

# A Novel Approach towards Polyfulvene: Cationic Polymerization of Ene-diyne

## Supporting Information

### Experimental section

#### Materials

Dichloromethane, dichloroethane, tetrahydrofuran (THF) and N,N-dimethylformamide (DMF) were dried over calcium hydride ( $\text{CaH}_2$ ) and distilled before use. All the other reagents were commercially available and used as received. 1,2-diiodocyclohexene (**1**), hept-1-ynyltrimethylsilane (**3a**) and trimethyl(5-methylhex-1-ynyl)silane (**3b**) were synthesized according to literature procedures with minor modifications. All the Sonogashira reactions were performed with dry Schlenk technique under an atmosphere of nitrogen.

#### Characterizations

$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were recorded in chloroform- $d$  ( $\text{CDCl}_3$ ) on an Ultra Shield 400 spectrometer (BRUKER BIOSPIN AG, Magnet System 400 MHz/54 mm). Chemical shifts were reported in parts per million (ppm) downfield from the tetramethylsilane resonance which was used as the internal standard when recording  $^1\text{H}$  NMR spectra. Mass spectra of ene-diyne compounds were recorded on a Micromass LCTTM mass spectrometer using the EI method. Fourier transform infrared analysis (FTIR) was performed using KBr pellets on a Nicolet Magna 5700 FTIR spectrometer. Emission spectra were recorded on a Shimadzu UV-2550 UV-vis spectrometer with ethyl acetate at room temperature. The weight averaged molecular weight ( $M_w$ ) and the polydispersity index (PDI) of the polymers were determined by a twice-detector gel permeation chromatography (GPC) equipped with a refractive index detector (Wyatt Technology Corp., Optilab REX) and a multi-angle static laser light scattering (Wyatt Technology Corp., DAWN HELEOS) detector was used, with a normal flow rate of 1 mL/min at 45°C, THF with 0.05M LiBr used as eluent. MS (MALDI-TOF) of polymers were performed on a Mass spectrometer 4800 plus MALDI-TOF/TOF MS Analyzer (AB Sciex, USA) equipped with a Nd:YAG laser emitting at 355 nm, and operating at an accelerating voltage of 20 kV in reflection mode. 4000 series Explorer and DATA Explorer (AB Sciex, USA) were used for data acquisition and processing. The extraction delay time used was 450 ns. All mass spectra were collected by averaging the signals of 500 individual laser shots. Dried-droplet samples were prepared by spotting 1 ml aliquot of a mixture of 2 ml of matrix (1,1,4,4-tetraphenyl-1,3-butadiene, 20  $\text{mg}\cdot\text{ml}^{-1}$  in THF) and 1 ml of

polymer (10mg\*ml<sup>-1</sup> in THF) on the target plate. UV-vis absorption spectra was recorded on a Shimadzu UV-2550 UV-vis spectrometer in ethyl acetate at room temperature. Gas chromatography (GC) was conducted on a GC-3010A (Shanghai Institute of Computer and Technology) with Agilent HP-5 column. The simulated <sup>1</sup>H NMR spectra of trifluoromethyl (2,6-difluorophenyl) (2-(2,6-difluorophenyl)-1H-inden-1-ylidene) methanesulfonate are simulated with WP04<sup>1</sup>/6-311++G(d,p) computational level and Gauge-Including Atomic Orbital (GIAO)<sup>2</sup> method. Structure optimizations are carried out with B3LYP/6-311++G(d,p) level in Gaussian09 package<sup>3</sup>. Frequency analyses are performed afterwards in order to make sure that they correspond to the local minima. During the optimization, TMS is constrained with T<sub>d</sub> symmetry.

#### Synthesis of enediyne compounds

1,2-di(hex-1-ynyl)cyclohex-1-ene (**EDY 1**): A 50 mL oven-dried flask was charged with CuI (57.1 mg, 0.3 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (100 mg, 0.15 mmol) and a stir bar. Then degassed THF (15 ml), n-BuNH<sub>2</sub> (0.5 ml), 1,2-diiodocyclohex-1-ene (0.5 g, 1.5 mmol) and hex-1-yne (0.37g, 4.5 mmol) were added successively under a nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 18 h. The dark brown resulting solution was partitioned with saturated aqueous NH<sub>4</sub>Cl and EtOAc, and the organic layer was dried over anhydrous MgSO<sub>4</sub>. After removal of the solvent, the crude product was purified through column chromatography (silica, PE:CH<sub>2</sub>Cl<sub>2</sub>=30 : 1) to yield a yellow liquid (0.21 g, 58%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 2.36-2.39 [t, 4H, cyclohexene 3(6)-H], 2.17 [m, 4H, cyclohexene 4(5)-H], 1.46-1.58 (m, 12H, CH<sub>2</sub>), 0.90-0.93 (t, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 125.2, 93.5, 81.6, 31.0, 30.3, 22.0, 21.9, 19.3, 13.7. HRMS (EI): m/z calcd for C<sub>18</sub>H<sub>26</sub> (242.2035); found: 242.2036.

The following enediynes were prepared and isolated under the similar procedure as described for EDY 1.

1,2-bis(phenylethynyl)cyclohex-1-ene (**EDY 2**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.47-7.50 (m, 4H, Ph), 7.30-7.31 (m, 6H, Ph), 2.38 [t, 4H, cyclohexene 3(6)-H], 1.71 [m, 4H, cyclohexene 4(5)-H]. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 131.5, 128.3, 128.0, 126.4, 123.6, 93.6, 90.4, 30.0, 21.8.

1,2-bis(p-tolylethynyl)cyclohex-1-ene (**EDY 3**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.38-7.40 (d, 4H, Ph), 7.12-7.14 (d, 4H, Ph), 2.39 [t, 4H, cyclohexene 3(6)-H], 2.36 (t, 6H, CH<sub>3</sub>), 1.71 [m, 4H, cyclohexene 4(5)-H]. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 138.1, 131.4, 129.0, 126.2, 120.6, 93.7, 89.9, 30.1, 21.9, 21.5. HRMS (EI): m/z calcd for C<sub>24</sub>H<sub>22</sub> (310.1722); found: 310.1723.

1,2-bis((4-fluorophenyl)ethynyl)cyclohex-1-ene (**EDY 4**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.42-7.45 (dd, 4H, Ph), 6.98-7.03 (t, 4H, Ph), 2.36 [t, 4H, cyclohexene 3(6)-H], 1.70 [m, 4H, cyclohexene 4(5)-H]. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 161.1-163.6 (d, 2C), 133.2-133.3 (d, 4C), 126.4, 119.6 (d, 2C), 115.5-115.7 (d, 4C), 92.5, 90.0, 30.0, 21.8.

1,2-di(hex-1-ynyl)benzene (**EDY 5**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.36-7.38

(m, 4H, Ph), 7.16-7.184 (m, 4H, Ph), 2.45-2.49 (t, 4H,  $\text{-C}\equiv\text{C-CH}_2$ ), 1.50-1.64 (m, 8H,  $\text{CH}_2$ ), 0.94-0.98 (t, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm): 131.8, 127.1, 126.3, 94.0, 79.6, 30.8, 22.0, 19.3, 13.7.

1,2-di(hept-1-ynyl)benzene (**EDY 6**): A 50 mL oven-dried flask was charged with CuI (70 mg, 0.368 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (130 mg, 0.184 mmol),  $\text{TBAF}\cdot 3\text{H}_2\text{O}$  (4.36g, 13.8 mmol) and a stir bar. Then degassed THF (20 ml),  $n\text{-BuNH}_2$  (1.54 ml), 1,2-diiodobenzene (1.52 g, 4.61 mmol) and hept-1-ynyltrimethylsilane (1.94g, 11.5 mmol) were added successively under a nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 18 h. The dark brown resulting solution was partitioned with saturated aqueous  $\text{NH}_4\text{Cl}$  and EtOAc, and the organic layer was dried over anhydrous  $\text{MgSO}_4$ . After removal of the solvent, the crude product was purified through column chromatography (silica, PE) to yield a colorless liquid (0.55 g, 45%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.36-7.38 (m, 4H, Ph), 7.16-7.18 (m, 4H, Ph), 2.44-2.47 (t, 4H,  $\text{-C}\equiv\text{C-CH}_2$ ), 1.61-1.67 (m, 4H,  $\text{CH}_2$ ), 1.43-1.51 (m, 4H,  $\text{CH}_2$ ), 1.32-1.39 (m, 4H,  $\text{CH}_2$ ), 0.90-0.94 (t, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm): 131.7, 127.1, 126.3, 94.1, 79.5, 31.1, 28.5, 22.3, 19.6, 14.0.

1,2-bis(5-methylhex-1-ynyl)benzene (**EDY 7**):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.35-7.37 (m, 4H, Ph), 7.15-7.18 (m, 4H, Ph), 2.45-2.48 (t, 4H,  $\text{-C}\equiv\text{C-CH}_2$ ), 1.77-1.87 (m, 2H, CH), 1.50-1.56 (m, 4H,  $\text{CH}_2$ ), 0.93-0.95 (d, 12H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm): 131.8, 127.1, 126.3, 94.1, 79.4, 37.7, 27.2, 22.2, 17.6. HRMS (EI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{26}$  (266.2035); found: 266.2036.

1,2-di(oct-1-ynyl)benzene (**EDY 8**):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.36-7.38 (m, 4H, Ph), 7.16-7.18 (m, 4H, Ph), 2.44-2.47 (t, 4H,  $\text{-C}\equiv\text{C-CH}_2$ ), 1.61-1.65 (m, 4H,  $\text{CH}_2$ ), 1.46-1.50 (m, 4H,  $\text{CH}_2$ ), 1.31-1.34 (m, 8H,  $\text{CH}_2$ ), 0.89-0.92 (t, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm): 131.8, 127.1, 126.3, 94.2, 79.5, 31.5, 28.8, 28.7, 22.6, 19.7, 14.1.

1,2-bis(phenylethynyl)benzene (**EDY 9**):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.56-7.59 (m, 6H, Ph), 7.31-7.36 (m, 9H, Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm): 131.8, 131.6, 128.4, 128.2, 128.0, 125.8, 123.3, 93.6, 88.3.

1,2-bis(p-tolylethynyl)benzene (**EDY 10**):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.55-7.57 (m, 2H, Ph), 7.47-7.49 (d, 4H, Ph), 7.29-7.31 (m, 2H, Ph), 7.16-7.18 (d, 4H, Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm): 138.5, 131.6, 131.5, 129.1, 127.8, 125.9, 120.2, 93.7, 87.7, 21.5.

1,2-bis((4-fluorophenyl)ethynyl)benzene (**EDY 11**):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.51-7.56 (m, 6H, Ph), 7.31-7.33 (m, 4H, Ph), 7.03-7.07 (t, 2H, Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm): 161.4-163.8 (d, 2C), 133.4-133.5 (d, 4C), 131.7, 128.1, 125.6, 119.3 (d, 2C), 115.6-115.8 (d, 4C), 92.4, 87.9.

((2,6-difluorophenyl)ethynyl)trimethylsilane (**3c**): A 50 mL oven-dried flask was charged with CuI (47.6 mg, 0.25 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (87.7 mg, 0.125 mmol) and a stir bar. Then degassed DMF (15 ml),  $\text{Et}_3\text{N}$  (3 ml), 1,3-difluoro-2-iodobenzene (3.0 g,

12.5 mmol) and TMSA (3.39g, 25 mmol) were added successively under a nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 18 h. The dark brown resulting solution was partitioned with saturated aqueous NH<sub>4</sub>Cl and EtOAc, and the organic layer was dried over anhydrous MgSO<sub>4</sub>. After removal of the solvent, the crude product was purified through column chromatography (silica, PE) to yield a yellow liquid (1.4 g, 54%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.23-7.26 (m, 1H, Ph), 6.86-6.90 (t, 2H, Ph), 1.46-1.58 (m, 12H, CH<sub>2</sub>), 0.28 (s, 9H, Si-CH<sub>3</sub>).

1,2-bis((2,6-difluorophenyl)ethynyl)benzene (**EDY 12**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.53-7.56 (m, 2H, Ph), 7.26-7.29 (m, 2H, Ph), 7.16-7.20 (m, 2H, Ph), 6.81-6.84 (d, 4H, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 161.7-164.3 (m, 4C), 132.3, 129.7-129.9 (t, 2C), 128.6, 125.1, 111.0-111.2 (m, 4C), 102.2 (t, 2C), 97.2, 80.4. HRMS (EI): m/z calcd for C<sub>22</sub>H<sub>10</sub>F<sub>4</sub> (350.0719); found: 350.0720.

E-trifluoromethyl (2,6-difluorophenyl) (2-(2,6-difluorophenyl)-1H-inden-1-ylidene) methanesulfonate (**M12**): A 50 mL oven-dried flask was charged with **EDY 12** (50 mg, 0.143 mmol) and a stir bar. Then degassed dichloroethane (10 ml), trifluoromethanesulfonic acid (1 eq) were added successively under a nitrogen atmosphere. After 24h of stirring at room temperature, the solution were quenched by saturated NaHCO<sub>3</sub>, and the aqueous layer were extracted with dichloromethane. Then the solvent was removed, and the crude product was purified through column chromatography (silica, PE:EtOAc=40:1) to yield a yellow solid (30 mg, 42%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 8.19-8.21 (m, 1H, Ph), 7.35-7.36 (m, 3H, Ph), 7.11-7.18 (m, 1H, CH), 6.94-6.98 (m, 2H, Ph), 6.65-6.63 (m, 4H, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 160.6 (dd, 2C), 160.0 (dd, 2C), 141.6, 139.8, 135.8, 135.6, 133.6, 133.6 (t, 1C), 129.8, 129.5 (t, 1C), 127.5, 126.5, 125.8, 122.0, 118.1 (q, 1C, CF<sub>3</sub>), 112.2 (t, 1C), 110.4-110.8 (m, 4C), 109.0 (t, 1C). HRMS (EI): m/z calcd for C<sub>23</sub>H<sub>11</sub>F<sub>7</sub>O<sub>3</sub>S (500.0317); found: 500.0316.

#### Polymerization

All the enediyne compounds were treated with trifluoromethanesulfonic acid (1 eq) as catalyst in redistilled dichloromethane (dichloroethane for **EDY 12**) under a dry nitrogen atmosphere. The mixture were stirred at -78°C for 1 h and then slowly warmed to room temperature. After 24h of stirring at room temperature (more than 3d at 100°C for **EDY 12**), the solution were quenched by saturated NaHCO<sub>3</sub>, and the aqueous layer were extracted with dichloromethane. Then the solvent was removed, and the product were precipitated into a large amount of methanol or hexane, collected by centrifugation, and dried under vacuum to afford dark brown polymers.

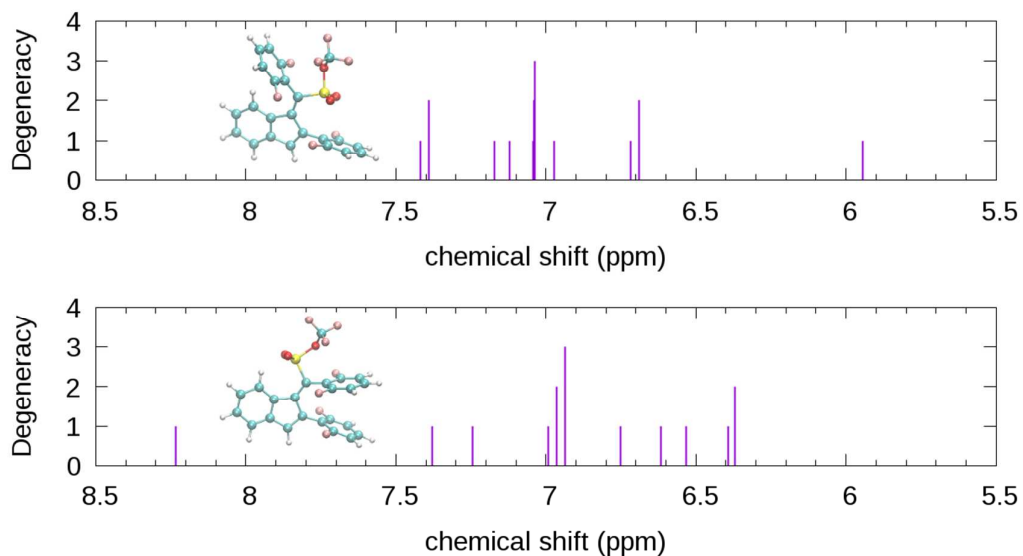


Figure S1. Simulated  $^1\text{H}$  NMR spectra of Z- (upper panel) and E- trifluoromethyl (2,6-difluorophenyl) (2-(2,6-difluorophenyl)-1H-inden-1-ylidene) methanesulfonate (bottom panel). Insets are the corresponding optimized structures, where H, C, S, O and F atoms are in white, cyan, yellow, red and pink respectively.

Representative UV-vis spectra of polymers:

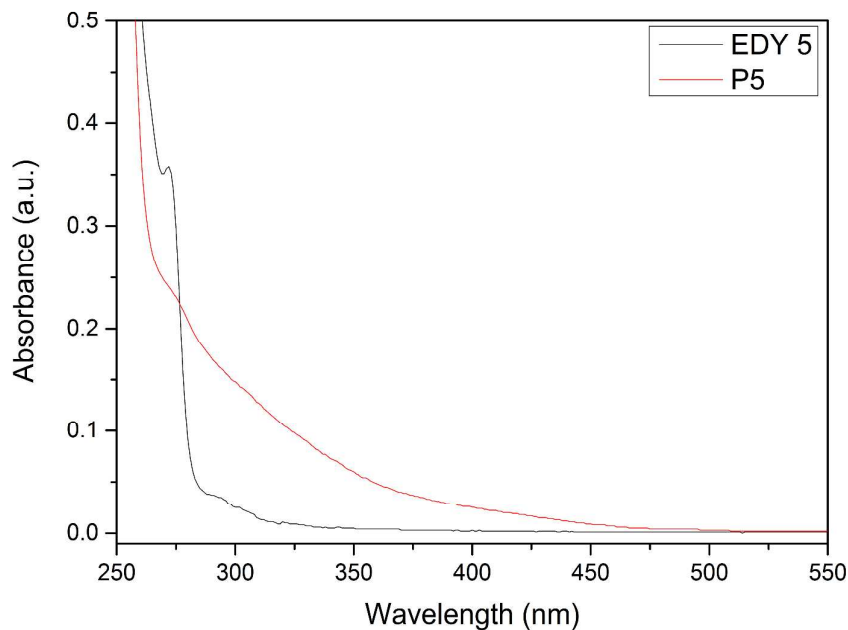
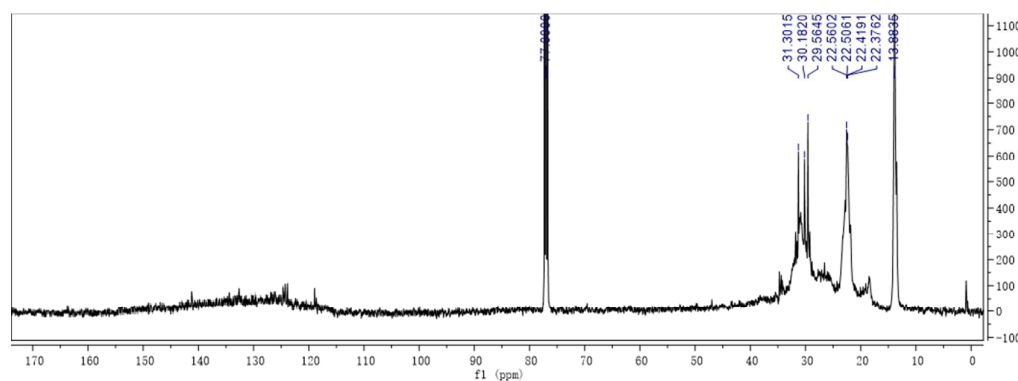
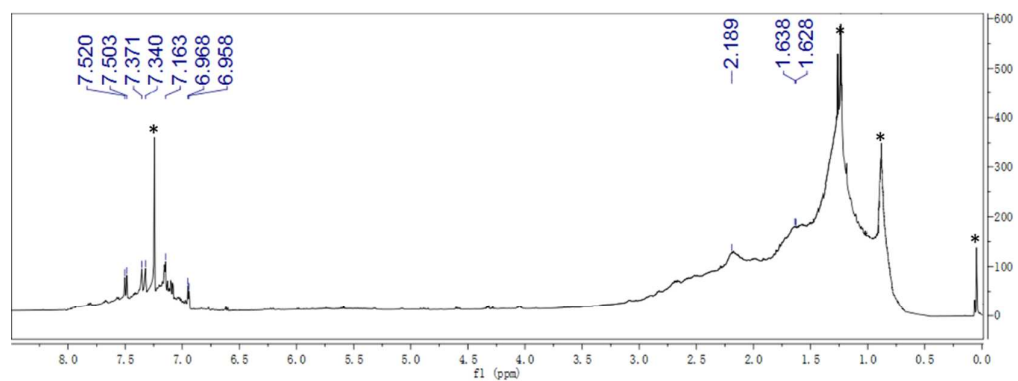


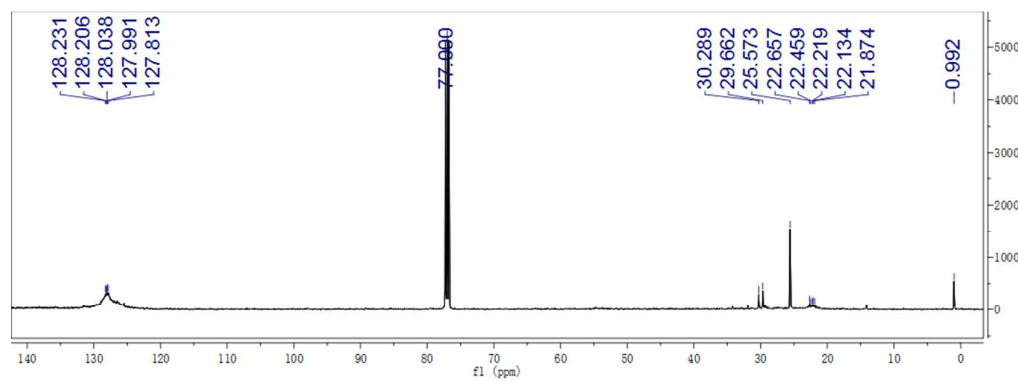
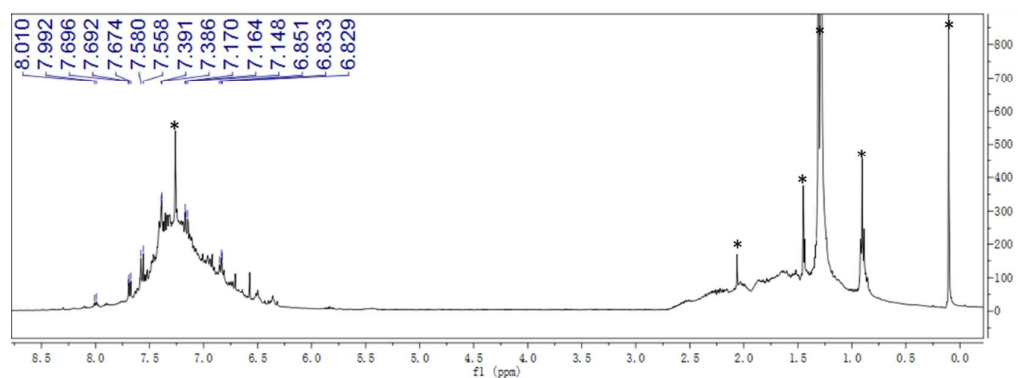
Figure S2. UV-vis spectra of EDY5 and P5 in ethyl acetate solution ( $c = 10^{-3}$  mg/mL) at room temperature.

# NMR spectra of polymers:

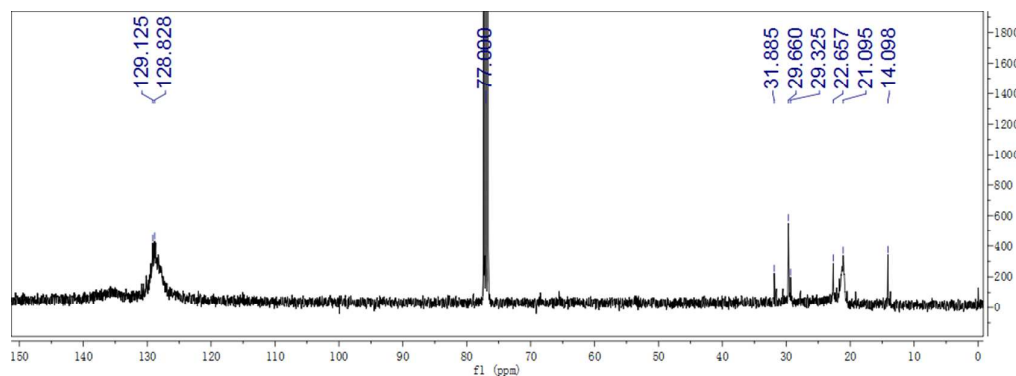
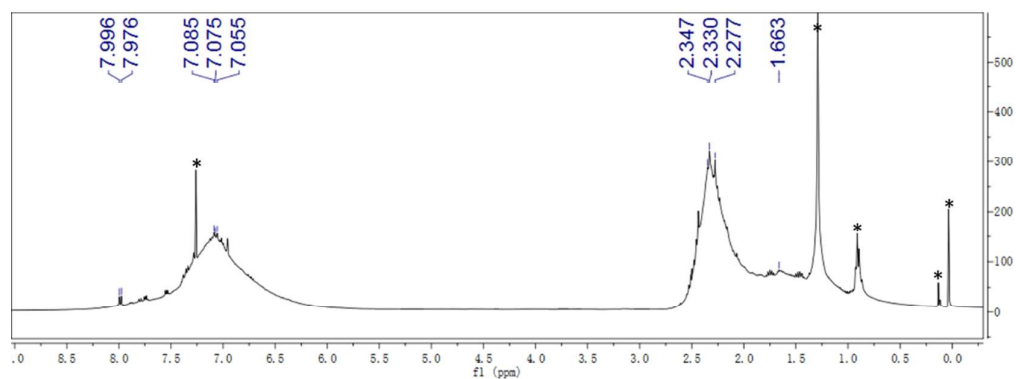
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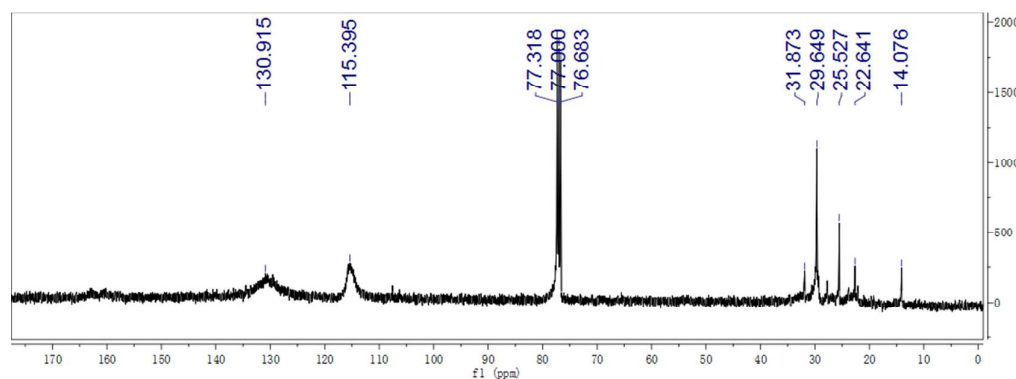
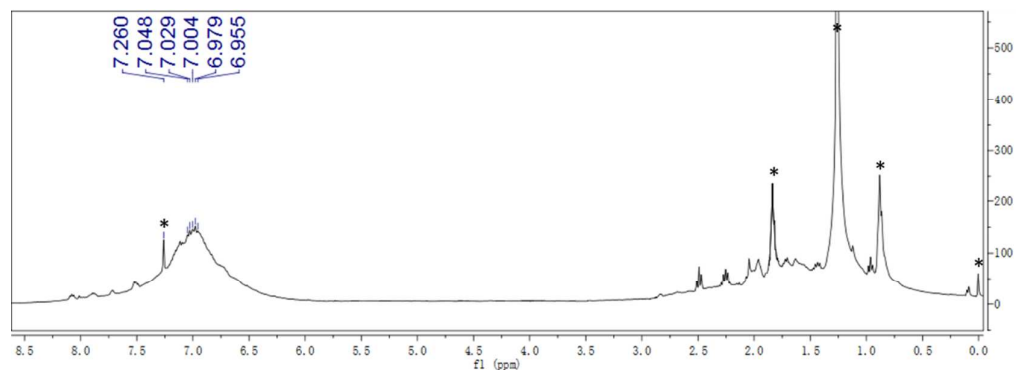
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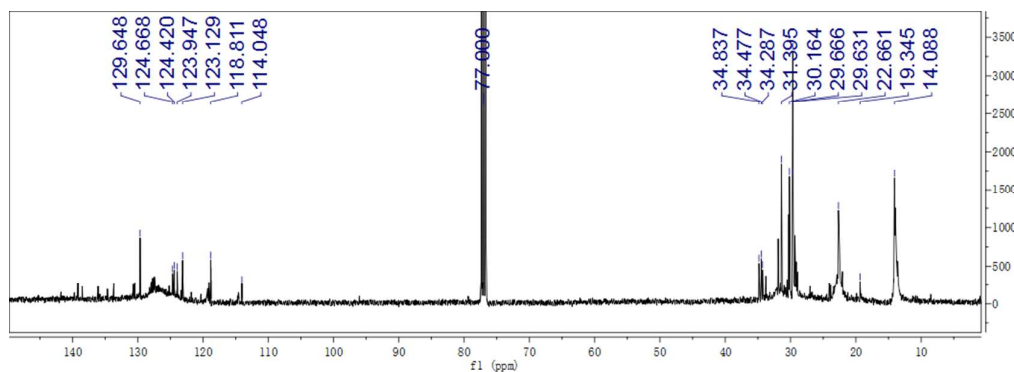
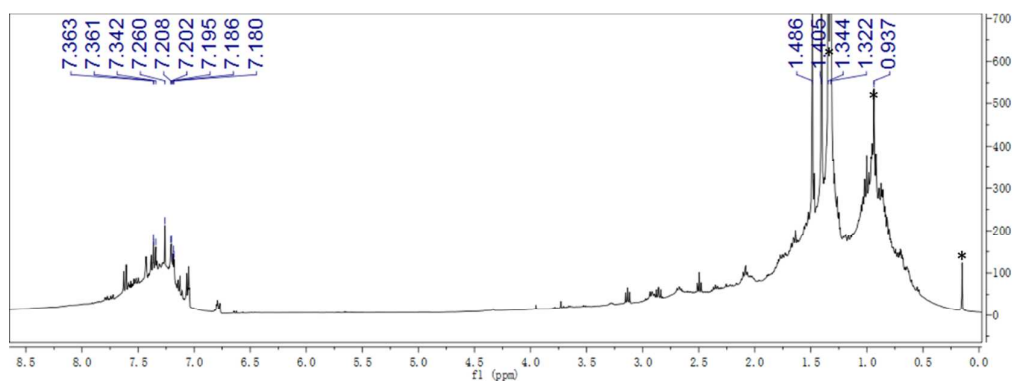
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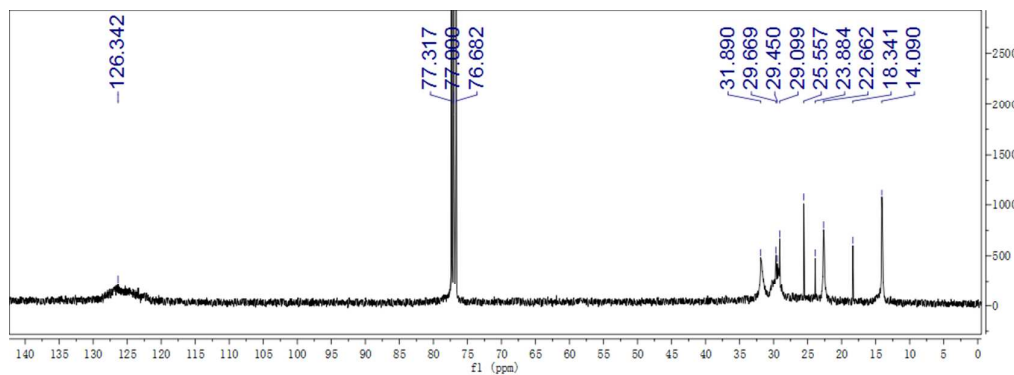
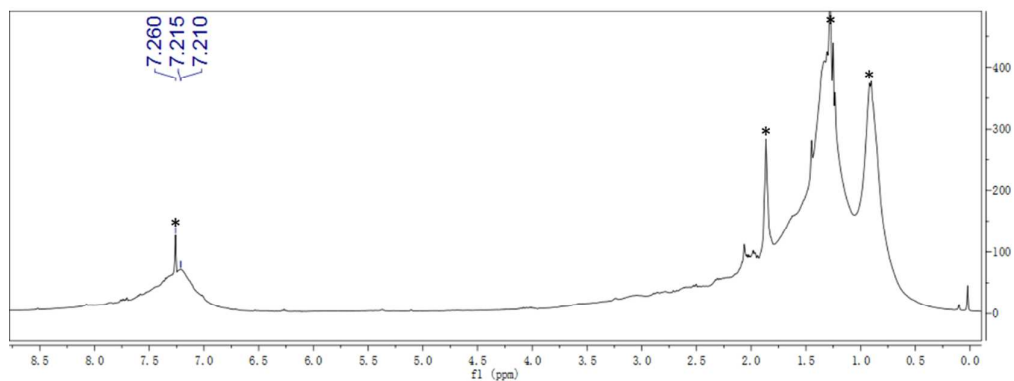
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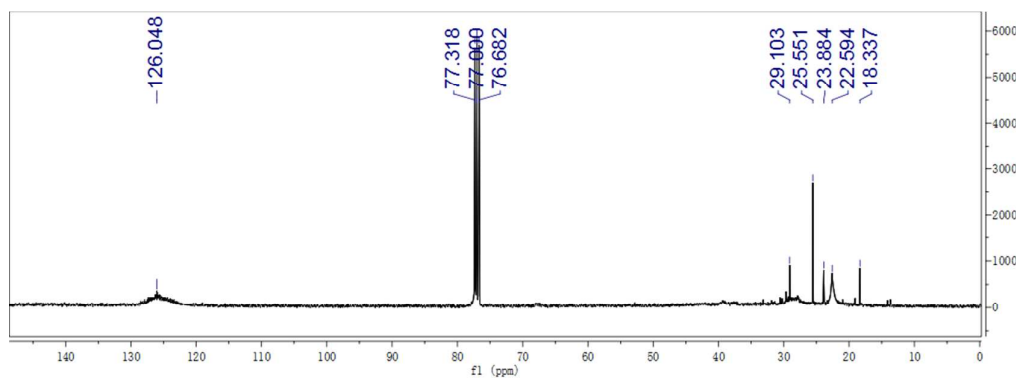
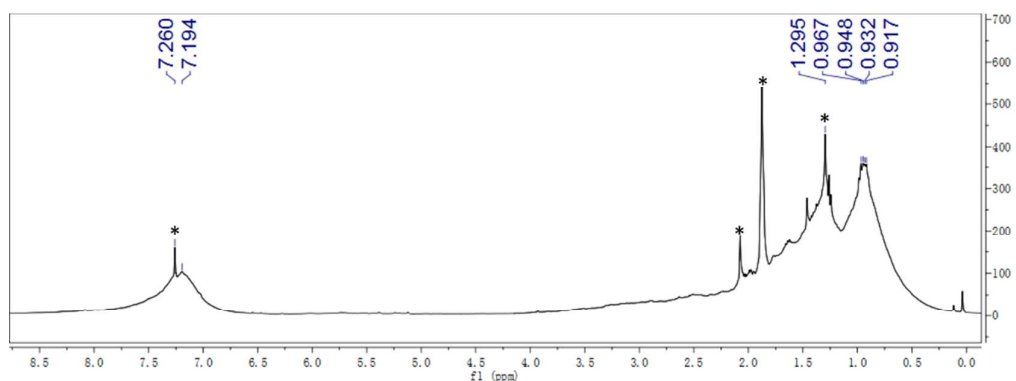


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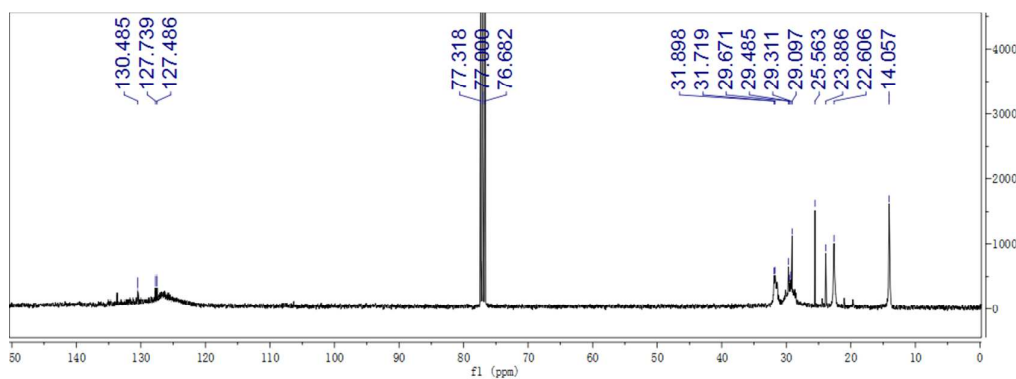
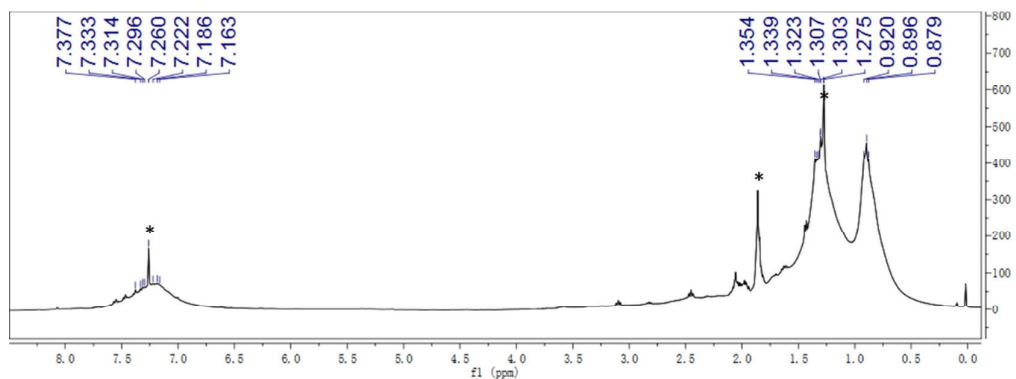




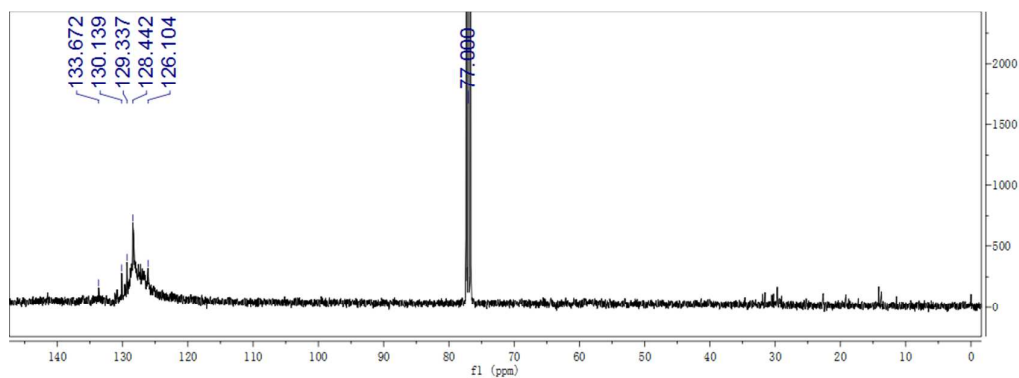
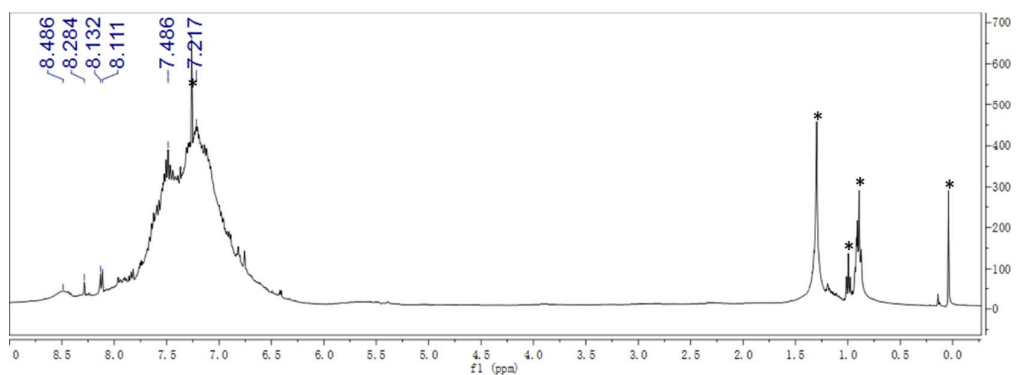
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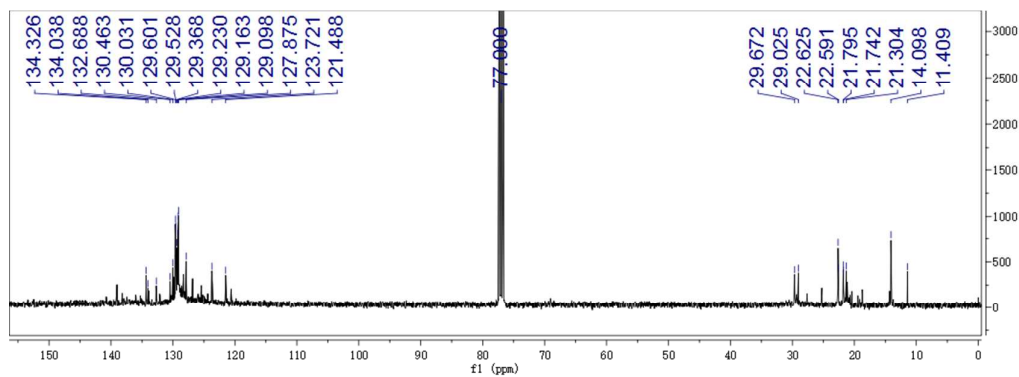
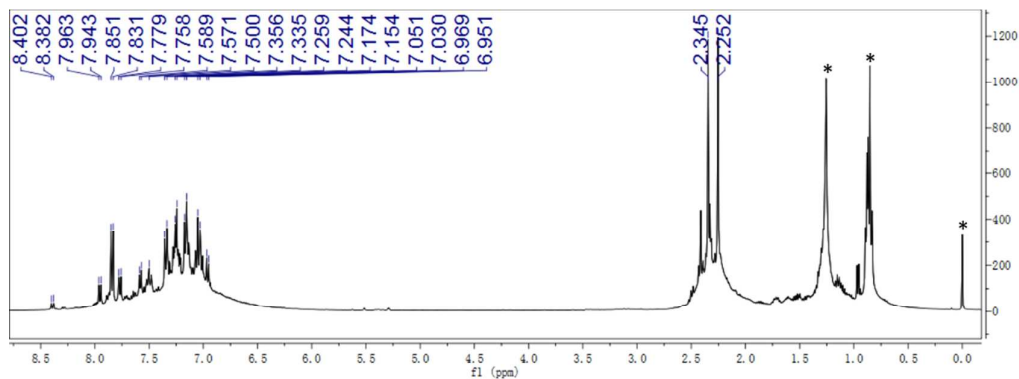
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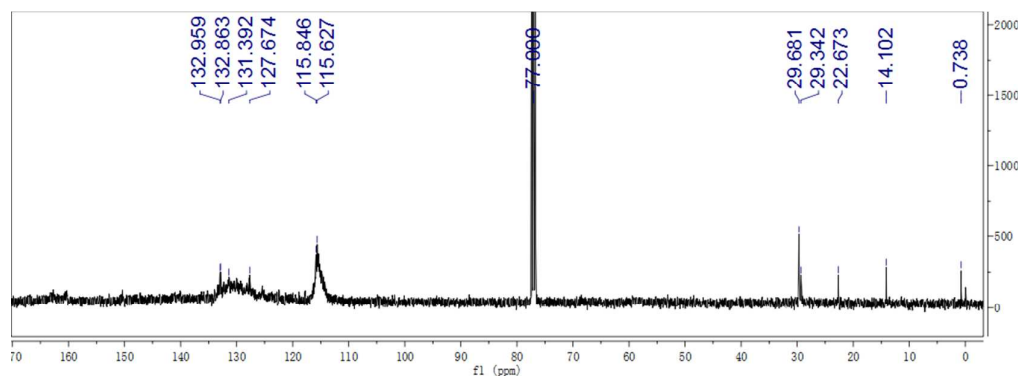
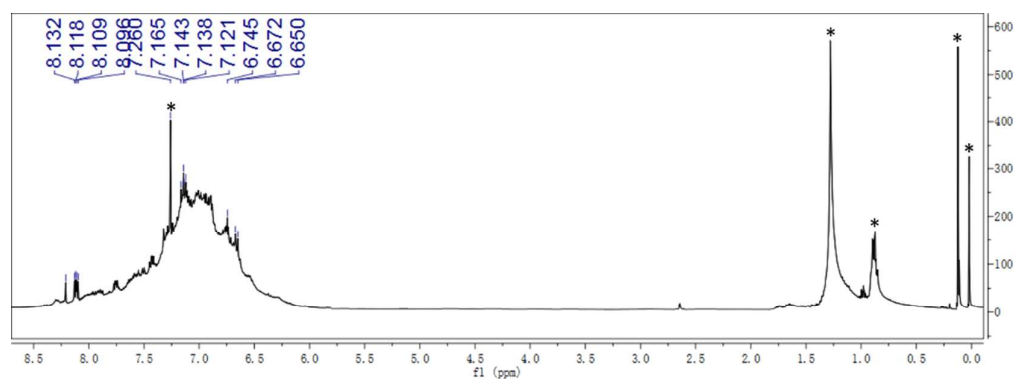
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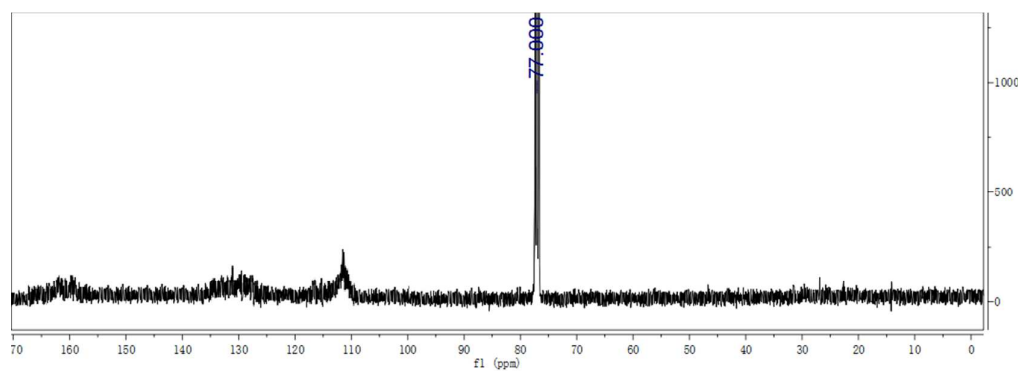
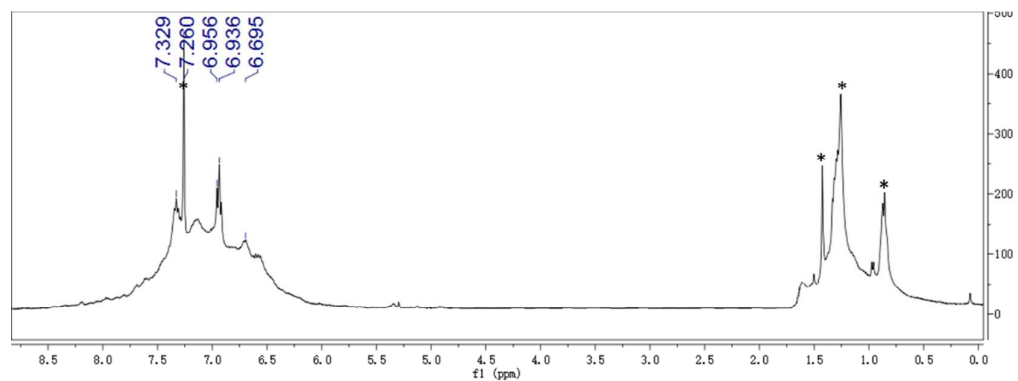
P10



P11

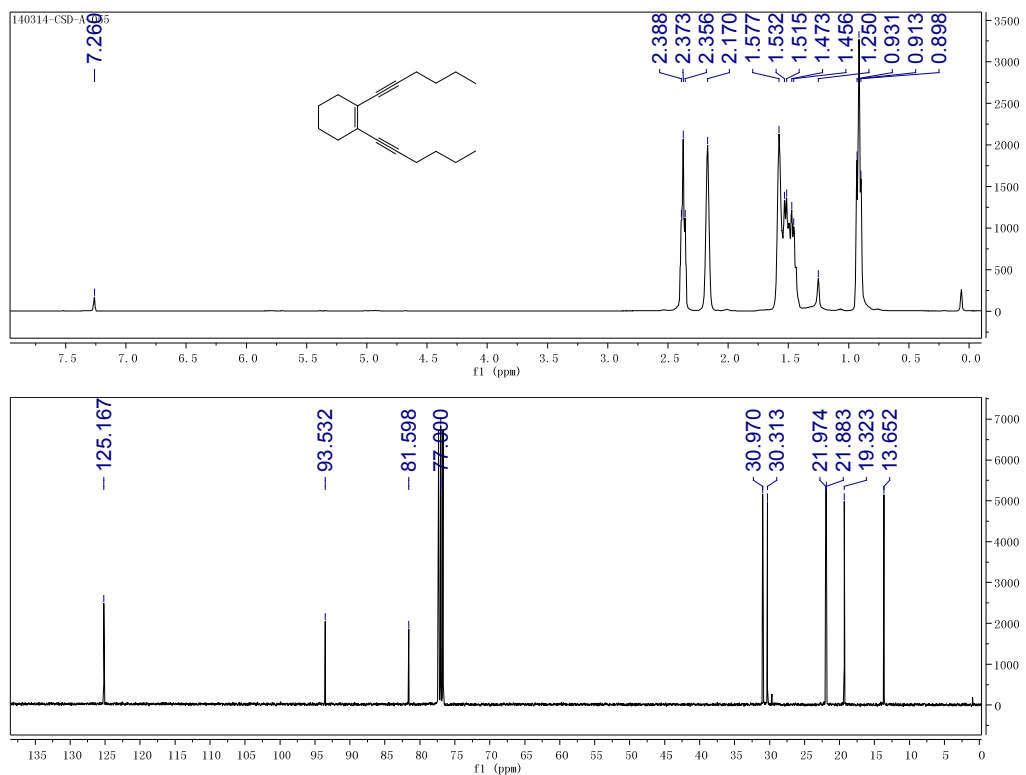


P12 (precipitated by hexane)

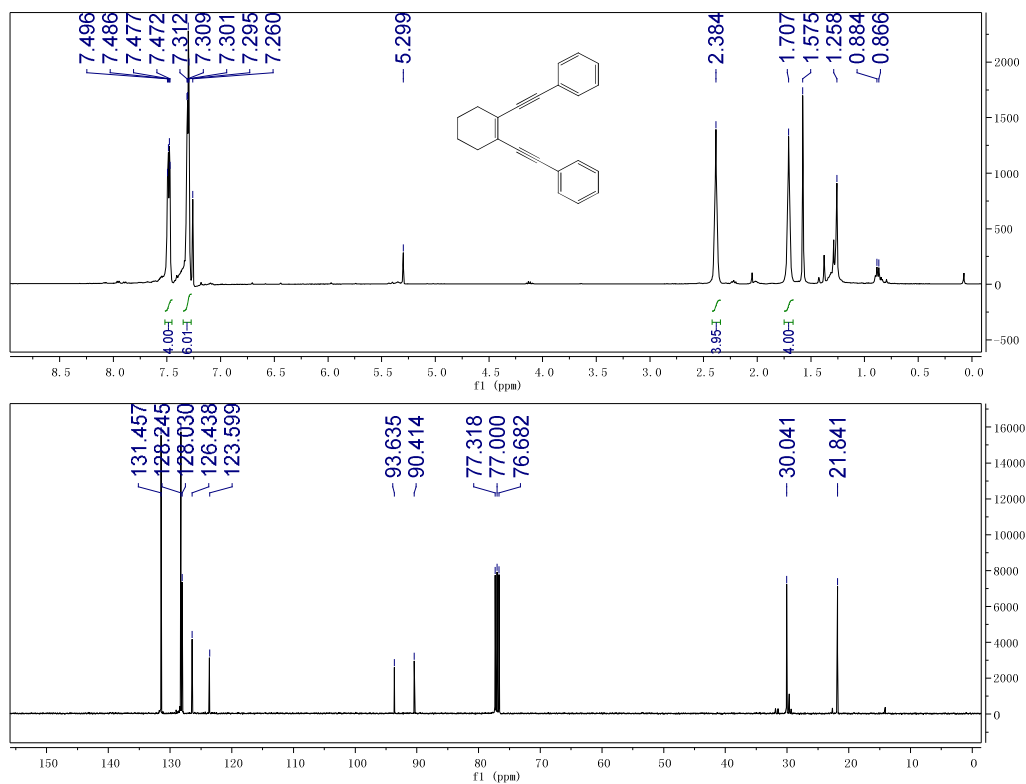


# NMR spectra of enediynes:

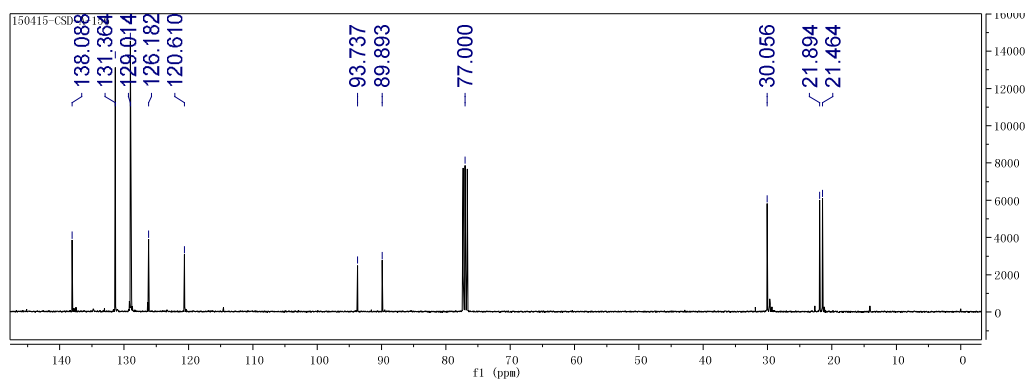
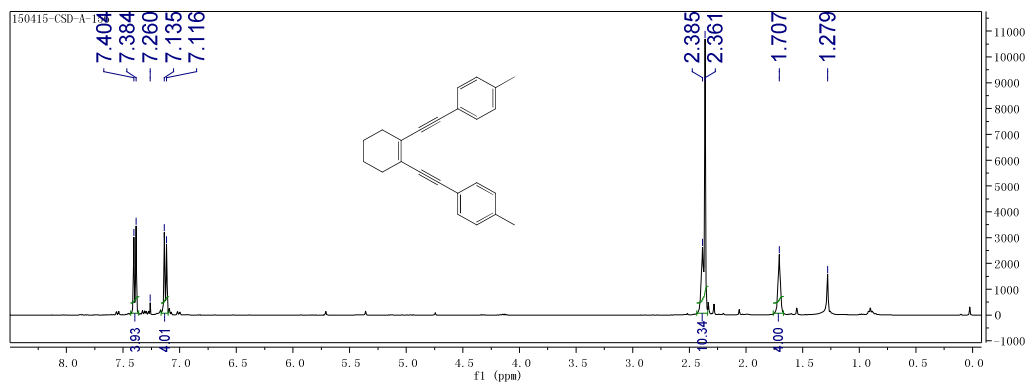
## EDY1



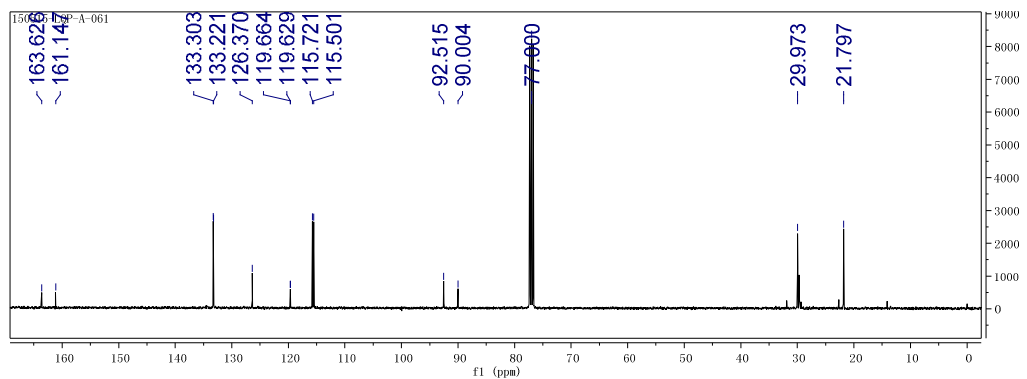
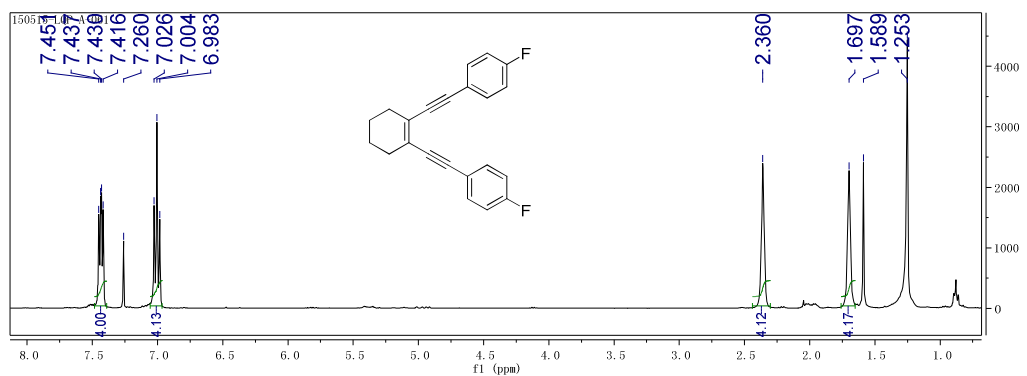
## EDY2



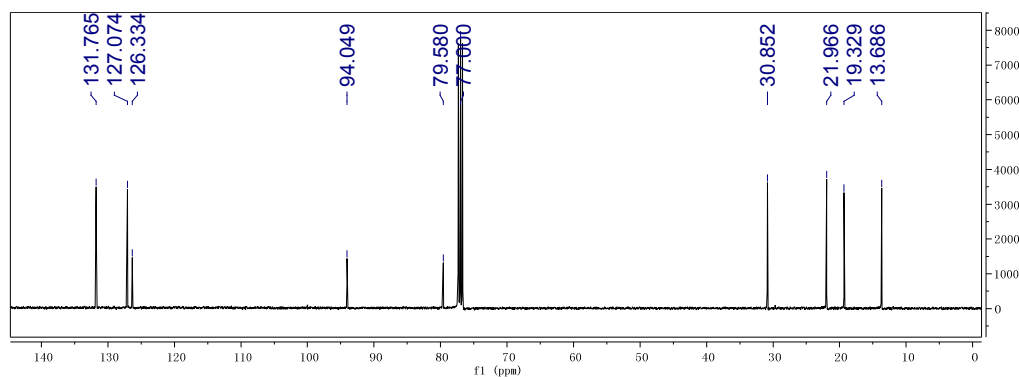
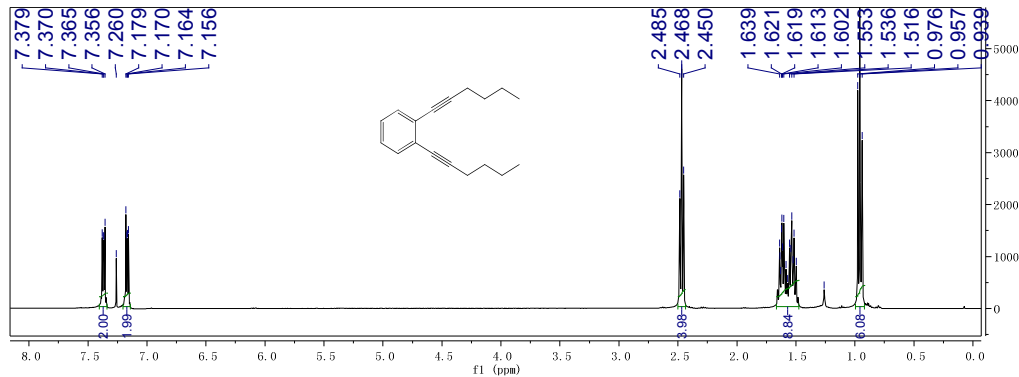
# EDY3



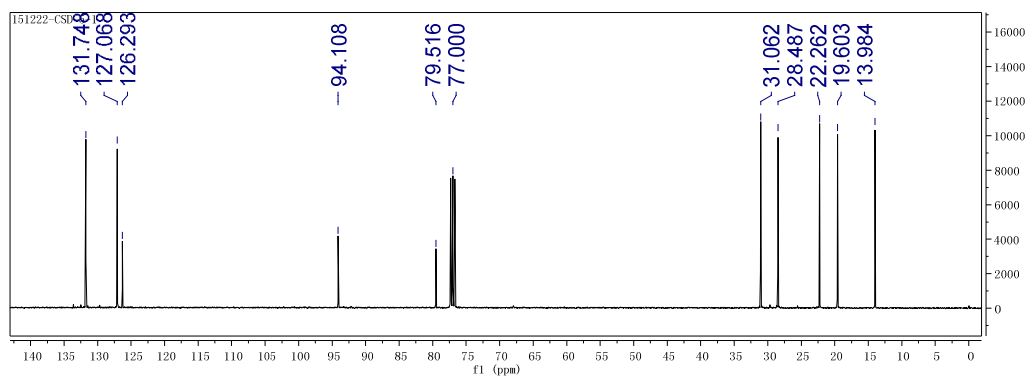
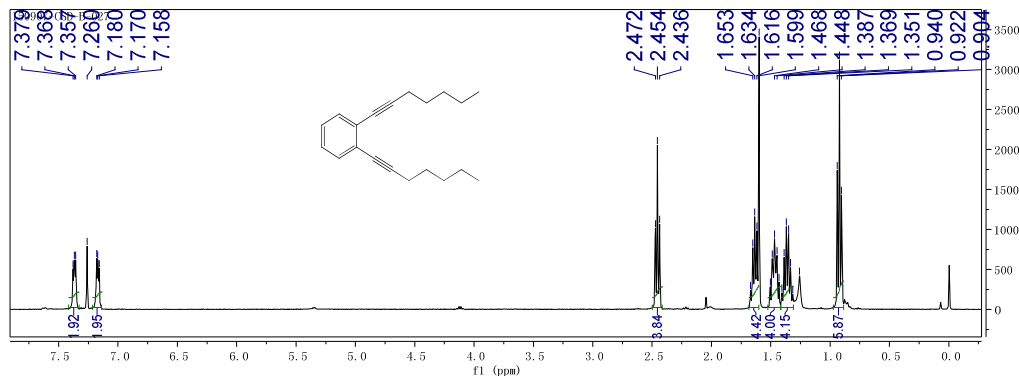
# EDY4



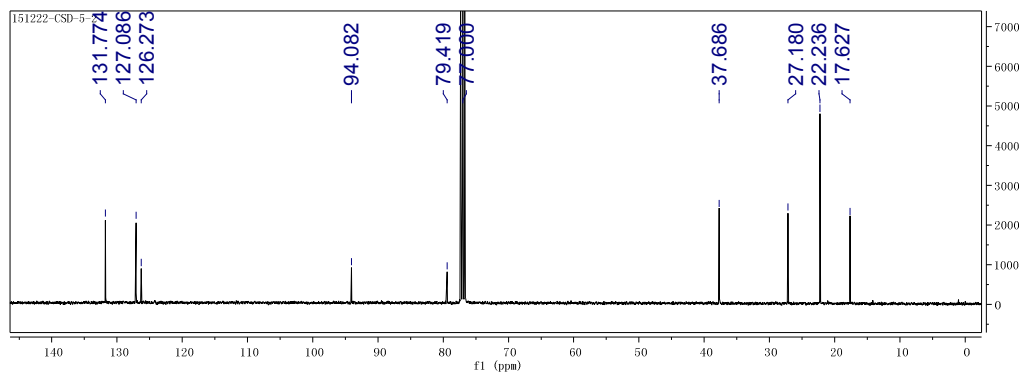
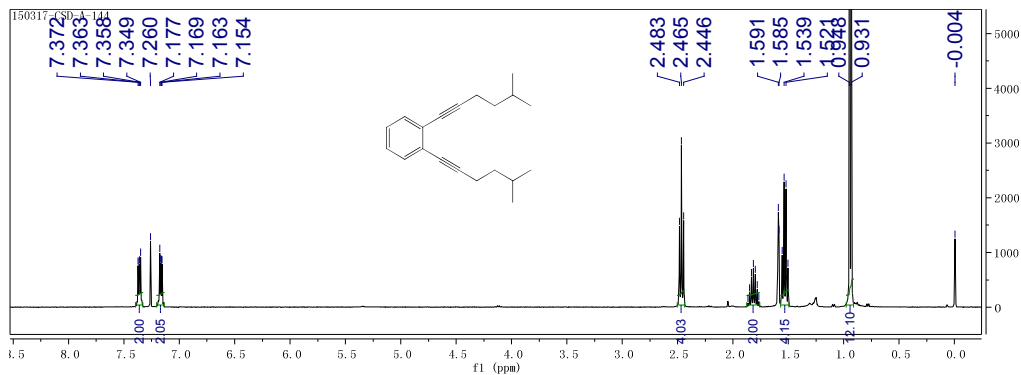
# EDY5



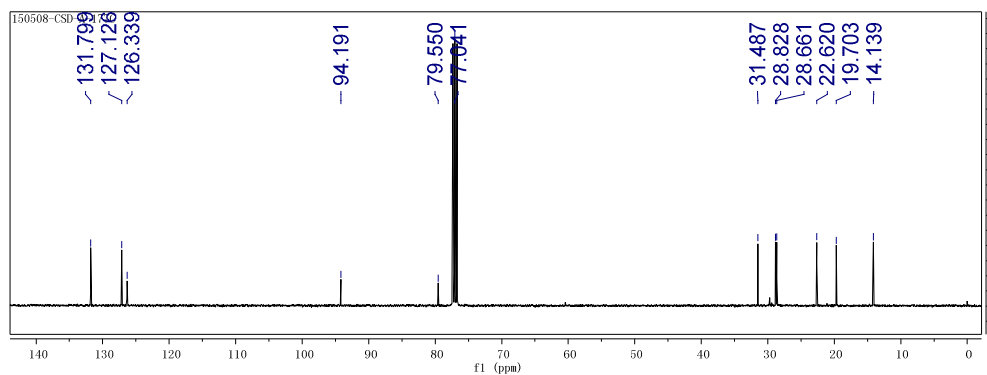
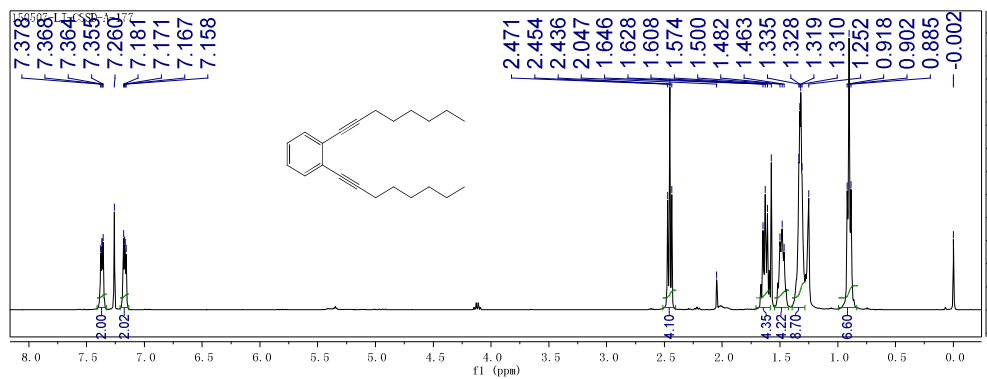
# EDY6



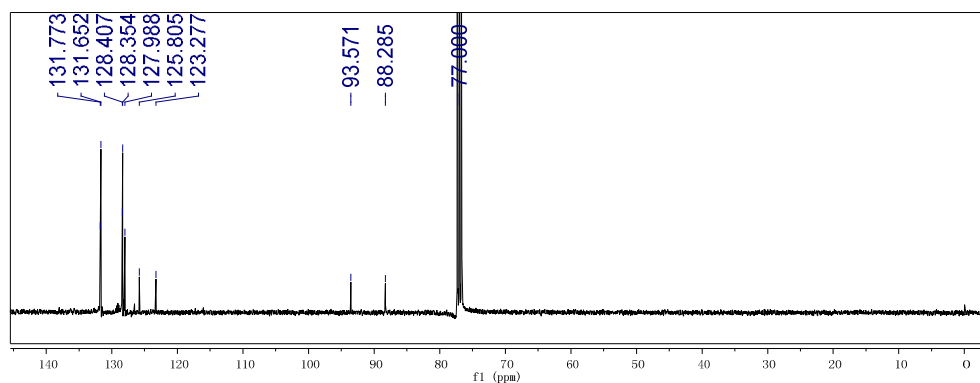
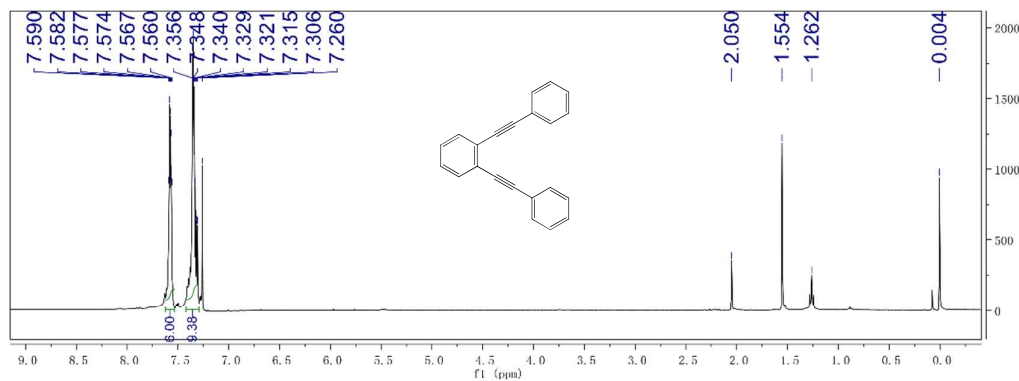
# EDY7



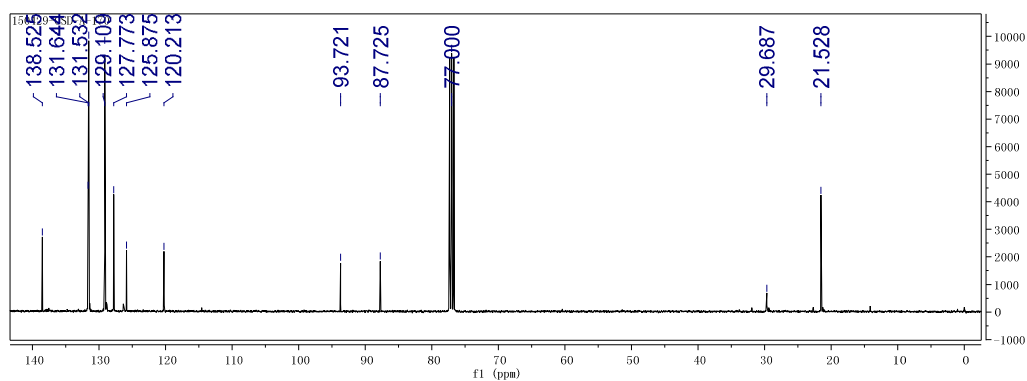
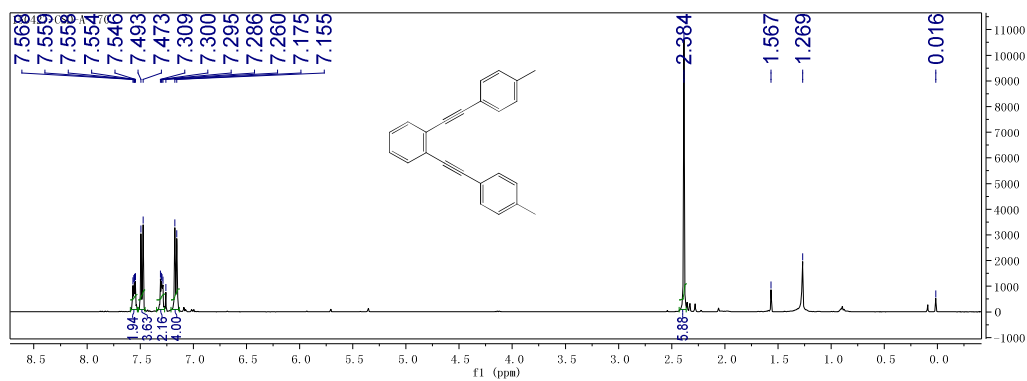
# EDY8



# EDY9

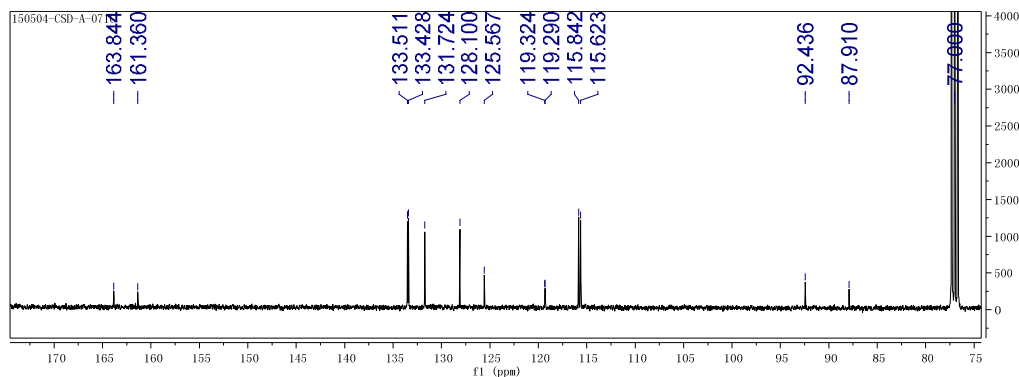
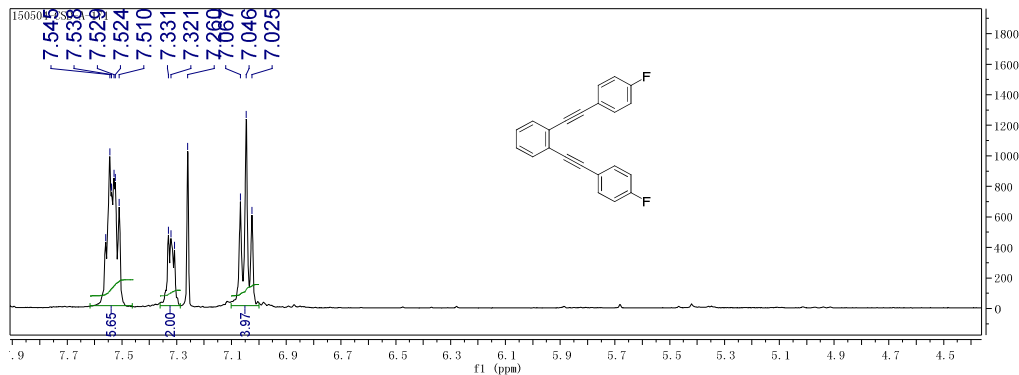


# EDY10

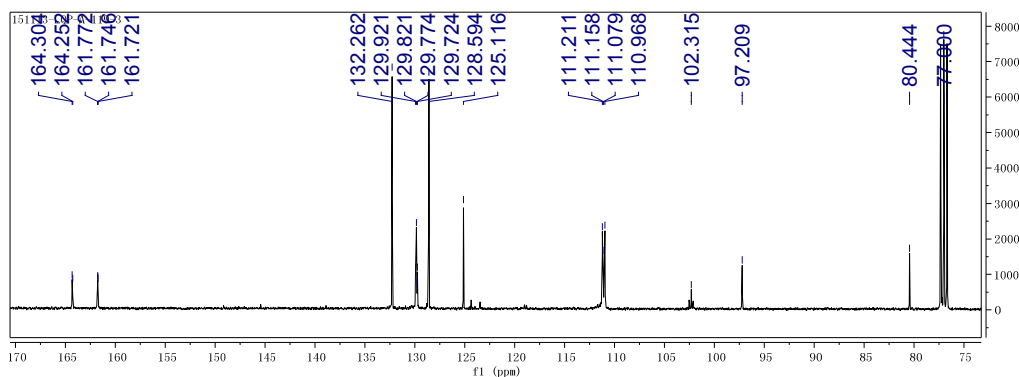
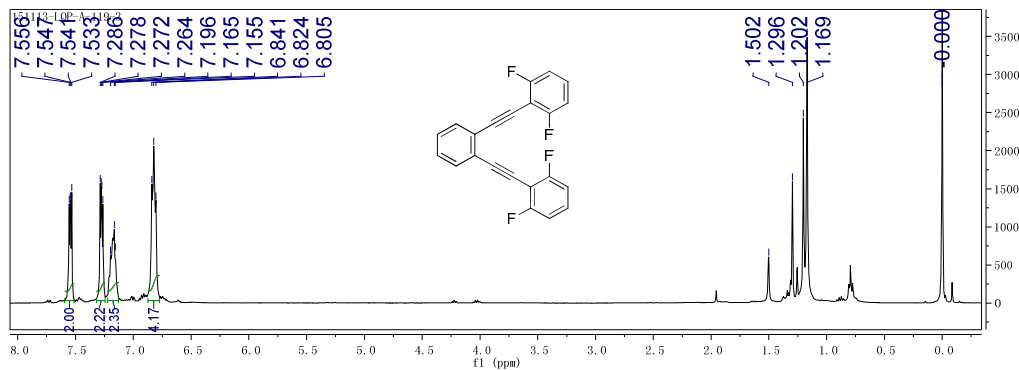




# EDY11



# EDY12



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