Electronic Supplementary Information for:

Dendronized hyperbranched polymers containing isolation chromophores: design, synthesis and further enhancement of the comprehensive NLO performance

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Synthesis

Materials

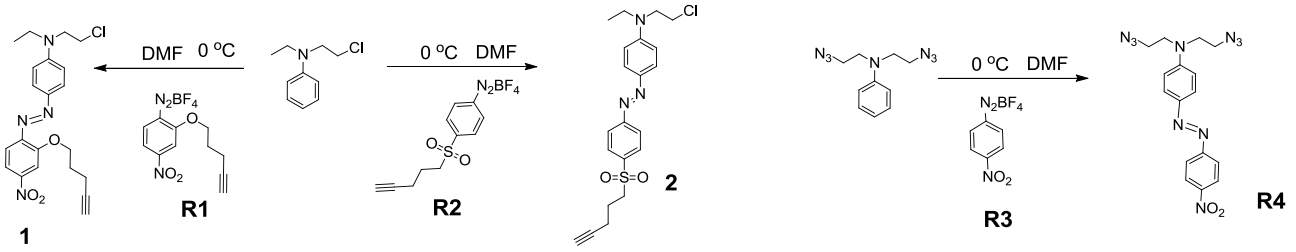
Tetrahydrofuran (THF) was dried over Na-K alloy and distilled under an atmosphere of dry nitrogen. *N*, *N*-Dimethylform amide (DMF) was dried over CaH_2 and distilled under an atmosphere of dry nitrogen. Compounds **R1-R6** were prepared according to literatures and our previous work[1-4]. All other reagents were used as received.

1. W. Wu, Z. Li, *Polym. Chem.*,2014, **5**, 5100-5108

2. Z. Li, C. Li, G. Yu, Y. Liu, C. Ye, J. Qin, Z. Li, *Chem. Eur. J.* 2012, **18**, 11019-11028.

3. Z. Li, G. Yu, P. Hu, C. Ye, Y. Liu, J. Qin, Z. Li, *Macromolecules*, 2009, **42**, 1589-1596.

4. J. Xie, L. Hu, W. Shi, X. Deng, Z. Cao, Q. Shen. *Polym. Int*., 2008, **57**: 965-974.

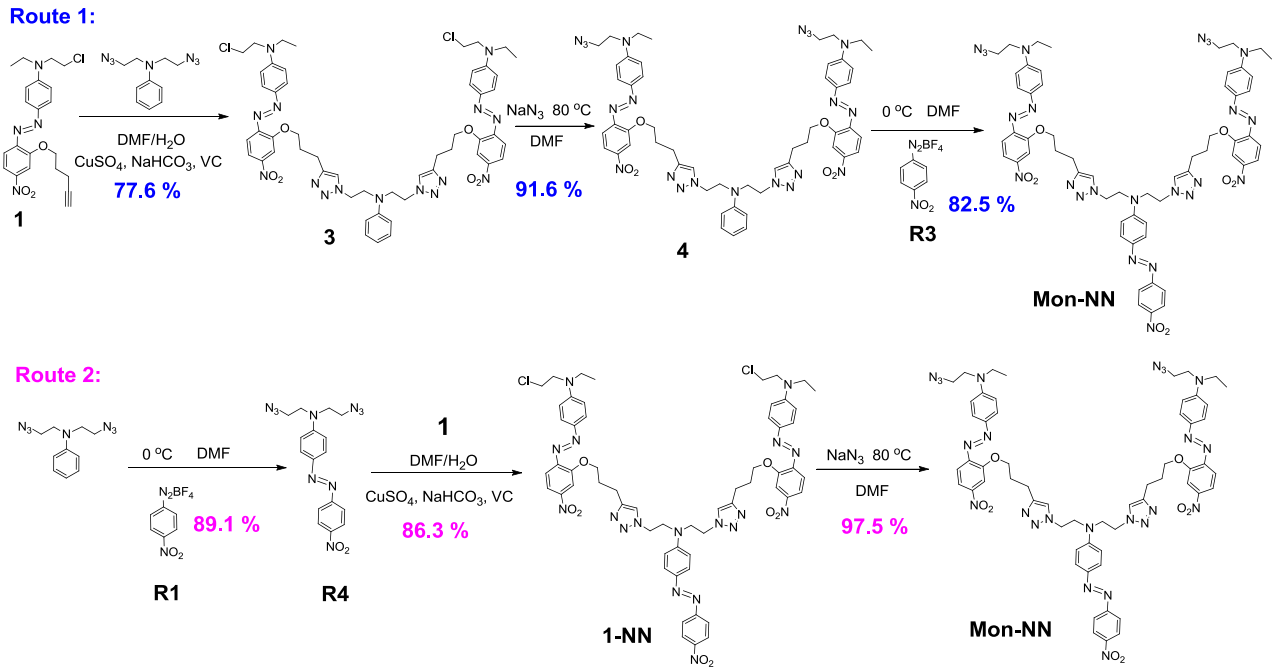


Scheme S1. The synthetic route to related compounds

Compound **1**: Compound **R1** (638.0 mg, 2.0 mmol), and *N*-(2-chloroethyl)-*N*-ethylaniline (367.3 mg,

2.0 mmol) were dissolved in DMF (8 mL), the resultant mixture was allowed to stir at 0 ℃ overnight, and then poured into a lot of water. The precipitate was collected and washed several times with water, and purified by column chromatography using ethyl acetate/petroleum ether (1/5) as eluent to yield red solid (680.0 mg, 82.0 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.26 (t, *J*=7.2 Hz, 3H, -CH_3), 2.00 (s, 1H, -C≡CH), 2.15 (m, 2H, -CH_2-), 2.50 (m, 2H, -CH_2-), 3.57 (m, 2H, -CH_2-), 3.70 (m, 2H, -CH_2-), 3.76 (m, 2H, -CH_2-), 4.35 (t, *J*=6.0 Hz, 2H, -CH_2-), 6.78 (d, *J*=9.0 Hz, 2H, -ArH), 7.69 (d, *J*=8.7 Hz, 1H, -ArH), 7.92 (m, 4H, -ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 155.30, 150.57, 148.46, 147.22, 144.85, 126.50, 117.63, 116.84, 111.55, 109.44, 83.43, 69.45, 68.31, 52.45, 46.13, 40.33, 28.26, 15.37, 12.76.

Compound **2**: Compound **R2** (300.0 mg, 0.93 mmol), and *N*-(2-chloroethyl)-*N*-ethylaniline (170.7 mg, 0.93 mmol) were dissolved in DMF (5 mL), the resultant mixture was allowed to stir at 0 ℃ overnight, and then poured into a lot of water. The precipitate was collected and washed several times with water, and purified by column chromatography using ethyl acetate/petroleum ether (1/5) as eluent to yield orange solid (250.0 mg, 64.4 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.27 (t, *J*=7.2 Hz, 3H, -CH_3), 1.99-1.94 (m, 3H, -C≡CH, -CH_2-), 2.33 (m, 2H, -CH_2-), 3.27 (t, *J*=8.1 Hz, 3H, -CH_3), 3.56 (q, *J*=7.2 Hz, 2H, -CH_2-), 3.67 (t, *J*=6.0 Hz, 2H, -CH_2-), 3.76 (t, *J*=6.0 Hz, 2H, -CH_2-), 6.77 (d, *J*=9.3 Hz, 2H, -ArH), 7.91 (d, *J*=9.3 Hz, 2H, -ArH), 8.02-7.95 (m, 4H, -ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 156.58, 150.72, 144.13, 138.61, 129.53, 126.40, 123.09, 111.62, 82.07, 70.52, 55.37, 52.48, 46.16, 40.43, 22.02, 17.56, 12.79



Scheme S2. The two synthetic routes to **Mon-NN**

Mon-NN was prepared through two different synthetic routes as following:

***Route 1*:**

Compound **3**: Compound **1** (348.5 mg, 0.84 mmol), *N*,*N*-bis(2-azidoethyl)aniline (92.5 mg, 0.40 mmol), $CuSO_4 \cdot 5H_2O$ (10 mol %), $NaHCO_3$ (20 mol %), and ascorbic acid (20 mol %) were dissolved in DMF (12 mL)/H_2O (2.4 mL) in a Schlenk flask under nitrogen. The mixture was stirred at room temperature for 3 h, then extracted with chloroform, and washed with 1N HCl, 1N NH_4OH, and water subsequently. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography using dichloromethane/ethyl acetate (4/1) as eluent to afford red solid (329.1 mg, 77.6%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.24 (t, *J*=6.9 Hz, 6H, -CH_3), 2.23 (m, 4H, -CH_2-), 2.94 (m, 4H, -CH_2-), 3.52 (t, *J*=6.9 Hz, 4H, -CH_2-), 3.67-3.61 (m, 8H, -CH_2-), 3.72 (t, *J*=6.9 Hz, 4H, -CH_2-), 4.15 (t, 4H, -CH_2-), 4.30 (t, 4H, -CH_2-), 6.53 (d, *J*=6.3 Hz, 2H, -ArH), 6.76 (d, *J*=9.0 Hz, 4H, -ArH), 7.13 (s, 2H, -ArH), 7.18 (m, 1H, -ArH), 7.66 (d, *J*=9.0 Hz, 2H, -ArH), 7.99 (s, 2H, -ArH). 7.89-7.84 (m, 5H, -ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 155.29, 150.69, 148.43, 147.23, 146.03, 144.84, 130.04, 126.54, 122.47, 118.57, 117.67, 116.78, 113.05, 111.64, 109.43, 68.78, 52.44, 51.79, 47.62, 46.15, 40.42, 28.74, 22.05, 12.77.

Compound **4**: Compound **3** (400.0 mg, 0.37 mmol), NaN_3 (152.5 mg, 2.34 mmol) and DMF (13 mL) were added into a flask, the resultant mixture was allowed to stir at 80 ℃ overnight, and then poured into a lot of water. The precipitate was collected and washed several times with water, dried under vacuum, and purified by column chromatography using ethyl dichloromethane/ethyl acetate (4/1) as eluent to yield red solid (459.0 mg, 91.6%).^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.24 (t, *J*=6.9 Hz, 6H, -CH_3), 2.24 (m, 4H, -CH_2-), 2.95 (m, 4H, -CH_2-), 3.62-3.53 (m, 16H, -CH_2-), 4.15 (t, *J*=6.0 Hz, 4H, -CH_2-), 4.29 (t, *J*=6.0 Hz, 4H, -CH_2-), 6.53 (d, *J*=7.8 Hz, 2H, -ArH), 6.78 (d, *J*=9.3 Hz, 4H, -ArH), 7.13 (s, 2H, -ArH), 7.18 (m, 1H, -ArH), 7.64 (d, *J*=9.0 Hz, 2H, -ArH), 7.79 (s, 2H, -ArH). 7.89-7.84 (m, 5H, -ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 155.25, 150.83, 148.36, 147.19, 145.99, 144.75, 130.00, 126.51, 122.44, 118.67, 117.61, 116.75, 112.97, 111.70, 109.37, 68.73, 51.76, 49.74, 49.14, 47.58, 46.09, 28.72, 22.04, 12.50.

Mon-NN: Compound **4** (132.0 mg, 0.12 mmol), and **R3** (29.2 mg, 0.12 mmol) were dissolved in DMF (6 mL), the resultant mixture was allowed to stir at 0 ℃ overnight, and then poured into a lot of water. The precipitate was collected and washed several times with water, and purified by column chromatography using dichloromethane/ethyl acetate (2/1) as eluent to yield orange solid (122.0 mg,

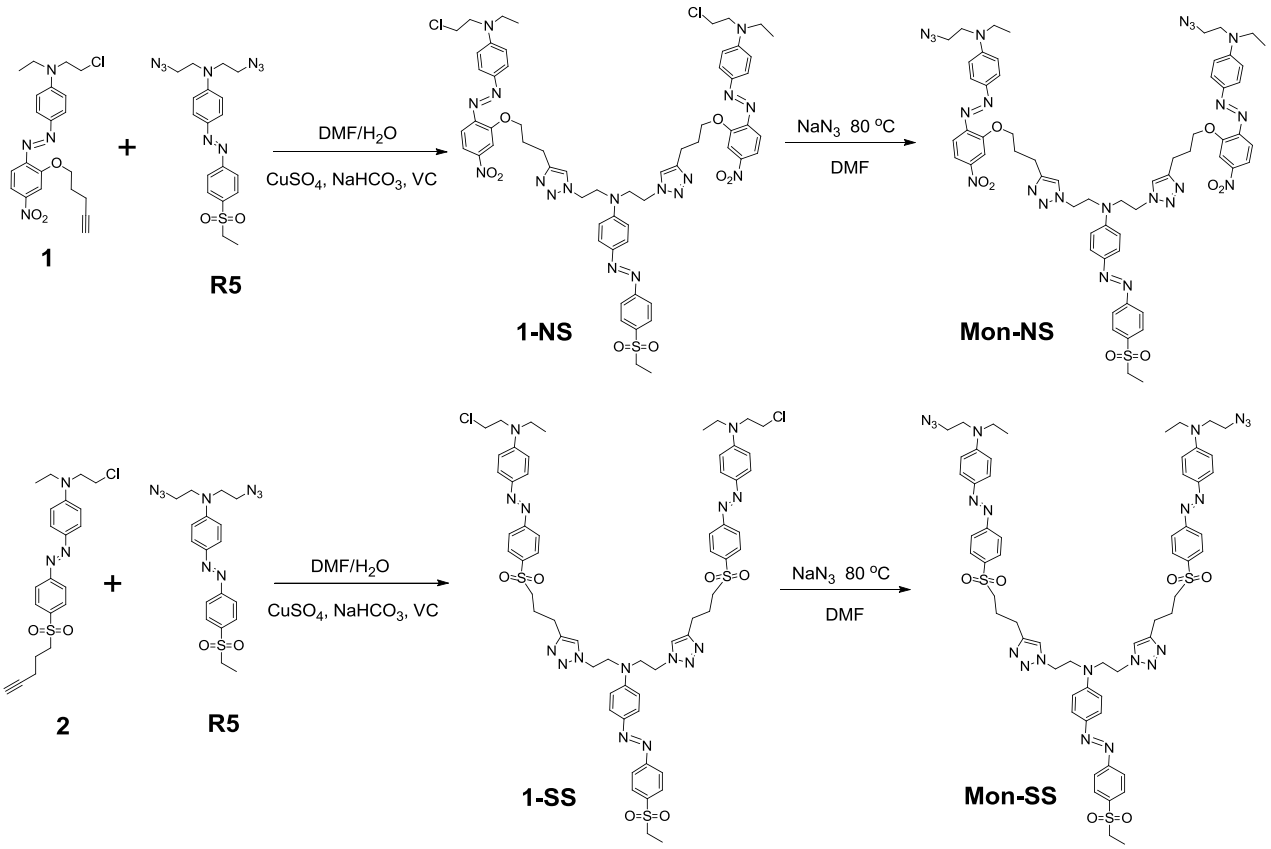
82.5 %). HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{58}H_{63}N_{24}O_8$, 1223.5260; found, 1223.5240. (EA) (%, found/Calcd): C, 56.84/56.95; H, 4.93/5.11; N, 27.13/27.48. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.25 (t, *J*=6.6 Hz, 6H, -CH_3), 2.24 (m, 4H, -CH_2-), 2.96 (m, 4H, -CH_2-), 3.60-3.53 (m, 12H, -CH_2-), 3.73 (br, 4H, -CH_2-), 4.12 (t, *J*=5.7 Hz, 4H, -CH_2-), 4.37 (br, 4H, -CH_2-), 6.55 (d, *J*=9.0 Hz, 2H, -ArH), 6.77 (d, *J*=8.7 Hz, 4H, -ArH), 7.23 (s, 2H, -ArH), 7.65 (d, *J*=9.0 Hz, 2H, -ArH), 7.75 (m, 4H, -ArH), 7.88-7.84 (m, 6H, -ArH), 8.29 (d, *J*=8.7 Hz, 2H, -ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 156.22, 155.16, 150.83, 149.62, 148.24, 147.85, 147.37, 147.11, 144.79, 144.64, 126.46, 126.23, 124.80, 123.05, 122.62, 117.54, 116.73, 111.82, 111.64, 109.34, 68.68, 51.37, 49.70, 49.09, 47.44, 46.02, 28.54, 22.00, 12.45.

***Route 2*:**

1-NN: Compound **1** (227.4 mg, 0.54 mmol), **R4** (99.2 mg, 0.26 mmol), $CuSO_4$ $5H_2O$ (10 mol %), $NaHCO_3$ (20 mol %), and ascorbic acid (20 mol %) were dissolved in DMF (20 mL)/H_2O (1.0 mL) in a Schlenk flask under nitrogen. The mixture was stirred at room temperature for 3 h, then extracted with chloroform, and washed with 1N HCl, 1N NH_4OH and water subsequently. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography using dichloromethane/ethyl acetate (4/1) as eluent to afford red solid (272.7 mg, 86.3 %). This compound was directly used in the next step.

Mon-NN: **1-NN** (252.7 mg, 0.21 mmol), NaN_3 (81.4 mg, 1.25 mmol) and DMF (8 mL) were added into a flask, the resultant mixture was allowed to stir at 80 ℃ overnight, and then poured into a lot of water. The precipitate was collected and washed several times with water, dried under vacuum, and purified by column chromatography using dichloromethane/ethyl acetate (2/1) as eluent to yield red solid (249.3 mg, 97.5%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.25 (t, *J*=6.6 Hz, 6H, -CH_3), 2.24 (m, 4H, -CH_2-), 2.96 (m, 4H, -CH_2-), 3.60-3.53 (m, 12H, -CH_2-), 3.73 (br, 4H, -CH_2-), 4.12 (t, *J*=5.7 Hz, 4H, -CH_2-), 4.37 (br, 4H, -CH_2-), 6.55 (d, *J*=9.0 Hz, 2H, -ArH), 6.77 (d, *J*=8.7 Hz, 4H, -ArH), 7.23 (s, 2H, -ArH), 7.65 (d, *J*=9.0 Hz, 2H, -ArH), 7.75 (m, 4H, -ArH), 7.88-7.84 (m, 6H, -ArH), 8.29 (d, *J*=8.7 Hz, 2H, -ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 156.22, 155.16, 150.83, 149.62, 148.24, 147.85, 147.37, 147.11, 144.79, 144.64, 126.46, 126.23, 124.80, 123.05, 122.62, 117.54, 116.73, 111.82, 111.64, 109.34, 68.68, 51.37, 49.70, 49.09, 47.44, 46.02, 28.54, 22.00, 12.45.

*In **Route 1**, azo-coupling reaction as the final step with relatively low yield, with low atom economy, while **Route 2** behaved better. Thus, the synthesis of **Mon-NS** and **Mon-SS** was through **Route 2**.*



Scheme S3. The synthetic route to **Mon-NS** and **Mon-SS**

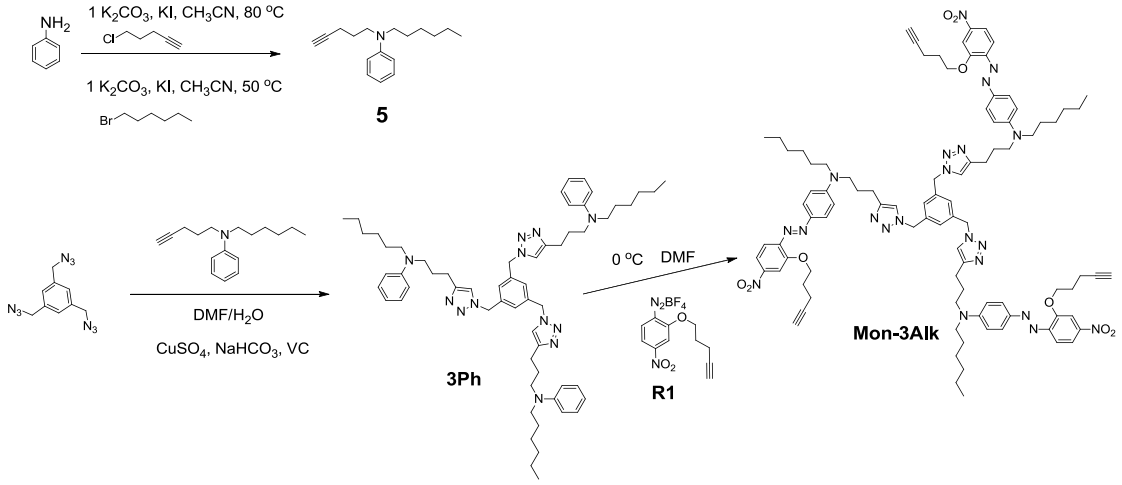
1-NS: Compound **R4** (305.8 mg, 0.73 mmol), **R5** (150.4 mg, 0.35 mmol), $CuSO_4$ $5H_2O$ (10 mol %), $NaHCO_3$ (20 mol %), ascorbic acid (20 mol %), DMF (20 mL)/H_2O (1.0 mL), 3 h, red solid (416.5 mg, 94.3 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.33-1.22 (m, 9H, -CH_3), 2.24 (m, 4H, -CH_2-), 2.96 (t, *J*=6.9 Hz, 4H, -CH_2-), 3.15 (m, 2H, -CH_2-), 3.53 (m, 4H, -CH_2-), 3.73-3.65 (m, 12H, -CH_2-), 4.14 (t, *J*=6.0 Hz, 4H, -CH_2-), 4.37 (br, 4H, -CH_2-), 6.57 (d, *J*=8.4 Hz, 2H, -ArH), 6.74 (d, *J*=9.0 Hz, 4H, -ArH), 7.21 (s, 2H, -ArH), 7.63 (d, *J*=9.0 Hz, 2H, -ArH), 7.88-7.77 (m, 8H, -ArH), 8.00-7.91 (m, 6H, -ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 155.71, 154.93, 150.39, 149.16, 148.06, 147.10, 146.88, 144.56, 144.48, 138.37, 129.14, 126.21, 125.87, 122.83, 122.24, 117.33, 116.46, 111.65, 111.32, 109.13, 68.47, 52.10, 51.12, 50.62, 47.12, 45.80, 40.11, 28.31, 21.74, 12.43, 7.37.

Mon-NS: **1-NS** (377.1 mg, 0.3 mmol), NaN_3 (135.3 mg, 2.08 mmol), DMF (15 mL), red solid (376.4 mg, 98.7%). HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{60}H_{68}N_{23}O_8S$, 1270.5342; found, 1270.5337. (EA) (%, found/Calcd): C, 56.52/56.73; H, 5.49/5.32; N, 15.19/25.36; S, 2.75/2.52. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.33-1.22 (m, 9H, -CH_3), 2.24 (m, 4H, -CH_2-), 2.96 (t, *J*=6.9 Hz, 4H, -CH_2-), 3.15 (m, 2H, -CH_2-), 3.53-3.59 (m, 12H, -CH_2-), 3.71 (br, 4H, -CH_2-), 4.14 (t, *J*=6.0 Hz, 4H, -CH_2-), 4.36 (br, 4H, -CH_2-), 6.57 (d, *J*=8.4 Hz, 2H, -ArH), 6.76 (d, *J*=9.0 Hz,

4H, -ArH), 7.22 (s, 2H, -ArH), 7.63 (d, *J*=9.0 Hz, 2H, -ArH), 7.88-7.77 (m, 8H, -ArH), 8.00-7.91 (m, 6H, -ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 156.06, 155.25, 150.91, 149.49, 148.38, 147.45, 147.28, 144.93, 144.78, 138.74, 129.49, 126.52, 126.20, 123.16, 122.58, 117.68, 116.82, 111.99, 111.77, 109.48, 77.71, 77.29, 76.86, 68.82, 51.44, 50.95, 49.77, 49.18, 47.45, 46.09, 28.63, 22.08, 12.52, 7.70.

1-SS: Compound **1** (186.7 mg, 0.44 mmol), **R5** (90.9 mg, 0.21 mmol) , DMF (10 mL)/H_2O (0.5 mL), 3 h, orange solid (242.1 mg, 90.1 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.33-1.24 (m, 9H, -CH_3), 2.08 (m, 4H, -CH_2-), 2.82 (t, *J*=7.2 Hz, 4H, -CH_2-), 3.15 (m, 6H, -CH_2-), 3.54 (m, 4H, -CH_2-), 3.75-3.67 (m, 12H, -CH_2-), 4.43 (br, 4H, -CH_2-), 6.57 (d, *J*=8.4 Hz, 2H, -ArH), 6.77-6.70 (m, 8H, -ArH), 7.22 (s, 2H, -ArH), 8.00-7.88 (d, 16H, -ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 156.17, 155.75, 150.43, 149.25, 146.19, 144.59, 143.75, 138.24, 129.18, 128.95, 126.06, 122.89, 122.74, 122.28, 111.85, 111.29, 55.12, 52.12, 51.24, 50.63, 47.14, 45.80, 40.11, 23.68, 22.56, 12.43, 7.40.

Mon-SS: **1-SS** (212.1 mg, 0.3 mmol), NaN_3 (65.0 mg, 1.0 mmol), DMF (15 mL), orange solid (200.7 mg, 94.1%). HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{60}H_{70}N_{21}O_6S_3$, 1276.4980; found, 1276.4983. (EA) (%, found/Calcd): C, 56.63/56.45; H, 5.69/5.45; N, 22.84/23.04; S, 7.48/7.54. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.33-1.23 (m, 9H, -CH_3), 2.09 (m, 4H, -CH_2-), 2.83 (t, *J*=7.2 Hz, 4H, -CH_2-), 3.15 (t, *J*=6.0 Hz, 6H, -CH_2-), 3.62-3.52 (m, 12H, -CH_2-), 3.73 (br, 4H, -CH_2-), 4.44 (br, 4H, -CH_2-), 6.79-6.70 (m, 8H, -ArH), 7.22 (s, 4H, -ArH), 7.94-7.88 (m, 8H, -ArH), 8.00 (m, 4H, -ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 156.61, 156.28, 151.21, 149.90, 146.59, 144.91, 144.05, 138.63, 129.63, 129.45, 126.55, 123.39, 123.21, 122.98, 112.26, 111.90, 78.23, 77.80, 77.38, 55.65, 51.54, 51.08, 49.86, 49.33, 47.61, 46.17, 24.21, 23.08, 12.69, 7.93.



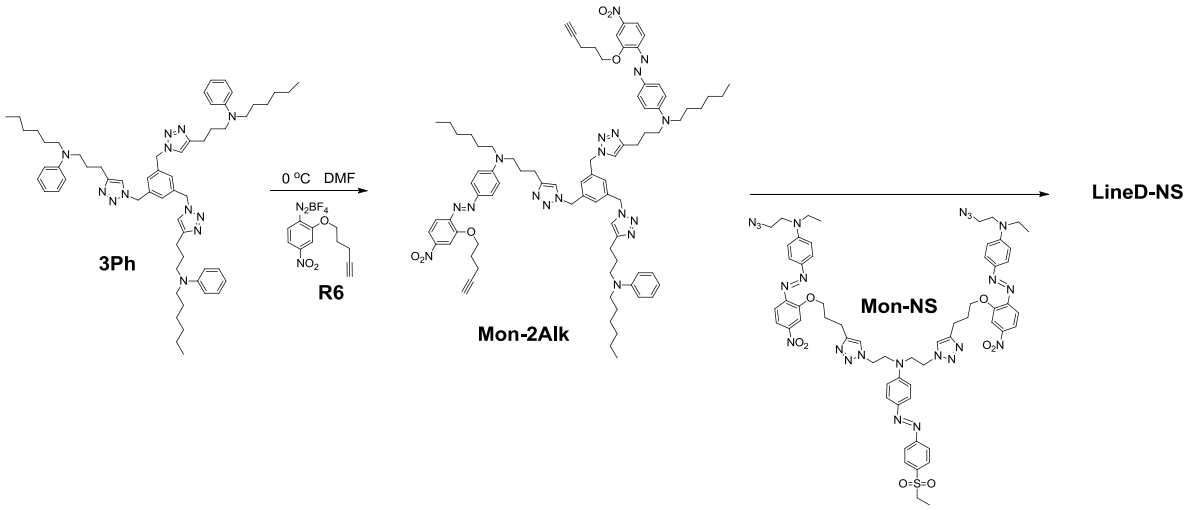
Scheme S4. The synthetic route to **Mon-3Alk**

Compound **5**: Aniline (1.86 g, 0.02 mol) were dissolved in CH_3CN, 5-chloropent-1-yne (0.24 g, 0.02 mol), K_2CO_3 (2.763 g, 0.02 mol) and KI (0.332 g, 0.002 mol) were added then. After the reaction was stirred for 24 h at 80 ^oC, another batch of 1-bromohexanel (0.328 g, 0.02 mol), K_2CO_3 ((2.763 g, 0.02 mol) and KI (0.332 g, 0.002 mol) were added. The reaction continued to stir for another 24 h. The mixture was cooled into room temperature, then filtered to remove the solid, the organic layer was poured into a lot of water. The mixture was extracted with chloroform, and washed with water for several times. The organic layer was dried over magnesium sulfate. The crude product was purified by column chromatography on silica gel using chloroform/petroleum ether (1/8) as eluent to afford colorless oil (0.357 g, 72.3 %). This compound was directly used in the next step.

Compound **3Ph**: 1,3,5-Tris(azidomethyl)benzene (107.9 mg, 0.44 mmol), **5** (356.2 mg, 1.46 mmol), $CuSO_4 \cdot 5H_2O$ (10 mol %), $NaHCO_3$ (20 mol %), and ascorbic acid (20 mol %) were dissolved in DMF (20 mL)/H_2O (1 mL) under nitrogen in a Schlenk flask. The mixture was stirred at 30 ^oC for 4 h, then extracted with chloroform, and washed with 1N HCl, 1N NH_4OH, and water subsequently. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography using dichloromethane/ethyl acetate (1/3) as eluent to afford colorless oil (370.0 mg, 85.7 %). ^1H NMR (300 MHz, $CDCl_3$, 298 K), δ(TMS, ppm): 0.89 (m, 9H, -CH_3), 1.29 (m, 18H, -CH_2-), 1.55 (br, 6H, -CH_2-), 1.93 (m, 6H, -CH_2-), 2.72 (t, *J*=7.8 Hz, 6H, -CH_2-), 3.24 (t, *J*=7.8 Hz, 6H, -CH_2-), 3.30 (t, *J*=7.8 Hz, 6H, -CH_2-), 5.39 (s, 6H, -CH_2-), 6.61 (m, 9H, -ArH), 7.07 (s, 3H, -ArH), 7.18-7.13 (m, 9H, -ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ(ppm): 148.3, 147.9, 137.0, 129.1, 127.0, 120.8, 115.4, 111.8, 64.1, 53.1, 51.3, 48.3, 31.6, 27.0, 26.8, 26.7, 23.1, 22.6, 13.9.

Mon-3Alk: Compound **3Ph** (245.0 mg, 0.25 mmol) and **R1** (241.1 mg, 0.75 mmol) were dissolved in DMF (20 mL), the resultant mixture was allowed to stir at 0 ℃ overnight, and then poured into a lot of water. The precipitate was collected and washed several times with water, and purified by column chromatography using dichloromethane/ethyl acetate (1/2) as eluent to yield red solid (380.0 mg, 90.1 %). HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{93}H_{112}N_{21}O_9$, 1666.8952; found, 1666.8962. (EA) (%, found/Calcd): C, 66.84/67.01; H, 6.94/6.71; N, 17.36/17.64. ^1H NMR (300 MHz, $CDCl_3$, 298 K), δ(TMS, ppm): 0.89 (br, 9H, -CH_3), 1.31 (br, 18H, -CH_2-), 2.00 (br, 9H, -CH_2-), 2.13 (br, 6H, -CH_2-), 2.48 (br, 6H, -CH_2-), 2.73 (br, 6H, -CH_2-), 3.37 (br, 6H, -CH_2-), 3.47 (br, 6H, -CH_2-), 4.33 (br, 6H, -CH_2-), 5.43 (s, 6H, -CH_2-), 6.65 (br, 6H, -ArH), 7.11 (s, 6H, -ArH), 7.67-7.64 (m, 3H, -ArH), 7.90-7.85 (m, 12H, -ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ(ppm): 154.82, 151.15, 147.86, 147.67, 147.12, 143.89, 136.96, 127.26, 126.22, 120.91, 117.21, 116.61, 111.14, 109.13, 83.18,

69.18, 68.00, 53.13, 51.24, 50.41, 31.54, 27.94, 27.19, 26.77, 26.62, 22.95, 22.57, 15.07, 13.97.



Scheme S5. The synthetic route to **Mon-2Alk** and **LineD-NS**

Mon-2Alk: Compound **3Ph** (97.3 mg, 0.1 mmol) and **R1** (63.9 mg, 0.20 mmol) were dissolved in DMF (20 mL), the resultant mixture was allowed to stir at 0 ℃ overnight, and then poured into a lot of water. The precipitate was collected and washed several times with water, and purified by column chromatography using dichloromethane/ethyl acetate (1/2) as eluent to yield red solid (64.5 mg, 45.2 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 0.90 (br, 9H, -CH_3), 1.32-1.25 (br, 18H, -CH_2-), 1.92 (m, 2H, -CH_2-), 2.00 (br, 6H, -CH_2-), 2.13 (m, 4H, -CH_2-), 2.48 (m, 4H, -CH_2-), 2.73 (br, 6H, -CH_2-), 3.24 (m, 2H, -CH_2-), 3.37 (m, 6H, -CH_2-), 3.47 (br, 4H, -CH_2-), 4.33 (br, 4H, -CH_2-), 5.42 (m, 6H, -CH_2-), 6.64 (m, 7H, -ArH), 7.21-7.11 (m, 6H, -ArH), 7.67-7.64 (m, 2H, -ArH), 7.91-7.81 (m, 10H, -ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 154.84, 151.19, 148.25, 147.87, 147.66, 147.18, 143.92, 137.05, 136.93, 129.11, 127.28, 127.20, 126.22, 120.91, 120.84, 117.24, 116.61, 115.34, 111.78, 111.17, 109.21, 83.18, 69.17, 68.06, 53.13, 52.06, 51.22, 51.07, 50.41, 50.17, 31.62, 31.54, 29.59, 27.96, 27.20, 27.0326.76, 26.72, 26.62, 23.13, 22.94, 22.56, 15.07, 13.96.

LineD-NS: **Mon-NS** (44.4 mg, 0.035 mmol), **Mon-2Alk** (50.2 mg, 0.035 mmol), $CuSO_4$ (30+30 μL), NaAsc (30+30 μL), in 5.5 mL DMF, deep red powder (70.7 mg, 76.1 %). M_w=13 650, M_w/M_n = 1.21 (GPC, polystyrene calibration). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 0.86 (-CH_3), 1.06 (-CH_3), 1.25 (-CH_2-), 1.60 (-CH_2-), 1.97-1.85 (-CH_2-, -CCH), 2.17 (-CH_2-), 2.69 (-CH_2-), 2.91 (-CCH_2-), 3.10 (-SCH_2-), 3.22 (-NCH_2-), 3.31 (-NCH_2-), 3.40 (-NCH_2-), 3.74 (-NCH_2-), 3.82 (-NCH_2-), 4.05 (-NCH_2-), 4.40 (-OCH_2-), 4.48 (-OCH_2-), 5.39 (-NCH_2-), 6.56 (-ArH), 7.11-7.08 (-ArH), 7.37 (-ArH), 7.56 (-ArH), 7.72 (-ArH), 7.86 (-ArH).

Table S1. The NLO properties of LineD-NS measured at 1064 nm fundamental beam.

@1064	T_e [a] (°C)	l_s [b] (nm)	λ_{max} [c] (nm)	d_{33} [d] (pm/V)	$d_{33(\infty)}$ [e] (pm/V)	Φ [f]	N [g] (%)	N_N [h] (%)	N_S [i] (%)	M_w [j] (10^4)	M_w/M_n [j]
LineD-NS	100	263	471	91.0	15.8	21.9	56.8	44.1	12.7	1.365	1.21

[a] The best poling temperature. [b] Film thickness. [c] The maximum absorption in thin films. [d] Second harmonic generation (SHG) coefficient. [e] The nonresonant d_{33} values calculated by using the approximate two-level model. [f] Order parameter $\Phi = 1\text{-}A_1/A_0$, A_1 and A_0 are the absorbance of the polymer film after and before corona poling, respectively. [g] The loading density of the effective chromophores. [h] The loading density of the nitro-chromophores. [i] The loading density of the sulfornly-chromophores. [j] Determined by GPC in THF, based on calibration with polystyrene.

The ^{1}H NMR and ^{13}C NMR spectra of related compounds:

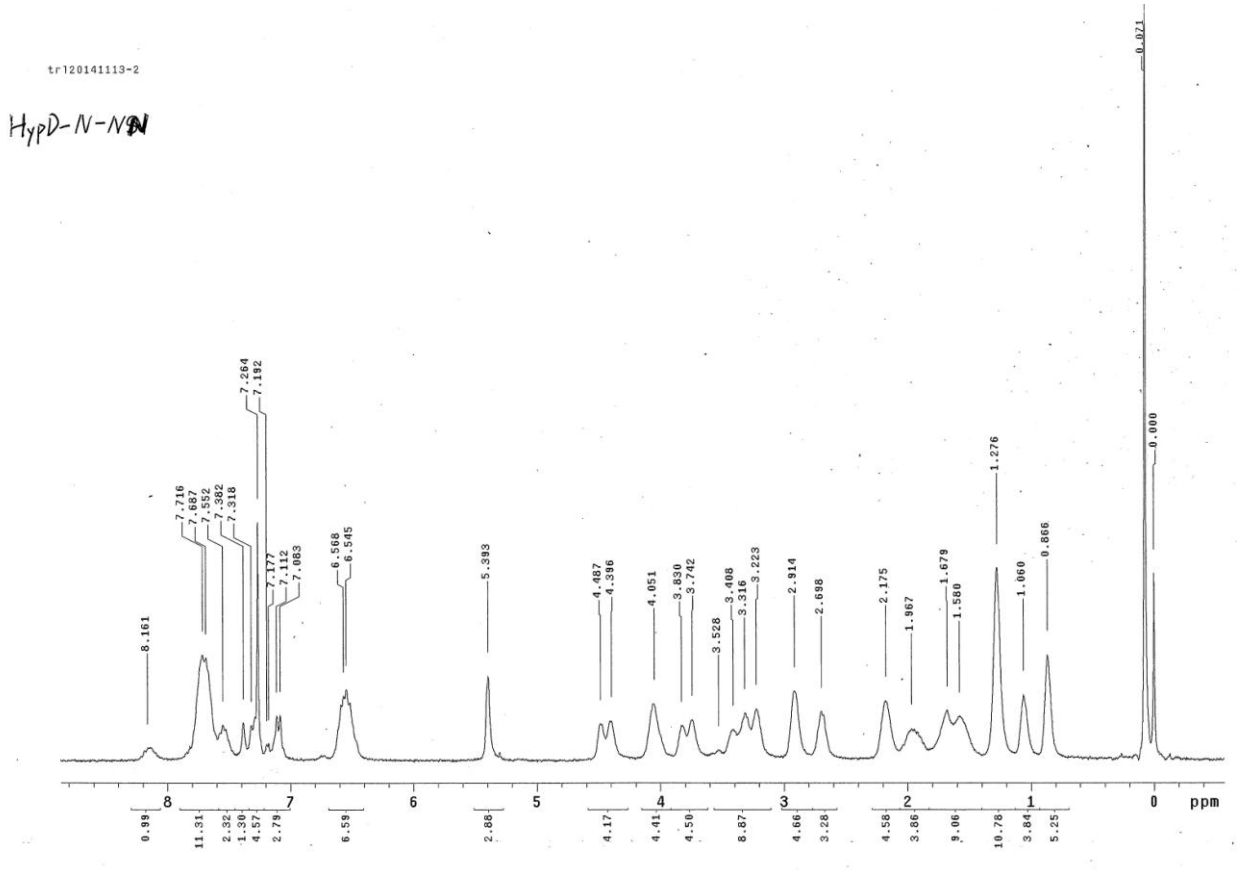


Fig.S1. ^{1}H NMR spectrum of polymer **HypD-NN** in chloroform-*d*.

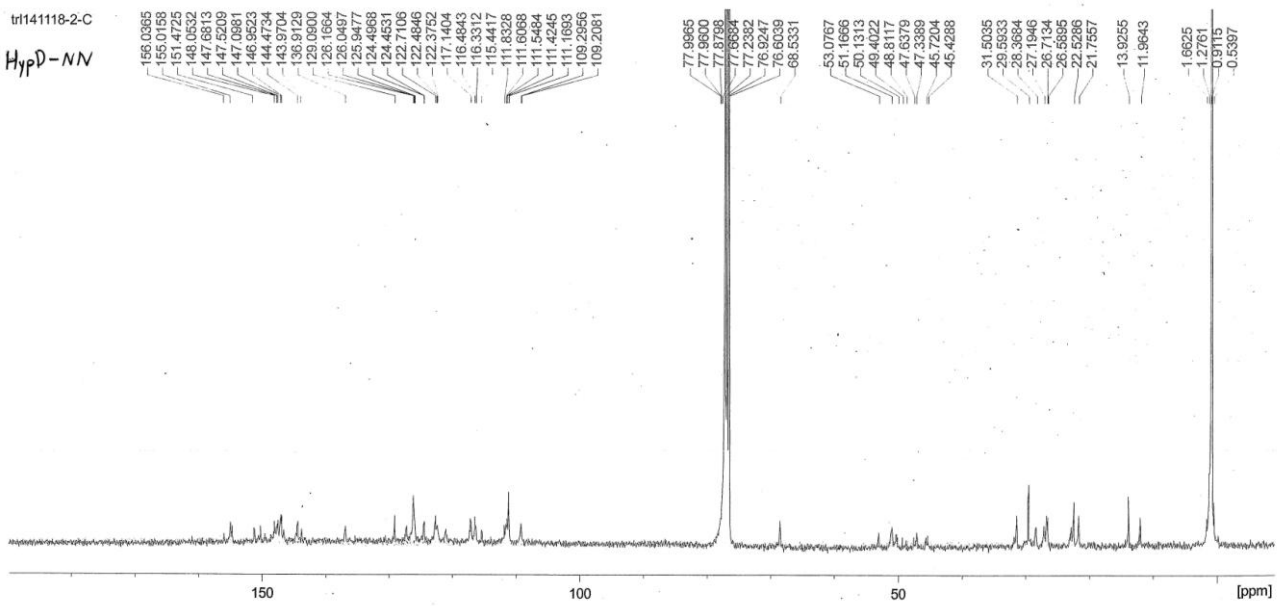


Fig.S2. ^{13}C NMR spectrum of polymer **HypD-NN** in chloroform-*d*.

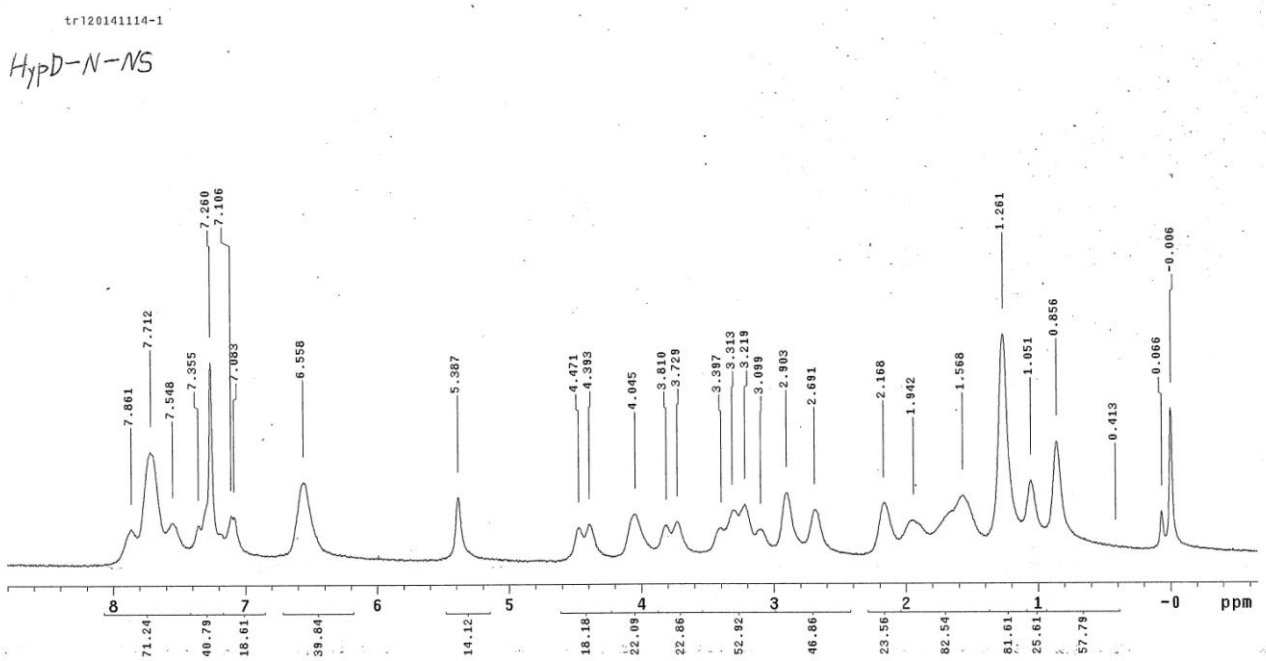


Fig.S3. ^{1}H NMR spectrum of polymer **HypD-NS** in chloroform-*d*.

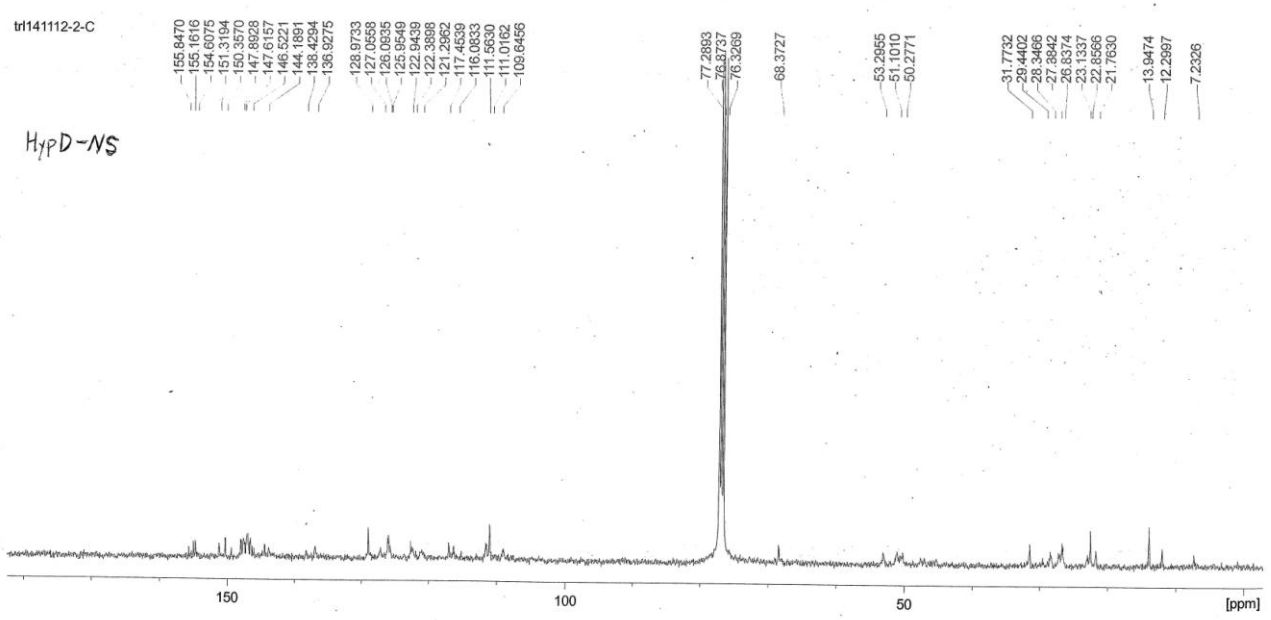


Fig.S4. ^{13}C NMR spectrum of polymer **HypD-NS** in chloroform-*d*.

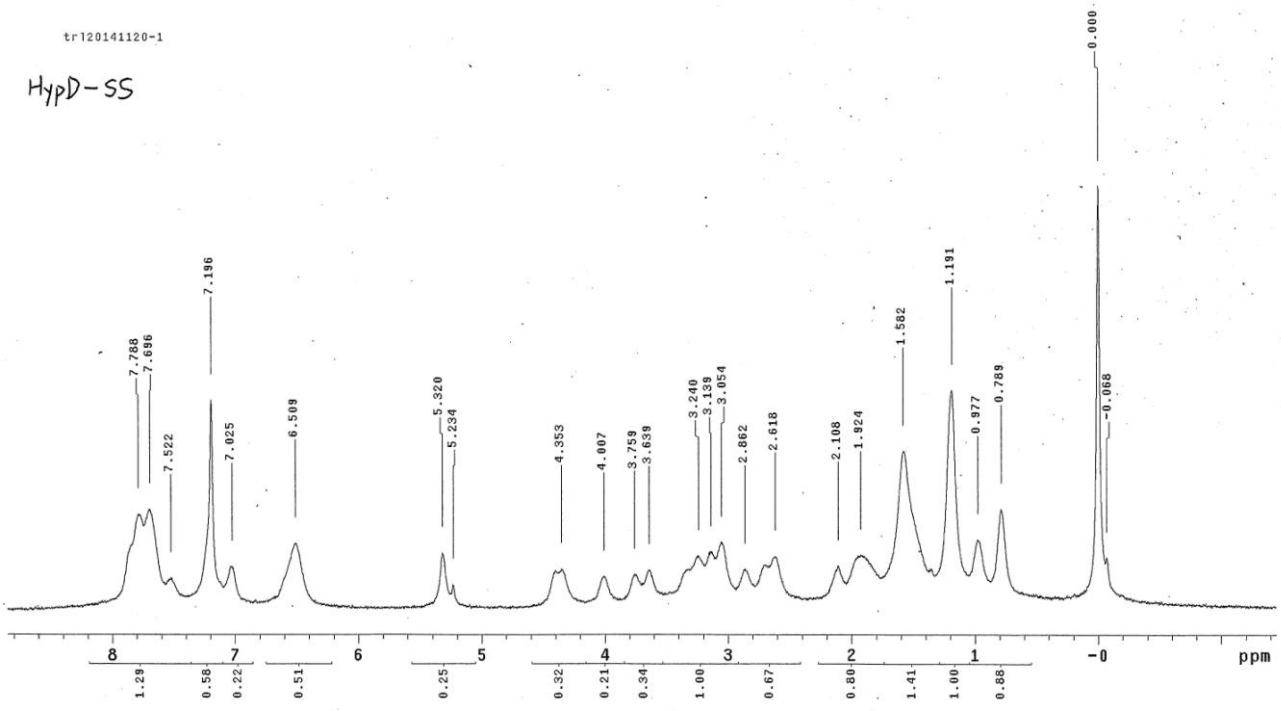


Fig.S5. ^{1}H NMR spectrum of polymer **HypD-SS** in chloroform-*d*.

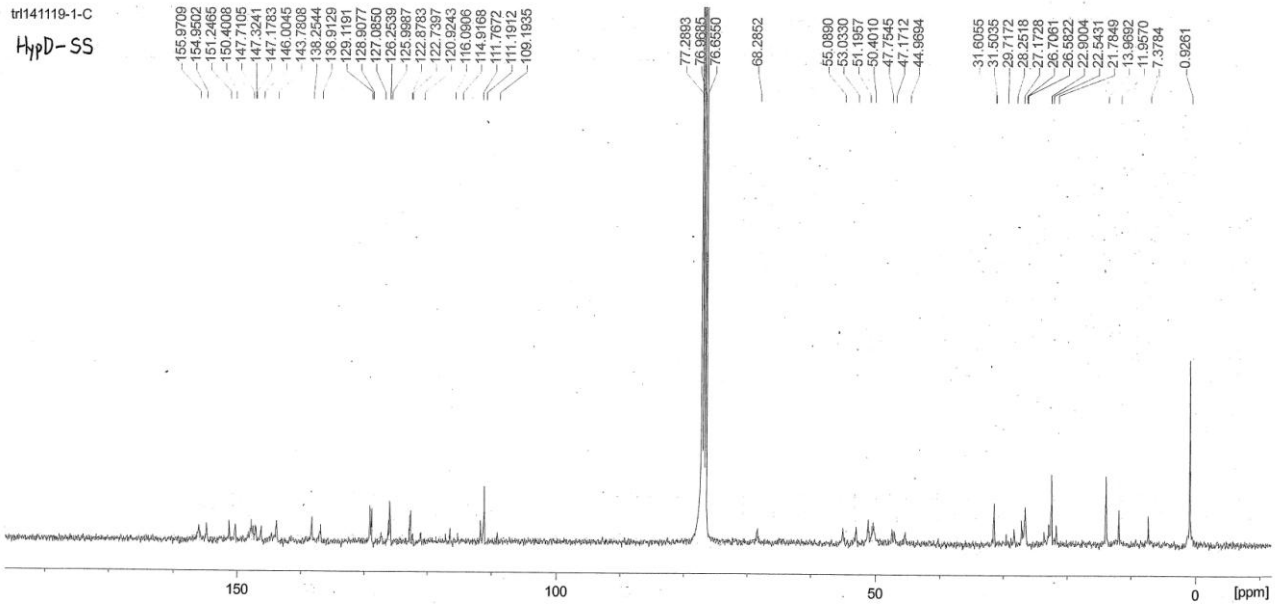


Fig.S6. ^{13}C NMR spectrum of polymer **HypD-SS** in chloroform-*d*.

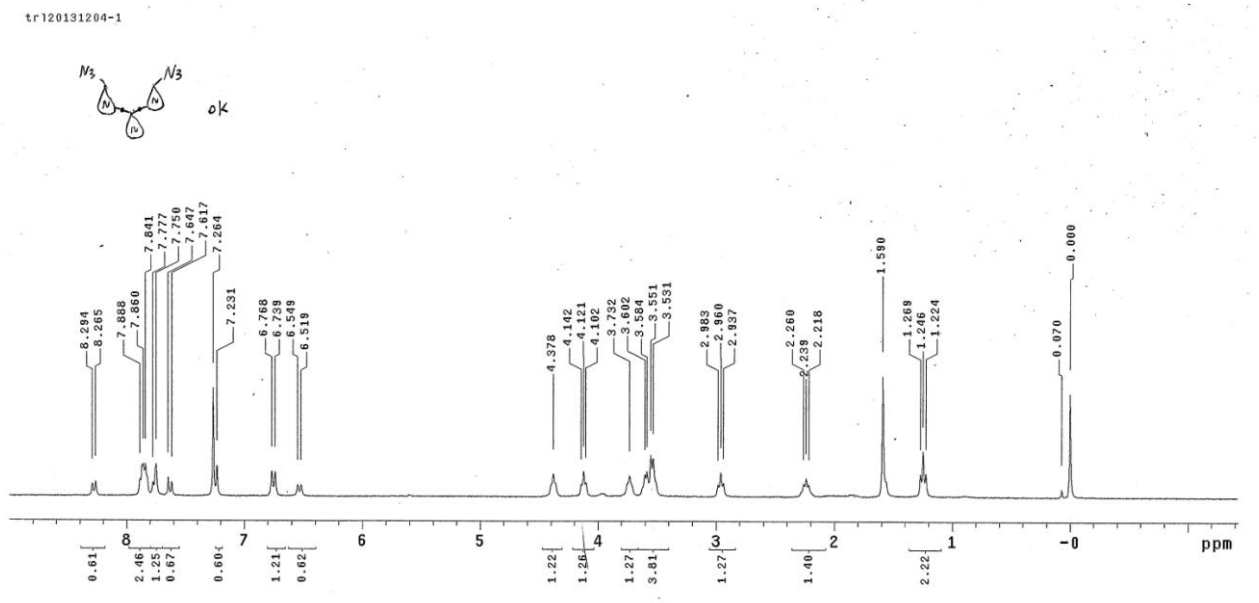


Fig.S7. ^{1}H NMR spectrum of **Mon-NN** in chloroform-*d*.

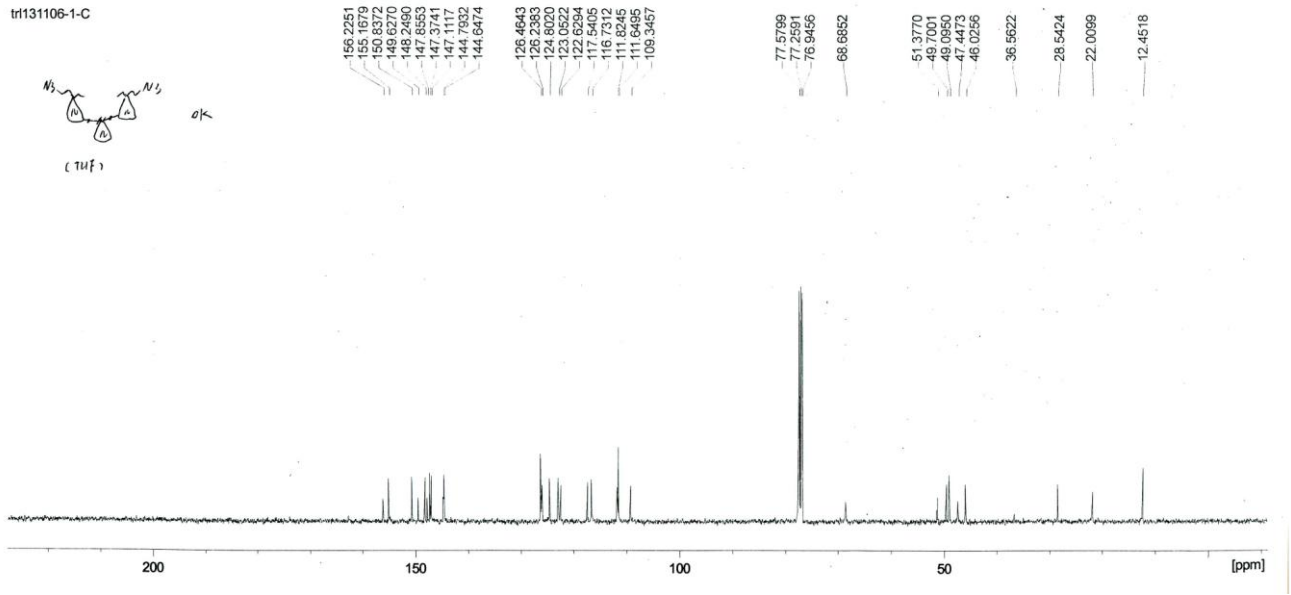


Fig.S8. ^{13}C NMR spectrum of **Mon-NN** in chloroform-*d*.

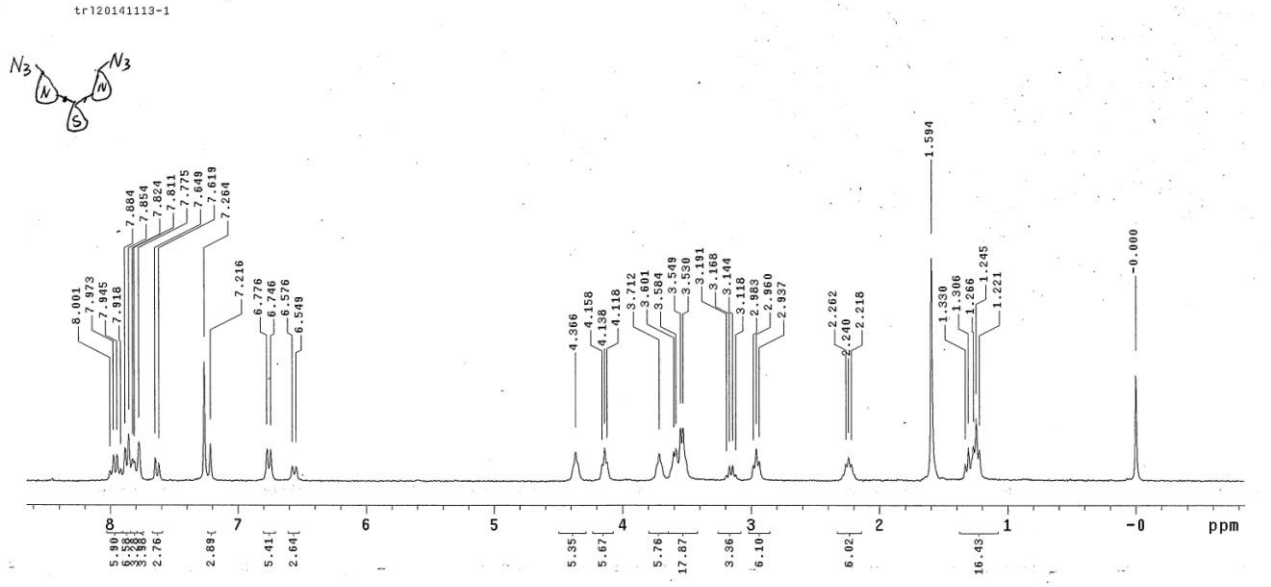


Fig.S9. ^{1}H NMR spectrum of **Mon-NS** in chloroform-*d*.

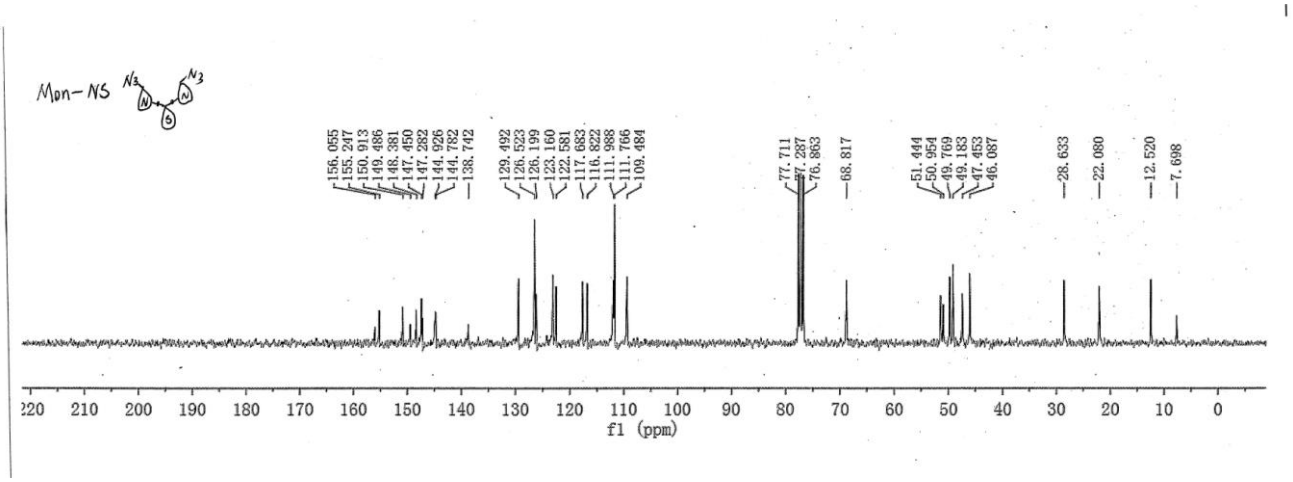


Fig.S10. ^{13}C NMR spectrum of **Mon-NS** in chloroform-*d*.

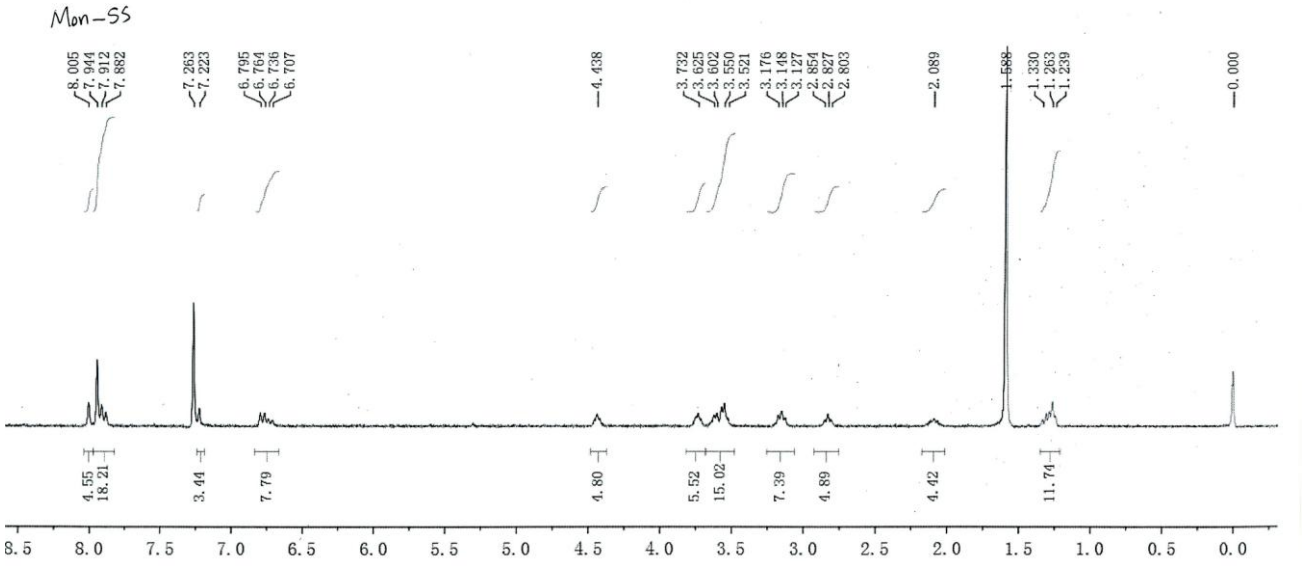


Fig.S11. ^{1}H NMR spectrum of **Mon-SS** in chloroform-*d*.

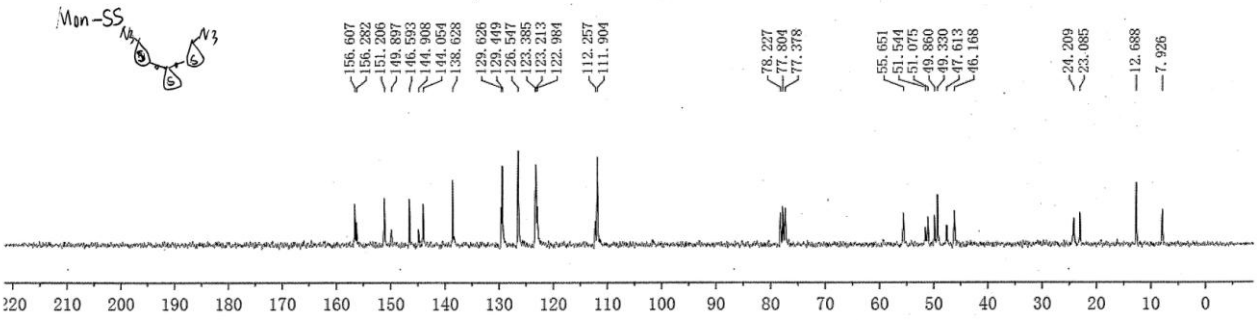


Fig.S12. ^{13}C NMR spectrum of **Mon-SS** in chloroform-*d*.

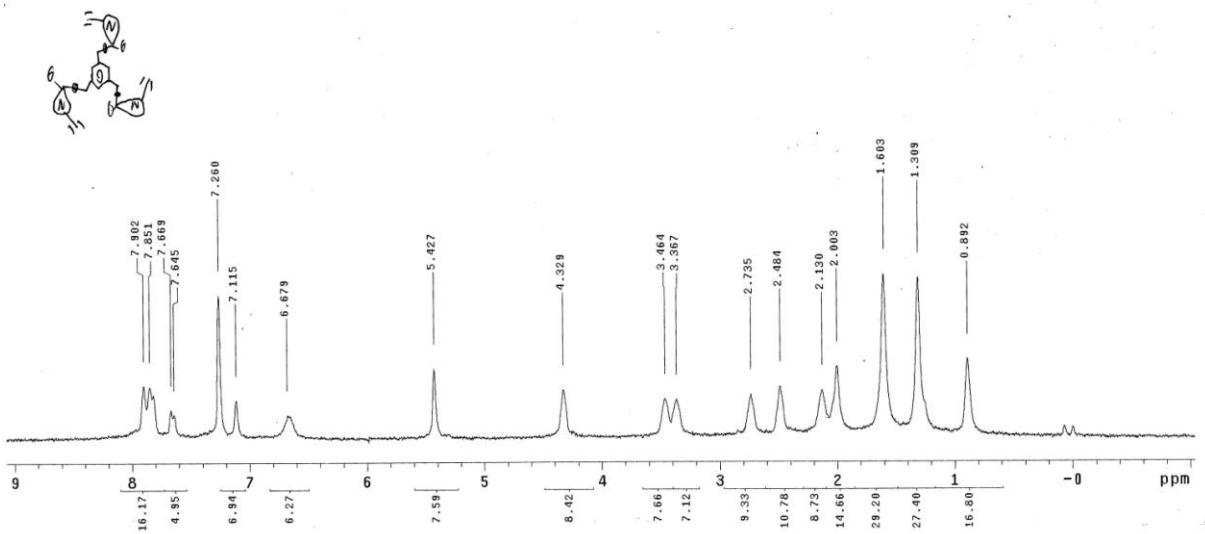


Fig.S13. ^{1}H NMR spectrum of **Mon-3Alk** in chloroform-*d*.

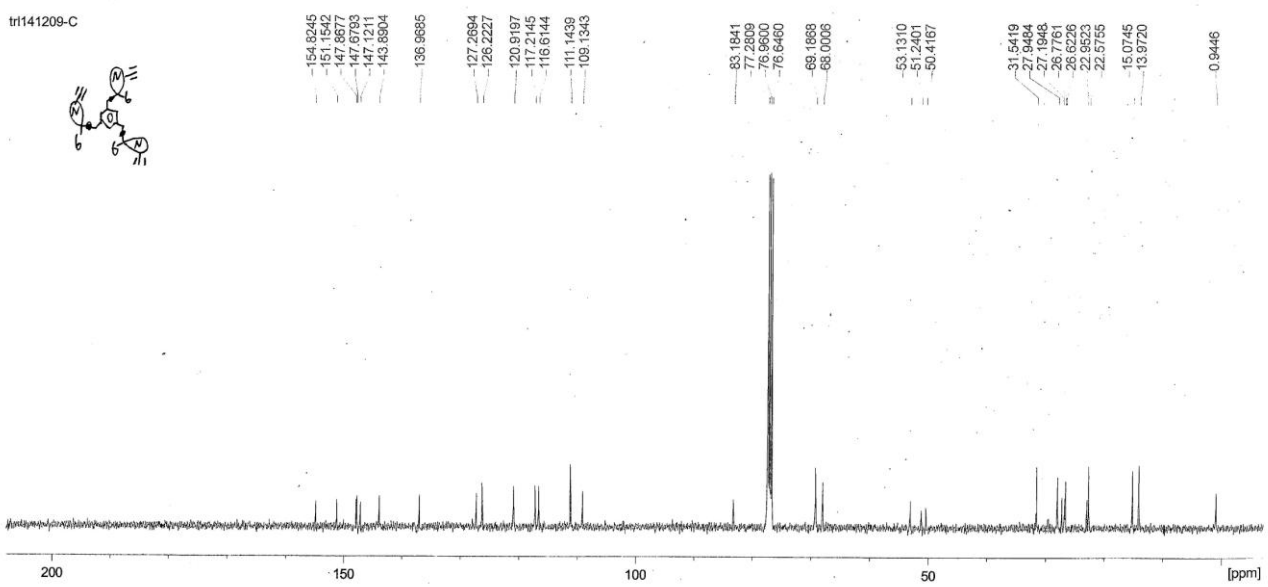


Fig.S14. ^{13}C NMR spectrum of **Mon-3≡** in chloroform-*d*.

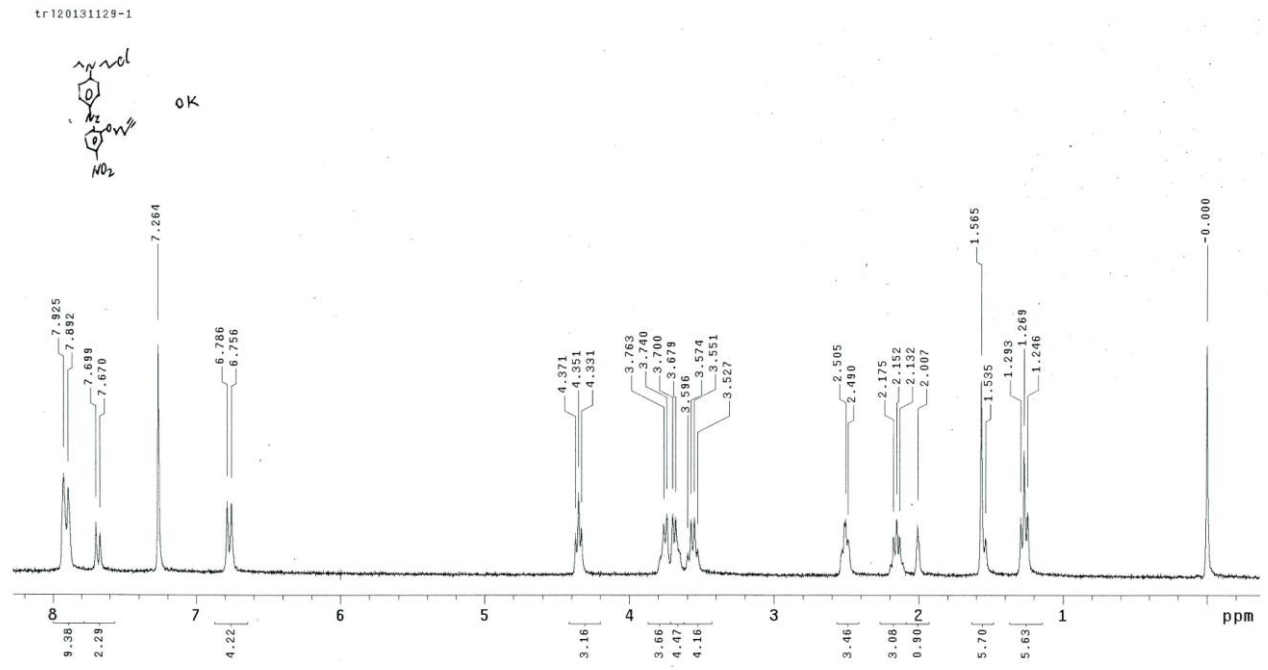


Fig.S15. ^{1}H NMR spectrum of **1** in chloroform-*d*.

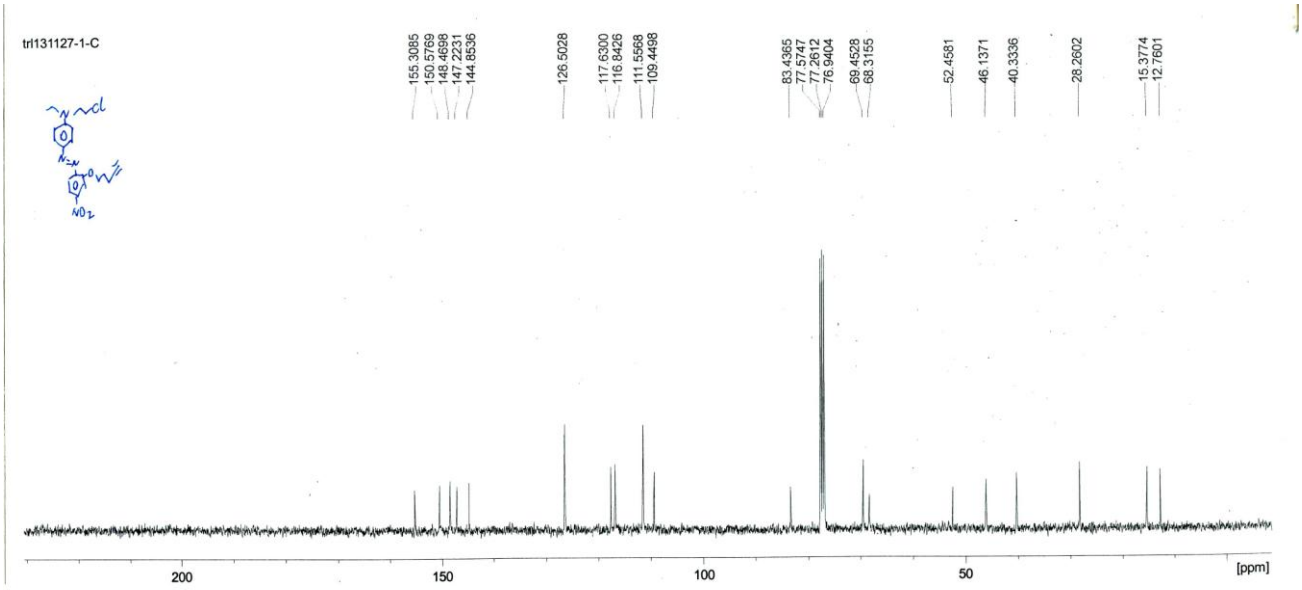


Fig.S16. ^{13}C NMR spectrum of **1** in chloroform-*d*.

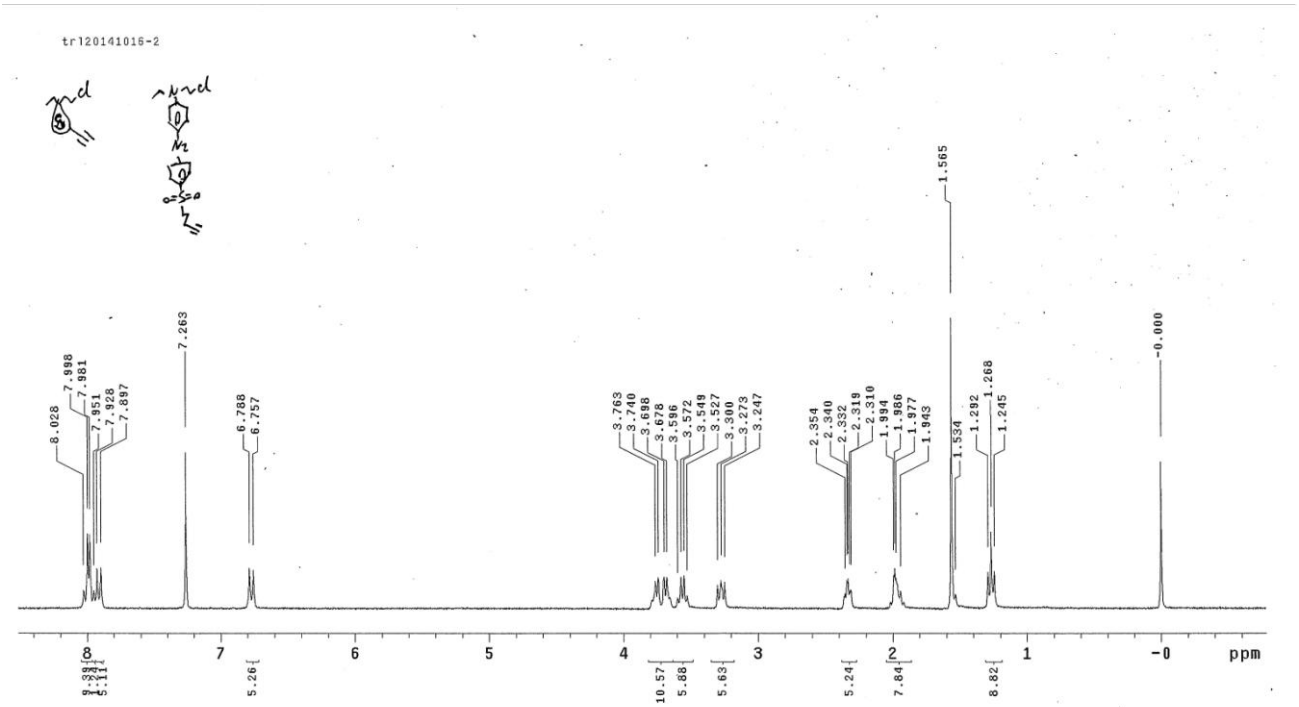


Fig.S17. ^{1}H NMR spectrum of **2** in chloroform-*d*.

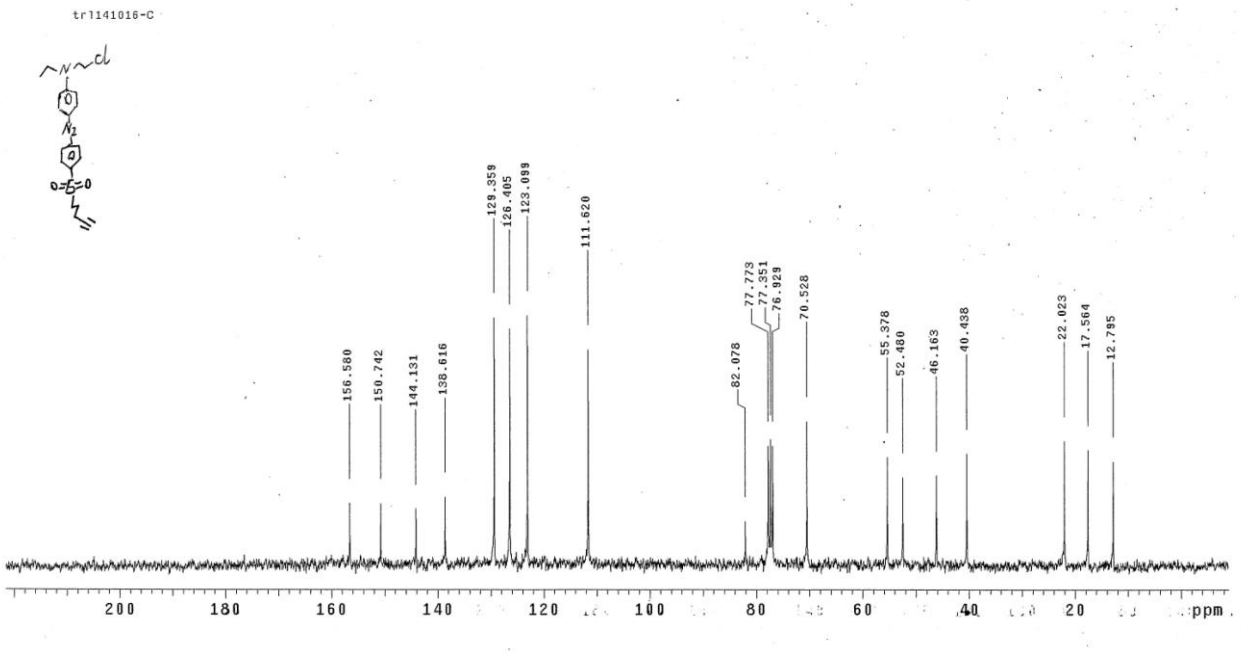


Fig.S18. ^{13}C NMR spectrum of **2** in chloroform-*d*.

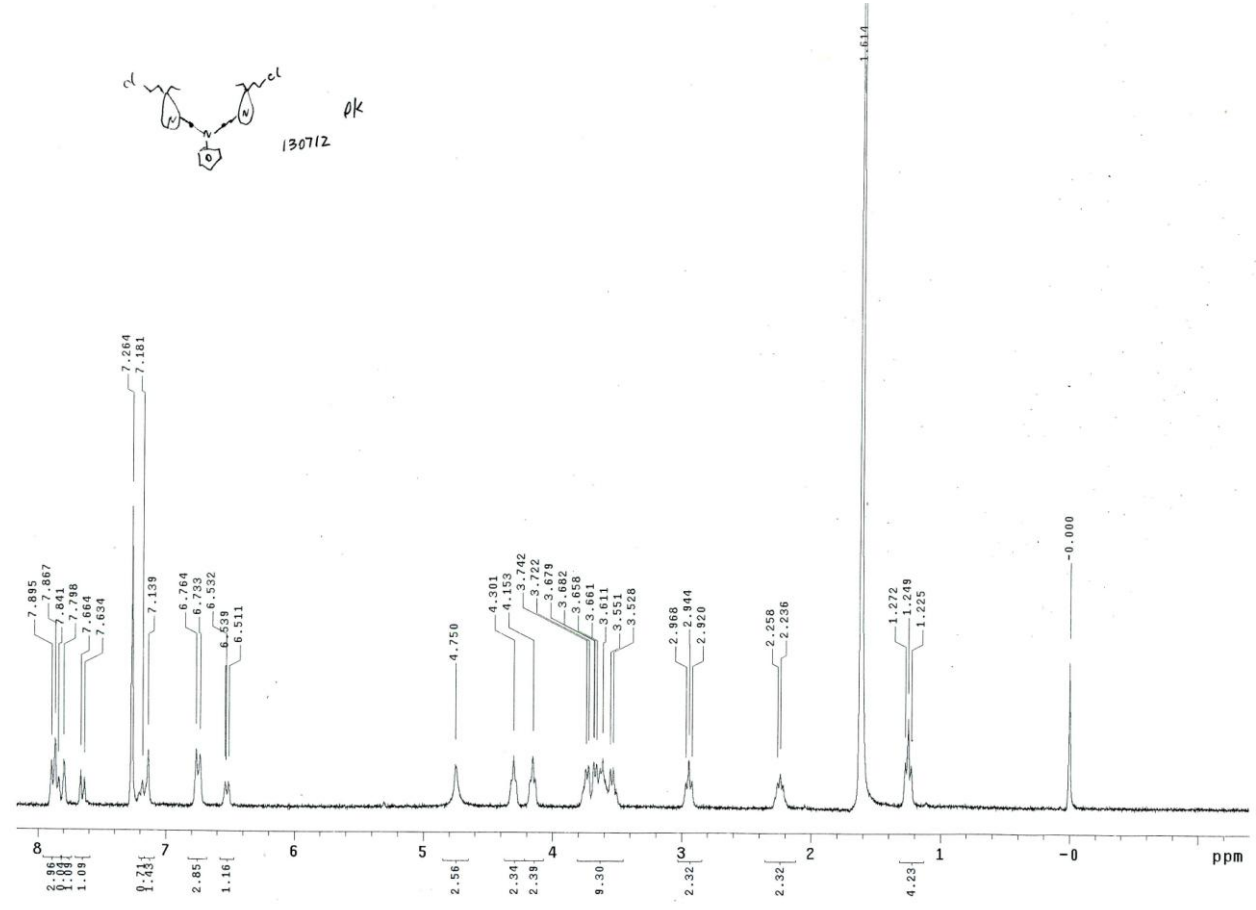


Fig.S19. ^{1}H NMR spectrum of **3** in chloroform-*d*.

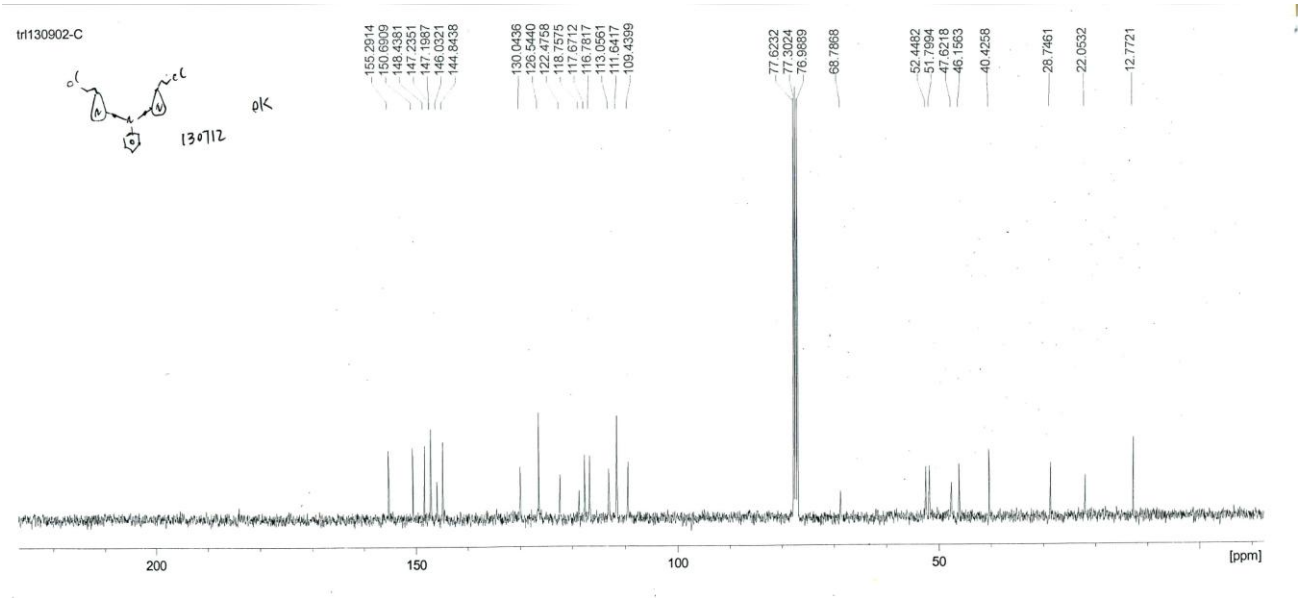


Fig.S20. ^{13}C NMR spectrum of **3** in chloroform-*d*.

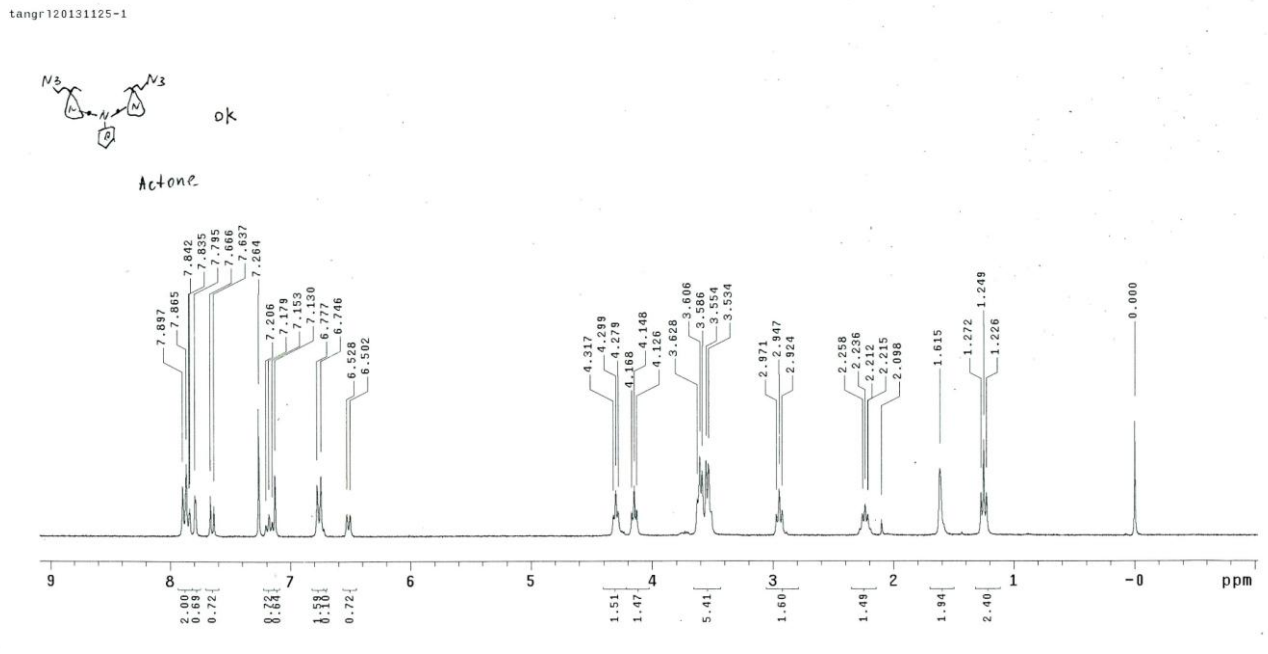


Fig.S21. ^{1}H NMR spectrum of **4** in chloroform-*d*.

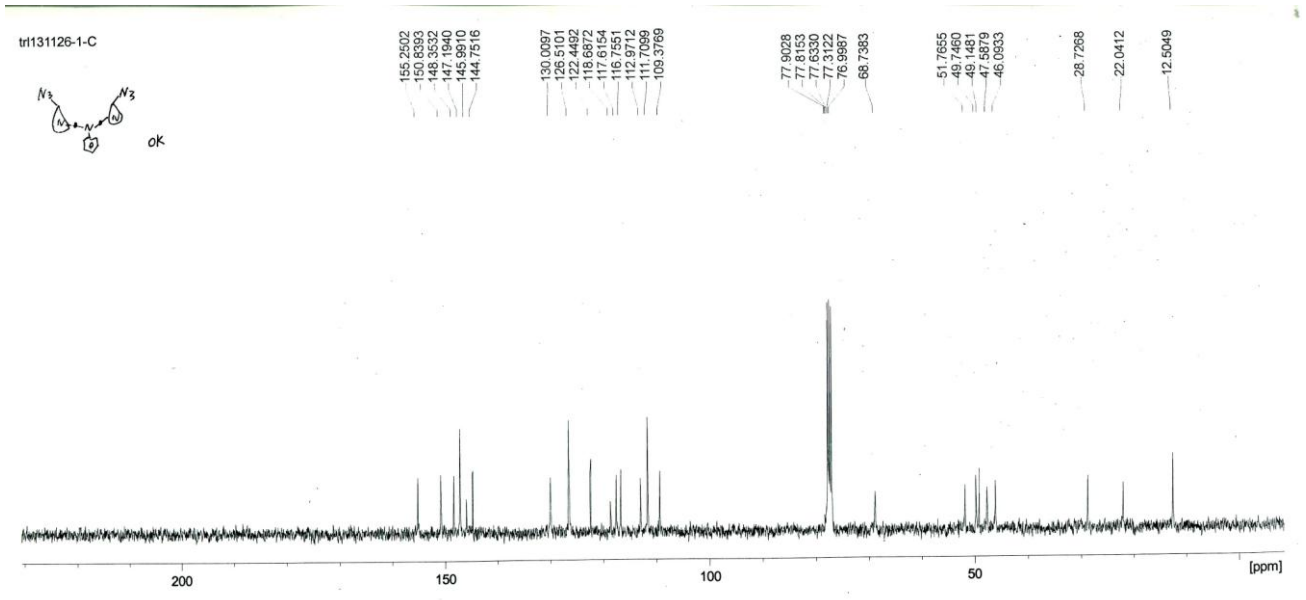


Fig.S22. ^{13}C NMR spectrum of **4** in chloroform-*d*.

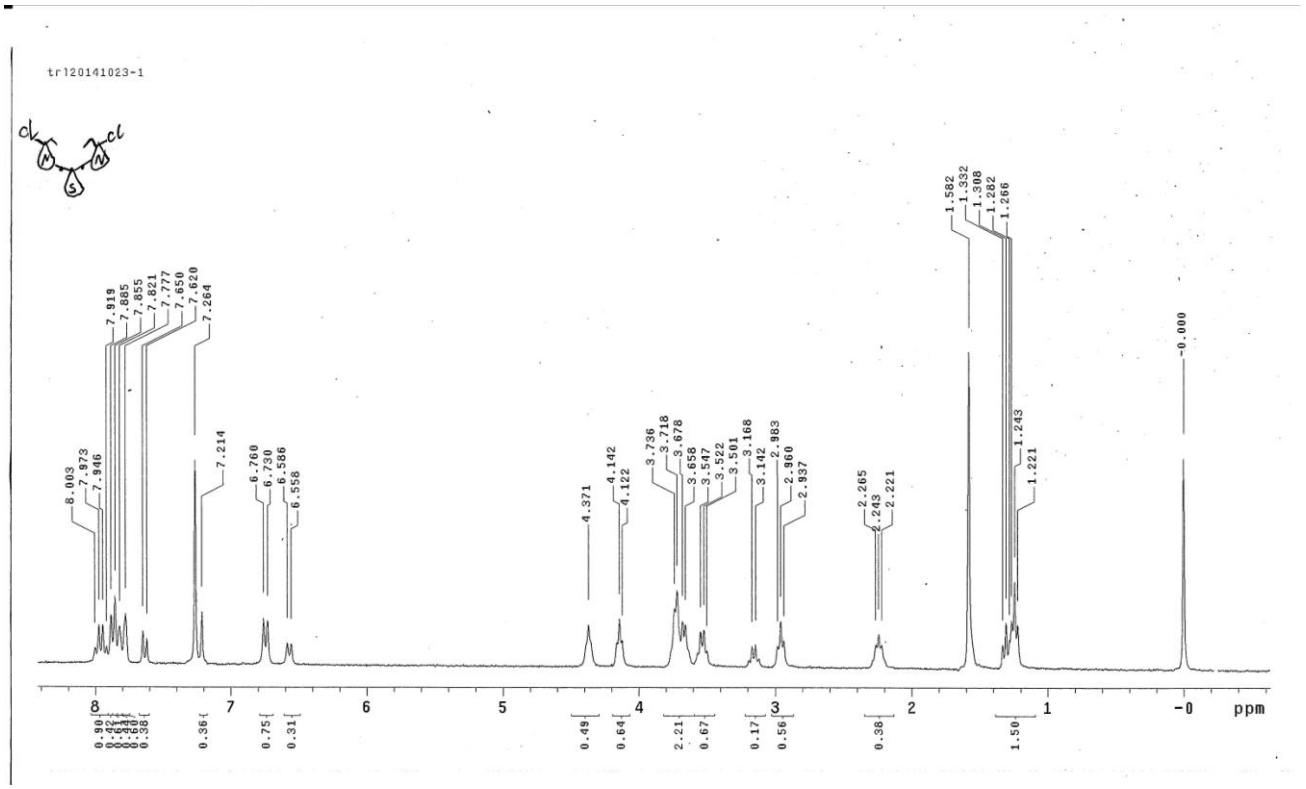


Fig.S23. ^{1}H NMR spectrum of **1-NS** in chloroform-*d*.

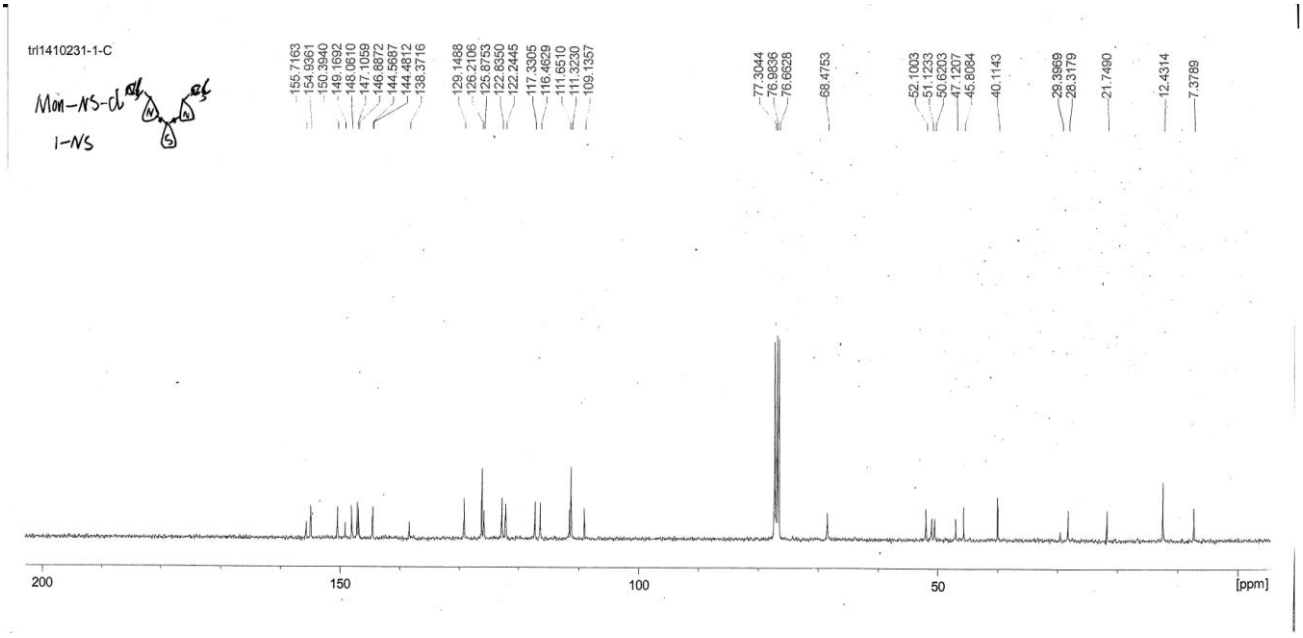


Fig.S24. ^{13}C NMR spectrum of **1-NS** in chloroform-*d*.

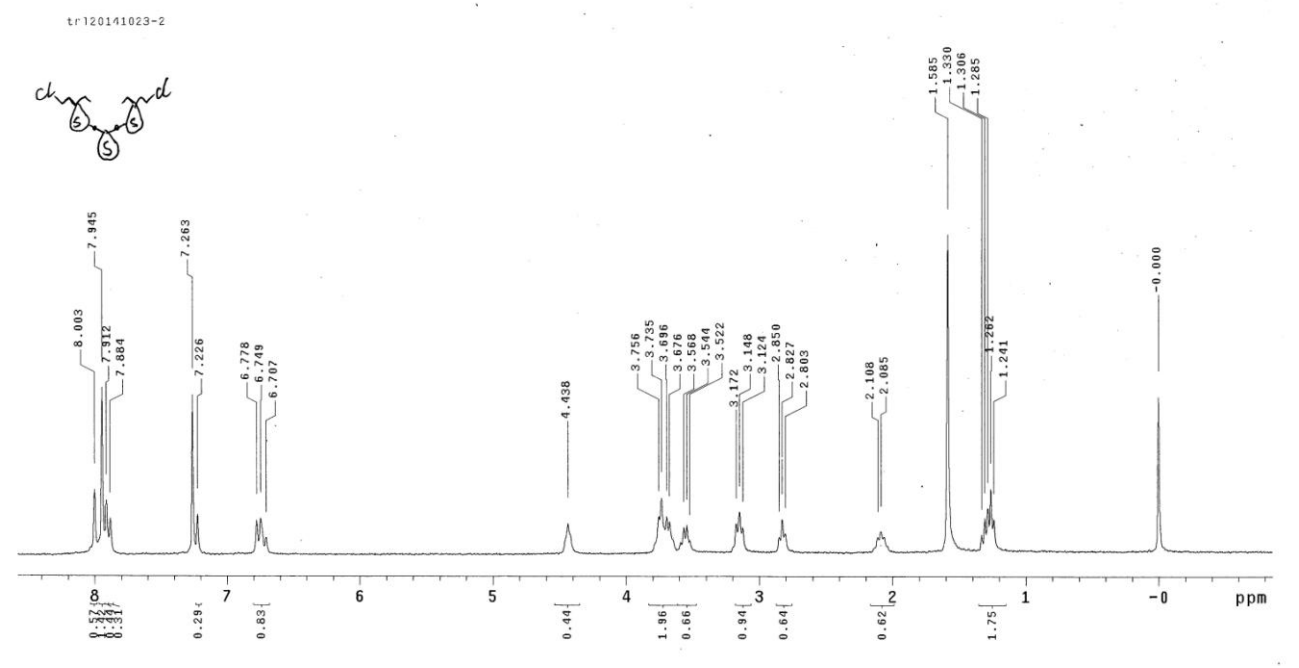


Fig.S25. ^{1}H NMR spectrum of **1-SS** in chloroform-*d*.

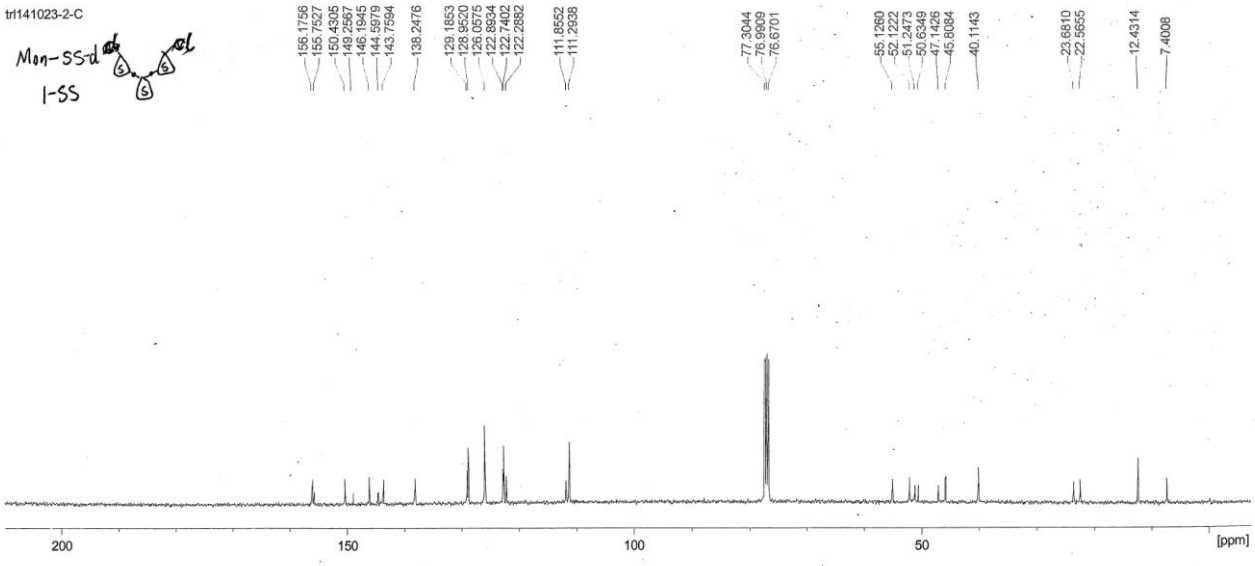


Fig.S26. ^{13}C NMR spectrum of **1-SS** in chloroform-*d*.

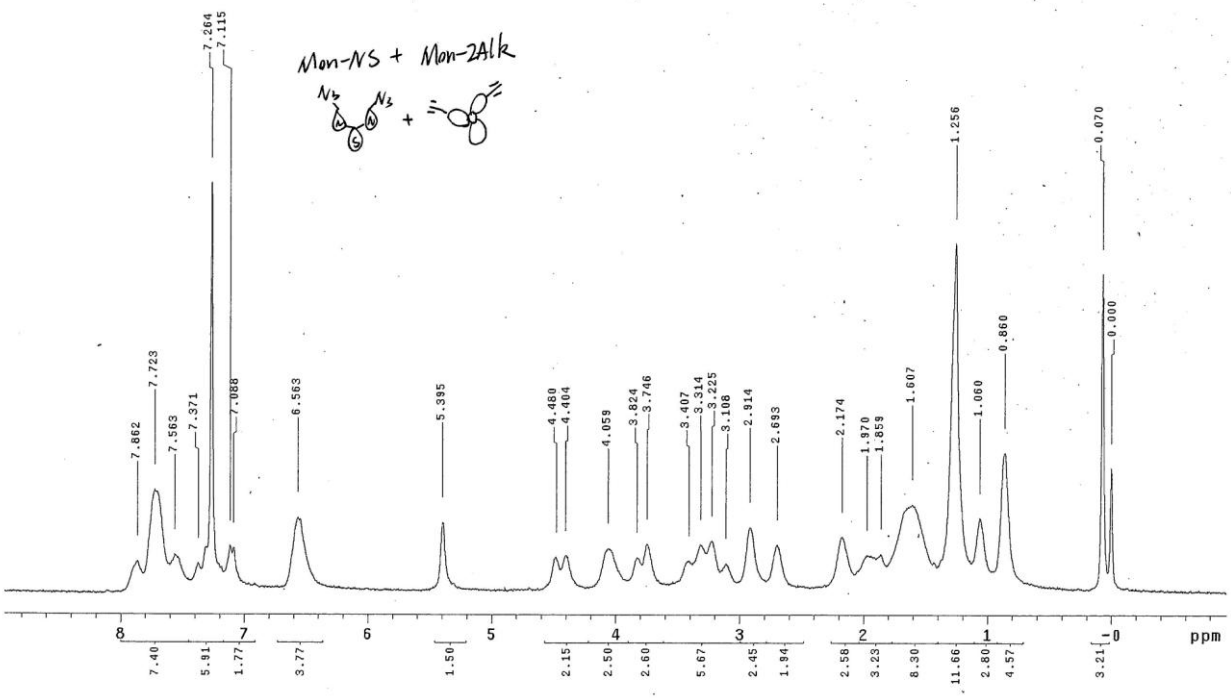


Fig.S27. ^{1}H NMR spectrum of **LineD-NS** in chloroform-*d*.

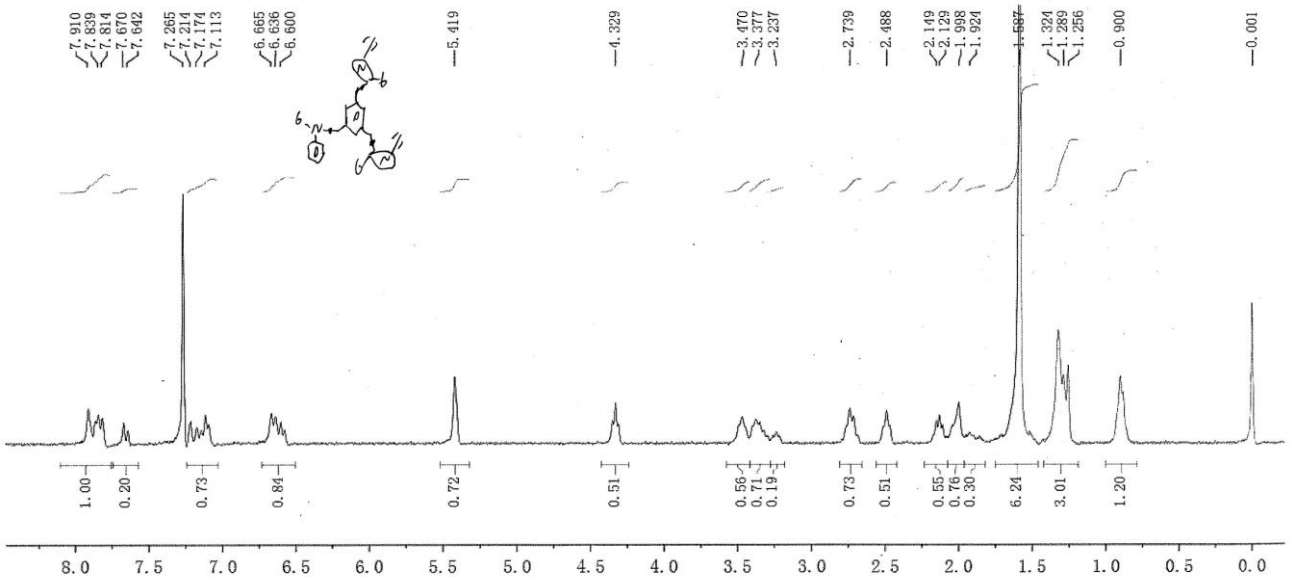


Fig.S28. ^{1}H NMR spectrum of **Mon-2Alk** in chloroform-*d*.

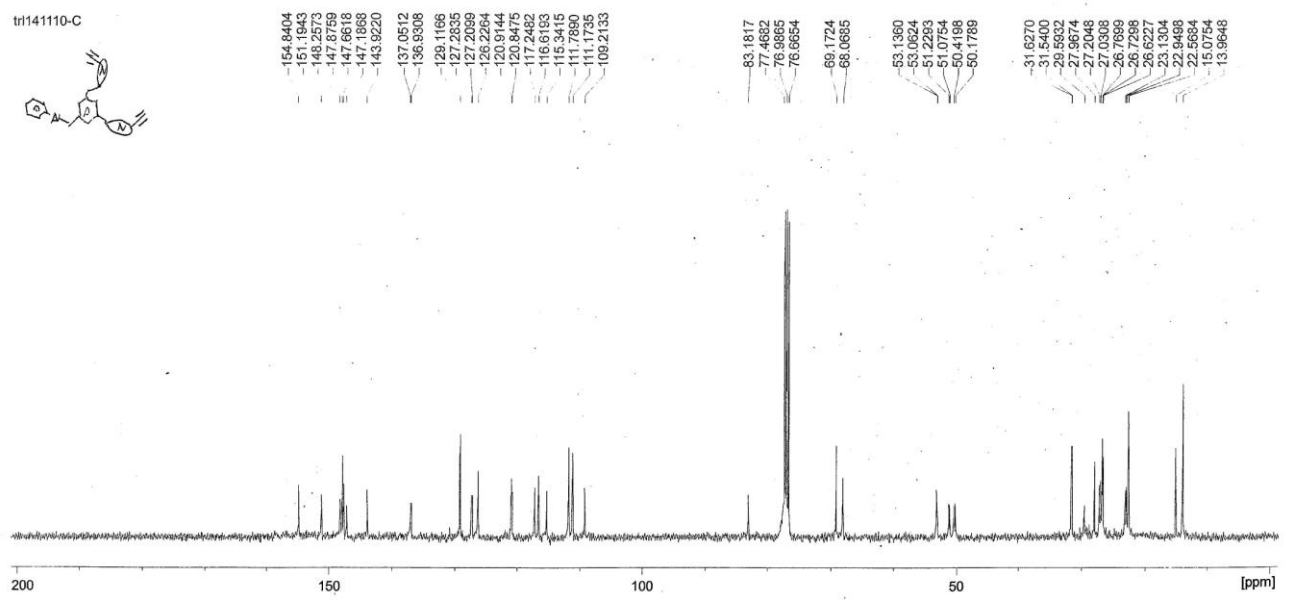


Fig.S29. ^{13}C NMR spectrum of **Mon-2Alk** in chloroform-*d*.

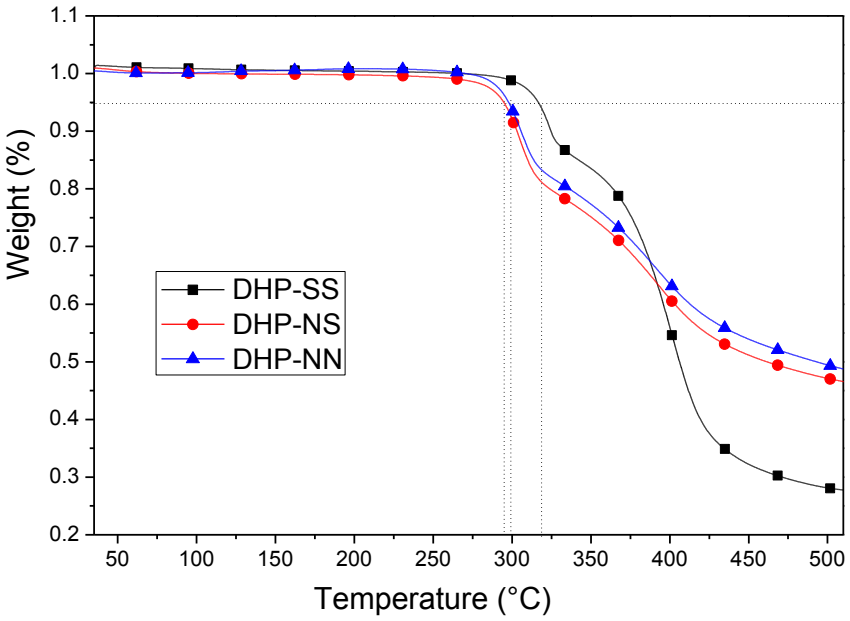


Fig. S30. TGA thermograms of **HDPs** measured in nitrogen at a heating rate of 10 ℃/min.

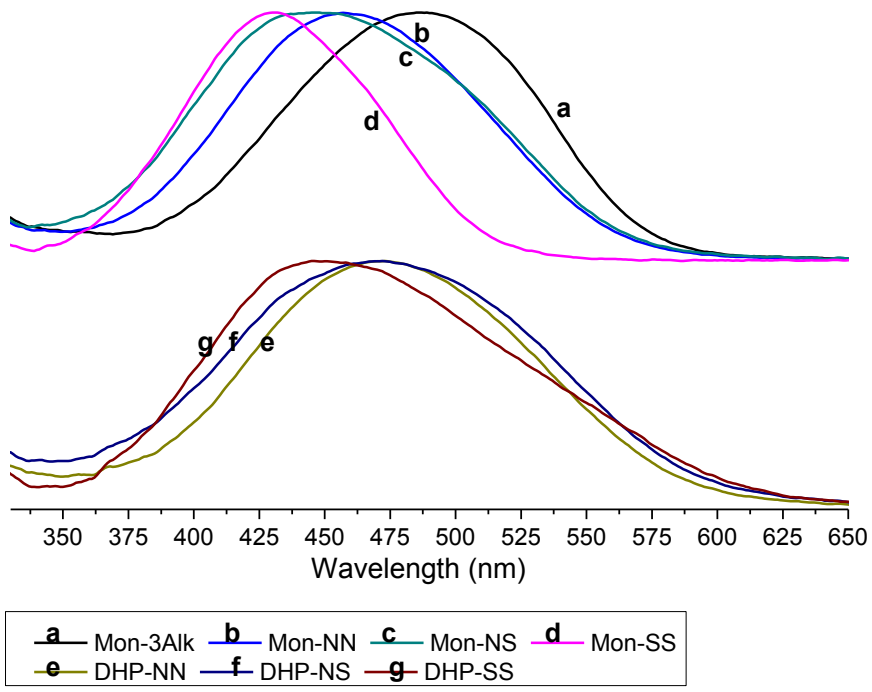


Fig. S31. UV-vis absorption spectra of monomers and polymers in 1,4-dioxane.

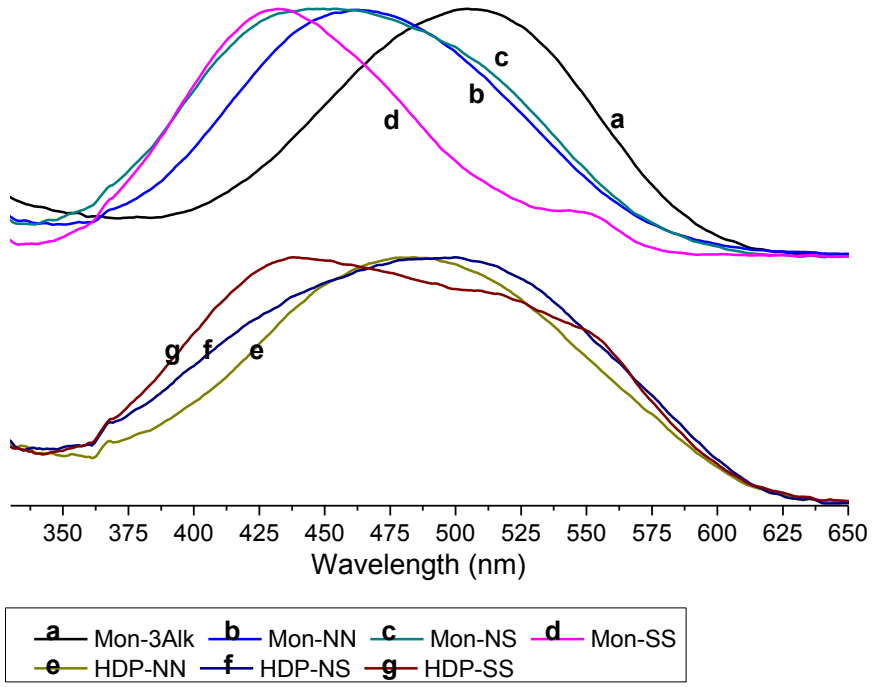


Fig. S32. UV-vis absorption spectra of monomers and polymers in CH_2Cl_2.

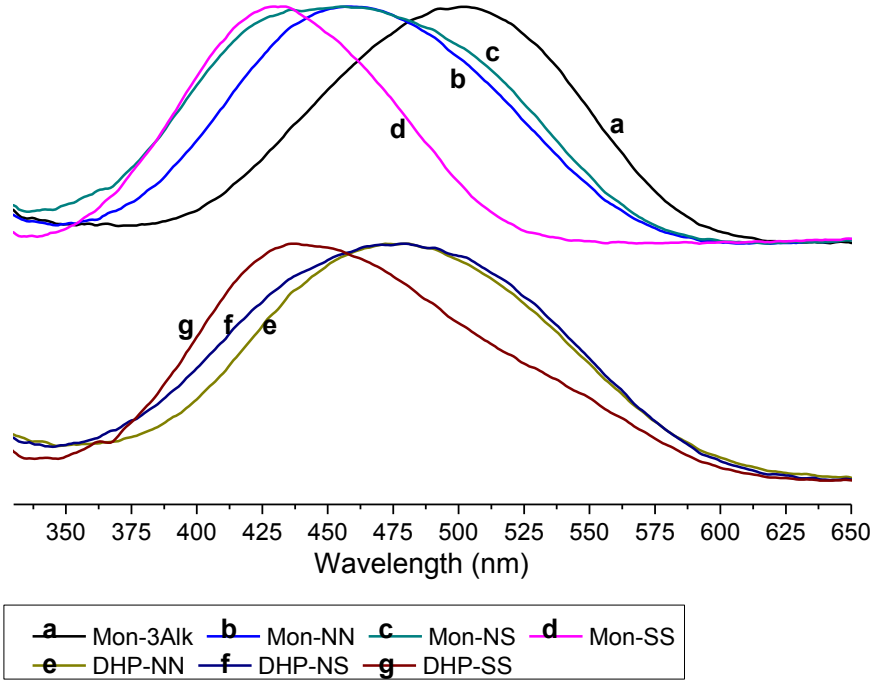


Fig. S33. UV-vis absorption spectra of monomers and polymers in $CHCl_3$.

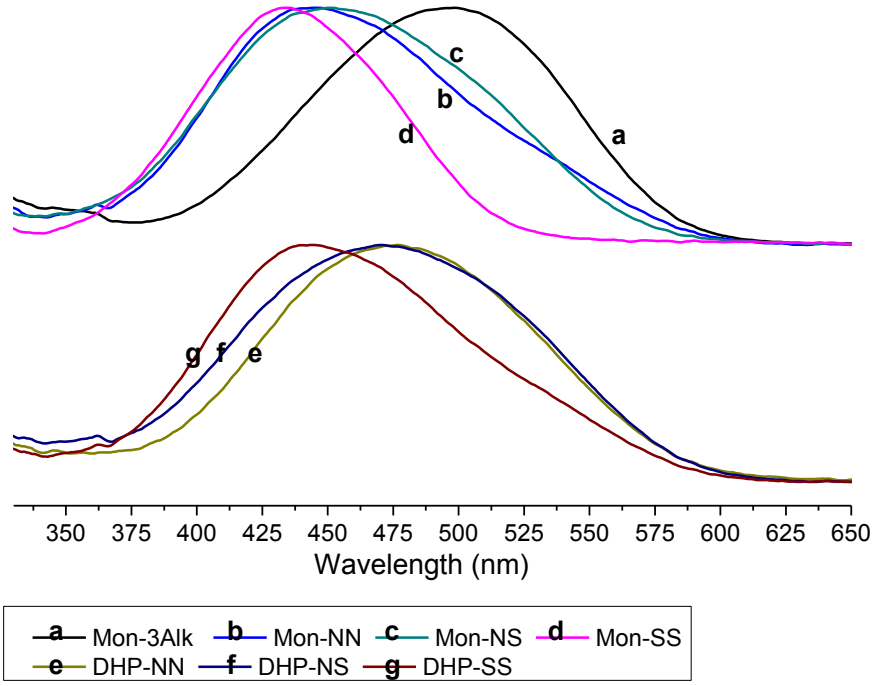


Fig. S34. UV-vis absorption spectra of monomers and polymers in THF.

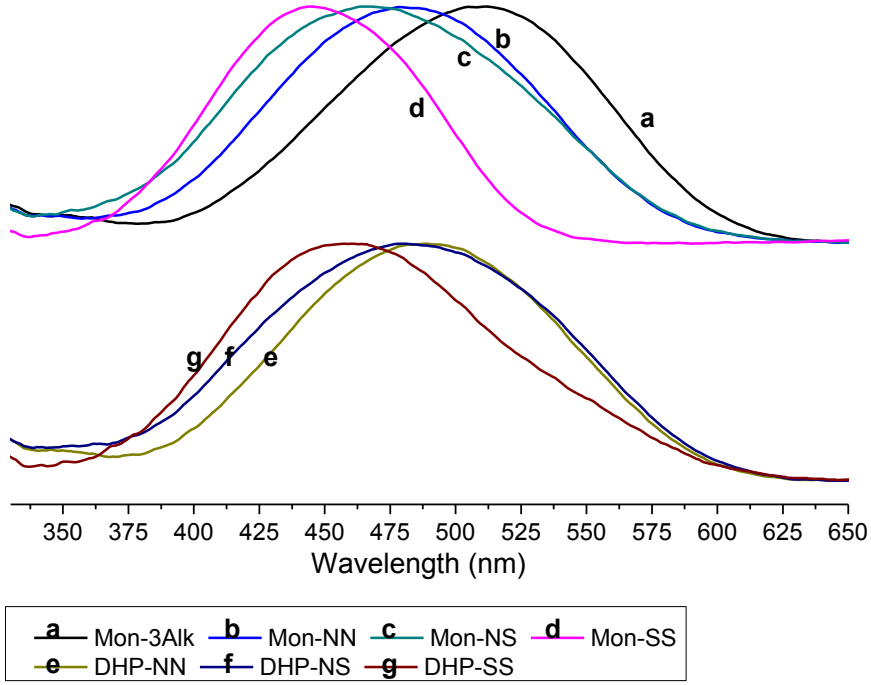


Fig. S35. UV-vis absorption spectra of monomers and polymers in DMF.

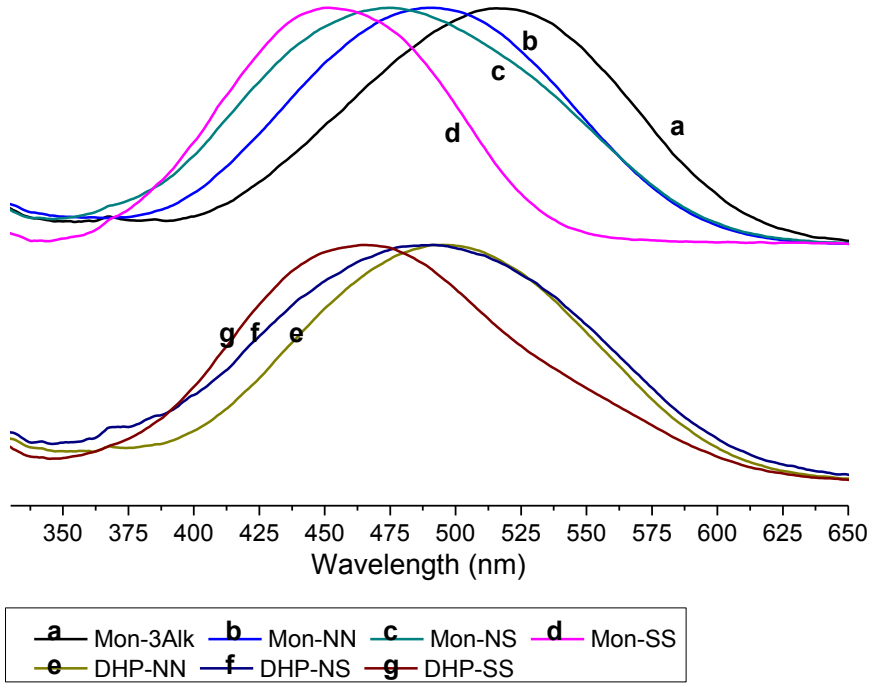


Fig. S36. UV-vis absorption spectra of monomers and polymers in DMSO.

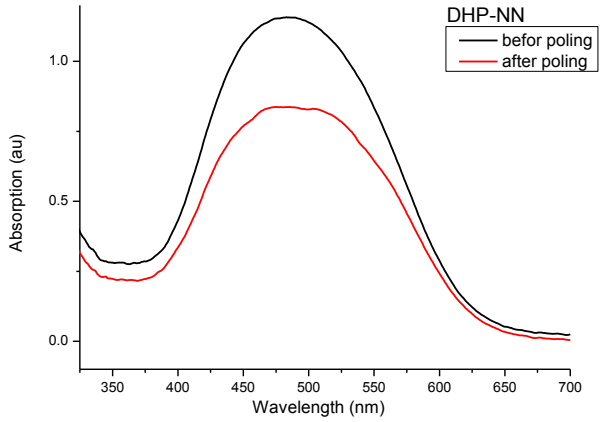


Fig. S37. UV-vis absorption spectra of the film of **DHP-NN** before and after poling.

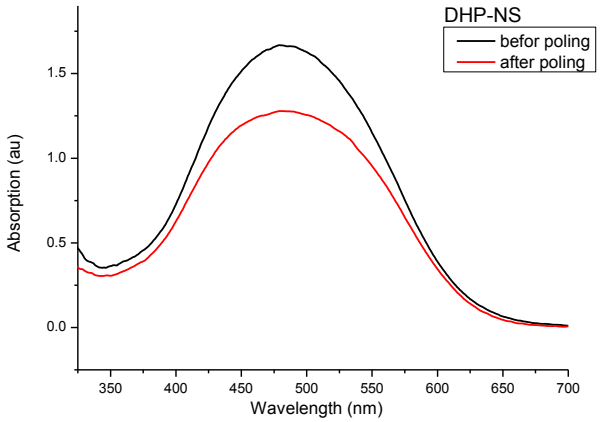


Fig. S38. UV-vis absorption spectra of the film of **DHP-NS** before and after poling.

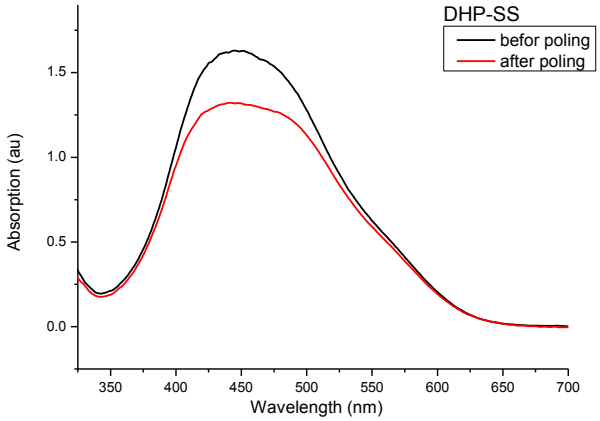


Fig. S39. UV-vis absorption spectra of the film of **DHP-SS** before and after poling.

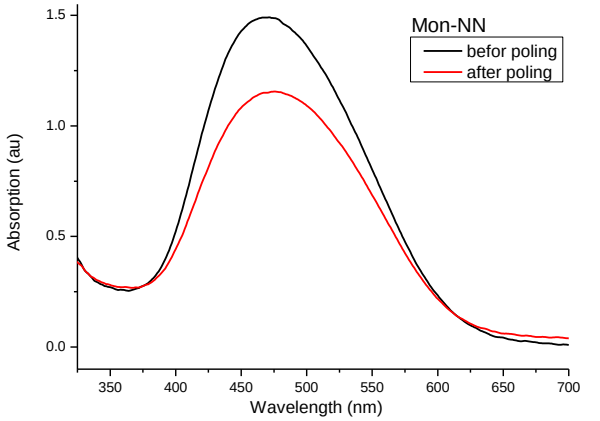


Fig. S40. UV-vis absorption spectra of the film of **Mon-NN** before and after poling.

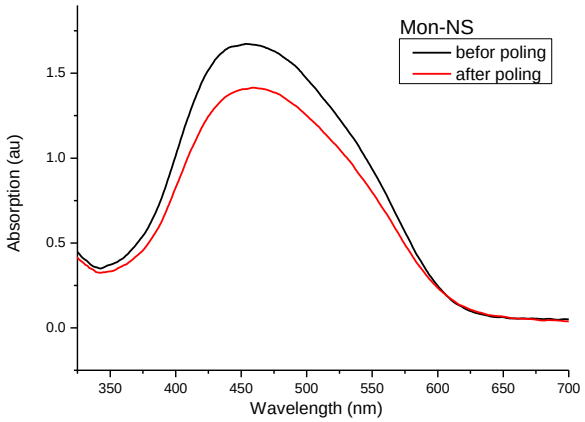


Fig. S41. UV-vis absorption spectra of the film of **Mon-NS** before and after poling.

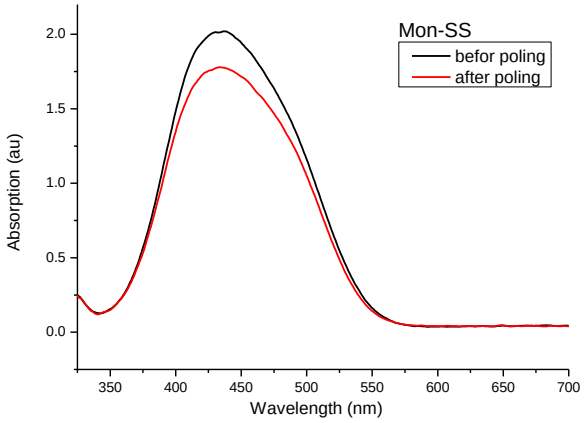


Fig. S42. UV-vis absorption spectra of the film of **Mon-SS** before and after poling.

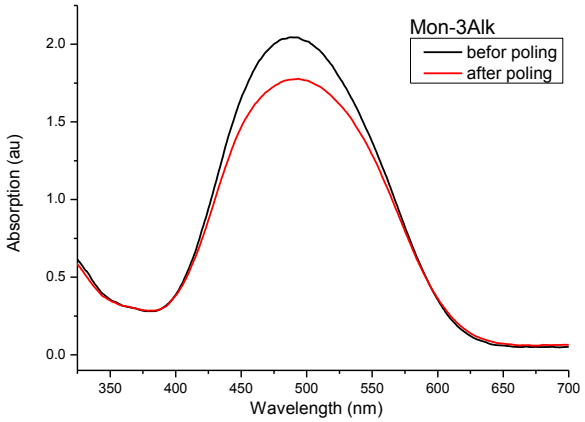


Fig. S43. UV-vis absorption spectra of the film of **Mon-3Alk** before and after poling.

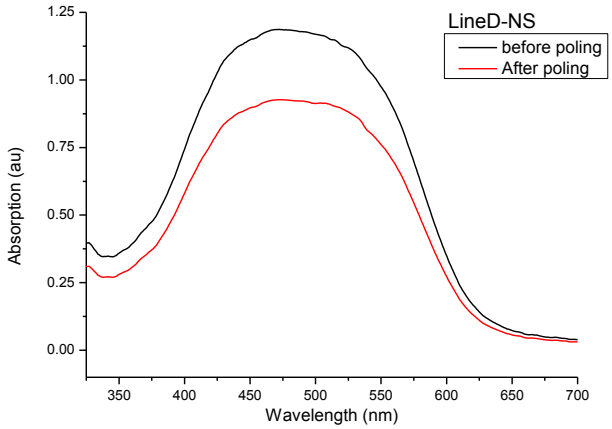


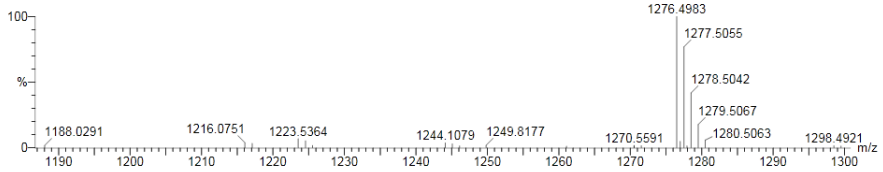
Fig. S44. UV-vis absorption spectra of the film of **LineD-NS** before and after poling.

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 1000.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 8 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 21-21 O: 6-6 S: 3-3

WH-ZHU ECUST institute of Fine Chem 18-Mar-2015 20:42:32
3-TRL-3 110 (0.775) Cm (109:112) 1: TOF MS ES+ 4.15e+003



Minimum:				-1.5			
Maximum:		1000.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1276.4983	1276.5919	-93.6	-73.3	29.5	29.5	0.0	C59 H82 N21 O6 S3

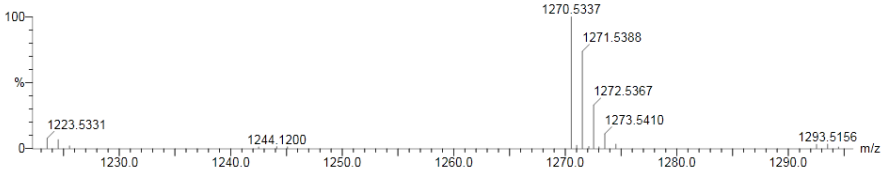
Fig. S45. HRMS report of **Mon-NN**.

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 1000.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
17 formula(e) evaluated with 17 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 23-23 O: 8-8 S: 0-1

WH-ZHU ECUST institute of Fine Chem 18-Mar-2015 20:40:16
2-TRL-2 11 (0.163) Cm (11) 1: TOF MS ES+ 1.99e+003



Minimum:				-1.5			
Maximum:		1000.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1270.5337	1270.6281	-94.4	-74.3	31.5	17.3	0.0	C59 H80 N23 O8 S

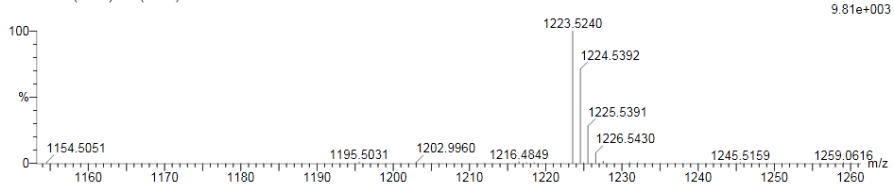
Fig. S46. HRMS report of **Mon-NS**.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 1000.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 9 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 24-24 O: 8-8

WH-ZHU ECUST institute of Fine Chem 18-Mar-2015 20:35:14
1-TRL-1 20 (0.219) Cm (20:22) 1: TOF MS ES+ 9.81e+003



Minimum:				-1.5			
Maximum:		1000.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1223.5240	1223.6200	-96.0	-78.5	32.5	23.2	0.0	C57 H75 N24 O8

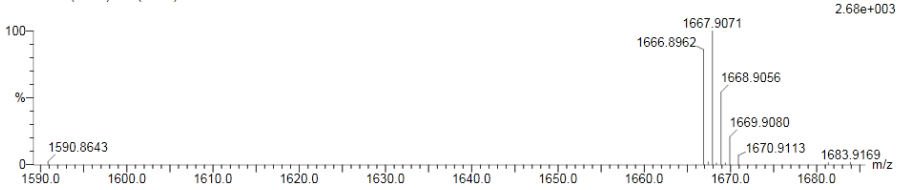
Fig. S47. HRMS report of **Mon-SS**.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 1000.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 5 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 21-21 O: 9-9

WH-ZHU ECUST institute of Fine Chem 18-Mar-2015 20:47:04
4-TRL-4 65 (0.494) Cm (65:67) 1: TOF MS ES+ 2.68e+003



Minimum:				-1.5			
Maximum:		1000.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1666.8962	1666.4257	470.5	282.3	83.5	54.4	0.0	C98 H52 N21 O9

Fig. S48. HRMS report of **Mon-3Alk**.