

Supporting Information

Aroylacetylene-Based Amino-Yne Click Polymerization toward Nitrogen-Containing Polymers

Xu Chen,[†] Tianwen Bai,[§] Rong Hu[†], Bo Song,[†] Lin Lu,[†] Jun Ling,[§] Anjun Qin,^{,†} Ben
Zhong Tang^{*,†,‡}*

[†]State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, Center for Aggregation-Induced Emission, South China University of Technology, Guangzhou 510640, China.

[‡]Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, Institute for Advanced Study, and Department of Chemical and Biological Engineering, the Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong 999077, China.

[§]MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China.

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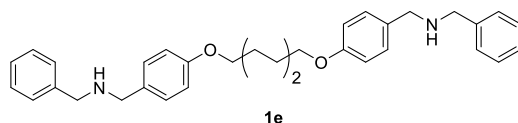
Materials and Instruments

All manipulations were carried out in a glove box or with the standard Schlenk techniques under dry nitrogen. Monomers 1,1'-((hexane-1,6-diylbis(oxy))-bis(4,1-phenylene))-bis(*N*-benzylmethanamine) (**1e**)¹ and **2b-2d**²⁻⁶ are prepared according to the references. *N,N'*-Diethylethylenediamine (**1a**), 1,3-bis(4-piperidyl)propane (**1c**), 4,13-diaza-18-crown-6-ether (**1d**), 1,5-diaminopentane (**1f**) and 2,2-bis(4-aminophenyl)propane (**1g**) were purchased from TCI (Shanghai, China) Co. Ltd., *N,N'*-Diisobutyl-1,6-hexanediamine (**1b**) was purchased from Alfa Aesar (Shanghai, China) Co., Inc. and used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen before use. All other chemicals and reagents were purchased from commercial sources and used as received without further purification. Water was purified with a Millipore filtration system. PBS buffer were purchased from Thermo Fisher Scientific (Shanghai, China). MTT was purchased from Tiangen Biotech (Beijing, China).

¹H and ¹³C NMR spectra were measured on a Bruker AVANCE 400 (400 MHz) or AVANCE DRX 500 (500 MHz) NMR spectrometer (Bruker, Germany) using deuterated chloroform (CDCl₃) or deuterated dimethyl sulfoxide (DMSO-*d*₆) as solvent and tetramethyl silane (TMS, $\delta = 0$) as internal reference. The weight-average molecular weights (M_w) and polydispersity indices ($\bar{D} = M_w/M_n$) of the polymers were measured by Waters 1515 gel permeation chromatography (GPC, Waters Associates, USA) system equipped with a RI detector. DMF containing 0.05 M LiBr was used as the eluent at a flow rate of 1.0 mL min⁻¹. A set of linear polymethylmethacrylate (PMMA) standards covering the M_n range of 10³~10⁷ were utilized for M_w and \bar{D} calibration. Fourier transform infrared (FT-IR) spectra were measured on a Bruker Vector 33 FT-IR (Germany) spectrometer (KBr disk). Thermogravimetric analysis (TGA) was carried out on a Netzsch TG 209 F3 (Germany) at a heating rate of 20 °C/min in a nitrogen flow. The glass transition temperature (T_g) of polymers was characterized by differential scanning calorimetry (DSC 200 F3 Maia, NETZSCH, Germany) in nitrogen flow at a heating rate of 10 °C/min. The absorbance for MTT analysis was recorded on a microplate reader (Thermo Fisher, USA) at a wavelength of 570 nm. Fluorescence spectra were recorded on a Horiba Fluoromax-4 fluorescence spectrophotometer (USA).

Preparation of Monomer 1e

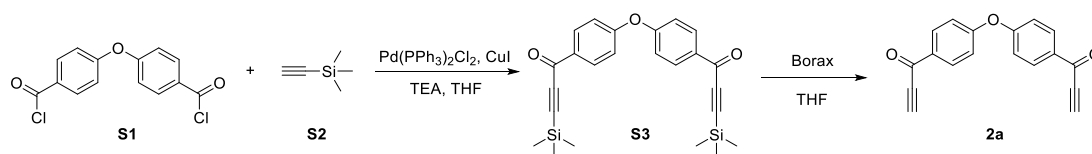
Monomer **1e** was synthesized according to the procedure reported by our group.¹



1,1'-((Hexane-1,6-diylbis(oxy))-bis(4,1-phenylene))-bis(*N*-benzylmethanamine) (1e**):** White solid in 92% yield. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.33 (m, 8H), 7.24 (m, 6H), 6.86 (d, J = 8.7 Hz, 4H), 3.96 (t, J = 6.8 Hz, 4H), 3.79 (s, 4H), 3.74 (s, 4H), 1.81 (m, 4H), 1.61 (s, 2H), 1.54 (m, 4H). ¹³C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 158.14, 140.39, 132.30, 129.30, 128.37, 128.15, 126.89, 114.39, 67.84, 53.06, 52.58, 29.25, 25.89. FT-IR (KBr disk), ν (cm⁻¹): 3341, 3058, 3026, 2938, 2868, 2821, 1609, 1581, 1510, 1474, 1448, 1289, 1250, 1165, 1105, 1025, 824, 730, 697, 609, 513.

Preparation of Monomers 2

Preparation of monomer 2a



Scheme S1. Synthetic routes to monomer **2a**.

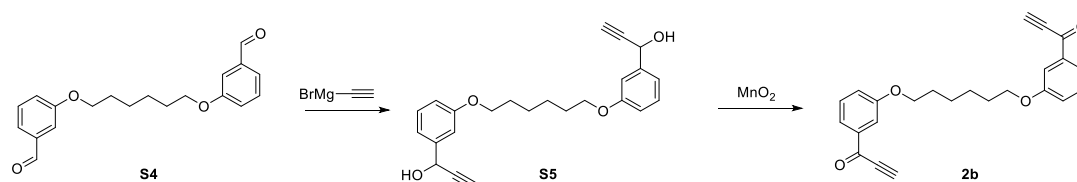
The synthetic routes to monomer **2a** are shown in Scheme S1.^{5,6}

1,1'-(Oxybis(4,1-phenylene))bis(3-(trimethylsilyl)prop-2-yn-1-one) (S3): Into a 250 mL round-bottom flask were added PdCl₂(PPh₃)₂ (140.4 mg, 0.2 mmol), CuI (38.1 mg, 0.2 mmol), **S1** (2.95 g, 10 mmol), and distilled THF (100 mL) under nitrogen. Trimethylsilylacetylene (**S2**, 3.53 mL, 25 mmol) was injected after triethylamine (1.39 mL, 10 mmol) was added into the solution. The mixture was stirred at room temperature for 2 h, and then the formed precipitates were removed by filtration. After concentrated by a rotary evaporator under reduced pressure, the crude product was purified by a silica gel column chromatography using petroleum ether/ethyl acetate (20:1 v/v) as eluent. White solid of **S3** was obtained in 31% yield (1.3 g). ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 8.18 (d, 4H), 7.12 (d, 4H), 0.32 (s, 18H).

1,1'-(Oxybis(4,1-phenylene))bis(prop-2-yn-1-one) (2a): In 3 mL THF solution of **S3** (83.7 mg, 0.2 mmol) was slowly added 0.3 mL aqueous solution of borax (0.01

M). The reaction was monitored with TLC, and **S3** can be totally consumed after 15 min. Then, the solution was quenched by adding 10 mL of water, and extracted with dichloromethane (DCM) for three times. The organic layer was dried over anhydrous Na₂SO₄. After filtration and solvent evaporation, crude product was purified by a silica gel column chromatography using petroleum ether/ethyl acetate (10:1, v/v) as eluent. White powder of compounds **2a** (47 mg) was obtained in 86% yield. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 8.21 (d, 4H), 7.14 (d, 4H), 3.44 (s, 2H). ¹³C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 175.81, 161.12, 132.35, 132.25, 118.98, 80.48, 80.13. FT-IR (KBr disk), ν (cm⁻¹): 3195, 2090, 1639, 1585, 1497, 1312, 1243, 1162, 1004, 766.

Preparation of monomer **2b**



Scheme **S2**. Synthetic routes to monomer **2b**.

Monomer **2b** was synthesized according to the procedures reported by our group,^{2,4} and the synthetic routes are shown in Scheme **S2**.

1,1'-((Hexane-1,6-diylbis(oxy))bis(3,1-phenylene))bis(prop-2-yn-1-ol) (**S5**):

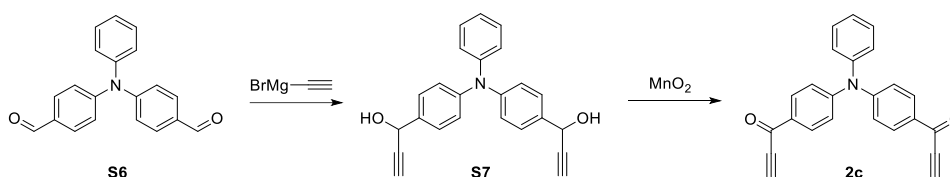
Into the solution of **S4** was slowly added ethynylmagnesium bromide (0.5 M in THF, 24 mL, 12 mmol) at 0 °C under N₂. The reaction mixture was stirred at room temperature for 12 h, and then quenched by saturated aqueous ammonium chloride solution. The crude product was obtained by extracting the solution with DCM for several times, and the organic phase was dried over anhydrous NaSO₄. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using petroleum ether/ethyl acetate (3:2, v/v) as eluent and 1.07 g of white solid was obtained in 71% yield. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.29 (m, 2H), 7.11 (m, 4H), 6.87 (m, 2H), 5.43 (d, J = 2.1 Hz, 2H), 3.99 (t, J = 6.4 Hz, 4H), 2.66 (d, J = 2.3 Hz, 2H), 1.83 (m, 4H), 1.55 (m, 4H).

1,1'-((Hexane-1,6-diylbis(oxy))bis(3,1-phenylene))bis(prop-2-yn-1-one) (**2b**):

Into the DCM (80 mL) solution of **S5** was added activated MnO₂ (10.4 g, 120 mmol) and reaction was monitored by TLC. after **S5** was consumed at 2 h, excess amount of MnO₂ power was removed by filtration through a pad of celite. The crude product was

further purified by a silica gel column chromatography using petroleum ether/dichloromethane (1:1, v/v) as eluent and 850 mg of white solid **2b** was obtained in 81% yield. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.78 (m, 2H), 7.62 (m, 2H), 7.40 (t, $J = 8.2$, 2H), 7.17 (m, 2H), 4.04 (t, $J = 6.5$, 4H), 3.42 (s, 2H), 1.85 (m, 4H), 1.57 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 177.24, 159.33, 137.47, 129.73, 122.91, 121.90, 113.49, 80.58, 80.37, 68.12, 29.08, 25.83. FT-IR (KBr disk), ν (cm^{-1}): 3213, 2947, 2911, 2868, 2094, 1632, 1592, 1475, 1441, 1397, 1347, 1322, 1269, 1207, 1153, 1072, 1022, 871, 760, 736, 673, 632, 479.

Preparation of monomer **2c**



Scheme **S3**. Synthetic routes to monomer **2c**.

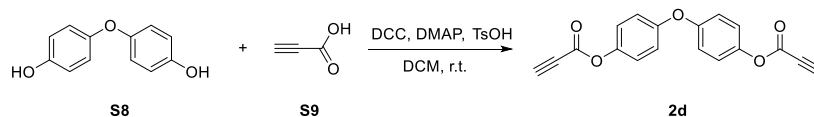
Monomer **2c** was synthesized in a similar procedure as **2b**, and the synthetic routes are shown in Scheme **S3**.

1,1'-((Phenylazanediyl)bis(4,1-phenylene))bis(prop-2-yn-1-ol) (S7): Yellow solid, 85% yield. ^1H NMR (500 MHz, $\text{DMSO}-d_6$), δ (TMS, ppm): 7.38 (m, 4H), 7.30 (m, 2H), 7.04 (m, 1H), 6.99 (m, 6H), 5.98 (d, $J = 5.9\text{ Hz}$, 2H), 5.30 (m, 2H), 3.48 (d, $J = 2.3\text{ Hz}$, 2H).

1,1'-((Phenylazanediyl)bis(4,1-phenylene))bis(prop-2-yn-1-one) (2c): Yellow solid, 71% yield. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.06 (d, $J = 8.9\text{ Hz}$, 4H), 7.40 (m, 2H), 7.28 (m, 1H), 7.16 (m, 6H), 3.38 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 175.55, 152.00, 145.31, 131.46, 131.05, 130.18, 127.16, 126.45, 122.32, 80.36, 80.30. FT-IR (KBr disk), ν (cm^{-1}): 3270, 3226, 2094, 1639, 1582, 1503, 1426, 1316, 1257, 1172, 1019, 999, 845, 757, 694, 529.

Preparation of monomer **2d**

Monomer **2d** was synthesized following the reported procedure.³ The synthetic route is shown in Scheme **S4**.



Scheme **S4**. Synthetic route to monomer **2d**.

Oxybis(4,1-phenylene)dipropiolate (2d): Into a 250 mL two-necked round bottom flask were added **S8** (10 mmol, 2.02 g), *N,N*-dicyclohexylcarbodiimide (DCC, 30 mmol, 6.19 g), 4-dimethylaminopyridine (DMAP, 4 mmol, 489 mg) and 4-methylbenzenesulfonic acid (TsOH, 4 mmol, 689 mg). The flask was evacuated under vacuum and flushed with dry nitrogen for three times and then 80 mL DCM was added. Then **S9** (30 mmol, 1.85 mL) in 20 mL DCM was added into the system dropwise. After finishing the addition, the mixture was stirred at room temperature overnight. Afterward, the solvent was evaporated and the crude product was purified by a silica gel column chromatography using petroleum ether/dichloromethane (7:3, v/v) as eluent. White solid **2d** was obtained in 75% yield. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.13 (d, *J* = 9.1 Hz, 4H), 7.03 (d, *J* = 9.1 Hz, 4H), 3.08 (s, 2H). ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 155.11, 151.05, 145.36, 122.59, 119.73, 74.17. FT-IR (KBr disk), ν (cm⁻¹): 3416, 3273, 3240, 3072, 2127, 1715, 1591, 1494, 1209, 1175, 1092, 1011, 915, 843, 750, 699, 677, 614, 582, 516.

Optimization of Polymerization Conditions

Table S1. Effect of solvent on the polymerization of **1a** and **2a**.^a

entry	solvent	yield (%)	<i>M_w</i> ^b	<i>Đ</i> ^b
1	THF	99	36 900	1.55
2	1,4-dioxane	86	38 000	1.80
3	acetone	87	27 900	1.82
4	DCM	98	22 200	1.82

^a Carried out under nitrogen at 25 °C for 1 h; [M] = 0.1 M. ^b Determined by gel-permeation chromatography (GPC) in *N,N*-dimethylformamide (DMF) containing 0.05 M LiBr using linear PMMA for calibration.

Table S2. Effect of monomer concentration on the polymerization of **1a** and **2a**.^a

entry	[M] (mol/L)	yield (%)	M_w^b	\bar{D}^b
1	0.05	99	12 500	1.62
2	0.1	98	22 200	1.85
3	0.2	98	31 400	1.98
4	0.25	99	78 300	2.58

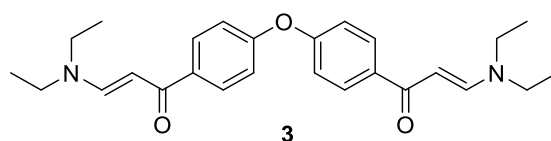
^a Carried out under nitrogen in anhydrous DCM at 25 °C for 1 h. ^b Determined by GPC in DMF containing 0.05 M LiBr using linear PMMA for calibration.

Table S3. Time course of the polymerization of **1a** and **2a**.^a

entry	time (h)	yield (%)	M_w^b	\bar{D}^b
1	0.5	31	8 800	1.41
2	1	98	12 800	1.62
3	2	99	24 000	1.93
4	3	98	20 600	1.90

^a Carried out under nitrogen in anhydrous DCM at 25 °C, [M] = 0.05 M. ^b Determined by GPC in DMF containing 0.05 M LiBr using linear PMMA for calibration.

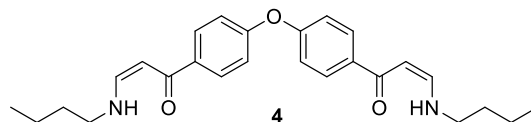
Model Reaction



(2*E*,2'*E*)-1,1'-(Oxybis(4,1-phenylene))bis(3-(diethylamino)prop-2-en-1-one)

(3): Into a 10 mL tube were added **2a** (27.4 mg, 0.1 mmol), diethylamine (22.7 μ L, 0.22 mmol) and 2 mL DCM. Then the solution was stirred at room temperature for 2 h. After removing the solvent with a rotary evaporator under reduced pressure, model compound **3** was obtained as yellow solid in 98% yield and further purification is needn't. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.91 (d, J = 8.7 Hz, 4H), 7.83 (d, J = 12.5 Hz, 2H), 7.04 (d, J = 8.7 Hz, 4H), 5.76 (d, J = 12.5 Hz, 2H), 3.34 (s, 8H),

1.25 (t, $J = 7.0$ Hz, 12H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 187.46, 158.98, 152.35, 136.16, 129.50, 118.33, 91.29, 50.61, 42.85, 14.80, 11.60. FT-IR (KBr disk), ν (cm^{-1}): 3064, 2975, 2932, 2873, 1639, 1587, 1547, 1500, 1470, 1361, 1282, 1217, 1163, 1054, 880, 777.

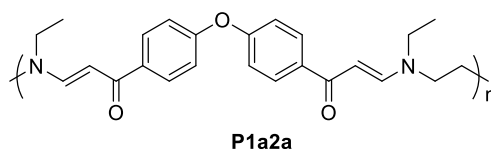


(2Z,2'Z)-1,1'-(Oxybis(4,1-phenylene))bis(3-(butylamino)prop-2-en-1-one) (4):

Into a 10 mL tube were added **2a** (27.4 mg, 0.1 mmol), *n*-butylamine (21.8 μL , 0.22 mmol) and DCM (2 mL). The solution was stirred at room temperature for 2 h. After removing the solvent with a rotary evaporator under reduced pressure, model compound **4** was obtained as yellow solid in 99% yield and further purification is needn't. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 10.33 (m, 2H), 7.88 (d, $J = 8.8$ Hz, 4H), 7.03 (d, $J = 8.8$ Hz, 4H), 6.94 (dd, $J = 12.9, 7.4$ Hz, 2H), 5.65 (d, $J = 7.4$ Hz, 2H), 3.27 (q, $J = 6.7$ Hz, 4H), 1.65 – 1.54 (m, 4H), 1.50 – 1.33 (m, 4H), 0.95 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 188.63, 158.96, 154.31, 135.32, 129.02, 118.47, 89.60, 49.00, 33.07, 19.74, 13.67. FT-IR (KBr disk), ν (cm^{-1}): 3394, 3243, 2955, 2928, 2867, 1637, 1588, 1550, 1480, 1370, 1286, 1245, 1217, 1155, 1054, 1009, 881, 864, 848, 774, 730.

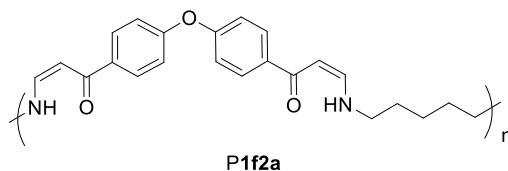
Typical Procedures for Polymerization

Without additional notes, all the polymerization reactions were conducted under a nitrogen atmosphere using standard Schlenk technique. A typical procedure of the polymerization of **P1a2a** and **P1f2a** are given below as examples.



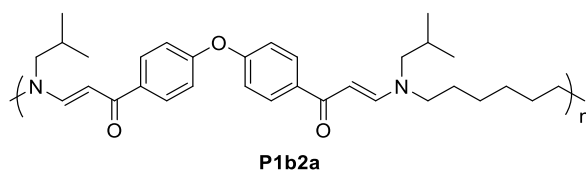
P1a2a. Into a 10 mL Schlenk tube, **2a** (27.4 mg, 0.1 mmol) was added, followed by 2 mL of DCM, then *N,N*-diethylethylenediamine (**1a**, 14.3 μL , 0.1 mmol) was added. The solution was stirred at room temperature for 2 h. Afterward, the polymer was precipitated by adding the solution dropwise into 125 mL of hexane under vigorous stirring. The precipitates were filtered and washed with hexane and dried in vacuum at 40 $^{\circ}\text{C}$ to a constant weight. A slightly-yellow solid was obtained in 99%

yield. M_w : 24 000, D : 1.93. FT-IR (KBr disk), ν (cm^{-1}): 3061, 2972, 2931, 2871, 1642, 1588, 1544, 1498, 1467, 1361, 1282, 1210, 1160, 1048, 877, 776. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.87 (d, 4H), 7.76 (d, 2H), 6.98 (d, 4H), 5.84 (s, 2H), 3.50 (s, 4H), 3.35 (d, 4H), 1.24 (t, 6H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 187.46, 159.16, 152.15, 135.52, 129.66, 118.44, 92.54, 51.46, 44.11, 14.65, 11.67.



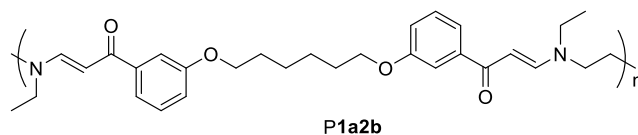
P1f2a. Into a 10 mL Schlenk tube, **2a** (27.4 mg, 0.1 mmol) was added, followed by 2 mL of dichloromethane, then 1,5-pentanediamine (**1f**, 11.8 μL , 0.1 mmol) was added. The solution was stirred at room temperature for 0.5 h. To terminate the polymer, 20 μL of *n*-propylamine was added and reacted for additional 0.5 h. The polymer was precipitated by adding the solution dropwise into 125 mL of hexane under vigorous stirring. The precipitates were filtered and washed with hexane and dried in vacuum at 40 $^{\circ}\text{C}$ to a constant weight. Slightly yellow solid was obtained in 93% yield. M_w : 12 300, D : 1.58. FT-IR (KBr disk), ν (cm^{-1}): 3267, 3056, 2934, 2860, 1631, 1588, 1540, 1480, 1381, 1279, 1236, 1159, 1054, 1008, 880, 848, 774, 730. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 10.44 – 10.20 (m, 2H), 7.87 (d, 4H), 7.03 (d, 4H), 6.97 – 6.88 (m, 2H), 5.65 (d, J = 7.4 Hz, 2H), 3.28 (d, 4H), 1.70 – 1.57 (m, 4H), 1.47 (d, 2H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 188.77, 159.00, 154.23, 135.23, 129.06, 118.49, 89.87, 49.04, 30.74, 23.62.

Characterization Data for Poly(β -enaminone)s

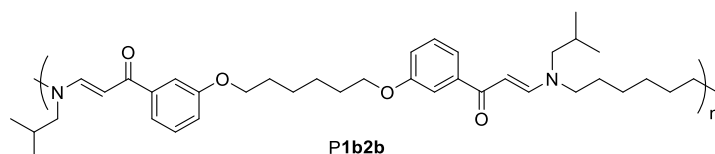


P1b2a. White solid was obtained in 99% yield. M_w : 19 900, D : 1.65. FT-IR (KBr disk), ν (cm^{-1}): 3062, 2957, 2898, 1641, 1587, 1547, 1500, 1467, 1366, 1282, 1235, 1215, 1162, 1052, 878, 776. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.95 – 7.69 (m, 6H), 7.03 (d, J = 8.7 Hz, 4H), 5.72 (d, J = 10.6 Hz, 2H), 3.26 (d, J = 24.7 Hz, 4H), 3.05 (s, 4H), 2.12 (s, 2H), 1.65 (s, 4H), 1.37 (s, 4H), 0.92 (d, J = 6.1 Hz, 12H). ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 187.43, 158.99, 153.58, 136.11, 129.51,

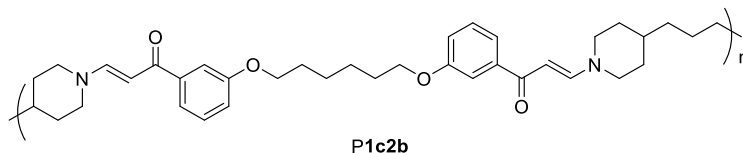
135.79, 129.62, 129.31, 128.92, 128.71, 128.20, 127.77, 127.25, 118.36, 114.83, 92.58, 67.91, 58.99, 50.55, 29.20, 25.90.



P1a2b. Light yellow solid was obtained in 82% yield. M_w : 6 200, D : 1.61. FT-IR (KBr disk), ν (cm^{-1}): 3066, 2934, 2864, 1644, 1534, 1464, 1434, 1361, 1276, 1247, 1189, 1041, 978, 768, 734. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.75 (s, 2H), 7.54 – 7.31 (m, 4H), 7.32 – 7.15 (m, 2H), 7.04 – 6.90 (m, 2H), 5.81 (d, J = 12.4 Hz, 2H), 4.00 (t, J = 6.4 Hz, 4H), 3.48 (s, 4H), 3.33 (d, J = 6.9 Hz, 4H), 1.80 (d, 4H), 1.53 (s, 4H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 188.65, 159.16, 152.20, 141.60, 129.17, 119.84, 117.87, 113.06, 93.28, 67.97, 51.76, 44.12, 29.24, 25.91, 15.17, 11.65.

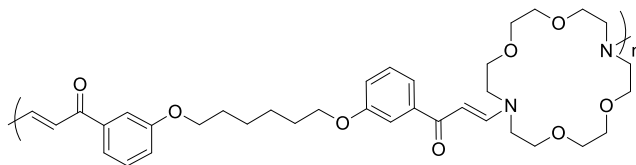


P1b2b. White solid was obtained in 59% yield. M_w : 17 000, D : 1.61. FT-IR (KBr disk), ν (cm^{-1}): 3071, 2935, 2865, 1644, 1550, 1465, 1367, 1277, 1247, 1044, 984, 872, 767, 734, 684, 663. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.78 (d, 2H), 7.50 – 7.32 (m, 4H), 7.28 (m, 2H), 6.98 (m, 2H), 5.71 (d, J = 11.5 Hz, 2H), 4.02 (t, J = 6.4 Hz, 4H), 3.24 (d, 4H), 3.04 (s, 4H), 2.00 – 1.25 (m, 18H), 0.91 (s, 12H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 188.65, 159.10, 153.67, 142.23, 128.99, 119.74, 117.48, 113.07, 92.53, 91.94, 67.97, 64.19, 56.75, 56.15, 48.91, 29.26, 27.97, 26.93, 26.40, 26.14, 25.92, 20.63, 20.38, 19.84.



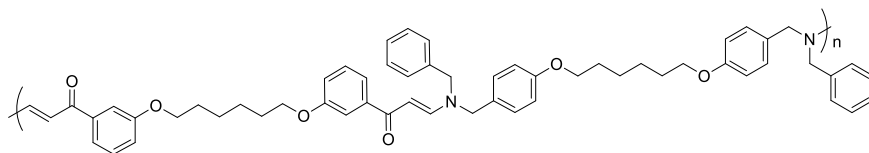
P1c2b. White solid was obtained in 91% yield. M_w : 14 800, D : 1.30. FT-IR (KBr disk), ν (cm^{-1}): 3068, 2930, 2854, 1639, 1550, 1454, 1367, 1270, 1249, 1180, 1046, 964, 768. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.76 (d, J = 12.4 Hz, 2H), 7.43 (d, J = 6.5 Hz, 4H), 7.29 (t, J = 7.4 Hz, 2H), 6.98 (d, J = 8.9 Hz, 2H), 5.80 (d, J = 12.4 Hz, 2H), 4.02 (t, J = 6.3 Hz, 4H), 3.66 (s, 4H), 3.31 – 2.72 (m, 4H), 1.88 – 1.69 (m, 8H), 1.61 – 1.43 (d, J = 21.9 Hz, 6H), 1.38 – 1.14 (m, 10H). ^{13}C NMR (100 MHz, CDCl_3),

δ (TMS, ppm): 188.81, 159.08, 153.03, 142.16, 129.04, 119.74, 117.48, 113.06, 91.53, 67.96, 36.32, 35.62, 29.26, 25.91, 23.54.



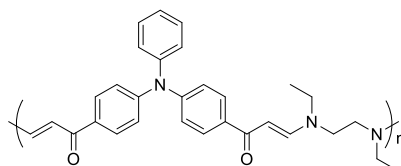
P1d2b

P1d2b. Yellow solid was obtained in 81% yield. M_w : 13 400, D : 1.09. FT-IR (KBr disk), ν (cm^{-1}): 3066, 2931, 2861, 1641, 1547, 1465, 1436, 1361, 1276, 1256, 1180, 1106, 1065, 981, 770, 738. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.79 (d, J = 12.6 Hz, 2H), 7.41 (d, 4H), 7.33 – 7.23 (m, 2H), 6.99 (m, 2H), 5.77 (d, J = 12.6 Hz, 2H), 4.01 (t, J = 6.4 Hz, 4H), 3.62 (t, 24H), 1.82 (s, 4H), 1.63 – 1.48 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 188.51, 159.10, 153.53, 141.93, 129.05, 119.79, 117.57, 113.11, 92.72, 70.87, 67.95, 56.78, 49.95, 29.24, 25.90.



P1e2b

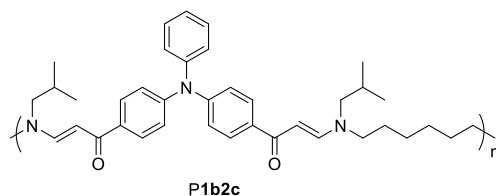
P1e2b. Light yellow solid was obtained in 77% yield. M_w : 22 500, D : 1.86. FT-IR (KBr disk), ν (cm^{-1}): 3061, 3028, 2934, 2860, 1642, 1547, 1510, 1443, 1359, 1242, 1170, 992, 877, 770, 733, 696. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 8.14 (d, J = 12.5 Hz, 2H), 7.50 – 7.23 (m, 12H), 7.19 (d, J = 6.9 Hz, 4H), 7.11 (d, J = 8.2 Hz, 4H), 6.98 (m, 2H), 6.86 (d, J = 8.5 Hz, 4H), 5.98 (s, 2H), 4.36 (s, 8H), 4.07 – 3.88 (m, 8H), 1.81 (s, 8H), 1.54 (d, 8H). ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 189.00, 159.13, 154.07, 141.90, 129.36, 129.09, 128.94, 128.20, 127.84, 127.39, 119.88, 117.88, 114.86, 113.00, 93.14, 67.96, 67.94, 58.96, 50.69, 29.27, 29.24, 25.94, 25.56.



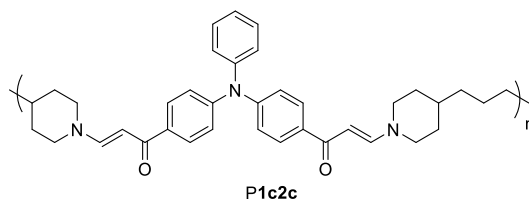
P1a2c

P1a2c. Yellow solid was obtained in 99% yield. M_w : 15 300, D : 1.68. FT-IR (KBr disk), ν (cm^{-1}): 3059, 2974, 2932, 2871, 1638, 1590, 1540, 1507, 1468, 1363,

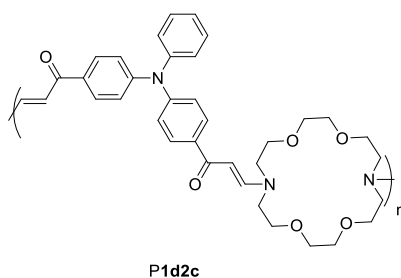
1276, 1213, 1175, 1051, 979, 780, 699, 520. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.93 – 7.44 (d, 6H), 7.33 (m, 1H), 7.20 – 6.88 (m, 8H), 5.82 (d, $J = 12.0$ Hz, 2H), 3.49 (s, 4H), 3.35 (s, 4H), 1.45 – 1.01 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 187.47, 151.84, 149.87, 146.46, 134.25, 129.65, 128.99, 126.12, 124.74, 122.55, 92.63.



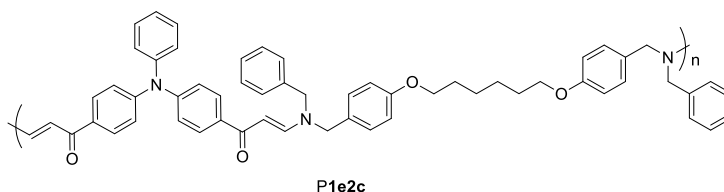
P1b2c. Yellow solid was obtained in 99% yield. M_w : 25 800, D : 1.62. FT-IR (KBr disk), ν (cm^{-1}): 3061, 2957, 2867, 1638, 1587, 1541, 1507, 1467, 1366, 1276, 1216, 1173, 1053, 982, 778, 697, 520. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.91 – 7.67 (m, 6H), 7.40 – 7.23 (d, 1H), 7.22 – 7.00 (m, 8H), 5.72 (d, $J = 12.4$ Hz, 2H), 3.38 – 3.13 (m, 4H), 3.04 (s, 4H), 2.26 – 1.99 (m, 2H), 1.64 (s, 4H), 1.35 (s, 4H), 0.91 (d, 12H). ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 187.37, 153.25, 149.68, 146.69, 134.83, 129.56, 128.84, 125.96, 124.48, 122.58, 91.98, 91.33, 64.18, 56.77, 56.17, 48.97, 29.12, 27.97, 26.98, 26.42, 26.17, 20.38, 19.85.



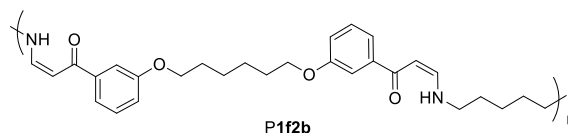
P1c2c. Yellow solid was obtained in 99% yield. M_w : 6 290, D : 1.25. FT-IR (KBr disk), ν (cm^{-1}): 3059, 2925, 2850, 1637, 1587, 1541, 1505, 1454, 1369, 1272, 1213, 1173, 1058, 964, 777, 699, 529. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.78 (m, 6H), 7.29 (m, 1H), 7.19 – 7.00 (m, 8H), 5.80 (d, $J = 12.3$ Hz, 2H), 3.66 (s, 4H), 3.34 – 2.83 (m, 4H), 1.77 (d, 4H), 1.50 (s, 2H), 1.41 – 1.15 (m, 10H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 187.71, 152.66, 149.70, 146.71, 134.85, 129.55, 128.82, 125.89, 124.43, 122.63, 91.07, 44.17, 36.34, 35.64, 31.43, 23.54.



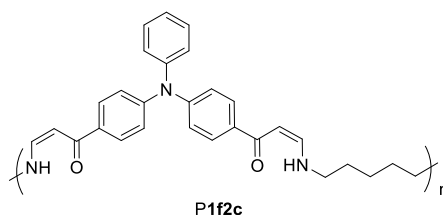
P1d2c. Yellow solid was obtained in 86% yield. M_w : 20 900, D : 1.78. FT-IR (KBr disk), ν (cm^{-1}): 3059, 2865, 1637, 1587, 1540, 1057, 1364, 1276, 1209, 1173, 1110, 1056, 978, 783, 699, 526. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.78 (t, J = 9.9 Hz, 6H), 7.29 (m, 1H), 7.09 (m, 8H), 5.77 (d, J = 12.5 Hz, 2H), 3.63 (t, 24H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 187.39, 153.11, 149.78, 146.61, 134.60, 129.60, 128.93, 126.02, 124.58, 122.58, 92.26, 70.89, 67.80, 56.79, 49.92.



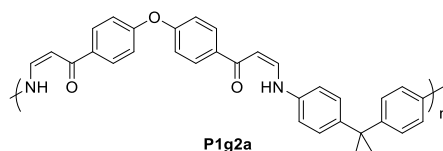
P1e2c. Light yellow solid was obtained in 95% yield. M_w : 24 300, D : 1.82. FT-IR (KBr disk), ν (cm^{-1}): 3061, 3031, 2937, 2861, 1639, 1587, 1544, 1508, 1448, 1361, 1274, 1203, 1172, 1052, 981, 894, 841, 781, 741, 697, 519. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 8.13 (d, J = 12.5 Hz, 2H), 7.75 (d, 4H), 7.42 – 7.26 (m, 8H), 7.19 (d, 4H), 7.15 – 6.98 (m, 11H), 6.86 (d, J = 8.2 Hz, 4H), 5.96 (s, 2H), 4.58 – 4.19 (m, 8H), 3.96 (t, 4H), 1.81 (s, 4H), 1.54 (s, 4H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 187.80, 153.65, 149.79, 146.59, 134.54, 129.56, 129.23, 128.94, 128.88, 127.77, 127.29, 125.99, 124.53, 122.55, 114.80, 92.67, 67.89, 58.96, 50.66, 29.20, 25.90.



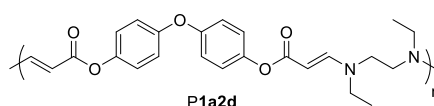
P1f2b. White solid, yield 90%. M_w : 22 700, D : 1.88. FT-IR (KBr disk), ν (cm^{-1}): 3270, 3064, 2935, 2863, 1631, 1585, 1548, 1497, 1470, 1383, 1267, 1179, 1022, 763, 683. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 10.35 (m, 2H), 7.41 (d, J = 8.5 Hz, 4H), 7.28 (d, 2H), 7.33 – 7.24 (m, 2H), 6.92 (m, 2H), 5.67 (d, J = 7.4 Hz, 2H), 4.01 (t, 4H), 3.26 (m, 4H), 1.81 (d, 4H), 1.68 – 1.49 (m, 8H), 1.50 – 1.35 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3), δ (TMS, ppm): 189.67, 159.19, 154.35, 141.20, 129.19, 119.38, 117.82, 112.33, 90.30, 67.95, 49.06, 30.74, 29.23, 25.90, 23.64.



P1f2c. Yellow solid was obtained in 97% yield. M_w : 15 900, D : 1.63. FT-IR (KBr disk), ν (cm^{-1}): 3275, 3035, 2934, 2861, 1631, 1588, 1481, 1380, 1273, 1173, 1051, 777, 728, 699, 522. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 10.29 (m, 2H), 7.76 (m, 4H), 7.29 (m, 2H), 7.15 – 7.09 (m, 3H), 7.09 – 7.01 (m, 4H), 6.90 (m, 2H), 5.63 (d, J = 7.4 Hz, 2H), 3.35 – 3.16 (m, 4H), 1.63 (m, 4H), 1.51 – 1.38 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 188.85, 153.92, 149.66, 146.63, 133.97, 129.58, 128.39, 126.00, 124.50, 122.70, 89.89, 49.02, 30.78, 23.63.

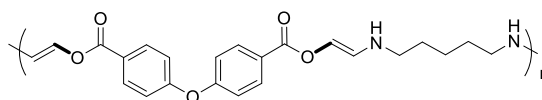


P1g2a. Into a 10 mL Schlenk tube, **2a** (27.4 mg, 0.1 mmol) was added, followed by 1 mL of THF, then 2,2-bis(4-aminophenyl)propane (**1g**, 22.6 mg, 0.1 mmol) in THF solution (1 mL) was added. The solution was stirred at room temperature for 14 h. The polymer was precipitated by adding the solution dropwise into 125 mL of hexane under vigorous stirring. The precipitates were filtered and washed with hexane and dried in vacuum at 40 °C to a constant weight. Yellow solid was obtained in 40% yield. M_w : 19 100, D : 2.16. FT-IR (KBr disk), ν (cm^{-1}): 3198, 2921, 2847, 1641, 1587, 1548, 1497, 1454, 1367, 1309, 1240, 1206, 1159, 1055, 1005, 859, 882, 845, 773, 614, 502. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 12.12 (d, J = 11.9 Hz, 2H), 7.96 (d, J = 7.6 Hz, 2H), 7.49 (m, 2H), 7.21 (d, J = 8.7 Hz, 2H), 7.09 (m, 2H), 7.03 (m, 2H), 5.98 (d, J = 7.7 Hz, 2H), 1.67(d, 6H).



P1a2d was prepared in similar procedures as **P1a2a**. Into a 10 mL Schlenk tube, **2d** (30.6 mg, 0.1 mmol) was added, followed by 2 mL of DCM, then *N,N*-diethylethylenediamine (**1a**, 14.3 μL , 0.1 mmol) was added. The solution was stirred at room temperature for 2 h. To terminate the reaction, 20 μL of diethylamine was added and reacted for 0.5 h. The polymer was precipitated by adding the solution dropwise into 125 mL of hexane under vigorous stirring. The precipitates were filtered and washed with hexane and dried in vacuum at 40 °C to a constant weight. A white solid was obtained in 98% yield. M_w : 11 000, D : 1.54. FT-IR (KBr disk), ν (cm^{-1}): 3314, 3045, 2930, 2857, 1695, 1609, 1493, 1376, 1314, 1242, 1188, 1110, 975, 918, 847, 776, 512. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.68 – 7.39 (m, 2H),

7.05 (d, 4H), 7.03 – 6.91 (d, 4H), 4.78 (d, $J = 12.7$, 2H), 3.35 (m, 8H), 1.37 – 1.16 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 167.89, 154.26, 152.08, 146.85, 123.08, 119.34, 84.48, 51.28, 43.77, 14.47, 11.32.



P1f2d

P1f2d was prepared with similar procedures as **P1f2a**. Light yellow solid was obtained in 96% yield. M_w : 13 400, D : 1.73. FT-IR (KBr disk), ν (cm^{-1}): 2975, 2934, 2875, 1703, 1605, 1494, 1359, 1186, 1096, 977, 852, 783, 516. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.96 (s, Z-N-H, 0.4H), 7.65 (s, E-N-H, 0.6H), 7.07 – 6.96 (d, 4H), 7.02 – 6.95 (m, E-C=CH-N, 0.6H), 6.83 – 6.95 (m, 4H), 6.82 – 6.73 (m, Z-C=CH-N, 0.4H), 4.88 (d, E-COCH=C, 0.6H), 4.72 – 4.56 (m, Z-COCH=C, 0.4H), 3.37 – 2.65 (m, 2H), 1.96 – 1.19 (m, 6H).

FT-IR Spectra of Polymers

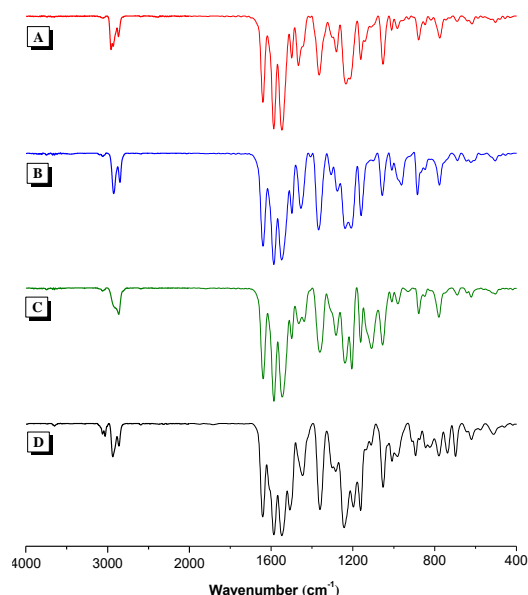


Figure S1. FT-IR spectra of (A) **P1b2a**, (B) **P1c2a**, (C) **P1d2a** and (D) **P1e2a**.

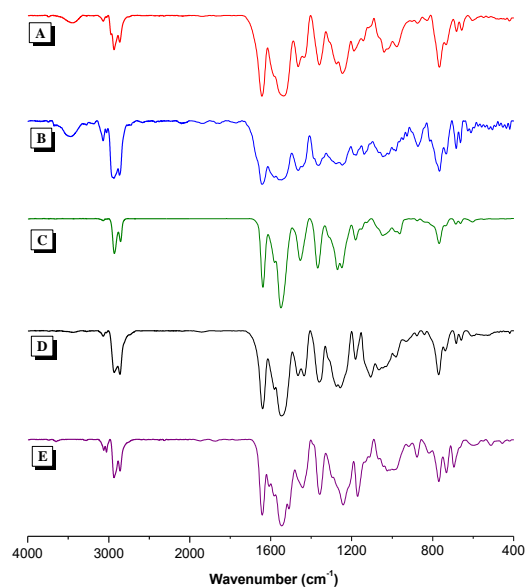


Figure S2. FT-IR spectra of (A) P1a2b, (B) P1b2b, (C) P1c2b, (D) P1d2b and (E) P1e2b.

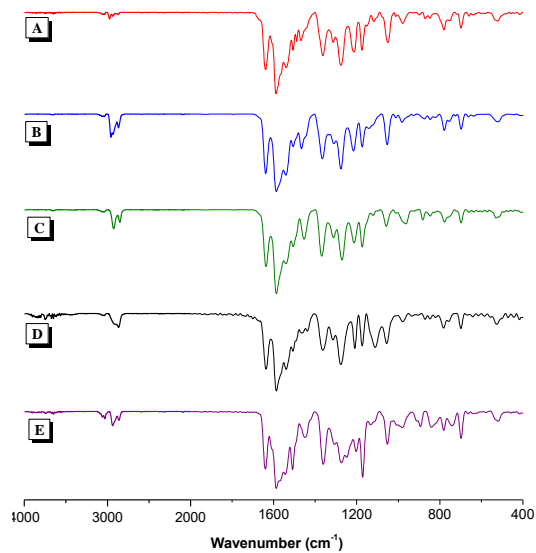


Figure S3. FT-IR spectra of (A) P1a2c, (B) P1b2c, (C) P1c2c, (D) P1d2c and (E) P1e2c.

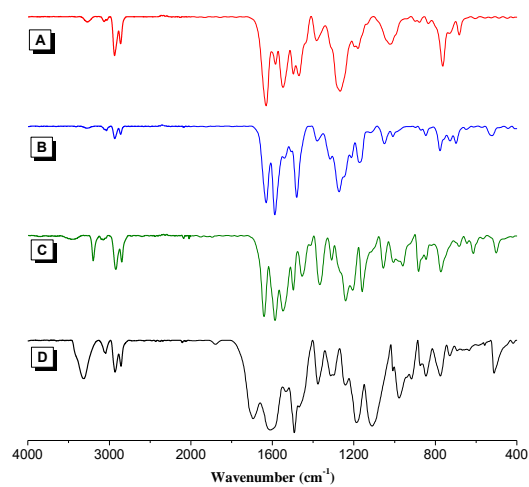


Figure S4. FT-IR spectra of (A) P1f2b, (B) P1f2c, (C) P1g2a and (D) P1f2d.

NMR Spectra of Polymers

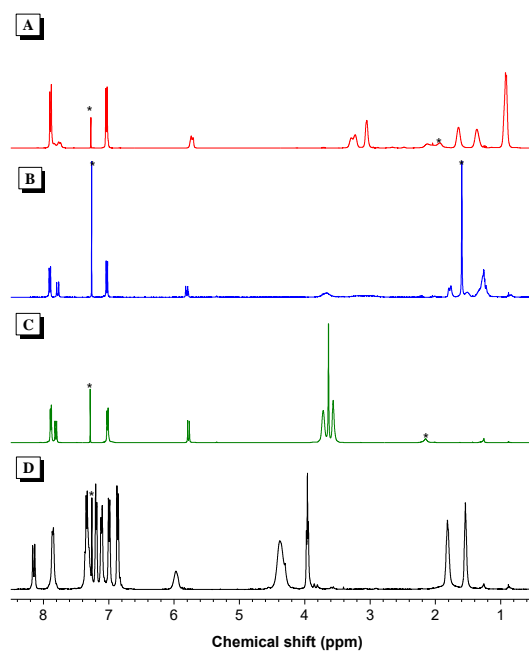


Figure S5. ^1H NMR spectra of (A) P1b2a, (B) P1c2a, (C) P1d2a and (D) P1e2a in CDCl_3 . The solvent peaks are marked with asterisks.

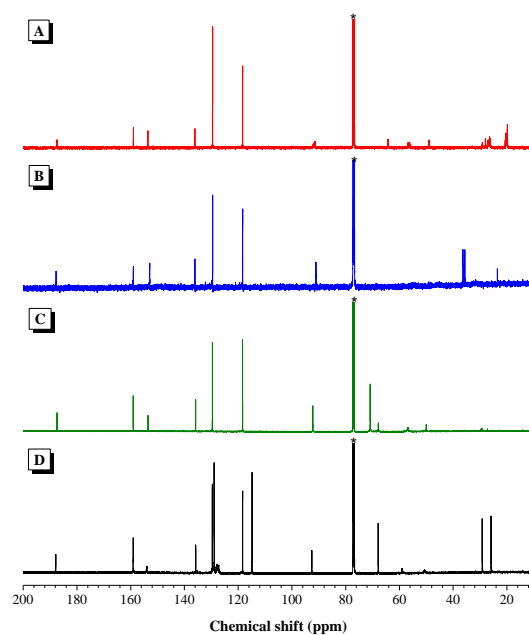


Figure S6. ^{13}C NMR spectra of (A) P1b2a, (B) P1c2a, (C) P1d2a and (D) P1e2a in CDCl_3 . The solvent peaks are marked with asterisks.

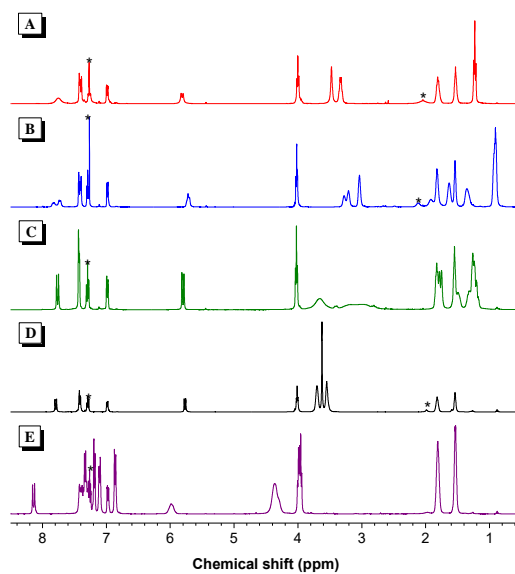


Figure S7. ^1H NMR spectra of (A) P1a2b, (B) P1b2b, (C) P1c2b, (D) P1d2b and (E) P1e2b in CDCl_3 . The solvent peaks are marked with asterisks.

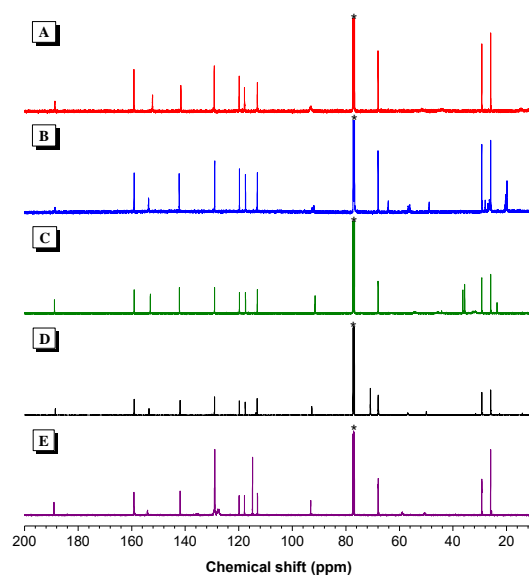


Figure S8. ^{13}C NMR spectra of (A) **P1a2b**, (B) **P1b2b**, (C) **P1c2b**, (D) **P1d2b** and (E) **P1e2b** in CDCl_3 . The solvent peaks are marked with asterisks.

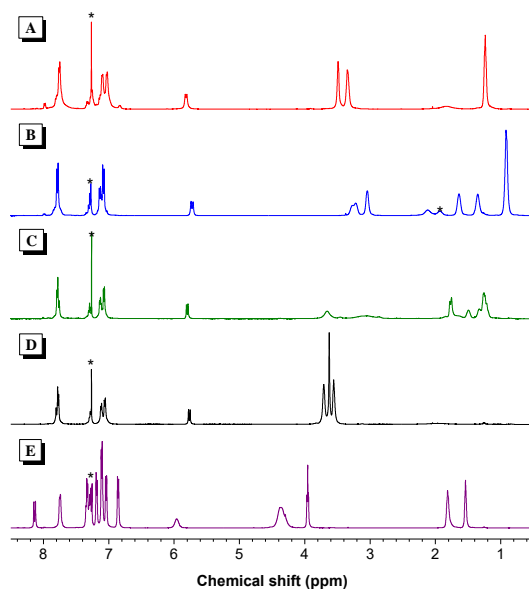


Figure S9. ^1H NMR spectra of (A) **P1a2c**, (B) **P1b2c**, (C) **P1c2c**, (D) **P1d2c** and (E) **P1e2c** in CDCl_3 . The solvent peaks are marked with asterisks.

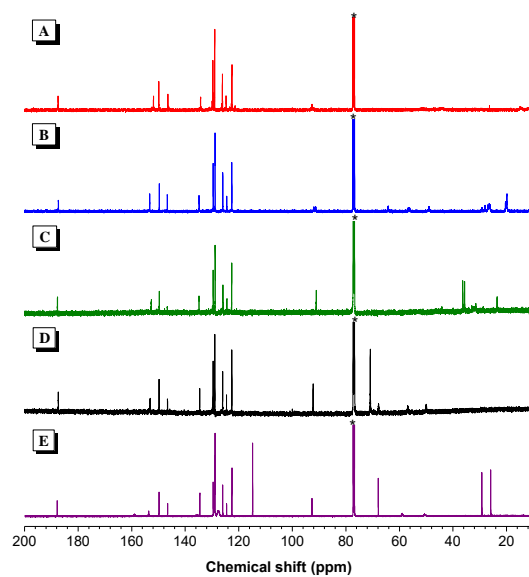


Figure S10. ^{13}C NMR spectra of (A) P1a2c, (B) P1b2c, (C) P1c2c, (D) P1d2c and (E) P1e2c in CDCl_3 . The solvent peaks are marked with asterisks.

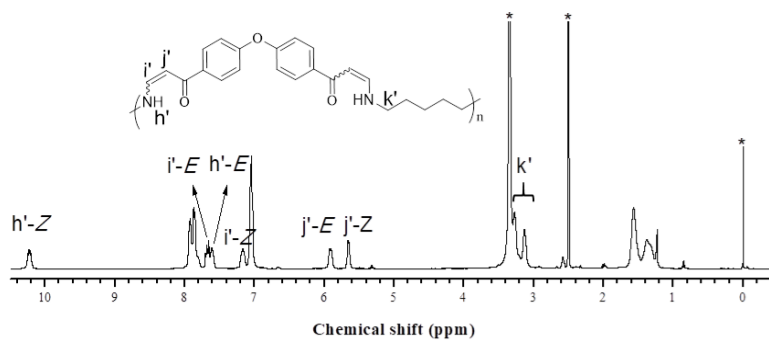


Figure S11. ^1H NMR spectra of P1f2a in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisks.

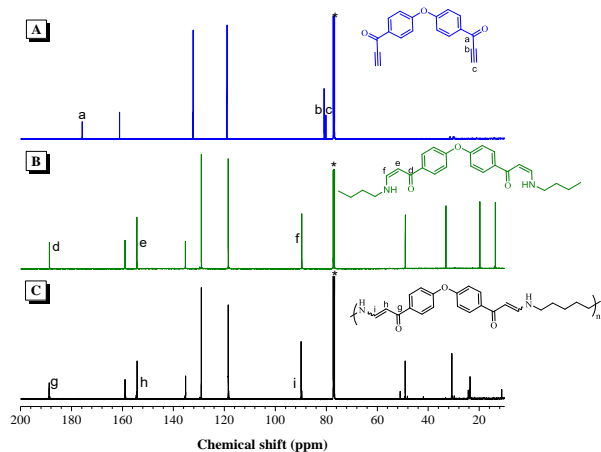


Figure S12. ^{13}C NMR spectra of (A) **2a**, (B) model compound **5**, and (C) **P1f2a** in CDCl_3 . The solvent peaks are marked with asterisks.

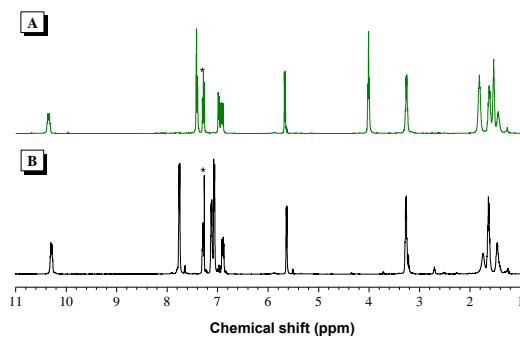


Figure S13. ^1H NMR spectra of (A) **P1f2b** and (B) **P1f2c** in CDCl_3 . The solvent peaks are marked with asterisks.

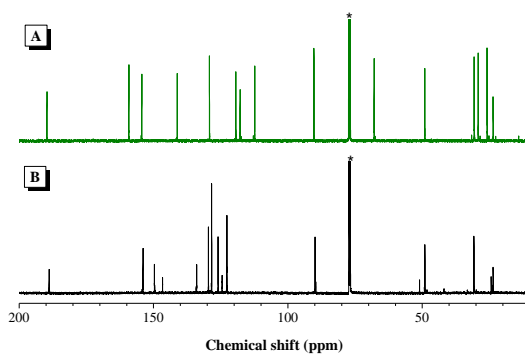
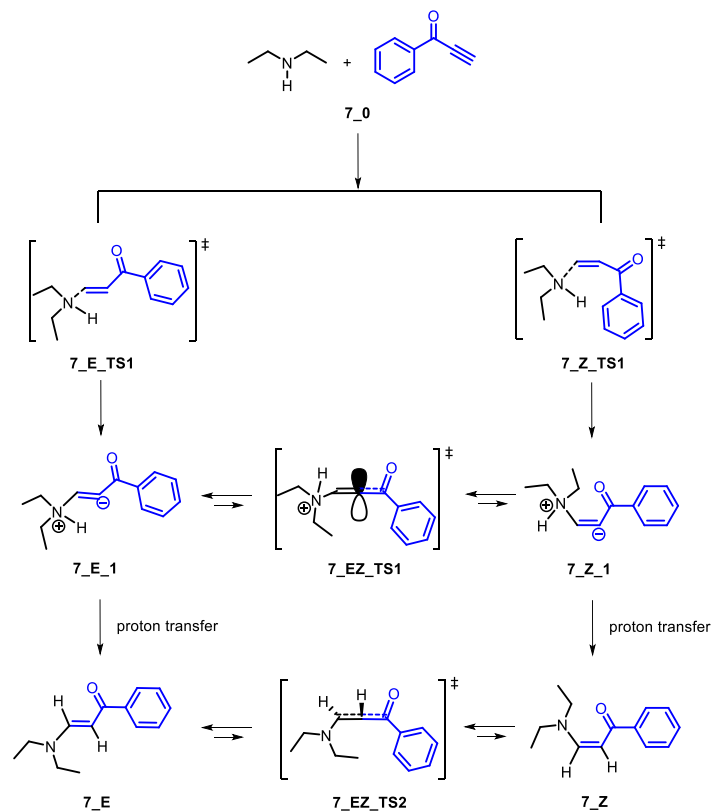


Figure S14. ^{13}C NMR spectra of (A) **P1f2b** and (B) **P1f2c** in CDCl_3 . The solvent peaks are marked with asterisks.

Calculation details



Scheme S5. Theoretical reaction pathways of benzoylacetylene **5** and diethylamine **6**.

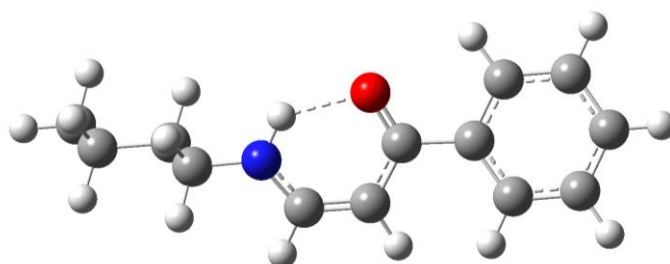


Figure S15. Illustration of hydrogen bonding of compound **9** in 3-D models.

Optimized geometries by M06-2x/6-31+G(d,p) (in Å):

7_0	C	-1.806828	0.841306	-5.160627
	C	-0.661151	0.561579	-4.892607
	C	0.723360	0.221435	-4.566507
	O	1.490462	-0.158843	-5.429158
	N	-4.910704	0.902170	-4.952805
	H	-5.620019	1.624419	-5.056888
	C	-5.238952	-0.246859	-5.796698
	H	-5.306715	0.116394	-6.827683
	H	-4.381753	-0.932476	-5.762509
	C	-6.517620	-1.003508	-5.431751
	H	-7.378374	-0.325941	-5.413325
	H	-6.719689	-1.785738	-6.169207
	H	-6.440573	-1.483205	-4.452270
	C	-4.727033	0.589365	-3.537287
	H	-3.930313	-0.164876	-3.472366
	H	-5.623718	0.145515	-3.077116
	C	-4.321387	1.837850	-2.765647
	H	-3.397381	2.259821	-3.171724
	H	-5.101146	2.604544	-2.829257
	H	-4.165593	1.607222	-1.708259
	H	-2.841690	1.087137	-5.365113
	C	1.138451	0.361139	-3.137570
	C	0.246976	0.790400	-2.151104
	C	2.459480	0.047491	-2.800337
	C	0.675437	0.904854	-0.830927
	H	-0.776915	1.033973	-2.419579
	C	2.883768	0.163205	-1.482244
	H	3.131363	-0.283584	-3.585899
	C	1.991812	0.591668	-0.496569
	H	-0.016482	1.239174	-0.064502
	H	3.908486	-0.079702	-1.219605
	H	2.325356	0.681107	0.532811

7_E_1	C	-1.764429	1.045811	0.567256
	C	-0.512364	1.224277	0.932412
	C	0.539954	0.775404	0.069728
	O	0.663629	1.177034	-1.109814
	N	-2.063444	0.354087	-0.773317
	H	-1.224644	0.598916	-1.332397
	C	-2.107989	-1.132136	-0.628707
	H	-1.251186	-1.387061	-0.000438
	H	-3.020388	-1.368745	-0.071663
	C	-2.028770	-1.864808	-1.959341
	H	-1.149157	-1.539983	-2.524602
	H	-1.922783	-2.935488	-1.769768
	H	-2.918722	-1.725962	-2.577309
	C	-3.256718	0.938787	-1.442612
	H	-4.092089	0.834549	-0.741714
	H	-3.478291	0.341929	-2.330215
	C	-3.008289	2.391411	-1.817400
	H	-2.814426	3.001613	-0.933434
	H	-2.141874	2.475615	-2.480115
	H	-3.882339	2.788781	-2.338193
	H	-2.692717	1.364375	1.038337
	C	1.509215	-0.236350	0.606090
	C	1.527495	-0.587059	1.960337
	C	2.376845	-0.875025	-0.286008
	C	2.395262	-1.579549	2.412050
	H	0.871783	-0.060794	2.647634
	C	3.248645	-1.859883	0.168444
	H	2.351229	-0.575974	-1.329597
	C	3.256479	-2.215661	1.518562
	H	2.410354	-1.846733	3.464432
	H	3.924674	-2.349738	-0.526060
	H	3.938975	-2.981682	1.874754

7_E_TS1	C	-5.263235	2.204465	0.709196
	C	-4.088630	2.618693	0.862200
	C	-2.790159	2.828715	0.318461
	O	-2.516990	3.800994	-0.389151
	N	-5.740857	1.350895	-0.926569
	H	-4.829390	1.036188	-1.261232
	C	-6.609874	0.206113	-0.626734
	H	-6.154397	-0.325065	0.215815
	H	-7.564125	0.615412	-0.273830
	C	-6.831696	-0.751239	-1.793550
	H	-5.878308	-1.150290	-2.153150
	H	-7.446927	-1.595076	-1.470243
	H	-7.342020	-0.269565	-2.630739
	C	-6.307228	2.354490	-1.844143
	H	-7.072283	2.899061	-1.276292
	H	-6.809180	1.860134	-2.685366
	C	-5.232453	3.302438	-2.354514
	H	-4.709424	3.804494	-1.536715
	H	-4.486581	2.759736	-2.945656
	H	-5.684589	4.057602	-3.001981
	H	-6.236365	2.139087	1.171932
	C	-1.734861	1.804978	0.644362
	C	-1.972975	0.746972	1.525769
	C	-0.488939	1.921532	0.022871
	C	-0.974277	-0.190767	1.778362
	H	-2.937416	0.670943	2.020769
	C	0.507911	0.983534	0.274702
	H	-0.327986	2.757216	-0.651080
	C	0.266299	-0.074822	1.151588
	H	-1.160495	-1.007665	2.468951
	H	1.475143	1.077266	-0.209676
	H	1.044899	-0.805579	1.349083

7_E_TS2	C	-0.837863	0.103884	0.554041
	C	0.356509	-0.033116	-0.008101
	C	1.646521	0.475326	0.455681
	O	1.974040	1.641638	0.274680
	N	-1.791017	-0.504638	-0.405329
	H	-0.646985	-0.631551	-0.953230
	C	-2.403549	-1.755364	0.095058
	H	-1.574738	-2.346293	0.496058
	H	-3.072419	-1.512201	0.931797
	C	-3.138026	-2.542902	-0.981749
	H	-2.510415	-2.655378	-1.871148
	H	-3.370610	-3.541205	-0.603212
	H	-4.080360	-2.075091	-1.275183
	C	-2.758649	0.442716	-1.007258
	H	-3.481124	0.739607	-0.233494
	H	-3.306309	-0.098370	-1.782372
	C	-2.073992	1.659813	-1.612712
	H	-1.568862	2.262872	-0.856498
	H	-1.323672	1.355680	-2.347871
	H	-2.822250	2.278152	-2.114851
	H	-1.221711	0.540835	1.474900
	C	2.605191	-0.490452	1.097590
	C	2.281638	-1.836307	1.286638
	C	3.844541	-0.009551	1.529389
	C	3.187896	-2.694011	1.906811
	H	1.322306	-2.208560	0.939380
	C	4.749399	-0.865477	2.148354
	H	4.071734	1.039792	1.368961
	C	4.421825	-2.209275	2.337796
	H	2.934644	-3.739912	2.050952
	H	5.710571	-0.488838	2.484505
	H	5.128829	-2.878240	2.819438

7_Z_1	C	4.041007	3.039420	0.769580
	C	2.850277	2.603192	1.122966
	C	2.737410	1.330004	1.770950
	O	3.325704	1.064348	2.844045
	N	5.272234	2.165771	1.067452
	H	4.971380	1.667457	1.926798
	C	5.509208	1.140783	0.005910
	H	4.518079	0.787181	0.287460
	H	5.952799	1.662941	0.848131
	C	6.361763	0.020586	0.493599
	H	5.901768	0.485929	1.371455
	H	6.419732	0.777643	0.291906
	H	7.383695	0.274493	0.743663
	C	6.469161	2.986539	1.393365
	H	6.625140	3.663883	0.546763
	H	7.332397	2.320265	1.460638
	C	6.266807	3.745123	2.695374
	H	5.418248	4.428607	2.628390
	H	6.076629	3.051995	3.520163
	H	7.165803	4.319996	2.928258
	H	4.348820	3.987989	0.333570
	C	1.902850	0.273560	1.109427
	C	1.102054	0.565296	0.000078
	C	1.976942	1.040803	1.582947
	C	0.397243	0.452750	0.639455
	H	1.028215	1.594847	0.337462
	C	1.265120	2.054529	0.948581
	H	2.595464	1.240644	2.452837
	C	0.477242	1.762283	0.166431
	H	0.224901	0.222017	1.498911
	H	1.321923	3.072935	1.321229
	H	0.078343	2.553661	0.660934

7_ZE_TS1	C	4.709033	2.458726	0.066266
	C	3.493671	2.389850	0.477236
	C	2.188910	2.471184	0.934183
	O	1.831959	3.236832	1.852513
	N	5.803356	1.608969	0.793620
	H	5.236350	0.953798	1.343002
	C	6.646884	0.847652	0.171823
	H	5.956362	0.450786	0.920206
	H	7.295798	1.577583	0.665346
	C	7.445678	0.273896	0.475244
	H	6.785699	0.975351	0.994609
	H	7.974071	0.831180	0.301830
	H	8.192338	0.092522	1.183096
	C	6.586471	2.471194	1.734767
	H	6.907689	3.335292	1.144486
	H	7.475526	1.919059	2.050533
	C	5.747061	2.891611	2.931175
	H	4.837268	3.411355	2.622401
	H	5.457182	2.022414	3.529794
	H	6.339109	3.554846	3.566122
	H	5.220255	3.054979	0.695052
	C	1.180012	1.542075	0.296530
	C	1.479570	0.760637	0.822279
	C	0.096346	1.478440	0.856256
	C	0.516214	0.080650	1.372723
	H	2.470123	0.824701	1.266889
	C	1.060939	0.635160	0.308337
	H	0.303866	2.104619	1.718443
	C	0.757117	0.147058	0.805733
	H	0.754858	0.680560	2.246157
	H	2.052410	0.587550	0.749279
	H	1.509422	0.803333	1.233242

7_ZE_TS2	C	0.329054	0.468109	0.505173
	C	0.836551	0.354319	0.762549
	C	0.964879	0.585673	2.135518
	O	0.055350	0.239175	2.941734
	N	1.499357	0.009590	0.191075
	H	1.602219	0.472729	0.008228
	C	1.738841	1.446412	0.091017
	H	1.180158	1.904071	0.909294
	H	2.808628	1.594977	0.259779
	C	1.303277	2.011050	1.254487
	H	0.225179	1.885801	1.374895
	H	1.532163	3.079199	1.290853
	H	1.815121	1.520216	2.086432
	C	2.670864	0.890296	0.069683
	H	2.334268	1.907285	0.281216
	H	3.371893	0.597839	0.857957
	C	3.323931	0.807721	1.303753
	H	2.607214	1.056077	2.091336
	H	3.729974	0.187751	1.501614
	H	4.150810	1.520221	1.352867
	H	0.315131	1.558037	0.639623
	C	2.192079	1.272306	2.679992
	C	3.138078	1.906235	1.868909
	C	2.376442	1.274733	4.064738
	C	4.253360	2.523036	2.430598
	H	2.998654	1.934474	0.792126
	C	3.493763	1.886195	4.628779
	H	1.620859	0.789428	4.674572
	C	4.436187	2.511824	3.813511
	H	4.978672	3.016124	1.789878
	H	3.629519	1.877280	5.706383
	H	5.306326	2.991222	4.252151

7_Z_TS1	C	4.085624	2.848817	1.299378
	C	3.043356	2.256017	1.677153
	C	2.525156	1.042978	2.221678
	O	2.598576	0.761044	3.418671
	N	5.715017	1.881223	1.361208
	H	5.671935	1.506396	2.309908
	C	5.625629	0.783989	0.385373
	H	4.616956	0.368428	0.474660
	H	5.704698	1.236702	0.609533
	C	6.667030	0.311631	0.584058
	H	6.567831	0.761026	1.577079
	H	6.517160	1.102465	0.155404
	H	7.689053	0.060157	0.471197
	C	6.862276	2.781847	1.205554
	H	6.644125	3.423369	0.340979
	H	7.771712	2.217461	0.967809
	C	7.067670	3.616990	2.460904
	H	6.159322	4.165431	2.723704
	H	7.337061	2.980859	3.309807
	H	7.875265	4.336719	2.310316
	H	4.473301	3.783724	0.923559
	C	1.258149	1.859278	0.092597
	C	1.659791	0.417628	0.086599
	C	1.453867	1.155634	1.736492
	C	1.064870	0.502231	0.947008
	H	1.962340	1.396737	0.448733
	C	0.858652	2.074142	0.876255
	H	1.614162	1.378332	2.786879
	C	0.665009	1.749342	0.466946
	H	0.905368	0.244739	1.989714
	H	0.542309	3.042711	1.251326
	H	0.198963	2.464844	1.137881

7_E	C	-1.585245	0.718759	-0.316623
	C	-0.442864	0.027085	-0.039004
	C	0.409745	0.531959	1.033272
	O	0.183097	1.586038	1.623845
	N	-2.511453	0.447389	-1.256755
	H	-0.142675	-0.844943	-0.604701
	C	-2.358121	-0.703318	-2.135847
	H	-2.059955	-1.563901	-1.524019
	H	-3.344390	-0.934063	-2.552226
	C	-1.347184	-0.473499	-3.259584
	H	-0.374756	-0.186260	-2.852250
	H	-1.220138	-1.387163	-3.847335
	H	-1.681882	0.323801	-3.928134
	C	-3.708054	1.266954	-1.396544
	H	-3.705052	1.993644	-0.580250
	H	-4.591725	0.628630	-1.259554
	C	-3.789650	1.986358	-2.739794
	H	-2.910659	2.619382	-2.890722
	H	-3.850025	1.275303	-3.569279
	H	-4.684117	2.614536	-2.774841
	H	-1.784118	1.597806	0.294517
	C	1.631708	-0.265195	1.411377
	C	1.780203	-1.622732	1.112180
	C	2.646200	0.393975	2.113509
	C	2.929116	-2.308583	1.502283
	H	0.989967	-2.159842	0.597410
	C	3.798984	-0.286190	2.491550
	H	2.504105	1.443289	2.351871
	C	3.942974	-1.640149	2.185886
	H	3.030732	-3.365488	1.275658
	H	4.585792	0.236300	3.026961
	H	4.840425	-2.174028	2.483596

7_Z	C	-1.018717	1.611337	-0.951426
	C	0.059423	1.118147	-0.261482
	C	0.099676	0.074789	0.748948
	O	-0.885536	-0.313192	1.379436
	N	-2.275653	1.159508	-1.129064
	H	0.985218	1.655203	-0.433394
	C	-2.708890	-0.208252	-0.828742
	H	-2.604382	-0.389452	0.242520
	H	-3.770673	-0.258446	-1.088364
	C	-1.931268	-1.262902	-1.611549
	H	-0.869217	-1.241814	-1.355984
	H	-2.314531	-2.256353	-1.363200
	H	-2.027217	-1.108705	-2.690747
	C	-3.206774	1.973373	-1.908377
	H	-2.853724	3.007651	-1.886792
	H	-4.176631	1.960130	-1.397791
	C	-3.361448	1.496389	-3.350534
	H	-2.394032	1.503901	-3.861883
	H	-3.762015	0.479268	-3.391573
	H	-4.048345	2.150929	-3.894804
	H	-0.832820	2.535446	-1.499236
	C	1.446087	-0.514041	1.082981
	C	2.521243	-0.489354	0.189811
	C	1.600513	-1.139284	2.324486
	C	3.737312	-1.075355	0.536878
	H	2.401842	-0.032595	-0.788263
	C	2.817082	-1.713998	2.676087
	H	0.748408	-1.162347	2.996409
	C	3.888444	-1.682828	1.782162
	H	4.564902	-1.061198	-0.165679
	H	2.932929	-2.188272	3.645864
	H	4.837582	-2.134710	2.054486

9_Z	C	-0.836223	2.143984	-1.863523
	C	0.213538	1.549869	-1.207018
	C	0.000845	0.724436	-0.043575
	O	-1.130662	0.538012	0.433176
	N	-2.132693	2.026476	-1.555662
	H	1.209550	1.743251	-1.577644
	C	-3.183779	2.767754	-2.224265
	H	-2.859287	2.970568	-3.252254
	H	-4.070552	2.127593	-2.290107
	C	-3.536395	4.078330	-1.520138
	H	-2.638424	4.708825	-1.476525
	H	-3.817156	3.861883	-0.481349
	H	-0.630605	2.772128	-2.730921
	C	1.178393	0.075625	0.631903
	C	2.434793	-0.043525	0.029210
	C	0.985977	-0.445691	1.915661
	C	3.482747	-0.667714	0.702740
	H	2.600527	0.328579	-0.976350
	C	2.034127	-1.060854	2.592143
	H	0.000832	-0.356533	2.361787
	C	3.286112	-1.172829	1.986563
	H	4.451865	-0.763384	0.222908
	H	1.876423	-1.457115	3.590553
	H	4.104178	-1.656953	2.511289
	C	-4.668997	4.827082	-2.219485
	H	-5.558258	4.184865	-2.258810
	H	-4.385128	5.026723	-3.261061
	C	-5.015720	6.140485	-1.521378
	H	-4.148643	6.808273	-1.495330
	H	-5.828192	6.663527	-2.032735
	H	-5.328847	5.961161	-0.487749
	H	-2.330241	1.474094	-0.722711

9_E	C	-1.564625	1.729514	-0.232415
	C	-0.606284	0.871903	0.209841
	C	0.598469	1.445398	0.807896
	O	0.733665	2.651461	0.996448
	N	-2.763149	1.408921	-0.764401
	H	-0.728896	-0.202133	0.152382
	C	-3.198170	0.042575	-0.985093
	H	-2.961092	-0.540226	-0.085373
	H	-4.288438	0.046513	-1.082315
	C	-2.563032	-0.606674	-2.216285
	H	-1.472377	-0.505788	-2.153511
	H	-2.876595	-0.055429	-3.112156
	H	-1.362480	2.794851	-0.141393
	C	1.709017	0.514440	1.218874
	C	1.844863	-0.782233	0.713896
	C	2.655367	0.995052	2.129974
	C	2.908509	-1.587509	1.117478
	H	1.138776	-1.163827	-0.016959
	C	3.709029	0.187360	2.543927
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	C	-2.943848	-2.079355	-2.350859
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	C	-5.819118	5.572478	-1.703518
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	C	3.945370	2.590948	2.574833
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	O	0.821226	1.169887	1.876433
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	H	1.416204	-0.856574	-0.688024
	C	-1.888047	-1.021989	0.539903
	H	-1.112694	-1.144709	1.297766
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	C	-2.403115	-3.490360	0.501289
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	C	3.792723	-0.898188	3.446204
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	H	3.648847	-1.925495	3.127508
	C	4.127771	1.756176	4.196485
	H	2.927216	2.237748	2.463573
	C	4.704232	0.744641	4.964196
	H	4.982114	-1.383010	5.167398
	H	4.254570	2.794968	4.486669
	H	5.280336	0.991565	5.850211

Thermal Properties of Polymers

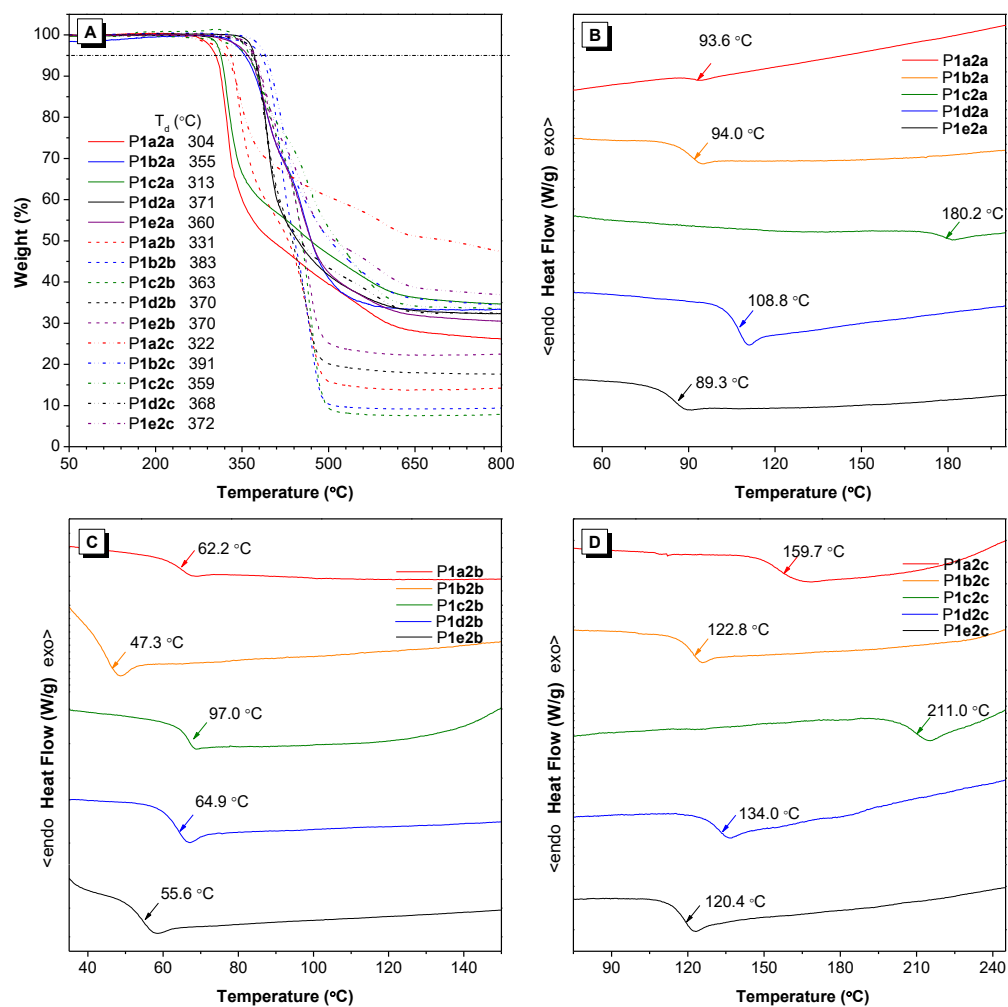


Figure S16. TGA thermograms of secondary amine-based polymers under nitrogen (A), and DSC curves of these polymers under nitrogen (B, C, D).

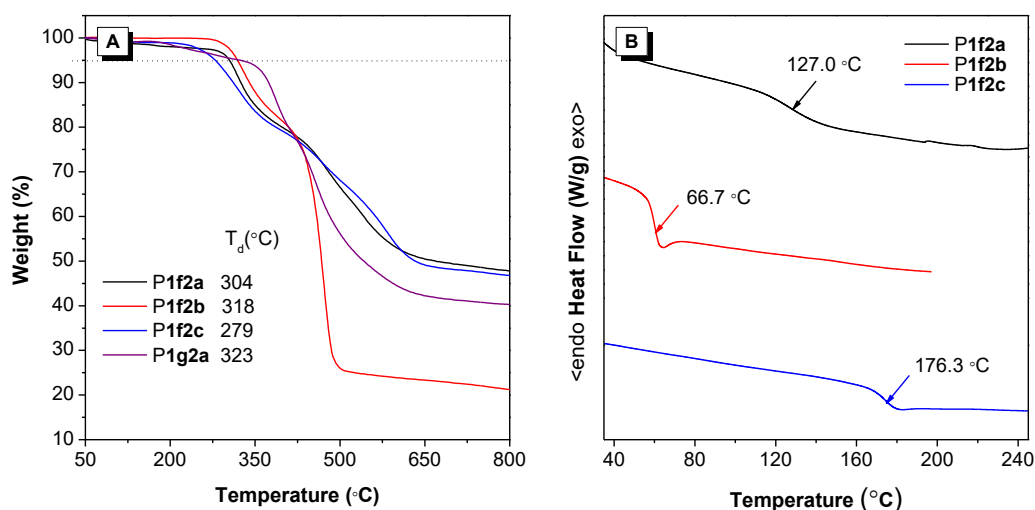


Figure S17. TGA thermograms of primary amine-based polymers under nitrogen (A), and DSC curves of these polymers under nitrogen (B).

Cell Viability Assay

HeLa cells were seeded in 96-well plate with 8×10^3 cells per well, and incubated with monomer **2a** or monomer **2d** in PBS with the final concentration ranging from 0 to 16 μM . After 20 min incubation, PBS with monomers was removed, followed with the addition of 100 μL of DMEM (10% FBS) to every well. After 24 h, 100 μL of MTT (50 $\mu\text{g/mL}$) in DMEM (10% FBS) was added, and incubated for additional 4 h. After removing the culture medium, 100 μL of DMSO was added to every well. The absorption was recorded by a microplate reader at 570 nm after shaking for 2 min. The cell viability ratio (VR) was evaluated according to the following equation:

$$\text{VR} = \frac{A}{A_0} \times 100\%$$

where A_0 is the absorbance of cells without any drugs, and A is the absorbance of cells incubated monomer **2a** or monomer **2d**.

Amine Exchange Reaction

The solution of compound **7** (48.7 mg, 0.24 mmol) dissolved in 3 mL DMF was divided into 6 equal parts. Kept one part for comparison and distributed the others into five 10 mL Schlenk tubes. Then dibenzylamine (**12**, 77 μL , 0.4 mmol) was added to the five tubes and heated at 60, 80, 100, 120, and 150 $^{\circ}\text{C}$ with magnetic stirring for 48 h, respectively. After cooled to room temperature, five samples was poured into

water and extracted with DCM for three times. The obtained mixture was measured by NMR spectroscopy after removing the solvent by rotary evaporation.

(*E*)-3-(dibenzylamino)-1-phenylprop-2-en-1-one (13): Into 2 mL of DCM solution of Compound **S11** (26.0 mg, 0.2 mmol) was added dibenzylamine (42.3 μ L, 0.22 mmol). After stirred for 2 h, the solvent was removed and the product was washed with hexane (6 mL) for three times. 62 mg (yield 95%) yellow solid was obtained after dried in vacuum for 4 h. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 8.17 (d, $J = 12.6$ Hz, 1H), 7.89 – 7.81 (m, 2H), 7.50 – 7.28 (m, 9H), 7.21 (d, $J = 6.7$ Hz, 4H), 6.01 (d, $J = 12.6$ Hz, 1H), 4.42 (d, $J = 18.5$ Hz, 4H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 189.27, 154.17, 140.30, 131.09, 128.94, 128.15, 127.56, 93.18.

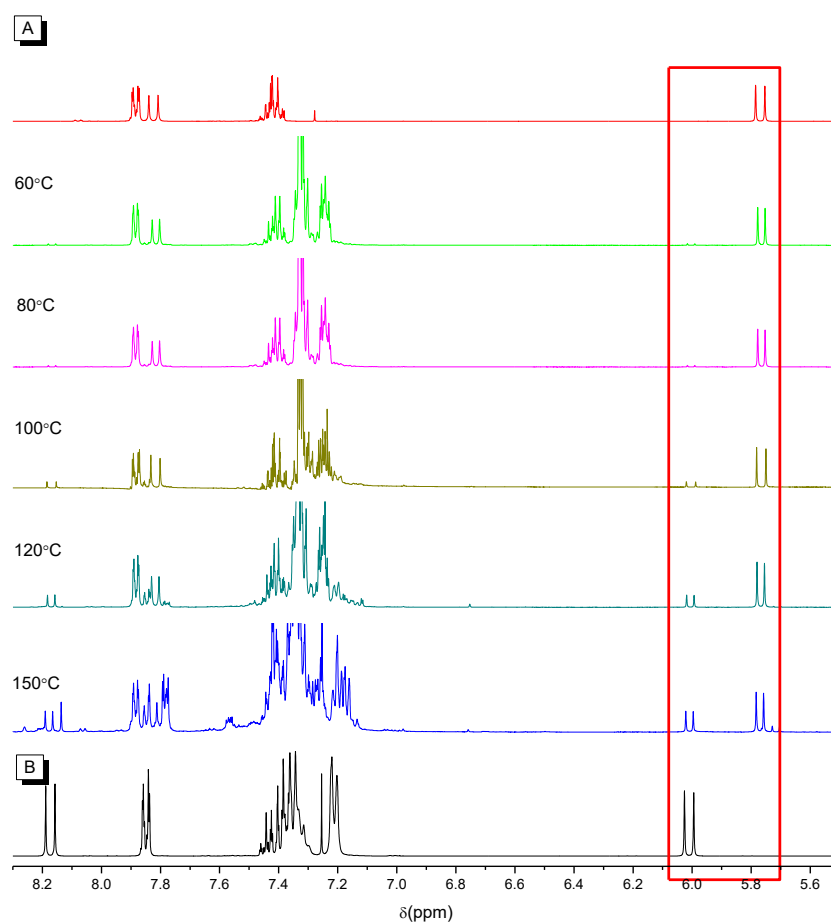


Figure S18. ^1H NMR spectra of (A) compound **7**, (B) compound **13** and the mixture of compound **7** with excessive dibenzylamine after heated under different temperatures for 48 h in CDCl_3 .

Table S4. The calculated conversion rate from compound **7** to **13** and corresponding temperatures.

temperature (°C)	60	80	100	120	150
equilibrium conversion ratio ^a (%)	2.0	2.9	11.5	20.6	36.7

^a Calculated from the integral area in ¹H NMR spectra, equilibrium conversion ratio is equal to the integral area of **13** divided by the total integral area of compound **13** and **7**, and then multiplied by 100%.

Typical Degradation Procedures of Polymer Catalyzed by Lewis Acid

(1) Degradation catalyzed by Fe³⁺

P1a2a (39 mg, 0.1 mmol) in 1 mL DMF was added dropwise into the aqueous solution of FeCl₃ (25 mL, 0.2 mol/L), followed by aniline (91.3 μL, 10 eq.). The suspension was stirred at room temperature for 6 h. Afterward, the crude product was collected by vacuum filtration, and further purified by dissolving in DCM, and washing with brine. After removing the solvent, yellow solid of **15** was obtained in 54% yield.

(2) Degradation catalyzed by KHSO₄

P1a2a (39 mg, 0.1 mmol) in 1 mL DMF was added dropwise into the aqueous solution of KHSO₄ (25 mL, 0.4 mol/L), followed by aniline (91.3 μL, 10 eq.). The formed suspension was stirred at 50 °C for 4 h. Afterward, the crude product was collected by vacuum filtration, and further purified by dissolving in DCM, and wash with brine. After removing the solvent, yellow solid of **15** was obtained in 79% yield.

(2Z,2'Z)-1,1'-(oxybis(4,1-phenylene))bis(3-(phenylamino)prop-2-en-1-one)

(15): ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 12.14 (d, *J* = 12.1 Hz, 2H), 8.03 – 7.95 (d, 4H), 7.54 (m, 2H), 7.36 (m, 6H), 7.16 – 7.09 (m, 8H), 6.01 (d, *J* = 7.8 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 189.56, 158.24, 145.12, 132.20, 129.80, 129.60, 123.85, 119.54, 118.11, 116.40, 93.41.

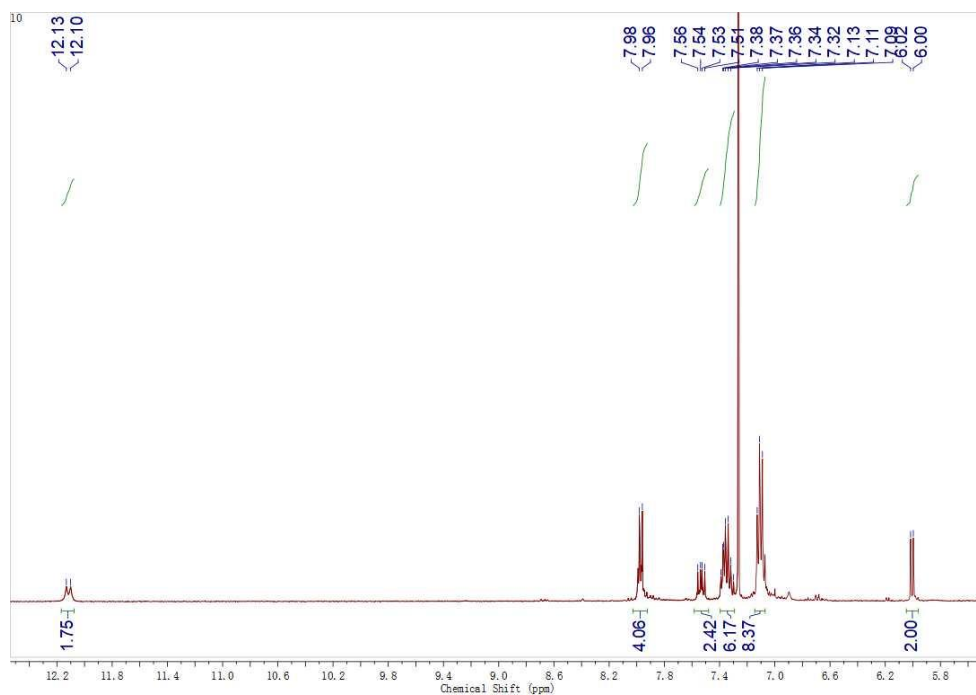


Figure S19. ^1H NMR spectra of compound **15** filtrated from the degradation mixture without further purification in CDCl_3 .

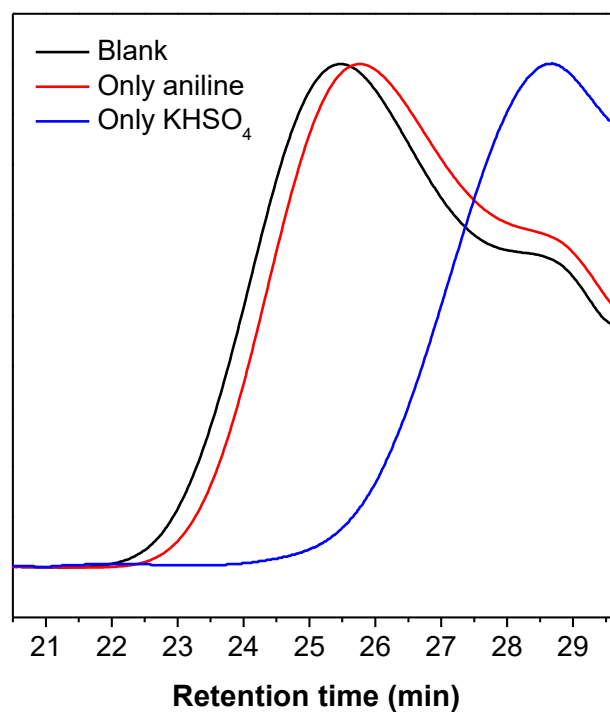
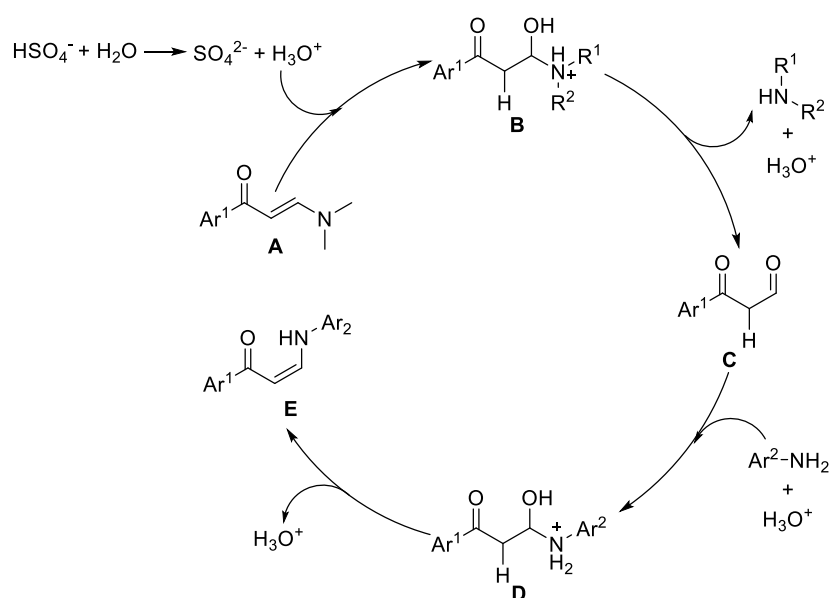


Figure S20. GPC curves of **P1a2a** before and after dealing with only KHSO_4 or only aniline.

Table S5. Molecular weights of **P1a2a** before and after dealing with only KHSO₄ or only aniline.

	M_w	\bar{D}
blank	24 200	1.99
only KHSO ₄ ^a	4 960	1.19
only aniline ^b	20 100	1.89

^a Performed by dispersing 1 mL DMF solution of **P1a2a** (0.1 mmol) in 25 mL aqueous solution of KHSO₄ (0.4 M), and heating at 50 °C for 4 h. ^b Carried out by dispersing 1 mL DMF solution of **P1a2a** (0.1 mmol) in 25 mL aqueous solution of aniline (10 eq.), and heating at 50 °C for 4 h.



Scheme S6. Possible mechanism of polymer degradation under the catalysis of KHSO₄.

References

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- (2) Qin, A.; Jim, C. K. W.; Lu, W.; Lam, J. W. Y.; Haussler, M.; Dong, Y.; Herman H. Y. Sung; Williams, I. D.; Wong, G. K. L.; Tang, B. Z. Click Polymerization: Facile Synthesis of Functional Poly(aroyltriazole)s by Metal-Free, Regioselective 1,3-Dipolar Polycycloaddition. *Macromolecules* **2007**, *40*, 2308-2317.
- (3) He, B.; Su, H.; Bai, T.; Wu, Y.; Li, S.; Gao, M.; Hu, R.; Zhao, Z.; Qin, A.; Ling, J.; Tang, B. Z. Spontaneous amino-yne click polymerization: A Powerful Tool toward Regio- and Stereospecific Poly(β -aminoacrylate)s. *J. Am. Chem. Soc.* **2017**, *139*, 5437-5443.
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- (6) Karpov, A. S.; Müller, T. J., Straightforward Novel One-Pot Enaminone and Pyrimidine Syntheses by Coupling-Addition-Cyclocondensation Sequences. *Synthesis* **2003**, *18*, 2815-2826.
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Additional Data

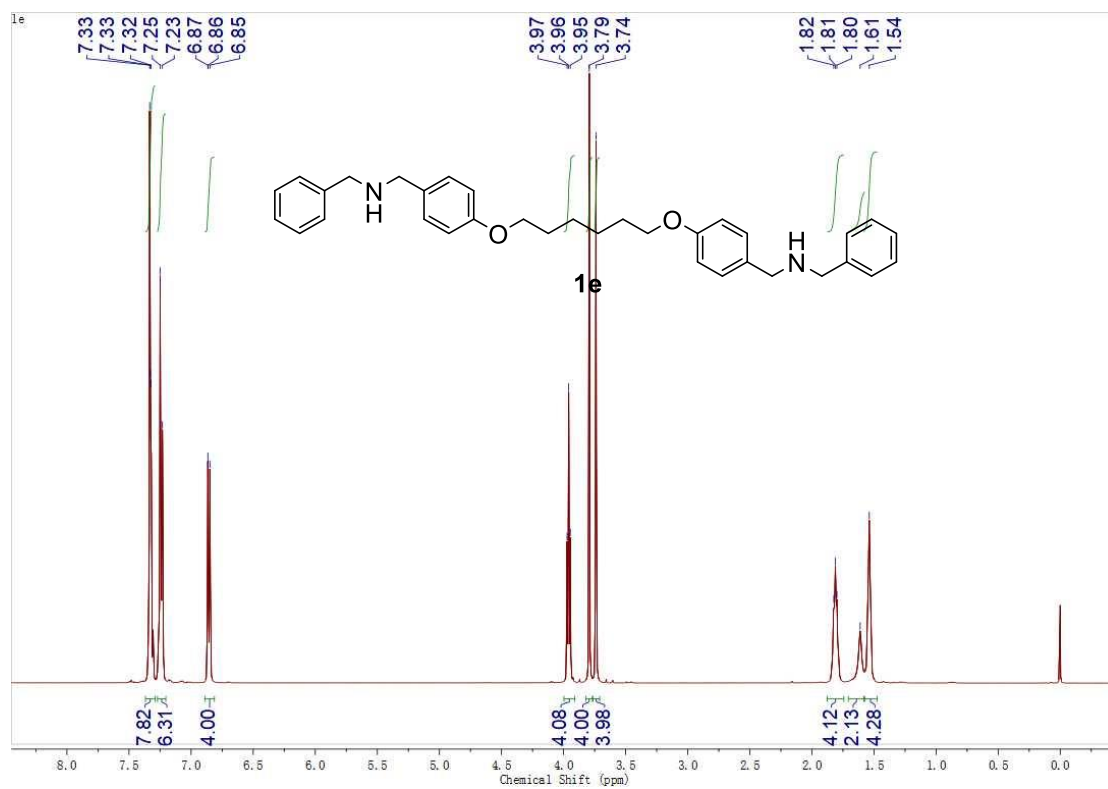


Figure S21. ^1H NMR spectrum of **1e** in CDCl_3 .

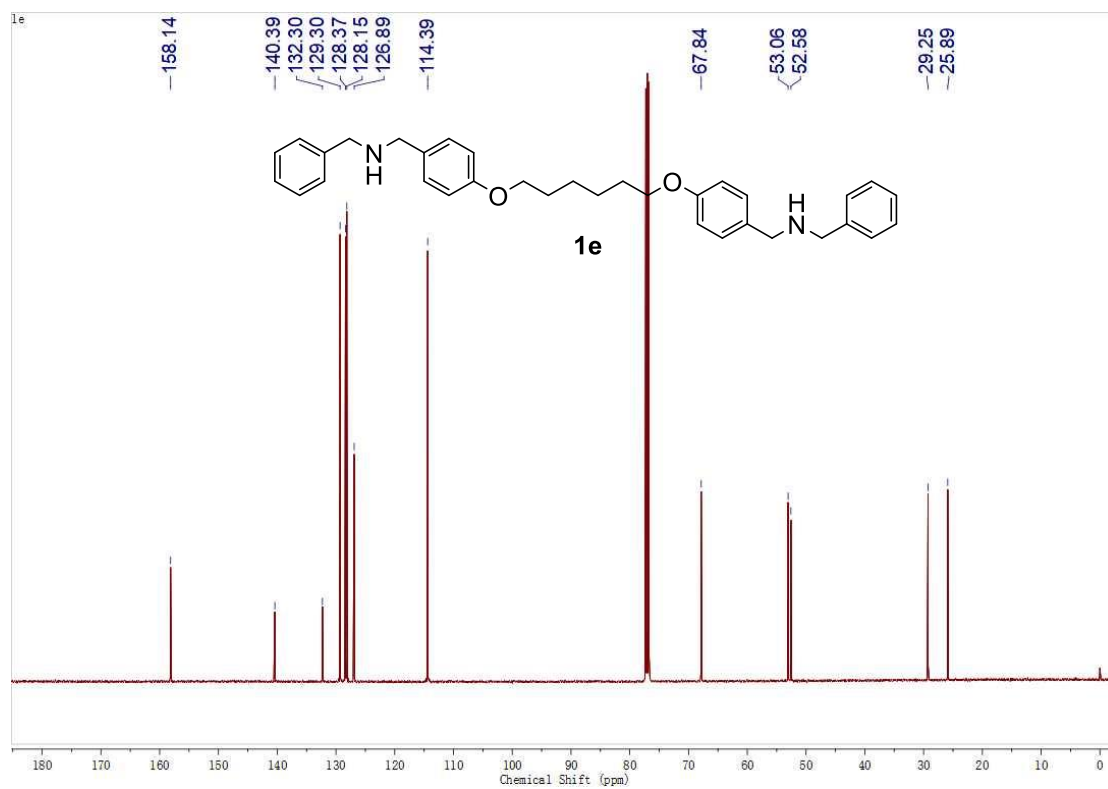


Figure S22. ^{13}C NMR spectrum of **1e** in CDCl_3 .

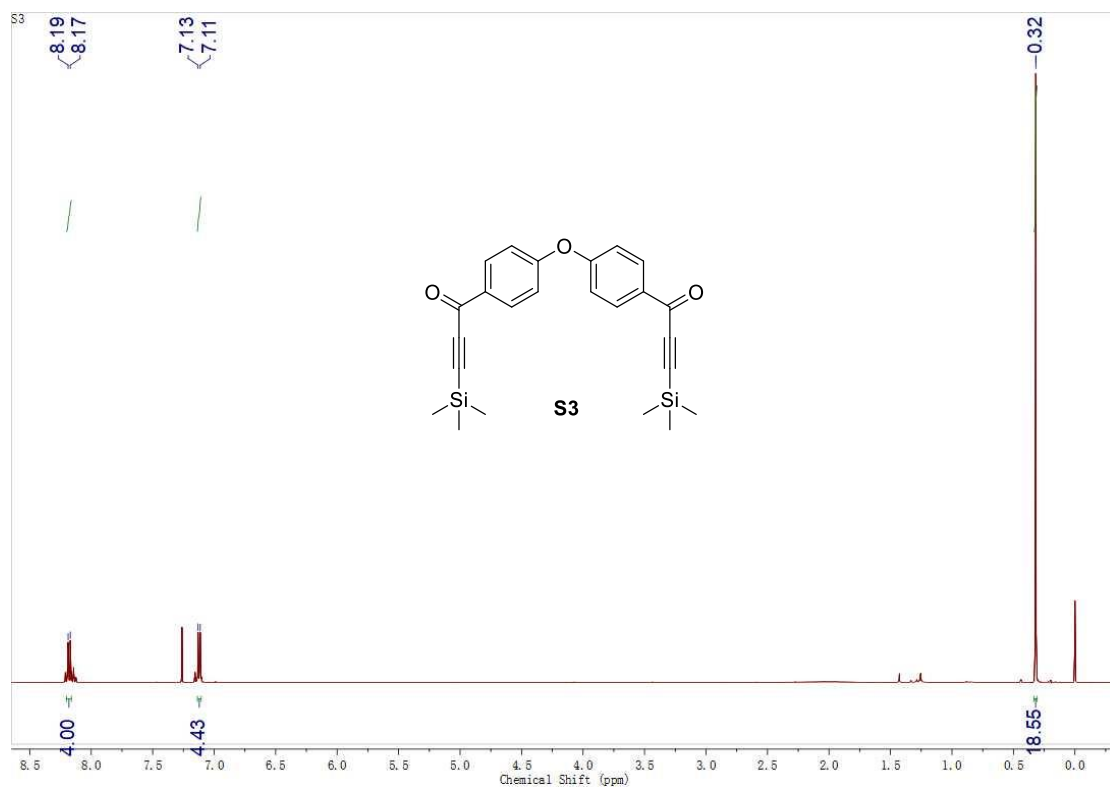


Figure S23. ^1H NMR spectrum of **S3** in CDCl_3 .

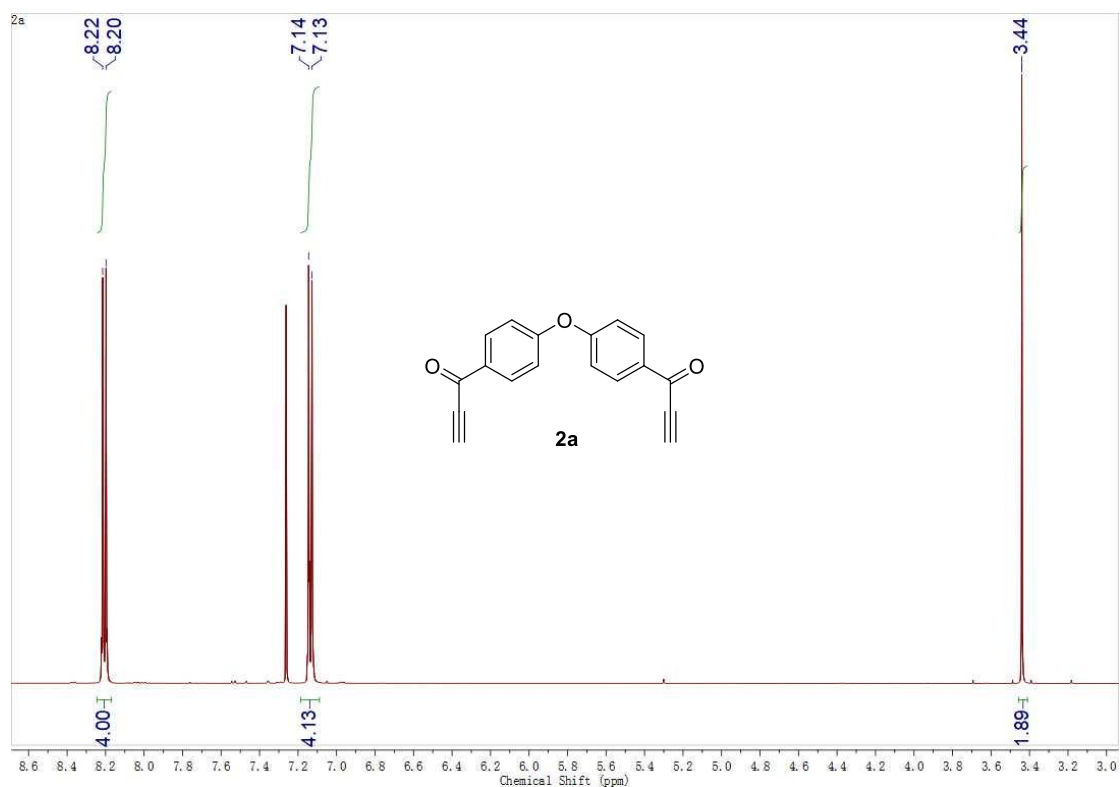


Figure S24. ^1H NMR spectrum of **2a** in CDCl_3 .

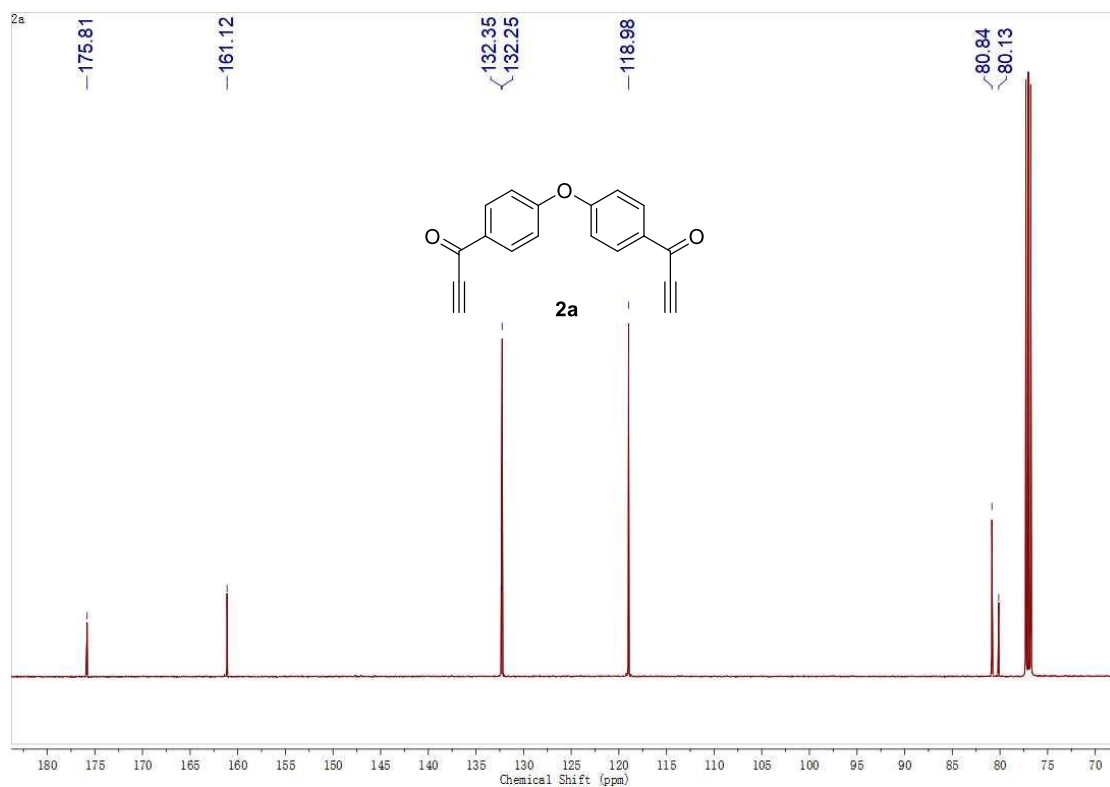


Figure S25. ^{13}C NMR spectrum of **2a** in CDCl_3 .

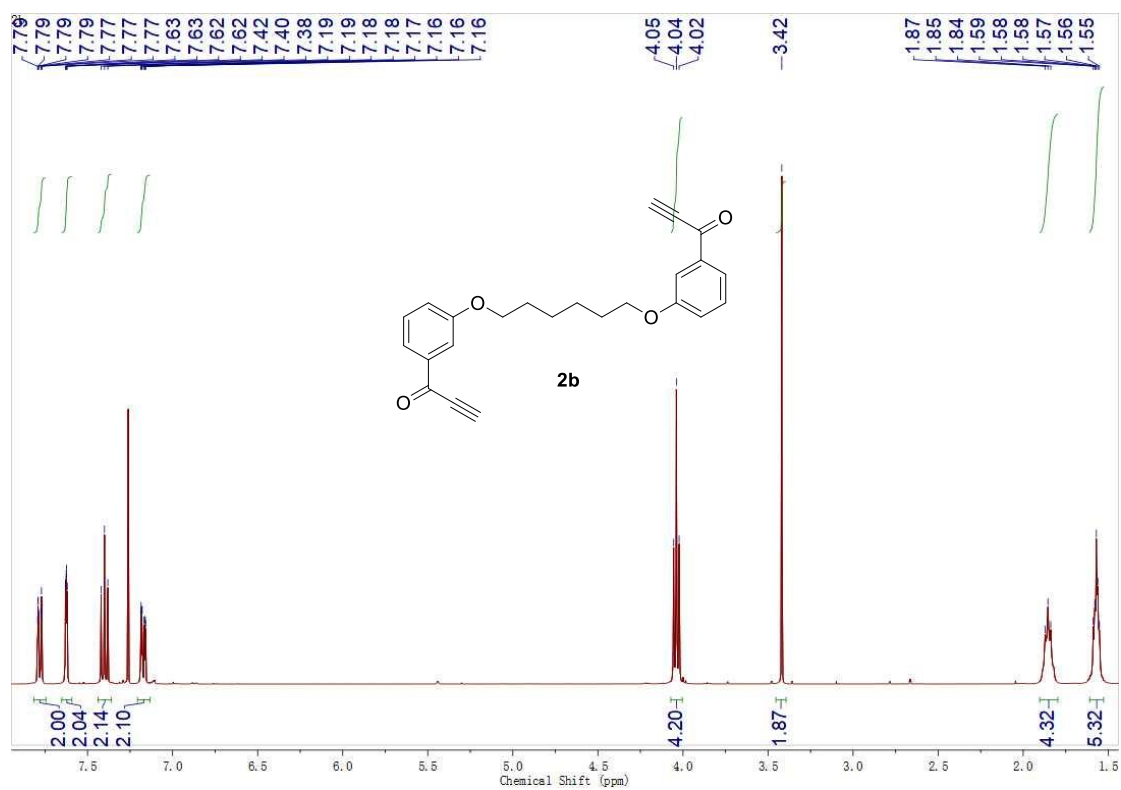


Figure S26. ^1H NMR spectrum of **2b** in CDCl_3 .

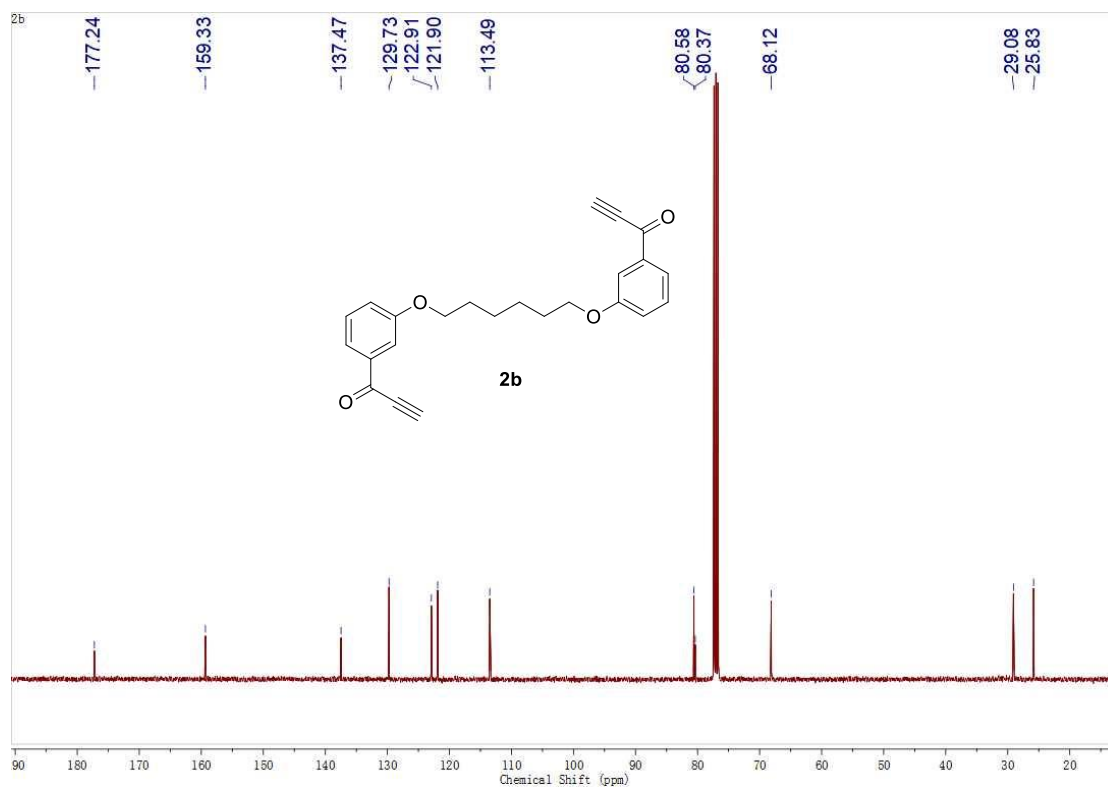


Figure S27. ^{13}C NMR spectrum of **2b** in CDCl_3 .

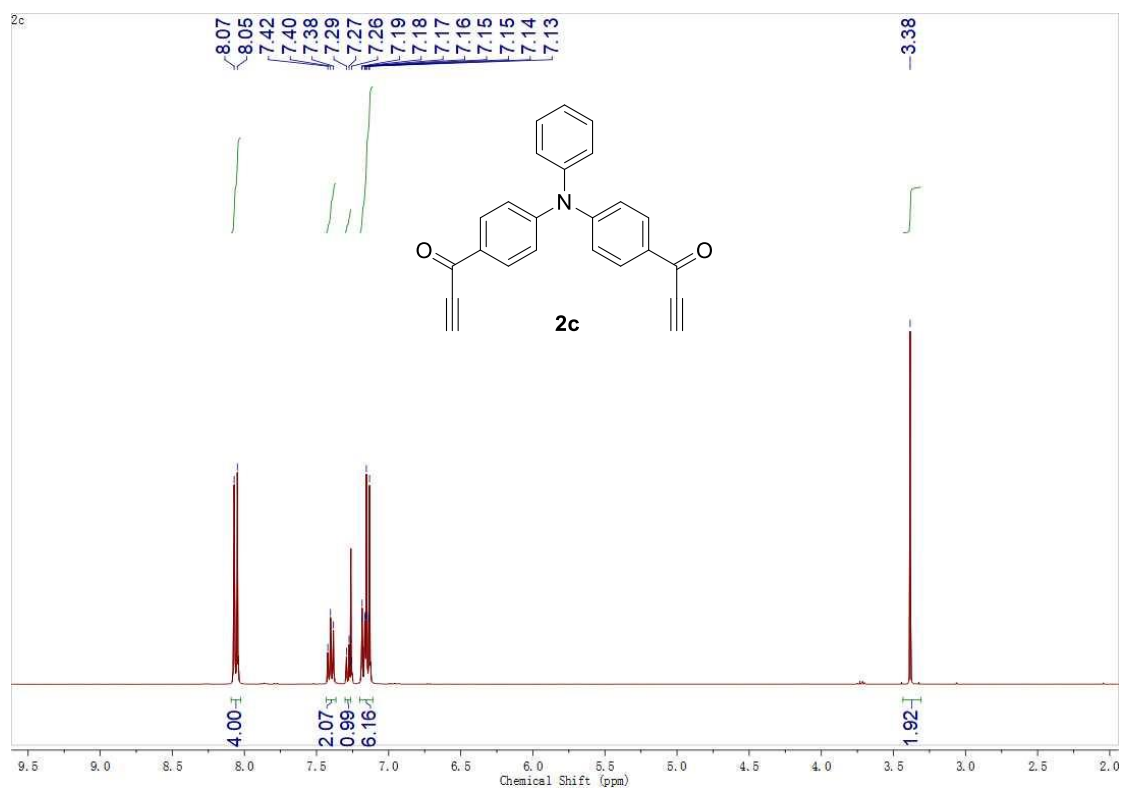


Figure S28. ^1H NMR spectrum of **2c** in CDCl_3 .

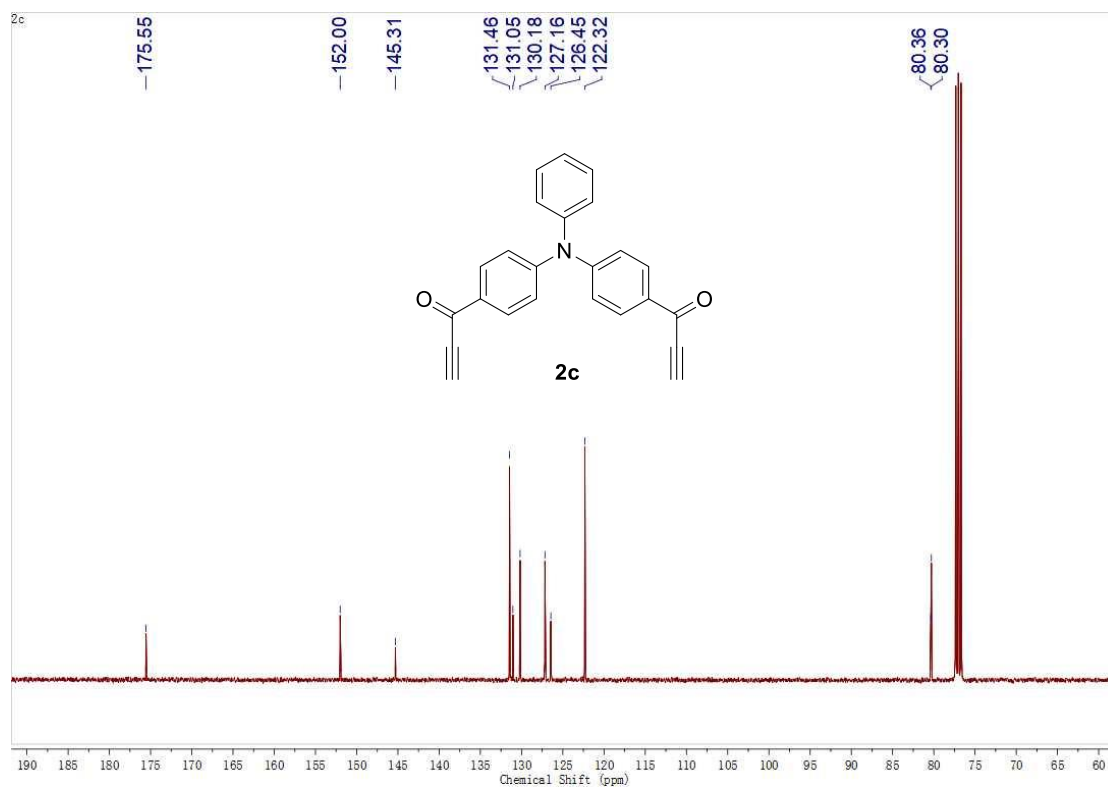


Figure S29. ^{13}C NMR spectrum of **2c** in CDCl_3 .

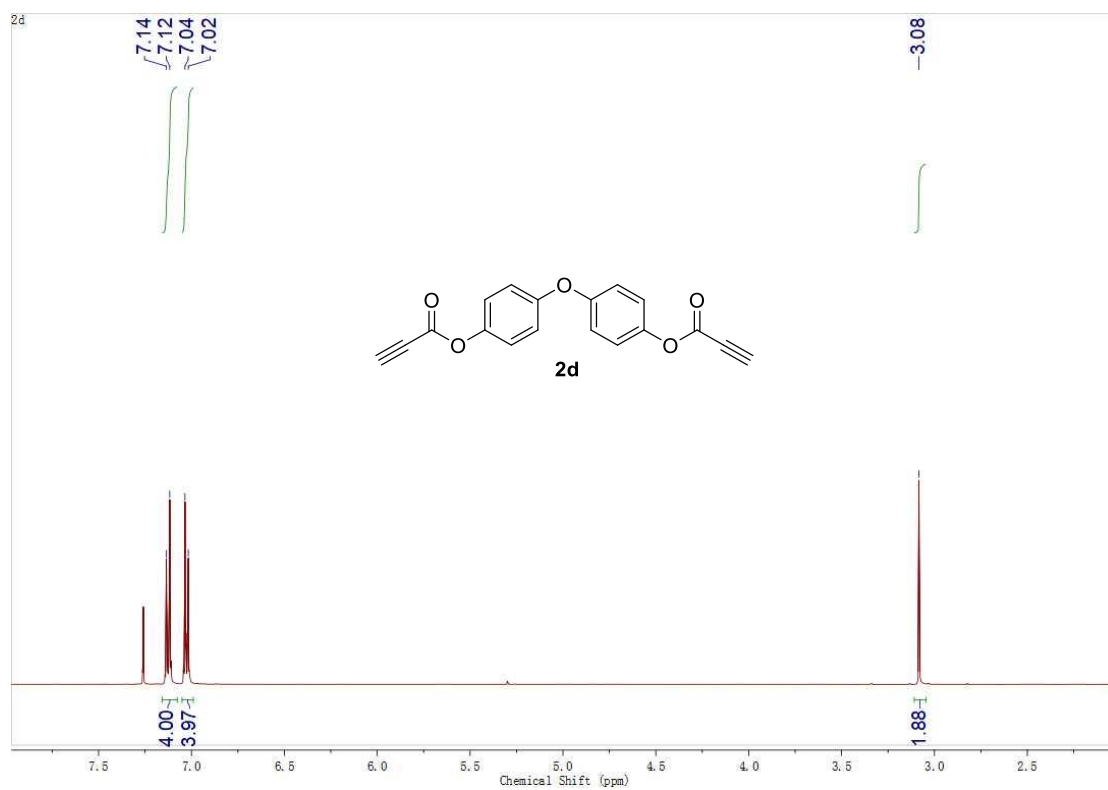


Figure S30. ^1H NMR spectrum of **2d** in CDCl_3 .

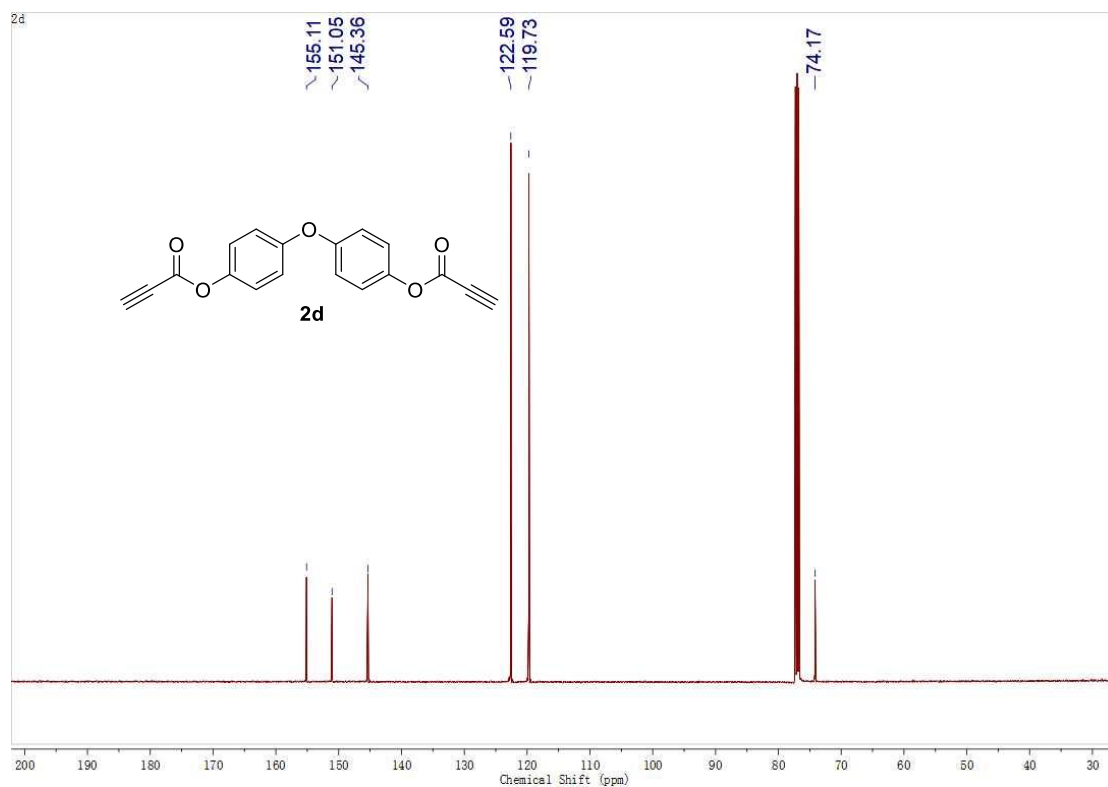


Figure S31. ¹³C NMR spectrum of **2d** in CDCl₃.

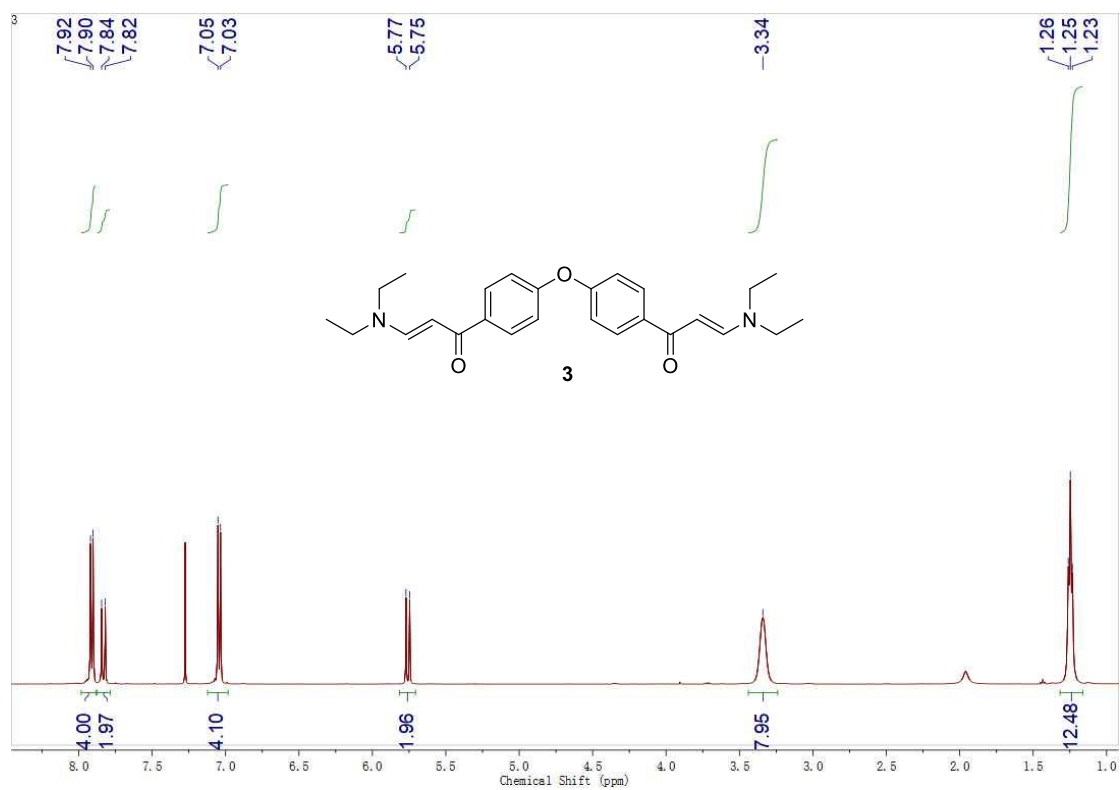


Figure S32. ¹H NMR spectrum of **3** in CDCl₃.

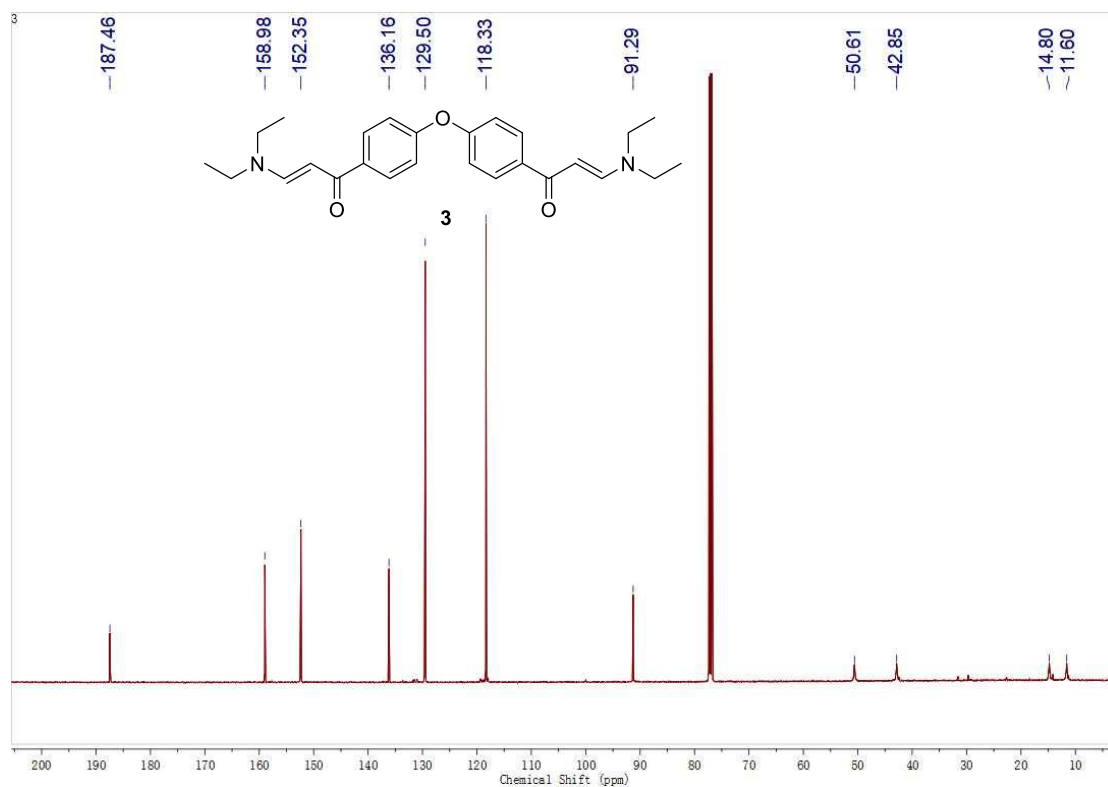


Figure S33. ^{13}C NMR spectrum of **3** in CDCl_3 .

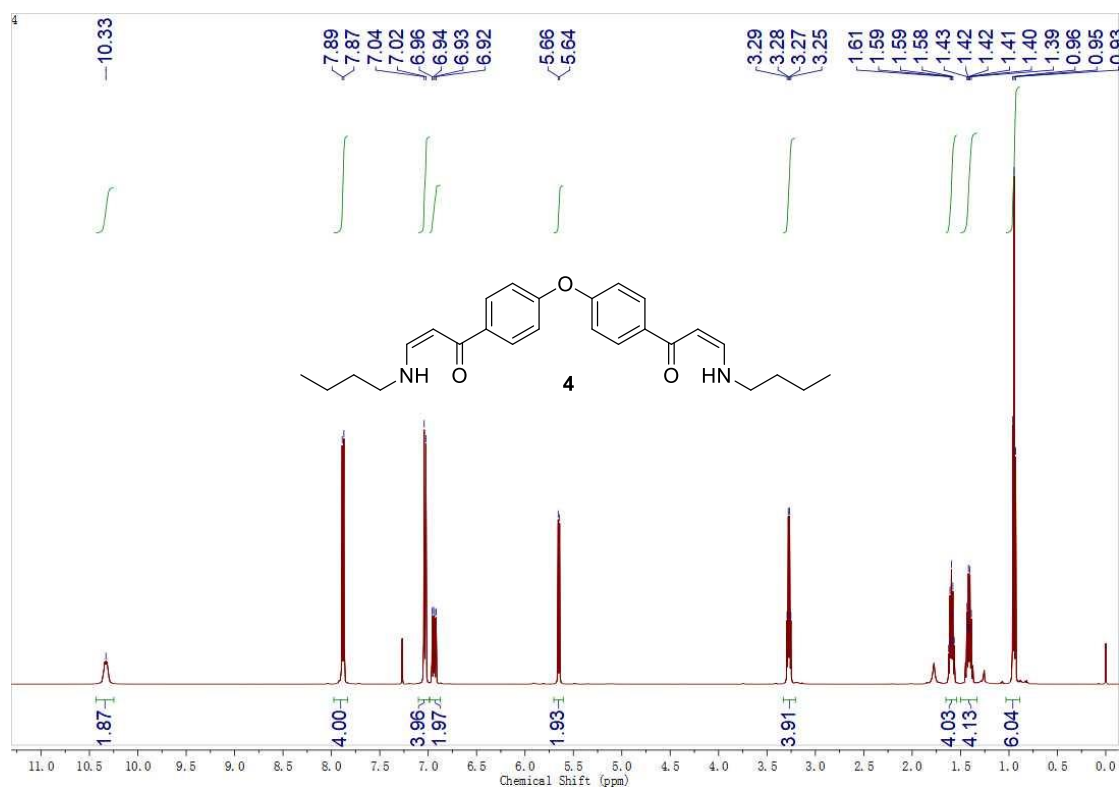


Figure S34. ^1H NMR spectrum of **4** in CDCl_3 .

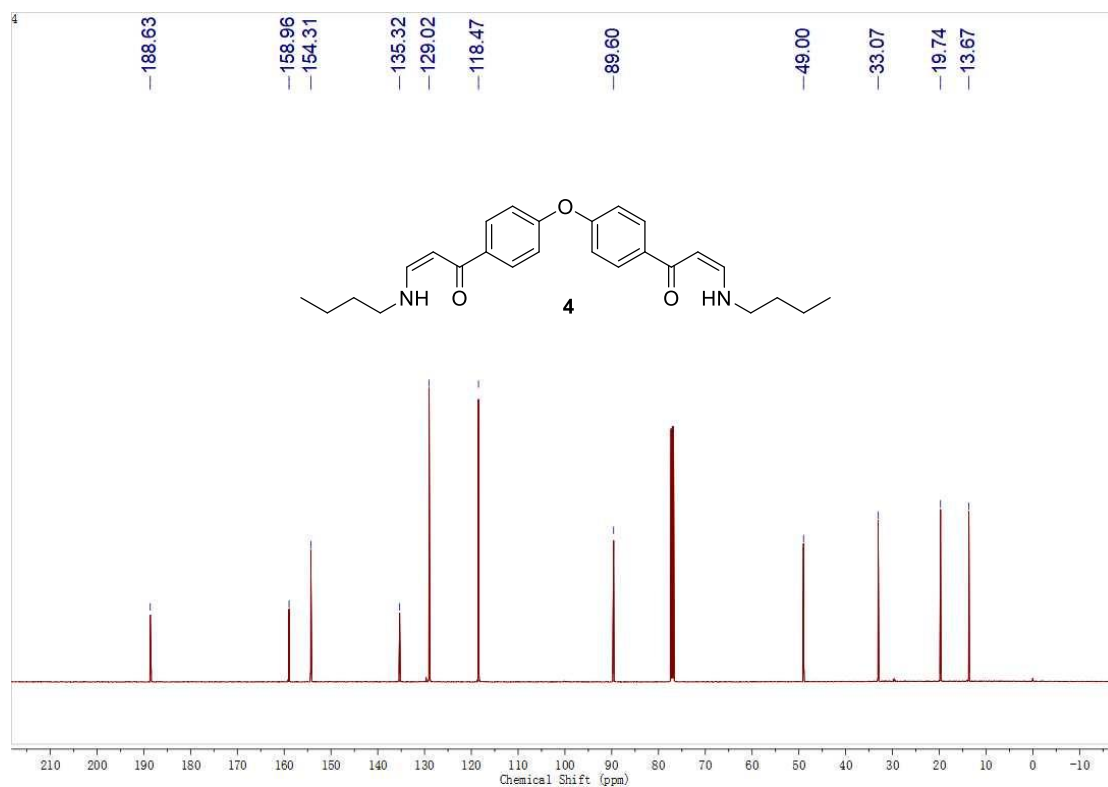


Figure S35. ¹³C NMR spectrum of **4** in CDCl₃.

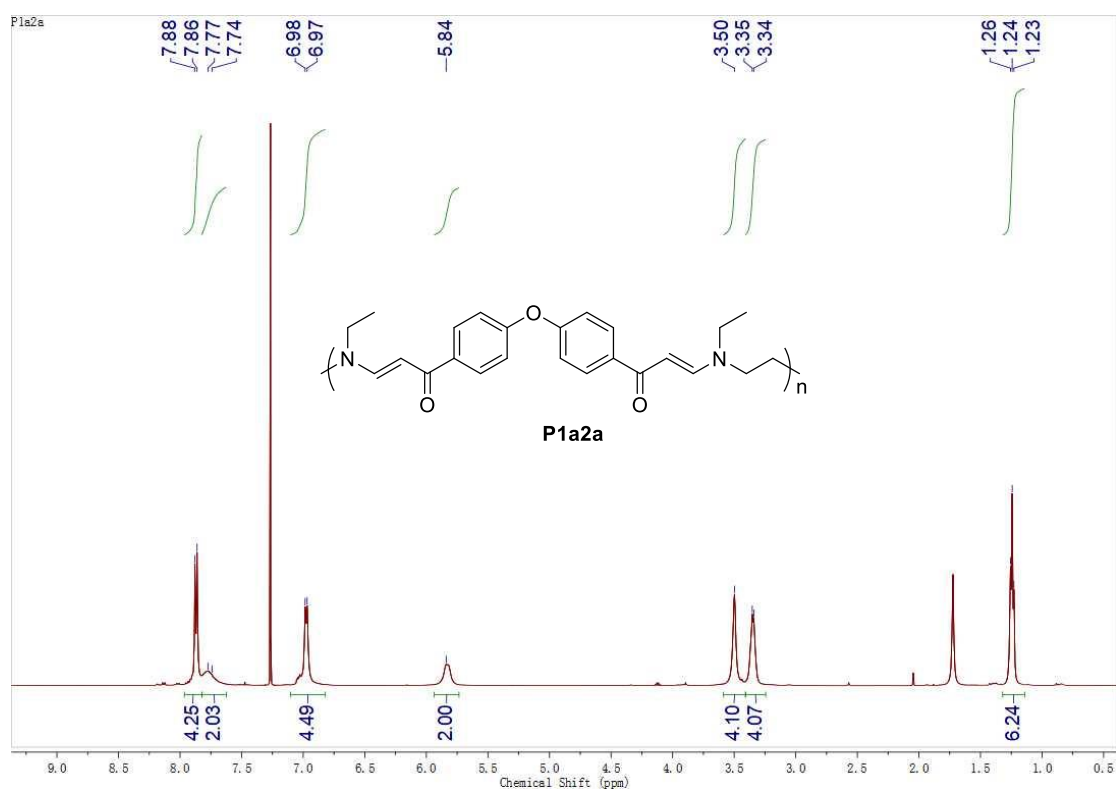


Figure S36. ¹H NMR spectrum of **P1a2a** in CDCl₃.

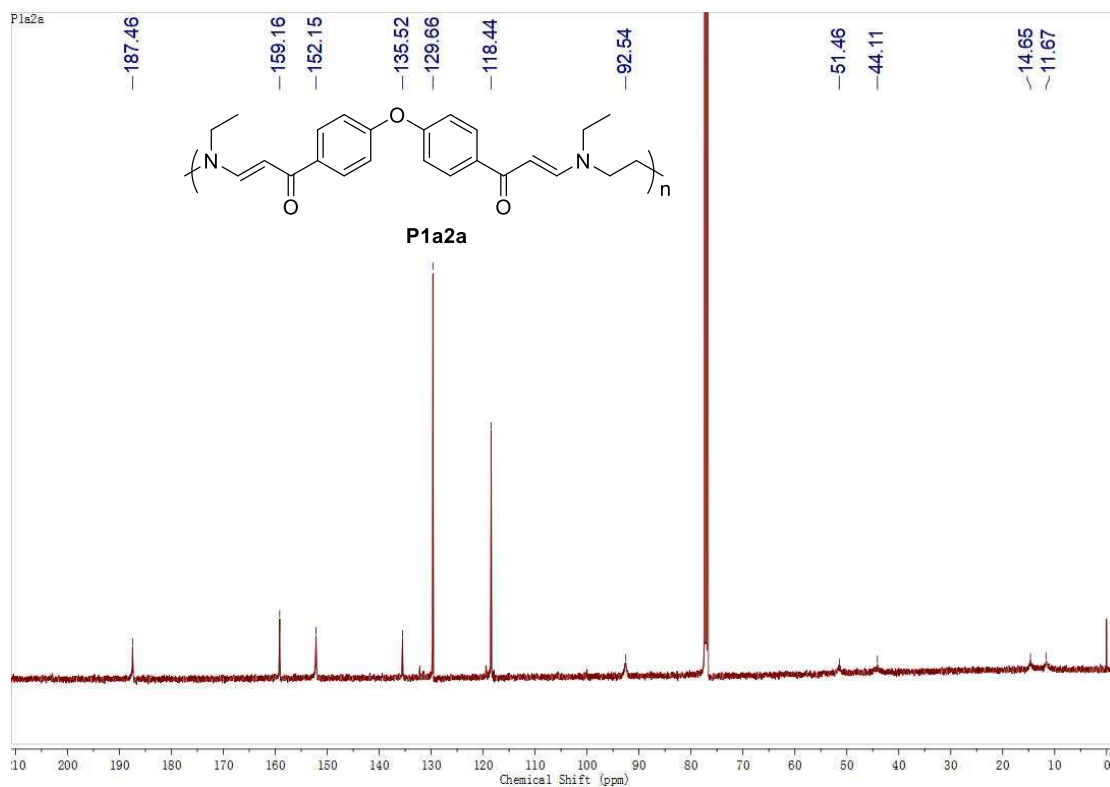


Figure S37. ^{13}C NMR spectrum of **P1a2a** in CDCl_3 .

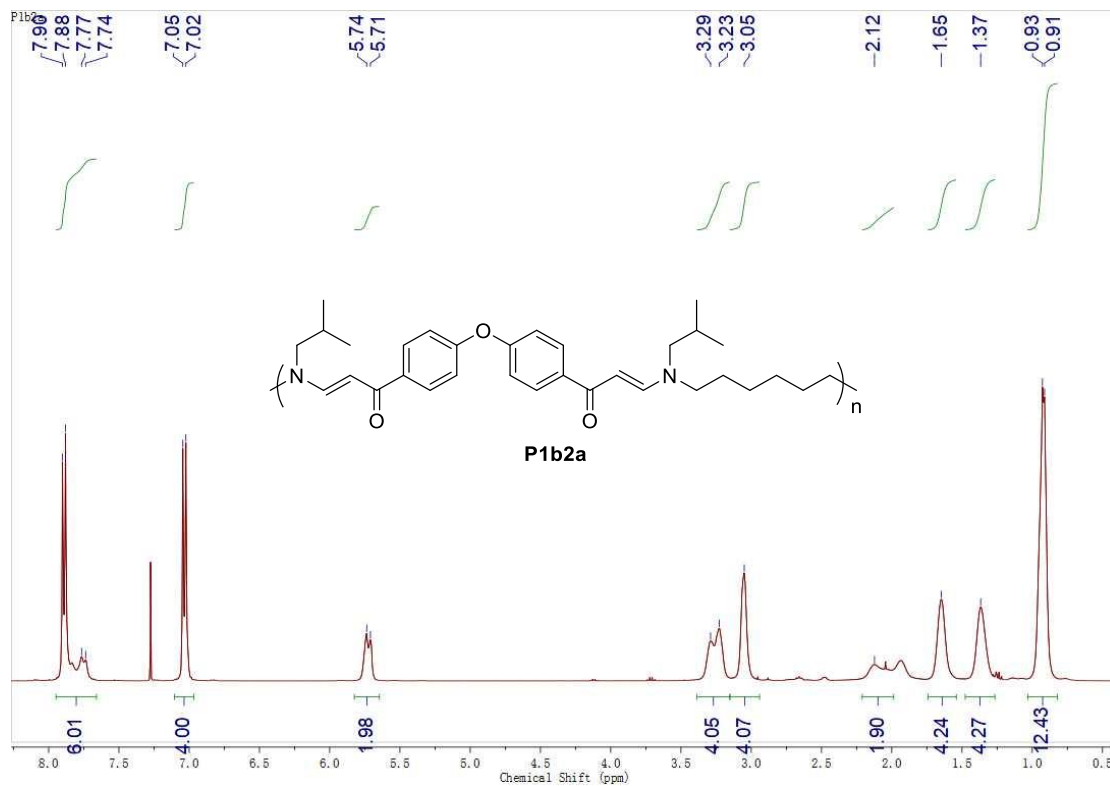


Figure S38. ^1H NMR spectrum of **P1b2a** in CDCl_3 .

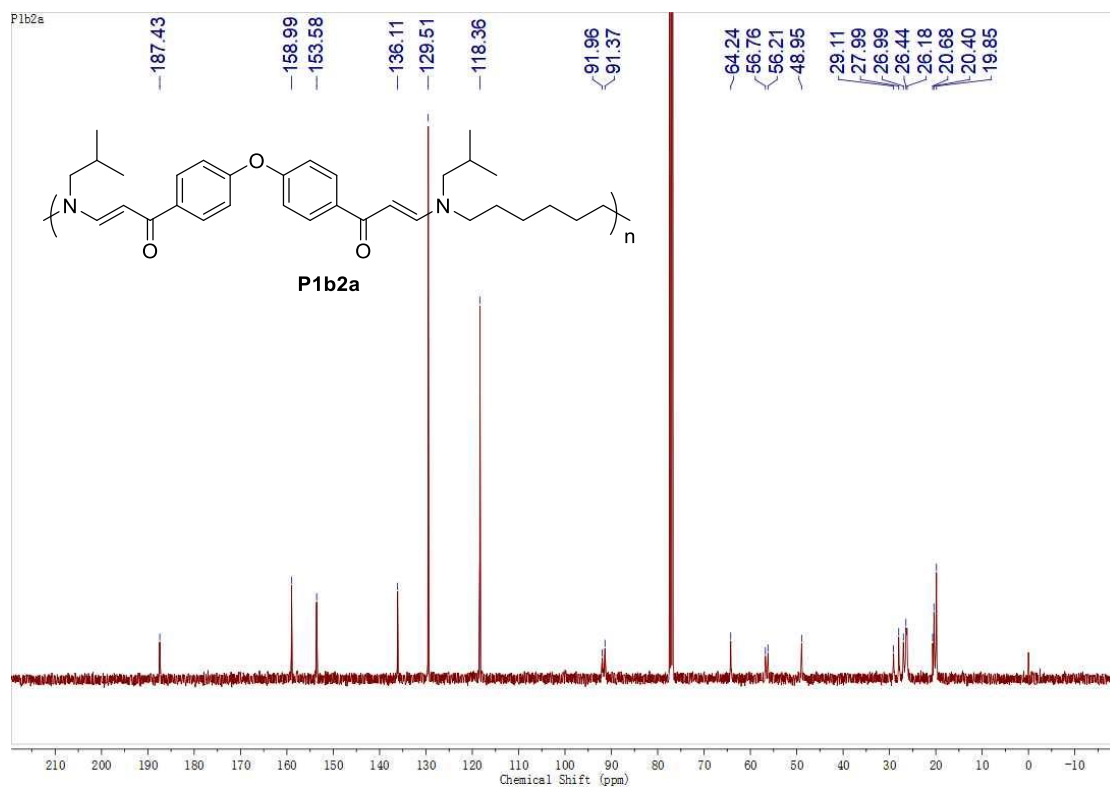


Figure S39. ^{13}C NMR spectrum of **P1b2a** in CDCl_3 .

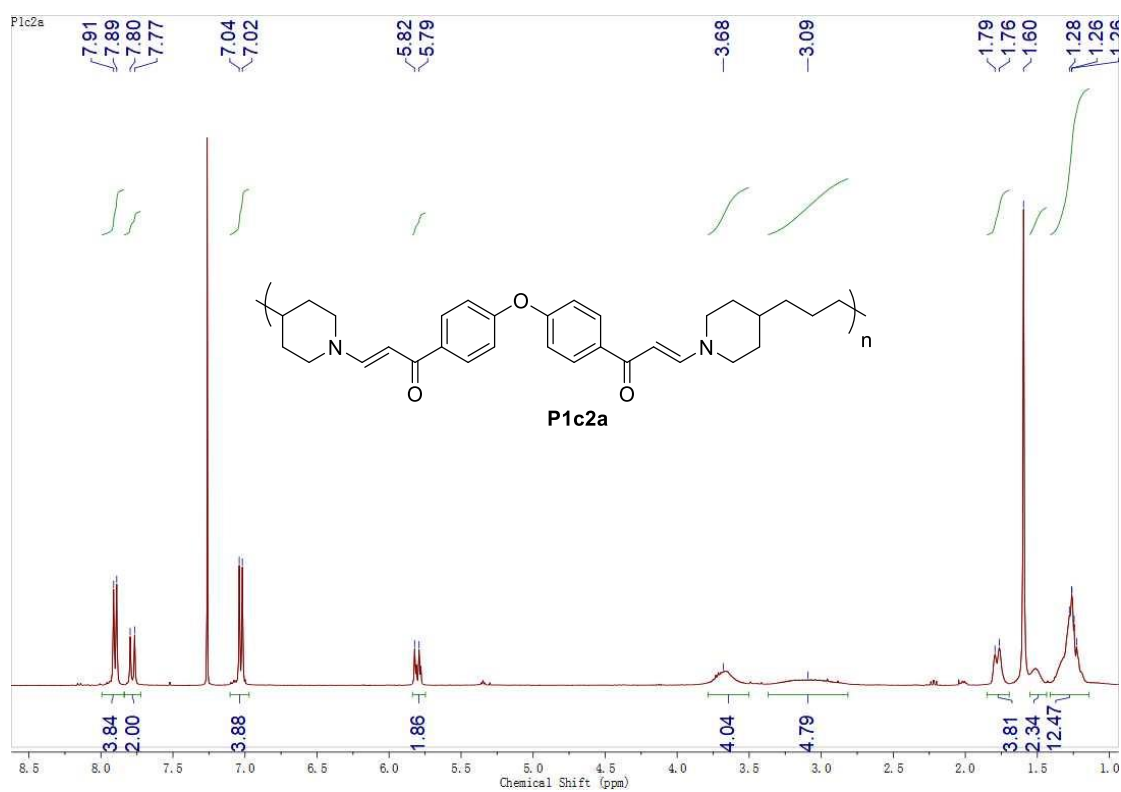


Figure S40. ^1H NMR spectrum of **P1c2a** in CDCl_3 .

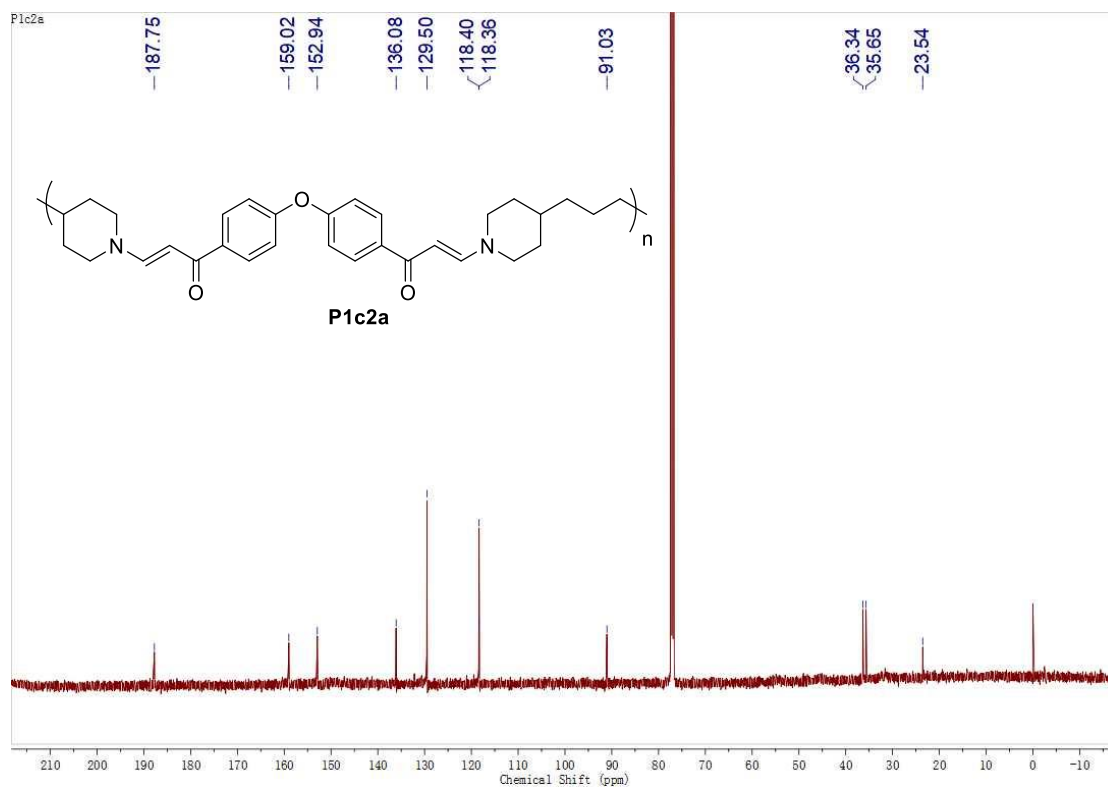


Figure S41. ^{13}C NMR spectrum of P1c2a in CDCl_3 .

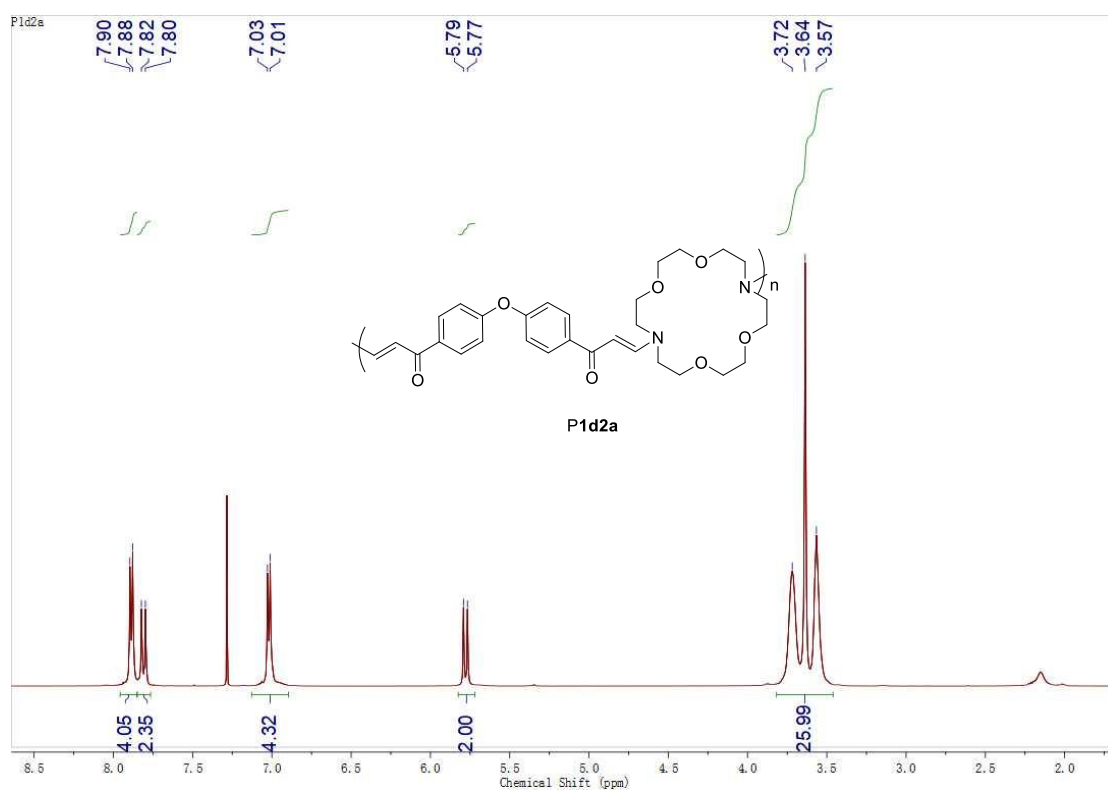


Figure S42. ^1H NMR spectrum of P1d2a in CDCl_3 .

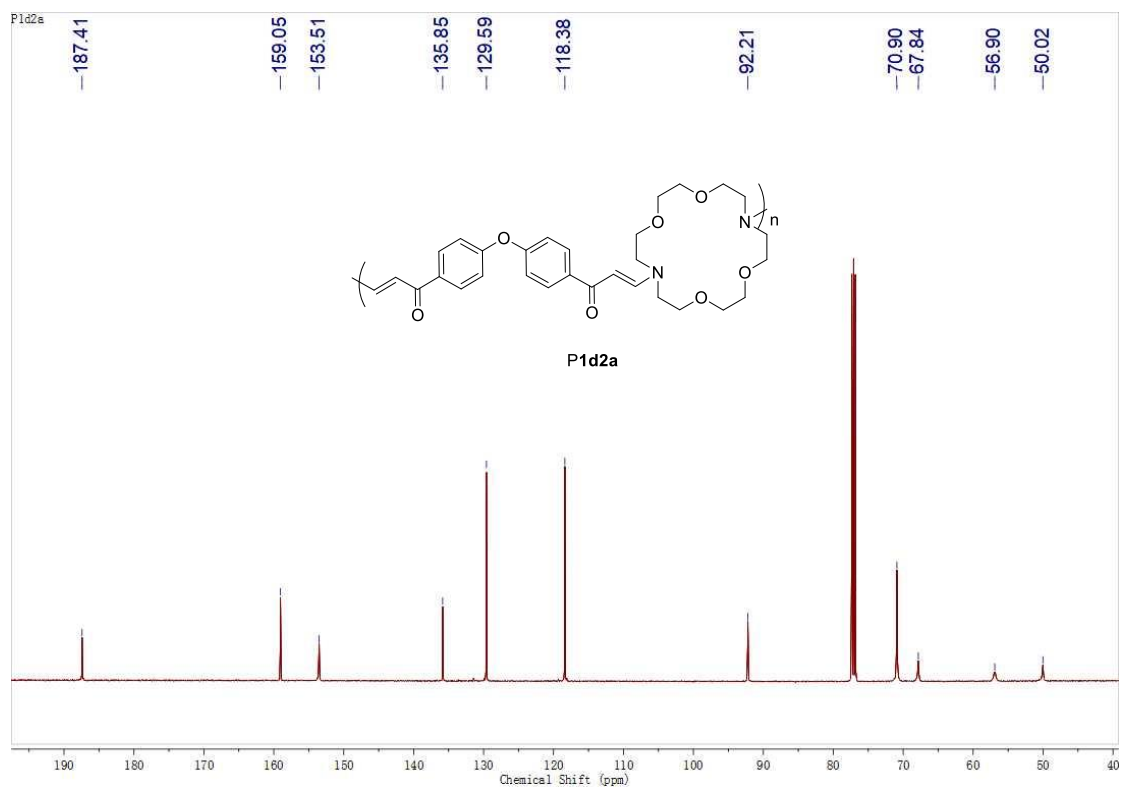


Figure S43. ^{13}C NMR spectrum of **P1d2a** in CDCl_3 .

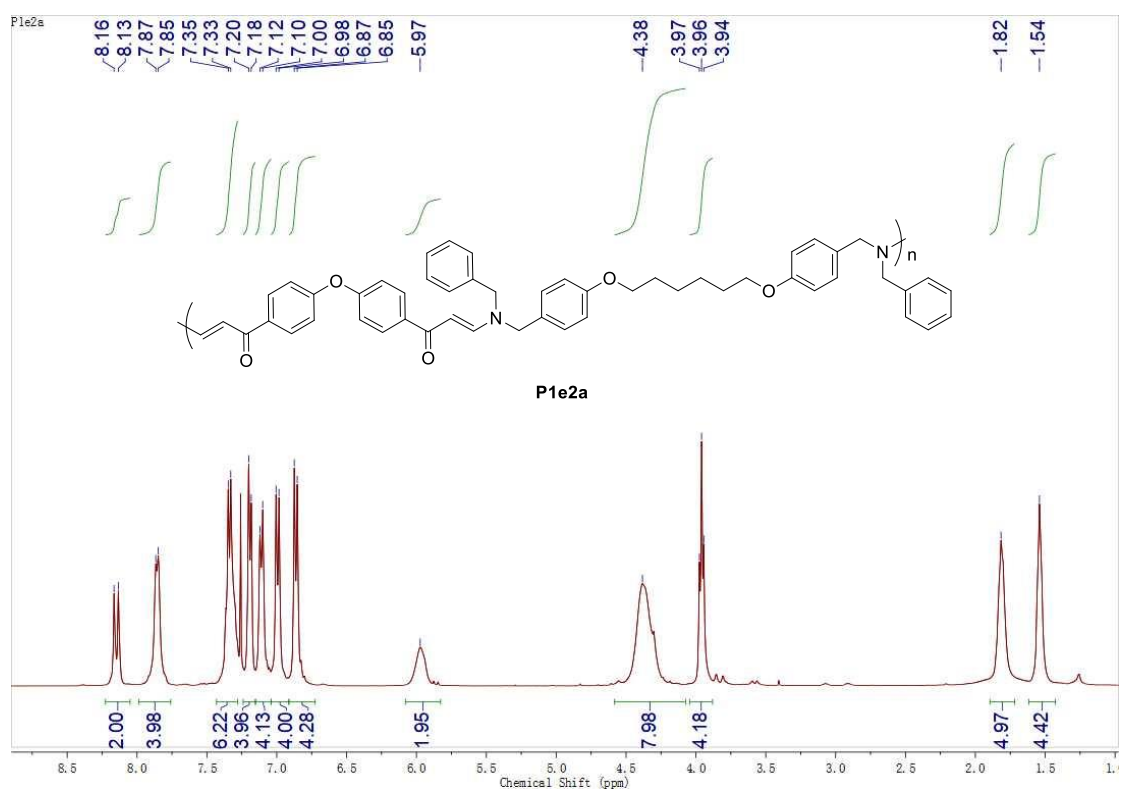


Figure S44. ^1H NMR spectrum of **P1e2a** in CDCl_3 .

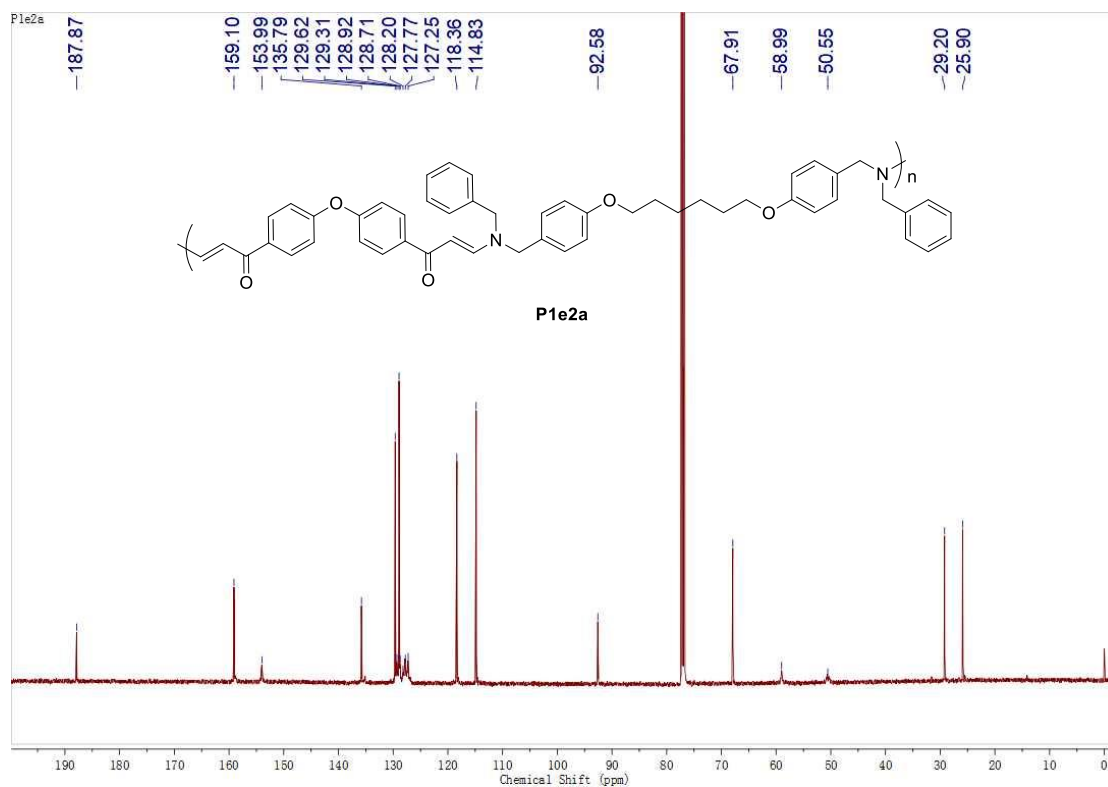


Figure S45. ^{13}C NMR spectrum of **P1e2a** in CDCl_3 .

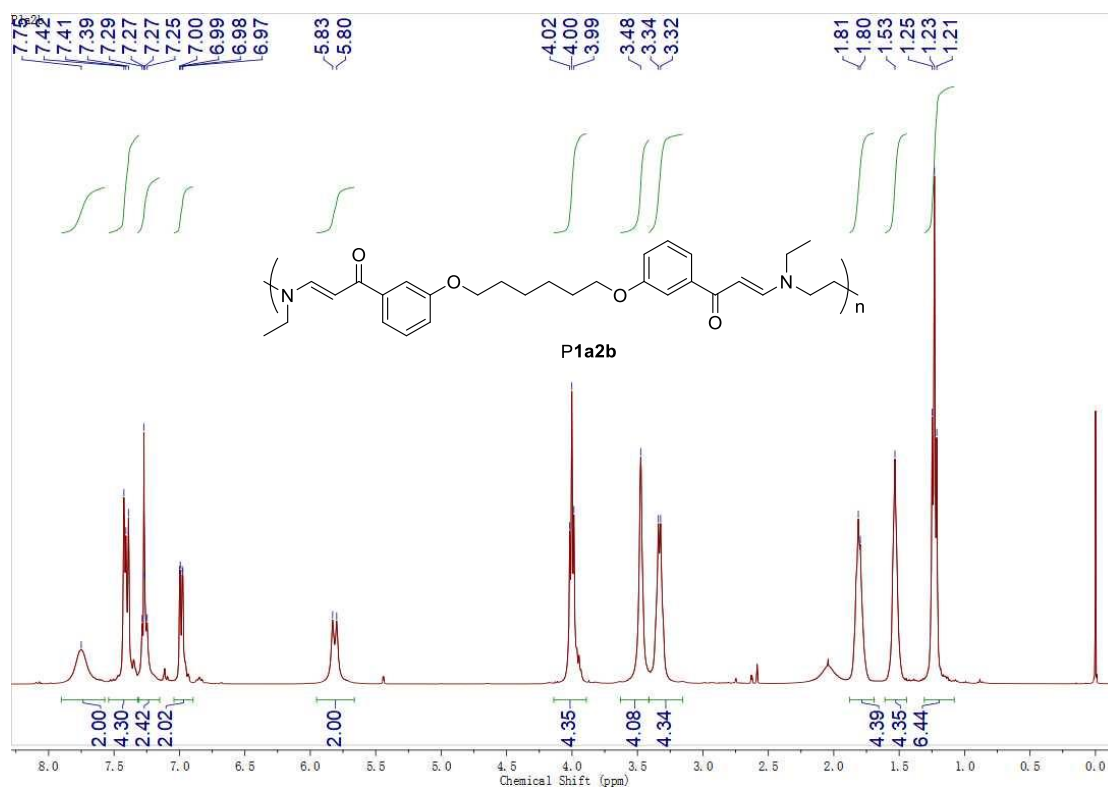


Figure S46. ^1H NMR spectrum of **P1a2b** in CDCl_3 .

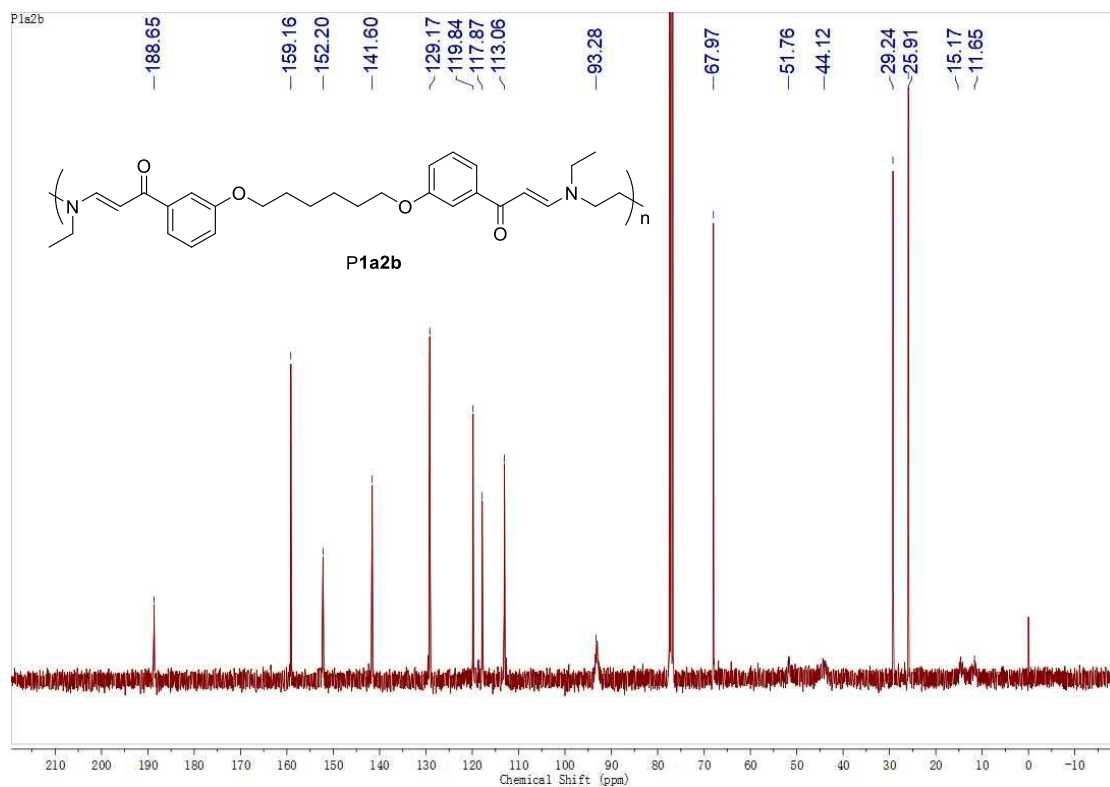


Figure S47. ^{13}C NMR spectrum of **P1a2b** in CDCl_3 .

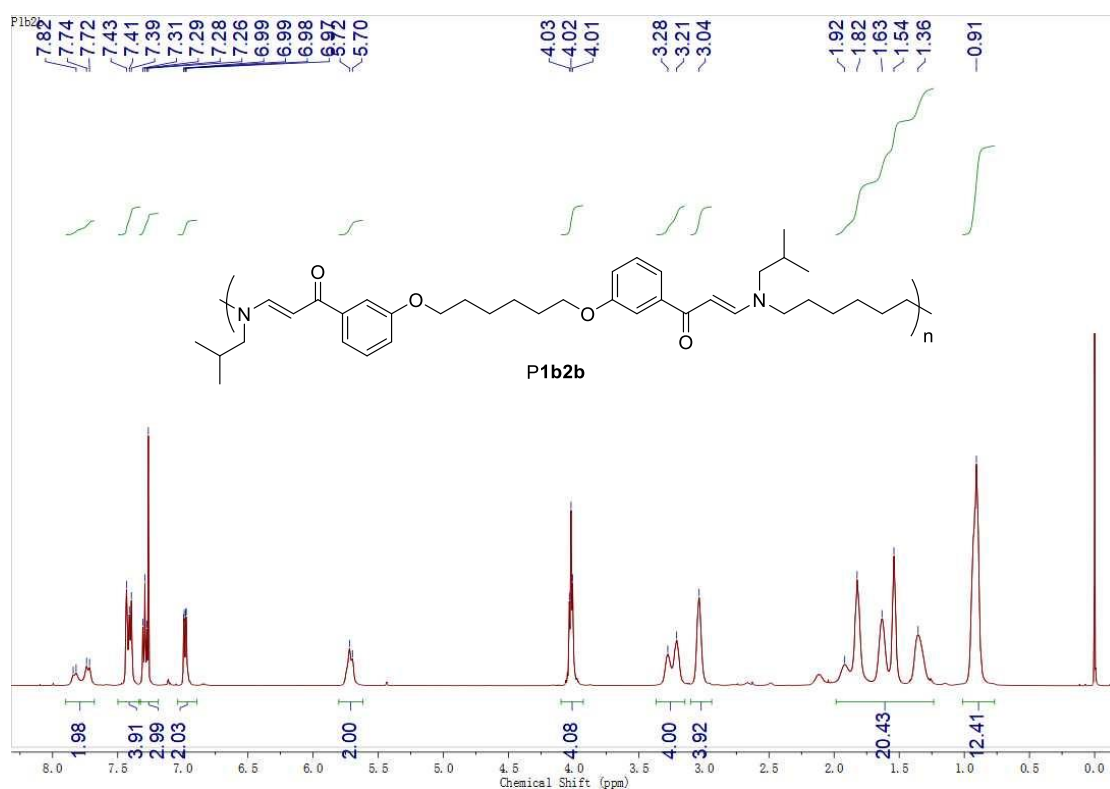


Figure S48. ^1H NMR spectrum of **P1b2b** in CDCl_3 .

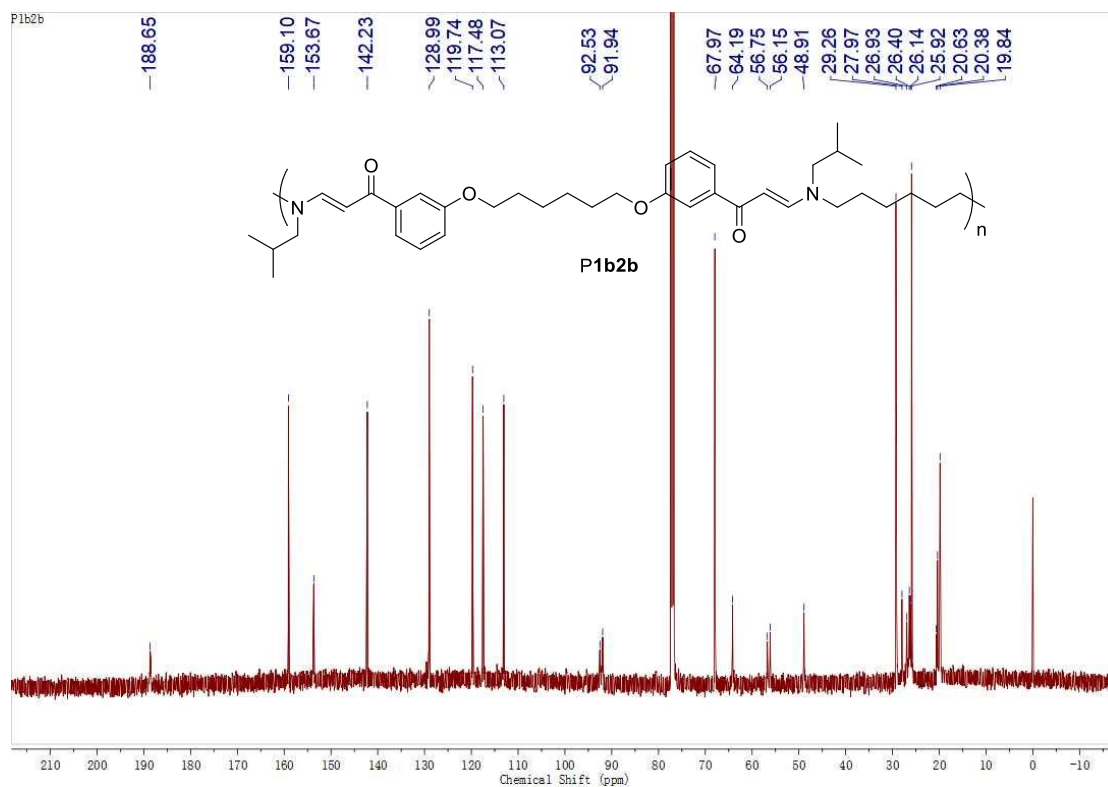


Figure S49. ^{13}C NMR spectrum of **P1b2b** in CDCl_3 .

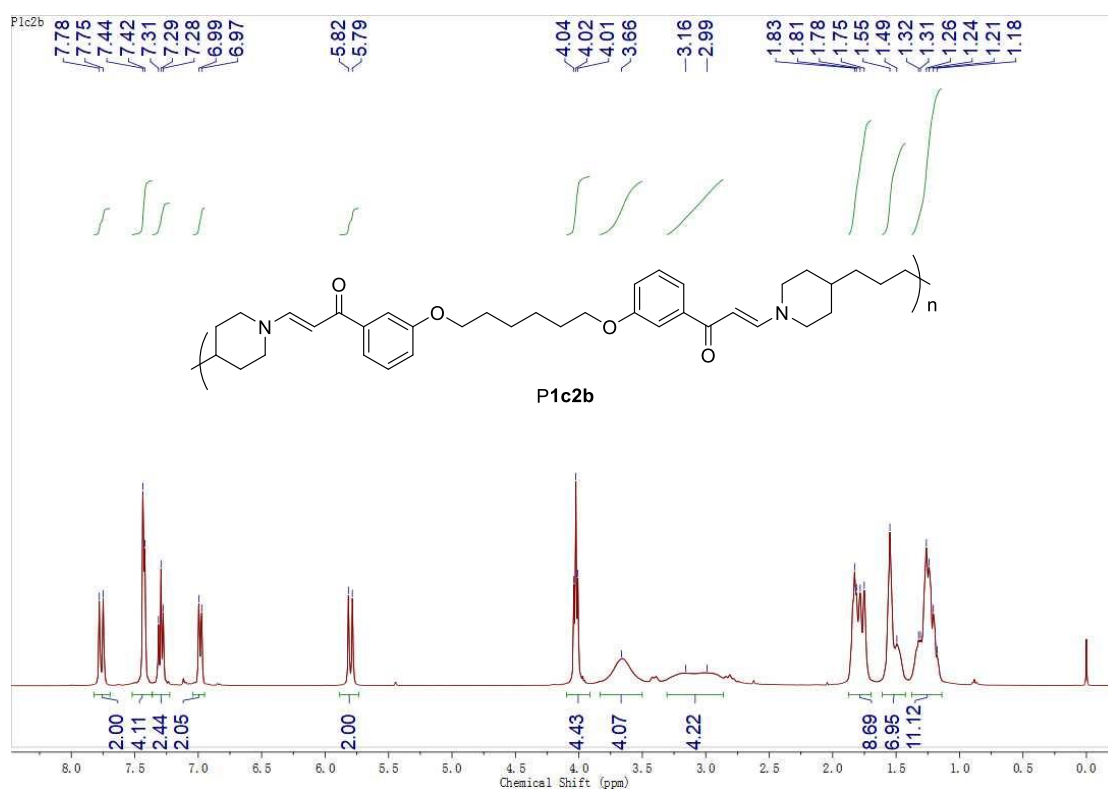


Figure S50. ^1H NMR spectrum of **P1c2b** in CDCl_3 .

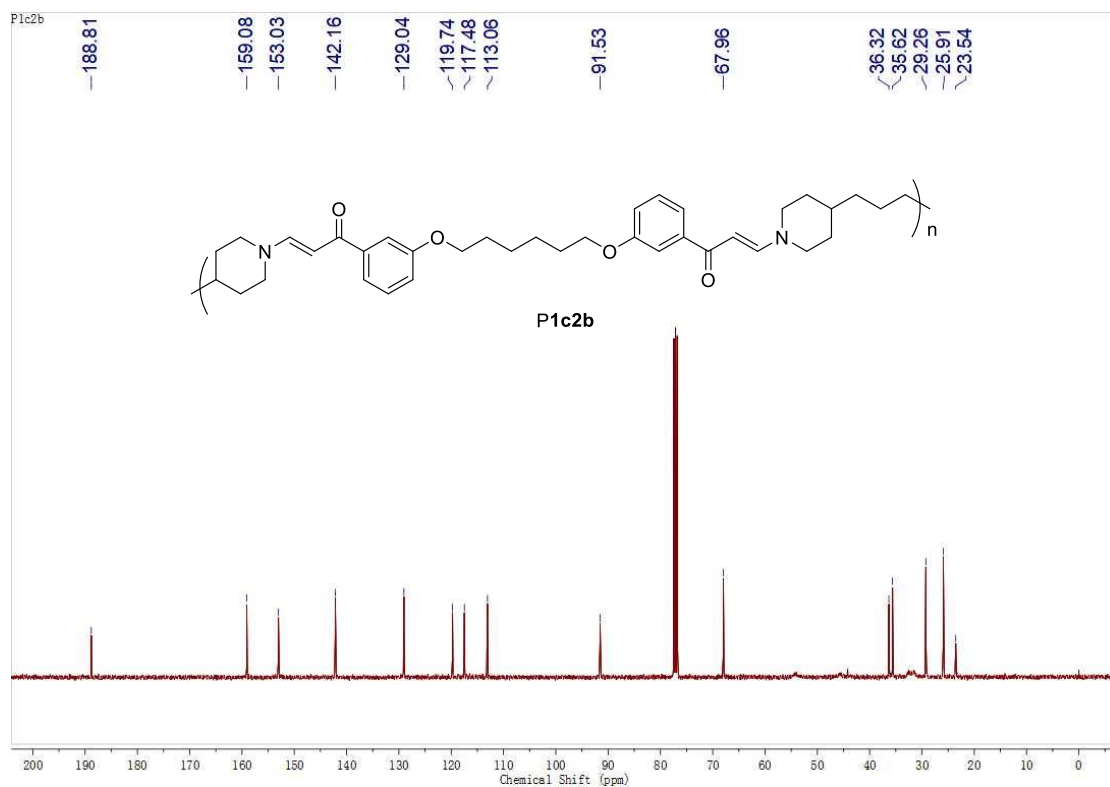


Figure S51. ^{13}C NMR spectrum of P1c2b in CDCl_3 .

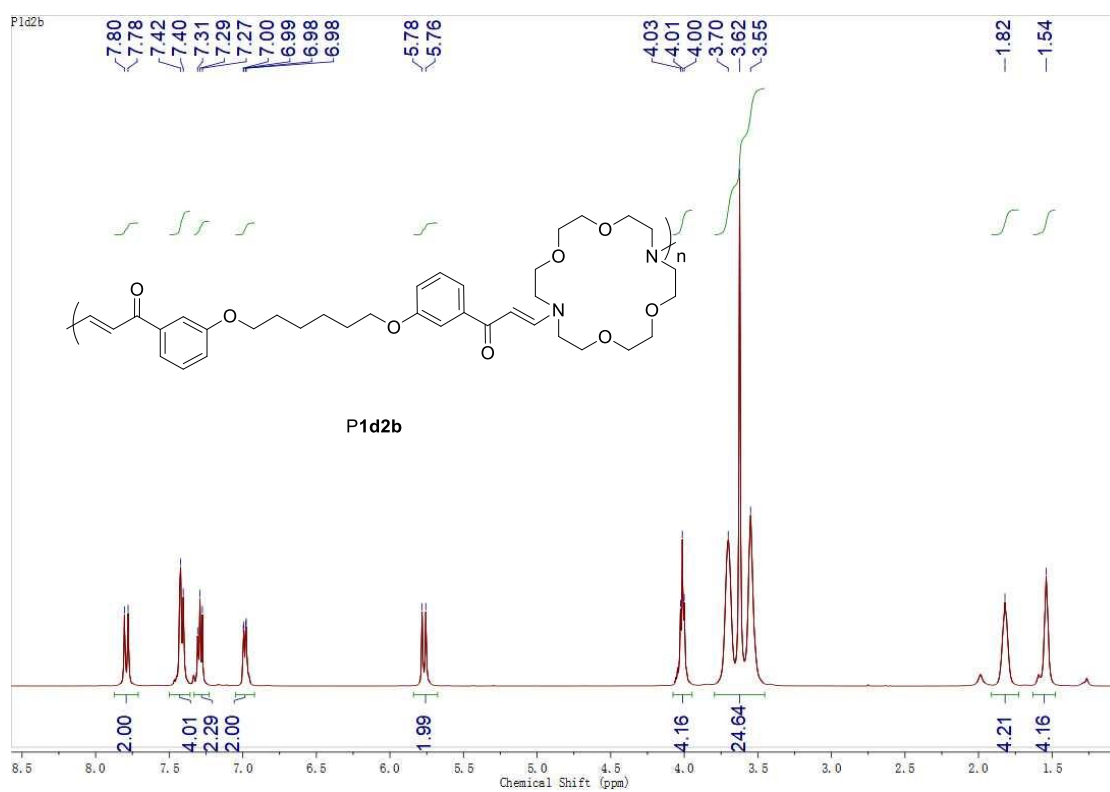


Figure S52. ^1H NMR spectrum of P1d2b in CDCl_3 .

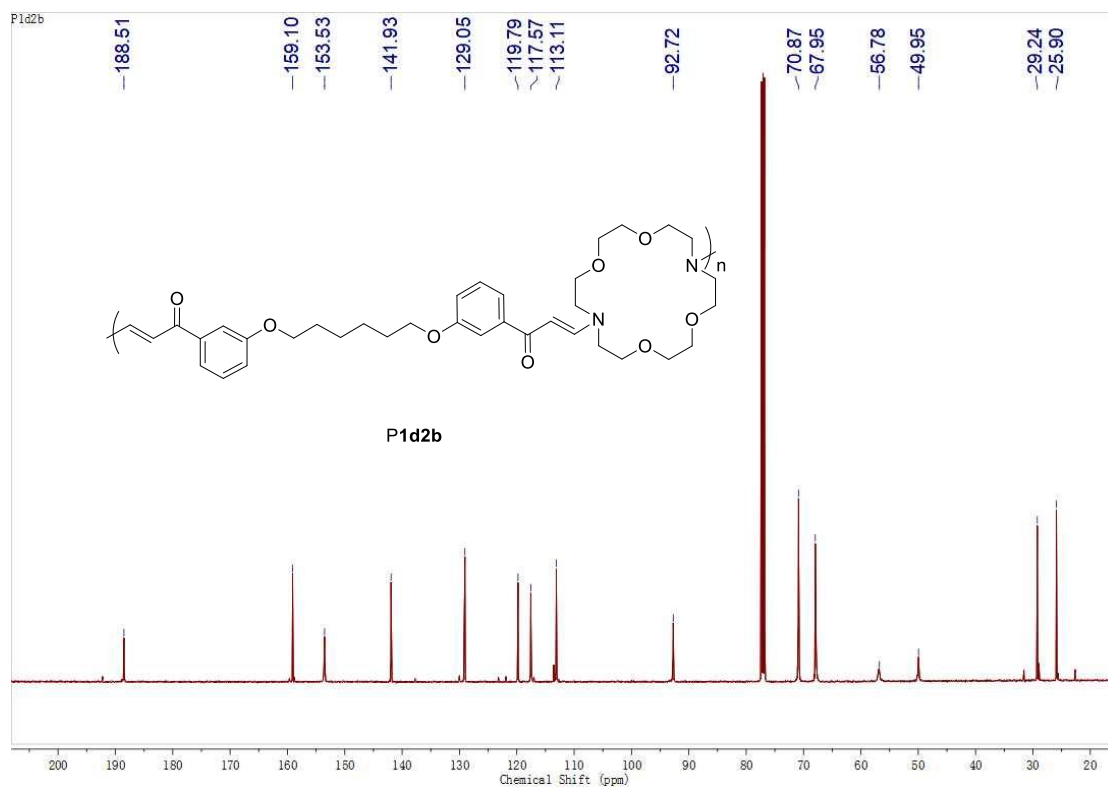


Figure S53. ^{13}C NMR spectrum of P1d2b in CDCl_3 .

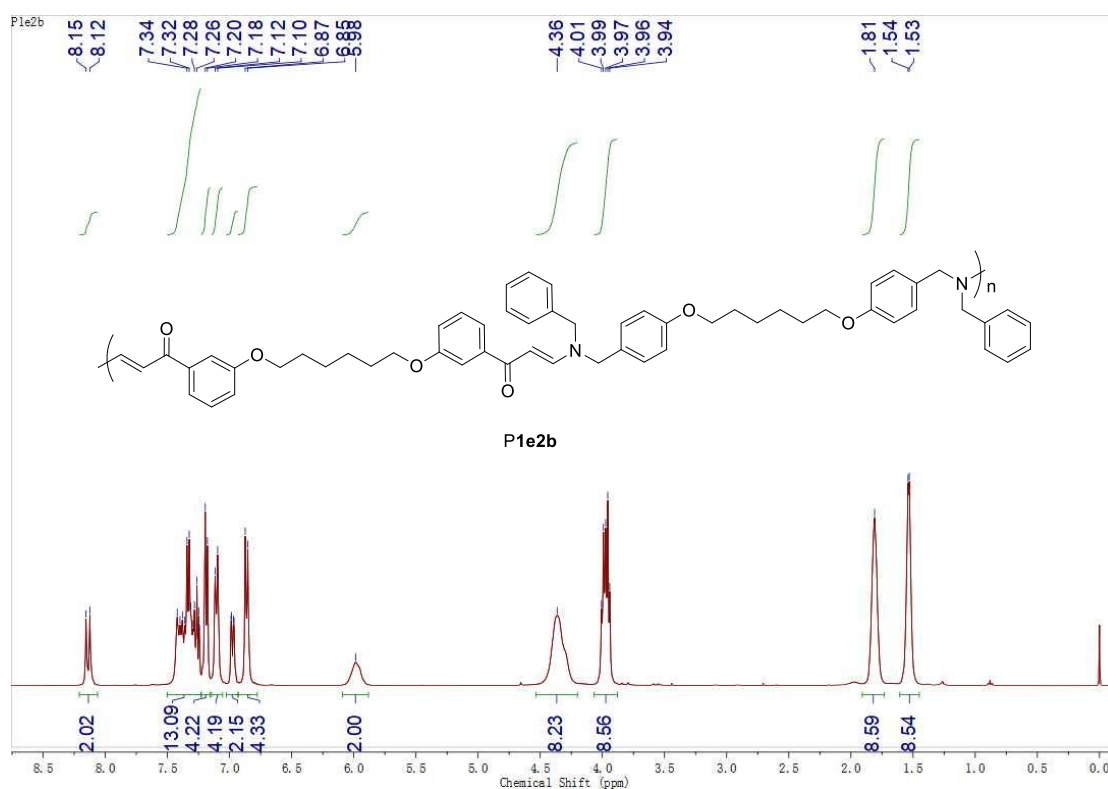


Figure S54. ^1H NMR spectrum of **P1e2b** in CDCl_3 .

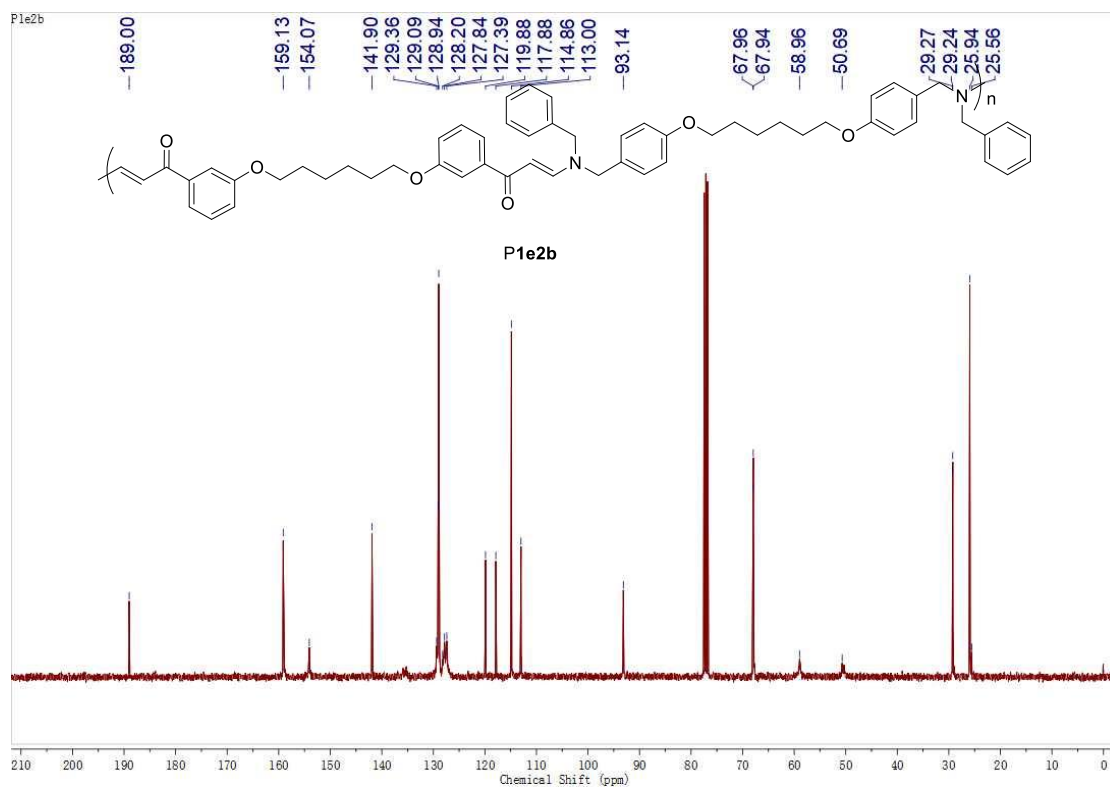


Figure S55. ^{13}C NMR spectrum of P1e2b in CDCl_3 .

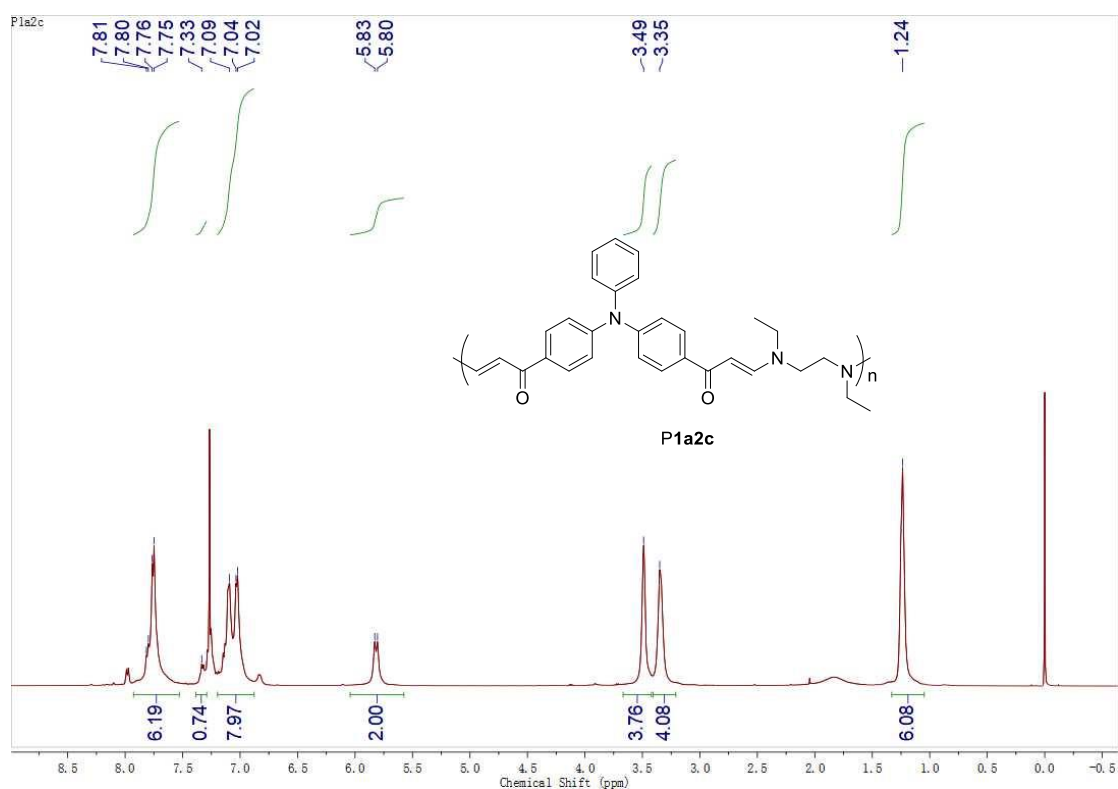


Figure S56. ^1H NMR spectrum of P1a2c in CDCl_3 .

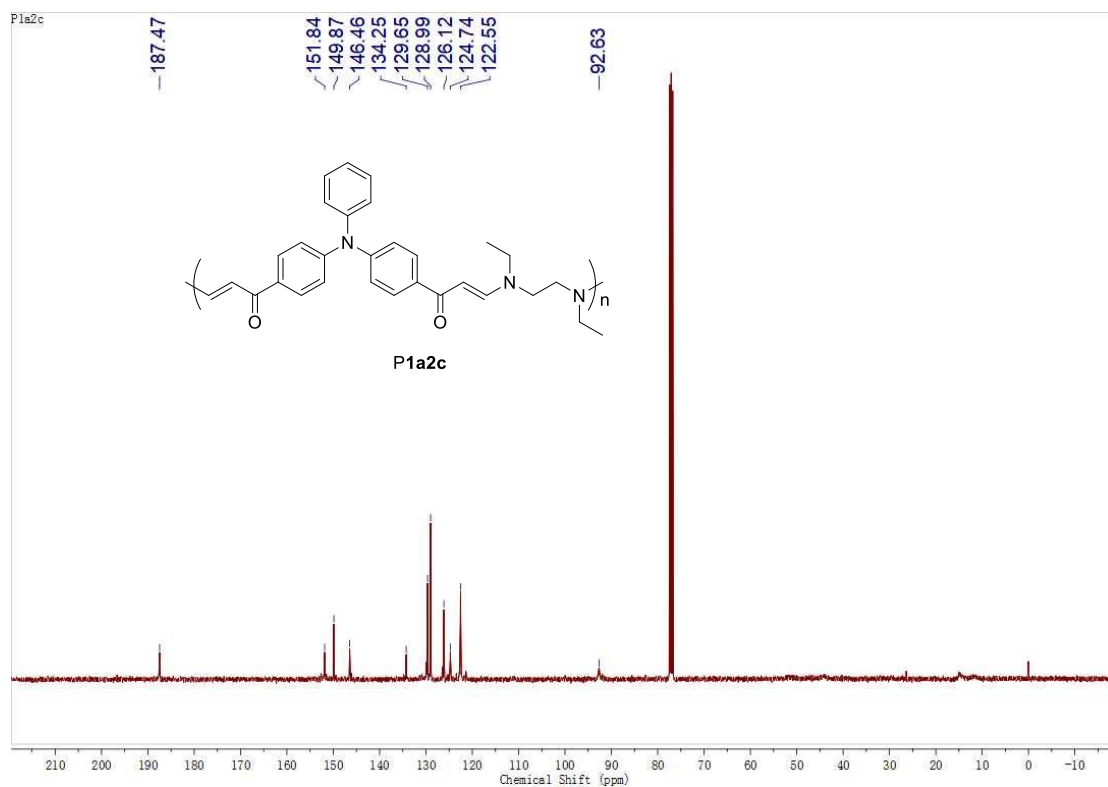


Figure S57. ^{13}C NMR spectrum of **P1a2c** in CDCl_3 .

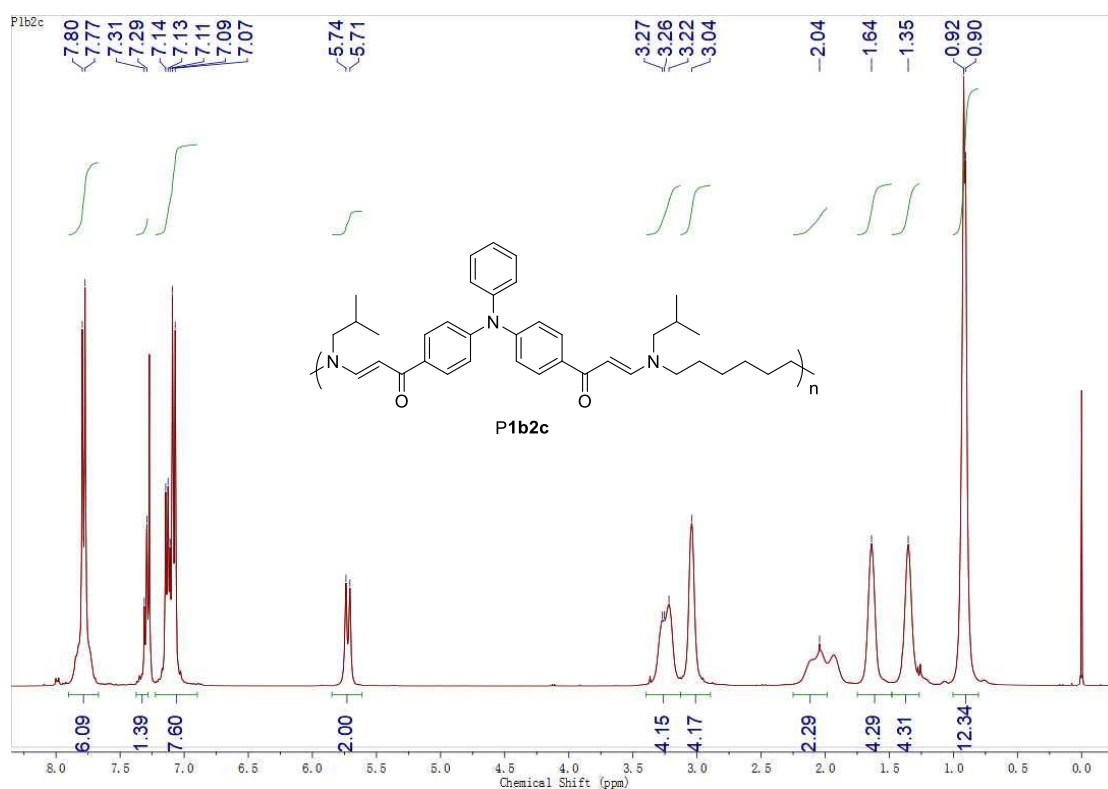


Figure S58. ^1H NMR spectrum of **P1b2c** in CDCl_3 .

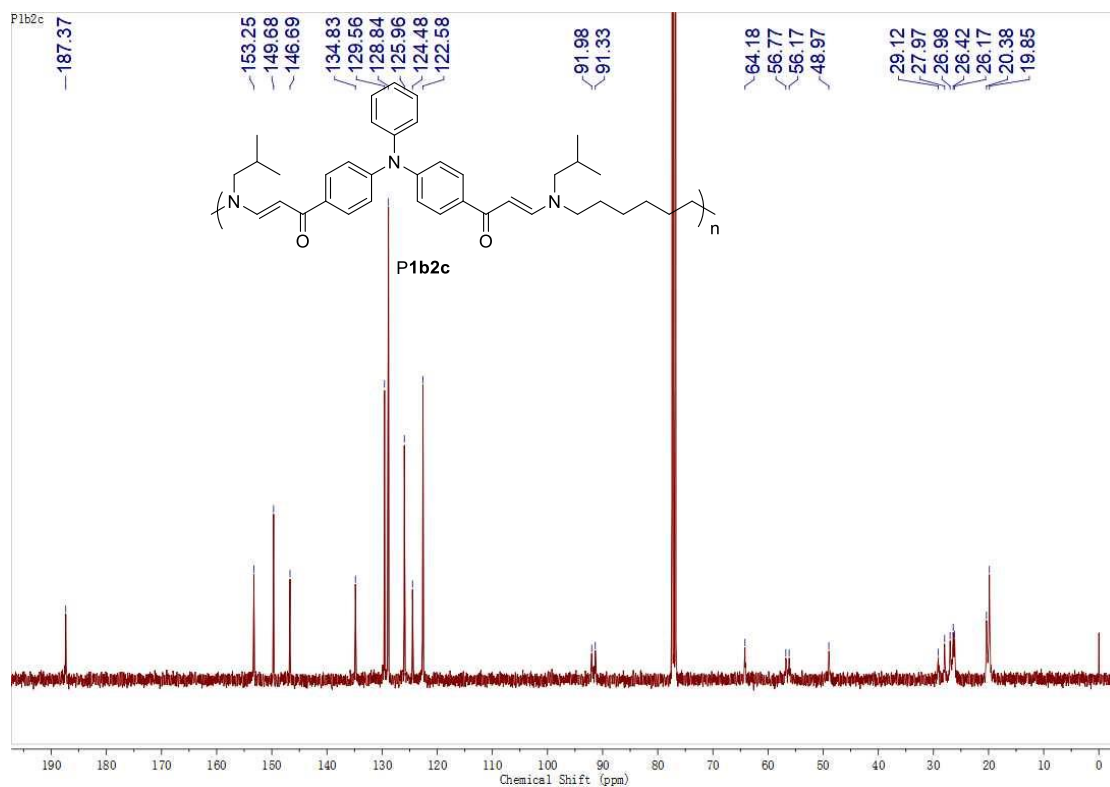


Figure S59. ^{13}C NMR spectrum of **P1b2c** in CDCl_3 .

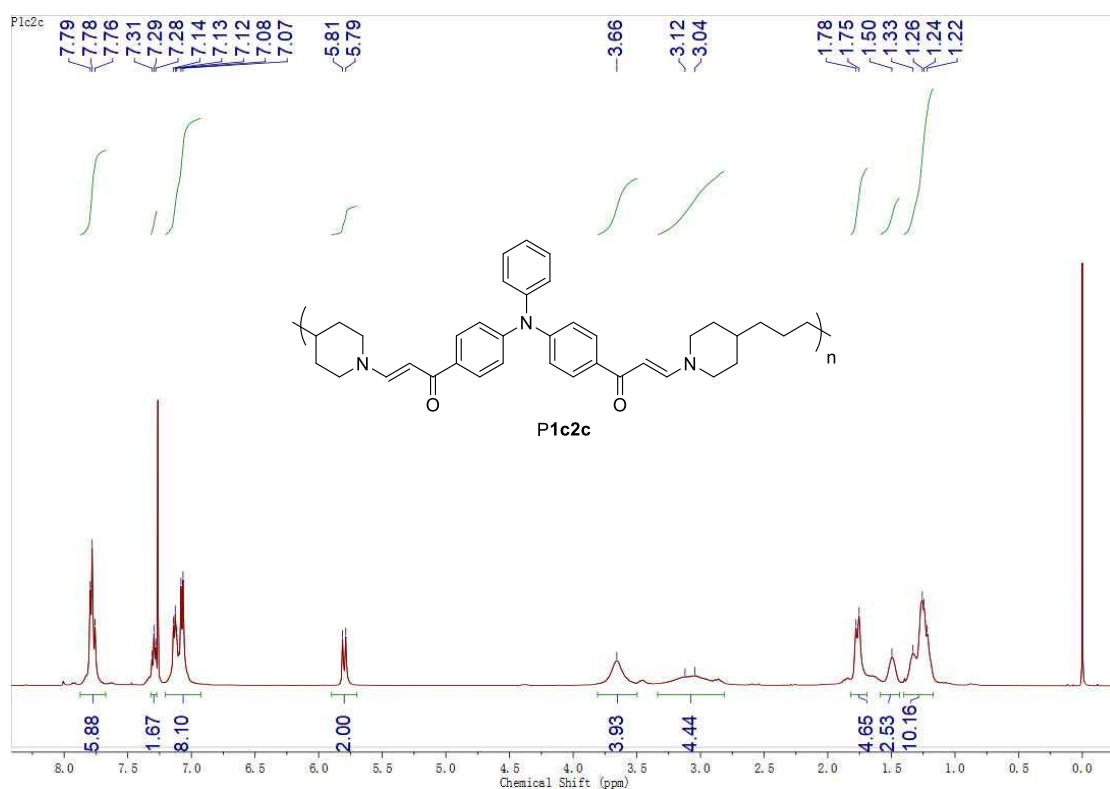


Figure S60. ^1H NMR spectrum of **P1c2c** in CDCl_3 .

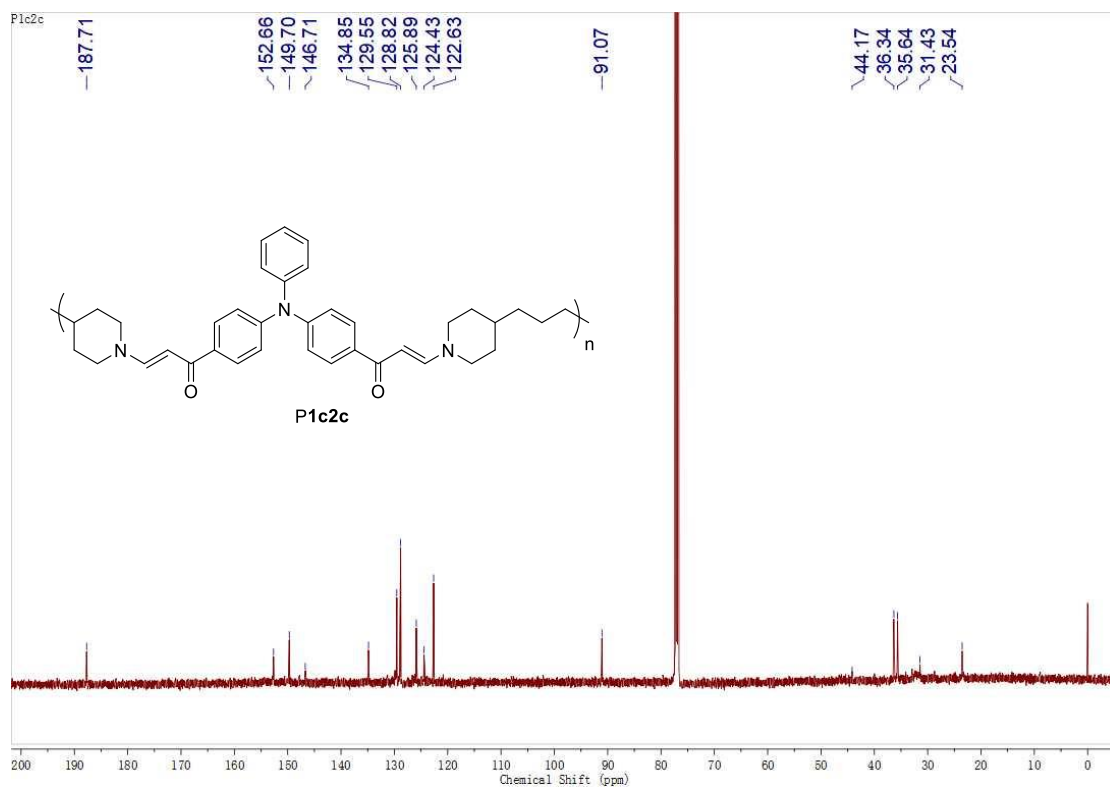


Figure S61. ^{13}C NMR spectrum of P1c2c in CDCl_3 .

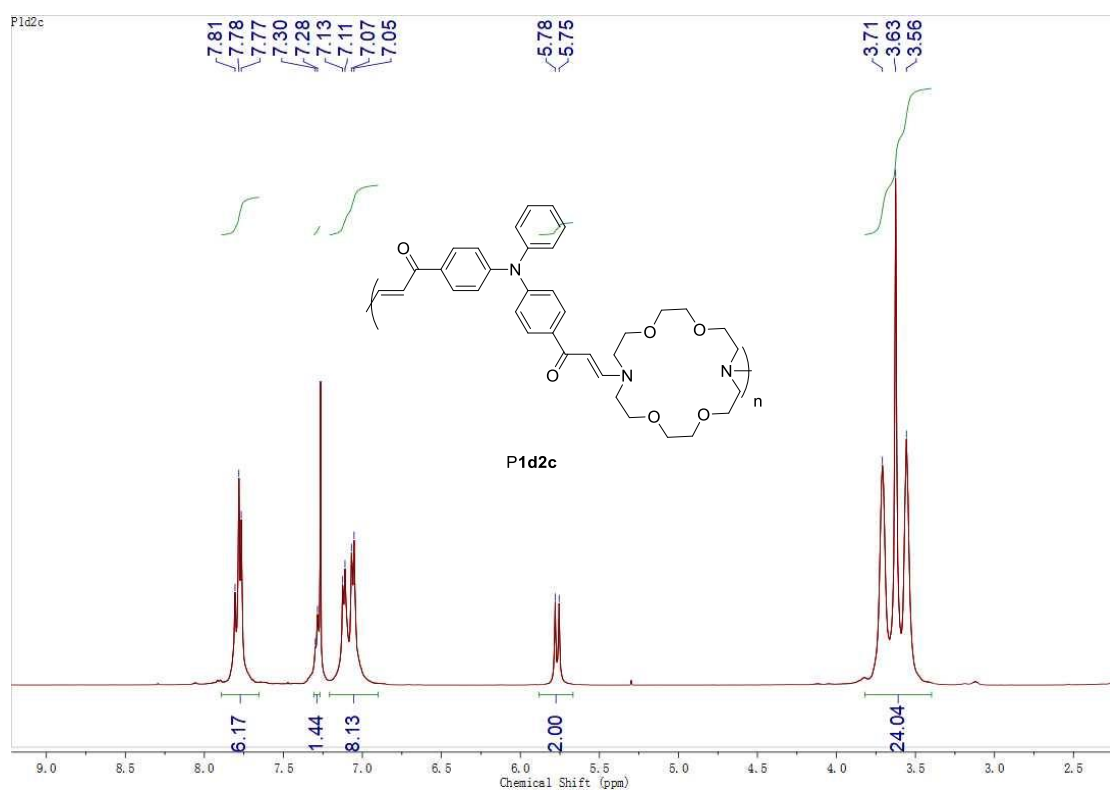


Figure S62. ^1H NMR spectrum of P1d2c in CDCl_3 .

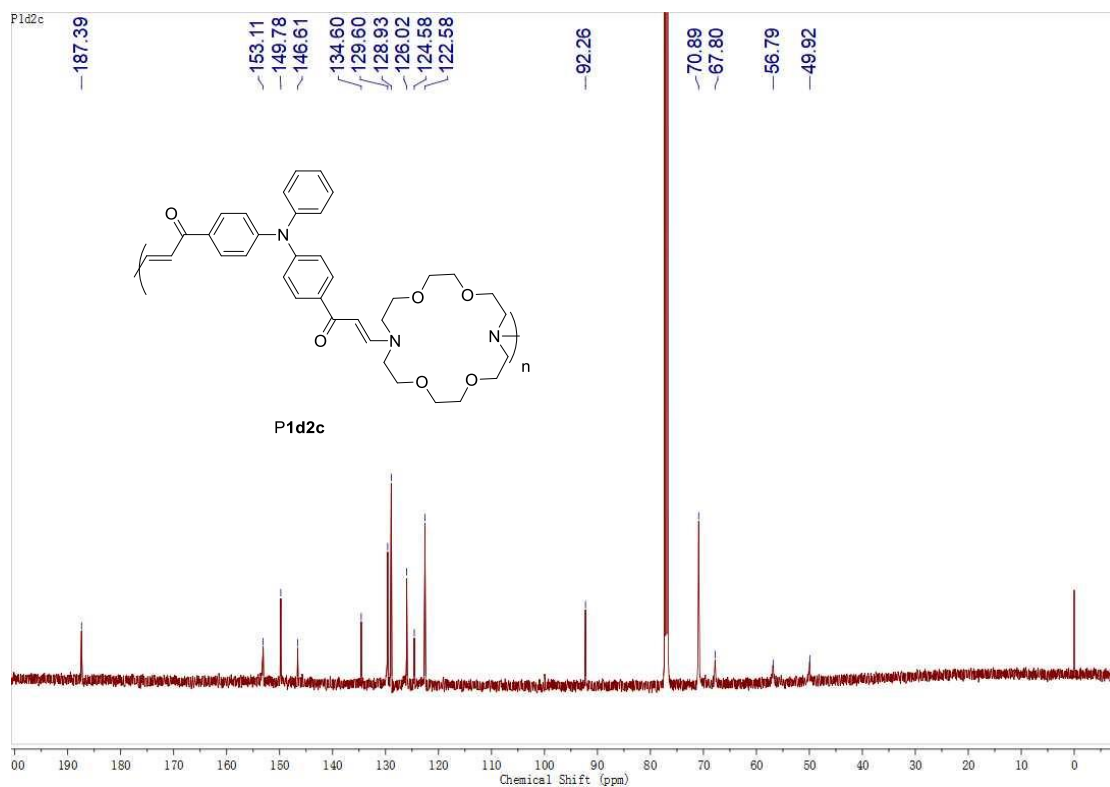


Figure S63. ^{13}C NMR spectrum of **P1d2c** in CDCl_3 .

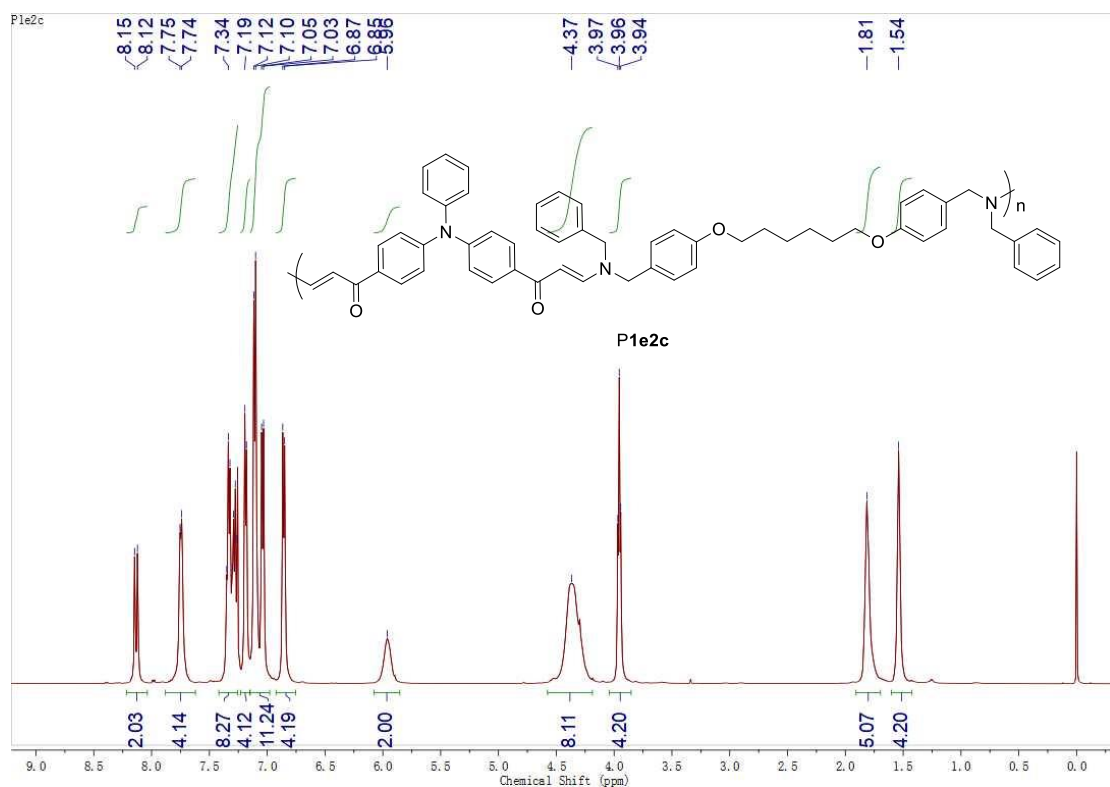


Figure S64. ^1H NMR spectrum of **P1e2c** in CDCl_3 .

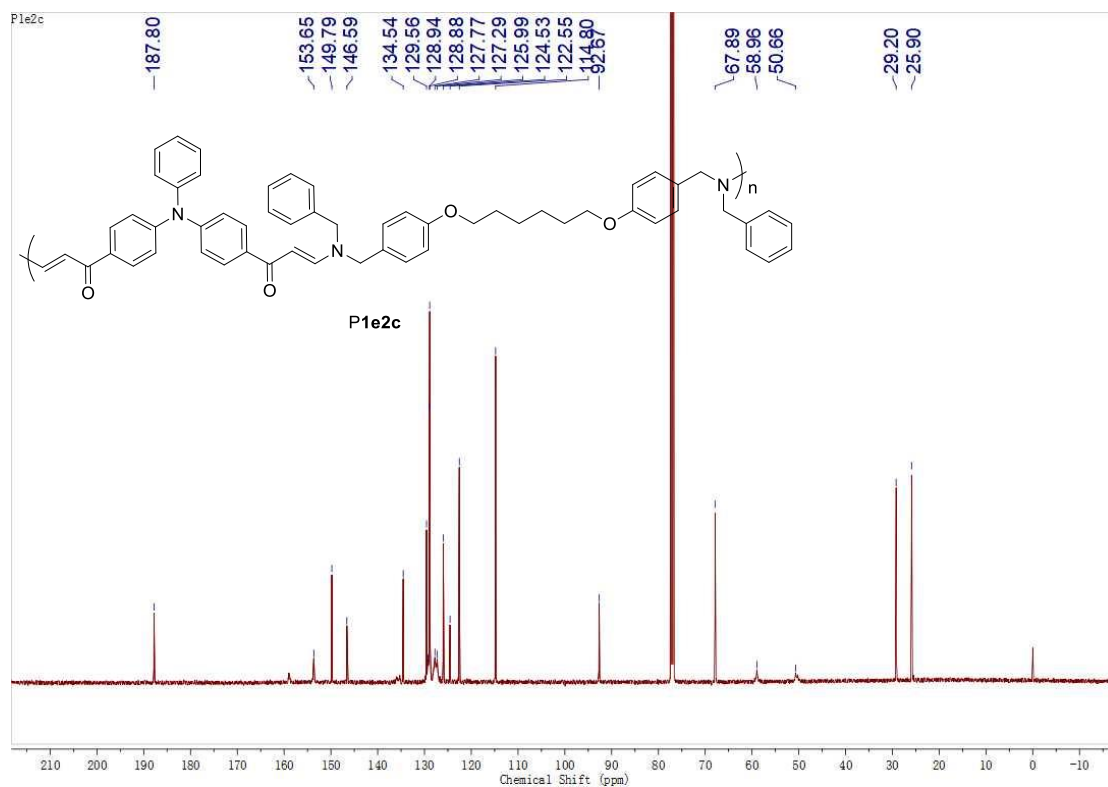


Figure S65. ^{13}C NMR spectrum of P1e2c in CDCl_3 .

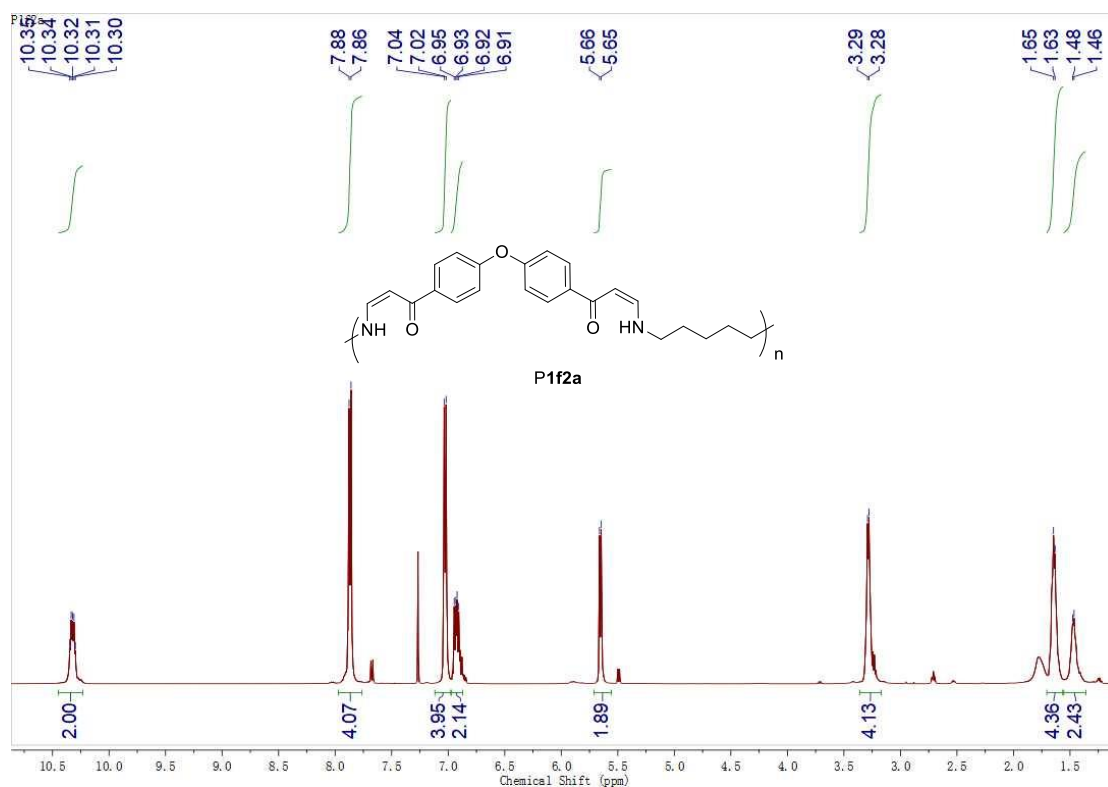


Figure S66. ^1H NMR spectrum of P1f2a in CDCl_3 .

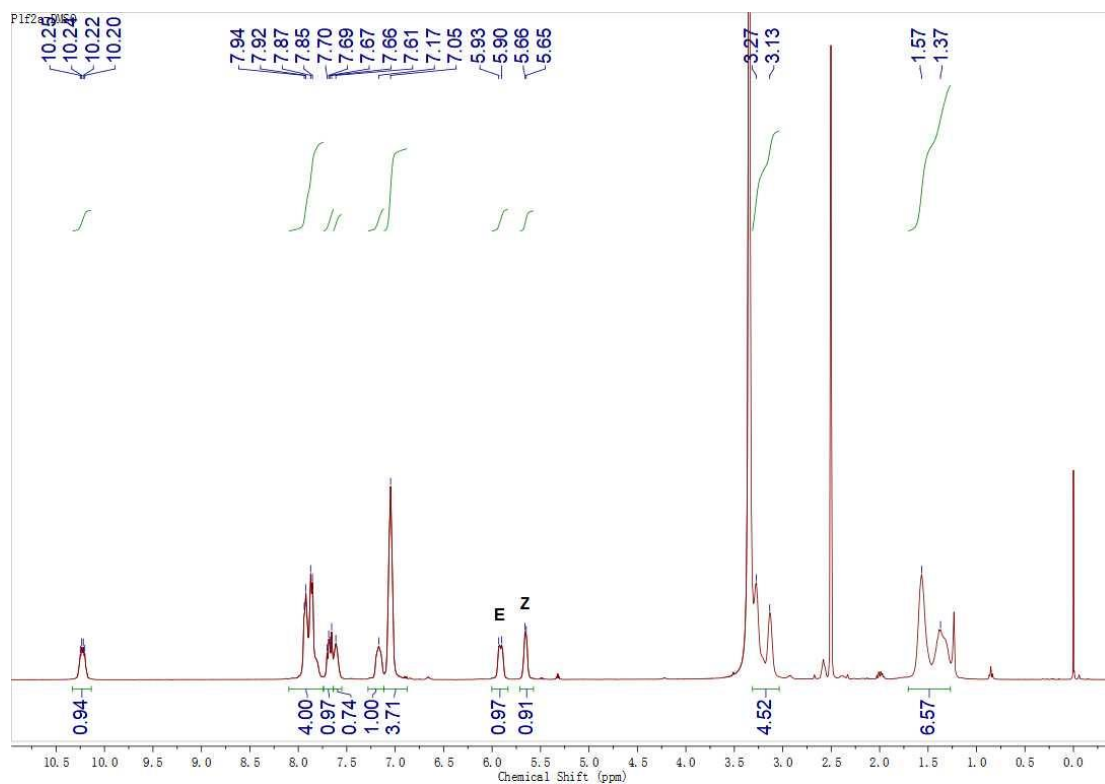


Figure S67. ¹H NMR spectrum of P1f2a in DMSO-*d*₆.

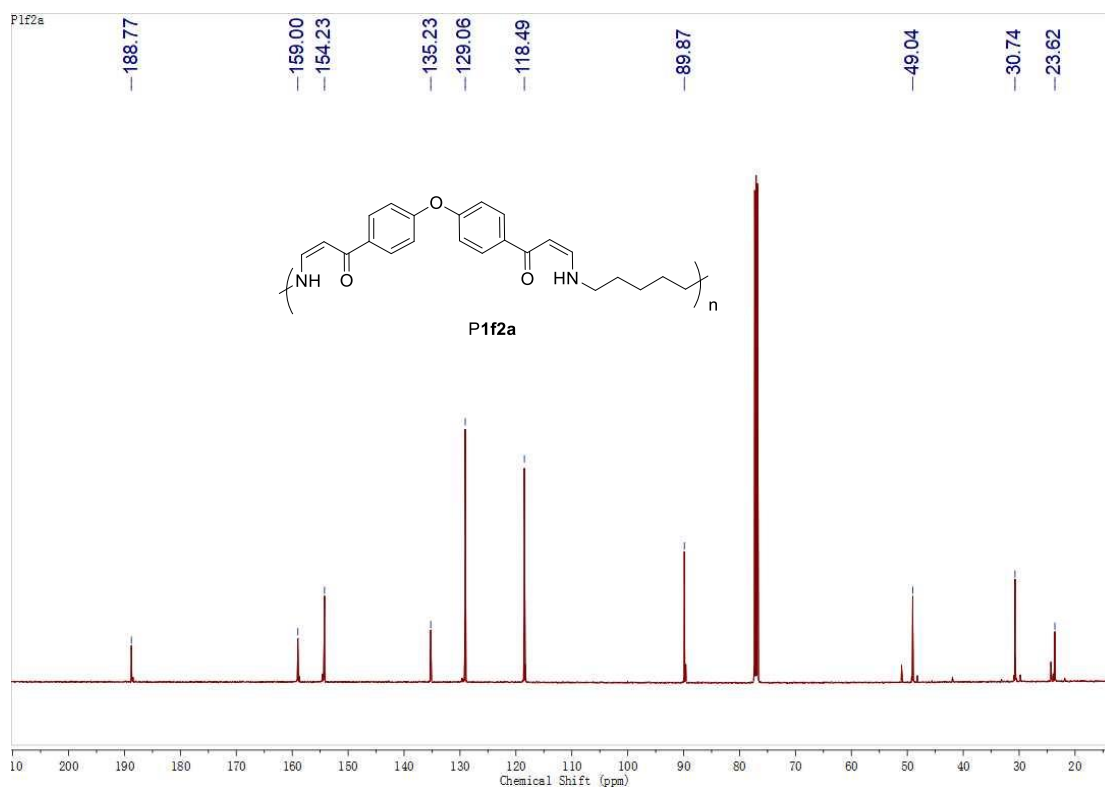


Figure S68. ¹³C NMR spectrum of P1f2a in CDCl₃.

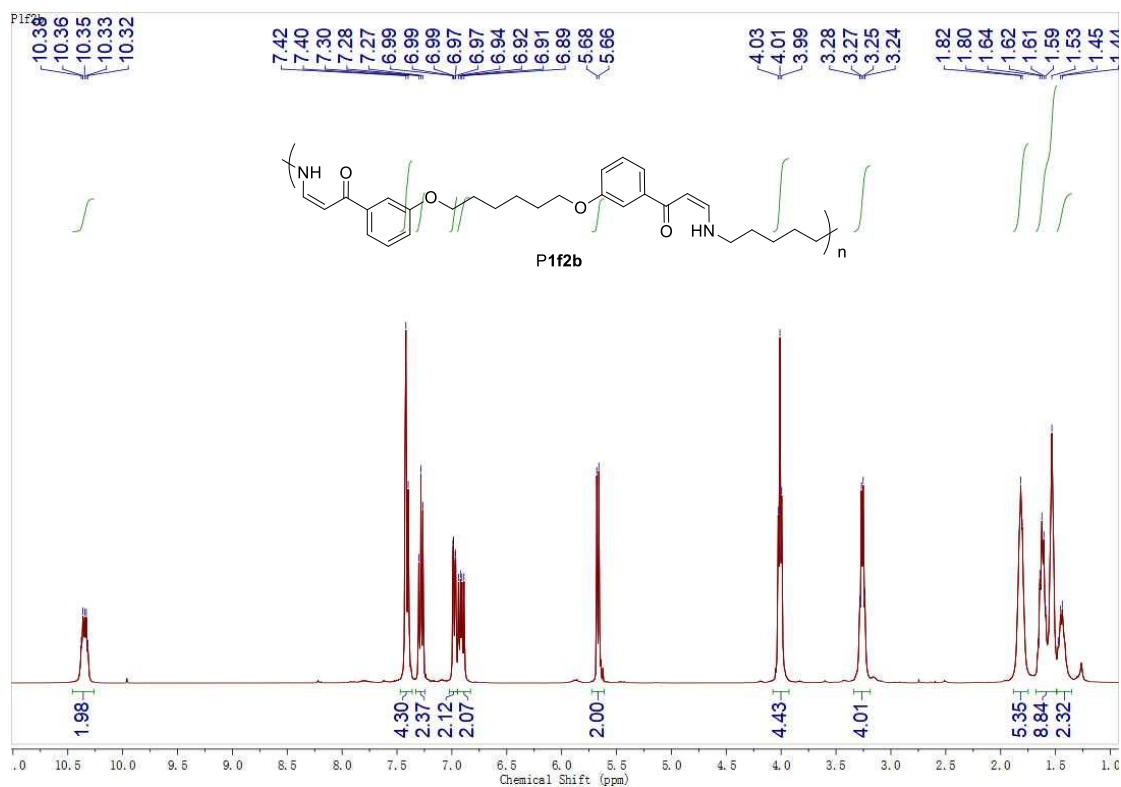


Figure S69. ¹H NMR spectrum of P1f2b in CDCl₃.

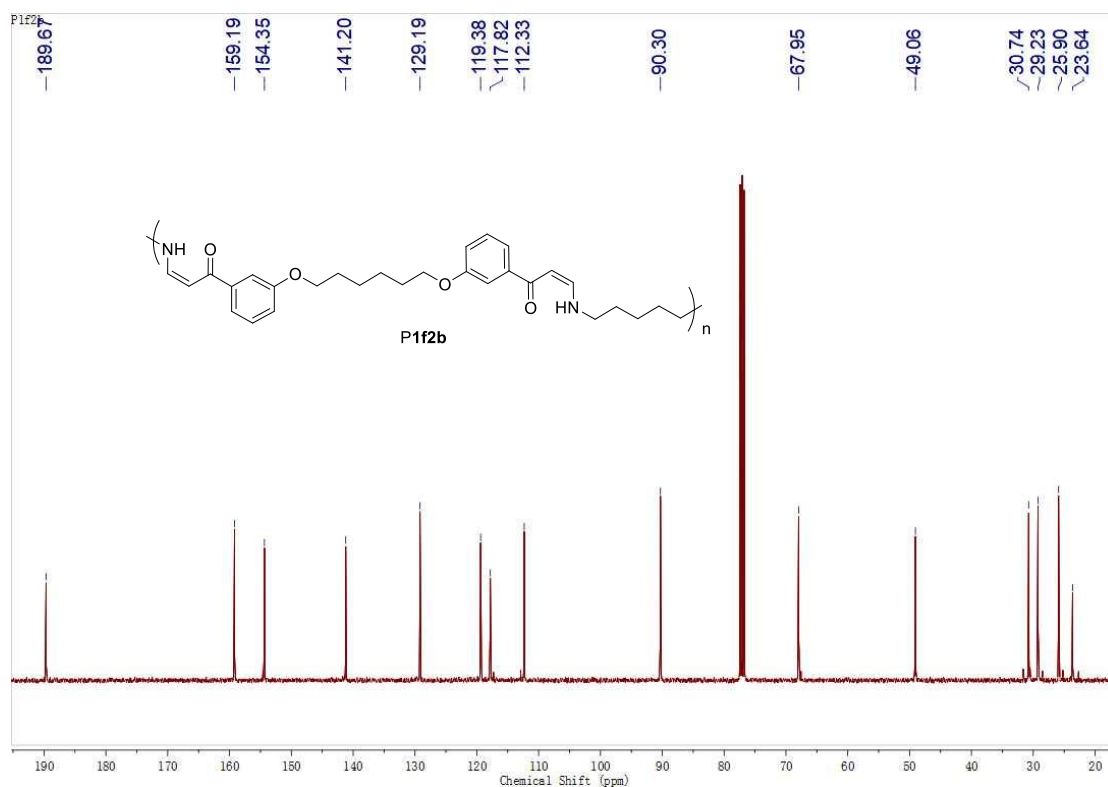


Figure S70. ¹³C NMR spectrum of P1f2b in CDCl₃.

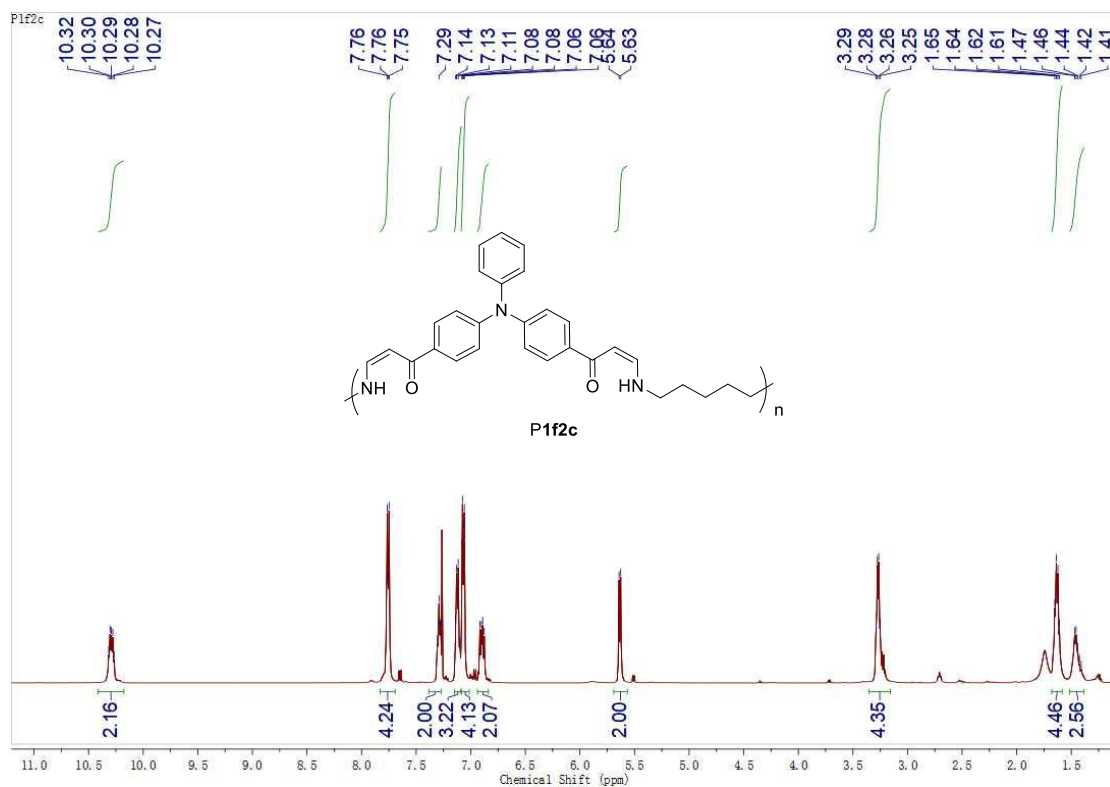


Figure S71. ^1H NMR spectrum of **P1f2c** in CDCl_3 .

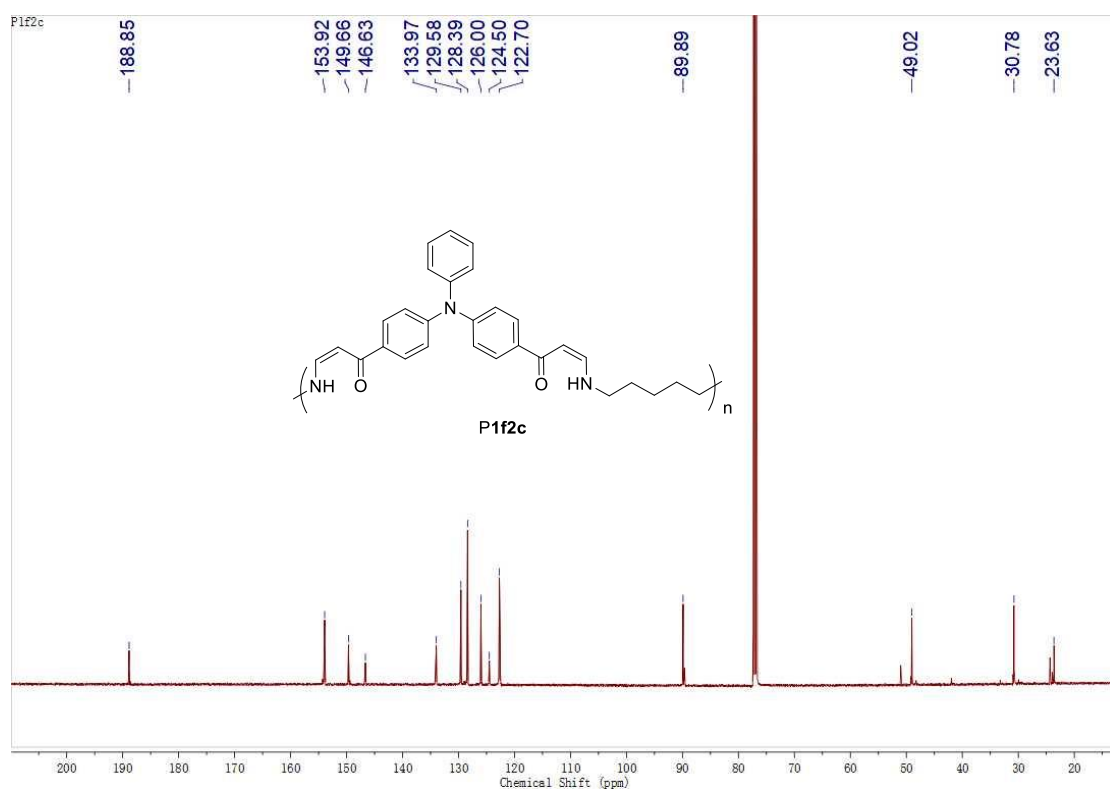


Figure S72. ^{13}C NMR spectrum of **P1f2c** in CDCl_3 .

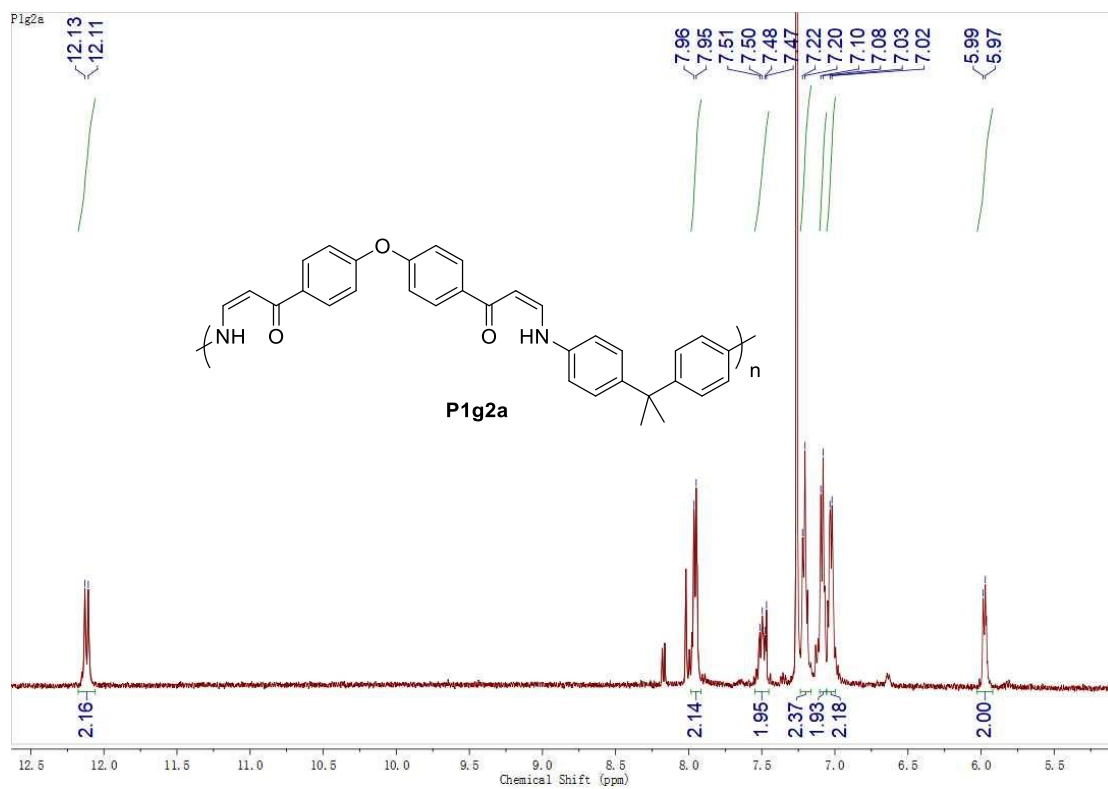


Figure S73. ^1H NMR spectra of **P1g2a** (soluble part) in CDCl_3 .