Electronic Supplementary Information

One-pot synthesis of polysulfonate by cascading sulfur(VI) fluorine exchange (SuFEx) reaction and cyanosilylation of aldehyde

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1. Experimental Section

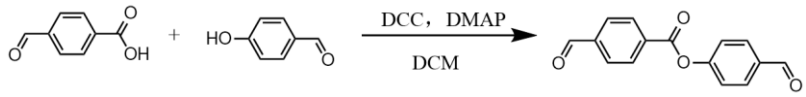
1.1. Materials and Instruments

p-Formylbenzoic acid, *p*-Hydroxybenzaldehyde, 4-Dimethylaminopyridine (DMAP), Trimethylsilylcyanide (TMSCN), Dicyclohexylcarbodiimide (DCC), phosphorus(V)oxychloride, *N*,*N*-dimethylformamide (DMF), *N*,*N*-Dimethylacetamide (DMAc), Bis(triphenylphosphine)iminiumchloride, Tetramethylguanidine (TMG), *N*-Methyl-pyrrolidone (NMP), Bis(4-chlorosulfonylphenyl)ether, 1,8-Dibicyclo[5,4,0]undec-7-ene (DBU), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), 4-Diphenylaminobenzaldehyde, 4,4-Biphenyldicarboxaldehyd, 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN), Sodium tungstate Chlorosulfonic acid and *p*-phenylenediamine were purchased from Sarn Chemical Technology (Shanghai) Co. Potassium hydrogen fluoride and Tetrabutylammonium chloride were purchased from McLean Ltd. $AgHF_2$ was purchased from Alfa Aesar. 4-Aminobenzaldehyde was purchased from Rohn Reagent Co. Cyclobutane sulfone (THT) was purchased from TCL. All reagents were used directly without further purification.

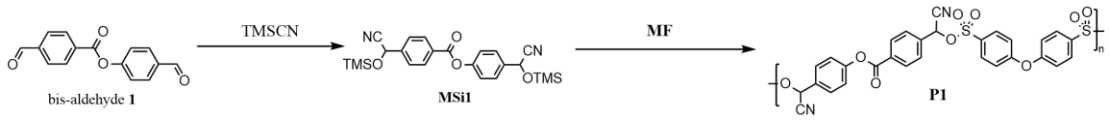
All ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were tested using a Bruker AVANCE 400 instrument at 295 K, ^{1}H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra were recorded at 101 MHz, and ^{19}F NMR spectra were recorded at 376 MHz in $CDCl_3$ or DMSO-d_6. Fourier infrared spectroscopy (FT-IR) was tested using a Bruker Tensor-27 instrument at ranging of 4000-500 cm^{-1}. GPC analysis was performed on Waters 1525 gel permeation chromatography system equipped with a Waters 2414 differential refractive index detector and an Agilent PLgel 5 μm MIXED-C (made in GB) column with narrowly dispersed polystyrene (PS) as standard. The column packing allows the separation of polymers in the molecular weight range of 500 - 2000000. The mobile phase was high performance liquid chromatography grade N,N-dimethylformamide (DMF), elution rate 1 mL/min (column temperature 35 ℃). The sample was tested at a concentration of 2 mg/mL. The thermogravimetric analysis (TGA) was tested using TA

SDT-Q600 instrument with a temperature rise of 10 ℃/min at 100 mL/min of N_2 atmosphere, with a temperature rise range of 25 ℃-800 ℃. Differential scanning calorimetry (DSC) analysis was performed using PE's diamond DSC instrument. Primary heating range: 0-200 ℃, heating rate of 10 ℃/min (eliminate thermal history). After staying for 5 min, the temperature drops to 0 ℃, and the cooling rate is 10 ℃/min. Secondary heating range: 0-250 ℃, heating rate of 10 ℃/min. X-ray diffraction (XRD)was tested using a Bruker D8 FOCUS instrument, with Cukα as the emitter, at a scan rate of 10 °/min and a scan range of 5-90 °. Atomic force microscope (AFM) were performed on Cyper ES (Asylum Research) equipment, where the probe (Radius:14nm) was AC160TS -R3 (Olympus). The elasticity factor was 26 nN/nm at 300 KHz.

1.2. Synthesis of P1



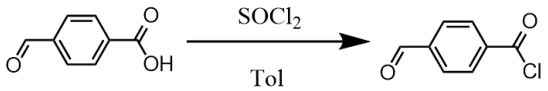
bis-aldehyde 1: To a 100 mL round bottom flask with 50 mL dichloromethane was added *p*-formylbenzoic acid (5 mmol, 766 mg), *p*-hydroxybenzaldehyde (5 mmol, 616.8 mg) and 4-dimethylaminopyridine (1 mmol, 124.7 mg). Then DCC (5.5 mmol, 1.16 g) was added to the flask and the mixture was stirred at room temperature. After 24 hours the insoluble matter was removed by filtration, and the filtrate was concentrated and purified by silica gel column chromatography (methylene chloride: methanol = 40:1). After vacuum, white solid was obtained (yield: 87%). ^{1}H NMR (400 MHz，$CDCl_3$) δ 10.16 (s, 1H)，10.05 (s, 1H)，8.47–8.33 (m, 2H)，8.19 – 8.03 (m, 2H)，8.03–7.85 (m, 2H)，7.44 (d, *J*=8.5 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 191.44, 190.88, 163.60, 155.36, 139.93, 134.43, 133.89, 131.42, 130.95, 129.79, 122.46.



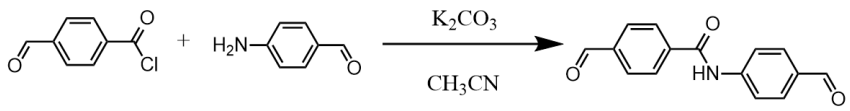
P1: To a 10 mL oblique two-pass reaction tube, bis-aldehyde **1** (1 mmol, 254 mg) was added under N_2 atmosphere, and the tube was placed in an oil bath at 100 ℃. TMSCN

(2 mmol, 0.26 mL) was injected and stirring for 1 h. Then monomer **MF** (1 mmol, 334 mg) and DMF (0.2 mL) were added into the reaction tube. When the system became a homogeneous solution, DBU (0.6 mmol, 90 μL) was slowly added into the solution with a syringe under agitation. The solution immediately turned black, and gradually became viscous as the reaction proceeded. After 3 hours, DMF (2 mL) was added and the reaction tube was placed in high temperature oil bath again. When the system became into a homogeneous solution, it was pipetted drop by drop into 100 mL of stirring methanol, the polymer immediately precipitated out and was filtered to obtain 294 mg of yellow solid which was washed with methanol, ethyl acetate and then dried in a vacuum oven at 70 ℃ (yield: 49%). **MSi1**: ^{1}H NMR (400MHz, $CDCl_3$) δ 8.47 (d, *J*=8.0 Hz, 2H), δ7.85 (d, *J*=8.0 Hz, 2H), δ7.77 (d, *J*=8.2 Hz, 2H), 7.50 (d, *J*=8.3 Hz, 2H), 5.81 (s, 1H), 5.75 (s, 1H), 0.49 (dd, *J*=7.6, 1.2 Hz, 18H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.61, 164.21, 155.65, 151.36, 143.68, 143.51, 142.89, 135.63, 135.05, 134.62, 131.66, 131.09, 131.00, 130.90, 129.73, 129.51, 128.31, 127.33, 123.36, 123.06, 122.85, 120.95, 120.60, 120.32, 119.96, 114.18, 62.93, 62.85, 61.96, 61.89, -0.18, -0.22. **P1**: ^{1}H NMR (400MHz, DMSO-d_6) δ 8.74–7.68 (m, 15H), 7.59 (t, *J*=10.7 Hz, 3H). ^{19}F NMR (376MHz, DMSO-d_6) δ 67.14.

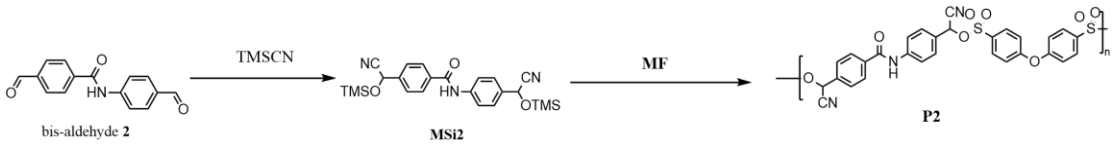
1.3. Synthesis of P2



4-formyl benzoyl chloride: To a 50 mL two-mouth flask with 10 mL toluene was added *p*-formylbenzoic acid (10 mmol, 1.5 g) and sulfoxide chloride (20 mmol, 2.38 g). The reaction was carried out at reflux (connected to a gas absorption unit). After the starting material disappeared by TLC, the solvent was evaporated under reduced pressure to obtain white solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.32 (d, *J*=8.1 Hz, 2H), 8.06 (d, *J*=8.0 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 193.44, 167.05, 166.94, 139.40, 136.09, 134.90, 130.42, 130.19, 130.03, 129.94.



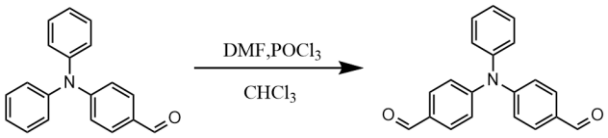
bis-aldehyde 2: To a 100 mL single-mouth flask with 35 mL acetonitrile, *p*-aminobenzaldehyde (5 mmol, 618 mg) and K_2CO_3 (5.5 mmol, 760 mg) were added at 0 ℃. *p*-Formylbenzoyl chloride (5.5 mmol, 927 mg, dissolved in 15 mL acetonitrile) was added dropwise to the flask, and the mixture was stirred at room temperature. After 24 h, the solution was poured into a large amount of distilled water. Yellow solid precipitated, and was washed with water and dried at 70 ℃ in a vacuum drying oven (yield: 81%). ^{1}H NMR (400MHz, DMSO-d_6) δ 10.83 (s, 1H), 10.13 (s, 1H), 9.93 (s, 1H), 8.16 (d, *J* = 8.1 Hz, 2H), 8.08 (d, *J* = 8.3 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ193.46, 192.24, 165.90, 145.01, 139.99, 138.95, 138.74, 137.70, 134.53, 132.38, 131.48, 131.21, 130.48, 130.00, 129.53, 129.15, 128.99, 120.51.



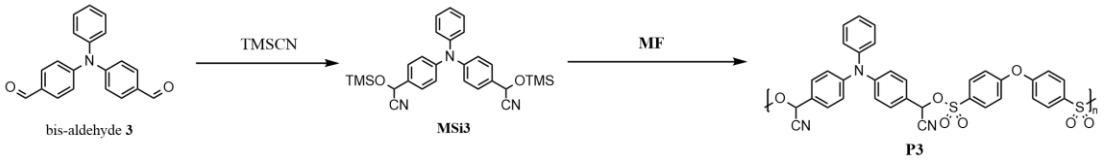
P2: To a 10 mL oblique two-pass reaction tube, bis-aldehyde **2** (1 mmol, 253 mg) was added under N_2 atmosphere, and the tube was placed in an oil bath at 100 ℃. TMSCN (2 mmol, 0.26 mL) was injected and stirred for 1 h. Then monomer **MF** (1 mmol, 334 mg) and DMF (0.2 mL) were added into the reaction tube. When the system was a homogeneous solution, DBU (0.6 mmol, 90 μL) was slowly added into the solution with a syringe under agitation. The solution immediately turned black, and gradually became viscous as the reaction proceeded. After 3 hours, DMF (2 mL) was added and the reaction tube was placed in high temperature oil bath again. When the system became into a homogeneous solution, it was pipetted drop by drop into 100 mL of stirring methanol, the polymer immediately precipitated out and was filtered to obtain 314 mg of yellow solid. The solid was washed with methanol, ethyl acetate and then dried in a vacuum oven at 70°C (yield: 52%). **MSi2**: ^{1}H NMR (400MHz, DMSO-d_6) δ 10.48 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 6.18 (s, 1H), 6.01 (s, 1H), 0.24 (s, 9H), 0.21 (s, 9H).^{13}C

NMR (101 MHz, DMSO-d_6) δ 165.65, 141.08, 140.09, 135.73, 132.96, 132.34, 128.97, 128.77, 127.52, 127.46, 126.83, 121.14, 121.09, 120.97, 120.81, 120.50, 120.17, 114.29, 63.05, 62.93, 62.00, 61.94, 0.14. **P2**: ^{1}H NMR (400MHz, DMSO-d_6) δ 10.83 (d, J = 19.3 Hz, 1H), δ 8.02 (d, J = 77.8 Hz, 18H), ^{19}F NMR (376MHz, DMSO-d_6) δ 67.47.

1.4. Synthesis of P3



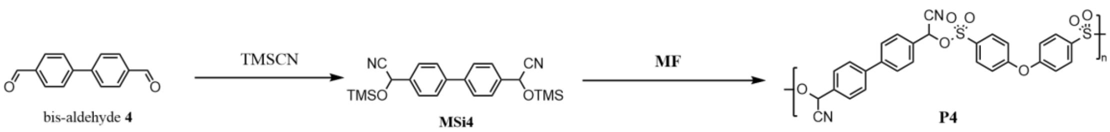
bis-aldehyde 2: *N,N*-dimethylformamide (12 mL, 0.15 mol) was added to a 100 mL round bottom flask, which was placed in an ice-water bath. Then phosphorus trichloride (14 mL, 0.15 mol) was added dropwise at a controlled rate of 6-10 drops per minute. The flask was placed in an oil bath until the solution turned white frozen salt, to which 4-diphenylaminobenzaldehyde (2.79 g, 10 mmol) was added. The temperature was raised to 50 ℃, and 20 mL of chloroform was poured into the bottle when the frozen salt was dissolved, followed by raising the temperature to 65 ℃. After stirring at reflux for three days, chloroform was evaporated and the mixture was slowly poured into a large amount of ice water and the pH was adjusted to 7-8 with NaOH. After filtration, the resulting solid was dissolved in dichloromethane and dried over anhydrous Na_2SO_4, and the crude product was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 10:1) to obtain a yellow solid (yield: 65%).^{1}H NMR (400MHz, DMSO-d_6) δ9.90 (s, 2H), 7.86 (d, J=8.1 Hz, 3H), 7.55–7.43 (m, 2H), 7.34 (d, J=7.3 Hz, 1H), 7.21 (dd, J=19.0, 7.8 Hz, 7H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 191.72, 151.96, 145.62, 131.83, 131.51, 130.89, 127.62, 126.88, 122.98.



P3: To a 10 mL oblique two-pass reaction tube, bis-aldehyde **2** (1 mmol, 301 mg) was added under N_2 atmosphere, and the tube was placed in an oil bath at 100 ℃. TMSCN (2 mmol, 0.26 mL) was injected and stirring for 1 h. Then monomer **MF** (1 mmol, 334

mg) and DMF (0.2 mL) were added into the reaction tube. When the system was a homogeneous solution, DBU (0.6 mmol, 90 μL) was slowly added into the solution with a syringe under agitation. The solution immediately turned black, and gradually became viscous as the reaction proceeded. After 3 hours, DMF (2 mL) was added and the reaction tube was placed in high temperature oil bath again. When the system became into a homogeneous solution, it was pipetted drop by drop into 100 mL of stirring methanol, the polymer immediately precipitated out and was filtered to obtain 365 mg of yellow solid. The solids were washed with methanol, ethyl acetate and then dried in a vacuum oven at 70 °C (yield: 56%). **MSi3**: ^{1}H NMR (400MHz, DMSO-d_6) δ 7.49–7.39 (m, 5H), 7.08 (p, *J*=3.4 Hz, 8H), 5.97 (s, 2H), 0.21 (s, 18H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.85, 148.20, 148.10, 147.91, 147.80, 147.01, 146.92, 146.84, 146.55, 145.82, 134.04, 131.99, 131.81, 131.67, 131.15, 130.97, 130.47, 130.17, 130.12, 129.43, 128.54, 128.30, 126.85, 126.80, 126.33, 125.98, 125.32, 125.20, 125.07, 124.51, 124.39, 124.26, 123.99, 123.76, 123.52, 122.78, 120.91, 120.81, 120.30, 119.37, 114.03, 62.80, 61.78, 61.73, -0.29. **P3**: ^{1}H NMR (400MHz, DMSO-d_6) δ7.82 (s, 3H), 7.12 (s, 20H) .^{19}F NMR (376MHz, DMSO-d_6) δ 67.32.

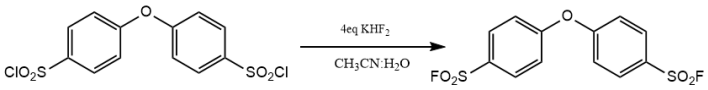
1.5. Synthesis of P4



P4: To a 10 mL oblique two-pass reaction tube, bis-aldehyde **2** (1 mmol, 216.7 mg) was added under N_2 atmosphere, and the tube was placed in an oil bath at 100 °C. TMSCN (2 mmol, 0.26 mL) was injected and stirring for 1 h. Then monomer **MF** (1 mmol, 334 mg) and DMF (1 mL) were added into the reaction tube, and the mixture was stirred in 50 °C oil bath to dissolve the monomer. When the system was a homogeneous solution, DBU (0.6 mmol, 90 μL) was slowly added into the solution with a syringe under agitation. The solution immediately turned black. After 3 hours, the solution was pipetted drop by drop into 100 mL of stirring methanol, The polymer

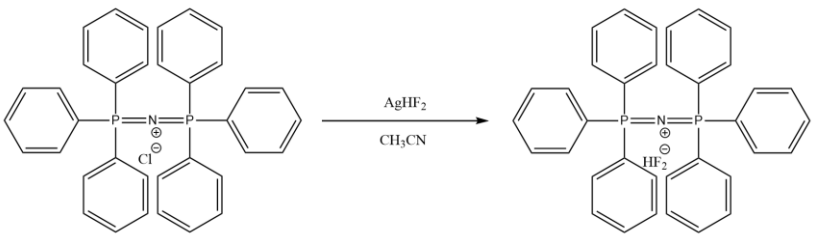
immediately precipitated out and was filtered to obtain 310 mg of yellow solid (yield: 55%). solids were washed with methanol, ethyl acetate and then dried in a vacuum oven at 70 °C. **MSi4**: ^{1}H NMR (400MHz, $CDCl_3$) δ 7.66 (d, *J*=8.1 Hz, 4H), δ7.58 (d, *J* = 8.0 Hz, 4H), 5.58 (d, *J* = 6.1 Hz, 2H), 0.37–0.21 (m, 18H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.75, 141.46, 141.33, 135.82, 135.17, 127.91, 127.79, 127.29, 127.01, 126.99, 119.12, 63.47, 63.30, -0.17. **P4**: ^{1}H NMR (400MHz, DMSO-d_6) δ 8.17 (s, 5H), 7.96 (d, *J*=11.8 Hz, 8H), 7.88 (s, 2H), 7.64 (s, 1H), 7.07 (s, 2H). ^{19}F NMR (376MHz, DMSO-d_6) δ 67.30.

1.6. Synthesis of monomer MF



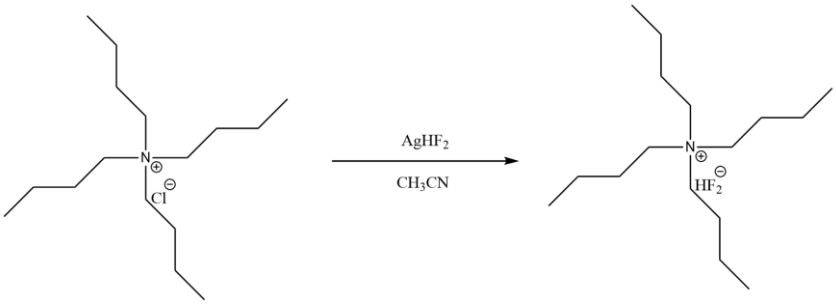
MF: To a 100 mL single-necked flask was added bis(4-chlorosulfonyl phenyl) ether (5 mmol, 1.87 g) with 30 mL of CH_3CN. KHF_2 (20 mmol, 1.58g) was dissolved in 30 mL distilled water. The aqueous solution of KHF_2 was injected into the flask. After stirring for 24 h at room temperature, the solution was extracted with ethyl acetate, and the organic phase was washed with distilled water and saturated salt solution, dried with anhydrous Na_2SO_4. After removing the solvent under reduced pressure, a white solid was obtained (yield: 84 %). ^{1}H NMR (400MHz, $CDCl_3$) δ 8.23–7.92 (m, 4H), 7.28 (d, *J* = 8.8 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.18, 131.44, 128.98, 128.72, 120.01. ^{19}F NMR (376MHz, DMSO-d_6) δ 67.04.

1.7. Preparation of catalysts $[Ph_3P{=}N{-}PPh_3]^+[HF_2]^-$ and $[^nBu_4]^+[HF_2]^-$



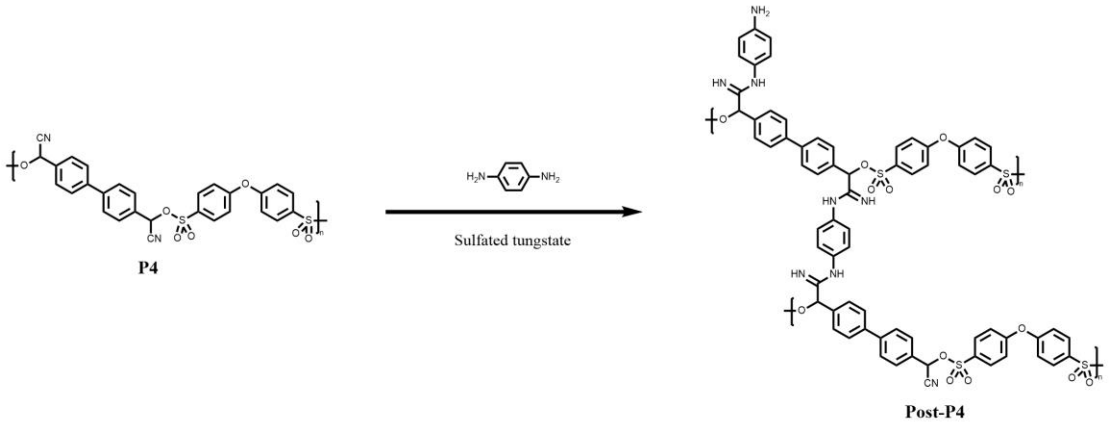
$[Ph_3P{=}N{-}PPh_3]^+[HF_2]^-$: To a 100 mL single-necked flask covered with tin foil, $AgHF_2$

(10 mmol, 1.47 g) was added and 35 mL of super-dry acetonitrile was poured. A solution of bis(triphenylphosphine)iminium chloride (10 mmol, 5.85 g) in acetonitrile (15 mL) was added dropwise to the flask. The mixture was stirred for 30 min at room temperature. Then sonicate was carried out for 30 min, and the mixture was centrifuged at 2000 rpm. After removing acetonitrile from the supernatant, a white solid was obtained, and stored away from light.



[^{n}Bu$_4$N]$^+$[HF$_2$]$^-$: To a 100 mL single-necked flask covered with tin foil, $AgHF_2$ (10 mmol, 1.47 g) was added and 35 mL of super-dry acetonitrile was poured. A solution of tetrabutylammonium chloride (10 mmol, 2.78 g) in acetonitrile (15 mL) was added dropwise to the flask. Stir for 30 min at room temperature and then continue to sonicate for 30 min, centrifuge at 2000 rpm and spin dry acetonitrile from the supernatant to obtain a yellow oily liquid, store away from light.

1.8. Synthesis of Post-P4



Post-P4: P4 (0.2 mmol, 111 mg) and *p*-phenylenediamine (0.2 mmol, 22 mg) were added into a 10 mL oblique two-pass tube, and 0.3 mL DMF was added. The reaction

tube was placed in an oil bath at 120 ℃ and sulfated tungstate[1] (20 wt%, 27 mg) was added to initiate the reaction. As the reaction proceeded, the mixture gradually became viscous and solid precipitated. After 24 h, the mixture was added into 100 mL of methanol, and the resulting solid was extracted with dichloromethane and distilled water with Soxhlet extractor and then dried at 80 ℃ to obtain 123 mg of red solid.

2. Data of the FT-IR, NMR and XRD

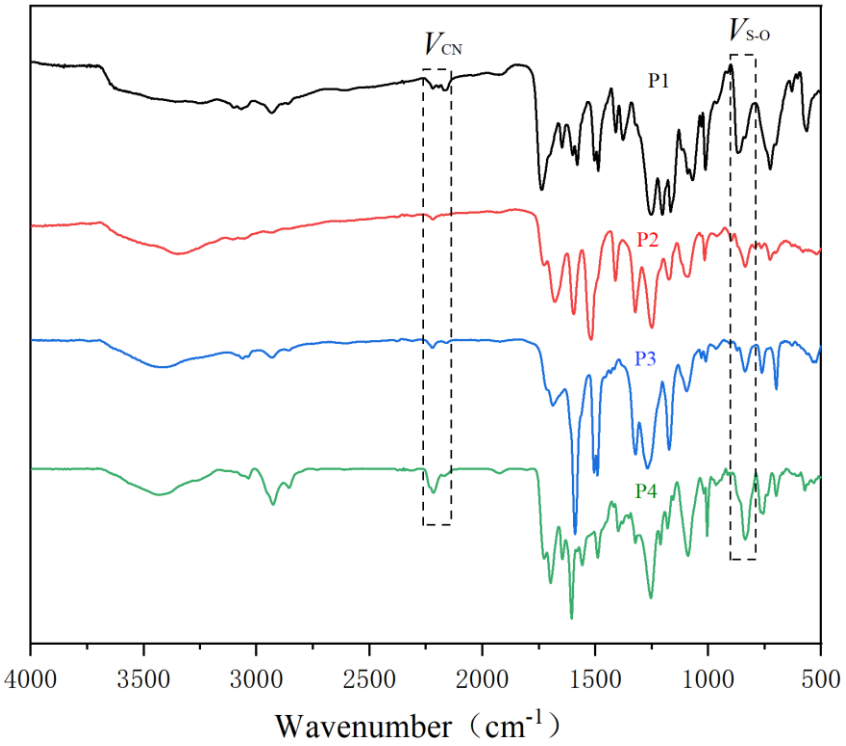


Figure S1. FT-IR spectrum of **P1-4**

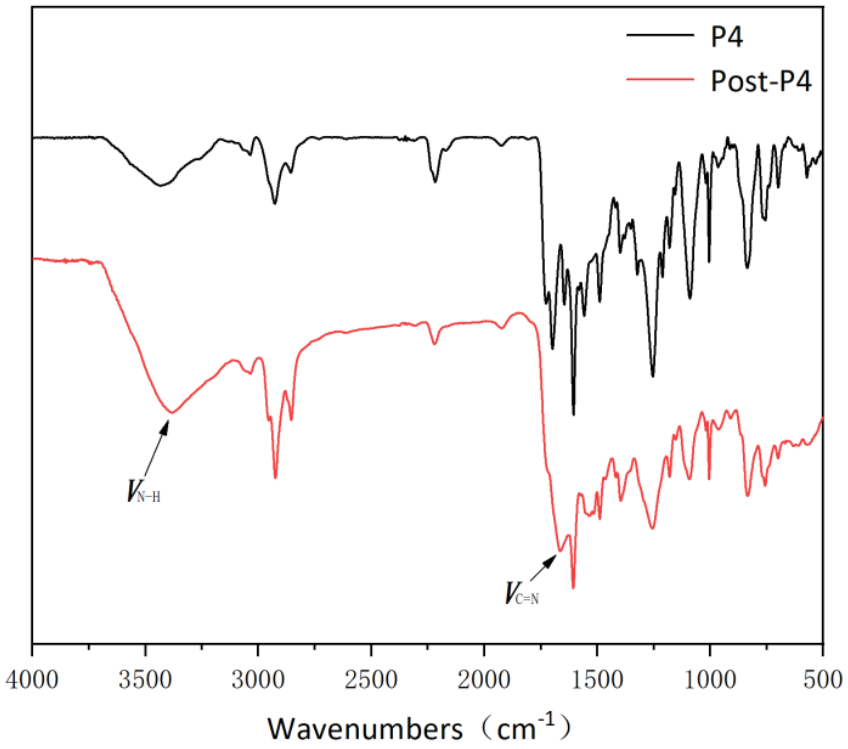


Figure S2. FT-IR spectra comparison of **P4** and **Post-P4**

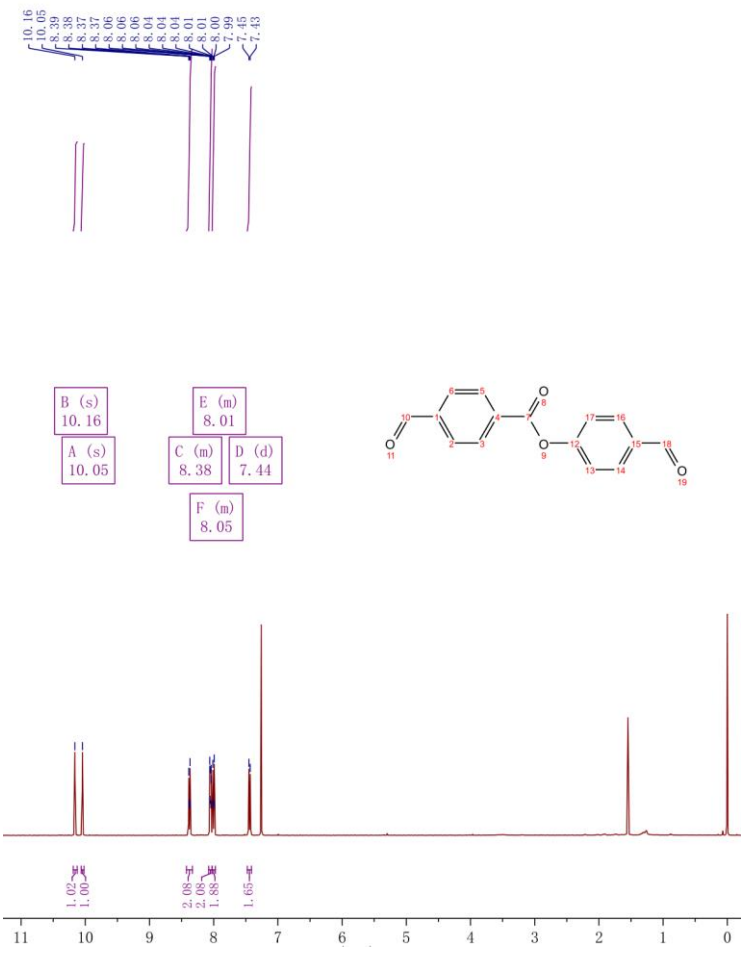


Figure S3. ^{1}H NMR spectrum of bis-aldehyde **1**

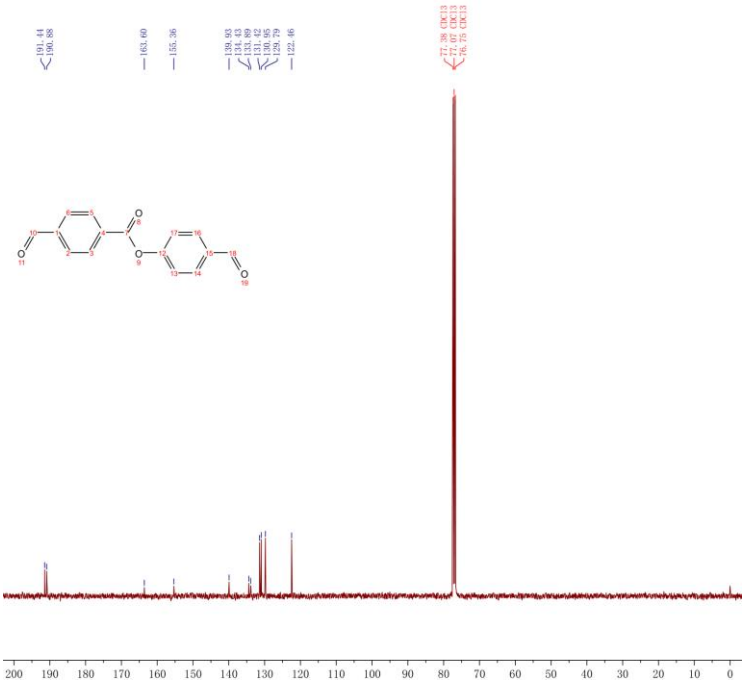


Figure S4. ^{13}C NMR spectrum of bis-aldehyde **1**

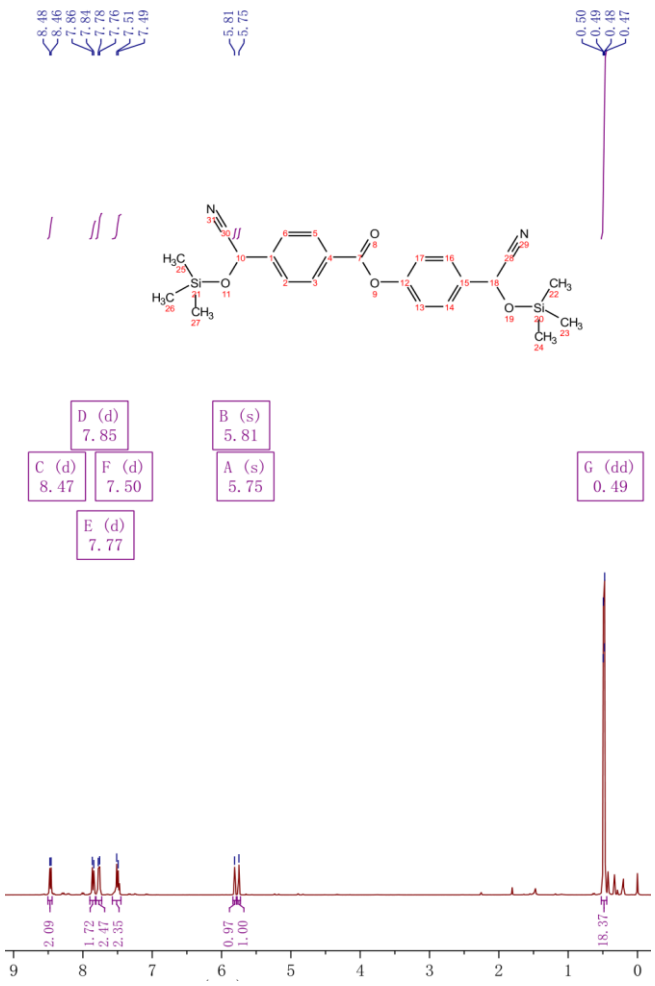


Figure S5 ^{1}H NMR spectrum of **MSi1**

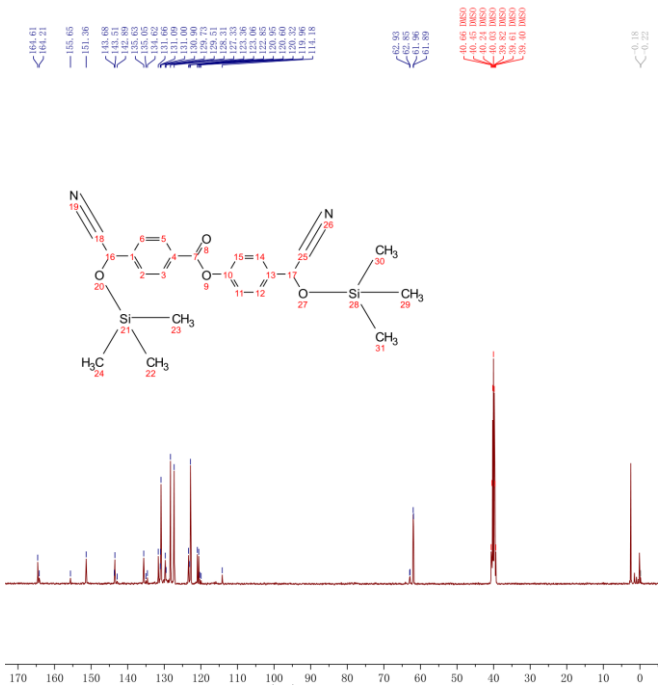


Figure S6. ^{13}C NMR spectrum of **MSi1**

Figure S7. ^{1}H NMR spectrum of 4-formyl benzoyl chloride

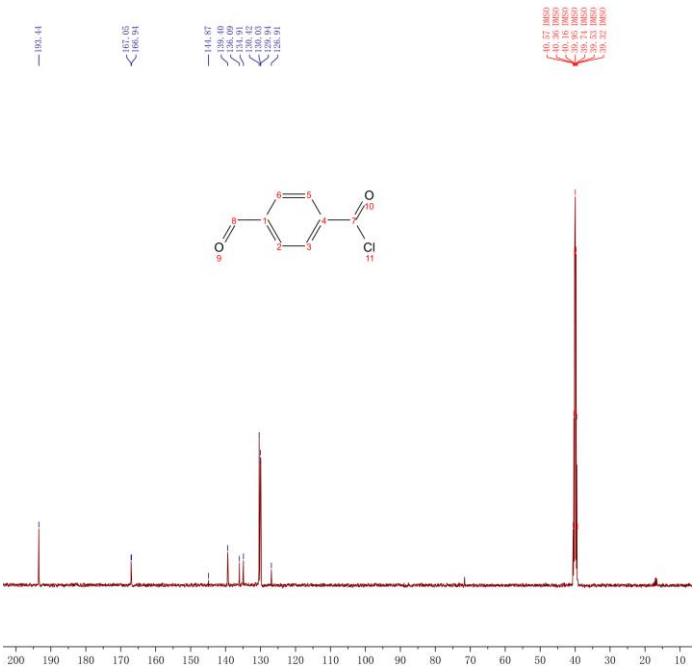


Figure S8. ^{13}C NMR spectrum of 4-formyl benzoyl chloride

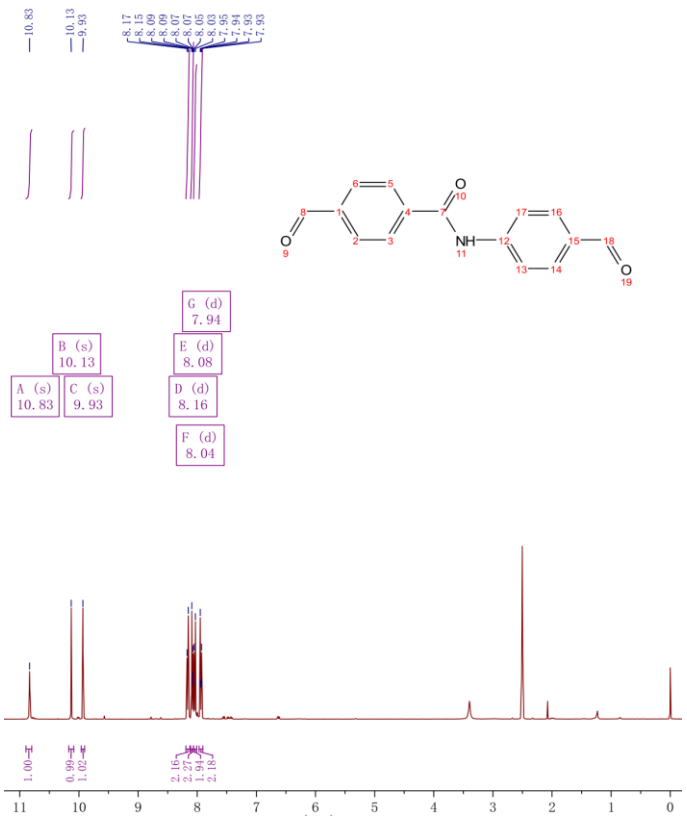


Figure S9. ^{1}H NMR spectrum of bis-aldehyde **3**

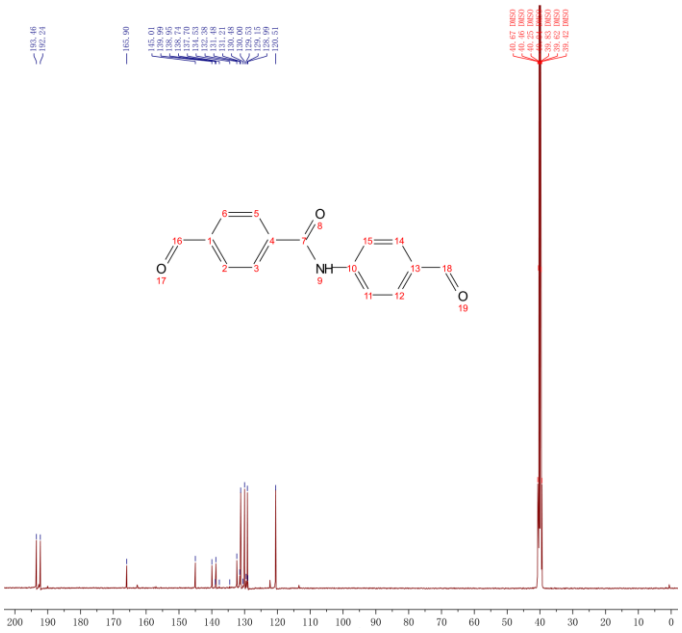


Figure S10. ^{1}H NMR spectrum of bis-aldehyde **3**

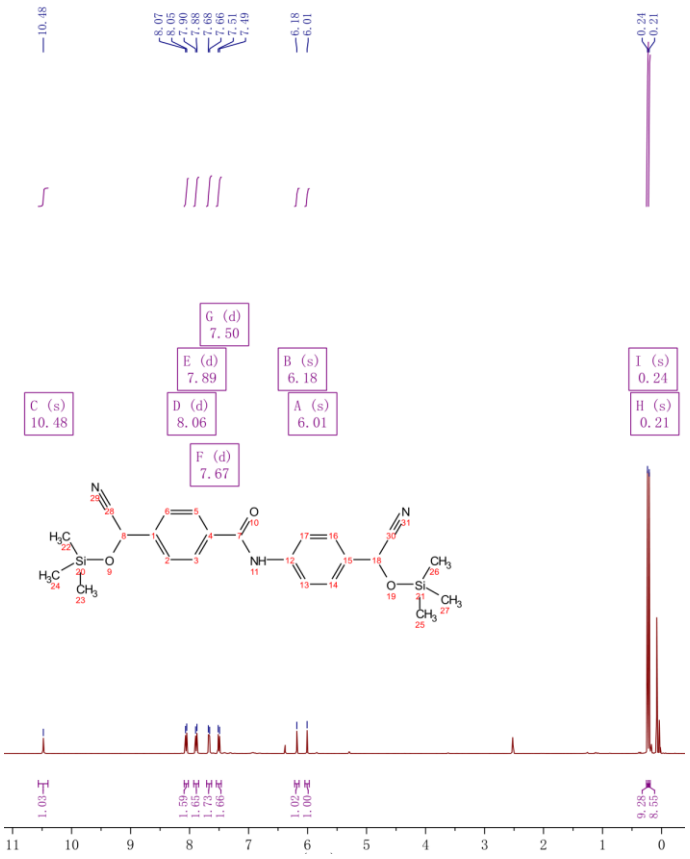


Figure S11. ^{1}H NMR spectrum of **MSi2**

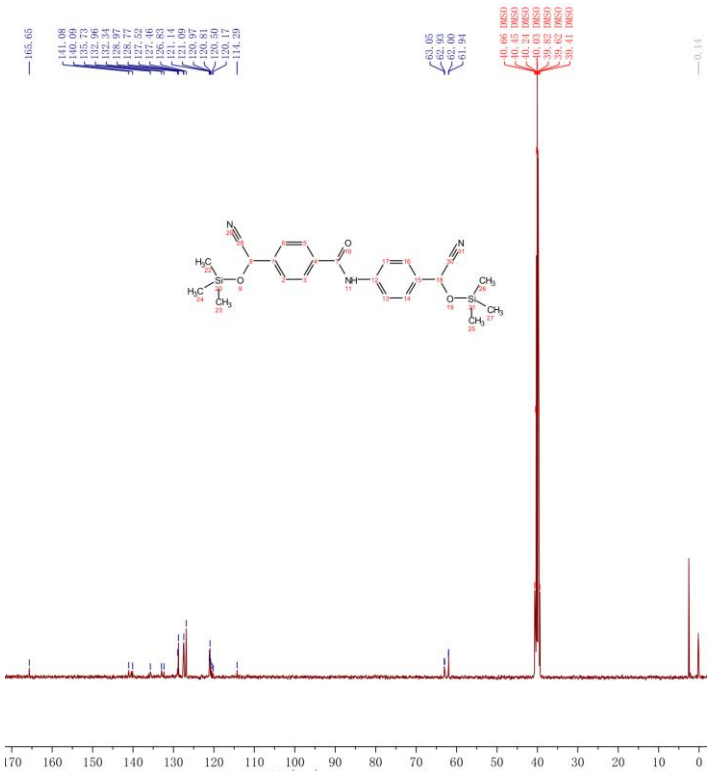


Figure S12. ^{13}C NMR spectrum of **MSi2**

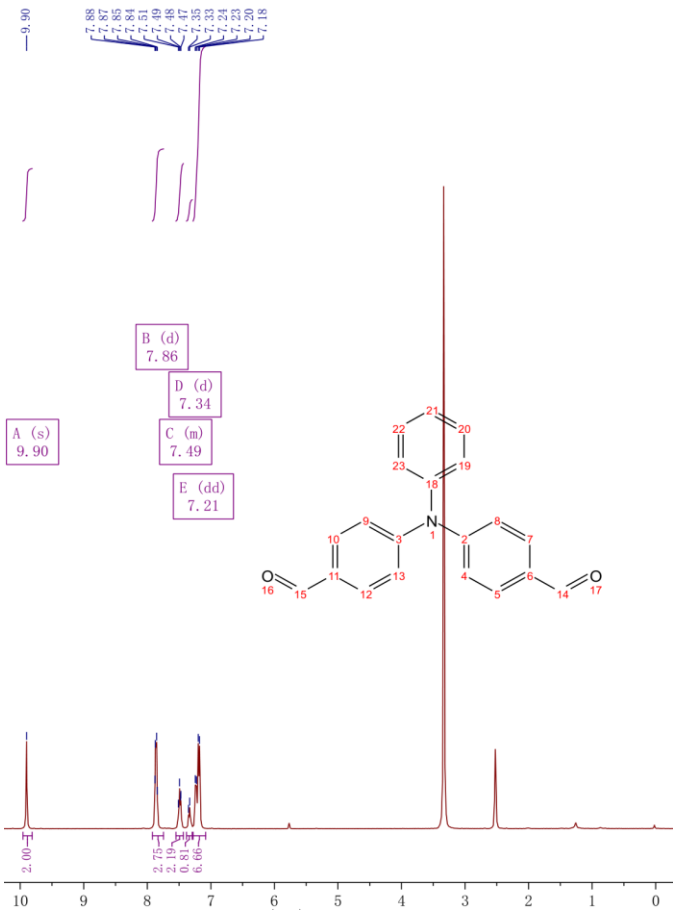


Figure S13. ^{1}H NMR spectrum of bis-aldehyde **4**

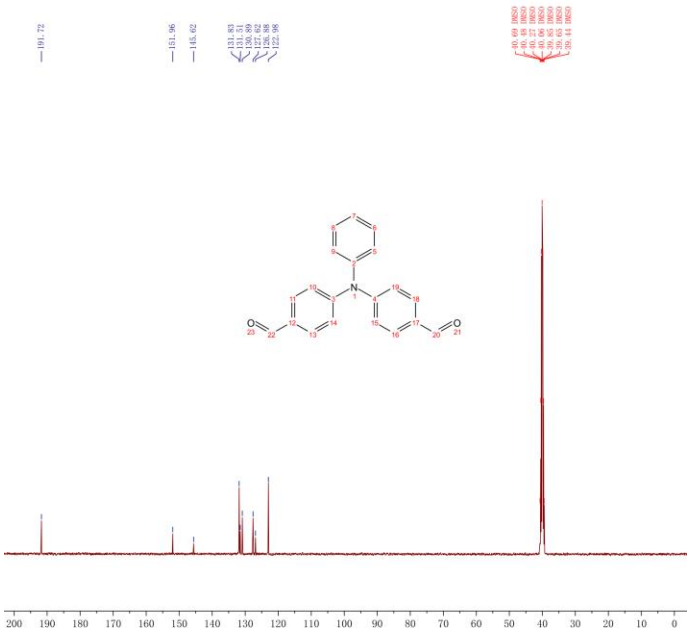


Figure S14. ^{13}C NMR spectrum of bis-aldehyde **4**

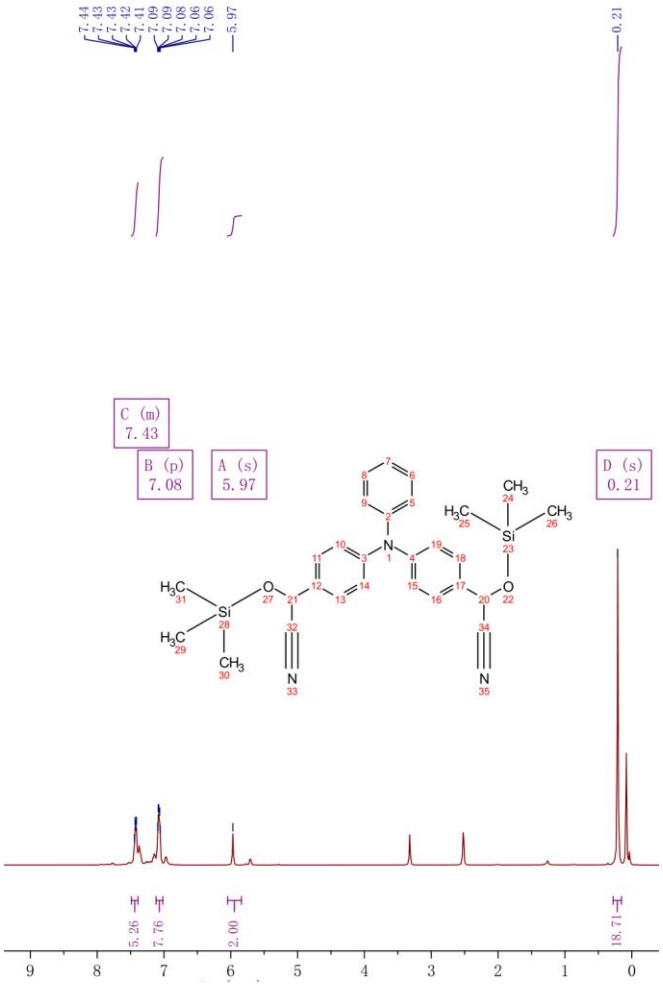


Figure S15. ^{1}H NMR spectrum of **MSi3**

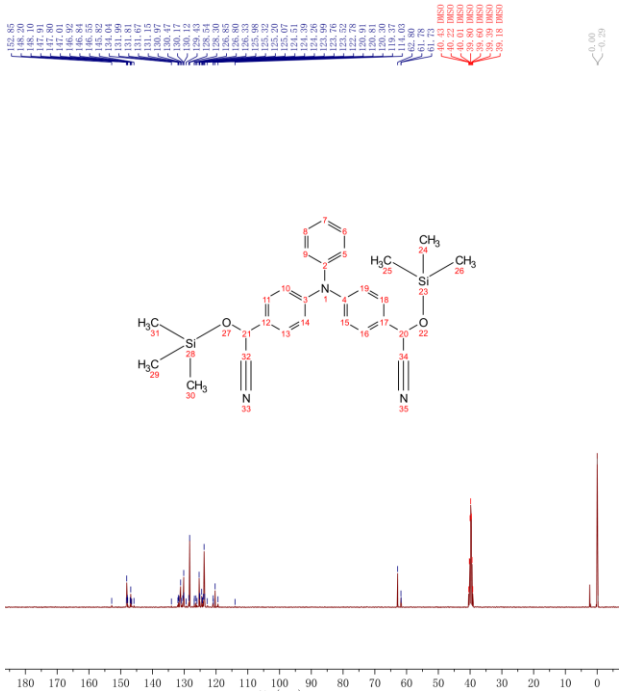


Figure S16. ^{13}C NMR spectrum of **MSi3**

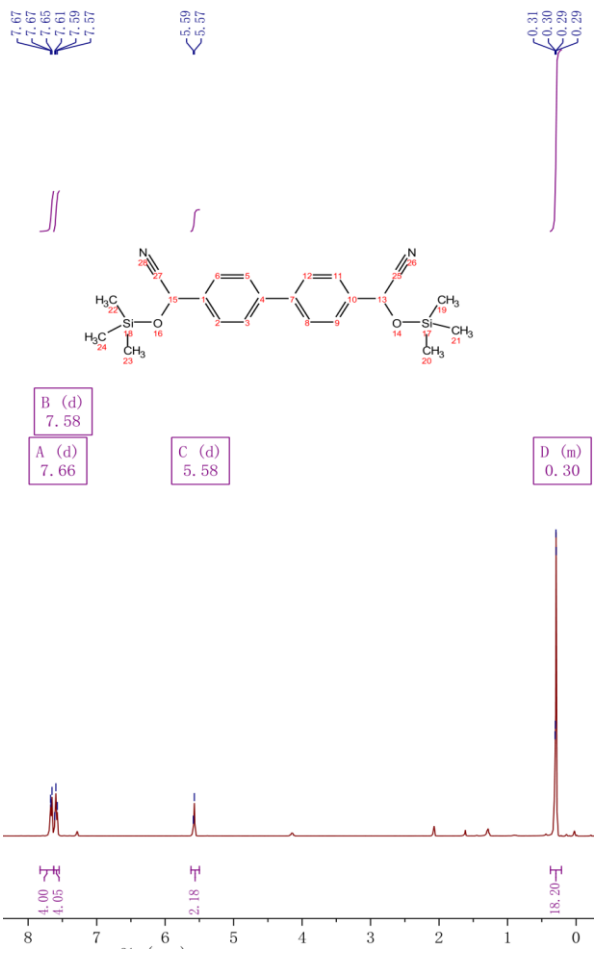


Figure S17. ^{1}H NMR spectrum of **MSi4**

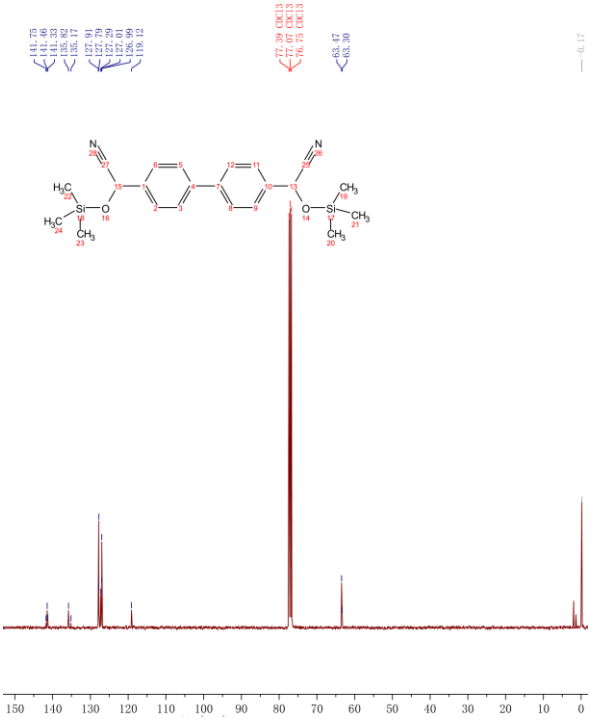


Figure S18. ^{13}C NMR spectrum of **MSi4**

Figure S19. ^{1}H NMR spectrum of **MF**

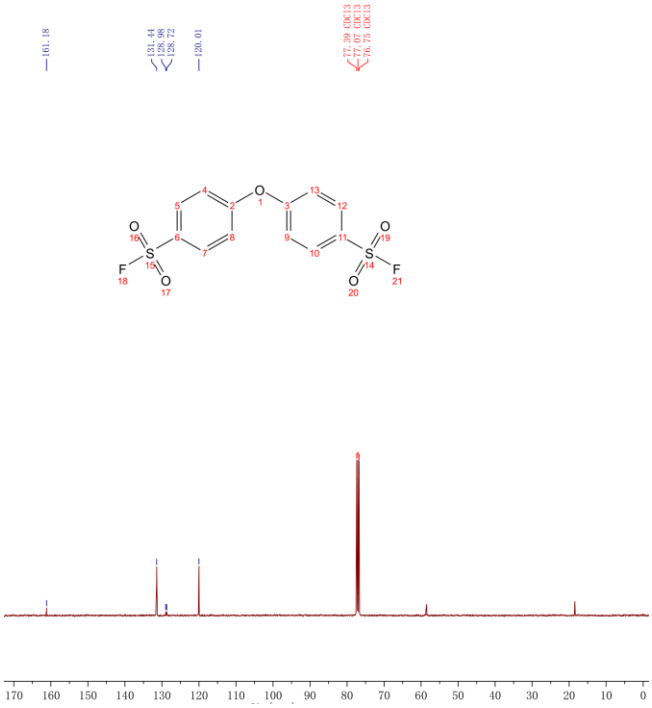


Figure S20. ^{13}C NMR spectrum of **MF**

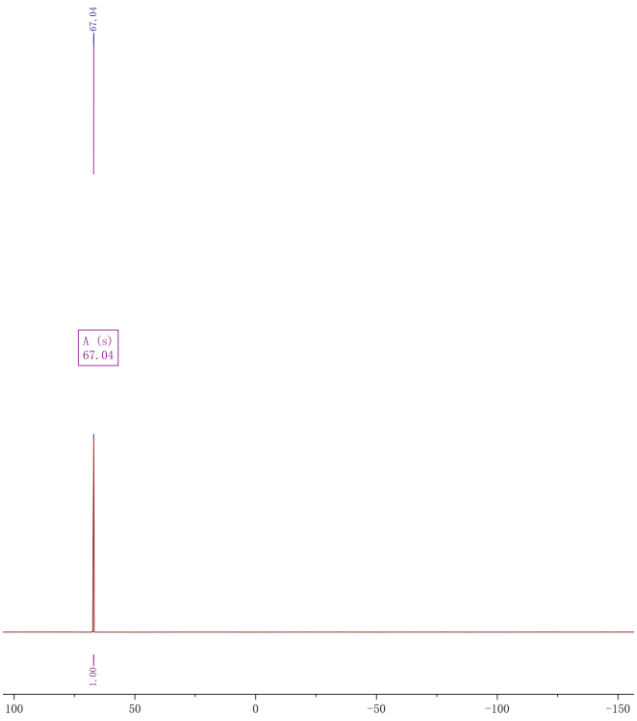


Figure S21. ^{19}F NMR spectrum of **MF**

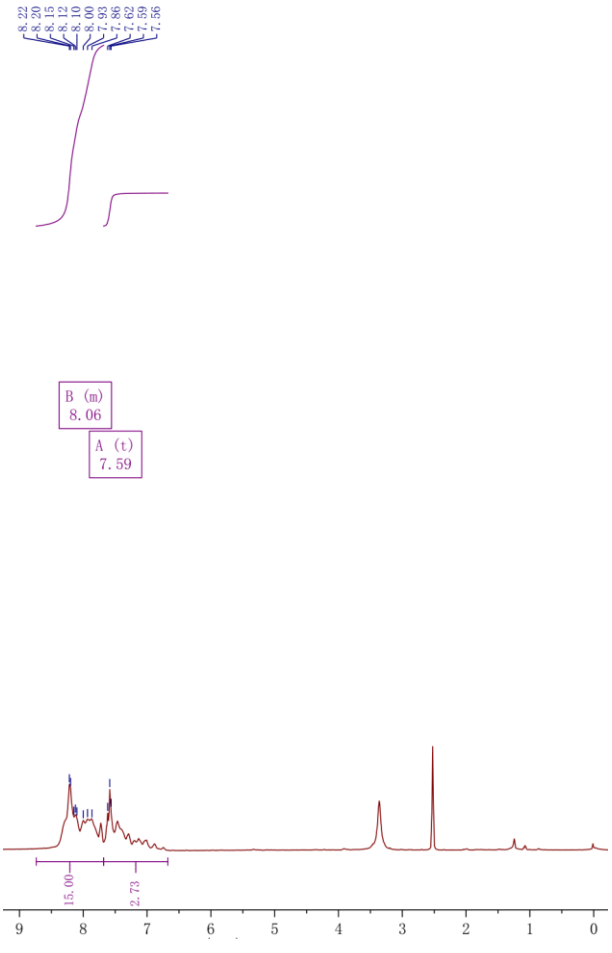


Figure S22. ^{1}H NMR spectrum of **P1**

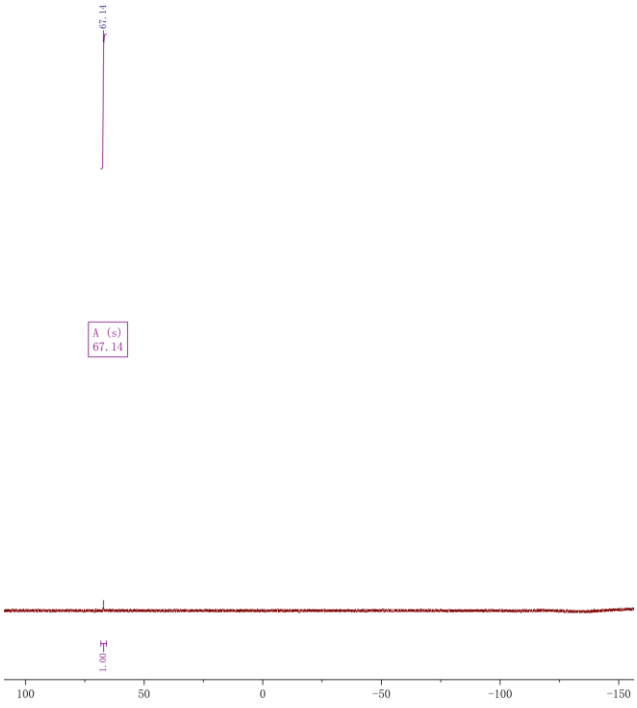


Figure S23. ^{19}F NMR spectrum of **P1**

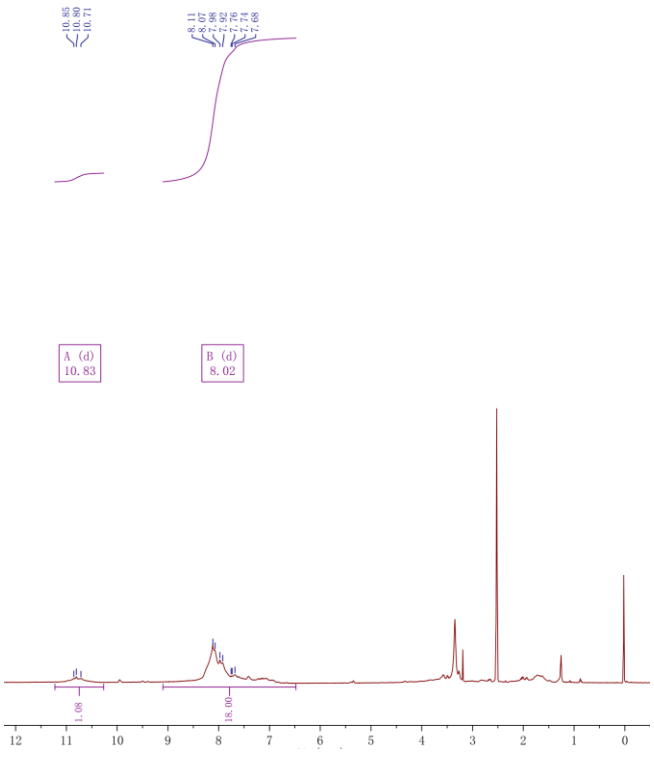


Figure S24. ^{1}H NMR spectrum of **P2**

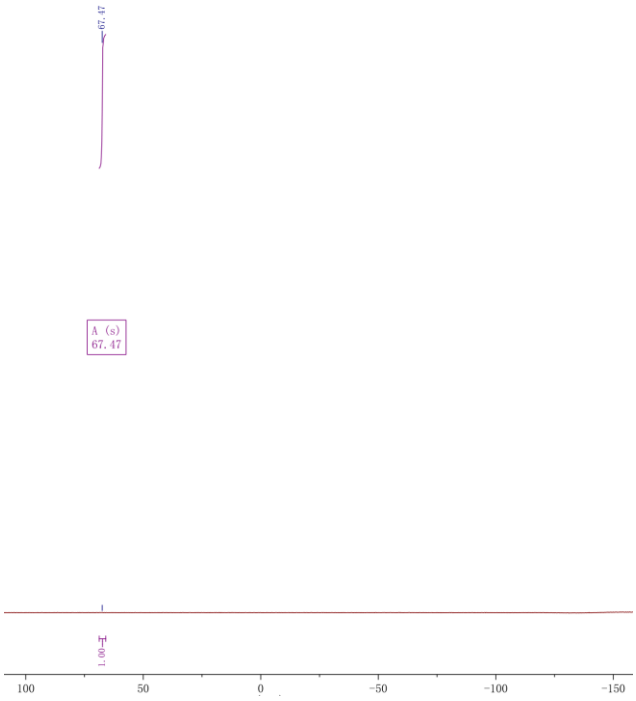


Figure S25. ^{19}F NMR spectrum of **P2**

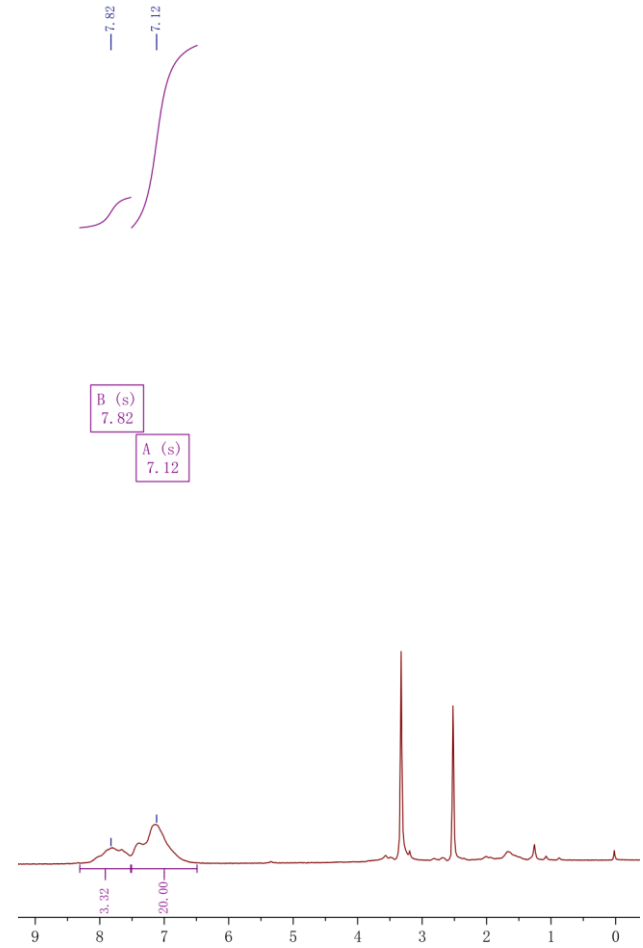


Figure S26. ^{1}H NMR spectrum of **P3**

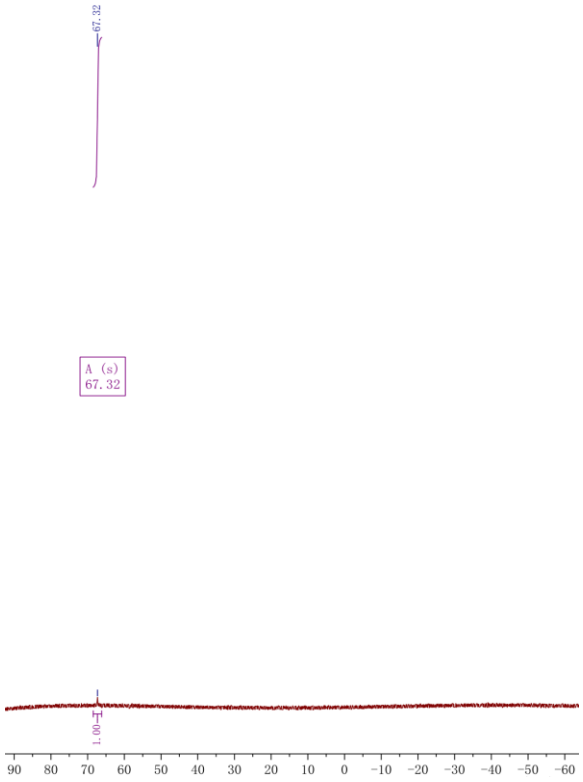


Figure S27. ^{19}F NMR spectrum of **P3**

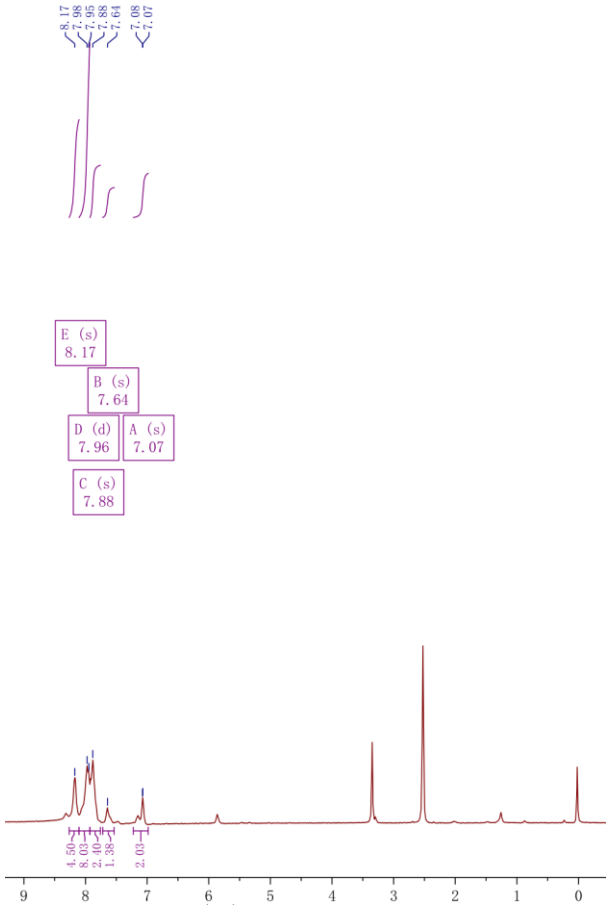


Figure S28. ^{1}H NMR spectrum of **P4**

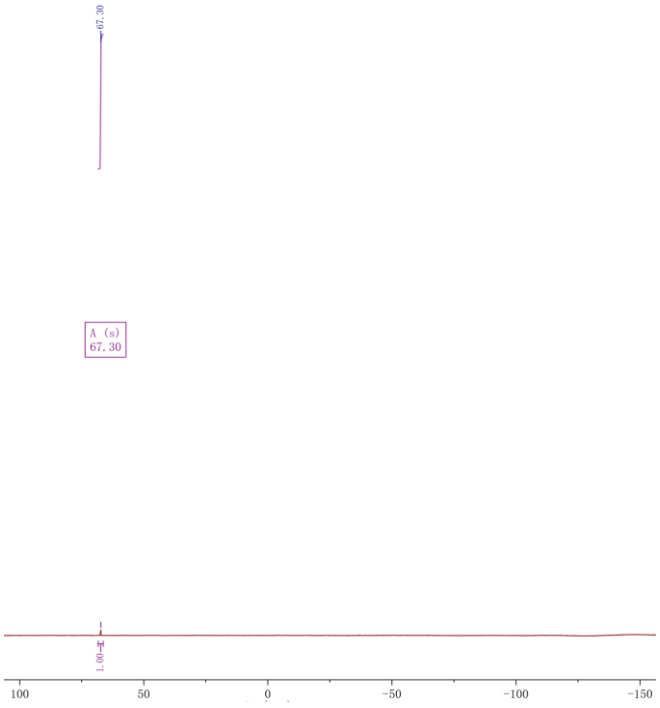


Figure S29. ^{19}F NMR spectrum of **P4**

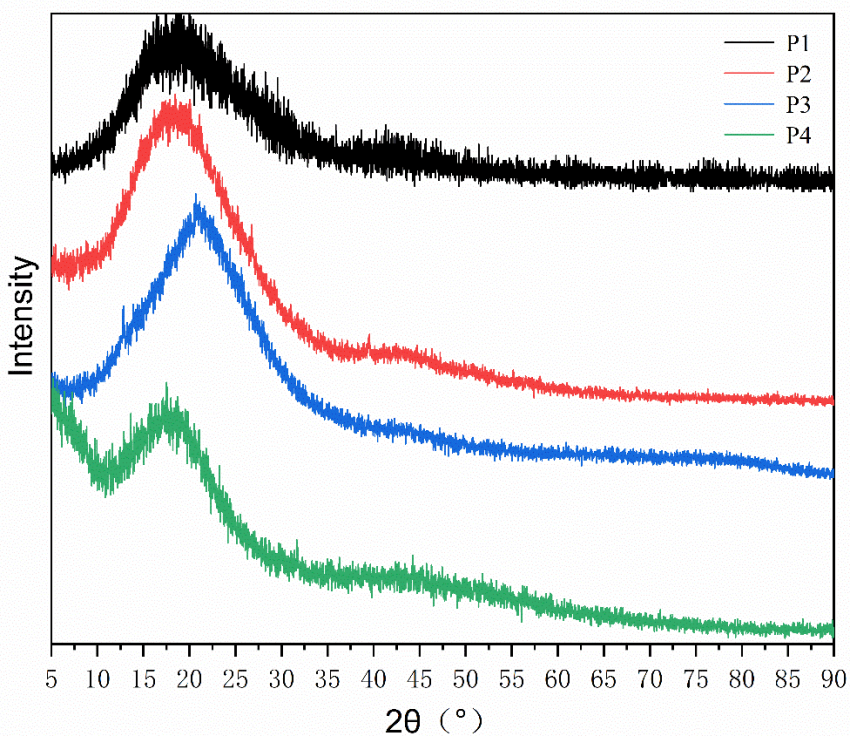


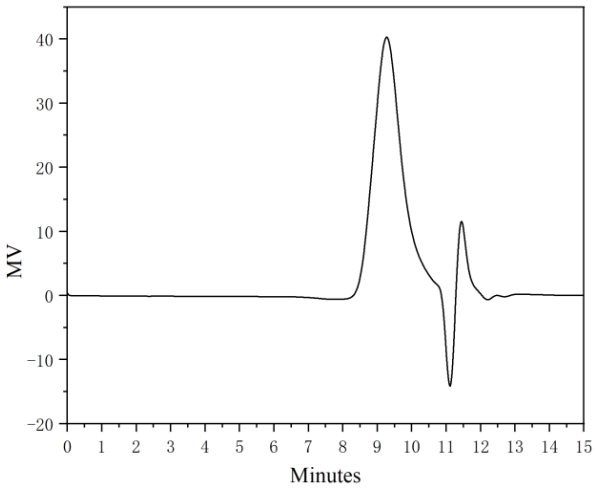
Figure S30. XRD analysis of polymers

3. GPC results

Entry	Polymer	Temperature (°C)	Solvent	Catalysts (equiv)	Mn[d] (g/mol)	Mw (g/mol)	PDI
1	P1	25	DMF	DBU (0.6)	Oligomer	Oligomer	—
2	P1	55	DMF	DBU (0.6)	5231	9152	1.75
3	P1	85	DMF	DBU (0.6)	9683	17391	1.80
4	P1	105	DMF	DBU (0.6)	12674	18411	1.45
5	P1	125	DMF	DBU (0.6)	11743	16875	1.44
6	P1	105	NMP	DBU (0.6)	8354	13576	1.45
7	P1	105	DMAc	DBU (0.6)	11256	17009	1.51
8	P1	105	THT	DBU (0.6)	9577	14530	1.52
9	P1	105	DMF	DBN (0.6)	7841	12159	1.55
10	P1	105	DMF	MTBD (0.6)	8822	16137	1.83
11	P1	105	DMF	TBD (0.6)	8808	14618	1.66
12	P1	105	DMF	TMG (0.6)	5522	9250	1.67
13	P1	105	DMF	$[Ph_3P{=}N{-}PPh_3]^+[HF_2]^-$ (0.6)	10367	14665	1.41
14	P1	105	DMF	$[^nBu_4N]^+[HF_2]^-$ (0.6)	11340	15897	1.40
15	P1	105	DMF	DBU (0.4)	11466	19563	1.71
16	P1	105	DMF	DBU (1)	8698	15588	1.79
17	P4	105	DMF	DBU (0.6)	2570	7088	2.76
18	P4	105	DMF	DBU (0.6)	6254	13342	2.13
19	P4	55	DMF	DBU (0.6)	12011	26383	2.19
20	P4	55	DMF	DBU (0.6)	12542	25041	1.99
21	P4	55	DMF	DBU (0.6)	7501	10050	1.34

Table S1 Polymerization reaction conditions screening results

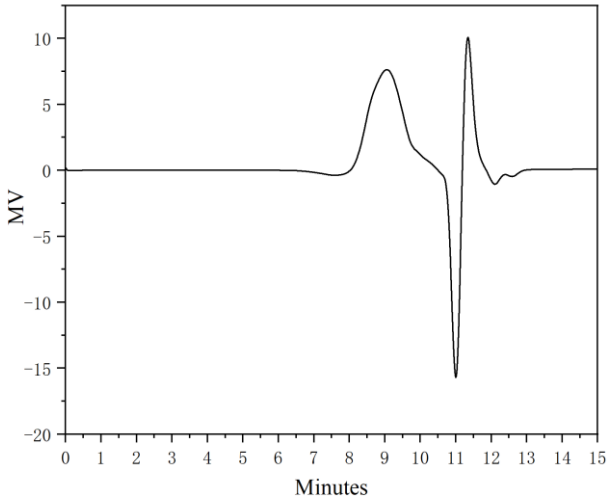
Entry 2 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	5231	9152	7855	1.749

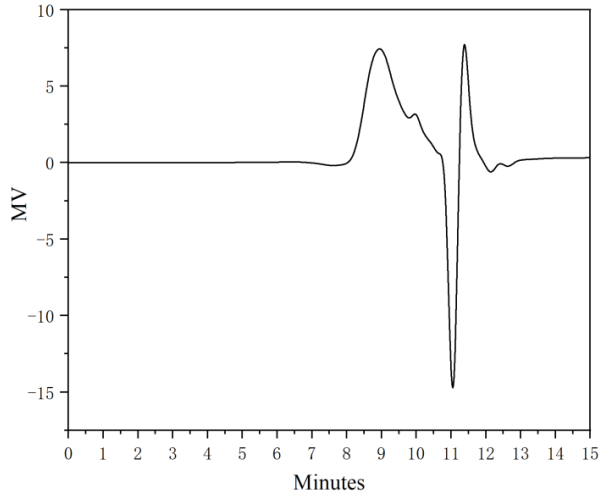
Entry 3 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	9633	17391	11912	1.805

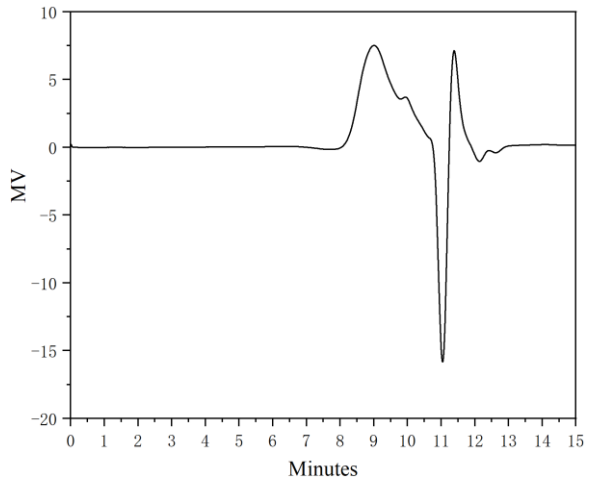
Entry 4 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	12674	18411	16143	1.452

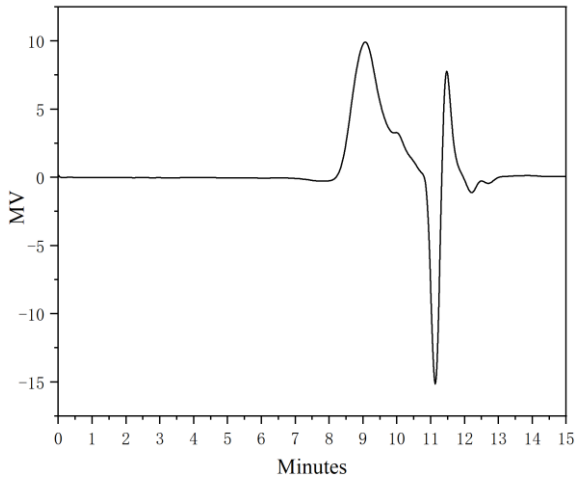
Entry 5 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	11743	16875	14173	1.437

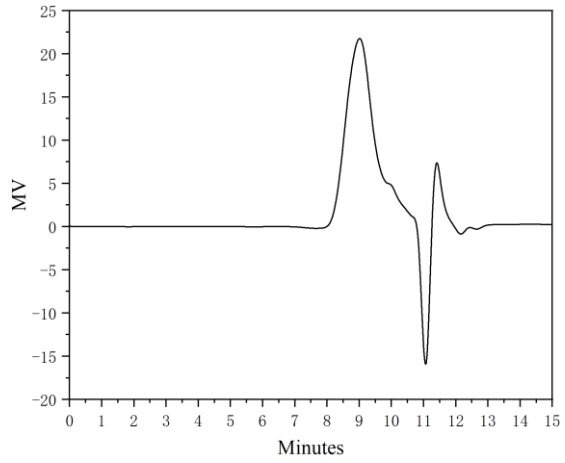
Entry 6 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	8354	13576	11715	1.451

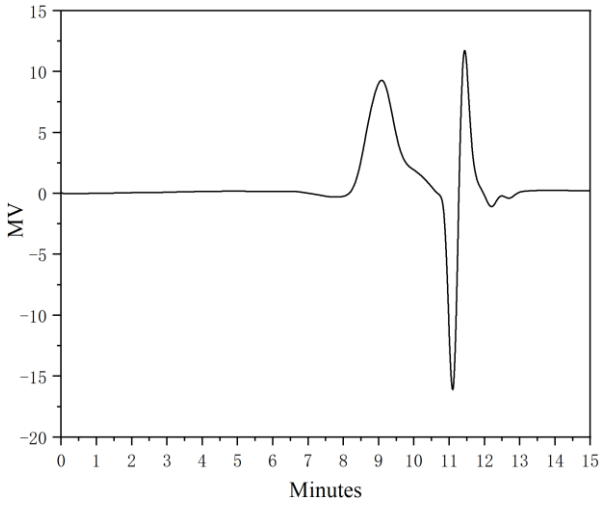
Entry 7 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	11256	17009	12985	1.511

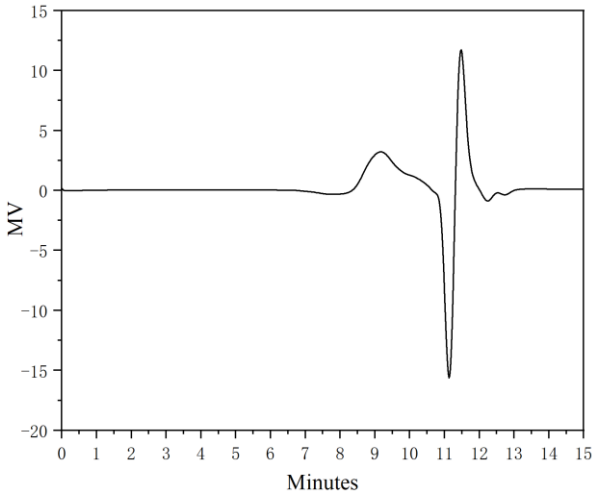
Entry 8 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	9577	14530	11271	1.517

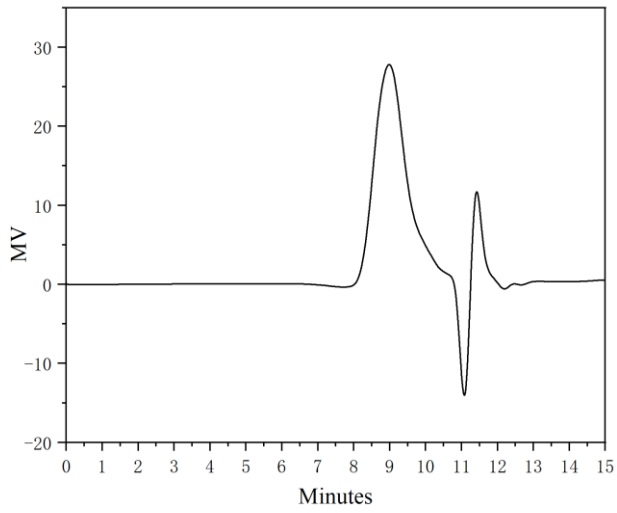
Entry 9 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	7841	12159	10263	1.551

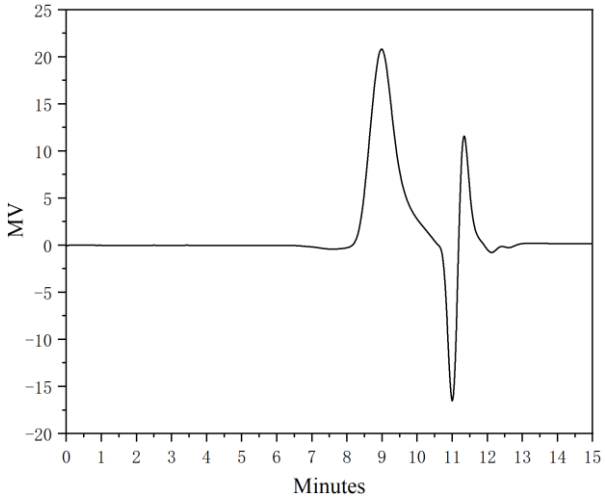
Entry 10 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	8822	16137	13659	1.829

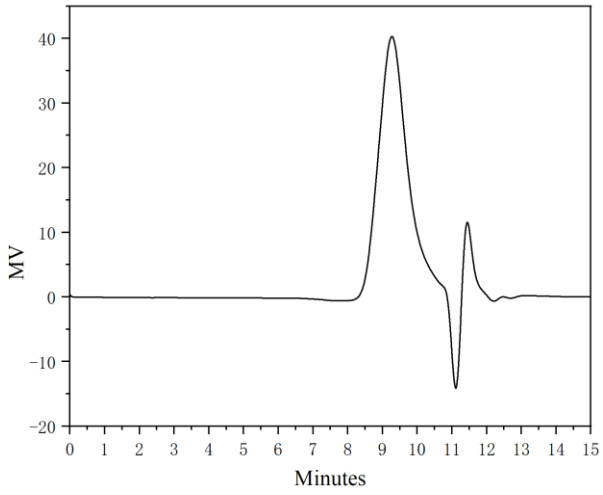
Entry 11 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	8808	14618	13650	1.659

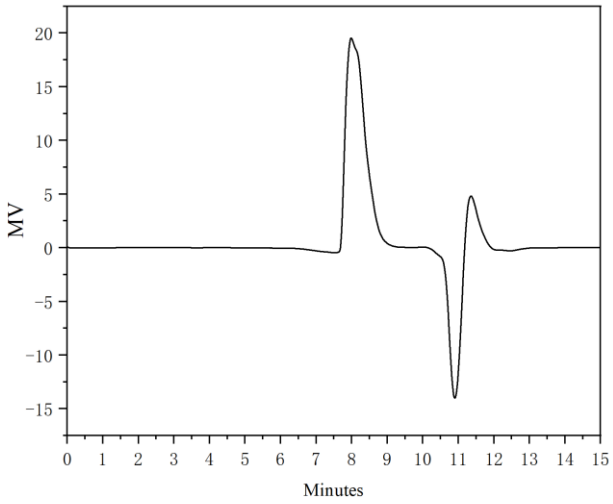
Entry 12 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	5522	9250	7855	1.675

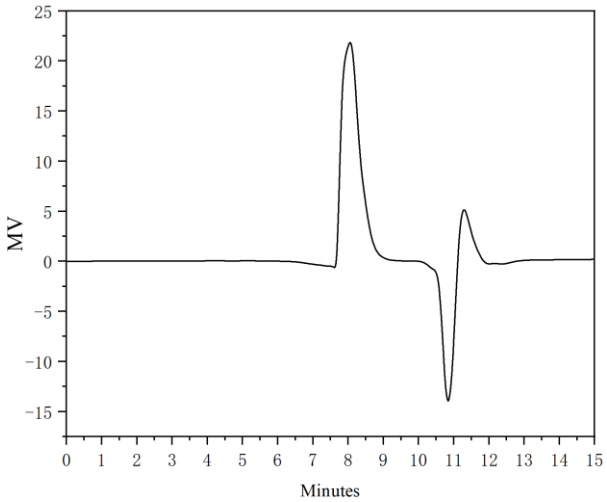
Entry 13 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	10367	14665	18633	1.414

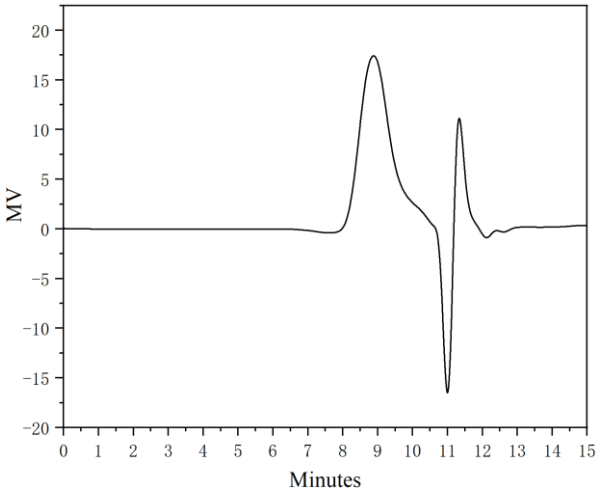
Entry 14 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	11340	15897	16032	1.402

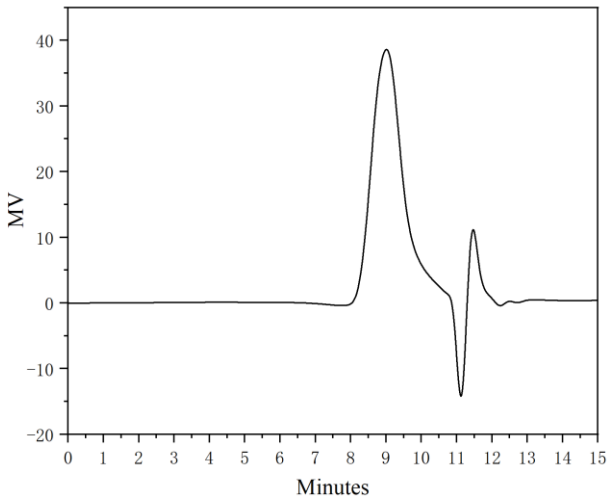
Entry 15 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	11466	19563	16685	1.706

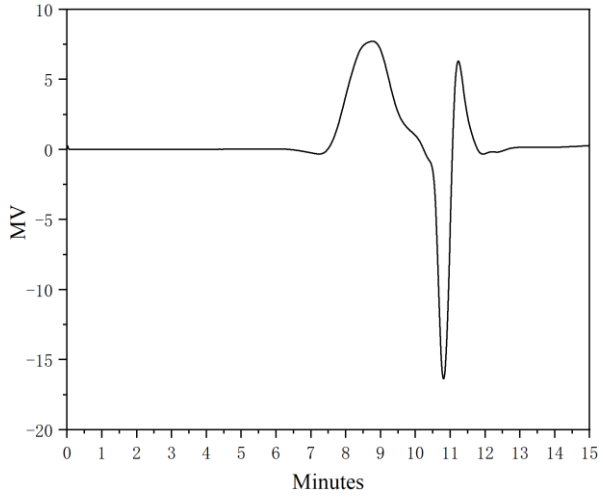
Entry 16 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	8698	15588	12959	1.792

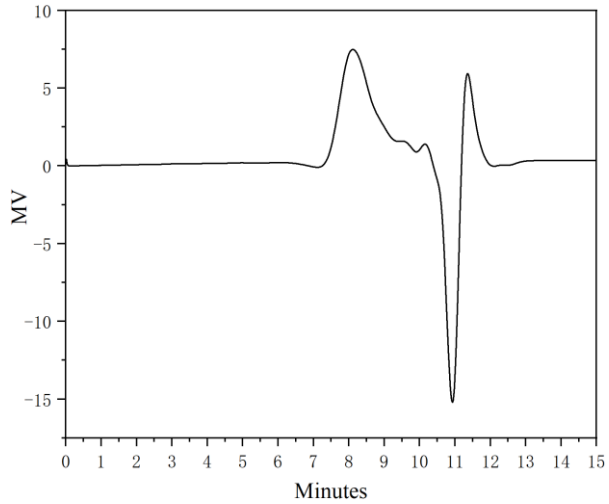
Entry 17 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P4	2570	7088	3194	2.758

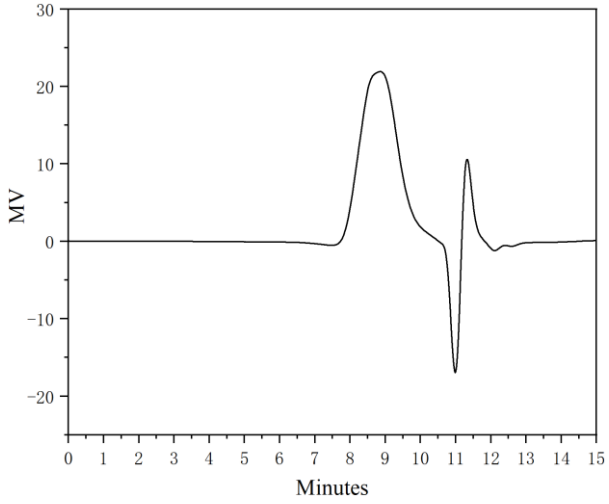
Entry 18 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P4	6254	13342	12161	2.133

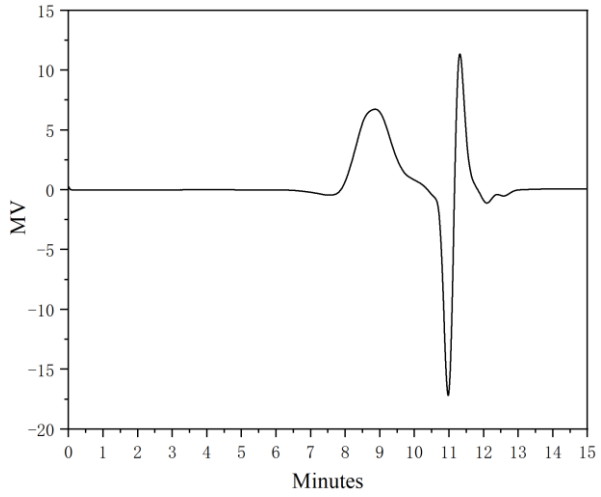
Entry 19 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P4	12011	26383	17516	2.196

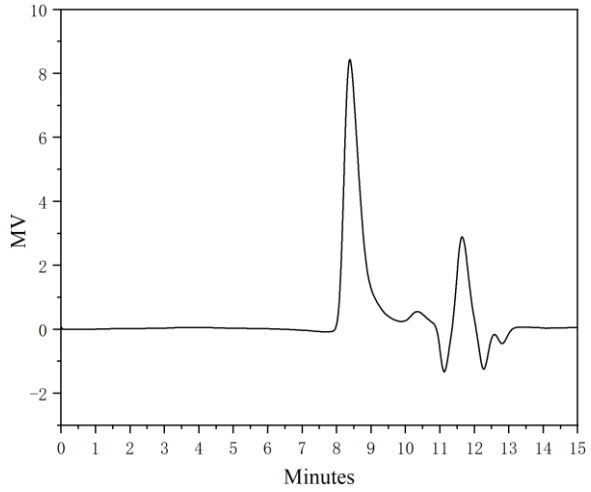
Entry 20 of Table S1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P4	12542	25041	17473	1.996

Entry 21 of Table S1



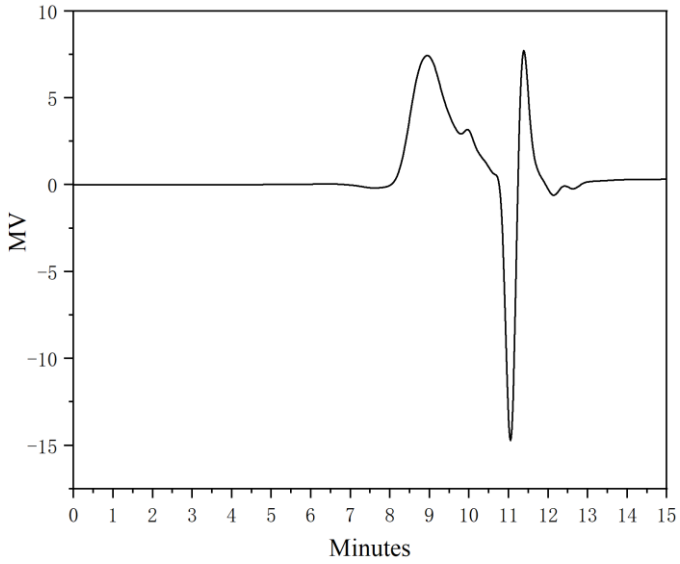
Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P4	7501	10050	11567	1.340

Entry	Polymer	Monomer	Monomer	Mn (g/mol)	Mw (g/mol)	PDI	Yield （%）
1	P1	MSi1	MF	12674	18411	1.45	49
2	P2	MSi2	MF	12565	20239	1.61	52
3	P3	MSi3	MF	11696	21997	1.88	56
4	P4	MSi4	MF	12542	25041	1.99	55

Table S2 Four Polysulfonates synthesized sequentially according to the optimal reaction conditions

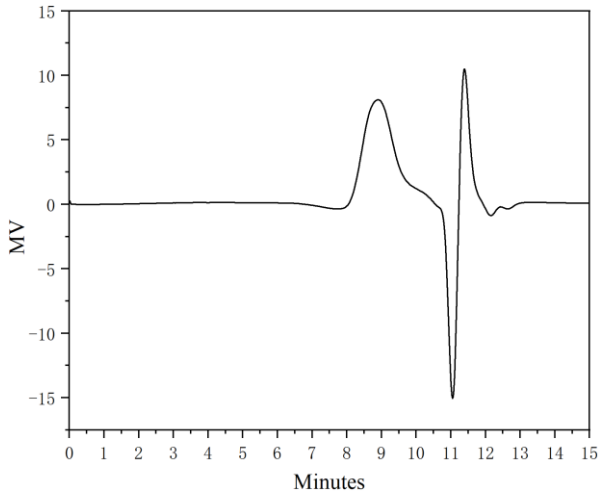
Entry 1 of Table S2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P1	12674	18411	16143	1.452

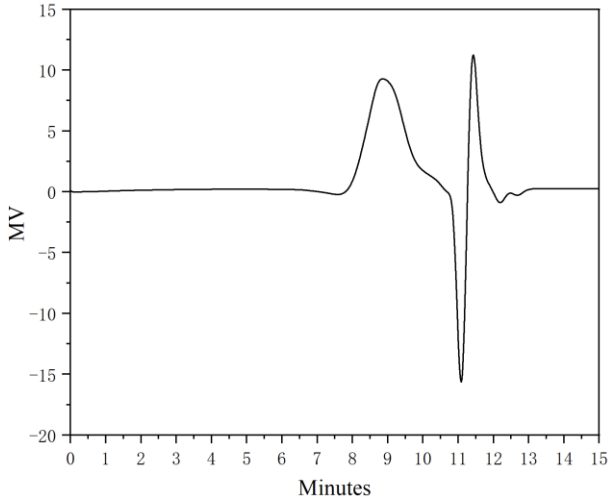
Entry 2 of Table S2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P2	12565	20239	16105	1.611

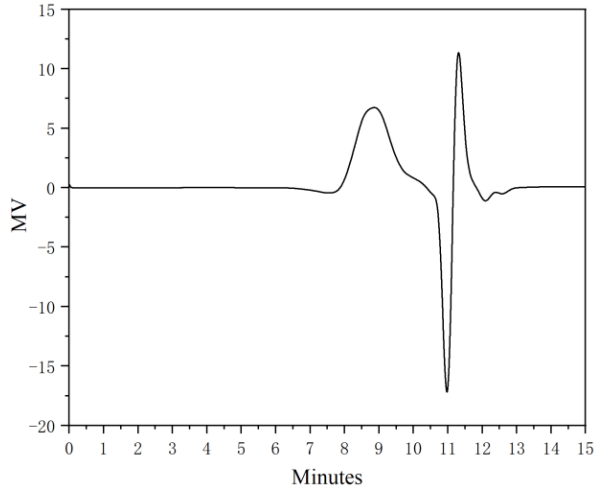
Entry 3 of Table S2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P3	11696	21997	17516	1.881

Entry 4 of Table S2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Polydispersity
P4	12542	25041	17473	1.996

Reference

[1] S. Veer, K. Katkar and K. Akamanchi, *Tetrahedron Lett*, 2016, **57**, 4039-4043.