Supporting Information

Catalytic stereoselective synthesis of all-carbon tetra-substituted alkenes via Z-selective alkyne difunctionalization

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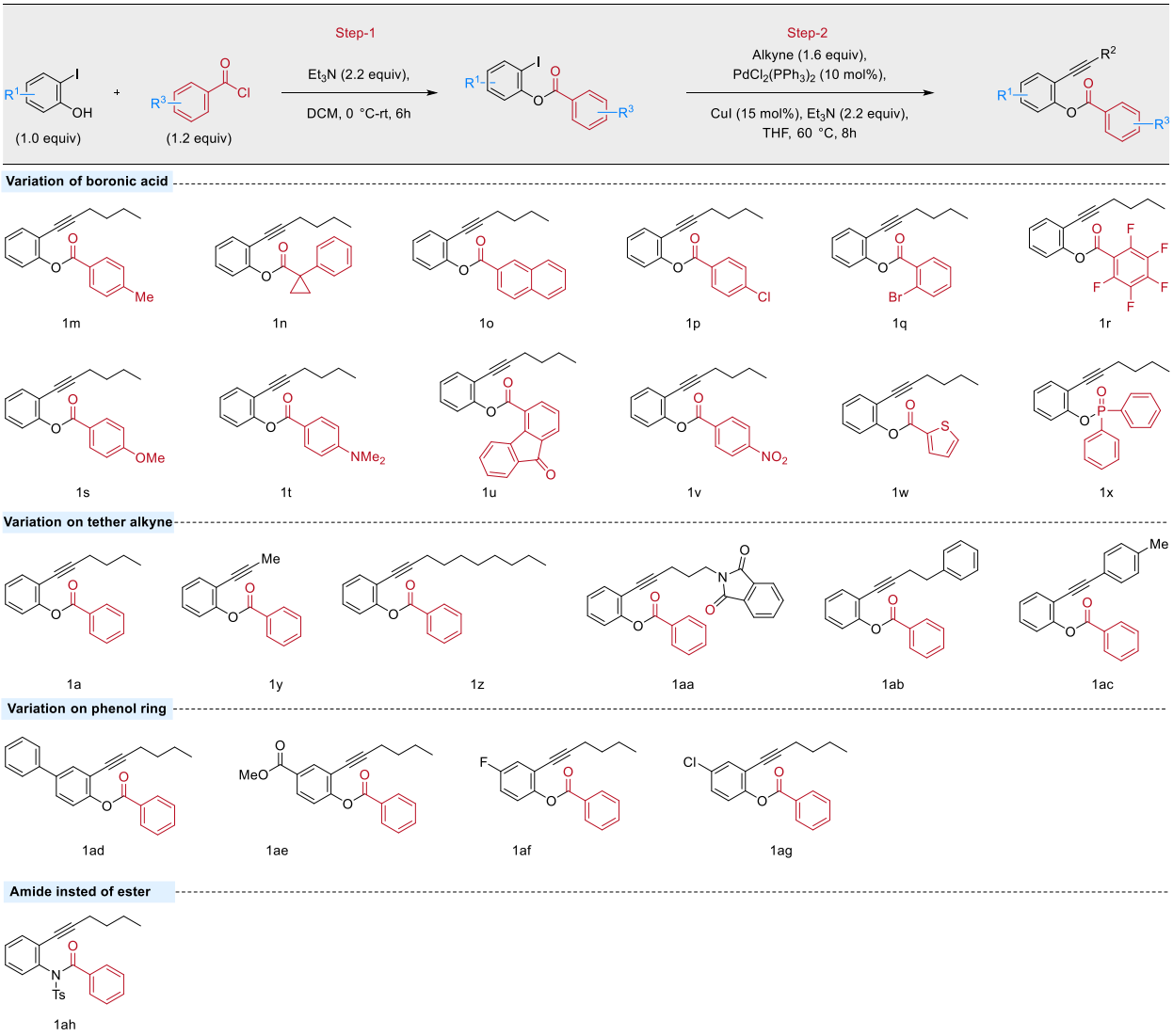
1. General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were HPLC grade. Anhydrous and degassed ACN used in reactions was purchased from Sigma-Aldrich in Sure/Seal™ bottle. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was performed on silica gel (particle size 0.043–0.063 mm) by using Interchim PuriFlash®430 automatic purification system. ^{1}H-NMR and ^{13}C-NMR were recorded on Bruker DRX-500 and AMX-400 instruments in $CDCl_3$ and are reported relative to the solvent residual peaks. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). Mass spectra (EI-MS, 70 eV) were conducted on the Agilent 7890 gas chromatograph equipped with 5975C EI-MSD Triple-Axis Detector using DB5MS and HP5MS columns. HRMS analysis was performed using a Thermo LTQ Velos Orbitrap mass spectrometer (Thermo Scientific, Pittsburgh, PA, USA) equipped with an ESI source. Single crystal X-ray diffraction data were collected in D8 VENTURE. The structure was solved with direct methods using the SHELXL programs. Single crystal suitable for X-ray diffraction obtained from methanol solution by slow evaporation.

2. General Procedure

2.1 General synthetic procedure for the preparation of 2-alkynyl phenol ester derivatives

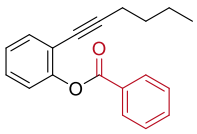


Step-1: To a stirred solution of 2-iodophenol (1.0 equiv.) in CH_2Cl_2, benzoyl chloride (1.2 equiv.) was added at 0 °C, followed by the dropwise addition of trimethylamine (2.2 equiv.). The reaction mixture was slowly warmed to room temperature and stirred for 6 hours. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with water and extracted three times with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure using a rotary evaporator. The crude product was purified by column chromatography on silica gel using a 5-10% mixture of petroleum ether and ethyl acetate to afford 2-iodophenyl benzoate.

Step-2: To a solution of 2-iodophenyl benzoate (1.0 equiv.), the corresponding alkyne (1.6 equiv.), and triethylamine (2.2 equiv.) in dry THF, $PdCl_2(PPh_3)_2$ (10 mol%) and CuI (20 mol%) were added under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 6 hours. Upon completion, the mixture was filtered through a Celite pad and washed with ethyl acetate. The combined filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel using a 10-15% mixture of petroleum ether and ethyl acetate to afford the corresponding 2-alkynyl phenyl benzoate.

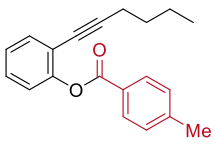
Analytical data for substrates:

2-(hex-1-yn-1-yl) phenyl benzoate (1a):



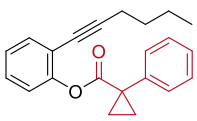
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.20 (m, 2H), 7.70 – 7.59 (m, 1H), 7.55 – 7.46 (m, 3H), 7.34 (td, *J* = 7.8, 1.7 Hz, 1H), 7.21 (ddd, *J* = 7.4, 3.6, 2.3 Hz, 2H), 2.26 (t, *J* = 6.8 Hz, 2H), 1.35 – 1.19 (m, 4H), 0.71 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.87, 152.07, 133.63, 133.06, 130.42, 129.71, 128.74, 128.61, 125.95, 122.36, 118.36, 96.00, 75.61, 30.59, 21.91, 19.27, 13.59. **HRMS** m/z (ESI) calcd for $[C_{19}H_{18}O_2$, M+Na$]^+$: 301.1200, Found: 301.1246.

2-(hex-1-yn-1-yl)phenyl 4-methylbenzoate (1m):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.12 (m, 2H), 7.51 – 7.45 (m, 1H), 7.33 (dd, *J* = 12.1, 7.8 Hz, 3H), 7.24 – 7.18 (m, 2H), 2.46 (s, 3H), 2.27 (t, *J* = 6.7 Hz, 2H), 1.36 – 1.19 (m, 4H), 0.73 (t, *J* = 7.0 Hz, 3H**). ^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.89, 152.12, 144.38, 132.99, 130.44, 129.28, 128.68, 126.91, 125.81, 122.39, 118.34, 95.87, 75.63, 30.57, 21.89, 21.85, 19.24, 13.56. **HRMS** m/z (ESI) calcd for $[C_{20}H_{20}O_2$, M+Na$]^+$: 315.1356, Found: 315.1374.

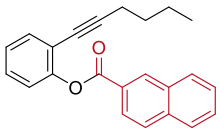
2-(hex-1-yn-1-yl)phenyl 1-phenylcyclopropane-1-carboxylate (1n):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.30 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.19 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.13 (td, *J* = 8.2, 2.1 Hz, 1H), 7.01 (td, *J* = 7.5, 1.3 Hz, 1H), 6.90 (dd, *J* = 8.1, 1.3 Hz, 1H), 2.39 (t, *J* = 7.1 Hz, 2H), 1.77 (q, *J* = 4.0 Hz, 2H), 1.60 – 1.51 (m, 2H), 1.43 (td, *J* = 9.5, 8.5, 6.2 Hz, 2H), 1.27 (q, *J* = 4.0 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H**). ^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.74, 151.82, 139.12,

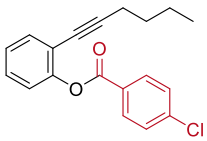
133.21, 130.75, 128.56, 128.30, 127.47, 125.68, 122.24, 118.04, 95.34, 75.79, 30.99, 29.34, 22.26, 19.52, 17.36, 13.83. **HRMS** m/z (ESI) calcd for [$C_{22}H_{22}O_2$, M+Na]$^+$: 341.1512, Found: 341.1588.

2-(hex-1-yn-1-yl)phenyl 2-naphthoate (1o):



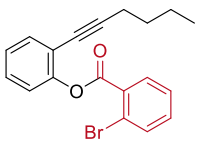
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.14 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.84 (dd, *J* = 11.2, 8.4 Hz, 2H), 7.50 (dt, *J* = 21.5, 7.2 Hz, 2H), 7.41 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.25 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.19 – 7.09 (m, 2H), 2.13 (t, *J* = 6.8 Hz, 2H), 1.12 (dq, *J* = 30.5, 7.3 Hz, 4H), 0.48 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.02, 152.18, 135.96, 133.11, 132.66, 132.16, 129.61, 128.78, 128.69, 128.42, 127.97, 126.94, 126.91, 125.98, 125.77, 122.42, 118.42, 96.08, 75.67, 30.59, 21.88, 19.27, 13.46. **HRMS** m/z (ESI) calcd for [$C_{23}H_{20}O_2$, M+Na]$^+$: 351.1356, Found: 351.1352.

2-(hex-1-yn-1-yl)phenyl 4-chlorobenzoate (1p) :



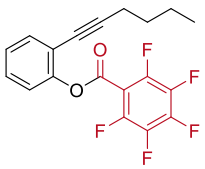
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.55 (ddd, *J* = 8.9, 4.2, 1.6 Hz, 3H), 7.44 – 7.37 (m, 1H), 7.34 – 7.22 (m, 2H), 2.33 (t, *J* = 6.6 Hz, 2H), 1.43 – 1.26 (m, 4H), 0.80 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.99, 151.81, 140.17, 133.12, 131.78, 131.06, 128.99, 128.78, 126.10, 122.24, 118.25, 96.07, 75.50, 30.60, 21.90, 19.23, 13.59. **HRMS** m/z (ESI) calcd for [$C_{19}H_{17}ClO_2$, M+Na]$^+$: 335.0809, Found: 335.0892.

2-(hex-1-yn-1-yl)phenyl 2-bromobenzoate (1q):



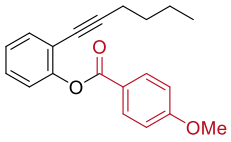
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dt, *J* = 7.5, 1.6 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.51 – 7.32 (m, 4H), 7.22 (t, *J* = 7.8 Hz, 2H), 2.34 (t, *J* = 6.9 Hz, 2H), 1.48 – 1.39 (m, 2H), 1.33 (h, *J* = 7.4 Hz, 2H), 0.80 (t, *J* = 7.2 Hz, 3H**). ^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.77, 151.56, 134.85, 133.37, 133.25, 132.36, 130.98, 128.81, 127.29, 126.18, 122.86, 122.31, 118.29, 96.09, 75.61, 30.68, 22.03, 19.39, 13.67. **HRMS** m/z (ESI) calcd for [$C_{19}H_{17}BrO_2$, M+Na]$^+$: 379.0304, Found: 379.0278.

2-(hex-1-yn-1-yl)phenyl 2,3,4,5,6-pentafluorobenzoate (1r):



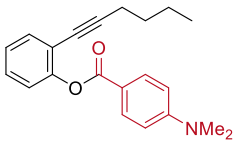
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.27 – 7.22 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 2.37 (td, *J* = 7.0, 1.2 Hz, 2H), 1.55 – 1.46 (m, 2H), 1.39 (p, *J* = 7.3 Hz, 2H), 0.86 (td, *J* = 7.2, 1.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.04, 150.73, 133.60, 145.8 (dddd, *J* = 248.1 Hz), 145.0 – 142.4 (m), 137.95 (dddd, *J* = 253.6 Hz), 128.92, 126.84, 121.86, 118.23, 96.76, 74.96, 30.68, 22.06, 19.31, 13.65. **HRMS** m/z (ESI) calcd for $[C_{19}H_{13}F_5O_2, M+Na]^+$: 391.0728, Found: 391.0696.

2-(hex-1-yn-1-yl)phenyl 4-methoxybenzoate (1s):



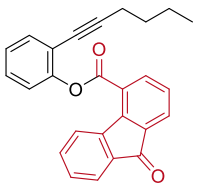
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.17 (m, 2H), 7.47 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.33 (td, *J* = 7.7, 1.7 Hz, 1H), 7.19 (ddd, *J* = 7.5, 3.7, 2.4 Hz, 2H), 7.02 – 6.94 (m, 2H), 3.89 (s, 3H), 2.26 (t, *J* = 6.7 Hz, 2H), 1.36 – 1.22 (m, 4H), 0.73 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.58, 163.95, 152.18, 132.99, 132.53, 128.69, 125.77, 122.46, 122.03, 118.38, 113.85, 95.83, 75.69, 55.62, 30.61, 21.90, 19.26, 13.63. **HRMS** m/z (ESI) calcd for $[C_{20}H_{20}O_3, M+Na]^+$: 331.1304, Found: 331.1315.

2-(hex-1-yn-1-yl)phenyl 4-(dimethylamino)benzoate (1t):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.05 (m, 2H), 7.46 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.31 (ddd, *J* = 8.4, 7.5, 1.7 Hz, 1H), 7.18 (ddd, *J* = 15.0, 7.8, 1.3 Hz, 2H), 6.78 – 6.65 (m, 2H), 3.08 (s, 6H), 2.27 (t, *J* = 6.8 Hz, 2H), 1.41 – 1.21 (m, 4H), 0.75 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.17, 153.73, 152.53, 132.92, 132.26, 128.60, 125.45, 122.68, 118.48, 116.40, 110.94, 95.62, 75.87, 40.28, 30.68, 21.97, 19.33, 13.70. **HRMS** m/z (ESI) calcd for $[C_{21}H_{23}NO_2, M+Na]^+$: 344.1621, Found: 344.1621.

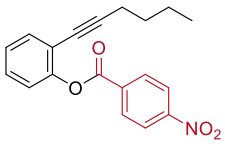
2-(hex-1-yn-1-yl)phenyl 9-oxo-9H-fluorene-4-carboxylate (1u):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 7.8 Hz, 1H), 8.36 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 7.3 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.56 – 7.32 (m, 5H), 7.30 – 7.21 (m, 2H), 2.23 (td, *J* = 7.0, 1.3 Hz, 2H), 1.38 – 1.29 (m, 2H), 1.23 (dt, *J* = 14.8, 7.3 Hz, 2H), 0.67 (td, *J* = 7.2, 1.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.99, 164.71, 151.61, 145.27, 143.05, 136.91, 135.90, 135.40, 134.48, 133.37, 130.12, 128.99,

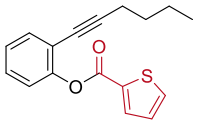
128.77, 128.07, 126.99, 126.43, 126.06, 124.22, 122.22, 118.40, 96.39, 75.56, 30.61, 21.98, 19.31, 13.57. **HRMS** m/z (ESI) calcd for [$C_{26}H_{20}O_3$, M+Na]$^+$: 403.1305, Found: 403.1364.

2-(hex-1-yn-1-yl)phenyl 4-nitrobenzoate (1v):



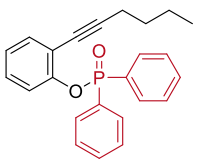
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 8.8, 1.5 Hz, 2H), 8.38 (dd, *J* = 8.7, 1.5 Hz, 2H), 7.52 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.30 – 7.21 (m, 2H), 2.27 (t, *J* = 6.7 Hz, 2H), 1.39 – 1.19 (m, 4H), 0.73 (td, *J* = 7.2, 1.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.95, 151.44, 150.98, 135.07, 133.29, 131.50, 128.90, 126.45, 123.79, 122.00, 118.11, 96.30, 75.36, 30.58, 21.87, 19.19, 13.58. **HRMS** m/z (ESI) calcd for [$C_{19}H_{17}NO_4$, M+Na]$^+$: 346.1050, Found: 346.1009.

2-(hex-1-yn-1-yl)phenyl thiophene-2-carboxylate (1w):



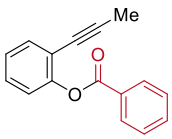
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 1H), 7.66 (d, *J* = 4.9 Hz, 1H), 7.52 – 7.44 (m, 1H), 7.36 – 7.29 (m, 1H), 7.24 – 7.15 (m, 3H), 2.30 (t, *J* = 6.7 Hz, 2H), 1.40 – 1.24 (m, 4H), 0.77 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.16, 151.61, 134.80, 133.50, 132.99, 132.96, 128.67, 128.01, 126.04, 122.33, 118.40, 96.22, 75.48, 30.57, 21.90, 19.26, 13.61. **HRMS** m/z (ESI) calcd for [$C_{17}H_{16}SO_4$, M+Na]$^+$: 307.0763, Found: 307.0750.

2-(hex-1-yn-1-yl)phenyl diphenylphosphinate (1x):



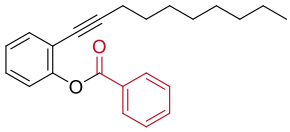
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.93 (m, 4H), 7.51 – 7.38 (m, 7H), 7.34 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.09 (td, *J* = 7.9, 1.8 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 2.50 (t, *J* = 7.1 Hz, 2H), 1.69 – 1.56 (m, 2H), 1.55 – 1.42 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.73 (d, $J_{C\text{-}P}$ = 7.9 Hz), 133.47, 132.49 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.99 (d, $J_{C\text{-}P}$ = 10.4 Hz), 131.06 (d, $J_{C\text{-}P}$ = 138.7 Hz), 128.89, 128.55 (d, $J_{C\text{-}P}$ = 13.6 Hz), 124.25, 120.42 (d, $J_{C\text{-}P}$ = 3.8 Hz), 116.52 (d, $J_{C\text{-}P}$ = 6.4 Hz), 95.59, 76.47, 30.89, 22.19, 19.49, 13.75. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 30.57. **HRMS** m/z (ESI) calcd for [$C_{14}H_{23}PO_2$, M+Na]$^+$: 397.1328, Found: 397.1362.

2-(prop-1-yn-1-yl)phenyl benzoate (1y):



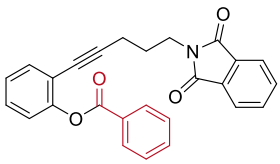
The title compound was prepared according to general procedure, and isolated as colorless liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 – 8.21 (m, 2H), 7.63 (td, *J* = 7.5, 1.5 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.36 – 7.30 (m, 1H), 7.23 – 7.16 (m, 2H), 1.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.98, 152.04, 133.63, 133.10, 130.36, 129.69, 128.79, 128.64, 125.94, 122.36, 118.22, 91.39, 74.75, 4.48. **HRMS** m/z (ESI) calcd for $[C_{16}H_{12}O_2$, M+Na$]^+$: 259.0730, Found: 259.0754.

2-(dec-1-yn-1-yl) phenyl benzoate (1z):



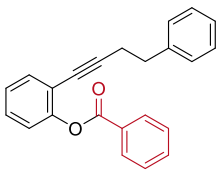
The title compound was prepared according to general procedure, and isolated as brown liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.33 (td, *J* = 7.8, 1.6 Hz, 1H), 7.25 – 7.16 (m, 2H), 2.24 (t, *J* = 6.9 Hz, 2H), 1.37 – 1.06 (m, 12H), 0.87 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.84, 152.08, 133.60, 133.05, 130.41, 129.74, 128.72, 128.60, 125.92, 122.35, 118.37, 96.10, 75.60, 31.97, 29.19, 29.16, 28.88, 28.58, 22.77, 19.59, 14.24. **HRMS** m/z (ESI) calcd for $[C_{23}H_{26}O_2$, M+Na$]^+$: 357.1825, Found: 357.1856.

2-(5-(1,3-dioxoisoindolin-2-yl)pent-1-yn-1-yl)phenyl benzoate (1aa):



The title compound was prepared according to general procedure, and isolated as brown solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 – 8.17 (m, 2H), 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.66 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.45 (dd, *J* = 8.2, 6.5 Hz, 2H), 7.39 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.32 (td, *J* = 7.7, 1.7 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 2H), 3.64 (t, *J* = 7.0 Hz, 2H), 2.33 (t, *J* = 7.1 Hz, 2H), 1.74 (p, *J* = 7.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.32, 164.83, 152.00, 133.98, 133.59, 133.05, 132.19, 130.42, 129.58, 128.87, 128.59, 125.85, 123.27, 122.31, 117.84, 94.21, 76.34, 37.26, 27.34, 17.46. **HRMS** m/z (ESI) calcd for $[C_{26}H_{19}NO_4$, M+Na$]^+$: 432.1206, Found: 432.1215.

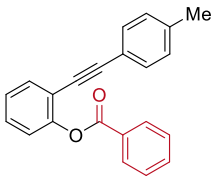
2-(4-phenylbut-1-yn-1-yl)phenyl benzoate (1ab):



The title compound was prepared according to general procedure, and isolated as colorless liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.38 (d, *J* = 7.8 Hz, 2H), 7.79 – 7.74 (m, 1H), 7.67 – 7.59 (m, 3H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.33 (dd, *J*

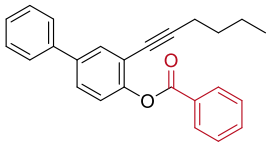
= 17.9, 8.0 Hz, 6H), 7.22 (d, *J* = 7.5 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.87, 152.07, 140.57, 133.67, 133.06, 130.38, 129.64, 128.91, 128.64, 128.42, 128.37, 126.32, 125.93, 122.36, 118.03, 95.08, 76.23, 34.94, 21.72. **HRMS** m/z (ESI) calcd for $[C_{23}H_{18}O_2, M+Na]^+$: 349.1200, Found: 349.1236.

2-(*p*-tolylethynyl)phenyl benzoate (1ac):



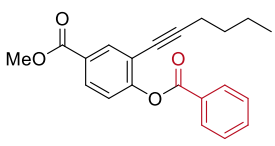
The title compound was prepared according to general procedure, and isolated as colorless liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.35 – 8.25 (m, 2H), 7.70 – 7.59 (m, 2H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 2.30 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.90, 151.95, 138.68, 133.77, 132.89, 131.46, 130.50, 129.62, 129.37, 129.09, 128.73, 126.05, 122.52, 119.88, 117.79, 94.90, 83.85, 21.60. **HRMS** m/z (ESI) calcd for $[C_{22}H_{16}O_2, M+Na]^+$: 335.1042, Found: 335.1052.

3-(hex-1-yn-1-yl)-[1,1'-biphenyl]-4-yl benzoate (1ad):



The title compound was prepared according to general procedure, and isolated as liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.54 (d, *J* = 2.3 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.33 (m, 5H), 7.27 (d, *J* = 15.1 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.14 – 7.06 (m, 1H), 2.11 (t, *J* = 6.7 Hz, 2H), 1.21 – 1.04 (m, 4H), 0.55 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.95, 151.37, 139.98, 139.20, 133.69, 131.73, 130.46, 129.65, 128.95, 128.64, 127.66, 127.51, 127.24, 122.65, 118.59, 96.12, 75.66, 30.58, 21.91, 19.27, 13.59. **HRMS** m/z (ESI) calcd for $[C_{25}H_{22}O_2, M+Na]^+$: 377.1522, Found: 377.1552.

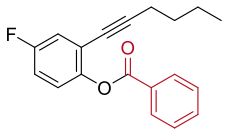
Methyl 4-(benzoyloxy)-3-(hex-1-yn-1-yl)benzoate (1ae):



The title compound was prepared according to general procedure, and isolated as liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (dd, *J* = 8.2, 1.4 Hz, 2H), 8.17 (d, *J* = 2.1 Hz, 1H), 8.01 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.65 (td, *J* = 7.3, 1.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 1H), 3.92 (s, 3H), 2.27 (t, *J* = 6.8 Hz, 2H), 1.39 – 1.19 (m, 4H), 0.72 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.06, 164.37, 155.50, 134.67, 133.91, 130.47, 130.04, 129.24, 128.70, 128.00, 122.53, 118.76, 97.07,

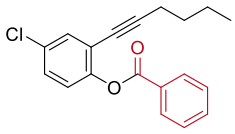
74.89, 52.43, 30.46, 21.89, 19.21, 13.56. **HRMS** m/z (ESI) calcd for $[C_{21}H_{20}O_4, M+Na]^+$: 359.1253, Found: 359.1274.

4-fluoro-2-(hex-1-yn-1-yl)phenyl benzoate (1af):



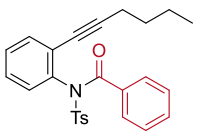
The title compound was prepared according to general procedure, and isolated as liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26 – 8.19 (m, 2H), 7.67 – 7.62 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.16 (ddd, *J* = 9.3, 5.3, 4.0 Hz, 2H), 7.07 – 7.00 (m, 1H), 2.25 (t, *J* = 6.8 Hz, 2H), 1.34 – 1.20 (m, 4H), 0.70 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.90, 159.98 (d, J_{C-F} = 244.34 Hz), 148.13 (d, J_{C-F} = 3.01 Hz), 133.78, 130.43, 130.32, 129.45, 128.67, 123.61 (d, J_{C-F} = 9.26 Hz), 119.42 (d, J_{C-F} = 24.46 Hz), 115.79 (d, J_{C-F} = 23.41 Hz), 97.20, 74.84 (d, J_{C-F} = 2.83 Hz), 30.43, 21.90, 19.22, 13.55. ^{19}F **NMR (377 MHz, $CDCl_3$)** δ -116.94. **HRMS** m/z (ESI) calcd for $[C_{19}H_{17}FO_2, M+Na]^+$: 319.1104, Found: 319.1126

4-chloro-2-(hex-1-yn-1-yl)phenyl benzoate (1ag):



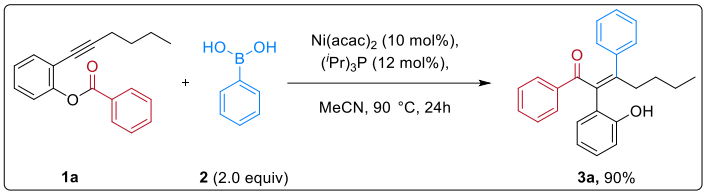
The title compound was prepared according to general procedure, and isolated as liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 – 8.10 (m, 2H), 7.62 – 7.52 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 2.5 Hz, 1H), 7.24 – 7.16 (m, 1H), 7.06 (d, *J* = 8.7 Hz, 1H), 2.17 (t, *J* = 6.8 Hz, 2H), 1.27 – 1.10 (m, 4H), 0.63 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.76, 150.72, 133.93, 132.82, 131.31, 130.55, 129.48, 128.86, 128.78, 123.70, 120.11, 97.55, 74.75, 30.54, 21.99, 19.33, 13.65. **HRMS** m/z (ESI) calcd for $[C_{19}H_{17}ClO_2, M+Na]^+$: 335.0809, Found: 335.0828.

N-(2-(hex-1-yn-1-yl)phenyl)-N-tosylbenzamide (1ah):



The title compound was prepared according to general procedure. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 – 7.94 (m, 2H), 7.60 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.34 – 7.10 (m, 8H), 2.44 (s, 3H), 2.03 – 1.93 (m, 2H), 1.29 (tq, *J* = 5.8, 2.7 Hz, 4H), 0.93 – 0.85 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.43, 144.56, 138.63, 136.55, 134.37, 132.99, 132.37, 131.41, 130.22, 129.16, 129.06, 128.17, 127.63, 124.83, 97.18, 76.55, 30.37, 22.31, 21.80, 19.13, 13.71

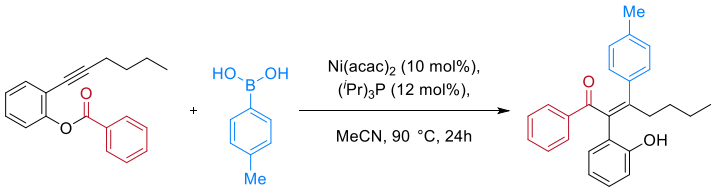
2.2 Experimental Procedure for Ni-Catalyzed Aryl acylation of alkynes:



An oven-dried screw-cap reaction vial equipped with a magnetic stir bar was charged with the 2-alkynyl phenol ester derivative (0.6 mmol, 1.0 equiv.), $Ni(acac)_2 \cdot 4H_2O$ (10 mol%), L4 (12 mol%), and arylboronic acid (1.2 mmol, 2.0 equiv.) in acetonitrile (6 mL). The reaction mixture was stirred at 90 °C for 24 hours, with progress monitored by thin-layer chromatography (TLC). After completion, the mixture was cooled to room temperature, quenched with H_2O (20 mL), and extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with a saturated sodium bicarbonate solution (20 mL, to remove excess phenylboronic acid) and brine (20 mL), then dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel using hexane/EtOAc as the eluent to yield the corresponding acyl-migrated product. In some cases, methanol washing was employed to remove byproducts such as homo-coupled phenylboronic acid and aryl ketone (see control experiment (d)).

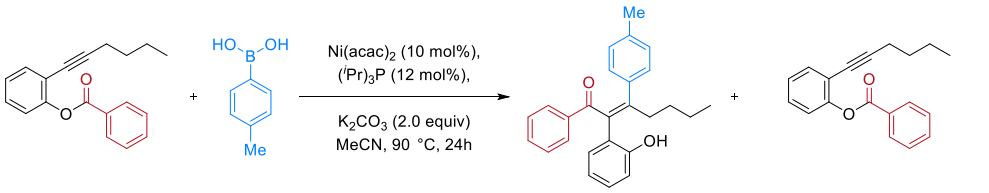
Control Experiments:

a) Standard reaction condition:



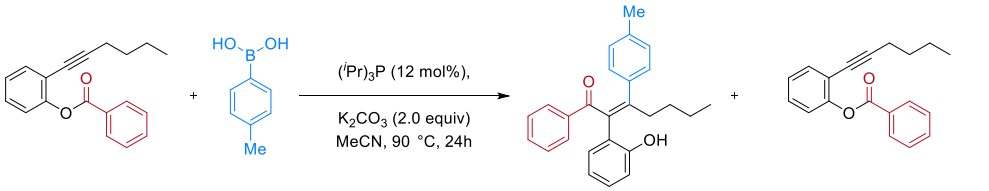
1a **2** (2.0 equiv) **3b,** 90%

b) Effect of base:



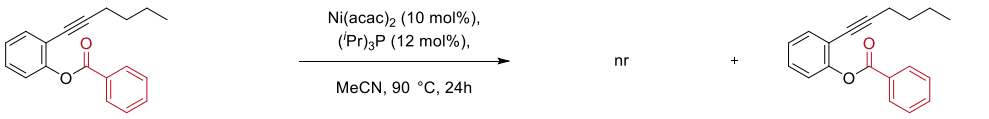
1a **2** (2.0 equiv) **3b,** nr Starting material recovered **(1a)**

c) Without $Ni(acac)_2$ (10 mol%):



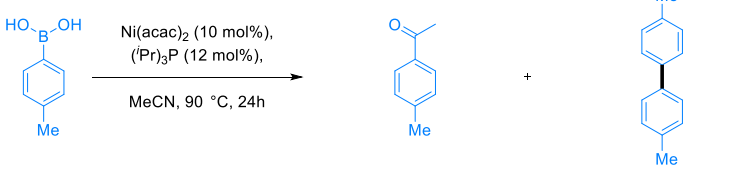
1a **2** (2.0 equiv) **3b,** nr Starting material recovered **(1a)**

c) Without boronic acid:



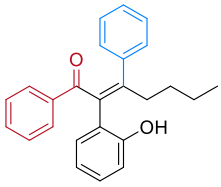
1a Starting material recovered **(1a)**

d) Without 2-(hex-1-yn-1-yl)phenyl benzoate:



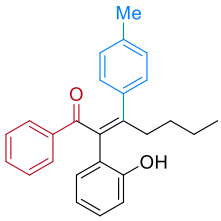
2 (2.0 equiv) ^{1}H, ^{13}C Confirmed ^{1}H, ^{13}C Confirmed

(*Z*)-2-(2-hydroxyphenyl)-1,3-diphenylhept-2-en-1-one (3a):



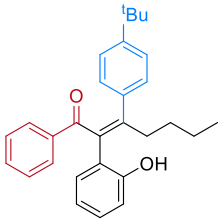
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 87% (187.4 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.00 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.24 (m, 6H), 7.23 – 7.11 (m, 4H), 7.04 (t, *J* = 7.4 Hz, 1H), 2.59 (s, 2H), 1.33 – 1.13 (m, *J* = 7.8, 6.9 Hz, 4H), 0.76 (t, *J* = 6.9 Hz, 3H)**. ^{1}H NMR (400 MHz, D_2O Exchange)**: δ 7.82 – 7.74 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.15 (m, 7H), 7.14 – 7.01 (m, 4H), 6.95 (t, *J* = 7.4 Hz, 1H), 2.49 (s, 2H), 1.23 – 1.03 (m, 4H), 0.73 – 0.59 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 201.72, 154.73, 147.35, 138.76, 134.48, 133.93, 132.70, 129.86, 129.00, 128.93, 127.76, 127.26, 127.16, 126.82, 122.77, 119.22, 117.29, 32.44, 28.88, 21.01, 12.75. **^{13}C-DEPT-90 NMR (101 MHz, $CDCl_3$)** δ 133.60, 130.76, 129.89, 129.82, 128.66, 128.15, 128.06, 127.71, 120.11, 118.18**. ^{13}C-DEPT-135 NMR (101 MHz, $CDCl_3$)** δ 133.60, 130.76, 129.89, 129.82, 128.66, 128.15, 128.06, 127.71, 120.11, 118.18, 13.65. **HRMS** m/z (ESI) calcd for $[C_{25}H_{24}O_2, M+Na]^+$: 379.1669, Found: 379.1678.

(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)hept-2-en-1-one (3b):



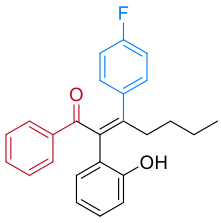
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 90% (200 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.92 (s, 1H), 7.88 – 7.80 (m, 2H), 7.44 – 7.36 (m, 1H), 7.28 (qd, *J* = 7.8, 7.2, 1.8 Hz, 4H), 7.10 (dd, *J* = 7.9, 5.5 Hz, 3H), 7.01 – 6.91 (m, 3H), 2.52 (s, 2H), 2.21 (s, 3H), 1.30 – 1.06 (m, 4H), 0.70 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 202.78, 155.74, 148.31, 137.56, 136.77, 135.48, 134.48, 133.63, 130.92, 129.98, 129.92, 128.87, 128.65, 128.24, 123.90, 120.18, 118.22, 33.43, 29.93, 22.02, 21.19, 13.76. **^{13}C-DEPT-45 NMR (101 MHz, $CDCl_3$):** δ 133.43, 130.72, 129.78, 129.71, 128.66, 128.45, 128.04, 119.97, 118.01, 33.22, 29.72, 21.81, 20.99, 13.55. **^{13}C-DEPT-90 NMR (101 MHz, $CDCl_3$):**130.82, 129.88, 129.81, 128.77, 128.55, 128.14, 120.07, 118.12. **^{13}C DEPT-135 NMR (101 MHz, $CDCl_3$):** δ 133.43, 130.72, 129.78, 129.72, 128.67, 128.45, 128.04, 119.98, 118.02, 20.99, 13.56. **HRMS** m/z (ESI) calcd for $[C_{26}H_{26}O_2, M+Na]^+$: 393.1825, Found: 393.1800.

(*Z*)-3-(4-(tert-butyl)phenyl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3c):



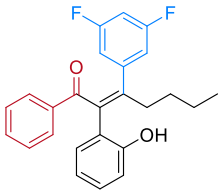
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 89% (220.3 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.19 (s, 1H), 7.95 – 7.84 (m, 2H), 7.54 – 7.41 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 5H), 7.14 (t, *J* = 7.4 Hz, 1H), 2.69 (s, 2H), 1.34 (s, 12H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 203.21, 155.75, 150.76, 149.11, 136.82, 136.08, 134.95, 133.22, 130.91, 129.90, 129.73, 128.53, 128.02, 124.89, 124.12, 120.15, 118.28, 34.48, 33.35, 31.16, 29.98, 22.07, 13.76. **HRMS** m/z (ESI) calcd for [$C_{29}H_{32}O_2$, M+Na]$^+$: 435.2295, Found: 435.2283.

(*Z*)-3-(4-fluorophenyl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3d):



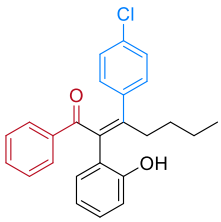
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 67% (150.5 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.82 (s, 1H), 7.83 – 7.74 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 4H), 7.18 – 7.12 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.81 (t, *J* = 8.6 Hz, 2H), 2.47 (s, 2H), 1.23 – 1.04 (m, 4H), 0.75 – 0.57 (m, 3H**). ^{13}C NMR (101 MHz, CDCl$_3$)** δ 202.58, 162.18 (d, *J* = 247.6 Hz) 155.66, 147.14, 135.71 (d, *J* = 3.4 Hz), 135.40 (d, *J* = 6.3 Hz), 133.93, 130.77, 130.52, 130.44, 130.11, 129.89, 128.41, 123.54, 120.29, 118.34, 115.23 (d, *J* = 21.4 Hz), 33.49, 29.83, 21.96, 13.74. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -113.77. **HRMS** m/z (ESI) calcd for [$C_{25}H_{23}$ FO_2, M+Na]$^+$: 397.1574, Found: 397.1584.

(*Z*)-3-(3,5-difluorophenyl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3e):



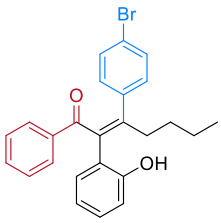
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 68% (160.1 mg). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.67 (s, 1H), 7.85 – 7.75 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.22 (m, 5H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.76 – 6.68 (m, 2H), 6.51 (tt, *J* = 8.8, 2.3 Hz, 1H), 2.45 (s, 2H), 1.15 (h, *J* = 3.5, 3.1 Hz, 4H), 0.73 – 0.63 (m, 3H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 200.85, 161.66 (dd, *J* = 250.0, 13.0 Hz), 154.58, 144.54, 142.06 (t, *J* = 9.2 Hz), 135.39, 134.08, 133.26, 129.46 (d, *J* = 19.6 Hz), 128.89, 127.58, 121.96, 119.42, 117.49, 111.32 – 110.35 (m), 102.30 (t, *J* = 25.1 Hz), 32.20, 28.81, 21.00, 12.73. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -108.77. **HRMS** m/z (ESI) calcd for [$C_{25}H_{22}F_2O_2$, M+Na]$^+$: 415.1480, Found: 415.1476.

(*Z*)-3-(4-chlorophenyl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3f):



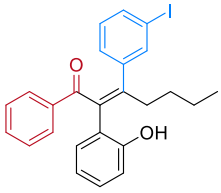
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 63% (147.7 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.77 (s, 1H), 7.86 – 7.76 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.34 – 7.23 (m, 4H), 7.18 – 7.05 (m, 5H), 7.01 – 6.92 (m, 1H), 2.49 (s, 2H), 1.23 – 1.06 (m, 4H), 0.76 – 0.58 (m, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 202.35, 155.65, 146.82, 138.21, 135.58, 135.27, 134.07, 133.76, 130.73, 130.17, 130.09, 129.96, 128.47, 123.38, 120.33, 118.36, 33.39, 29.84, 21.99, 13.75. **HRMS** m/z (ESI) calcd for [$C_{25}H_{23}ClO_2$, M+Na]$^+$: 413.1279, Found: 413.1269.

(*Z*)-3-(4-bromophenyl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3g):



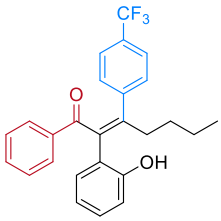
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 57% (149 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.74 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.21 (m, 6H), 7.07 (d, *J* = 8.2 Hz, 3H), 6.96 (t, *J* = 7.4 Hz, 1H), 2.48 (s, 2H), 1.15 (q, *J* = 3.7 Hz, 4H), 0.76 – 0.61 (m, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 202.30, 155.62, 146.78, 138.68, 135.55, 135.25, 134.08, 131.41, 130.71, 130.37, 130.17, 129.96, 128.49, 123.33, 121.99, 120.33, 118.35, 33.35, 29.82, 21.99, 13.74. **HRMS** m/z (EI) calcd for [$C_{25}H_{23}BrO_2$, M+Na]$^+$: 457.0774, Found: 457.0767.

(*Z*)-2-(2-hydroxyphenyl)-3-(3-iodophenyl)-1-phenylhept-2-en-1-one (3h):



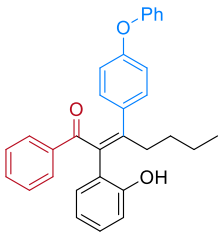
The title compound was prepared according to general procedure, and isolated as pale yellow semiliquid. Yield: 58% (167.8 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.84 (s, 1H), 7.84 – 7.76 (m, 2H), 7.53 (d, *J* = 1.8 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.34 – 7.25 (m, 5H), 7.19 – 7.13 (m, 1H), 7.12 – 7.04 (m, 1H), 7.01 – 6.94 (m, 1H), 6.86 (t, *J* = 7.8 Hz, 1H), 2.48 (s, 2H), 1.17 (tt, *J* = 10.6, 6.2 Hz, 4H), 0.71 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 202.29, 155.61, 146.68, 141.93, 137.42, 136.73, 136.03, 135.45, 133.94, 130.65, 130.17, 129.76, 128.39, 128.07, 123.38, 120.32, 118.39, 94.09, 33.30, 29.82, 22.00. **HRMS** m/z (ESI) calcd for [$C_{25}H_{23}IO_2$, M+Na]$^+$: 505.0635, Found: 505.0616.

(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)hept-2-en-1-one (3i):



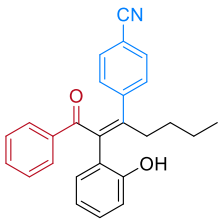
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 64% (163 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.72 (s, 1H), 7.84 – 7.75 (m, 2H), 7.46 – 7.38 (m, 3H), 7.35 – 7.23 (m, 7H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 2.53 (s, 2H), 1.18 (q, *J* = 3.8 Hz, 4H), 0.80 – 0.53 (m, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 202.12, 155.61, 146.66, 143.53, 136.32, 135.31, 134.13, 130.63, 130.30, 129.87, 129.81(d, *J* = 32.6 Hz), 129.13, 128.48, 125.15 (q, *J* = 3.8 Hz), 123.94 (q, *J* = 272.6 Hz), 123.09, 120.41, 118.42, 33.42, 29.78, 22.02, 13.72. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -62.81. **HRMS** m/z (ESI) calcd for $[C_{26}H_{23}F_3O_2, M+Na]^+$: 447.1542, Found: 447.1533.

(*Z*)-2-(2-hydroxyphenyl)-3-(4-phenoxyphenyl)-1-phenylhept-2-en-1-one (3j):



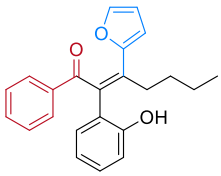
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 87% (234 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.94 (s, 1H), 7.82 – 7.76 (m, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.32 – 7.21 (m, 7H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.06 (dd, *J* = 7.8, 5.8 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.78 – 6.72 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 2H), 2.50 (s, 2H), 1.16 (dp, *J* = 22.1, 7.6 Hz, 4H), 0.68 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 202.89, 157.43, 156.62, 155.72, 148.16, 135.78, 135.20, 135.11, 133.58, 130.86, 130.30, 130.05, 129.99, 129.76, 128.30, 123.94, 123.24, 120.23, 119.11, 118.44, 118.39, 33.35, 29.97, 22.01, 13.78. **HRMS** m/z (ESI) calcd for $[C_{31}H_{28}O_3, M+Na]^+$: 471.1904, Found: 471.1900.

(*Z*)-4-(2-(2-hydroxyphenyl)-1-oxo-1-phenylhept-2-en-3-yl)benzonitrile (3k):



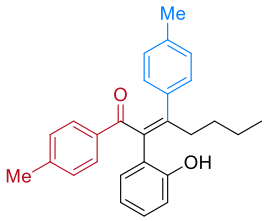
The title compound was prepared according to general procedure, and isolated as colorless liquid. Yield: 59% (135.1 mg). (59% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.58 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.45 – 7.39 (m, 3H), 7.32 – 7.23 (m, 8H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 2.50 (d, *J* = 6.8 Hz, 2H), 1.13 (q, *J* = 6.9, 5.3 Hz, 4H), 0.73 – 0.63 (m, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 201.72, 155.51, 146.05, 144.77, 136.76, 135.10, 134.36, 132.02, 130.50, 130.41, 129.89, 129.48, 128.61, 122.85, 120.49, 118.51, 118.45, 111.62, 33.24, 29.79, 21.99, 13.68. **HRMS** m/z (ESI) calcd for $[C_{26}H_{23}NO_3, M+Na]^+$: 404.1621, Found: 404.1609.

(*Z*)-3-(furan-2-yl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3l):



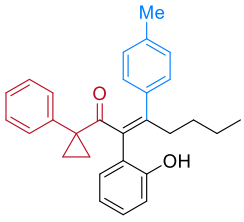
The title compound was prepared according to general procedure, and isolated as brown liquid. Yield: 53% (110.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.32 (s, 1H), 7.94 – 7.86 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.17 – 7.04 (m, 2H), 7.00 (d, *J* = 1.8 Hz, 1H), 6.91 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.79 (td, *J* = 7.5, 1.2 Hz, 1H), 6.29 (d, *J* = 3.4 Hz, 1H), 6.13 (dd, *J* = 3.5, 1.8 Hz, 1H), 2.46 – 2.11 (m, 2H), 1.32 (p, *J* = 7.6 Hz, 2H), 1.17 – 1.05 (m, 2H), 0.64 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 201.41, 155.66, 152.09, 143.10, 135.46, 134.51, 133.85, 132.00, 130.74, 130.13, 129.69, 128.73, 122.85, 120.28, 118.14, 111.38, 111.02, 31.61, 30.22, 22.52, 13.77. **HRMS** m/z (ESI) calcd for $[C_{23}H_{22}O_3, M+Na]^+$: 369.1461, Found: 369.1498.

(*Z*)-2-(2-hydroxyphenyl)-1,3-di-*p*-tolylhept-2-en-1-one (3m):



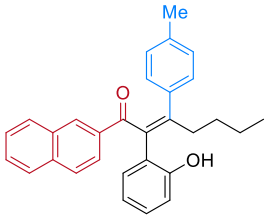
The title compound was prepared according to general procedure, and isolated as off white solid. Yield: 89% (206 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.98 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.24 (m, 2H), 7.12 (dd, *J* = 21.0, 8.0 Hz, 5H), 7.01 – 6.94 (m, 3H), 2.52 (s, 2H), 2.34 (s, 3H), 2.24 (s, 3H), 1.20 (s, 4H), 0.72 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.21, 155.80, 147.50, 144.77, 137.46, 136.85, 134.47, 132.73, 130.90, 130.28, 129.84, 129.09, 128.89, 128.61, 123.94, 120.12, 118.16, 33.40, 29.95, 22.03, 21.86, 21.24, 13.77. **HRMS** m/z (ESI) calcd for $[C_{27}H_{28}O_2, M+Na]^+$: 407.1982, Found: 407.1978.

(*Z*)-2-(2-hydroxyphenyl)-1-(1-phenylcyclopropyl)-3-(*p*-tolyl)hept-2-en-1-one (3n):



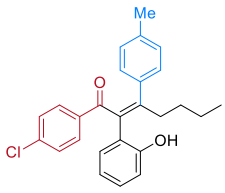
The title compound was prepared according to general procedure, and isolated as off white solid. Yield: 41% (101 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (s, 1H), 7.31 – 7.16 (m, 6H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 7.1 Hz, 2H), 6.64 (dd, *J* = 7.7, 1.7 Hz, 1H), 2.47 (s, 3H), 2.13 (d, *J* = 73.0 Hz, 2H), 1.81 – 1.51 (m, 2H), 0.98 (s, 6H), 0.58 (t, *J* = 6.6 Hz, 3H**). ^{13}C NMR (101 MHz, $CDCl_3$)** δ 213.78, 155.60, 145.31, 139.00, 138.05, 136.97, 134.88, 131.49, 131.46, 129.75, 129.47, 129.00, 127.78, 127.50, 123.57, 119.76, 117.82, 37.93, 32.81, 29.84, 29.71, 21.80, 21.46, 13.64. **HRMS** m/z (ESI) calcd for $[C_{29}H_{30}O_2, M+Na]^+$ 433.2138, Found: 433.2135.

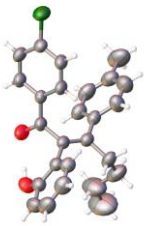
(*Z*)-2-(2-hydroxyphenyl)-1-(naphthalen-2-yl)-3-(*p*-tolyl)hept-2-en-1-one (3o):



The title compound was prepared according to general procedure, and isolated as yellow solid. Yield: 90% (227 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.10 – 9.02 (m, 1H), 8.51 (d, *J* = 1.8 Hz, 1H), 8.04 – 7.94 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.71 – 7.58 (m, 2H), 7.48 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.31 – 7.19 (m, 3H), 7.09 (td, *J* = 7.4, 1.3 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 2H), 2.68 (s, 2H), 2.21 (s, 3H), 1.33 (dq, *J* = 12.3, 8.1, 6.8 Hz, 4H), 0.83 (t, *J* = 6.9 Hz, 3H**). ^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.54, 155.77, 148.23, 137.57, 136.88, 135.85, 134.50, 132.83, 132.71, 132.30, 130.95, 129.94, 129.83, 128.96, 128.85, 128.51, 128.24, 127.79, 126.67, 124.82, 123.97, 120.22, 118.24, 33.53, 29.98, 22.06, 21.13, 13.78. **HRMS** m/z (ESI) calcd for $[C_{30}H_{28}O_2, M+Na]^+$: 443.1982, Found: 443.1968.

(*Z*)-1-(4-chlorophenyl)-2-(2-hydroxyphenyl)-3-(*p*-tolyl)hept-2-en-1-one (3p):

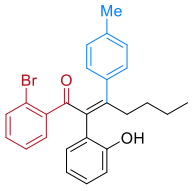




CCDC: 2288884

The title compound was prepared according to general procedure, and isolated as yellow solid. Yield: 69% (168 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (s, 1H), 7.78 – 7.69 (m, 2H), 7.30 – 7.16 (m, 5H), 7.10 – 7.02 (m, 3H), 6.98 – 6.88 (m, 3H), 2.48 (s, 2H), 2.20 (s, 3H), 1.21 – 1.05 (m, 4H), 0.66 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 201.43, 155.63, 148.77, 140.05, 137.90, 136.60, 134.07, 133.87, 131.28, 130.86, 130.06, 129.04, 128.66, 128.59, 123.67, 120.28, 118.28, 33.42, 29.92, 22.00, 21.24, 13.74. **HRMS** m/z (ESI) calcd for $[C_{26}H_{25}ClO_2, M+Na]^+$ 427.1435, Found: 427.1428.

(*Z*)-1-(2-bromophenyl)-2-(2-hydroxyphenyl)-3-(*p*-tolyl)hept-2-en-1-one (3q):

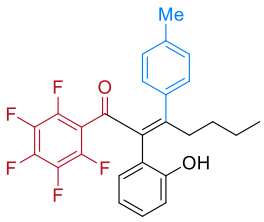


CCDC: 2288883

The title compound was prepared according to general procedure, and isolated as white solid. Yield: 62% (167 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (s, 1H), 7.41 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.29 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.04 – 6.78 (m, 8H), 2.32 (s, 2H), 2.11 (s, 3H), 1.04 (dd, *J* = 10.5, 6.1 Hz, 4H), 0.56 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.07, 155.36, 153.49, 138.72, 137.60, 136.90, 135.92, 134.11, 132.18, 131.72, 131.31, 129.86, 128.93, 128.26, 126.48, 125.25,

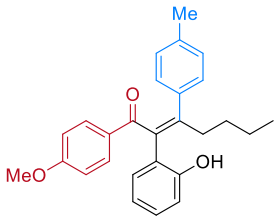
121.63, 120.13, 118.45, 34.73, 29.77, 22.09, 21.16, 13.70. **HRMS** m/z (ESI) calcd for $[C_{26}H_{25}BrO_2, M+Na]^+$: 471.0930, Found: 471.0934.

(*Z*)-2-(2-hydroxyphenyl)-1-(perfluorophenyl)-3-(*p*-tolyl)hept-2-en-1-one (3r):



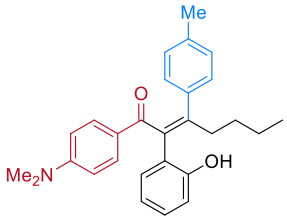
The title compound was prepared according to general procedure, and isolated as brown oil. Yield: 26% (73 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.19 (m, 3H), 7.15 – 6.84 (m, 6H), 2.40 (s, 2H), 2.28 (s, 3H), 1.20 – 0.97 (m, 4H), 0.64 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.73, 157.33, 154.52, 142.3 (dddd, *J* = 261.1 Hz), 143.9 (dddd, *J* = 253.8 Hz), 139.05, 137.06 (dddd, *J* = 254.8 Hz), 136.96, 136.78, 131.65, 130.25, 129.09, 128.06, 124.24, 120.63, 118.14, 116.10, 35.34, 29.74, 22.16, 21.09, 13.67. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -138.16 (d, *J* = 22.6 Hz), -149.83 (t, *J* = 20.8 Hz), -161.91 (t, *J* = 20.9 Hz). **HRMS** m/z (ESI) calcd for $[C_{26}H_{21}F_5O_2, M+Na]^+$: 483.1354, Found:483.1563.

(*Z*)-2-(2-hydroxyphenyl)-1-(4-methoxyphenyl)-3-(*p*-tolyl)hept-2-en-1-one (3s):



The title compound was prepared according to general procedure, and isolated as yellow solid. Yield: 58% (140 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.08 (s, 1H), 7.85 – 7.76 (m, 2H), 7.25 – 7.18 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.04 (dd, *J* = 8.5, 1.2 Hz, 1H), 6.97 – 6.88 (m, 3H), 6.75 – 6.67 (m, 2H), 3.77 (s, 3H), 2.40 (d, *J* = 43.7 Hz, 2H), 2.19 (s, 3H), 1.14 (s, 4H), 0.66 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 201.00, 164.11, 155.88, 147.10, 137.40, 136.91, 134.43, 132.64, 130.84, 129.80, 128.90, 128.54, 128.12, 124.01, 120.06, 118.18, 113.64, 55.53, 33.37, 29.94, 22.02, 21.25, 13.77. **HRMS** m/z (ESI) calcd for $[C_{27}H_{28}O_3, M+Na]^+$: 423.1931, Found: 423.1934.

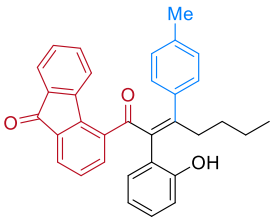
(*Z*)-1-(4-(dimethylamino)phenyl)-2-(2-hydroxyphenyl)-3-(*p*-tolyl)hept-2-en-1-one (3t):



The title compound was prepared according to general procedure, and isolated as white solid. Yield: 72% (178 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.49 (s, 1H), 7.75 (d, *J* = 8.6 Hz, 2H), 7.22 – 7.12 (m, 4H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 2H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.46 (d, *J* = 9.1 Hz, 2H), 2.98 (s, 6H), 2.62 – 2.25 (m, 2H), 1.13 (s, 4H), 0.73 –

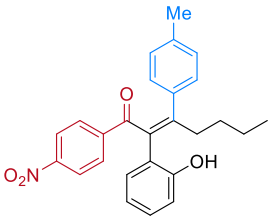
0.60 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 199.78, 156.09, 153.83, 145.47, 137.26, 136.98, 134.75, 132.83, 130.79, 129.48, 128.82, 128.51, 124.52, 122.76, 119.82, 118.05, 110.68, 40.15, 33.35, 29.99, 22.04, 21.30, 13.80. **HRMS** m/z (ESI) calcd for $[C_{28}H_{31}NO_2, M+Na]^+$: 436.2247, Found: 436.2242.

(*Z*)-4-(2-(2-hydroxyphenyl)-3-(*p*-tolyl)hept-2-enoyl)-9*H*-fluoren-9-one (3u):



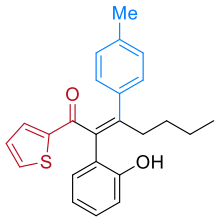
The title compound was prepared according to general procedure, and isolated as yellow solid. Yield: 70% (198 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.43 (s, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.58 – 7.47 (m, 2H), 7.38 – 7.27 (m, 3H), 7.18 – 6.99 (m, 3H), 6.84 (d, *J* = 7.5 Hz, 2H), 6.51 (d, *J* = 7.5 Hz, 2H), 2.64 – 2.29 (m, 2H), 1.88 (s, 3H), 1.15 (qd, *J* = 8.2, 4.8, 4.2 Hz, 4H), 0.66 (t, *J* = 6.7 Hz, 3H**). ^{13}C NMR (101 MHz, $CDCl_3$)** δ 203.67, 193.19, 155.15, 154.08, 143.65, 143.14, 137.79, 137.47, 137.27, 136.09, 135.09, 134.95, 134.65, 134.00, 131.01, 130.11, 129.77, 129.01, 128.13, 127.79, 126.42, 126.08, 124.99, 123.81, 120.54, 118.35, 34.46, 30.01, 22.16, 20.90, 13.74. **HRMS** m/z (ESI) calcd for $[C_{33}H_{28}O_3, M+Na]^+$: 495.1930, Found: 495.1926.

(*Z*)-2-(2-hydroxyphenyl)-1-(4-nitrophenyl)-3-(*p*-tolyl)hept-2-en-1-one (3v):



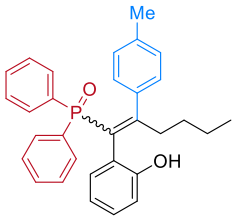
The title compound was prepared according to general procedure, and isolated as yellow solid. Yield: 63% (157 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.05 – 6.86 (m, 6H), 2.47 (d, *J* = 7.2 Hz, 2H), 2.14 (s, 3H), 1.12 (dp, *J* = 8.6, 5.5 Hz, 4H), 0.64 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 201.02, 155.26, 150.89, 150.08, 141.05, 138.46, 136.48, 134.12, 130.95, 130.48, 130.32, 129.20, 128.77, 123.64, 123.33, 120.57, 118.30, 33.64, 29.99, 22.06, 21.22, 13.72. **HRMS** m/z (ESI) calcd for $[C_{26}H_{25}NO_4, M+Na]^+$: 438.1676, Found:438.1684.

(*Z*)-2-(2-hydroxyphenyl)-1-(thiophen-2-yl)-3-(*p*-tolyl)hept-2-en-1-one (3w):



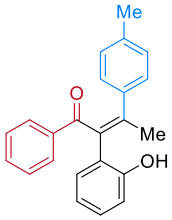
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 72% (163 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.83 (s, 1H), 7.67 (dd, *J* = 3.9, 1.2 Hz, 1H), 7.60 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.38 – 7.23 (m, 5H), 7.18 – 6.96 (m, 5H), 2.68 – 2.45 (m, 2H), 2.32 (s, 3H), 1.24 (dd, *J* = 10.7, 5.7 Hz, 4H), 0.75 (t, *J* = 6.9 Hz, 3H**). ^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.25, 155.69, 148.20, 142.36, 137.69, 136.82, 135.92, 135.75, 134.82, 131.02, 129.99, 129.03, 128.62, 128.11, 123.68, 120.22, 118.24, 33.34, 29.88, 21.98, 21.27, 13.74. **HRMS** m/z (ESI) calcd for $[C_{24}H_{24}O_2S, M+Na]^+$: 399.1389, Found: 399.1380.

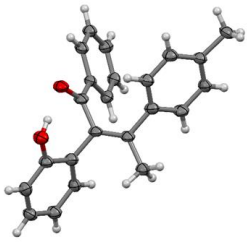
(*E*/*Z*)-(1-(2-hydroxyphenyl)-2-(*p*-tolyl)hex-1-en-1-yl)diphenylphosphine oxide (3x):



The title compound was prepared according to general procedure, and isolated as yellow liquid. *Z*/*E* = 77.23, Yield: 54% (151 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 – 7.80 (m, 2H), 7.78 – 7.68 (m, 4H), 7.46 – 7.40 (m, 1H), 7.39 – 7.32 (m, 5H), 7.31 – 7.21 (m, 7H), 7.18 – 7.12 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.05 – 6.93 (m, 2H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 7.3 Hz, 1H), 6.63 (s, 1H), 6.60 – 6.49 (m, 2H), 2.42 (q, *J* = 7.6, 6.5 Hz, 3H), 2.17 (s, 2H), 1.33 – 1.08 (m, 7H), 0.85 – 0.74 (m, 2H), 0.67 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.20 (d, *J* = 8.2 Hz), 149.08 (d, *J* = 8.2 Hz), 144.62, 144.41, 139.41, 137.39, 137.06, 136.55, 132.51 (d, *J* = 2.9 Hz), 132.40 (d, *J* = 2.9 Hz), 132.03, 131.97, 131.91, 131.86, 131.80, 131.19, 130.65, 130.48, 130.37, 130.16 (d, *J* = 5.8 Hz), 129.81, 129.74, 129.15, 128.96, 128.70, 128.62, 128.57, 128.48, 128.12, 127.38, 126.48, 124.25, 123.81, 122.58,120.60 (d, *J* = 3.8 Hz), 120.47, 120.31 (d, *J* = 3.8 Hz), 115.41, 39.69, 30.86, 30.37, 29.93, 22.71, 22.46, 21.24, 14.13, 13.92. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 29.97 (d, *J* = 4.3 Hz). **HRMS** m/z (ESI) calcd for $[C_{31}H_{31}O_2P, M+Na]^+$: 489.1953, Found: 489.1946.

(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)but-2-en-1-one (3y):



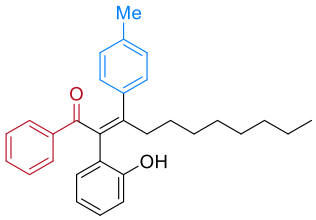


3y, CCDC: 2110836

The title compound was prepared according to general procedure, and isolated as white solid. Yield: 76% (149.7 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.92 (d, *J* = 2.9 Hz, 1H), 7.90 – 7.80 (m, 2H), 7.41 (td, *J* = 7.4, 1.4 Hz, 1H), 7.33 – 7.25 (m, 4H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.13 – 7.08 (m, 1H), 6.97 (t, *J* = 6.5 Hz, 3H), 2.21 (s, 3H), 2.13 (s, 3H). **^{1}H NMR D_2O Exchange (400 MHz, $CDCl_3$)** δ 7.86

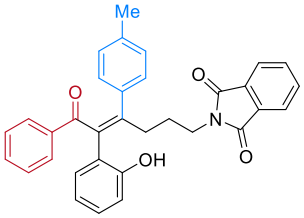
(d, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.34 – 7.24 (m, 4H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 6.9 Hz, 3H), 2.21 (s, 3H), 2.13 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.85, 155.37, 143.67, 138.39, 137.83, 135.52, 134.18, 133.70, 130.96, 130.02, 129.99, 128.97, 128.31, 128.00, 124.25, 120.29, 118.27, 21.47, 21.19. **HRMS** m/z (ESI) calcd for [$C_{23}H_{20}O_2$, M+Na]$^+$: 351.1355, Found: 351.1359.

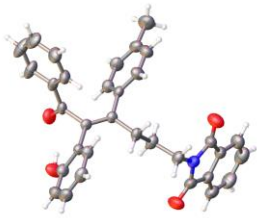
(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)undec-2-en-1-one (3z):



The title compound was prepared according to general procedure, and isolated as off white solid. Yield: 84% (215 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.84 (s, 1H), 7.83 – 7.77 (m, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.21 (m, 4H), 7.05 (dd, *J* = 7.8, 5.1 Hz, 3H), 6.91 (dd, *J* = 7.7, 5.8 Hz, 3H), 2.57 – 2.34 (m, 2H), 2.17 (s, 3H), 1.28 – 1.07 (m, 12H), 0.83 (t, *J* = 7.2 Hz, 3H**). ^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.78, 155.77, 148.40, 137.56, 136.82, 135.52, 134.47, 133.62, 130.91, 130.00, 129.92, 128.87, 128.68, 128.25, 123.88, 120.16, 118.24, 33.66, 31.92, 29.15, 28.87, 27.71, 22.74, 21.20, 14.24. **HRMS** m/z (ESI) calcd for [$C_{30}H_{34}O_2$, M+Na]$^+$: 449.2451, Found: 449.2458.

(*Z*)-2-(5-(2-hydroxyphenyl)-6-oxo-6-phenyl-4-(*p*-tolyl)hex-4-en-1-yl)isoindoline-1,3-dione (3aa):

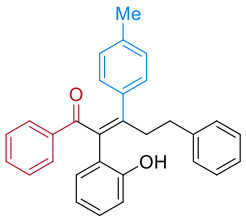




3aa, CCDC: 228885

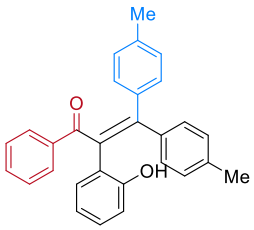
The title compound was prepared according to general procedure, and isolated as yellow solid. Yield: 66% (198.6 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.59 (s, 1H), 7.68 – 7.57 (m, 4H), 7.53 (dq, *J* = 5.5, 3.4 Hz, 2H), 7.25 – 7.17 (m, 1H), 7.12 – 7.01 (m, 3H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.87 – 6.81 (m, 1H), 6.75 (dd, *J* = 8.2, 1.9 Hz, 3H), 6.60 (t, *J* = 7.4 Hz, 1H), 3.35 (d, *J* = 10.2 Hz, 2H), 2.31 (d, *J* = 45.8 Hz, 2H), 2.00 (s, 3H), 1.54 – 1.32 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.26, 168.25, 155.32, 146.85, 137.82, 136.12, 135.34, 135.21, 133.85, 133.70, 132.16, 130.47, 129.94, 129.91, 129.00, 128.62, 128.27, 123.53, 123.22, 120.16, 118.20, 37.35, 31.52, 27.03, 21.18. **HRMS** m/z (ESI) calcd for [$C_{33}H_{27}NO_4$, M+Na]$^+$: 524.1832, Found: 524.1826.

(*Z*)-2-(2-hydroxyphenyl)-1,5-diphenyl-3-(*p*-tolyl)pent-2-en-1-one (3ab):



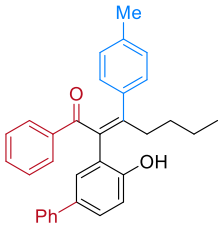
The title compound was prepared according to general procedure, and isolated as yellow solid. Yield: 77% (193.4 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.71 (s, 1H), 7.87 (d, *J* = 7.7 Hz, 2H), 7.48 – 7.40 (m, 1H), 7.33 – 7.28 (m, 3H), 7.18 (ddd, *J* = 32.7, 13.9, 7.7 Hz, 7H), 7.03 – 6.90 (m, 5H), 2.84 (s, 2H), 2.56 (t, *J* = 8.1 Hz, 2H), 2.25 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 202.36, 155.57, 147.22, 141.25, 137.80, 136.50, 135.38, 135.11, 133.74, 130.78, 130.08, 130.02, 129.02, 128.68, 128.40, 128.37, 128.31, 126.00, 123.54, 120.32, 118.20, 36.06, 34.22, 21.22. **HRMS** m/z (ESI) calcd for [$C_{30}H_{26}O_2$, M+Na]$^+$: 441.1825, Found: 441.1828.

(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3,3-di-*p*-tolylprop-2-en-1-one (3ac):



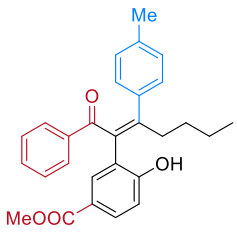
The title compound was prepared according to general procedure, and isolated as yellow solid. Yield: 61% (148 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.18 – 8.10 (m, 2H), 7.67 – 7.57 (m, 1H), 7.55 – 7.45 (m, 2H), 7.32 – 7.20 (m, 6H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 7.01 – 6.91 (m, 2H), 6.55 (s, 1H), 2.46 (s, 3H), 2.40 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 199.84, 153.69, 147.18, 138.12, 137.92, 137.15, 136.93, 135.11, 133.19, 131.27, 130.04, 129.92, 129.85, 129.64, 128.89, 128.42, 125.19, 120.82, 117.06, 21.40, 21.28. **HRMS** m/z (ESI) calcd for [$C_{29}H_{24}O_2$, M+Na]$^+$: 427.1668, Found: 427.1665.

(*Z*)-2-(4-hydroxy-[1,1'-biphenyl]-3-yl)-1-phenyl-3-(*p*-tolyl)hept-2-en-1-one (3ad):



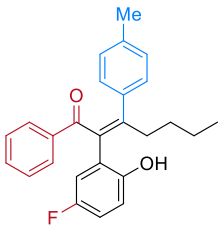
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 79% (211.6 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.02 (s, 1H), 7.85 – 7.78 (m, 2H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.50 – 7.20 (m, 9H), 7.11 (dd, *J* = 18.6, 8.0 Hz, 3H), 6.92 (d, *J* = 7.8 Hz, 2H), 2.76 – 2.30 (m, 2H), 2.18 (s, 3H), 1.17 (s, 4H), 0.67 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 202.94, 155.54, 148.76, 141.08, 137.77, 136.84, 135.57, 134.52, 133.82, 133.55, 130.13, 129.62, 129.02, 129.00, 128.85, 128.78, 128.41, 127.05, 126.98, 124.32, 118.78, 33.65, 30.10, 22.13, 21.32, 13.90. **HRMS** m/z (ESI) calcd for [$C_{32}H_{30}O_2$, M+Na]$^+$: 469.2138, Found: 469.2142.

(*Z*)-methyl-4-hydroxy-3-(1-oxo-1-phenyl-3-(*p*-tolyl)hept-2-en-2-yl)benzoate (3ae):



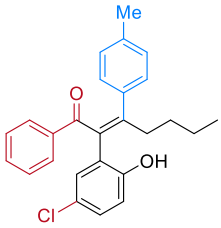
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 82% (210.8 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.66 (s, 1H), 7.99 (d, *J* = 2.2 Hz, 1H), 7.93 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.83 – 7.76 (m, 2H), 7.37 (td, *J* = 7.2, 1.4 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.10 – 7.01 (m, 3H), 6.91 (d, *J* = 7.8 Hz, 2H), 3.91 (s, 3H), 2.65 – 2.28 (m, 2H), 2.16 (s, 3H), 1.11 (s, 4H), 0.64 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 203.05, 166.97, 160.35, 149.66, 137.84, 136.50, 135.18, 133.94, 133.40, 133.19, 131.79, 130.10, 128.94, 128.61, 128.36, 123.86, 122.15, 118.24, 52.09, 33.50, 29.86, 21.91, 21.20, 13.74. **HRMS** m/z (ESI) calcd for [$C_{28}H_{28}O_4$, M+Na]$^+$: 451.1879, Found: 451.1885.

(*Z*)-2-(5-fluoro-2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)hept-2-en-1-one (3af):



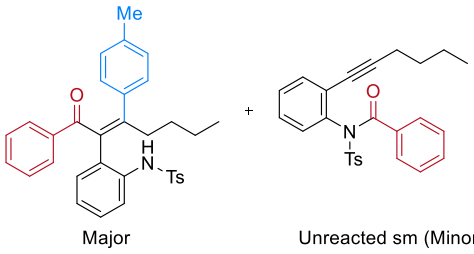
The title compound was prepared according to general procedure, and isolated as white solid. Yield: 66% (153.8 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.79 (s, 1H), 7.85 – 7.75 (m, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 2H), 7.12 – 6.91 (m, 7H), 2.52 (s, 2H), 2.20 (s, 3H), 1.27 – 1.10 (m, 4H), 0.71 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 202.42, 156.55 (d, *J* = 238.6 Hz), 151.85, 149.14, 137.83, 136.45, 135.33, 133.83, 133.33, 129.96, 128.95, 128.60, 128.35, 124.79 (d, *J* = 7.5 Hz), 119.18 (d, *J* = 8.3 Hz), 116.62 (dd, *J* = 47.8, 22.7 Hz), 33.53, 29.91, 22.03, 21.21, 13.76. **^{19}F NMR (377 MHz, CDCl$_3$)** δ -124.91. **HRMS** m/z (ESI) calcd for [$C_{26}H_{25}FO_2$, M+Na]$^+$: 411.1730, Found: 411.1742.

(*Z*)-2-(5-chloro-2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)hept-2-en-1-one (3ag):



The title compound was prepared according to general procedure, and isolated as white solid. Yield: 77% (174.9 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.04 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.17 (m, 4H), 7.03 (dd, *J* = 20.3, 8.2 Hz, 3H), 6.92 (d, *J* = 7.8 Hz, 2H), 2.46 (d, *J* = 35.2 Hz, 2H), 2.18 (s, 3H), 1.16 (s, 4H), 0.75 – 0.60 (m, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 202.56, 154.60, 149.36, 137.87, 136.42, 135.21, 133.90, 133.15, 130.26, 130.01, 129.77, 128.97, 128.59, 128.37, 125.44, 124.71, 119.69, 33.53, 29.90, 21.97, 21.20, 13.78. **HRMS** m/z (ESI) calcd for [$C_{26}H_{25}ClO_2$, M+Na]$^+$: 427.1435, Found: 427.1438.

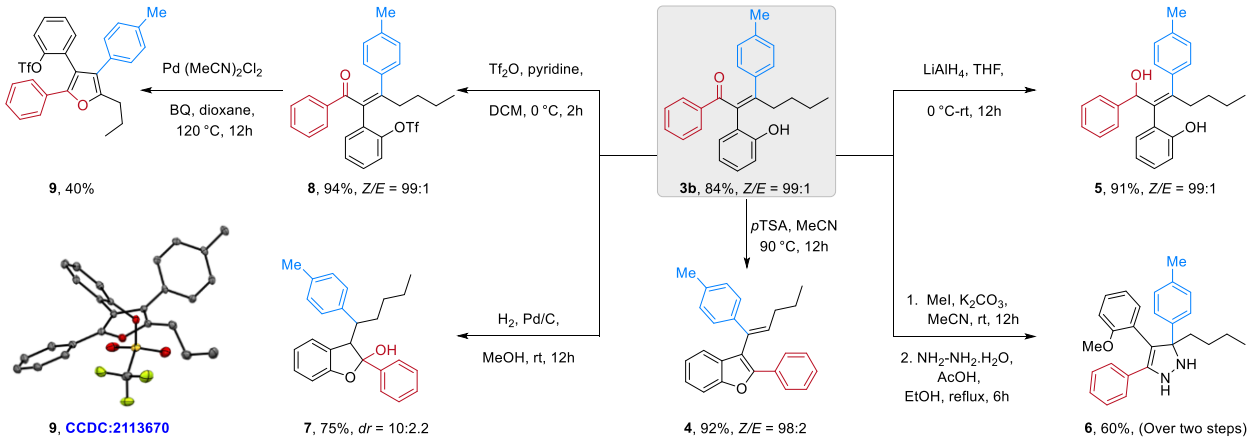
(*Z*)-4-methyl-N-(2-(1-oxo-1-phenyl-3-(*p*-tolyl)hept-2-en-2-yl)phenyl)benzenesulfonamide (3ah):



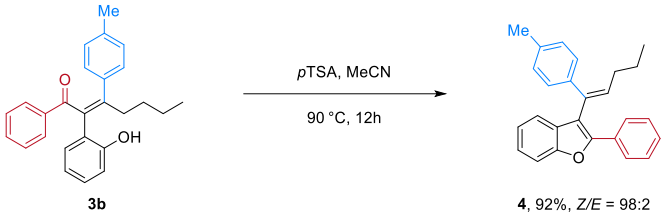
Major Unreacted sm (Minor)

The title compound was prepared according to general procedure, and isolated as colorless thick gel (52% yield). Isolated as mixture due to difficulty in separation by column chromatography. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.31 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 4H), 7.90 – 7.85 (m, 2H), 7.80 – 7.75 (m, 2H), 7.58 (ddd, *J* = 15.9, 8.1, 1.2 Hz, 3H), 7.44 – 7.40 (m, 4H), 7.40 – 7.10 (m, 26H), 7.05 (d, *J* = 7.9 Hz, 3H), 6.93 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 6H), 2.32 (s, 3H), 2.18 (s, 3H), 2.09 (t, *J* = 7.7 Hz, 2H), 2.00 (d, *J* = 14.1 Hz, 4H), 1.33 – 1.26 (m, 7H), 1.22 – 1.03 (m, 5H), 0.92 – 0.87 (m, 6H), 0.69 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.46, 169.39, 149.05, 144.55, 143.49, 138.57, 137.69, 137.59, 136.86, 136.49, 136.42, 135.60, 134.32, 133.95, 133.48, 132.94, 132.31, 131.38, 130.99, 130.16, 129.79, 129.68, 129.15, 129.11, 129.02, 128.85, 128.49, 128.28, 128.13, 127.59, 127.51, 127.45, 124.78, 123.68, 119.43, 97.14, 33.88, 30.32, 29.99, 22.59, 22.26, 21.74, 21.55, 21.15, 19.08, 13.70, 13.68. **HRMS** m/z (ESI) calcd for [$C_{33}H_{33}NO_3S$, M+Na]$^+$: 546.2073, Found: 546.2088.

3. Chemical transformations of 3b to synthetically valuable building blocks



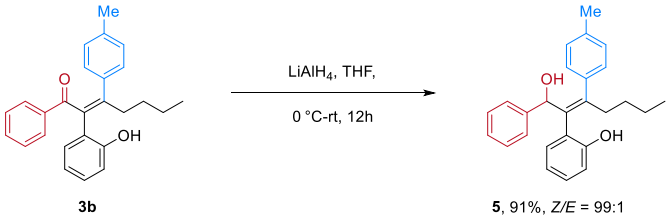
(*E*)-2-phenyl-3-(1-(*p*-tolyl) pent-1-en-1-yl)benzofuran (4):



3b **4**, 92%, *Z*/*E* = 98:2

To a solution of the substrate (100 mg, 0.27 mmol, 1.0 equiv.) in acetonitrile, p-toluenesulfonic acid (61.6 mg, 0.32 mmol, 1.2 equiv.) was added. The reaction mixture was then heated to reflux and stirred for 12 hours, with the progress monitored by TLC. Upon completion, the reaction mixture was quenched with water and extracted with ethyl acetate (2 × 10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using hexane/ethyl acetate as the eluent. Yield: 92% (87.5 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 – 7.94 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.29 (m, 8H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.50 (t, *J* = 7.2 Hz, 1H), 2.36 (s, 3H), 2.01 (dq, *J* = 19.6, 7.4 Hz, 2H), 1.37 (dtt, *J* = 14.0, 6.5, 3.5 Hz, 2H), 0.82 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.11, 150.88, 137.41, 137.07, 132.73, 131.69, 131.07, 130.76, 129.34, 129.22, 128.93, 128.64, 128.44, 128.27, 126.89, 126.20, 126.00, 124.64, 122.89, 120.59, 115.11, 111.08, 32.15, 22.49, 21.20, 14.01. **HRMS (ESI)** for $C_{26}H_{24}O$: calculated for $[M+Na]^+$: 375.1719, found 375.1722.

(*Z*)-2-(1-hydroxy-1-phenyl-3-(*p*-tolyl)hept-2-en-2-yl)phenol (5):

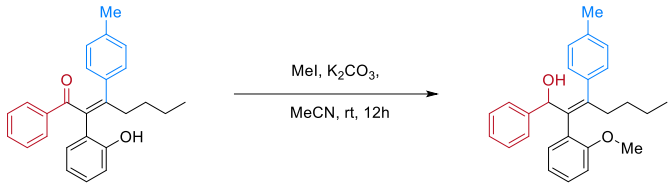


3b **5**, 91%, *Z*/*E* = 99:1

To an ice-cooled solution of the substrate (100 mg, 0.27 mmol, 1.0 equiv.) in THF, $LiAlH_4$ (30.7 mg, 0.81 mmol, 3.0 equiv.) was added. The reaction mixture was then warmed to room temperature and stirred for 12 hours. The reaction progress was monitored by TLC. Upon completion, the mixture was quenched with aqueous KOH and extracted with diethyl ether. The organic layer was dried, and the solvent was removed under reduced pressure. The crude product was purified by

flash column chromatography on silica gel using hexane/ethyl acetate as the eluent. Yield: 91% (90.5 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (q, *J* = 3.6 Hz, 1H), 7.28 (s, 4H), 7.13 (tt, *J* = 8.5, 5.0 Hz, 4H), 7.02 – 6.92 (m, 3H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.35 (dd, *J* = 7.5, 1.7 Hz, 1H), 5.67 (d, *J* = 2.9 Hz, 1H), 2.60 – 2.50 (m, 1H), 2.43 (s, 3H), 2.18 – 1.99 (m, 2H), 1.20 – 0.98 (m, 4H), 0.65 (t, *J* = 7.0 Hz, 3H). **^{1}H NMR (400 MHz, D_2O exchange)** δ 7.28 (s, 4H), 7.18 – 7.08 (m, 4H), 7.02 – 6.92 (m, 3H), 6.62 (t, *J* = 7.1 Hz, 1H), 6.34 (dd, *J* = 7.5, 1.8 Hz, 1H), 5.66 (s, 1H), 2.42 (s, 3H), 2.15 – 1.99 (m, 2H), 1.09 (ddq, *J* = 28.5, 15.3, 7.5 Hz, 4H), 0.64 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.88, 147.33, 141.78, 138.65, 136.85, 134.28, 132.69, 129.22, 128.75, 128.59, 128.01, 127.39, 125.83, 124.94, 119.59, 116.73, 75.73, 35.80, 29.83, 22.46, 21.37, 13.84. **HRMS (ESI)** for $C_{26}H_{28}O_2$: calculated for $[M+Na]^+$: 395.1982, found 395.1964.

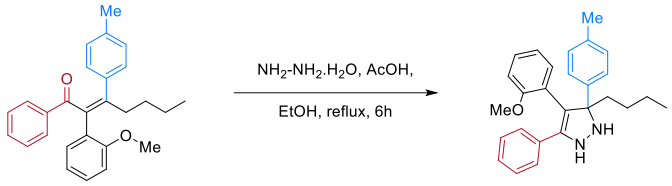
(*Z*)-2-(2-methoxyphenyl)-1-phenyl-3-(*p*-tolyl)hept-2-en-1-one (6'):



3b **6'**, 96%, *Z*/*E* = 99:1

To a solution of the starting material (100 mg, 0.27 mmol, 1.0 equiv.) and methyl iodide (MeI, 114.9 mg, 0.8 mmol, 3.0 equiv.) in acetonitrile, K_2CO_3 (93.1 mg, 0.67 mmol, 2.5 equiv.) was added. The reaction mixture was stirred at room temperature for 12 hours, with the progress monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was quenched with water and extracted with ethyl acetate (2 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel using hexane/ethyl acetate as the eluent. Yield: 96% (99.6 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 – 7.75 (m, 2H), 7.42 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.02 (dd, *J* = 16.0, 7.6 Hz, 3H), 6.91 – 6.82 (m, 3H), 3.69 (s, 3H), 2.53 – 2.40 (m, 2H), 2.17 (s, 3H), 1.36 – 1.13 (m, 5H), 0.76 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 199.62, 156.86, 147.75, 138.38, 137.97, 137.16, 134.95, 131.69, 131.62, 129.78, 129.21, 128.79, 128.70, 127.96, 127.49, 120.72, 111.01, 55.24, 34.99, 30.71, 22.87, 21.19, 13.95. **HRMS (ESI)** for $C_{27}H_{28}O_2$: calculated for $[M+Na]^+$: 407.1982, found 407.1943

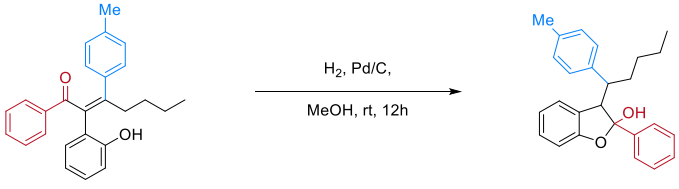
3-butyl-4-(2-methoxyphenyl)-5-phenyl-3-(*p*-tolyl)-2,3-dihydro-*1H*-pyrazole (6):



6' **6**, 60%

A mixture of the starting material (76.9 mg, 0.2 mmol, 1.0 equiv.), hydrazine hydrate (20.0 mg, 0.4 mmol, 2.0 equiv.), and acetic acid (3.8 mg, 0.02 mmol, 0.1 equiv.) in ethanol was refluxed for 6 hours. Upon completion, the reaction mixture was concentrated under vacuum and then diluted with water (10 mL). The aqueous mixture was extracted with ethyl acetate (2 × 20 mL), and the combined organic layers were concentrated using a rotary evaporator. The crude product was purified by flash column chromatography on silica gel using hexane/ethyl acetate as the eluent. Yield: 60% (47.8 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.22 – 7.10 (m, 4H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.78 (dd, *J* = 19.1, 7.9 Hz, 3H), 6.68 (d, *J* = 7.4 Hz, 1H), 6.44 (t, *J* = 8.2 Hz, 2H), 4.88 (s, 1H), 3.72 (s, 3H), 2.08 (s, 3H), 2.04 (dd, *J* = 12.6, 4.0 Hz, 1H), 1.90 (td, *J* = 13.5, 13.0, 4.4 Hz, 1H), 1.19 (dq, *J* = 11.9, 5.9, 5.3 Hz, 4H), 0.74 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 155.73, 154.82, 137.21, 135.05, 132.54, 129.51, 128.16, 128.08, 127.54, 127.44, 126.71, 125.87, 125.04, 120.16, 109.45, 75.37, 54.95, 40.24, 26.22, 22.84, 20.73, 13.76. **HRMS (ESI)** for $C_{27}H_{30}N_2O$: calculated for $[M+Na]^+$: 407.1981, found 407.1998.

2-phenyl-3-(1-(*p*-tolyl)pentyl)-2,3-dihydrobenzofuran-2-ol (7):

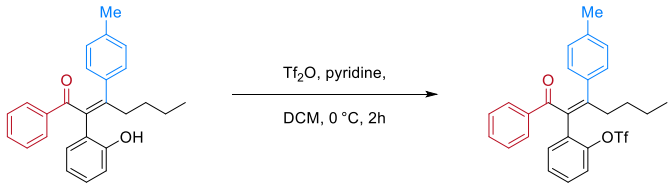


3b **7**, 75%, *dr* = 10:2.2

To a solution of the substrate (74.0 mg, 0.2 mmol, 1.0 equiv.) and Pd/C (2.1 mg, 0.02 mmol, 10 mol%) in methanol, hydrogen gas (1.0 atm) was introduced directly at room temperature. The reaction mixture was stirred for 12 hours. Upon completion, the mixture was filtered through a Celite pad and washed with ethyl acetate. The combined filtrate was concentrated using a rotary evaporator. The resulting crude product was purified by flash column chromatography on silica gel using hexane/ethyl acetate as the eluent. Yield: 75% (55.8 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.21 – 6.85 (m, 12H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.48 (d, *J* = 7.9 Hz, 1H), 4.28 (s, 1H), 3.59 (dt, *J*

= 11.1, 5.4 Hz, 1H), 3.23 (dd, *J* = 13.8, 4.7 Hz, 1H), 3.07 – 2.85 (m, 2H), 2.26 (s, 3H), 1.97 (dtd, *J* = 12.5, 8.0, 3.8 Hz, 1H), 1.71 (tt, *J* = 14.1, 7.4 Hz, 1H), 1.27 (tt, *J* = 13.8, 6.9 Hz, 2H), 1.11 (p, *J* = 7.7 Hz, 2H), 0.83 (t, *J* = 7.3 Hz, 3H). **^{1}H NMR (400 MHz, D$_2$O exchange)** δ 7.16 – 6.80 (m, 12H), 6.66 (t, *J* = 7.5 Hz, 1H), 6.44 (d, *J* = 7.9 Hz, 1H), 3.62 – 3.50 (m, 1H), 3.19 (dd, *J* = 13.8, 4.7 Hz, 1H), 3.02 – 2.81 (m, 2H), 2.22 (s, 3H), 1.92 (dtd, *J* = 12.4, 8.0, 3.9 Hz, 1H), 1.67 (tt, *J* = 13.6, 7.6 Hz, 1H), 1.23 (ddt, *J* = 21.5, 13.9, 6.8 Hz, 2H), 1.08 (q, *J* = 7.7 Hz, 2H), 0.79 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 153.48, 141.12, 140.47, 135.24, 129.97, 129.45, 129.33, 129.08, 128.88, 128.69, 128.55, 128.07, 127.95, 126.66, 125.69, 125.61, 120.35, 115.56, 49.77, 38.59, 32.78, 30.04, 23.00, 21.17, 14.18. **HRMS (ESI)** for $C_{26}H_{28}O_2$: calculated for $[M+Na]^+$: 395.1982, found 395.1942.

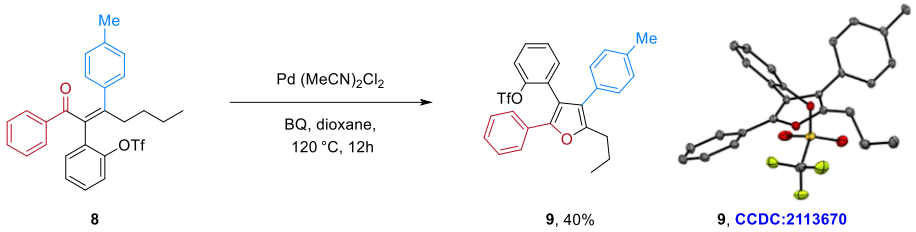
(*Z*)-2-(1-oxo-1-phenyl-3-(*p*-tolyl)hept-2-en-2-yl)phenyl trifluoromethanesulfonate (8):



3b **8**, 94%, *Z*/*E* = 99:1

A flame-dried flask was charged with the starting material (100 mg, 0.27 mmol, 1.0 equiv.) in CH2Cl2 (2.0 mL). Pyridine (43.4 mg, 0.54 mmol, 2.0 equiv.) was added at 0°C. A solution of trifluoromethanesulfonic anhydride (54.7 mg, 0.32 mmol, 1.2 equiv.) in CH2Cl2 (2.0 mL) was then added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 2 hours. The reaction was quenched with Et2O (5 mL) and 10% aqueous HCl (4 mL), then washed sequentially with saturated NaHCO3 (4 mL) and brine (5 mL). The organic layer was dried over Na2SO4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using a hexane/EtOAc gradient as the eluent. Yield: 94% (127.4 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.75 (d, *J* = 7.7 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.46 – 7.38 (m, 2H), 7.37 – 7.31 (m, 1H), 7.24 (d, *J* = 3.0 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 7.7 Hz, 2H), 2.43 (s, 2H), 2.14 (s, 3H), 1.21 (d, *J* = 29.1 Hz, 4H), 0.70 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 197.12, 150.82, 147.63, 137.94, 136.86, 136.65, 133.36, 132.35, 132.08, 131.30, 129.90, 129.77, 128.90, 128.75, 128.24, 127.85, 121.12, 120.21 (q, J_{CF} = 320.3 Hz), 35.34, 30.19, 22.63, 21.21, 13.84. **HRMS** m/z (ESI) calcd for $[C_{27}H_{25}F_3O_4S, M+Na]^+$: 525.1318, Found: 525.1296.

2-(2-phenyl-5-propyl-4-(*p*-tolyl)furan-3-yl)phenyl trifluoromethanesulfonate (9):

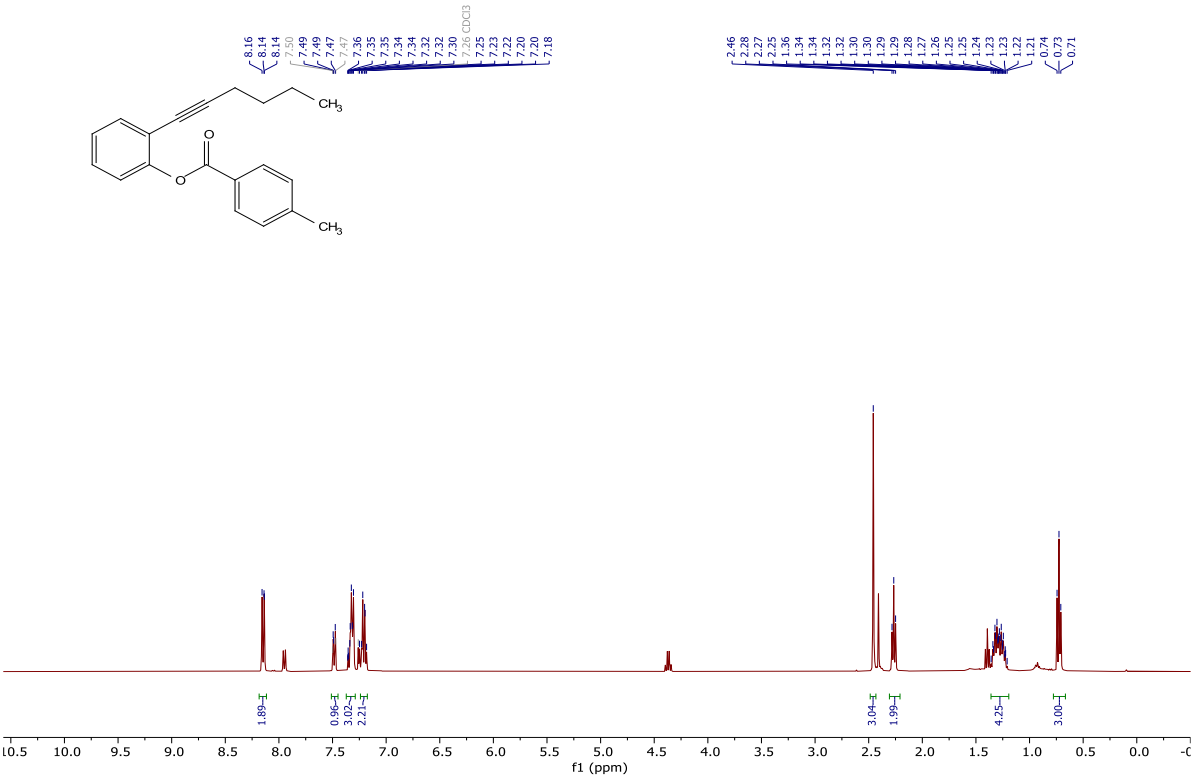


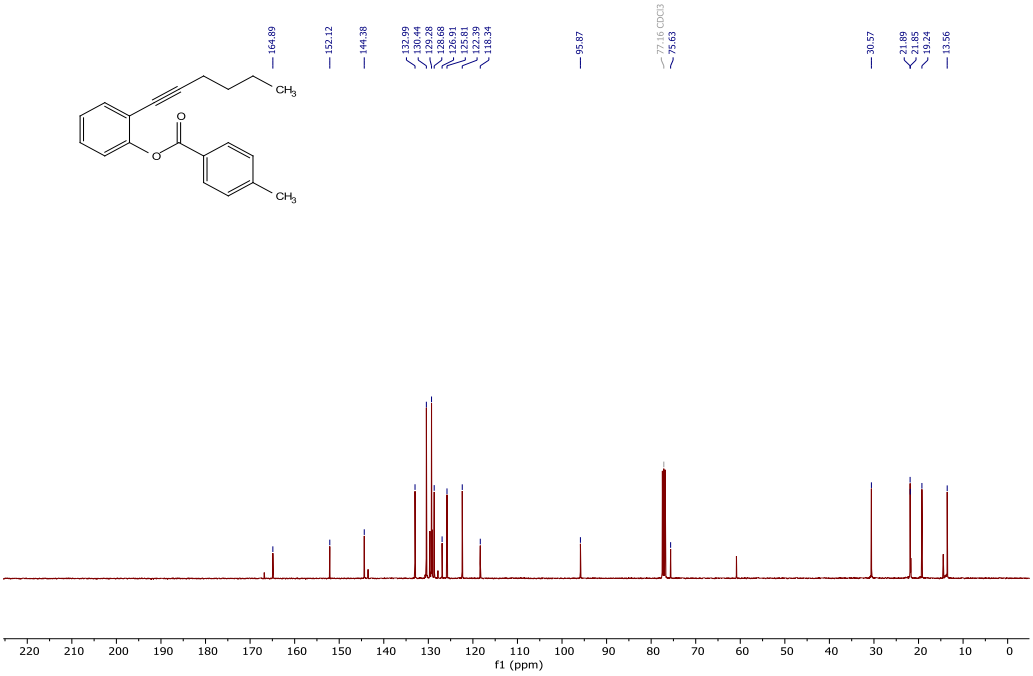
8 **9**, 40% **9**, CCDC:2113670

To a stirred solution of the starting material (100 mg, 0.2 mmol, 1.0 equiv.) in 1,4-dioxane (4 mL), Pd(CH3CN)Cl2 (5.1 mg, 0.02 mmol, 10 mol %) and 1,4-benzoquinone (28.1 mg, 0.26 mmol, 1.3 equiv.) were added. The mixture was stirred at 120°C for 12 hours under an air atmosphere. After completion, the reaction was cooled to room temperature, filtered through a small bed of Celite, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using a hexane/EtOAc gradient as the eluent. Yield: 40% (40.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 – 7.03 (m, 9H), 6.89 (d, *J* = 7.7 Hz, 2H), 6.81 – 6.76 (m, 2H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.16 (s, 3H), 1.64 (dp, *J* = 10.4, 6.7 Hz, 2H), 0.85 (td, *J* = 7.3, 1.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.32, 148.30, 147.60, 136.34, 133.53, 130.89, 129.78, 129.40, 129.03, 128.95, 128.56, 128.44, 127.45, 125.86, 125.63, 123.86, 122.29, 119.6 (q, J_{CF} = 319.9 Hz), 116.01, 28.56, 22.14, 21.34, 13.90. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -74.52. **HRMS** m/z (ESI) calcd for $[C_{27}H_{23}F_3O_4S, M+Na]^+$: 523.1161, Found: 523.1196

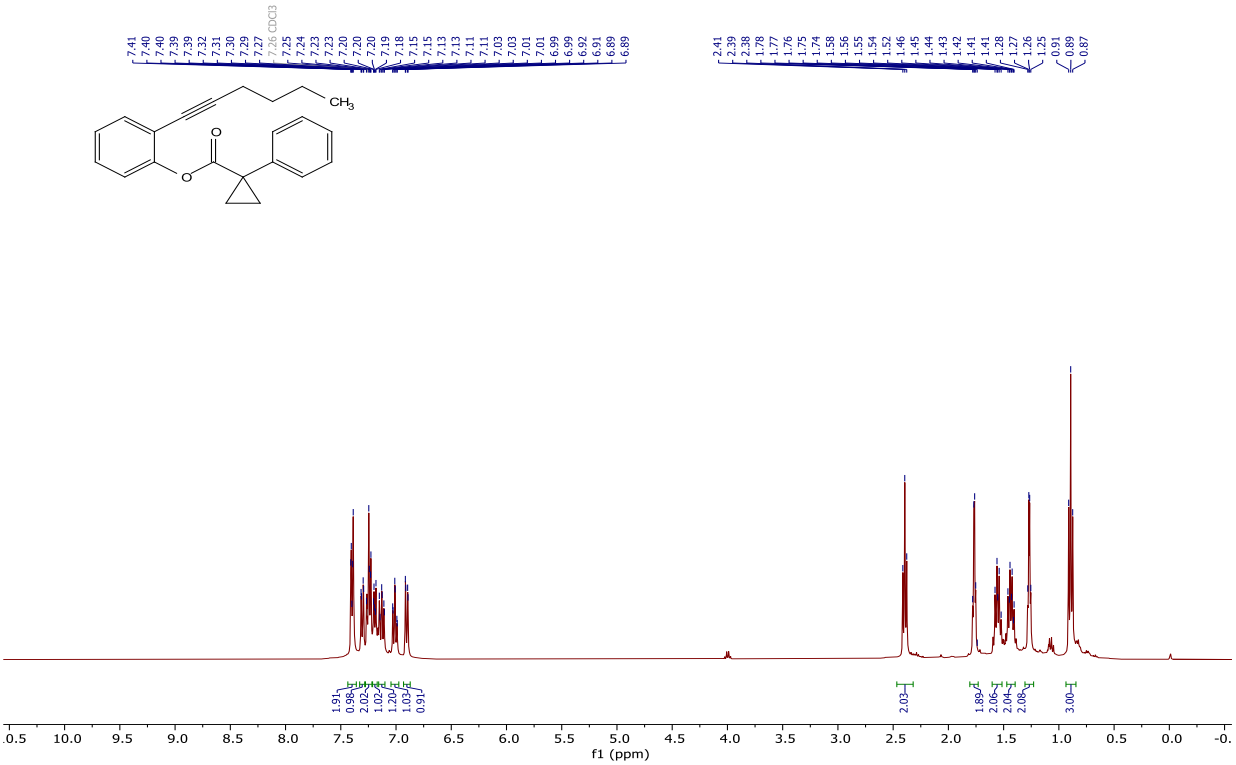
4. Copies of NMR Spectra

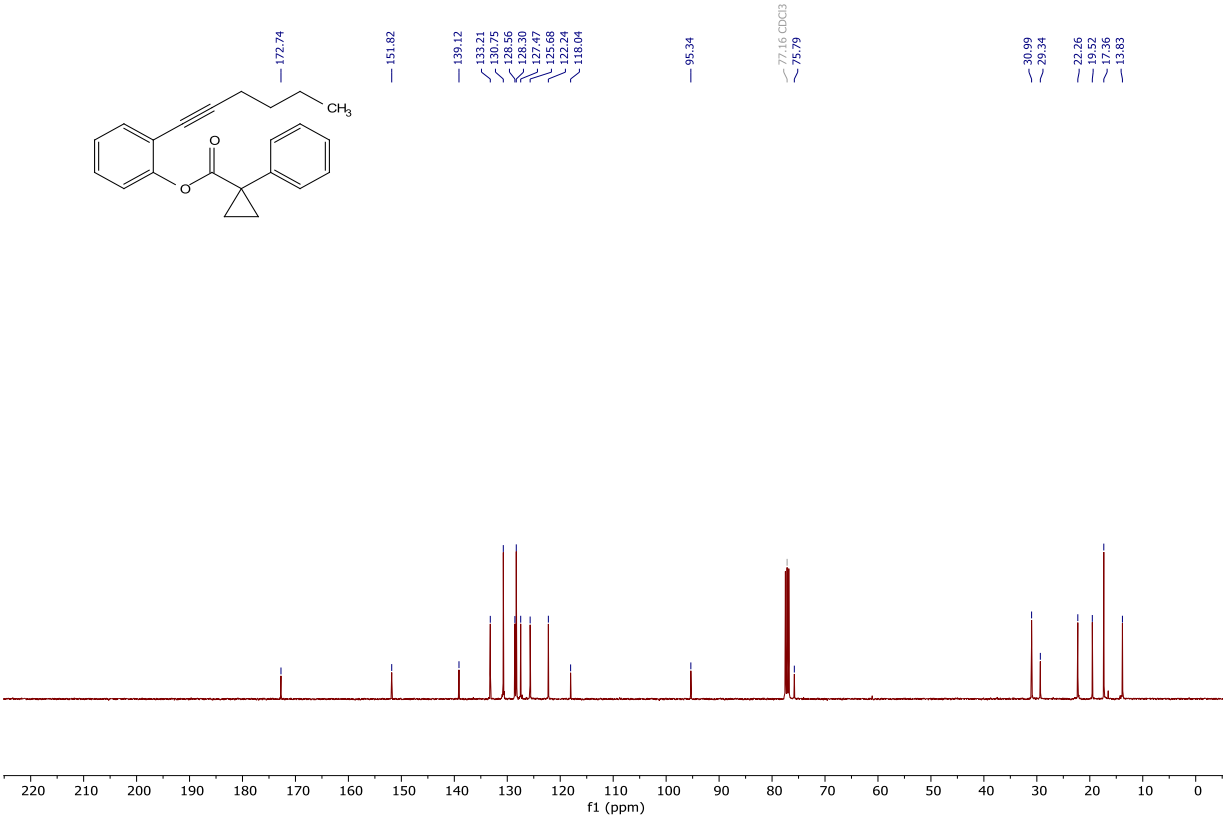
2-(hex-1-yn-1-yl)phenyl 4-methylbenzoate (1m):



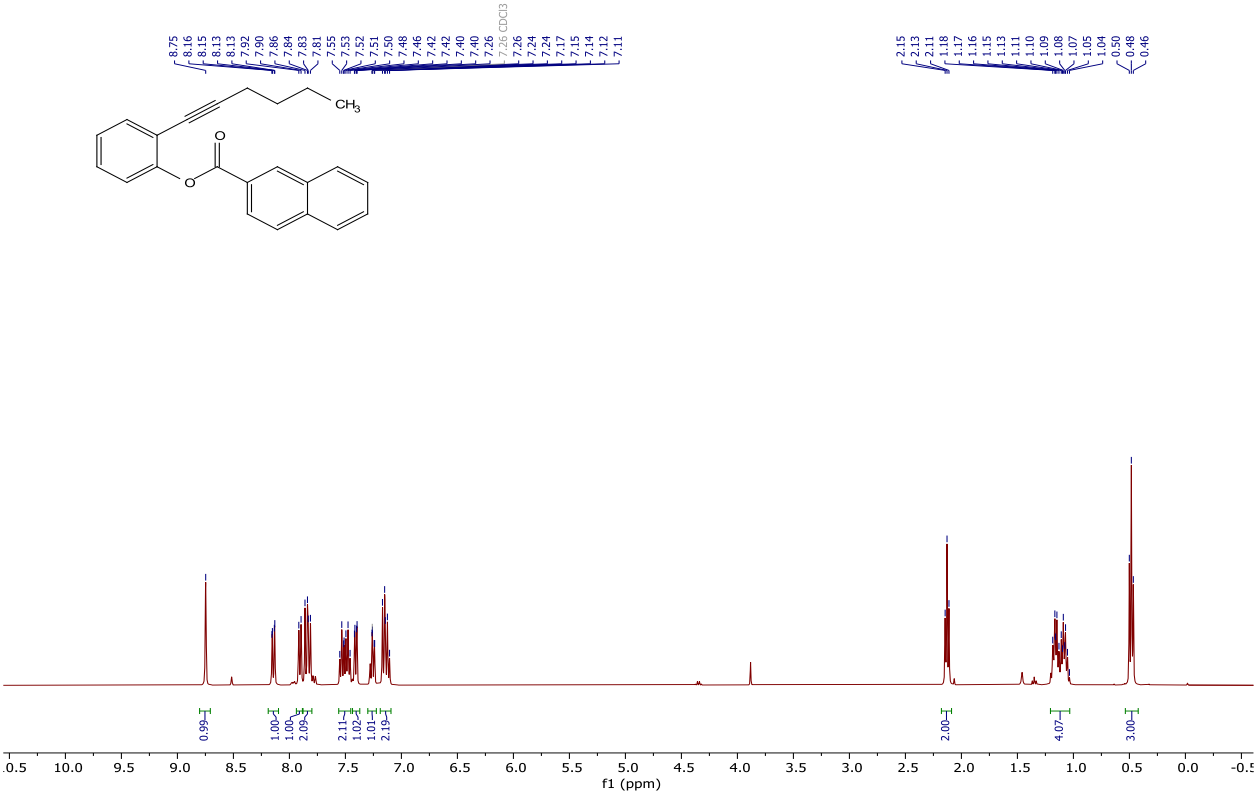


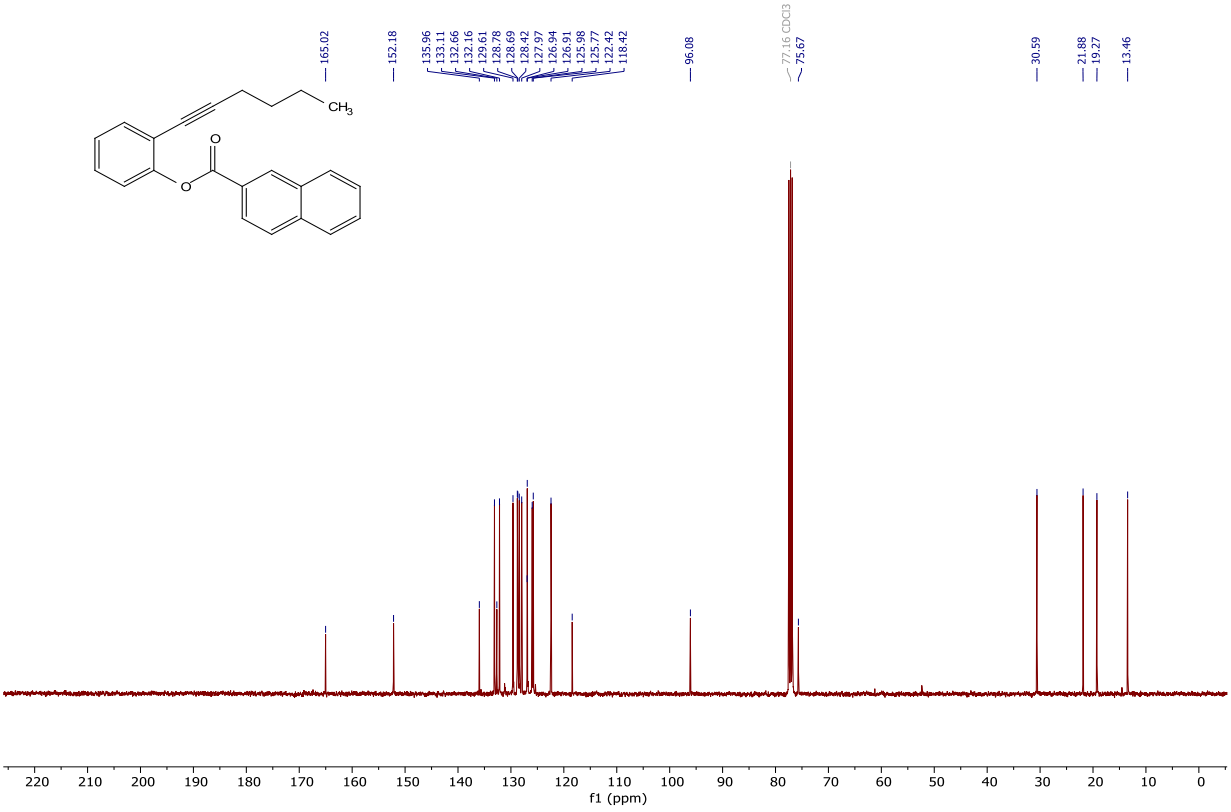
2-(hex-1-yn-1-yl)phenyl 1-phenylcyclopropane-1-carboxylate (1n):



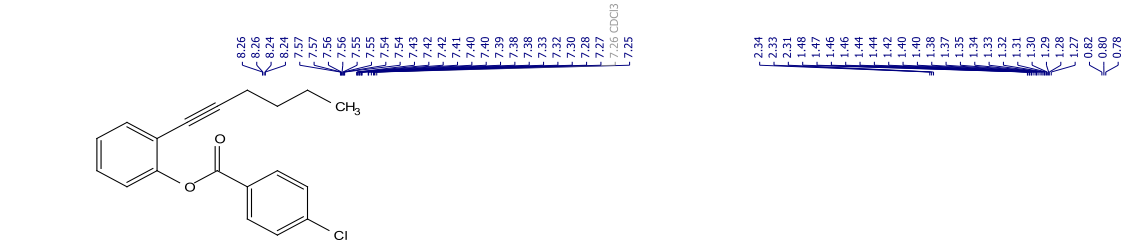


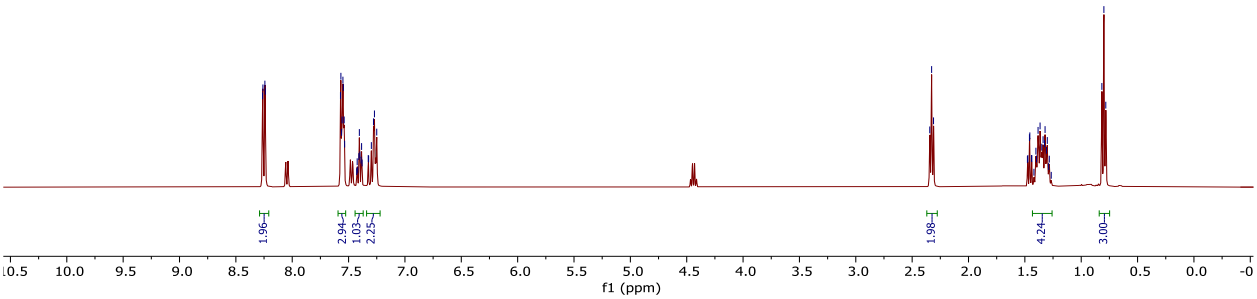
2-(hex-1-yn-1-yl)phenyl 2-naphthoate (1o):

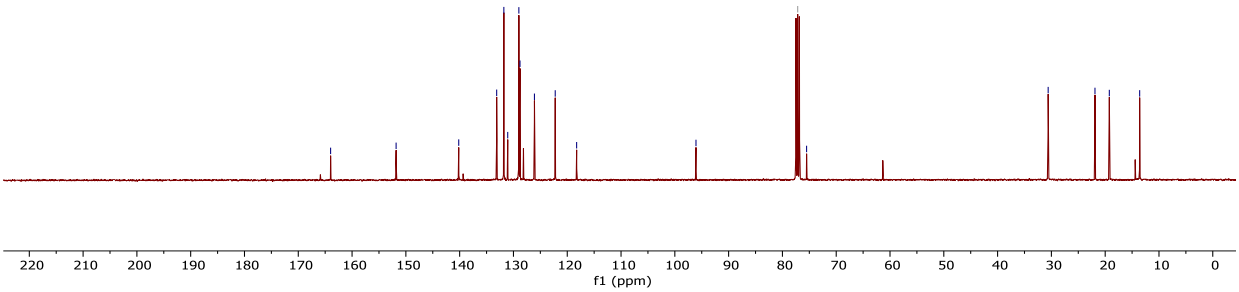




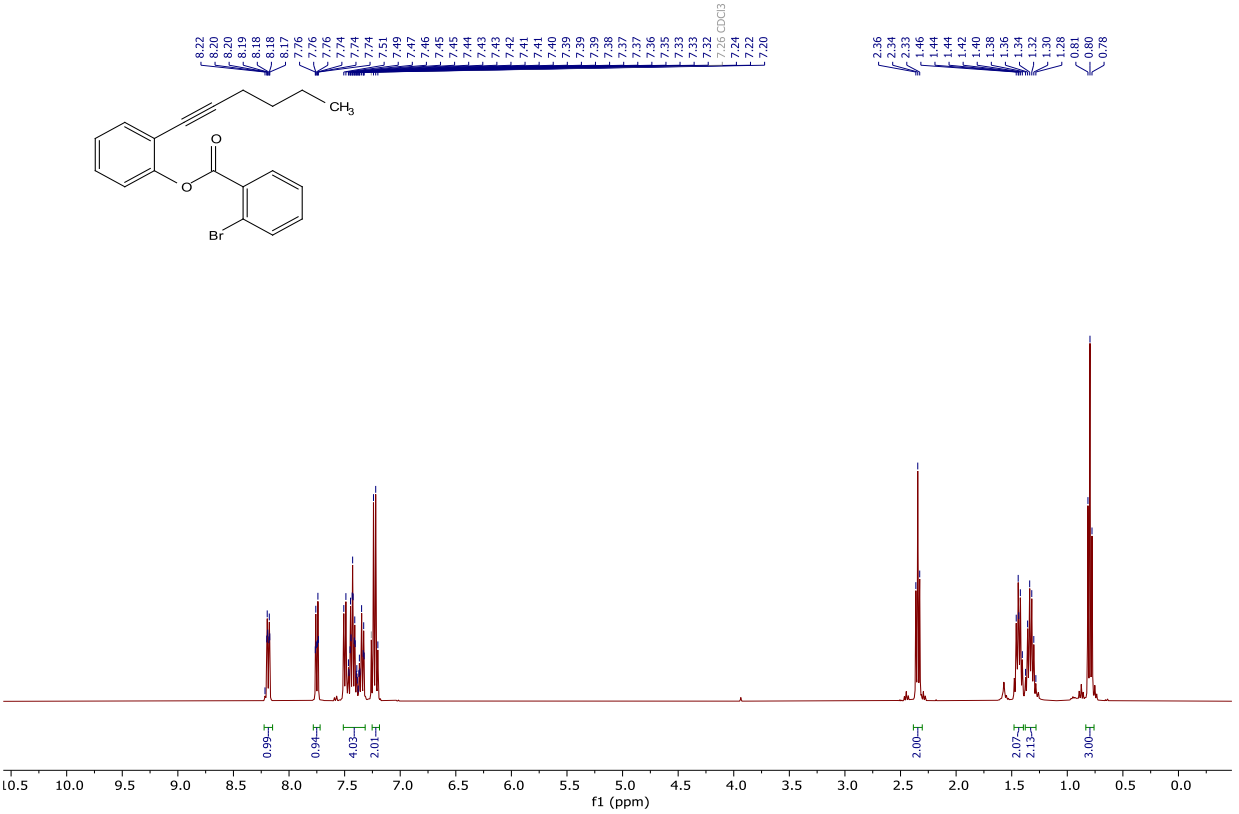
2-(hex-1-yn-1-yl)phenyl 4-chlorobenzoate (1p) :

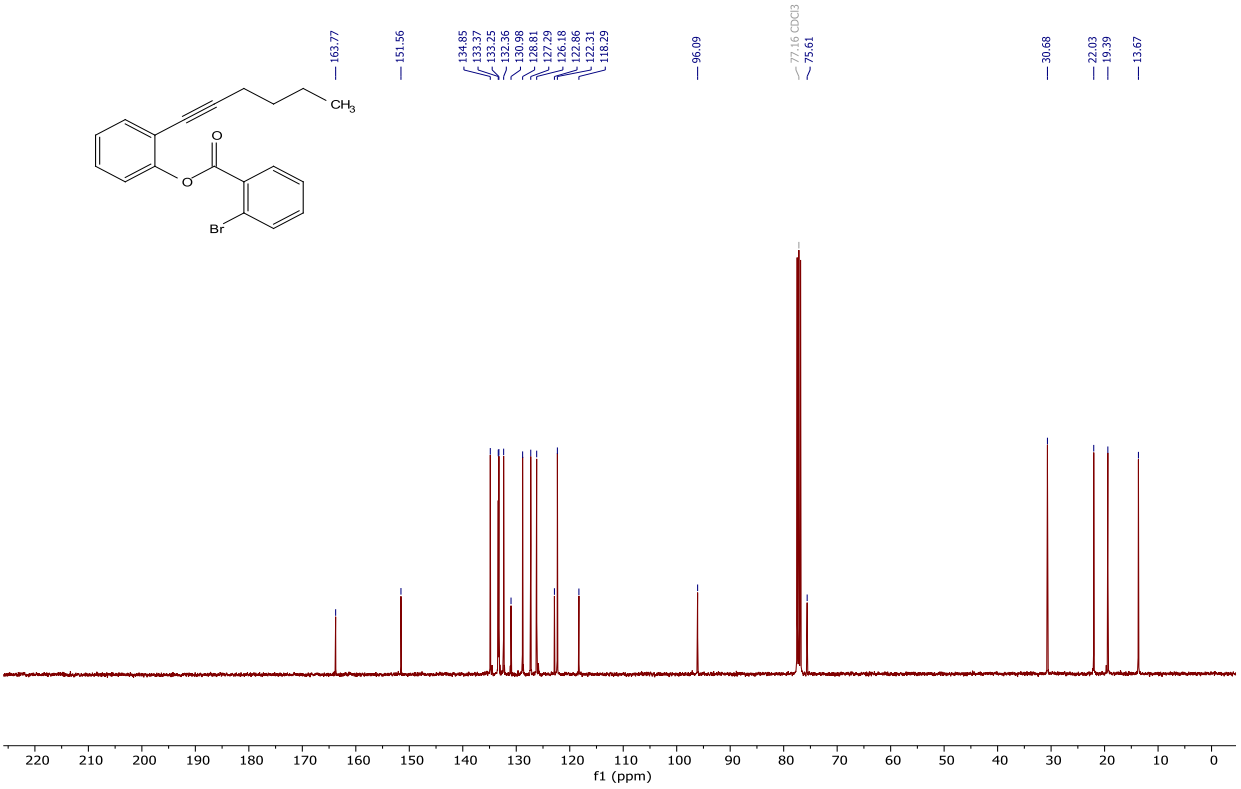




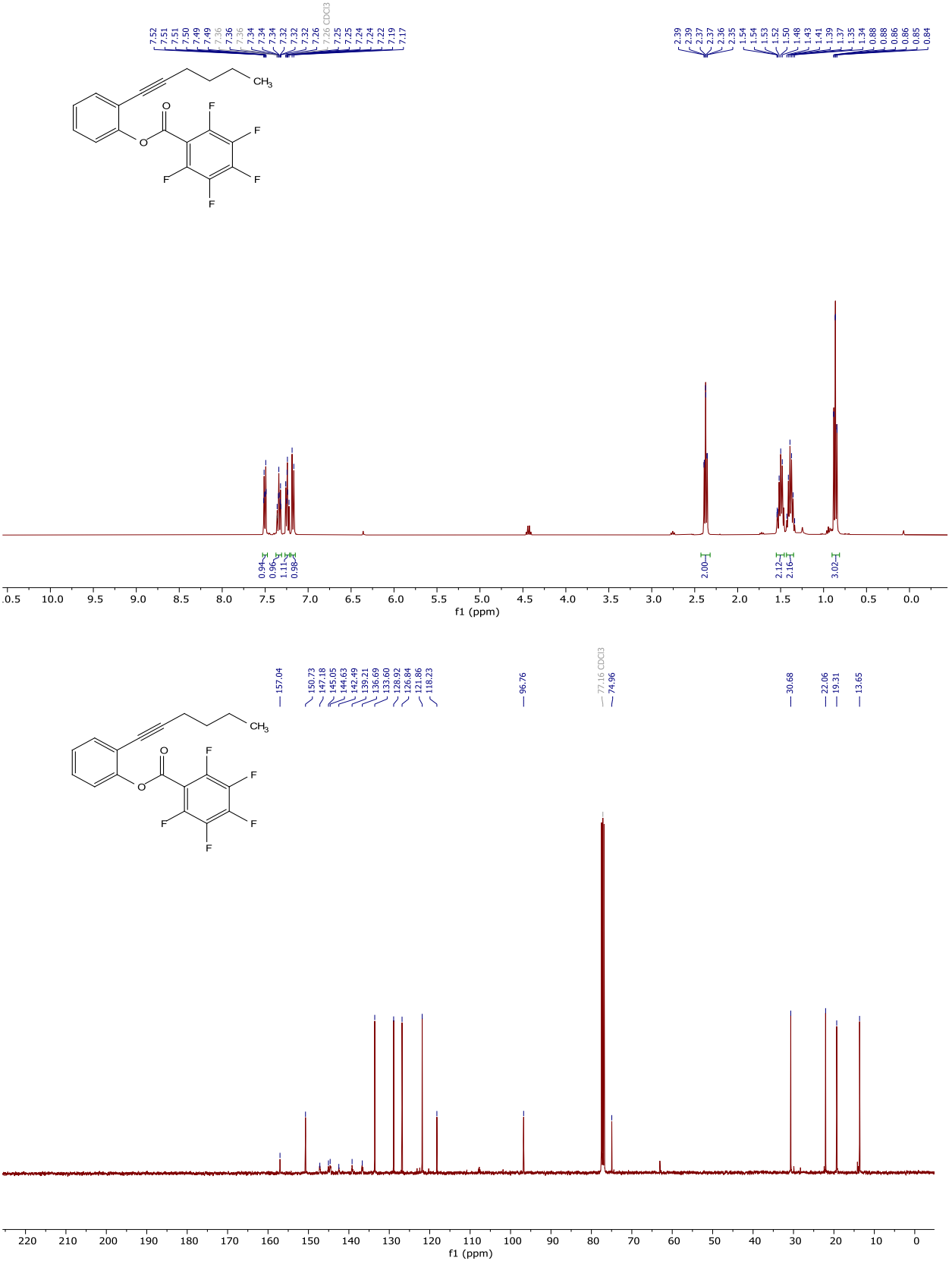


2-(hex-1-yn-1-yl)phenyl 2-bromobenzoate (1q):

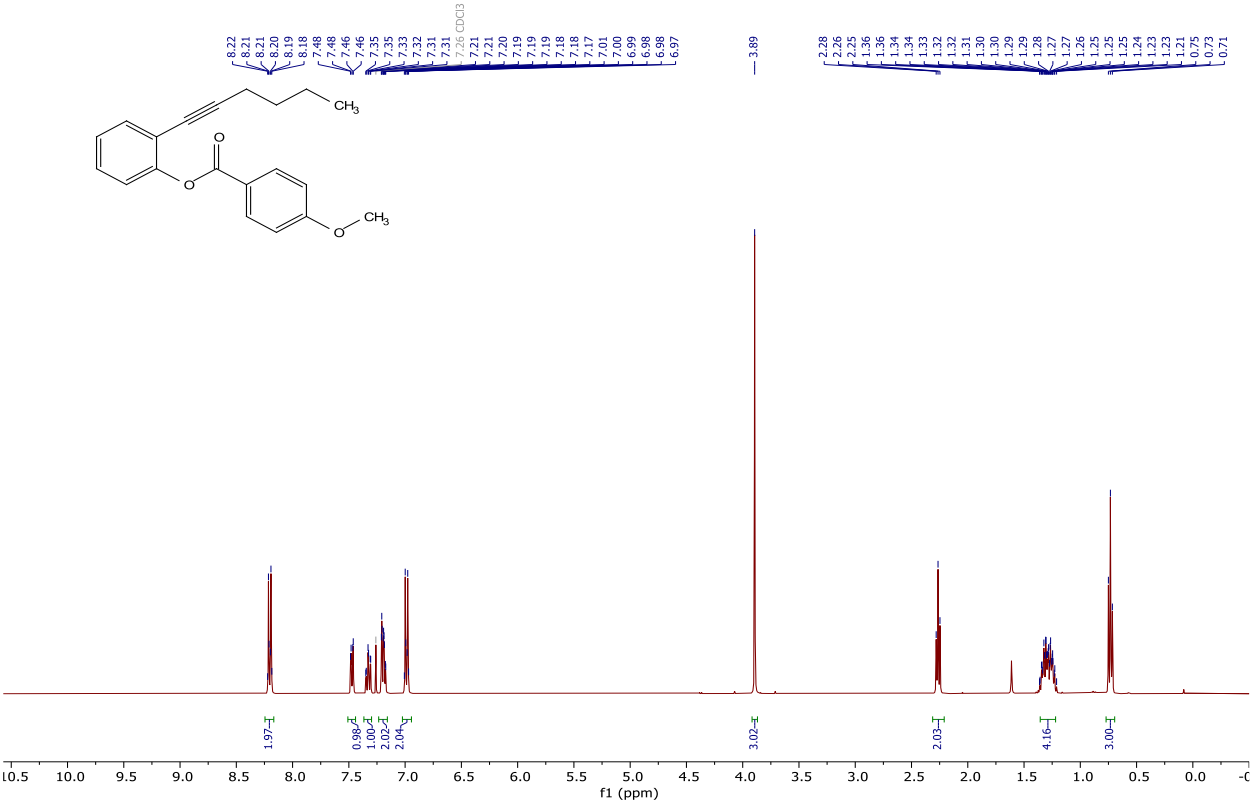


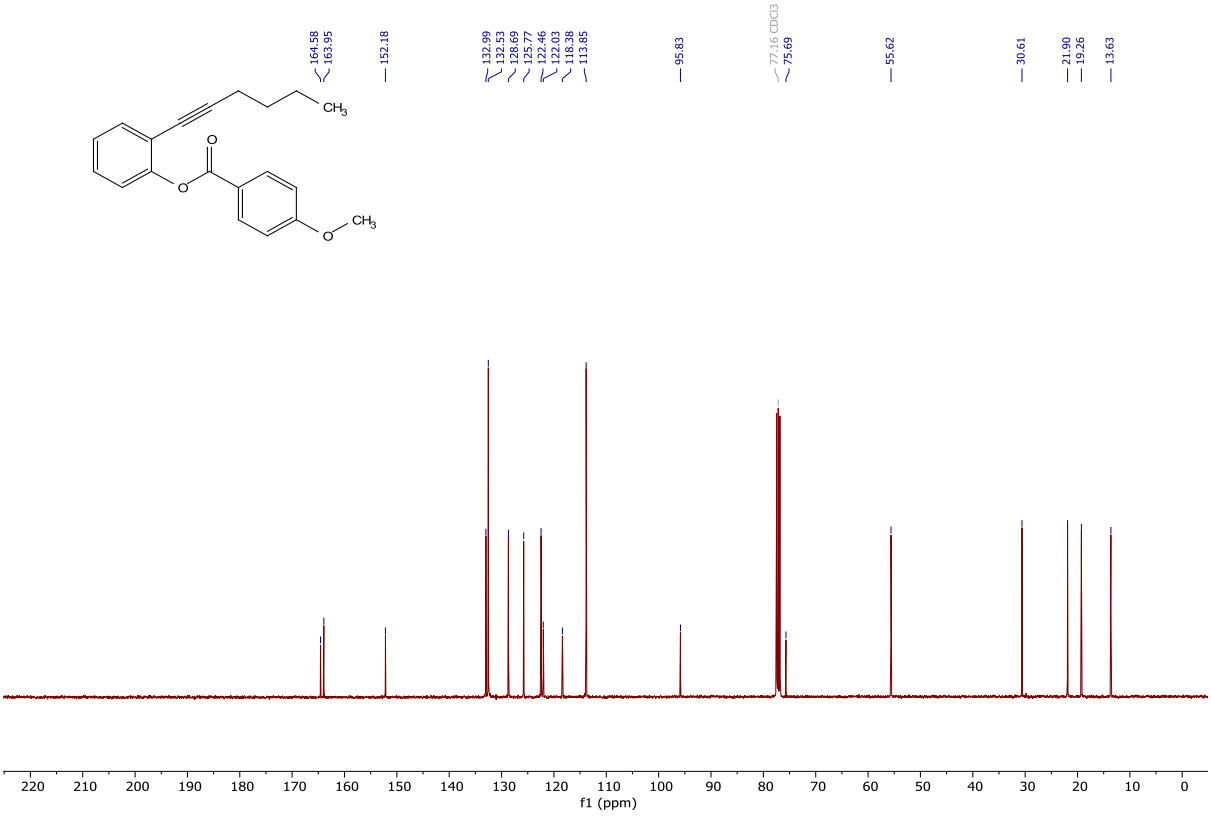


2-(hex-1-yn-1-yl)phenyl 2,3,4,5,6-pentafluorobenzoate (1r):

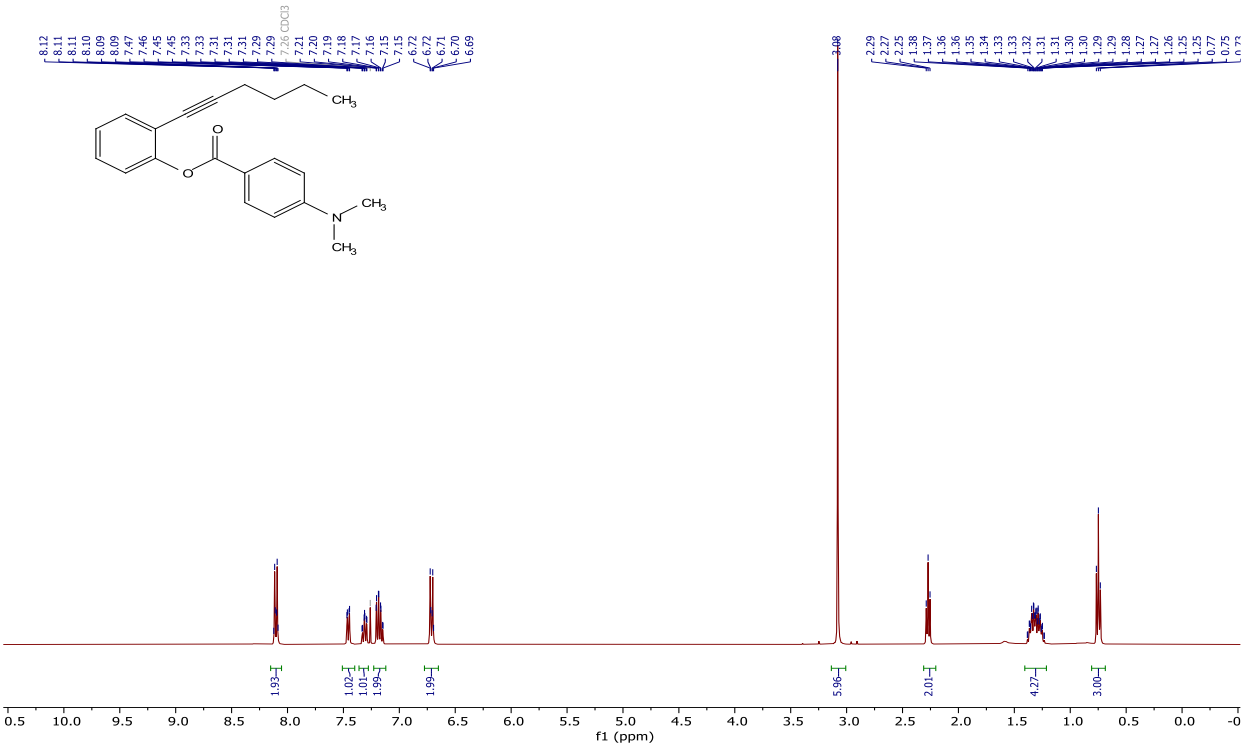


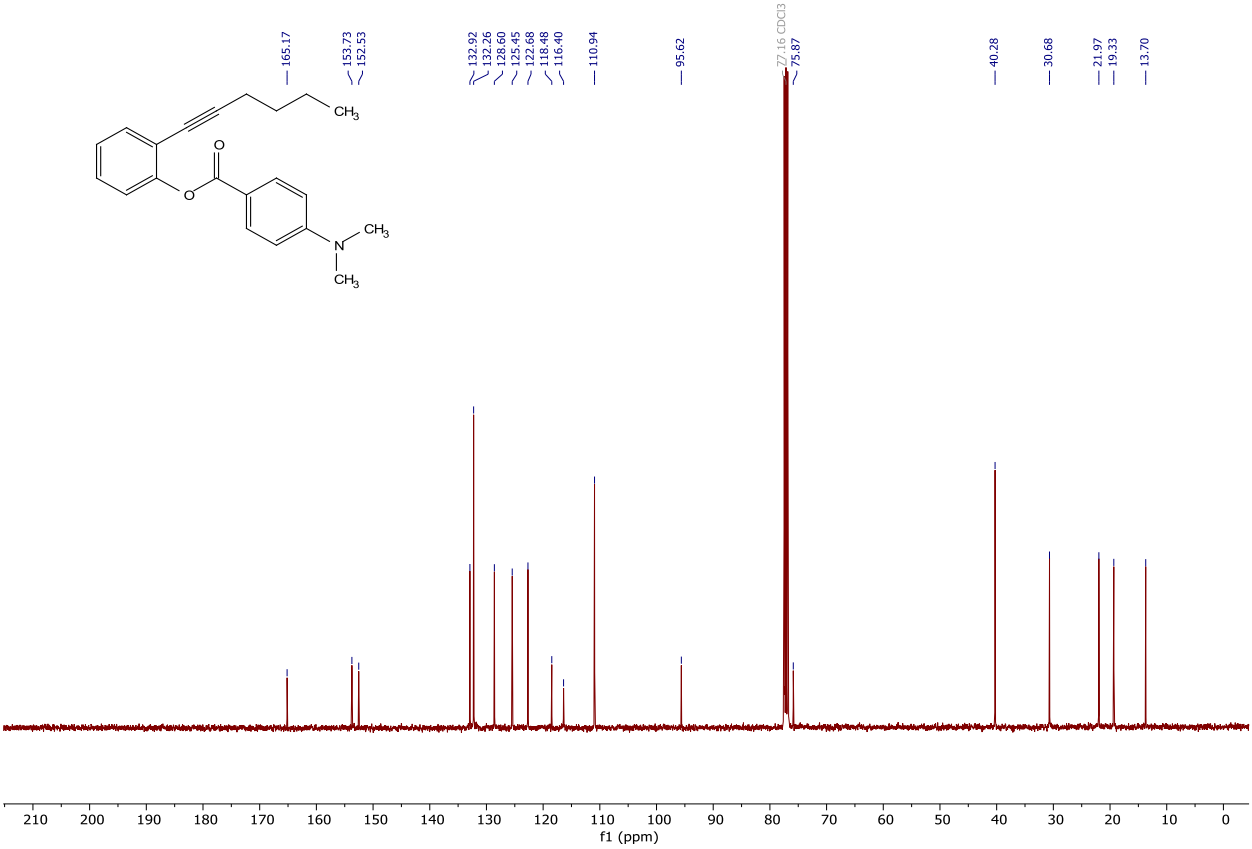
2-(hex-1-yn-1-yl)phenyl 4-methoxybenzoate (1s):



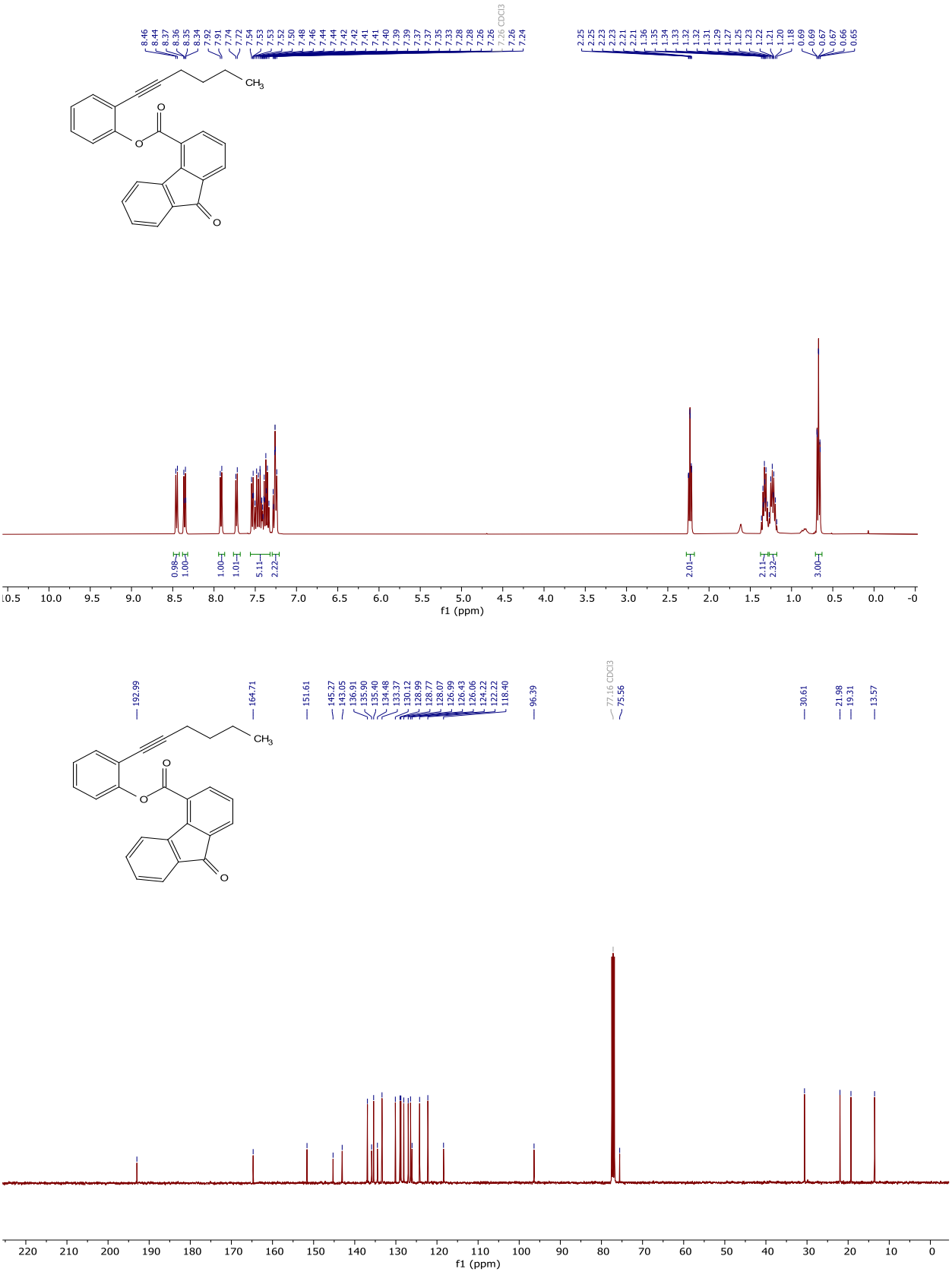


2-(hex-1-yn-1-yl)phenyl 4-(dimethylamino)benzoate (1t):

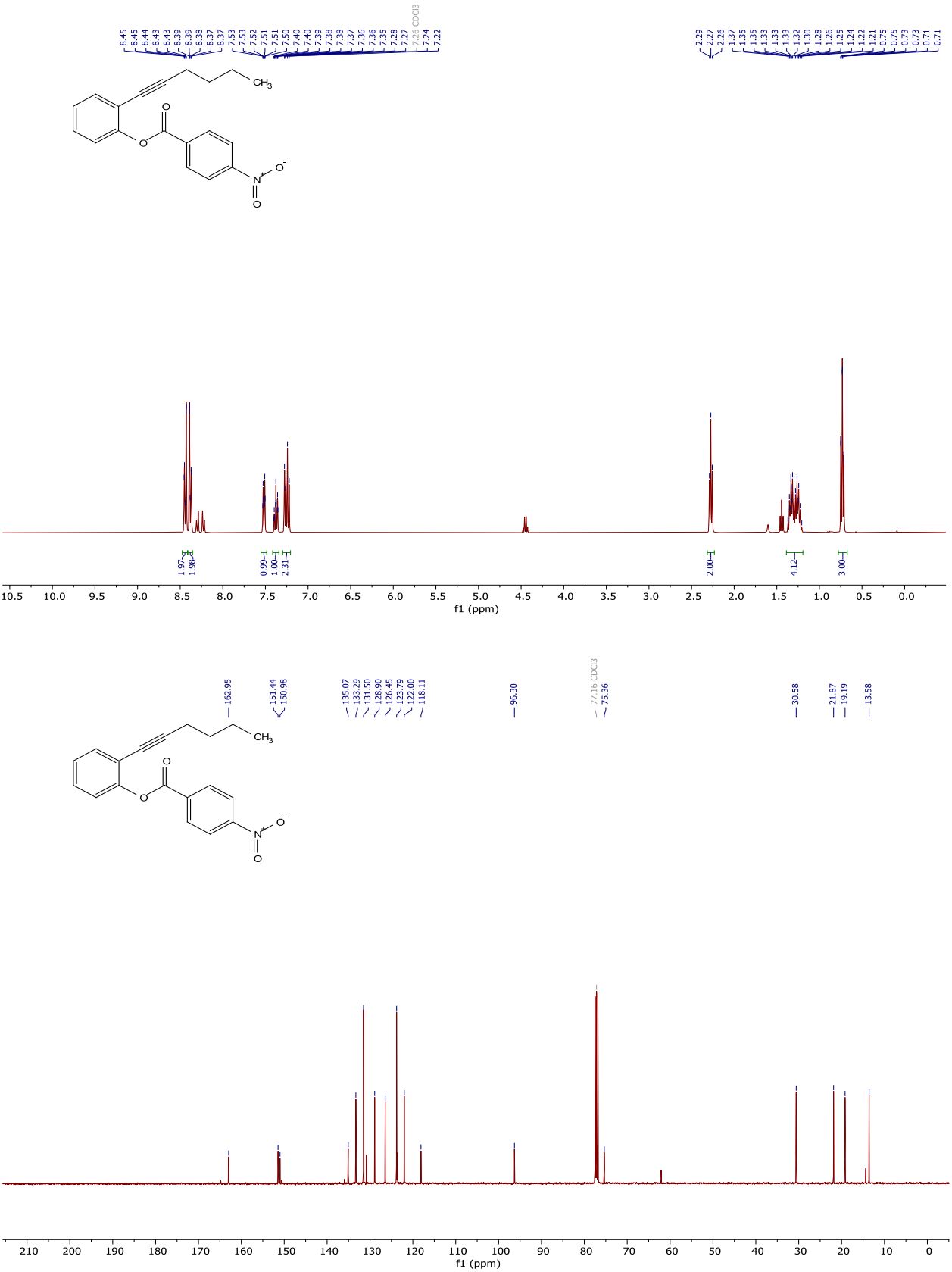




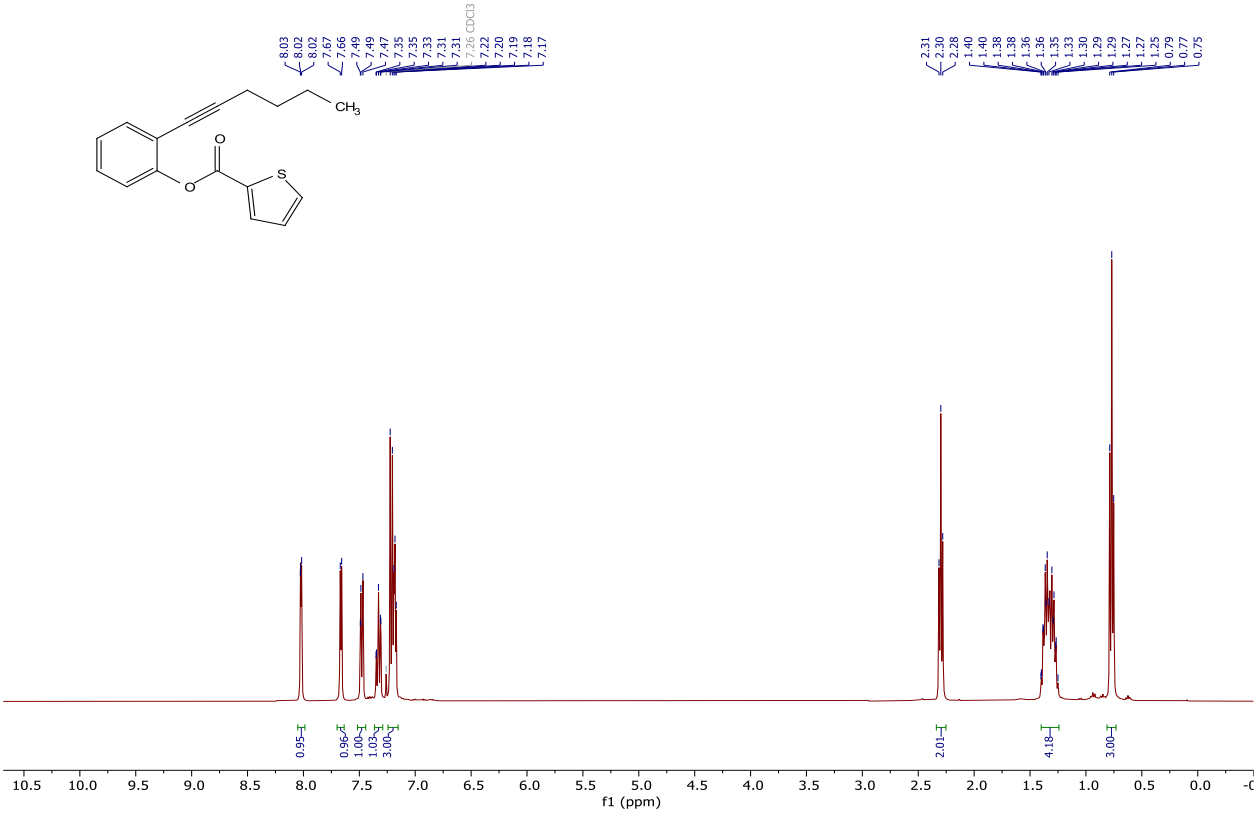
2-(hex-1-yn-1-yl)phenyl 9-oxo-9H-fluorene-4-carboxylate (1u):

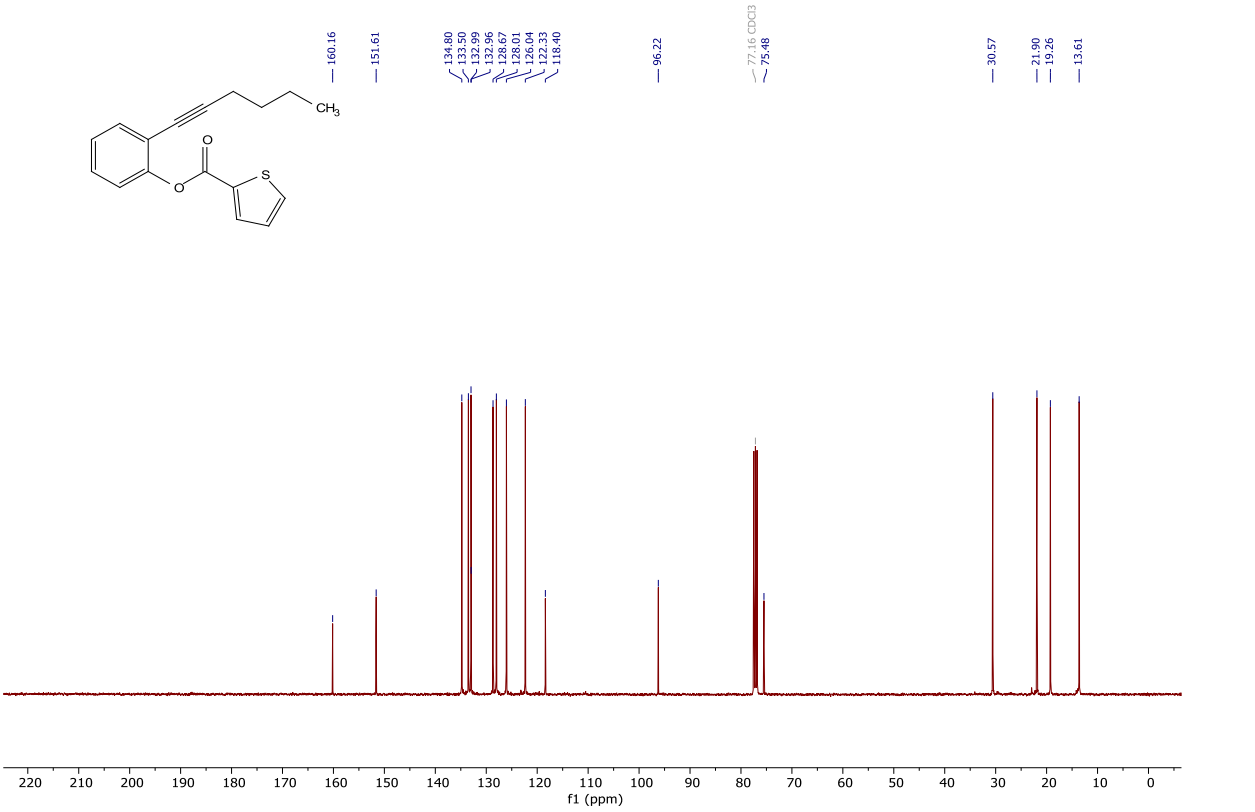


2-(hex-1-yn-1-yl)phenyl 4-nitrobenzoate (1v):

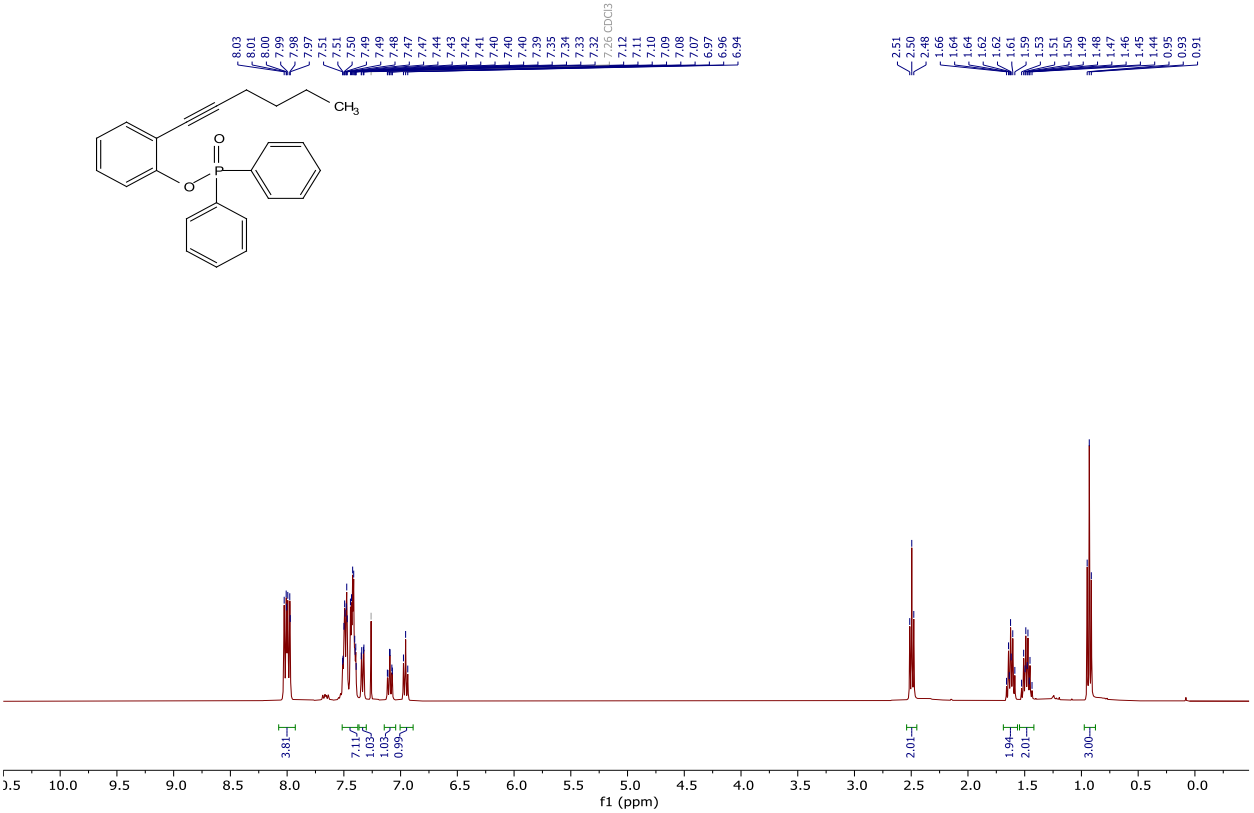


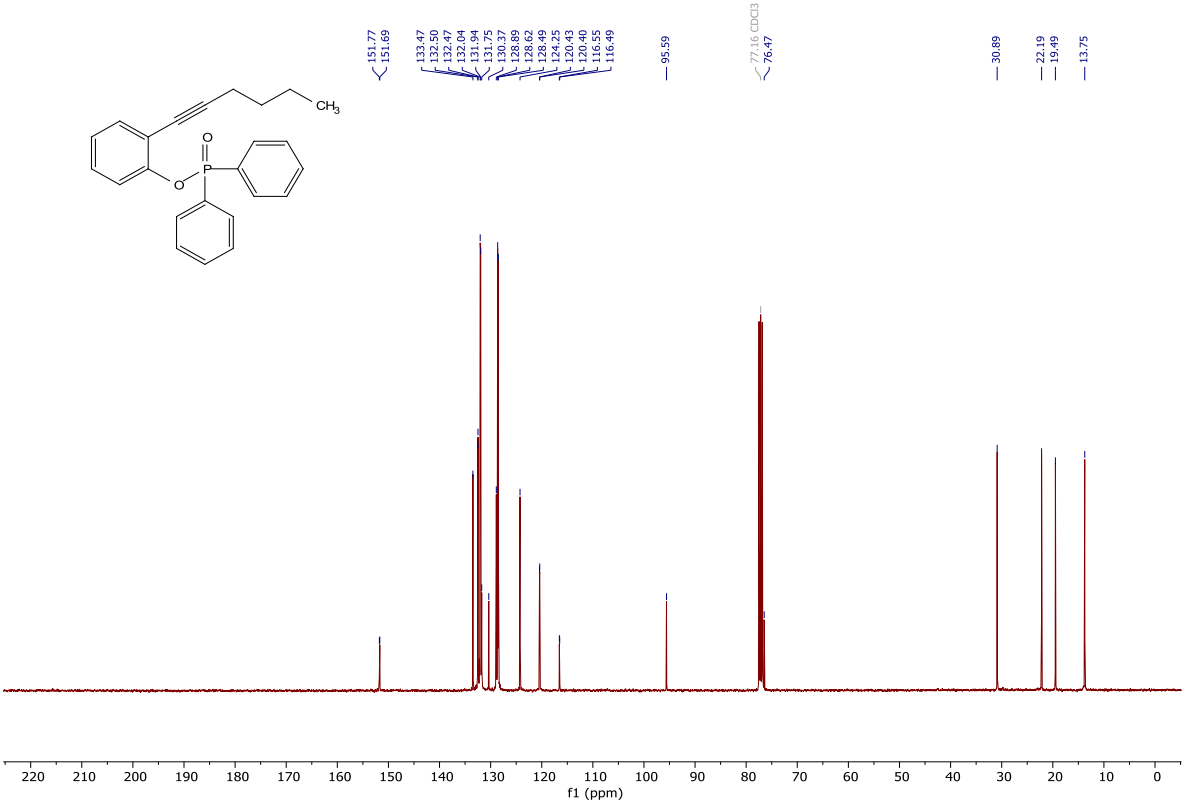
2-(hex-1-yn-1-yl)phenyl thiophene-2-carboxylate (1w):

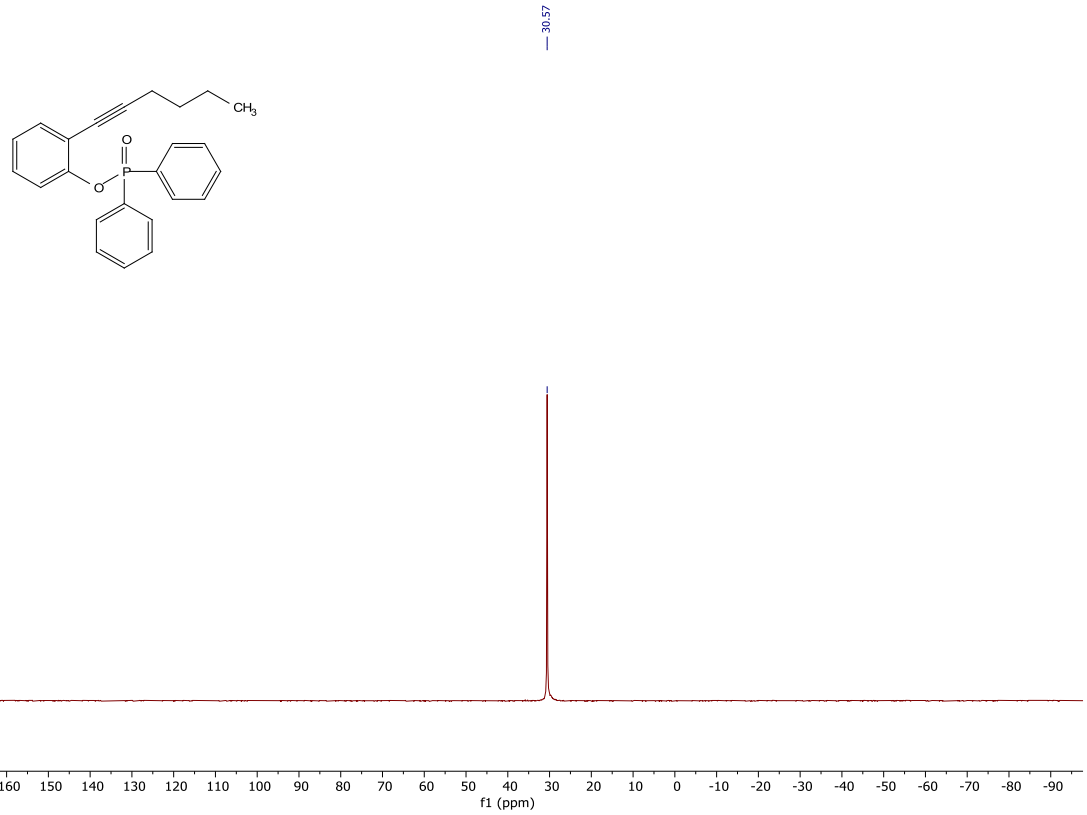




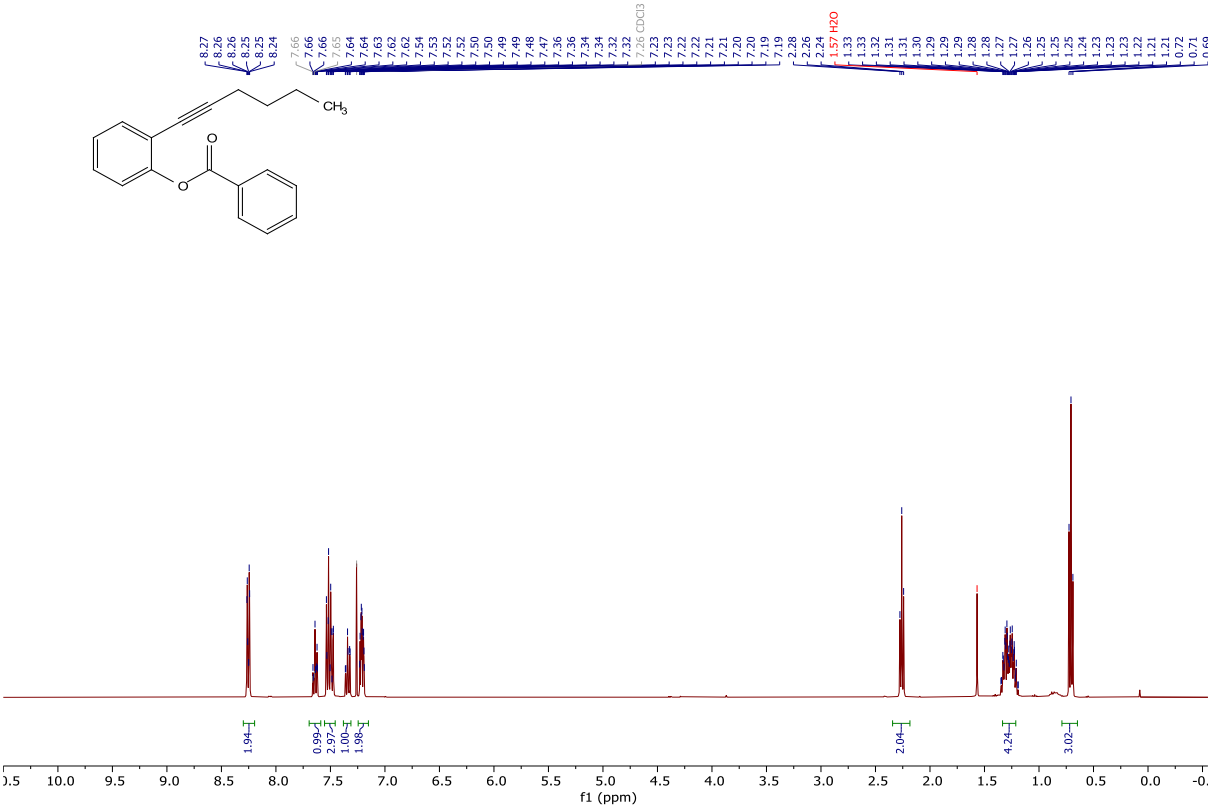
2-(hex-1-yn-1-yl)phenyl diphenylphosphinate (1x):

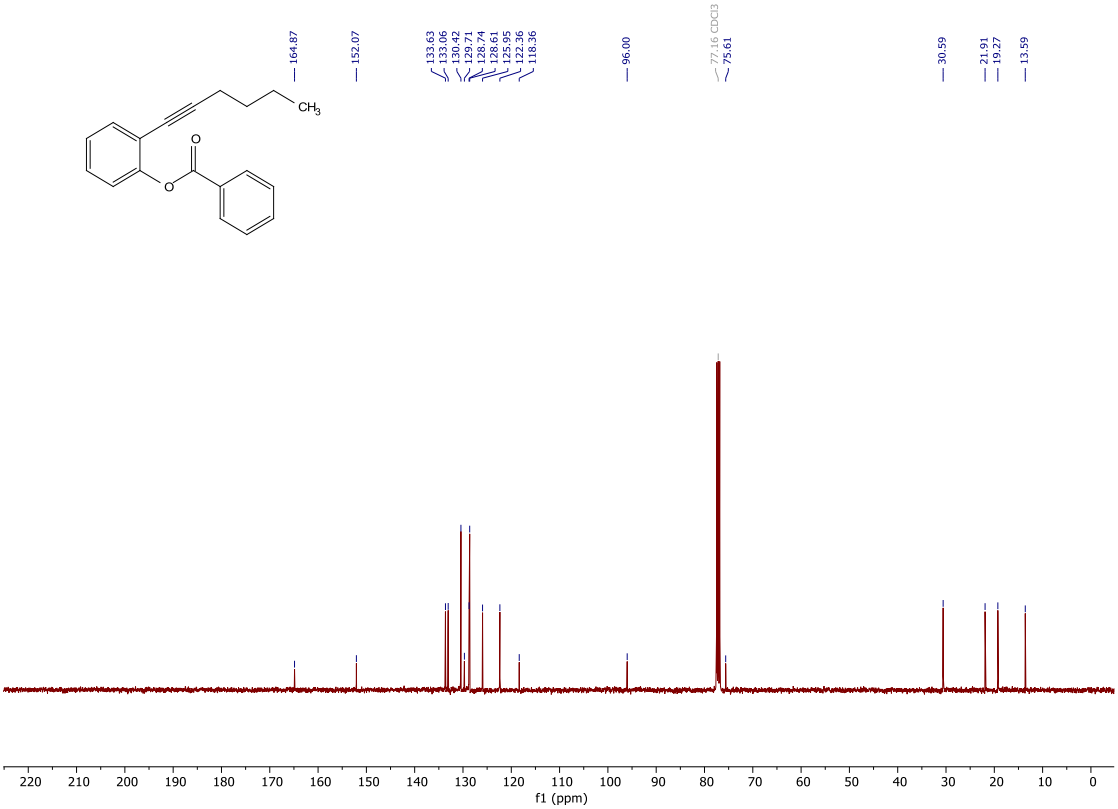




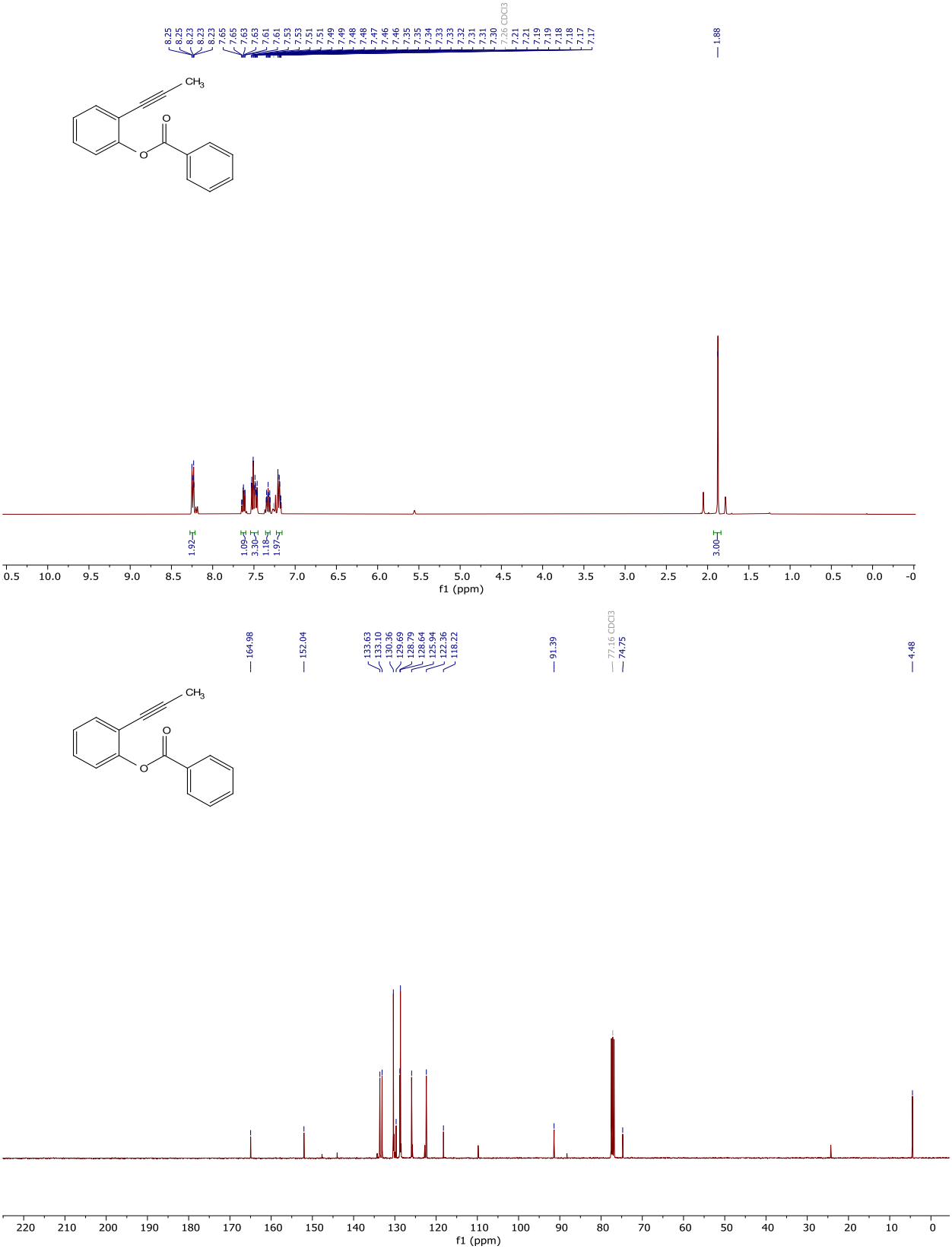

30.57
CH3
O
P
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

2-(hex-1-yn-1-yl)phenyl benzoate (1a):

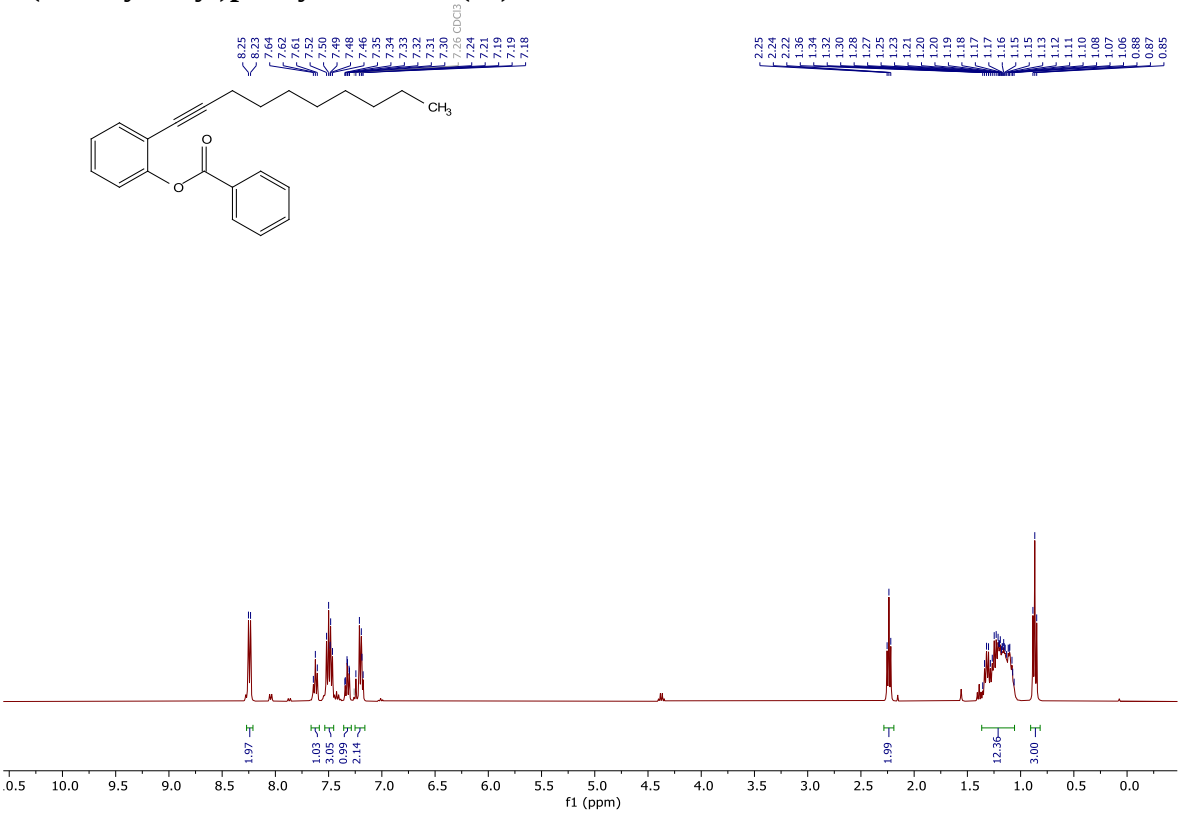


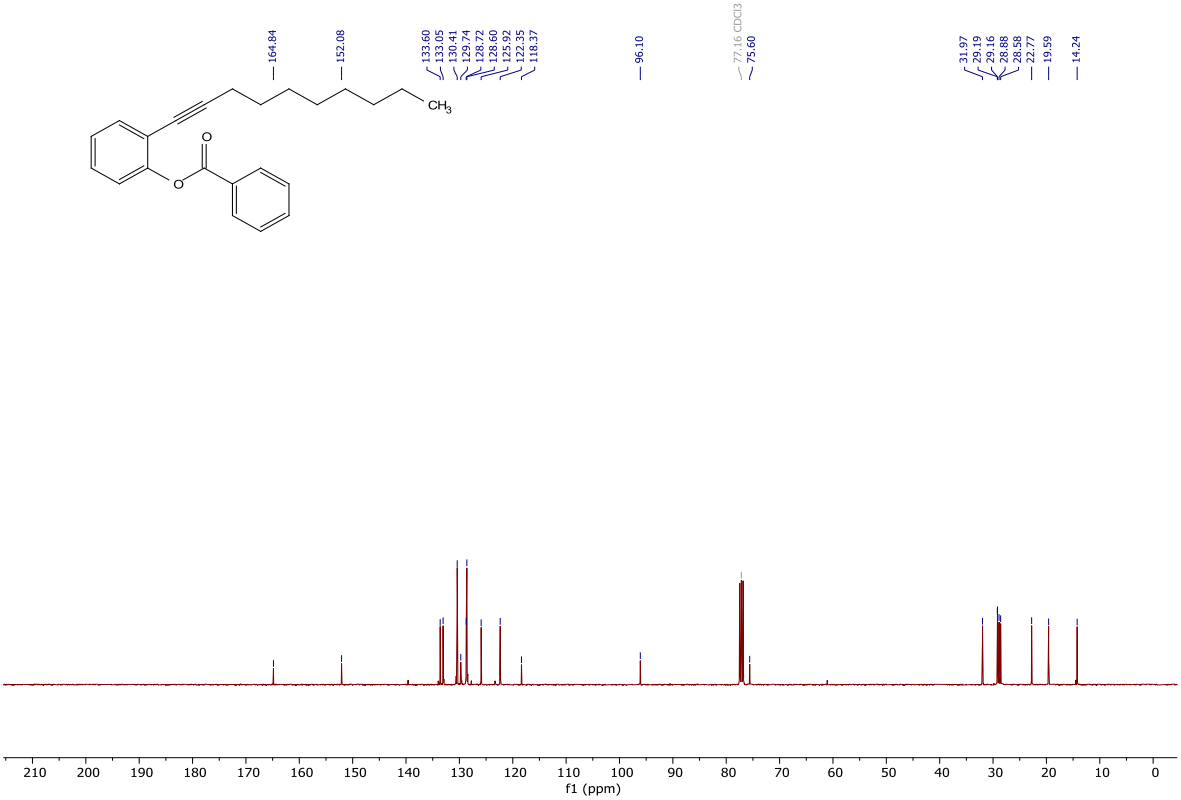


2-(prop-1-yn-1-yl)phenyl benzoate (1y):

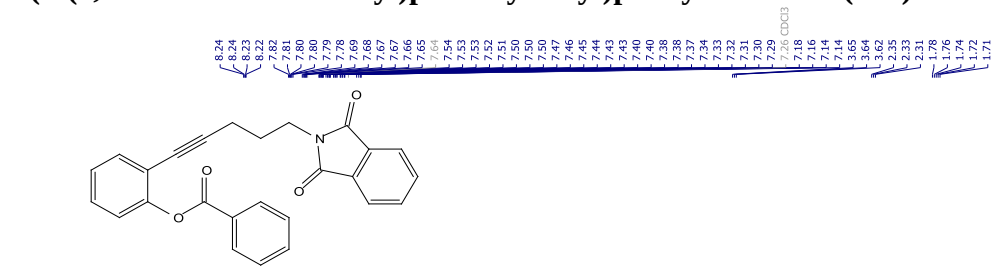


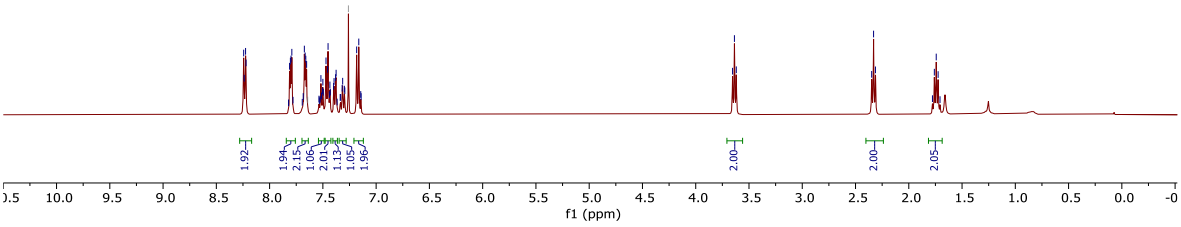
2-(dec-1-yn-1-yl)phenyl benzoate (1z):

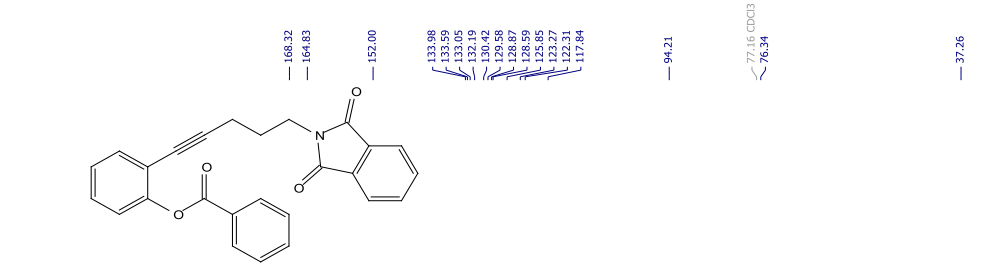


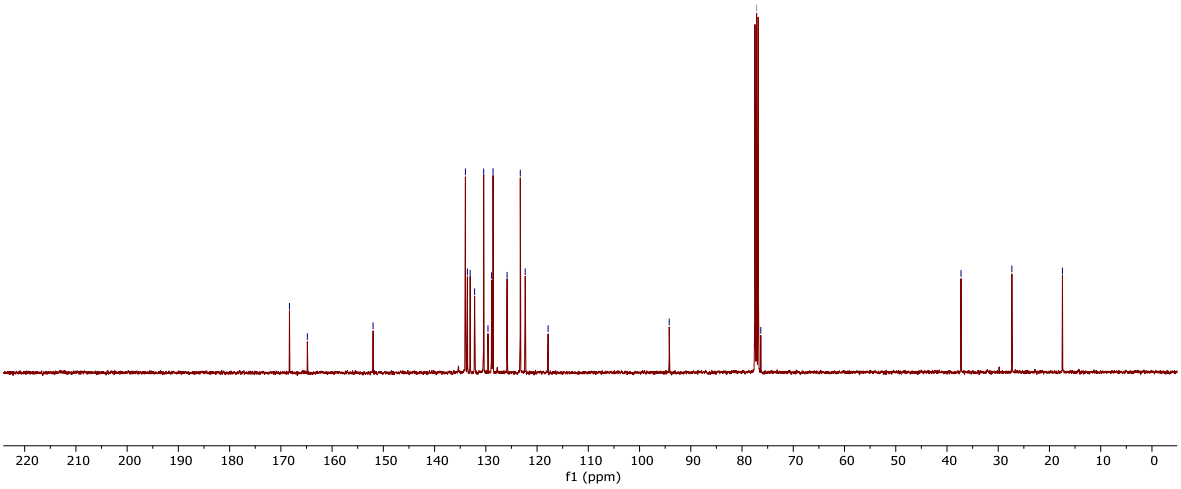


2-(5-(1,3-dioxoisoindolin-2-yl)pent-1-yn-1-yl)phenyl benzoate (1aa):

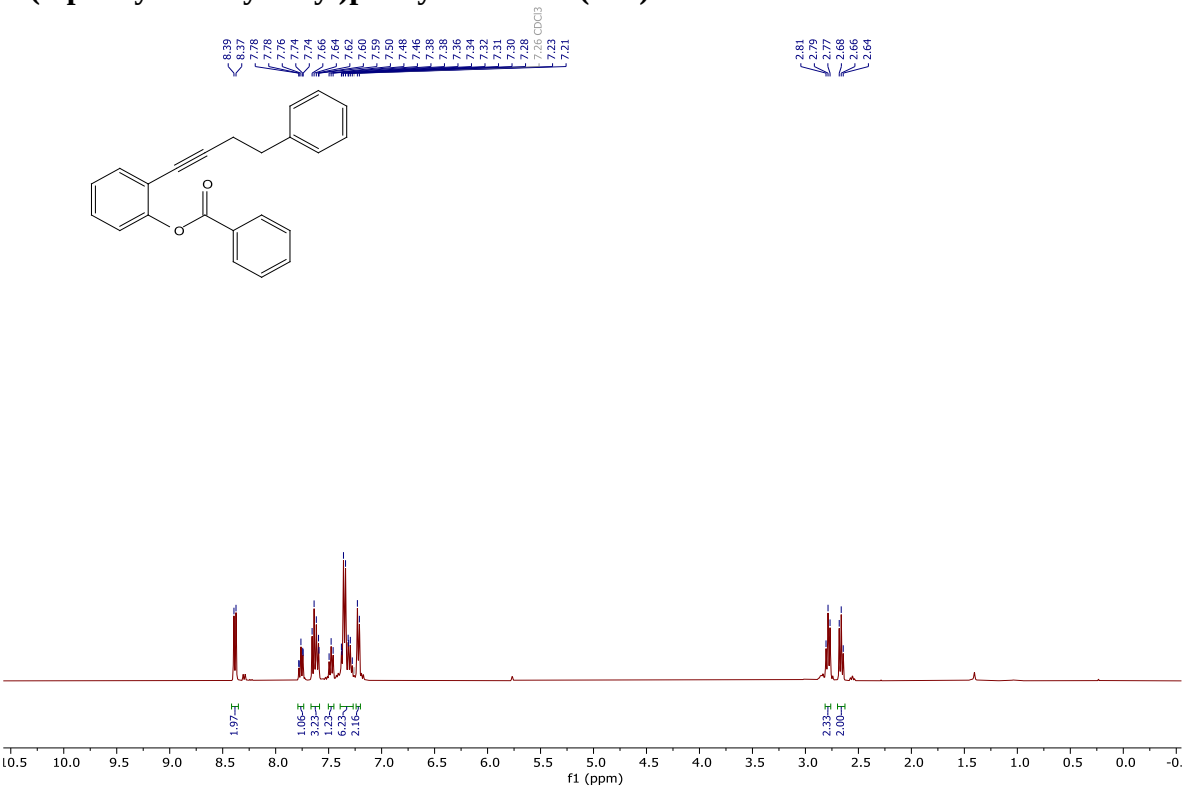


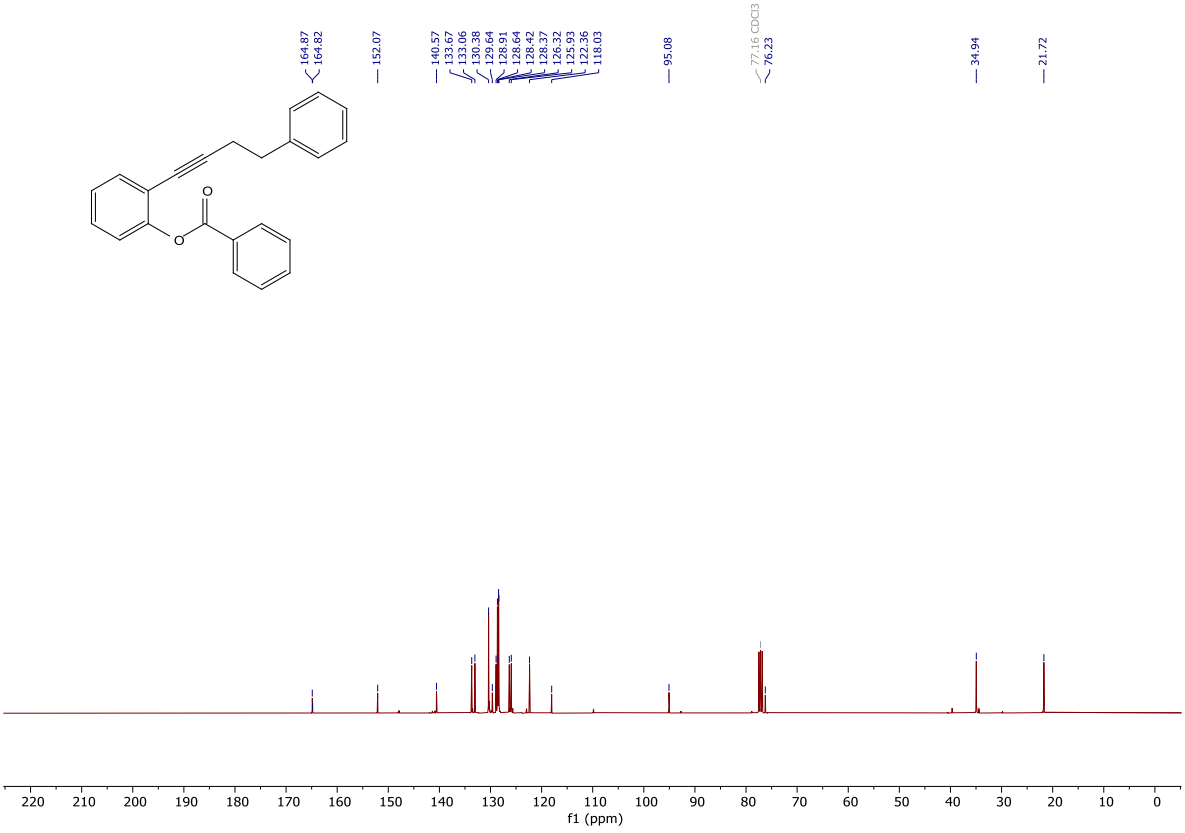




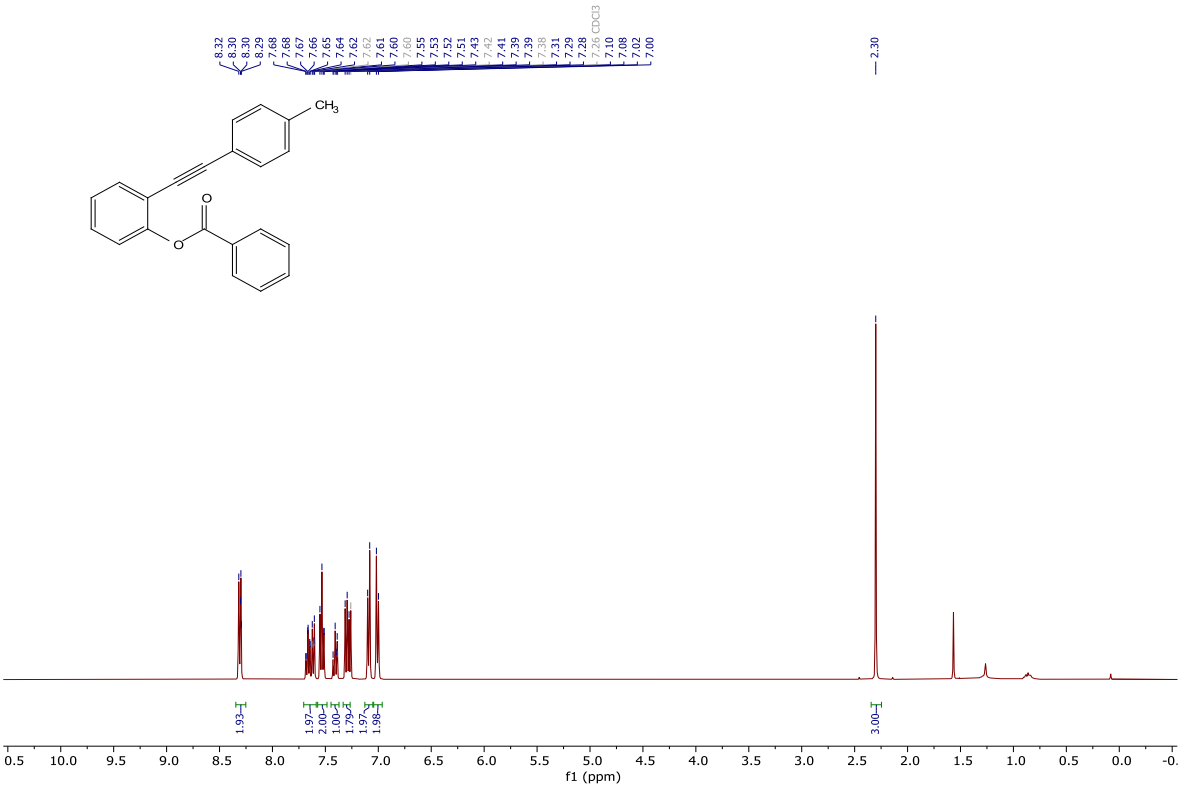


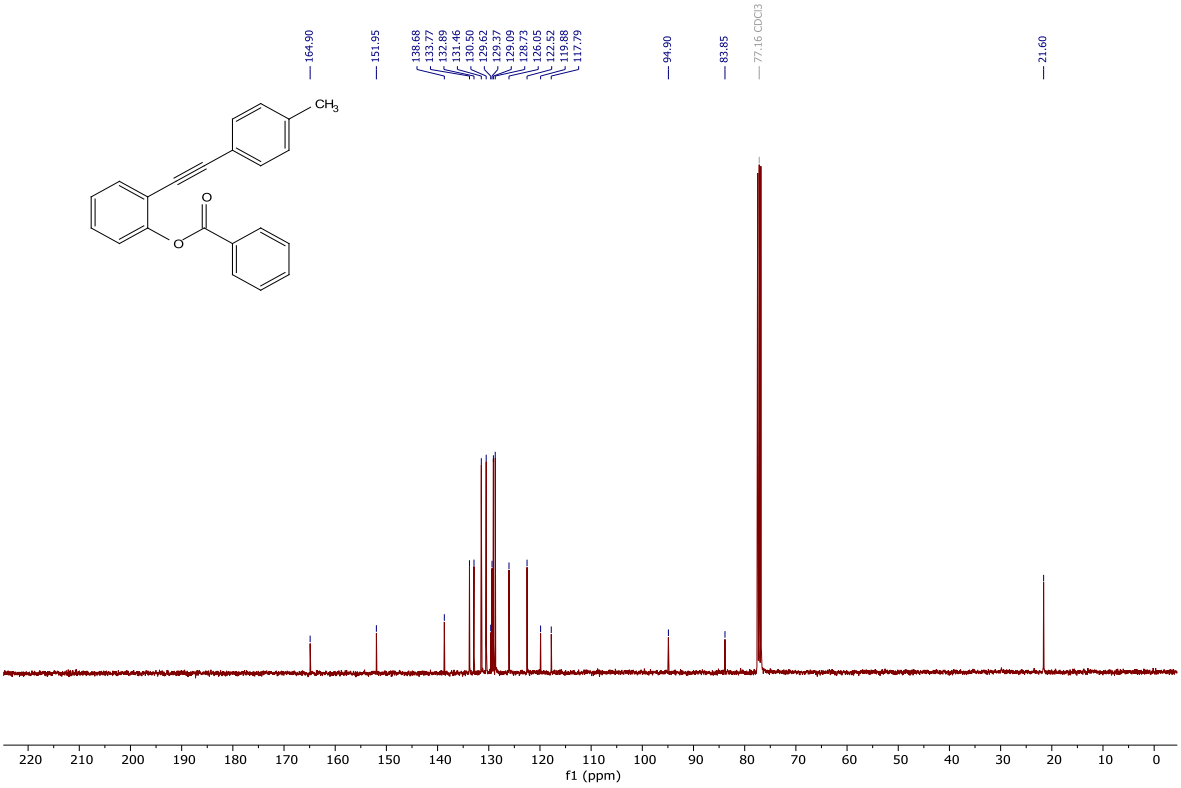
2-(4-phenylbut-1-yn-1-yl)phenyl benzoate (1ab):



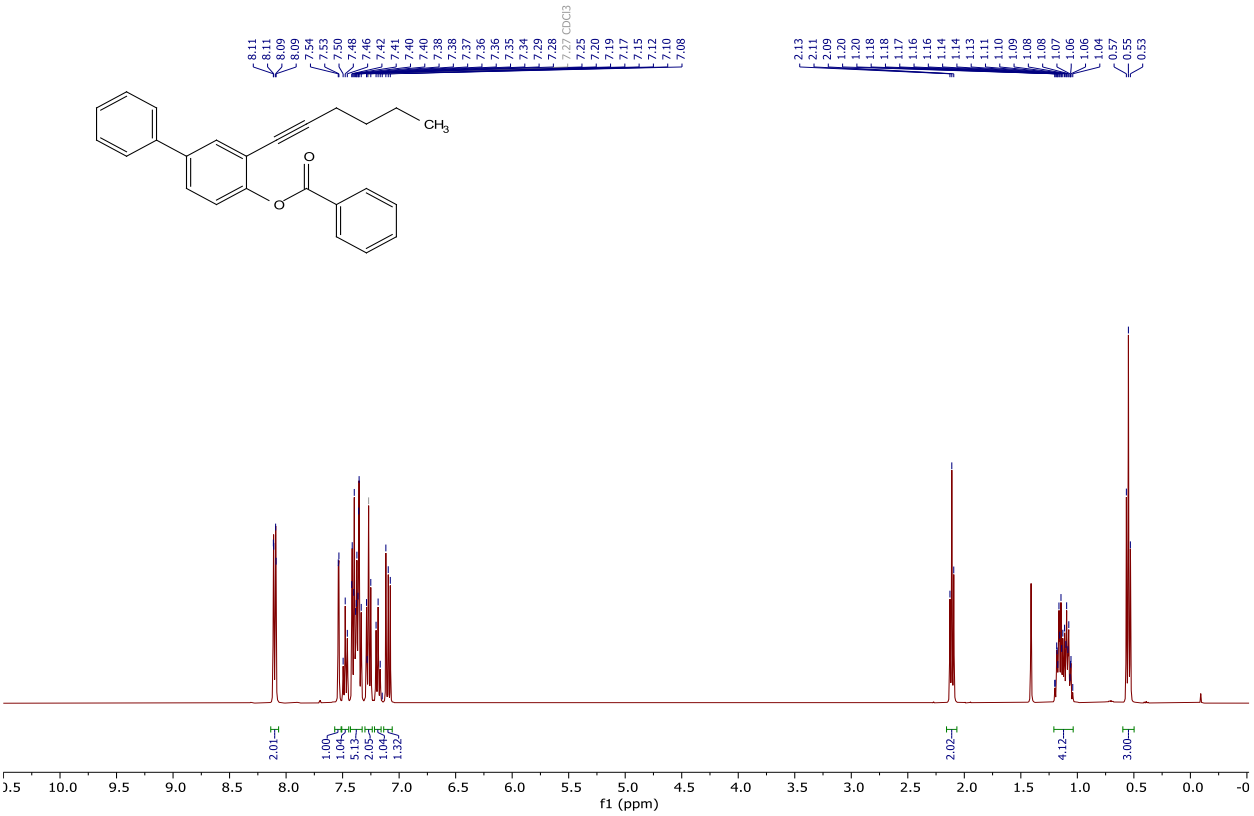


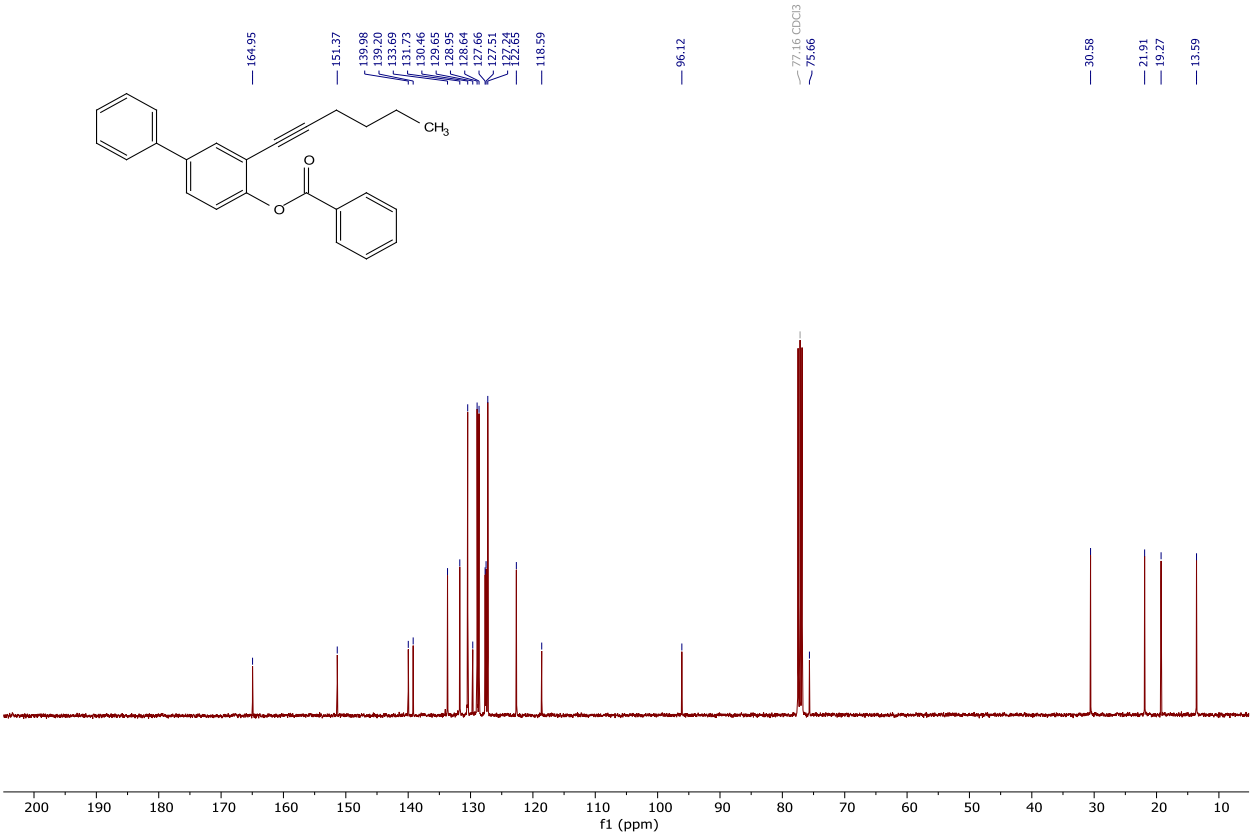
2-(p-tolylethynyl)phenyl benzoate (1ac):



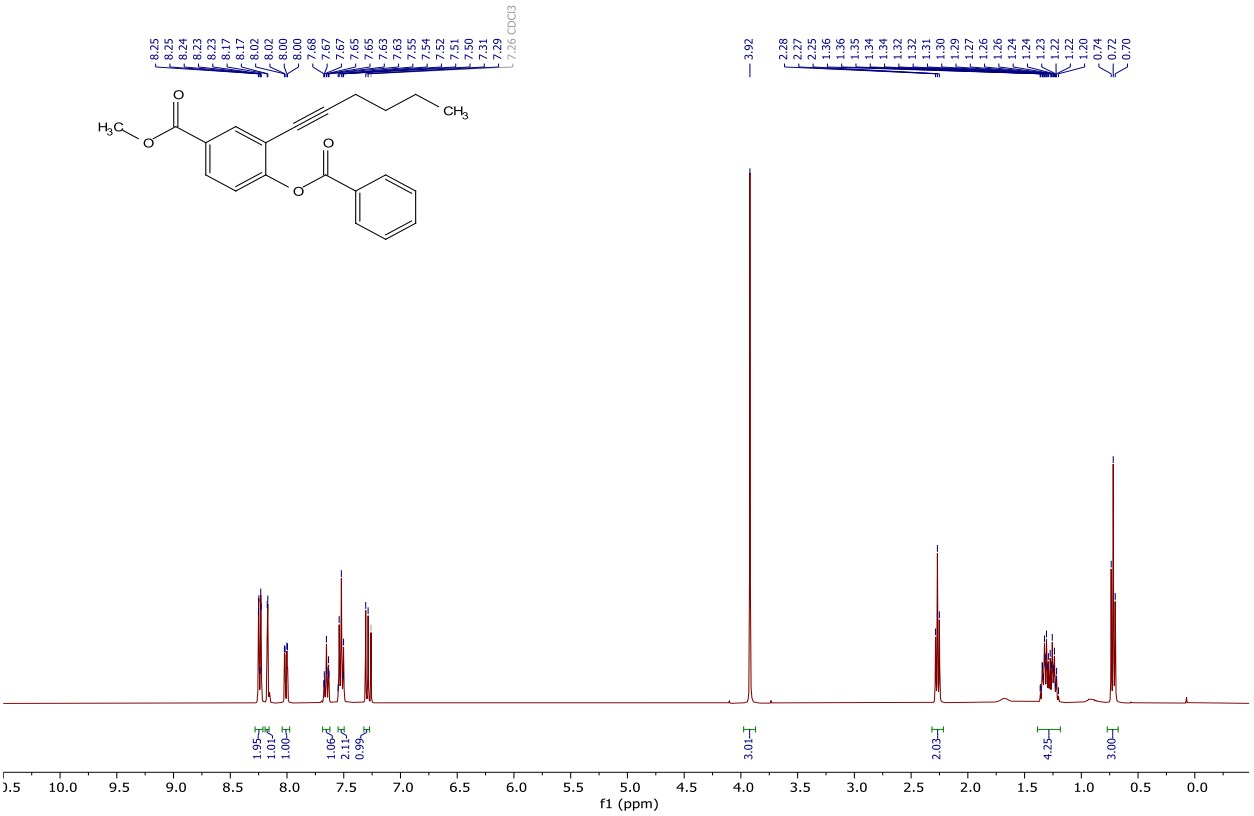


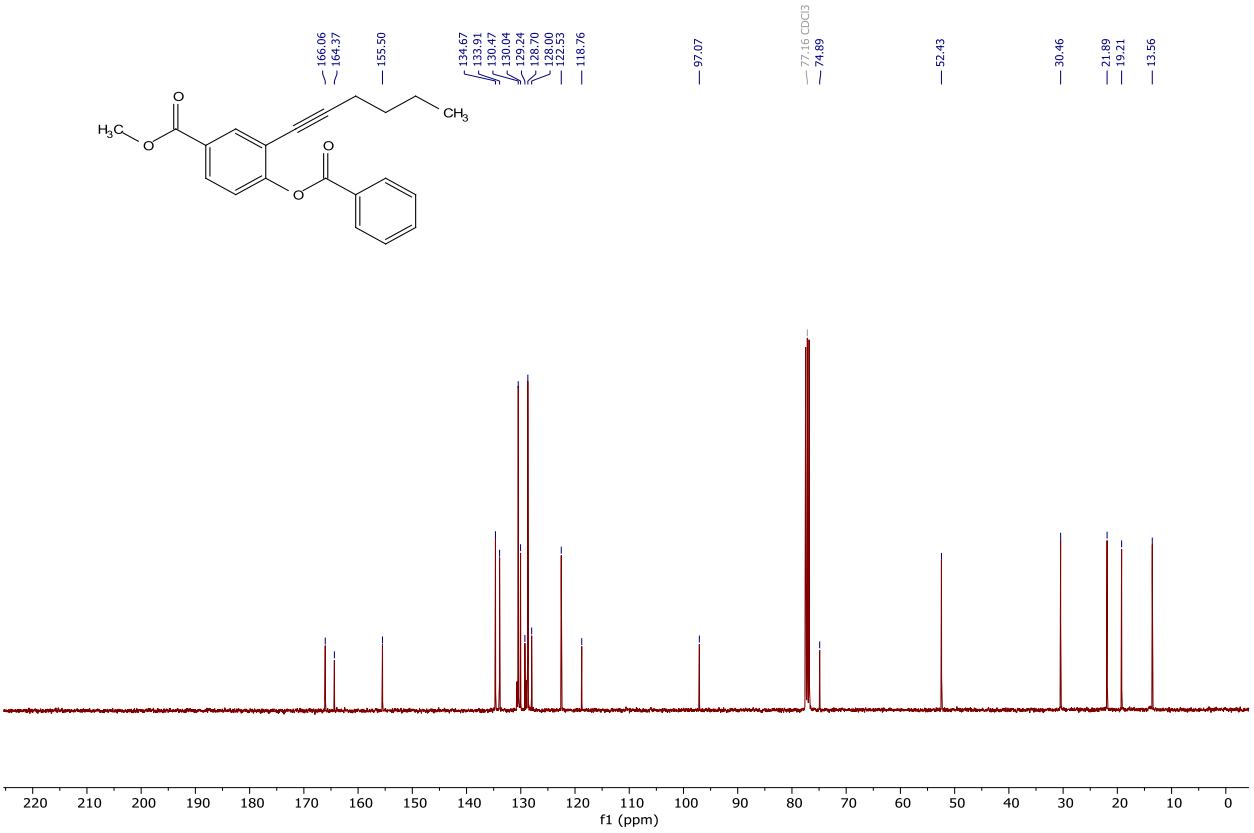
3-(hex-1-yn-1-yl)-[1,1'-biphenyl]-4-yl benzoate (1ad):



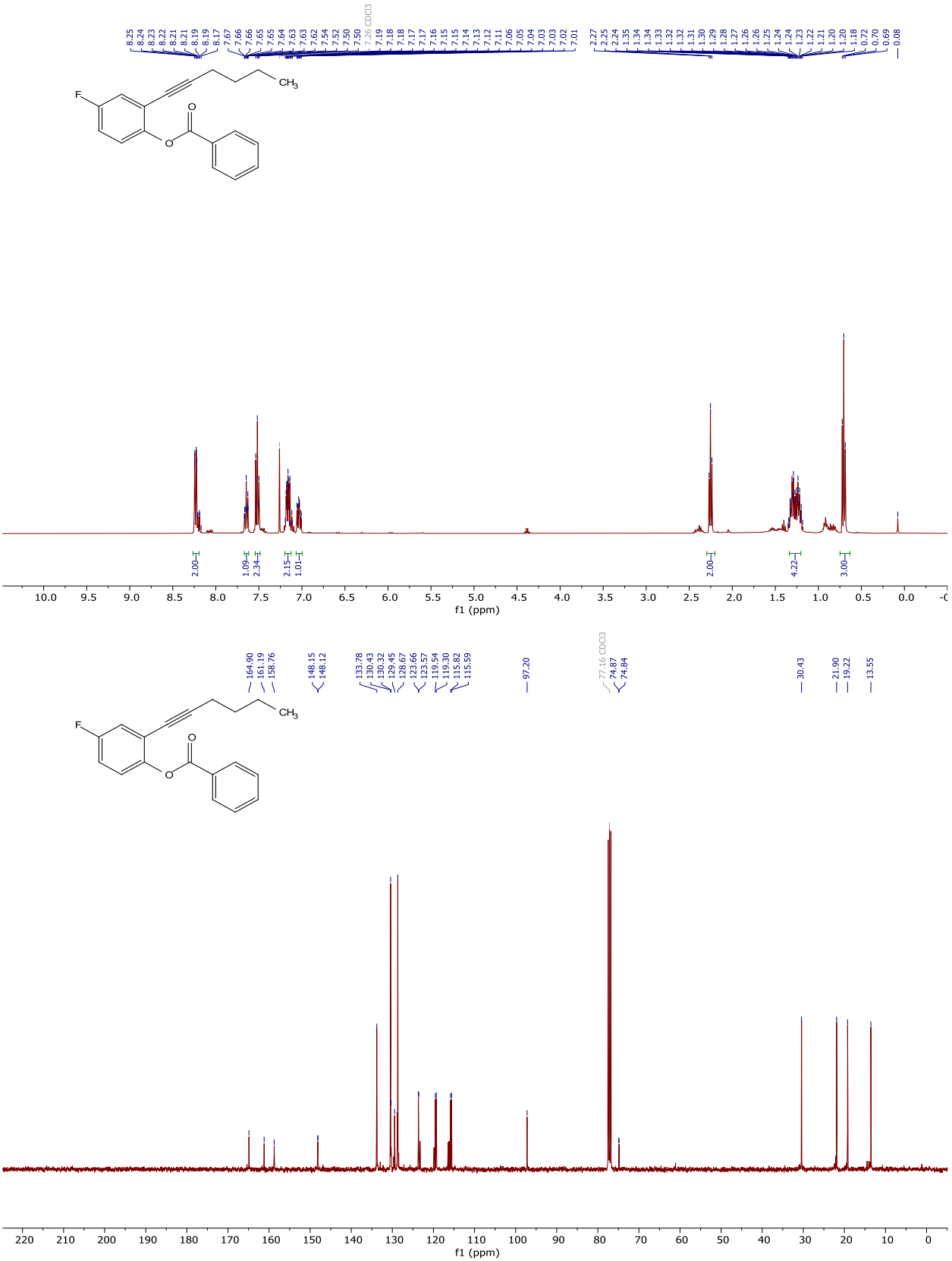


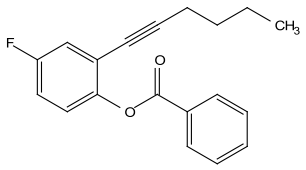
methyl 4-(benzoyloxy)-3-(hex-1-yn-1-yl)benzoate (1ae):





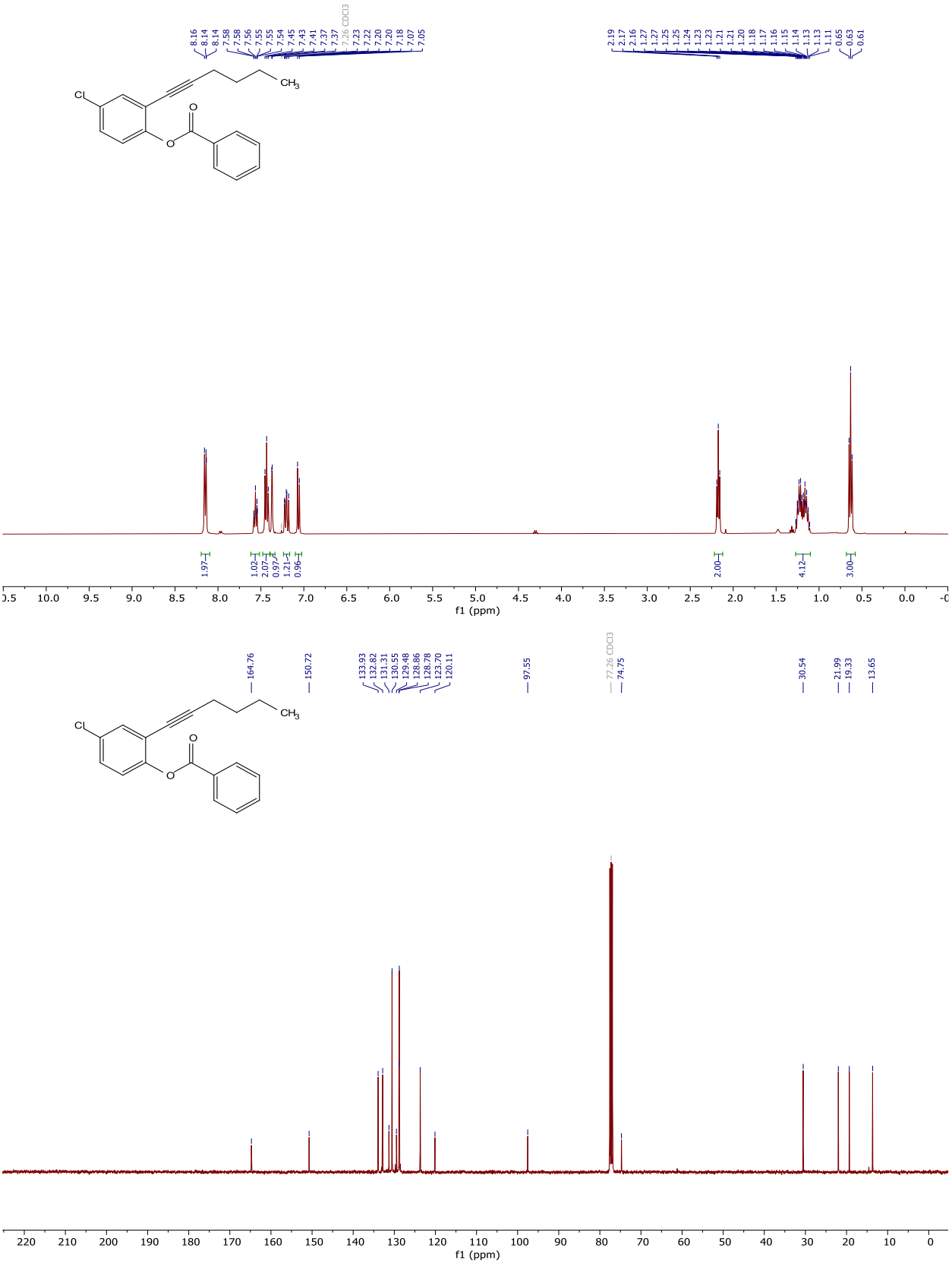
4-fluoro-2-(hex-1-yn-1-yl)phenyl benzoate (1af):



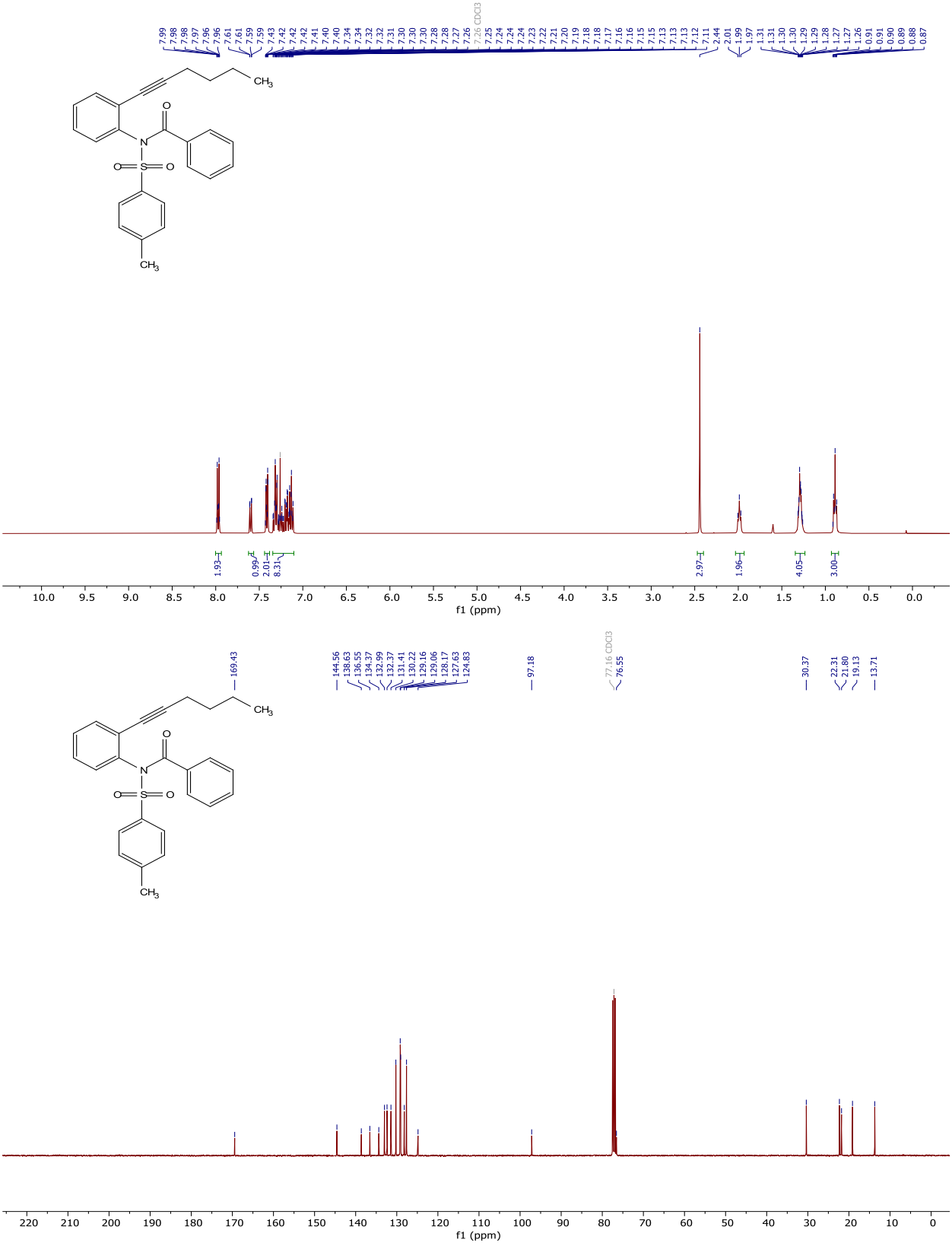

F
O
O
CH3

-116.94
00 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300 -320
f1 (ppm)

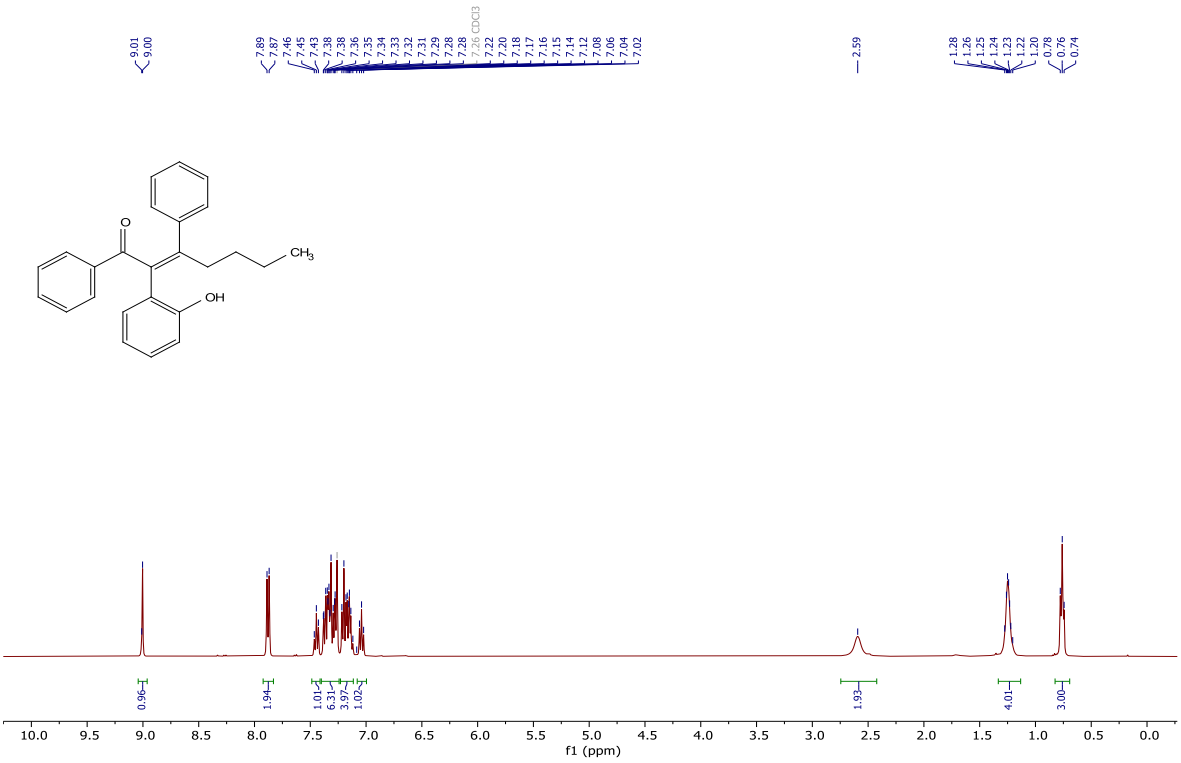
4-chloro-2-(hex-1-yn-1-yl)phenyl benzoate (1ag):



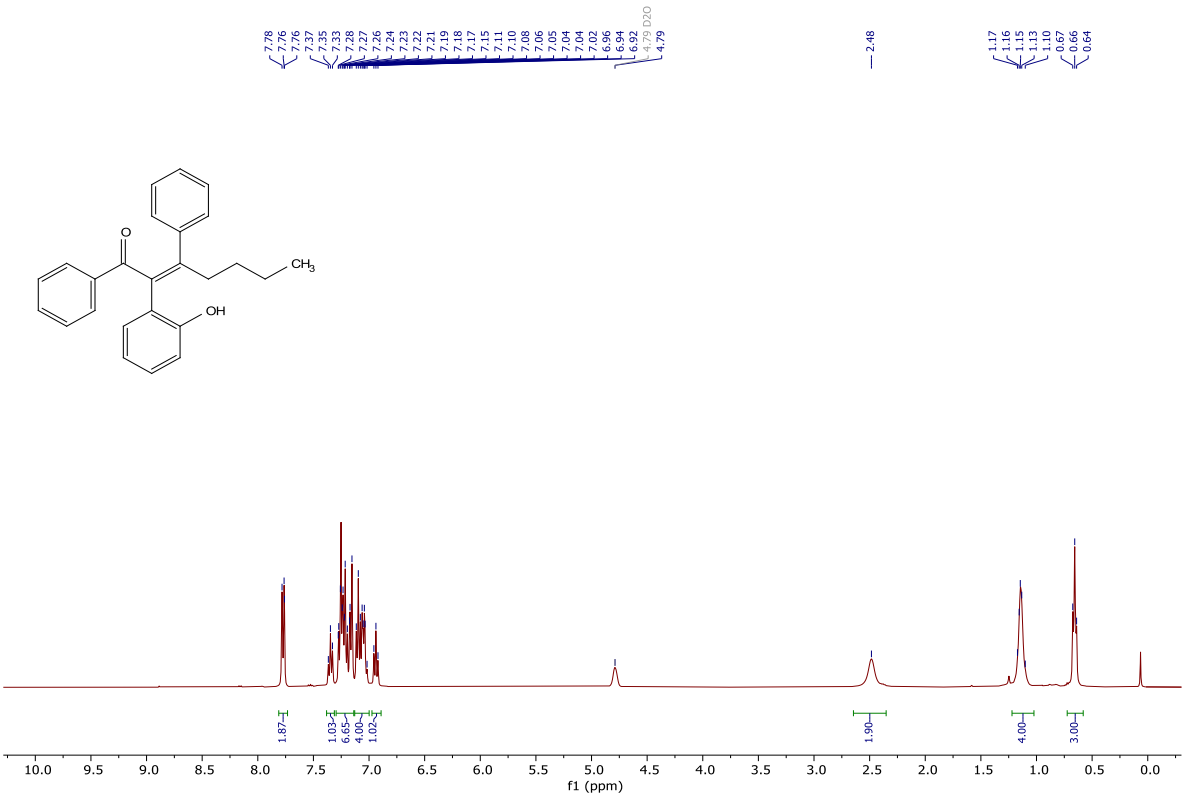
N-(2-(hex-1-yn-1-yl)phenyl)-N-tosylbenzamide (1ah):



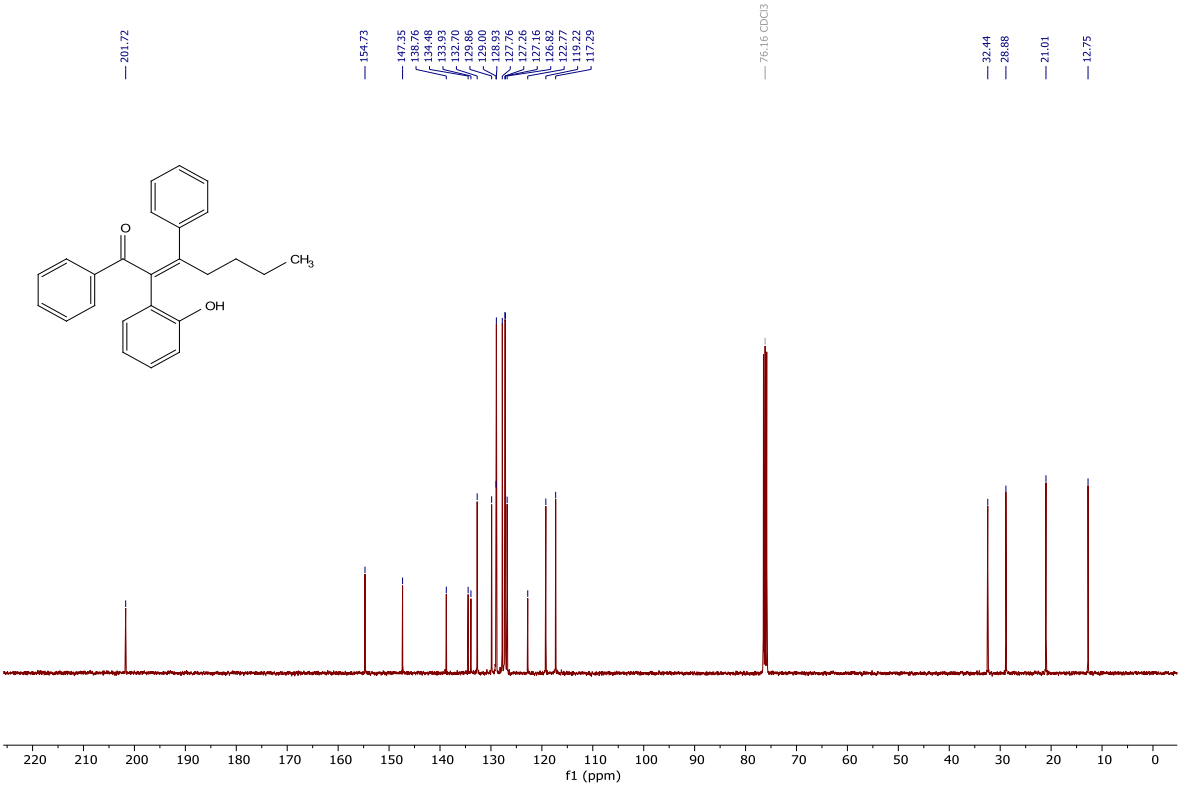
(*Z*)-2-(2-hydroxyphenyl)-1,3-diphenylhept-2-en-1-one (3a):



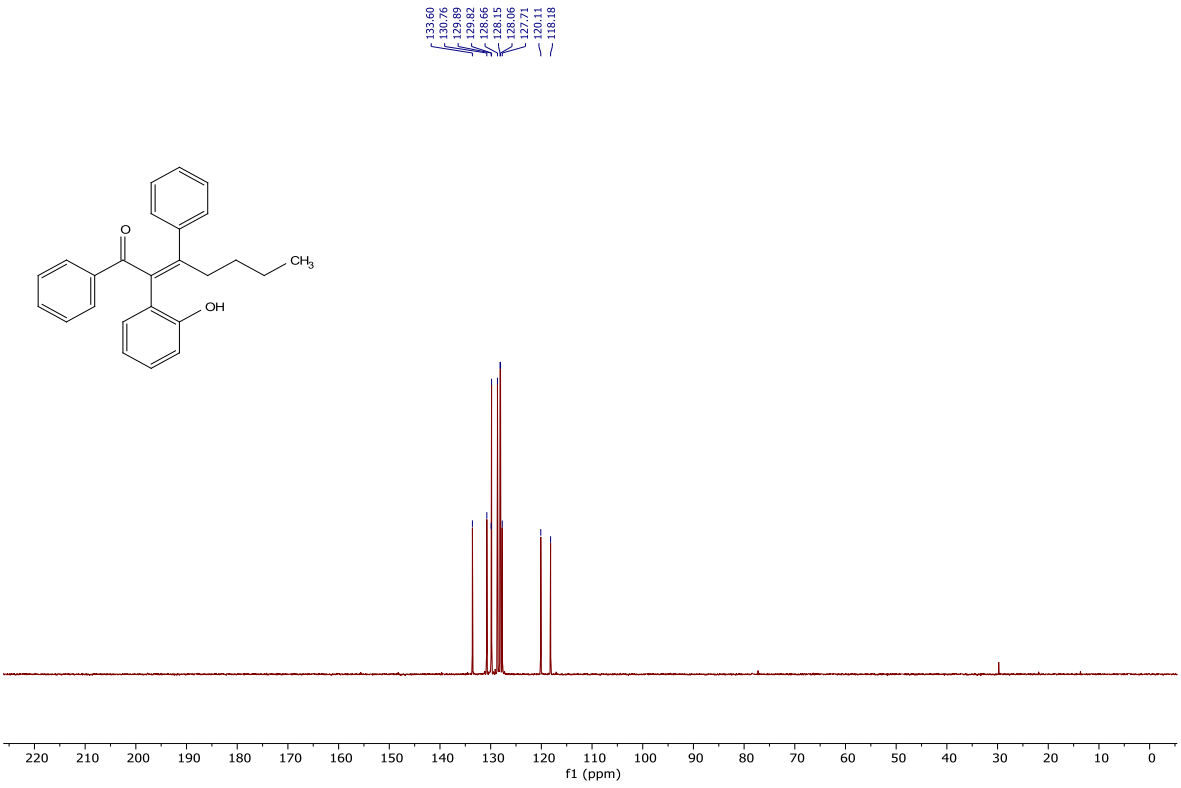
D_2O Exchange study



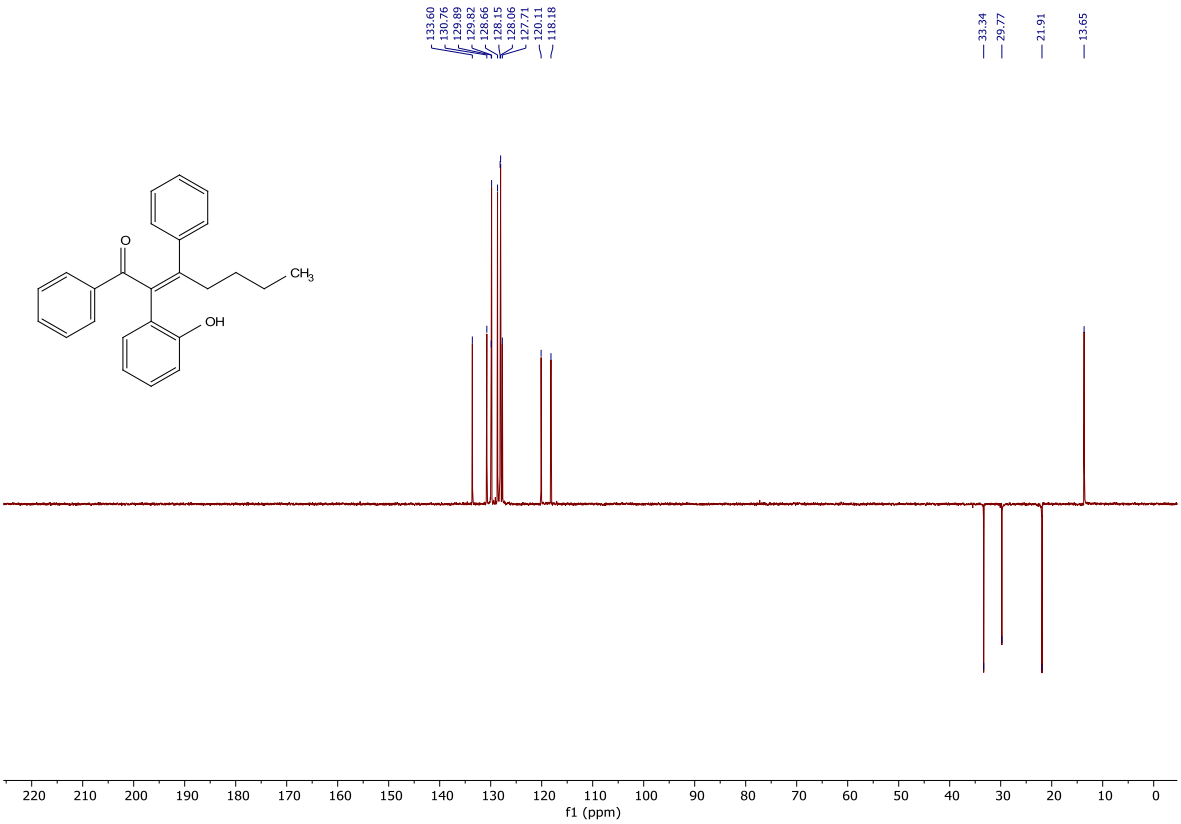
(*Z*)-2-(2-hydroxyphenyl)-1,3-diphenylhept-2-en-1-one (3a): ^{13}C NMR



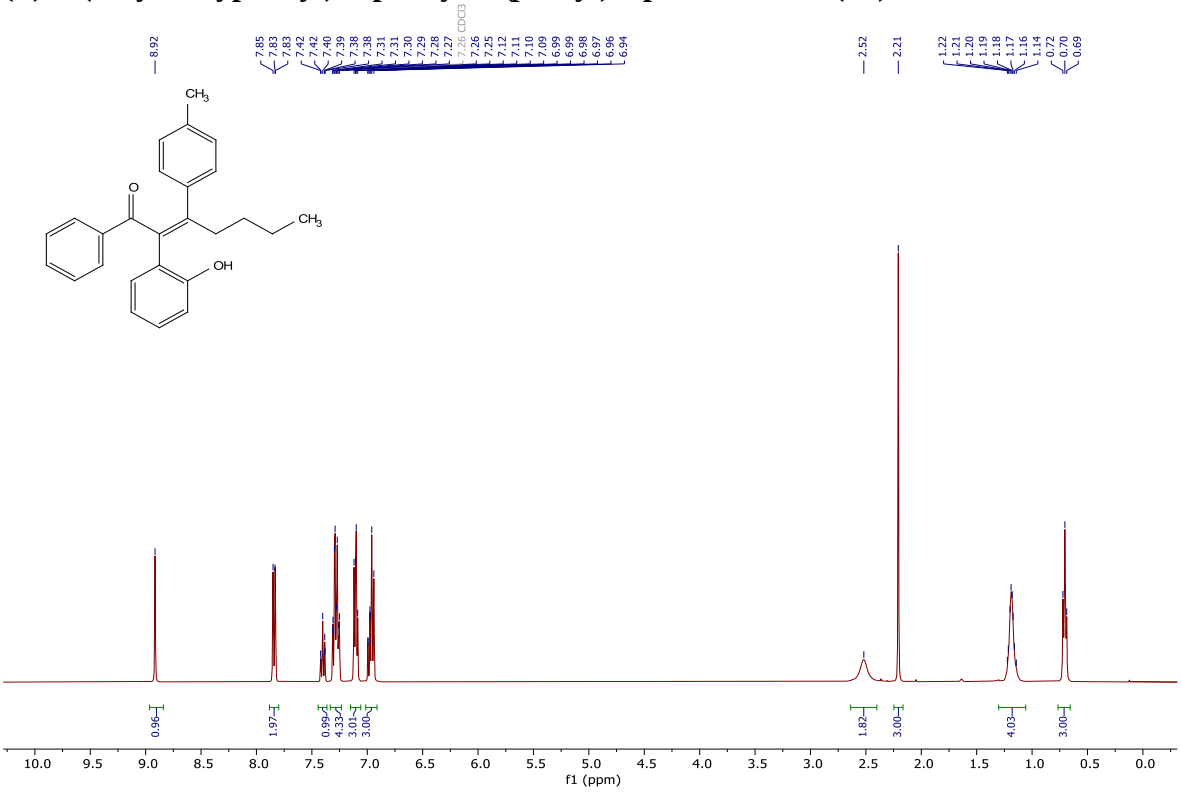
(*Z*)-2-(2-hydroxyphenyl)-1,3-diphenylhept-2-en-1-one (3a): DEPT-90 spectra

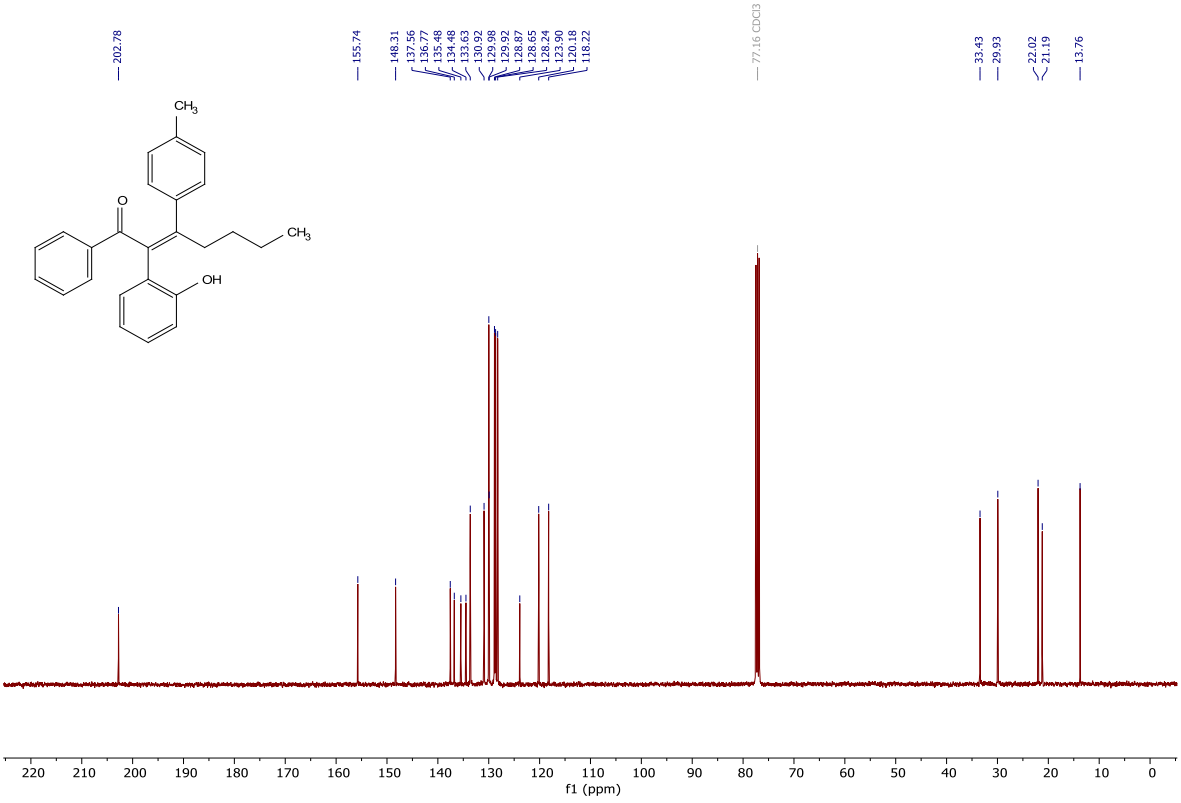


(*Z*)-2-(2-hydroxyphenyl)-1,3-diphenylhept-2-en-1-one (3a): DEPT-135 spectra

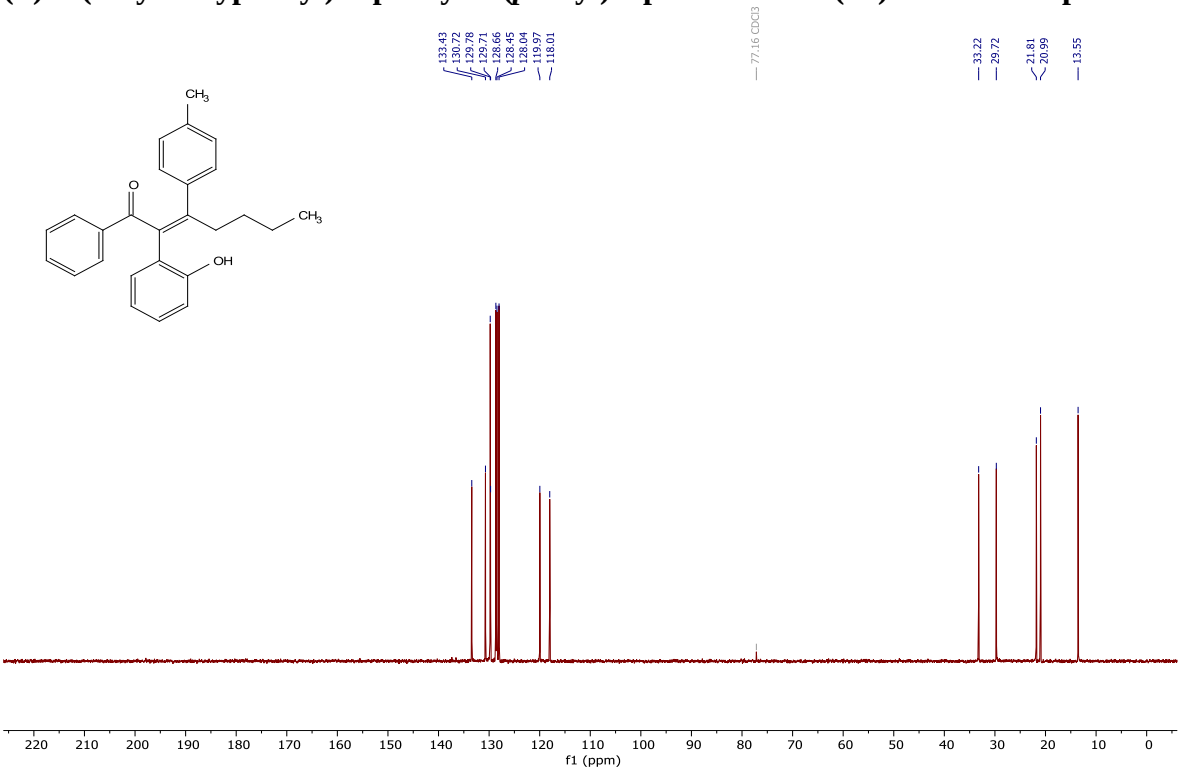


(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)hept-2-en-1-one (3b):

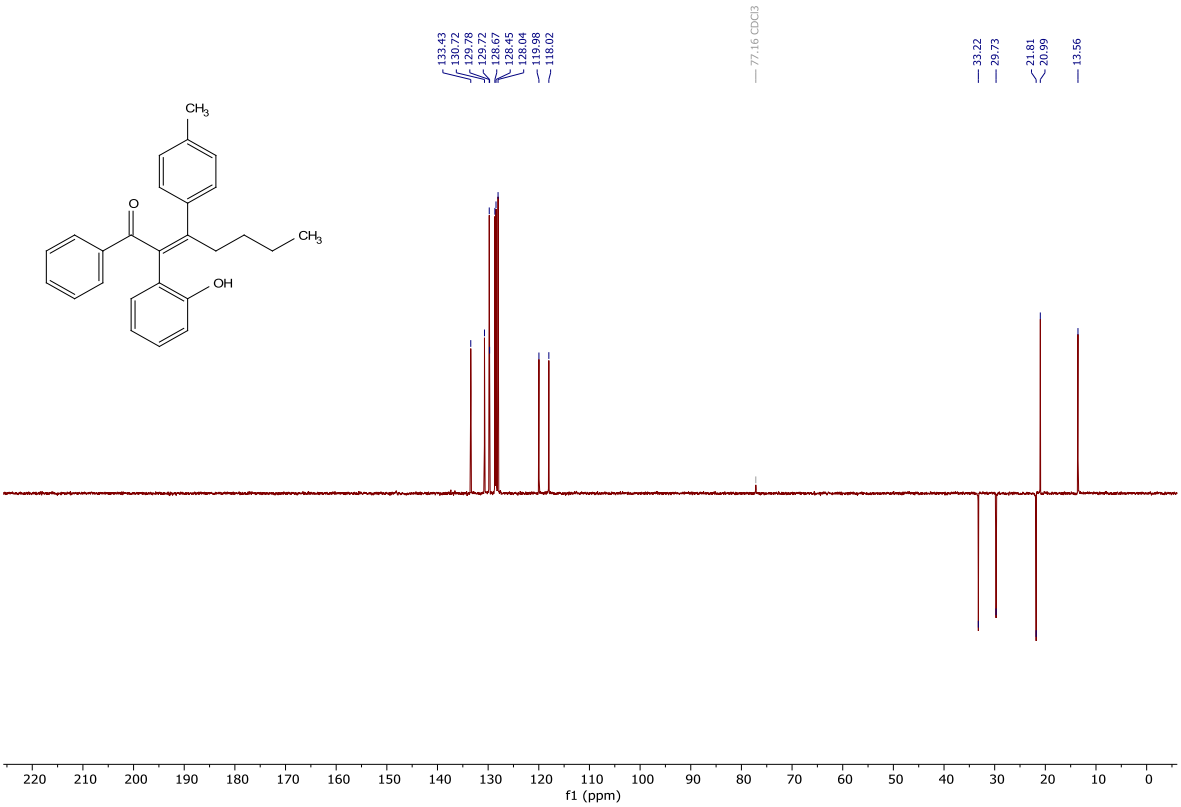




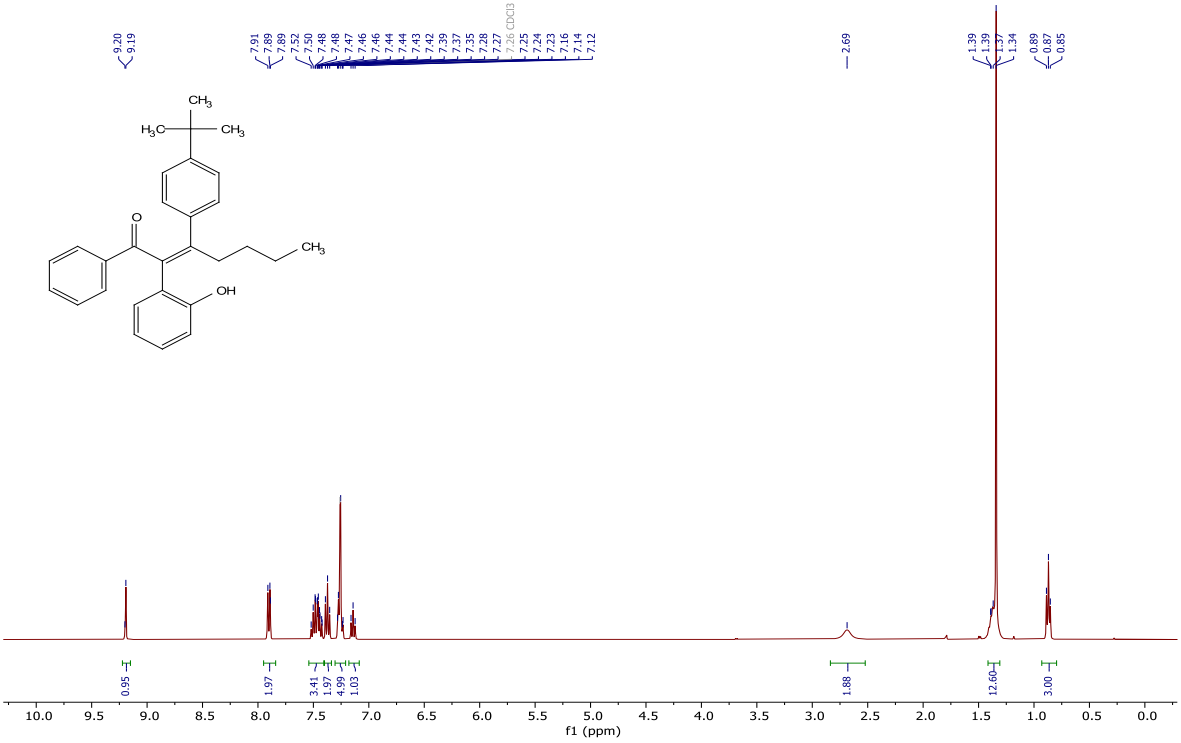
(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)hept-2-en-1-one (3b): DEPT-45 Spectra

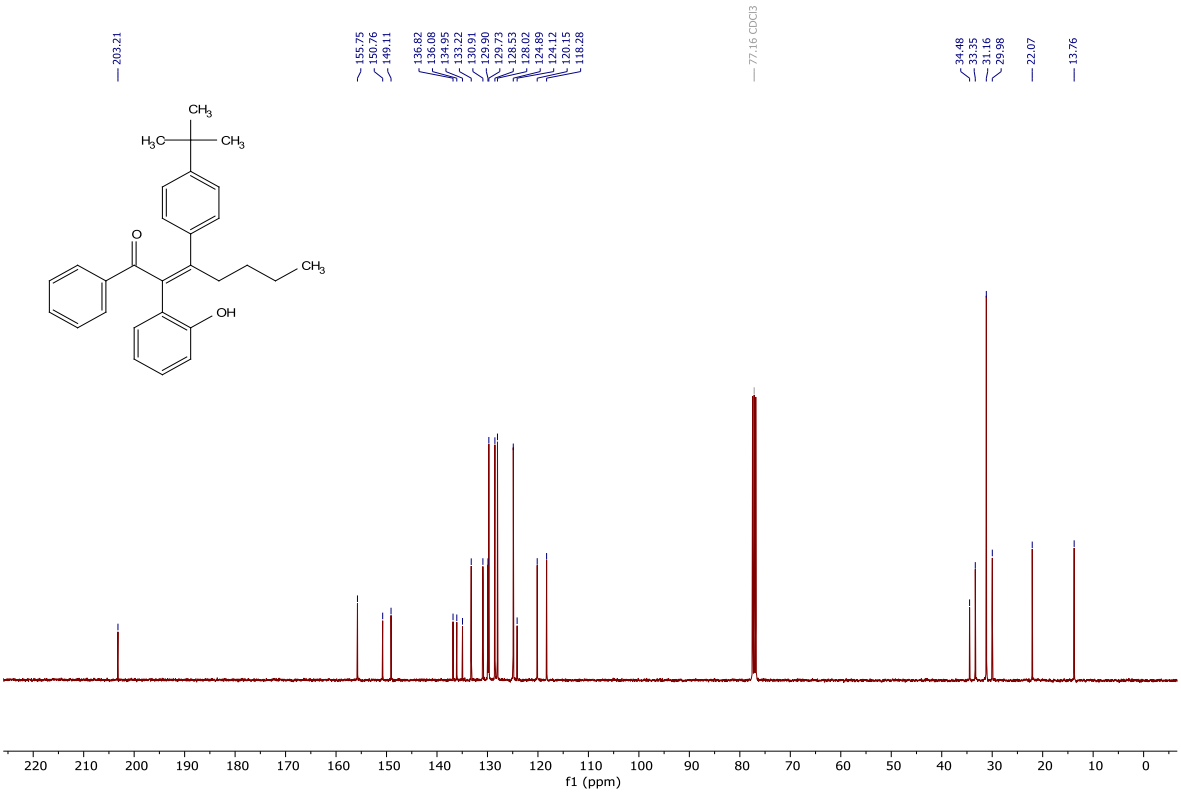


DEPT-90 Spectra

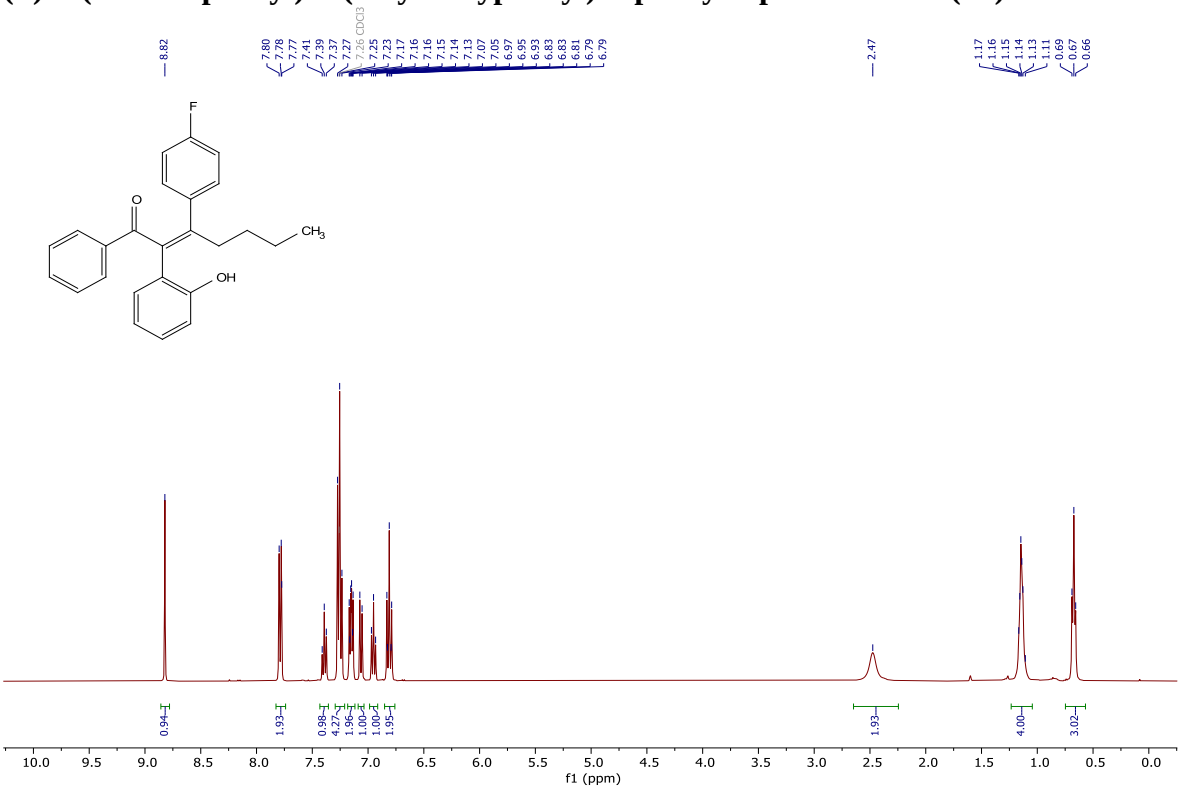


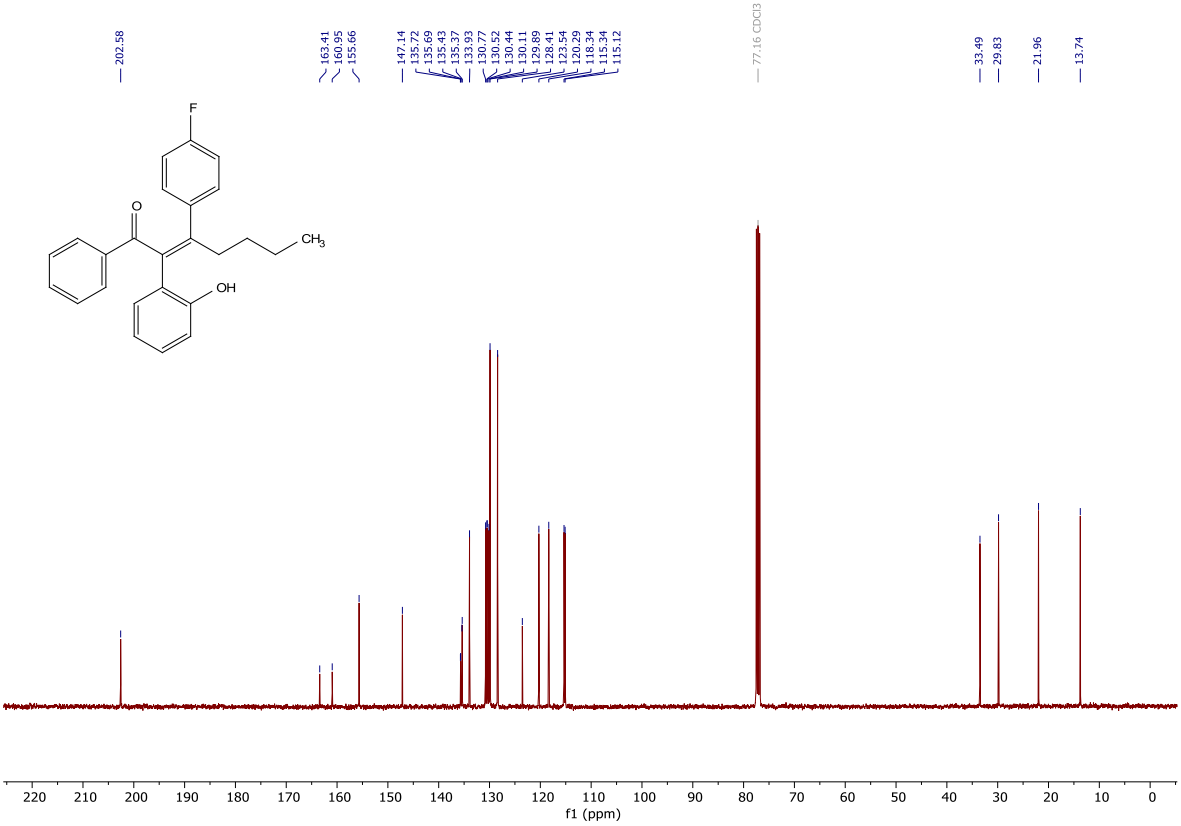
(*Z*)-3-(4-(tert-butyl)phenyl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3c):



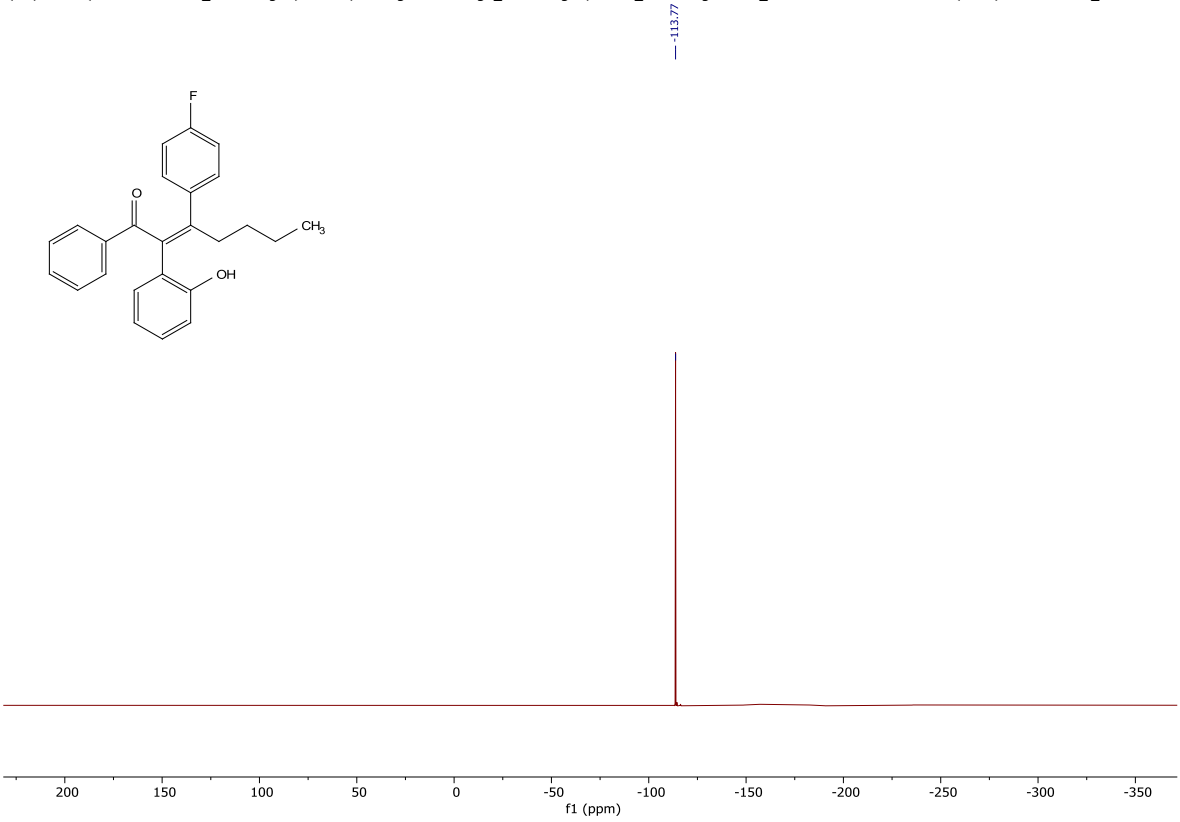


(*Z*)-3-(4-fluorophenyl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3d):

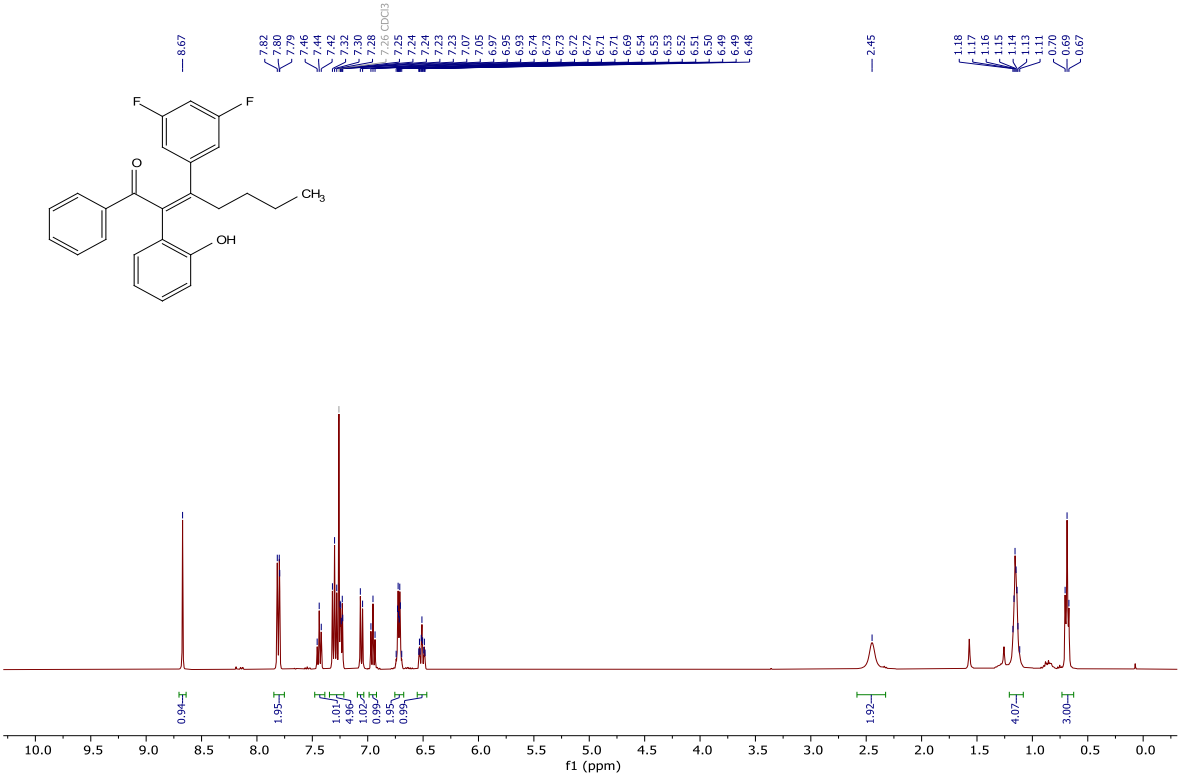


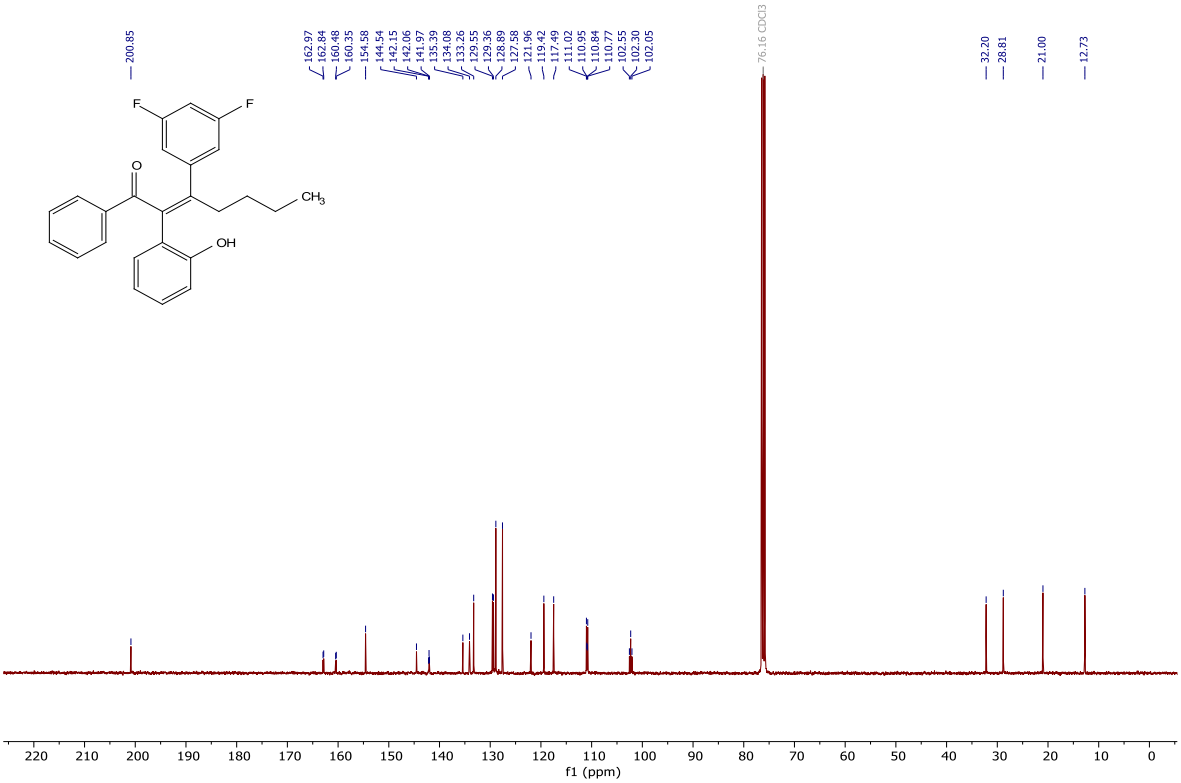


(*Z*)-3-(4-fluorophenyl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3d): ^{19}F Spectra

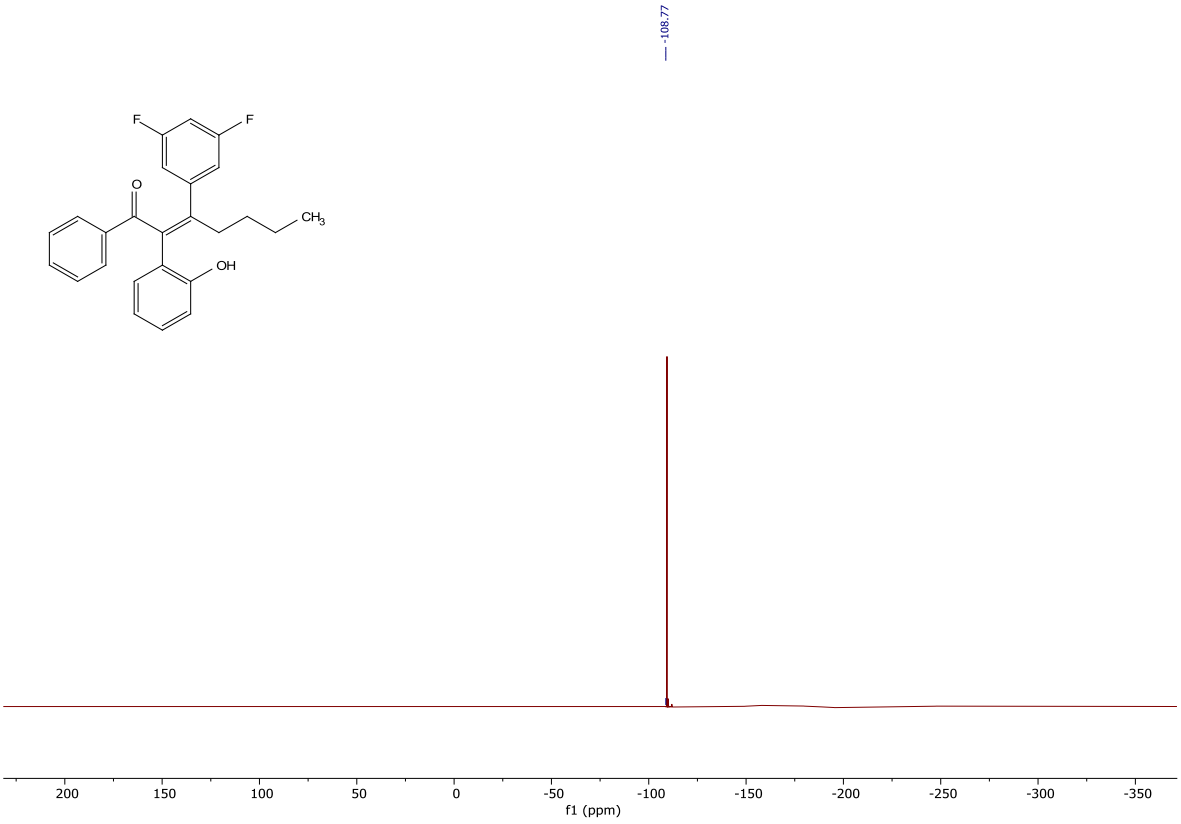


(*Z*)-3-(3,5-difluorophenyl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3e):

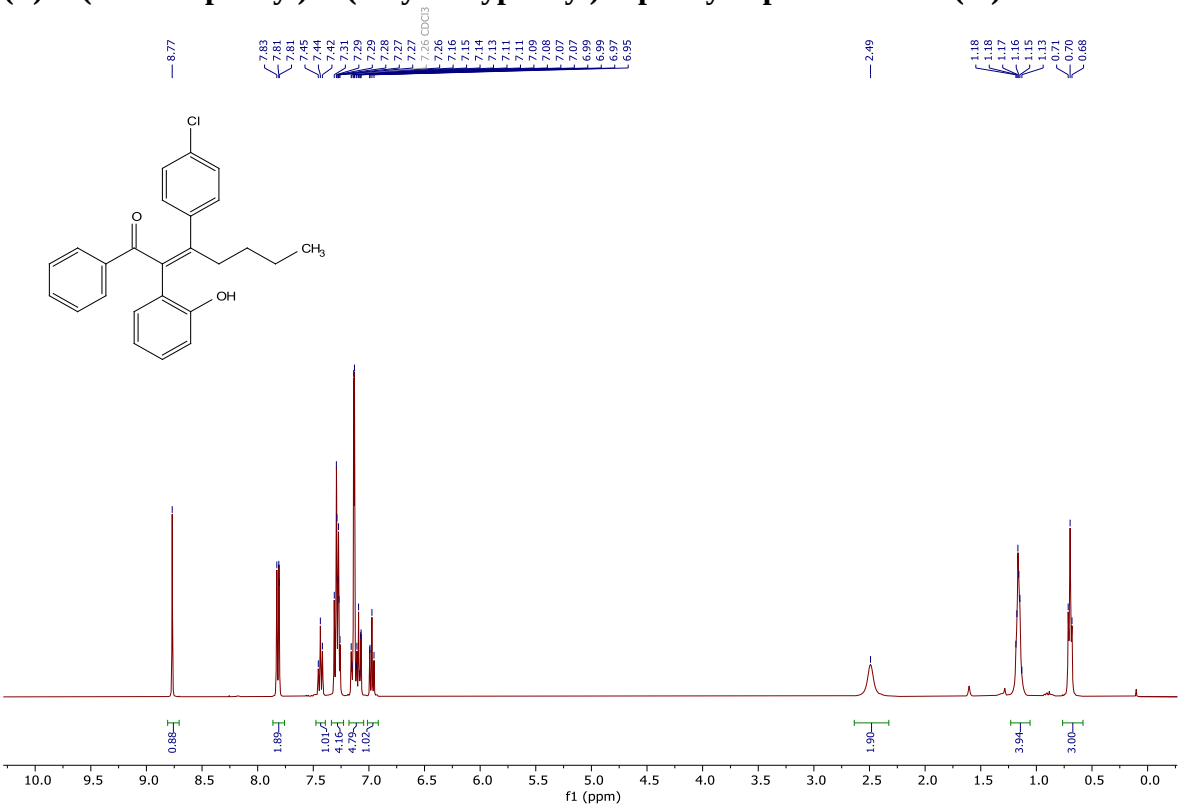


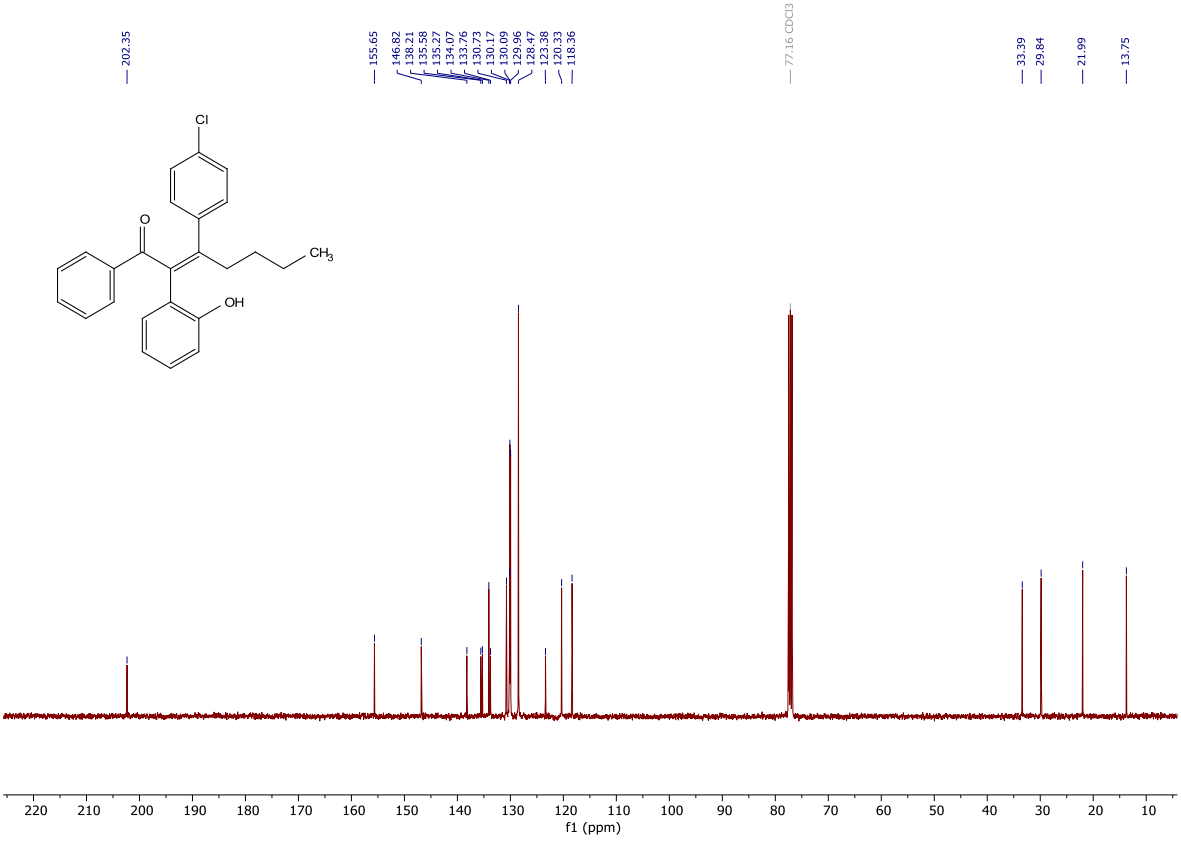


(*Z*)-3-(3,5-difluorophenyl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3e): ^{19}F Spectra

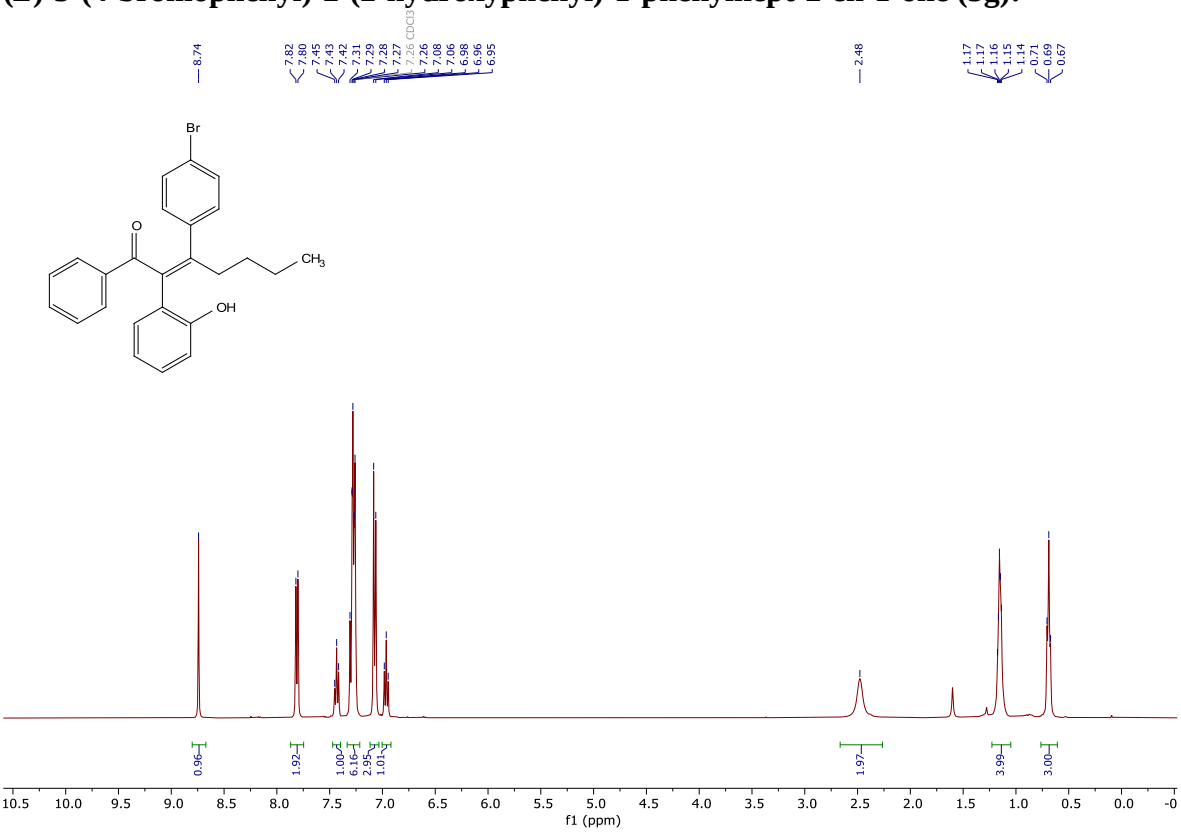


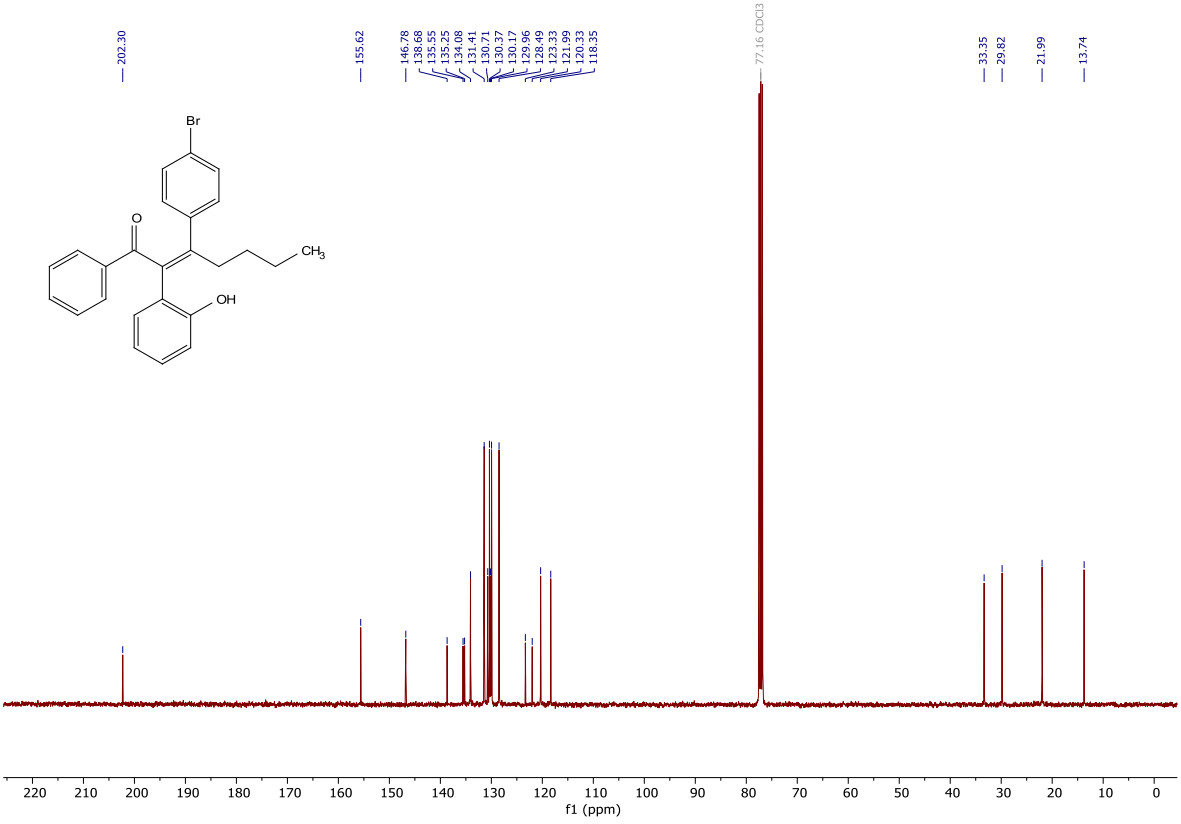
(*Z*)-3-(4-chlorophenyl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3f):



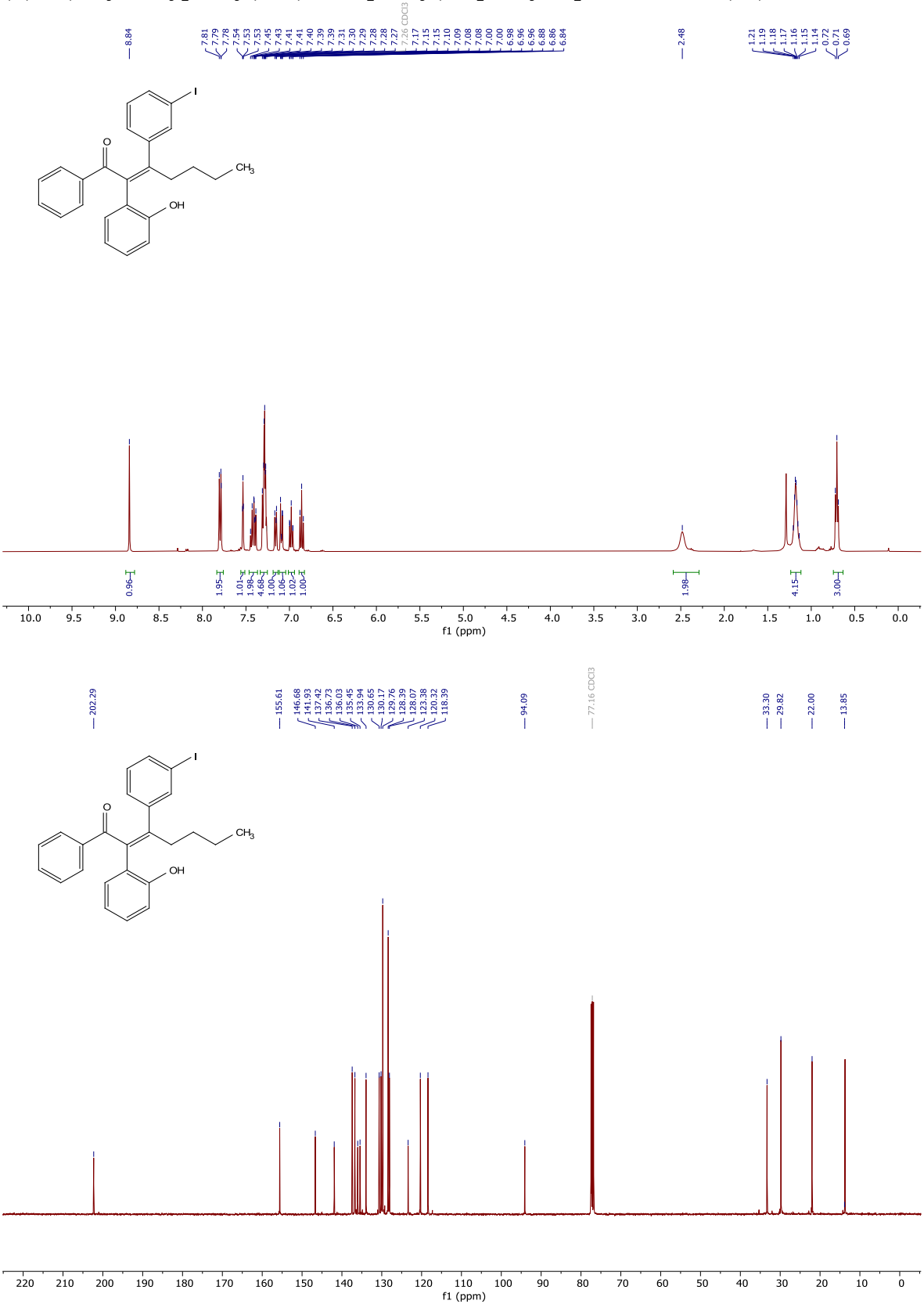


(*Z*)-3-(4-bromophenyl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3g):

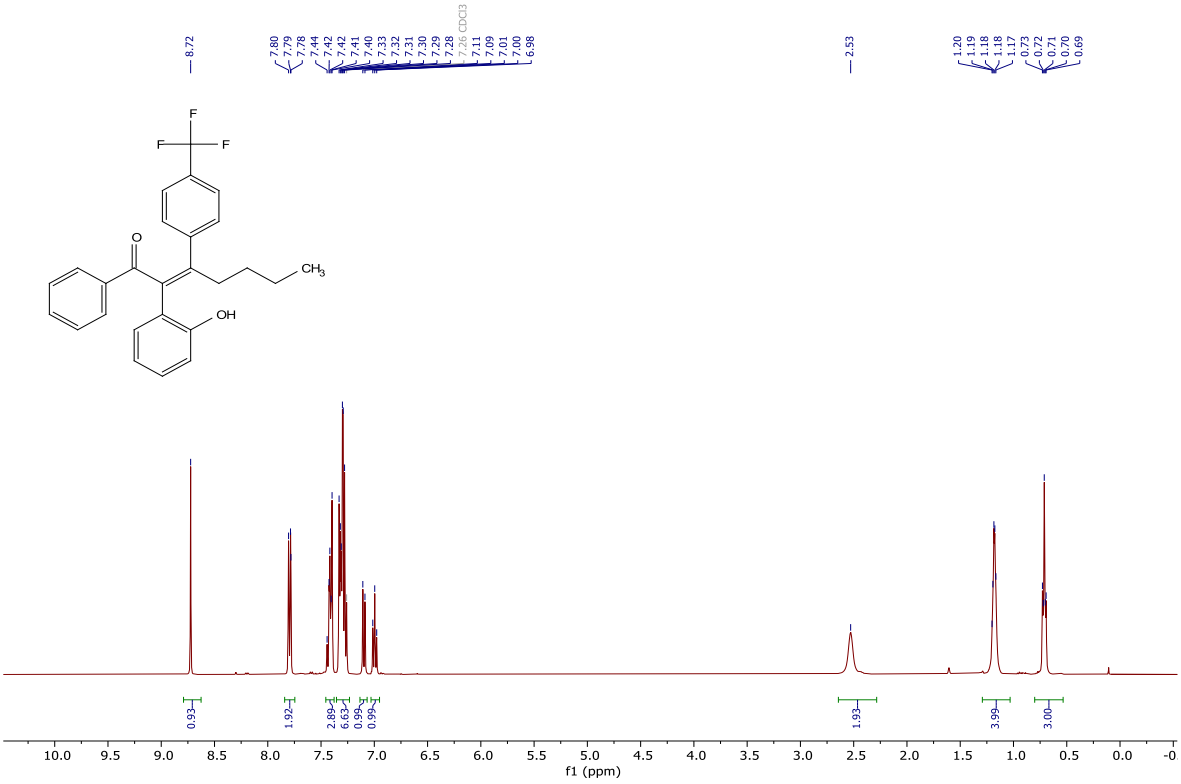


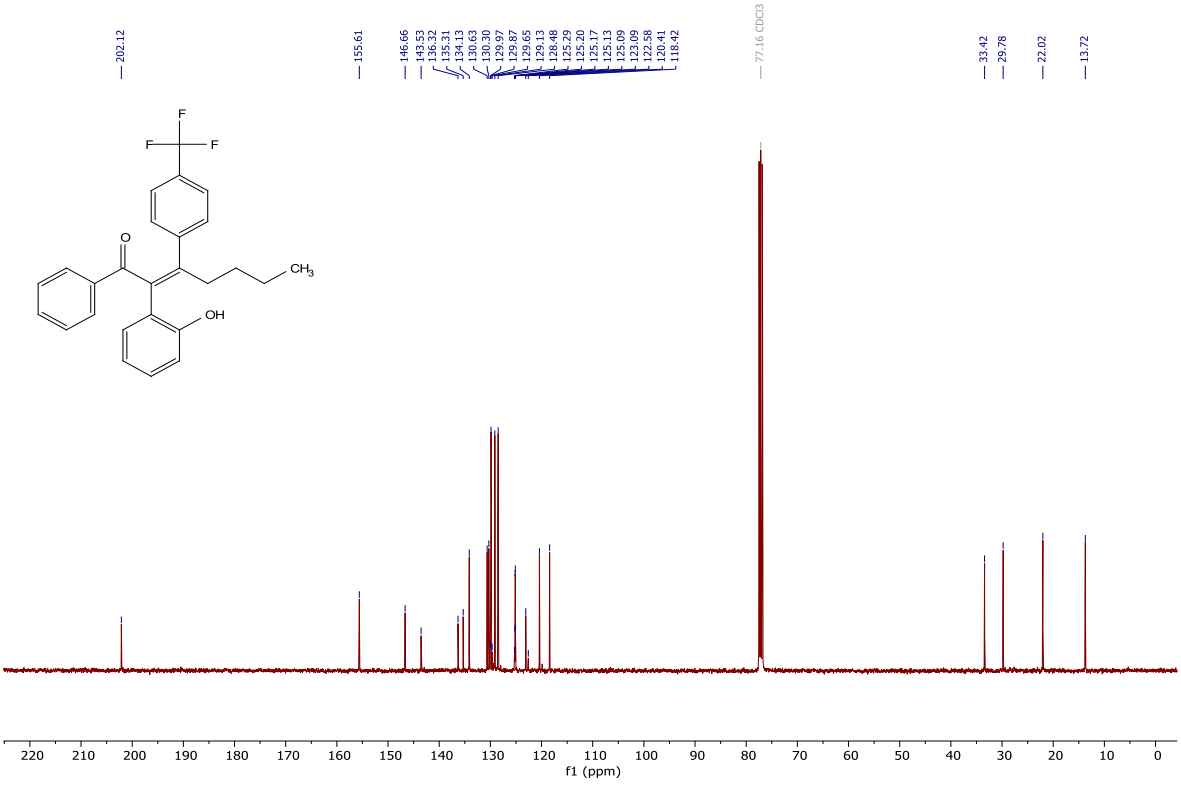


(*Z*)-2-(2-hydroxyphenyl)-3-(3-iodophenyl)-1-phenylhept-2-en-1-one (3h):

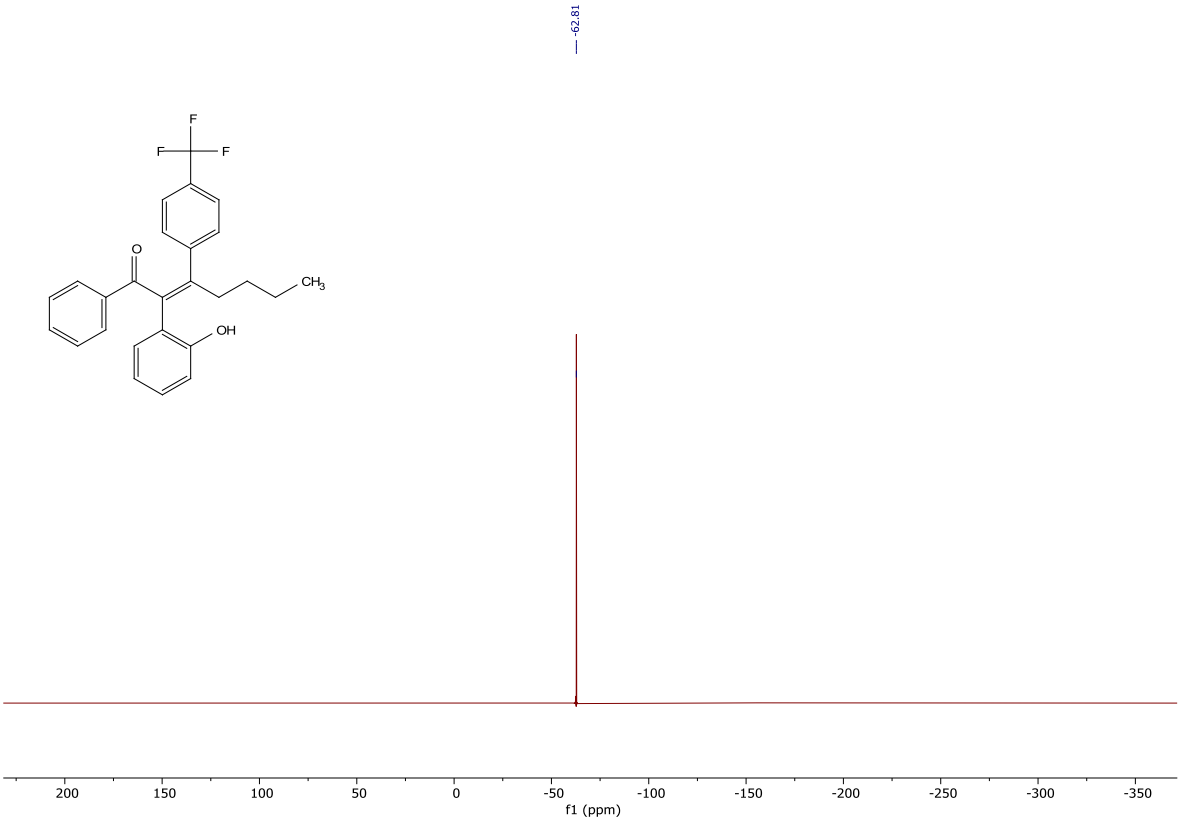


(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)hept-2-en-1-one (3i):

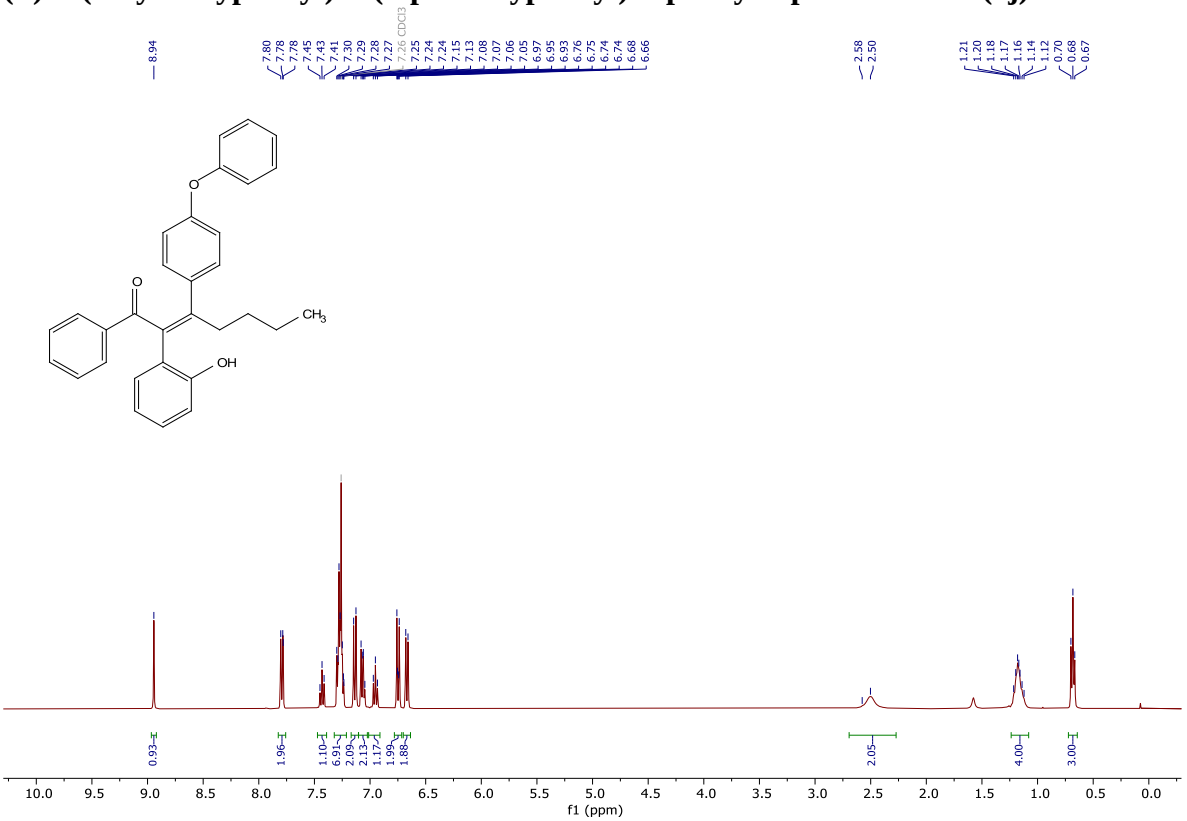


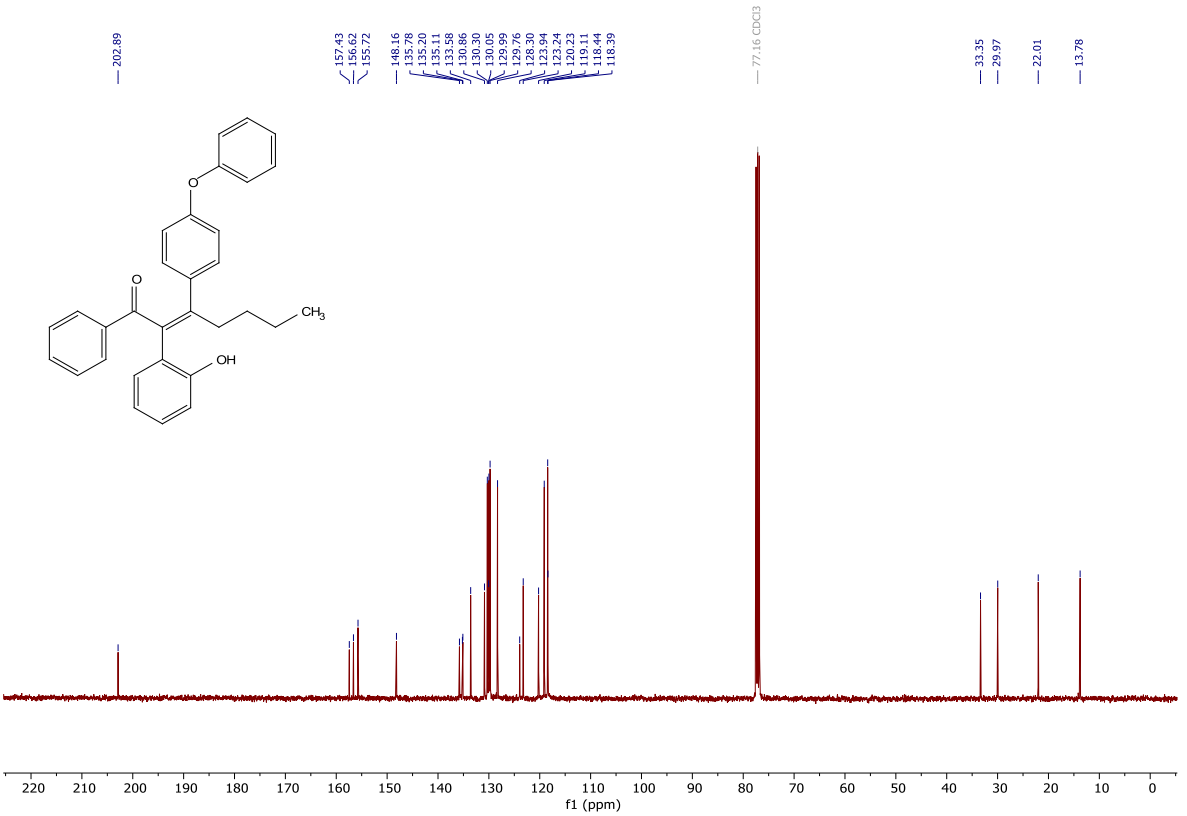


(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)hept-2-en-1-one (3i): ^{19}F Spectra

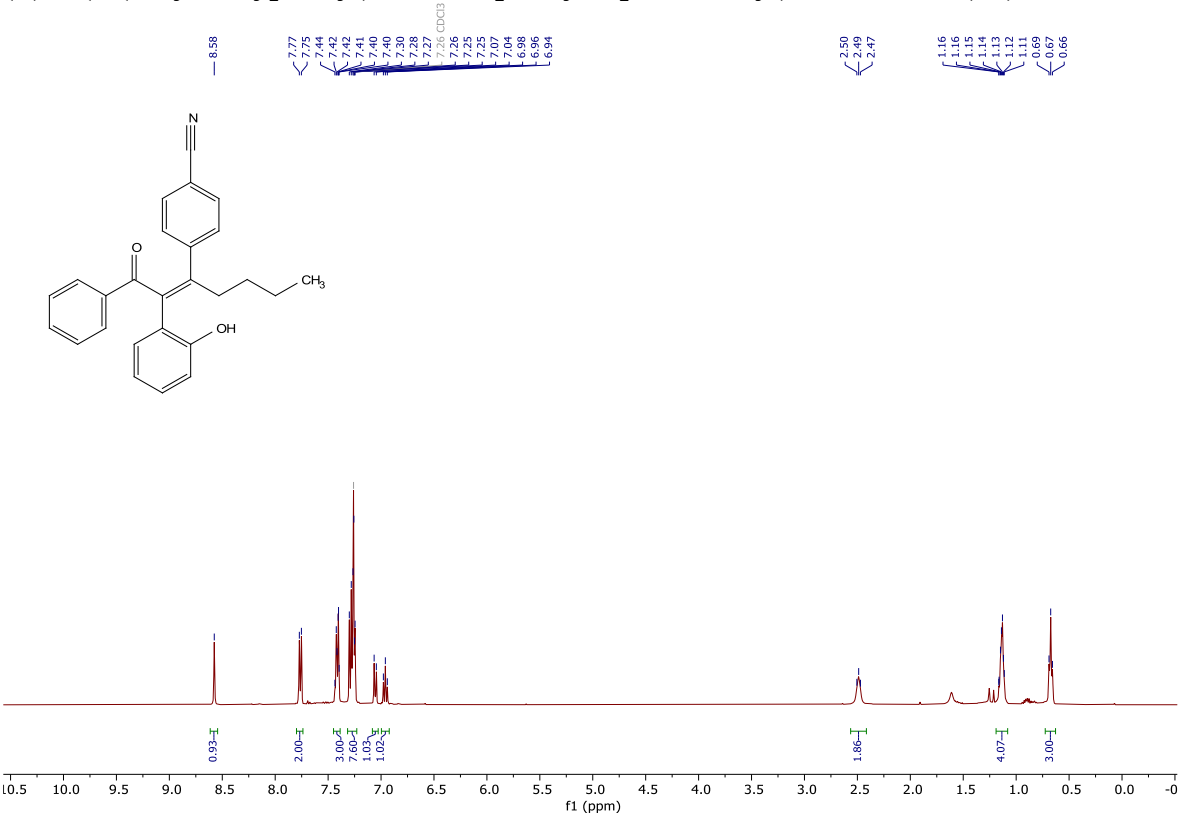


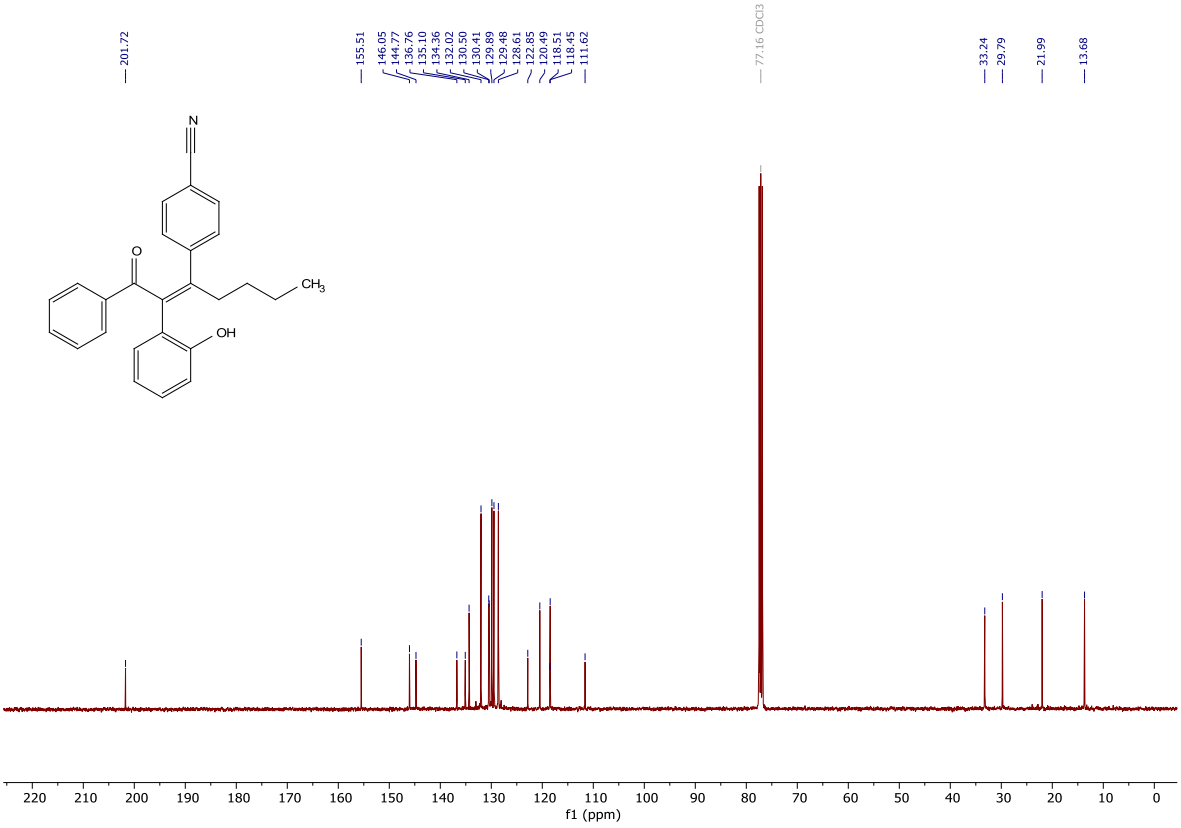
(*Z*)-2-(2-hydroxyphenyl)-3-(4-phenoxyphenyl)-1-phenylhept-2-en-1-one (3j):



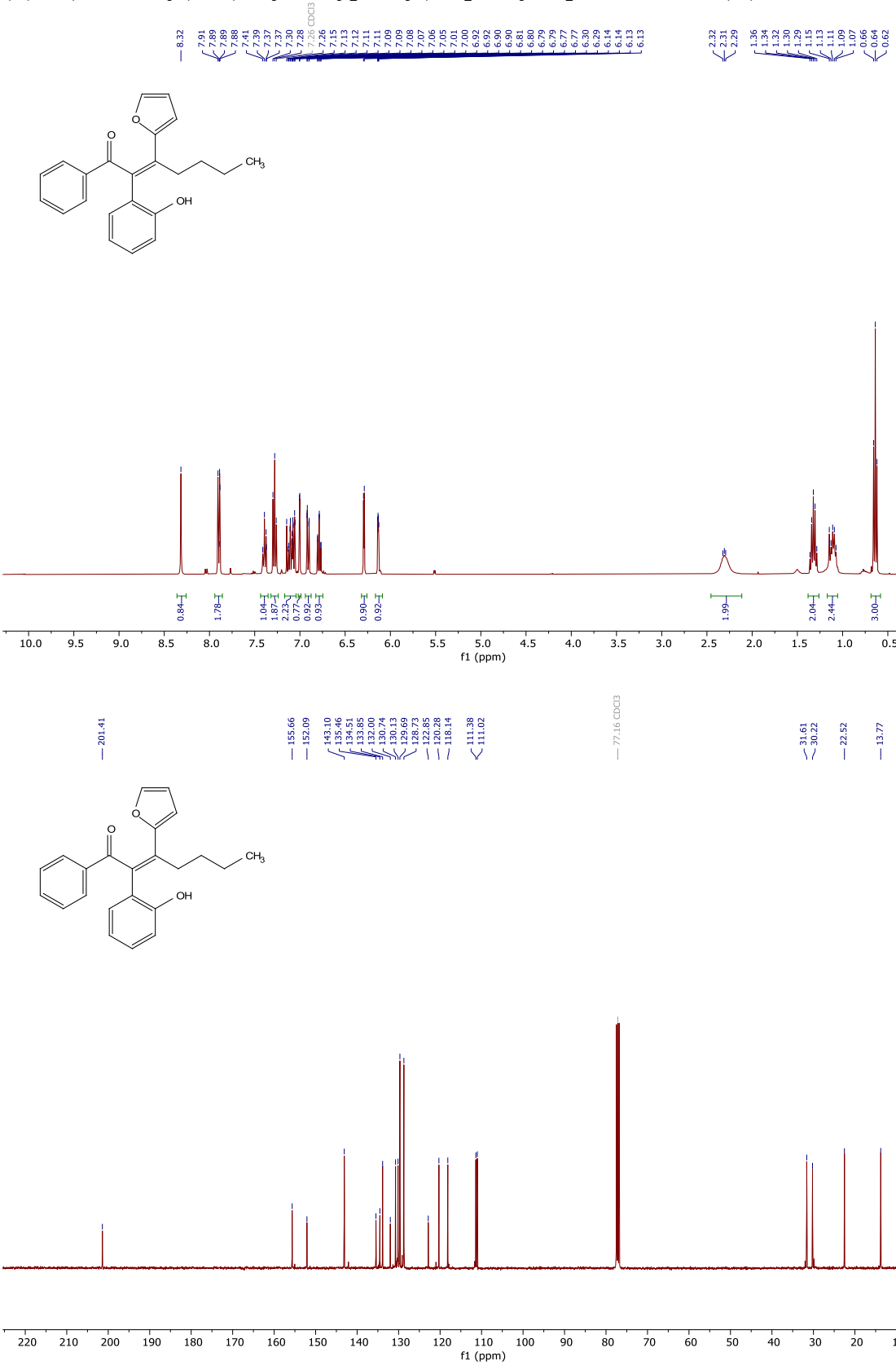


(*Z*)-4-(2-(2-hydroxyphenyl)-1-oxo-1-phenylhept-2-en-3-yl)benzonitrile (3k):

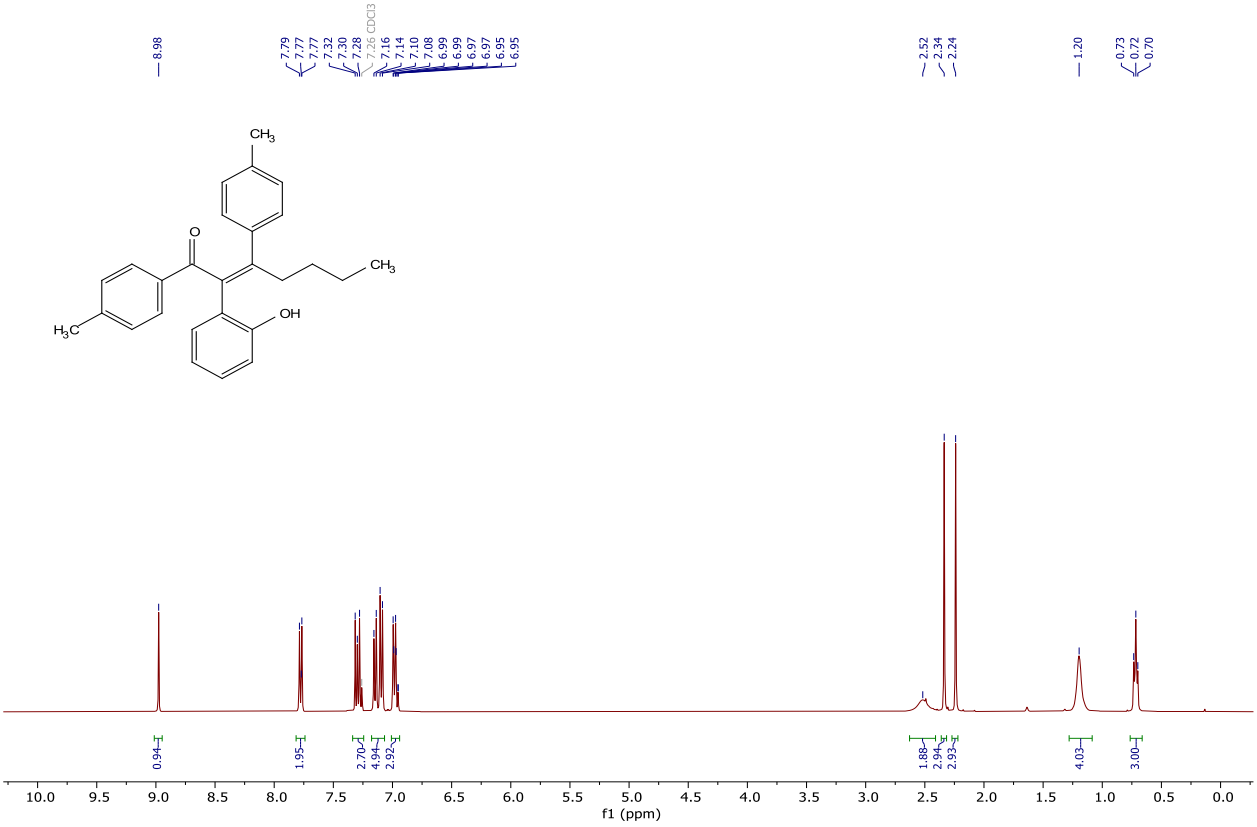


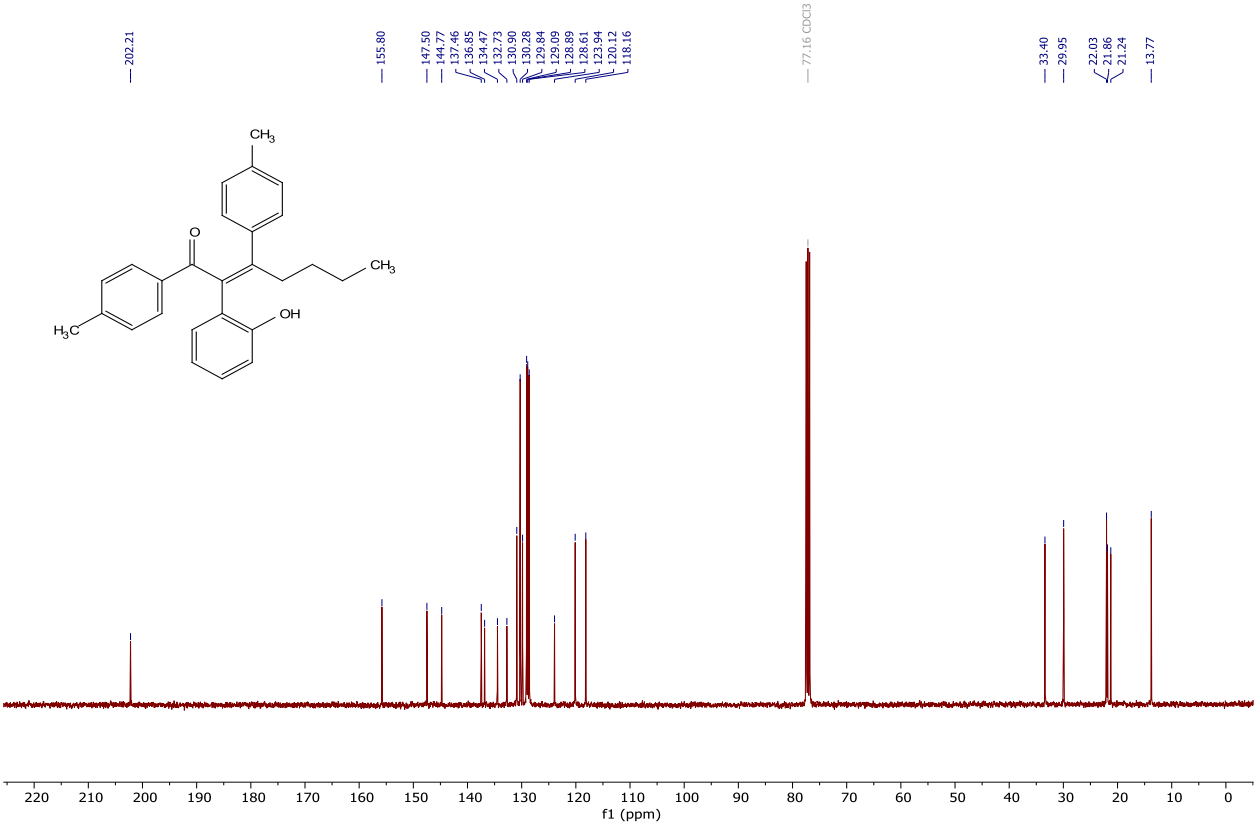


(*Z*)-3-(furan-2-yl)-2-(2-hydroxyphenyl)-1-phenylhept-2-en-1-one (3l):

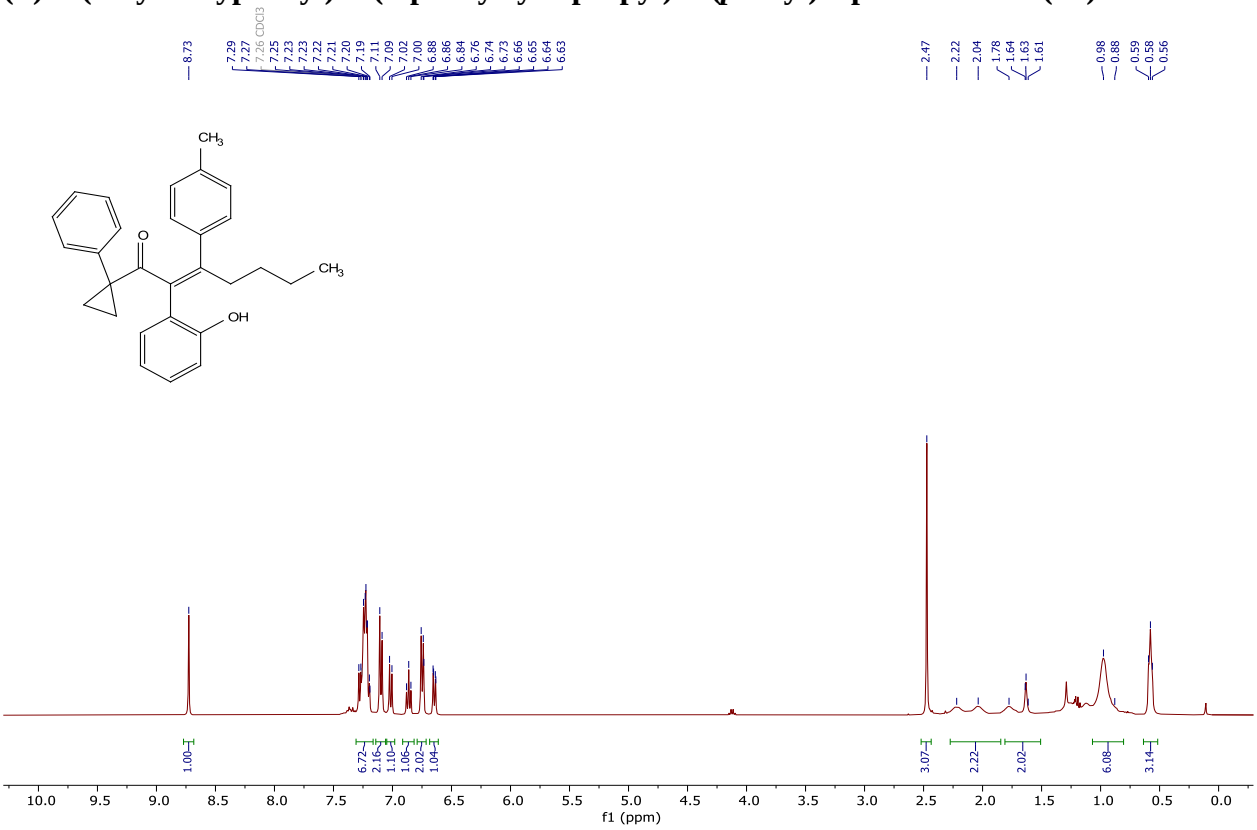


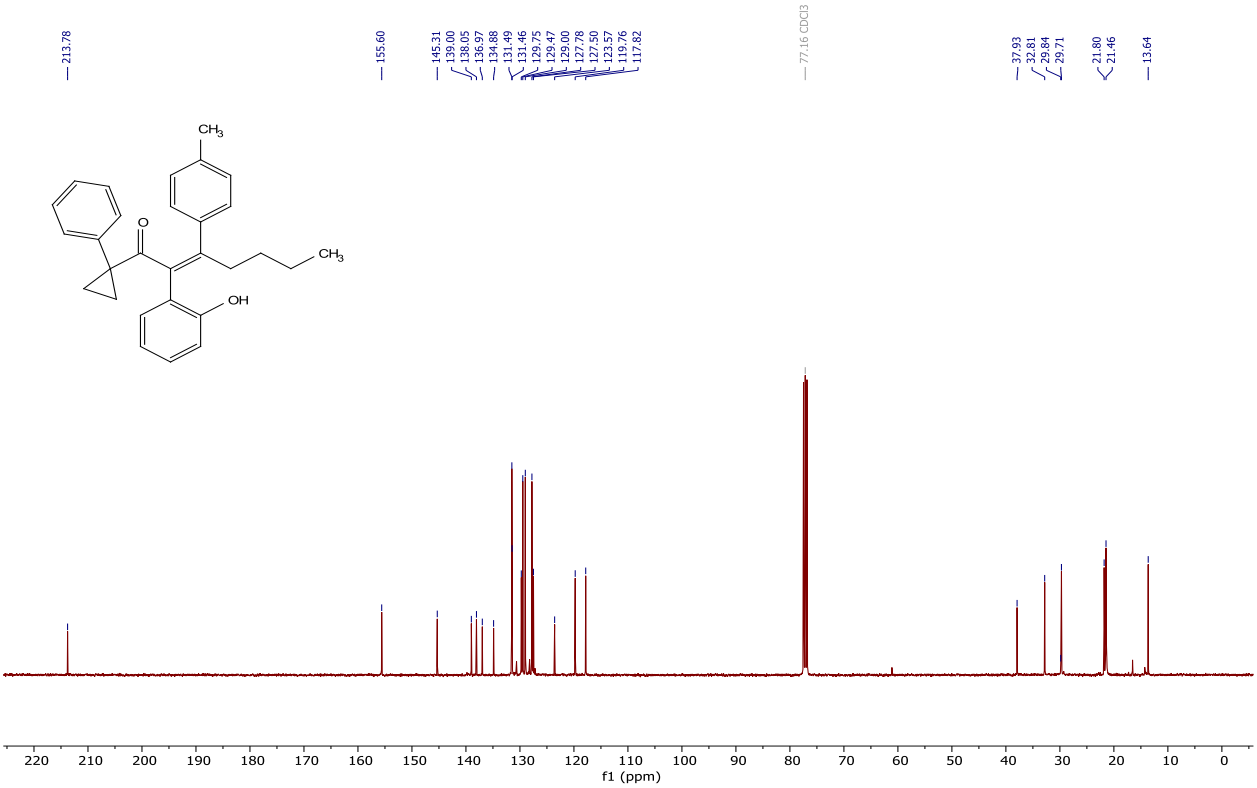
(*Z*)-2-(2-hydroxyphenyl)-1,3-di-*p*-tolylhept-2-en-1-one (3m):



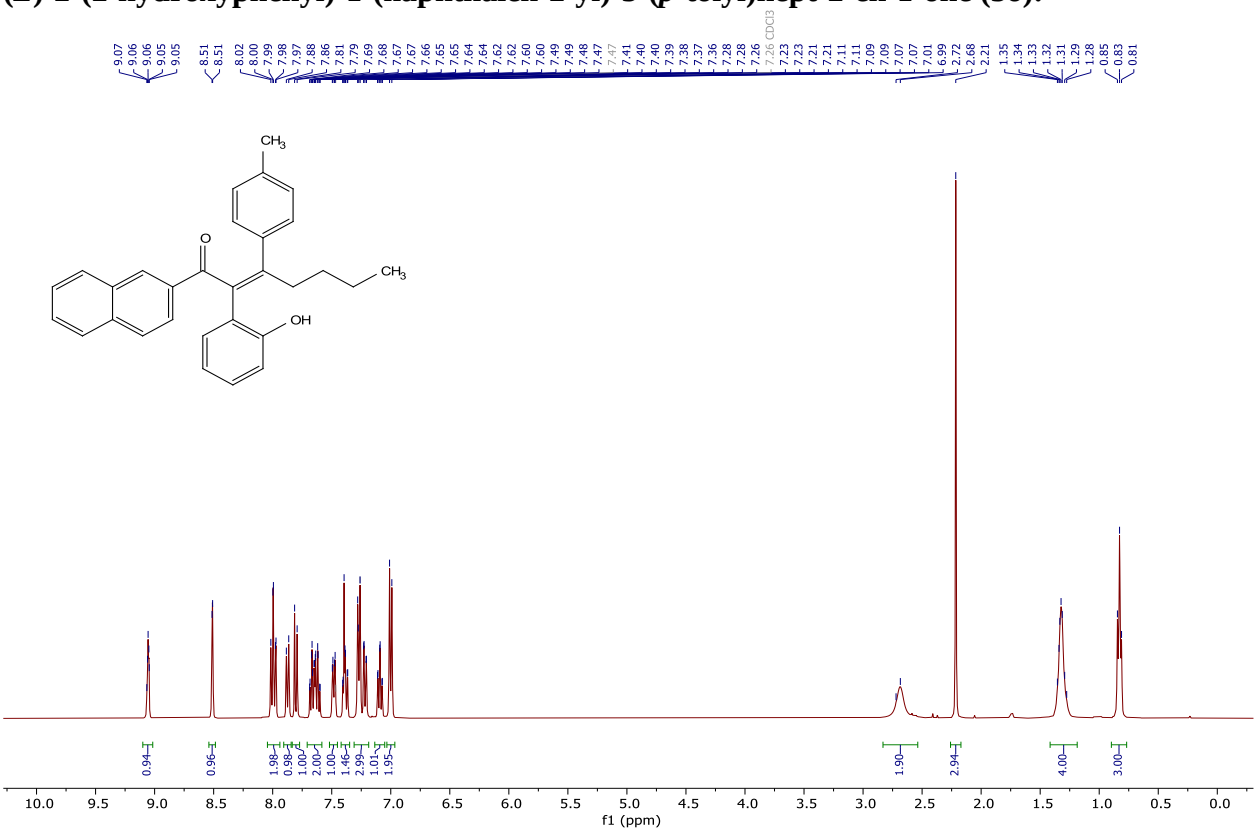


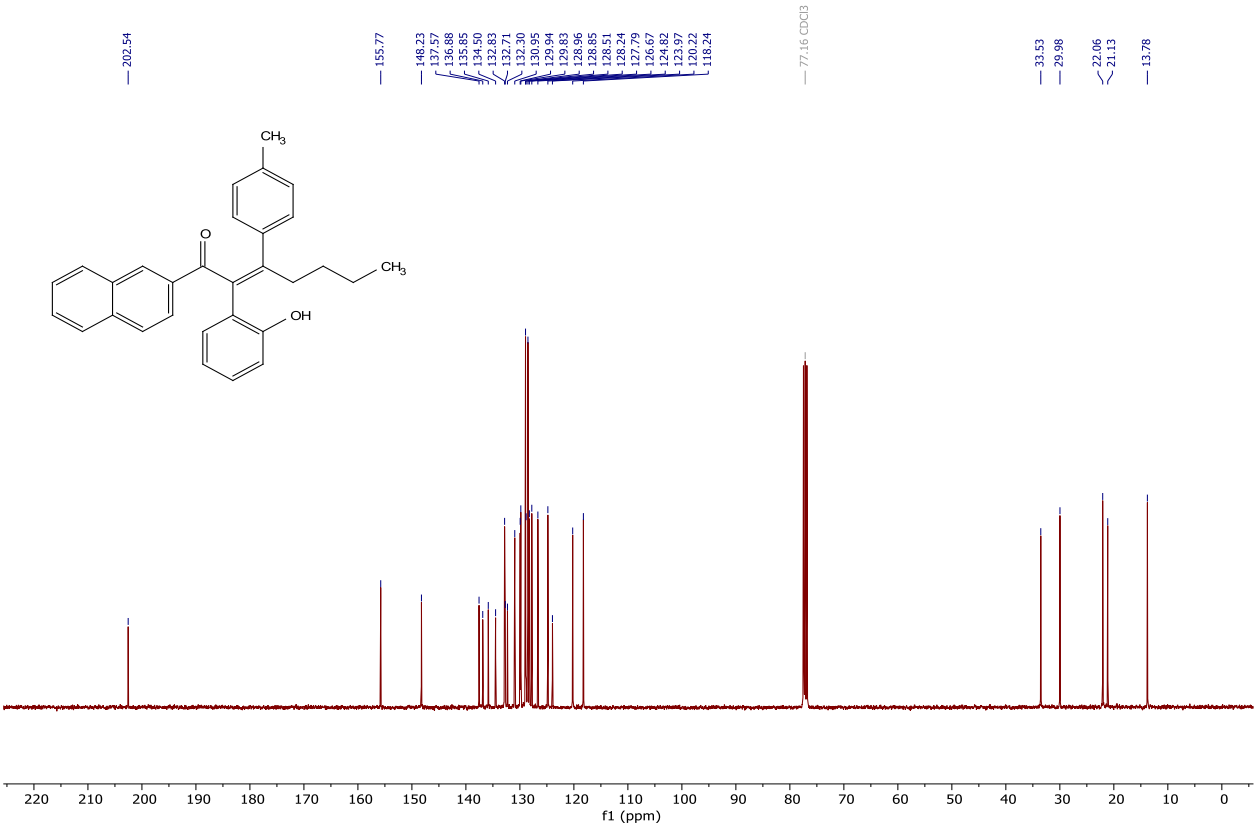
(*Z*)-2-(2-hydroxyphenyl)-1-(1-phenylcyclopropyl)-3-(*p*-tolyl)hept-2-en-1-one (3n):



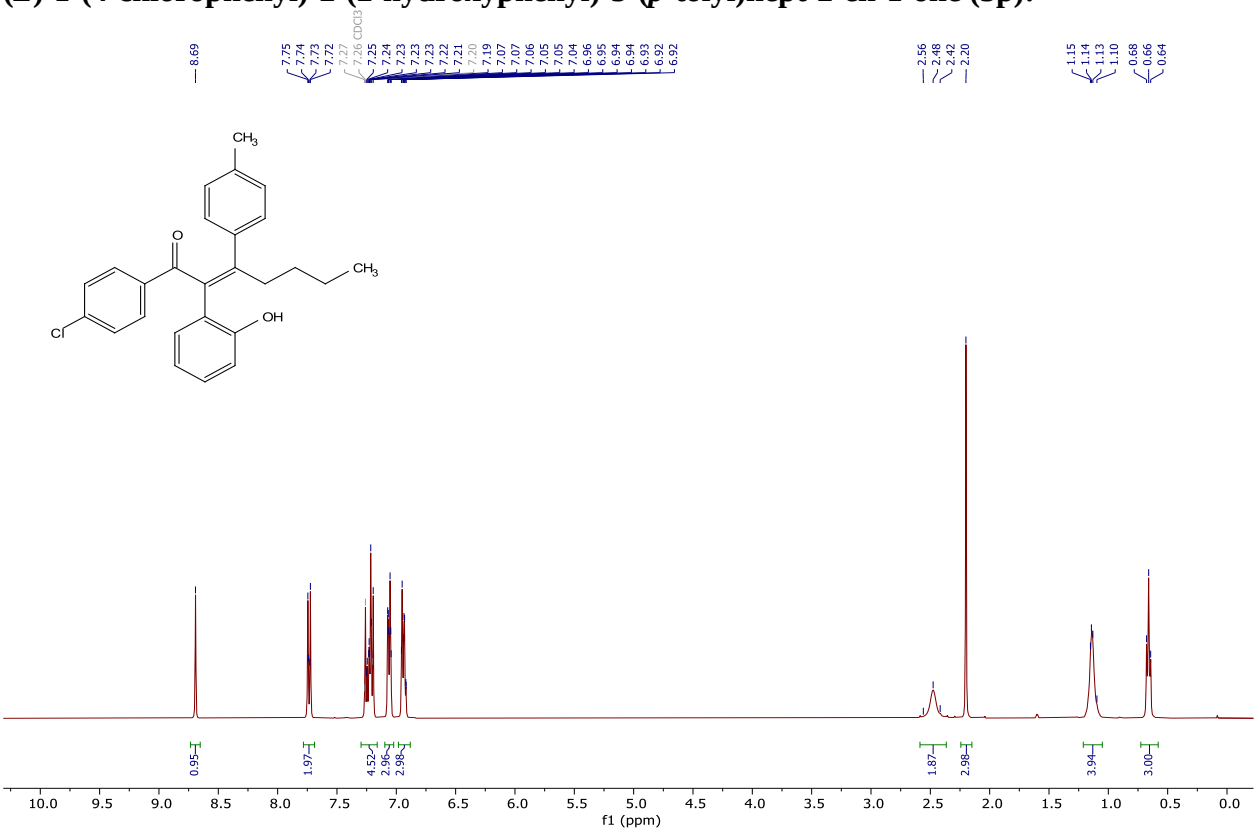


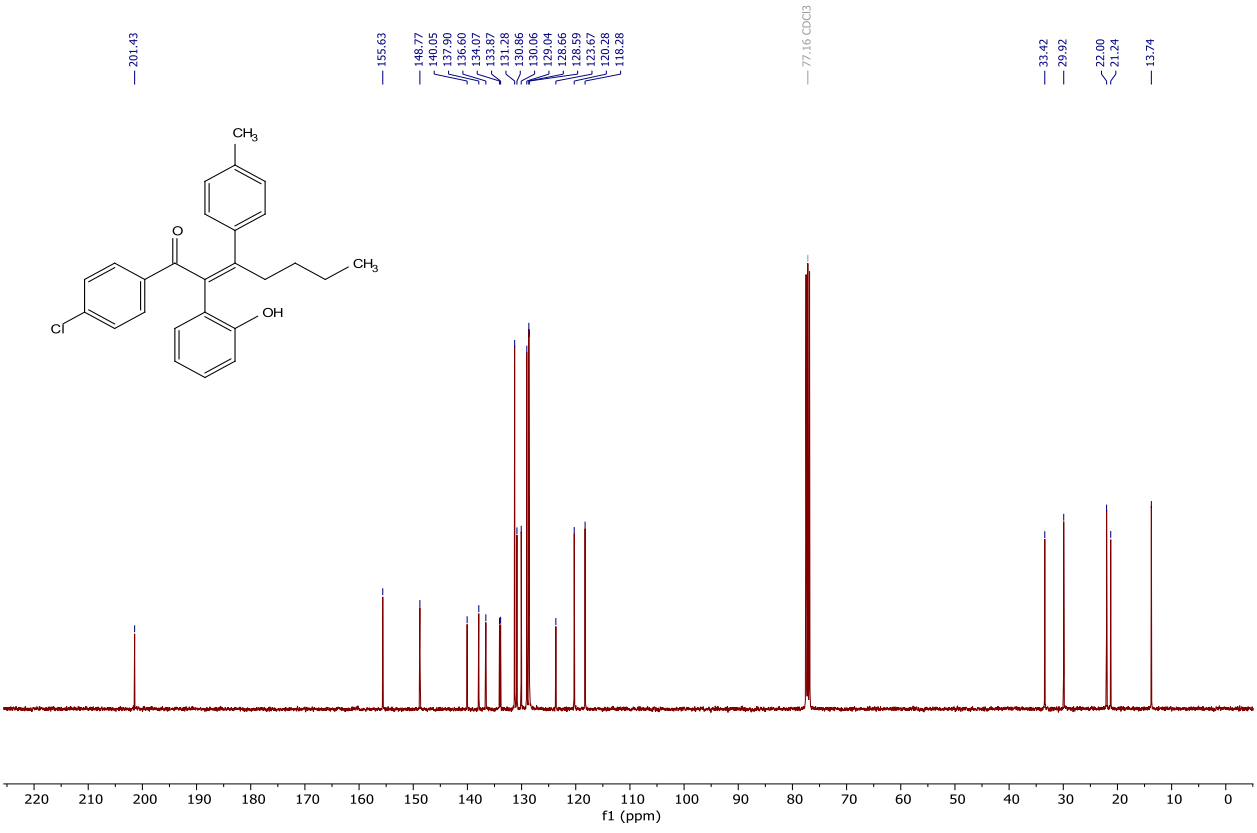
(*Z*)-2-(2-hydroxyphenyl)-1-(naphthalen-2-yl)-3-(*p*-tolyl)hept-2-en-1-one (3o):



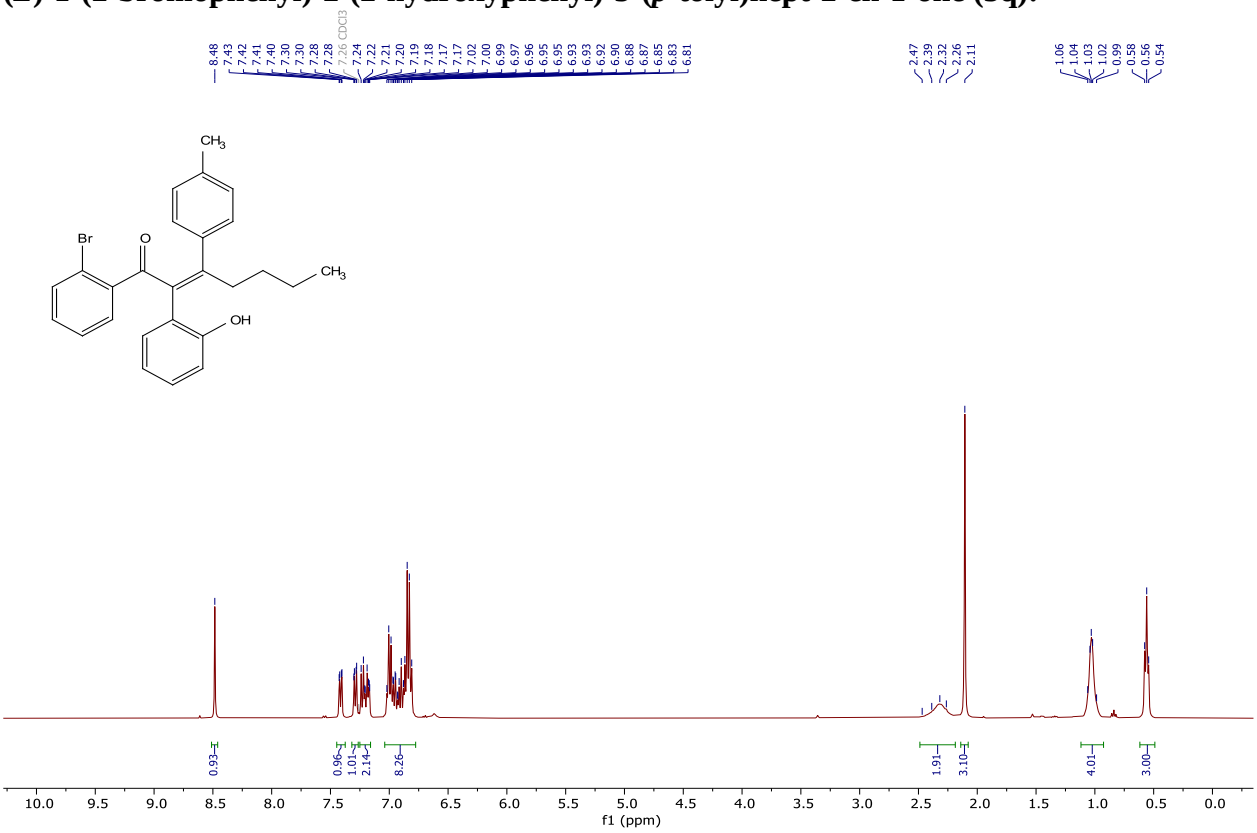


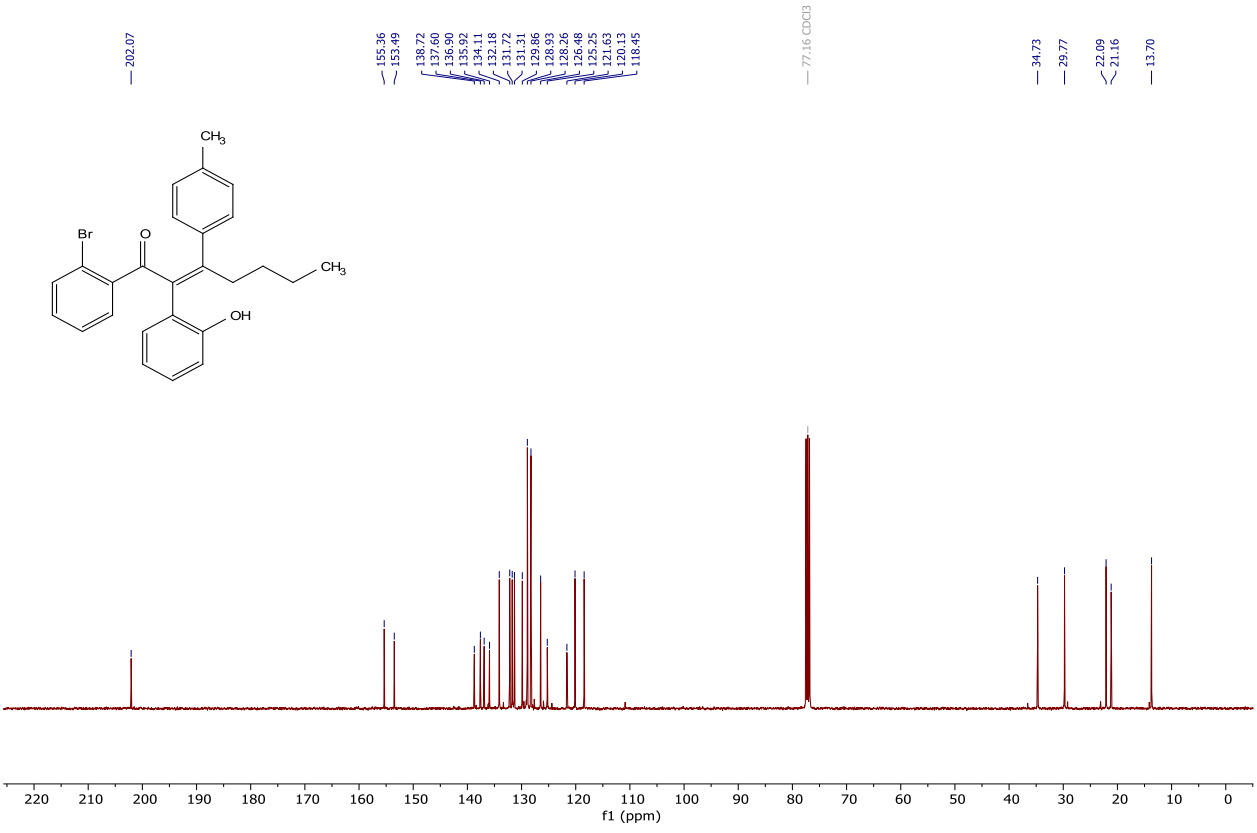
(*Z*)-1-(4-chlorophenyl)-2-(2-hydroxyphenyl)-3-(*p*-tolyl)hept-2-en-1-one (3p):



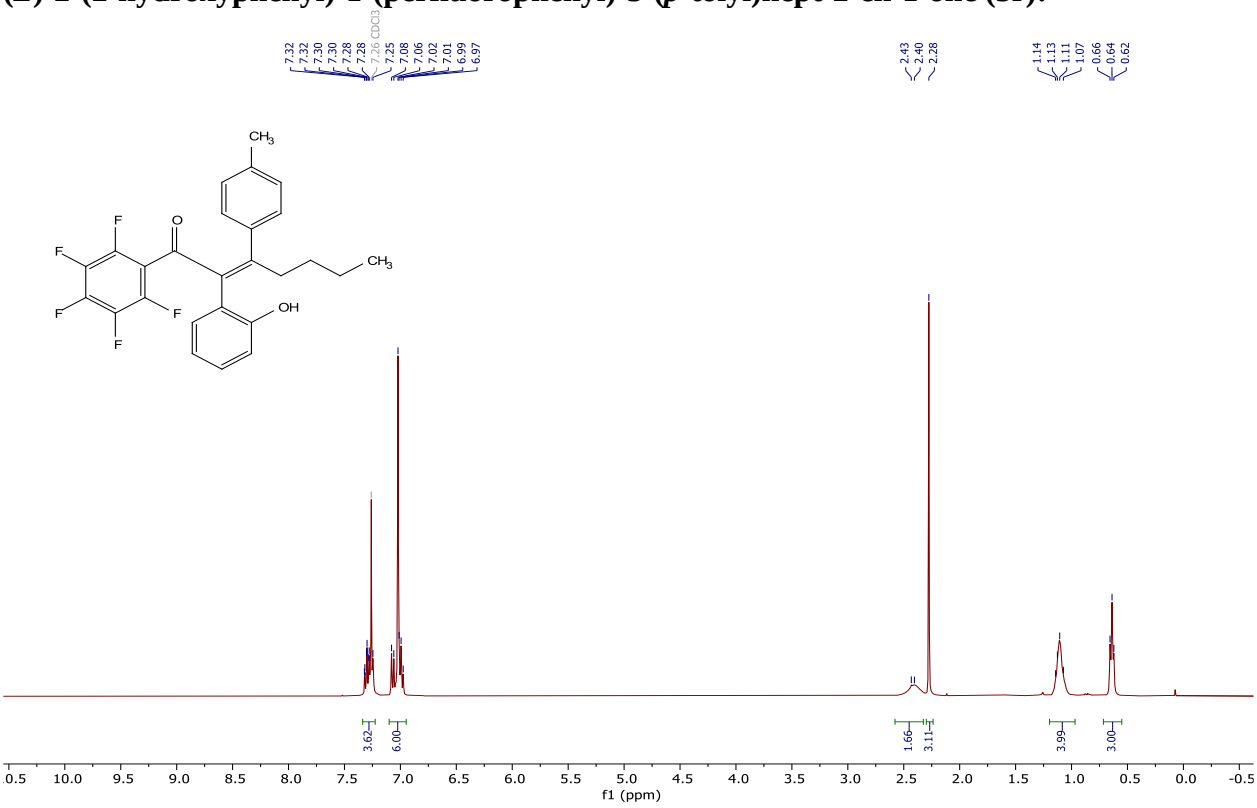


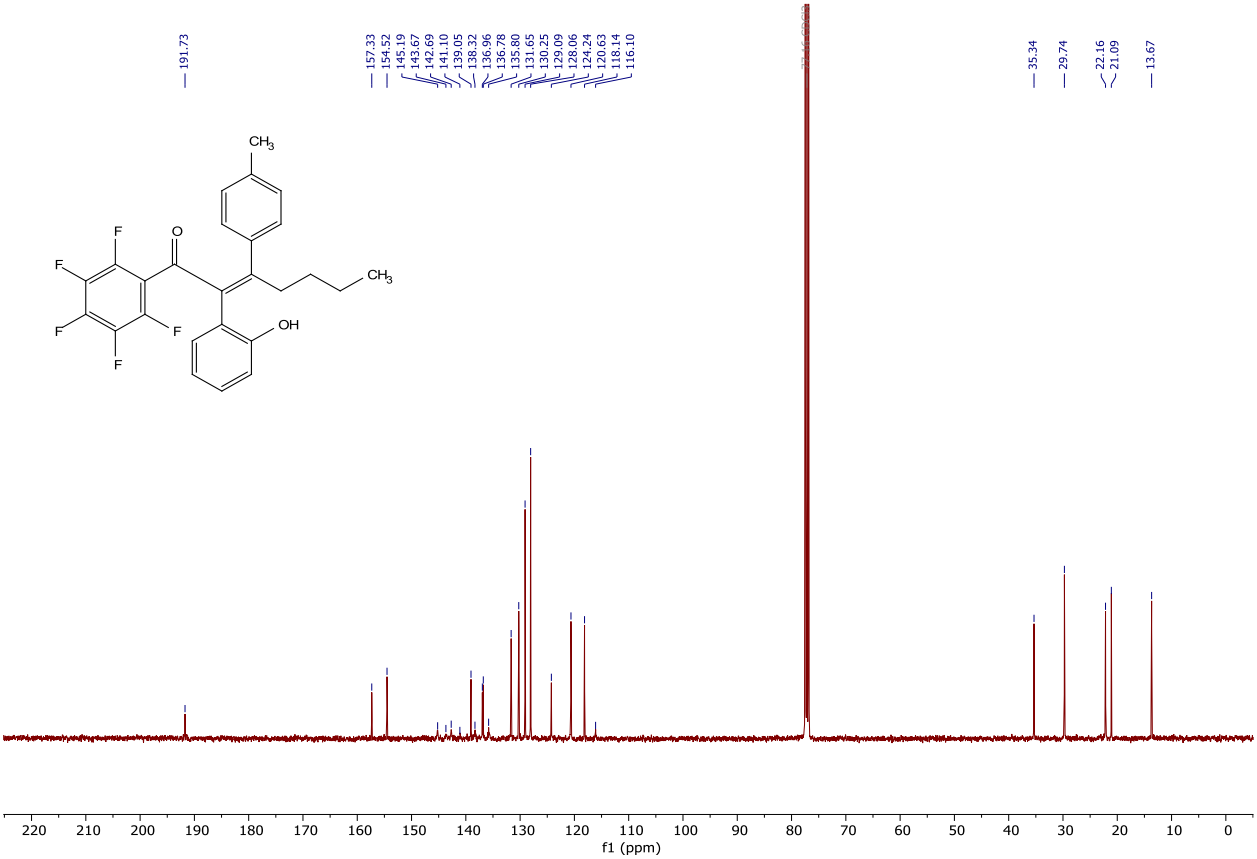
(*Z*)-1-(2-bromophenyl)-2-(2-hydroxyphenyl)-3-(*p*-tolyl)hept-2-en-1-one (3q):



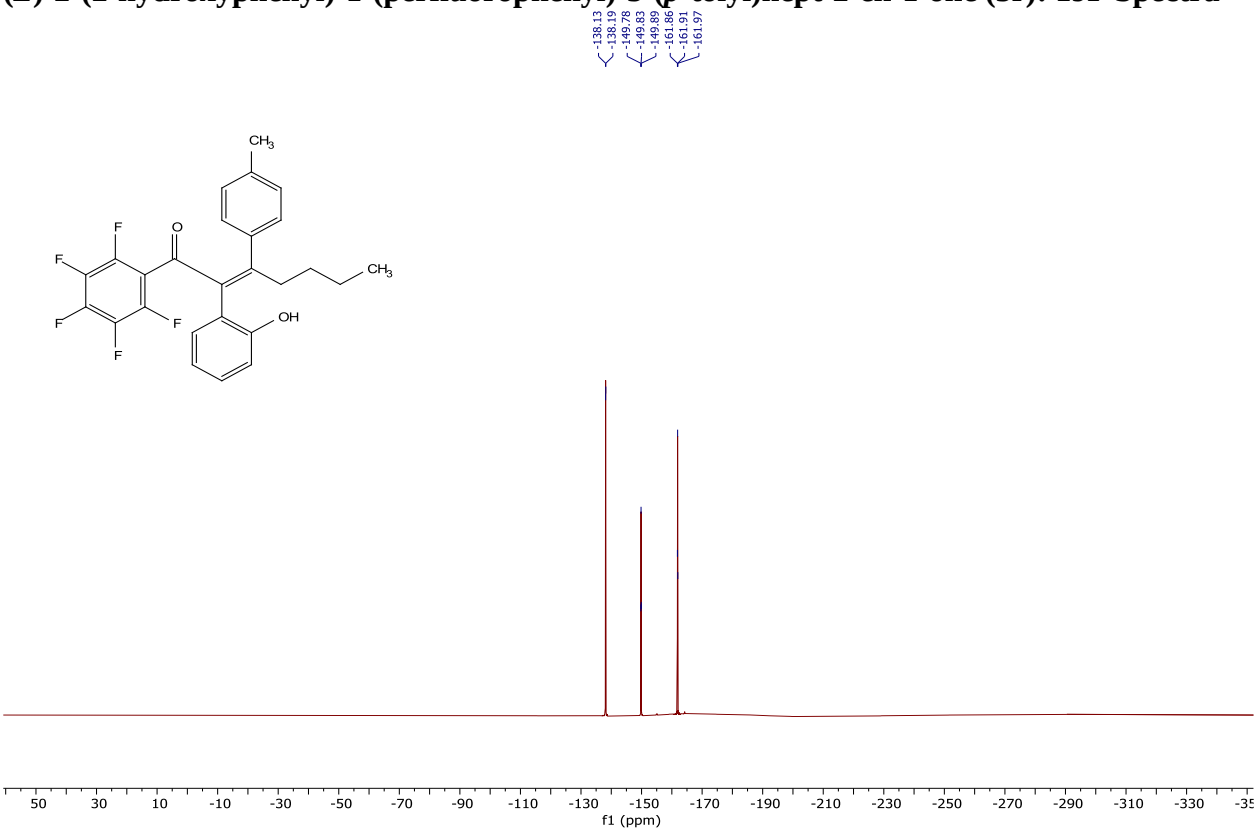


(*Z*)-2-(2-hydroxyphenyl)-1-(perfluorophenyl)-3-(*p*-tolyl)hept-2-en-1-one (3r):

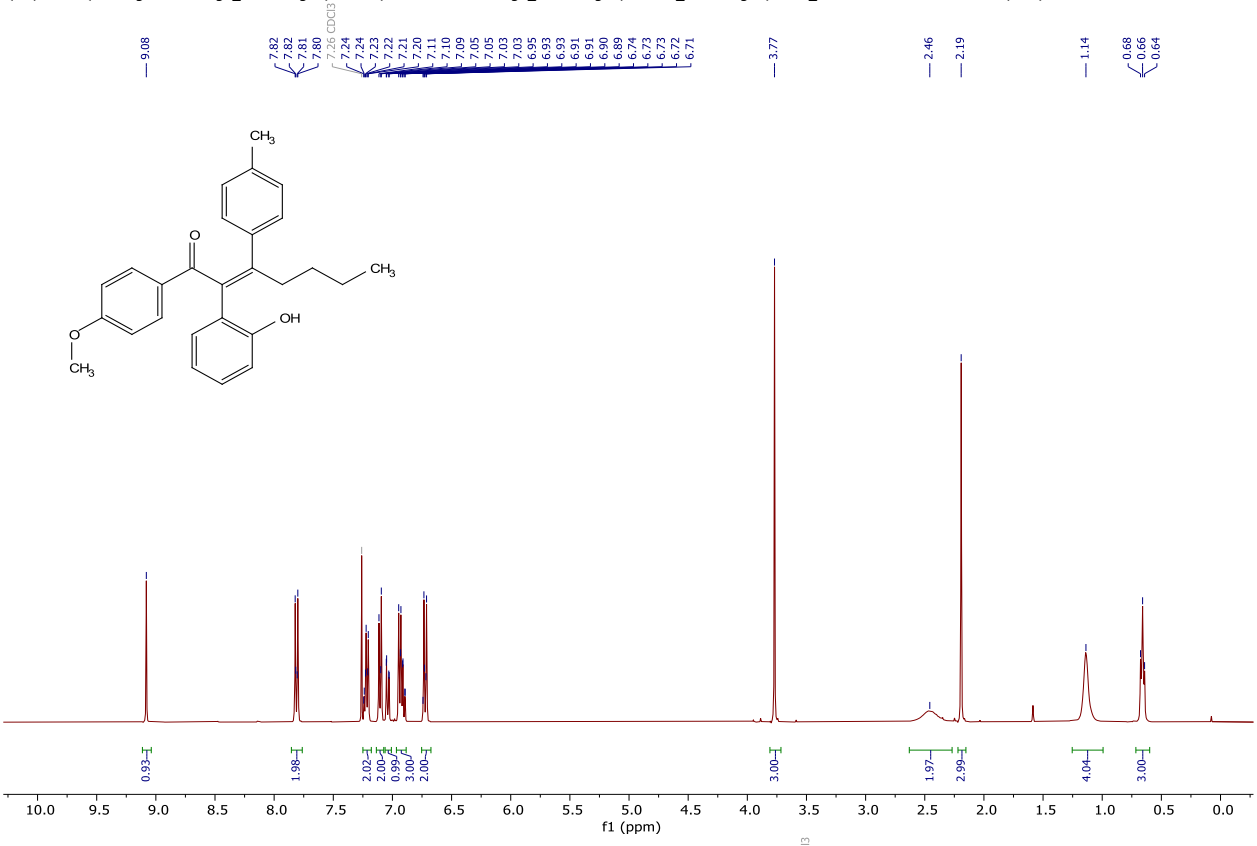


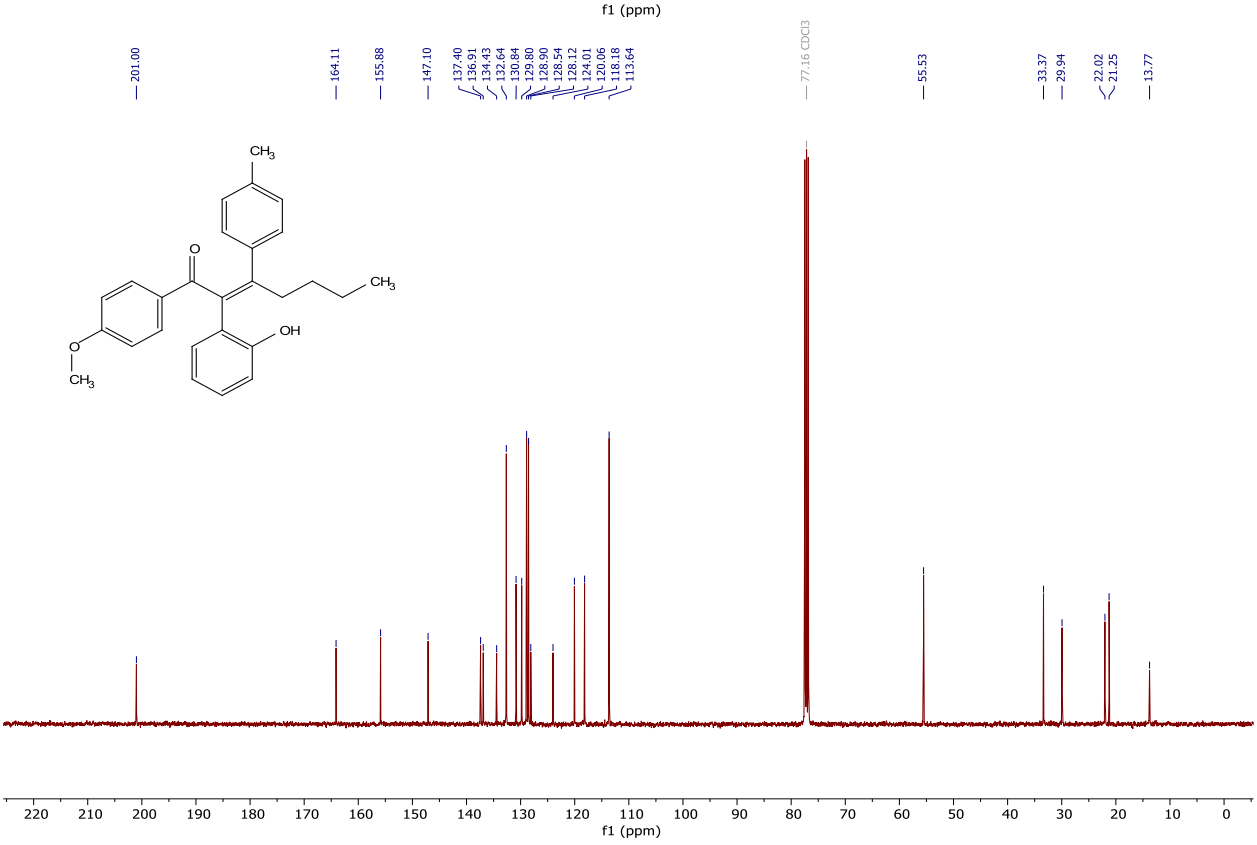


(*Z*)-2-(2-hydroxyphenyl)-1-(perfluorophenyl)-3-(*p*-tolyl)hept-2-en-1-one (3r): 19F Spectra

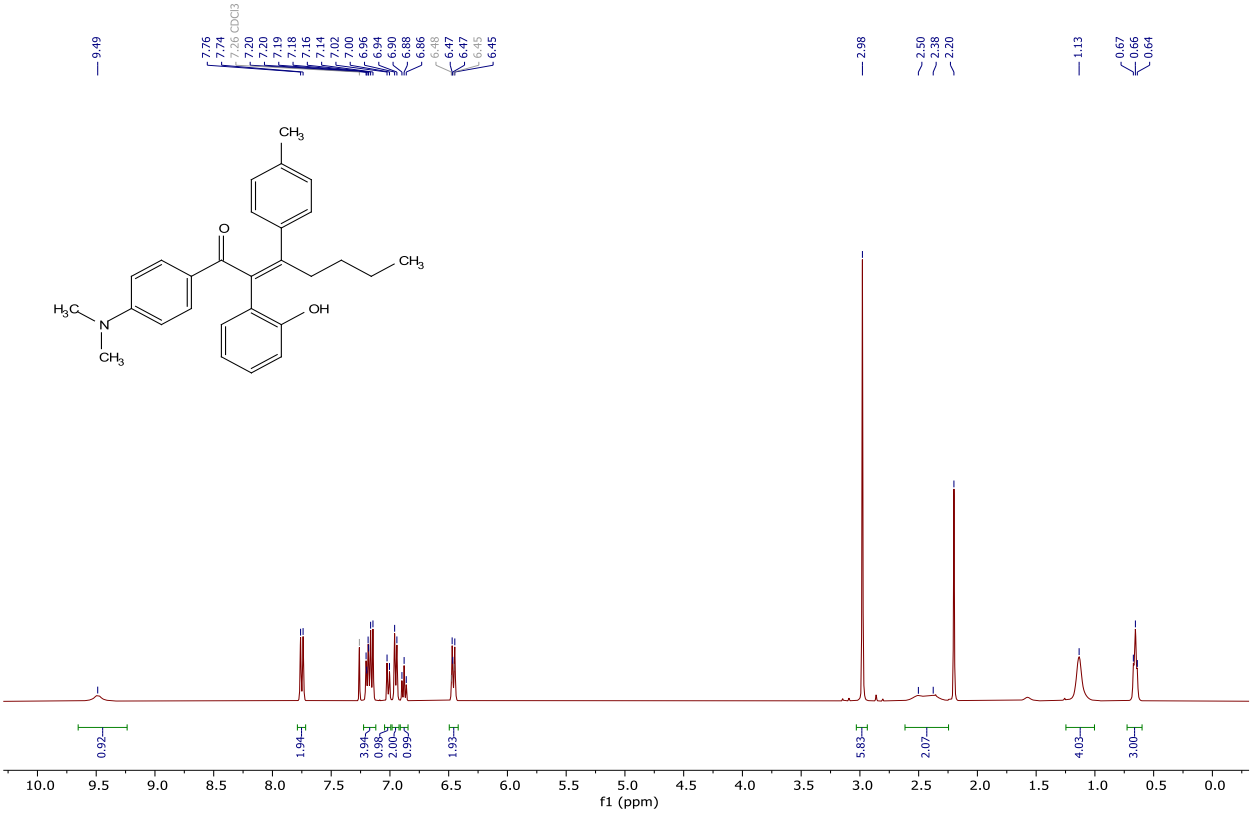


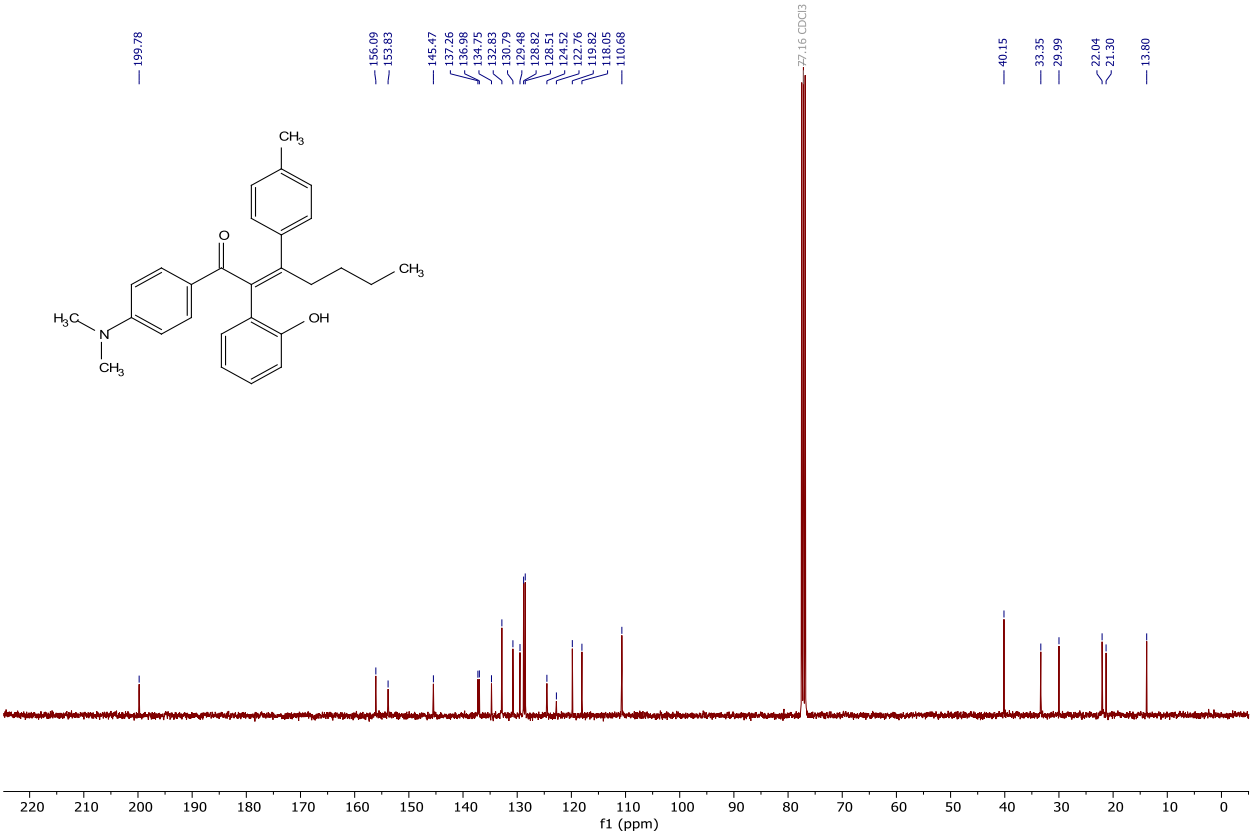
(*Z*)-2-(2-hydroxyphenyl)-1-(4-methoxyphenyl)-3-(*p*-tolyl)hept-2-en-1-one (3s):



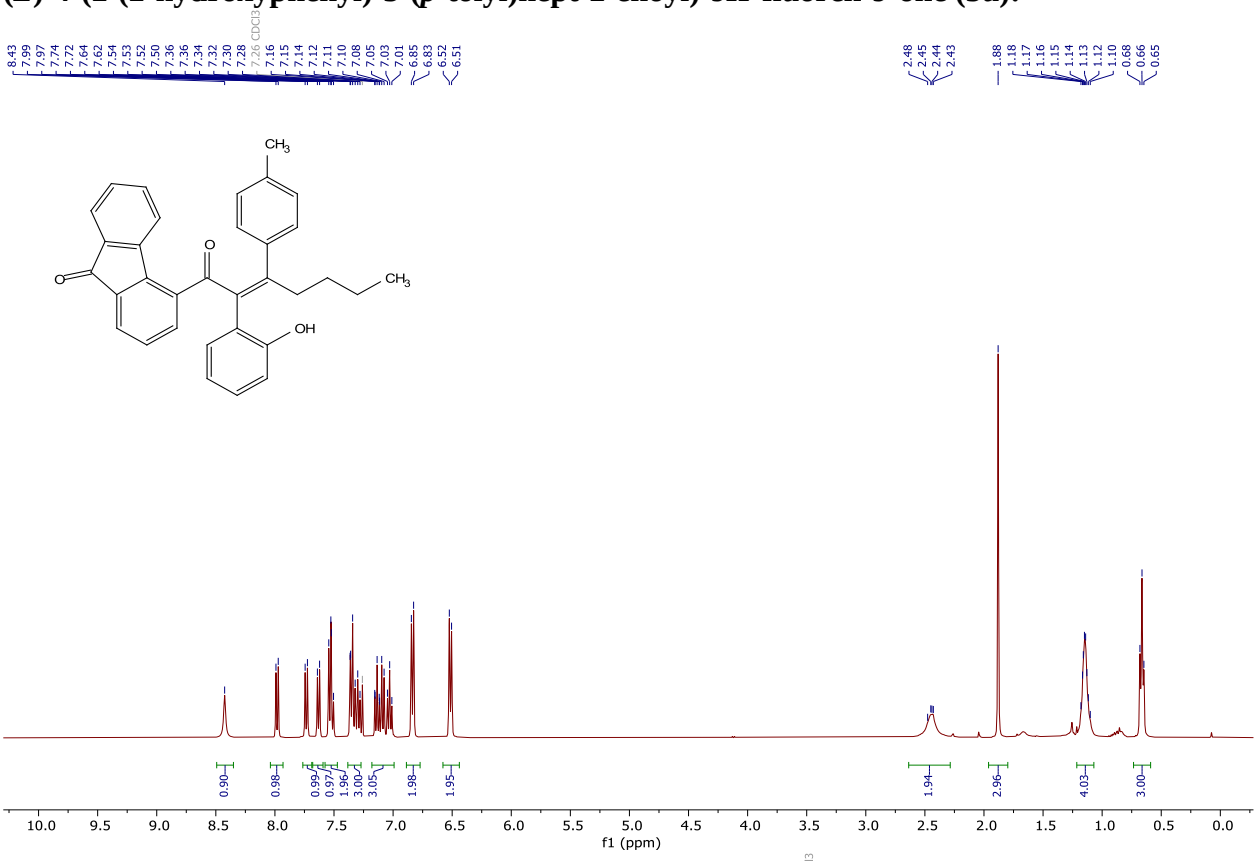


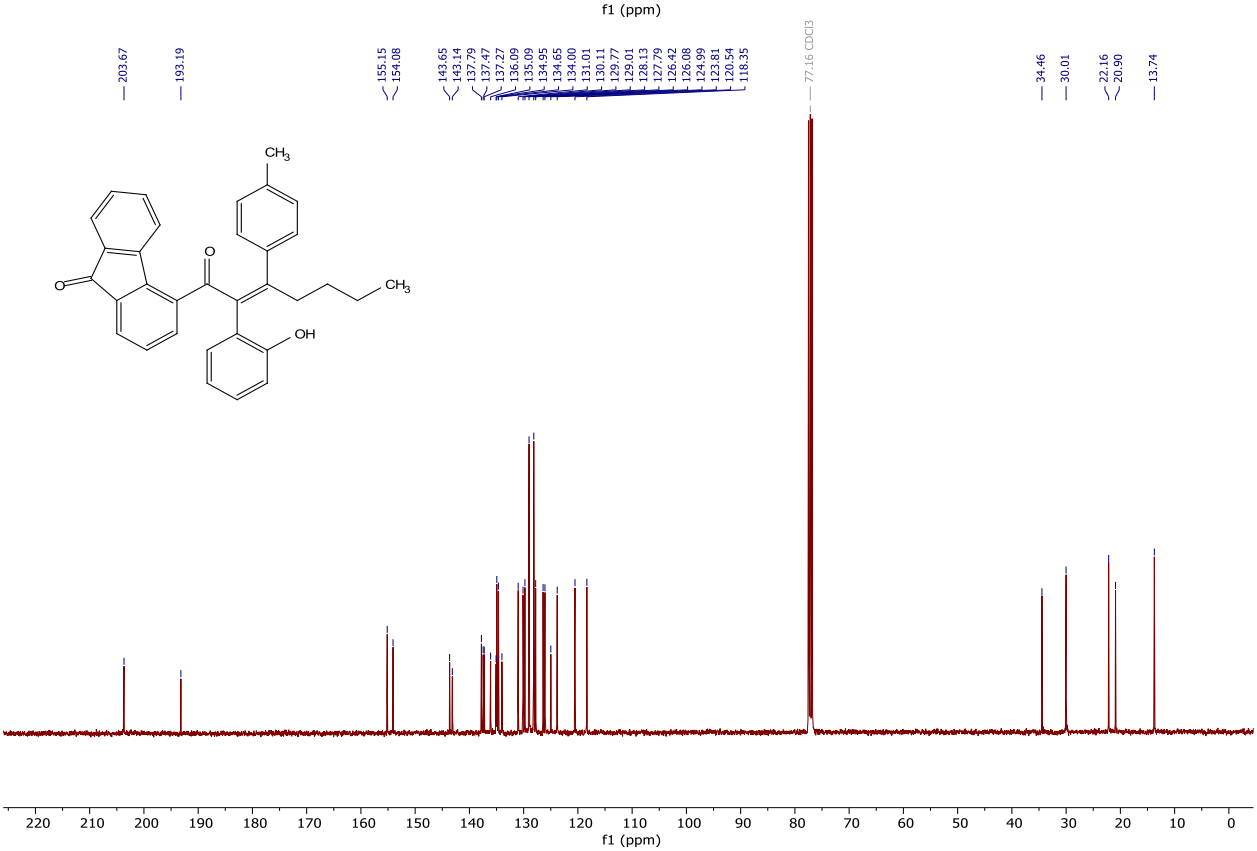
(*Z*)-1-(4-(dimethylamino)phenyl)-2-(2-hydroxyphenyl)-3-(*p*-tolyl)hept-2-en-1-one (3t):



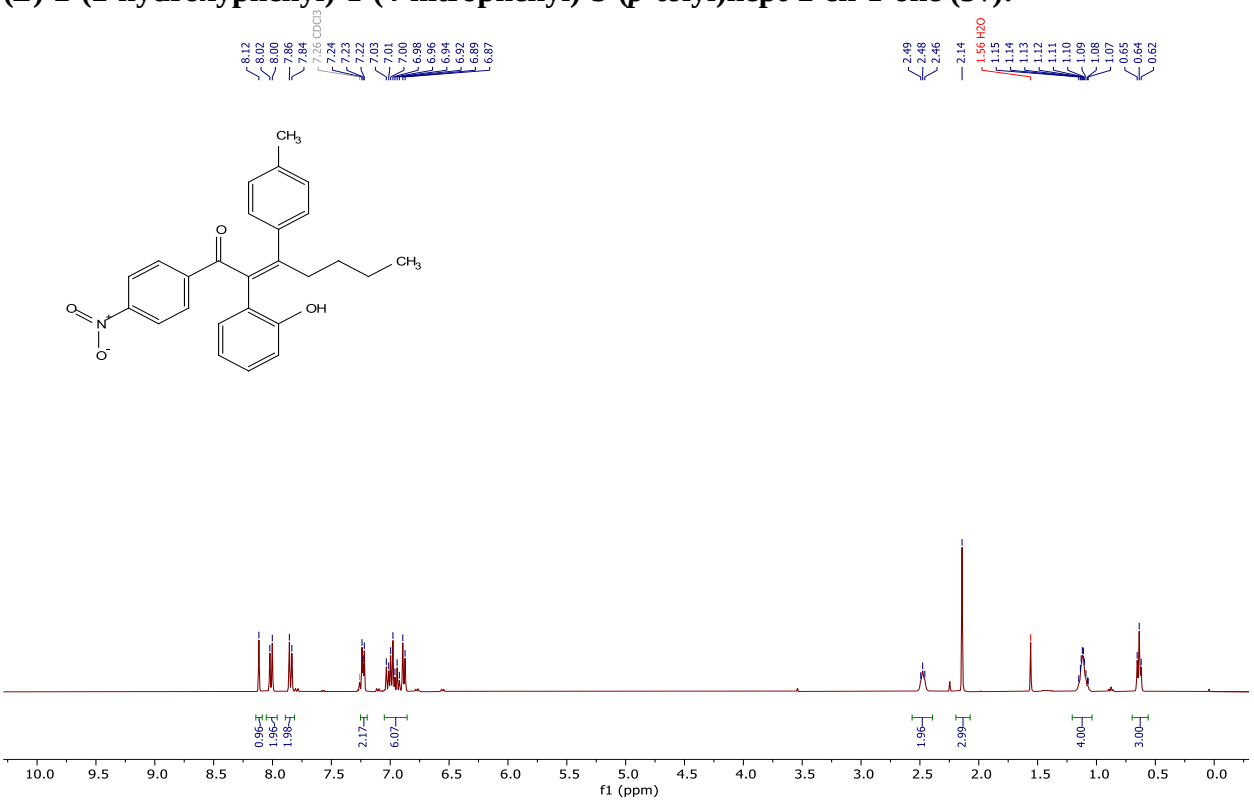


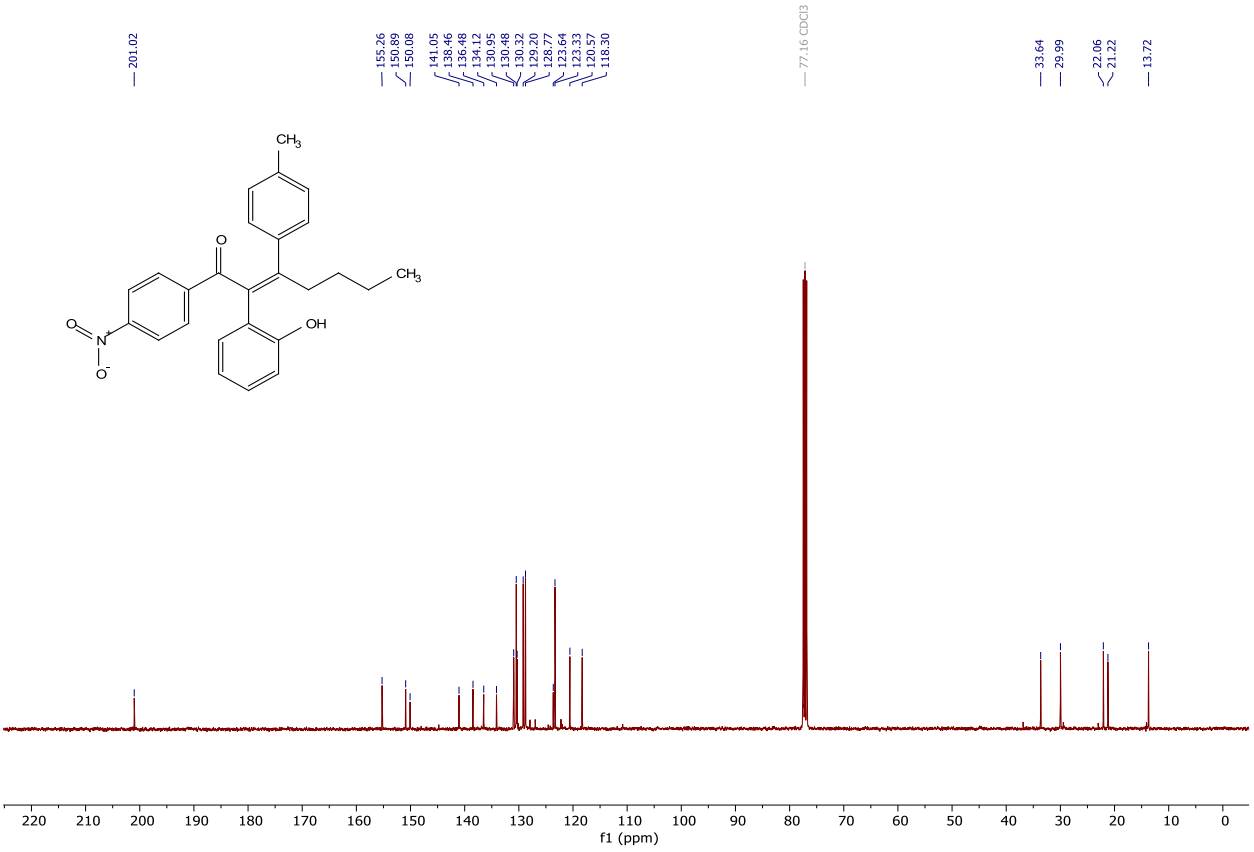
(*Z*)-4-(2-(2-hydroxyphenyl)-3-(*p*-tolyl)hept-2-enoyl)-9*H*-fluoren-9-one (3u):



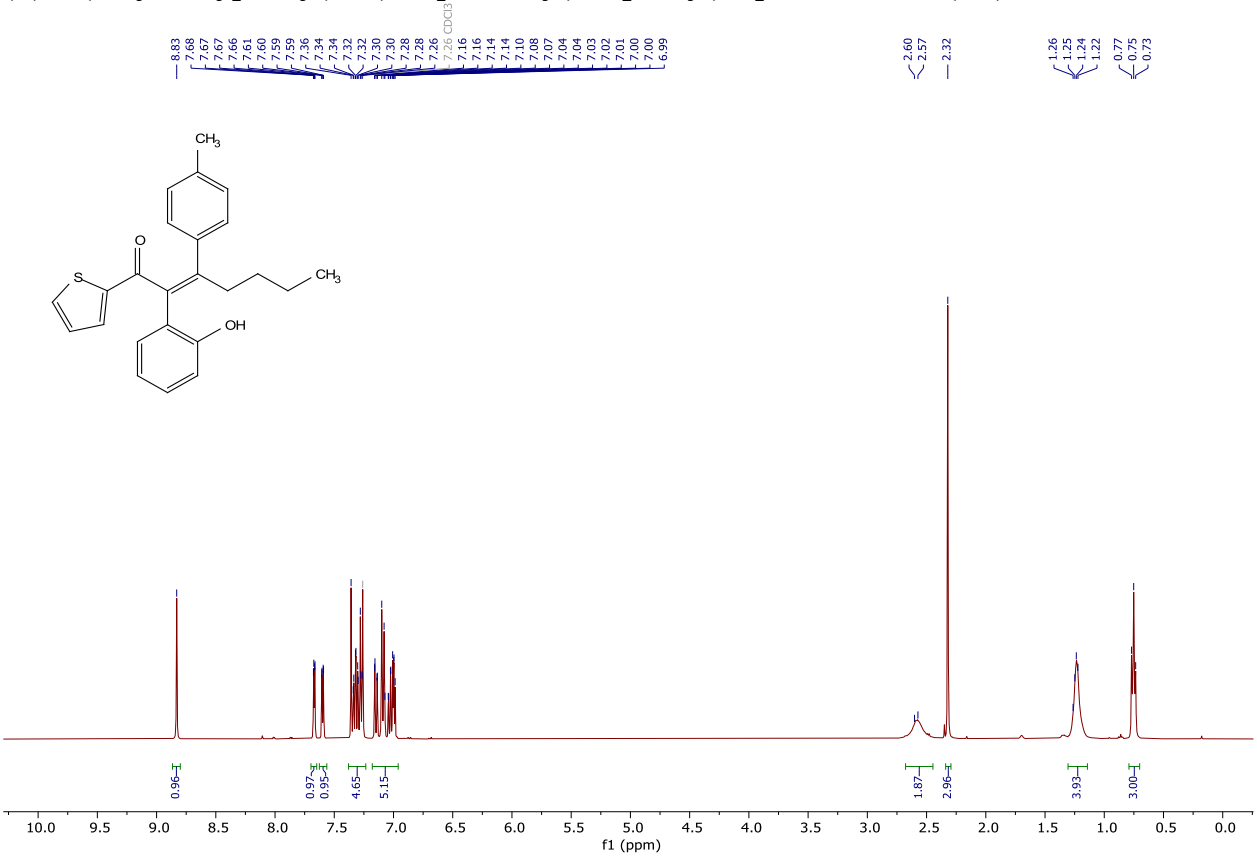


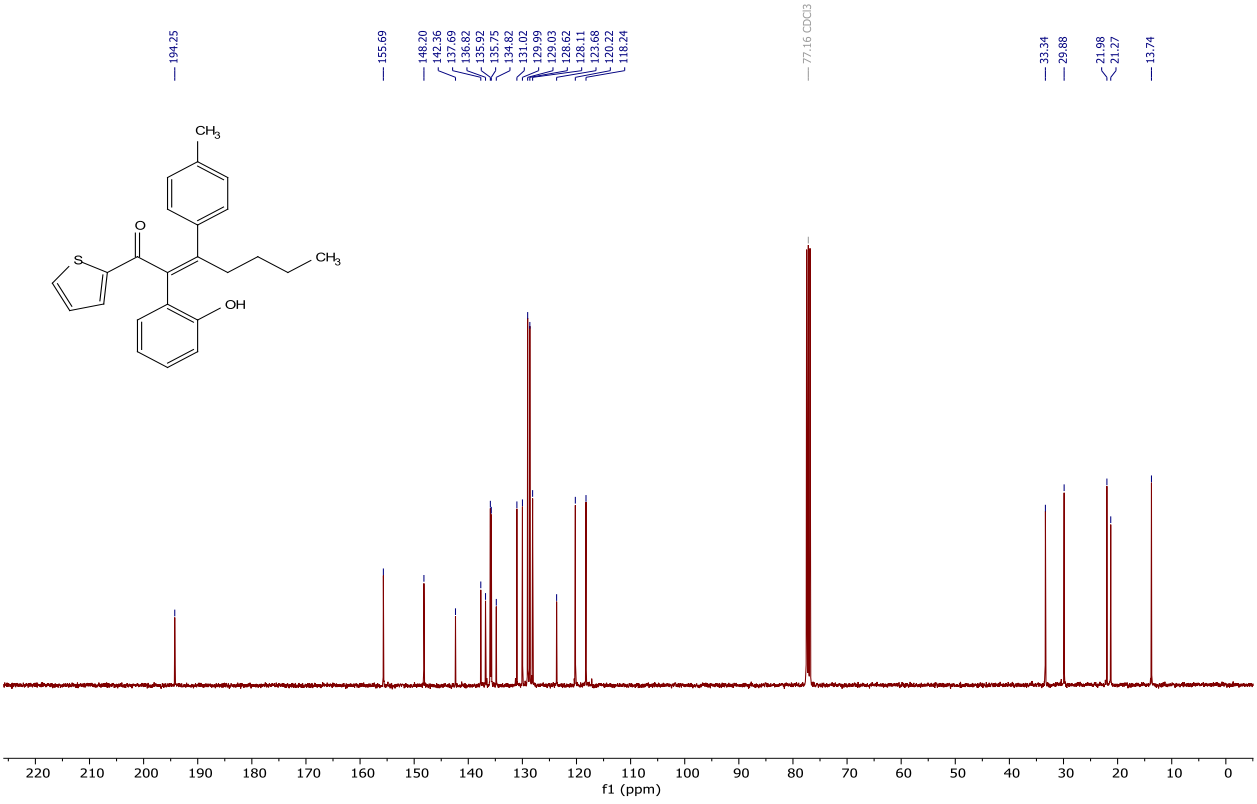
(*Z*)-2-(2-hydroxyphenyl)-1-(4-nitrophenyl)-3-(*p*-tolyl)hept-2-en-1-one (3v):



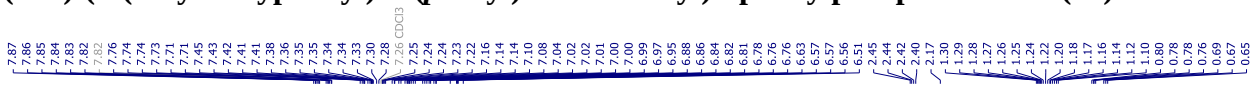


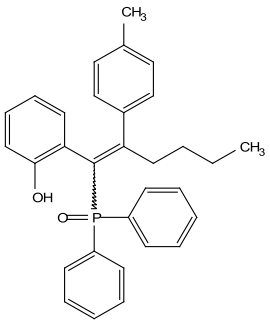
(*Z*)-2-(2-hydroxyphenyl)-1-(thiophen-2-yl)-3-(*p*-tolyl)hept-2-en-1-one (3w):

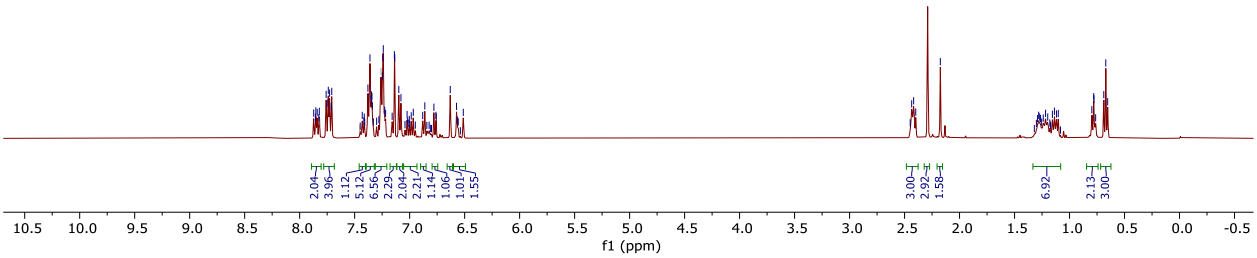


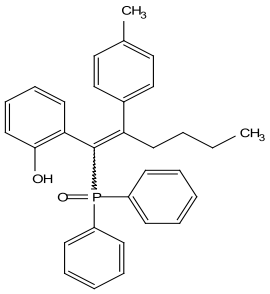


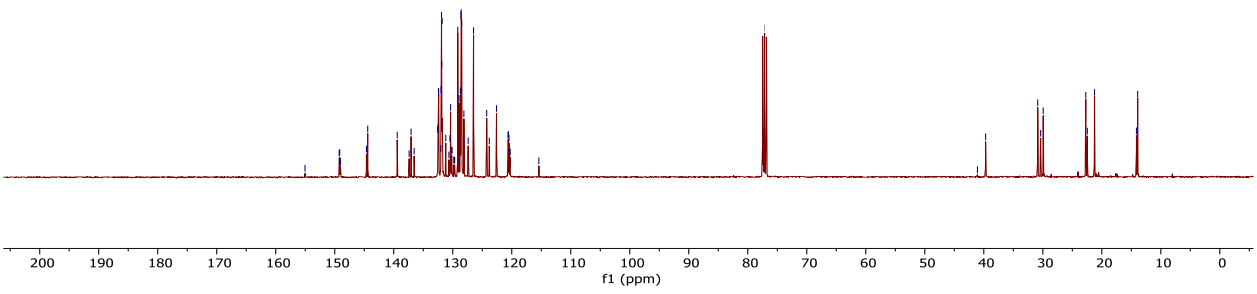
(*E*/*Z*)-(1-(2-hydroxyphenyl)-2-(*p*-tolyl)hex-1-en-1-yl)diphenylphosphine oxide (3x):



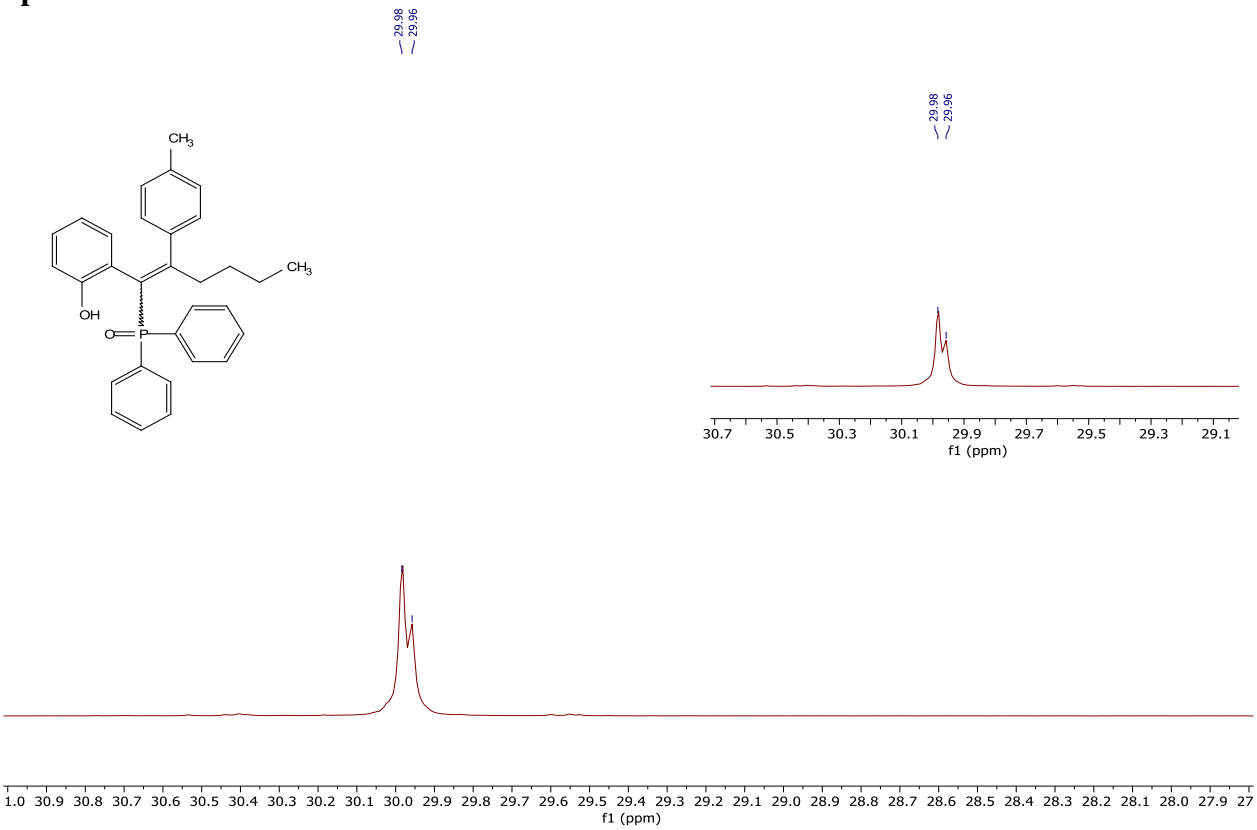




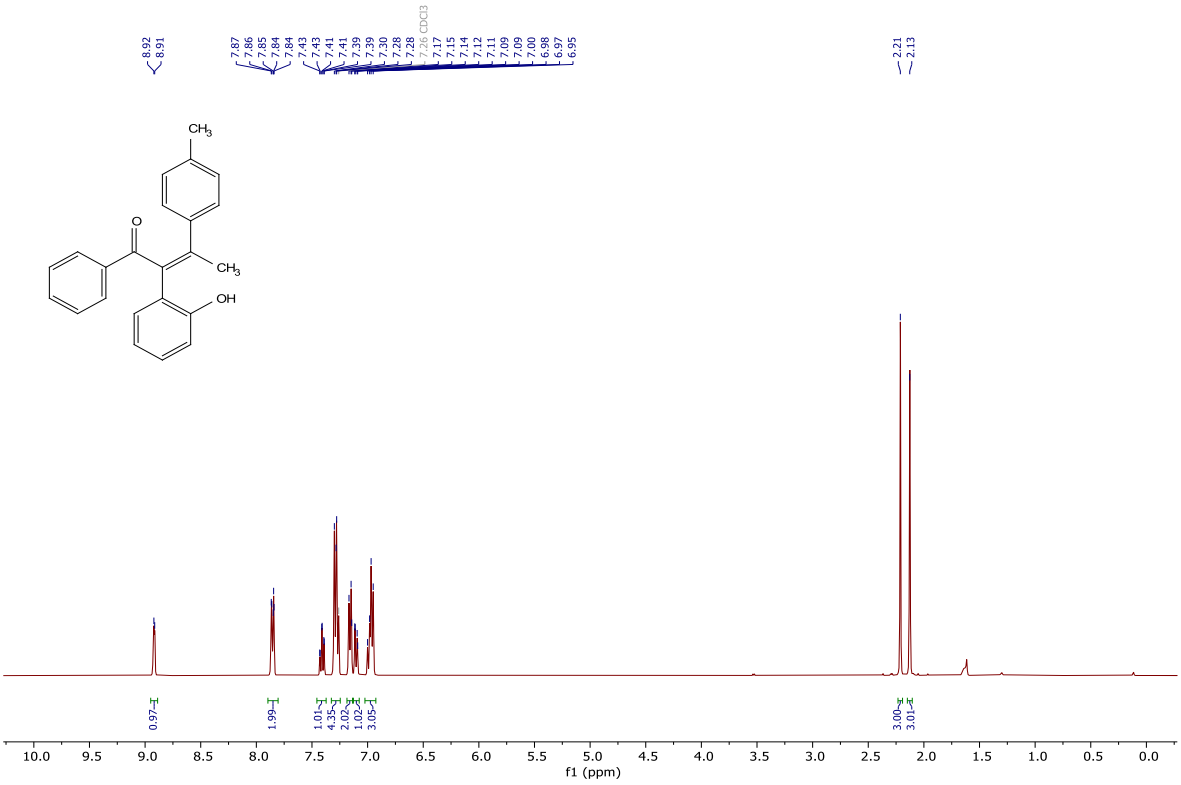




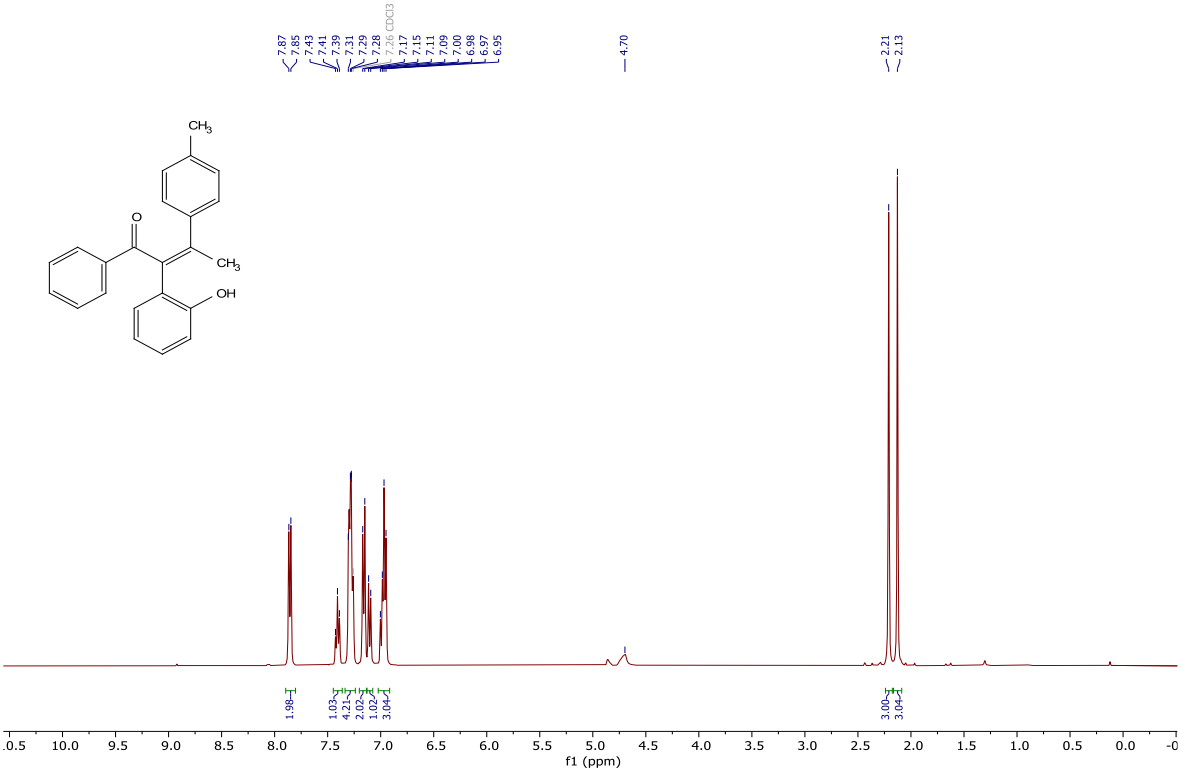
(*E*/*Z*)-(1-(2-hydroxyphenyl)-2-(*p*-tolyl)hex-1-en-1-yl)diphenylphosphine oxide (3x): ^{15}P Spectra



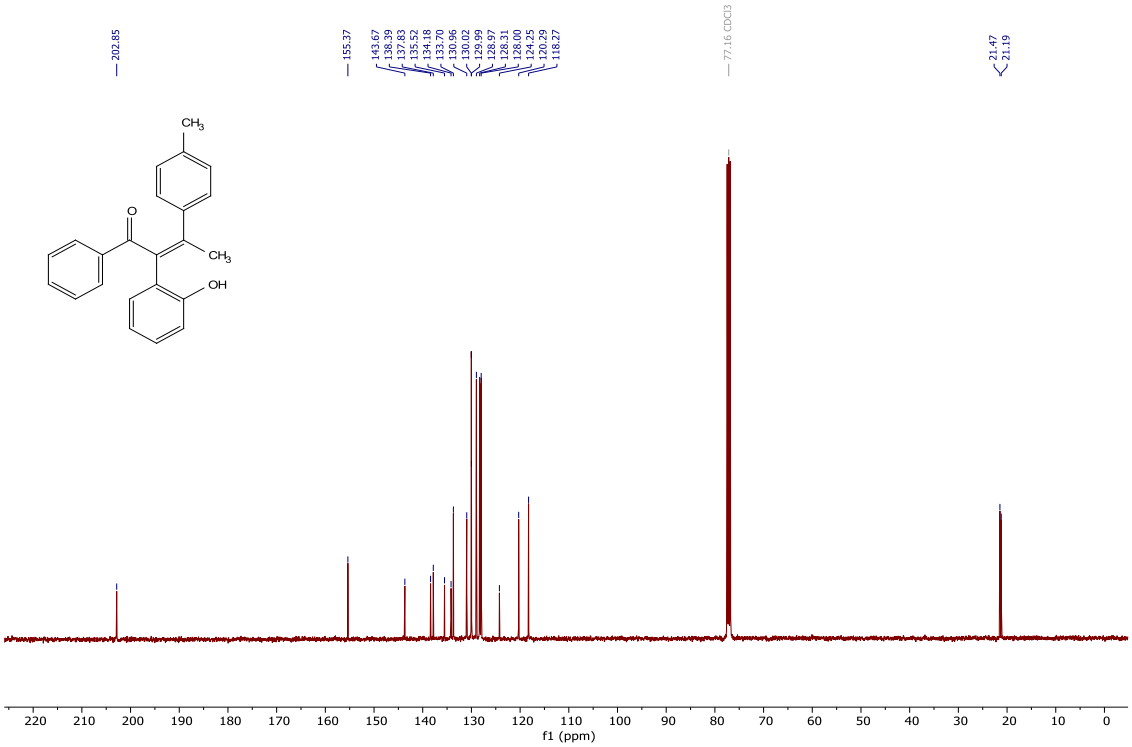
(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)but-2-en-1-one (3y):



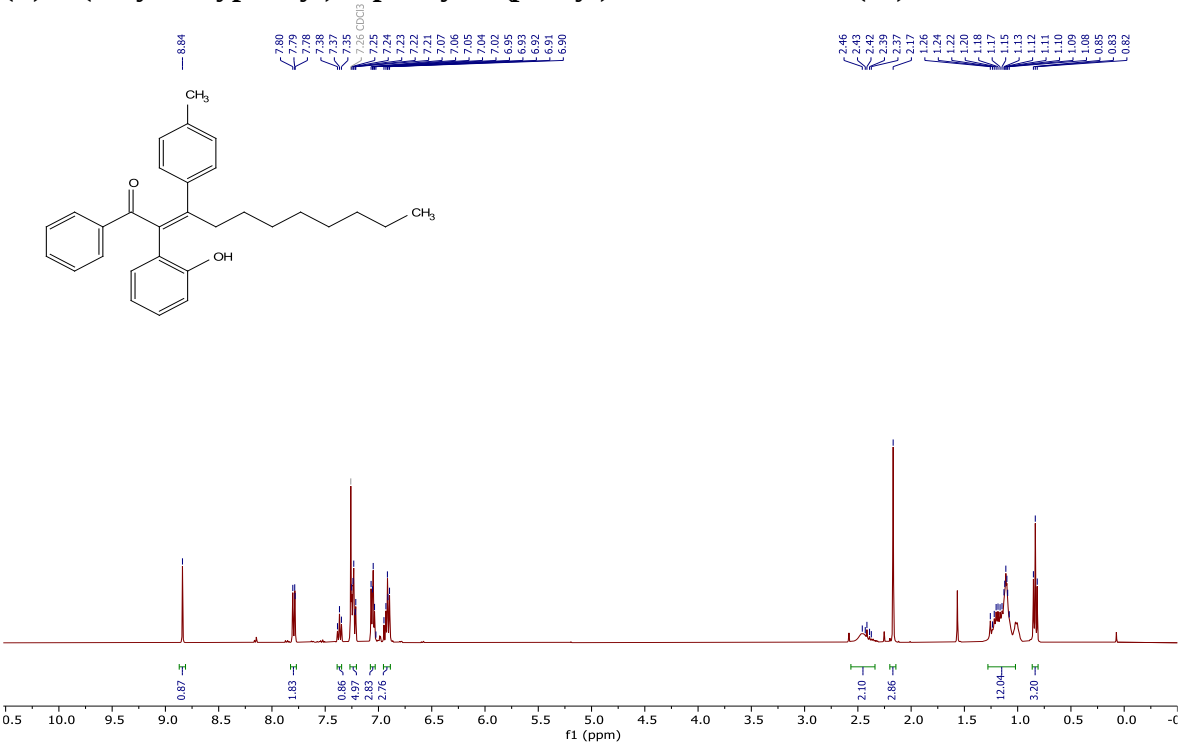
D_2O Exchange

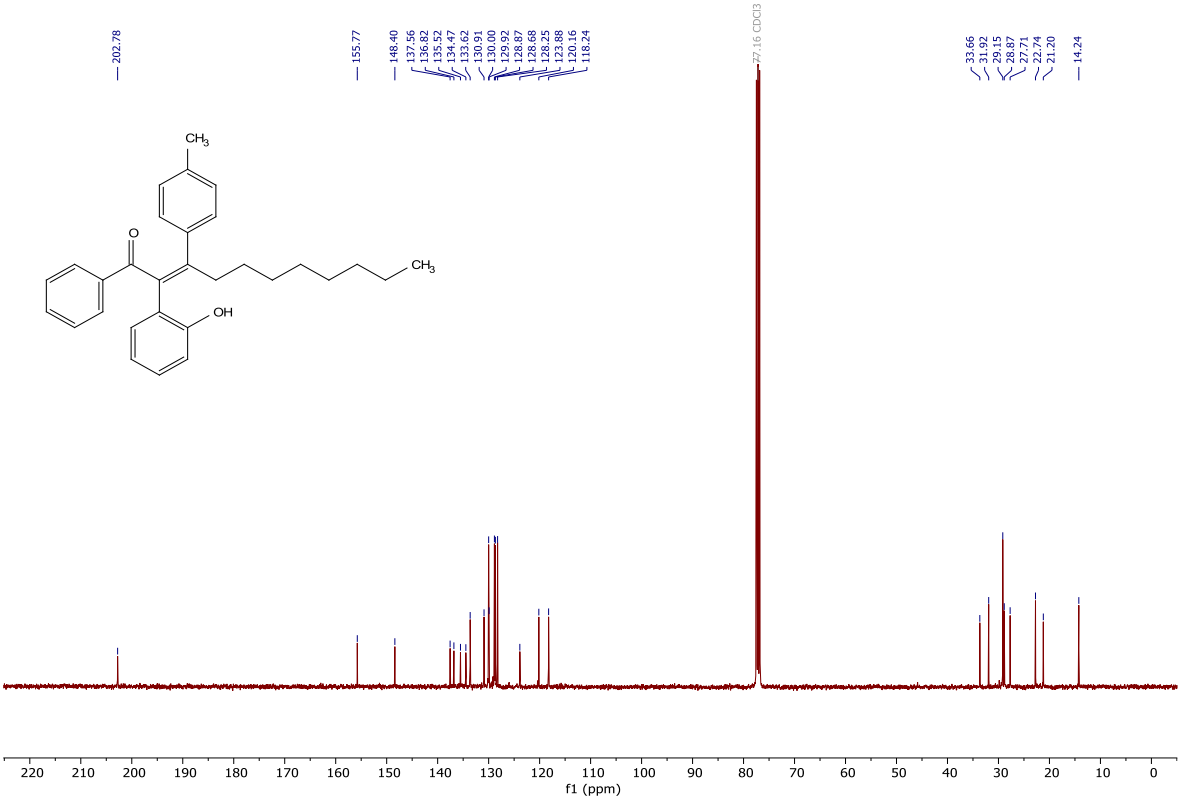


(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)but-2-en-1-one (3y): ^{13}C NMR spectra

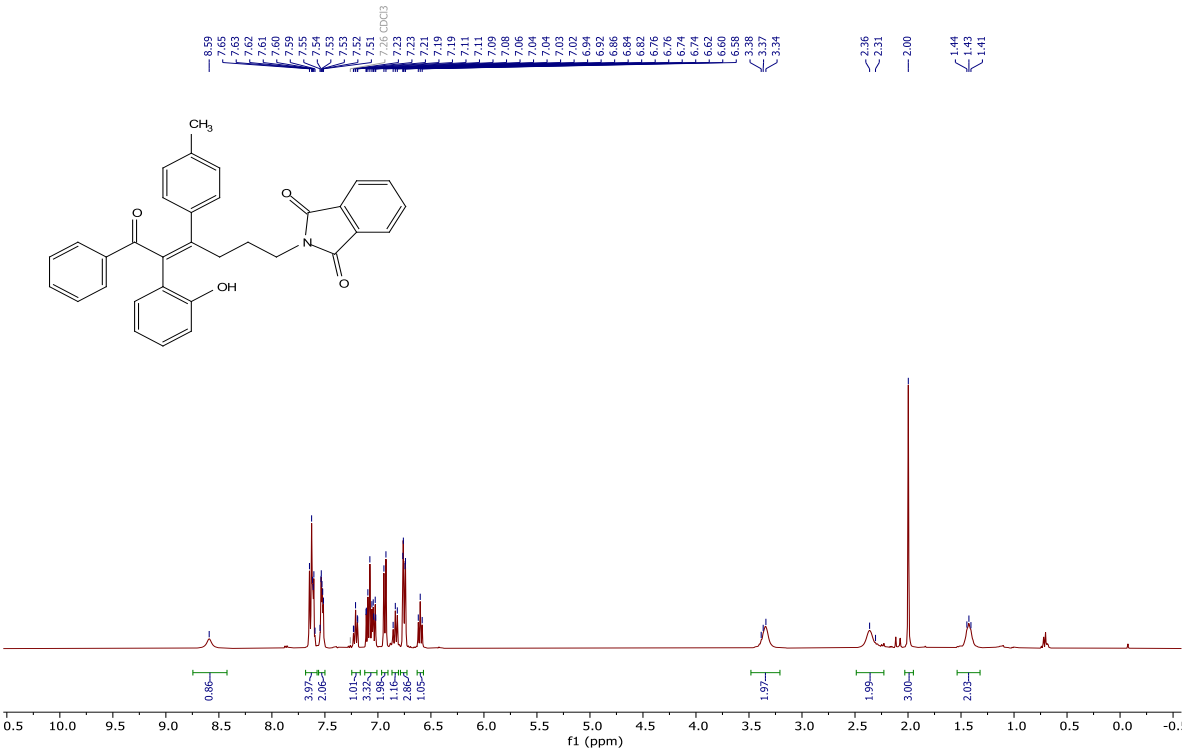


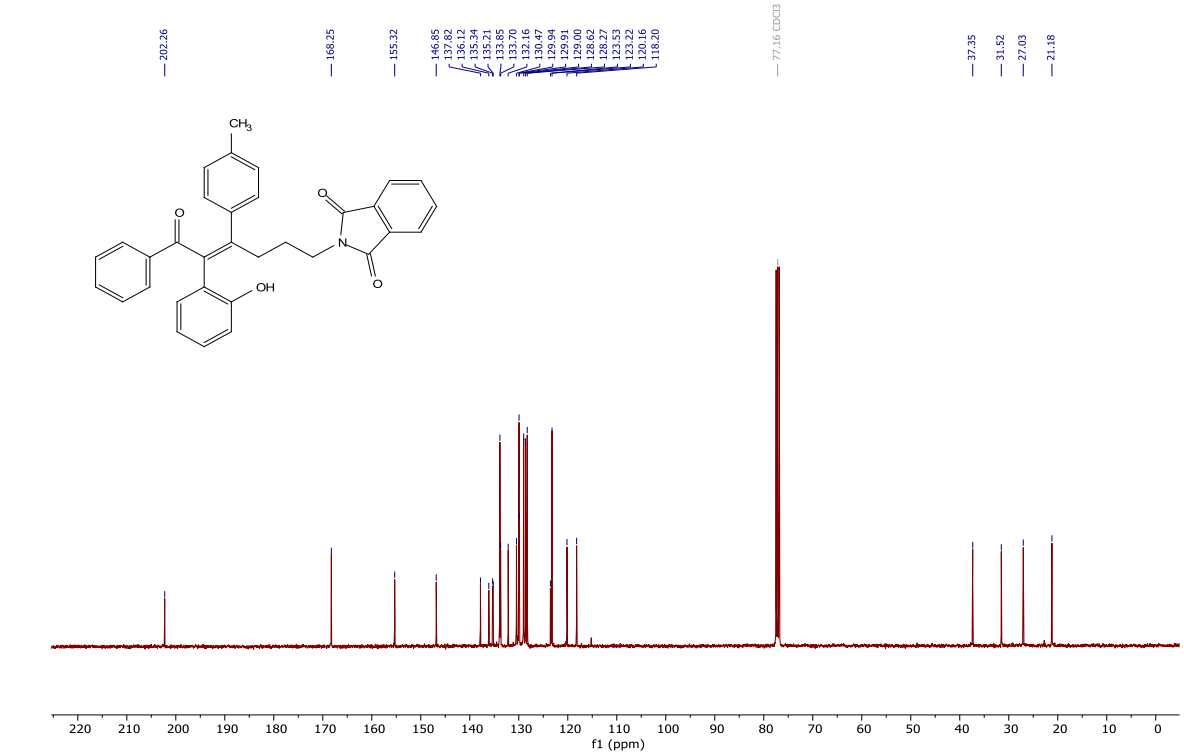
(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)undec-2-en-1-one (3z):



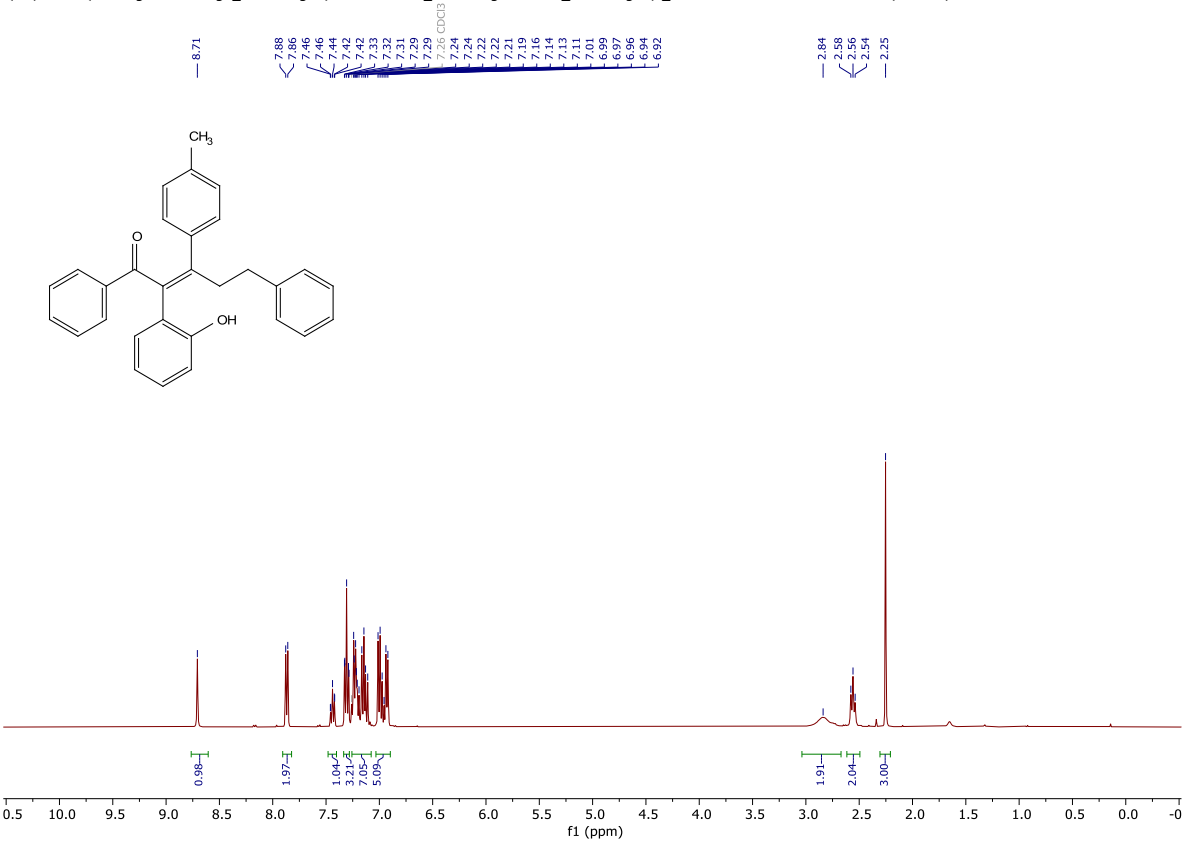


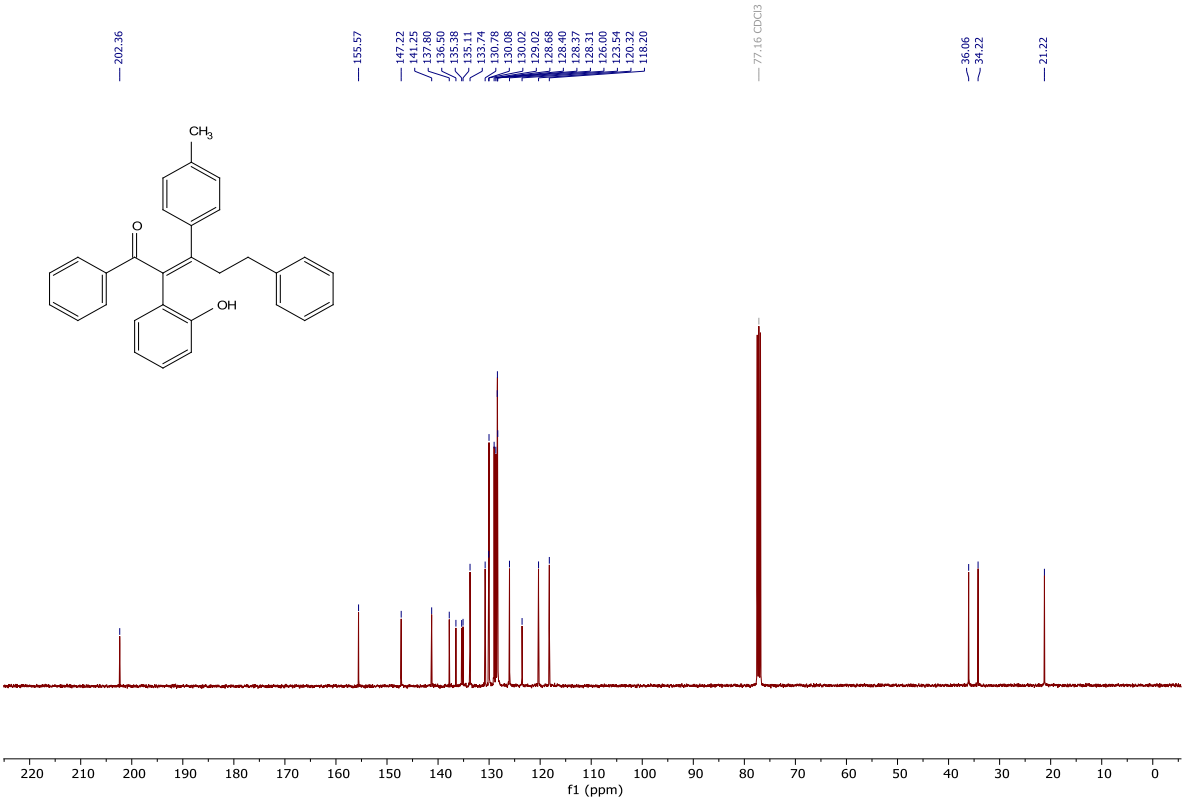
(*Z*)-2-(5-(2-hydroxyphenyl)-6-oxo-6-phenyl-4-(*p*-tolyl)hex-4-en-1-yl)isoindoline-1,3-dione (3aa):



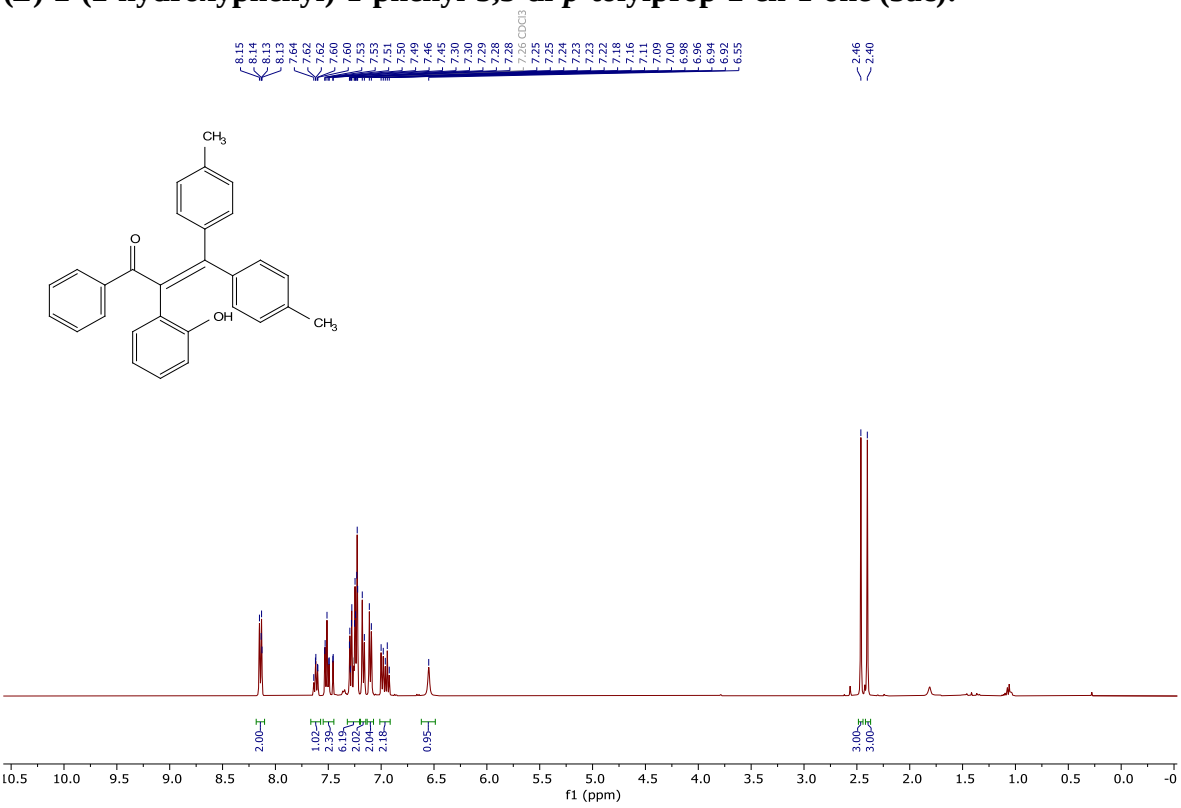


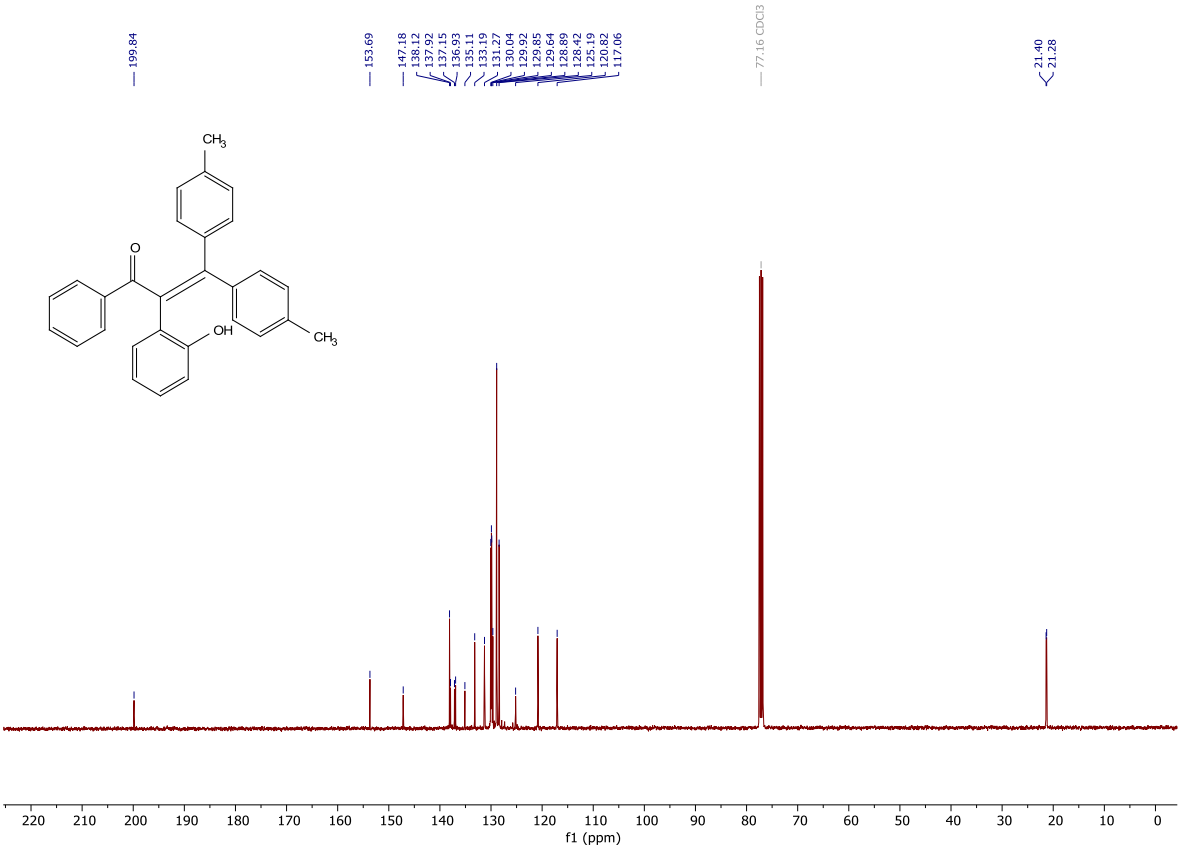
(*Z*)-2-(2-hydroxyphenyl)-1,5-diphenyl-3-(*p*-tolyl)pent-2-en-1-one (3ab):



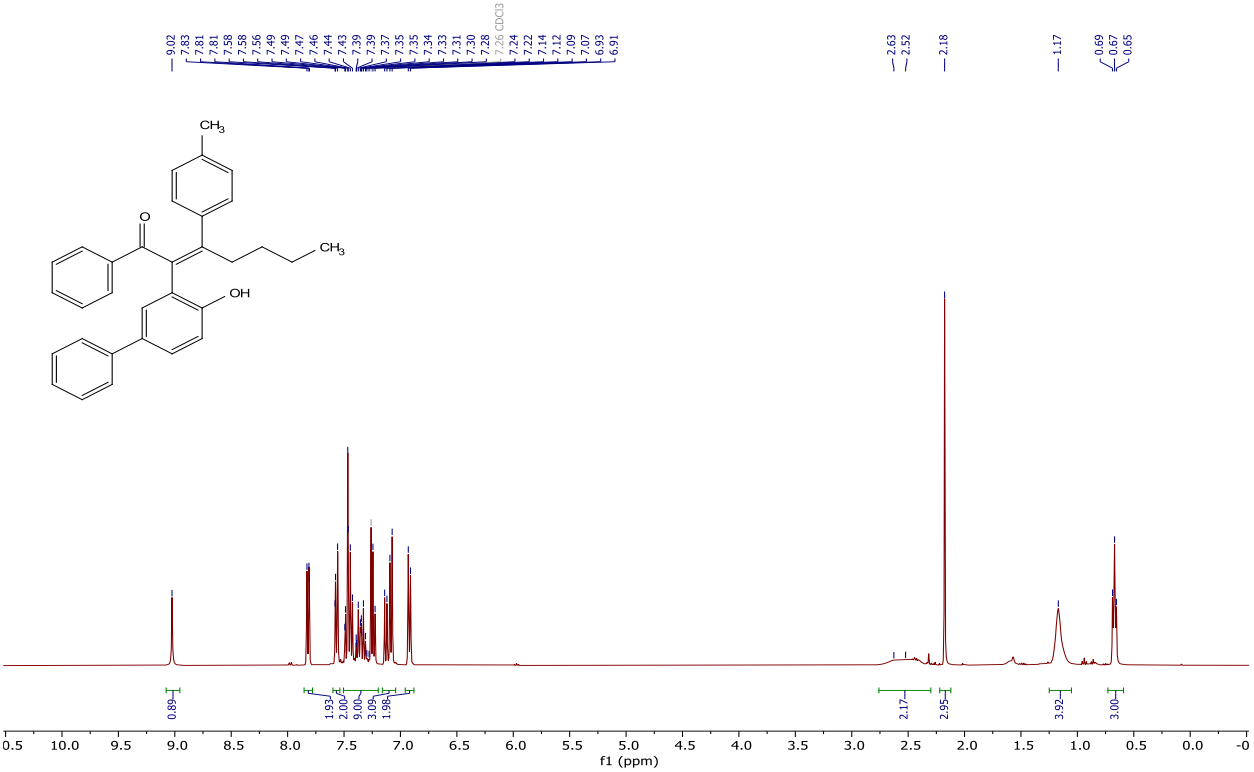


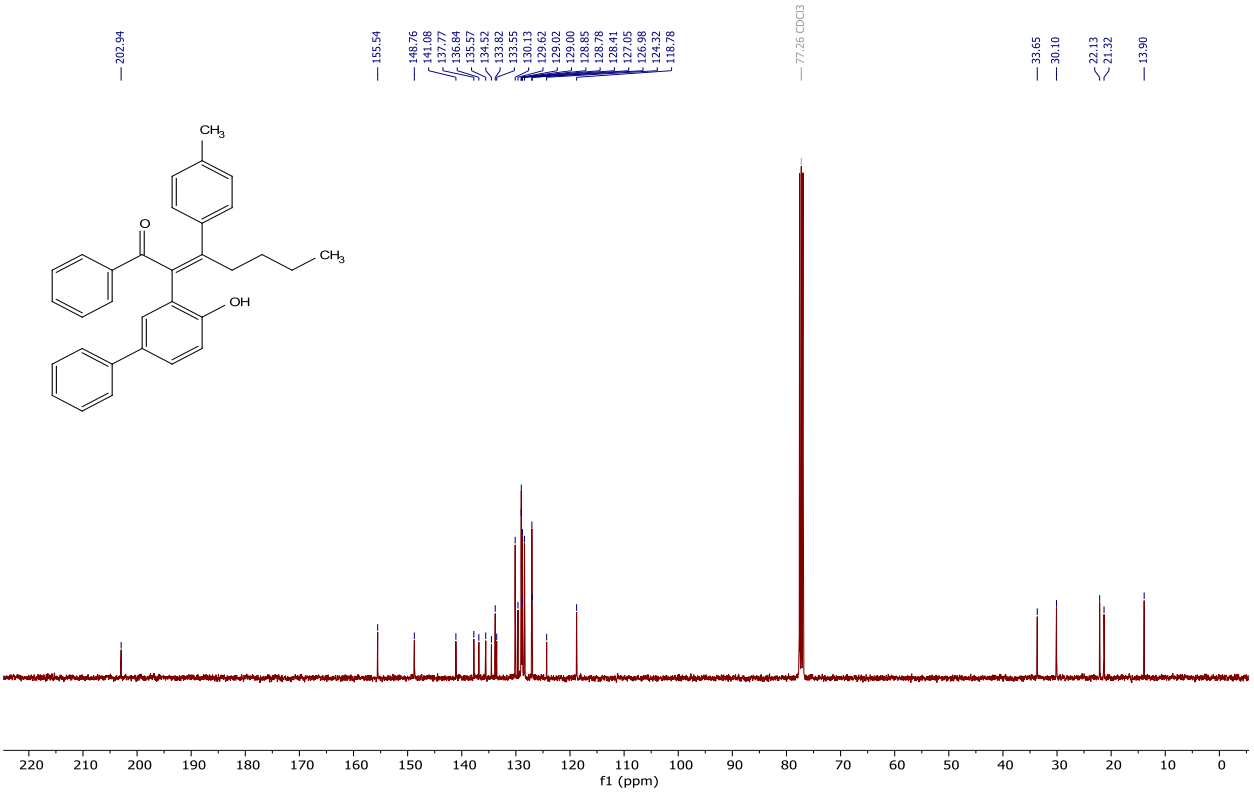
(*Z*)-2-(2-hydroxyphenyl)-1-phenyl-3,3-di-*p*-tolylprop-2-en-1-one (3ac):



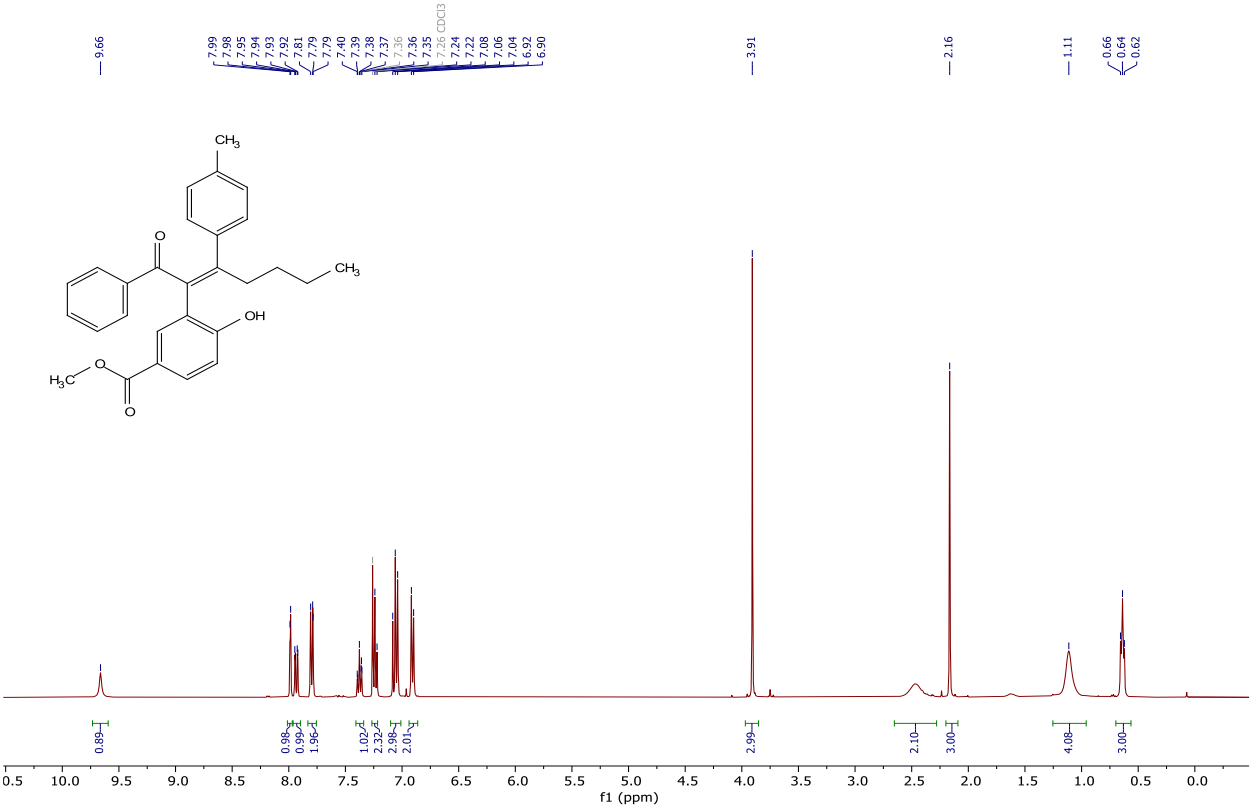


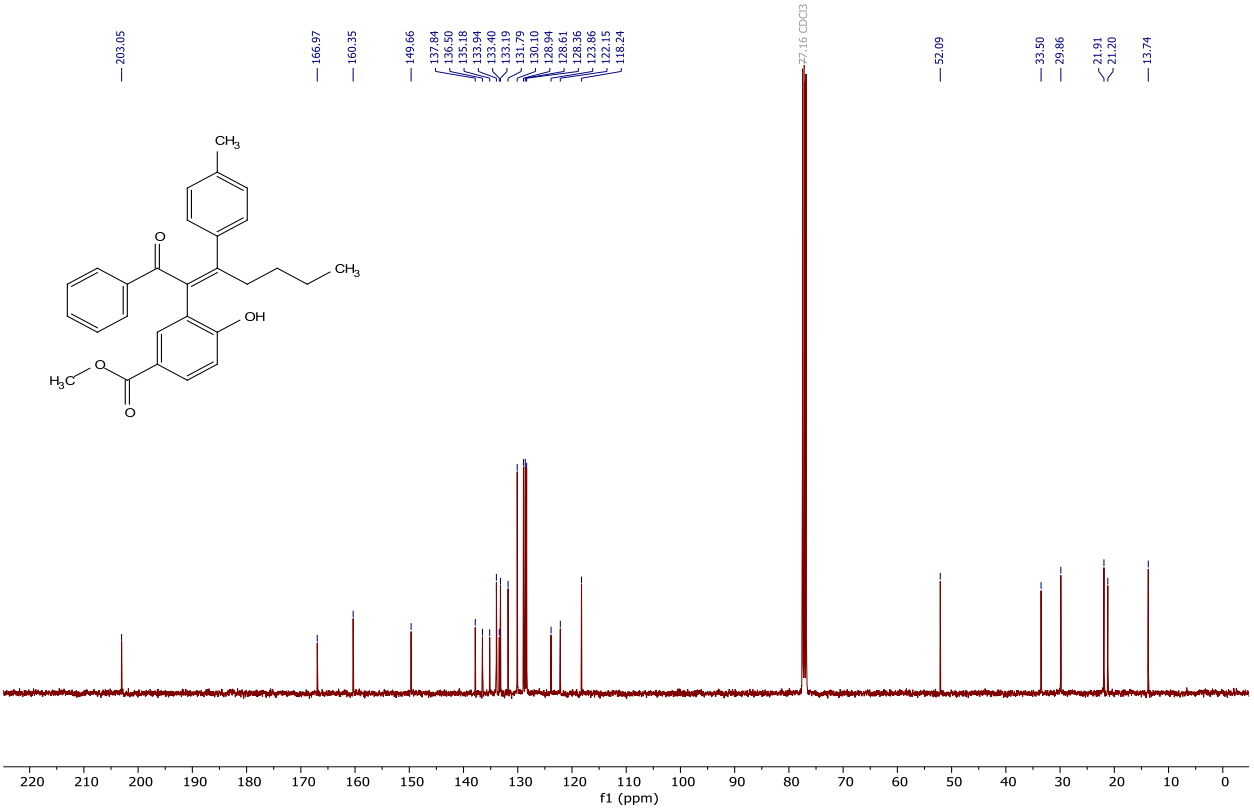
(*Z*)-2-(4-hydroxy-[1,1'-biphenyl]-3-yl)-1-phenyl-3-(*p*-tolyl)hept-2-en-1-one (3ad):



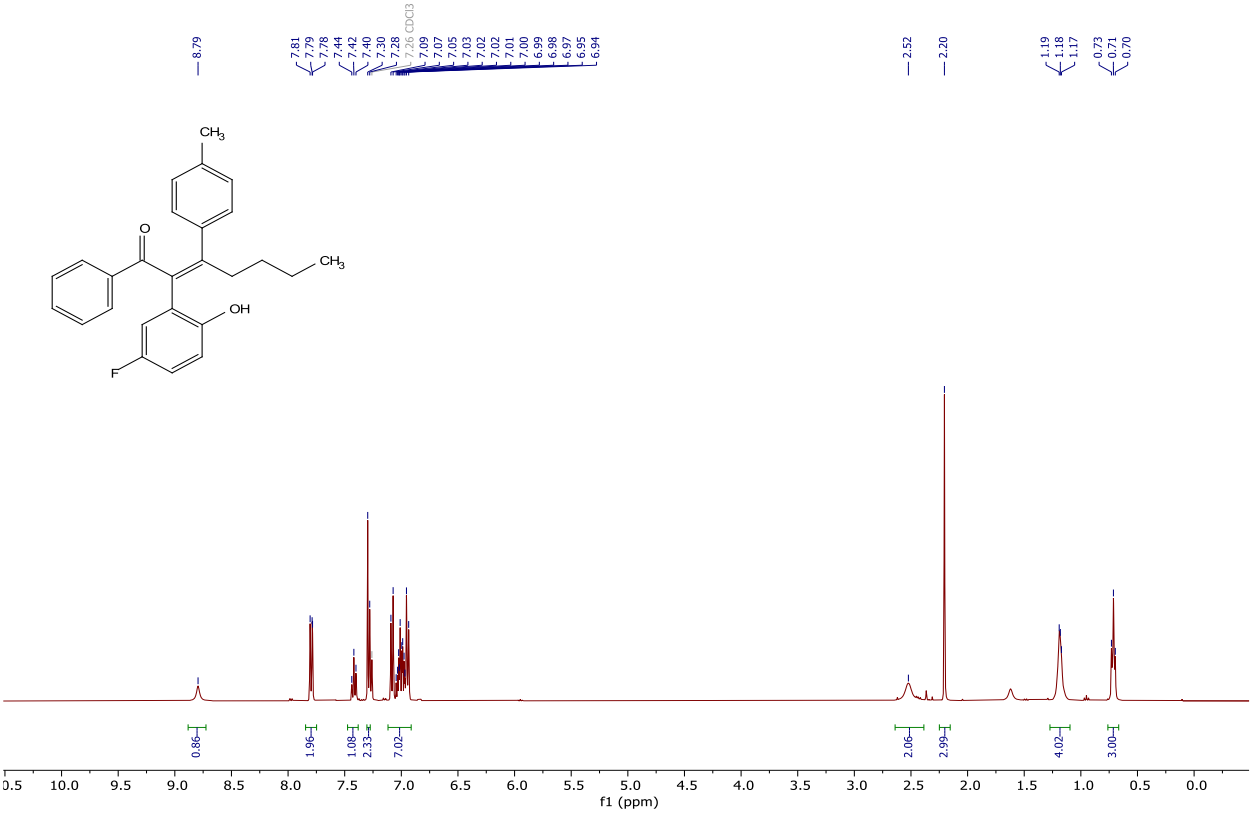


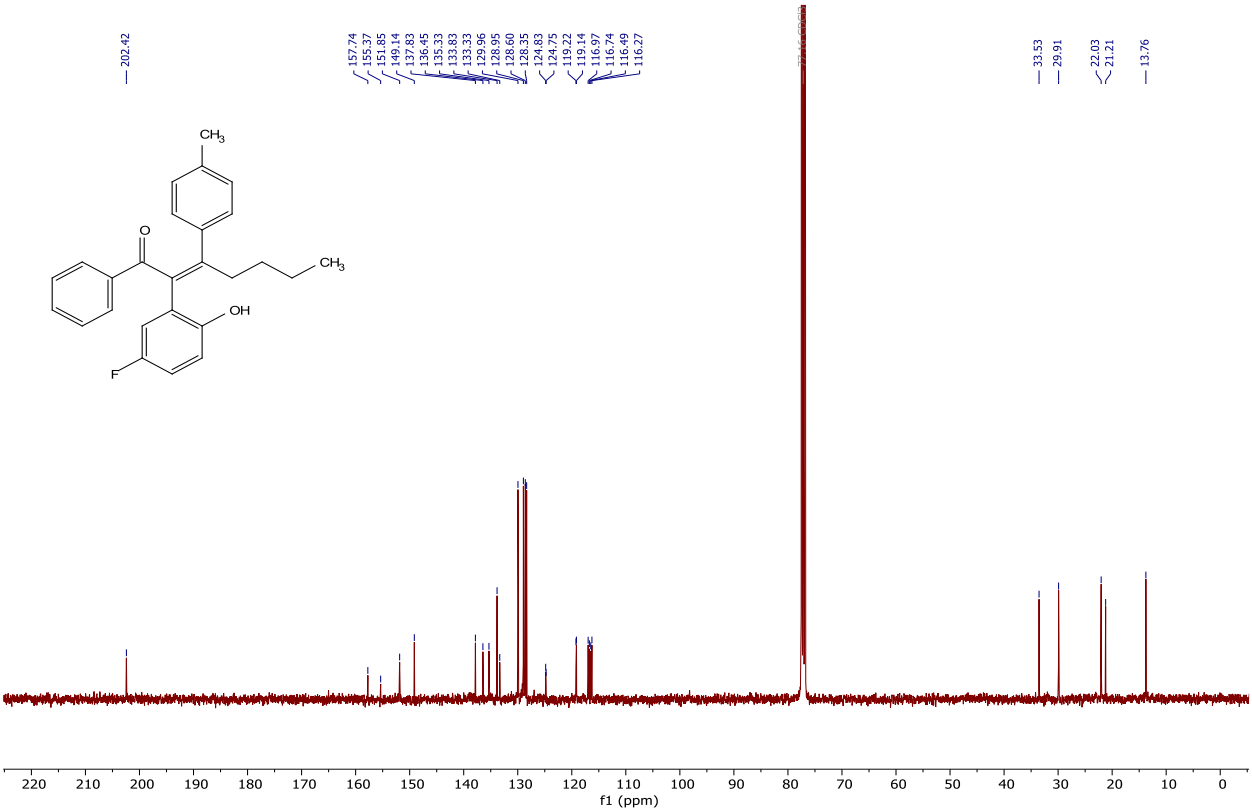
Z)-methyl-(-4-hydroxy-3-(1-oxo-1-phenyl-3-(*p*-tolyl)hept-2-en-2-yl)benzoate (3ae):



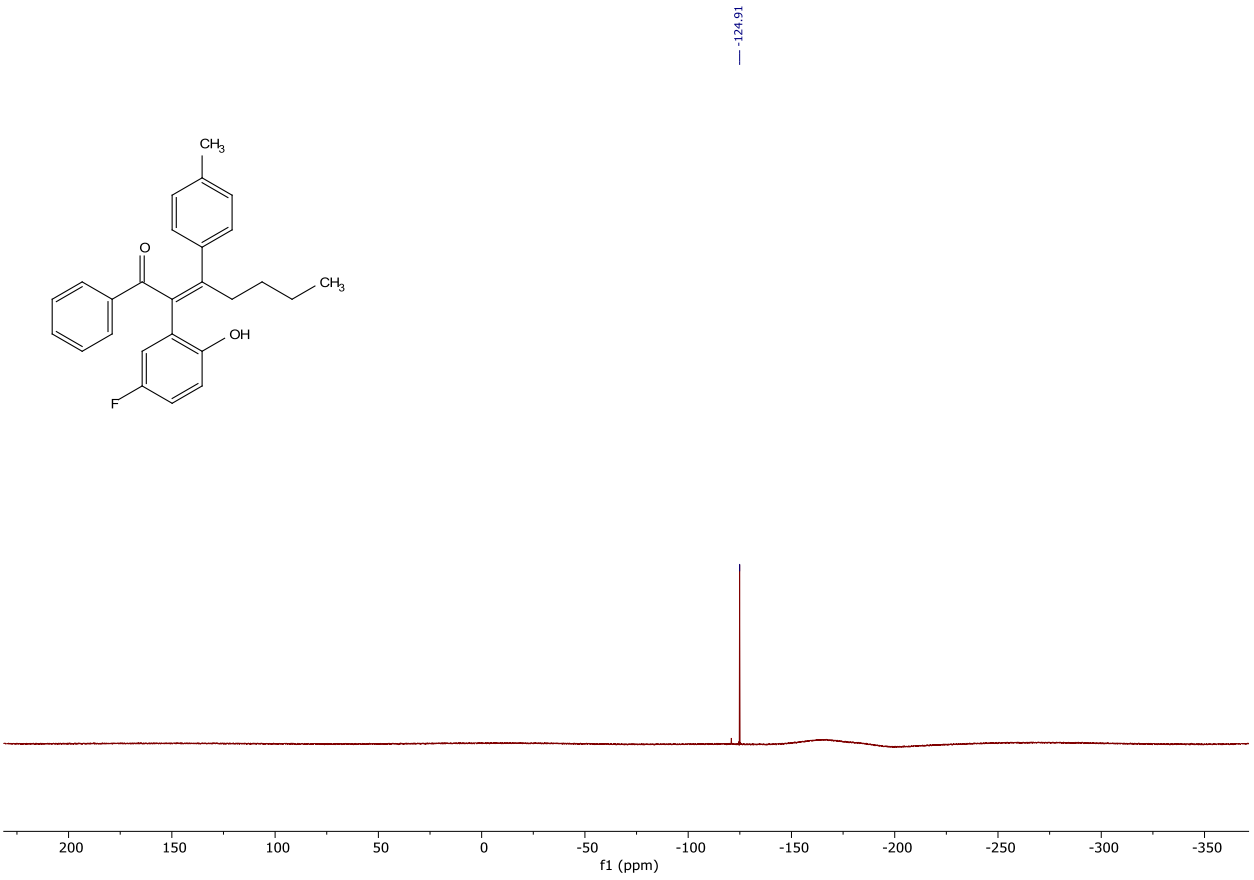


(*Z*)-2-(5-fluoro-2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)hept-2-en-1-one (3af):

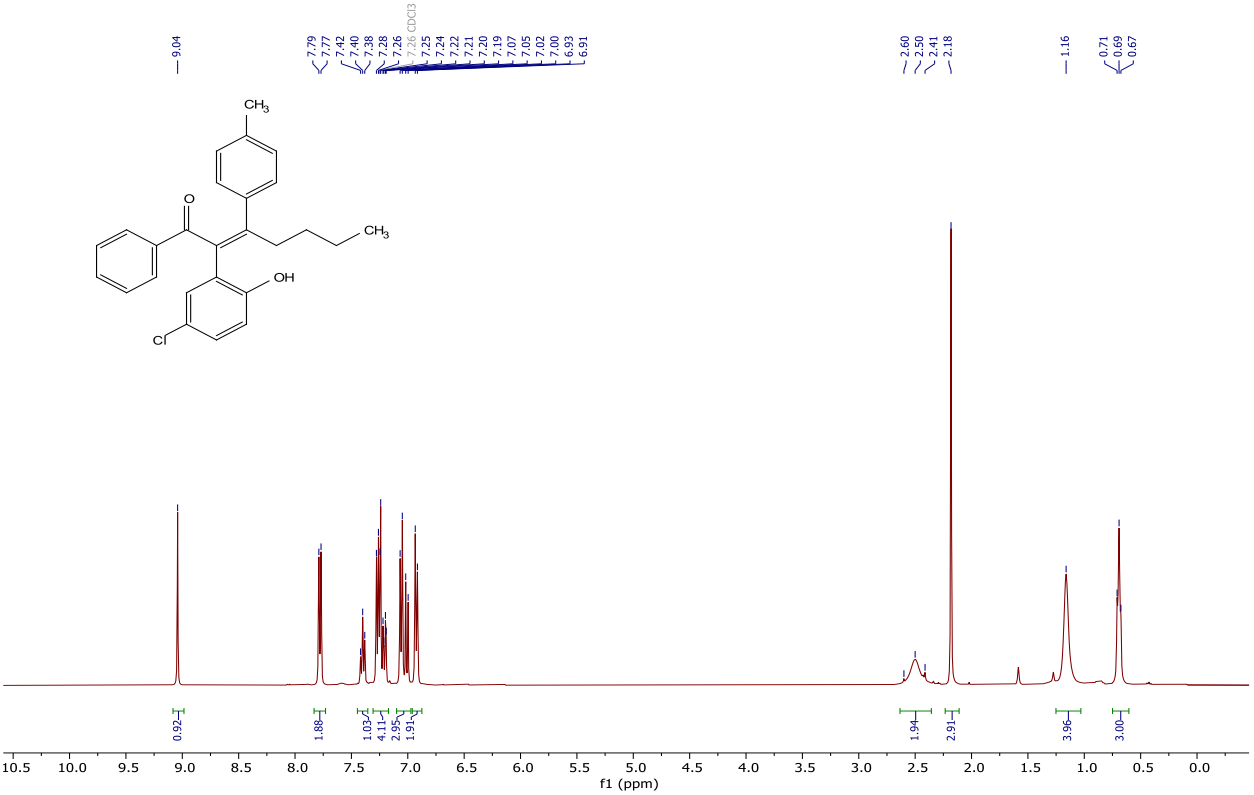


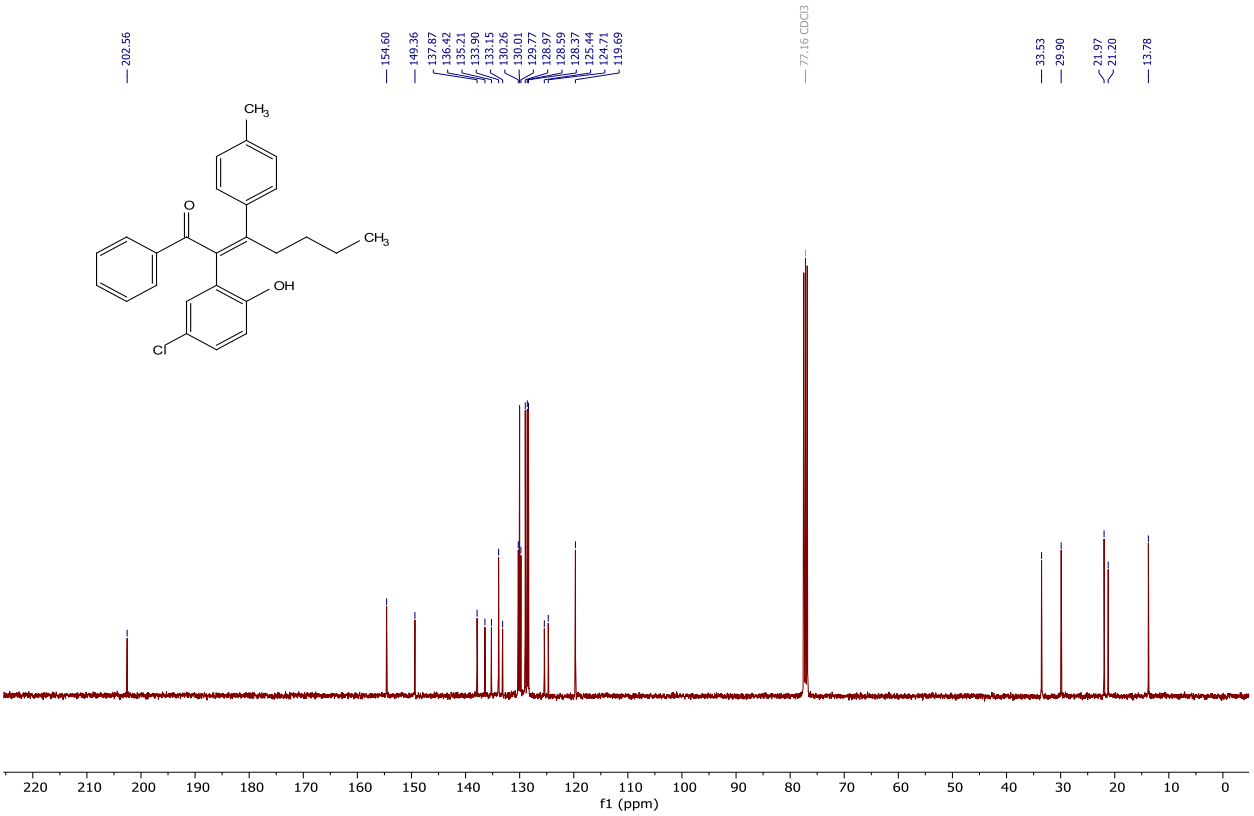


(*Z*)-2-(5-fluoro-2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)hept-2-en-1-one (3af): ^{19}F Spectra

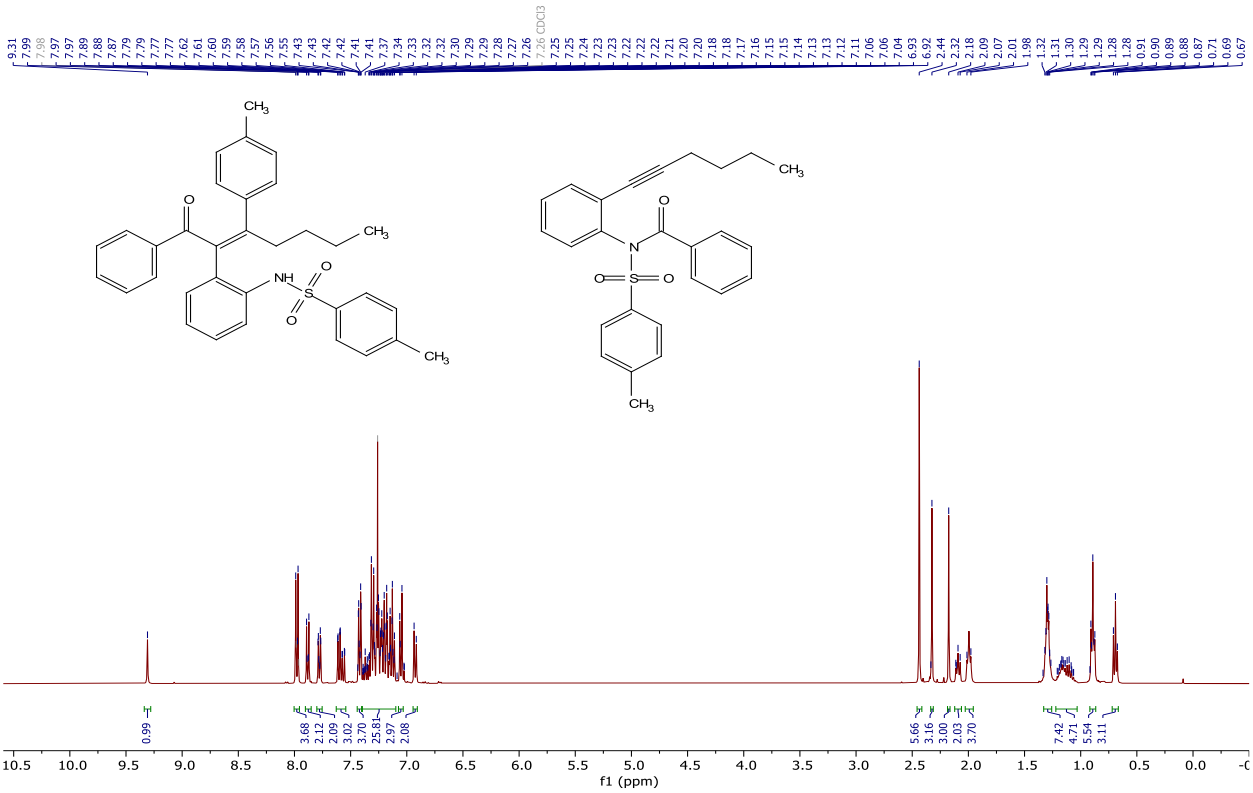


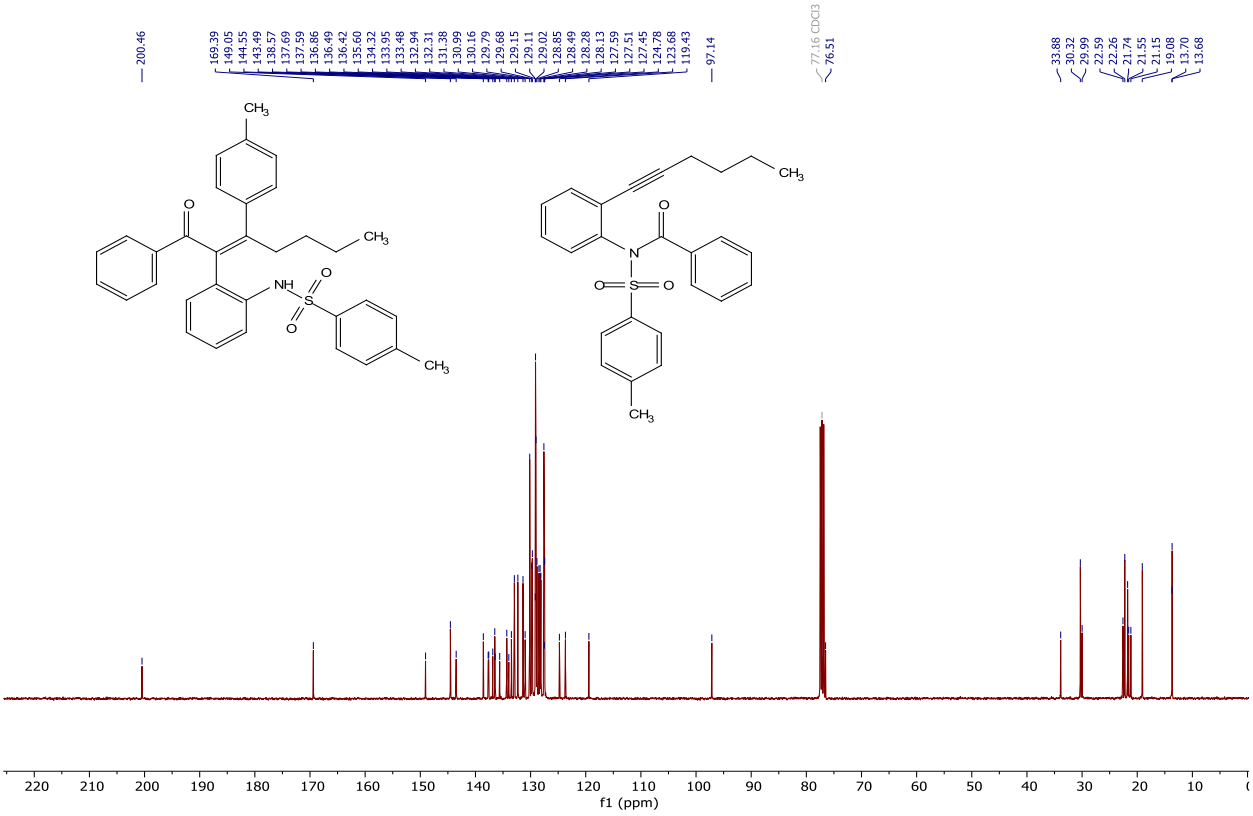
(*Z*)-2-(5-chloro-2-hydroxyphenyl)-1-phenyl-3-(*p*-tolyl)hept-2-en-1-one (ag):



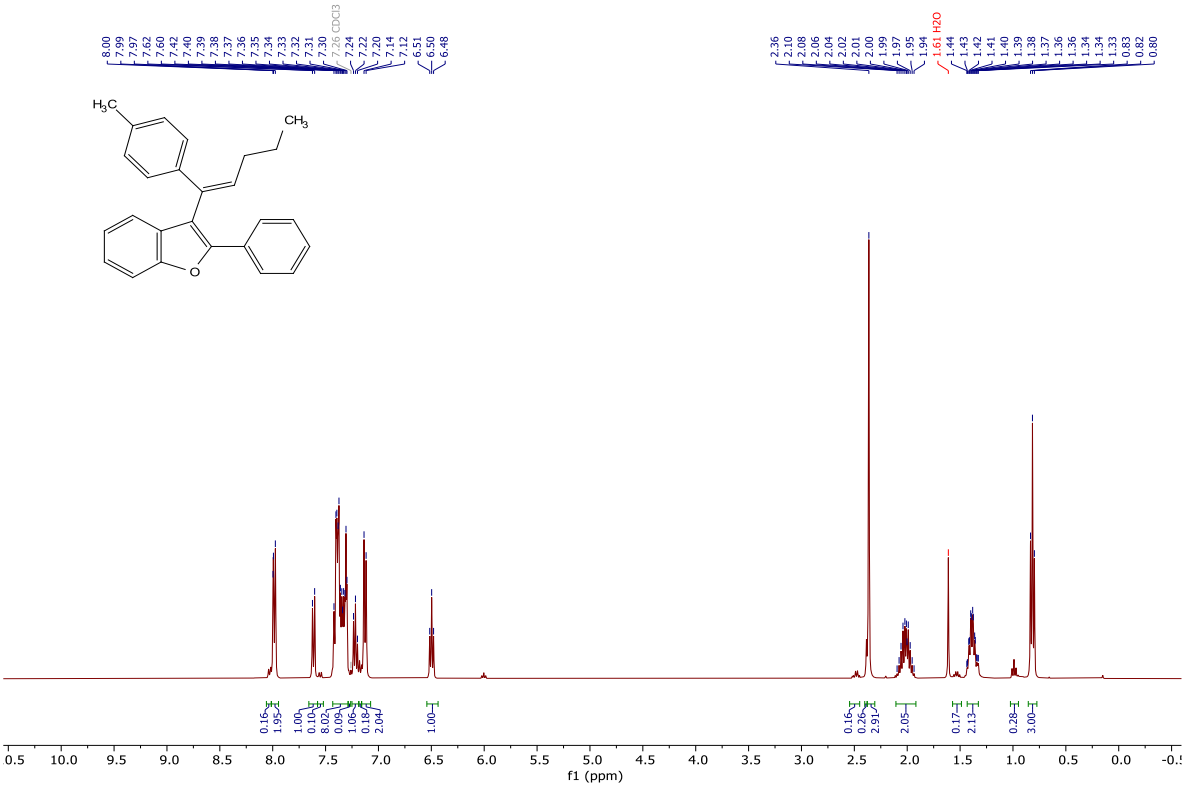


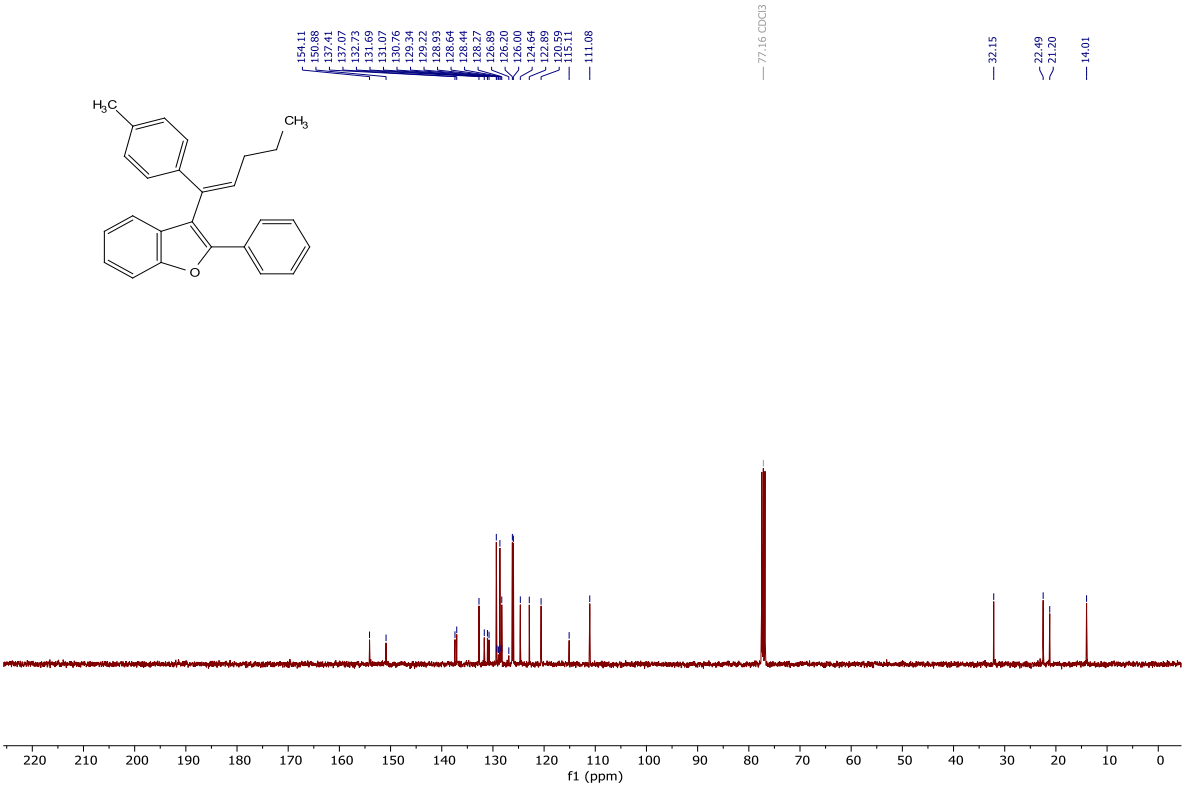
(*Z*)-4-methyl-N-(2-(1-oxo-1-phenyl-3-(*p*-tolyl)hept-2-en-2-yl)phenyl)benzenesulfonamide (3ah):



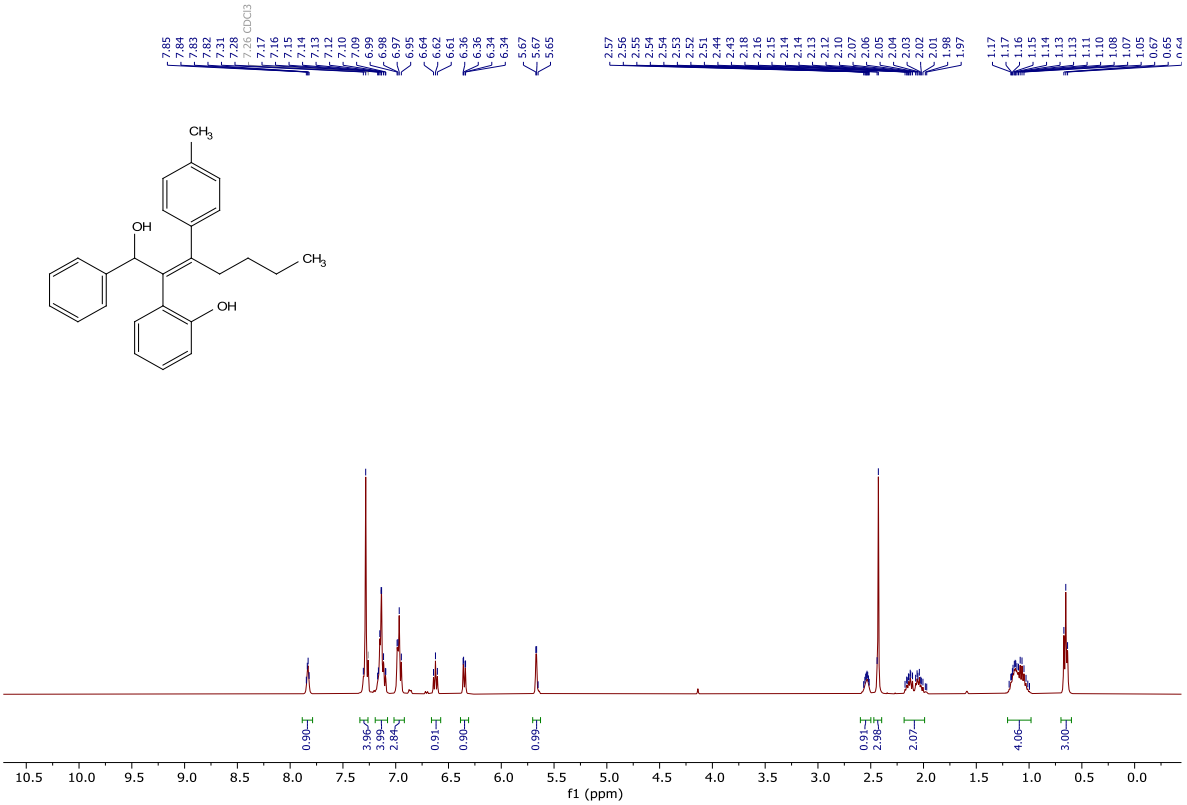


(*Z*)-2-phenyl-3-(1-(*p*-tolyl)pent-1-en-1-yl)benzofuran (4):

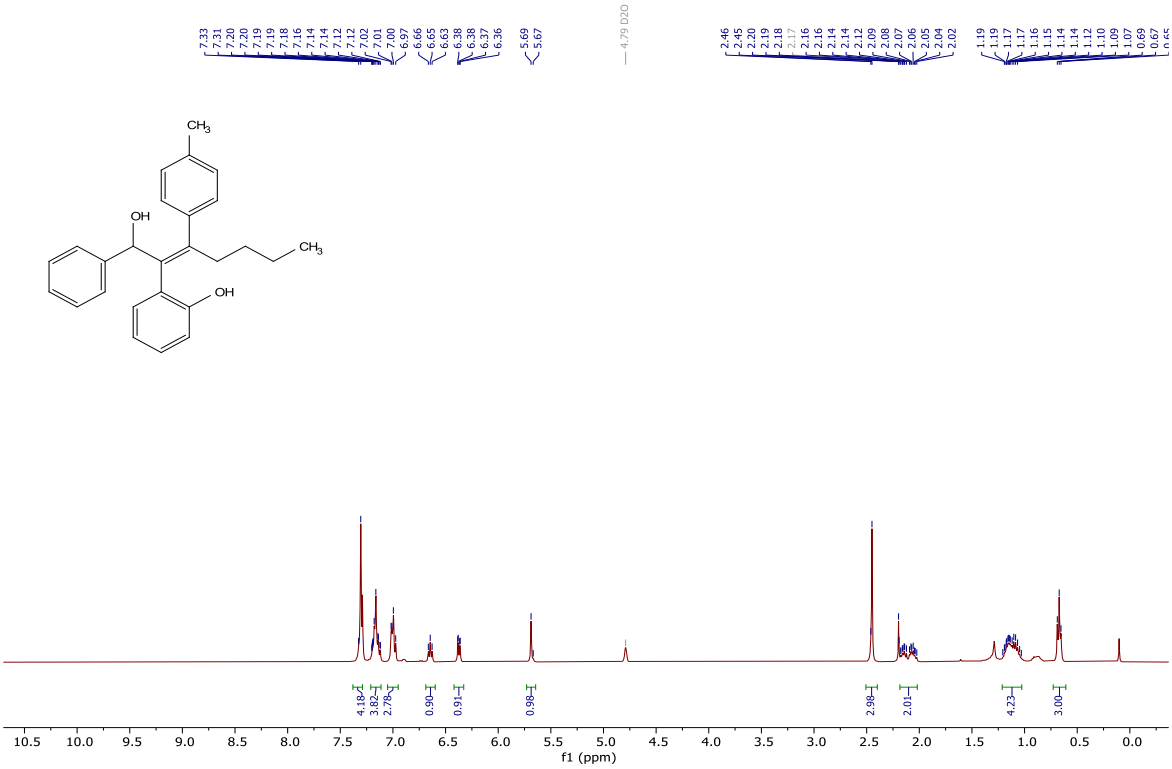




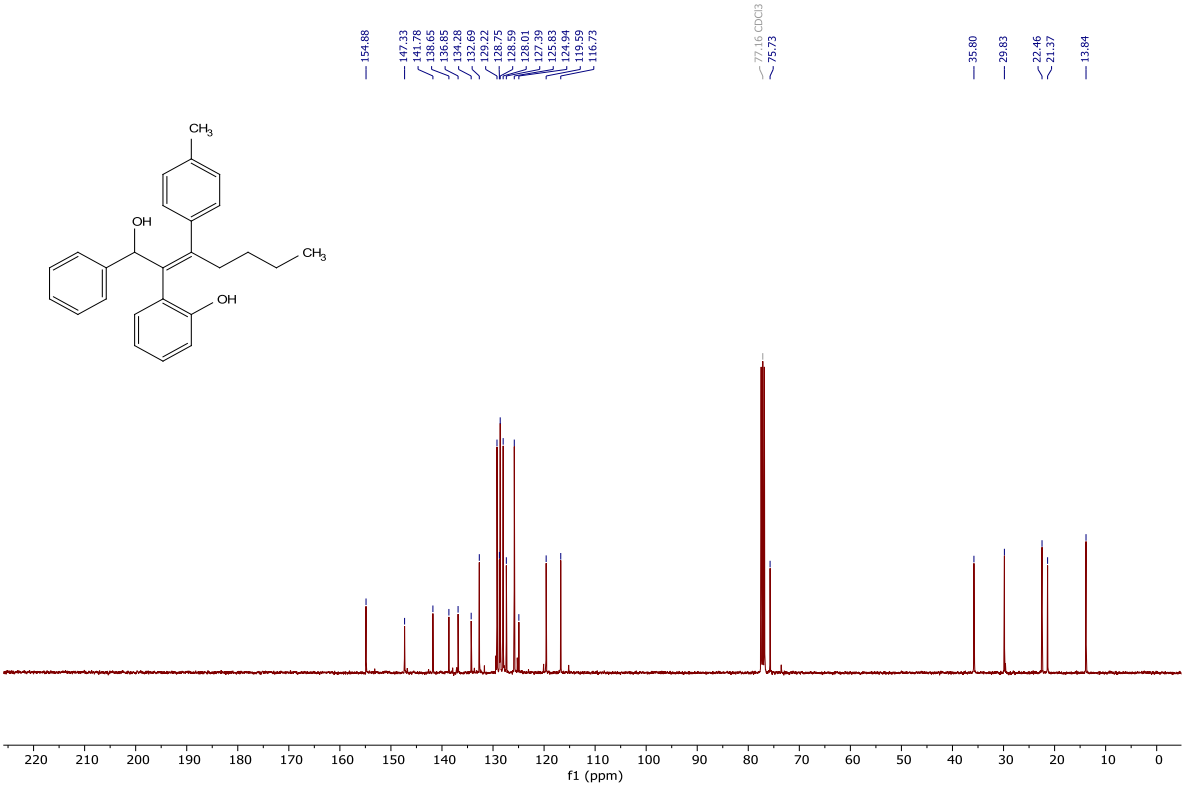
(*Z*)-2-(1-hydroxy-1-phenyl-3-(*p*-tolyl)hept-2-en-2-yl)phenol (5):



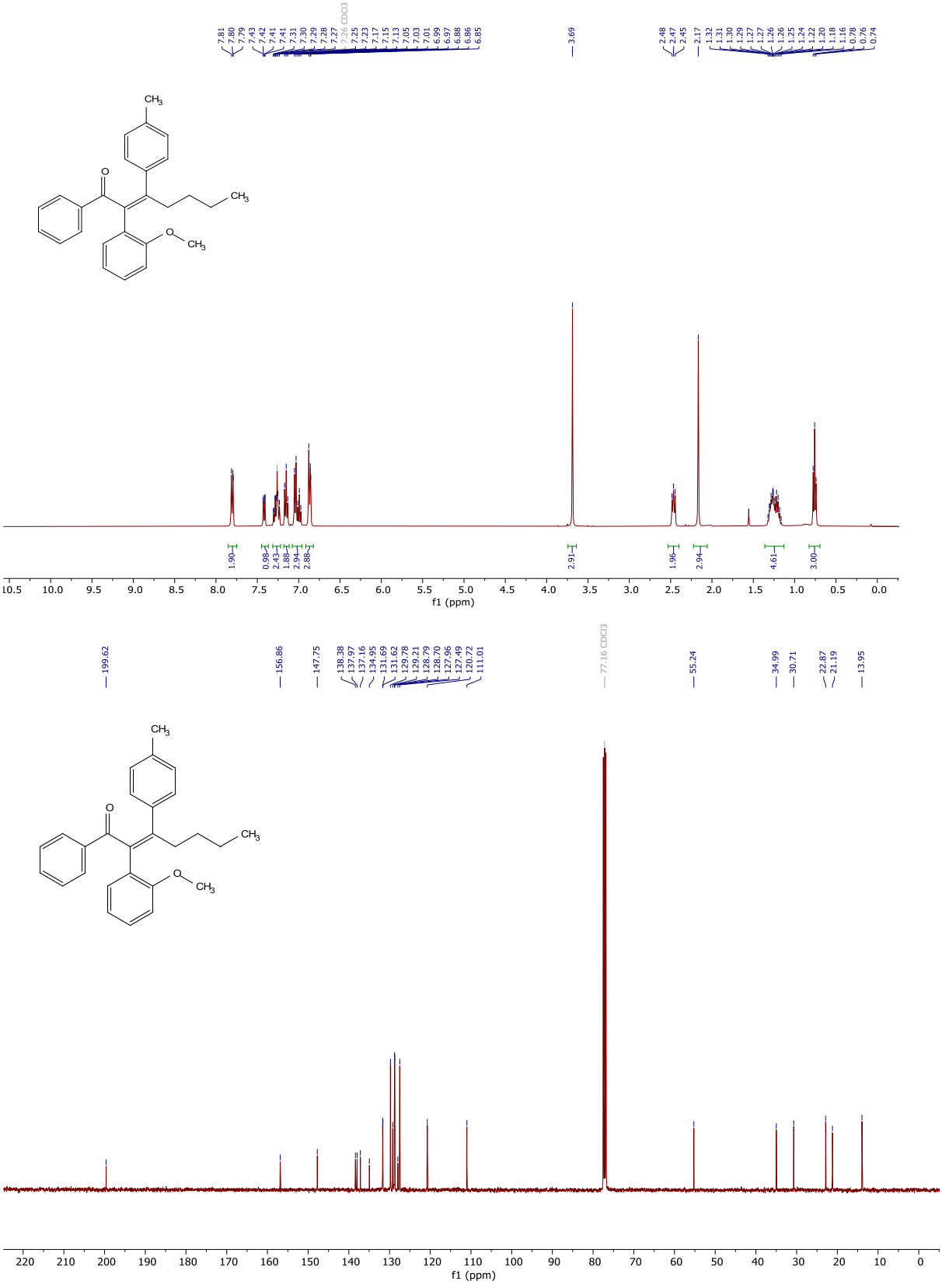
D_2O Exchange study



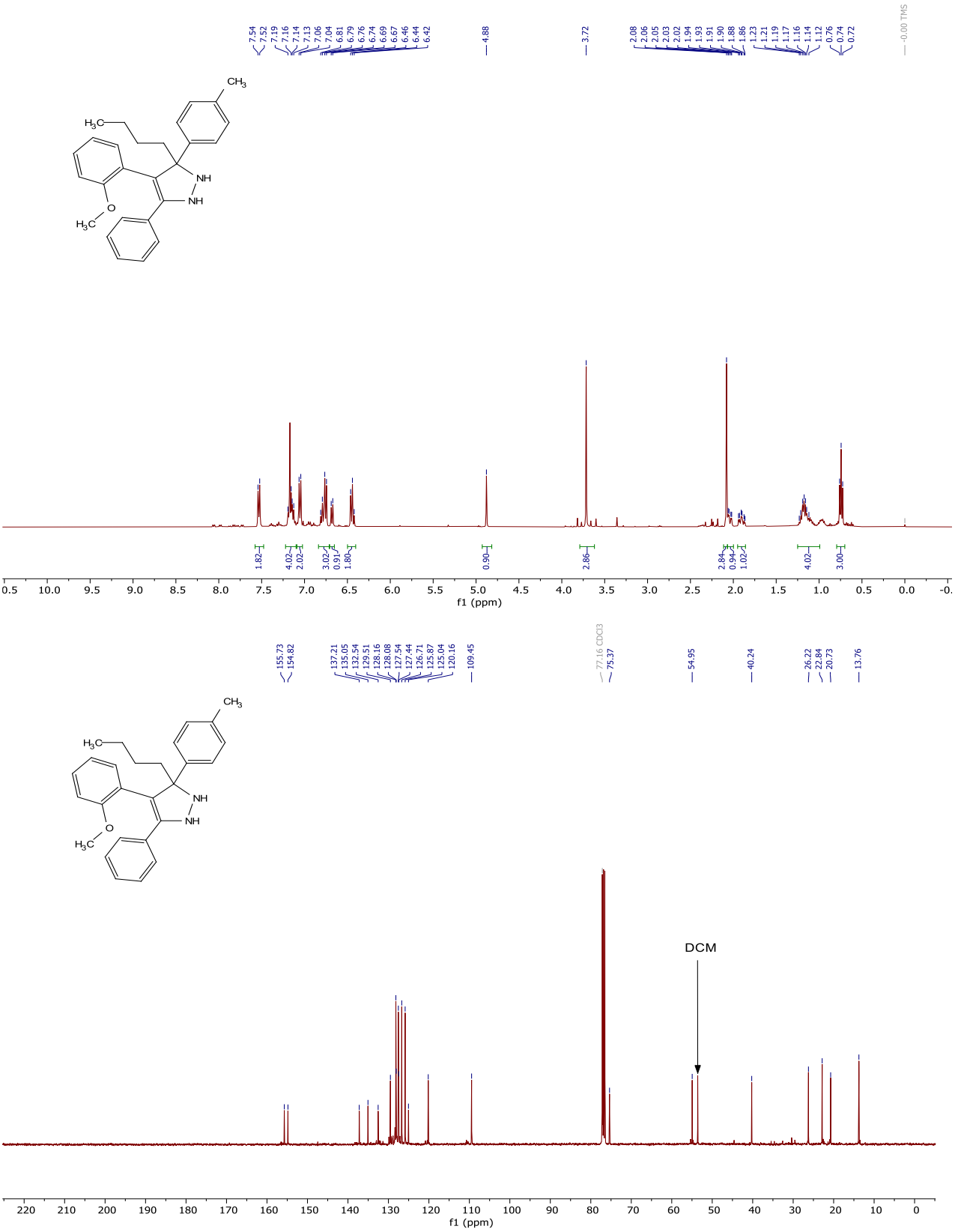
(*Z*)-2-(1-hydroxy-1-phenyl-3-(*p*-tolyl)hept-2-en-2-yl)phenol (5):



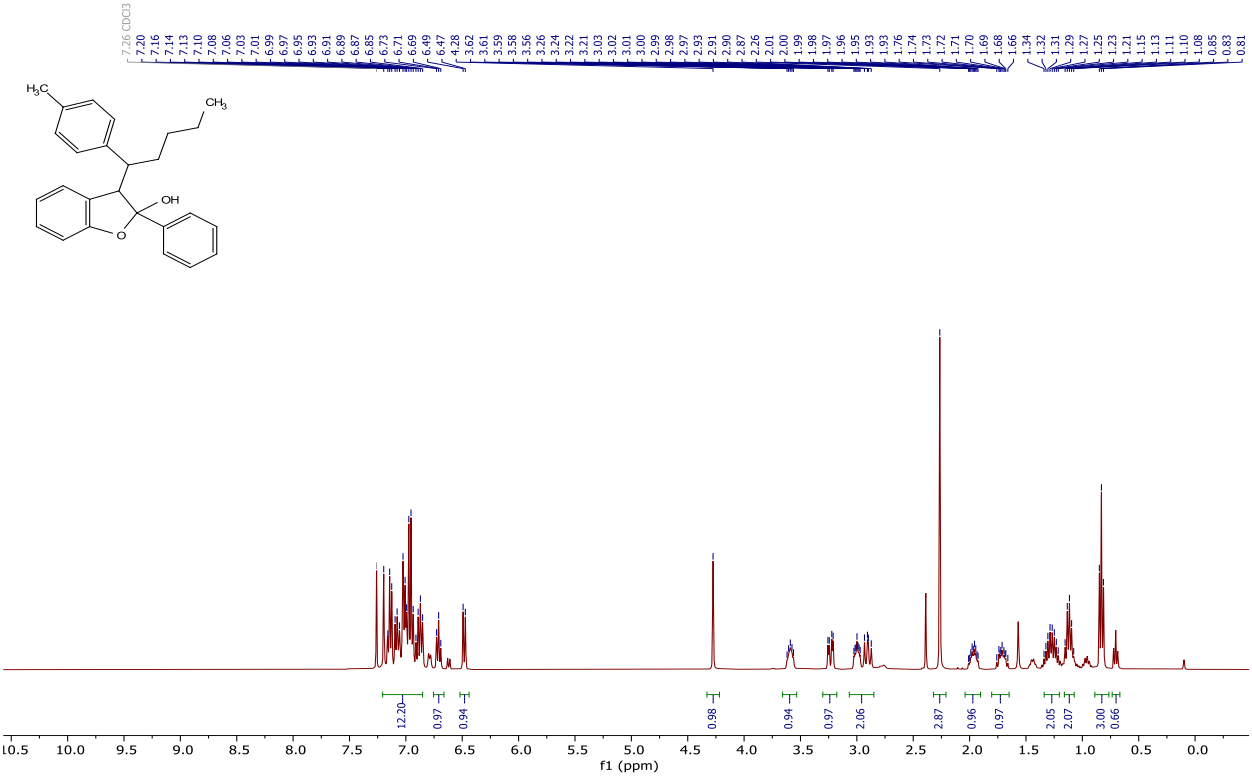
(*Z*)-2-(2-methoxyphenyl)-1-phenyl-3-(*p*-tolyl)hept-2-en-1-one (6”)



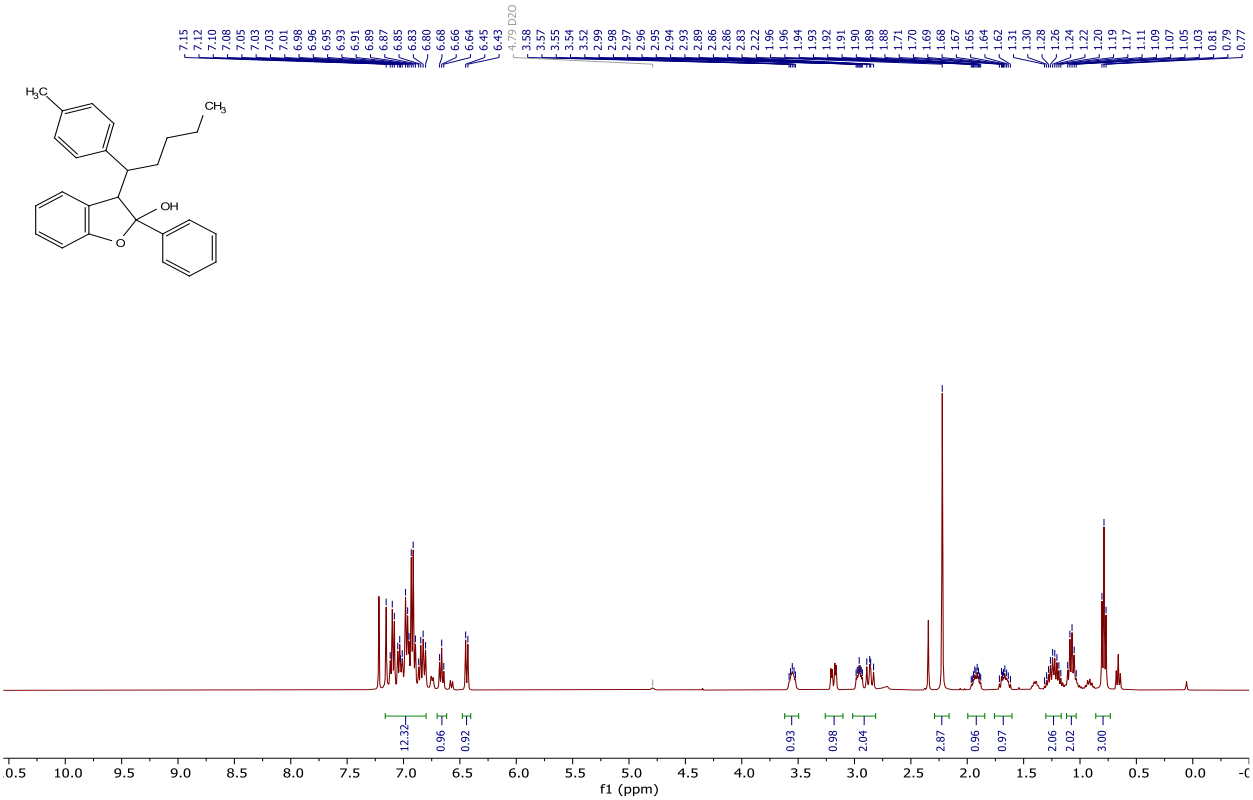
3-butyl-4-(2-methoxyphenyl)-5-phenyl-3-(*p*-tolyl)-2,3-dihydro-1H-pyrazole (6):



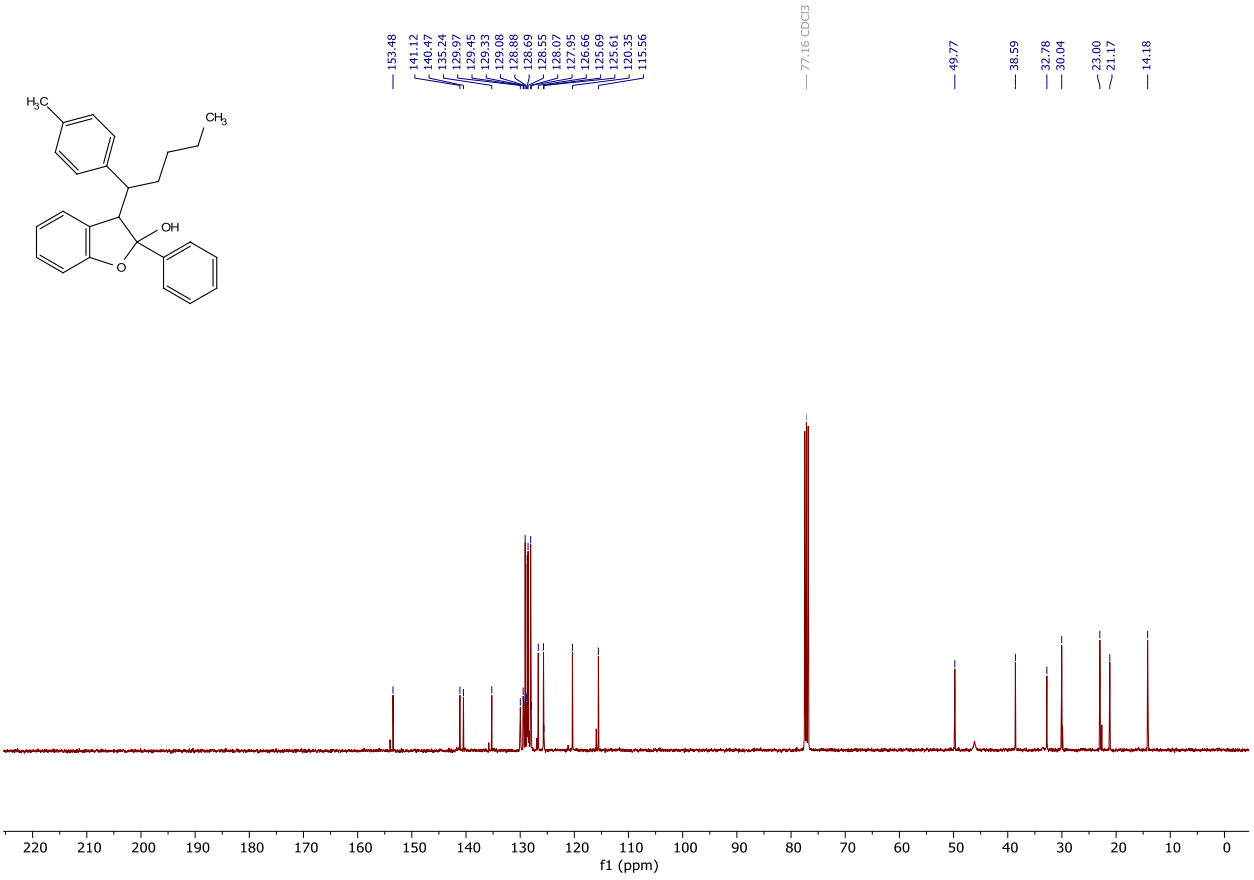
2-phenyl-3-(1-(*p*-tolyl)pentyl)-2,3-dihydrobenzofuran-2-ol (7):



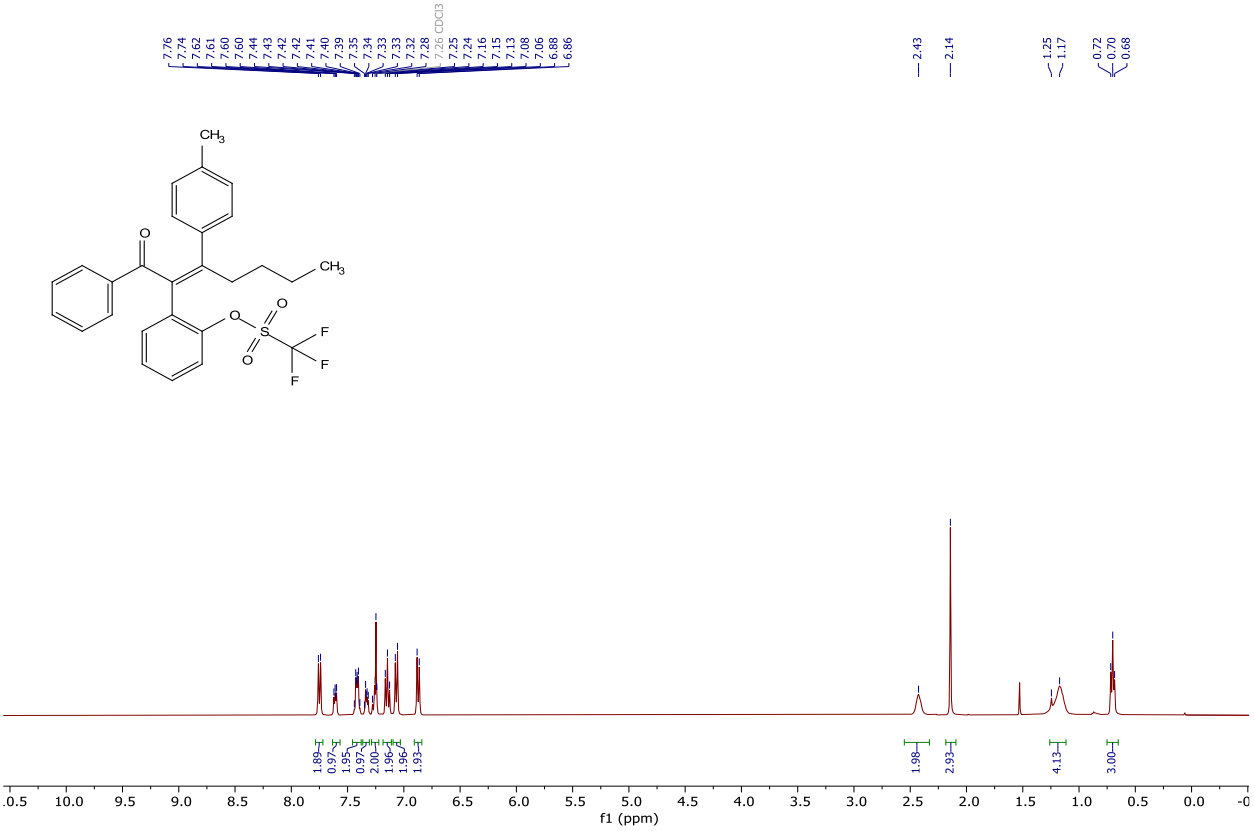
D_2O exchange study

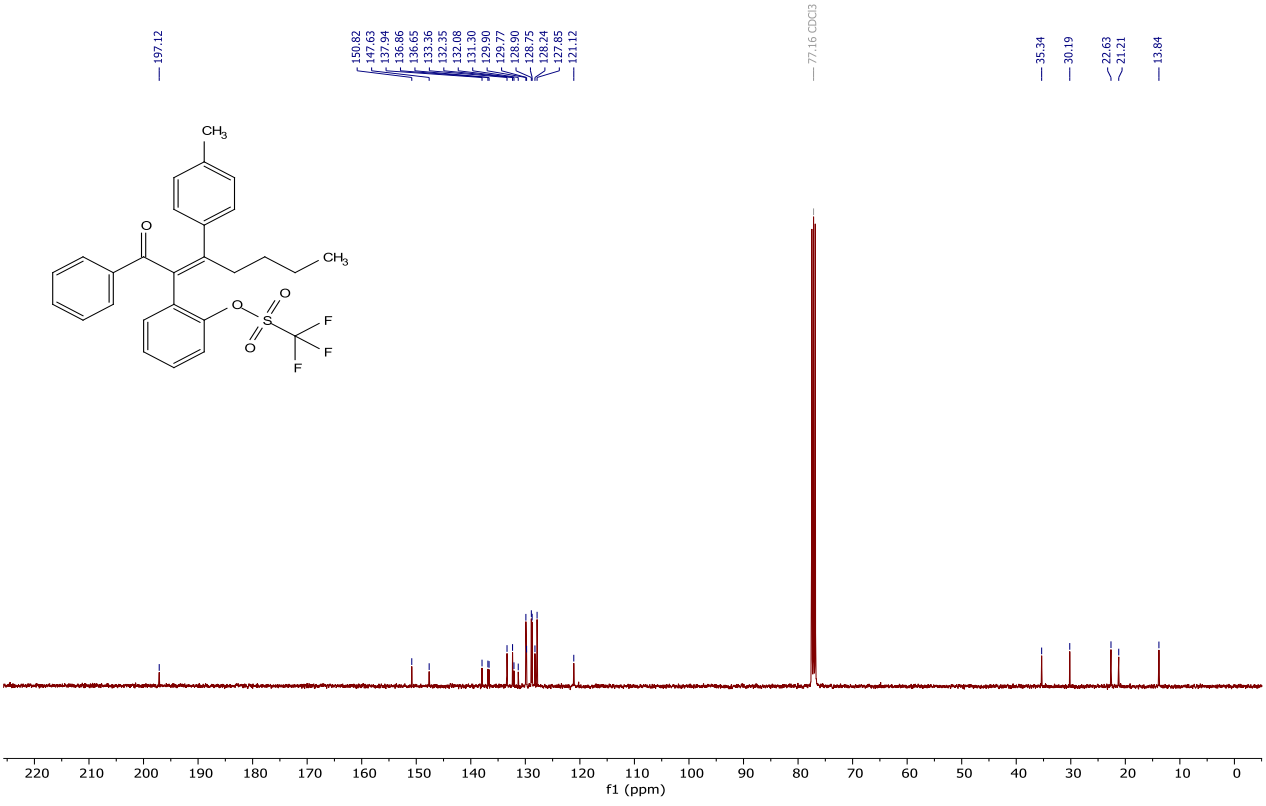


2-phenyl-3-(1-(*p*-tolyl)pentyl)-2,3-dihydrobenzofuran-2-ol (7): ^{13}C NMR spectra

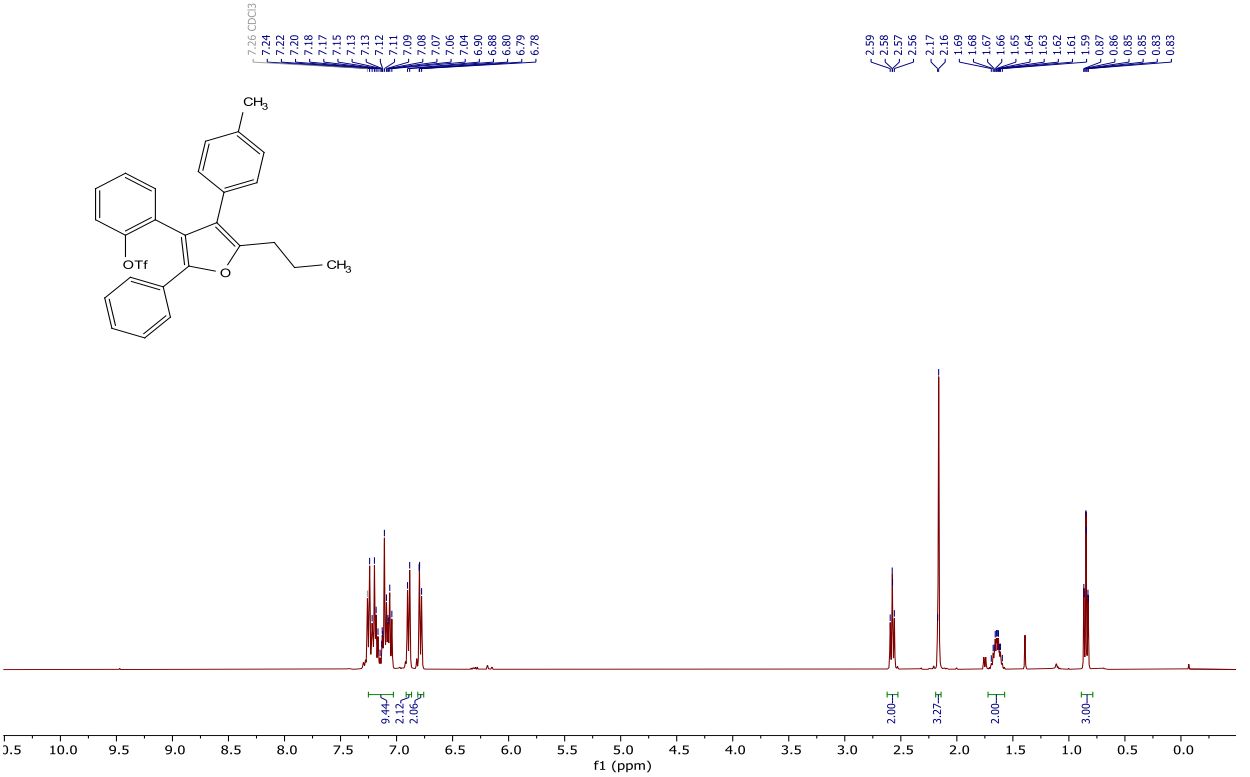


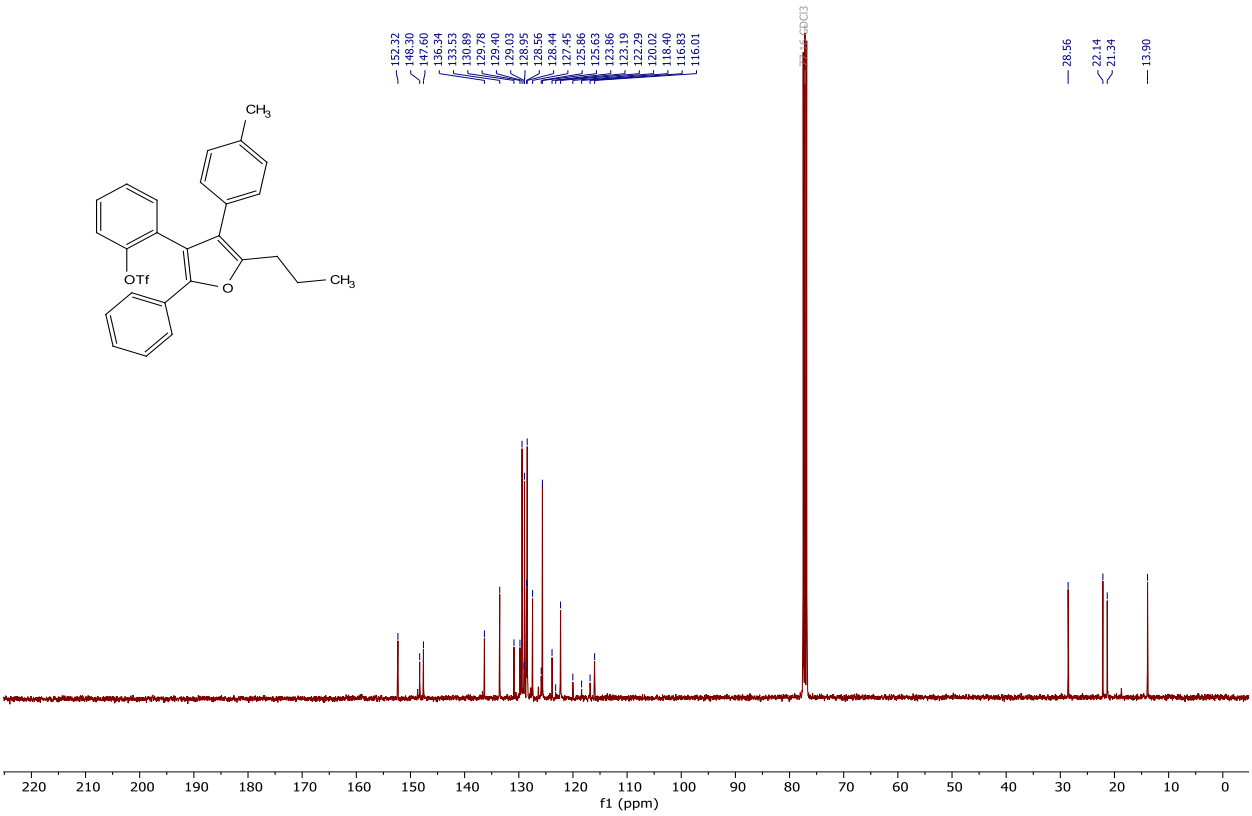
(*Z*)-2-(1-oxo-1-phenyl-3-(*p*-tolyl)hept-2-en-2-yl)phenyl trifluoromethanesulfonate (8)



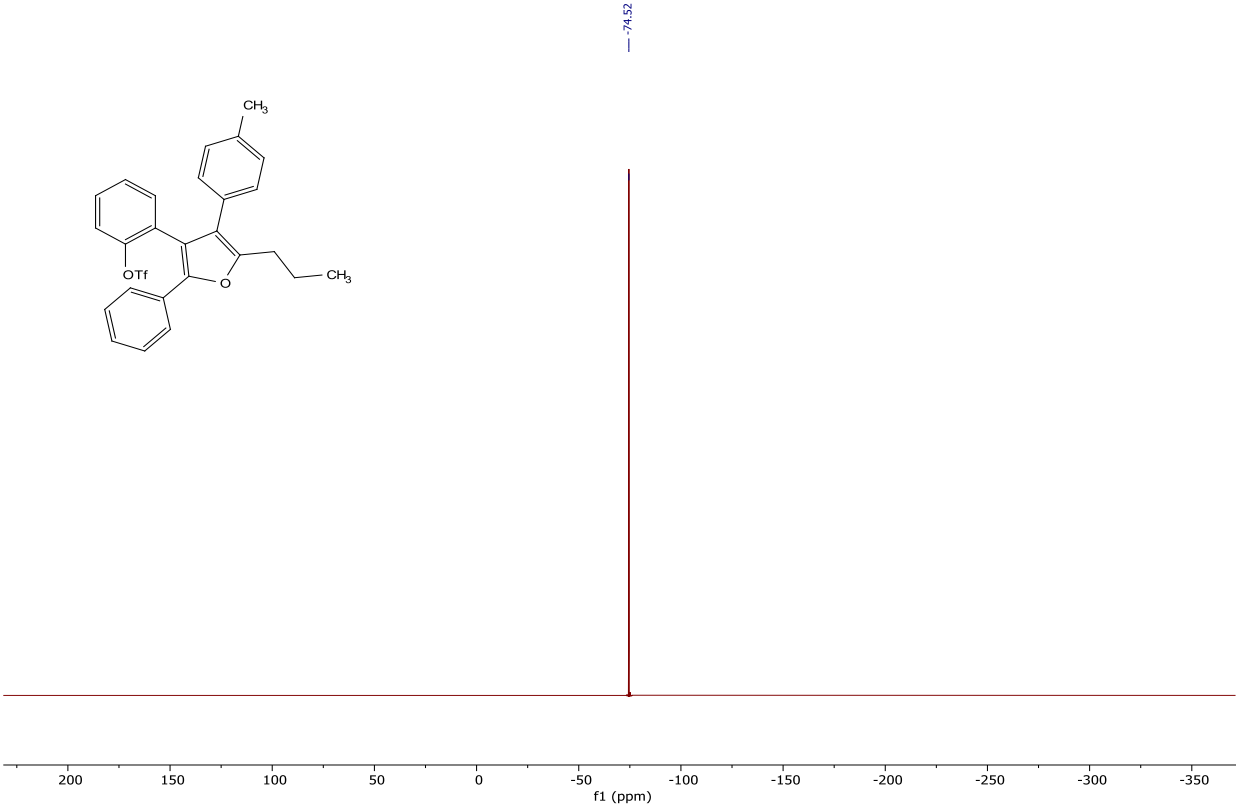


2-(2-phenyl-5-propyl-4-(*p*-tolyl)furan-3-yl)phenyl trifluoromethanesulfonate (9):





^{19}F NMR


-74.52
CH3
OTf
O
CH3
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150
100
50
0
-50
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-150
-200
-250
-300
-350
f1 (ppm)