-phenylethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10b):



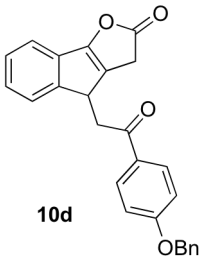
Colorless solid; mp 124-125 ^{o}C, yield: 78%; IR (neat) 3086, 2887, 1805, 1679, 1596, 1398, 1227, 1064 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.02 (dd, *J* = 18.0, 10.5 Hz, 1H), 3.40 (d, *J* = 24.6 Hz, 1H), 3.64 -3.73 (m, 2H), 4.13 (dd, J = 10.5, 4.8 Hz, 1H), 7.29-7.41 (m, 3H), 7.47-7.52 (m, 3H), 7.58-7.63 (m, 1H) 7.95-7.98 (m, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ 35.3, 40.1, 40.3, 118.0, 122.5, 123.9, 126.4, 127.4, 128.1, 128.8, 132.4, 133.7, 136.4, 147.9, 157.2, 177.9, 198.1. HRMS (ESI): calcd for $C_{19}H_{14}NaO_3$, m/z 313.0841 ([M+Na]$^{+}$); found, m/z 313.0835.

4-(2-Oxopentyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10c):



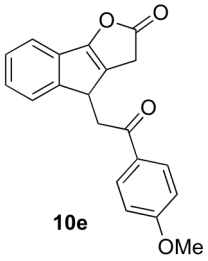
Yellow liquid; yield: 60%; IR (neat) 3043, 2918, 1810, 1672, 1426, 1131, 1051 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.5 Hz, 3H), 1.69-1.74 (m, 2H), 2.34-2.50 (m, 3H), 3.10 (dd, *J* = 18.0, 5.4 Hz, 1H), 3.38 (d, *J* = 24.6 Hz, 1H), 3.61 (dd, *J* = 24.6, 1.8 Hz, 1H), 3.93 (dd, *J* = 9.9, 5.4 Hz, 1H), 7.24-7.40 (m, 4H); ^{13}C NMR (75MHz, $CDCl_3$): 13.7, 17.3, 35.1, 38.7, 43.8, 44.8, 117.9, 122.2, 123.8, 126.3, 127.3, 128.8, 132.3, 147.8, 157.1, 177.9, 209.0. HRMS (ESI): calcd for $C_{16}H_{16}NaO_3$, m/z 279.0997 ([M+Na]$^{+}$); found, m/z 279.0992.

4-(2-(4-(Benzyloxy)phenyl)-2-oxoethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10d):



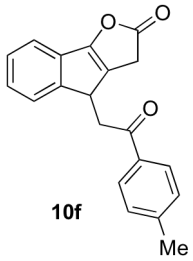
Colorless solid; mp 166-167 ^{o}C, yield: 90%; IR (neat) 3062, 2900, 1808, 1682, 1396, 1122, 1038 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.95 (dd, *J* = 17.4, 10.2 Hz, 1H), 3.38 (d, *J* = 24.9 Hz, 1H), 3.56 -3.71 (m, 2H), 4.12 (dd, *J* = 10.2, 4.5 Hz, 1H), 5.14 (S, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 7.28-7.48 (m, 9H), 7.94 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ 33.8, 38.4, 38.7, 68.7, 113.3, 116.5, 121.2, 122.4, 124.8, 125.9, 126.0, 126.8, 127.2, 128.2, 128.9, 130.9, 134.5, 146.5, 155.6, 161.5, 176.4, 195.0 HRMS (ESI): calcd for $C_{26}H_{20}NaO_4$, m/z 419.1259 ([M+Na]$^{+}$); found, m/z 419.1252.

4-(2-(4-Methoxyphenyl)-2-oxoethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10e):



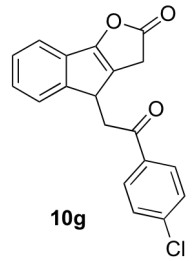
Colorless solid; mp 137-138 ^{o}C, yield: 87%; IR (neat) 3060, 2899, 1797, 1677, 1596, 1392, 1225, 1167, 1038 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.96 (dd, *J* = 17.7, 10.5 Hz, 1H), 3.39 (d, *J* = 24.9 Hz, 1H), 3.57-3.71 (m, 2H), 3.88 (s, 3H), 4.12 (dd, *J* = 10.5, 4.5 Hz, 1H) 6.95 (d, *J* = 8.7 Hz, 2H), 7.29-7.40 (m, 3H), 7.48 (d, *J* = 6.9 Hz, 1H), 7.95(d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 35.3, 39.9, 40.2, 55.6, 114.0, 117.9, 122.7, 123.9, 126.3, 127.4, 129.5, 130.4, 132.4, 148.0, 157.1, 163.9, 178.0, 196.5. HRMS (ESI): calcd for $C_{20}H_{16}NaO_4$, m/z 343.0946 ($[M+Na]^+$); found, m/z 343.0942.

4-(2-Oxo-2-*p*-tolylethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10f):



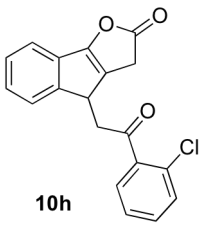
Colorless solid; mp 113-114 ^{o}C, yield: 80%; IR (neat) 3048, 1788, 1669, 1606, 1389, 1341, 1229, 1182, 1069 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H), 2.98 (dd, *J* = 17.7, 10.5 Hz, 1H), 3.39 (d, *J* = 25.2 Hz, 1H), 3.60-3.72 (m, 2H), 4.13 (dd, *J* = 10.5, 4.5 Hz, 1H) 7.29-7.33 (m, 3H), 7.35-7.41 (m, 2H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.86(d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 21.7, 35.3, 40.1, 40.2, 117.8, 122.6, 123.9, 126.3, 127.4, 128.2, 129.5, 132.4, 133.9, 144.6, 148.0, 157.1, 177.9, 197.7. Anal Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.63; H, 5.30.

4-(2-(4-Chlorophenyl)-2-oxoethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10g):



Colorless solid; mp 167-168 ^{o}C, yield: 76%; IR (neat) 2935, 1801, 1665, 1465, 1232, 1165 cm-1; 1H NMR (300 MHz, $CDCl_3$): δ 2.98 (dd, *J* = 17.7, 10.2 Hz, 1H), 3.39 (d, *J* = 24.6 Hz, 1H), 3.64 (dd, *J* = 17.7, 4.8 Hz, 1H), 3.68 (dd, *J* = 24.6, 1.8 Hz, 1H), 4.12 (dd, *J* = 10.2, 4.8 Hz, 1H) 7.29-7.41 (m, 3H), 7.45-7.48 (m, 3H), 7.89-7.92 (d, *J* = 8.7Hz, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 35.3, 39.9, 40.3, 118.1, 122.3, 123.9, 126.4, 127.5, 129.2, 129.5, 132.3, 134.7, 140.2, 147.7, 157.3, 177.8, 196.8. Anal Calcd for $C_{19}H_{13}ClO_3$: C, 70.27; H, 4.03. Found: C, 69.98; H, 3.93.

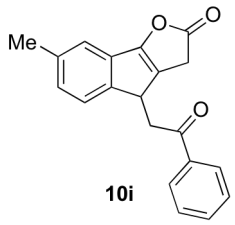
4-(2-(2-Chlorophenyl)-2-oxoethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10h):



Yellow gummy solid; yield: 64%; IR (neat) 2919, 1796, 1704, 1587, 1467, 1431, 1258 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.03 (dd, *J* = 18.0, 10.2 Hz, 1H), 3.49 (d, *J* = 24.3 Hz, 1H), 3.60 -3.73 (m, 2H), 4.11 (dd, *J* = 10.2, 4.5 Hz, 1H), 7.28-7.50 (m, 8H); ^{13}C NMR (75MHz, $CDCl_3$)*: δ 34.2, 39.2, 43.3,

117.0, 120.9, 122.8, 125.4, 126.1, 126.4, 128.0, 129.8, 130.1, 131.3, 137.5, 146.4, 156.3, 176.8, 200.2. Anal Calcd for $C_{19}H_{13}ClO_3$: C, 70.27; H, 4.03. Found: C, 69.99; H, 3.92. *One aromatic carbon is merged with others.

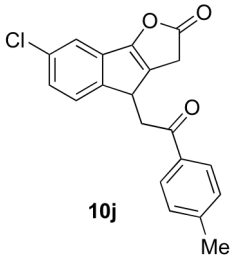
7-Methyl-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10i):



10i

Colorless solid; mp 144-145 ^{o}C, yield: 81%; IR (neat) 2917, 1811, 1676, 1446, 1375, 1222, 1185 cm-1; 1H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H) 2.99 (dd, *J* = 18.0, 10.5 Hz, 1H), 3.38 (d, *J* = 24.6 Hz, 1H), 3.60 - 3.71 (m, 2H), 4.09 (dd, *J* = 10.5, 4.8 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.21 (s, 1H), 7.35 (d, *J* = 7.8 Hz, 1H) 7.46-7.51 (m, 2H) 7.60 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.95-7.97 (m, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 21.4, 35.3, 39.8, 40.4, 118.7, 122.6, 123.5, 127.0, 128.0, 128.8, 132.5, 133.6, 136.4, 137.3, 145.0, 157.1, 178.0, 198.2. Anal Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.72; H, 5.21.

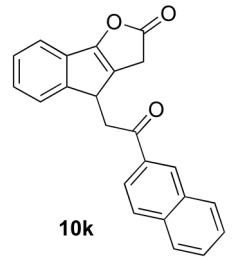
7-Chloro-4-(2-oxo-2-*p*-tolylethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10j):



10j

Yellow solid; mp 89-90 ^{o}C, yield: 60%; IR (neat) 2922, 1802, 1694, 1572, 1455, 1223 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H), 2.99 (dd, *J* = 18.0, 10.2 Hz, 1H), 3.40 (d, *J* = 24.6 Hz, 1H), 3.58 (dd, *J* = 18.0, 5.1 Hz, 1H), 3.68 (d, *J* = 24.6 Hz, 1H), 4.12 (dd, *J* = 10.2, 5.1 Hz, 1H), 7.25- 7.30 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ 21.7, 35.3, 39.9, 40.0, 118.4, 124.5, 124.8, 126.1, 128.2, 129.5, 133.5, 133.8, 133.9, 144.7, 146.2, 156.1, 177.3, 197.3. Anal Calcd for $C_{20}H_{15}ClO_3$: C, 70.90; H, 4.46. Found: C, 70.61; H, 4.35.

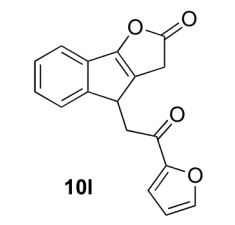
4-(2-(Naphthalen-2-yl)-2-oxoethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10k):



10k

Colorless solid; mp 114-115 ^{o}C, yield: 80%; IR (neat) 2917, 1792, 1663, 1602, 1391, 1267, 1172, 1036 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$): δ 3.17 (dd, *J* = 17.7, 10.5 Hz, 1H), 3.43 (d, *J* = 24.6 Hz, 1H), 3.71 (d, *J* = 24.6 Hz, 1H), 3.80 (dd, *J* = 17.7, 4.5 Hz, 1H), 4.20 (dd, *J* = 10.5, 4.5 Hz, 1H), 7.29-7.43 (m, 3H), 7.52-7.65 (m, 3H), 7.89-7.95 (m, 3H) 8.05 (dd, *J* = 8.4, 1.5 Hz, 1H), 8.46 (s, 1H); ^{13}C NMR (75MHz, $CDCl_3$): δ 35.4, 40.3, 40.5, 118.2, 122.7, 123.7, 124.1, 126.5, 127.2, 127.6, 128.0, 128.9, 129.0, 129.7, 130.1, 132.5, 132.6, 133.8, 135.9, 148.1, 157.4, 178.1, 198.2. HRMS (ESI): calcd for $C_{23}H_{16}NaO_3$, m/z 363.0997 ($[M+Na]^+$); found, m/z 363.0992.

4-(2-(Furan-2-yl)-2-oxoethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10l):

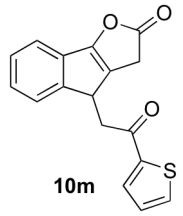


10l

Colorless solid; mp 111-112 ^{o}C, yield: 60%; IR (neat) 3011, 1810, 1701, 1633, 1341, 1177, 1043 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.89 (dd, *J* = 17.4, 10.2

Hz, 1H), 3.42 (d, *J* = 24.9 Hz, 1H), 3.52 (dd, *J* = 17.4, 5.1 Hz, 1H), 3.64 (dd, *J* = 24.9, 1.8 Hz, 1H), 4.09 (dd, *J* = 10.2, 5.1 Hz, 1H) 6.57 (dd, *J* = 3.6, 1.8 Hz, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.29-7.40 (m, 3H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 0.9 Hz, 1H); ^{13}C NMR (75MHz, $CDCl_3$): δ 35.1, 39.8, 39.9, 112.5, 117.6, 118.0, 122.1, 123.9, 126.4, 127.4, 132.3, 146.8, 147.7, 152.3, 157.3, 177.8, 187.2. Anal Calcd for $C_{17}H_{12}O_4$: C, 72.85; H, 4.32. Found: C, 72.52; H, 4.21.

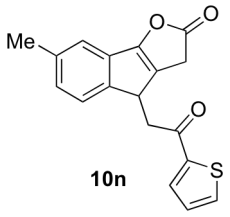
4-(2-Oxo-2-(thiophen-2-yl)ethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10m):



10m

Colorless solid; mp 145-146 ^{o}C, yield: 67%; IR (neat) 3106, 2921, 1792, 1722, 1657, 1414, 1387, 1229 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.95 (dd, *J* = 17.1, 10.2 Hz, 1H), 3.42 (d, *J* = 24.0 Hz, 1H), 3.55-3.70 (m, 2H), 4.12 (dd, *J* = 10.2, 5.1 Hz, 1H), 7.15 (t, *J* = 4.5, 1H), 7.30-7.41 (m, 3H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.69-7.71 (m, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 34.2, 39.2, 39.8, 117.1, 121.3, 123.0, 125.5, 126.6, 127.5, 131.3, 131.4, 133.4, 142.6, 146.7, 156.3, 176.9, 190.0. Anal Calcd for $C_{17}H_{12}O_3S$: C, 68.90; H, 4.08; S, 10.82. Found: C, 68.62; H, 4.04; S, 10.65.

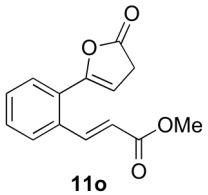
7-Methyl-4-(2-oxo-2-(thiophen-2-yl)ethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10n):



10n

Brown solid; mp 119-120 ^{o}C, yield: 55%; IR (neat) 3093, 2918, 1794, 1718, 1660, 1413, 1228 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H) 2.93 (dd, *J* = 17.1, 10.2 Hz, 1H), 3.40 (d, *J* = 24.6 Hz, 1H), 3.52 - 3.67 (m, 2H), 4.07 (dd, *J* = 10.2, 4.8 Hz, 1H), 7.09-7.16 (m, 2H), 7.21 (s, 1H), 7.34 (d, *J* = 7.8 Hz, 1H) 7.68-7.70 (m, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 19.7, 33.4, 38.1, 39.2, 117.0, 120.6, 121.8, 125.3, 126.6, 130.5, 132.5, 135.7, 141.8, 143.0, 155.5, 176.2, 189.3. Anal Calcd for $C_{18}H_{14}O_3S$: C, 69.66; H, 4.55; S, 10.33. Found: C, 69.34; H, 4.42; S, 10.09.

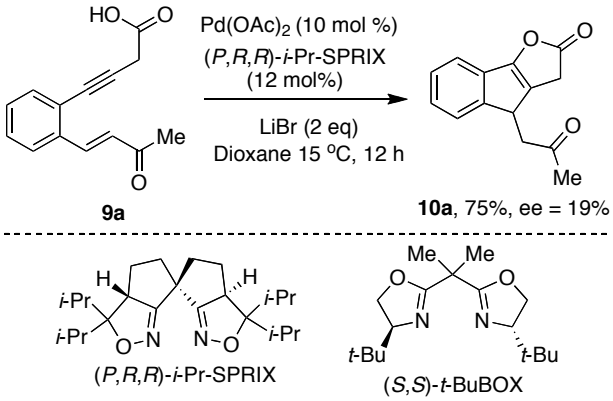
(*E*)-Methyl 3-(2-(5-oxo-4,5-dihydrofuran-2-yl)phenyl)acrylate (11o):



11o

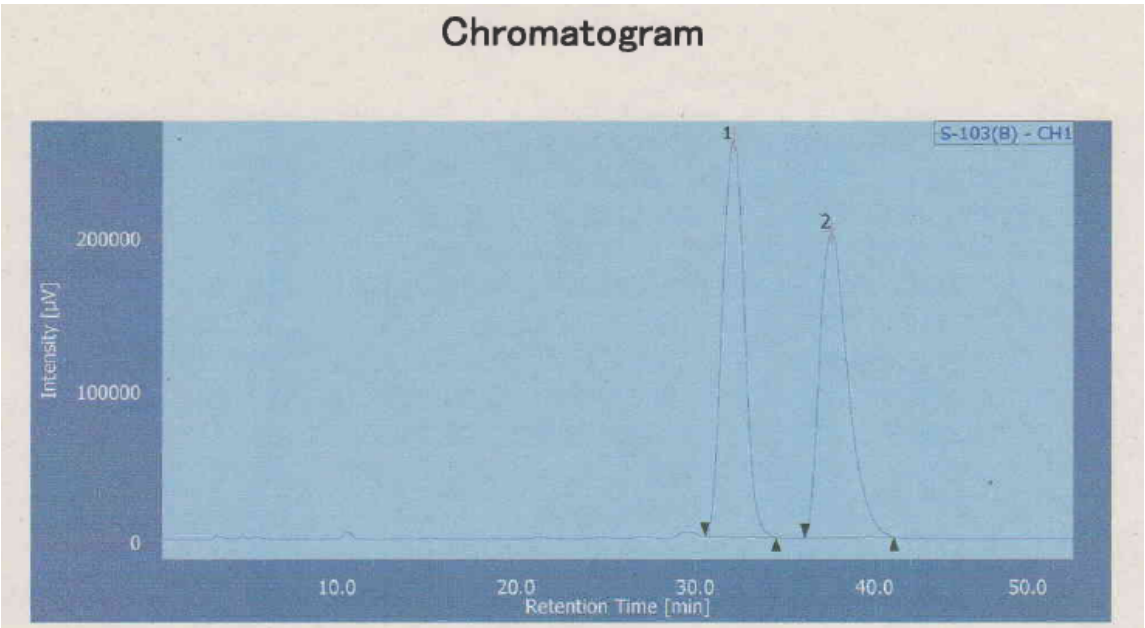
Off-white solid; mp 94-95^{o}C, yield: 54%; IR (neat) 2914, 2117, 1782, 1706, 1634, 1433, 1321, 1170 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.50 (d, *J* = 2.4 Hz, 2H), 3.83 (s, 3H), 5.56 (t, *J* = 2.4 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 7.43-7.49 (m, 2H), 7.58-7.67 (m, 2H), 8.04 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 35.1, 51.9, 105.1, 120.6, 127.7, 127.9, 128.5, 129.8, 129.9, 133.3, 142.9, 152.0, 167.0, 175.3. Anal Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.66; H, 5.06.

7. Attempts to enantioselective synthesis of compound 10a.



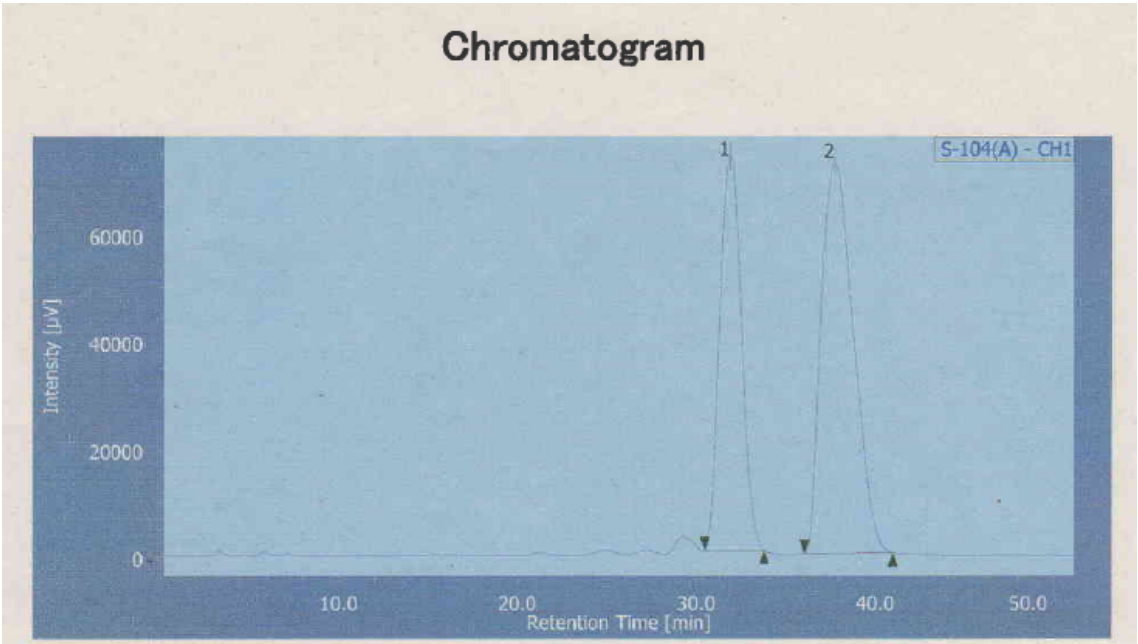
A mixture of $Pd(OAc)_2$ (0.05 mmol, 10 mol%) and (*P*,*R*,*R*)-*i*-Pr-SPRIX (0.06 mmol, 12 mol%) in dioxane (0.2 M) was stirred at 15 °C for 1 h under nitrogen atmosphere. To this *in situ* generated Pd(II)-SPRIX complex, acid **9a** (0.5 mmol 1 equiv) and LiBr (1 mmol, 2 equiv) were added and stirring was continued until completion of the reaction (12 h). Then the mixture was filtered through a pad of silica and purified through silica column chromatography using petroleum ether-ethyl acetate mixture (95:5, v/v) as eluent. The enantiomeric excess (19%) was determined by HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 98/2, flow rate: 1 mL/min, 254 nm, major enantiomer: t_R = 37.7 min, minor enantiomer: t_R = 31.9 min). No enantioselectivity was observed in case of Pd(II)-(*S*,*S*)-*t*-BuBOX complex.

HPLC of racemic 10a:



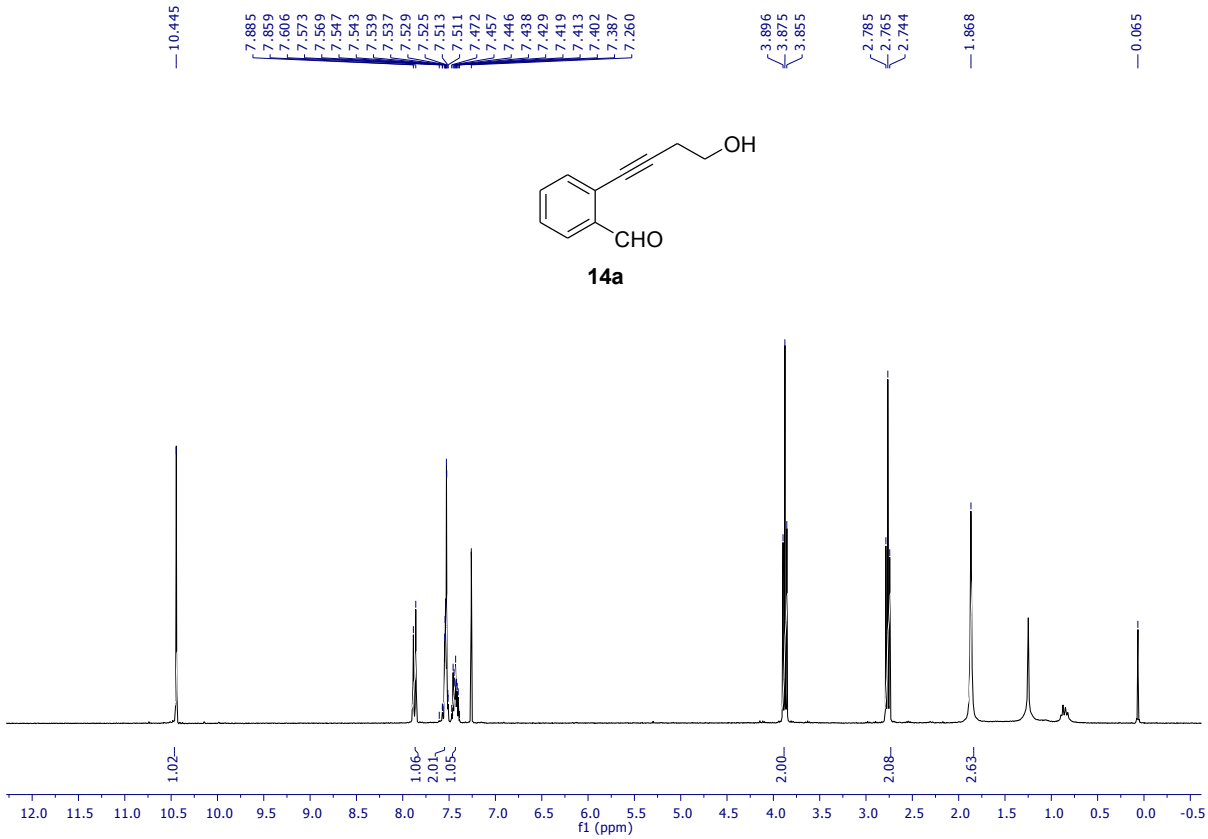
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	32.100	22286161	261556	50.327	56.576	N/A	3074	2.118	1.093	
2	Unknown	1	37.583	21996331	200752	49.673	43.424	N/A	2723	N/A	1.483	

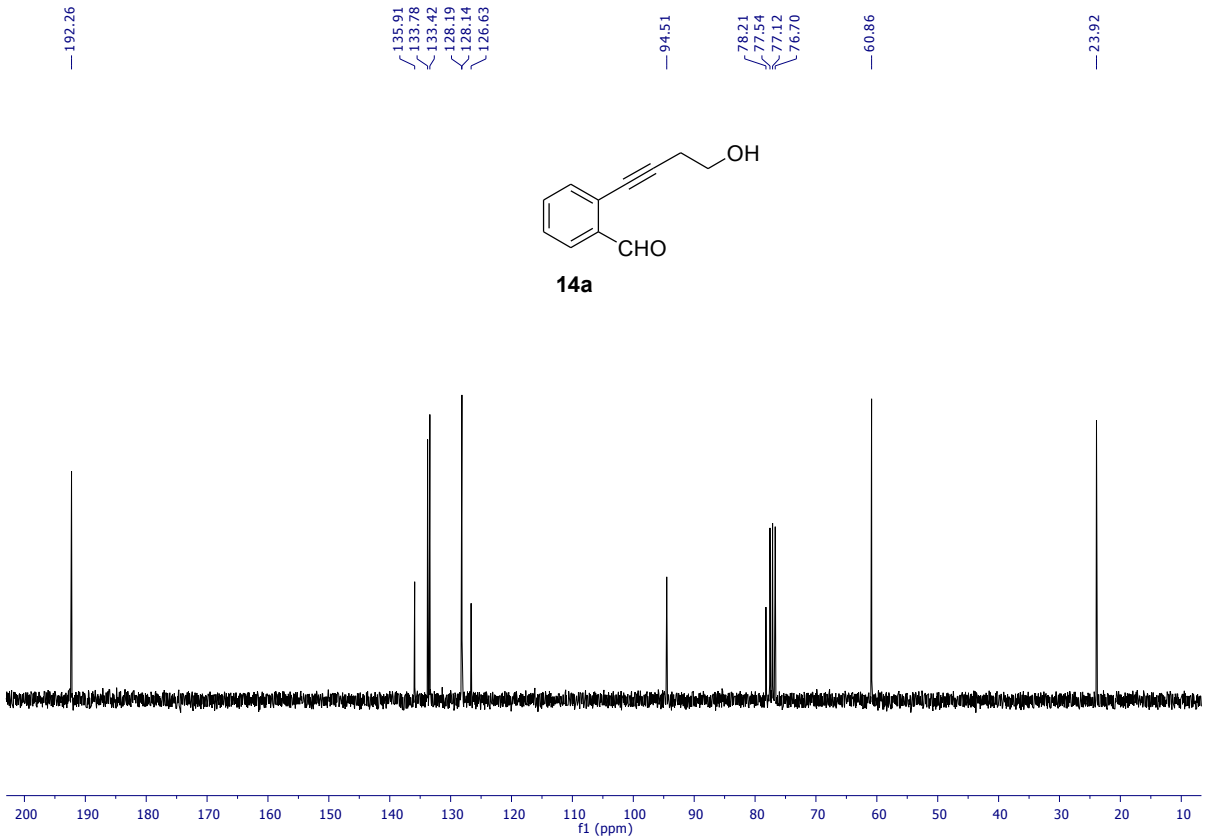
HPLC of 10a obtained from Scheme 3:

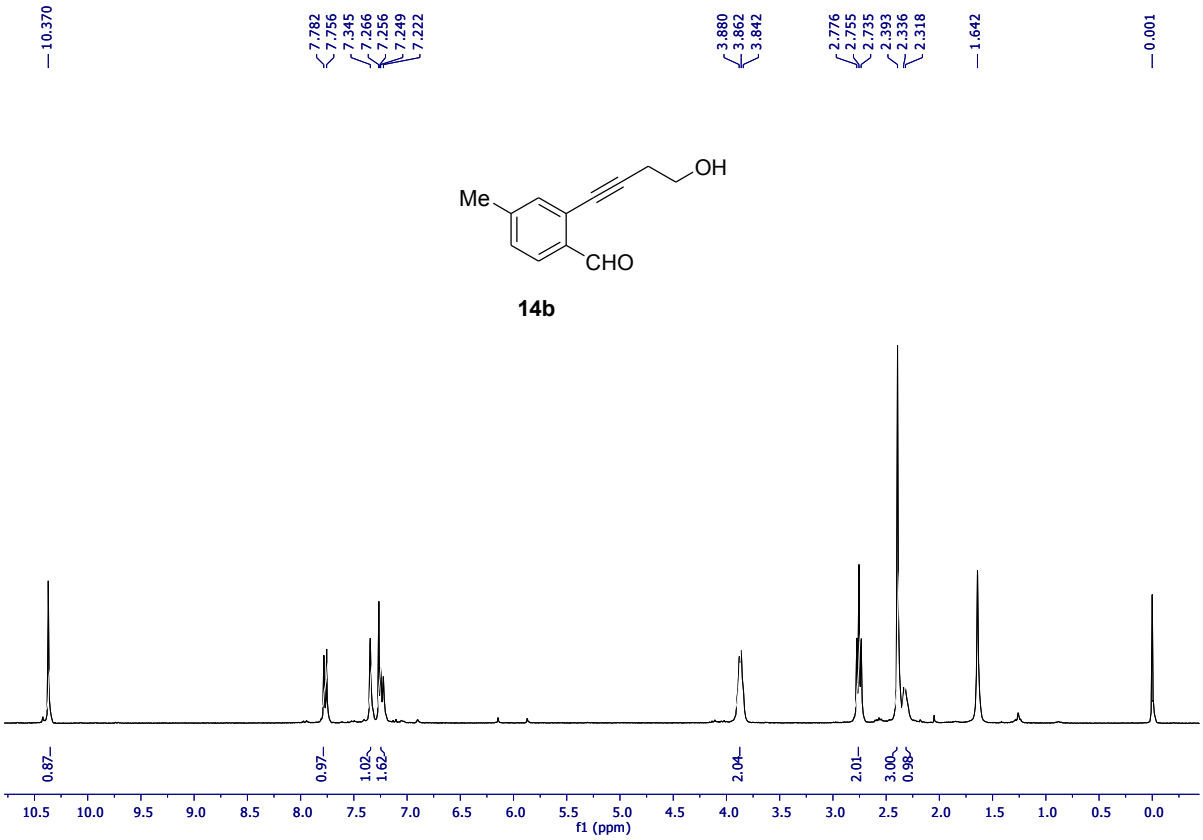


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	31.900	6177495	73231	40.643	50.201	N/A	3037	2.028	1.119	
2	Unknown	1	37.733	9021795	72644	59.357	49.799	N/A	1912	N/A	1.356	

^{1}H and ^{13}C NMR Spectra of compounds:



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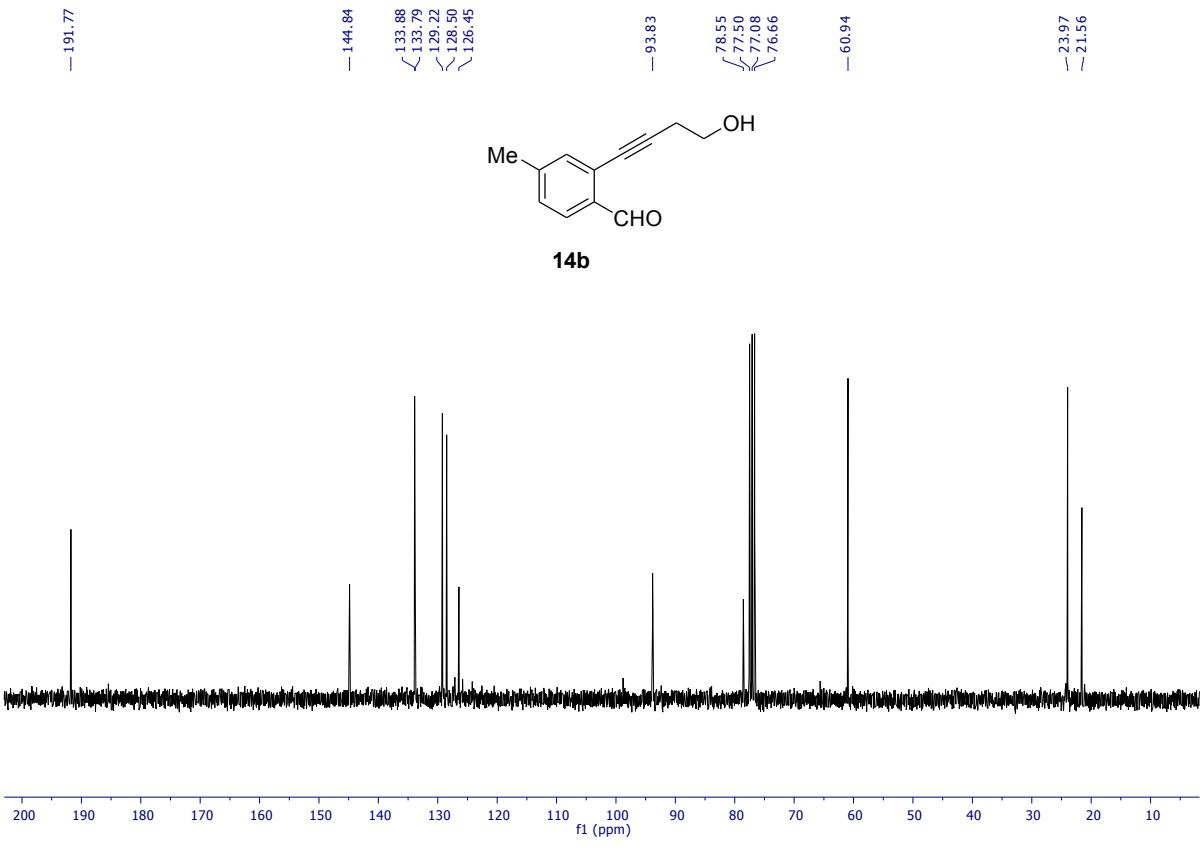
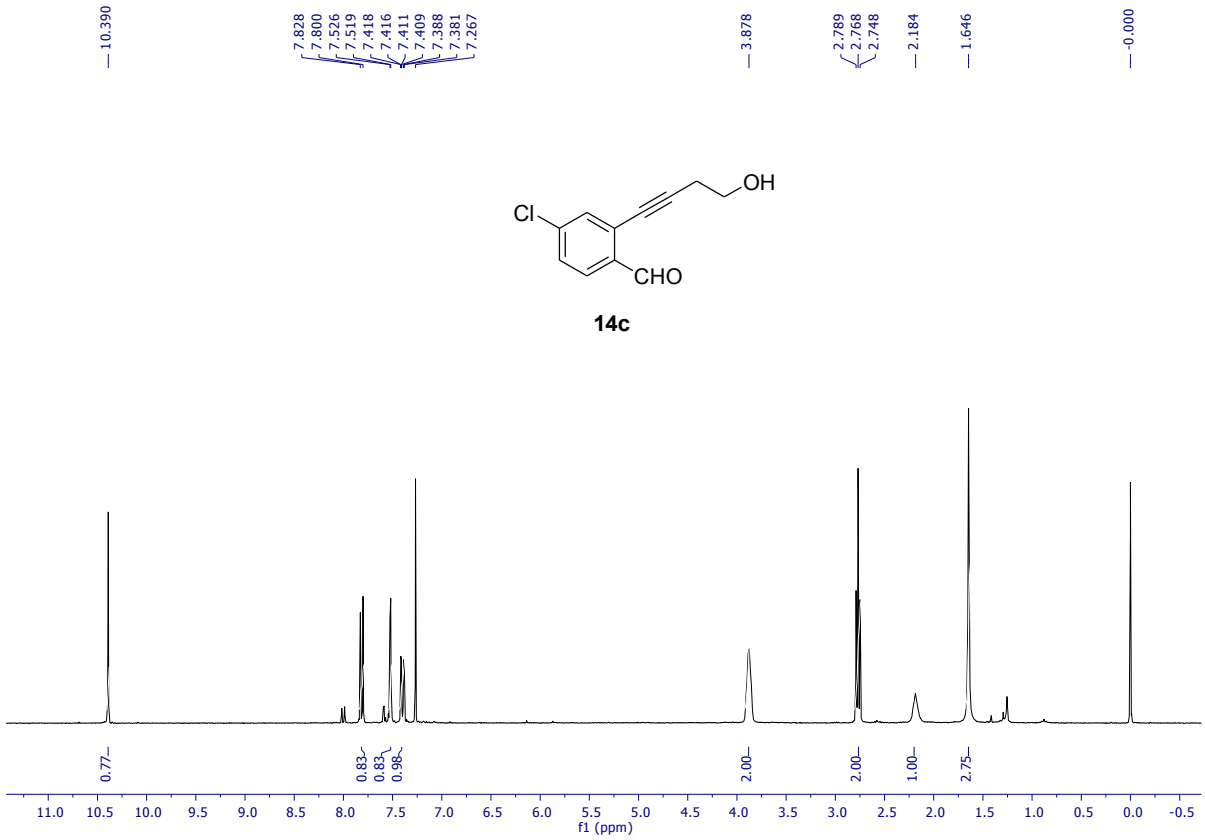
7.756
7.345
7.266
7.256
7.249
7.222
3.880
3.862
3.842
2.776
2.755
2.735
2.393
2.336
2.318
1.642
0.001
OH
Me
CHO
0.87
0.97
1.02
1.62
2.04
2.01
3.00
0.98
f1 (ppm)

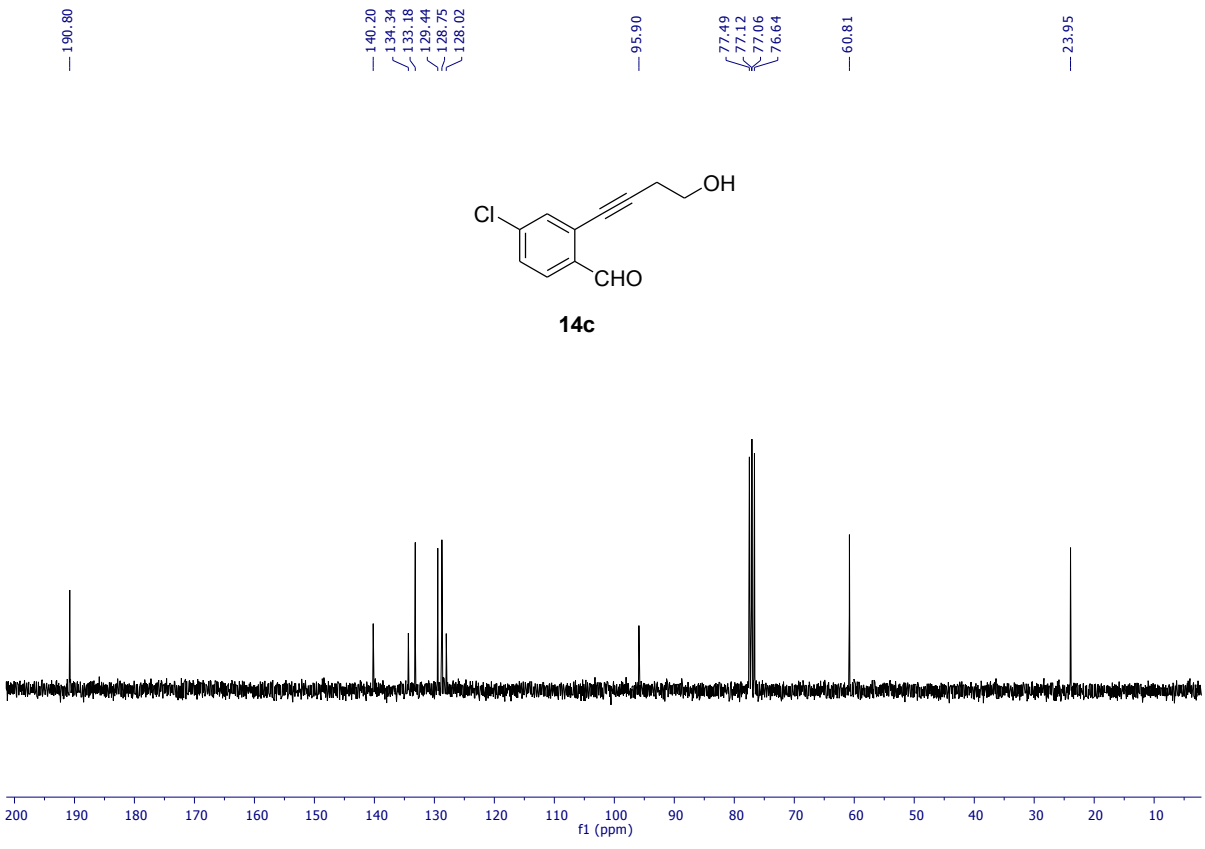
14b


191.77
144.84
133.88
133.79
129.22
128.50
126.45
93.83
78.55
77.50
77.08
76.66
60.94
23.97
21.56
OH
Me
CHO
f1 (ppm)

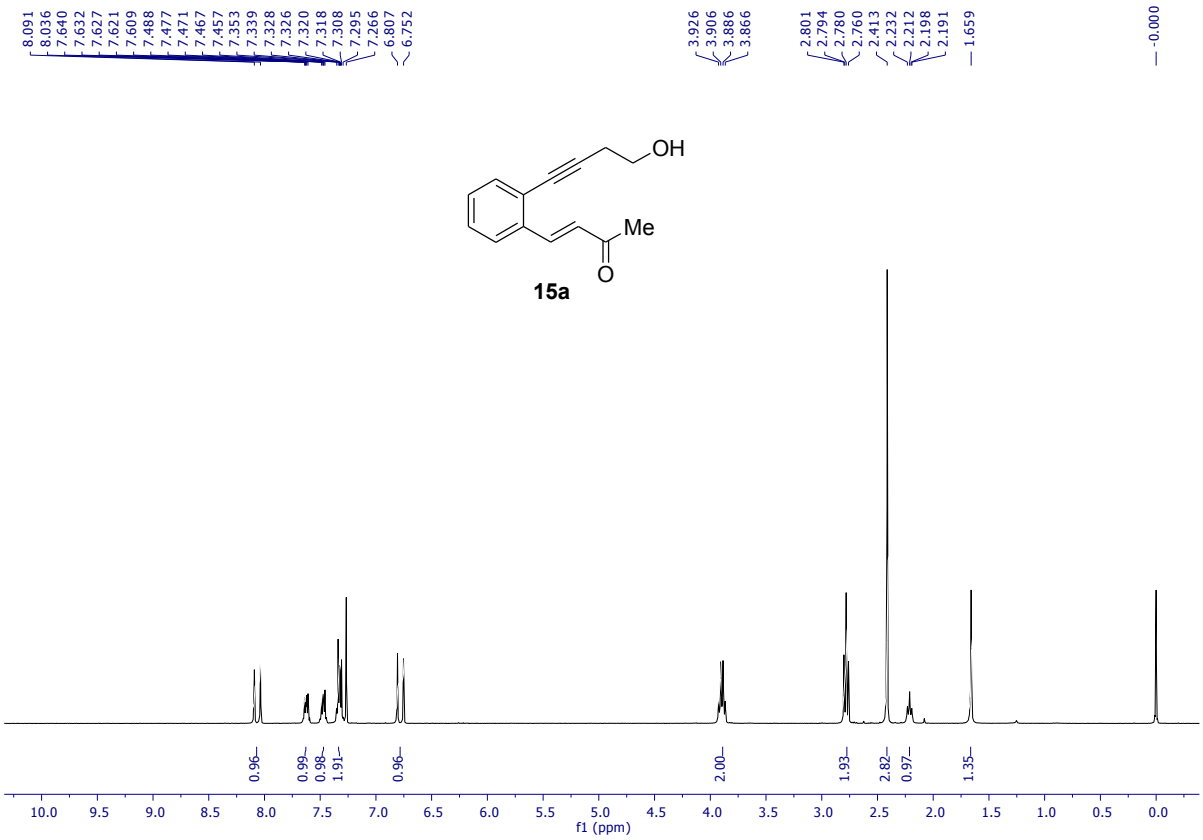
14b


10.390
7.828
7.800
7.526
7.519
7.418
7.416
7.411
7.409
7.388
7.381
7.267
3.878
2.789
2.768
2.748
2.184
1.646
-0.000
Cl
OH
CHO
0.77
0.83
0.83
0.98
2.00
2.00
1.00
2.75
f1 (ppm)

14c


190.80
140.20
134.34
133.18
129.44
128.75
128.02
95.90
77.49
77.12
77.06
76.64
60.81
23.95
Cl
OH
CHO
f1 (ppm)

14c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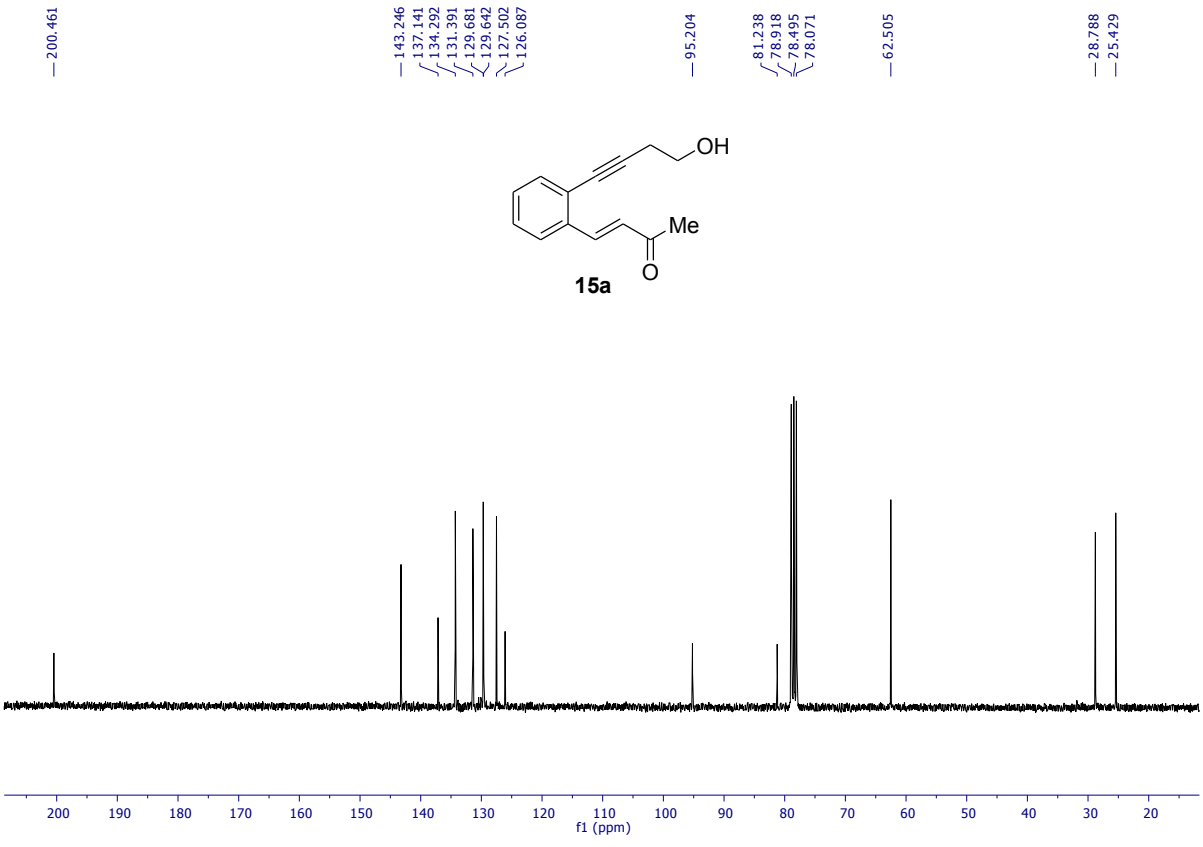
8.036
7.640
7.632
7.627
7.621
7.609
7.488
7.477
7.471
7.467
7.457
7.353
7.339
7.328
7.326
7.320
7.318
7.308
7.295
7.266
6.807
6.752
3.926
3.906
3.886
3.866
2.801
2.794
2.780
2.760
2.413
2.232
2.212
2.198
2.191
1.659
-0.000
OH
Me
O
15a
0.96
0.99
0.98
1.91
0.96
2.00
1.93
2.82
0.97
1.35
f1 (ppm)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137.141
134.292
131.391
129.681
129.642
127.502
126.087
95.204
81.238
78.918
78.495
78.071
62.505
28.788
25.429
OH
Me
O
15a
f1 (ppm)


8.309
8.256
7.974
7.970
7.965
7.947
7.942
7.709
7.695
7.684
7.680
7.672
7.664
7.652
7.557
7.553
7.548
7.538
7.529
7.520
7.509
7.504
7.499
7.476
7.465
7.459
7.444
7.439
7.425
7.416
7.411
7.406
7.395
7.381
7.302
7.297
7.286
7.277
7.272
7.268
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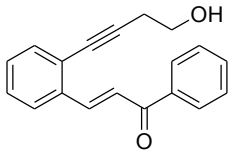
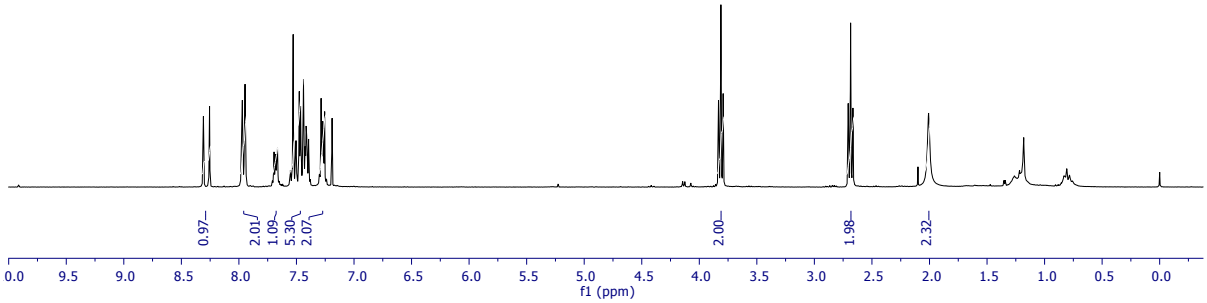
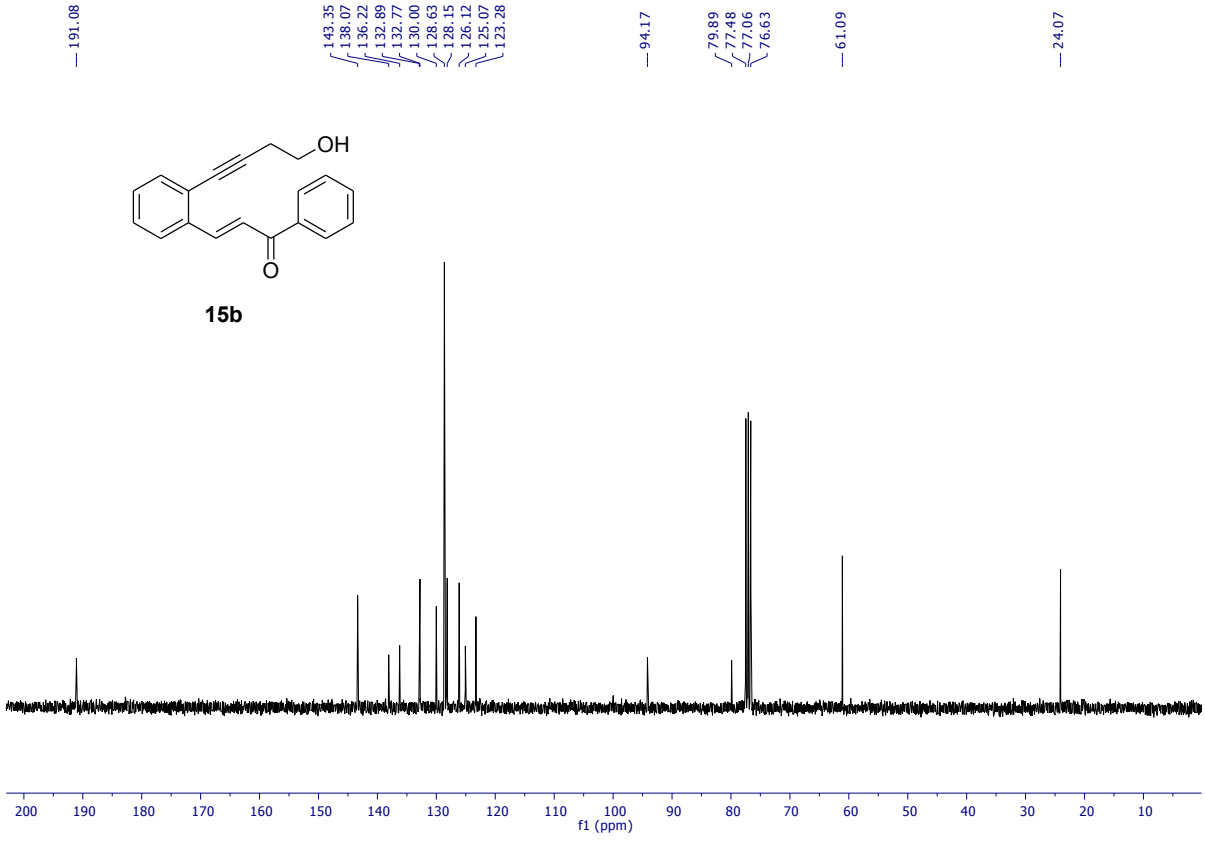
3.813
2.686
2.665
2.007
0.000

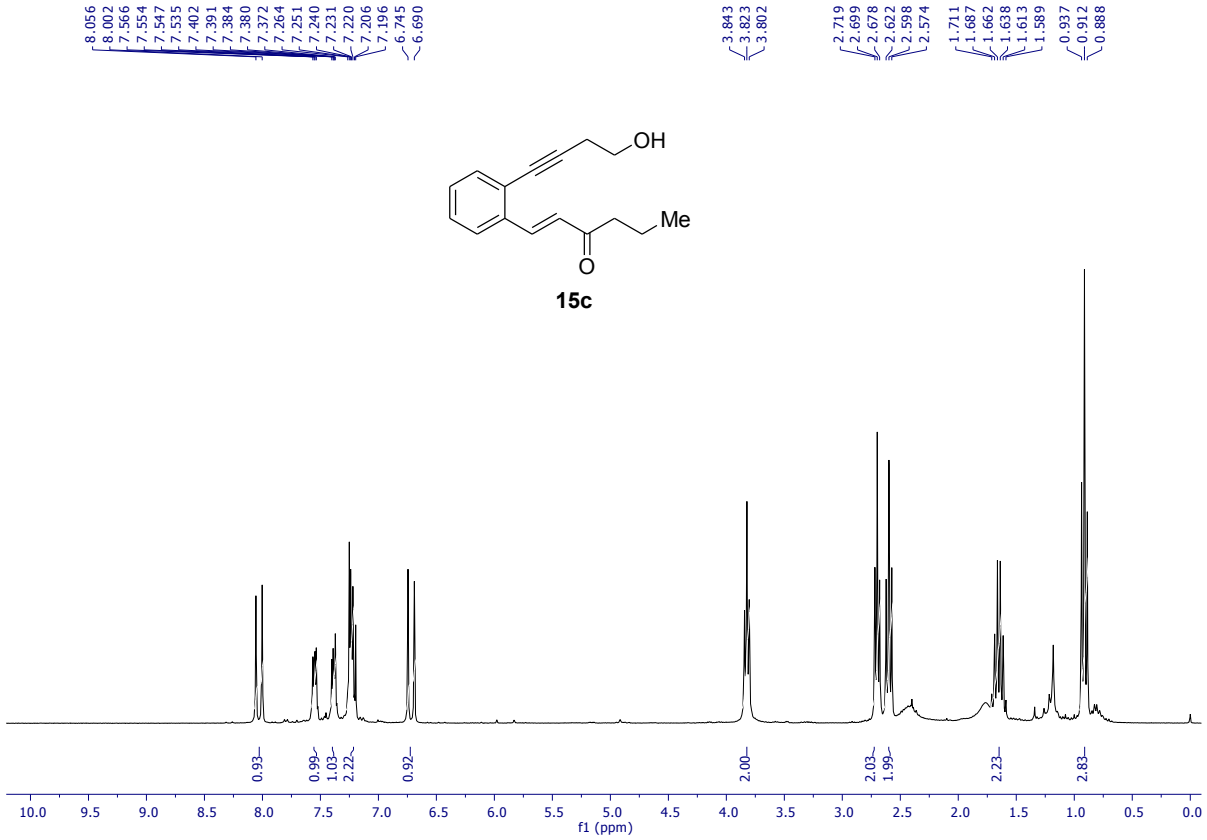

OH
O

15b


0.97
2.01
1.09
5.30
2.07
2.00
1.98
2.32
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


191.08
143.35
138.07
136.22
132.89
132.77
130.00
128.63
128.15
126.12
125.07
123.28
94.17
79.89
77.48
77.06
76.63
61.09
24.07
OH
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

15b


8.056
8.002
7.566
7.554
7.547
7.535
7.402
7.391
7.384
7.380
7.372
7.264
7.251
7.240
7.231
7.220
7.206
7.196
6.745
6.690
3.843
3.823
3.802
2.719
2.699
2.678
2.622
2.598
2.574
1.711
1.687
1.662
1.638
1.613
1.589
0.937
0.912
0.888
OH
Me
O
0.93
0.99
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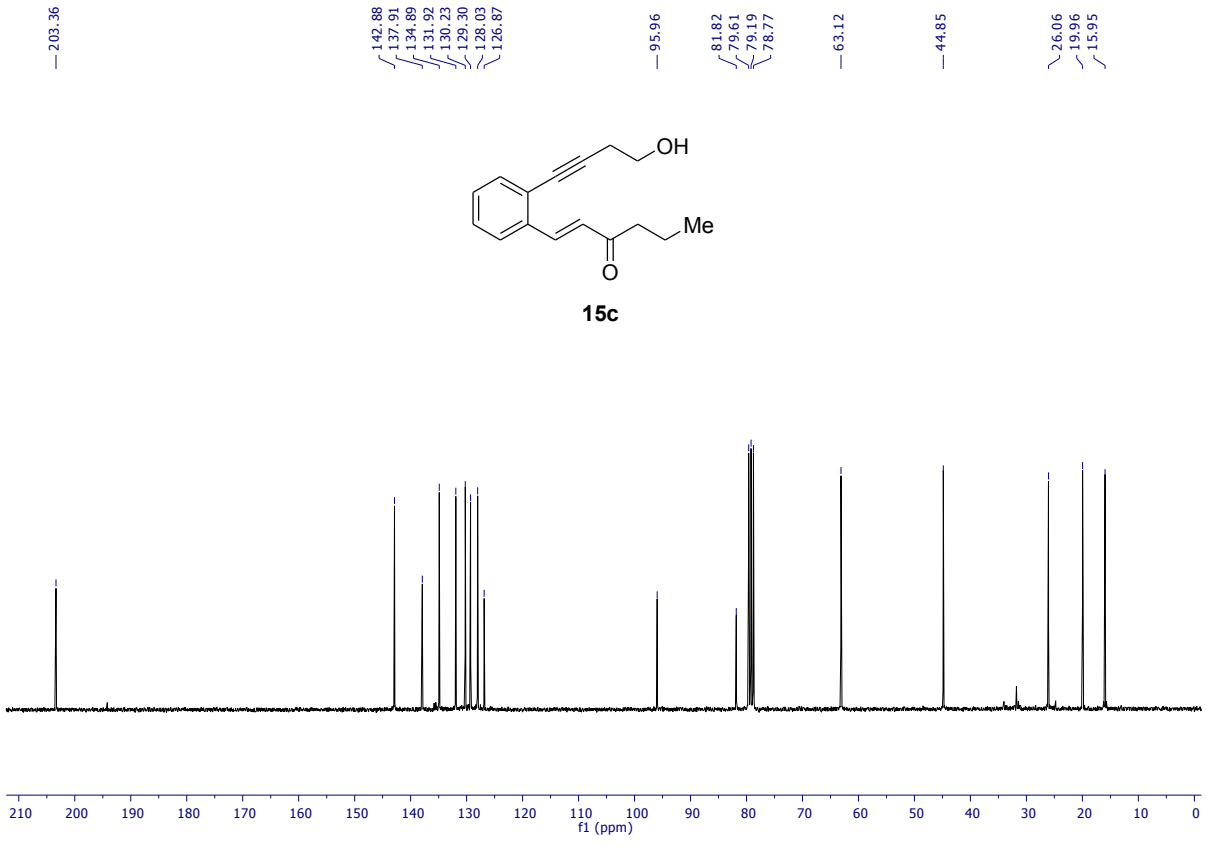
2.22
0.92
2.00
2.03
1.99
2.23
2.83
f1 (ppm)

15c


203.36
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137.91
134.89
131.92
130.23
129.30
128.03
126.87
95.96
81.82
79.61
79.19
78.77
63.12
44.85
26.06
19.96
15.95
OH
Me
O
f1 (ppm)

15c


8.311
8.258
7.996
7.974
7.967
7.686
7.676
7.671
7.662
7.655
7.539
7.487
7.420
7.412
7.404
7.399
7.390
7.375
7.370
7.365
7.361
7.354
7.346
7.342
7.339
7.332
7.320
7.314
7.309
7.303
7.294
7.279
7.276
7.270
7.264
7.261
7.254
7.247
7.191
7.007
7.000
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2.708
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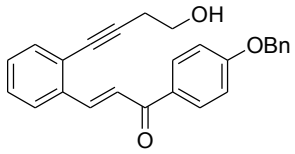
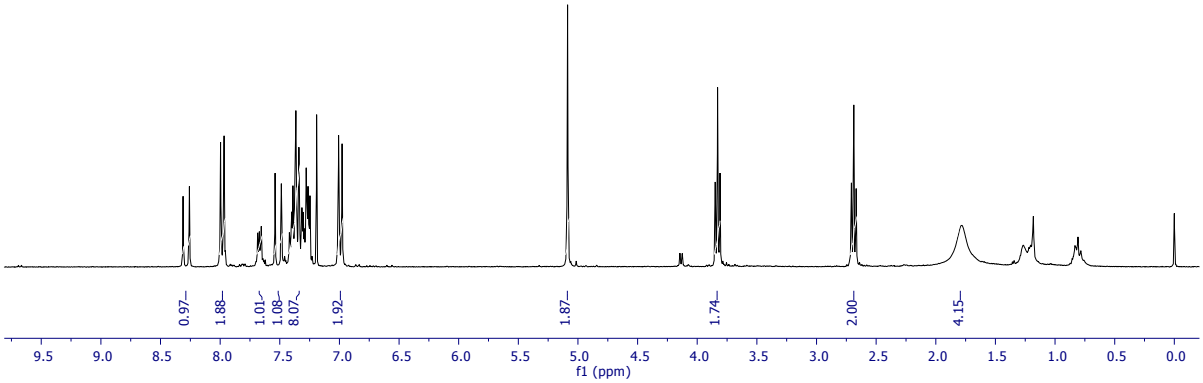
2.667
1.783
-0.000


OH
OBn
O

15d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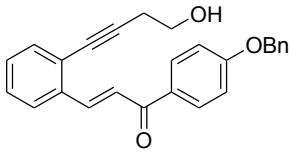
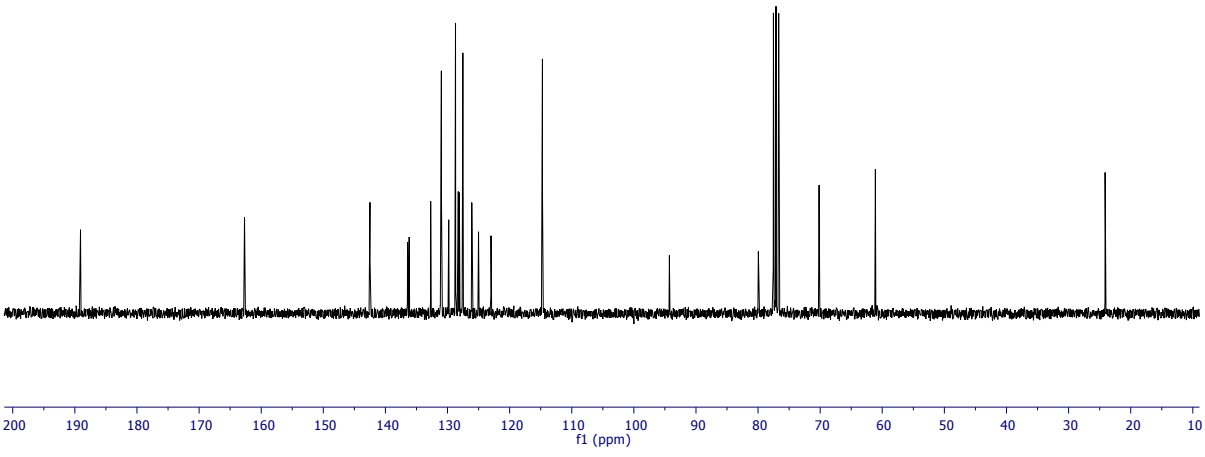
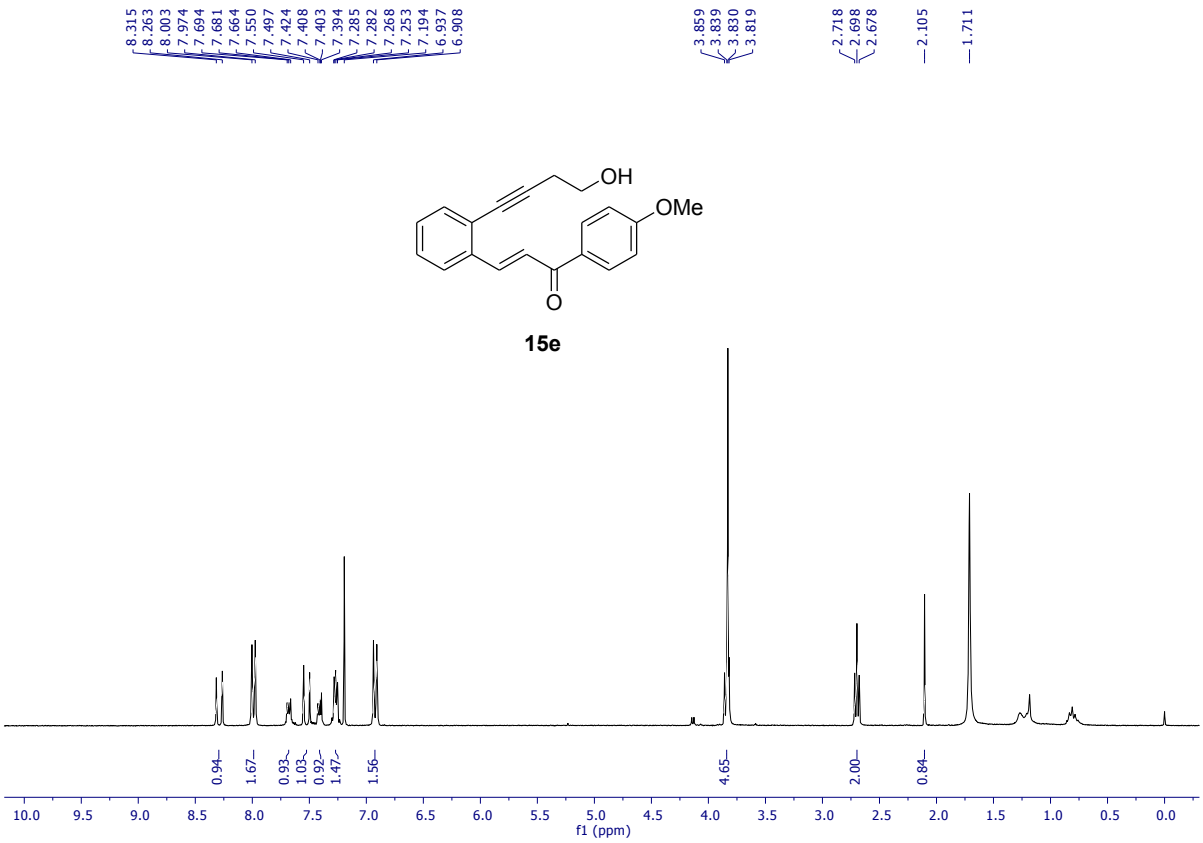
1.08
8.07
1.92
1.87
1.74
2.00
4.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

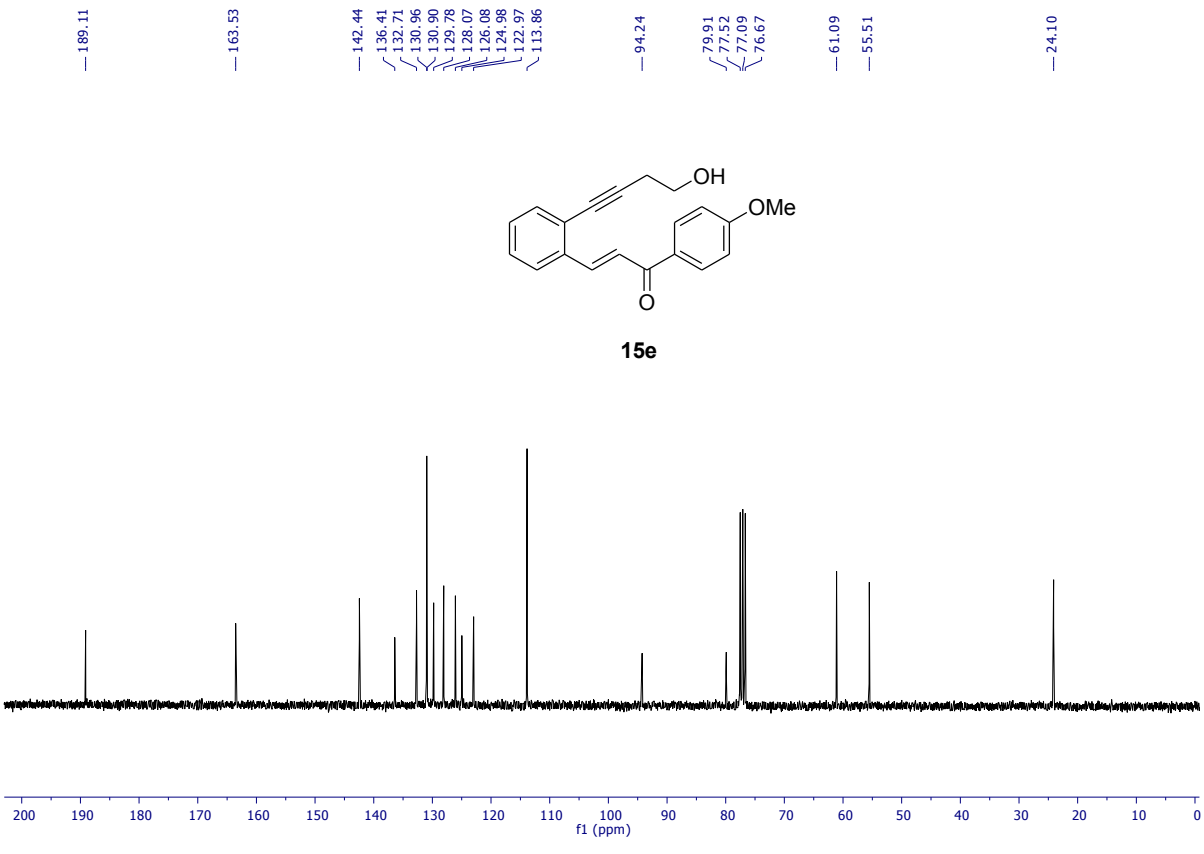

162.68
142.49
136.44
136.18
132.72
131.13
130.99
129.80
128.71
128.27
128.09
127.53
126.09
125.00
122.99
114.72
94.28
79.94
77.53
77.10
76.68
70.17
61.11
24.12

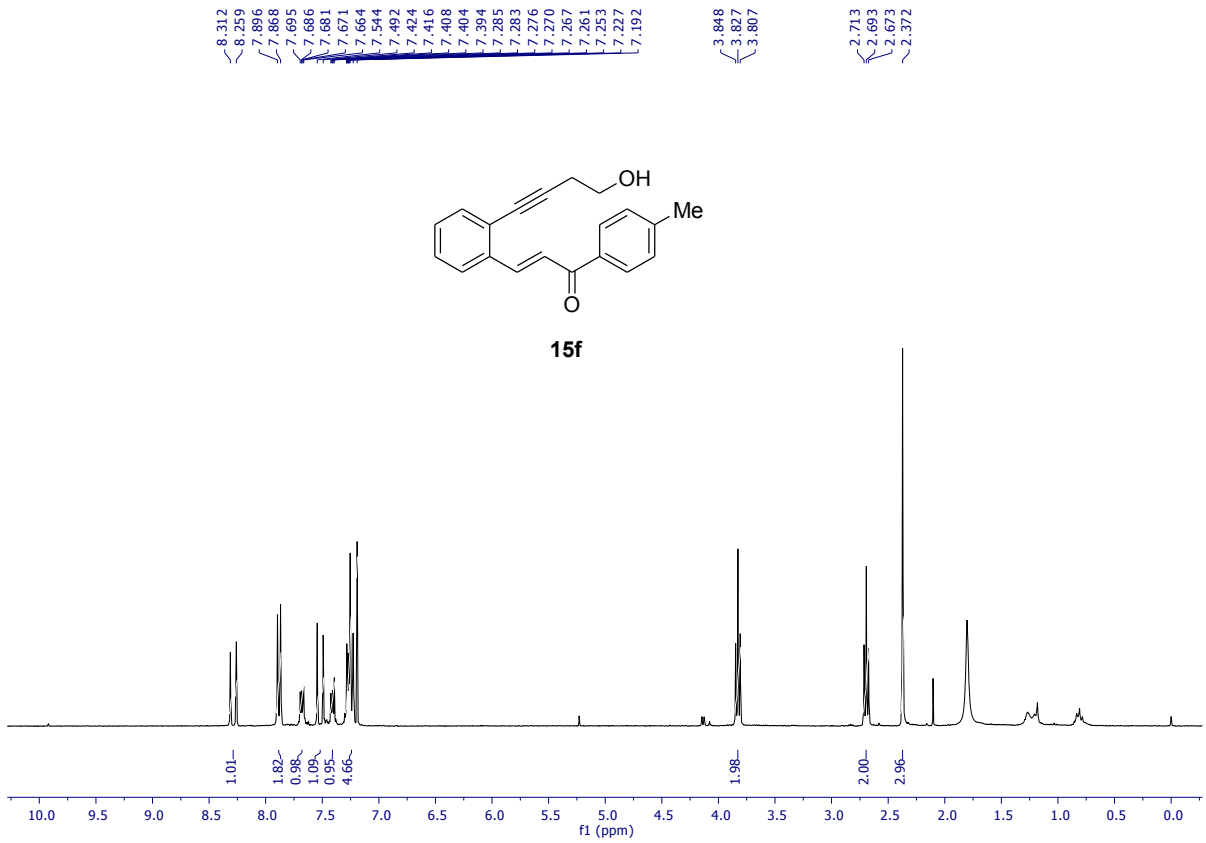

OH
OBn
O

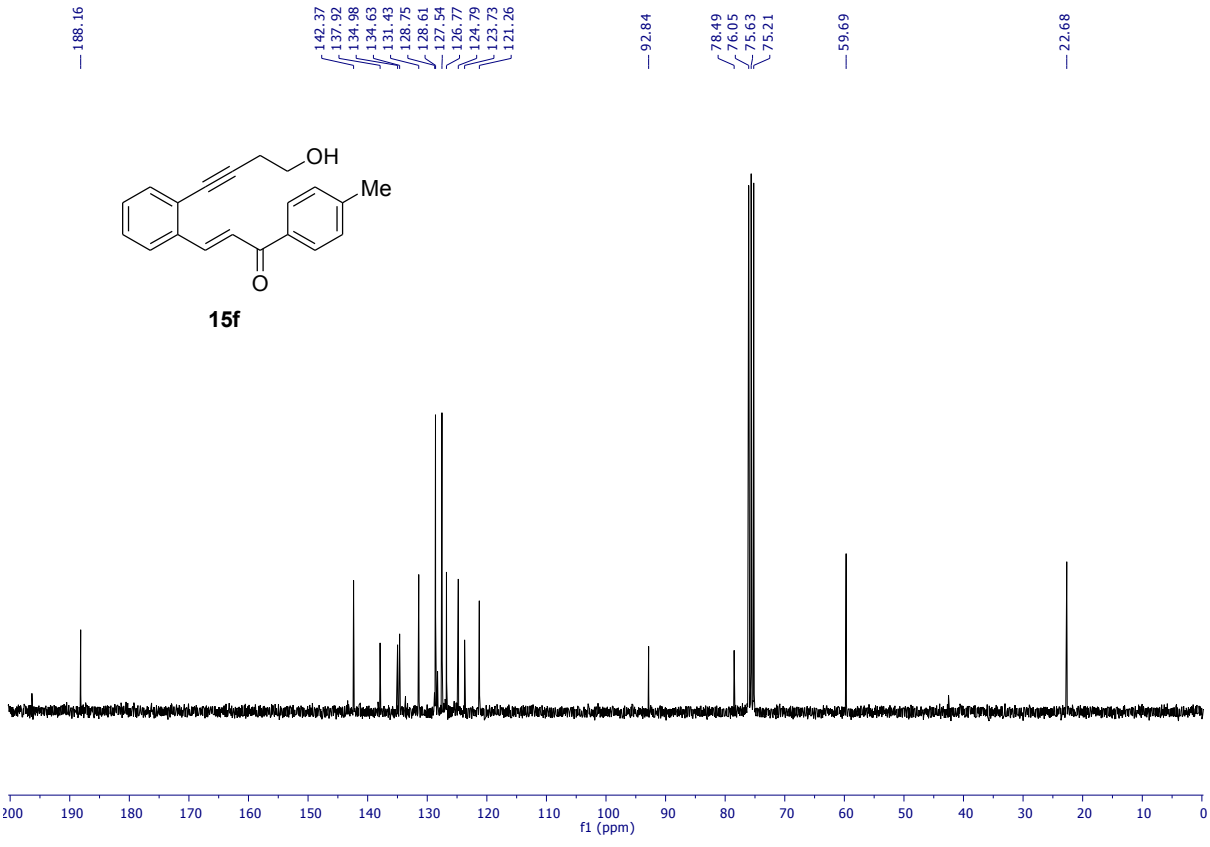
15d


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

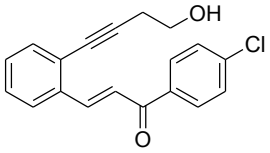

8.315
8.263
8.003
7.974
7.694
7.681
7.664
7.550
7.497
7.424
7.408
7.403
7.394
7.285
7.282
7.268
7.253
7.194
6.937
6.908
3.859
3.839
3.830
3.819
2.718
2.698
2.678
2.105
1.711
OH
OMe
O
15e
0.94
1.67
0.93
1.03
0.92
1.47
1.56
4.65
2.00
0.84
f1 (ppm)


189.11
163.53
142.44
136.41
132.71
130.96
130.90
129.78
128.07
126.08
124.98
122.97
113.86
94.24
79.91
77.52
77.09
76.67
61.09
55.51
24.10
OH
OMe
O
15e
f1 (ppm)

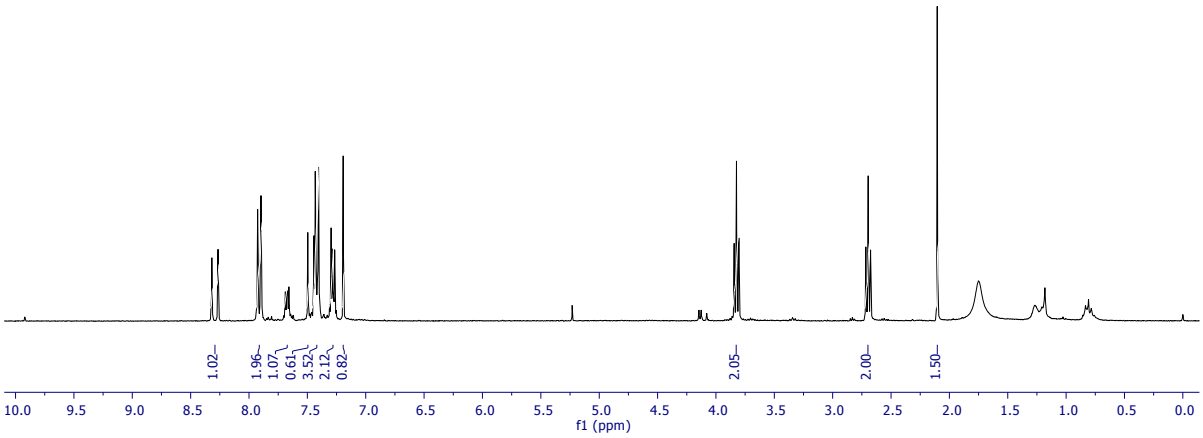

8.312
8.259
7.896
7.868
7.695
7.686
7.681
7.671
7.664
7.544
7.492
7.424
7.416
7.408
7.404
7.394
7.285
7.283
7.276
7.270
7.267
7.261
7.253
7.227
7.192
3.848
3.827
3.807
2.713
2.693
2.673
2.372
OH
Me
O
15f
1.01
1.82
0.98
1.09
0.95
4.66
1.98
2.00
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


188.16
142.37
137.92
134.98
134.63
131.43
128.75
128.61
127.54
126.77
124.79
123.73
121.26
92.84
78.49
76.05
75.63
75.21
59.69
22.68
OH
Me
O
15f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

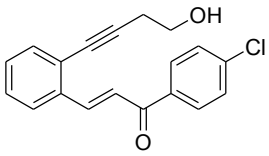

8.318
8.265
7.934
7.926
7.920
7.904
7.897
7.889
7.689
7.677
7.670
7.658
7.496
7.481
7.469
7.462
7.444
7.432
7.425
7.423
7.416
7.410
7.404
7.395
7.391
7.297
7.286
7.277
7.266
7.193
3.844
3.824
3.804
2.716
2.695
2.675
2.104


OH
Cl
O

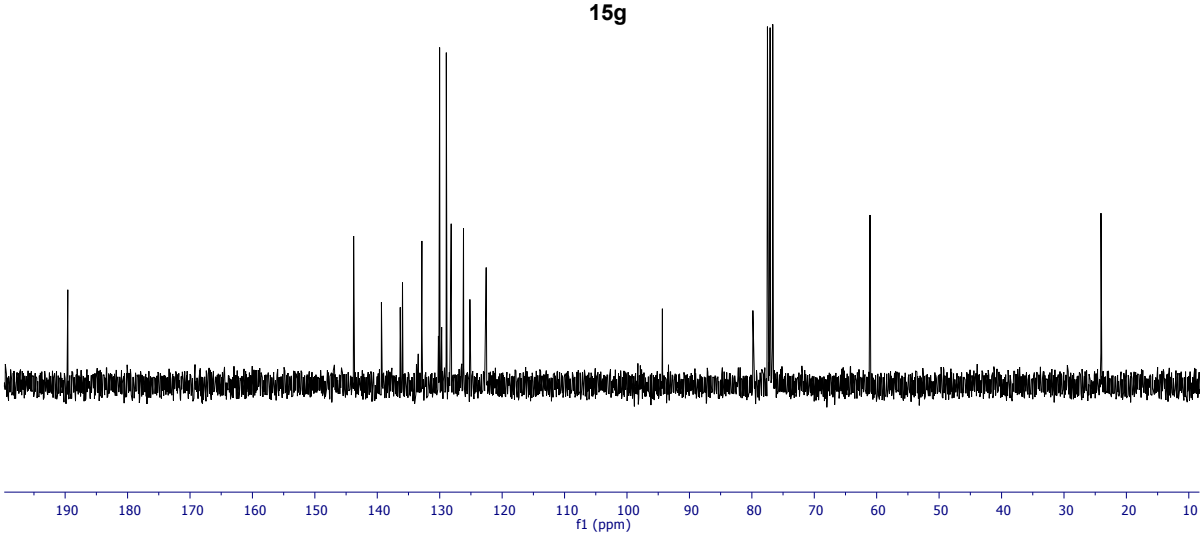
15g

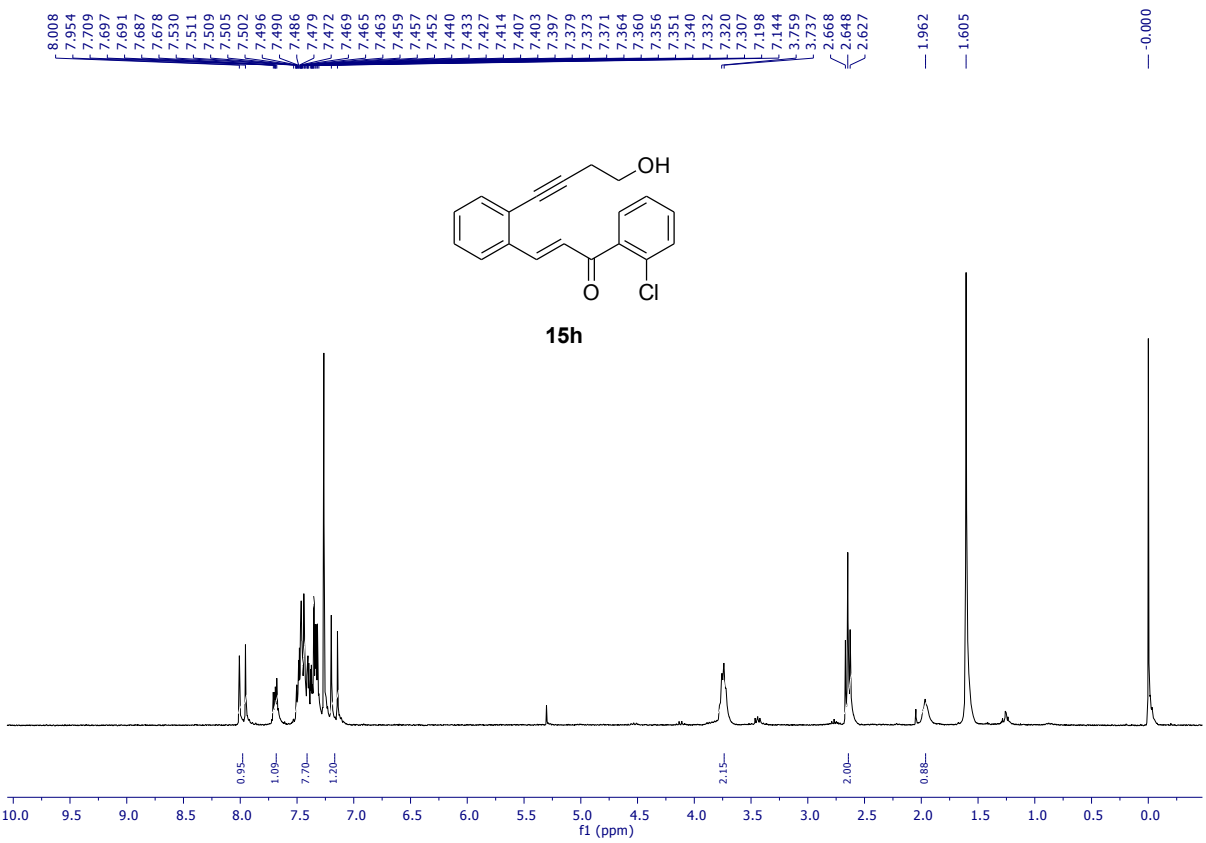

1.02
1.96
1.07
0.61
3.52
2.12
0.82
2.05
2.00
1.50
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

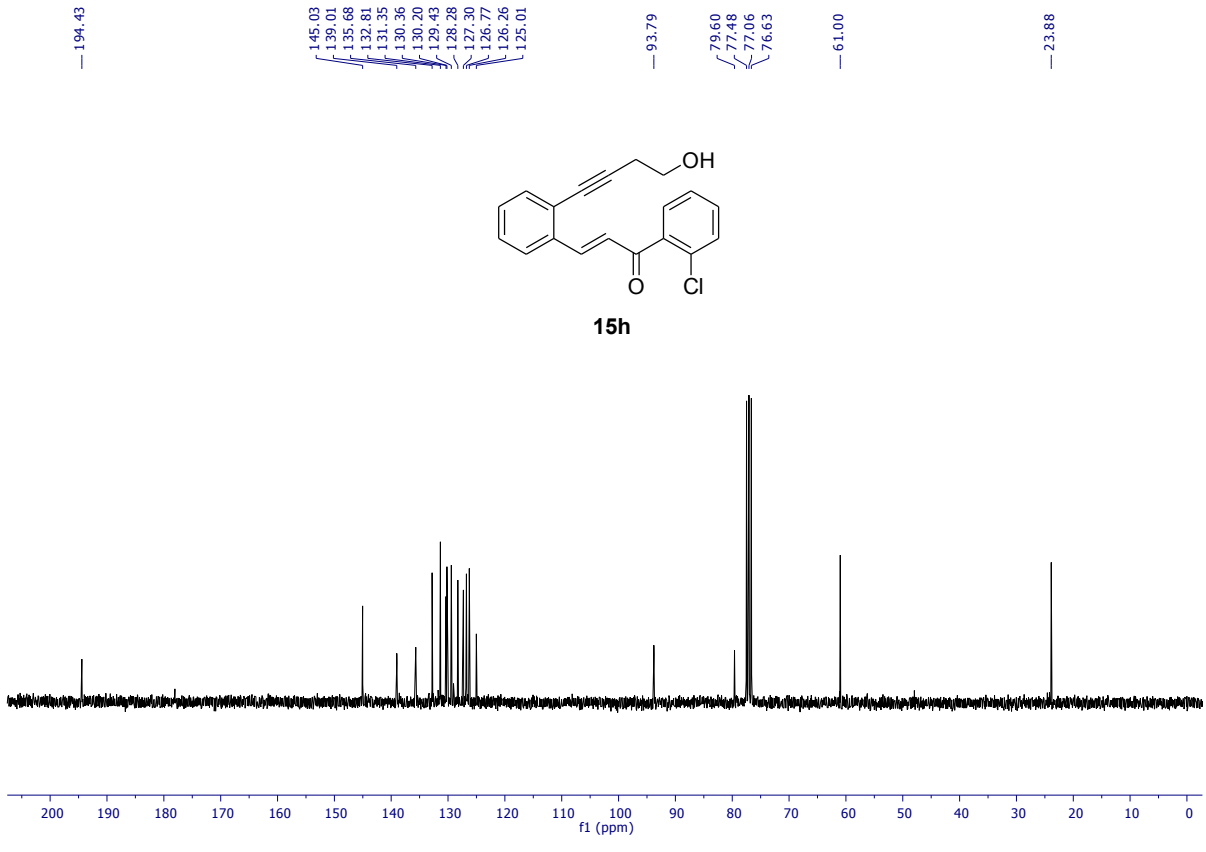

189.58
143.78
139.33
136.32
135.96
132.85
130.19
130.02
128.94
128.16
126.19
125.17
122.55
94.33
79.83
77.50
77.08
76.65
61.07
24.07


OH
Cl
O

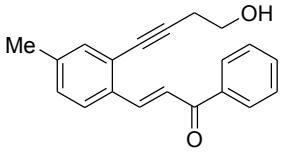
15g


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

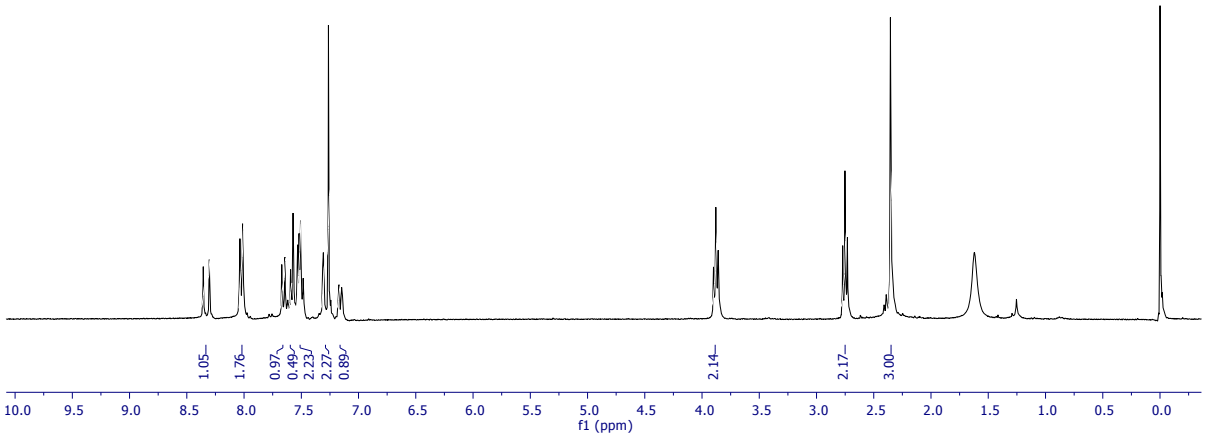

8.008
7.954
7.709
7.697
7.691
7.687
7.678
7.530
7.511
7.509
7.505
7.502
7.496
7.490
7.486
7.479
7.472
7.469
7.465
7.463
7.459
7.457
7.452
7.440
7.433
7.427
7.414
7.407
7.403
7.397
7.379
7.373
7.371
7.364
7.360
7.356
7.351
7.340
7.332
7.320
7.307
7.198
7.144
3.759
3.737
2.668
2.648
2.627
1.962
1.605
-0.000
OH
O
Cl
15h
0.95
1.09
7.70
1.20
2.15
2.00
0.88
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


194.43
145.03
139.01
135.68
132.81
131.35
130.36
130.20
129.43
128.28
127.30
126.77
126.26
125.01
93.79
79.60
77.48
77.06
76.63
61.00
23.88
OH
O
Cl
15h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

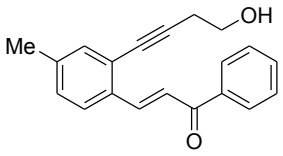

8.356
8.303
8.040
8.036
8.030
8.020
8.013
8.007
7.670
7.643
7.594
7.586
7.572
7.565
7.539
7.535
7.532
7.527
7.519
7.512
7.507
7.489
7.484
7.479
7.308
7.263
7.259
7.254
7.175
7.169
7.146
3.900
3.879
3.859
2.772
2.751
2.731
2.354
-0.000


OH
Me
O

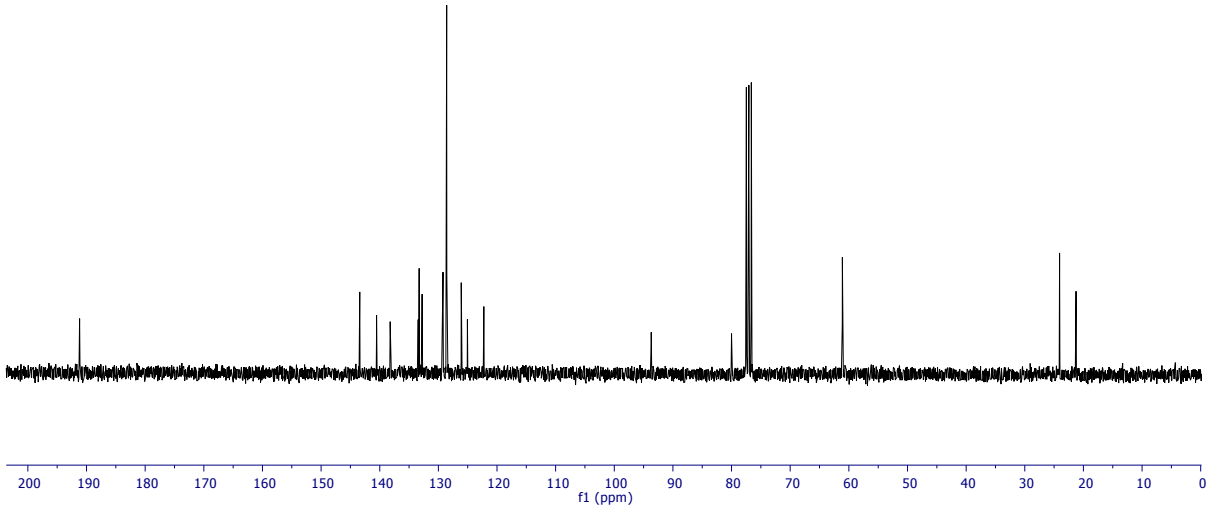
15i

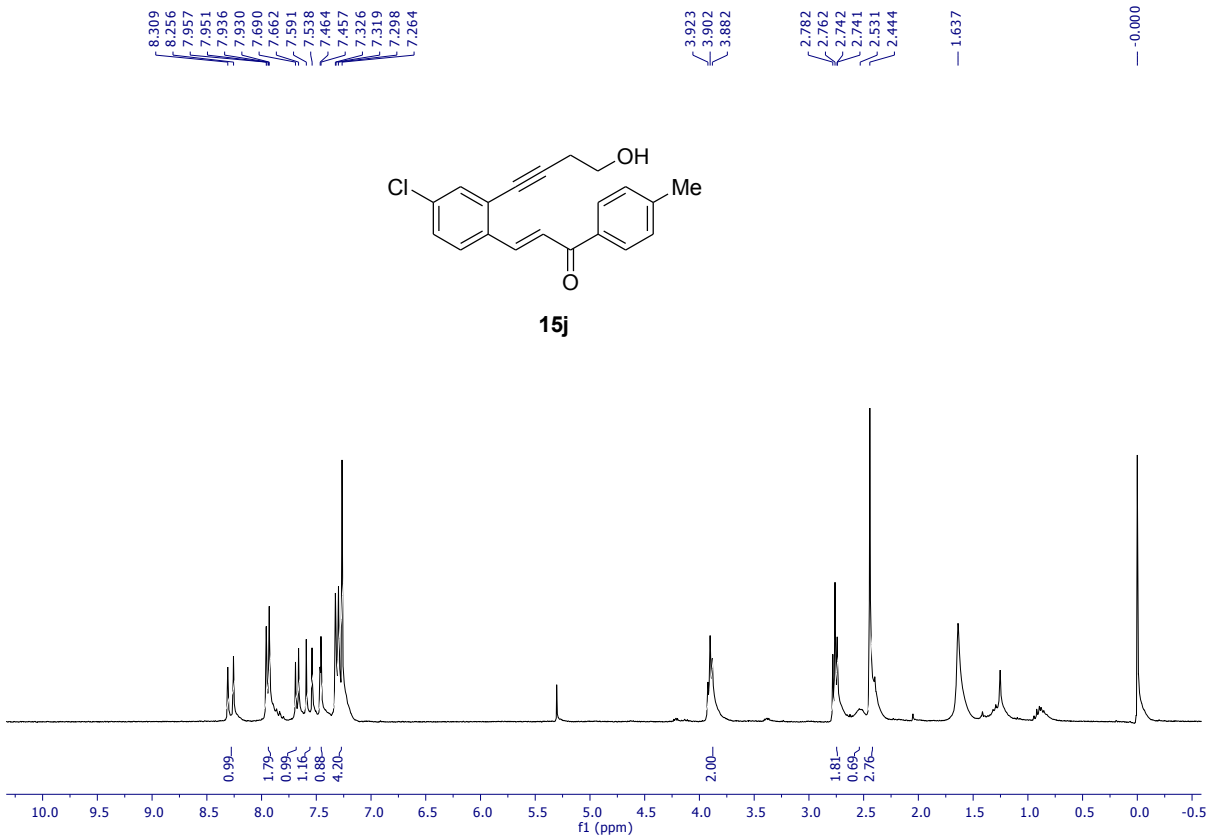

1.05
1.76
0.97
0.49
2.23
2.27
0.89
2.14
2.17
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

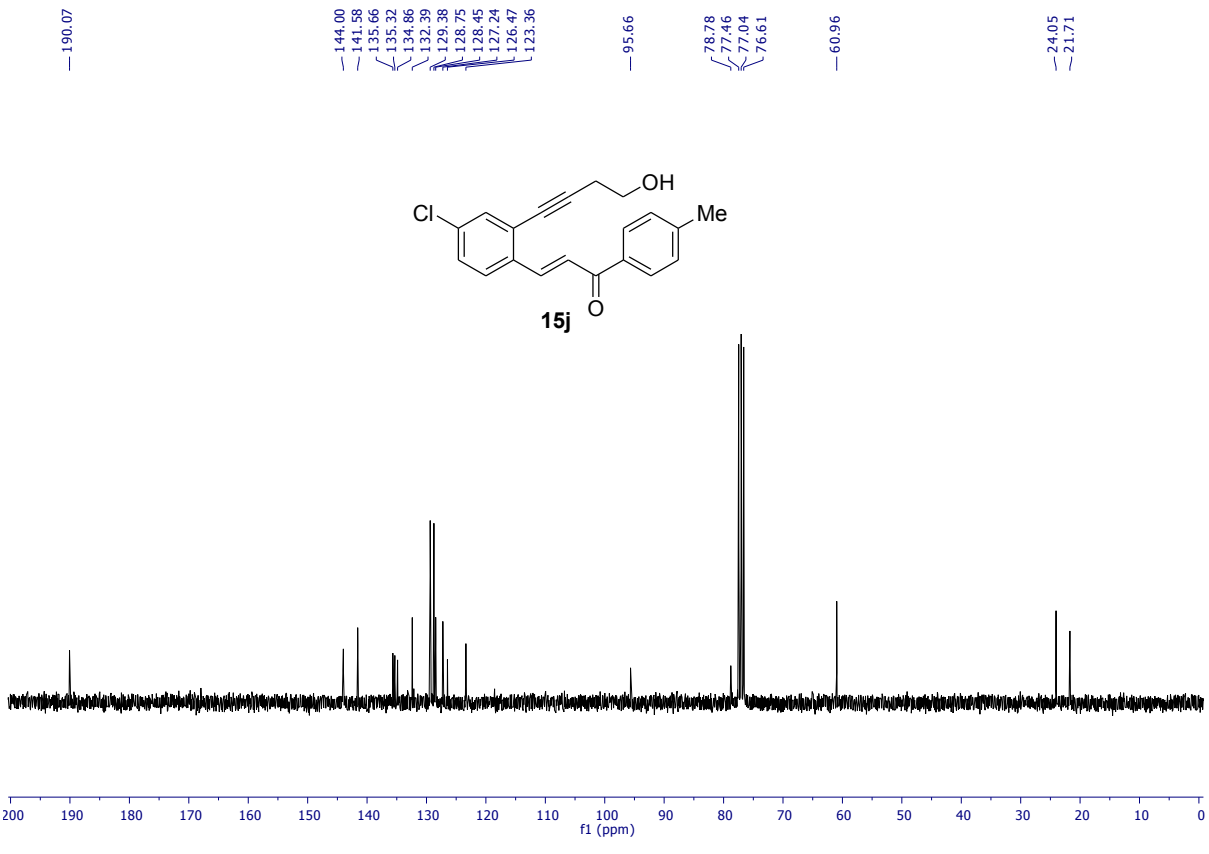

191.17
143.41
140.54
138.22
133.44
133.28
132.77
129.20
128.58
126.10
125.04
122.25
93.71
80.00
77.48
77.06
76.63
61.11
24.06
21.26

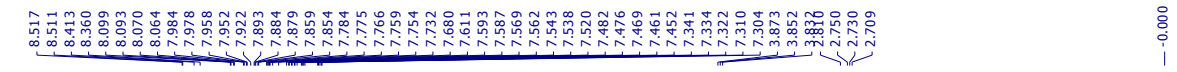

OH
Me
O

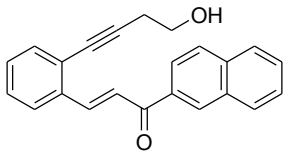
15i


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

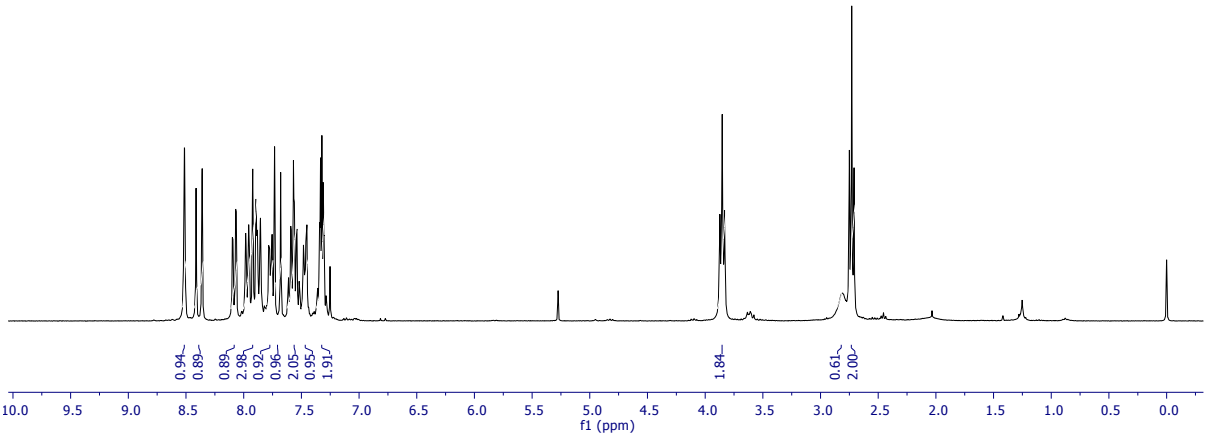

8.309
8.256
7.957
7.951
7.936
7.930
7.690
7.662
7.591
7.538
7.464
7.457
7.326
7.319
7.298
7.264
3.923
3.902
3.882
2.782
2.762
2.742
2.741
2.531
2.444
1.637
-0.000
OH
Cl
Me
O
15j
0.99
1.79
0.99
1.16
0.88
4.20
2.00
1.81
0.69
2.76
f1 (ppm)

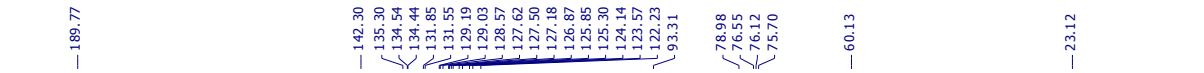

190.07
144.00
141.58
135.66
135.32
134.86
132.39
129.38
128.75
128.45
127.24
126.47
123.36
95.66
78.78
77.46
77.04
76.61
60.96
24.05
21.71
OH
Cl
Me
O
15j
f1 (ppm)

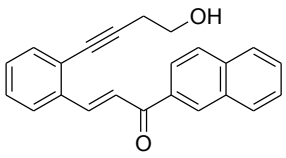

8.517
8.511
8.413
8.360
8.099
8.093
8.070
8.064
7.984
7.978
7.958
7.952
7.922
7.893
7.884
7.879
7.859
7.854
7.784
7.775
7.766
7.759
7.754
7.732
7.680
7.611
7.593
7.587
7.569
7.562
7.543
7.538
7.520
7.482
7.476
7.469
7.461
7.452
7.341
7.334
7.322
7.310
7.304
3.873
3.852
2.832
2.810
2.750
2.730
2.709
-0.000


OH
O

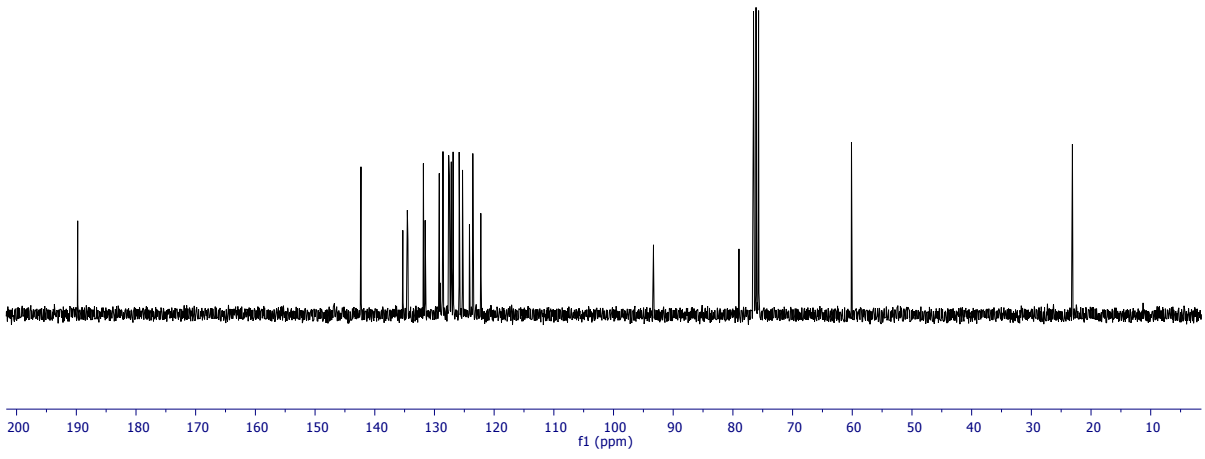
15k


0.94
0.89
0.89
2.98
0.92
0.96
2.05
0.95
1.91
1.84
0.61
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

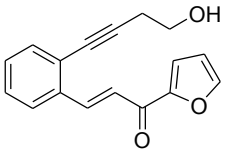

189.77
142.30
135.30
134.54
134.44
131.85
131.55
129.19
129.03
128.57
127.62
127.50
127.18
126.87
125.85
125.30
124.14
123.57
122.23
93.31
78.98
76.55
76.12
75.70
60.13
23.12


OH
O

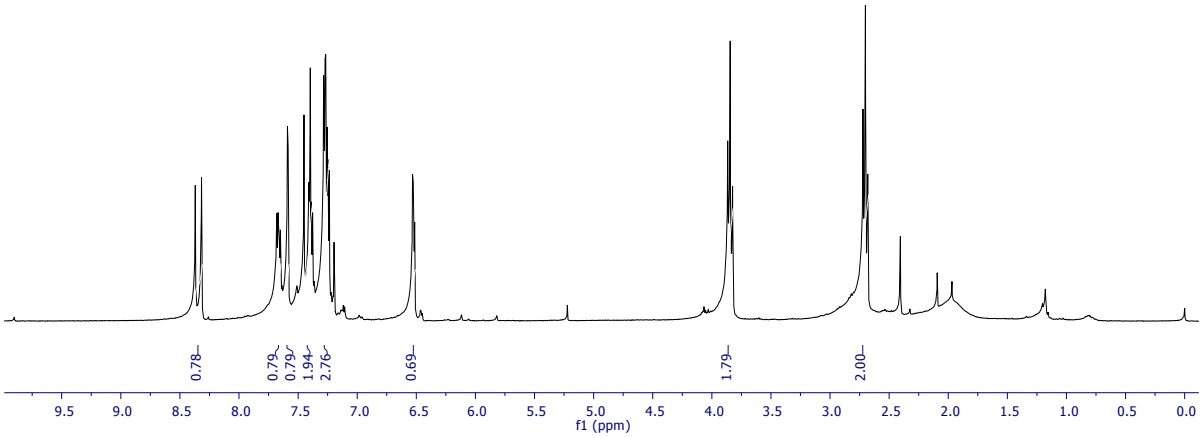
15k


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

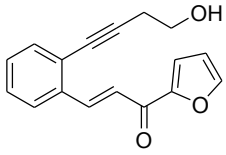

8.370
8.317
7.681
7.670
7.663
7.650
7.590
7.585
7.451
7.407
7.398
7.388
7.291
7.283
7.272
7.266
7.255
7.247
7.236
6.532
6.526
6.520
6.514
3.866
3.845
3.825
2.721
2.701
2.681


OH
O
O

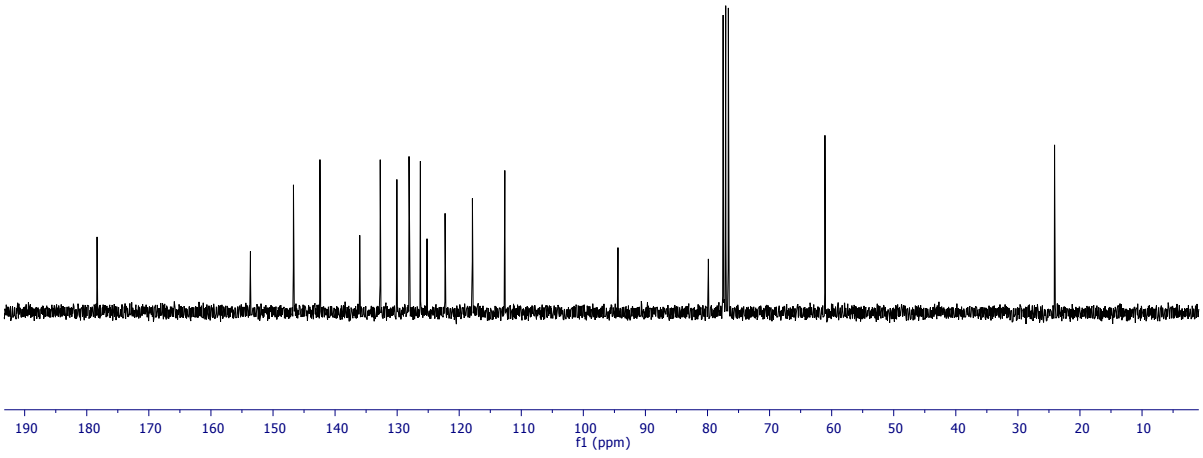
15l

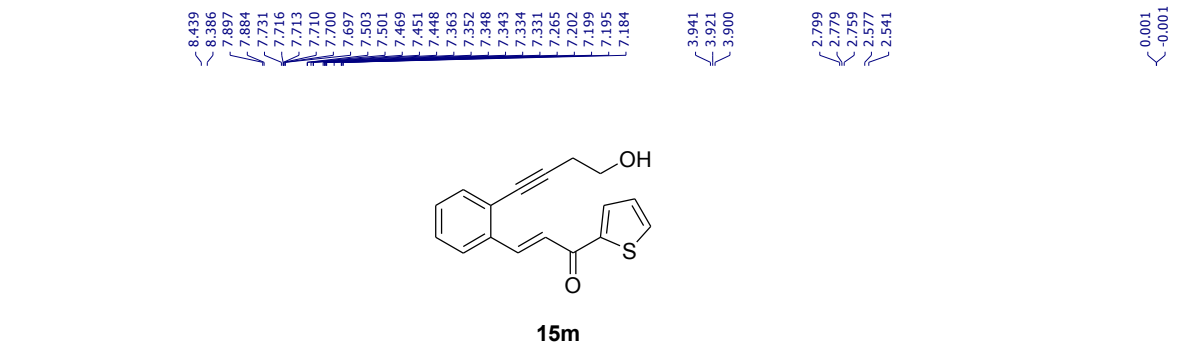

0.78
0.79
0.79
1.94
2.76
0.69
1.79
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


178.34
153.63
146.70
142.44
136.02
132.73
130.04
128.08
126.26
125.18
122.27
117.87
112.65
94.43
79.86
77.49
77.07
76.65
61.09
24.09

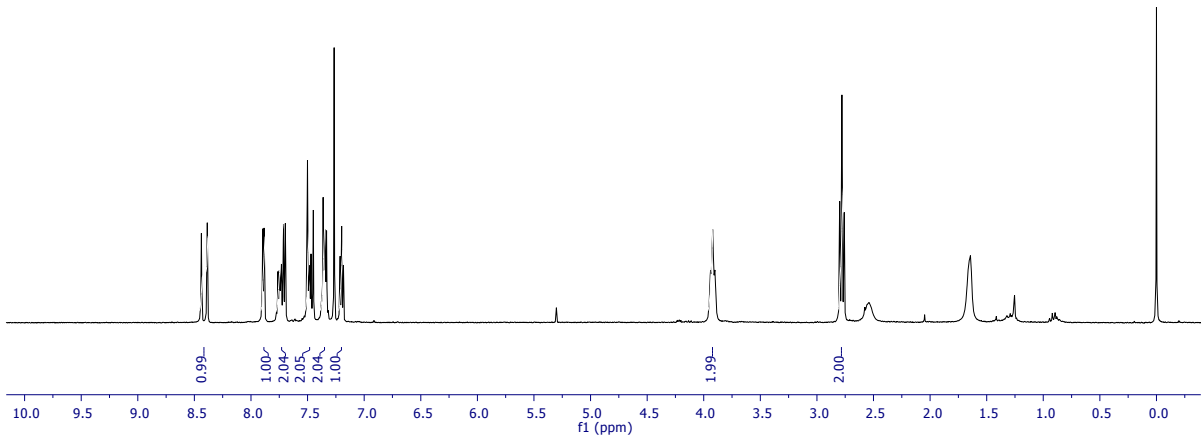

OH
O
O

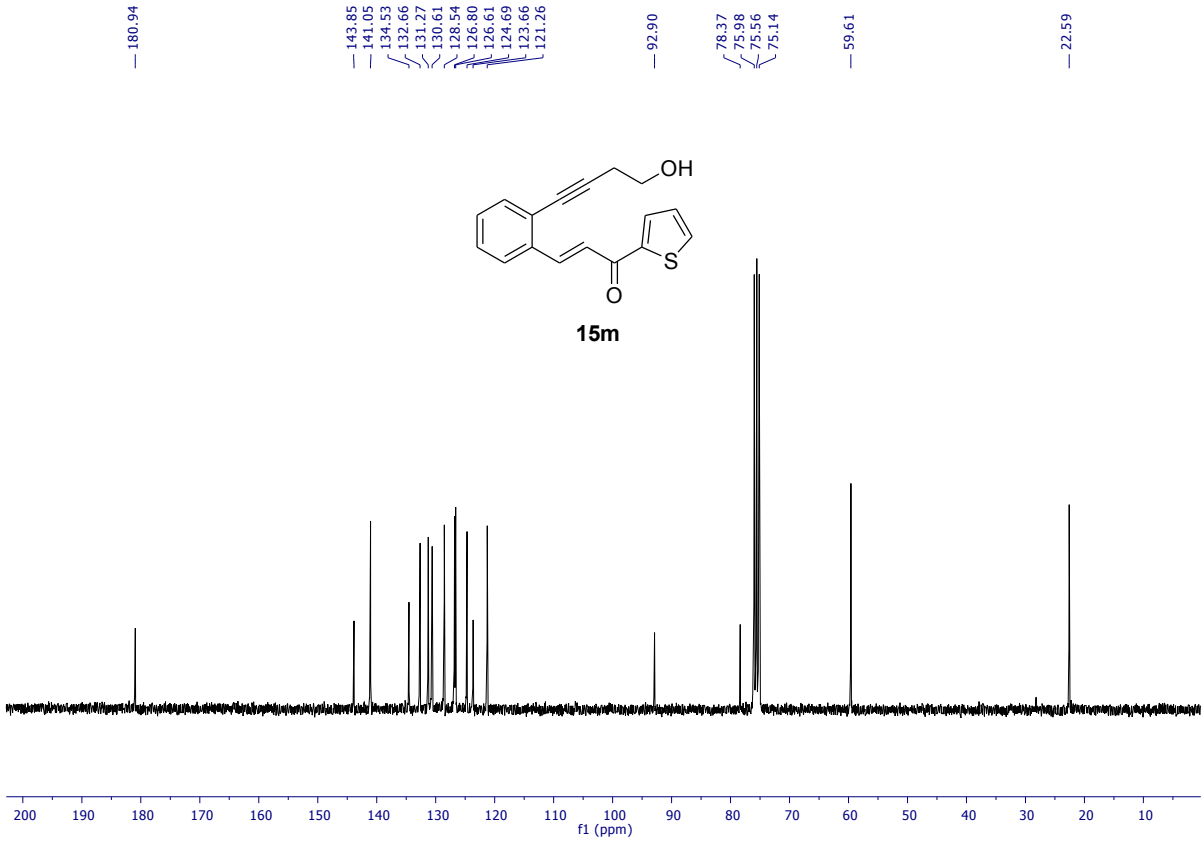
15l


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


8.439
8.386
7.897
7.884
7.731
7.716
7.713
7.710
7.700
7.697
7.503
7.501
7.469
7.451
7.448
7.363
7.352
7.348
7.343
7.334
7.331
7.265
7.202
7.199
7.195
7.184
3.941
3.921
3.900
2.799
2.779
2.759
2.577
2.541
0.001
-0.001
OH
S
O

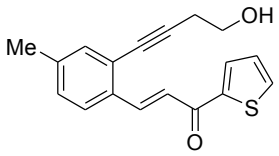
15m


0.99
1.00
2.04
2.05
2.04
1.00
1.99
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

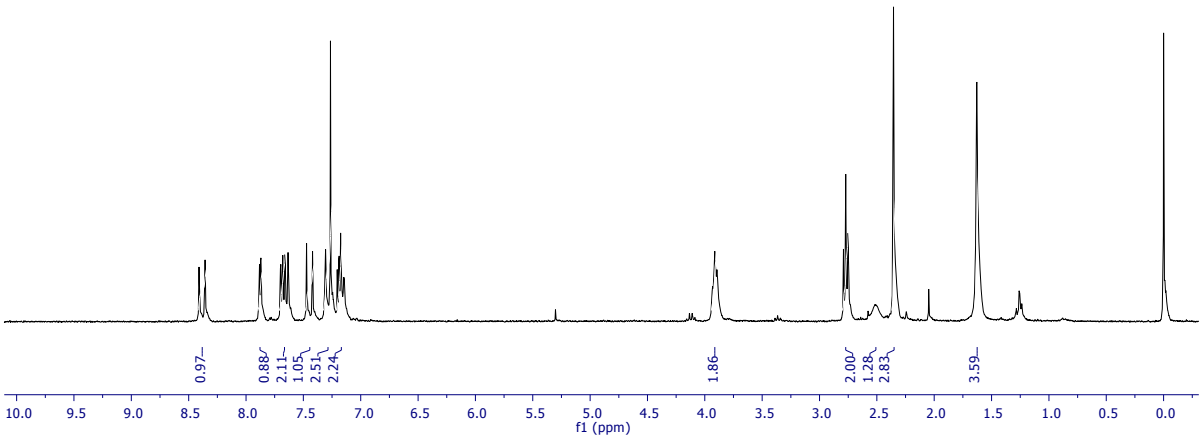

180.94
143.85
141.05
134.53
132.66
131.27
130.61
128.54
126.80
126.61
124.69
123.66
121.26
92.90
78.37
75.98
75.56
75.14
59.61
22.59
OH
S
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

15m

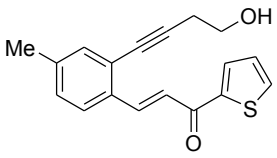

8.409
8.357
7.887
7.883
7.874
7.870
7.700
7.696
7.684
7.680
7.660
7.648
7.633
7.472
7.420
7.307
7.264
7.244
7.204
7.192
7.188
7.175
7.168
7.145
3.933
3.913
3.892
2.791
2.771
2.751
2.355
1.629
-0.000


OH
Me
S
O

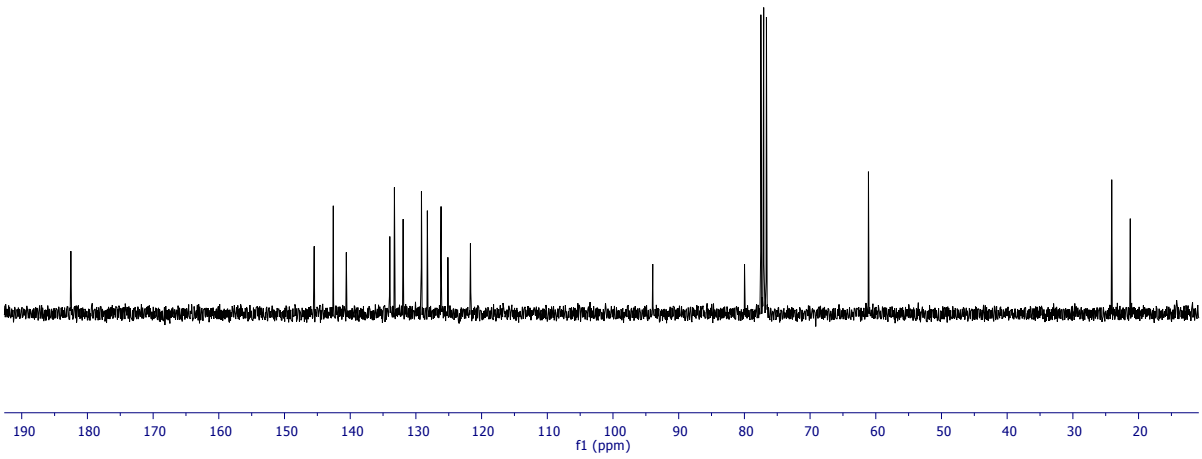
15n

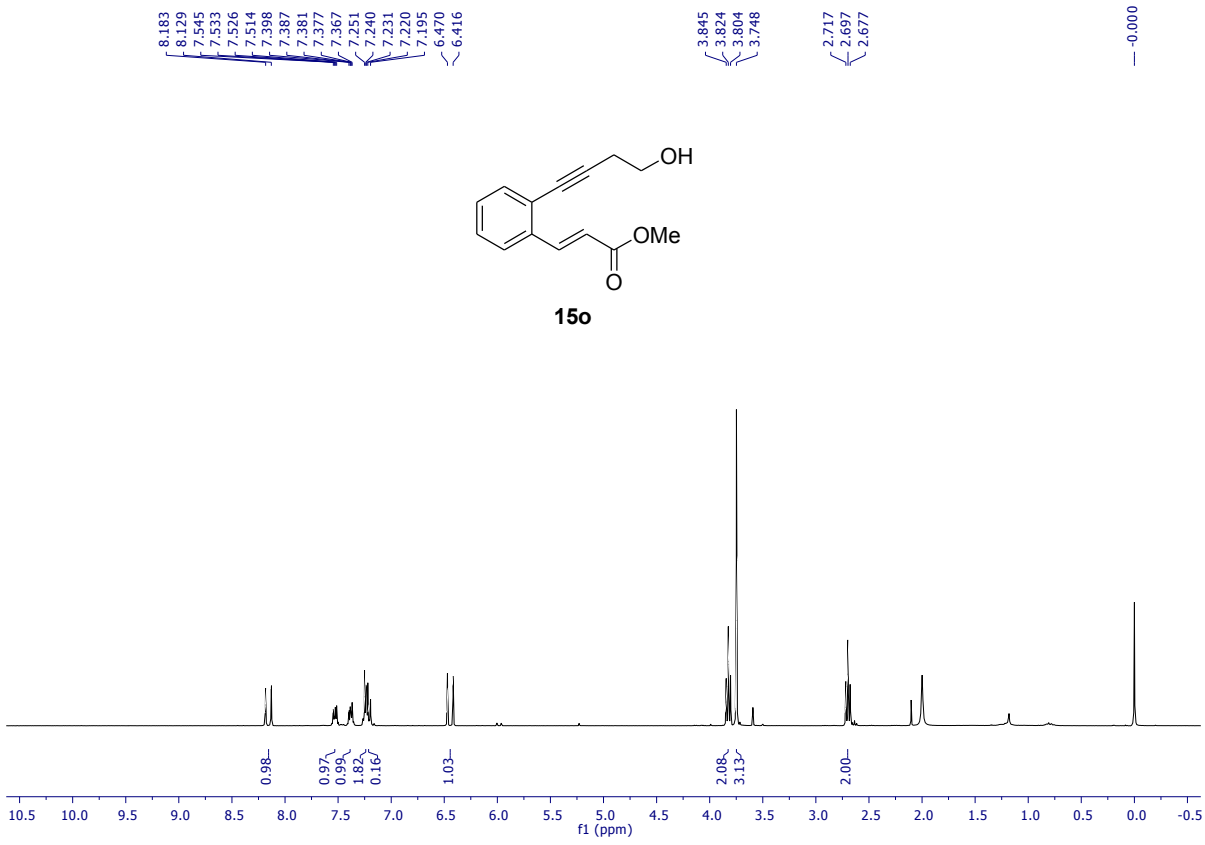

0.97
0.88
2.11
1.05
2.51
2.24
1.86
2.00
1.28
2.83
3.59
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

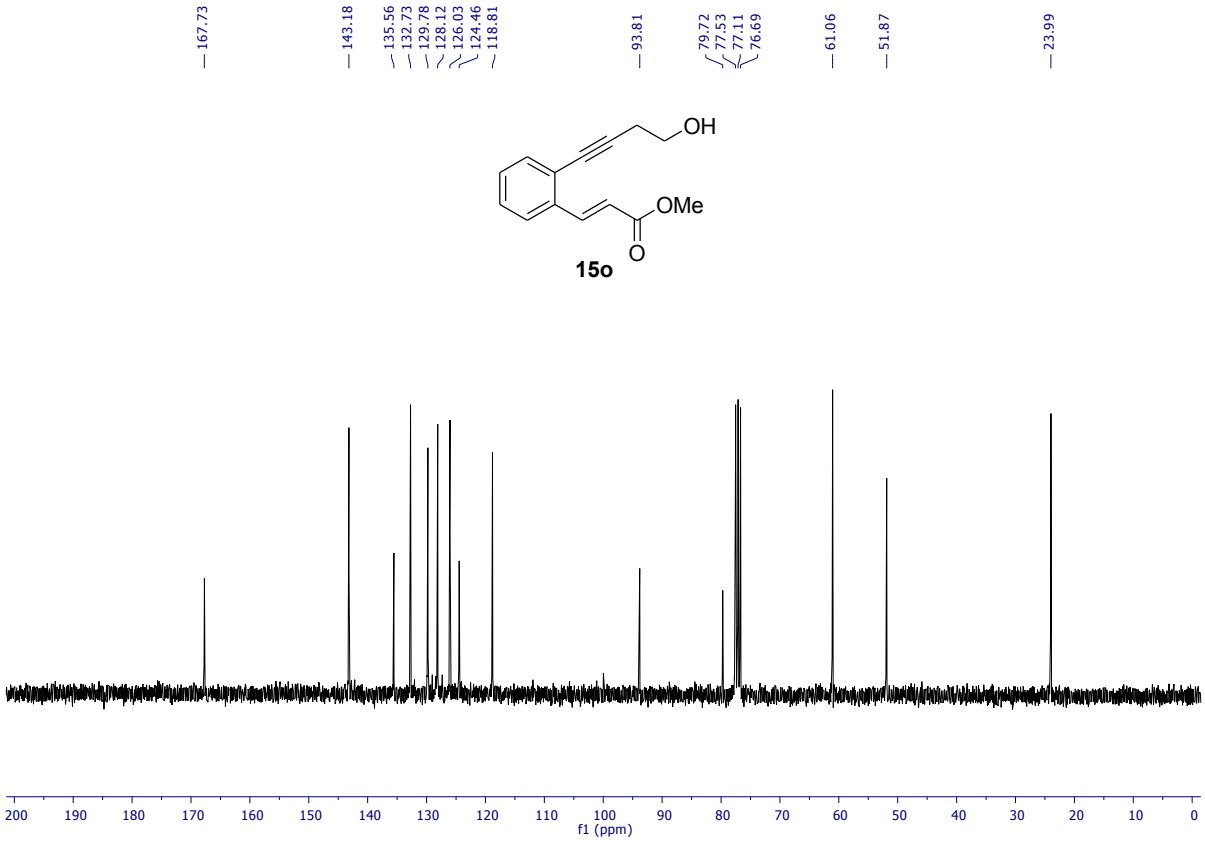

182.52
145.48
142.58
140.60
133.98
133.27
133.24
131.95
129.15
128.26
126.17
125.13
121.69
93.95
79.97
77.49
77.06
76.64
61.12
24.08
21.26

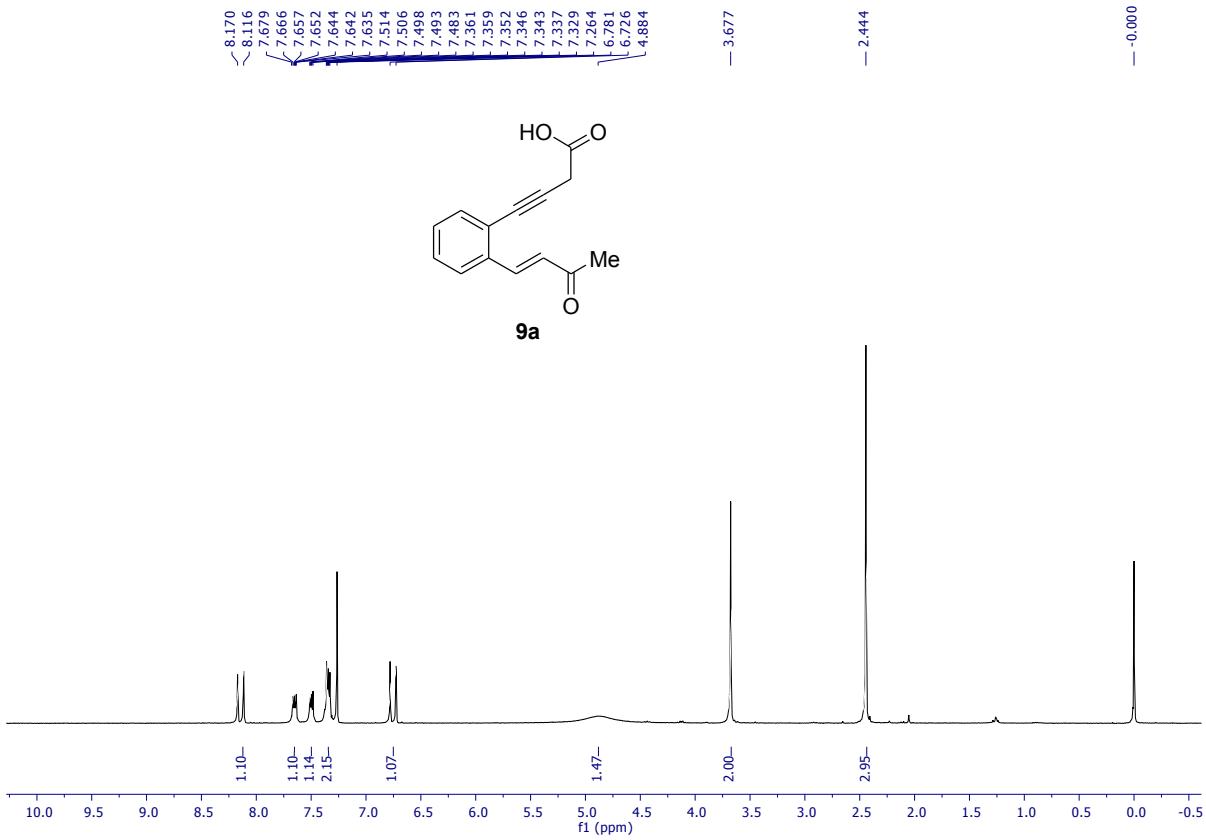

OH
Me
S
O

15n

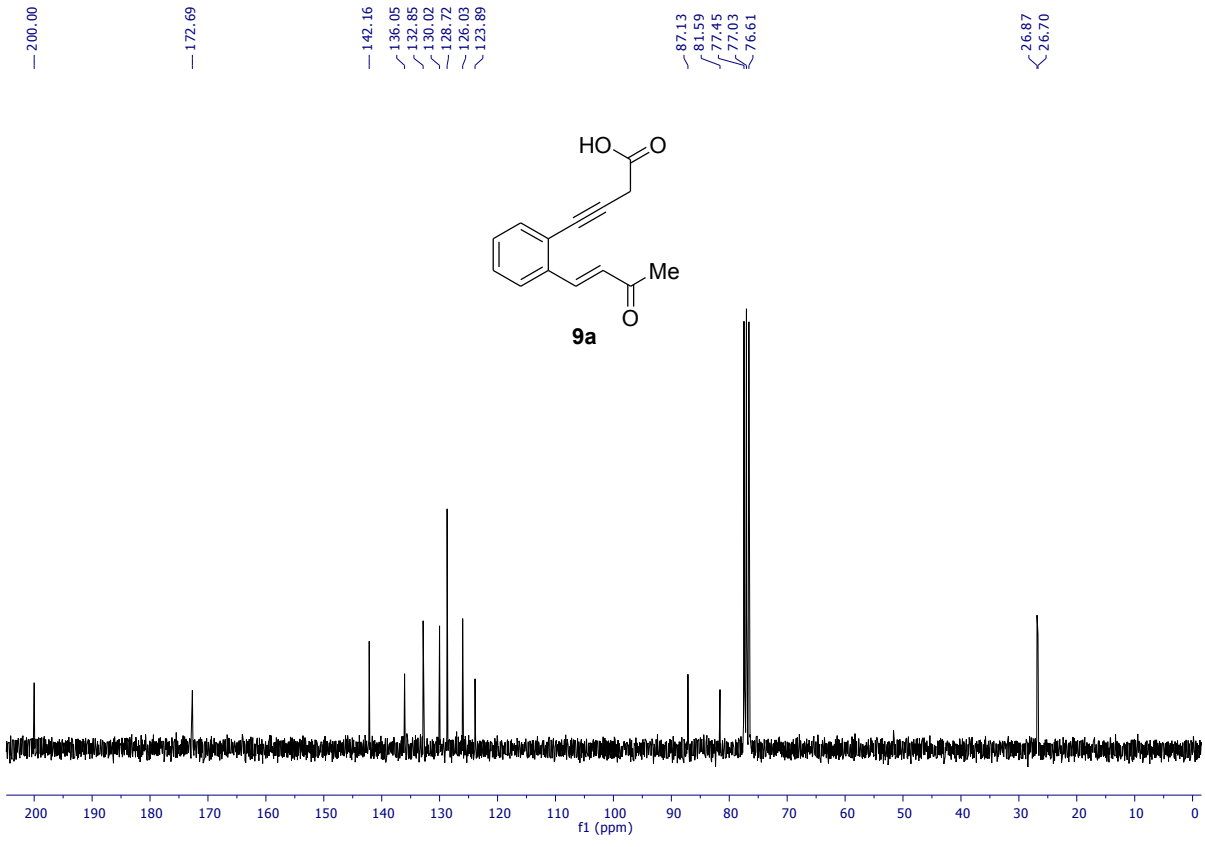

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


8.183
8.129
7.545
7.533
7.526
7.514
7.398
7.387
7.381
7.377
7.367
7.251
7.240
7.231
7.220
7.195
6.470
6.416
3.845
3.824
3.804
3.748
2.717
2.697
2.677
-0.000
OH
OMe
O
15o
0.98
0.97
0.99
1.82
0.16
1.03
2.08
3.13
2.00
f1 (ppm)

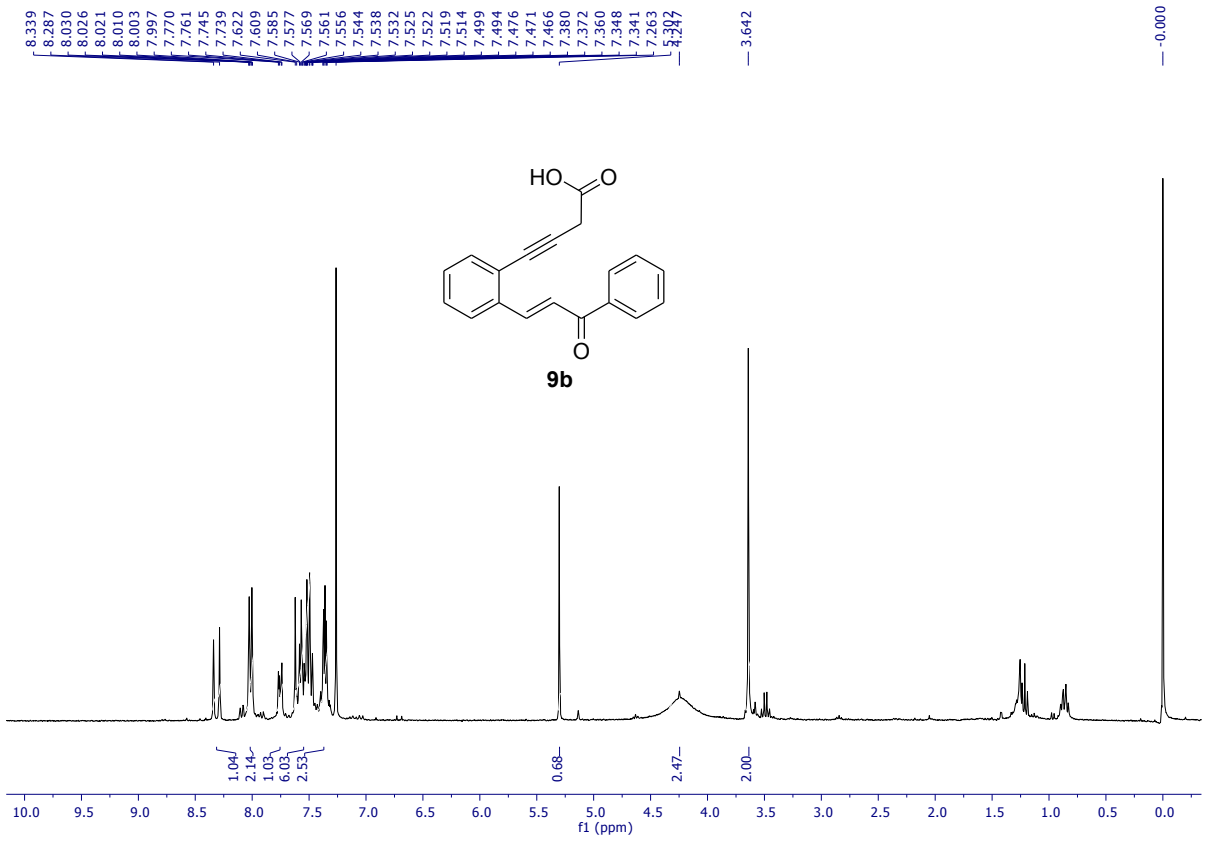

167.73
143.18
135.56
132.73
129.78
128.12
126.03
124.46
118.81
93.81
79.72
77.53
77.11
76.69
61.06
51.87
23.99
OH
OMe
O
15o
f1 (ppm)

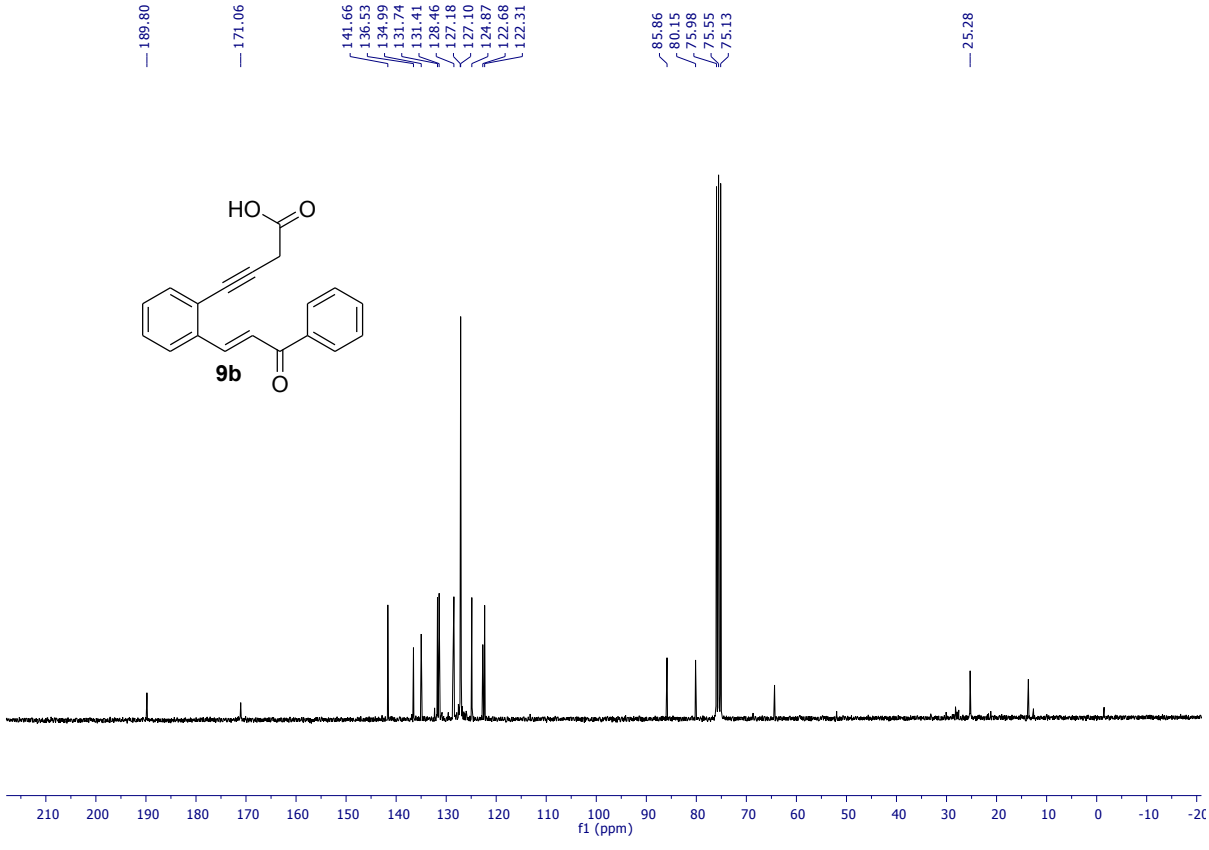

8.170
8.116
7.679
7.666
7.657
7.652
7.644
7.642
7.635
7.514
7.506
7.498
7.493
7.483
7.361
7.359
7.352
7.346
7.343
7.337
7.329
7.264
6.781
6.726
4.884
3.677
2.444
-0.000
HO
O
Me
O
1.10
1.10
1.14
2.15
1.07
1.47
2.00
2.95
f1 (ppm)

9a

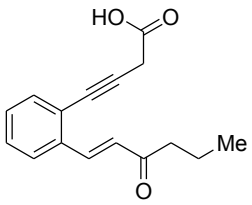

200.00
172.69
142.16
136.05
132.85
130.02
128.72
126.03
123.89
87.13
81.59
77.45
77.03
76.61
26.87
26.70
HO
O
Me
O
f1 (ppm)

9a

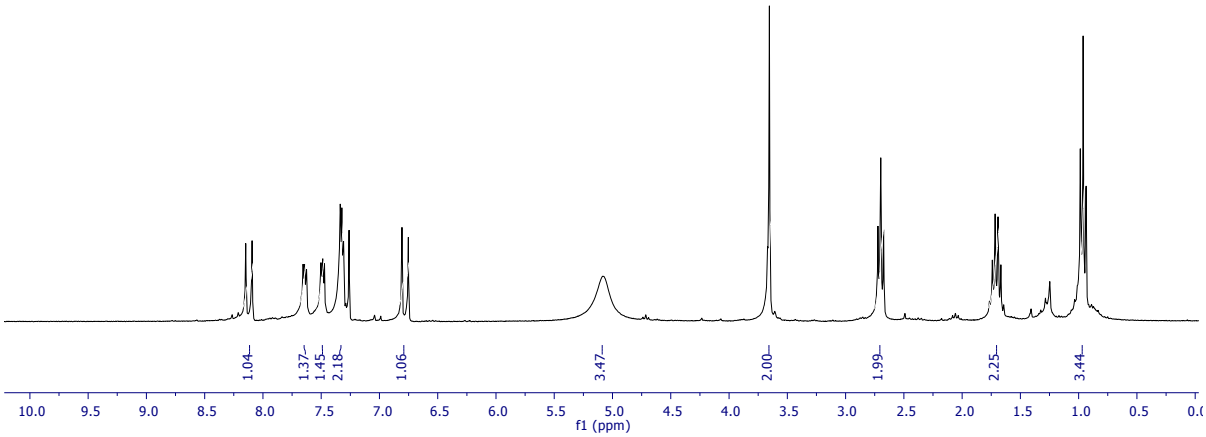

8.339
8.287
8.030
8.026
8.021
8.010
8.003
7.997
7.770
7.761
7.745
7.739
7.622
7.609
7.585
7.577
7.569
7.561
7.556
7.544
7.538
7.532
7.525
7.522
7.519
7.514
7.499
7.494
7.476
7.471
7.466
7.380
7.372
7.360
7.348
7.341
7.263
5.302
4.247
3.642
-0.000
HO
O
O
9b
1.04
2.14
1.03
6.03
2.53
0.68
2.47
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


189.80
171.06
141.66
136.53
134.99
131.74
131.41
128.46
127.18
127.10
124.87
122.68
122.31
85.86
80.15
75.98
75.55
75.13
25.28
HO
O
O
9b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

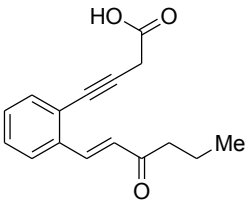

8.148
8.093
7.656
7.647
7.642
7.632
7.625
7.519
7.512
7.502
7.494
7.486
7.481
7.472
7.354
7.340
7.336
7.331
7.323
7.314
7.307
7.261
6.807
6.753
5.081
3.654
2.722
2.698
2.674
1.741
1.716
1.692
1.667
0.986
0.961
0.937


HO
O
Me
O

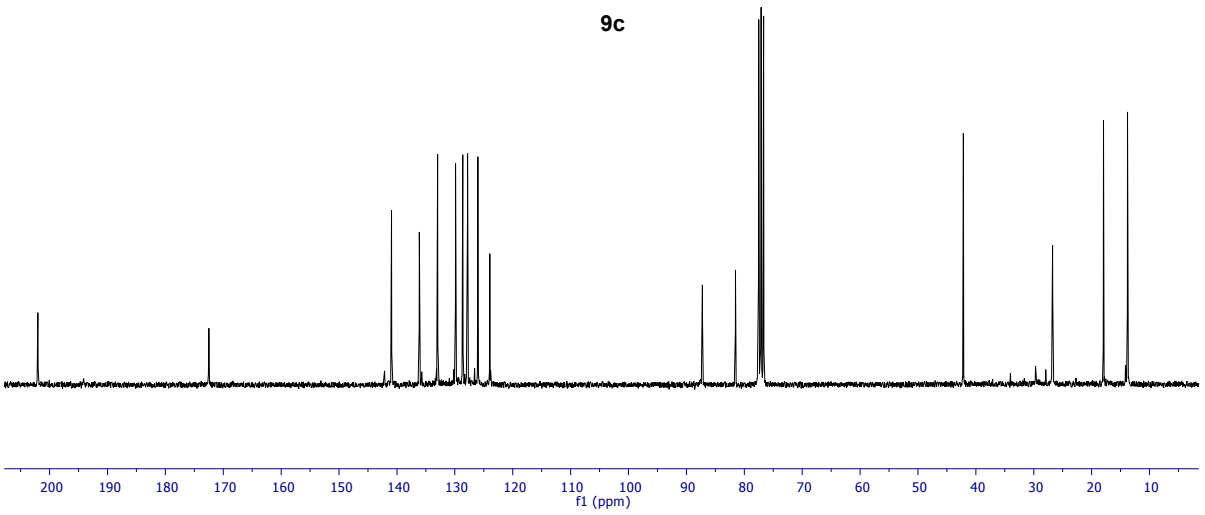
9c

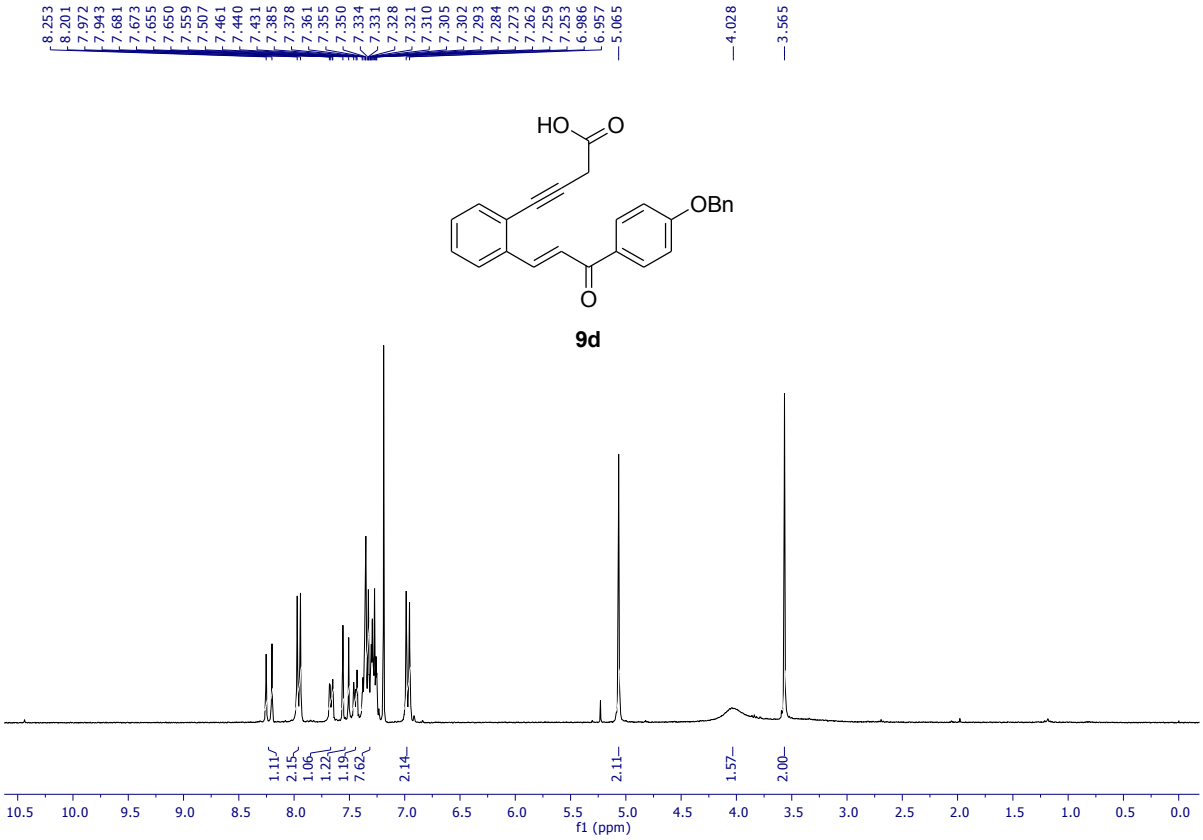

1.04
1.37
1.45
2.18
1.06
3.47
2.00
1.99
2.25
3.44
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


202.02
172.49
140.94
136.14
132.97
129.87
128.63
127.81
126.02
123.96
87.24
81.53
77.51
77.09
76.66
42.16
26.74
17.95
13.80

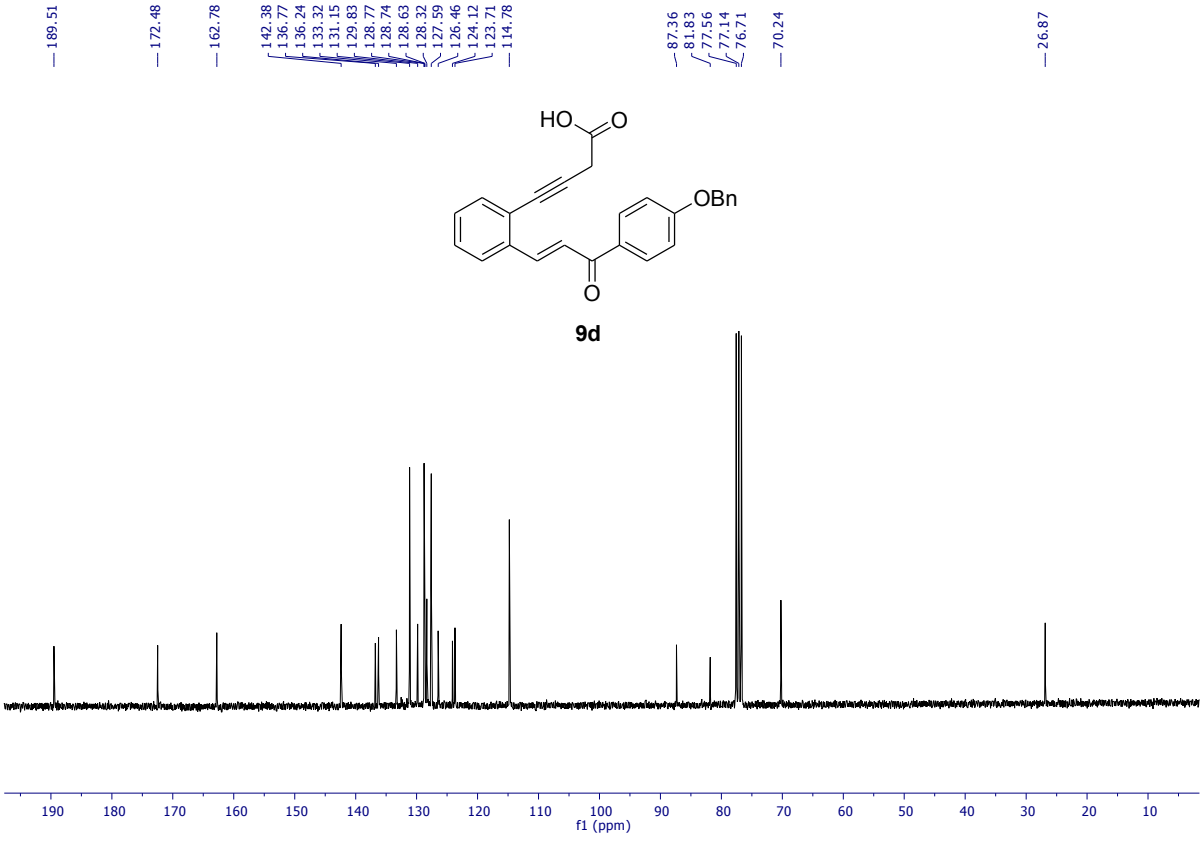

HO
O
Me
O

9c

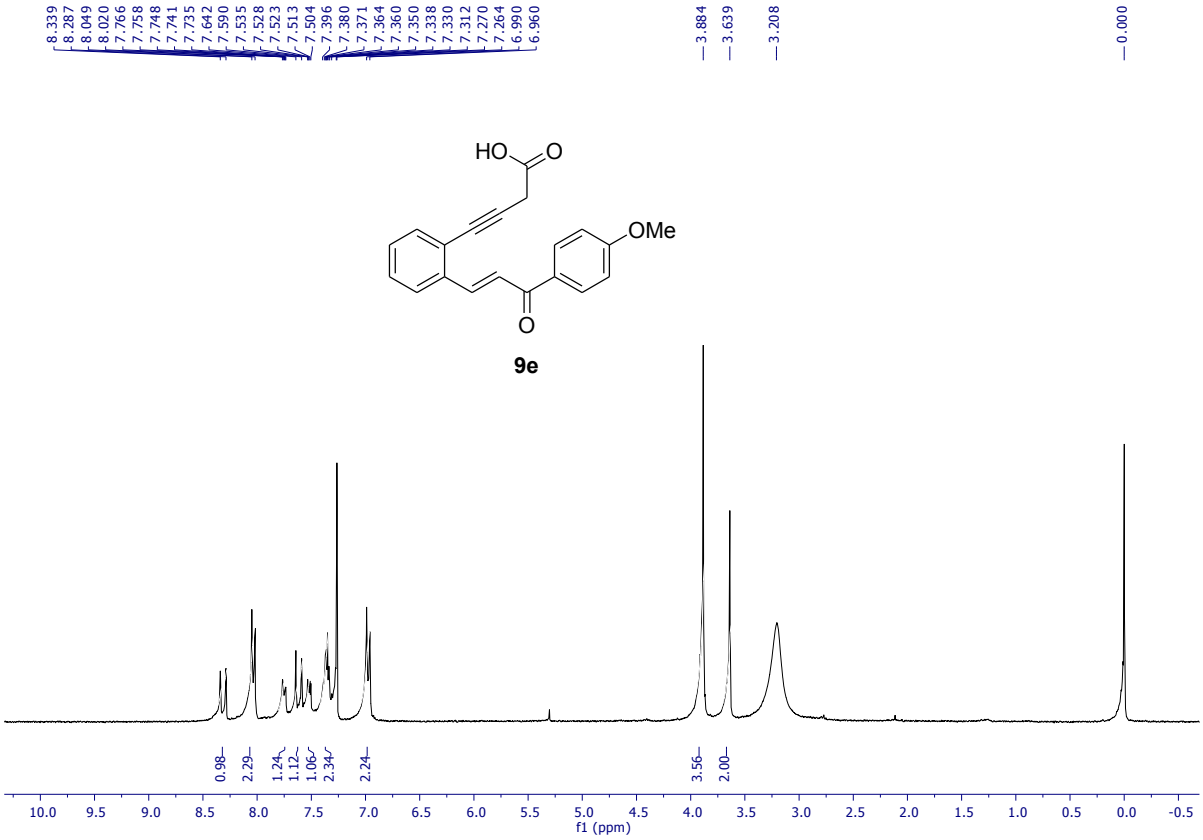

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

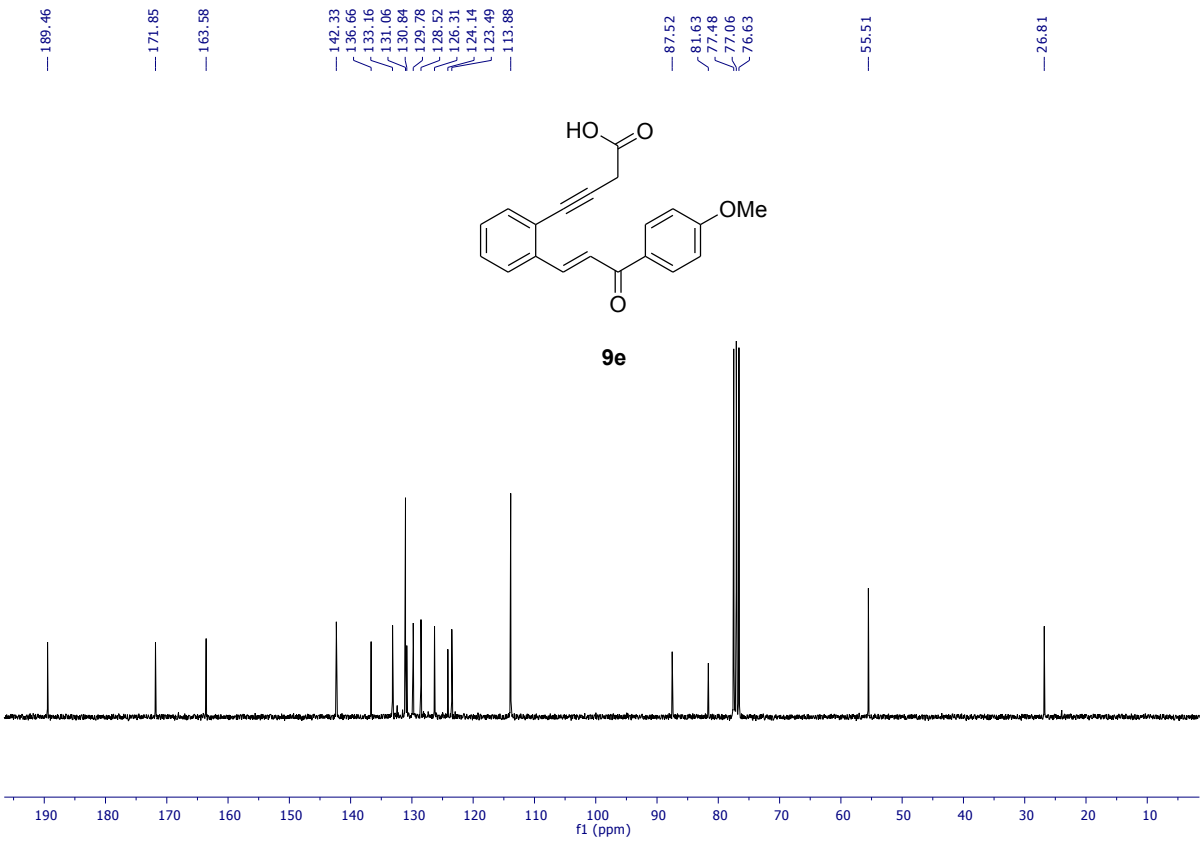

8.253
8.201
7.972
7.943
7.681
7.673
7.655
7.650
7.559
7.507
7.461
7.440
7.431
7.385
7.378
7.361
7.355
7.350
7.334
7.331
7.328
7.321
7.310
7.305
7.302
7.293
7.284
7.273
7.262
7.259
7.253
6.986
6.957
5.065
4.028
3.565
HO
O
OBn
O
1.11
2.15
1.06
1.22
1.19
7.62
2.14
2.11
1.57
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

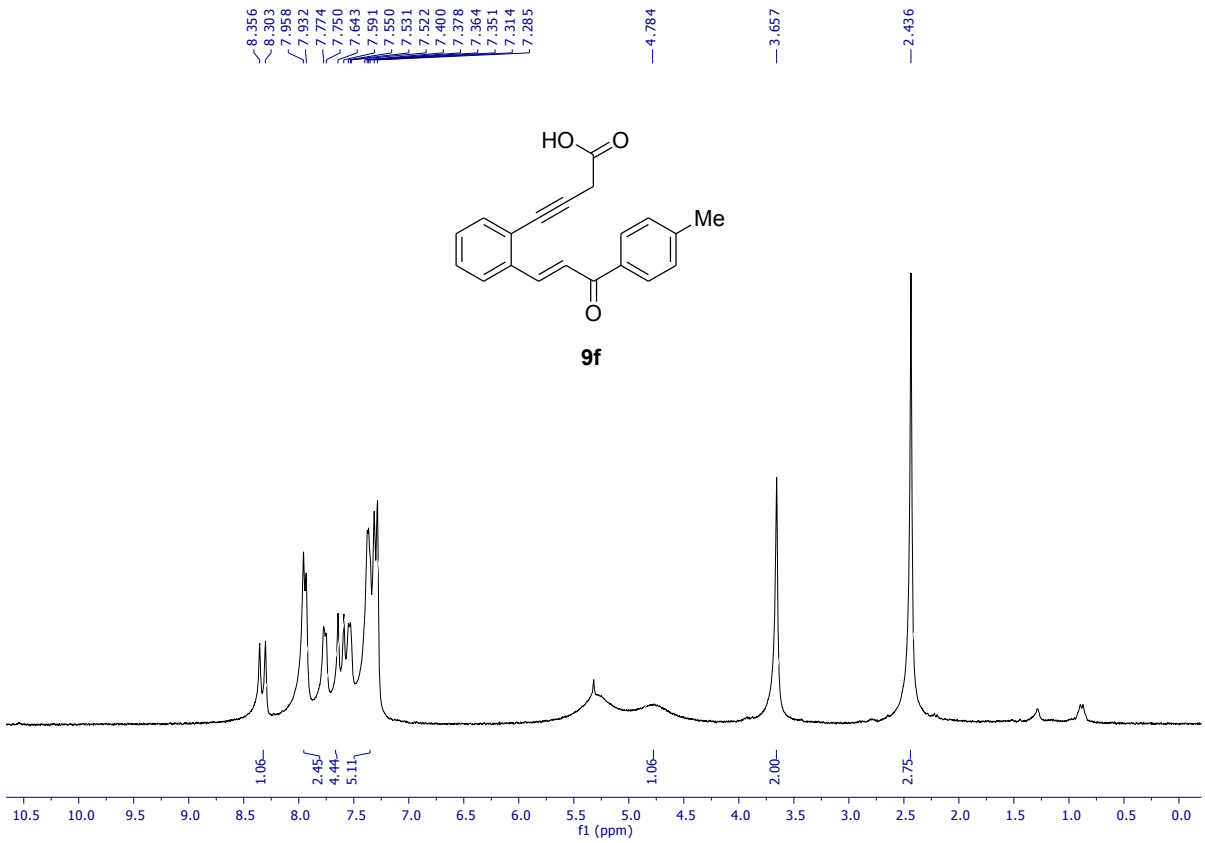
9d


189.51
172.48
162.78
142.38
136.77
136.24
133.32
131.15
129.83
128.77
128.74
128.63
128.32
127.59
126.46
124.12
123.71
114.78
87.36
81.83
77.56
77.14
76.71
70.24
26.87
HO
O
OBn
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

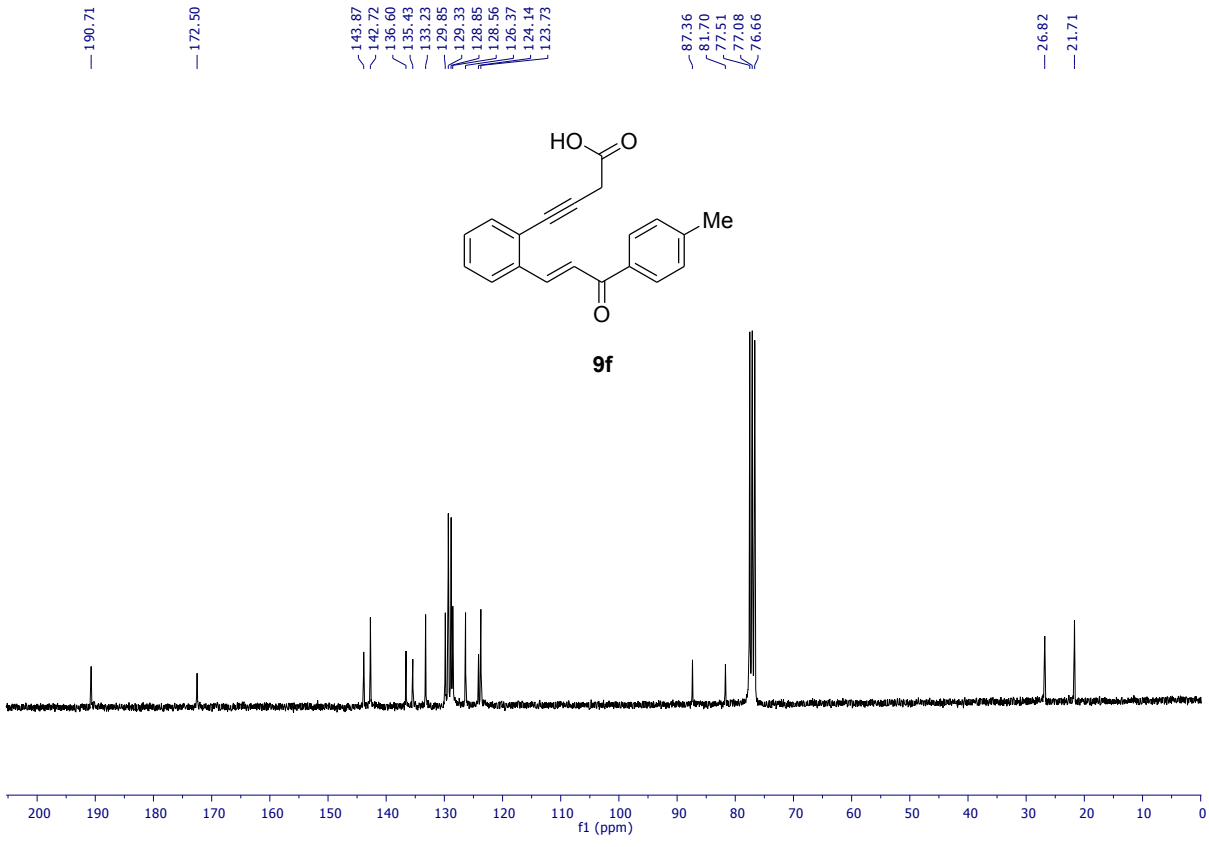
9d


8.339
8.287
8.049
8.020
7.766
7.758
7.748
7.741
7.735
7.642
7.590
7.535
7.528
7.523
7.513
7.504
7.396
7.380
7.371
7.364
7.360
7.350
7.338
7.330
7.312
7.270
7.264
6.990
6.960
3.884
3.639
3.208
0.000
HO
O
OMe
O
9e
0.98
2.29
1.24
1.12
1.06
2.34
2.24
3.56
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

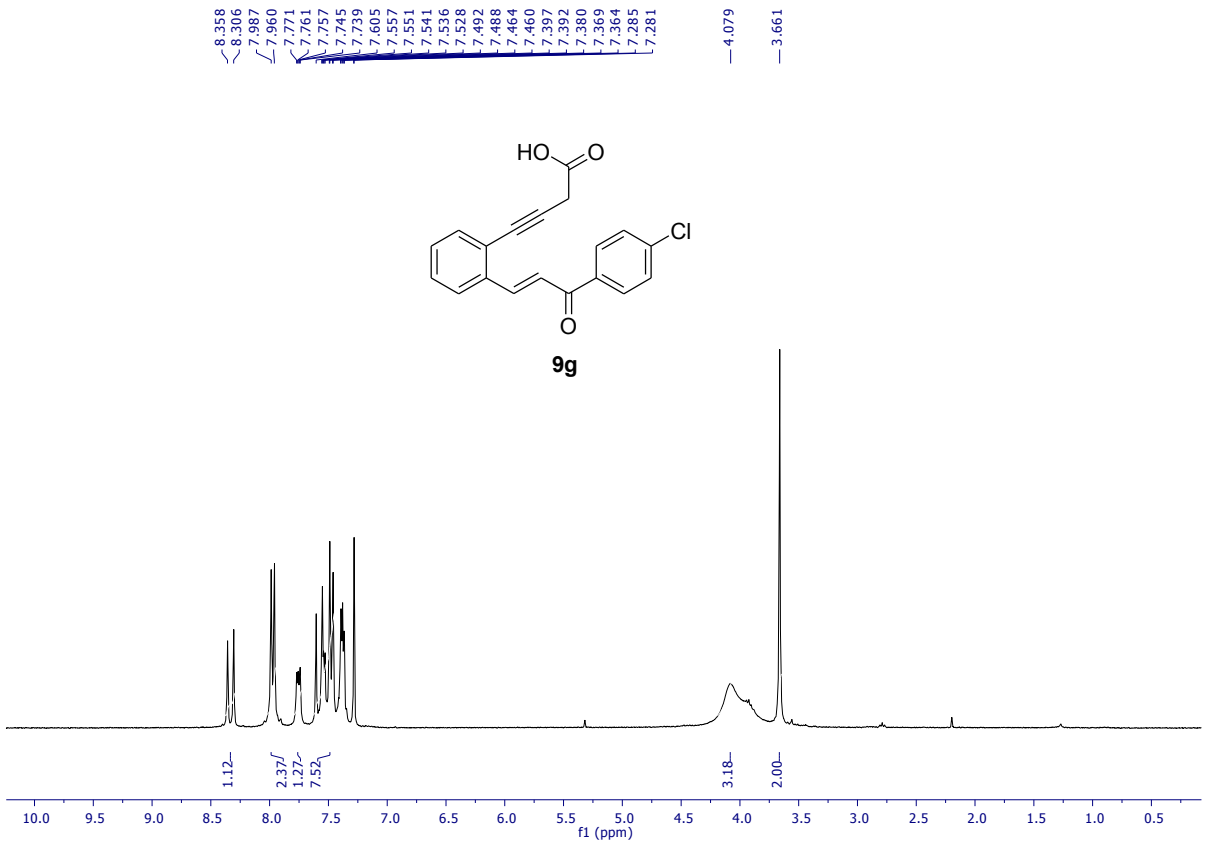

189.46
171.85
163.58
142.33
136.66
133.16
131.06
130.84
129.78
128.52
126.31
124.14
123.49
113.88
87.52
81.63
77.48
77.06
76.63
55.51
26.81
HO
O
OMe
O
9e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


8.356
8.303
7.958
7.932
7.774
7.750
7.643
7.591
7.550
7.531
7.522
7.400
7.378
7.364
7.351
7.314
7.285
4.784
3.657
2.436
HO
O
Me
O
1.06
2.45
4.44
5.11
1.06
2.00
2.75
f1 (ppm)

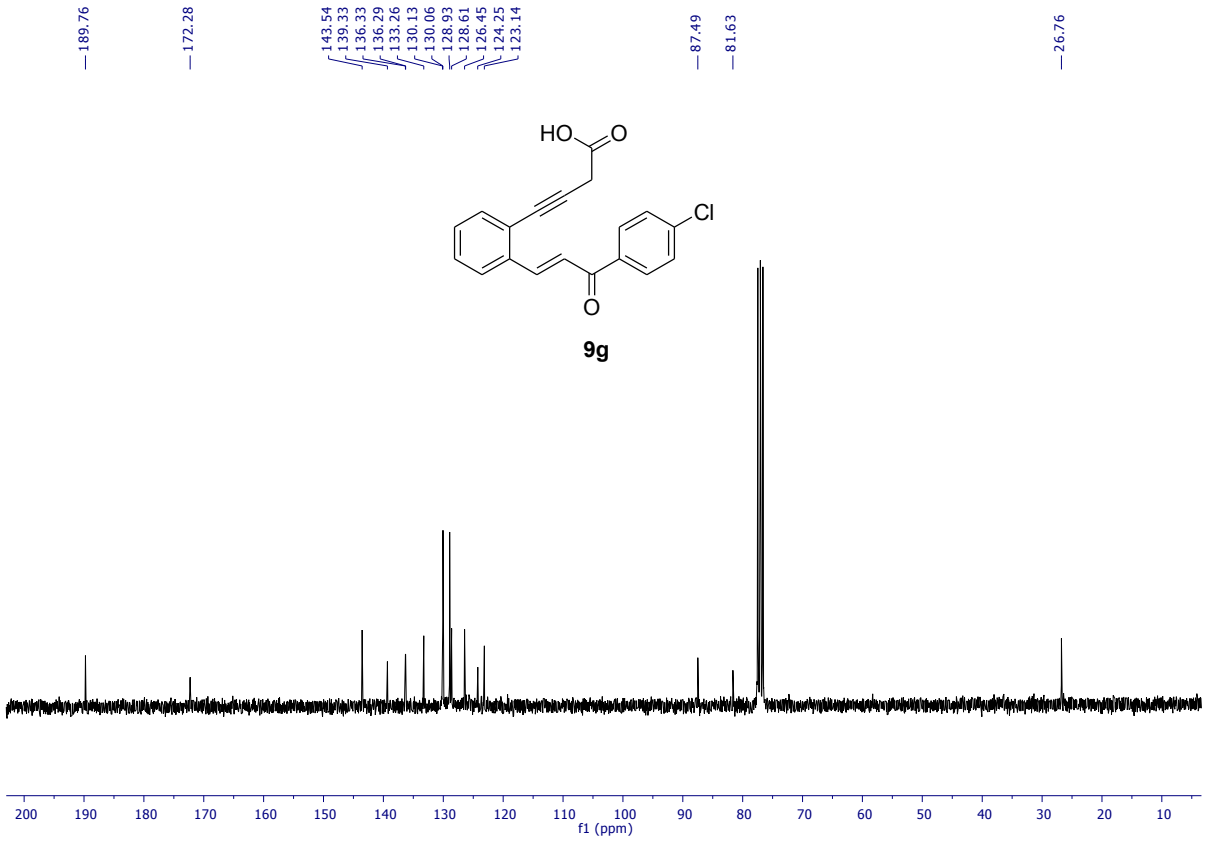
9f


190.71
172.50
143.87
142.72
136.60
135.43
133.23
129.85
129.33
128.85
128.56
126.37
124.14
123.73
87.36
81.70
77.51
77.08
76.66
26.82
21.71
HO
O
Me
O
f1 (ppm)

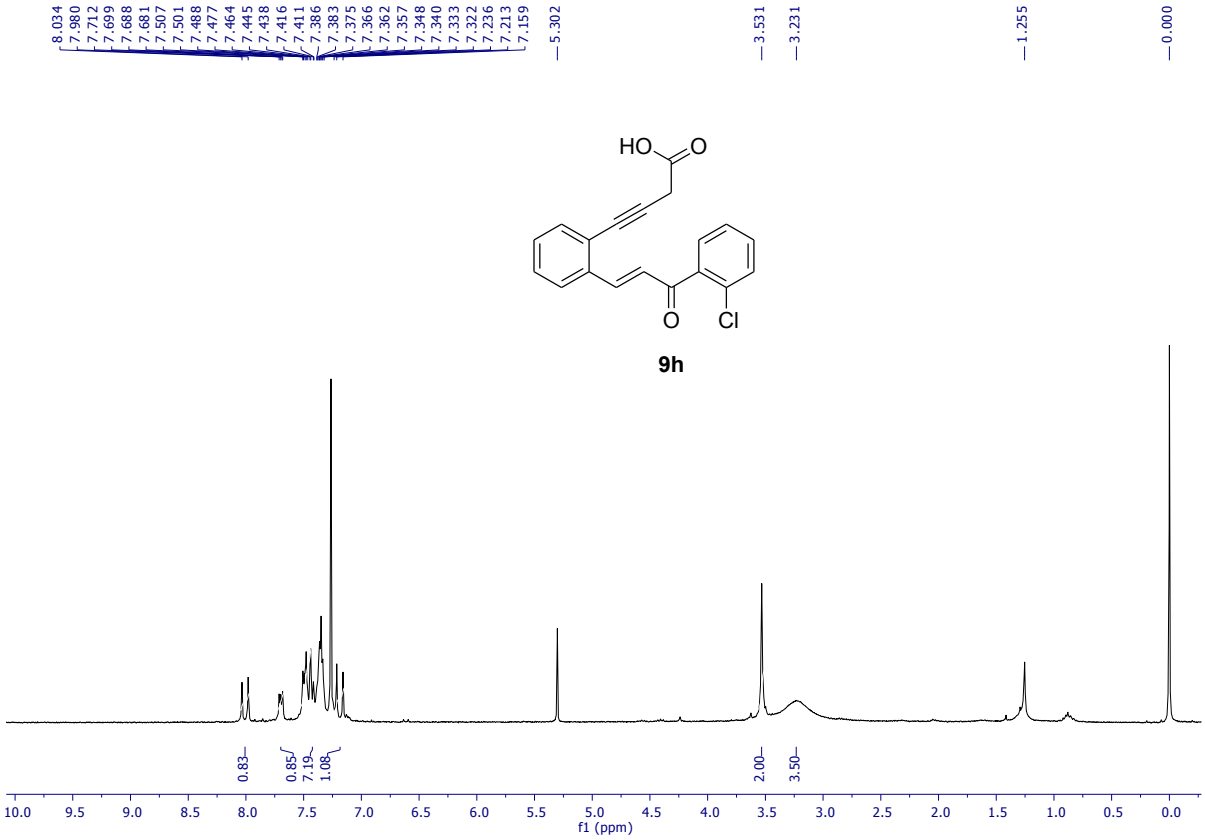
9f


8.358
8.306
7.987
7.960
7.771
7.761
7.757
7.745
7.739
7.605
7.557
7.551
7.541
7.536
7.528
7.492
7.488
7.464
7.460
7.397
7.392
7.380
7.369
7.364
7.285
7.281
4.079
3.661
HO
O
Cl
O
1.12
2.37
1.27
7.52
3.18
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

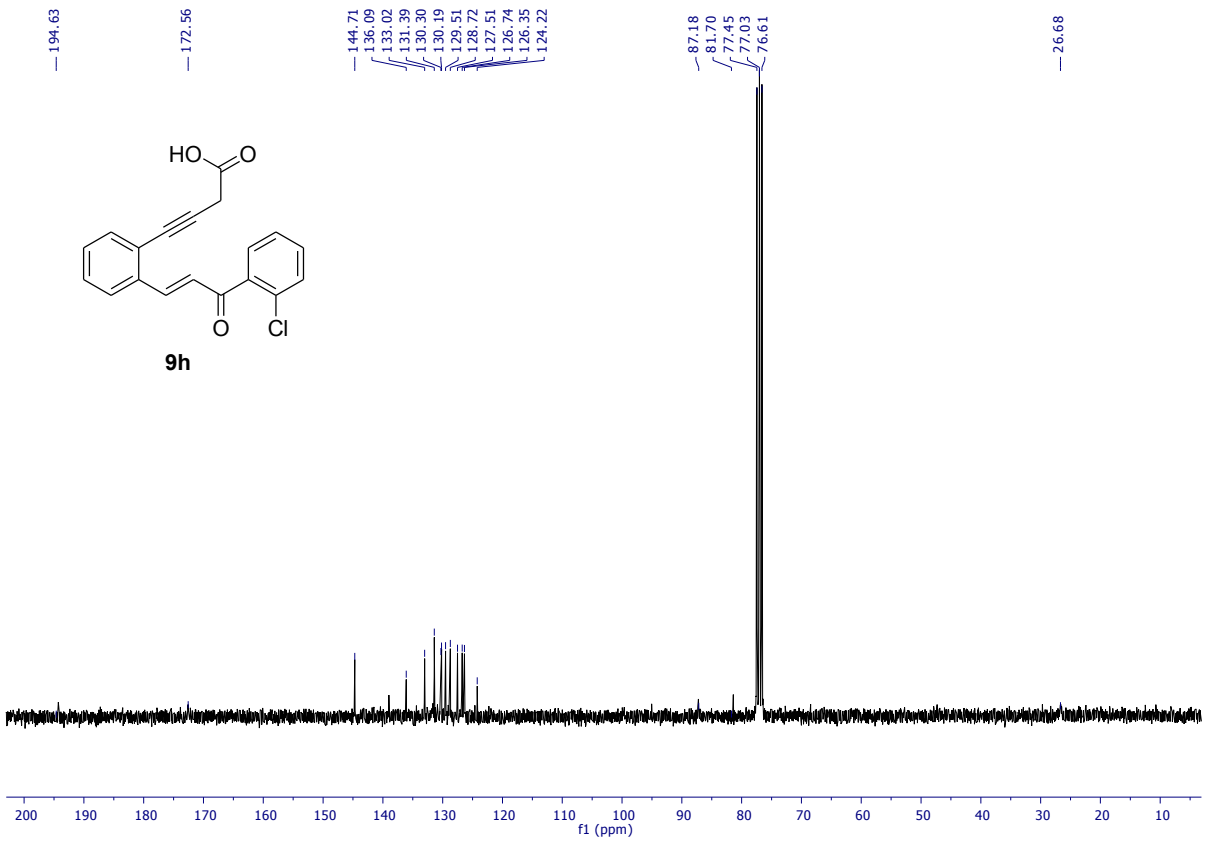
9g


189.76
172.28
143.54
139.33
136.33
136.29
133.26
130.13
130.06
128.93
128.61
126.45
124.25
123.14
87.49
81.63
26.76
HO
O
Cl
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

9g

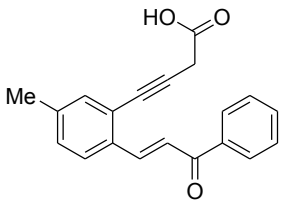

8.034
7.980
7.712
7.699
7.688
7.681
7.507
7.501
7.488
7.477
7.464
7.445
7.438
7.416
7.411
7.386
7.383
7.375
7.366
7.362
7.357
7.348
7.340
7.333
7.322
7.236
7.213
7.159
5.302
3.531
3.231
1.255
0.000
HO
O
O
Cl
0.83
0.85
7.19
1.08
2.00
3.50
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

9h

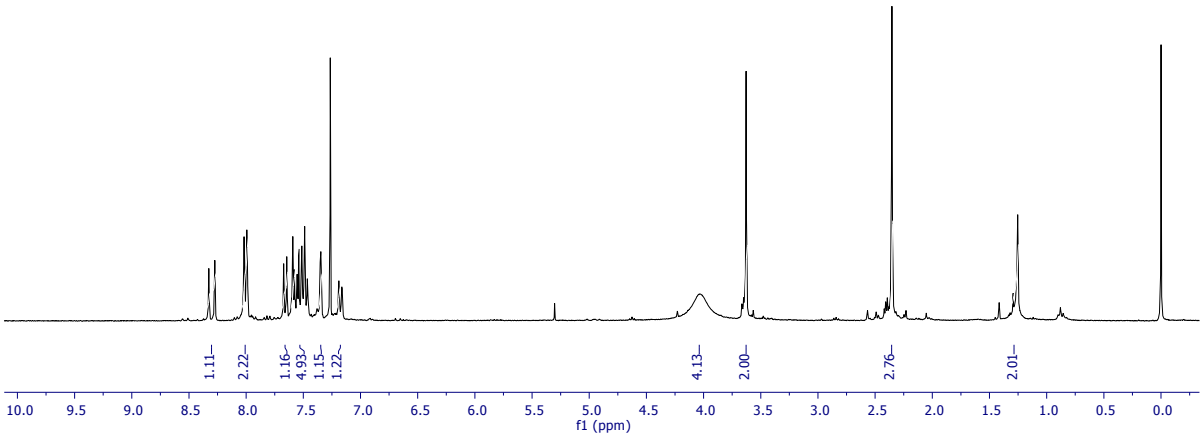

194.63
172.56
144.71
136.09
133.02
131.39
130.30
130.19
129.51
128.72
127.51
126.74
126.35
124.22
87.18
81.70
77.45
77.03
76.61
26.68
HO
O
O
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

9h

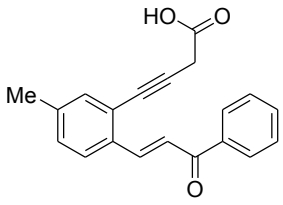

8.326
8.274
8.022
8.018
8.013
8.001
7.994
7.989
7.672
7.645
7.607
7.603
7.592
7.578
7.570
7.559
7.554
7.549
7.540
7.516
7.514
7.509
7.494
7.488
7.470
7.465
7.460
7.346
7.264
7.192
7.186
7.165
7.158
4.031
3.628
2.353
1.254
-0.000


HO
O
Me
O

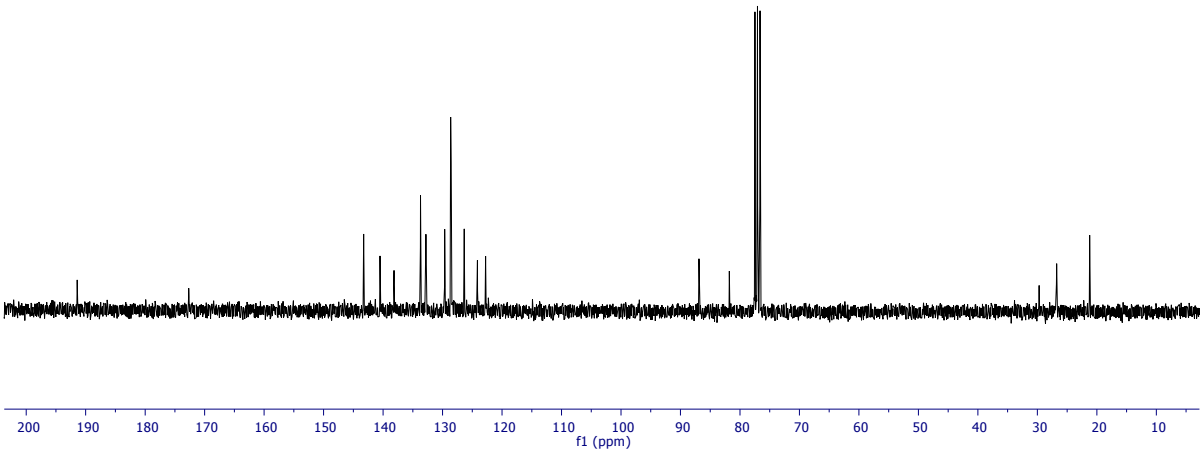
9i

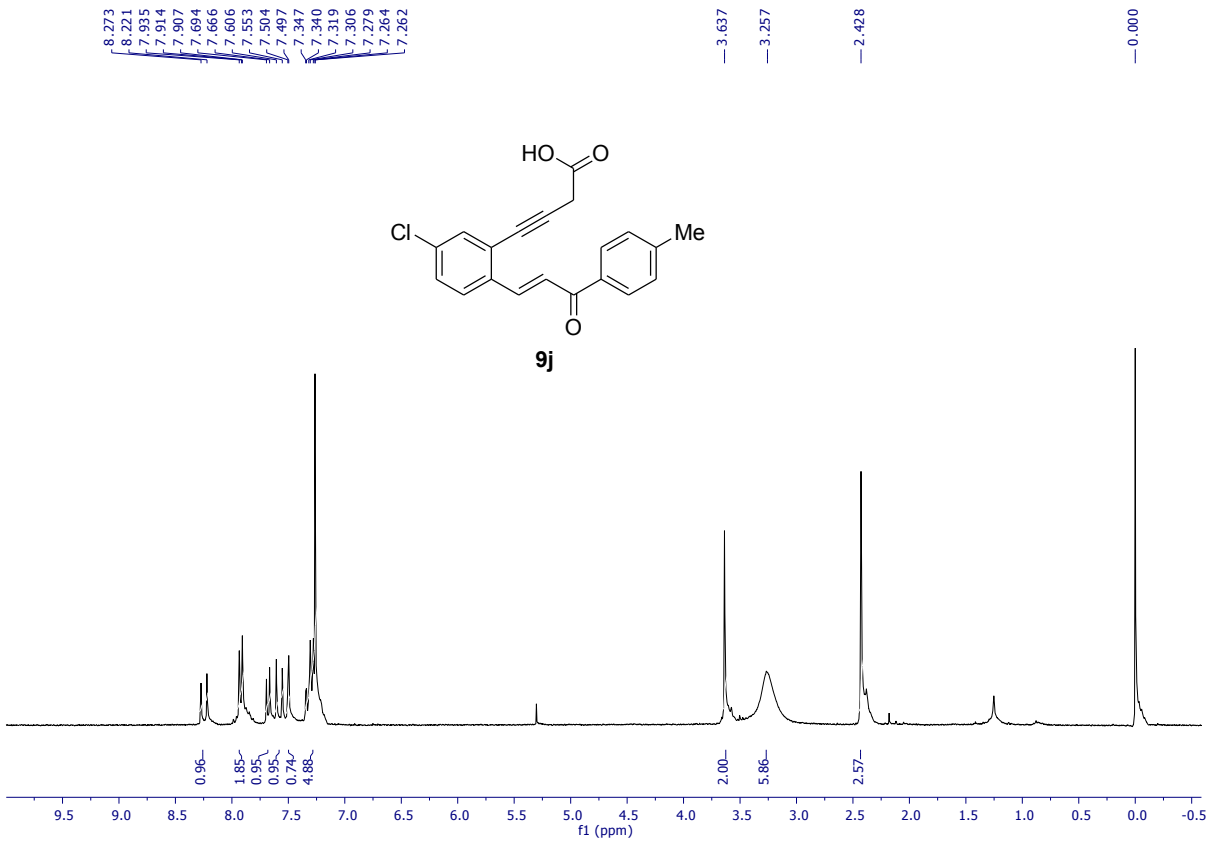

1.11
2.22
1.16
4.93
1.15
1.22
4.13
2.00
2.76
2.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

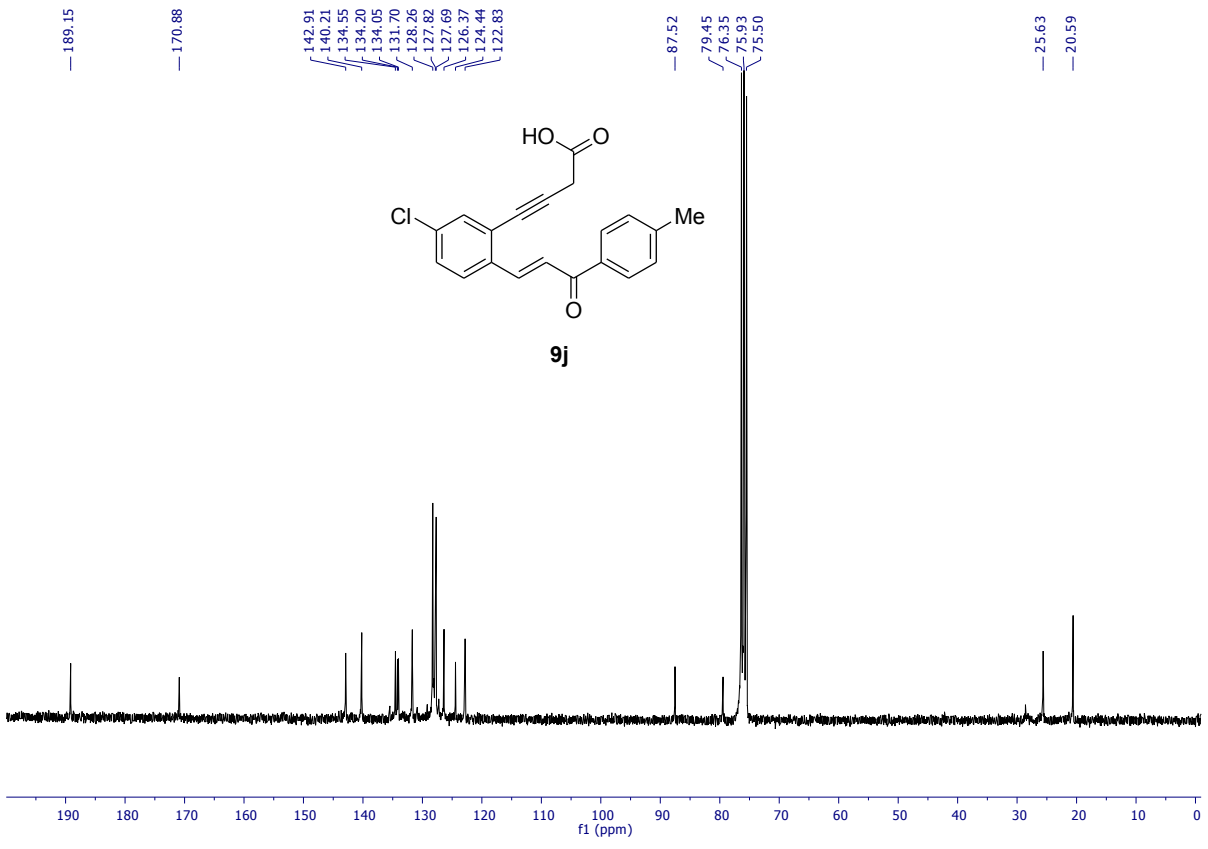

191.42
172.68
143.26
140.52
138.16
133.71
132.80
129.64
128.64
128.56
126.35
124.14
122.77
86.88
81.79
77.48
77.05
76.63
26.77
21.21

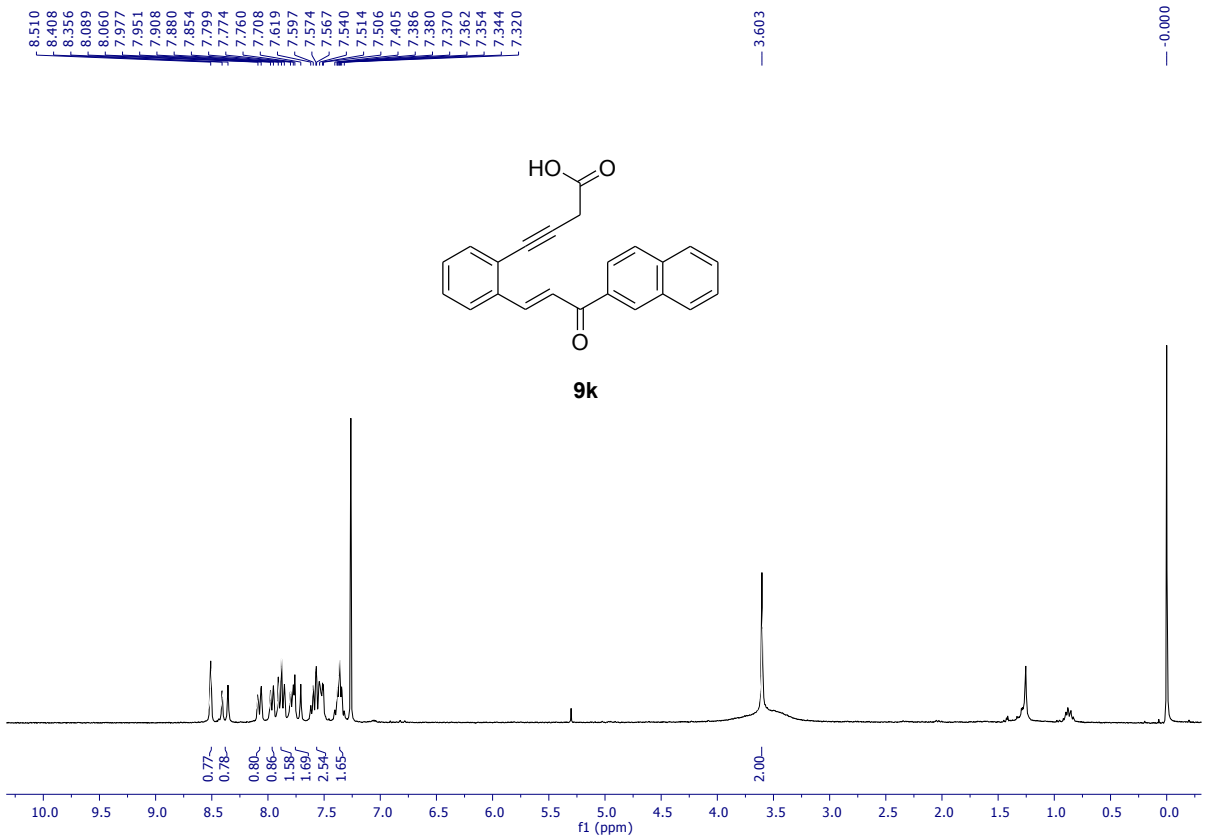

HO
O
Me
O

9i

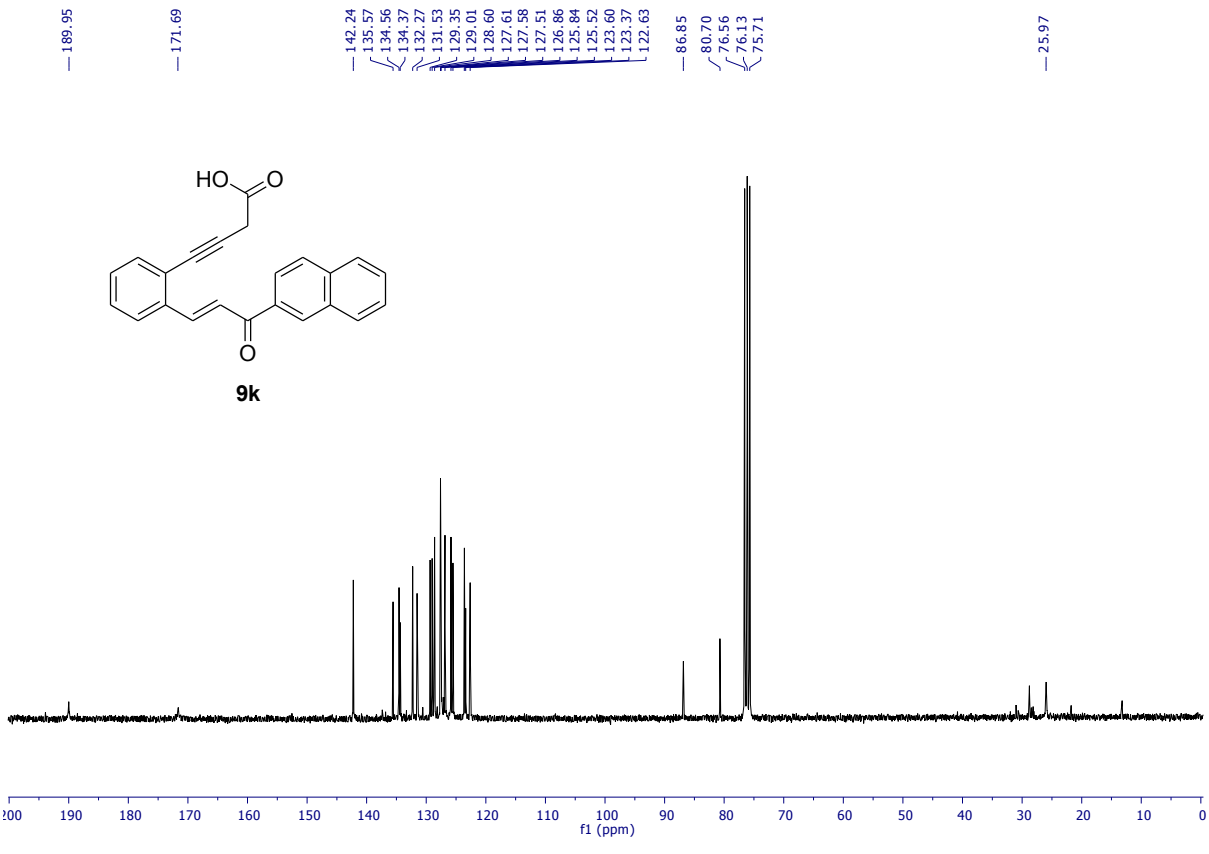

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.273
8.221
7.935
7.914
7.907
7.694
7.666
7.606
7.553
7.504
7.497
7.347
7.340
7.319
7.306
7.279
7.264
7.262
3.637
3.257
2.428
0.000
HO
O
Cl
Me
O
9j
0.96
1.85
0.95
0.95
0.74
4.88
2.00
5.86
2.57
f1 (ppm)


189.15
170.88
142.91
140.21
134.55
134.20
134.05
131.70
128.26
127.82
127.69
126.37
124.44
122.83
87.52
79.45
76.35
75.93
75.50
25.63
20.59
HO
O
Cl
Me
O
9j
f1 (ppm)

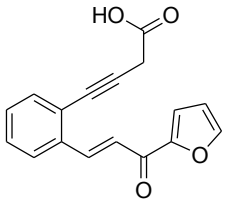

8.510
8.408
8.356
8.089
8.060
7.977
7.951
7.908
7.880
7.854
7.799
7.774
7.760
7.708
7.619
7.597
7.574
7.567
7.540
7.514
7.506
7.405
7.386
7.380
7.370
7.362
7.354
7.344
7.320
3.603
-0.000
HO
O
O
0.77
0.78
0.80
0.86
1.58
1.69
2.54
1.65
2.00
f1 (ppm)

9k

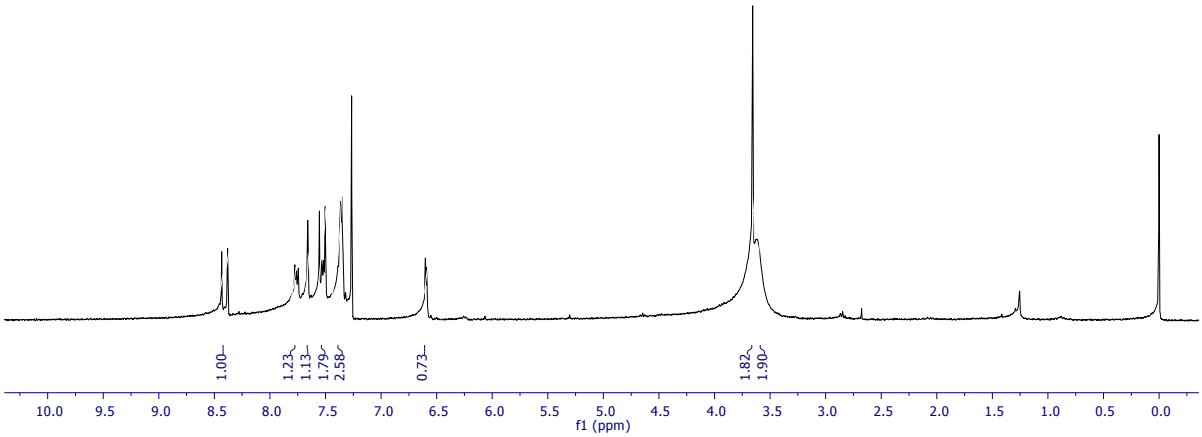

189.95
171.69
142.24
135.57
134.56
134.37
132.27
131.53
129.35
129.01
128.60
127.61
127.58
127.51
126.86
125.84
125.52
123.60
123.37
122.63
86.85
80.70
76.56
76.13
75.71
25.97
HO
O
O
f1 (ppm)

9k


8.434
8.381
7.775
7.766
7.762
7.751
7.744
7.661
7.655
7.630
7.555
7.535
7.527
7.518
7.512
7.503
7.389
7.372
7.367
7.362
7.354
7.349
7.340
7.337
7.319
7.266
6.602
6.596
6.590
6.585
3.657
0.001


HO
O
O
O

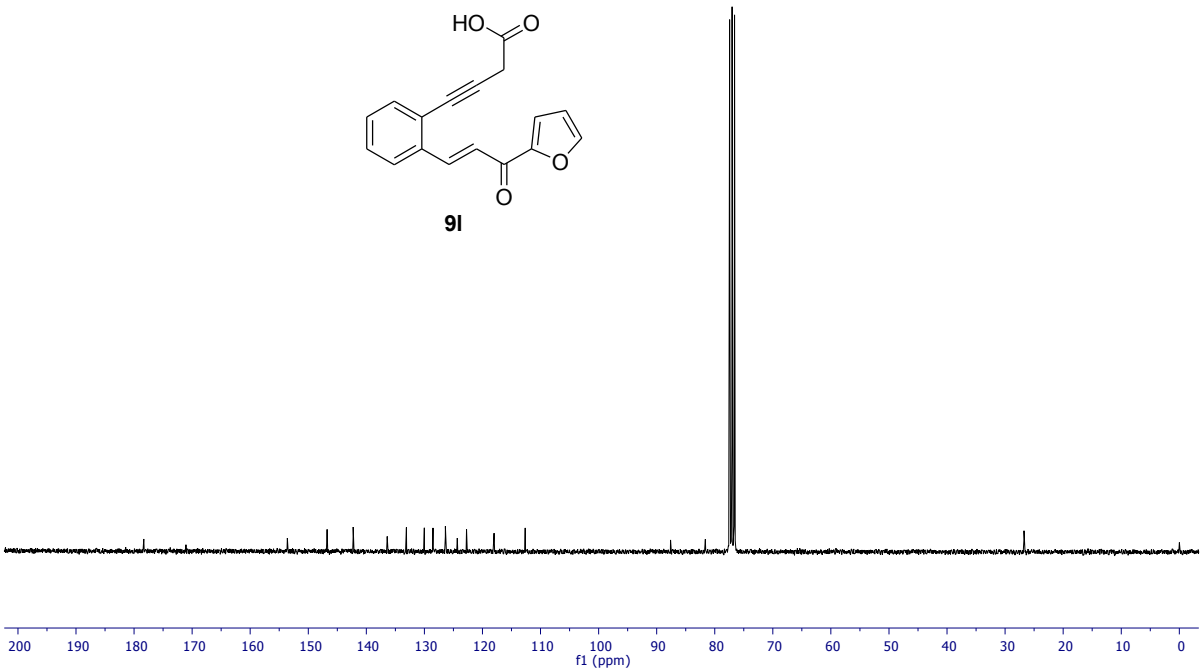
9l

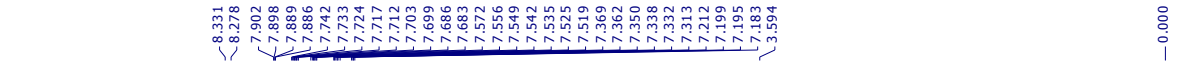

1.00
1.23
1.13
1.79
2.58
0.73
1.82
1.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

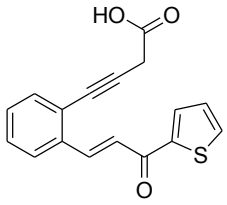

178.40
171.11
153.60
146.75
142.27
136.41
133.10
130.02
128.52
126.38
124.39
122.74
118.01
112.64
87.70
81.71
77.43
77.01
76.58
26.74

HO
O
O
O

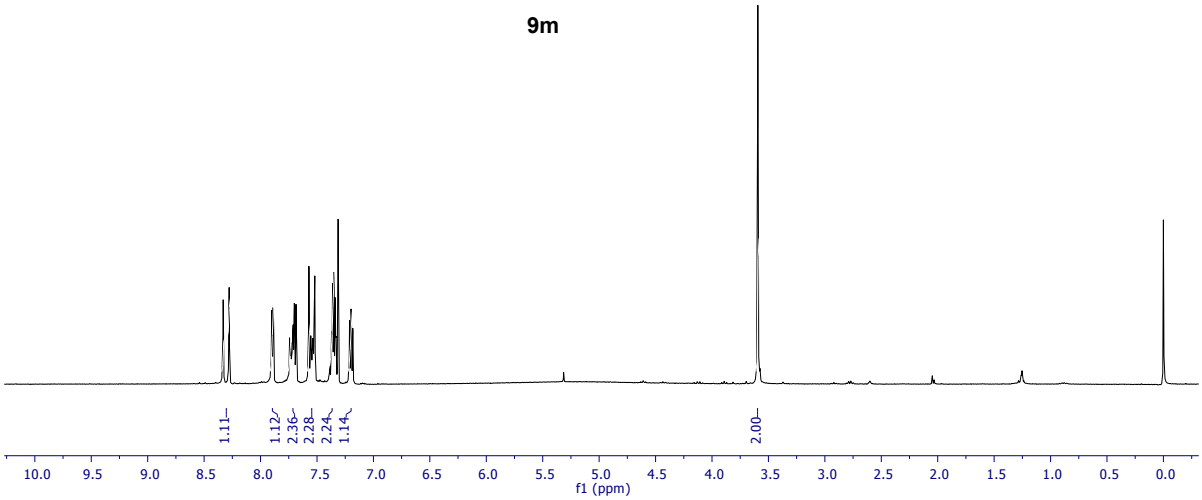
9l


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

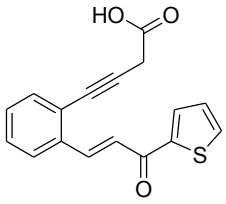

8.331
8.278
7.902
7.898
7.889
7.886
7.742
7.733
7.724
7.717
7.712
7.703
7.699
7.686
7.683
7.572
7.556
7.549
7.542
7.535
7.525
7.519
7.369
7.362
7.350
7.338
7.332
7.313
7.212
7.199
7.195
7.183
3.594
0.000


HO
O
S
O

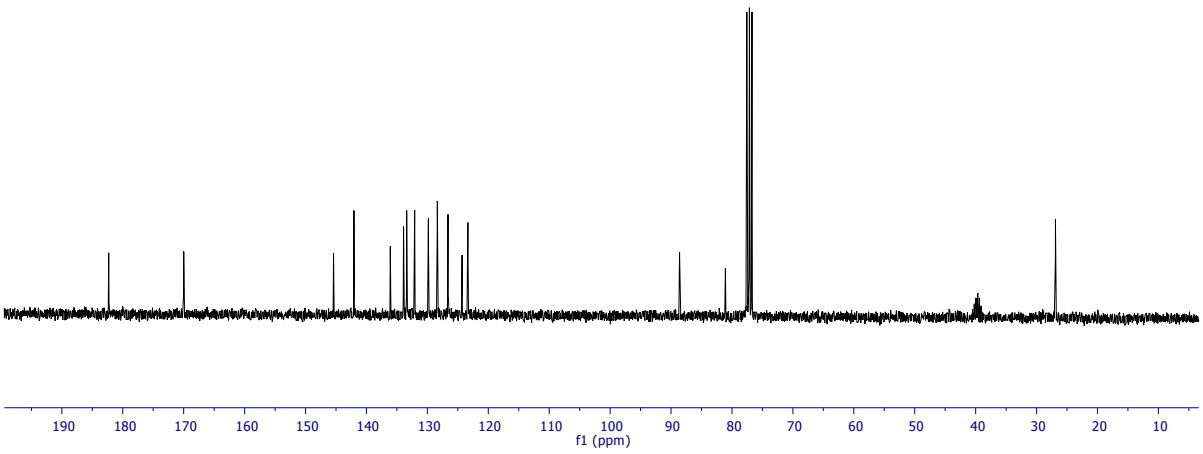
9m

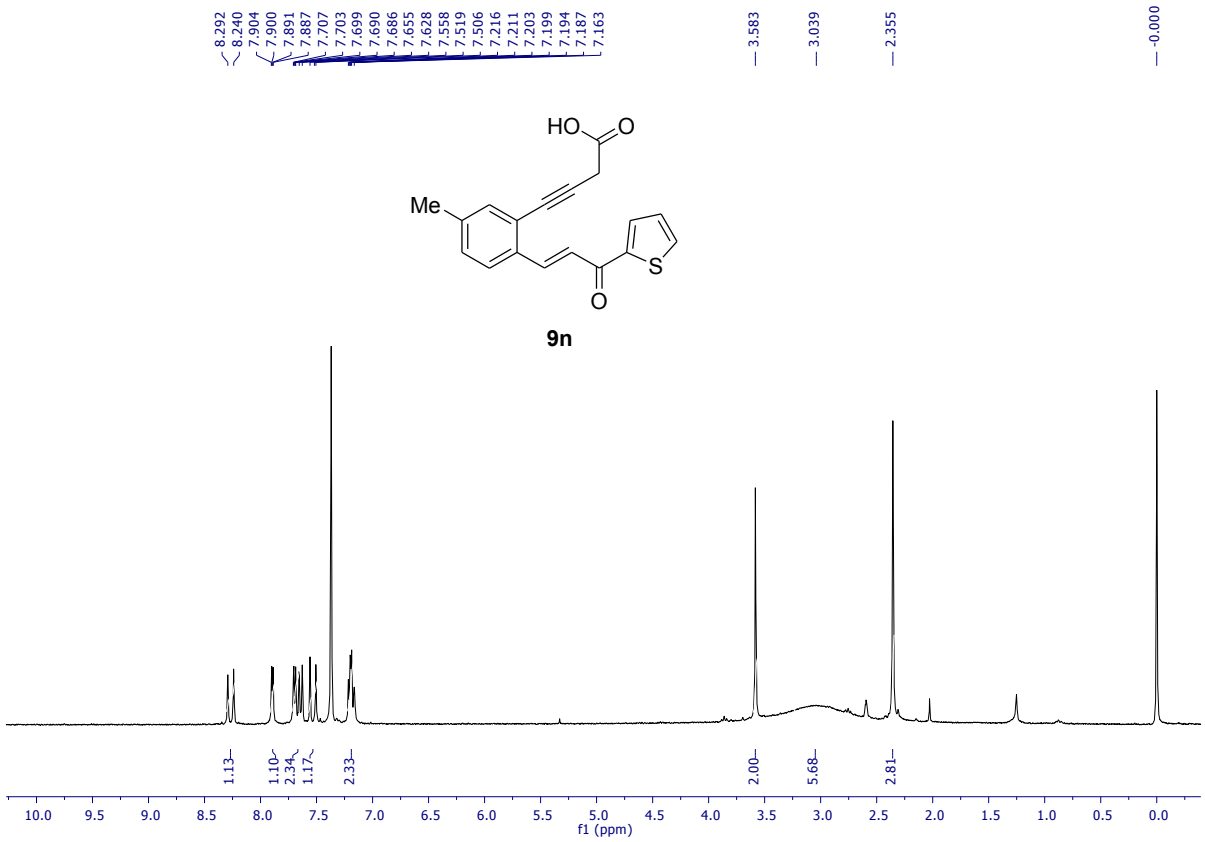

1.11
1.12
2.36
2.28
2.24
1.14
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


182.30
169.99
145.40
142.06
136.08
133.92
133.40
132.09
129.83
128.38
128.32
126.61
124.30
123.34
88.61
81.08
77.56
77.13
76.71
26.90

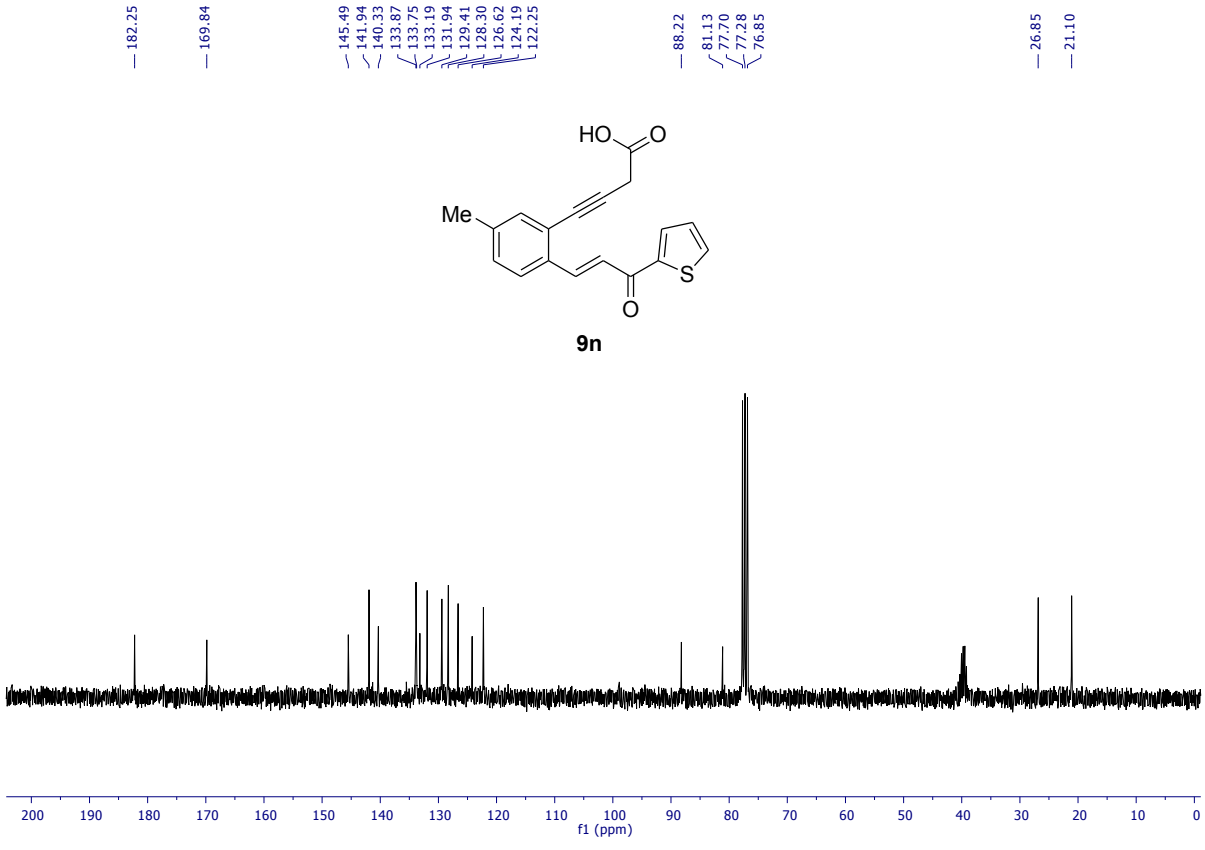

HO
O
S
O

9m

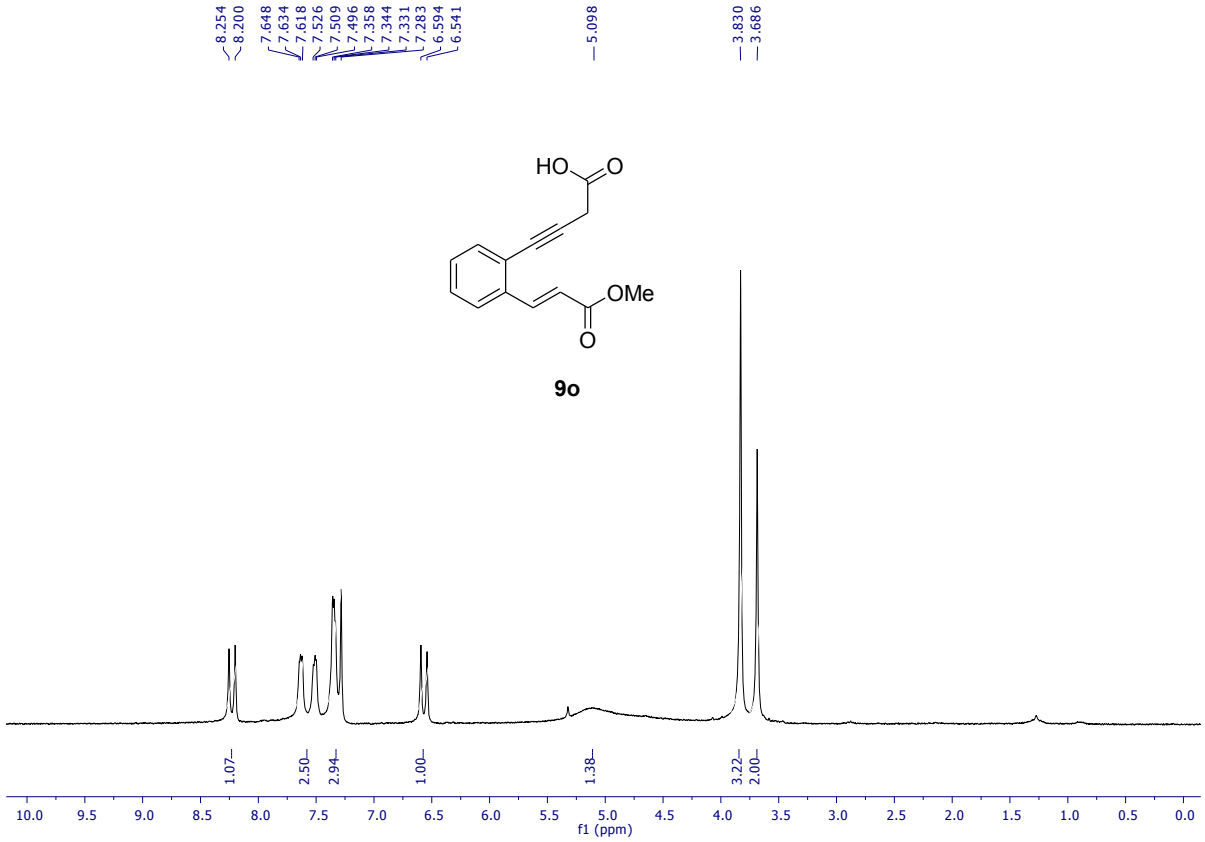

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.292
8.240
7.904
7.900
7.891
7.887
7.707
7.703
7.699
7.690
7.686
7.655
7.628
7.558
7.519
7.506
7.216
7.211
7.203
7.199
7.194
7.187
7.163
3.583
3.039
2.355
-0.000
HO
O
Me
S
O
1.13
1.10
2.34
1.17
2.33
2.00
5.68
2.81
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

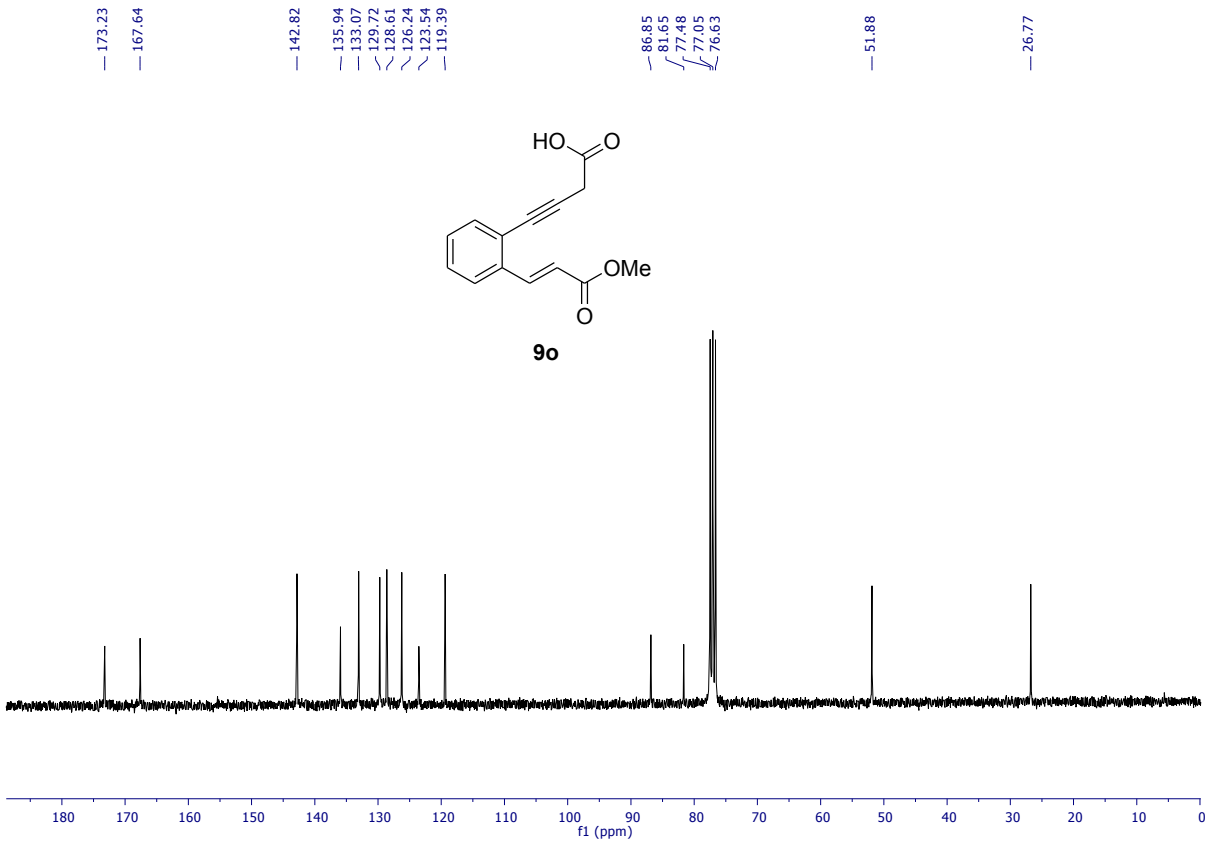
9n


182.25
169.84
145.49
141.94
140.33
133.87
133.75
133.19
131.94
129.41
128.30
126.62
124.19
122.25
88.22
81.13
77.70
77.28
76.85
26.85
21.10
HO
O
Me
S
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

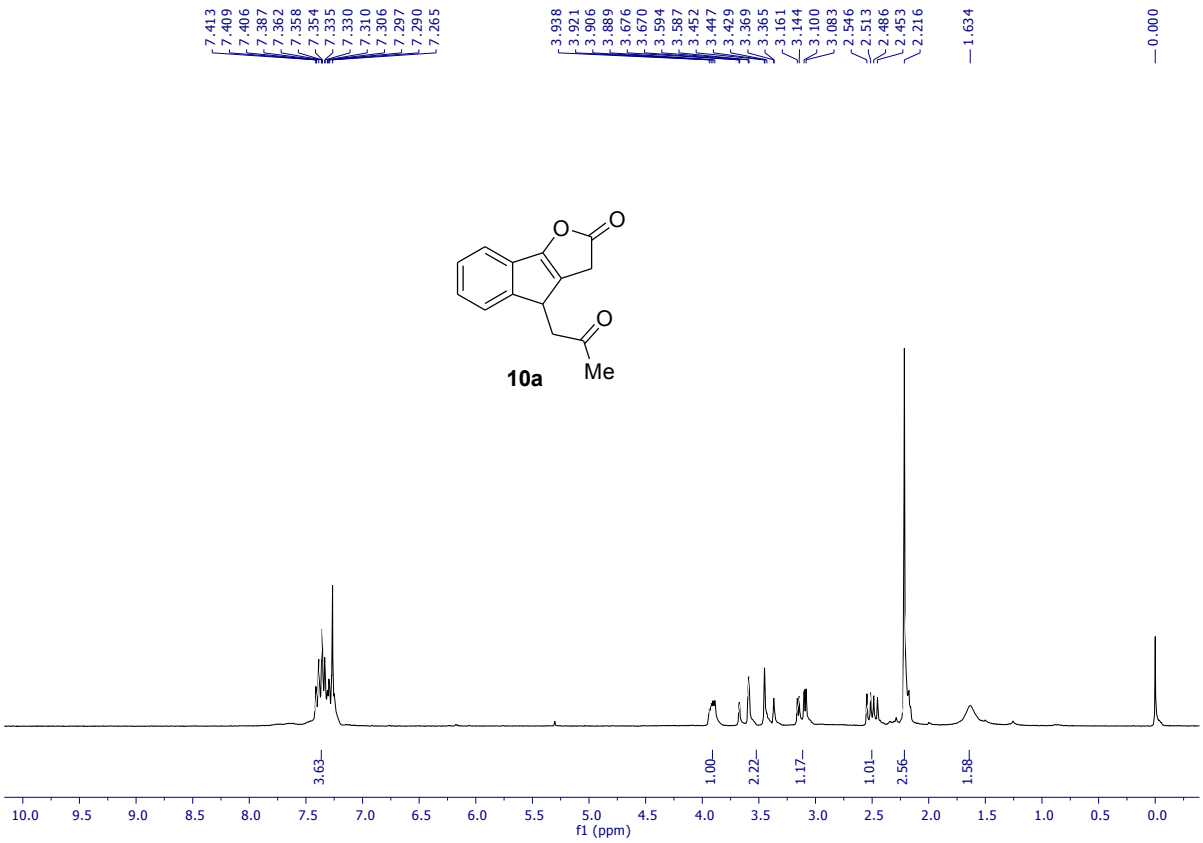
9n

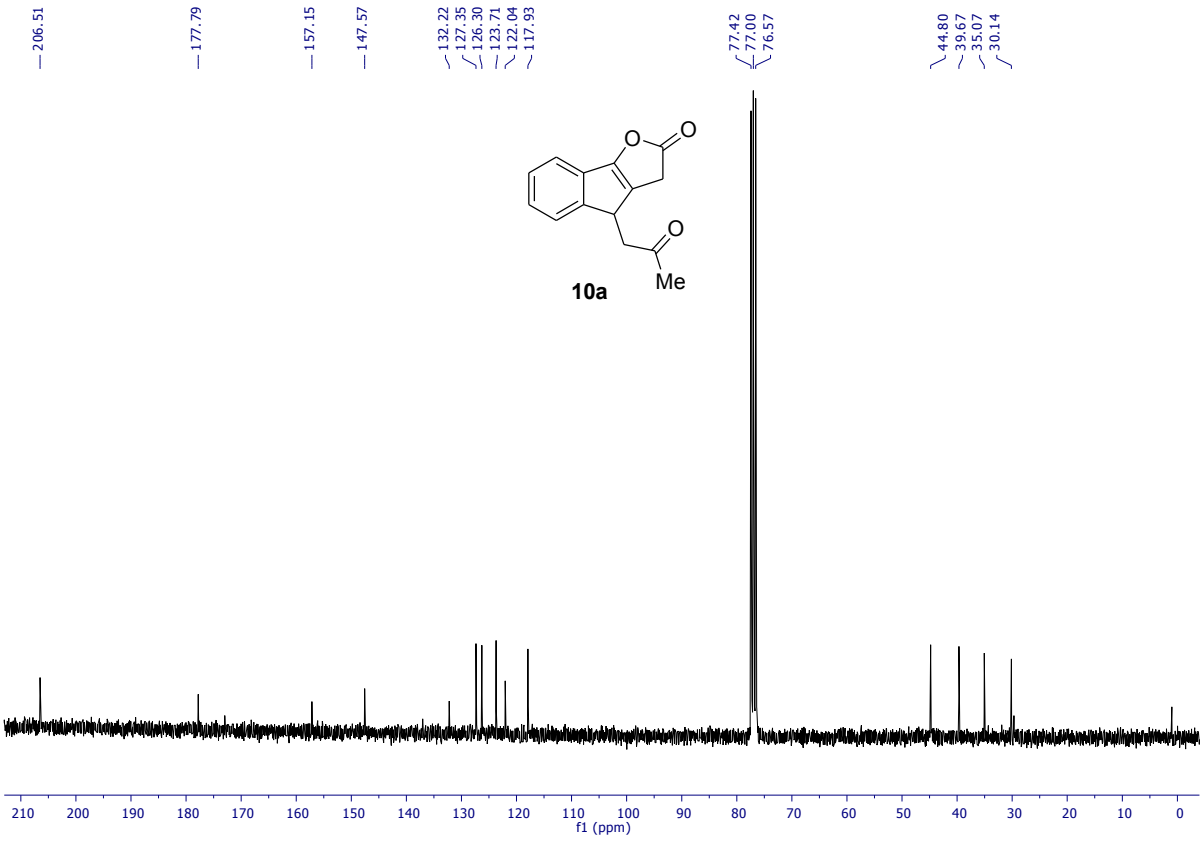

8.254
8.200
7.648
7.634
7.618
7.526
7.509
7.496
7.358
7.344
7.331
7.283
6.594
6.541
5.098
3.830
3.686
HO
O
OMe
O
1.07
2.50
2.94
1.00
1.38
3.22
2.00
f1 (ppm)

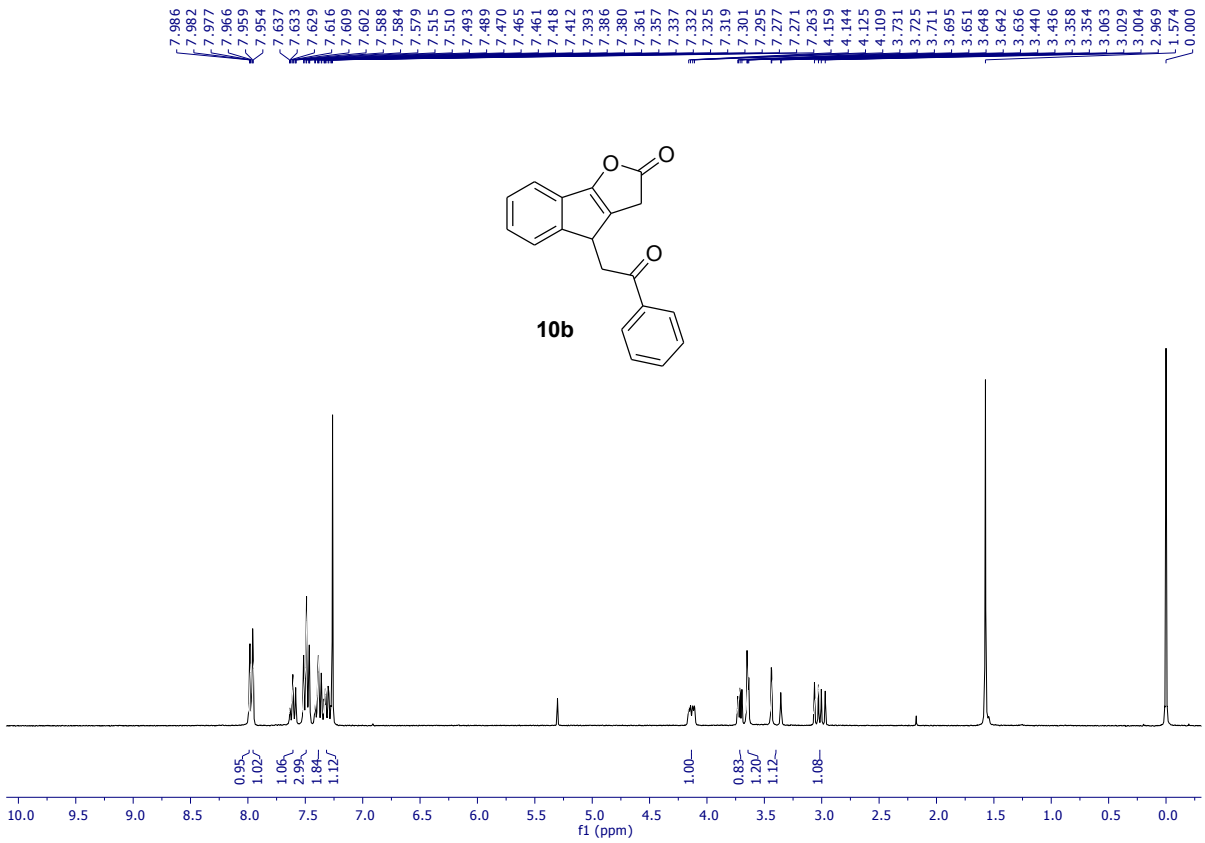
9o

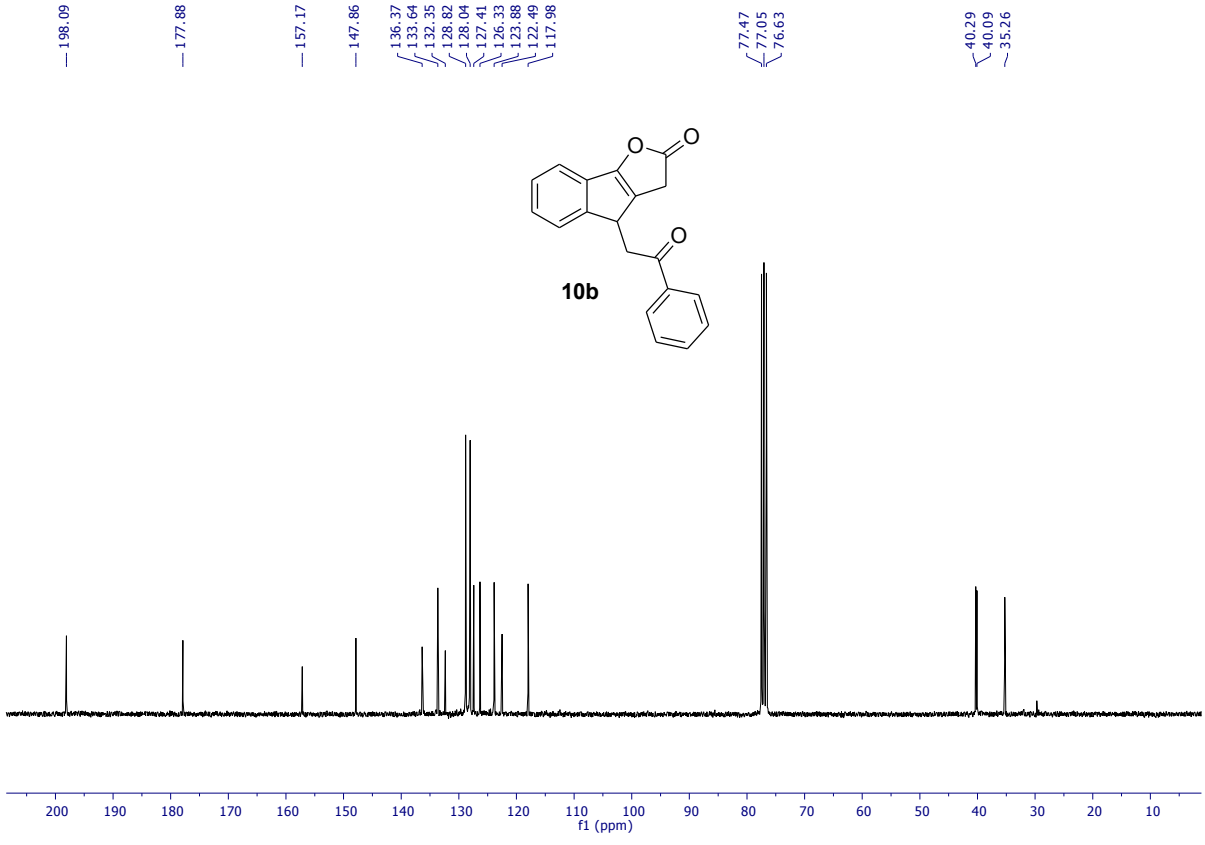

173.23
167.64
142.82
135.94
133.07
129.72
128.61
126.24
123.54
119.39
86.85
81.65
77.48
77.05
76.63
51.88
26.77
HO
O
OMe
O
f1 (ppm)

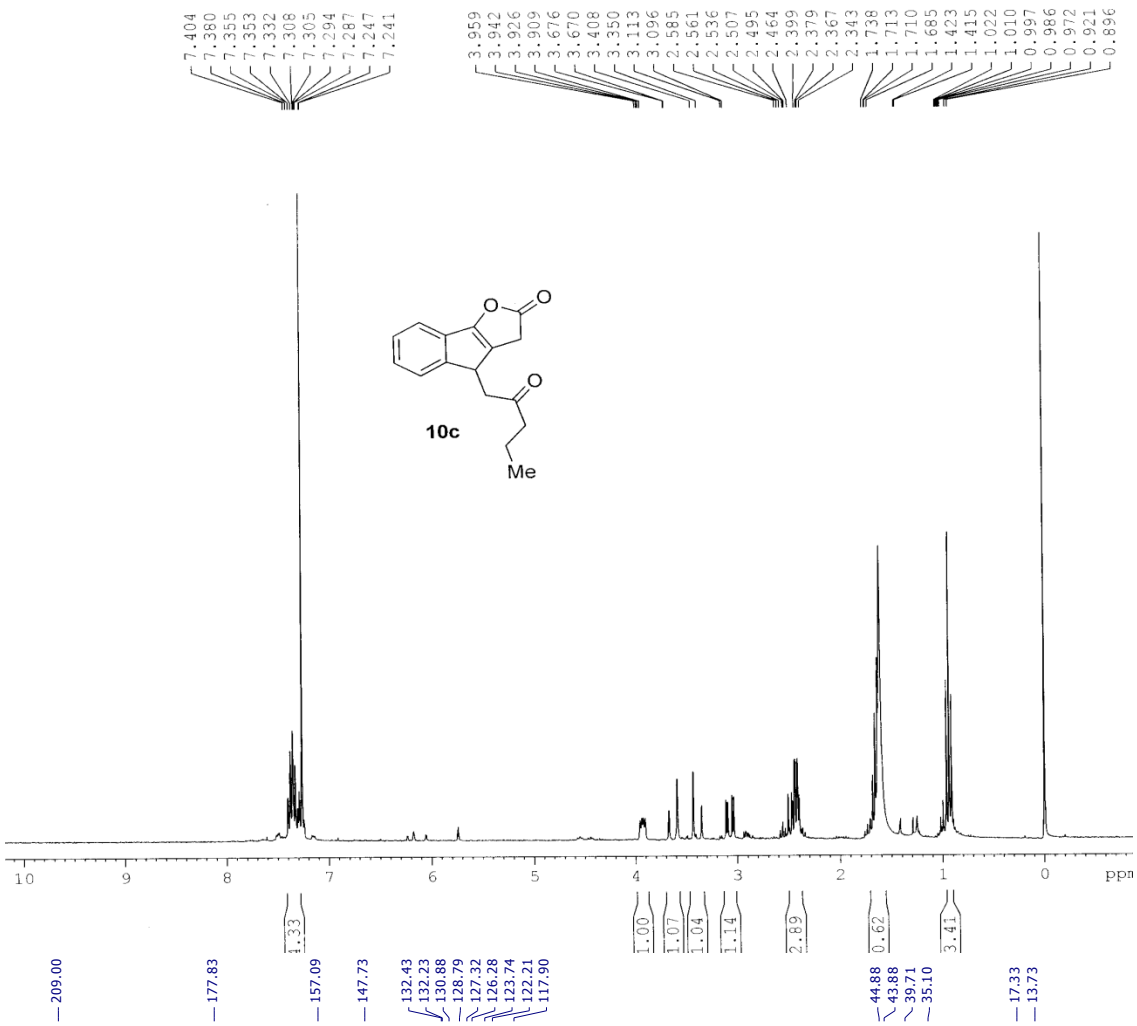
9o

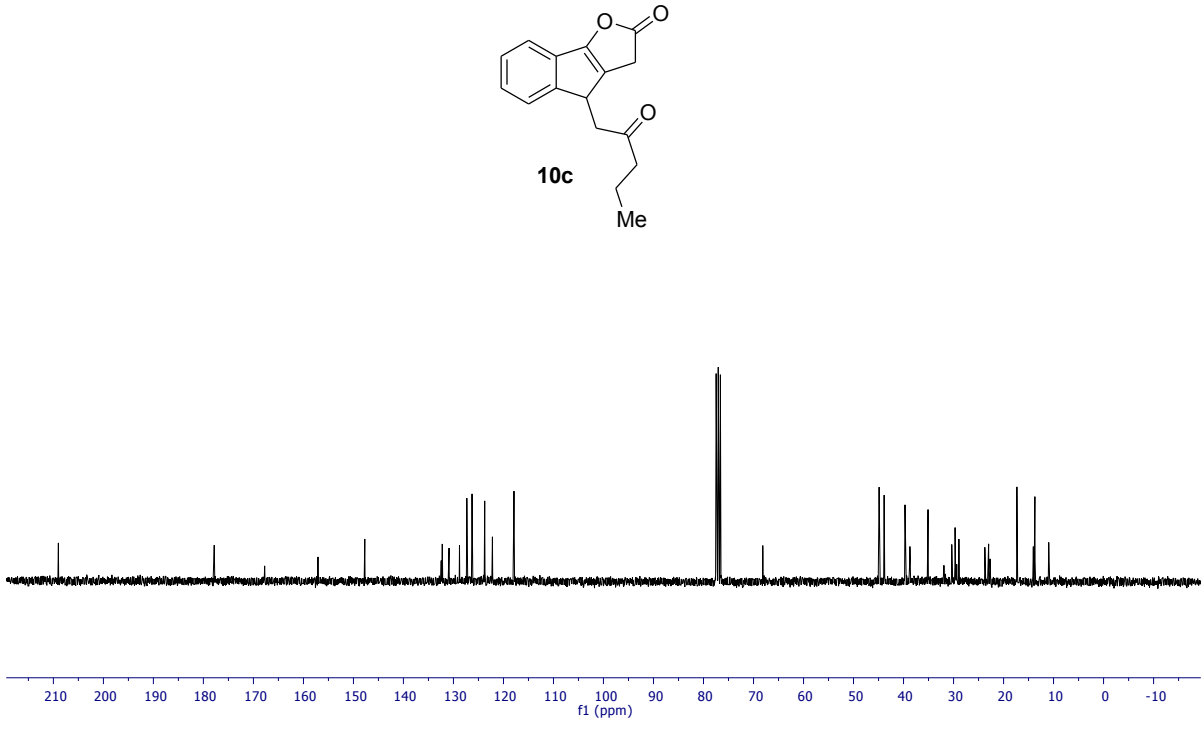

7.413
7.409
7.406
7.387
7.362
7.358
7.354
7.335
7.330
7.310
7.306
7.297
7.290
7.265
3.938
3.921
3.906
3.889
3.676
3.670
3.594
3.587
3.452
3.447
3.429
3.369
3.365
3.161
3.144
3.100
3.083
2.546
2.513
2.486
2.453
2.216
1.634
0.000
O
O
O
Me
10a
3.63
1.00
2.22
1.17
1.01
2.56
1.58
f1 (ppm)

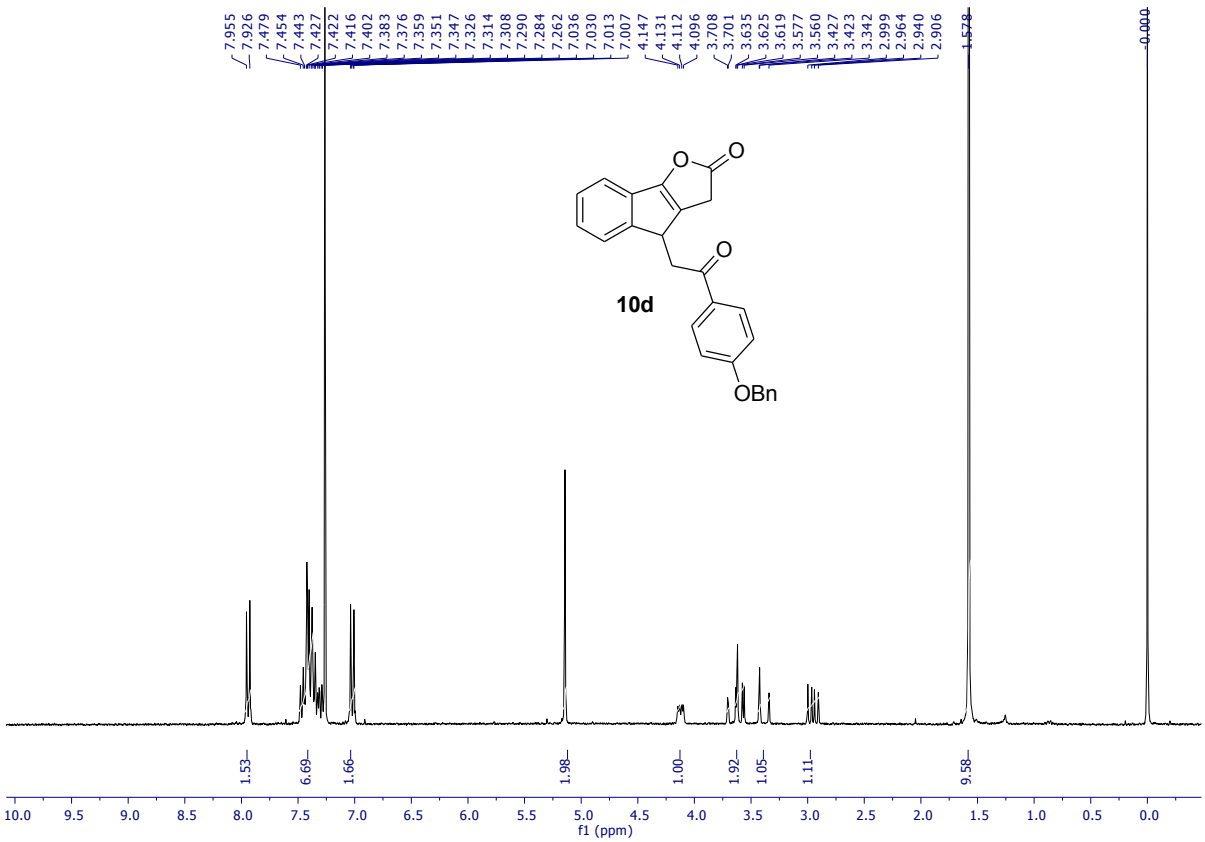

206.51
177.79
157.15
147.57
132.22
127.35
126.30
123.71
122.04
117.93
77.42
77.00
76.57
44.80
39.67
35.07
30.14
O
O
O
Me
10a
f1 (ppm)

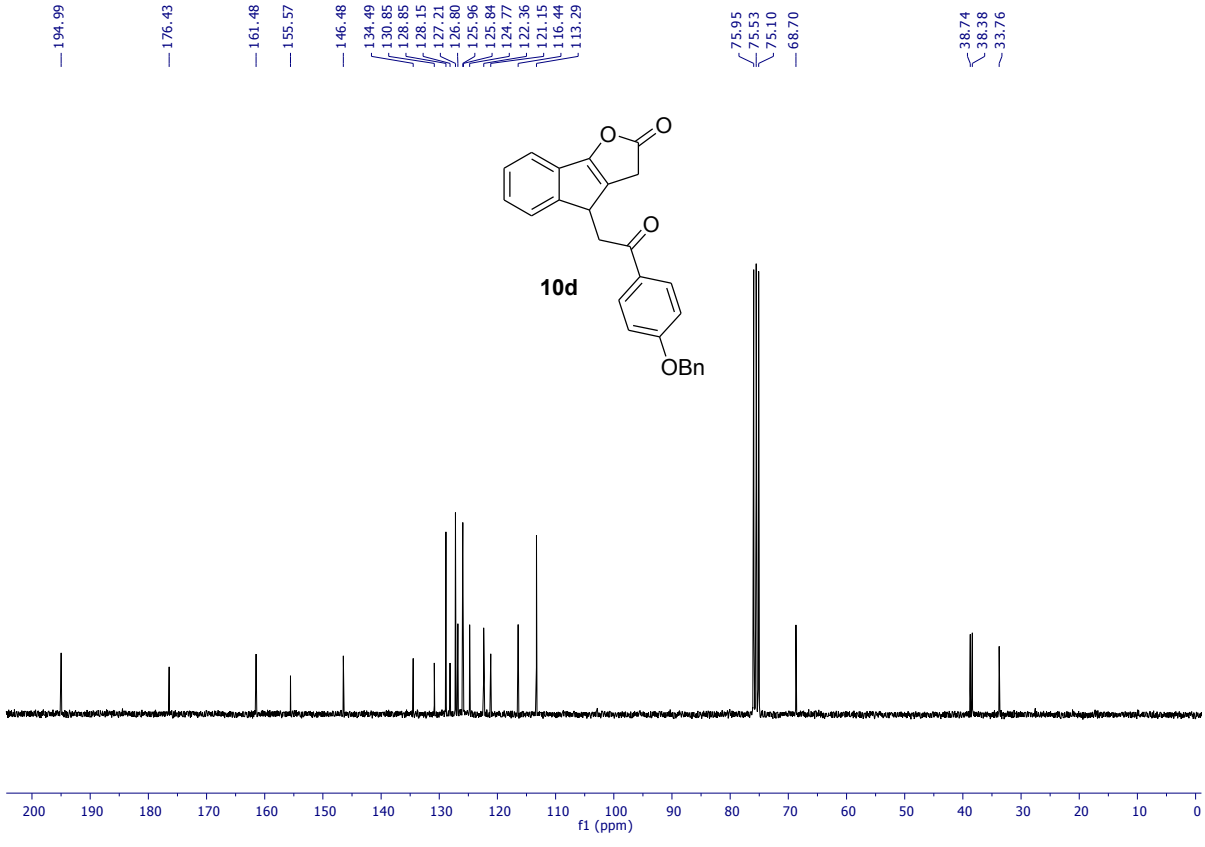

7.986
7.982
7.977
7.966
7.959
7.954
7.637
7.633
7.629
7.616
7.609
7.602
7.588
7.584
7.579
7.515
7.510
7.493
7.489
7.470
7.465
7.461
7.418
7.412
7.393
7.386
7.380
7.361
7.357
7.337
7.332
7.325
7.319
7.301
7.295
7.277
7.271
7.263
4.159
4.144
4.125
4.109
3.731
3.725
3.711
3.695
3.651
3.648
3.642
3.636
3.440
3.436
3.358
3.354
3.063
3.029
3.004
2.969
1.574
0.000
10b
0.95
1.02
1.06
2.99
1.84
1.12
1.00
0.83
1.20
1.12
1.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

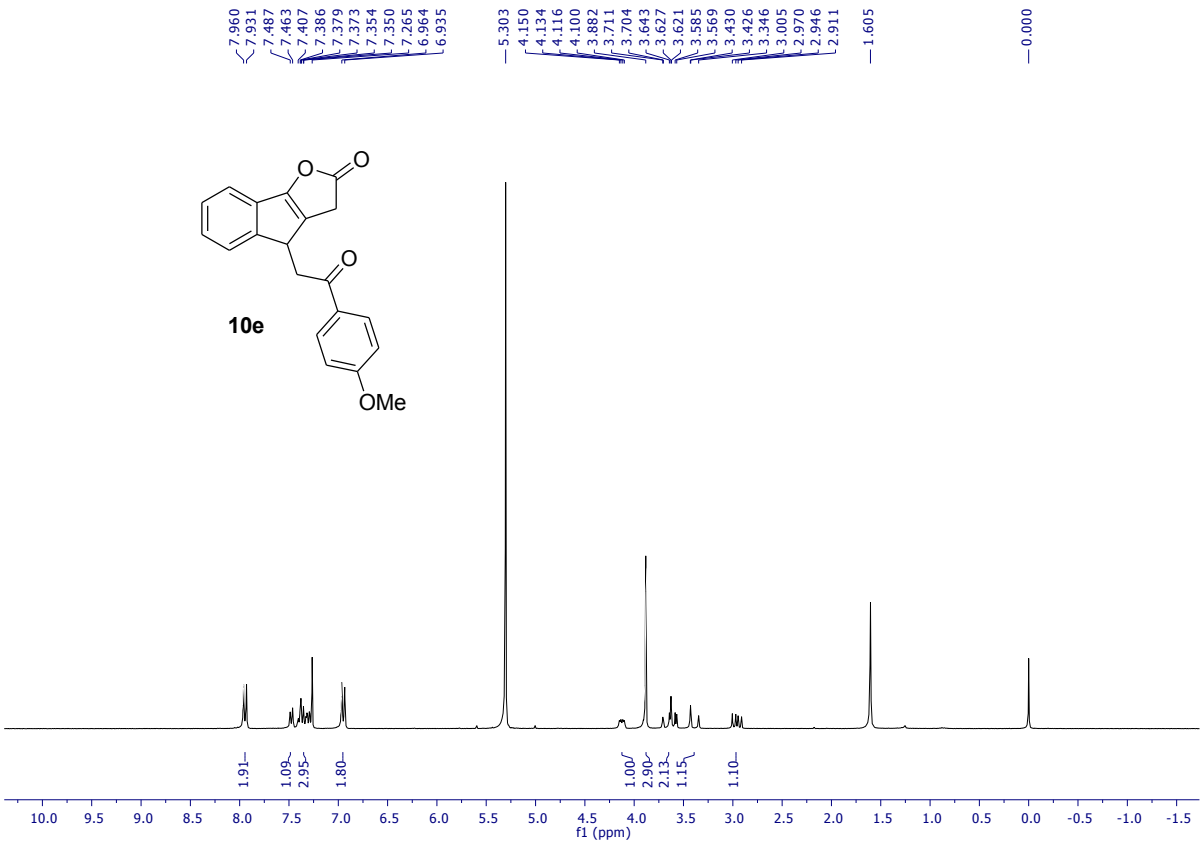

198.09
177.88
157.17
147.86
136.37
133.64
132.35
128.82
128.04
127.41
126.33
123.88
122.49
117.98
77.47
77.05
76.63
40.29
40.09
35.26
10b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

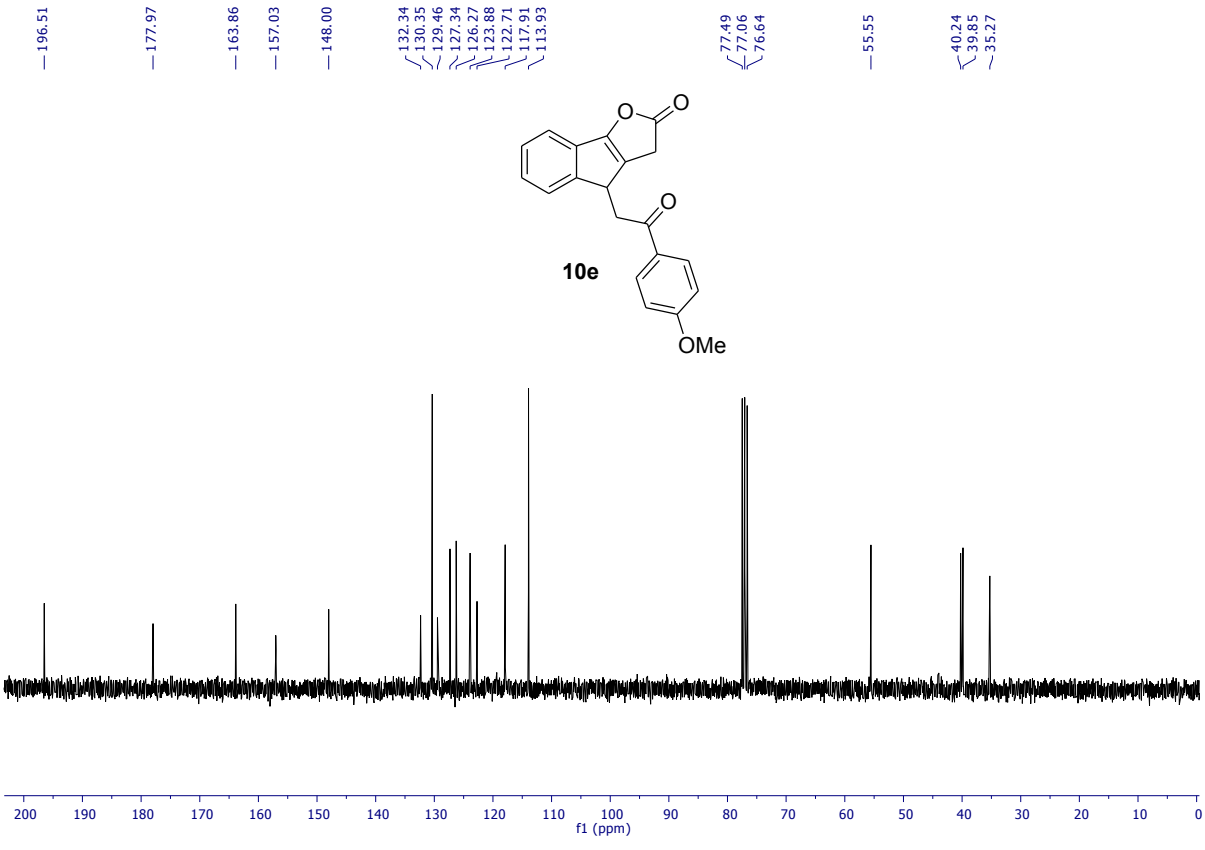

7.404
7.380
7.355
7.353
7.332
7.308
7.305
7.294
7.287
7.247
7.241
3.959
3.942
3.926
3.909
3.676
3.670
3.408
3.350
3.113
3.096
2.585
2.561
2.536
2.507
2.495
2.464
2.399
2.379
2.367
2.343
1.738
1.713
1.710
1.685
1.423
1.415
1.022
1.010
0.997
0.986
0.972
0.921
0.896
10c
Me
ppm
1.33
1.00
1.07
1.04
1.14
2.89
0.62
3.41
209.00
177.83
157.09
147.73
132.43
132.23
130.88
128.79
127.32
126.28
123.74
122.21
117.90
44.88
43.88
39.71
35.10
17.33
13.73

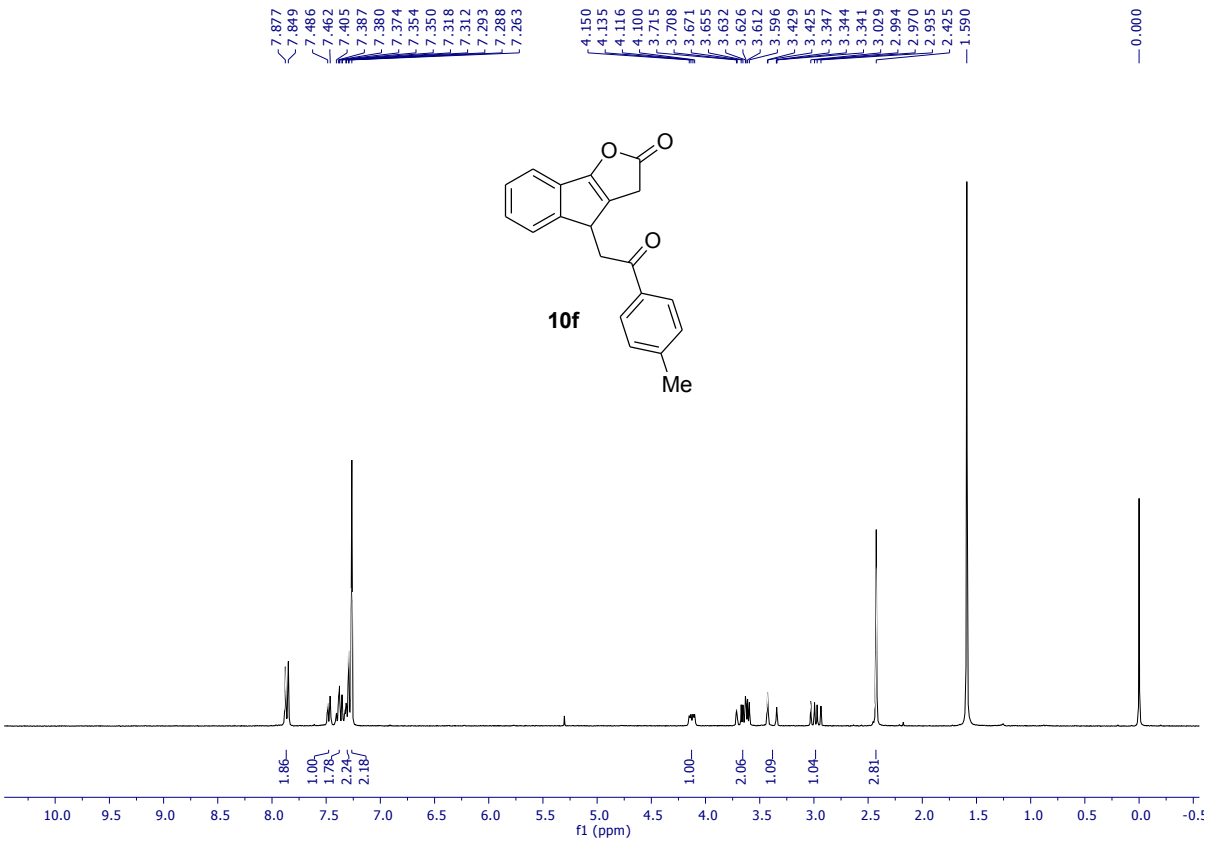

10c
Me
f1 (ppm)


7.955
7.926
7.479
7.454
7.443
7.427
7.422
7.416
7.402
7.383
7.376
7.359
7.351
7.347
7.326
7.314
7.308
7.290
7.284
7.262
7.036
7.030
7.013
7.007
4.147
4.131
4.112
4.096
3.708
3.701
3.635
3.625
3.619
3.577
3.560
3.427
3.423
3.342
2.999
2.964
2.940
2.906
1.578
0.000
10d
OBn
1.53
6.69
1.66
1.98
1.00
1.92
1.05
1.11
9.58
f1 (ppm)


194.99
176.43
161.48
155.57
146.48
134.49
130.85
128.85
128.15
127.21
126.80
125.96
125.84
124.77
122.36
121.15
116.44
113.29
75.95
75.53
75.10
68.70
38.74
38.38
33.76
10d
OBn
f1 (ppm)


7.960
7.931
7.487
7.463
7.407
7.386
7.379
7.373
7.354
7.350
7.265
6.964
6.935
5.303
4.150
4.134
4.116
4.100
3.882
3.711
3.704
3.643
3.627
3.621
3.585
3.569
3.430
3.426
3.346
3.005
2.970
2.946
2.911
1.605
0.000
O
O
O
10e
OMe
1.91
1.09
2.95
1.80
1.00
2.90
2.13
1.15
1.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


196.51
177.97
163.86
157.03
148.00
132.34
130.35
129.46
127.34
126.27
123.88
122.71
117.91
113.93
77.49
77.06
76.64
55.55
40.24
39.85
35.27
O
O
O
10e
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.354
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7.312
7.293
7.288
7.263
4.150
4.135
4.116
4.100
3.715
3.708
3.671
3.655
3.632
3.626
3.612
3.596
3.429
3.425
3.347
3.344
3.341
3.029
2.994
2.970
2.935
2.425
1.590
0.000
O
O
O
10f
Me
1.86
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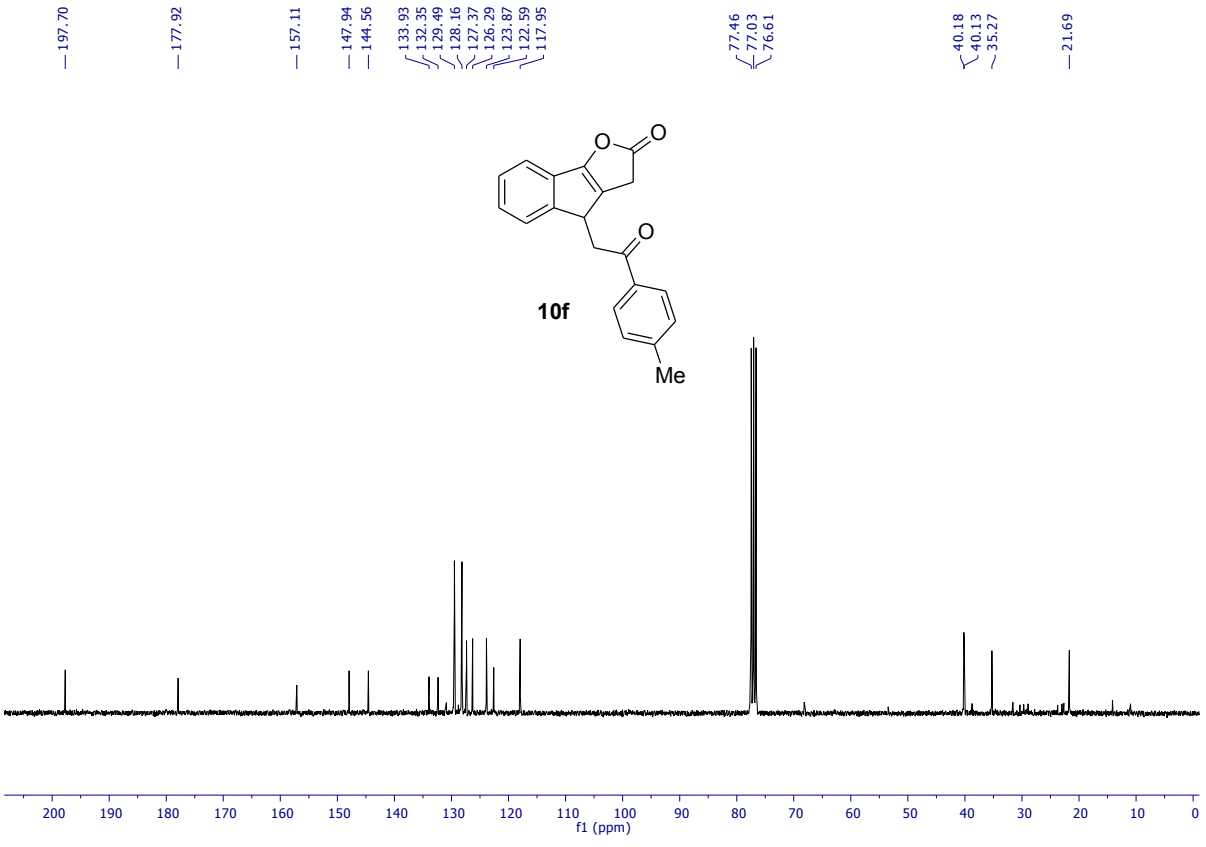
1.78
2.24
2.18
1.00
2.06
1.09
1.04
2.81
f1 (ppm)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129.49
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127.37
126.29
123.87
122.59
117.95
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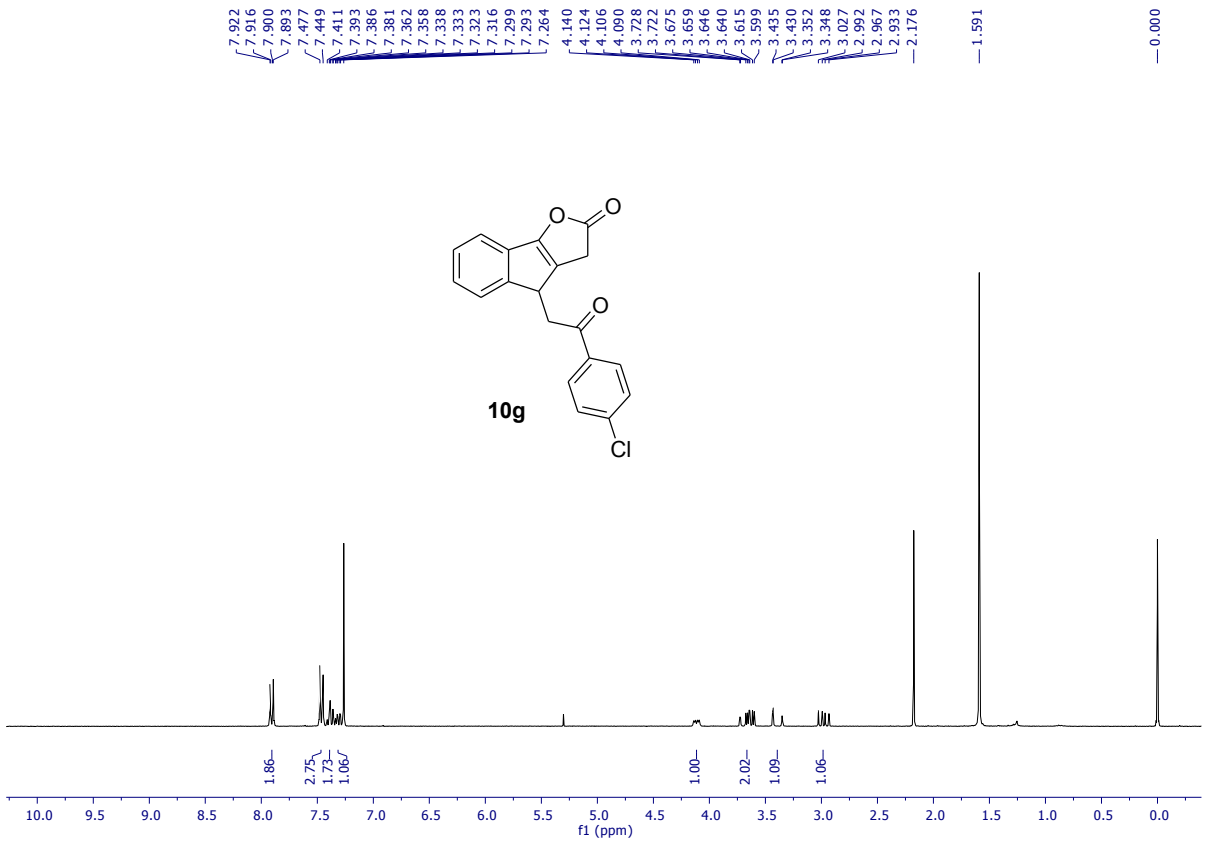
77.03
76.61
40.18
40.13
35.27
21.69
O
O
O
10f
Me
f1 (ppm)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7.386
7.381
7.362
7.358
7.338
7.333
7.323
7.316
7.299
7.293
7.264
4.140
4.124
4.106
4.090
3.728
3.722
3.675
3.659
3.646
3.640
3.615
3.599
3.435
3.430
3.352
3.348
3.027
2.992
2.967
2.933
2.176
1.591
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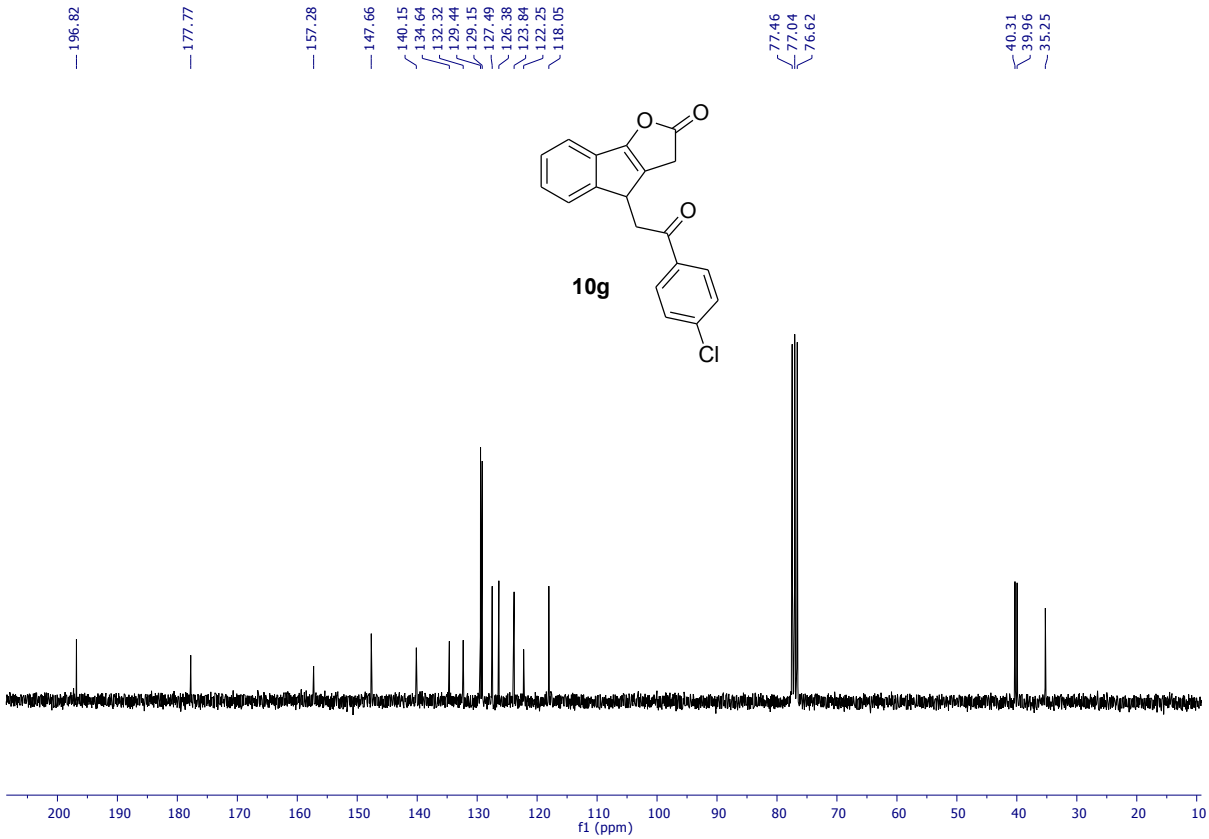
10g
Cl
1.86
2.75
1.73
1.06
1.00
2.02
1.09
1.06
f1 (ppm)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134.64
132.32
129.44
129.15
127.49
126.38
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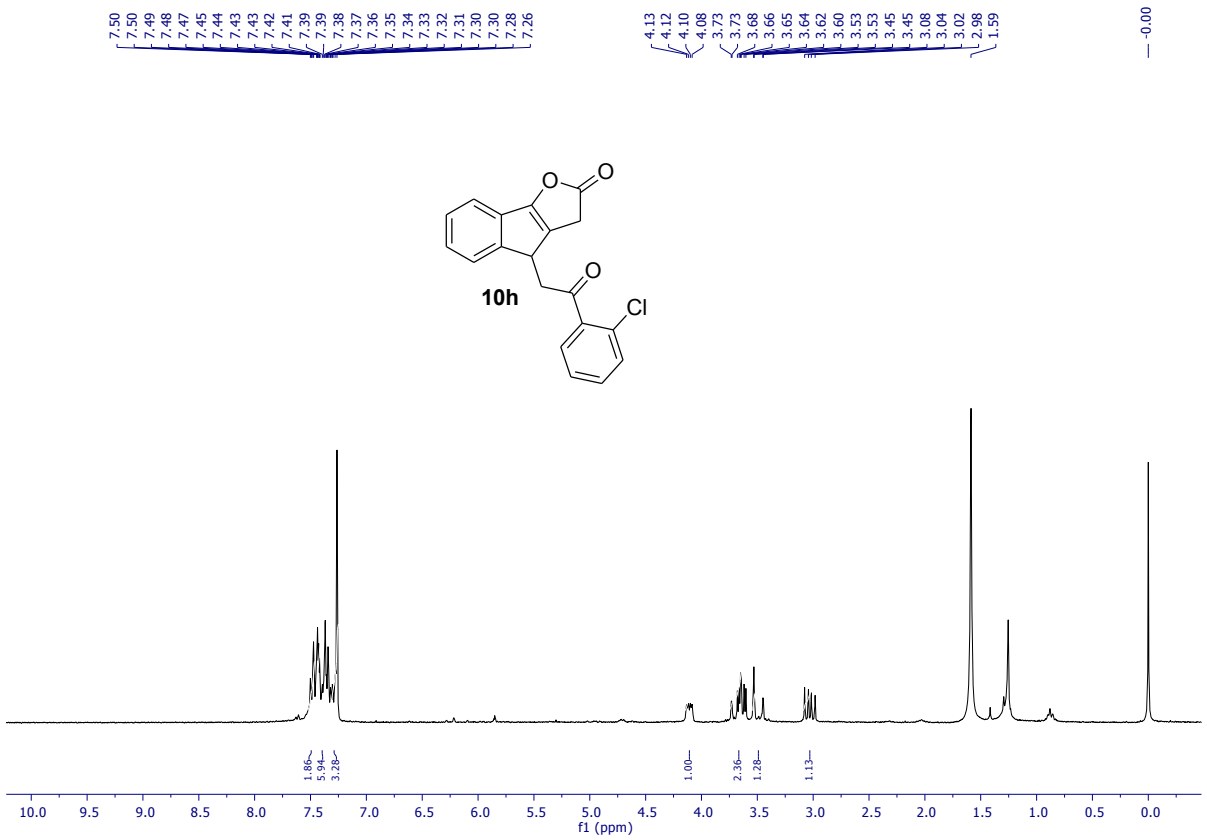
118.05
77.46
77.04
76.62
40.31
39.96
35.25
10g
Cl
f1 (ppm)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7.50
7.49
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7.47
7.45
7.44
7.43
7.43
7.42
7.41
7.39
7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.28
7.26
4.13
4.12
4.10
4.08
3.73
3.73
3.68
3.66
3.65
3.64
3.62
3.60
3.53
3.53
3.45
3.45
3.08
3.04
3.02
2.98
1.59
0.00
O
O
O
Cl
10h
1.86
5.94
3.28
1.00
2.36
1.28
1.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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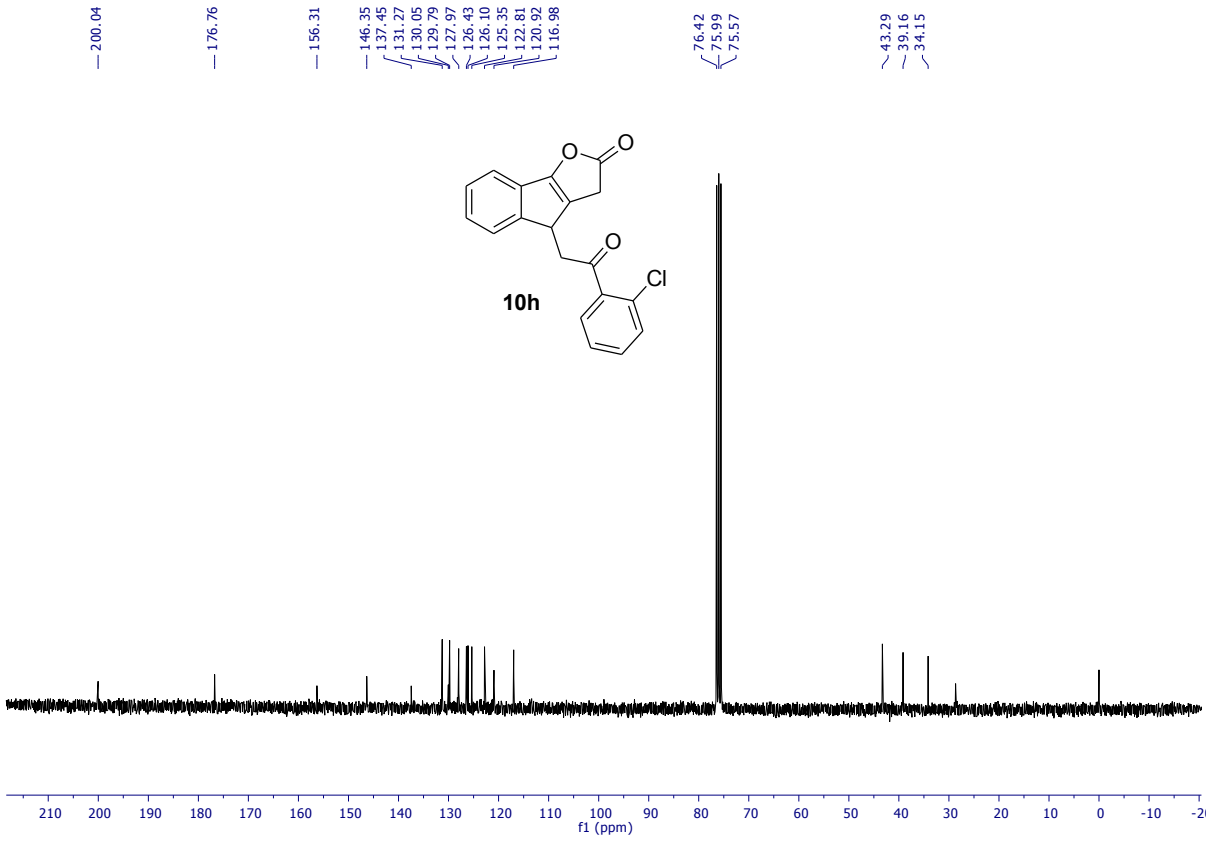
1.5
1.0
0.5
0.0
f1 (ppm)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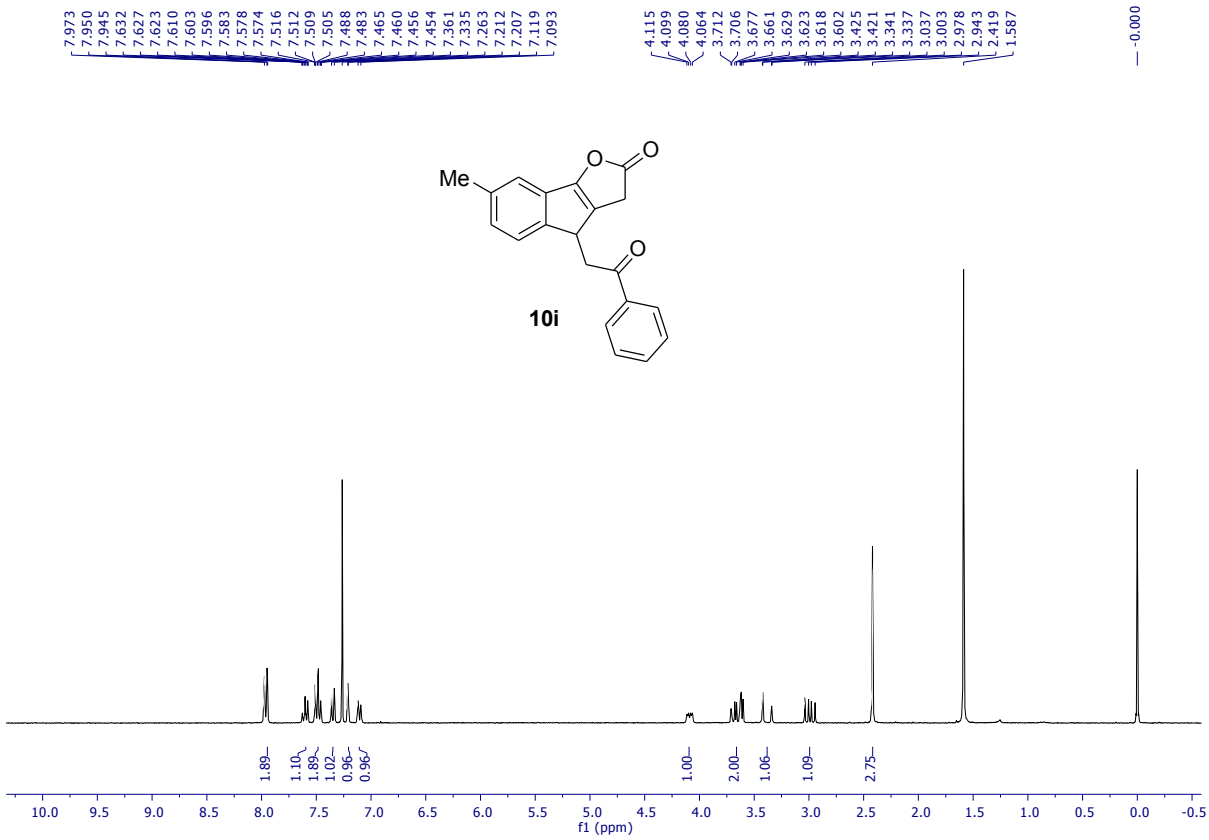
137.45
131.27
130.05
129.79
127.97
126.43
126.10
125.35
122.81
120.92
116.98
76.42
75.99
75.57
43.29
39.16
34.15
O
O
O
Cl
10h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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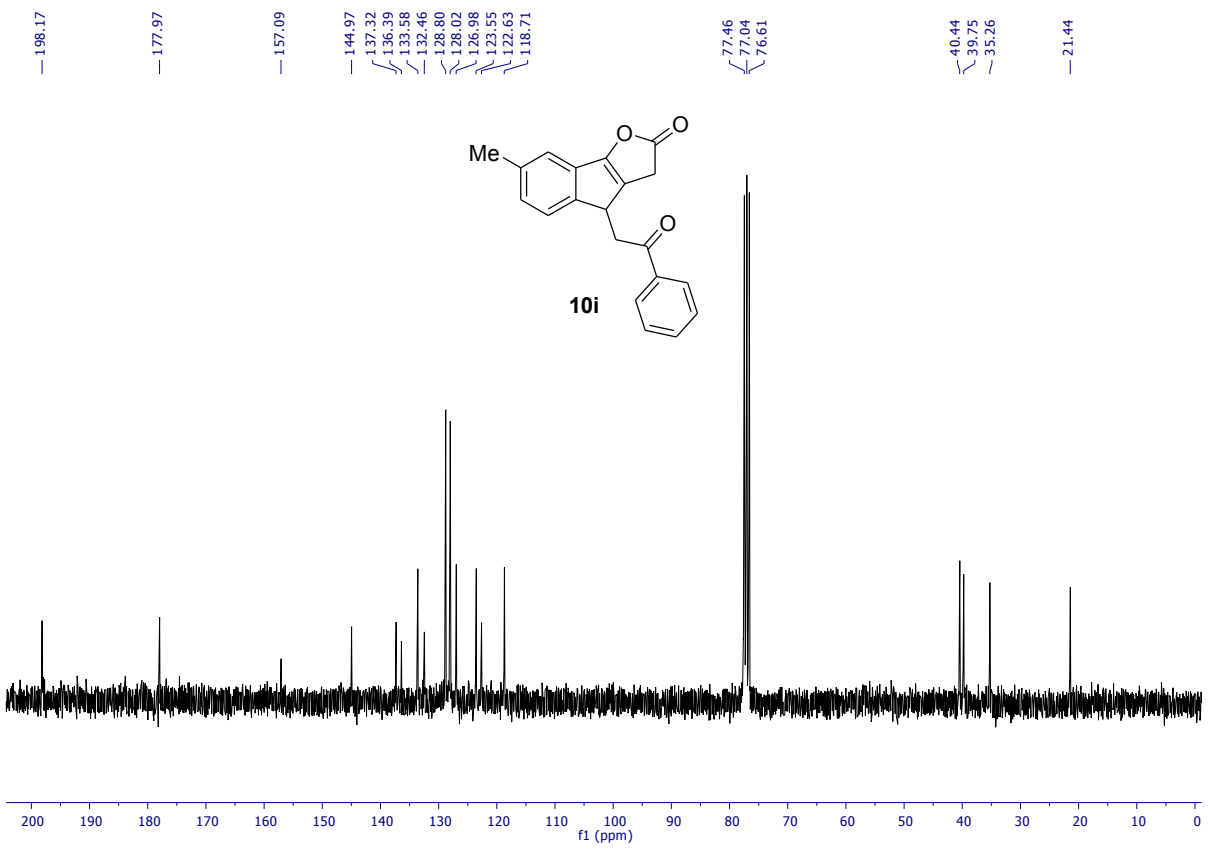
7.945
7.632
7.627
7.623
7.610
7.603
7.596
7.583
7.578
7.574
7.516
7.512
7.509
7.505
7.488
7.483
7.465
7.460
7.456
7.454
7.361
7.335
7.263
7.212
7.207
7.119
7.093
4.115
4.099
4.080
4.064
3.712
3.706
3.677
3.661
3.629
3.623
3.618
3.602
3.425
3.421
3.341
3.337
3.037
3.003
2.978
2.943
2.419
1.587
-0.000
Me
O
O
O
10i
1.89
1.10
1.89
1.02
0.96
0.96
1.00
2.00
1.06
1.09
2.75
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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177.97
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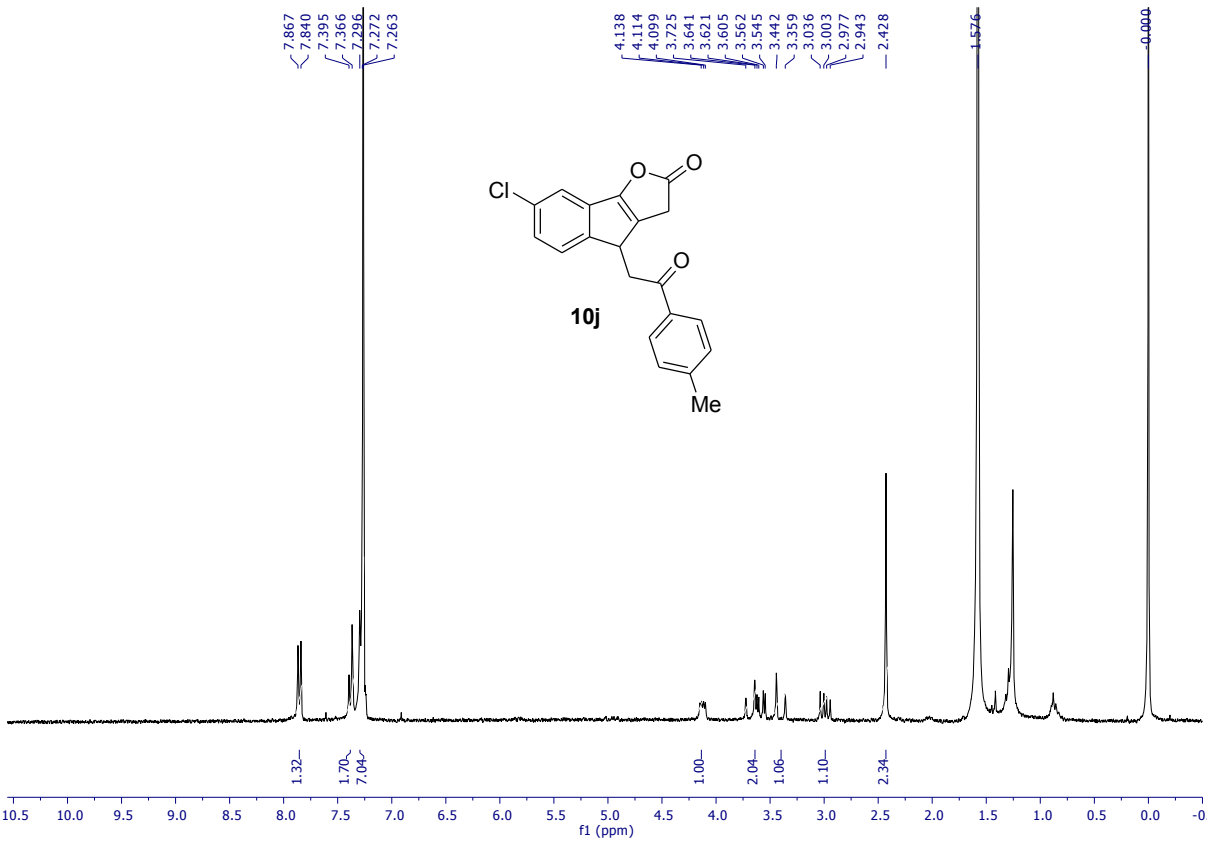
137.32
136.39
133.58
132.46
128.80
128.02
126.98
123.55
122.63
118.71
77.46
77.04
76.61
40.44
39.75
35.26
21.44
Me
O
O
O
10i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.395
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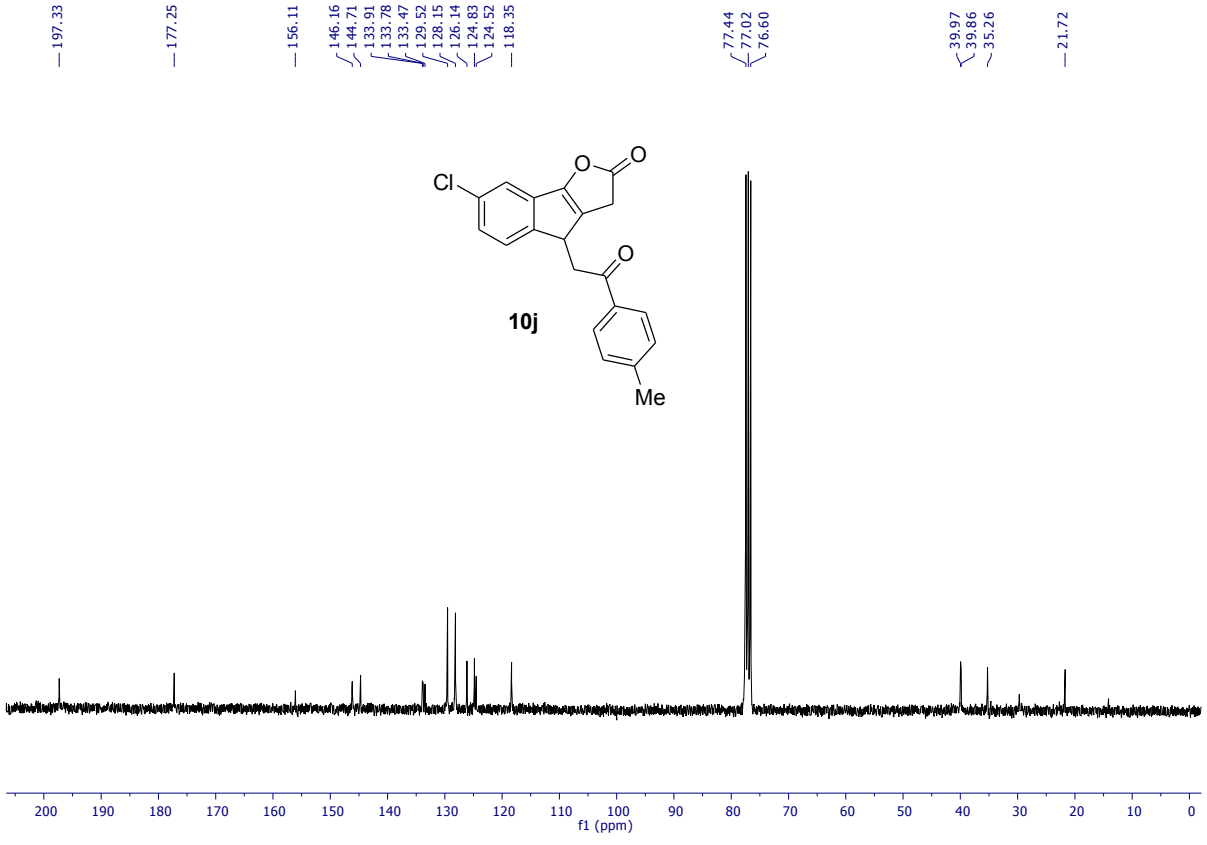
7.296
7.272
7.263
4.138
4.114
4.099
3.725
3.641
3.621
3.605
3.562
3.545
3.442
3.359
3.036
3.003
2.977
2.943
2.428
1.576
0.000
Cl
O
O
O
10j
Me
1.32
1.70
7.04
1.00
2.04
1.06
1.10
2.34
f1 (ppm)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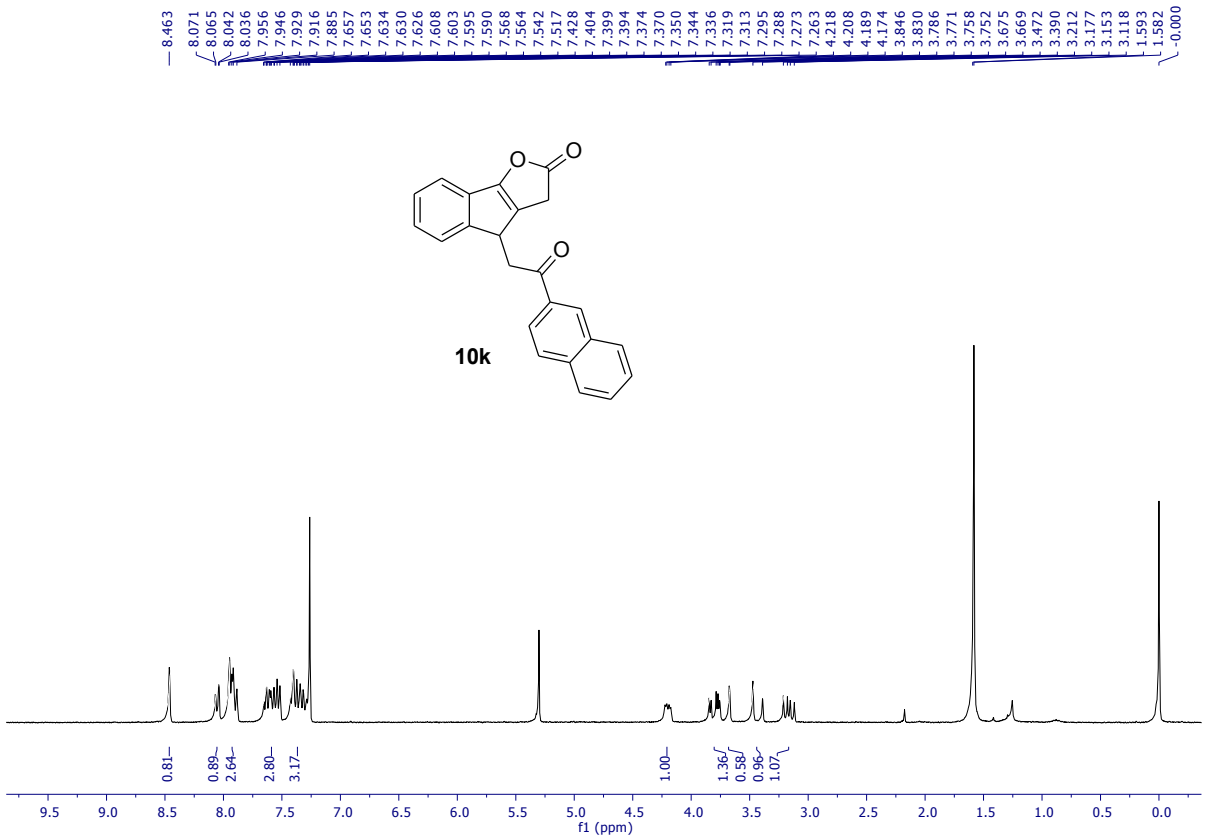
177.25
156.11
146.16
144.71
133.91
133.78
133.47
129.52
128.15
126.14
124.83
124.52
118.35
77.44
77.02
76.60
39.97
39.86
35.26
21.72
Cl
O
O
O
10j
Me
f1 (ppm)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7.929
7.916
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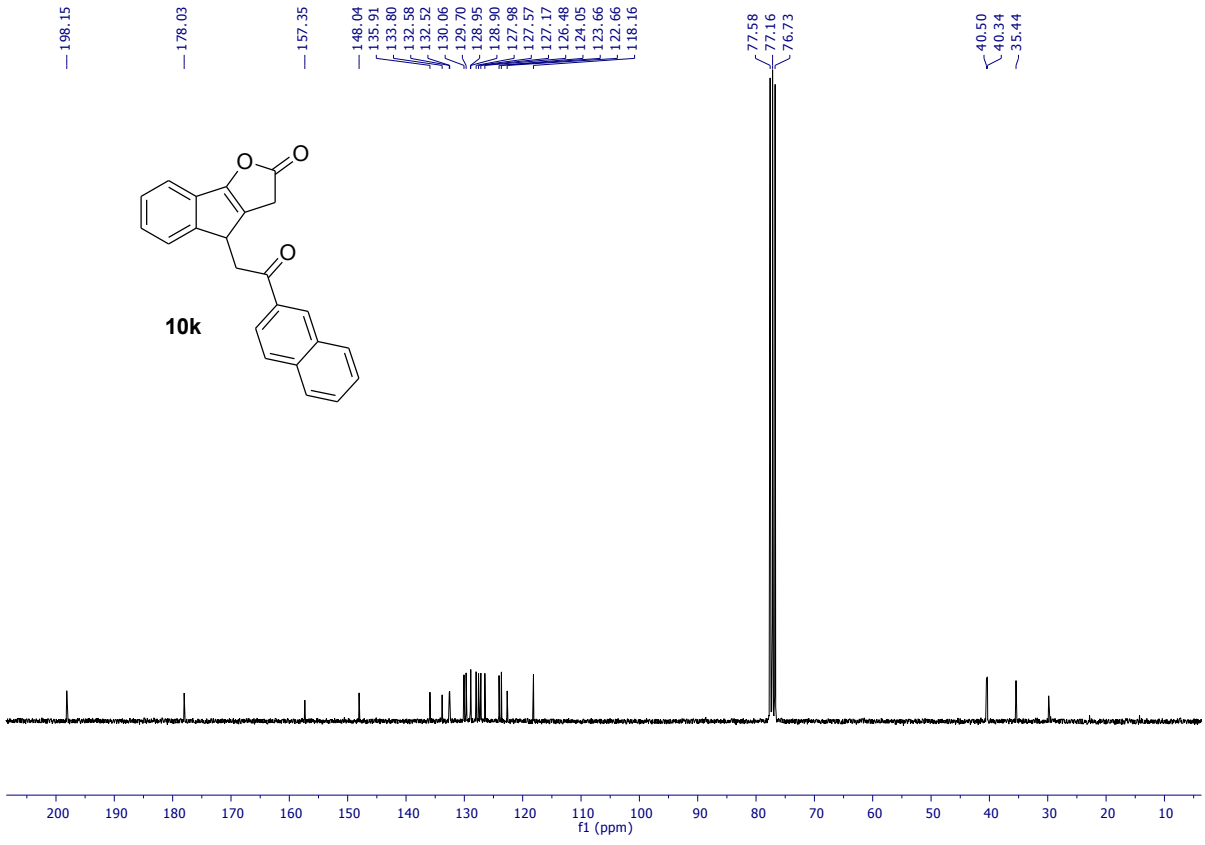
7.653
7.634
7.630
7.626
7.608
7.603
7.595
7.590
7.568
7.564
7.542
7.517
7.428
7.404
7.399
7.394
7.374
7.370
7.350
7.344
7.336
7.319
7.313
7.295
7.288
7.273
7.263
4.218
4.208
4.189
4.174
3.846
3.830
3.786
3.771
3.758
3.752
3.675
3.669
3.472
3.390
3.212
3.177
3.153
3.118
1.593
1.582
-0.000
10k
0.81
0.89
2.64
2.80
3.17
1.00
1.36
0.58
0.96
1.07
f1 (ppm)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157.35
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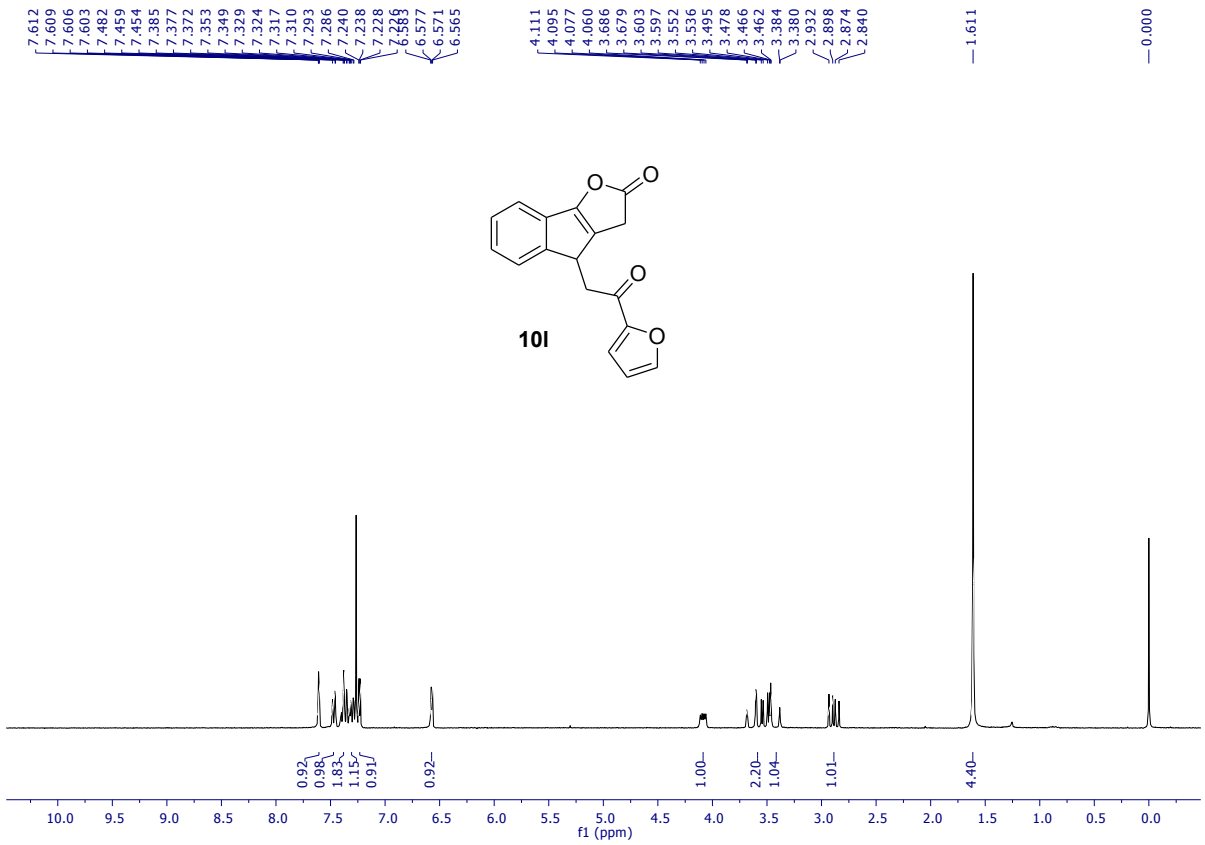
135.91
133.80
132.58
132.52
130.06
129.70
128.95
128.90
127.98
127.57
127.17
126.48
124.05
123.66
122.66
118.16
77.58
77.16
76.73
40.50
40.34
35.44
10k
f1 (ppm)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7.329
7.324
7.317
7.310
7.293
7.286
7.240
7.238
7.228
6.577
6.571
6.565
4.111
4.095
4.077
4.060
3.686
3.679
3.603
3.597
3.552
3.536
3.495
3.478
3.466
3.462
3.384
3.380
2.932
2.898
2.874
2.840
1.611
0.000
10l
0.92
0.98
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1.15
0.91
0.92
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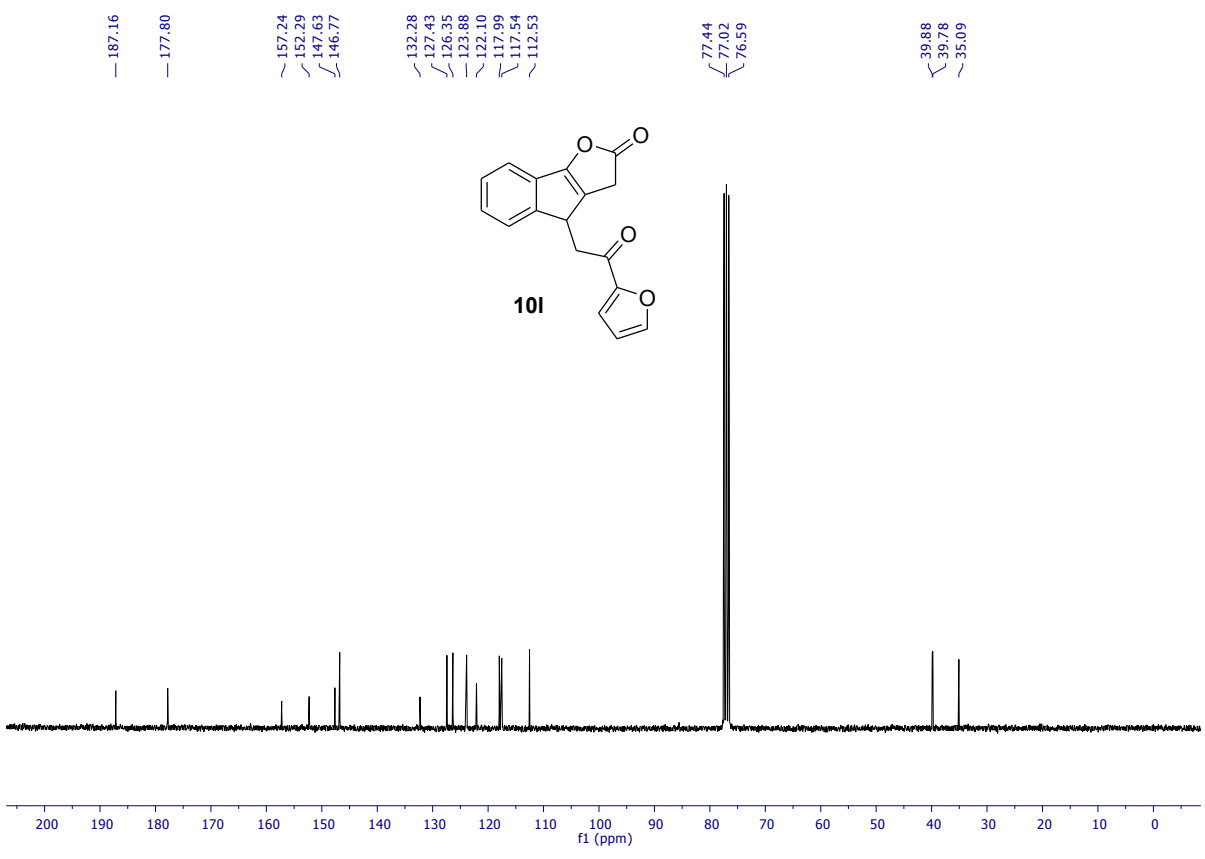
2.20
1.04
1.01
4.40
f1 (ppm)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152.29
147.63
146.77
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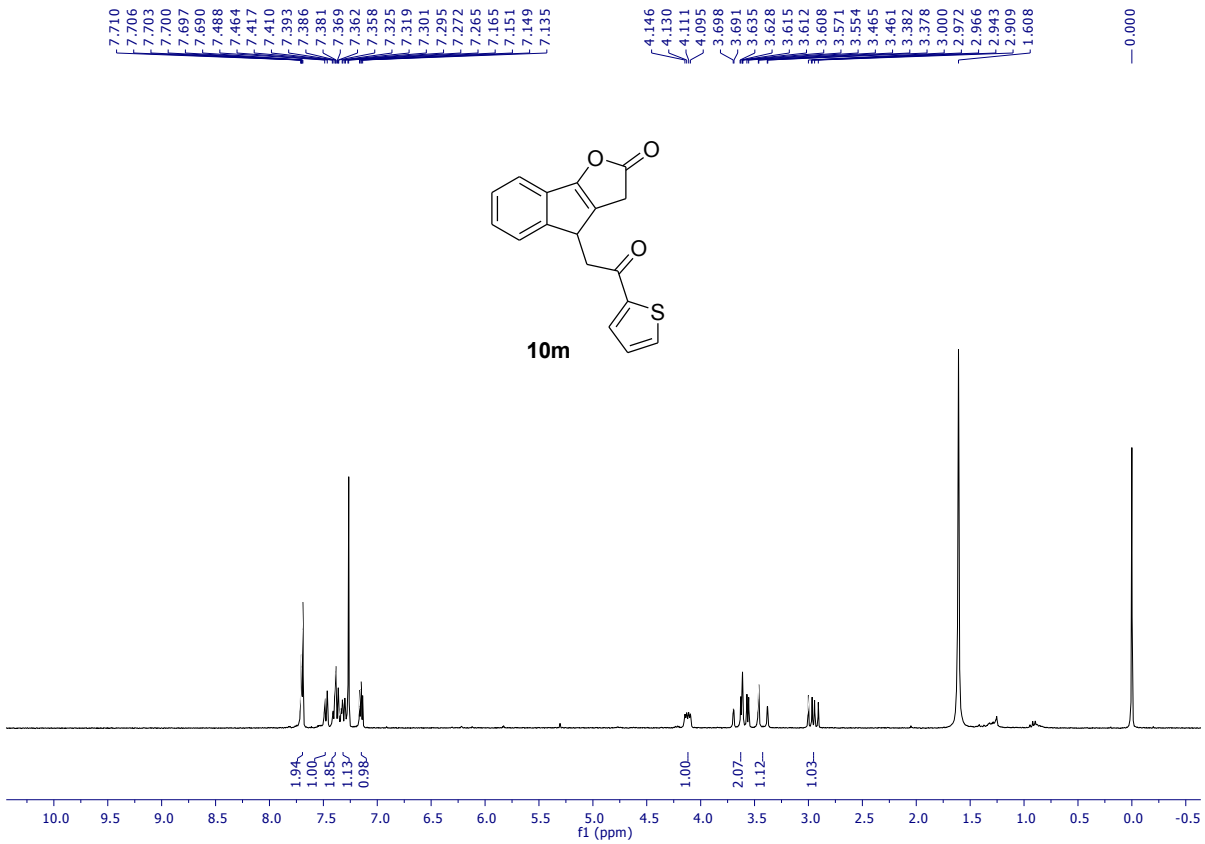
127.43
126.35
123.88
122.10
117.99
117.54
112.53
77.44
77.02
76.59
39.88
39.78
35.09
10l
f1 (ppm)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7.410
7.393
7.386
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7.369
7.362
7.358
7.325
7.319
7.301
7.295
7.272
7.265
7.165
7.151
7.149
7.135
4.146
4.130
4.111
4.095
3.698
3.691
3.635
3.628
3.615
3.612
3.608
3.571
3.554
3.465
3.461
3.382
3.378
3.000
2.972
2.966
2.943
2.909
1.608
0.000
O
O
O
S
10m
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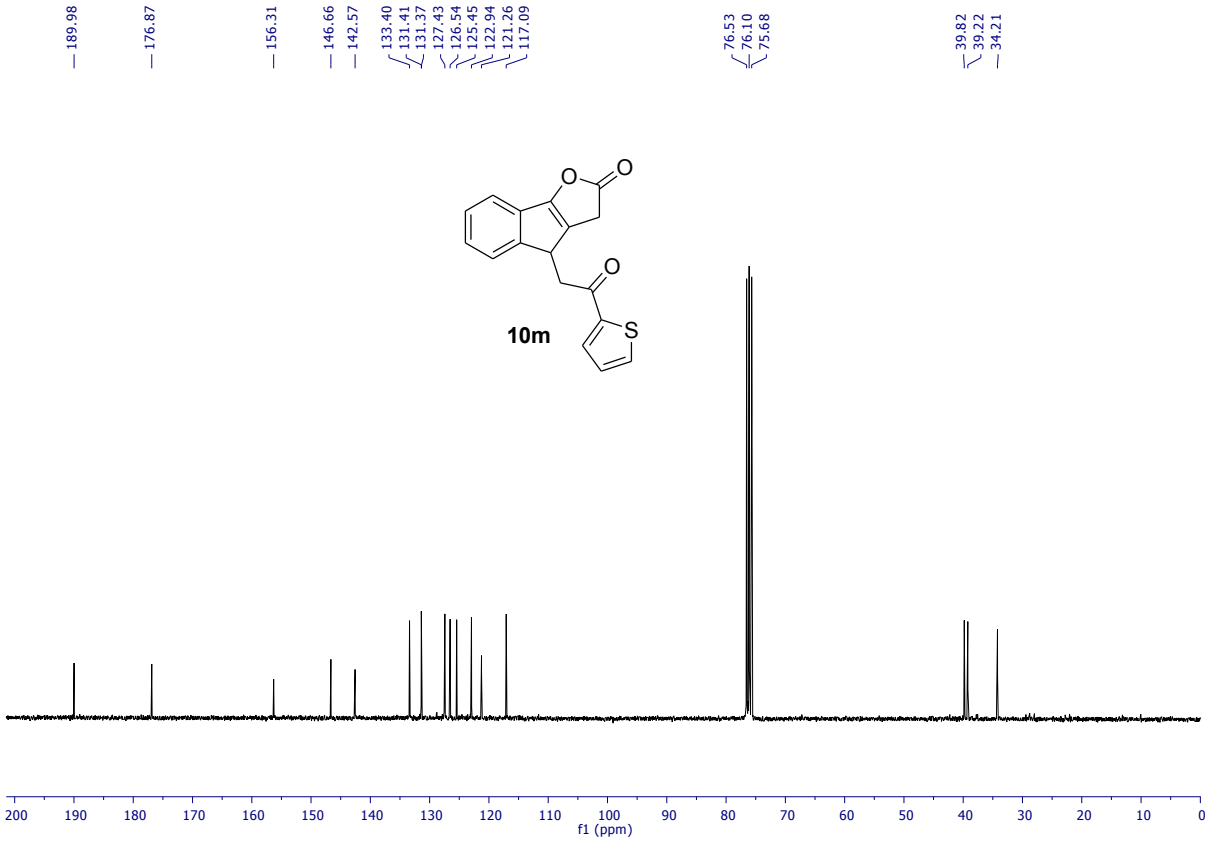
1.00
1.85
1.13
0.98
1.00
2.07
1.12
1.03
f1 (ppm)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127.43
126.54
125.45
122.94
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76.10
75.68
39.82
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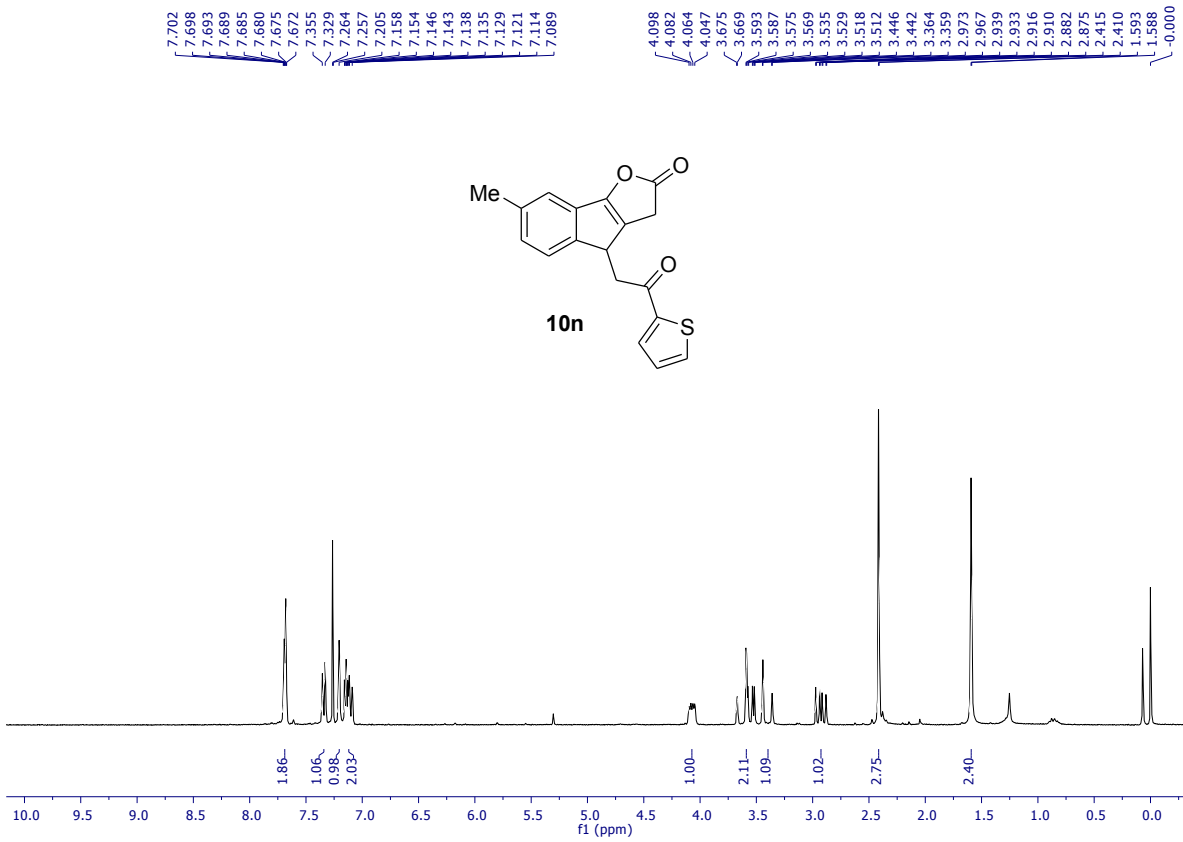
O
O
O
S
10m
f1 (ppm)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7.675
7.672
7.355
7.329
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7.257
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7.158
7.154
7.146
7.143
7.138
7.135
7.129
7.121
7.114
7.089
4.098
4.082
4.064
4.047
3.675
3.669
3.593
3.587
3.575
3.569
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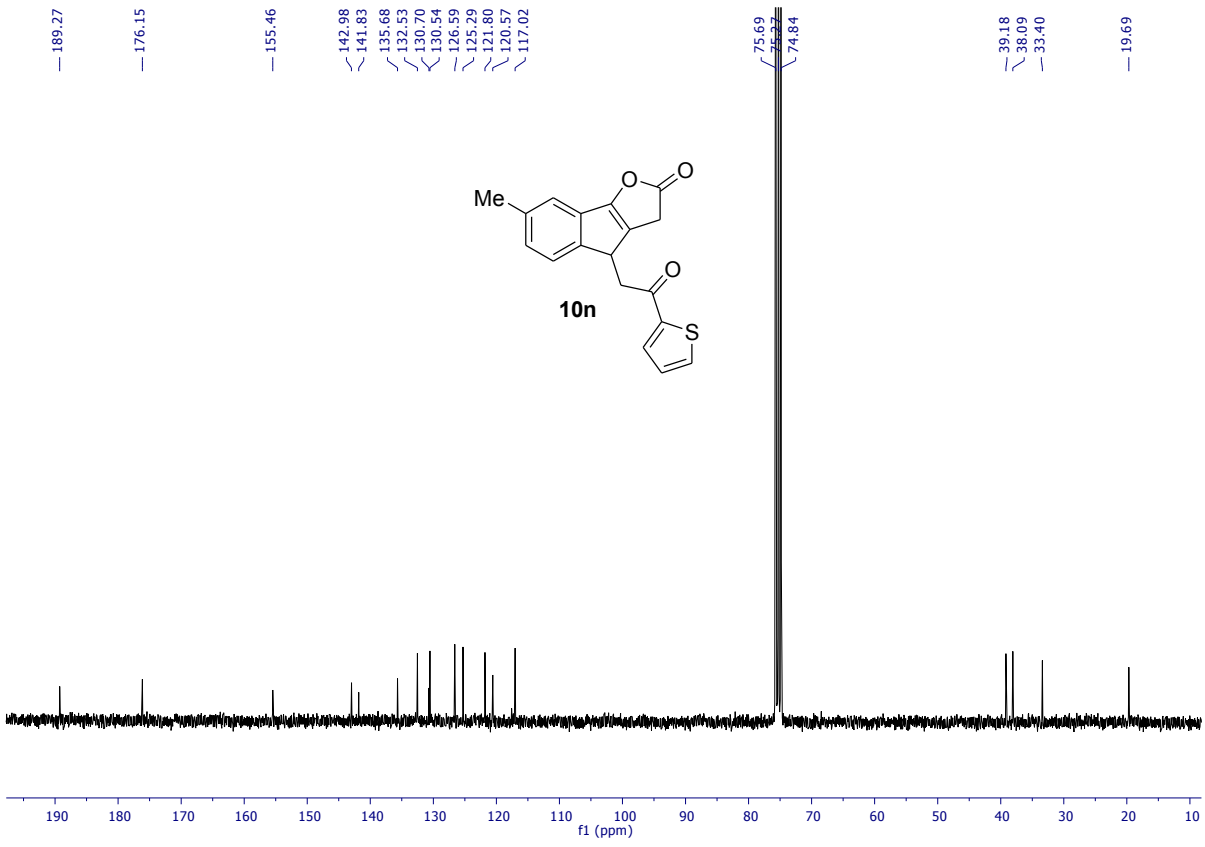
3.529
3.518
3.512
3.446
3.442
3.364
3.359
2.973
2.967
2.939
2.933
2.916
2.910
2.882
2.875
2.415
2.410
1.593
1.588
-0.000
Me
O
O
O
S
10n
1.86
1.06
0.98
2.03
1.00
2.11
1.09
1.02
2.75
2.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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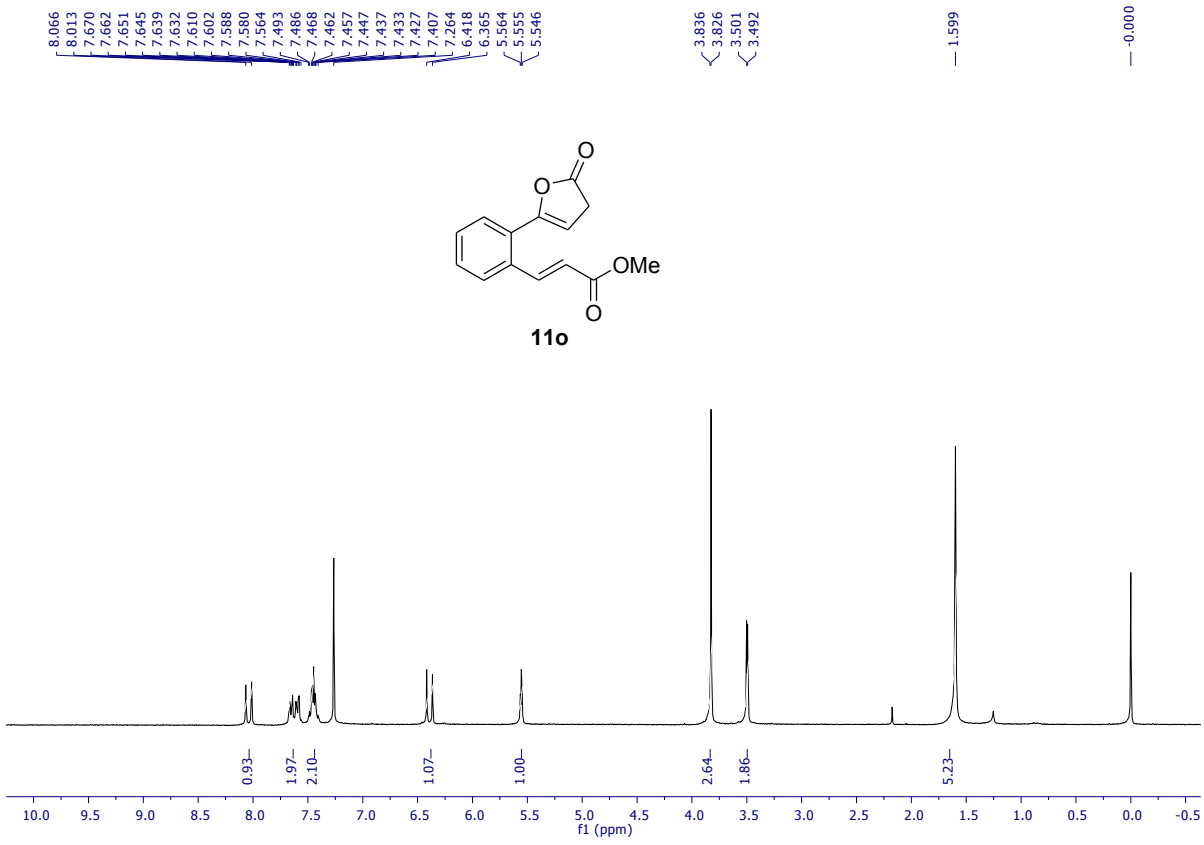
142.98
141.83
135.68
132.53
130.70
130.54
126.59
125.29
121.80
120.57
117.02
75.69
75.32
74.84
39.18
38.09
33.40
19.69
Me
O
O
O
S
10n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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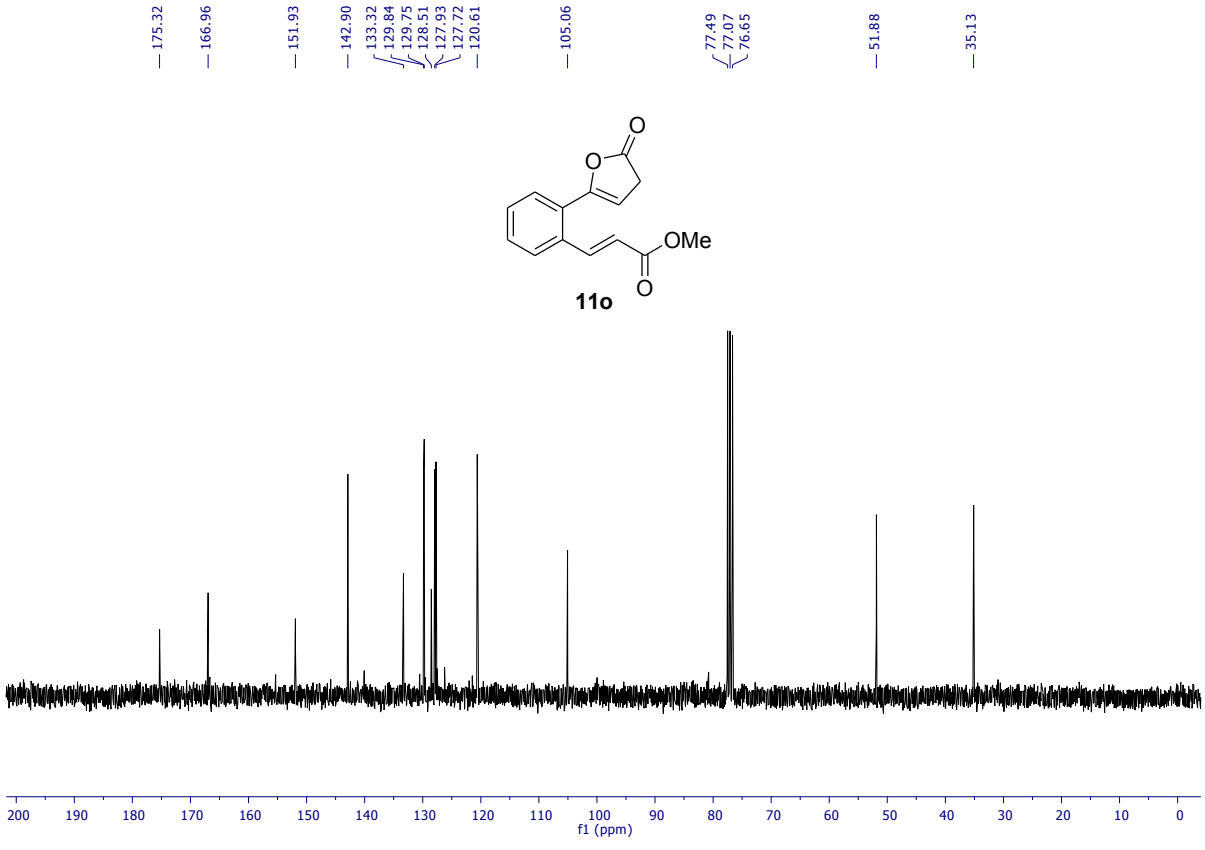
7.564
7.493
7.486
7.468
7.462
7.457
7.447
7.437
7.433
7.427
7.407
7.264
6.418
6.365
5.564
5.555
5.546
3.836
3.826
3.501
3.492
1.599
-0.000
O
O
OMe
O
11o
0.93
1.97
2.10
1.07
1.00
2.64
1.86
5.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


175.32
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151.93
142.90
133.32
129.84
129.75
128.51
127.93
127.72
120.61
105.06
77.49
77.07
76.65
51.88
35.13
O
O
OMe
O
11o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)