**Electronic Supplementary Information**

**for**

# Synthesis and Characterization of Poly(Ethene-Ketone-Arylene-Ketone)s Containing Pendant Methylthio Groups via Metal-Free Catalyzed Copolymerization of Aryldiynes with DMSO

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## 1 Experimental

### 1.1 Materials

Unless stated otherwise, all chemicals were obtained from commercial suppliers and used without further purification. The monomers **M-1 - 10** were synthesized according to the commonly used synthetic routes as shown in Scheme S1 - S10. Dimethyl sulfoxide (DMSO) and $I_2$ were bought from Energy Chemical. $BF_3 \cdot Et_2O$ was bought from Aladdin. Chloroform-d was bought from Innochem.

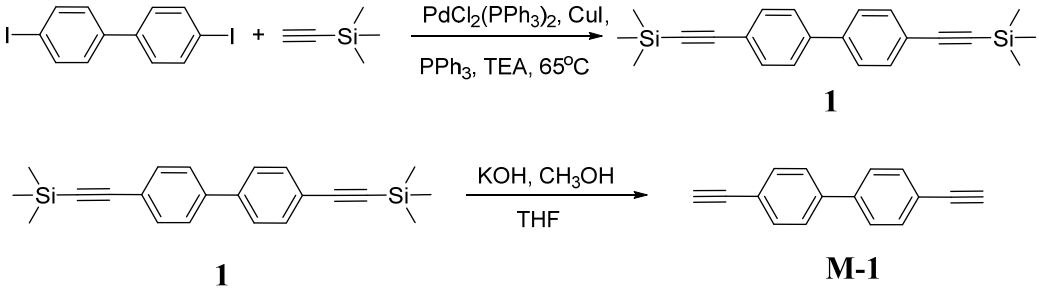
### 1.2 Equipments

Weight-average molecular weights ($M_w$) and polydispersity indices ($M_w/M_n$) of the polymers were obtained from gel permeation chromatography (GPC) system equipped with a Waters 1515 isocratic HPLC pump and Waters 2414 refractive index detector. Polystyrene standard was utilized and THF was used as the eluent at a flow rate of 1.0 mL min$^{-1}$. Fourier transform infrared (FT-IR) spectra were measured on a Bruker (ALPHA) spectrometer. $^{1}$H NMR spectra were measured on a Bruker AV 400 spectrometer. Mass spectra were collected by using a Finnigan BIFLEX III mass spectrometer. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer STA 8000 and mass spectrometer was carried out on a PerkinElmer Clarus SQ 8T at a heating rate of 10 $^{o}$C min$^{-1}$ under a nitrogen flow. UV-Vis spectra were recorded on a TU-1901 double beam UV-Vis spectrophotometer. Fluorescence spectra were

measured on a Hitachi F-7000 fluorescence spectrophotometer. Refractive index was measured on a SENTECH SE 850 DUV spectroscopic ellipsometer. The size of aggregates was measured by a Malvern ZEN3600 Zetasizer. Morphologies of the films were imaged on a FEI Quanta 450 scanning electron microscope (SEM) operating at an accelerating voltage of 5 kV.

### 1.3 Synthesis of Monomers M-1~10

#### 1.3.1 Preparation of 4,4'-diethynylbiphenyl (M-1)




**1** **M-1**

**Scheme S1.** The synthetic route to **M-1**

To a 500 mL round-bottom flask were added 4,4'-Diiodobiphenyl (8.1201 g, 20 mmol), $PdCl_2(PPh_3)_2$ (356.0 mg, 0.5 mmol), CuI (95.0 mg, 0.5 mmol), $PPh_3$ (262.0 mg, 1 mmol) and anaerobic TEA (150 mL) under nitrogen atmosphere. The reaction mixture was heated under stirring to 65 °C. The (trimethylsilyl)acetylene (8.48 mL, 60 mmol) was injected into the flask after 30 min. After 24 hours, product **1** was separated by flash column chromatograph. Yield: 77%.

Product **1** (3.4600 g, 10 mmol), KOH (560.0 mg, 10 mmol,), methanol (50 mL) and THF (50 mL) were added to a 500 mL flask. The reaction mixture was stirred at room temperature. After 12 hours, the organic layer was combined and washed with brine and water, and then dried over $MgSO_4$ for an hour. Product **M-1** was separated by flash column chromatograph. Yield: 98%. $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.53 (m, 8H), 3.16 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 140.60, 132.73, 126.98, 121.57, 83.48, 78.22. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{16}H_{10}$: 202.0783, Found: 202.0783, error: 0 ppm.

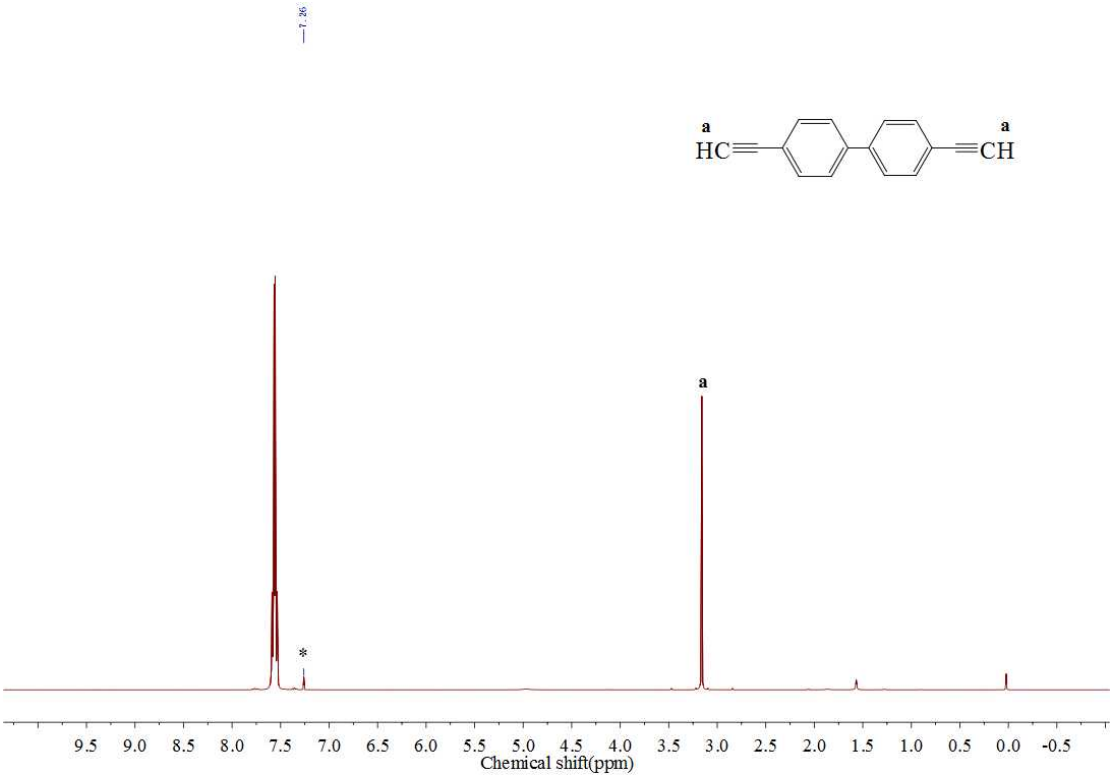



**Figure S1.** $^{1}$H NMR spectrum of **M-1** in $CDCl_3$

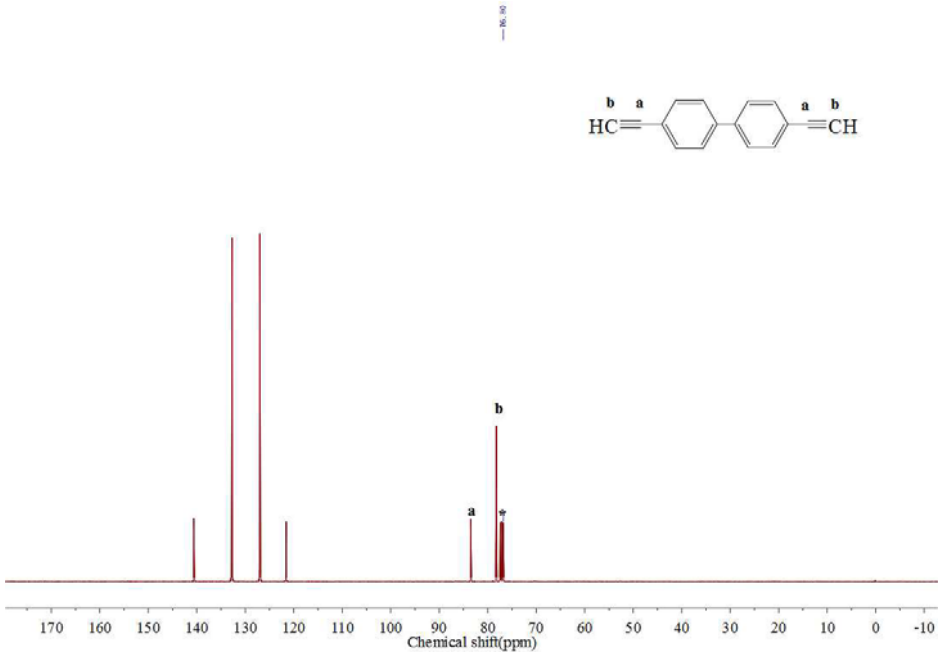



**Figure S2.** $^{13}$C NMR spectrum of **M-1** in $CDCl_3$

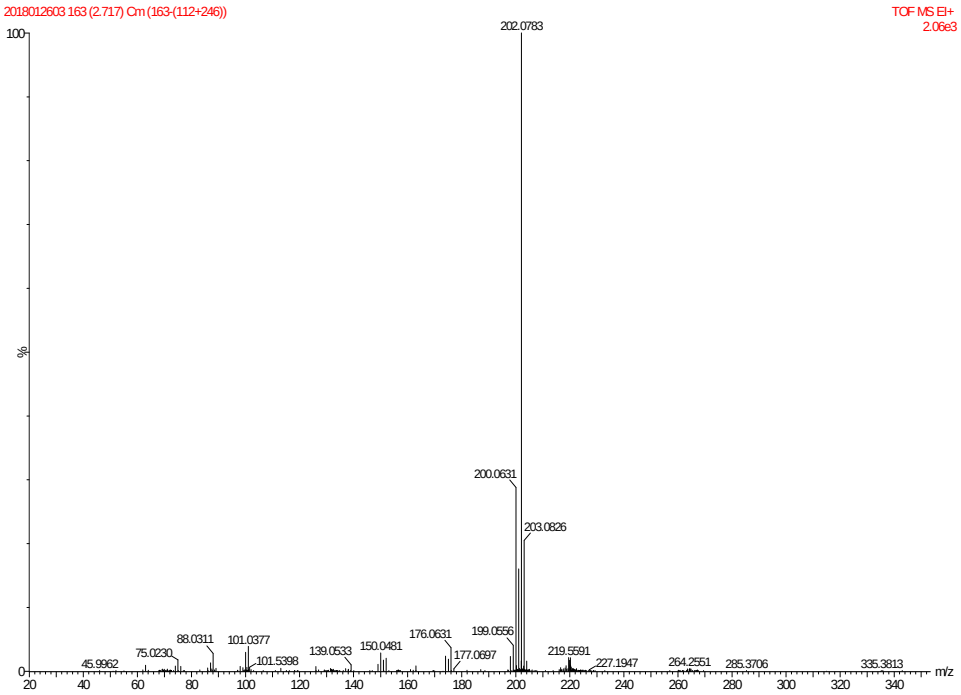
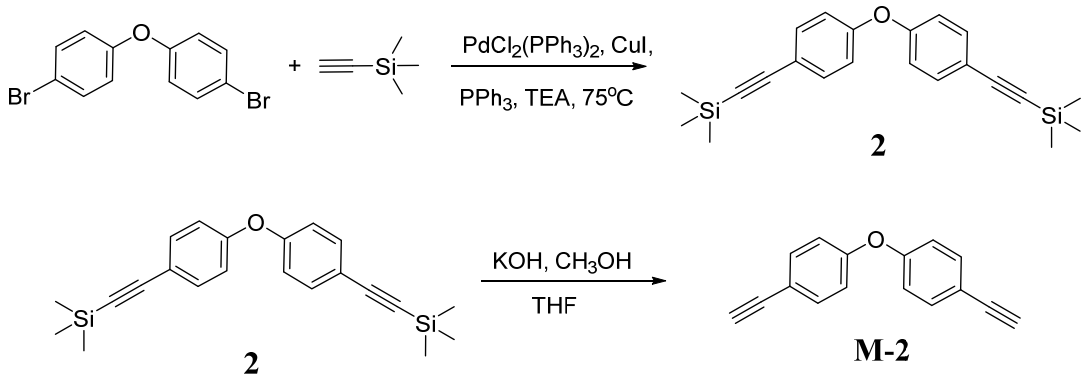



**Figure S3.** MS spectrum of **M-1**.

### 1.3.2 Preparation of 4,4'-diethynyldiphenyl ether (M-2)




**Scheme S2.** The synthetic route to **M-2**

To a 500 mL round-bottom flask were added bis(4-bromophenyl) ether (6.5600 g, 20 mmol), $PdCl_2(PPh_3)_2$ (356.0 mg, 0.5 mmol), CuI (95.0 mg, 0.5 mmol), $PPh_3$ (262.0 mg, 1 mmol) and anaerobic TEA (150 mL) under nitrogen atmosphere. The reaction mixture was heated under stirring to 75 °C. The (trimethylsilyl)acetylene (8.48 mL, 60 mmol) was injected into the flask after 30 min. After 24 hours, product **2** was separated by flash column chromatograph. Yield: 77%.

Product **2** (3.6200 g, 10 mmol,), KOH (560.0 mg, 10 mmol), methanol (50 mL) and THF (50 mL) were added into a 500 mL flask. The reaction mixture was stirred at

room temperature. After 12 hours, the organic layer was combined and washed with brine and water, and then dried over $MgSO_4$ for an hour. Product **M-2** was separated by flash column chromatograph. Yield: 95%. $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.46 (d, *J* = 8.4 Hz, 2H), 6.95-6.93 (d, *J* = 8.4 Hz, 2H), 3.16 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 157.07, 133.95, 118.95, 117.43, 83.12, 77.00. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{16}H_{10}O$: 218.0732, Found: 218.0732, error: 0 ppm.

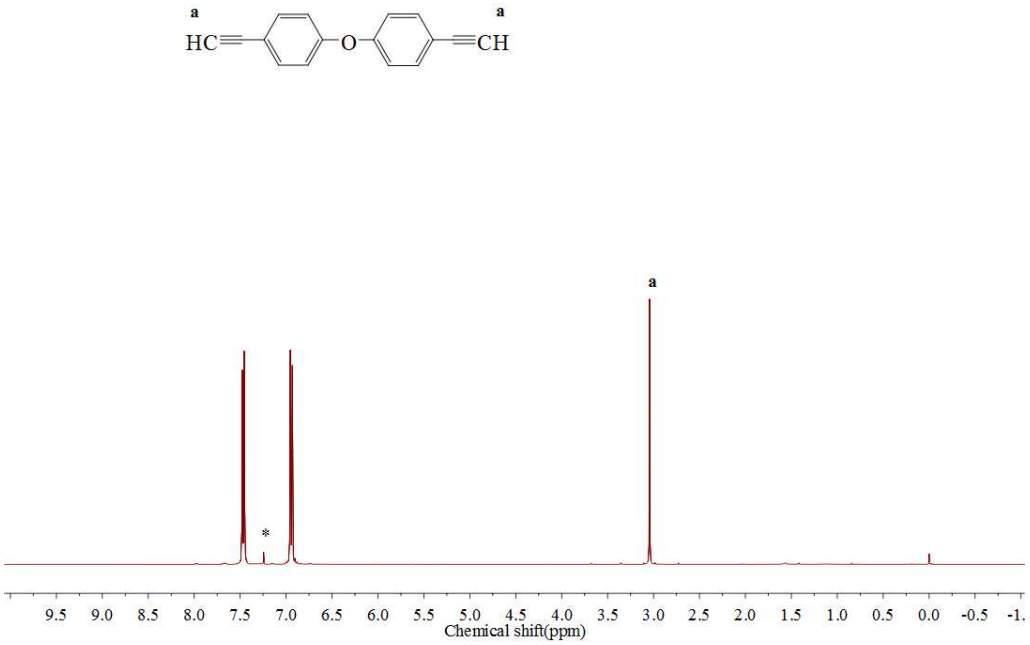



**Figure S4.** $^1$H NMR spectrum of **M-2** in $CDCl_3$

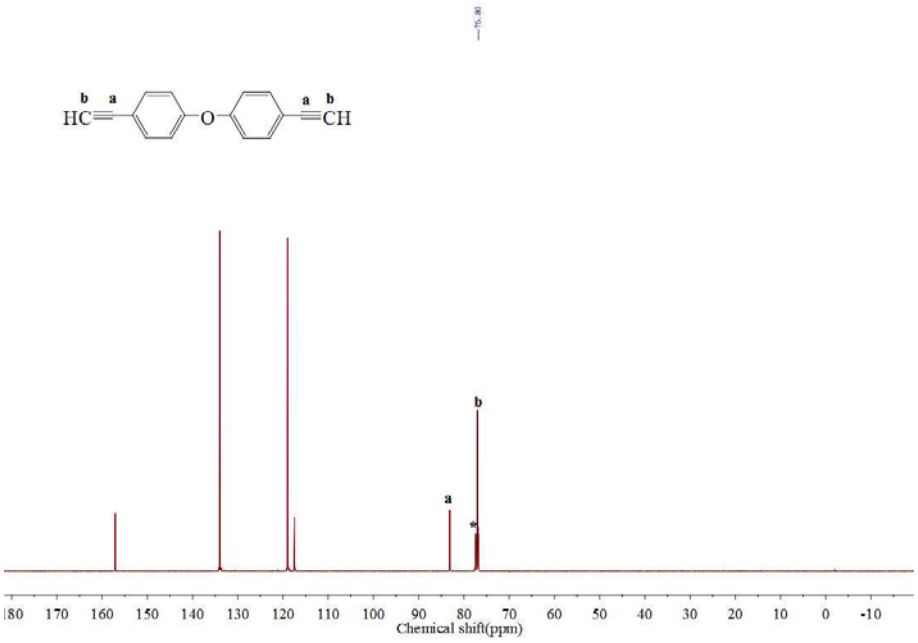



**Figure S5.** $^{13}$C NMR spectrum of **M-2** in $CDCl_3$

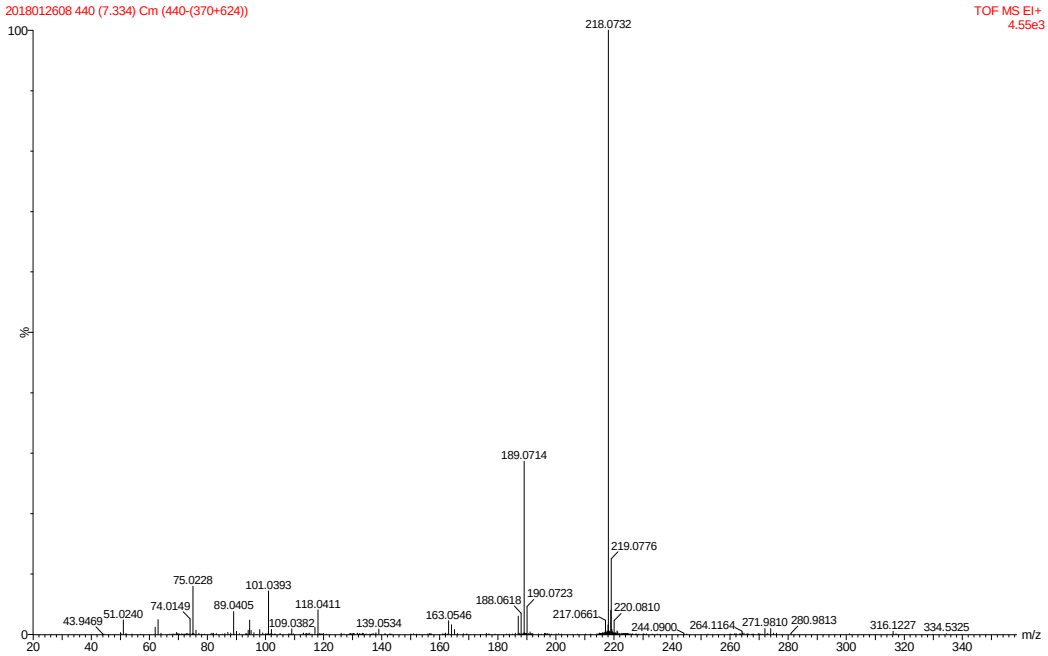
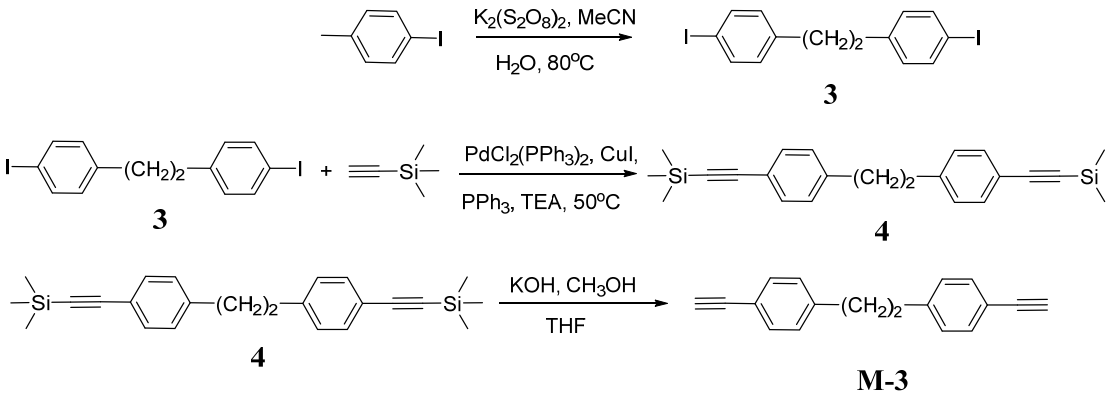



**Figure S6.** MS spectrum of **M-2**.

### 1.3.3 Preparation of 1,2-Bis(4-ethynylphenyl)ethane M-3




**Scheme S3.** The synthetic route to **M-3**

To a 500 mL round-bottom flask were added 4-iodotoluene (4.3600 g, 20 mmol), $K_2(S_2O_8)_2$ (10.8000 g, 40 mmol), MeCN (80 mL) and water (10 mL). The reaction mixture was heated at 80 ºC. After 12 hours, $K_2(S_2O_8)_2$ was removed by filtration. Product **3** was recrystallized from acetone. Yield: 35%.

To a 500 mL round-bottom flask were added **3** (3.5600 g, 10 mmol), $PdCl_2(PPh_3)_2$ (175.0 mg, 0.25 mmol), CuI (47.5 mg, 0.25 mmol), $PPh_3$ (131.0 mg, 0.5 mmol) and anaerobic TEA (80 mL) under nitrogen atmosphere. The reaction mixture

was heated under stirring to 50 ºC. The (trimethylsilyl)acetylene (4.24 mL, 30 mmol) was injected into the flask after 30 min. After 24 hours, product **4** was separated by flash column chromatograph. Yield: 89%.

Product **4** (1.8700 g, 5 mmol), KOH (280.0 g, 5 mmol), methanol (25 mL) and THF (25 mL) were adding into 500 mL flask. The reaction mixture was stirred at room temperature. After 12 hours, the organic layer was combined and washed with brine and water, and then dried over $MgSO_4$ for an hour. Product **M-3** was separated by flash column chromatograph. Yield: 97%. $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.39 (m, 2H), 7.09-7.07 (m, 2H), 3.05 (s, 2H), 2.90 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 142.25, 132.19, 128.55, 119.77, 83.74, 76.84, 37.48. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{16}H_{14}$: 230.1096, Found: 230.1095, error: -0.4 ppm.

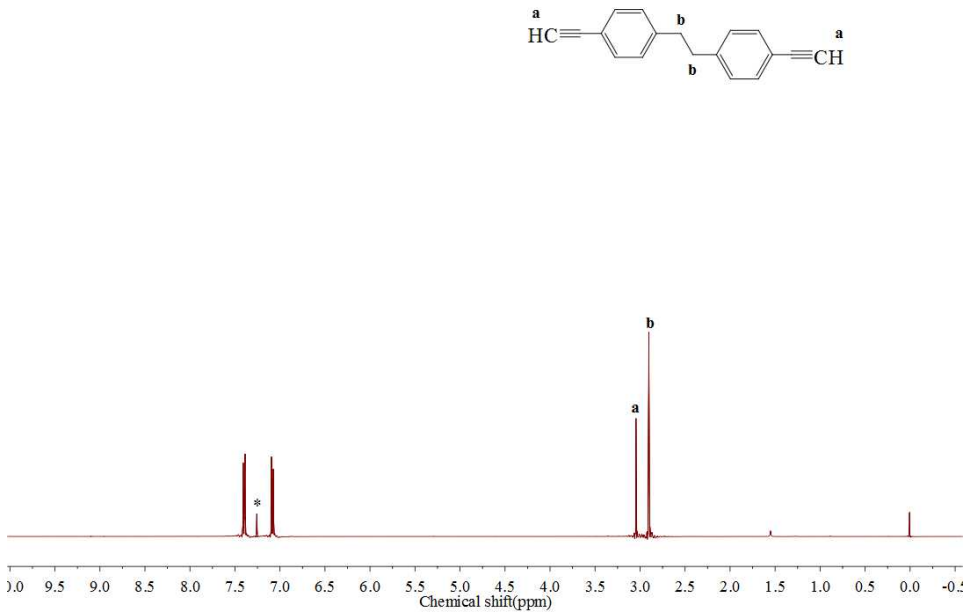



**Figure S7.** $^1$H NMR spectrum of **M-3** in $CDCl_3$.

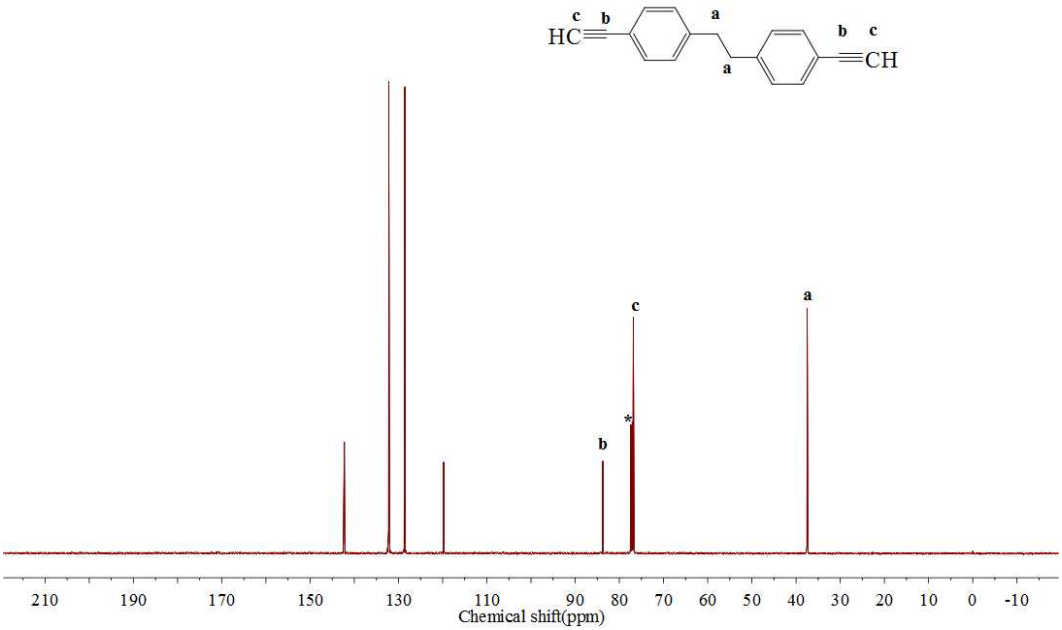



**Figure S8.** $^{13}C$ NMR spectrum of **M-3** in $CDCl_3$.

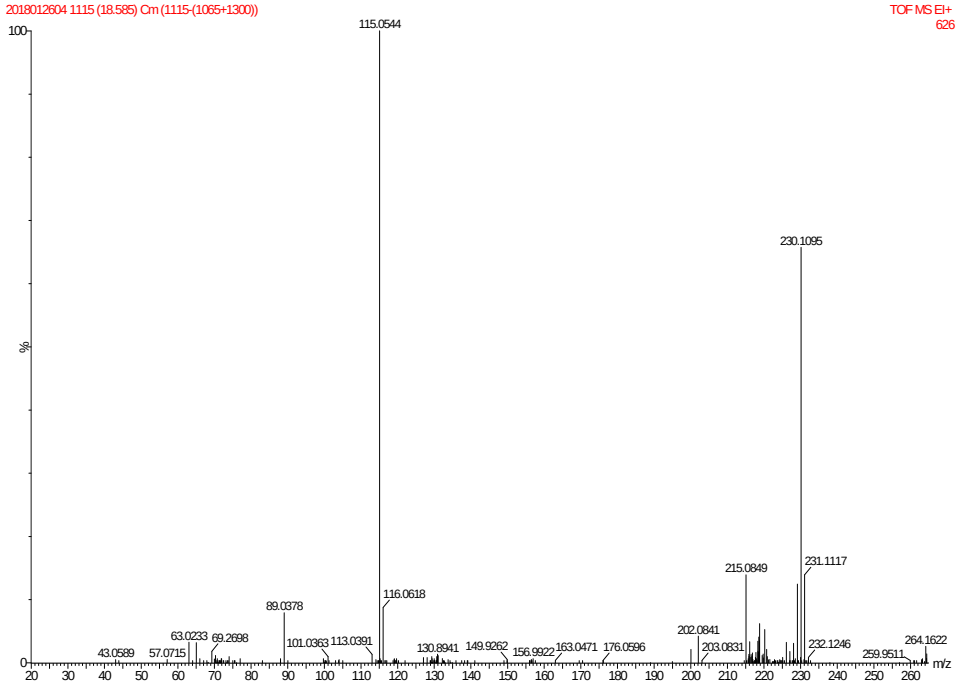
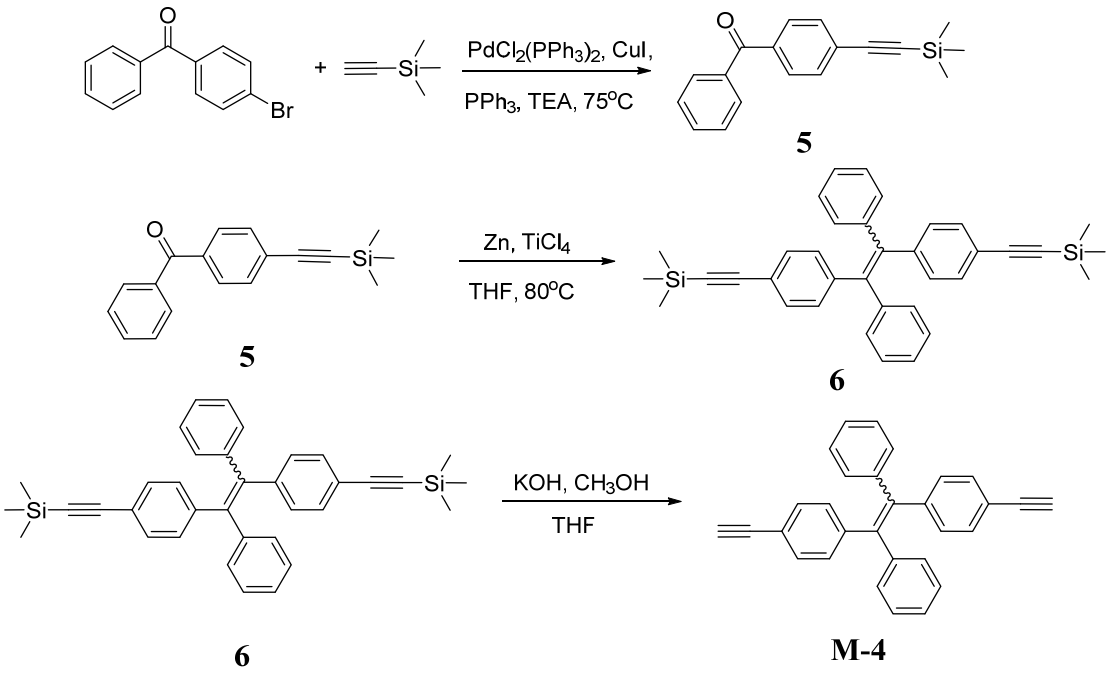



**Figure S9.** MS spectrum of **M-3**.

### 1.3.4 Preparation of 1,2-bis(4-ethynylphenyl)-1,2-diphenylethene (M-4)




**Scheme S4.** The synthetic route to **M-4**

To a 500 mL round-bottom flask were added 4-bromobenzophenone (10.4001 g, 40 mmol), $PdCl_2(PPh_3)_2$ (701.0 mg, 1 mmol), CuI (190.0 mg, 1 mmol), $PPh_3$ (524.0 mg, 2 mmol) and anaerobic TEA (250 mL) under nitrogen atmosphere. The reaction mixture was heated under stirring to 75 °C. The (trimethylsilyl)acetylene (8.48 mL, 60 mmol) was injected into the flask after 30 min. After 24 hours, product **5** was separated by flash column chromatograph. Yield: 92%.

To a 500 mL round-bottom flask were added product **5** (4.1800 g, 15 mmol), zinc powder (12.1000 g, 18 mmol), anhydrous THF (50 mL) under nitrogen atmosphere. The mixture was cooled to 0 °C and 1 mL of $TiCl_4$ (9 mmol) was slowly added. The mixture was slowly warmed to room temperature, stirred at 80 °C for 12 hours. The reaction was quenched with 10% aqueous $K_2CO_3$ solution and large amount of water was added until the solid turned to grey or white. The mixture was extracted with DCM for three times. The organic layer was combined and washed with brine twice. After solvent evaporation, the crude product **6** was purified by column chromatography. Yield: 77%.

Product **6** (5.0000 g, 10 mmol), KOH (560.0 mg, 10 mmol), methanol (50 mL)

and THF (50 mL) were adding in 500 mL flask. The reaction mixture was stirred at room temperature. After 12 hours, the organic layer was combined and washed with brine and water, and then dried over $MgSO_4$ for an hour. Product **M-4** was separated by flash column chromatograph. Yield: 96%. $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.21 (t, *J* = 8.4 Hz, 2H), 7.13-7.09 (m, 4H), 7.00-6.95 (m, 4H), 3.05-3.03 (d, *J* = 6.8 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 144.24, 144.14, 143.03, 142.94, 141.00, 131.73, 131.59, 131.36, 131.32, 128.04, 127.88, 127.01, 126.91, 120.32, 120.17, 83.79, 83.73, 77.52, 77.43. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{30}H_{20}$: 380.1565, Found: 380.1565. , error: 0 ppm.

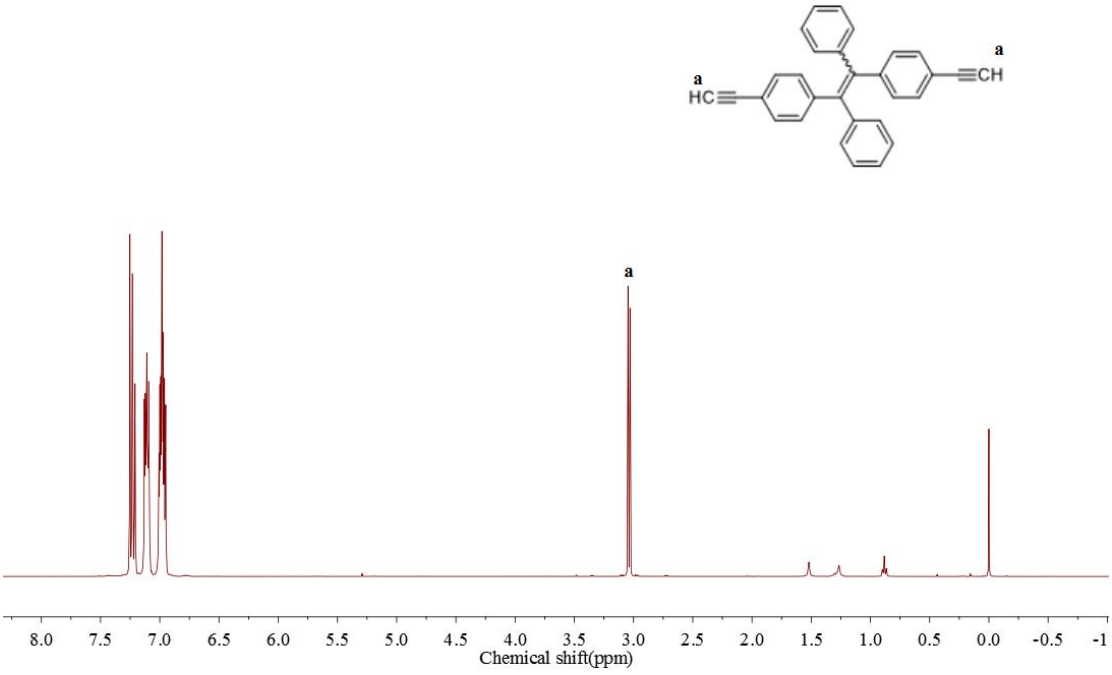



**Figure S10.** $^1$H NMR spectrum of **M-4** in $CDCl_3$.

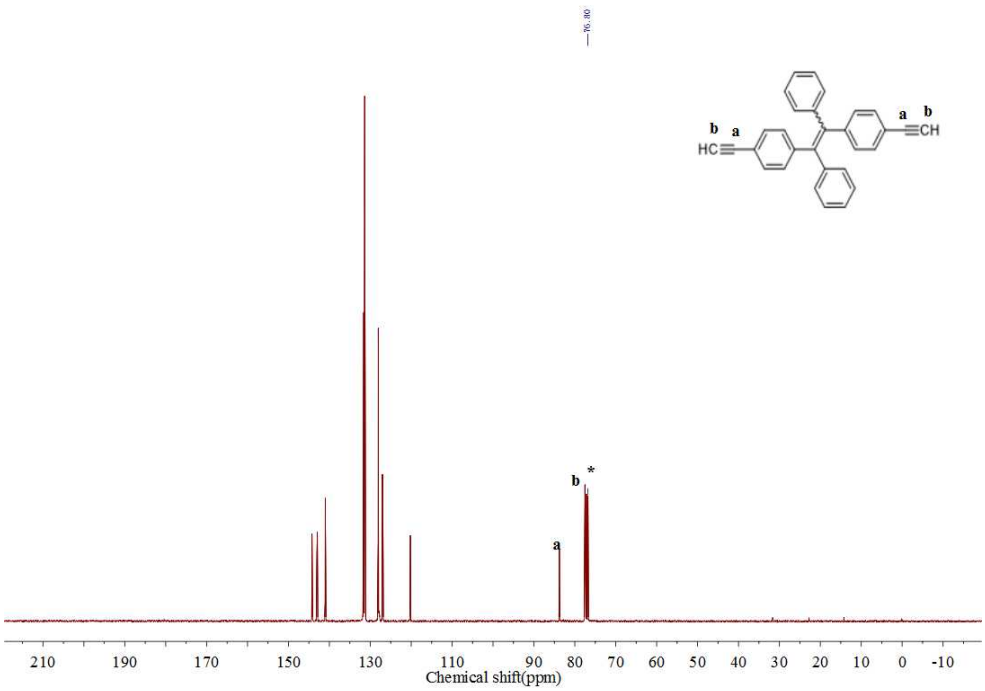



**Figure S11.** $^{13}C$ NMR spectrum of **M-4** in $CDCl_3$.

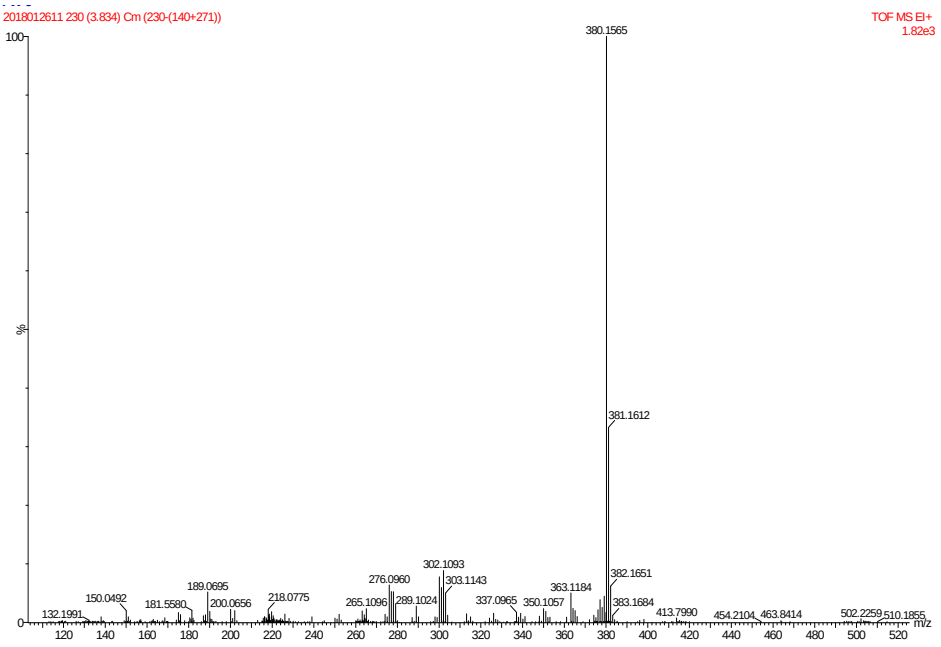
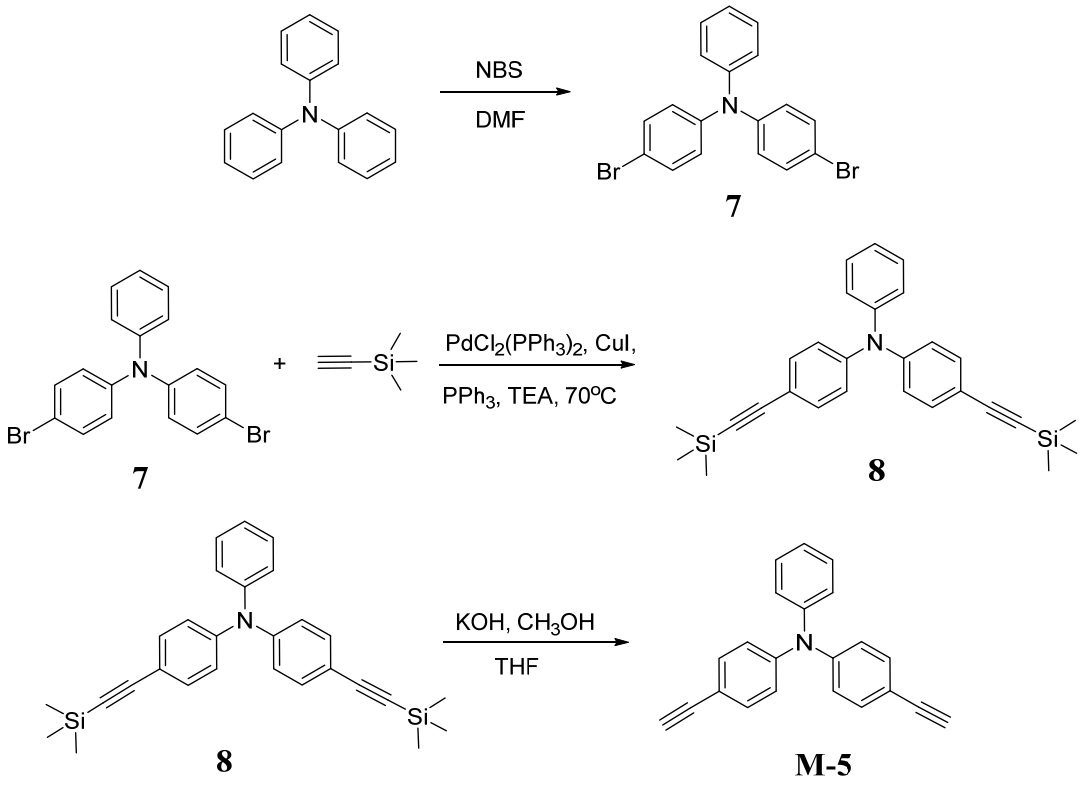



**Figure S12.** MS spectrum of **M-4**.

### 1.3.5 Preparation of 4-ethynyl-N-(4-ethynylphenyl)-N-phenylbenzenamine (M-5)




**Scheme S5.** The synthetic route to **M-5**

To a 500 mL round-bottom flask were added triphenylamine (4.9000 g, 20 mmol), N-bromobutanimide (7.0800 g, 40 mmol), DMF (30 mL). The reaction mixture was stirred at room temperature. After 12 hours, the organic layer was washed with ether and water three times, and then dried over $MgSO_4$ for an hour. The product **7** was separated by flash column chromatograph. Yield: 90%.

To a 500 mL round-bottom flask were added product **7** (4.0300 g, 10 mmol), $PdCl_2(PPh_3)_2$ (175.0 mg, 0.25 mmol), CuI (47.5 mg, 0.25 mmol), $PPh_3$ (131.0 mg, 0.5 mmol) and anaerobic TEA (80 mL) under nitrogen atmosphere. The reaction mixture was heated under stirring to 70 $^oC$. The (trimethylsilyl)acetylene (4.24 mL, 30 mmol) was injected into the flask after 30 min. After 24 hours, product **8** was separated by flash column chromatograph. Yield: 79%.

Product **8** (4.3700 g, 10 mmol), KOH (560.0 mg, 10 mmol), methanol (50 mL) and THF (50 mL) were adding in 500 mL flask. The reaction mixture was stirred at

room temperature. After 12 hours, the organic layer was combined and washed with brine and water, and then dried over $MgSO_4$ for an hour. Product **M-5** was separated by flash column chromatograph. Yield: 94%. $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.38 (d, *J* = 8.4 Hz, 4H), 7.33-7.29 (t, *J* = 8.0 Hz, 2H), 7.15-7.11 (d, *J* = 8.4 Hz, 3H), 7.04-7.02 (d, *J* = 8.0 Hz, 4H), 3.06 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 147.67, 146.60, 133.26, 129.66, 125.62, 124.39, 123.22, 116.00, 83.68, 76.70. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{22}H_{15}N$: 293.1204, Found: 293.1204, error: 0 ppm.

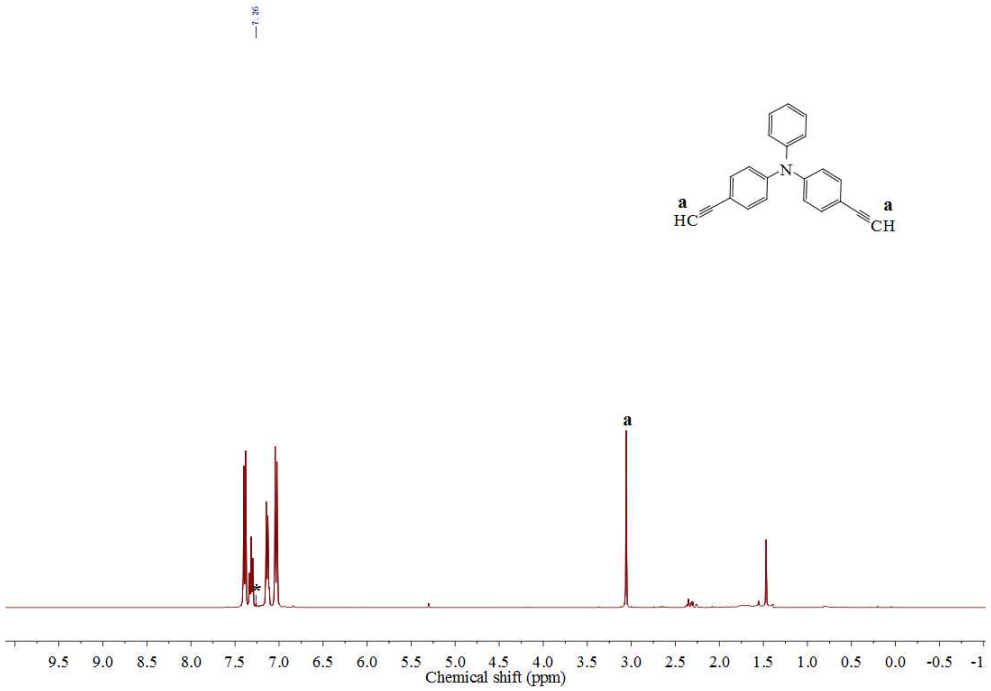



**Figure S13.** $^1$H NMR spectrum of **M-5** in $CDCl_3$.

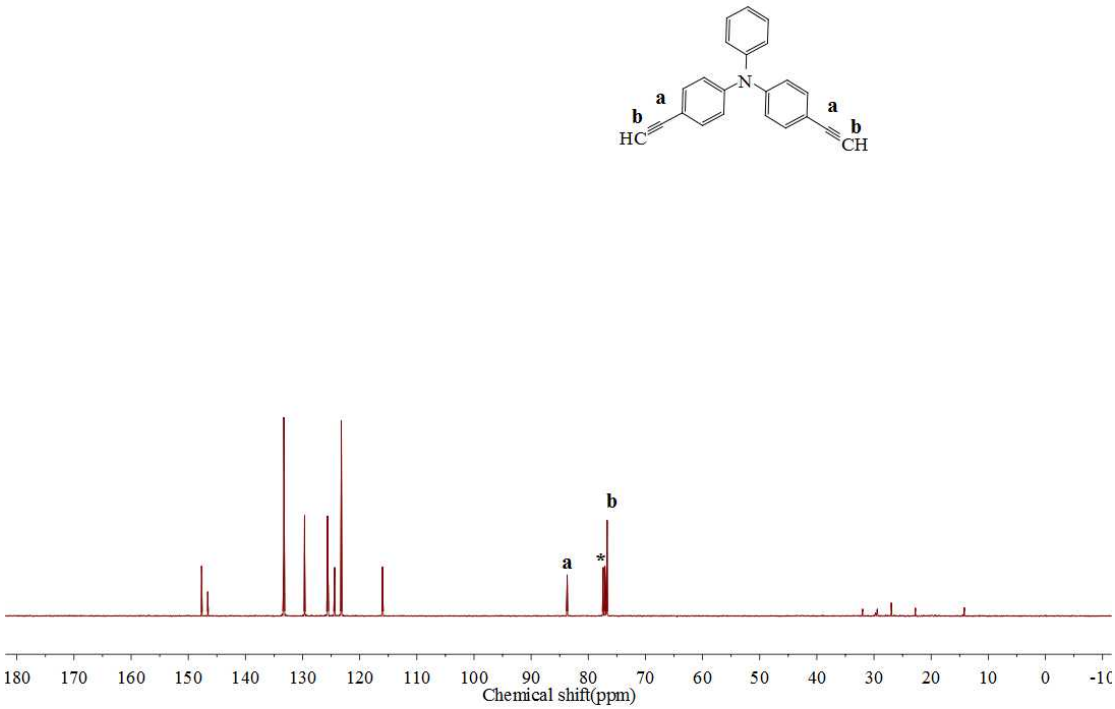



**Figure S14.** $^{13}C$ NMR spectrum of **M-5** in $CDCl_3$.

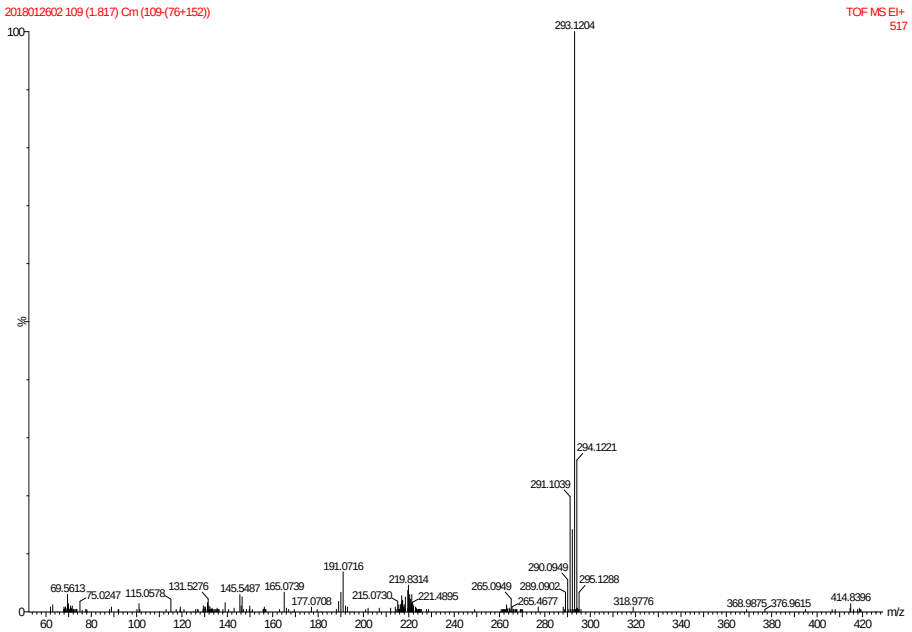
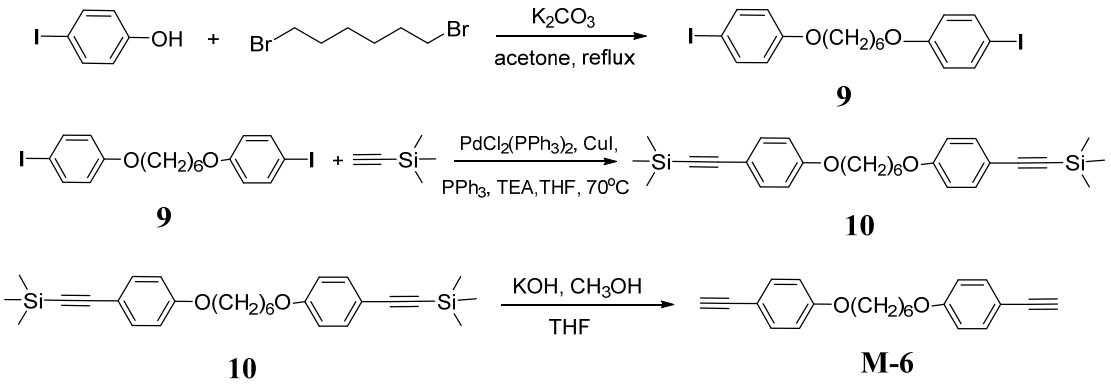



**Figure S15.** MS spectrum of **M-5**.

### 1.3.6 Preparation of 1,6-bis(4-ethynylphenoxy)hexane (M-6)




**Scheme S6.** The synthetic route to **M-6**

To a 500 mL round-bottom flask were added 4-iodophenol (8.8000 g, 40 mmol), 1,2-dibromoethane (3.7600 g, 20 mmol), $K_2CO_3$ (2.7600 g, 20 mmol ) and acetone (60 mL). The reaction mixture was refluxed for 12 hours. After 24 hours, $K_2CO_3$ was removed by filtration. Product **11** was separated by flash column chromatograph. Yield: 98%.

To a 500 mL round-bottom flask were added product **9** (5.2200 g, 10 mmol), $PdCl_2(PPh_3)_2$ (175.0 mg, 0.25 mmol), CuI (47.5 mg, 0.25 mmol), $PPh_3$ (131.0 mg, 0.5 mmol), THF (10 mL) and anaerobic TEA (80 mL) under nitrogen atmosphere. The reaction mixture was heated under stirring to 70 °C. The (trimethylsilyl)acetylene (4.24 mL, 30 mmol) was injected into the flask after 30 min. After 24 hours, product **10** was separated by flash column chromatograph. Yield: 83%.

Product **10** (2.3100 g, 5 mmol), KOH (280.0 mg, 5 mmol), methanol (25 mL) and THF (25 mL) were adding in 500 mL flask. The reaction mixture was stirred at room temperature. After 12 hours, the organic layer was combined and washed with brine and water, and then dried over $MgSO_4$ for an hour. Product **M-6** was separated by flash column chromatograph. Yield: 96%. $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.41 (d, *J* = 8.4 Hz, 4H), 6.84-6.82 (d, *J* = 8.4 Hz, 4H), 3.98-3.95 (t, *J* = 6.4 Hz, 4H), 2.99 (s, 2H), 1.83-1.80 (t, *J* = 6.4 Hz, 4H), 1.55-1.53 (t, *J* = 6.4 Hz, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 159.49, 133.61, 114.48, 114.00, 83.78, 75.80, 67.87, 29.13, 25.85. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{22}H_{22}O_2$: 318.1620, Found: 318.1621, error: +0.3 ppm.

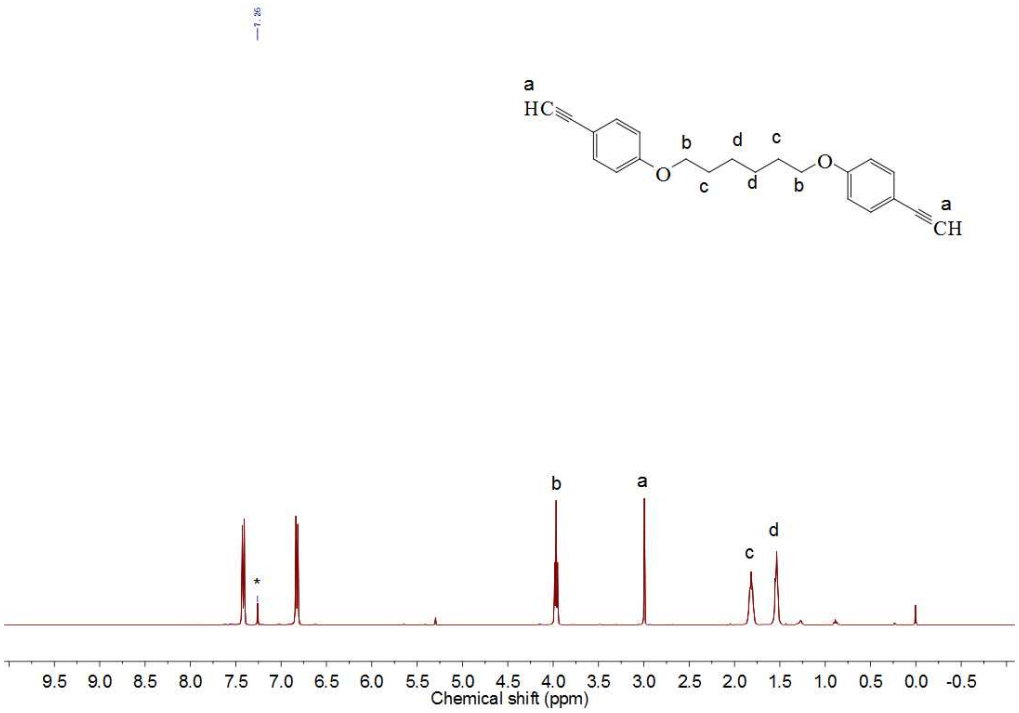



**Figure S16.** $^{1}$H NMR spectrum of **M-6** in $CDCl_3$.

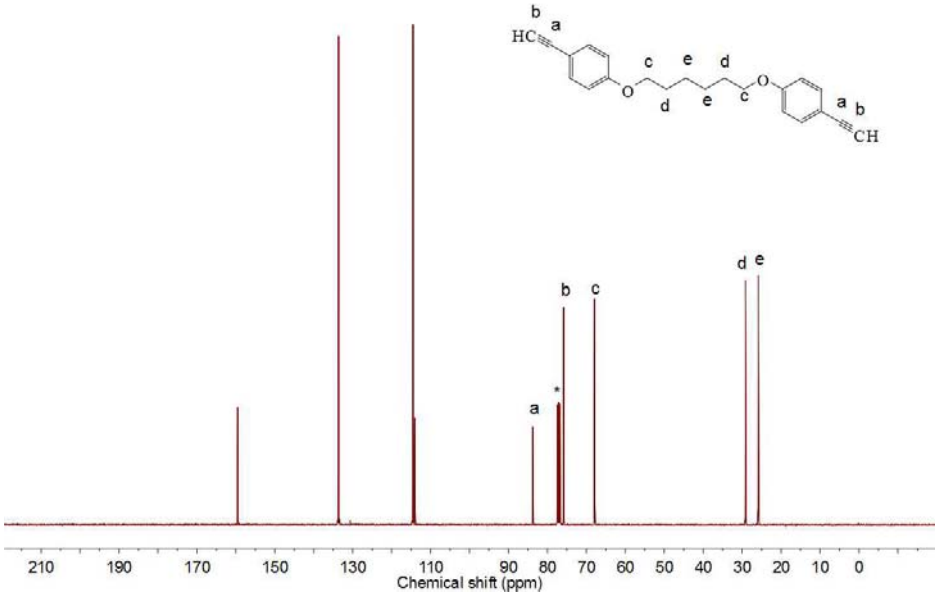



**Figure S17.** $^{13}$C NMR spectrum of **M-6** in $CDCl_3$.

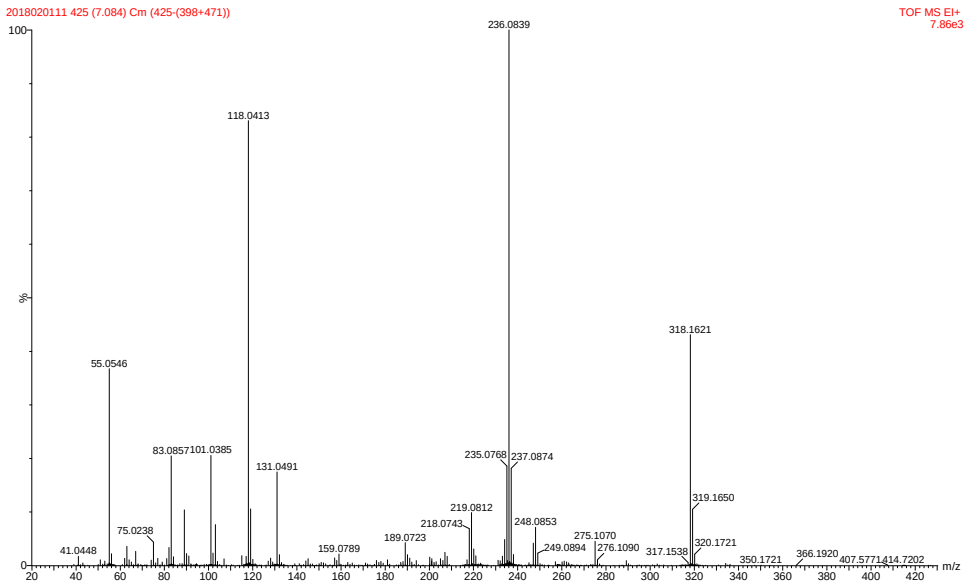
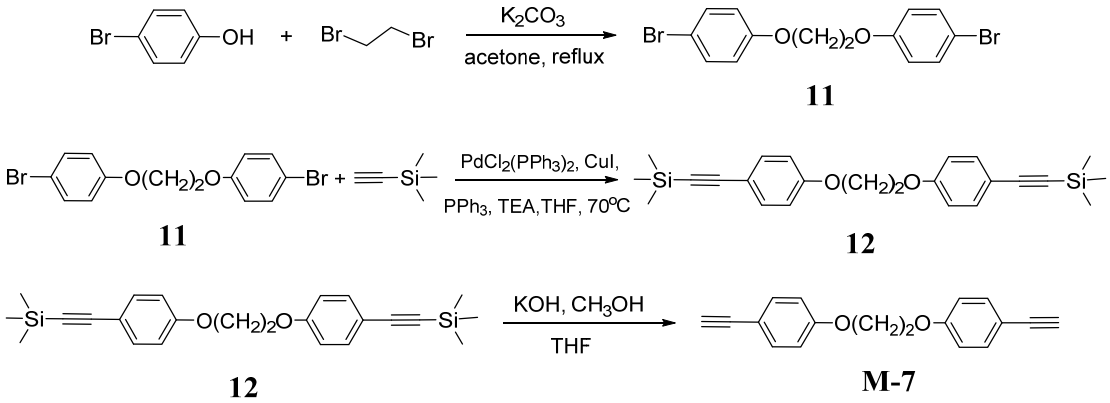



**Figure S18.** MS spectrum of **M-6**.

### 1.3.7 Preparation of 1,2-bis(4-ethynylphenoxy)ethane (M-7)




**Scheme S7.** The synthetic route to **M-7**

To a 500 mL round-bottom flask were added 4-bromophenol (6.9200 g, 40 mmol), 1,2-dibromoethane (3.7600 g, 20 mmol), $K_2CO_3$ (2.7600 g, 20 mmol) and acetone (60 mL). The reaction mixture was refluxed for 12 hours. After 24 hours, $K_2CO_3$ was removed by filtration. Product **11** was separated by flash column chromatograph. Yield: 85%.

To a 500 mL round-bottom flask were added **11** (3.8800 g, 10 mmol), $PdCl_2(PPh_3)_2$ (175.0 mg, 0.25 mmol), CuI (47.5 mg, 0.25 mmol), $PPh_3$ (131 mg, 0.5 mmol), THF (10 mL) and anaerobic TEA (80 mL) under nitrogen atmosphere. The reaction mixture was heated under stirring to 70 ºC. The (trimethylsilyl)acetylene

(4.24 mL, 30 mmol) was injected into the flask after 30 min. After 24 hours, product **12** was separated by flash column chromatograph. Yield: 69%.

Product **12** (2.0300 g, 5 mmol), KOH (280.0 mg, 5 mmol), methanol (25 mL) and THF (25 mL) were adding in 500 mL flask. The reaction mixture was stirred at room temperature. After 12 hours, the organic layer was combined and washed with brine and water, and then dried over $MgSO_4$ for an hour. The product **M-7** was separated by flash column chromatograph. Yield: 90%. $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.43 (d, *J* = 8.8 Hz, 4H), 6.90-6.88 (d, *J* = 8.4 Hz, 4H), δ = 4.32 (s, 4H), δ = 3.01 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.99, 133.75, 114.83, 114.73, 83.61, 76.10, 66.52. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{18}H_{14}O_2$: 262.0994, Found: 262.0995, error: +0.4 ppm.

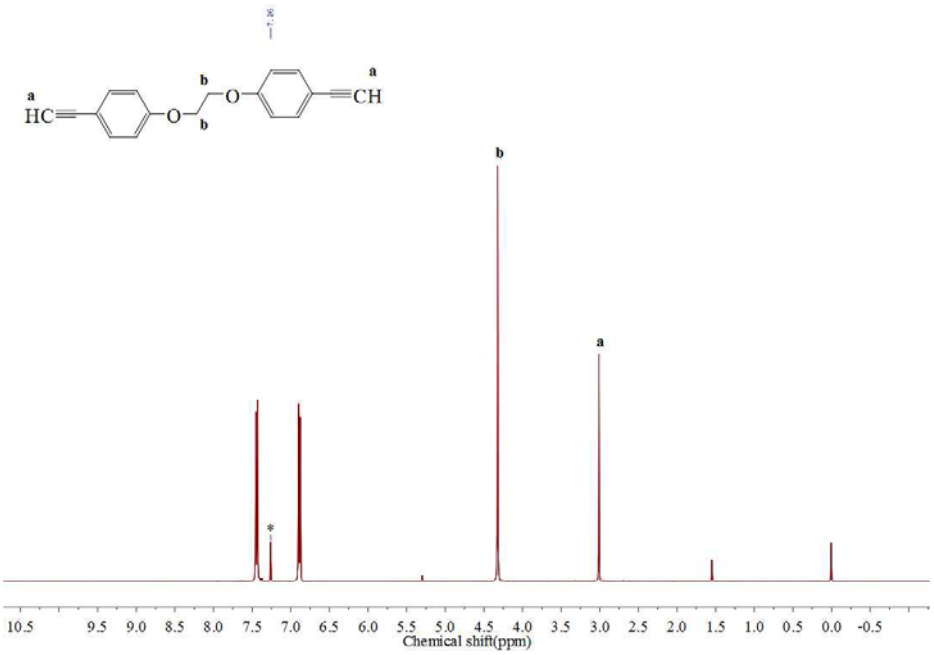



**Figure S19.** $^1$H NMR spectrum of **M-7** in $CDCl_3$.

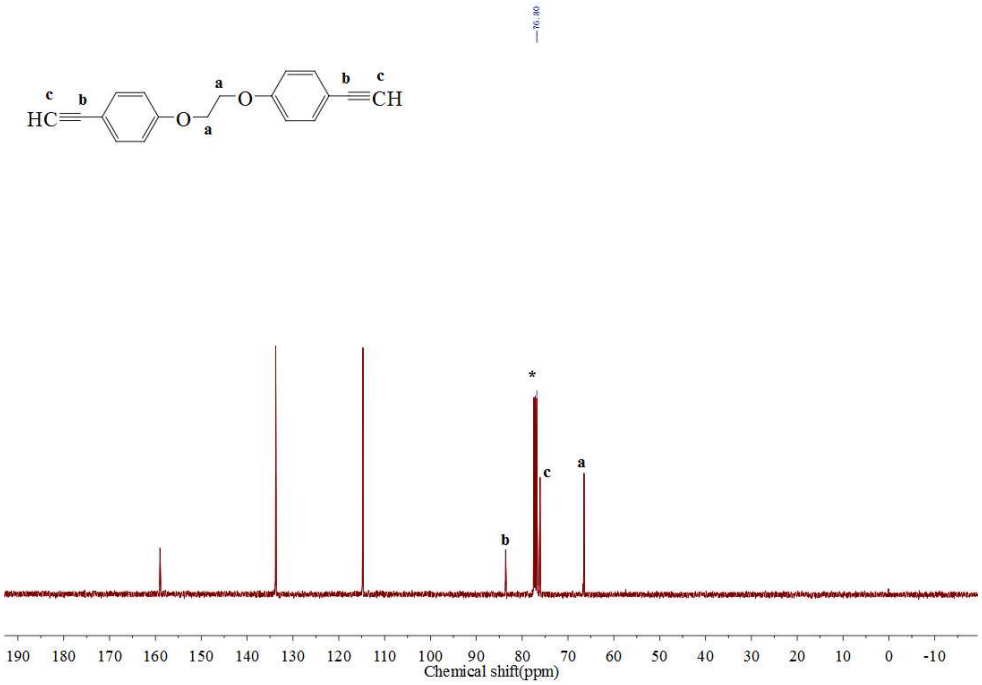



**Figure S20.** $^{13}$C NMR spectrum of **M-7** in $CDCl_3$.

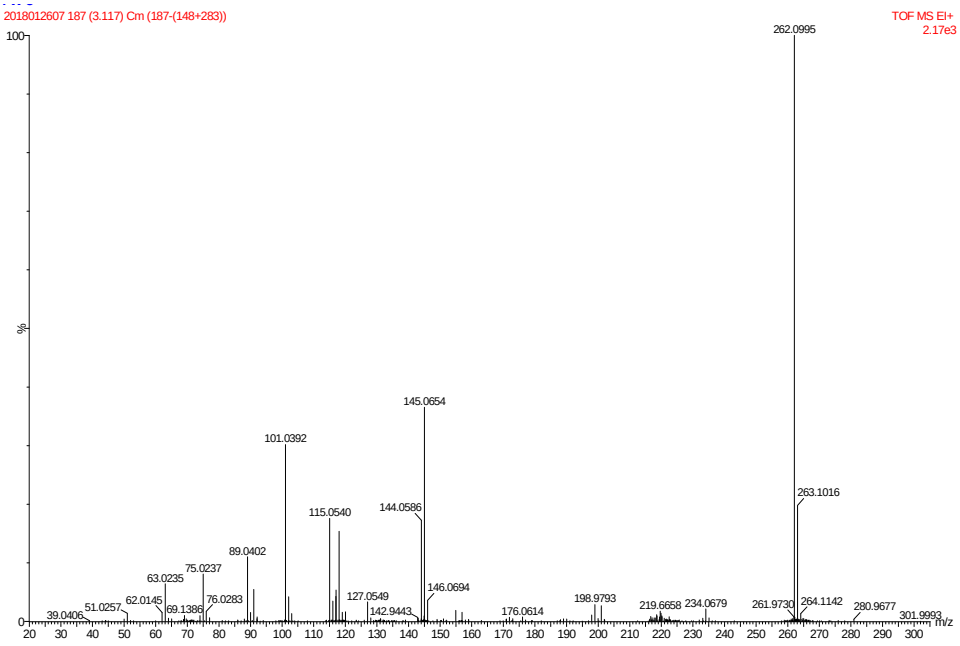
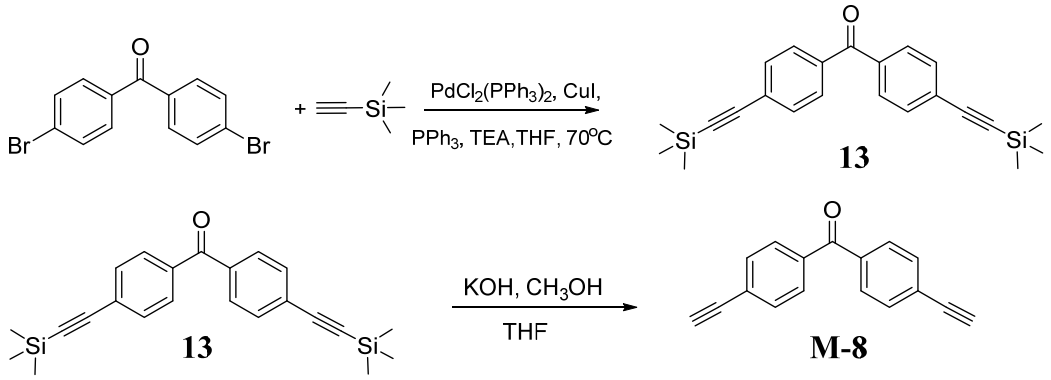



**Figure S21.** MS spectrum of **M-7**.

### 1.3.8 Preparation of 4,4'-diethynyl benzophenone (M-8)




**Scheme S8.** The synthetic route to **M-8**

To a 500 mL round-bottom flask were added 4,4'-dibromobenzophenone (6.8000 g, 20 mmol), $PdCl_2(PPh_3)_2$ (356.0 mg, 0.5 mmol), CuI (95.0 mg, 0.5 mmol), $PPh_3$ (262.0 mg, 1 mmol), THF (20 mL) and anaerobic TEA (150 mL) under nitrogen atmosphere. The reaction mixture was heated under stirring to 70 °C. The (trimethylsilyl)acetylene (8.48 mL, 60 mmol) was injected into the flask after 30 min. After 24 hours, product **13** was separated by flash column chromatograph. Yield: 86%.

Product **13** (3.7400 g, 10 mmol), KOH (560.0 mg, 10 mmol), methanol (50 mL) and THF (50 mL) were added into 500 mL flask. The reaction mixture was stirred at room temperature. After 12 hours, the organic layer was combined and washed with brine and water, and then dried over $MgSO_4$ for an hour. The product **M-8** was separated by flash column chromatograph. Yield: 99%. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.62-8.60 (m, 4H), 7.63-7.61 (m, 4H), 4.07 (s, 2H). $^{13}$C NMR (100 MHz, CDCl3): δ = 194.83, 136.92, 131.96, 129.73, 126.38, 82.61, 80.24. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{17}H_{10}O$: 230.0732, Found: 230.0732, error: 0 ppm.

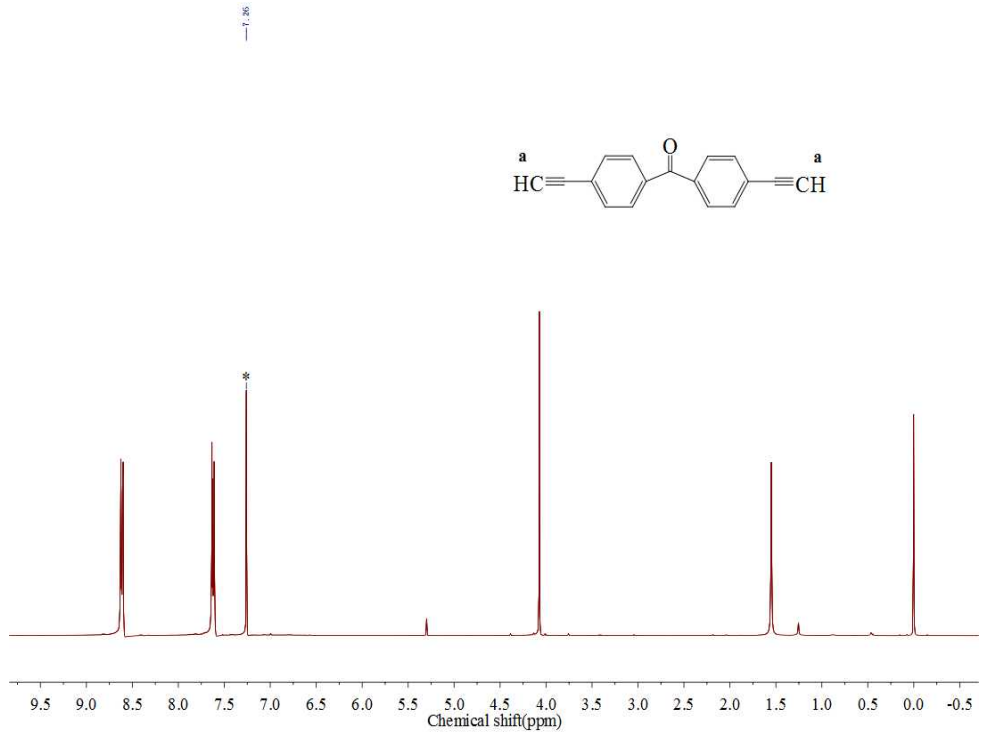



**Figure S22.** $^{1}$H NMR spectrum of **M-8** in $CDCl_3$.

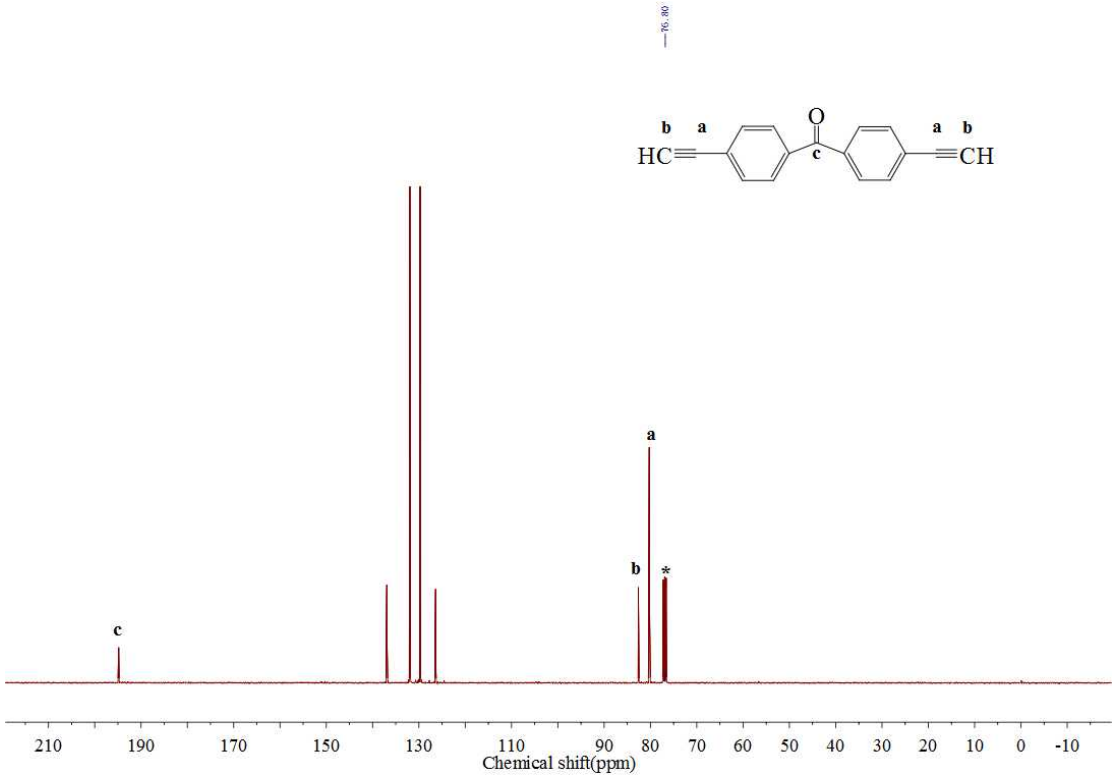



**Figure S23.** $^{13}$C NMR spectrum of **M-8** in $CDCl_3$.

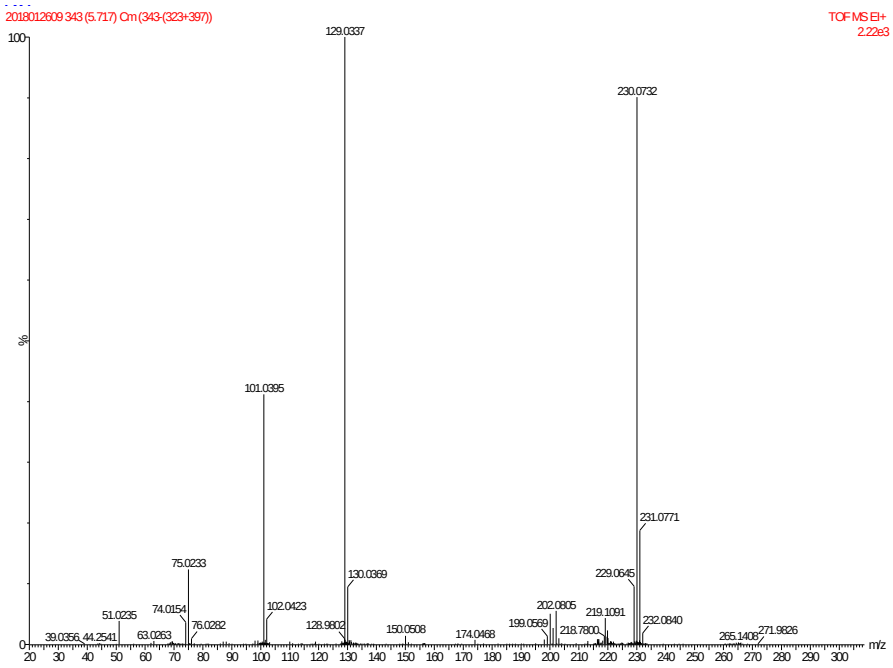
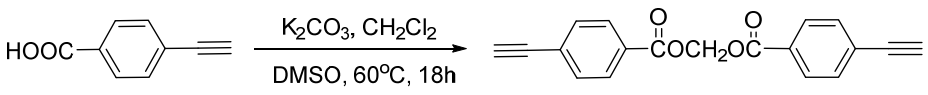



**Figure S24.** MS spectrum of **M-8**.

### 1.3.9 Preparation of bis(4-ethynylbenzoyloxy)methane (M-9)




**M-9**

**Scheme S9.** The synthetic route to **M-9**

To a 500 mL round-bottom flask were added 4-ethynylbenzoic acid (5.8400 g, 40 mmol), $K_2CO_3$ (2.7600 g, 20mmol), DCM (10 mL) and DMSO (60 ml). The reaction mixture was heated under stirring to 60 °C. After 18 hours, the formed solid was removed by filtration and extracted by DCM three times. Product **M-9** was separated by flash column chromatograph. Yield: 68%. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.05-8.03 (d, *J* = 8.4 Hz, 4H), 7.56-7.54 (d, *J* = 8.4 Hz, 4H), 6.24 (s, 2H), 3.27 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 159.77, 127.44, 125.19, 124.07, 122.85, 77.91, 76.11, 75.47. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{19}H_{12}O_4$: 304.0736, Found: 304.0731, error: -1.64 ppm.

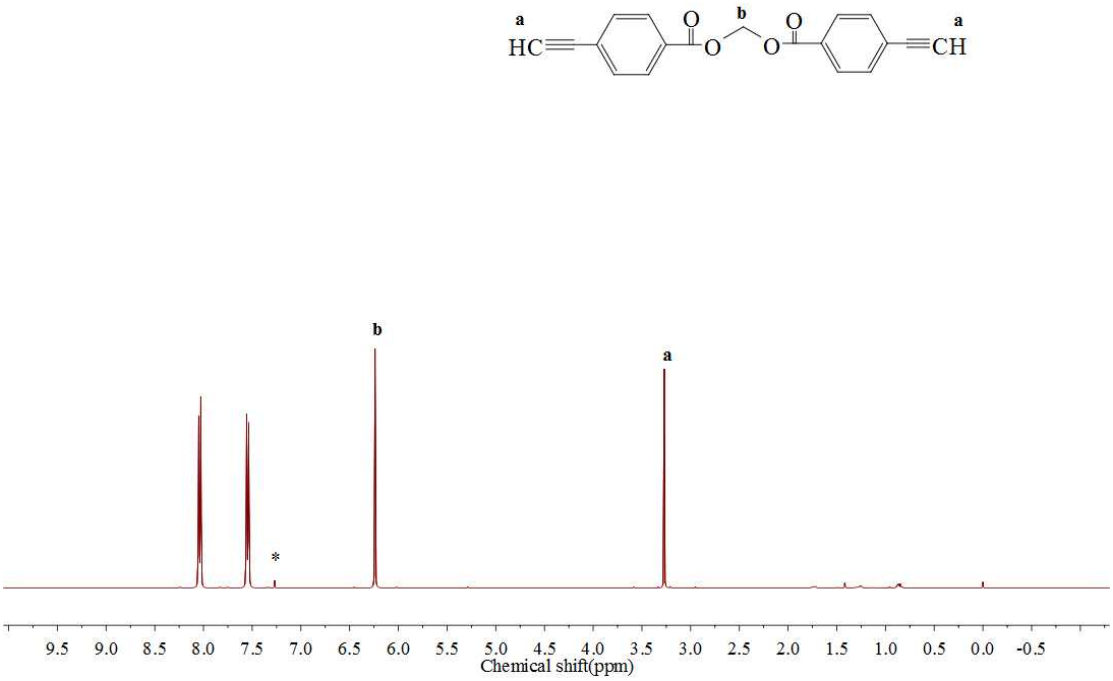



**Figure S25.** $^{1}$H NMR spectrum of **M-9** in $CDCl_3$.

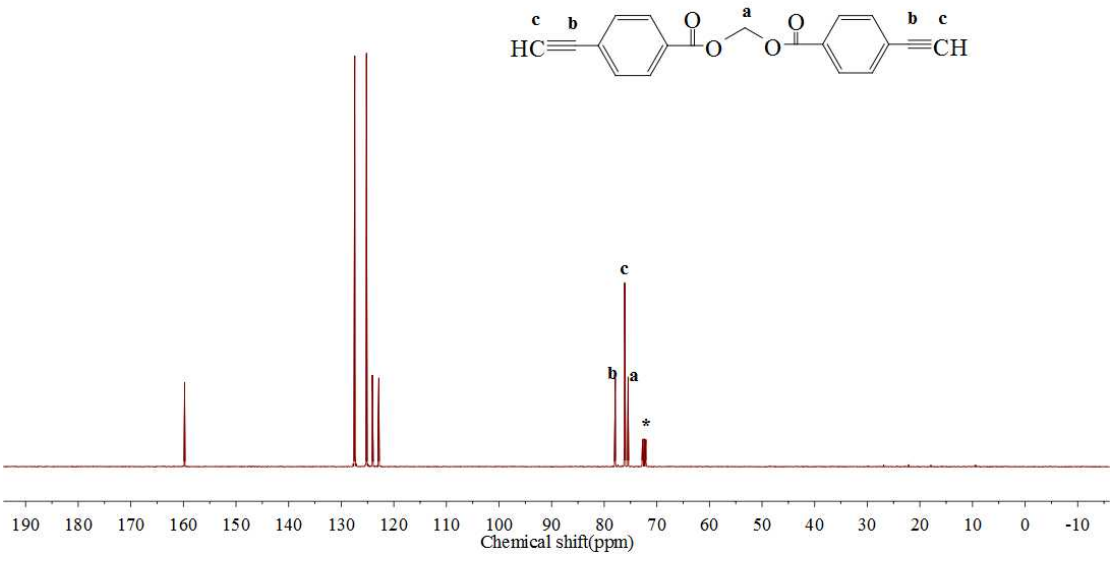



**Figure S26.** $^{13}$C NMR spectrum of **M-9** in $CDCl_3$.

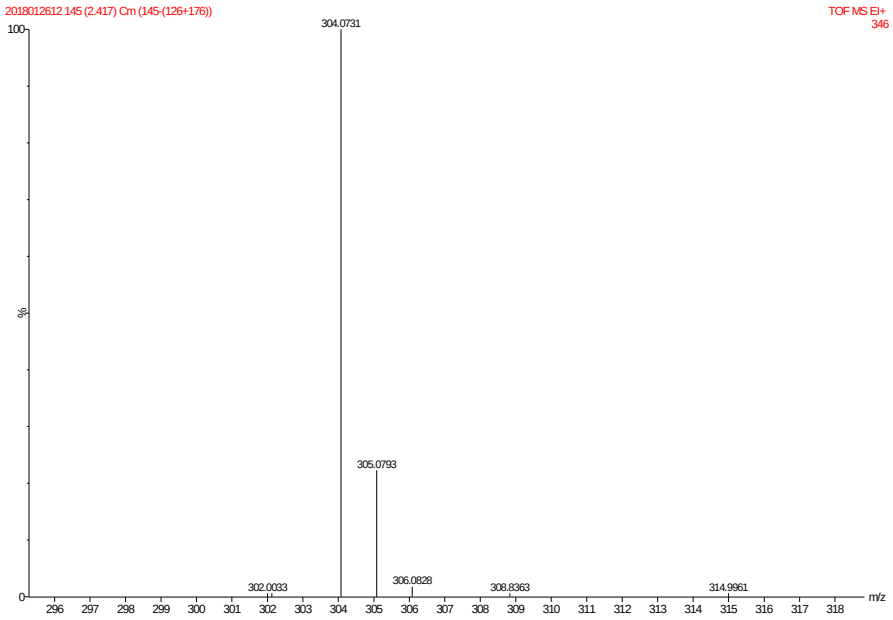
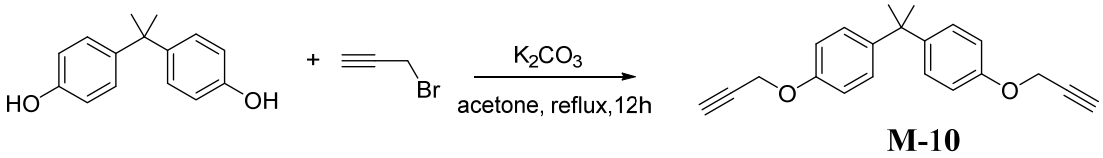



**Figure S27.** MS spectrum of **M-9**.

### 1.3.10 Preparation of 2,2-bis[(4-propargyloxy)phenyl]propane (M-10)




**M-10**

**Scheme S10.** The synthetic route to **M-10**

To a 500 mL round-bottom flask were added 4, 4'-bisphenol (2.2800 g, 10 mmol), propargyl bromide (1.49 ml, 20 mmol), $K_2CO_3$ (2.7600 g, 20 mmol) and acetone (60 mL). The reaction mixture was refluxed for 12 hours. After 24 hours, $K_2CO_3$ was removed by filtration. Product **M-10** was separated by flash column chromatograph. Yield: 91%. $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.18-7.16 (d, *J* = 8.4 Hz, 4H), δ = 6.90-6.88 (d, *J* = 8.8 Hz, 4H), 4.67 (s, 4H), 2.52 (s, 2H), 1.66 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 155.46, 143.90, 127.77, 114.24, 78.85, 75.47, 55.77, 41.76, 31.03. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{21}H_{20}O_2$: 304.1463, Found: 304.1467, error: +1.31 ppm.

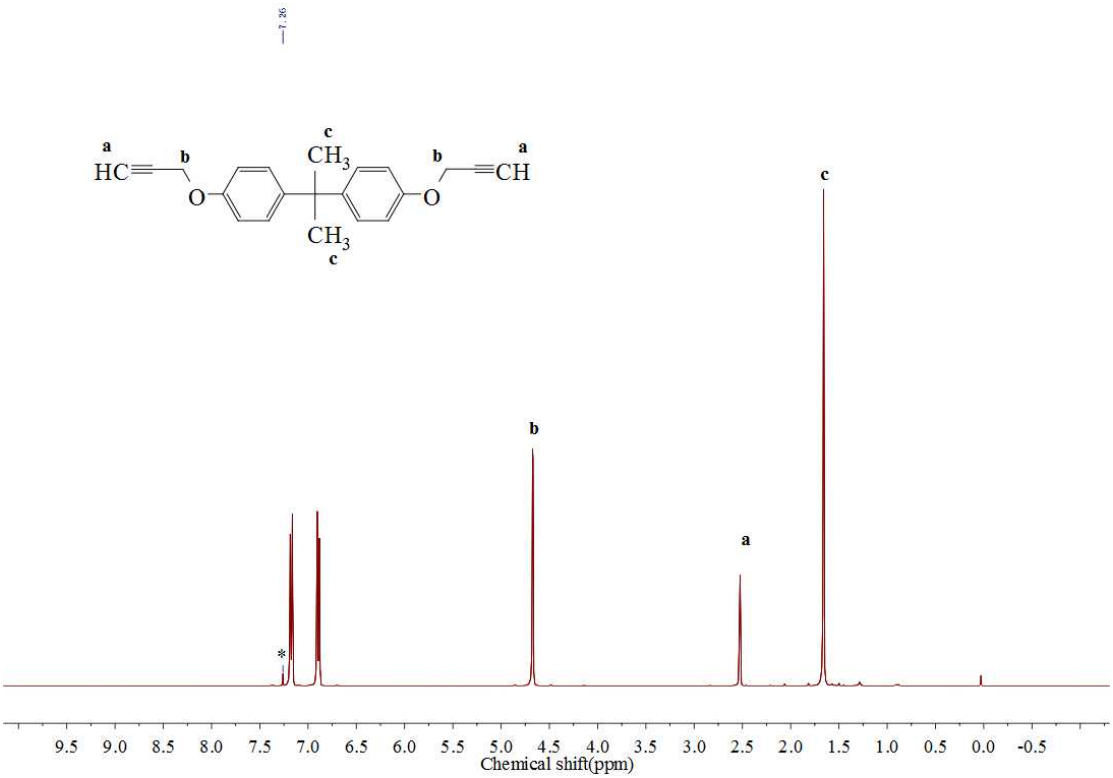



**Figure S28.** $^{1}$H NMR spectrum of **M-10** in $CDCl_3$

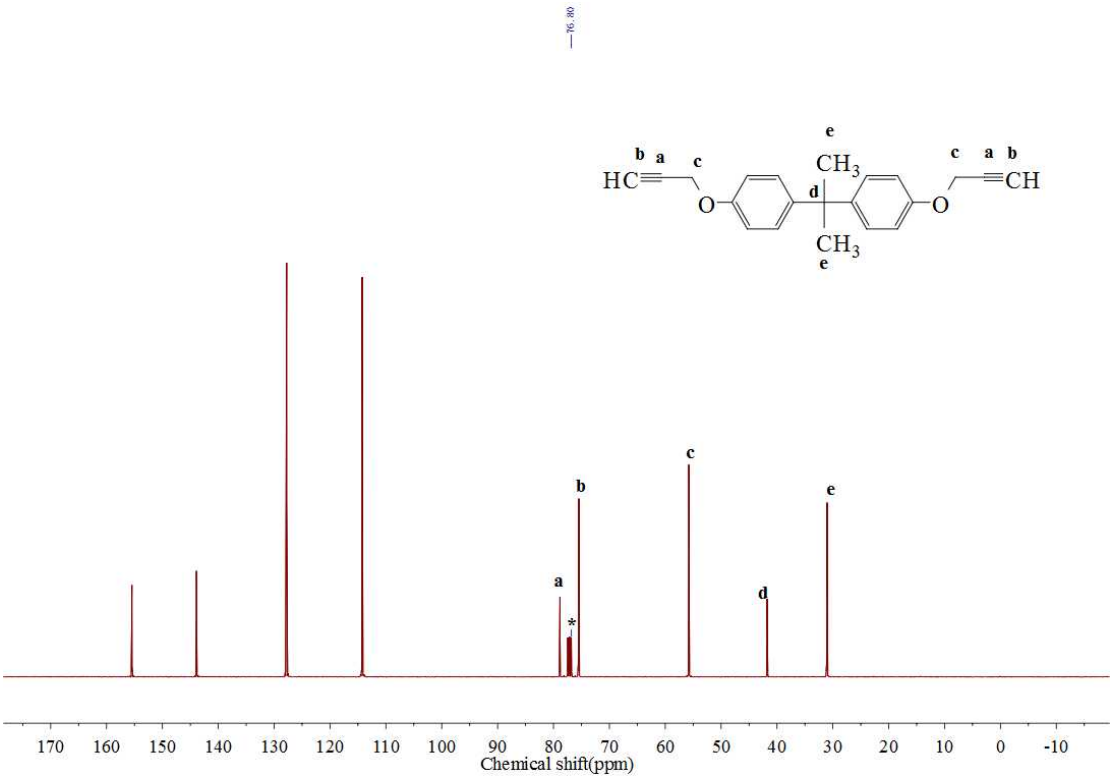



**Figure S29.** $^{13}$C NMR spectrum of **M-10** in $CDCl_3$

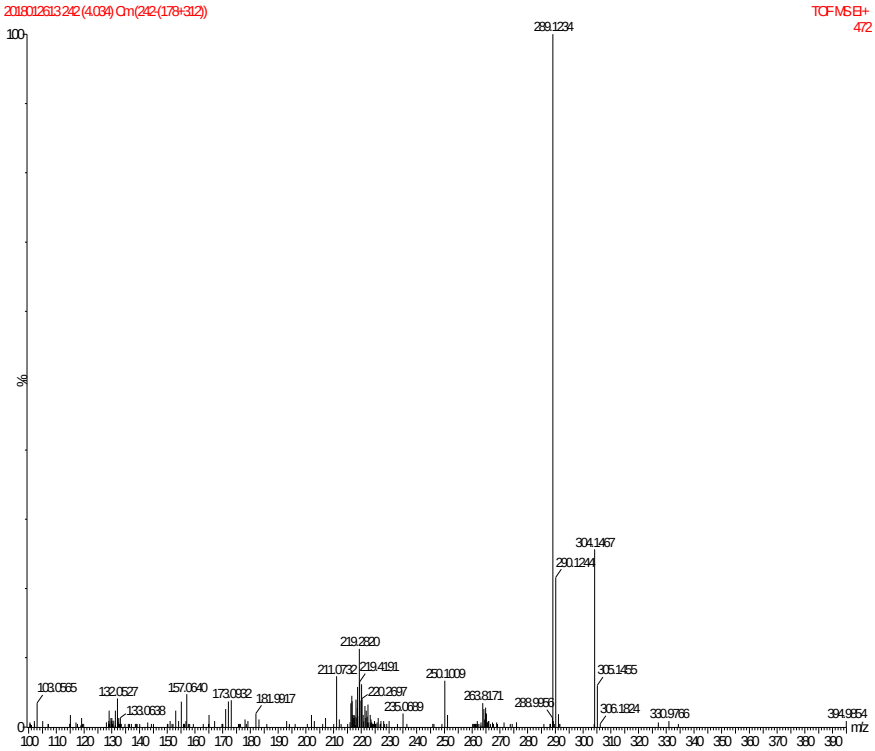



**Figure S30.** MS spectrum of **M-10**.

### 1.3.11 Preparation of model compound 2-methylthio-1,4-ene-diones (MC)

The synthetic route has shown in Scheme 2. To a 30 mL Schlenk tube equipped with a magnetic stir bar were added phenylacetylene (712.0 mg, 6.0 mmol), DMSO (236.0 mg, 3 mmol), $I_2$ (378.0 mg, 3 mmol), $BF_3 \cdot Et_2O$ (423.0 mg, 3 mmol) and 6 mL of dry DMF. The reaction mixture was heated in an oil bath at 100 °C for 24 h under constant stirring under nitrogen atmosphere, cooled to room temperature. The organic layer was combined and washed with brine and water, and then dried over $MgSO_4$ for an hour. Yield: 78%. The two isomers, *Z*-**MC** and *E*-**MC**, were easily separated by column chromatography and the ratio of *Z*-**MC** and *E*-**MC** is approximately 1:1.

*Z*-**MC** $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.07-8.05 (d, *J* = 7.6 Hz, 2H), 7.94-7.92 (d, *J* = 7.2 Hz, 2H), 7.68-7.65 (t, *J* = 7.6 Hz, 1H), 7.54-7.50 (t, *J* = 8.0 Hz, 3H), 7.45-7.41 (t, *J* = 7.6 Hz, 2H), 7.09 (s, 1H), 2.15 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 193.85, 185.12, 160.95, 137.21, 134.84, 133.64, 133.03, 128.83, 128.74, 128.66, 128.49, 115.73, 15.00. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{17}H_{14}O_2S$: 282.1715, Found: 282.1715, error: 0 ppm.

*E*-**MC** $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 8.02-8.00 (d, *J* = 8.0 Hz, 2H), 7.91-7.89 (d, *J* = 7.6 Hz, 2H), 7.57-7.51 (q, *J* = 7.2 Hz, 2H), 7.48-7.40 (m, 4H), 7.03 (s, 1H), 2.44 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 191.85, 188.18, 160.64, 137.88, 134.92, 134.85, 132.74, 130.01, 129.17, 128.69, 128.09, 116.02, 15.47. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{17}H_{14}O_2S$: 282.1715, Found: 282.1714, error: -0.4 ppm.

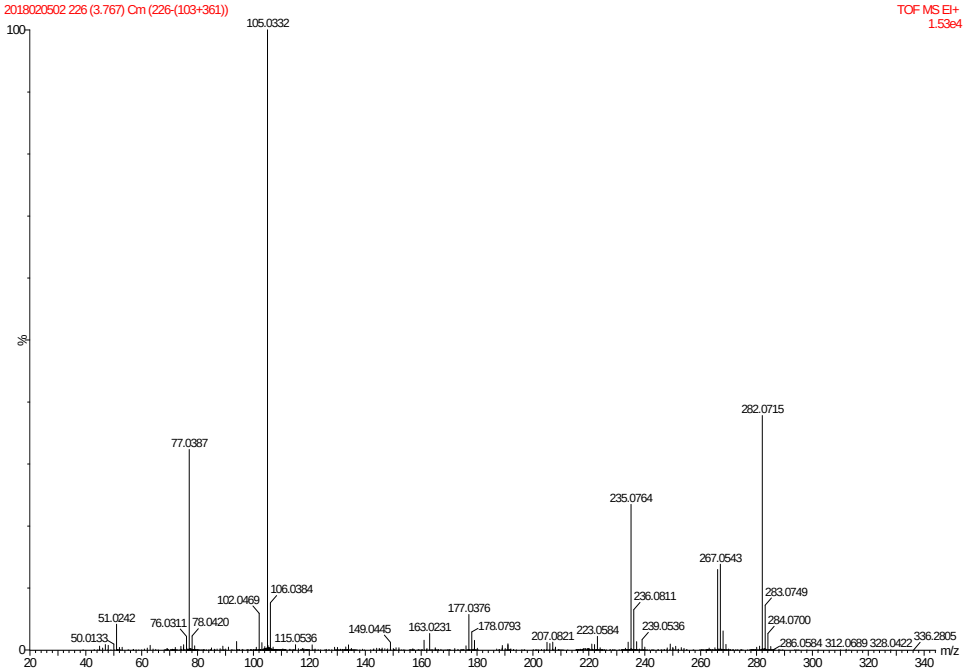



**Figure S31.** MS spectrum of *Z*-**MC**.

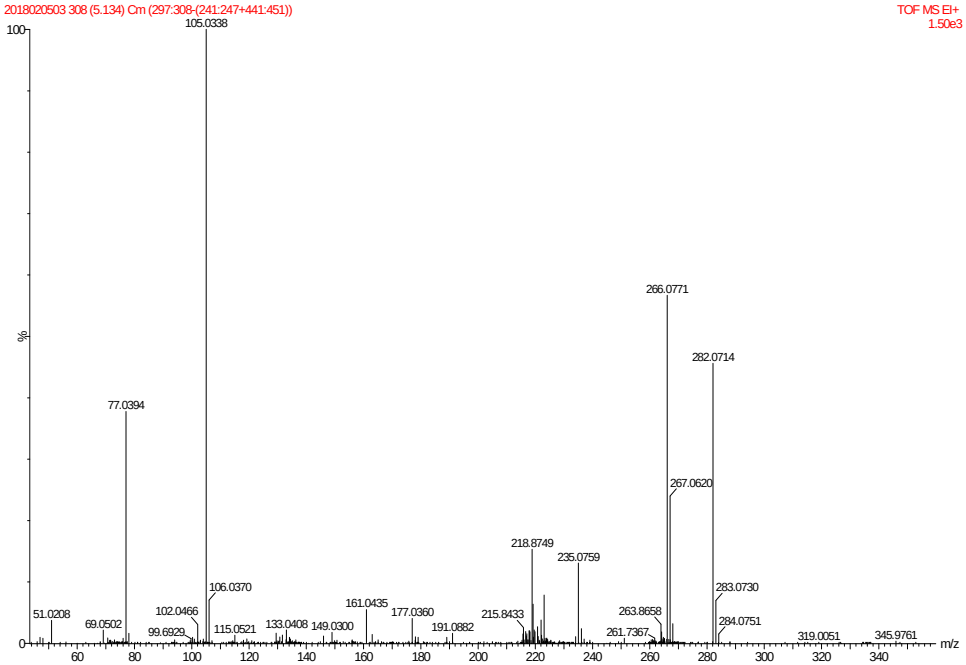



**Figure S32.** MS spectrum of *E*-**MC**.

## 2 The GPC curve of polymers in Table 4

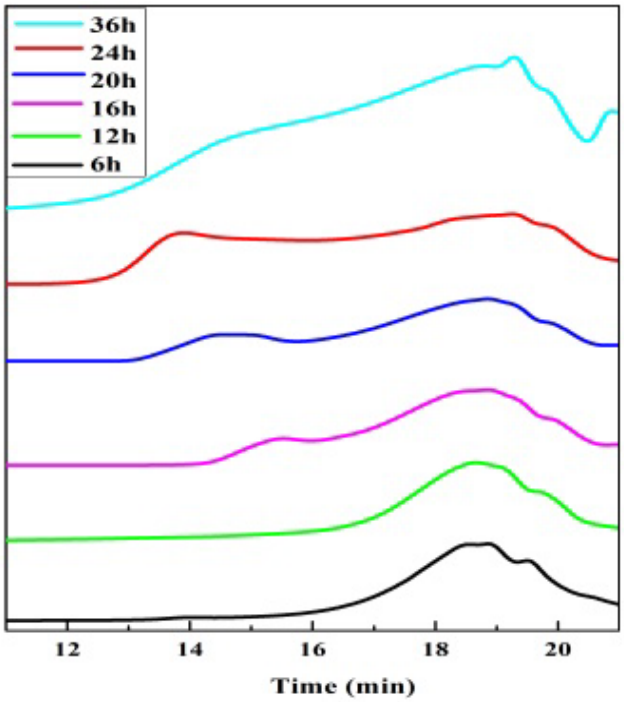



**Figure S33.** The GPC curve of obtained polymers taken from Entries 1-6 in Table 4.

## 3 FT-IR spectra of **PEKAK-2**, **PEKAK-3** and **PEKAK-4**

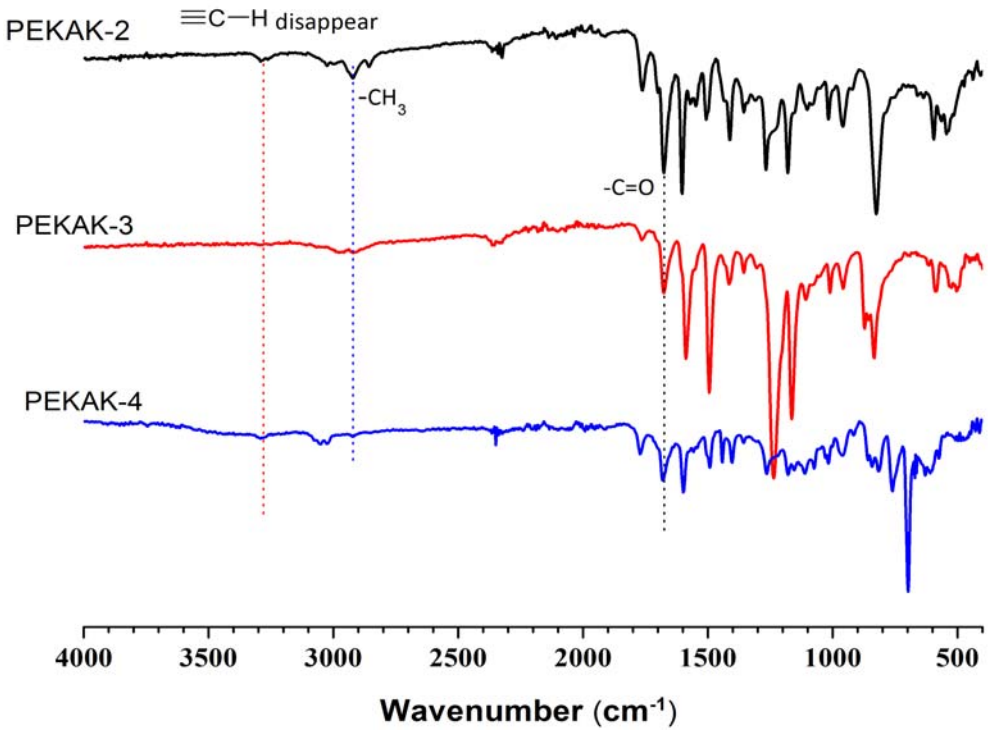



**Figure S34.** FT-IR spectra of **PEKAK-2**, **PEKAK-3** and **PEKAK-4**

## 4 $^{1}$H NMR spectra of **PEKAK-2**, **PEKAK-3** and **PEKAK-4**

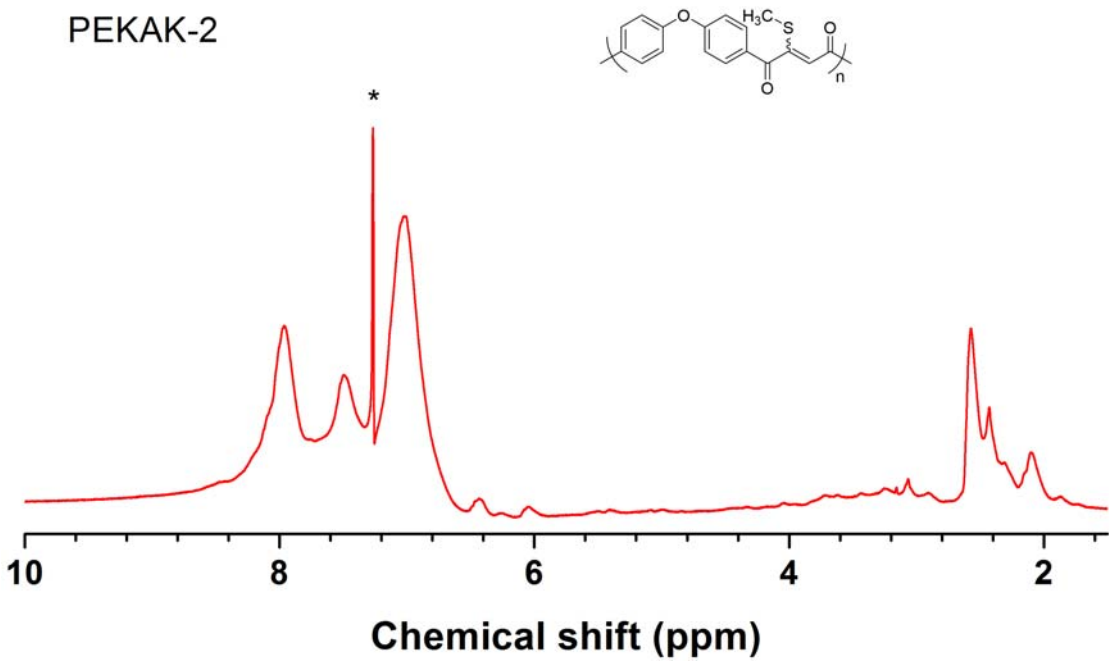



**Figure 35.** $^{1}$H NMR spectrum of **PEKAK-2** in $CDCl_3$. The solvent peaks are marked with asterisks.

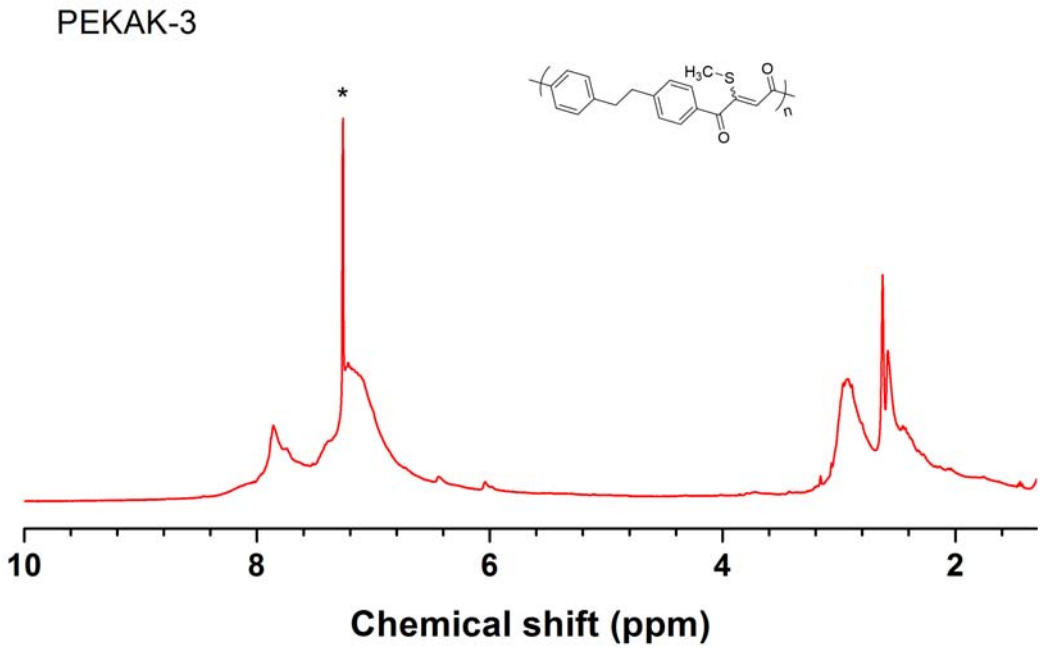



**Figure S36.** $^{1}$H NMR spectraum of **PEKAK-3** in $CDCl_3$. The solvent peaks are marked with asterisks.

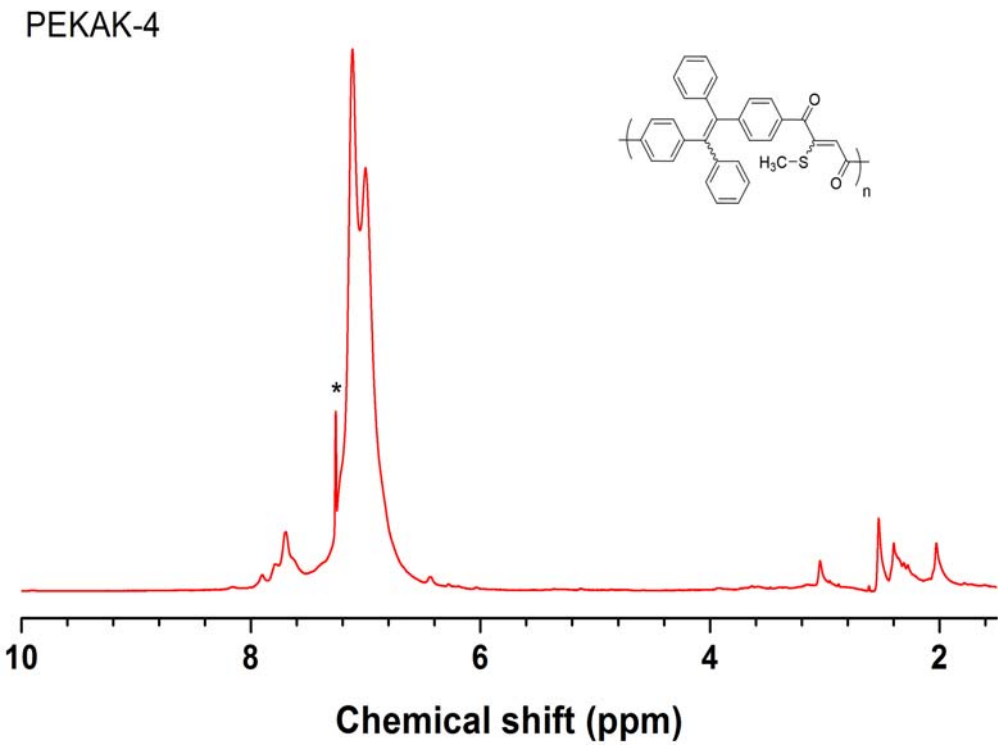



**Figure S37.** $^{1}$H NMR spectrum of **PEKAK-4** in $CDCl_3$. The solvent peaks are marked with asterisks.

## 5 TGA-MS curve of PEKAK-1

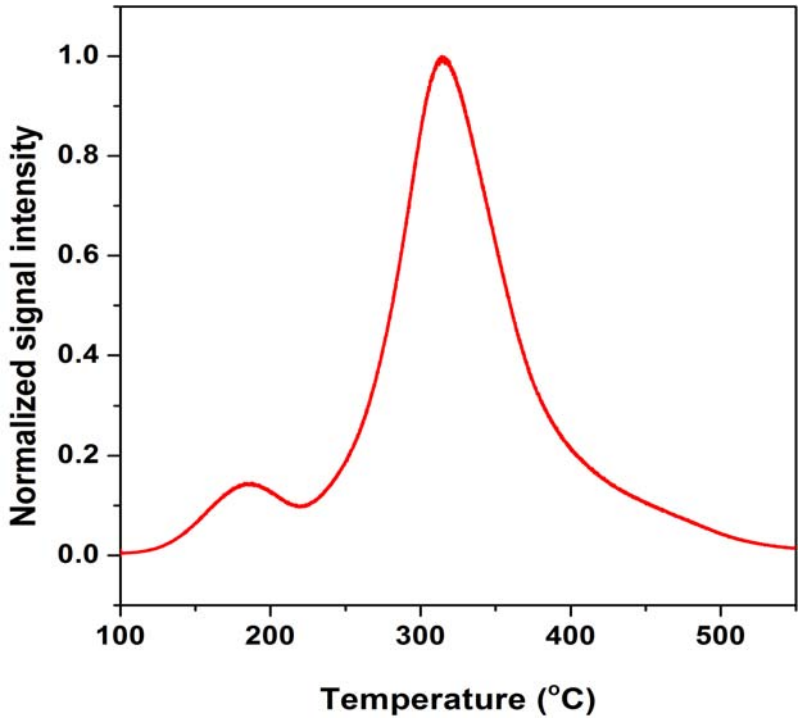



**Figure S38.** The methanethiol signal intensity in TGA-MS curve of **PEKAK-1**.

## 6 The DLS results of PEKAK-1 and PEKAK-4

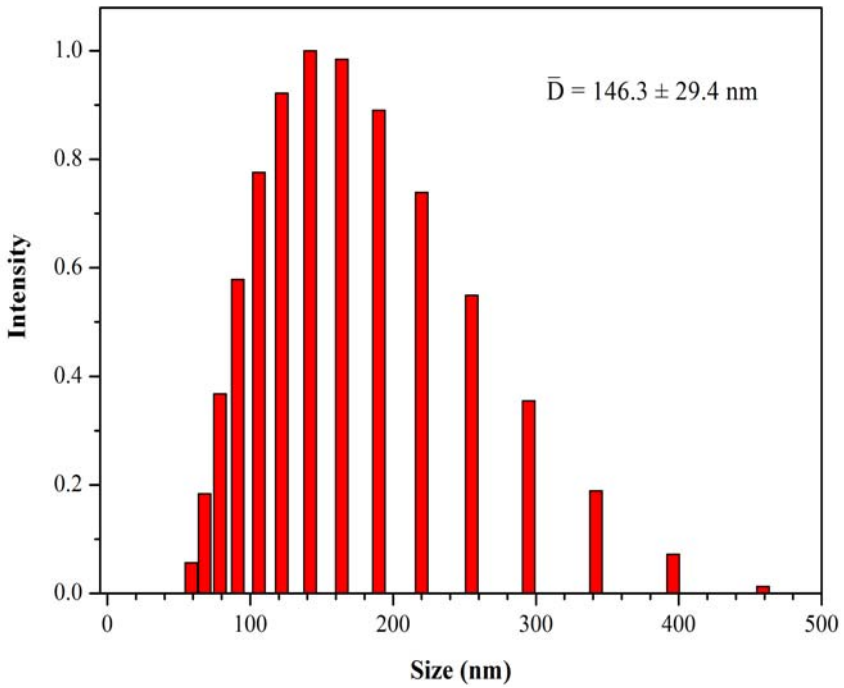



**Figure S39.** Dynamic light scattering result of **PEKAK-1** in the THF-water mixtures at 90% water fraction. [PEKAK-1] = 10 $\mu$mol/L.

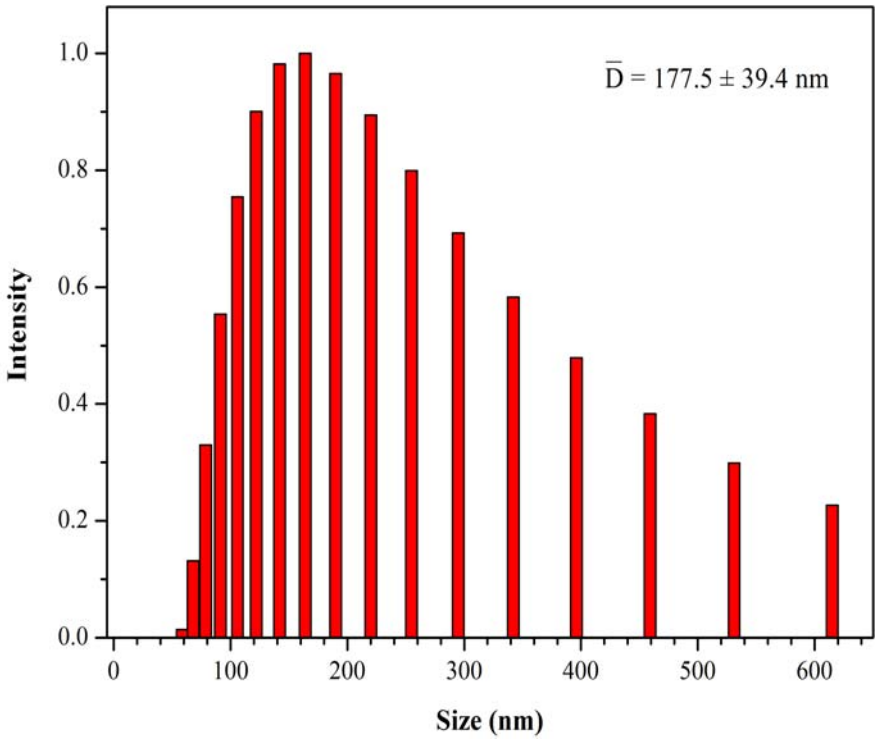



**Figure S40.** Dynamic light scattering result of **PEKAK-4** in the THF-water mixtures at 90% water fraction. [PEKAK-4] = 10 $\mu$mol/L.

## 7 SEM images of the polymer's film

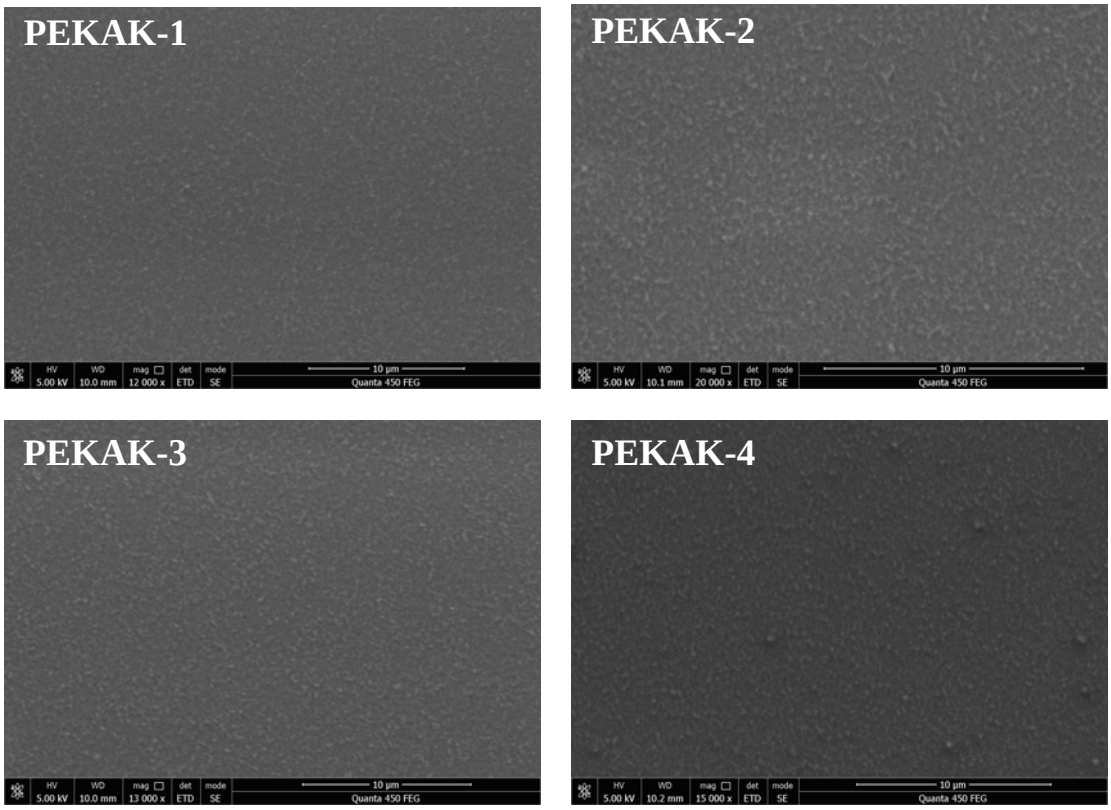



**Figure S41.** SEM images of thin solid films of **PEKAK-1**, **PEKAK-2**, **PEKAK-3** and **PEKAK-4**.