Supporting Information

Synthesis of 1,4-Enyne-3-ones via Palladium-Catalyzed Sequential Decarboxylation and Carbonylation of Allyl Alkynoates

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General methods

Melting points were measured using a melting point instrument and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform was used as a solvent with TMS as the internal standard. IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC-MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed using commercially available 100-400 mesh silica gel plates (GF_{254}). Unless otherwise noted, purchased chemicals were used without further purification. The allyl alkynoates were prepared according to the literature.

Preparation of the staring materials

To a mixture of propiolic acid (10.0 mmol) and allyl alcohol (1.2 equiv) in CH_2Cl_2 (5 mL) was added a solution of 4-DMAP (10 mol %) and DCC (1.5 equiv) in CH_2Cl_2 (5 mL) at 0 °C. The reaction mixture was stirred for 10 h at 25 °C and filtered through a short plug of silica gel, which was rinsed with PE/EA = 10/1. The filtrate was concentrated in vacuum. Purification was achieved by flash chromatography (PE/EA = 30/1).

Typical procedure for the preparation of 1,4-enyne-3-ones 4

To a mixture of allyl alkynoates **1** (0.2 mmol), $Pd(PPh_3)_4$ (0.01 mmol, 5 mol %), toluene (1.0 mL) was added under nitrogen at room temperature. Then *t*-butylisonitrile (45 μL, 0.4 mmol) was dropped into the mixture. The resulting mixture was stirred at 50 °C for 12 h. After the mixture was cooled to room temperature, silica power (2 g), and DCM (2 mL) was added sequentially. The resulting mixture was stirred at room temperature for 12 hours. Then the resulting solution was directly filtered through a pad of silica by EtOAc. The solvent was evaporated in vacuum to give the crude product. GC yields were determined by gas chromatography using decane as an internal standard. Purification was achieved by flash chromatography.

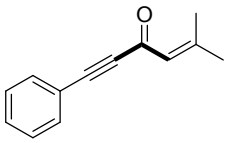
Typical procedure for the preparation of 5

A mixture of 1,4-enyne-3-one **4aa** (92 mg, 0.50 mmol), $Na_2S·9H_2O$ (82 mg, 1.05 mmol), THF (2 mL), and H_2O (2 mL) was stirred for 35 h at room temperature. CH_2Cl_2 (5 mL) was added, and the mixture was further stirred for 10 h. The organic layer was separated. The aqueous phase was neutralized with saturated NH_4Cl solution (10 mL) and then extracted with CH_2Cl_2 (80 mL). The combined organic layers were washed with brine (12 mL) and dried ($MgSO_4$). After filtration, the solvent was stripped off and the residue purified by flash chromatography (PE/EA = 5:1) to yield the title compound **5**.

Typical procedure for the preparation of 6

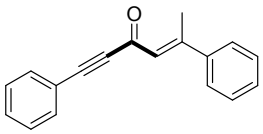
To indole (69 mg, 0.6 mmol) in a round bottomed flask was added a solution of 1,4-enyne-3one **4aa** (89 mg, 0.5 mmol) in acetonitrile (0.5 mL) followed by a solution of sodium tetrachloroaurate (III) hydrate (0.025 mmol) in acetonitrile (0.5 mL) and stirred at room temperature for 12 h. The solution was filtered through celite and concentrated in vacuum. Subsequent purification by flash chromatography (PE/EA = 8:1) afforded **6**.

Characterization data for all products



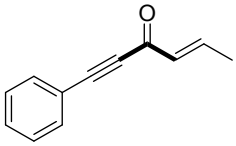
5-Methyl-1-phenylhex-4-en-1-yn-3-one (4aa)[1]

Yield: 81% (32.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 - 7.54 (m, 2 H), 7.45 - 7.39 (m, 1 H), 7.38 - 7.33 (m, 2 H), 6.28 - 6.26 (m, 1 H), 2.27 (d, J = 0.9 Hz, 3 H), 1.96 (d, J = 1.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 158.1, 132.8, 130.4, 128.6, 126.2, 120.5, 90.4, 89.1, 27.9, 21.2 ppm; ν_{max}(KBr)/cm^{-1} 2965, 2923, 2854, 1652, 1599, 1492, 1442, 1377, 1266, 1205, 1119; MS (EI) m/z 75, 82, 115, 129, 141, 155, 168, 183; HRMS (ESI): m/z Calcd for $C_{13}H_{12}NaO$ $[M + Na]^+$ 207.0780, Found: 207.0784.



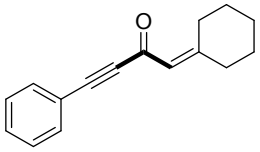
(*Z*)-1,5-diphenylhex-4-en-1-yn-3-one (4ab)[1]

Yield: 65% (32.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 - 7.59 (m, 2 H), 7.57 - 7.53 (m, 2 H), 7.46 - 7.36 (m, 6 H), 6.75 - 6.72 (m, 1 H), 2.68 (d, J = 1.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 156.3, 141.9, 133.0, 130.5, 129. 7, 128.7, 128.6, 126.6, 126.3, 120. 5, 90.8, 89.7, 18.9 ppm; ν_{max}(KBr)/cm^{-1} 2964, 2919, 2852, 1641, 1584, 1438, 1263, 1106; MS (EI) m/z 75, 101, 115, 129, 202, 215, 231, 245; HRMS(ESI): m/z calcd for $C_{18}H_{14}NaO$ $[M + Na]^+$ 269.0937, Found: 269.0942.



(*E*)-1-phenylhex-4-en-1-yn-3-one (3ad)[2]

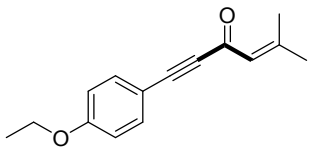
Yield: 40% (15.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 - 7.54 (m, 2 H), 7.45 - 7.39 (m, 1 H), 7.38 - 7.33 (m, 2 H), 7.31 - 7.21 (m, 1 H), 6.24 (dq, J = 15.6, 3.2, 1.6 Hz, 1 H), 1.99 (dd, J = 6.9, 1.6 Hz, 3 H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 149.5, 133.9, 132.8, 130.5, 128.6, 120.2, 91.1, 86.2, 18.5 ppm; ν_{max}(KBr)/cm^{-1} 2960, 2919, 2851, 1648, 1624, 1489, 1441, 1307, 1292, 1189, 1174, 1130; MS (EI) m/z 75, 102, 115, 129, 141, 155, 170; HRMS(ESI): m/z calcd for $C_{12}H_{10}NaO$ $[M + Na]^+$ 193.0624, Found: 193.0626.



1-cyclohexylidene-4-phenylbut-3-yn-2-one (4ah)[3]

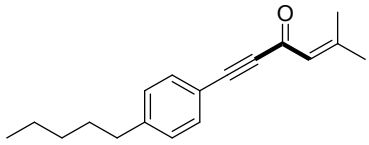
Yield: 54% (25.3 mg) as a faint yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.5, 2H), 7.45 - 7.41 (m, 1H), 7.38 - 7.35 (m, 2H), 6.17 (s, 1H), 2.94 (t, J = 6.0, 2H), 2.24 (t, J = 6.0, 2H),

1.75 - 1.67 (m, 4H), 1.66 - 1.61 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 165.2, 132.9, 130.4, 128.6, 123.4, 120.5, 90.4, 89.2, 38.3, 30.6, 28.8, 28.0, 26.2 ppm; ν_{max}(KBr)/cm^{-1} 2966, 2925, 2856, 1645, 1606, 1449, 1268, 1103; MS (EI) m/z 75, 101, 129, 167, 182, 196, 223; HRMS(ESI): m/z calcd for $C_{16}H_{16}NaO$ $[M + Na]^+$ 247.1093, Found:247.1091.



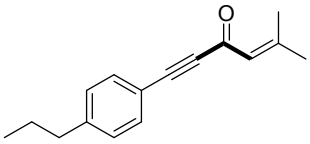
1-(4-ethoxyphenyl)-5-methylhex-4-en-1-yn-3-one (4ba)

Yield: 88% (42.9 mg) as a faint yellow solid; mp = 88.9 - 90.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 - 7.47 (m, 2 H), 6.89 - 6.84 (m, 2 H), 6.25 - 6.23 (m, 1 H), 4.05 (q, J = 7.0 Hz, 2 H), 2.27 (d, J = 1.0 Hz, 3 H), 1.96 (d, J = 1.1 Hz, 3 H), 1.42 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 160.8, 157.3, 134.8, 126.3, 114.8, 112.0, 90.4, 90.2, 63. 7, 27.9, 21.1, 14.6 ppm; ν_{max}(KBr)/cm^{-1} 2965, 2920, 2853, 1647, 1593, 1508, 1439, 1250, 1111; HRMS(ESI): m/z calcd for $C_{15}H_{16}NaO_2$ $[M + Na]^+$ 251.1043, Found:251.1046.



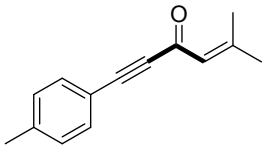
5-methyl-1-(4-pentylphenyl)hex-4-en-1-yn-3-one (4ca)

Yield: 81% (41.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.2 Hz, 2 H), 7.18 (d, J = 8.2 Hz, 2 H), 6.28 - 6.23 (m, 1 H), 2.62 (t, J = 4.0 Hz, 2 H), 2.27 (d, J = 1.0 Hz, 3 H), 1.96 (d, J = 1.0 Hz, 3 H), 1.61 (m, 2 H), 1.36 - 1.27 (m, 4 H), 0.89 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176. 7, 157.7, 146.0, 132.9, 128.7, 126.3, 117.6, 90.2, 89.9, 36.0, 31.4, 30.8, 27. 9, 22.5, 21.1, 14.0 ppm; ν_{max}(KBr)/cm^{-1} 2962, 2923, 2856, 1652, 1600, 1449, 1267, 1115; HRMS(ESI): m/z calcd for $C_{18}H_{22}NaO$ $[M + Na]^+$ 277.1563; Found: 277.1559.



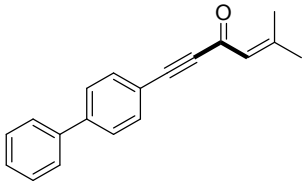
5-methyl-1-(4-propylphenyl)hex-4-en-1-yn-3-one (4da)

Yield: 87% (39.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 - 7.46 (m, 2 H), 7.17 (d, J = 8.4 Hz, 2 H), 6.27 - 6.24 (m, 1 H), 2.59 (t, J = 8.0 Hz, 1 H), 2.26 (d, J = 1.0 Hz, 3 H), 1.95 (d, J = 1.1 Hz, 3 H), 1.67 - 1.57 (m, 2 H), 0.92 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 157.7, 145.7, 132.9, 128.8, 126.3, 117.6, 90.2, 89.8, 38.0, 27. 9, 24.2, 21.1, 13.7 ppm; ν_{max}(KBr)/cm^{-1} 2955, 2925, 2863, 1653, 1605, 1510, 1447, 1379, 1265, 1112, 1045; HRMS(ESI): m/z calcd for $C_{14}H_{14}NaO$ $[M + Na]^+$ 249.1250, Found: 249.1248.



5-methyl-1-(4-methylphenyl)hex-4-en-1-yn-3-one (4ea)

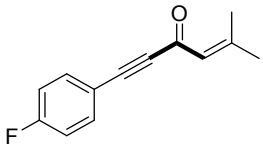
Yield: 82% (34.2 mg) as a faint yellow solid; mp = 90.7 - 92.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.1 Hz, 2 H), 7.17 (d, J = 8.0 Hz, 2 H), 6.27 - 6.25 (m, 1 H), 2.37 (s, 3 H), 2.27 (s, 3 H), 1.96 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 157.7, 141.0, 132.9, 129.4, 126.3, 117.4, 90.2, 89. 8, 27.88, 21.68, 21.1 ppm; ν_{max}(KBr)/cm^{-1} 2960, 2918, 2851, 1649, 1593, 1509, 1438, 1265, 1114, 1043; HRMS(ESI): m/z calcd for $C_{14}H_{14}NaO$ $[M + Na]^+$ 221.0937, Found: 221.0936.



1-([1,1'-biphenyl]-4-yl)-5-methylhex-4-en-1-yn-3-one (4fa)

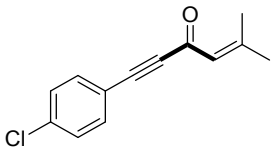
Yield: 89% (47.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 - 7.62 (m, 2 H), 7.61 -

7.58 (m, 4 H), 7.47 - 7.43 (m, 2 H), 7.40 - 7.35 (m, 1 H), 6.31 - 6.28 (m, 1 H), 2.30 (d, J = 1.0 Hz, 1 H), 1.98 (d, J = 1.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 158.1, 143.2, 139.8, 133.4, 129.0, 128.1, 127.2, 127.1, 126.2, 119.3, 91.1, 89.2, 27.9, 21.2 ppm; ν_{max}(KBr)/cm^{-1} 2960, 2921, 2854, 1648, 1602, 1486, 1441, 1381, 1272, 1117, 1050; HRMS(ESI): m/z calcd for $C_{19}H_{16}NaO$ $[M + Na]^+$ 283.1093, Found: 283.1088.



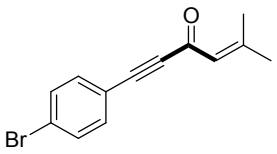
1-(4-fluorophenyl)-5-methylhex-4-en-1-yn-3-one (4ga)

Yield: 73% (29.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 - 7.54 (m, 2 H), 7.09 - 7.04 (m, 2 H), 6.29 - 6.24 (m, 1 H), 2.27 (d, J = 0.8 Hz, 3 H), 1.97 (d, J = 0.9 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 163.8 (d, $J_{C\text{-}F}$ = 253.1 Hz), 158.3, 135.1 (d, $J_{C\text{-}F}$ = 8.8 Hz), 126.0, 116.6 (d, $J_{C\text{-}F}$ = 3.5 Hz), 116.2, 116.0, 90.2, 87.9, 27.9, 21.2 ppm; ν_{max}(KBr)/cm^{-1} 2960, 2925, 2854, 1650, 1600, 1506, 1445, 1378, 1274, 1228, 1116, 1048; HRMS(ESI): m/z calcd for $C_{13}H_{11}FNaO$ $[M + Na]^+$ 225.0686, Found: 225.0688.



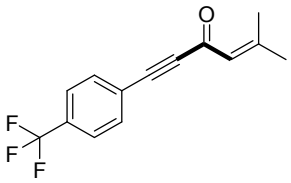
1-(4-chlorophenyl)-5-methylhex-4-en-1-yn-3-one (4ha)

Yield: 76% (34.0 mg) as a yellow solid; mp = 87.8 - 89.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 - 7.45 (m, 2 H), 7.35 - 7.31 (m, 2 H), 6.30 - 6.19 (m, 1H), 2.25 (d, J = 0.8 Hz, 3 H), 1.95 (d, J = 0.9 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 158.6, 136.7, 134.0, 129.0, 126.0, 119.0, 91.0, 87.5, 21.2 ppm; ν_{max}(KBr)/cm^{-1} 2962, 2926, 2858, 1647, 1604, 1485, 1441, 1384, 1265, 1114, 1094, 1047; HRMS(ESI): m/z calcd for $C_{13}H_{11}ClNaO$ $[M + Na]^+$ 241.0391, Found: 241.0390.



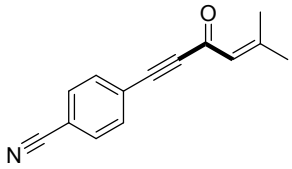
1-(4-bromophenyl)-5-methylhex-4-en-1-yn-3-one (4ia)

Yield: 75% (40.3 mg) as a yellow solid; mp = 87.3 - 88.5 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 - 7.49 (m, 2 H), 7.45 - 7.40 (m, 2 H), 6.29 - 6.24 (m, 1 H), 2.27 (d, J = 0.8 Hz, 3 H), 1.97 (d, J = 0.9 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 158.6, 134.1, 132.0, 126.0, 125.1, 119.4, 91.1, 87. 6, 27.9, 21.3 ppm; ν_{max}(KBr)/cm^{-1} 2960, 2921, 2852, 1649, 1600, 1471, 1379, 1263, 1117, 1050; HRMS(ESI): m/z calcd for $C_{13}H_{11}BrNaO$ $[M + Na]^+$, 284.9885; Found: 284.9884.



5-methyl-1-(4-(trifluoromethyl)phenyl)hex-4-en-1-yn-3-one (4ja)

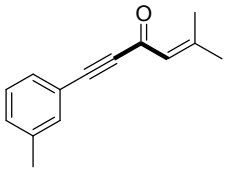
Yield: 66% (34.2 mg) as a brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 - 7.61 (m, 4 H), 6.34 - 6.16 (m, 1 H), 2.26 (d, J = 0.9 Hz, 3 H), 1.97 (d, J = 1.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 159.3, 132.9, 131.8 (d, J = 33.3 Hz), 125. 8, 125.5 (q, J = 3.8 Hz), 125.0, 124.4, 122.2, 91.5, 86.4, 27.9, 21.3 ppm; ν_{max}(KBr)/cm^{-1} 2968, 2925, 2857, 1663, 1612, 1456, 1409, 1324, 1172, 1125, 1067; HRMS(ESI): m/z calcd for $C_{14}H_{11}F_3NaO$ $[M + Na]^+$, 275.0654, Found: 275.0651.



4-(5-methyl-3-oxohex-4-en-1-yn-1-yl)benzonitrile (4ka)

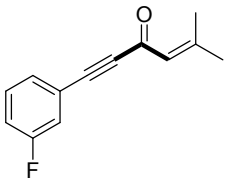
Yield: 49% (20.9 mg) as a yellow solid; mp = 78.4 - 80.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 - 7.58 (m, 4 H), 6.31 - 6.22 (m, 1 H), 2.26 (d, J = 0.8 Hz, 3 H), 1.98 (d, J = 0.9 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 159.8, 133.1, 132.2, 125.6, 125.4, 118.0, 113.6, 92.8, 85.6, 28.0, 21.4

ppm; ν_{max}(KBr)/cm^{-1} 2960, 2922, 2854, 1645, 1602, 1498, 1438, 1262, 1110, 1042; HRMS(ESI): m/z calcd for $C_{14}H_{11}NNaO$ $[M + Na]^+$, 232.0733, Found: 232.0736.



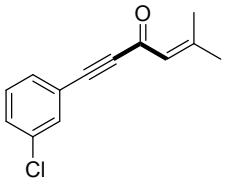
1-(3-methylphenyl)-5-methylhex-4-en-1-yn-3-one (4la)

Yield: 86% (35.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.35 (m, 2 H), 7.26 - 7.22 (m, 2 H), 6.29 - 6.24 (m, 1 H), 2.35 (s, 3H), 2.27 (d, J = 0.9 Hz, 3 H), 1.97 (d, J = 1.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 156.0, 138.4, 133.4, 131.3, 130.0, 128.5, 126.2, 120.3, 90.1, 89.5, 27.9, 21.2, 21.2 ppm; ν_{max}(KBr)/cm^{-1} 2968, 2924, 2855, 1652, 1604, 1447, 1377, 1266, 1116, 1047; HRMS(ESI): m/z calcd for $C_{14}H_{14}NaO$ $[M + Na]^+$, 221.0937, Found: 221.0940.



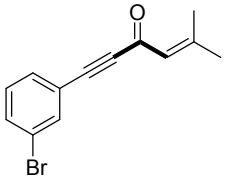
1-(3-fluorophenyl)-5-methylhex-4-en-1-yn-3-one (4ma)

Yield: 67% (27.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.31 (m, 2 H), 7.26 - 7.22 (m, 1 H), 7.17 - 7.10 (m, 2 H), 6.29 - 6.23 (m, 1 H), 2.26 (d, J = 0.9 Hz, 3 H), 1.97 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 162.3 (d, $J_{C\text{-}F}$ = 247.8 Hz), 158.8, 130.3 (d, $J_{C\text{-}F}$ = 8.5 Hz), 128.7 (d, $J_{C\text{-}F}$ = 3.2 Hz), 125.9, 122.4 (d, $J_{C\text{-}F}$ = 9.3 Hz), 119.4 (d, J = 23.2 Hz), 117.8 (d, $J_{C\text{-}F}$ = 21.2 Hz), 90.6, 87.0, 27.9, 21.3 ppm; ν_{max}(KBr)/cm^{-1} 2965, 2926, 2855, 1652, 1600, 1586, 1437, 1377, 1216, 1161, 1113, 1047; HRMS(ESI): m/z calcd for $C_{13}H_{11}FNaO$ $[M + Na]^+$, 225.0686, Found: 225.0690.



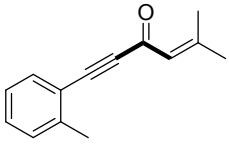
1-(3-chlorophenyl)-5-methylhex-4-en-1-yn-3-one (4na)

Yield: 80% (35.8 mg) as a brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (t, J = 1.8 Hz, 1 H), 7.44 (dt, J = 7.6, 1.2 Hz, 1 H), 7.43 - 7.38 (m, 1 H), 7.30 (t, J = 7.9 Hz, 1 H), 6.29 - 6.23 (m, 1 H), 2.27 (d, J = 1.0 Hz, 3 H), 1.97 (d, J = 1.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 158.9, 134.5, 132.4, 130.9, 130.6, 129.8, 125.9, 122.2, 90.8, 86.9, 28.0, 21.3 ppm; ν_{max}(KBr)/cm^{-1} 2965, 2926, 2855, 1663, 1595, 1466, 1377, 1260, 1092, 1017; HRMS(ESI): m/z calcd for $C_{13}H_{11}ClNaO$ $[M + Na]^+$, 241.0391, Found:241.0390.



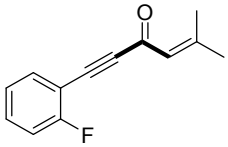
1-(3-bromophenyl)-5-methylhex-4-en-1-yn-3-one (4oa)

Yield: 78% (41.6 mg) as a yellow solid; mp = 63.9 - 65.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (t, J = 1.6, 1 H), 7.58 - 7.53 (m, 1 H), 7.49 (dd, J = 7.7 Hz, 1.2, 1 H), 7.23 (d, J = 7.9 Hz, 1 H), 6.29 - 6.23 (m, 1 H), 2.27 (d, J = 0.8 Hz, 3 H), 1.97 (d, J = 0.9 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 158.9, 135.3, 133.5, 131.3, 130.0, 125.9, 122.5, 122.3, 90.9, 86.8, 28.0, 21.3 ppm; ν_{max}(KBr)/cm^{-1} 2865, 2924, 2858, 1646, 1601, 1556, 1473, 1431, 1378, 1252, 1197, 1116, 1046; HRMS(ESI): m/z calcd for $C_{13}H_{11}BrNaO$ $[M + Na]^+$, 284.9885, Found: 284.9884.



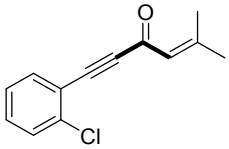
5-methyl-1-(o-tolyl)hex-4-en-1-yn-3-one (4pa)

Yield: 85% (33.3 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.7, 1.1 Hz, 1 H), 7.35 - 7.28 (m, 1 H), 7.25 - 7.22 (m, 1 H), 7.20 - 7.15 (m, 1 H), 6.29 - 6.26 (m, 1 H), 2.49 (s, 3 H), 2.27 (d, J = 1.0 Hz, 3 H), 1.97 (d, J = 1.1 Hz, 3 H);^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 157.9, 141.9, 133.3, 130.4, 129.7, 126.2, 125.8, 120.3, 94.3, 88.1, 27.9, 21.2, 20.6 ppm; ν_{max}(KBr)/cm^{-1} 2965, 2924, 2858, 1647, 1606, 1444, 1378, 1264, 1206, 1121, 1047; HRMS(ESI): m/z calcd for $C_{14}H_{14}NaO$ $[M + Na]^+$, 221.0937, Found: 221.0937.



1-(2-fluorophenyl)-5-methylhex-4-en-1-yn-3-one (4qa)

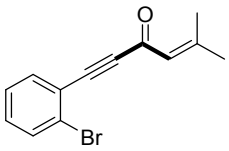
Yield: 61% (24.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (td, J = 7.5 Hz, 1.7, 1 H), 7.44 - 7.36 (m, 1 H), 7.16 - 7.06 (m, 2 H), 6.26 - 6.24 (m, 1 H), 2.26 (d, J = 1.0 Hz, 3 H), 1.95 (d, J = 1.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 163.5 (d, $J_{C\text{-}F}$ = 255.1 Hz), 158.7, 134.6, 132.3 (d, $J_{C\text{-}F}$ = 8.2 Hz), 126.1, 124.3 (d, $J_{C\text{-}F}$ =3.7 Hz), 115.8 (d, $J_{C\text{-}F}$ = 20.5 Hz), 109.4 (d, $J_{C\text{-}F}$ = 15.4 Hz), 94.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 82.4, 28.0, 21.2 ppm; ν_{max}(KBr)/cm^{-1} 2965, 2925, 2856, 1648, 1604, 1490, 1446, 1378, 1264, 1218, 1117, 1048; HRMS(ESI): m/z calcd for $C_{13}H_{11}FNaO$ $[M + Na]^+$, 225.0686; Found: 225.0684.



1-(2-chlorophenyl)-5-methylhex-4-en-1-yn-3-one (4ra)

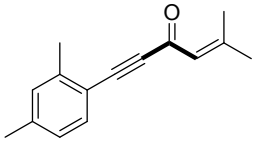
Yield: 67% (30.5 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.7, 1.6 Hz, 1 H), 7.43 (dd, J = 8.0, 1.0 Hz, 1 H), 7.35 (td, J = 7.8, 1.7 Hz, 1 H), 7.26 (dd, J = 15.2, 1.2 Hz, 1 H), 6.34 - 6.28 (m, 1 H), 2.28 (d, J = 0.9 Hz, 3 H), 1.97 (d, J = 1.0, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 158.8, 137.2, 134.7, 131.4, 129. 6, 126.7, 126.0, 120.7, 94.4, 85.2, 28.0, 21.4 ppm;

ν_{max}(KBr)/cm^{-1} 2965, 2923, 2853, 1650, 1603, 1472, 1433, 1378, 1291, 1247, 1121, 1047; HRMS(ESI): m/z calcd for $C_{13}H_{11}ClNaO$ [M + Na]$^+$, 241.0391, Found: 241.0390.



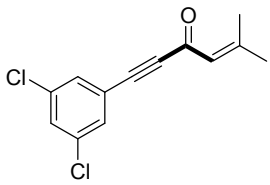
1-(2-bromophenyl)-5-methylhex-4-en-1-yn-3-one (4sa)

Yield: 72% (38.4 mg) as a brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 7.8, 1.3 Hz, 1 H), 7.58 (dd, J = 7.4, 2.0 Hz, 1 H), 7.32 - 7.25 (m, 2 H), 6.36 - 6.27 (m, 1 H), 2.28 (d, J = 0.8, 3 H), 1.97 (d, J = 0.9, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 158.8, 134. 8, 132.7, 131.4, 127.2, 126.5, 126.0, 123.0, 93.7, 86.8, 27.9, 21.4 ppm; ν_{max}(KBr)/cm^{-1} 2968, 2820, 2852, 1651, 1597, 1429, 1374, 1255, 1201, 1119, 1033; HRMS(ESI): m/z calcd for $C_{13}H_{11}BrNaO$ [M + Na]$^+$: 284.9885, Found: 284.9886.



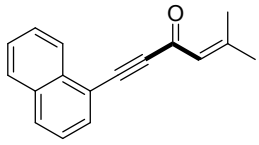
1-(2,4-dimethylphenyl)-5-methylhex-4-en-1-yn-3-one (4ta)

Yield: 83% (37.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.8 Hz, 1 H), 7.04 (s, 1 H), 6.98 (d, J = 7.8 Hz, 1 H), 6.28 - 6.25 (m, 1 H), 2.45 (s, 3 H), 2.32 (s, 3 H), 2.26 (d, J = 1.0 Hz, 3 H), 1.95 (d, J = 1.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 157.5, 142.0, 141.0, 133.4, 130.6, 126.7, 126.3, 117.2, 94.1, 88.8, 27.8, 21.6, 21.2, 20.5 ppm; ν_{max}(KBr)/cm^{-1} 2969, 2921, 2854, 1651, 1602, 1500, 1444, 1376, 1267, 1125, 1044; HRMS(ESI): m/z calcd for $C_{15}H_{16}NaO$ [M + Na]$^+$: 235.1093, Found, 235.1097.



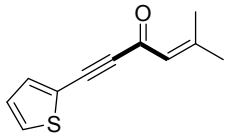
1-(3,5-dichlorophenyl)-5-methylhex-4-en-1-yn-3-one (4ua)

Yield: 64% (34.6 mg) as a brown solid; mp = 94.5 - 96.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.42 (m, 2 H), 7.42 - 7.40 (m, 1 H), 6.26 - 6.23 (m, 1 H), 2.26 (d, J = 1.0 Hz, 3 H), 1.97 (d, J = 1.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 159.5, 135.3, 130.7, 130.6, 125.6, 123.4, 91.3, 84.9, 28.0, 21.4 ppm; ν_{max}(KBr)/cm^{-1} 2971, 2922, 2854, 1653, 1602, 1556, 1435, 1378, 1263, 1207, 1124, 1050; HRMS(ESI): m/z calcd for $C_{13}H_{10}Cl_2NaO$ $[M + Na]^+$, 275.0001, Found: 275.0000.



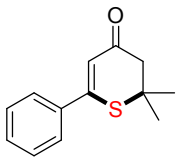
5-methyl-1-(naphthalen-1-yl)hex-4-en-1-yn-3-one (4va)

Yield: 92% (43.9 mg) as a brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.4 Hz, 1 H), 7.91 (d, J = 8.3 Hz, 1 H), 7.85 (d, J = 8.1 Hz, 1 H), 7.82 (dd, J = 7.2, 1.1 Hz, 1 H), 7.61 (ddd, J = 8.3, 6.9, 1.3 Hz, 1 H), 7.54 (ddd, J = 8.1, 6.9, 1.2 Hz, 1 H), 7.44 (dd, J = 8.2, 7.2 Hz, 1 H), 6.43 - 6.33 (m, 1 H), 2.32 (d, J = 1.0 Hz, 3 H), 1.99 (d, J = 1.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 158.3, 133.6, 133.1, 132.8, 131.1, 128.5, 127.5, 126.9, 126.2, 125.9, 125.2, 118.1, 95.2, 87.3, 27.9, 21.4 ppm; ν_{max}(KBr)/cm^{-1} 2965, 2915, 2852, 1649, 1601, 1506, 1444, 1386, 1262, 1208, 1126, 1021; HRMS(ESI): m/z calcd for $C_{17}H_{14}NaO$ $[M + Na]^+$, 257.0937, Found: 257.0941.



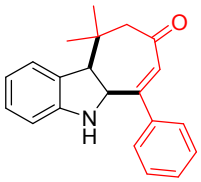
5-methyl-1-(thiophen-2-yl)hex-4-en-1-yn-3-one (4wa)

Yield: 68% (27.0 mg) as a gray solid; mp = 63.2 - 64.7 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 - 7.42 (m, 2 H), 7.04 (dd, J = 5.0, 3.8 Hz, 1 H), 6.27 - 6.21 (m, 1 H), 2.25 (d, J = 0.9 Hz, 3 H), 1.96 (d, J = 1.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 158.2, 136.1, 131.1, 127.6, 125.9, 120.4, 94.8, 83.0, 27.9, 21.2 ppm; ν_{max}(KBr)/cm^{-1} 2970, 2922, 2852, 1648, 1593, 1516, 1434, 1364, 1256, 1207, 1108, 1024; HRMS(ESI): m/z calcd for $C_{11}H_{10}NaOS$ $[M + Na]^+$, 213.0345, Found: 213.0346.



2,2-dimethyl-6-phenyl-2,3-dihydro-4*H*-thiopyran-4-one (5)

Yield: 87% (94.7 mg) as a brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 - 7.55 (m, 2 H), 7.48 - 7.34 (m, 3 H), 6.49 (s, 1 H), 2.68 (s, 2 H), 1.52 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 159.2, 137.4, 130.9, 128.8, 127.1, 119.6, 51.9, 45. 8, 28.0 ppm; ν_{max}(KBr)/cm^{-1} 2963, 2923, 2852, 1651, 1551, 1490, 1445, 1368, 1318, 1272, 1229, 1148, 1101; HRMS(ESI): m/z calcd for $C_{13}H_{14}NaOS$ $[M + Na]^+$, 241.0658, Found: 241.0659.



10,10-dimethyl-6-phenyl-5a,9,10,10a-tetrahydrocyclohepta[b]indol-8(5*H*)-one (6)

Yield: 84% (122.3 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1 H), 7.94 (s, 1 H), 7.5 - 7.48 (m , 2 H), 7.45 - 7.42 (m, 3 H), 7.45 - 7.41 (m, 2 H), 7.14 - 7.08 (m, 1 H), 6.18 (s, 1 H), 3.01 (s, 2 H), 1.69 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 146.0, 140.2, 135.9, 129.9, 129.3, 129.0, 128.6, 128.6, 126.1, 124.1, 122.4, 120.3, 111.7, 58.2, 33.5, 28.4 ppm; ν_{max}(KBr)/cm^{-1} 33646, 3304, 2955, 2906, 2863, 2836, 1627, 1585, 1516, 1440, 1338, 1295, 1224, 1153, 1071; HRMS(ESI): m/z calcd for $C_{21}H_{19}NNaO$ $[M + Na]^+$, 324.1359, Found: 324.1361.

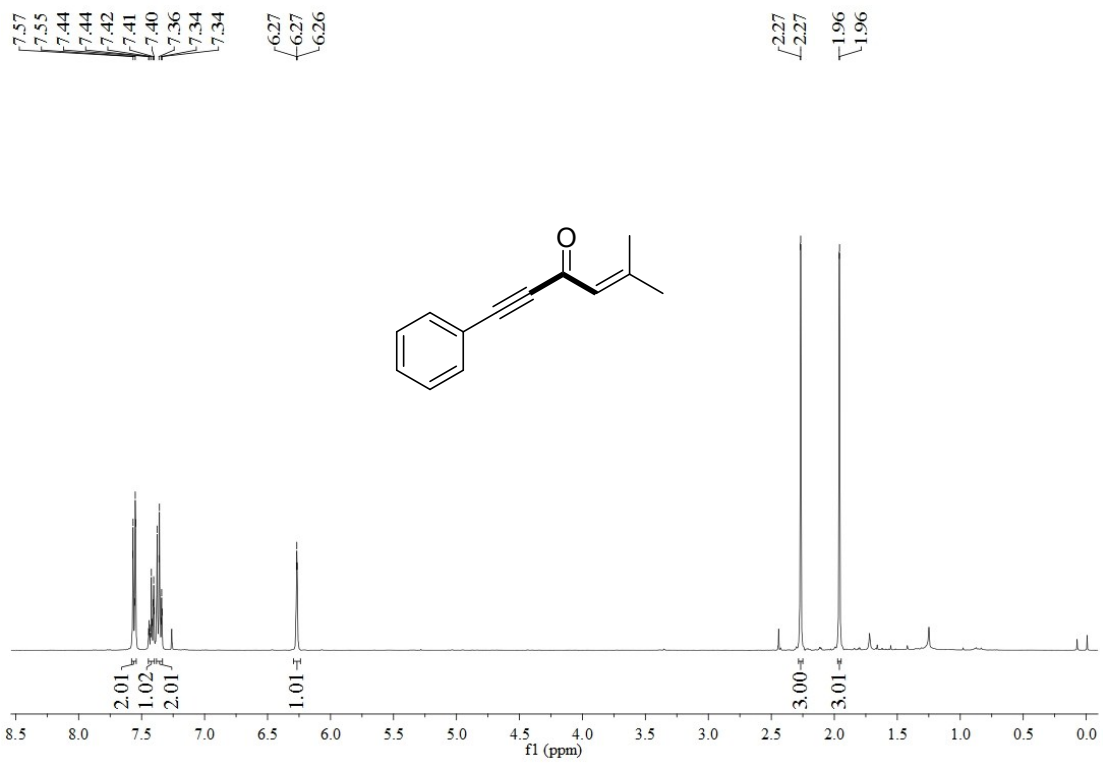
References

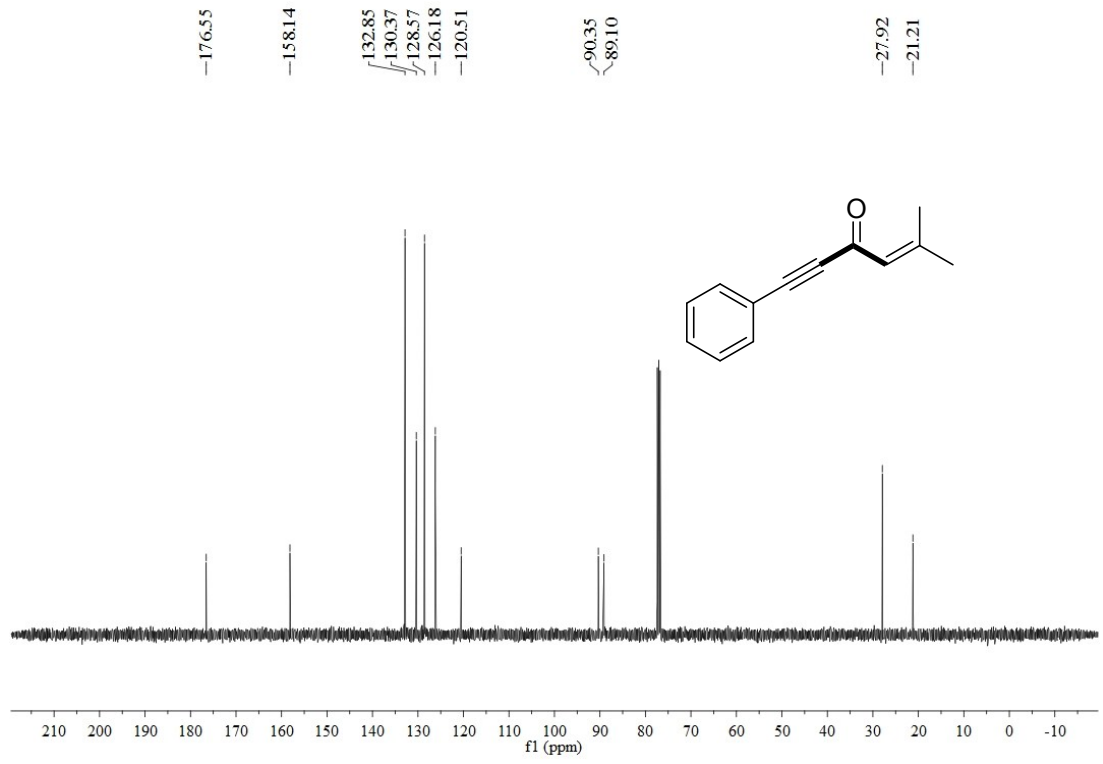
(1) M. H. Babu, V. Dwivedi, R. Kant, and M. S. Reddy, *Angew. Chem. Int. Ed*., 2015, **54**, 3783-3786.

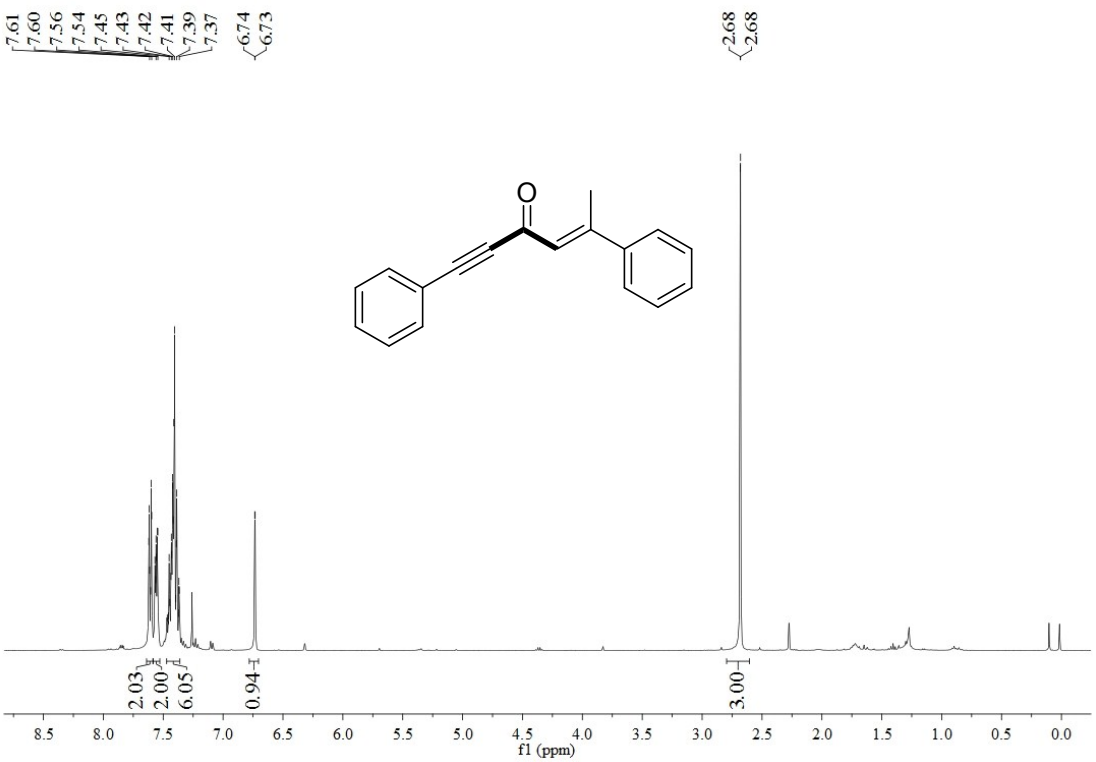
(2) S. J. Heffernan, J. P. Tellam, M. F. Mahon, A. J. Hennessy B. I. Andrews and David R. Carbery, *Adv. Synth. Catal.,* 2013, **355**, 1149-1159.

(3) Y. Wang, Z. Zheng and L. Zhang, *J. Am. Chem. Soc.*, 2015, **137**, 5316-5319.

NMR spectra for all compounds



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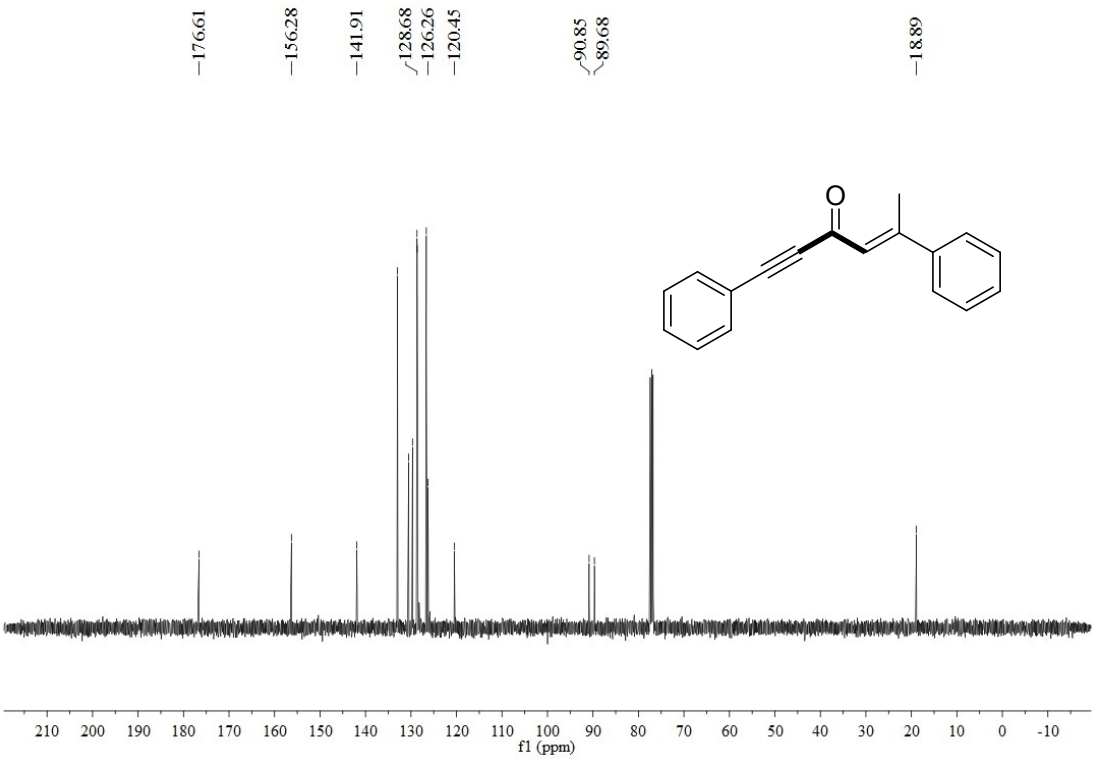
2.68
O
2.03
2.00
6.05
0.94
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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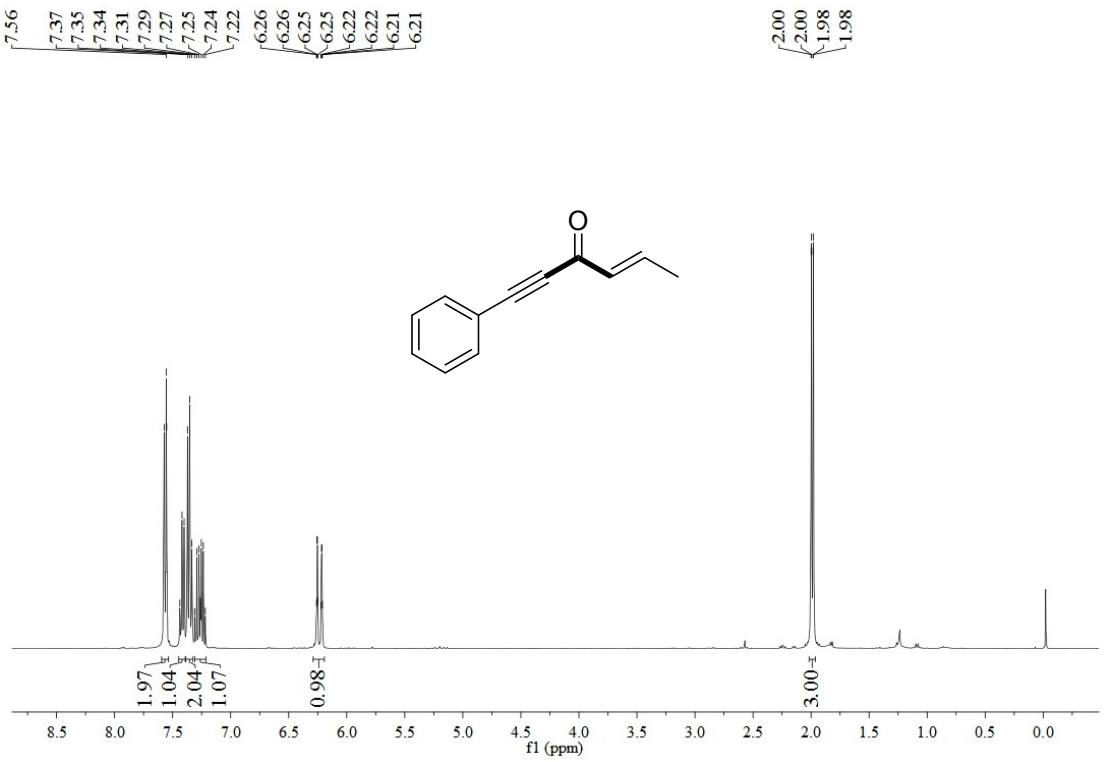
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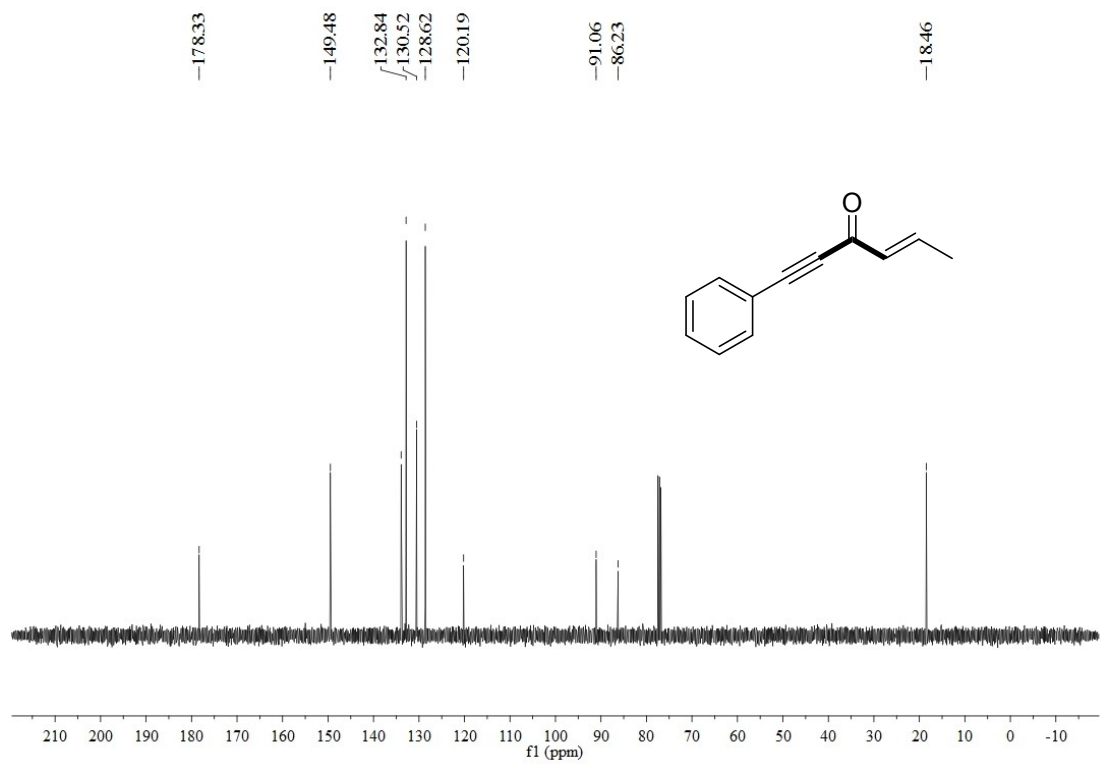
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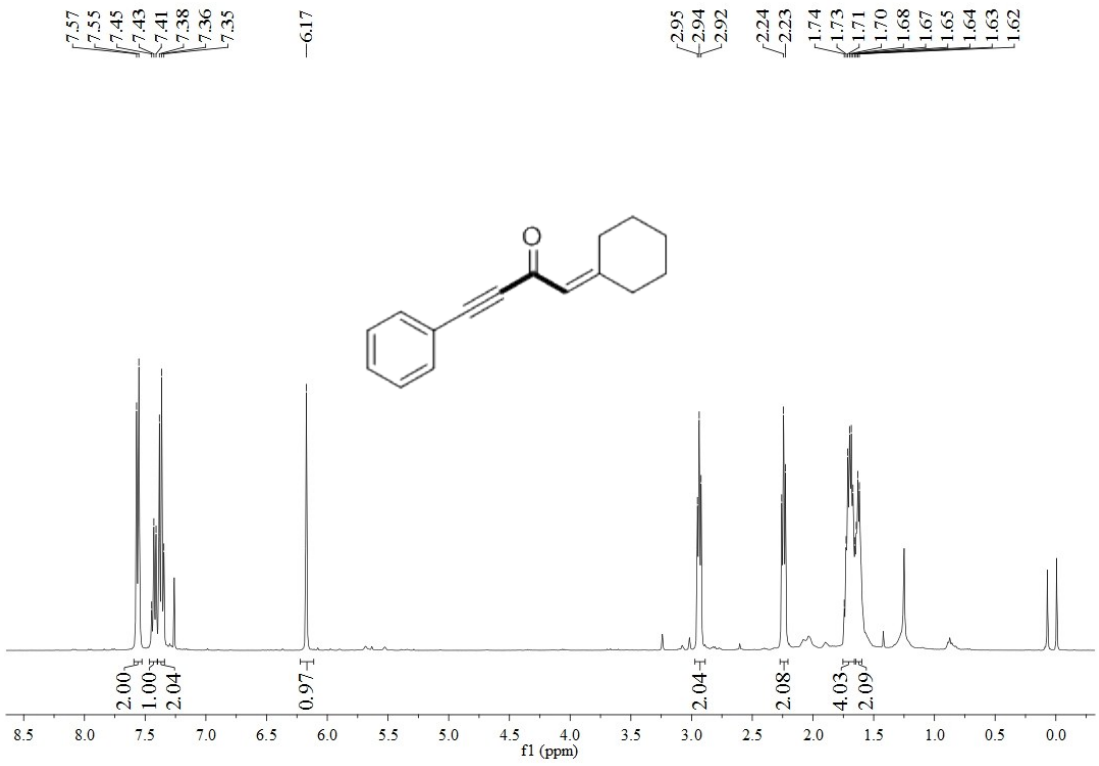
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2.09
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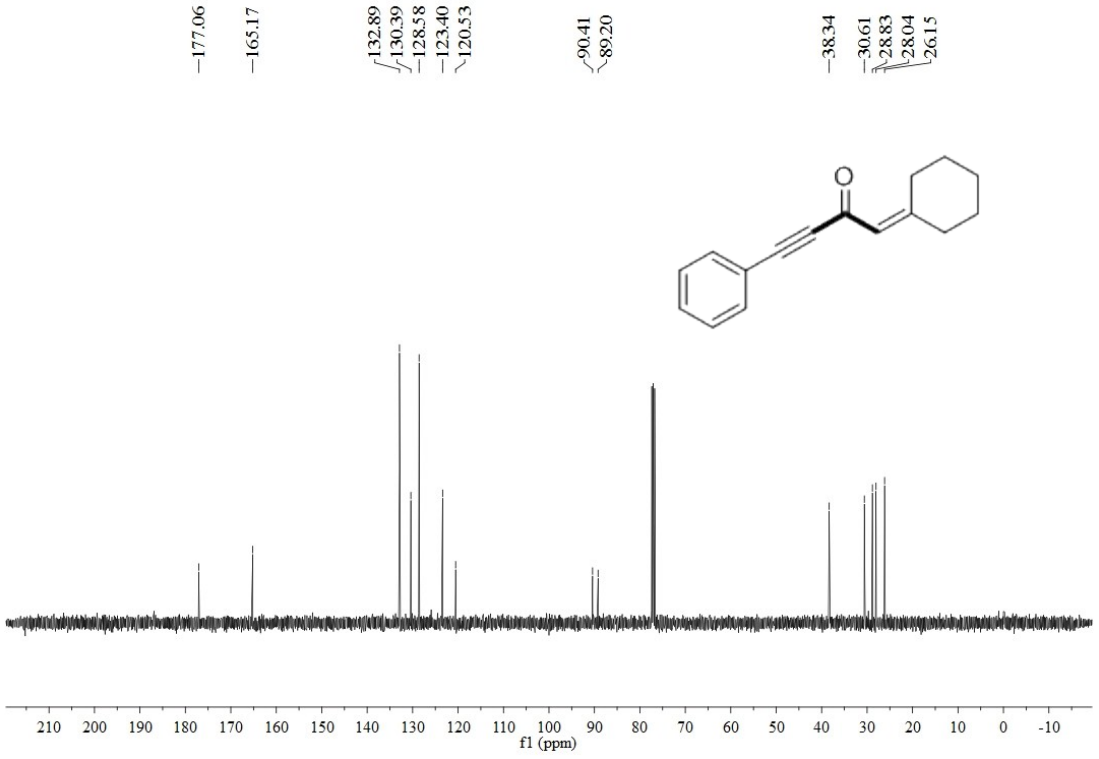
f1 (ppm)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28.04
26.15
O
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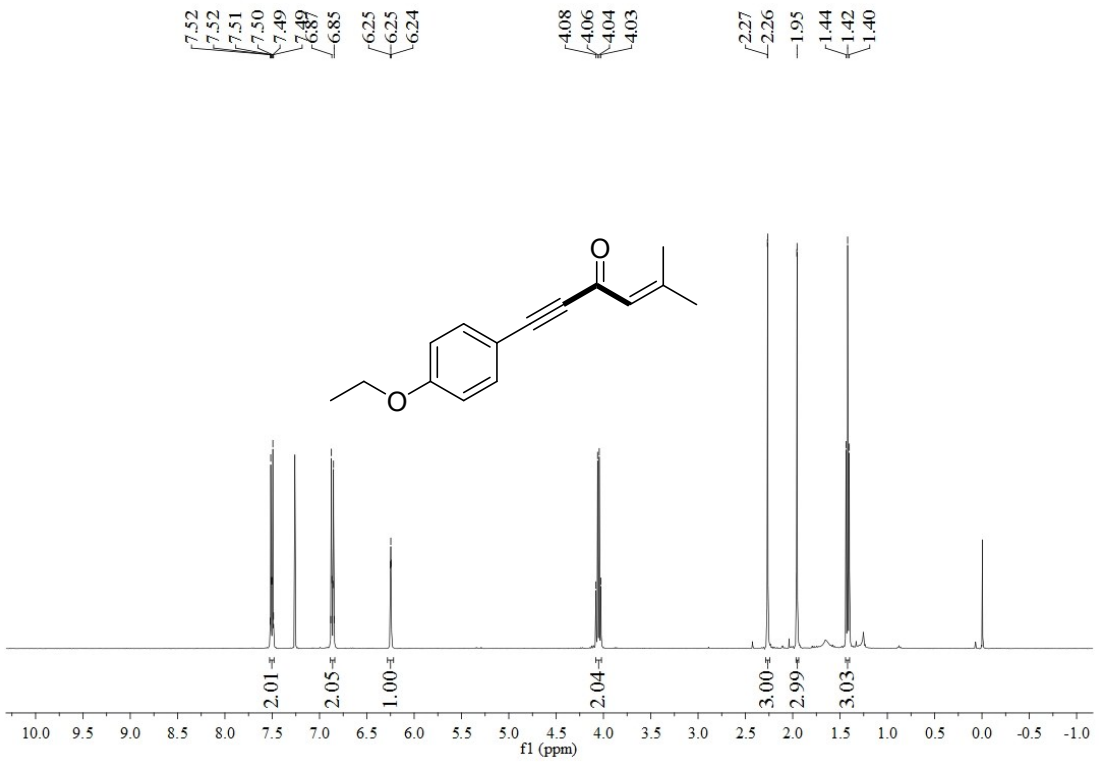
f1 (ppm)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4.06
4.04
4.03
2.27
2.26
1.95
1.44
1.42
1.40
O
O
2.01
2.05
1.00
2.04
3.00
2.99
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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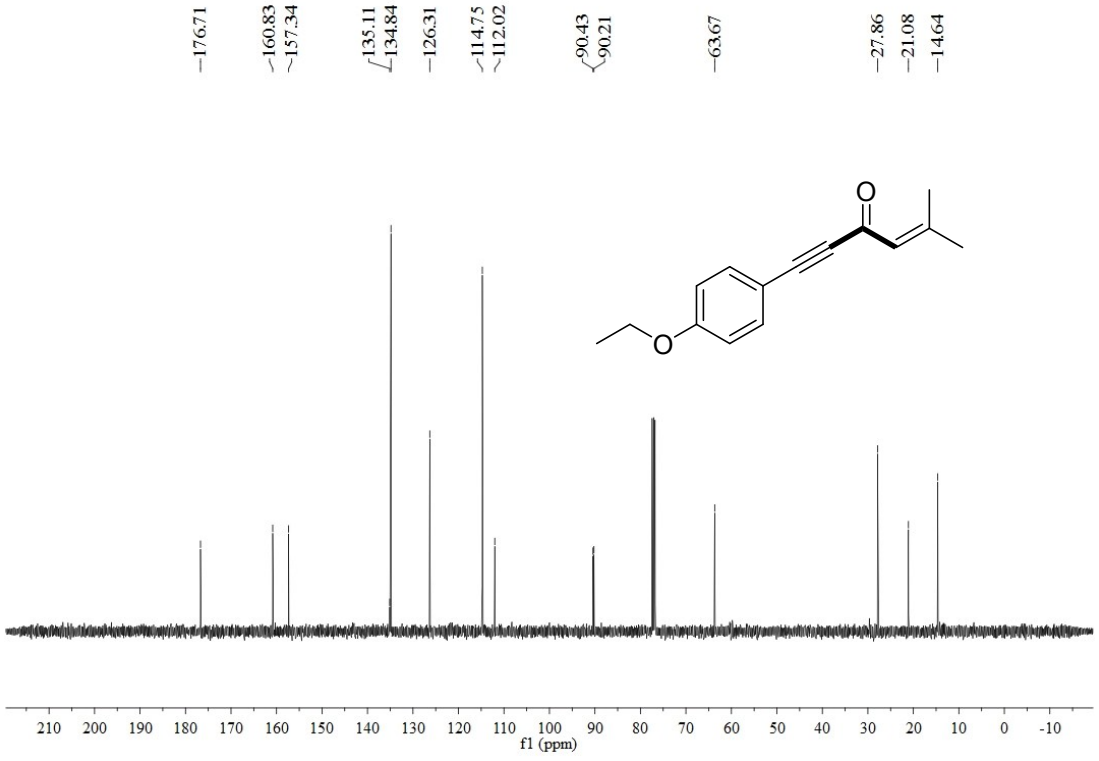
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14.64
O
O
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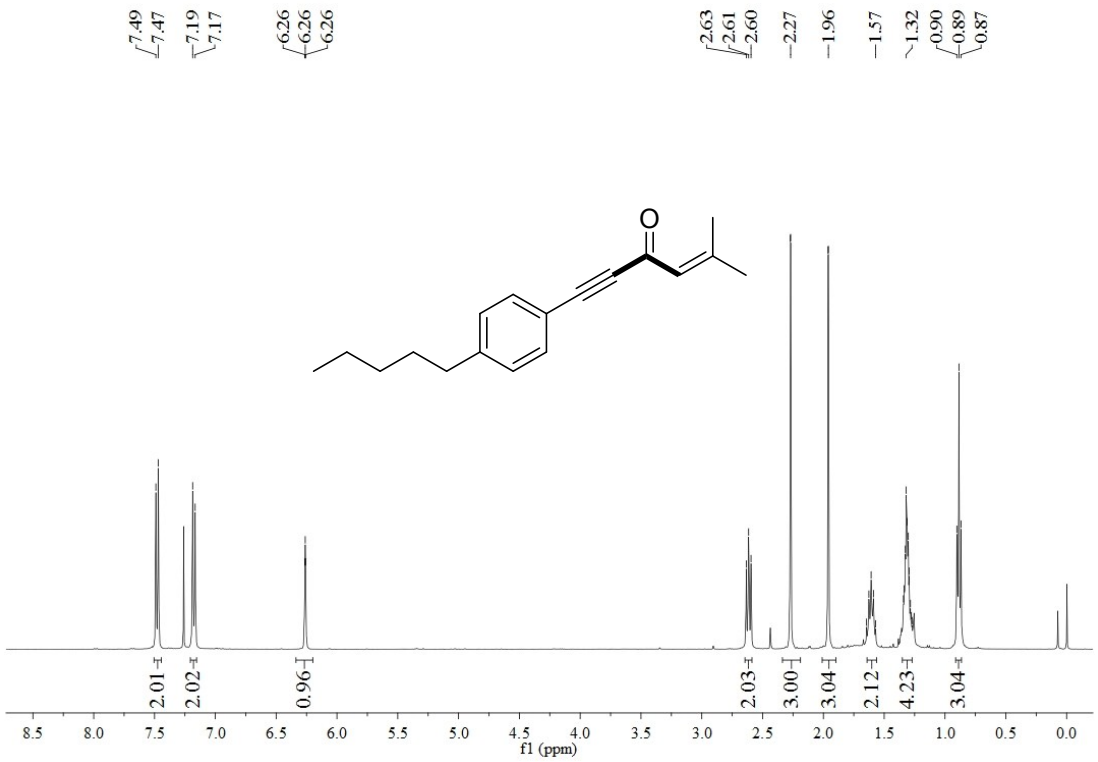
f1 (ppm)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1.57
1.32
0.90
0.89
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0.96
2.03
3.00
3.04
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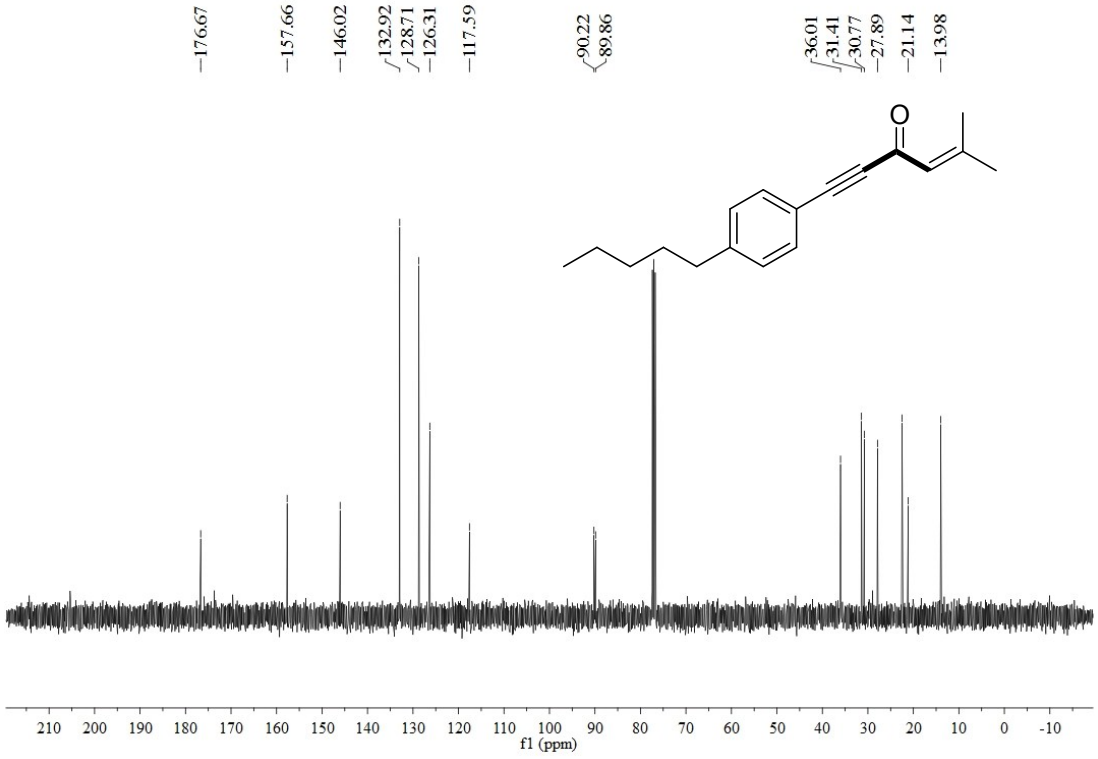
4.23
3.04
f1 (ppm)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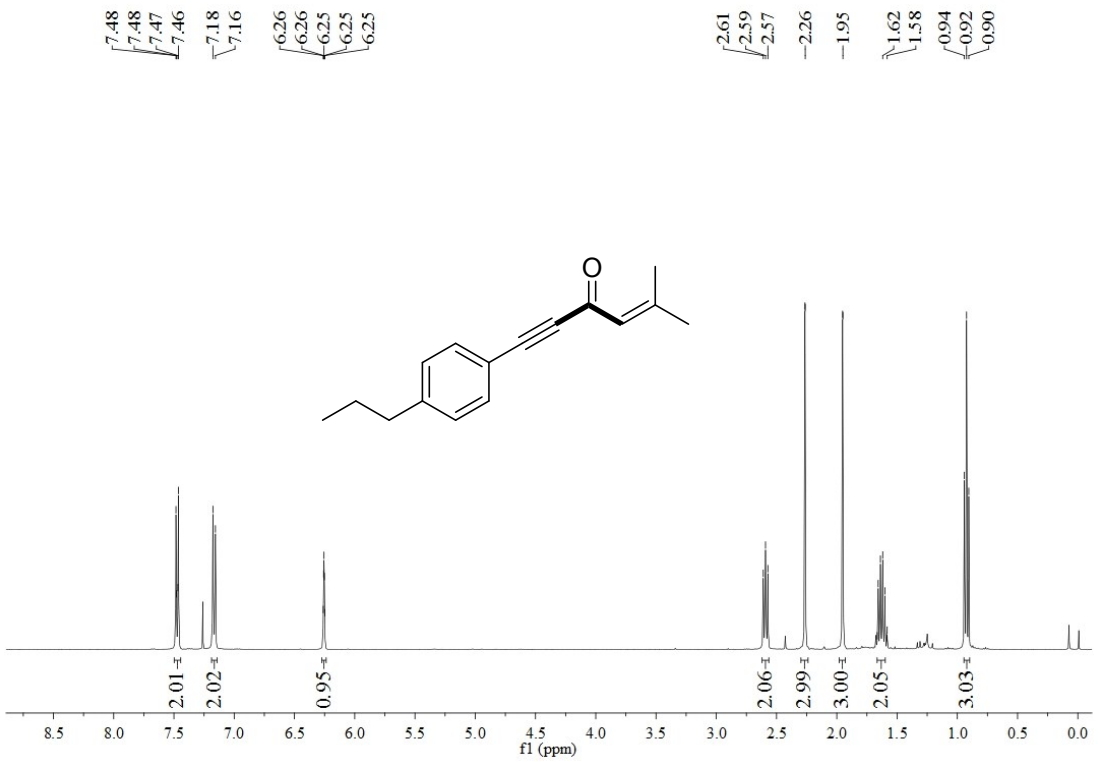
f1 (ppm)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6.25
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2.59
2.57
2.26
1.95
1.62
1.58
0.94
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2.02
0.95
2.06
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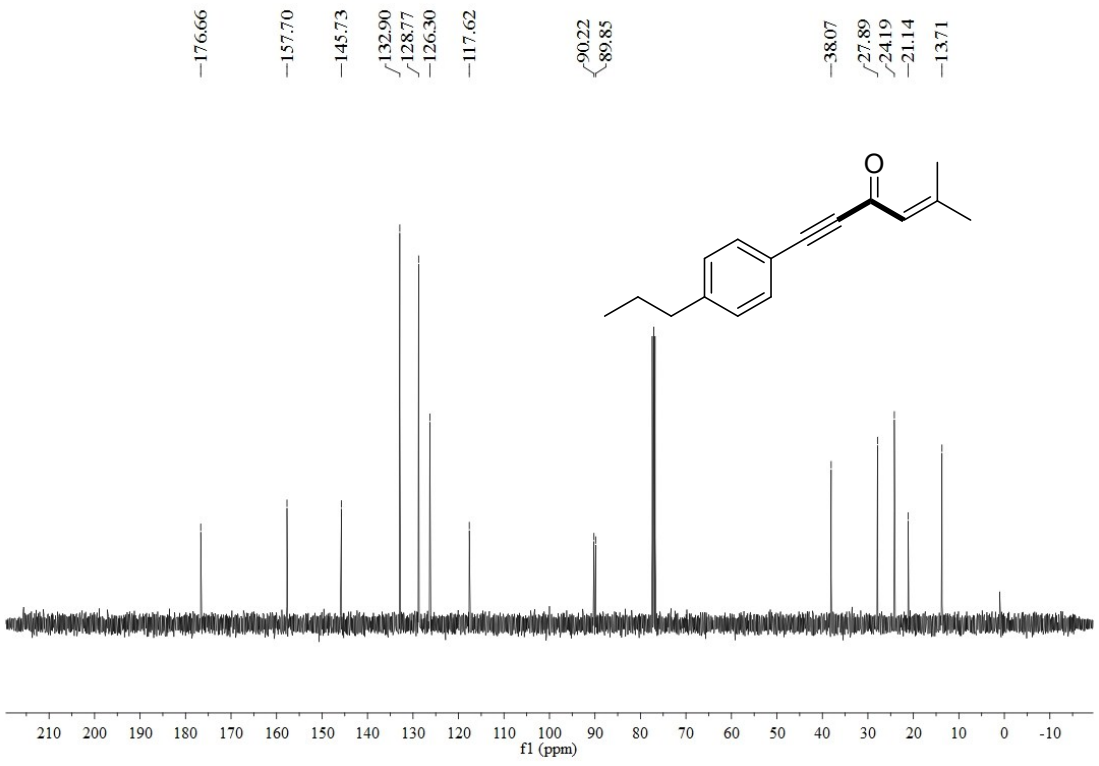
3.00
2.05
3.03
f1 (ppm)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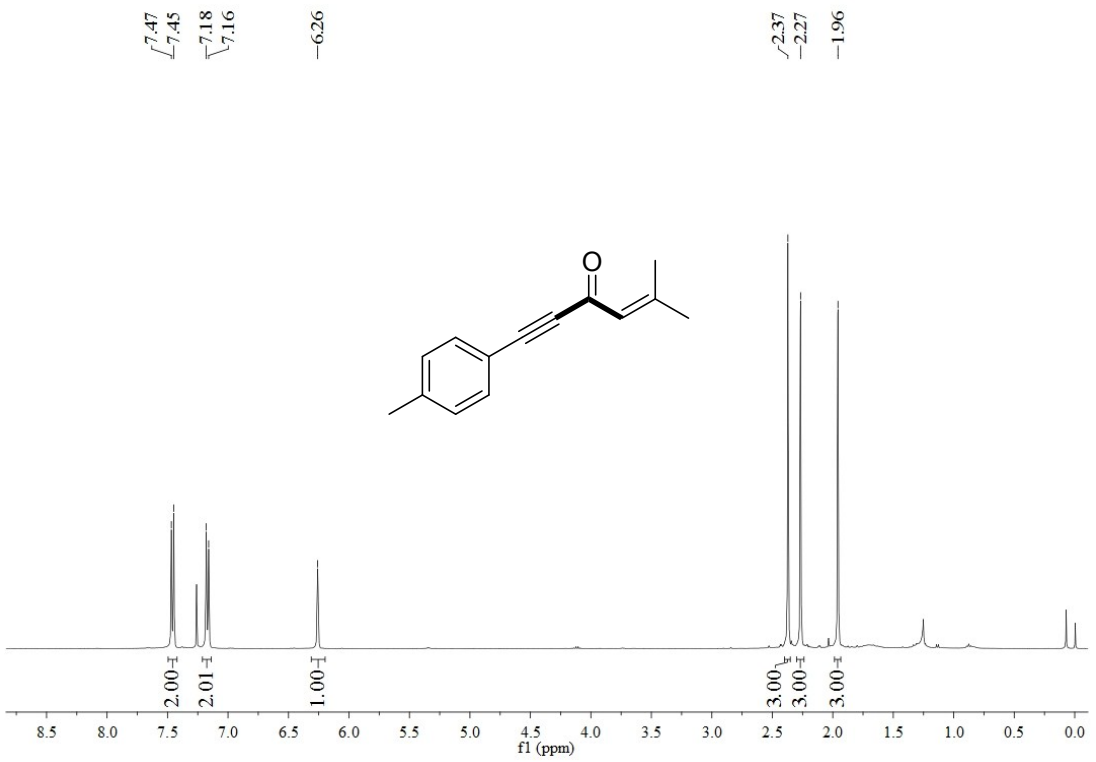
f1 (ppm)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2.00
2.01
1.00
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3.00
3.00
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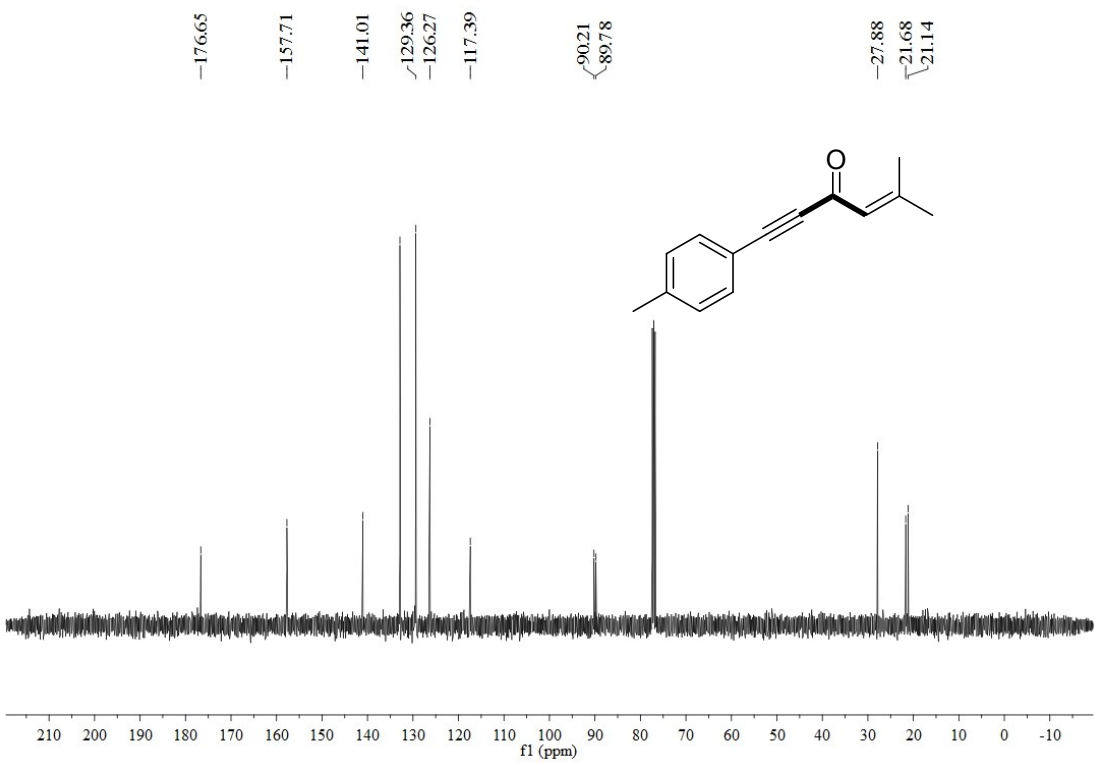
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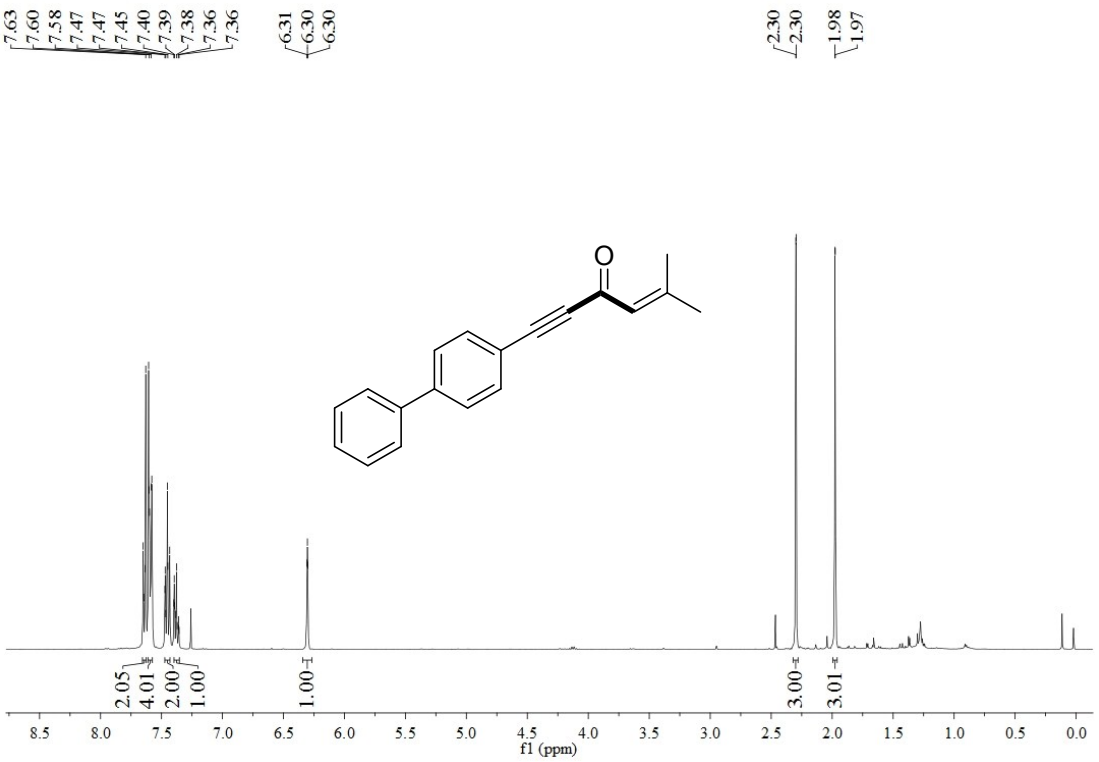
f1 (ppm)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7.36
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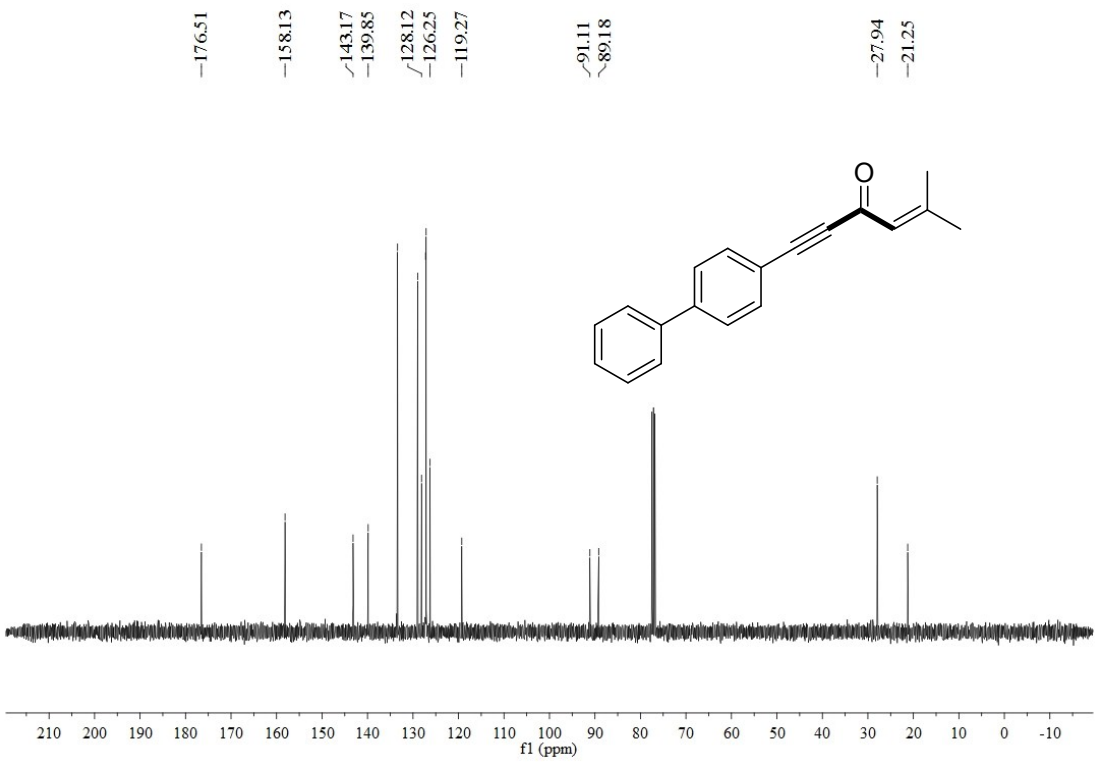
6.31
6.30
6.30
2.30
2.30
1.98
1.97
O
2.05
4.01
2.00
1.00
1.00
3.00
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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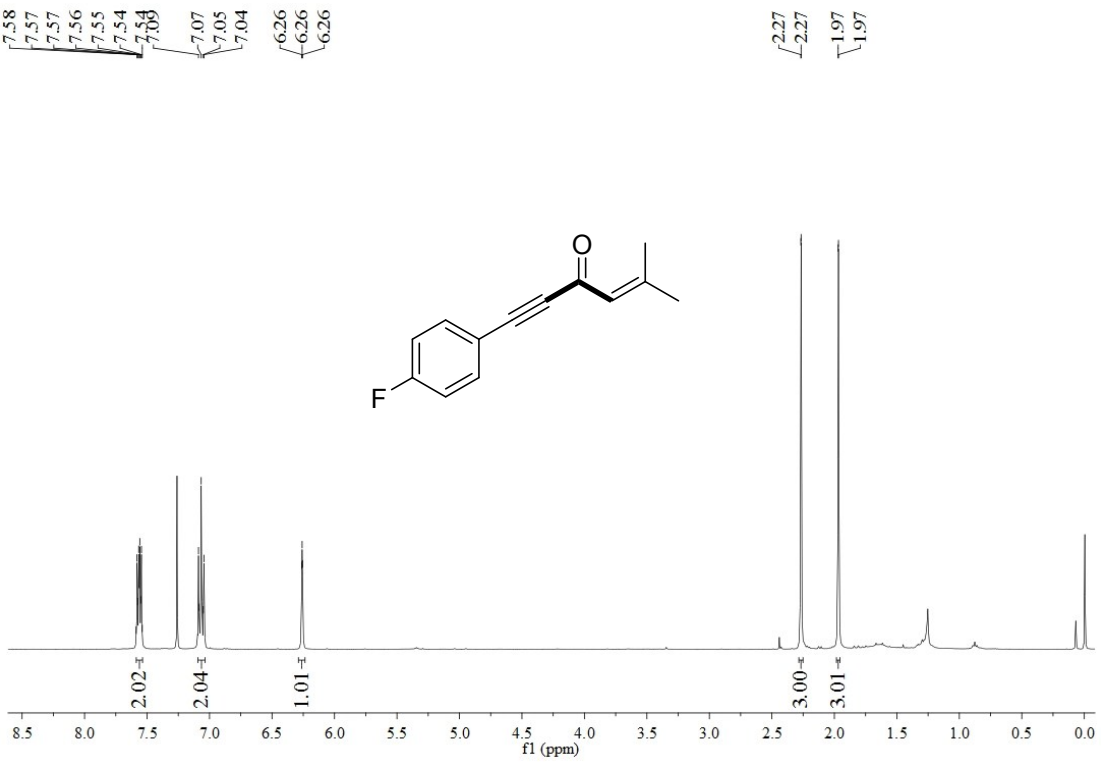
f1 (ppm)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2.27
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1.97
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F
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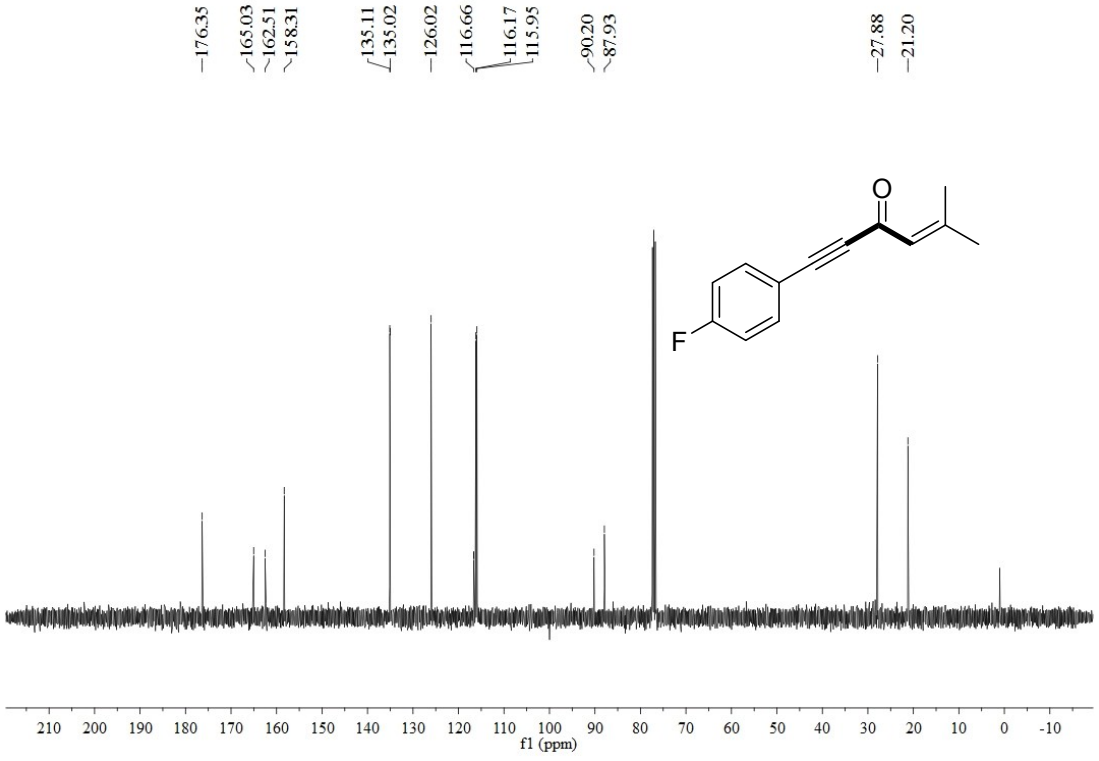
2.04
1.01
3.00
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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116.66
116.17
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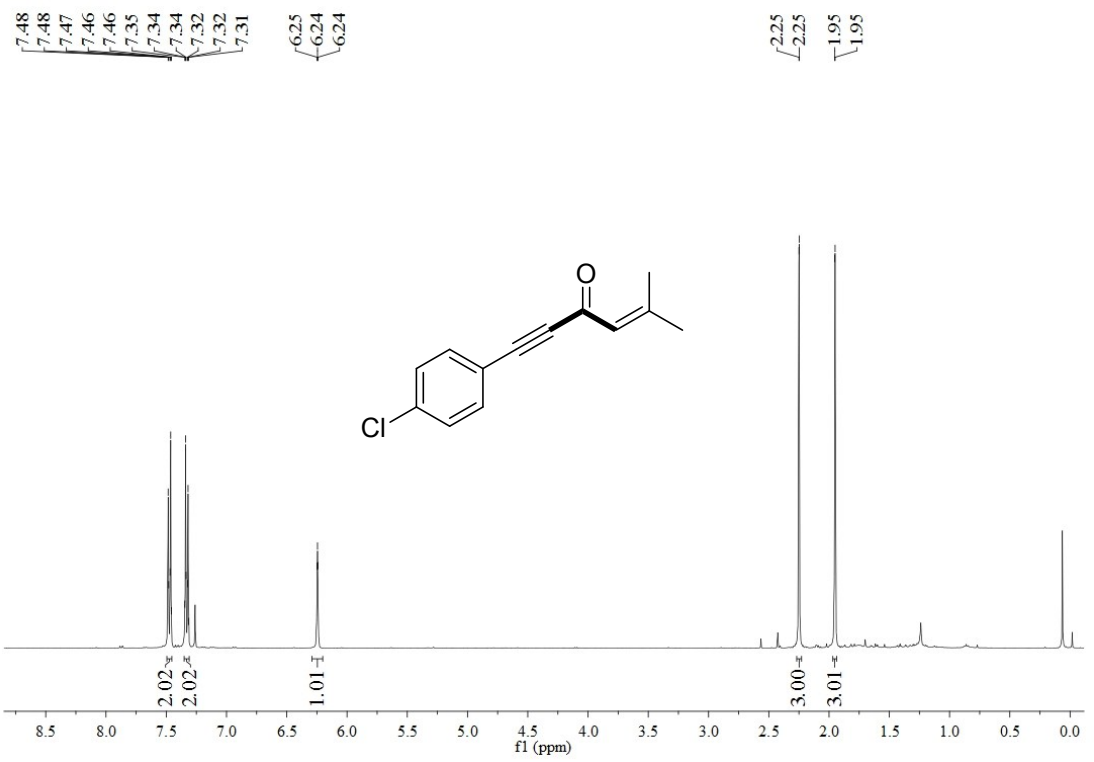
27.88
21.20
O
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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2.25
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1.95
O
Cl
2.02
2.02
1.01
3.00
3.01
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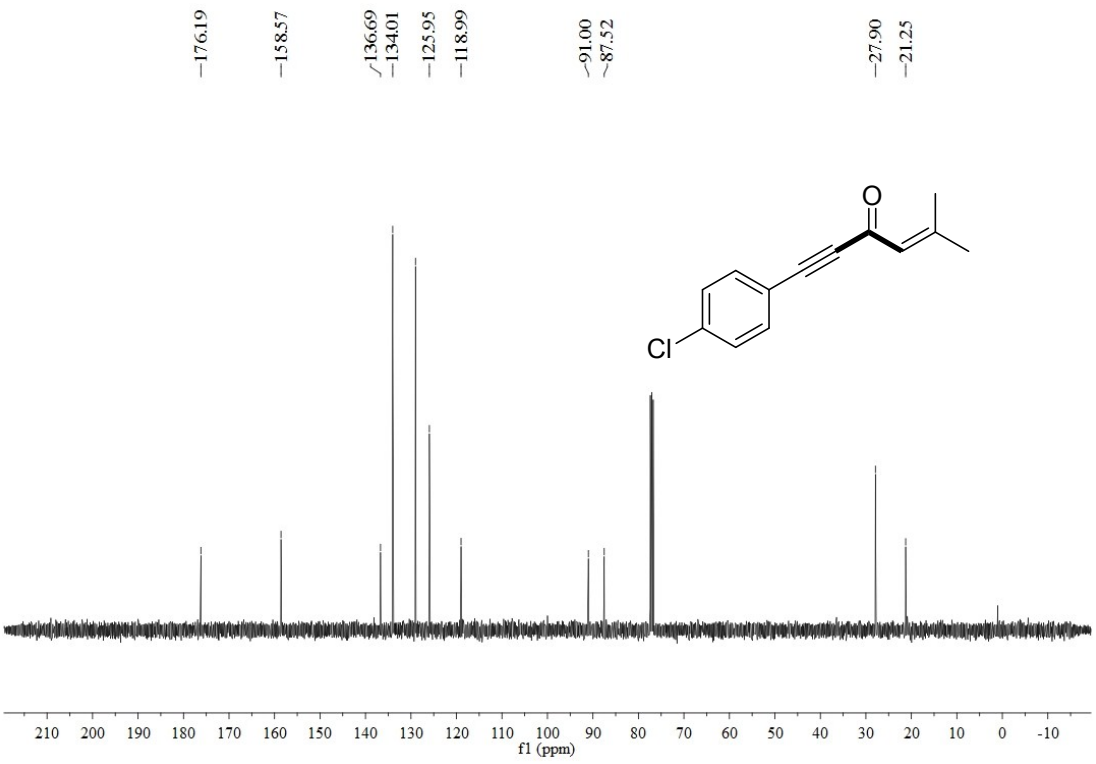
f1 (ppm)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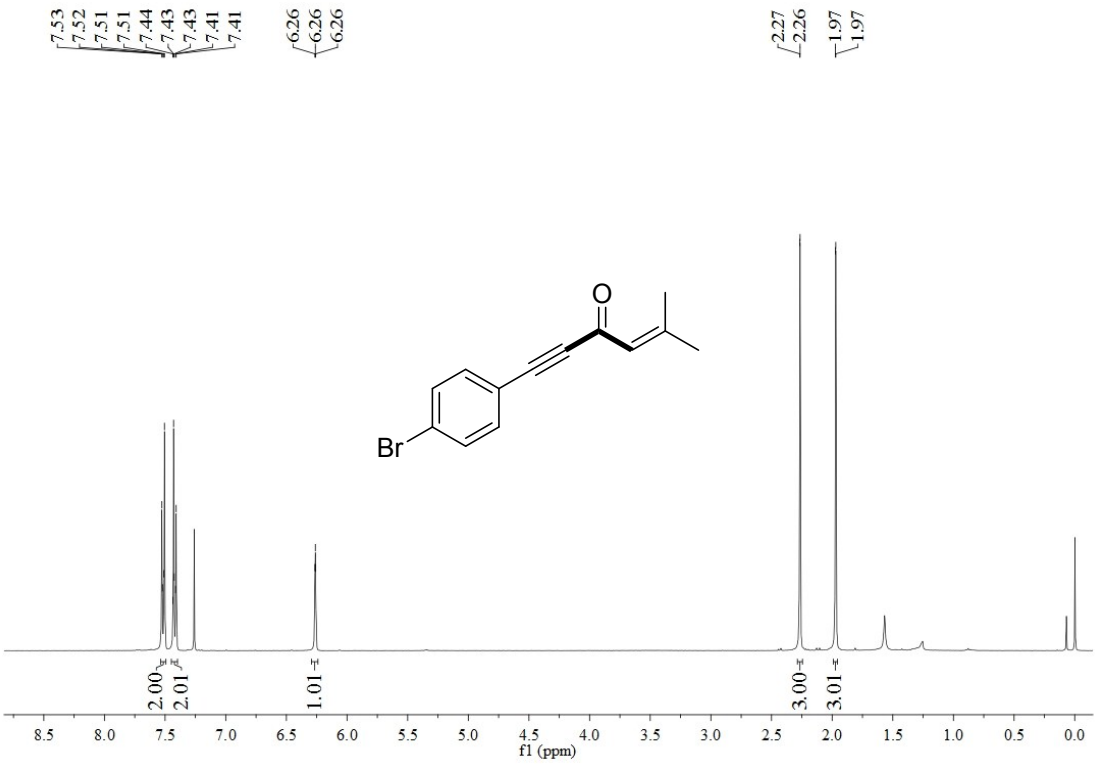
f1 (ppm)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6.26
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1.97
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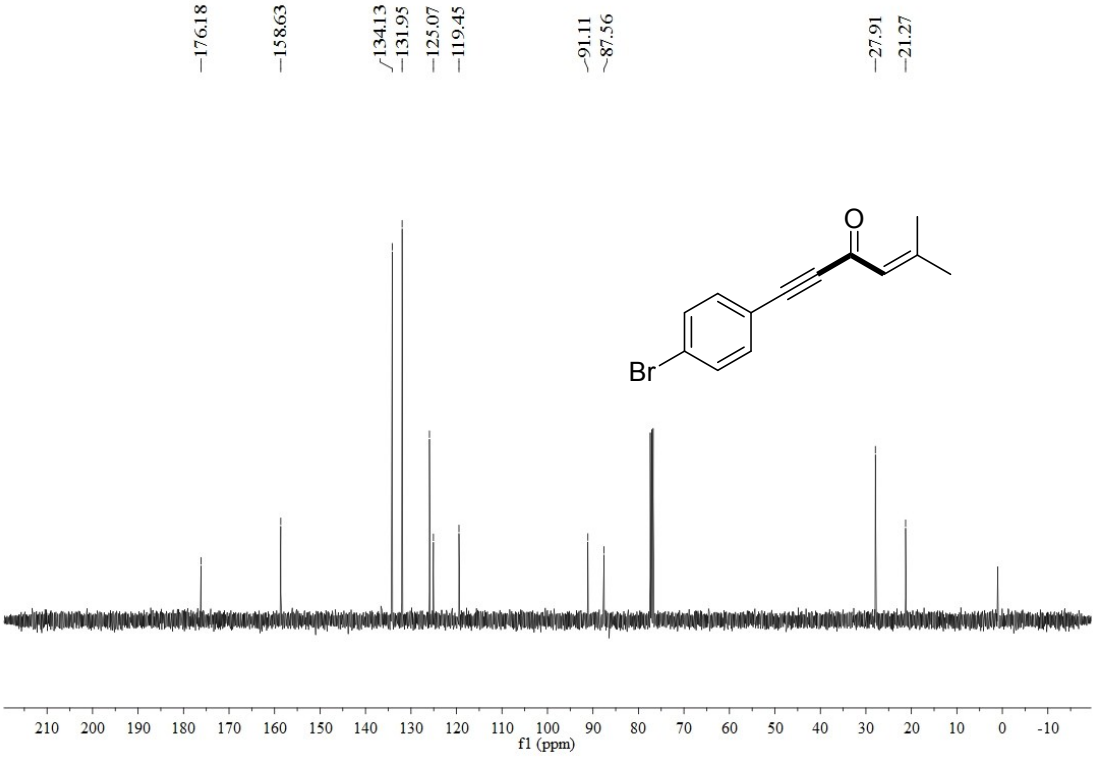
1.01
3.00
3.01
f1 (ppm)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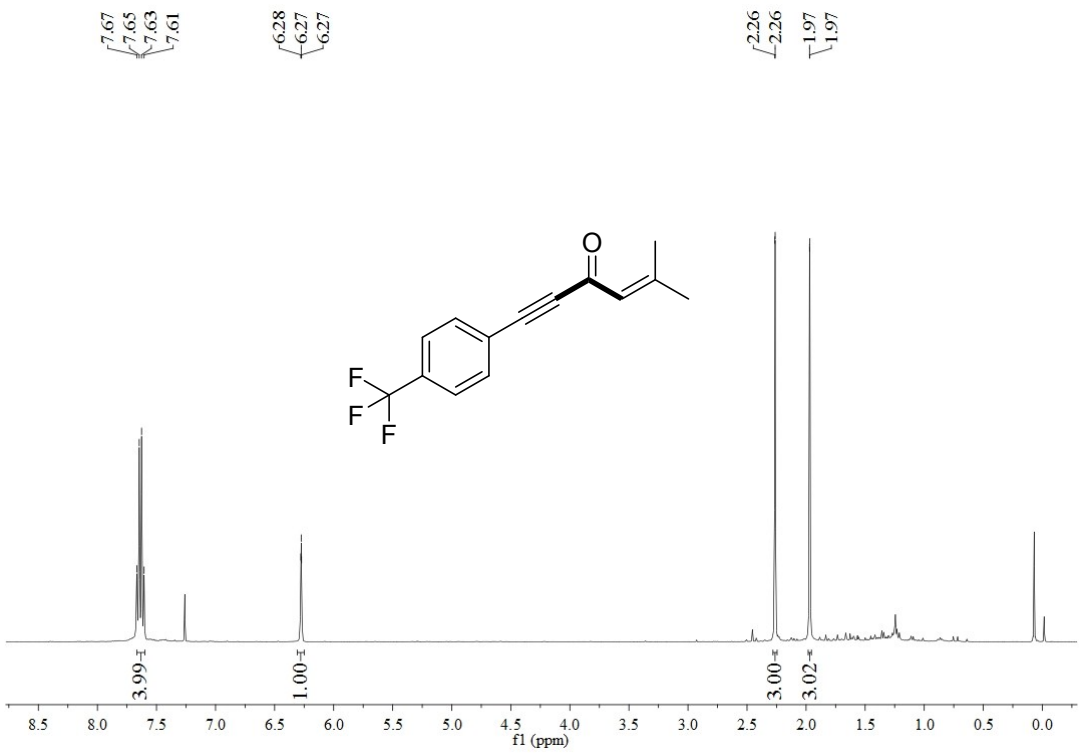
Br
f1 (ppm)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O
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F
F
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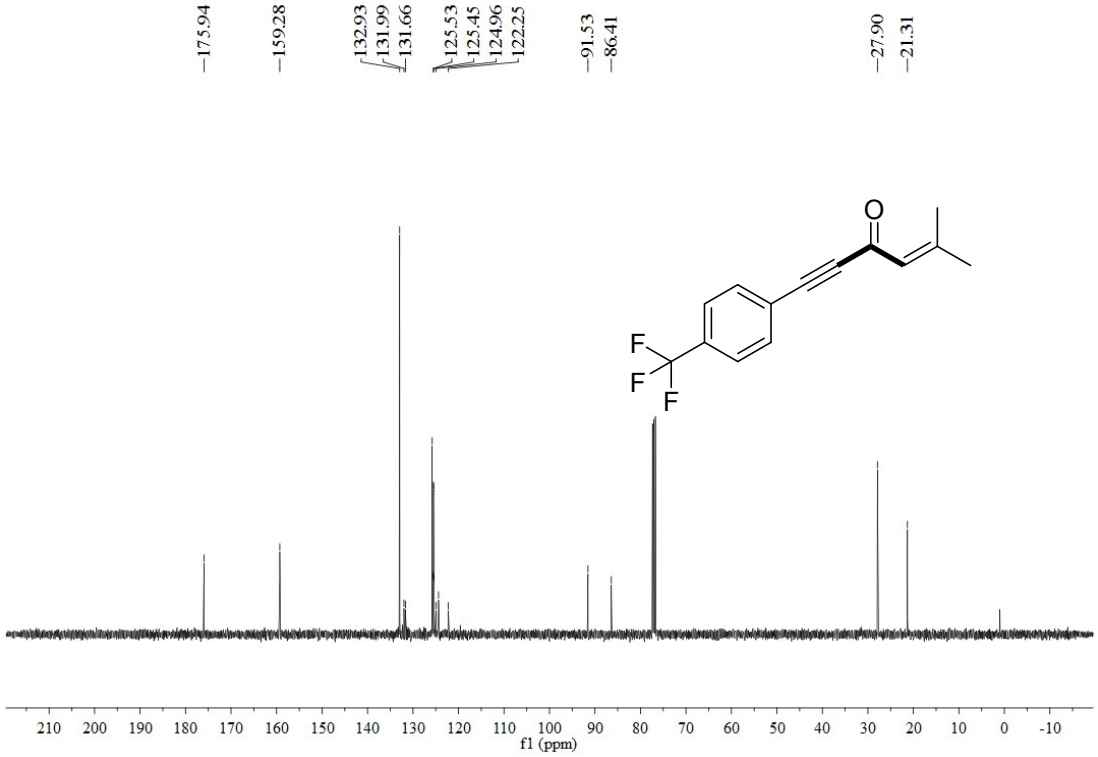
1.00
3.00
3.02
f1 (ppm)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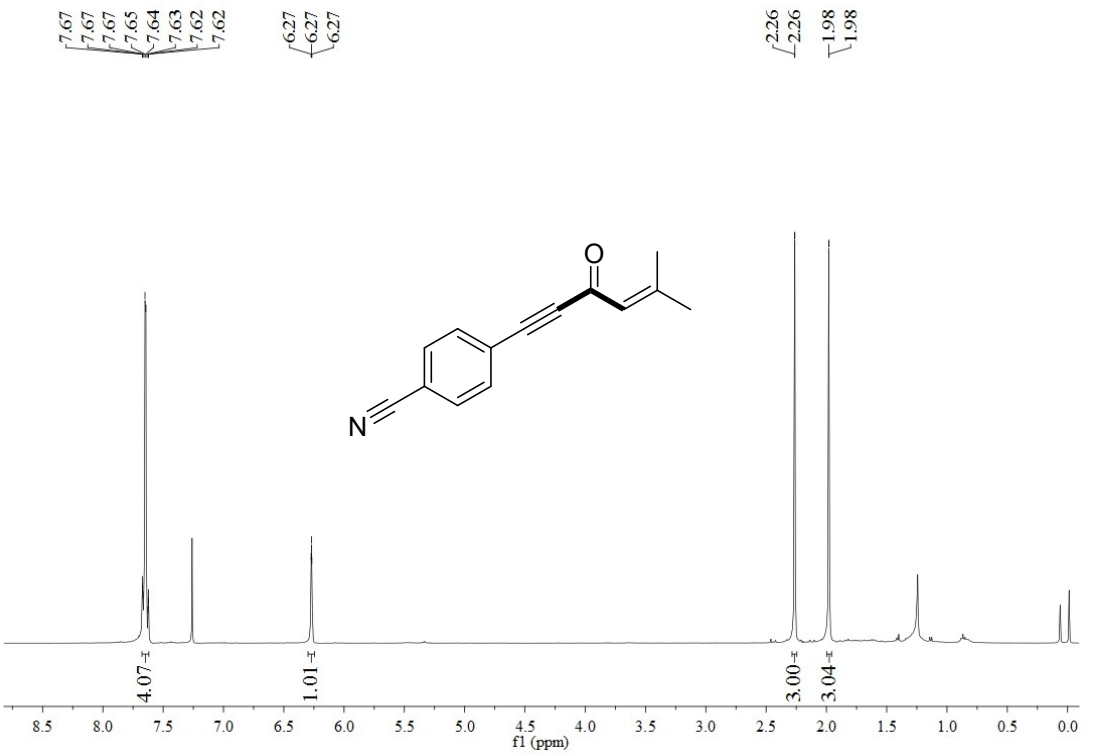
21.31
O
F
F
F
f1 (ppm)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2.26
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1.98
O
N
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1.01
3.00
3.04
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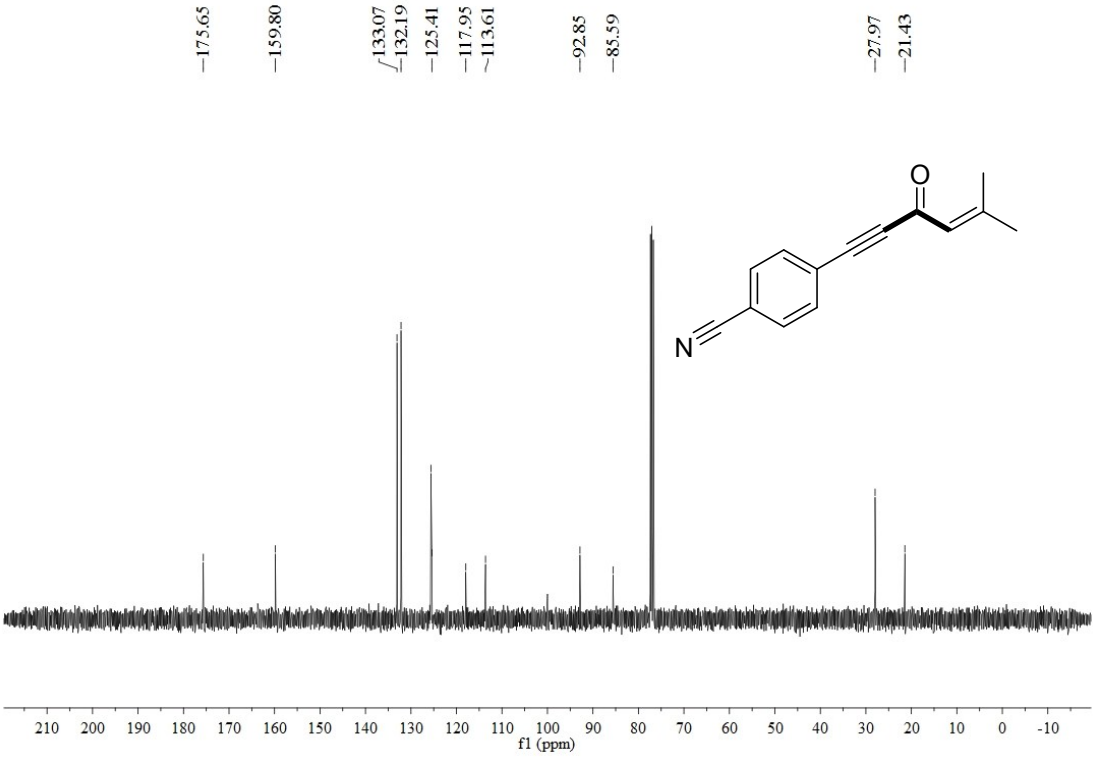
f1 (ppm)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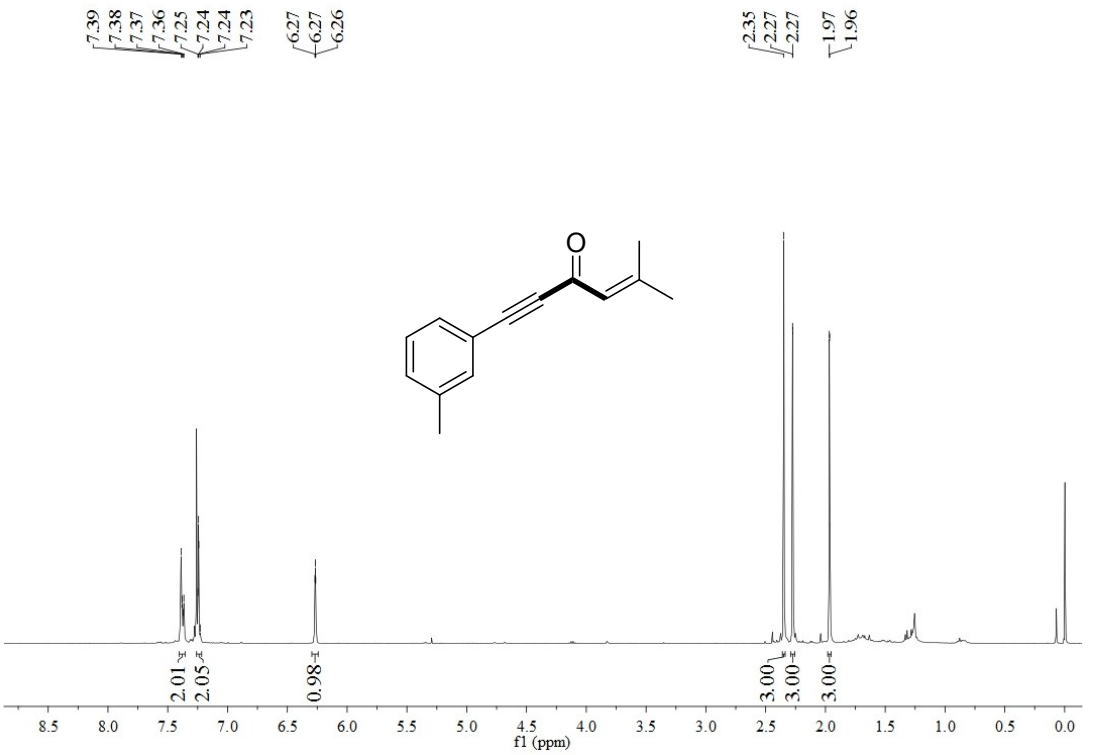
f1 (ppm)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2.27
2.27
1.97
1.96
O
2.01
2.05
0.98
3.00
3.00
3.00
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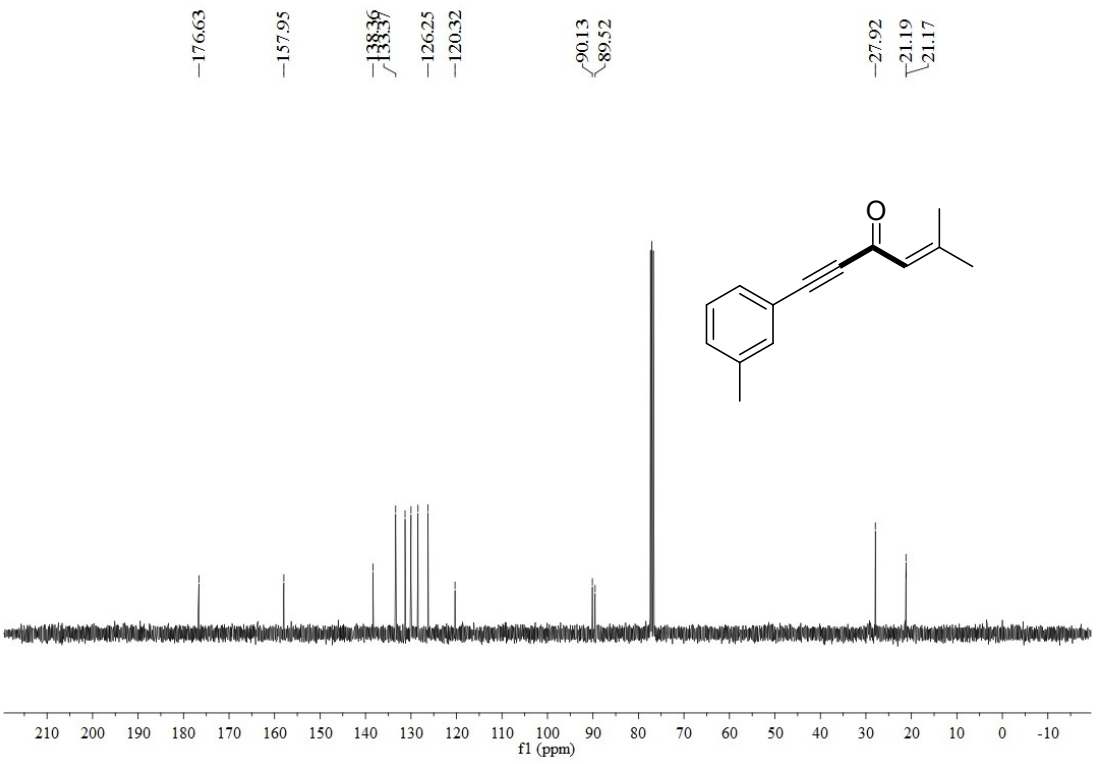
f1 (ppm)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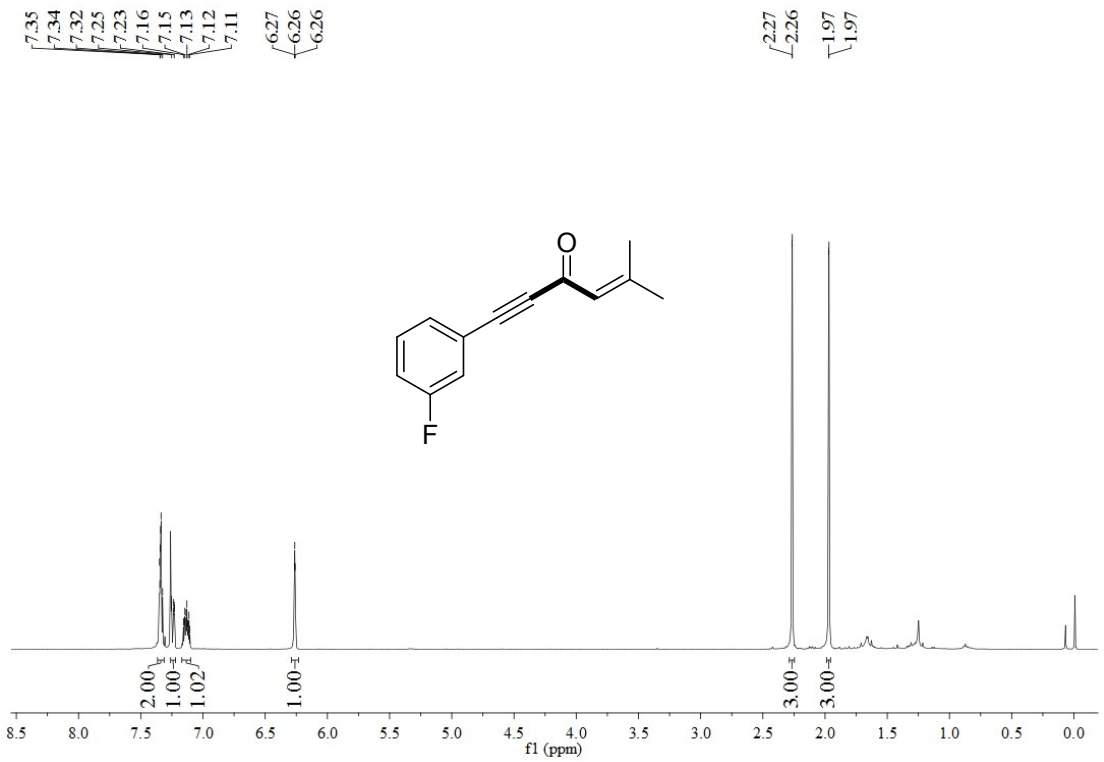
f1 (ppm)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6.26
6.26
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1.97
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F
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1.00
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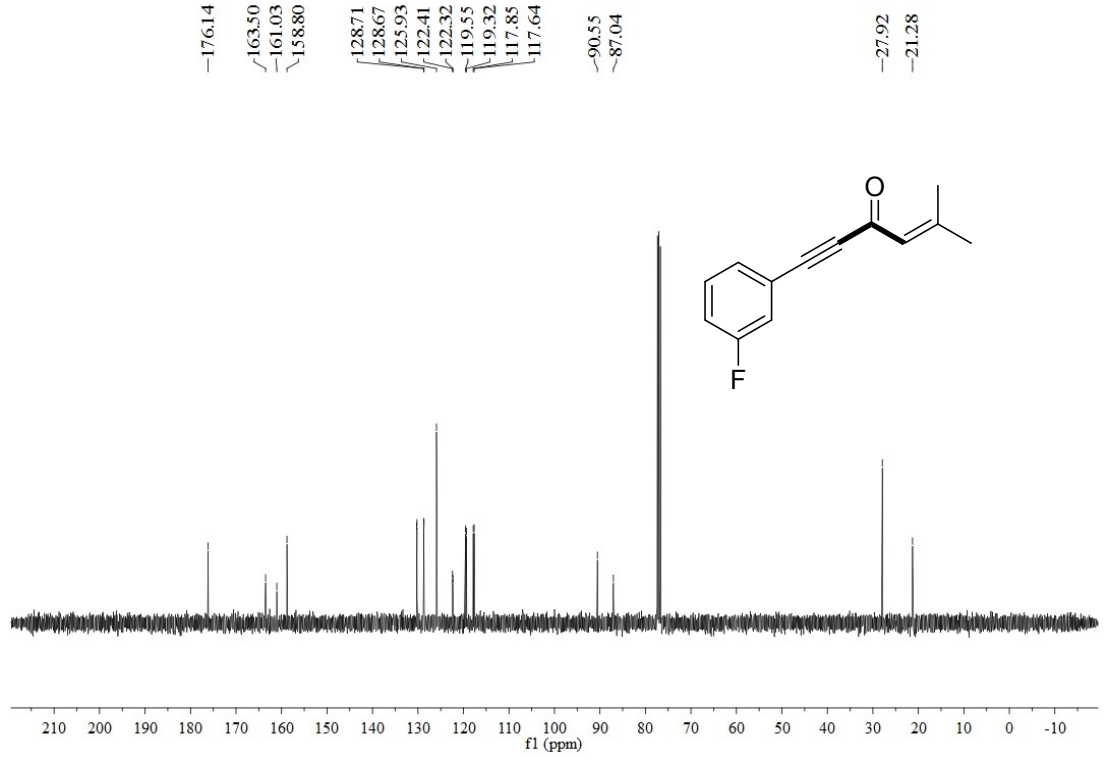
1.00
3.00
3.00
f1 (ppm)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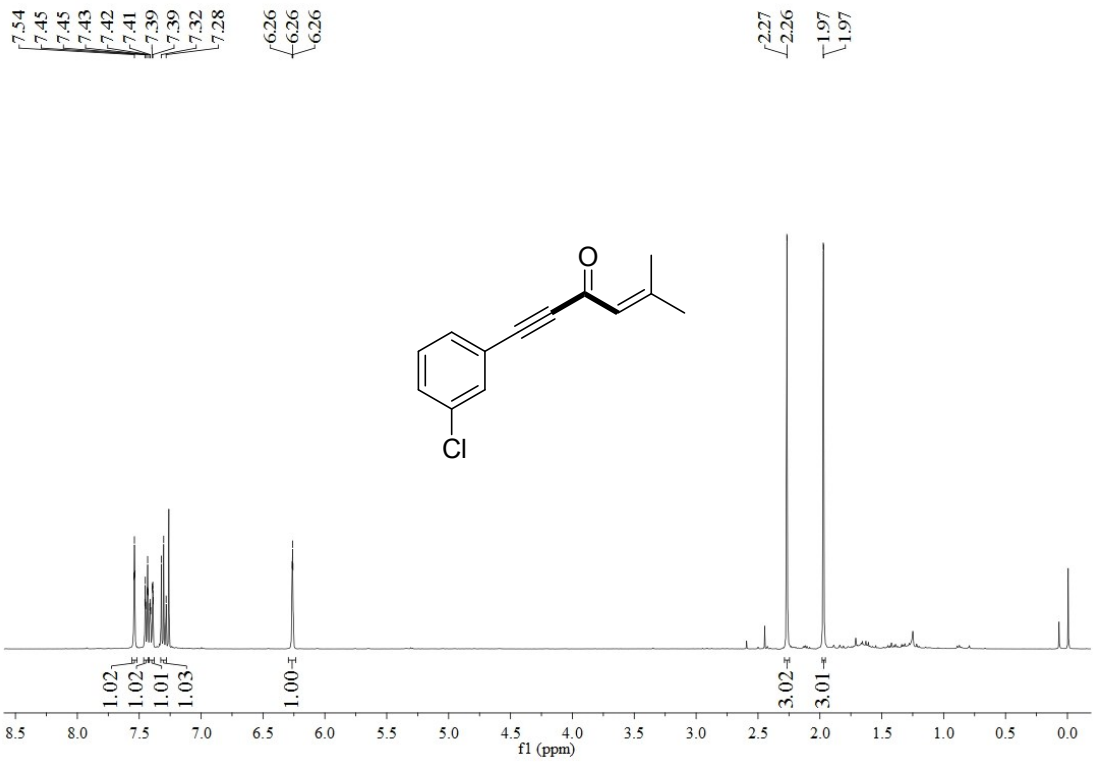
27.92
21.28
O
F
f1 (ppm)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6.26
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2.26
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Cl
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1.02
1.01
1.03
1.00
3.02
3.01
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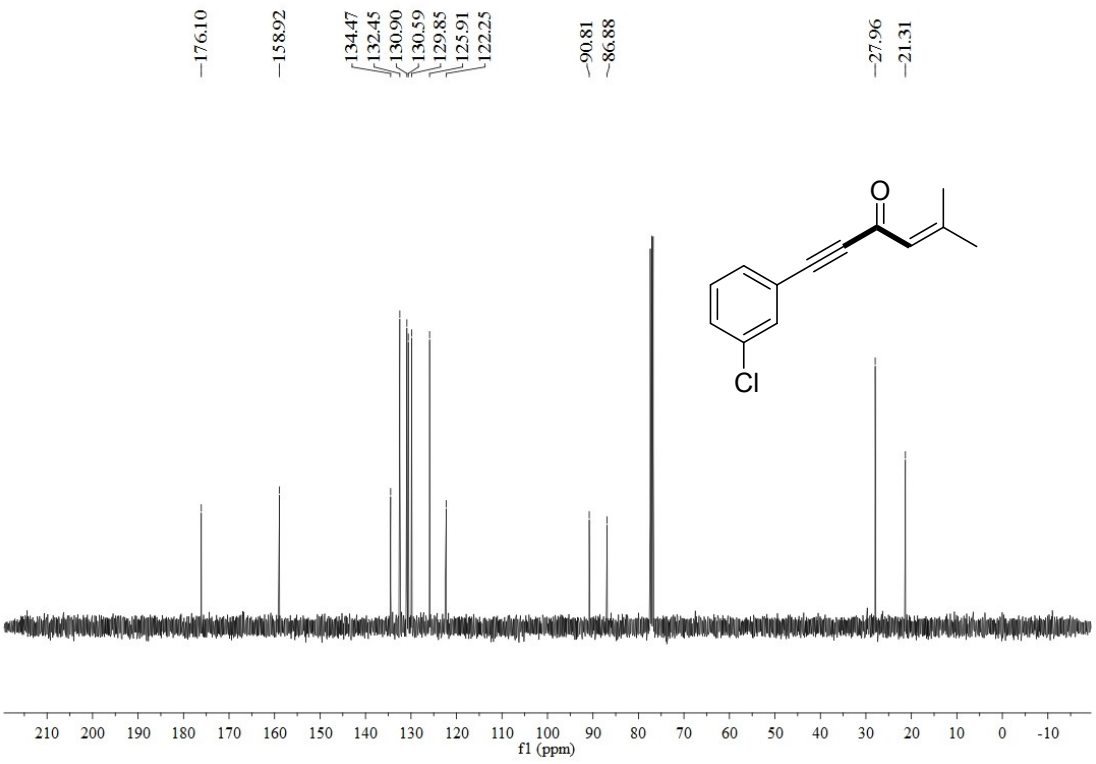
f1 (ppm)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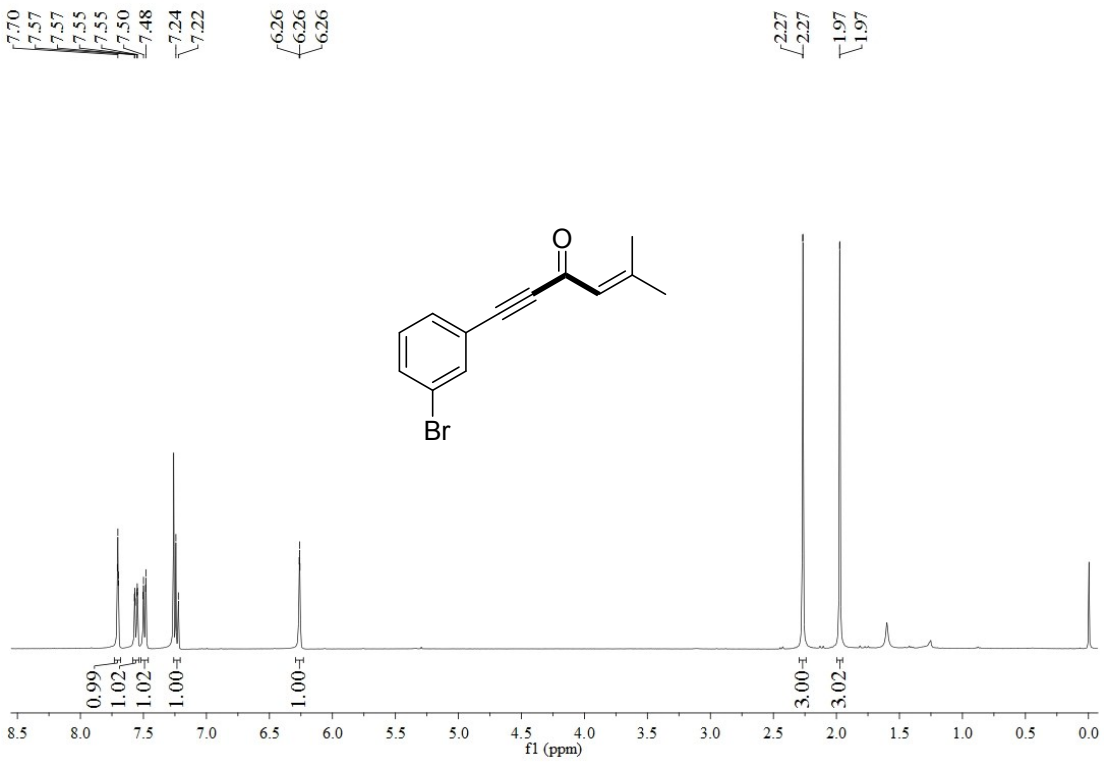
f1 (ppm)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2.27
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1.97
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Br
0.99
1.02
1.02
1.00
1.00
3.00
3.02
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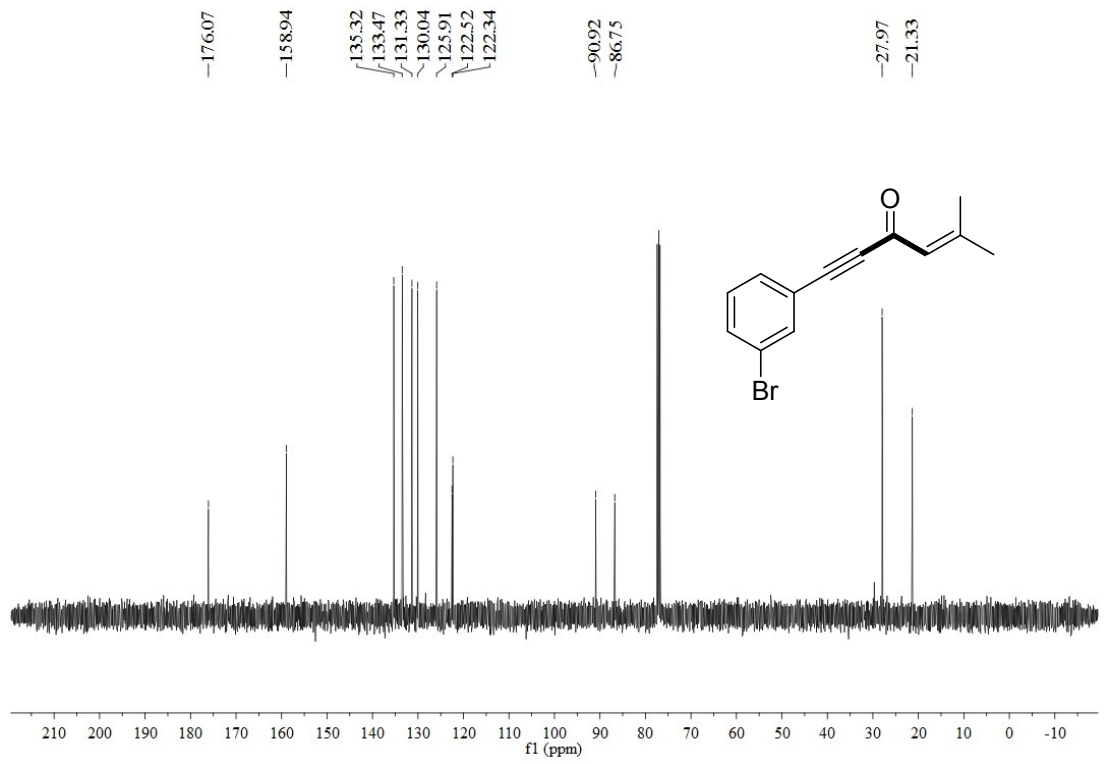
f1 (ppm)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Br
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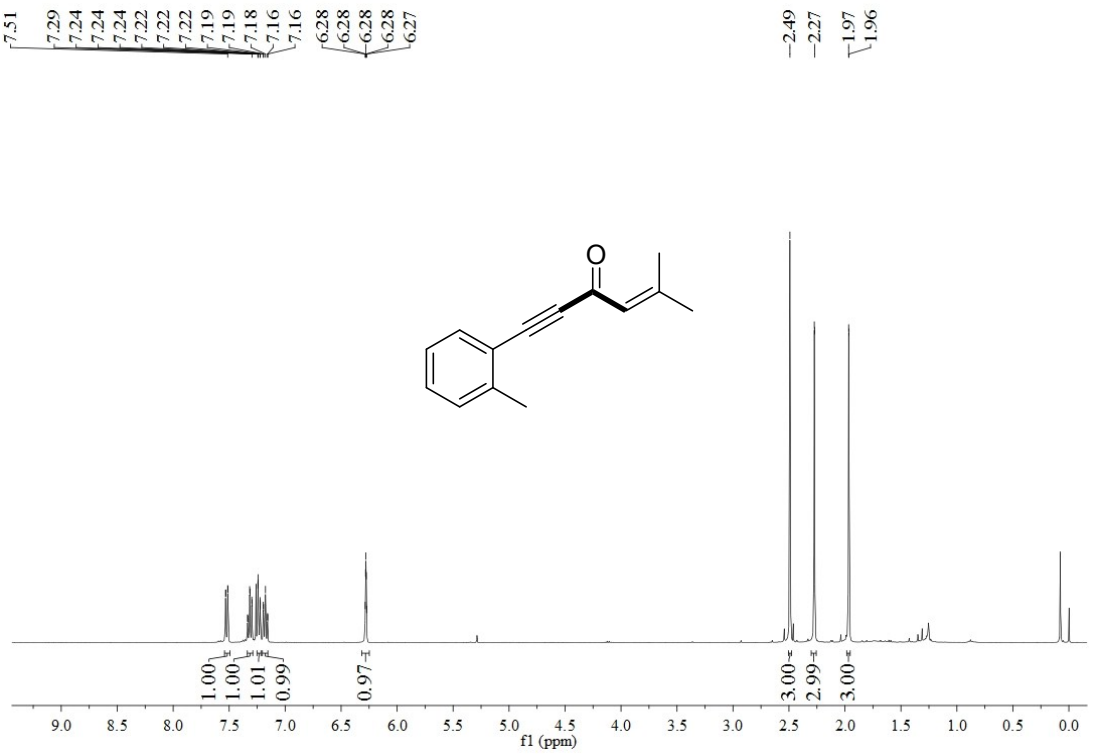
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1.96
O
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1.00
1.01
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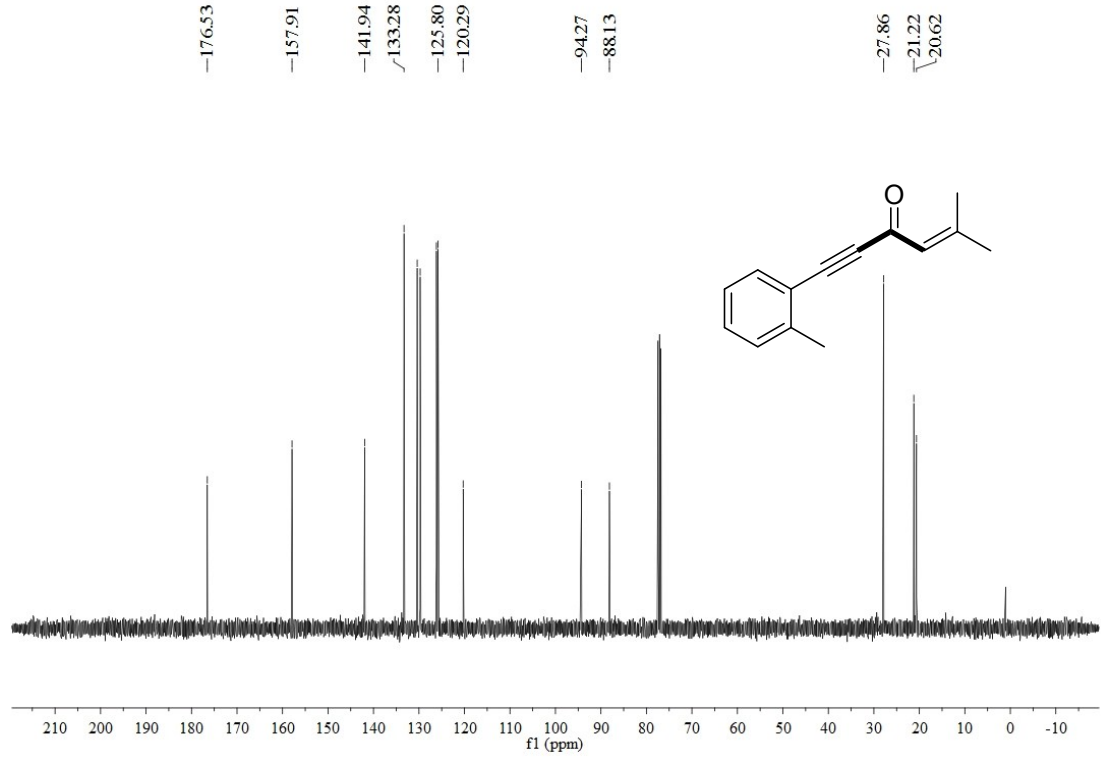
0.97
3.00
2.99
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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O
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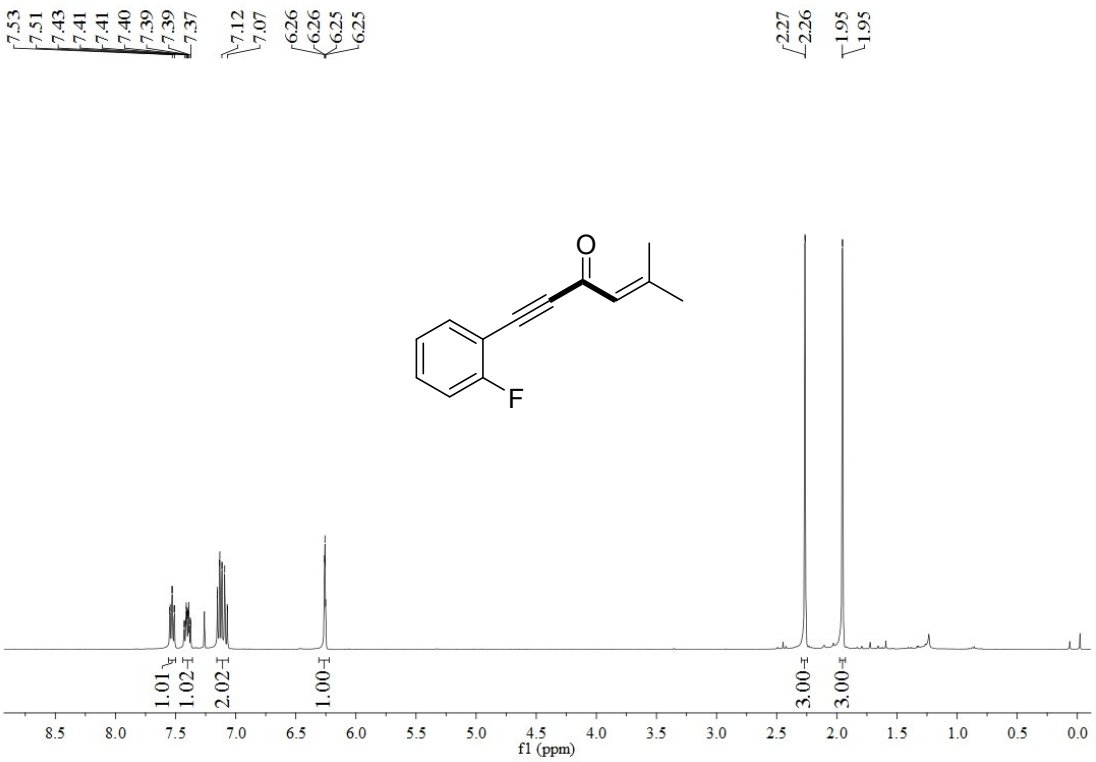
f1 (ppm)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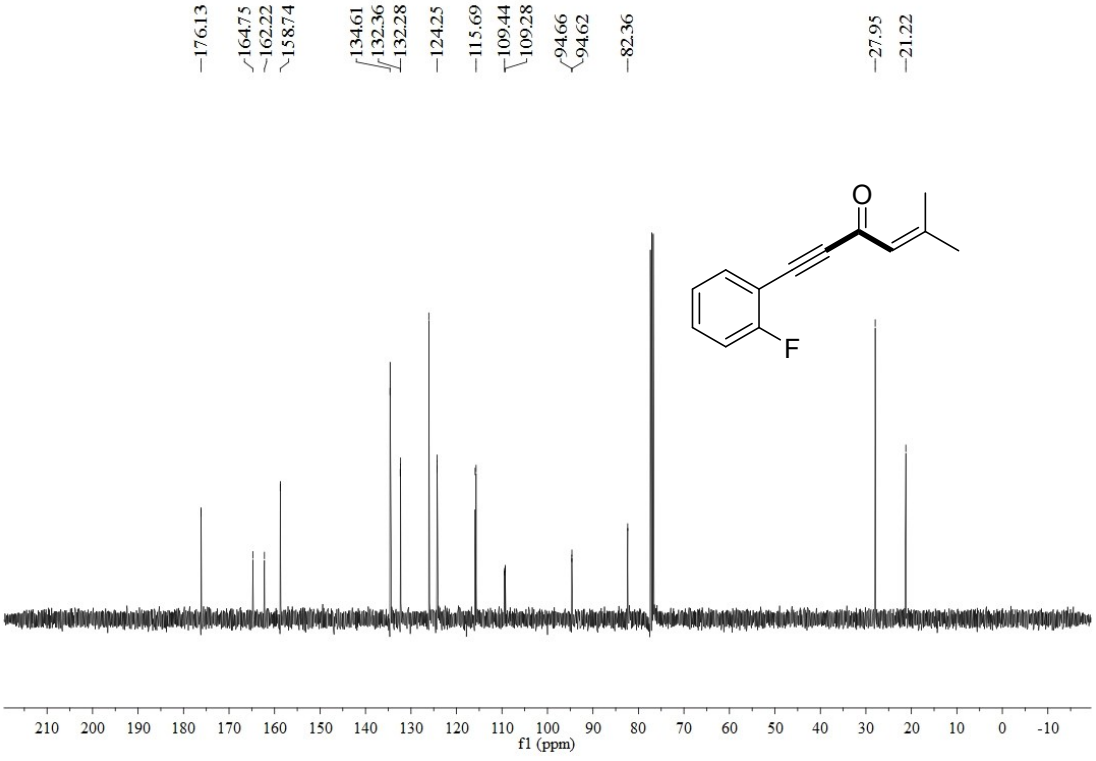
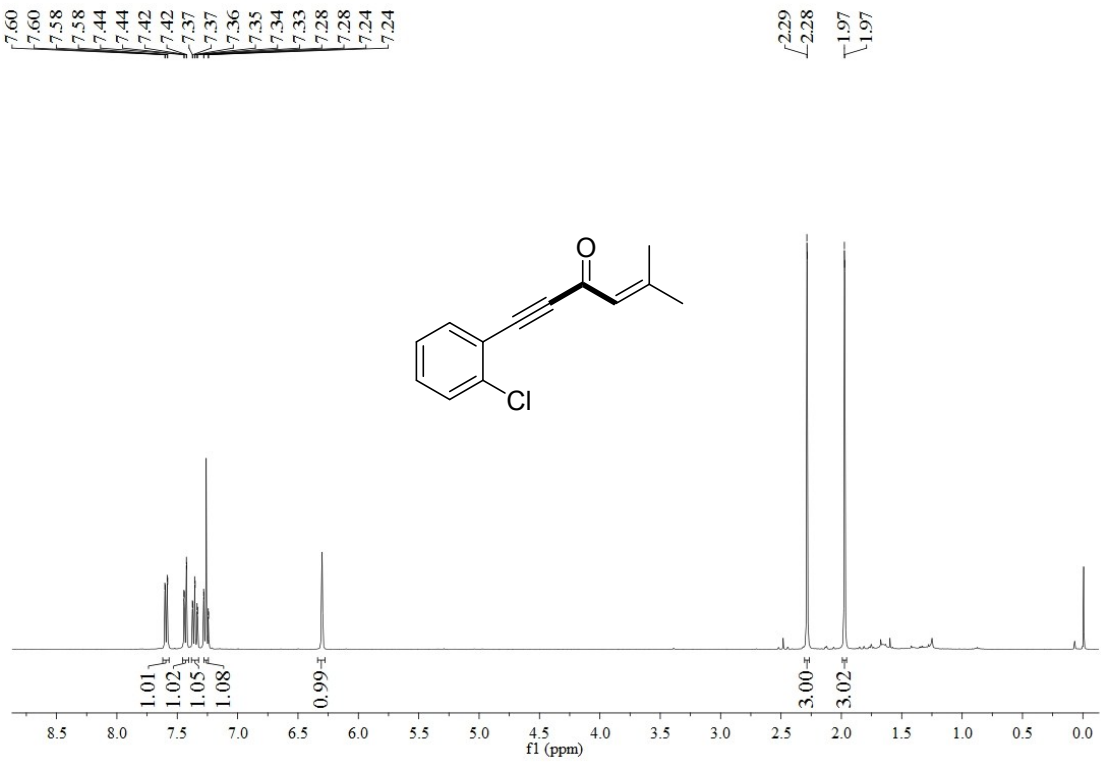
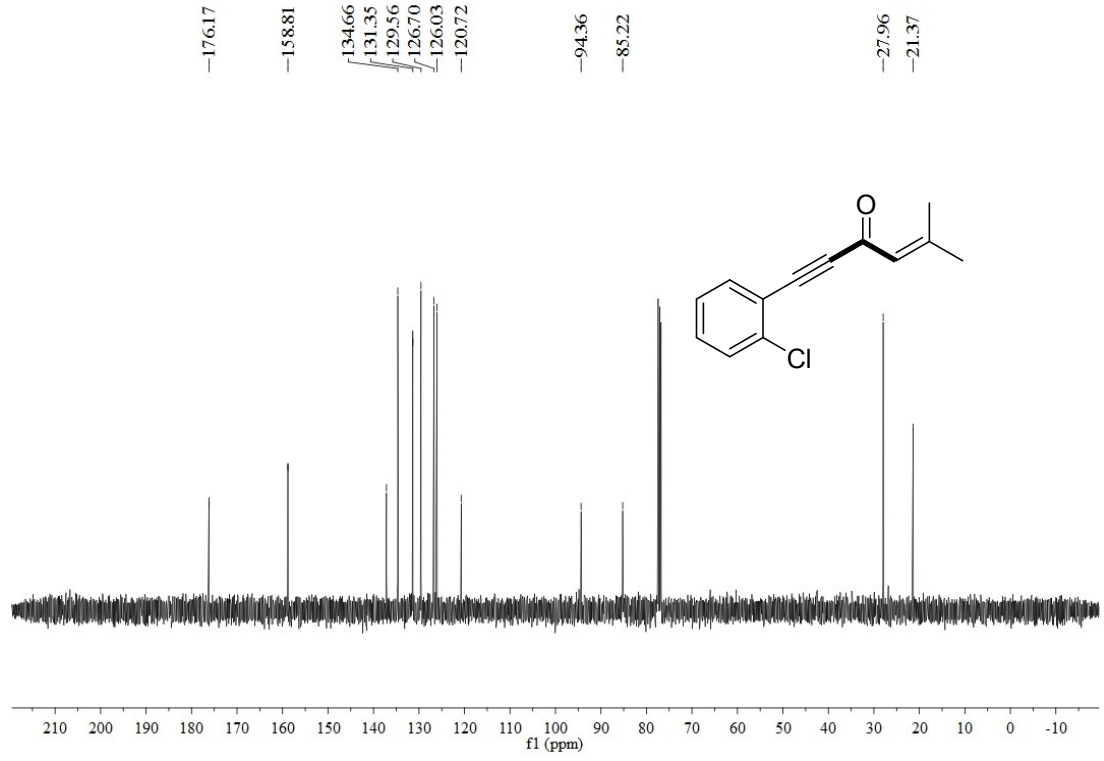
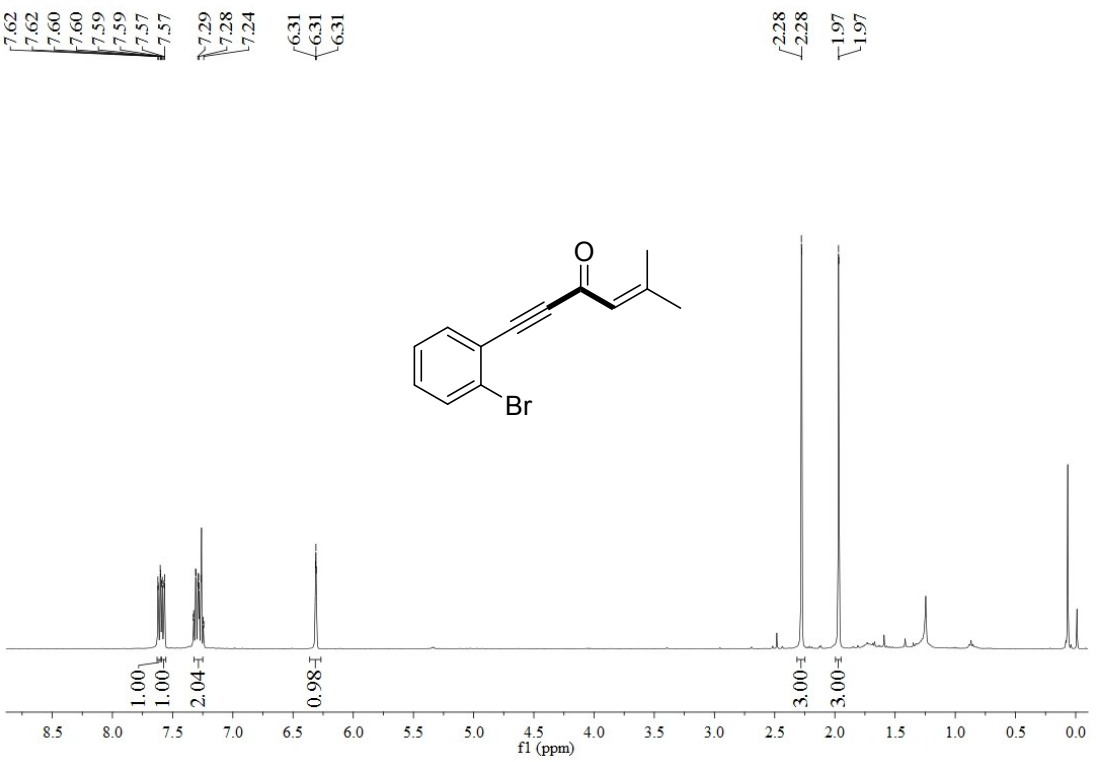
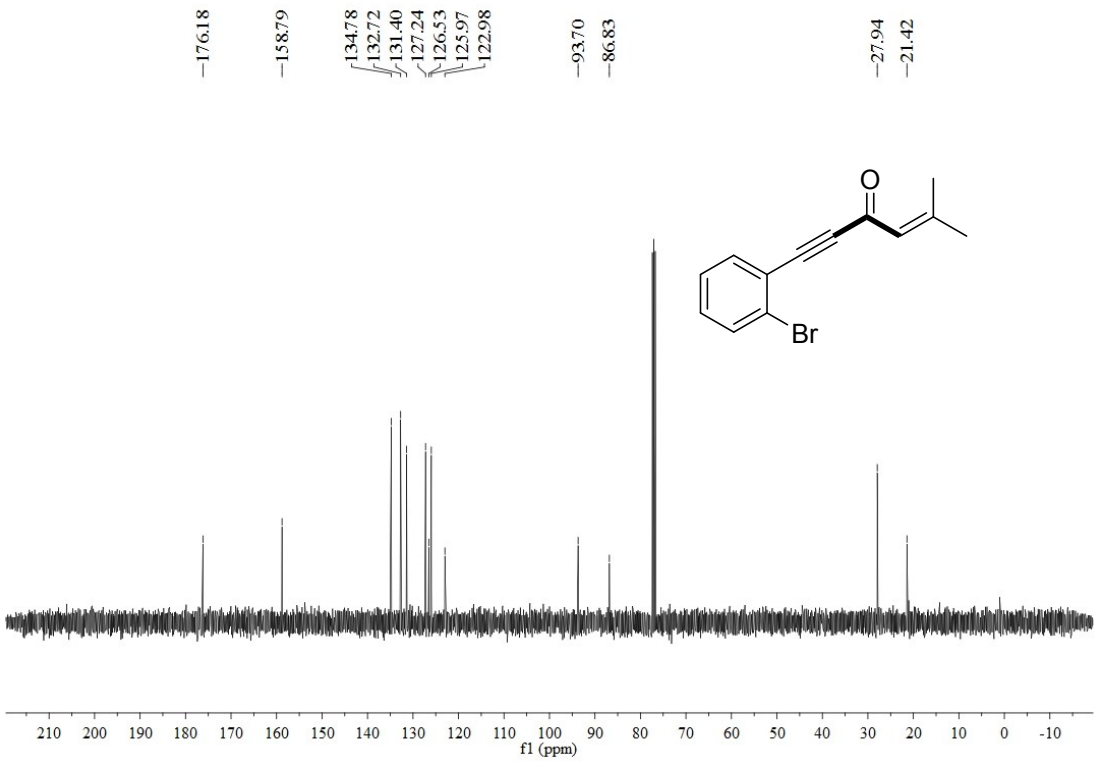
7.51
7.43
7.41
7.41
7.40
7.39
7.39
7.37
7.12
7.07
6.26
6.26
6.25
6.25
2.27
2.26
1.95
1.95
O
F
1.01
1.02
2.02
1.00
3.00
3.00
f1 (ppm)

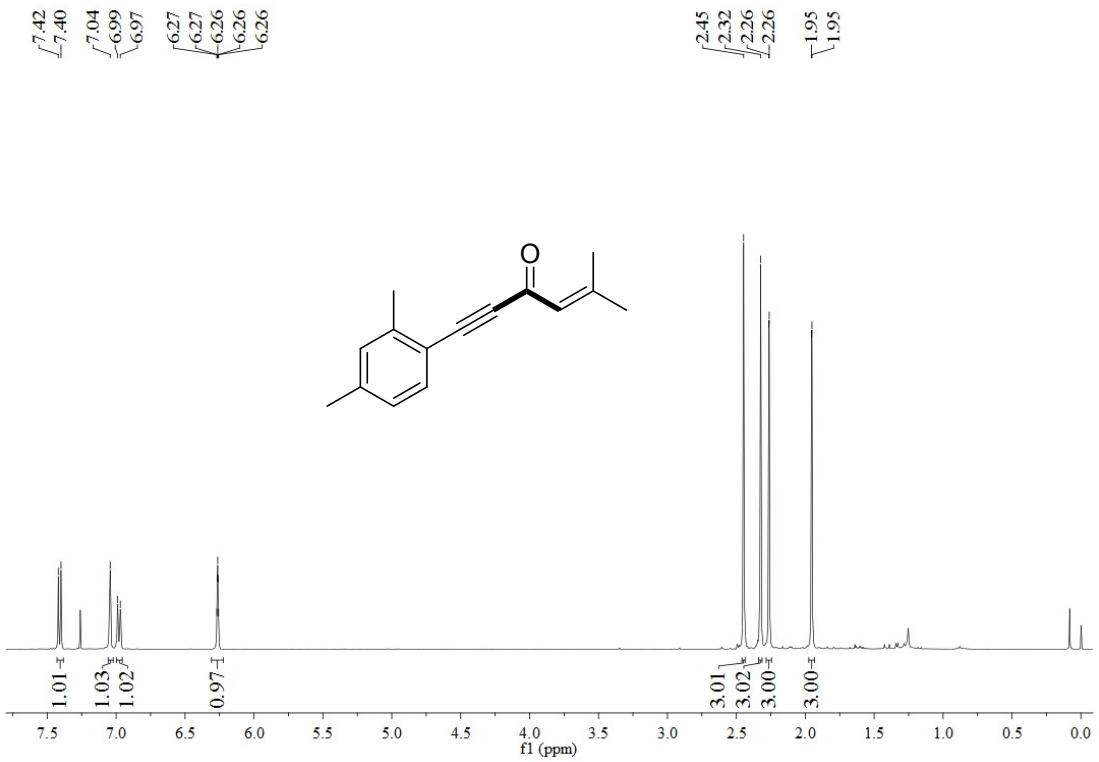

176.13
164.75
162.22
158.74
134.61
132.36
132.28
124.25
115.69
109.44
109.28
94.66
94.62
82.36
27.95
21.22
O
F
f1 (ppm)

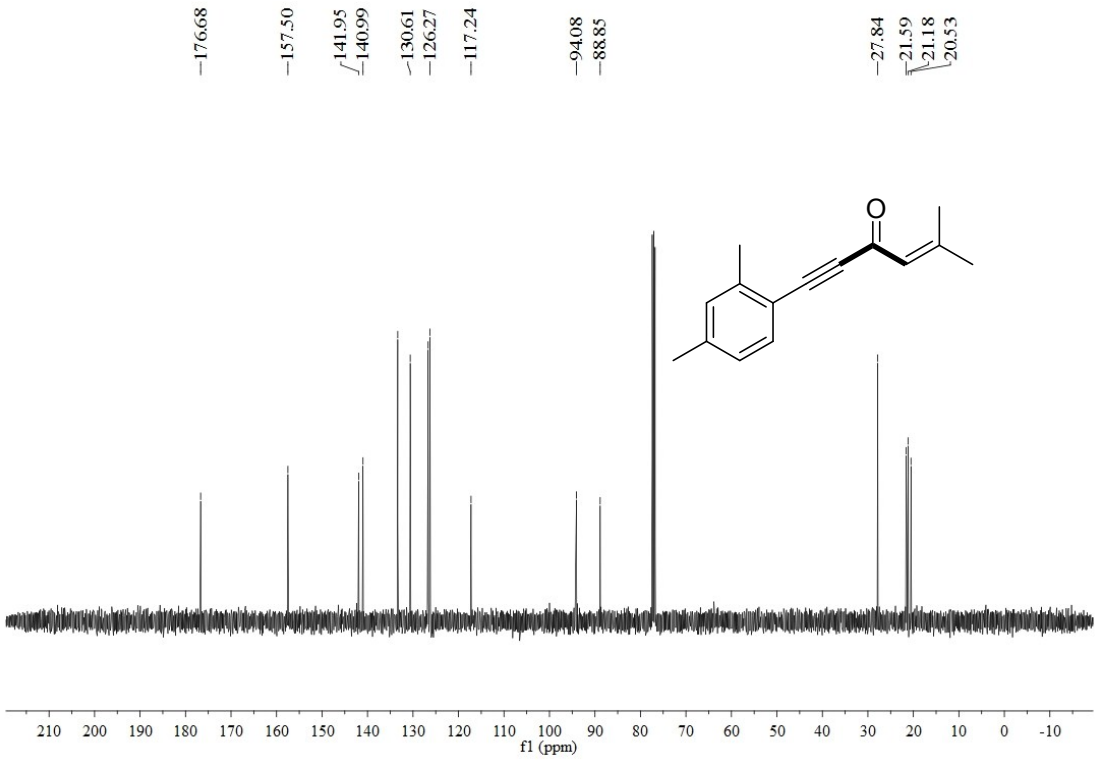

7.60
7.60
7.58
7.58
7.44
7.44
7.42
7.42
7.37
7.37
7.36
7.35
7.34
7.33
7.28
7.28
7.24
7.24
2.29
2.28
1.97
1.97
O
Cl
1.01
1.02
1.05
1.08
0.99
3.00
3.02
f1 (ppm)


176.17
158.81
134.66
131.35
129.56
126.70
126.03
120.72
94.36
85.22
27.96
21.37
O
Cl
f1 (ppm)


7.62
7.62
7.60
7.60
7.59
7.59
7.57
7.57
7.29
7.28
7.24
6.31
6.31
6.31
2.28
2.28
1.97
1.97
O
Br
1.00
1.00
2.04
0.98
3.00
3.00
f1 (ppm)


176.18
158.79
134.78
132.72
131.40
127.24
126.53
125.97
122.98
93.70
86.83
27.94
21.42
O
Br
f1 (ppm)


7.42
7.40
7.04
6.99
6.97
6.27
6.27
6.26
6.26
6.26
2.45
2.32
2.26
2.26
1.95
1.95
O
1.01
1.03
1.02
0.97
3.01
3.02
3.00
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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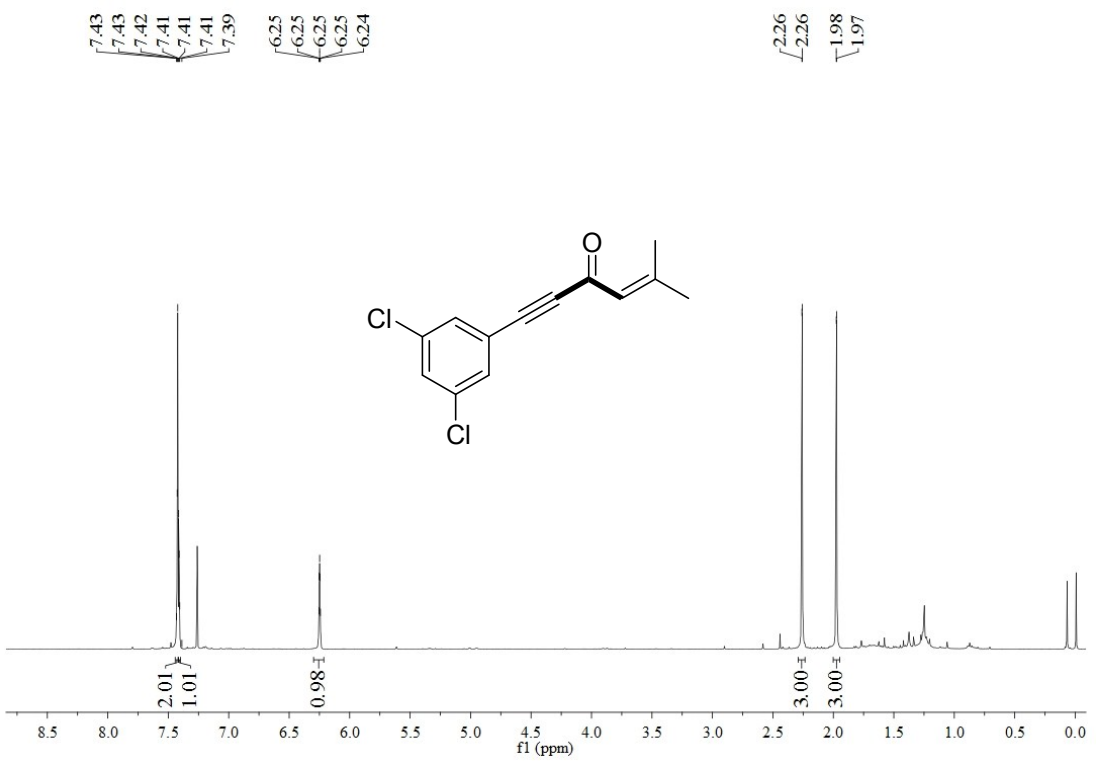
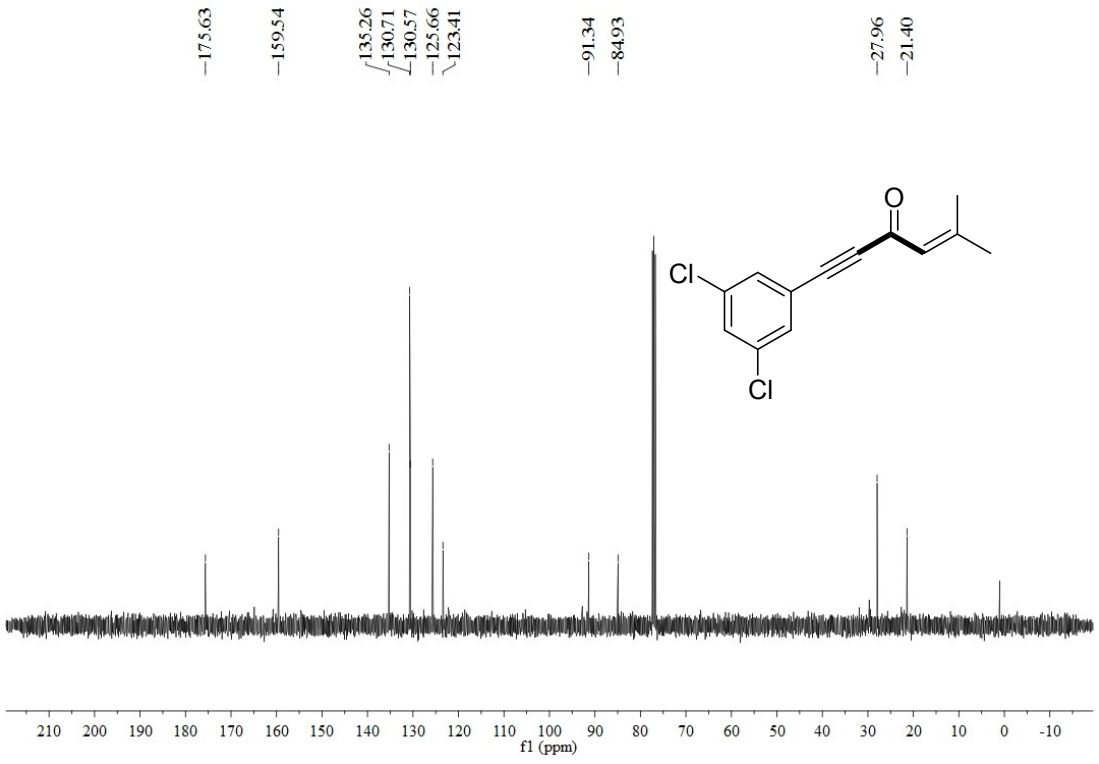
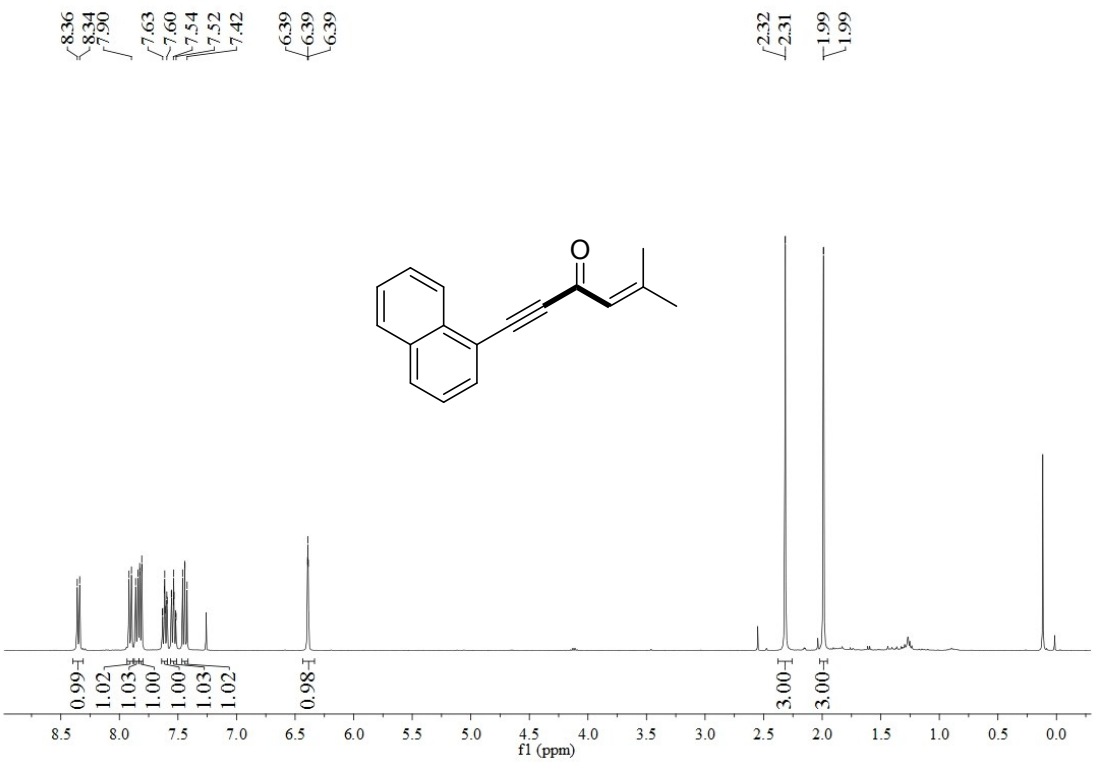
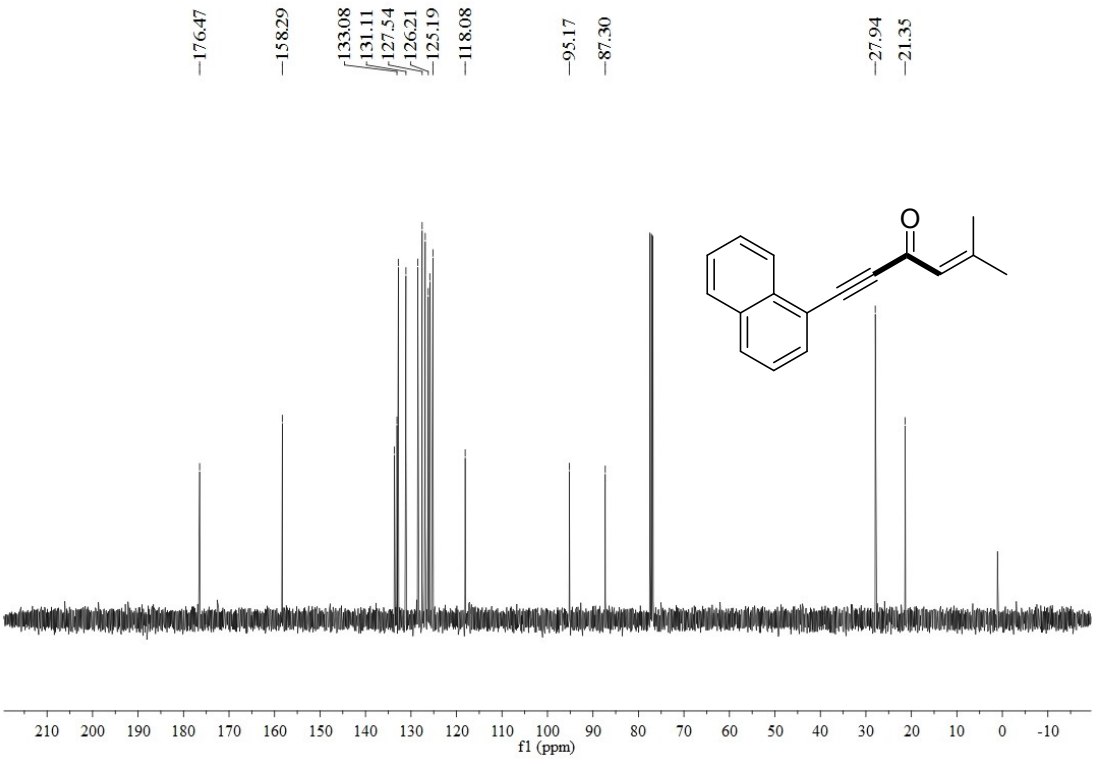
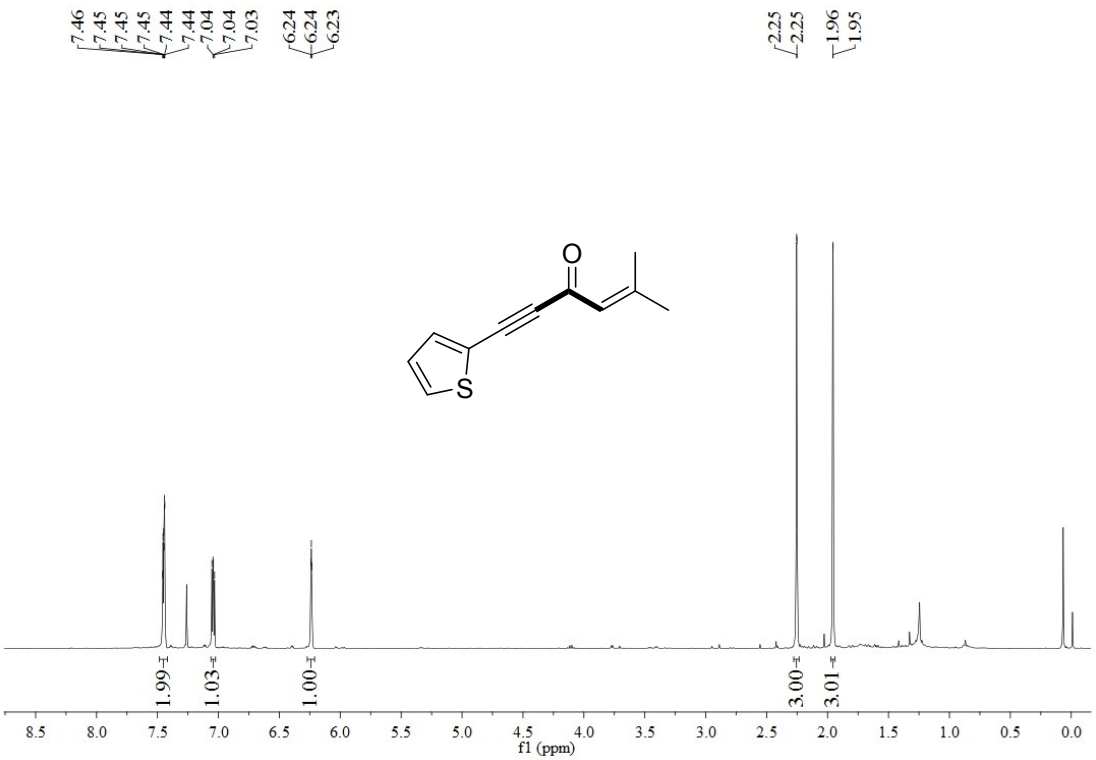
157.50
141.95
140.99
130.61
126.27
117.24
94.08
88.85
27.84
21.59
21.18
20.53
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

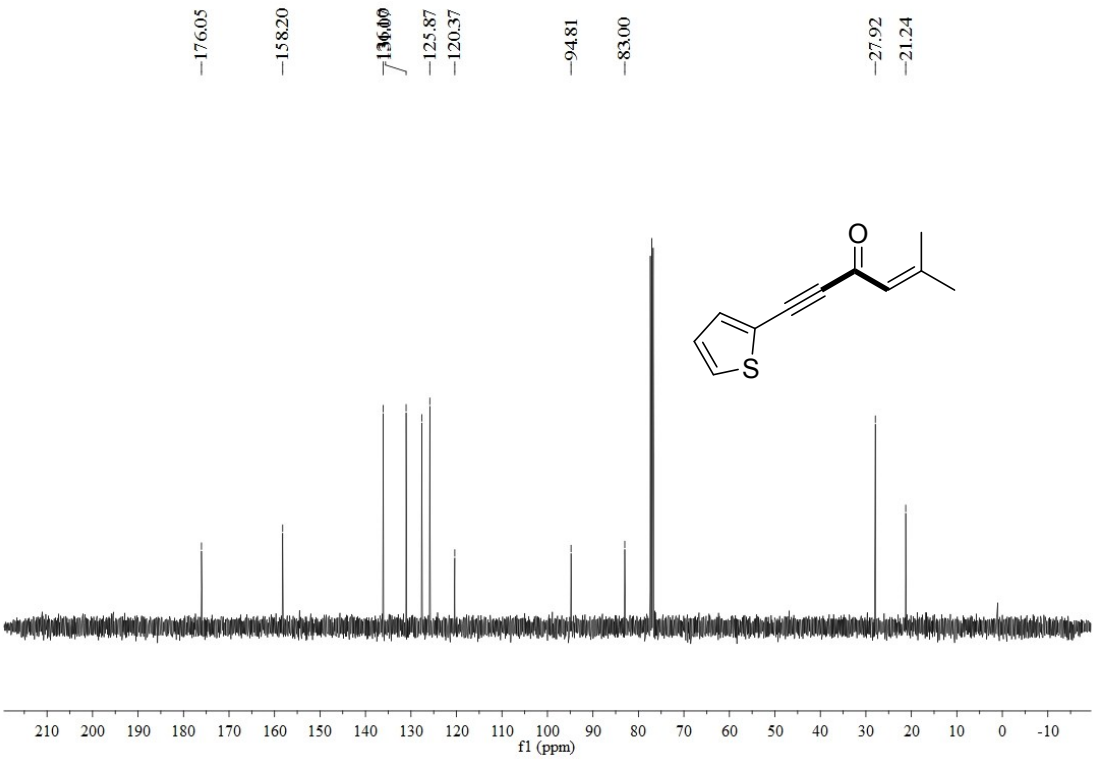

7.43
7.43
7.42
7.41
7.41
7.41
7.39
6.25
6.25
6.25
6.24
2.26
2.26
1.98
1.97
O
Cl
Cl
2.01
1.01
0.98
3.00
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


175.63
159.54
135.26
130.71
130.57
125.66
123.41
91.34
84.93
27.96
21.40
O
Cl
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.36
8.34
7.90
7.63
7.60
7.54
7.52
7.42
6.39
6.39
6.39
2.32
2.31
1.99
1.99
O
0.99
1.02
1.03
1.00
1.00
1.03
1.02
0.98
3.00
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


176.47
158.29
133.08
131.11
127.54
126.21
125.19
118.08
95.17
87.30
27.94
21.35
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.46
7.45
7.45
7.45
7.44
7.44
7.04
7.04
7.03
6.24
6.24
6.23
2.25
2.25
1.96
1.95
O
S
1.99
1.03
1.00
3.00
3.01
f1 (ppm)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158.20
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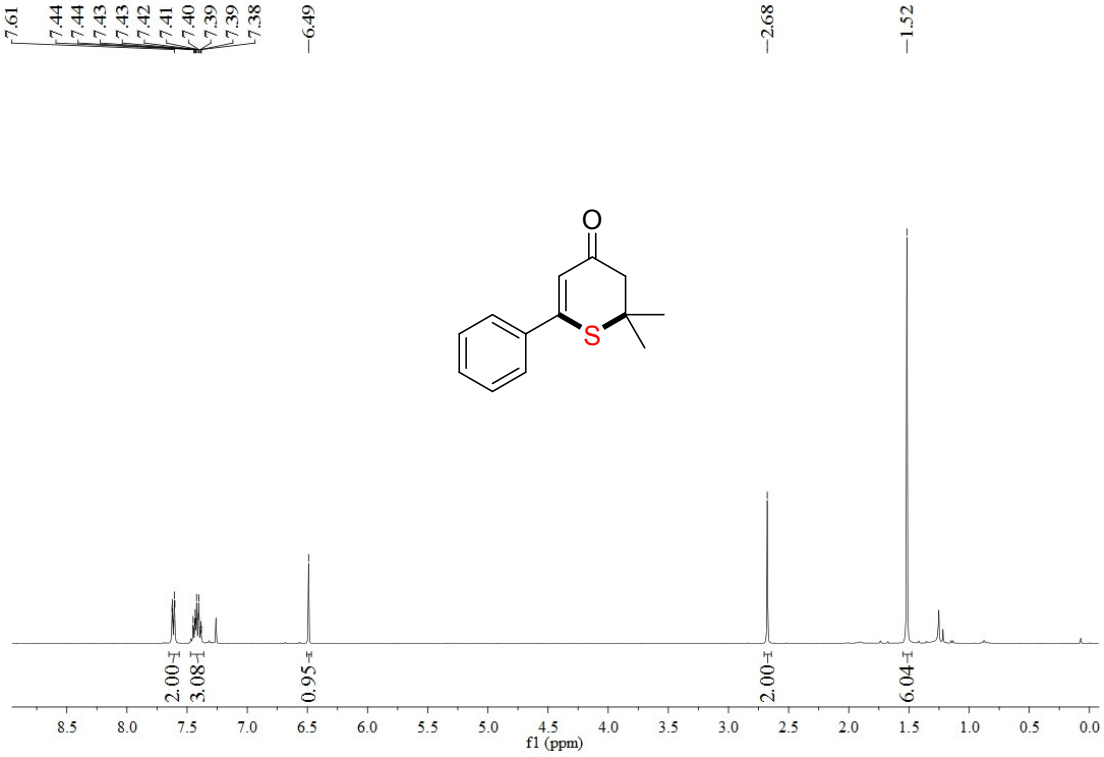
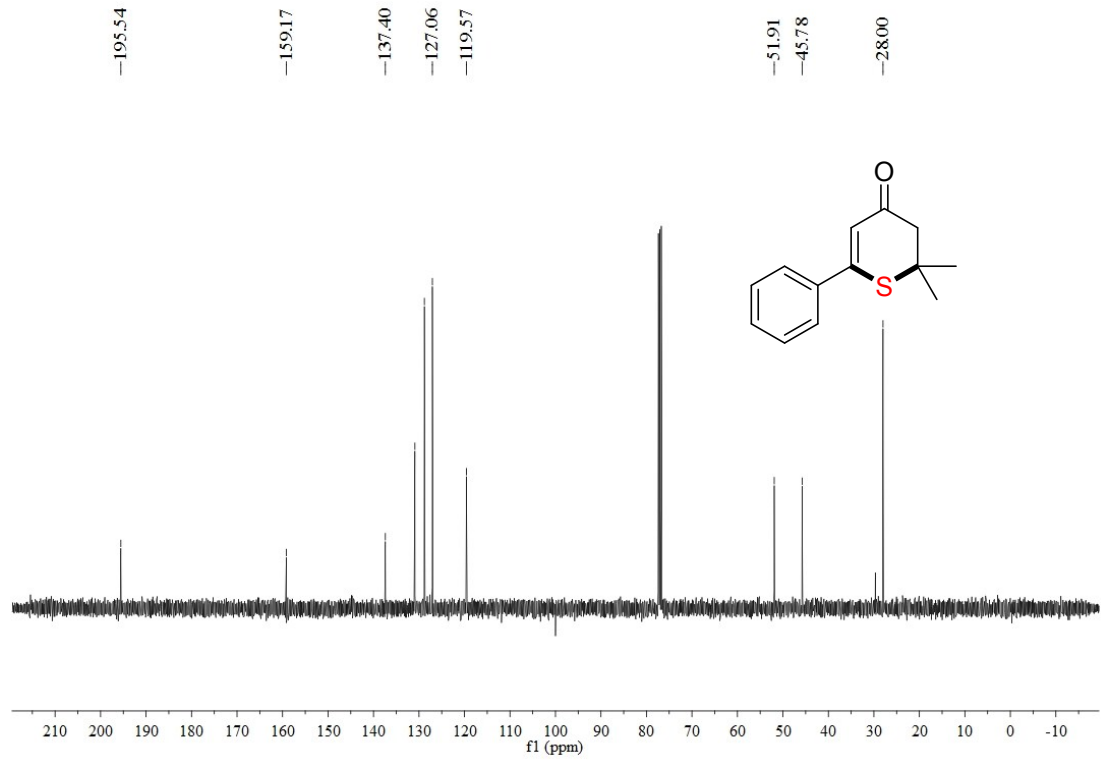
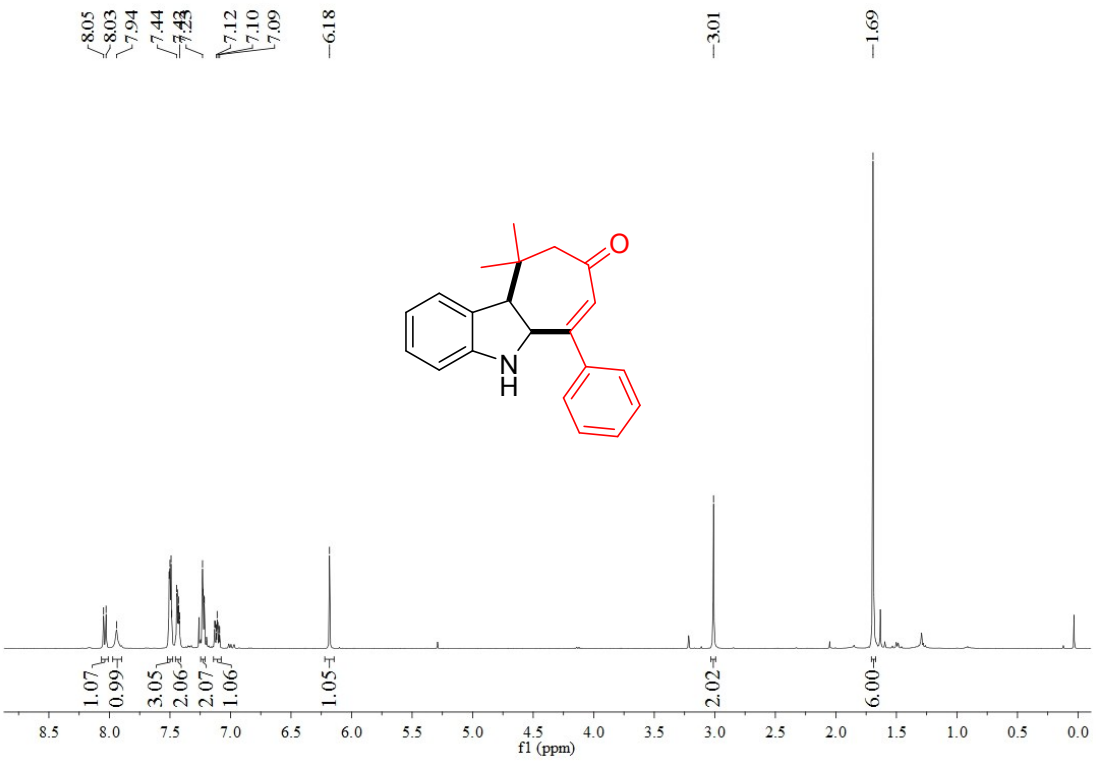
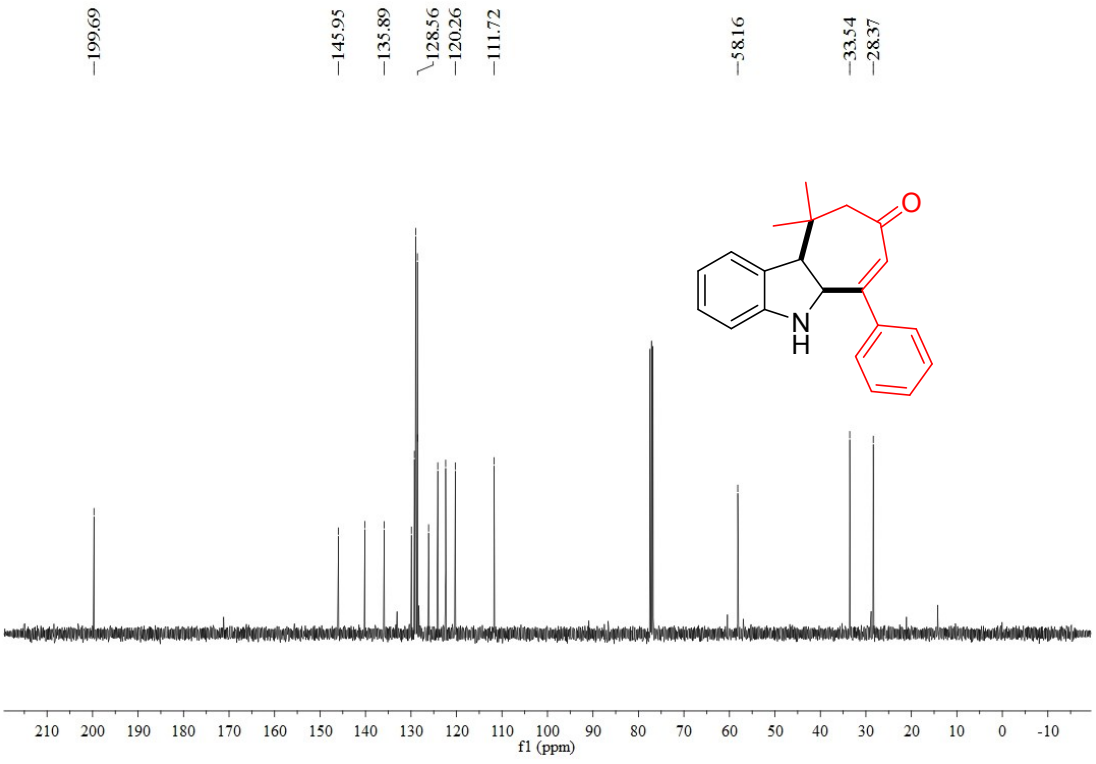
125.87
120.37
94.81
83.00
27.92
21.24
O
S
f1 (ppm)


7.61
7.44
7.44
7.43
7.43
7.42
7.41
7.40
7.39
7.39
7.38
6.49
2.68
1.52
O
S
2.00
3.08
0.95
2.00
6.04
f1 (ppm)


195.54
159.17
137.40
127.06
119.57
51.91
45.78
28.00
O
S
f1 (ppm)


8.05
8.03
7.94
7.44
7.43
7.12
7.10
7.09
6.18
3.01
1.69
O
N
H
1.07
0.99
3.05
2.06
2.07
1.06
1.05
2.02
6.00
f1 (ppm)


199.69
145.95
135.89
128.56
120.26
111.72
58.16
33.54
28.37
O
N
H
f1 (ppm)