Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information (ESI)

Photo-crosslinkable second order nonlinear AB_2-type monomers: convenient synthesis and the enhanced NLO thermostability

Ruifang Wang, Ziyao Cheng, Xiaocong Deng, Wenjing Zhao, Qianqian Li and Zhen Li *

1. Additional data and analysis

Chart S1 Some NLO molecules using the photo-crosslink method.[1,2]

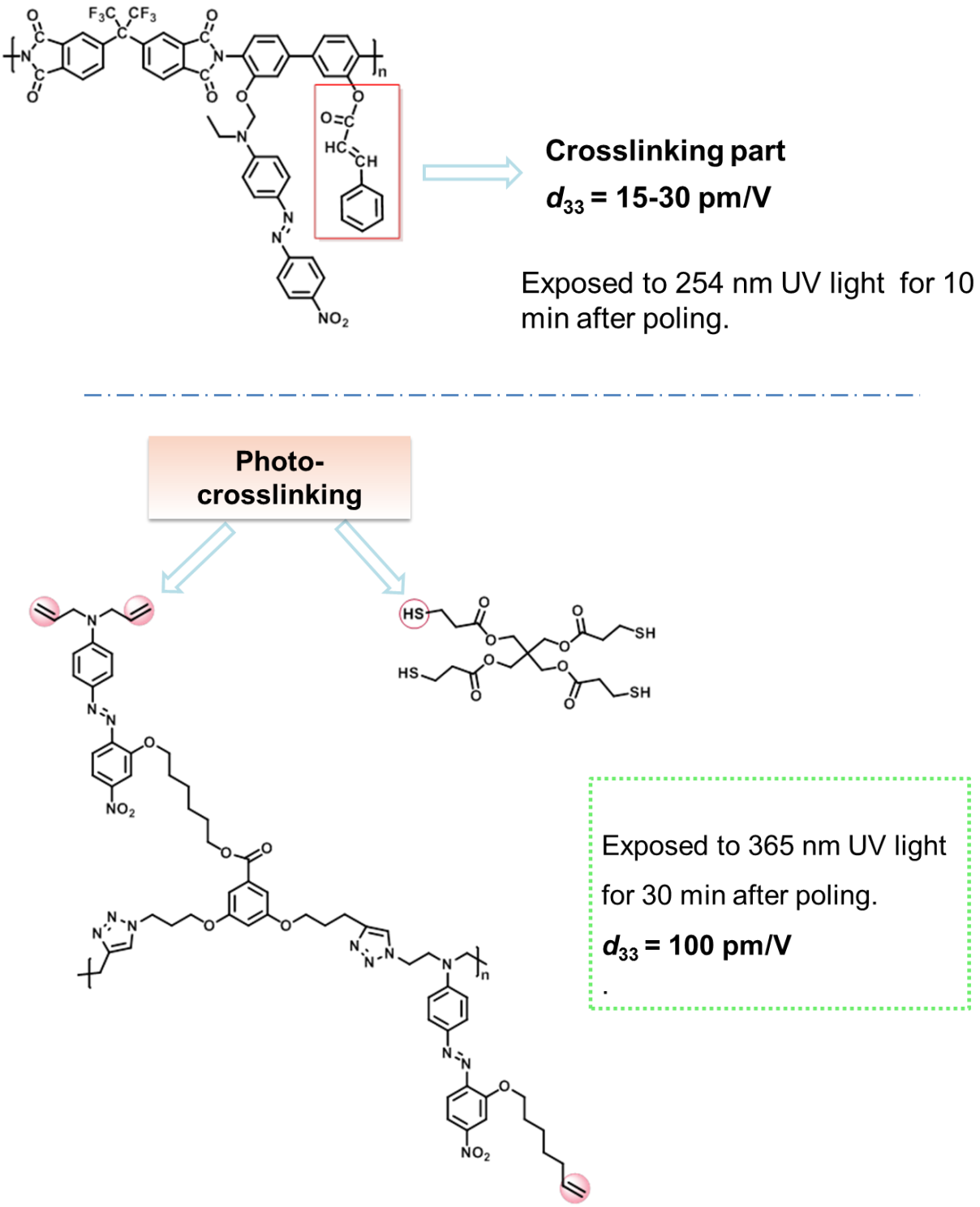
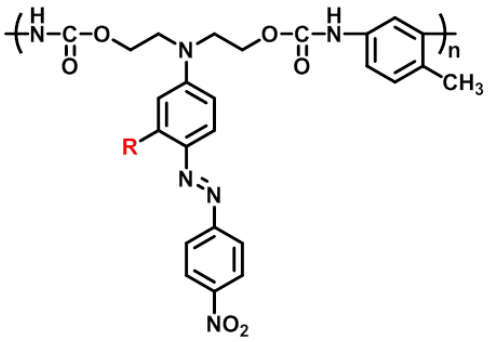
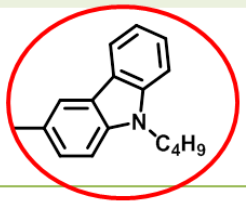
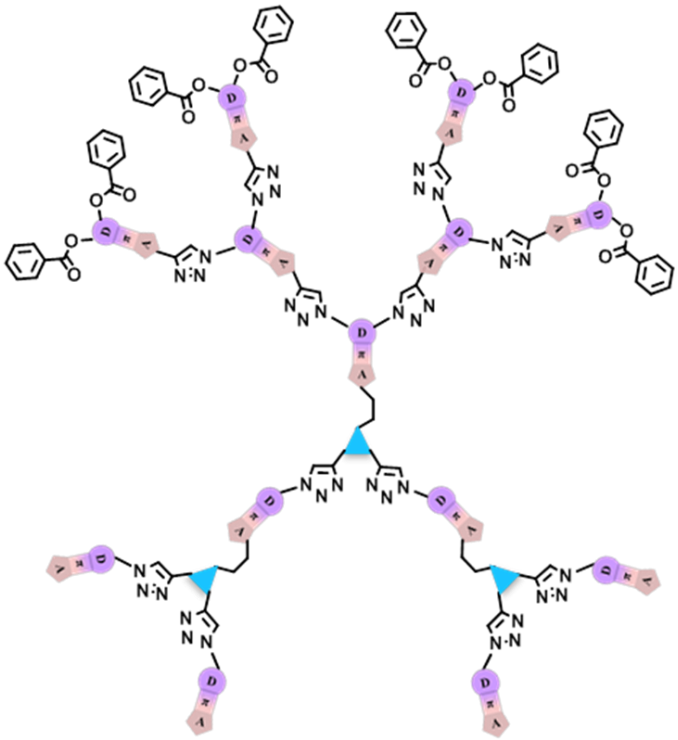


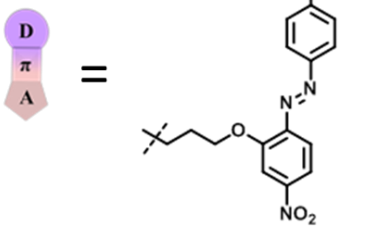
Chart S2 Some molecules we have synthesized in our previous works.[3,4]

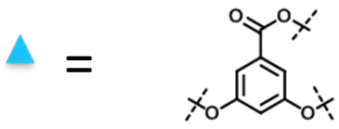


	R	d_{33} (pm/V)
p1	H	56.4
p2	Br	51.9
p3		49.4
p4		**82.3**

Suitable isolation group







D13N

d_{33} = 299 pm/V

Table S1 Characterization results of **DN-SH** and **DS-SH**.

No.	m/z [a]	m/z(cal) [b]	T_g [c] (°C)	T_d [d] (°C)
DN-SH	1369.6033	1369.6047	60.5	245.9
DS-SH	1316.5202	1316.5241	70.5	216.3

[a] Measured by HRMS spectroscopy. [b] Calculated for $[M + H]^+$. [c] detected by DSC analysis under nitrogen at a heating rate of 10 °C min^{-1}. [d] The 5% weight loss temperature of monomers detected by TGA analysis under nitrogen at a heating rate of 20 °C min^{-1}.

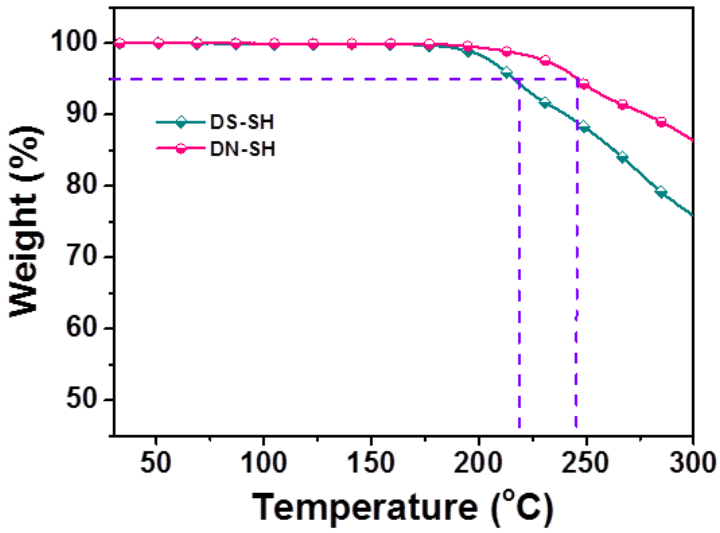


Fig S1 TGA curves of **DN-SH** and **DS-SH**.

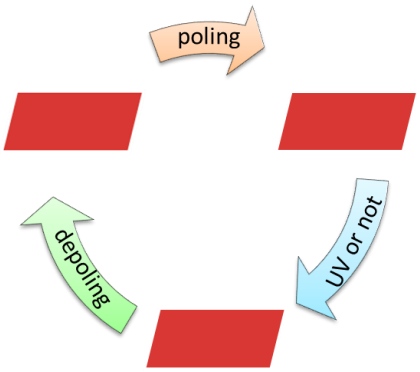


Fig S2 Schematic illustrations of the photo-crosslinking process.

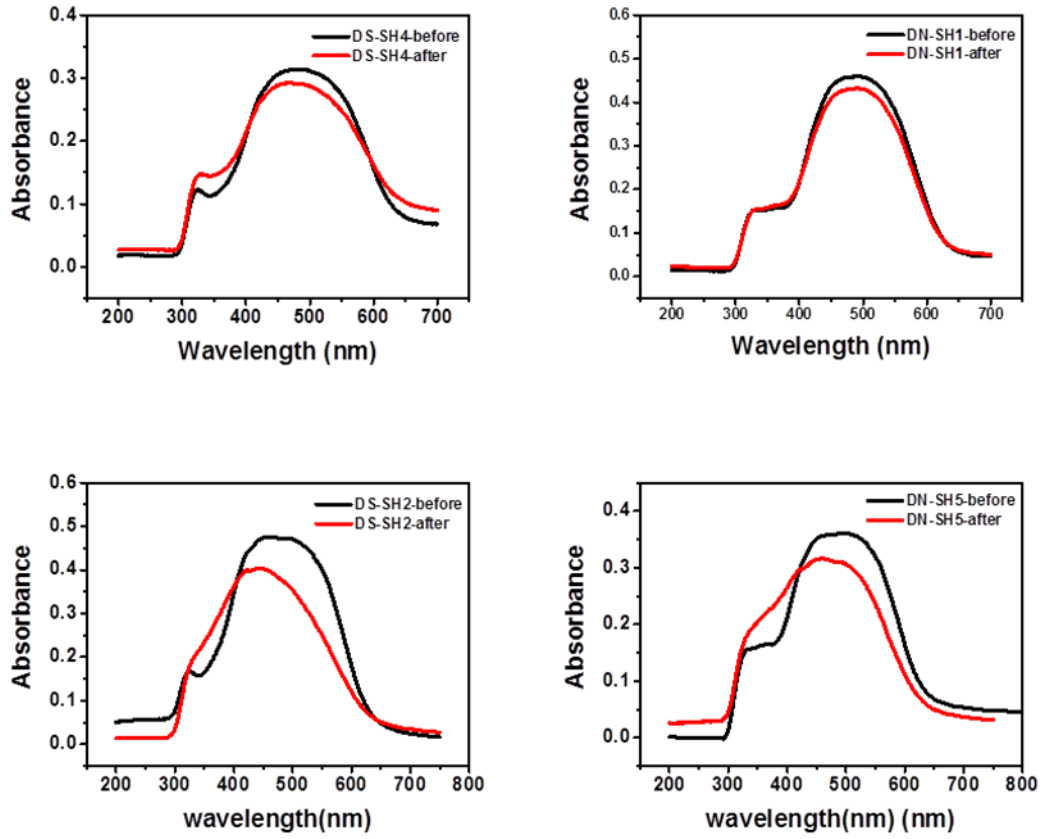


Fig S3 The UV-vis spectra of the films before and after poling. (**DS-SH4** and **DN-SH1** were illuminated for 0 min, **DS-SH2** and **DN-SH5** were illuminated for 30 min).

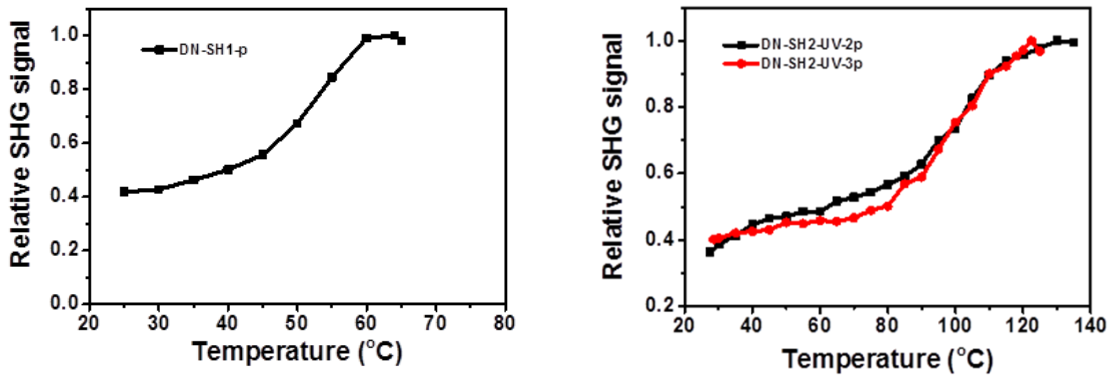


Fig S4 The poling curves of film **DN-SH1** and **DN-SH2** (illuminated at room temperature for 30 min).

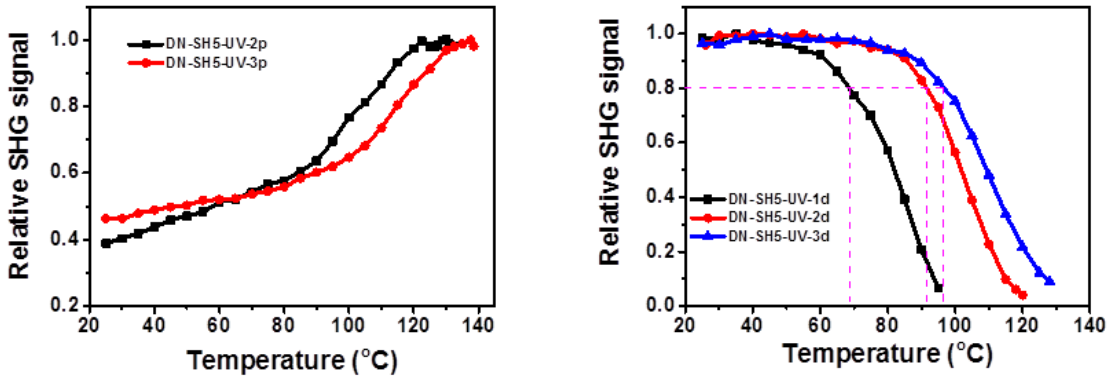


Fig S5 The poling (left) and depoling curves of film **DN-SH5** (illuminated at best temperature for 30 min).

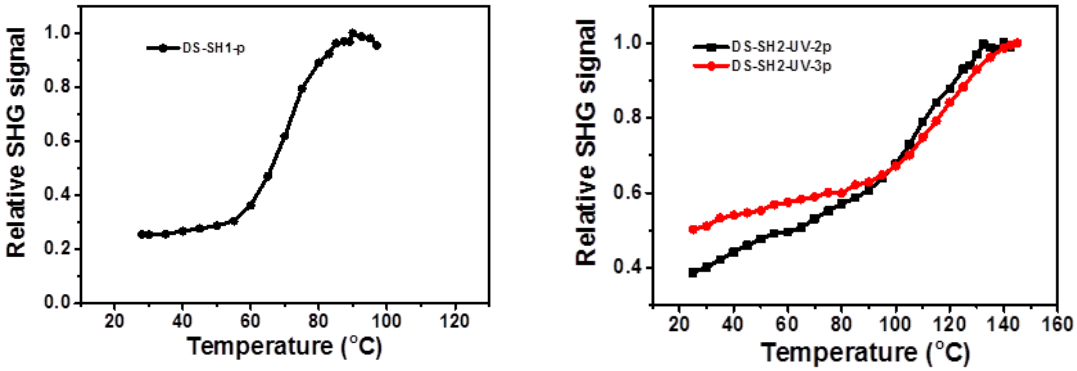


Fig S6 The poling curves of film **DS-SH1** and **DS-SH2** (illuminated at room temperature for 30 min).

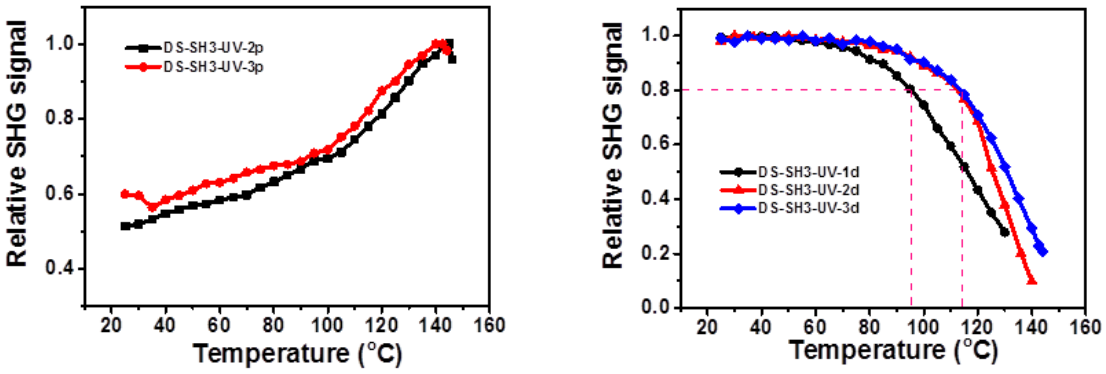


Fig S7 The poling and depoling curves of film **DS-SH3** (illuminated at best temperature for 30 min).

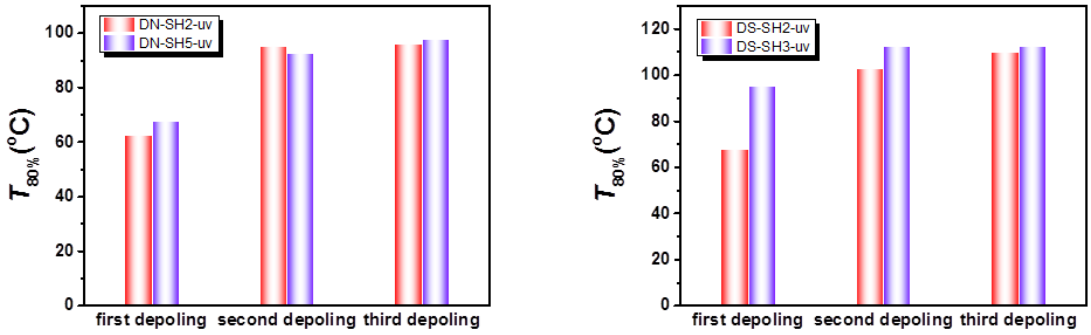


Fig S8 The $T_{80\%}$ of the films of monomers **DN-SH** and **DS-SH**. (Red: illuminated at room temperature, Purple: illuminated at best poling temperature).

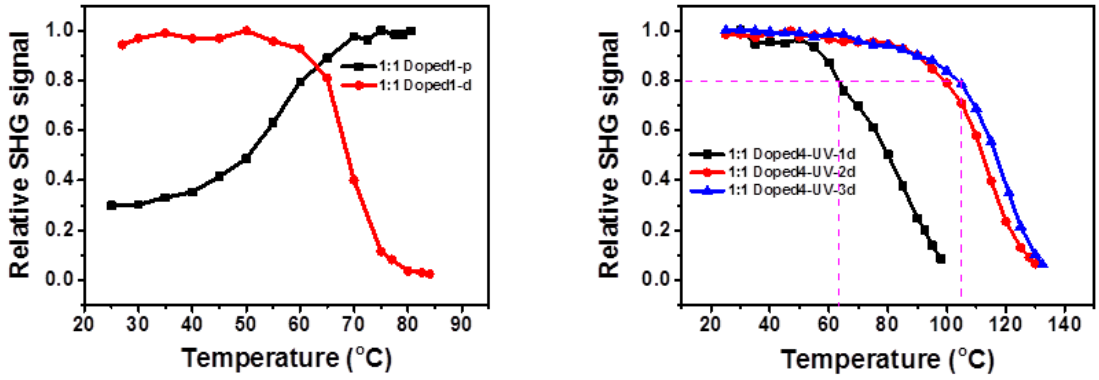


Fig S9 The poling and depoling curves of films **1:1 Doped1** and **1:1 Doped4** (**1:1 Doped4** was illuminated at room temperature for 30 min).

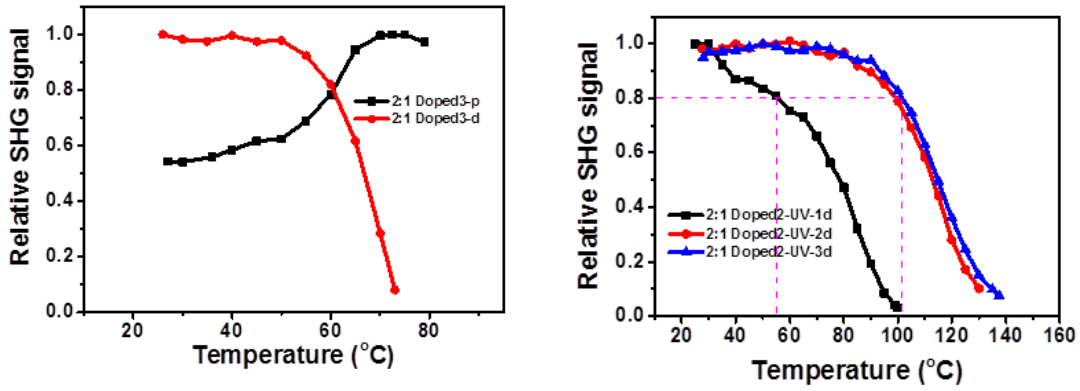


Fig S10 The poling and depoling curves of films **2:1 Doped3** and **2:1 Doped2** (**2:1 Doped2** was illuminated at room temperature for 30 min).

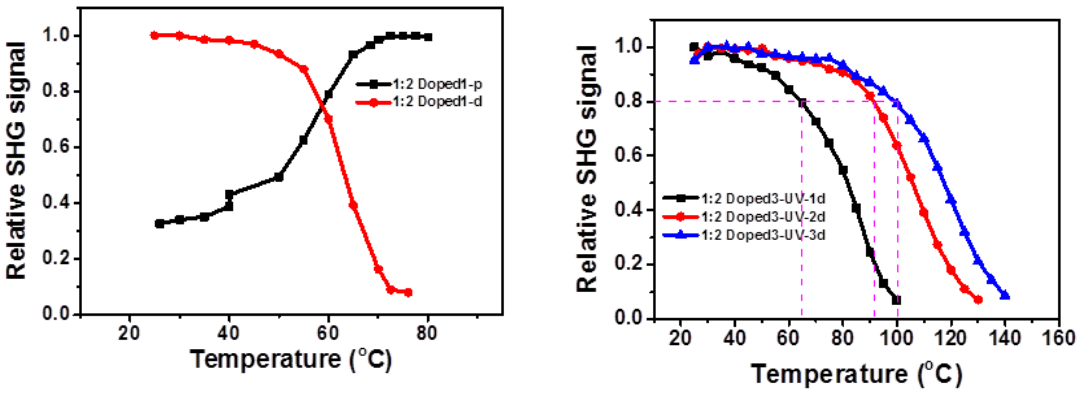
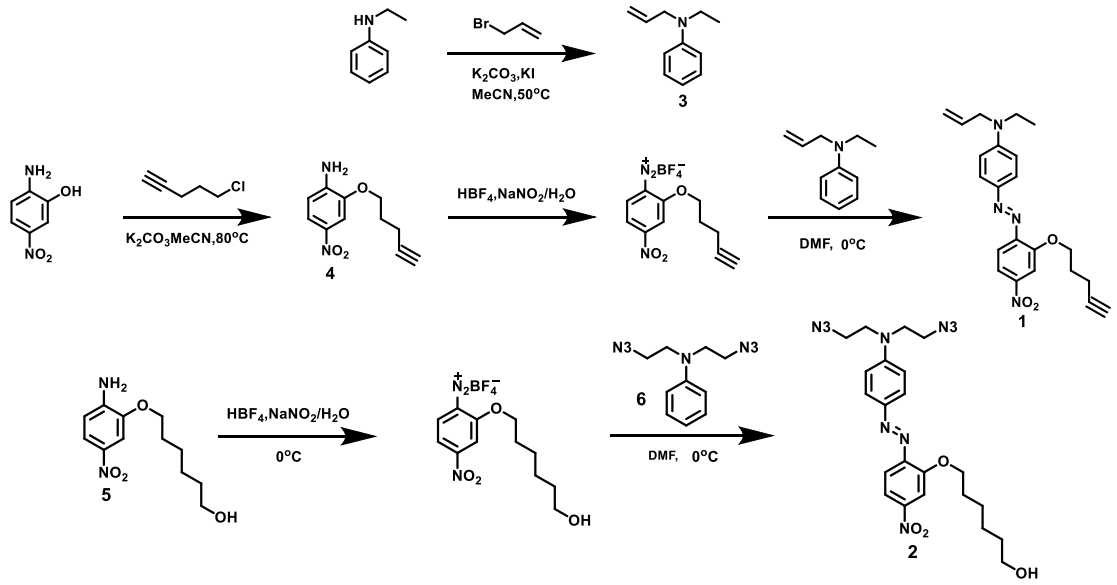


Fig S11 The poling and depoling curves of films **1:2 Doped1** and **1:2 Doped3** (**1:2 Doped3** was illuminated at room temperature for 30 min).

2. Synthesis



Compound **3**: *N*-Ethylaniline (6.06 g, 0.05 mol), allyl bromide (12.1 g, 0.1 mol), potassium carbonate (13.8 g, 0.1 mol) and potassium iodide (1.66 g, 0.01 mol) were added in acetonitrile (50 mL). The resultant mixture was stirred at 50 °C until the starting reactant consumed completely. After cooling to room temperature, the reaction mixture was filtered to remove the salt, and then the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent, to yield the colorless oil (6.25 g, 77.5%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.15 (t, J = 6.0 Hz, 3H, -CH_3), 3.36 (q, 2H, -CH_2-), 3.88 (m, 2H, -CH_2-), 5.19-5.11 (m, 2H, -C=CH_2), 5.89-5.80 (m, 1H, -CH=C), 6.63-6.69 (m, 3H, ArH), 7.22-7.18

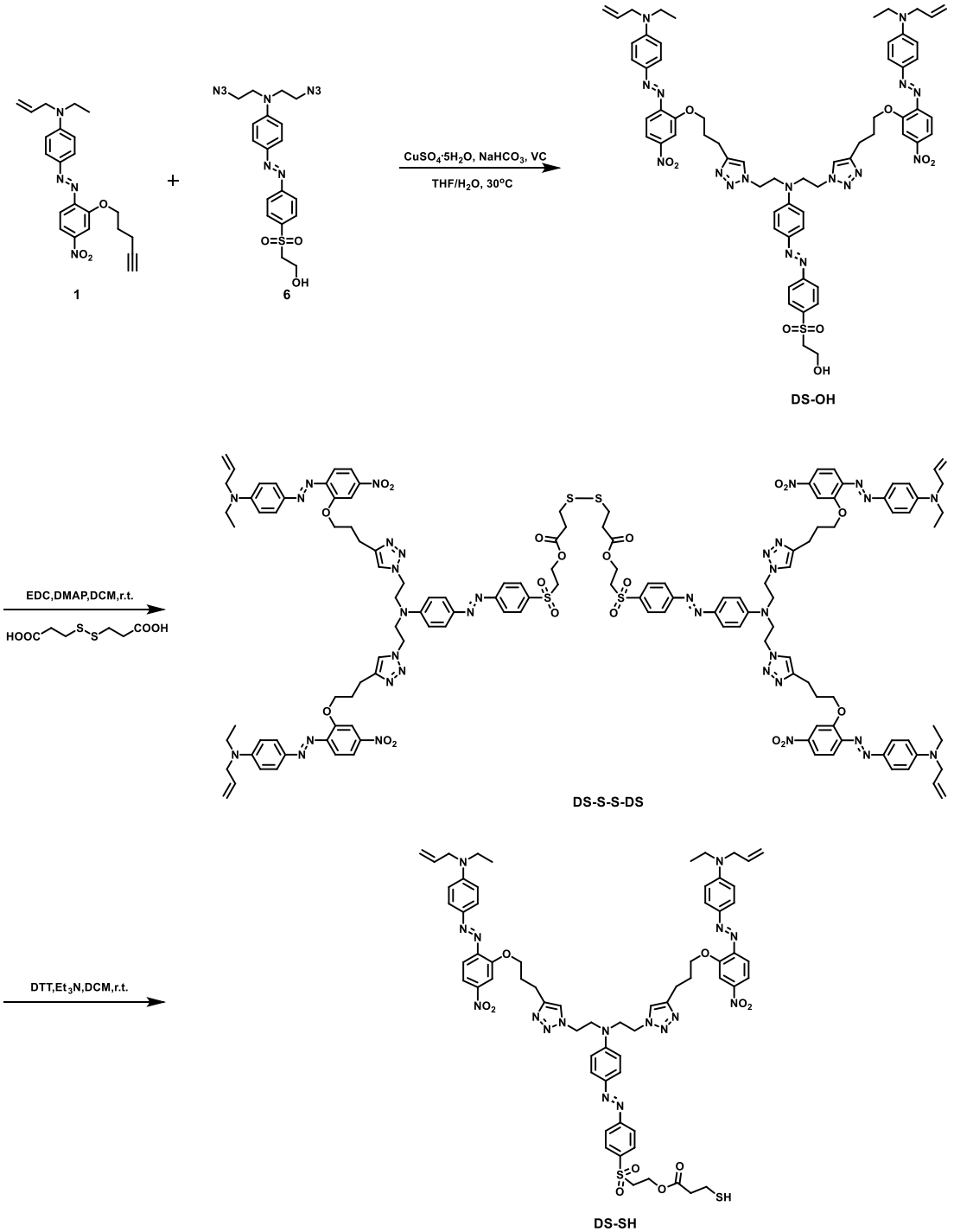
(m, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 148.24, 134.52, 129.24, 115.84, 115.80, 112.08, 52.67, 44.75, 12.36.

Compound **4**: 2-Amino-5-nitrophenol (7.00 g, 0.04 mol), 5-chloro-1-pentyne (4.66 g, 0.04 mol), potassium carbonate (12.55 g, 0.09 mol) and potassium iodide (1.51 g, 0.01 mol) were added in acetonitrile (50 mL). The resultant mixture was stirred at 80 ºC overnight. After cooling to room temperature, the reaction mixture was filtered to remove the salt, and then the solvent was removed by rotary evaporation. The crude product was purified by column chromatography using petroleum ether and dichloromethane (3/1) as eluent to yield yellow solid (5.00 g, 50%).

Monomer **1**: Compound **4** (800 mg, 3.63 mmol) was dissolved in 48% fluoroboric acid (3.8 mL), then the sodium nitrite saturated solution (300.93 mg, 4.36 mmol) was added in an ice bath. After the reaction mixture was stirred at 0 ºC for 12 h, the solution of Compound **3** (732.48 mg, 4.54 mmol) in DMF (12 mL) was added. The resultant mixture was further stirred at 0 ºC overnight. The reasultant mixture was further stirred at 0 ºC overnight. Then dichloromethane (200 mL) was added into the reaction mixture, DMF was washed out by water. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel using petroleum ether and dichloromethane (4/1) as eluent to yield the red solid (1.00 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.26 (t, J = 4.0 Hz, 3H, -CH_3), 2.00 (t, J = 4.0 Hz, 1H, -C≡CH), 2.18-2.11 (m, 2H, -CH_2-), 2.52-2.48 (m, 2H, -CH_2-), 3.50 (q, 2H, -CH_2-), 4.03 (m, 2H, -CH_2-), 4.34 (t, J = 8.0 Hz, 2H, -CH_2-), 5.23-5.16 (m, 2H, -C=CH_2), 5.91-5.83 (m, 1H, -CH=C), 6.73 (d, J = 12.0 Hz, 2H, ArH), 7.66 (d, J = 8.0 Hz, 1H, ArH), 7.66-7.93 (m, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 154.97, 151.54, 148.01, 147.29, 144.29, 132.75, 126.30, 117.39, 116.74, 116.56, 111.45, 109.26, 83.30, 69.24, 68.14, 52.68, 45.37, 28.07, 15.18, 12.50.

Monomer **2**: Compound **5** (700 mg, 2.75 mmol) was dissolved in 48% fluoroboric acid, then the sodium nitrite saturated solution (237.40 mg, 3.44 mmol) was added in an ice bath. After the reaction mixture was stirred at 0 ºC for 6 h, the solution of Compound **6** (795 mg, 3.44 mmol) in DMF (4.3 mL) was added. The resultant mixture was further stirred at 0 ºC overnight. Then dichloromethane (150 ml) was added into the reaction mixture, DMF was washed out by water. The solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel using dichloromethane as eluent, to yield the red solid (900 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.73-1.46 (m, 7H, -CH_2-, OH), 1.94 (m, 2H, -CH_2-), 3.59 (t, J = 8.0

Hz, 4H, -CH_2-), 3.65 (t, *J* = 8.0 Hz, 2H, -CH_2-), 3.71 (t, *J* = 8.0 Hz, 4H, -CH_2-), 4.23 (t, *J* = 4.0 Hz, 2H, -CH_2-), 6.80 (d, *J* = 8.0 Hz, 2H, ArH), 7.67-7.65 (m, 1H, ArH), 7.93-7.85 (m, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 155.45, 149.70, 148.54, 146.79, 145.20 , 126.21, 117.43, 116.35, 111.87, 109.08 , 69.91, 62.83, 50.79, 48.79 ,32.65, 28.96, 25.86, 25.50.



DS-OH: Under an atmosphere of nitrogen, Compound **6** (140.7 mg, 0.32 mmol), Compound **1** (274

mg, 0.698 mmol), $CuSO_4 \cdot 5H_2O$ (11.8 mg, 0.05 mmol), $NaHCO_3$ (6.66 mg, 0.08 mmol), VC (13.96 mg, 0.08 mmol), THF (6.67 mL) and water (1 mL) were added in a Schlenk flask. The resultant mixture was stirred at room temperature for 3 h. The reaction solution was extracted by water, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel using ethyl acetate as eluent, to yield the red solid (300 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$, 298K), δ (TMS, ppm): 1.24 (t, *J* = 8.0 Hz, 6H, -CH_3), 2.22 (m, 4H, -CH_2-), 3.02-2.93 (q, 5H, -CH_2, -OH), 3.39 (t, *J* = 4.0 Hz, 2H, -CH_2-), 3.47 (q, 4H, -CH_2-), 3.70 (t, *J* = 8.0 Hz, 4H, -CH_2-), 4.01 (m, *J* = 4.0 Hz, 6H, -CH_2-), 4.12 (t, *J* = 4.0 Hz, 4H, -CH_2-), 4.36 (t, *J* = 8.0 Hz, 4H, -CH_2-), 5.20-5.13 (m, 4H, -C=CH_2), 5.89-5.79 (m, 2H, -CH=C), 6.53 (d, *J* = 12.0 Hz, 2H, ArH), 6.73 (d, *J* = 12.0 Hz, 4H, ArH), 7.25 (s, 2H, -C=CH-), 7.63 (d, *J* = 8.0 Hz, 2H, ArH), 7.85-7.74 (m, 10H, ArH), 7.99-7.91 (m, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 155.99, 154.87, 151.60, 149.31, 147.90, 147.23, 147.21, 144.63, 144.19, 138.83, 132.69, 129.09, 126.31, 126.05, 123.11, 122.44, 117.40, 116.67, 116.59, 111.70, 111.48, 109.15, 68.49, 58.40, 56.36, 52.67, 51.15, 47.21, 45.38, 28.35, 21.58, 12.49. HRMS (ESI, m/z): calcd for $C_{62}H_{70}N_{17}O_9S$, 1228.5258 $[M+H]^+$; found, 1228.5245. (EA) (%, found/Calcd): C, 60.47/60.62; H, 5.377/5.66; N, 19.23/19.38; S, 2.453/2.61.

DS-S-S-DS: Compound **DS-OH** (219 mg, 0.18 mmol), 3,3'-dithiodipropionic acid (18.74 mg, 0.09 mmol), EDC (51.18 mg, 0.27 mmol) and DMAP (3.26 mg, 0.03 mmol) were added in dichloromethane (2.3 mL). The resultant mixture was stirred at 30 ^{o}C for 7 h. The organic layer was extracted by citric acid aqueous solution and water, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel using ethyl acetate and methyl alcohol (150/1) as eluent, to yield the red solid (200 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$, 298K), δ (TMS, ppm): 1.21 (t, *J* = 8.0 Hz, 12H, -CH_3), 2.20 (m, 8H, -CH_2-), 2.45 (t, *J* = 8.0 Hz, 4H, -CH_2-), 2.69 (t, *J* = 8.0 Hz, 4H, -CH_2-), 2.91 (t, *J* = 8.0 Hz, 8H, -CH_2-), 3.48 (m, 12H, -CH_2-), 3.67(t, *J* = 8.0 Hz, 8H, -CH_2-), 4.00 (t, *J* = 4.0 Hz, 8H, -CH_2-), 4.15 (t, *J* = 8.0 Hz, 8H, -CH_2-), 4.43-4.35 (m, 12H, -CH_2-), 5.18-5.12 (m, 8H, -C=CH_2), 5.90-5.81 (m, 4H, -CH=C), 6.63 (d, *J* = 8.0 Hz, 4H, ArH), 6.73 (d, *J* = 8.0 Hz, 8H, ArH), 7.26 (s, 4H, -CH=C-), 7.63 (d, *J* = 12.0 Hz, 4H, ArH), 7.83-7.79 (m, 20H, ArH), 7.97-7.92 (m, 8H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 172.77, 157.93, 156.99, 153.56, 151.48, 149.92, 149.05, 149.01, 146.41, 146.03, 141.28, 134.88, 131.13, 128.00, 127.87, 124.83, 124.15, 119.06, 118.35, 118.04, 113.67, 113.39, 111.18, 70.63, 59.82, 56.97, 54.54, 53.11, 49.02, 47.29, 35.43, 34.49, 30.46, 23.73, 14.14. (EA) (%,

found/Calcd): C, 59.04/59.35; H, 5.225/5.52; N, 17.98/18.10; S, 4.7/4.87.

DS-SH: Under an atmosphere of nitrogen, Compound **DS-S-S-DS** (125 mg, 0.05 mmol), DTT (16.12 mg, 0.1 mmol), Et_3N (10.7 mg, 0.1 mmol) and distilled dichloromethane (1.5 mL) were added into a schlenk flask. The reaction mixture was stirred at room temperature for 5h. The organic layer was washed with HCl (0.1 mol/L) and water, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel using dichloromethane and ethyl acetate (1/2) as eluent, to yield the red solid (60 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$, 298K), δ (TMS, ppm): 1.14 (t, *J* = 4.0 Hz, 6H, -CH_3), 1.50 (m, 1H, -SH), 2.13 (m, 4H, -CH_2-), 2.32 (t, *J* = 4.0 Hz, 2H, -CH_2-), 2.51 (q, 2H, -CH_2-), 2.84 (t, *J* = 8.0 Hz, 4H, -CH_2-), 3.43-3.37 (m, 6H, -CH_2-), 3.60 (t, *J* = 4.0 Hz, 4H, -CH_2-), 3.93(t, *J* = 4.0 Hz, 4H, -CH_2-), 4.08 (t, *J* = 8.0 Hz, 4H, -CH_2-), 4.29 (t, *J* = 8.0 Hz, 4H, -CH_2-), 4.37 (t, *J* = 8.0 Hz, 2H, -CH_2-), 5.11-5.04 (m, 4H, -C=CH_2), 5.82-5.74 (m, 2H, -CH=C), 6.52 (d, *J* = 8.0 Hz, 2H, ArH), 6.64 (d, *J* = 8.0 Hz, 4H, ArH), 7.16 (s, 2H, -CH=C-), 7.56 (d, *J* = 8.0 Hz, 2H, ArH), 7.76-7.72 (m, 10H, ArH), 7.92-7.86 (q, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm) : 170.85, 156.06, 155.07, 151.65, 149.54, 148.01, 147.14, 144.10, 144.52, 144.11, 139.37, 132.96, 129.25, 126.08, 125.94, 122.91, 122.23, 117.15, 116.45, 116.12, 111.75, 111.47, 109.26, 68.70, 57.80, 55.12, 52.62, 51.17, 47.11, 45.38, 38.05, 28.53, 21.80, 19.36 , 12.22. HRMS (ESI, m/z): calcd for $C_{65}H_{74}N_{17}O_{10}S_2$, 1316.5240 $[M+H]^+$, found, 1316.5202. (EA) (%, found/Calcd): C, 59.07/59.30; H, 5.293/5.59; N, 17.89/18.09; S, 4.708/4.87.

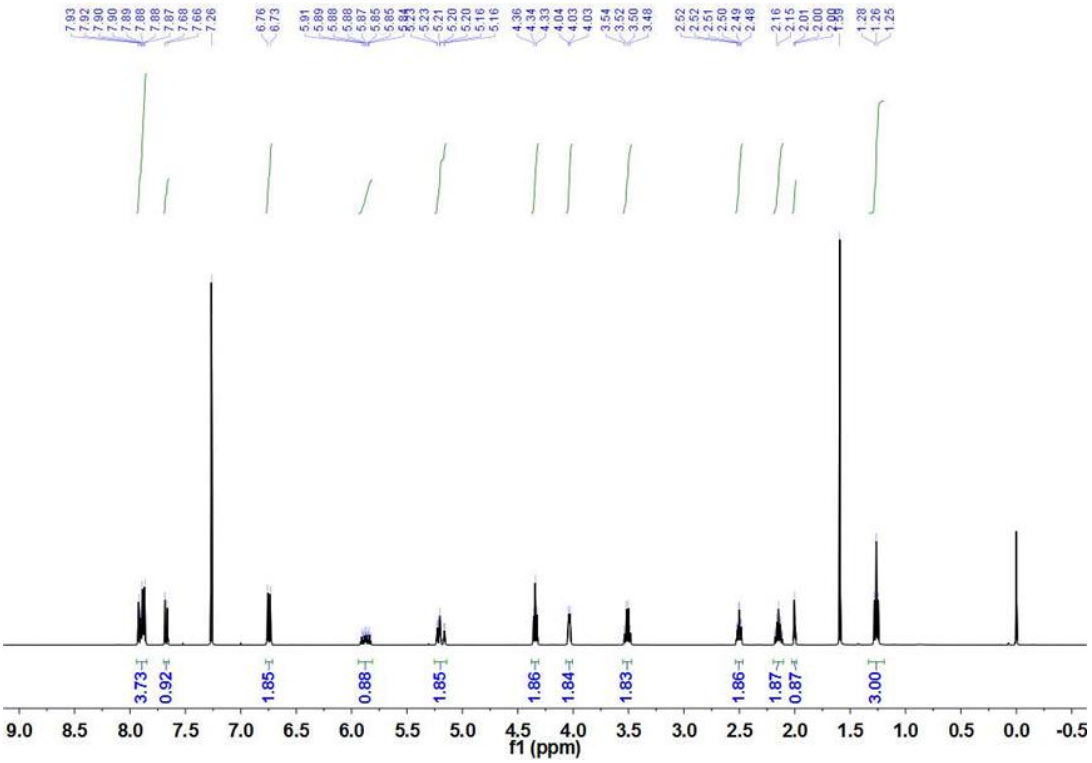


Figure S12 The ^{1}H NMR spectrum of Compound **1**.

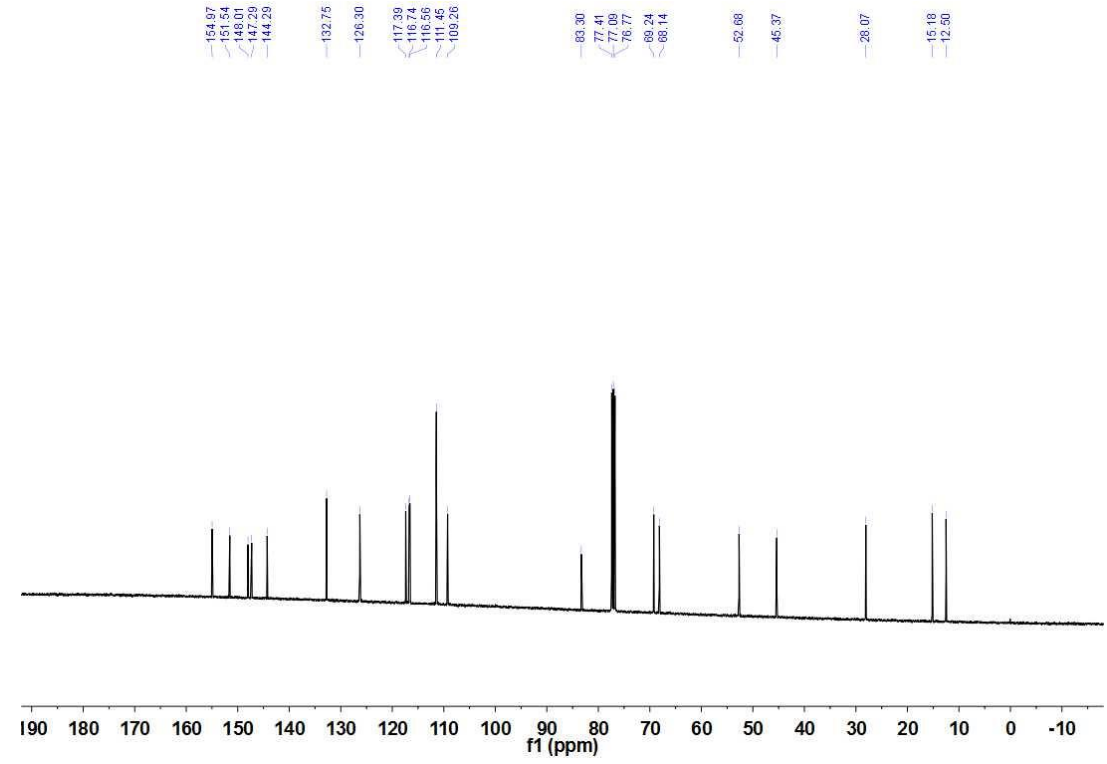


Figure S13 The ^{13}C NMR spectrum of Compound **1**.

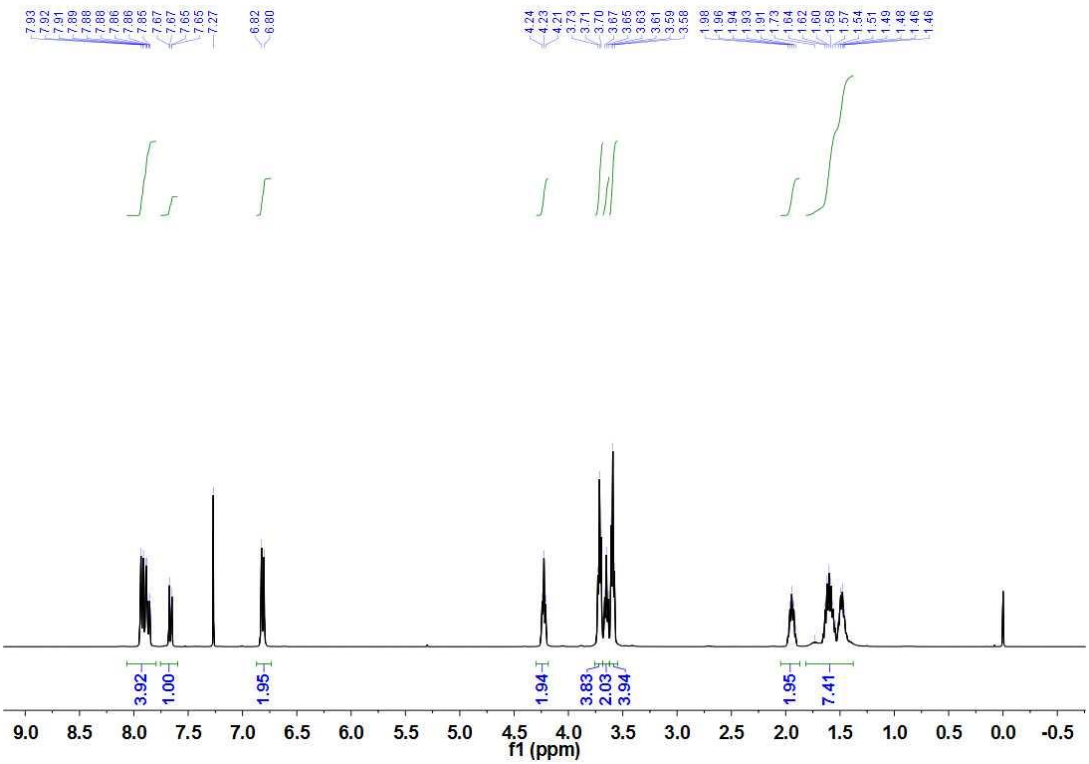


Figure S14 The ^{1}H NMR spectrum of Compound **2**.

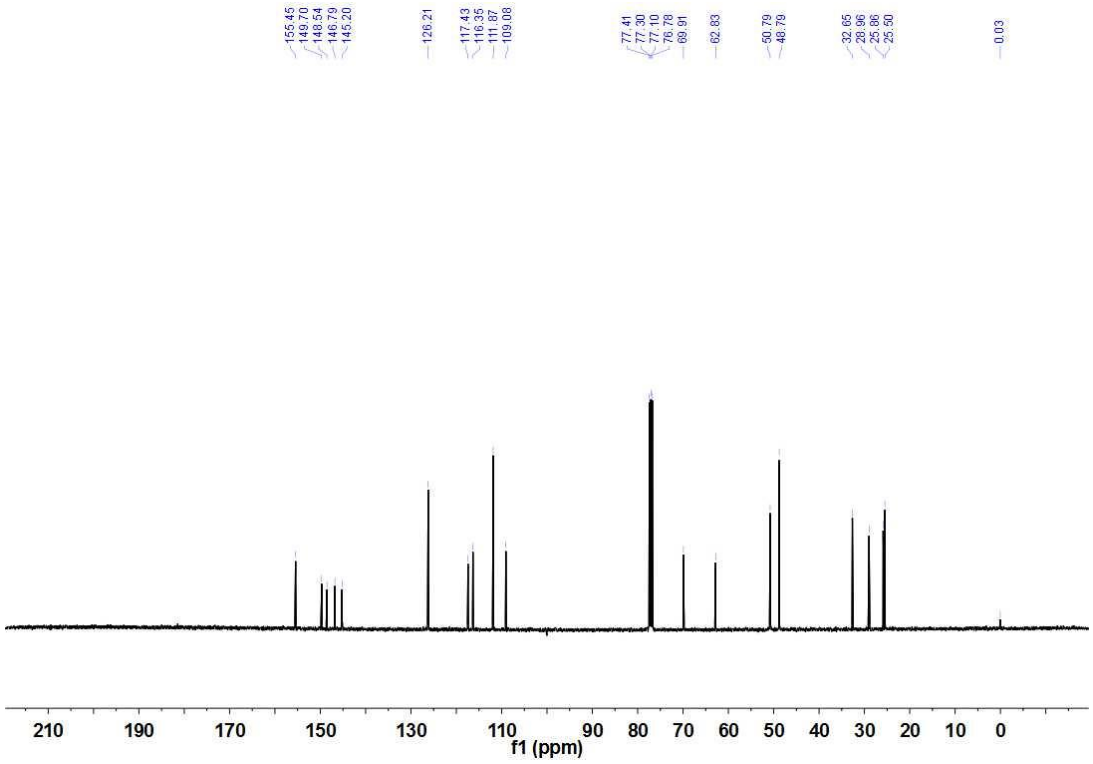


Figure S15 The ^{13}C NMR spectrum of Compound **2**.

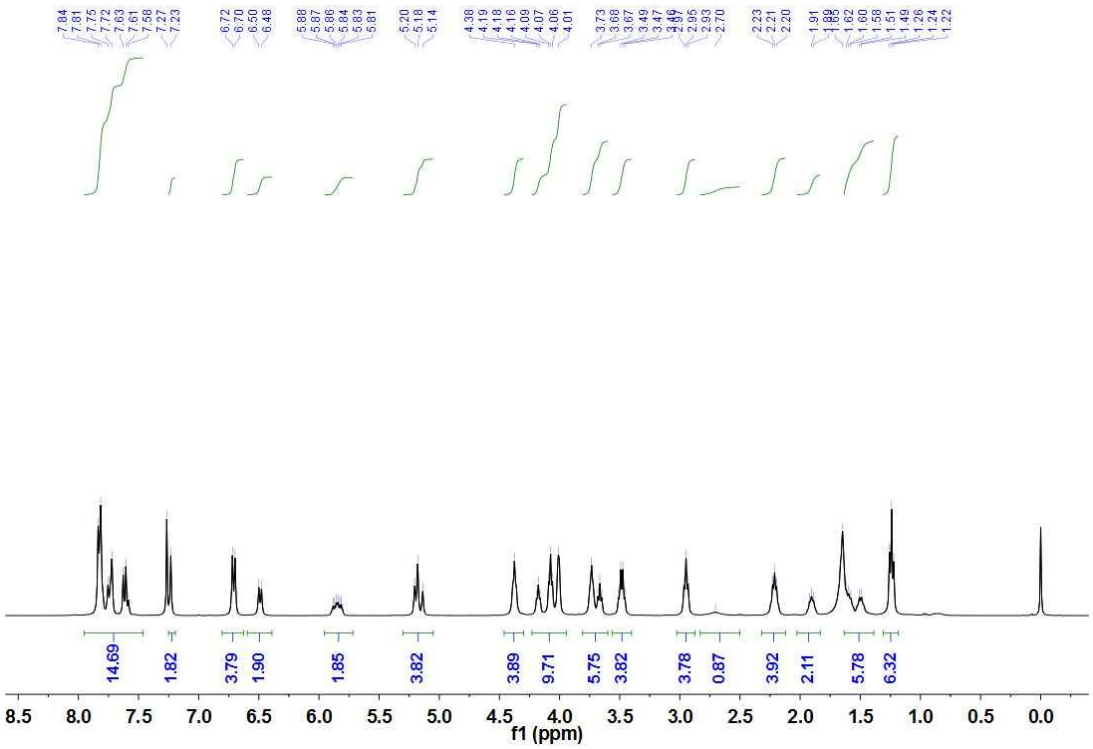


Figure S16 The ^{1}H NMR spectrum of Compound **DN-OH**.

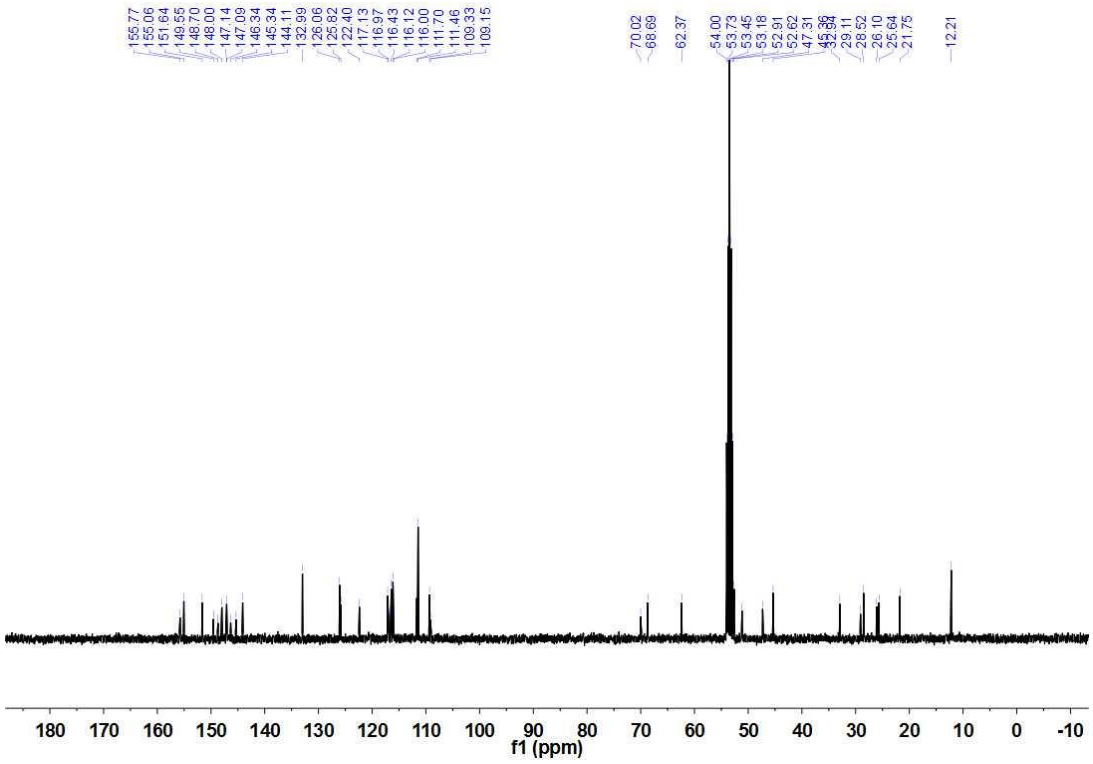


Figure S17 The ^{13}C NMR spectrum of Compound **DN-OH**.

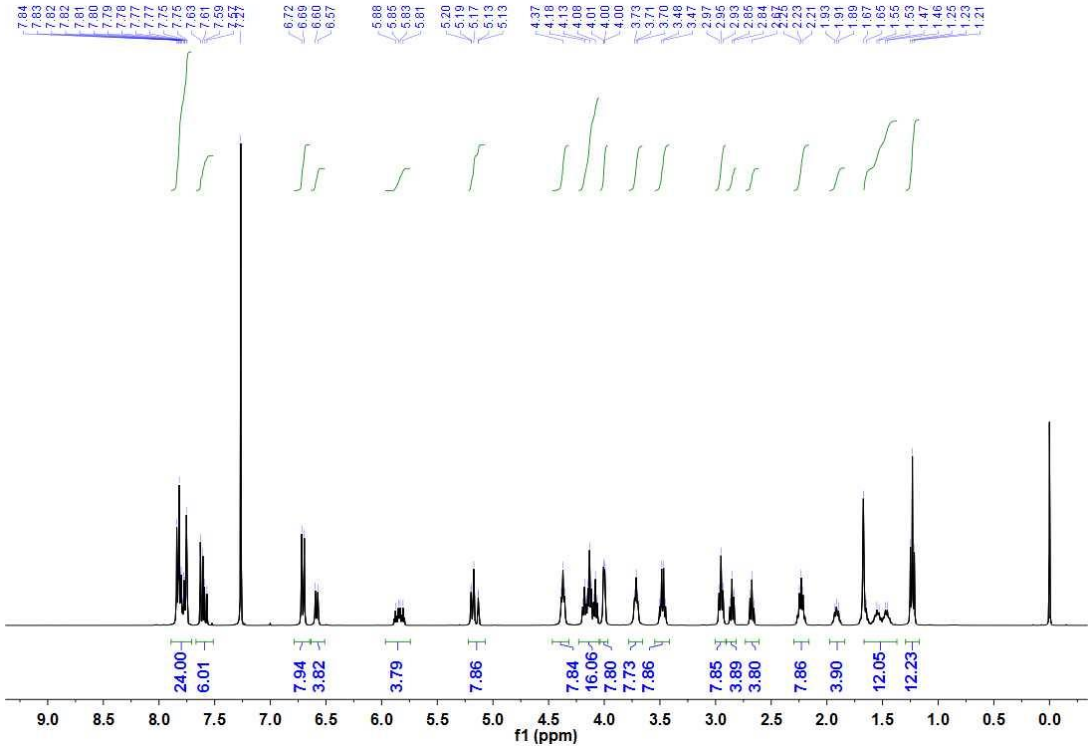


Figure S18 The ^{1}H NMR spectrum of Compound **DN-S-S-DN**.

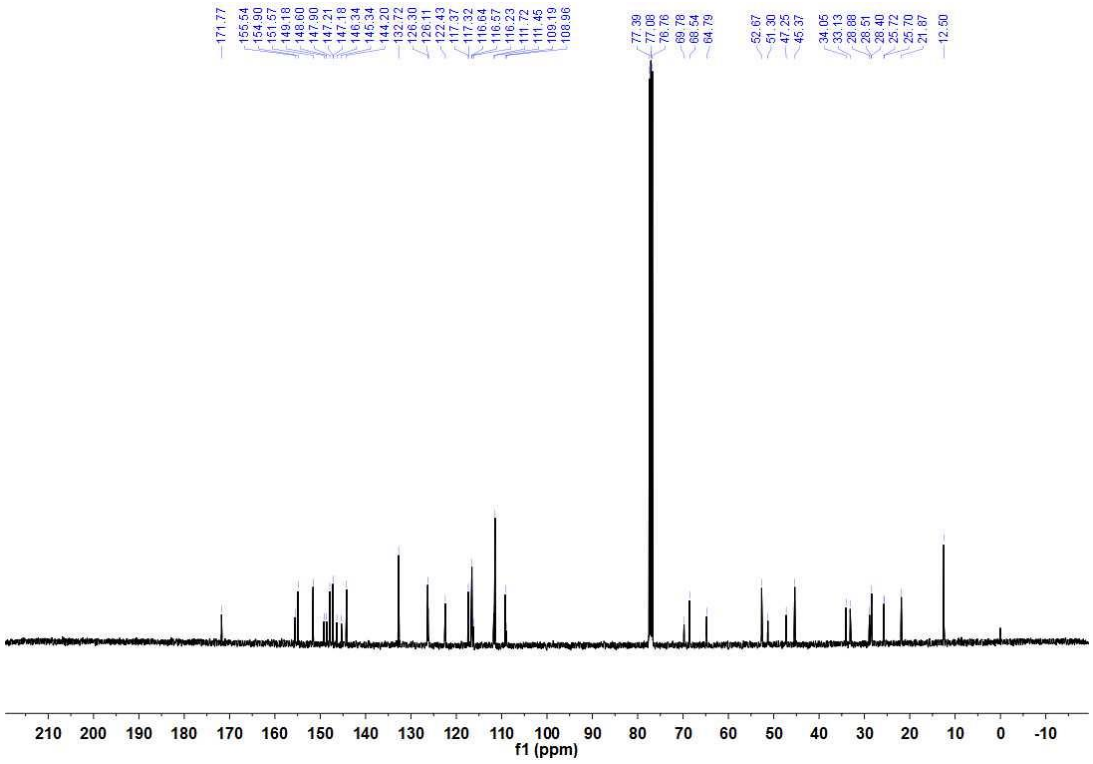


Figure S19 The ^{13}C NMR spectrum of Compound **DN-S-S-DN**.

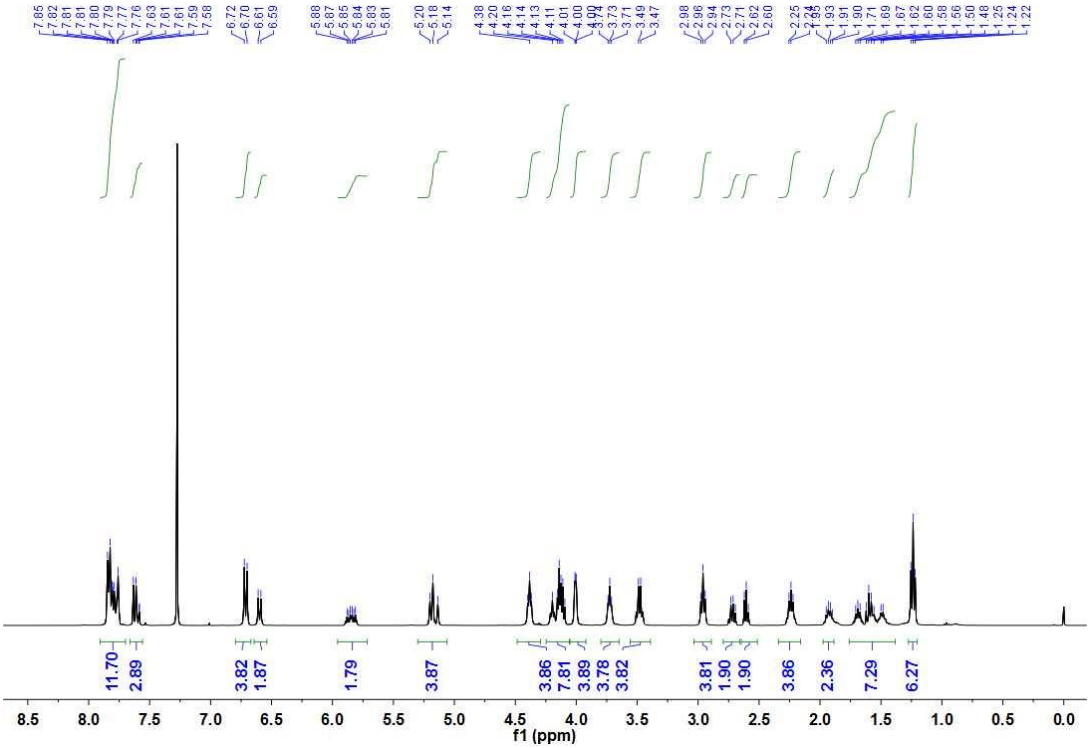


Figure S20 The ^{1}H NMR spectrum of Compound **DN-SH**.

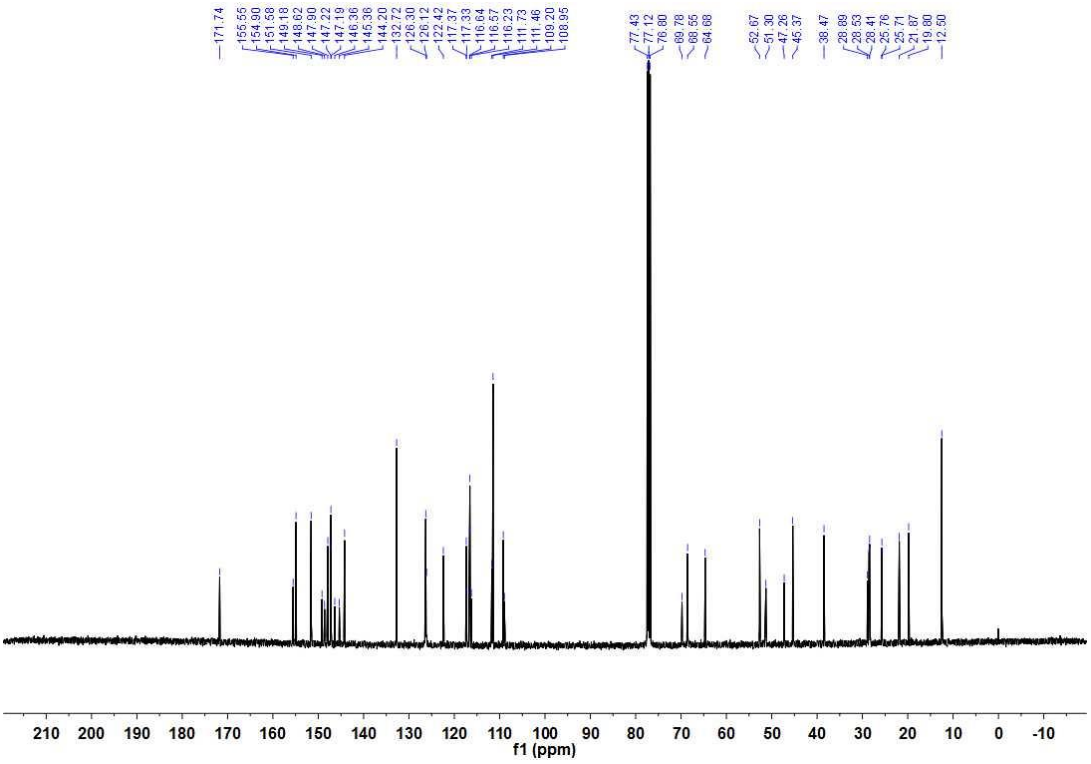


Figure S21 The ^{13}C NMR spectrum of Compound **DN-SH**.

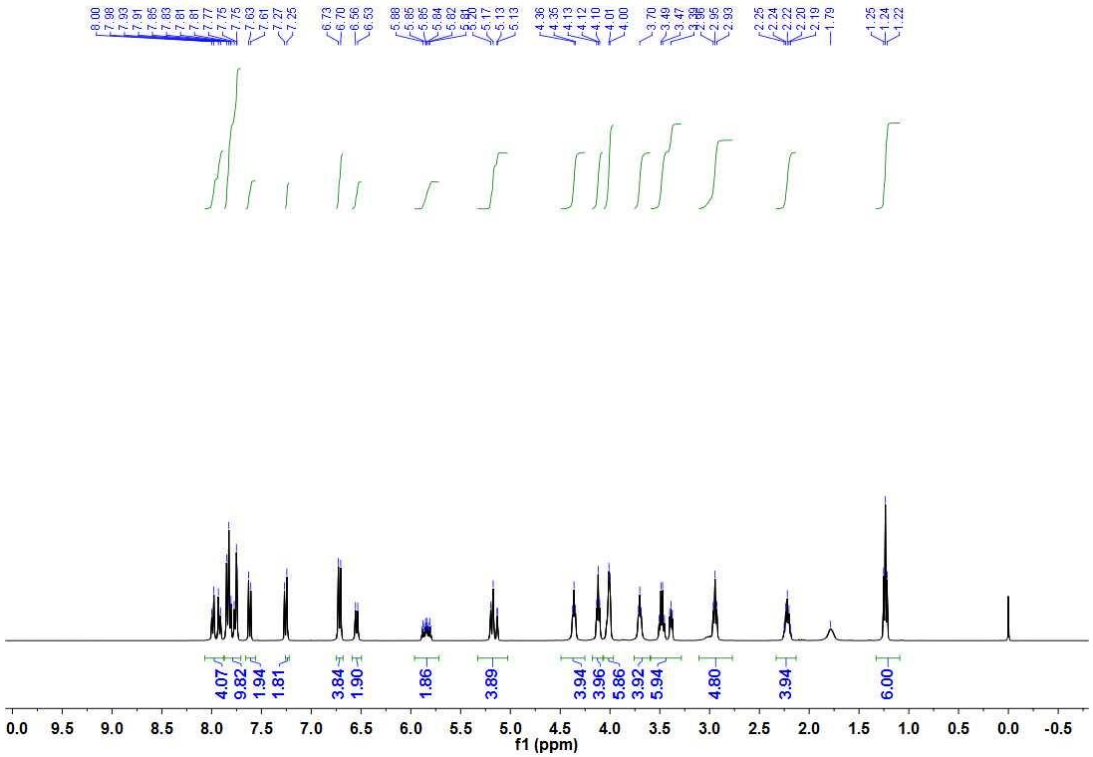


Figure S22 The ^{1}H NMR spectrum of Compound **DS-OH**.

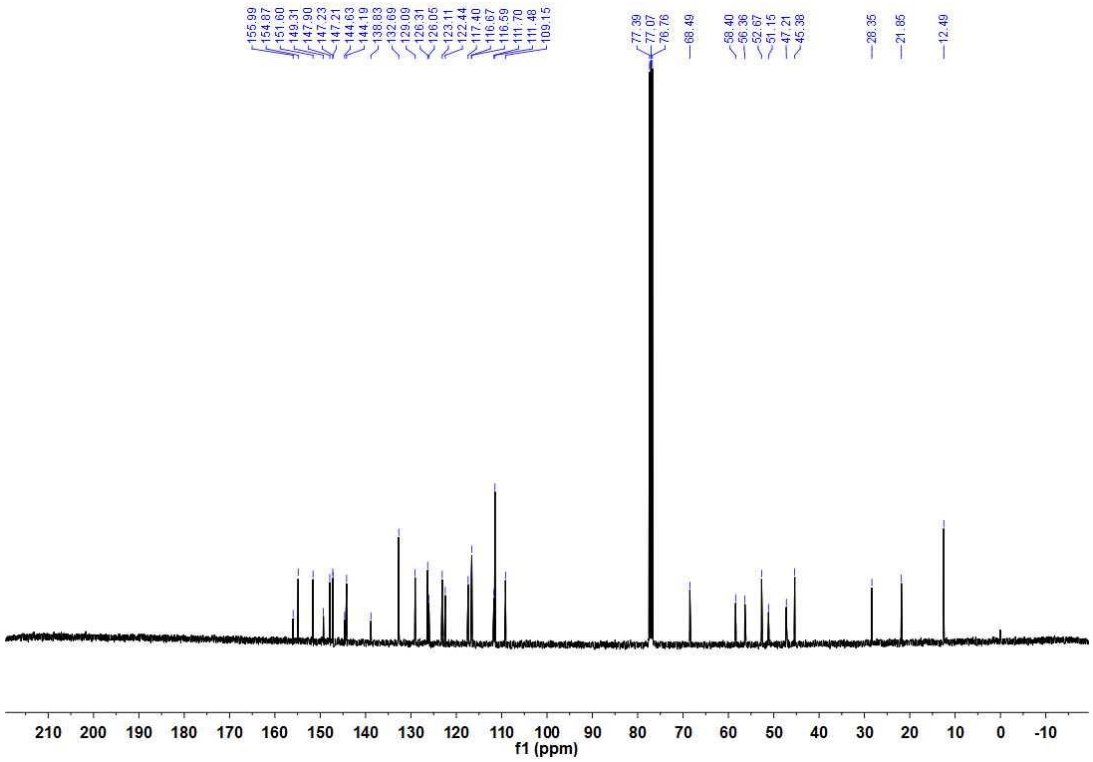


Figure S23 The ^{13}C NMR spectrum of Compound **DS-OH**.

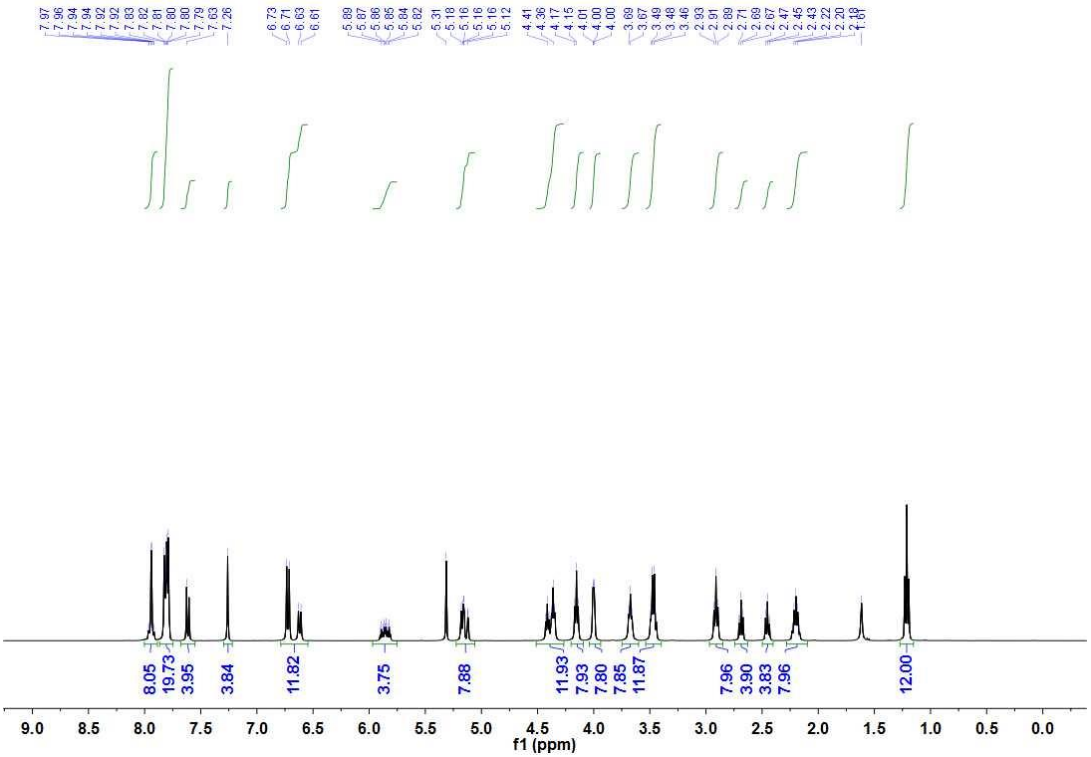


Figure S24 The ^{1}H NMR spectrum of Compound **DS-S-S-DS**.

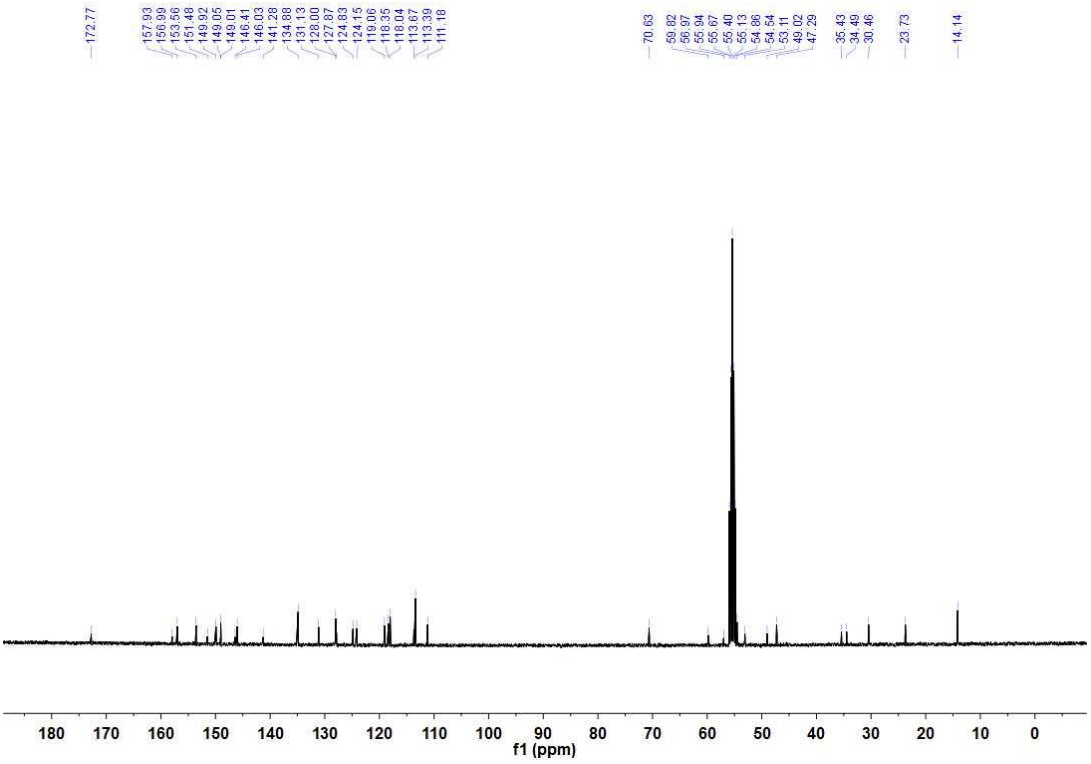


Figure S25 The ^{13}C NMR spectrum of Compound **DS-S-S-DS**.

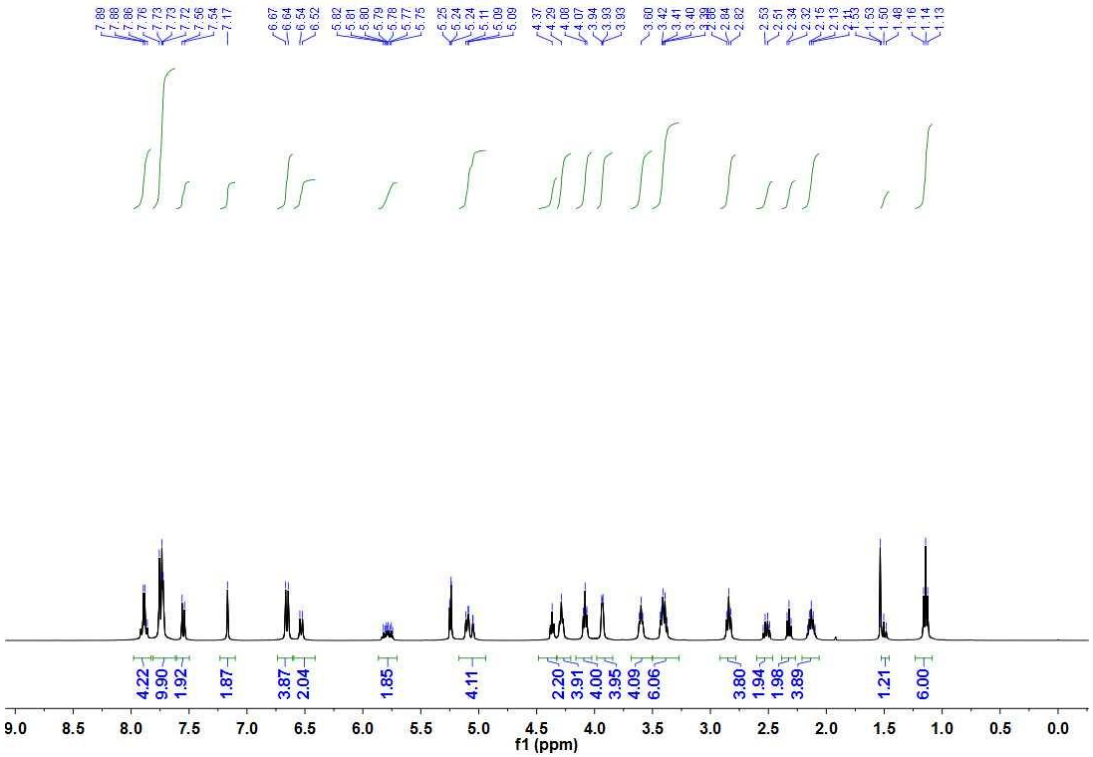


Figure S26 The ^{1}H NMR spectrum of Compound **DS-SH**.

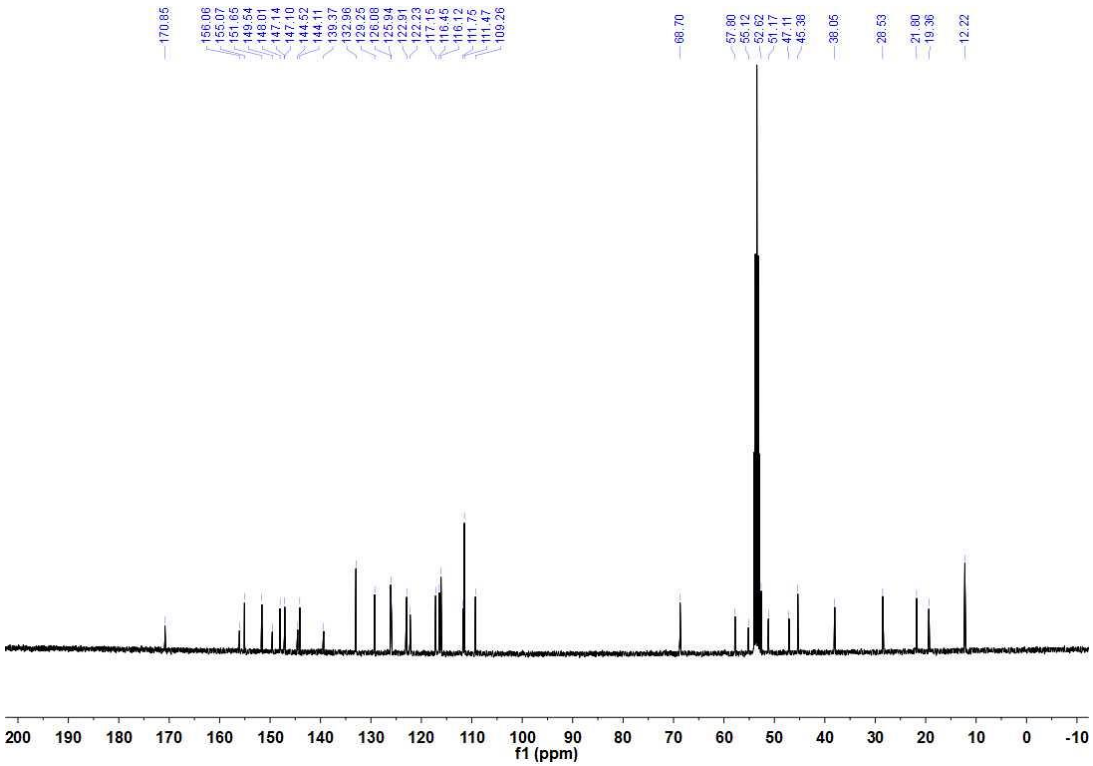


Figure S27 The ^{13}C NMR spectrum of Compound **DS-SH**.

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