

## Electronic supplementary information (ESI)

### Photo-crosslinkable second-order nonlinear optical polymer: facile synthesis and enhanced NLO thermostability

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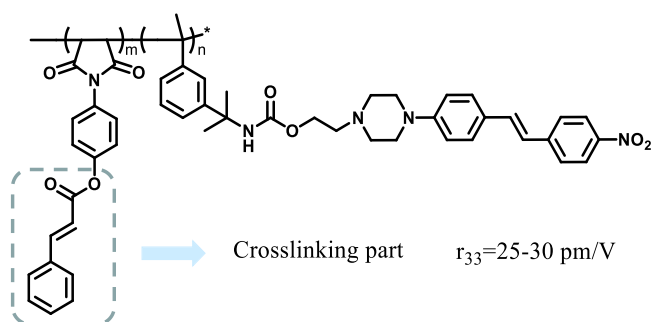
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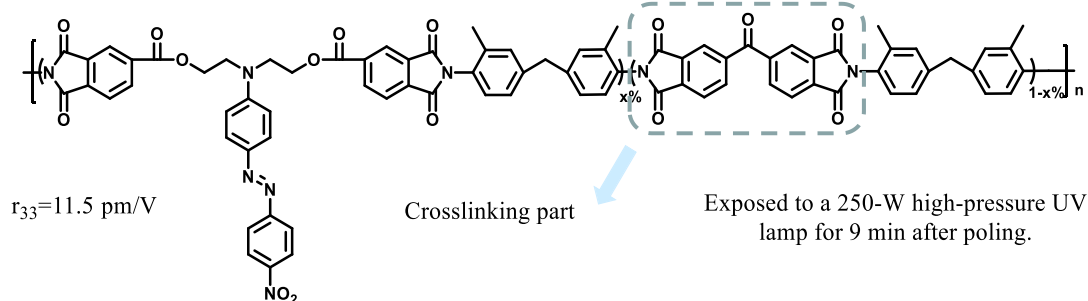
##### 3. Reference

## 1. Additional data and analysis

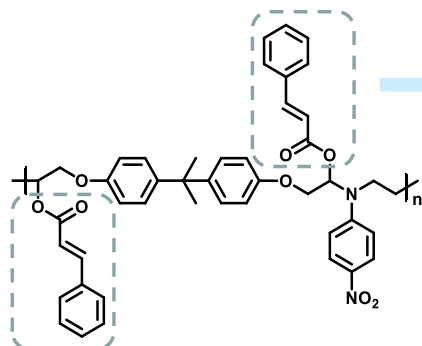
**Chart S1.** Some typical NLO molecules using the photo-crosslink method.<sup>1-3</sup>



Exposed to 254 nm UV light for 30 min during poling.



Exposed to a 250-W high-pressure UV lamp for 9 min after poling.

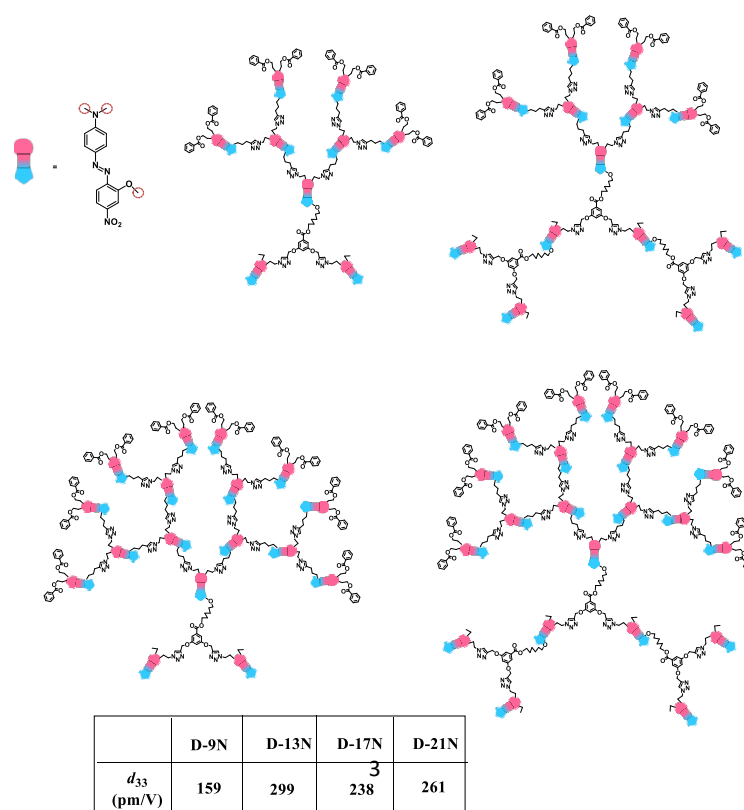
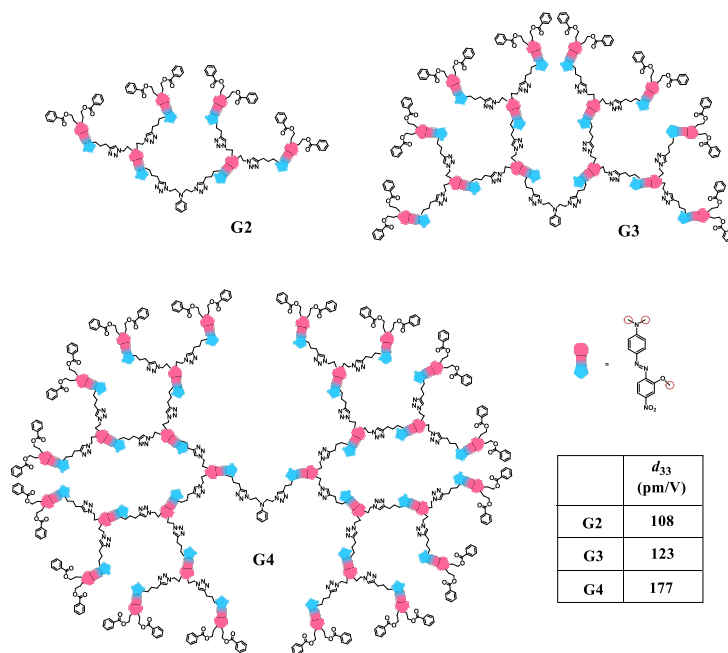
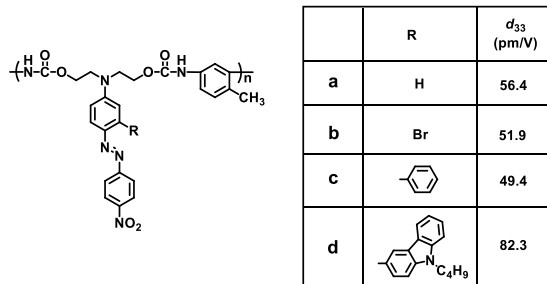


Crosslinking part

Exposed to a 40-W UV lamp for 45 min after poling.

No clear information for the NLO performance in the literature

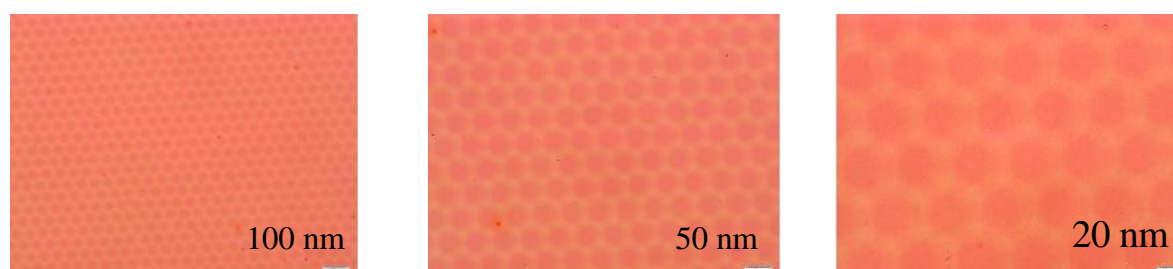
**Chart S2.** Some typical molecules synthesized in our preview works.<sup>4-8</sup>



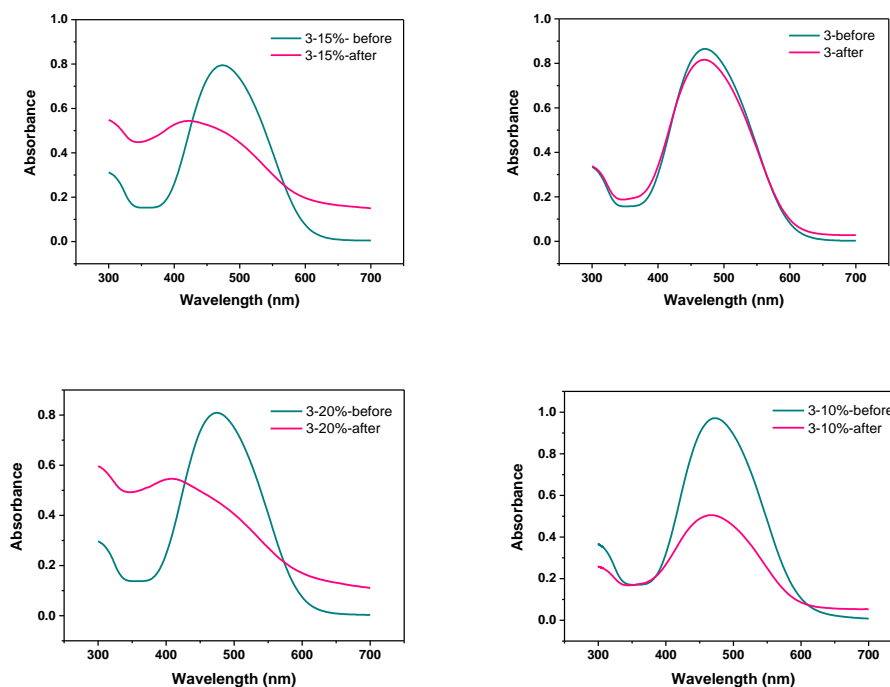
**Table S1** The maximum absorption wavelength ( $\lambda_{\max}$ , nm) in different solvents ( $0.02 \text{ mg mL}^{-1}$ ) (UV-vis) and the characterization data of the polymer.

	$\lambda_{\max}$ (nm)						$\Delta^a$	$M_w$ ( $10^4$ ) <sup>b</sup>	$M_w/M_n$ (PDI) <sup>b</sup>	$T_d$ ( $^{\circ}\text{C}$ ) <sup>c</sup>	$T_g$ ( $^{\circ}\text{C}$ ) <sup>d</sup>
	1,4-Dioxane	$\text{CHCl}_3$	DCM	THF	DMF	DMSO					
<b>4</b>	467.5	482.5	482	473	489	497.5	30	/	/	/	/
<b>3</b>	463.5	469	468	465.5	481	485.5	22	7.25	1.89	276	89

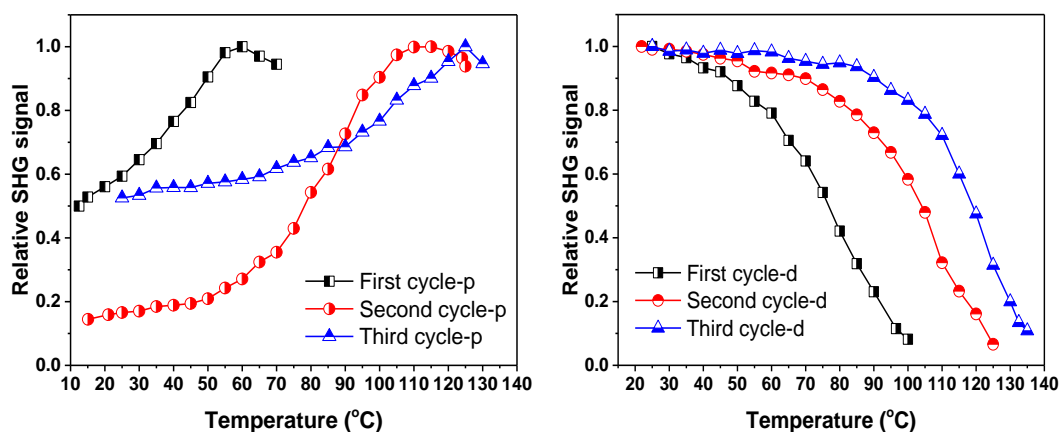
<sup>a</sup> $\Delta = \lambda_{\max, \text{DMSO}} - \lambda_{\max, \text{1,4-Dioxane}}$ . <sup>b</sup>Determined by GPC in DMF, based on laser light scattering technology. <sup>c</sup>The 5% weight loss temperature of polymer detected by the TGA analysis. <sup>d</sup>The glass transition temperature of the polymer detected by the DSC analysis.



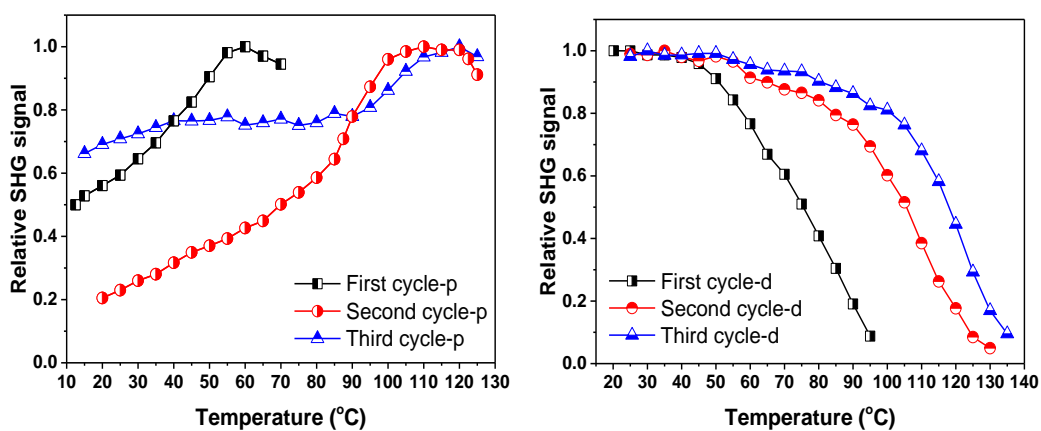
**Figure S1** The photo-controllable pattern pictures taken by electron microscope (10 min, irradiation time).



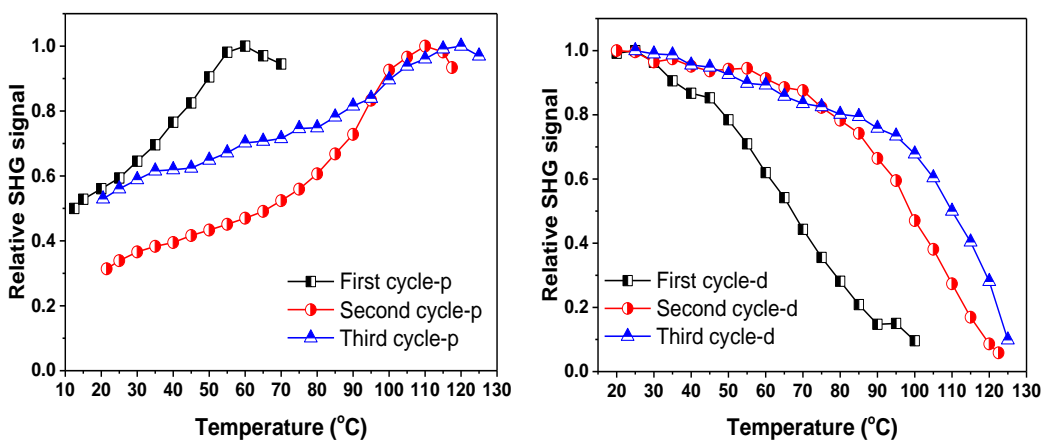
**Figure S2** The UV-vis spectra of the film before (blue) and after poling (red).



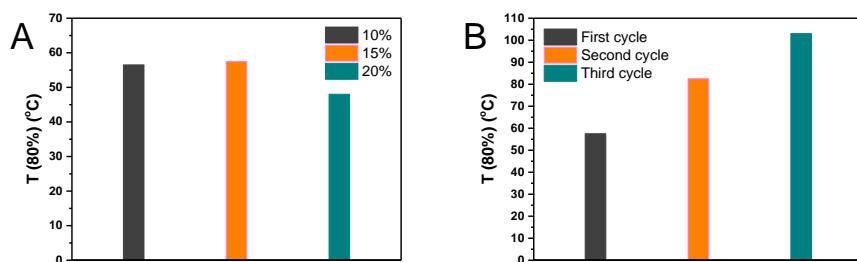
**Figure S3** The poling (left) and depoling (right) curves of the film (**PETMP: 3** (wt%)= 10%).



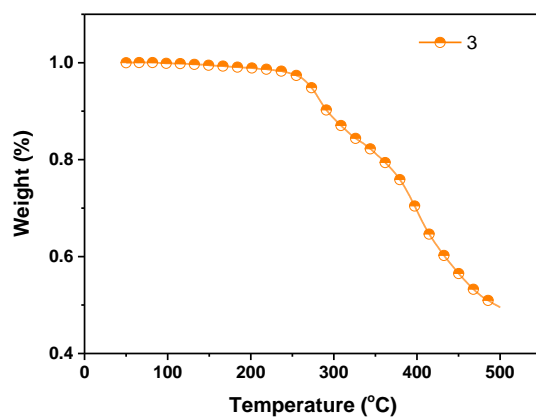
**Figure S4** The poling (left) and depoling (right) curves of the film (**PETMP: 3** (wt%)= 15%).



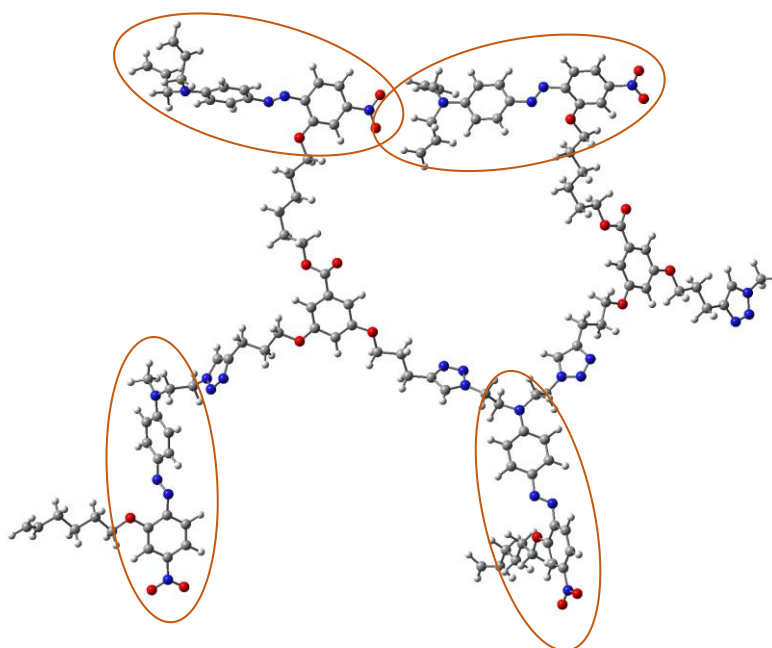
**Figure S5** The poling (left) and depoling (right) curves of the film (**PETMP: 3** (wt%)= 20%).



**Figure S6** The  $T_{80\%}$  of the PETMP: **3** system with different mixing ratio (first cycle); (B) The  $T_{80\%}$  of the PETMP: **3** system (wt%=10%);



**Figure S7** The TGA spectra of **3**.



**Figure S8** The optimized structure of **3**.

## 2. Experimental details

### 2.1 Instrumentation

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE III HD 400 MHz spectrometer using tetramethylsilane (TMS;  $\delta=0$  ppm) as the internal standard. UV-visible spectra were obtained using a Shimadzu UV-2550 spectrometer. The Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer-2 spectrometer in the region of  $3000\text{-}400\text{ cm}^{-1}$  on KBr pellets. Thermogravimetric analysis (TGA) was performed on a METTLER TOLEDO ATARe TGA/DSC 1 thermal analyzer at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  in nitrogen at a flow rate of  $50\text{ cm}^3\text{ min}^{-1}$ . Gel permeation chromatography (GPC) was used to determine the molecular weights of the polymer. GPC analysis was tested by the laser light scattering (DOWN-EOS, Wyatt, US), DMF was used as an eluent. The thickness of the films was measured by the profiler of BRUKER DEKTAKXT. All the raw material were purchased from Energy Chemical, HEOWNS and Innochem.

### 2.2 Preparation and measurement of the polymer films

#### Preparation of the polymer films:

The mixture of the polymer and PETMP in different ratio were dissolved in THF at a concentration of 35 mg/mL. After filtering by the syringe filters, the mixed solution was coated onto indium-tin-oxide (ITO)-coated glass substrates to obtain the thin films. And the ITO-coated glass substrates were subjected to ultra-sonication in different solvent systems in advance, in the order of soapy water, acetone, deionized water, DMF, and THF. The thin films was dried in a vacuum oven at  $45\text{ }^\circ\text{C}$  overnight before poling.

#### NLO measurement and photo-crosslinking process of the poled films:

The second-order optical nonlinearity of the polymers was determined by in situ second harmonic generation (SHG) experiment using a closed temperature-controlled oven with optical windows and three needle electrodes. The films were kept at  $45\text{ }^\circ$  to the incident beam and poled inside the oven, and the SHG intensity

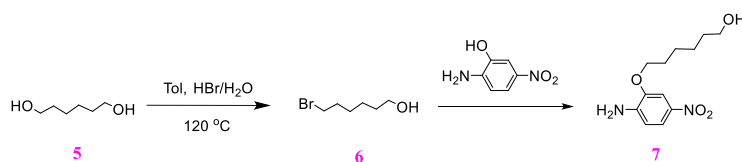
was monitored simultaneously. The poling voltage was 7.0 KV. The SHG measurements were carried out with a Nd:YAG laser operating at a 10 Hz repetition rate and an 8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

The thin films was heated to the optimum poling temperature ( $T_e$ ) under the electric field. After maintaining for 10 mins at  $T_e$ , the photo-crosslinking process was proceed at room temperature. The poled films were exposed to the 365 nm UV light for 30 mins with the voltage still on, then the photo-crosslinked films were obtained.

The orientation stability test was proceed as followed: The photo-crosslinked films were heated without voltage on until the SHG signals disappeared. The heating rate was 4 °C/min.  $T_{80\%}$  represent the temperature at which the SHG signals decreased to 80%.

## 2.3 synthesis

### The synthetic route of chromophore

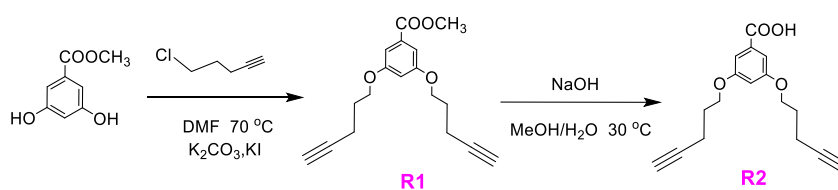


Compound 6: Compound 5 (12.90 g, 0.11 mol) was dissolved in toluene (250 mL), and then hydrobromic acid (48%, 15 mL) was added dropwise. The resultant mixture was stirred at 120 °C for 24 h. After cooling to the room temperature, the reaction mixture was dried by rotary evaporator, and the crude product was purified by column chromatography on silica gel using dichloromethane/ethyl acetate (3/1) as eluent, to yield the colorless oil (3.62g, 18.3%).

Compound 7: Compound 6 (3.62 g, 20.0 mmol), 2-amino-5-nitrophenol (3.08 g, 20.0 mmol) and potassium carbonate (4.14 g, 30 mmol) were added in DMF (40 mL), and the resultant mixture was stirred at 50 °C until the starting reactant consumed completely as monitored by TLC. Then dichloromethane (100 mL) was added,



and the salt and DMF in the resultant mixture was washed away by water. The solvent was removed by rotary evaporator, and the crude product was purified by column chromatography on silica gel using dichloromethane/ethyl acetate (10/1) as eluent to yield the yellow solid (3.2 g, 63.0%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.32 (s, 1H, -OH), 1.64-1.46 (m, 6H, -CH<sub>2</sub>-), 1.88 (m, 2H, -CH<sub>2</sub>-), 3.68 (m, 2H, -CH<sub>2</sub>-), 4.09 (m, 2H, -CH<sub>2</sub>-), 4.55 (s, 2H, -NH<sub>2</sub>), 6.63 (d, *J*=8 Hz, 1H, ArH), 7.65 (d, *J*=4 Hz, 1H, ArH), 7.81 (m, 1H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 144.8, 143.5, 138.6, 119.0, 111.8, 106.6, 68.7, 62.8, 32.6, 29.0, 25.9, 25.5. HRMS (ESI, *m/z*): calcd for C<sub>12</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>, 277.1159 [M+Na]<sup>+</sup>; found, 277.1148.



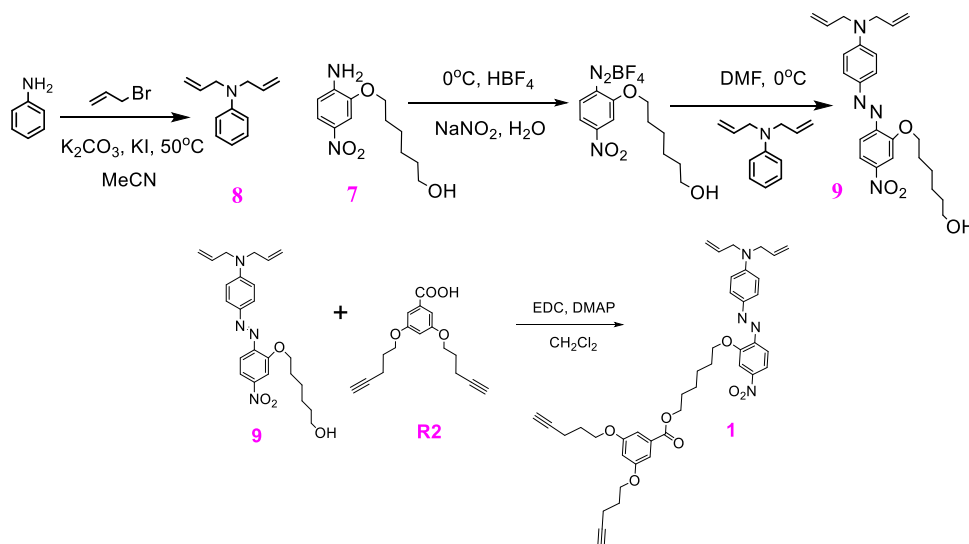
Compound **R1**: Methyl 3,5-dihydroxybenzoate (6.81 g, 0.04 mol), 5-chloro-1-pentyne (10.2 g, 0.10 mol), K<sub>2</sub>CO<sub>3</sub> (13.8 g, 0.10 mol) and KI (2.2 g, 0.02 mol) were added in acetone (20 mL). After stirred at 55 °C for 24h, the mixture was cooled to room temperature, and then remove the solid by rotary evaporator. The crude product was washed by methanol, and recrystallized from acetone/methanol (V/V, 1/2), to yield the yellow solid (7.18 g, 59.8%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.99 (m, 4H, -CH<sub>2</sub>-), 2.02 (m, 2H, -C≡CH), 2.41 (m, 4H, -CH<sub>2</sub>-), 3.90 (s, 3H, -CH<sub>3</sub>), 4.09 (m, 4H, -CH<sub>2</sub>-), 6.66 (t, *J*=4 Hz, 1H, ArH), 7.18 (d, *J*=4 Hz, 1H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 166.8, 159.8, 131.9, 107.7, 106.6, 83.3, 69.1, 66.4, 52.2, 28.0, 15.1. HRMS (ESI, *m/z*): calcd for C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>, 323.1259 [M+Na]<sup>+</sup>; found, 323.1272.

Compound **R2**: Compound **R1** (6.91 g, 23.0 mmol) was dissolved in methanol (20 mL), and the solution of sodium hydroxide was added (sodium hydroxide (9.20 g, 23.0 mmol) in 15 mL water). After stirred at 30 °C for 6 h, dilute hydrochloric acid was added to adjust the pH to 7.0. The crude product was precipitated out, collected and washed several times with water and ethanol, and then recrystallized from acetone/methanol (V/V, 1/1), to yield the white solid (5.58 g, 84.7%). <sup>1</sup>H NMR (400 MHz, DMSO, 298 K),  $\delta$  (TMS, ppm): 1.89 (m, 4H,

-CH<sub>2</sub>-), 2.33 (m, 4H, -CH<sub>2</sub>-), 2.83 (m, 2H, -C≡CH), 4.06 (m, 4H, -CH<sub>2</sub>-), 6.75 (m, 1H, ArH), 7.05 (m, 2H, ArH).

<sup>13</sup>C NMR (100 MHz, DMSO, 298 K),  $\delta$  (ppm): 167.0, 159.6, 132.9, 107.5, 105.7, 83.6, 71.7, 66.3, 27.6, 14.5.

HRMS (ESI, m/z): calcd for C<sub>17</sub>H<sub>18</sub>O<sub>4</sub>, 285.1132 [M-H]<sup>-</sup>, found, 285.1146.

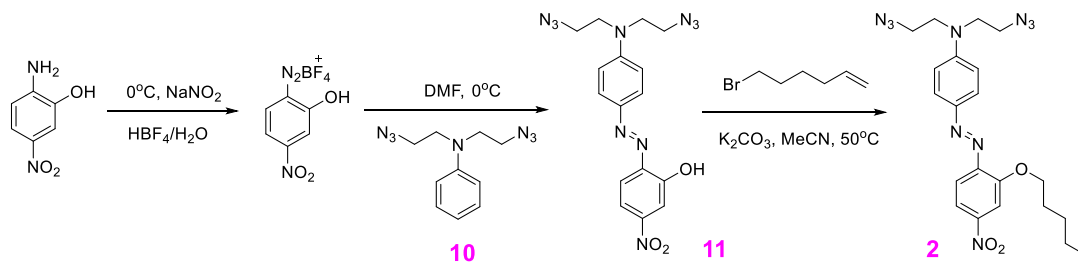


Compound **8**: Aniline (1.86 g, 0.02 mol), allyl bromide (6.04 g, 0.05 mol) and potassium carbonate (5.52 g, 0.04 mol) were added in acetonitrile (30 mL). The resultant mixture was stirred at 50 °C until the starting reactant consumed completely as monitored by TLC. After cooling to room temperature, the reaction mixture was filtered to remove the salt, and then the solvent was removed by rotary evaporator. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent, to yield the colorless oil (1.54 g, 44.5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 3.91 (d, *J*=4.5 Hz, 4H, -CH<sub>2</sub>-), 5.17 (m, 4H, -C=CH<sub>2</sub>), 5.85 (m, 2H, -CH=C), 7.20 (m, 2H, ArH), 6.58 (m, 3H, ArH).

Compound **9**: Compound **7** (580.2 mg, 2.28 mmol) was dissolved in 48% fluoroboric acid (3 mL), then the sodium nitrite saturated solution (196.7 mg, 1.43 mmol) was added in an ice bath. The resultant mixture was stirred at 0 °C for 12 h, before the addition of the solution of Compound **8** (493.4 mg, 2.85 mmol) in DMF (15 mL) at 0 °C. Then, the reaction mixture was further stirred at 0 °C overnight. Dichloromethane (150 mL) was added into the reaction mixture, then washed with water to remove DMF. The solvent was removed by rotary evaporator, and the crude product was purified by column chromatography on silica gel using dichloromethane as eluent, to yield the red solid (788.9 mg, 79%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.61-1.43

(m, 6H, -CH<sub>2</sub>-), 1.75 (s, 1H, -OH), 1.94 (m, 2H, -CH<sub>2</sub>-), 3.65 (m, 2H, -CH<sub>2</sub>-), 4.03 (t, 4H, -CH<sub>2</sub>-), 4.21 (t, 2H, -CH<sub>2</sub>-), 5.21 (m, 4H, -C=CH<sub>2</sub>), 5.89 (m, 2H, -CH=C), 6.75 (d, *J* = 6.4 Hz, 2H, ArH), 7.66 (d, *J* = 8.0 Hz, 1H, ArH), 7.89-7.85 (m, 4H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 155.2, 152.0, 148.1, 147.2, 144.6, 132.5, 129.9, 126.1, 121.7, 117.4, 116.7, 116.5, 115.6, 111.8, 109.0, 108.6, 69.9, 68.6, 62.8, 52.8, 32.6, 28.9, 25.8, 25.5. MS (EI), *m/z*: 438.18 ([M<sup>+</sup>], calcd for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>, 438.22). (EA) (%), found/Calcd): C, 65.88/65.73; H, 6.88/6.90; N, 12.98/12.78.

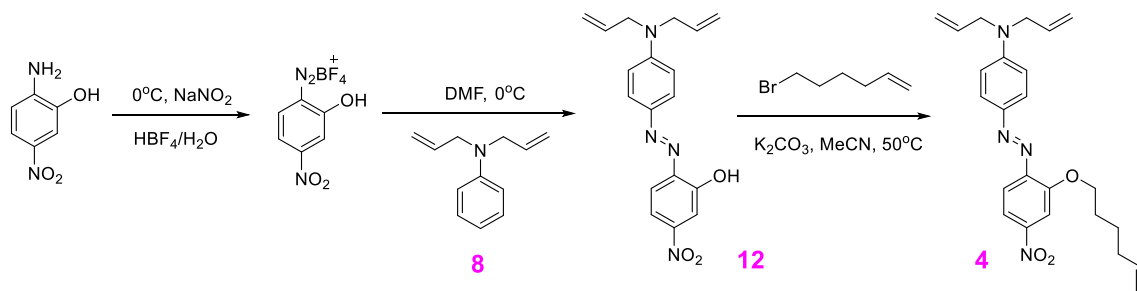
**Monomer 1:** Under an atmosphere of nitrogen, Compound **9** (300.0 mg, 0.68 mmol), Compound **R2** (393.6 mg, 1.71 mmol), EDC (393.6 mg, 2.1 mmol) and DMAP (25.1 mg, 0.21 mmol) were dissolved in anhydrous trichloromethane (7 mL), and the resultant mixture was stirred at 30 °C overnight. Then the reaction mixture was washed by the solution of citric acid and deionized water respectively for several times. The organic layer was dried over anhydrous magnesium sulfate, and then the solvent was removed by rotary evaporator. The crude product was purified by column chromatography on silica gel using dichloromethane as eluent, to give the red solid (308.8 mg, 69.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.70-1.50 (m, 4H, -CH<sub>2</sub>-), 1.82 (m, 2H, -CH<sub>2</sub>-), 2.02 (m, 2H, -C≡CH), 2.05-1.90 (m, 6H, -CH<sub>2</sub>-), 2.40 (m, 4H, -CH<sub>2</sub>-), 4.02 (d, *J* = 3.6 Hz, 4H, -CH<sub>2</sub>-), 4.08 (t, *J* = 6.0 Hz, 4H, -CH<sub>2</sub>-), 4.23 (t, *J* = 6.4 Hz, 2H, -CH<sub>2</sub>-), 4.32 (t, *J* = 6.8 Hz, 2H, -CH<sub>2</sub>-), 5.20 (t, *J* = 10 Hz, 4H, -C=CH<sub>2</sub>), 5.83 (m, 2H, -CH=C), 6.65 (t, *J* = 2.4 Hz, 1H, ArH), 6.75 (d, *J* = 8.8 Hz, 2H, ArH), 7.17 (d, *J* = 2.4, Hz, 2H, ArH), 7.65(d, *J* = 8.4, Hz, 1H, ArH), 7.91-7.84 (m, 4H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 155.3, 152.1, 148.2, 147.1, 144.7, 132.3, 126.2, 117.4, 116.8, 116.5, 111.7, 109.0, 107.8, 106.2, 82.8, 70.0, 68.9, 66.5, 65.0, 52.8, 29.0, 28.6, 28.0, 25.8. HRMS (ESI, *m/z*): calcd for C<sub>41</sub>H<sub>46</sub>N<sub>4</sub>O<sub>7</sub>, 707.3439 [M+H]<sup>+</sup>; found, 707.3444. (EA) (%), found/Calcd): C, 69.73/69.67; H, 6.65/6.56; N, 7.65/7.93.



Compound **11**: 2-Amino-5-nitrophenol (500 mg, 3.24 mmol) was dissolved in 48% fluoroboric acid (3.5 mL), then the saturated solution of sodium nitrite (279.8 mg, 4.06 mmol) was added in an ice bath. The resultant mixture was stirred at 0 °C for 12 h, before the addition of the solution of Compound **10** (937.7 mg, 4.06 mmol) in DMF (12 mL) at 0 °C. The reaction was further stirred at 0 °C overnight. Dichloromethane (150 mL) was added into the reaction mixture, and washed with water to remove DMF. The solvent was removed by rotary evaporator, and the crude product was purified by column chromatography on silica gel using dichloromethane as eluent, to yield the red solid (200 mg, 15.56%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 3.61 (t,  $J$  = 8.0 Hz, 4H, -CH<sub>2</sub>-), 3.73 (t,  $J$  = 8.0 Hz, 4H, -CH<sub>2</sub>-), 6.81 (d,  $J$  = 8.0 Hz, 2H, ArH), 7.86-7.75 (t, 4H, ArH), 7.93 (d,  $J$  = 8.0 Hz, 1H, ArH), 13.15 (s, 1H, Ar-OH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 152.8, 150.3, 148.1, 141.7, 140.3, 132.0, 125.6, 114.7, 113.8, 50.7. HRMS (ESI,  $m/z$ ): calcd for C<sub>16</sub>H<sub>16</sub>N<sub>10</sub>O<sub>3</sub>, 395.1334 [M-H]<sup>-</sup>, found, 395.1336.

Monomer **2**: Compound **11** (150 mg, 0.38 mmol), 6-bromo-1-hexene (185 mg, 1.14 mmol) and anhydrous potassium carbonate (157.5 mg, 1.14 mmol) were added in acetonitrile (10 mL). The reaction was stirred at 50 °C overnight, then poured into ice water and filtered. After dried in vacuum oven, the solid product was purified by column chromatography on silica gel using dichloromethane as eluent, to give the red solid (147 mg, 81.2%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.68 (m, 2H, -CH<sub>2</sub>-), 1.95 (m, 2H, -CH<sub>2</sub>-), 2.19 (m, 2H, -CH<sub>2</sub>-), 3.58 (t,  $J$  = 4.0 Hz, 4H, -CH<sub>2</sub>-), 3.72 (t, 4H,  $J$  = 8.0 Hz, -CH<sub>2</sub>-), 4.24 (t,  $J$  = 8.0 Hz, 2H, -CH<sub>2</sub>-), 5.05 (m, 2H, -C=CH<sub>2</sub>), 5.96 (m, 1H, -CH=C), 6.81 (d,  $J$  = 12.0 Hz, 2H, ArH), 7.67 (d,  $J$  = 8.8 Hz, 1H, ArH), 7.97-7.84 (m, 4H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 155.4, 148.7, 146.8, 145.3, 133.5, 126.2, 117.5, 114.9,

111.8, 109.1, 69.8, 51.4, 48.2, 33.8, 28.2, 25.0. HRMS (ESI, m/z): calcd for C<sub>22</sub>H<sub>26</sub>N<sub>10</sub>O<sub>3</sub>, 479.2262 [M+H]<sup>+</sup>; found, 479.2274.



Compound **12**: 2-Amino-5-nitrophenol (500 mg, 3.24 mmol) was dissolved in 48% fluoroboric acid (3.5 mL), then the sodium nitrite saturated solution (279.8 mg, 4.06 mmol) was added in an ice bath. The resultant mixture was stirred at 0 °C for 12 h, before the addition of the solution of Compound **8** (702.6 mg, 4.06 mmol) DMF (8 mL) at 0 °C. The reaction was further stirred at 0 °C overnight. Dichloromethane (150 mL) was added into the reaction mixture, then washed with water to remove DMF. The solvent of dichloromethane was removed by rotary evaporator, and the crude product was purified by column chromatography on silica gel using dichloromethane as eluent, to give the red solid (230 mg, 21.0%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K), δ (TMS, ppm): 4.05 (t, *J*=2.0 Hz, 4H, -CH<sub>2</sub>-), 5.26-5.17 (m, 4H, -C=CH<sub>2</sub>), 5.87 (m, 2H, -CH=C), 6.74 (d, *J*=8.0 Hz, 2H, ArH), 7.82-7.76 (m, 4H, ArH), 7.86 (d, *J*=8.0 Hz, 1H, ArH), 13.32 (s, 1H, Ar-OH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K), δ (ppm): 152.8, 152.5, 147.7, 140.9, 140.6, 132.1, 131.6, 125.4, 116.9, 114.6, 113.6, 112.3, 52.9. HRMS (ESI, m/z): calcd for C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>, 337.1306 [M-H]<sup>-</sup>; found, 337.1303. (EA) (%), found/Calcd): C, 63.67/63.89; H, 5.21/5.36; N, 16.62/16.56.

Monomer **4**: Compound **12** (101.5 mg, 0.30 mmol), 6-bromo-1-hexene (146.7 mg, 0.90 mmol) and anhydrous potassium carbonate (124.4 mg, 0.90 mmol) were added in acetonitrile (5 mL). The reaction was stirred at 50 °C overnight, and poured into ice water, and filtered. After dried in vacuum oven, the crude solid was purified by column chromatography on silica gel using dichloromethane as eluent, to give the red solid (115 mg, 91.2%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K), δ (TMS, ppm): 1.65 (m, 2H, -CH<sub>2</sub>-), 1.94 ((m, 2H, -CH<sub>2</sub>-), 2.18 (m, 2H,

-CH<sub>2</sub>-), 4.04 (t, *J*=3.0 Hz, 4H, -CH<sub>2</sub>-), 4.22 (t, *J*=6.0 Hz, 2H, -CH<sub>2</sub>-), 5.02 (m, 2H, -C=CH<sub>2</sub>), 5.22 (m, 4H, -C=CH<sub>2</sub>), 5.86 (m, 3H, -CH=C), 6.77-6.74 (m, 2H, ArH), 7.64 (d, *J*=12.0 Hz, 1H, ArH), 7.89-7.85 (m, 4H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 155.2, 152.0, 148.2, 147.2, 144.6, 138.5, 132.5, 126.1, 117.4, 116.7, 116.5, 114.9, 111.8, 109.1, 69.8, 52.8, 33.4, 28.4, 25.3. HRMS (ESI, *m/z*): calcd for C<sub>24</sub>H<sub>28</sub>N<sub>4</sub>O<sub>3</sub>, 421.2240 [M+H]<sup>+</sup>; found, 421.2239. (EA) (%), found/Calcd): C, 68.29/68.55; H, 6.54/6.71; N, 13.27/13.32.

### Synthesis of polymer

Polymer(**3**): Under an atmosphere of nitrogen, a Schlenk flask was charged with **1** (121.12 mg, 0.171 mmol), **2** (82 mg, 0.171 mmol), CuSO<sub>4</sub> · 5H<sub>2</sub>O (10 mol %), NaHCO<sub>3</sub> (20 mol %), ascorbic acid (20 mol %) and DMF (5 mL). The resultant mixture was stirred at 28 °C for 36 h, then poured into ice water and filtered. The crude solid product was washed several times with methanol, methanol/acetone (2/1) and deionized water. The obtained solid was dissolved in THF, and the insoluble solid was filtered out. After removal of the solvent, the residue was dried in a vacuum oven to a constant weight, as a red powder (103 mg, 50.7%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (TMS, ppm): 1.60 (-CH<sub>2</sub>-), 1.91 (-CH<sub>2</sub>-), 2.13 (-CH<sub>2</sub>-), 2.84 (-CH<sub>2</sub>-), 3.72 (-CH<sub>2</sub>-), 4.00 (-CH<sub>2</sub>-), 4.41-4.17 (-CH<sub>2</sub>-), 4.97 (-CH<sub>2</sub>-), 5.17 (-CH<sub>2</sub>-), 5.84 (-CH-), 6.73-6.55 (-ArH), 7.08 (-ArH), 7.21 (-ArH), 7.61 (-ArH), 7.80 (-ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K),  $\delta$  (ppm): 165.2, 158.8, 154.4, 154.1, 150.9, 147.9, 147.5, 146.9, 146.3, 145.9, 145.2, 144.2, 143.3, 137.4, 131.4, 130.1, 125.2, 124.8, 121.1, 116.1, 115.6, 115.3, 115.1, 113.8, 110.7, 108.0, 106.6, 105.0, 102.6, 68.7, 65.6, 65.4, 64.1, 51.7, 51.2, 50.3, 46.1, 32.2, 27.8, 27.6, 27.3, 26.6, 24.8, 24.6, 24.1, 20.9, 20.6.

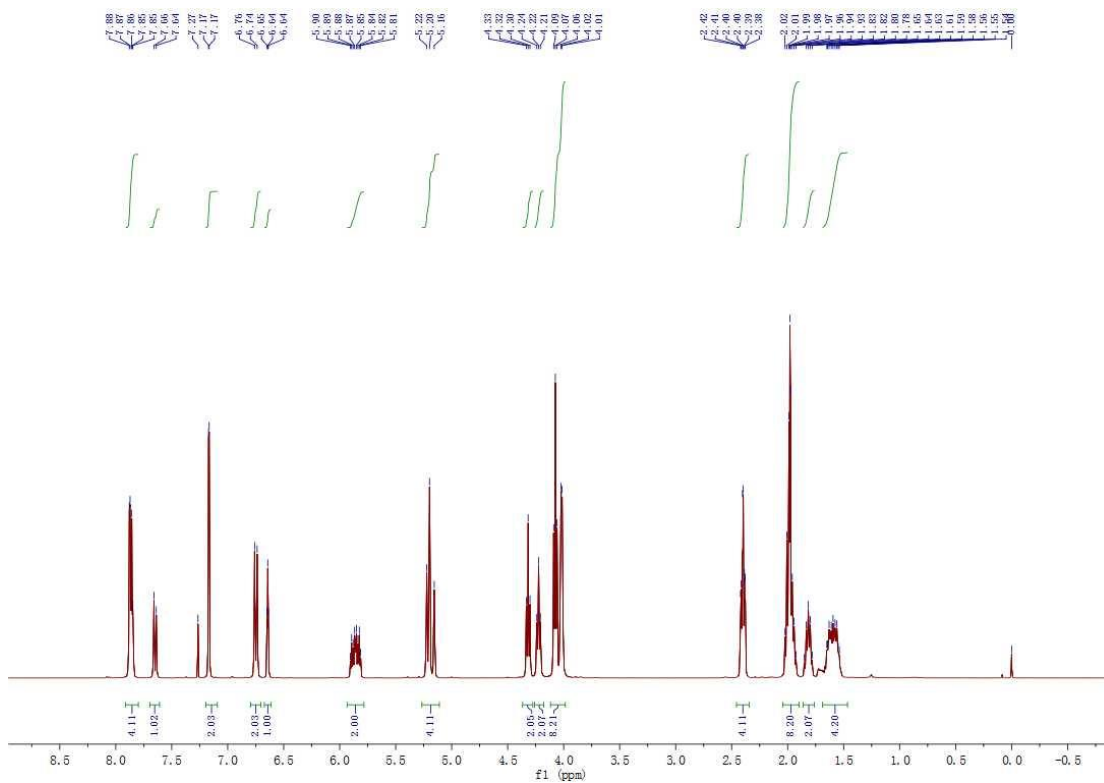


Figure S9 The  $^1\text{H}$  NMR spectrum of **1**.

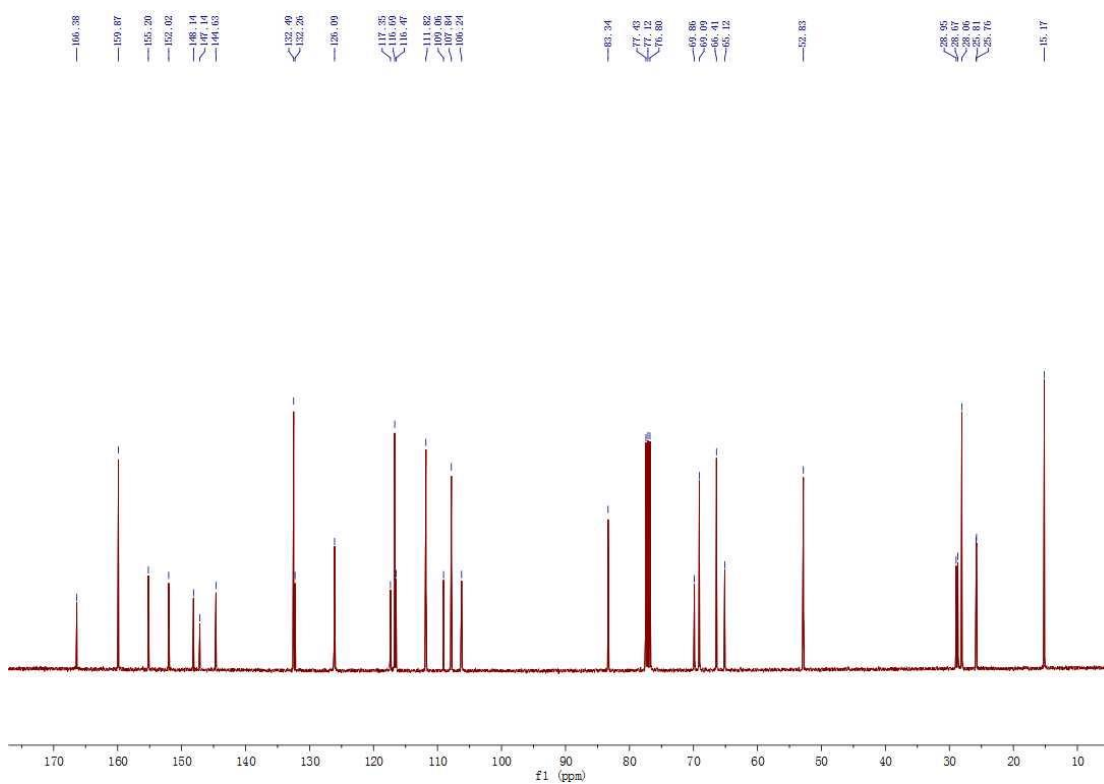
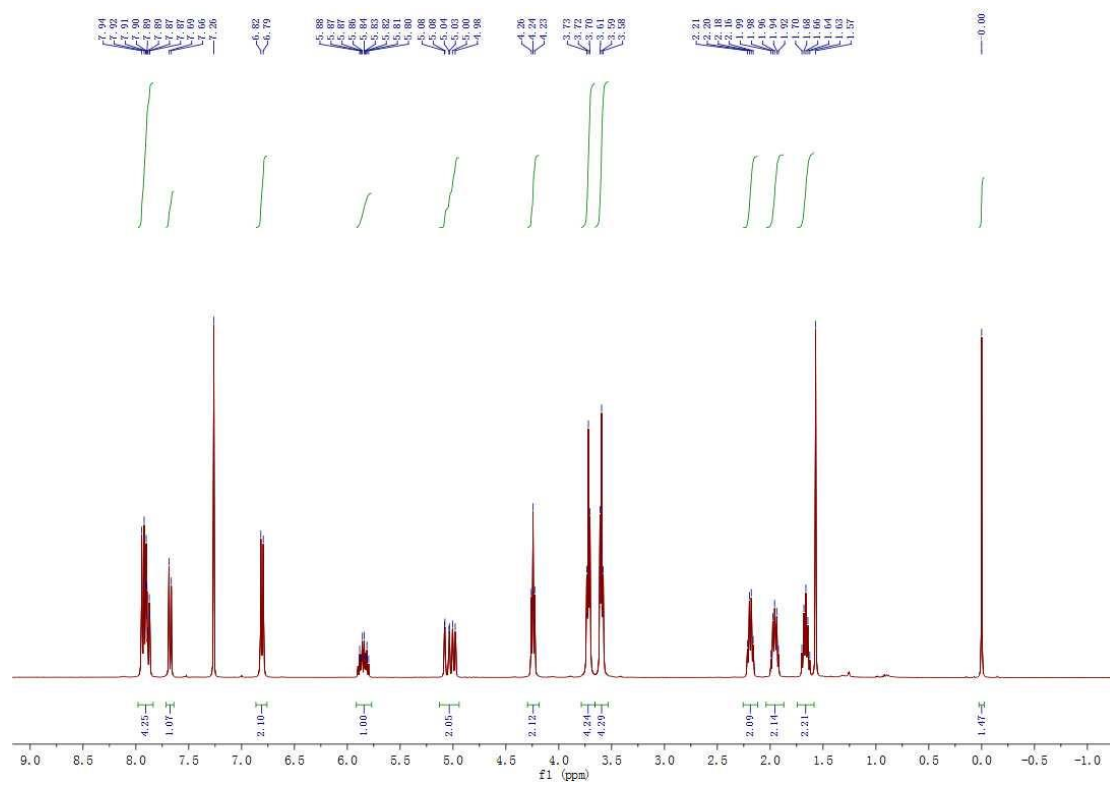
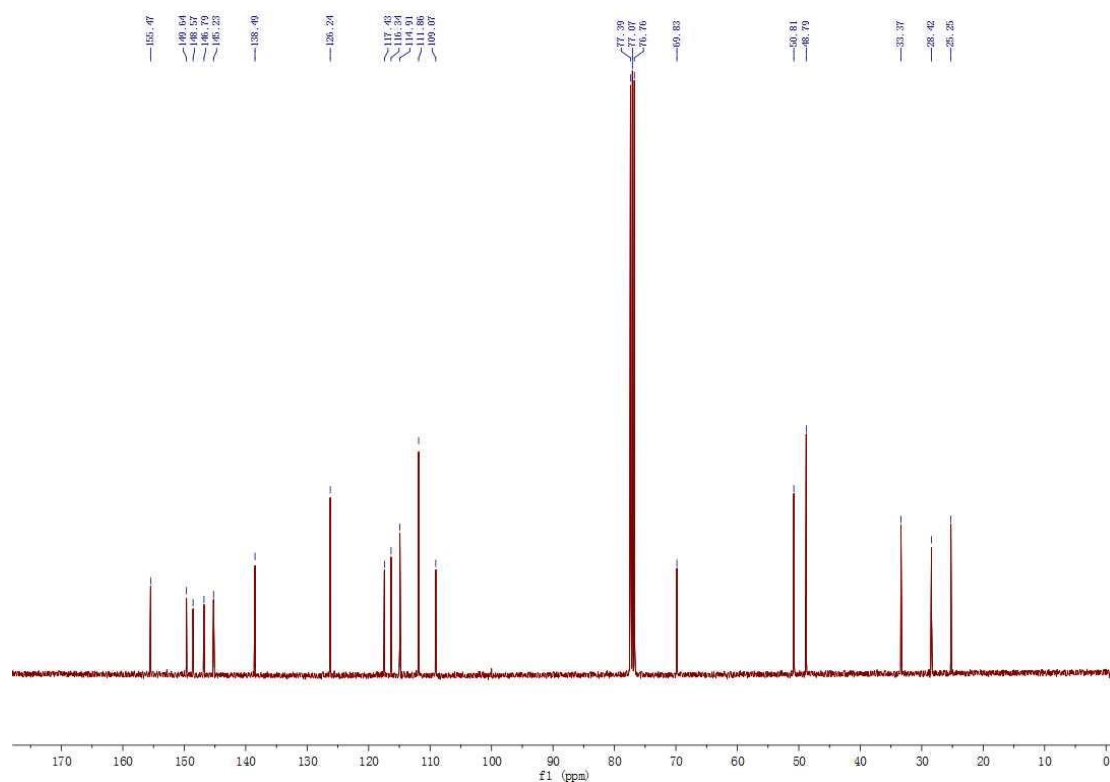


Figure S10 The  $^{13}\text{C}$  NMR spectrum of **1**.



**Figure S11** The  $^1\text{H}$  NMR spectrum of **2**.



**Figure S12** The  $^{13}\text{C}$  NMR spectrum of **2**.



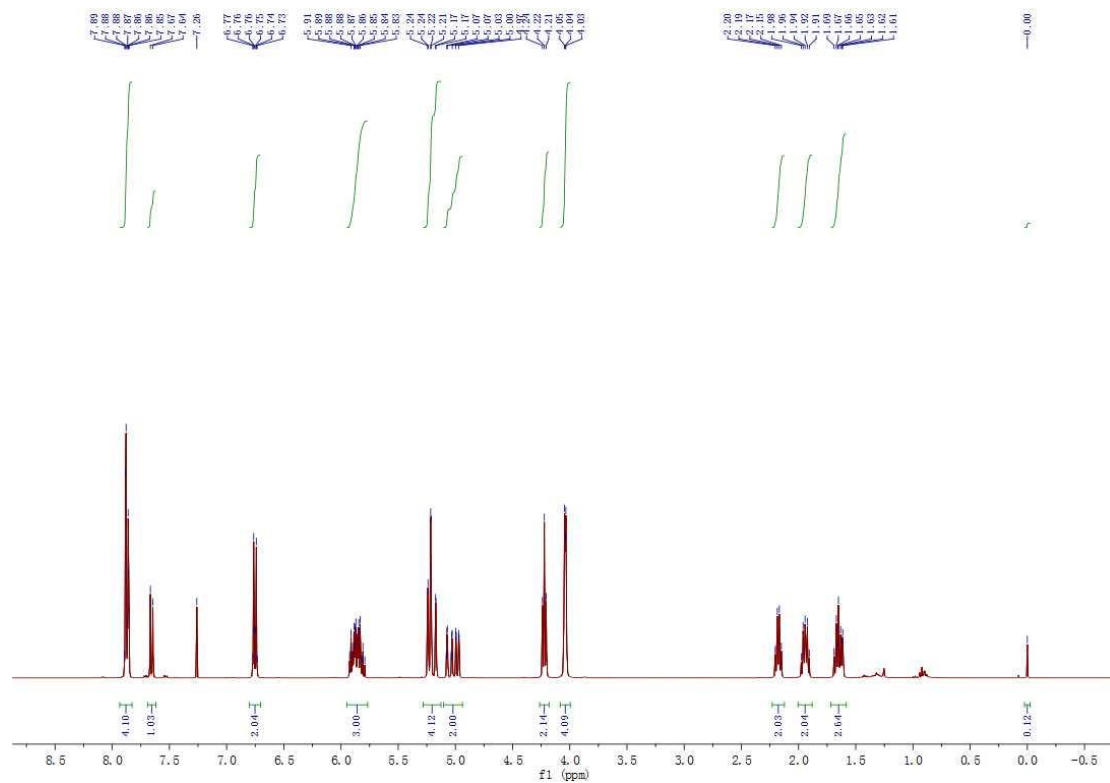


Figure S13 The  $^1\text{H}$  NMR spectrum of **4**.

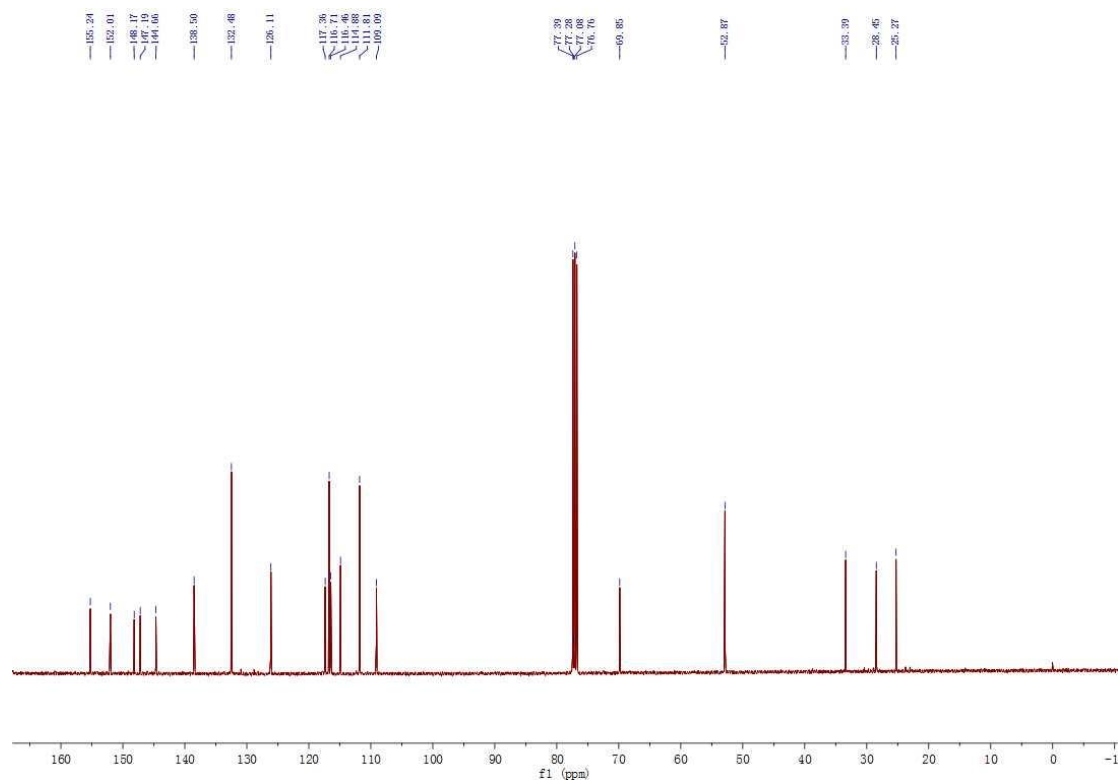


Figure S14 The  $^{13}\text{C}$  NMR spectrum of **4**.

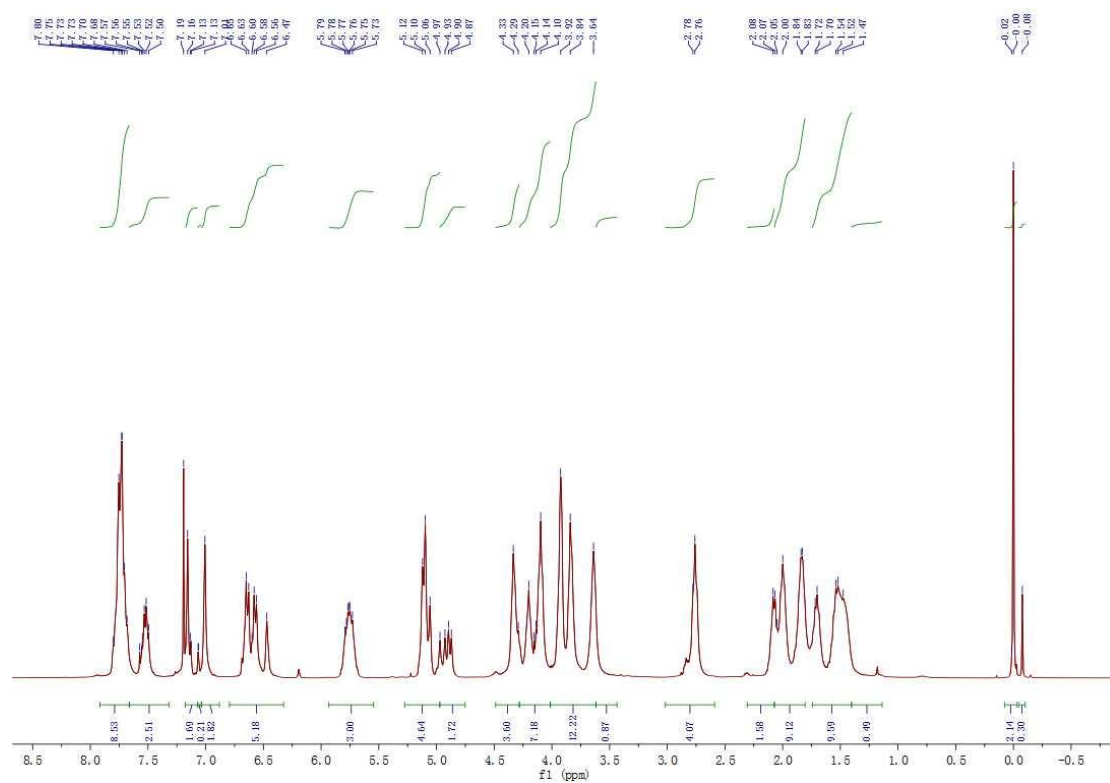


Figure S15 The  $^1\text{H}$  NMR spectrum of **3**.

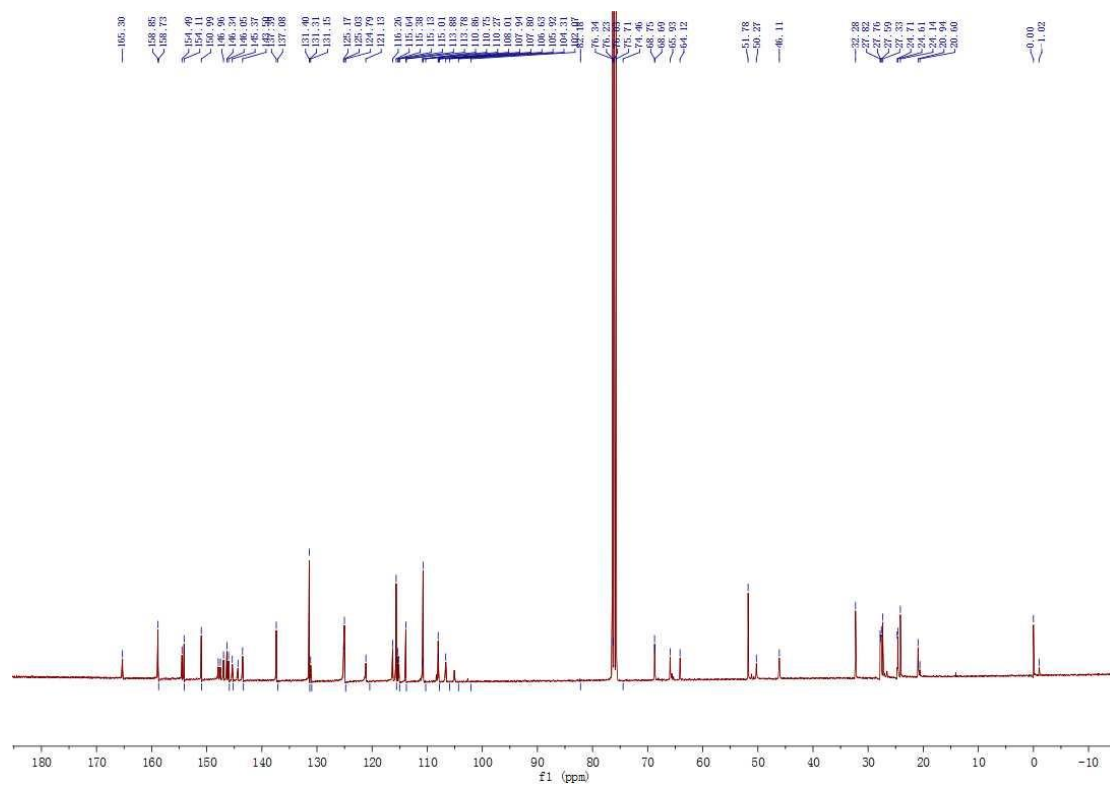
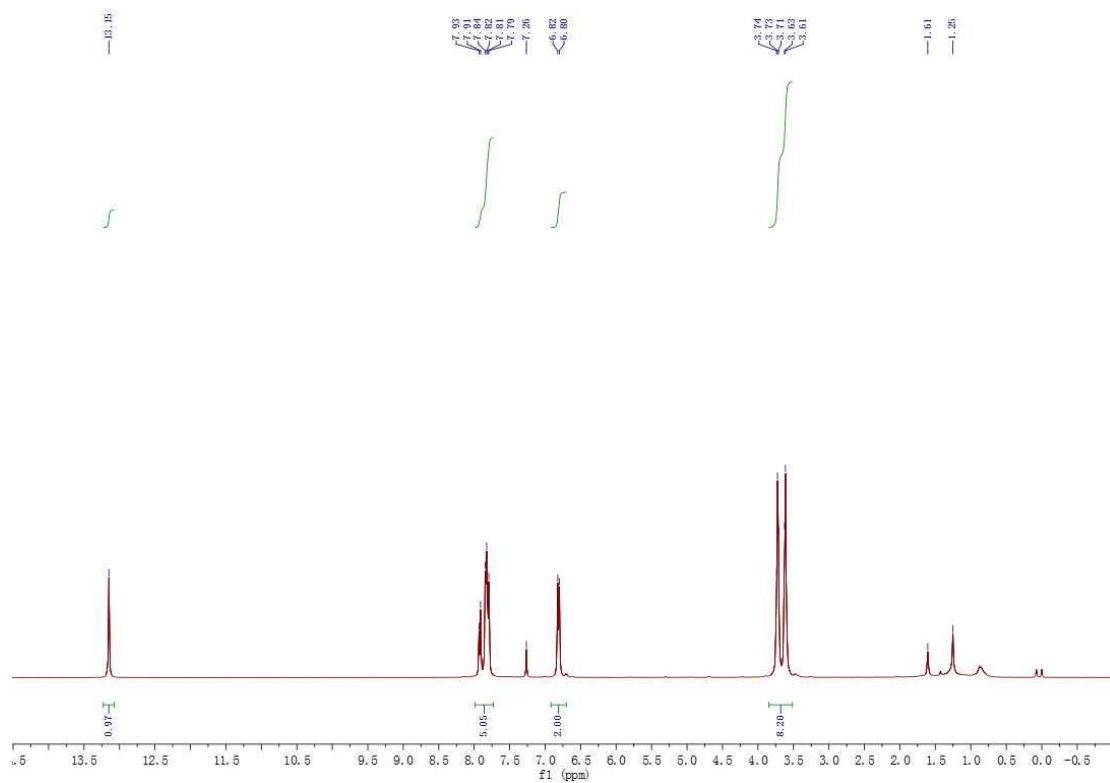
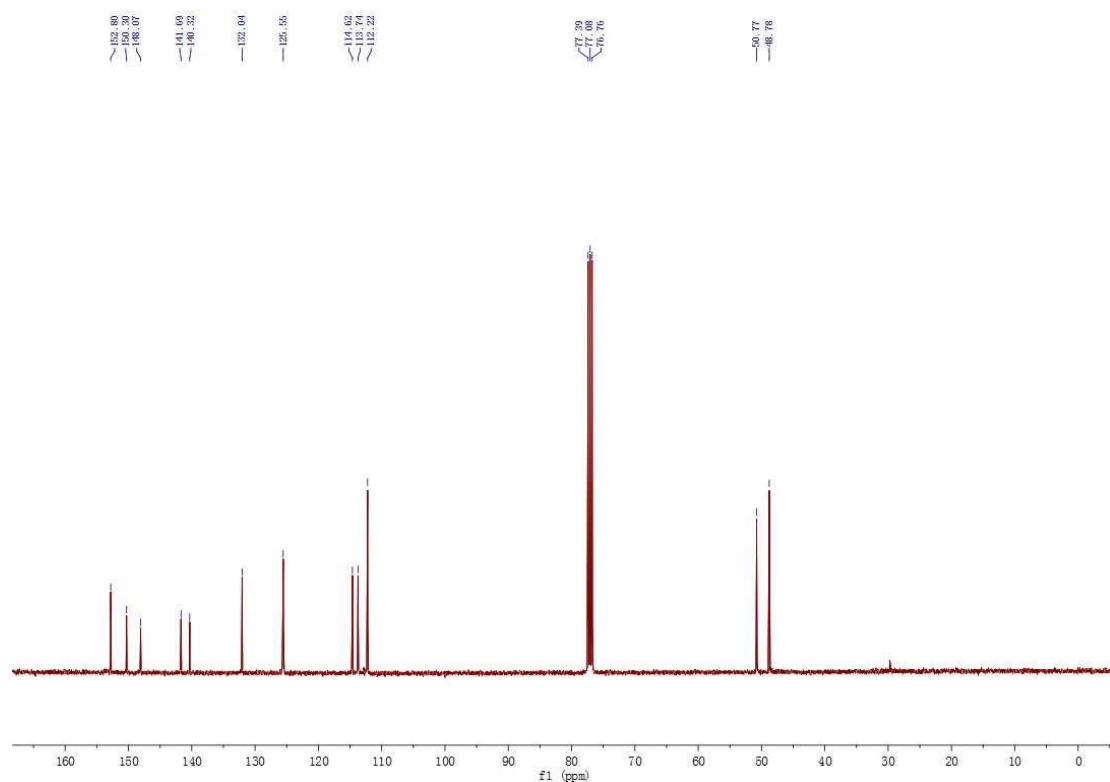


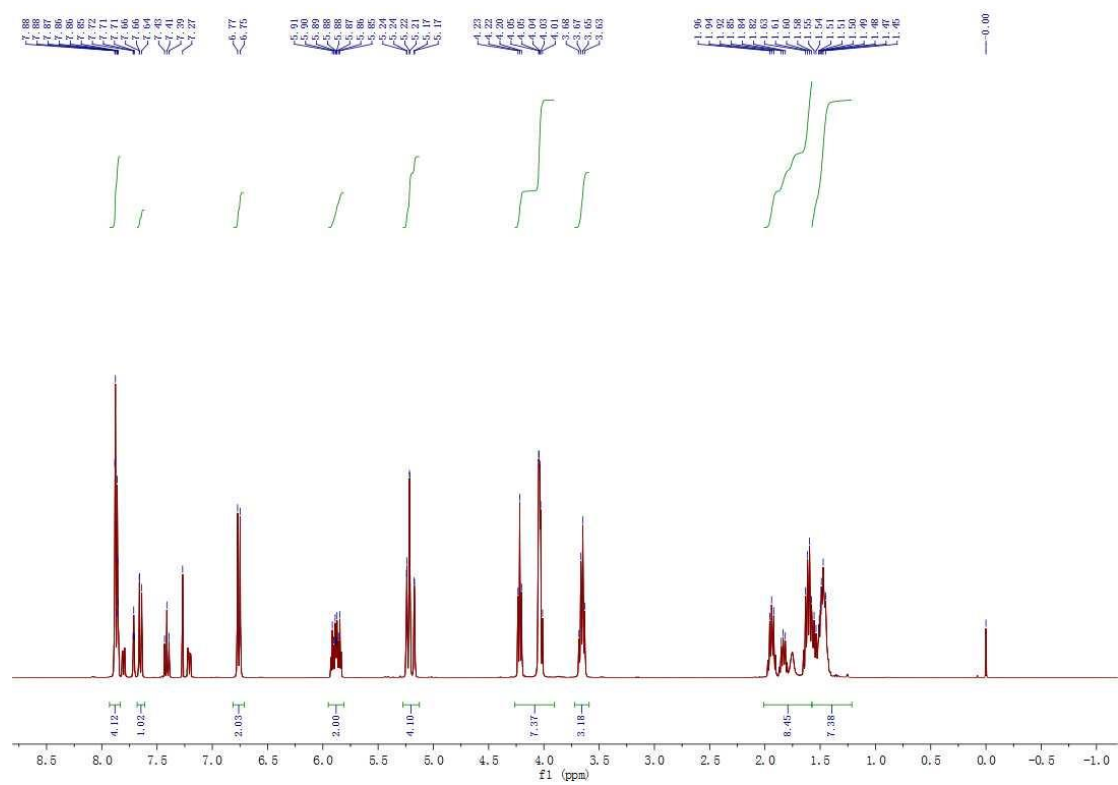
Figure S16 The  $^{13}\text{C}$  NMR spectrum of **3**.



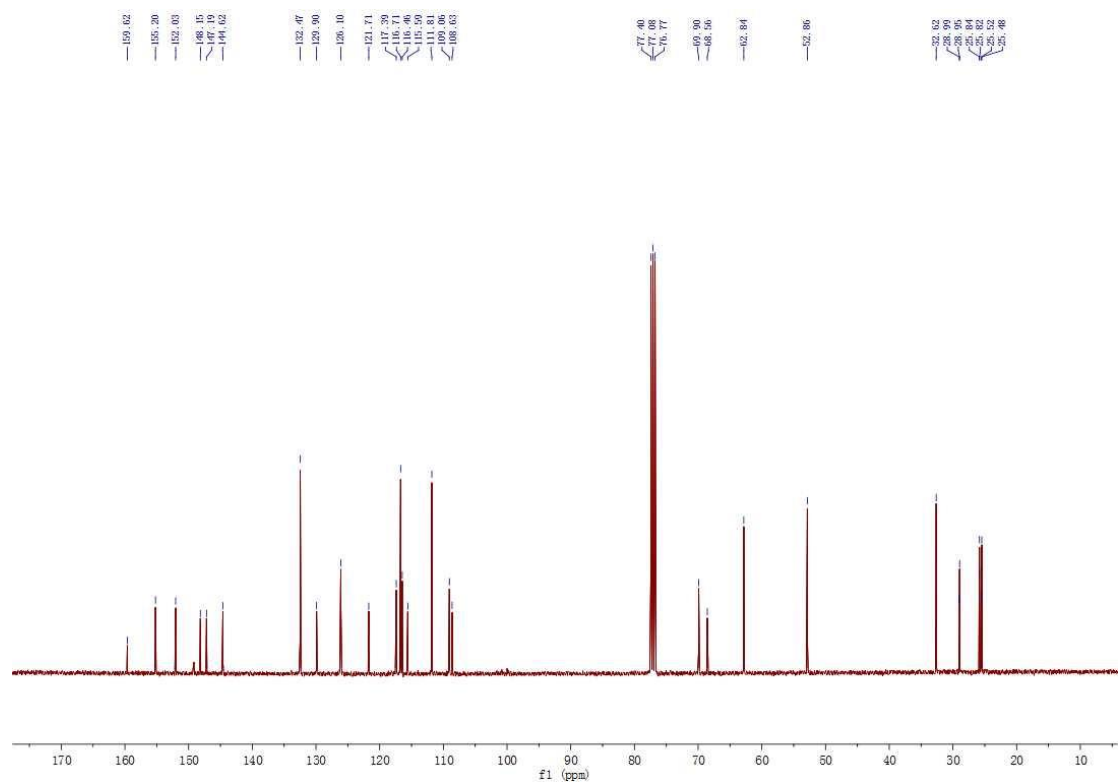
**Figure S17** The  $^1\text{H}$  NMR spectrum of **11**.



**Figure S18** The  $^{13}\text{C}$  NMR spectrum of **11**.



**Figure S19** The  $^1\text{H}$  NMR spectrum of **9**.



**Figure S20** The  $^{13}\text{C}$  NMR spectrum of **9**.

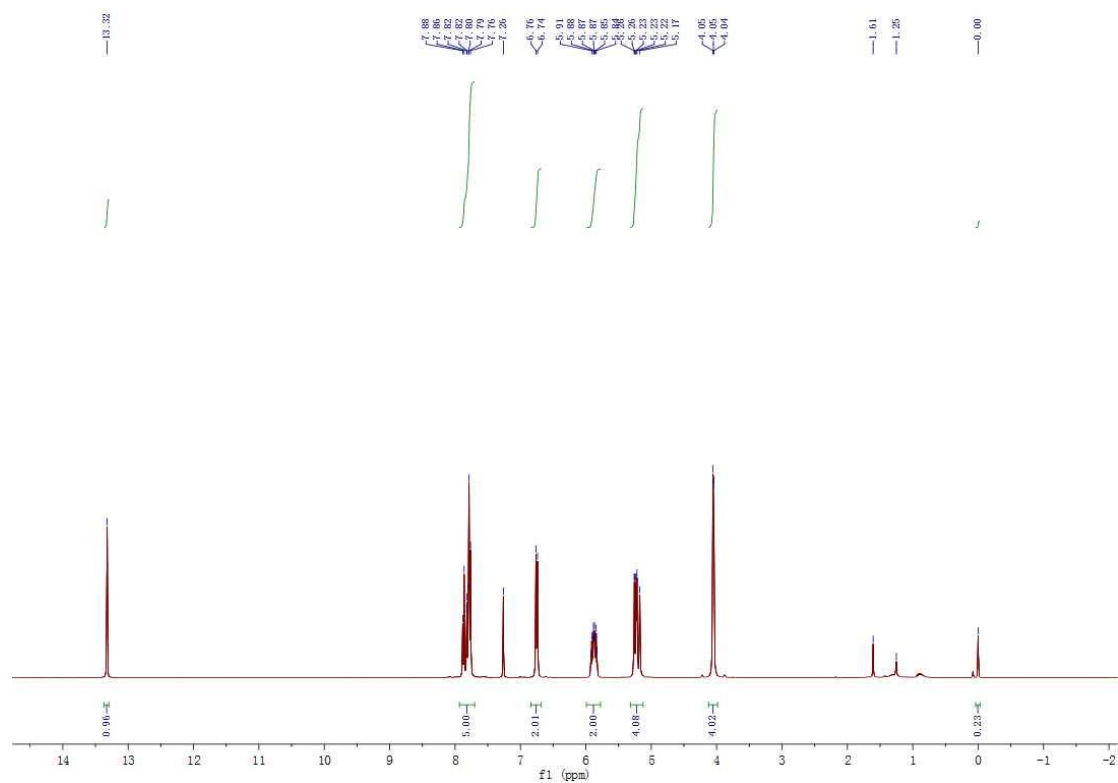


Figure S21 The  $^1\text{H}$  NMR spectrum of **12**.

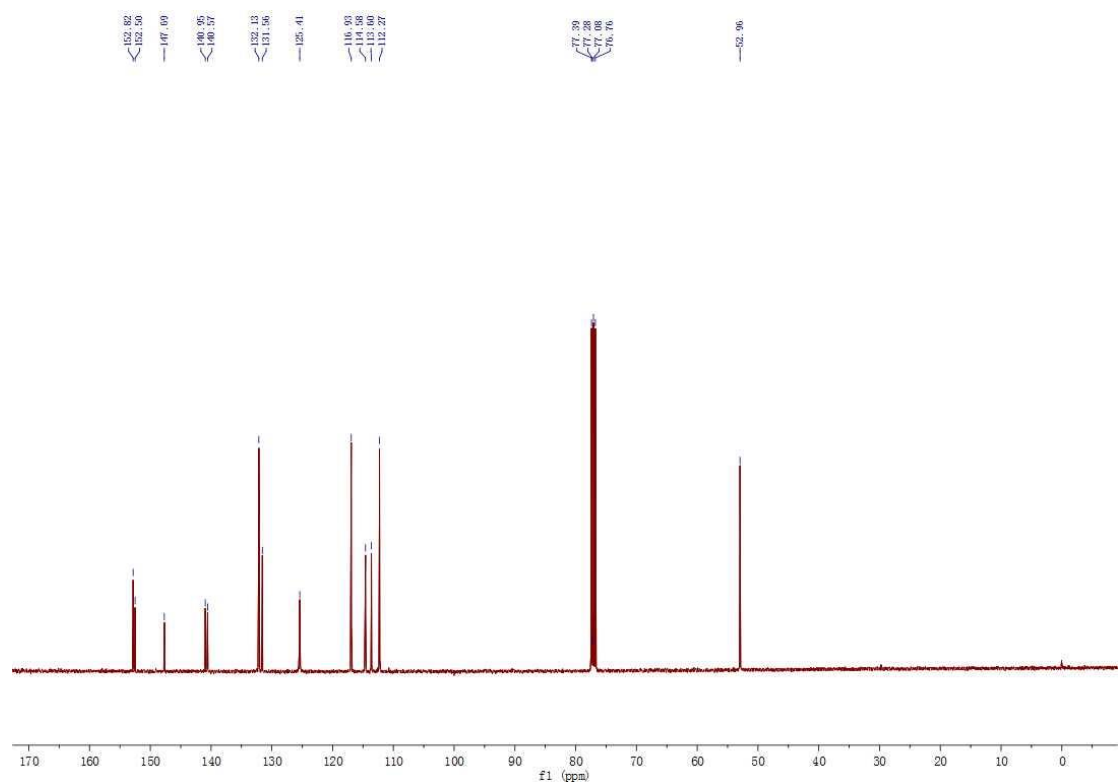


Figure S22 The  $^{13}\text{C}$  NMR spectrum of **12**.

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