Electronic supplementary information (ESI)

High Second-Order Nonlinear Optical Effect Achieved by Gradually Decreased Rotational Energy Barriers

Panpan Qiao[a], Wentao Yuan[a], Qianqian Li*[a] and Zhen Li*[a,b]

[a]Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Department of Chemistry, Wuhan University, Wuhan, 430072, China.
E-mail: liqianqian@whu.edu.cn, lizhen@whu.edu.cn.
[b]TaiKang Center for Life and Medical Sciences, Wuhan University, Wuhan, 430072, China.

Contents

1. Additional data and analysis

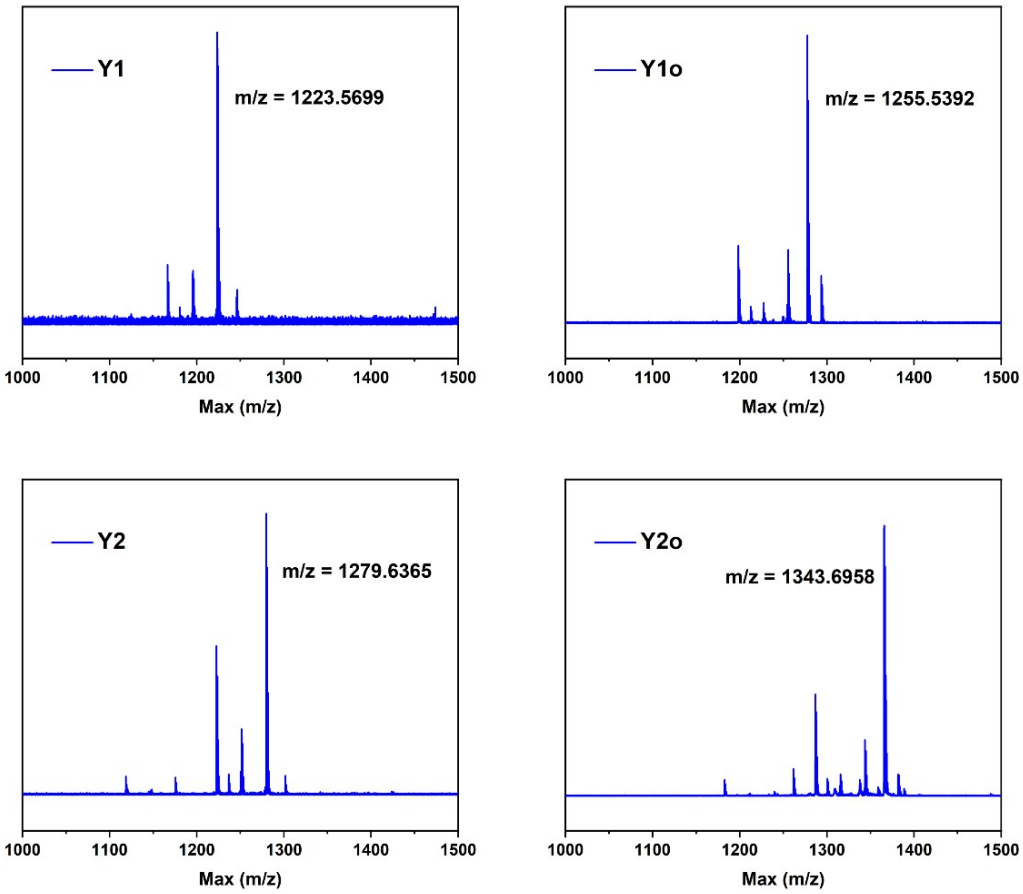


Fig. S1 MALDI-TOF spectra of target monomers.

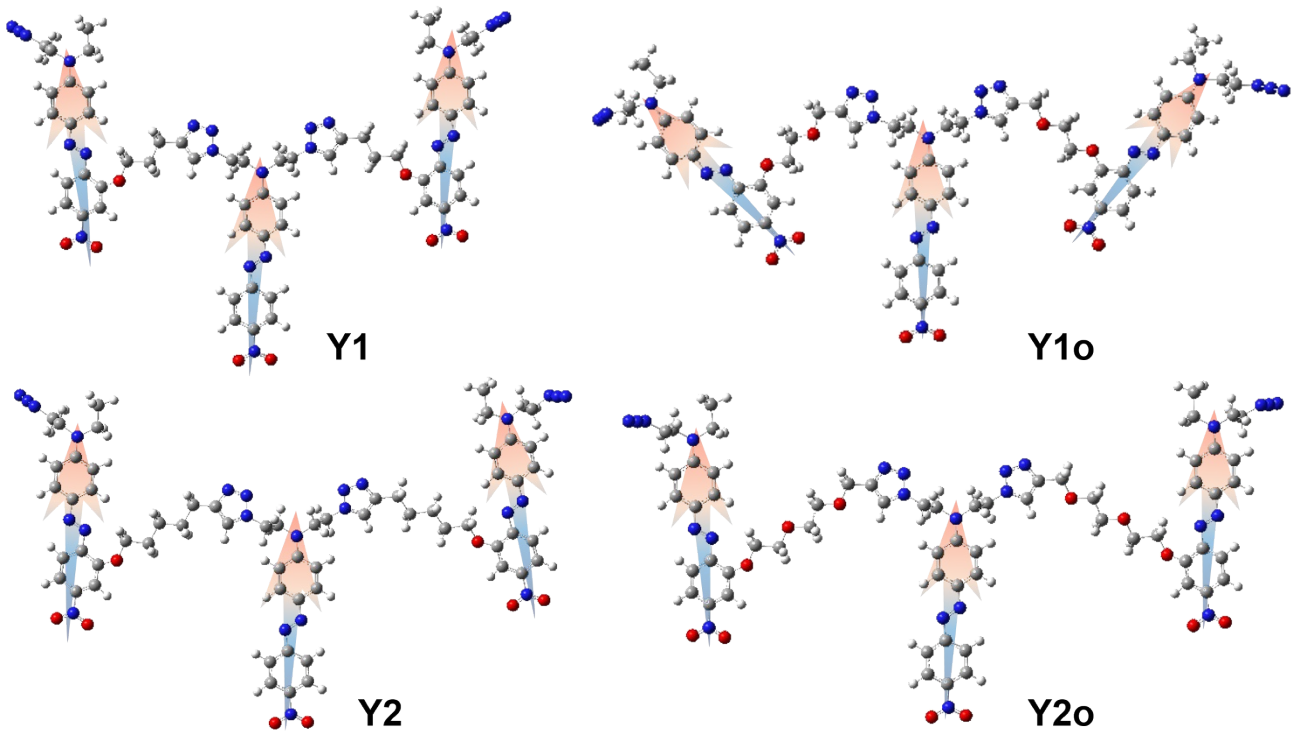


Fig. S2 Molecular conformations of Y-type monomers optimized by Guassian 16 based on M062X functional with 6-31G(d) basis set.

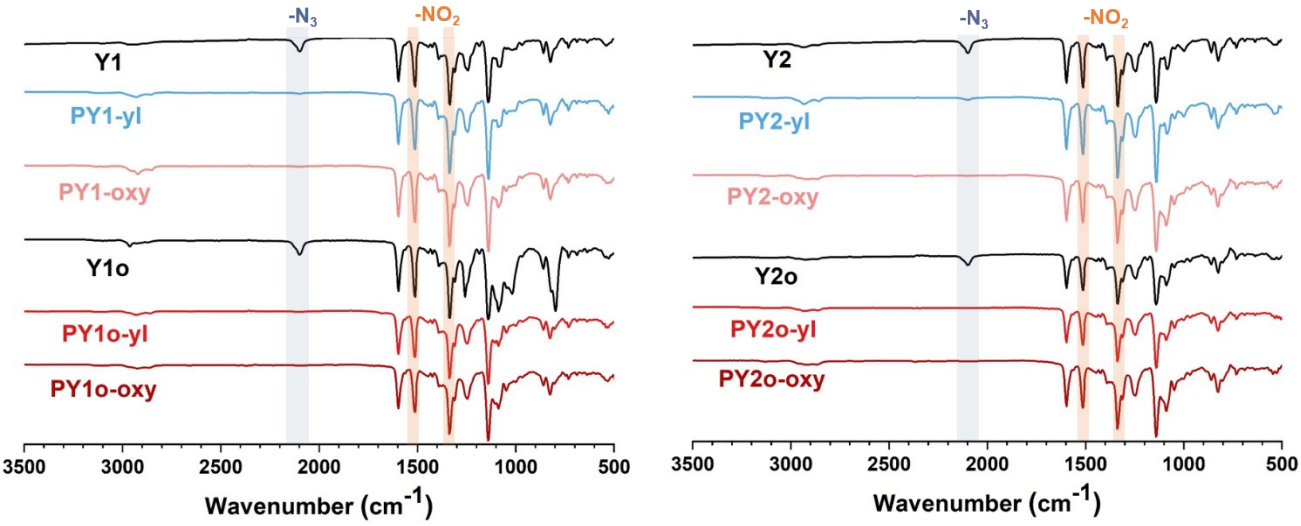
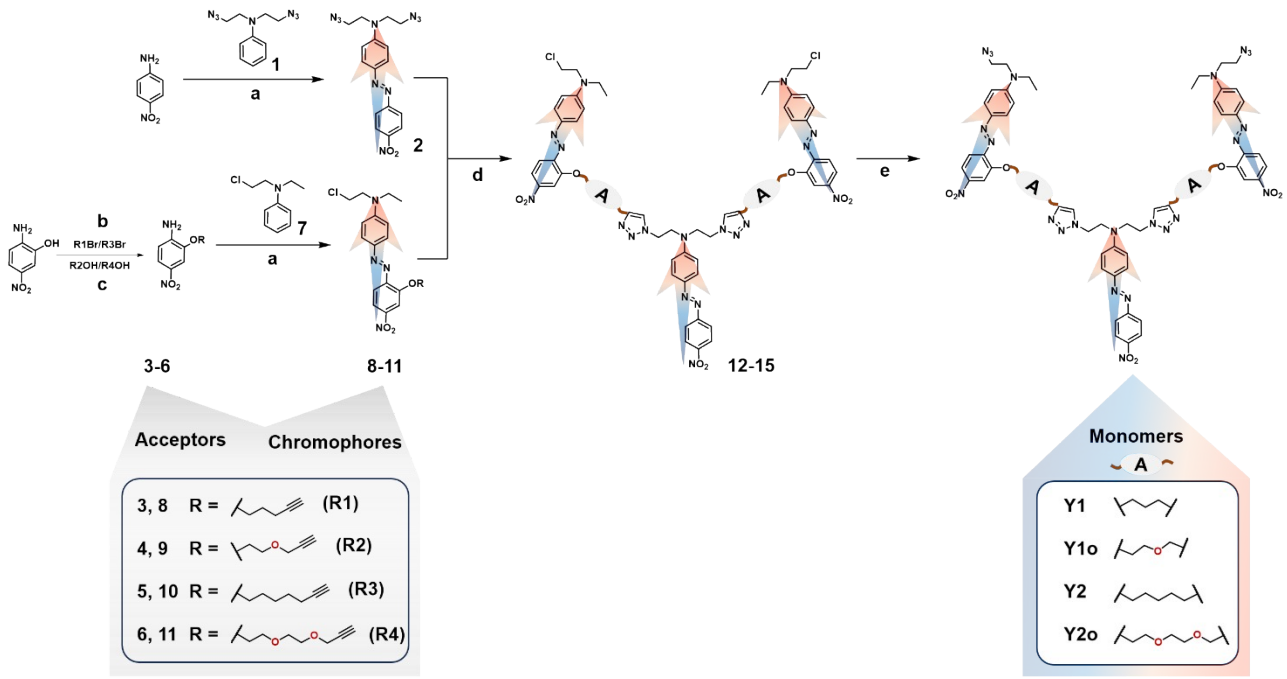


Fig. S3 FTIR-ATR spectra of polymers and their corresponding monomers.



Reaction conditions: a) HCl (38%), $NaNO_2/H_2O$, CH_3CN, 0-5 °C; b) K_2CO_3, DMF, 80 °C; c) DIAD, PPh_3, THF, 30 °C; d) $CuSO_4 \cdot H_2O$, VcNa, THF/H2O, 30 °C; e) NaN_3, DMF, 80 °C; f) $CuSO_4 \cdot H_2O$, VcNa, DMF, 25 °C.

Scheme S1. The synthetic route of monomer **Y1**, **Y1o**, **Y2**, **Y2o**.

2. Synthesis

Compounds **1**, **2**, **3**, **7** and **8** were prepared in our previous work.[1, 2] Compound **5** was synthesized through a simple substitution reaction. Compounds **4** and **6** were synthesized by the classical Mitsunobu reaction. Compounds **9-11** were synthesized by an azo coupling reaction[3, 4] between donor **7** and receptors **4-6** respectively. Products **12-15** were generated by chromophores **2** and **8-11** through "Click chemistry" reaction,[5, 6] and then the corresponding target monomers **Y1**, **Y1o**, **Y2**, and **Y2o** were synthesized by azide reaction.

The general synthetic route of compounds 9-11

The acceptor nitroaniline **4-6** (1.1 eq.) was dissolved in acetonitrile and stirred at 0-5 °C, then the concentrated hydrochloric acid and sodium nitrite (1.2 eq.) dissolved in a small amount of ice water were added dropwise successively. After the reaction mixture was continued to stir at 0-5 °C for 0.5 h, the donor aniline **7** (1.0 eq) was added to the mixture respectively. Sodium bicarbonate was used to adjust the pH to 7 after half an hour. The reaction was then continued for 3-4 hours and monitored by thin-layer chromatography (TLC). After the completion of the reaction, the mixture was poured into

water and extracted with CH_2Cl_2 for three times. The combined organic solution was dried over anhydrous sodium sulfate and condensed via rotary evaporation. The residue was purified by column chromatography on silica gel to give the desired product.

Compound 9: **7** (551 mg, 3.0 mmol), **4** (780 mg, 3.3 mmol), HCl (38%, 66 μL), $NaNO_2$ (248 mg, 3.6 mmol), CH_2Cl_2/petroleum ether = 1/1 as an eluent to yield a red solid (1.28 g, 89.8 %). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K), δ (TMS, ppm): 7.98 (d, J = 2.3 Hz, 1H, -ArH), 7.94-7.87 (m, 1H, -ArH), 7.87-7.78 (m, 2H, -ArH), 7.65 (d, J = 8.8 Hz, 1H, -ArH), 6.93-6.85 (m, 2H, -ArH), 4.48-4.41 (m, 2H, -CH_2-), 4.30 (d, J = 2.4 Hz, 2H, -CH_2-), 3.95-3.89 (m, 2H, -CH_2-), 3.84 (t, J = 7.3 Hz, 2H, -CH_2-), 3.65 (t, J = 7.2 Hz, 2H, -CH_2-), 3.57 (q, J = 6.9 Hz, 2H, -CH_2-), 3.44 (t, J = 2.4 Hz, 1H, -C≡H), 1.17 (t, J = 7.0 Hz, 3H, -CH_3). ^{13}C NMR (101 MHz, DMSO-d_6, 298 K), δ (ppm): 155.15, 151.11, 148.26, 146.76, 144.23, 126.48, 117.54, 117.04, 112.10, 110.12, 80.66, 77.70, 69.82, 67.85, 58.29, 51.69, 45.29, 30.20, 12.72.

Compound 10: **7** (551 mg, 3.0 mmol), **5** (819 mg, 3.3 mmol), HCl (38%, 66 μL), $NaNO_2$ (248mg, 3.6 mmol), CH_2Cl_2/petroleum ether = 1/1 as an eluent to yield a red solid (1.13 g, 85.1 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 7.94-7.83 (m, 4H, -ArH), 7.66 (d, J = 8.5 Hz, 1H, -ArH), 6.76 (d, J = 9.2 Hz, 2H, -ArH), 4.23 (t, J = 6.4 Hz, 2H, -CH_2-), 3.78-3.71 (m, 2H, -CH_2-), 3.70-3.63 (m, 2H, -CH_2-), 3.55 (q, J = 7.1 Hz, 2H, -CH_2-), 2.29-2.20 (m, 2H, -CH_2-), 1.97 (t, J = 5.3 Hz, 1H, -C≡H), 1.95-1.88 (m, 2H, -CH_2-), 1.70-1.63 (m, 4H, -CH_2-), 1.26 (t, J = 7.1 Hz, 3H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K), δ (ppm): 155.30, 150.38, 148.32, 147.03, 144.70, 126.32, 117.39, 116.45, 111.36, 109.16, 84.33, 69.86, 68.50, 52.27, 45.93, 40.17, 28.55, 28.15, 25.22, 18.40, 12.57.

Compound 11: **7** (551 mg, 3.0 mmol), **6** (925 mg, 3.3 mmol), HCl (38%, 66 μL), $NaNO_2$ (248mg, 3.6 mmol), CH_2Cl_2/petroleum ether = 1/2 as an eluent to yield red solid (1.25 g, 88.0 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 7.95 (d, J = 2.3 Hz, 1H, -ArH), 7.93-7.85 (m, 3H, -ArH), 7.67 (d, J = 8.8 Hz, 1H, -ArH), 6.80-6.71 (m, 2H, -ArH), 4.45-4.38 (m, 2H, -CH_2-), 4.19 (d, J = 2.3 Hz, 2H, -CH_2-), 4.03-3.96 (m, 2H, -CH_2-), 3.86-3.80 (m, 2H, -CH_2-), 3.77-3.69 (m, 4H, -CH_2-), 3.71-3.62 (m, 2H, -CH_2-), 3.55 (q, J = 7.1 Hz, 2H, -CH_2-), 2.42 (t, J = 2.3 Hz, 1H, -C≡H), 1.26 (t, J = 7.1 Hz, 3H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K), δ (ppm): 155.17, 150.42, 148.26, 147.14, 144.68, 126.37, 117.49, 116.90, 111.36, 110.01, 79.65, 74.59, 70.95, 70.15, 69.60, 69.21, 58.46, 52.26, 45.93, 40.15,

12.56.

The general synthetic route of compounds 12-15

Chromophore **2** (1.00 eq), chromophores **8-11** (2.20 eq), $CuSO_4 \cdot 5H_2O$ (0.20 eq), and VcNa (0.40 eq) were added to a Schlenk tube under an argon atmosphere. Degassed THF/H_2O (v/v = 5/1) were added and reacted for about 12 hours at 30 °C. The mixture was poured into water and extracted with CH_2Cl_2 for three times. The combined organic solution was dried over anhydrous sodium sulfate and condensed via rotary evaporation. The residue was purified by column chromatography on silica gel to give the product.

Compound 12: Chromophore **2** (190 mg, 0.50 mmol), chromophores **8** (500 mg, 1.10 mmol), $CuSO_4 \cdot 5H_2O$ (25 mg, 0.10 mmol) and VcNa (40 mg, 0.20 mmol). CH_2Cl_2/EtOAc = 5/1 as an eluent to yield deep red solid. (625 mg, 96.3 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 8.28-8.18 (m, 2H, -ArH), 7.88-7.78 (m, 8H, -ArH), 7.79-7.70 (m, 4H, -ArH), 7.25 (s, 2H, -ArH), 6.72 (d, J = 9.2 Hz, 4H, -ArH), 6.54 (d, J = 9.2 Hz, 2H, -ArH), 4.38 (t, J = 5.9 Hz, 4H, -CH_2-), 4.12 (t, J = 6.3 Hz, 4H, -CH_2-), 3.84-3.66 (m, 8H, -CH_2-), 3.63-3.35 (m, 8H, -CH_2-), 2.95 (t, J = 7.1 Hz, 4H, -CH_2-), 2.23 (p, J = 6.6 Hz, 4H, -CH_2-), 1.24 (t, J = 7.0 Hz, 6H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K), δ (ppm): 156.10, 155.06, 150.28, 149.45, 148.19, 147.78, 147.22, 146.96, 144.72, 144.62, 126.34, 126.09, 124.65, 122.91, 122.39, 117.43, 116.58, 111.72, 111.38, 109.26, 68.57, 53.47, 52.29, 51.26, 47.30, 45.77, 28.39, 27.79, 21.85, 12.67.

Compound 13: Chromophore **2** (133 mg, 0.35 mmol), chromophores **9** (377 mg, 0.77 mmol), $CuSO_4 \cdot 5H_2O$ (17.5 mg, 0.07 mmol) and VcNa (28 mg, 0.14 mmol), CH_2Cl_2/EtOAc = 4/1 as an eluent to yield deep red solid (405 mg, 86.9 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 8.28-8.23 (m, 2H, -ArH), 7.89 (d, J = 2.3 Hz, 2H, -ArH), 7.87-7.79 (m, 8H, -ArH), 7.72 (d, J = 9.0 Hz, 2H, -ArH), 7.61 (d, J = 8.8 Hz, 2H, -ArH), 7.55 (s, 2H, -ArH), 6.70 (d, J = 9.2 Hz, 4H, -ArH), 6.54 (d, J = 9.1 Hz, 2H, -ArH), 4.76 (s, 4H, -CH_2-), 4.38-4.33 (m, 4H, -CH_2-), 4.30 (t, J = 6.0 Hz, 4H, -CH_2-), 3.92-3.86 (m, 4H, -CH_2-), 3.76 (t, J = 7.6 Hz, 4H, -CH_2-), 3.66 (t, J = 6.0 Hz, 4H, -CH_2-), 3.54-3.43 (m, 8H, -CH_2-), 1.22 (t, J = 7.1 Hz, 6H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K), δ (ppm): 156.10, 155.22, 150.35, 149.30, 148.10, 147.80, 147.08, 145.60, 144.66, 144.57, 126.42, 126.13, 124.69, 123.66, 122.89, 117.48, 116.99, 111.66, 111.38, 110.38, 70.08, 68.86, 65.07, 52.24, 51.03, 47.12, 45.77, 27.84,

12.66.

Compound 14: Chromophore **2** (228 mg, 0.60 mmol), chromophores **10** (585 mg, 1.20 mmol), $CuSO_4 \cdot 5H_2O$ (30 mg, 0.12 mmol) and VcNa (48 mg, 0.24 mmol), petroleum ether/EtOAc = 1/4 as an eluent to yield deep red solid (760 mg, 94.7 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 8.25-8.20 (m, 2H, -ArH), 7.87-7.78 (m, 12H, -ArH), 7.66-7.61 (m, 2H, -ArH), 7.18 (s, 2H, -ArH), 6.73 (d, J = 9.3 Hz, 4H, -ArH), 6.60 (d, J = 9.2 Hz, 2H, -ArH), 4.34 (t, J = 6.0 Hz, 4H, -CH_2-), 4.14 (t, J = 6.4 Hz, 4H, -CH_2-), 3.77-3.62 (m, 12H, -CH_2-), 3.52 (q, J = 7.1 Hz, 4H, -CH_2-), 2.71 (t, J = 7.5 Hz, 4H, -CH_2-), 1.90 (p, J = 6.8 Hz, 4H, -CH_2-), 1.71 (p, J = 7.6 Hz, 4H, -CH_2-), 1.53 (p, J = 7.9, 7.3 Hz, 4H, -CH_2-), 1.23 (t, J = 7.1 Hz, 6H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K), δ (ppm): 156.14, 155.28, 150.46, 149.42, 148.38, 148.24, 147.76, 146.90, 144.70, 144.59, 126.29, 126.16, 124.67, 122.86, 121.89, 117.33, 116.42, 111.74, 111.41, 109.15, 69.82, 52.22, 51.28, 47.14, 45.93, 40.25, 29.10, 28.65, 25.53, 25.44, 12.55.

Compound 15: Chromophore **2** (228 mg, 0.60 mmol), chromophores **11** (627 mg, 1.20 mmol), $CuSO_4 \cdot 5H_2O$ (30 mg, 0.12 mmol) and VcNa (48 mg, 0.24 mmol), CH_2Cl_2/EtOAc = 1/1 as an eluent to yield deep red solid (680 mg, 85.4 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 8.28-8.24 (m, 2H, -ArH), 7.90-7.86 (m, 4H, -ArH), 7.86-7.75 (m, 8H, -ArH), 7.62 (d, J = 8.8 Hz, 2H, -ArH), 7.52 (s, 2H, -ArH), 6.70 (d, J = 9.2 Hz, 4H, -ArH), 6.64 (d, J = 9.2 Hz, 2H, -ArH), 4.63 (s, 4H, -CH_2-), 4.41-4.32 (m, 8H, -CH_2-), 3.93-3.89 (m, 4H, -CH_2-), 3.75-3.62 (m, 20H, -CH_2-), 3.51 (q, J = 7.1 Hz, 4H, -CH_2-), 1.22 (t, J = 7.1 Hz, 6H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K), δ (ppm): 156.18, 155.14, 150.55, 149.25, 148.12, 147.78, 147.09, 145.48, 144.71, 144.50, 126.35, 126.17, 124.68, 123.78, 122.91, 117.47, 116.92, 111.83, 111.37, 110.22, 70.98, 70.16, 69.77, 69.63, 64.57, 52.20, 51.27, 47.13, 45.93, 40.25, 12.53.

The general synthetic route of target monomers Y1, **Y1o**, **Y2**, **Y2o**[7]

To a mixture solution of compounds **12-15** (1.0 eq.) and NaN_3 (0.5 eq.) dissolved in *N,N*-dimethylformamide and reacted at 80 ^{o}C for 5-6 h. The mixture was poured into water and extracted with EtOAc for several times. The combined organic solution was dried over anhydrous sodium sulfate and condensed via rotary evaporation. The residue was purified by column chromatography on silica gel to give the product.

Monomer Y1: Compound **12** (548 mg, 0.42 mmol), NaN_3 (60 mg, 0.92 mmol), CH_2Cl_2/EtOAc = 2/1 as an eluent to yield deep red solid (500 mg, 59.0 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 8.29-8.21 (m, 2H, -ArH), 7.85 (d, J = 9.0 Hz, 6H, -ArH), 7.81 (t, J = 2.2 Hz, 2H, -ArH), 7.78-7.71 (m, 4H, -ArH), 7.62 (d, J = 8.8 Hz, 2H, -ArH), 7.25 (d, J =2.5 Hz, 2H, -ArH), 6.75 (d, J = 9.1 Hz, 4H, -ArH), 6.54 (d, J = 9.1 Hz, 2H, -ArH), 4.38 (t, J = 5.8 Hz, 4H, -CH_2-), 4.13 (t, J = 6.2 Hz, 4H, -CH_2-), 3.73 (t, J = 5.8 Hz, 4H, -CH_2-), 3.60 (t, J = 5.9 Hz, 4H, -CH_2-), 3.57-3.50 (m, 8H, -CH_2-), 2.96 (t, J = 7.1 Hz, 4H, -CH_2-), 2.28-2.18 (m, 4H, -CH_2-), 1.24 (t, J = 6.9 Hz, 6H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K), δ (ppm): 156.11, 155.03, 150.67, 149.46, 148.15, 147.81, 147.23, 147.02, 144.74, 144.55, 126.29, 126.08, 124.65, 122.91, 122.39, 117.43, 116.60, 111.71, 111.52, 109.27, 68.58, 51.25, 49.55, 48.95, 47.29, 45.88, 28.37, 21.86, 12.29. MS (MALDI-TOF, m/z): $[M + H]^+$ calcd for $C_{58}H_{62}N_{24}O_8$: 1223.5216, found 1223.5966. (EA) (%, found/Calcd): C, 56.95/56.37; H, 5.11/5.14; N, 27.48/26.97; O, 10.46/10.81.

Monomer Y1o: Compound **13** (373 mg, 0.28 mmol), NaN_3 (91 mg, 1.4 mmol), petroleum ether/EtOAc = 1/2 as an eluent to yield deep red solid (300 mg, 85.7 %).^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 8.23 (d, J = 8.7 Hz, 2H, -ArH), 7.87 (d, J = 1.9 Hz, 2H, -ArH), 7.84-7.77 (m, 8H, -ArH), 7.69 (d, J = 8.6 Hz, 2H, -ArH), 7.59 (d, J = 8.8 Hz, 2H, -ArH), 7.56 (s, 2H, -ArH), 6.72 (d, J = 8.8 Hz, 4H, -ArH), 6.51 (d, J = 8.7 Hz, 2H, -ArH), 4.76 (s, 4H, -CH_2-), 4.36-4.31 (m, 4H, -CH_2-), 4.29 (t, J = 5.8 Hz, 4H, -CH_2-), 3.90-3.84 (m, 4H, -CH_2-), 3.64 (t, J = 5.6 Hz, 4H, -CH_2-), 3.59-3.55 (m, 4H, -CH_2-), 3.54-3.47 (m, 8H, -CH_2-), 1.21 (t, J = 7.0 Hz, 6H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K), δ (ppm): 156.08, 155.16, 150.76, 149.34, 148.04, 147.74, 147.09, 145.56, 144.60, 144.47, 126.37, 126.11, 124.67, 123.72, 122.87, 117.46, 116.97, 111.63, 111.51, 110.27, 70.04, 68.77, 65.05, 50.95, 49.53, 48.94, 47.08, 45.85, 12.28. MS (MALDI-TOF, m/z): $[M + H]^+$ calcd for $C_{58}H_{62}N_{24}O_{10}$: 1255.5114, found 1255.5392. (EA) (%, found/Calcd): C, 55.90/55.56; H, 5.08/5.32; N, 26.88/26.82; O, 12.15/11.56.

Monomer Y2: Compound **14** (373 mg, 0.28 mmol), NaN_3 (91 mg, 1.4 mmol), CH_2Cl_2/EtOAc = 1/1 as an eluent to yield deep red solid (300 mg, 85.7 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 8.26-8.21 (m, 2H, -ArH), 7.88-7.78 (m, 12H, -ArH), 7.67-7.62 (m, 2H, -ArH), 7.20 (s, 2H, -ArH), 6.76 (d, J = 9.2 Hz, 4H, -ArH), 6.60 (d, J = 9.2 Hz, 4H,), 4.35 (t, J = 6.0 Hz, 4H, -CH_2-), 4.15

(t, J = 6.4 Hz, 4H, -CH_2-), 3.70 (t, J = 6.0 Hz, 4H, -CH_2-), 3.63 – 3.58 (m, 4H, -CH_2-), 3.57-3.51 (m, 8H, -CH_2-), 2.72 (t, J = 7.5 Hz, 4H, -CH_2-), 1.91 (p, J = 6.8 Hz, 4H, -CH_2-), 1.72 (p, J = 7.6 Hz, 4H, -CH_2-), 1.60-1.50 (m, 4, -CH_2-), 1.24 (t, J = 7.0 Hz, 6H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K), δ (ppm): 156.12, 155.27, 150.66, 149.46, 148.36, 148.18, 147.70, 146.93, 144.65, 144.53, 126.26, 126.14, 124.64, 122.85, 121.92, 117.30, 116.41, 111.72, 111.52, 109.16, 69.83, 51.25, 49.54, 48.96, 47.12, 45.87, 29.10, 28.66, 25.54, 25.45, 12.30. MS (MALDI-TOF, m/z): $[M + H]^+$ calcd for $C_{62}H_{70}N_{24}O_8$: 1279.5842, found 1279.6365. (EA) (%, found/Calcd): C, 58.21/57.40; H, 5.52/5.61; N, 26.28/25.95; O, 10.00/10.30.

Monomer Y2o: Compound **15** (464 mg, 0.35 mmol), NaN_3 (68 mg, 3.0 mmol), CH_2Cl_2/EtOAc = 2/1 as an eluent to yield deep red solid (437 mg, 93.2 %).^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 8.31-8.23 (m, 2H, -ArH), 7.92-7.86 (m, 4H, -ArH), 7.84-7.77 (m, 8H, -ArH), 7.62 (d, J = 8.8 Hz, 2H, -ArH), 7.51 (s, 2H, -ArH), 6.74-6.69 (m, 4H, -ArH), 6.64 (d, J = 9.1 Hz, 2H, -ArH), 4.64 (s, 4H, -CH_2-), 4.39-4.31 (m, 8H, -CH_2-), 3.93-3.89 (m, 4H, -CH_2-), 3.76-3.72 (m, 4H, -CH_2-), 3.68 (t, J = 6.1 Hz, 4H, -CH_2-), 3.66-3.62 (m, 4H, -CH_2-), 3.61-3.56 (m, 4H, -CH_2-), 3.56-3.49 (m, 8H, -CH_2-), 1.23 (t, J = 7.1 Hz, 6H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K), δ (ppm): 156.19, 155.12, 150.74, 149.25, 148.09, 147.79, 147.14, 145.50, 144.72, 144.47, 126.33, 126.17, 124.68, 123.78, 122.91, 117.47, 116.94, 111.83, 111.48, 110.22, 70.99, 70.18, 69.77, 69.63, 64.57, 51.26, 49.54, 48.96, 47.12, 45.87, 12.29. MS (MALDI-TOF, m/z): $[M + H]^+$ calcd for $C_{62}H_{70}N_{24}O_{12}$: 1343.5639, found 1343.6958. (EA) (%, found/Calcd): C, 55.43/54.55; H, 5.25/5.25; N, 25.02/24.55; O, 14.29/14.79.

3. NMR spectra

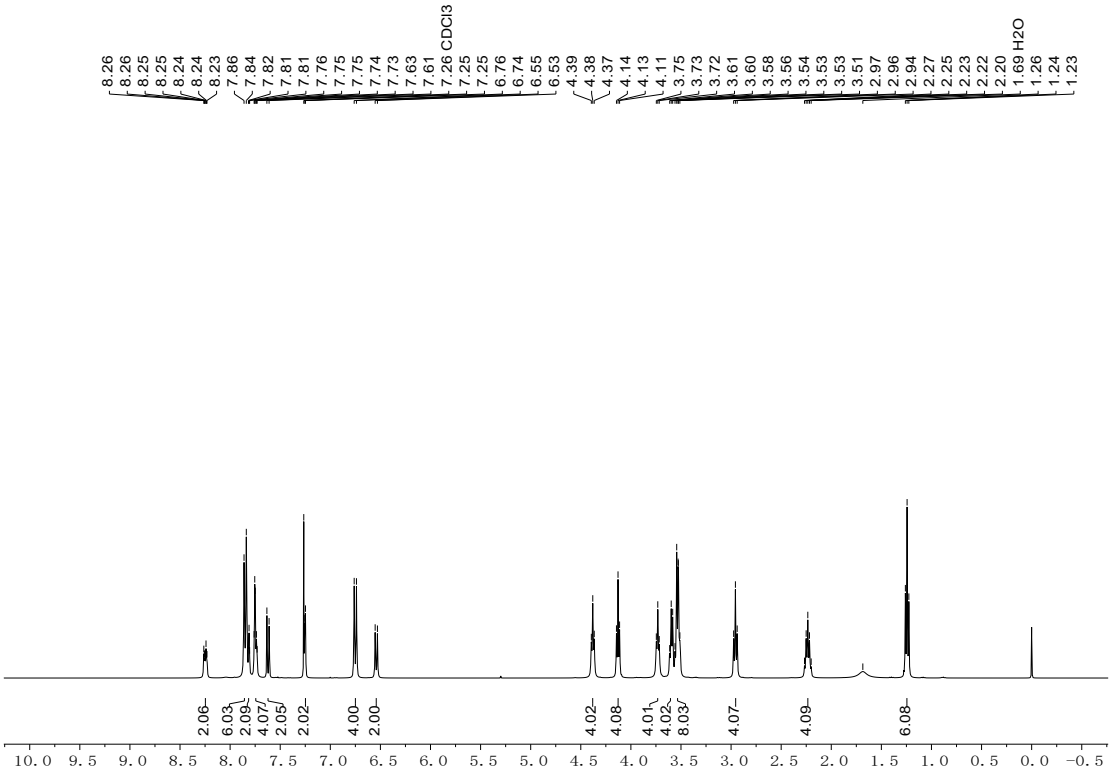


Fig. S4 The ^{1}H NMR spectrum of **Y1** in $CDCl_3$.

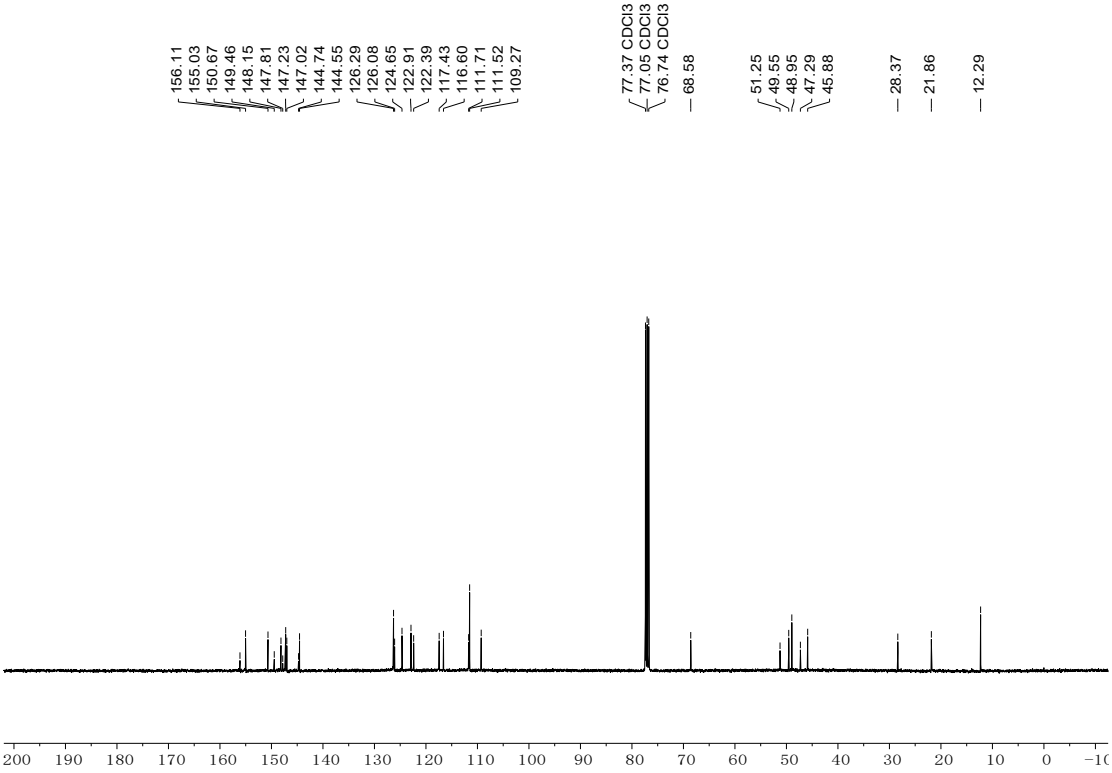


Fig. S5 The ^{13}C NMR spectrum of **Y1** in $CDCl_3$.

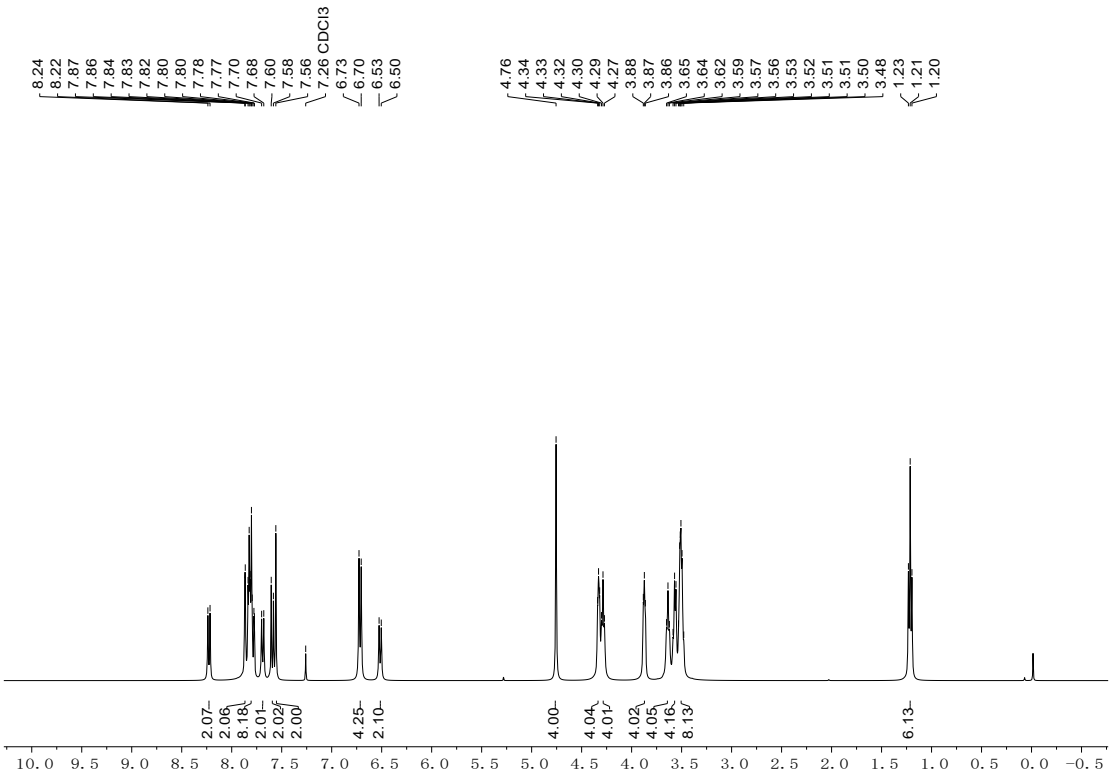


Fig. S6 The ^{1}H NMR spectrum of **Y1o** in $CDCl_3$.

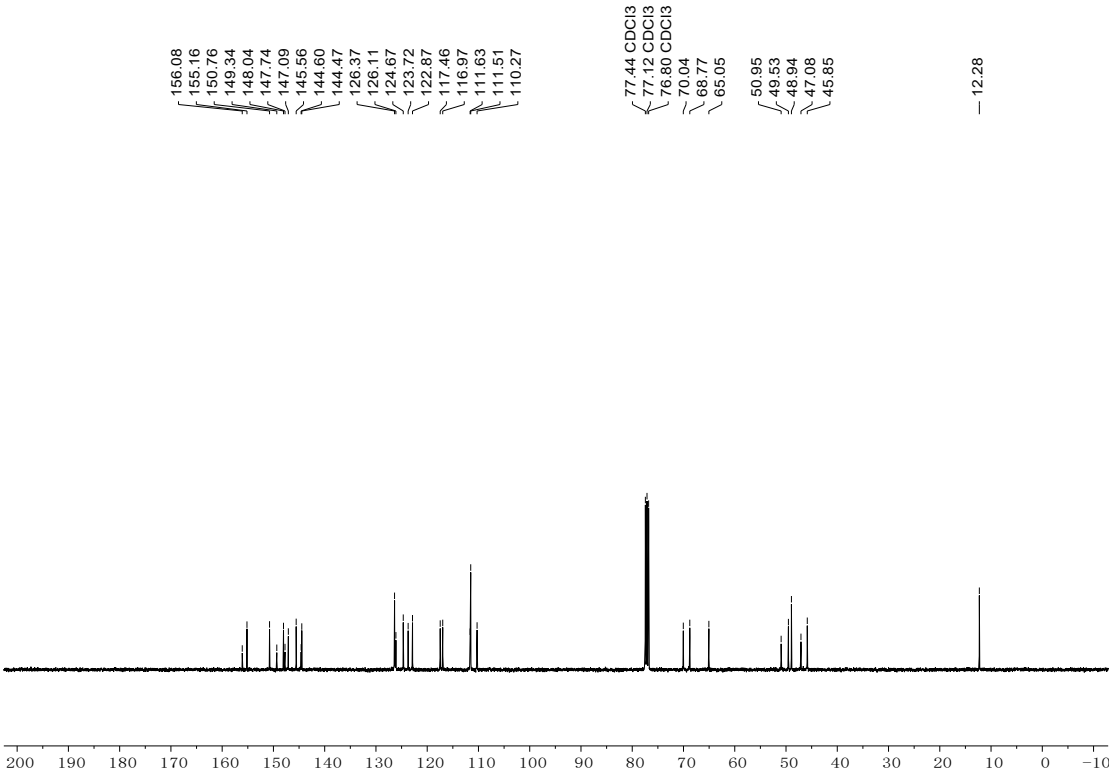


Fig. S7 The ^{13}C NMR spectrum of **Y1o** in $CDCl_3$.

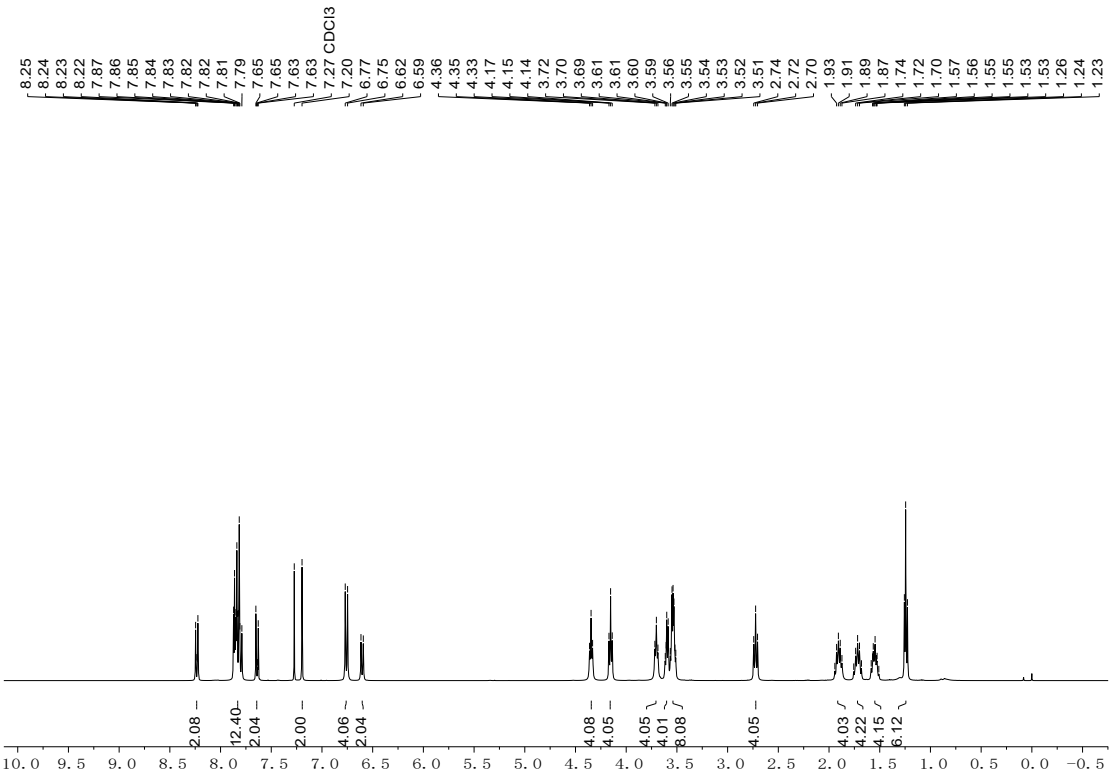


Fig. S8 The ^{1}H NMR spectrum of **Y2** in $CDCl_3$.

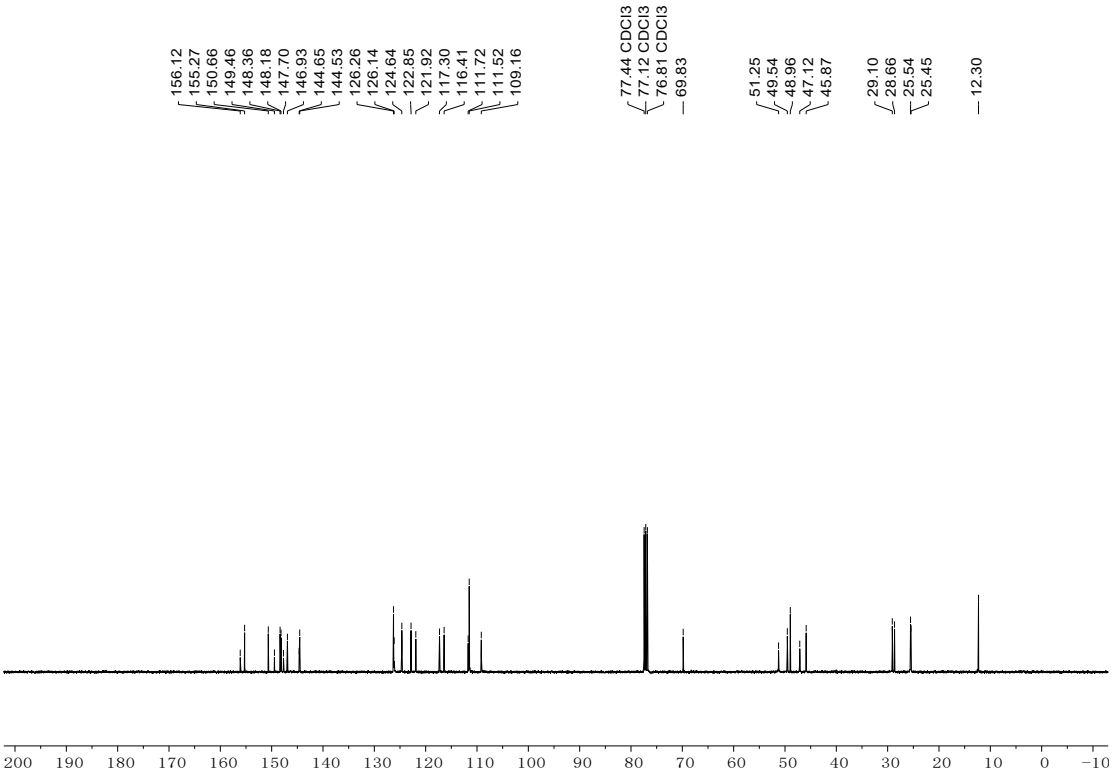


Fig. S9 The ^{13}C NMR spectrum of **Y2** in $CDCl_3$.

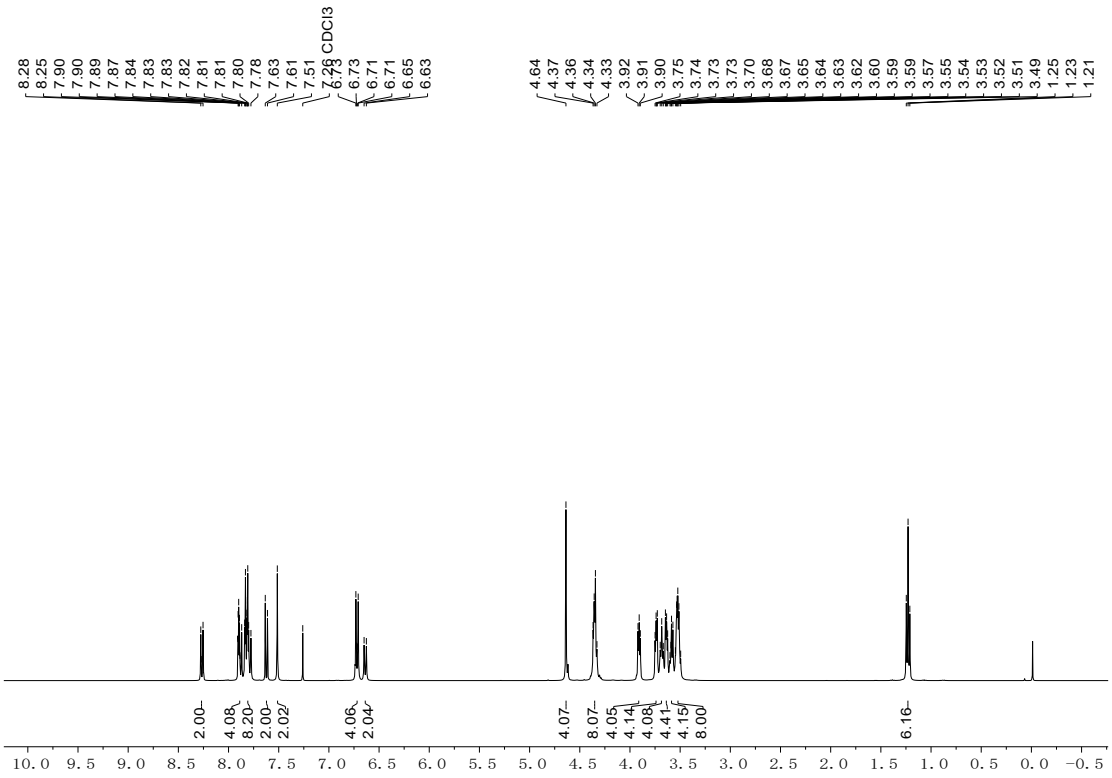


Fig. S10 The ^{1}H NMR spectrum of **Y2o** in $CDCl_3$.

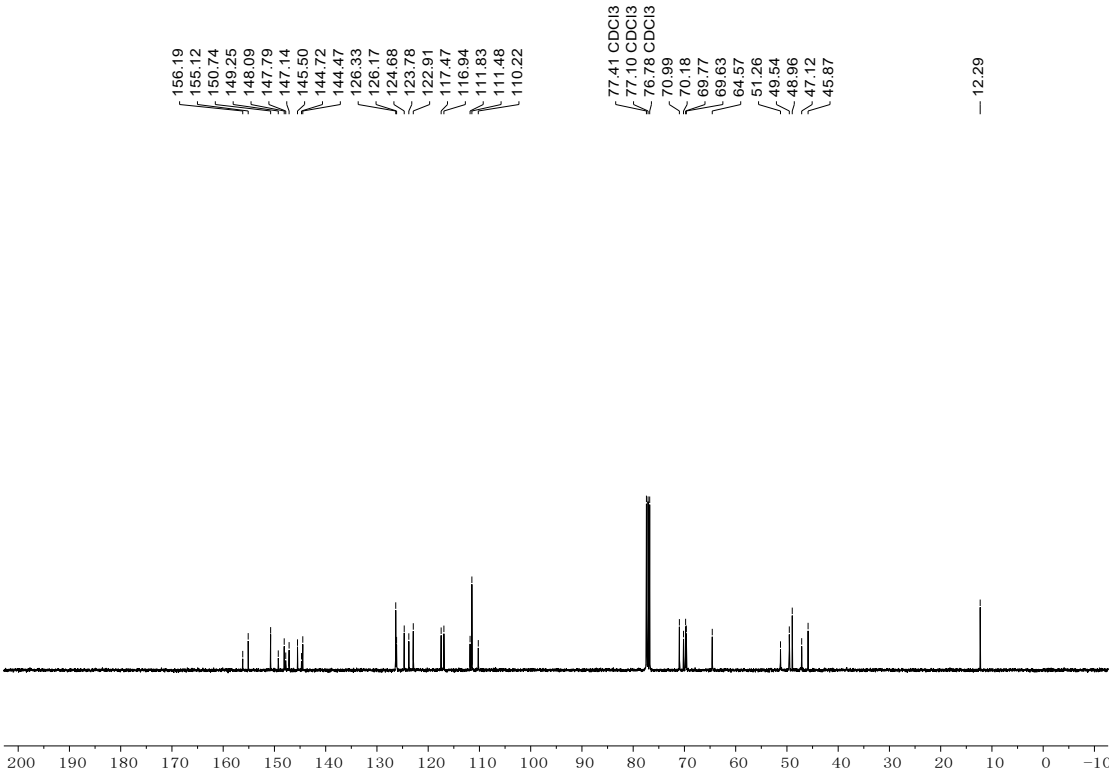


Fig. S11 The ^{13}C NMR spectrum of **Y2o** in $CDCl_3$.

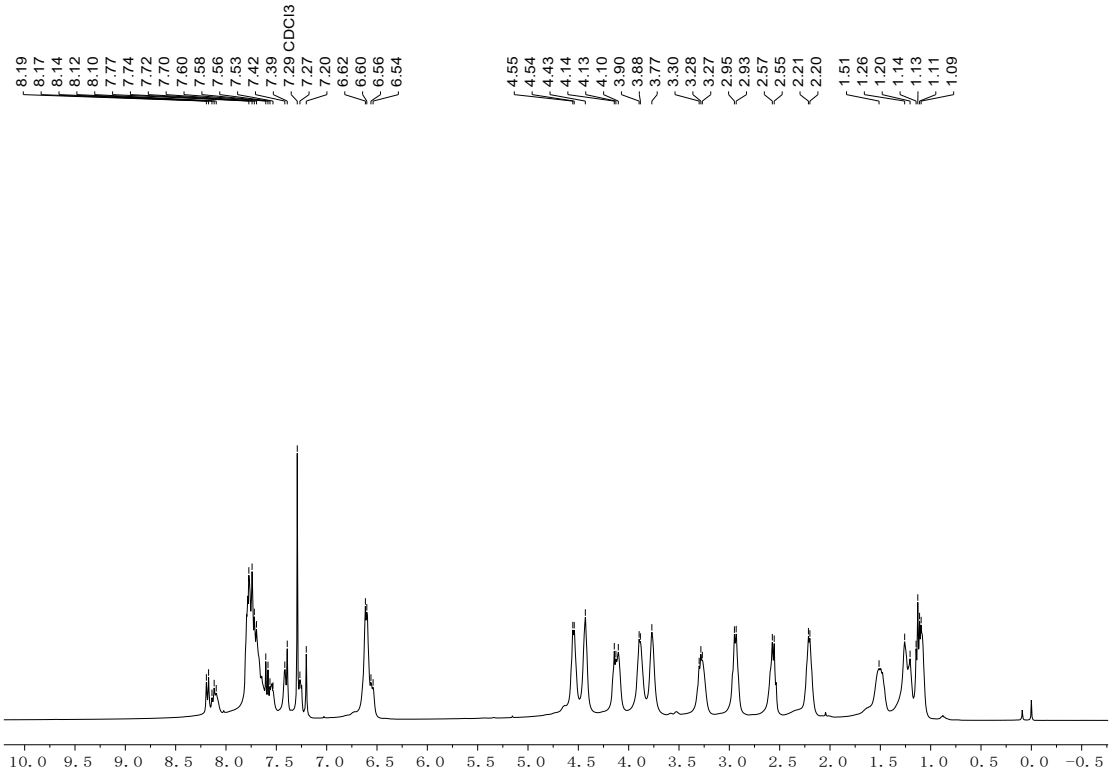


Fig. S12 The ^{1}H NMR spectrum of **PY1-yl** in $CDCl_3$.

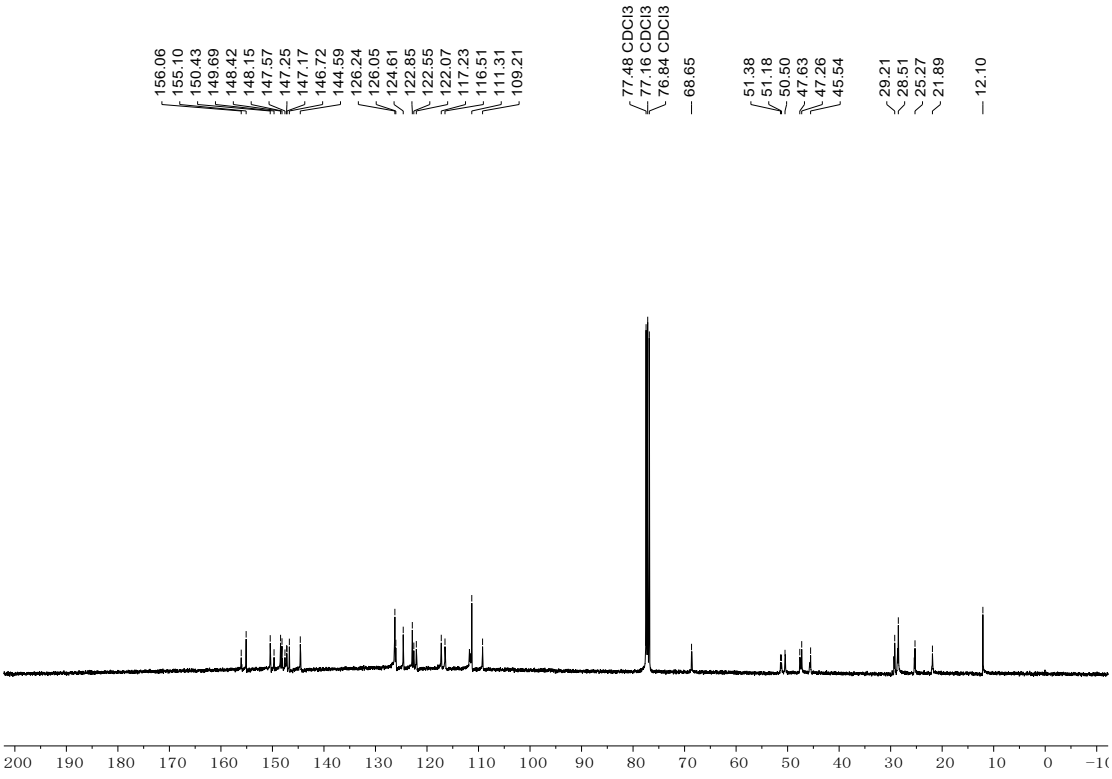


Fig. S13 The ^{13}C NMR spectrum of **PY1-yl** in $CDCl_3$.

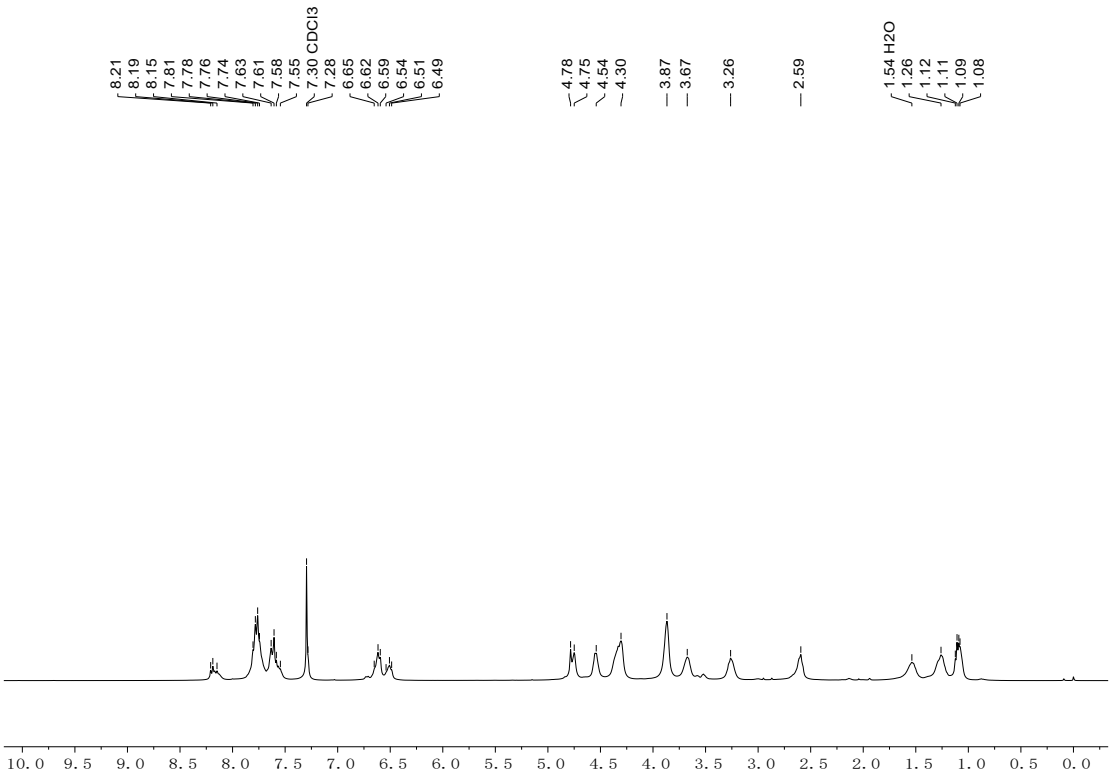


Fig. S14 The ^{1}H NMR spectrum of **PY1o-yl** in $CDCl_3$.

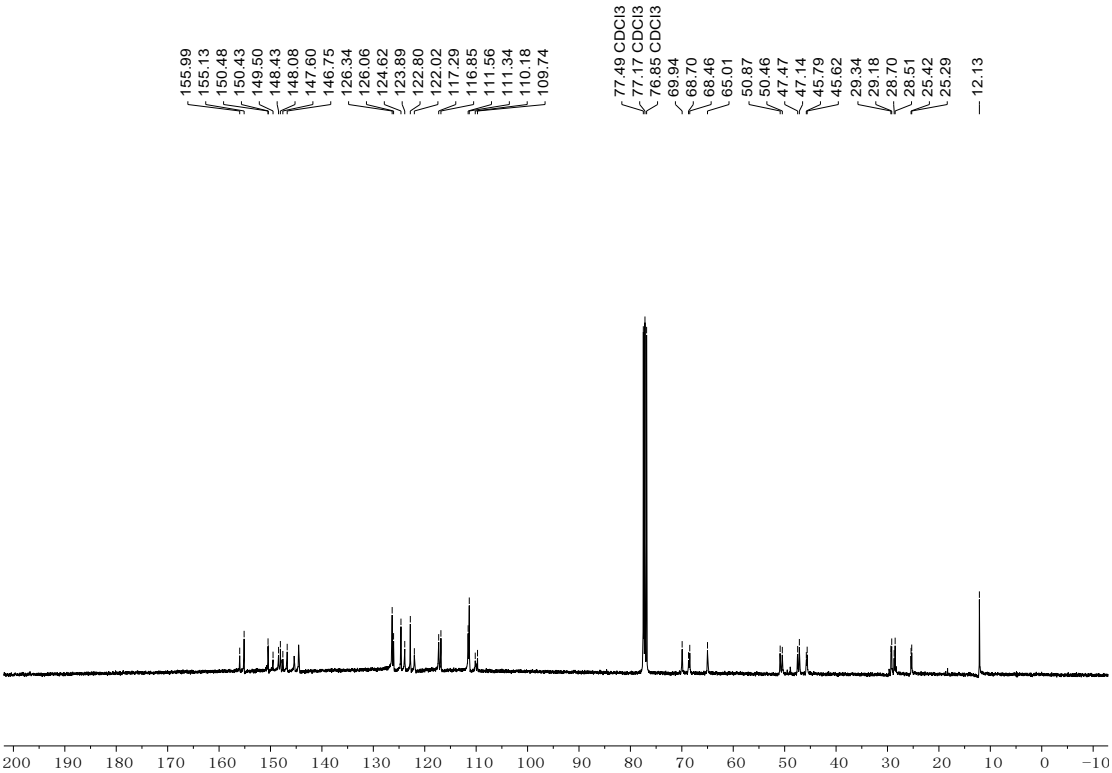


Fig. S15 The ^{13}C NMR spectrum of **PY1o-yl** in $CDCl_3$.

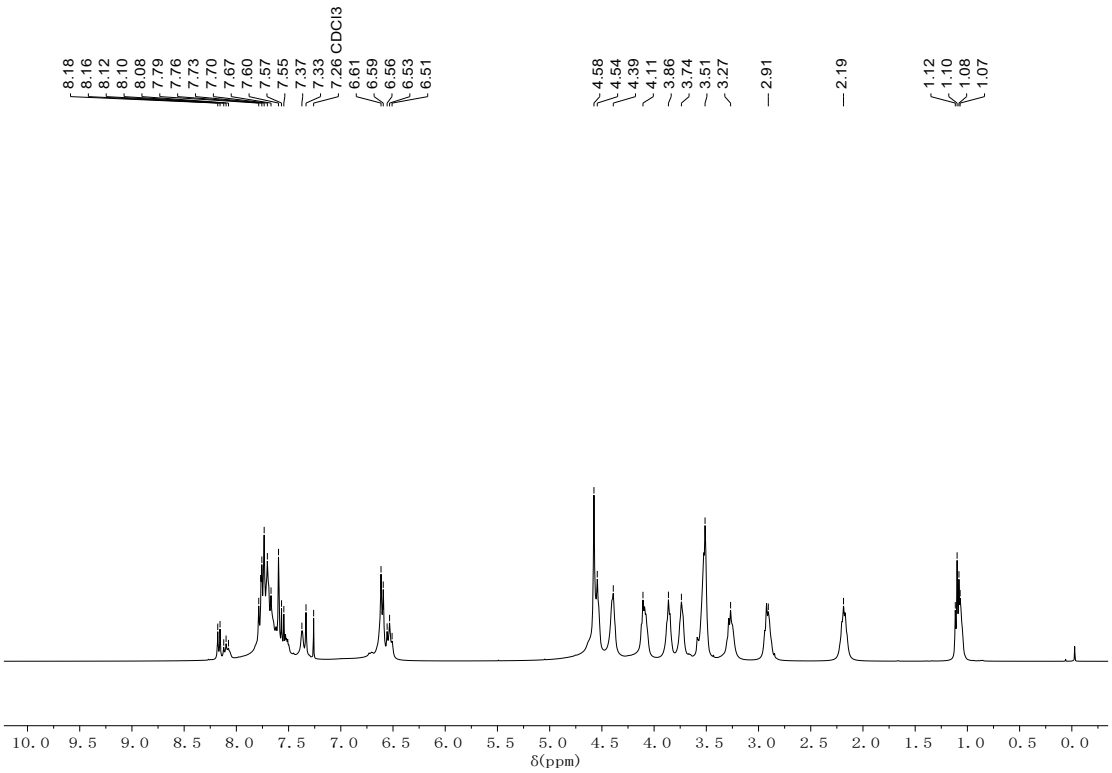


Fig. S16 The ^{1}H NMR spectrum of **PY1-oxy** in $CDCl_3$.

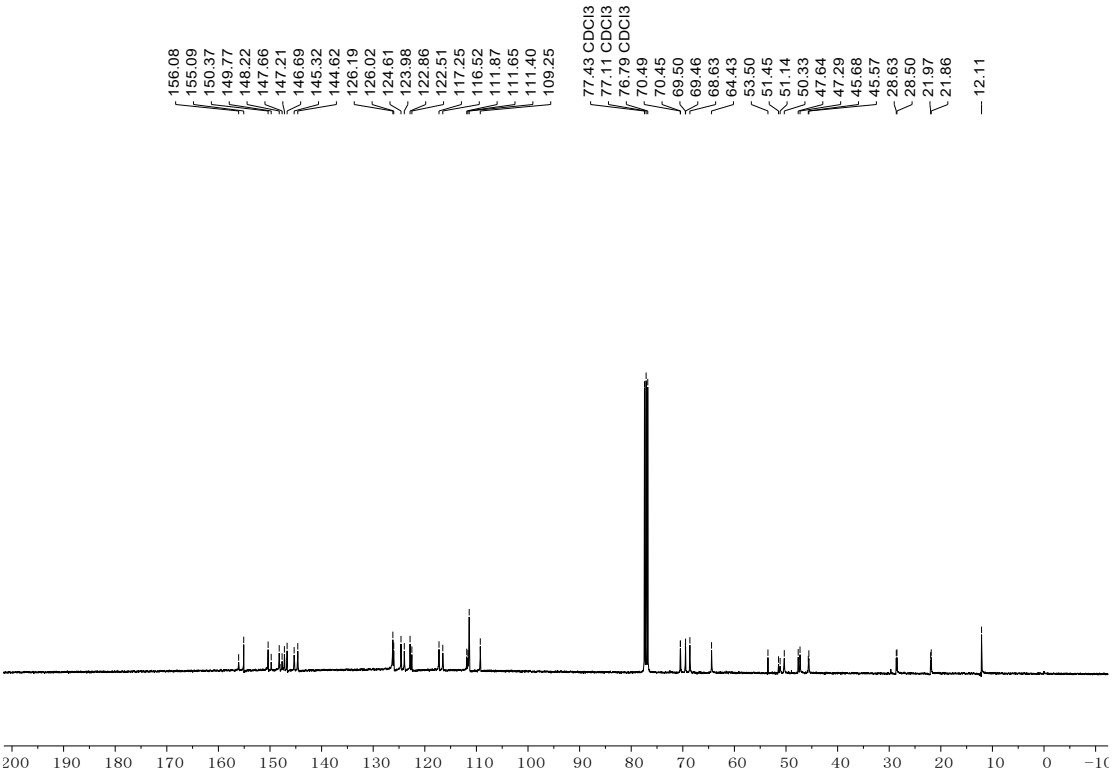


Fig. S17 The ^{13}C NMR spectrum of **PY1-oxy** in $CDCl_3$.

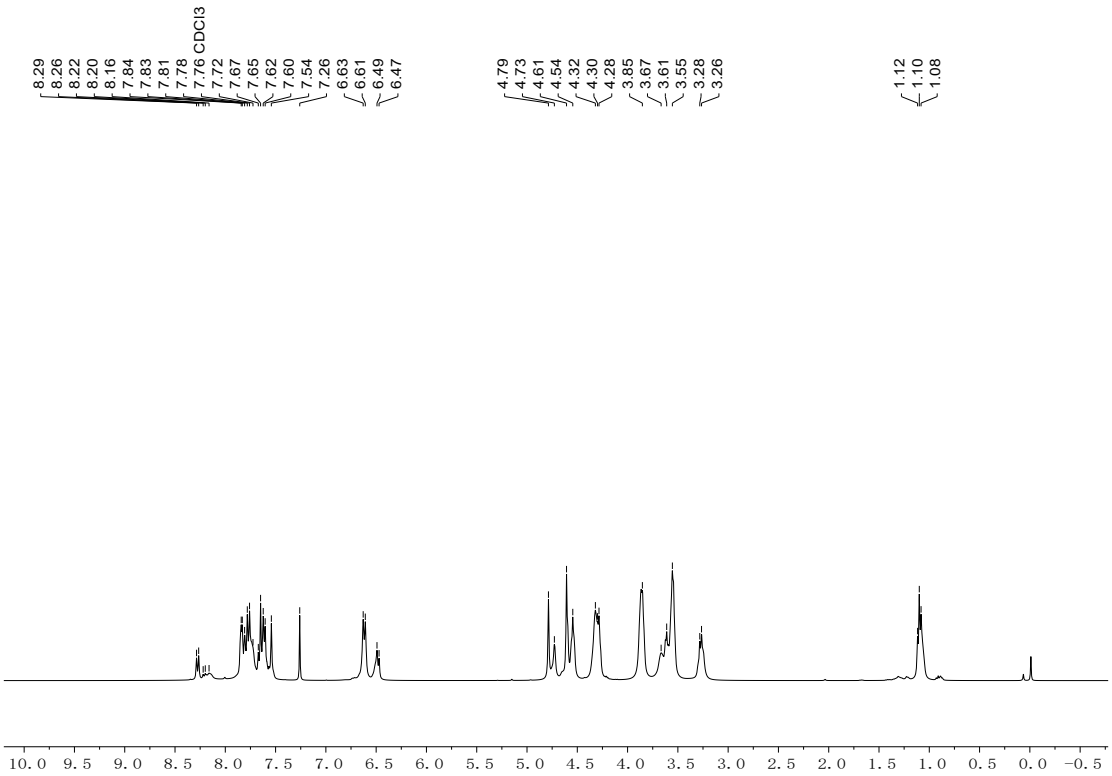


Fig. S18 The ^{1}H NMR spectrum of **PY1o-oxy** in $CDCl_3$.

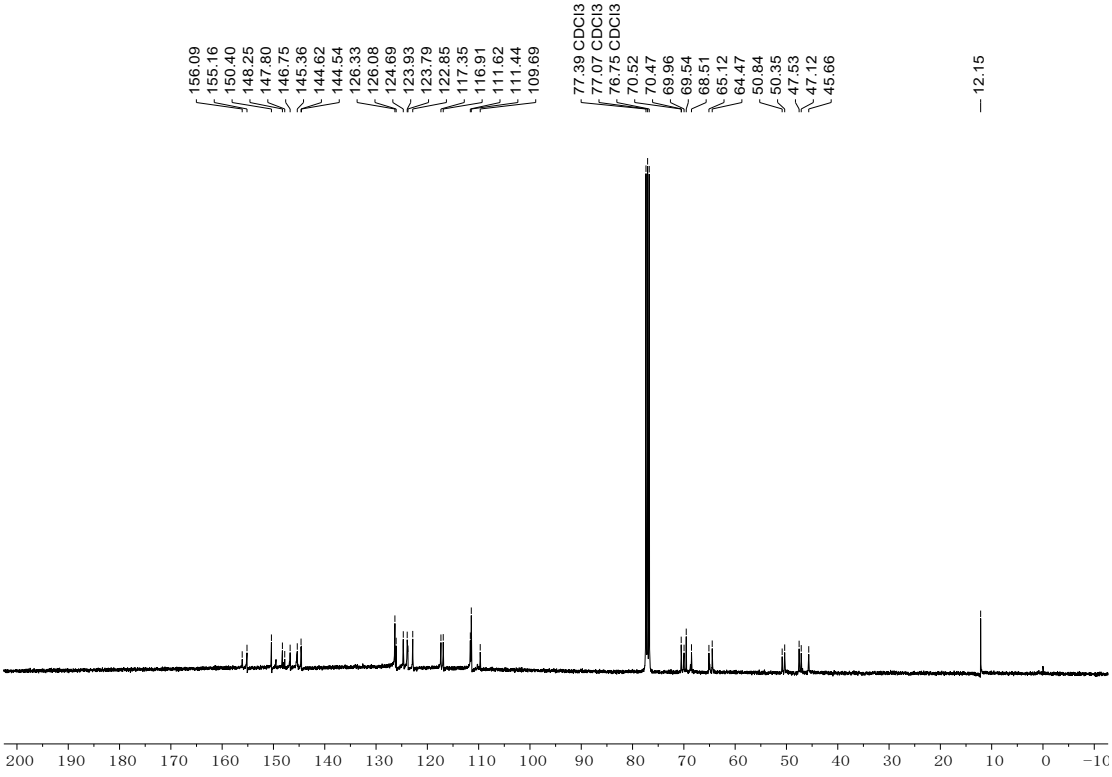


Fig. S19 The ^{13}C NMR spectrum of **PY1o-oxy** in $CDCl_3$.

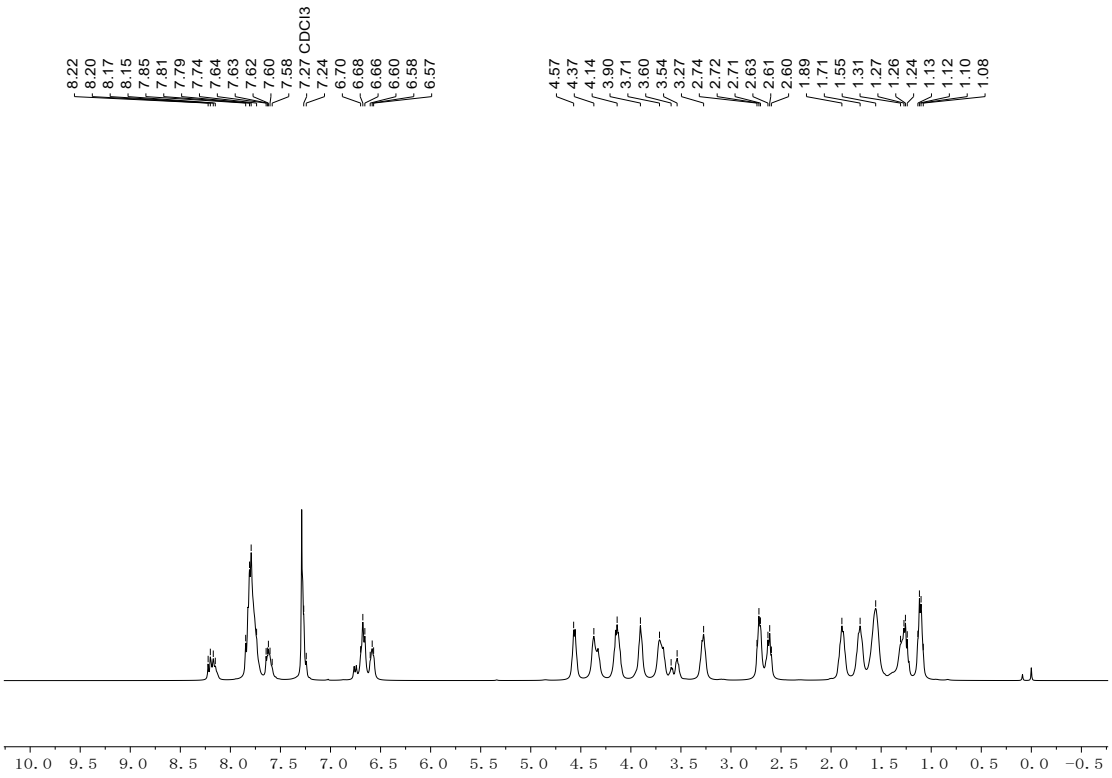


Fig. S20 The ^{1}H NMR spectrum of **PY2-yl** in $CDCl_3$.

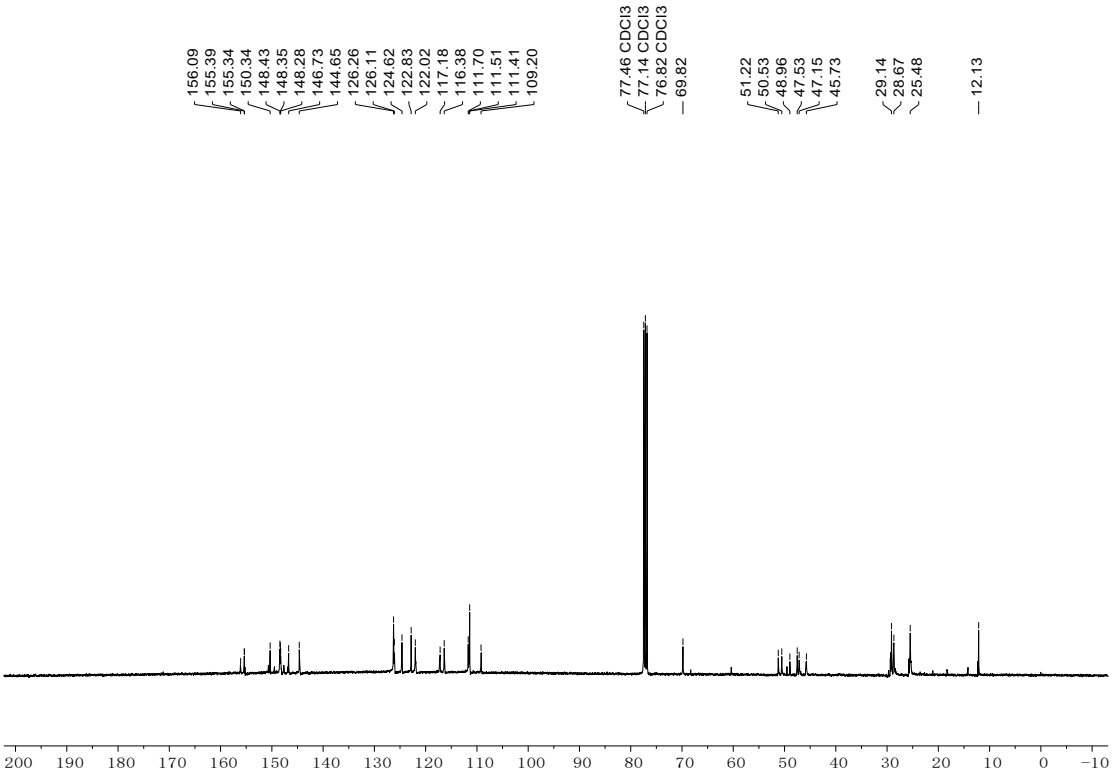


Fig. S21 The ^{13}C NMR spectrum of **PY2-yl** in $CDCl_3$.

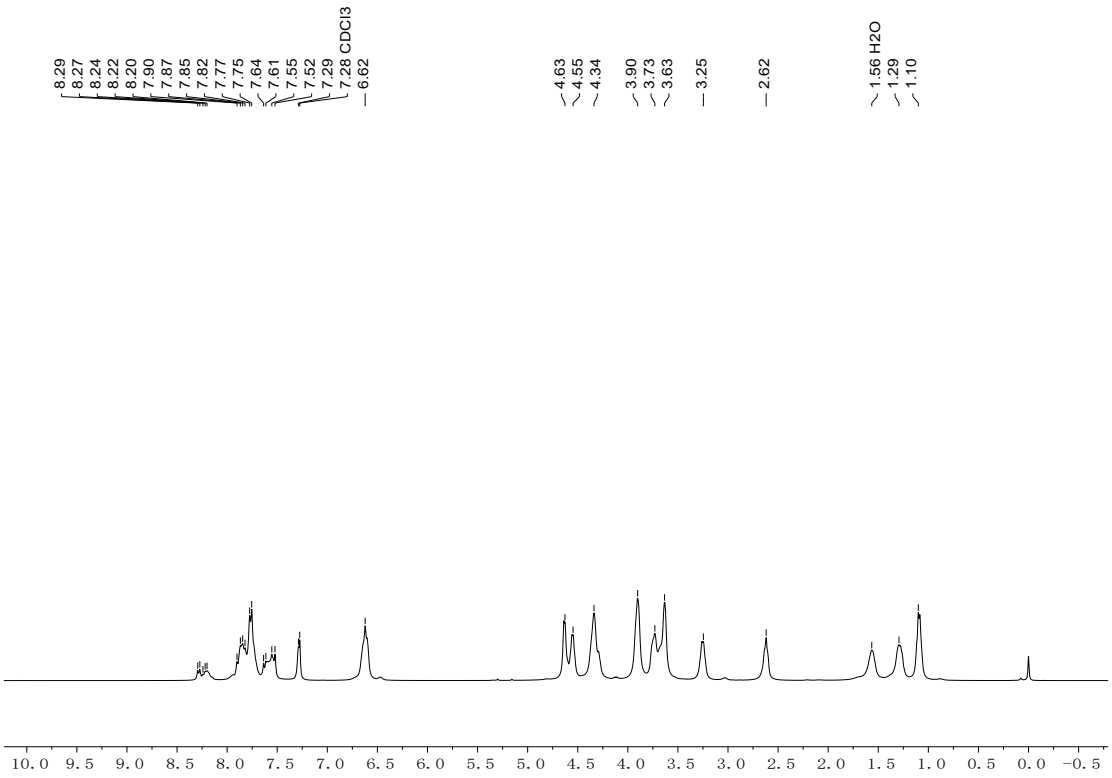


Fig. S22 The ^{1}H NMR spectrum of **PY2o-yl** in $CDCl_3$.

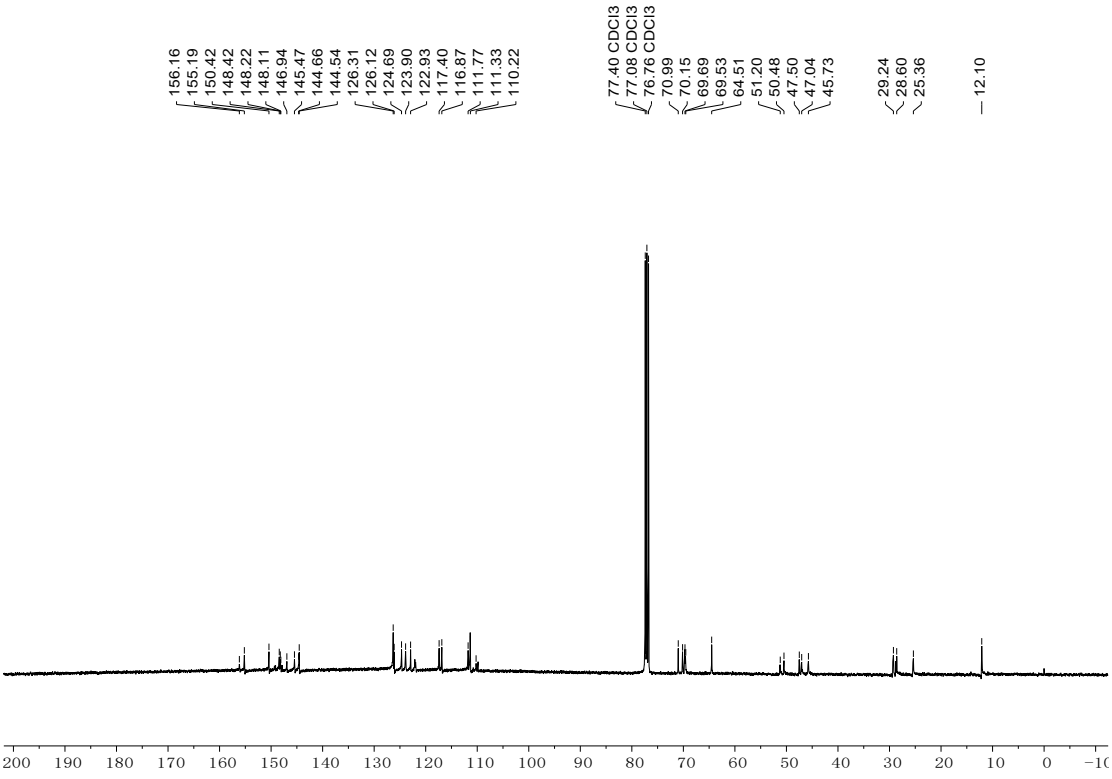


Fig. S23 The ^{13}C NMR spectrum of **PY2o-yl** in $CDCl_3$.

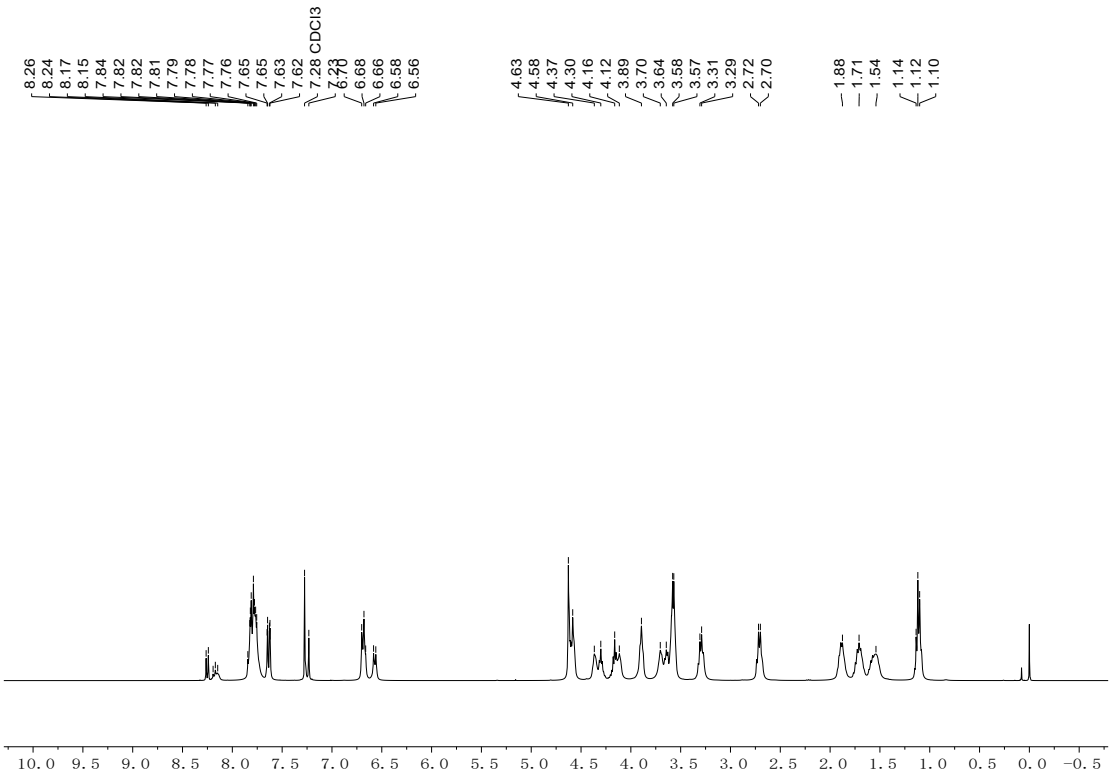


Fig. S24 The ^{1}H NMR spectrum of **PY2-oxy** in $CDCl_3$.

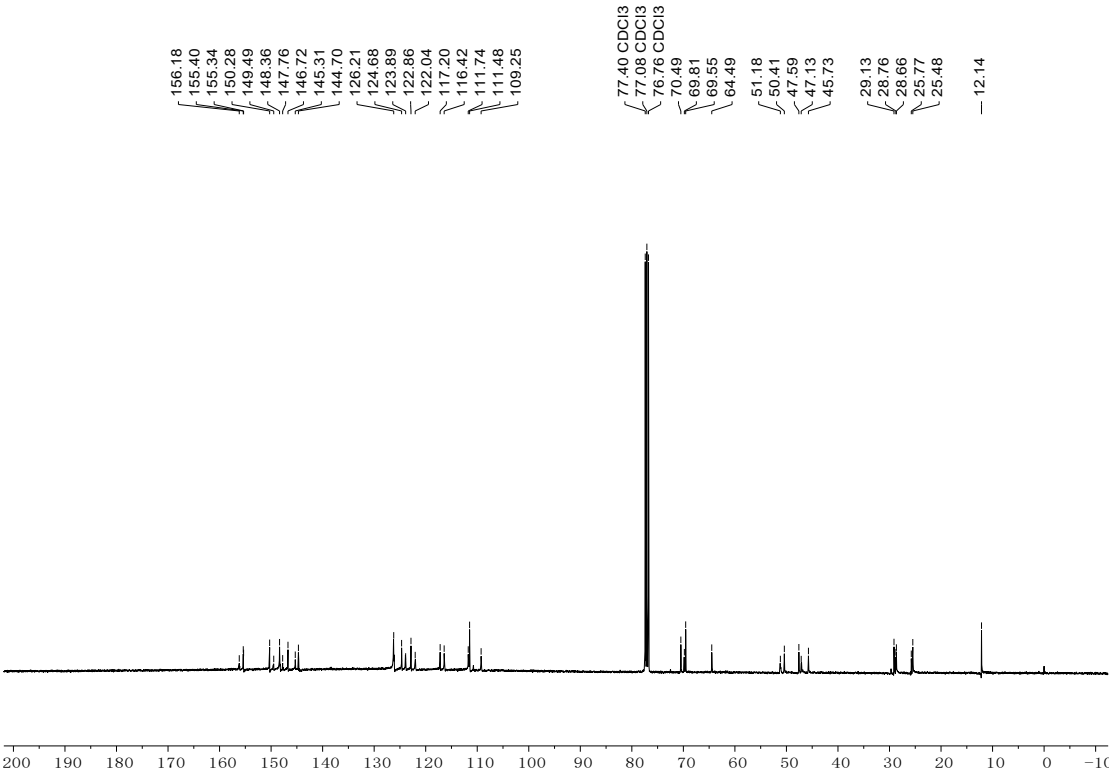


Fig. S25 The ^{13}C NMR spectrum of **PY2-oxy** in $CDCl_3$.

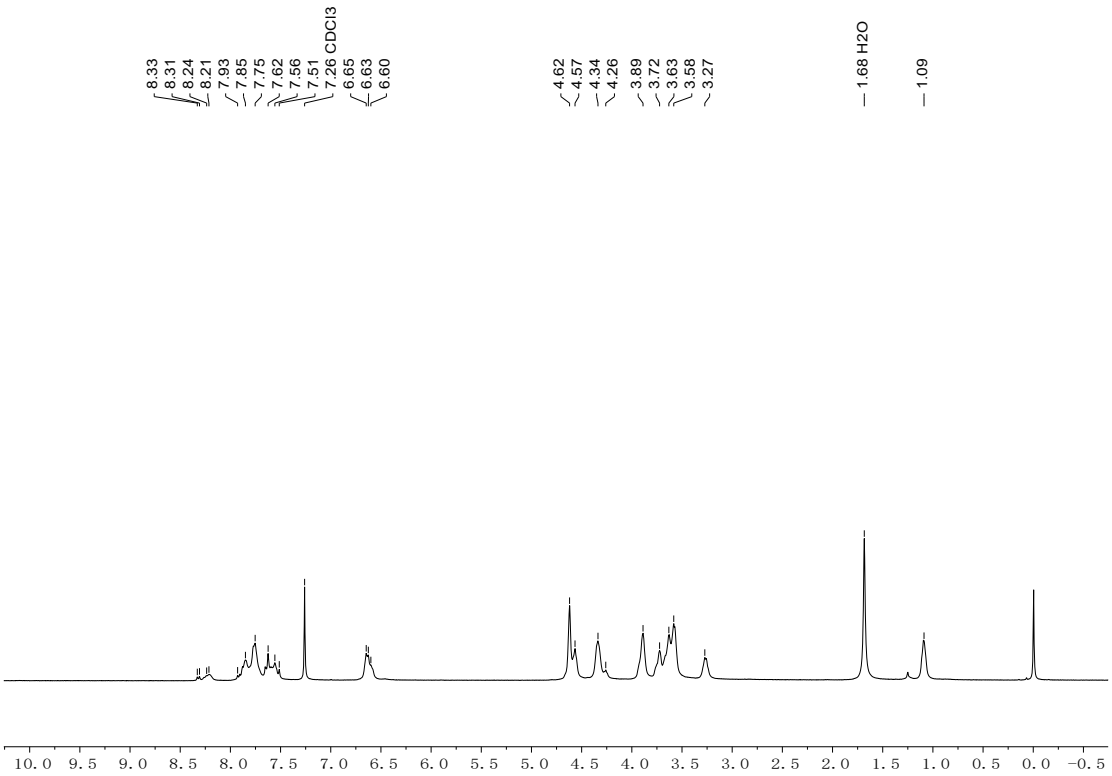


Fig. S26 The ^{1}H NMR spectrum of **PY2o-oxy** in $CDCl_3$.

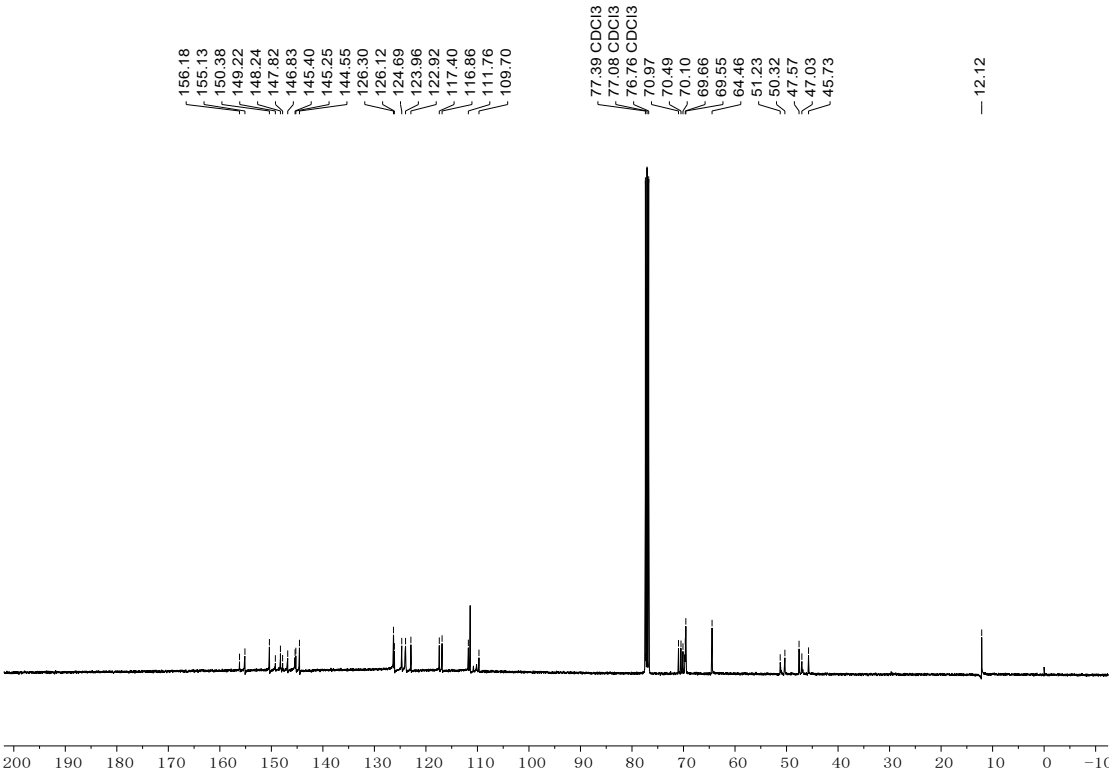


Fig. S27 The ^{13}C NMR spectrum of **PY2o-oxy** in $CDCl_3$.

4. Reference

1. X. Deng, K. Wang, Q. Li and Z. Li, *Mater. Chem. Front.*, 2022, **6**, 3349-3358.
2. R. Tang, H. Chen, S. Zhou, B. Liu, D. Gao, H. Zeng and Z. Li, *Polym. Chem.*, 2015, **6**, 6680-6688.
3. Z. Zhu, Z. a. Li, Y. Tan, Z. Li, Q. Li, Q. Zeng, C. Ye and J. Qin, *Polymer*, 2006, **47**, 7881-7888.
4. J. Xie, L. Hu, W. Shi, X. Deng, Z. Cao and Q. Shen, *Polym. Int.*, 2008, **57**, 965-974.
5. H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2001, **40**, 2004-2021.
6. V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2002, **41**, 2596-2599.
7. R. Tang, H. Chen, S. Zhou, W. Xiang, X. Tang, B. Liu, Y. Dong, H. Zeng and Z. Li, *Polym. Chem.*, 2015, **6**, 5580-5589.