Supporting Information

Atom-economic, room-temperature, and high-efficiency synthesis of polyamides via a three-component polymerization involving benzoxazine, odorless isocyanide, and water

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Experimental Section.

Materials. $CHCl_3$, CH_2Cl_2, THF and toluene were dried and distilled prior to use as well as Et_3N. DMSO, DMF, ethyl ether, octylphosphonic acid (OPA), tosylmethyl isocyanide **2**, paraformaldehyde and other reagents and chemicals were purchased from Adamas or Aladdin and used as received. Benzoxazines[1, 2] and isocyanides[3, 4] were prepared according to the reported procedures.

Characterization. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III HD NMR spectrometer at 400 MHz and 100 MHz in $CDCl_3$ or DMSO-d_6 using tetramethylsilane (TMS; $\delta = 0$) as internal standard. FT-IR spectra were performed on a WQF-520 FT-IR spectrometer as thin films on KBr pellets. High resolution mass spectra (HRMS) were measured on a Waters Q-TOF Premier mass spectrometer. Relative weight-average and number-average molecular weights (M_w and M_n) and polydispersity indices (Đ, M_w/M_n) of the polymers were estimated by an Aglient 1260 gel permeation chromatography (GPC) system equipped with a UV detector (eluent: THF, at a flow rate of 1.0 mL/min; calibration standards: polystyrene). Cyclic voltammograms carried out on a CHI650e electrochemical workstation with platinum electrodes at a scan rate of 50 mV/s against a saturated calomel reference electrode with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN).

Monomer Preparation.

Preparation of benzoxazines.

3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine (1). In a standard Schlenk tube, phenol (470 mg, 5 mmol), aniline (465 mg, 5 mmol), and paraformaldehyde (300 mg, 10 mmol) were dissolved in 10 mL toluene. The reaction mixture was refluxed for 10 h, afterwards, the mixture was cooled down to room temperature and was washed several times with 0.1 M NaOH solution and distilled water. After this, the solution was dried over anhydrous $MgSO_4$. The volatile was removed under vacuum and the residue was purified by column chromatography (SiO_2, petroleum ether/EtOAc 30:1).

Benzoxazines **1a**, **1b** and **1c** were prepared according to the synthesis of **1**.

Characterization data of 1: White powder was obtained (538 mg, 51%). FT-IR (KBr, cm^{-1}): 3009, 2909, 2857, 1602, 1573, 1488, 1225 (C-O-C), 1031, 932 (benzoxazine related band), 755. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32–7.26 (m, 2H), 7.17–7.11 (m, 3H), 7.06–7.01 (m, 1H), 6.98–6.88 (m, 2H), 6.86–6.82 (m, 1H), 5.39 (s, 2H), 4.66 (s, 2H).

Characterization data of 1a: Light yellow solids was obtained (50%). FT-IR (KBr, cm^{-1}): 3035, 2959, 2868, 1613, 1504, 1454, 1237 (C-O-C), 1017, 945 (benzoxazine related band), 829. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.10 (dd, J = 10.8, 4.2 Hz, 9H), 7.02–6.80 (m, 7H), 6.72 (dd, J = 8.4, 3.9 Hz, 2H), 5.30 (s, 4H), 4.57 (s, 4H), 1.70–1.51 (m, 16H), 1.33–1.07 (m, 16H), 0.90–0.49 (m, 18H).

Characterization data of 1b: Yellow oil was obtained (35%). FT-IR (KBr, cm^{-1}):3006, 2963, 2922, 2864, 1614, 1509, 1454, 1236 (C-O-C), 945 (benzoxazine related band), 822. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55–7.36 (m, 2H), 7.06–6.74 (m, 12H), 5.30 (d, J = 8.3 Hz, 4H), 4.56 (s, 4H), 3.80 (s, 2H), 1.64–0.57 (m, 38H).

Characterization data of 1c: White solid was obtained (61%). FT-IR (KBr, cm^{-1}):3002, 2922, 2857, 1607, 1578, 1484, 1222 (C-O-C), 927 (benzoxazine related band), 811. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.27 (dd, J = 8.3, 2.1 Hz, 2H), 7.11 (d, J = 2.1 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 4.89 (s, 4H), 4.03 (s, 4H), 2.80–2.71 (m, 4H), 1.62–1.51 (m, 4H), 1.36–1.26 (m, 12H), 0.88 (t, J = 6.8 Hz, 6H).

Preparation of isocyanides.

4-isocyano-1,1'-biphenyl (3). 4-aminobiphenyl (845 mg, 5 mmol) in 10 ml CH_2Cl_2 in a Schlenk tube, added chloroform (407 μL, 5 mmol), tetrabutylammonium hydroxide (26 mg, 0.1 mmol) and 10 mL 50% aqueous solution of sodium hydroxide. The mixture was heated to reflux for 3 hours. Afterwards, cooling down the reaction mixture and washed with distilled water, dried over anhydrous $MgSO_4$. After the drying agent was filtered off and removed the solvent, the residue was purified by column chromatography (Al_2O_3, petroleum ether/EtOAc 30:1).

Other isocyanides **4a**, **4b**, **4c**, **4d**, **4e** and **4f** were prepared according to the synthesis of **3**.

Characterization data of 3: Yellow powder was obtained (500 mg, 56%). FT-IR (KBr, cm^{-1}): 3071, 2963, 2120 (C≡N stretching), 1585, 1473, 845, 761. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.67–7.61 (m, 2H), 7.61–7.55 (m, 2H), 7.53–7.45 (m, 4H), 7.45–7.39 (m, 1H).

Characterization data of 4a: Yellow powder was obtained (573 mg, 52%).FT-IR (KBr, cm^{-1}): 3070, 2125 (C≡N stretching), 1589, 1486, 1245, 837. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43–7.35 (m, 4H), 7.04–6.98 (m, 4H).

Characterization data of 4b: White powder was obtained (477 mg, 47%). FT-IR (KBr, cm^{-1}): 3030, 2124 (C≡N stretching), 1640, 1486, 816. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.63–7.55 (m, 4H), 7.52–7.44 (m, 4H).

Characterization data of 4c: Yellow powder was obtained (455 mg, 25%). FT-IR (KBr, cm^{-1}): 3020, 2960, 2120 (C≡N stretching), 1604, 1500, 1457, 833. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31–7.20 (m, 8H), 7.07 (s, 4H), 1.26 (dt, J = 11.6, 5.2 Hz, 12H).

Characterization data of 4d: Brown powder was obtained (281 mg, 21%). FT-IR (KBr, cm^{-1}): 3070, 2135 (C≡N stretching), 1591, 1480, 1300, 1145, 810. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.04-7.97 (m, 2H), 7.95 (s, 2H), 7.68-7.59 (m, 4H).

Characterization data of 4e: White powder was obtained (678 mg, 30%).FT-IR (KBr, cm^{-1}): 3070, 2130 (C≡N stretching), 1583, 1503, 1325, 1250, 1155, 847. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.96–7.89 (m, 4H), 7.44–7.36 (m, 4H), 7.10–7.01 (m, 8H).

Characterization data of 4f: Red powder was obtained (320 mg, 20%). FT-IR (KBr, cm^{-1}): 3020, 2923, 2851, 2115 (C≡N stretching), 1593, 1499, 1318, 1268, 833. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.35–7.28 (m, 6H), 7.09–7.02 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 164.55 (s), 146.83 (s), 127.98 (s), 124.74 (s), 122.22 (s). HRMS (MALDI−TOF): m/z [M+Cl^-]: calcd for $C_{21}H_{12}N_4$, 320.3201; found 355.0735.

Preparation of model compounds.

Model compound M1. 1 (0.2 mmol), **2** (0.2 mmol), water (0.2 mmol), and OPA (0.04 mmol) were stirred at room temperature in $CHCl_3$ (2 mL) for 18 h. Solvent was

removed under reduced pressure and the crude product was purified by column chromatography (SiO_2, petroleum ether/EtOAc 3:1).

Model compound M2. 1 (0.2 mmol), **3** (0.2 mmol), water (0.2 mmol) and OPA (0.04 mmol) stirred at room temperature in $CHCl_3$ (2 mL) for 6 h. After removed solvent under reduced pressure and the crude product was purified by column chromatography (SiO_2, petroleum ether/EtOAc 8:1).

Characterization data of M1: White powder was obtained (65 mg, 77%). FT-IR (KBr, cm^{-1}): 3496(-OH), 3243(-NH), 3040, 2923, 1668, 1570, 1326, 1230, 1140, 754. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.61 (s, 1H), 8.95 (t, J = 6.6 Hz, 1H), 7.70 (dd, J = 24.8, 8.3 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.14–7.00 (m, 3H), 6.91 (d, J = 7.4 Hz, 1H), 6.83 (d, J = 7.5 Hz, 1H), 6.68 (t, J = 7.4 Hz, 1H), 6.62 (t, J = 7.2 Hz, 1H), 6.42 (d, J = 8.2 Hz, 2H), 4.68 (d, J = 6.6 Hz, 2H), 4.36 (s, 2H), 3.94 (s, 2H), 2.40 (d, J = 10.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm): 170.51 (s), 155.39 (s), 148.68 (s), 145.02 (s), 134.95 (s), 130.19 (s), 129.23 (s), 129.01 (s), 128.02 (s), 127.73 (s), 124.41 (s), 119.26 (s), 116.71 (s), 115.39 (s), 112.39 (s), 60.69 (s), 54.07 (s), 50.77 (s), 21.60 (s). HRMS (MALDI−TOF): m/z [M+H^+]: calcd for $C_{23}H_{24}N_2O_4S$, 424.1457; found 425.1498.

Characterization data of M2: White powder was obtained (60 mg, 73%). FT-IR (KBr, cm^{-1}): 3279, 3069, 2956, 1640, 1530, 1497, 1450, 1312, 837. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.06 (s, 1H), 9.64 (s, 1H), 7.71 (d, J = 8.6 Hz, 2H), 7.64 (dd, J = 7.8, 4.6 Hz, 4H), 7.44 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.10 (dt, J = 23.8, 8.2 Hz, 4H), 6.85 (d, J = 7.8 Hz, 1H), 6.73 (t, J = 7.4 Hz, 1H), 6.62 (t, J = 8.5 Hz, 3H), 4.59 (s, 2H), 4.24 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm): 169.50 (s), 155.45 (s), 149.05 (s), 149.04 (s), 140.13 (s), 138.79 (s), 135.46 (s), 135.43 (s), 129.37 (s), 128.07 (s), 127.50 (s), 127.38 (s), 126.71 (s), 124.77 (s), 120.11 (s), 119.34 (s), 116.75 (s), 115.46 (s), 112.49 (s), 55.24 (s), 51.29 (s). HRMS (MALDI−TOF): m/z [M+H^+]: calcd for $C_{27}H_{24}N_2O_2$, 408.4682; found 409.1919.

Polymer Synthesis. The polymerization reactions were carried out using a standard Schlenk technique under nitrogen atmosphere and a typical synthetic method for the

preparation of **P1** (1a/4a) was given as an example: **1a** (0.25 mmol), **4a** (0.25 mmol), water (0.5 mmol) and OPA (0.1 mmol) was stirred at room temperature in 5 mL $CHCl_3$ for 6 h. A portion of $CHCl_3$ was removed from the mixture and the residue was added dropwise into 200 mL ethyl ether, the precipitate was collected by filtration and dried under vacuum at 40 ^oC to a constant weight.

Characterization data of P1 (1a+4a): Yellow powder was obtained (204 mg, 75%). FT-IR (KBr, cm^{-1}): 3301, 3035, 2963, 2922, 2868, 1672, 1611, 1501, 1302, 1214, 822. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.17 (hydroxyl protons), 7.23–6.17 (aromatic protons), 4.25 (CH_2 protons), 3.84 (CH_2 protons), 2.03–0.21 (CH_2 and CH_3 protons).

Characterization data of P2 (1a+4b): Yellow powder was obtained (153 mg, 57%). FT-IR (KBr, cm^{-1}): 3315, 3032, 2963, 2922, 2865, 1668, 1607, 1505, 1316, 822. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.34 (O-H), 9.15 (N-H), 8.42–7.30 (aromatic protons), 7.21–5.55 (aromatic protons), 4.49 (CH_2 protons), 3.82 (CH_2 protons), 2.15–0.16 (CH_2 and CH_3 protons).

Characterization data of P3 (1a+4c): Yellow powder was obtained (160 mg, 52%). FT-IR (KBr, cm^{-1}): 3307, 3026, 2959, 2923, 2864, 1665, 1603, 1505, 1404, 1315, 826. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.66 (hydroxyl protons), 7.16–6.49 (aromatic protons), 4.50 (CH_2 protons), 3.77 (CH_2 protons), 1.91–0.30 (CH_2 and CH_3 protons).

Characterization data of P4 (1a+4d): Red powder was obtained (70 mg, 25%). FT-IR (KBr, cm^{-1}): 3286, 3025, 2922, 2861, 1672, 1601, 1509, 1418, 1302, 822. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.21 (hydroxyl protons), 7.89–7.33 (aromatic protons), 7.21–6.47 (aromatic protons), 4.51 (CH_2 protons), 3.83 (CH_2 protons), 1.78–0.21 (CH_2 and CH_3 protons).

Characterization data of P5 (1a+4e): Light yellow powder was obtained (240 mg, 73%). FT-IR (KBr, cm^{-1}): 3293, 3027, 2963, 2922, 2864, 1672, 1596, 1501, 1418, 1302, 822. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.98 (hydroxyl protons), 8.03–7.54 (aromatic protons), 7.22–6.35 (aromatic protons), 4.52 (CH_2 protons), 4.10 (CH_2 protons), 1.81–0.15 (CH_2 and CH_3 protons).

Characterization data of P6 (1b+4a): Brown powder was obtained (141 mg, 60%). FT-IR (KBr, cm^{-1}): 3293, 3028, 2959, 2922, 2864, 1669, 1611, 1504, 1415, 1305, 1211, 822. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.20 (hydroxyl protons), 7.19–5.98 (aromatic protons), 4.40 (CH_2 protons), 3.82 (CH_2 protons), 1.97–0.17 (CH_2 and CH_3 protons).

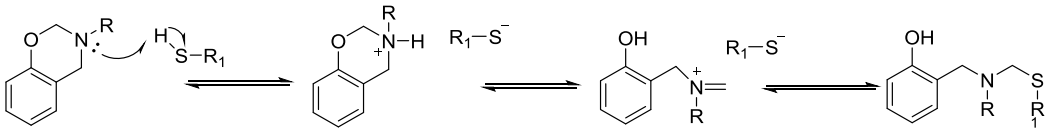
Characterization data of P7 (1c+4a): White powder was obtained (60 mg, 35%). FT-IR (KBr, cm^{-1}): 3275, 3046, 2955, 2923, 2854, 1663, 1611, 1494, 1410, 1305, 1229, 826. ^1H NMR (400 MHz, $CDCl_3/CD_3OD$=20:1) δ (ppm): 7.78–6.52 (aromatic protons), 4.38 (CH_2 protons), 3.81 (CH_2 protons), 3.36 (CH_2 protons), 2.6 (CH_2 protons), 1.97–0.56 (CH_3 and CH_2 protons). We envisaged that the peaks of active protons (O-H and N-H) not appeared in the existence of CD_3OD and the peaks of CH_2 protons splitting in the mixed deuterated reagents.

Characterization data of P1-air (1a+4a): Yellow powder was obtained (135 mg, 50%). FT-IR (KBr, cm^{-1}): 3297, 3039, 2963, 2922, 2864, 1665, 1607, 1501, 1305, 1214, 822. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.17 (hydroxyl protons), 7.23–6.13 (aromatic protons), 4.45 (CH_2 protons), 3.86 (CH_2 protons), 1.99–0.20 (CH_3 and CH_2 protons).

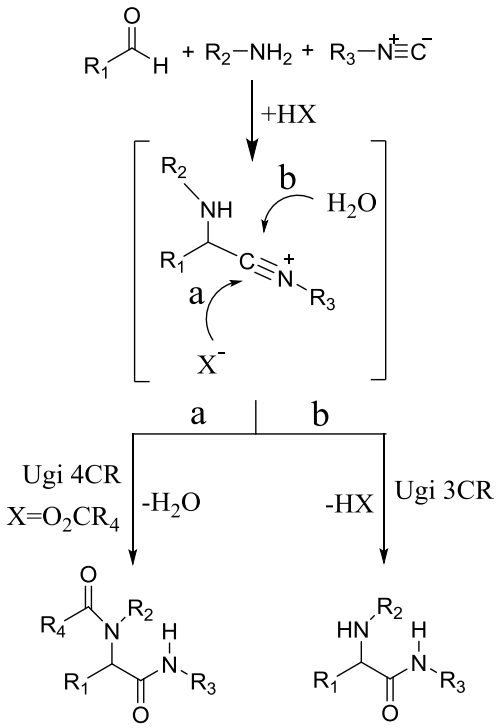
Characterization data of P8 (1a+4a/4f=10:1): Red powder was obtained (120 mg, 57%). FT-IR (KBr, cm^{-1}): 3297, 3039, 2963, 2926, 2864, 1665, 1607, 1501, 1309, 1214, 818. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.11 (hydroxyl protons), 7.22–6.11 (aromatic protons), 4.40 (CH_2 protons), 3.83 (CH_2 protons), 2.00–0.15 (CH_3 and CH_2 protons).

Characterization data of P9 (1a+4a/4f=5:1): Red powder was obtained (110 mg, 52%). FT-IR (KBr, cm^{-1}): 3296, 3038, 2962, 2926, 2865, 1668, 1607, 1501, 1309, 1215, 821. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.15 (hydroxyl protons), 7.25–6.12 (aromatic protons), 4.43 (CH_2 protons), 3.81 (CH_2 protons), 1.92–0.15 (CH_3 and CH_2 protons).

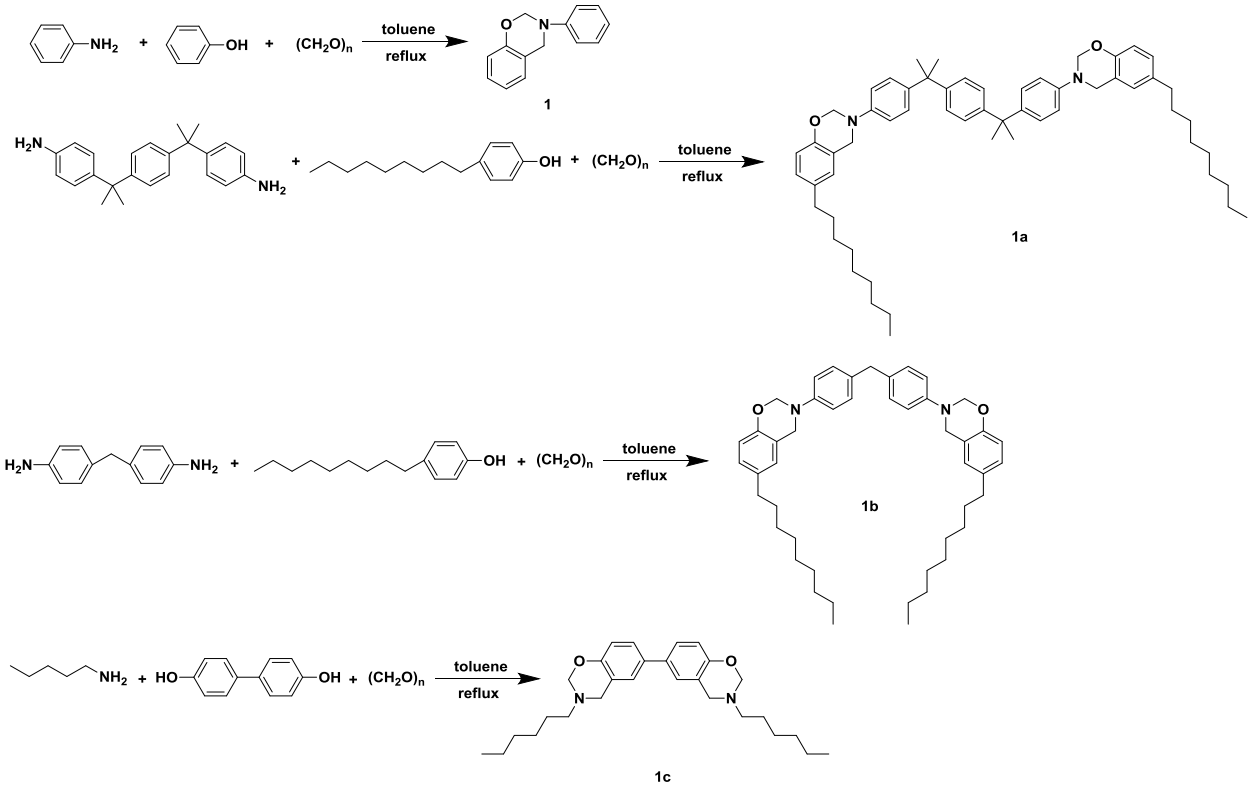
Scheme S1. Proposed reaction mechanism of CLOBERT reaction.[5]



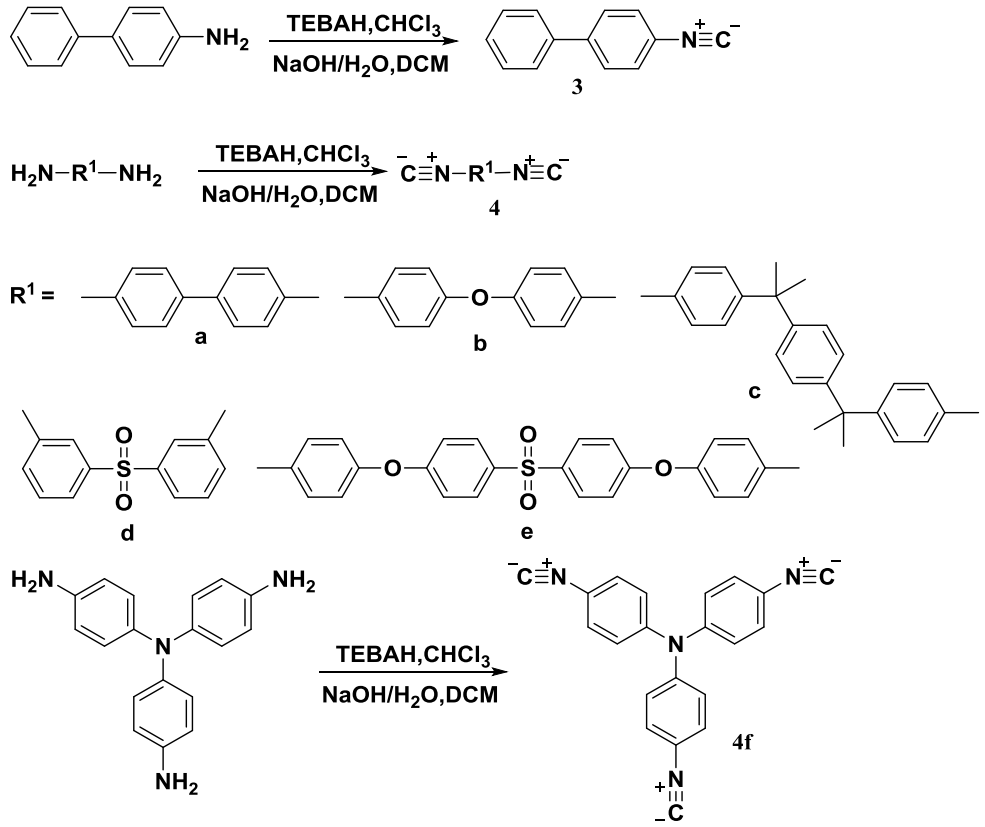
Scheme S2. The mechanism for Ugi 4CR and Ugi 3CR.[6]



Scheme S3. Synthetic route of benzoxazines **1**, **1a**, **1b** and **1c**.



Scheme S4. Synthetic route of isocyanides **3**, **4a**, **4b**, **4c**, **4d** and **4e**.



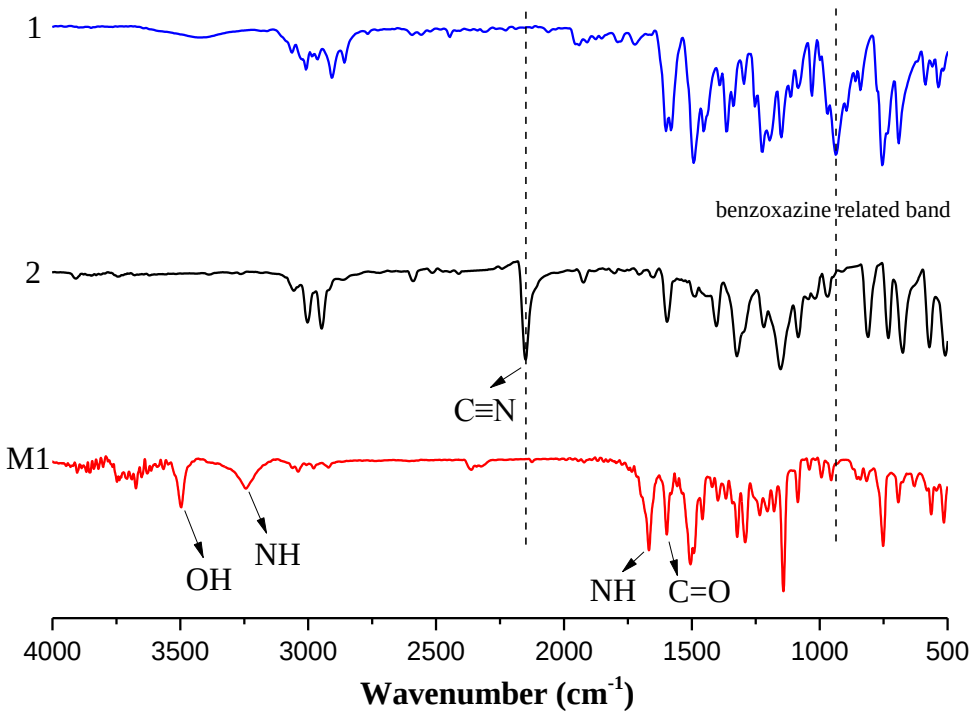


Figure S1. FT-IR spectra of **1**, **2** and **M1**.

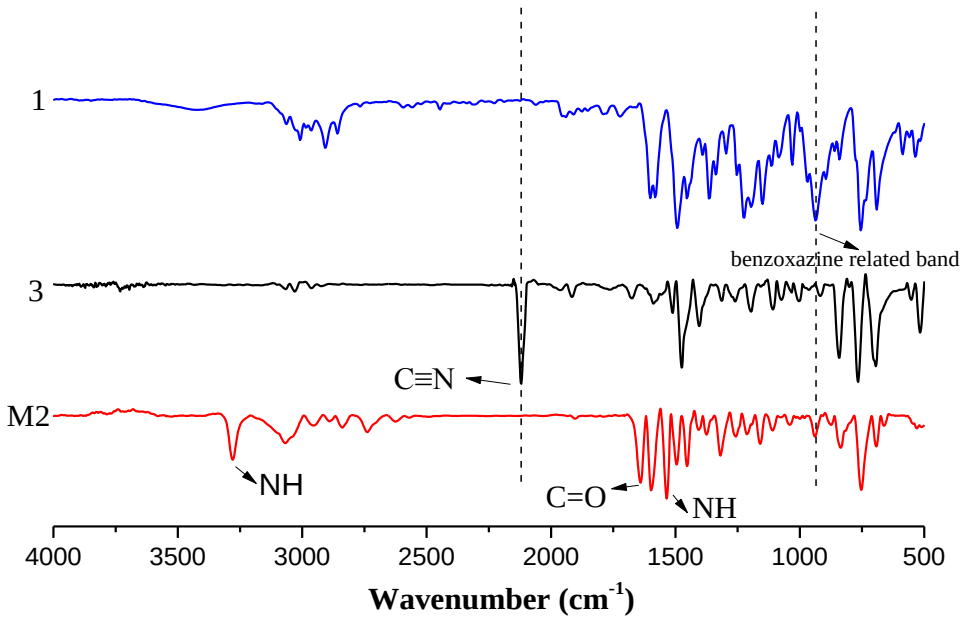


Figure S2. FT-IR spectra of **1**, **3** and **M2**.

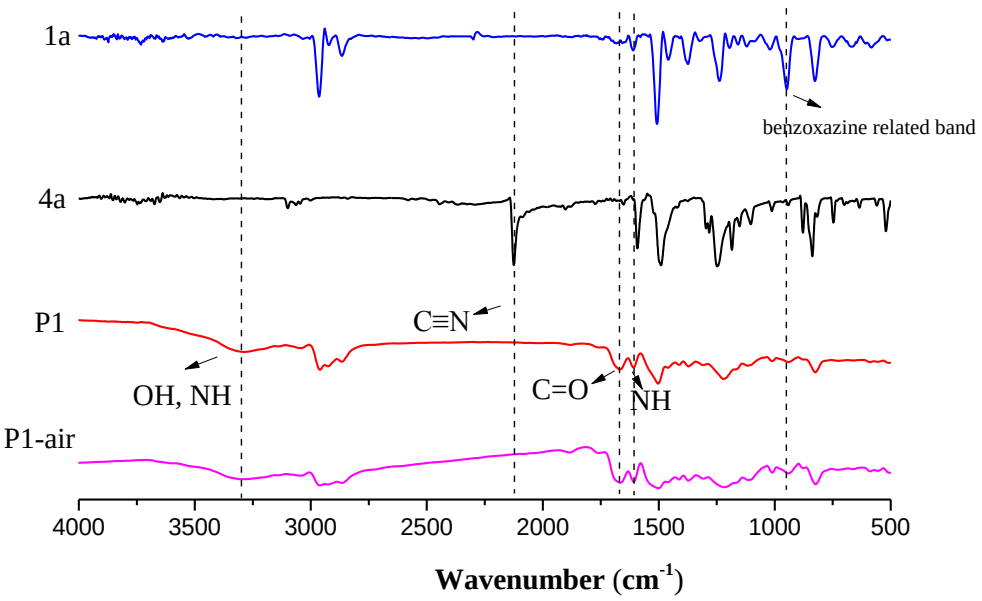


Figure S3. FT-IR spectra of **1a**, **4a**, **P1** and **P1-air**.

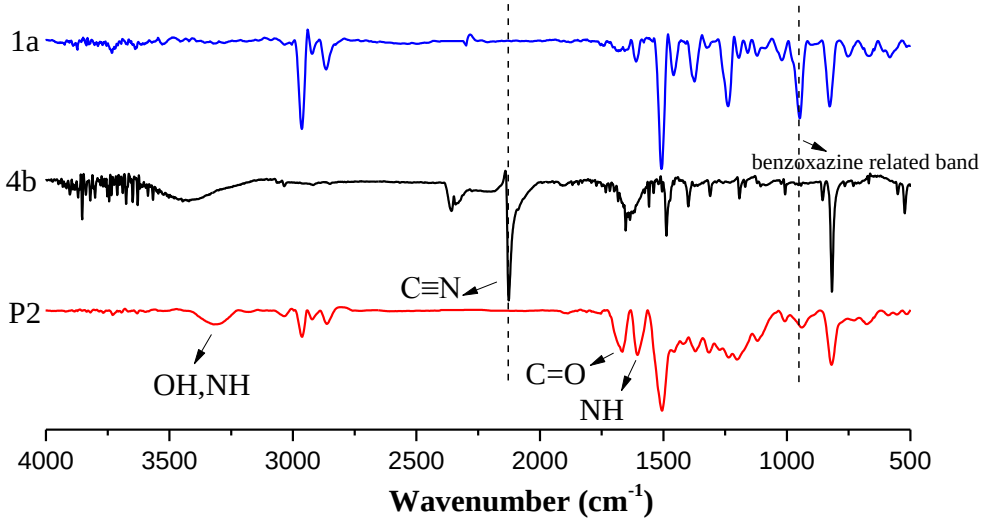


Figure S4. FT-IR spectra of **1a**, **4b** and **P2**.

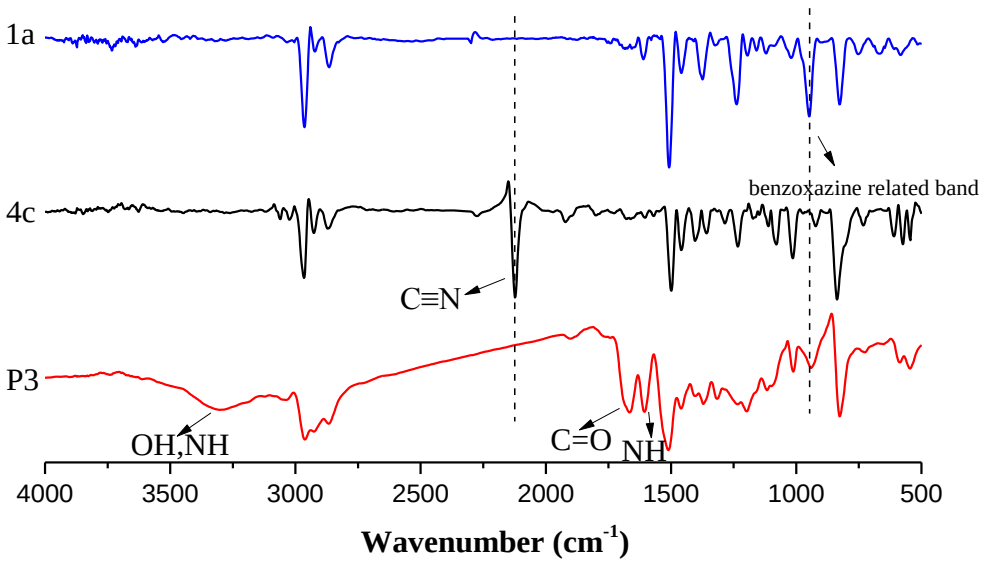


Figure S5. FT-IR spectra of **1a**, **4c** and **P3**.

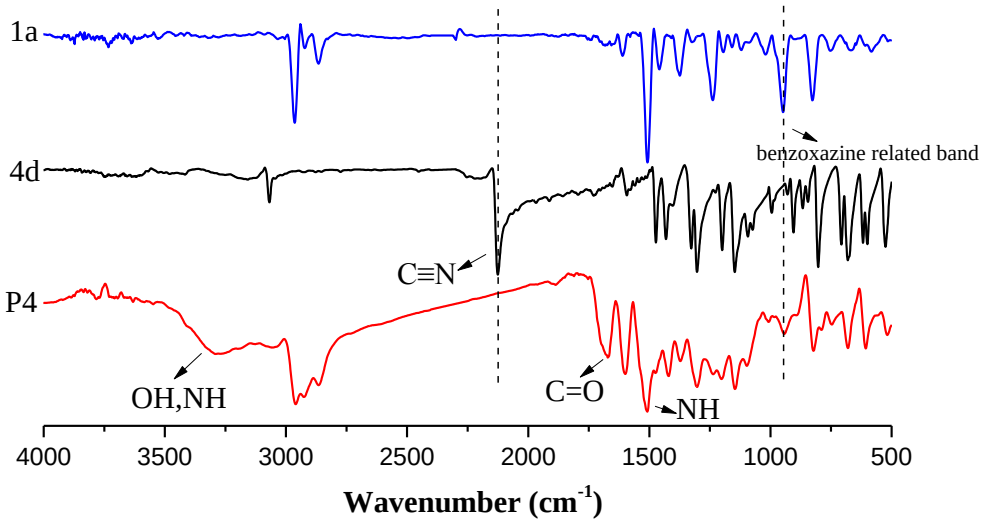


Figure S6. FT-IR spectra of **1a**, **4d** and **P4**.

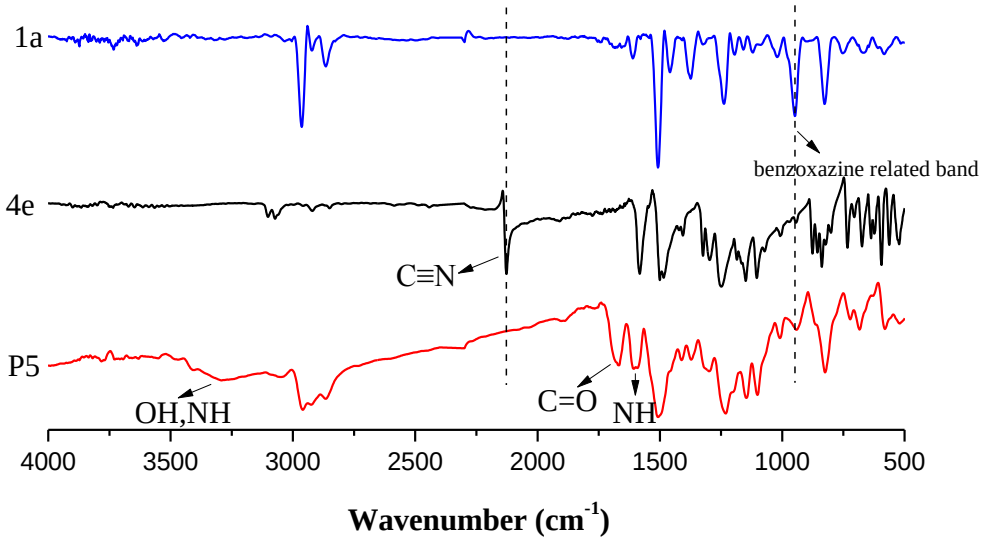


Figure S7. FT-IR spectra of **1a**, **4e** and **P5**.

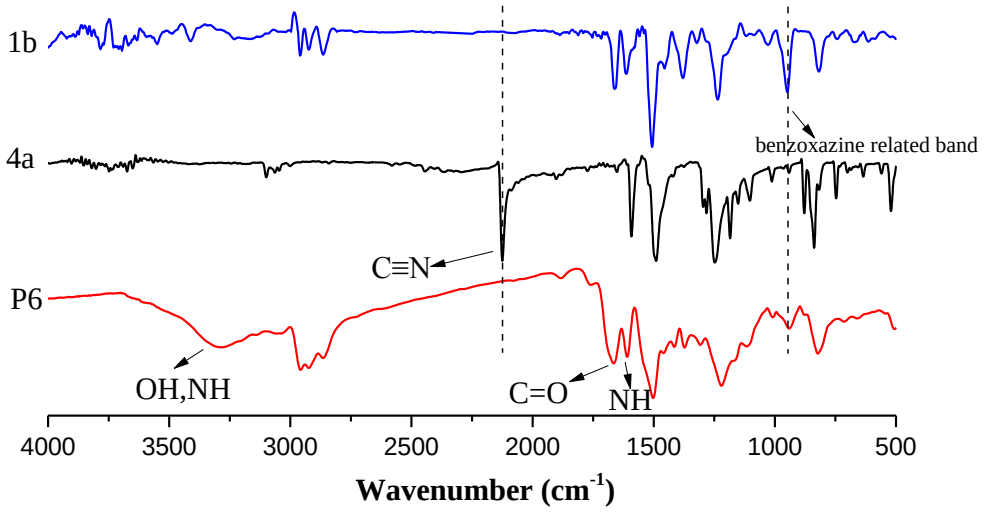


Figure S8. FT-IR spectra of **1b**, **4a** and **P6**.

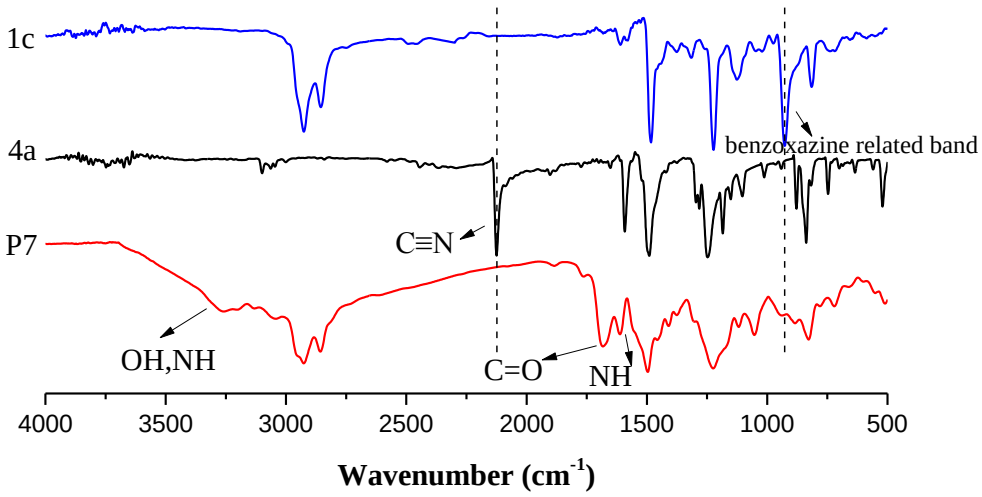


Figure S9. FT-IR spectra of **1c**, **4a** and **P7**.

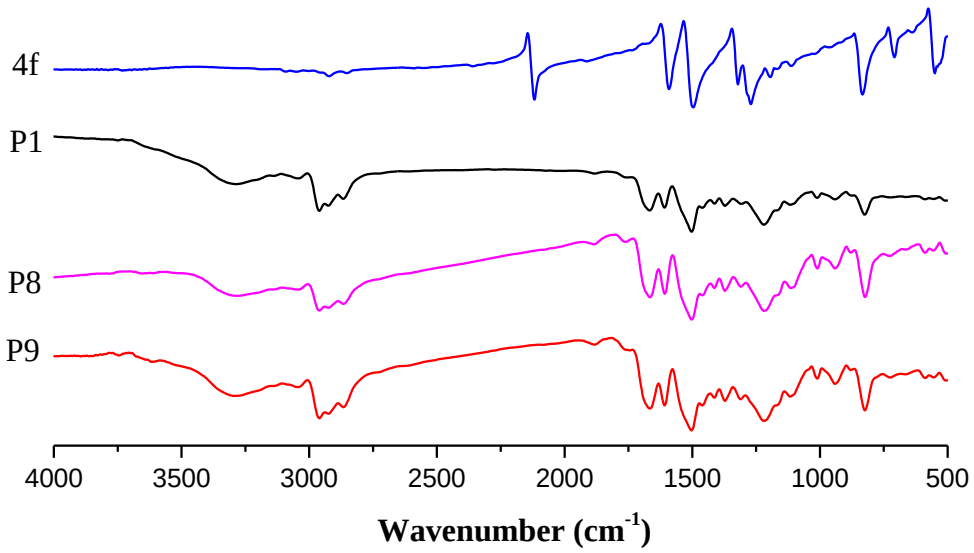


Figure S10. FT-IR spectra of **4f**, **P1**, **P8** and **P9**.

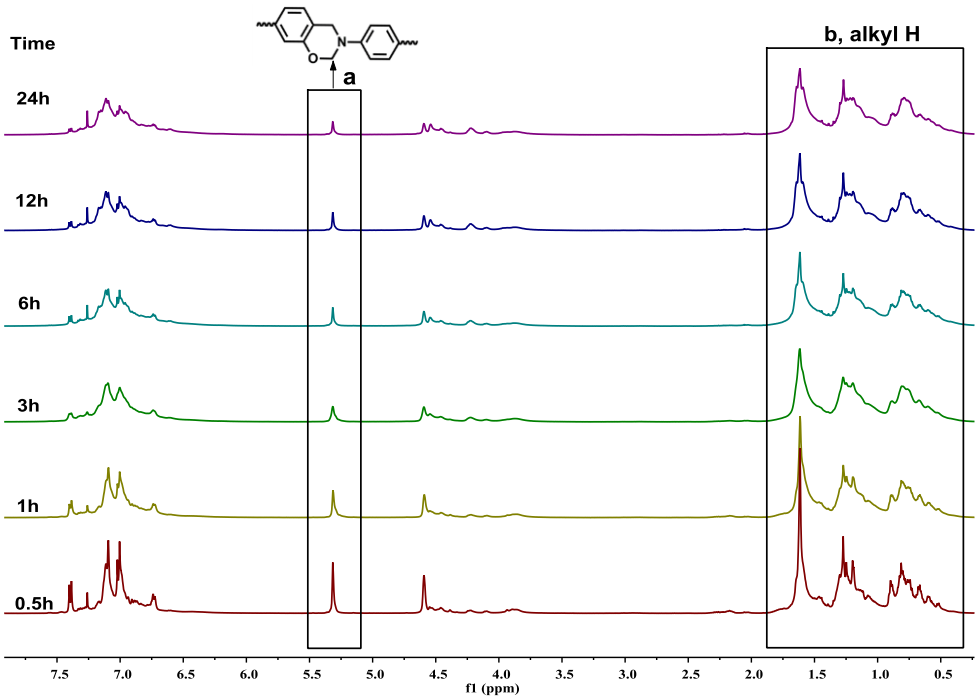


Figure S11. In-situ ^{1}H NMR study of the polymerization between **1a** and **4a** in $CDCl_3$ under room temperature.

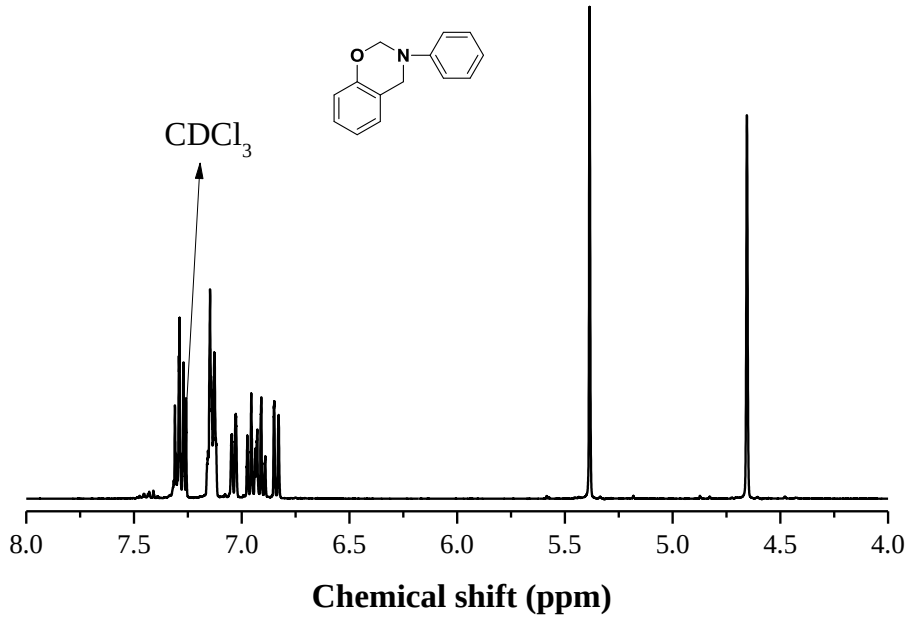


Figure S12. ^{1}H NMR spectrum of **1** in $CDCl_3$.

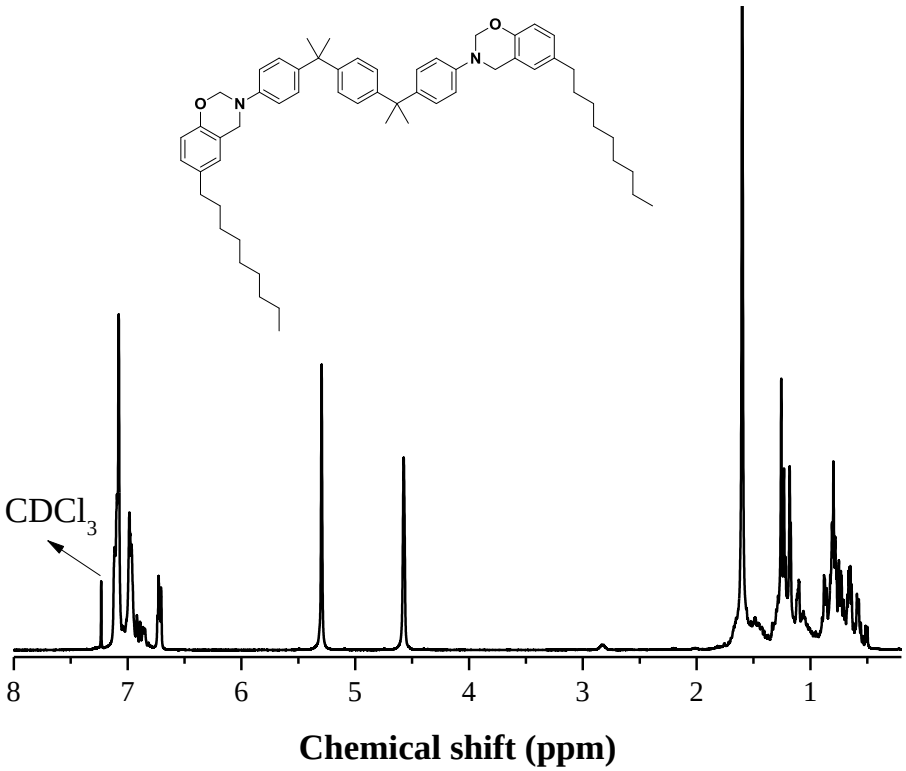


Figure S13. ^{1}H NMR spectrum of **1a** in $CDCl_3$.

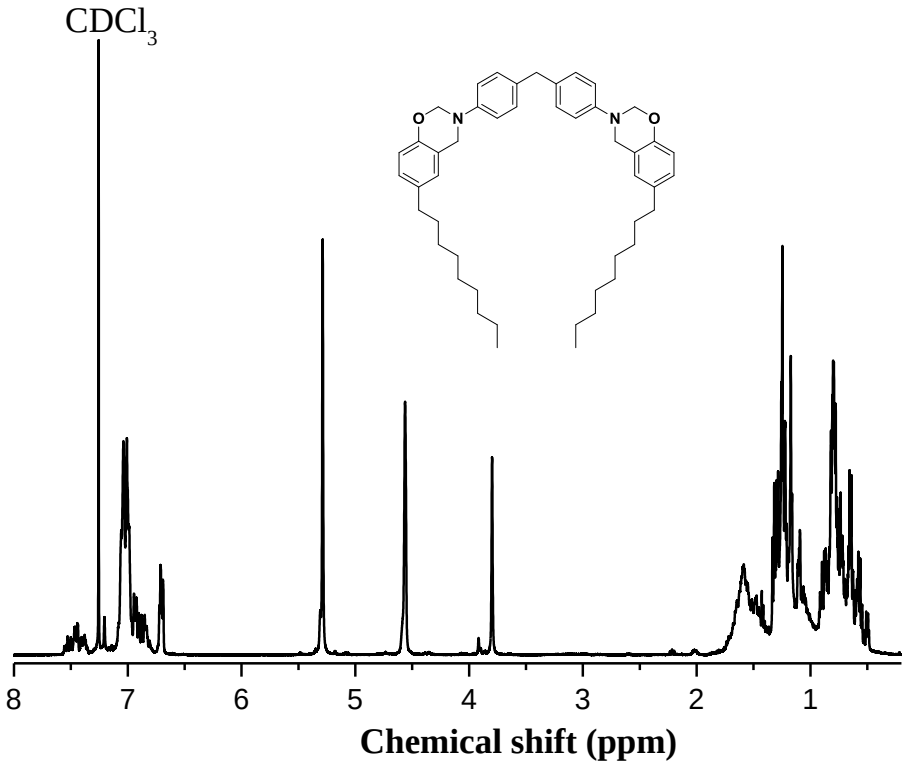


Figure S14. ^{1}H NMR spectrum of **1b** in $CDCl_3$.

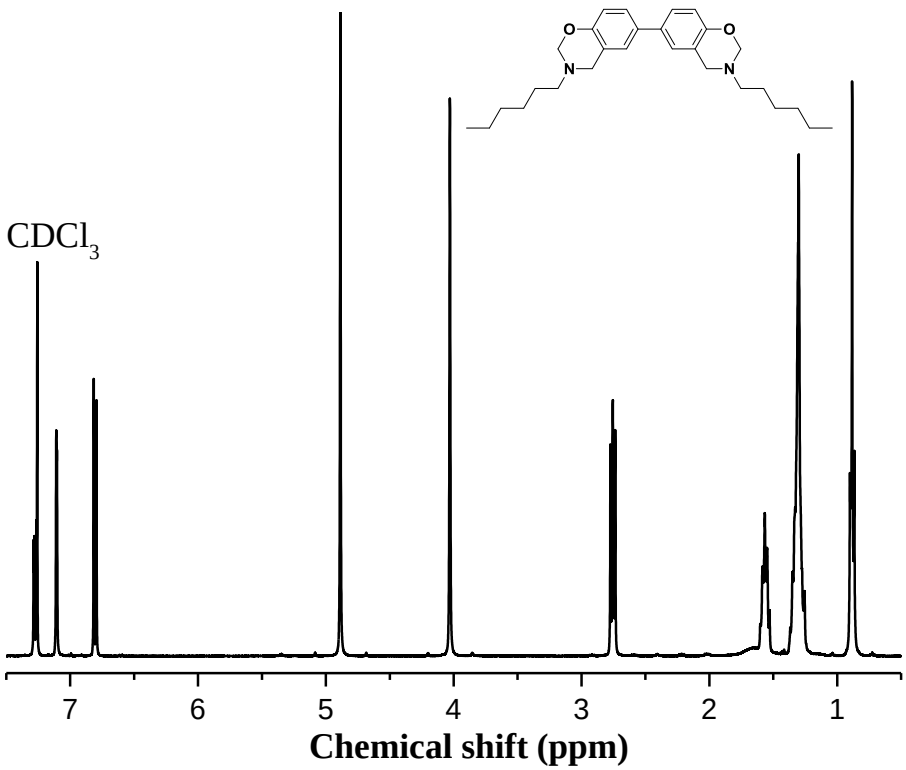


Figure S15. ^{1}H NMR spectrum of **1c** in $CDCl_3$.

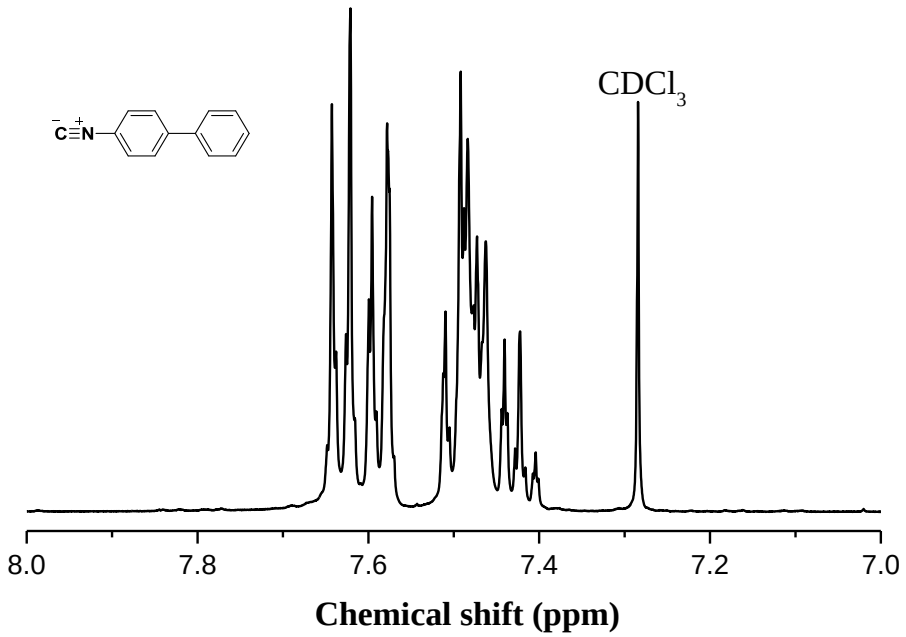


Figure S16. ^{1}H NMR spectrum of **4** in $CDCl_3$.

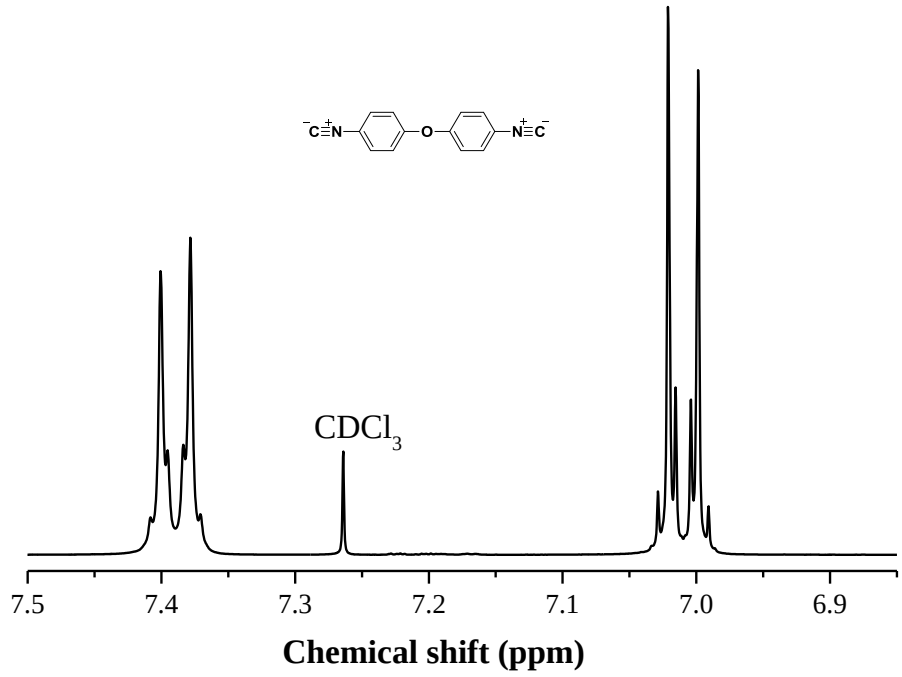


Figure S17. ^{1}H NMR spectrum of **4a** in $CDCl_3$.

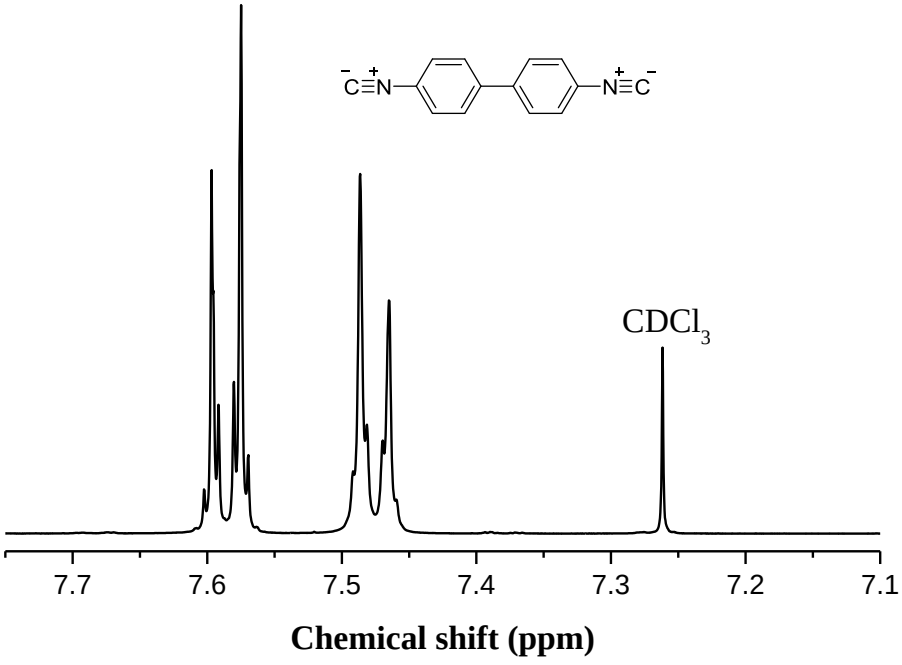


Figure S18. ^{1}H NMR spectrum of **4b** in $CDCl_3$.

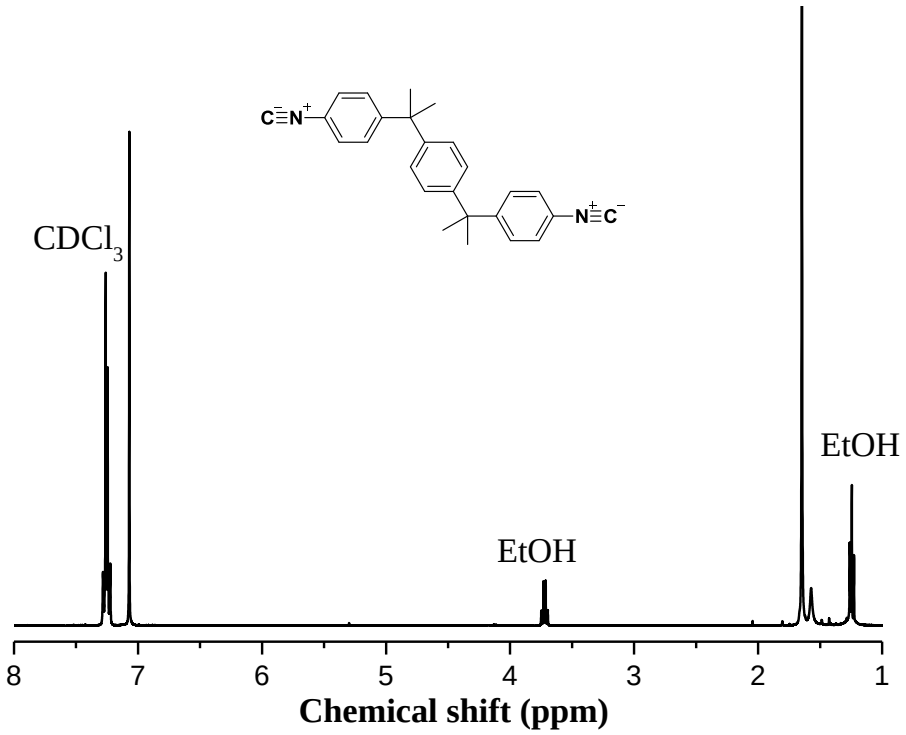


Figure S19. ^{1}H NMR spectrum of **4c** in $CDCl_3$.

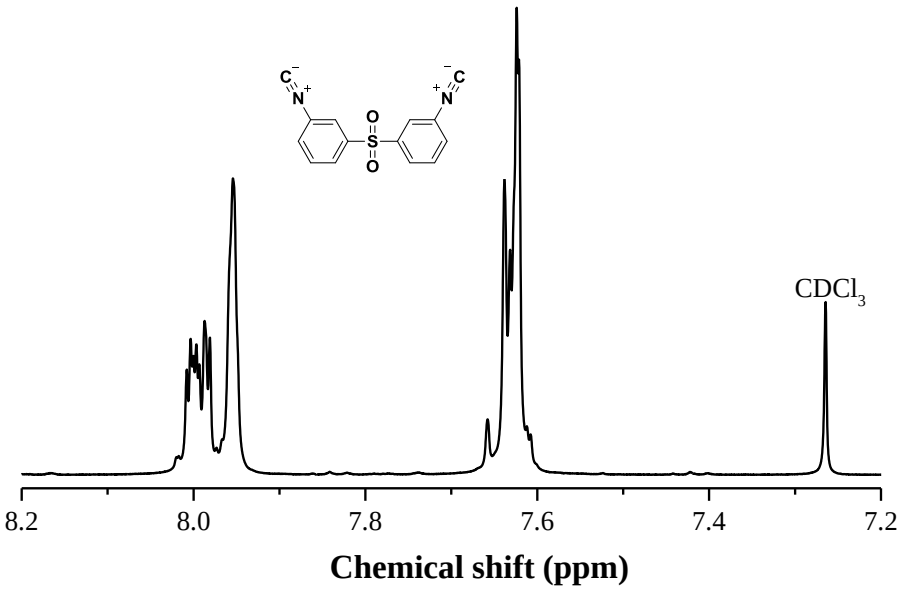


Figure S20. ^{1}H NMR spectrum of **4d** in $CDCl_3$.

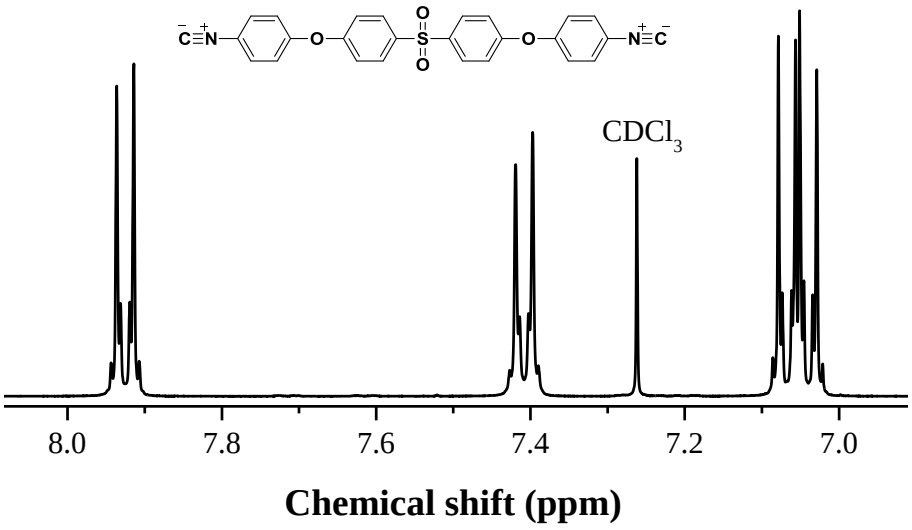


Figure S21. ^{1}H NMR spectrum of **4e** in $CDCl_3$.

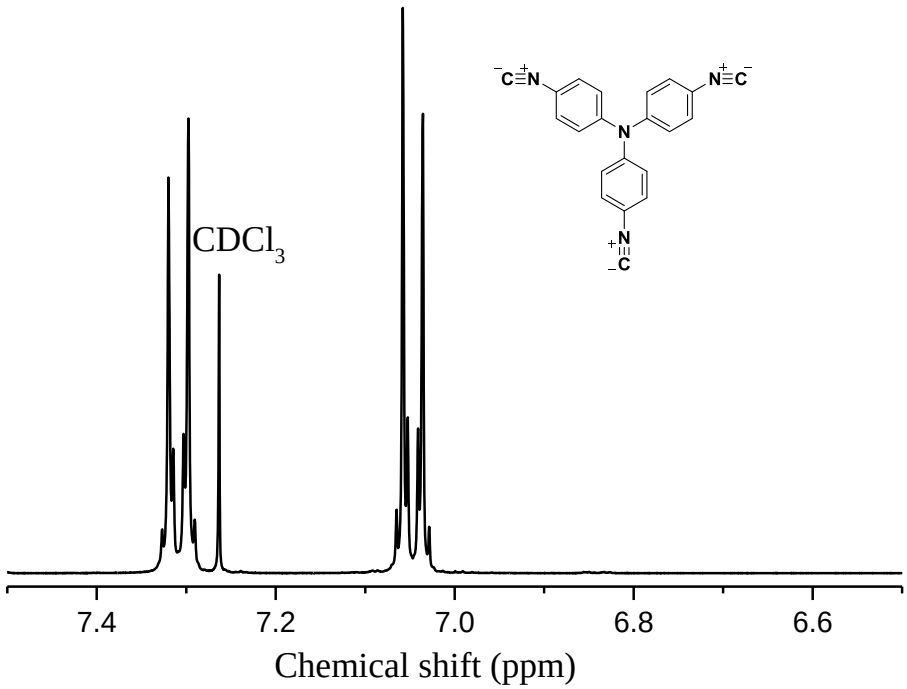


Figure S22. ^{1}H NMR spectrum of **4f** in $CDCl_3$.

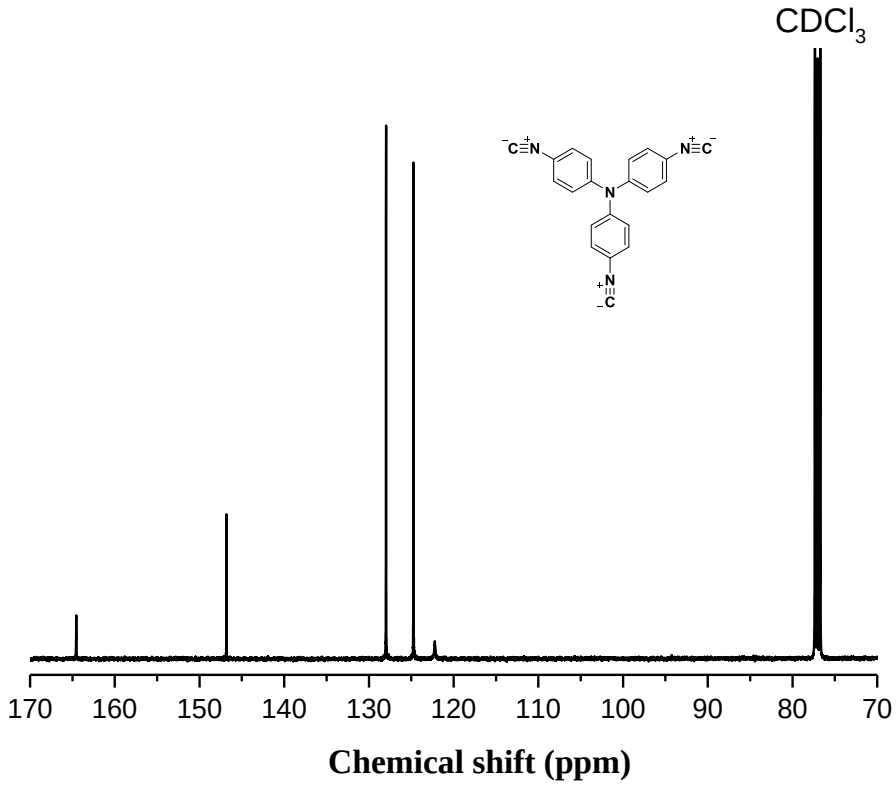


Figure S23. ^{13}C NMR spectrum of **4f** in $CDCl_3$.

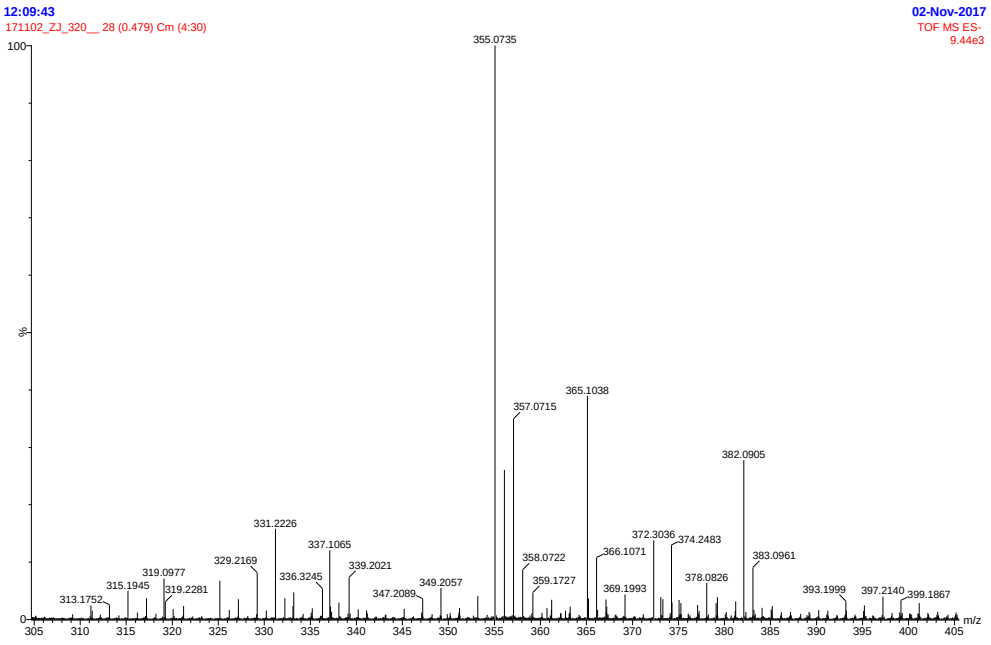


Figure S24. High resolution mass spectrum of **4f**.

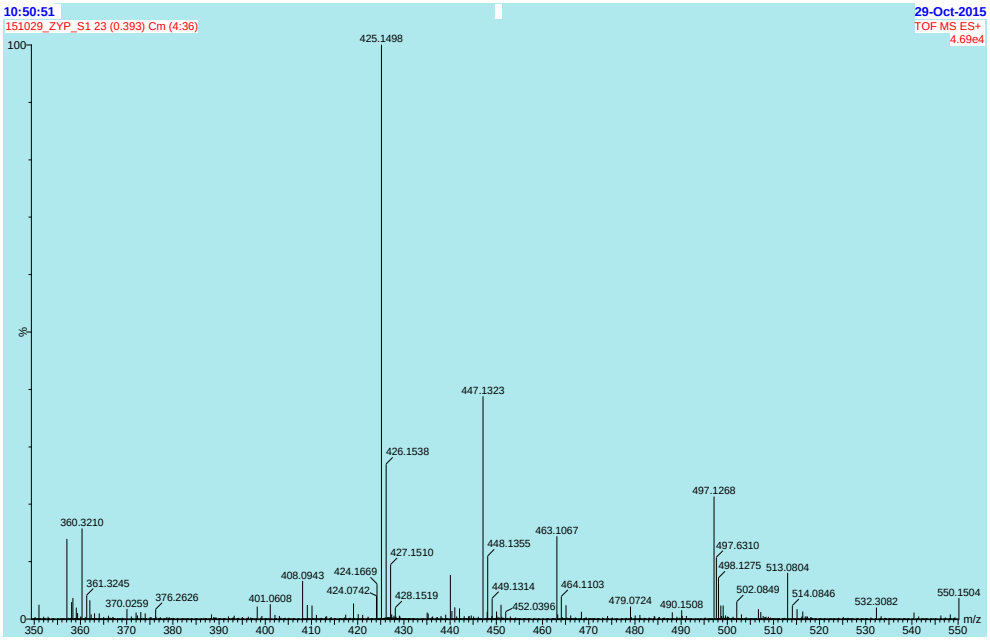


Figure S25. High resolution mass spectrum of model compound **M1.**

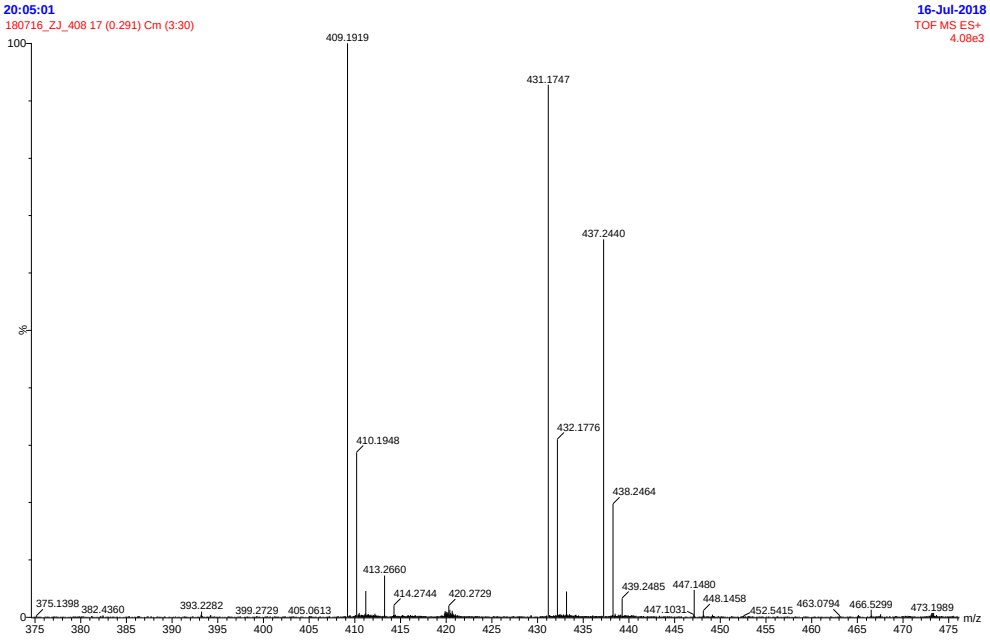


Figure S26. High resolution mass spectrum of model compound **M2.**

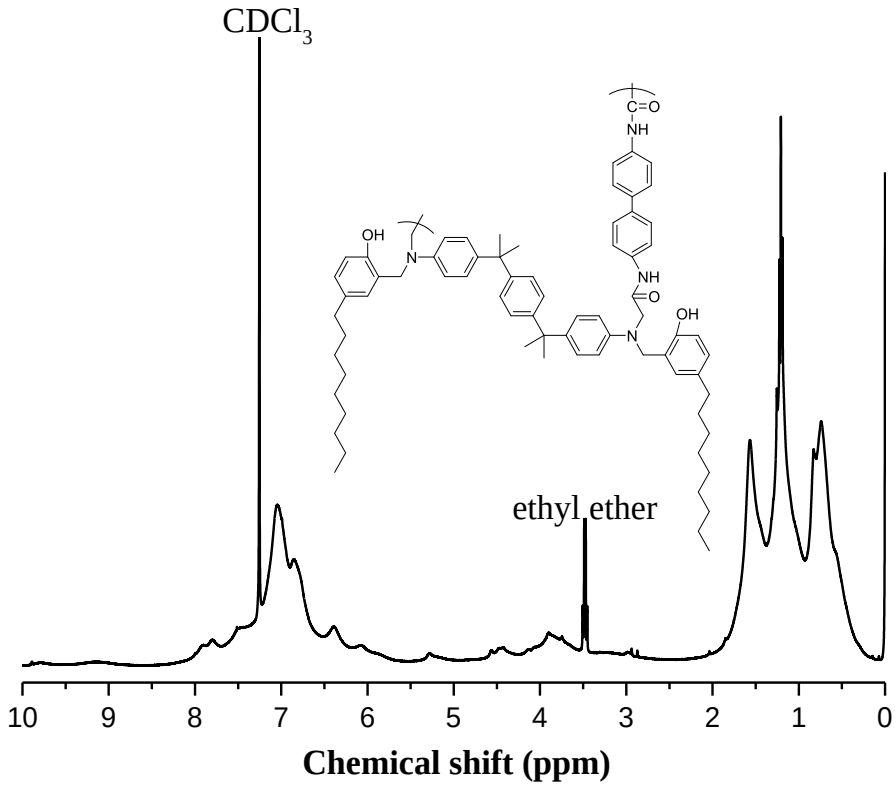


Figure S27. ^{1}H NMR spectrum of **P2** in $CDCl_3$.

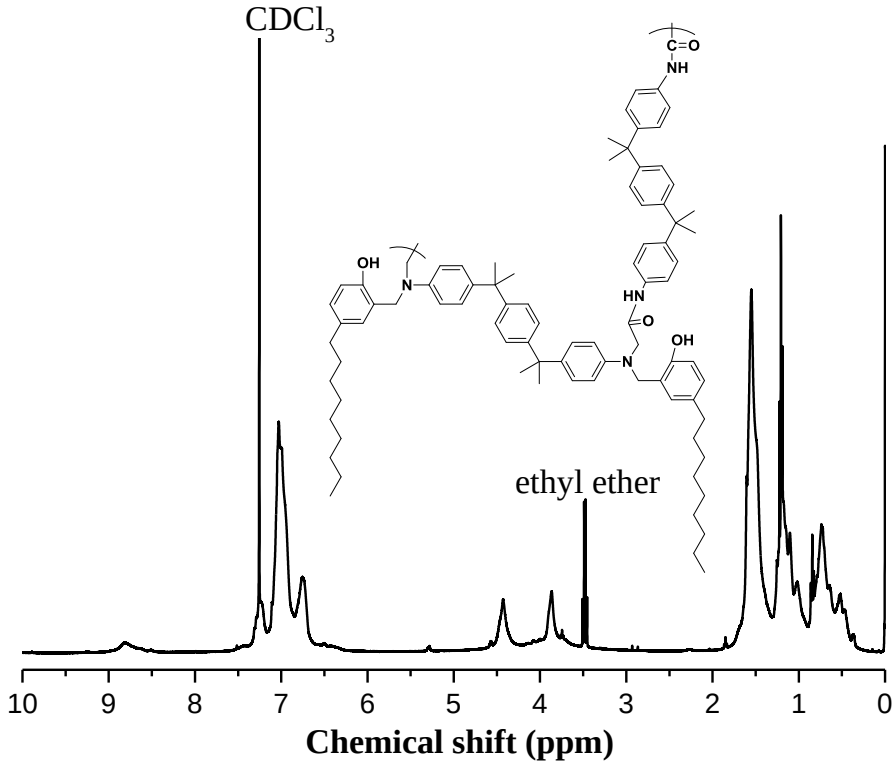


Figure S28. ^{1}H NMR spectrum of **P3** in $CDCl_3$.

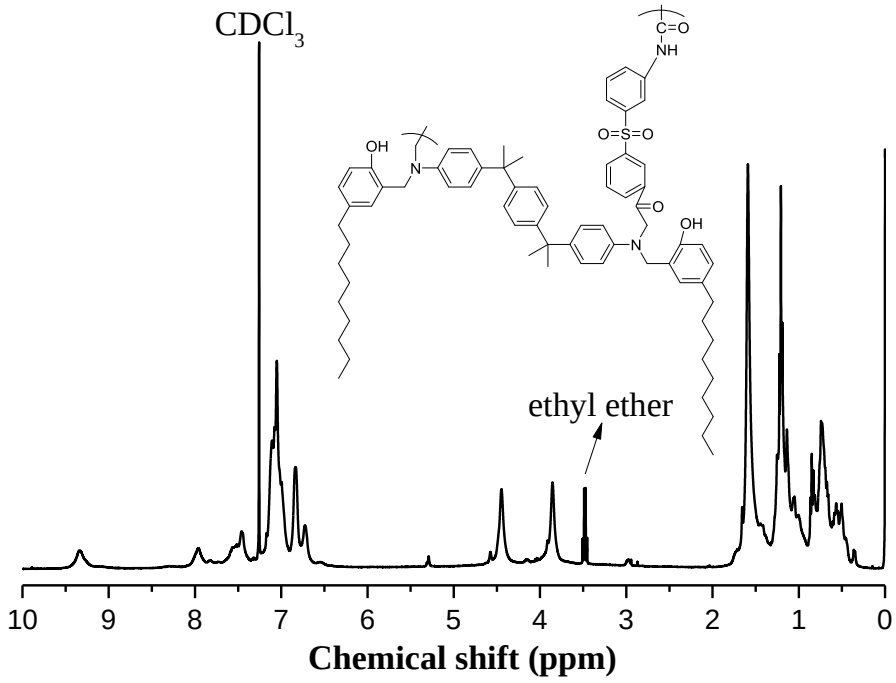


Figure S29. ^{1}H NMR spectrum of **P4** in $CDCl_3$.

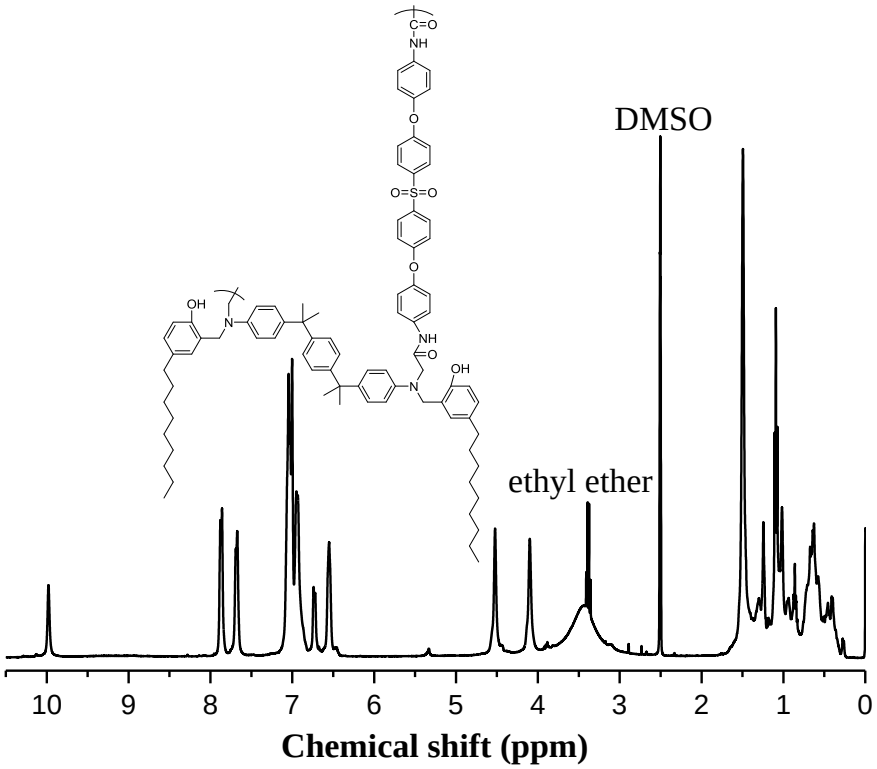


Figure S30. ^{1}H NMR spectrum of **P5** in DMSO-d_6.

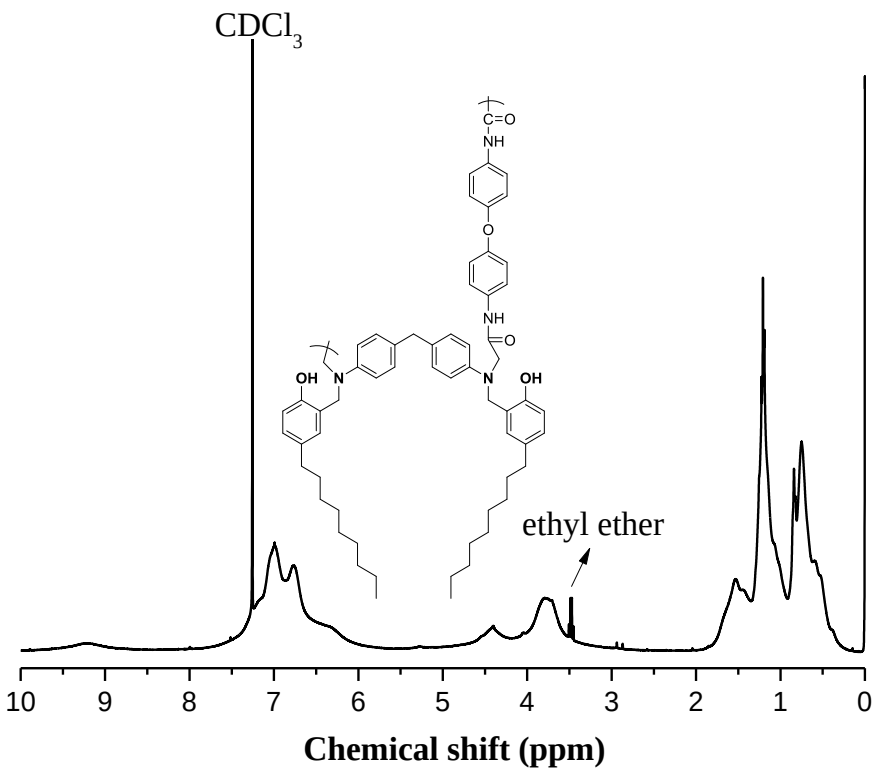


Figure S31. ^{1}H NMR spectrum of **P6** in $CDCl_3$.

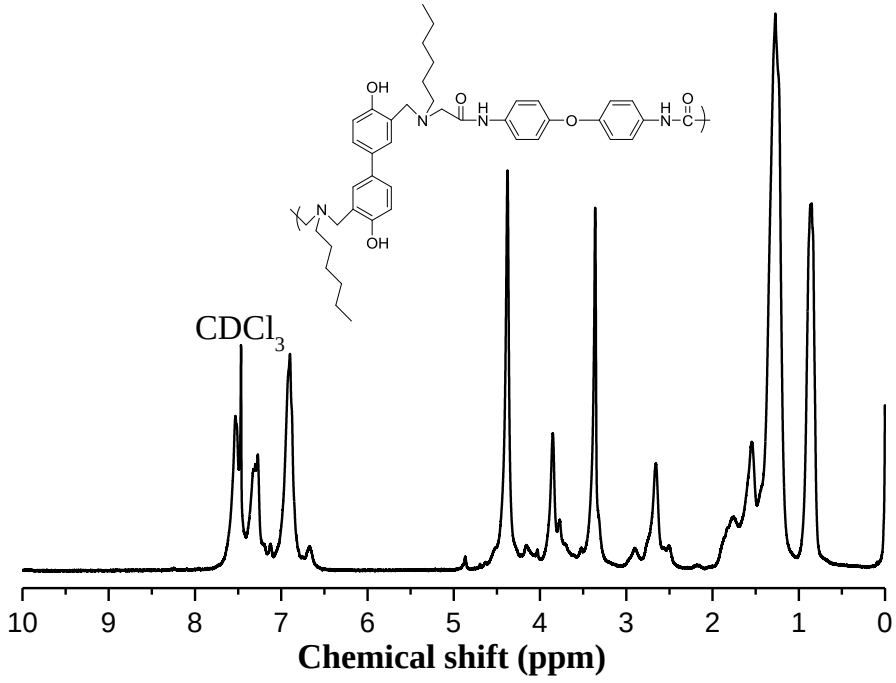


Figure S32. ^{1}H NMR spectrum of **P7** in $CDCl_3/CD_3OD$ (20:1, v:v).

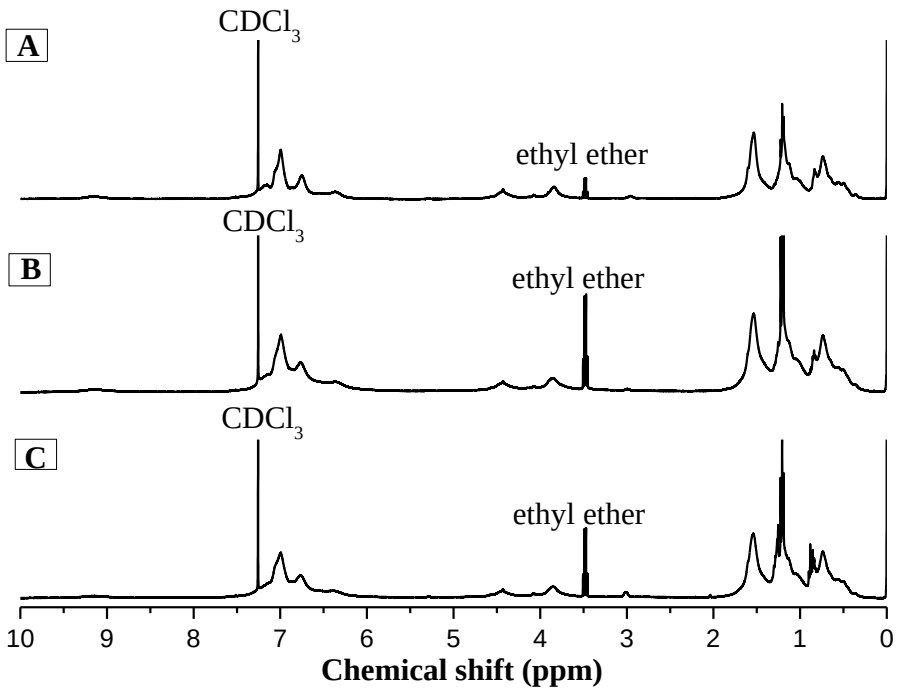


Figure S33. ^{1}H NMR spectra of **P1** (A), **P8** (B) and **P9** (C) in $CDCl_3$.

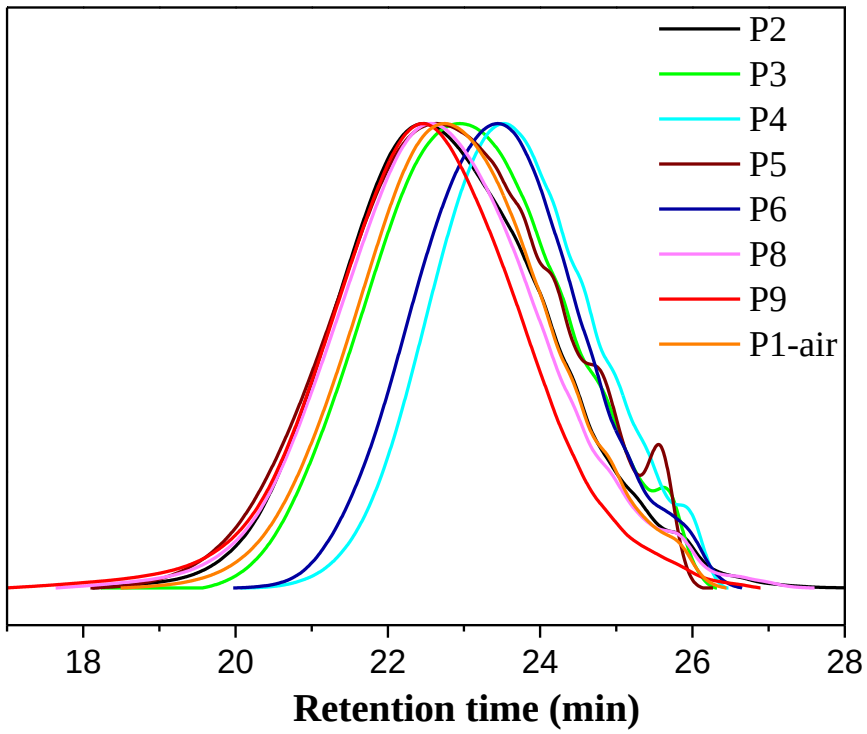


Figure S34. GPC curves of other polymers (**P2-P9** and **P1-air**).

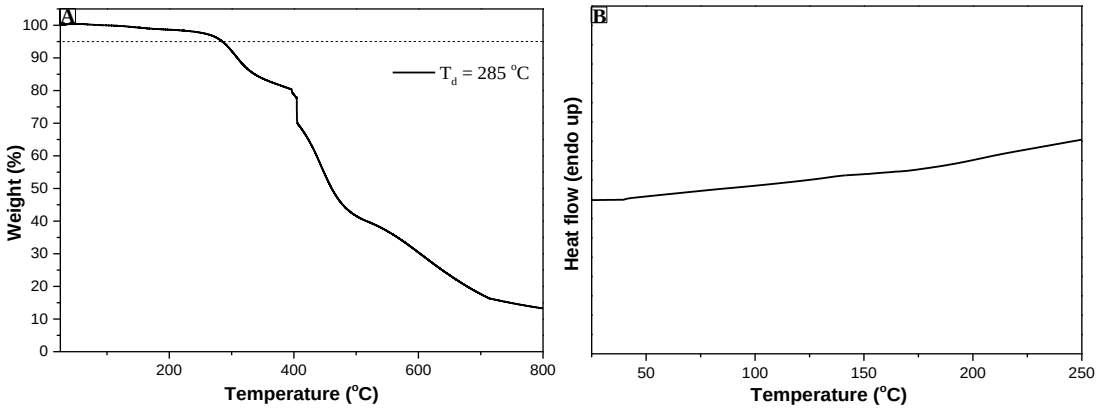


Figure S35. TG (A) and DSC thermograms (B) of **P1** (recorded under nitrogen with the heating rate of 10 °C/min).

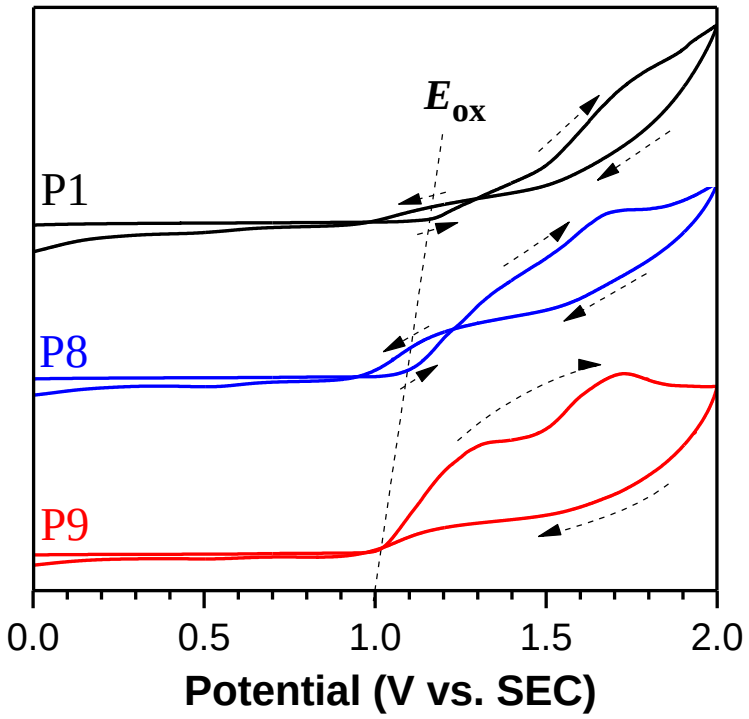


Figure S36. Cyclic voltammograms of polymer films coated on platinum electrodes in 0.1 M Bu_4NPF_6, CH_3CN solution.

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