Supporting Information

Cumulene Wires Display Increasing Conductance with Increasing Length

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1. Additional Data

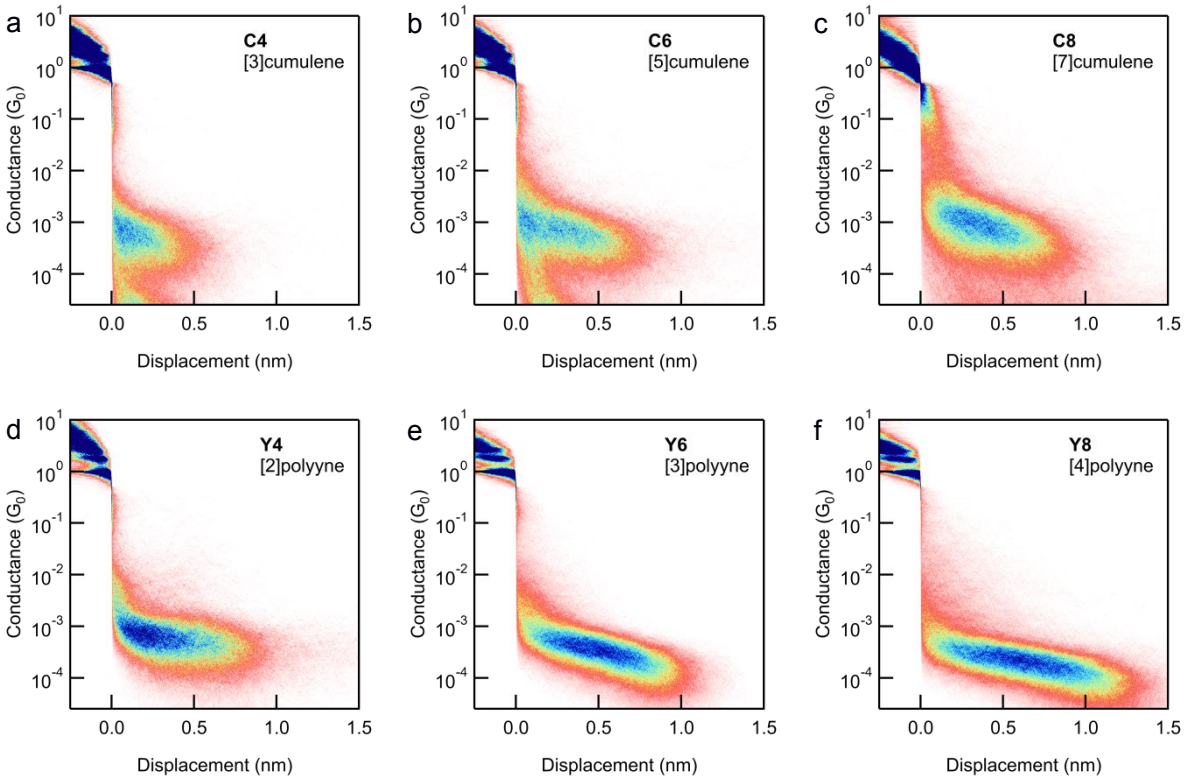


Figure S1. Two-dimensional conductance histograms of (a) **C4**, (b) **C6**, (c) **C8**, (d) **Y4**, (e) **Y6** and (f) **Y8** in 1,2,4-trichlorobenzene (TCB) solution. The corresponding one-dimensional histograms are in the Figure 1b and 1c.

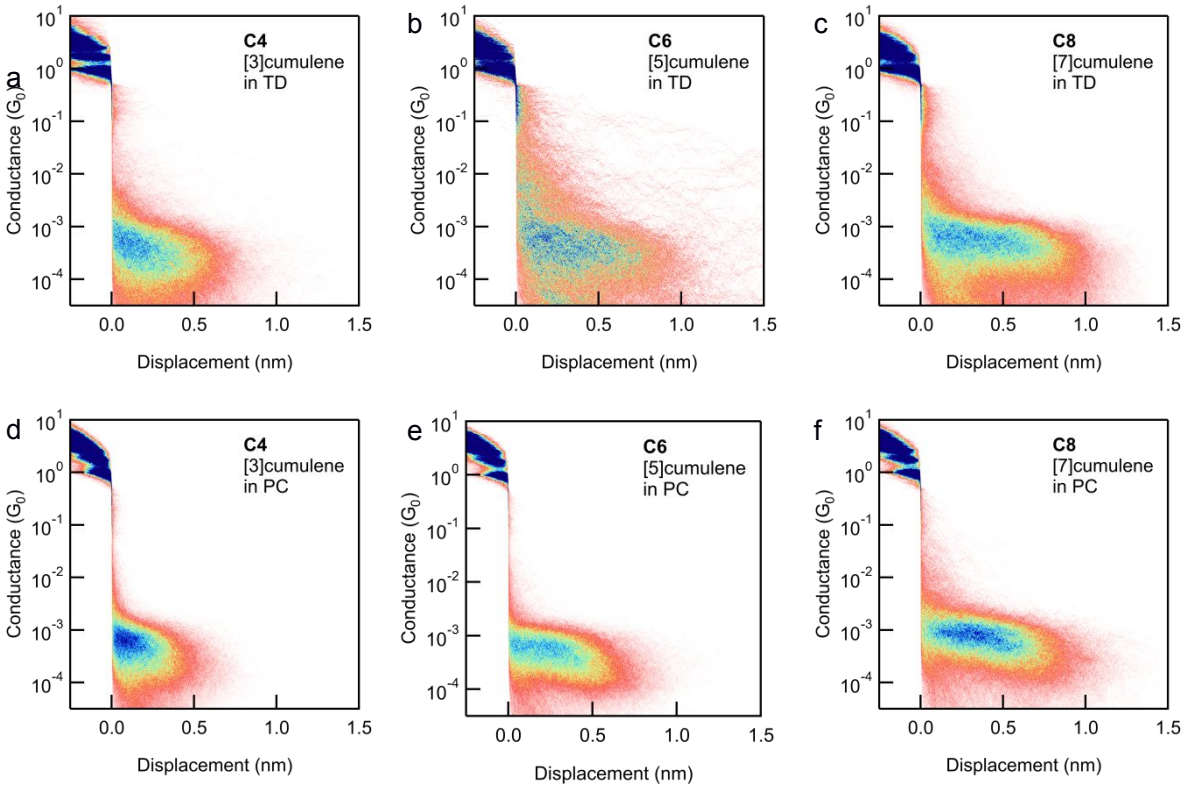


Figure S2. Two-dimensional conductance histograms of (a) **C4**, (b) **C6** and (c) **C8** in *n*-tetradecane (TD) and (d) **C4**, (e) **C6** and (f) **C8** in propylene carbonate (PC). The corresponding one-dimensional histograms are in the Figure 3a and 3b.

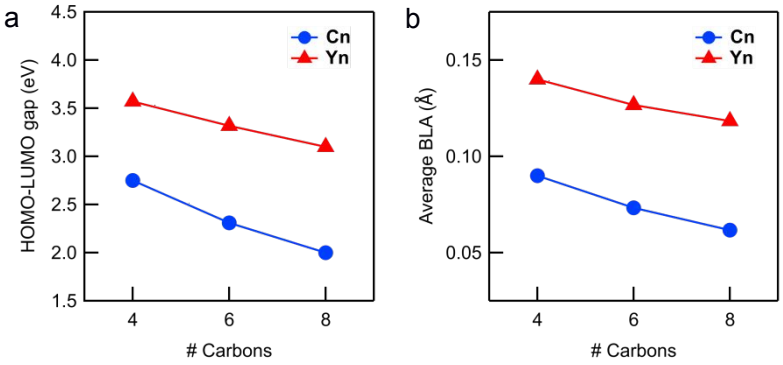


Figure S3. (a) The theoretical HOMO-LUMO gap for cumulenes (**Cn**-series) and polyynes (**Yn**-series). (b) The average bond length alternation (BLA) values for cumulenes and polyynes. The average BLA is the difference between the average bond length of bonds with odd bond indices and even bond indices.

2. Synthetic Details

2.1 General

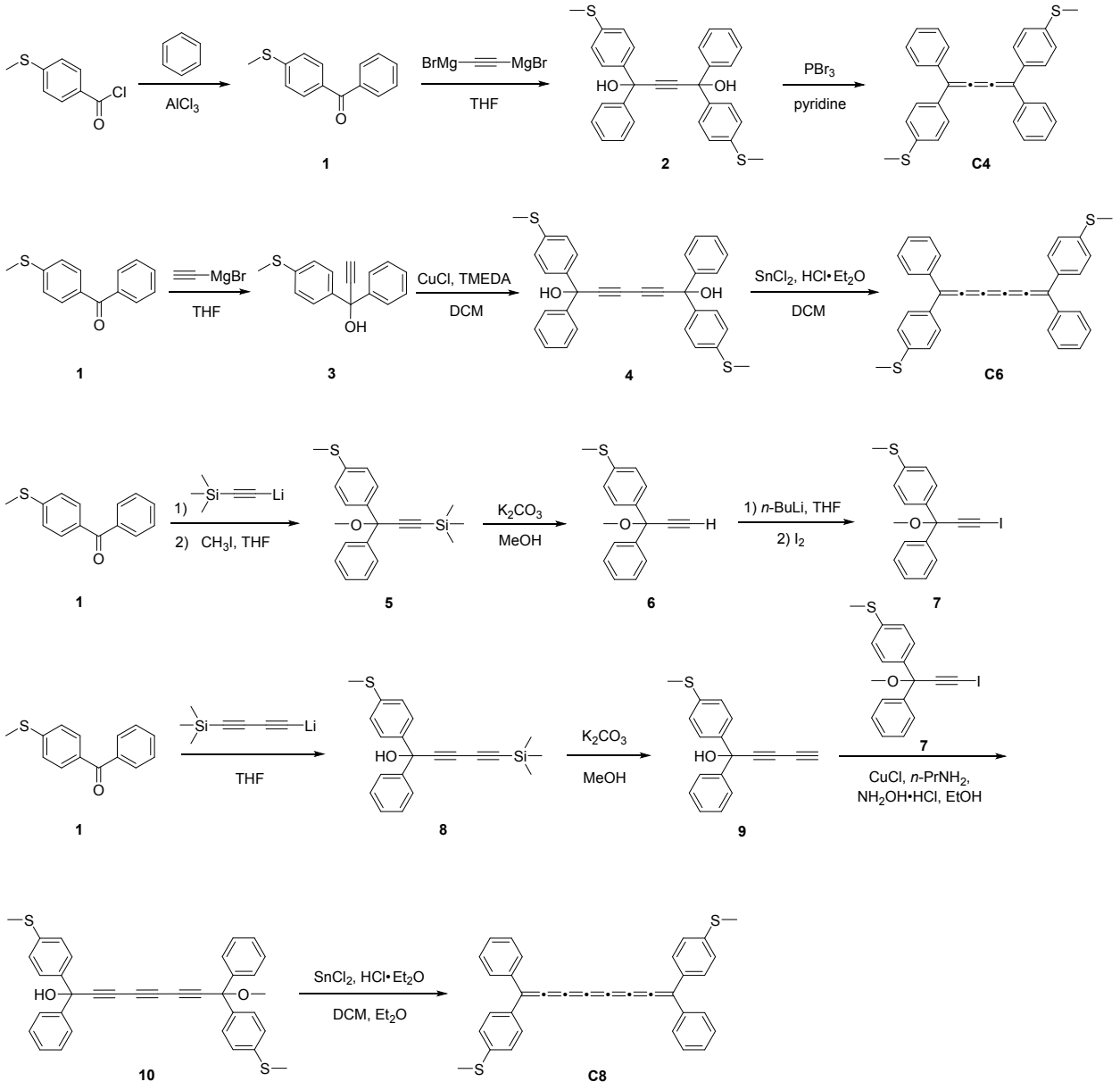
All reactions were performed in oven-dried round bottom flasks, unless otherwise noted. The flasks were fitted with Teflon magnetic stir bar, rubber septa and reactions were conducted under a positive pressure of nitrogen, unless otherwise noted. Anhydrous and anaerobic solvents were obtained from Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst (Glass Contour, Irvine, CA). For the synthesis of compounds **C6** and **C8**, the post-treatment procedures were carried out in Aldrich® AtmosBag filled with nitrogen. Automated flash chromatography was performed using a Teledyne Isco Combiflash R_f 200 and Redisep R_f Silica/Alumina columns.

Materials. All chemicals were purchased from commercial sources and used without further purification unless otherwise specified. The syntheses of compounds **Y4**,[1] **Y6**,[2] **Y8**[2] and **C4**[3] were based on the literature procedures, respectively.

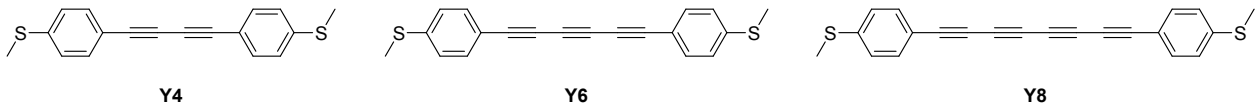
Instrumentation. ^{1}H NMR and ^{13}C NMR spectra in deuterated solvents were recorded on Brucker DRX400 (400 MHz) or a Bruker DMX500 (500 MHz) spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents ($CDCl_3$: δ 7.26; $C_2D_2Cl_4$: δ 6.00; CD_2Cl_2: δ 5.32). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0; $C_2D_2Cl_4$: δ 74.0; CD_2Cl_2: δ 53.8). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz, and integration.

High-resolution mass spectrometry (HRMS) was recorded on a Waters XEVO G2-XS QTOF spectrometer with dichloromethane as solvent.

2.2 Synthetic Procedures

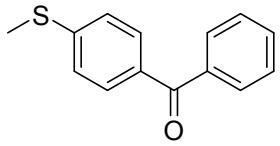


Scheme S1. Synthetic route of cumulene compounds.

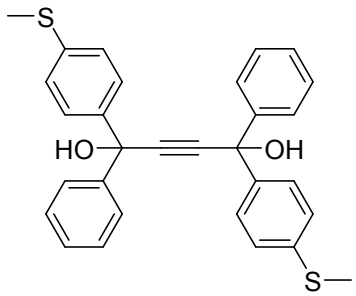


Scheme S2. Structures of polyyne compounds.

*2.2.1 Synthesis of **C4***

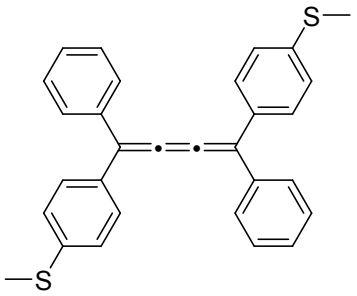


Synthesis of 4-methylthio-benzophenone (1). Under nitrogen atmosphere, to the mixture of $AlCl_3$ (0.784 g, 5.88 mmol) and 4-(methylthio)benzoyl chloride (0.548 g, 2.94 mmol), benzene (5.0 mL) was added dropwise over a 10 min period at 0 °C, with stirring. The cooling bath was removed and the mixture was stirred at room temperature for 5 h. The resulting solution was poured into icy 1 M HCl aqueous solution (40.0 mL), extracted with dichloromethane (20.0 mL×3), combined organic layers were washed with water (30.0 mL×2) and dried over anhydrous Na_2SO_4. Then the mixture was filtered through a pad of silica gel and eluted with dichloromethane (50.0 mL), and concentrated to afford the compound **1** (0.625 g, 93%) as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 2.54 (s, 3H, -SCH_3), 7.30 (d, *J* 8.0 Hz, 2H, benzene-H), 7.46-7.50 (m, 2H, benzene-H), 7.56-7.60 (m, 1H, benzene-H), 7.74-7.78 (m, 4H, benzene-H). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ (ppm): 14.77, 124.75, 128.19, 129.75, 130.58, 132.12, 133.55, 137.78, 145.23, 195.73. HRMS (ASAP+, *m/z*): $[M+H]^+$ calcd. for $C_{14}H_{13}OS$, 229.0687; found, 229.0678.



Synthesis of 1,4-bis(4-(methylthio)phenyl)-1,4-diphenylbut-2-yne-1,4-diol (2). Under nitrogen atmosphere, ethynylmagnesium bromide (5.44 mL, 2.72 mmol, 0.5 M in THF) was added

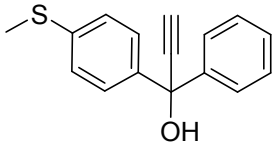
dropwise to the solution of ethylmagnesium bromide (1.0 mL, 3.0 mmol, 3.0 M in Et_2O) in anhydrous THF (4.4 mL) over a 10 min period at room temperature, with stirring. After completing the addition, the reaction mixture was refluxed for 2 h to give a product which was white bis(bromomagnesium)acetylene. After cooling to room temperature, the solution of compound **1** (1.242 g, 5.44 mmol) in anhydrous THF (3.6 mL) was added dropwise over a 10 min period. Then the mixture was refluxed again for 3.5 h. After cooling to room temperature, the solution was poured into icy 1 M HCl aqueous solution (50.0 mL), extracted with ethyl acetate (30.0 mL×3), combined organic layers were washed with saturated $NaHCO_3$ solution (30.0 mL) and saturated NaCl solution (30.0 mL), and dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (24 g Redisep R_f Silica) using a gradient from 0% to 40% ethyl acetate/hexanes to give the compound **2** (1.052 g, 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 2.46 (s, 6H, -SCH_3), 2.86 (s, 2H, -OH), 7.19 (d, *J* 8.0 Hz, 4H, benzene-H), 7.27-7.34 (m, 6H, benzene-H), 7.49 (d, *J* 8.0 Hz, 4H, benzene-H), 7.57 (d, *J* 8.0 Hz, 4H, benzene-H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 15.65, 74.29, 89.86, 125.90, 126.26, 126.49, 127.89, 128.37, 138.26, 141.52, 144.50. HRMS (ASAP+, m/z): $[M]^+$ calcd. for $C_{30}H_{26}O_2S_2$, 482.1374; found, 482.1372.



Synthesis of 1,4-bis(4-(methylthio)phenyl)-1,4-diphenylbuta-1,2,3-triene (C4). Under nitrogen atmosphere, to the solution of compound **2** (0.150 g, 0.31 mmol) in anhydrous pyridine (2.7 mL), phosphorus tribromide (0.09 mL, 0.93 mmol) was added dropwise over a 5 min period at room

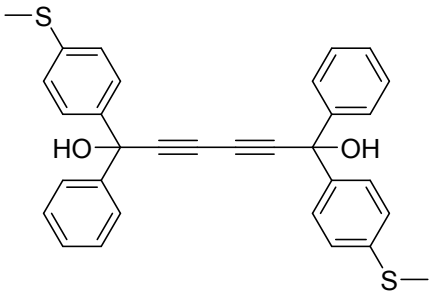
temperature and stirred for another 2 h. After cooling to 0 °C, water (15.0 mL) was added dropwise to quench the reaction. The resulting yellow mixture was extracted with dichloromethane (20.0 mL×3), combined organic layers were washed with saturated $NaHCO_3$ solution (20.0 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (24 g Redisep R_f Alumina) using hexanes to give the crude product as a red solid. Recrystallization from ethyl acetate and hexanes (1:2, v/v) afforded the compound **C4** (0.062 g, 44%) as a yellow solid that was isolated as the 2:1 mixture of *E* and *Z* isomers. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ (ppm): 2.52 (s, 2H, -SCH_3), 2.54 (s, 4H, -SCH_3), 7.24-7.28 (m, 4H, benzene-H), 7.32-7.43 (m, 6H, benzene-H), 7.47-7.50 (m, 4H, benzene-H), 7.53-7.57 (m, 4H, benzene-H). ^{13}C NMR (101 MHz, CD_2Cl_2, 298 K) δ (ppm): 15.63, 122.17, 126.27, 126.29, 128.40, 128.83, 128.86, 129.66, 129.69, 129.91, 129.95, 135.69, 135.76, 138.94, 139.01, 139.42, 150.75. HRMS (ASAP+, m/z): $[M]^+$ calcd. for $C_{30}H_{24}S_2$, 448.1319; found, 448.1320.

*2.2.2 Synthesis of **C6***



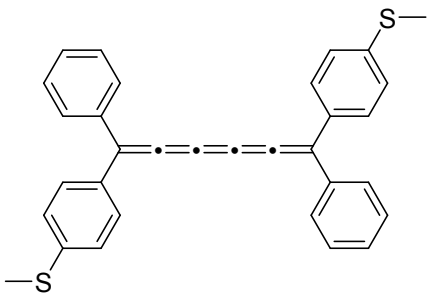
Synthesis of 1-(4-(methylthio)phenyl)-1-phenylprop-2-yn-1-ol (3). Under nitrogen atmosphere, ethynylmagnesium bromide (5.60 mL, 2.80 mmol, 0.5 M in THF) was added dropwise to a solution of compound **1** (0.559 g, 2.45 mmol) in anhydrous THF (5.0 mL) over a 15 min period at room temperature, with stirring. After completing the addition, the solution was stirred for 6 h at room temperature. Then the solution was poured into icy 1 M HCl aqueous solution (40.0 mL), extracted with ethyl acetate (20.0 mL×3), combined organic layers were washed with saturated $NaHCO_3$ solution (30.0 mL) and saturated NaCl solution (30.0 mL), and dried over anhydrous

Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (24 g Redisep R_f Silica) using a gradient from 0% to 35% ethyl acetate/hexanes to give the compound **3** (0.498 g, 80%) as a pink liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 2.46 (s, 3H, -SCH_3), 2.78 (s, 1H, -OH), 2.88 (s, 1H, -C≡CH), 7.21 (d, *J* 8.0 Hz, 2H, benzene-H), 7.27-7.30 (m, 1H, benzene-H), 7.32-7.36 (m, 2H, benzene-H), 7.52 (d, *J* 12.0 Hz, 2H, benzene-H), 7.59-7.61 (m, 2H, benzene-H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 15.65, 73.98, 75.56, 86.19, 125.90, 126.21, 126.49, 127.92, 128.32, 138.30, 141.27, 144.24. HRMS (ASAP+, m/z): $[M\text{-}OH]^+$ calcd. for $C_{16}H_{13}S$, 237.0732; found, 237.0742.



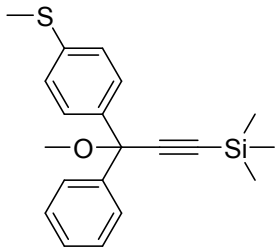
Synthesis of 1,6-bis(4-(methylthio)phenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol (4). Hay catalyst was prepared by stirring the mixture of TMEDA (1.18 mL, 7.84 mmol) and CuCl (0.388 g, 3.92 mmol) in dichloromethane (45.0 mL) for 30 min at room temperature. Then Hay catalyst was added to the solution of compound **3** (0.499 g, 1.96 mmol) in dichloromethane (45.0 mL) and stirred for 8 h at room temperature open to air. The organic phase was washed with saturated NH_4Cl solution (30.0 mL×2) and saturated NaCl solution (30.0 mL), and dried over anhydrous Na_2SO_4. Then the mixture was filtered through a pad of silica gel and eluted with dichloromethane (100.0 mL), and concentrated to afford the compound **4** (0.493 g, 99%) as a pink solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 2.46 (s, 6H, -SCH_3), 2.81 (s, 2H, -OH), 7.21 (d, *J* 8.0 Hz, 4H, benzene-H), 7.27-7.36 (m, 6H, benzene-H), 7.46 (d, *J* 8.0 Hz, 4H, benzene-H), 7.53-7.56 (m, 4H, benzene-H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 15.61, 71.16, 74.66, 82.62, 126.02,

126.24, 126.57, 128.16, 128.43, 138.68, 140.66, 143.69. HRMS (ASAP+, m/z): $[M]^+$ calcd. for $C_{32}H_{26}O_2S_2$, 506.1374; found, 506.1376.

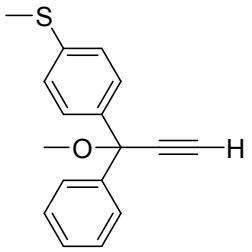


Synthesis of 1,6-bis(4-(methylthio)phenyl)-1,6-diphenylhexa-1,2,3,4,5-pentaene (C6). Under nitrogen atmosphere, hydrogen chloride solution (0.60 mL, 0.6 mmol, 1.0 M in Et_2O) was added to the mixture of compound **4** (0.051 g, 0.1 mmol) and anhydrous $SnCl_2$ (0.076 g, 0.4 mmol) in degassed dichloromethane (5.0 mL) over a 10 min period at -78 °C and stirred for another 50 min at -78 °C. Then the solution was filtered through a plug of basic alumina oxide and eluted with degassed dichloromethane (16.0 mL) under nitrogen atmosphere. Degassed hexanes (4.0 mL) was added to the eluent and reduced to around 7 mL in vacuum at 30 °C. The resulting suspension was kept at -20 °C for 1 h, filtered and washed with diethyl ether (2.0 mL) to yield the compound **C6** (0.024 g, 51%) as a red solid that was isolated as the 1:1 mixture of *E* and *Z* isomers. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 298 K) δ (ppm): 2.56 (s, 3H, -SCH_3), 2.57 (s, 3H, -SCH_3), 7.28-7.30 (m, 4H, benzene-H), 7.39-7.48 (m, 6H, benzene-H), 7.54-7.56 (m, 4H, benzene-H), 7.60-7.62 (m, 4H, benzene-H). ^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 320 K) δ (ppm): 15.68, 123.98, 126.42, 128.69, 128.72, 129.41, 129.63, 135.05, 138.03, 139.85, 148.06. HRMS (ESI+, m/z): $[M]^+$ calcd. for $C_{32}H_{24}S_2$, 472.1319; found, 472.1324.

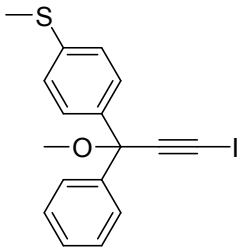
2.2.3 Synthesis of ***C8***



Synthesis of (3-methoxy-3-(4-(methylthio)phenyl)-3-phenylprop-1-yn-1-yl)trimethylsilane (5). Under nitrogen atmosphere, *n*-butyl lithium (1.38 mL, 3.44 mmol, 2.5 M in hexane) was added dropwise to the solution of trimethylsilylacetylene (0.67 mL, 4.86 mmol) in anhydrous THF (6.0 mL) at -78 °C over a 6 min period, with stirring. The mixture was stirred for 1 h at -78 °C and then the reaction mixture was quenched with the solution of compound **1** (0.740 g, 3.24 mmol) in anhydrous THF (12.0 mL). The cooling bath was removed and the solution was stirred for 3 h at room temperature, before iodomethane (1.21 mL, 19.44 mmol) was added. After completing the addition, the solution was stirred for 16 h at room temperature. Then the solution was poured into saturated NH_4Cl aqueous solution (50.0 mL), extracted with ethyl acetate (30.0 mL×3), combined organic layers were washed with saturated NaCl solution (30.0 mL), and dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (24 g Redisep R_f Silica) using a gradient from 0% to 10% ethyl acetate/hexanes to give the compound **5** (1.070 g, 97%) as a light-pink liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 0.25 (s, 9H, -$Si(CH_3)_3$), 2.46 (s, 3H, -SCH_3), 3.33 (s, 3H, -OCH_3), 7.19 (d, *J* 12.0 Hz, 2H, benzene-H), 7.22-7.24 (m, 1H, benzene-H), 7.30 (t, *J* 6.0 Hz, 2H, benzene-H), 7.45 (d, *J* 8.0 Hz, 2H, benzene-H), 7.53 (d, *J* 8.0 Hz, 2H, benzene-H). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ (ppm): -0.08, 15.66, 52.35, 80.82, 94.60, 104.18, 126.09, 126.57, 127.15, 127.57, 128.12, 137.74, 140.19, 143.05. HRMS (ASAP+, m/z): $[M+H]^+$ calcd. for $C_{20}H_{25}OSSi$, 341.1395; found, 341.1403.

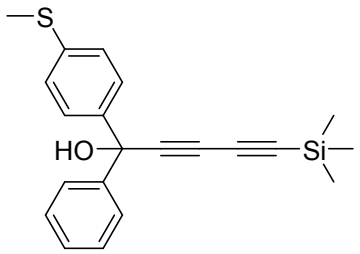


Synthesis of (4-(1-methoxy-1-phenylprop-2-yn-1-yl)phenyl)(methyl)sulfane (6). To the solution of compound **5** (1.05 g, 3.08 mmol) in methanol (75.0 mL) was added K_2CO_3 (0.638 g, 4.62 mmol). The reaction mixture was stirred for 3 h at room temperature, and subsequently quenched by the addition of saturated NH_4Cl aqueous solution (100.0 mL), extracted with dichloromethane (40.0 mL×3), combined organic layers were washed with saturated NaCl solution (40.0 mL), and dried over anhydrous Na_2SO_4, filtered, and concentrated to yield the compound **6** (0.818 g, 99%) as a pink liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 2.46 (s, 3H, -SCH_3), 2.88 (s, 1H, -C≡CH), 3.34 (s, 3H, -OCH_3), 7.20 (d, *J* 8.0 Hz, 2H, benzene-H), 7.26-7.28 (m, 1H, benzene-H), 7.32 (t, *J* 8.0 Hz, 2H, benzene-H), 7.46 (d, *J* 8.0 Hz, 2H, benzene-H), 7.52-7.55 (m, 2H, benzene-H). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ (ppm): 15.64, 52.43, 77.61, 80.38, 82.86, 126.11, 126.58, 127.17, 127.76, 128.18, 138.05, 139.81, 142.75. HRMS (ASAP+, m/z): $[M+H]^+$ calcd. for $C_{17}H_{17}OS$, 269.1000; found, 269.0999.



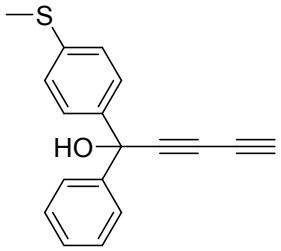
Synthesis of (4-(3-iodo-1-methoxy-1-phenylprop-2-yn-1-yl)phenyl)(methyl)sulfane (7). Under nitrogen atmosphere, *n*-butyl lithium (1.37 mL, 3.43 mmol, 2.5 M in hexane) was added dropwise to the solution of compound **6** (0.838 g, 3.12 mmol) in anhydrous THF (50.0 mL) over a 5 min period at -78 °C, with stirring. The mixture was stirred for 1.5 h at -78 °C. Then the reaction

mixture was quenched with the solution of iodine (0.949 g, 3.74 mmol) in anhydrous THF (5.0 mL). The cooling bath was removed and the solution was stirred for 12 h at room temperature. Then the solution was poured into saturated NH_4Cl aqueous solution (100.0 mL), extracted with ethyl acetate (40.0 mL×3), combined organic layers were washed with saturated $Na_2S_2O_3$ aqueous solution (50.0 mL) and saturated NaCl solution (50.0 mL), and dried over anhydrous Na_2SO_4, filtered, and concentrated to yield the compound **7** (1.218 g, 99%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 2.46 (s, 3H, -SCH_3), 3.33 (s, 3H, -OCH_3), 7.19 (d, *J* 8.0 Hz, 2H, benzene-H), 7.26-7.34 (m, 3H, benzene-H), 7.41 (d, *J* 8.0 Hz, 2H, benzene-H), 7.49 (d, *J* 8.0 Hz, 2H, benzene-H). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ (ppm): 6.11, 15.65, 52.66, 81.96, 94.05, 126.13, 126.64, 127.20, 127.81, 128.20, 138.11, 139.87, 142.77. HRMS (ASAP+, m/z): $[M]^+$ calcd. for $C_{17}H_{15}OSI$, 393.9888; found, 393.9883.



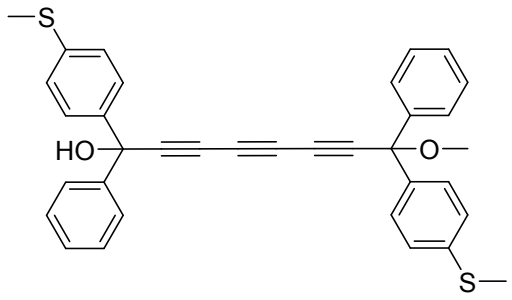
Synthesis of 1-(4-(methylthio)phenyl)-1-phenyl-5-(trimethylsilyl)penta-2,4-diyn-1-ol (8). Under nitrogen atmosphere, methyllithium lithium bromide complex solution (1.54 mL, 2.31 mmol, 1.5 M in Et_2O) was added dropwise to the solution of 1,4-bis(trimethylsilyl)-1,3-butadiyne (0.428 g, 2.2 mmol) in anhydrous THF (6.0 mL) over a 5 min period at 0 °C, with stirring. The resulting solution was warmed to room temperature and stirred for 45 min. Then the solution of compound **1** (0.502 g, 2.2 mmol) in anhydrous THF (3.0 mL) was added over a 5 min period at 0 °C. The solution was stirred for 12 h at room temperature. Then the solution was poured into saturated NH_4Cl aqueous solution (20.0 mL), extracted with diethyl ether (20.0 mL×3), combined

organic layers were washed with saturated NaCl solution (20.0 mL), and dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (24 g Redisep R_f Silica) using a gradient from 0% to 20% ethyl acetate/hexanes to give the compound **8** (0.402 g, 52%) as a light-pink liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 0.21 (s, 9H, -$Si(CH_3)_3$), 2.46 (s, 3H, -SCH_3), 2.72 (s, 1H, -OH), 7.21 (d, *J* 12.0 Hz, 2H, benzene-H), 7.28-7.35 (m, 3H, benzene-H), 7.46 (d, *J* 12.0 Hz, 2H, benzene-H), 7.52-7.55 (m, 2H, benzene-H). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ (ppm): -0.51, 15.63, 72.18, 74.57, 79.03, 87.03, 89.47, 126.01, 126.21, 126.56, 128.09, 128.39, 138.57, 140.78, 143.78. HRMS (ASAP+, m/z): $[M]^+$ calcd. for $C_{21}H_{22}OSSi$, 350.1161; found, 350.1153.

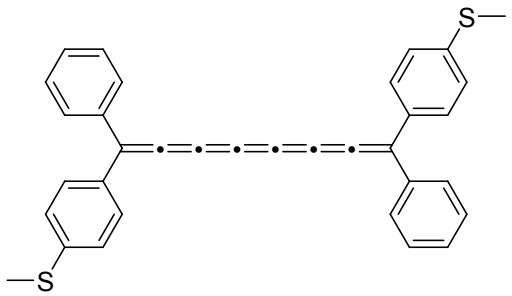


Synthesis of 1-(4-(methylthio)phenyl)-1-phenylpenta-2,4-diyn-1-ol (9). To the solution of compound **8** (0.40 g, 1.14 mmol) in methanol (25.0 mL) was added K_2CO_3 (0.236 g, 1.71 mmol). The reaction mixture was stirred for 3 h at room temperature, and subsequently quenched by the addition of saturated NH_4Cl aqueous solution (50.0 mL), extracted with dichloromethane (20.0 mL×3), combined organic layers were washed with saturated NaCl solution (20.0 mL), and dried over anhydrous Na_2SO_4, filtered, and concentrated to yield the compound **9** (0.310 g, 98%) as a purple liquid. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm): 2.32 (s, 1H, -C≡CH), 2.47 (s, 3H, -SCH_3), 2.80 (s, 1H, -OH), 7.21 (d, *J* 10.0 Hz, 2H, benzene-H), 7.30 (t, *J* 7.5 Hz, 1H, benzene-H), 7.35 (t, *J* 7.5 Hz, 2H, benzene-H), 7.46 (d, *J* 10.0 Hz, 2H, benzene-H), 7.53-7.55 (m, 2H, benzene-H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 15.61, 67.32, 70.06, 71.41, 74.48, 77.86, 125.96,

126.25, 126.52, 128.17, 128.44, 138.71, 140.59, 143.62. HRMS (ASAP+, m/z): $[M]^+$ calcd. for $C_{18}H_{14}OS$, 278.0765; found, 278.0767.



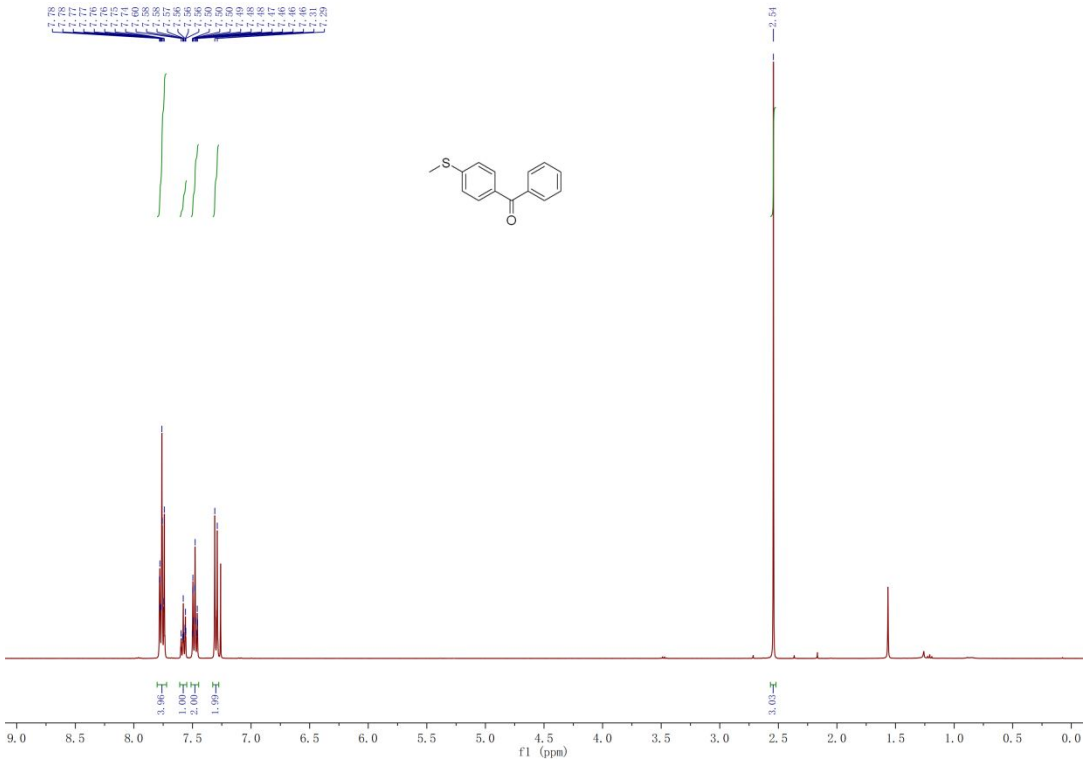
Synthesis of 8-methoxy-1,8-bis(4-(methylthio)phenyl)-1,8-diphenylocta-2,4,6-triyn-1-ol (10). To the solution of compound **9** (0.298 g, 1.07 mmol) and compound **7** (0.568 g, 1.44 mmol) in degassed ethanol (80.0 mL) were added CuCl (0.178 g, 1.80 mmol) and NH_2OH•HCl (0.149 g, 2.14 mmol) at room temperature, and the mixture was purged with nitrogen for 15 min. Then *n*-$PrNH_2$ (0.38 mL, 4.60 mmol) was added dropwise using a syringe. The mixture was purged with nitrogen for further 10 min and stirred for 19 h at room temperature. The reaction was quenched by addition of H_2O (150.0 mL), extracted with dichloromethane (30.0 mL×3), combined organic layers were washed with saturated NH_4Cl solution (30.0 mL×2) and saturated NaCl solution (30.0 mL), and dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (24 g Redisep R_f Silica) using a gradient from 0% to 20% ethyl acetate/hexanes to give the compound **10** (0.292 g, 50%) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm): 2.46 (s, 3H, -SCH_3), 2.47 (s, 3H, -SCH_3), 2.80 (s, 1H, -OH), 3.32 (s, 3H, -OCH_3), 7.20 (t, *J* 10.0 Hz, 4H, benzene-H), 7.28-7.38 (m, 8H, benzene-H), 7.43-7.47 (m, 4H, benzene-H), 7.51-7.54 (m, 2H, benzene-H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 15.58, 15.60, 52.85, 63.79, 64.42, 71.92, 73.83, 74.72, 78.64, 80.55, 81.15, 125.97, 126.14, 126.26, 126.52, 126.66, 127.19, 128.12, 128.28, 128.34, 128.50, 128.52, 138.63, 138.90, 138.94, 140.38, 141.94, 143.45. HRMS (ASAP+, m/z): $[M-OH]^+$ calcd. for $C_{35}H_{27}OS_2$, 527.1498; found, 527.1503.



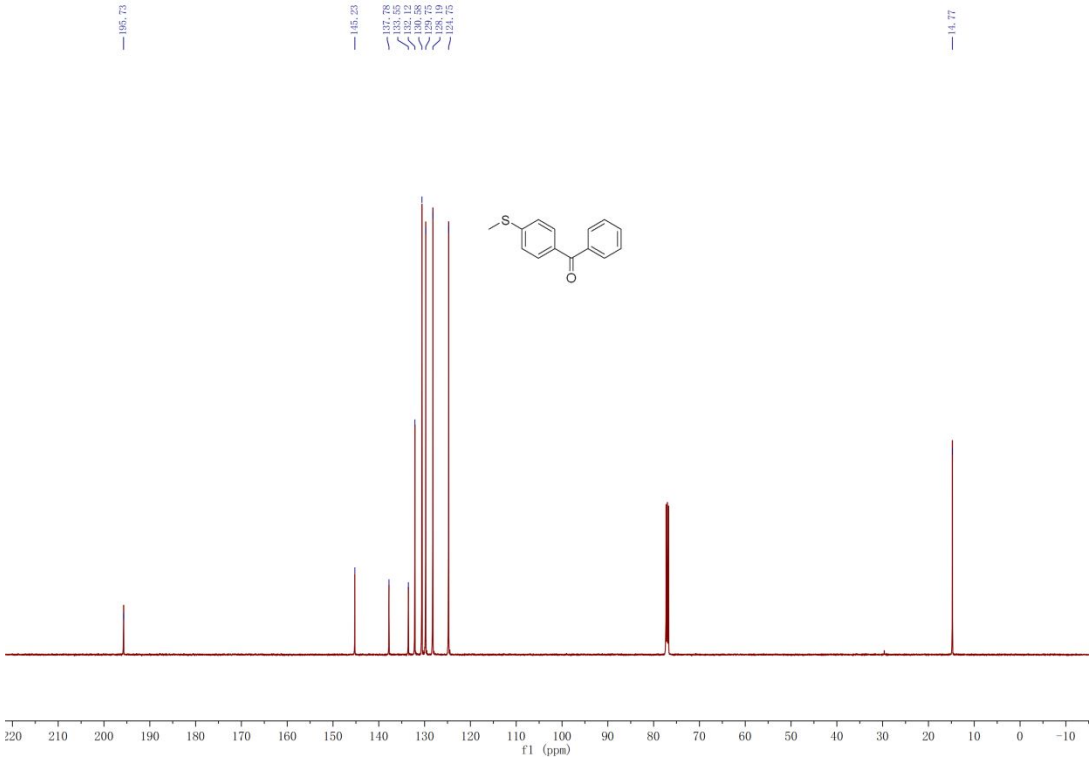
Synthesis of 1,8-bis(4-(methylthio)phenyl)-1,8-diphenylocta-1,2,3,4,5,6,7-heptaene (C8). Under nitrogen atmosphere, hydrogen chloride solution (0.12 mL, 0.12 mmol, 1.0 M in Et_2O) was added dropwise to the mixture of compound **10** (0.022 g, 0.04 mmol) and anhydrous $SnCl_2$ (0.023 g, 0.12 mmol) in degassed dichloromethane (3.2 mL) and diethyl ether (0.8 mL) over a 5 min period at -78 °C and stirred for another 45 min at -78 °C. Then the solution was filtered through a plug of basic alumina oxide and eluted with degassed dichloromethane (20.0 mL) to afford the purified compound **C8** as a blue solution under nitrogen atmosphere. The yield could not be determined due to instability of this compound in solid state. The resulting solution was added to various degassed solvents, respectively, and concentrated in vacuum to give the corresponding samples that were tested immediately. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 298 K) δ (ppm): 2.54 (s, 6H, -SCH_3), 7.26 (d, *J* 5.0 Hz, 4H, benzene-H), 7.38-7.45 (m, 6H, benzene-H), 7.52 (d, *J* 10.0 Hz, 4H, benzene-H), 7.58 (dd, *J* 10.0 Hz, 4H, benzene-H). ^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 298 K) δ (ppm): 15.39, 124.18, 124.92, 125.92, 128.87, 129.26, 129.62, 129.84, 134.27, 137.44, 140.57, 144.27, 145.89. HRMS (ESI+, m/z): $[M]^+$ calcd. for $C_{34}H_{24}S_2$, 496.1319; found, 496.1337.

3. NMR Spectra

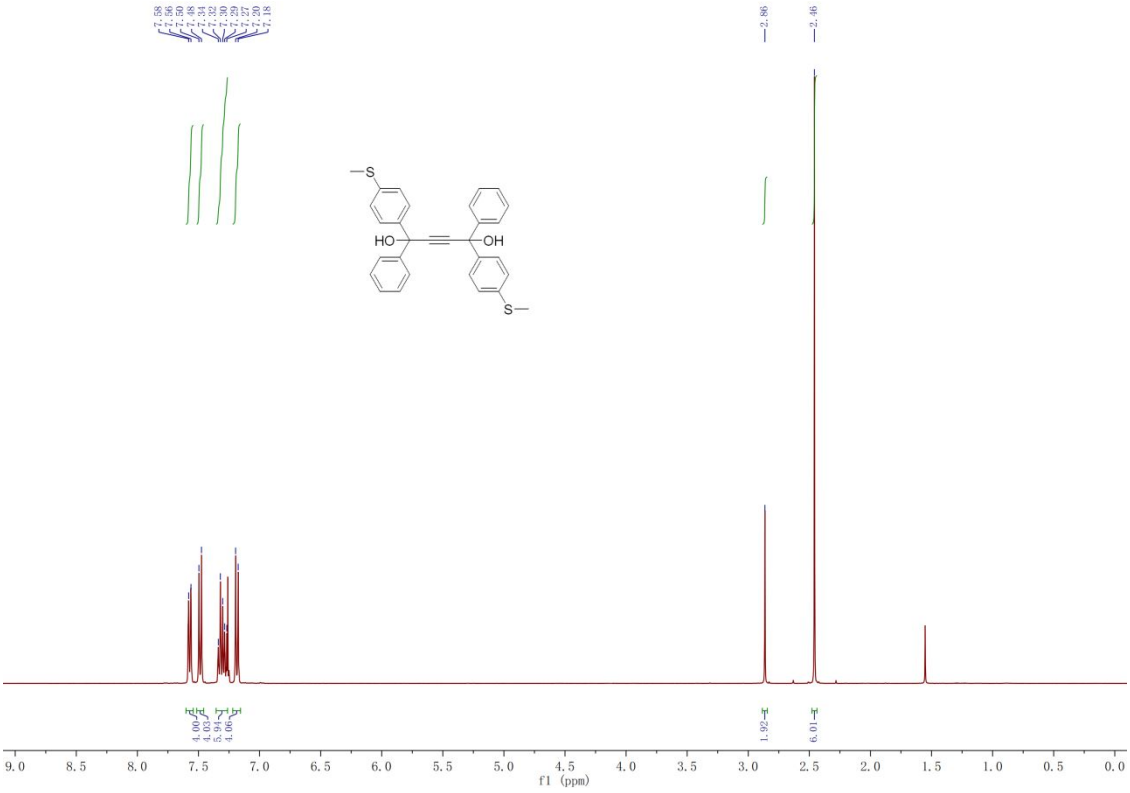
[1]H NMR spectrum of 1



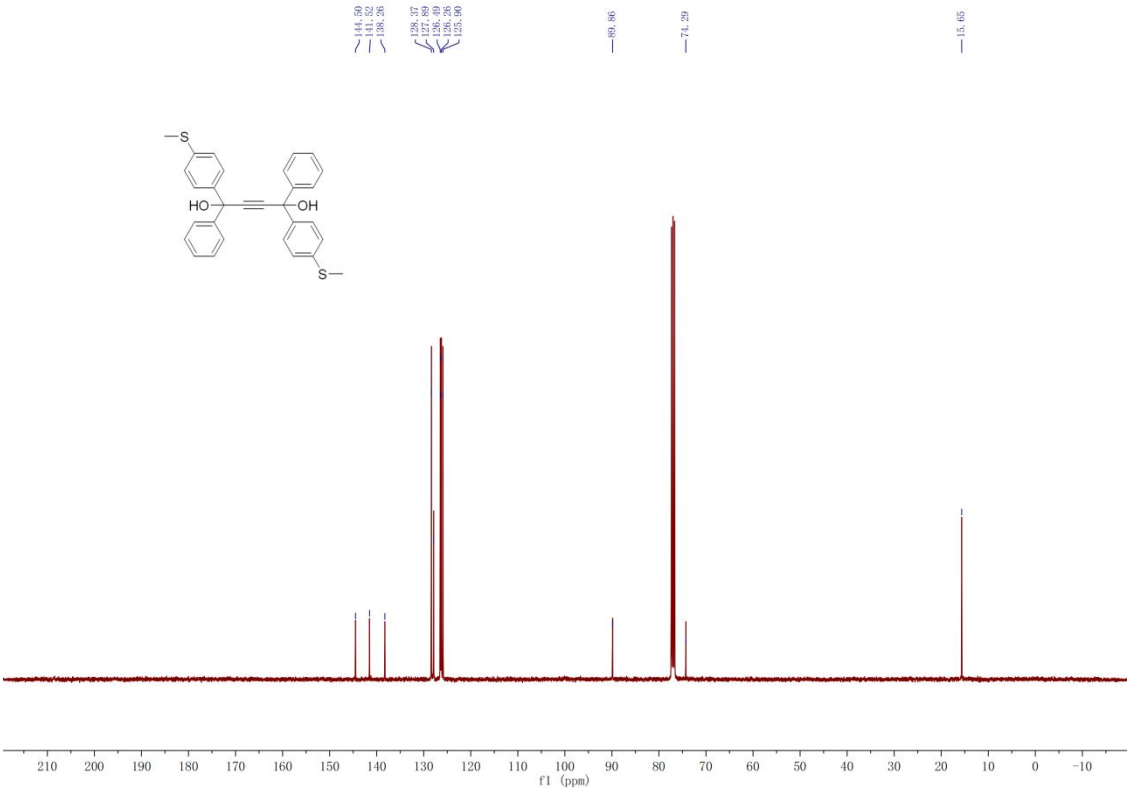
[13]C NMR spectrum of 1



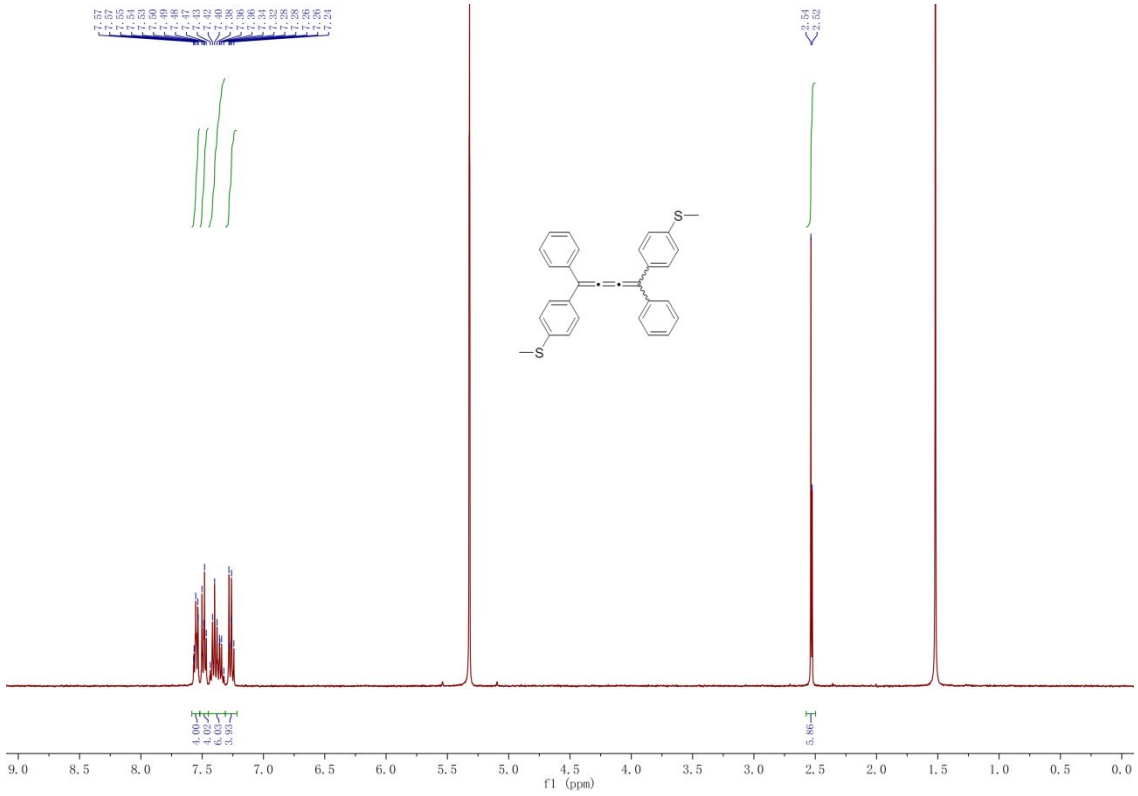
[1]H NMR spectrum of 2



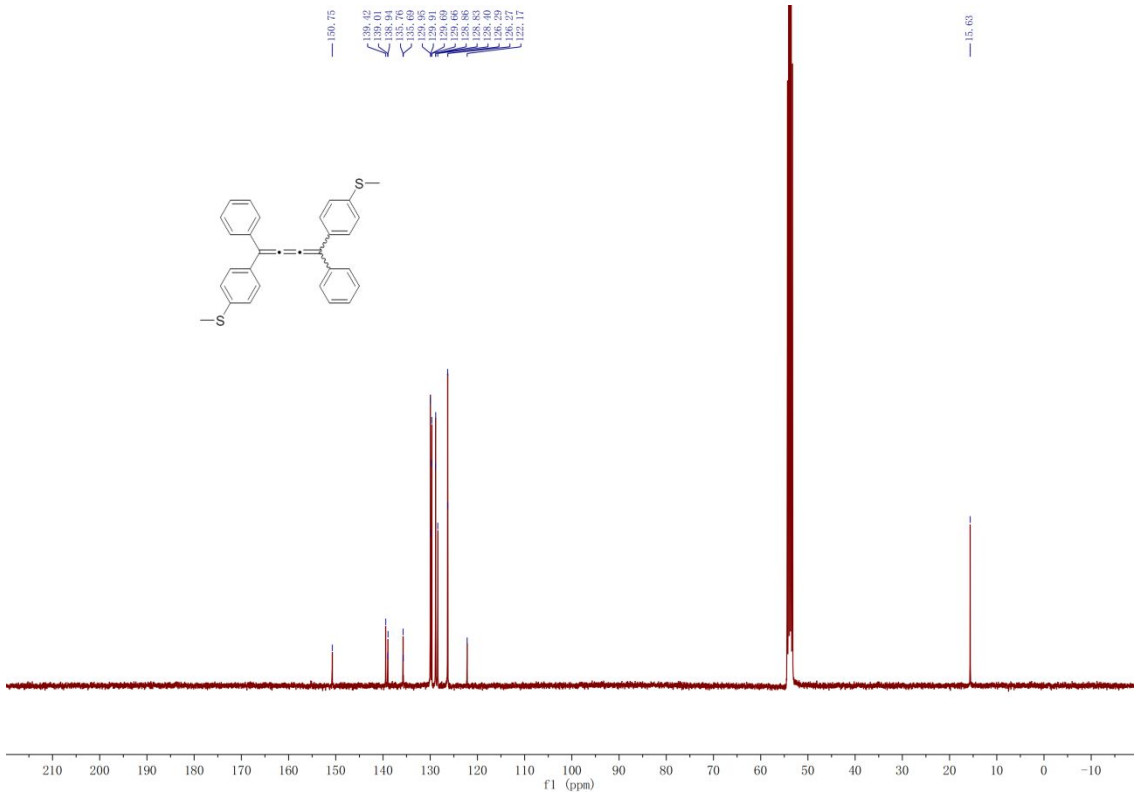
[13]C NMR spectrum of 2



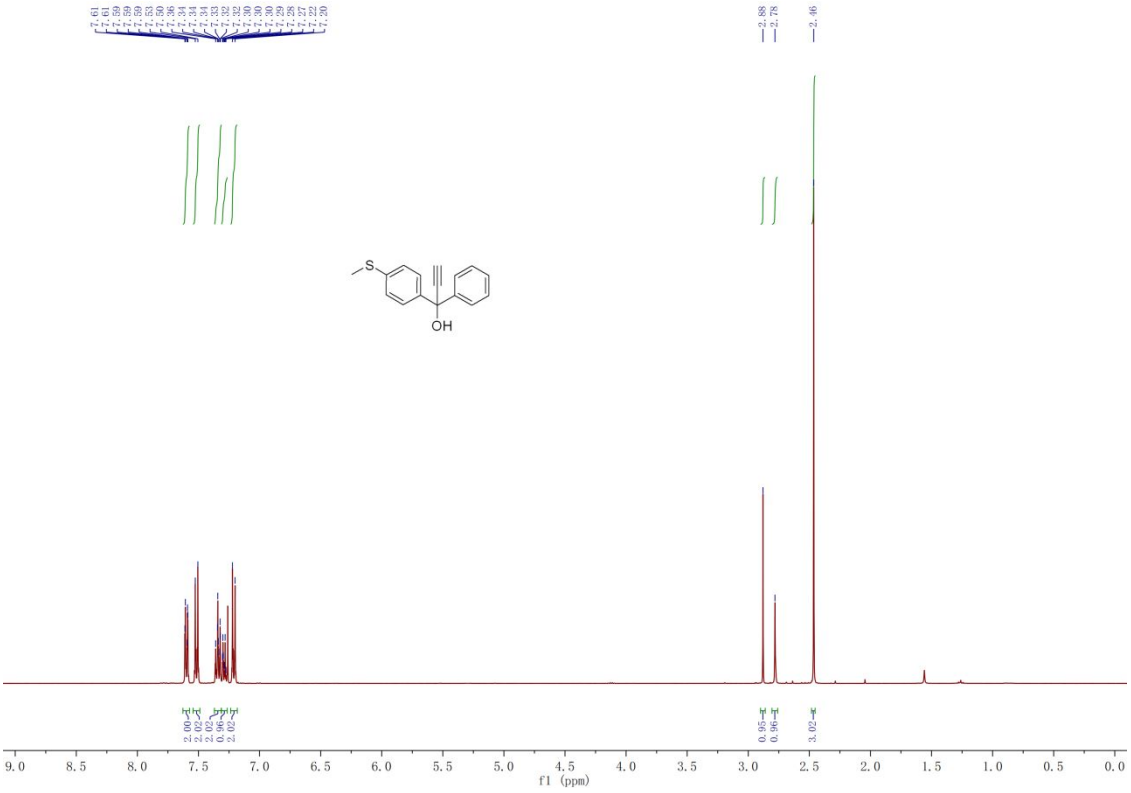
[1]H NMR spectrum of C4



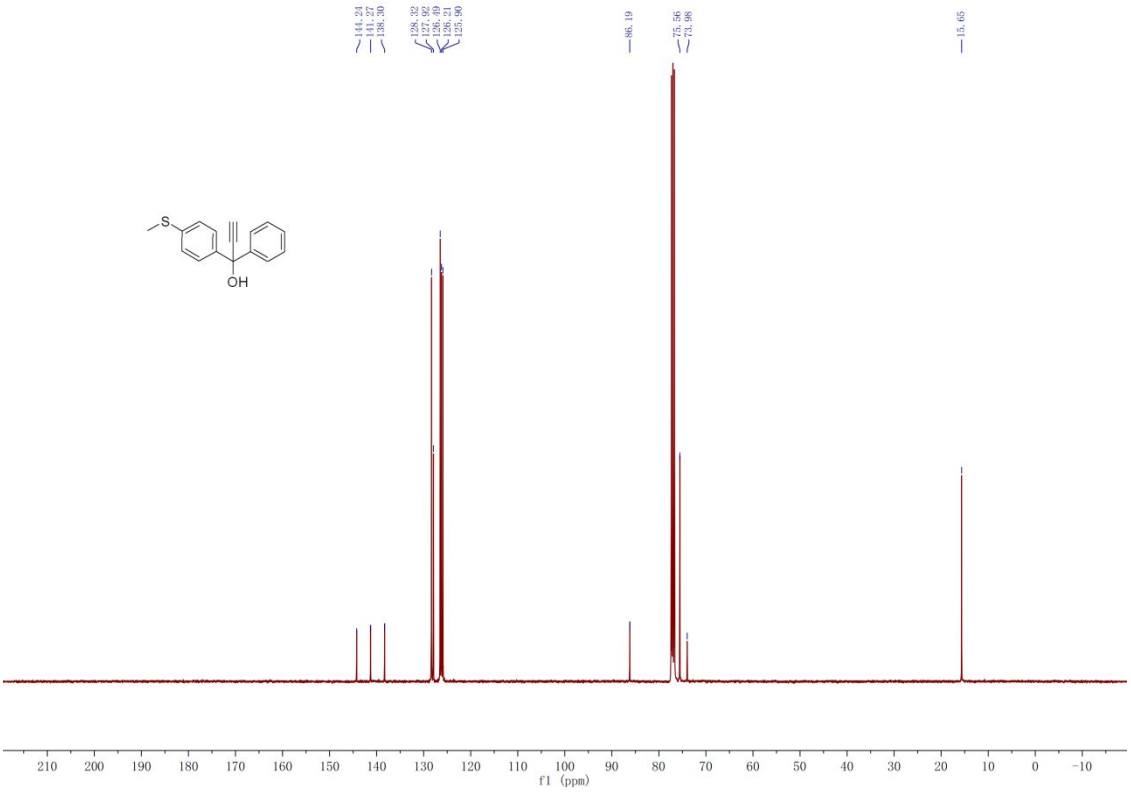
[13]C NMR spectrum of C4



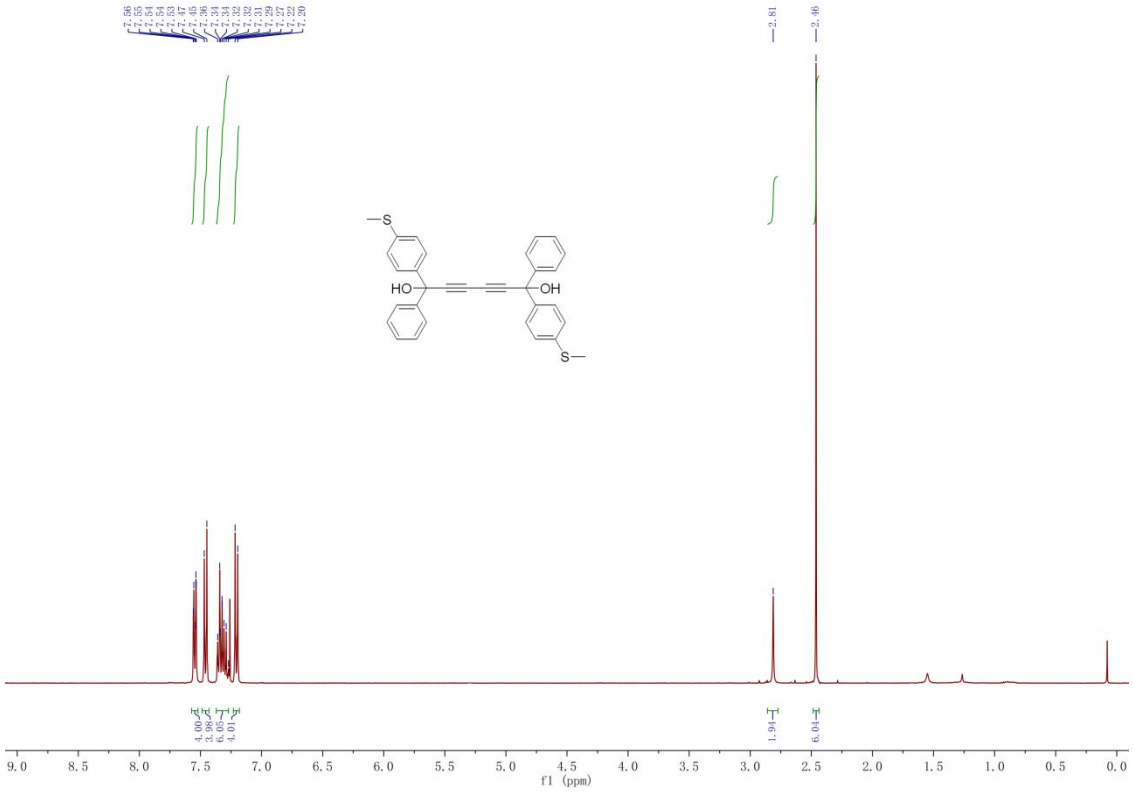
[1]H NMR spectrum of 3



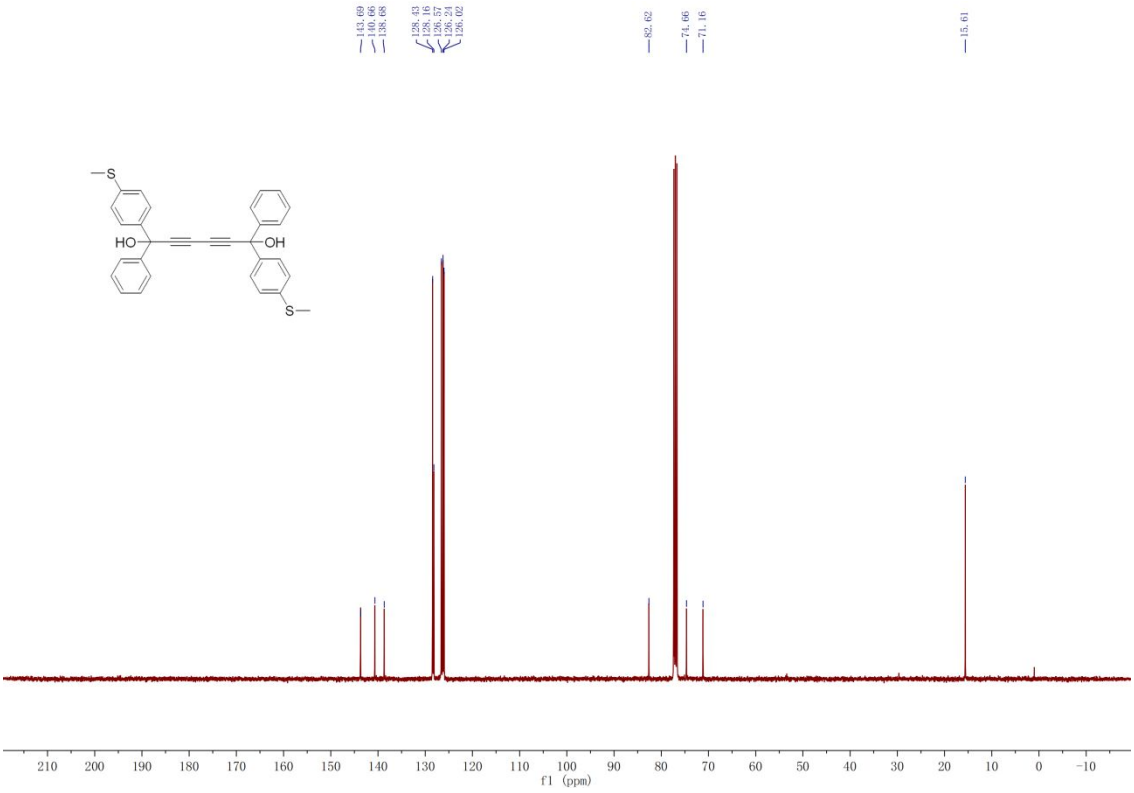
[13]C NMR spectrum of 3



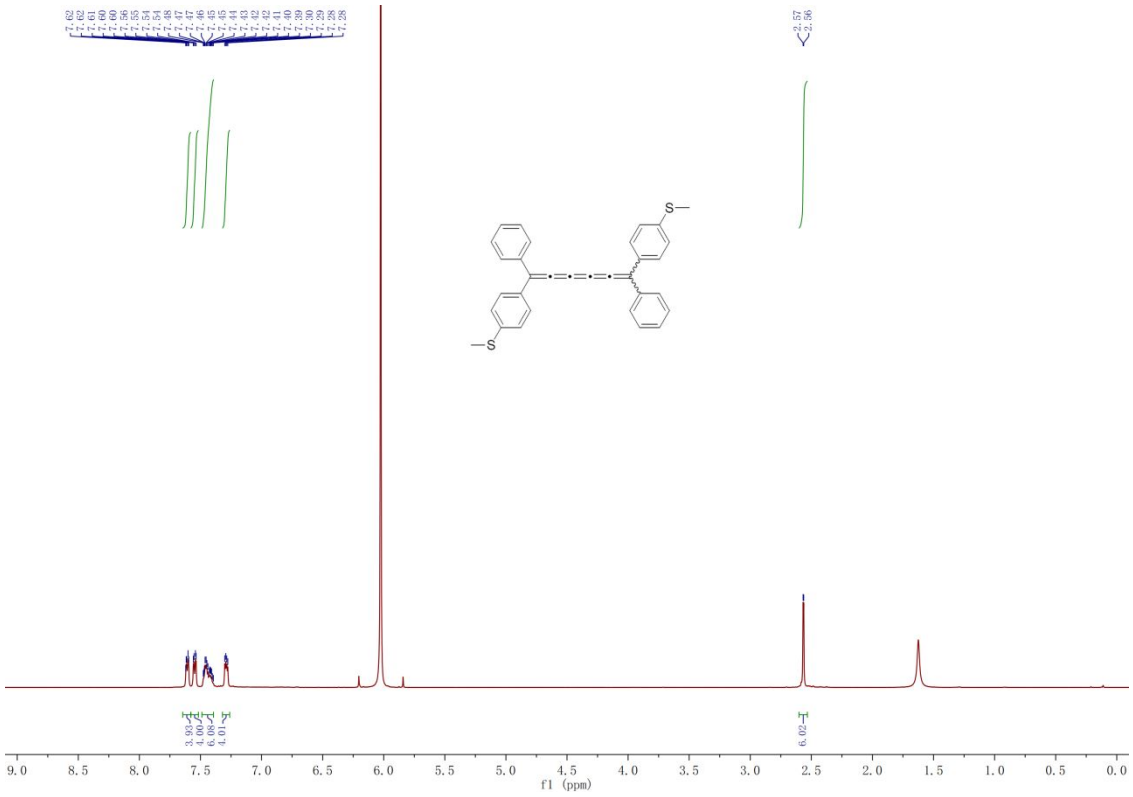
[1]H NMR spectrum of 4



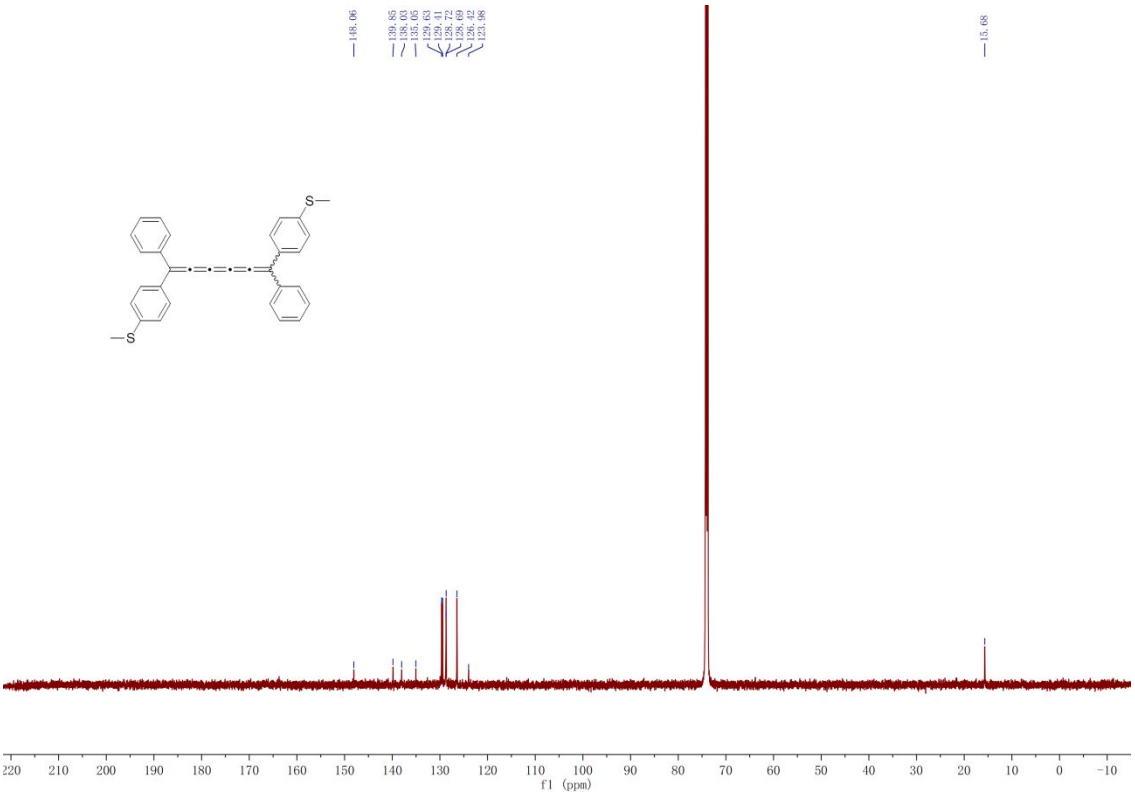
[13]C NMR spectrum of 4



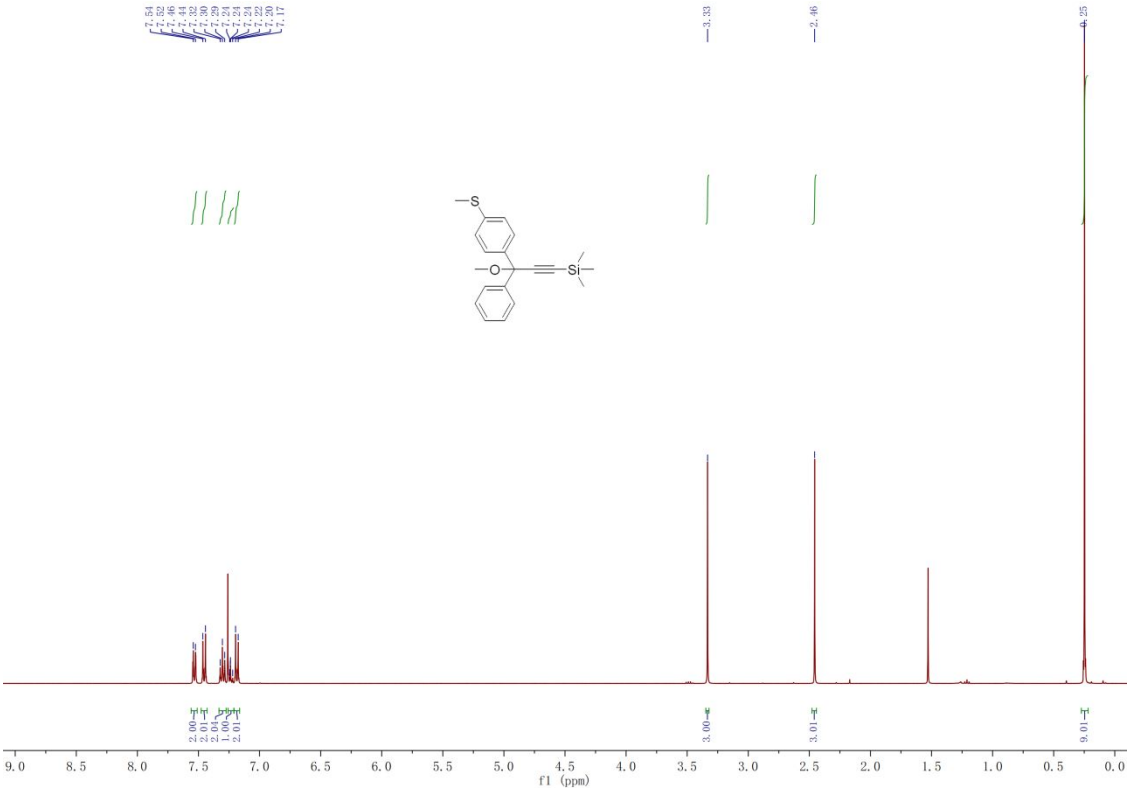
[1]H NMR spectrum of C6



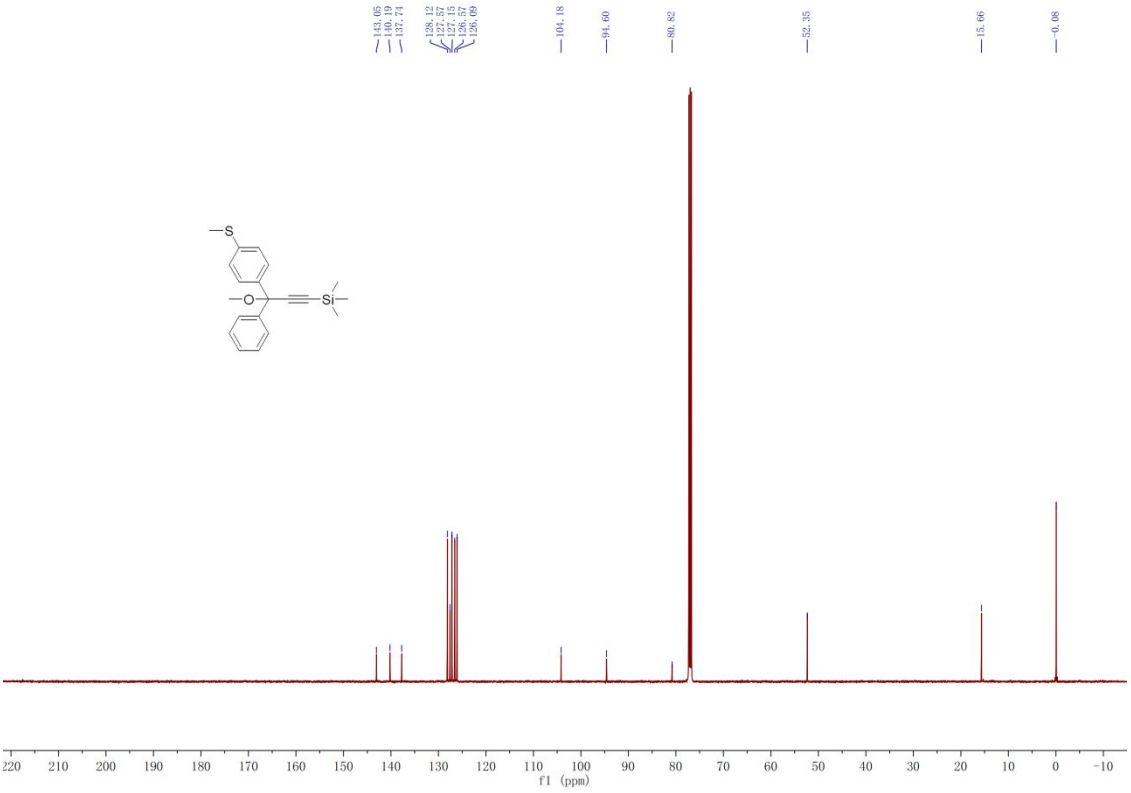
[13]C NMR spectrum of C6



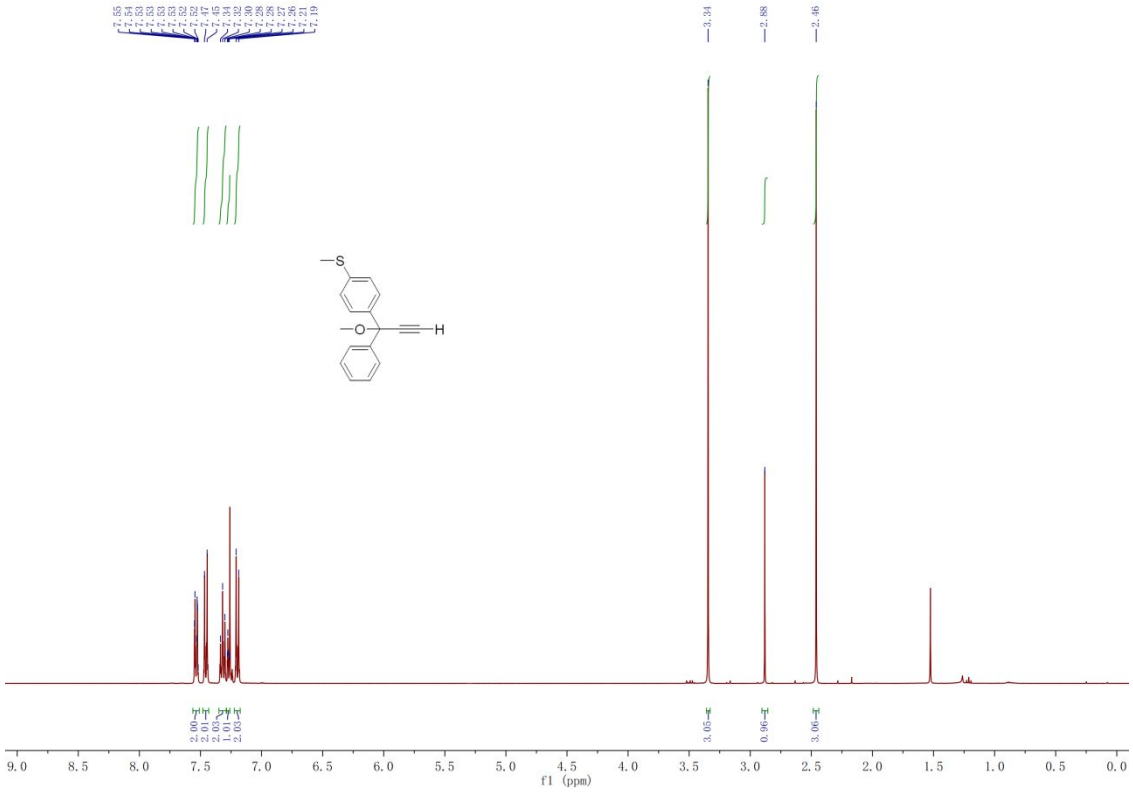
[1]H NMR spectrum of 5



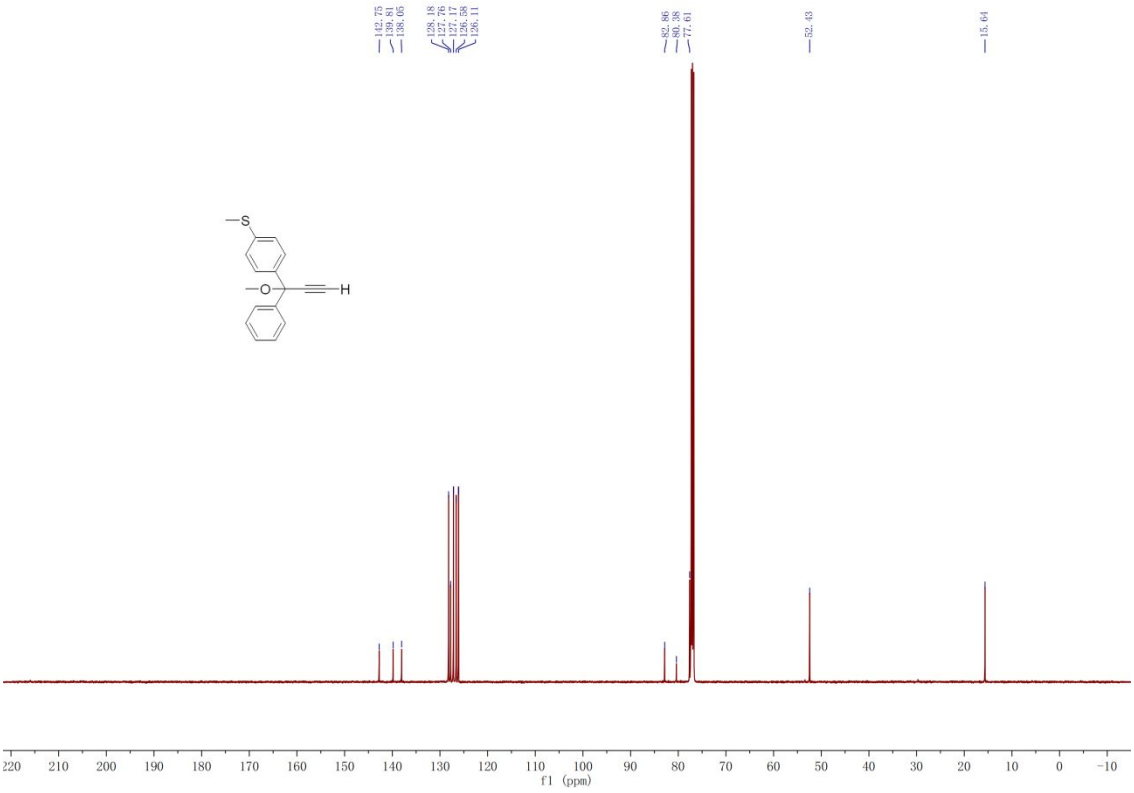
[13]C NMR spectrum of 5



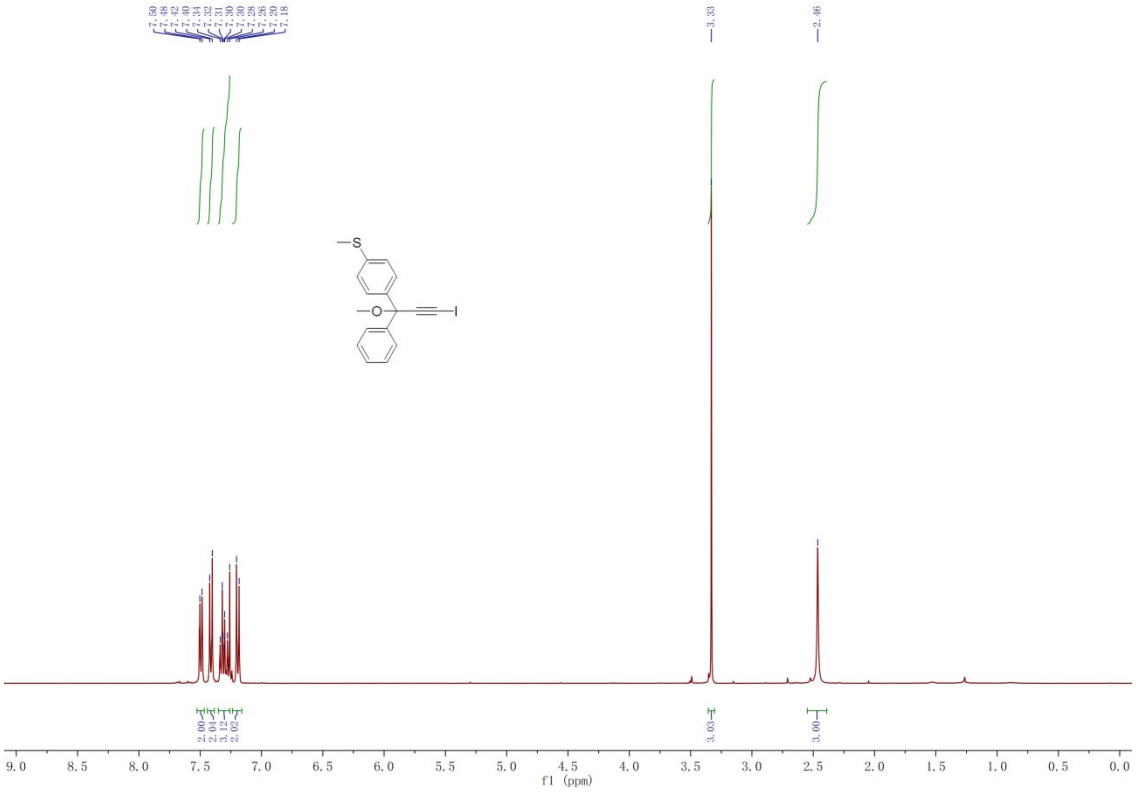
[1]H NMR spectrum of 6



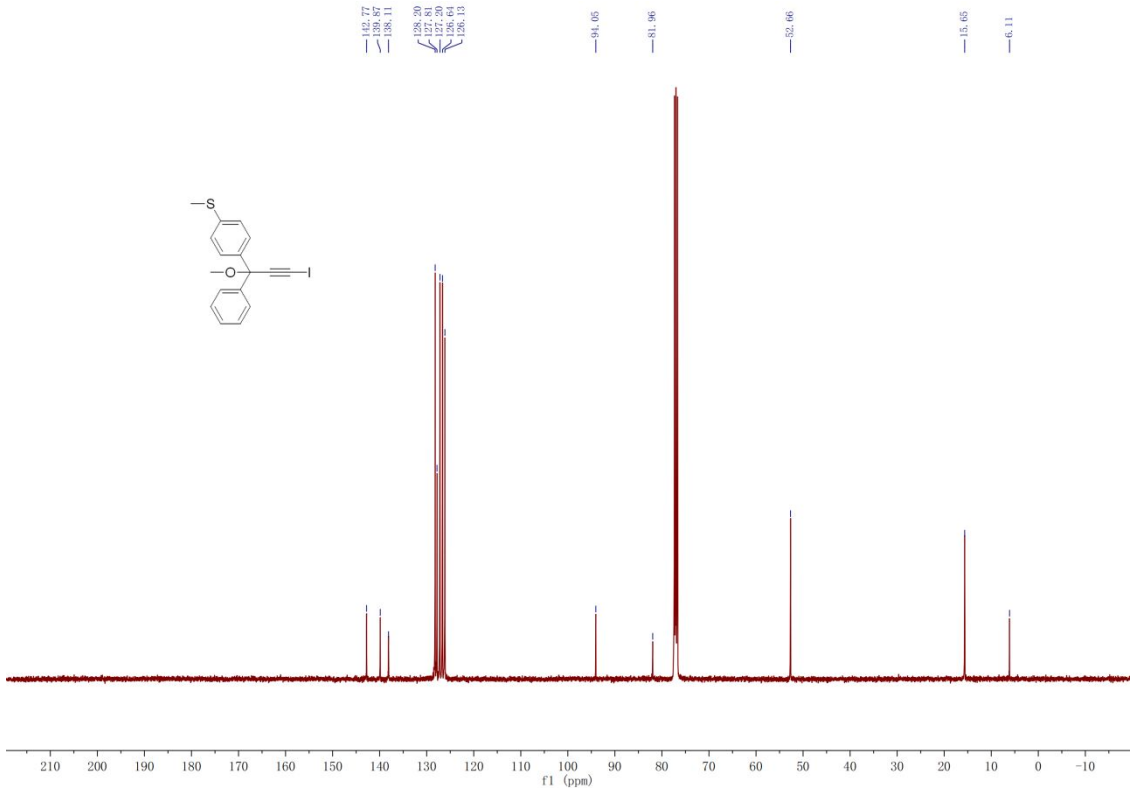
[13]C NMR spectrum of 6



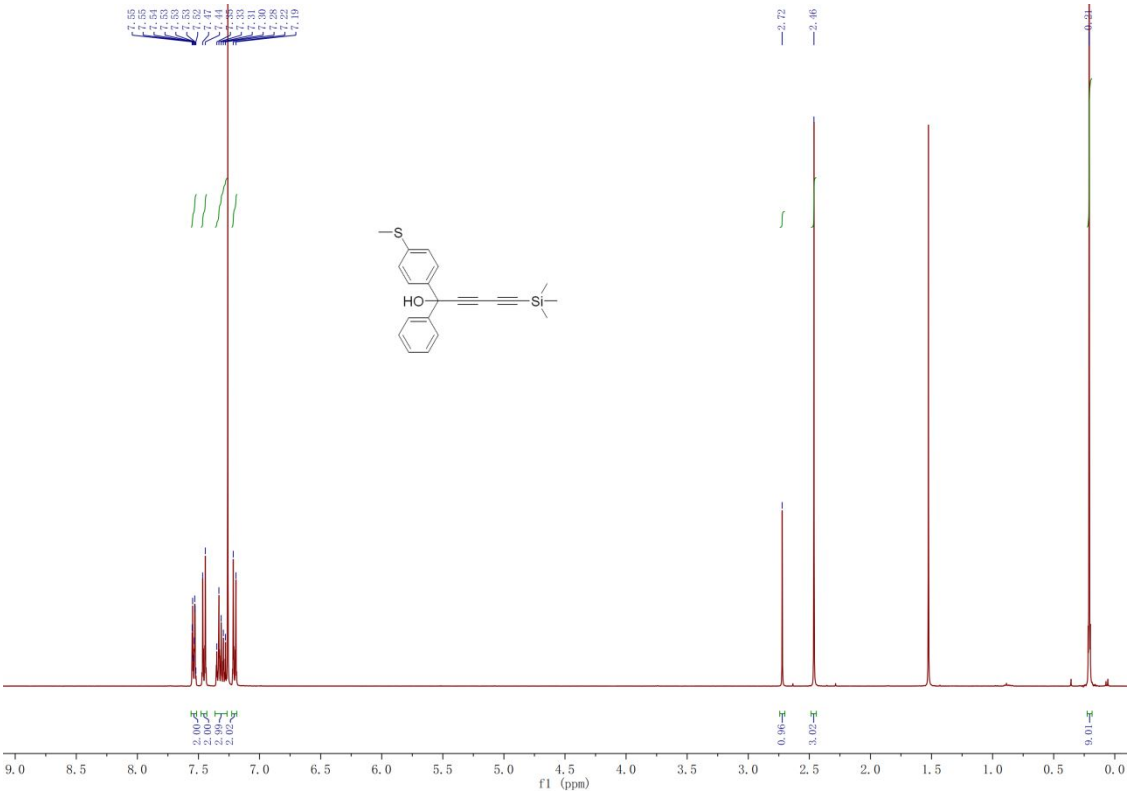
[1]H NMR spectrum of 7



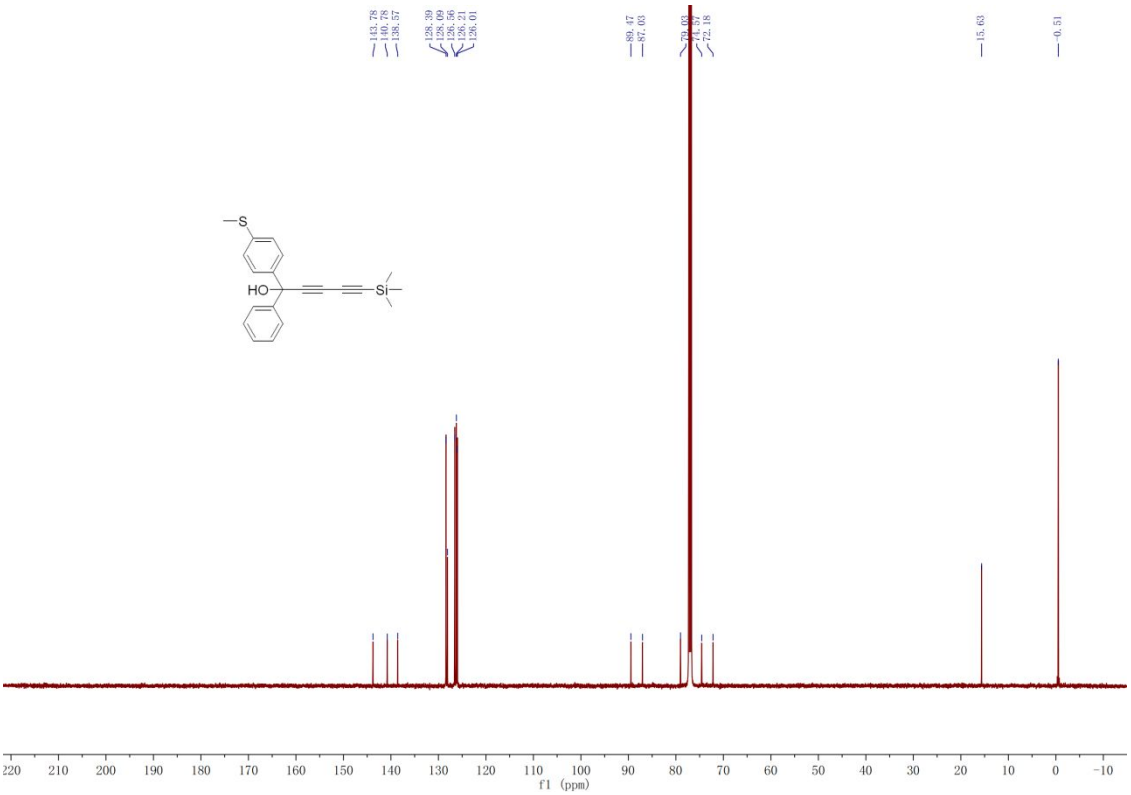
[13]C NMR spectrum of 7



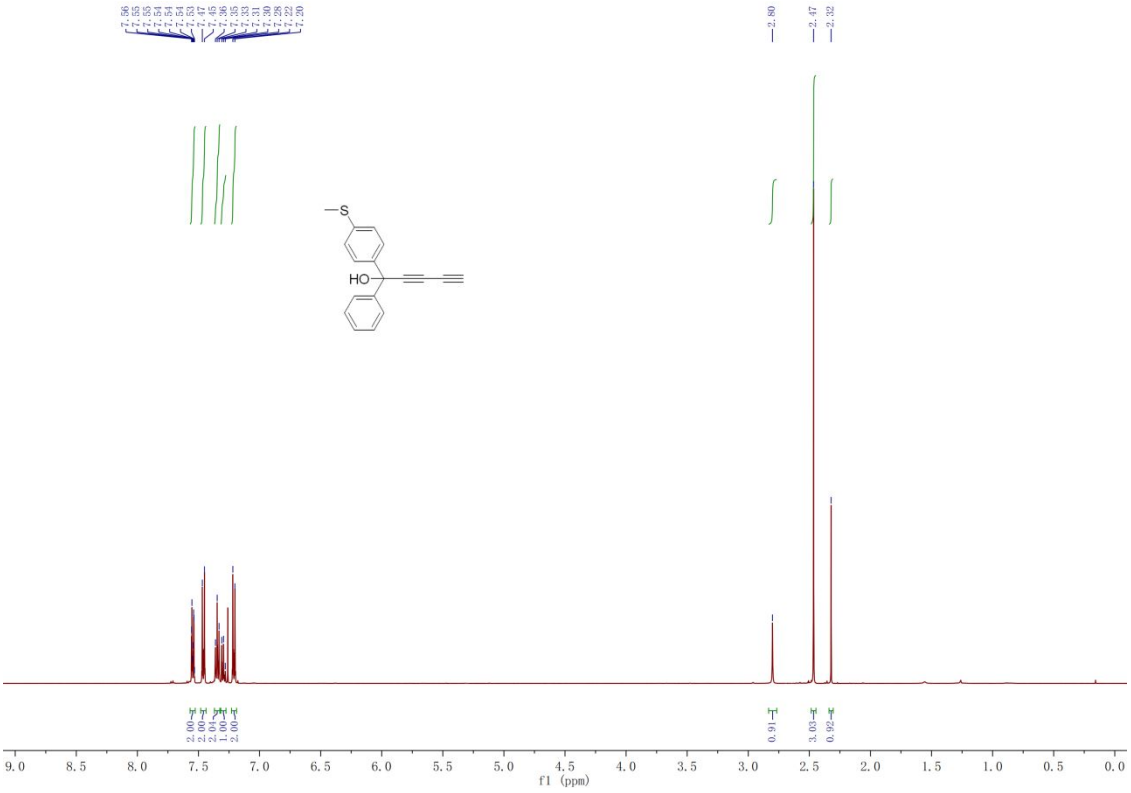
[1]H NMR spectrum of 8



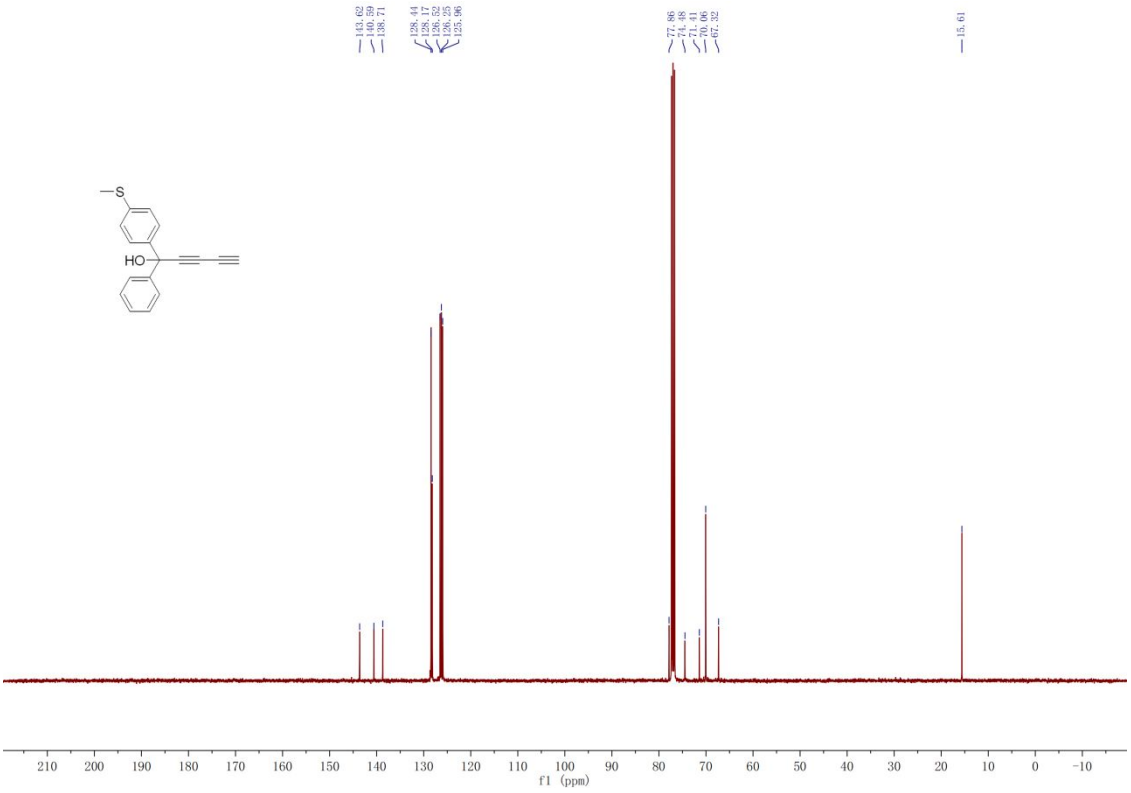
[13]C NMR spectrum of 8



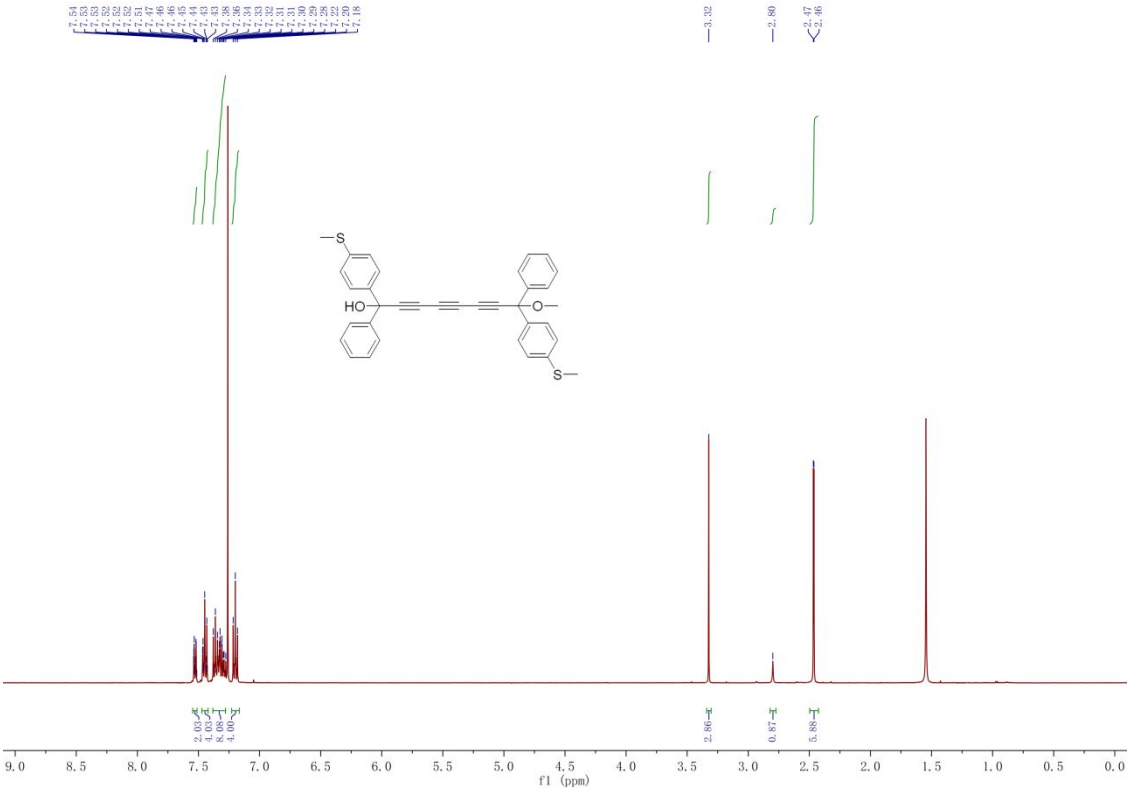
[1]H NMR spectrum of 9



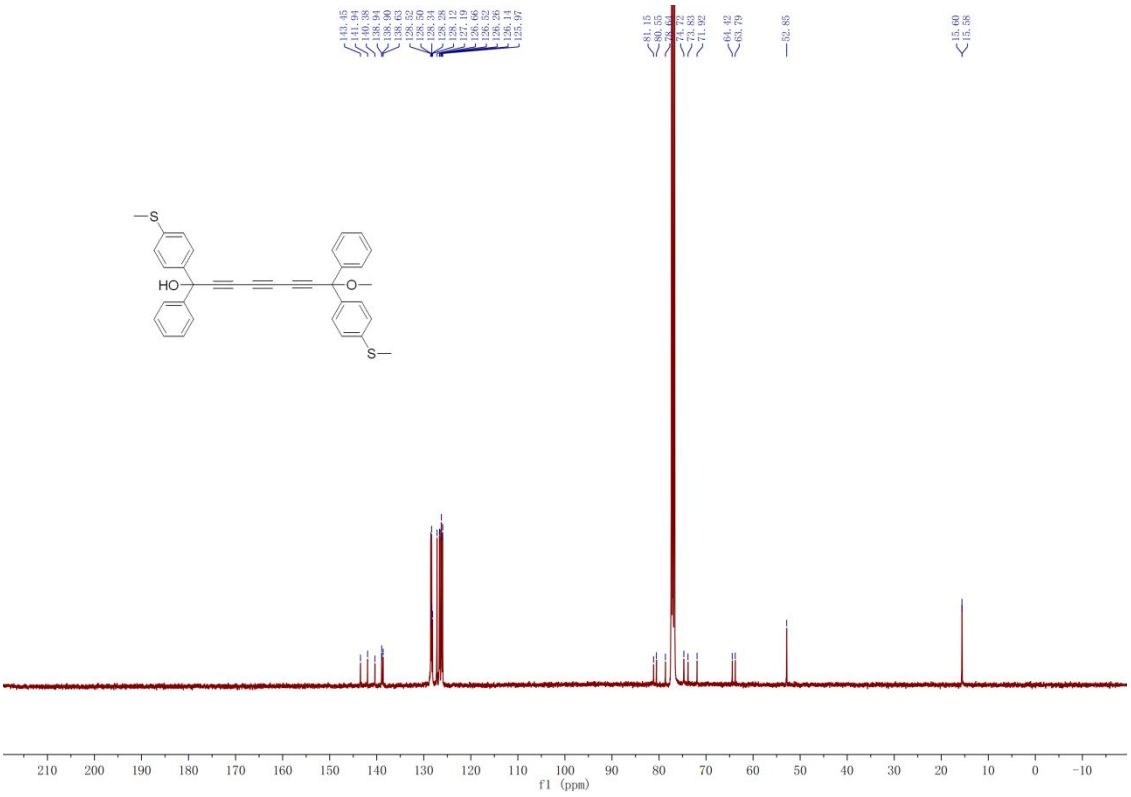
[13]C NMR spectrum of 9



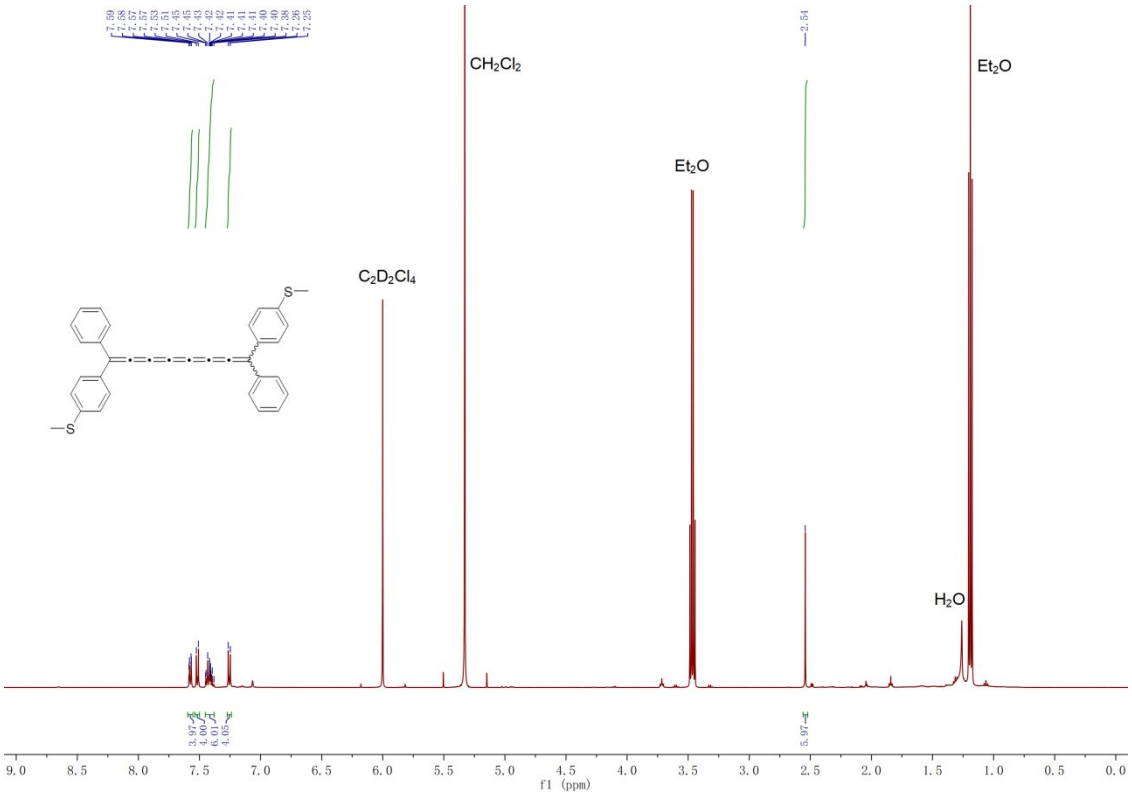
[1]H NMR spectrum of 10



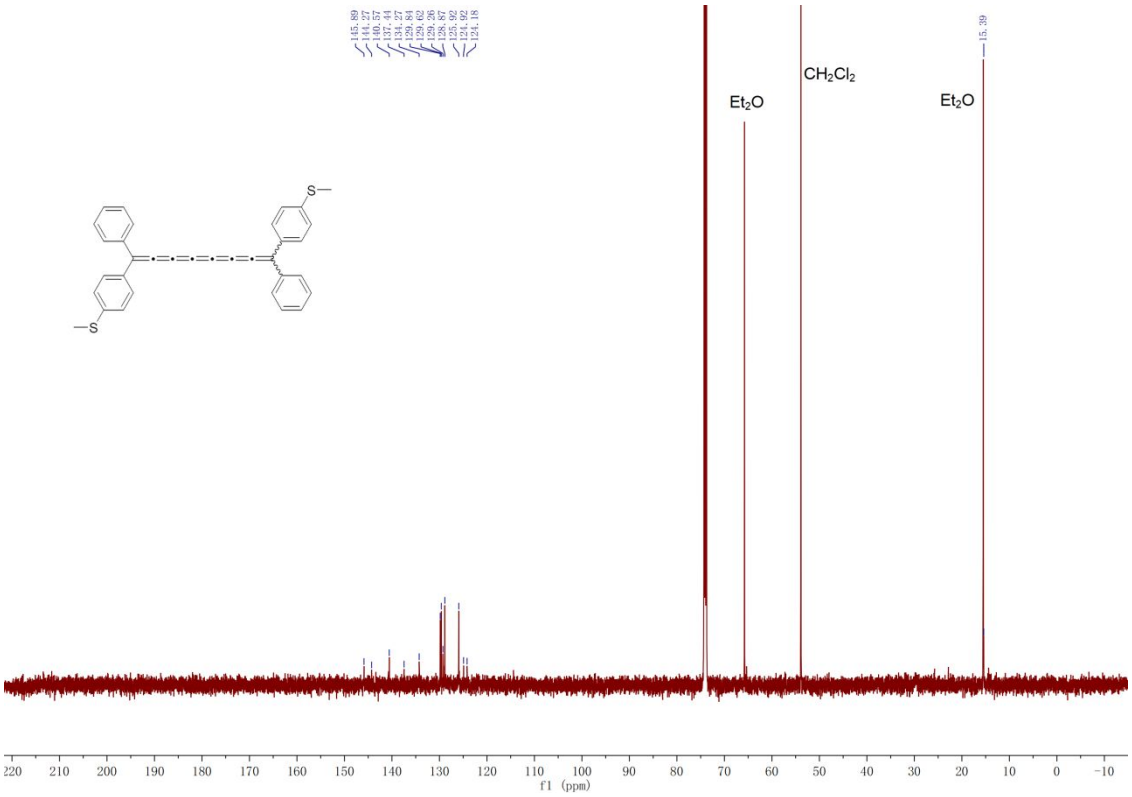
[13]C NMR spectrum of 10



[1]H NMR spectrum of C8



[13]C NMR spectrum of C8



References

1. Batsanov, A. S.; Collings, J. C.; Fairlamb, lan J. S.; Holland, J. P.; Howard, J. A. K.; Lin, Z.; Marder, T. B.; Parsons, A. C.; Ward R. M.; Zhu, J. *J. Org. Chem.* **2005**, *70*, 703−706.
2. Zhang, L.-Y.; Duan, P.; Wang, J.-Y.; Zhang, Q.-C.; Chen, Z.-N. *J. Phys. Chem. C* **2019**, *123*, 5282−5288.
3. Zang, Y.; Zou, Q.; Fu, T.; Ng, F.; Fowler, B.; Yang, J.; Li, H.; Steigerwald, M. L; Nuckolls, C.; Venkataraman, L. *Nat. Comm.* **2019**, *10*, 4482.