Supporting Information

for

Living Cascade Enyne Metathesis Polymerization of an Allylic Acetate Monomer and Post-Polymerization Modification via Tsuji-Trost Reaction

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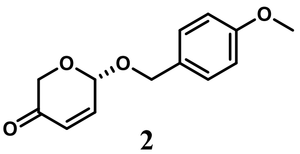
General methods: All reagents are commercially available and used without further purification unless otherwise noted. All polymerization reactions were carried out under nitrogen atmosphere. Dry, degassed tetrahydrofuran (THF) and dichloromethane (DCM) were obtained from a Vigor solvent purification system. Greagent gel (100-200 mesh) was used for flash column chromatography. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz magnetic resonance spectrometer and calibrated using residual undeuterated solvent as an internal reference ($CHCl_3$ @ 7.26 ppm for ^1H NMR; 77.16 ppm for ^{13}C NMR; DMSO @ 2.50 ppm for ^1H NMR; 39.53 ppm for ^{13}C NMR; CH_2Cl_2 @ 5.30 ppm for ^1H NMR). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High Resolution Mass spectra were recorded on Thermo scientific Q Exactive Ultimate 3000 UPLC. Polymer samples were analyzed using a Waters 2414 Refractive Index Detector size exclusion chromatography (SEC) system with Waters (WAT045870) columns eluting THF (0.3 mL /min) and Tosoh EcoSEC HLC 8420GPC system with TSKgel SuperHM-N columns eluting $CHCl_3$ containing 0.25% Et_3N at a flow rate of 0.6 mL/min. All number-average molecular weights and polydispersities were calculated from refractive index chromatography using polyacrylate or polystyrene standards. Melting points were measured on RY-1G Digital Melting Point Apparatus. Thermogravimetric analysis (TGA) of the polymers was conducted using a METTLER TOLEDO Thermal Analysis System TGA2 under nitrogen atmosphere at a heating speed of 10 °C per minute from 30°C to 800 °C.

The monomer synthesis and experiment method.



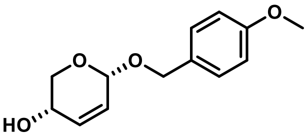
2

2: A dry DCM (80 mL) solution of PMB (5.80 g, 42 mmol, 1.4 eq) and **1** (6.422 g, 30 mmol, 1.0 eq) was purged with nitrogen. Then a solution of the $Pd_2(dba)_3$ (686 mg, 0.75 mmol, 0.025 eq) and PPh_3 (786 mg, 3 mmol, 0.1 eq) in dry DCM (4 mL) was added at 0 °C under nitrogen. The reaction was stirred at RT for 4 h before it was quenched with sat. aq. $NaHCO_3$. Then the reaction was extracted with DCM (3×20 mL), dried over Na_2SO_4. After evaporation, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 8:1) to afford the desired product as a yellowish oil (5.62 g, 80%).

HRMS (ESI) $[M+H]^+$ calcd. for $C_{13}H_{14}O_4$, 233.0819, found, 233.0819.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.26 (m, 2H), 6.92–6.87 (m, 2H), 6.85 (dd, *J* = 10.3, 3.4 Hz, 1H), 6.11 (d, *J* = 10.3 Hz, 1H), 5.26 (dd, *J* = 3.4, 0.8 Hz, 1H), 4.77 (d, *J* = 11.4 Hz, 1H), 4.58 (d, *J* = 11.4 Hz, 1H), 4.46 (d, *J* = 16.9 Hz, 1H), 4.10 (d, *J* = 16.9 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.69, 159.63, 144.54, 129.96, 128.94, 127.87, 114.02, 91.80, 70.40, 66.30, 55.30.



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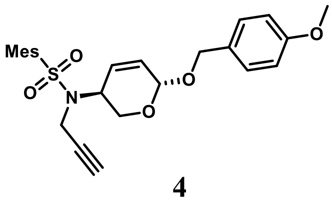
3: A solution of **2** (5.62 g, 24 mmol, 1.0 eq) and $CeCl_3$ (2.37 g, 9.6 mmol, 0.4 eq) in dry DCM (60 mL) and MeOH (60 mL) was cooled to -78 °C. $NaBH_4$ (998 mg, 26.4 mmol, 1.1 eq) was added and the reaction mixture was stirred for 2 h at -78 °C. The resulting solution was quenched with saturated $NaHCO_3$ (20 mL), extracted (3x20 mL) with DCM, dried over Na_2SO_4, and concentrated under reduced pressure. After evaporation, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) to afford the desired product as a colorless oil (3.97 g, 70%).

HRMS (ESI) [M] calcd. for $C_{13}H_{16}O_4$, 235.0976, found, 235.0975.

^{1}H NMR (400 MHz, DMSO): δ 7.30–7.23 (m, 2H), 6.95–6.88 (m, 2H), 5.91 (dq, *J* = 10.3, 1.4 Hz, 1H), 5.67 (ddd, *J* = 10.3, 2.6, 2.0 Hz, 1H), 5.08 (d, *J* = 6.1 Hz, 1H), 4.97 (dt, *J* =

2.8, 1.4 Hz, 1H), 4.61 (d, *J* = 11.4 Hz, 1H), 4.42 (d, *J* = 11.4 Hz, 1H), 4.10 (dtq, *J* = 9.7, 6.0, 1.8 Hz, 1H), 3.75 (s, 3H), 3.69–3.61 (m, 1H), 3.52–3.45 (m, 1H).

^{13}C NMR (100 MHz, DMSO): δ 159.20, 135.21, 130.54, 129.88, 126.18, 114.11, 93.03, 69.20, 62.76, 62.23, 55.52.



4

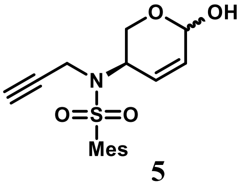
4: To a solution of **3** (1.89 g, 8 mmol, 1.0 eq), 2,4,6-trimethyl-N-2-propyn-1-ylbenzenesulfonamide (1.90 g, 8 mmol, 1.0 eq) and PPh$_3$ (3.36 g, 12.8 mmol, 1.6 eq) in dry THF (100 mL, 0.08 M) was added DEAD (2.09 g, 1.84 mL, 12 mmol, 1.5 eq) at 0 °C. The mixture was then stirred for 24 h (TLC monitoring) while warmed to room temperature. After evaporation, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 6:1) to afford the desired product as a white solid (3.06 g, 84%).

Melting point: 72–74 °C.

HRMS (ESI) [M] calcd. for $C_{25}H_{29}NO_5S$, 456.1839, found, 456.1833.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29–7.23 (m, 2H), 6.95 (s, 2H), 6.91–6.83 (m, 2H), 6.05 (ddd, *J* = 10.1, 3.2, 1.6 Hz, 1H), 5.89 (ddt, *J* = 10.1, 5.0, 1.3 Hz, 1H), 5.12–5.01 (m, 1H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.48 (d, *J* = 11.4 Hz, 1H), 4.21 (dd, *J* = 12.7, 4.4 Hz, 1H), 4.18–4.10 (m, 1H), 4.07 (dd, *J* = 7.3, 1.9 Hz, 1H), 4.06–4.00 (m, 1H), 4.00–3.92 (m, 1H), 3.80 (s, 3H), 2.62 (s, 6H), 2.30 (s, 3H), 2.09 (t, *J* = 2.4 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 159.37, 142.95, 140.49, 132.47, 132.07, 131.20, 129.74, 129.66, 126.13, 113.90, 91.76, 80.17, 71.52, 69.40, 62.19, 55.30, 48.27, 33.23, 22.81, 21.00.



5

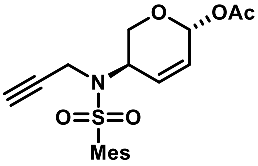
5: A solution of **4** (2.9 g, 6.4 mmol, 1.0 eq) in CH$_3$CN (60 mL) and H$_2$O (15 mL) was cooled to 0 °C. Ceric Ammonium Nitrate (8.77 g, 16 mmol, 2.5 eq) was added and the reaction mixture was stirred for 25 min at 0 °C. The resulting solution was quenched with saturated

$NaHCO_3$ (60 mL), extracted (3x20 mL) with EtOAc, dried over Na_2SO_4, and concentrated under reduced pressure. After evaporation, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) to afford the desired product as a mixture of diastereomers as a white solid (1.93 g, 90%).

Melting point: 116–118 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (s, 2H), 6.17–5.89 (m, 2H), 5.54–5.26 (m, 1H), 4.36–3.94 (m, 5H), 2.98–2.74 (m, 1H), 2.64 (s, 6H), 2.33 (s, 3H), 2.22–2.09 (m, 1H).

HRMS (ESI) [M] calcd. for $C_{17}H_{21}NO_4S$, 334.1119, found, 334.1121.



M1

M1: A solution of **5** (1.91 g, 5.7 mmol, 1.0 eq) and DMAP (0.033 g, 0.27 mmol, 0.05 eq) in DCM (90 mL) was cooled to -15 °C. Et_3N (1.16 g, 11.4 mmol, 2 eq) and Ac_2O (1.16 g, 11.4 mmol, 2 eq) was added and the reaction mixture was stirred for 4 h at -15 °C. The resulting solution was quenched with H_2O (20 mL), extracted (3x20 mL) with DCM, dried over Na_2SO_4, and concentrated under reduced pressure. After evaporation, the residue was recrystallized twice by (petroleum ether/EtOAc = 4:1) to afford the product as a white solid (1.02 g, 50%).

Melting point: 118–120 °C.

HRMS (ESI) [M] calcd. for $C_{19}H_{23}NO_5S$, 378.1370, found, 378.1366.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (s, 2H), 6.31 (d, J = 1.9 Hz, 1H), 6.08 (d, J = 2.3 Hz, 2H), 4.20–4.12 (m, 2H), 4.09 (d, J = 2.5 Hz, 1H), 4.08–4.06 (m, 1H), 4.03 (dd, J = 18.4, 2.5 Hz, 1H), 2.62 (s, 6H), 2.30 (s, 3H), 2.09 (t, J = 2.4 Hz, 1H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.90, 143.10, 140.50, 132.29, 132.12, 129.06, 127.45, 86.96, 79.70, 71.88, 64.10, 47.65, 33.39, 22.81, 21.10, 21.01.

General procedure for the polymerization of M1: Monomer **M1** (25-75 eq) was added to a 10 mL vial equipped with a stir bar, placed under a nitrogen atmosphere, and was dissolved in degassed THF at RT. In a separate 3 mL vial, a solution of Grubbs 3rd generation (Grubbs 3) initiator (1 eq) in degassed THF was prepared. An appropriate volume of Grubbs 3 solution was rapidly added to the stirred reaction mixture containing monomer solution using a microliter syringe to make a total concentration of 0.08 M for the monomer. After the indicated time, the polymerization was quenched by addition of mixed solution of excess ethyl vinyl ether (0.1mL) and triethylamine (0.05 mL). The reaction mixture was stirred for 1 minute, and the reaction mixture was concentrated under vacuum. A small portion of the crude sample was analyzed by SEC and ^{1}H NMR. The remaining material was precipitated from DCM into 20-fold volume of diethyl ether. The precipitated polymer was then characterized using ^{1}H NMR.

P1: **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.02–7.00 (m, 2H), 6.56–6.14 (m, 1H), 6.14–5.74 (m, 2H), 5.61–5.39 (m, 1H), 4.91–4.65 (m, 1H), 4.48–4.22 (m, 1H), 4.17-3.87 (m, 1H), 3.74–3.67 (m, 1H), 3.50–3.15 (m, 1H), 2.72–2.58 (m, 6H), 2.41–2.27 (m, 3H), 2.15–1.94 (m, 3H).

Kinetic Studies on the polymerization of M1 targeting DP75: A solution of Grubbs 3 in degassed THF (2.4 mg/620 µL) was prepared. Monomer **M1** (30.2 mg, 0.08 mmol, 75 eq) was dissolved in 800 µL THF. Then 200 µL of Grubbs 3 was added. The reaction mixture was stirred at 0 °C and aliquots (100 µl each) were taken and quenched by mixed solution of excess ethyl vinyl ether (50 µL) and triethylamine (20 µL) at 5 min, 10 min, 20 min, 30 min, 40 min, 60 min, 80 min and 100 min. Each aliquot was concentrated rapidly and analyzed by SEC and ^{1}H NMR.

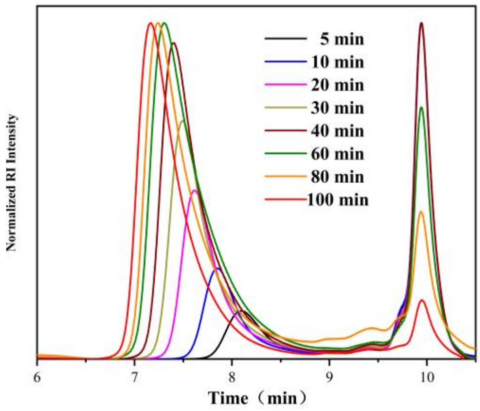


Fig. S1 SEC traces for different time points of the **P1**

General procedure of the diblock copolymer P_{Bn}-*b*-P1 by sequential monomer addition: Monomer **M_{Bn}** and **M1** were respectively added to two different 5 mL vials equipped with a stir bar, placed under a nitrogen atmosphere, and was dissolved in degassed THF at RT. In a separate 4 mL vial, a stock solution of G3 in degassed THF was prepared. An appropriate volume of G3 solution was rapidly added to the stirred solution that contained **M_{Bn}** using a microliter syringe to make a concentration of 0.08 M for the monomer. The reaction mixture was stirred before the **M1** solution was rapidly added to the reaction solution using a microliter syringe to make a concentration of 0.08 M. Then the mixture was stirred at RT. After the indicated time, the polymerization was quenched by addition of mixed solution of excess ethyl vinyl ether (0.1mL）and triethylamine (0.05 mL). The reaction mixture was stirred for 1 minute, and the reaction mixture was concentrated under vacuum. The polymer was precipitated from DCM into 20-fold volume of diethyl ether. The precipitated polymer was then characterized using ^{1}H NMR and SEC.

General procedure of the copolymerization CP1: Monomer **M1** and **M_{Bn}** (25, 50 eq respectively) were added to a 10 mL vial equipped with a stir bar, placed under a nitrogen atmosphere, and was dissolved in degassed THF at RT. In a separate 4 mL vial, a solution of Grubbs 3 in degassed THF was prepared. An appropriate volume of G3 solution was rapidly transferred to the stirred vial containing monomer solution using a microliter syringe to make a total monomer concentration of 0.1 M. Then the mixture was stirred at RT. After the indicated time, the polymerization was quenched by addition of mixed solution of excess ethyl vinyl ether (0.1mL） and triethylamine (0.05 mL). The reaction mixture was stirred for 1 minute, and the reaction mixture was concentrated under vacuum. The polymer was precipitated from DCM into 20-fold volume of diethyl ether. The precipitated polymer was then characterized using ^{1}H NMR and SEC.

General procedures of post-polymerization modifications: A dry DCM (1 mL) solution of **P1** (0.08 mmol monomer unit of **P1**, 30 mg, 1 eq), PPh_3 (0.04 mmol, 10.4mg, 0.5 eq), NaOAc (0.08 mmol, 6.5mg, 1 eq) and an appropriate nucleophile (such as PMB; 0.08 mmol, 3-5 eq) was added with nitrogen condition. Then a solution of the $Pd_2(dba)_3$ (0.012 mmol, 10.9mg, 0.15 eq) was added at 0 ºC under nitrogen. The reaction was stirred at room temperature for 8 h, then the reaction was extracted with DCM/H_2O, The resulting DCM solution was subsequently filtered with a filter membrane of 0.22 μm, The filtrate was slowly dropped into the diethyl ether solution, and subsequently centrifuged at 4000 r/min for 5min, the polymer solid obtained by centrifugation was dissolved in a small amount of DCM, then slowly dropped into n-hexane solution, centrifuged again at 4000 r/min for 5 min, The resulting polymer solid was dried in a vacuum drying chamber to obtain the target polymer. For the purification of **P2c**, precipitation used *n*-hexane instead, which was subsequently centrifuged at 4000 r/min for 5min and dried in a vacuum drying chamber.

P2a: **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.28−7.16 (m, 2H), 7.04−6.93 (m, 2H), 6.93−6.77 (m, 2H), 6.54−6.34 (m, 1H), 5.86 (d, *J* = 9.4 Hz, 1H), 5.47−5.36 (m, 1H), 5.03−4.76 (m, 2H), 4.54−4.42 (m, 1H), 4.41−4,24 (m, 2H), 4.05−3.91 (m, 1H), 3.80 (s, 3H), 3.66−3.53 (m, 1H), 3.42−3.16 (m, 1H), 2.69−2.58 (m, 6H), 2.33−2.23 (m, 3H).

P2b: **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.02−6.86 (m, 2H), 6.50−6.3 (m, 1H), 5.81 (d, *J* = 11.0 Hz, 1H), 5.38−5.22 (m, 1H), 5.03−4.76 (m, 2H), 4.55−4.41 (m, 1H), 4.41−4.24 (m, 1H), 3.65−3.15 (m, 4H), 2.59 (m, 6H), 2.42−2.31 (m, 2H), 2.31−2.17 (m, 3H), 2.00−1.93 (m, 1H).

P2c: **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.07−6.88 (m, 2H), 6.55−6.30 (m, 1H), 6.17−5.71 (m, 2H), 5.42-5.26 (m, 1H), 5.17−4.88 (m, 1.4H), 4.87−4.67 (m, 1.8H), 4.48−4.20 (m, 1H), 4.06−4.85 (m, 1H), 3.74−3.16 (m, 4H), 2.75−2.50 (m, 6H), 2.39−2.21 (m, 3H), 2.11−2.02 (m, 2.2H), 1.56−1.31 (m, 11H).

P2d: **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.06−6.95 (m, 2H), 6.53−6.33 (m 1H), 6.25–5.72 (m, 3H), 5.45–5.25 (m, 1H), 5.00–4.62 (m, 2H), 4.50–4.24 (m, 1H), 4.07–3.84 (m, 1H), 3.78–2.76 (m, 6H), 2.70–2.52 (m, 6H), 2.38–2.21 (m, 3.6H), 1.85-1.74 (m, 0.6H), 1.56–1.42 (m, 1H), 1.34–1.20 (m, 2H), 1.19–1.03 (m, 0.5H), 0.56–0.39 (m, 0.6H).

P2e: **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.15−7.95 (m, 0.7H), 7.81−7.61 (m, 1.3H), 7.53−7.42 (m, 0.7H), 7.08−6.88 (m, 2H), 6.59−6.25 (m, 1H), 6.32−5.38 (m, 3H), 5.09−4.74 (m, 3H), 4.45−4.16 (m, 1H), 4.13−3.85 (m, 1H), 3.69−3.34 (m, 2H), 2.74−2.53 (m, 6H), 2.39−2.16 (m, 3H), 2.08−2.01 (m, 1H).

P2f: **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.85–7.49 (m, 1.4H), 7.43–7.21 (m, 1.4H), 7.09–6.89 (m, 2H), 6.57–5.40 (m, 3H), 5.33–5.13 (m, 1H), 4.94–4.64 (m, 1H), 4.48–4.11 (m, 1H), 4.04–3.07 (m, 5H), 2.77–2.54 (m, 6H), 2.54–2.36 (m, 2H), 2.33 (7.36-7.23, 3H), 2.14–1.94 (m, 1.5H).

P2g: **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.68−6.70 (m, 4.6H), 6.53−5.38 (m, 4H), 4.90−4.56 (m, 1H), 4.44−4.10 (m, 1H), 4.08−3.75 (m, 1H), 3.66−3.06 (m, 2H), 2.7−2.36 (m, 6H), 2.36−2.14 (m, 3H), 2.36−2.14 (m, 0.3H).

P2h: **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.00−7.84 (m, 2H), 7.68−7.56 (m, 1H), 7.55−7.41 (m, 2H), 7.01−6.82 (m, 2H), 6.70−5.49 (m, 4H), 4.81−4.67 (m, 1H), 4.54−4.23 (m, 1H), 4.10−3.85 (m, 1H), 3.72−3.27 (m, 2H), 2.79−2.44 (m, 6H), 2.35−2.09 (m, 3H), 2.08−2.00 (m, 0.3H).

Studies toward the degradation of representative polymers under different acidic conditions

Degradation studies of **P1** (M_n = 15.8 kDa) was examined under different acidic conditions in tetrahydrofuran using acetic acid or trifluoroacetic acid.

Procedure for degradation with acetic acid: In a 10 mL vial equipped with a stir bar, 15 mg of polymer **P1/P2a/P2f** (0.04 mmol monomer unit for each polymer) was dissolved in THF (6.5 mL). In a separate 10 mL vial, add acetic acid (55 μL) to THF (6 mL), then dilute acetic acid solution (1 mL, 4 eq/monomer unit of **P1/P2a/P2f**) was rapidly added to the stirred mixture **P1/P2a/P2f** solution using a pipette to make a total concentration of 2 mg/mL for the **P1/P2a/P2f** polymer. The degradations were followed by size exclusion chromatography after concentration to monitor the decrease in molecular weight at 10 min, 20 min, 40 min, 1 hour, 2 hours, 4 hours, 12 hours, and 24 hours. Each aliquot was quenched with 0.05 mL triethylamine, concentrated under vacuum, and analyzed by SEC.

Procedure for degradation with trifluoroacetic acid: In a 10 mL vial equipped with a stir bar, 15 mg of polymer **P1** (0.04 mmol monomer unit for each polymer) was dissolved in THF (6.5mL). In a separate 10 mL vial, add trifluoroacetic acid (71 μL) to TH F (6 mL), then dilute trifluoroacetic acid solution (1 mL, 4 eq/monomer unit of **P1**) was rapidly added to the stirred mixture **P1** solution using a pipette to make a total concentration of 2mg/mL for the **P1** polymer. The degradations were followed by size exclusion chromatography after concentration to follow the decrease in molecular weight at 2min, 5min, 10 min, 20 min, 40 min, 80min, and 4 hours. Each aliquot was quenched with 0.05 mL triethylamine, concentrated under vacuum, and analyzed by SEC.

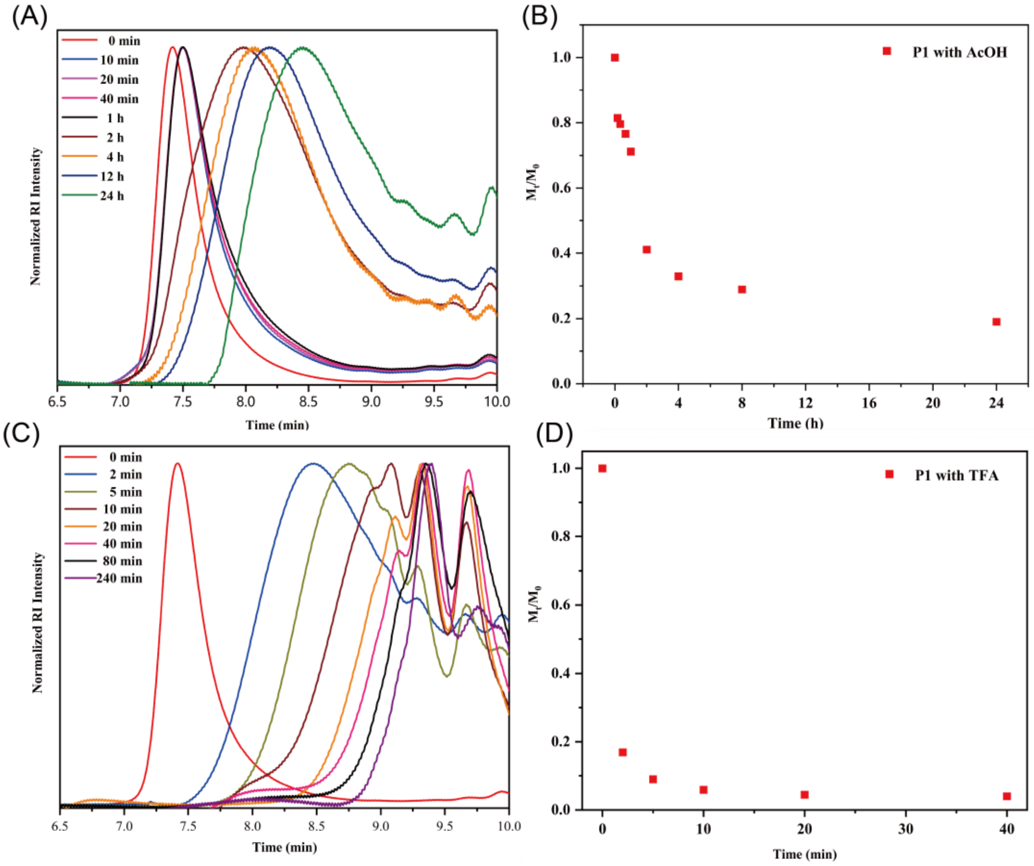


Fig. S2 (A) SEC trace of **P1** polymer at different times under acetic acid conditions. (B) M_n of the P1 polymer at different times under acetate conditions. (C) SEC trace of **P1** polymer at different times under trifluoroacetic acid. (D) M_n of polymer **P1** at different times under trifluoroacetic acid.

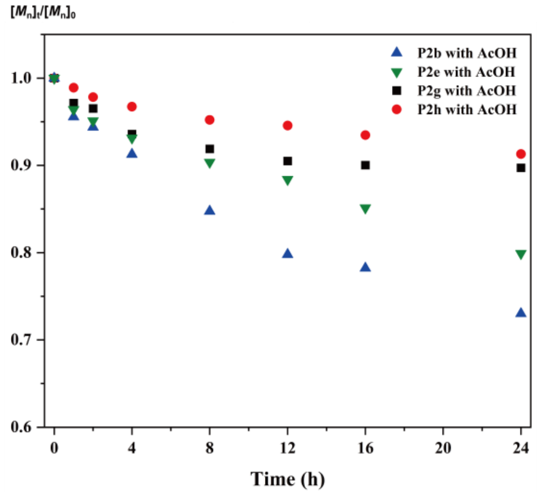


Fig. S3a M_n of P2b, P2e, P2g, and P2h at different times under acetic acid conditions.

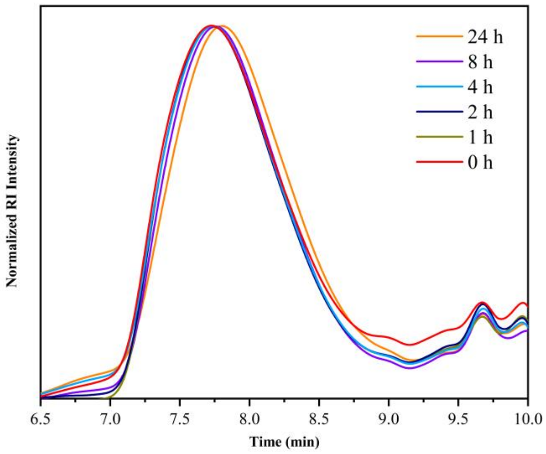


Fig. S3b SEC trace of **P2f** at different times under acetic acid conditions.

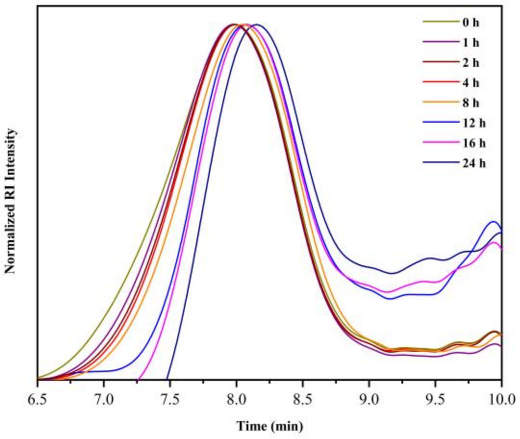


Fig. S3c SEC trace of **P2b** at different times under acetic acid conditions.

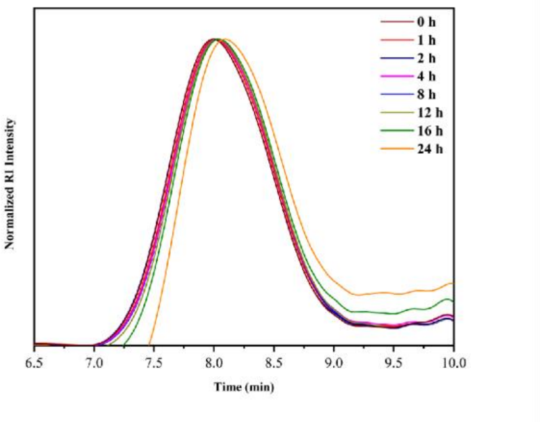


Fig. S3d SEC trace of **P2e** at different times under acetic acid conditions.

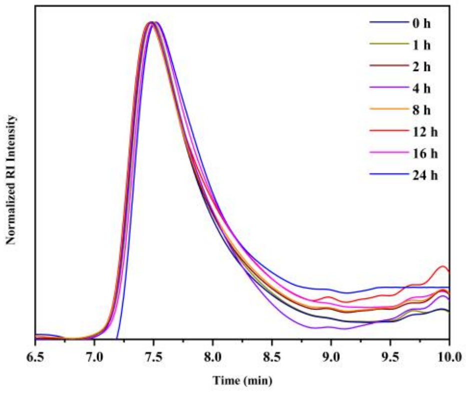


Fig. S3e SEC trace of **P2g** at different times under acetic acid conditions.

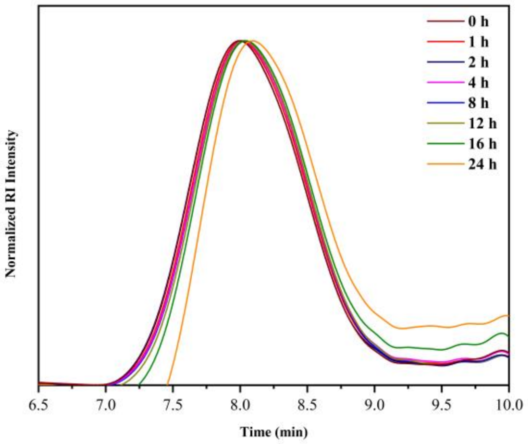
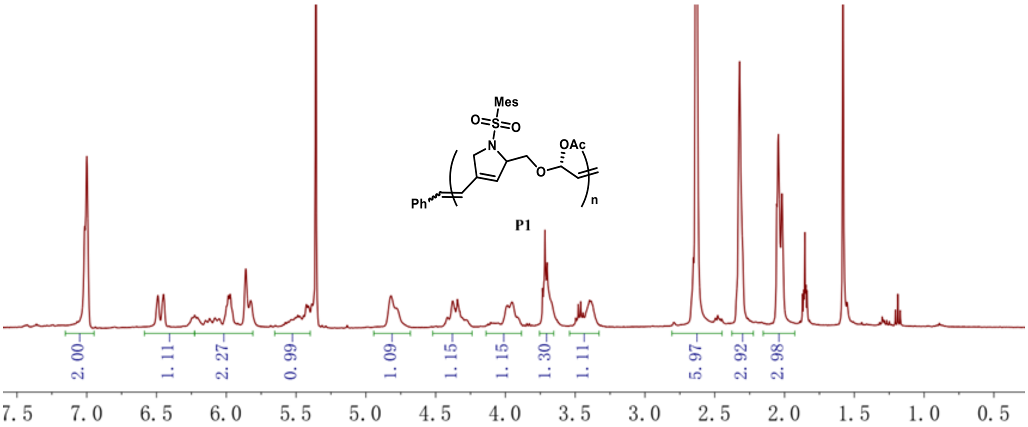
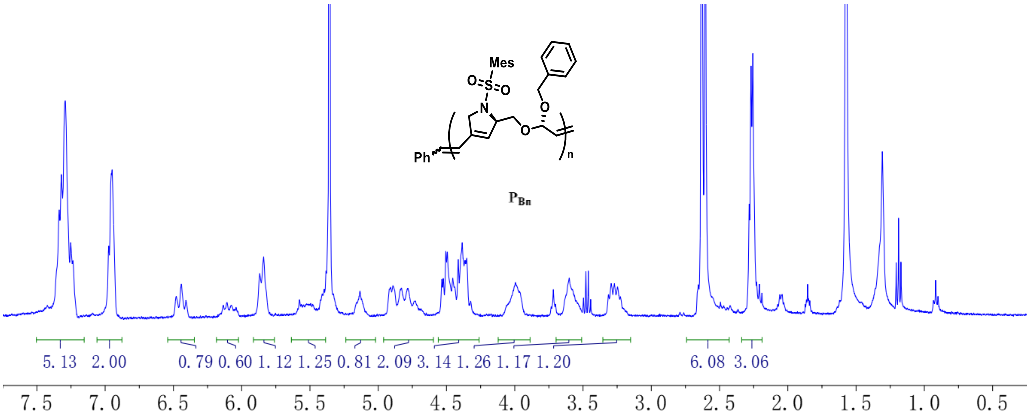
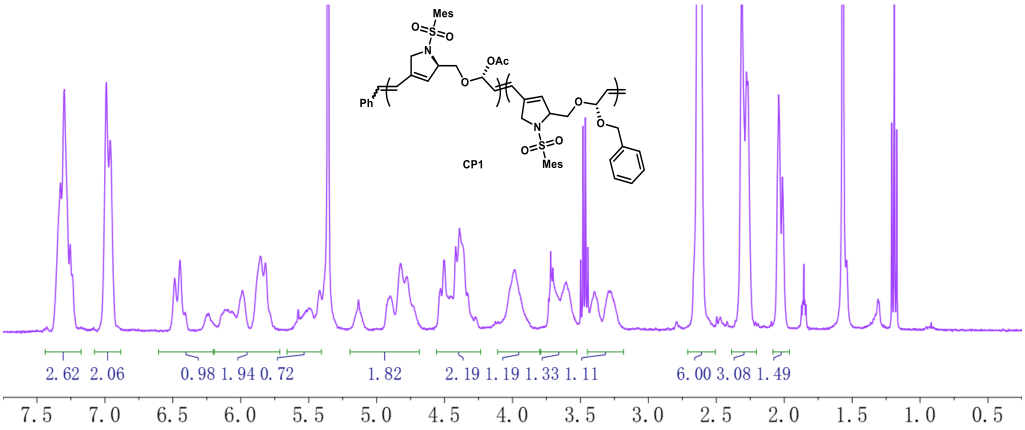


Fig. S3f SEC trace of **P2h** polymer at different times under acetic acid conditions.


Mes
O=S=O
N
OAc
O
Ph
n
P1
2.00
1.11
2.27
0.99
1.09
1.15
1.15
1.30
1.11
5.97
2.92
2.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


Mes
O=S=O
N
O
O
Ph
n
P_{Bn}
5.13
2.00
0.79
0.60
1.12
1.25
0.81
2.09
3.14
1.26
1.17
1.20
6.08
3.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


Mes
O=S=O
N
OAc
O
Ph
O
O
N
O=S=O
Mes
CP1
2.62
2.06
0.98
1.94
0.72
1.82
2.19
1.19
1.33
1.11
6.00
3.08
1.49
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

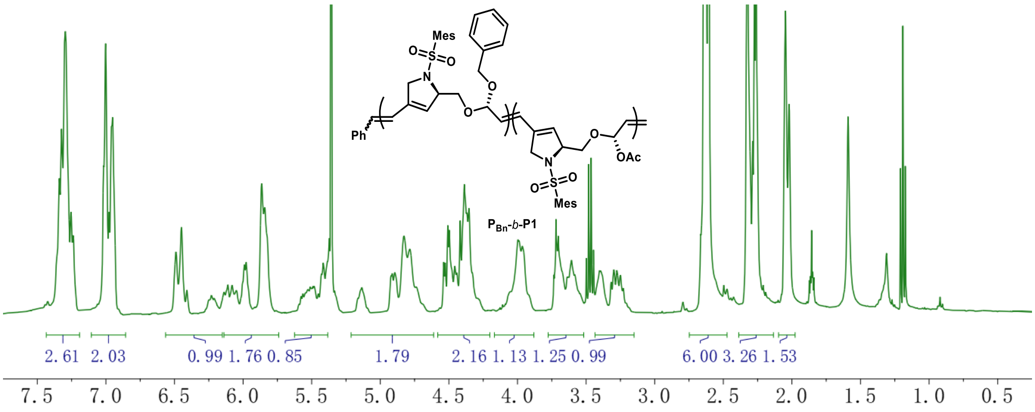

Mes
O=S=O
N
O
O
Ph
O
OAc
N
O=S=O
Mes
P_{Bn}-b-P1
2.61
2.03
0.99
1.76
0.85
1.79
2.16
1.13
1.25
0.99
6.00
3.26
1.53
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

Fig. S4 Comparison of ^{1}H NMR of polymer **P1**, **P**$_{Bn}$, **CP1** and **P**$_{Bn}$-*b*-**P1**

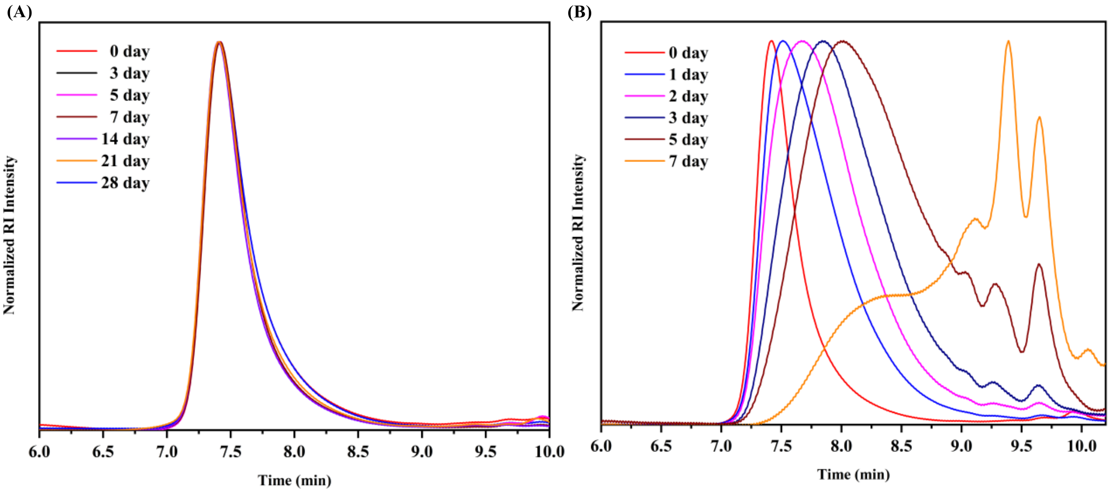


Fig. S5 Stability testing for the **P1**. (A) **P1** was stored under −20℃ sealed conditions. (B) **P1** was exposed to air at room temperature.

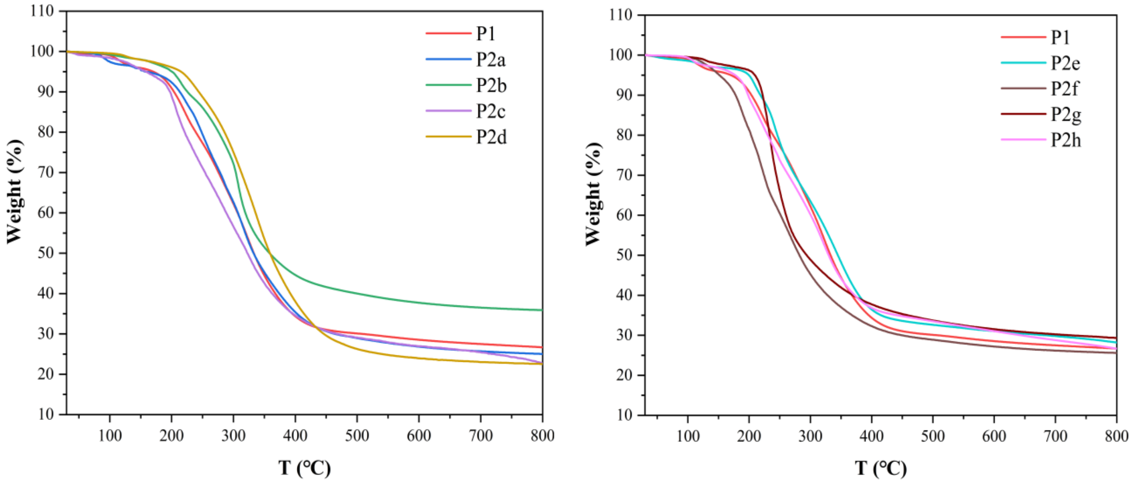


Fig. S6 TGA curves of the polymers before and after post-polymerization modification with different nucleophiles.

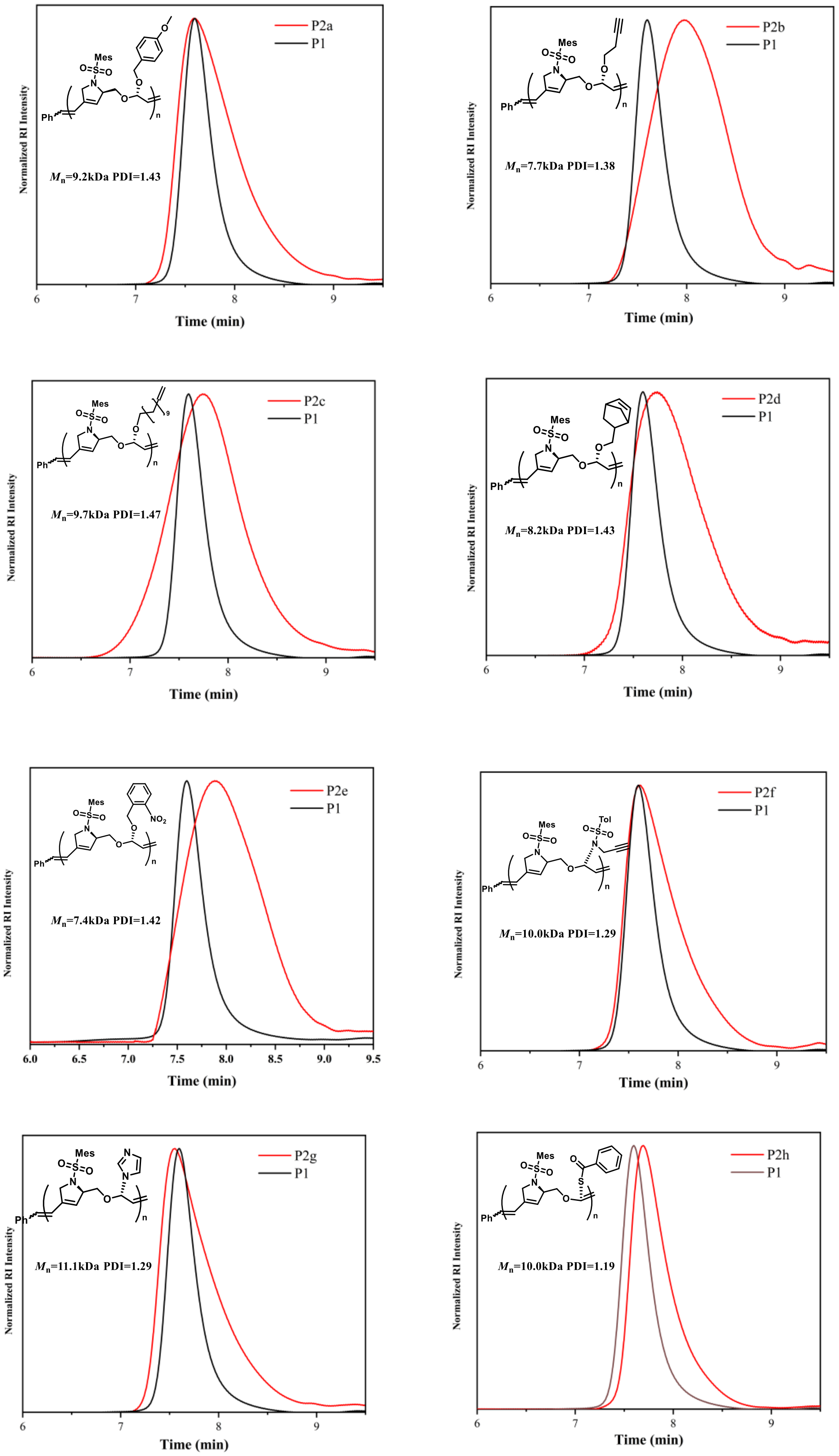


Fig. S7 SEC data of before and after post-polymerization modification of **P1** (M_n = 13.7 kDa; PDI = 1.12)

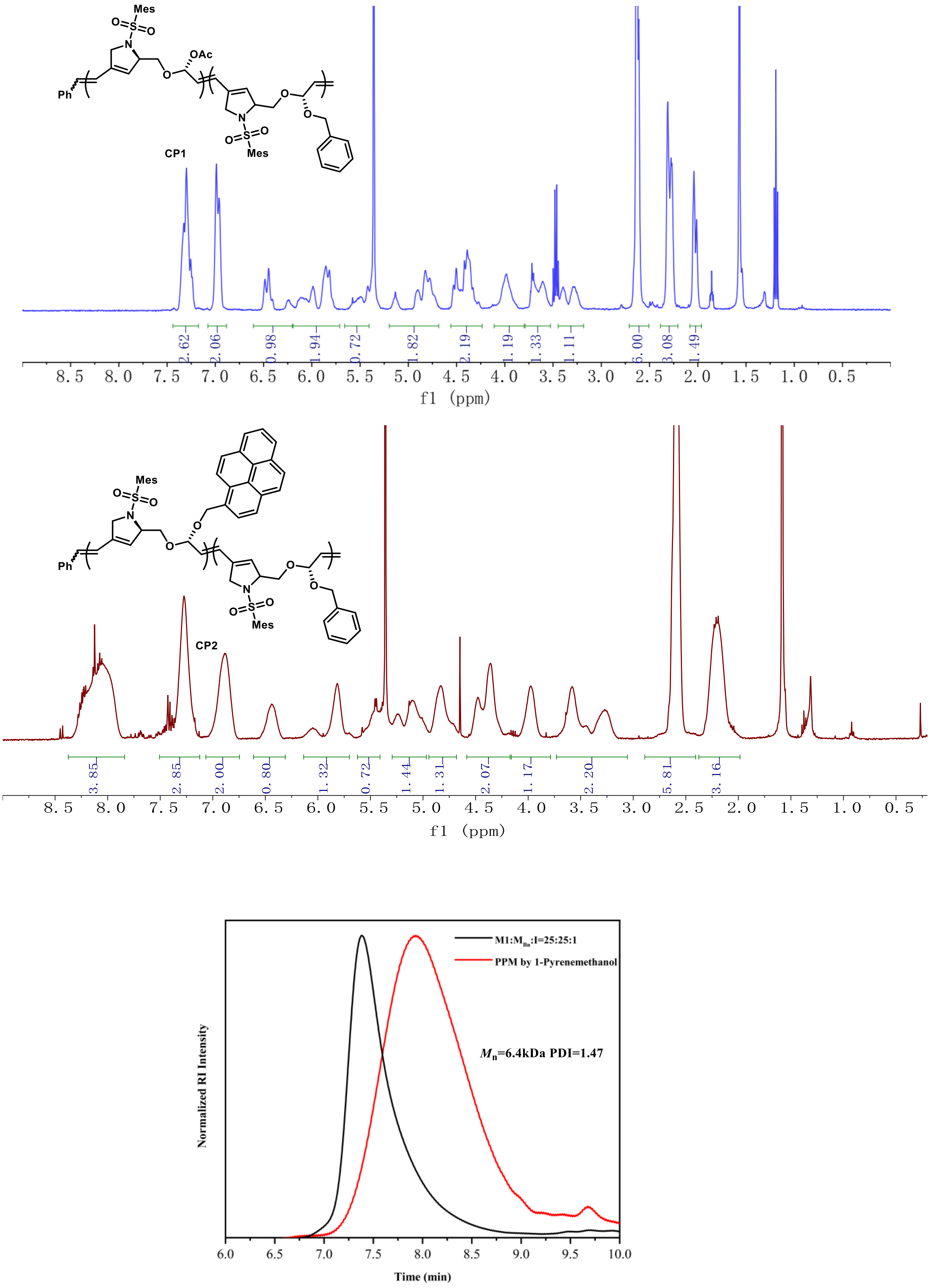


Fig. S8 Comparison of ^{1}H NMR and SEC of polymer **CP1** (M_n = 15.9 kDa, PDI=1.26): before and after PPM with 1-pyrenemethanol

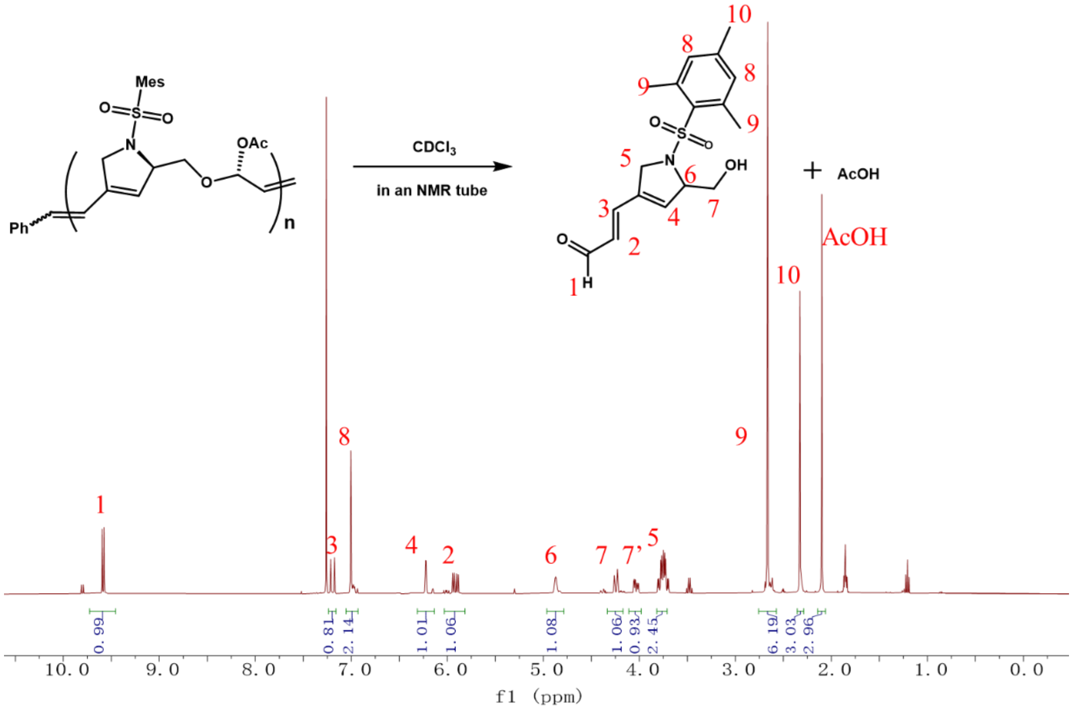


Fig. S9 ^{1}H NMR spectrum of **P1** after 0.5 hour in deuterated chloroform and tentative assignment of resonance peaks for plausible products

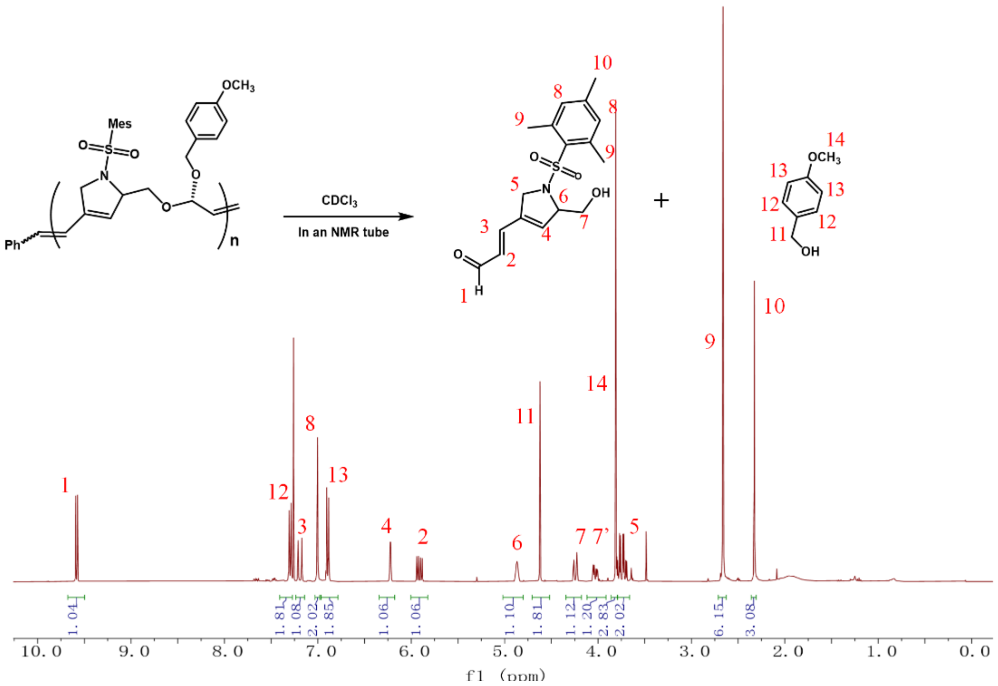


Fig. S10 ^{1}H NMR spectrum of **P2a** after 1 hour in deuterated chloroform and tentative assignment of resonance peaks for plausible products

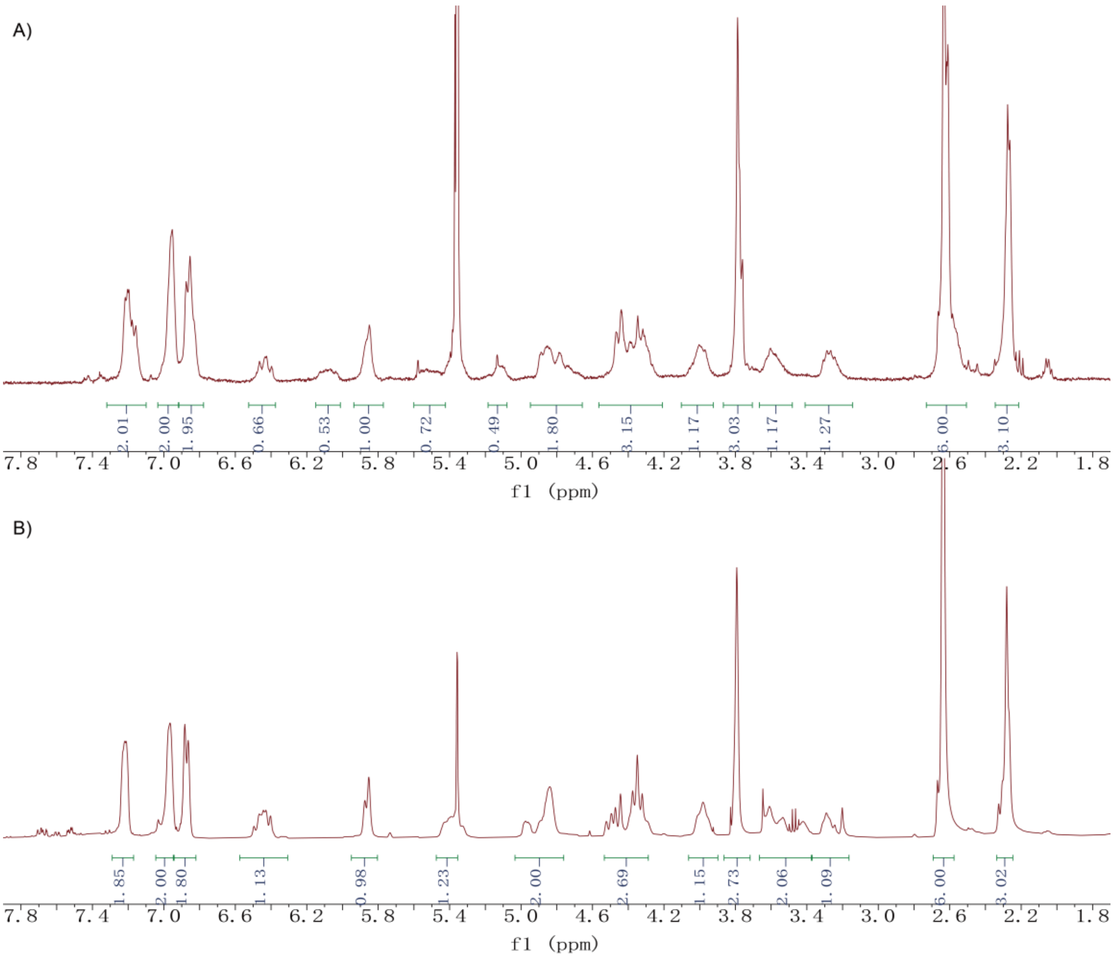
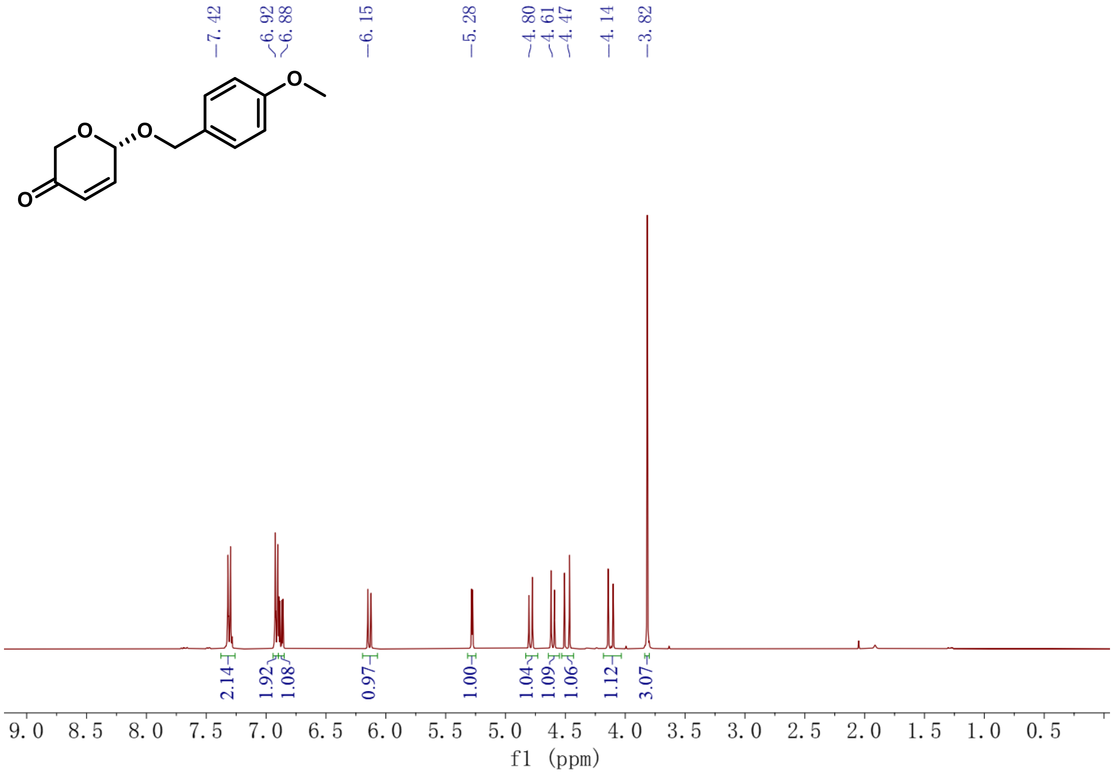
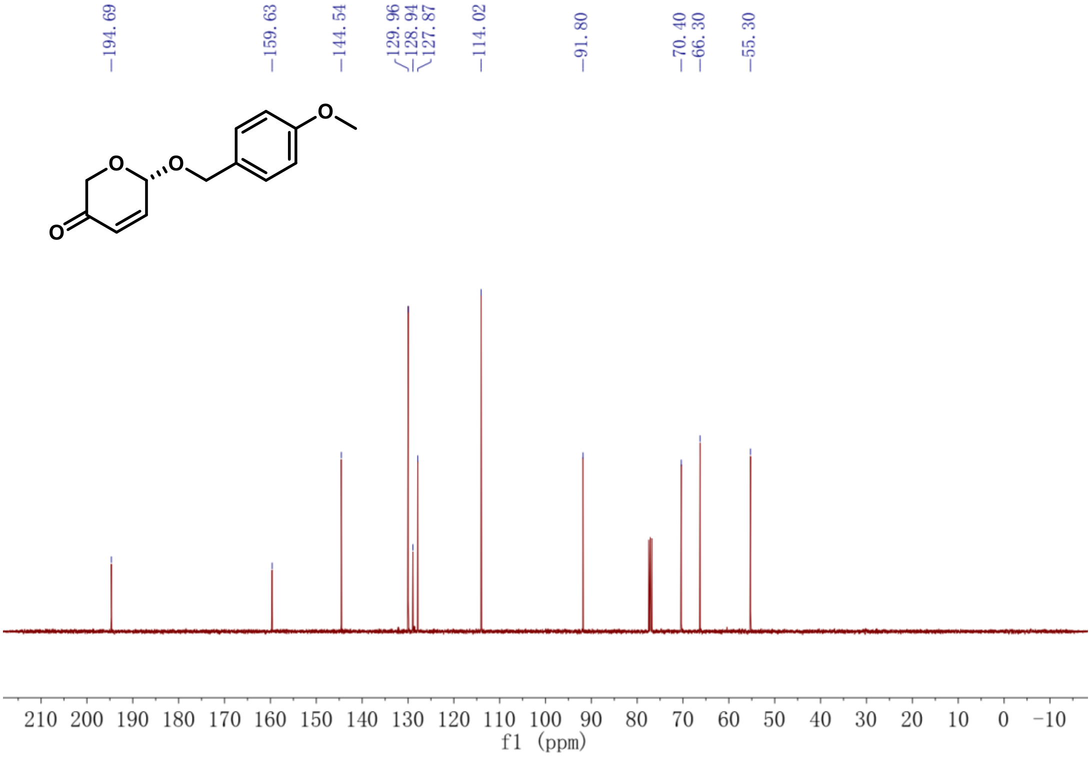


Fig. S11 Comparison of ^{1}H NMR spectra of $\mathbf{P_{int4}}$ (A) and **P2a** (B)

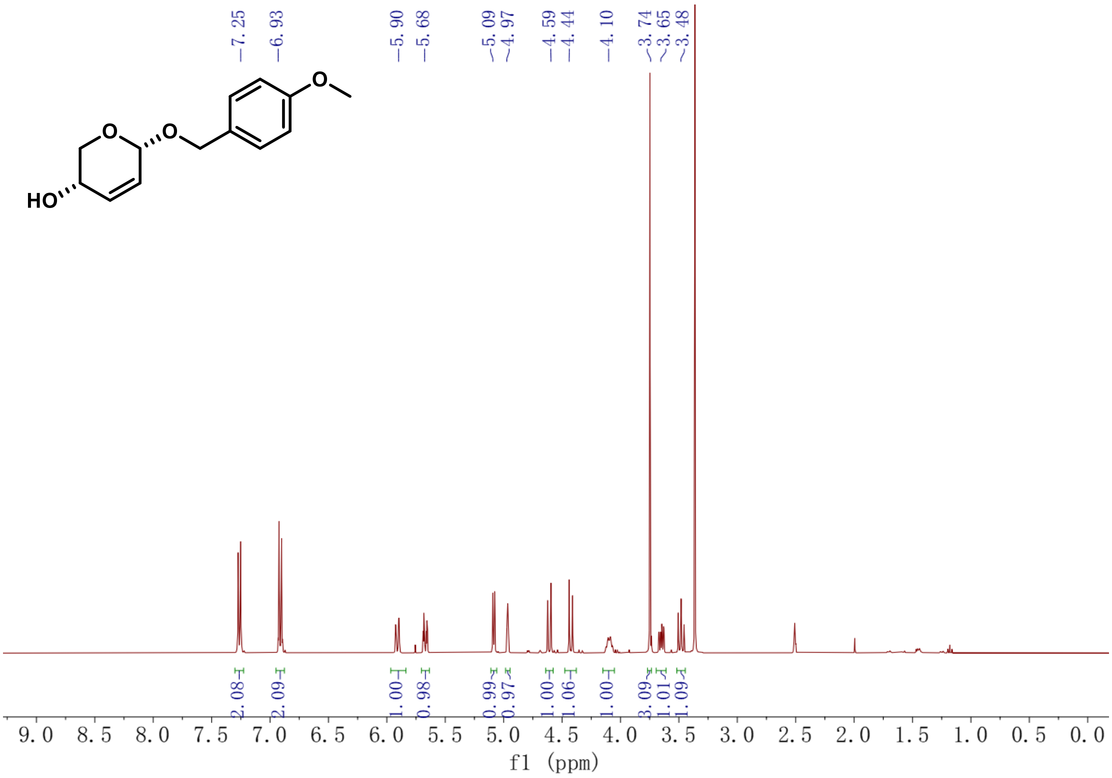
^{1}H NMR and ^{13}C NMR spectra

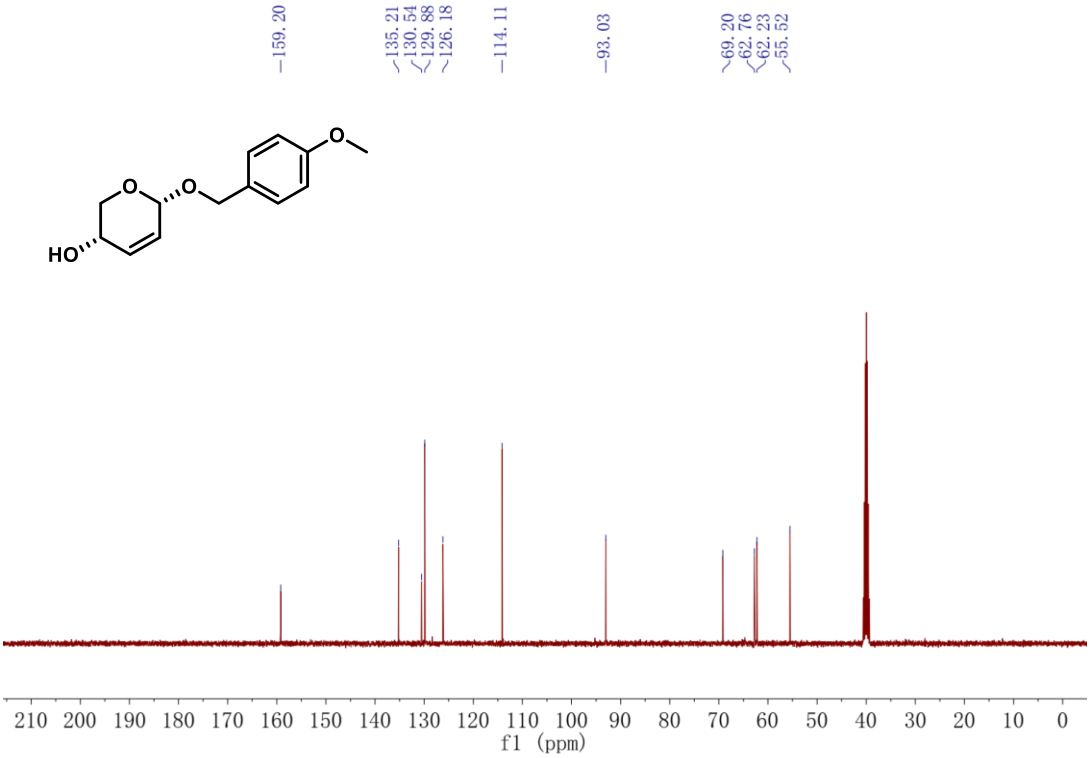
^{1}H NMR and ^{13}C NMR spectra of **2**



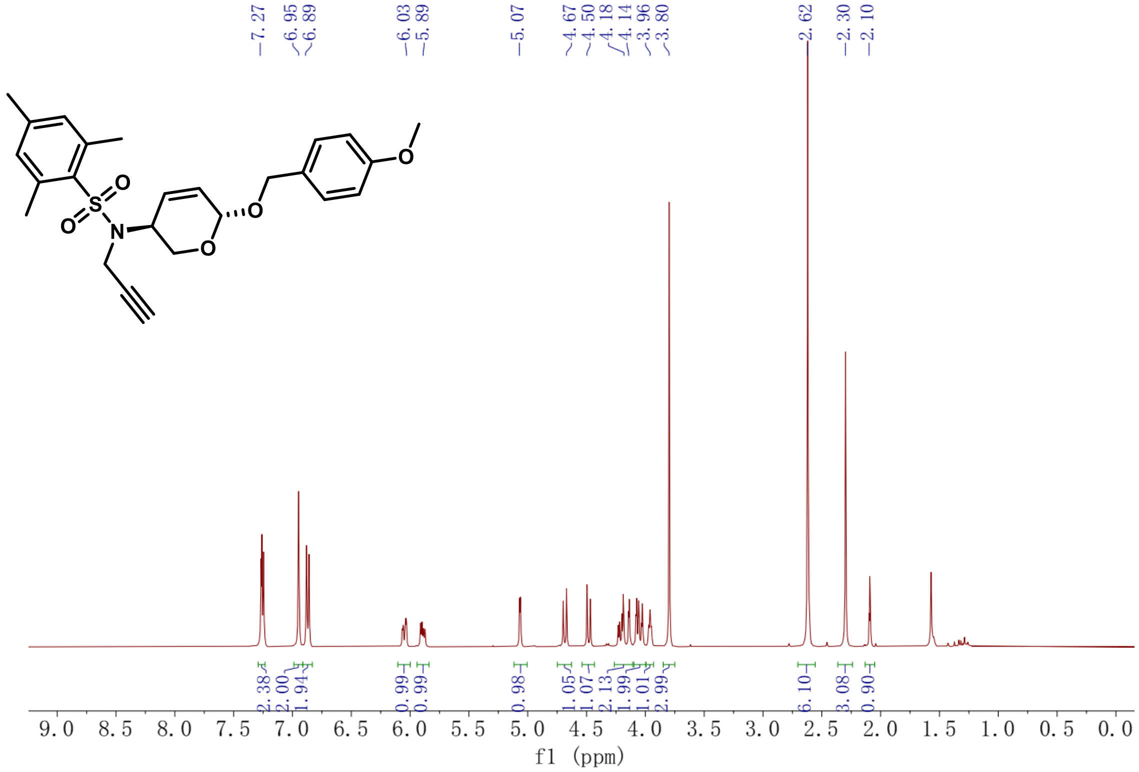


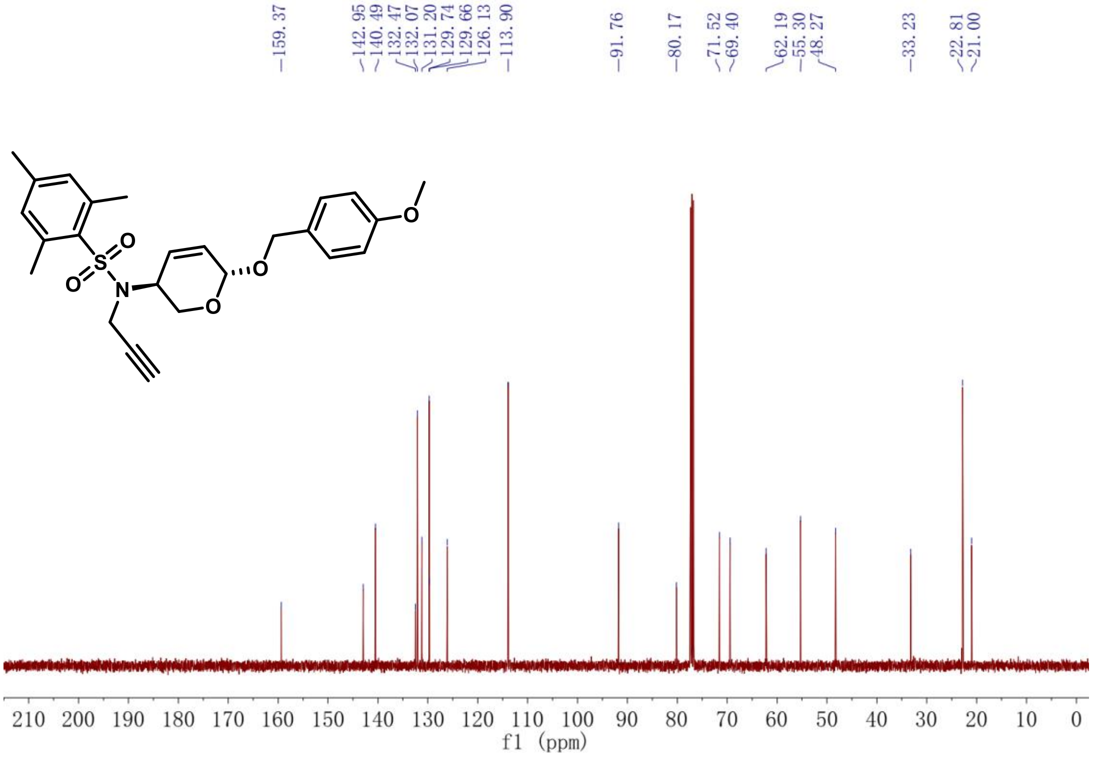
^{1}H NMR and ^{13}C NMR spectra of **3**



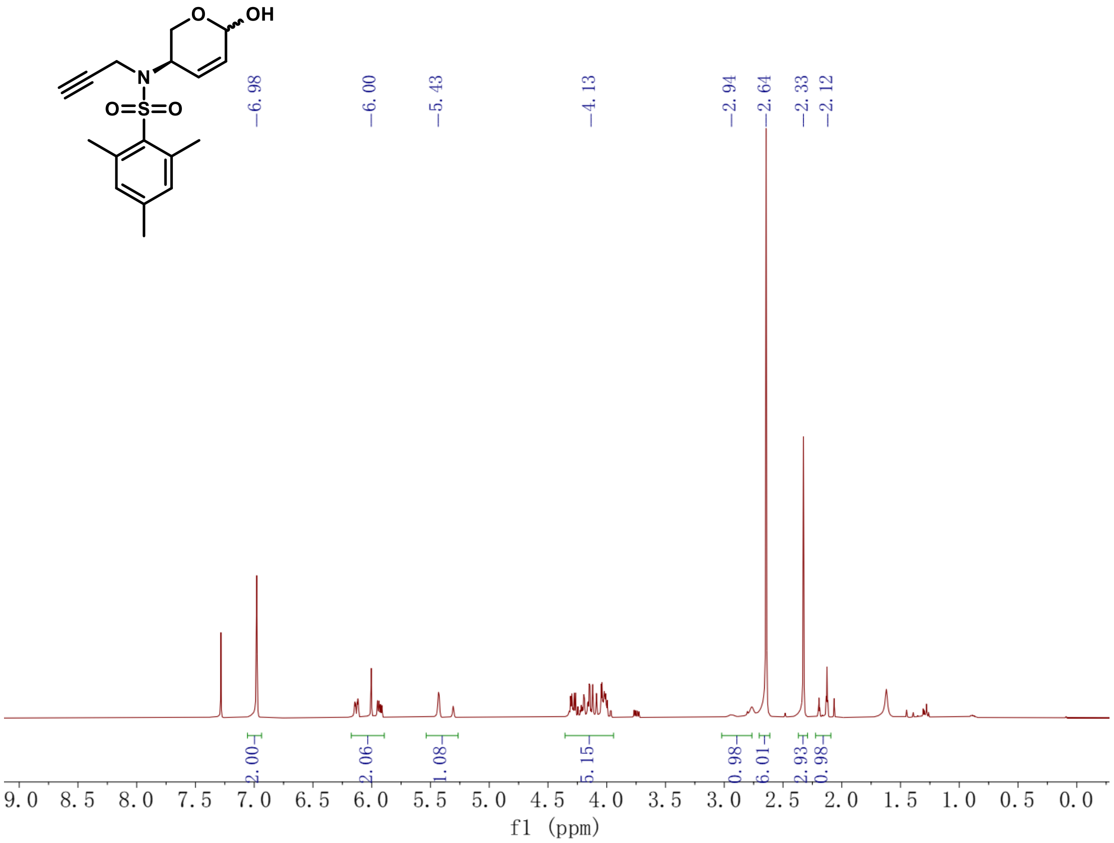


^{1}H NMR and ^{13}C NMR spectra of **4**



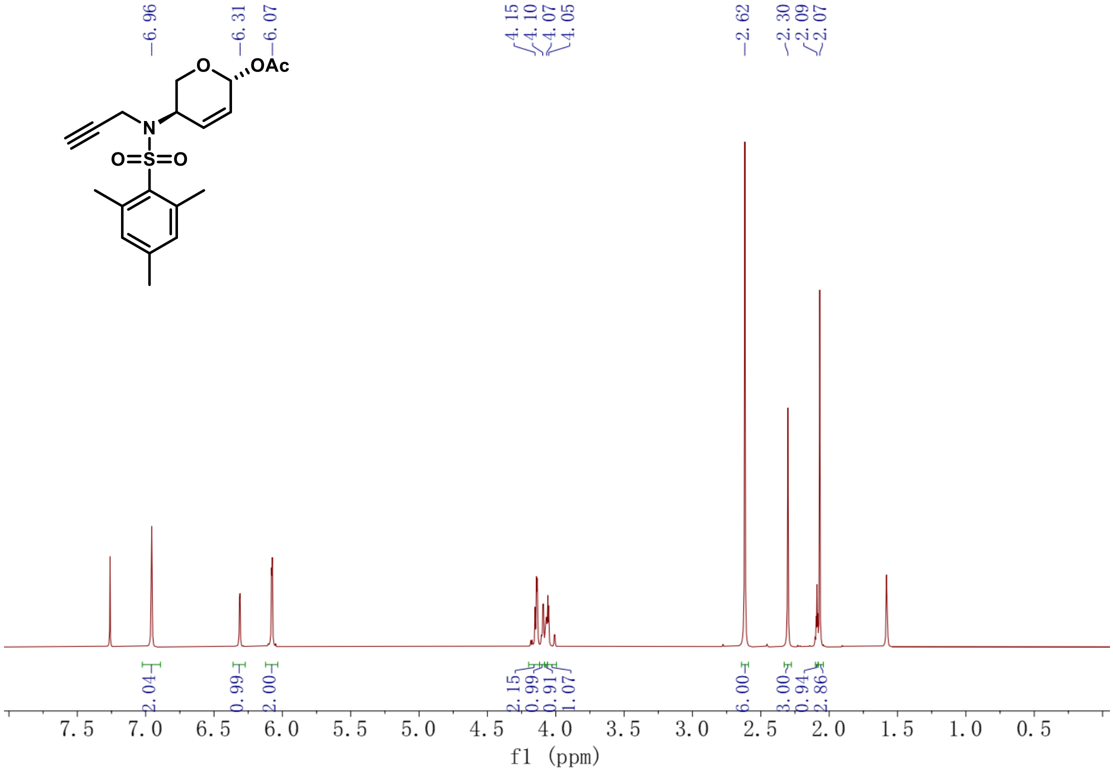


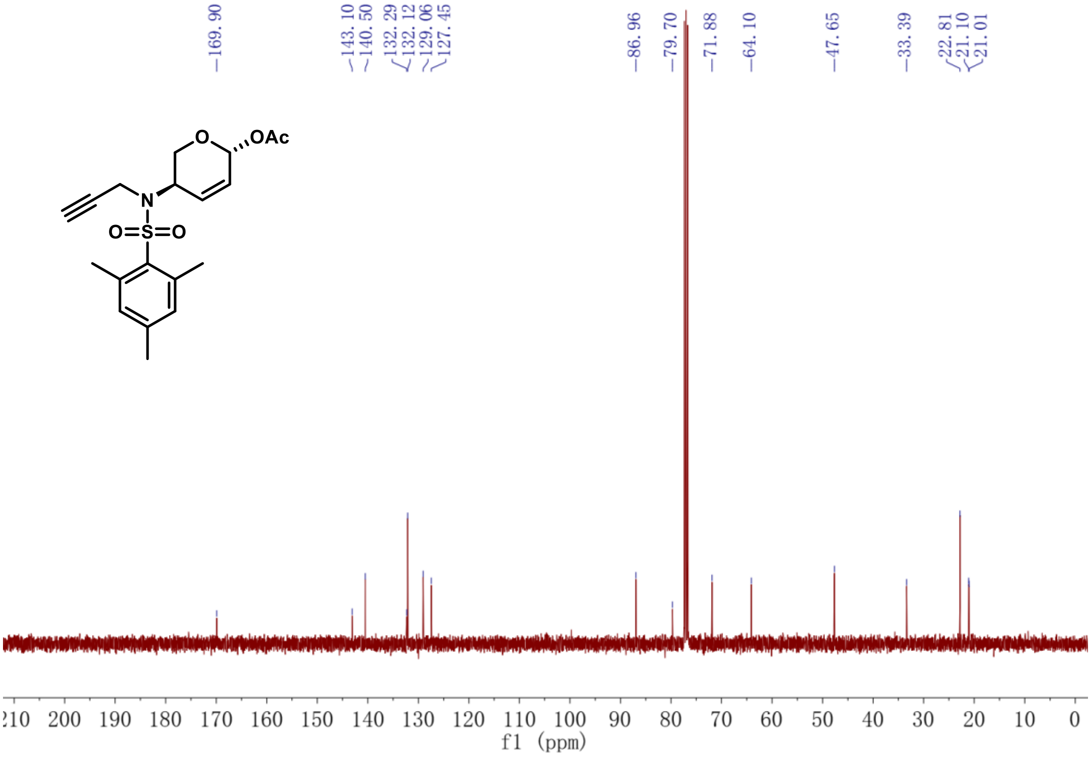
^{1}H NMR spectrum of **5**



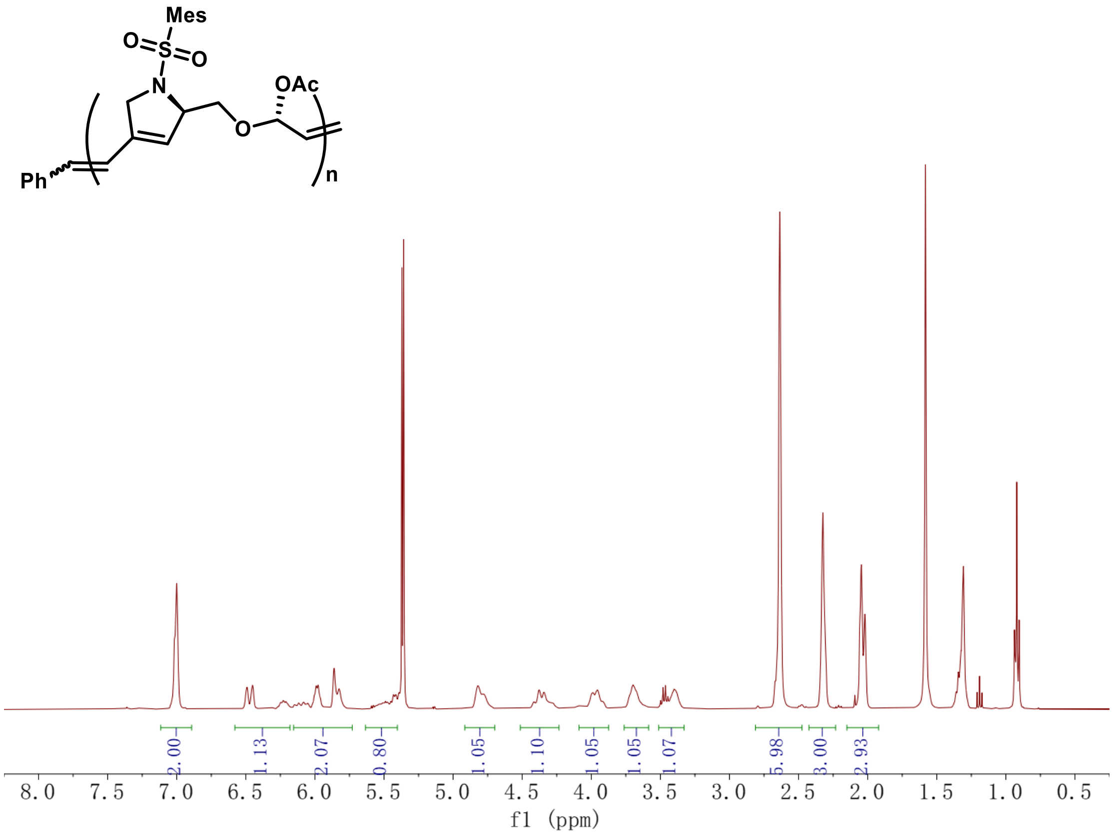
OH
O
N
O=S=O
6.98
6.00
5.43
4.13
2.94
2.64
2.33
2.12
2.00
2.06
1.08
5.15
0.98
6.01
2.93
0.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

^{1}H NMR and ^{13}C NMR spectra of **M1**

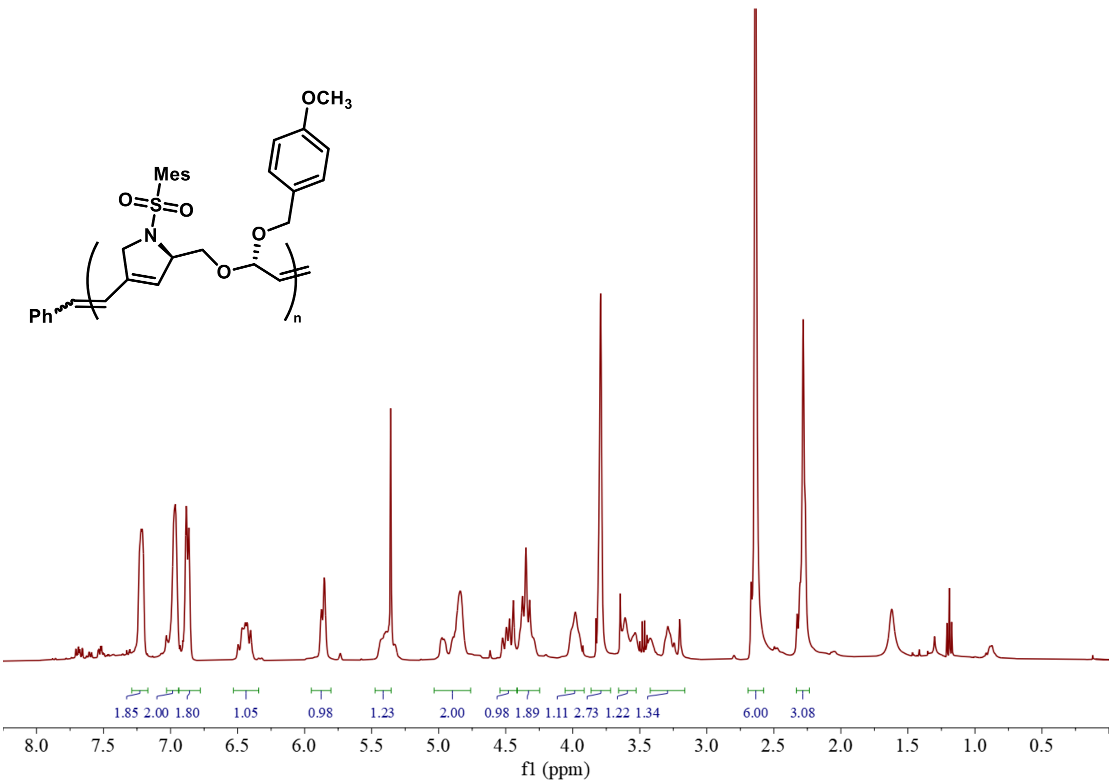




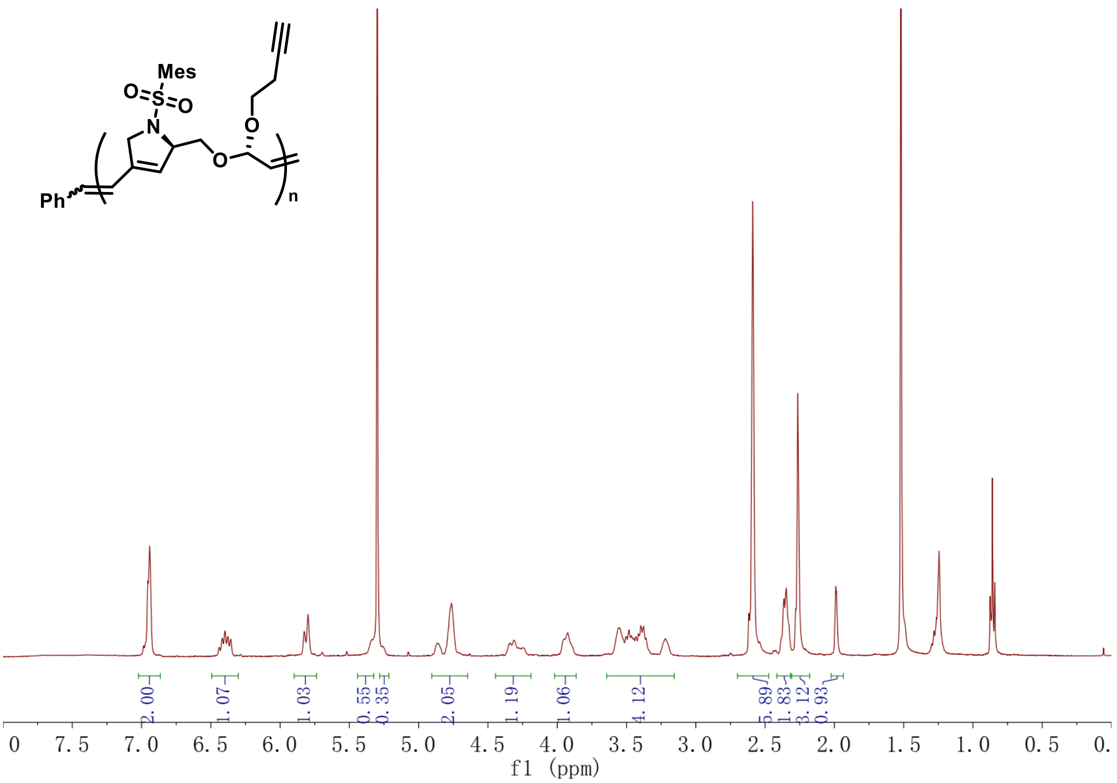
^{1}H NMR spectrum of polymer **P1**



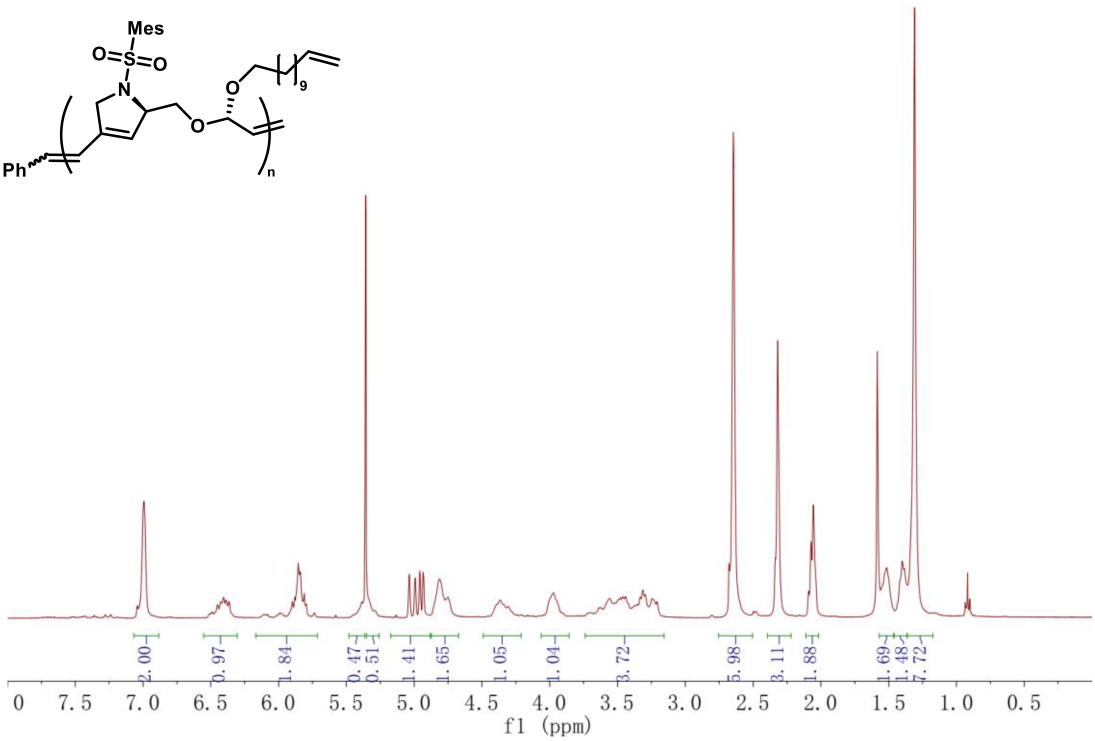
^{1}H NMR spectrum of polymer **P2a**



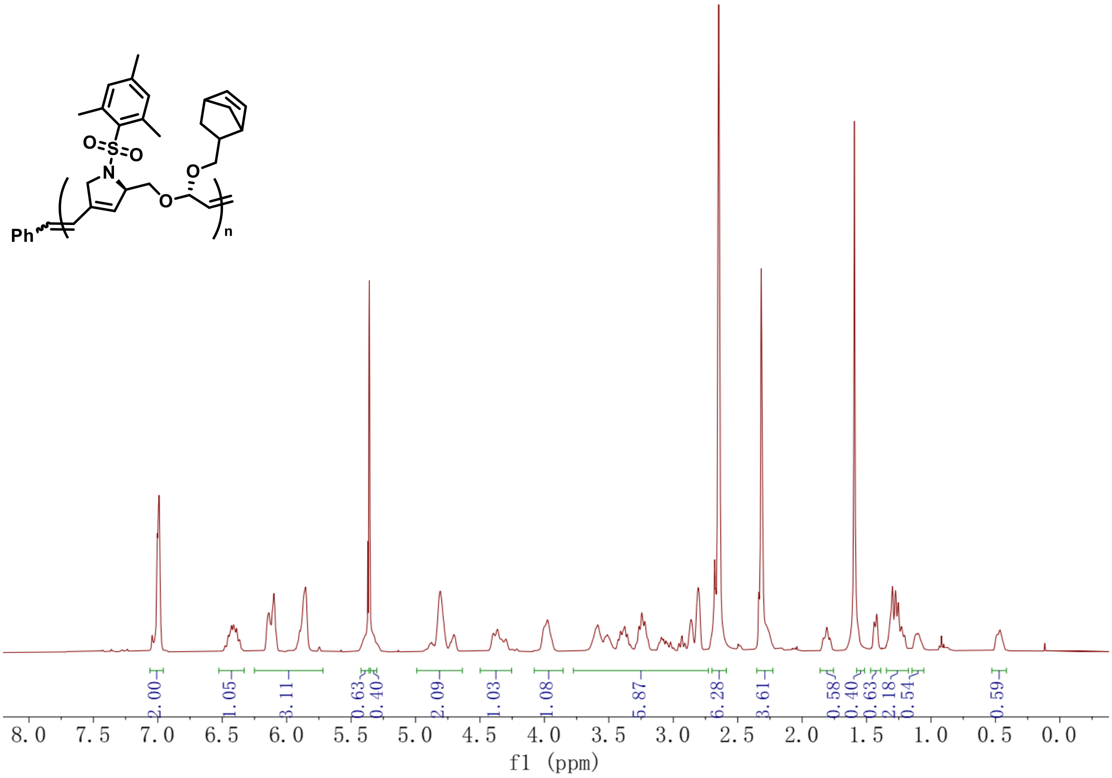
^{1}H NMR spectrum of polymer **P2b**



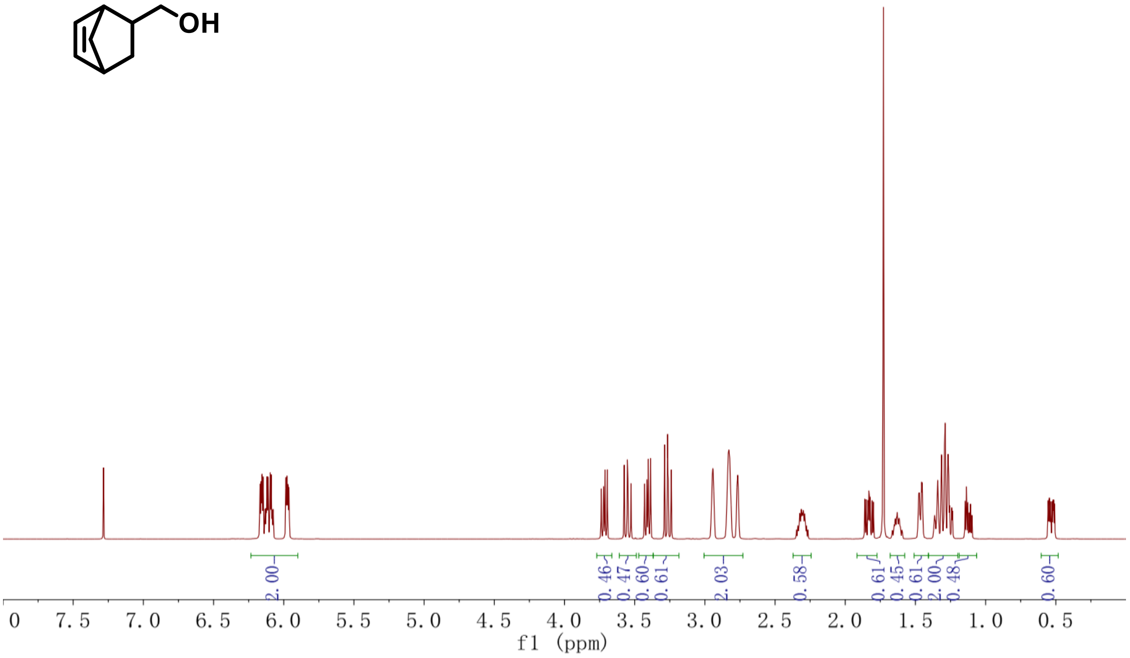
^{1}H NMR spectrum of polymer **P2c**



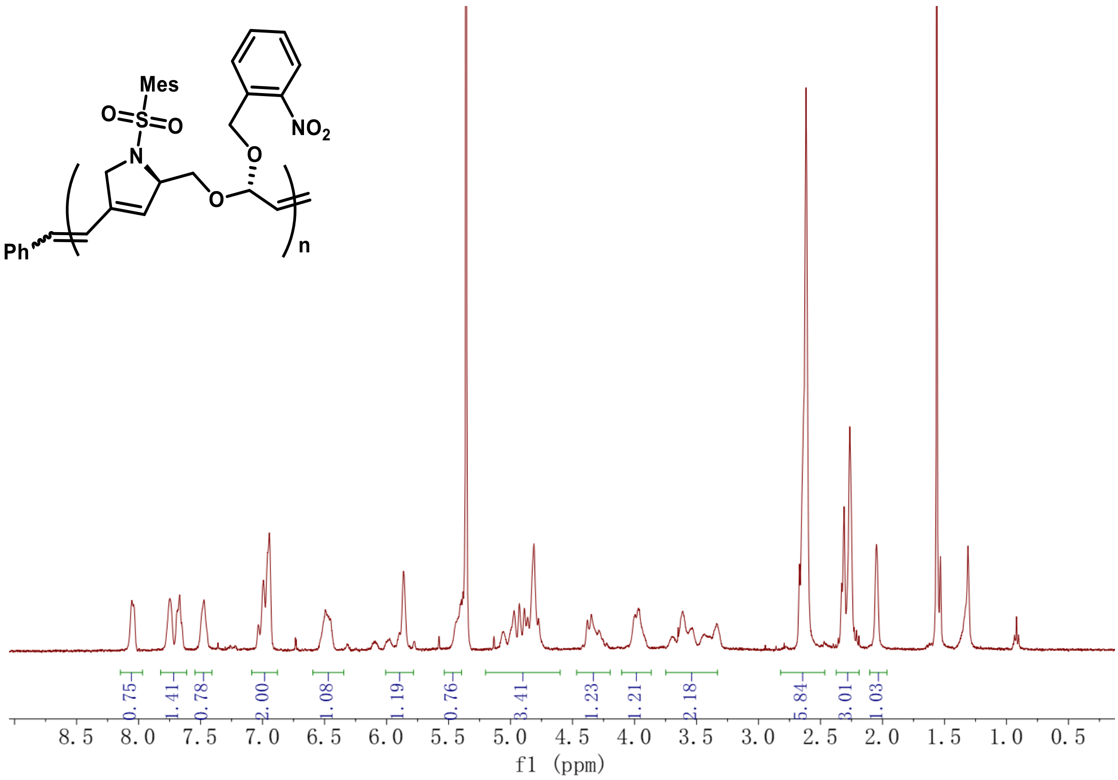
^{1}H NMR spectrum of polymer **P2d**



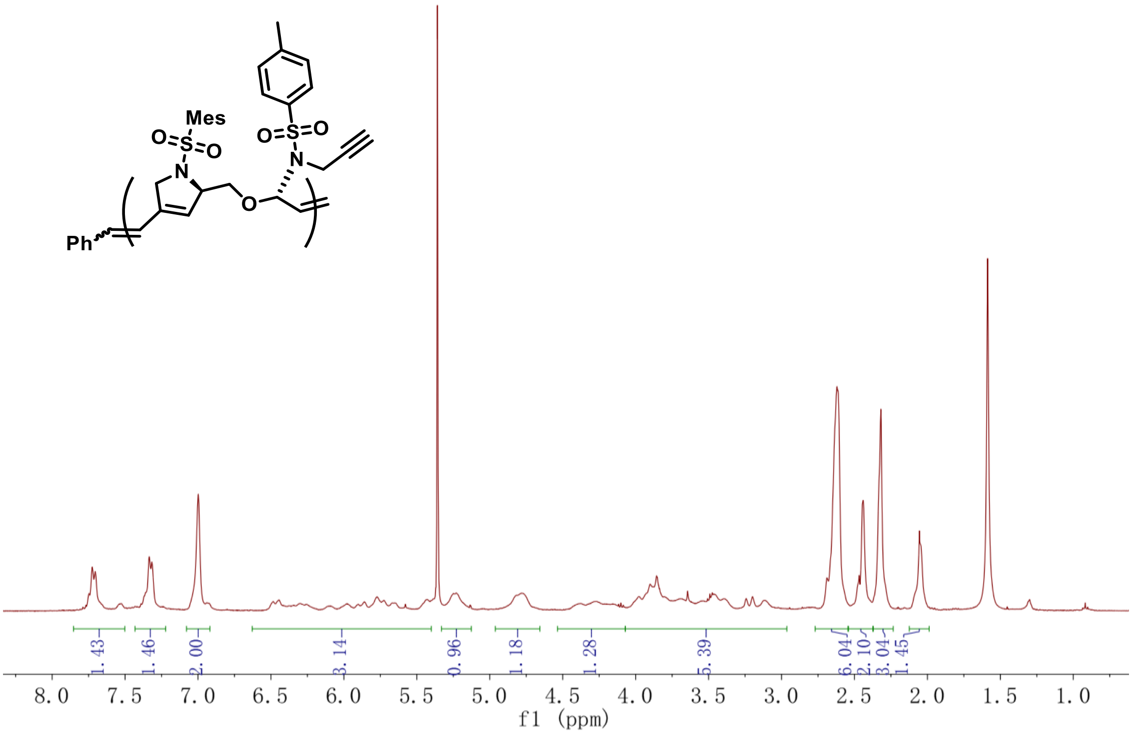
^{1}H NMR spectrum of 5-norbornene-2-methanol



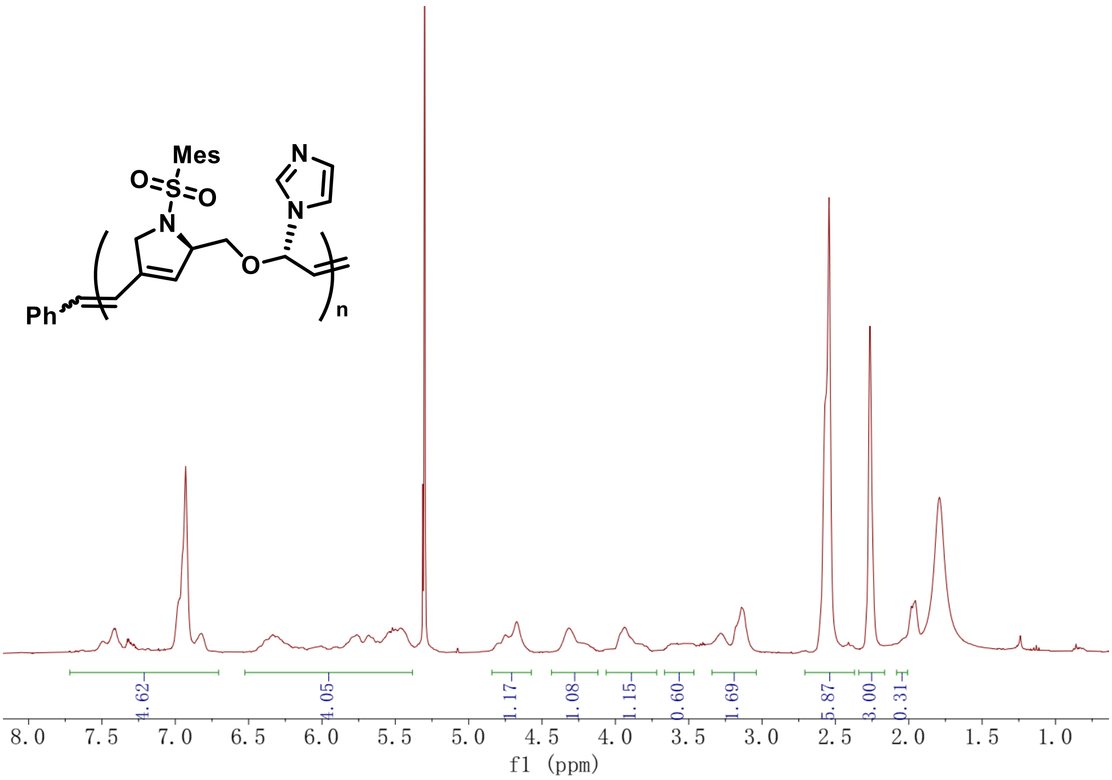
^{1}H NMR spectrum of polymer **P2e**



^{1}H NMR spectrum of polymer **P2f**



^{1}H NMR spectrum of polymer **P2g**



^{1}H NMR spectrum of polymer **P2h**