Electronic supplementary information (ESI)

Promotion of Second-order Nonlinear Optical Effect by Introducing Ether Linkage into Polymer Main Chains

Kai Wang, Xiaocong Deng, Qianqian Li* and Zhen Li*[a]

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

Additional data and analysis

Table S1 The maximum absorption wavelength (λ_{max}, nm) in different solvents (0.02 mg/mL).

	$CHCl_3$	DCM	THF	DMF	DMSO	Δ
Mon-NN	458	460	462	479	488	30
P1	457	460	463	478	485	28
P2	457	459	463	478	486	29
P3	457	458	463	477	485	28
P4	458	460	467	479	486	28
P5	456	458	462	477	484	28

$\Delta = \lambda_{max}$ (DMSO)- λ_{max} ($CHCl_3$)

Dielectric constant of solvents: ε ($CHCl_3$) = 4.8 $C^2/(N \cdot M^2)$, ε (THF) = 7.5 $C^2/(N \cdot M^2)$, ε (CH_2Cl_2) = 8.9 $C^2/(N \cdot M^2)$, ε (DMF) = 37.6 $C^2/(N \cdot M^2)$, ε (DMSO) = 46.7 $C^2/(N \cdot M^2)$

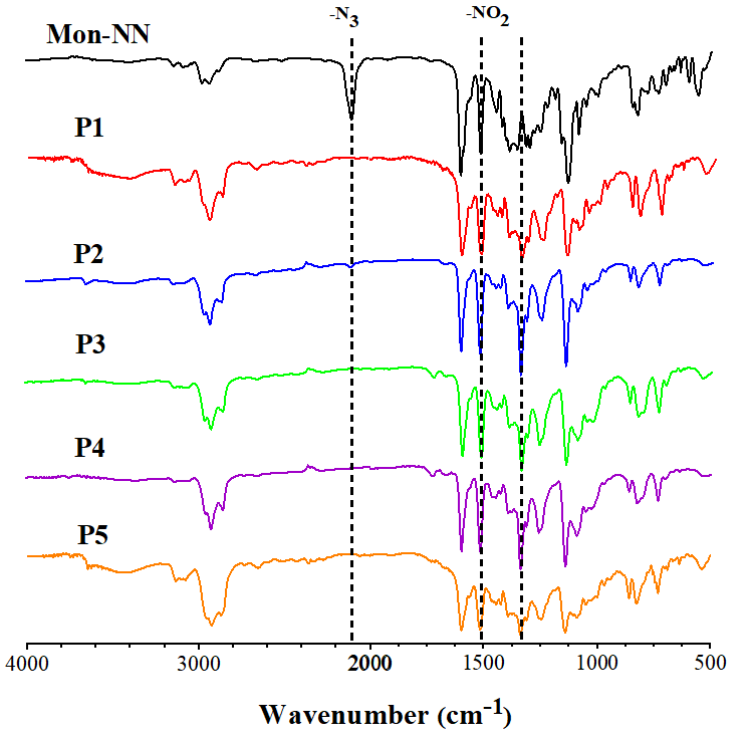


Fig. S1 FT-IR spectra of polymers.

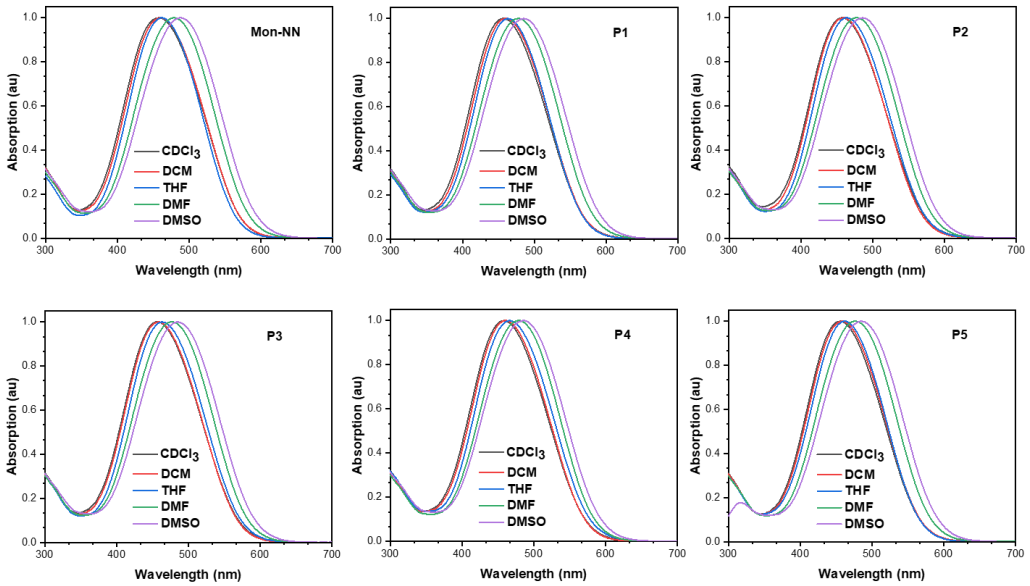


Fig. S2 UV-vis spectra of polymers and Mon-NN in different solvents ($CHCl_3$, DCM, THF, DMF, DMSO, concentration: 0.02 mg mL^{-1}).

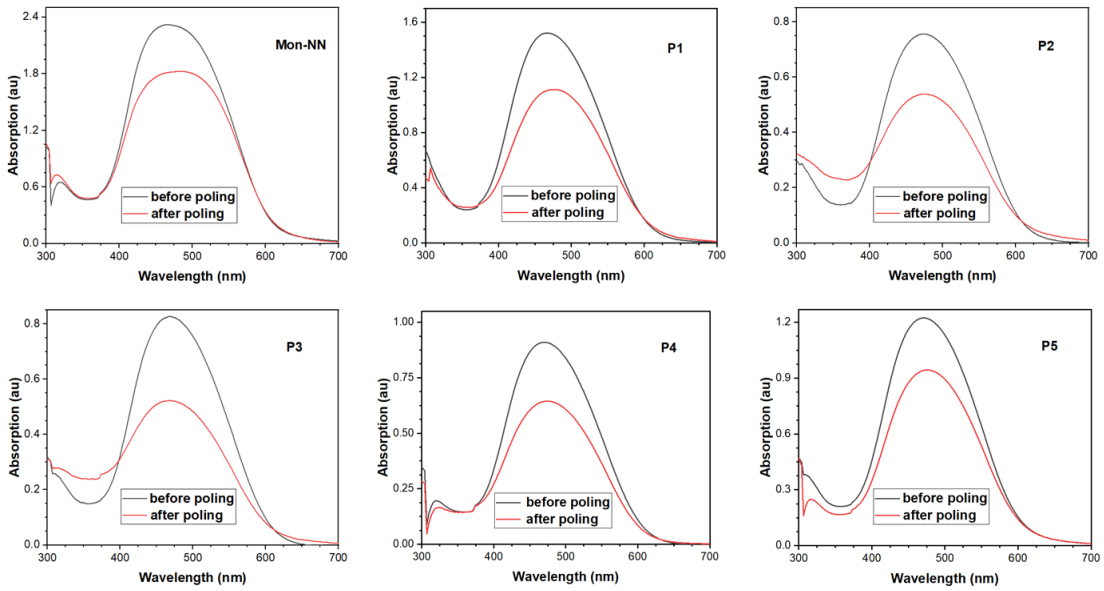


Fig. S3 UV-vis absorption spectra of polymer films and monomer **Mon-NN** before and after poling.

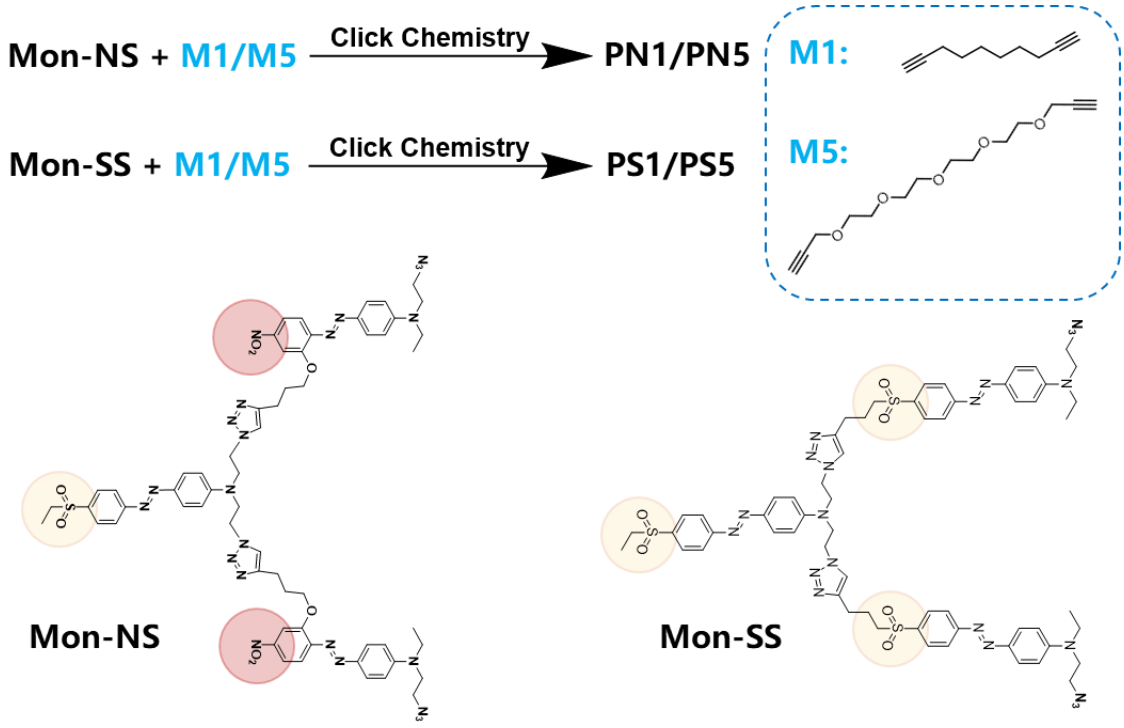


Fig. S4 Synthesis of polymer **PN1, PN5, PS1 and PS5** and molecular structures of monomers.

General synthesis of PN1, PN5, PS1 and PS5

Two monomers (at a molar ratio of 1 : 1) were dissolved in DMF (the concentrate of all monomers was about 15 mg/mL) in a Schlenk flask under nitrogen. A certain volume of $CuSO_4$ aqueous solution (0.08 mol/L) and ascorbic acid sodium aqueous solution (NaAsc, 0.16 mol/L) were added into the

mixture. After the reaction was stirred for 24 h, another batch of $CuSO_4$ and NaAsc aqueous solution was added. The mixture was then stirred for another 12 h, and another batch of $CuSO_4$ and NaAsc aqueous solution was added. After another 12 h, the mixture was poured into water. The precipitate was collected and washed by deionized water and anhydrous methanol in turn. The obtained solid was further purified by reprecipitation from its DCM solution into methanol.

PN1: Mon-NS (139.4 mg, 0.110 mmol), **M1** (14.8 mg, 0.110 mmol), $CuSO_4$ (250 + 150 + 150 μL), NaAsc (250 + 150 + 150 μL) in DMF (10 mL), a red powder (80.0 mg, 51.9%). M_w =60500, M_w/M_n = 1.87 (GPC, PMMA calibration). IR (thin film), v (cm^{-1}): 1516, 1338 (-NO_2), 1138 (-SO_2-). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ(ppm): 7.92-7.86 (ArH), 7.77 (ArH), 7.72 (ArH), 7.57 (ArH), 7.34 (ArH), 7.21 (ArH), 6.97 (ArH), 6.63 (ArH), 4.52 (-CH_2-), 4.40 (-CH_2-), 4.11 (-CH_2-), 3.87 (-CH_2-), 3.74 (-CH_2-), 3.27 (-CH_2-), 3.13 (-CH_2-), 2.92 (-CH_2-), 2.56 (-CH_2-), 2.27 (-CH_2-), 2.19 (-CH_2-), 1.75 (-CH_2-), 1.43 (-CH_2-), 1.26 (-CH_2-), 1.10 (-CH_2-), 0.88 (-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ(ppm): 155.78, 155.11, 150.41, 129.24, 126.26, 125.94, 125.54, 122.90, 117.38, 116.61, 111.37, 109.24, 68.62, 50.72, 47.59, 34.30, 30.33, 29.72, 29.34, 21.72, 12.14, 7.47.

PN5: Mon-NS (142.3 mg, 0.112 mmol), **M5** (30.2 mg, 0.112 mmol), $CuSO_4$ (210 + 100 + 100 μL), NaAsc (210 + 100 + 100 μL), in DMF (9 mL), a red powder (79.0 mg, 45.8%). M_w =17500, M_w/M_n = 1.87 (GPC, PMMA calibration). IR (thin film), v (cm^{-1}): 1516, 1338 (-NO_2), 1142 (-SO_2-). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ(ppm): 7.86 (ArH), 7.77-7.74 (ArH), 7.57 (ArH), 7.33 (ArH), 6.65 (ArH), 6.58 (ArH), 4.58 (-CH_2-), 4.40 (-CH_2-), 4.11 (-CH_2-), 3.88 (-CH_2-), 3.74 (-CH_2-), 3.54 (-CH_2-), 3.28 (-CH_2-), 3.11 (-CH_2-), 2.92 (-CH_2-), 2.19 (-CH_2-), 1.24 (-CH_2-), 1.09 (-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 155.80, 155.11, 150.36, 148.20, 146.81, 144.66, 129.23, 126.28, 125.96, 122.91, 117.36, 116.51, 111.73, 111.44, 109.26, 70.46, 69.56, 68.62, 64.43, 51.17, 50.71, 50.40, 47.65, 47.26, 45.70, 28.51, 21.87, 12.15, 7.47.

PS1: Mon-SS (144.6 mg, 0.113 mmol), **M1** (15.2 mg, 0.113 mmol), $CuSO_4$ (250 + 150 + 150 μL), NaAsc (250 + 150 + 150 μL) in DMF (10 mL), a yellow powder (102.0 mg, 63.8%). M_w =88800, M_w/M_n = 1.78 (GPC, PMMA calibration). IR (thin film), v (cm^{-1}): 1132 (-SO_2-). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ(ppm): 7.94 (ArH), 7.89 (ArH), 7.17 (ArH), 6.65-6.63 (ArH), 4.54 (-CH_2-), 4.42 (-CH_2-), 3.91 (-CH_2-), 3.72 (-CH_2-), 3.29 (-CH_2-), 3.13 (-CH_2-), 2.78 (-CH_2-), 2.57 (-CH_2-), 2.05 (-CH_2-), 1.72 (-CH_2-), 1.51 (-CH_2-), 1.25 (-CH_2-), 1.11 (-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ(ppm):

150.50, 148.47, 146.29, 138.42, 129.30, 129.06, 126.17, 123.00, 122.86, 121.93, 111.39, 55.22, 50.74, 50.36, 29.72, 29.33, 28.74, 25.39, 23.78, 22.66, 12.14, 7.49.

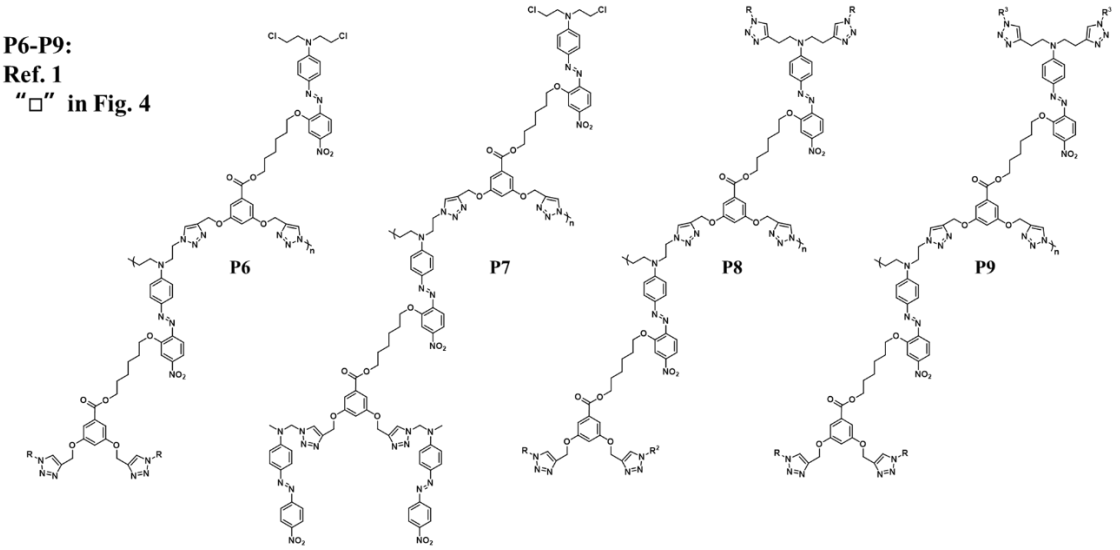
PS5: Mon-SS (148.1 mg, 0.116 mmol), **M5** (31.3 mg, 0.116 mmol), $CuSO_4$ (210 + 100 + 100 μL), NaAsc (210 + 100 + 100 μL) in DMF (10 mL), a yellow powder (60.0 mg, 33.4%). M_w = 28100, M_w/M_n = 1.86 (GPC, PMMA calibration). IR (thin film), v (cm^{-1}): 1132 (-SO_2-). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ(ppm): 7.91 (ArH), 7.84 (ArH), 7.56 (ArH), 6.69 (ArH), 4.63 (-CH_2-), 4.57 (-CH_2-), 4.44 (-CH_2-), 3.91 (-CH_2-), 3.73 (-CH_2-), 3.58 (-CH_2-), 3.28 (-CH_2-), 3.15 (-CH_2-), 2.79 (-CH_2-), 2.07 (-CH_2-), 1.78 (-CH_2-), 1.25 (-CH_2-), 1.12 (-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ(ppm): 156.17, 155.60, 150.54, 138.48, 129.30, 129.07, 126.17, 123.01, 122.88, 111.97, 111.46, 70.50, 69.60, 64.52, 55.21, 50.74, 50.38, 47.62, 47.27, 45.76, 23.79, 22.65, 12.15, 7.50.

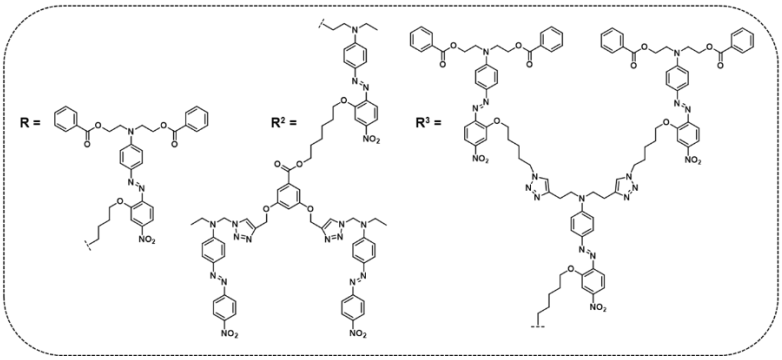
Table S2 Characterization data and NLO properties of polymers

	Yield (%)	M_w [a] (10^4)	M_w/M_n [a] (PDI)	T_g [b] (°C)	T_d [c] (°C)	T_e [d] (°C)	l_s [e] (nm)	λ_{max} [f] (nm)	d_{33} [g] (pm/V)	$d_{33(\infty)}$ [h] (pm/V)	Φ [i]	N [j] (%)
PN1	51.9	6.05	1.87	111	278	161	412	461	50	10	0.11	69.1
PN5	45.8	1.75	1.87	92	270	115	287	463	84	17	0.20	62.2
PS1	63.8	8.88	1.78	109	302	144	228	433	60	17	0.14	75.8
PS5	33.4	2.81	1.86	95	262	128	292	442	66	17	0.16	68.2

[a] Determined by GPC in DMF, based on calibration with PMMA. [b] Glass transition temperature (T_g) detected by the DSC analyses under nitrogen at a heating rate of 10 °C min^{-1}. [c] The 5 % weight loss temperature of polymers detected by the TGA under nitrogen at a heating rate of 10 °C min^{-1}. [d] The best poling temperature. [e] Film thickness. [f] The maximum absorption wavelength of thin films. [g] Second harmonic generation (SHG) coefficient measured at 1064 nm fundamental beam at a voltage of 7.0 kV. [h] The non-resonant d_{33} values calculated using the approximate two-level model. [i] Order parameter $\Phi = 1 - A_1/A_0$, A_1 and A_0 are the absorbance values of the polymer film after and before corona poling, respectively. [j] The loading density of the effective chromophores.

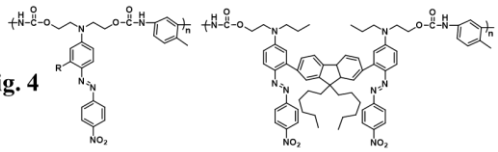
P6-P9:
Ref. 1
"□" in Fig. 4

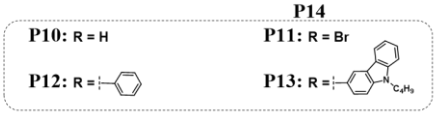




No.	d_{33} (pm/V)	Φ
P6	172	0.25
P7	189	0.24
P8	232	0.23
P9	227	0.26

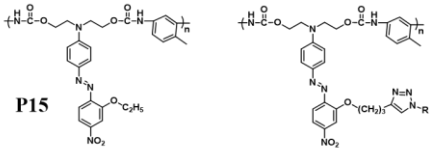
P10-P14:
Ref. 2
"○" in Fig. 4

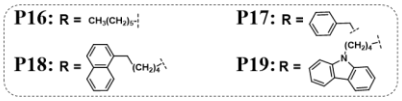




No.	P10	P11	P12	P13	P14
d_{33} (pm/V)	56	52	49	82	56
Φ	0.15	0.18	0.20	0.34	0.31

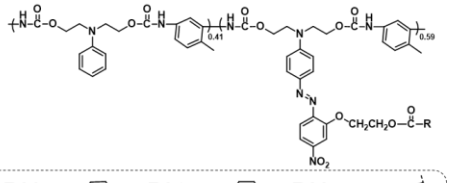
P15-P19:
Ref. 3
"△" in Fig. 4

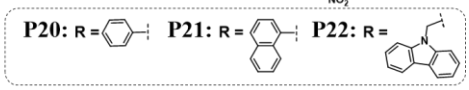




No.	P15	P16	P17	P18	P19
d_{33} (pm/V)	54	69	75	56	45
Φ	0.08	0.14	0.22	0.20	0.17

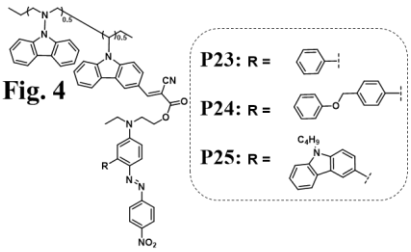
P20-P22:
Ref. 4





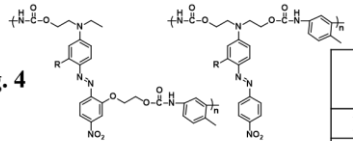
No.	P20	P21	P22
d_{33} (pm/V)	35	40	58
Φ	-	-	-

P23-P25:
Ref. 5
"▽" in Fig. 4



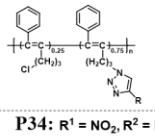
No.	P23	P25	P25
d_{33} (pm/V)	29	40	34
Φ	0.11	0.19	0.17

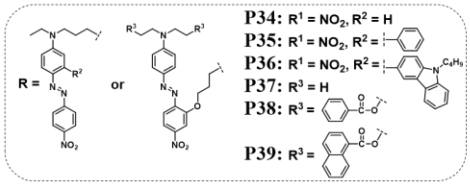
P26-P33:
Ref. 6
"◇" in Fig. 4



No.	d_{33} (pm/V)	Φ
P26	65	0.16
P27	106	0.24
P28	74	0.16
P29	67	0.14
P30	60	0.15
P31	84	0.22
P32	58	0.20
P33	64	0.18

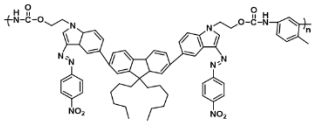
P34-P39:
Ref. 7
"◁" in Fig. 4





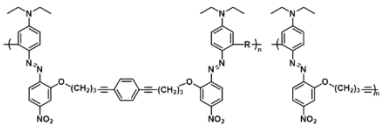
No.	d_{33} (pm/V)	Φ
P34	72	0.14
P35	131	0.19
P36	53	0.15
P37	63	0.12
P38	34	0.10
P39	25	0.09

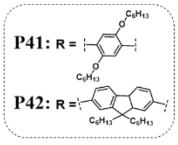
P40:
Ref. 8



No.	d_{33} (pm/V)	Φ
P34	43	-

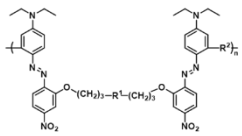
P41-P43:
Ref. 9
"▷" in Fig. 4

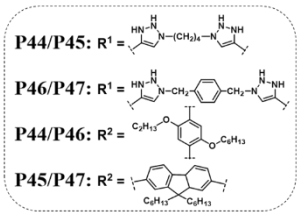




No.	d_{33} (pm/V)	Φ
P41	88	0.15
P42	90	0.18
P43	13	0.02

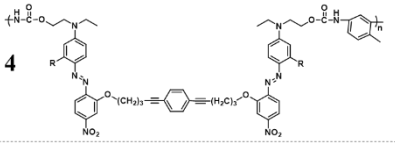
P44-P47:
Ref. 10

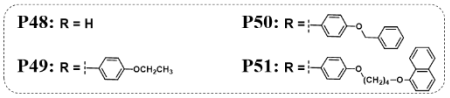




No.	P44	P45	P46	P47
d_{33} (pm/V)	75	64	65	95
Φ	-	-	-	-

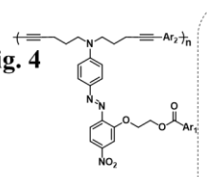
P48-P51:
Ref. 11
"◒" in Fig. 4

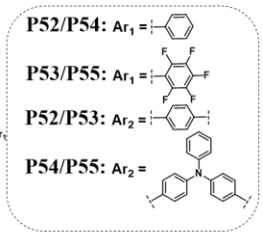




No.	P48	P49	P50	P51
d_{33} (pm/V)	119	128	108	84
Φ	0.20	0.26	0.22	0.14

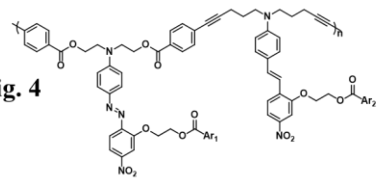
P52-P55:
Ref. 12
"◬" in Fig. 4

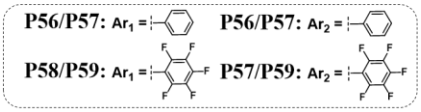




No.	P52	P53	P54	P55
d_{33} (pm/V)	12	129	50	167
Φ	0.08	0.15	0.11	0.24

P56-P59:
Ref. 13
"◭" in Fig. 4

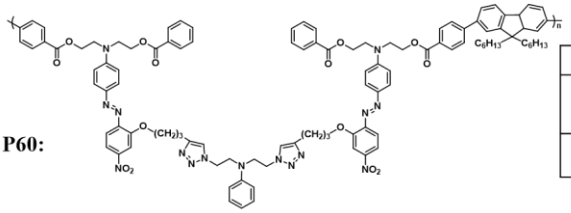




No.	P56	P57	P58	P59
d_{33} (pm/V)	100	162	94	150
Φ	0.21	0.33	0.15	0.29

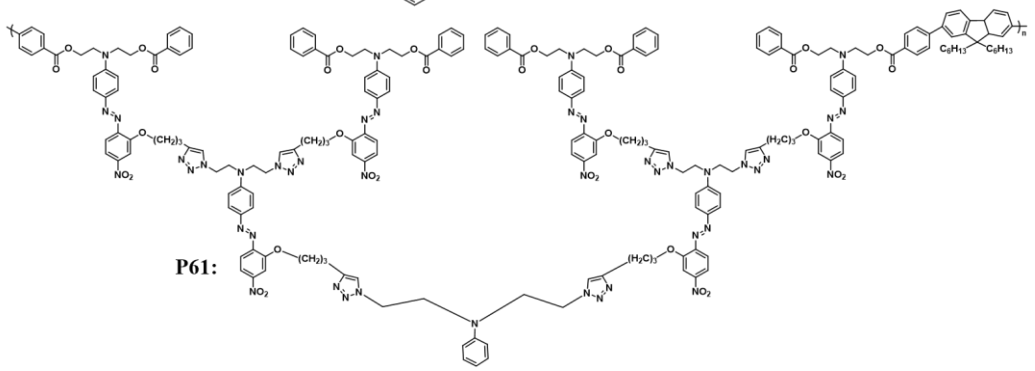
P60-P61:
Ref. 14
"◭" in Fig. 4

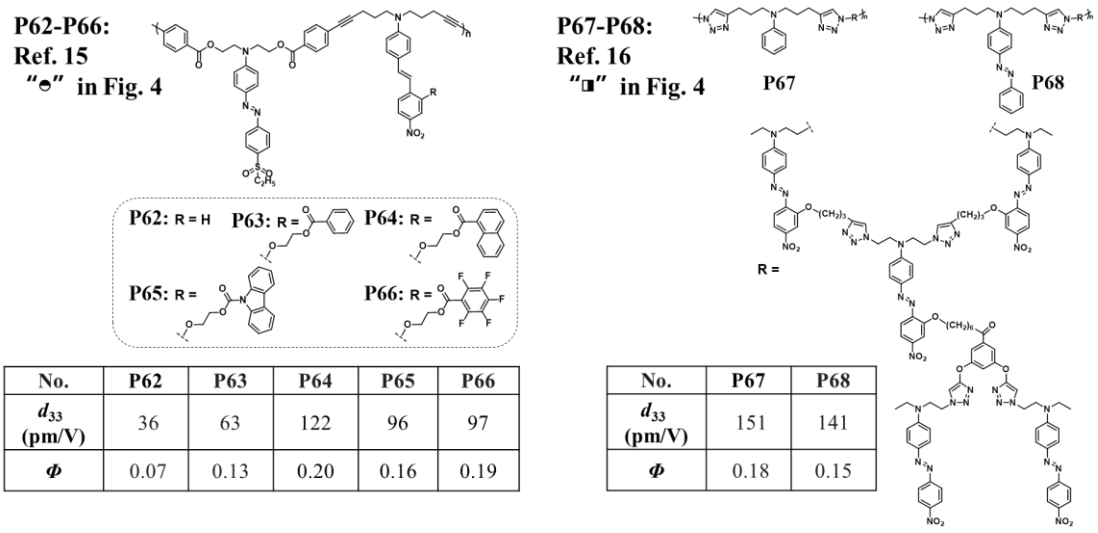
P60:



No.	P60	P61
d_{33} (pm/V)	99	116
Φ	0.15	0.23

P61:





No.	P62	P63	P64	P65	P66
d_{33} (pm/V)	36	63	122	96	97
Φ	0.07	0.13	0.20	0.16	0.19

No.	P67	P68
d_{33} (pm/V)	151	141
Φ	0.18	0.15

Fig. S5 Chemical structures and d_{33} values of linear polymers and L-D copolymers based on nitroazobenzene chromophore in previous study.

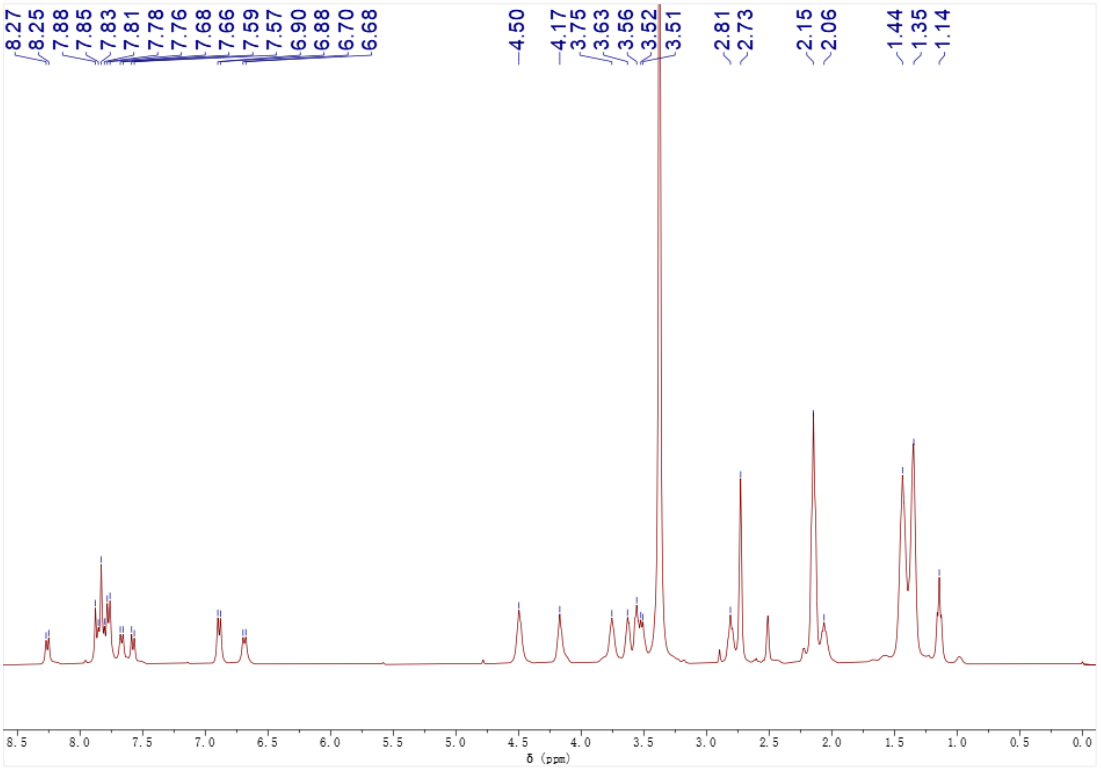


Fig. S6 The ^{1}H NMR spectrum of **P1** in DMSO-d_6.

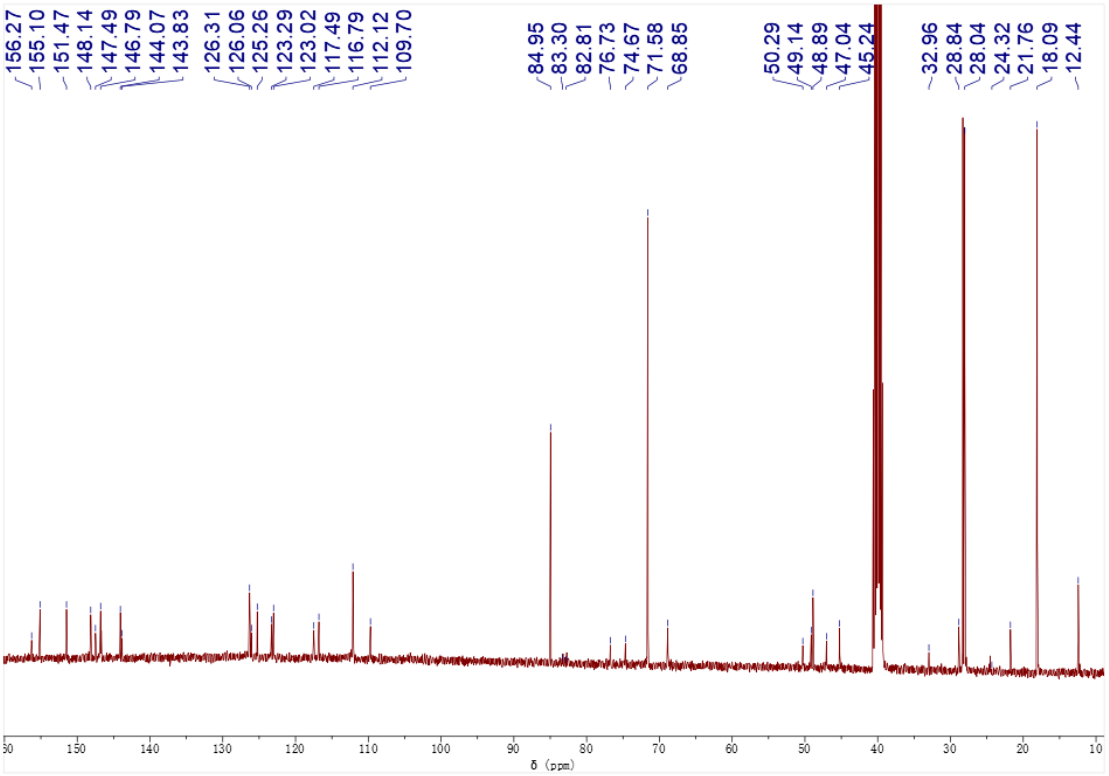


Fig. S7 The ^{13}C NMR spectrum of **P1** in $CDCl_3$.

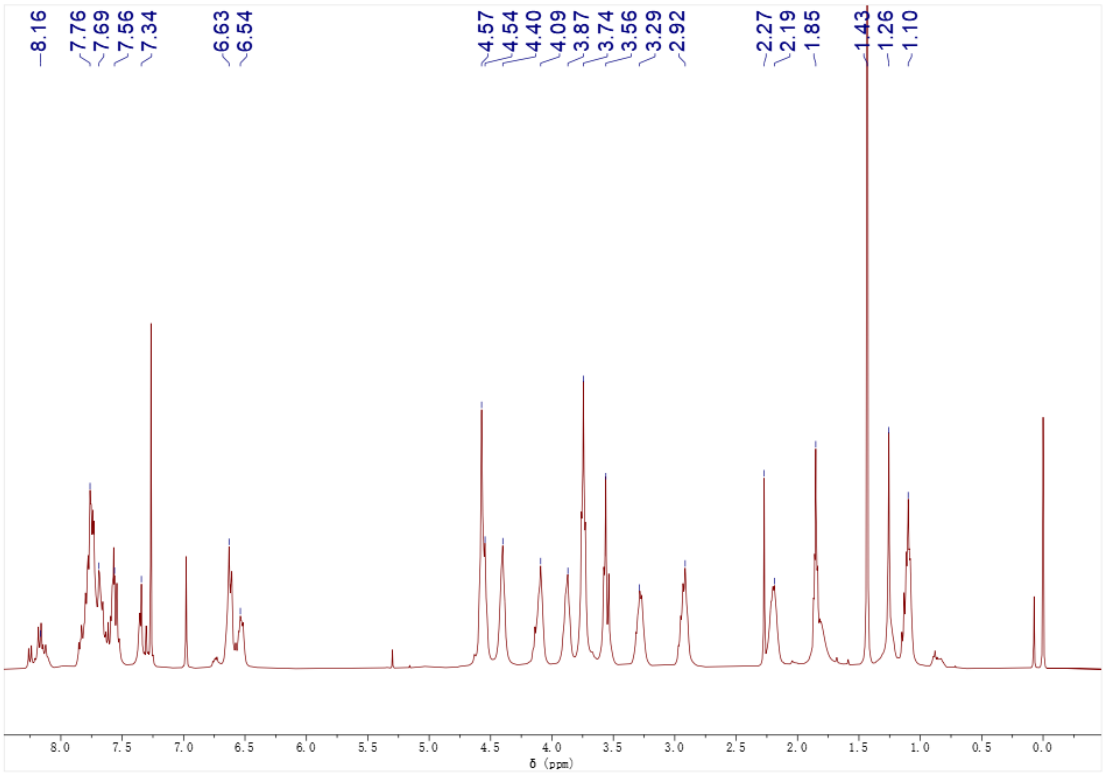


Fig. S8 The ^{1}H NMR spectrum of **P2** in $CDCl_3$.

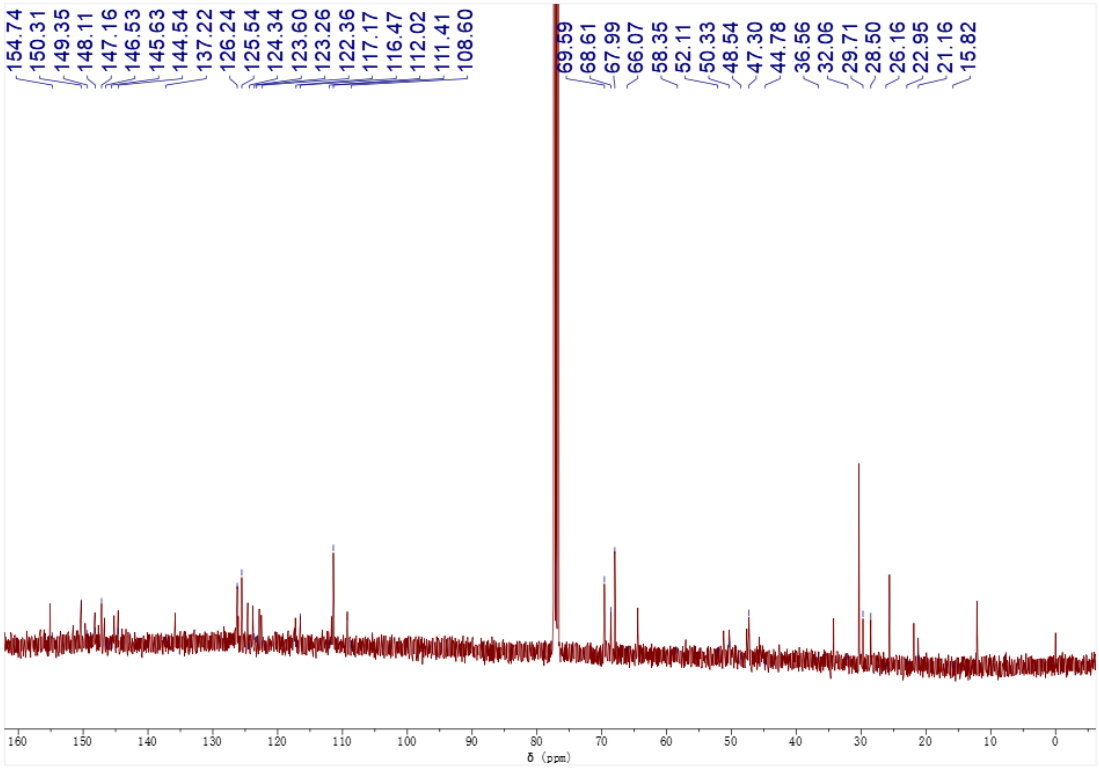


Fig. S9 The ^{13}C NMR spectrum of **P2** in $CDCl_3$.

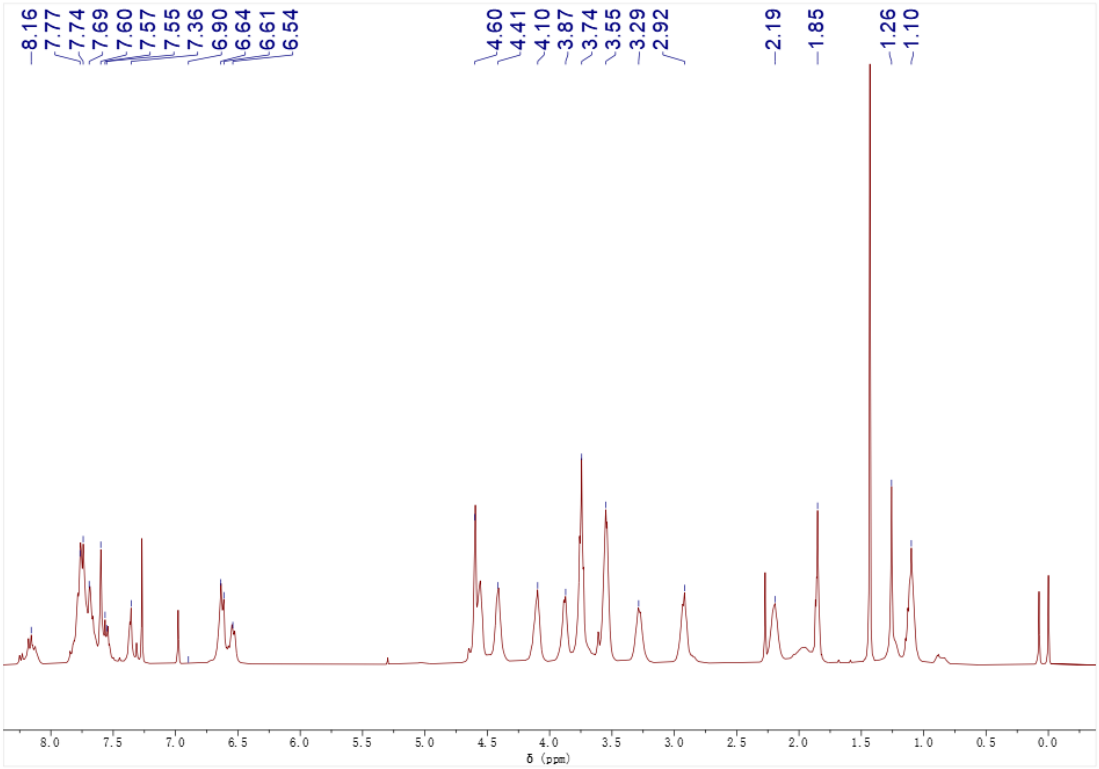


Fig. S10 The ^{1}H NMR spectrum of **P3** in $CDCl_3$.

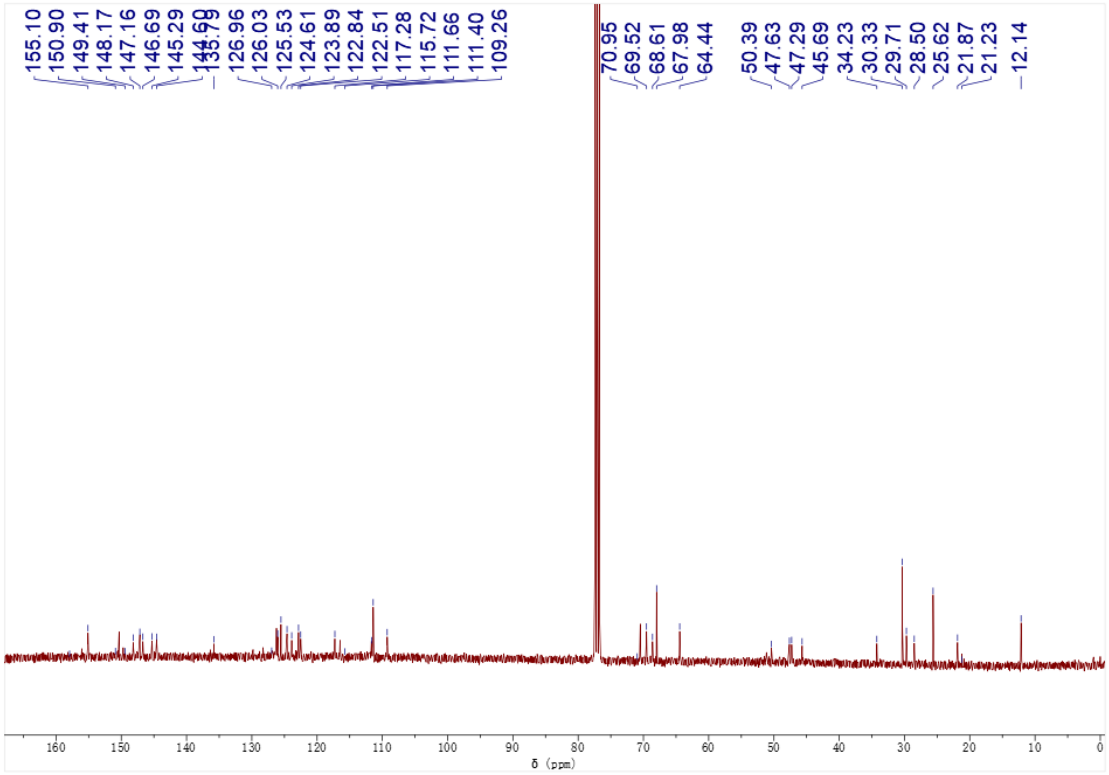


Fig. S11 The ^{13}C NMR spectrum of **P3** in $CDCl_3$.

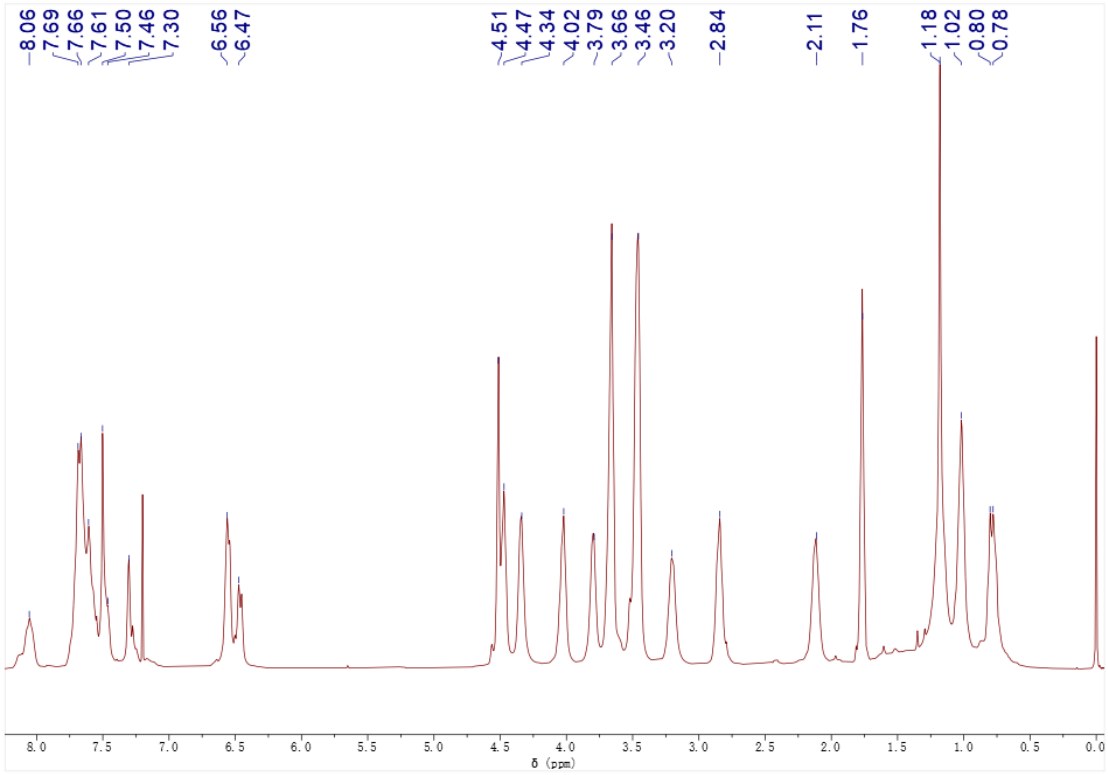


Fig. S12 The ^{1}H NMR spectrum of **P4** in $CDCl_3$.

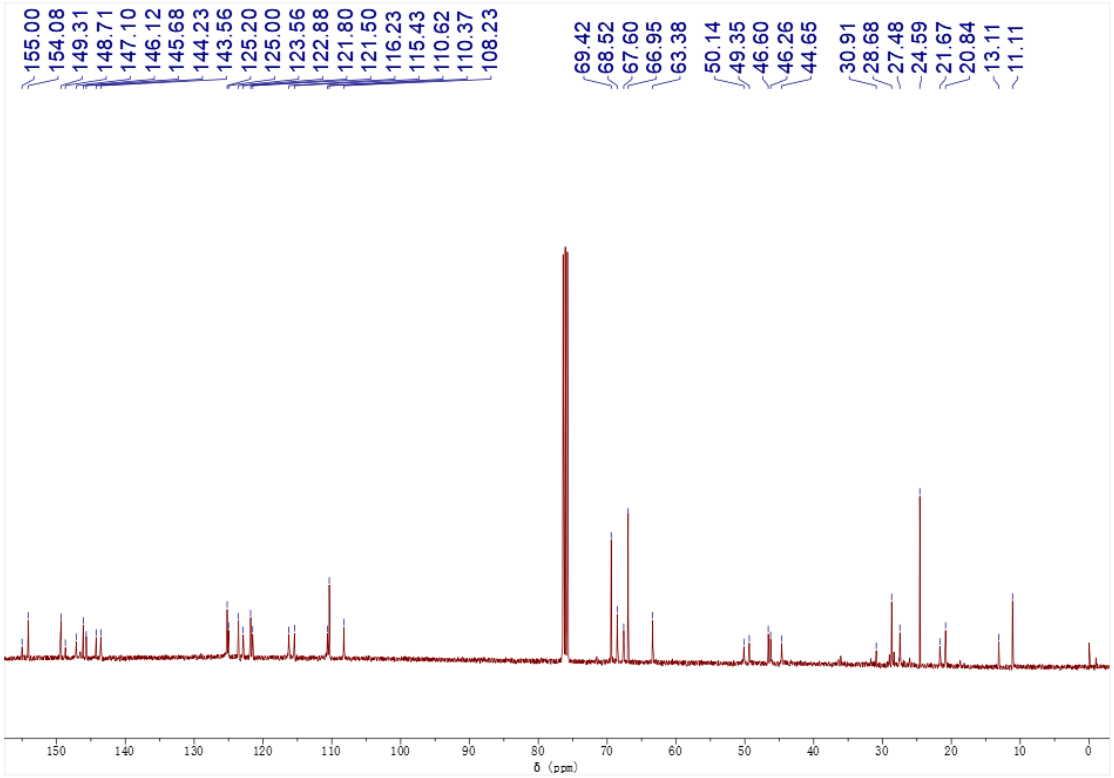


Fig. S13 The ^{13}C NMR spectrum of **P4** in $CDCl_3$.

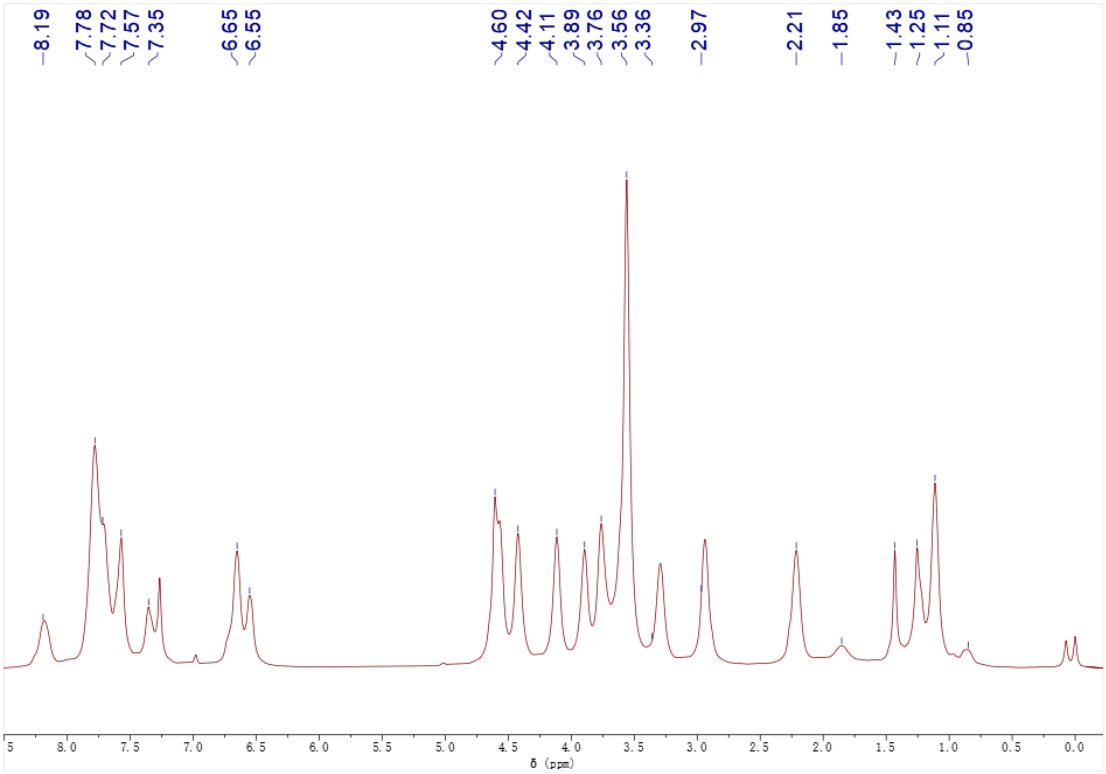


Fig. S14 The ^{1}H NMR spectrum of **P5** in $CDCl_3$.

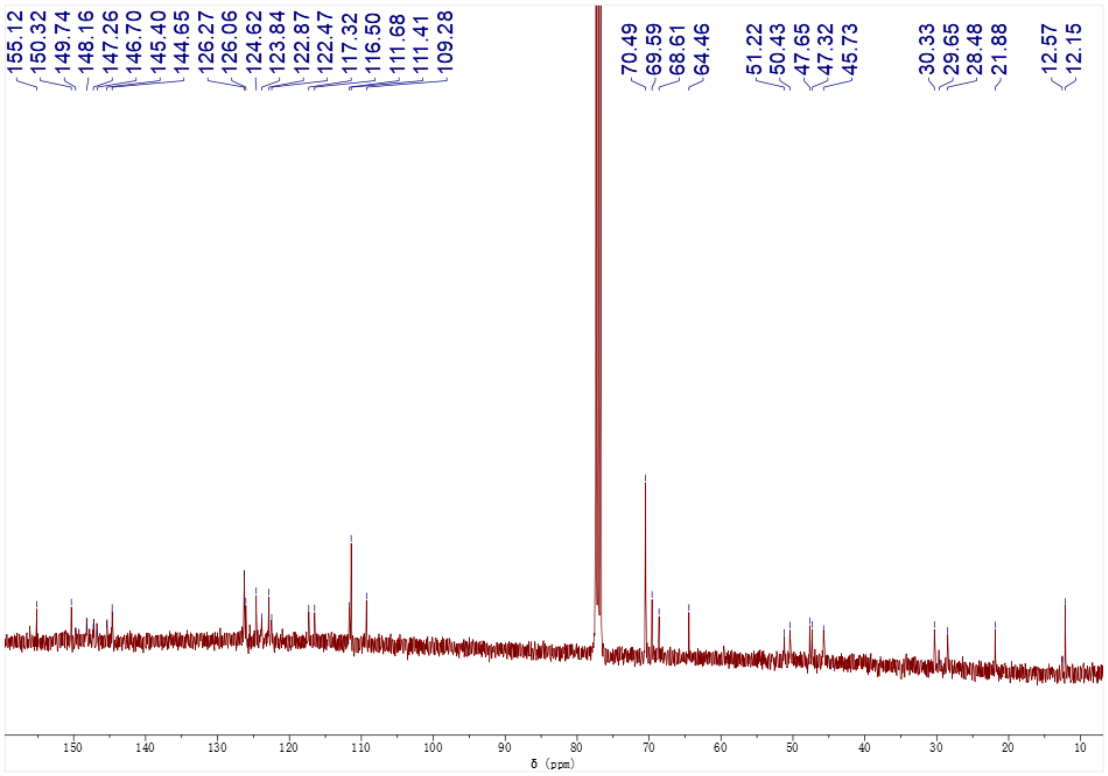


Fig. S15 The ^{13}C NMR spectrum of **P5** in $CDCl_3$.

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