Supplementary Information

Migratory Insertion of Copper-Allenylidene from Propargyl Ester

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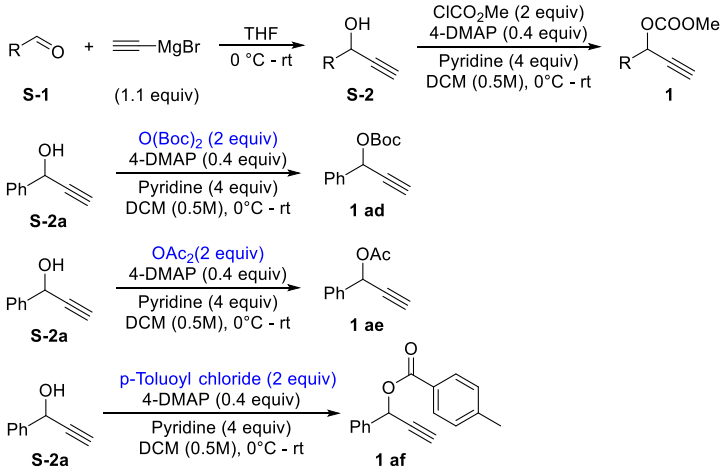
1. Experimental procedures and spectroscopic data

1.1. General information

Unless stated otherwise, reactions were conducted in Schlenk tube under an inert atmosphere of dry N_2. ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ^1H; 101 MHz for ^{13}C; 376 MHz for ^{19}F) or Bruker AVANCE 500 (500 MHz for ^1H; 126 MHz for ^{13}C; 471 MHz for ^{19}F). ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (HRMS) were obtained using Agilent UHD Accurate Mass Q-TOF LC/MS (ESI) mass spectrometer, Thermo Fisher Scientific LTQ FTICR-MS and Thermo Scientific Q Exactive HF Orbitrap-FTMS. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

1.2. General procedure for 1



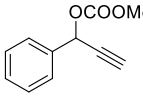
Starting aldehyde (10 mmol) was dissolved in dry-THF (5mL) under N_2 and cooled to 0 °C. Ethynylmagnesium bromide (0.5 M in THF, 1.1 equiv, 22mL) was added. After completion of the addition, the reaction mixture was warmed to room temperature. After 3 hours the reaction mixture was quenched with saturated ammonium chloride solution and extracted with AcOEt. The combined organic extracts were dried with anhydrous sodium sulfate, filtered, and concentrated in vacuo to provide the crude product **S-2**.

To a stirred solution of crude product **S-2** (about 10mmol) in CH_2Cl_2 (20 mL) were added pyridine (4.0 equiv, 40mmol, 3.2g, 3.2mL), 4-Dimethylaminopyridine (0.4 equiv, 4 mmol, 488.7mg) and methyl chloroformate (2.0 equiv, 20 mmol, 1.9g, 1.5mL) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with aqueous NH_4Cl and extracted with AcOEt. The combined extracts were washed with brine. The residue upon workup was chromatographed on silica gel with PE/EA as eluent to give propargylic carbonate **1**.

1ad, **1ae** and **1af** were prepared from **S-2a** in the same way as **1** using corresponding acylation reagents.

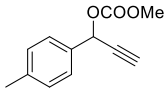
The characterization of compound **1a-b**[1], **1c**[2], **1e-f**[1], **1i**[1], **1l**[3], **1v**[4], **1ad**[5], **1ae**[6], **1af**[7] were previously reported.

Methyl (1-phenylprop-2-yn-1-yl) carbonate (**1a**)



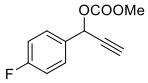
Colorless oil (1.6 g), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 85 %. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 2H), 7.47 – 7.39 (m, 3H), 6.32 (d, *J* = 2.3 Hz, 1H), 3.84 (s, 3H), 2.75 (d, *J* = 2.3 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 154.9, 135.9, 129.4, 128.9, 127.8, 79.6, 76.5, 69.4, 55.2.

methyl (1-(p-tolyl)prop-2-yn-1-yl) carbonate (**1b**)



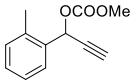
Colorless oil (1.7 g), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 83 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.25 (d, *J* = 2.3 Hz, 1H), 3.81 (s, 3H), 2.70 (d, *J* = 2.3 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 154.9, 139.4, 133.0, 129.4, 127.7, 79.8, 76.2, 69.3, 55.1, 21.2.

1-(4-fluorophenyl)prop-2-yn-1-yl methyl carbonate (**1c**)



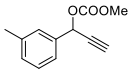
Colorless oil (1.6 g), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 77 %. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 (ddt, *J* = 8.2, 5.0, 2.4 Hz, 2H), 7.13 – 7.02 (m, 2H), 6.26 (d, *J* = 2.2 Hz, 1H), 3.81 (s, 3H), 2.73 (d, *J* = 2.3 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.4 (d, *J* = 248.7 Hz), 154.9, 131.92 (d, *J* = 3.3 Hz), 129.93 (d, *J* = 8.6 Hz), 115.8 (d, *J* = 21.9 Hz), 79.5, 76.8, 68.7, 55.3. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -111.86.

methyl (1-(o-tolyl)prop-2-yn-1-yl) carbonate (**1e**)



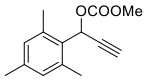
Colorless oil (1.8 g), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 88 %.**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.3 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 2.0 Hz, 1H), 3.79 (s, 3H), 2.69 (d, *J* = 2.1 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.0, 136.4, 134.1, 134.0, 129.5, 128.1, 126.5, 79.6, 76.4, 67.5, 55.3, 19.2.

methyl (1-(m-tolyl)prop-2-yn-1-yl) carbonate(**1f**)



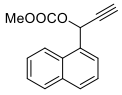
Colorless oil (1.6 g), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 80 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 12.2 Hz, 2H), 7.29 – 7.21 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.24 (s, 1H), 3.79 (s, 3H), 2.70 (d, *J* = 1.7 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.0, 138.7, 135.8, 130.3, 128.8, 128.43, 124.9, 79.8, 76.4, 69.5, 55.3, 21.5.

1-mesitylprop-2-yn-1-yl methyl carbonate(**1g**)



White solid (1.9 g), m.p. = 59-61 °C, purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 83 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.90 (s, 2H), 6.77 (s, 1H), 3.80 (s, 3H), 2.69 – 2.66 (m, 1H), 2.57 (s, 6H), 2.30 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.0, 138.8, 137.3, 130.0, 129.8, 79.4, 75.6, 65.4, 55.0, 21.0, 20.2. **IR** (KBr, cm^{-1}): 3267, 2958, 2124, 1774, 1607, 1447, 1327, 1268, 1009, 919, 849, 792, 716, 677, 578, 541. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{16}NaO_3$ 255.0992; found 255.0987.

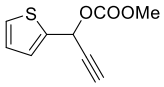
methyl (1-(naphthalen-1-yl)prop-2-yn-1-yl) carbonate(**1h**)



Colorless oil (1.8 g), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 80 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 7.0 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* =

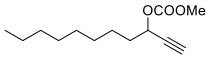
7.7 Hz, 1H), 6.98 (s, 1H), 3.84 (s, 3H), 2.82 (d, *J* = 2.1 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.0, 134.1, 131.2, 130.4, 128.9, 126.9, 126.8, 126.2, 125.2, 123.7, 79.7, 77.1, 68.0, 55.3. **IR** (KBr, cm^{-1}): 3290, 2957, 2126, 1762, 1593, 1512, 1446, 1270, 1095, 1048, 917, 863, 797, 645, 554, 516, 439. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{12}NaO_3$ 263.0679; found 263.0669.

methyl (1-(thiophen-2-yl)prop-2-yn-1-yl) carbonate(**1i**)



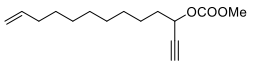
Yellow oil (0.6 g), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 33 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.37 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.30 (d, *J* = 3.6 Hz, 1H), 6.99 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.52 (d, *J* = 2.3 Hz, 1H), 3.82 (s, 3H), 2.74 (d, *J* = 2.3 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 154.8, 138.4, 128.5, 127.8, 126.9, 79.0, 76.1, 64.5, 55.4.

methyl undec-1-yn-3-yl carbonate(**1j**)



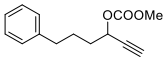
Colorless oil (1.3 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 60 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.20 (td, *J* = 6.7, 2.1 Hz, 1H), 3.81 (s, 3H), 2.51 (d, *J* = 2.1 Hz, 1H), 1.89 – 1.74 (m, 2H), 1.46 (h, *J* = 6.7 Hz, 2H), 1.29 (td, *J* = 11.3, 4.3 Hz, 7H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.1, 80.7, 74.5, 68.0, 55.0, 34.7, 31.9, 29.5, 29.3, 29.1, 24.9, 22.7, 14.2. **IR** (KBr, cm^{-1}): 3301, 2927, 2860, 2124, 1754, 1451, 1268, 1125, 1032, 961, 791, 671, 456. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{22}NaO_3$ 249.1461; found 249.1459.

methyl tridec-12-en-1-yn-3-yl carbonate(**1k**)



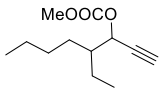
Colorless oil (1.4 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 56 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.78 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.18 (td, *J* = 6.7, 2.0 Hz, 1H), 5.02 – 4.93 (m, 1H), 4.93 – 4.86 (m, 1H), 3.79 (s, 3H), 2.49 (d, *J* = 2.1 Hz, 1H), 2.02 (q, *J* = 6.9 Hz, 2H), 1.87 – 1.72 (m, *J* = 6.9 Hz, 2H), 1.44 (q, *J* = 8.1, 7.4 Hz, 2H), 1.38 – 1.23 (m, 10H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.1, 139.2, 114.2, 80.7, 74.5, 68.0, 55.0, 34.7, 33.9, 29.4, 29.4, 29.1, 29.1, 29.0, 24.8.

methyl (6-phenylhex-1-yn-3-yl) carbonate(**1l**)



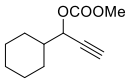
Colorless oil (1.7 g), purified by chromatography (petroleum/ethyl acetate = 60/1), yield = 72 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.20 (q, *J* = 7.2, 6.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 3H), 5.15 (d, *J* = 6.4 Hz, 1H), 3.73 (s, 3H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 1H), 1.77 (ddq, *J* = 19.5, 11.3, 5.3, 4.1 Hz, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.3, 142.0, 128.8, 126.3, 80.8, 75.0, 68.1, 55.4, 35.6, 34.5, 26.9. **IR** (KBr, cm^{-1}): 3288, 3027, 2950, 2125, 1757, 1595, 1448, 1271, 954, 791, 747, 687, 497. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{16}NaO_3$ 255.0992; found 255.0994.

4-ethyloct-1-yn-3-yl methyl carbonate(**1m**)



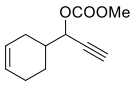
Colorless oil (1.3 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 62 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.26 (q, *J* = 6.2, 3.4 Hz, 1H), 3.80 (s, 3H), 2.48 (s, 1H), 1.64 (td, J = 12.1, 6.3 Hz, 1H), 1.49 (dddd, *J* = 55.8, 26.1, 13.3, 6.0 Hz, 4H), 1.37 – 1.23 (m, 4H), 0.97 – 0.86 (m, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.3, 79.7, 79.6, 75.2, 75.2, 70.7, 70.7, 55.1, 43.7, 43.7, 29.4, 29.3, 29.0, 23.0, 23.0, 22.8, 22.5, 14.1, 14.1, 11.6, 11.6. **IR** (KBr, cm^{-1}): 3300, 2960, 1755, 1706, 1449, 1269, 964, 790, 669. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{20}NaO_3$ 235.1305; found 235.1302.

1-cyclohexylprop-2-yn-1-yl methyl carbonate(**1n**)



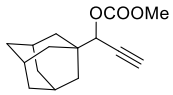
Colorless oil (1.3 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 66 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.03 – 5.00 (m, 1H), 3.78 (s, 2H), 2.49 (d, *J* = 2.0 Hz, 1H), 1.88 – 1.62 (m, 6H), 1.28 – 1.05 (m, 5H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.2, 79.6, 75.2, 72.3, 55.0, 41.7, 28.3, 28.0, 26.2, 25.7, 25.7. **IR** (KBr, cm^{-1}): 3298, 2931, 2857, 2124, 1751, 1447, 1262, 1106, 968, 791, 673, 466. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{16}NaO_3$ 219.0992; found 219.0984.

1-(cyclohex-3-en-1-yl)prop-2-yn-1-yl methyl carbonate(**1o**)



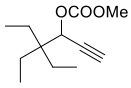
Colorless oil (1.0 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 51 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.71 – 5.60 (m, 2H), 5.13 (dd, *J* = 6.3, 2.2 Hz, 1H), 3.81 (s, 3H), 2.51 (t, *J* = 1.6 Hz, 1H), 2.25 – 1.81 (m, 6H), 1.55 – 1.35 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.0, 155.0, 126.9, 126.7, 125.2, 125.1, 79.2, 79.2, 75.3, 75.1, 71.4, 71.3, 54.8, 54.81, 37.8, 37.7, 26.9, 26.6, 24.6, 24.5, 24.1, 23.8. **IR** (KBr, cm^{-1}): 3284, 2953, 2867, 2694, 2203, 2123, 1751, 1582, 1447, 1269, 1166, 1098, 959, 878, 791, 680, 552, 453. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{14}NaO_3$ 217.0835; found 217.0833.

1-((3r,5r,7r)-adamantan-1-yl)prop-2-yn-1-yl methyl carbonate (**1p**)



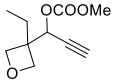
White solid (1.7 g), m.p. = 60-61 ºC, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 70 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.78 (d, *J* = 2.1 Hz, 1H), 3.78 (s, 3H), 2.48 (d, *J* = 2.2 Hz, 1H), 1.99 (s, 3H), 1.66 (d, *J* = 14.6 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.5, 78.7, 76.2, 75.5, 55.0, 37.6, 36.8, 36.7, 28.1. **IR** (KBr, cm^{-1}): 3288, 3030, 2957, 2126, 1763, 1707, 1581, 1495, 1448, 1284, 961, 790, 748, 698, 539, 447. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}O_3$ 249.1485; found 249.1482.

4,4-diethylhex-1-yn-3-yl methyl carbonate(**1q**)



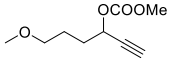
Colorless oil (1.2 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 55 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.14 (d, *J* = 2.1 Hz, 1H), 3.80 (s, 3H), 2.51 (d, *J* = 2.1 Hz, 1H), 1.45 (qt, *J* = 14.6, 7.3 Hz, 6H), 0.86 (t, *J* = 7.6 Hz, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 156.0, 79.7, 75.9, 73.9, 55.1, 42.3, 26.0, 8.2. **IR** (KBr, cm^{-1}): 3300, 2968, 1754, 1449, 1347, 1263, 1083, 971, 925, 794, 669, 459. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{20}NaO_3$ 235.1305; found 235.1302.

1-(3-ethyloxetan-3-yl)prop-2-yn-1-yl methyl carbonate(**1r**)



Colorless oil (1.2 g), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 60 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.34 (d, *J* = 1.8 Hz, 1H), 4.62 – 4.56 (m, 2H), 4.39 – 4.33 (m, 2H), 3.80 (s, 3H), 2.56 (d, *J* = 2.1 Hz, 1H), 1.88 – 1.78 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ, 76.3, 76.1, 75.8, 70.0, 55.3, 45.8, 25.9, 8.2. 155.1, 77.9. **IR** (KBr, cm^{-1}): 3290, 2953, 2882, 2122, 1756, 1450, 1266, 1107, 976, 831, 790, 688, 470. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{15}O_4$ 199.0965; found 199.0963.

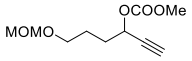
6-methoxyhex-1-yn-3-yl methyl carbonate(**1s**)



Colorless oil (0.9 g), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 47 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.24 (td, *J* = 6.5, 2.1 Hz, 1H), 3.80 (s, 3H), 3.40 (t, *J* = 6.2 Hz, 2H), 3.32 (s, 3H), 2.51 (d, *J* = 2.1 Hz, 1H), 1.96 – 1.82 (m, 2H), 1.76 (dt, *J* = 9.0, 6.1 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.1, 80.5, 74.7, 71.9, 67.7, 58.7, 55.1, 31.6,

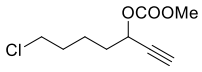
25.1. **IR** (KBr, cm^{-1}): 3293, 2951, 2880, 2123, 1754, 1449, 1268, 1117, 959, 791, 684, 502. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{14}O_4$ 187.0965; found 187.0966.

6-(methoxymethoxy)hex-1-yn-3-yl methyl carbonate(**1t**)



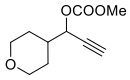
Colorless oil (1.1 g), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 49 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.24 (td, *J* = 6.5, 1.8 Hz, 1H), 4.59 (s, 2H), 3.79 (s, 3H), 3.54 (t, *J* = 6.2 Hz, 2H), 3.34 (s, 3H), 2.52 (d, *J* = 2.0 Hz, 1H), 1.99 – 1.88 (m, 2H), 1.76 (dq, *J* = 13.3, 7.2, 6.7 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.0, 96.5, 80.4, 74.8, 67.7, 66.9, 55.3, 55.1, 31.7, 25.2. **IR** (KBr, cm^{-1}): 3287, 2950, 2885, 2123, 1754, 1448, 1269, 1150, 1110, 1042, 955, 791, 679, 454. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{16}NaO_5$ 239.0890; found 239.0887.

7-chlorohept-1-yn-3-yl methyl carbonate(**1u**)



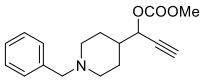
Colorless oil (1.3 g), purified by chromatography (petroleum/ethyl acetate = 60/1), yield = 66 %. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.22 (td, *J* = 6.5, 2.1 Hz, 1H), 3.81 (s, 3H), 3.54 (t, *J* = 6.6 Hz, 2H), 2.53 (d, *J* = 2.1 Hz, 1H), 1.93 – 1.74 (m, 4H), 1.71 – 1.57 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.0, 80.3, 74.9, 67.6, 55.2, 44.7, 33.9, 32.1, 22.3. **IR** (KBr, cm^{-1}): 3292, 2956, 2126, 1761, 1707, 1449, 1278, 1152, 1051, 959, 791, 652, 554, 449. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_9H_{13}ClNaO_3$ 227.0445; found 227.0441.

methyl (1-(tetrahydro-2H-pyran-4-yl)prop-2-yn-1-yl) carbonate(**1v**)



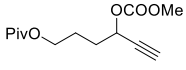
Colorless oil (1.4 g), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 71 %. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.05 (dd, *J* = 6.5, 2.1 Hz, 1H), 4.00 (dt, *J* = 9.7, 4.2 Hz, 2H), 3.81 (s, 3H), 3.37 (tdd, *J* = 11.8, 6.1, 2.1 Hz, 2H), 2.54 (d, *J* = 2.2 Hz, 1H), 1.99 (tdd, *J* = 11.8, 6.8, 3.6 Hz, 1H), 1.78 – 1.65 (m, 2H), 1.54 (dqd, *J* = 24.9, 12.2, 4.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.1, 78.9, 75.8, 71.4, 67.4, 55.2, 39.3, 28.5, 28.0.

1-(1-benzylpiperidin-4-yl)prop-2-yn-1-yl methyl carbonate(**1w**)



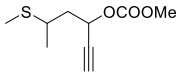
Yellow oil (1.8 g), purified by chromatography (petroleum/ethyl acetate = 5/1), yield = 63 %. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 4.4 Hz, 4H), 7.30 – 7.24 (m, 1H), 5.10 (dd, *J* = 6.1, 2.1 Hz, 1H), 3.83 (s, 3H), 3.52 (s, 2H), 3.00 – 2.92 (m, 2H), 2.55 (d, *J* = 2.2 Hz, 1H), 1.98 (tdd, *J* = 11.8, 7.0, 2.2 Hz, 2H), 1.87 – 1.70 (m, 3H), 1.54 (dqd, *J* = 25.5, 13.1, 12.6, 3.9 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.2, 138.5, 129.2, 128.3, 127.1, 79.3, 75.5, 71.6, 63.3, 55.1, 53.2, 40.2, 27.9, 27.4. **IR** (KBr, cm^{-1}): 3292, 3027, 2948, 2763, 2204, 2122, 1752, 1587, 1449, 1258, 1114, 1075, 964, 789, 739, 695, 463. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}NO_3$ 288.1594; found 288.1591.

4-((methoxycarbonyl)oxy)hex-5-yn-1-yl pivalate(**1x**)



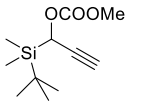
Colorless oil (1.4 g), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 55 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.23 (dt, *J* = 6.3, 3.0 Hz, 1H), 4.06 (hept, *J* = 6.0, 5.4 Hz, 2H), 3.78 (s, 3H), 2.52 (d, *J* = 2.0 Hz, 1H), 1.92 – 1.85 (m, 2H), 1.85 – 1.78 (m, 2H), 1.17 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 178.5, 154.9, 80.1, 75.0, 67.4, 63.6, 55.1, 38.83, 31.34, 27.25, 24.19. **IR** (KBr, cm^{-1}): 3292, 2968, 2124, 1754, 1449, 1270, 1161, 1036, 961, 787, 678, 462. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{21}O_5$ 257.1384; found 257.1383.

methyl (5-(methylthio)hex-1-yn-3-yl) carbonate(**1y**)



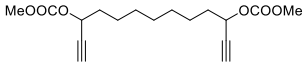
Colorless oil (0.9 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 46 %. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.41 (qd, *J* = 6.5, 5.4, 2.1 Hz, 1H), 3.81 (d, *J* = 2.3 Hz, 3H), 2.83 (dq, *J* = 14.8, 7.9, 7.4 Hz, 1H), 2.54 (dd, *J* = 6.5, 2.1 Hz, 1H), 2.18 – 1.87 (m, 5H), 1.33 (dd, *J* = 6.8, 4.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.9, 154.9, 80.5, 80.3, 75.1, 74.9, 66.6, 65.9, 55.2, 41.3, 41.0, 37.1, 37.0, 21.1, 21.0, 12.7, 12.5. **IR** (KBr, cm^{-1}): 3293, 2922, 1754, 1446, 1269, 1116, 1029, 969, 790, 681. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{15}O_3S$ 203.0737; found 203.0733.

1-(tert-butyldimethylsilyl)prop-2-yn-1-yl methyl carbonate(**1z**)



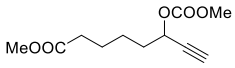
The corresponding propargylic alcohol was prepared according the literature[8]. Colorless oil (1.4 g), purified by chromatography (petroleum), yield = 60 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 4.94 (t, *J* = 2.8 Hz, 1H), 3.68 – 3.63 (m, 3H), 2.55 (t, *J* = 2.5 Hz, 1H), 0.86 – 0.81 (m, 9H), 0.00 (d, *J* = 3.4 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 156.0, 80.6, 77.2, 60.7, 54.8, 26.6, 16.8, -7.9, -8.6. **IR** (KBr, cm^{-1}): 3302, 2945, 2862, 1753, 1452, 1362, 1331, 1261, 1097, 1000, 946, 836, 795, 674, 599, 445. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{20}NaO_3Si$ 251.1074; found 251.1072.

dimethyl trideca-1,12-diyne-3,11-diyl bis(carbonate) (**1aa**)



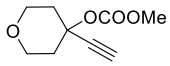
Colorless oil (1.8 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 55 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.20 – 5.14 (m, 2H), 3.78 (s, 6H), 2.50 (d, *J* = 1.7 Hz, 2H), 1.86 – 1.71 (m, *J* = 6.9 Hz, 4H), 1.47 – 1.41 (m, 4H), 1.30 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.1, 80.6, 74.6, 67.9, 55.1, 34.6, 29.2, 28.9, 24.8. **IR** (KBr, cm^{-1}): 3280, 2860, 2125, 1765, 1706, 1456, 1319, 958, 791, 674, 556, 450. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{24}NaO_6$ 347.1465; found 347.1466.

methyl 6-((methoxycarbonyl)oxy)oct-7-ynoate(**1ab**)



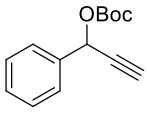
Colorless oil (1.4 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 62 %. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.18 (dt, *J* = 6.5, 3.3 Hz, 1H), 3.78 (s, 3H), 3.64 (s, 3H), 2.50 (d, *J* = 2.0 Hz, 1H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.81 (ddt, *J* = 11.2, 6.8, 3.0 Hz, 2H), 1.65 (p, *J* = 7.6 Hz, 2H), 1.55 – 1.43 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.9, 155.0, 80.4, 74.7, 67.6, 55.1, 51.6, 34.3, 33.9, 24.4, 24.4. **IR** (KBr, cm^{-1}): 3284, 2953, 2867, 2694, 2203, 2123, 1751, 1582, 1447, 1269, 1166, 1098, 959, 878, 791, 680, 552, 453. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{19}O_5$ 229.1071; found 229.1074.

4-ethynyltetrahydro-2H-pyran-4-yl methyl carbonate(**1ac**)



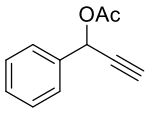
Colorless oil (1.5 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 80 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 3.86 (dt, *J* = 11.7, 4.3 Hz, 2H), 3.77 (s, 3H), 3.73 – 3.66 (m, 2H), 2.69 (s, 1H), 2.24 (d, *J* = 13.2 Hz, 2H), 2.04 (ddd, *J* = 13.2, 9.5, 4.0 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 153.4, 81.8, 75.9, 74.5, 64.4, 54.7, 37.3. **IR** (KBr, cm^{-1}): 3286, 2967, 2863, 2768, 2707, 2118, 1824, 1757, 1578, 1443, 1354, 1247, 1157, 1098, 1034, 950, 910, 844, 791, 678, 562, 509, 454. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{13}O_4$ 185.0808; found 185.0807.

tert-butyl (1-phenylprop-2-yn-1-yl) carbonate (**1ad**)



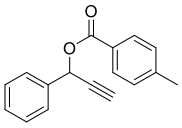
Colorless oil (1.5 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 65 %. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.38 (d, *J* = 6.9 Hz, 3H), 6.25 (d, *J* = 2.2 Hz, 1H), 2.69 (d, *J* = 2.3 Hz, 1H), 1.50 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.57, 136.35, 129.25, 128.79, 127.80, 83.24, 80.14, 76.08, 68.30, 27.86.

1-phenylprop-2-yn-1-yl acetate (**1ae**)



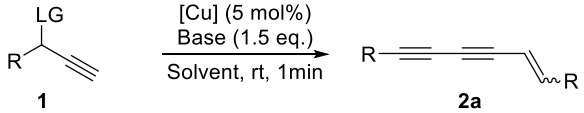
Colorless oil (1.3 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 75 %. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.54 (dd, J = 7.6, 1.8 Hz, 2H), 7.39 (d, J = 6.9 Hz, 3H), 6.46 (d, J = 2.2 Hz, 1H), 2.66 (d, J = 2.3 Hz, 1H), 2.12 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.82, 136.60, 129.22, 128.84, 127.82, 80.39, 75.50, 65.43, 21.14.

1-phenylprop-2-yn-1-yl 4-methylbenzoate (**1af**)



Colorless oil (2.1 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 84 %. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 6.7 Hz, 2H), 7.38 (dd, *J* = 9.3, 7.2 Hz, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 2.0 Hz, 1H), 2.68 (d, *J* = 2.2 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.49, 144.21, 136.79, 130.06, 129.23, 129.11, 128.82, 127.75, 126.96, 80.52, 75.64, 65.72, 21.79.

1.3. Optimization of 1-en-3,5-diynes[a]

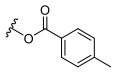


1 **2a**

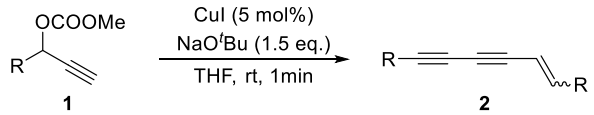
Entry	Catalyst (5 mol%)	Liangd (10 mol%)	Base (1.5 equiv)	LG	Solvent (2 mL)	Yield (%)[b]	E/Z
1	CuI	-	NaO^{t}Bu	OCO_2Me	THF	86 (78[c])	1:1.0
2	-	-	NaO^{t}Bu	OCO_2Me	THF	0	-
3	SIMesCuCl	-	NaO^{t}Bu	OCO_2Me	THF	55	1:1.1
4	SIPrCuCl	-	NaO^{t}Bu	OCO_2Me	THF	10	1.1:1
5	IMesCuCl	-	NaO^{t}Bu	OCO_2Me	THF	51	1:1.1
6	IPrCuCl	-	NaO^{t}Bu	OCO_2Me	THF	36	1.1:1
7	CuCl	PCy_3	NaO^{t}Bu	OCO_2Me	THF	16	1.4:1
8	CuCl	PPh_3	NaO^{t}Bu	OCO_2Me	THF	61	1:1.1
9	CuCl	XPhos	NaO^{t}Bu	OCO_2Me	THF	39	1:1.1
10	CuCl	XantPhos	NaO^{t}Bu	OCO_2Me	THF		1.3:1
11	CuCl	JohnPhos	NaO^{t}Bu	OCO_2Me	THF	56	1:1.3
12	CuCl	dppf	NaO^{t}Bu	OCO_2Me	THF	20	1.2:1
13	CuCl	dppBz	NaO^{t}Bu	OCO_2Me	THF	13	1.5:1
14	CuCl	DPEPhos	NaO^{t}Bu	OCO_2Me	THF	37	1:1.1
15	Me_2S-CuBr	-	NaO^{t}Bu	OCO_2Me	THF	75	1:1.2
16	$Cu(CH_3CN)_4PF_6$	-	NaO^{t}Bu	OCO_2Me	THF	81	1:1.2
17	CuBr	-	NaO^{t}Bu	OCO_2Me	THF	72	1:1.2
18	CuSCN	-	NaO^{t}Bu	OCO_2Me	THF	76	1:1.2

19	CuOAc	-	NaO^{t}Bu	OCO_2Me	THF	81	1:1.2
20	CuI	-	KO^{t}Bu	OCO_2Me	THF	56 (53[c])	5:1
21	CuI	-	LiO^{t}Bu	OCO_2Me	THF	trace	-
22	CuI	-	$Mg(O^tBu)_2$	OCO_2Me	THF	0	-
23	CuI	-	$Al(O^tBu)_3$	OCO_2Me	THF	0	-
24[d]	CuI	-	Et_3N	OCO_2Me	THF	0	-
25[e]	CuI	-	K_2CO_3	OCO_2Me	THF	0	-
26	CuI	-	TMSONa	OCO_2Me	THF	trace	-
27	CuI	-	TMSOK	OCO_2Me	THF	trace	-
28	CuI	-	EtONa	OCO_2Me	THF	11	1:1.0
29[f]	CuI	-	NaHMDS	OCO_2Me	THF	0	-
30[g]	CuI	-	*n*-BuLi	OCO_2Me	THF	0	-
31	CuI	-	NaO^{t}Bu	OCO_2Me	DCE	0	-
32	CuI	-	NaO^{t}Bu	OCO_2Me	CH_3CN	13	5.6:1
33	CuI	-	NaO^{t}Bu	OCO_2Me	DME	51	1:1.0
34	CuI	-	NaO^{t}Bu	OCO_2Me	1,4-Di-oxane	70	1:1.2
35	CuI	-	NaO^{t}Bu	OBoc	THF	32	1:1.0
36	CuI	-	NaO^{t}Bu	OAc	THF	13	1:1.1
37	CuI	-	NaO^{t}Bu	LG_x[h]	THF	61	1:1.2

[a]Reaction conditions: **1a** (0.2 mmol), Cu (5 mol%), base (0.3 mmol, 1.5 equiv), 2 mL of THF, 25 °C. [b]NMR yield. [c]Isolated yield [d] Reaction for 4 h. [e]Overnight. [f]Reation at -20 °C. [g]Reation at -78 °C. [h]LG_x =



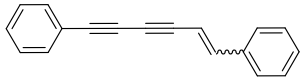
1.4. General procedure for 2



To a 25 mL Schlenk tube with a magnetic bar under nitrogen atmosphere was added CuI (1.9mg, 5 mol%), dry-THF (0.7 mL), and NaO^{t}Bu (1.0 M in THF, 300 μL) sequentially at room temperature (about 25 °C). solution of **1** (0.2 mmol) in 1 mL dry-THF was dropped to the mixture within 1 min. After the drop was finished, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel to afford the pure product **2**.

The melting point of *E*/*Z* mixtures were not measured because of the excessively wide melting range. The characterization of compound *E*-**2a**[9] was previously reported.

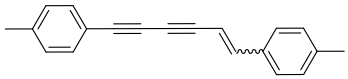
(*E*/*Z*)-hexa-1-en-3,5-diyne-1,6-diyldibenzene (**2a**)



White solid (17.8 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 78%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 8.8 Hz, 4H), 7.46 – 7.41 (m, 4H), 7.36 (m, 10H), 7.14 (d, *J* = 16.2 Hz, 1H, *E*-isomer), 6.81 (d, *J* = 12.0 Hz, 1H, *Z*-isomer), 6.29 (d, *J* = 16.2 Hz, 1H, *E*-isomer), 5.84 (d, *J* = 12.0 Hz, 1H, *Z*-isomer). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.7, 142.5, 136.1, 135.9, 132.6, 132.6, 129.4, 129.4, 129.3, 128.9, 128.7, 128.6, 128.6, 128.6, 126.6, 122.0, 121.9, 106.9, 106.0, 83.6, 82.3, 81.5, 80.5, 80.3, 76.2, 74.3, 74.3. **IR** (KBr, cm^{-1}): 3054, 2919, 2203, 1681, 1595,

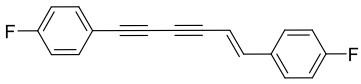
1486, 1442, 1265, 1069, 1022, 953, 916, 783, 749, 684, 519. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}$ 229.1012; found 229.1003.

(*E/Z*)-4,4'-(hexa-1-en-3,5-diyne-1,6-diyl)bis(methylbenzene) (**2b**)



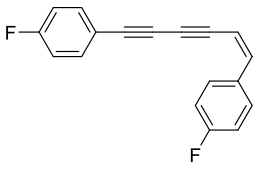
White solid (21.6 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 84 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.44 (dd, *J* = 10.7, 7.9 Hz, 4H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.0 Hz, 6H), 7.10 (d, *J* = 16.2 Hz, 1H , *E*-isomer), 6.76 (d, *J* = 12.0 Hz, 1H , *Z*-isomer), 6.23 (d, *J* = 16.2 Hz, 1H , *E*-isomer), 5.77 (d, *J* = 12.0 Hz, 1H , *Z*-isomer), 2.41 – 2.35 (m, 12H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.5, 142.2, 139.7, 139.6, 139.6, 139.4, 133.6, 133.2, 132.5, 132.5, 129.6, 129.4, 129.3, 129.3, 128.7, 126.5, 118.9, 118.9, 105.8, 105.0, 83.8, 82.5, 81.5, 80.5, 80.3, 76.0, 73.8, 73.8, 21.8, 21.7, 21.6, 21.5. **IR** (KBr, cm^{-1}): 2920, 1899, 1599, 1506, 1176, 955, 817, 705, 557, 519, 442. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{16}Na$ 279.1144; found 279.1142.

(*E*)-4,4'-(hexa-1-en-3,5-diyne-1,6-diyl)bis(fluorobenzene) (*E*-**2c**)



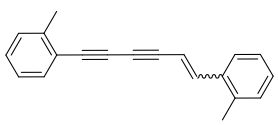
White solid (7.9 mg), m.p. = 153-155 ºC, purified by chromatography (petroleum/ethyl acetate = 80/1), yield = 30 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.55 – 7.44 (m, 2H), 7.43 – 7.35 (m, 2H), 7.11 – 6.99 (m, 5H), 6.17 (d, *J* = 16.2 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 163.5 (d, *J* = 250.1 Hz), 163.2 (d, *J* = 251.5 Hz), 143.5, 134.6 (d, *J* = 8.5 Hz), 132.1 (d, *J* = 3.5 Hz), 128.3 (d, *J* = 8.2 Hz), 118.1 (d, *J* = 3.6 Hz), 116.1 (d, *J* = 21.9 Hz), 116.0 (d, *J* = 22.3 Hz), 106.6 (d, *J* = 2.5 Hz), 81.3, 81.2,76.0, 73.0 (d, *J* = 1.3 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -108.61, -111.19. **IR** (KBr, cm^{-1}): 3149, 3042, 2918, 2851, 1597, 1503, 1317, 1227, 1157, 1093, 834, 747, 614, 528, 468. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{11}F_2$ 265.0823; found 265.0822.

(*Z*)-4,4'-(hexa-1-en-3,5-diyne-1,6-diyl)bis(fluorobenzene) (*Z*-**2c**)



White solid (8.7 mg), m.p. = 71-73 ºC, purified by chromatography (petroleum/ethyl acetate = 80/1), yield = 33 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 – 7.82 (m, 2H), 7.55 – 7.48 (m, 2H), 7.06 (dt, *J* = 21.2, 8.7 Hz, 4H), 6.75 (d, *J* = 12.0 Hz, 1H), 5.79 (d, *J* = 12.0 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 163.1 (d, *J* = 251.7 Hz), δ 162.9 (d, *J* = 250.2 Hz), 134.6 (d, *J* = 8.6 Hz), δ 132.3 (d, *J* = 3.4 Hz), 130.5 (d, *J* = 8.2 Hz), 117.9 (d, *J* = 3.5 Hz), 115.9 (d, *J* = 22.3 Hz), 115.5 (d, *J* = 21.7 Hz), 105.4 (d, *J* = 2.3 Hz), 141.1, 105.43, 105.41, 82.4, 80.2, 79.9, 73.8 (d, *J* = 1.3 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -108.39, -110.75. **IR** (KBr, cm^{-1}): 3132, 2128, 1883, 1630, 1598, 1502, 1402, 1301, 1225, 1153, 1093, 940, 818, 802, 617, 520, 479. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{11}F_2$ 265.0823; found 265.0822.

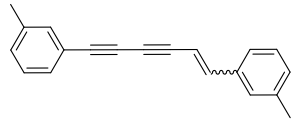
(*E/Z*)-2,2'-(hexa-1-en-3,5-diyne-1,6-diyl)bis(methylbenzene) (**2e**)



White solid (22.2 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 86 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 7.3 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.38 (d, *J* = 16.2 Hz, 1H , *E*-isomer), 7.18 (ddq, *J* = 33.9, 20.9, 7.4 Hz, 12H), 6.99 (d, *J* = 12.0 Hz, 1H , *Z*-isomer), 6.18 (d, *J* = 16.1 Hz, 1H , *E*-isomer), 5.87 (d, *J* = 12.0 Hz, 1H , *Z*-isomer), 2.46 (s, 3H), 2.44 (s, 3H), 2.36 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 142.3, 141.8, 140.4, 136.6, 136.2, 134.9, 134.8, 133.02, 133.00, 130.8, 130.4, 129.69, 129.67, 129.26, 129.25, 129.2, 129.0, 127.9, 126.4, 126.0, 125.78,

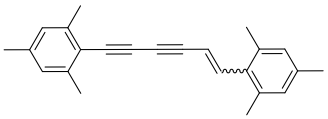
125.76, 125.0, 121.81, 121.75, 107.8, 107.0, 82.4, 82.1, 81.4, 80.8, 79.5, 77.8, 76.0, 20.8, 20.8, 19.9, 19.9. **IR** (KBr, cm^{-1}): 3022, 2921, 2203, 2131, 1917, 1697, 1599, 1454, 1379, 1300, 1195, 1195, 1160, 1093, 1039, 949, 871, 750, 710, 544, 444. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{16}Na$ 279.1144; found 279.1134.

(*E/Z*)-3,3'-(hexa-1-en-3,5-diyne-1,6-diyl)bis(methylbenzene) (**2f**)



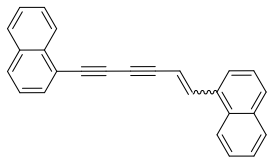
White solid (20.8 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 81 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.60 (s, 1H), 7.31 (dd, *J* = 16.1, 8.2 Hz, 5H), 7.20 (dd, *J* = 12.3, 5.5 Hz, 5H), 7.18 – 7.10 (m, 4H), 7.07 (d, *J* = 16.2 Hz, 1H , *E*-isomer), 6.74 (d, *J* = 12.0 Hz, 1H , *Z*-isomer), 6.23 (d, *J* = 16.2 Hz, 1H , *E*-isomer), 5.78 (d, *J* = 12.0 Hz, 1H , *Z*-isomer), 2.37 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.8, 142.6, 138.6, 138.3, 138.3, 138.1, 136.1, 135.8, 133.08, 133.06, 130.3, 130.2, 130.1, 129.73, 129.71, 129.6, 128.8, 128.51, 128.46, 128.44, 127.3, 125.7, 123.8, 121.82, 121.76, 106.7, 105.8, 83.8, 82.5, 81.5, 80.6, 80.3, 76.2, 74.0, 73.9, 21.6, 21.5, 21.3. **IR** (KBr, cm^{-1}): 3027, 2921, 2203, 2133, 1783, 1600, 1484, 1304, 1089, 1040, 951, 880, 793, 688, 496, 437. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{16}Na$ 279.1144; found 279.1142.

(*E/Z*)-2,2'-(hexa-1-en-3,5-diyne-1,6-diyl)bis(1,3,5-trimethylbenzene) (**2g**)



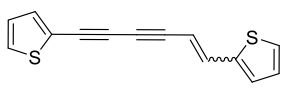
White solid (30.9 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 99 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 16.5 Hz, 1H , *E*-isomer), 6.96 – 6.89 (m, 7H), 6.86 (s, 2H), 6.03 (d, *J* = 11.6 Hz, 1H , *Z*-isomer), 5.92 (d, *J* = 16.5 Hz, 1H , *E*-isomer), 2.48 (s, 6H), 2.39 (s, 6H), 2.36 (s, 6H), 2.35 – 2.29 (m, 18H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 142.9, 142.6, 142.0, 141.9, 138.9, 138.8, 137.7, 137.2, 136.3, 136.1, 132.7, 132.5, 129.2, 128.4, 127.9, 127.8, 118.8, 118.8, 112.2, 111.2, 82.2, 81.1, 81.1, 80.8, 80.5, 80.4, 78.8, 75.7, 21.54, 21.51, 21.20, 21.17, 21.12, 21.07, 21.01, 20.48. **IR** (KBr, cm^{-1}): 2918, 2857, 2205, 1607, 1443, 1379, 1030, 854, 737, 570. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{24}Na$ 335.1770; found 335.1771.

(*E/Z*)-1,1'-(hexa-1-en-3,5-diyne-1,6-diyl)dinaphthalene (**2h**)



White solid (23.0 g), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 70 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.3 Hz, 1H), 8.22 (d, *J* = 6.9 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 16.0 Hz, 1H, *E*-isomer), 7.78 – 7.69 (m, 7H), 7.67 (d, *J* = 7.1 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.52 – 7.37 (m, 11H), 7.35 – 7.25 (m, 3H), 6.28 (d, *J* = 16.0 Hz, 1H, *E*-isomer), 5.99 (d, *J* = 11.8 Hz, 1H , *Z*-isomer). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.7, 140.0, 134.0, 133.9, 133.8, 133.7, 133.20, 133.16, 133.14, 132.6, 132.1, 131.4, 130.9, 129.9, 129.8, 129.6, 128.9, 128.8, 128.5, 128.5, 127.34, 127.30, 126.81, 126.78, 126.59, 126.55, 126.24, 126.20, 126.17, 126.0, 125.63, 125.58, 125.33, 125.29, 123.7, 123.5, 123.4, 119.7, 119.6, 109.4, 108.5, 82.9, 81.4, 81.3, 80.9, 79.4, 79.00, 78.95, 76.4. **IR** (KBr, cm^{-1}): 3046, 1582, 1502, 1332, 1246, 942, 792, 760, 556, 468. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{16}Na$ 351.1144; found 351.1142.

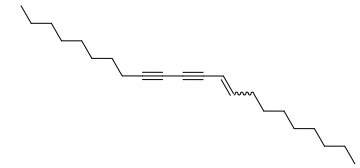
(*E/Z*)-2,2'-(hexa-1-en-3,5-diyne-1,6-diyl)dithiophene (**2i**)



White solid (13.0 mg), purified by chromatography (petroleum/ethyl acetate = 80/1), yield = 54 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.41 – 7.29 (m,

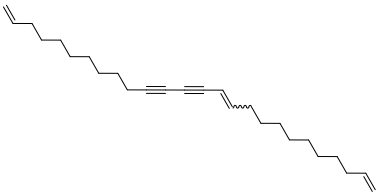
6H), 7.25 (d, *J* = 5.5 Hz, 1H), 7.21 (d, *J* = 15.9 Hz, 1H, *E*-isomer), 7.10 – 6.97 (m, 6H), 6.07 (d, *J* = 15.9 Hz, 1H, *E*-isomer), 5.66 (d, *J* = 11.4 Hz, 1H, *Z*-isomer). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.0, 140.6, 137.4, 135.8, 134.5, 134.3, 130.4, 129.0, 128.8, 128.3, 128.1, 127.7, 127.4, 127.3, 126.9, 126.6, 122.3, 122.2, 105.7, 103.0, 83.4, 83.2, 82.6, 78.4, 78.3, 77.6, 76.4, 75.6. **IR** (KBr, cm^{-1}): 2921, 2130, 1584, 1425, 1210, 1041, 936, 830, 701. **HRMS** (ESI) m/z: [M+H]$^+$ Calcd for $C_{14}H_9S_2$ 241.0140; found 241.0131.

(*E/Z*)-docosa-9-en-11,13-diyne (**2j**)



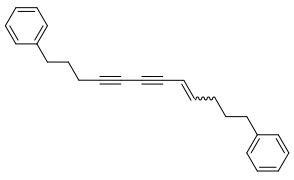
Colorless oil (18.7 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 62%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.26 (dt, *J* = 15.0, 7.1 Hz, 1H , *E*-isomer), 6.02 (dt, *J* = 10.8, 7.5 Hz, 1H , *Z*-isomer), 5.50 – 5.43 (m, 2H), 2.36 – 2.27 (m, 7H), 2.10 (q, *J* = 7.2 Hz, 2H), 1.53 (h, *J* = 7.4 Hz, 5H), 1.39 (q, *J* = 6.5 Hz, 9H), 1.29 – 1.24 (m, 41H), 0.88 (t, *J* = 6.9 Hz, 14H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.4, 147.9, 108.8, 108.2, 85.0, 83.8, 78.3, 74.2, 73.0, 72.2, 65.34, 65.31, 33.4, 32.0, 31.99, 31.97, 30.8, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.03, 28.99, 28.96, 28.7, 28.5, 22.8, 22.8, 19.8, 19.7, 14.24, 14.22. **IR** (KBr, cm^{-1}): 2926, 2857, 2233, 1667, 1460, 1373, 954, 730. **HRMS** (ESI) m/z: [M+Na]$^+$ Calcd for $C_{22}H_{36}Na$ 323.2709; found 323.2706.

(*E/Z*)-hexacosa-1,11,25-trien-13,15-diyne (**2k**)



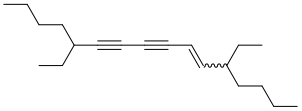
Colorless oil (23.3 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 66%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.26 (dt, *J* = 14.7, 7.1 Hz, 1H, *E*-isomer), 6.02 (dt, *J* = 10.7, 7.5 Hz, 1H, *Z*-isomer), 5.87 – 5.75 (m, 4H), 5.51 – 5.44 (m, 2H), 4.99 (d, *J* = 17.1 Hz, 4H), 4.93 (d, *J* = 10.1 Hz, 4H), 2.37 – 2.25 (m, 6H), 2.10 (q, *J* = 7.1 Hz, 2H), 2.04 (q, *J* = 6.9 Hz, 8H), 1.53 (h, *J* = 7.3 Hz, 4H), 1.42 – 1.34 (m, 16H), 1.32 – 1.24 (m, 28H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.3, 147.9, 139.4, 139.3, 114.3, 114.2, 108.8, 108.3, 85.0, 83.8, 78.3, 74.2, 73.0, 72.2, 65.4, 65.3, 34.0, 33.9, 33.3, 30.8, 30.5, 29.8, 29.54, 29.52, 29.47, 29.44, 29.26, 29.25, 29.22, 29.20, 29.17, 29.07, 29.04, 29.0, 28.9, 28.7, 28.4, 19.8, 19.7. **IR** (KBr, cm^{-1}): 3118, 3027, 2934, 2802, 2761, 1742, 1623, 1494, 1448, 1400, 1230, 1116, 979, 911, 786, 737, 697, 617, 471. **HRMS** (ESI) m/z: [M+H]$^+$ Calcd for $C_{26}H_{41}$ 353.3203; found 353.3203.

(*E/Z*)-dodeca-4-en-6,8-diyne-1,12-diyldibenzene (**2l**)



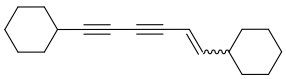
Colorless oil (17.5 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 56%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.31 (q, *J* = 7.0 Hz, 8H), 7.21 (dd, *J* = 11.9, 5.1 Hz, 12H), 6.33 (dt, *J* = 15.3, 7.1 Hz, 1H, *E*-isomer), 6.09 (dt, *J* = 10.6, 7.5 Hz, 1H, *E*-isomer), 5.57 – 5.50 (m, 2H), 2.80 – 2.72 (m, 4H), 2.70 – 2.60 (m, 4H), 2.45 – 2.32 (m, 6H), 2.18 (q, *J* = 7.2 Hz, 2H), 1.94 – 1.84 (m, 4H), 1.82 – 1.72 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 147.8, 147.3, 142.3, 142.0, 141.4, 128.7, 128.60, 128.56, 128.54, 128.53, 128.5, 128.4, 126.2, 126.1, 121.0, 125.9, 109.3, 108.8, 84.5, 83.3, 78.6, 74.2, 73.2, 72.3, 65.89, 65.85, 35.5, 35.3, 34.9, 34.8, 32.8, 30.8, 30.5, 30.3, 30.0, 29.8, 19.14, 19.05. **IR** (KBr, cm^{-1}):3123, 2927, 2857, 1714, 1604, 1401, 1265, 1154, 739, 534. **HRMS** (ESI) m/z: [M+Na]$^+$ Calcd for $C_{24}H_{24}Na$ 335.1770; found 335.1765.

(*E/Z*)-5,12-diethylhexadeca-6-en-8,10-diyne (**2m**)



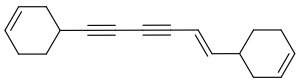
Colorless oil (19.1 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 70%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.03 (dd, *J* = 15.9, 9.2 Hz, 1H, *E*-isomer), 5.73 (t, *J* = 10.5 Hz, 1H, *Z*-isomer), 5.52 (d, *J* = 10.9 Hz, 1H, *Z*-isomer), 5.44 (d, *J* = 15.9 Hz, 1H, *E*-isomer), 2.58 (dq, *J* = 8.8, 4.7 Hz, 1H), 2.42 – 2.32 (m, 2H), 1.92 (dt, *J* = 8.6, 4.3 Hz, 1H), 1.57 – 1.39 (m, 14H), 1.38 – 1.29 (m, 6H), 1.29 – 1.18 (m, 12H), 1.04 – 0.96 (m, 6H), 0.94 – 0.79 (m, 18H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 152.7, 152.3, 108.6, 108.4, 87.9, 87.1, 77.6, 74.6, 73.0, 72.9, 66.5, 66.4, 45.6, 42.6, 34.7, 34.49, 34.45, 34.34, 34.32, 34.29, 29.8, 29.6, 29.5, 28.2, 28.1, 28.0, 27.8, 23.01, 22.89, 22.7, 14.19, 14.15, 14.13, 12.0, 11.9, 11.8. **IR** (KBr, cm^{-1}): 3125, 2960, 2929, 2866, 2226, 1709, 1458, 1397, 1263, 1148, 960, 740. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{33}$ 273.2577; found 273.2572.

(*E/Z*)-hexa-1-en-3,5-diyne-1,6-diyldicyclohexane (**2n**)



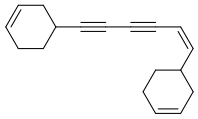
Colorless oil (16.4 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 68%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.22 (dd, *J* = 16.0, 7.0 Hz, 1H , *E*-isomer), 5.84 (t, *J* = 10.2 Hz, 1H , *Z*-isomer), 5.44 (d, *J* = 16.0 Hz, 1H , *E*-isomer), 5.37 (d, *J* = 10.9 Hz, 1H , *Z*-isomer), 2.64 – 2.55 (m, 1H), 2.54 – 2.44 (m, 2H), 2.08 – 1.98 (m, 1H), 1.80 (m, 4H), 1.75 – 1.61 (m, 14H), 1.48 (m, 6H), 1.35 – 1.25 (m, 10H), 1.20 – 1.01 (m, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 153.5, 153.0, 106.5, 106.2, 88.6, 87.5, 77.8, 75.0, 73.1, 72.8, 65.3, 41.5, 39.8, 32.4, 32.3, 32.2, 30.0, 29.8, 26.1, 26.0, 25.9, 25.6, 24.9, 24.8. **IR** (KBr, cm^{-1}): 3128, 2930, 2855, 2228, 1624, 1401, 1152, 617, 530. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{24}Na$ 263.1770; found 263.1770.

(*E*)-4,4'-(hexa-1-en-3,5-diyne-1,6-diyl)dicyclohex-1-ene (*E*-**2o**)



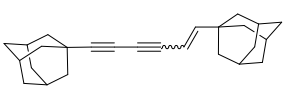
Colorless oil (7.5 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 32%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.29 (dd, *J* = 16.0, 7.3 Hz, 1H), 5.72 – 5.57 (m, 4H), 5.50 (d, *J* = 16.0 Hz, 1H), 2.70 (td, *J* = 9.3, 8.7, 4.2 Hz, 1H), 2.31 (dq, *J* = 22.6, 6.2, 5.0 Hz, 2H), 2.19 – 1.99 (m, 6H), 1.76 (dt, *J* = 13.1, 4.0 Hz, 1H), 1.73 – 1.62 (m, 1H), 1.40 (ddt, *J* = 15.8, 7.9, 3.4 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 152.5, 127.1, 126.9, 125.6, 124.9, 107.2, 87.2, 74.9, 73.3, 65.2, 37.5, 31.1, 30.6, 28.2, 28.0, 26.4, 24.6, 24.0. **IR** (KBr, cm^{-1}): 3025, 2921, 2844, 2230, 1715, 1442, 1259, 1047, 745, 655. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{20}Na$ 259.1457; found 259.1462.

(*Z*)-4,4'-(hexa-1-en-3,5-diyne-1,6-diyl)dicyclohex-1-ene (*Z*-**2o**)



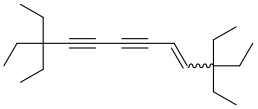
Colorless oil (9.9 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 42%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.95 (t, *J* = 10.2 Hz, 1H), 5.68 (q, *J* = 11.9, 10.4 Hz, 3H), 5.64 – 5.59 (m, 1H), 5.44 (d, *J* = 10.8 Hz, 1H), 2.90 (qd, *J* = 11.7, 9.5, 4.9 Hz, 1H), 2.73 (tt, *J* = 8.6, 3.3 Hz, 1H), 2.31 (d, *J* = 17.8 Hz, 1H), 2.17 – 2.02 (m, 6H), 1.96 – 1.90 (m, 1H), 1.81 (ddt, *J* = 14.0, 5.0, 2.2 Hz, 1H), 1.77 – 1.72 (m, 1H), 1.71 – 1.64 (m, 1H), 1.50 – 1.39 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 152.2, 127.1, 126.9, 125.8, 124.9, 107.0, 88.3, 78.0, 72.8, 65.2, 35.5, 31.1, 30.7, 28.2, 28.1, 26.5, 24.3, 24.0. **IR** (KBr, cm^{-1}): 3143, 3025, 2923, 2844, 2226, 1625, 1401, 1259, 1083, 958, 871, 806, 752, 651, 474. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{20}Na$ 259.1457; found 259.1462.

(*E/Z*)- (3r,3'r,5r,5'r,7r,7'r)-1,1'-(hexa-1-en-3,5-diyne-1,6-diyl)bis(adamantane) (**2p**)



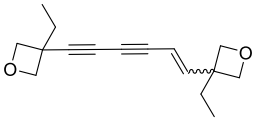
Colorless oil (21.8 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 63%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.14 (d, *J* = 16.2 Hz, 1H, *E*-isomer), 5.63 (d, *J* = 12.2 Hz, 1H, *Z*-isomer), 5.39 (d, *J* = 12.2 Hz, 1H, *Z*-isomer), 5.33 (d, *J* = 16.2 Hz, 1H, *E*-isomer), 1.97 (d, *J* = 14.6 Hz, 12H), 1.91 – 1.82 (m, 18H), 1.68 (p, *J* = 12.1, 11.5 Hz, 24H), 1.55 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 158.2, 155.9, 104.8, 104.2, 92.5, 90.9, 79.0, 76.1, 74.2, 73.3, 64.4, 64.3, 42.4, 41.8, 41.5, 37.3, 36.84, 36.79, 36.4, 36.3, 30.6, 30.5, 29.8, 28.6, 28.3, 27.9, 27.9. **IR** (KBr, cm^{-1}): 3137, 2909, 2851, 2667, 2226, 1625, 1450, 1316, 1264, 1101, 962, 739, 484. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{33}$ 345.2577; found 345.2573.

(*E/Z*)-3,3,10,10-tetraethyldodeca-4-en-6,8-diyne (**2q**)



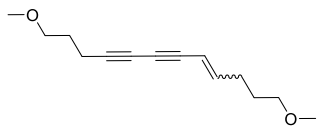
Colorless oil (18.2 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 67%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.10 (d, *J* = 16.5 Hz, 1H, *E*-isomer), 5.64 – 5.54 (m, 2H, *Z*-isomer), 5.36 (d, *J* = 16.5 Hz, 1H, *E*-isomer), 1.57 (q, *J* = 7.4 Hz, 6H), 1.48 (p, *J* = 7.3 Hz, 12H), 1.31 (q, *J* = 7.4 Hz, 6H), 0.95 – 0.88 (m, 18H), 0.79 (t, *J* = 7.4 Hz, 9H), 0.72 (t, *J* = 7.4 Hz, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 156.3, 154.2, 107.4, 107.2, 91.1, 89.6, 79.1, 75.0, 73.4, 73.3, 66.9, 66.8, 44.5, 43.3, 40.7, 40.6, 29.8, 29.7, 28.5, 27.8, 8.8, 8.3, 7.9. **IR** (KBr, cm^{-1}): 3098, 2968, 2931, 2877, 2226, 1614, 1456, 1398, 1297, 1155, 1079, 964, 912, 741, 623, 469. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{33}$ 273.2577; found 273.2573.

(*E/Z*)-3,3'-(hexa-1-en-3,5-diyne-1,6-diyl)bis(3-ethyloxetane) (**2r**)



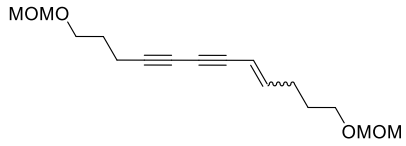
Colorless oil (12.9 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 53%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.39 (d, *J* = 16.3 Hz, 1H, *E*-isomer), 6.11 (d, *J* = 11.3 Hz, 1H, *Z*-isomer), 5.60 (d, J = 11.4 Hz, 1H, *Z*-isomer), 5.60 (d, J = 16.1 Hz, 1H, *E*-isomer), 4.84 (d, *J* = 5.9 Hz, 2H), 4.77 (d, *J* = 5.5 Hz, 2H), 4.56 (d, *J* = 5.8 Hz, 2H), 4.45 (d, *J* = 5.9 Hz, 2H), 4.42 (d, *J* = 5.8 Hz, 2H), 4.39 (d, *J* = 5.5 Hz, 4H), 2.02 (q, J = 7.4 Hz, 2H), 1.95 (q, J = 7.4 Hz, 4H), 1.85 (q, J = 7.4 Hz, 2H), 1.00 (td, *J* = 7.4, 2.9 Hz, 6H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.1, 149.6, 108.7, 108.4, 85.8, 84.2, 80.86, 80.85, 80.8, 80.2, 79.6, 76.1, 74.3, 73.9, 69.0, 68.8, 46.4, 46.2, 39.2, 39.1, 31.7, 31.3, 31.3, 30.3, 9.4, 8.9, 8.7. **IR** (KBr, cm^{-1}): 3129, 2967, 2877, 1724, 1611, 1401, 1154, 985, 822, 753, 530. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}O_2$ 245.1536; found 245.1533.

(*E/Z*)-1,12-dimethoxydodeca-4-en-6,8-diyne (**2s**)



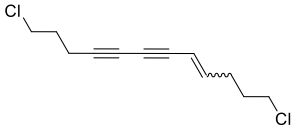
Colorless oil (8.4 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 38%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.27 (dt, *J* = 15.3, 7.1 Hz, 1H, *E*-isomer), 6.09 – 6.00 (m, 1H, *Z*-isomer), 5.51 (d, J = 16.1 Hz, 1H, *E*-isomer), 5.49 (d, J = 10.4 Hz, 1H, *Z*-isomer), 3.48 – 3.42 (m, 4H), 3.41 – 3.35 (m, 4H), 3.35 – 3.29 (m, 12H), 2.46 – 2.36 (m, 6H), 2.19 (q, *J* = 7.3 Hz, 2H), 1.80 (h, *J* = 6.6 Hz, 4H), 1.67 (tt, *J* = 12.0, 5.7 Hz, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 147.5, 147.1, 109.3, 108.8, 84.3, 84.2, 83.1, 78.5, 74.1, 73.1, 72.2, 72.1, 71.8, 71.09, 71.08, 65.5, 58.8, 58.7, 29.9, 28.9, 28.7, 28.49, 28.47, 27.5, 16.6, 16.5. **IR** (KBr, cm^{-1}): 3133, 1623, 1401, 1266, 1115, 740, 617, 531, 476. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{20}NaO_2$ 243.1356; found 243.1357.

(*E/Z*)-2,4,17,19-tetraoxaicosa-8-en-10,12-diyne (**2t**)



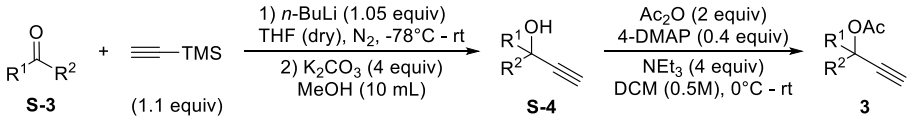
Colorless oil (15.1 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 54%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.27 (dt, *J* = 15.2, 7.1 Hz, 1H, *E*-isomer), 6.05 (q, *J* = 7.7 Hz, 1H, *Z*-isomer), 5.55 – 5.45 (m, 2H), 4.62 (s, 4H), 4.60 (s, 4H), 3.64 – 3.58 (m, 4H), 3.55 – 3.48 (m, 4H), 3.36 (s, 6H), 3.34 (s, 6H), 2.44 (dt, *J* = 13.4, 6.9 Hz, 6H), 2.22 (q, *J* = 7.2 Hz, 2H), 1.91 – 1.62 (m, 8H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 147.4, 146.9, 109.4, 108.9, 96.63, 96.58, 96.57, 96.53, 84.1, 82.9, 78.5, 74.1, 73.8, 73.2, 72.1, 67.2, 67.1, 66.9, 66.08, 66.06, 65.7, 65.6, 63.6, 55.3, 31.6, 30.0, 29.8, 29.0, 28.8, 28.56, 28.55, 27.6, 25.3, 21.1, 16.6, 16.5. **IR** (KBr, cm^{-1}): 3242, 2940, 2236, 1736, 1624, 1398, 1226, 1150, 1110, 919, 742, 620, 474. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{24}NaO_4$ 303.1567; found 303.1567.

(*E/Z*)-1,12-dichlorododeca-4-en-6,8-diyne (**2u**)



Colorless oil (14.6 mg), purified by chromatography (petroleum/ethyl acetate = 80/1), yield = 53%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.25 (dt, *J* = 15.7, 7.1 Hz, 1H, *E*-isomer), 6.03 (dt, *J* = 10.8, 7.5 Hz, 1H, *Z*-isomer), 5.53 – 5.47 (m, 2H), 3.61 – 3.49 (m, 8H), 2.38 (dq, *J* = 13.2, 6.6 Hz, 6H), 2.16 (qd, *J* = 7.3, 1.3 Hz, 2H), 1.90 (dq, *J* = 11.9, 6.5 Hz, 4H), 1.84 – 1.74 (m, 4H), 1.70 (dt, *J* = 15.1, 7.5 Hz, 4H), 1.61 – 1.52 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 147.4, 146.9, 109.4, 109.0, 84.1, 82.8, 78.4, 74.2, 73.1, 65.9, 65.9, 44.9, 44.8, 44.5, 32.5, 32.00, 31.97, 31.6, 31.5, 29.9, 26.1, 25.9, 25.6, 19.1, 19.0. **IR** (KBr, cm^{-1}): 3138, 2945, 2866, 2238, 1717, 1445, 1401, 1303, 1080, 735, 649, 474. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}Cl_2$ 257.0858; found 257.0853.

1.5. General procedure for 3

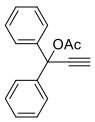


n-BuLi (2.5M in hexane, 1.05 equiv, 4.2 mL, 10.5 mmol) was added dropwise under N_2 to a solution of ethynyltrimethylsilane (1.1 equiv, 1.6 mL, 11 mmol) in dry-THF (16 mL) at –78 ºC. After stirring for 30 min at –78 ºC, ketone **S-3** (1 equiv, 10 mmol) was added. The mixture was stirred at room temperature for 4 h. A solution of potassium hydroxide (4 equiv, 5.5g, 40 mmol) in MeOH (10 mL) was added to the mixture. Desilylation was complete within 30 min as monitored by TLC. The mixture was poured into a satured solution of NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over MgSO4, filtered and the solvent was evaporated under reduced pressure. The combined organic extracts were dried with anhydrous sodium sulfate, filtered and concentrated in vacuo to provide the crude product **S-4**.

To a stirred solution of crude product **S-4** (about 10mmol) in CH_2Cl_2 (20 mL) were added NEt_3 (4.0 equiv, 40mmol, 4.0g, 5.6mL), 4-Dimethylaminopyridine (0.4 equiv, 4 mmol, 488.7mg) and acetic anhydride (2.0 equiv, 20 mmol, 1.9g, 1.5mL) at 0 °C, Warm the reaction mixture to room temperature and stir for 6 h. Quench the reaction with a satured solution of NH_4Cl and extract the aqueous layer with DCM. Wash the combine organic extracts with sat. aq. $NaHCO_3$ and brine. Concentrate the dried ($NaSO_4$) extract in vacuo. The residue was purified by flash column chromatography on silica gel to afford the desired product.

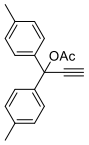
The characterization of compound **3a**[10] was previously reported.

1,1-diphenylprop-2-yn-1-yl acetate (**3a**)



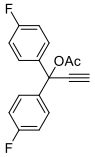
White solid (2.2 g), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 90%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.5 Hz, 4H), 7.37 (t, *J* = 7.4 Hz, 4H), 7.31 (t, *J* = 7.2 Hz, 2H), 3.03 (s, 1H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.2, 142.1, 128.4, 128.1, 126.2, 82.4, 79.1, 78.2, 21.9.

1,1-di-p-tolylprop-2-yn-1-yl acetate (**3b**)



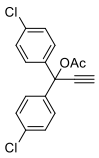
White solid (2.6 g), m.p. = 87-89 °C, purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 93%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 5.6 Hz, 4H), 7.20 (d, *J* = 6.4 Hz, 4H), 3.03 (dd, *J* = 3.5, 1.9 Hz, 1H), 2.38 (s, 6H), 2.23 – 2.17 (m, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.3, 139.4, 137.7, 129.0, 126.1, 82.7, 79.0, 77.9, 21.9, 21.1. **IR** (KBr, cm^{-1}): 3291, 1753, 1510, 1368, 1227, 1053, 984, 814, 738, 568, 497. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{18}NaO_2$ 301.1199; found 301.1198.

1,1-bis(4-fluorophenyl)prop-2-yn-1-yl acetate (**3c**)



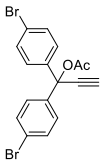
White solid (2,5 g), m.p. = 73-75 °C, purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 88%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.48 (ddt, *J* = 8.2, 5.1, 2.5 Hz, 4H), 7.07 – 6.98 (m, 4H), 3.01 (s, 1H), 2.16 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.2, 162.5 (d, *J* = 247.8 Hz), 137.9 (d, *J* = 3.3 Hz), 128.2 (d, *J* = 8.4 Hz), 115.4 (d, *J* = 21.8 Hz), 82.1, 78.6, 78.1, 21.9. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -113.90. **IR** (KBr, cm^{-1}): 3265, 2120, 1737, 1602, 1503, 1428, 1371, 1301, 1233, 1163, 1113, 1056, 1013, 946, 832, 734, 685, 609, 568, 506. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{12}F_2NaO_2$ 309.0698; found 309.0703.

1,1-bis(4-chlorophenyl)prop-2-yn-1-yl acetate (**3d**)



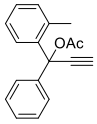
White solid (2.6 g), m.p. = 124-125 °C, purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 82%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.2 Hz, 5H), 7.30 (d, *J* = 8.3 Hz, 5H), 3.00 (s, 1H), 2.15 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.1, 140.3, 134.3, 128.7, 127.7, 81.6, 78.9, 78.0, 21.8. **IR** (KBr, cm^{-1}): 3288, 3130, 2122, 1756, 1601, 1487, 1401, 1282, 1225, 1093, 1054, 1001, 943, 869, 822, 682, 637, 524. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{12}Cl_2NaO_2$ 341.0107; found 341.0108.

1,1-bis(4-bromophenyl)prop-2-yn-1-yl acetate (**3e**)



White solid (3.1 g), m.p. = 117-119 °C, purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 77%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.5 Hz, 4H), 7.40 (d, *J* = 8.5 Hz, 4H), 3.03 (s, 1H), 2.18 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.0, 140.8, 131.6, 127.9, 122.5, 81.4, 78.9, 78.0, 21.8. **IR** (KBr, cm^{-1}): 3291, 3956, 2935, 2122, 1905, 1755, 1630, 1584, 1484, 1434, 1367, 1224, 1114, 1063, 999, 941, 818, 738, 680, 637, 563, 504, 456. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{12}Br_2NaO_2$ 428.9096; found 428.9096.

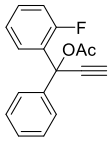
1-phenyl-1-(o-tolyl)prop-2-yn-1-yl acetate (**3f**)



White solid (2.2 g), m.p. = 64-66 °C, purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 85%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.84 – 7.78 (m, 1H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.31 (q, *J* = 8.3, 7.2 Hz, 3H), 7.27 – 7.21 (m, 2H), 7.13 – 7.09 (m, 1H), 2.99 (s, 1H), 2.15 (s, 3H), 2.10 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.1, 141.4, 138.8, 136.0, 132.6, 128.6, 128.31, 128.30, 128.1, 126.8, 125.6, 82.1, 79.6, 78.8, 21.8, 21.2. **IR** (KBr, cm^{-1}): 3293, 3027, 2928, 2115, 1753, 1667, 1595, 1452, 1371, 1228, 1033, 758, 563, 462. **HRMS** (ESI) m/z:

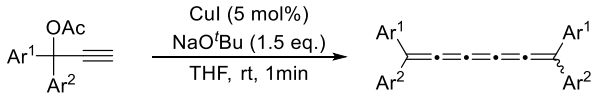
$[M+Na]^+$ Calcd for $C_{18}H_{16}NaO_2$ 287.1043; found 287.1041.

1-(2-fluorophenyl)-1-phenylprop-2-yn-1-yl acetate (**3g**)



White solid (2.1 g), m.p. = 117-119 °C, purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 79%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.82 (t, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.21 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.92 (dd, *J* = 11.0, 8.7 Hz, 1H), 2.96 (s, 1H), 2.12 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.2, 159.4 (d, *J* = 251.5 Hz), 140.8, 130.3 (d, *J* = 8.4 Hz), 128.8 (d, *J* = 9.8 Hz), 128.6 (d, *J* = 2.3 Hz), 128.23, 128.18, 126.0, 123.8 (d, *J* = 3.6 Hz), 116.6 (d, *J* = 21.7 Hz), 81.2, 78.1, 21.5. **IR** (KBr, cm^{-1}): 3287, 3121, 2120, 1753, 1668, 1586, 1488, 1449, 1402, 1371, 1228, 1115, 1041, 989, 945, 812, 760, 692, 642, 556, 476. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{13}FNaO_2$ 291.0792; found 291.0795.

1.6. General procedure for 4



3 **4**

To a 25 mL schlenk tube with a magnetic bar under nitrogen atmosphere was added CuI (1.9mg, 5 mol%), dry-THF (0.7 mL), and NaO^{t}Bu (1.0 M in THF, 300 μL) sequentially at room temperature (about 25 °C). Solution of **3** (0.2 mmol) in 1 mL dry-THF was dropped to the mixture within 1 min.

Gram scale reaction: To a 100 mL schlenk tube with a magnetic bar under nitrogen atmosphere was added CuI (47.6mg, 5 mol%), dry-THF (32.5 mL), and NaO^{t}Bu (1.0 M in THF, 7.5 mL) sequentially at room temperature (about 25 °C). Solution of **3a** (1.25 g, 5 mmol) in 10 mL dry-THF was dropped to the mixture within 1 min. After the drop was finished, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator to afford a red solid. The solid was washed with petroleum ether (50 ml) to obtain the pure product.

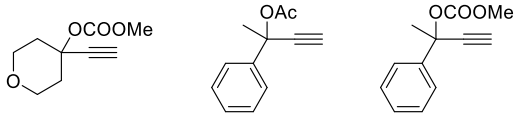
Purification of **4a** and **4c** (poor solubility): After the drop was finished, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator to afford a red solid. The solid was washed with petroleum ether (10 ml) to obtain the pure product.

Purification of **4b** and **4d-e** (terribly poor solubility): After the drop was finished, water (2 mL) and ammonium hydroxide solution (1 mL) were added. After stirring for 5 min, the mixture was filtered to afford the corresponding solid. The solid was washed with ethyl acetate (5 mL) and petroleum ether (10 mL) to obtain the pure product.

Purification of **4f-g** (good solubility): After the drop was finished, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel to afford the pure product.

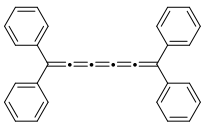
*Caution: **4c** and **4h** are relatively unstable, don't heat them during evaporating by rotary evaporator.*

Failed substrates were listed below:



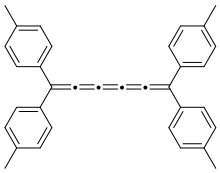
The characterization of compound **4a**–**b**[11] were previously reported.

1,1,6,6-tetraphenylhexa-1,2,3,4,5-pentaene (**4a**)



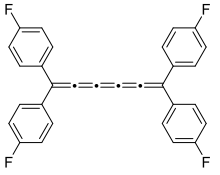
Red solid (37.8 mg), purified by filtration and wash, yield = 99%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.4 Hz, 8H), 7.40 (t, *J* = 7.4 Hz, 8H), 7.36 (d, *J* = 7.2 Hz, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.5, 138.2, 129.5, 128.7, 128.7, 127.5, 124.9.

1,1,6,6-tetra-p-tolylhexa-1,2,3,4,5-pentaene (**4b**)



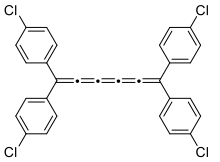
Red solid (39.8 mg), purified by filtration and wash, yield = 91%. **^{1}H NMR** (500 MHz, Chloroform-*d*–CS_2) δ 7.43 (d, *J* = 8.1 Hz, 8H), 7.18 (d, *J* = 8.0 Hz, 8H), 2.41 (s, 12H). **^{13}C NMR** (126 MHz, Chloroform-*d*–CS_2) δ 148.0, 138.4, 135.5, 129.3, 129.3, 126.3, 123.7, 21.5.

1,1,6,6-tetrakis(4-fluorophenyl)hexa-1,2,3,4,5-pentaene (**4c**)



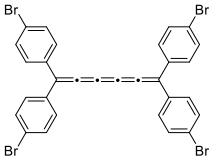
Red solid (44.7 mg), m.p.＞250 °C, purified by filtration and wash, yield = 99%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 8H), 7.10 (t, *J* = 8.6 Hz, 8H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 163.1 (d, *J* = 250.6 Hz), 134.1(d, *J* = 3.3 Hz), 131.1 (d, *J* = 8.1 Hz), 126.9, 122.5, 116.0, 115.8. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -111.62. **IR** (KBr, cm^{-1}): 3125, 2043, 1725, 1660, 1601, 1506, 1403, 1233, 1160, 1100, 1015, 932, 836, 732, 578. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{17}F_4$ 453.1261; found 453.1260.

1,1,6,6-tetrakis(4-chlorophenyl)hexa-1,2,3,4,5-pentaene (**4d**)



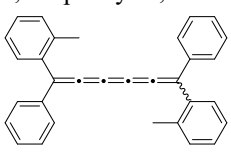
Red solid (35.2 mg), m.p.＞250 °C, purified by filtration and wash, yield = 68%. **^{1}H NMR** (500 MHz, Chloroform-*d*–CS_2) δ 7.47 (d, *J* = 8.4 Hz, 8H), 7.36 (d, *J* = 8.5 Hz, 8H). **^{13}C NMR** (126 MHz, Chloroform-*d*–CS_2) δ 149.0, 135.9, 135.1, 130.4, 128.9, 127.6, 122.9. **IR** (KBr, cm^{-1}): 3234, 3126, 1623, 1485, 1401, 1094, 1012, 832, 619, 480. **HRMS** (DART) m/z: $[M+H]^+$ Calcd for $C_{30}H_{17}Cl_4$ 517.0079; found 517.0080.

1,1,6,6-tetrakis(4-bromophenyl)hexa-1,2,3,4,5-pentaene (**4e**)



Purplish red solid (54.1 mg), m.p.＞250 °C, purified by filtration and wash, yield = 78%. **H NMR** (500 MHz, Chloroform-*d*–CS_2) δ 7.53 (d, *J* = 8.5 Hz, 8H), 7.40 (d, *J* = 8.5 Hz, 8H). **^{13}C NMR** (126 MHz, Chloroform-*d*–CS_2) δ 149.1, 136.4, 132.0, 130.7, 127.7, 123.6, 123.3. **IR** (KBr, cm^{-1}): 3131, 2005, 1900, 1624, 1576, 1479, 1400, 1285, 1174, 1070, 1004, 962, 906, 825, 716, 612, 492. **HRMS** (MALDI) m/z: [M] Calcd for $C_{30}H_{16}Br_4$ 691.7986; found 691.7988.

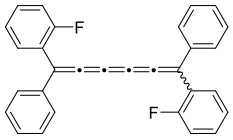
1,6-diphenyl-1,6-di-o-tolylhexa-1,2,3,4,5-pentaene (**4f**)



Red solid (36.4 mg), thermal decomposition, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 89%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.8 Hz, 4H), 7.39 – 7.19 (m, 32H), 2.28 (s, 6H), 2.24 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.94, 150.89, 138.8, 138.7, 137.4, 137.3, 137.1, 137.1, 130.8, 130.8, 130.42, 130.35, 129.2, 129.1, 128.8, 128.7, 128.58, 128.55, 128.50, 128.12, 128.07, 126.1, 126.0, 124.1, 124.0, 20.5. **IR** (KBr, cm^{-1}): 3062, 2929, 2856, 1906, 1732, 1598, 1487,

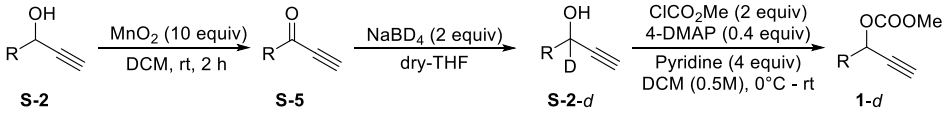
1447, 1391, 1245, 1170, 1090, 1044, 926, 849, 758, 697, 627, 530, 464. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{24}Na$ 431.1770; found 431.1771.

1,6-bis(2-fluorophenyl)-1,6-diphenylhexa-1,2,3,4,5-pentaene (**4g**)



Red solid (41.1 mg), thermal decomposition, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 99%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.55 – 7.06 (m, 18H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.4 (d, *J* = 251.5 Hz), 160.3 (d, *J* = 251.5 Hz), 151.53, 151.51, 138.02, 137.97, 132.08, 132.06, 132.04, 130.58 (d, *J* = 8.1 Hz), 130.55 (d, *J* = 8.1 Hz), 128.89, 128.86, 128.69, 128.66, 128.32, 128.30, 125.6, 125.5, 124.44, 124.40, 124.37, 119.42, 119.36, 116.40 (d, *J* = 21.8 Hz), 116.36 (d, *J* = 21.9 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -110.25, -110.26. **IR** (KBr, cm^{-1}): 3093, 2004, 1726, 1613, 1487, 1447, 1401, 1221, 1163, 1101, 923, 868, 811, 758, 684, 622, 535, 480. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{18}F_2Na$ 439.1269; found 439.1269.

1.7. Deuterium-labeled Experiments



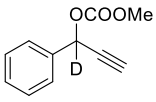
S-2 **S-5** **S-2-*d*** **1-*d***

S-5 was prepared according the literature[12]: Dissolve propargyl alcohol (5 mmol, 1 equiv) in dichloromethane. Treat the solution with MnO_2 (4.3 g, 10 equiv). Stir the solution at room temperature over 2 hours. Remove the excess MnO_2 by filtration of the reaction mixture through a pad of celite. Remove the solvent of filtrate under reduced pressure. Purify the residue by column chromatography on silica gel. Elute the residue with petroleum/ethyl acetate to afford **S-5**.

d-**S-2a** was prepared according the literature[13]: Add $NaBD_4$ (251 mg, 2 equiv) to a solution of **S-5** (3 mmol) in dry-THF (10 mL). Stir the reaction mixture for 3 hours at room temperature. Add saturated NH_4Cl aqueous solution to the reaction mixture. Dilute the resulting mixture with dichloromethane. Wash the reaction mixture by water. Dry the combined organic layers with Na_2SO_4. Concentrate the combined organic layers. Purify the product by column chromatography on silica gel.

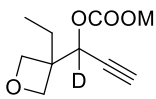
d-**1** was prepared from *d*-**S-2** in the same way as **1**.

methyl (1-phenylprop-2-yn-1-yl-1-d) carbonate (**1a-*d***)



Colorless oil (343 mg), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 60 %. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.61 – 7.52 (m, 1H), 7.44 – 7.35 (m, 1H), 3.81 (s, 2H), 2.74 (s, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 154.9, 135.8, 129.4, 128.8, 127.8, 79.6, 76.5, 69.7 – 68.3 (m), 55.2. **IR** (KBr, cm^{-1}): 3291, 3031, 2960, 2855, 2199, 2124, 1962, 1752, 1493, 1446, 1401, 1282, 1112, 1077, 1006, 952, 913, 792, 757, 692, 520, 440. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_9DNaO_3$ 214.0585; found 214.0584.

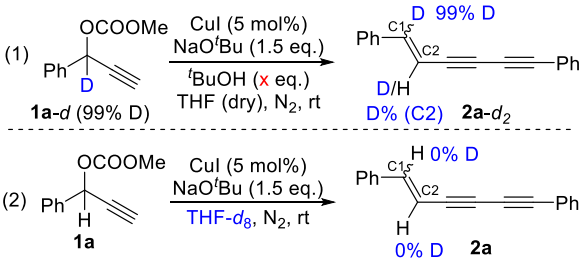
1-(3-ethyloxetan-3-yl)prop-2-yn-1-yl-1-d methyl carbonate (**1r-*d***)



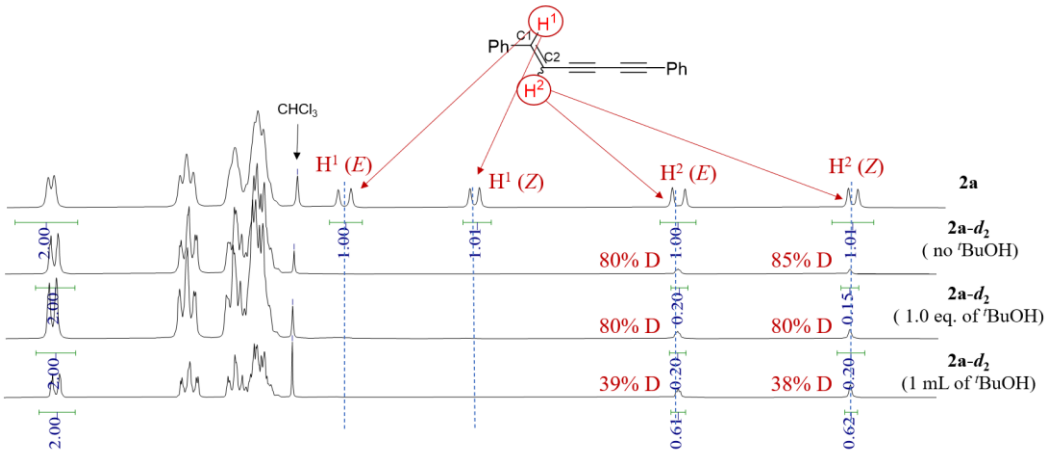
Colorless oil (424 g), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 71 %.**1H NMR** (400 MHz, Chloroform-d) δ 4.63 – 4.55 (m, 2H), 4.36 (dd, J = 6.3, 4.4 Hz, 2H), 3.80 (s, 3H), 2.55 (s, 1H), 1.84 (qd, J = 7.4, 2.2 Hz, 2H), 0.99 (t, J

= 7.5 Hz, 3H). **13C NMR** (101 MHz, Chloroform-d) δ 155.06, 77.88, 76.30, 76.07, 75.82, 70.34 – 69.34 (m), 55.27, 45.71, 25.89, 8.19. **IR** (KBr, cm^{-1}): 3290, 2953, 2882, 2122, 1756, 1450, 1266, 1107, 976, 831, 790, 688, 470. **HRMS** (ESI) m/z: [M+H]+ Calcd for $C_{10}H_{13}DO_4$ 200.1028; found 200.1029.

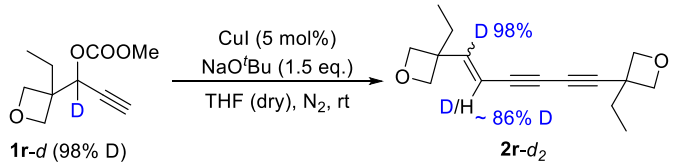
2-d_2 was synthesized according to general procedure for **2**

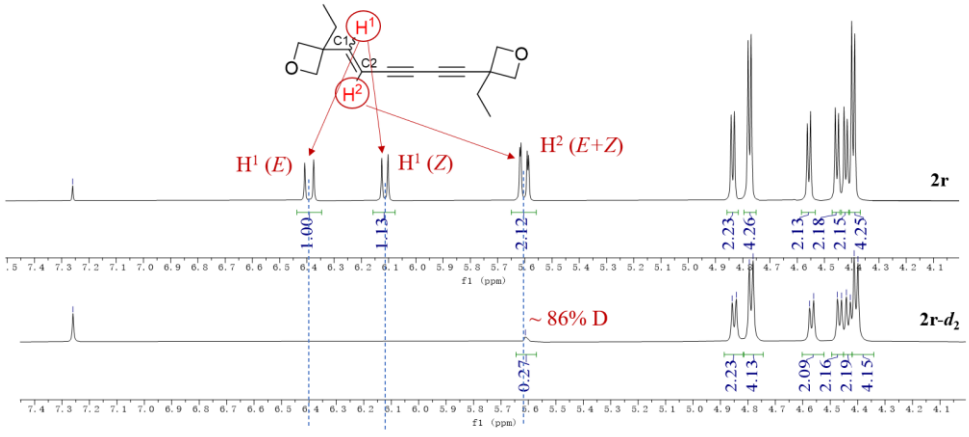


entry	x	yield	D% (C2) *E*-iso	D% (C2) *Z*-iso
a	0	75%	80%	85%
b	1.0	71%	80%	80%
c	52[a]	19%	39%	38%



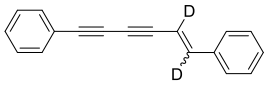
Deuterium-labelling experiment for **1a**-*d*





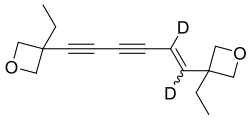
Deuterium-labelling experiment for **1r**-*d*

(*E*/*Z*)-(hexa-1-en-3,5-diyne-1,6-diyl-d2)dibenzene (**2a**-d_2)



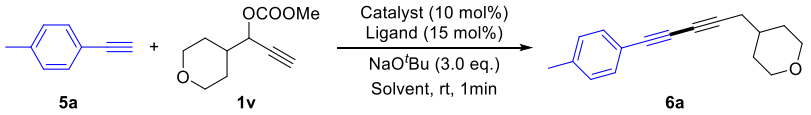
White solid (17.3 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 75%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 – 7.85 (m, 2H), 7.58 – 7.49 (m, 4H), 7.44 – 7.39 (m, 4H), 7.39 – 7.30 (m, 10H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.6 – 143.8 (m), 142.2 – 141.4 (m), 136.0, 135.7, 132.52, 132.50, 129.3, 129.2, 128.8, 128.6, 128.52, 128.47, 128.45, 126.5, 121.9, 121.8, 106.7 – 106.1 (m), 105.8 – 105.2 (m), 83.5, 82.2, 81.3, 80.4, 80.2, 76.1, 74.22, 74.17. **IR** (KBr, cm^{-1}): 3054, 2921, 2855, 2207, 1959, 1890, 1750, 1576, 1490, 1446, 1330, 1262, 1183, 1074, 1026, 915, 750, 694, 615, 521. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{11}D_2$ 231.1137; found 231.1137.

(*E*/*Z*)-3,3'-(hexa-1-en-3,5-diyne-1,6-diyl-d2)bis(3-ethyloxetane) (**2r**-d_2)



White solid (15.5 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 63%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.85 (d, *J* = 5.8 Hz, 2H), 4.79 (d, *J* = 5.5 Hz, 2H), 4.57 (d, *J* = 5.8 Hz, 2H), 4.47 (d, *J* = 5.8 Hz, 2H), 4.43 (d, *J* = 5.9 Hz, 2H), 4.41 (d, *J* = 5.5 Hz, 4H), 2.07 – 2.00 (m, 2H), 1.97 (q, *J* = 7.4 Hz, 4H), 1.86 (q, *J* = 7.4 Hz, 2H), 1.01 (td, *J* = 7.3, 1.9 Hz, 6H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 149.81 – 149.42 (m), 149.42 – 149.03 (m), 108.61 – 108.31 (m), 108.28 – 107.80 (m), 85.76, 84.24, 80.90, 80.85, 80.25, 79.57, 76.04, 74.27, 73.87, 69.04, 68.78, 46.30, 46.08, 39.19, 39.17, 31.75, 31.34, 31.31, 30.33, 29.82, 9.39, 8.91, 8.67. **IR** (KBr, cm^{-1}): 3129, 2967, 2877, 1724, 1611, 1401, 1154, 985, 822, 753, 530. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}D_2O_2$ 247.1662; found 247.1660.

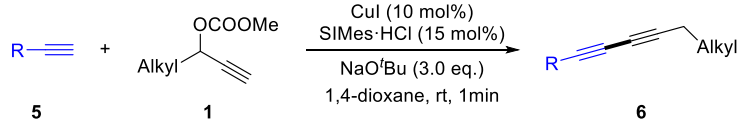
1.8. Optimization for 1,3-diynes[a]



Entry	Catalyst (10mol%)	Liangd (15 mol%)	Solvent (2 mL)	Yield (%)[b]
1	SIMesCuCl	-	THF	68
2	CuI	SIMes•HCl	THF	75
3	CuI	Xantphos	THF	trace
4	CuI	2,2'-Bipyridine	THF	trace
5	CuI	6,6'-Dimethyl-2,2'-dipyridyl	THF	trace
6	CuI	SIMes•HCl	DCE	0
7	CuI	SIMes•HCl	CH_3CN (dry)	46
8	CuI	SIMes•HCl	toluene	47
9	CuI	SIMes•HCl	1,4-Dioxane	81
10	CuI	SIMes•HCl	MTBE (dry)	46
11[c]	CuI	SIMes•HCl	1,4-Dioxane	65

[a]Reaction conditions: **5b** (0.1 mmol), **1v** (1.5 equiv), catalyst (10 mol%), ligand (15 mol%), NaO^{t}Bu (3.0 equiv), 2 mL of solvent, 25 ° C. [b]Isolated yield. [c]**1v** (1.2 equiv)

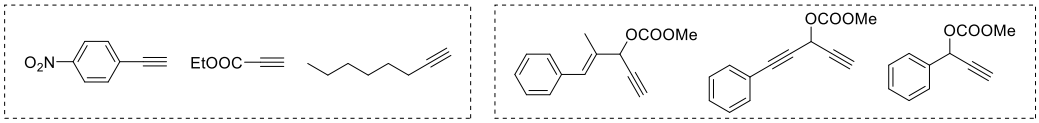
1.9. General procedure for 6



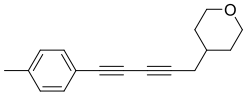
5 1 6

To a 25 mL Schlenk tube with a magnetic bar under nitrogen atmosphere was added CuI (3.8mg, 10 mol%), SIMes·HCl (5.2 mg, 15 mol%), dry-1,4-Dioxane (0.7 mL), NaO^{t}Bu (1.0 M in THF, 300 μL) and **6** (0.1 mmol, 1 equiv) sequentially at room temperature (about 25 °C) and the mixture was stired for 15 min. Solution of **1** (0.2 mmol) in 1 mL dry-1,4-Dioxane was dropped to the mixture within 1 min. After the drop was finished, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel to afford the pure product **2**.

Failed substrates were listed below:



4-(5-(p-tolyl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6a**)

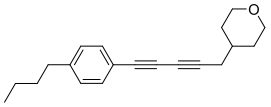


White solid (19.3 mg), m.p. = 67-69 °C, purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 81%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 3.98 (dd, *J* = 11.3, 4.2 Hz, 2H), 3.39 (td, *J* = 11.9, 1.8 Hz, 2H), 2.36 – 2.29 (m, 5H), 1.80 (ddt, *J* = 13.2, 6.5, 3.2 Hz, 1H), 1.75 – 1.70 (m, 2H), 1.41 (qd, *J* = 12.8, 12.3, 4.5 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 139.3, 132.5, 129.3, 118.9, 82.2, 75.4, 73.7, 67.9, 66.7, 34.7, 32.5, 27.0, 21.7. **IR** (KBr, cm^{-1}): 3042, 2926, 2848, 2760, 2233, 2149, 1943, 1720, 1597, 1444, 1377, 1265, 1199, 1125, 1089, 1017, 896, 847, 785, 742, 690, 522, 443. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}O$ 239.1431; found 239.1428.

4-(5-phenylpenta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6b**)

White solid (18.4 mg), m.p. = 69-71 °C, purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 82%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.50 – 7.44 (m, 2H), 7.36 – 7.27 (m, 3H), 3.98 (dd, *J* = 11.3, 4.1 Hz, 2H), 3.39 (td, *J* = 11.9, 1.7 Hz, 2H), 2.32 (d, *J* = 6.6 Hz, 2H), 1.79 (ddd, *J* = 14.7, 7.5, 3.9 Hz, 1H), 1.73 (d, *J* = 13.5 Hz, 2H), 1.41 (qd, *J* = 12.3, 4.5 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 132.6, 129.0, 128.5, 122.1, 82.6, 75.2, 74.3, 67.8, 66.6, 34.7, 32.5, 27.0. **IR** (KBr, cm^{-1}): 3060, 2925, 2846, 2759, 2705, 2238, 1964, 1721, 1605, 1484, 1441, 1376, 1265, 1125, 1085, 1017, 981, 922, 846, 755, 692, 615, 522, 462. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}O$ 225.1274; found 225.1270.

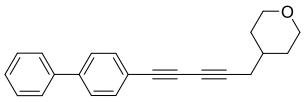
4-(5-(4-butylphenyl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6c**)



Colorless oil (25.3 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 90%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 3.98 (dd, *J* = 11.2, 4.2 Hz, 2H), 3.39 (td, *J* = 11.9, 1.8 Hz, 2H), 2.63 – 2.55 (m, 2H), 2.32 (d, *J* = 6.5 Hz, 2H), 1.80 (ddt, *J* = 13.2, 6.5, 3.2 Hz, 1H), 1.76 – 1.70 (m, 2H), 1.61 – 1.51 (m, 2H), 1.48 – 1.38 (m, 2H), 1.37 – 1.30 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.3, 132.5, 128.6, 119.1, 82.1, 75.5, 73.7, 67.9, 66.8, 35.8, 34.7, 33.4, 32.5, 27.0, 22.4, 14.0. **IR** (KBr, cm^{-1}): 3033, 2927, 2855, 2760, 2207, 1915, 1720, 1609, 1507,

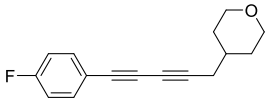
1454, 1377, 1266, 1183, 1124, 1088, 1016, 981, 892, 838, 611, 544, 475. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{25}O$ 281.1900; found 281.1897.

4-(5-([1,1'-biphenyl]-4-yl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6d**)



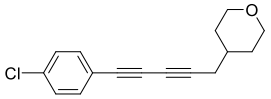
White solid (27.0 mg), m.p. = 95-97 °C, purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 90%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.63 – 7.51 (m, 5H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 4.00 (dd, *J* = 11.3, 3.9 Hz, 3H), 3.45 – 3.36 (m, 3H), 2.35 (d, *J* = 6.6 Hz, 2H), 1.81 (ddq, *J* = 15.3, 8.8, 4.4, 3.8 Hz, 1H), 1.77 – 1.72 (m, 3H), 1.44 (qd, *J* = 12.3, 4.4 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.8, 140.3, 133.1, 129.0, 127.9, 127.2 (d, *J* = 2.4 Hz), 121.0, 75.1, 75.0, 67.9, 66.7, 34.8, 32.6, 27.1. **IR** (KBr, cm^{-1}): 3048, 2923, 2845, 1915, 1583, 1444, 1375, 1270, 1129, 1087, 1008, 839, 764, 722, 698, 560, 516. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}O$ 301.1587; found 301.1584.

4-(5-(4-fluorophenyl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6e**)



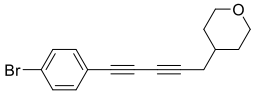
White solid (18.4 mg), m.p. = 73-75 °C, purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 76%.**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 3.98 (dd, *J* = 11.4, 4.1 Hz, 2H), 3.42 – 3.34 (m, 2H), 2.32 (d, *J* = 6.6 Hz, 2H), 1.79 (ddq, *J* = 15.3, 8.7, 4.0 Hz, 1H), 1.72 (d, *J* = 13.5 Hz, 2H), 1.41 (qd, *J* = 12.3, 4.5 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 163.0 (d, *J* = 251.0 Hz), 134.6 (d, *J* = 8.5 Hz), 118.2 (d, *J* = 3.6 Hz), 115.9 (d, *J* = 22.2 Hz), 82.6, 74.1, 67.9, 66.5, 66.3, 34.7, 32.5, 27.0. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -109.18. **IR** (KBr, cm^{-1}): 3059, 2927, 2851, 2762, 2709, 2560, 2444, 2239, 2151, 1895, 1721, 1646, 1595, 1440, 1377, 1265, 1226, 1144, 1122, 1083, 1016, 980, 892, 838, 734, 599, 524, 467. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}FO$ 243.1180; found 243.1177.

4-(5-(4-chlorophenyl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6f**)



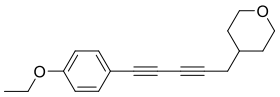
White solid (22.3 mg), m.p. = 90-91 °C, purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 86%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.98 (dd, *J* = 11.4, 4.0 Hz, 2H), 3.39 (t, *J* = 11.2 Hz, 2H), 2.33 (d, *J* = 6.5 Hz, 2H), 1.86 – 1.75 (m, 1H), 1.73 (d, *J* = 13.6 Hz, 2H), 1.42 (qd, *J* = 12.3, 4.4 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.2, 133.8, 128.9, 120.7, 83.2, 75.4, 74.0, 67.9, 66.5, 34.7, 32.5, 27.1. **IR** (KBr, cm^{-1}): 2925, 2847, 2241, 1585, 1482, 1395, 1270, 1130, 1086, 1012, 891, 830, 526, 472. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}ClO$ 259.0884; found 259.0884.

4-(5-(4-bromophenyl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6g**)



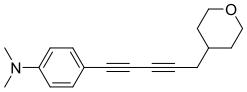
White solid (26.9 mg), m.p. = 98-100 °C, purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 89%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.98 (dd, *J* = 11.3, 4.1 Hz, 2H), 3.42 – 3.35 (m, 2H), 2.32 (d, *J* = 6.6 Hz, 2H), 1.80 (tdt, *J* = 11.3, 8.6, 4.1 Hz, 1H), 1.72 (d, *J* = 13.3 Hz, 2H), 1.41 (qd, *J* = 12.3, 4.5 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.0, 131.8, 123.5, 121.1, 83.3, 75.5, 74.0, 67.9, 66.5, 34.7, 32.5, 27.1. **IR** (KBr, cm^{-1}): 3129, 3063, 2925, 2845, 2236, 1629, 1580, 1477, 1390, 1299, 1231, 1124, 1077, 1003, 979, 827, 724, 523. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}BrO$ 303.0379; found 303.0376.

4-(5-(4-ethoxyphenyl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6h**)



Colorless oil (18.3 mg), purified by chromatography (petroleum/ethyl acetate = 15/1), yield = 68%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.06 – 3.93 (m, 4H), 3.38 (td, *J* = 11.9, 1.6 Hz, 2H), 2.31 (d, *J* = 6.5 Hz, 2H), 1.78 (dq, *J* = 9.9, 3.0, 2.5 Hz, 1H), 1.72 (d, *J* = 13.3 Hz, 2H), 1.39 (t, *J* = 6.9 Hz, 5H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.6, 134.2, 114.7, 113.7, 81.8, 75.4, 73.0, 67.9, 66.8, 63.6, 34.7, 32.5, 27.0, 14.8. **IR** (KBr, cm^{-1}): 3071, 2928, 2846, 2760, 2703, 2238, 2151, 1939, 1723, 1580, 1481, 1436, 1373, 1264, 1197, 1129, 1089, 983, 931, 864, 785, 679, 611, 520, 450. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}O_2$ 269.1536; found 269.1533.

N, N-dimethyl-4-(5-(tetrahydro-2H-pyran-4-yl)penta-1,3-diyn-1-yl)aniline (**6i**)



White solid (16.1 mg), m.p. = 102-104 ºC, purified by chromatography (petroleum/ethyl acetate = 5/1), yield = 60%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 3.98 (dd, *J* = 11.3, 4.0 Hz, 2H), 3.38 (t, *J* = 11.1 Hz, 2H), 2.97 (s, 6H), 2.31 (d, *J* = 6.5 Hz, 2H), 1.79 (ddt, *J* = 13.3, 6.5, 3.2 Hz, 1H), 1.73 (d, *J* = 13.4 Hz, 2H), 1.41 (qd, *J* = 12.3, 4.4 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.6, 133.9, 111.8, 108.3, 81.4, 72.4, 67.9, 67.2, 40.2, 34.9, 32.6, 27.1. **IR** (KBr, cm^{-1}): 3043, 2923, 2844, 2708, 2233, 2140, 1887, 1684, 1607, 1526, 1451, 1368, 1299, 1227, 1197, 1120, 1015, 981, 944, 817, 735, 644, 585, 531, 476. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}NO$ 268.1696; found 268.1697.

4-(5-(o-tolyl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6j**)

Colorless oil (20.1 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 84%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 3.99 (dd, *J* = 11.5, 4.5 Hz, 2H), 3.39 (td, *J* = 11.9, 1.9 Hz, 2H), 2.45 (s, 3H), 2.34 (d, *J* = 6.5 Hz, 2H), 1.82 (ddt, *J* = 13.2, 6.6, 3.2 Hz, 1H), 1.77 – 1.71 (m, 2H), 1.48 – 1.35 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.7, 133.1, 129.6, 129.0, 125.7, 121.9, 83.0, 77.9, 74.2, 67.9, 66.7, 34.7, 32.5, 27.1, 20.8. **IR** (KBr, cm^{-1}): 2925, 2846, 2760, 2203, 1720, 1650, 1450, 1396, 1266, 1127, 1085, 1016, 980, 849, 756, 657, 536, 444. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}O$ 239.1431; found 239.1427.

4-(5-(2-fluorophenyl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6k**)

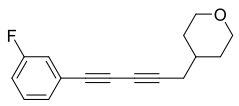
Colorless oil (21.8 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 90%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.49 – 7.42 (m, 1H), 7.35 – 7.27 (m, 1H), 7.11 – 7.02 (m, 2H), 3.98 (dd, *J* = 11.3, 4.0 Hz, 2H), 3.43 – 3.34 (m, 2H), 2.33 (d, *J* = 6.6 Hz, 2H), 1.80 (dtt, *J* = 15.3, 8.6, 4.0 Hz, 1H), 1.73 (d, *J* = 13.3 Hz, 2H), 1.41 (qd, *J* = 12.3, 4.5 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 164.0 (d, *J* = 253.0 Hz), 134.5, 130.7 (d, *J* = 8.0 Hz), 124.1 (d, *J* = 3.8 Hz), 115.7 (d, *J* = 20.7 Hz), 110.9 (d, *J* = 15.6 Hz), 83.8, 79.2 (d, *J* = 3.1 Hz), 68.4, 67.9, 66.5, 34.7, 32.5, 27.1. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -109.06. **IR** (KBr, cm^{-1}): 3049, 2924, 2845, 2758, 2243, 1726, 1571, 1490, 1449, 1374, 1299, 1261, 1219, 1125, 1086, 1016, 980, 911, 847, 796, 751, 656, 575, 450. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}FO$ 243.1180; found 243.1176.

4-(5-(m-tolyl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6l**)

Colorless oil (19.4 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 81%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 2H), 7.17 (dt, *J* = 14.3, 7.6 Hz, 2H), 3.98 (dd, *J* = 11.2, 4.2 Hz, 2H), 3.38 (td, *J* =

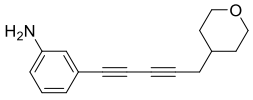
11.9, 1.9 Hz, 2H), 2.33 – 2.27(m, 5H), 1.81 (ddd, *J* = 15.2, 7.2, 3.9 Hz, 1H), 1.76 – 1.69 (m, 2H), 1.41 (qd, *J* = 12.8, 12.3, 4.5 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.2, 133.1, 130.0, 129.7, 128.4, 121.8, 82.3, 75.4, 74.0, 67.9, 66.7, 34.7, 32.5, 27.0, 21.3. **IR** (KBr, cm^{-1}): 3042, 2926, 2848, 2760, 2233, 2149, 1943, 1720, 1597, 1444, 1377, 1265, 1199, 1125, 1089, 1017, 896, 847, 785, 742, 690, 522, 443. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}O$ 239.1431; found 239.1430.

4-(5-(3-fluorophenyl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6m**)



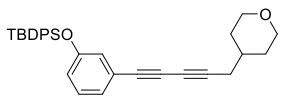
Colorless oil (18.7 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 77%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.28 – 7.23 (m, 2H), 7.15 (d, *J* = 9.6 Hz, 1H), 7.08 – 7.01 (m, 1H), 3.99 (dd, *J* = 11.3, 4.1 Hz, 2H), 3.39 (td, *J* = 11.9, 1.5 Hz, 2H), 2.33 (d, *J* = 6.6 Hz, 2H), 1.80 (dtt, *J* = 15.3, 8.6, 4.1 Hz, 1H), 1.75 – 1.70 (m, 2H), 1.42 (qd, *J* = 12.3, 4.5 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 247.1 Hz), 130.1 (d, *J* = 8.6 Hz), 128.5 (d, *J* = 3.1 Hz), 124.0 (d, *J* = 9.5 Hz), 119.3 (d, *J* = 23.0 Hz), 116.5 (d, *J* = 21.2 Hz), 83.4, 75.2, 73.7 (d, *J* = 3.5 Hz), 67.8, 66.4, 34.7, 32.5, 27.0. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -112.52. **IR** (KBr, cm^{-1}): 3069, 2926, 2845, 2759, 2706, 2239, 2150, 1939, 1726, 1604, 1506, 1476, 1435, 1386, 1249, 1185, 1123, 1101, 1045, 981, 927, 839, 787, 733, 680, 615, 527, 461. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}FO$ 243.1180; found 243.1177.

3-(5-(tetrahydro-2H-pyran-4-yl)penta-1,3-diyn-1-yl)aniline (**6n**)



White solid (22.5 mg), m.p. = 104-106 °C, purified by chromatography (petroleum/ethyl acetate = 3/1), yield = 94%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.65 (t, *J* = 8.8 Hz, 2H), 4.26 (s, 2H), 3.99 (dd, *J* = 11.3, 3.7 Hz, 3H), 3.39 (t, *J* = 11.3 Hz, 2H), 2.34 (d, *J* = 6.5 Hz, 2H), 1.80 (ddt, *J* = 15.3, 11.3, 5.6 Hz, 1H), 1.73 (d, *J* = 13.7 Hz, 2H), 1.42 (qd, *J* = 12.4, 4.4 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.7, 133.3, 130.4, 118.0, 114.5, 106.5, 83.6, 79.4, 72.2, 67.9, 66.6, 34.7, 32.5, 27.1. **IR** (KBr, cm^{-1}): 3345, 3034, 2925, 2848, 2761, 2238, 2144, 1927, 1688, 1618, 1491, 1451, 1368, 1311, 1257, 1127, 1086, 1018, 981, 892, 845, 751, 654, 609, 483. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}NO$ 240.1383; found 240.1383.

tert-butyldiphenyl(3-(5-(tetrahydro-2H-pyran-4-yl)penta-1,3-diyn-1-yl)phenoxy)silane (**6o**)



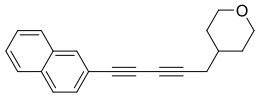
Colorless oil (38.2 mg), purified by chromatography (petroleum/ethyl acetate = 50/1), yield = 80%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.72 – 7.68 (m, 4H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 4H), 7.03 – 6.95 (m, 3H), 6.72 – 6.67 (m, 1H), 3.99 (dd, *J* = 11.3, 4.0 Hz, 2H), 3.39 (t, *J* = 11.2 Hz, 2H), 2.31 (d, *J* = 6.5 Hz, 2H), 1.79 (ddt, *J* = 14.4, 6.9, 3.8 Hz, 1H), 1.73 (d, *J* = 13.8 Hz, 2H), 1.41 (qd, *J* = 12.3, 4.4 Hz, 2H), 1.10 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.5, 135.6, 132.6, 130.2, 129.3, 128.0, 125.7, 123.7, 122.9, 121.1, 82.5, 75.0, 74.0, 67.9, 66.6, 34.7, 32.5, 27.0, 26.6, 19.6. **IR** (KBr, cm^{-1}): 3133, 2937, 2853, 2241, 1585, 1477, 1422, 1316, 1271, 1224, 1111, 971, 835, 786, 701, 614, 499. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{34}NaO_2Si$ 501.2220; found 501.2216.

4-(5-(naphthalen-1-yl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6p**)

White solid (25.2 mg), m.p. = 64-66 °C, purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 92%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 8.3 Hz, 1H), 7.84 (dd, *J* = 8.0, 2.9 Hz, 2H), 7.73 (d, *J* = 7.1 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 4.01 (dd, *J* = 11.3, 4.0 Hz, 2H), 3.41 (td, *J* = 11.9, 1.6 Hz, 2H), 2.39 (d, *J* = 6.6 Hz, 2H), 1.84 (dddd, *J* = 15.3, 11.3, 7.8, 4.0 Hz, 1H), 1.77

(d, *J* = 13.4 Hz, 2H), 1.46 (qd, *J* = 12.2, 4.4 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.1, 133.2, 132.1, 129.5, 128.5, 127.2, 126.7, 126.2, 125.3, 119.8, 83.7, 79.0, 73.5, 67.9, 66.8, 34.8, 32.6, 27.2. **IR** (KBr, cm^{-1}): 3132, 2924, 2843, 2760, 2235, 1935, 1628, 1585, 1504, 1400, 1265, 1203, 1127, 1086, 1014, 978, 848, 802, 769, 740, 560, 425. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}O$ 275.1431; found 275.1427.

4-(5-(naphthalen-2-yl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6q**)



White solid (25.8 mg), m.p. = 82-84 °C, purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 94%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.83 – 7.74 (m, 3H), 7.49 (dd, *J* = 6.3, 3.3 Hz, 3H), 4.00 (dd, *J* = 11.3, 3.9 Hz, 3H), 3.44 – 3.36 (m, 3H), 2.36 (s, 1H), 1.81 (tdt, *J* = 11.3, 8.7, 3.6 Hz, 2H), 1.75 (d, *J* = 13.6 Hz, 3H), 1.44 (qd, *J* = 12.3, 4.5 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 133.2, 133.04, 132.95, 128.7, 128.2, 127.91, 127.88, 127.2, 126.8, 119.4, 82.9, 75.6, 74.7, 67.9, 66.8, 34.8, 32.5, 27.1. **IR** (KBr, cm^{-1}): 3056, 2924, 2844, 2757, 2704, 2237, 2148, 1924, 1724, 1629, 1596, 1500, 1435, 1374, 1298, 1265, 1232, 1202, 1127, 1087, 1015, 980, 894, 854, 817, 744, 597, 508, 472. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}O$ 275.1431; found 275.1427.

4-(5-(thiophen-2-yl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6r**)

Colorless oil (19.8 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 86%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.27 (dd, *J* = 9.6, 4.0 Hz, 2H), 6.96 (dd, *J* = 5.0, 3.8 Hz, 1H), 3.98 (dd, *J* = 11.3, 4.1 Hz, 2H), 3.39 (td, *J* = 11.9, 1.7 Hz, 2H), 2.34 (d, *J* = 6.6 Hz, 2H), 1.80 (tdt, *J* = 11.3, 8.6, 4.0 Hz, 1H), 1.73 (d, *J* = 13.2 Hz, 2H), 1.41 (qd, *J* = 12.3, 4.5 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.1, 128.3, 127.2, 122.4, 84.8, 78.4, 68.2, 67.9, 66.5, 34.7, 32.5, 27.1. **IR** (KBr, cm^{-1}): 3100, 2924, 2844, 2757, 2705, 2231, 2149, 1725, 1628, 1429, 1373, 1298, 1266, 1207, 1126, 1087, 1017, 980, 893, 845, 706, 612, 513, 457. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}OS$ 231.0838; found 231.0835.

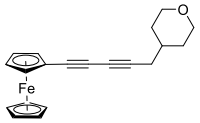
4-(5-(thiophen-3-yl)penta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6s**)

Colorless oil (20.7 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 90%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 2.2 Hz, 1H), 7.25 (dt, *J* = 4.9, 2.9 Hz, 1H), 7.12 (d, *J* = 4.5 Hz, 1H), 3.98 (dd, *J* = 11.3, 4.1 Hz, 2H), 3.39 (td, *J* = 11.9, 1.6 Hz, 2H), 2.32 (d, *J* = 6.6 Hz, 2H), 1.79 (dddd, *J* = 15.3, 11.3, 7.7, 4.0 Hz, 1H), 1.73 (d, *J* = 13.4 Hz, 2H), 1.41 (qd, *J* = 12.3, 4.5 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 131.0, 130.3, 125.6, 121.2, 82.4, 74.0, 70.4, 67.9, 66.6, 34.7, 32.5, 27.0. **IR** (KBr, cm^{-1}): 3104, 2924, 2844, 2758, 2705, 2239, 2150, 1722, 1577, 1431, 1360, 1300, 1264, 1233, 1202, 1125, 1087, 1015, 981, 932, 842, 785, 695, 620, 516. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}OS$ 231.0838; found 231.0835.

3-(5-(tetrahydro-2H-pyran-4-yl)penta-1,3-diyn-1-yl)pyridine (**6t**)

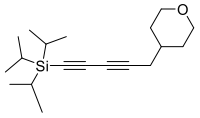
Yellow oil (80 mg), purified by chromatography (petroleum/ethyl acetate = 10/1), yield = 80%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.71 (s, 1H), 8.56 (s, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.22 (m, 2H), 3.99 (dd, *J* = 11.3, 4.0 Hz, 3H), 3.40 (td, *J* = 11.9, 1.5 Hz, 3H), 2.35 (d, *J* = 6.6 Hz, 2H), 1.81 (dddt, *J* = 18.0, 10.7, 6.6, 4.0 Hz, 2H), 1.74 (d, *J* = 13.2 Hz, 3H), 1.43 (qd, *J* = 12.3, 4.5 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 153.3, 149.0, 139.5, 123.2, 84.0, 77.7, 71.7, 67.8, 66.2, 34.7, 32.5, 27.0. **IR** (KBr, cm^{-1}): 3037, 2924, 2845, 2758, 2705, 2244, 1707, 1565, 1472, 1418, 1374, 1264, 1198, 1125, 1087, 1018, 981, 893, 846, 805, 702, 619, 515, 451. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}NO$ 226.1226; found 226.1226.

4-(5-ferrocenyl -2,4-diyn-1-yl)tetrahydro-2H-pyran (**6u**)



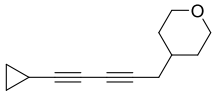
Orange solid (24.0 mg), m.p. = 95-97 °C, purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 72%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 4.22 (d, *J* = 9.5 Hz, 3H), 3.98 (dd, *J* = 11.2, 3.8 Hz, 1H), 3.39 (t, *J* = 11.2 Hz, 1H), 2.28 (d, *J* = 6.5 Hz, 1H), 1.83 – 1.75 (m, 1H), 1.73 (d, *J* = 13.2 Hz, 1H), 1.41 (qd, *J* = 12.4, 4.4 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 79.7, 75.2, 72.3, 70.6, 70.2, 69.2, 67.9, 67.3, 63.6, 34.7, 32.6, 27.1. **IR** (KBr, cm^{-1}): 3096, 2925, 2844, 2758, 2703, 2233, 2151, 1688, 1446, 1370, 1271, 1207, 1125, 1093, 1012, 913, 824, 609, 490. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}FeO$ 333.0936; found 333.0938.

triisopropyl(5-(tetrahydro-2H-pyran-4-yl)penta-1,3-diyn-1-yl)silane (**6v**)



Colorless oil (24.6 mg), purified by chromatography (petroleum/ethyl acetate = 80/1), yield = 80%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.97 (dd, *J* = 11.4, 3.9 Hz, 2H), 3.43 – 3.32 (m, 2H), 2.24 (d, *J* = 6.5 Hz, 2H), 1.77 (dq, *J* = 10.6, 3.8 Hz, 1H), 1.71 (d, *J* = 13.1 Hz, 2H), 1.38 (qd, *J* = 13.2, 12.5, 4.5 Hz, 2H), 1.07 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 90.0, 80.6, 76.6, 67.9, 67.4, 34.6, 32.6, 26.8, 18.7, 11.5. **IR** (KBr, cm^{-1}): 2947, 2862, 2757, 2718, 2223, 2104, 1983, 1734, 1630, 1460, 1376, 1299, 1239, 1183, 1128, 1085, 1002, 923, 884, 849, 810, 756, 670, 597, 481. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{33}OSi$ 305.2295; found 305.2292.

4-(5-cyclopropylpenta-2,4-diyn-1-yl)tetrahydro-2H-pyran (**6w**)

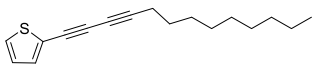


Colorless oil (10.0 mg), purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 53%. **^{1}H NMR** (500 MHz,) δ 3.97 – 3.92 (m, 2H), 3.39 – 3.31 (m, 2H), 2.22 – 2.17 (m, 2H), 1.70 – 1.64 (m, 3H), 1.42 – 1.22 (m, 3H), 0.89 – 0.64 (m, 4H). **^{13}C NMR** (126 MHz,) δ 81.0, 74.8, 67.9, 67.0, 60.7, 34.7, 32.5, 26.7, 8.8, 0.1. **IR** (KBr, cm^{-1}): 3012, 2925, 2843, 2758, 2259, 2150, 1437, 1374, 1300, 1234, 1127, 1087, 1020, 982, 935, 844, 816, 723, 512. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}O$ 189.1274; found 189.1272.

4-(7-(4-methoxyphenyl)hepta-2,4,6-triyn-1-yl)tetrahydro-2H-pyran (**6x**)

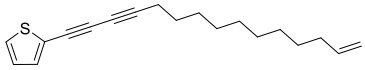
White solid (13.7 mg), m.p. = 75-77 °C, purified by chromatography (petroleum/ethyl acetate = 20/1), yield = 49%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.98 (dd, *J* = 11.5, 4.1 Hz, 2H), 3.81 (s, 3H), 3.38 (t, *J* = 11.7 Hz, 2H), 2.30 (d, *J* = 6.6 Hz, 2H), 1.78 (dtt, *J* = 17.9, 10.9, 4.9 Hz, 1H), 1.71 (d, *J* = 13.4 Hz, 2H), 1.39 (qd, *J* = 12.4, 4.5 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.8, 134.8, 114.4, 113.1, 80.2, 76.1, 73.6, 67.9, 67.3, 66.8, 60.4, 55.5, 34.7, 32.5, 27.0. **IR** (KBr, cm^{-1}): 2922, 2845, 2193, 1601, 1509, 1457, 1365, 1294, 1252, 1170, 1091, 1027, 833, 738, 574, 531. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{18}NaO_2$ 301.1199; found 301.1201.

2-(trideca-1,3-diyn-1-yl)thiophene (**6y**)



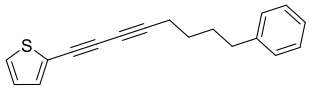
Colorless oil (21.3 mg), purified by chromatography (petroleum/ethyl acetate =100/1), yield = 82%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 2H), 6.95 (dd, *J* = 5.1, 3.7 Hz, 1H), 2.36 (t, *J* = 7.0 Hz, 2H), 1.57 (p, *J* = 7.0 Hz, 2H), 1.45 – 1.37 (m, 2H), 1.29 (d, *J* = 10.7 Hz, 10H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 133.9, 128.1, 127.1, 122.6, 87.3, 78.7, 67.8, 65.1, 32.0, 29.6, 29.4, 29.2, 29.0, 28.4, 22.8, 19.8, 14.3. **IR** (KBr, cm^{-1}): 3128, 2927, 2858, 2232, 2151, 1625, 1456, 1401, 1296, 1206, 1153, 1088, 965, 846, 766, 702, 534. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}S$ 259.1515; found 259.1514.

2-(pentadeca-14-en-1,3-diyn-1-yl)thiophene (**6z**)



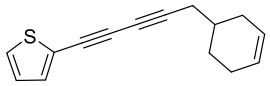
Colorless oil (24.4 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 86%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.29 – 7.23 (m, 2H), 6.95 (t, *J* = 4.1 Hz, 1H), 5.87 – 5.75 (m, 1H), 4.99 (d, *J* = 17.1 Hz, 1H), 4.93 (d, *J* = 10.2 Hz, 1H), 2.36 (t, *J* = 7.0 Hz, 2H), 2.04 (q, *J* = 6.8 Hz, 2H), 1.56 (q, *J* = 7.5 Hz, 2H), 1.42 – 1.36 (m, 4H), 1.29 (s, 8H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 139.4, 134.0, 128.1, 127.1, 122.6, 114.3, 87.3, 78.6, 67.8, 65.1, 34.0, 29.8, 29.56, 29.55, 29.24, 29.20, 29.1, 29.0, 28.3, 19.8. **IR** (KBr, cm^{-1}): 3137, 2926, 2854, 2233, 2148, 1718, 1637, 1401, 1300, 1209, 1086, 990, 908, 842, 791, 704. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{25}S$ 285.1672; found 285.1667.

2-(8-phenylocta-1,3-diyn-1-yl)thiophene (**6aa**)



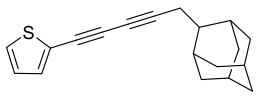
Colorless oil (23.5 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 89%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.27 (dt, *J* = 12.8, 6.3 Hz, 4H), 7.18 (d, *J* = 7.5 Hz, 3H), 6.95 (t, *J* = 4.2 Hz, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.39 (t, *J* = 7.0 Hz, 2H), 1.76 (p, *J* = 8.2, 7.7 Hz, 2H), 1.61 (p, *J* = 7.2 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 142.2, 134.0, 128.6, 128.5, 128.2, 127.1, 126.0, 122.6, 86.8, 78.6, 68.0, 65.3, 35.5, 30.7, 27.9, 19.7. **IR** (KBr, cm^{-1}): 3151, 3026, 2930, 2858, 2149, 1626, 1453, 1324, 1209, 1084, 1033, 966, 843, 702, 621, 479. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{16}NaS$ 287.0865; found 287.0865.

2-(5-(cyclohex-3-en-1-yl)penta-1,3-diyn-1-yl)thiophene (**6ab**)



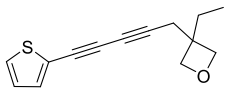
Colorless oil (18.6 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 82%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.26 (dd, *J* = 11.0, 3.9 Hz, 2H), 6.96 (t, *J* = 4.0 Hz, 1H), 5.65 (d, *J* = 14.6 Hz, 2H), 2.43 – 2.31 (m, 2H), 2.19 (d, *J* = 15.9 Hz, 1H), 2.08 (s, 2H), 1.83 (d, *J* = 27.5 Hz, 3H), 1.40 (p, *J* = 9.8, 9.2 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.0, 128.2, 127.1, 127.0, 125.9, 122.6, 85.9, 78.6, 67.9, 66.0, 33.2, 31.2, 28.2, 26.6, 24.9. **IR** (KBr, cm^{-1}): 3138, 3024, 2917, 2840, 2230, 2148, 1635, 1403, 1318, 1267, 1209, 1145, 1088, 1047, 963, 923, 843, 768, 702, 654, 538, 497. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}S$ 227.0889; found 227.0890.

2-(5-((1r,3r,5r,7r)-adamantan-2-yl)penta-1,3-diyn-1-yl)thiophene (**6ac**)



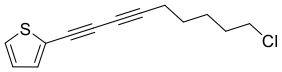
White solid (25.8 mg), m.p. = 97-100 ºC, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 92%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 2H), 6.98 – 6.93 (m, 1H), 2.13 (s, 1H), 2.00 (s, 3H), 1.75 – 1.54 (m, 15H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 133.9, 128.1, 127.1, 122.7, 85.0, 78.8, 67.7, 67.0, 42.2, 36.9, 35.1, 33.6, 28.9. **IR** (KBr, cm^{-1}): 3139, 2906, 2848, 2230, 1624, 1401, 1306, 1205, 1152, 962, 846, 701, 538. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}S$ 281.1359; found 281.1358.

3-ethyl-3-(5-(thiophen-2-yl)penta-2,4-diyn-1-yl)oxetane (**6ad**)



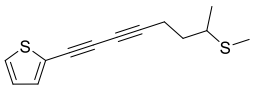
Colorless oil (19.8 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 86%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.28 (dd, *J* = 11.8, 4.5 Hz, 2H), 6.99 – 6.94 (m, 1H), 4.48 – 4.41 (m, 4H), 2.73 (s, 2H), 1.83 (q, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.3, 128.4, 127.2, 122.2, 83.1, 80.1, 78.3, 68.3, 66.8, 42.8, 28.7, 27.0, 8.5. **IR** (KBr, cm^{-1}): 3132, 2967, 2870, 2231, 2149, 1626, 1401, 1295, 1210, 1153, 1091, 979, 841, 774, 706, 618, 477. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}OS$ 231.0838; found 231.0835.

2-(9-chlorononona-1,3-diyn-1-yl)thiophene (**6ae**)



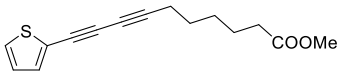
Colorless oil (12.8 mg), purified by chromatography (petroleum/ethyl acetate = 80/1), yield = 54%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 2H), 6.96 (dd, *J* = 5.1, 3.7 Hz, 1H), 3.55 (t, *J* = 6.7 Hz, 2H), 2.40 (t, *J* = 6.6 Hz, 2H), 1.81 (p, *J* = 6.8 Hz, 2H), 1.65 – 1.57 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.1, 128.2, 127.2, 122.5, 86.5, 78.5, 68.1, 65.5, 44.9, 32.2, 27.6, 26.3, 19.8. **IR** (KBr, cm^{-1}): 3132, 2942, 2231, 2149, 1631, 1402, 1209, 1089, 843, 705, 646. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}ClS$ 237.0499; found 237.0499.

2-(7-(methylthio)octa-1,3-diyn-1-yl)thiophene (**6af**)



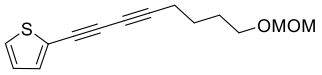
Colorless oil (20.1 mg), purified by chromatography (petroleum/ethyl acetate = 80/1), yield = 86%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.27 (dd, *J* = 10.1, 4.3 Hz, 2H), 6.99 – 6.93 (m, 1H), 2.81 (h, *J* = 6.8 Hz, 1H), 2.63 – 2.46 (m, 2H), 2.08 (s, 3H), 1.78 (ddp, *J* = 21.0, 13.9, 7.0 Hz, 2H), 1.31 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.1, 128.2, 127.2, 122.4, 86.2, 78.5, 68.1, 65.6, 40.2, 34.7, 20.8, 17.7, 13.0. **IR** (KBr, cm^{-1}): 3133, 2966, 2922, 2231, 2149, 1607, 1403, 1210, 1095, 955, 843, 705, 553. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}S_2$ 235.0610; found 235.0608.

methyl 10-(thiophen-2-yl)deca-7,9-diynoate (**6ag**)



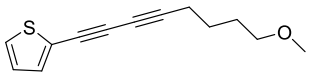
Colorless oil (12.8 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 49%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.26 (dd, *J* = 7.0, 4.6 Hz, 2H), 6.96 (dd, *J* = 5.1, 3.7 Hz, 1H), 3.68 (s, 3H), 2.36 (dt, *J* = 20.9, 7.2 Hz, 4H), 1.70 – 1.63 (m, 2H), 1.59 (q, *J* = 7.0 Hz, 3H), 1.51 – 1.41 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.2, 134.0, 128.2, 127.1, 122.5, 86.7, 78.5, 68.0, 65.4, 51.7, 34.0, 28.4, 28.0, 24.5, 19.7. **IR** (KBr, cm^{-1}): 2939, 1736, 1434, 1364, 1207, 1082, 844, 709, 505. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}OS_2$ 261.0944; found 261.0941.

2-(8-(methoxymethoxy)octa-1,3-diyn-1-yl)thiophene (**6ah**)



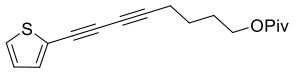
Colorless oil (22.0 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 89%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.27 (dd, *J* = 9.6, 4.4 Hz, 2H), 6.96 (t, *J* = 4.0 Hz, 1H), 4.62 (s, 2H), 3.56 (t, *J* = 6.0 Hz, 2H), 3.37 (s, 3H), 2.42 (t, *J* = 6.6 Hz, 2H), 1.72 (dp, *J* = 22.7, 6.9 Hz, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.0, 128.2, 127.1, 96.6, 86.6, 78.5, 68.0, 67.2, 65.4, 29.0, 25.2, 19.6. **IR** (KBr, cm^{-1}): 2935, 2231, 2149, 1733, 1432, 1375, 1315, 1212, 1148, 1108, 1040, 921, 844, 706. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}O_2S$ 249.0944; found 249.0947.

2-(8-methoxyocta-1,3-diyn-1-yl)thiophene (**6ai**)



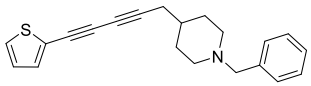
Colorless oil (18.2 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 73%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.29 – 7.23 (m, 2H), 6.98 – 6.93 (m, 1H), 3.40 (t, *J* = 6.1 Hz, 2H), 3.33 (s, 3H), 2.41 (t, *J* = 6.7 Hz, 2H), 1.68 (dh, *J* = 28.0, 6.3 Hz, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.0, 128.2, 127.1, 122.6, 86.7, 78.6, 72.2, 68.0, 65.4, 58.7, 28.8, 25.1, 19.6. **IR** (KBr, cm^{-1}): 3130, 2930, 2803, 2230, 2147, 1626, 1401, 1293, 1204, 1147, 970, 845, 744, 701, 616, 533, 479. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}OS$ 219.0838; found 219.0838.

8-(thiophen-2-yl)octa-5,7-diyn-1-yl pivalate (**6aj**)



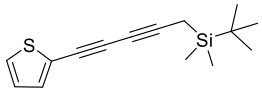
Colorless oil (25.1 mg), purified by chromatography (petroleum/ethyl acetate = 30/1), yield = 87%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 2H), 6.96 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.09 (t, *J* = 6.3 Hz, 2H), 2.43 (t, *J* = 6.9 Hz, 2H), 1.84 – 1.74 (m, 2H), 1.65 (dt, *J* = 14.1, 6.9 Hz, 2H), 1.21 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.7, 134.1, 128.2, 127.2, 122.4, 86.2, 78.5, 68.1, 65.6, 63.8, 38.9, 27.9, 27.3, 24.9, 19.5. **IR** (KBr, cm^{-1}): 3105, 2966, 2232, 2151, 1726, 1538, 1469, 1368, 1284, 1158, 1091, 1042, 945, 895, 845, 777, 708, 635, 597, 505. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}O_2S$ 289.1257; found 289.1254.

1-benzyl-4-(5-(thiophen-2-yl)penta-2,4-diyn-1-yl)piperidine (**6ak**)



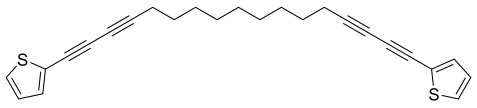
Yellow oil (23.0 mg), purified by chromatography (petroleum/ethyl acetate = 4/1), yield = 72%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 4.3 Hz, 4H), 7.26 (dd, *J* = 11.1, 4.2 Hz, 3H), 6.98 – 6.92 (m, 1H), 3.49 (s, 2H), 2.89 (d, *J* = 11.5 Hz, 2H), 2.31 (d, *J* = 6.6 Hz, 2H), 1.96 (t, *J* = 11.0 Hz, 2H), 1.76 (d, *J* = 12.6 Hz, 2H), 1.55 (ddt, *J* = 11.0, 8.0, 3.8 Hz, 1H), 1.38 (qd, *J* = 12.7, 3.9 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 138.6, 134.0, 129.3, 128.3, 128.2, 127.13, 127.07, 122.5, 85.6, 78.6, 68.0, 66.2, 63.5, 53.6, 35.7, 32.0, 26.8. **IR** (KBr, cm^{-1}): 3114, 2944, 2869, 2231, 2150, 1727, 1625, 1401, 1299, 1208, 1116, 962, 845, 706, 638, 509. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}NS$ 320.1468; found 320.1465.

tert-butyldimethyl(5-(thiophen-2-yl)penta-2,4-diyn-1-yl)silane (**6al**)



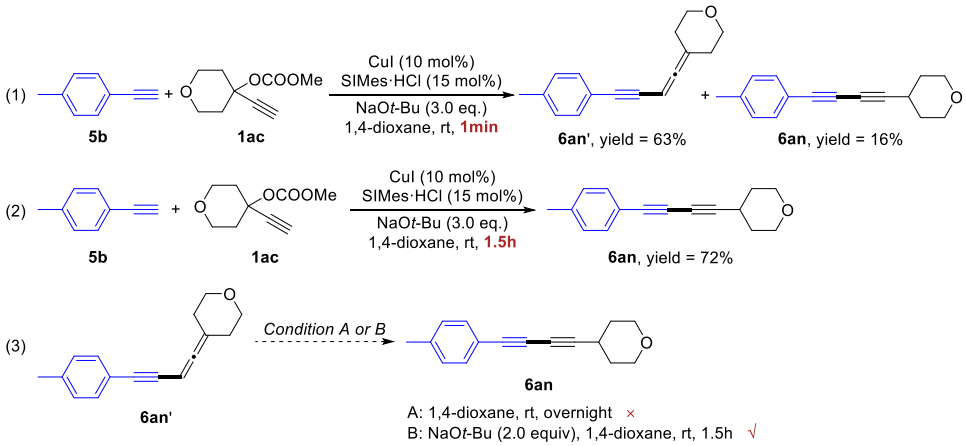
Colorless oil (12.5 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 48%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 5.0 Hz, 1H), 6.96 (s, 1H), 6.95 – 6.92 (m, 1H), 3.85 (s, 2H), 0.95 (s, 9H), 0.13 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 137.5, 127.1, 125.8, 124.7, 88.7, 83.8, 75.4, 67.5, 26.2, 20.6, 16.9, -4.7. **IR** (KBr, cm^{-1}): 3120, 2946, 2861, 2227, 2109, 1712, 1622, 1463, 1404, 1299, 1251, 1183, 1076, 1010, 832, 780, 694, 582, 454. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}SSi$ 261.1128; found 261.1129.

1,17-di(thiophen-2-yl)heptadeca-1,3,14,16-tetrayne (**6am**)



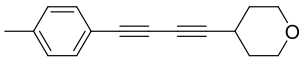
Colorless oil (19.8 mg), purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 51%. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.26 (dd, *J* = 11.7, 4.3 Hz, 4H), 6.98 – 6.93 (m, 2H), 2.37 (t, *J* = 7.0 Hz, 4H), 1.57 (p, *J* = 7.1 Hz, 5H), 1.41 (s, 4H), 1.31 (s, 5H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.0, 128.1, 127.1, 122.6, 87.2, 78.7, 67.8, 65.1, 29.4, 29.1, 28.9, 28.3, 19.8. **IR** (KBr, cm^{-1}): 3115, 2930, 2856, 2231, 2149, 1798, 1616, 1531, 1406, 1210, 1090, 1037, 842, 703, 633, 503. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{24}NaS_2$ 411.1212; found 411.1210.

1.10. Base-assisted proton transfer from 6' to 6



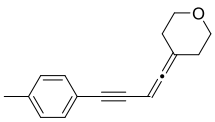
When tertiary propargyl ether **1ab** was tested under the standard conditions, a mixture of allenyne **6an'** (63%) and 1,3-diyne **6an** (16%) was obtained (eq 1). However, there was only **6an** when the reaction time was extended to 1.5h (eq 2). To figure out what has caused this isomerization, **6an'** was subjected to condition A and B (eq 3). This isomerization didn't occur under condition A but occurred under condition B, meaning that base could promote this allene–alkyne isomerization. Learned from these experiments, we believe that the final 1,3-diyne products were generated through isomerization of allenyne.

4-(p-tolylbuta-1,3-diyn-1-yl)tetrahydro-2H-pyran (**6an**)



White solid [3.6 mg (1 min) or 16.2 mg (1.5 h)], m.p. = 80-82 °C, purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 16% (1 min) or 72% (1.5 h).**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 3.92 (dt, *J* = 10.5, 4.3 Hz, 2H), 3.56 – 3.49 (m, 2H), 2.80 (dt, *J* = 8.2, 4.2 Hz, 1H), 2.35 (s, 3H), 1.90 – 1.84 (m, 2H), 1.73 (dtd, *J* = 12.6, 8.5, 3.3 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 139.47, 132.56, 129.31, 118.87, 85.90, 76.32, 73.45, 66.38, 66.30, 31.88, 27.14, 21.73. **IR** (KBr, cm^{-1}): 3170, 3132, 2960, 2913, 1851, 2195, 1950, 1625, 1509, 1401, 1292, 1244, 1161, 1097, 1006, 967, 813, 753, 682, 637, 533, 477. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}O$ 225.1274; found 225.1272.

4-(4-(p-tolyl)but-1-en-3-yn-1-ylidene)tetrahydro-2H-pyran (**6an'**)



White solid (14.1 mg), m.p. = 141-143 °C, purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 63% (1 min). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 5.58 – 5.54 (m, 1H), 3.81 (ddd, *J* = 10.8, 6.3, 4.2 Hz, 2H), 3.73 (ddd, *J* = 11.1, 7.0, 4.1 Hz, 2H), 2.41 – 2.23 (m, 7H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 207.23, 138.28, 131.43, 129.16, 120.49, 100.14, 89.60, 82.59, 75.14, 68.27, 30.93, 21.59. **IR** (KBr, cm^{-1}): 3126, 2965, 2840, 2142, 1627, 1505, 1401, 1241, 1170, 1122, 1082, 1018, 889, 819, 752, 619, 527, 462. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}O$ 225.1274; found 225.1271.

1.11. References

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2. X-Ray diffraction analysis

2.1. Crystal data and structure refinement for 4a

Experimental Procedure

Single crystal of **4a** was grown from slow evaporation of DCM/PE solvent. A suitable crystal was selected and measured on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 169.99(10) K during data collection.

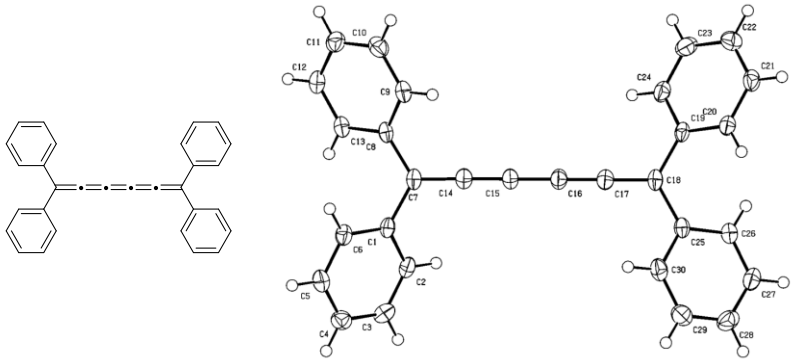


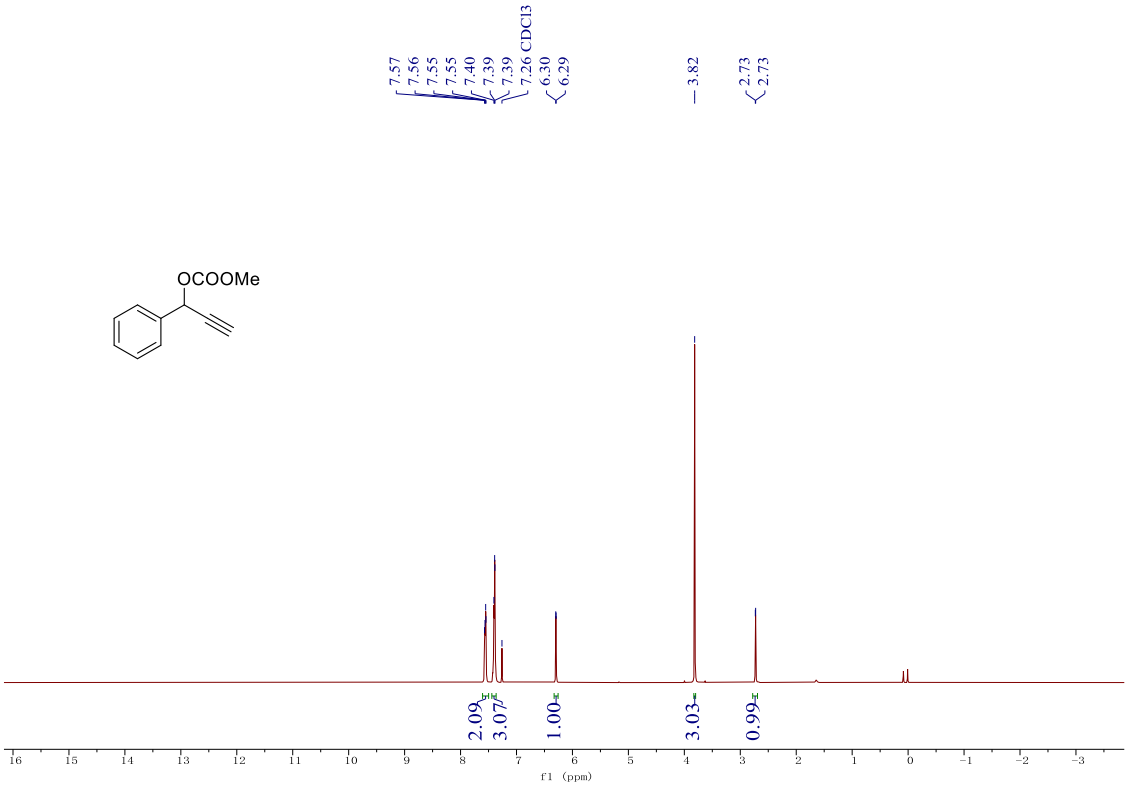
Figure S1. Ellipsoid plot of the crystal structure of **4a** (Prob = 50, Temp = 170 K).

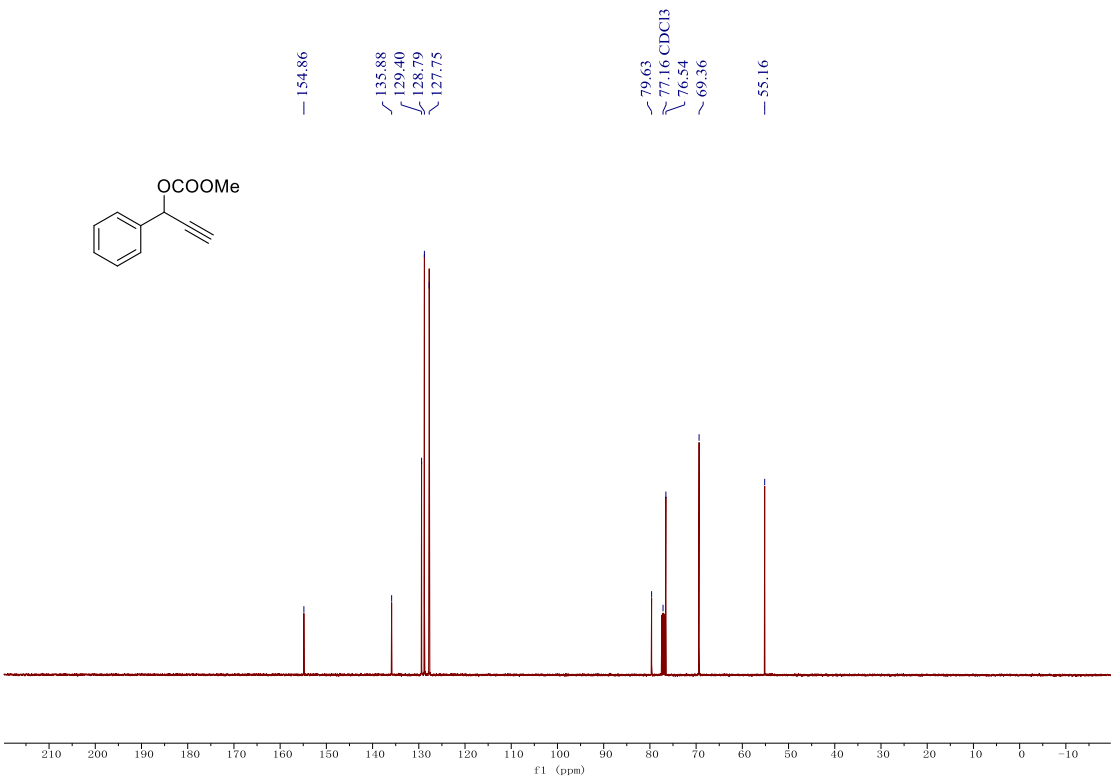
Identification code	**4a** (CCDC 2142926)
Empirical formula	$C_{30}H_{20}$
Formula weight	380.46
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.7343(13)
b/Å	7.8467(5)
c/Å	18.5969(16)
α/°	90
β/°	107.975(9)
γ/°	90
Volume/Å^3	2045.1(3)
Z	4
ρ_{calc}g/cm^3	1.236
μ/mm^{-1}	0.070
F(000)	800.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.606 to 49.998
Index ranges	$-17 \le h \le 17$, $-9 \le k \le 8$, $-16 \le l \le 22$

Reflections collected	9228
Independent reflections	3606 [R_{int} = 0.0242, R_{sigma} = 0.0329]
Data/restraints/parameters	3606/0/271
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0417, wR_2 = 0.0947
Final R indexes [all data]	R_1 = 0.0569, wR_2 = 0.1048
Largest diff. peak/hole / e $Å^{-3}$	0.13/-0.19

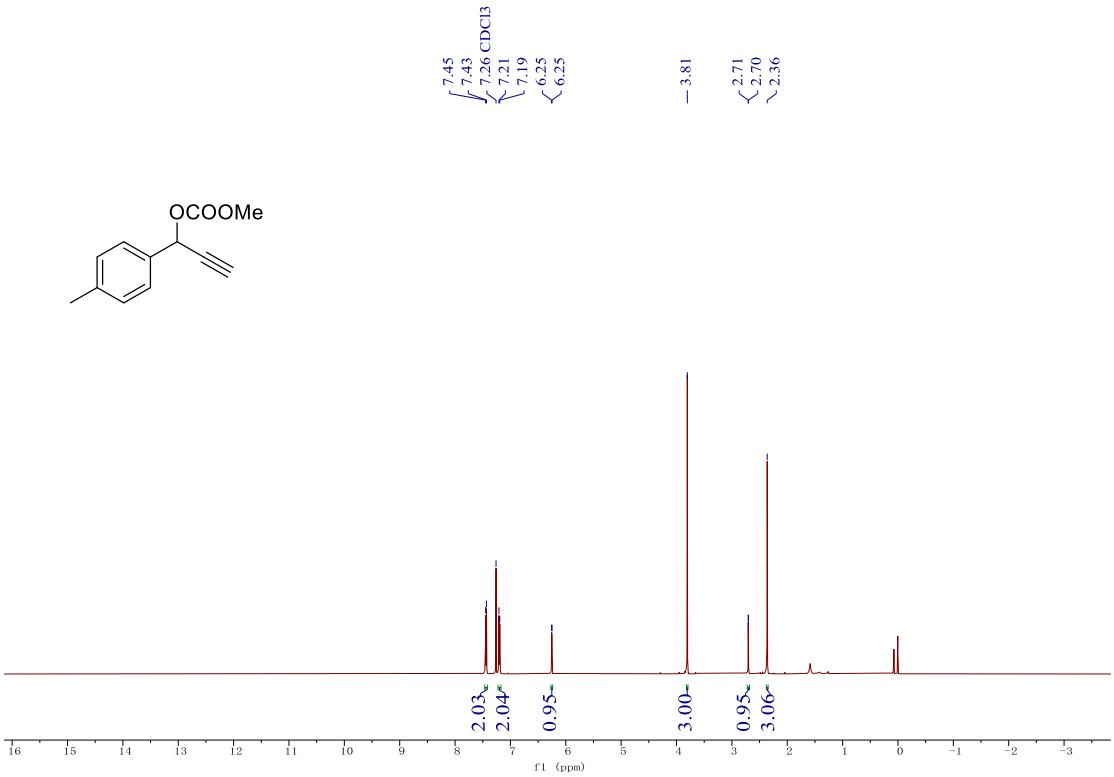
3. Data of NMR spectra

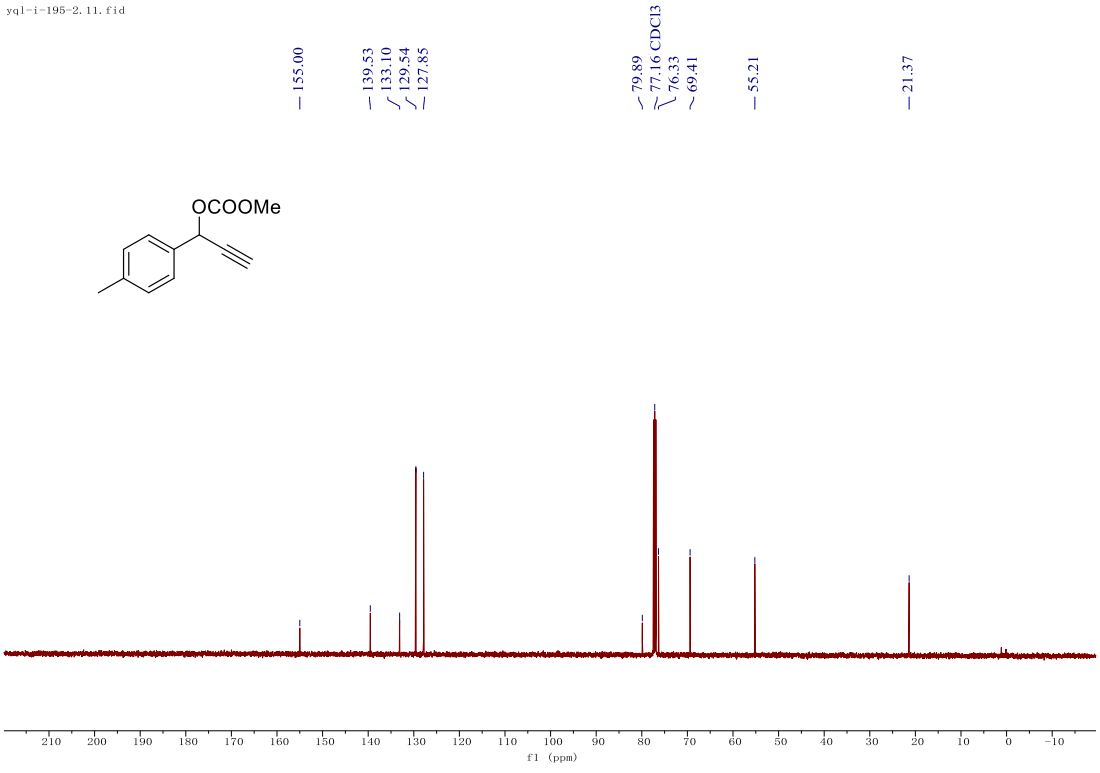
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1a



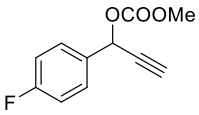


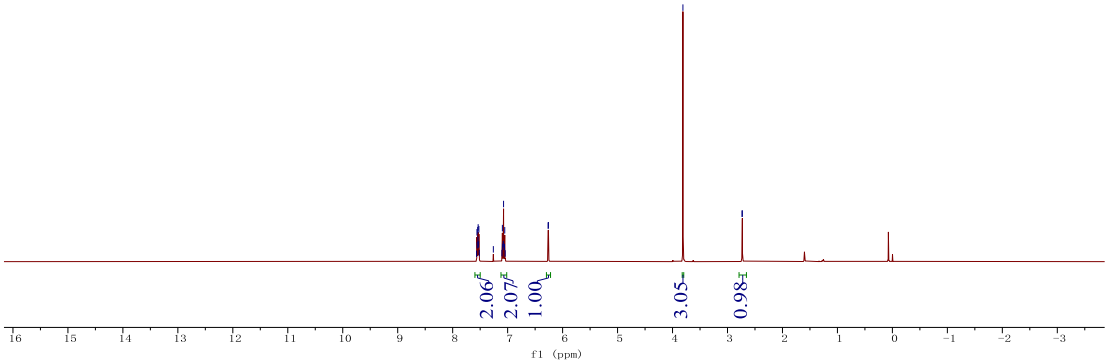
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1b

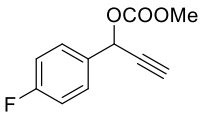


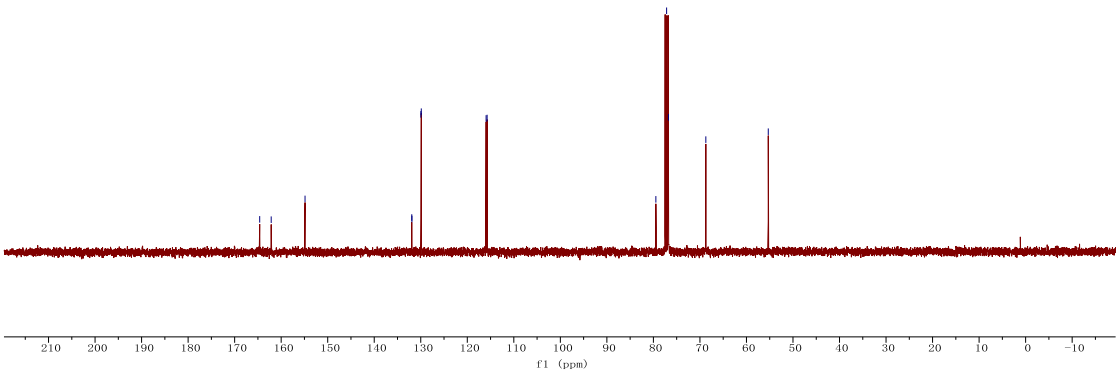


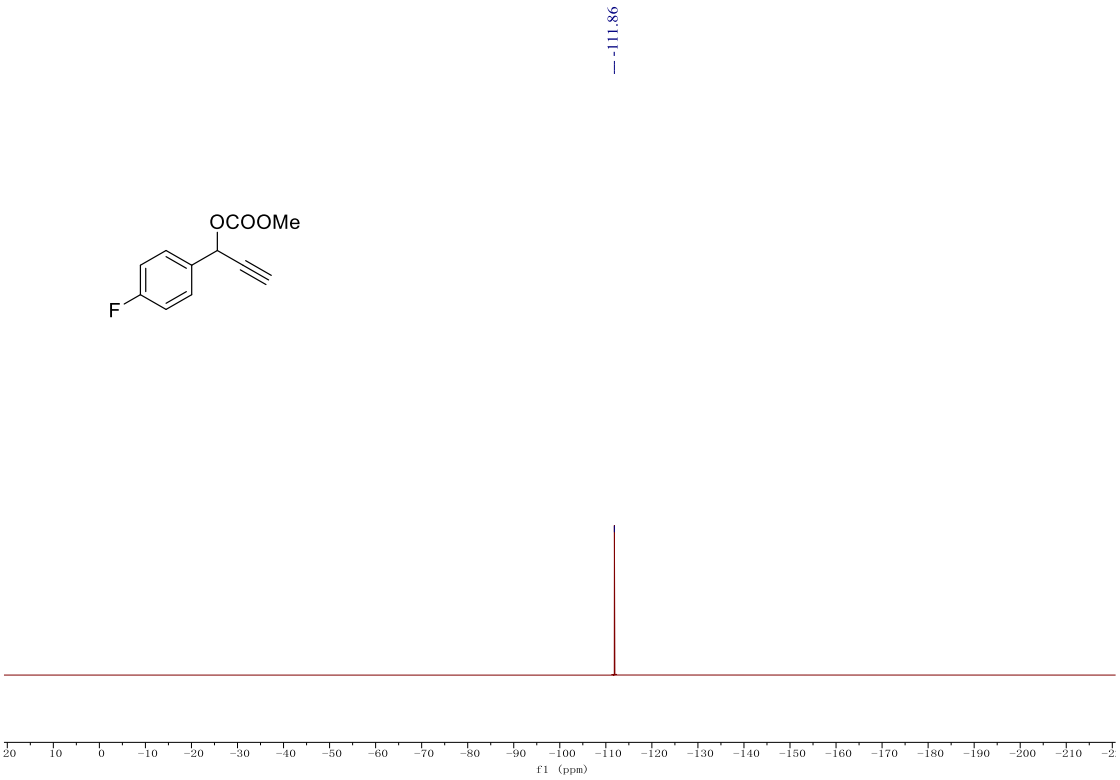
^{1}H NMR spectrum (400 MHz, $CDCl_3$), ^{13}C NMR spectrum (101 MHz, $CDCl_3$) and ^{19}F spectrum NMR (471 MHz, $CDCl_3$) of 1c



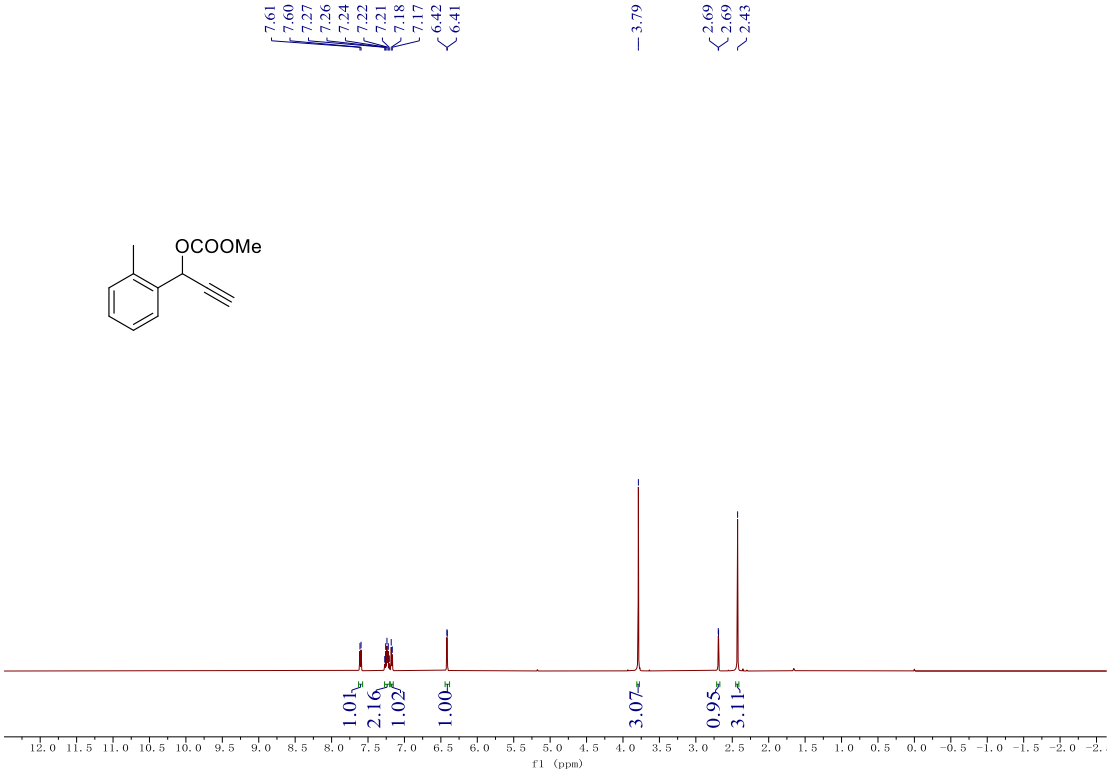


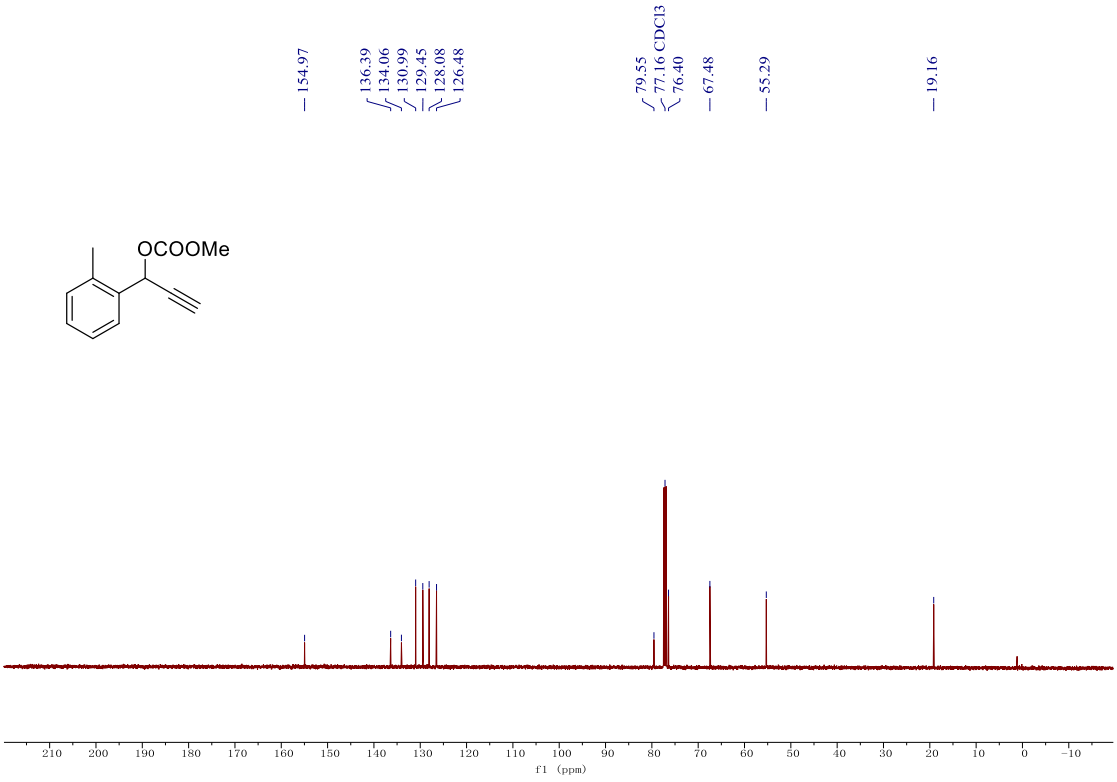




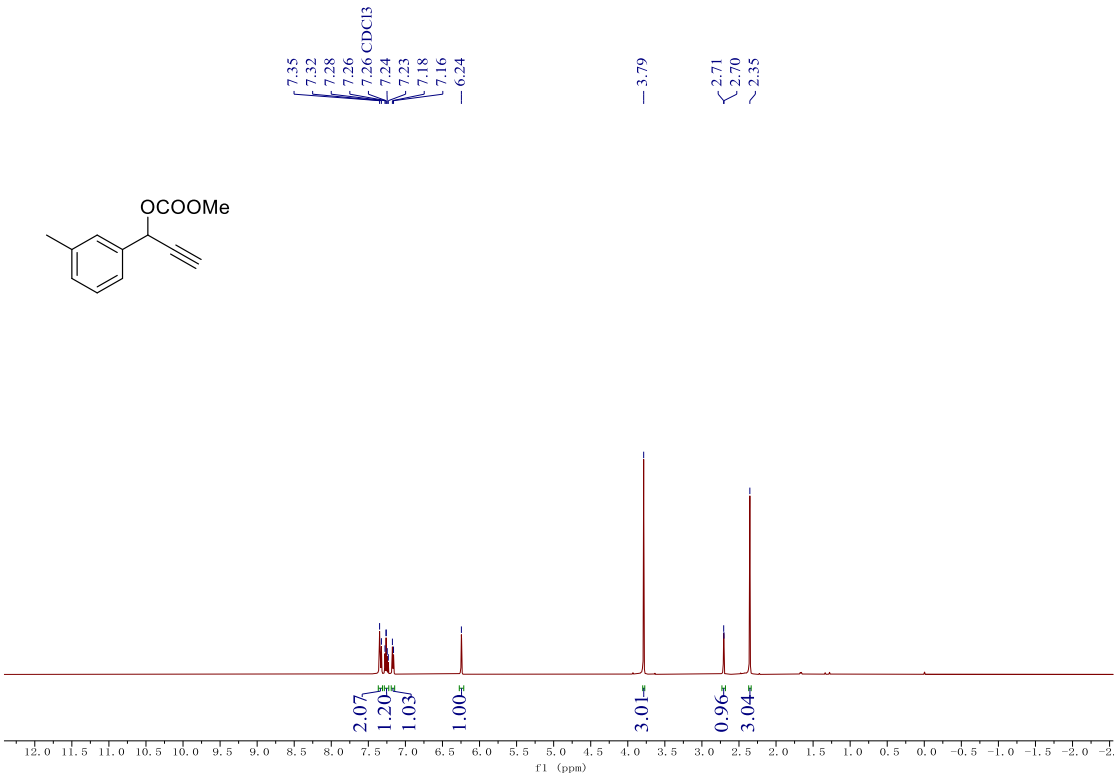


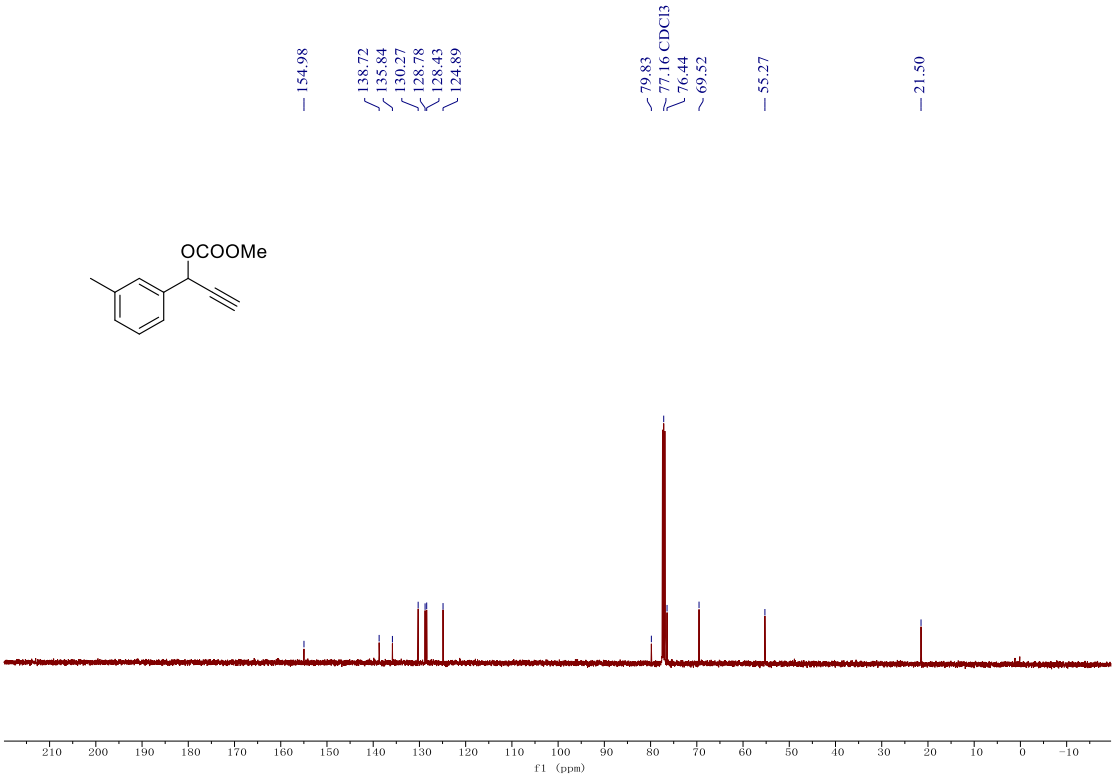
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1e



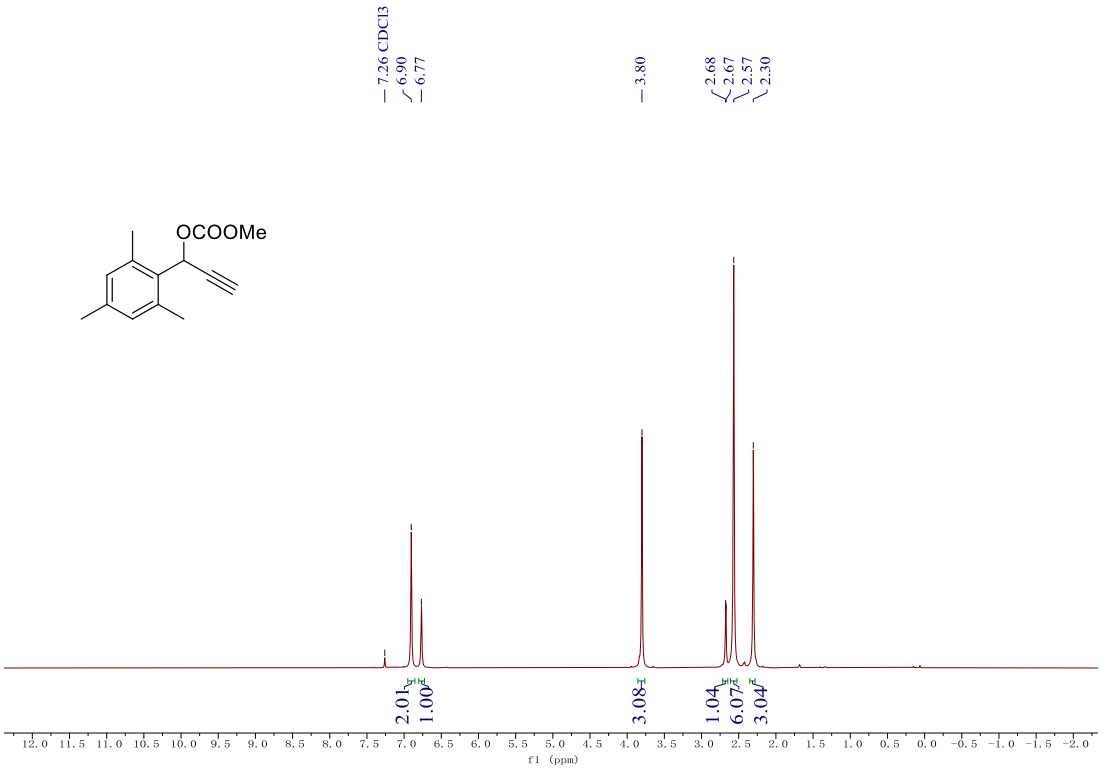


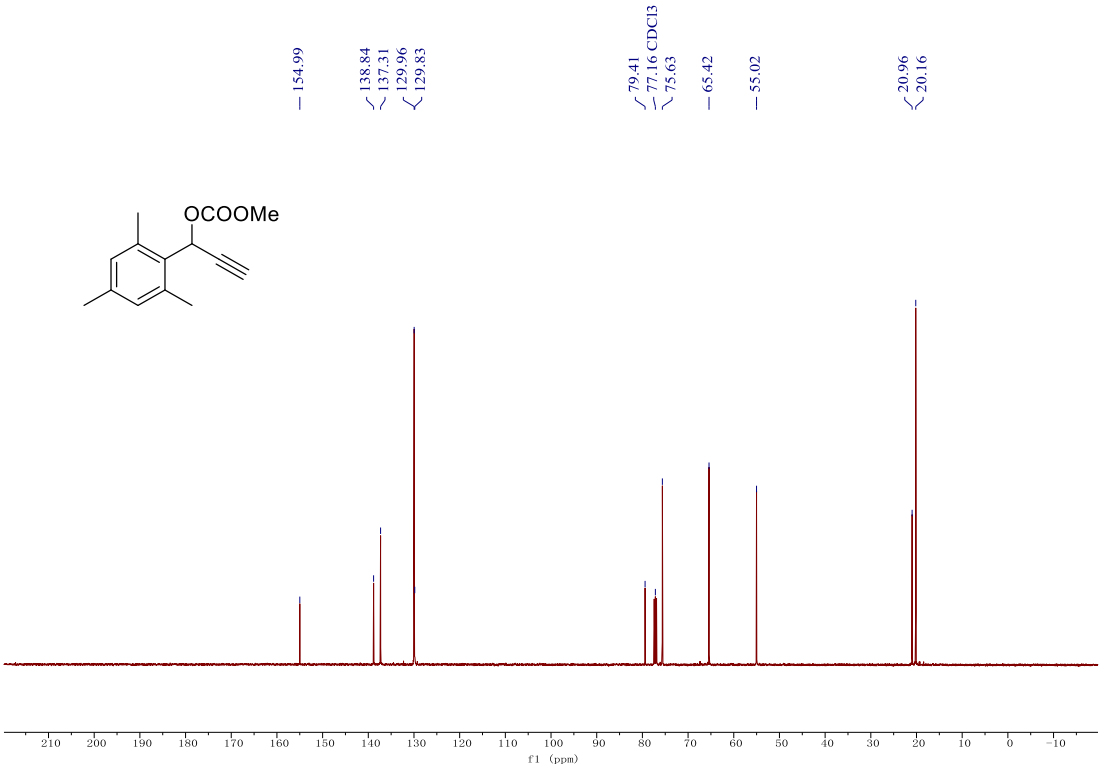
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1f



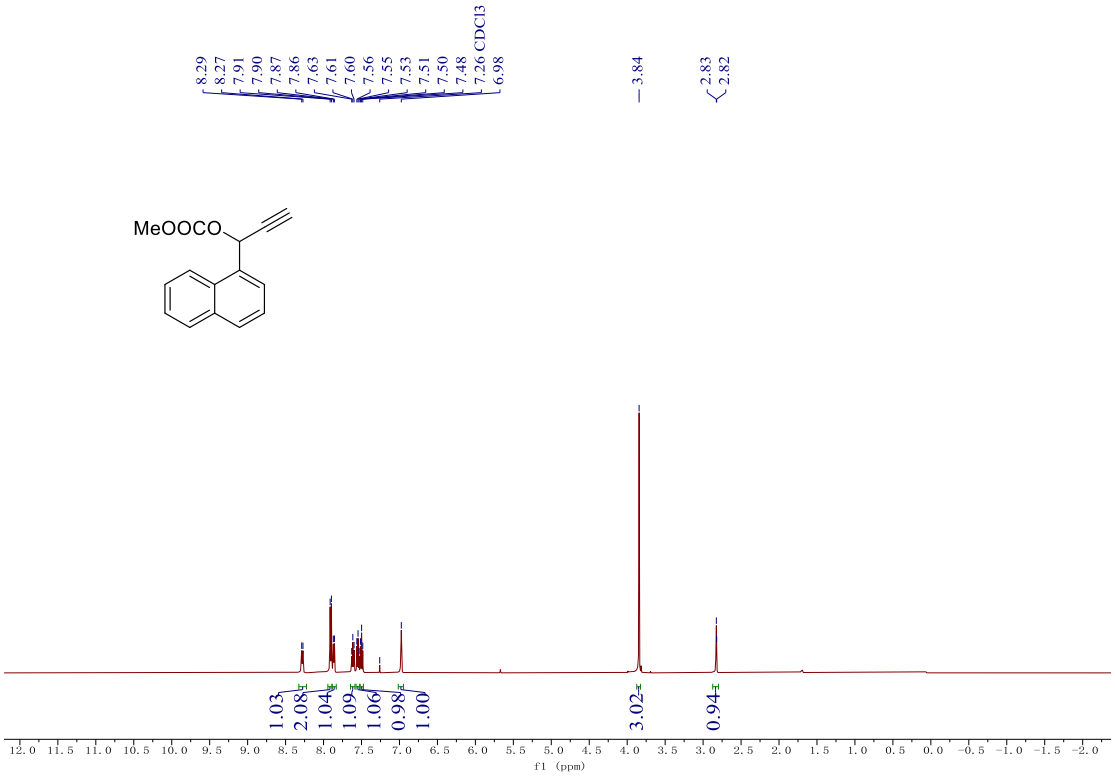


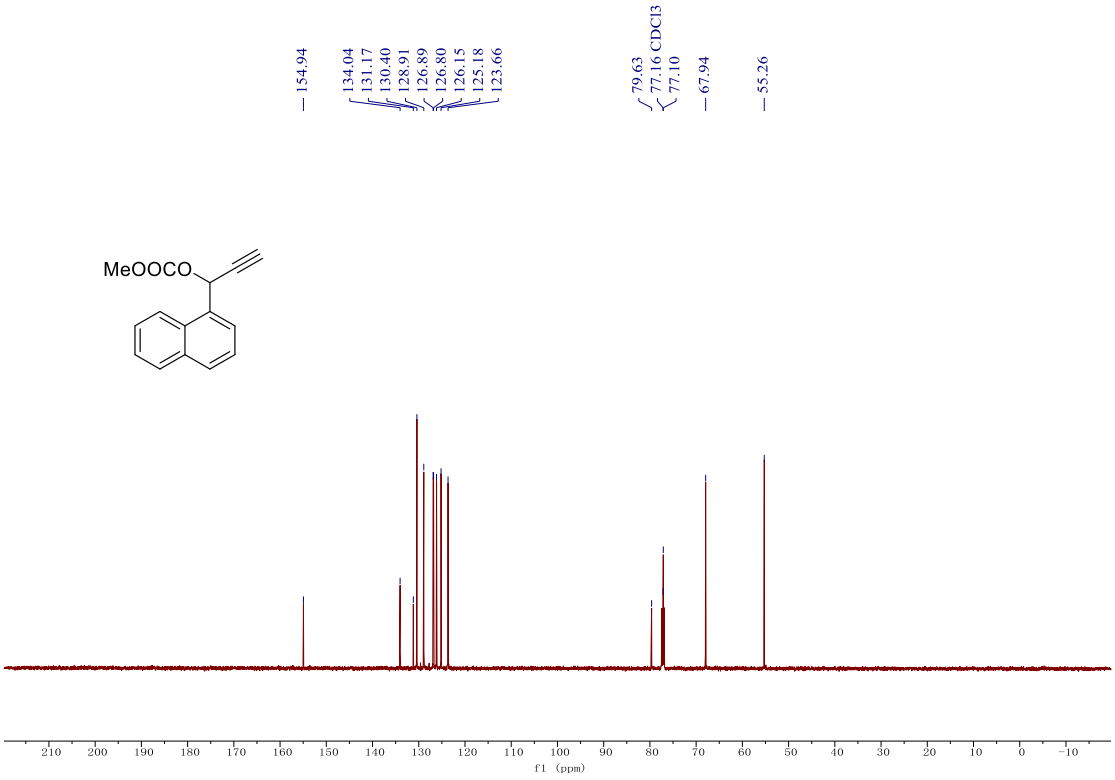
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1g



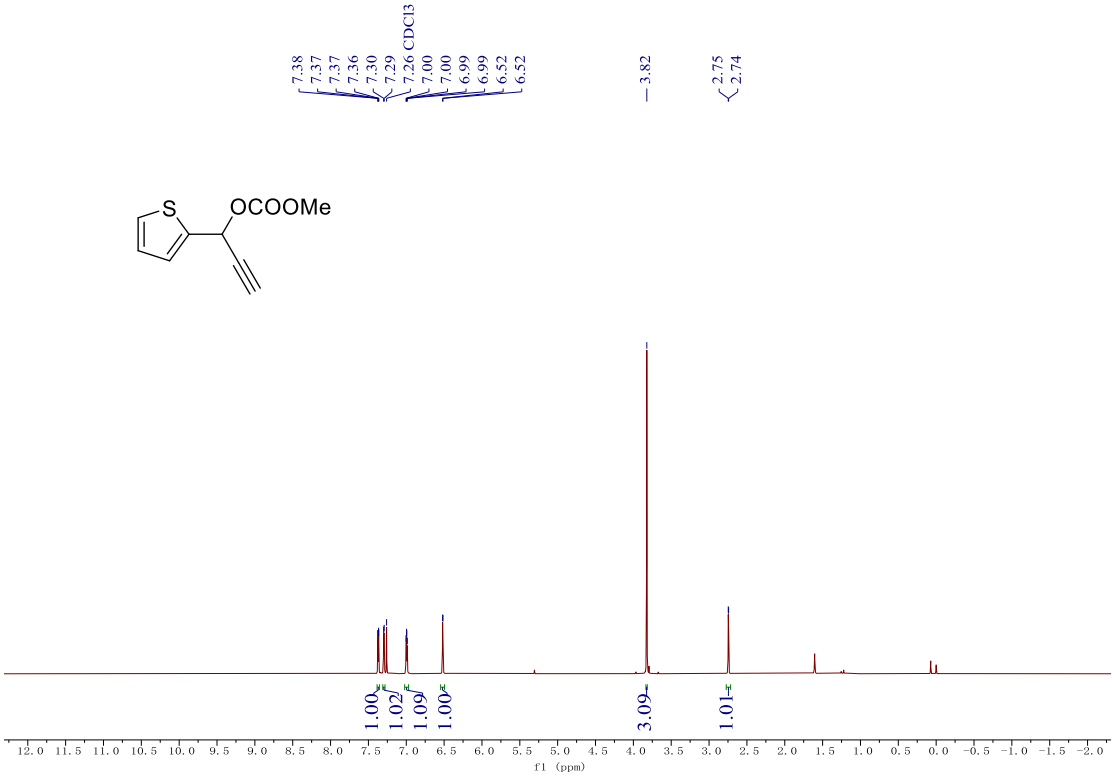


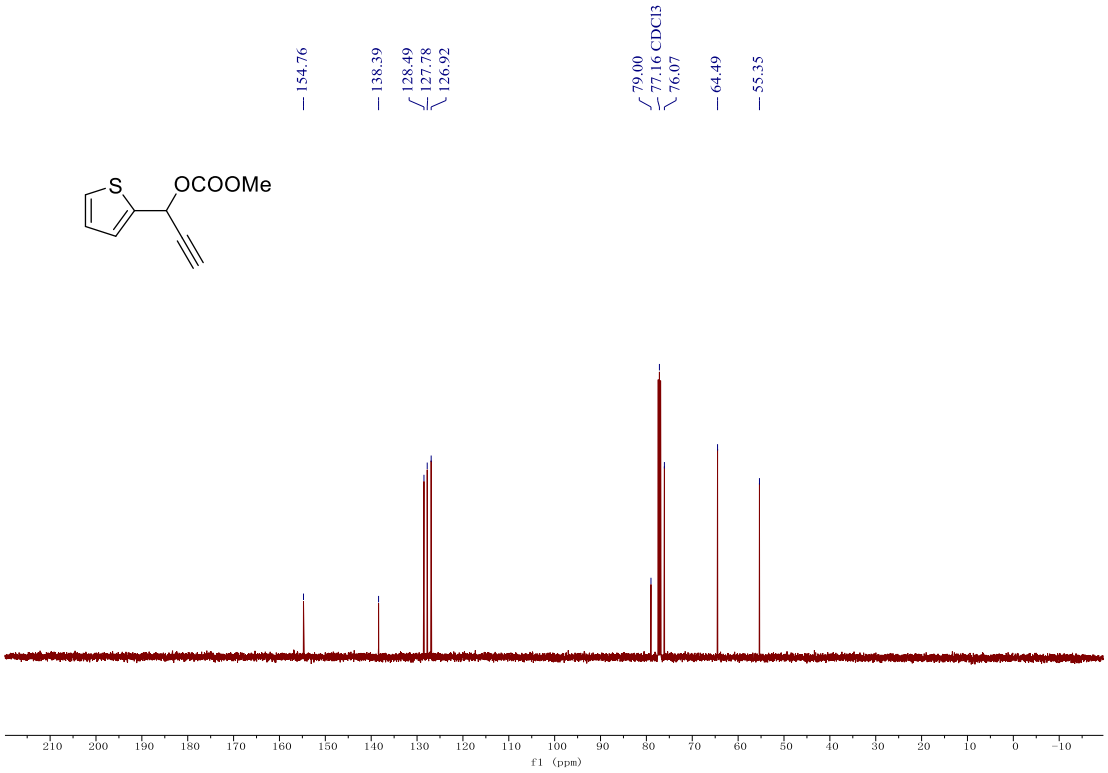
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1h



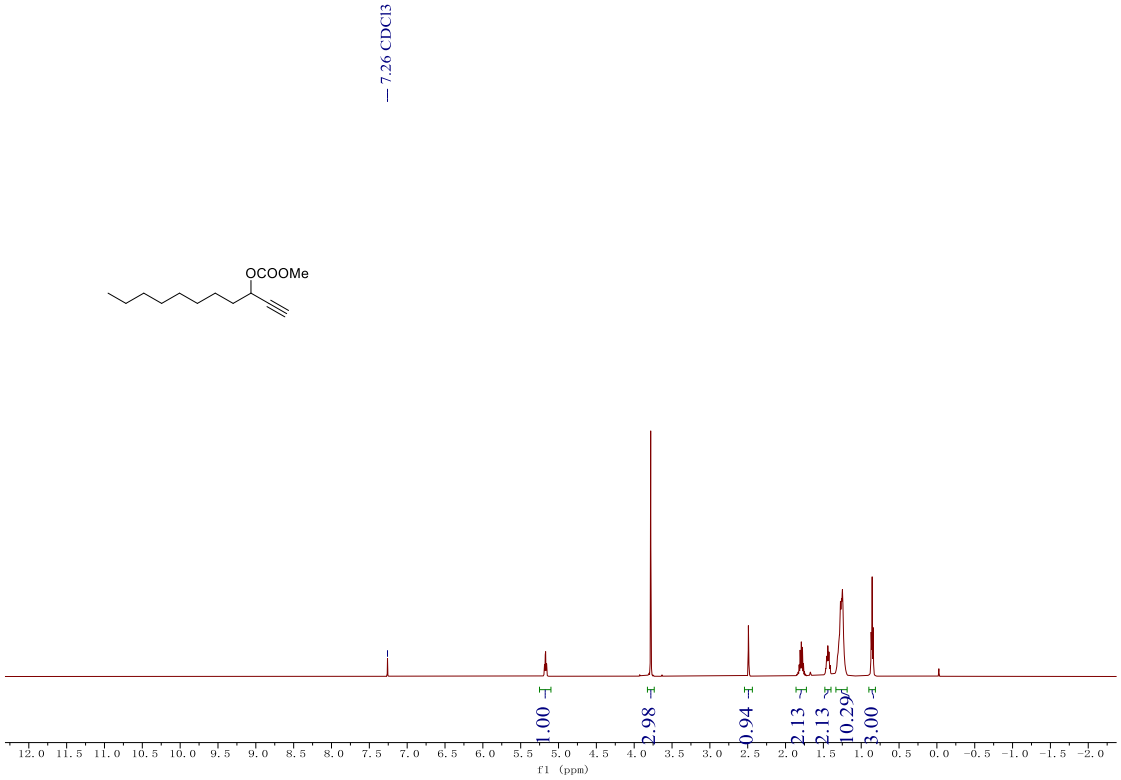


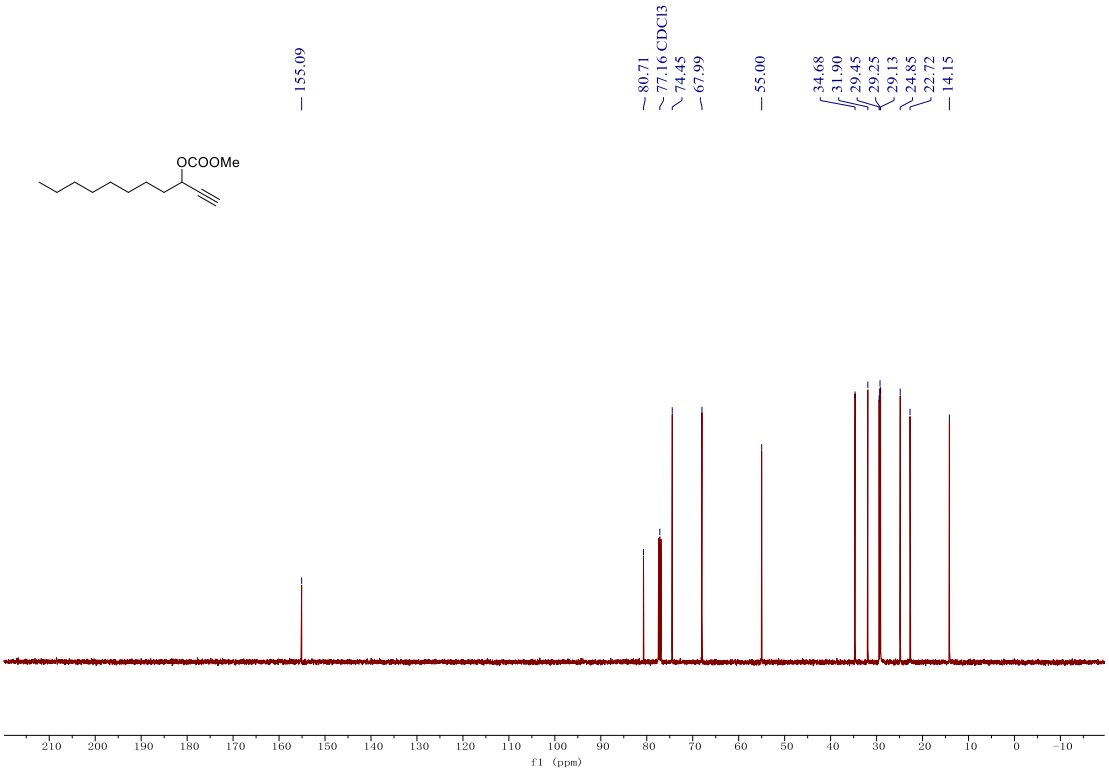
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1i



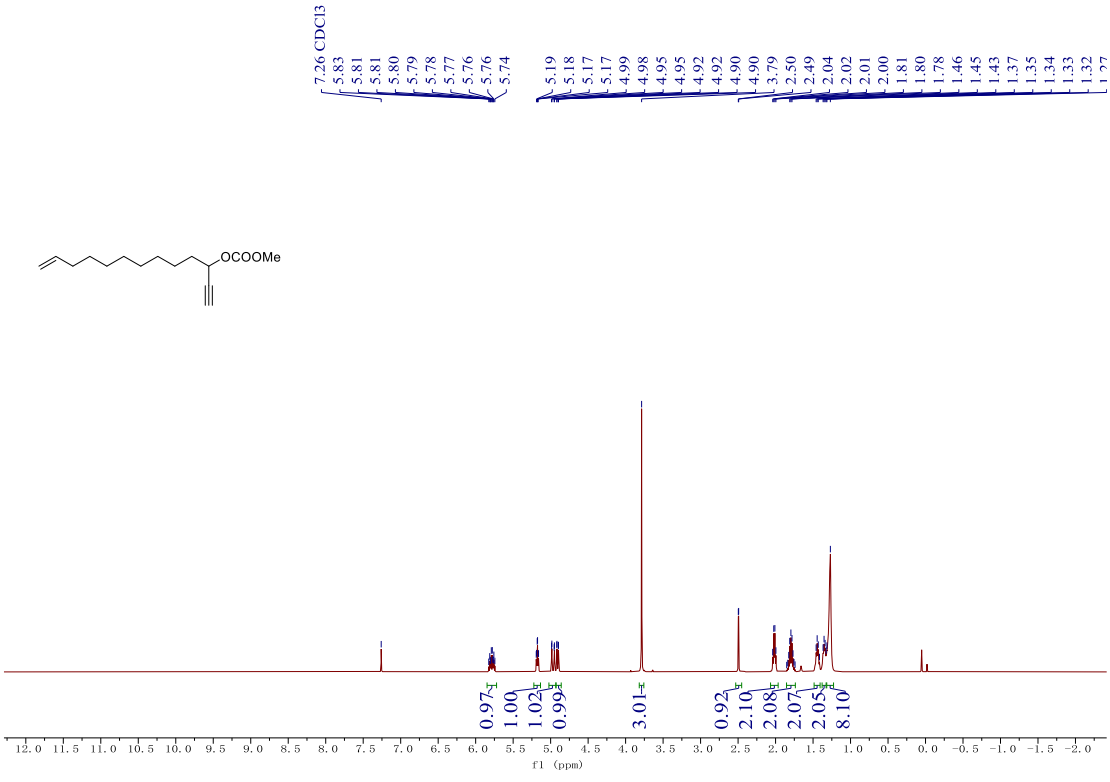


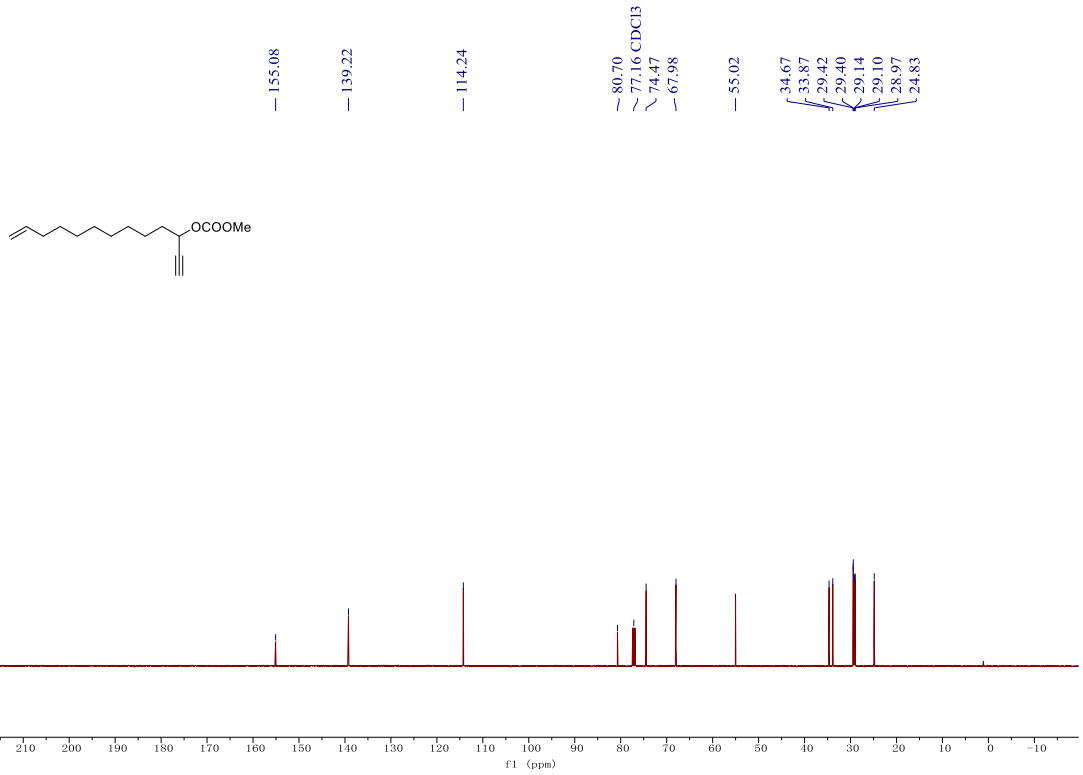
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1j



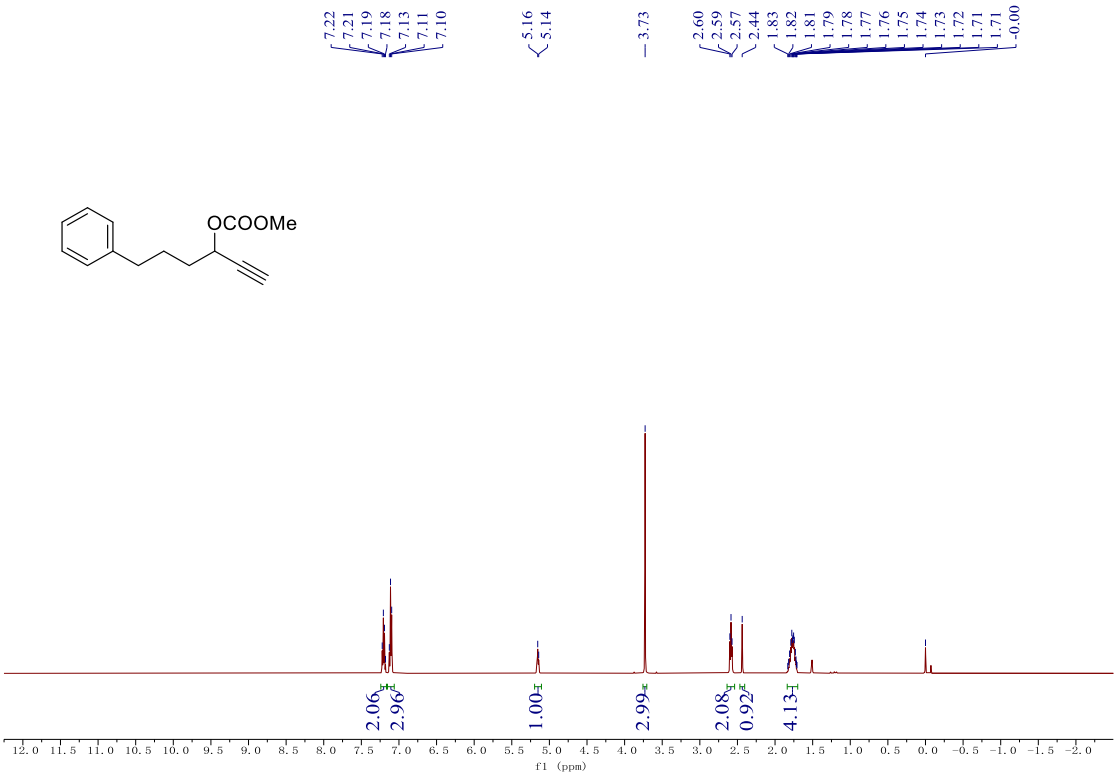


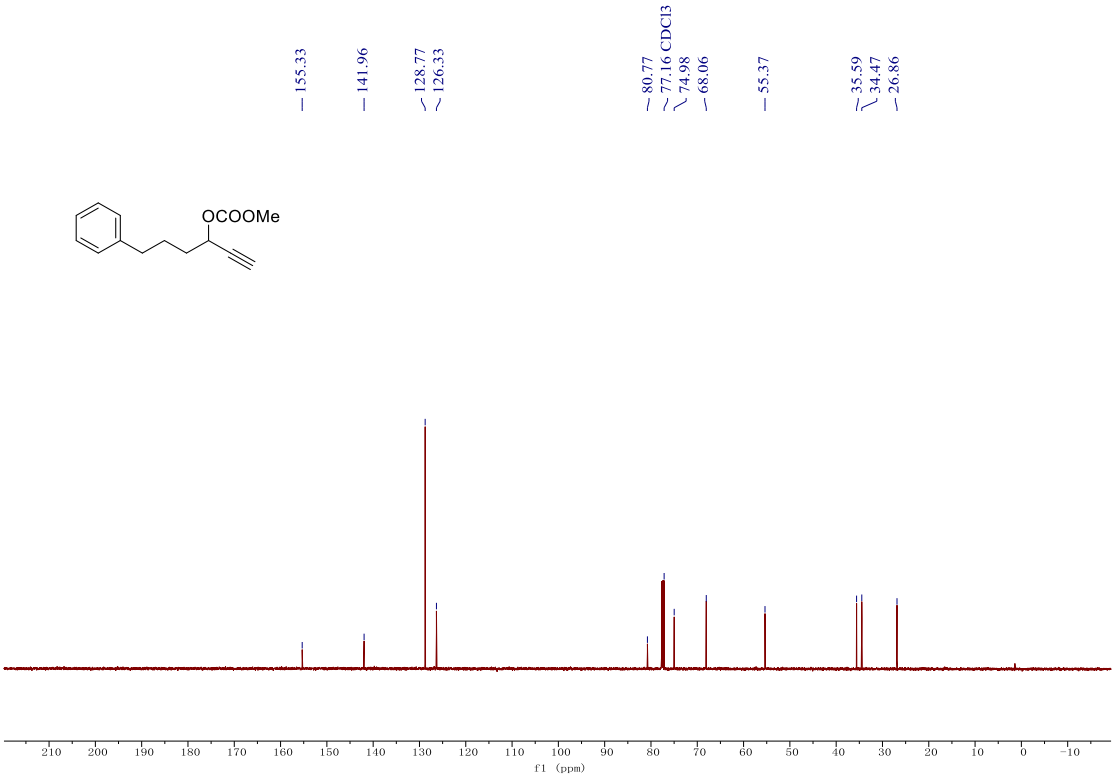
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1k



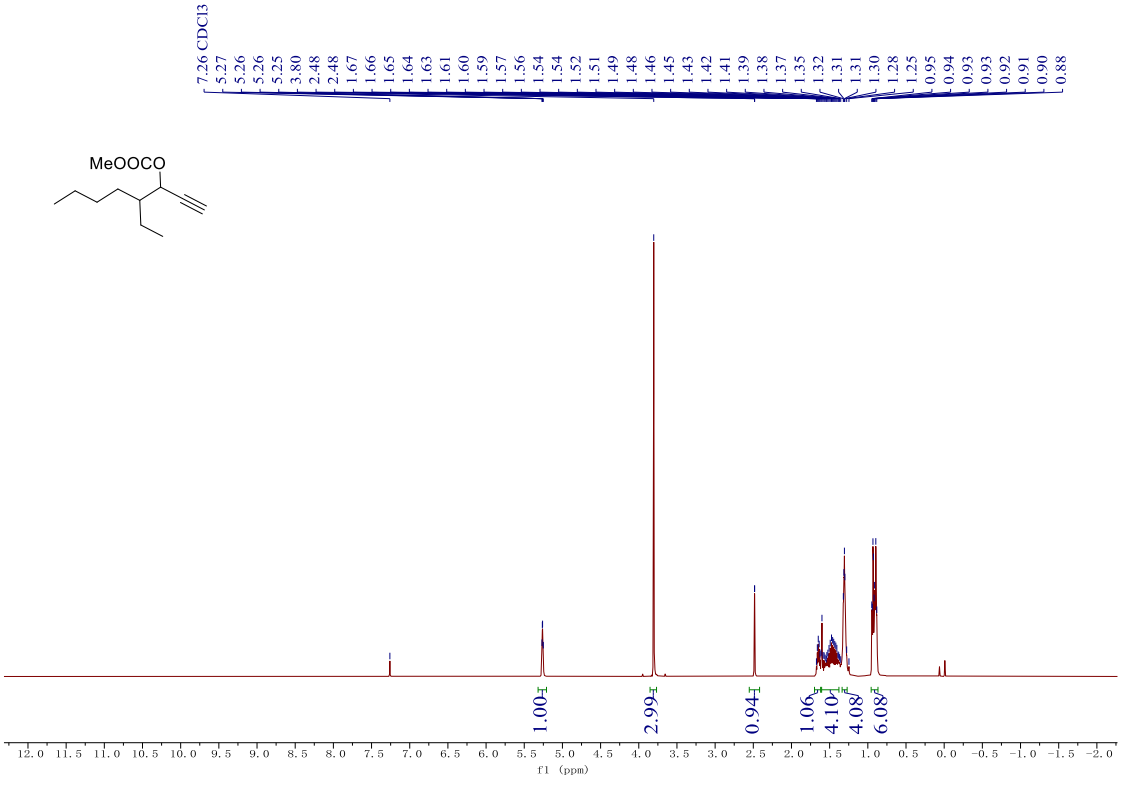


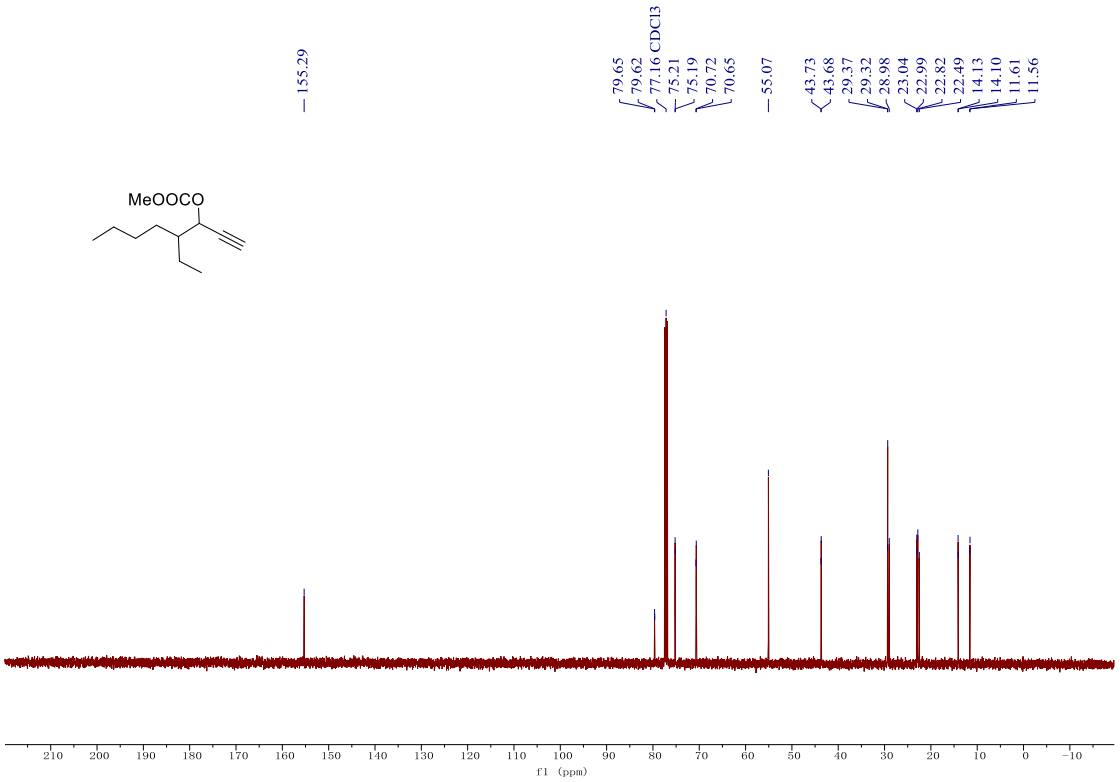
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1l



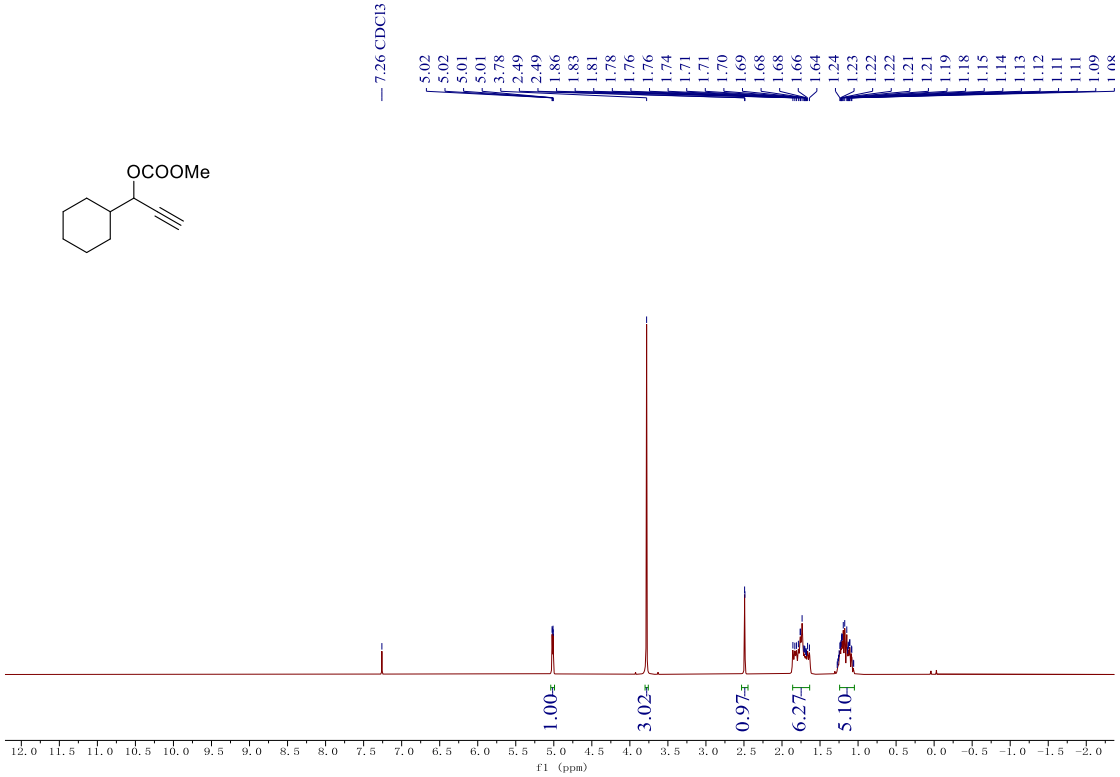


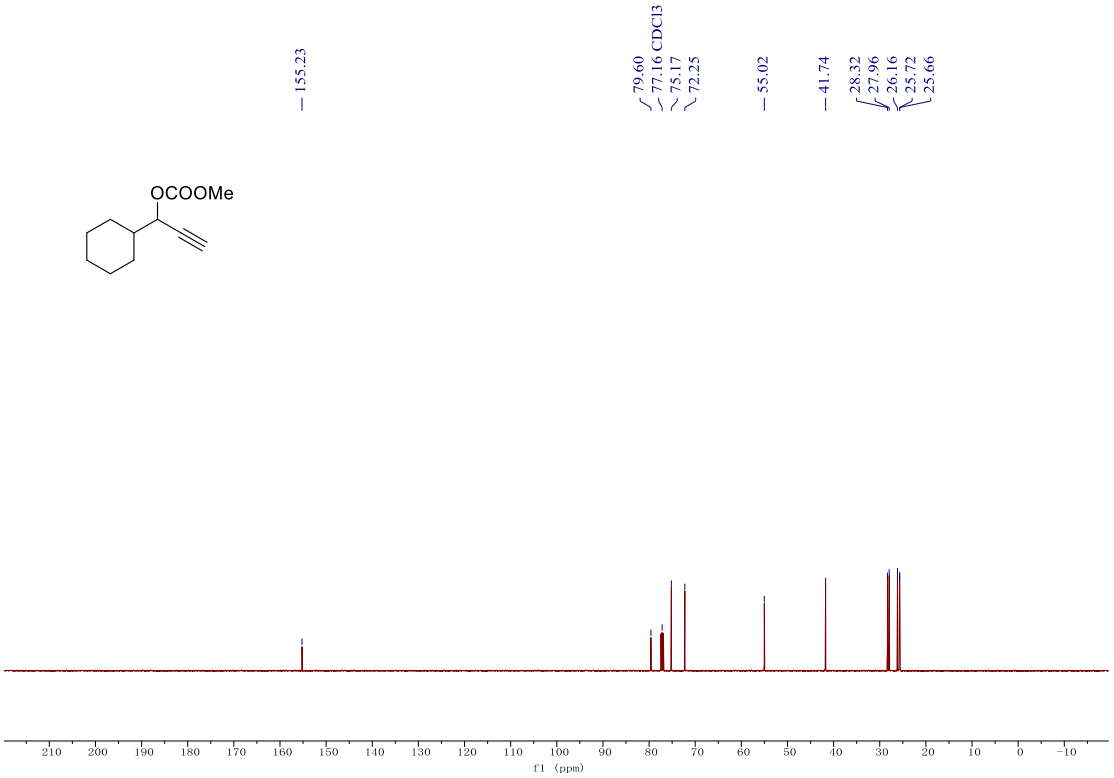
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1m



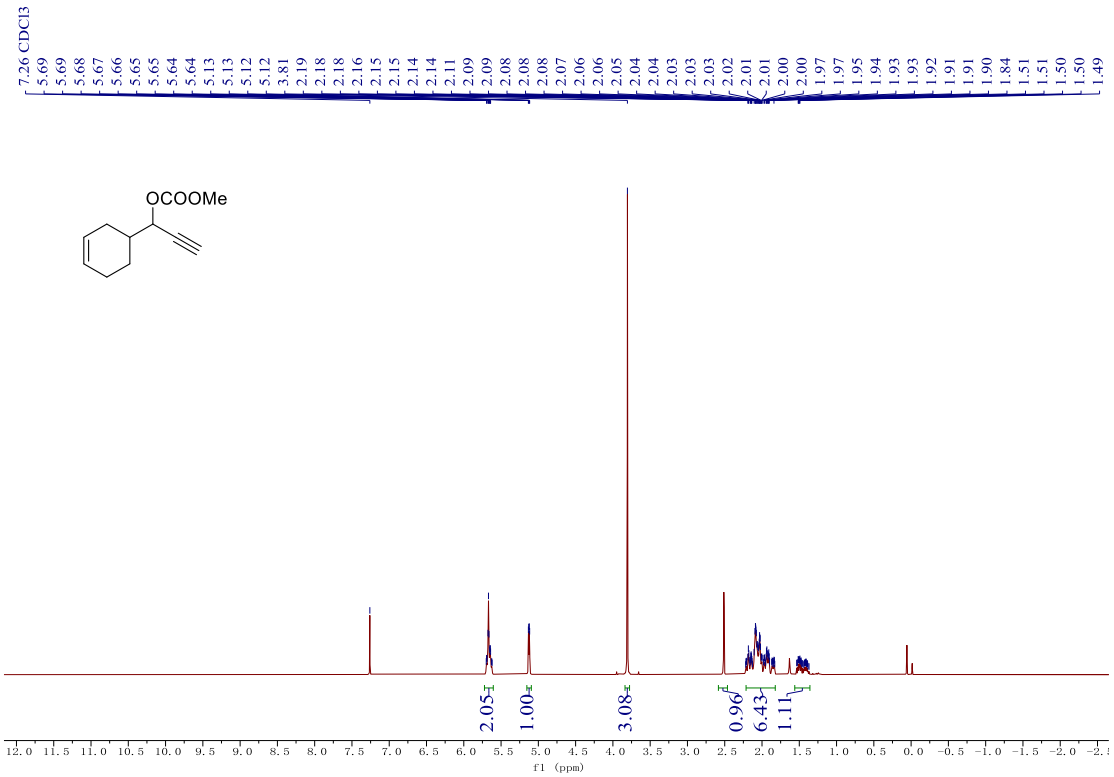


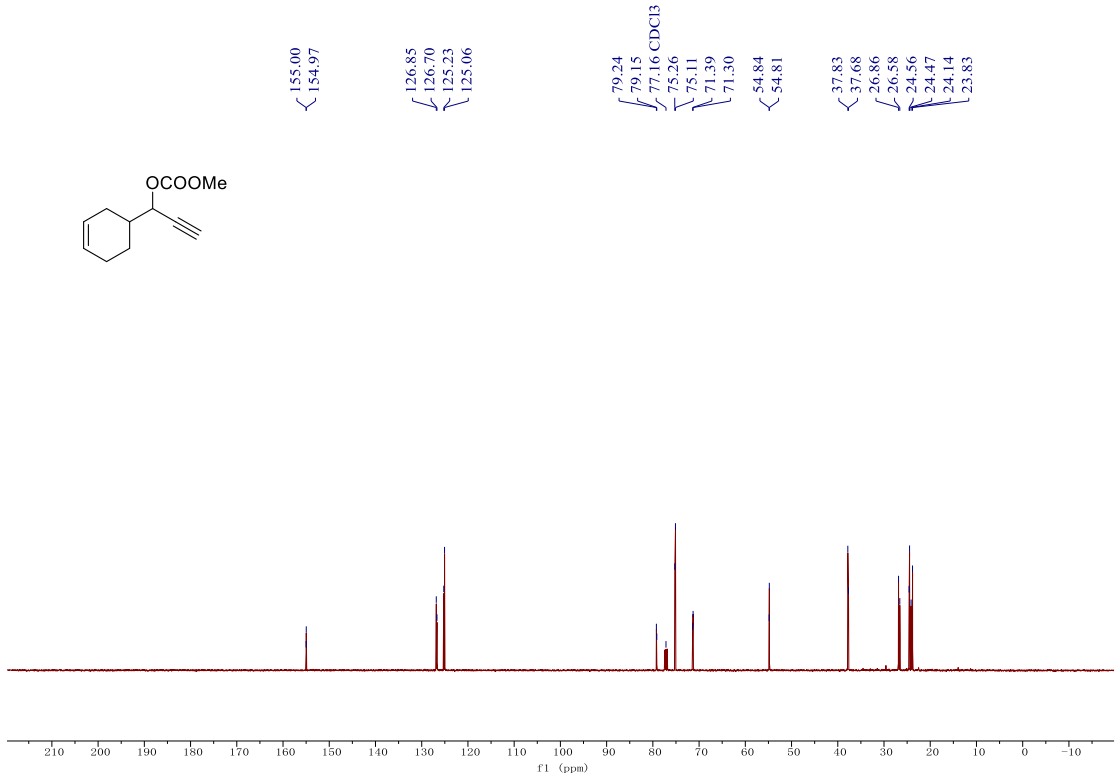
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1n



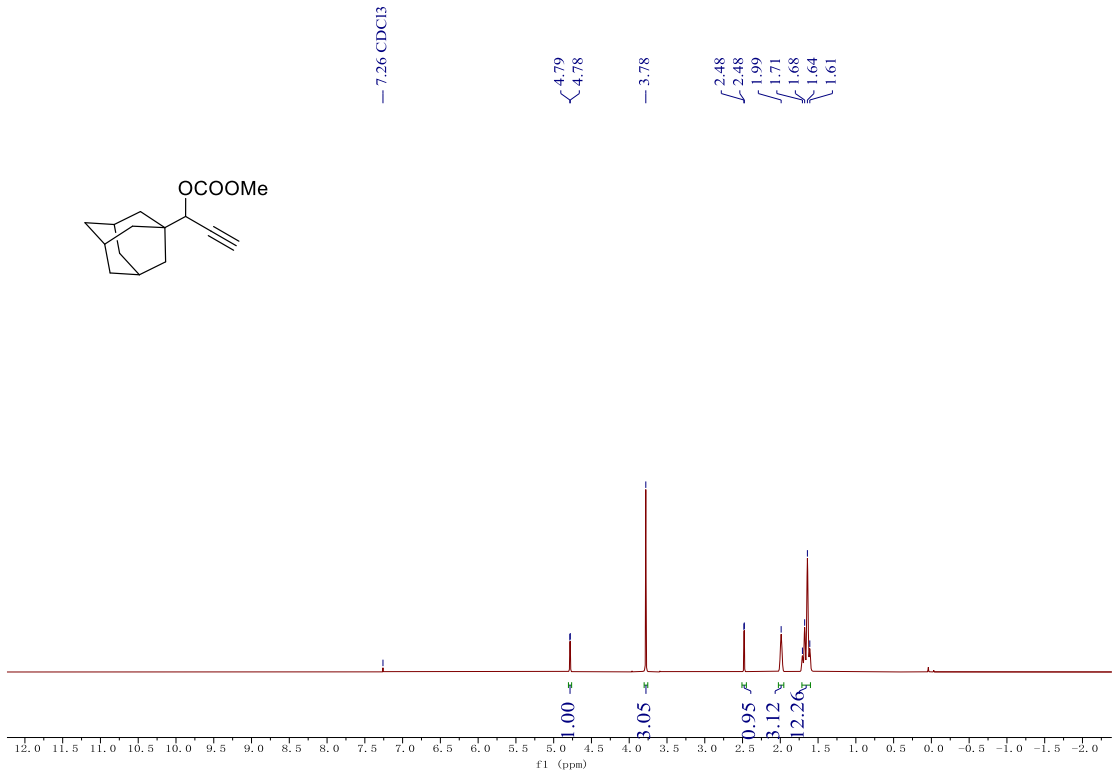


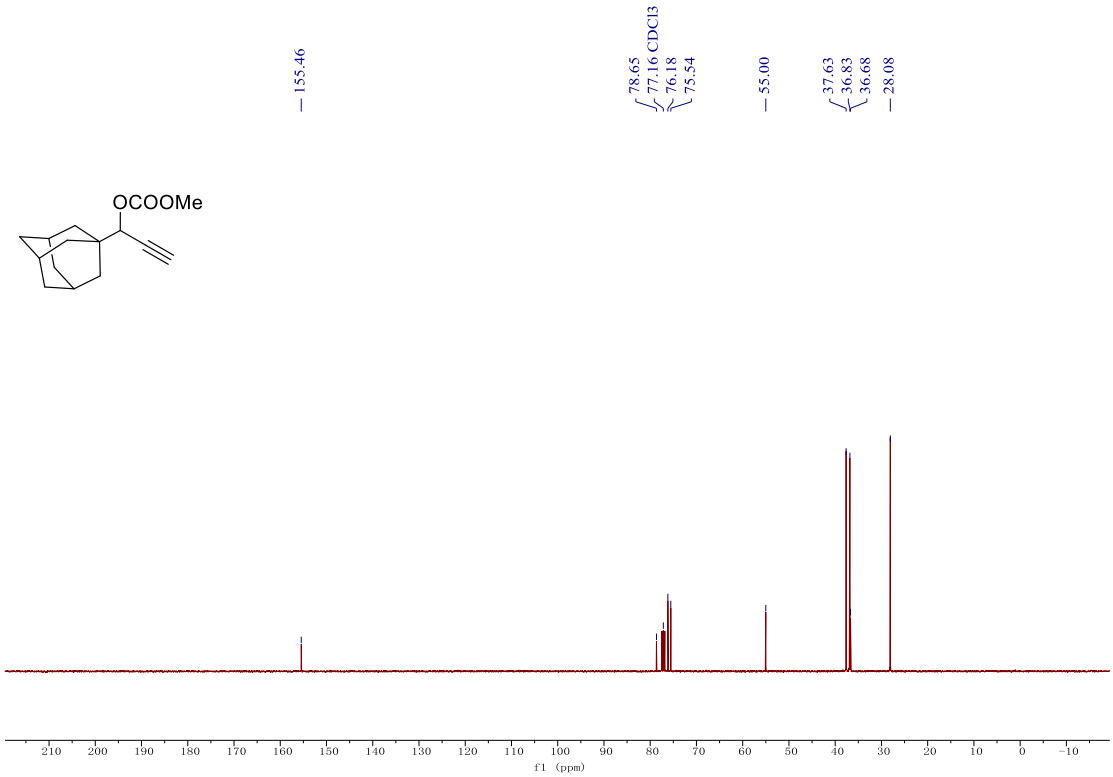
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1o



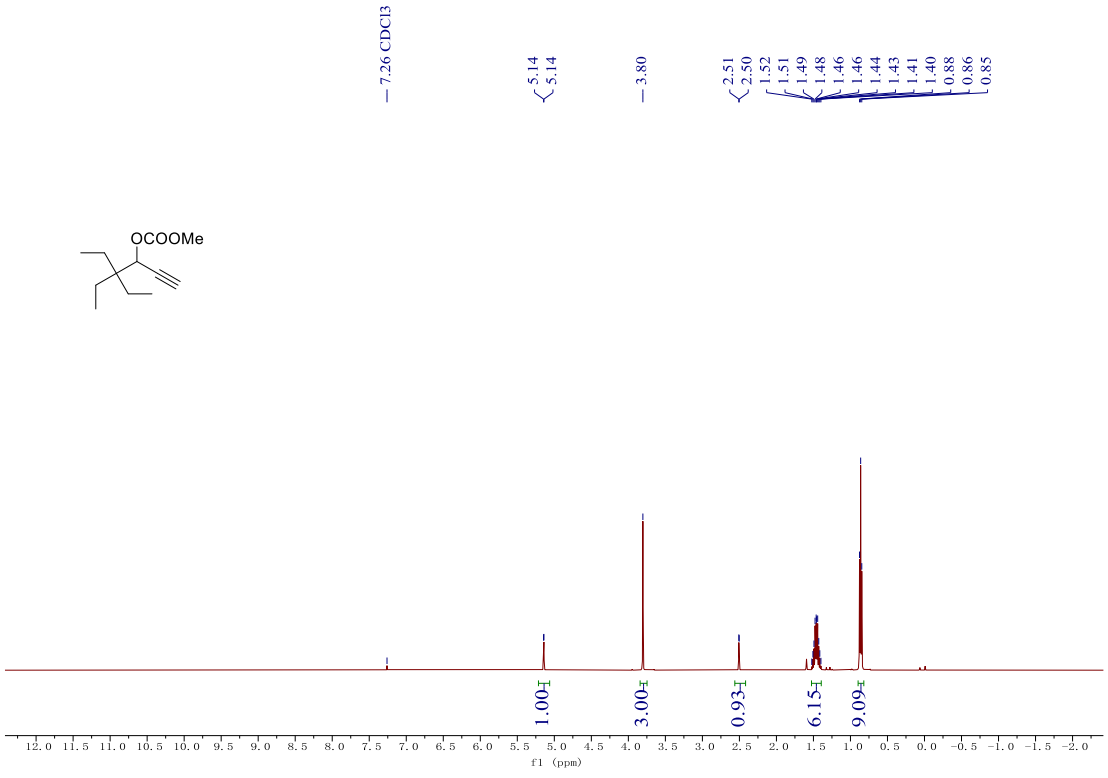


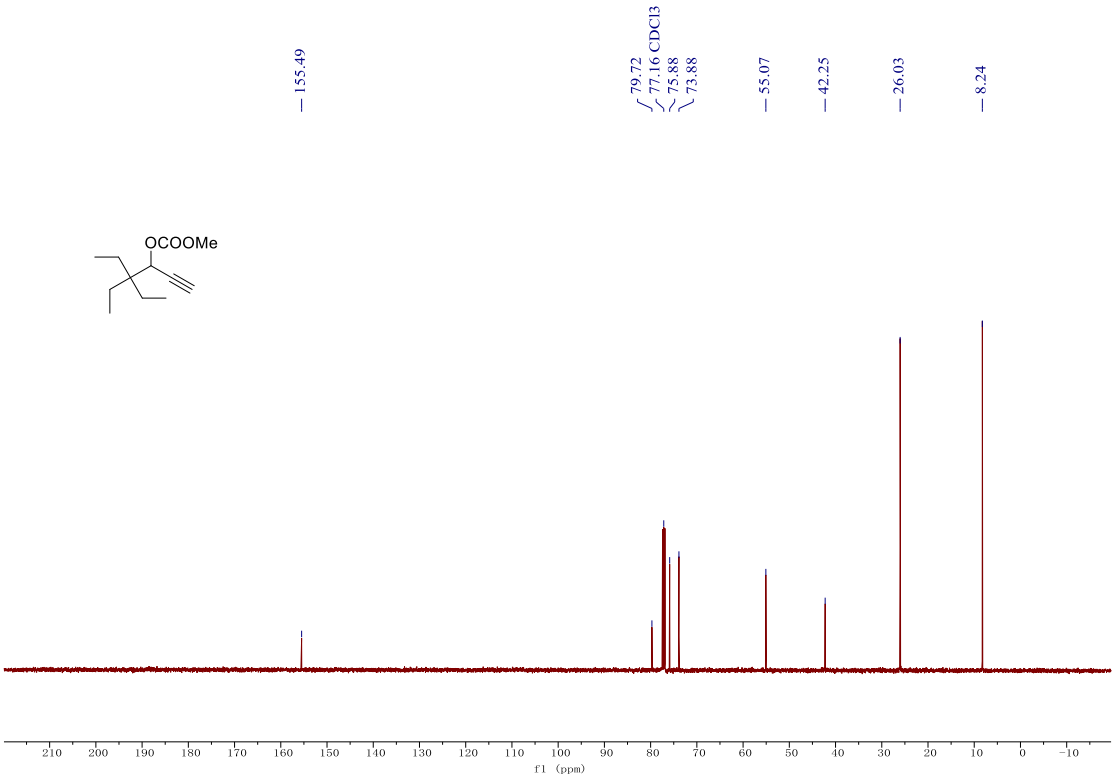
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1p



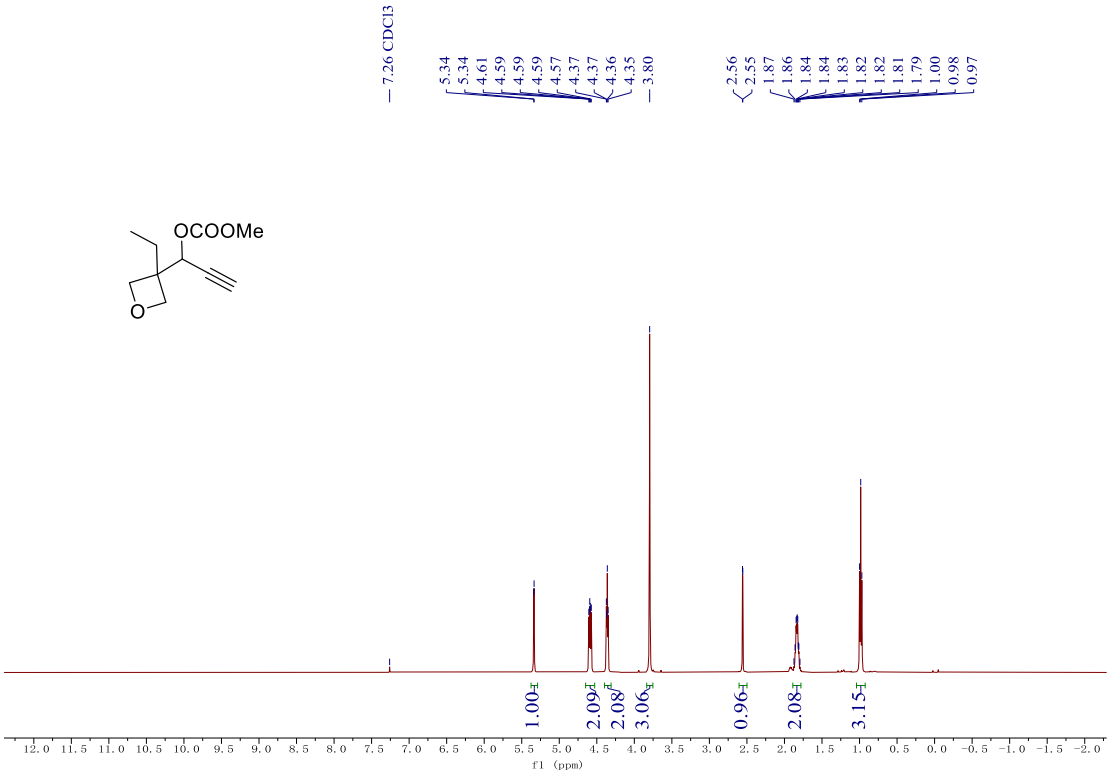


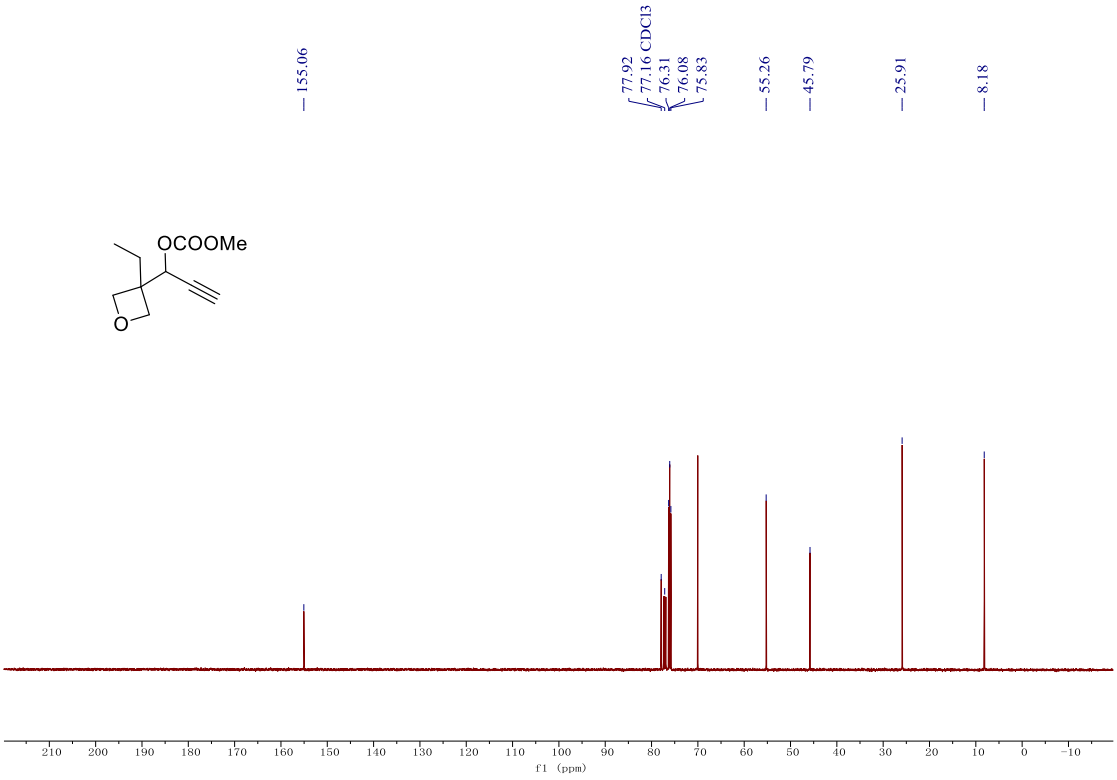
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1q



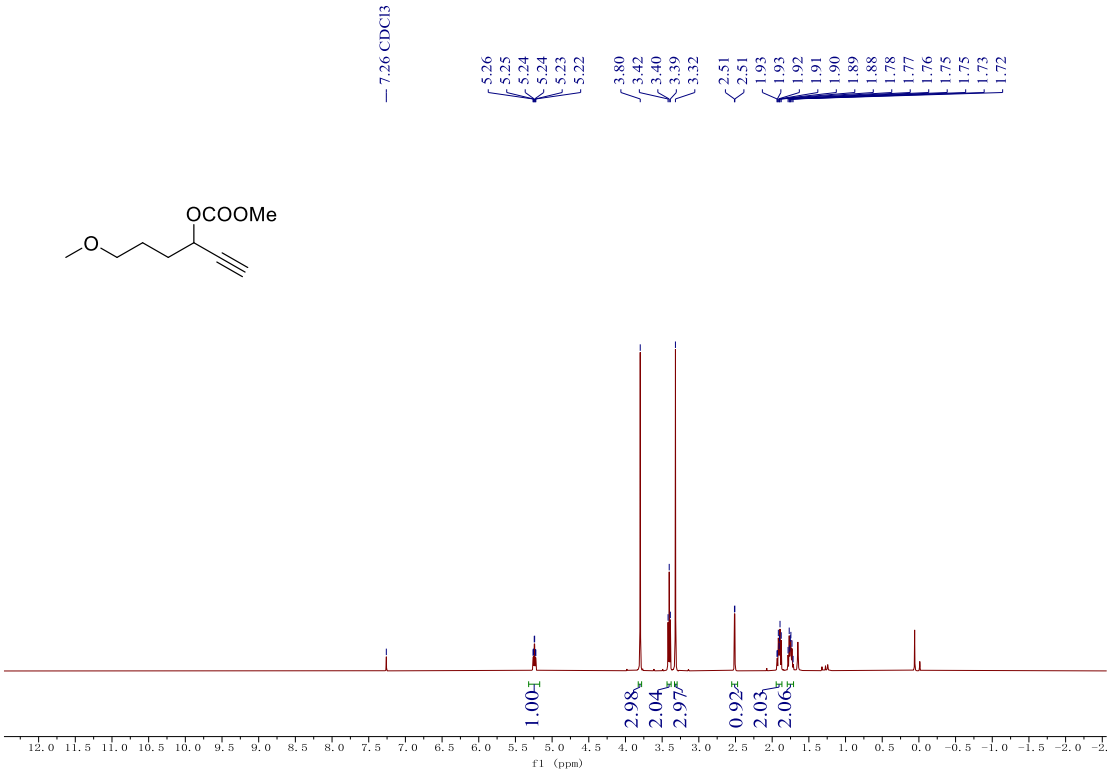


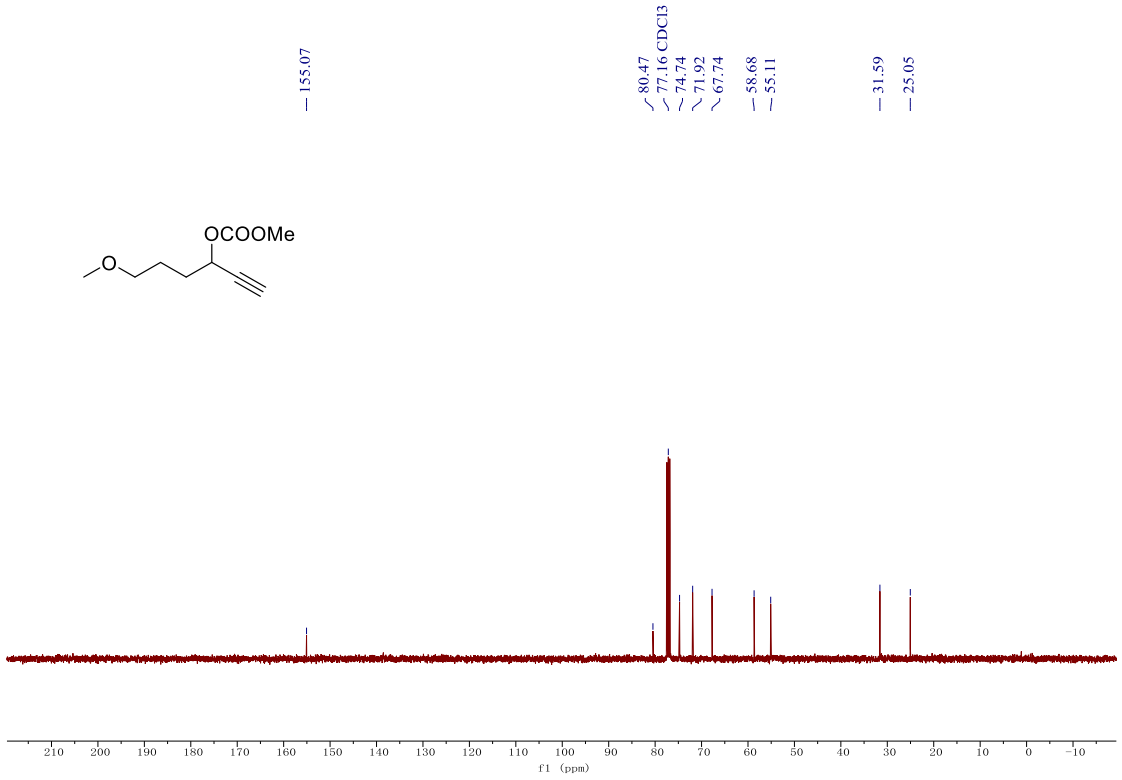
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1r



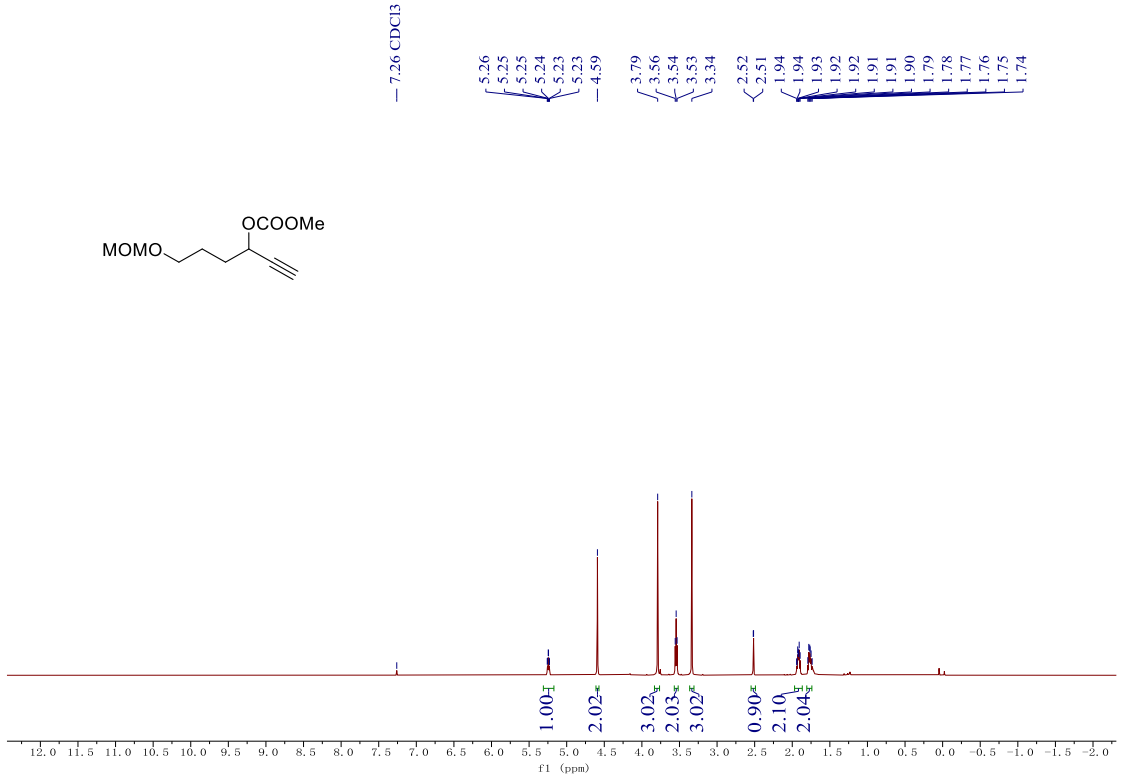


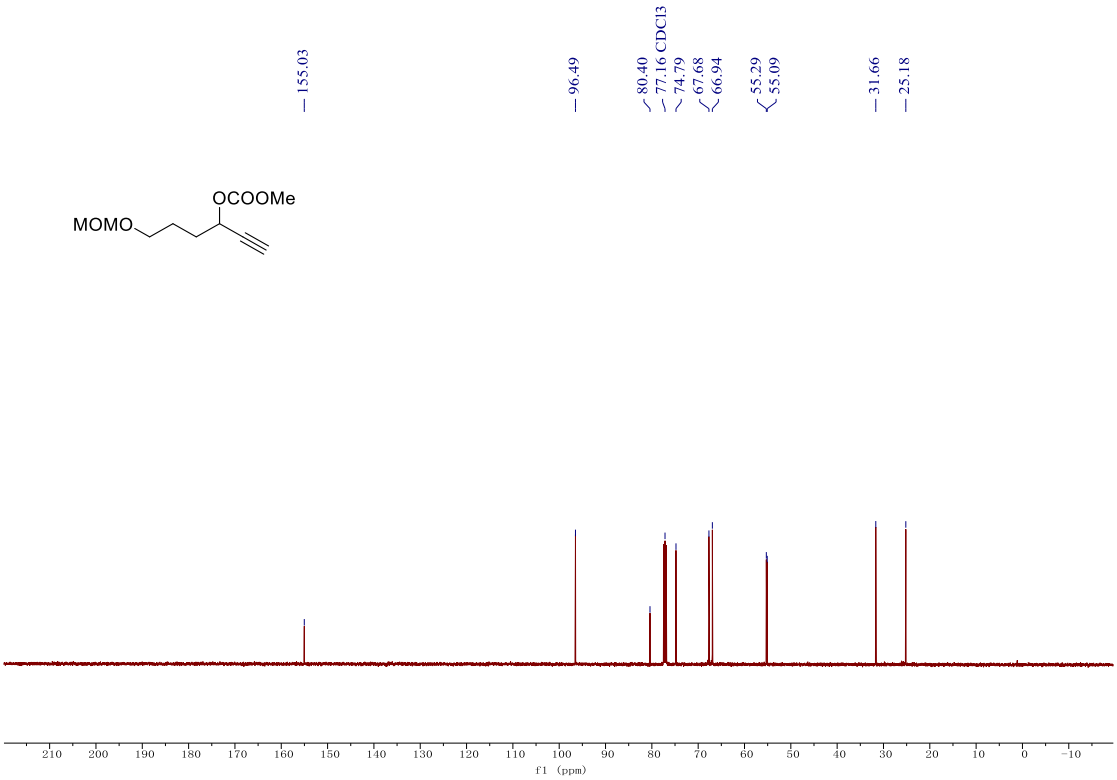
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1s



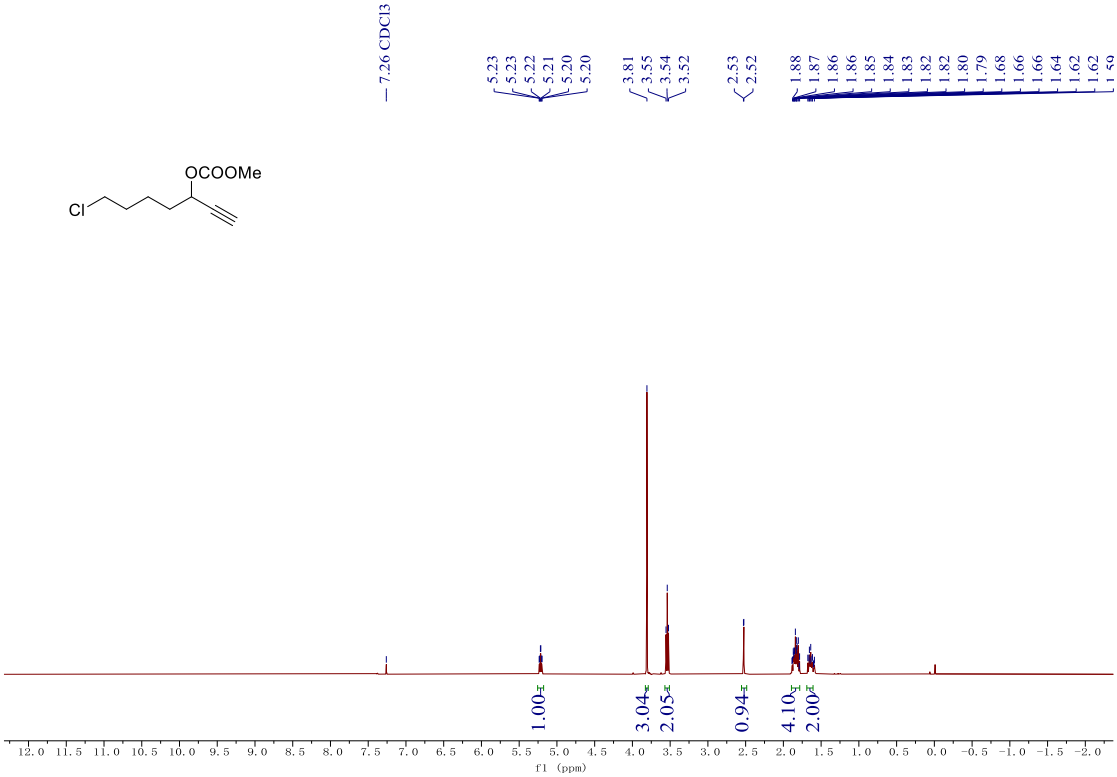


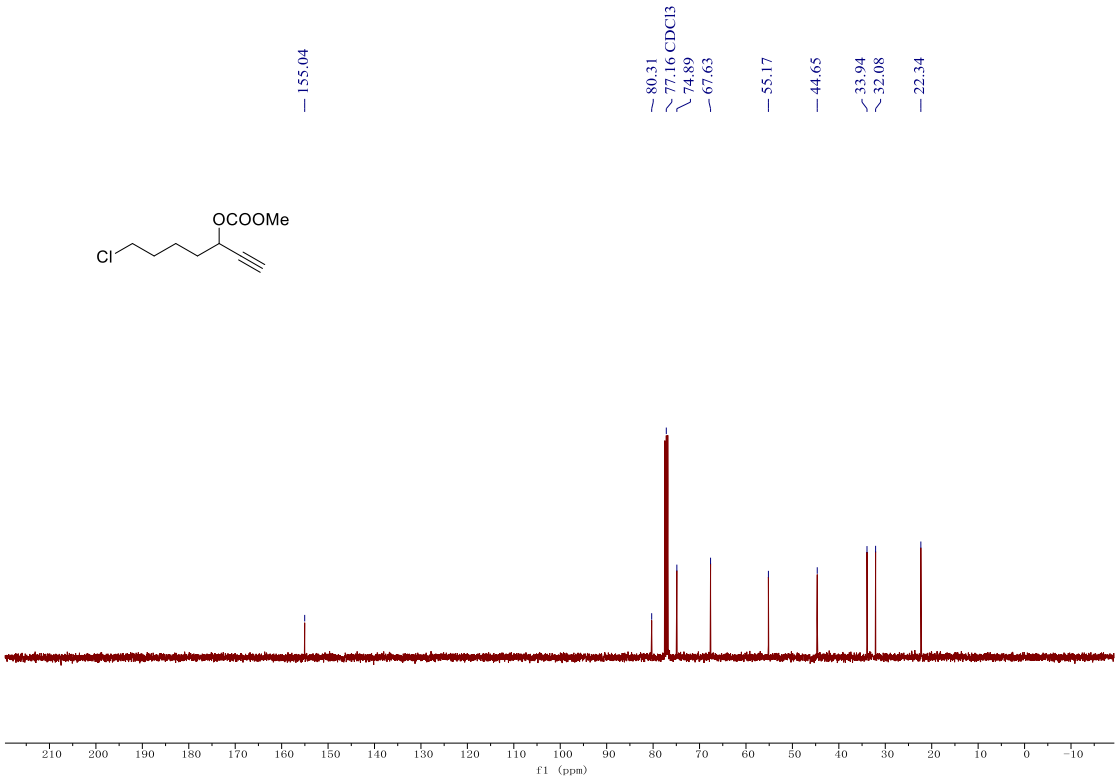
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1t



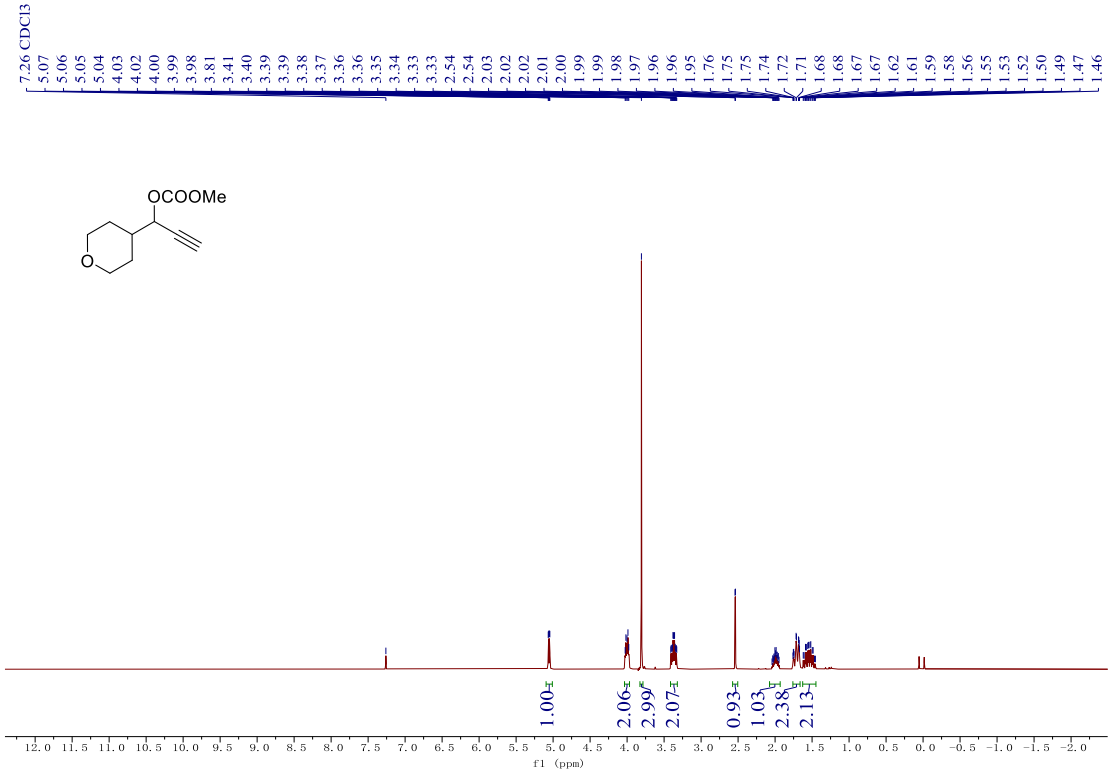


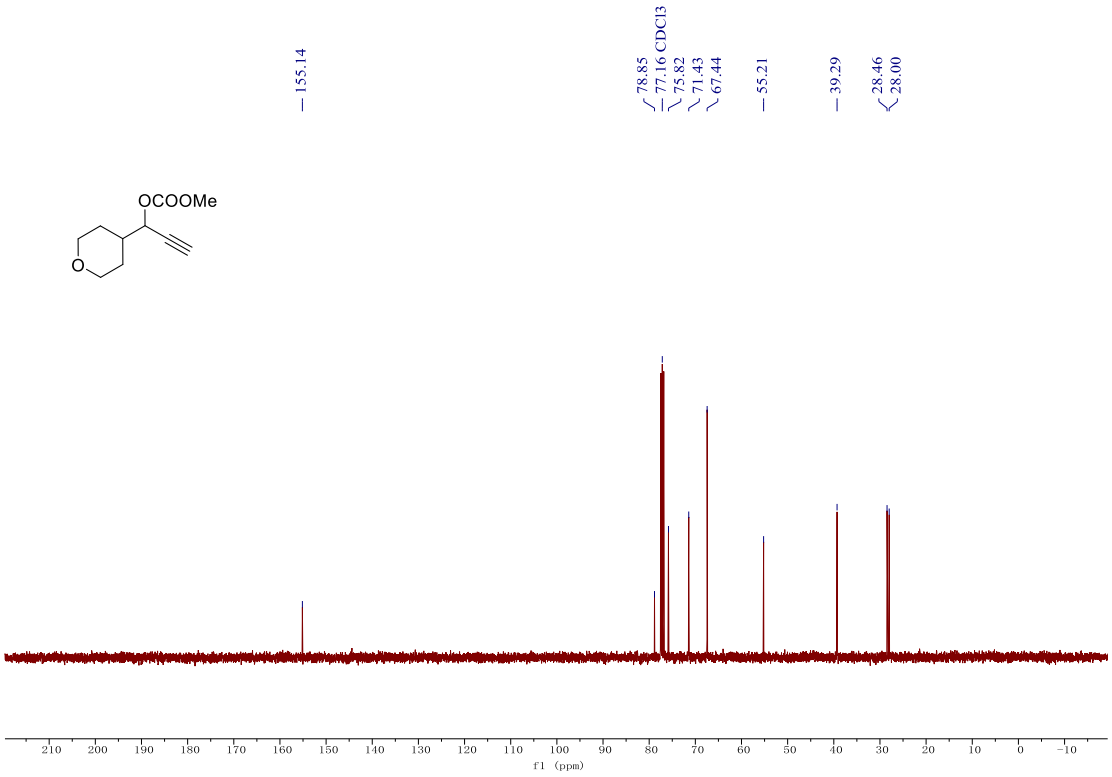
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1u



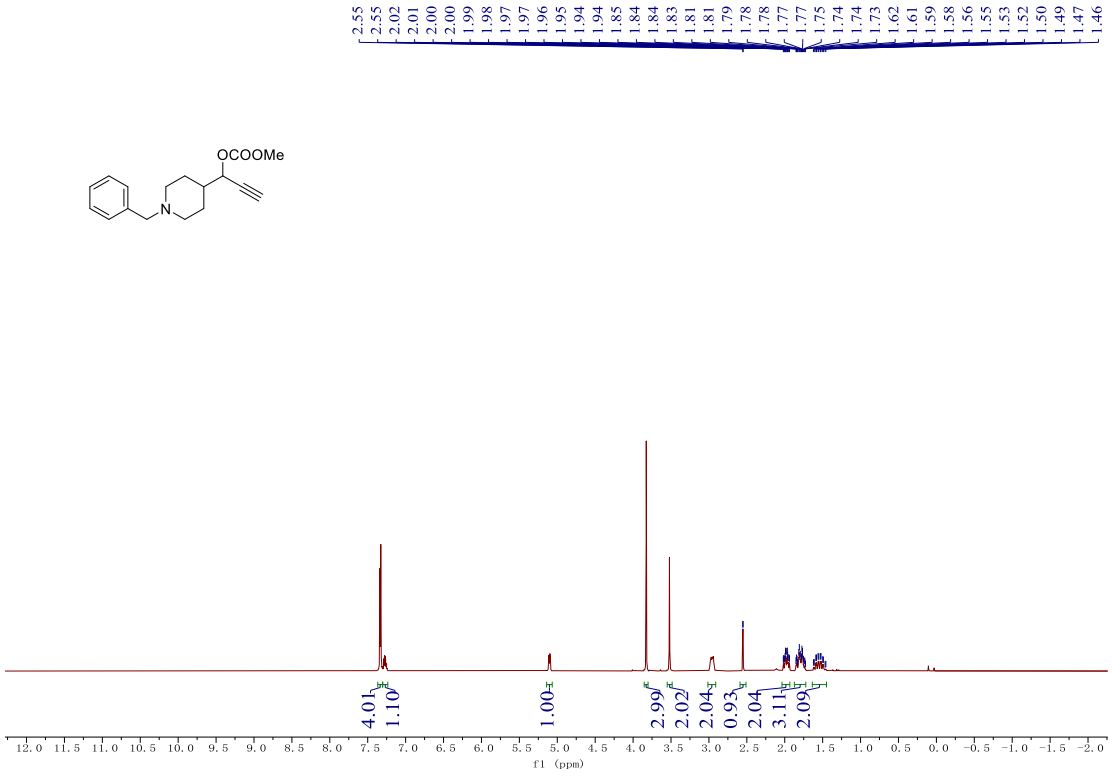


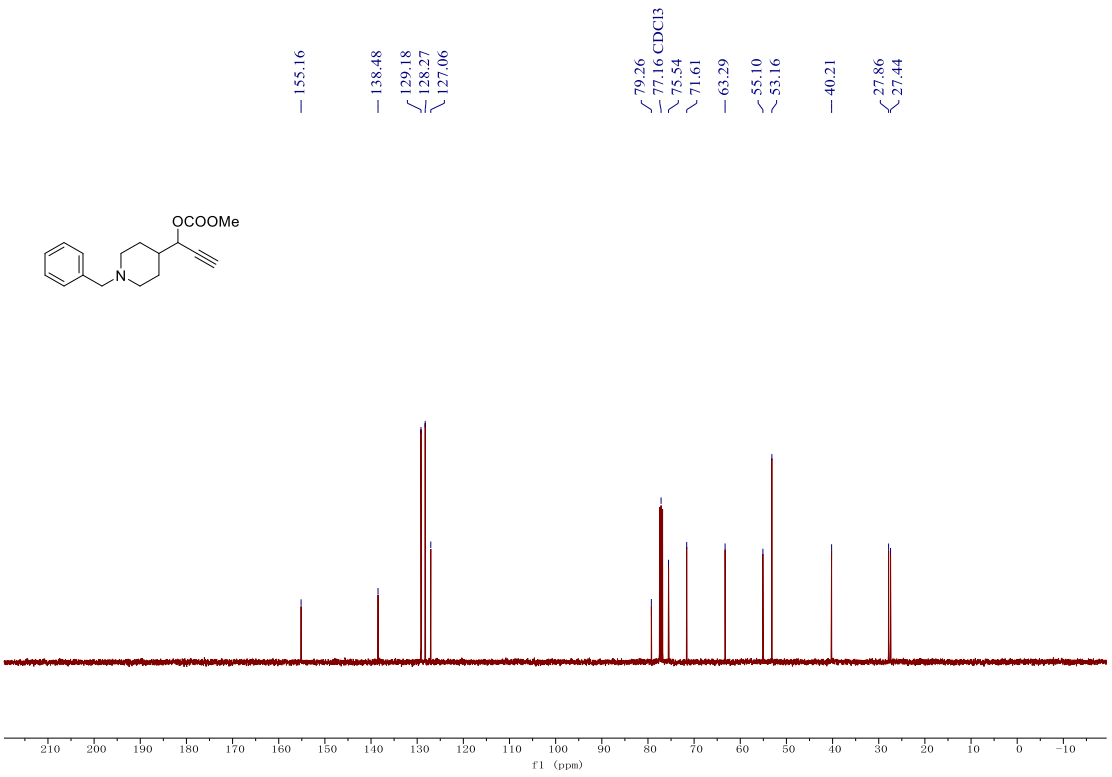
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1v



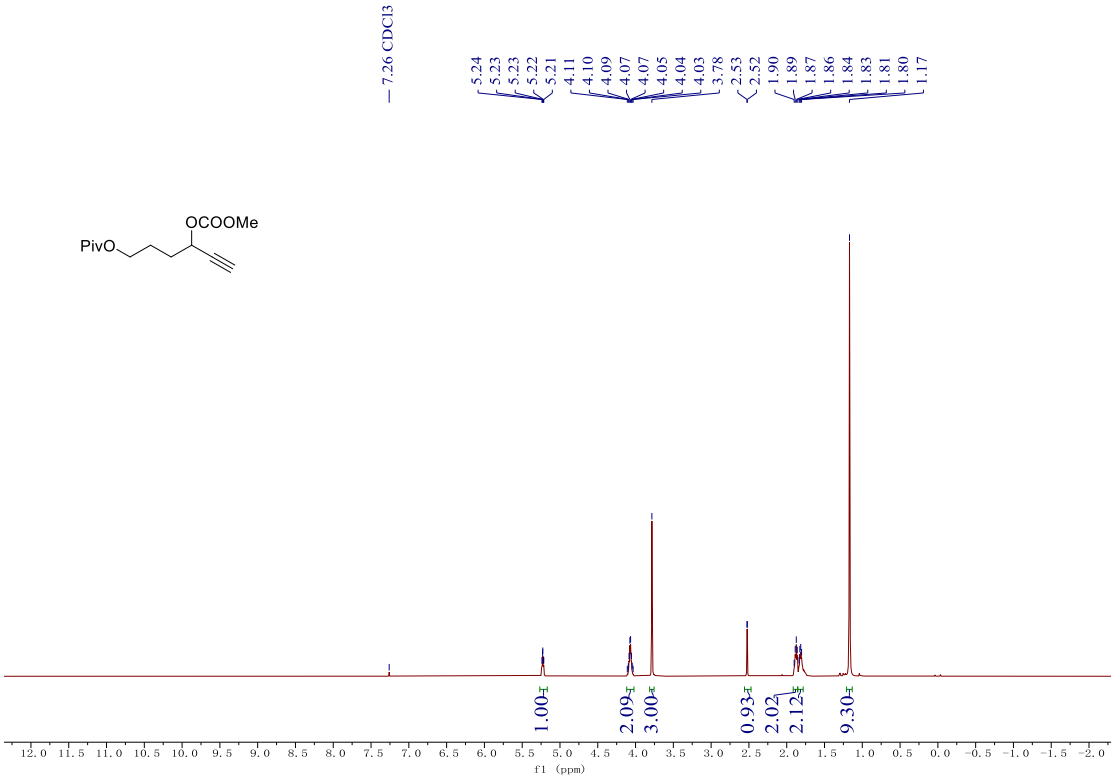


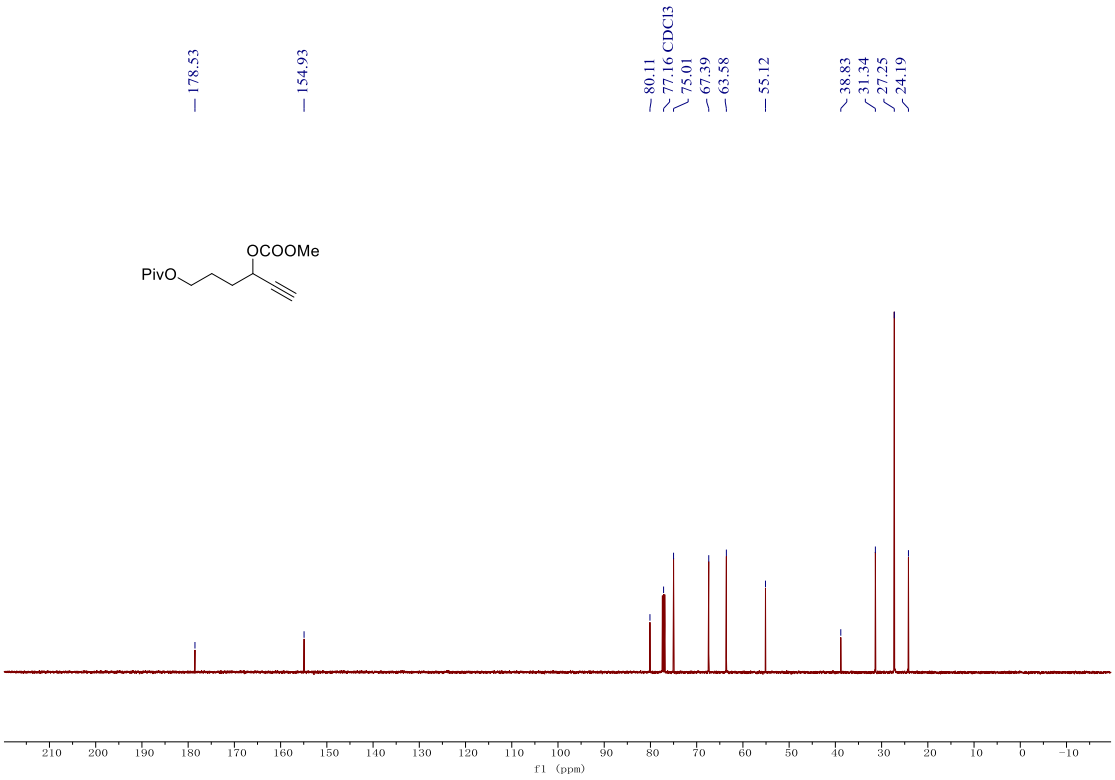
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1w



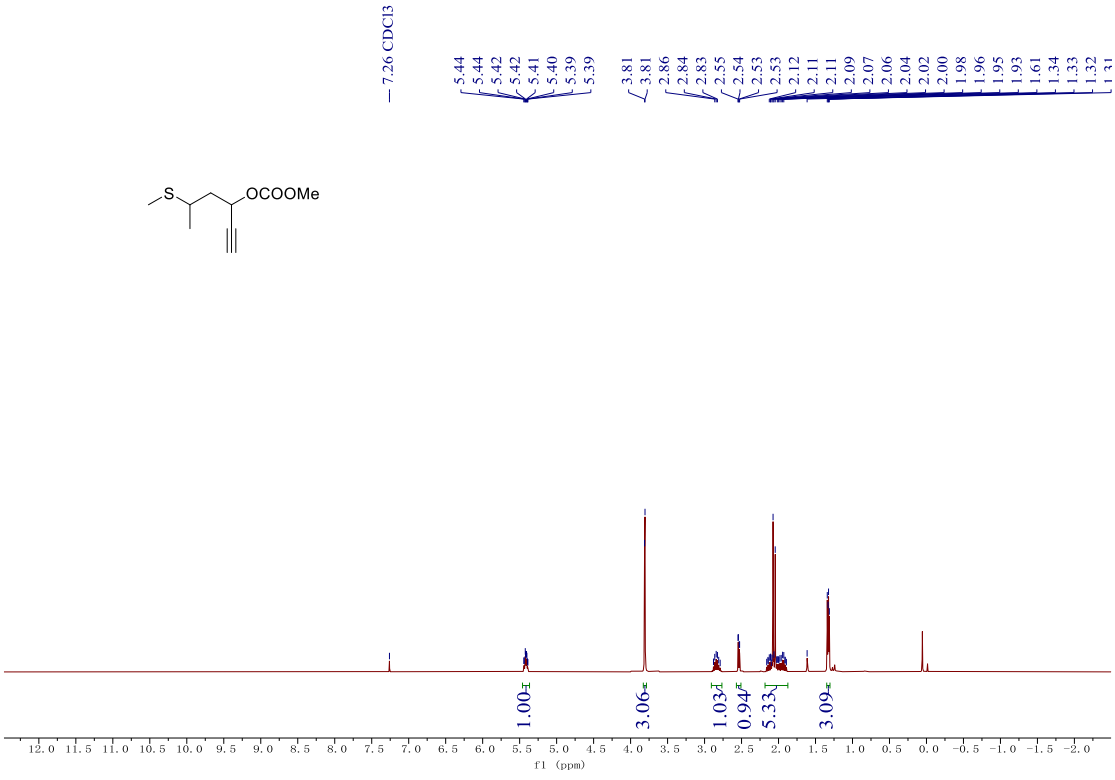


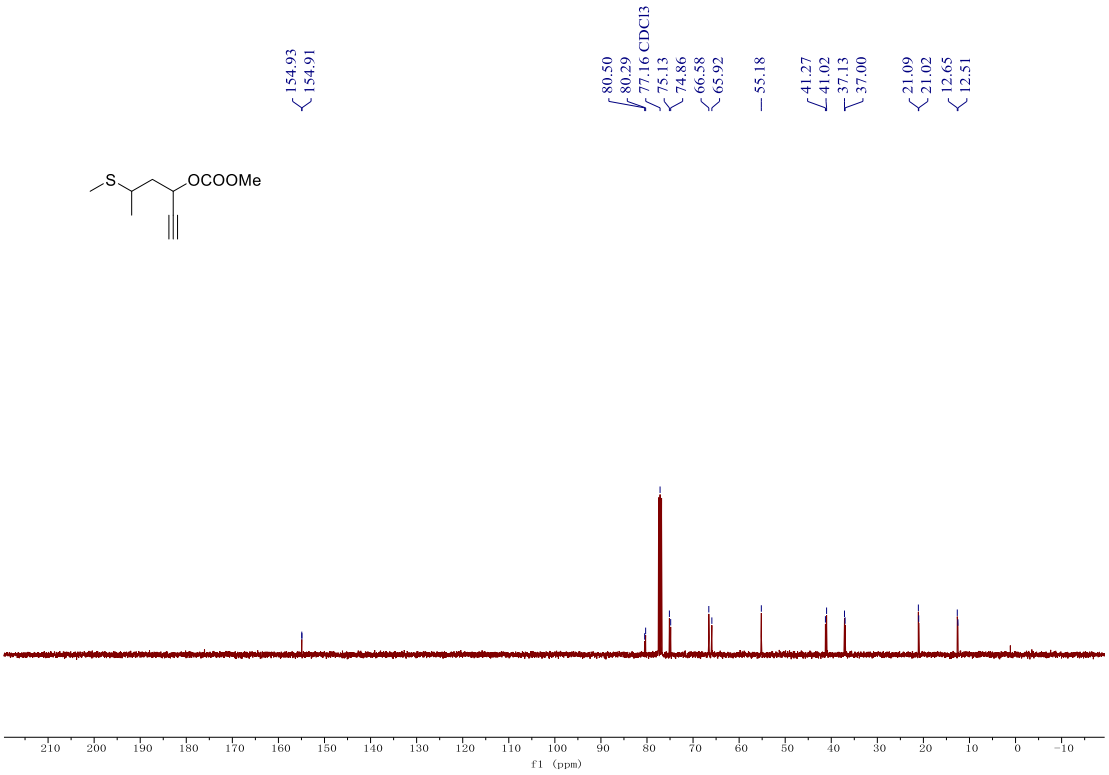
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1x



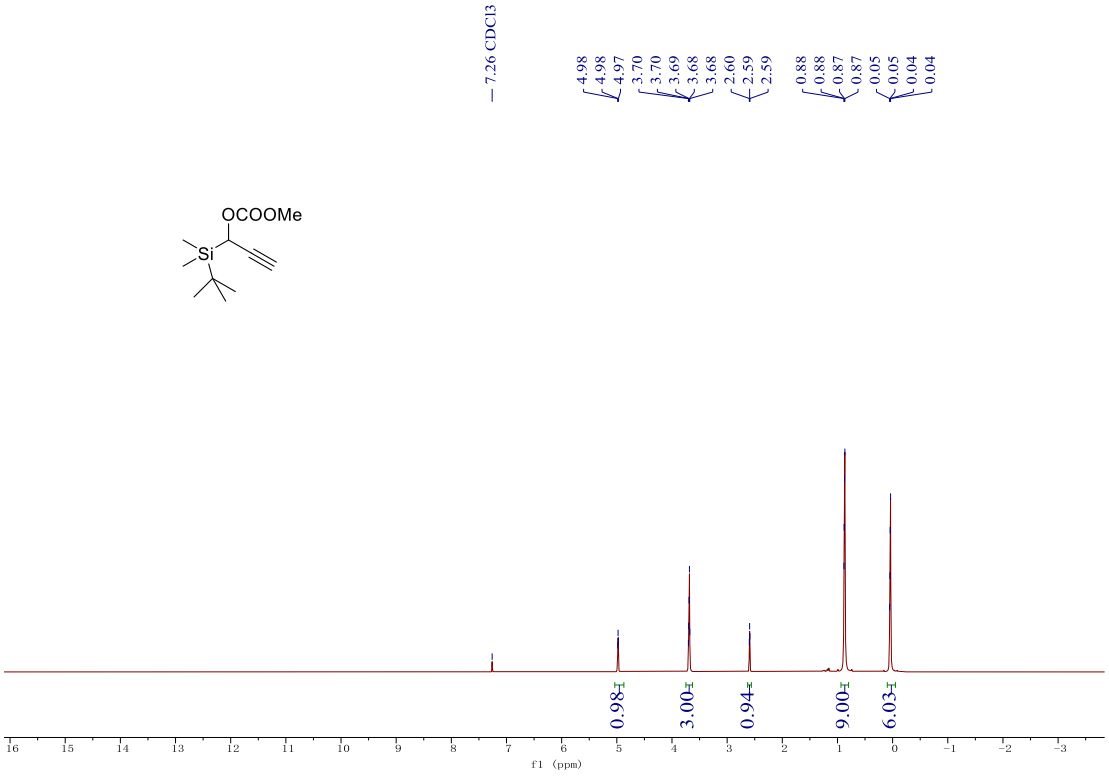


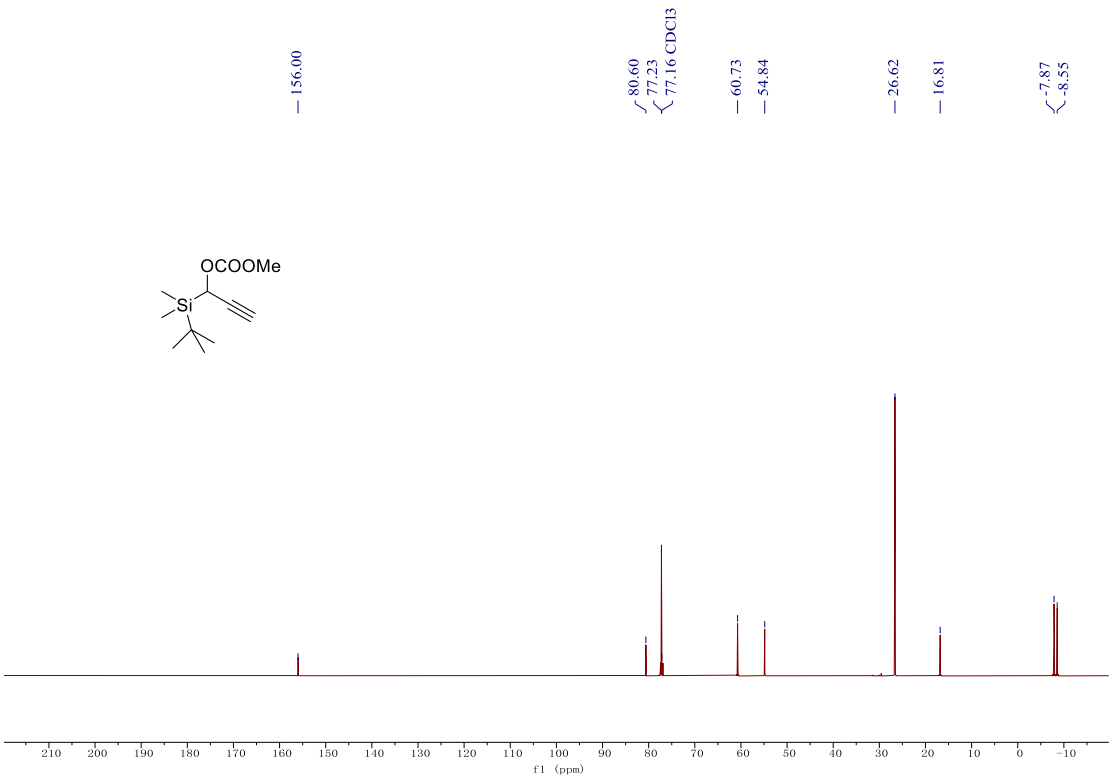
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1y



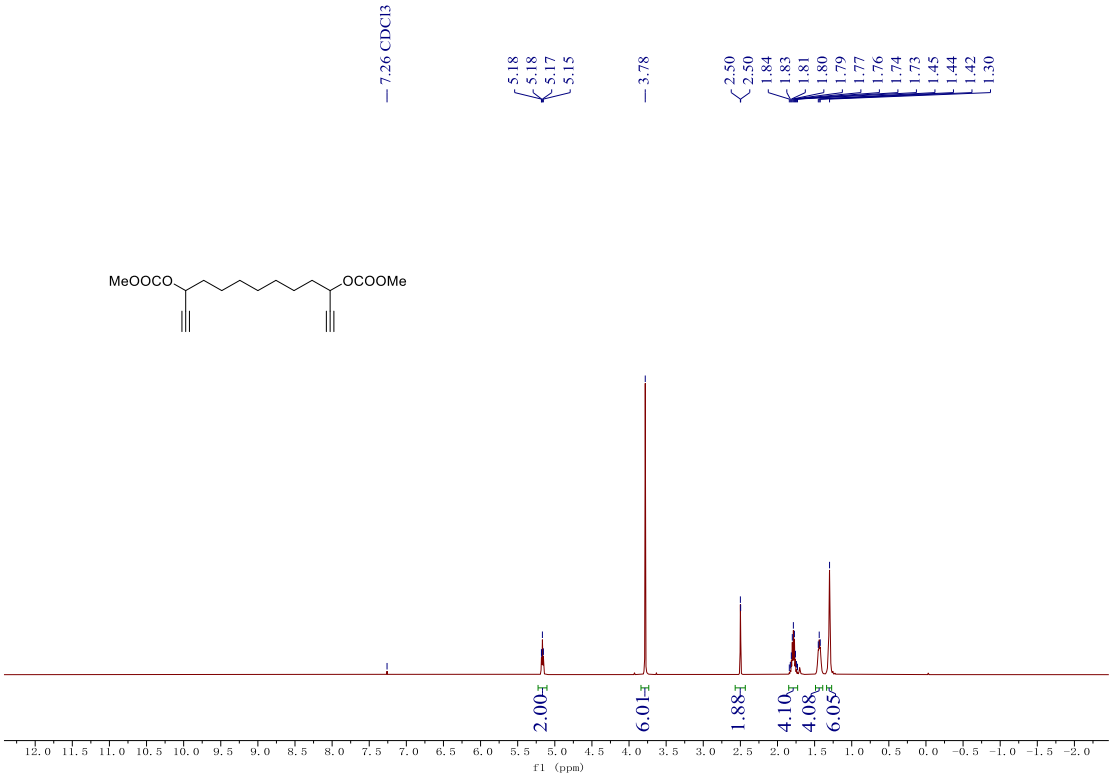


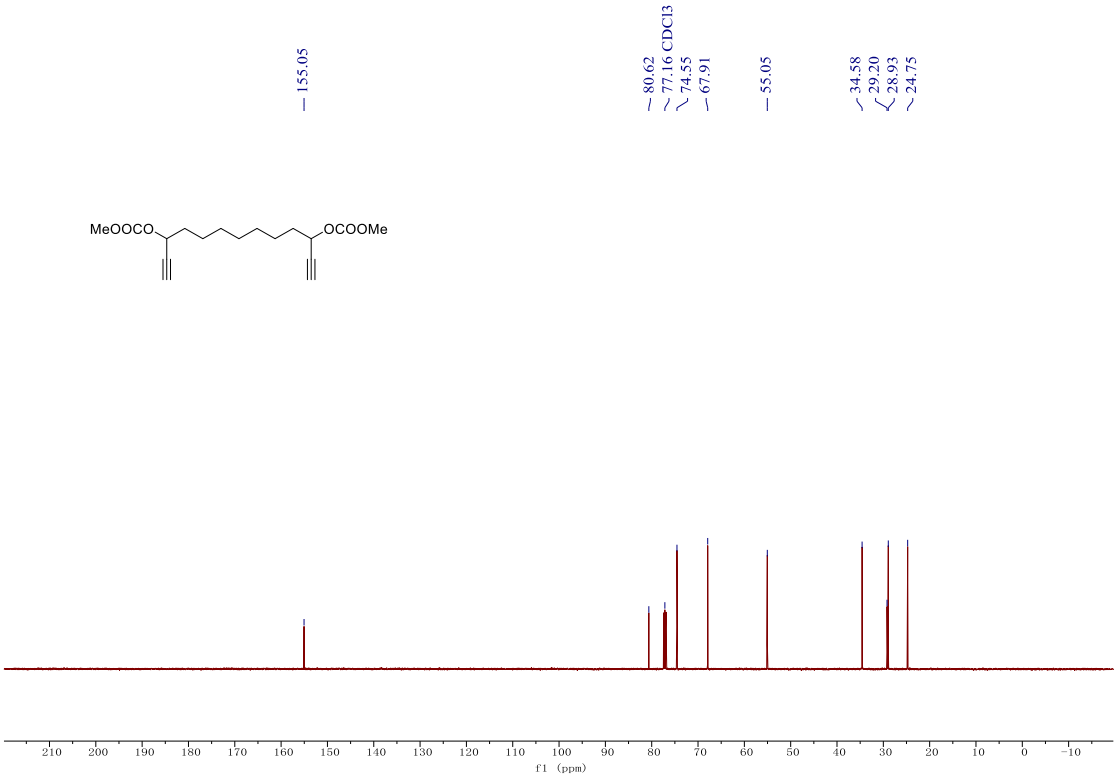
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1z



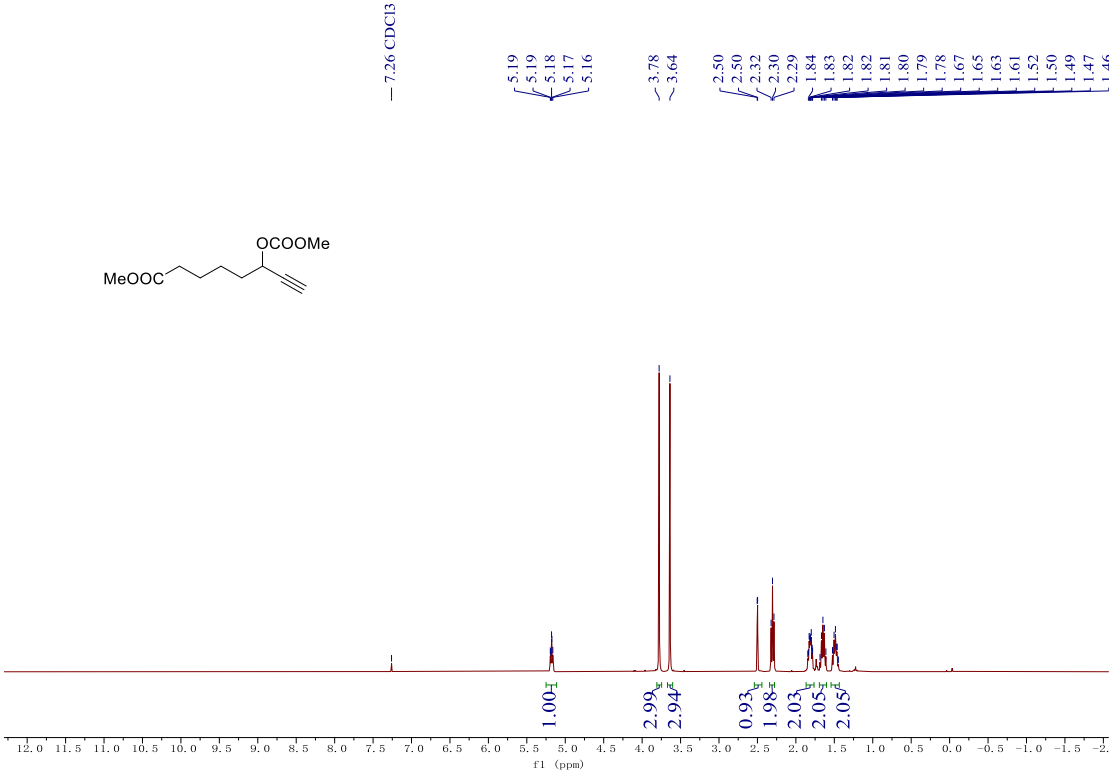


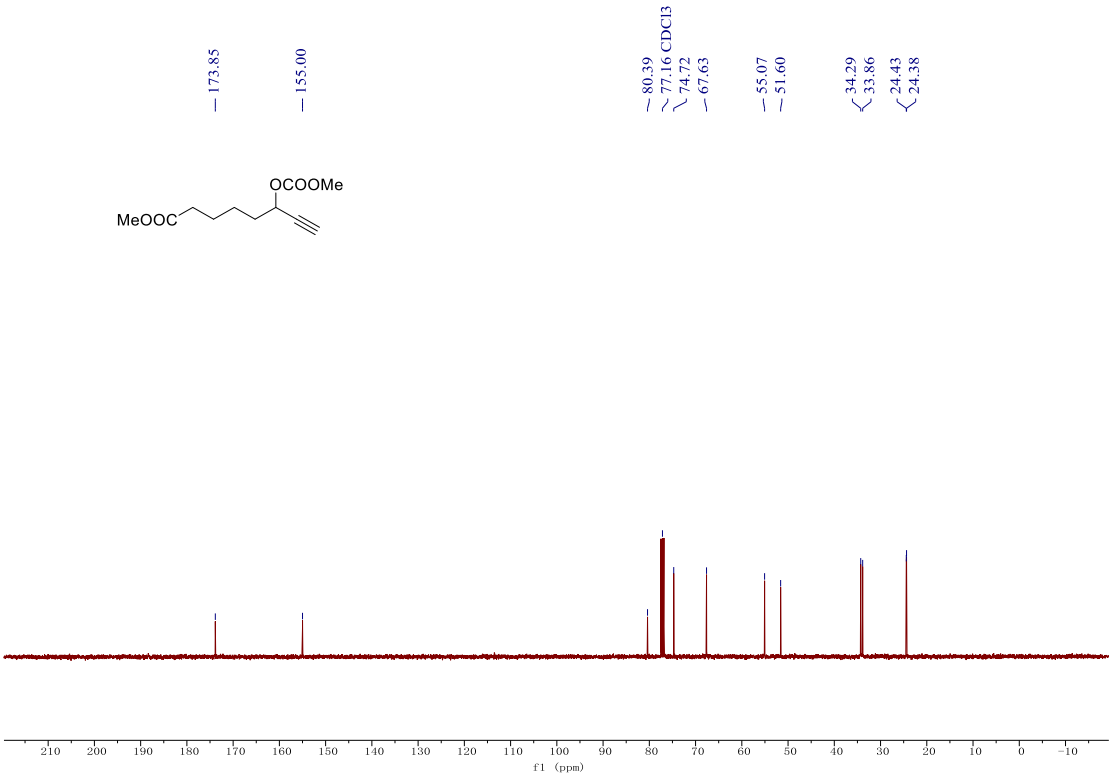
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1aa



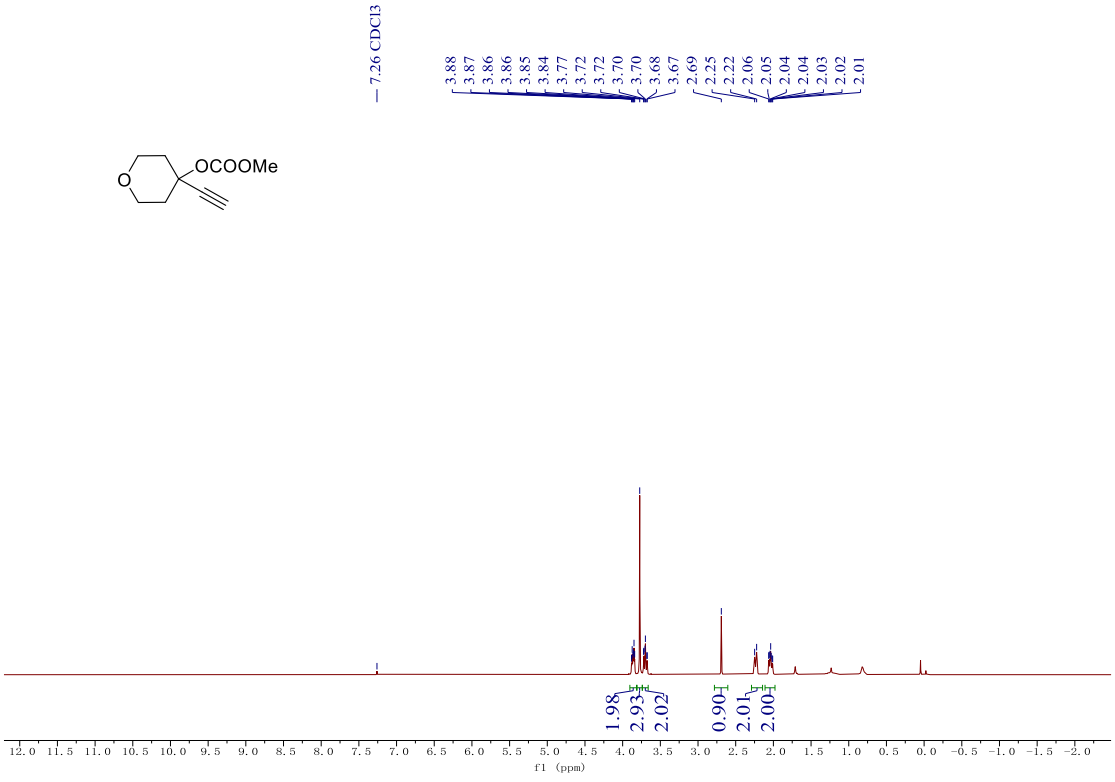


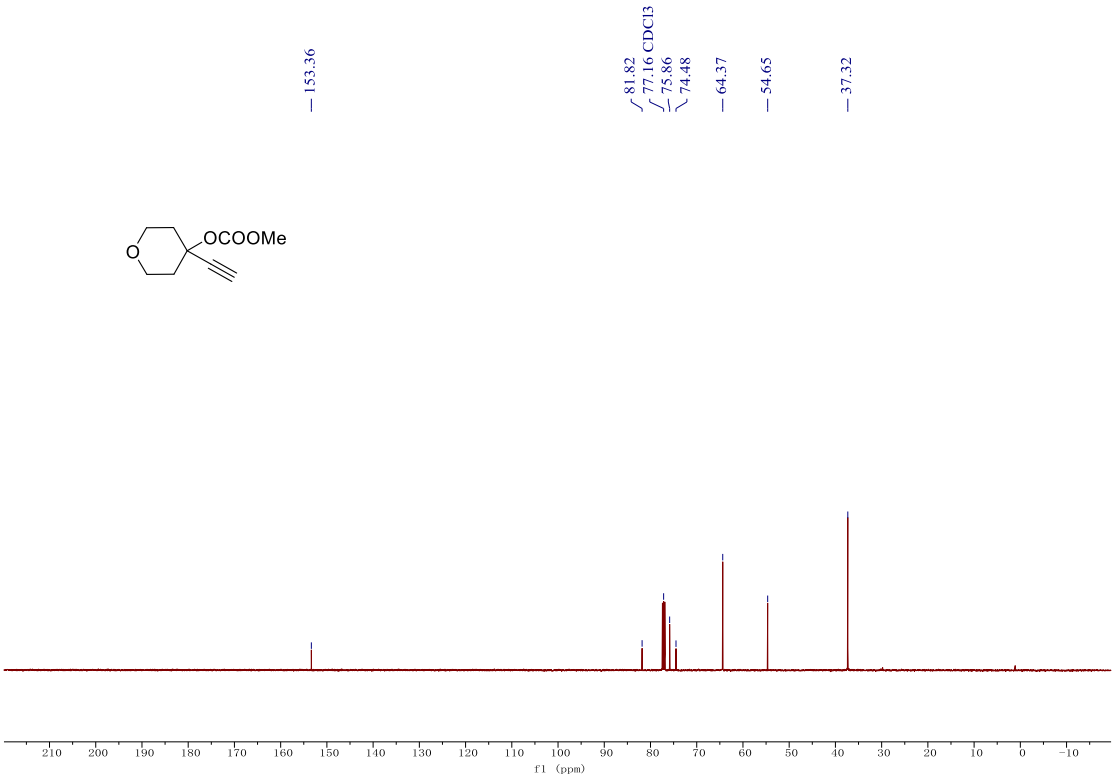
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1ab



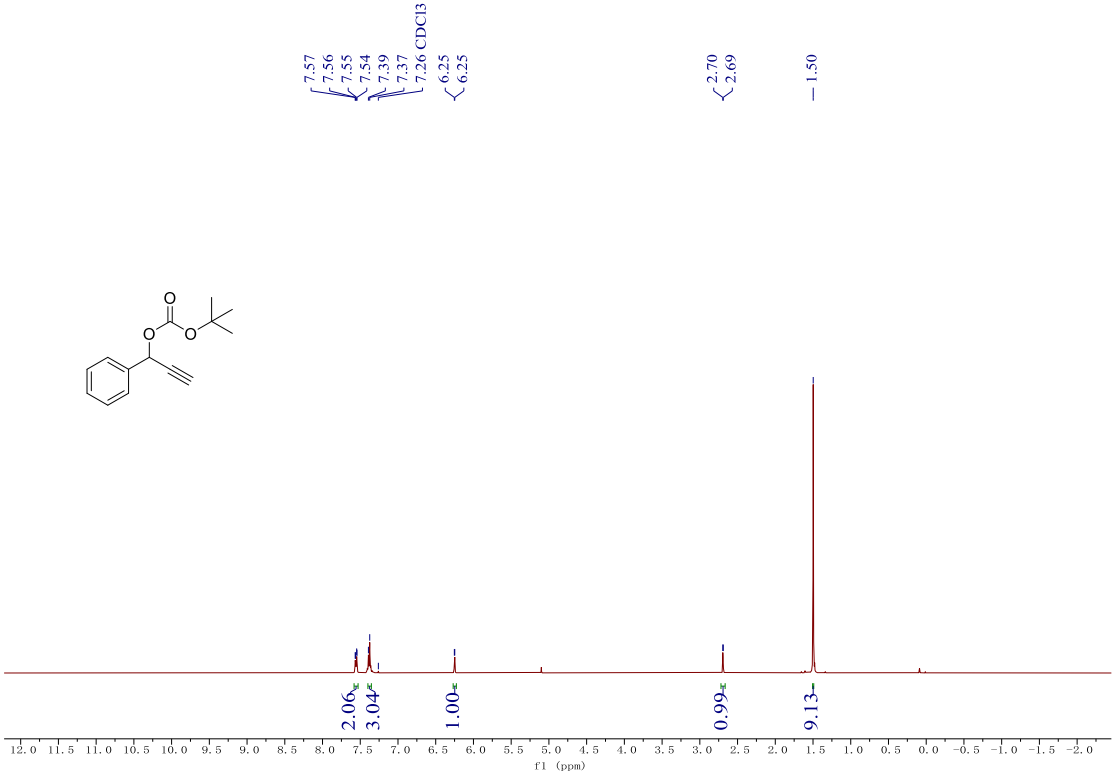


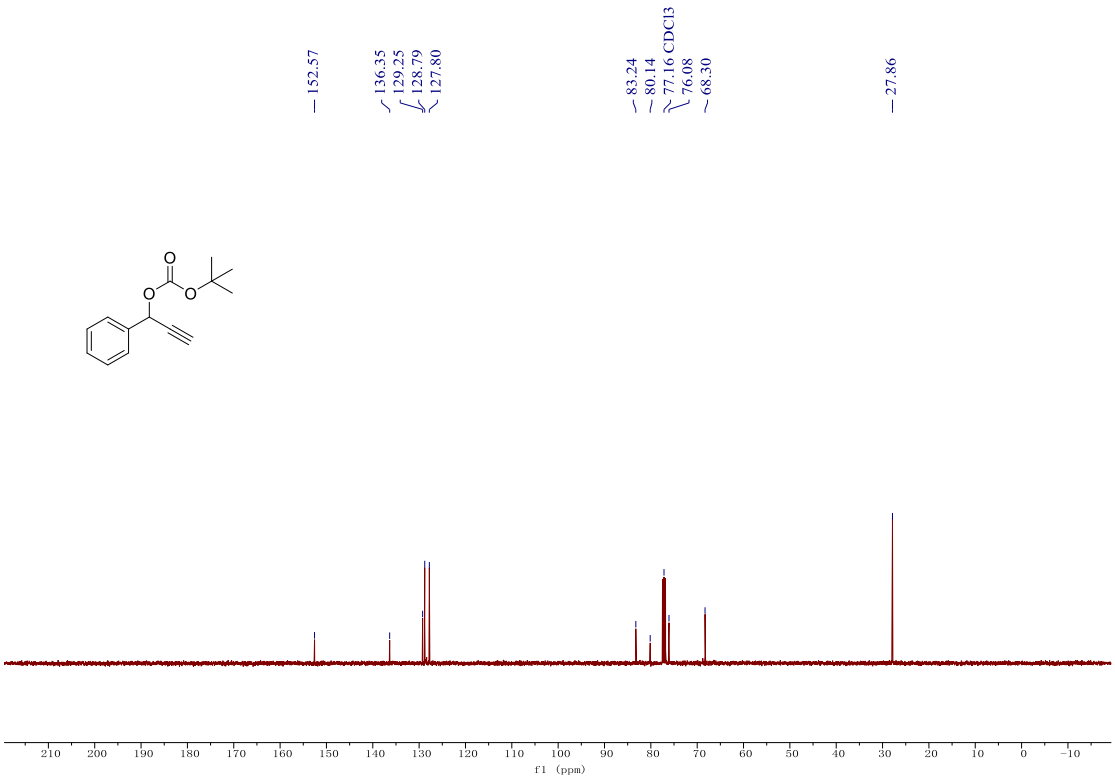
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 1ac



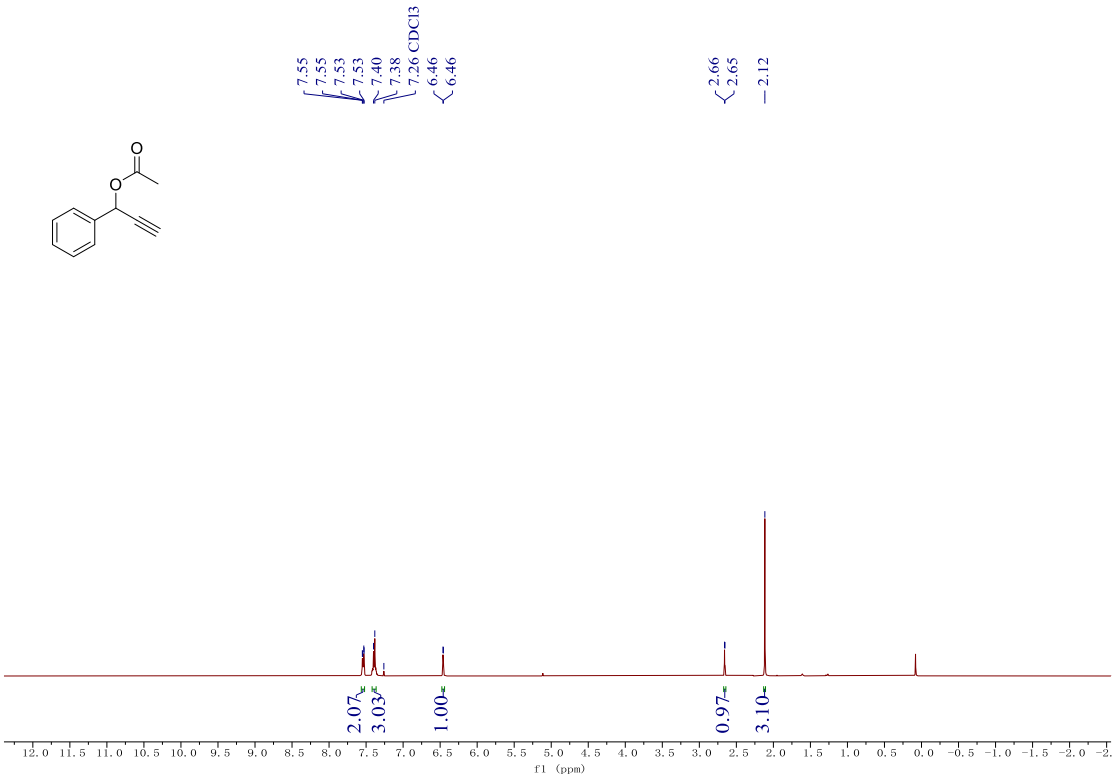


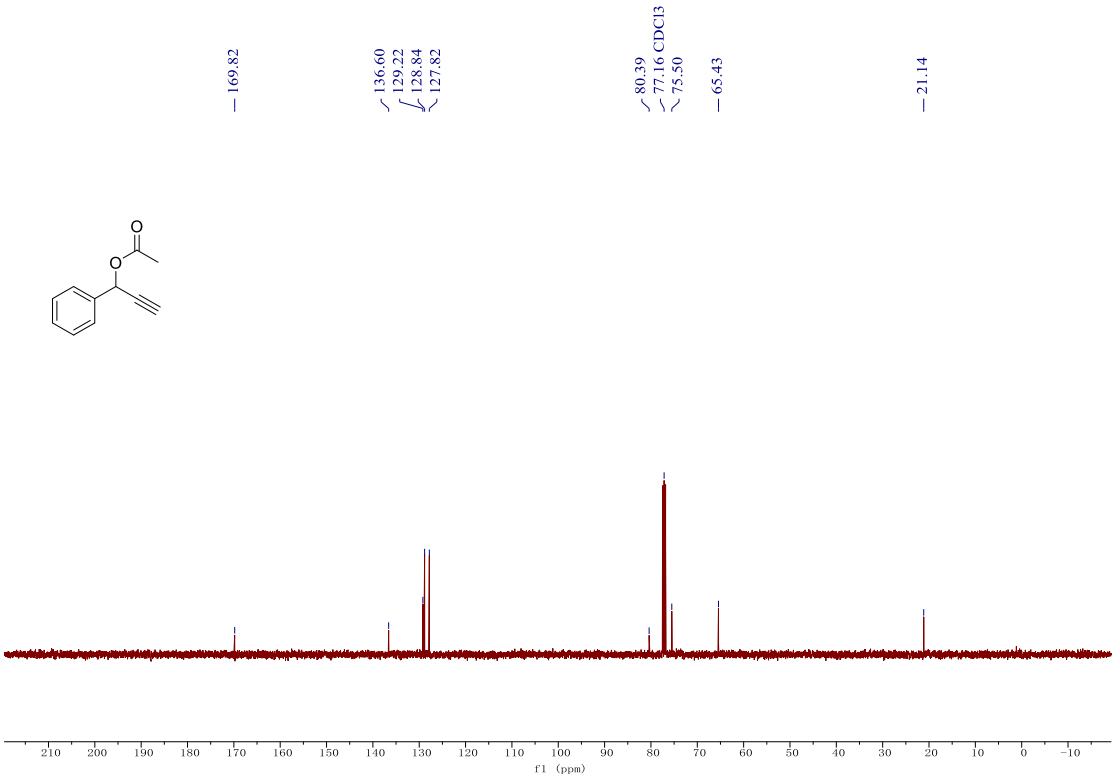
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1ad



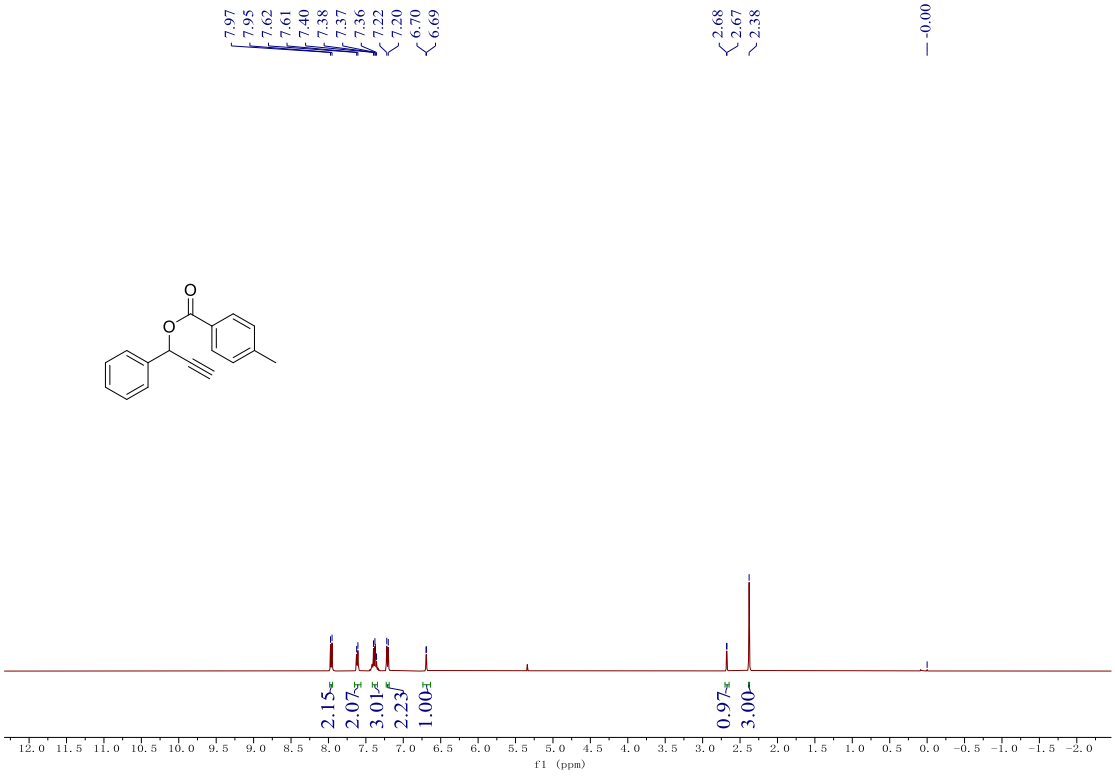


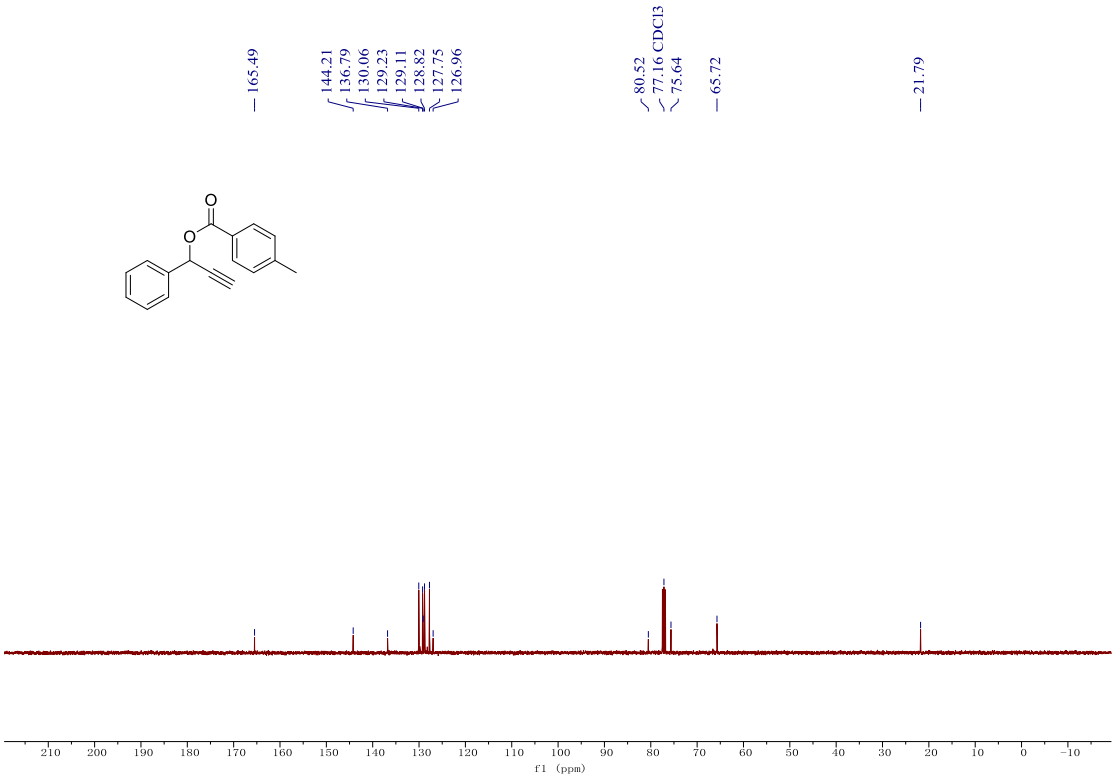
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1ae



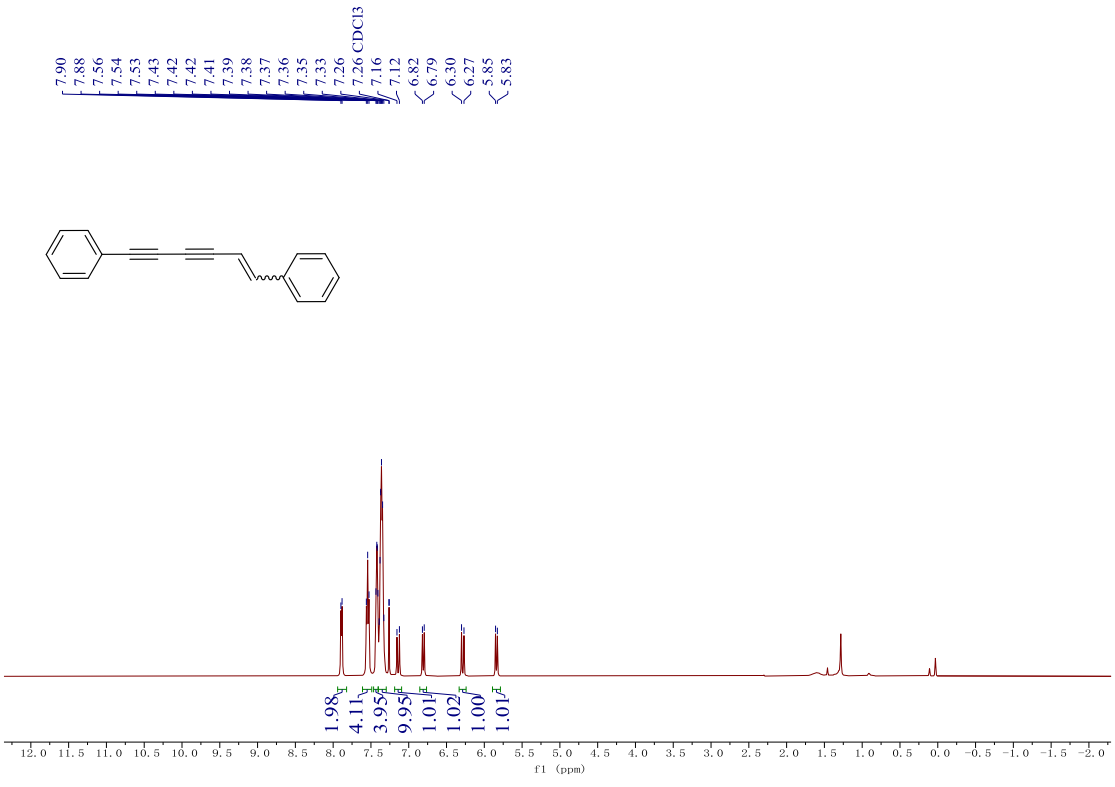


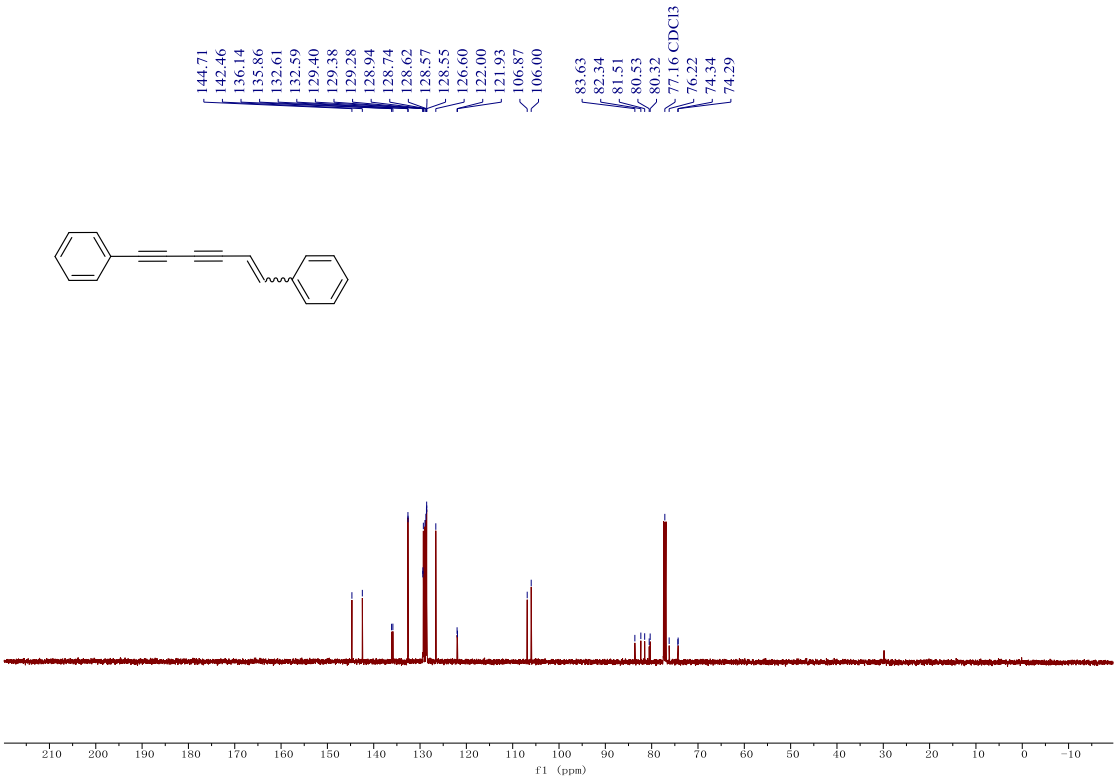
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1af



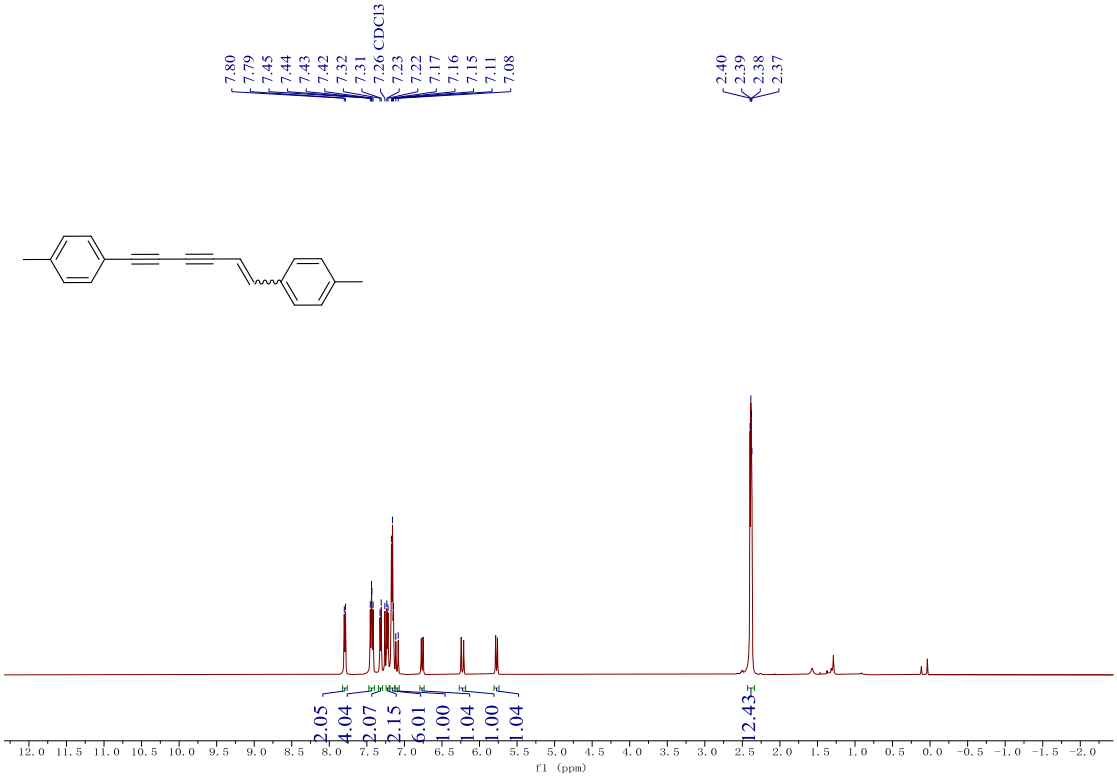


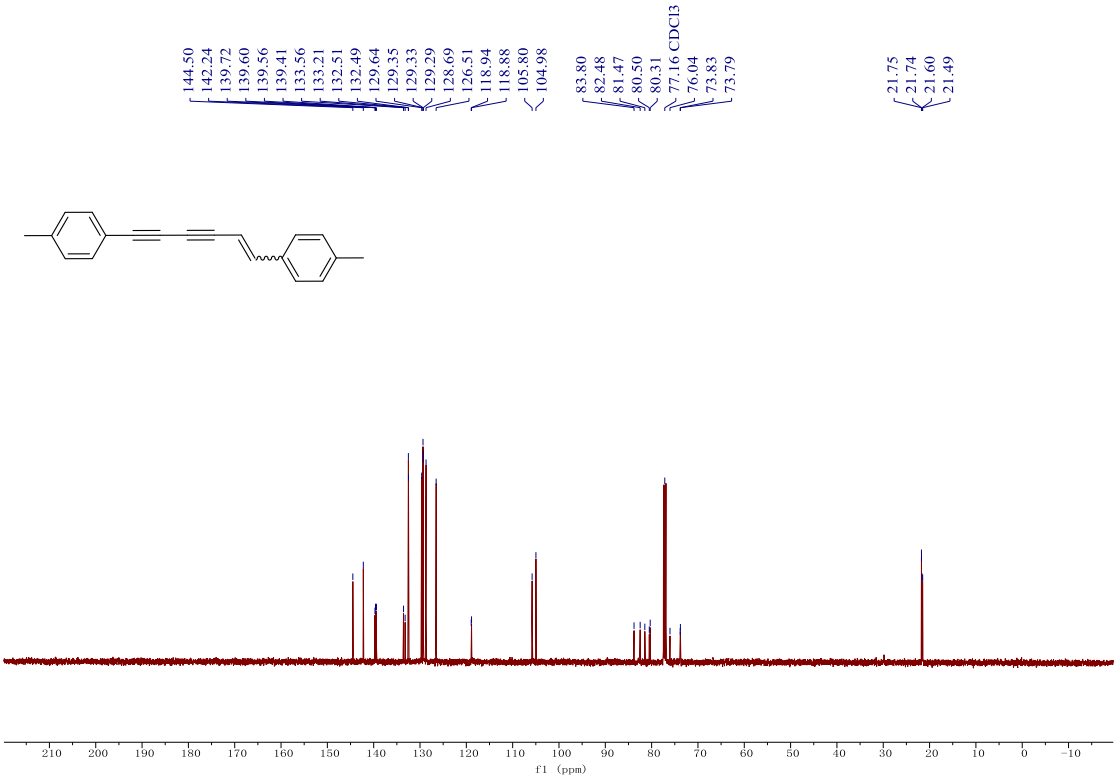
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2a



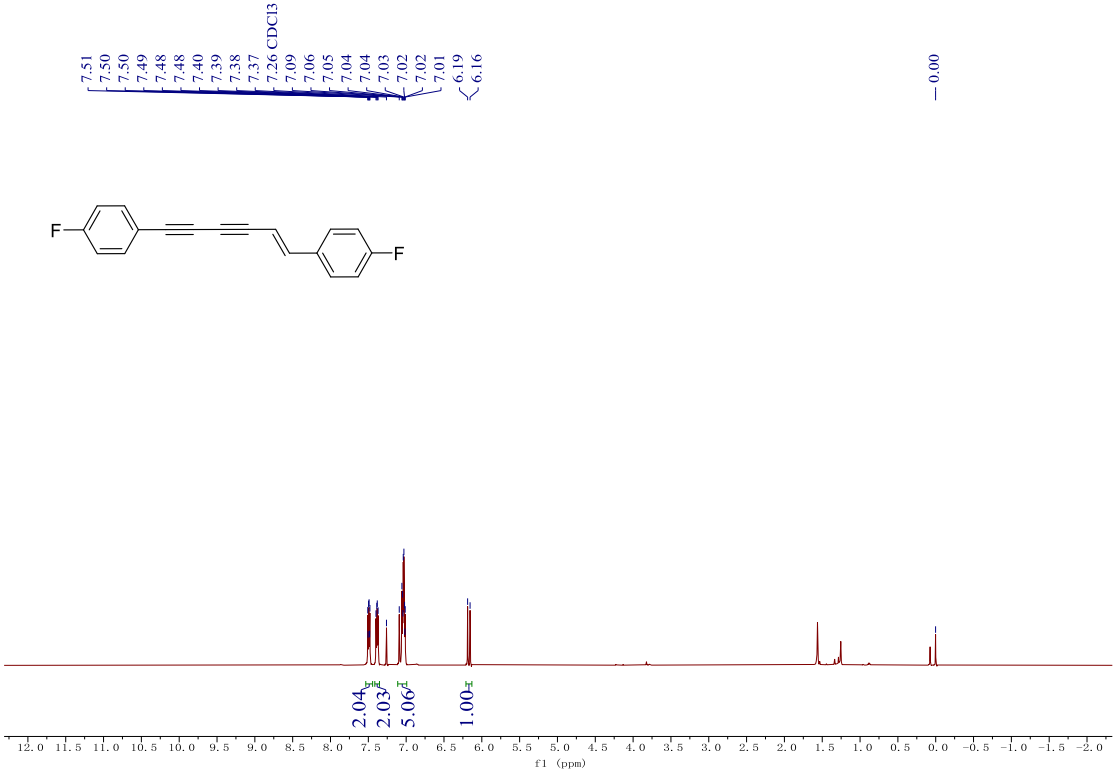


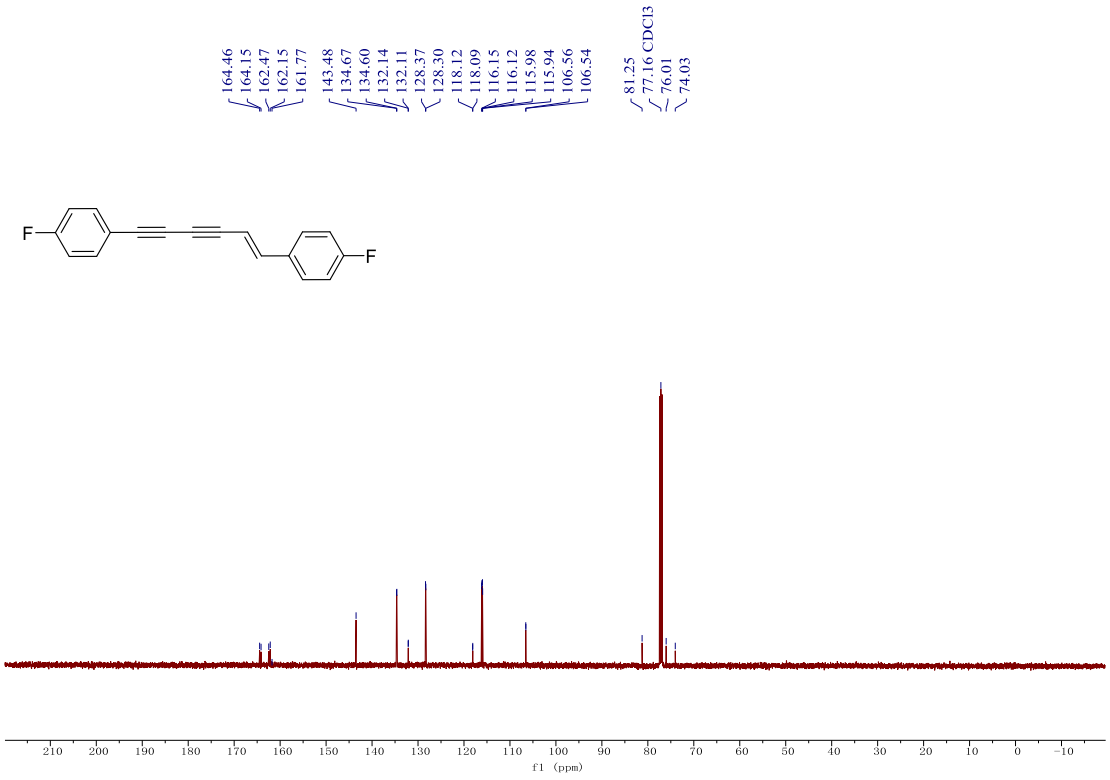
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2b

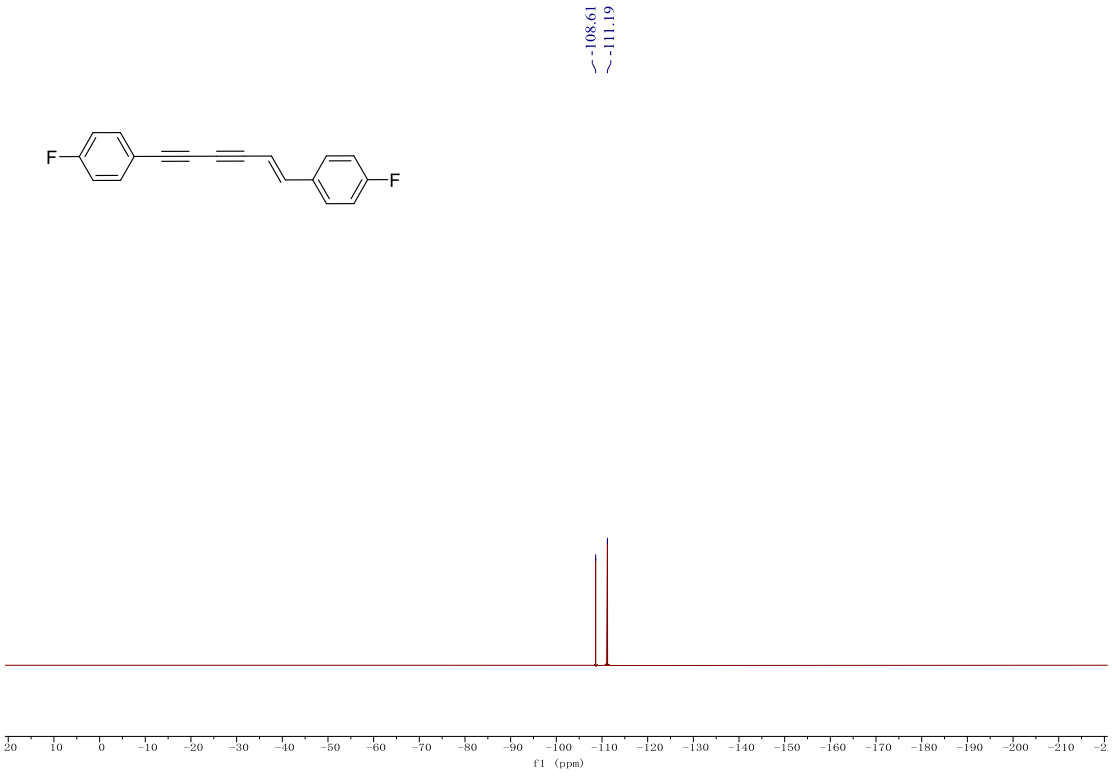




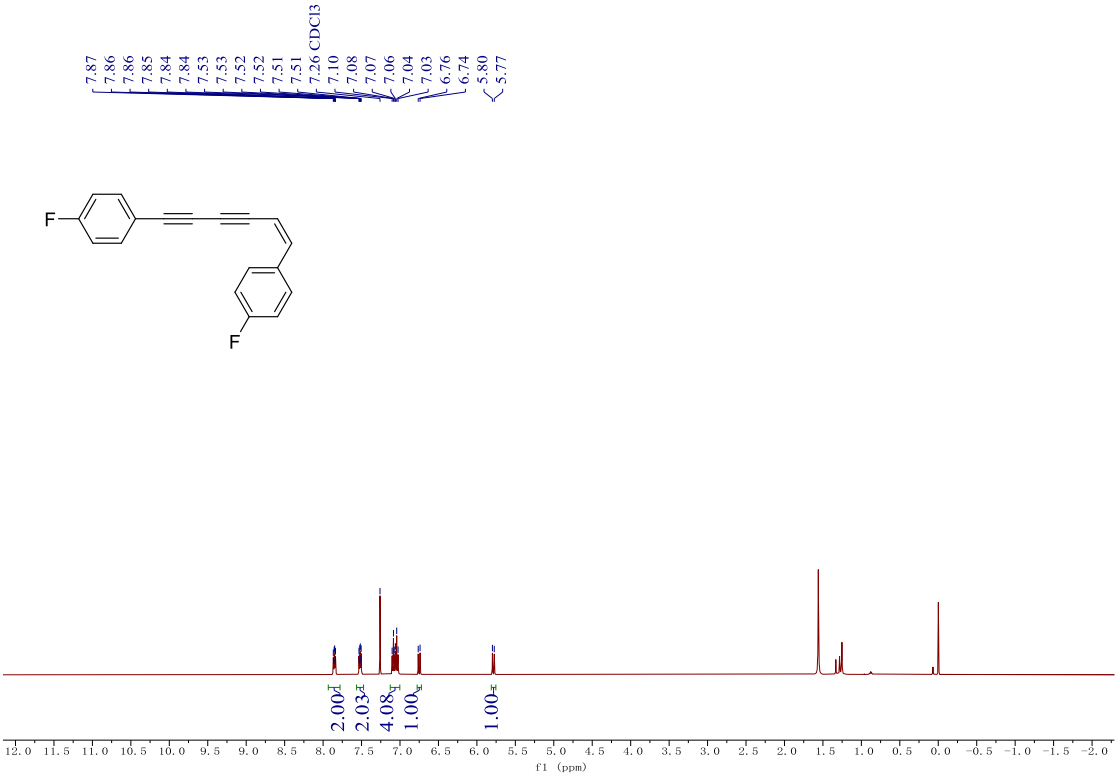
^{1}H NMR spectrum (500 MHz, $CDCl_3$), ^{13}C NMR spectrum (126 MHz, $CDCl_3$) and ^{19}F spectrum NMR (471 MHz, $CDCl_3$) of *E*-2c

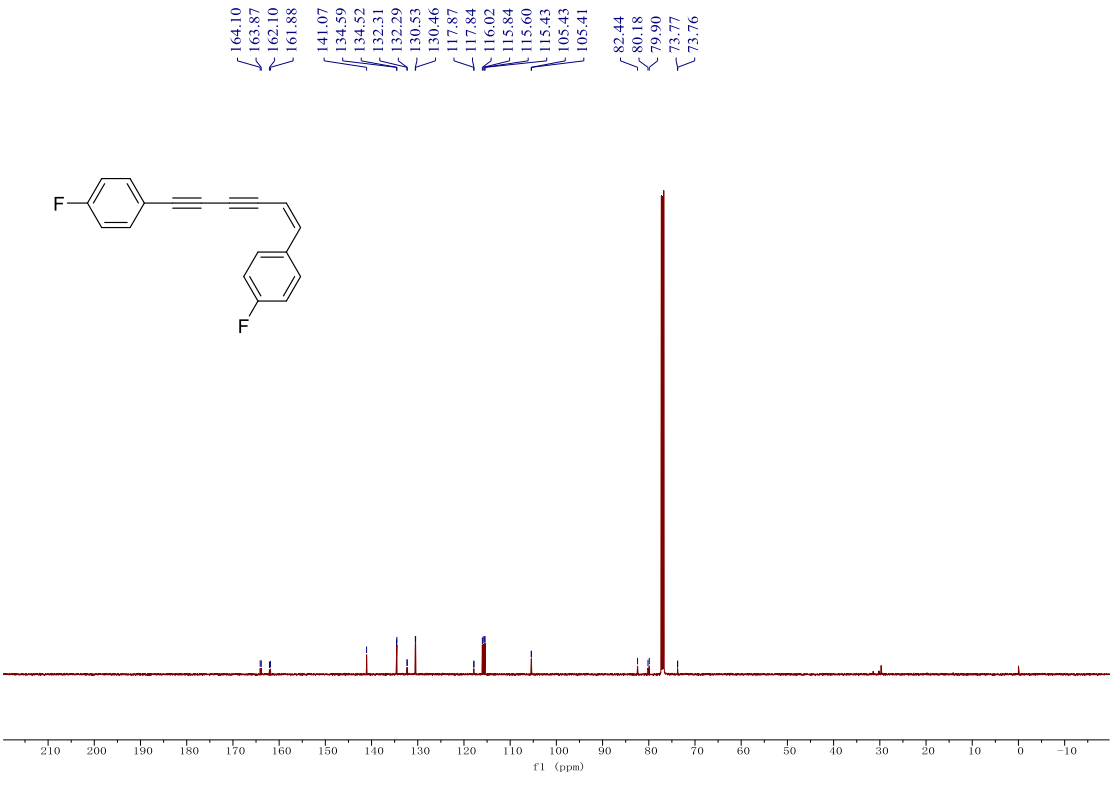


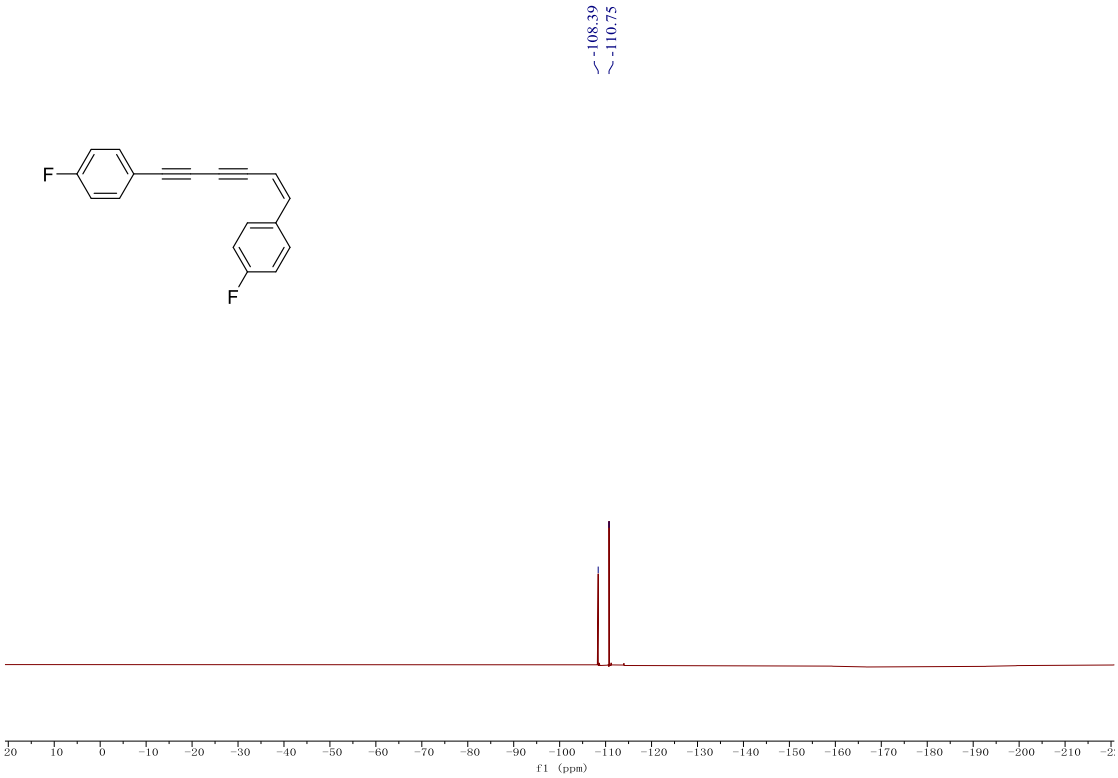

164.46
164.15
162.47
162.15
161.77
143.48
134.67
134.60
132.14
132.11
128.37
128.30
118.12
118.09
116.15
116.12
115.98
115.94
106.56
106.54
81.25
77.16 CDCl3
76.01
74.03
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-108.61
-111.19
F
F
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

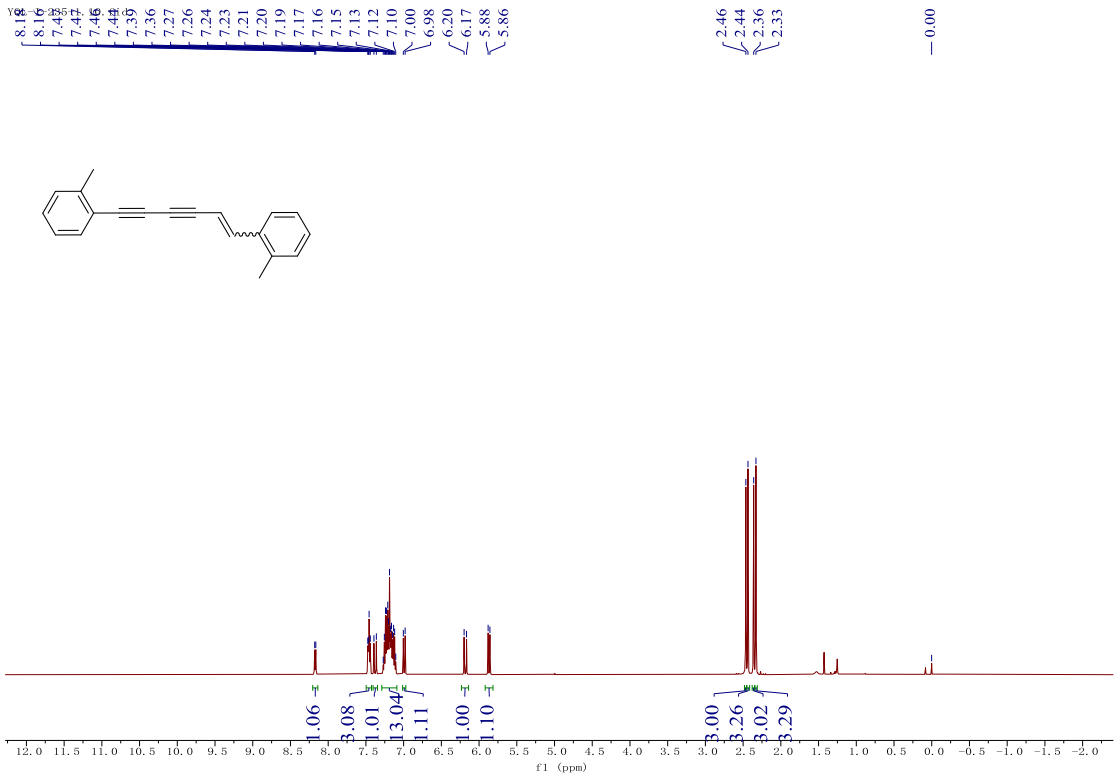
^{1}H NMR spectrum (500 MHz, $CDCl_3$), ^{13}C NMR spectrum (126 MHz, $CDCl_3$) and ^{19}F spectrum NMR (471 MHz, $CDCl_3$) of *Z*-2c

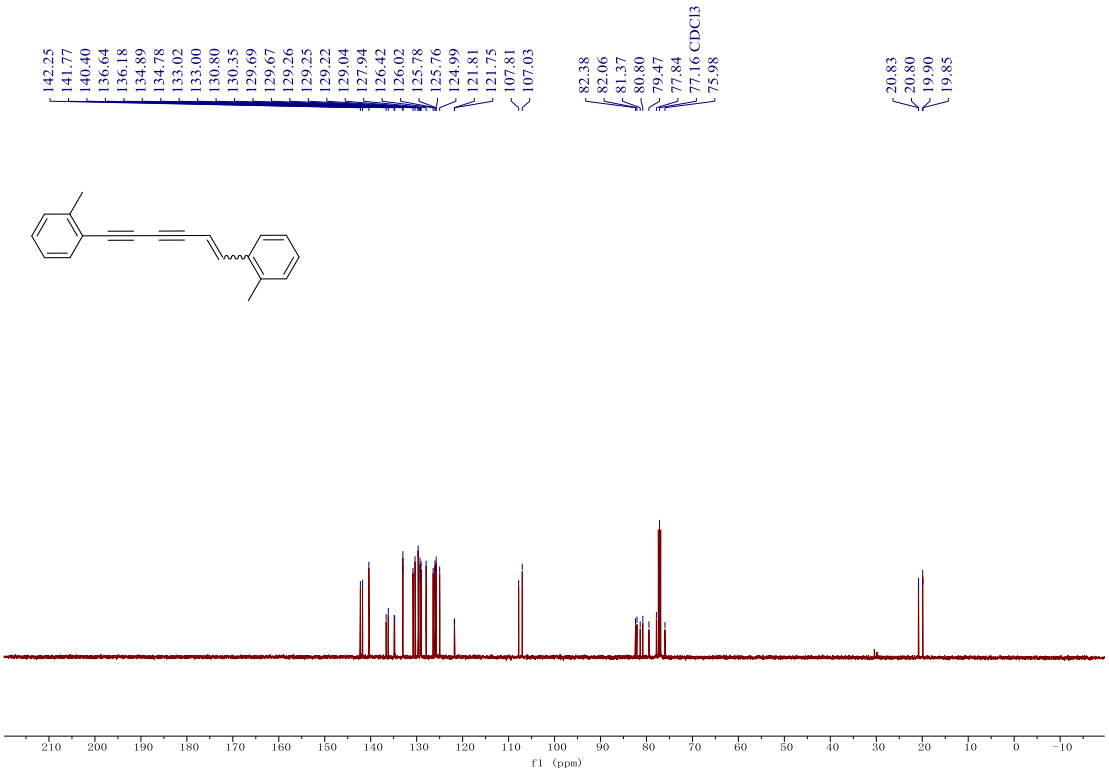




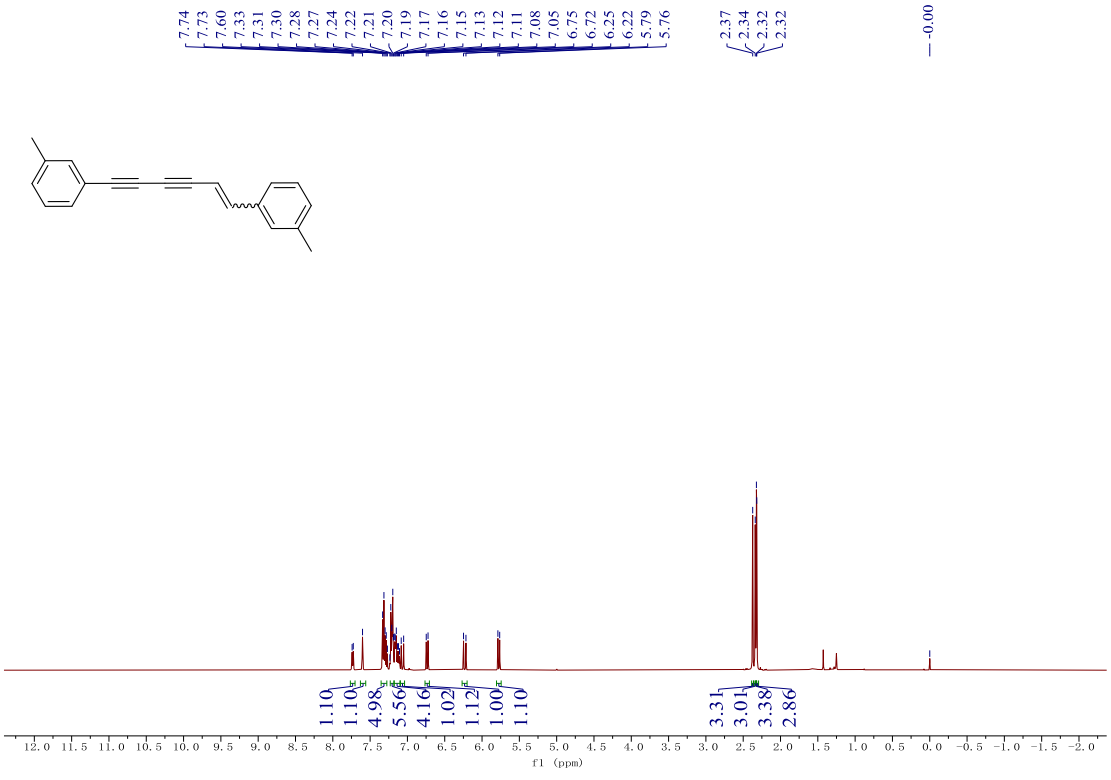


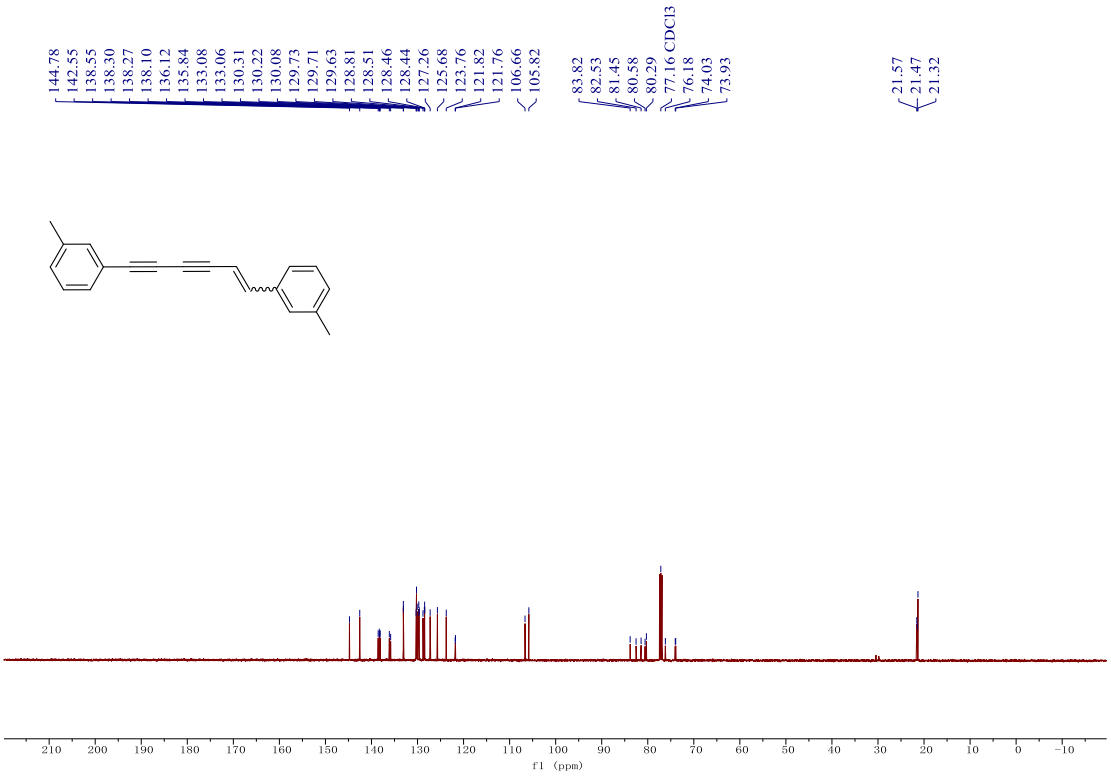
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2e



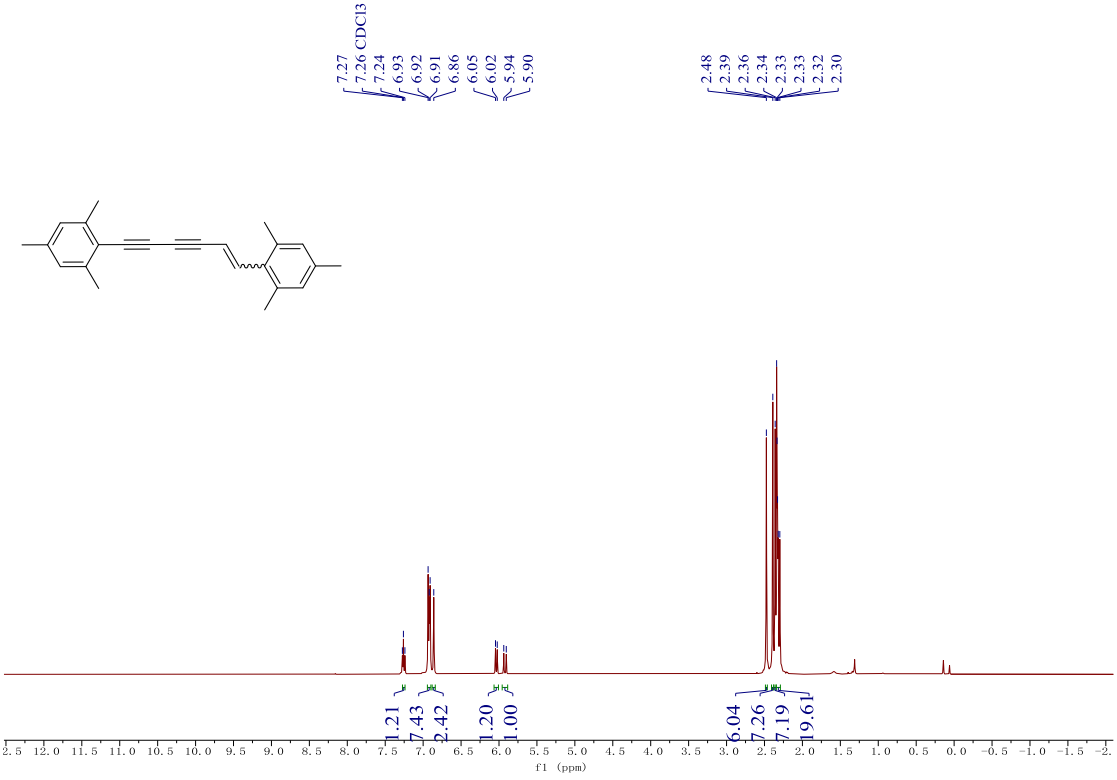


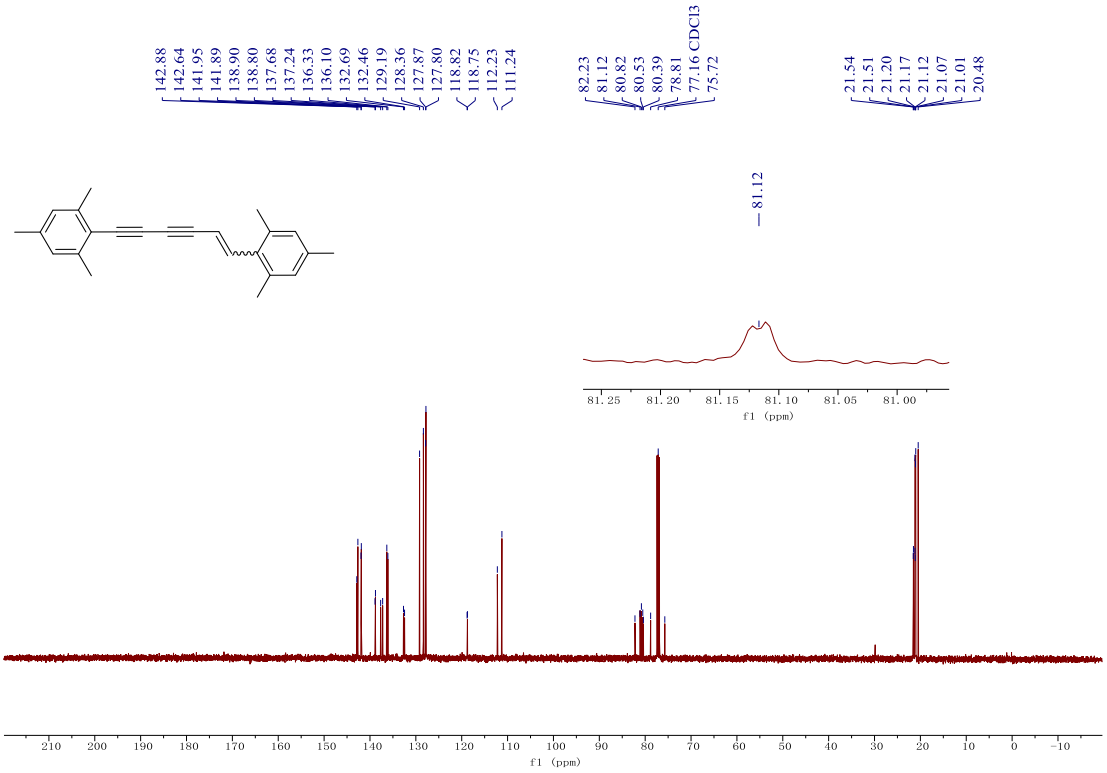
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2f



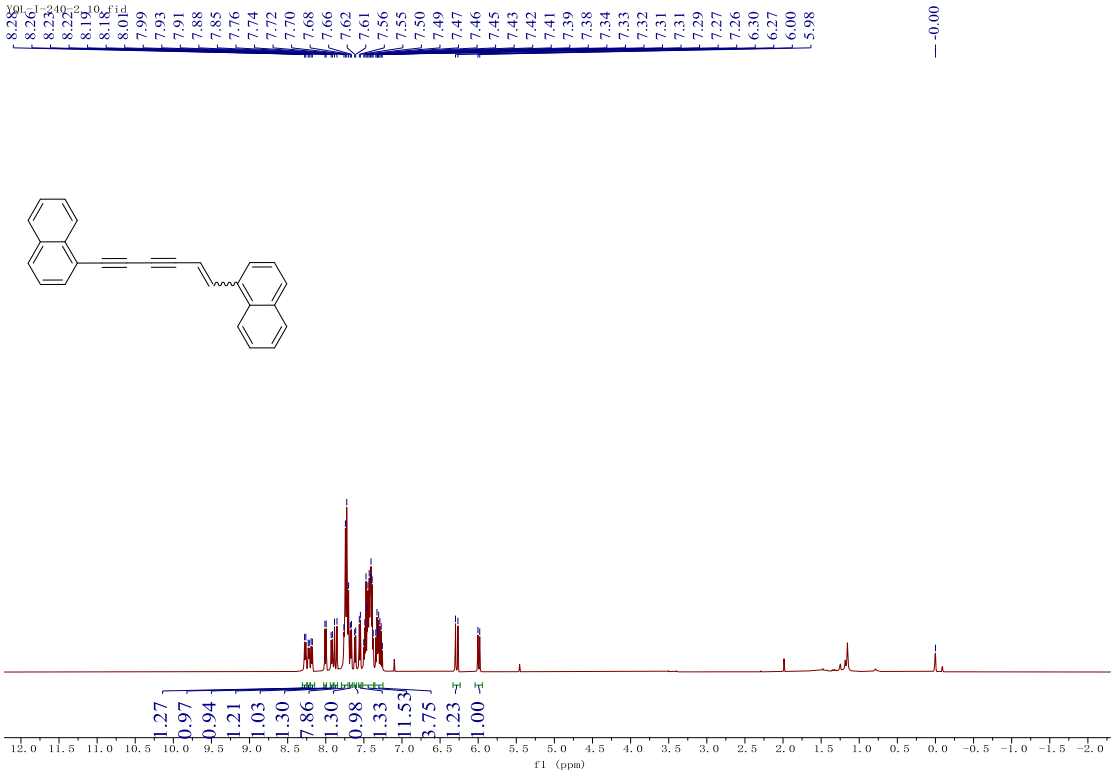


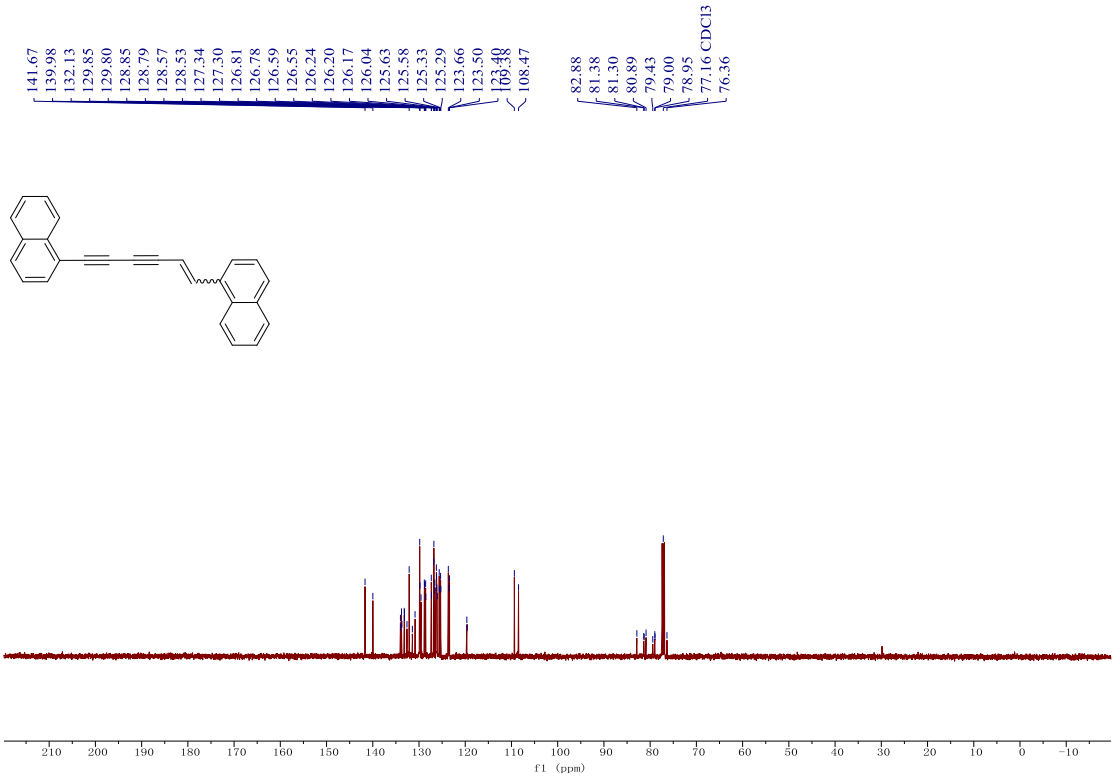
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2g



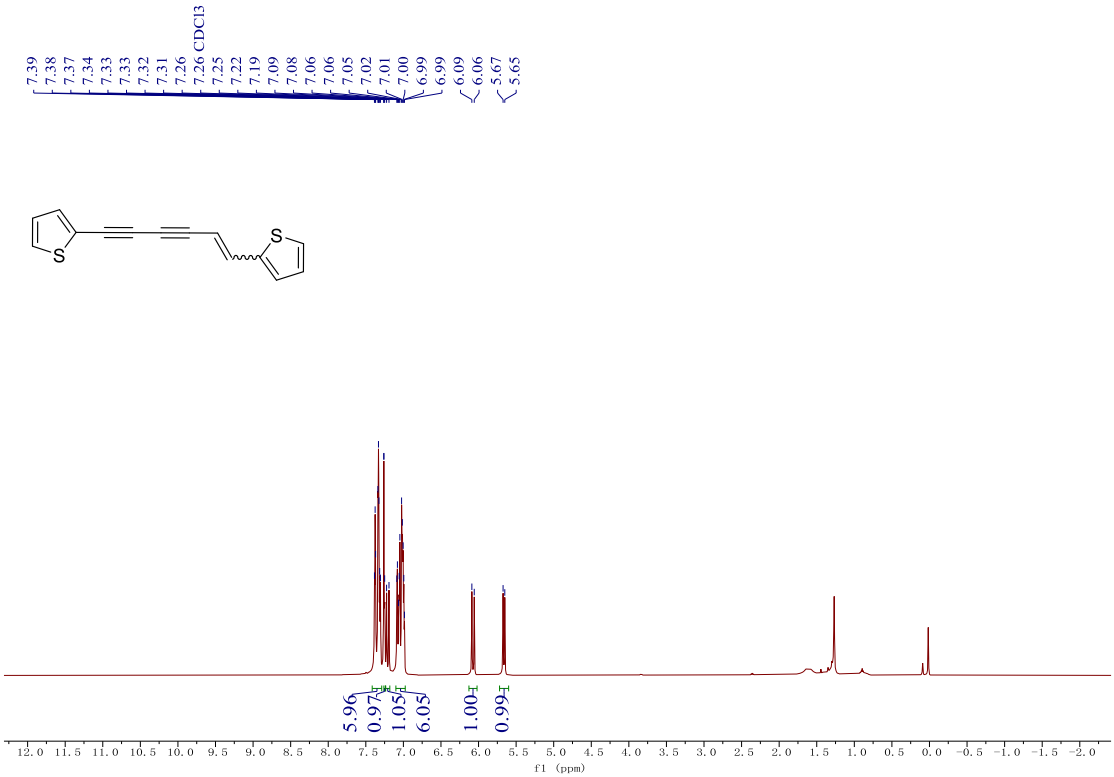


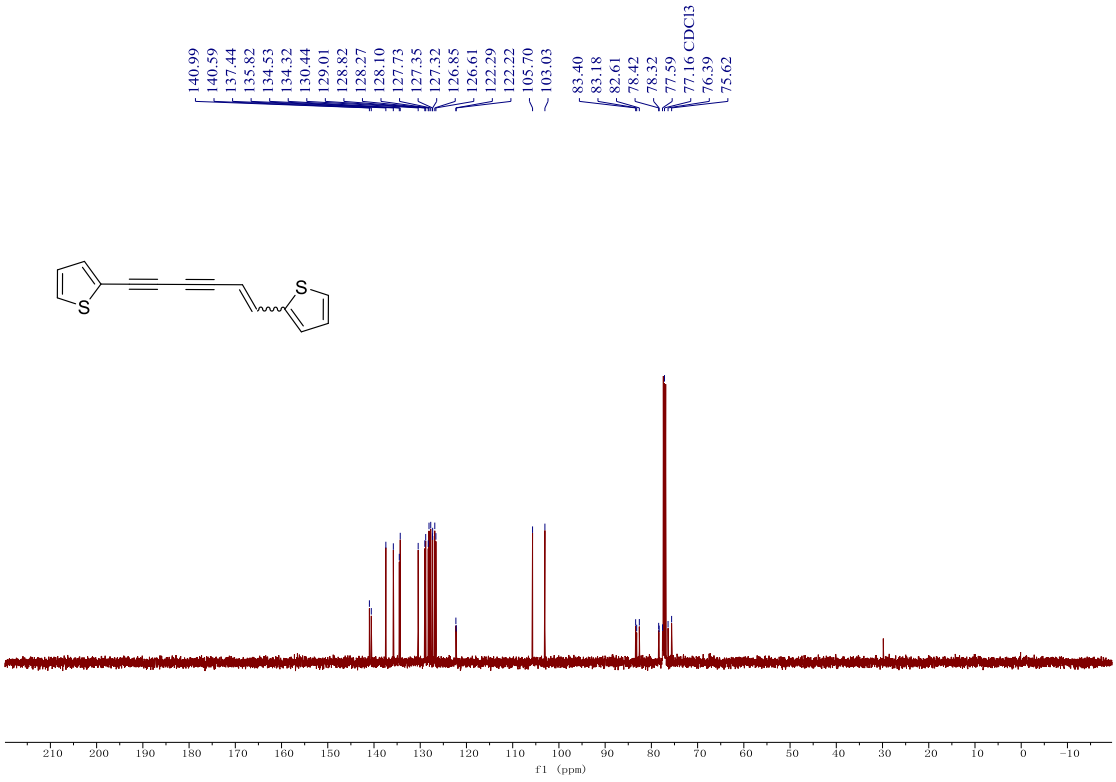
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2h



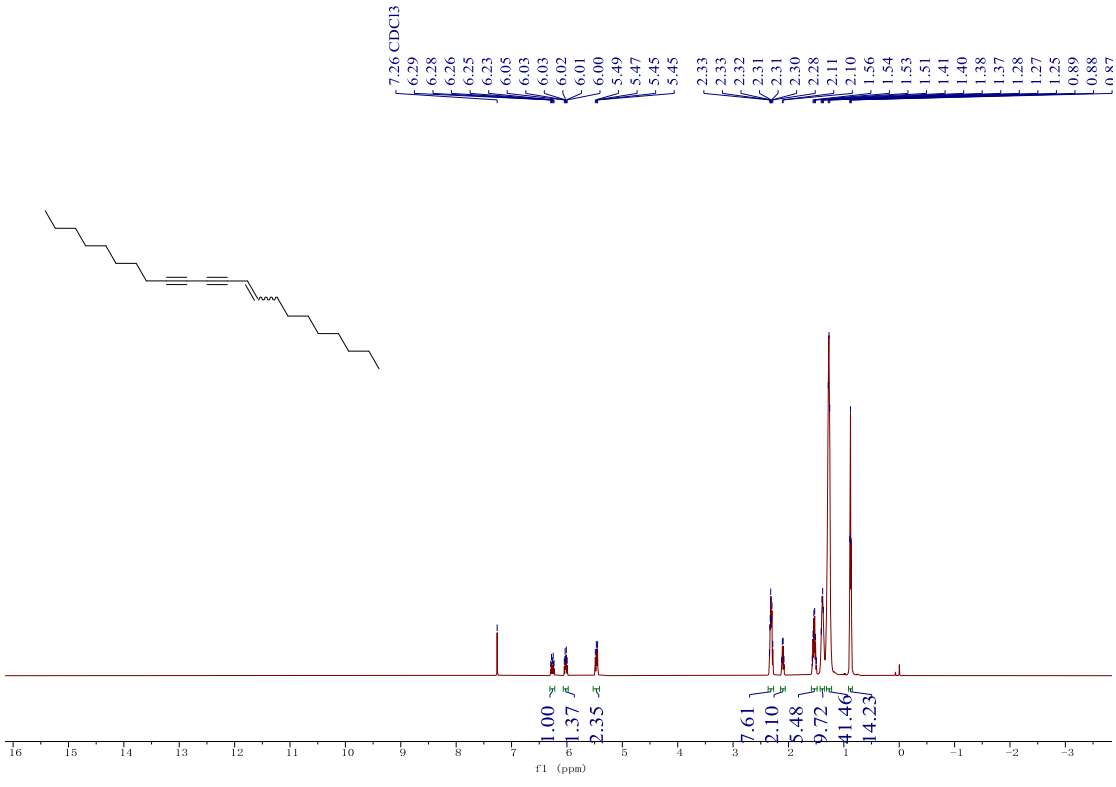


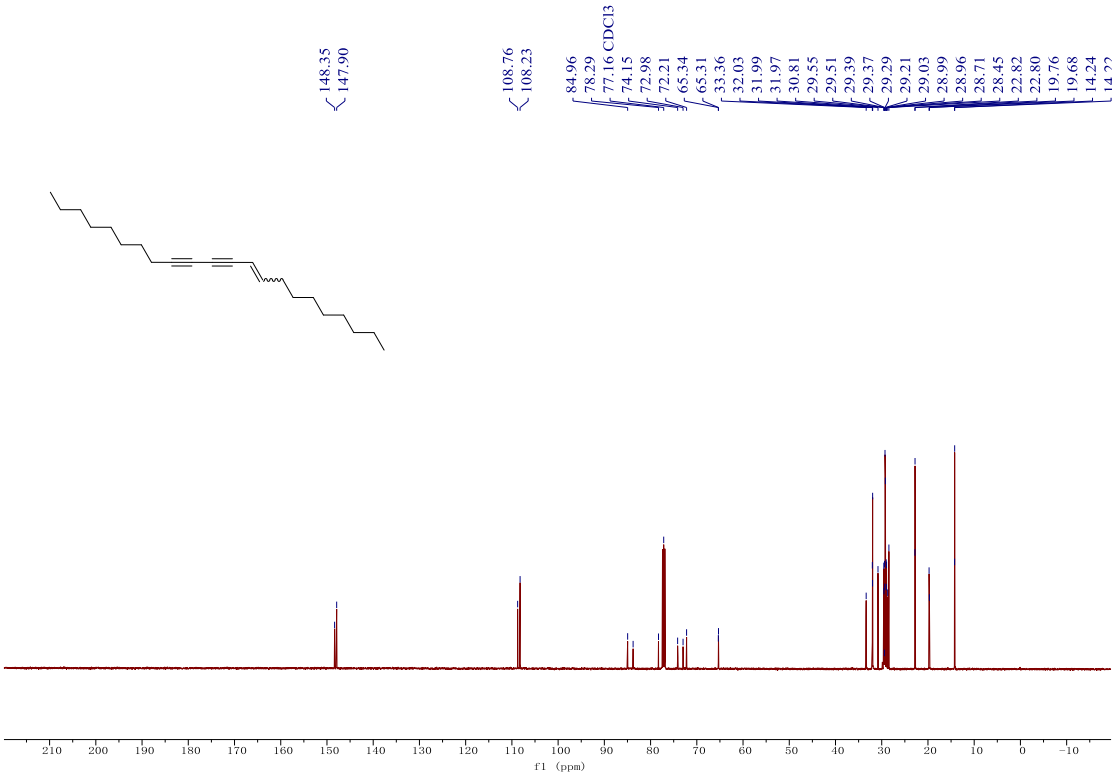
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2i



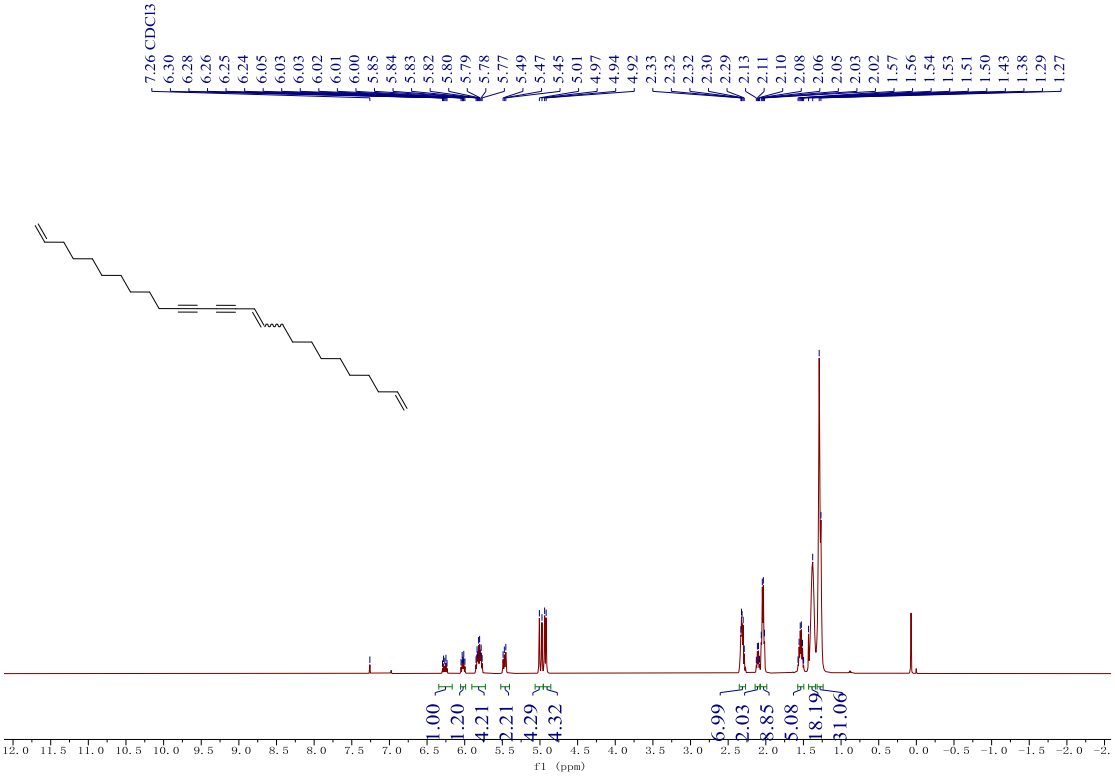


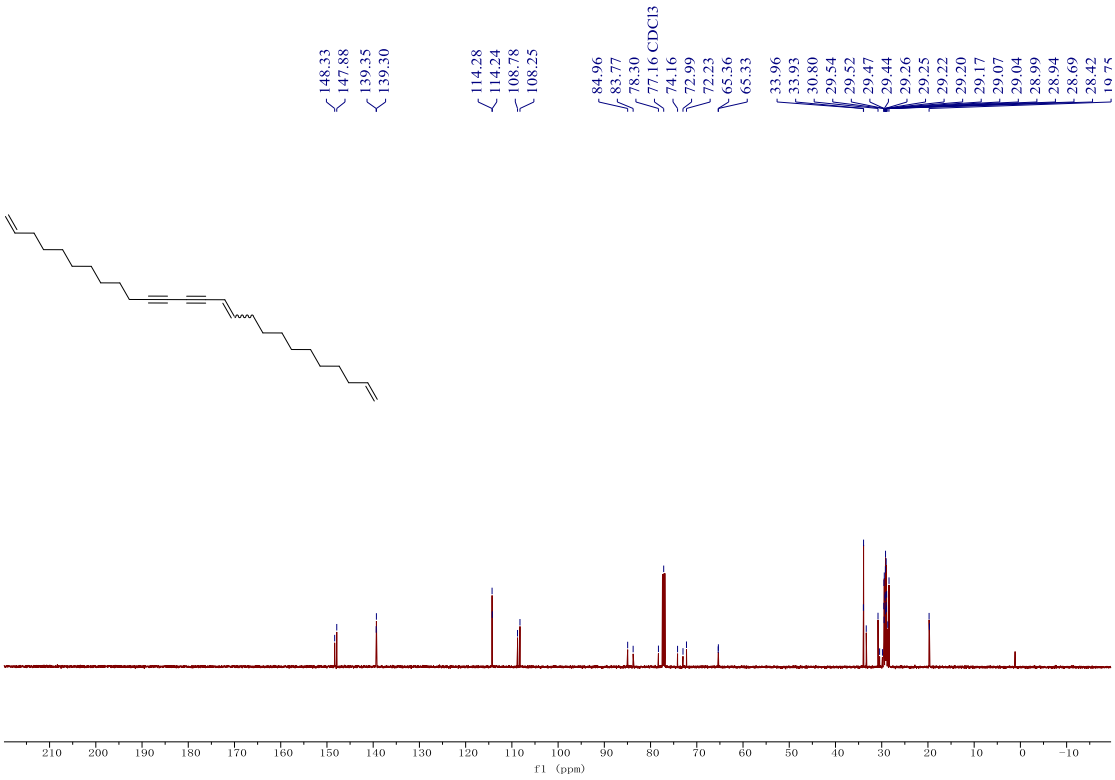
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2j



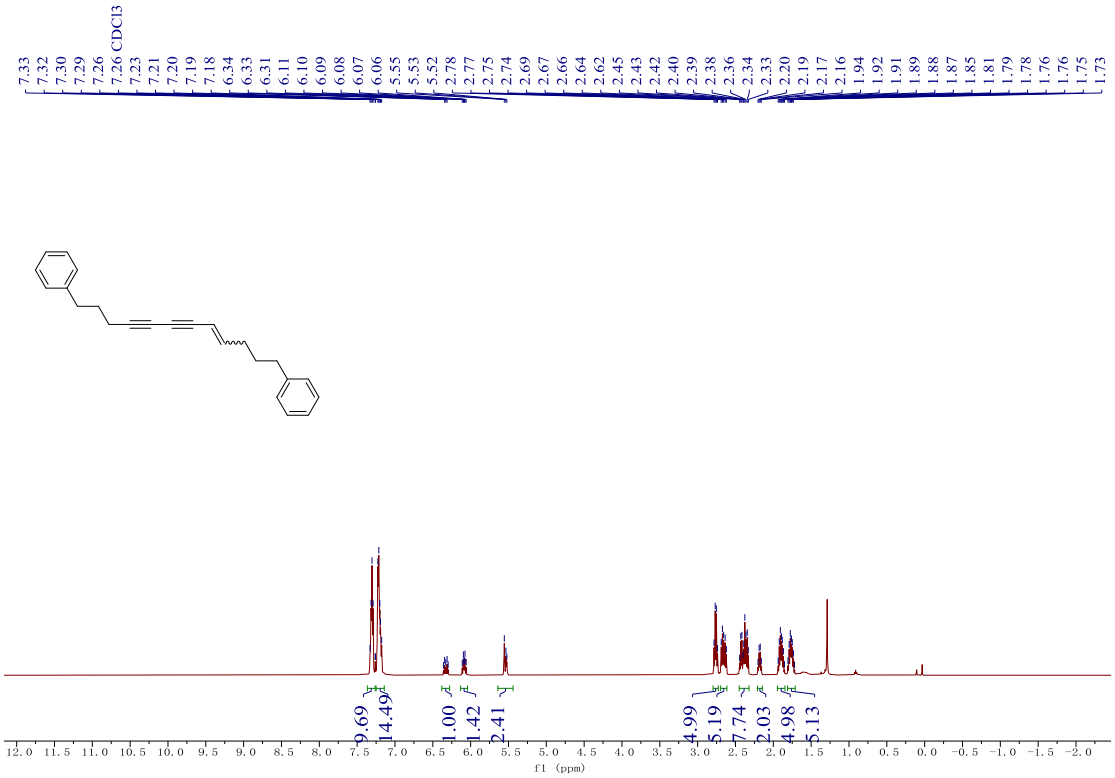


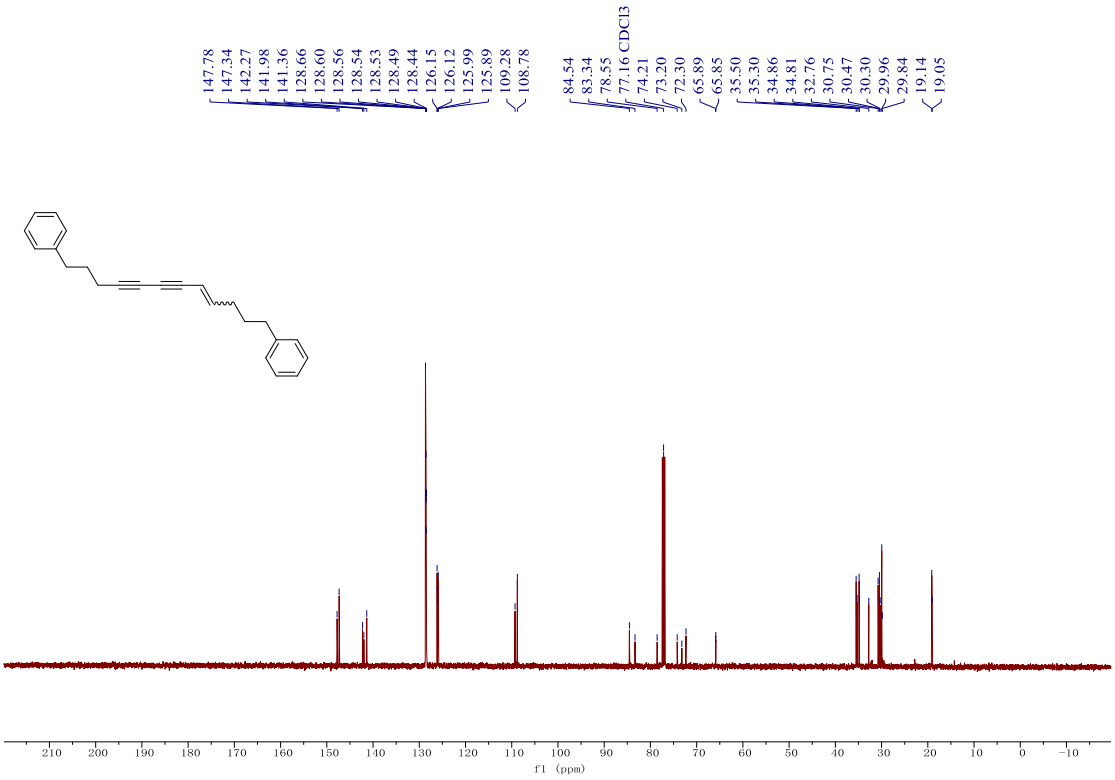
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2k



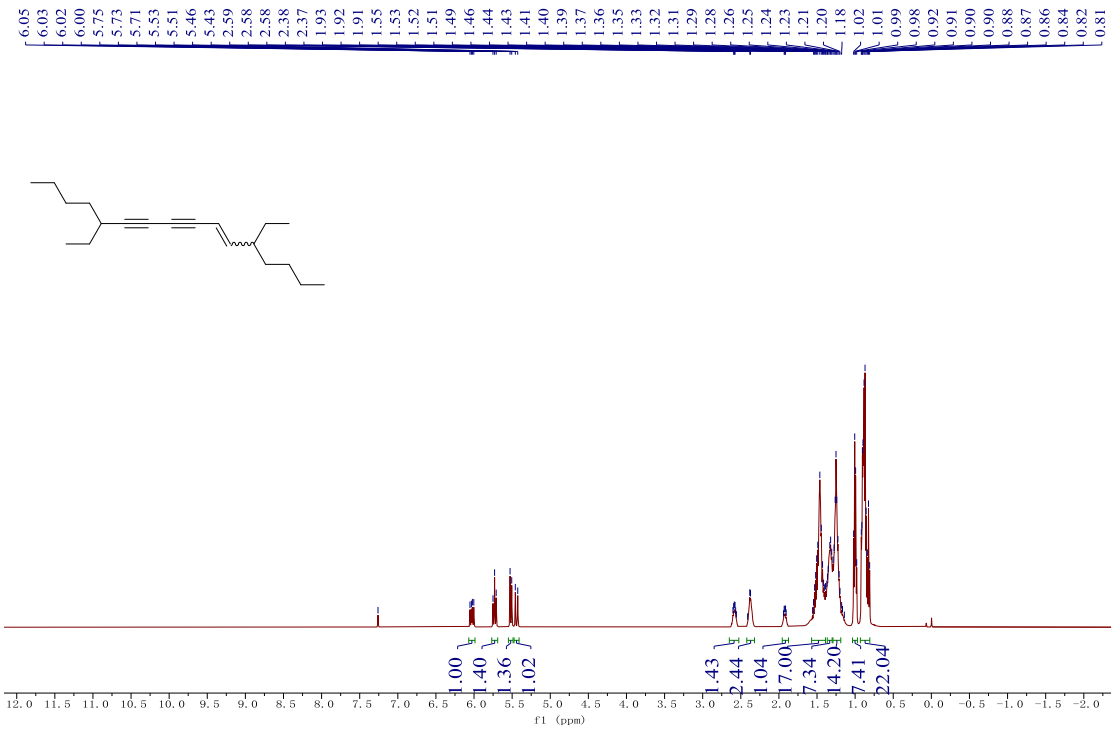


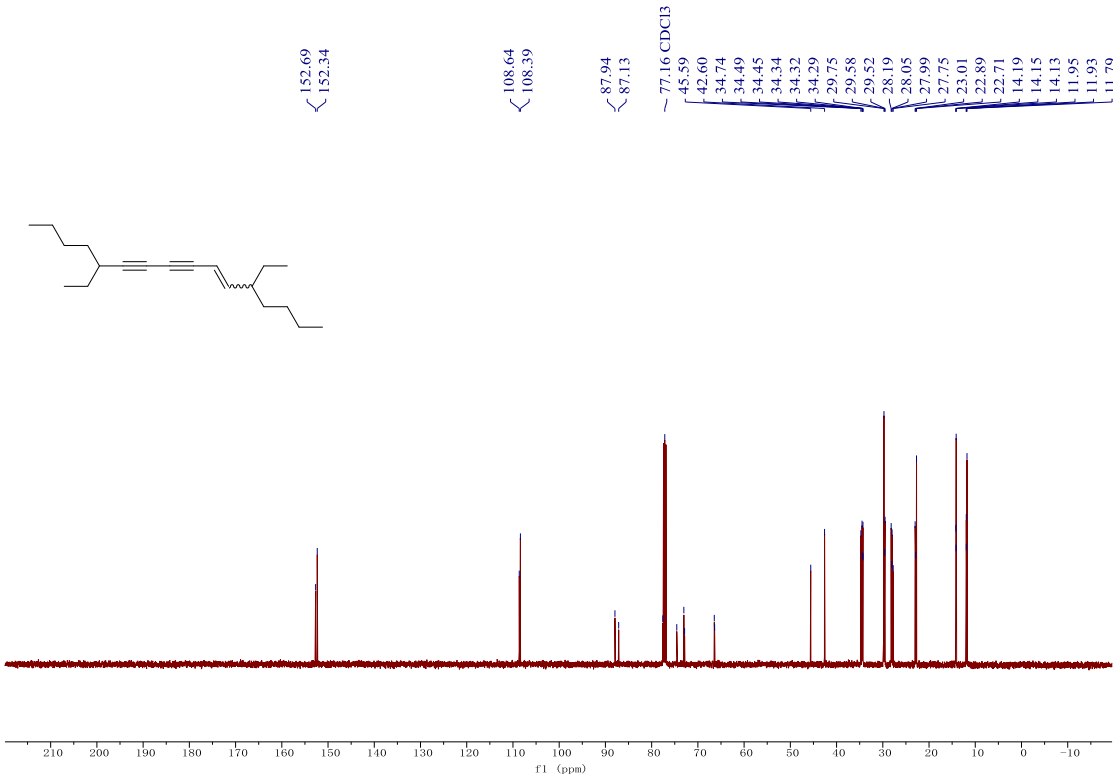
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2l



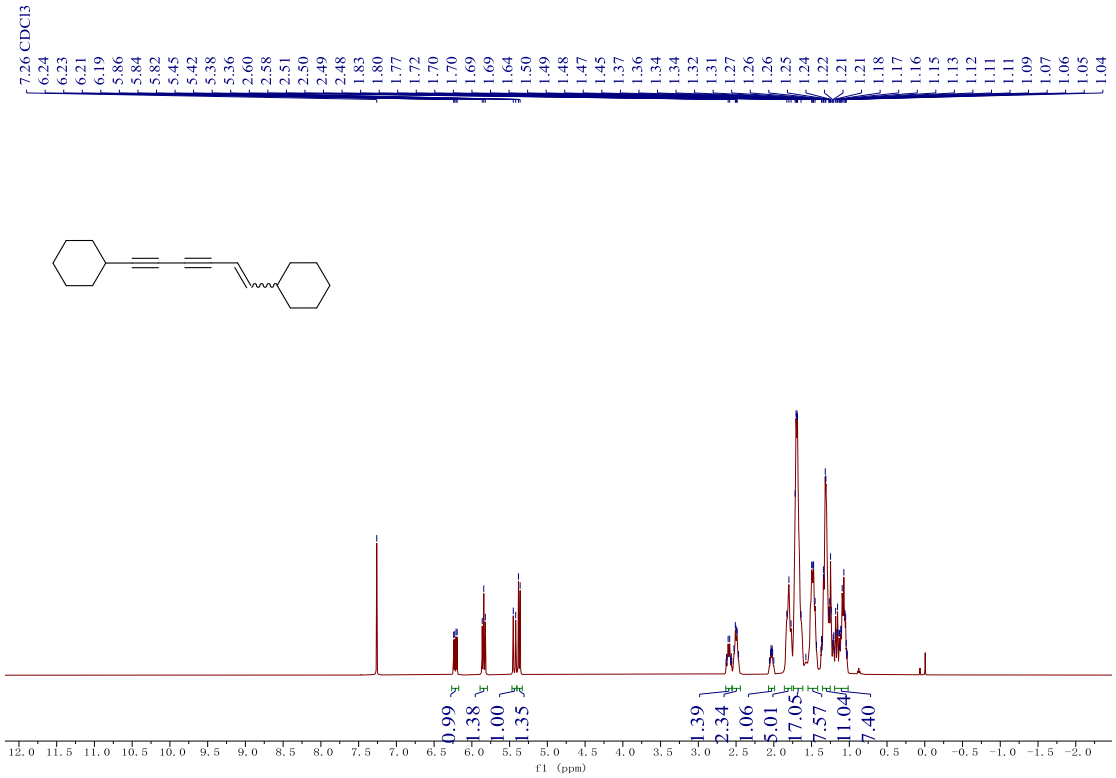


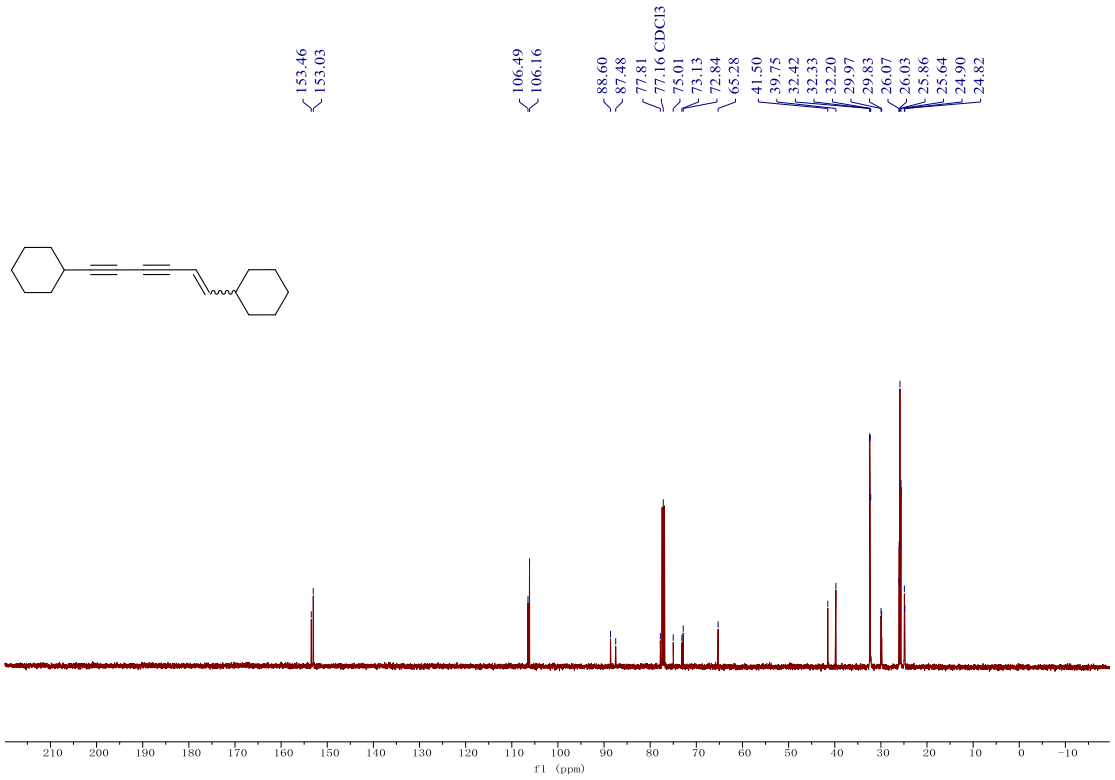
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2m



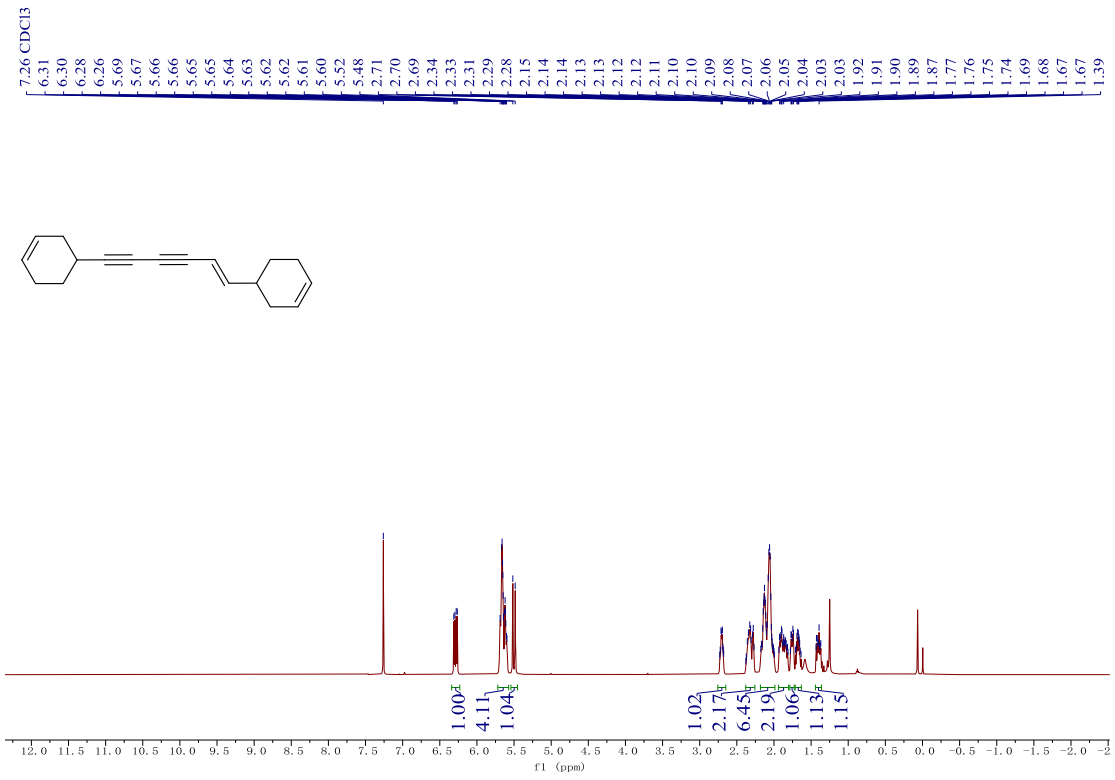


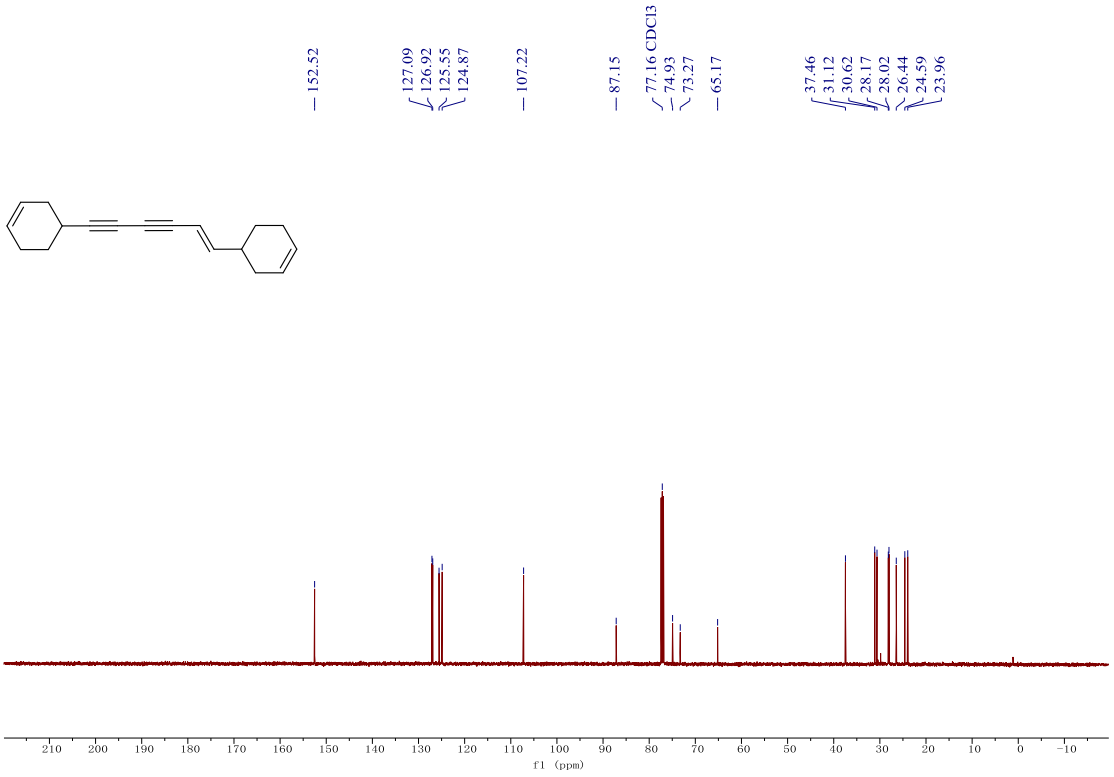
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2n



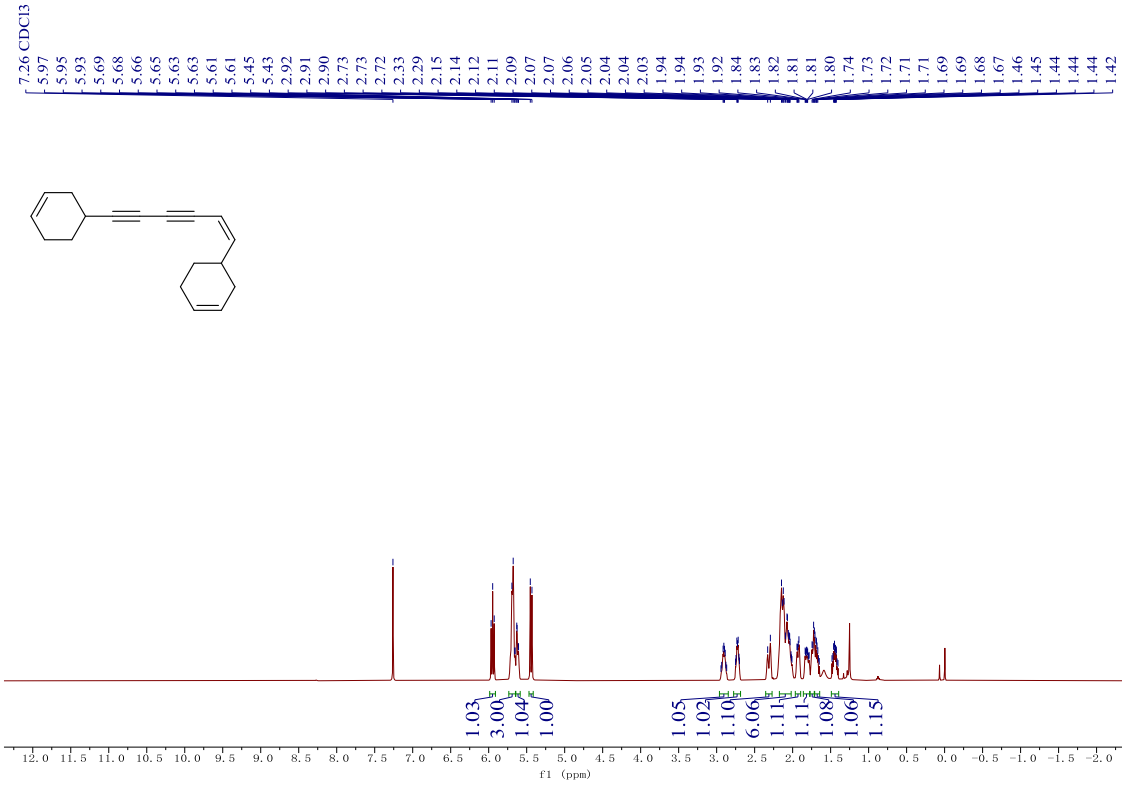


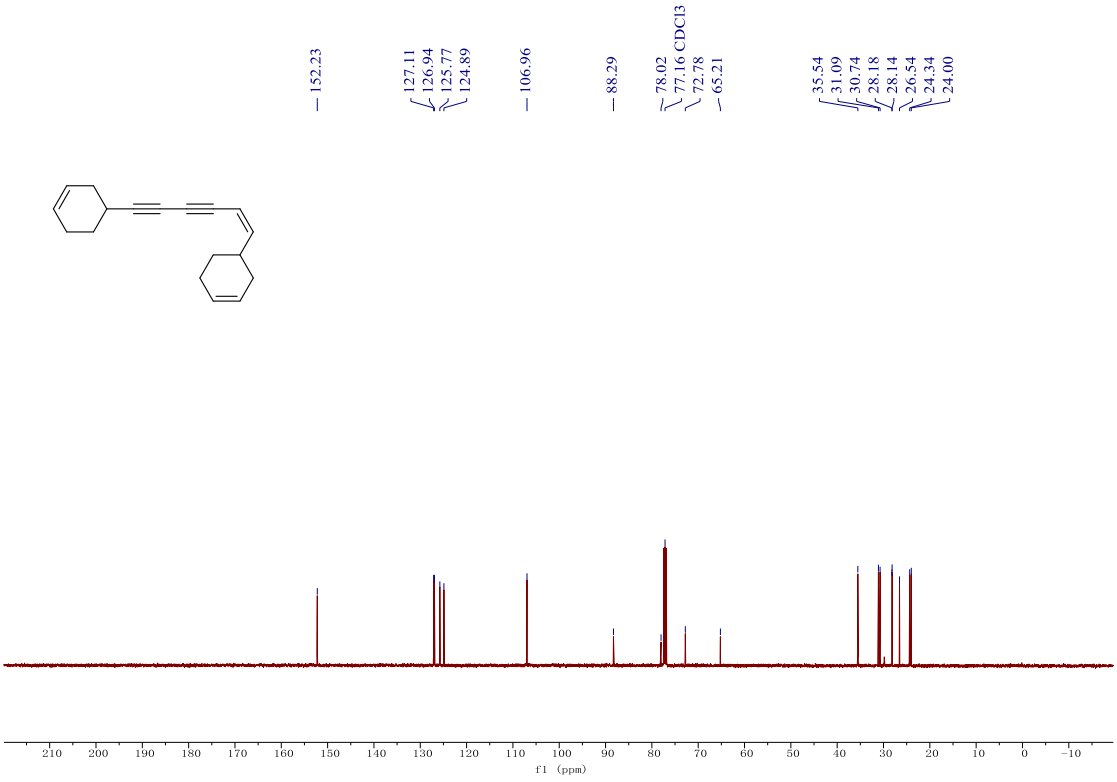
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of *E*-2o



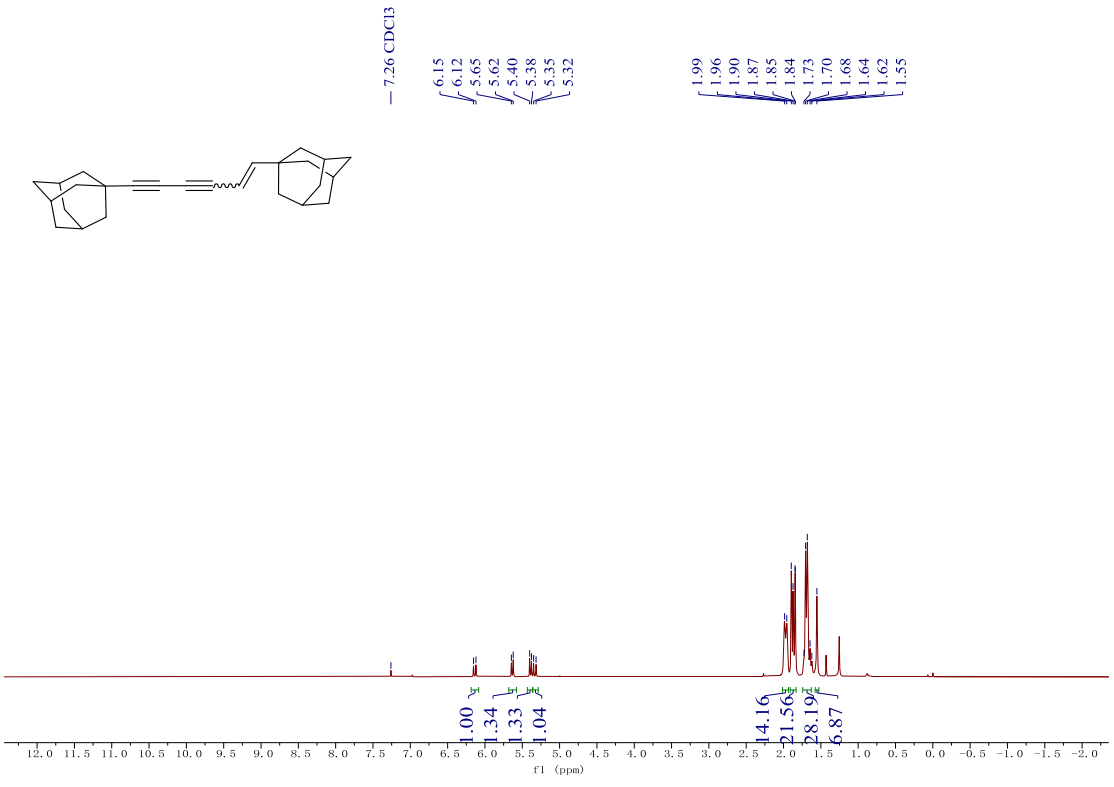


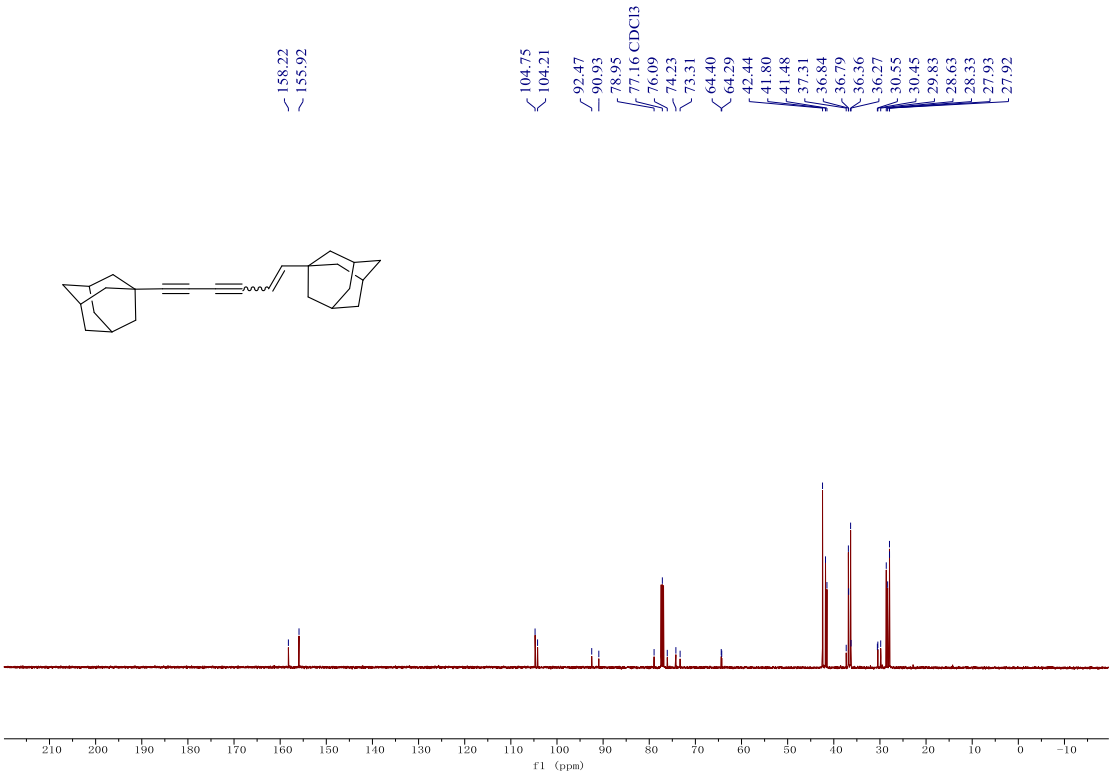
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of *Z*-2o



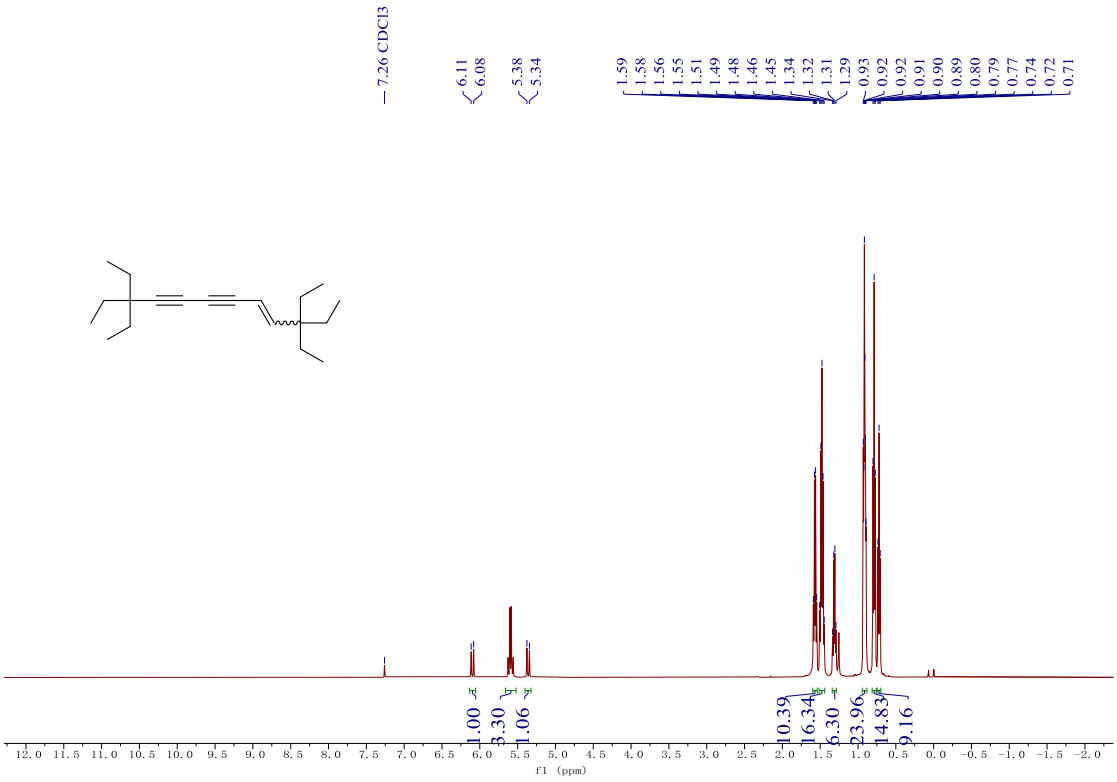


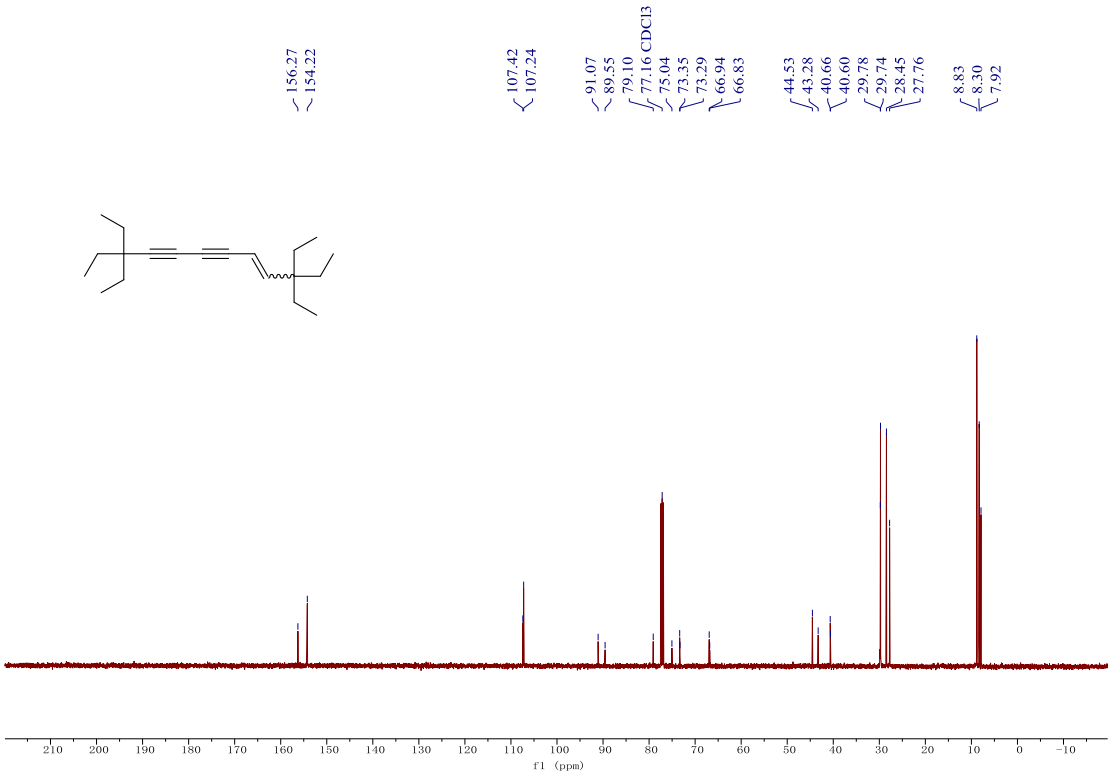
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2p



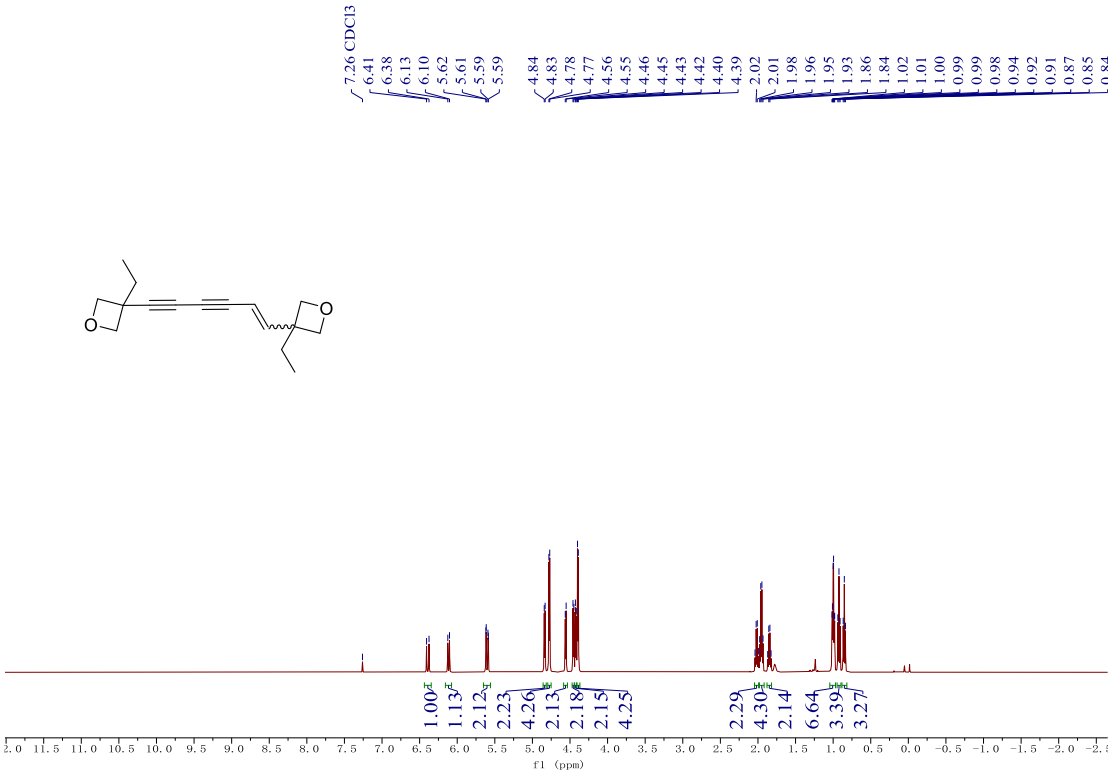


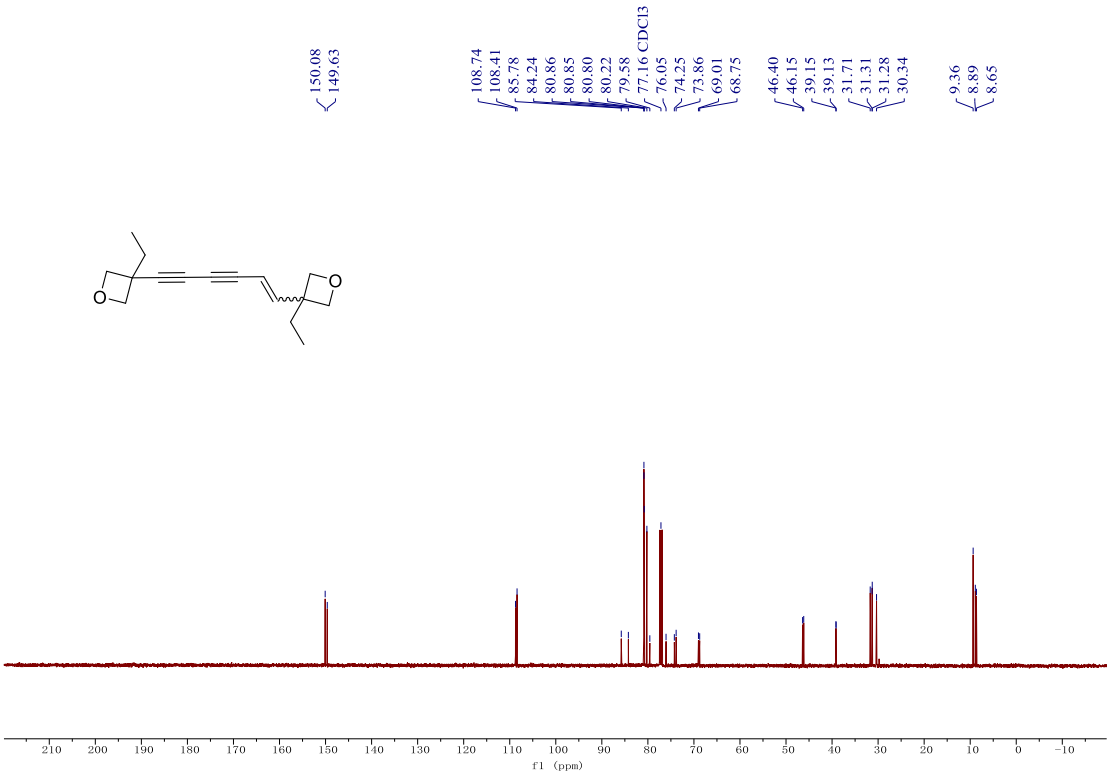
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2q



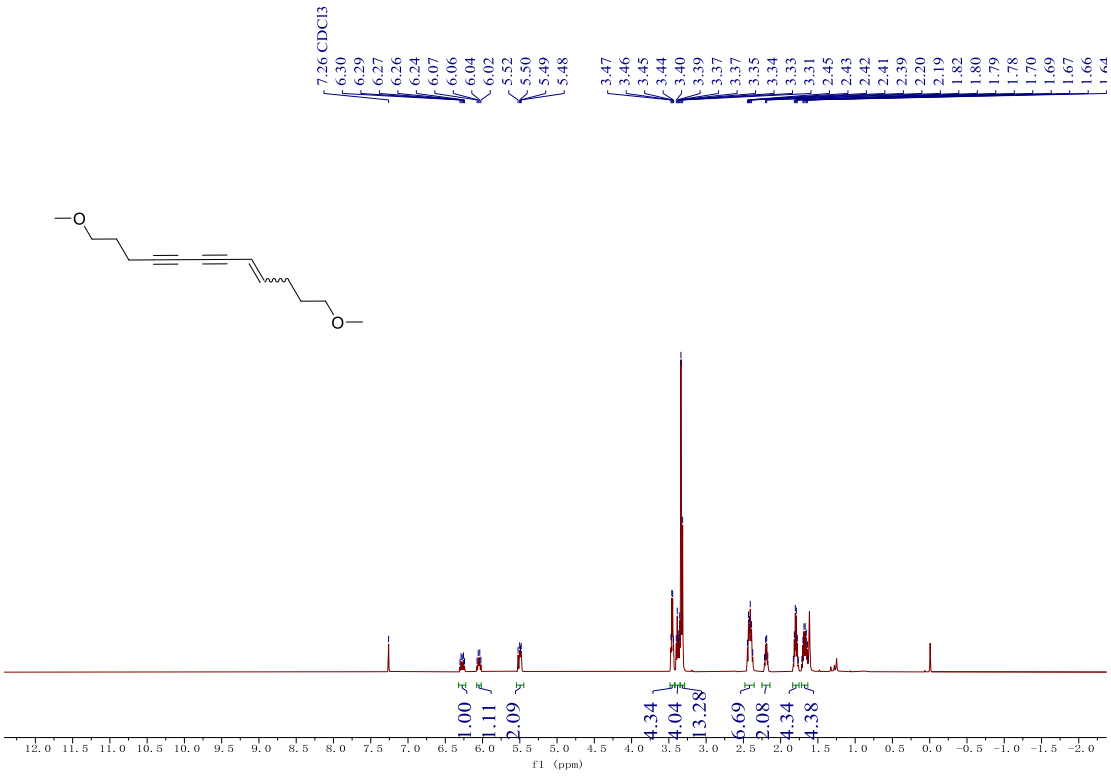


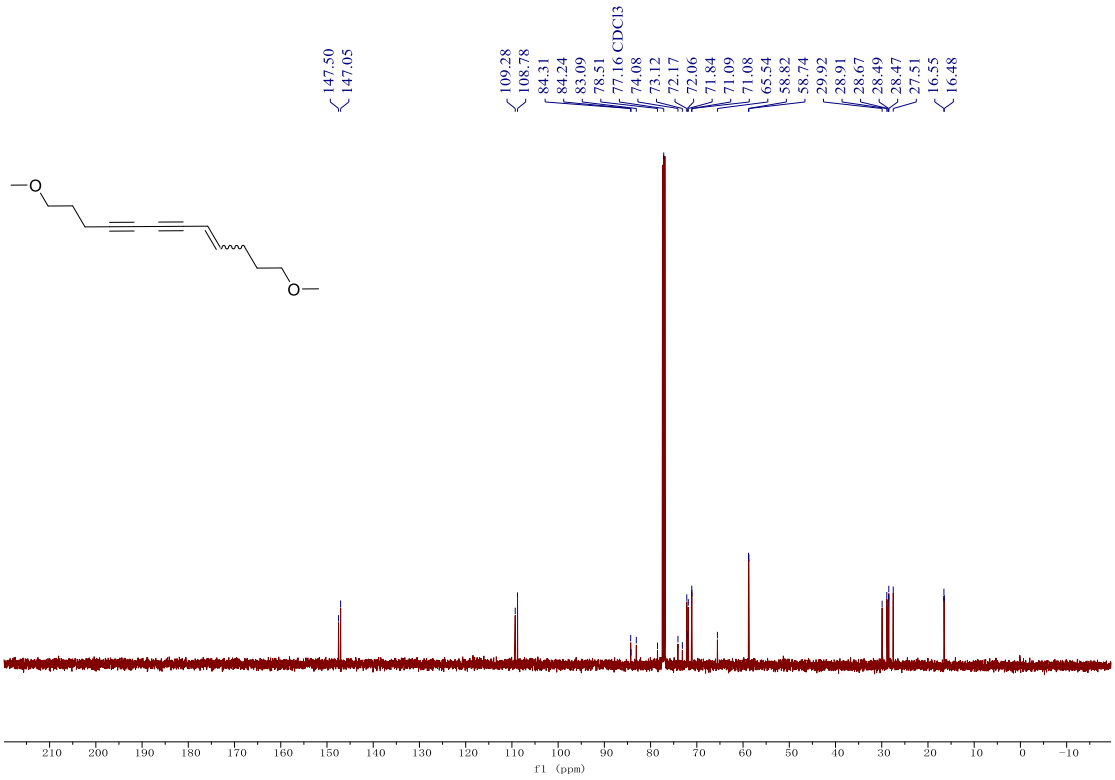
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2r



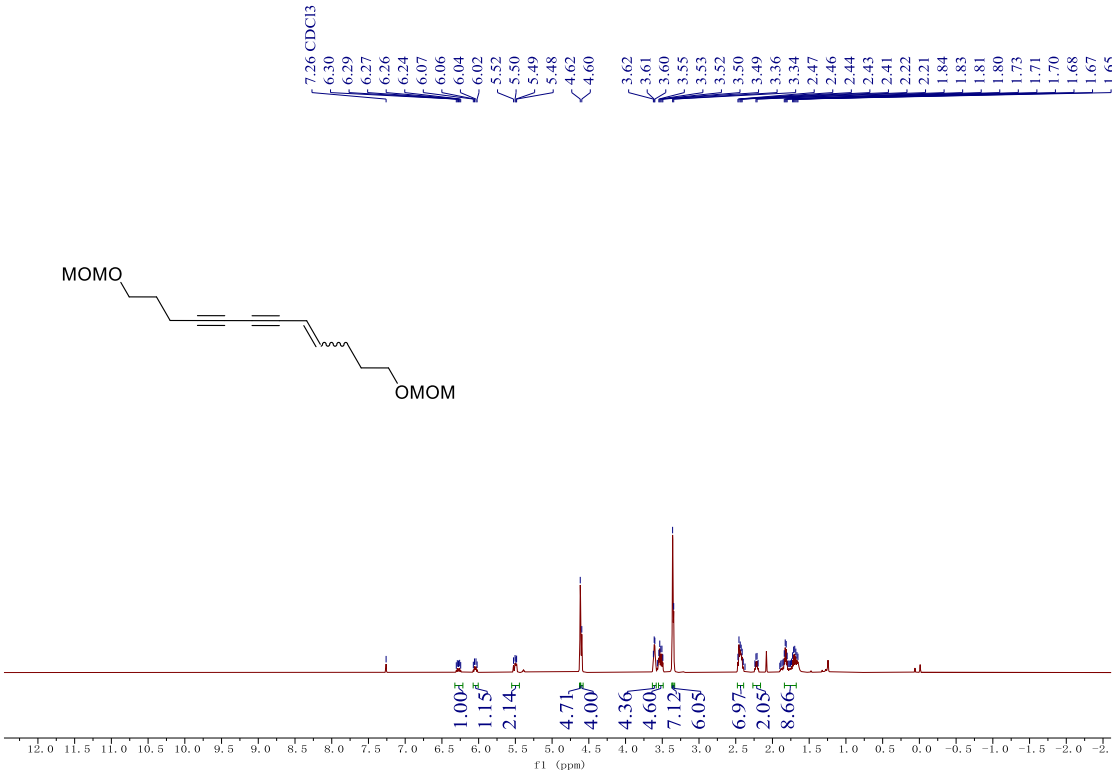


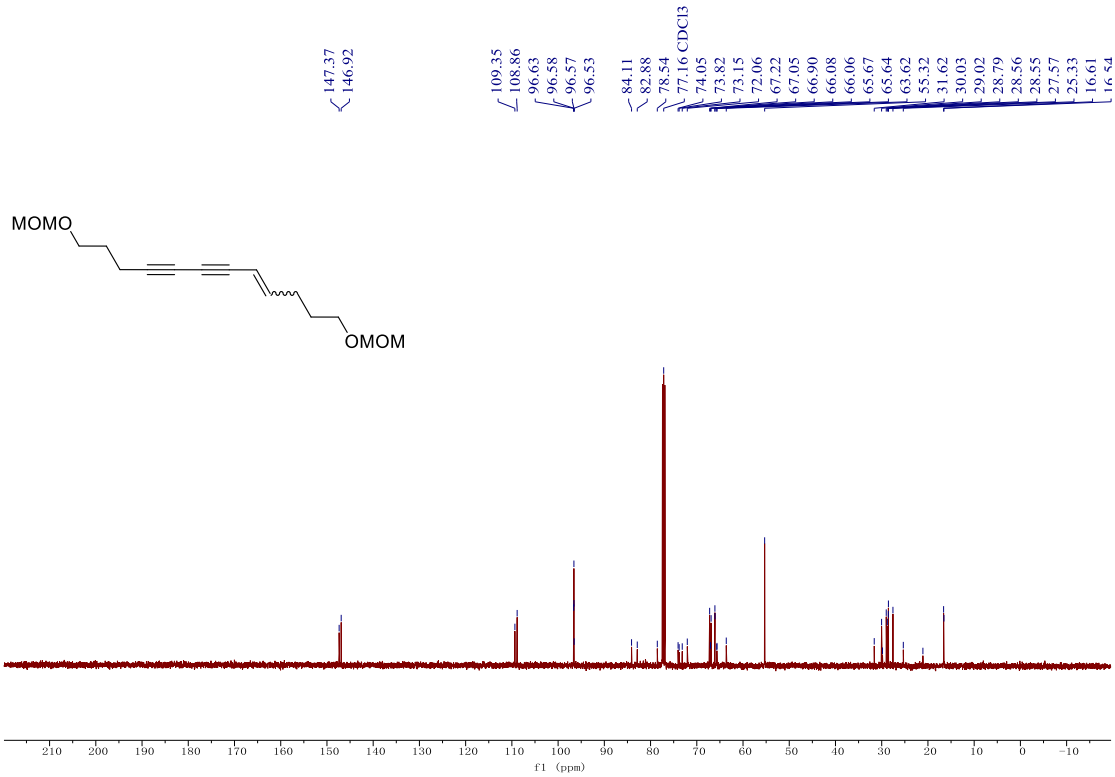
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2s



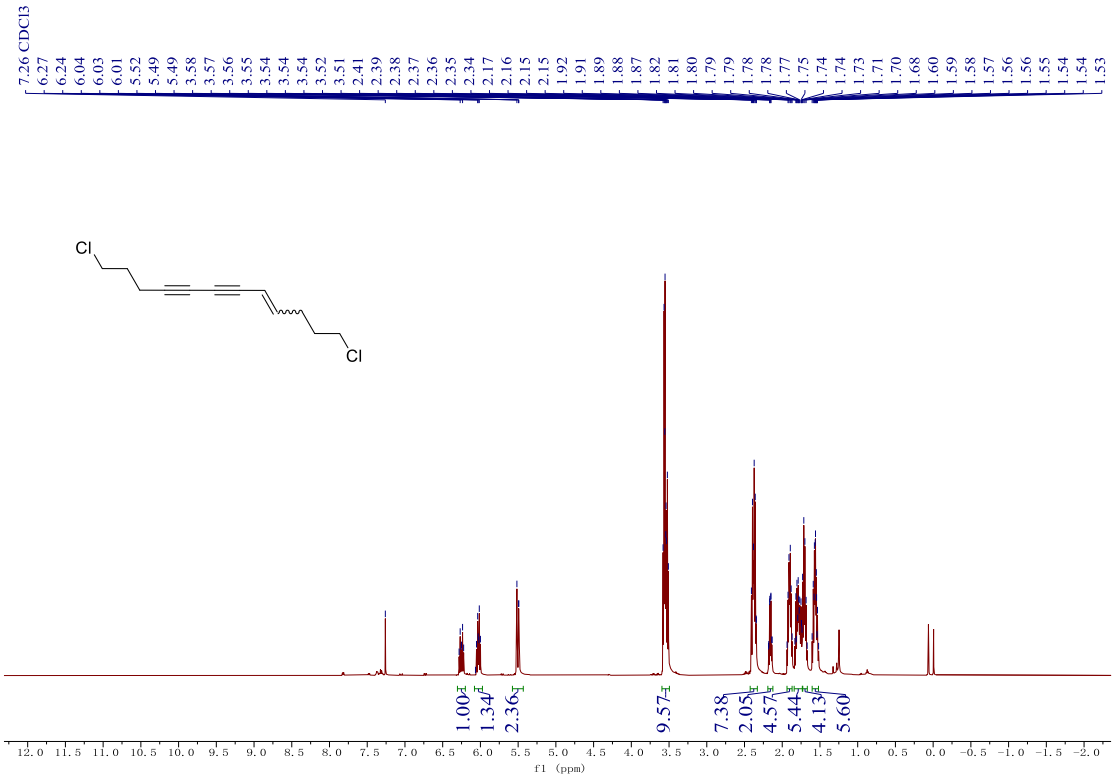


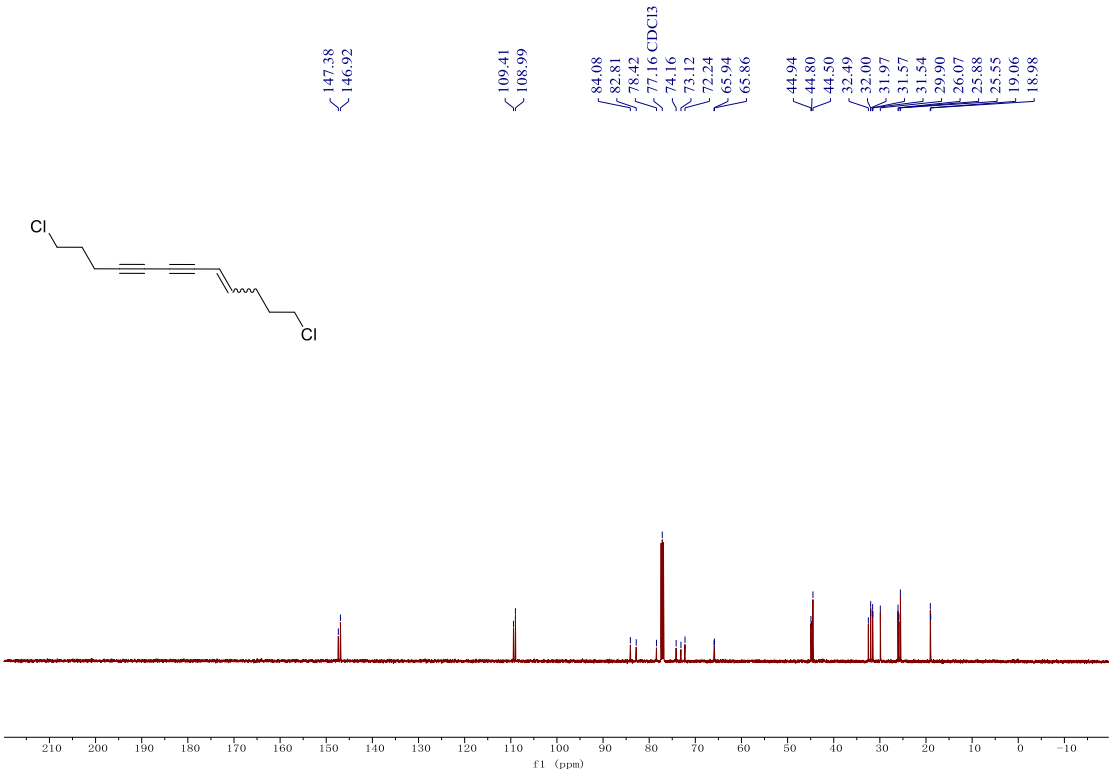
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2t



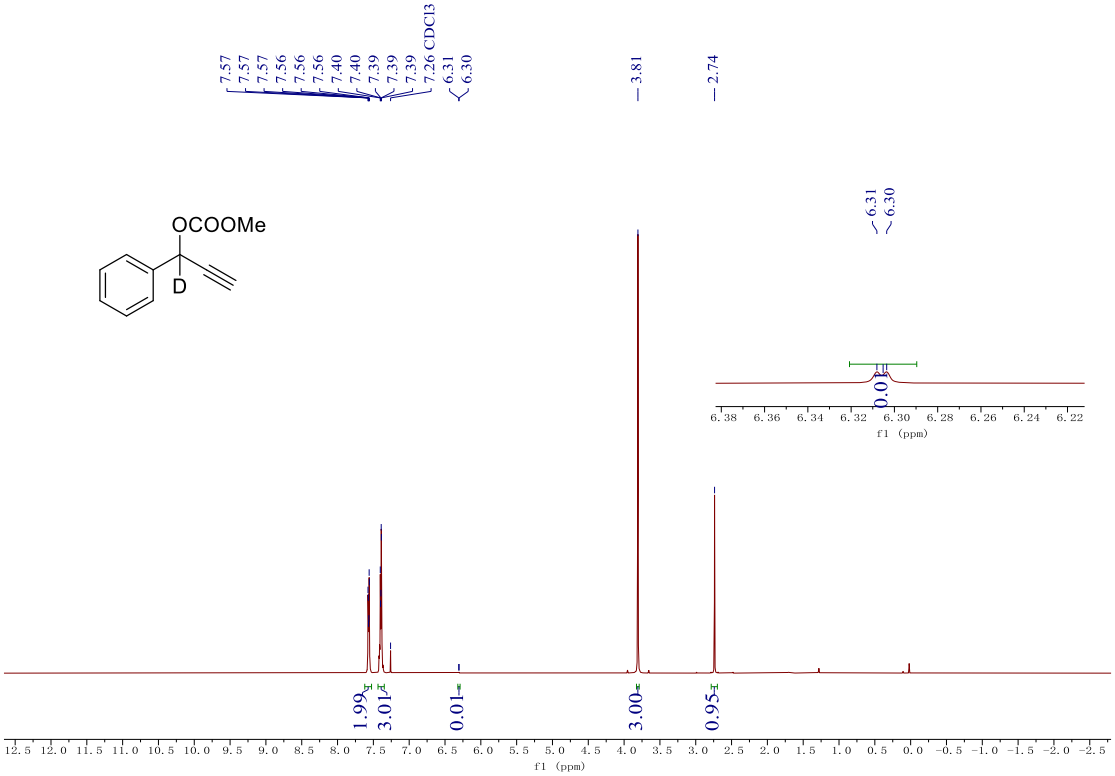


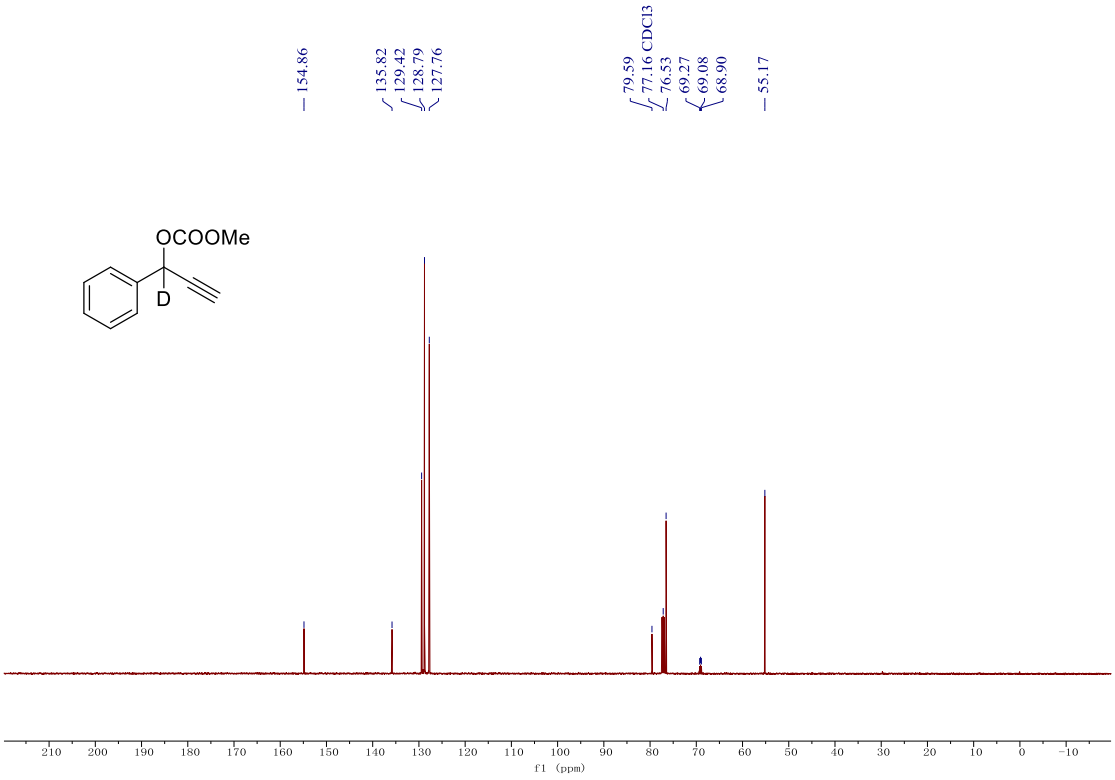
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 2u



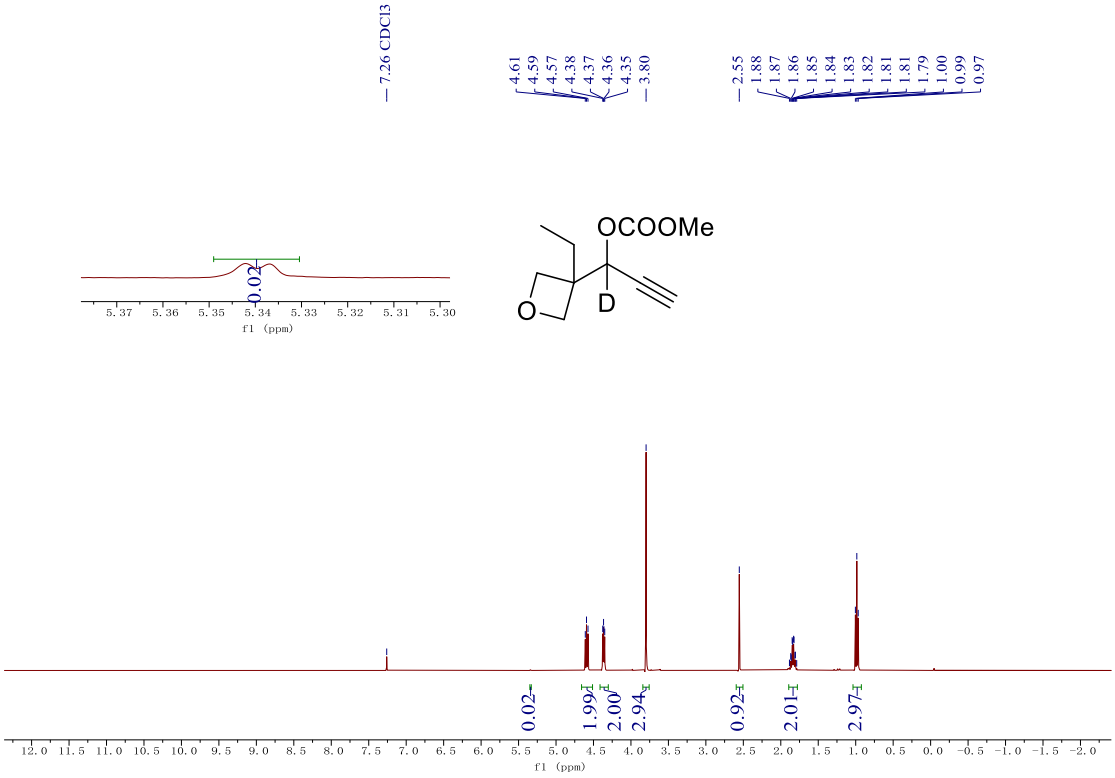


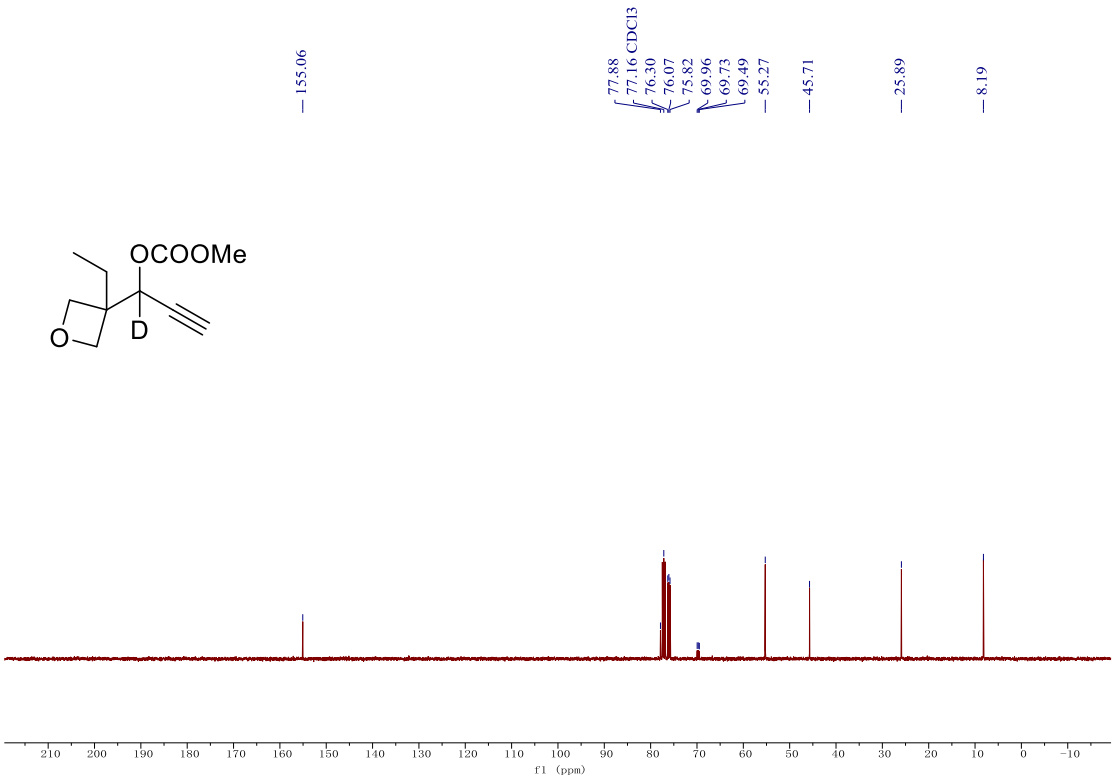
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of *d*-1a



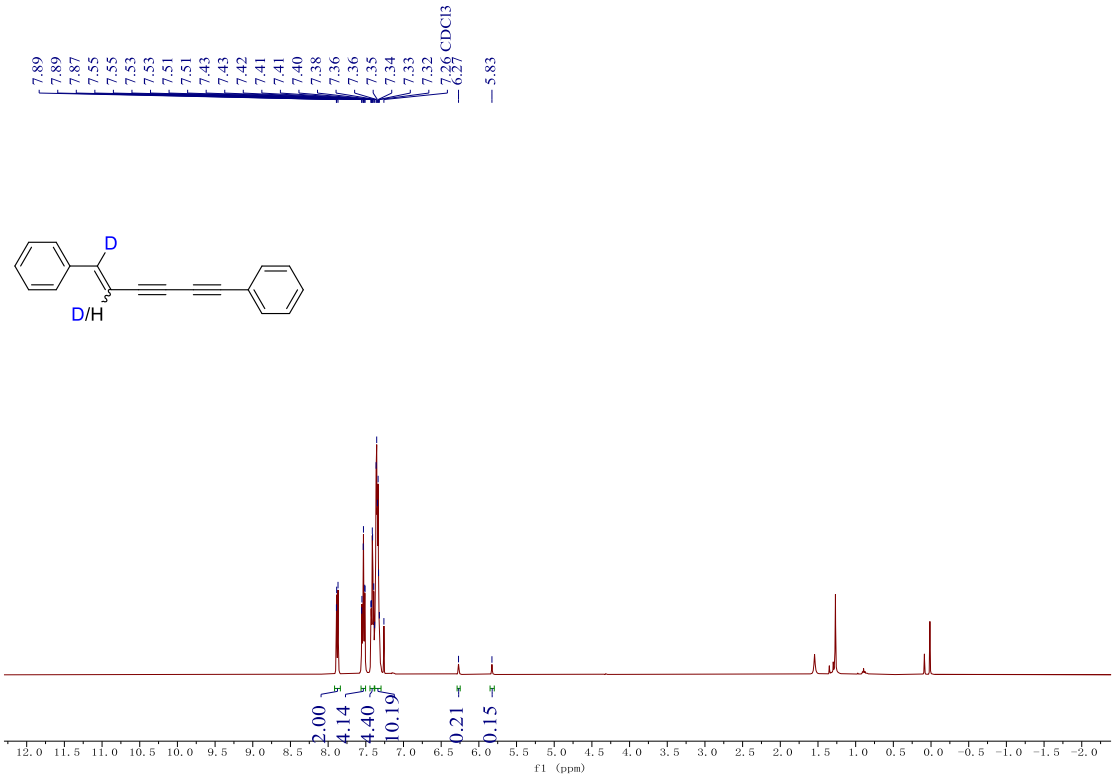


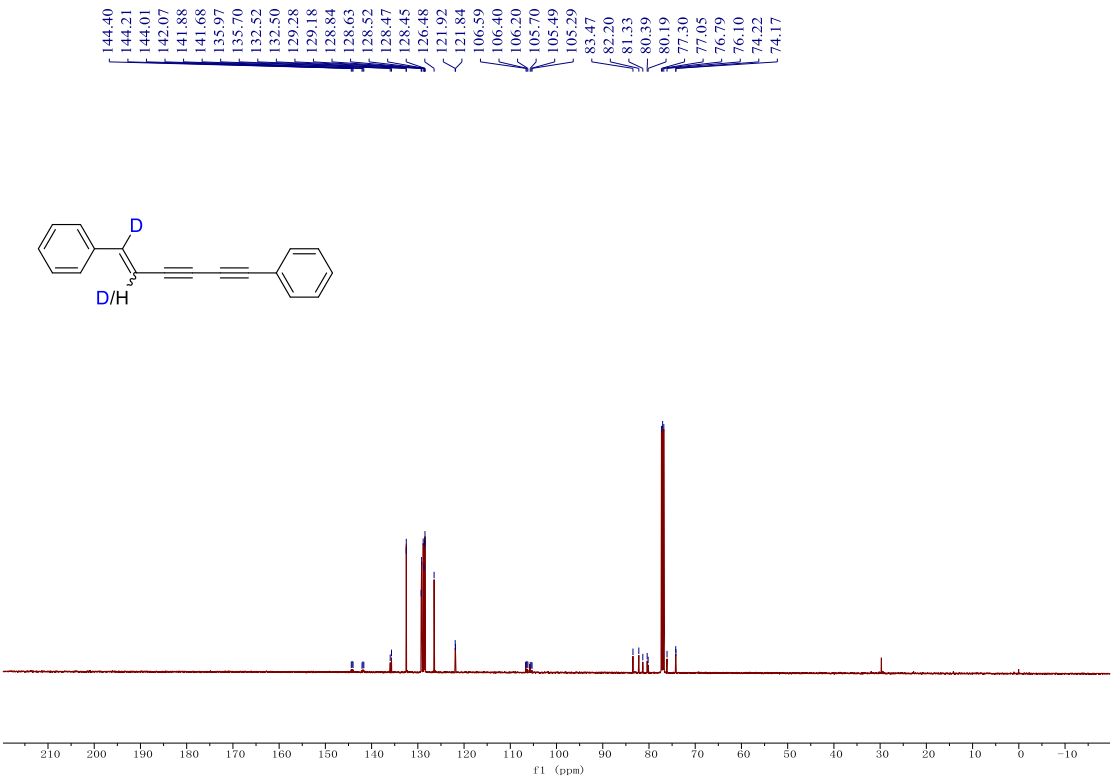
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of *d*-1r



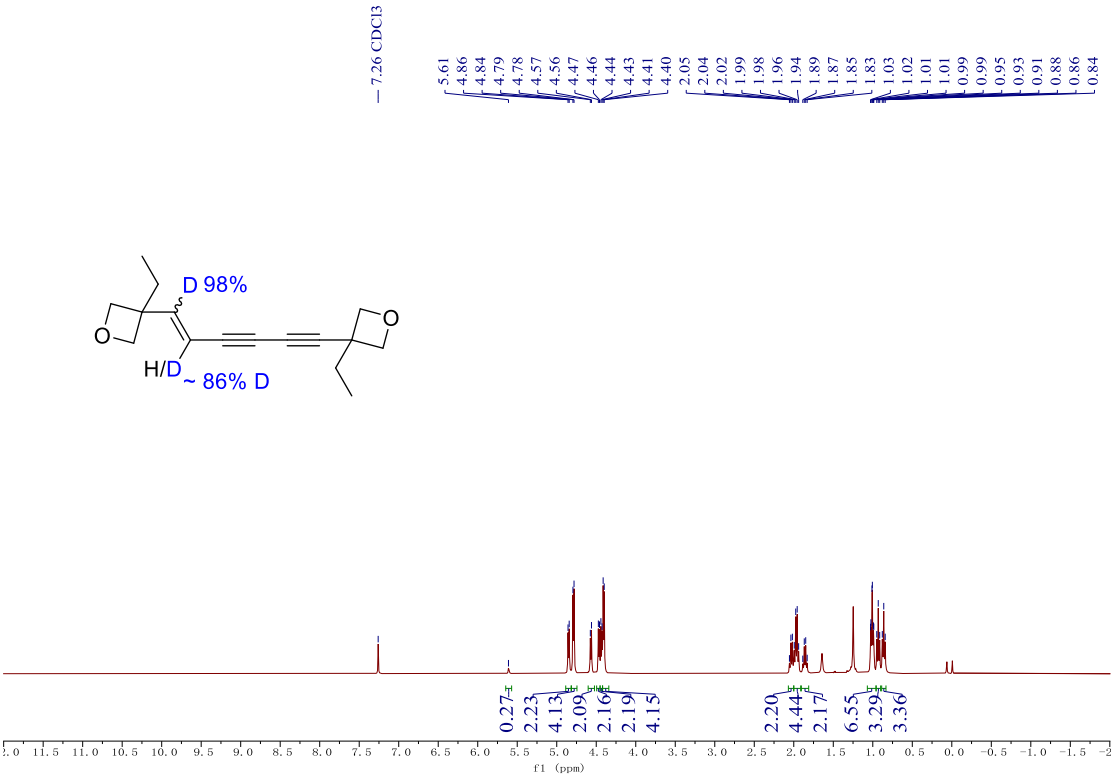


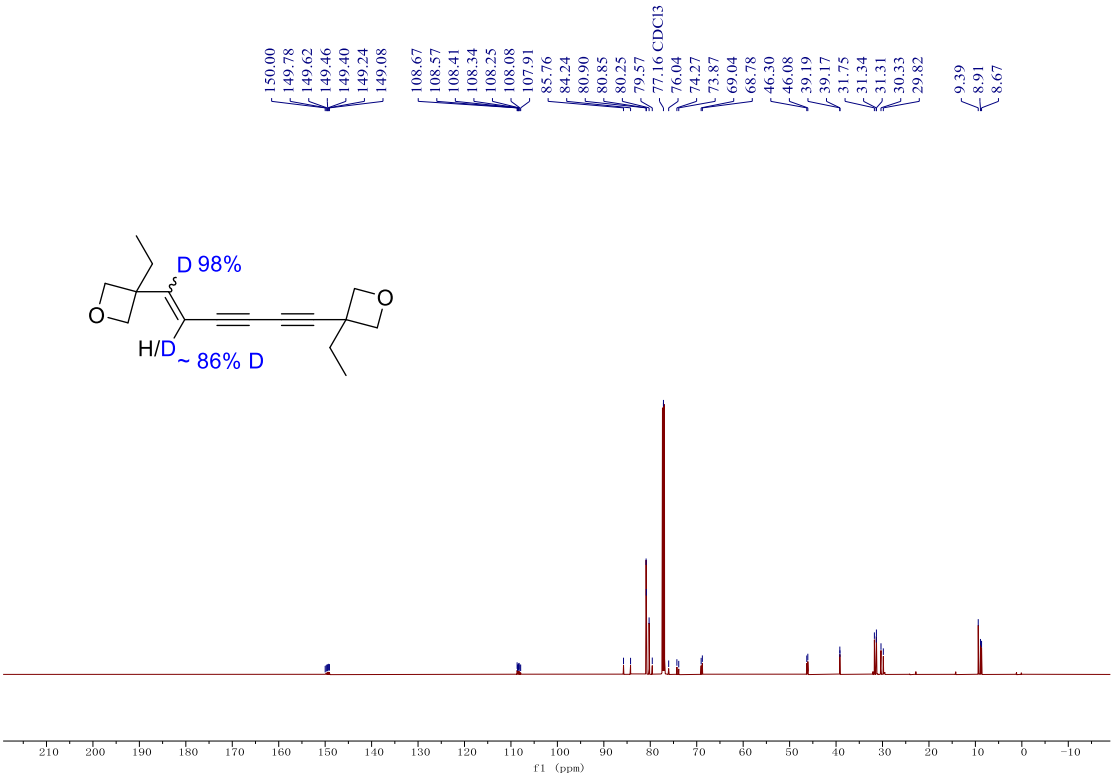
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of *d_2*-2a



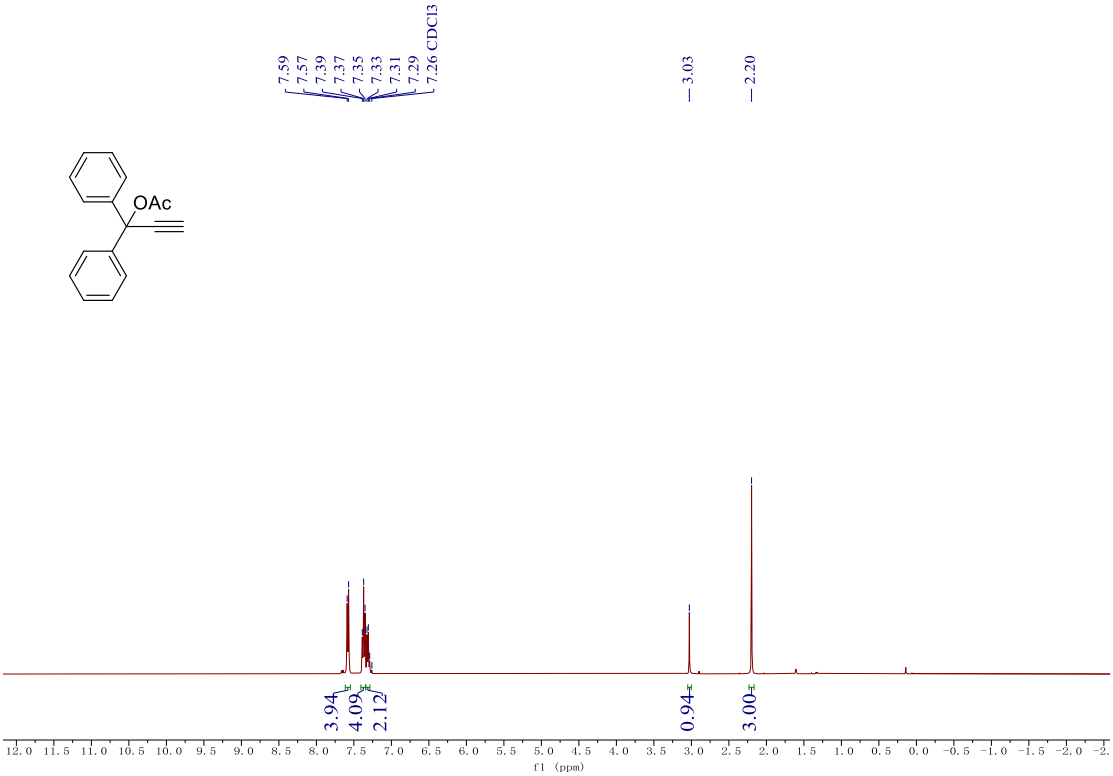


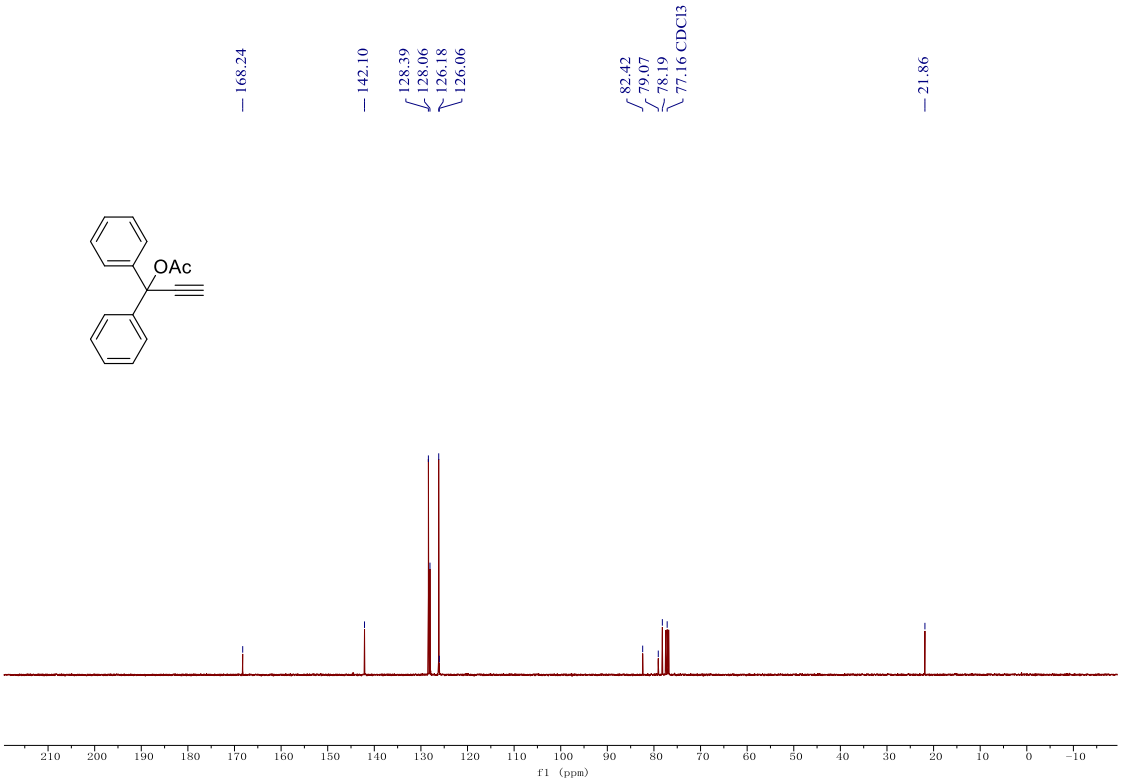
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of *d_2*-2r



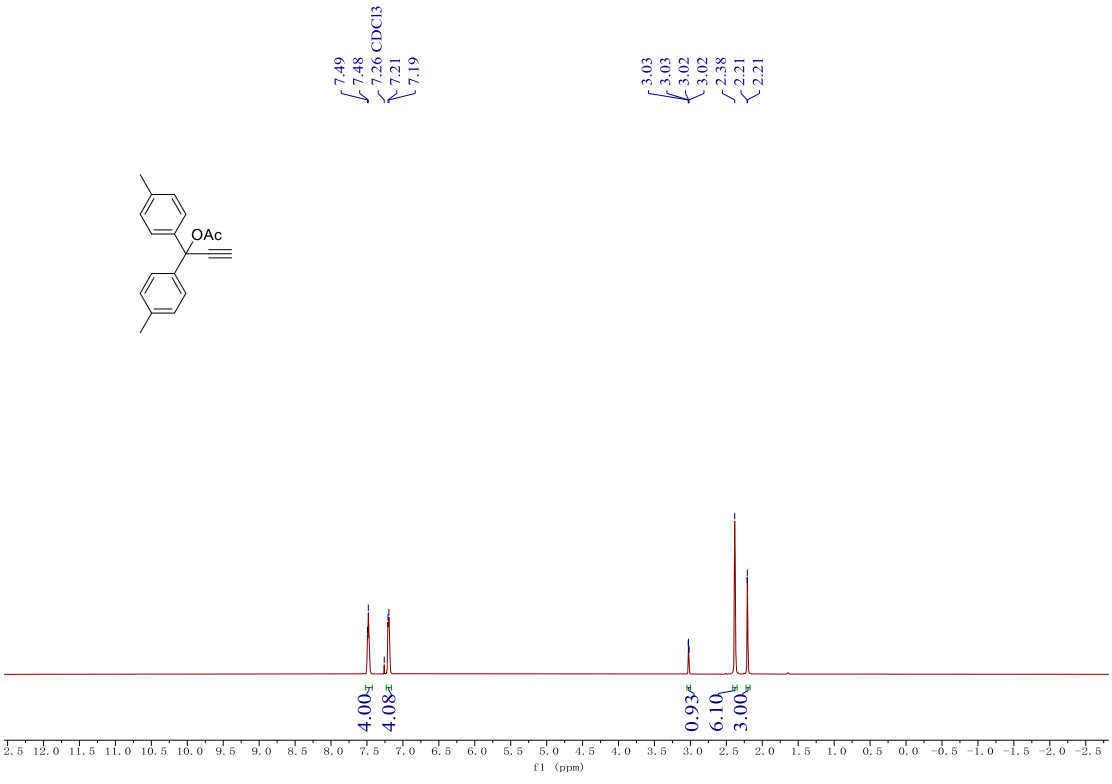


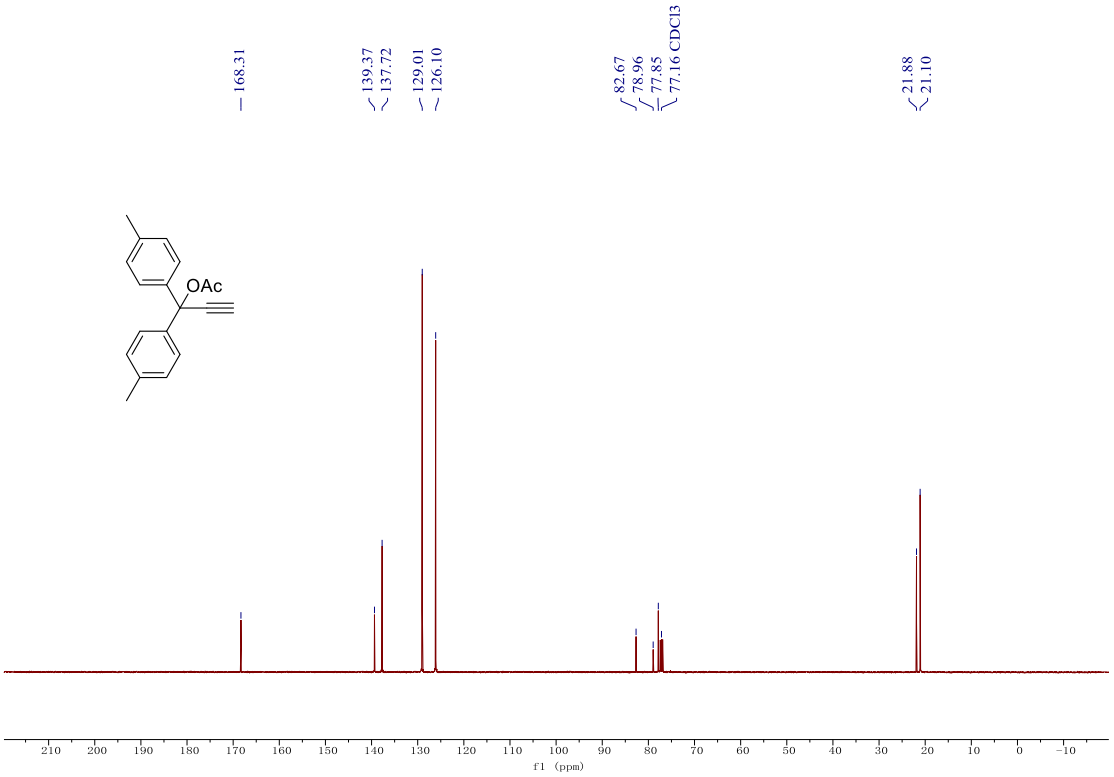
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3a



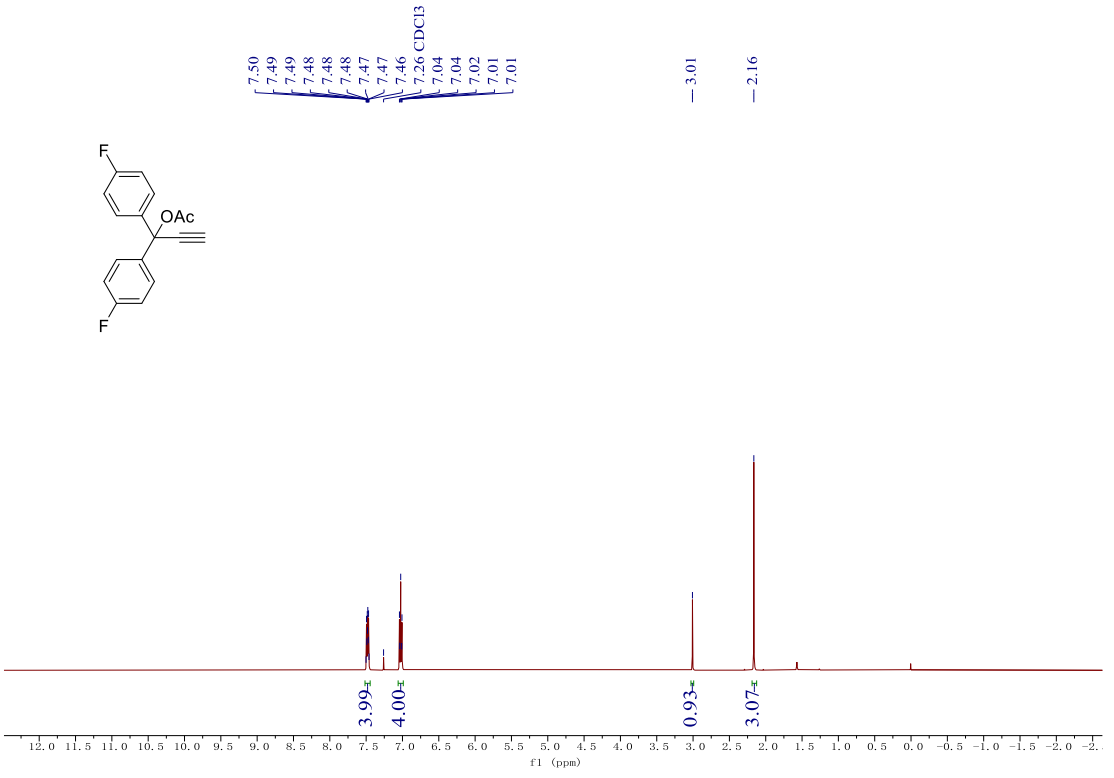


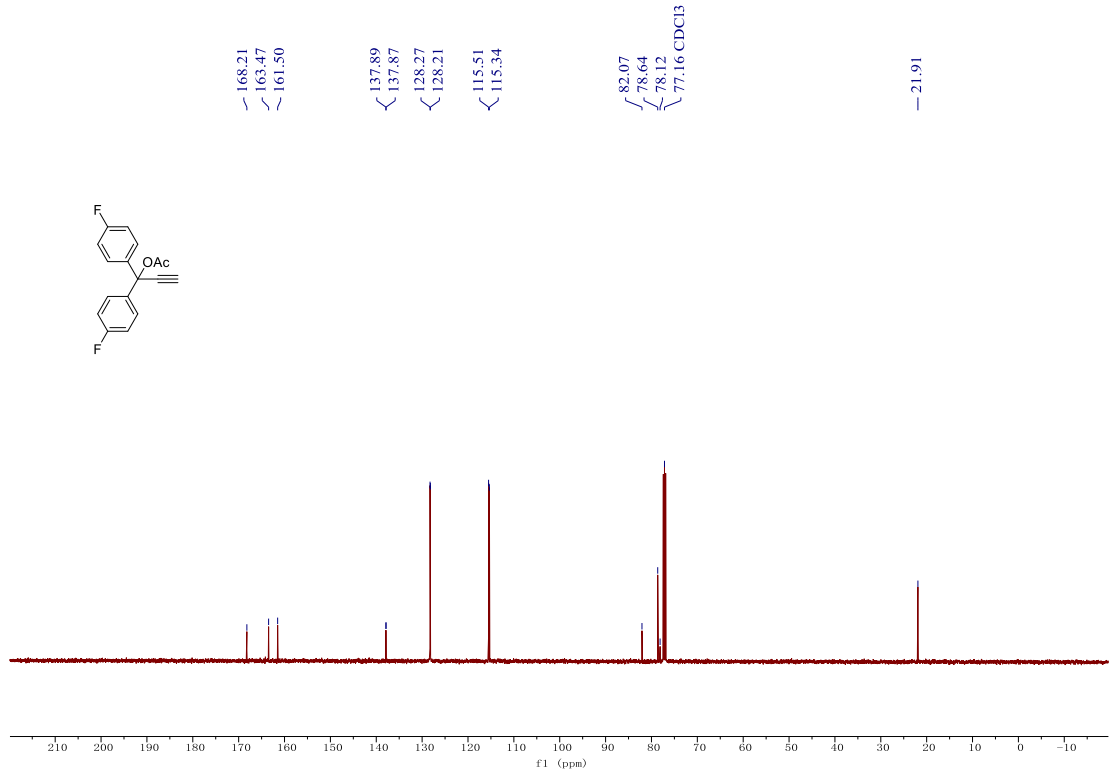
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 3b

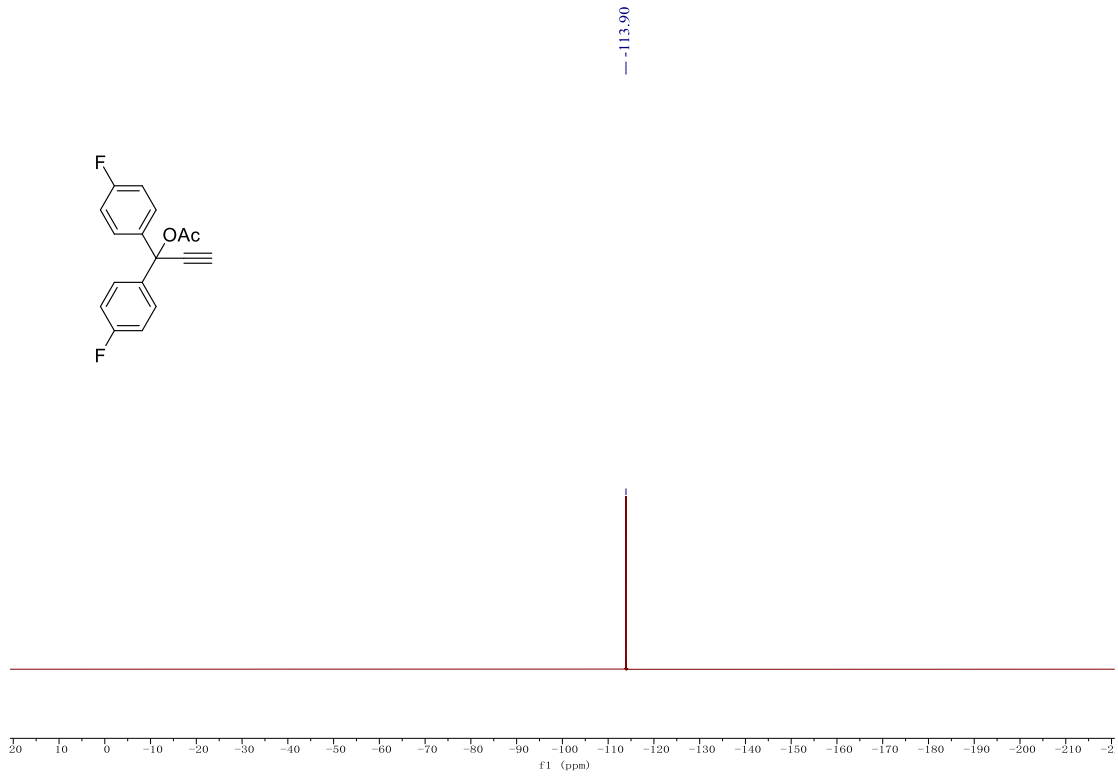




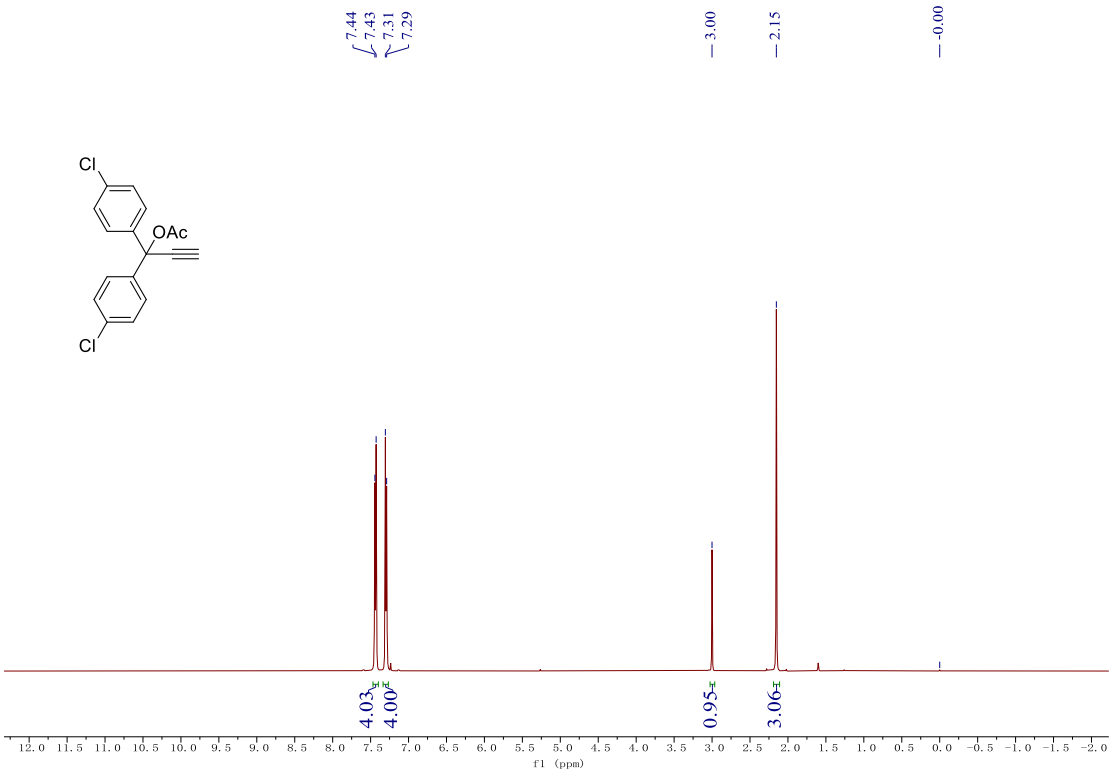
^{1}H NMR spectrum (500 MHz, $CDCl_3$), ^{13}C NMR spectrum (126 MHz, $CDCl_3$) and ^{19}F spectrum NMR (471 MHz, $CDCl_3$) of 3c

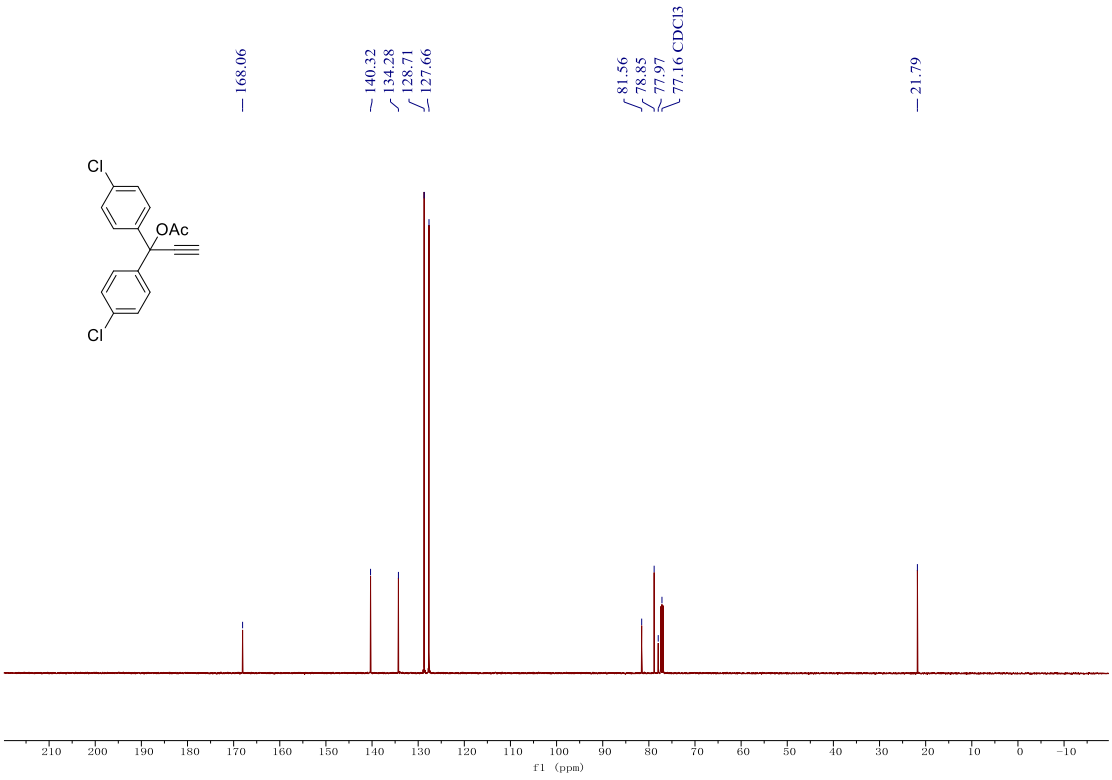



168.21
163.47
161.50
137.89
137.87
128.27
128.21
115.51
115.34
82.07
78.64
78.12
77.16 CDCl3
21.91
F
OAc
F
f1 (ppm)

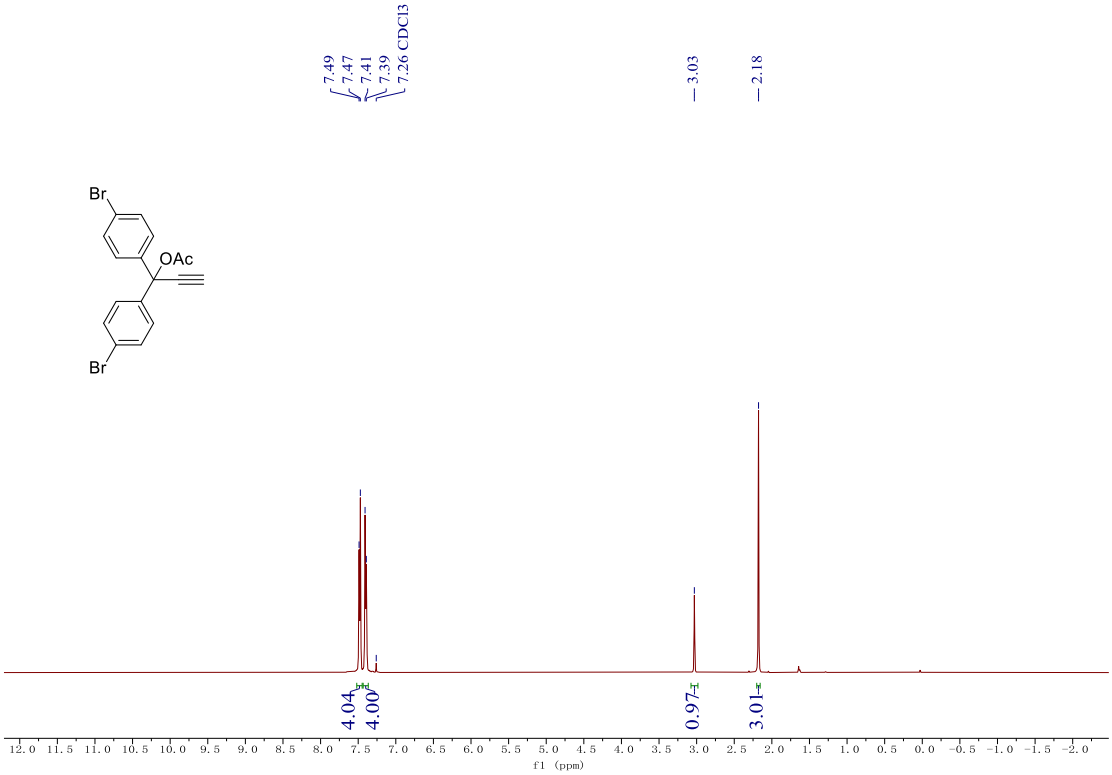

-113.90
F
OAc
F
f1 (ppm)

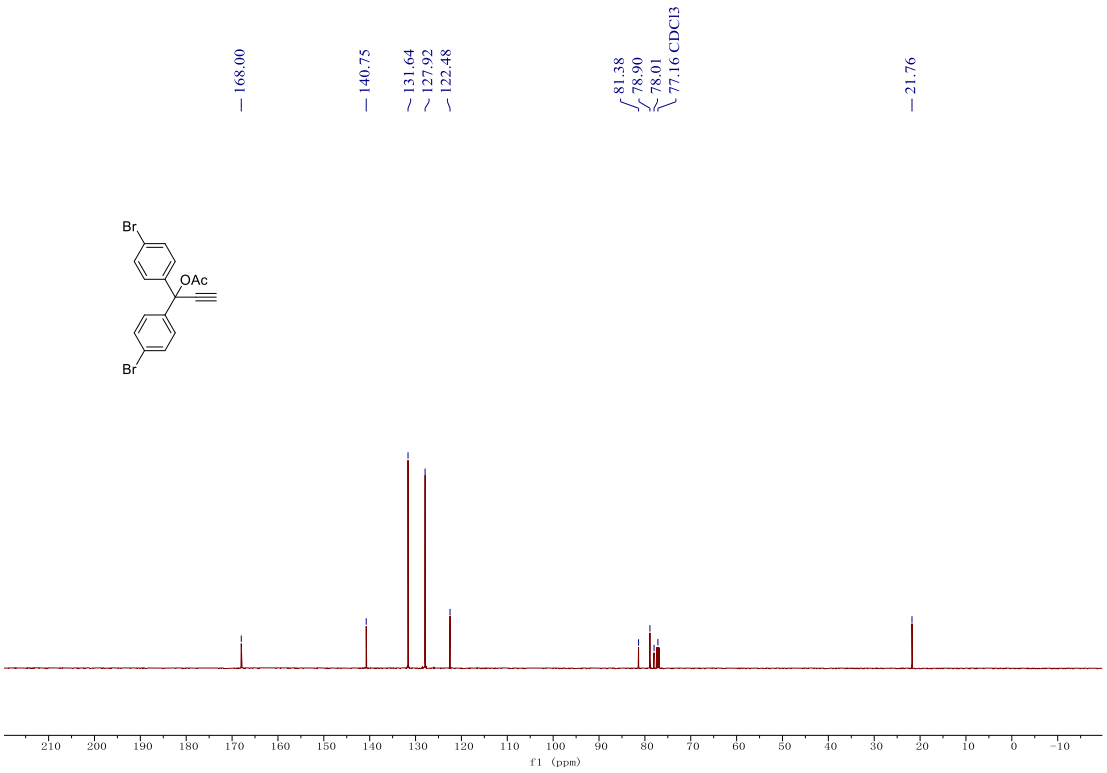
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 3d



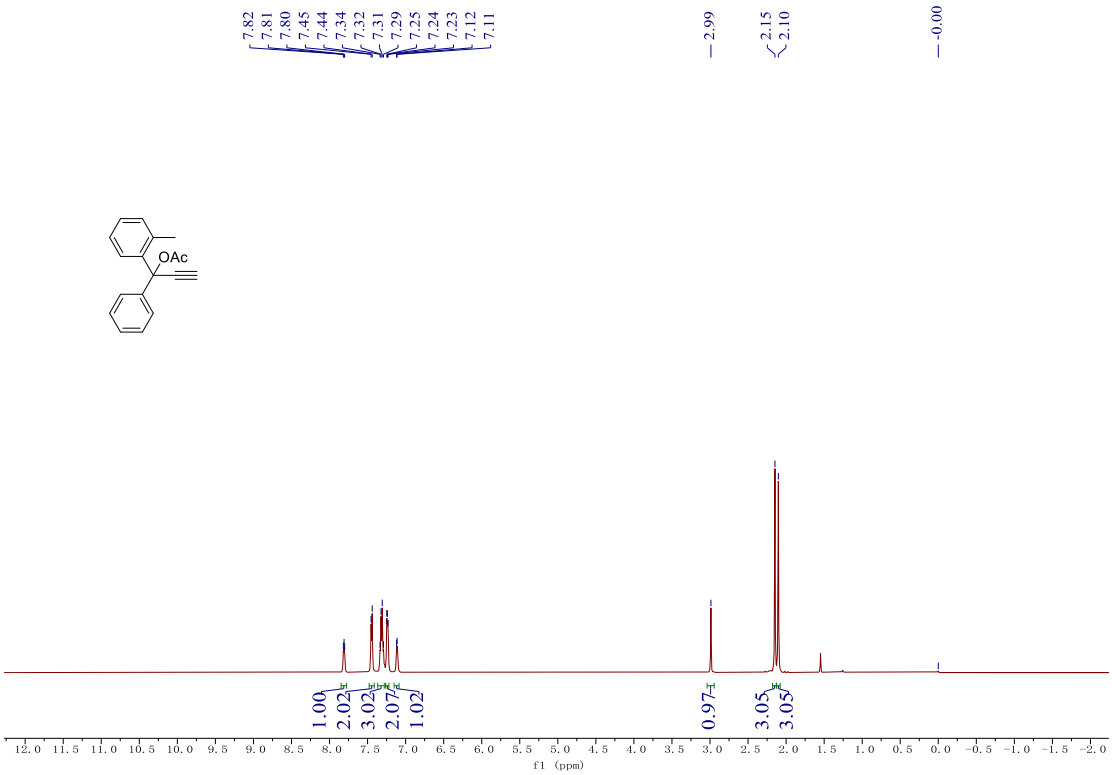


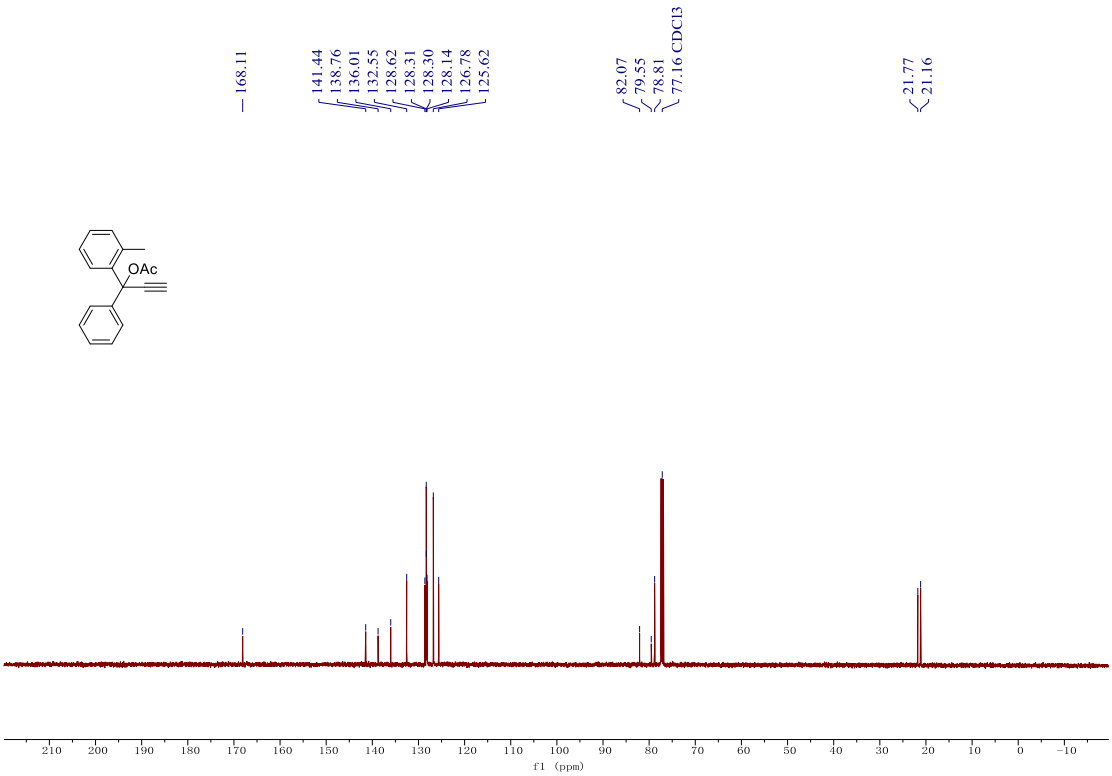
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 3e



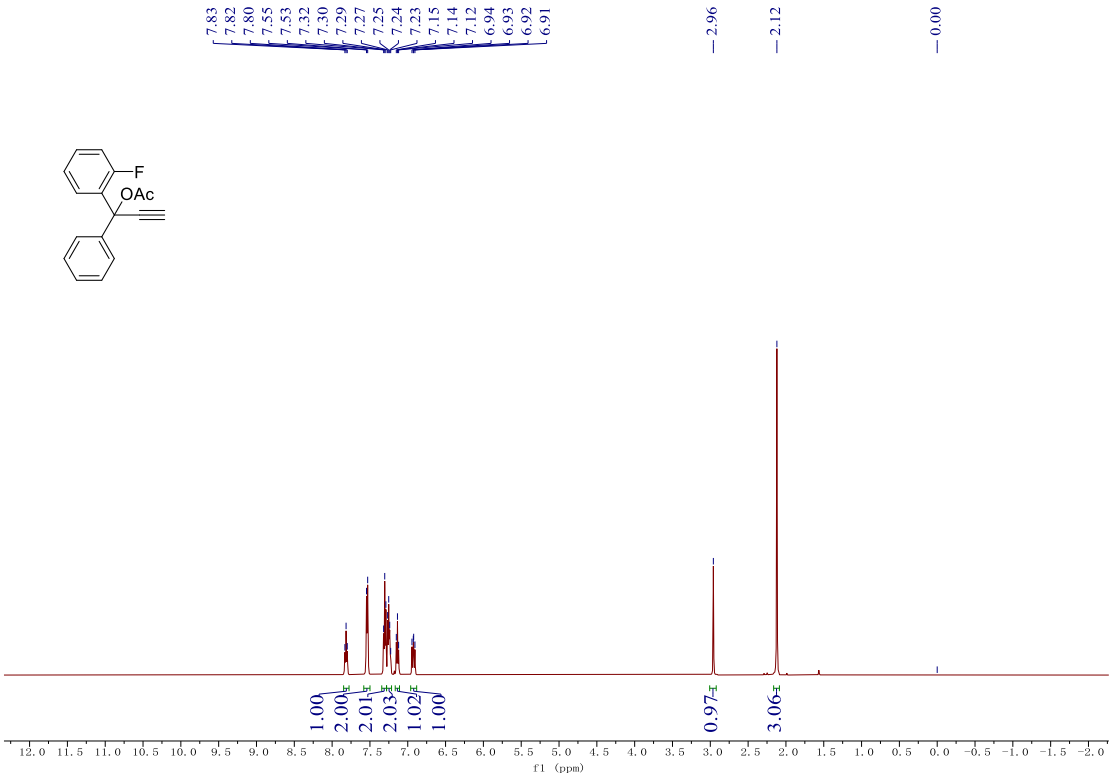


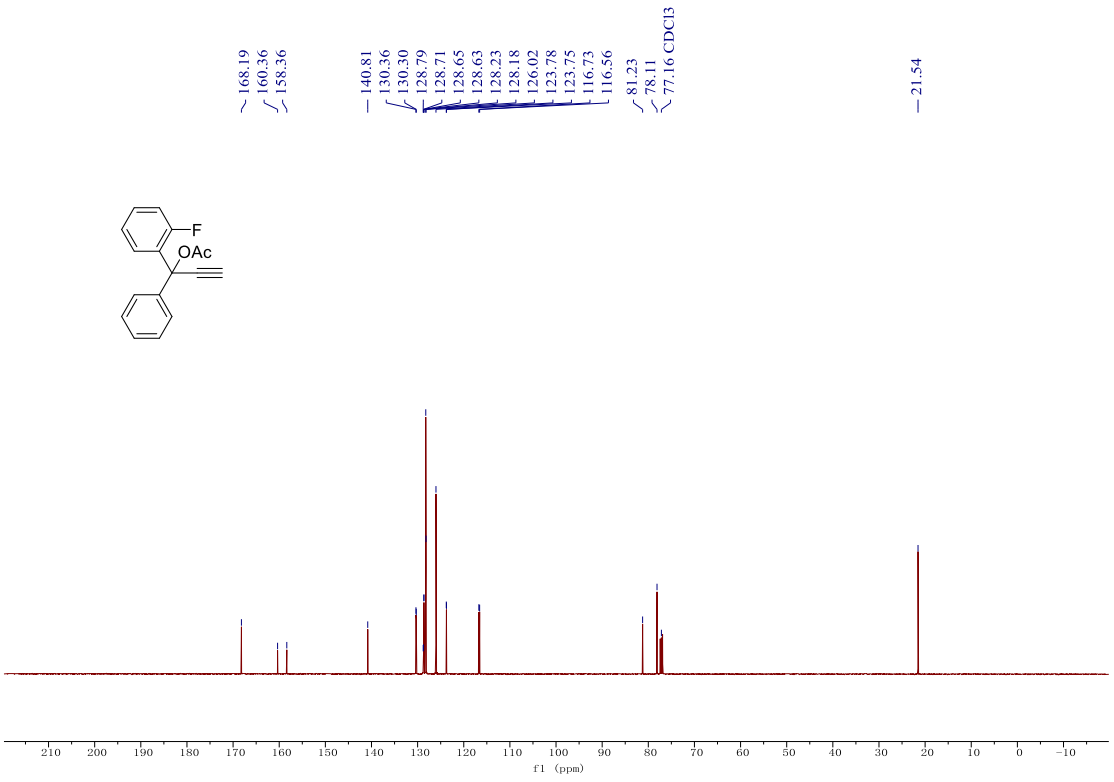
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 3f

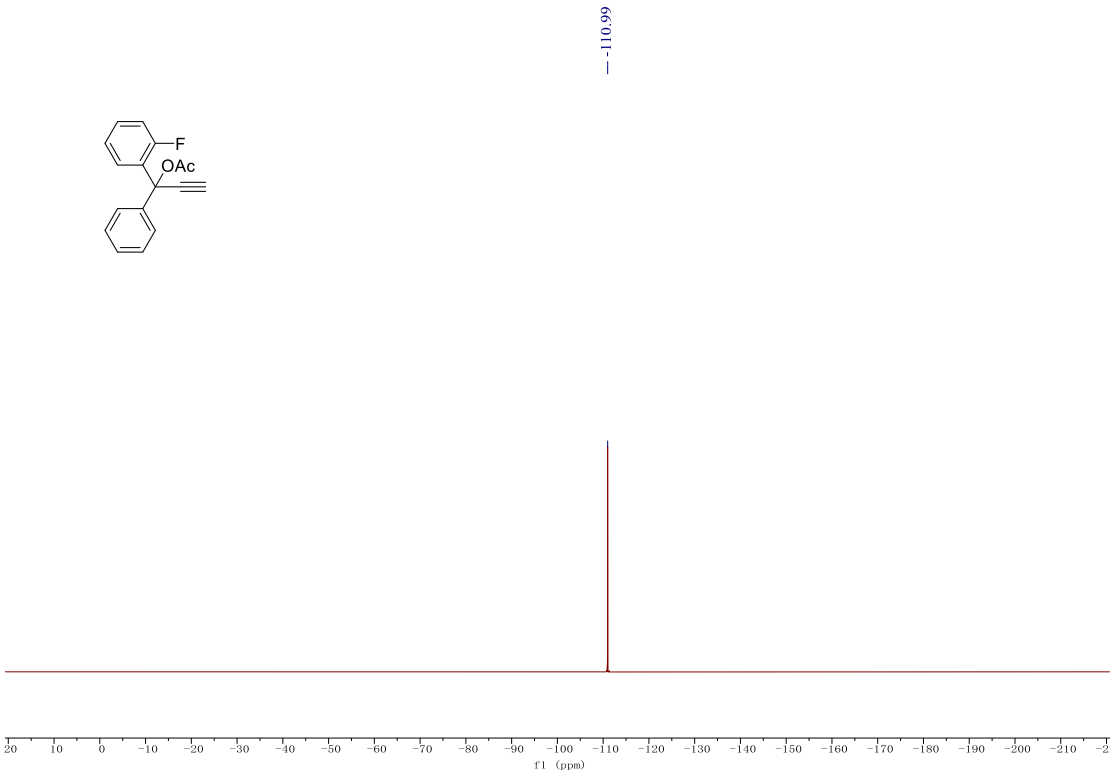




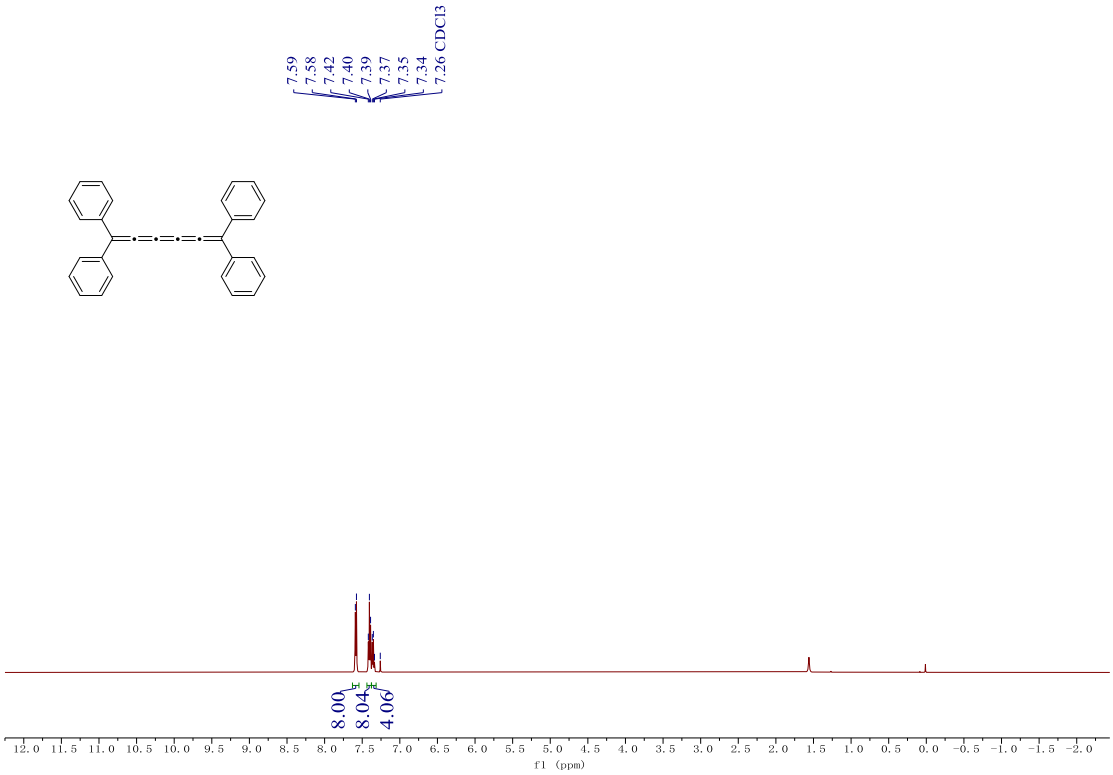
^{1}H NMR spectrum (500 MHz, $CDCl_3$), ^{13}C NMR spectrum (126 MHz, $CDCl_3$) and ^{19}F spectrum NMR (471 MHz, $CDCl_3$) of 3g

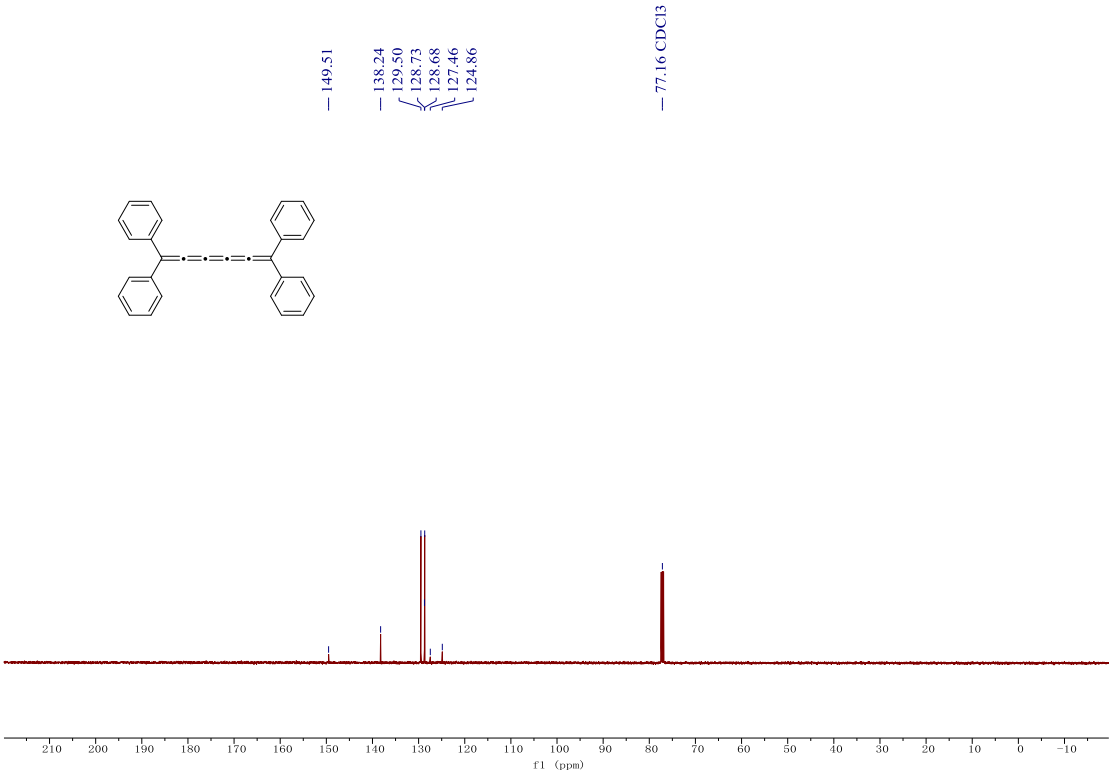




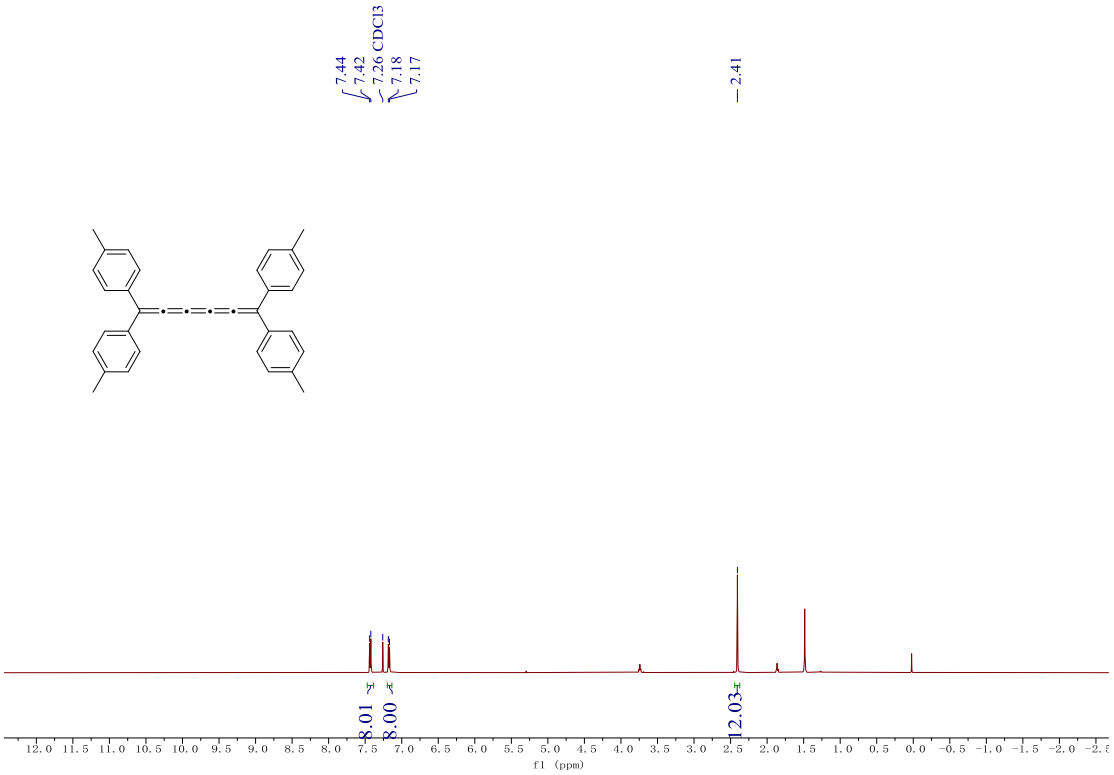


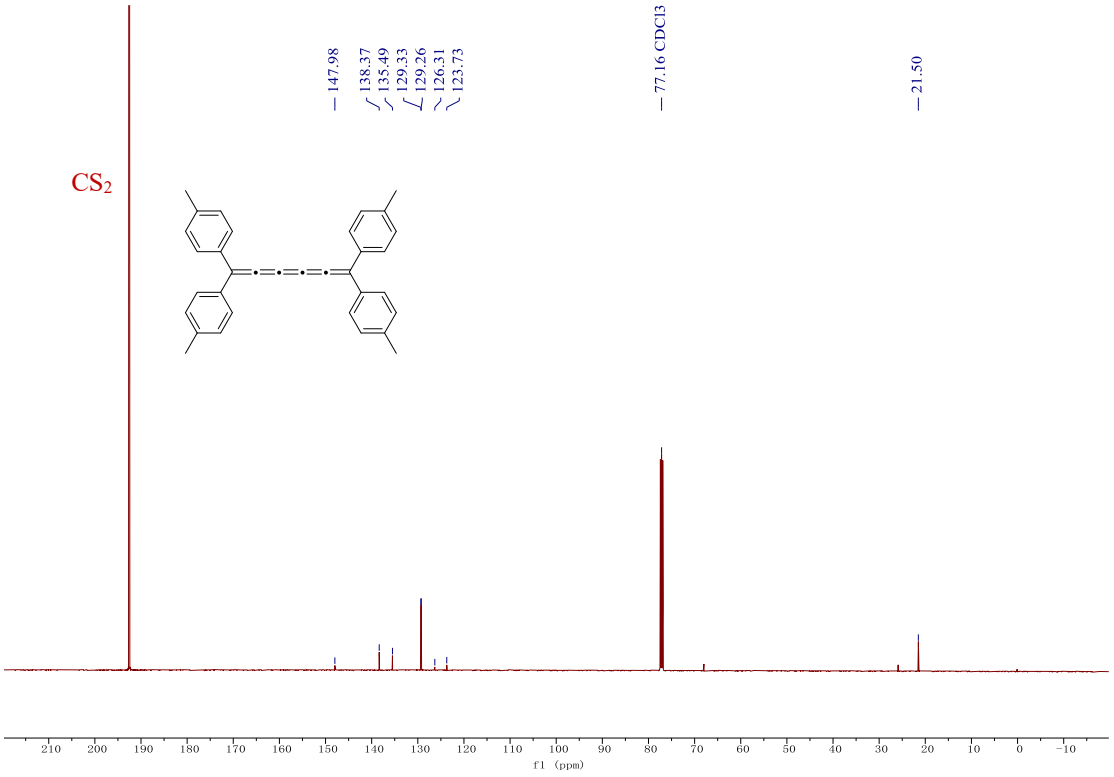
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 4a



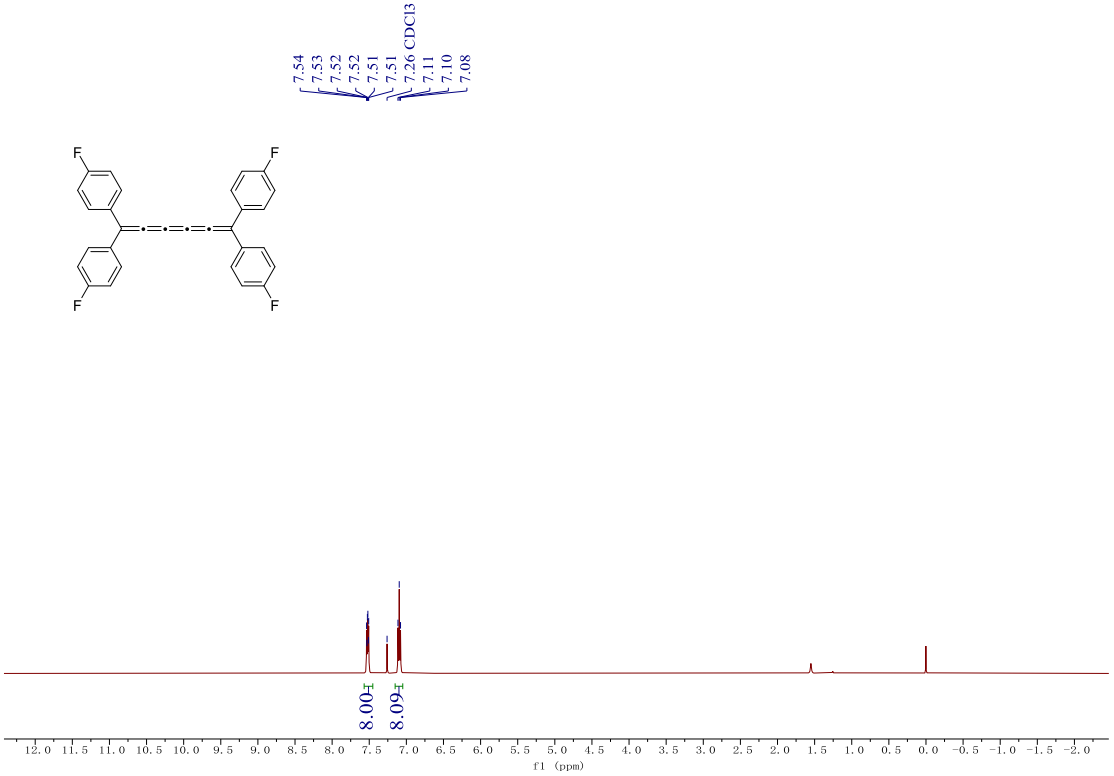


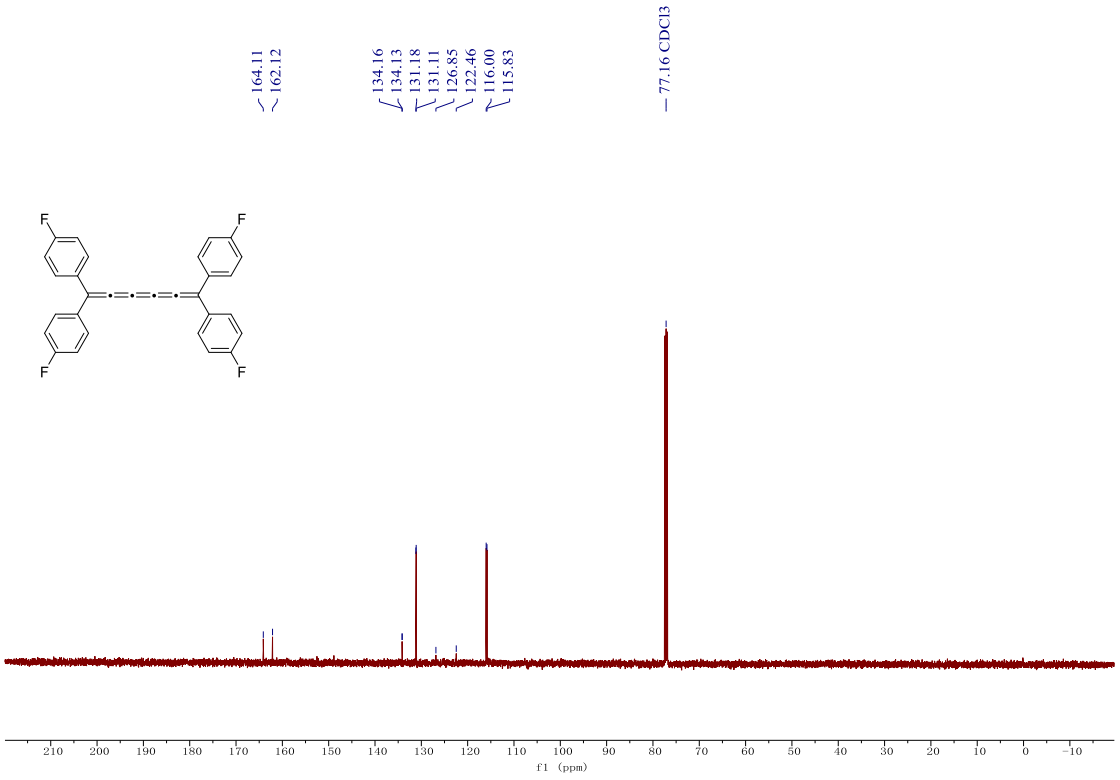
^{1}H NMR spectrum (500 MHz, $CDCl_3$−CS_2) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$−CS_2) of 4b

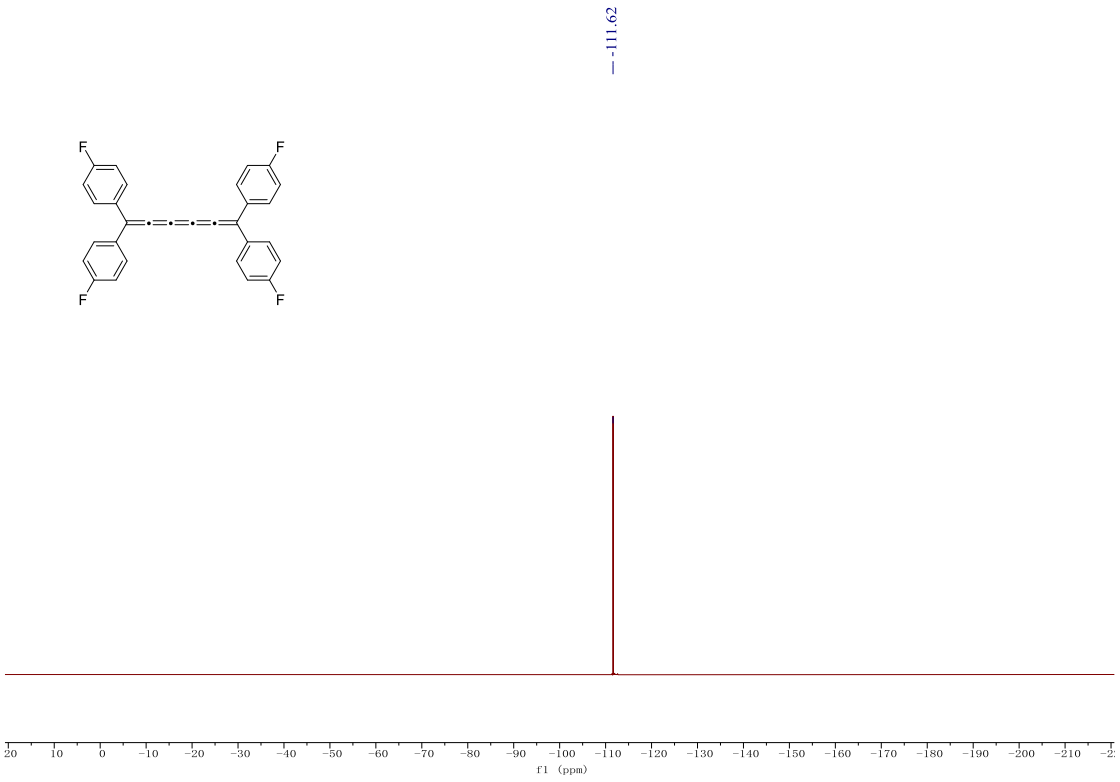




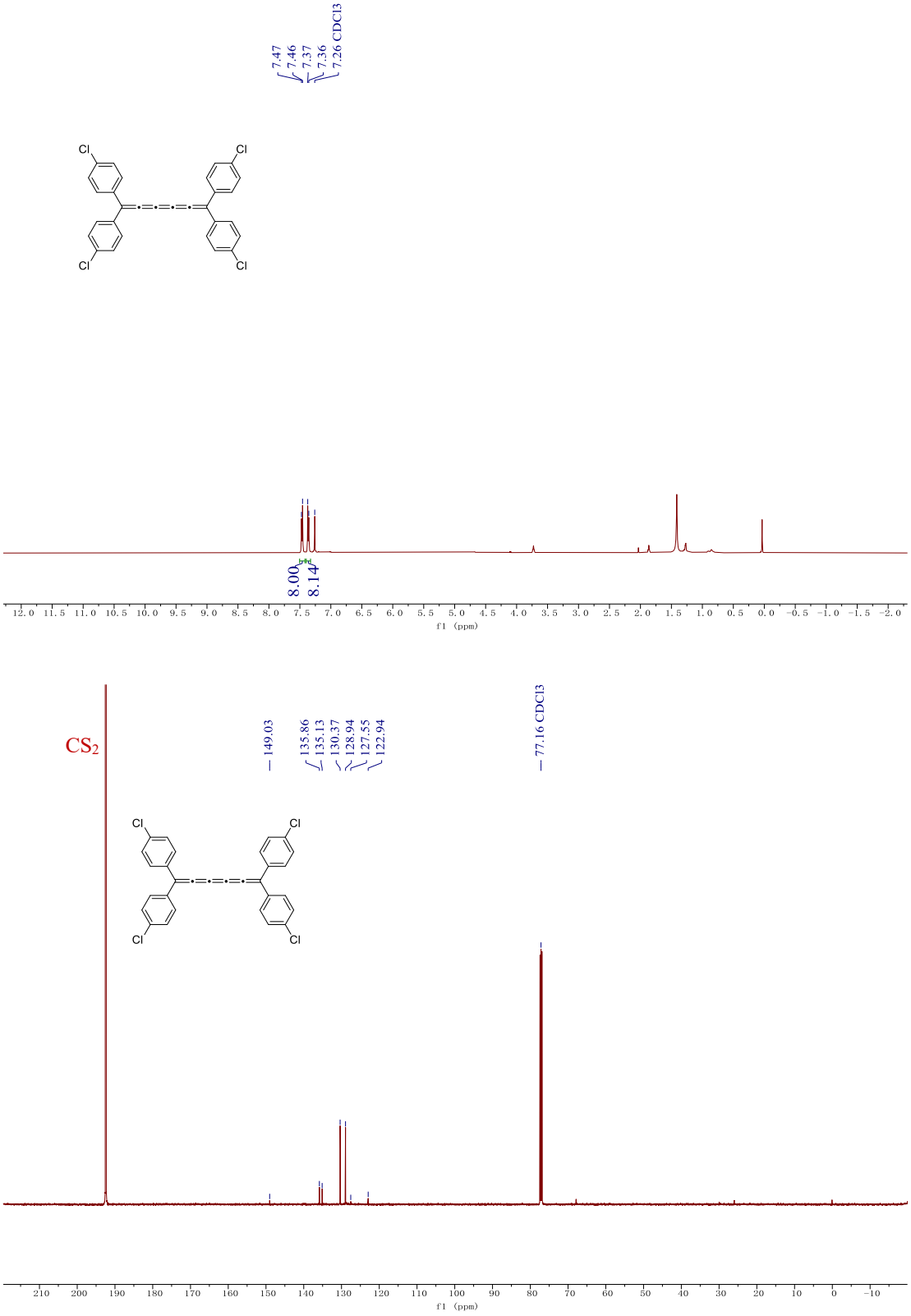
^{1}H NMR spectrum (500 MHz, $CDCl_3$), ^{13}C NMR spectrum (126 MHz, $CDCl_3$) and ^{19}F spectrum NMR (471 MHz, $CDCl_3$) of 4c



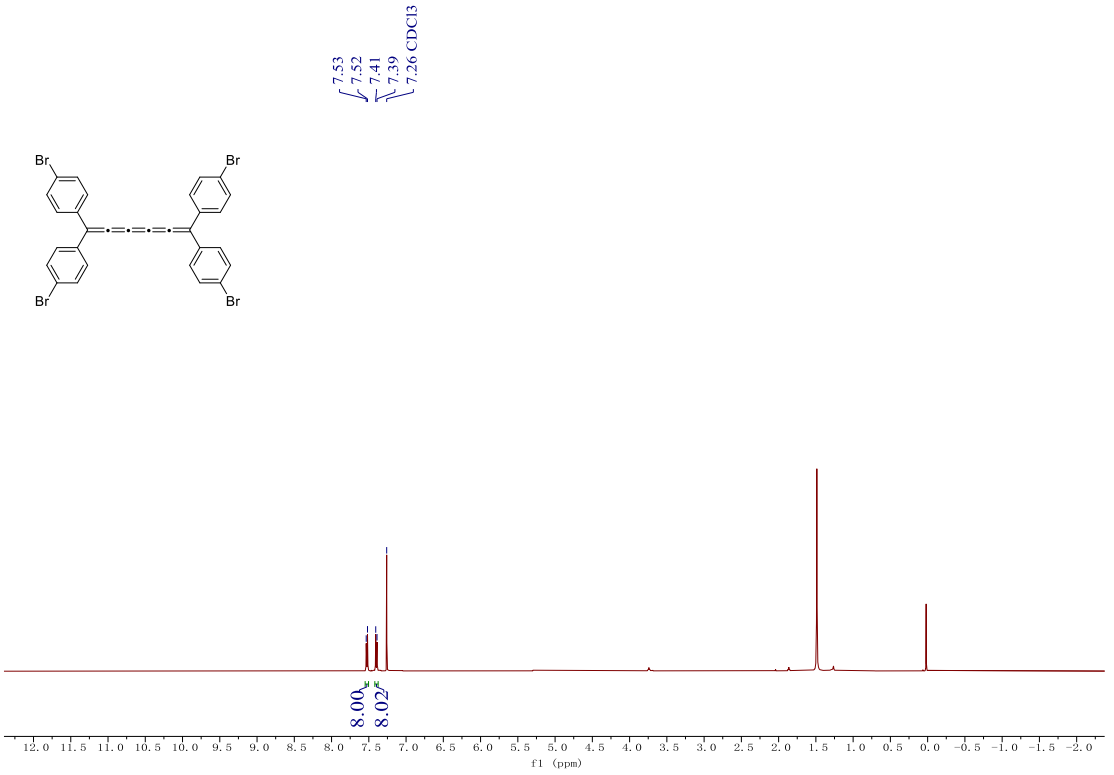

164.11
162.12
134.16
134.13
131.18
131.11
126.85
122.46
116.00
115.83
77.16 CDCl3
F
F
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

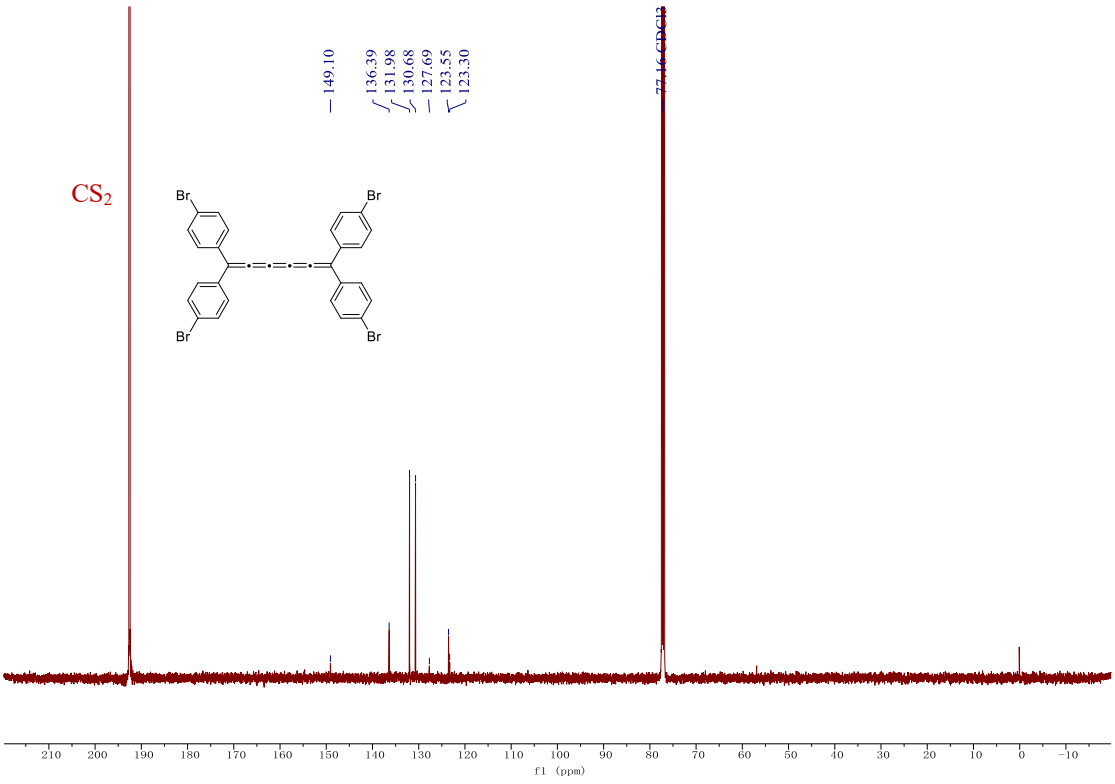

-111.62
F
F
F
F
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

^{1}H NMR spectrum (500 MHz, $CDCl_3$−CS_2) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$−CS_2) of 4d

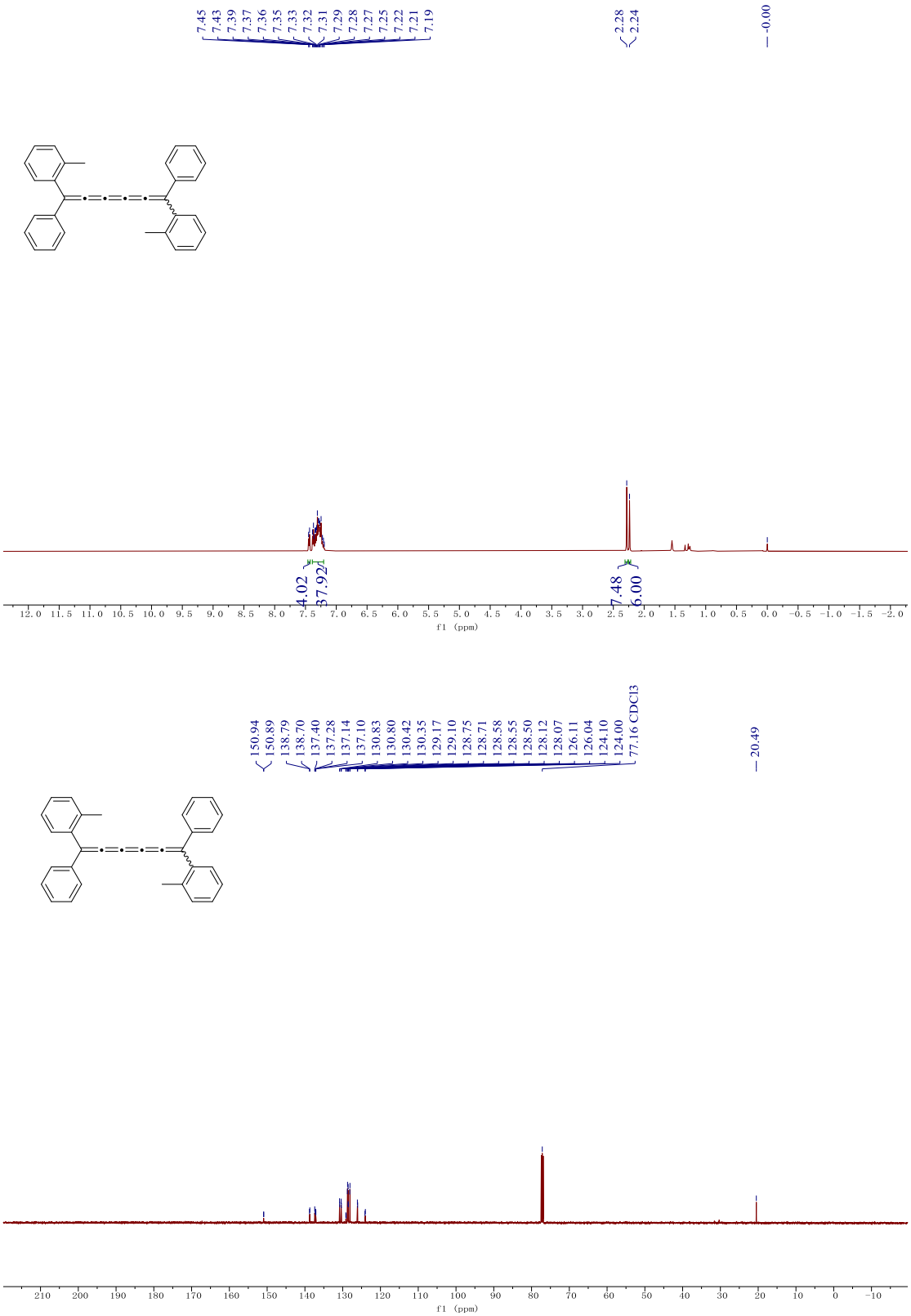


^{1}H NMR spectrum (500 MHz, $CDCl_3$–CS_2) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$–CS_2) of 4e

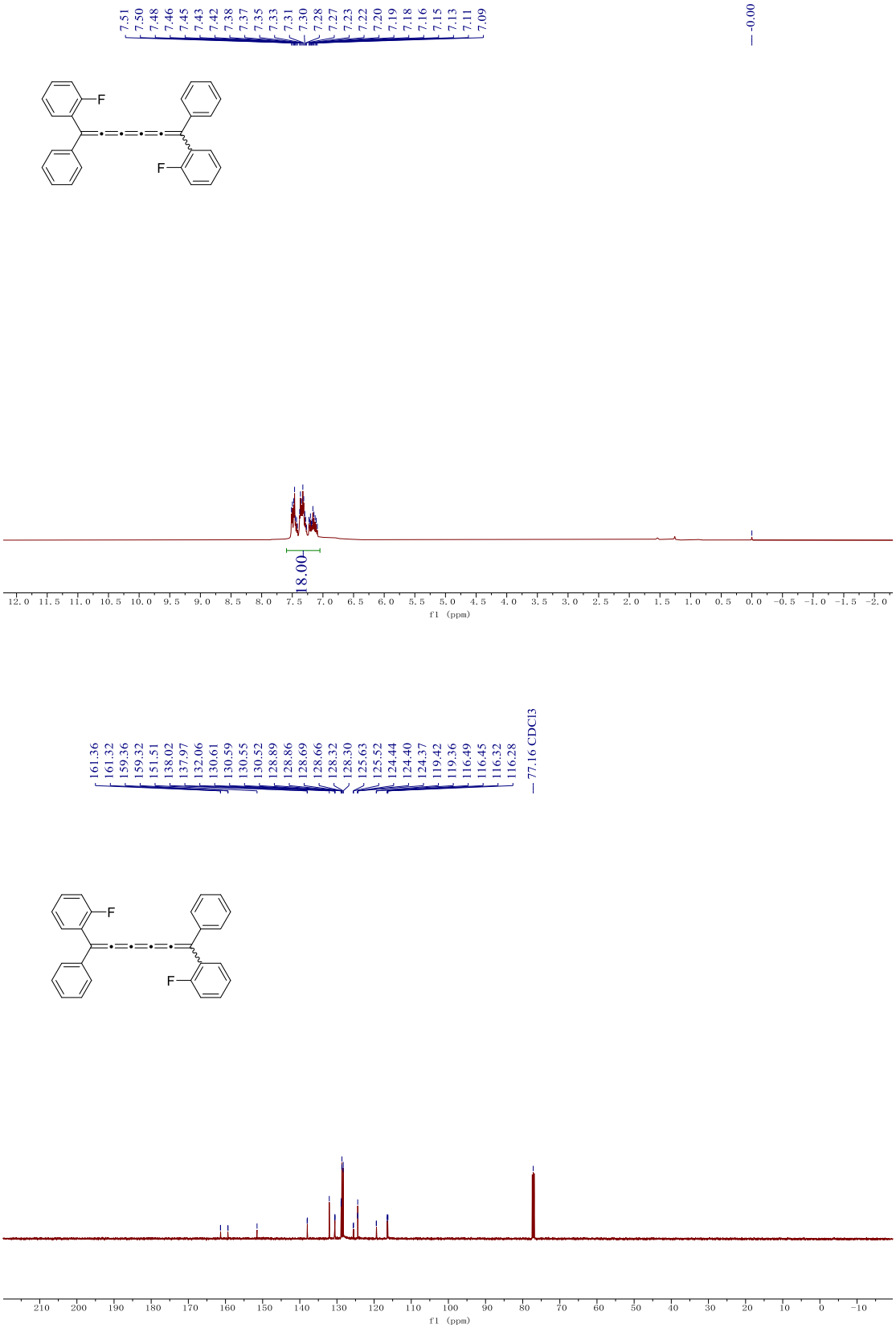


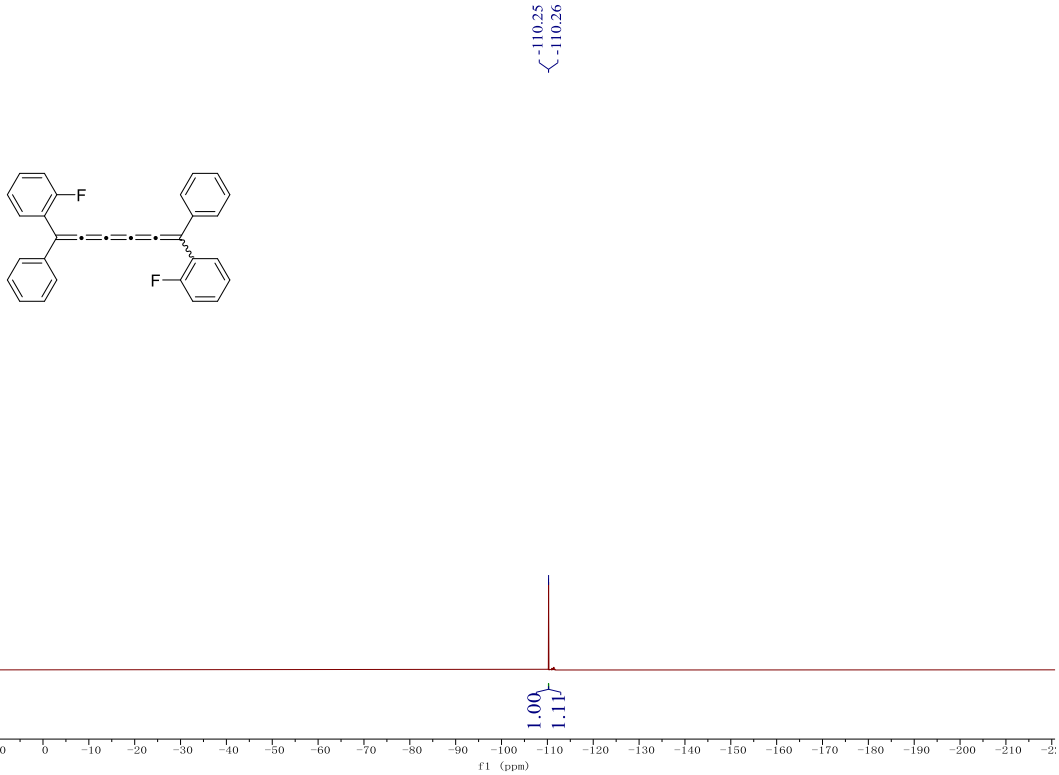


^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 4f

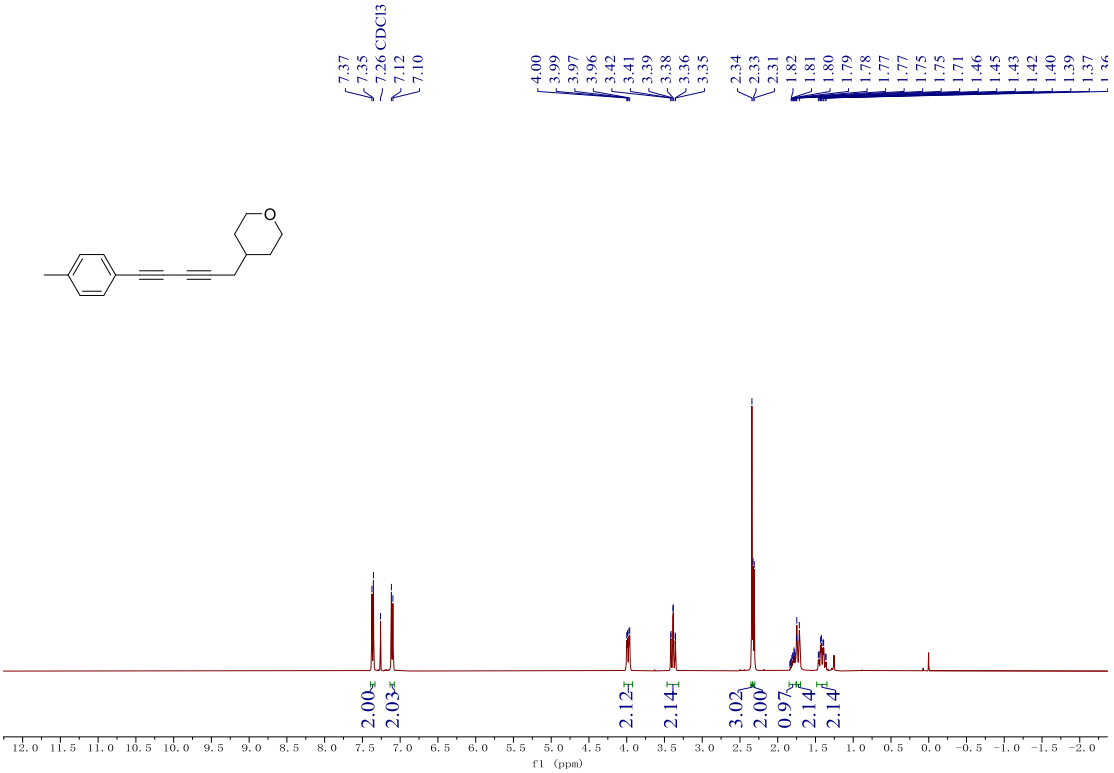


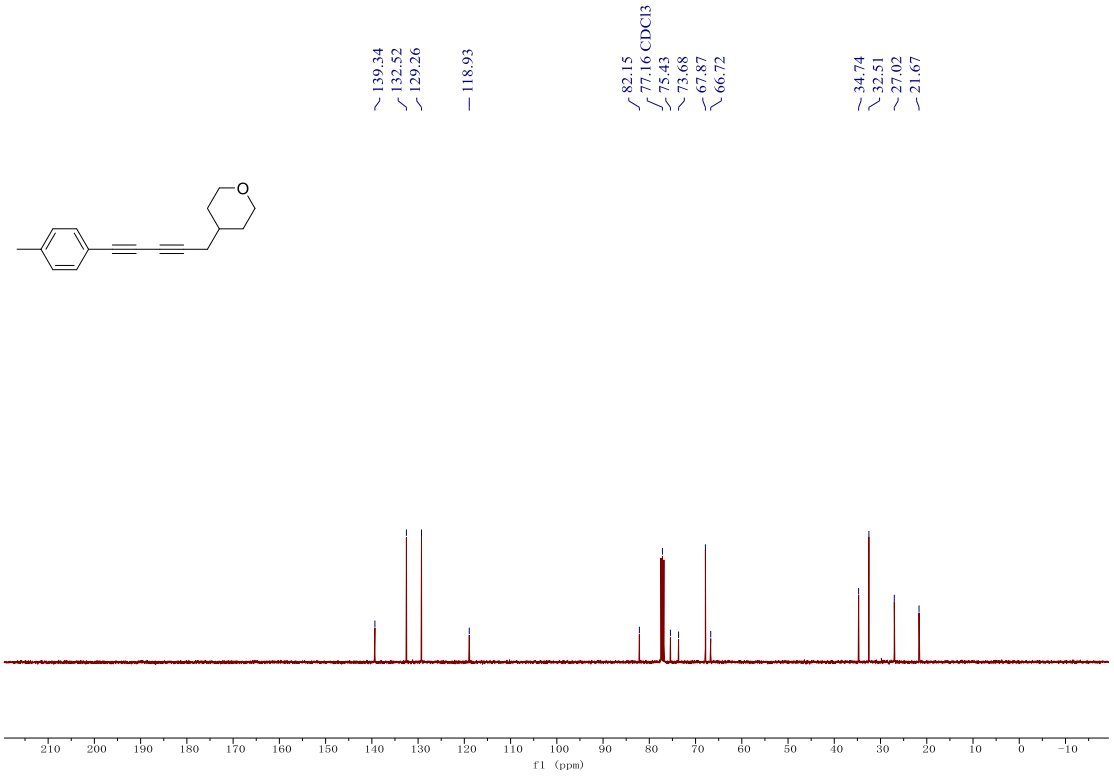
^{1}H NMR spectrum (500 MHz, $CDCl_3$), ^{13}C NMR spectrum (126 MHz, $CDCl_3$) and ^{19}F spectrum NMR (471 MHz, $CDCl_3$) of 4g



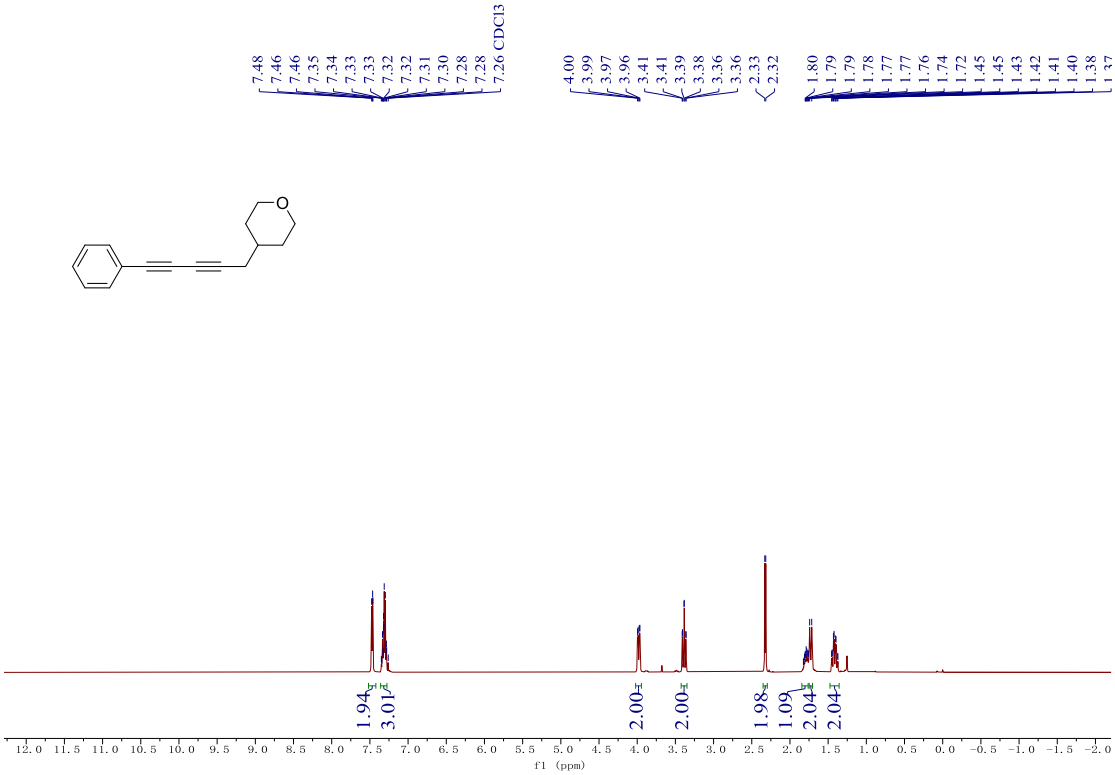


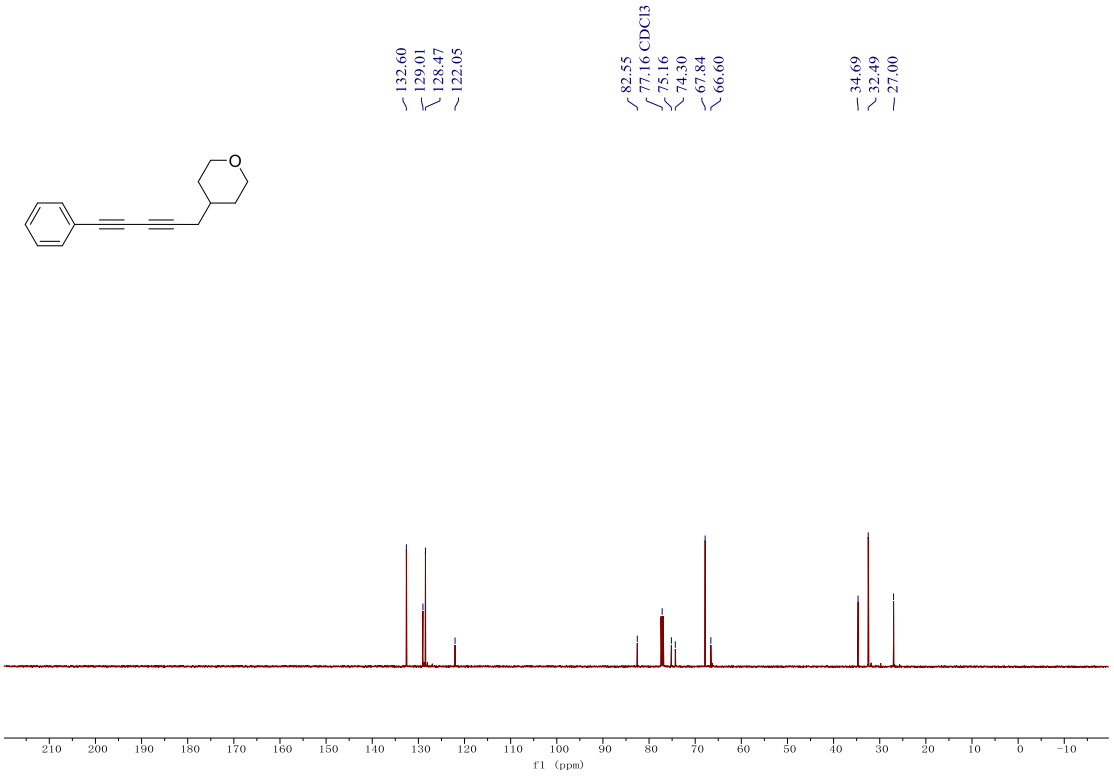
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 6a



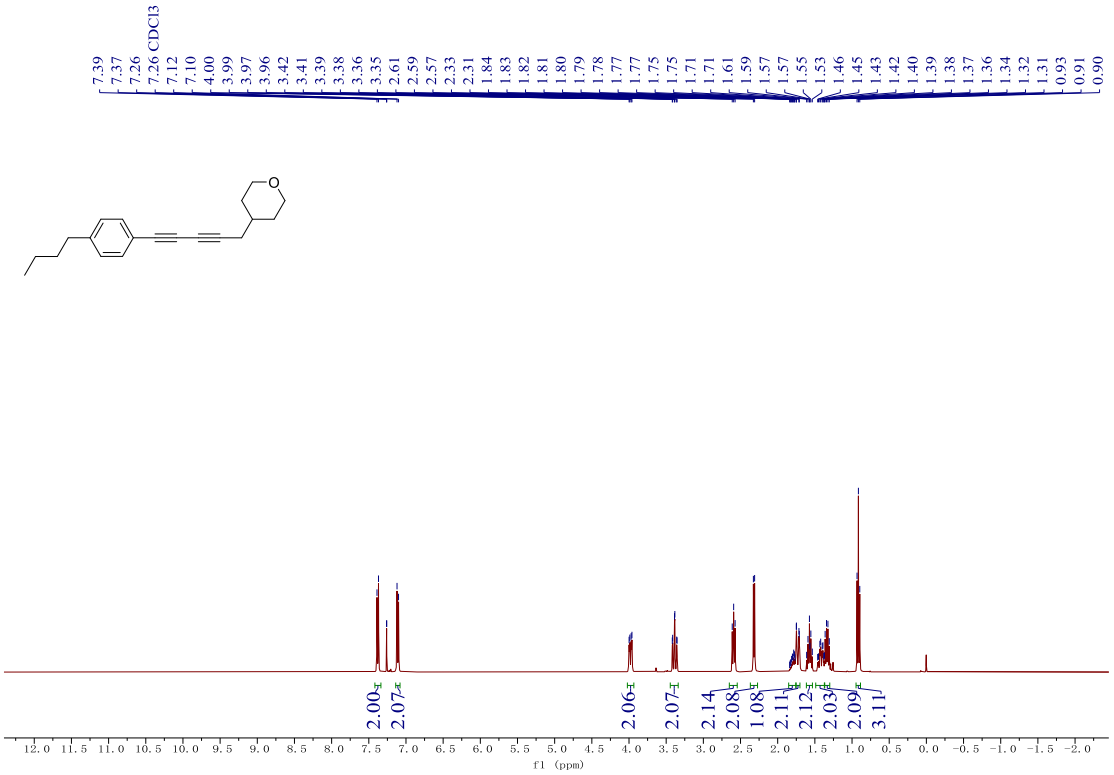


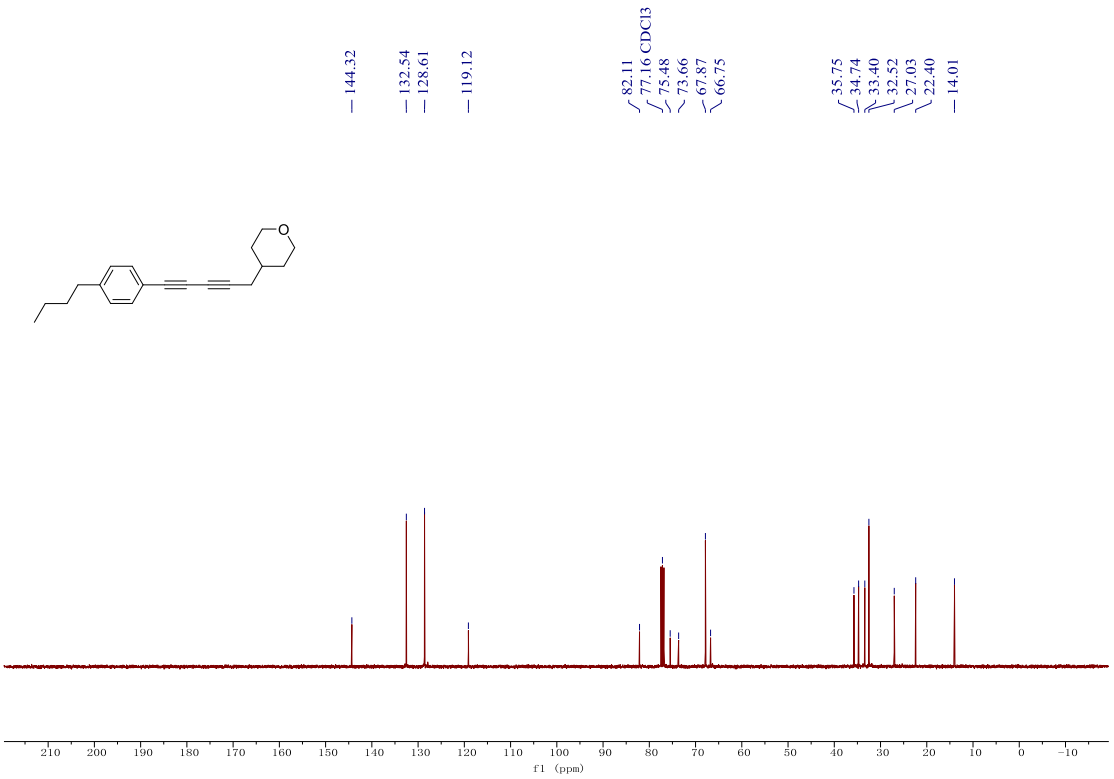
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6b



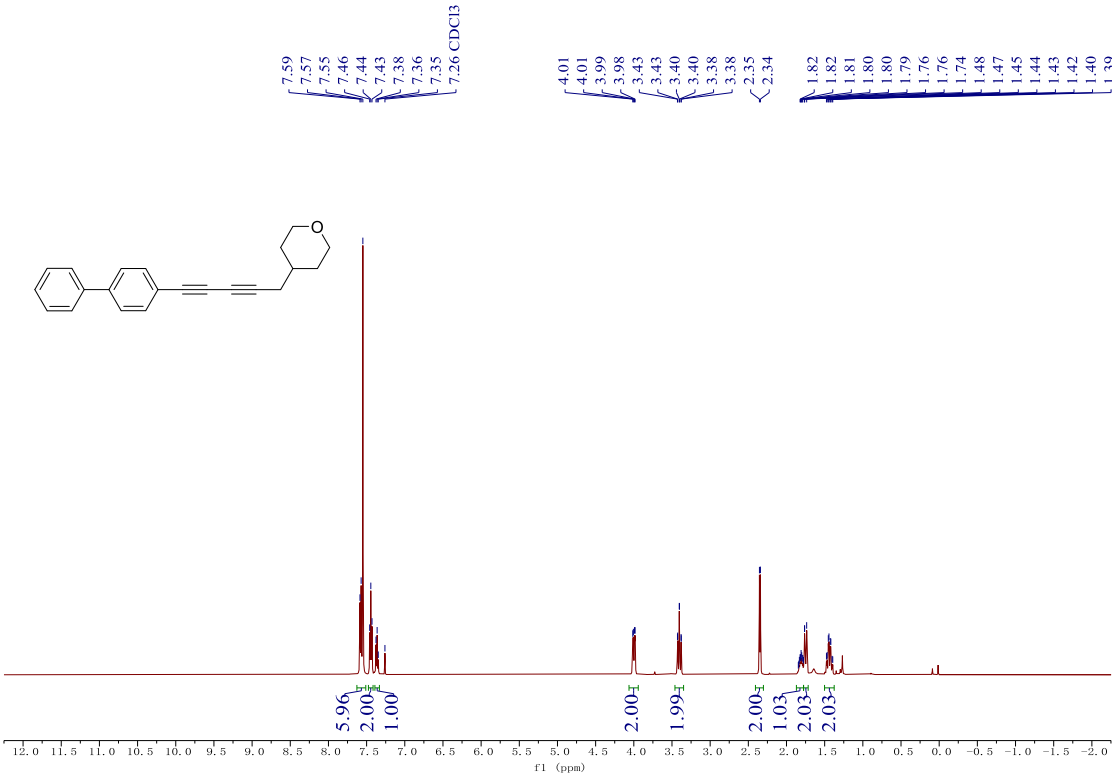


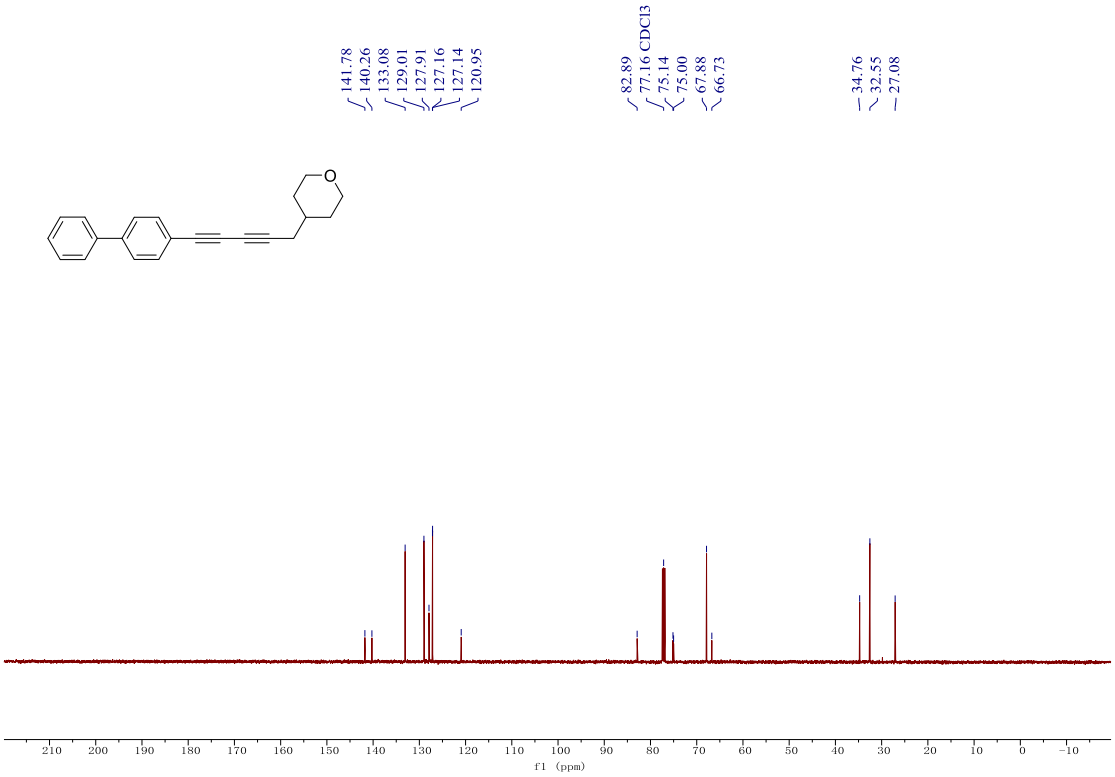
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 6c



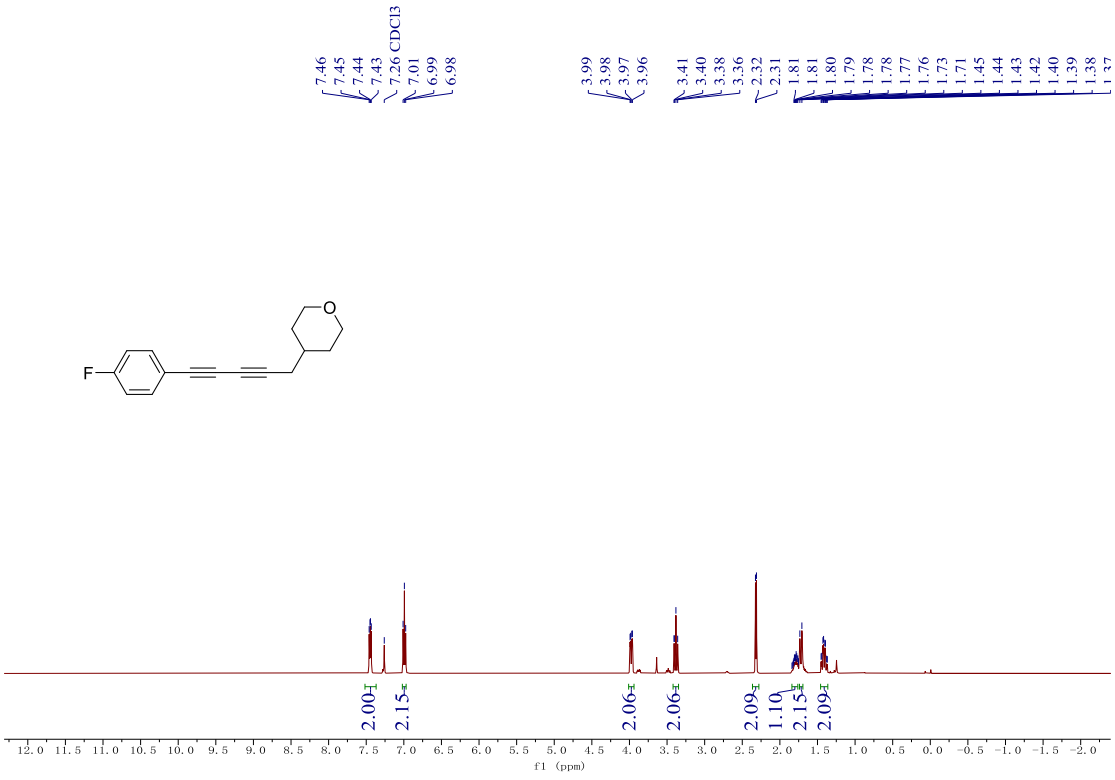


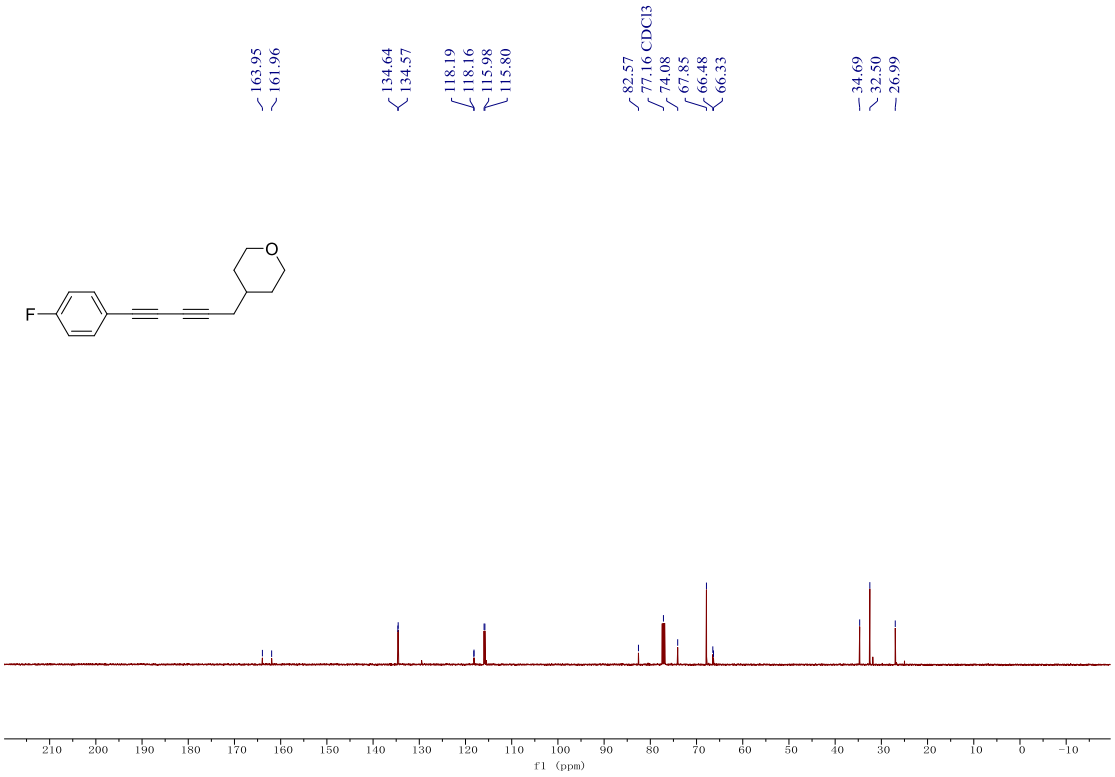
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6d

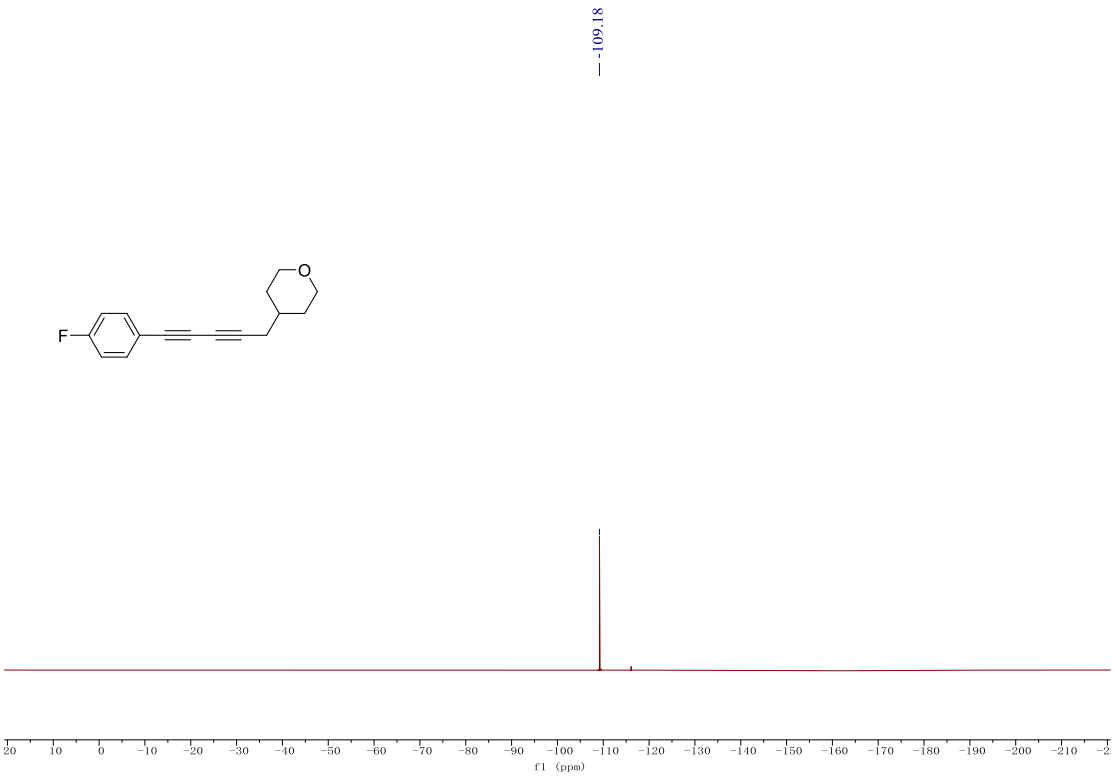




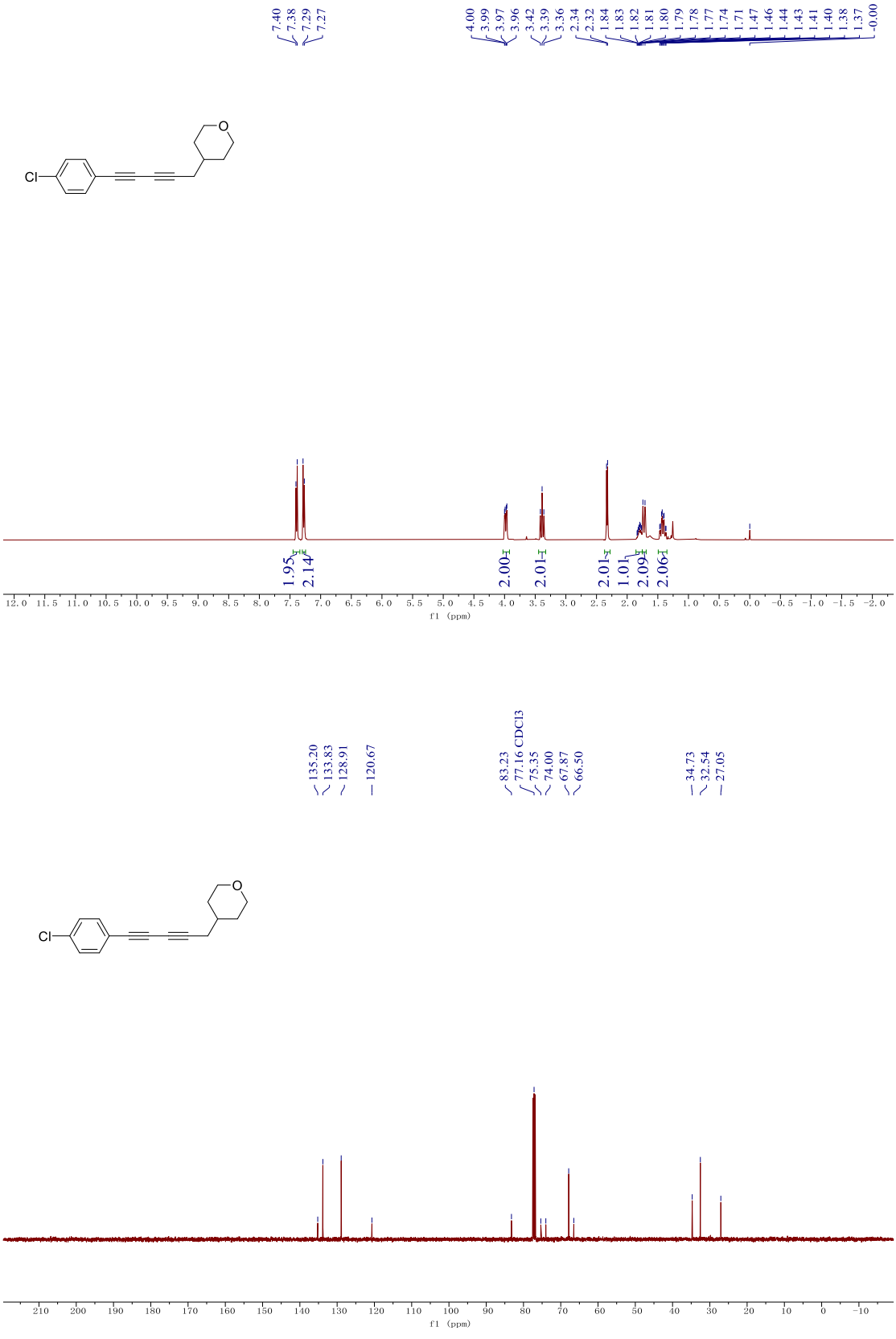
^{1}H NMR spectrum (500 MHz, $CDCl_3$), ^{13}C NMR spectrum (126 MHz, $CDCl_3$) and ^{19}F spectrum NMR (471 MHz, $CDCl_3$) of 6e



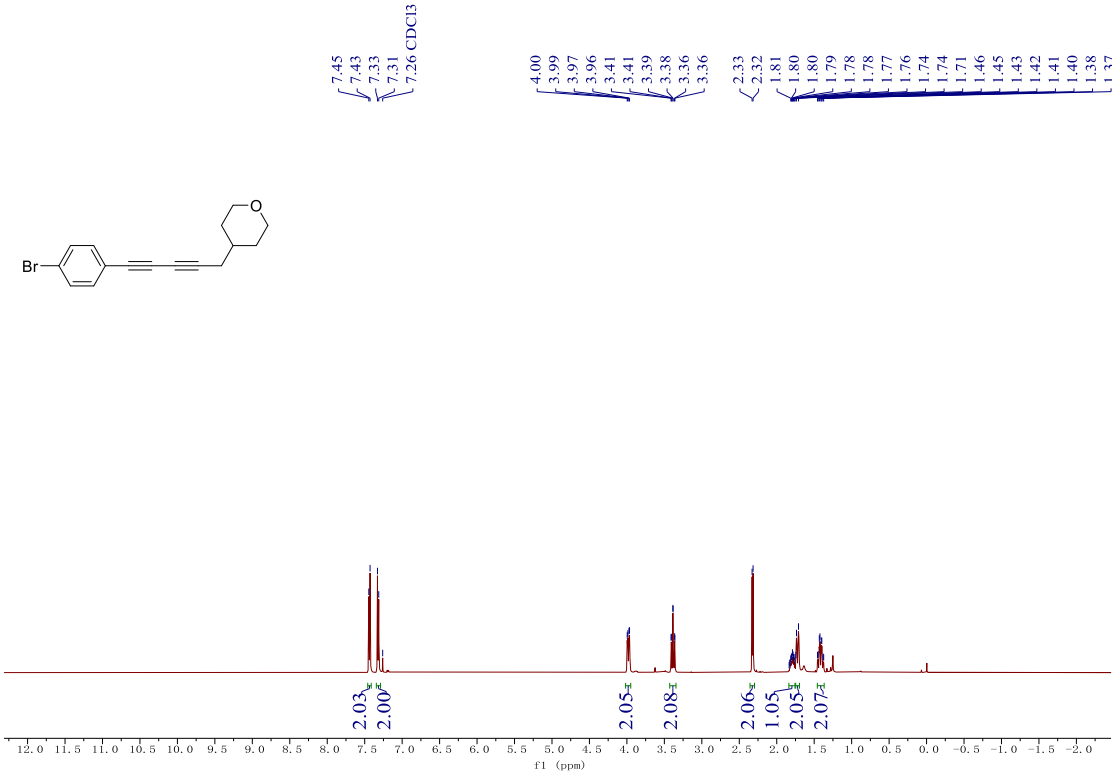

163.95
161.96
134.64
134.57
118.19
118.16
115.98
115.80
82.57
77.16 CDCl3
74.08
67.85
66.48
66.33
34.69
32.50
26.99
O
F
f1 (ppm)

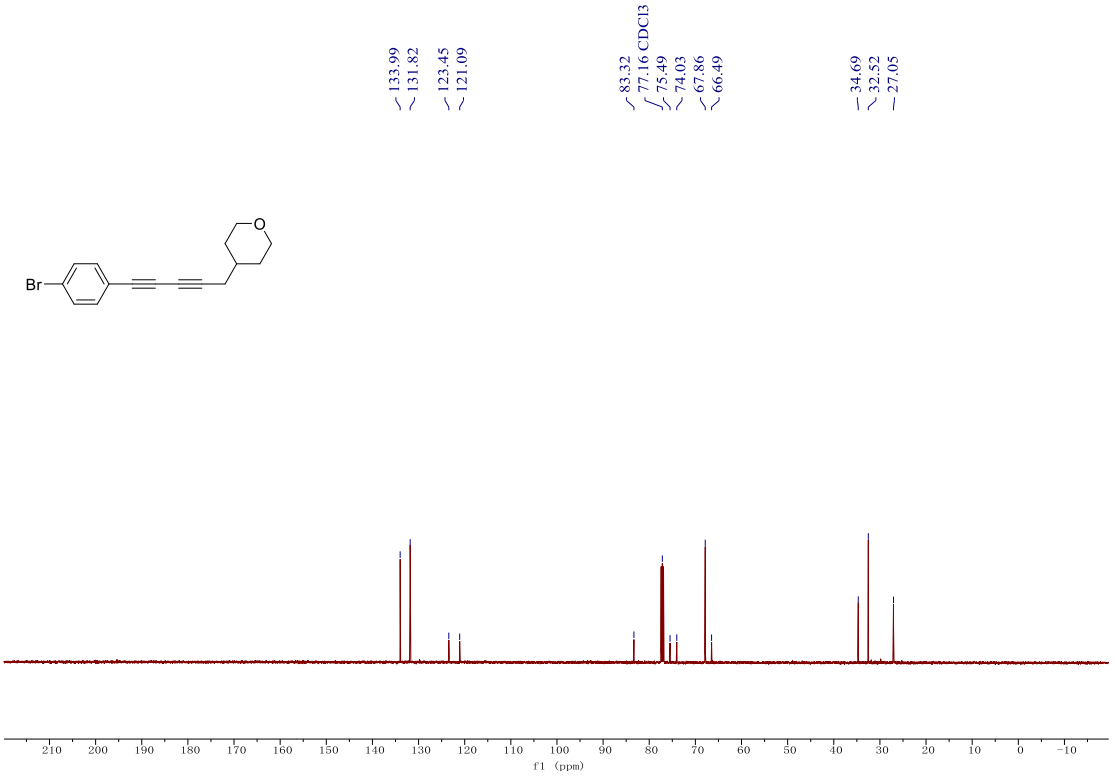

-109.18
O
F
f1 (ppm)

^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 6f

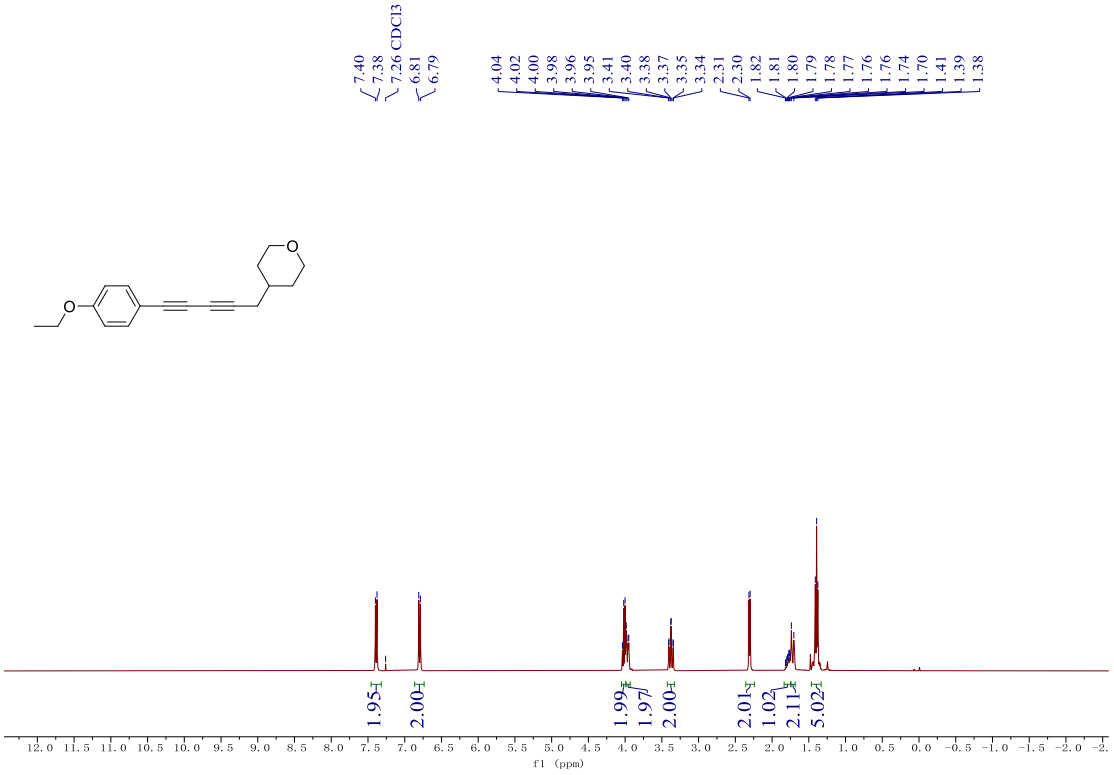


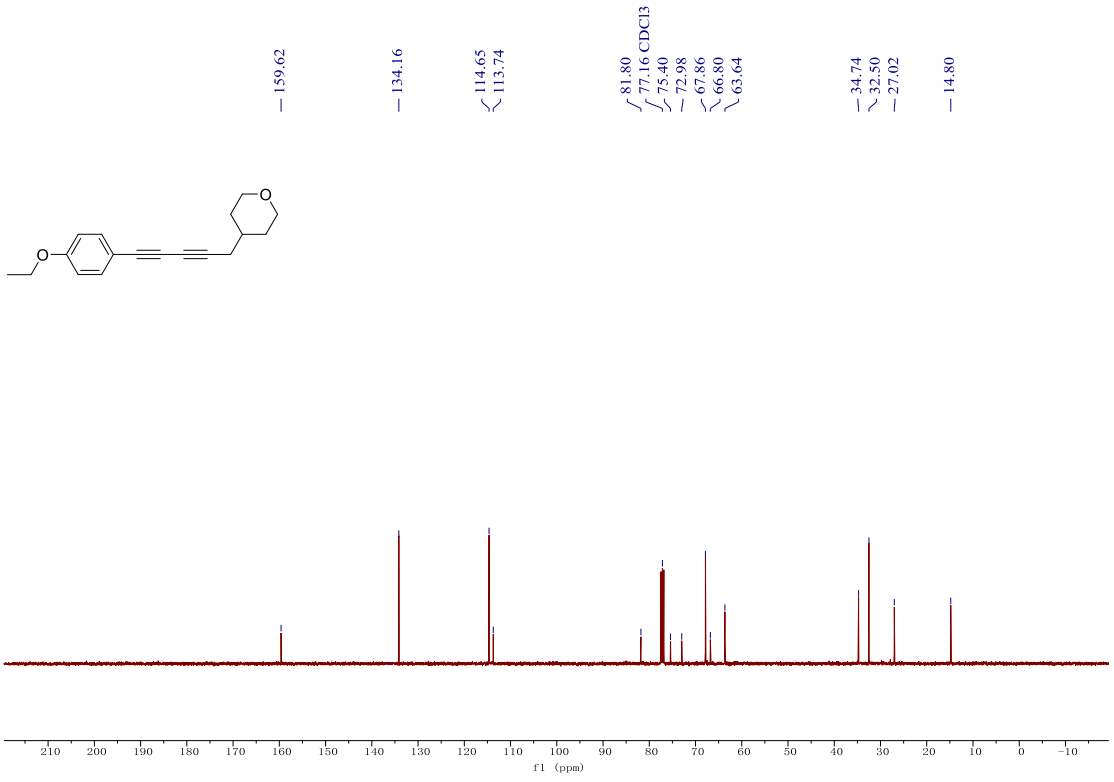
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6g



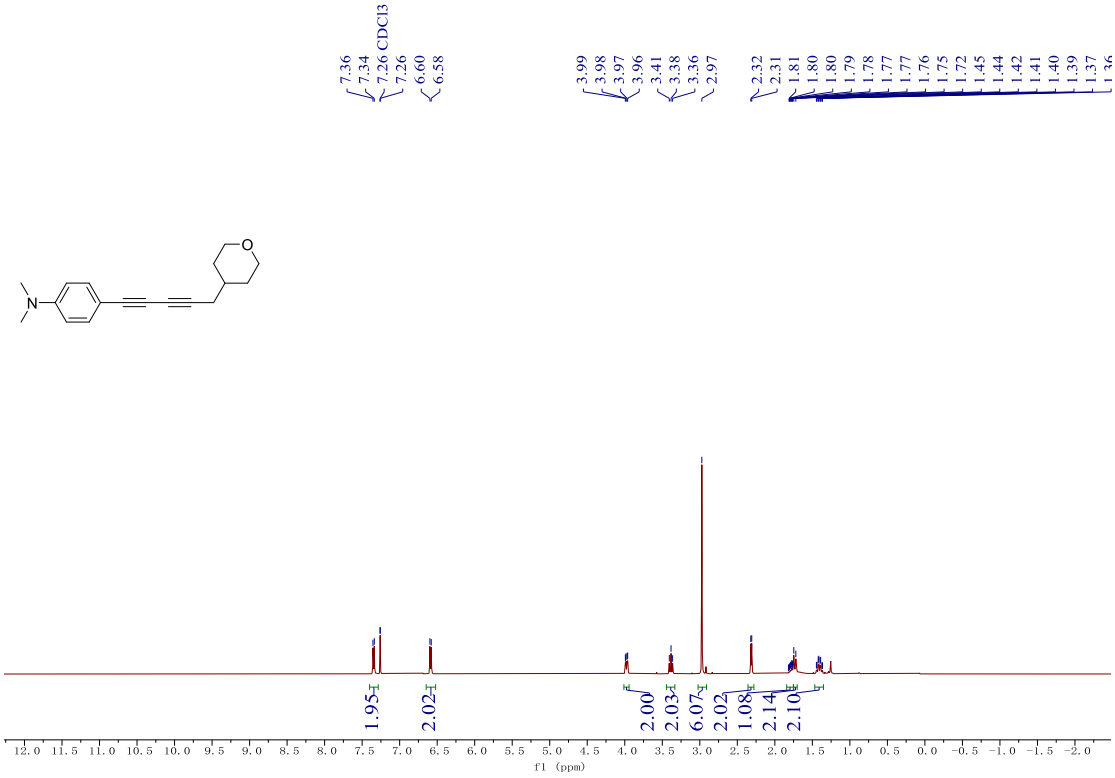


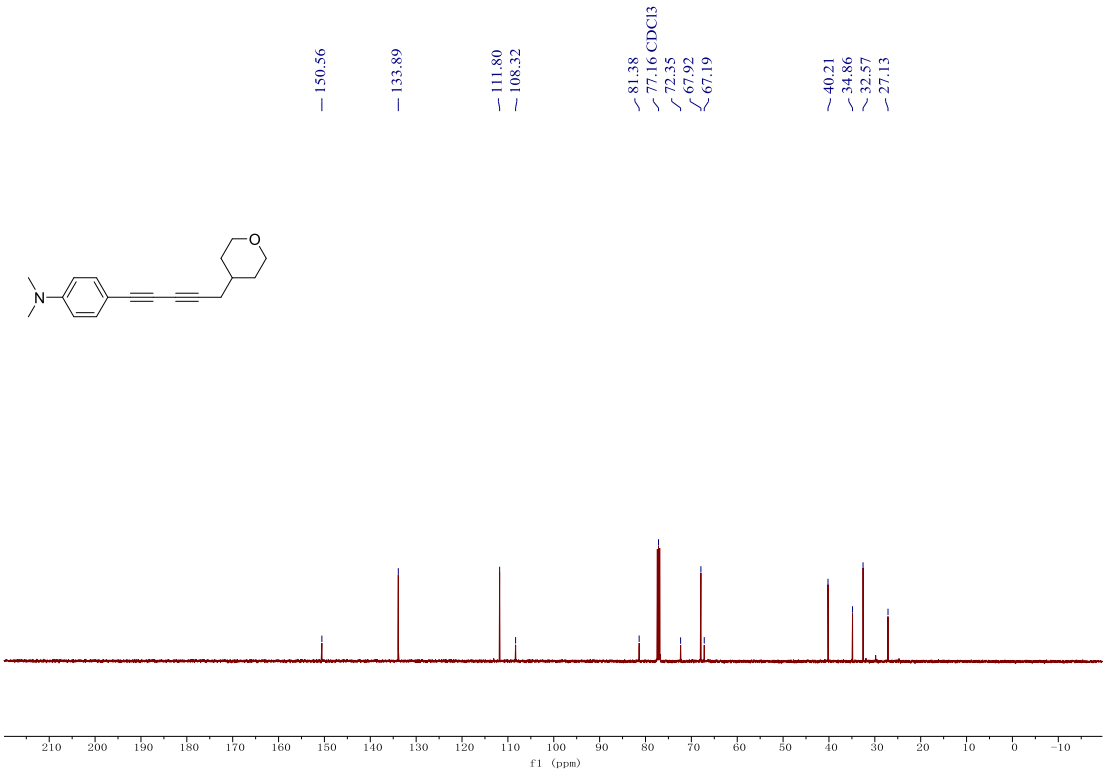
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 6h



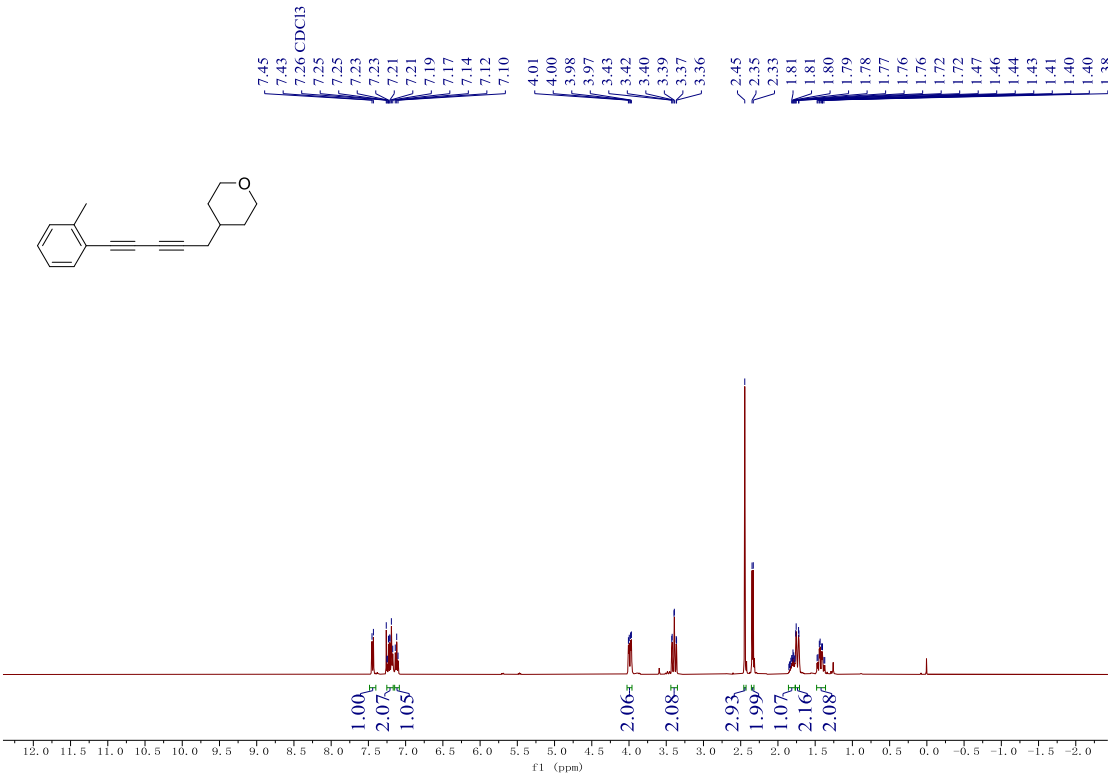


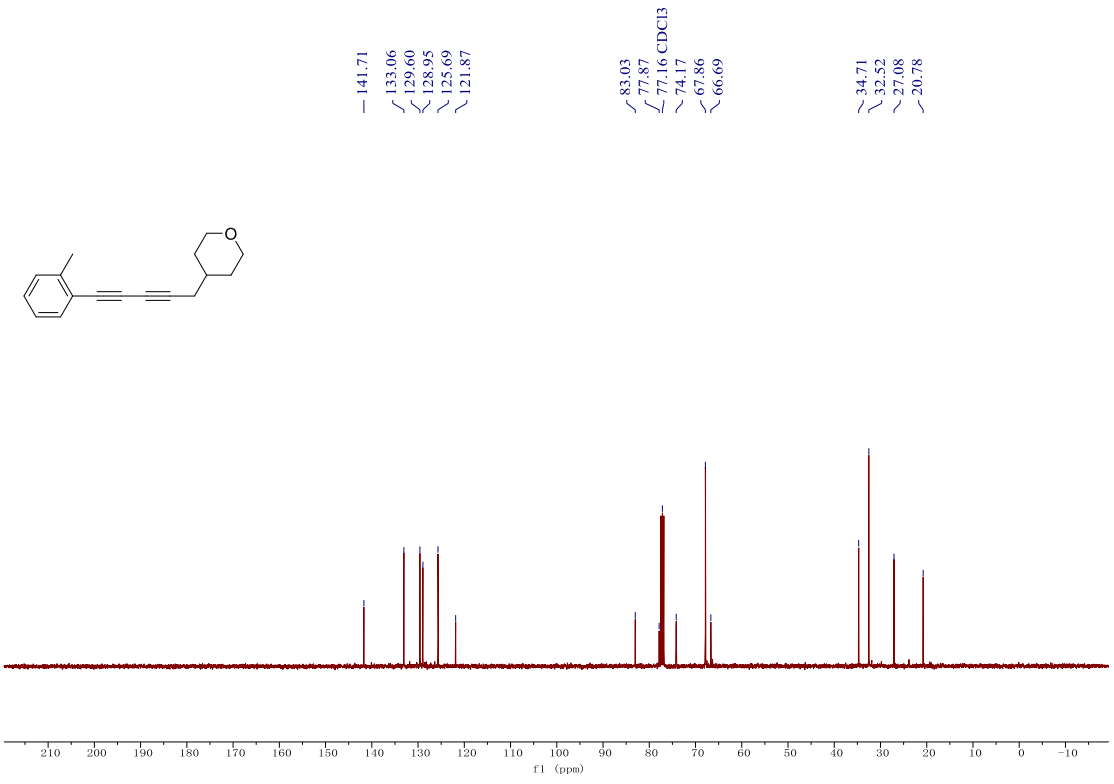
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6i



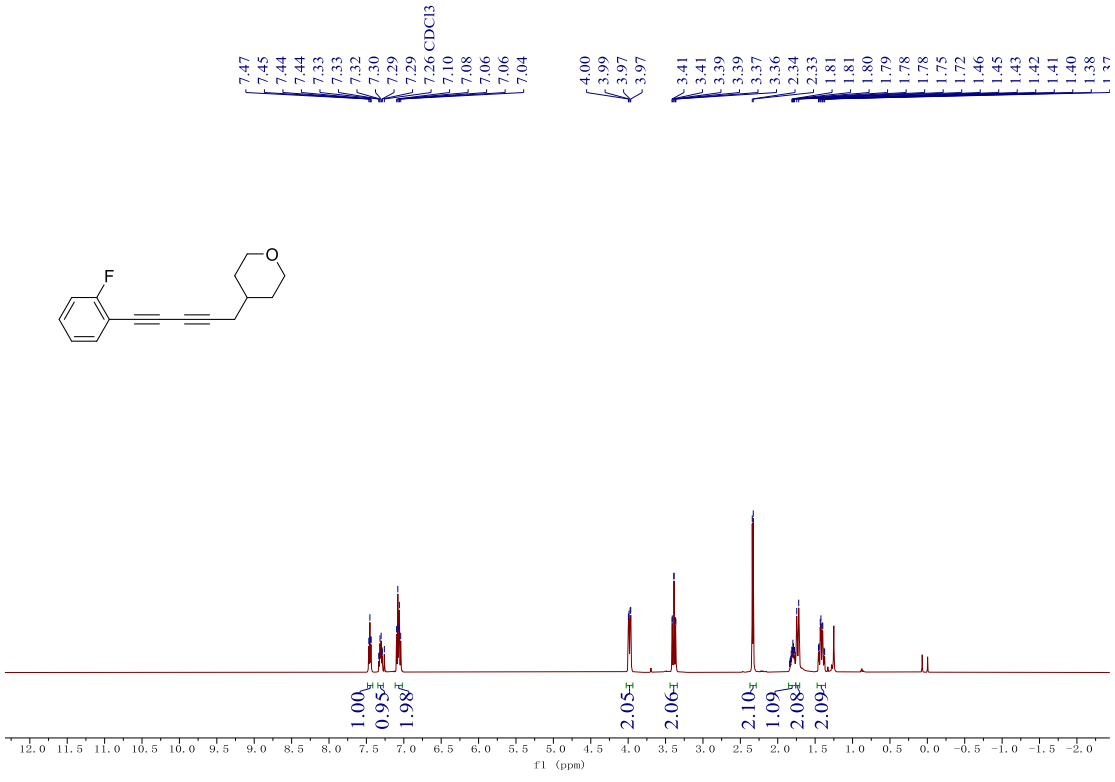


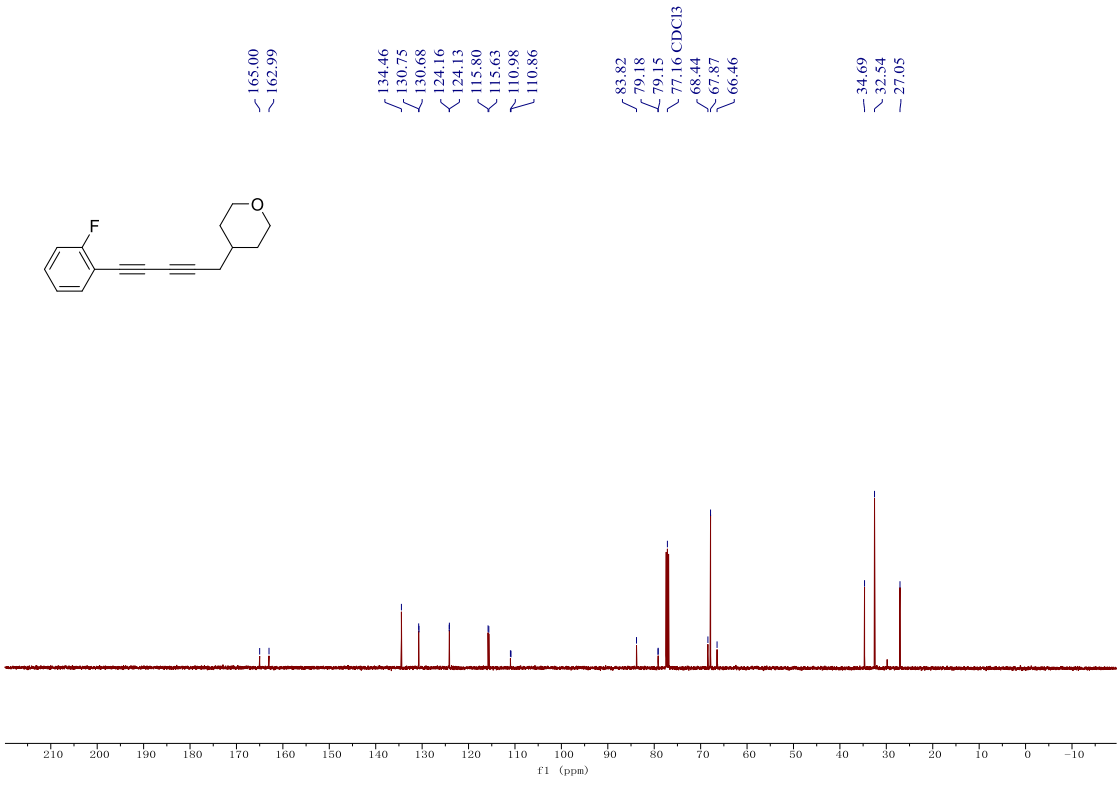
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 6j

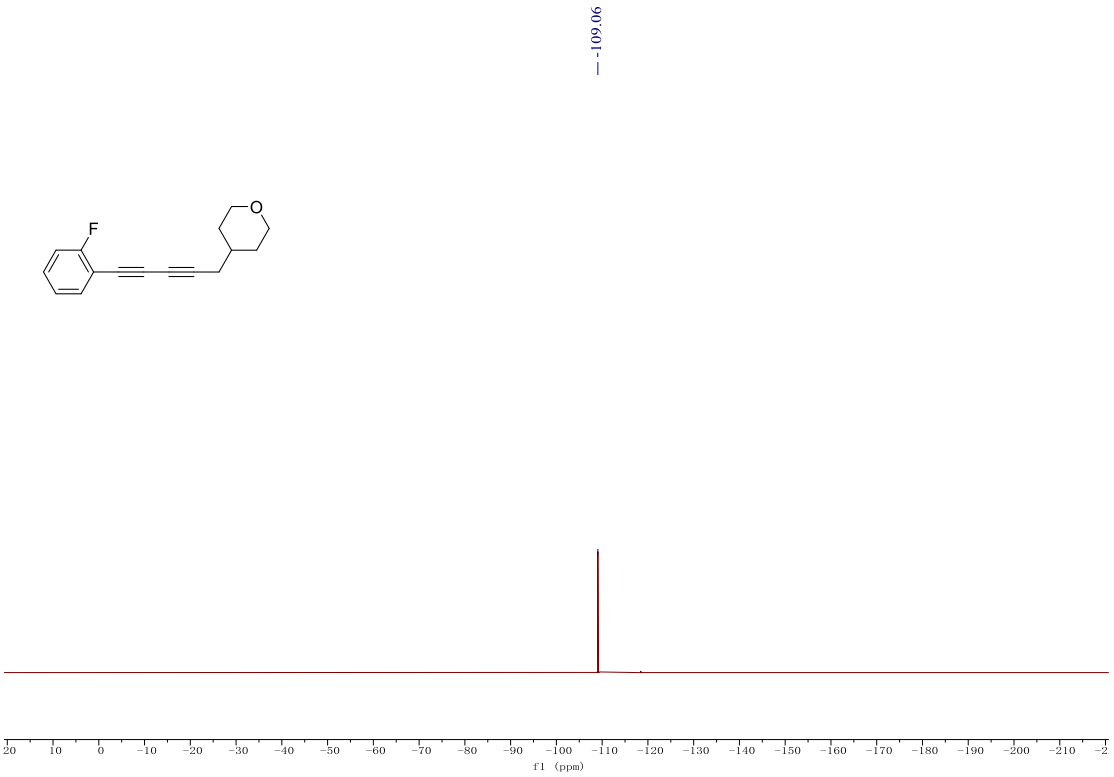




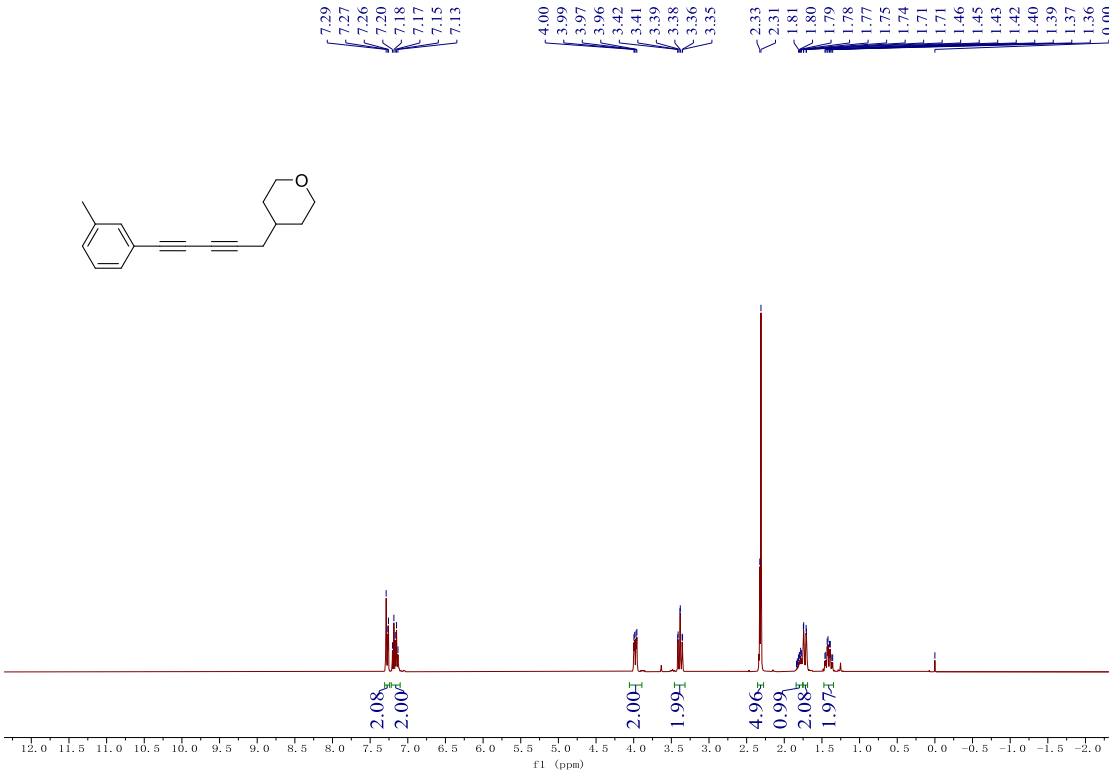
^{1}H NMR spectrum (500 MHz, $CDCl_3$), ^{13}C NMR spectrum (126 MHz, $CDCl_3$) and ^{19}F spectrum NMR (471 MHz, $CDCl_3$) of 6k

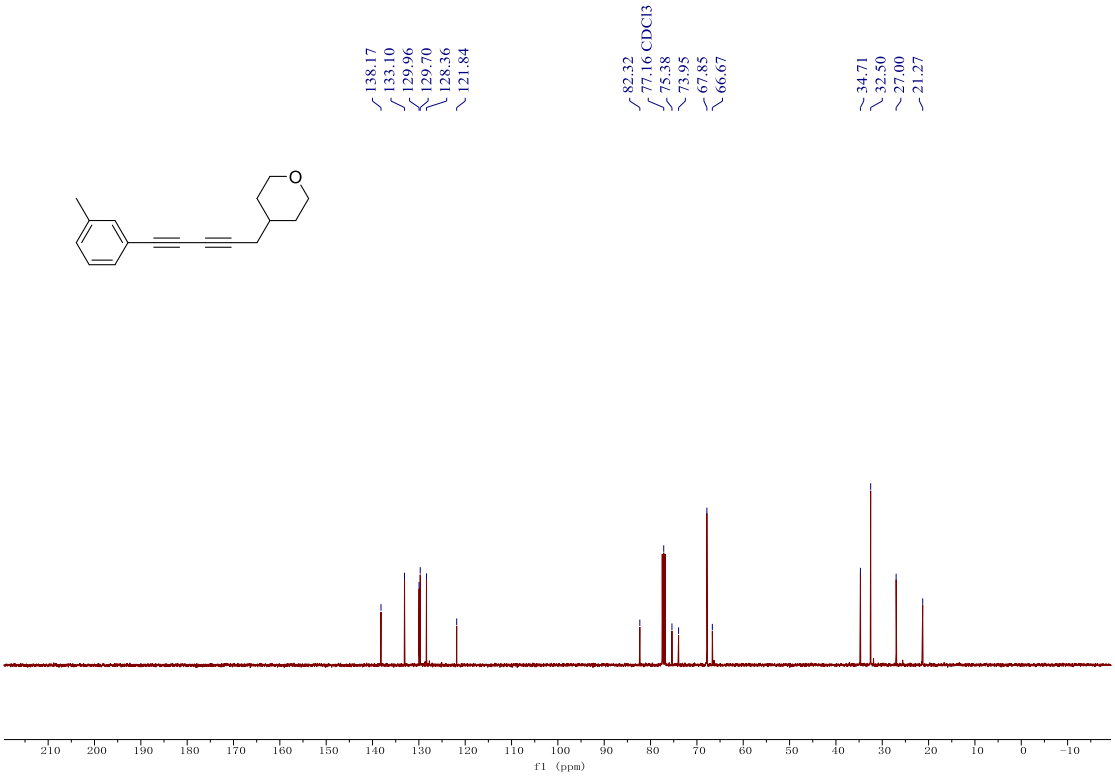




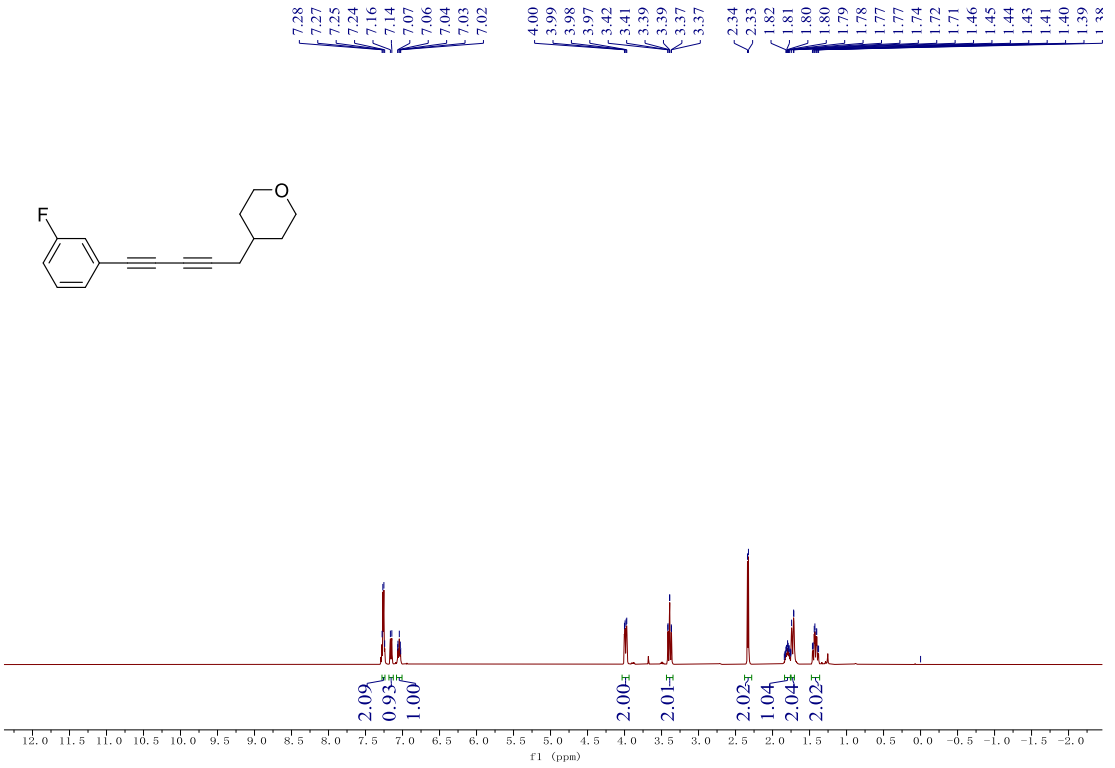


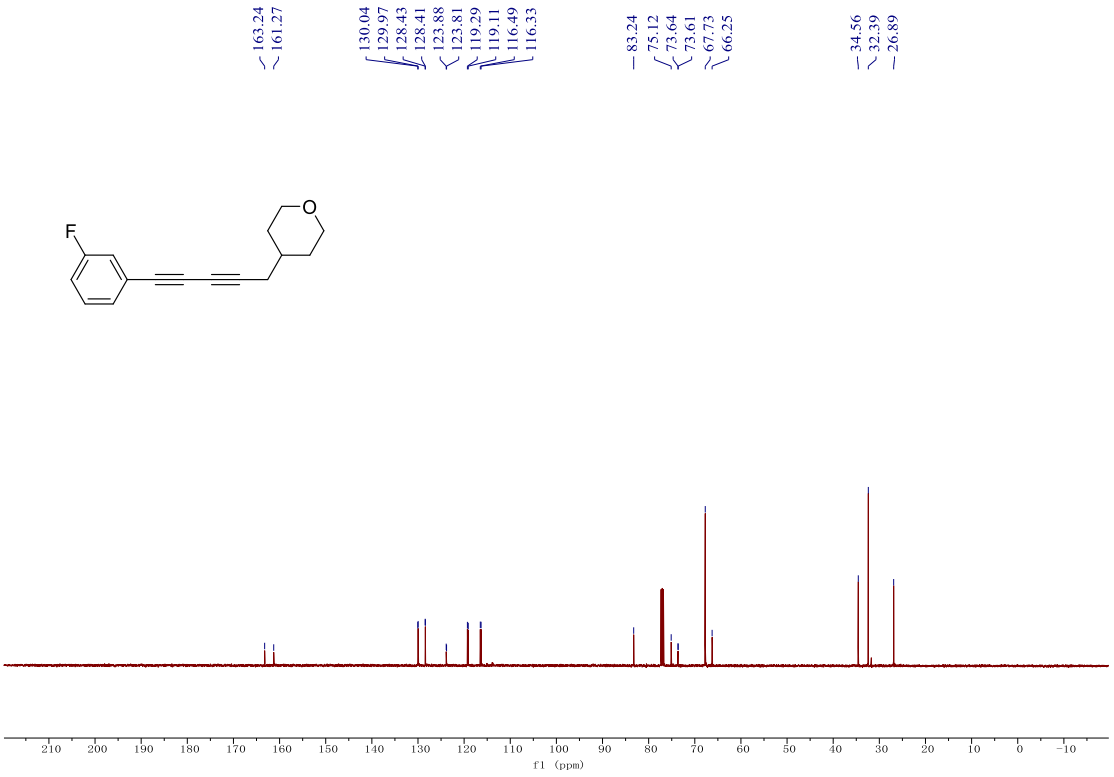
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 6l





^{1}H NMR spectrum (500 MHz, $CDCl_3$), ^{13}C NMR spectrum (126 MHz, $CDCl_3$) and ^{19}F spectrum NMR (471 MHz, $CDCl_3$) of 6m




163.24
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123.81
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119.11
116.49
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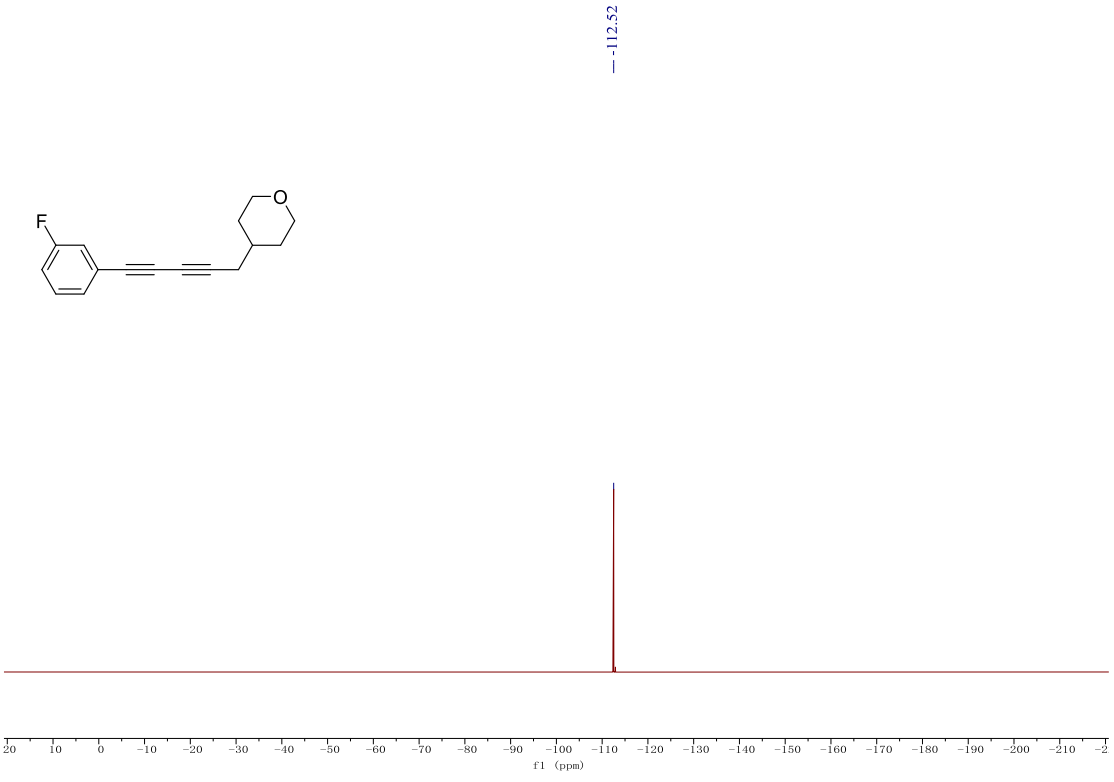
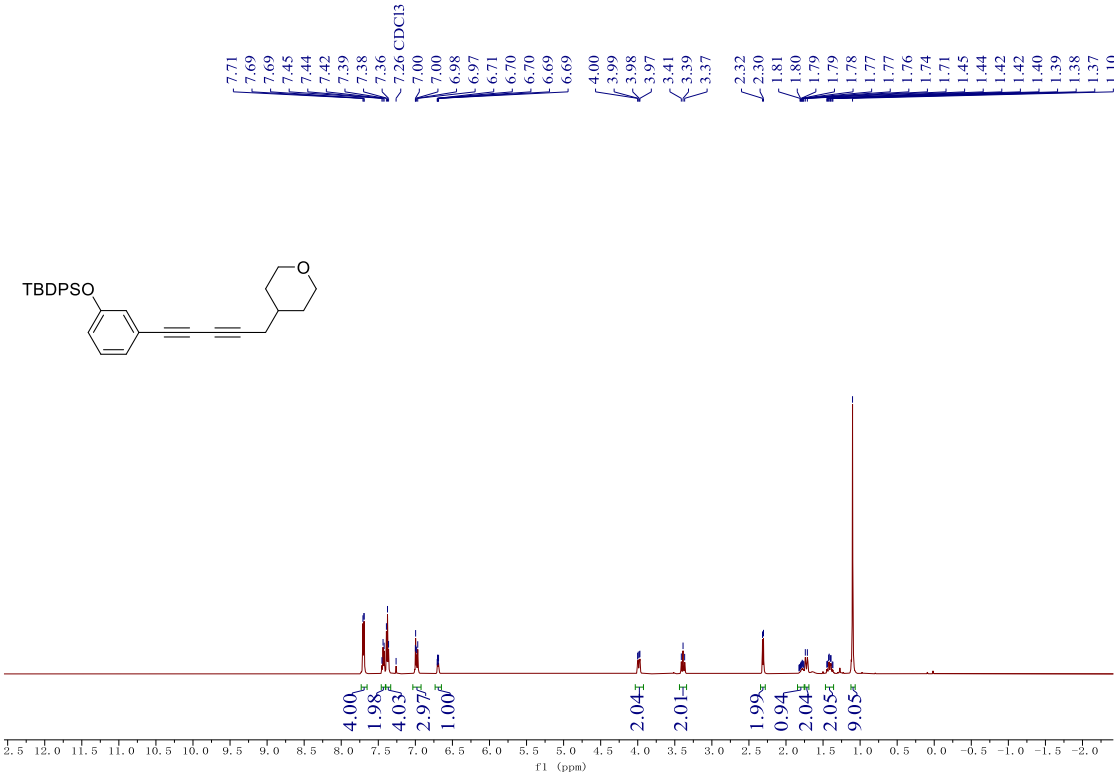
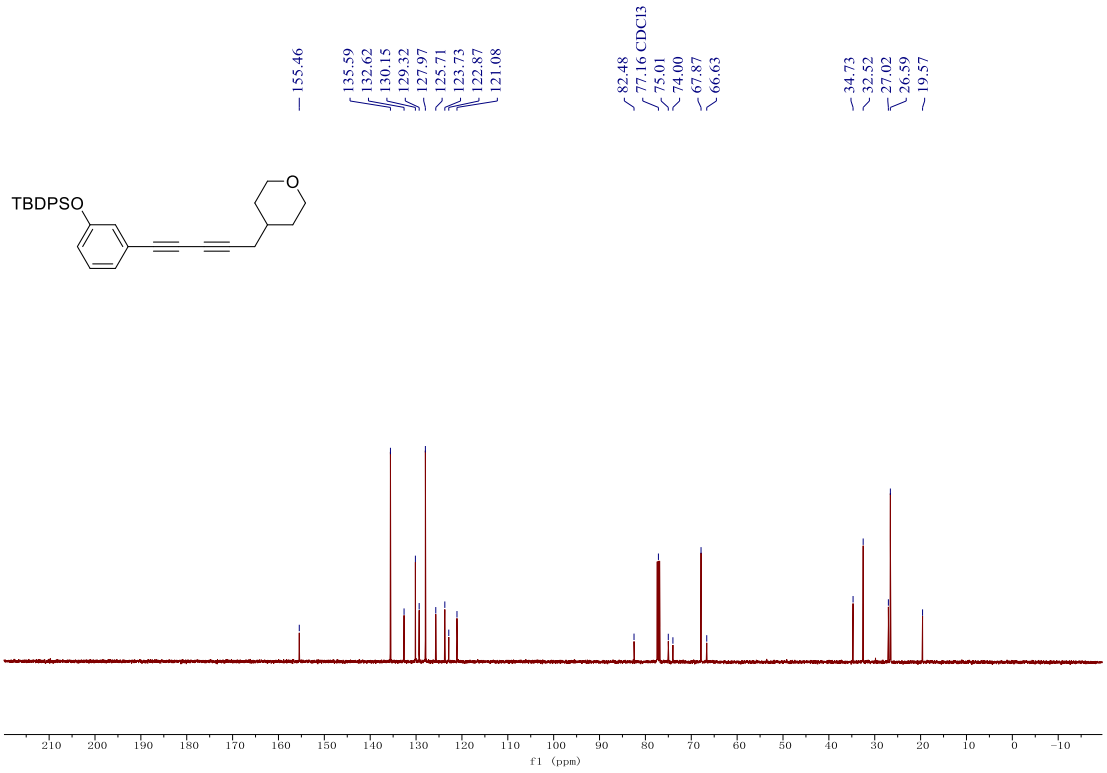
73.64
73.61
67.73
66.25
34.56
32.39
26.89
F
O
f1 (ppm)


-112.52
F
O
f1 (ppm)

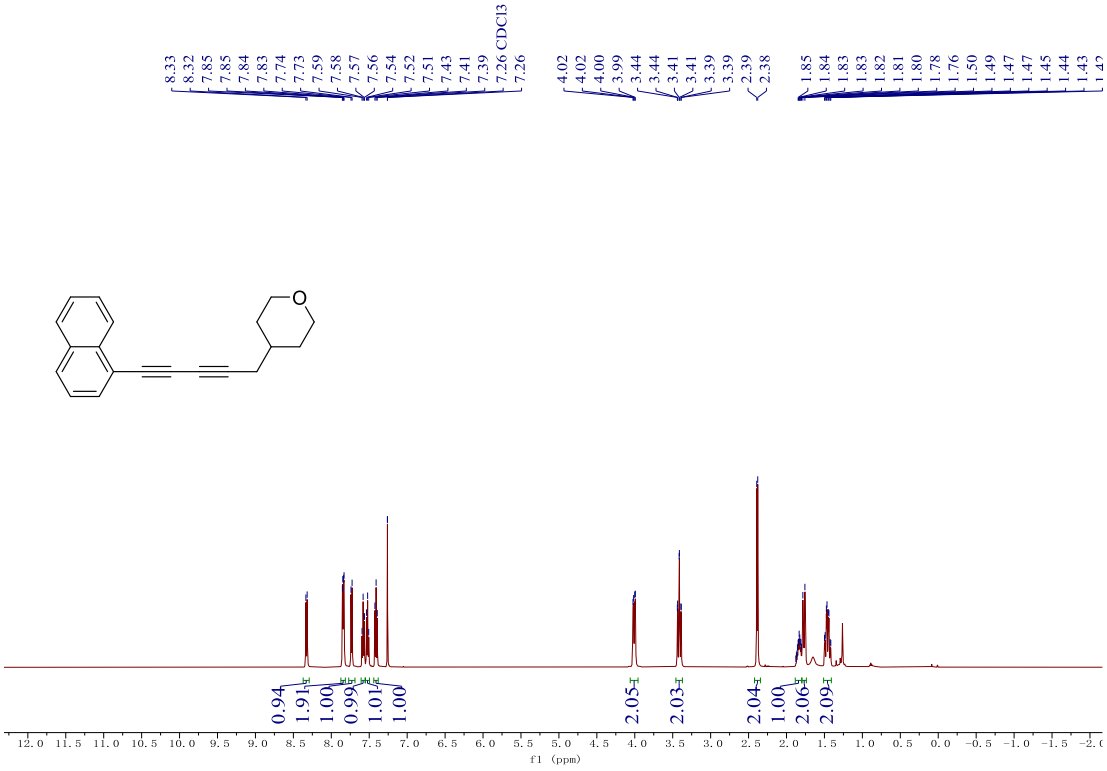
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6n

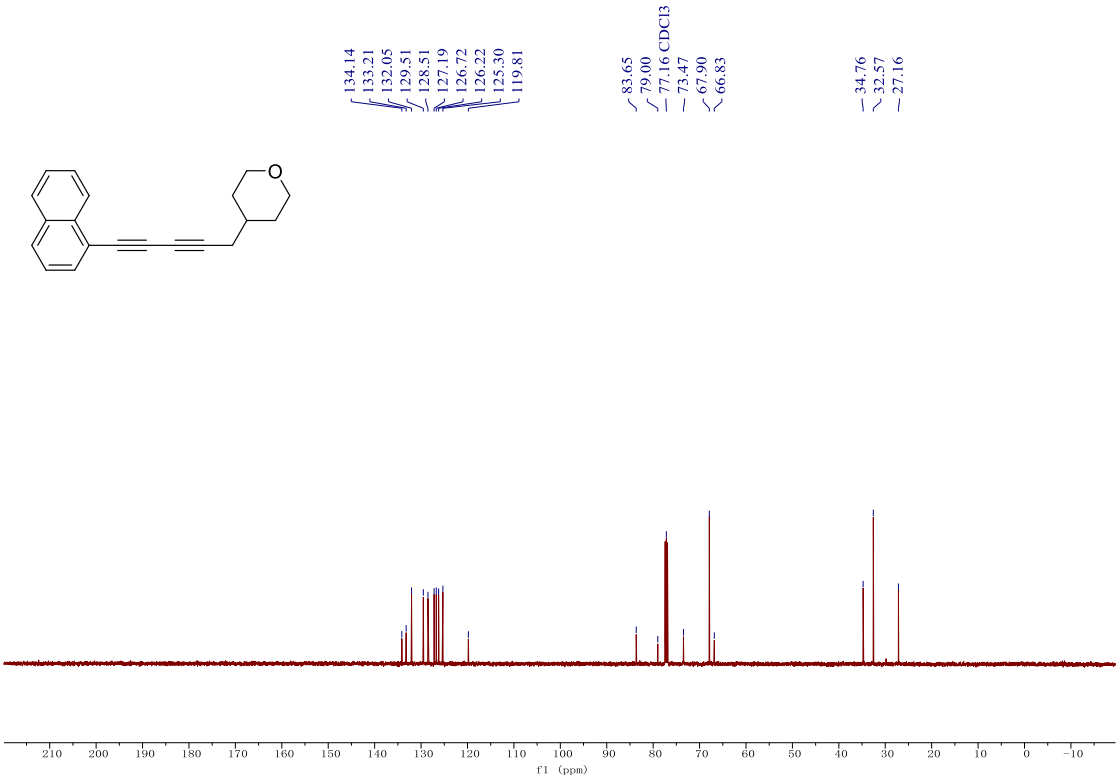
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6o



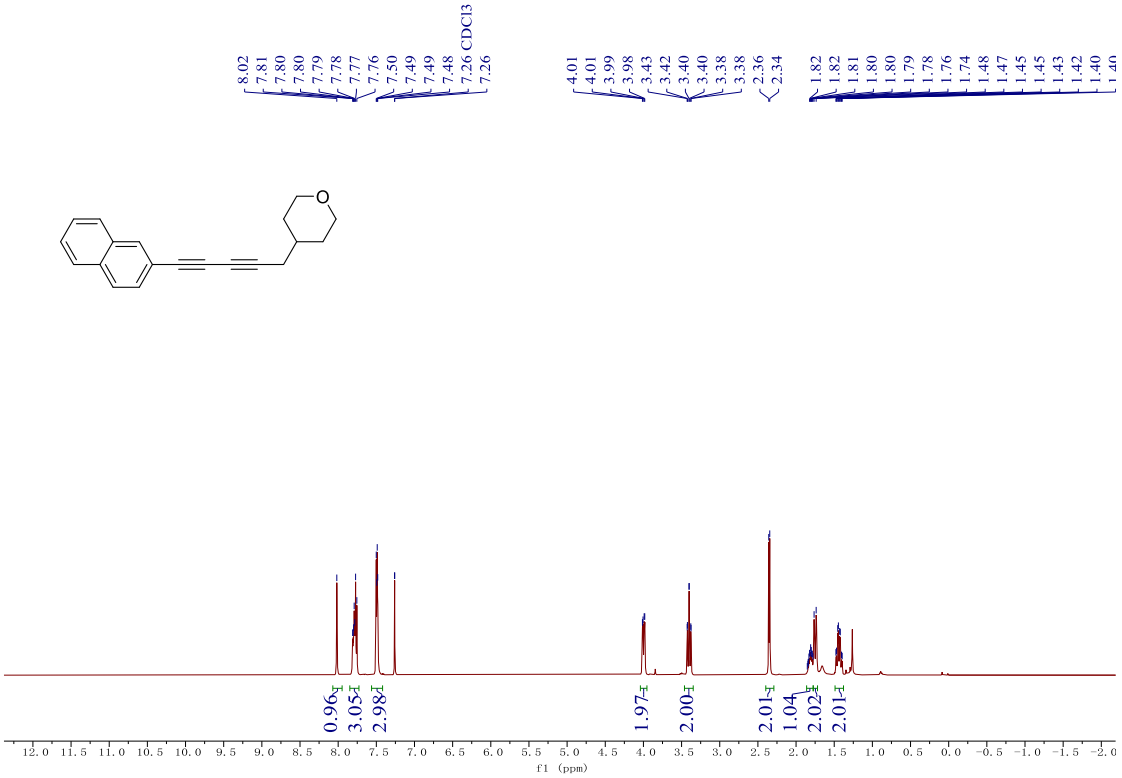


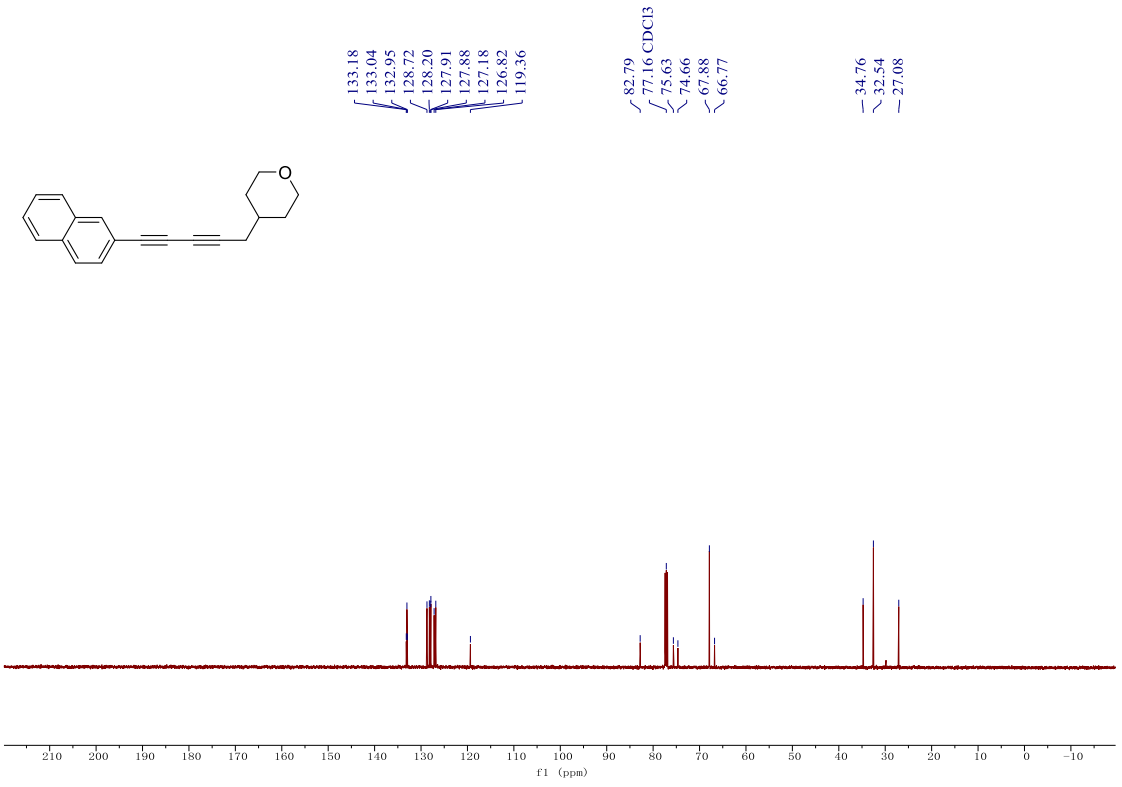
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6p



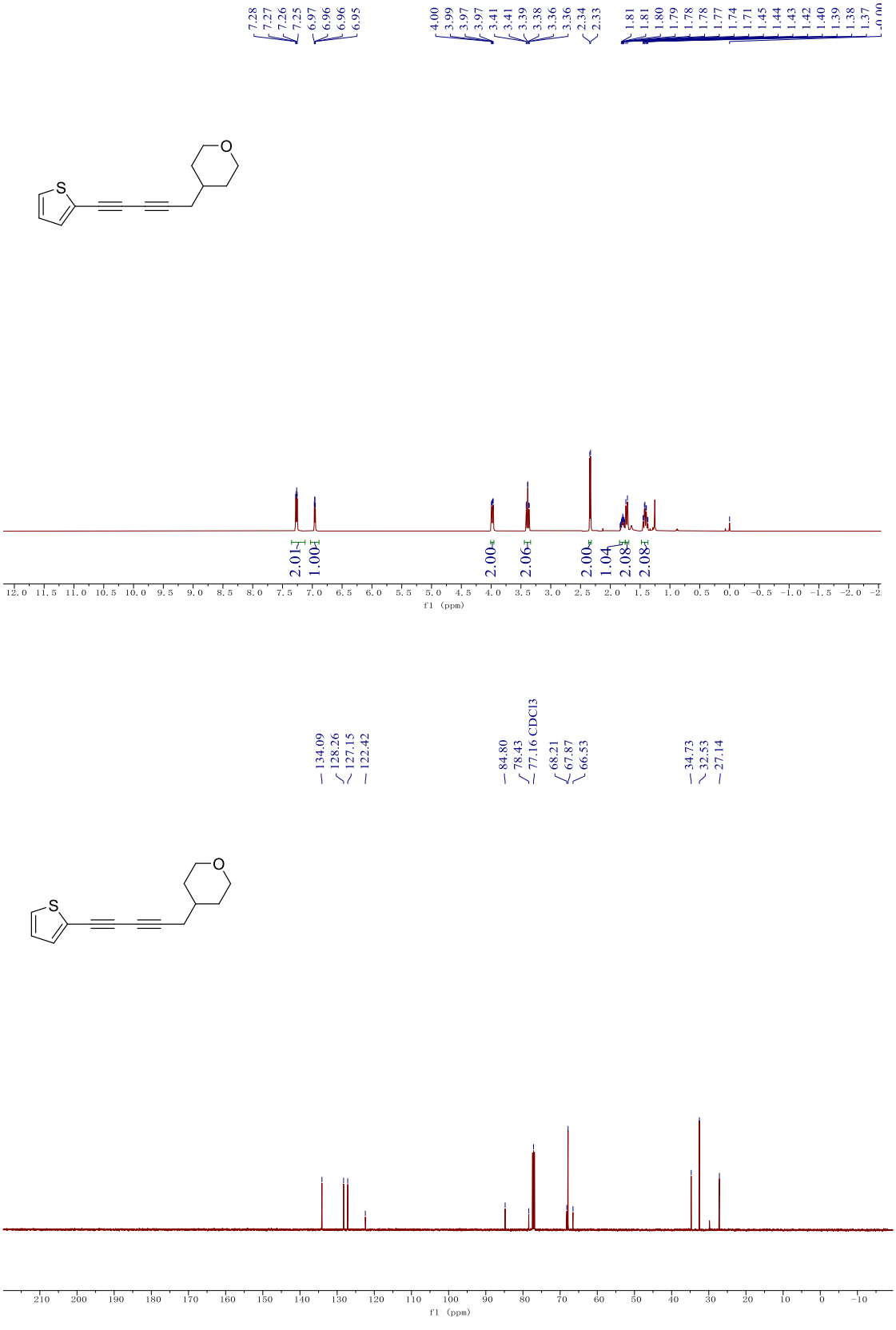


^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6q

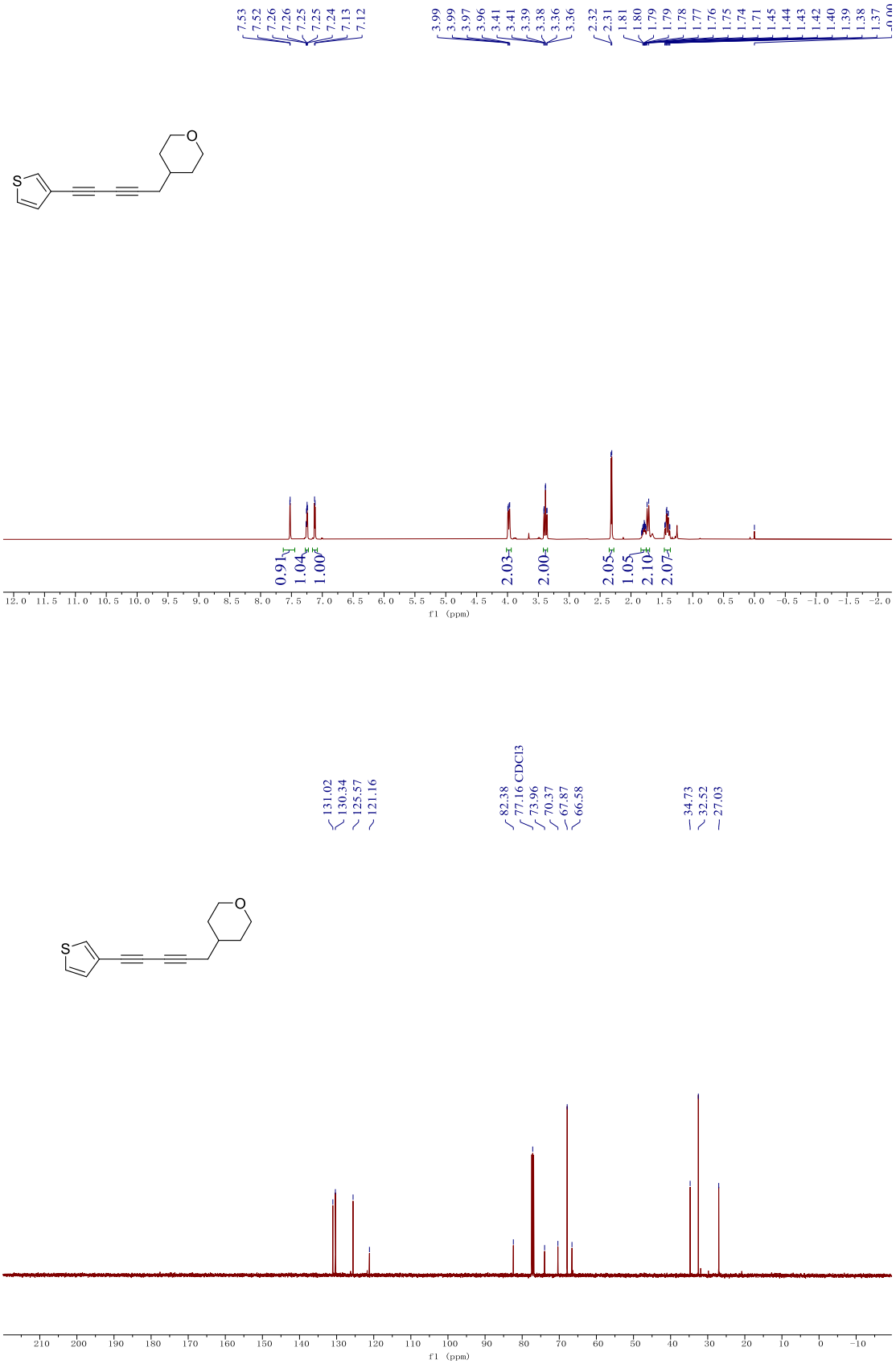




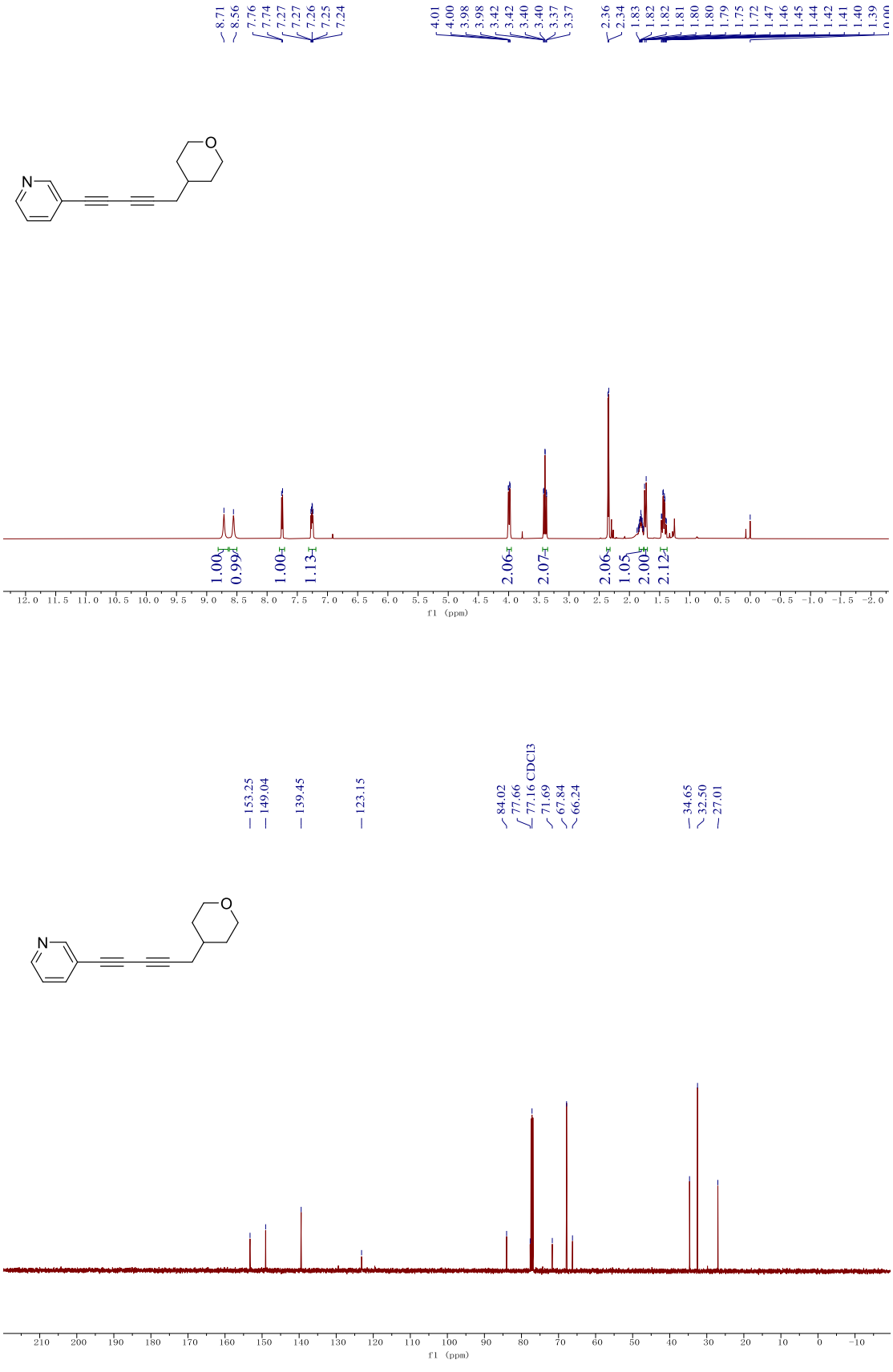
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6r



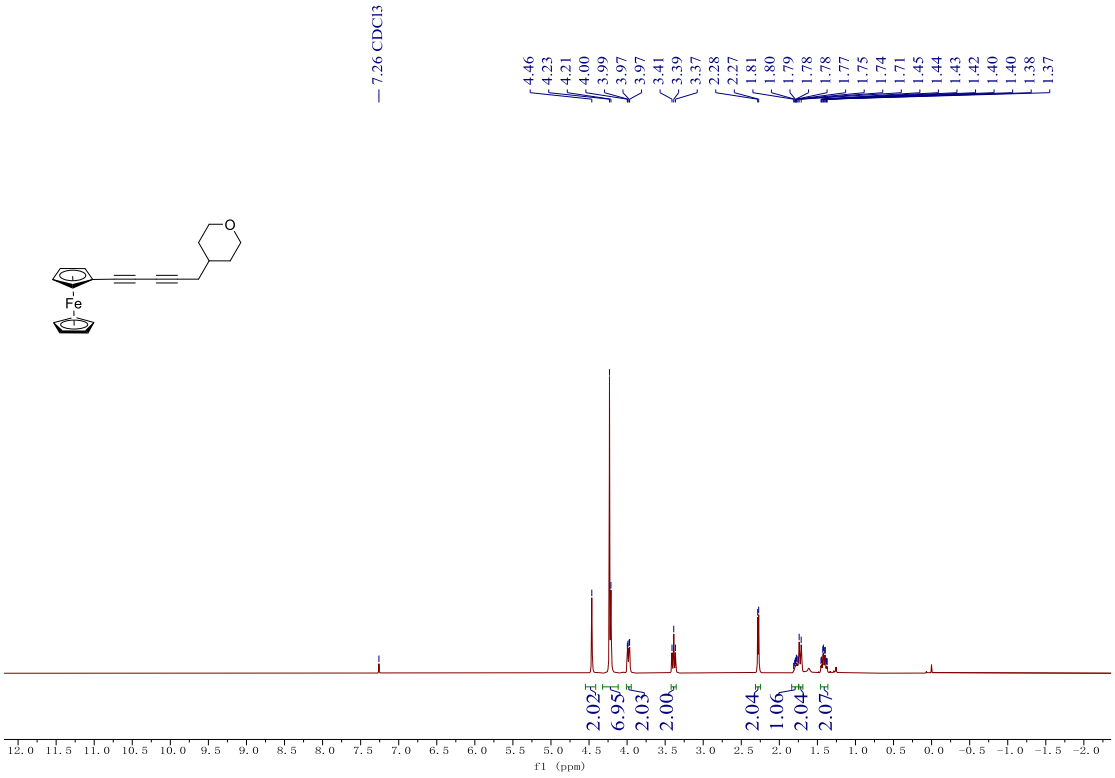
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6s

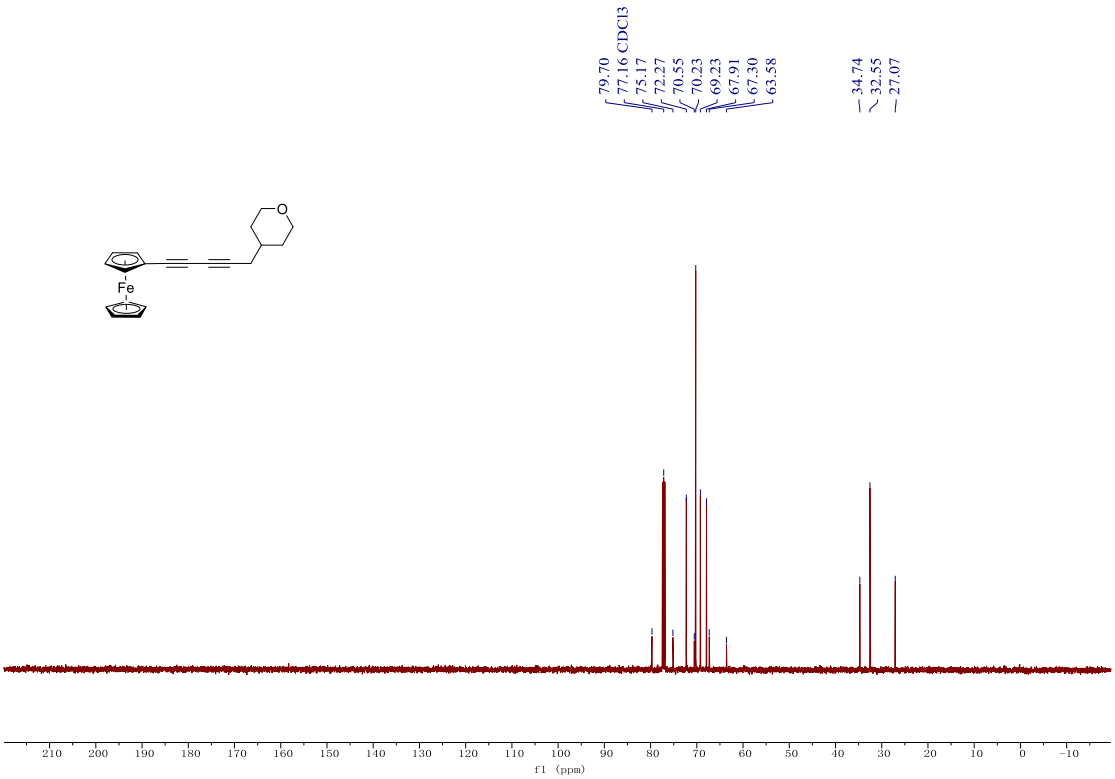


^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6t

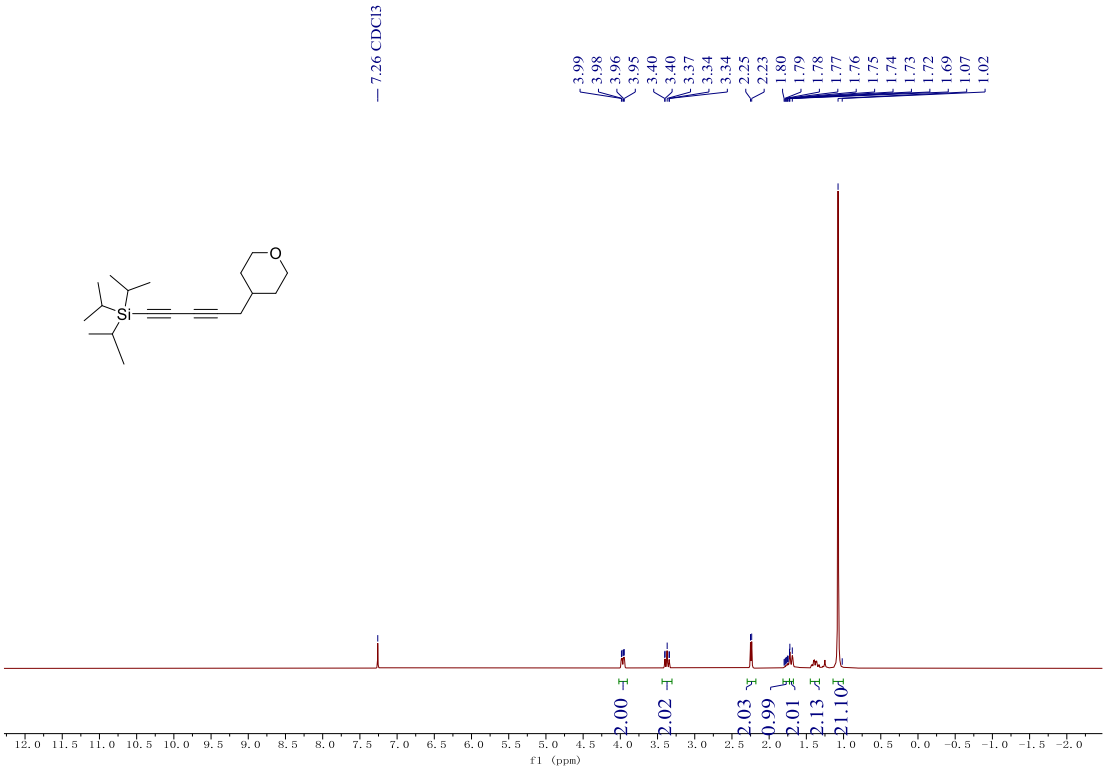


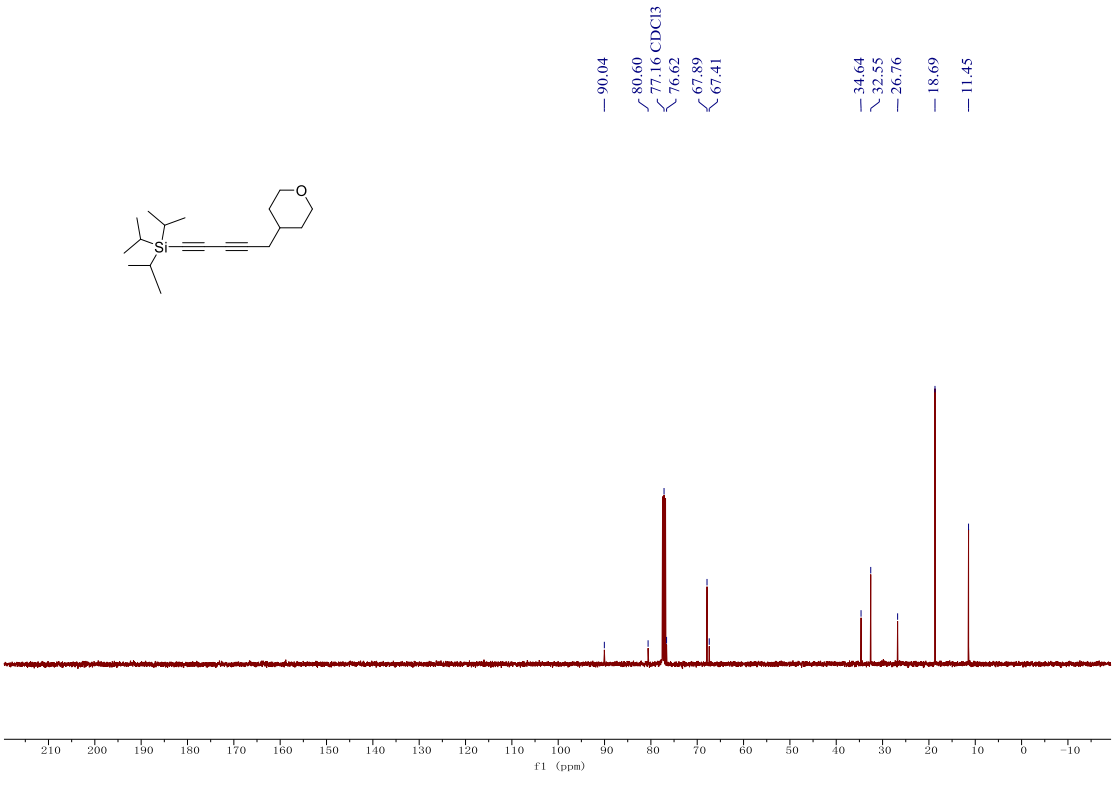
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6u



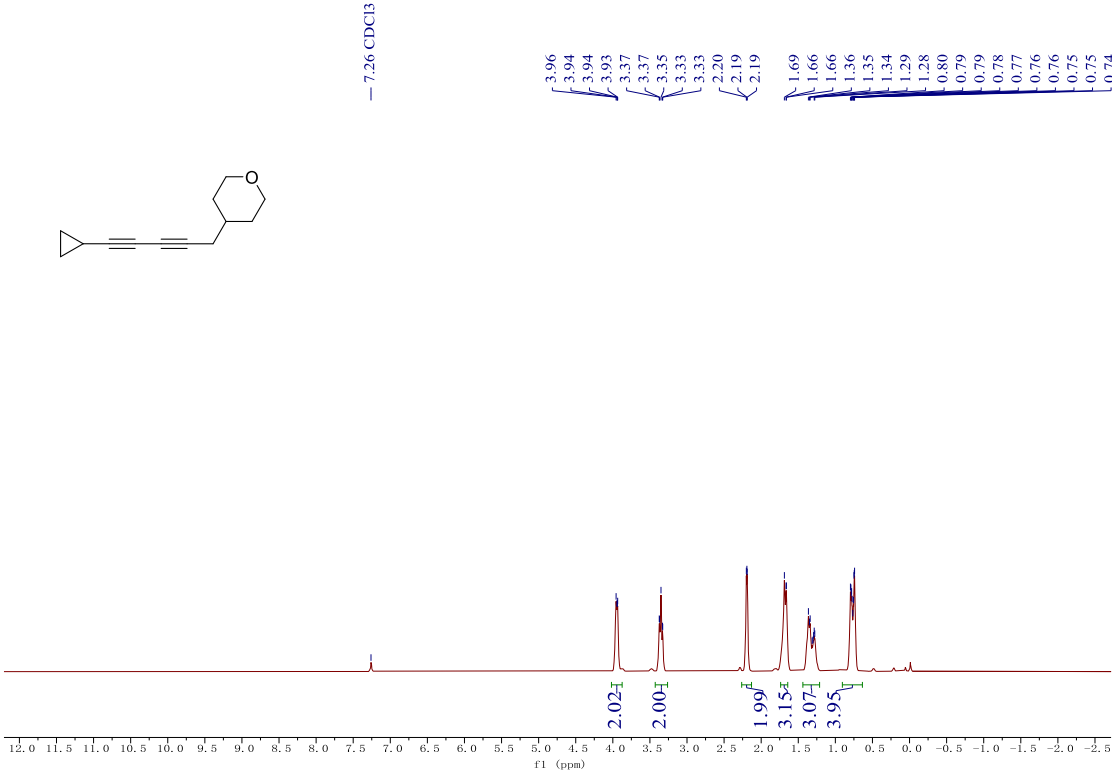


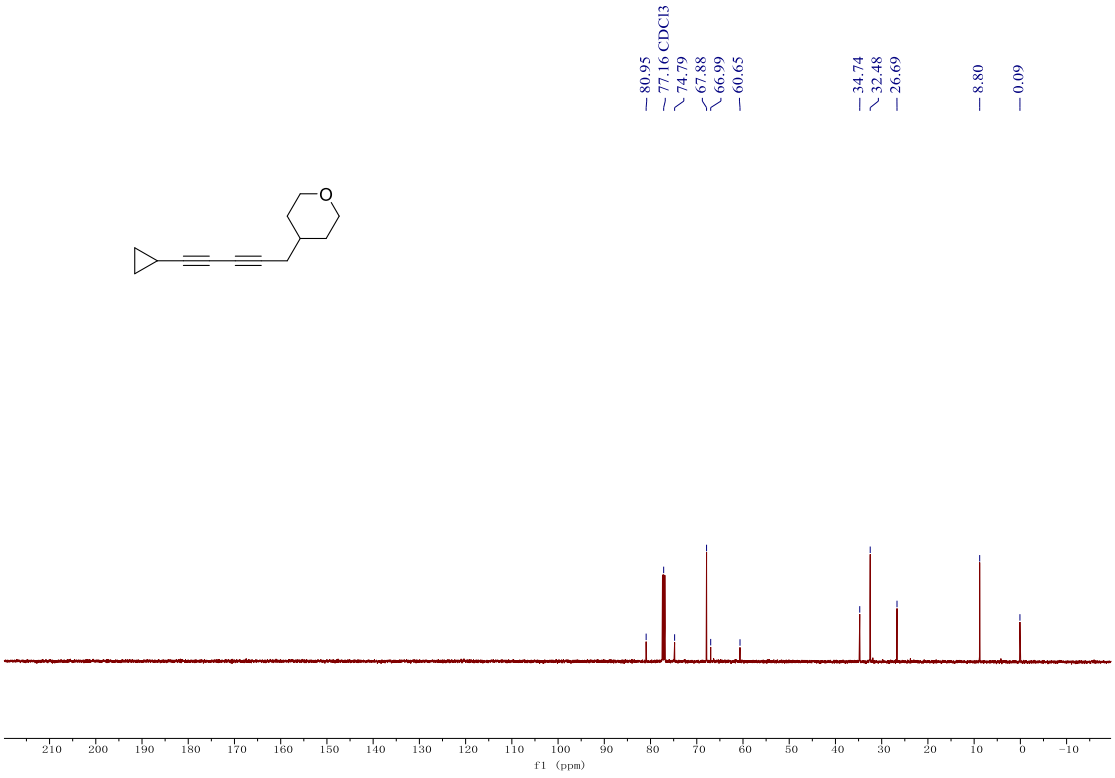
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 6v



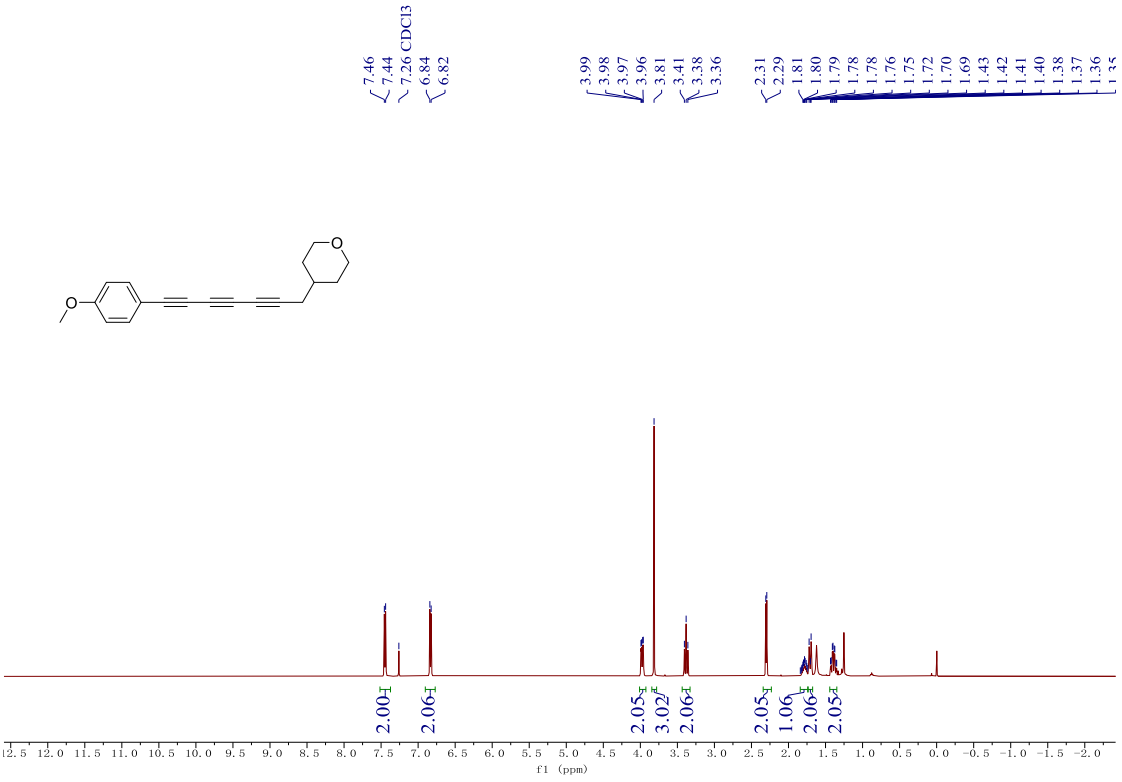


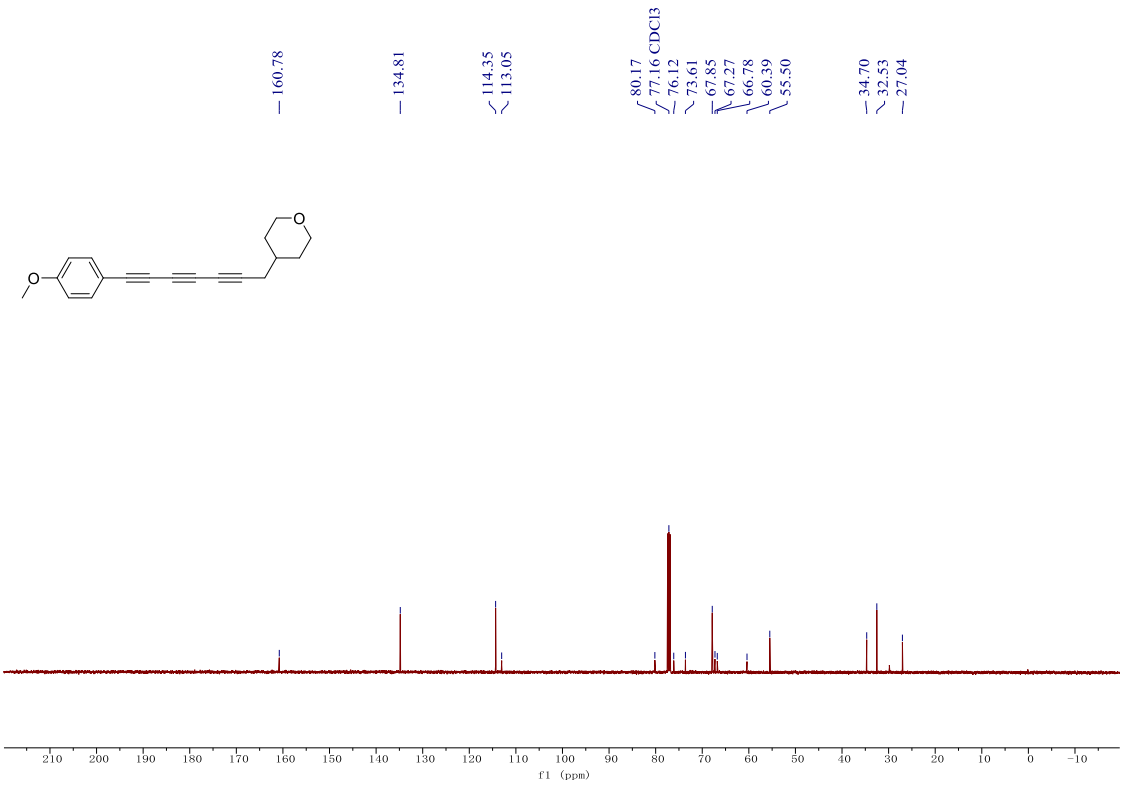
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6w



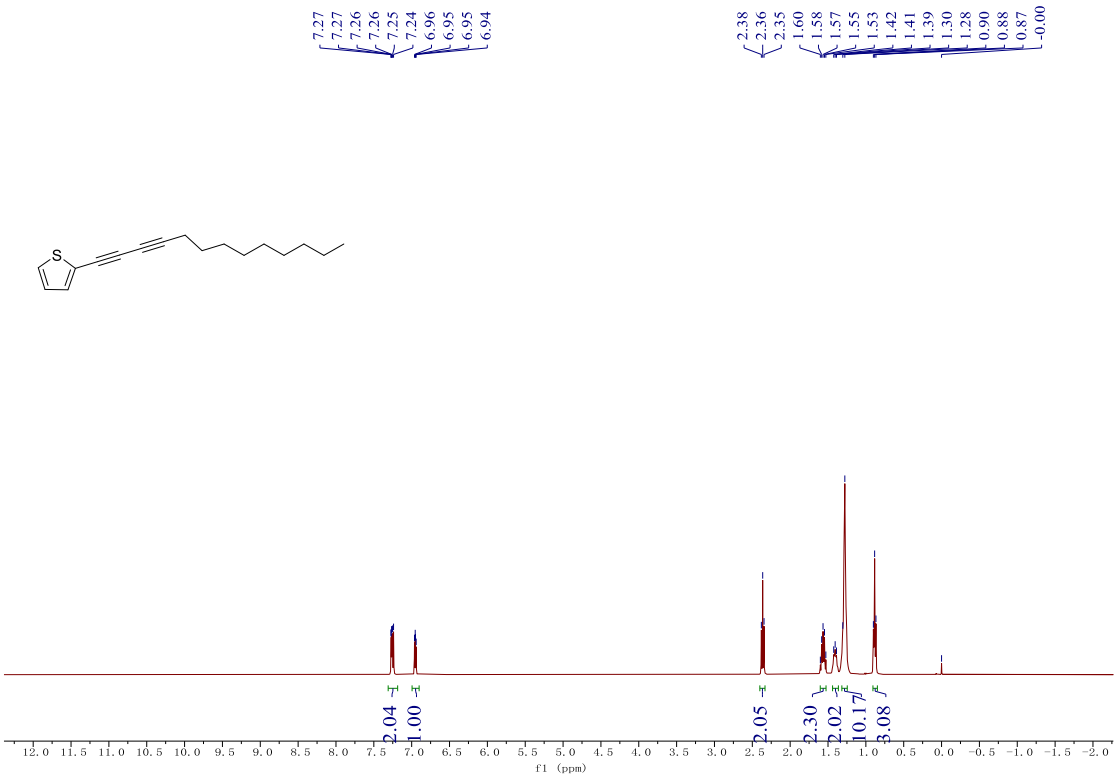


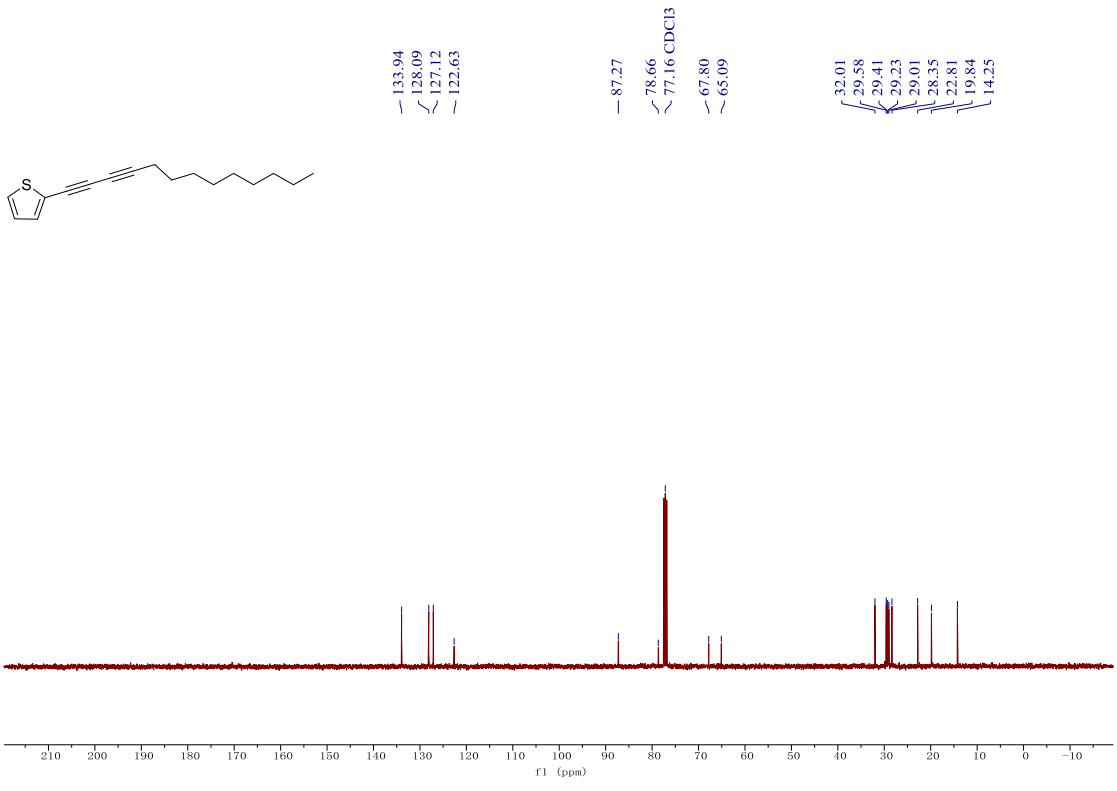
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6x



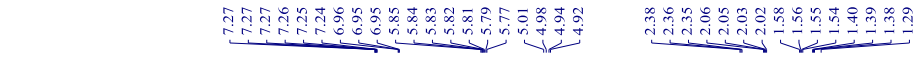


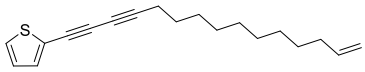
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 6y

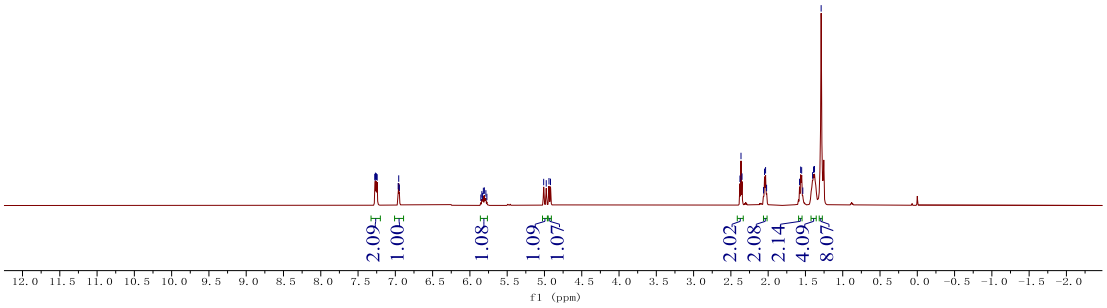


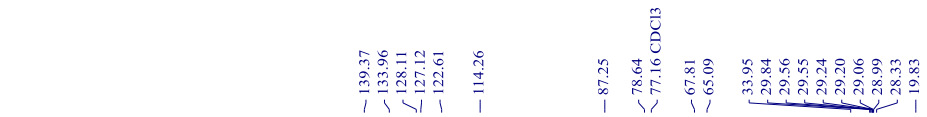


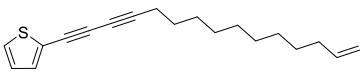
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6z

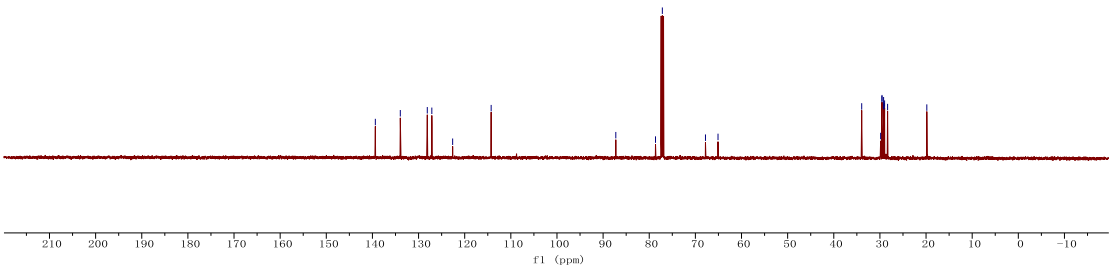




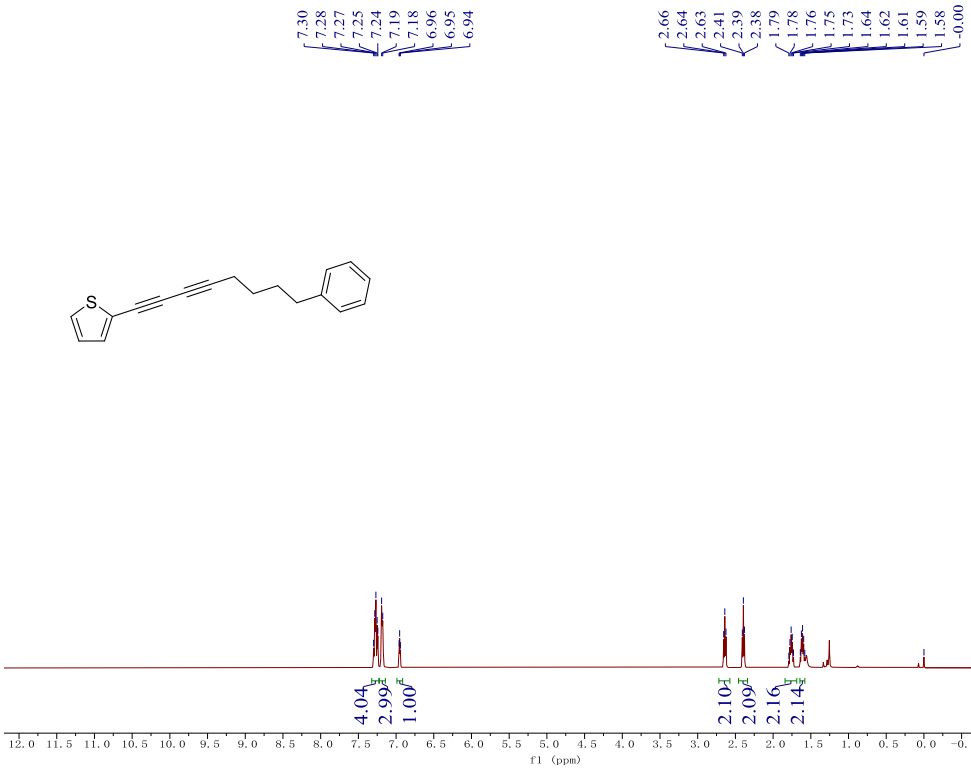


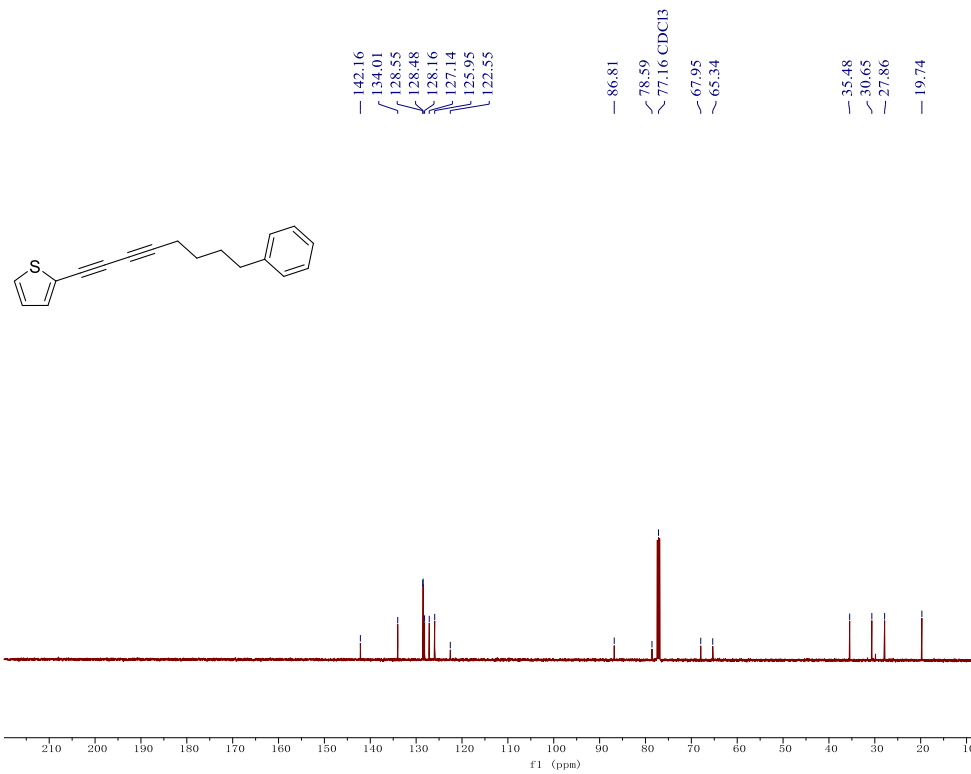




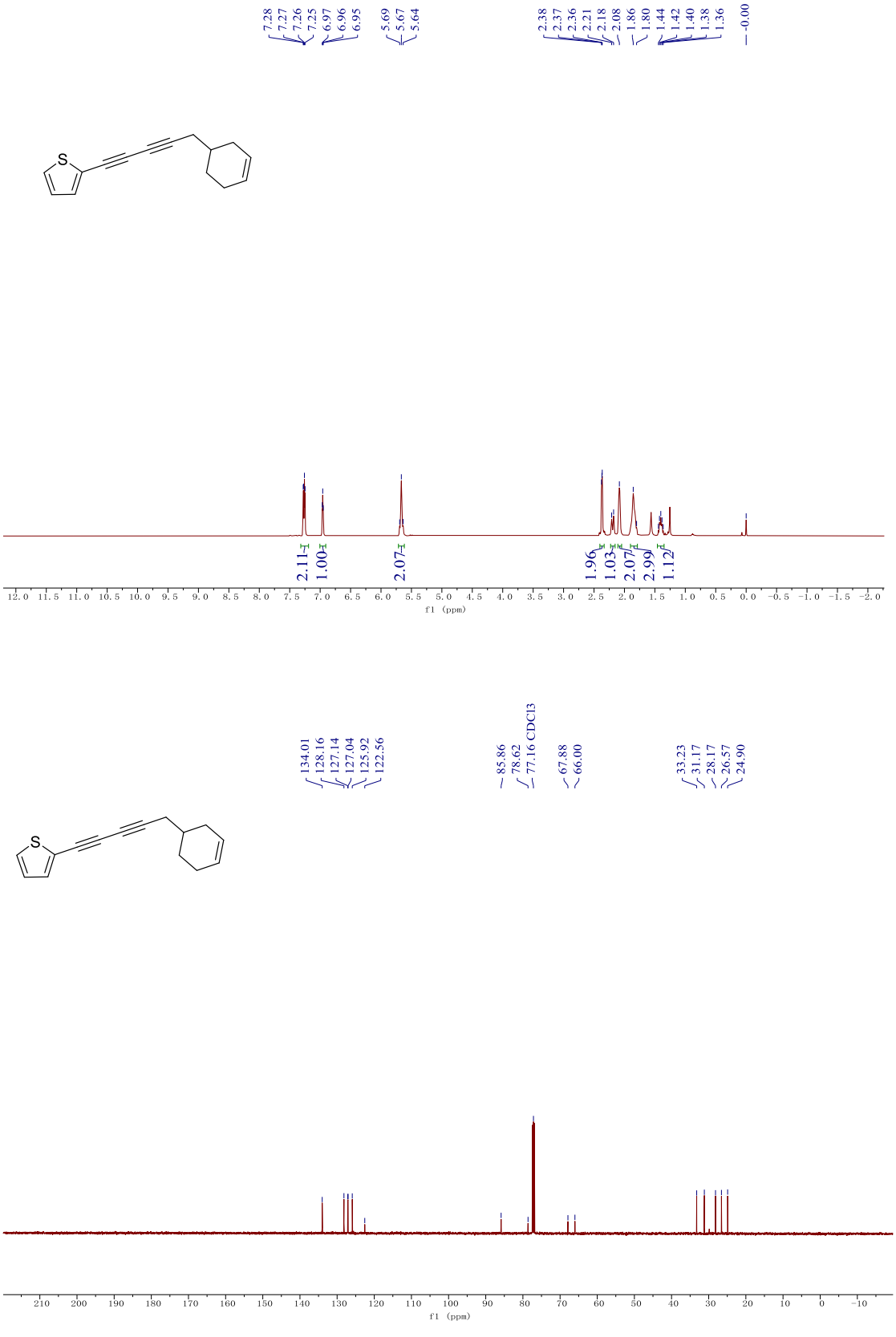


^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6aa

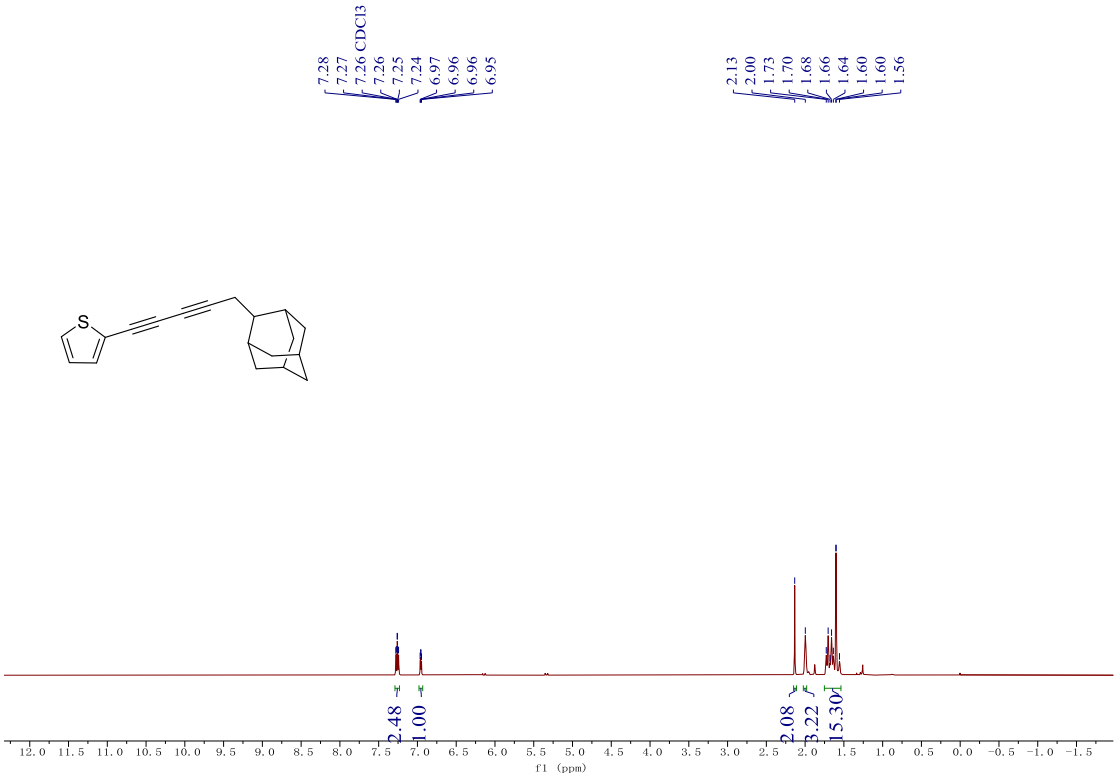


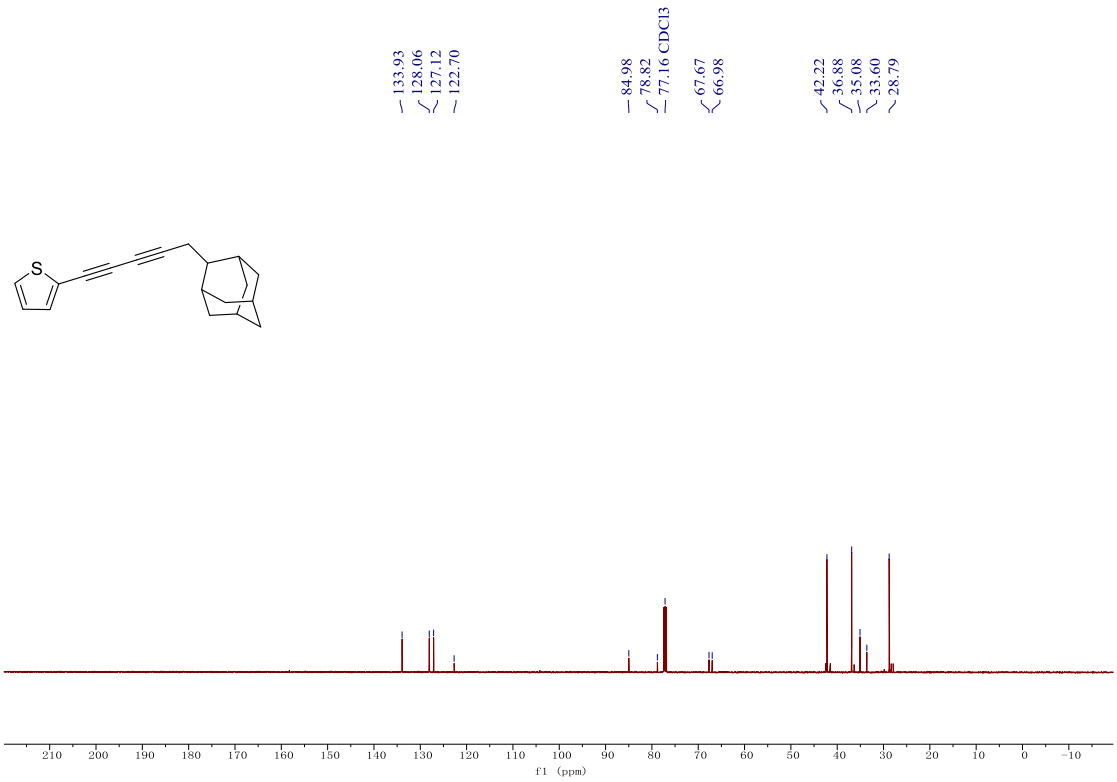


^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6ab

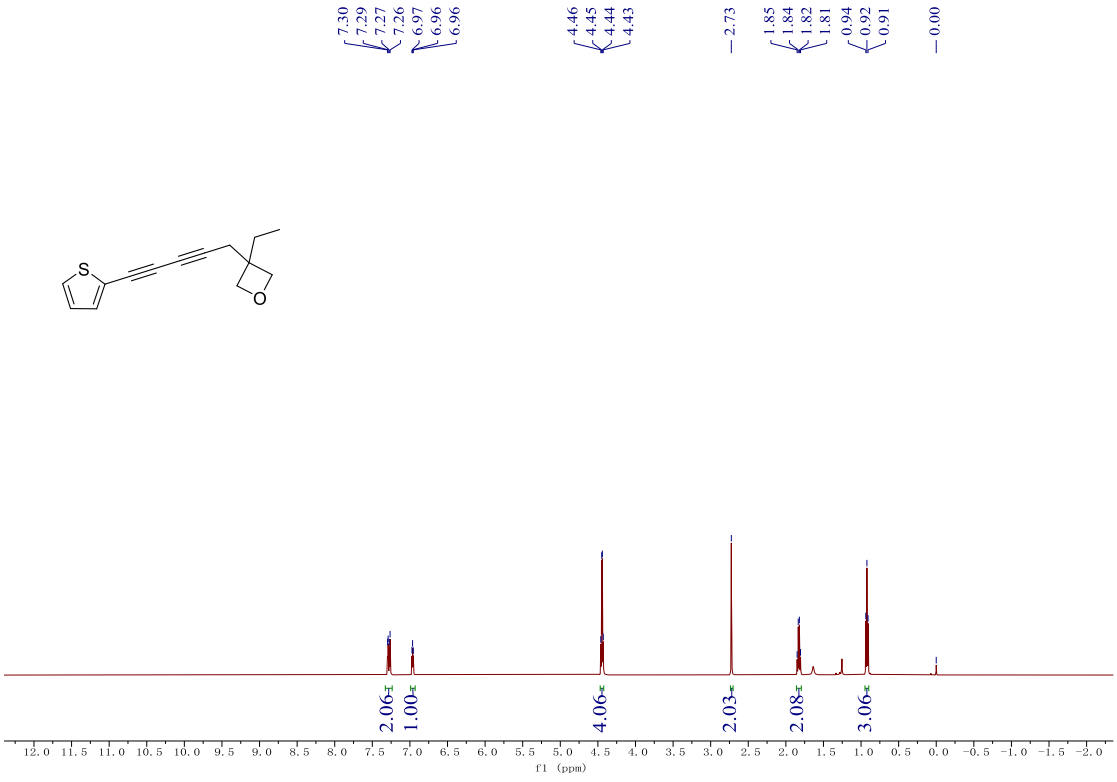


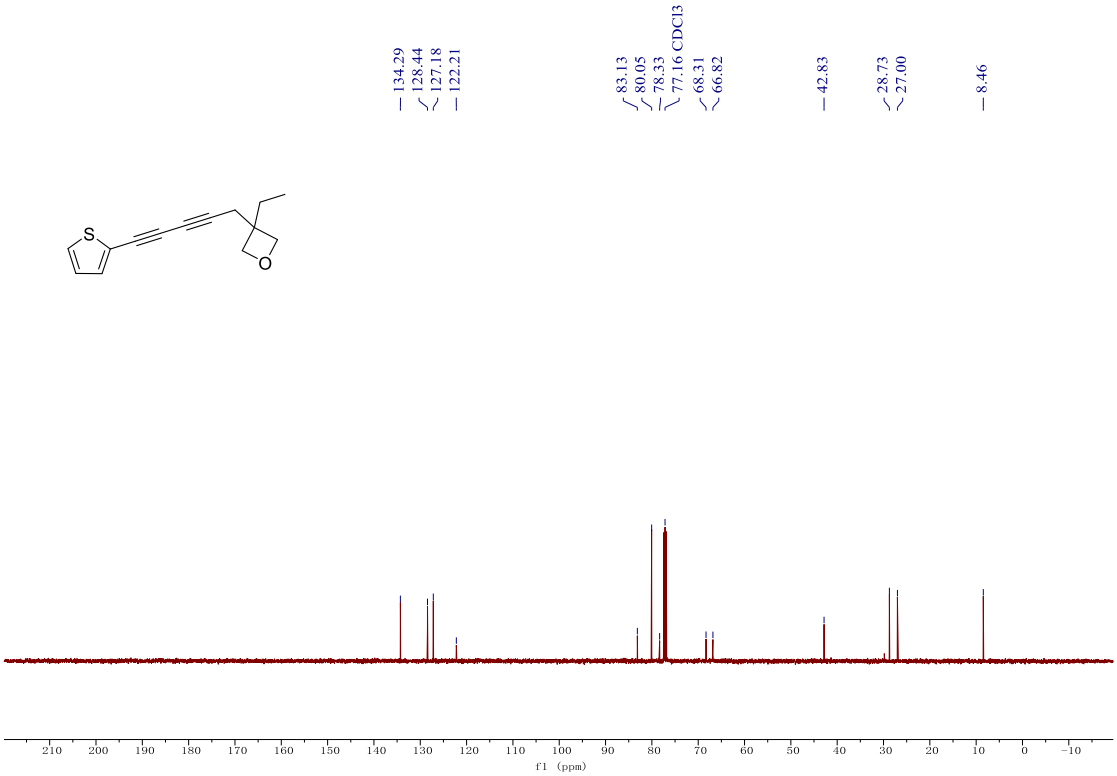
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6ac



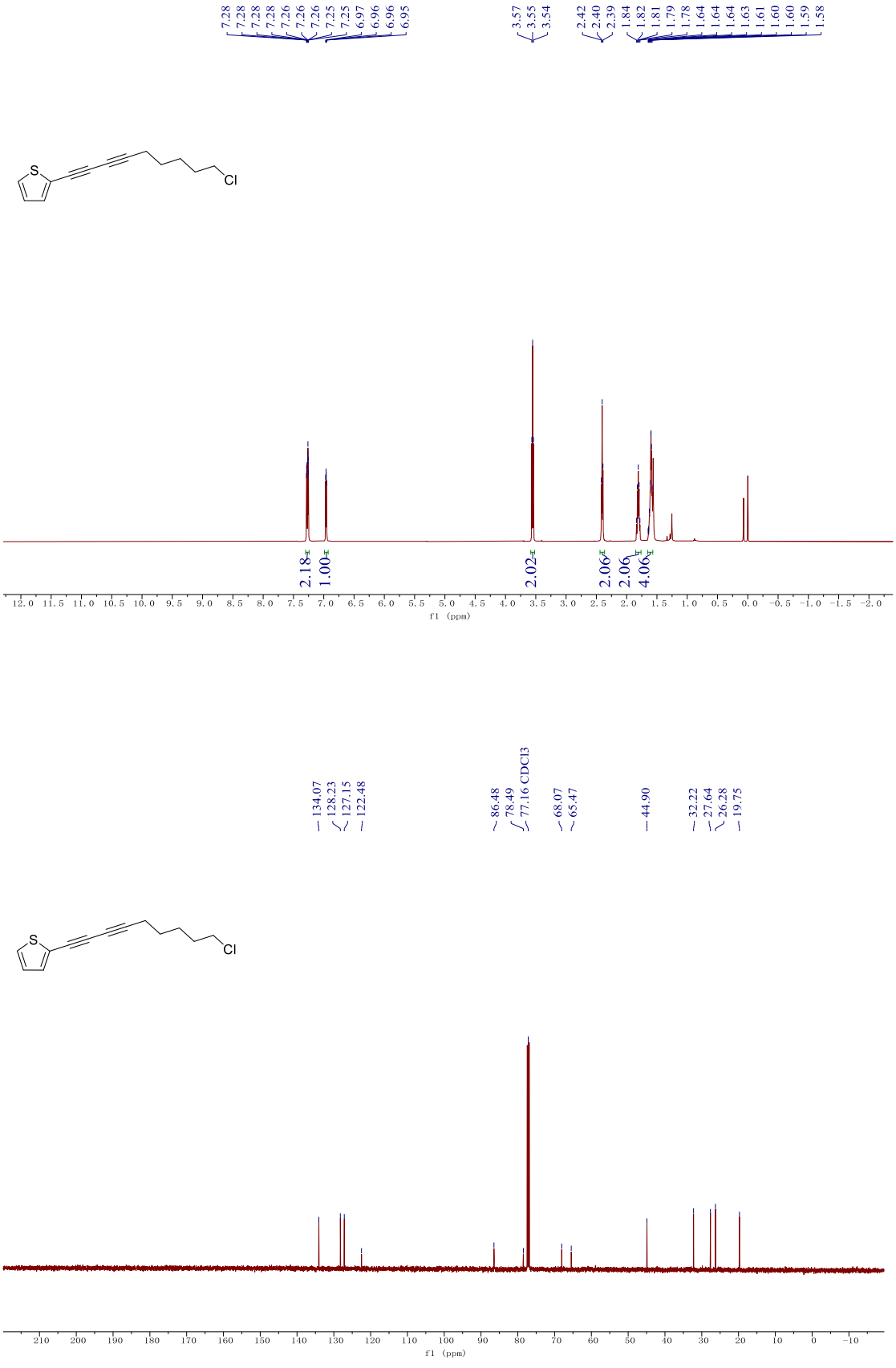


^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6ad

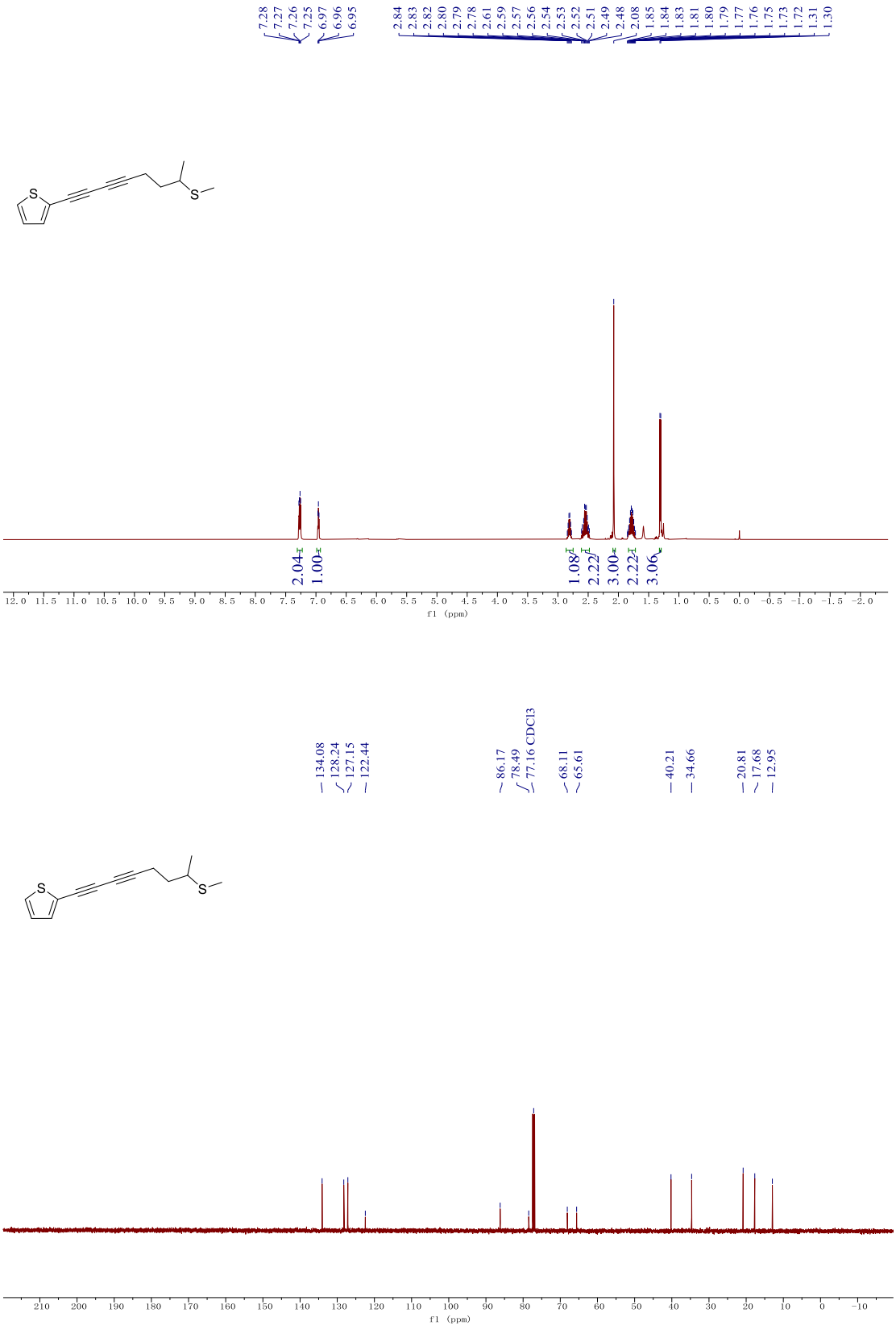




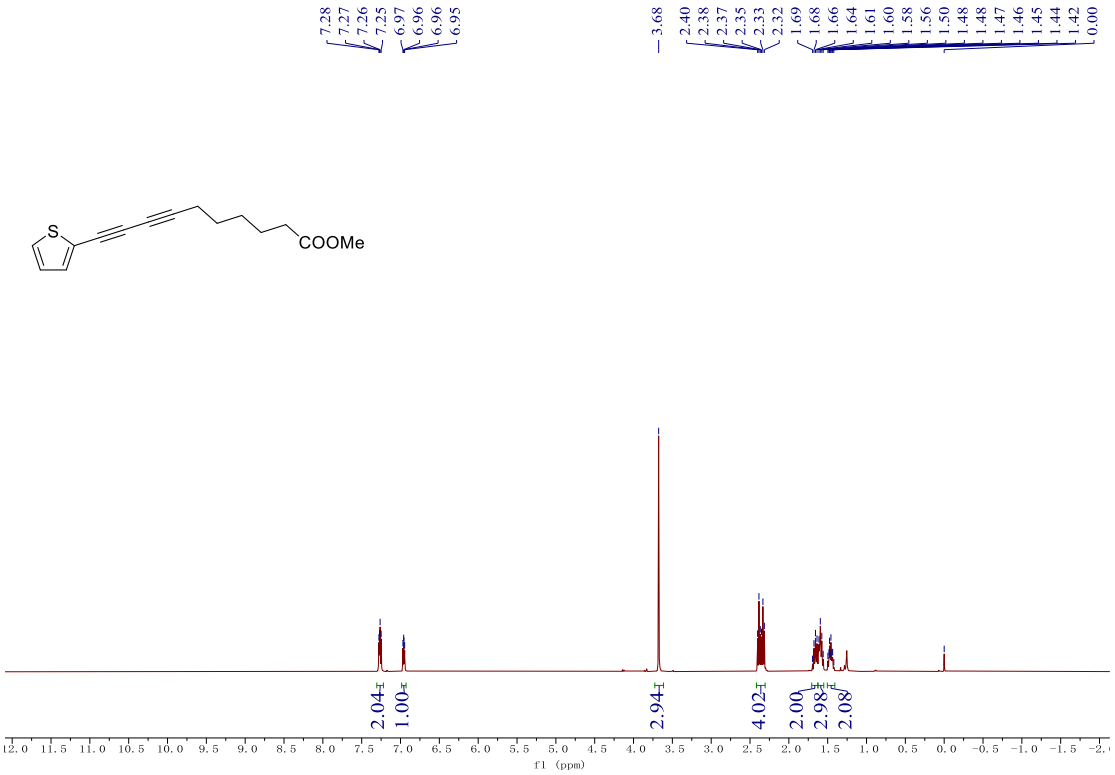
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6ae

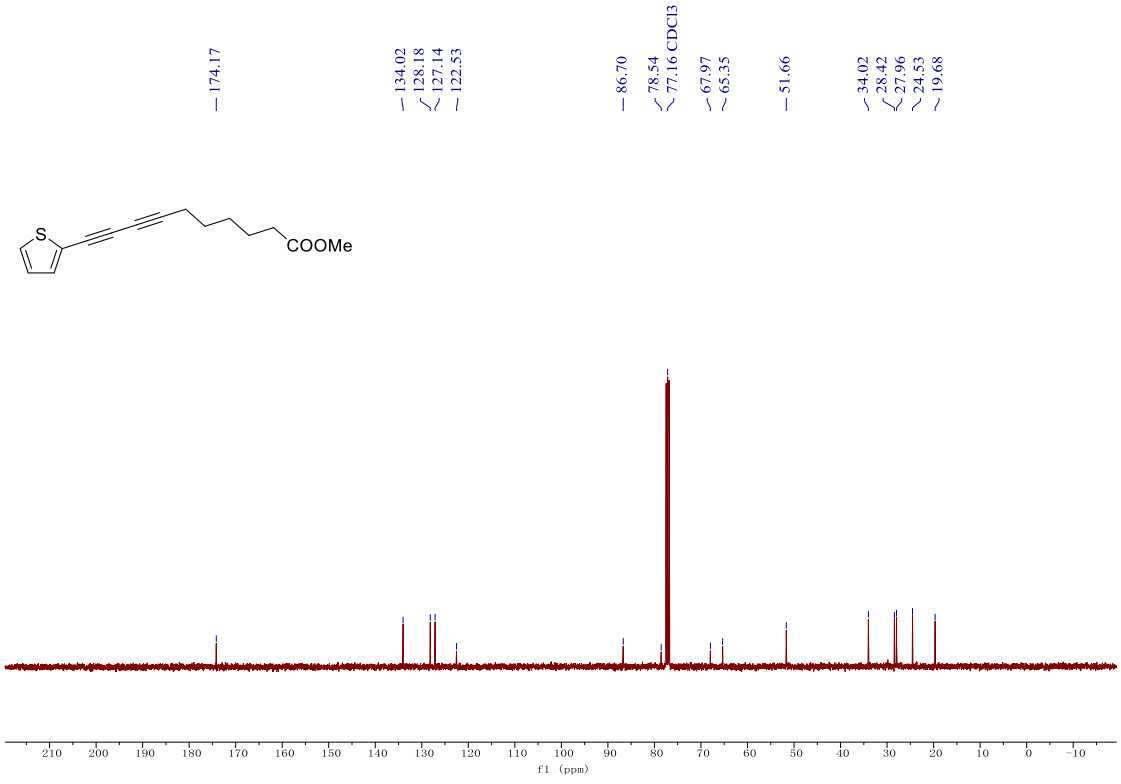


^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6af

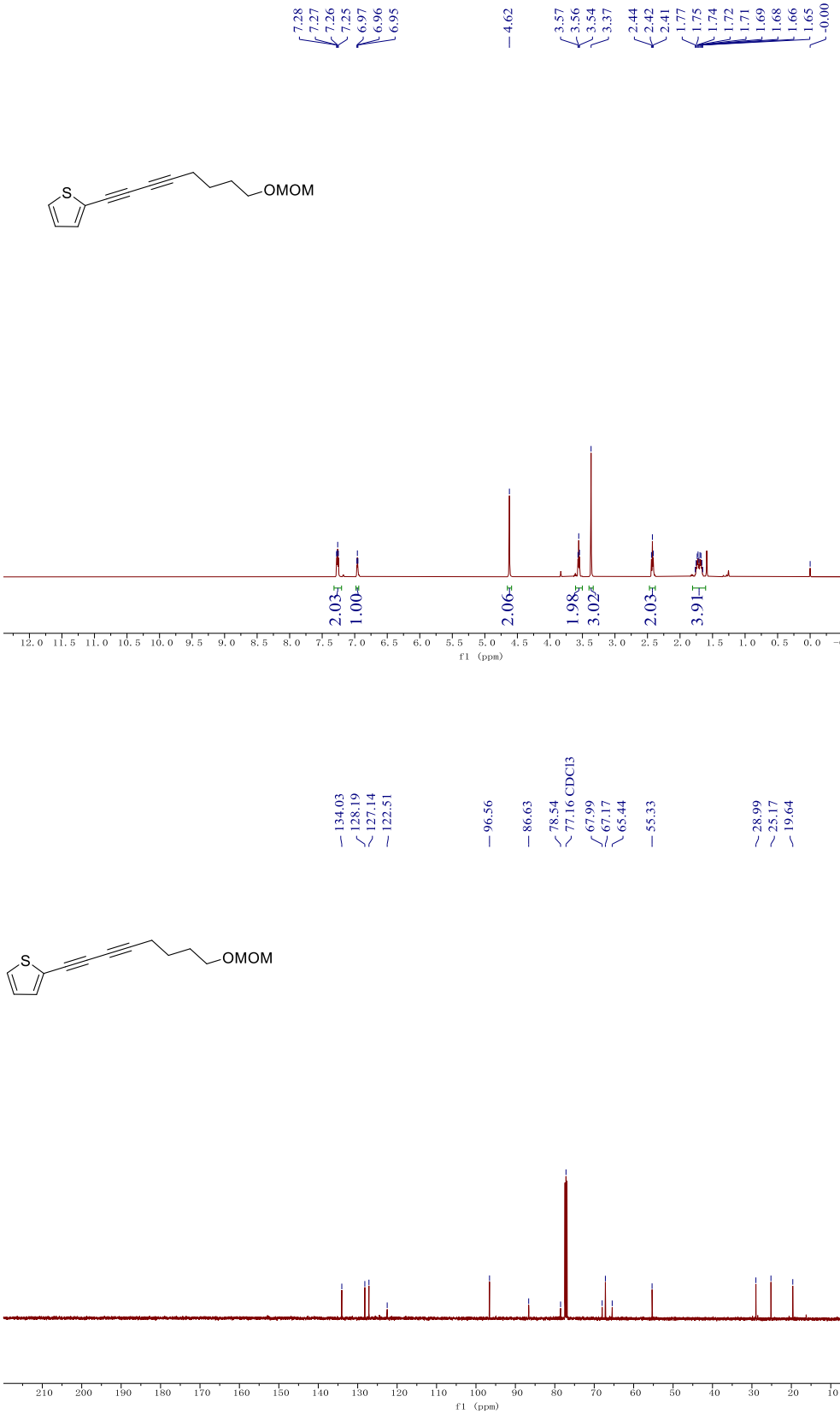


^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 6ag

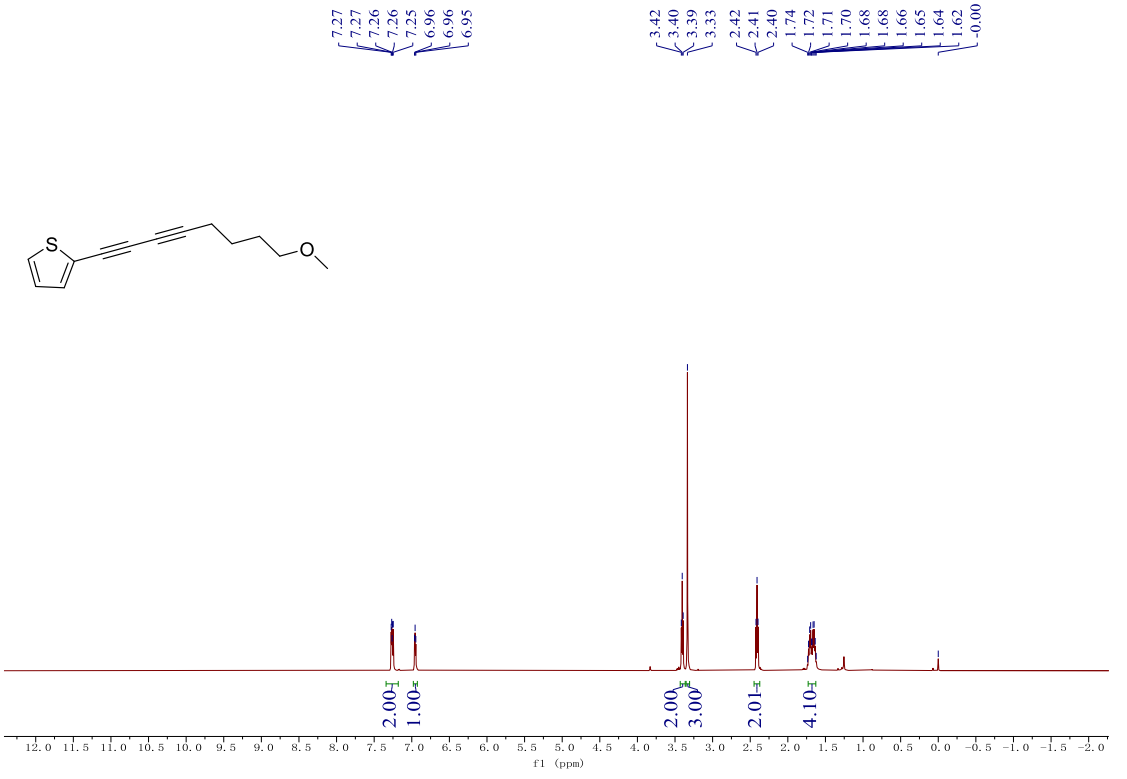


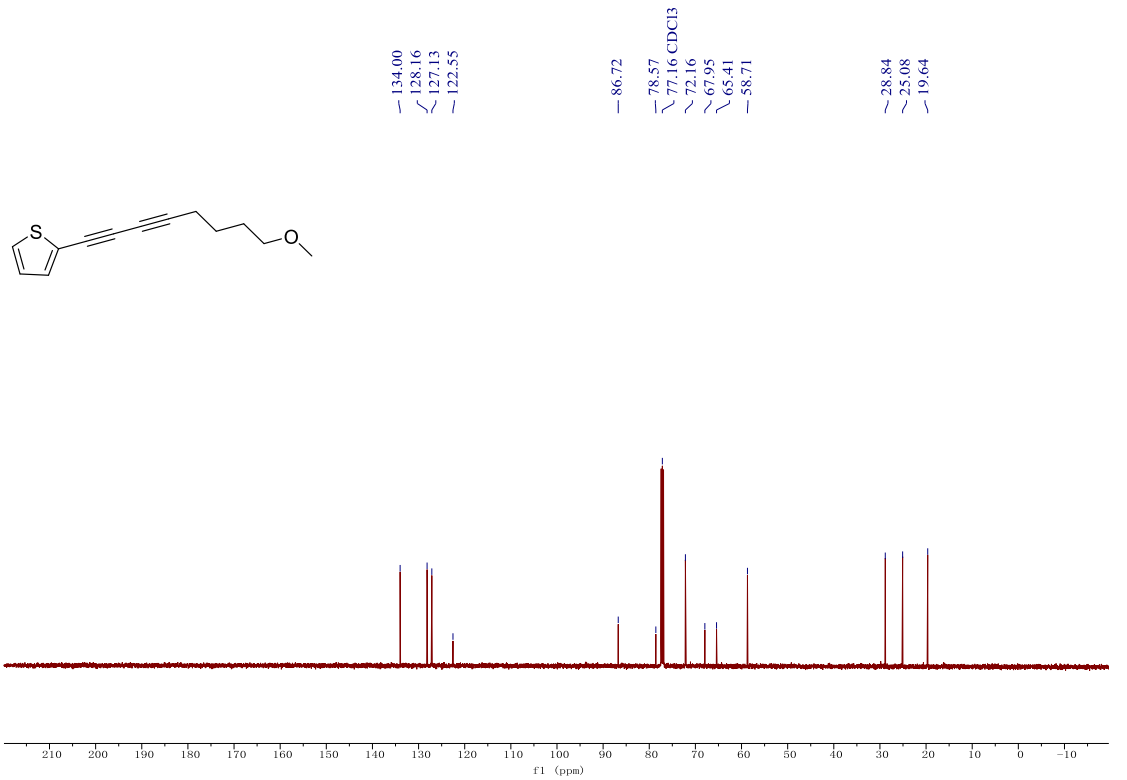


^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6ah

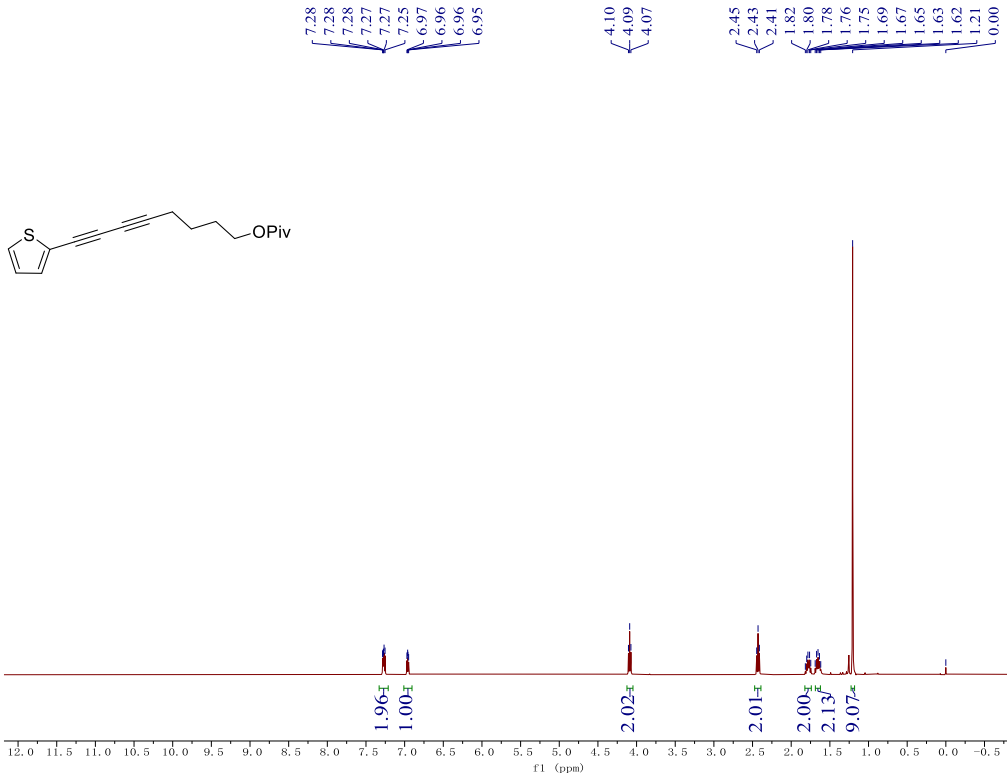


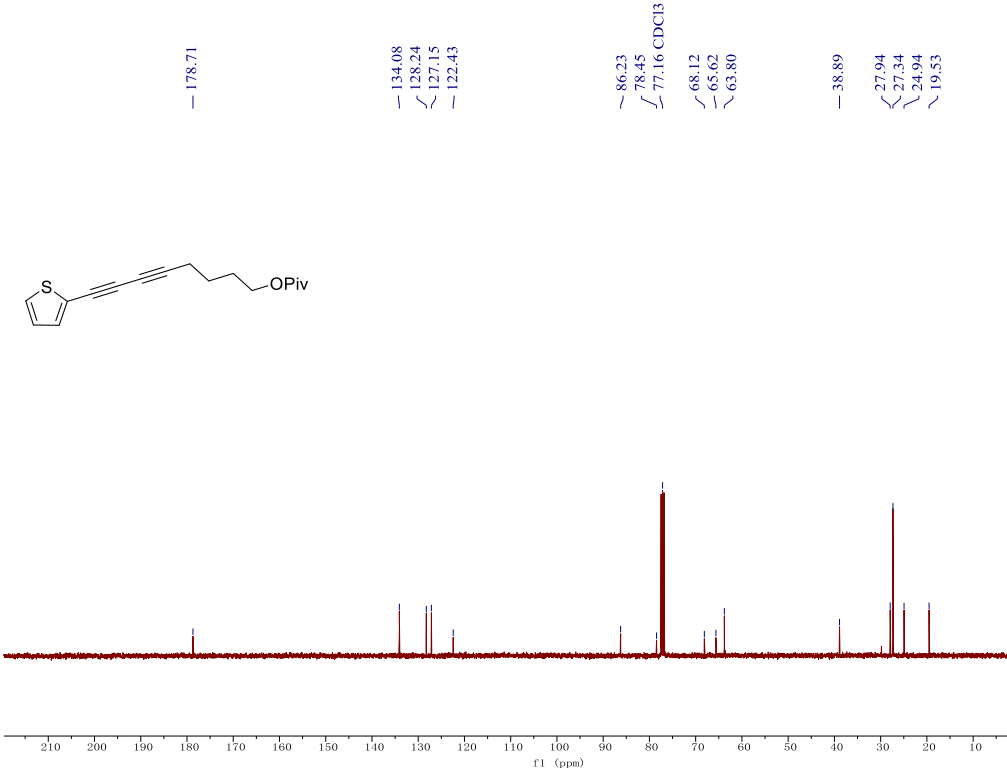
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6ai



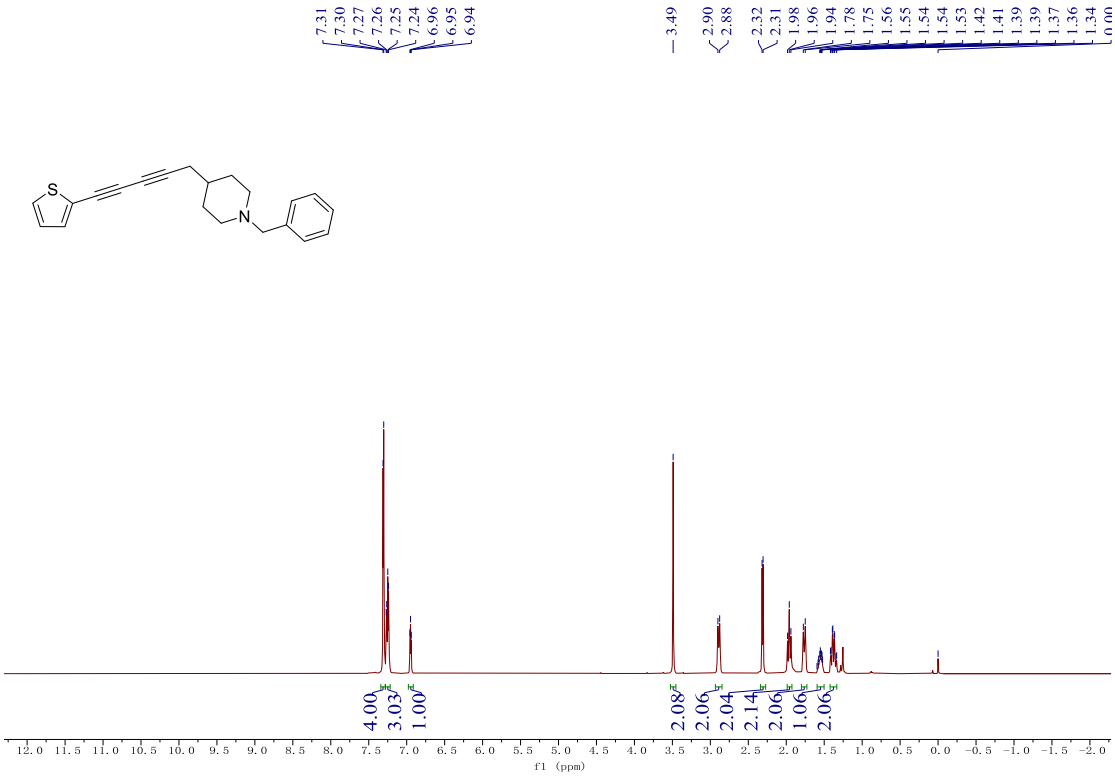


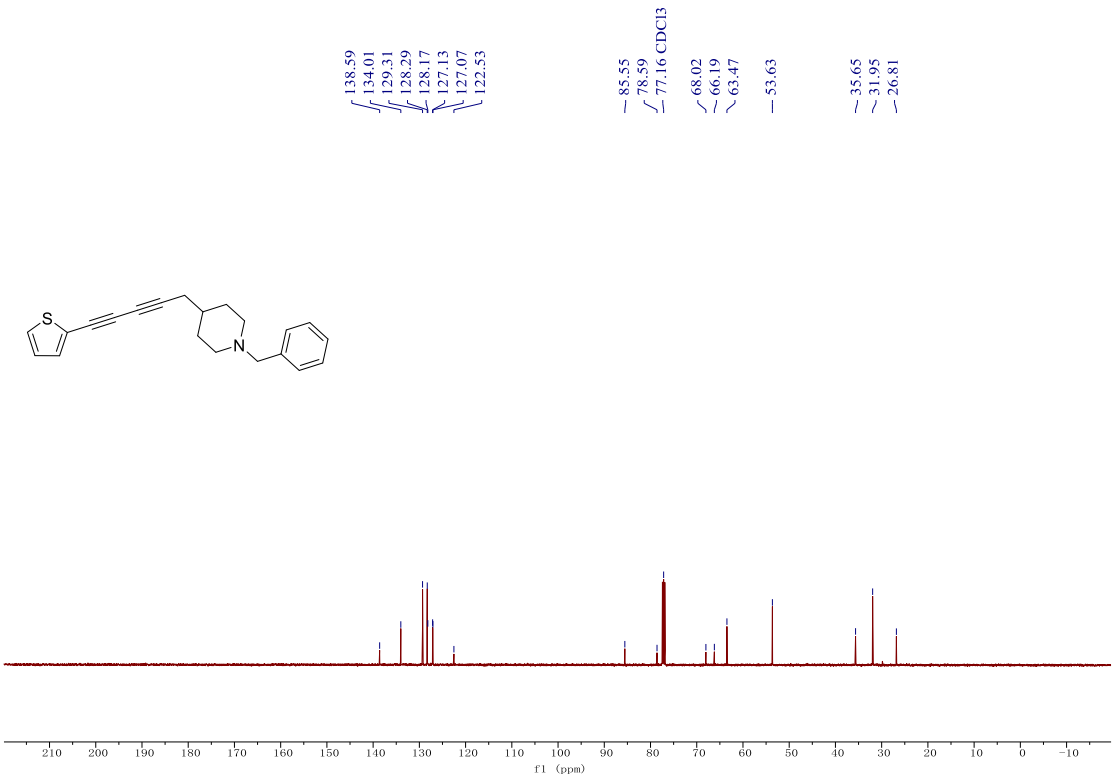
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 6aj



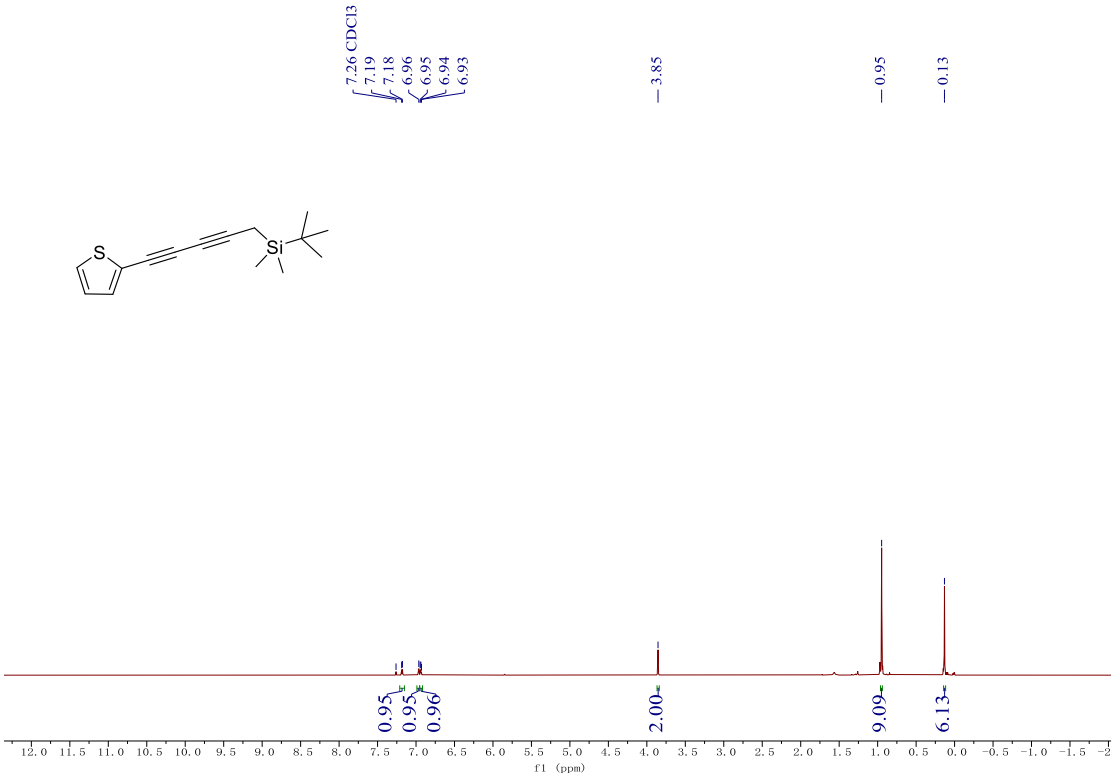


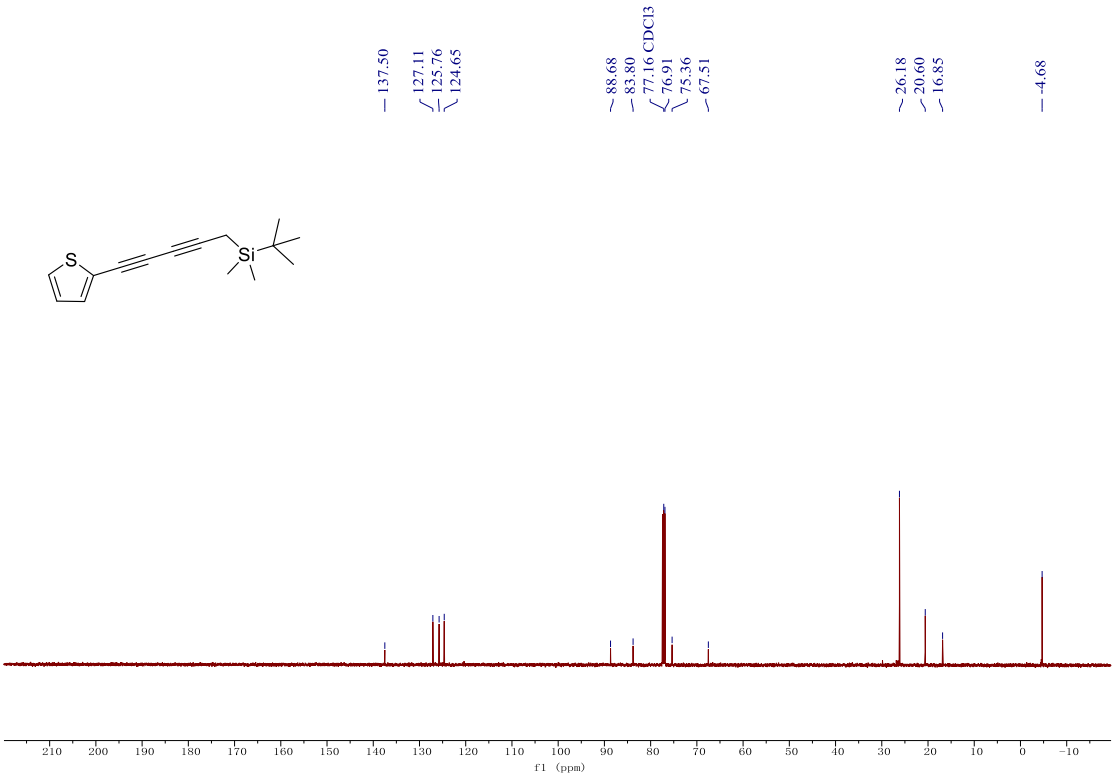
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6ak



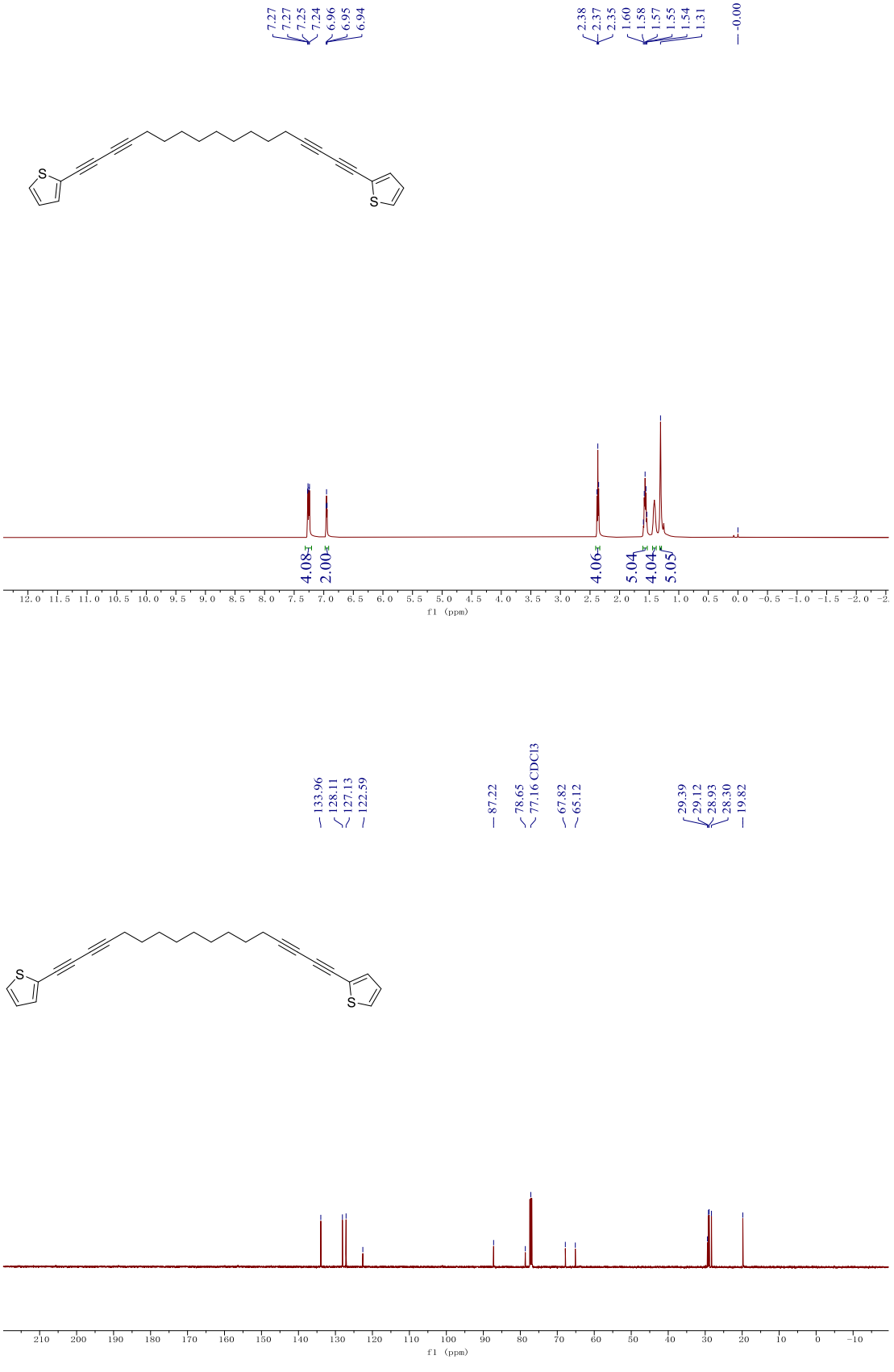


^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6al

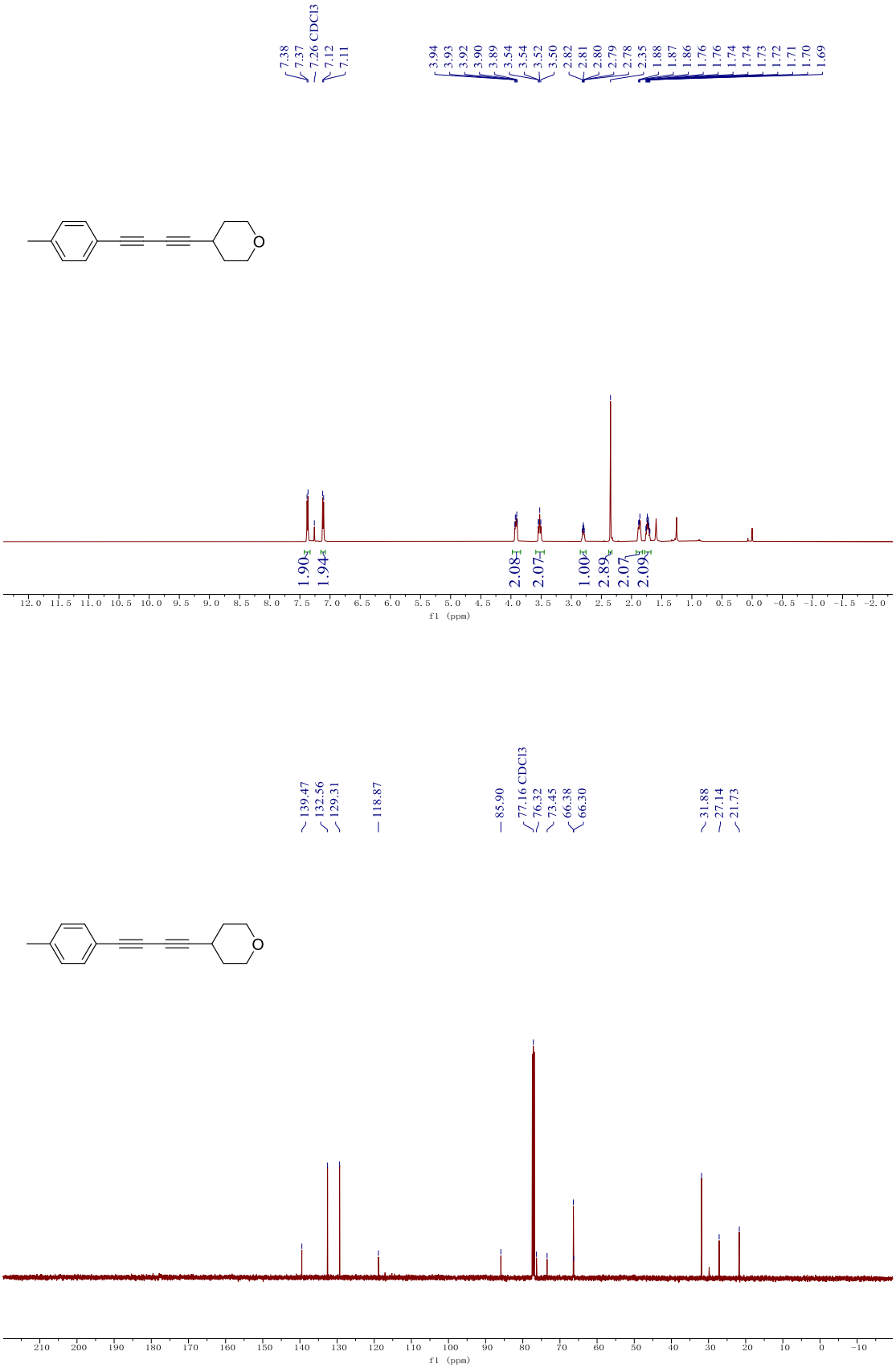




^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6am



^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6an



^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6an'