SUPPORTING INFORMATION

Solvent Controlled Mechanistic Dichotomy in a Au(III)-catalyzed, Heterocyclization Triggered, Nazarov Reaction

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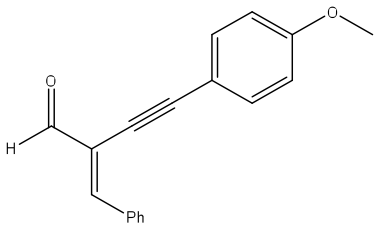
General Consideration: All commercially procured chemicals were used as received. Dichloromethane (DCM), triethylamine (Et_3N), diethyl ether (Et_2O) were distilled from calcium hydride (CaH_2). Tetrahydrofuran (THF) was distilled from lithium aluminum hydride (LAH). Reagent grade solvents were used for solvent extraction and organic extracts were dried over anhydrous sodium sulfate (Na_2SO_4). Silica gel 60 (230-400 mesh ASTM) was used for Flash Chromatography with dry hexane/ethyl acetate eluent system.^{1}H NMR spectra were recorded on 700 MHz Bruker, 500 MHz Varian, 500 MHz Bruker, 400 MHz Varian, or 300 MHz Varian spectrometers. ^{13}C spectra were recorded on 300 MHz Varian spectrometers. The proton chemical shifts (δ) are reported as parts per million relative to 7.26 ppm for $CDCl_3$, 7.14 ppm for C_6D_6, 5.32 for CD_2Cl_2. The carbon chemical shifts (d) were reported as the centerline of triplet at 77.0 ppm for $CDCl_3$, pentate at 54.00 ppm for CD_2Cl_2 and triplet at 128.0 for C_6D_6. Infrared spectra were recorded on sodium chloride plates using a Perkin-Elmer FT-IR Paragon 1000 spectrometer and frequencies were reported as reciprocal of centimeters (cm^{-1}). Mass spectra were recorded using a Jeol JMS-600 instrument. The computations were performed using Gaussian98 on High Performance Computing facility (HPC) at Florida State University.

General procedure for the synthesis of α-alkynyl enals.

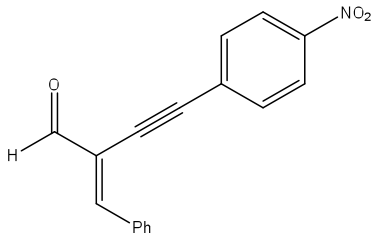
α-alkynyl enals **Ia-f** were synthesized using a Sonogashira protocol.[1] A solution containing 5mL THF, 5mL Et_3N and 274 mg $Pd(PPh_3)_4$ was degassed for 15 minutes before adding 1g (4.74mmols) of α-bromocinnamaldehyde and 190mg of copper (I) iodide. The resulting solution was stirred for 15 minutes before adding 5mmols (0.51g) of phenyl acetylene. The solution was stirred for 3 hours in argon atmosphere before quenching with saturated ammonium chloride solution. The organic layer was extracted using diethyl ether and dried over anhydrous sodium sulfate. Solvent was removed on rotary evaporator and crude was purified on silica column using 10% ethyl acetate and hexane to give 85% (E)-2-benzylidene-4-phenylbut-3-ynal.

Aldehyde **Ia**



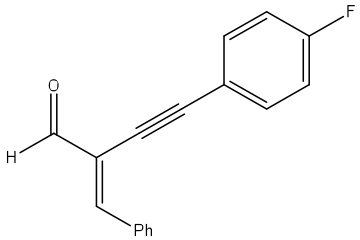
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.64 (s, 1H), 8.15 (m, 2H), 7.52 (d, *J* = 10 Hz, 2H), 7.50 (s, 1H), 7.48 (m, 2H), 6.91 (d, *J* = 5 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.2, 160.3, 150.5, 134.3, 133.4, 131.4, 130.6, 130.2, 128.8, 122.9, 114.6, 114.1, 107.6, 101.3, 82.2, 55.3. FTIR (neat): 3063, 2979, 2936, 2838, 2201, 1735, 1695, 1607, 1594, 1568, 1509, 1450, 1373, 1292, 1251, 1173, 1137, 1107, 1074, 1045, 1030. HRMS (CI+) Calcd. For $C_{18}H_{15}O_2$ (M+1): 263.1072, Found: 263.1066.

Aldehyde **Ib**



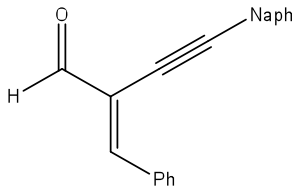
^{1}H NMR (300 MHz, $CDCl_3$): δ 9.66(s, 1H), 8.26(d, *J* = 9Hz 2H), 8.10(m, 2H), 7.73(d, *J* = 9 Hz, 2H), 7.64(s, 1H), 7.52(m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.36, 153.17, 147.05, 133.76, 132.57, 132.18, 130.78, 129.22, 128.99, 123.73, 121.89, 98.28, 87.89. FTIR (neat): 3103, 3067, 2843, 2367, 2345, 2203, 2102, 1696, 1691, 1594, 1515, 1340, 1140, 1107. HRMS (CI+) Calcd. For $C_{17}H_{11}NO_3$ (M+1): 278.0817, Found: 278.0820.

Aldehyde **Ic**



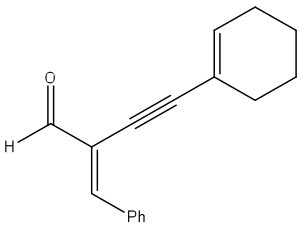
^{1}H NMR (300 MHz, $CDCl_3$): δ 9.63 (s, 1H), 8.16 (m, 2H), 7.63- 7.58 (m, 3H), 7.52 (m, 3H), 7.13 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.05, 164.90, 161.58, 152.02, 134.13, 134.01, 131.94, 130.89, 129.10, 122.80, 118.99, 118.94, 116.27, 115.97, 99.93, 83.32. FTIR (neat): 3368, 3065, 3029, 2985, 2940, 2836, 2716, 2205, 1894, 1734, 1694, 1593, 1569, 1505, 1450, 1414, 1373, 1324, 1304, 1233, 1156, 1137, 1094, 1075, 1046. HRMS (EI+) Calcd. For $C_{17}H_{11}OF$ (M^+): 250.07940, Found: 250.07958.

Aldehyde **Id**



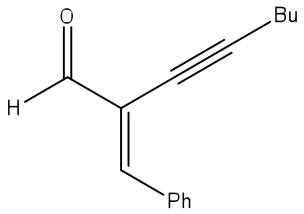
^{1}H NMR (300 MHz, C_6D_6): δ 9.31(s, 1H), 8.18(m, 1H), 7.81(m, 2H) 7.45(m, 3H), 7.25-7.05(m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.33, 151.42 134.48, 133.53, 133.42, 131.91, 131.25, 130.95, 129.98, 129.12, 128.57, 127.54, 126.94, 126.62, 125.48, 123.26, 120.52, 99.78, 88.16. FTIR (neat): 3057, 2827, 2712, 2193, 1693, 1595, 1449, 1416, 1323, 1304, 1239, 1217, 1179, 1160, 1143, 1081, 1072. HRMS (EI+) Calcd. For $C_{21}H_{14}O$ (M^+): 282.10447, Found: 282.10373.

Aldehyde **Ie**



^{1}H NMR (500 MHz, $CDCl_3$): δ 9.59 (s, 1H), 8.1 (m, 2H), 7.46 (m, 3H), 7.44 (s, 1H), 6.35 (tt, *J* = 2, 4 Hz, 1H), 2.3 (dtt, *J* = 2,5,4.5Hz, 2H), 2.19 (dtt, *J* = 2,5,2.5Hz, 2H), 1.72 (m, 2H), 1.65(m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 189.08, 157.89, 146.09, 134.72, 130.98, 130.65, 128.61, 120.51, 106.31, 101.25, 93.74, 64.13, 31.83, 22.89, 14.35. FTIR (neat): 3062, 3026, 2932, 2859, 2838, 2194, 1694, 1625, 1593, 1567, 1493, 1449, 1434, 1414, 1221, 1124, 1070. HRMS (CI+) Calcd. For $C_{17}H_{16}O$ (M+1): 237.1279, Found: 237.1278.

Aldehyde **If**

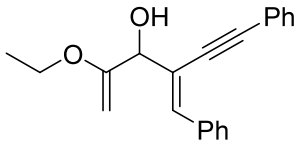


^{1}H NMR (500 MHz, $CDCl_3$): 9.56 (s, 1H), 8.10 (m, 2H), 7.46(m, 2H), 7.42(s, 1H), 2.57(q, *J* = 7Hz, 2H), 1.54 (sextet, *J* = 6.8Hz, 2H), 0.97 (t, *J* = 7Hz, 3H).

General Procedure for Synthesis of Alcohol IIa.

A 5M THF solution of ethyl vinylether (10 mmol) was prepared in dry round bottom flask that was filled with argon gas. The flask was cooled to -78^{o}C using acetone and dry ice. To this solution, a solution ^{t}BuLi (5 mmol) in hexane was added very slowly and carefully using a syringe. The solution turns bright yellow with precipitates. Next, the flask was placed in an ice bath and the reaction mixture was warmed to 0 ^{o}C and stirred until the bright yellow color disappears. The reaction mixture was then cooled to -78^{o}C in an acetone-dry ice bath and a 0.3M THF solution of aldehyde **Ia** **(**0.232g**,** 1mmol) was added slowly. The resulting reaction mixture was then stirred for another 3 hours before slowly quenching with the aqueous saturated ammonium chloride solution. The organic layer was then extracted using ethyl acetate and dried over anhydrous sodium sulfate before concentrating *in vacuo*. Finally, alcohol **IIa** was isolated in 90% yield (0.27g) using flash silica gel column chromatography with 25% ethyl acetate-hexane mixture. The reaction was performed by placing the entire reaction assembly behind an acrylic shield.

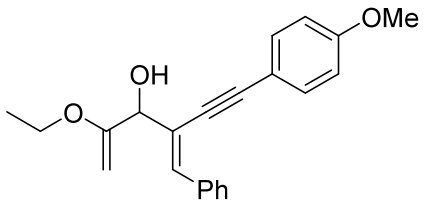
Alcohol **IIa**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (m, 2H), 7.48 (m, 2H), 7.44 – 7.28 (m, 6H), 6.94 (s, 1H), 4.77 (d, *J* = 7.6 Hz, 1H), 4.39 (d, *J* = 2.4 Hz, 1H), 4.15 (d, *J* = 2.4 Hz, 1H), 3.86 (d, *J* = 7.1 Hz,

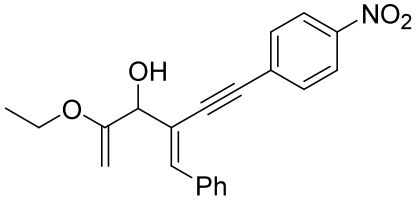
1H), 3.83 (qd, *J* = 7.0, 3.5 Hz, 2H), 2.65 (d, *J* = 7.6 Hz, 1H), 1.31 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 161.58, 136.34, 135, 131.69, 129.13, 128.82, 128.17, 128.68, 128.54, 123.42, 122.77, 97.68, 87.17, 82.87, 76.53, 63.67, 14.41. FTIR (neat): 3446, 3058, 3024, 2980, 2931, 2198, 1736, 1661, 1627, 1490, 1443, 1373, 1290, 1242, 1116, 1070, 1046. HRMS (EI+) Calcd. For $C_{21}H_{20}O_2$ (M^+): 304.14633, Found: 304.14601.

Alcohol **IIb**



Alcohol **IIb** was synthesized in 71% yield (0.24g) using the general procedure described for alcohol **IIa**. ^{1}H NMR (300 MHz, C_6D_6) δ: 8.00 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.9 Hz, 2H), 7.22 – 7.01 (m, 3H), 6.99 (s, 1H), 6.58 (d, *J* = 8.9 Hz, 2H), 4.87 (d, *J* = 7.1 Hz, 1H), 4.58 (d, *J* = 1.2 Hz, 1H), 4.07 (d, *J* = 1.9 Hz, 1H), 3.43 (q, *J* = 7.0 Hz, 2H), 3.13 (s, 3H), 2.30 (d, *J* = 7.1 Hz, 1H), 0.95 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ: 162.17, 160.08, 136.86, 134.52, 133.26, 129.23, 128.37, 128.22, 123.56, 115.90, 114.29, 98.04, 86.63, 82.47, 76.65, 63.11, 54.63, 14.18. FTIR (neat): 3464, 3055, 3023, 2981, 2936, 2906, 2882, 2195, 1736, 1648, 1602, 1568, 1509, 1445, 1374, 1289, 1249, 1155, 1172, 1098, 1046. HRMS (CI+) Calcd. For $C_{22}H_{23}O_3$ (M+1): 335.1647, Found: 335.1638.

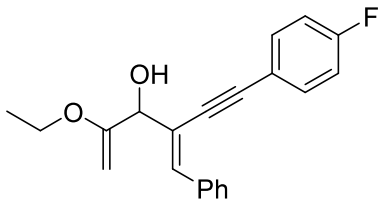
Alcohol **IIc**



Alcohol **IIc** was synthesized in 88% yield (0.31g) using the general procedure described for alcohol **IIa**. ^{1}H NMR (300 MHz, C_6D_6) δ: 7.79 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 8.9 Hz, 2H), 7.20 – 6.99 (m, 3H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.74 (d, *J* = 6.5 Hz, 1H), 4.46 (d, *J* = 2.1 Hz, 1H), 4.01 (d, *J* = 2.2 Hz, 1H), 3.39 (q, *J* = 7.0 Hz, 2H), 2.11 (d, *J* = 6.6 Hz, 1H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ: 161.72, 147.06, 137.26, 136.22, 131.89, 129.61, 129.31,

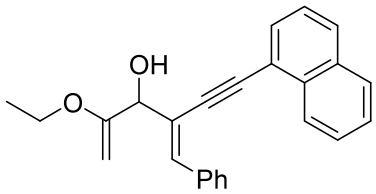
128.89, 128.47, 123.47, 122.43, 95.26, 92.69, 82.64, 76.30, 63.23, 14.13. FTIR (neat):3445, 3065, 3025, 2979, 2929, 2195, 1718, 1590, 1517, 1492, 1341, 1286, 1233, 1106, 1075. HRMS (CI+) Calcd. For $C_{21}H_{19}NO_4$ (M+1): 350.13923, Found: 350.13750.

Alcohol **IId**



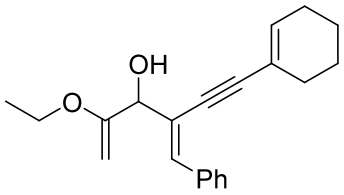
Alcohol **IId** was synthesized in 87% yield (0.28g) using the general procedure described for alcohol **IIa**.^{1}H NMR (300 MHz, CD_2Cl_2) δ: 7.92 (d, J = 8.1 Hz, 2H), 7.55 – 7.28 (m, 5H), 7.09 (t, J = 8.8 Hz, 2H), 6.95 (s, 1H), 5.44 – 5.18 (m, 1H), 4.75 (d, J = 7.3 Hz, 1H), 4.38 (d, J = 2.2 Hz, 1H), 4.18 (d, J = 2.3 Hz, 1H), 3.83 (q, J = 7.0 Hz, 2H), 2.68 (d, J = 7.4 Hz, 1H), 1.31 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 164.56, 161.65, 161.25, 136.37, 135.17, 133.76, 133.64, 129.15, 128.72, 128.56, 122.70, 119.74, 119.69, 116.13, 115.84, 96.53, 87.08, 82.94, 76.54, 63.68, 14.44. FTIR (neat): 3446, 3059, 3025, 2981, 2932, 2905, 2883, 2201, 1891, 1736, 1661, 1626, 1598, 1507, 1478, 1457, 1374, 1235, 1156, 1093, 1074, 1046. HRMS (EI+) Calcd. For $C_{21}H_{19}O_2F$ (M^+): 322.13691, Found: 322.13690.

Alcohol **IIe**



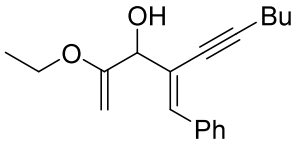
Alcohol **IIe** was synthesized in 71% yield (0.25g) using the general procedure described for alcohol **IIa**. ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 8.49 – 7.25 (m, 12H), 7.04 (s, 1H), 4.87 (d, J = 7.1 Hz, 1H), 4.49 (d, J = 2.2 Hz, 1H), 4.25 (d, J = 2.3 Hz, 1H), 3.87 (q, J = 7.0 Hz, 2H), 2.74 (d, J = 7.2 Hz, 1H), 1.32 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 161.82, 136.49, 135.28, 133.51, 133.42, 130.89, 129.25, 128.77, 128.62, 128.57, 127.11, 126.83, 126.60, 125.63, 123.16, 121.17, 95.86, 92.05, 83.14, 76.76, 63.79, 14.49. FT IR (neat):3419, 3057, 3025, 2979, 2930, 2189, 1660, 1623, 1446, 1402, 1289, 1272, 1240, 1129, 1117, 1087, 1071. HRMS (EI+) Calcd. For $C_{25}H_{22}O_2$ (M^+): 354.16198, Found: 354.16115.

Alcohol **IIf**



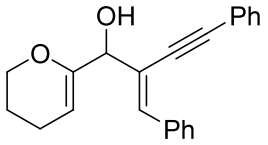
Alcohol **IIf** was synthesized in 72% yield (0.22g) using the general procedure described for alcohol **IIa**. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.23-7.11 (m, 3H), 6.99 (s, 1H), 6.24 – 6.12 (m, 1H), 4.87 (d, *J* = 6.8 Hz, 1H), 4.60 (d, *J* = 2.0 Hz, 1H), 4.11 (d, *J* = 2.0 Hz, 1H), 3.50 (qd, *J* = 7.0, 3.5 Hz, 2H), 2.35 (d, *J* = 7.1 Hz, 1H), 2.35(m, 2H)1.85 (m, 2H), 1.41 (m, 2H), 1.34 (m, 2H), 1.02 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ: 162.21, 136.88, 135.37, 134.13, 129.16, 128.27, 128.14, 123.63, 121.40, 100.10, 85.22, 82.30, 76.61, 63.06, 29.07, 25.77, 22.33, 21.54, 14.15. FTIR (neat): 3450, 3058, 3024, 2978, 2930, 2860, 2181, 1738, 1660, 1626, 1599, 1493, 1447, 1374, 1290, 1239, 1116, 1074, 1048. HRMS (EI+) Calcd. For $C_{21}H_{24}O_2$ (M^+): 308.17763, Found: 308.17659.

Alcohol **IIg**



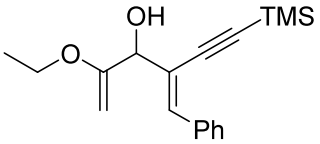
Alcohol **IIg** was synthesized in 75% yield (0.23g) using the general procedure described for alcohol **IIa**. ^{1}H NMR (400 MHz, C_6D_6) δ: 7.95(d, *J*= 8Hz, 2H), 7.18 (m, 2H), 7.05(m, 1H), 6.89(s, 1H), 4.78 (d, *J* = 8Hz, 1H), 4.52(d, *J* = 4Hz, 1H), 4.04(d, *J* = 4Hz, 1H), 3.44 (q, *J* = 8Hz, 2H), 2.29 (d, *J* = 8Hz, 1H), 2.14 (t, *J* = 8Hz, 2H), 1.3 (m, 4H), 0.97 (t, *J* = 8Hz, 3H), 0.75 (t, *J* = 8Hz, 3H) ^{13}C NMR (75 MHz, C_6D_6) δ: 162.35, 136.86, 133.89, 129.01, 128.07, 123.79, 99.26, 82.22, 78.54, 76.72, 63.03, 30.70, 22.05, 19.57, 14.16, 13.54. FTIR (neat):3448, 3057, 3025, 2958, 2931, 2872, 2214, 1661, 1624, 1494, 1447, 1378, 1291, 1235, 1072. HRMS (ESI+) Calcd. For $C_{19}H_{24}O_2Na$ (M + Na): 307.16740, Found: 307.16841.

Alcohol **IIh**



Alcohol **IIh** was synthesized in 66% yield (0.21g) using the general procedure described for alcohol **IIa**. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (d, J = 7.6 Hz, 1H), 7.67 – 7.17 (m, 4H), 6.96 (s, 1H), 5.02 (t, J = 3.8 Hz, 1H), 4.70 (d, J = 7.2 Hz, 1H), 4.11 – 4.02 (m, 2H), 2.54 (d, J = 7.2 Hz, 1H), 2.30 – 2.02 (m, 2H), 1.89 – 1.83 (m, 2H). ^{13}C NMR (75 MHz, C_6D_6) δ: 153.69, 136.76, 135.09, 131.70, 129.29, 128.52, 128.38, 128.35, 128.32, 123.91,123.22, 97.73, 97.52, 88.34, 76.08, 66.28, 22.46, 20.20. HRMS (EI+) Calcd. For $C_{22}H_{20}O_2$ (M^+): 316.14633, Found: 316.14592.

Alcohol **IIi**

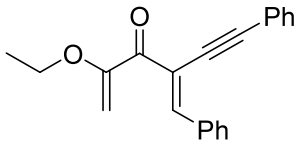


Alcohol **IIi** was synthesized in 68% yield (0.2g) using the general procedure described for alcohol **IIa**. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (m, 2H), 7.17(m, 2H), 7.04(m, 1H), 6.94(s, 1H), 4.72(d, J = 7.33Hz, 1H), 4.45(d, J = 2.16Hz, 1H), 3.98 (d, J = 1.83Hz, 1H), 3.39 (qd, J = 7Hz, J = 2.01Hz, 1H), 3.37 (qd, J = 7.01 Hz, J = 2.3Hz, 1H), 2.22 (d, J = 7.3Hz, 1H), 0.92 (t, J = 7.12Hz, 3H), 0.16 (s, 9H). ^{13}C NMR (75 MHz, C_6D_6) δ: 161.96, 136.50, 136.33, 129.43, 128.65, 128.32, 123.25, 103.59, 82.61, 76.32, 63.17, 14.24, 0.22. FTIR (neat): 3449, 3059, 3025, 2980, 2961, 2139, 1740, 1661, 1627, 1494, 1478, 1448, 1374, 1249, 1116, 1071, 1047. HRMS (EI+) Calcd. For $C_{18}H_{24}O_2Si$ (M^+): 300.15456, Found: 300.15417.

General Procedure for Oxidation of Alcohol IIa-i

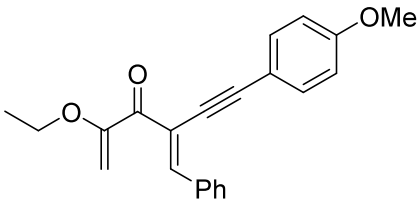
A 0.1M solution of alcohol **IIa** (1 mmol) was prepared in dry methylene chloride containing 4A^{o} molecular sieves. To this solution active manganese oxide (10 mmol) was added at room temperature. The reaction mixture was stirred for 18 hours at room temperature before filtering it through celite pad and concentrating *in vacuo*. Ketone **1** was isolated in 56% yield (0.17g) using silica gel column (ethyl acetate: hexane, 1:5 v/v).

Ketone **1**



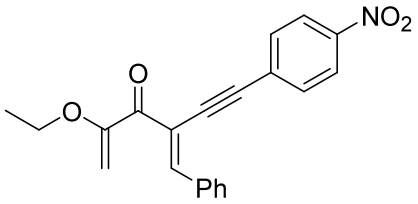
^{1}H NMR (400 MHz, C_6D_6) δ: 7.93 (m, 2H), 7.71 (s, 1H), 7.41 (m, 2H), 7.09 – 6.94 (m, 6H), 5.19 (d, *J* = 2.5 Hz, 1H), 4.31 (d, *J* = 2.5 Hz, 1H), 3.42 (q, *J* = 7.0 Hz, 2H), 1.03 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ: 188.31, 158.75, 144.84, 135.22, 131.60, 130.54, 130.41, 128.71, 128.60, 128.57, 123.47, 120.92, 99.47, 92.53, 87.01, 63.73, 14.18. FTIR (neat): 3060, 3030, 2981, 2928, 2882, 2196, 1676, 1607, 1566, 1490, 1445, 1381, 1363, 1304, 1243, 1215, 1155, 1138, 1115, 1058, 1029. HRMS (EI+) Calcd. For $C_{21}H_{18}O_2$ (M^+): 302.13068, Found: 302.13046.

Ketone **4**



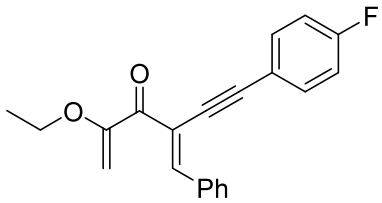
Alcohol **IIb** was oxidized to ketone **4** in 60% yield (0.2g) using the general procedure described for the oxidation of alcohol **IIa**. ^{1}H NMR (300 MHz, C_6D_6) δ: 7.96 (d, *J* = 7.3 Hz, 2H), 7.68 (s, 1H), 7.36 (d, *J* = 8.9 Hz, 2H), 7.06 (m, 3H), 6.55 (d, *J* = 8.8 Hz, 2H), 5.20 (d, *J* = 2.5 Hz, 1H), 4.31 (d, *J* = 2.4 Hz, 1H), 3.39 (q, *J* = 7.0 Hz, 2H), 3.11 (s, 3H), 1.02 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 189.38, 160.51, 158.06, 144.13, 135.14, 133.19, 130.73, 130.50, 128.82, 120.80, 115.13, 114.47, 99.84, 93.93, 85.20, 64.26, 14.41. FTIR (neat): 3060, 2929, 2195, 1736, 1676, 1606, 1566, 1509, 1446, 1379, 1303, 1291, 1250, 1173, 1137, 1075, 1057, 1031. HRMS (CI+) Calcd. For $C_{22}H_{21}O_3$ (M+1): 333.1491, Found: 333.1482.

Ketone **6**



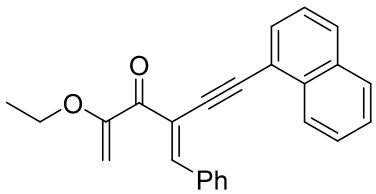
Alcohol **IIc** was oxidized to ketone **6** in 61% yield (0.21g) using the general procedure described for the oxidation of alcohol **IIa**. ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 8.23 (d, J = 8.8 Hz, 2H), 8.06 (m, 2H), 7.71 (s, 1H), 7.66 (d, J = 8.8 Hz, 2H), 7.49 (m, 3H)., 5.14 (d, J = 2.8 Hz, 1H), 4.76 (d, J = 2.8 Hz, 1H), 3.93 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 188.56, 157.86, 147.54, 147.15, 134.62, 132.38, 131.33, 130.68, 129.84, 128.92, 123.94, 119.66, 96.92, 93.92, 91.13, 64.32, 14.33. FTIR (neat):3105, 3063, 2980, 2927, 2196, 1674, 1594, 1565, 1517, 1491, 1447, 1341, 1306, 1261, 1134, 1106, 1056. HRMS (EI+) Calcd. For $C_{21}H_{17}NO_4$ (M^+): 347.1158, Found: 347.1147.

Ketone **8**



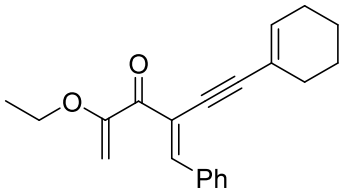
Alcohol **IId** was oxidized to ketone **8** in 50% yield (0.16g) using the general procedure described for the oxidation of alcohol **IIa**. ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 8.09 (m, 2H), 7.61 (s, 1H), 7.55-7.45 (m, 5H), 7.12 (m, J = 2H), 5.14 (d, J = 3 Hz, 1H), 4.76 (d, J = 3 Hz, 1H), 3.91 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 189.11, 164.72, 161.41, 157.97, 145.18, 133.70, 130.90, 130.52, 128.82, 120.36, 119.35, 116.21, 115.92, 98.26, 93.89, 85.97, 64.25, 14.35. FTIR (neat): 3055, 2986, 2203, 1734, 1683, 1600, 1507, 1265, 1234, 1156, 1093, 1059. HRMS (EI+) Calcd. For $C_{21}H_{17}O_2F$ (M^+): 320.1203, Found: 320.1213.

Ketone **10**



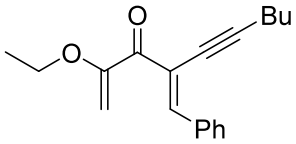
Alcohol **IIe** was oxidized to ketone **10** in 55% yield (0.19g) using the general procedure described for the oxidation of alcohol **IIa** in 48hrs. ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 8.65 (d, *J* = 8.3 Hz, 1H), 8.25 – 7.21 (m, 7H), 7.17 (m, 4H), 5.20 (d, *J* = 2.5 Hz, 1H), 4.33 (d, *J* = 2.5 Hz, 1H), 3.40 (q, *J* = 7.0 Hz, 2H), 0.96 (t, *J* = 7.0 Hz 2H). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.54 – 7.16 (m, 12H), 5.22 (d, *J* = 2.9 Hz, 1H), 4.81 (d, *J* = 2.9 Hz, 1H), 3.95 (q, *J* = 7.0 Hz, 2H), 1.39 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 189.39, 158.16, 145.06, 135.08, 133.51, 133.46, 130.96, 130.81, 130.62, 129.62, 128.90, 128.60, 127.29, 126.91, 126.42, 125.61, 120.84, 97.98, 93.94, 91.01, 64.33, 14.40. FTIR (neat):3057, 3027, 2980, 2929, 2193, 1676, 1607, 1586, 1565, 1493, 1446, 1303, 1272, 1181, 1141, 1088, 1056. HRMS (EI+) Calcd. For $C_{25}H_{20}O_2$ (M^+): 352.14633, Found: 352.14685.

Ketone **12**



Alcohol **IIf** was oxidized to ketone **12** in 65% yield (0.12g) using the general procedure described for the oxidation of alcohol **IIa**. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.02 (m, 2H), 7.48 (s, 1H), 7.46 – 7.35 (m, 3H), 6.22 (ddd, *J* = 5.9, 3.9, 1.8 Hz, 1H), 5.16 (d, *J* = 2.9 Hz, 1H), 4.70 (d, *J* = 2.9 Hz, 1H), 3.90 (q, *J* = 7.0 Hz, 2H), 2.24 (m, 2H), 2.17 (m, 2H), 1.70 (m, 2H), 1.64 (m, 1H), 1.41 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6) δ: 188.58, 158.73, 145.81, 143.36, 135.90, 135.49, 131.14, 130.99, 130.41, 130.05, 101.81, 92.39, 84.64, 63.61, 28.84, 25.79, 22.27, 21.49, 14.16. FTIR (neat): 3060, 3025, 2934, 2861, 2185, 1718, 1682, 1670, 1582, 1561, 1493, 1448, 1352, 1323, 1119, 1109, 1098, 1075, 1046. HRMS (CI+) Calcd. For $C_{21}H_{22}O_2$ (M+1): 307.16981, Found: 307.16867.

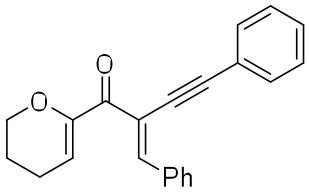
Ketone **14**



Alcohol **IIg** was oxidized to ketone **14** in 55% yield (0.15g) using the general procedure described for the oxidation of alcohol **IIa**. ^{1}H NMR (400 MHz, C_6D_6) δ: 7.92 (d, *J* = 7.5 Hz,

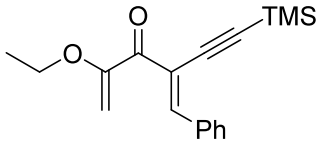
2H), 7.54 (s, 1H), 7.21 – 6.98 (m, 3H), 5.09 (d, J = 2.5 Hz, 1H), 4.29 (d, J = 2.5 Hz, 1H), 3.38 (q, J = 7.0 Hz, 2H), 2.14 (t, J = 6.6 Hz, 2H), 1.45 – 1.15 (m, 2H), 1.02 (t, J = 7.0 Hz, 3H), 0.72 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ: 189.02, 158.69, 143.41, 135.44, 130.21, 130.01, 128.39, 121.90, 101.46, 92.39, 77.87, 63.56, 30.50, 22.06, 19.70, 14.15, 13.53. FTIR (neat): 3062, 3026, 2959, 2933, 2219, 1717, 1700, 1585, 1566, 1448, 1353, 1324, 1154, 1066. HRMS (ESI+) Calcd. For $C_{19}H_{22}O_2Na$ (M + Na): 305.151575, Found: 305.15349.

Ketone **22**



Alcohol **IIh** was oxidized to ketone **22** in 67% yield (0.21g) using the general procedure described for the oxidation of alcohol **IIa**. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.05(m, 2H), 7.50(m, 2H), 7.47(s, 1H), 7.36-7.45(m, 6H), 6.24(t, J = 4.27Hz, 1H), 4.19(t, J = 4.88Hz, 2H), 2.30(td, J = 6.41, 4.27Hz, 2H), 1.94(tt, J = 6.41, 5.19Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6) δ: 187.13, 151.80, 143.80, 135.42, 131.64, 130.36, 130.12, 128.65, 128.57, 128.54, 123.59, 121.28, 111.97, 99.43, 87.33, 65.90, 21.67, 20.74. FTIR (neat): 3060, 3032, 2954, 2934, 2875, 2198, 1668, 1662, 1627, 1598, 1490, 1446, 1388, 1291, 1274, 1259, 1184, 1112, 1070, 1054, 1027. HRMS (EI+) Calcd. For $C_{22}H_{18}O_2$ (M^+): 314.13068, Found: 314.13038.

Ketone **20**



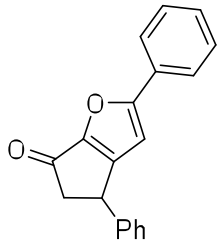
Alcohol **IIi** was oxidized to ketone **20** in 43% yield (0.13g) using the general procedure described for the oxidation of alcohol **IIa**. ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 8.08(m, 2H), 7.55(s, 1H), 7.41-7.46(m, 3H), 5.09(d, J = 2.7 Hz , 1H), 4.70(d, J = 2.8 Hz , 1H), 3.89 (q, J = 6.9 Hz , 2H), 1.40 (t, J = 7 Hz , 3H), 0.28(s, 9H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 189.08, 157.89, 146.09, 134.72, 130.98, 130.65, 128.61, 120.51, 106.31, 101.25, 93.74, 64.13, 14.15, 0.47. FTIR (neat):3062, 3026, 2981, 2960, 2140, 1739, 1681, 1608, 1566, 1494, 1447, 1373, 1305, 1250,

1163, 1116, 1092, 1059. HRMS (EI+) Calcd. For $C_{18}H_{22}O_2Si$ (M^+): 298.13891, Found: 298.13849.

General Procedure for Gold Catalyzed Heterocyclization – Nazarov Cyclization

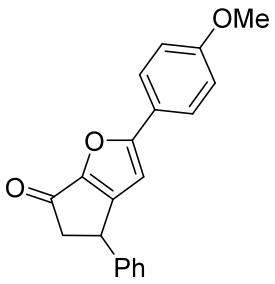
To a solution of 5 mol% of gold trichloride and15 mol% of silver hexafluoro antimonate, under an argon atmosphere, a 0.2M solution of ketone **1** (0.2mmol, 60mg) in methylene chloride was added via syringe. The mixture was stirred for 3hrs at ambient temperature before filtering through plug silica. The solution was then concentrated *in vacuo* and the product was isolated using silica gel column chromatography (ethyl acetate: hexane, 1:5 v/v) in 67% yield (36mg)

Heterocycle **2**



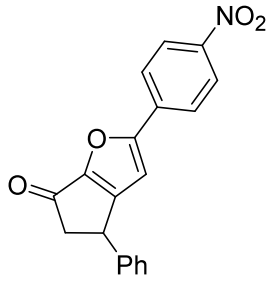
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.79(m, 2H), 7.43 (m, 3H), 7.36 (m, 2H), 7.29(m, 1H), 7.23(m, 2H), 6.71 (s, 1H), 4.43 (dd, J = 6.71, 1.83 Hz, 1H), 3.46 (dd, J = 18, 7Hz, 1H), 2.87 (dd, J = 18, 2.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 186.98, 165.62, 160.36, 153.97, 141.68, 131.62, 130.07, 129.59, 129.17, 127.46, 127.25, 125.49, 104.69, 50.96, 38.32. FTIR (Methylene chloride solution): 3054, 2986, 2927, 1792, 1696, 1451, 1421, 1358, 1265, 1178, 1087, 1083, 1035. HRMS (EI+) Calcd. For $C_{19}H_{14}O_2$ (M^+): 274.09938, Found: 274.09922.

Heterocycle **5**



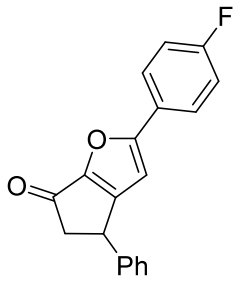
Heterocycle **5** was obtained in 75% yield (45mg) from ketone **4** (0.2mmol, 66mg) in 5 minutes using general procedure described for the synthesis of heterocycle **2**. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.9 Hz, 2H), 7.29 (m, 5H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.56 (s, 1H), 4.39 (dd, *J* = 6.5, 1.8 Hz, 1H), 3.86 (s, 1H), 3.43 (dd, *J* = 18.2, 6.7 Hz, 1H), 2.83 (dd, *J* = 18.2, 2.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 186.68, 166.03.62, 160.24, 160.91, 141.83, 129.19, 127.46, 127.32, 127.20, 122.36 114.68, 103.24, 55.63, 50.97, 38.38. FTIR (Methylene chloride solution): 3054, 2987, 1694, 1610, 1481, 1434, 1422, 1265, 1177, 1086, 1058, 1035. HRMS (EI+) Calcd. For $C_{20}H_{16}O_3$ (M^+): 304.1100, Found: 304.1096.

Heterocycle **7**



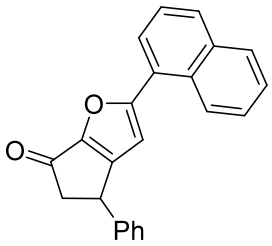
Heterocycle **7** was obtained in 54% yield (33mg) from ketone **6** in 36 hours using the general procedure described for the synthesis of the heterocycle **2**. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.15 – 7.06 (m, 3H), 6.89 – 6.86 (m, 2H), 6.48 (m, 1H), 3.77 (d, *J* = 6.7 Hz, 1H), 3.02 (dd, *J* = 18.0, 6.8 Hz, 1H), 2.60 (dd, *J* = 18.0, 2.3 Hz, 1H), 2.04 – 1.80 (m, 4H), 1.54 – 1.26 (m, 4H). ^{1}H NMR (300 MHz, $CDCl3l_3$) δ: 7.13 – 6.98 (m, 3H), 6.90 – 6.77 (m, 2H), 6.44 (t, *J* = 4.0 Hz, 1H), 5.69 (s, 1H), 3.71 (dd, *J* = 6.8, 2.3 Hz, 1H), 2.97 (dd, *J* = 18.0, 6.8 Hz, 1H), 2.52 (dd, *J* = 18.0, 2.4 Hz, 1H), 2.01 – 1.74 (m, 4H), 1.48 – 1.25 (m, 4H). ^{13}C NMR (125 MHz, C_6D_6) δ: 186.26, 162.01, 158.76, 156.18, 148.41, 142.12, 135.12, 129.52, 128.68, 128.58, 125.77, 124.50, 107.64, 51.08, 38.37. FTIR(neat): 3102, 2963, 1699, 1601, 1516, 1473, 1435, 1341, 1257, 1106, 1086, 1057, 1026. HRMS (EI+) Calcd. For $C_{19}H_{13}NO_4$ (M^+): 319.0845, Found: 319.0849.

Heterocycle **9**



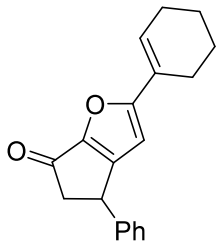
Heterocycle **9** was obtained in 60% yield (35mg) from ketone **8** in 18 hours using the general procedure described for the synthesis of heterocycle **2**. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.8 (m, 2H), 7.14 – 7.39 (m, 7H), 6.69 (s, 1H), 4.43 (dd, J = 6 Hz, J = 3 Hz,1H), 3.42 (dd, J = 18.0, 6 Hz, 1H), 2.80 (dd, J = 18.0, 3 Hz, 1H. ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 186.65, 165.44, 164.37, 162.13, 160.28, 154.13, 141.94, 129.12, 127.57, 127.46, 127.38, 127.32, 126.19, 116.51, 116.21, 104.65, 50.95, 38.26. FTIR(neat): 3363, 3111, 3087, 3058, 3035, 2979, 2924, 2304, 2197, 1928, 1811, 1751, 1694, 1607, 1479, 1434, 1370, 1292, 1238, 1194, 1160, 1088, 1058. HRMS (EI+) Calcd. For $C_{19}H_{13}O_2F$ (M^+): 292.0900, Found: 292.0888.

Heterocycle **11**



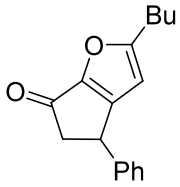
Heterocycle **11** was obtained in 52% yield (33mg) from ketone **10** in 24 hours using the general procedure described for the synthesis of heterocycle **2**. ^{1}H NMR (300 MHz, C_6D_6) δ: 8.35 (dd, J = 6.1, 3.6 Hz, 1H), 7.64 – 7.42 (m, 3H), 7.19 (m, 2H), 7.08 – 6.95 (m, 3H), 6.81 (dd, J = 7.6, 1.5 Hz, 2H), 6.15 (s, 1H), 3.74 (dd, J = 6.7, 2.2 Hz, 1H), 2.99 (dd, J = 18.1, 6.8 Hz, 1H), 2.56 (dd, J = 18.1, 2.4 Hz, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 186.85, 165.34, 159.79, 154.59, 142.05, 134.15, 130.84, 130.34, 129.15, 128.96, 127.91, 127.61, 127.38, 127.29, 126.62, 125.45, 125.20, 109.24, 51.08, 38.40. FTIR (neat): 3058, 3028, 2962, 2922, 1697, 1496, 1439, 1391, 1363, 1419, 1268, 1084, 1047, 1027. HRMS (EI+) Calcd. For $C_{23}H_{16}O_2$ (M^+): 324.1150, Found: 324.1140.

Heterocycle **13**



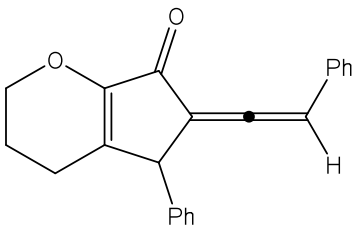
Heterocycle **13** was obtained in 51% yield (28mg) from ketone **12** in 6 hours using the general procedure described for the synthesis of heterocycle **2**. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.21 – 7.13 (m, 3H), 6.93 (m, 2H), 6.55 (t, *J* = 4.0 Hz, 1H), 5.80 (s, 1H), 3.81 (dd, *J* = 6.8, 2.3 Hz, 1H), 3.07 (dd, *J* = 18.0, 6.8 Hz, 1H), 2.68 (dd, *J* = 18.0, 2.4 Hz, 1H), 2.06 – 1.91 (m, 4H), 1.55 – 1.37 (m, 4H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 186.7, 167.2, 160.2, 152.8, 141.7, 138.6, 129.7, 128.9, 127.2,127, 103.2, 50.7, 38.1, 25.5, 24.6, 22, 21.8. FTIR (neat): 3060, 3029, 2931, 2859, 1663, 1639, 1577, 1499, 1450, 1406, 1359, 1307, 1276, 1250, 1138, 1079, 1061, 1021. . HRMS (CI+) Calcd. For $C_{19}H_{18}O_2$ (M+1): 279.13851, Found: 279.13776.

Heterocycle **15**



Heterocycle **15** was obtained in 85% yield (43mg) from ketone **14** in 12 hours using the general procedure described for the synthesis of heterocycle **2**. ^{1}H NMR (500 MHz, C_6D_6) δ: 7.16 – 7.04 (m, 3H), 6.89 (dd, *J* = 5.1, 3.1 Hz, 2H), 5.50 (s, 1H), 3.70 (dd, *J* = 6.8, 2.2 Hz, 1H), 3.94 (dd, *J* = 17.9, 6.8 Hz, 1H), 2.53 (dd, *J* = 17.9, 2.3 Hz, 1H), 2.25 (td, *J* = 7.4, 2.0 Hz, 2H), 1.31 (tt, *J* = *15.6, 7.5* Hz, 2H), 1.07 (qt, *J* = 7.6, 7.6 Hz, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ: 185.10, 169.15, 158.94, 154.11, 142.37, 128.89, 127.17, 127.00, 105.53, 50.55, 38.05, 29.56, 28.64, 22.26, 13.66. FTIR (neat): 3062, 3029, 2958, 2931, 2872, 1704, 1524, 1425, 1080, 1045, 1029. HRMS (EI+) Calcd. For $C_{17}H_{18}O_2$ (M^+): 254.1307, Found: 254.1297.

Cyclopentenone **23**



[a]To a solution of ketone **22** in 0.01M distilled methylene chloride, a standard solution of 5 mol% $AuCl_3$ and 15 mol% $AgSbF_6$ was added. The reaction was monitored using silica gel TLC. The work up of this reaction was done using the general procedure described above.

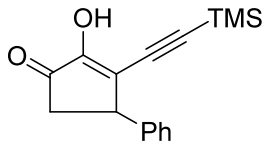
[b] To a solution of ketone **22** in 0.01M distilled acetonitrile, a standard solution of 5 mol% $AuCl_3$ and 15 mol% $AgSbF_6$ was added. The reaction was monitored using silica TLC. The work up of this reaction was done using the general procedure described above.

[c] To a solution of ketone **22** in 0.01M distilled methylene chloride, a standard solution of 5 mol% Ph_3PAuCl and 5 mol% $AgSbF_6$ was added. The reaction was monitored using silica TLC. The work up of this reaction was done using the general procedure described above.

[d]To a solution of ketone **22** in 0.01M distilled acetonitrile, a standard solution of 5 mol% Ph_3PAuCl and 5 mol% $AgSbF_6$ was added. The reaction was monitored using silica TLC. The work up of this reaction was done using the general procedure described above.

[e]To a solution of ketone **22** in 0.005M distilled methylene chloride, a standard solution of 5 mol% $AuCl_3$ and 15 mol% $AgSbF_6$ was added. The reaction was monitored using silica TLC. The work up of this reaction was done using the general procedure described above giving the pure compound as a single diastereomer.^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34-7.15 (m, 10H), 6.62 (d, J = 1.89Hz, 1H), 4.57 (d, J = 1.8Hz 1H), 4.23 H_A(dt, J = 11.6, 3.3 Hz, 1H), 4.21 H_B(dt, J = 11.9, 3.0 Hz, 1H), 2.27 H_A(dt, J = 18.9, 6.5 Hz, 1H), 2.17 H_B(dt, J = 18.6, 6.0 Hz, 1H), 1.99 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 206.66, 186.88, 152.56, 142.51, 139.89, 132.23, 131.71, 131.42, 130.33, 129.40, 129.18, 129.15, 129.04, 128.99, 128.92, 128.85, 128.43, 128.24, 128.11, 128.00, 127.80, 127.69, 127.59, 127.48, 110.36, 102.35, 102.06, 67.71, 48.42, 22.20, 21.97. IR (neat): 3055, 2987, 2960, 1948, 1694, 1643, 1493, 1454, 1422, 1396, 1298, 1265, 1183, 1115, 1101, 1074, 1043. HRMS (EI+) Calcd. For $C_{22}H_{18}O_2$ (M^+): 314.13068, Found: 314.12998.

Cyclopentenone **21**



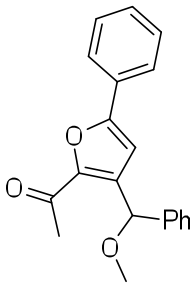
[a]To a solution of ketone **20** in 0.3M distilled methylene chloride, a standard solution of 5 mol% $AuCl_3$ and 15 mol% $AgSbF_6$ was added. The reaction was monitored using silica gel TLC. The work up of this reaction was done using the general procedure described above.

[b] To a solution of ketone **20** in 0.3M distilled acetonitrile, a standard solution of 5 mol% $AuCl_3$ and 15 mol% $AgSbF_6$ was added. The reaction was monitored using silica TLC. The work up of this reaction was done using the general procedure described above.

[c] To a solution of ketone **20** in 0.3M distilled methylene chloride, a standard solution of 5 mol% Ph_3PAuCl and 5 mol% $AgSbF_6$ was added. The reaction was monitored using silica gel TLC. The work up of this reaction was done using the general procedure described above.

[d]To a solution of ketone **20** in 0.3M distilled acetonitrile, a standard solution of 5 mol% Ph_3PAuCl and 5 mol% $AgSbF_6$ was added. The reaction was monitored using silica TLC. The work up of this reaction was done using the general procedure described above. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.24-7.08(m, 5H), 5.89(s, 1H), 3.89(dd, *J = 6.8, 2.1 Hz*, 1H), 2.84(dd, *J = 19.4, 6.9 Hz*, 1H), 2.30 (dd, *J = 19.4, 2.1 Hz*, 1H), 0.0(s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 201.95, 153.84, 140.94, 128.64, 127.28, 126.10, 113.64, 97.16, 43.50, 41.47, 14.10, 0.00. FTIR (neat): 3273, 3064, 3029, 2958, 2899, 2134, 1702, 1645, 1405, 1385, 1247, 1228, 1125. HRMS (CI+) Calcd. For $C_{16}H_{19}O_2Si$ (M+1): 271.1154, Found: 271.1154.

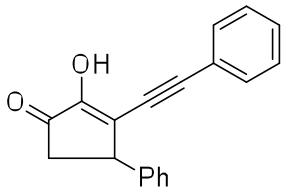
Furan **B**



To a 0.2 mmol solution of ketone **1** in 0.3M distilled methylene chloride, 0.2mmol of HPLC grade methanol was added followed by addition of a standard solution containing 5 mole % $AuCl_3$ and 15 mol% of $AgSbF_6$ in methylene chloride. The methoxy adduct was obtained in 97% yield (60mg) upon the work up described above in the general procedure. ^{1}H NMR (300 MHz,

CD_2Cl_2) δ: 7.82(m, 2H), 7.58(m, 2H), 7.5-7.28(m, 5H), 7.06(s, 1H), 6.13(s, 1H), 3.43(s, 3H), 2.60(s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 188.68, 155.93, 147.20, 141.50, 137.57, 129.64, 129.39, 129.12, 128.54, 127.92, 127.09, 124.99, 107.09, 76.92, 57.01, 27.03. FTIR (neat):3316, 3063, 3032, 2933, 2822, 1728, 1663, 1591, 1577, 1529, 1476, 1400, 1359, 1321, 1190, 1176, 1142, 1096, 1073, 1027. HRMS (EI+) Calcd. For $C_{20}H_{18}O_3$ (M^+): 306.1256, Found: 306.1254.

Nazarov Product **A**



To a solution of 5 mol% of gold trichloride and15 mol% of silver hexafluoro antimonate, under an argon atmosphere, a 0.2M solution of Ketone **1** (1mmol, 300mg) in dry acetonitrile was added via syringe. The mixture was stirred for 3hrs at ambient temperature before filtering through plug silica. The solution was then concentrated *in vacuo* and the Nazarov Product **A** was isolated using silica gel column chromatography (ethyl acetate: hexane, 1:5 v/v) in 15% yield (40mg) along with 40% (100mg) heterocycle **2**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.24(m, 10H), 6.03 (s, 1H), 4.03 (dd, J = 6.6, 1.89 Hz, 1H), 2.96 (dd, J = 19.3, 6.7Hz, 1H), 2.41 (dd, J = 19.5, 2.1 Hz, 1H). ^{13}C NMR (700 MHz, $CDCl_3$) δ: 201.02, 153.65, 141.53, 131.60, 129.27, 128.74, 128.40, 127.31, 127.23, 125.44, 122.07, 105.52, 82.46, 43.54, 41.62. FTIR (Methylene chloride solution): 3054, 2987, 2928, 1718, 1654, 1604, 1550, 1421, 1358, 1157. HRMS (EI+) Calcd. For $C_{19}H_{14}O_2$ (M^+): 274.09938, Found: 274.09938.

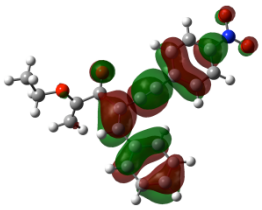
Computational Study

Methodology: All geometries were optimized by DFT computations at the B3LYP level with the LANL2DZ basis set which frequently performs well for the transition metal compounds (e.g. Xia, Y.; Dudnik, A. S.; Gevorgyan, V.; Li, Y. *J Am Chem Soc.* **2008**, *130*, 6940–6941 and Soriano, E.; Marco-Contelles, J. *Acc. Chem. Res.* **2009**, *42*, 1026–1036) using Gaussian 03 program (see below the reference). Force Field calculation indicated that optimized structures were found to be true minima with no imaginary frequency.

Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford, CT, 2003.

Cartesian coordinates of geometries optimized at the B3LYP/LANL2DZ level (Absolute Energies are given in Hartree)

6



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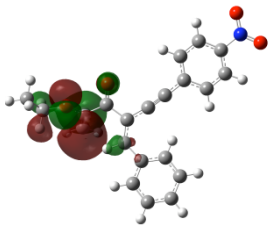
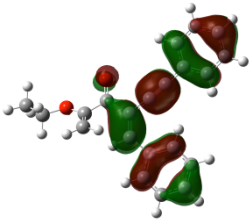


Energy: -159.19 kcals

1



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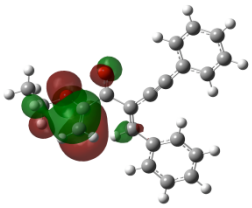
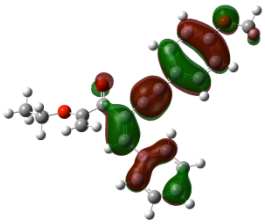


Energy: -153.08 kcals

4



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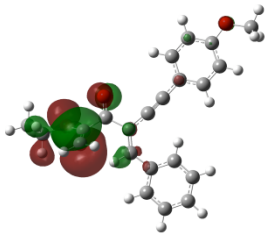
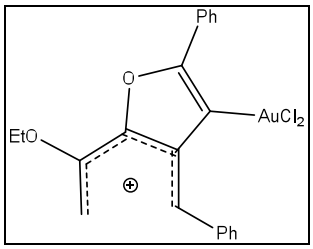


Energy: -151.83 kcals

Furan_Intermediate

Total Energy: -1126.444



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C	2.725201	0.154678	-3.251589
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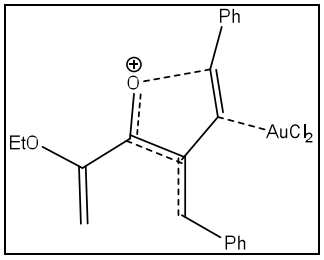
Cl	0.285884	-0.392347	4.875645

TS_Furan_Pathway

Total Energy: -1126.395



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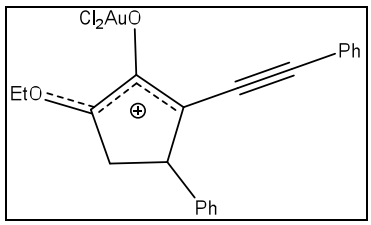
Nazarov_Intermediate

Total Energy: -1126.428



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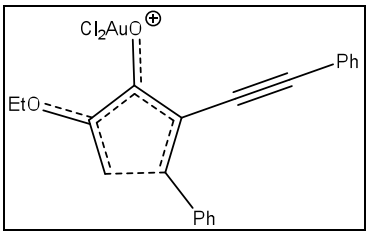
O	-0.663968	-1.348089	-3.478287
C	-0.502412	-1.060950	-4.968060
H	-0.422705	0.030458	-5.029006
H	0.427521	-1.540290	-5.294626
C	-1.738007	-1.608781	-5.657082
H	-2.644730	-1.140971	-5.262650
H	-1.672928	-1.383668	-6.728966
H	-1.816007	-2.693884	-5.537983
Au	-2.117445	0.710432	-0.052127
Cl	-3.372530	0.127633	1.890809
Cl	-0.647189	1.522921	-1.865267
C	0.948122	-0.835427	3.513569
C	2.065959	-0.749078	4.412100
C	1.839887	-0.642964	5.782753
C	0.511427	-0.612168	6.279944
C	-0.598020	-0.685481	5.404575
C	-0.394949	-0.795697	4.028240
H	3.075118	-0.773000	4.011352
H	2.675857	-0.581713	6.472390
H	0.344172	-0.525376	7.350516
H	-1.607431	-0.648144	5.801524
H	-1.236518	-0.829838	3.340855

TS_Nazarov_Pathway

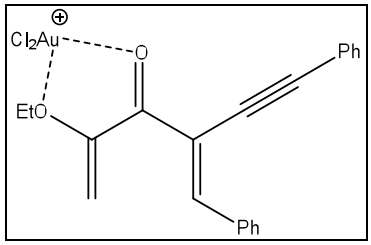
Total Energy: -1126.377



C	-1.985908	-0.956606	3.320617
C	-0.072637	0.336631	2.878415
C	-0.030856	-0.263262	1.543576
C	-1.309502	-0.648130	0.987698
C	-2.379662	-0.686255	2.003220
H	-1.194844	-1.667450	3.523590
H	-2.646026	-0.741751	4.158153
H	-0.771940	1.162241	2.993231
O	-1.532609	-0.964077	-0.245280
O	-3.602216	-0.347653	1.567569
C	-4.819350	-0.516445	2.431044
H	-4.760117	-1.507692	2.899068

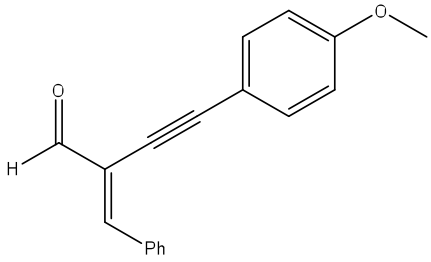
H	-4.786692	0.264568	3.200773
C	-6.026891	-0.368097	1.518178
H	-6.031667	0.613712	1.034193
H	-6.030350	-1.141324	0.743724
H	-6.944711	-0.465609	2.111181
C	1.127173	-0.362600	0.779880
C	2.087707	-0.379783	-0.006686
C	3.175816	-0.372816	-0.900357
C	4.460709	0.086716	-0.468853
C	5.528953	0.108631	-1.367508
C	5.338925	-0.315805	-2.704738
C	4.073125	-0.766203	-3.143727
C	2.996031	-0.801778	-2.254380
H	4.590757	0.421903	0.556062
H	6.505439	0.457005	-1.044941
H	6.173611	-0.292834	-3.400244
H	3.936107	-1.082384	-4.173043
H	2.021101	-1.145124	-2.586113
C	0.976934	0.262837	3.870994
C	1.008978	1.250456	4.899591
C	2.003298	1.220935	5.883827
C	2.971831	0.193874	5.870721
C	2.944191	-0.802332	4.867637
C	1.958198	-0.772593	3.876356
H	0.259545	2.039415	4.909510
H	2.028734	1.982295	6.657386
H	3.738742	0.164421	6.640084
H	3.686469	-1.595050	4.874337
H	1.935364	-1.547717	3.115494
Au	-1.026215	0.022997	-2.055550
Cl	-0.914376	2.128763	-0.799914
Cl	-0.481056	0.228541	-4.359815

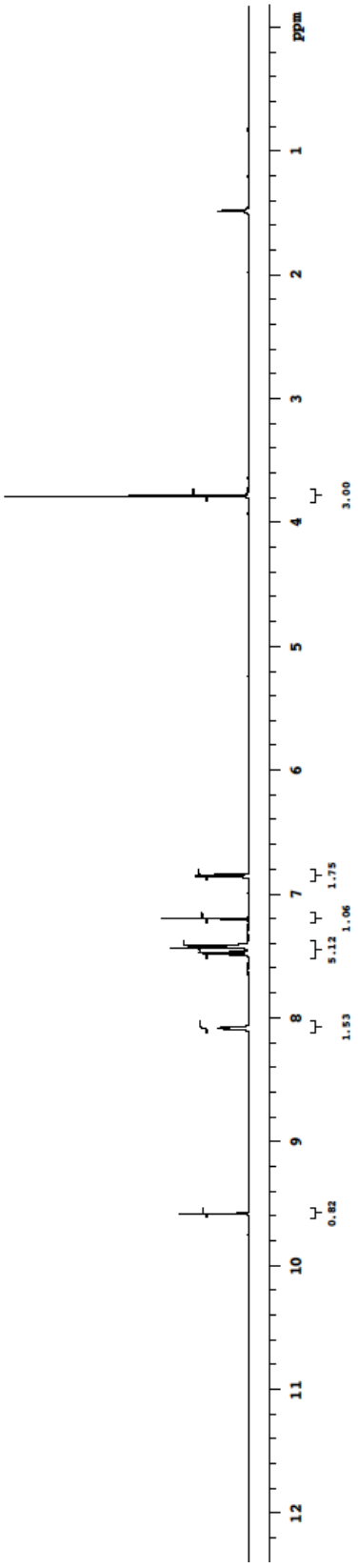
Substrate_Gold(III)_Complex:
Total Energy: -1126.403

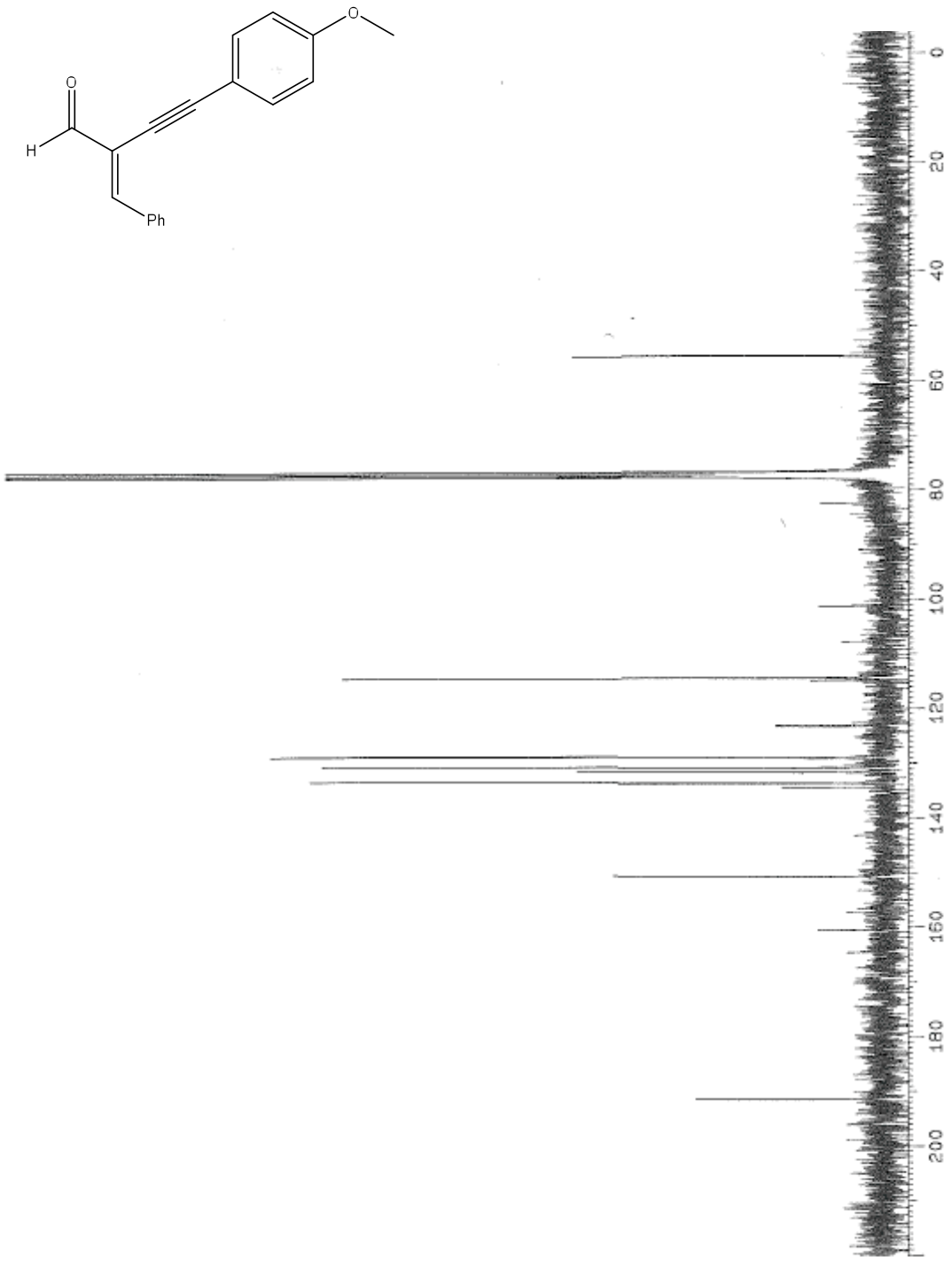


C	-0.964227	0.283954	-1.540451
C	-2.239003	0.080821	-2.099891
H	-3.059104	0.019759	-1.387390
C	-0.837193	0.440953	-0.101208

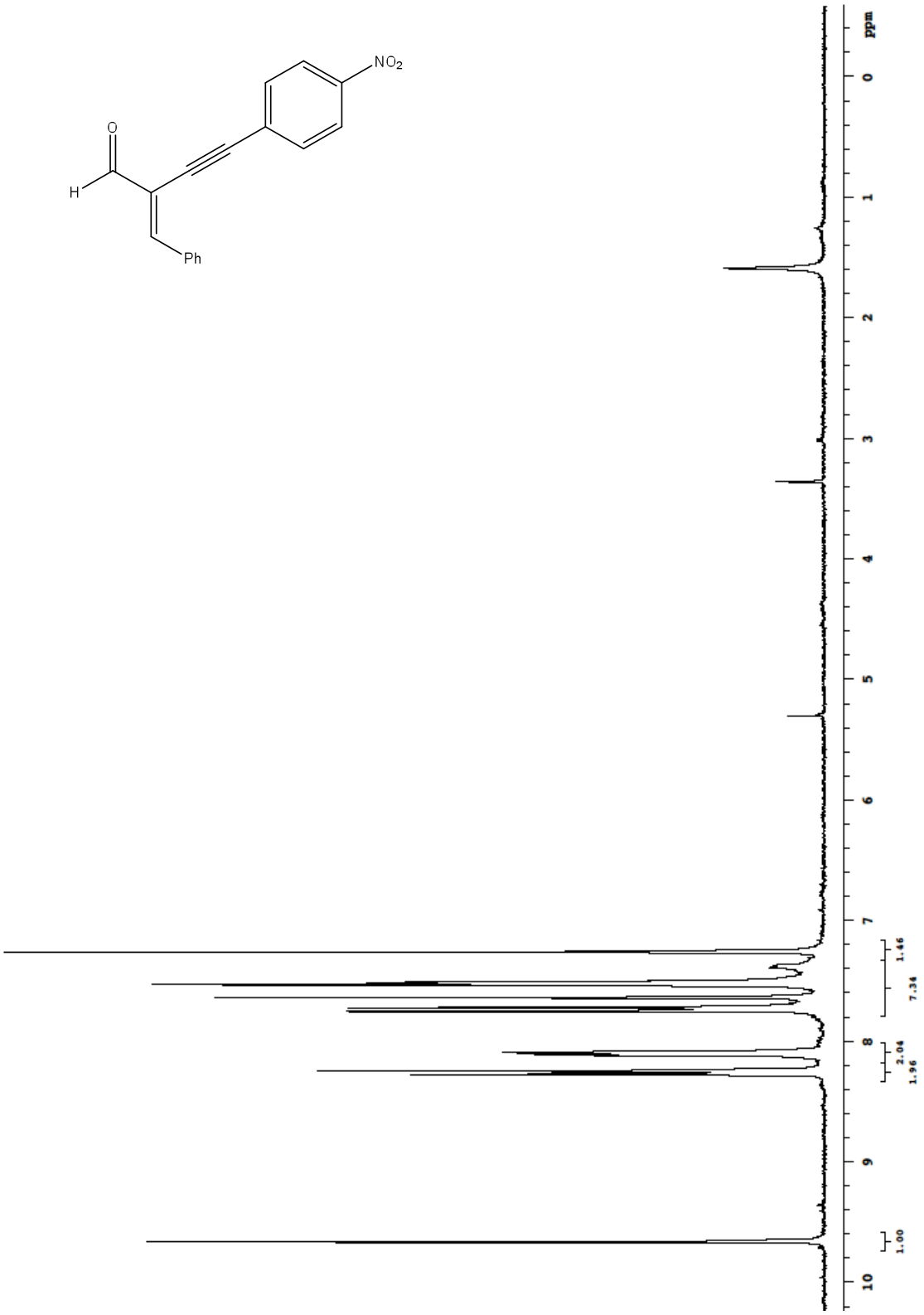
C	-1.936266	0.857321	0.812203
C	-2.907954	1.753075	0.532438
H	-3.641309	2.072744	1.264536
H	-2.957961	2.222918	-0.441913
O	0.343329	0.252680	0.430980
O	-1.732167	0.284608	2.106617
C	-2.780533	0.399213	3.199399
H	-2.221462	0.123472	4.095397
H	-3.066417	1.454176	3.264205
C	-3.943385	-0.547169	2.929302
H	-3.595326	-1.582857	2.860744
H	-4.641686	-0.483116	3.773851
H	-4.496733	-0.294513	2.018952
C	0.270856	0.236665	-2.241559
C	1.402354	0.198694	-2.724408
C	2.725201	0.154678	-3.251589
C	2.960819	-0.187867	-4.612131
C	4.269913	-0.227415	-5.108843
C	5.358752	0.070956	-4.260963
C	5.133971	0.408723	-2.909273
C	3.828727	0.451901	-2.402202
H	2.121532	-0.424614	-5.260559
H	4.448609	-0.490597	-6.147439
H	6.372823	0.038268	-4.650078
H	5.974699	0.634263	-2.259648
H	3.647334	0.707153	-1.362100
C	-2.635524	-0.124944	-3.468336
C	-4.010173	-0.453614	-3.700251
C	-4.494072	-0.656044	-4.994997
C	-3.618628	-0.527509	-6.095996
C	-2.260258	-0.196362	-5.890437
C	-1.766662	-0.000124	-4.597249
H	-4.685563	-0.549867	-2.852306
H	-5.537602	-0.908573	-5.156333
H	-3.991836	-0.680831	-7.105085
H	-1.597461	-0.092585	-6.744482
H	-0.725293	0.256626	-4.451135
Au	0.403889	-0.073841	2.516335
Cl	2.744464	-0.488954	2.571894
Cl	0.285884	-0.392347	4.875645

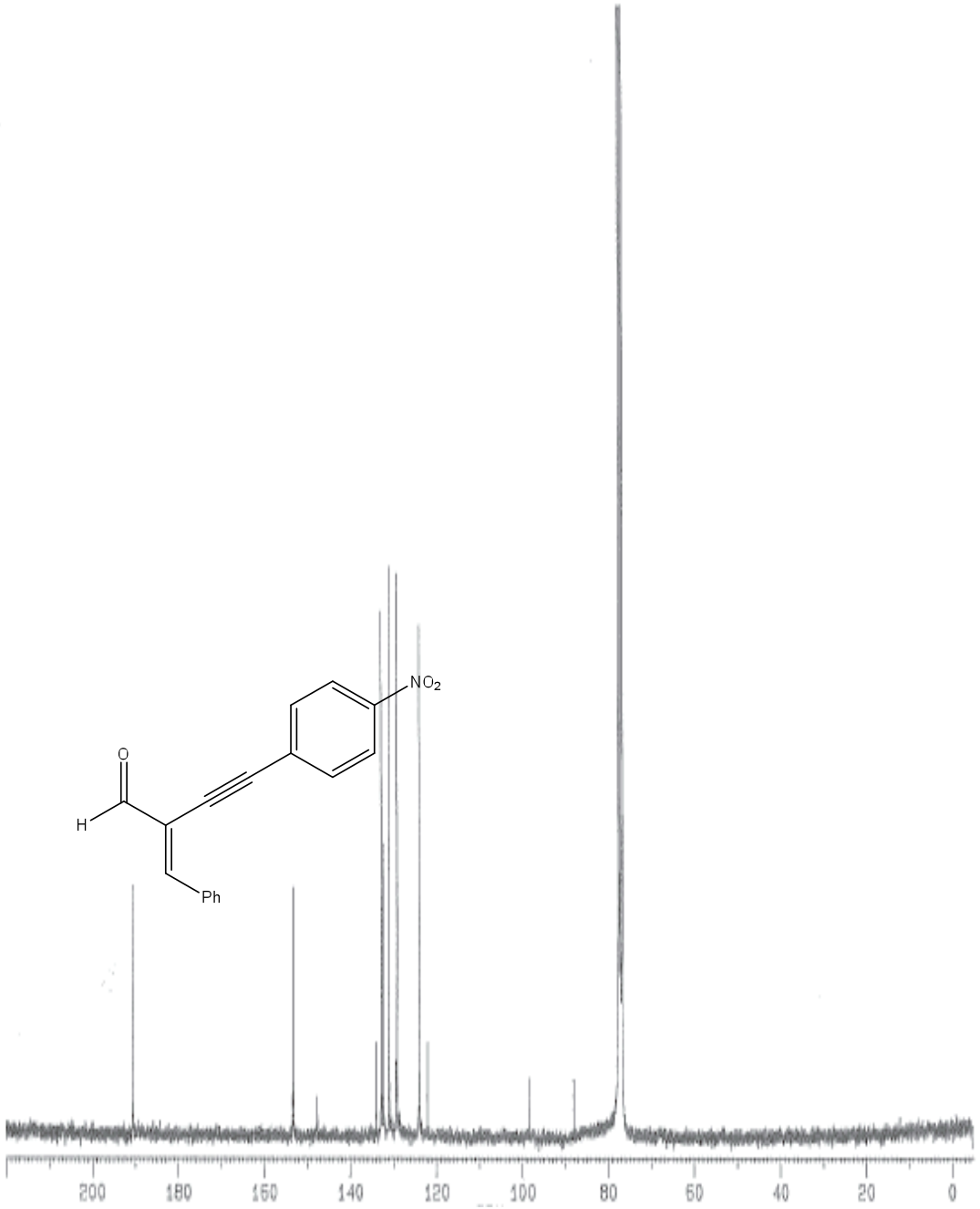


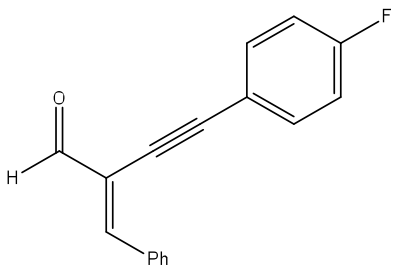


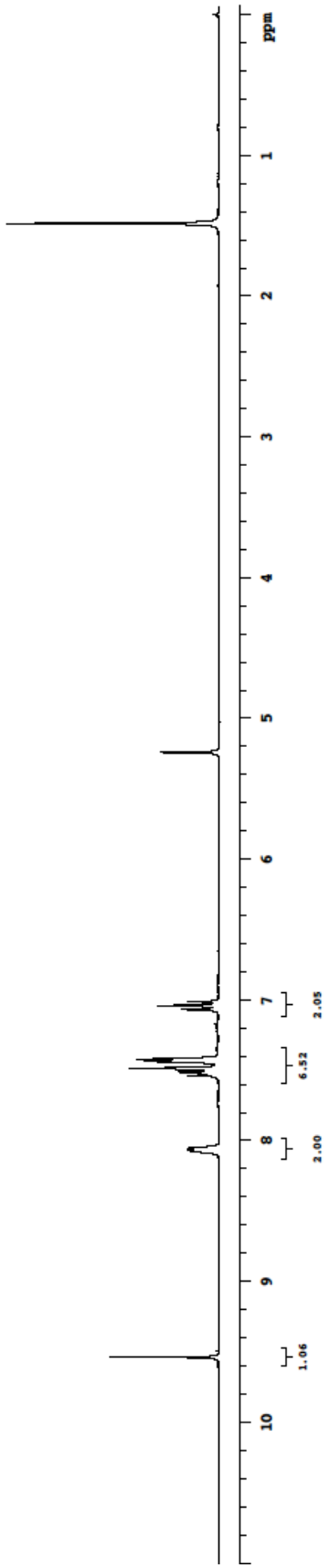


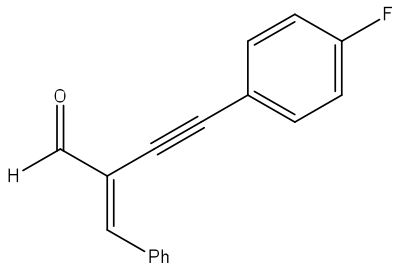
Electronic Supplementary Material (ESI) for Chemical Communications

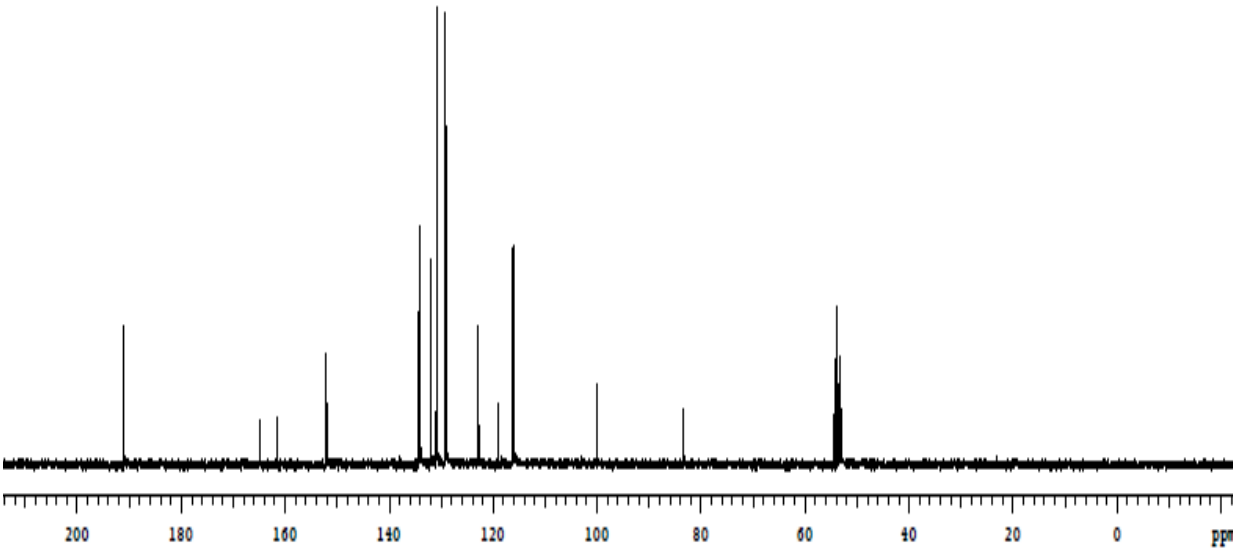


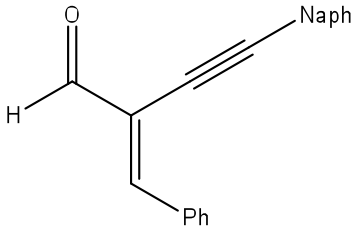


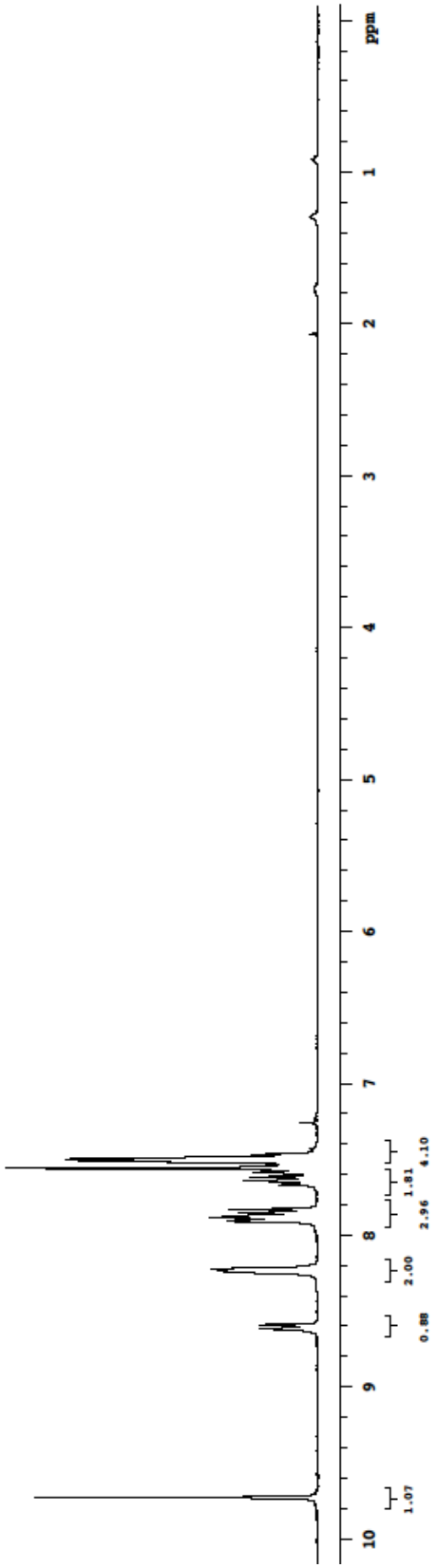


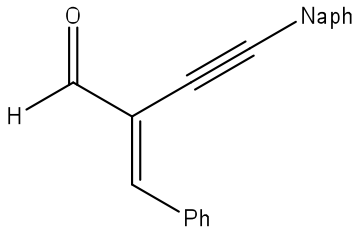


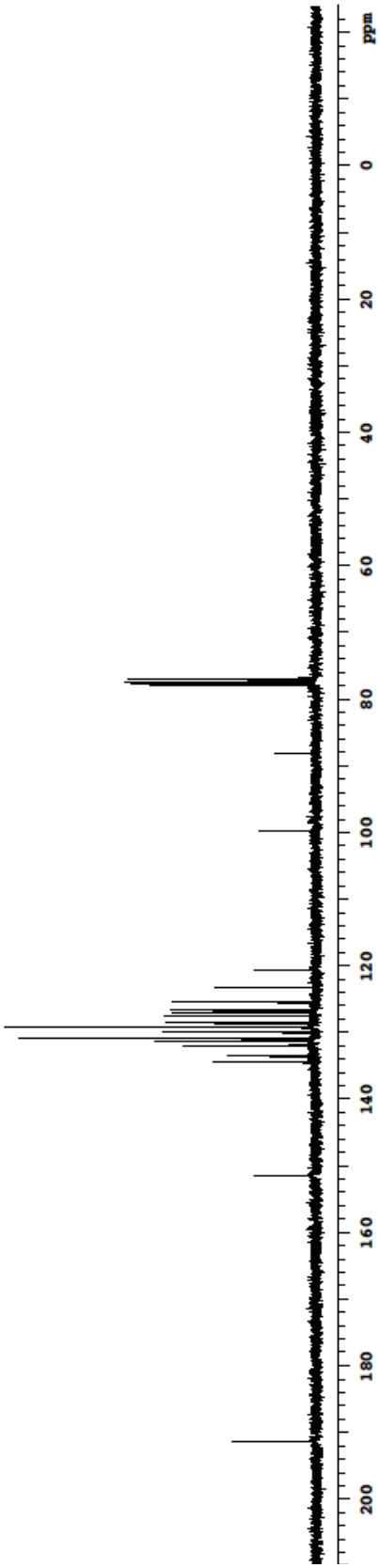


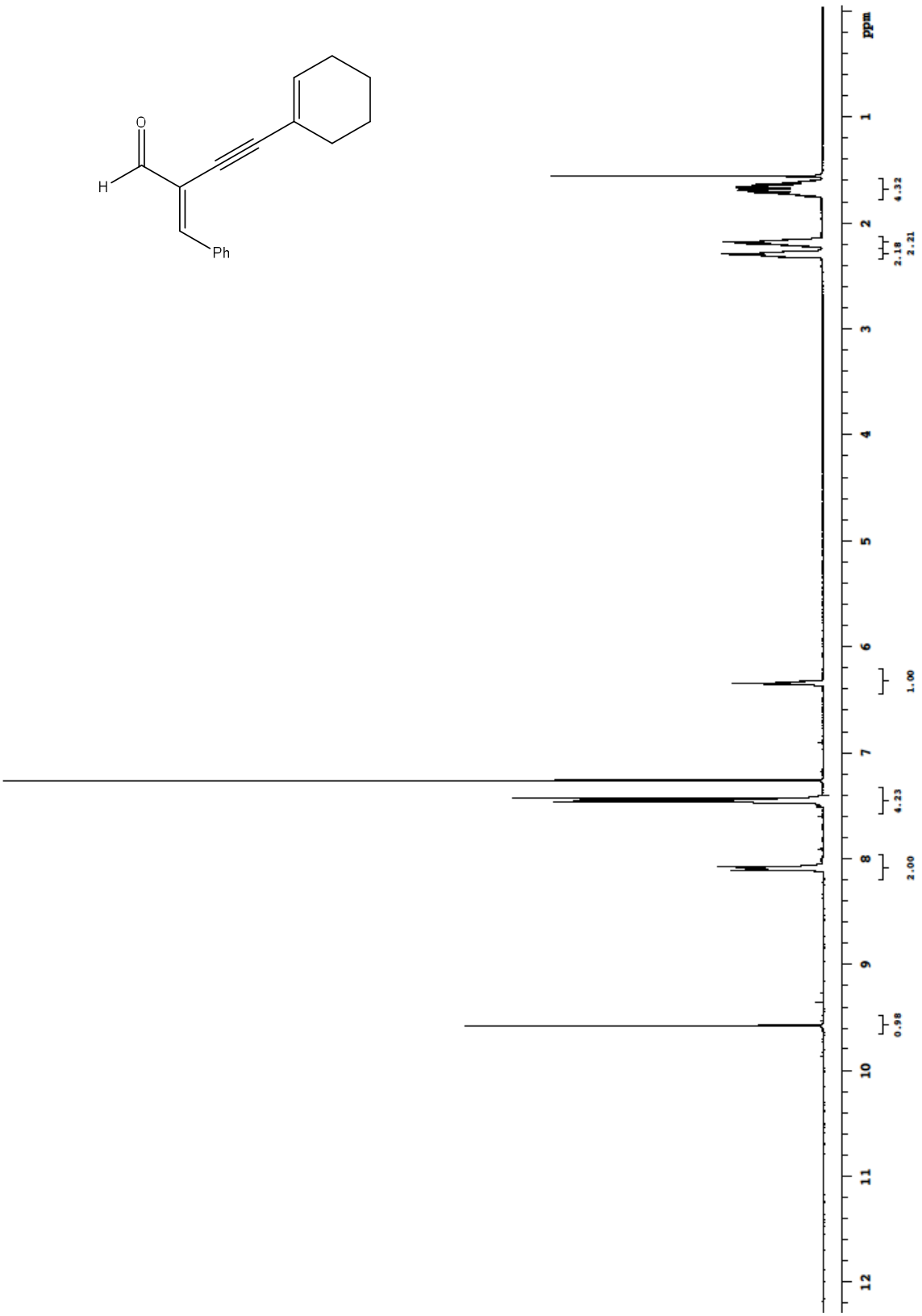


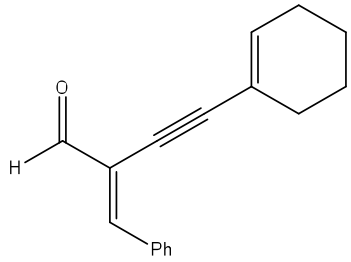


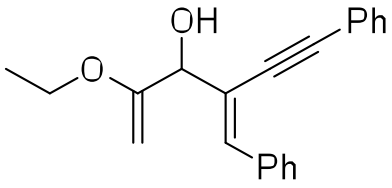


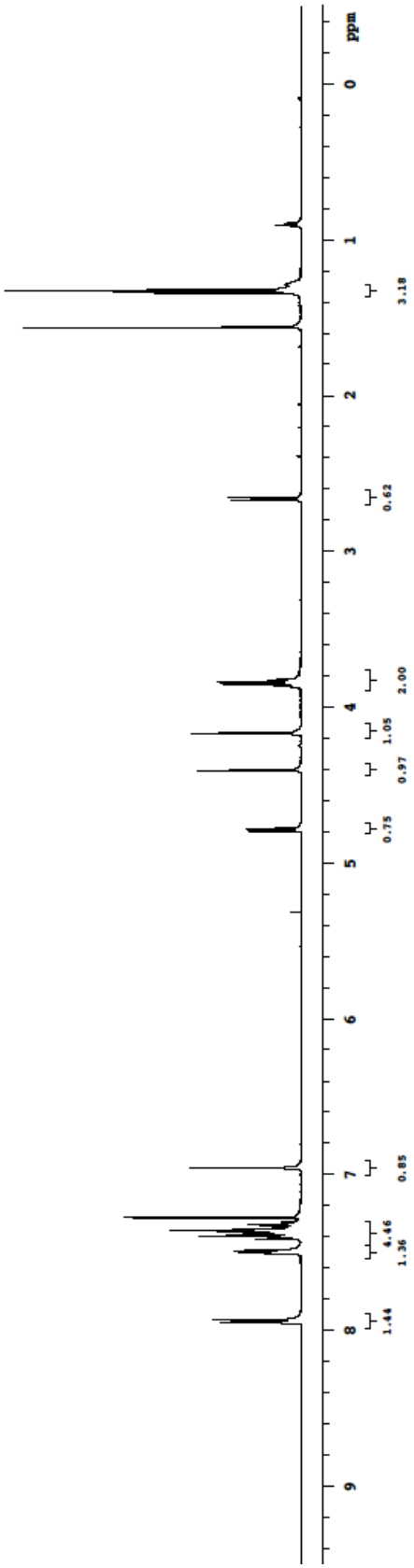


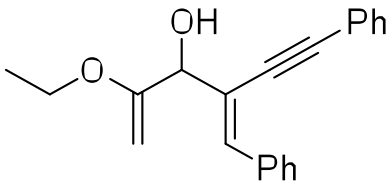


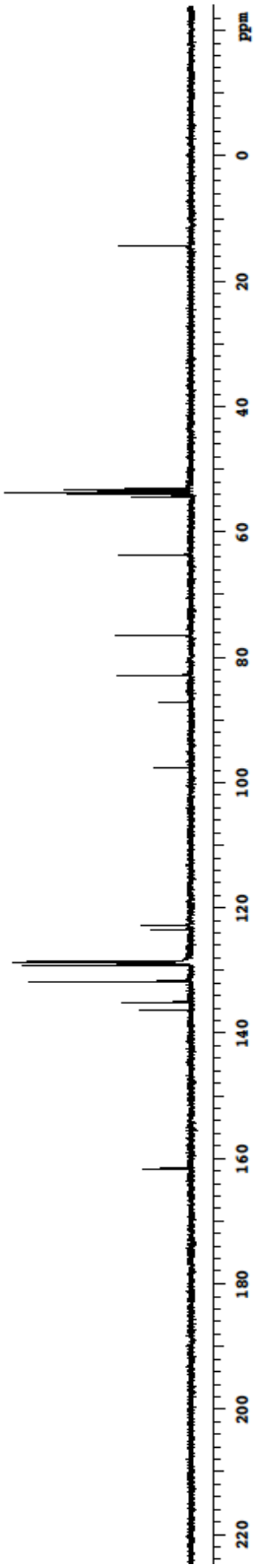


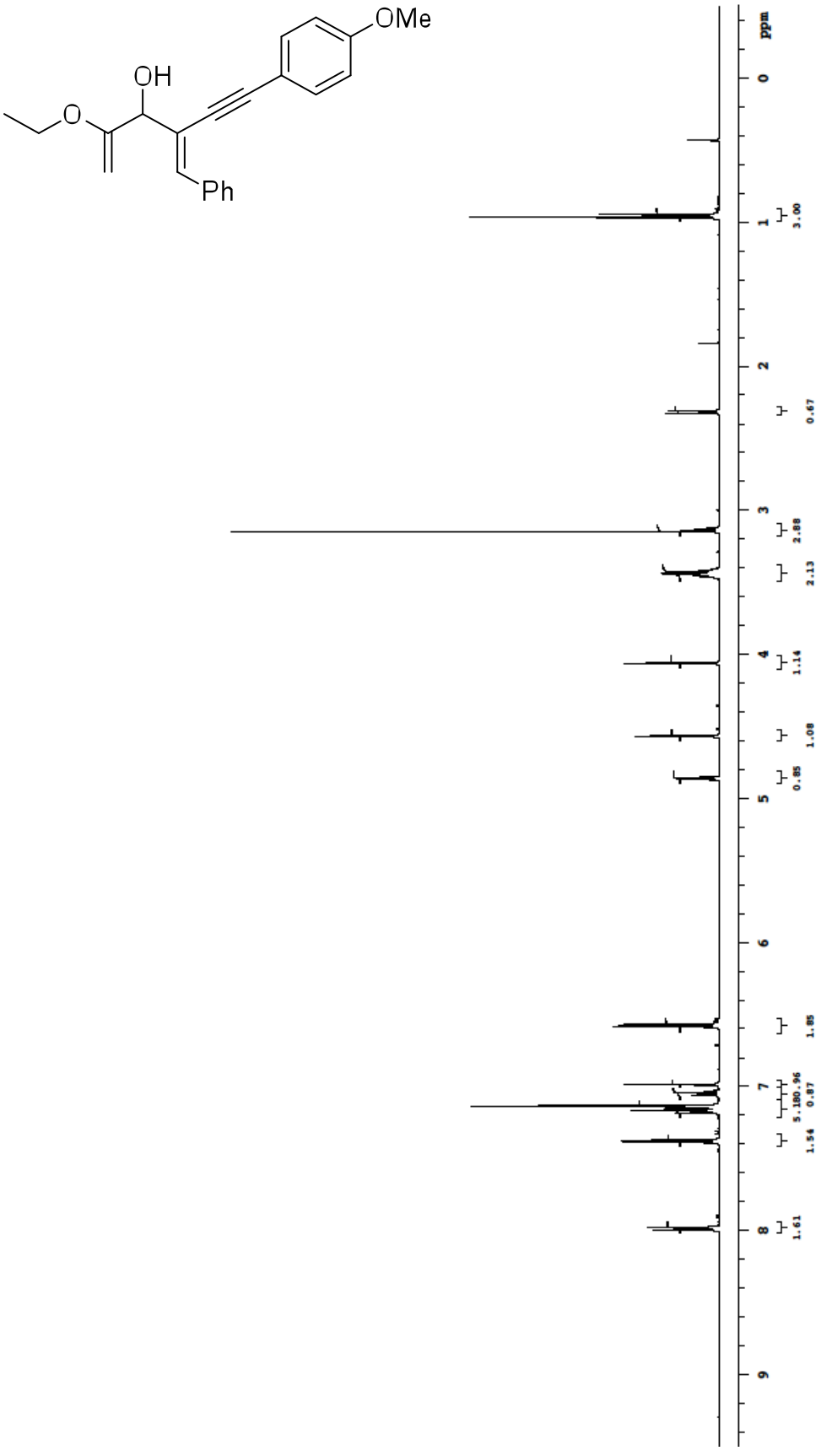


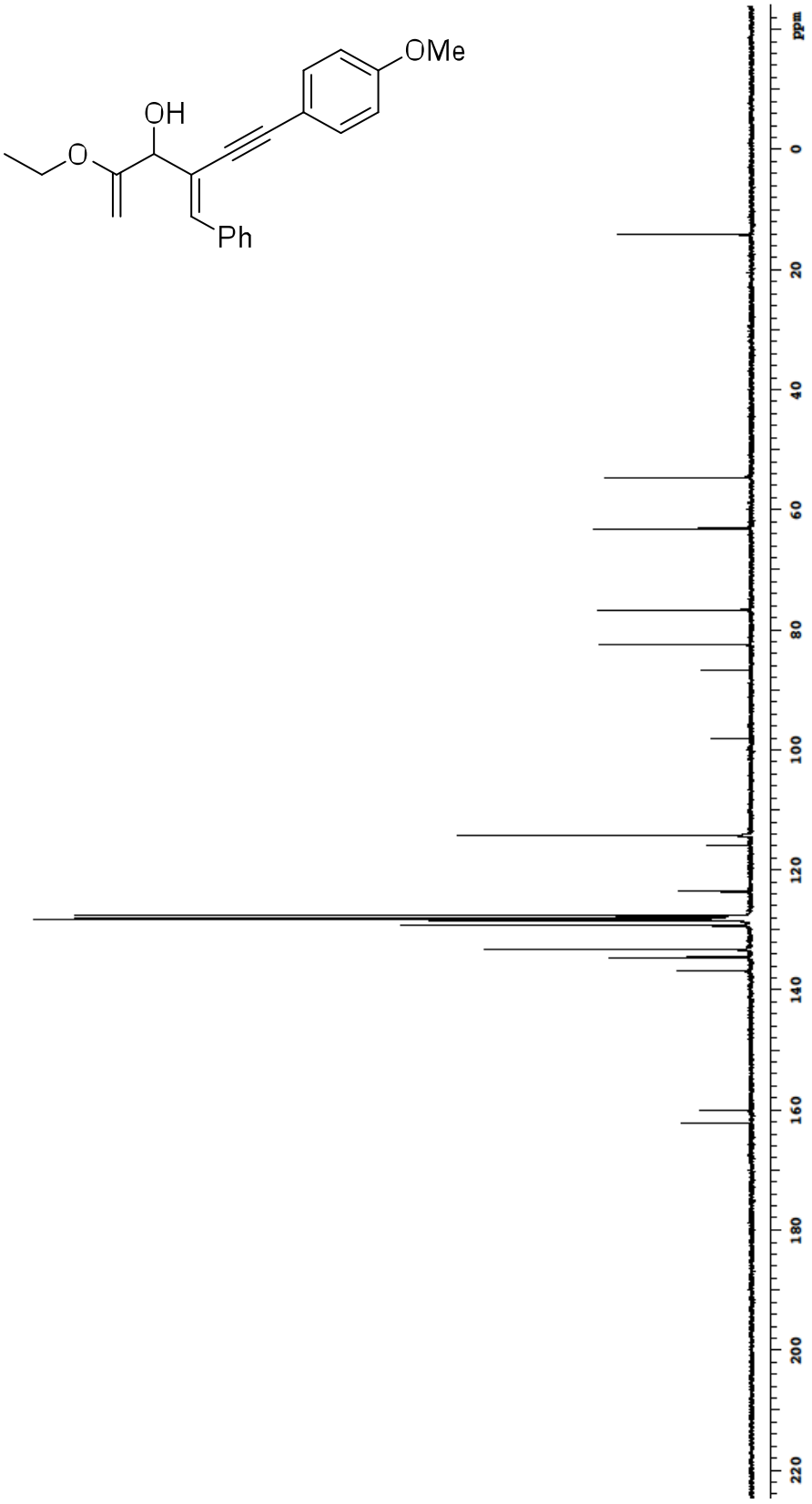


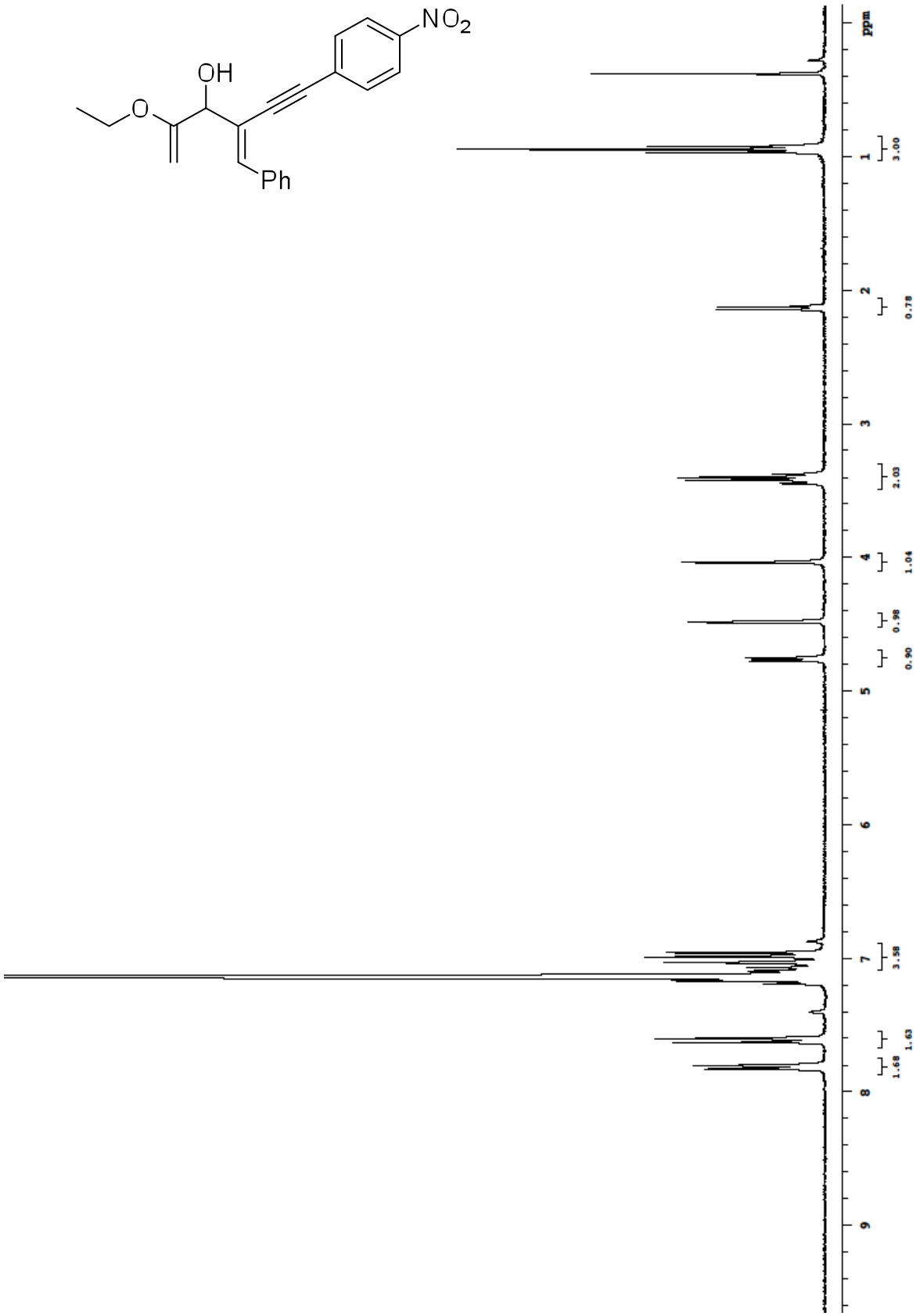


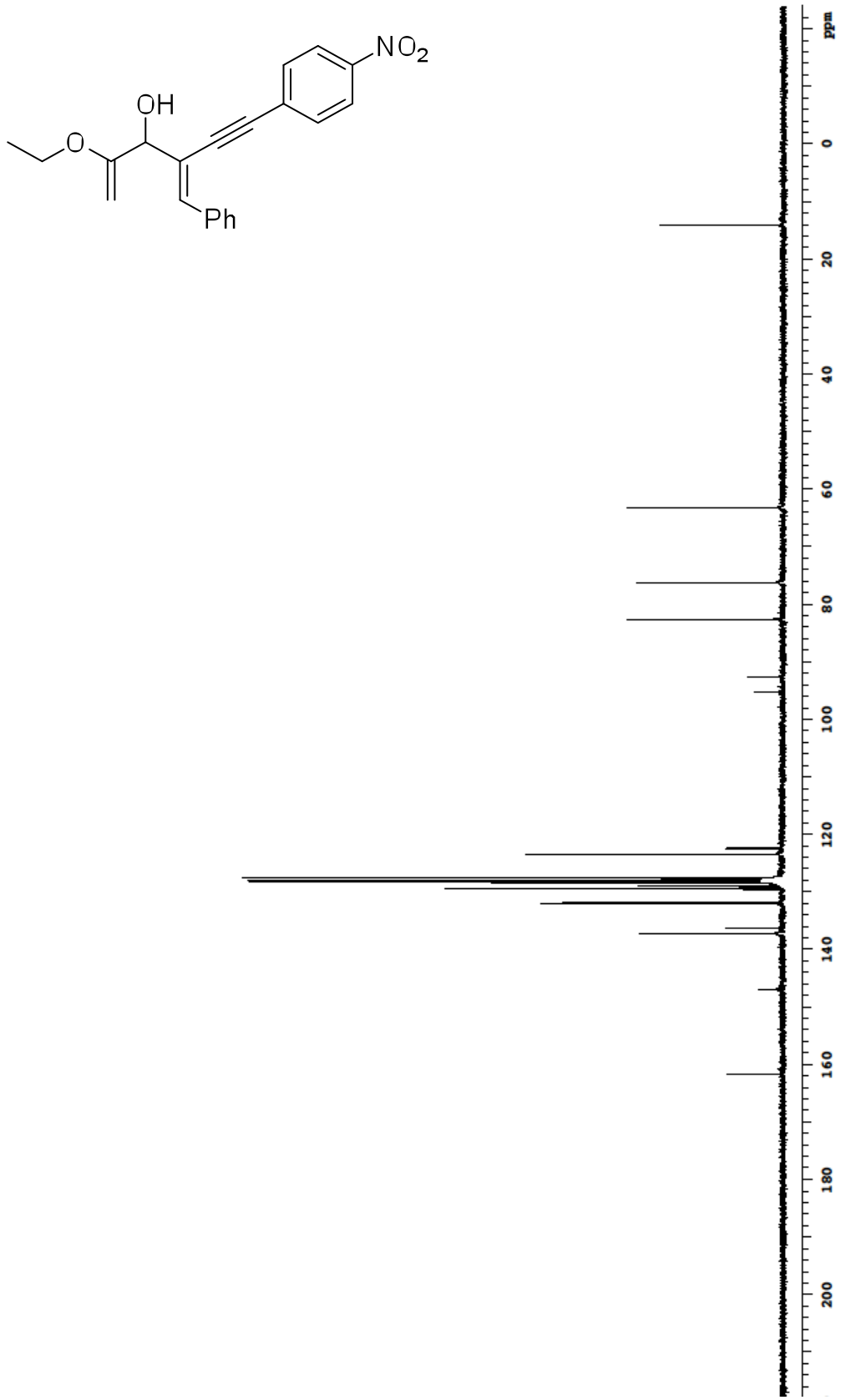


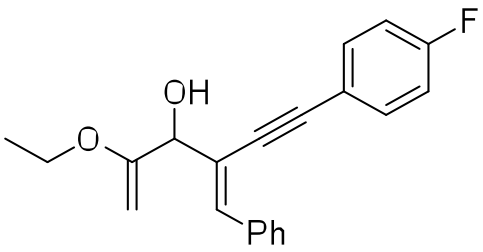


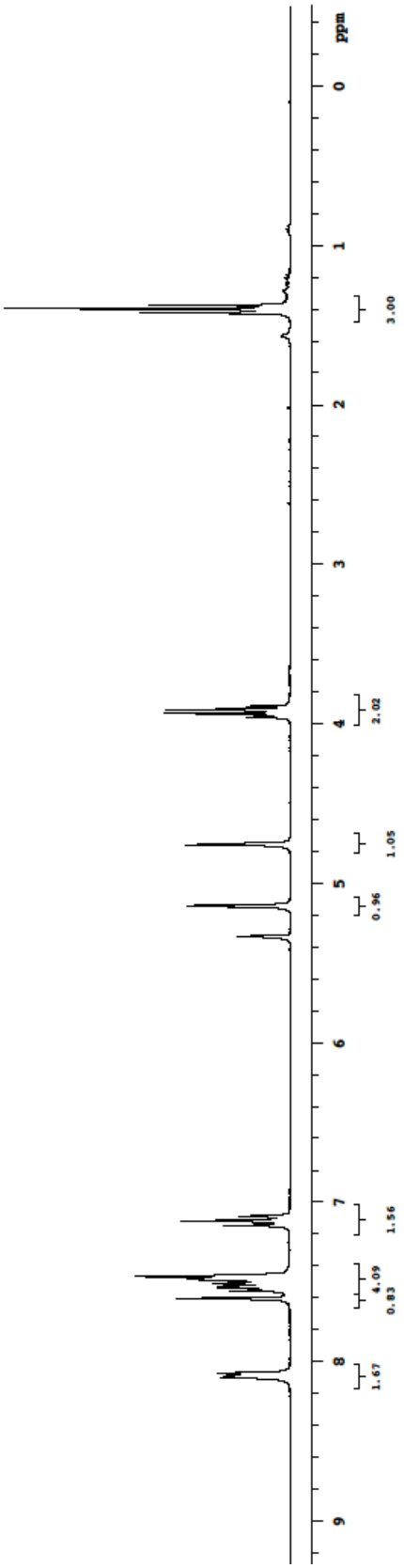


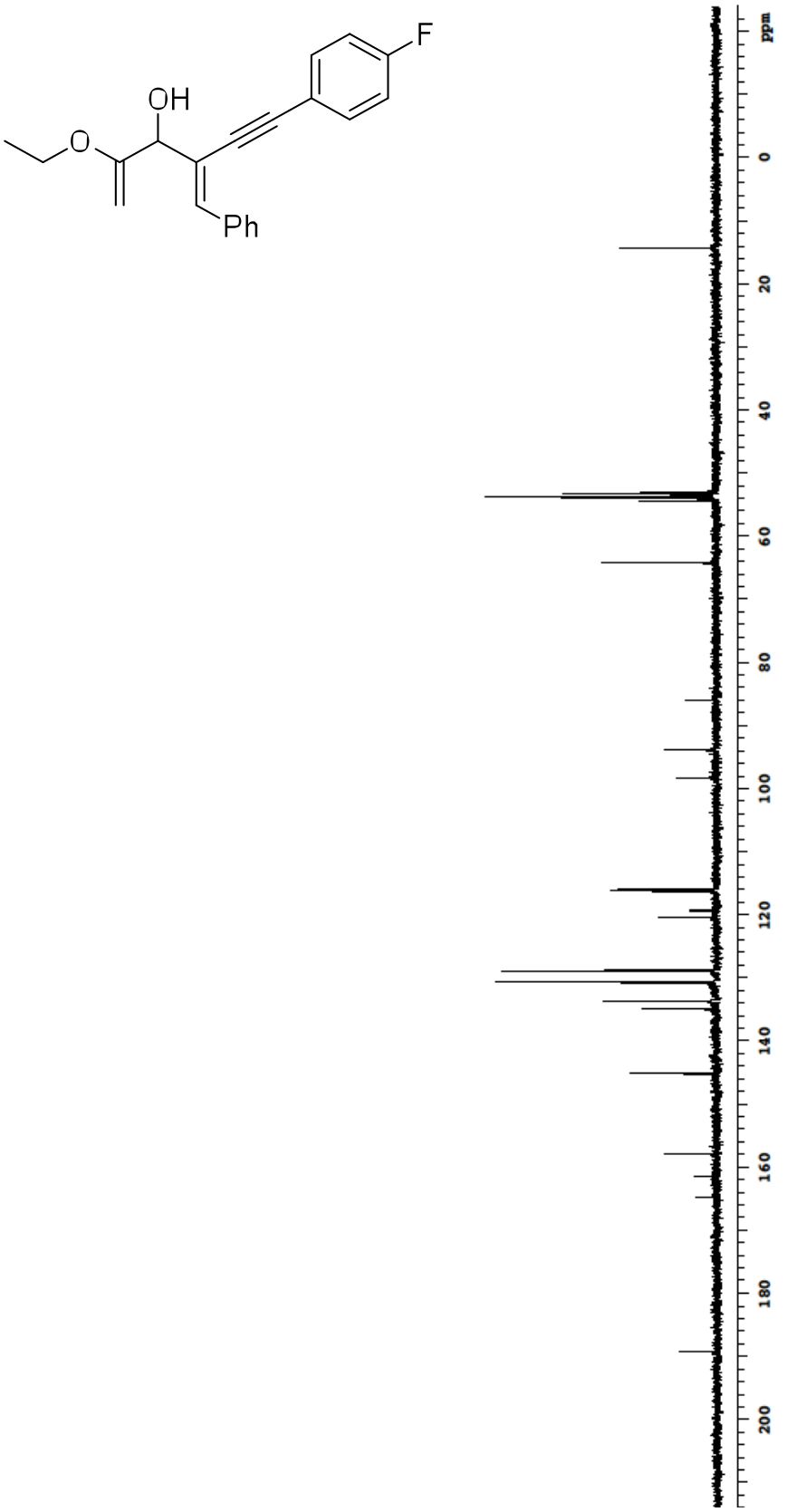


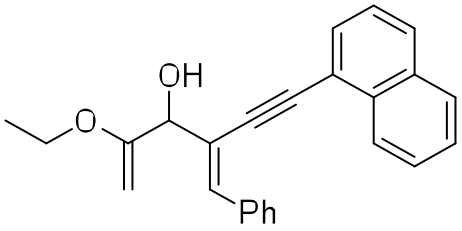


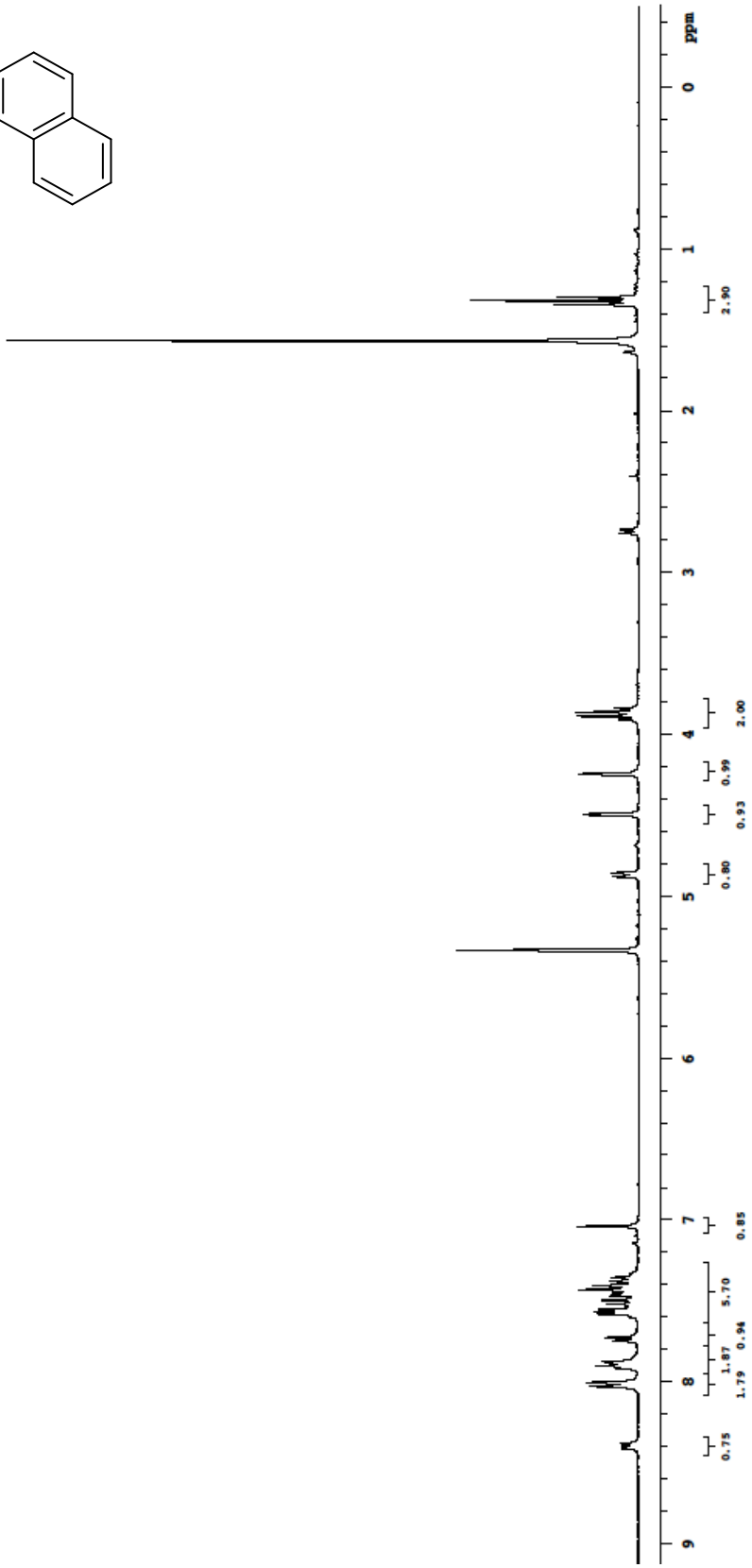


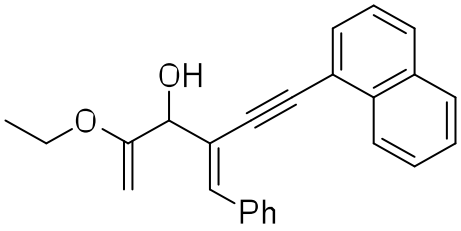


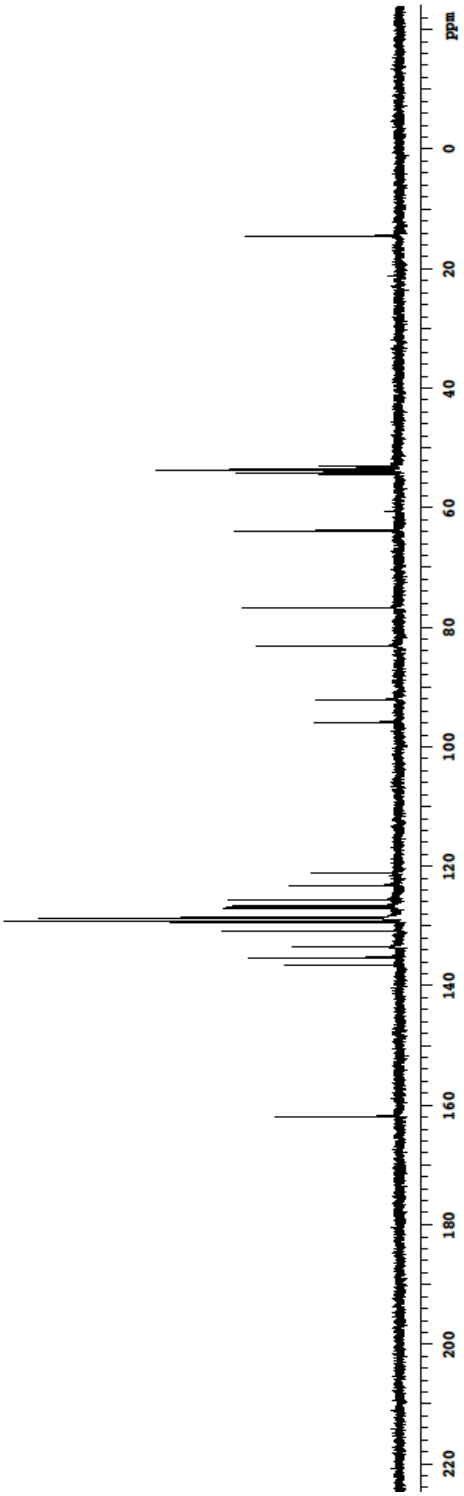


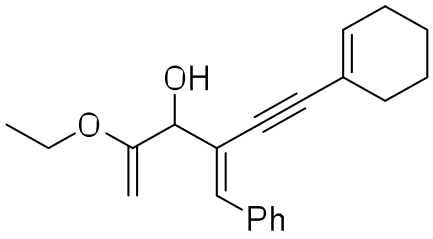


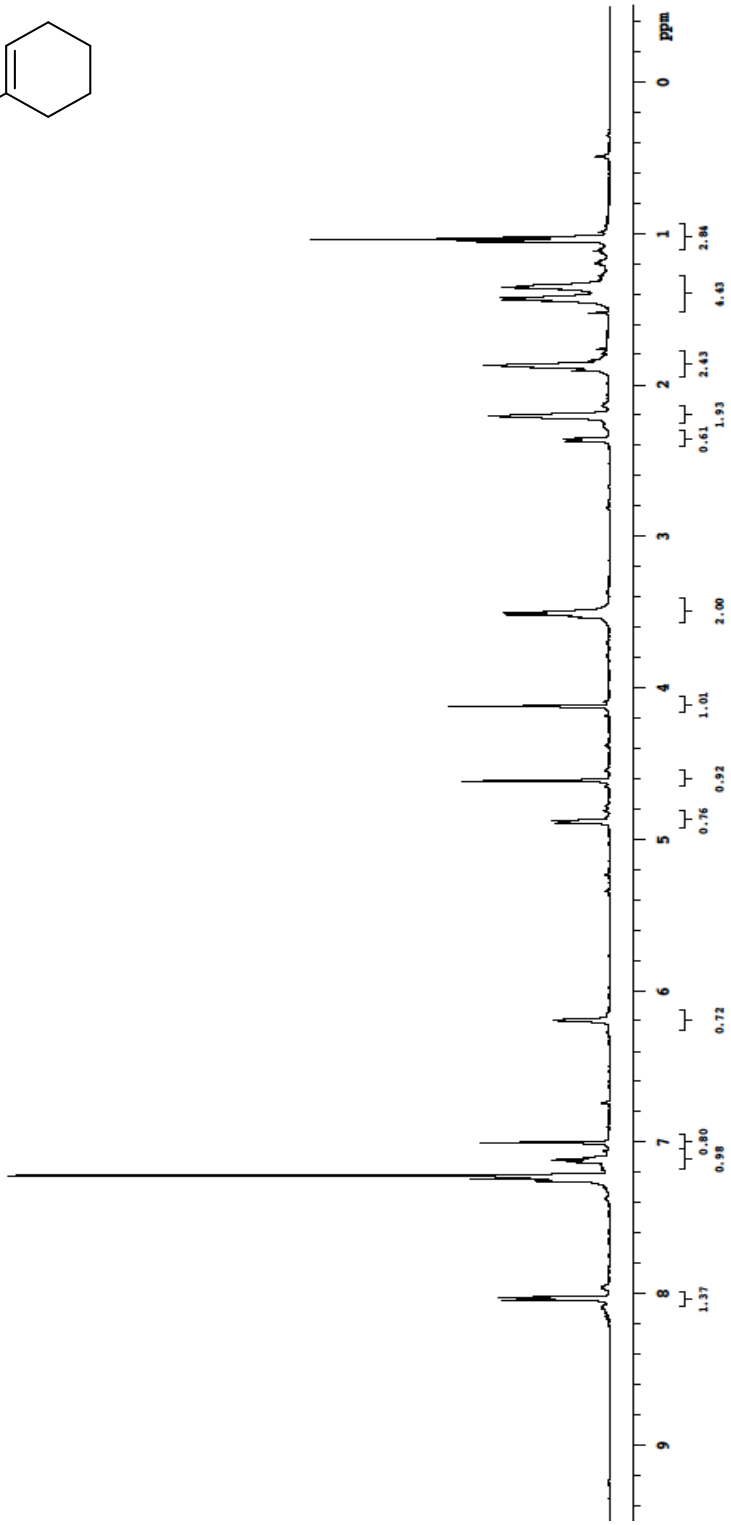


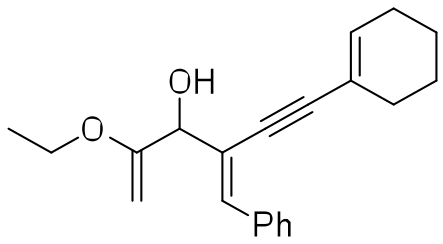


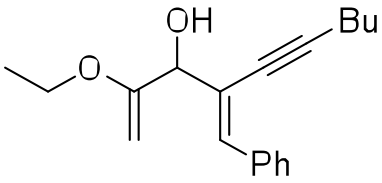


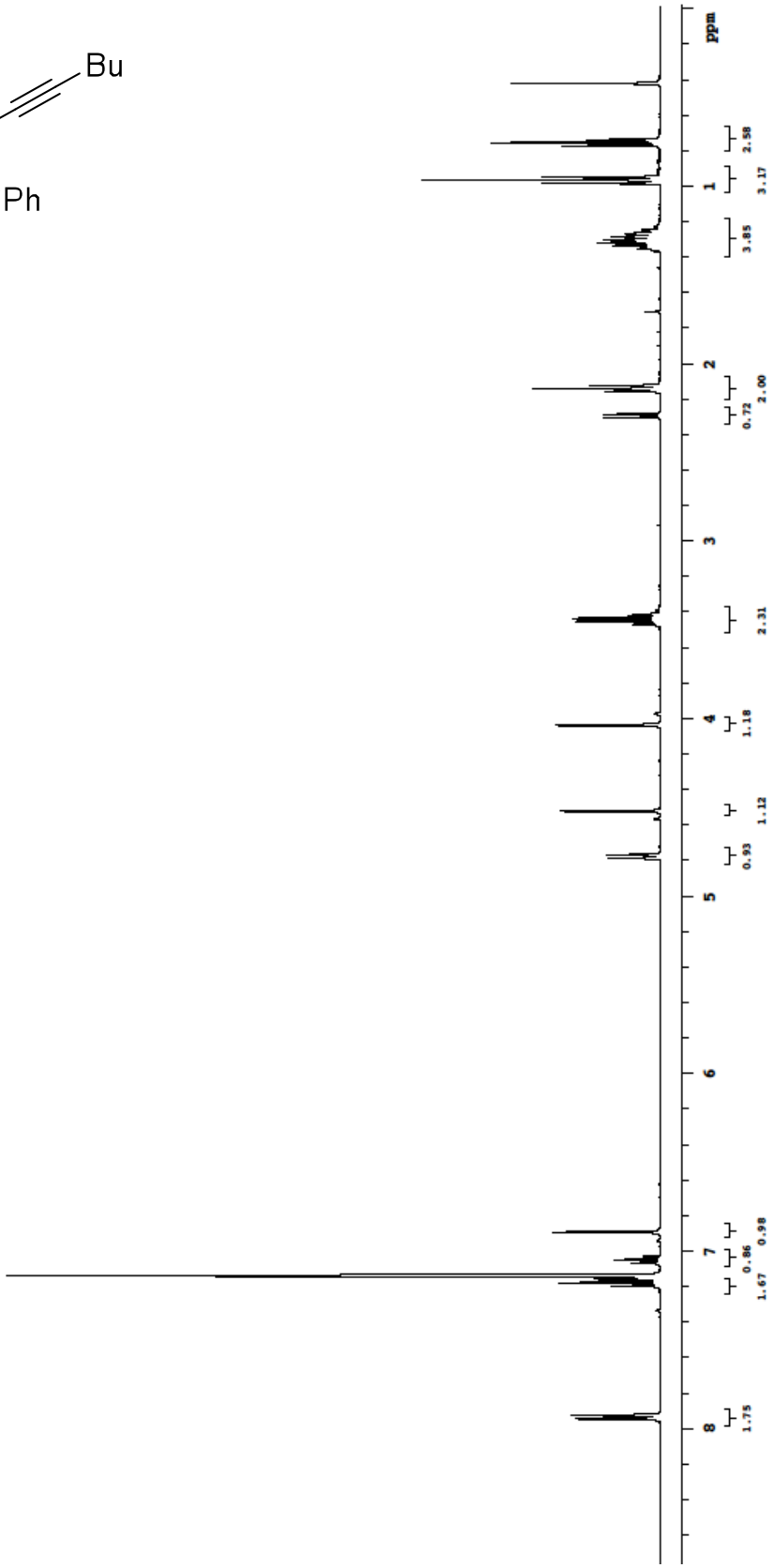


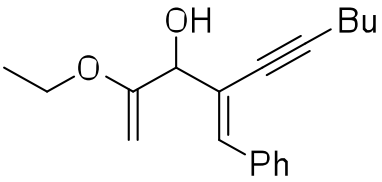


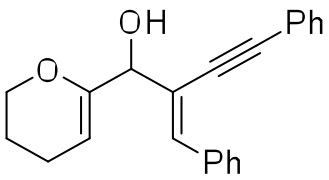


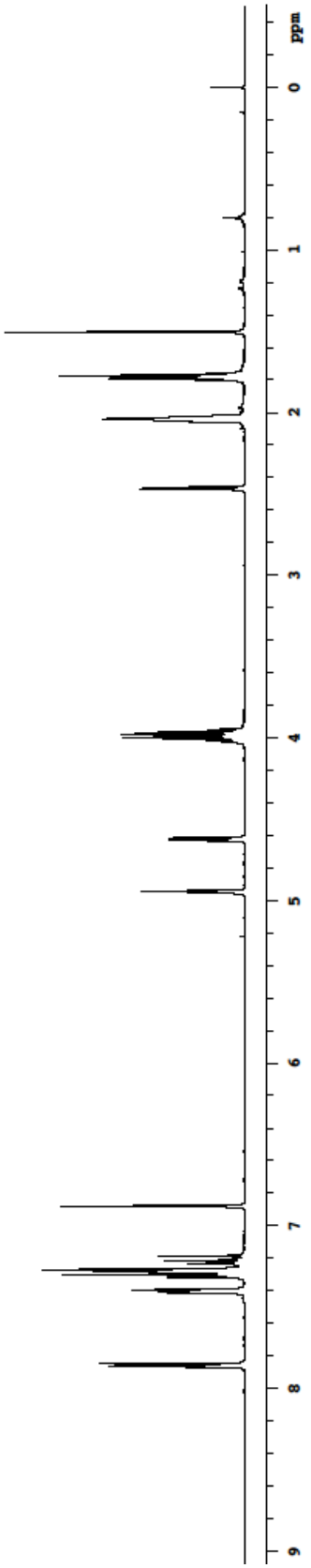


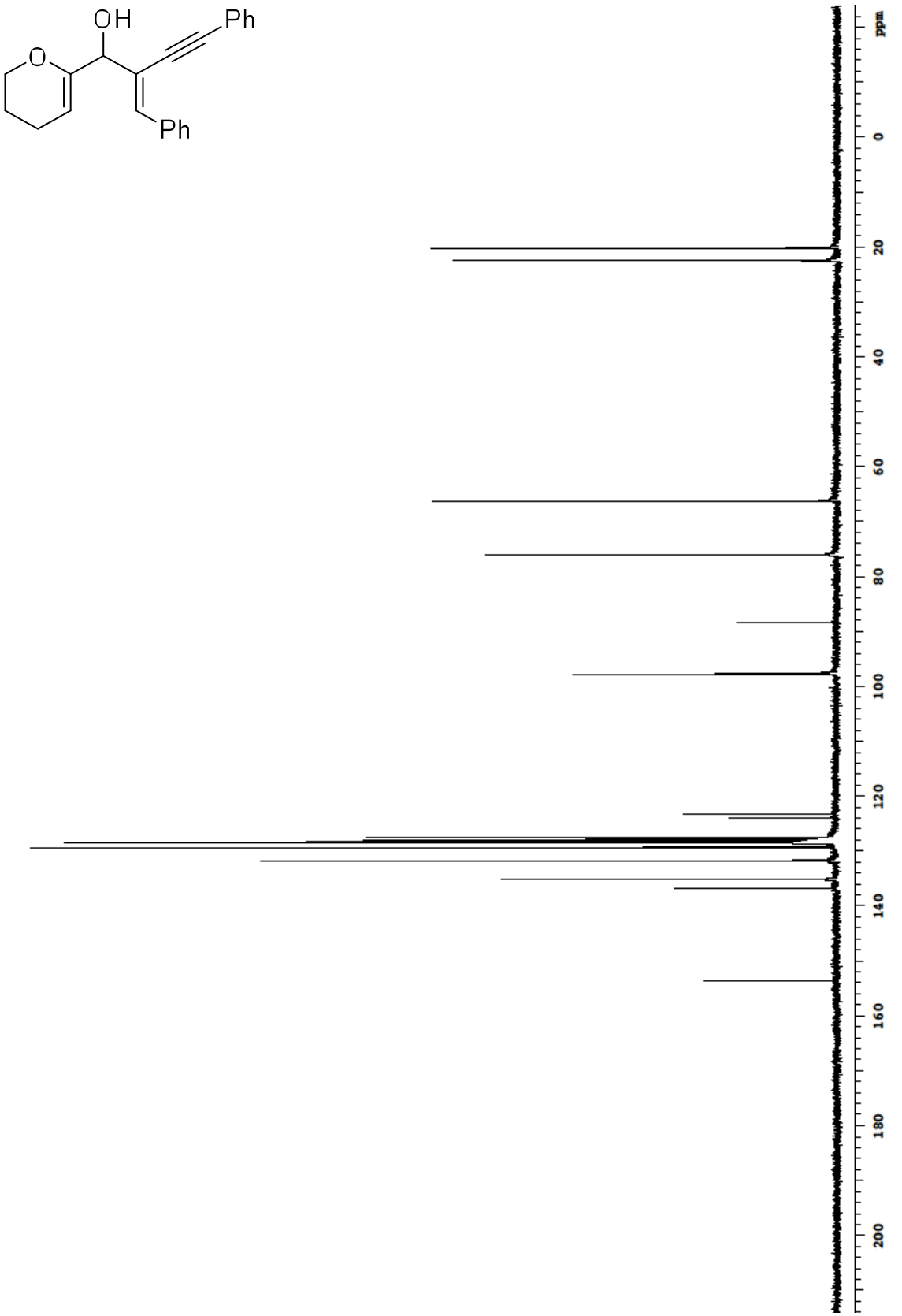


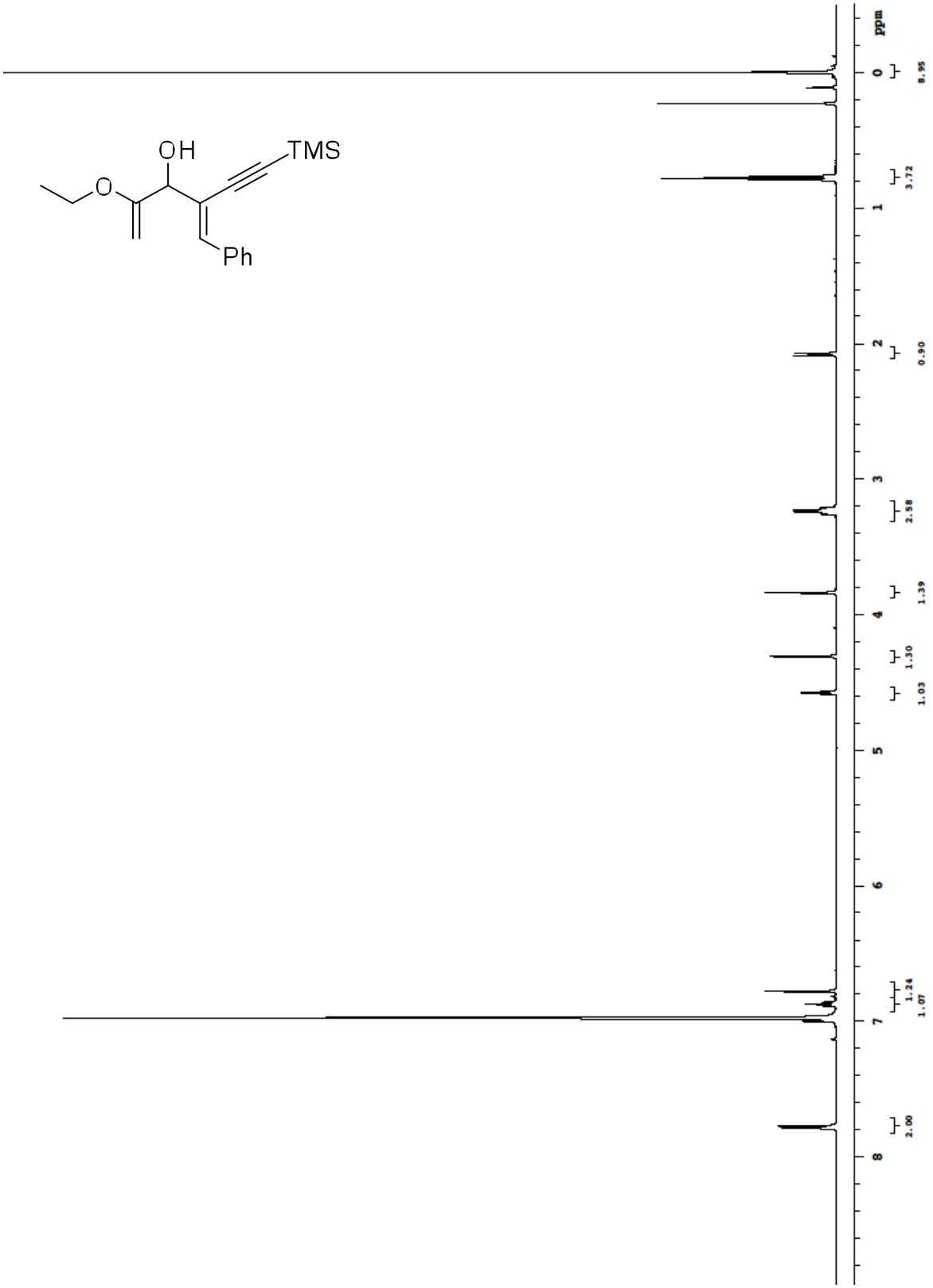


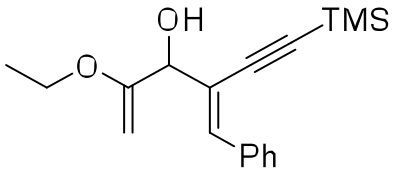


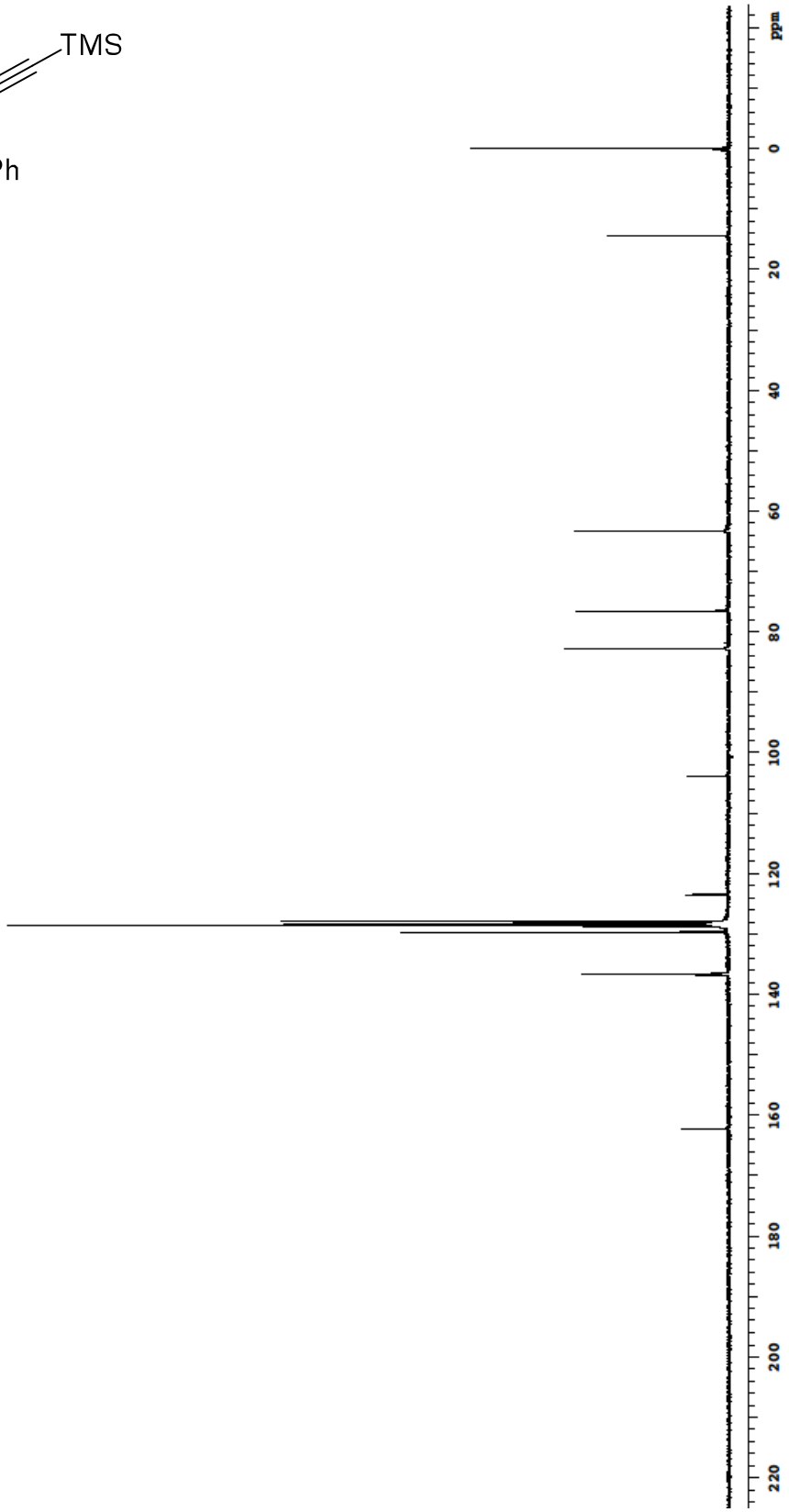


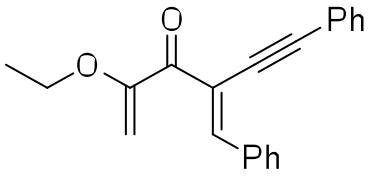


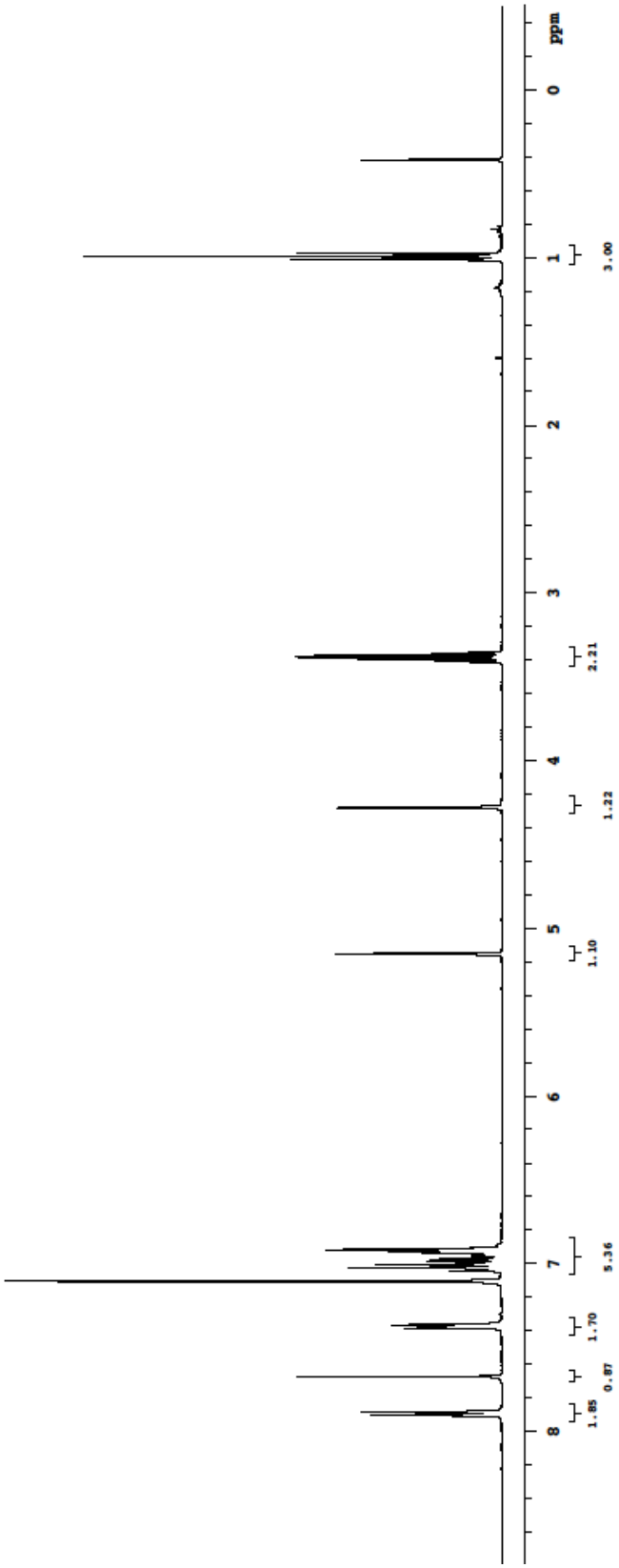


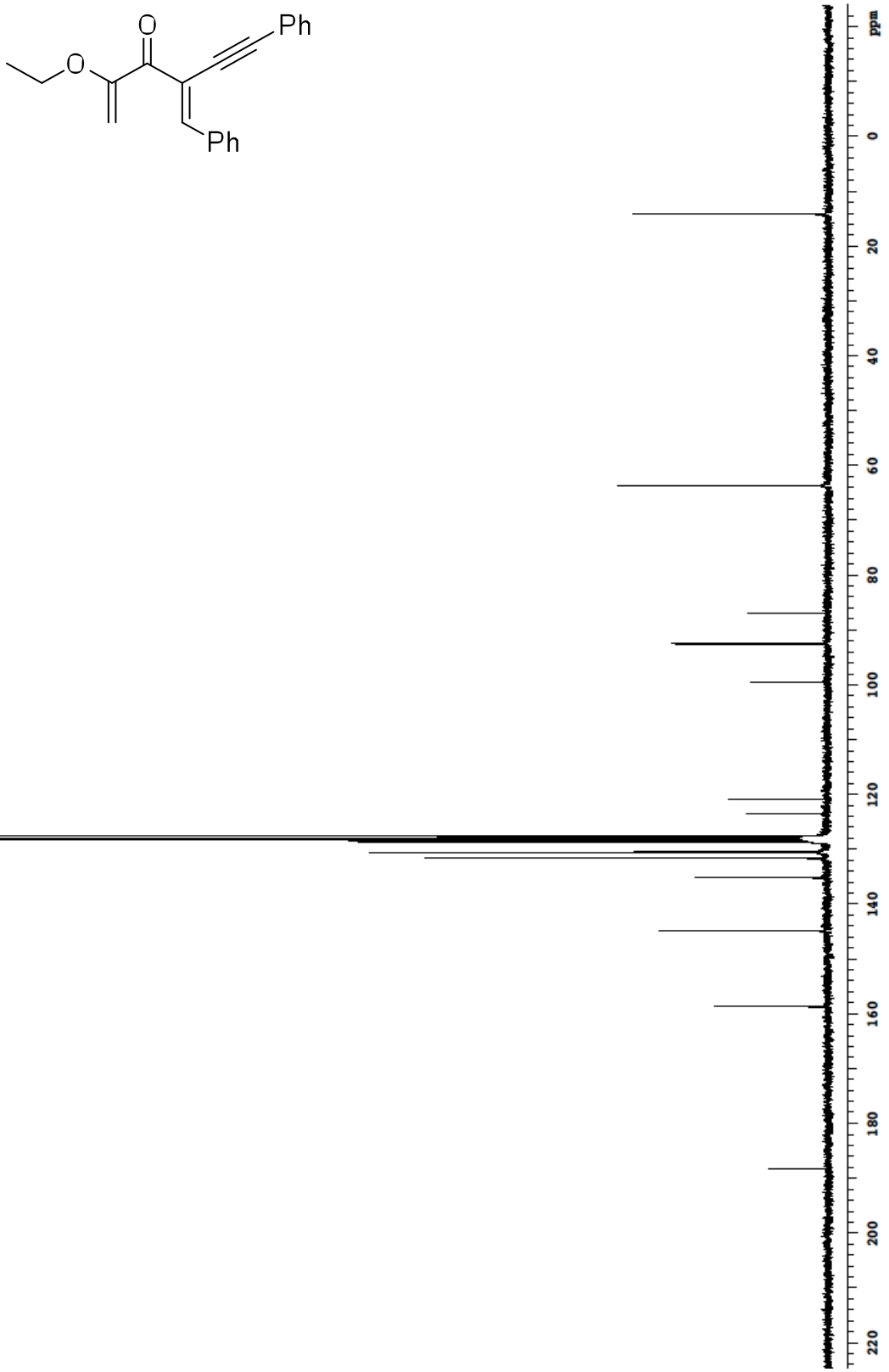


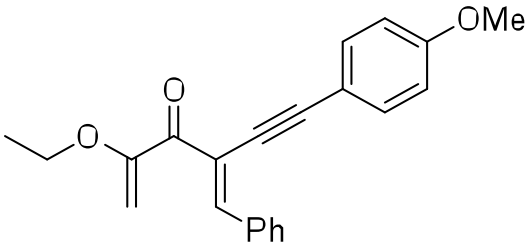


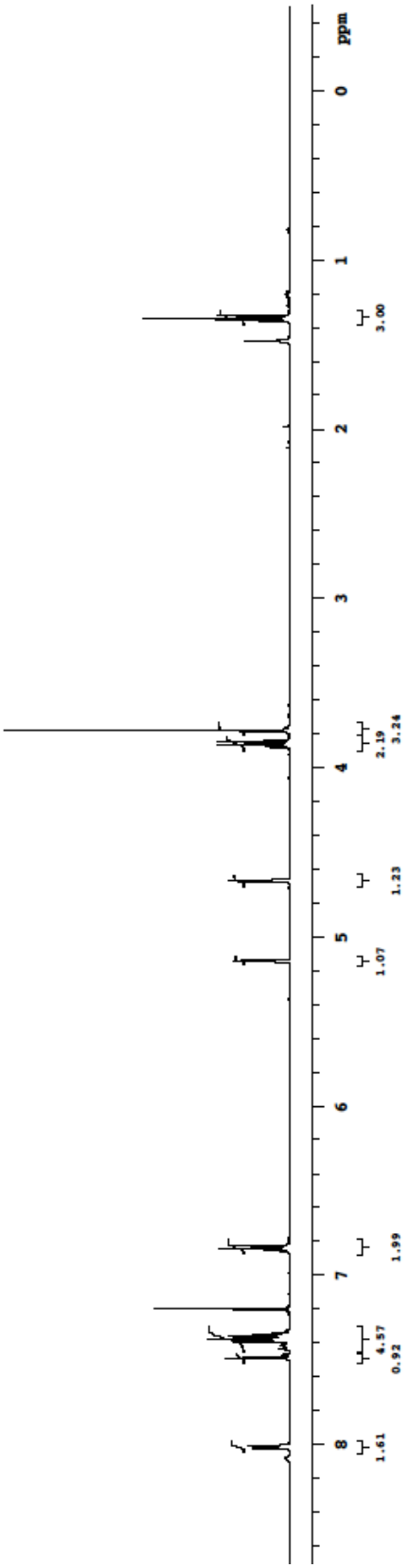


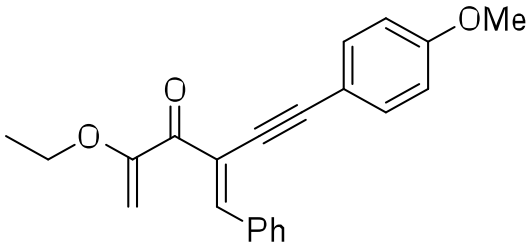


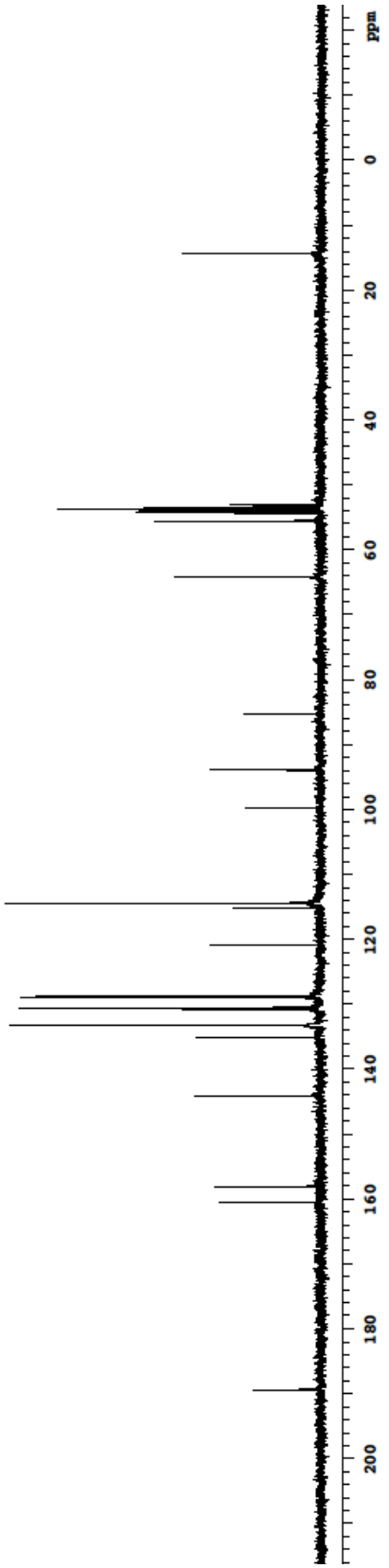


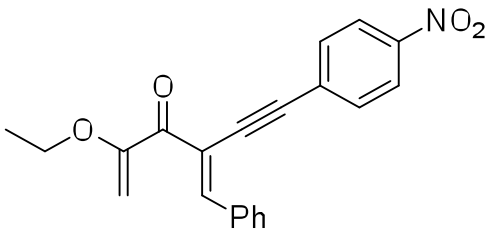


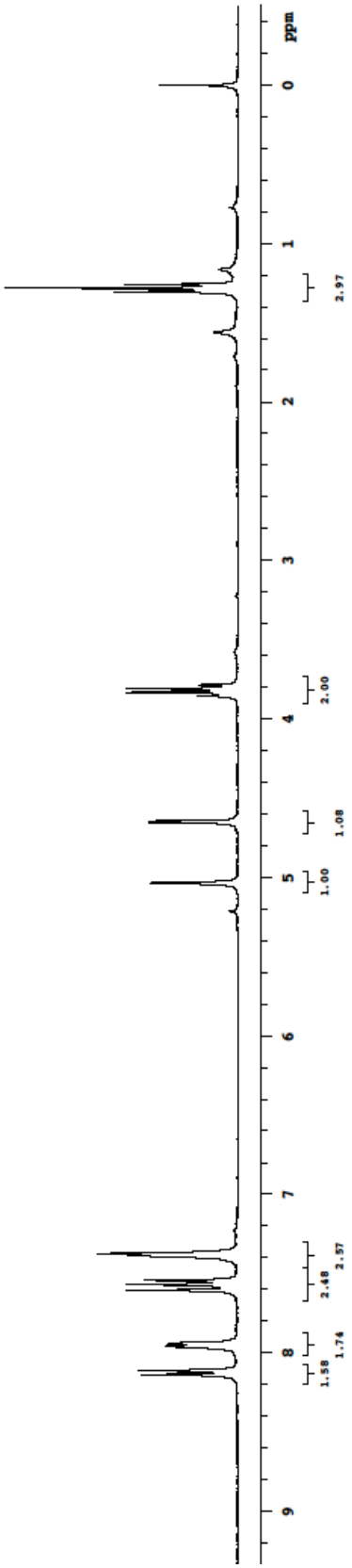


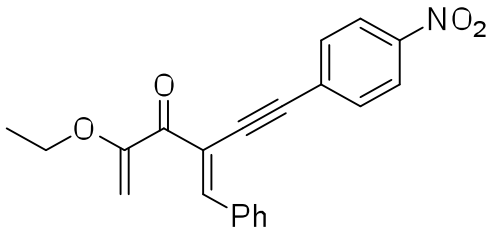


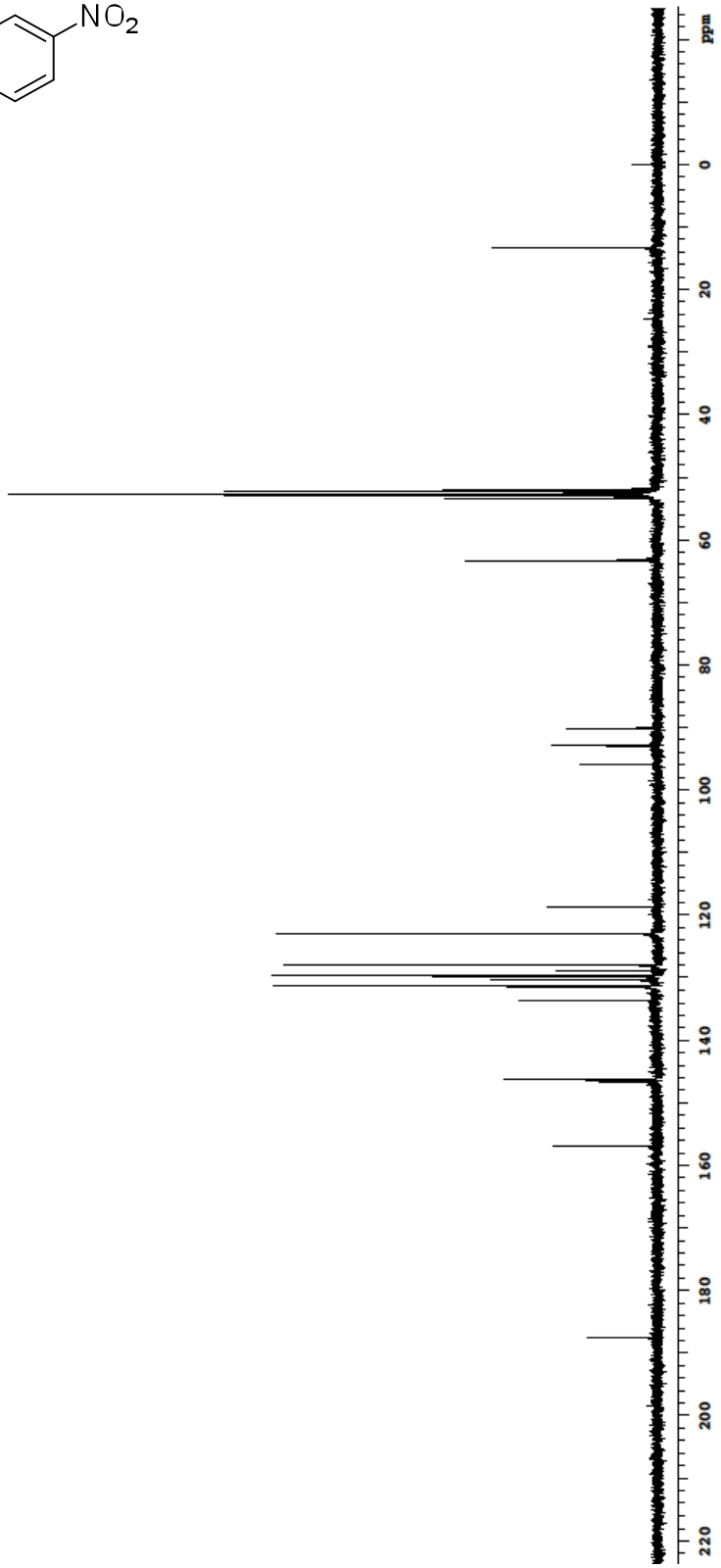


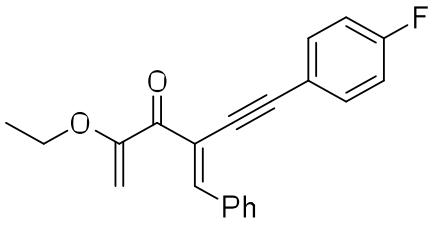


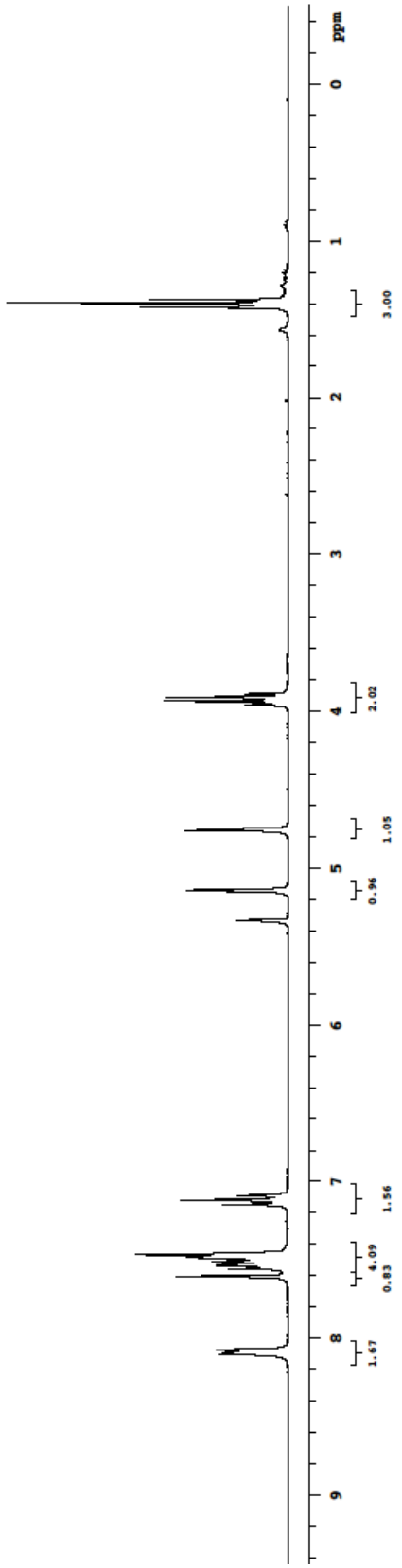


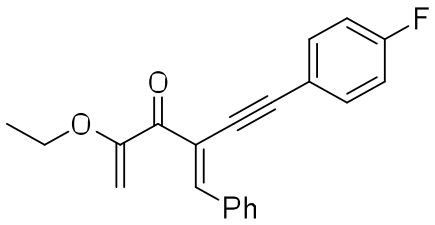


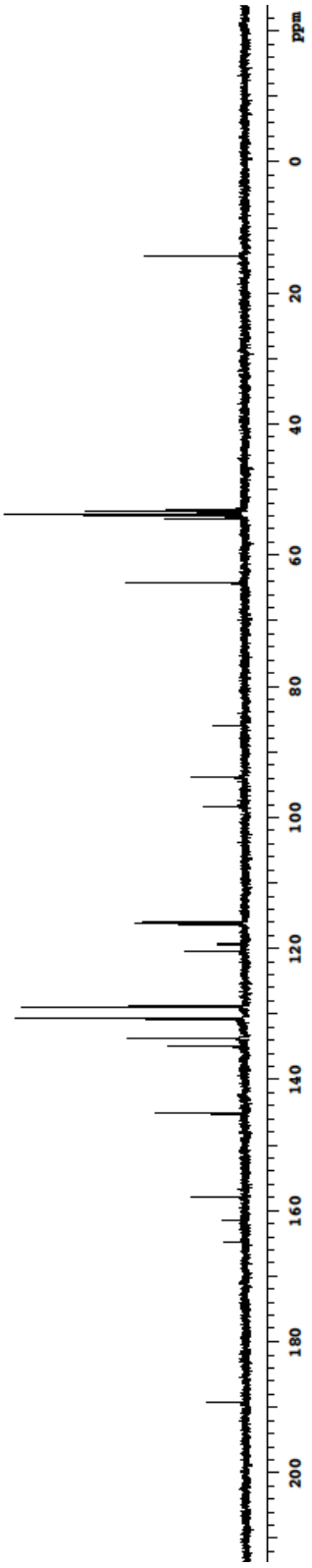


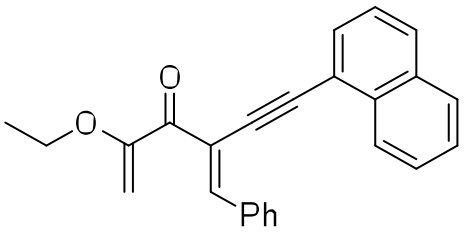


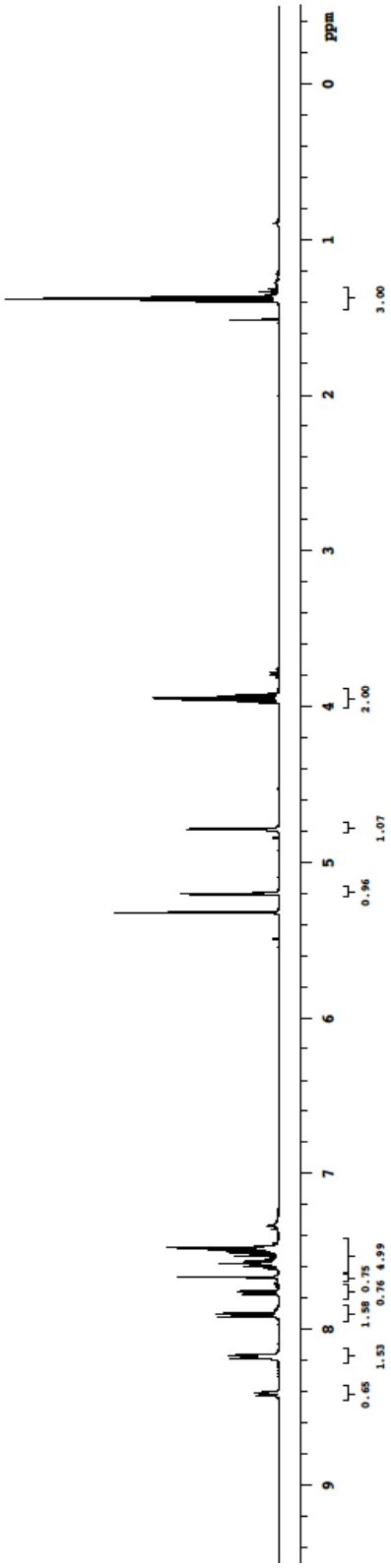


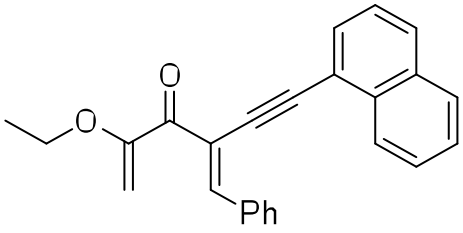


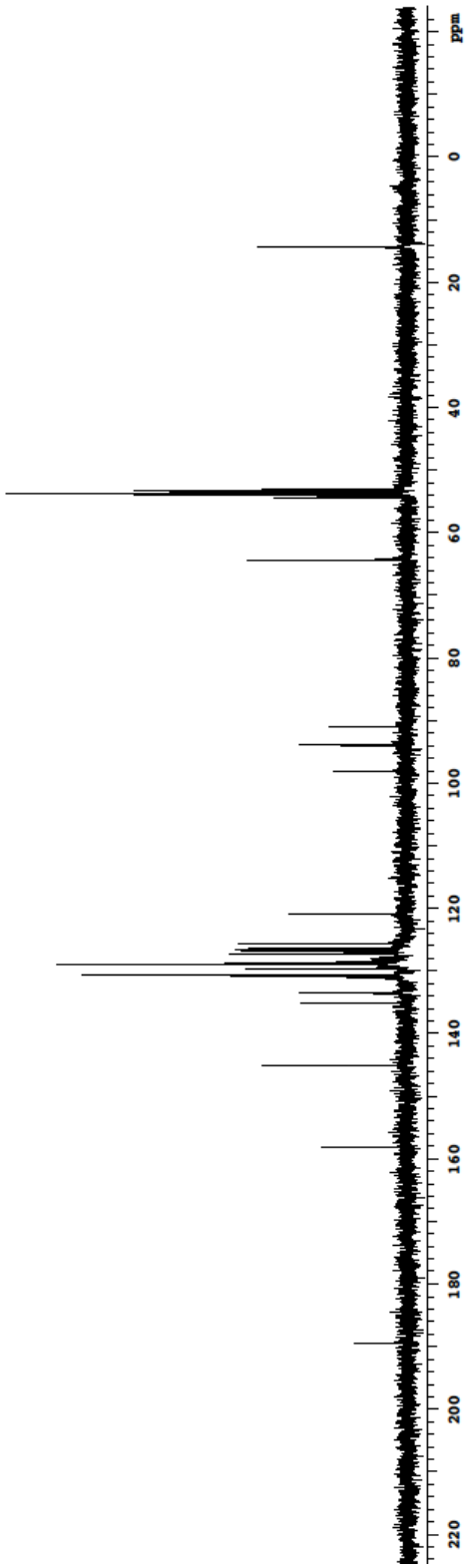


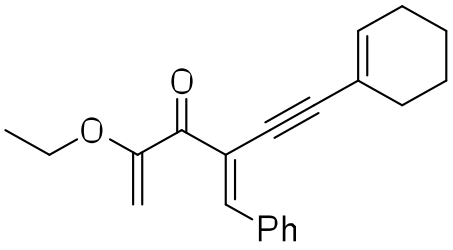


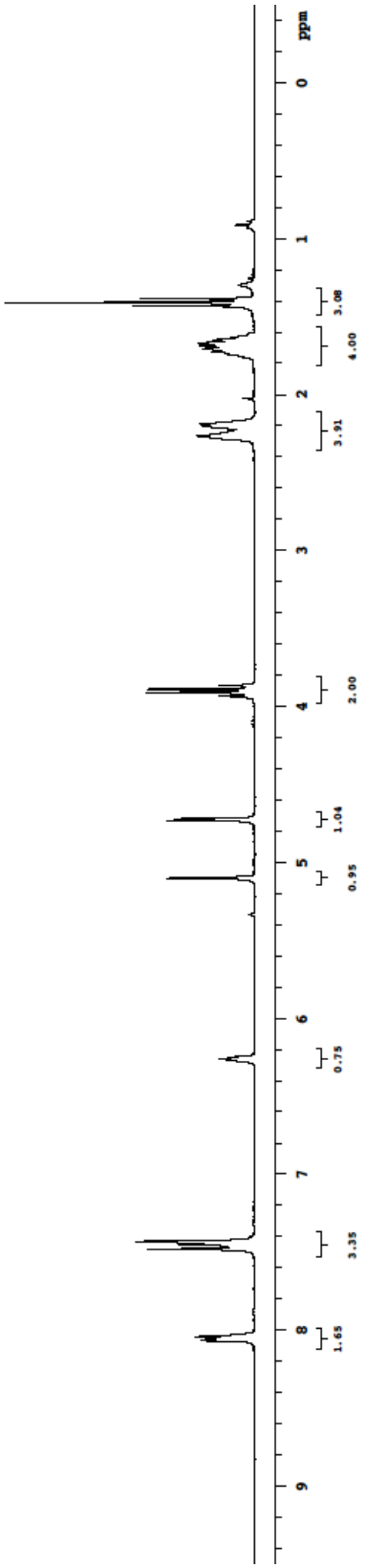


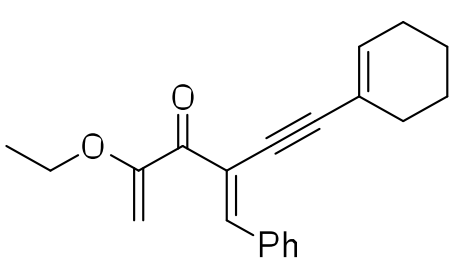


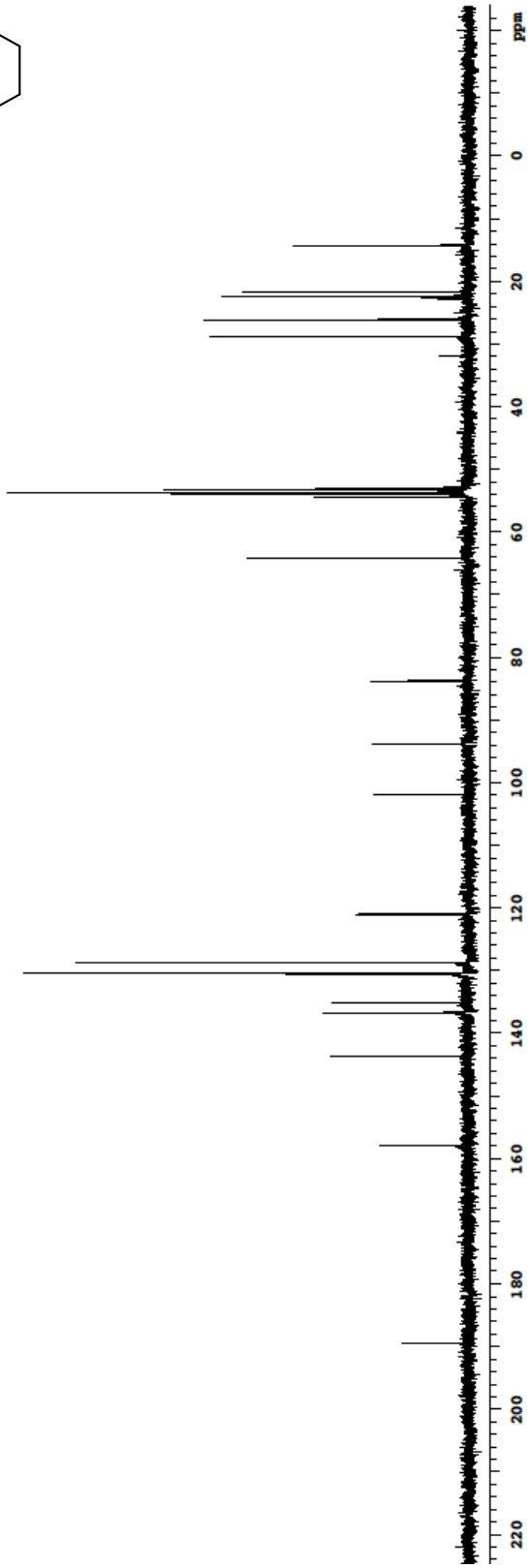


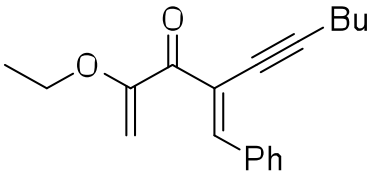


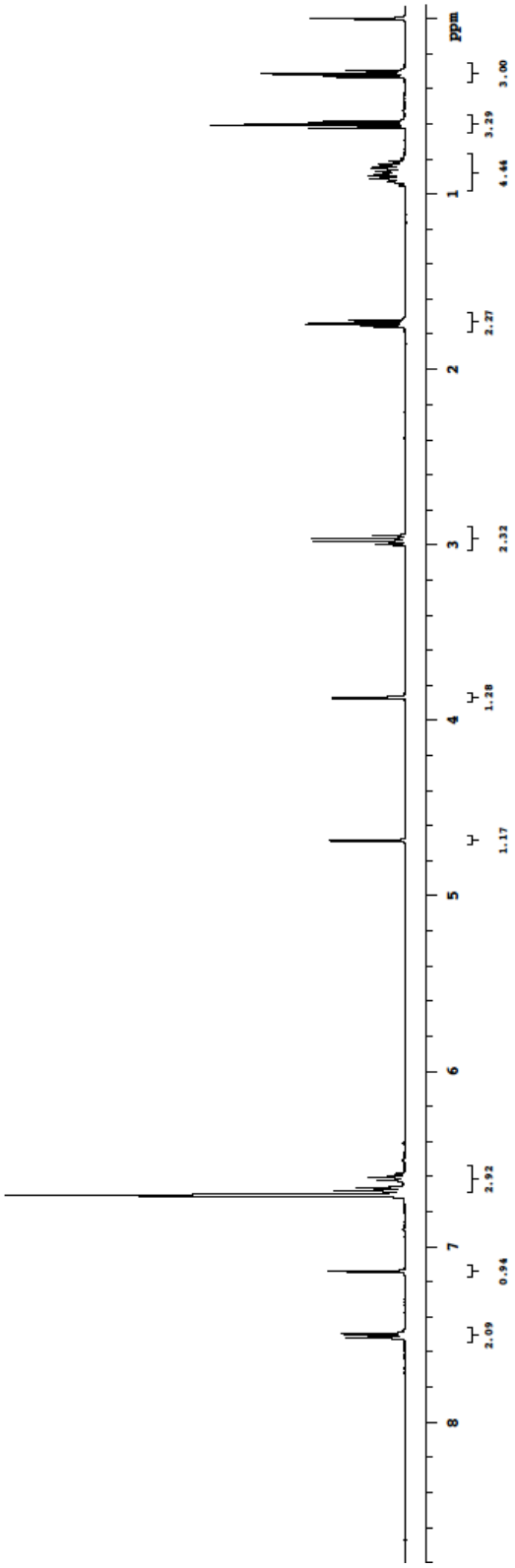


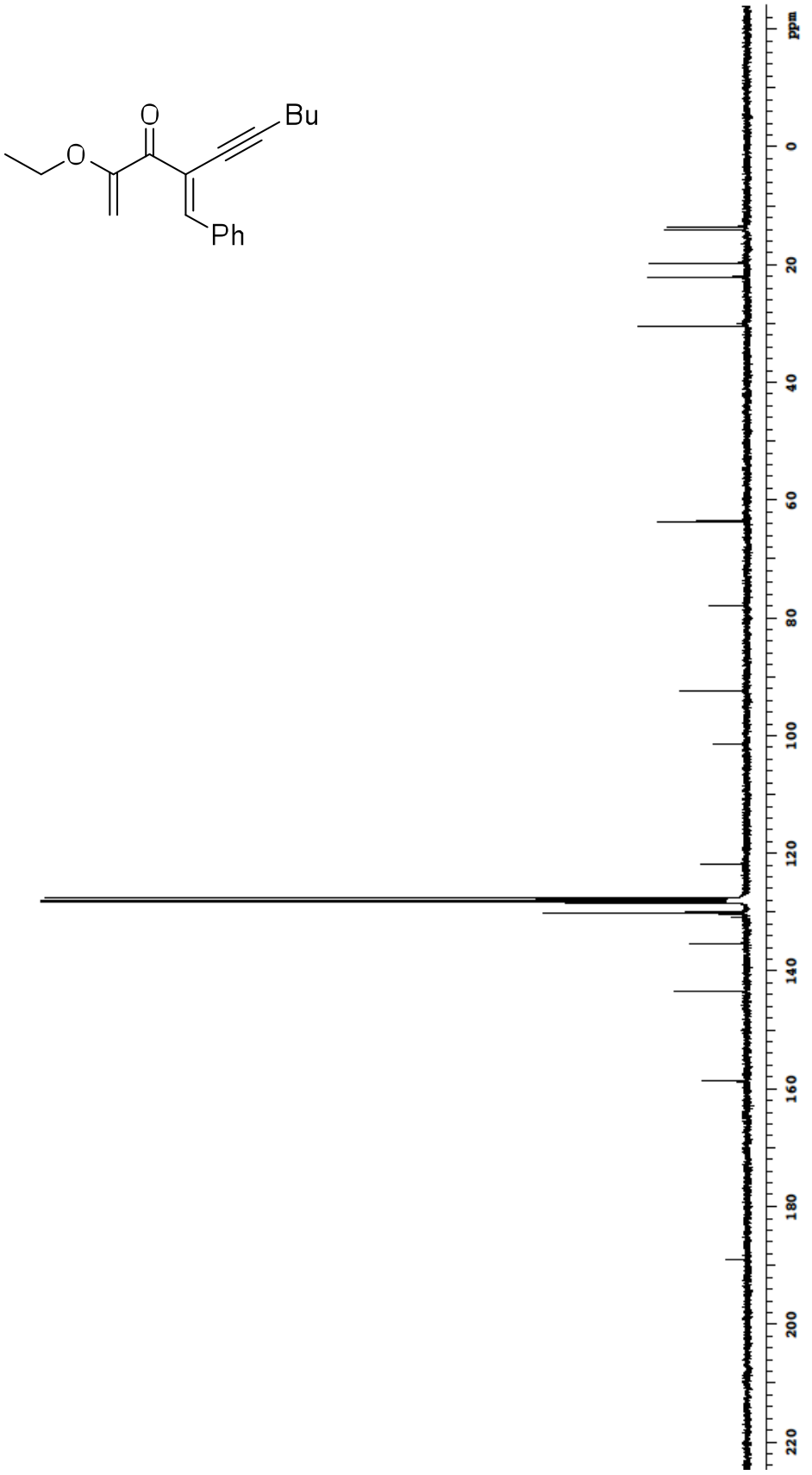


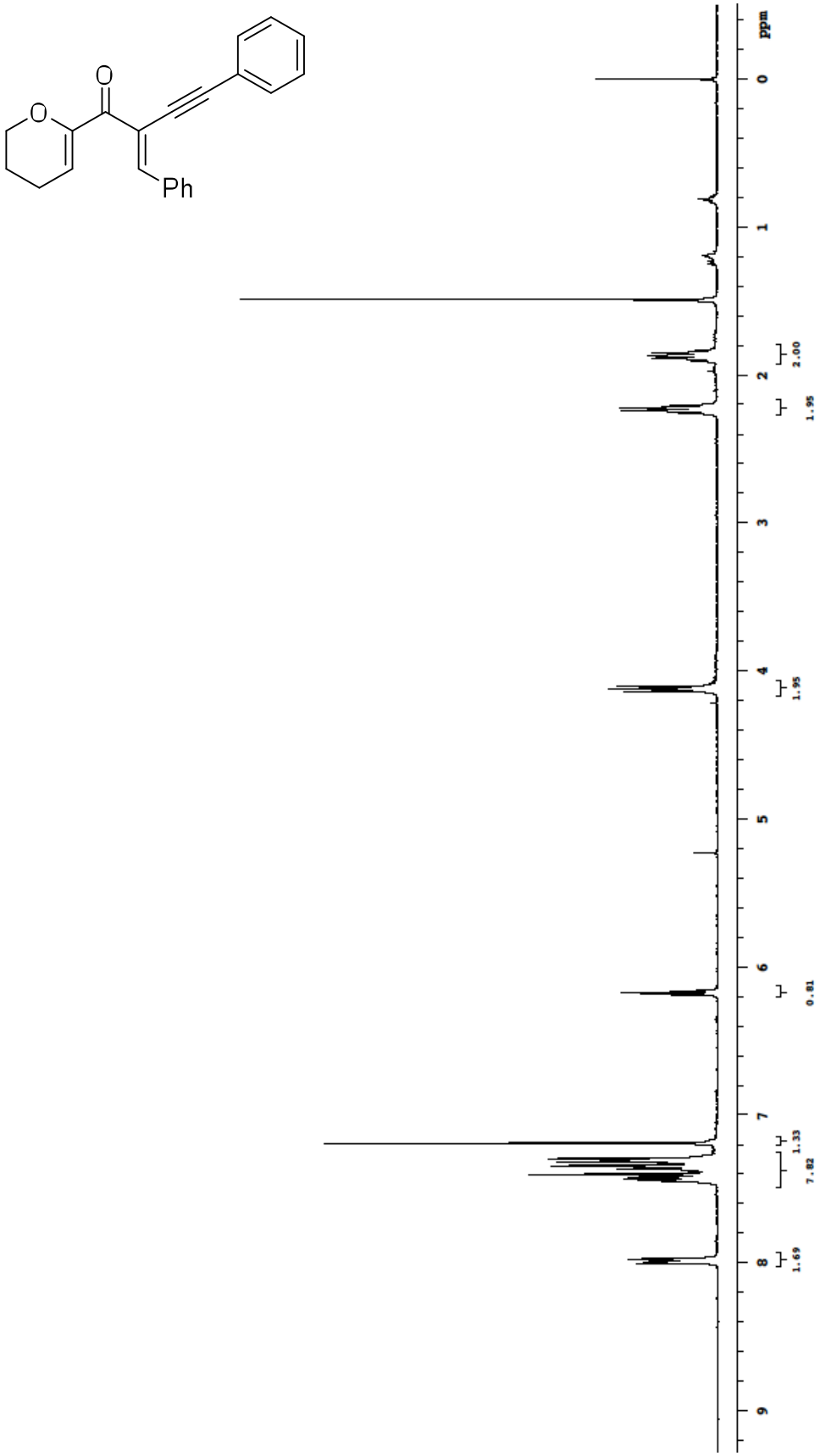


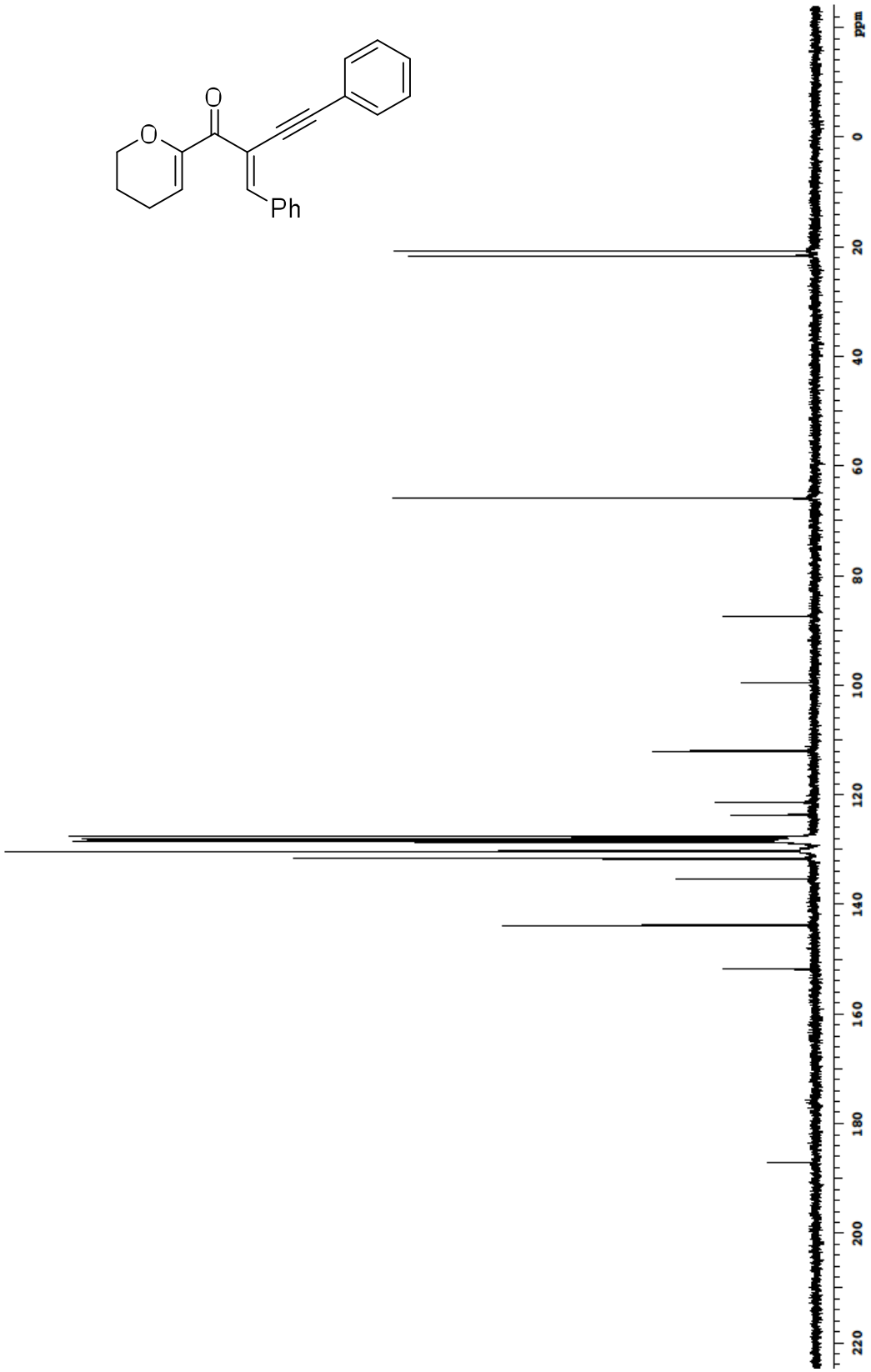


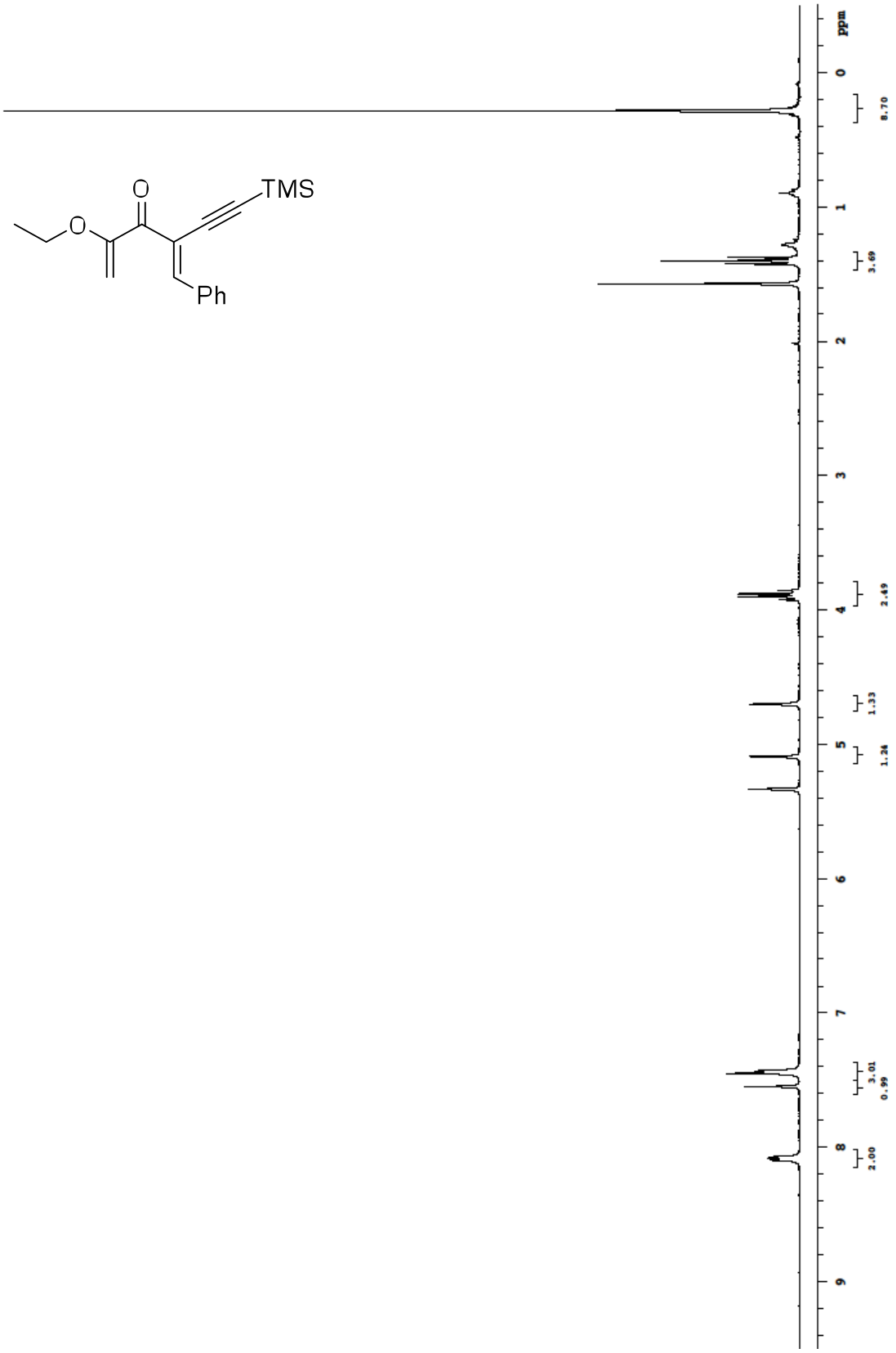


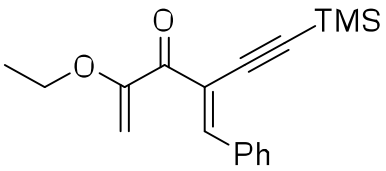


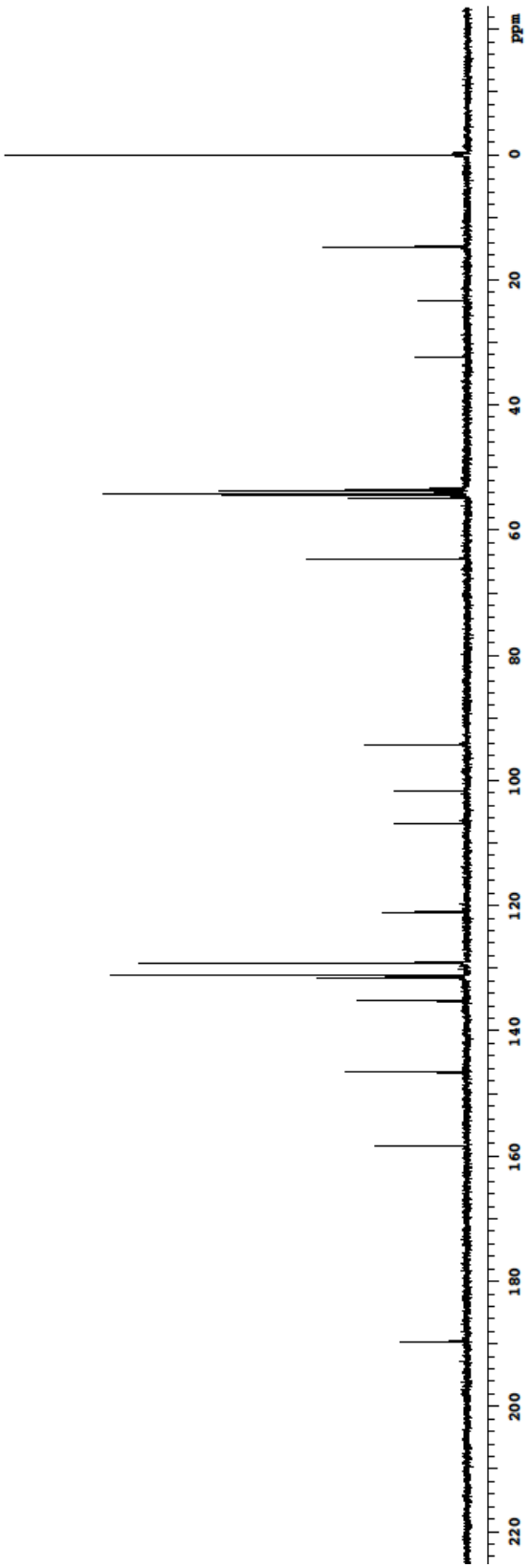


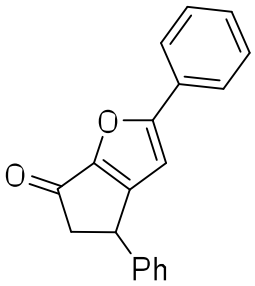


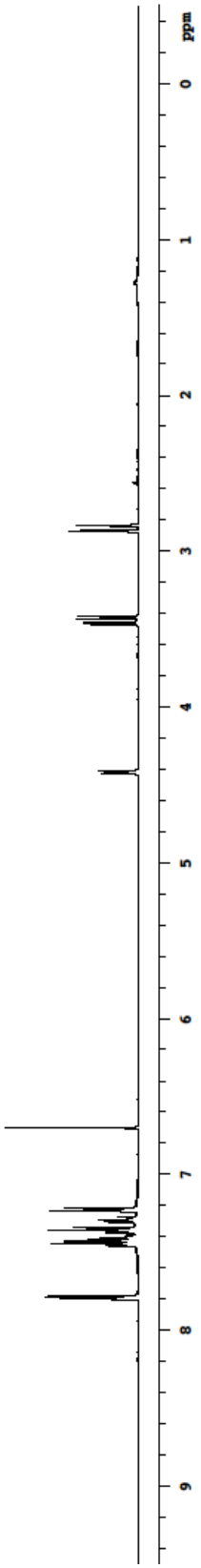


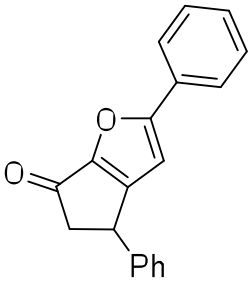


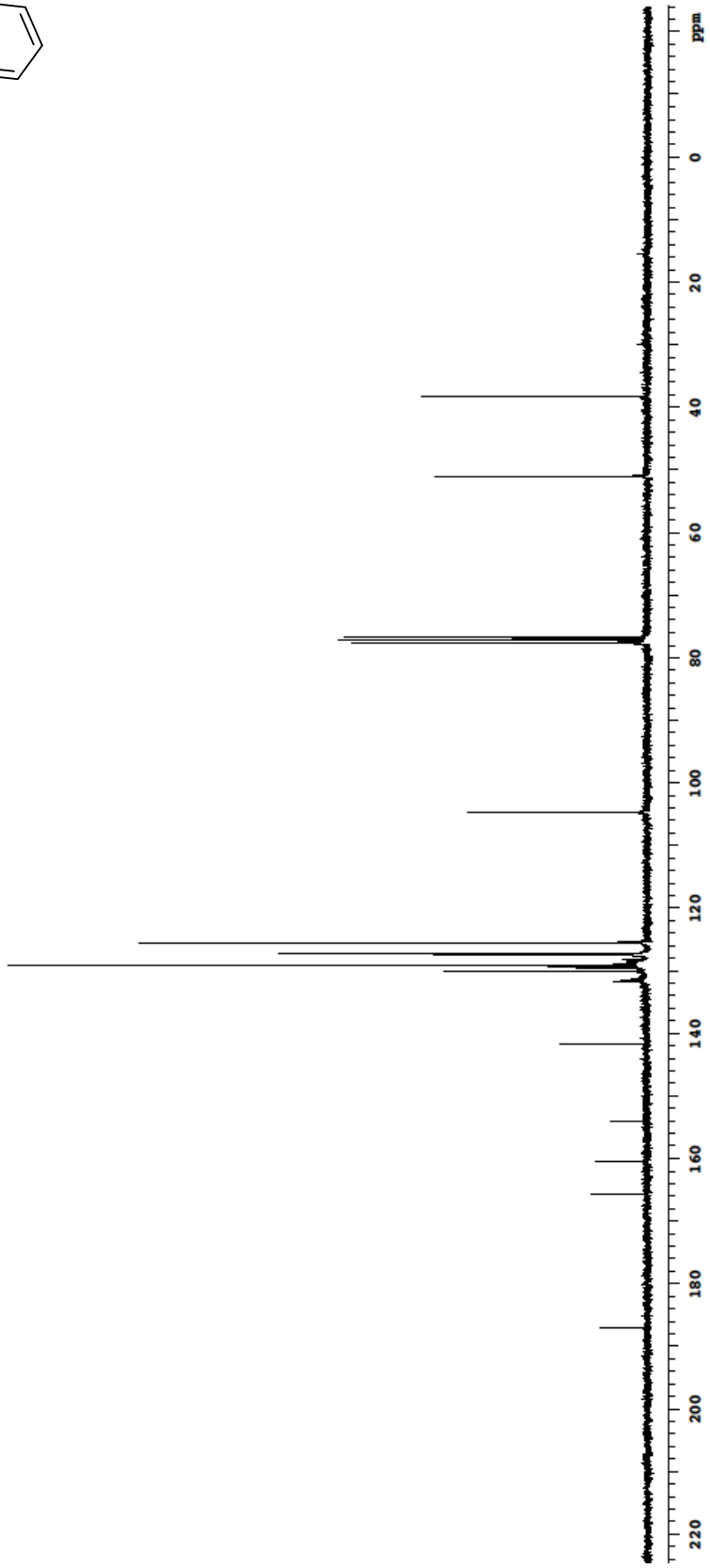


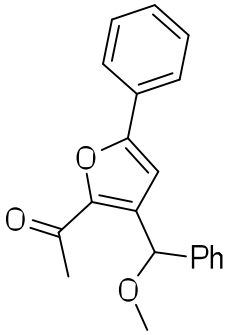


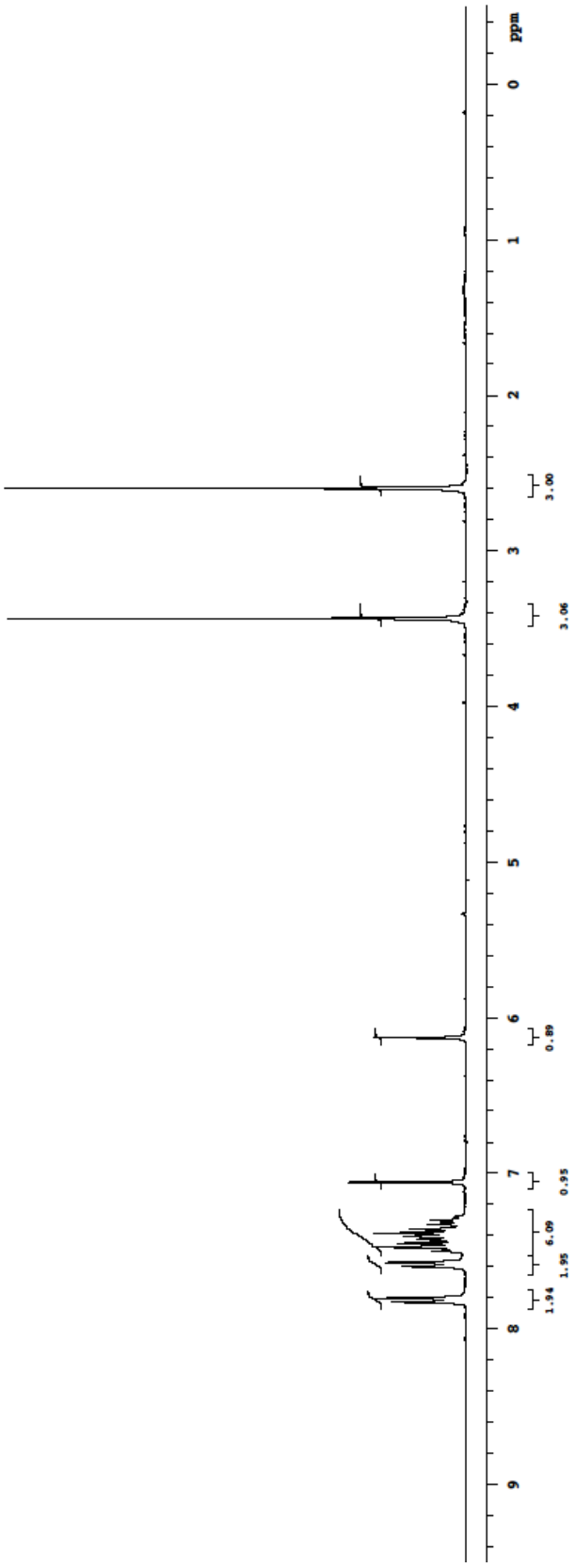


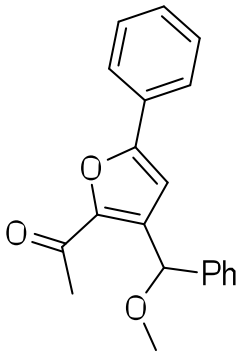


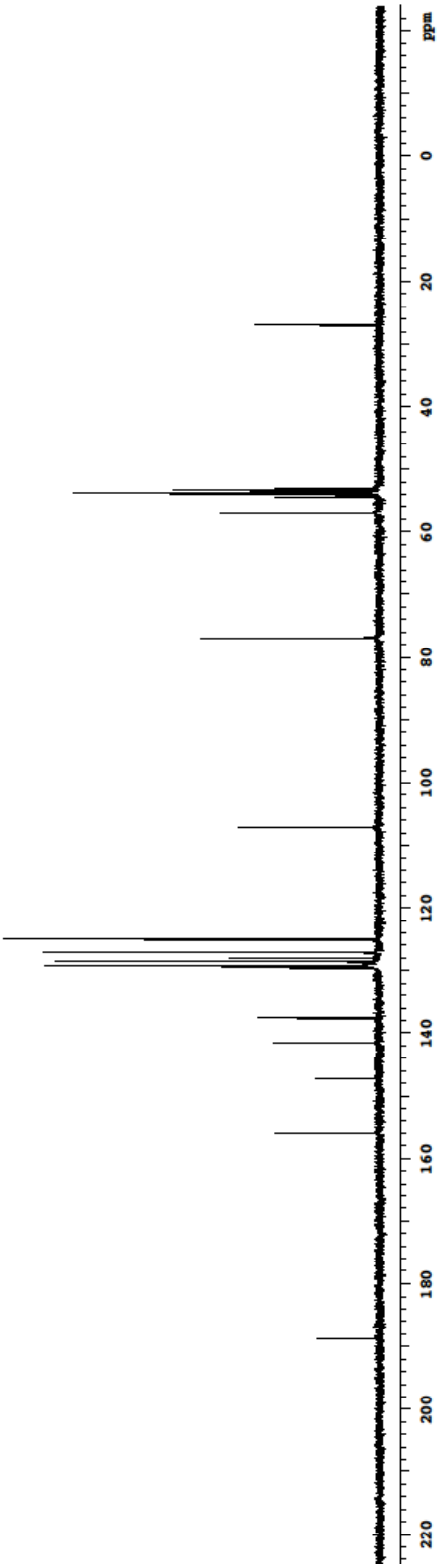


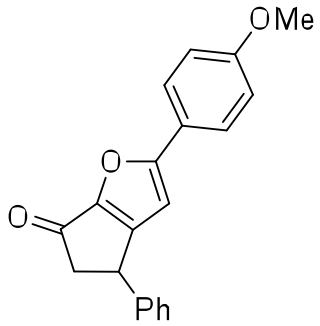


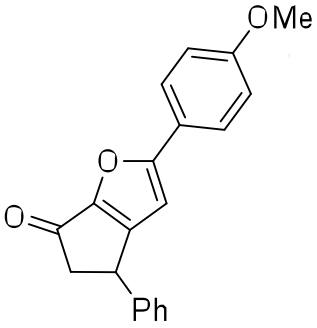


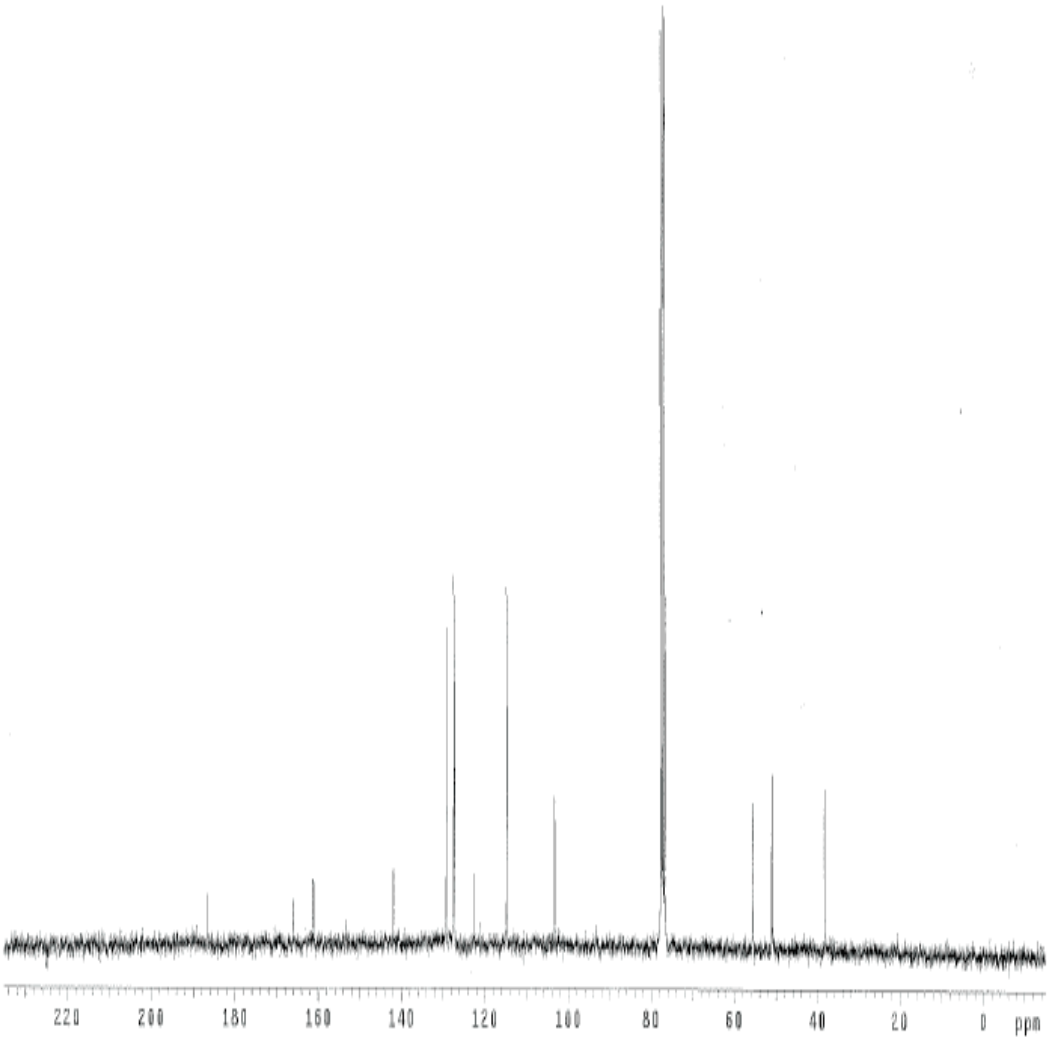


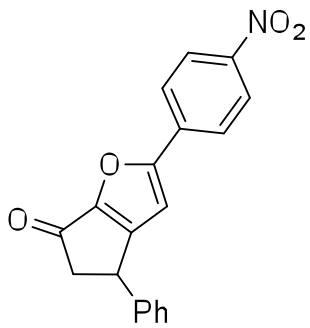


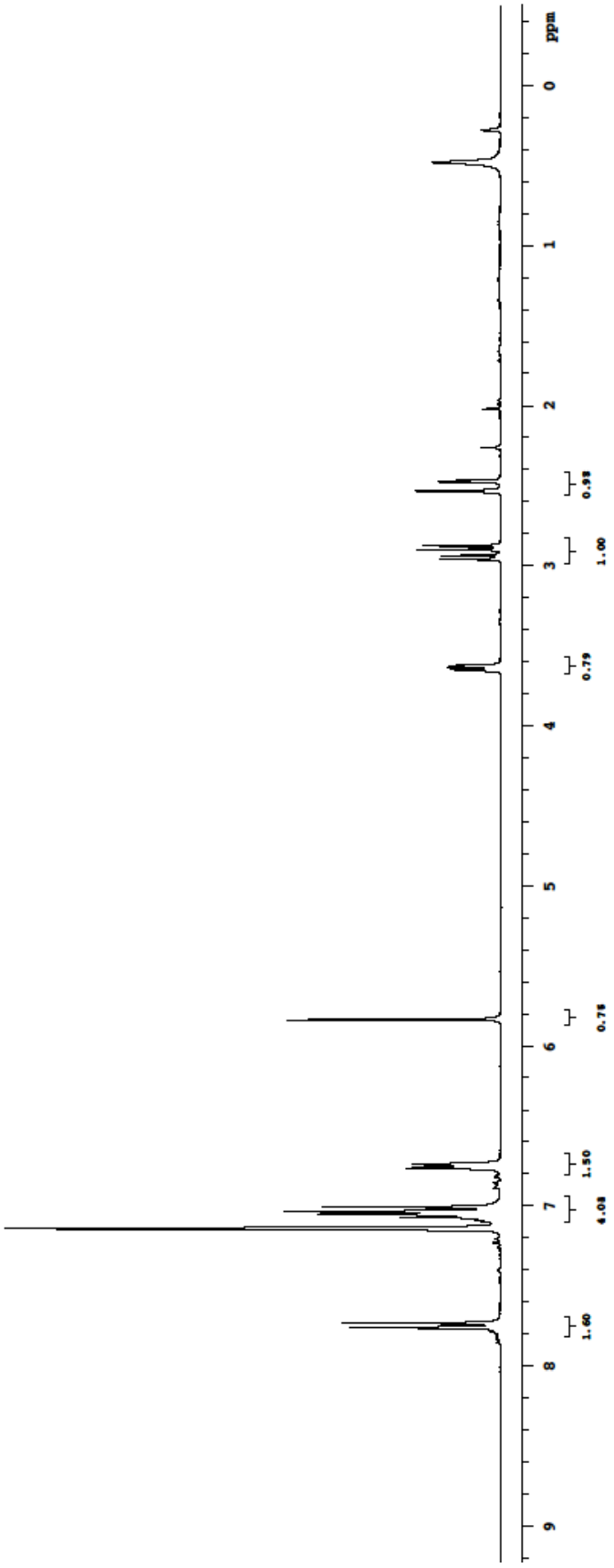


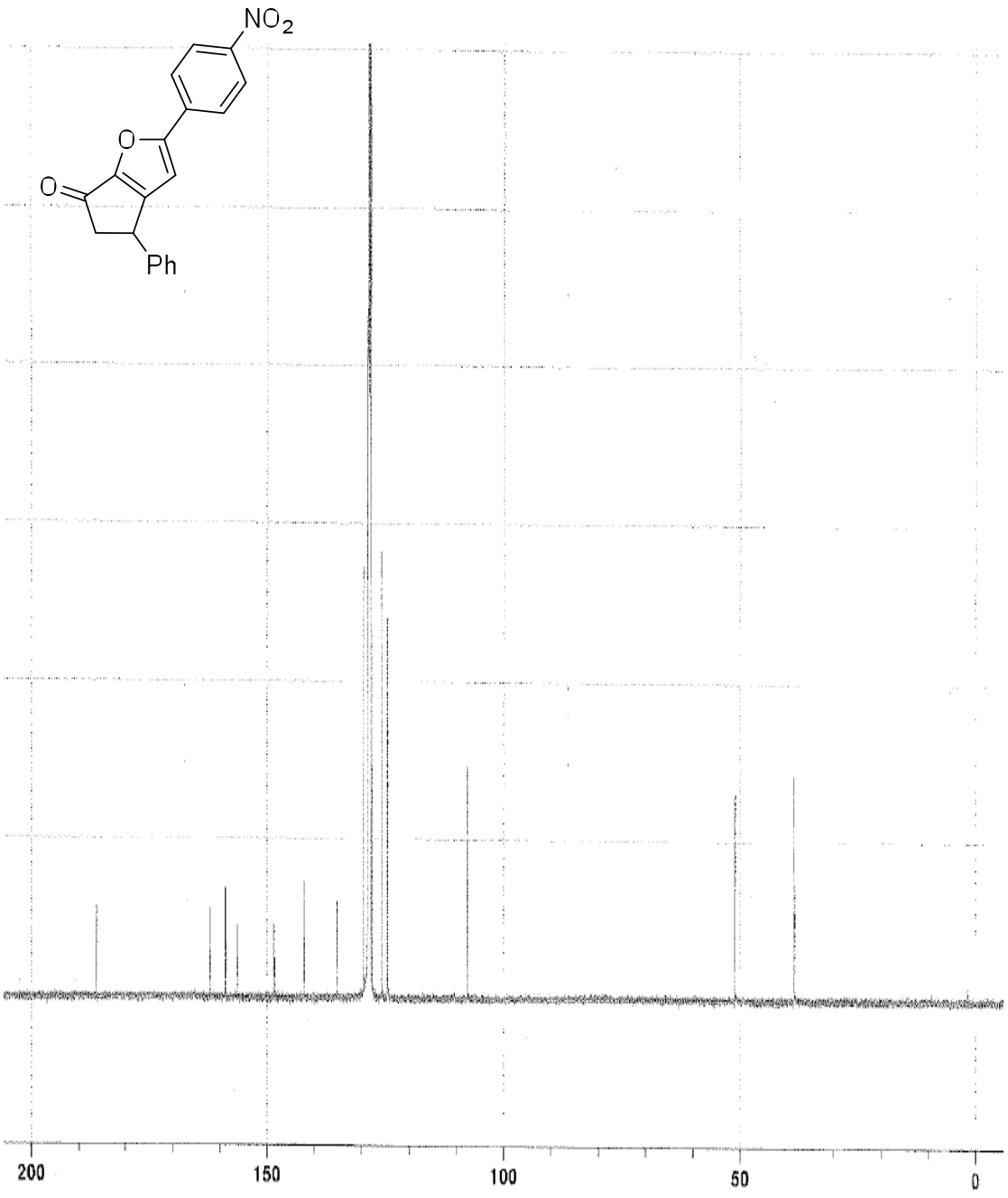


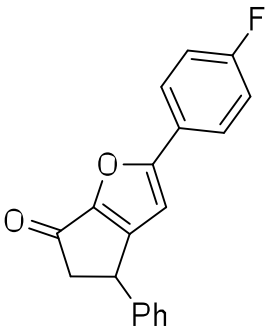


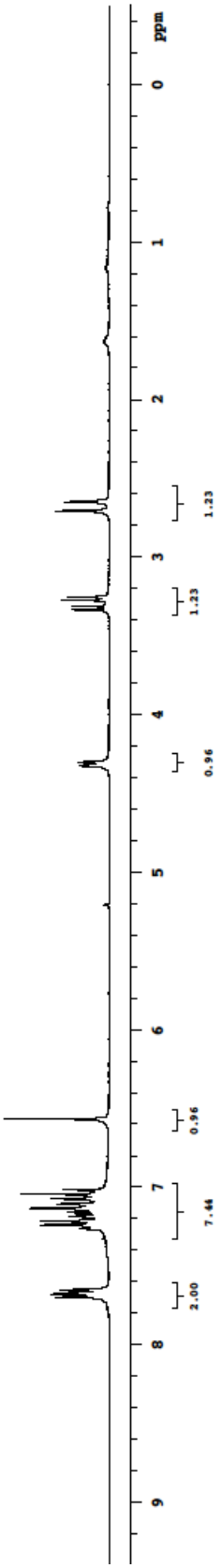


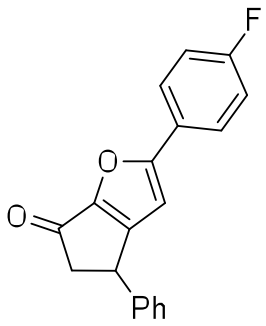


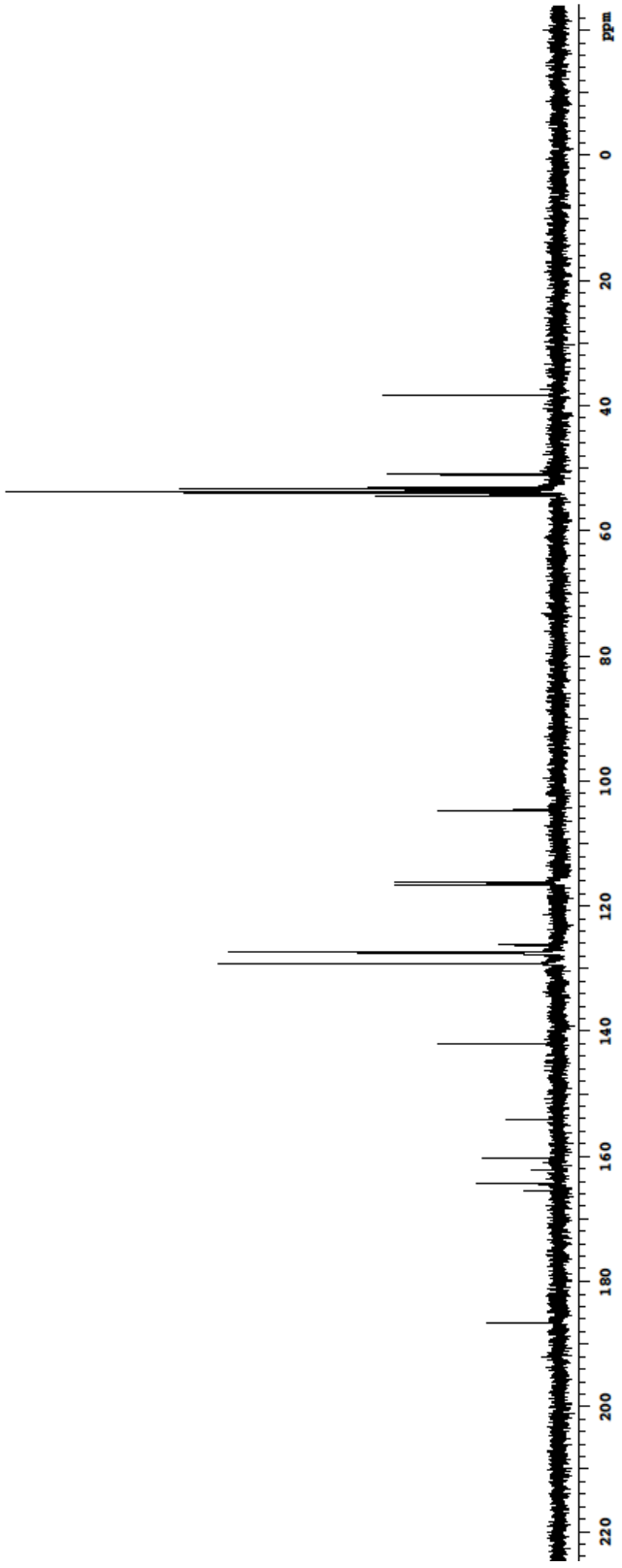


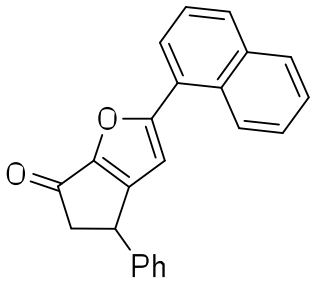


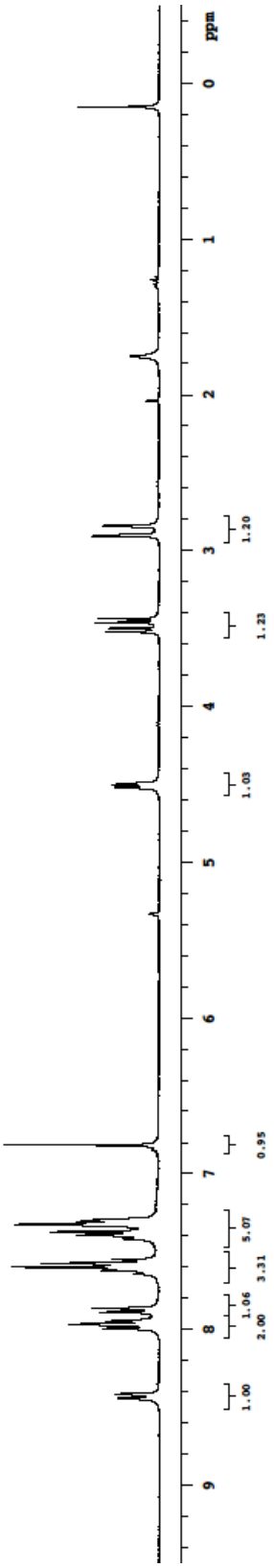


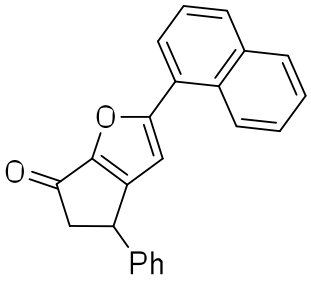


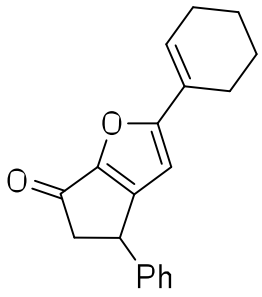


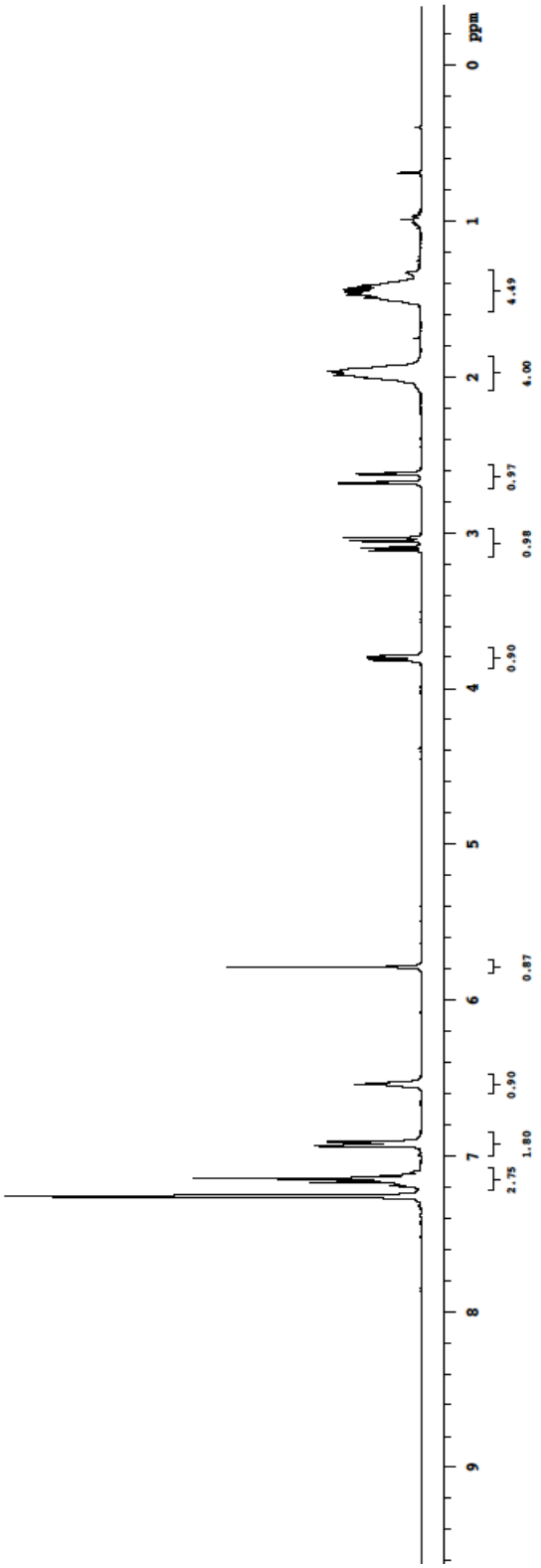


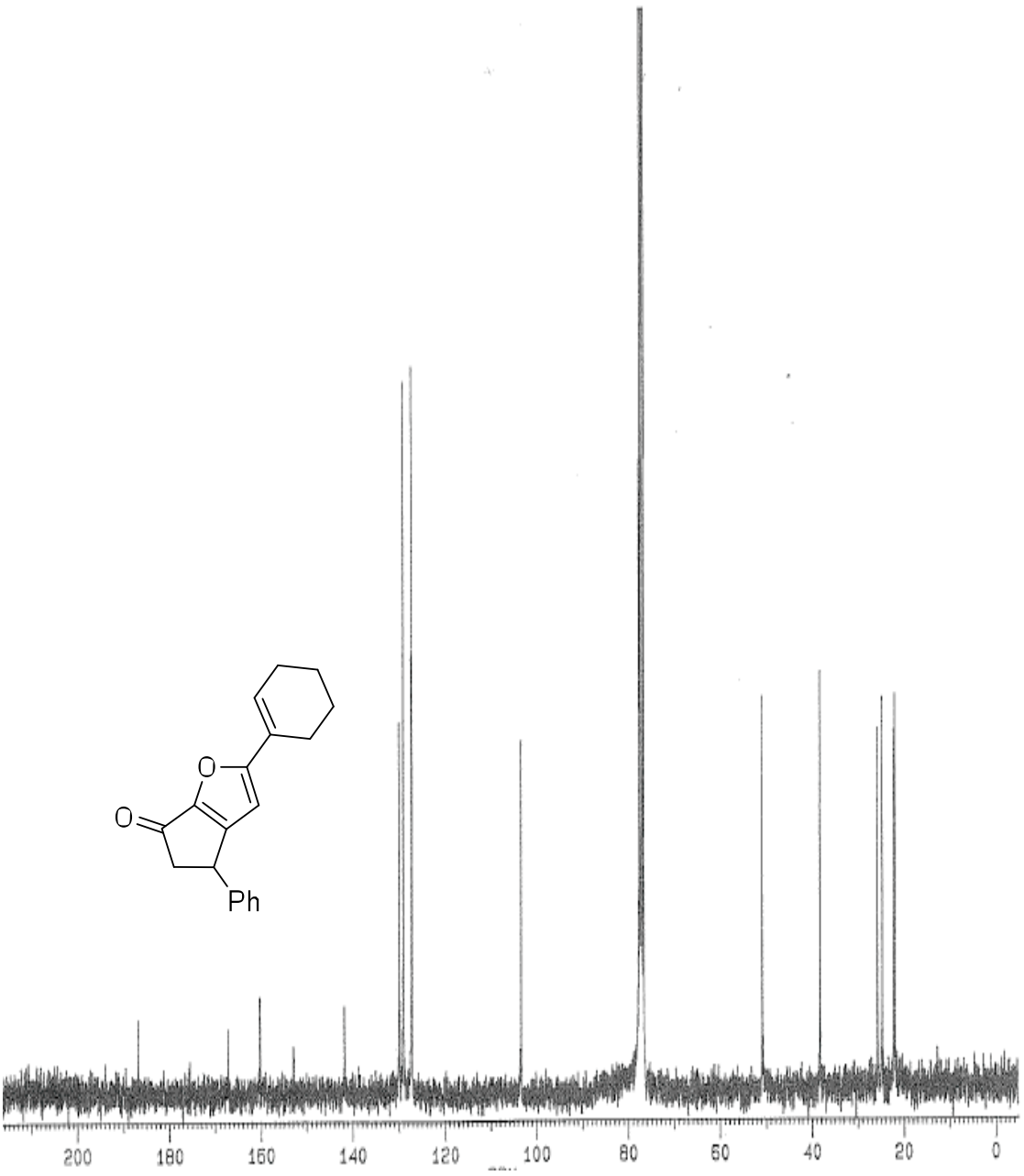


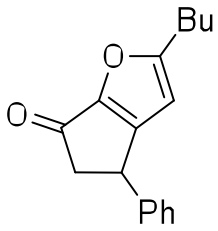


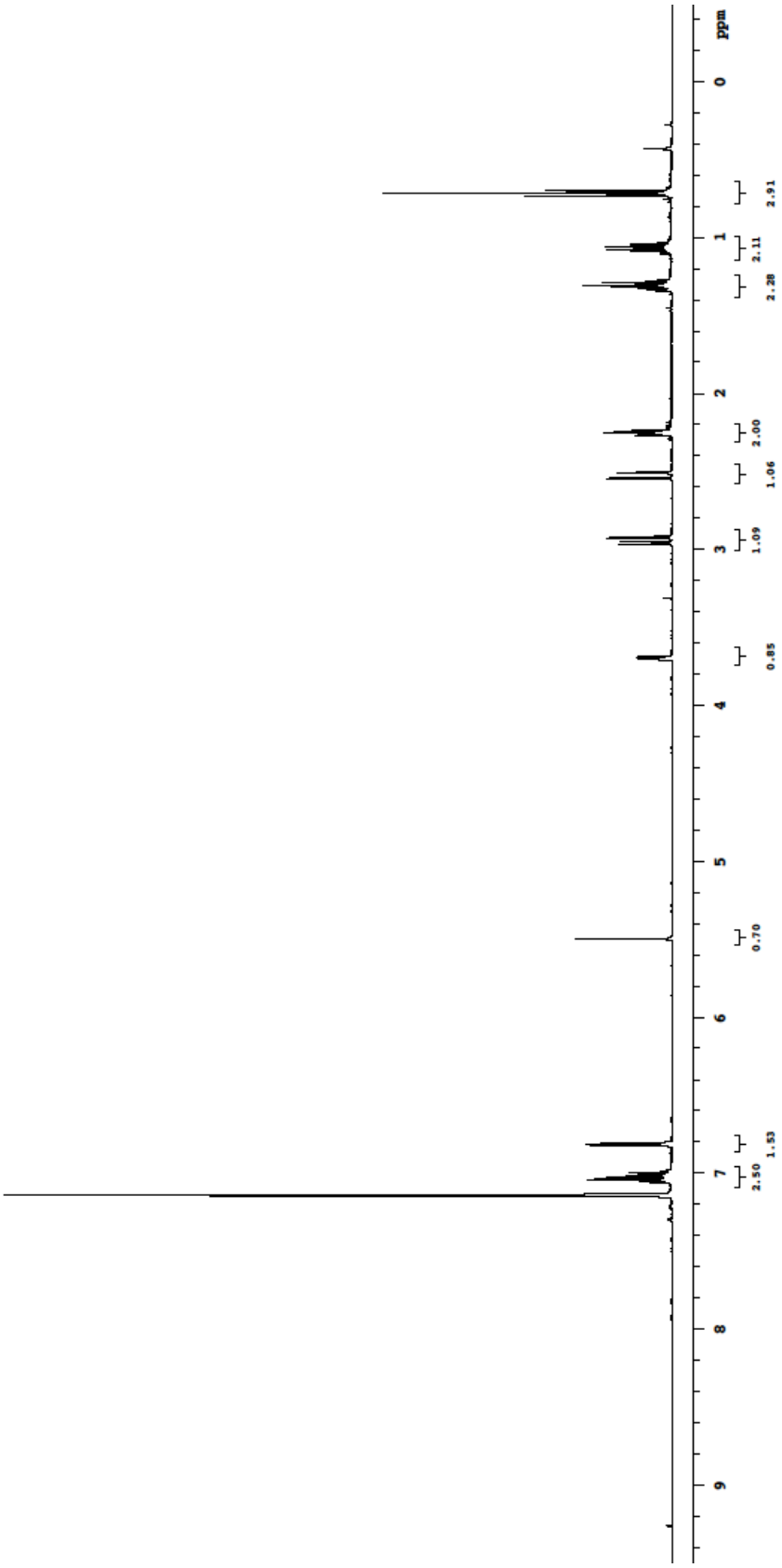


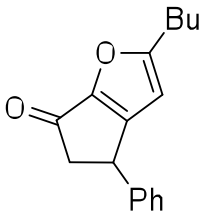


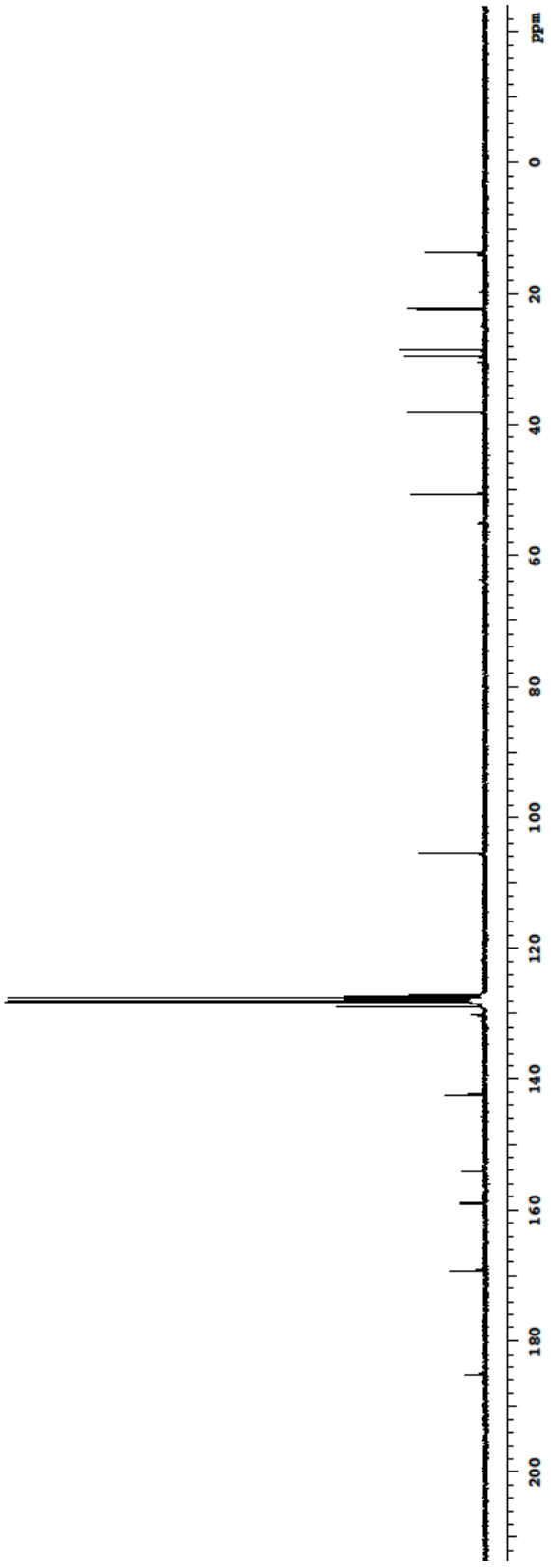


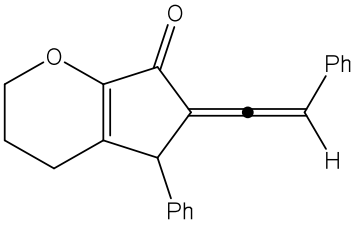


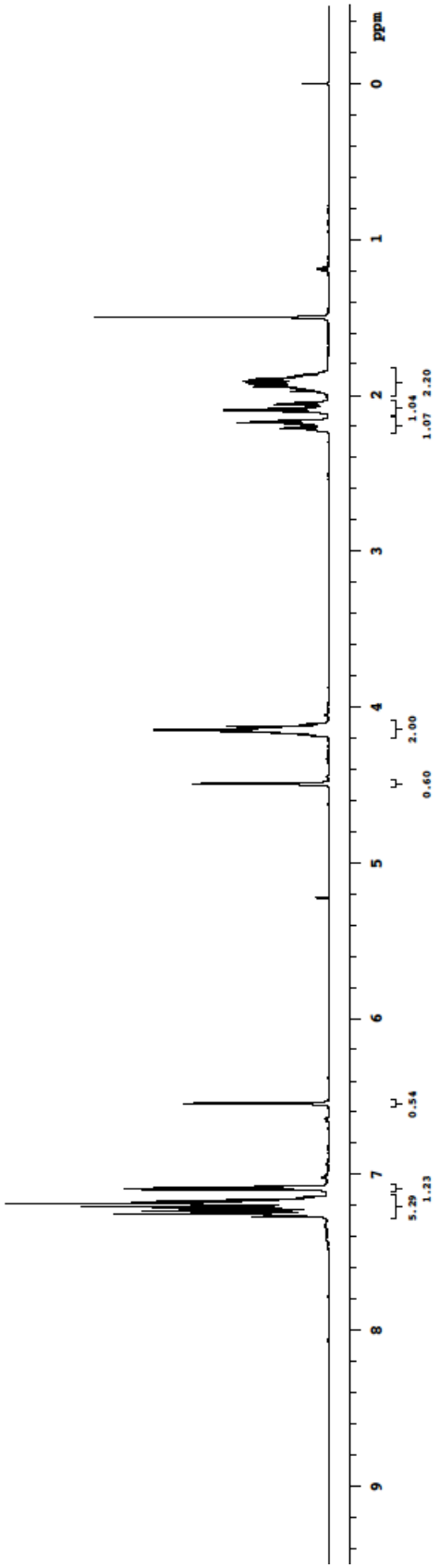


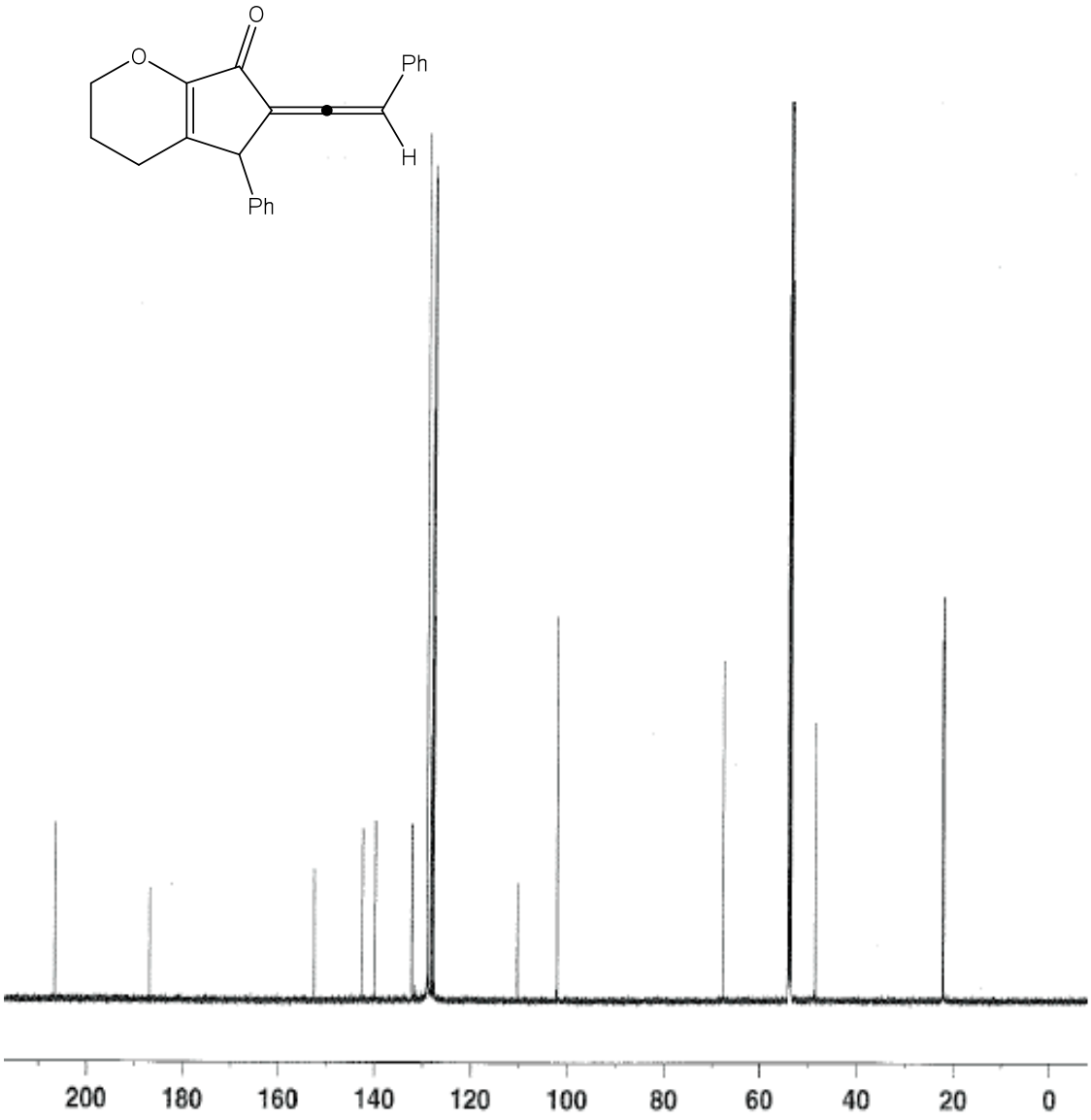


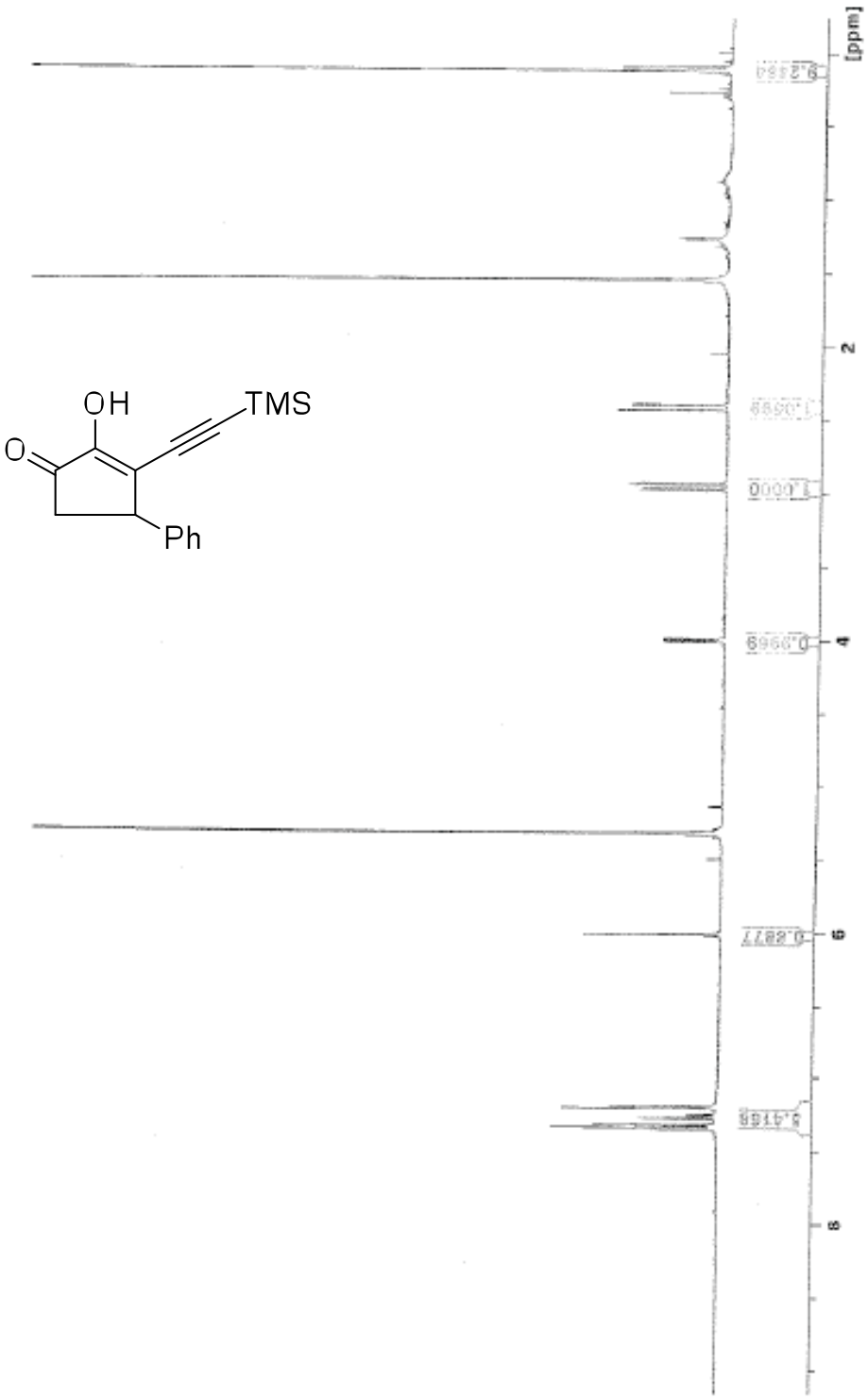


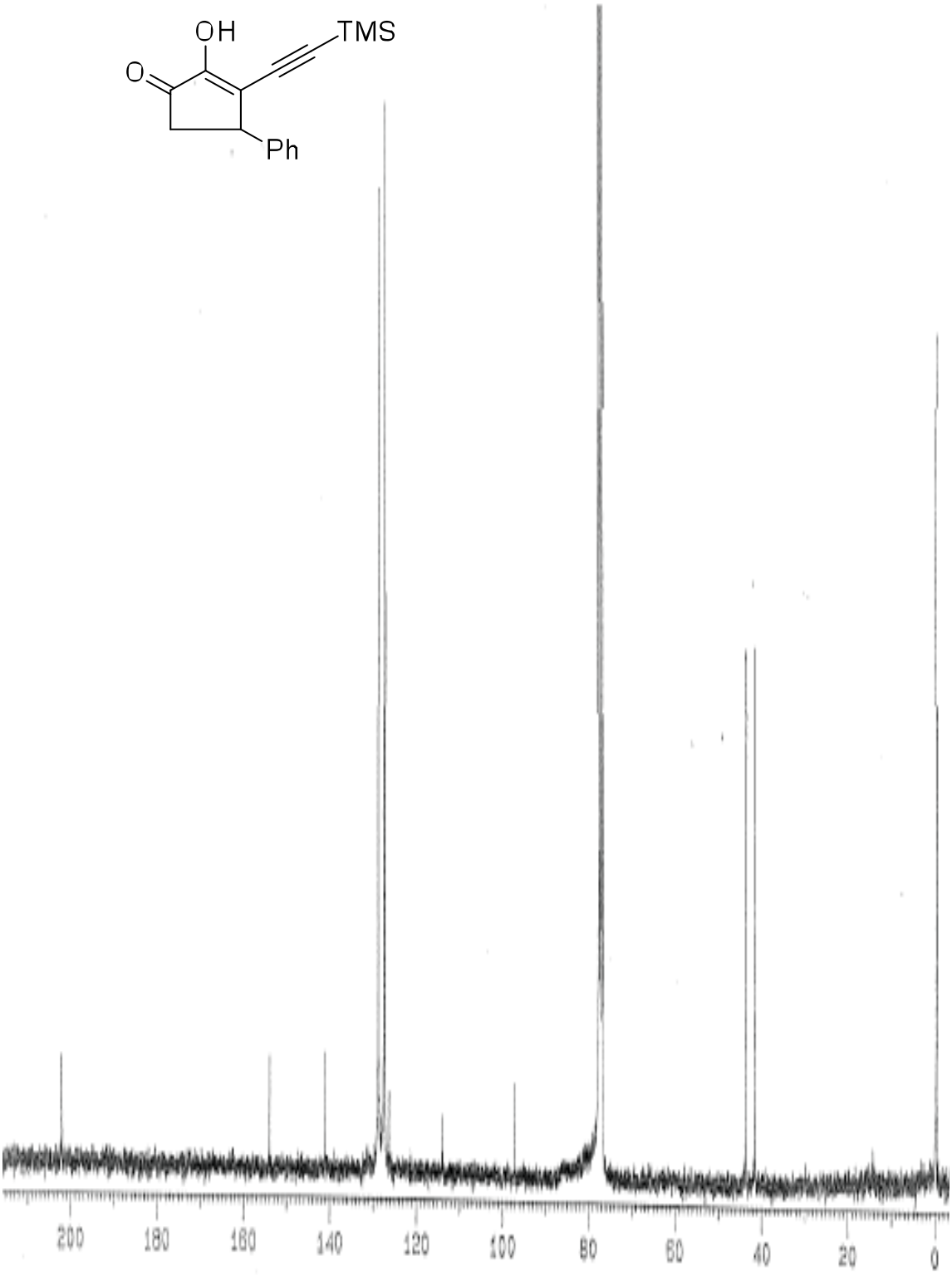


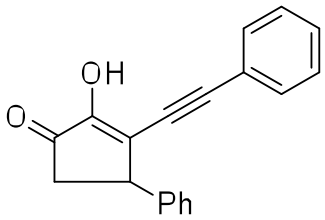


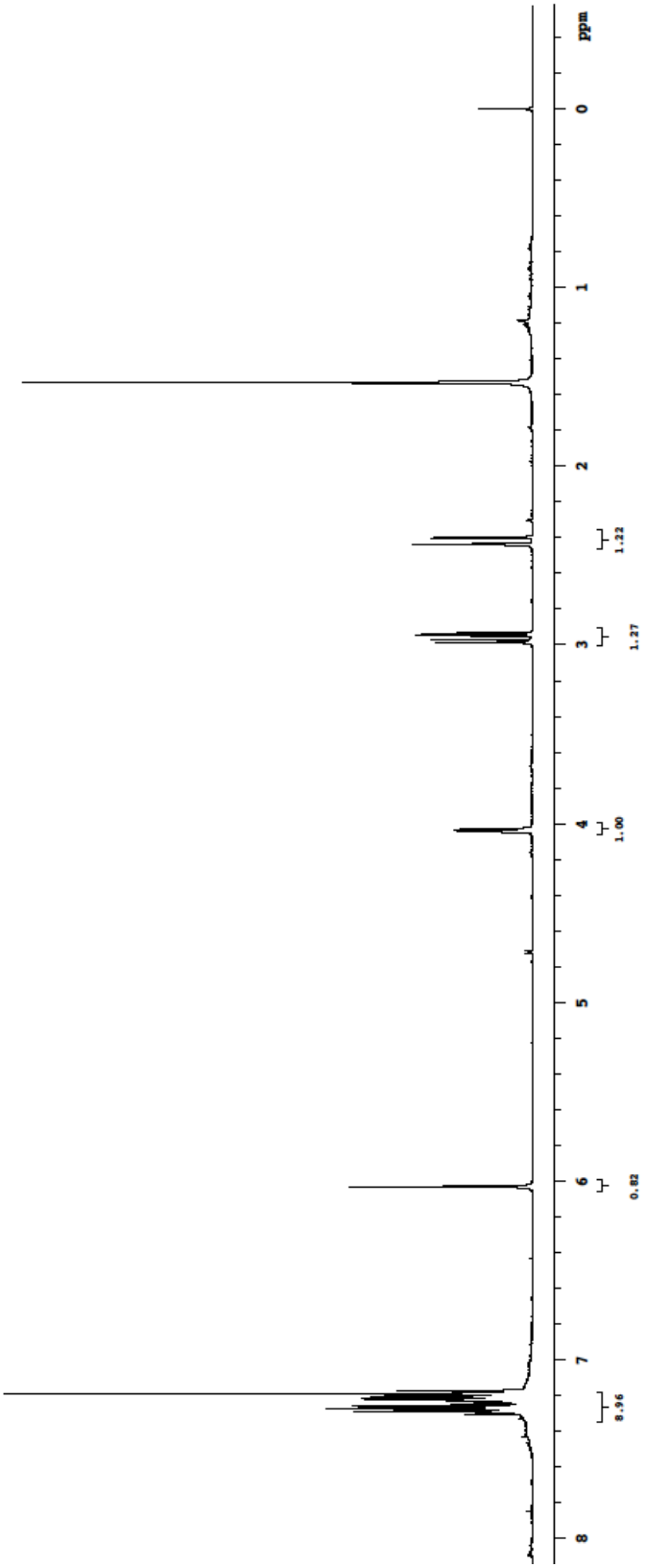


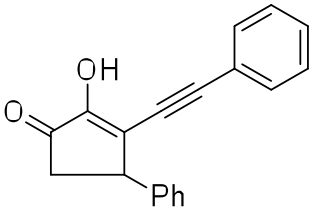


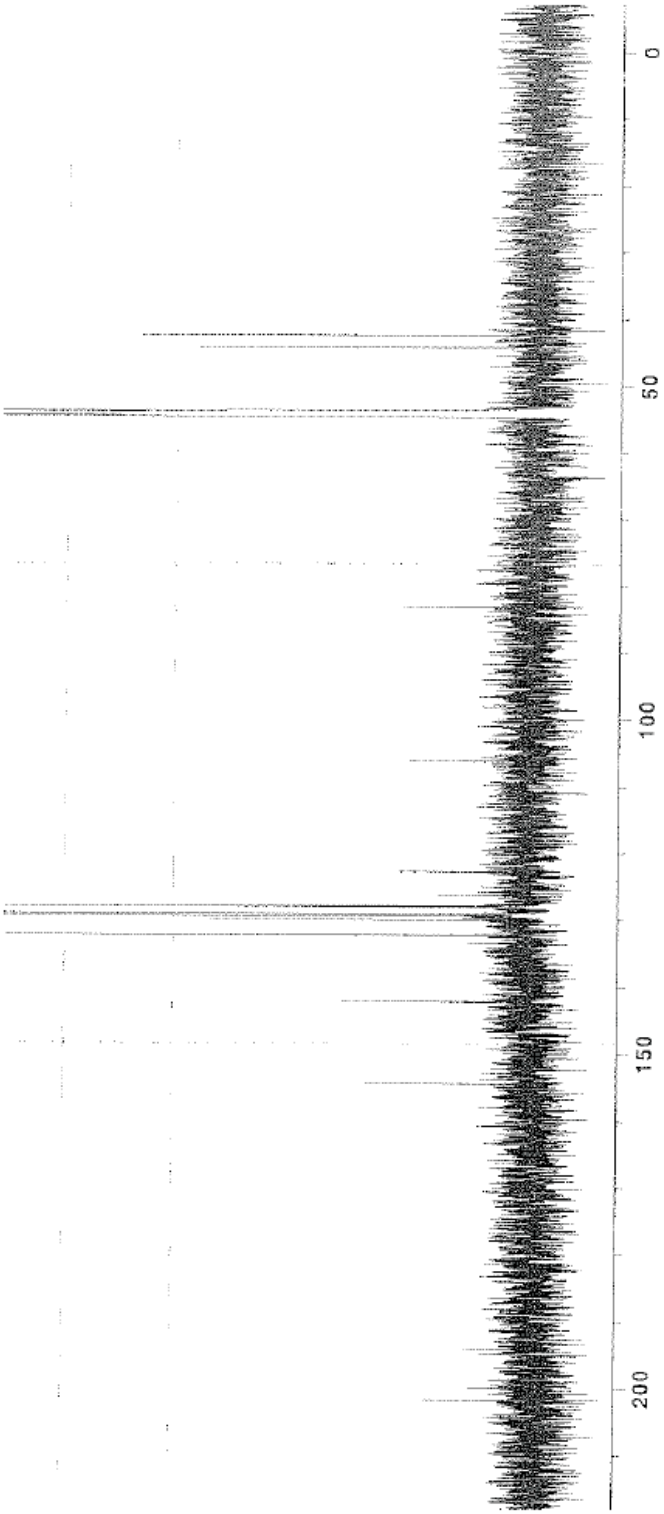












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[1] Lautens, M.; Maddess, M. L.; Sauer, E. L. O.; Ouellet, S. G. *Org. Lett.* **2002**, *4*, 83.