

Supporting Information

Tributylphosphine-Catalyzed Aziridine-Based Cycloaddition Polymerization toward Thiacyclic Polymers

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1. Supporting Schemes and Figures

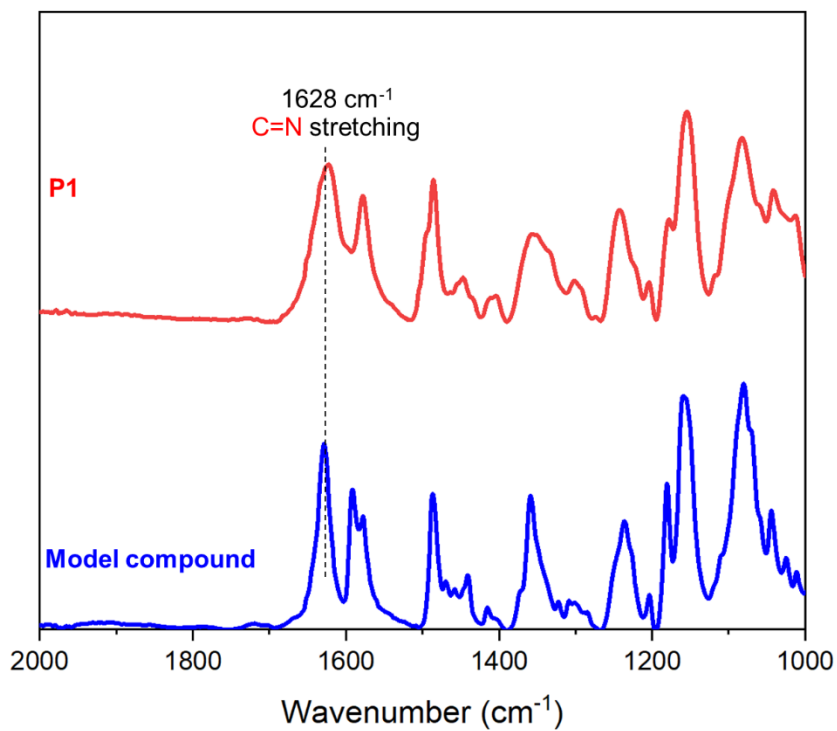


Fig. S1 FT-IR spectra of **P1** and the model compound (Scheme 2).

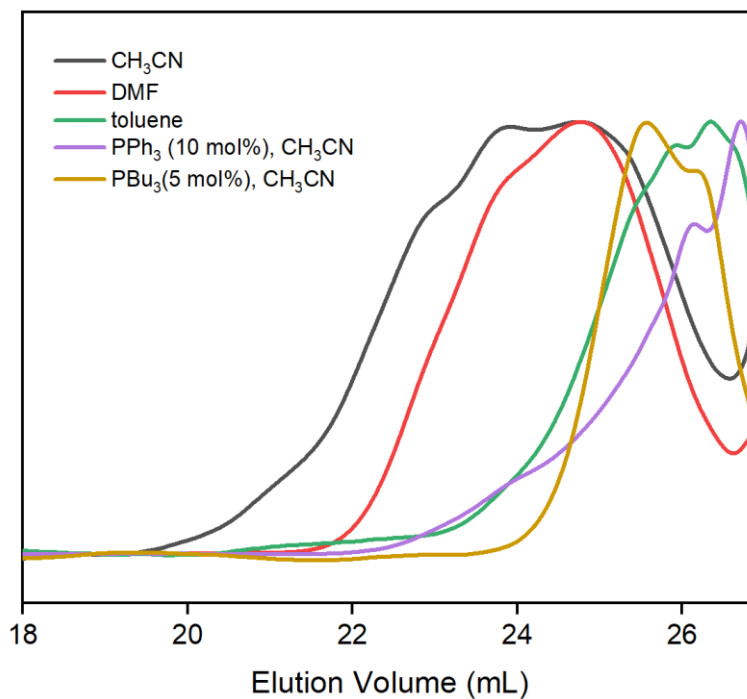


Fig. S2 SEC traces (DMF, $60 \text{ }^\circ\text{C}$) of polymers synthesized in Table 1.

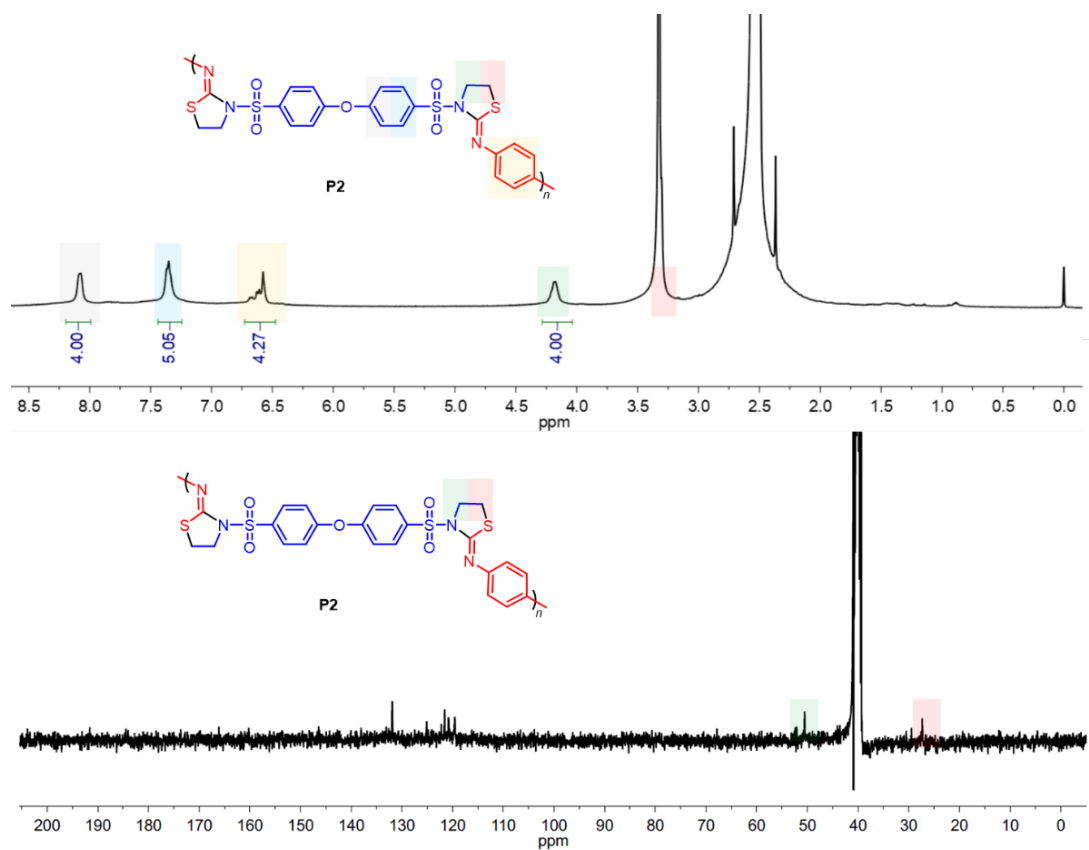


Fig. S3 ^1H NMR (400 MHz, $\text{DMSO-}d_6$, 25 °C) and ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$, 25 °C) spectra of **P2**.

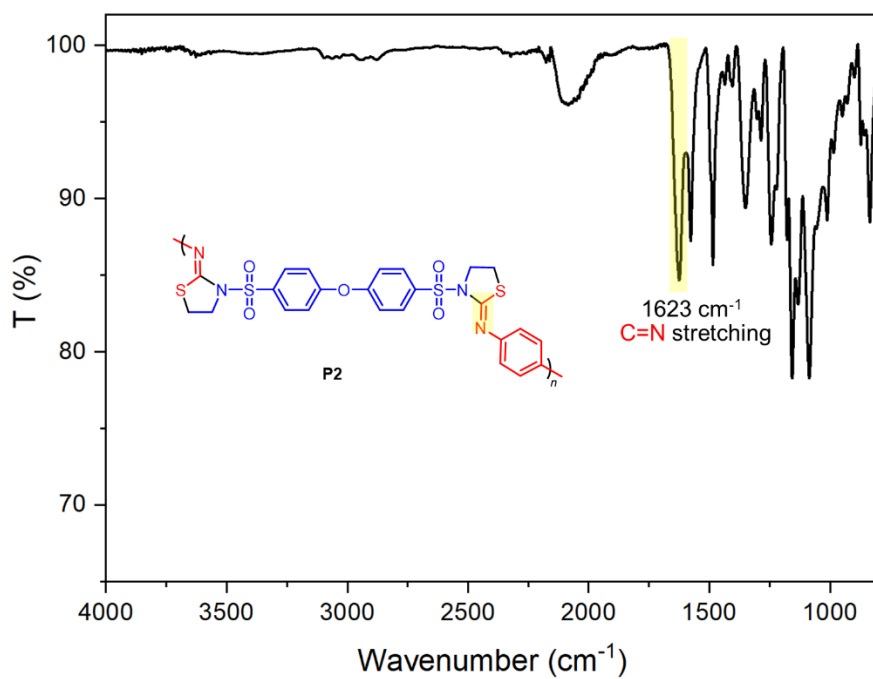


Fig. S4 FT-IR spectrum of **P2**.

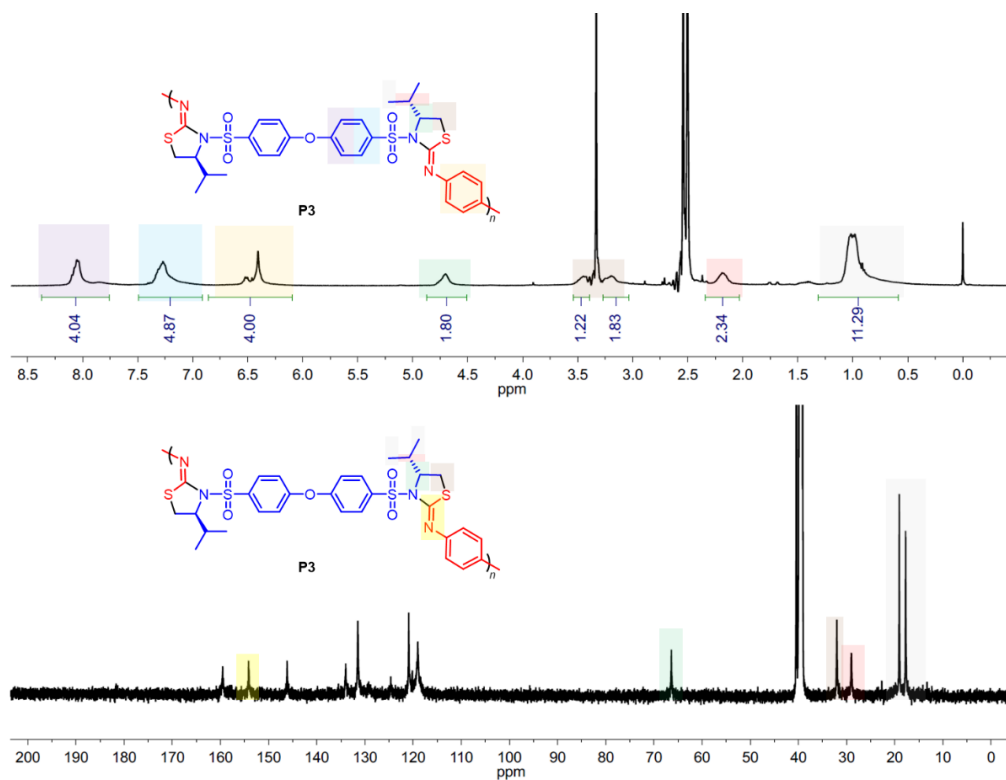


Fig. S5 ^1H NMR (400 MHz, $\text{DMSO-}d_6$, 25 °C) and ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$, 25 °C) spectra of **P3**.

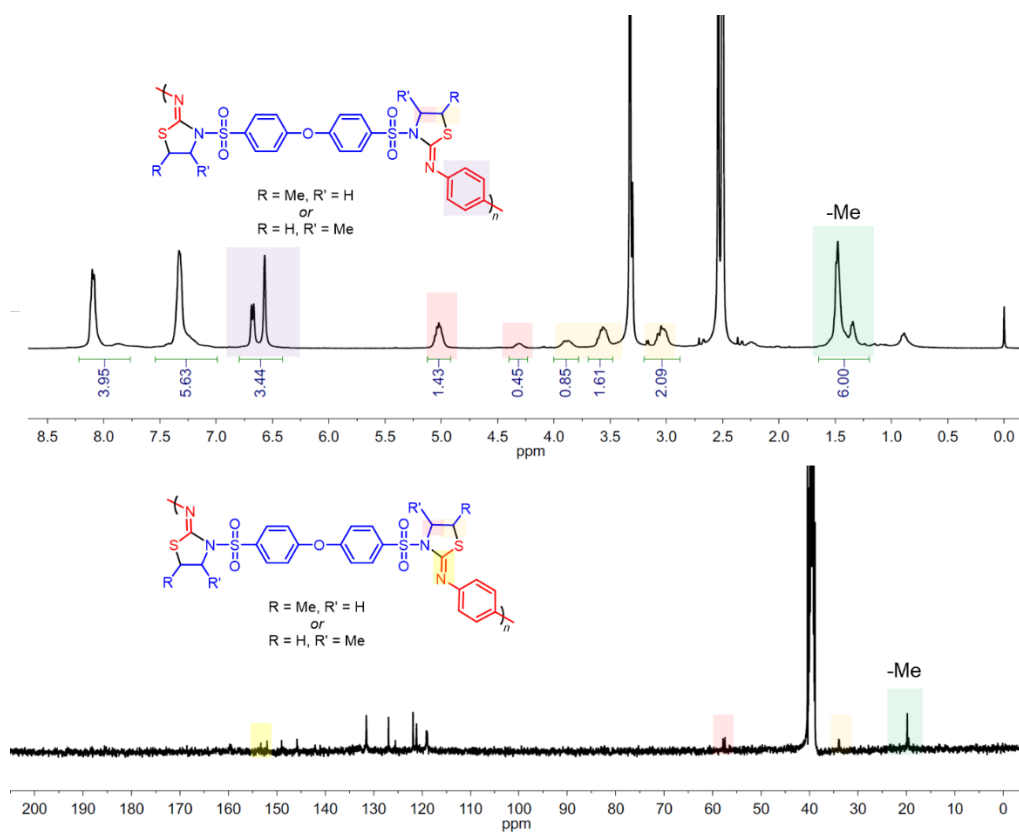
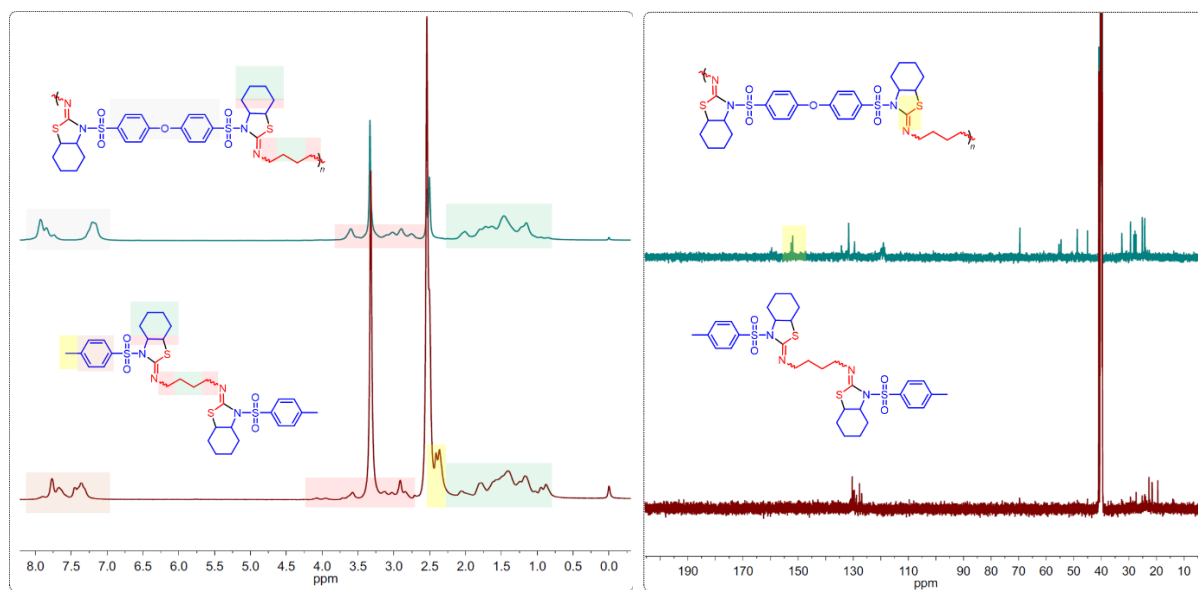
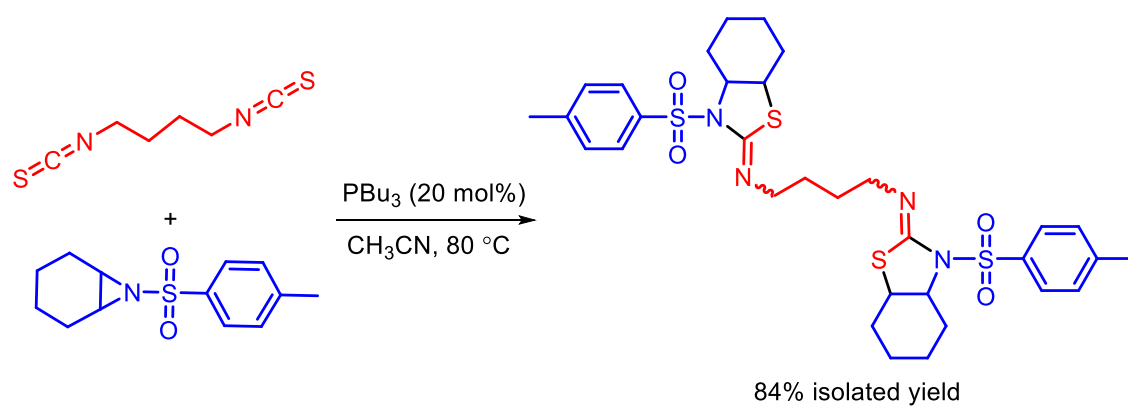


Fig. S6 ^1H NMR (400 MHz, $\text{DMSO-}d_6$, 25 °C) and ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$, 25 °C) spectra of **P4**.

Scheme S1. Model Cycloaddition Reaction



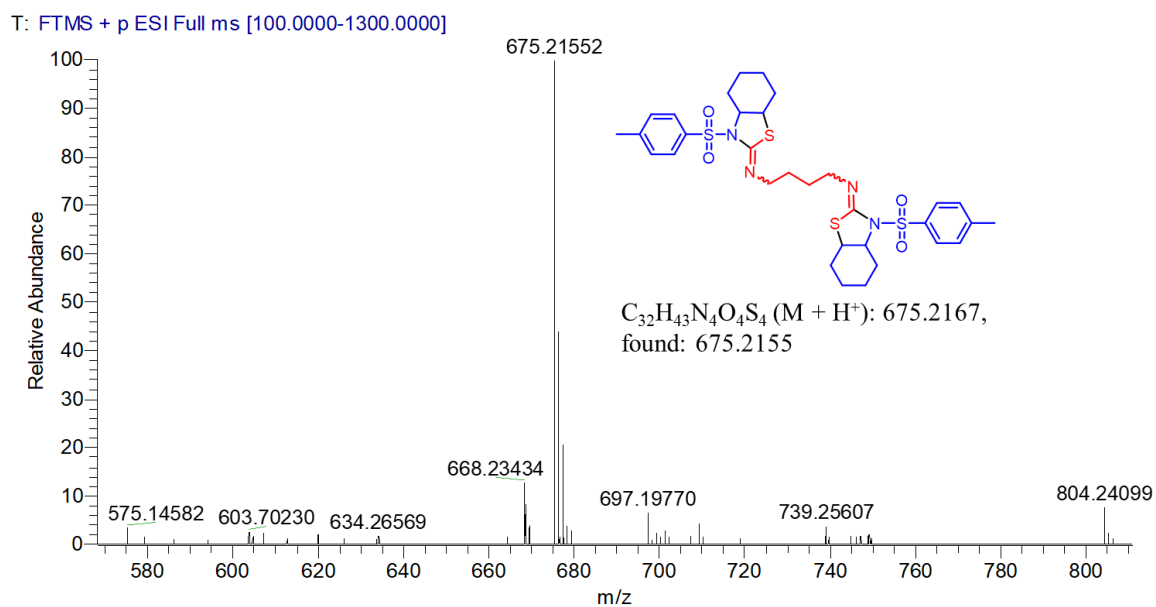


Fig. S8 HRMS spectrum of the model compound (Scheme S1).

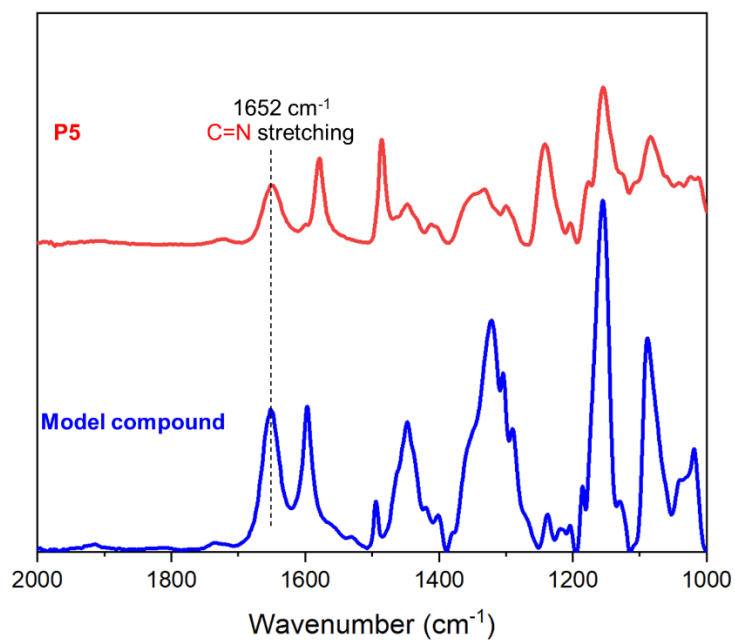


Fig. S9 FT-IR spectrum of **P5** and the model compound (Scheme S1).

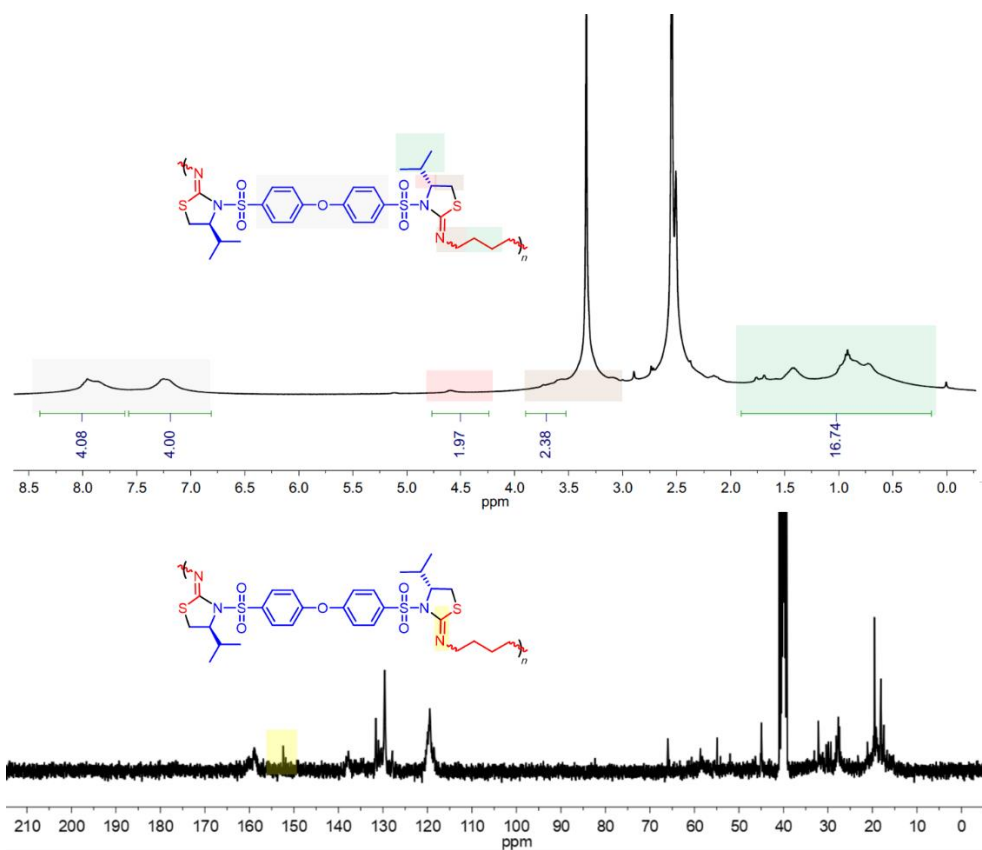


Fig. S10 ^1H NMR (400 MHz, $\text{DMSO-}d_6$, 25 °C) and ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$, 25 °C) spectra of **P6**.

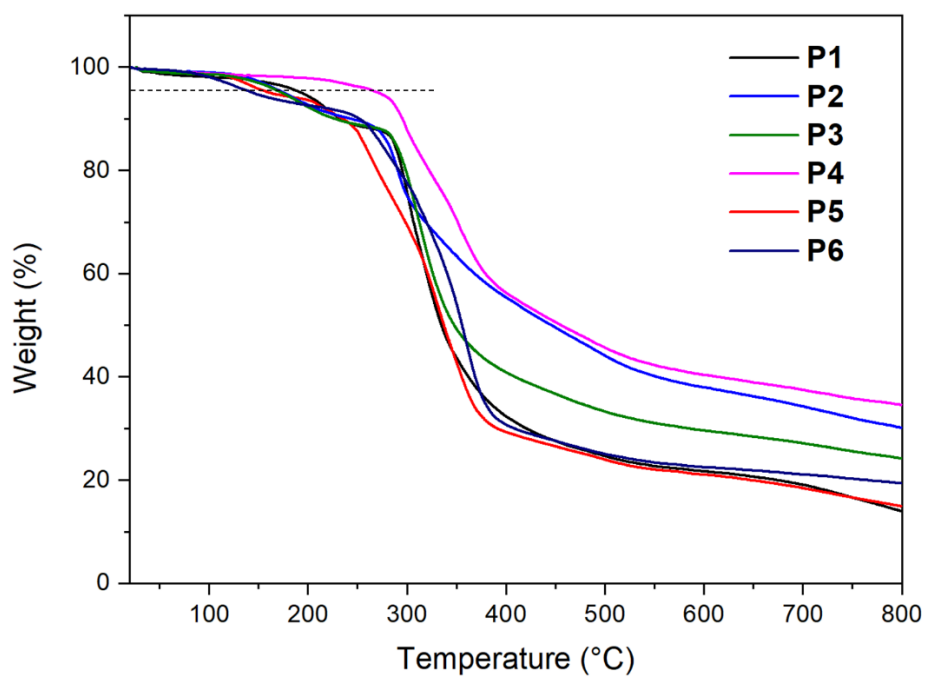


Fig. S11 The TG curves of **P1-P6**.

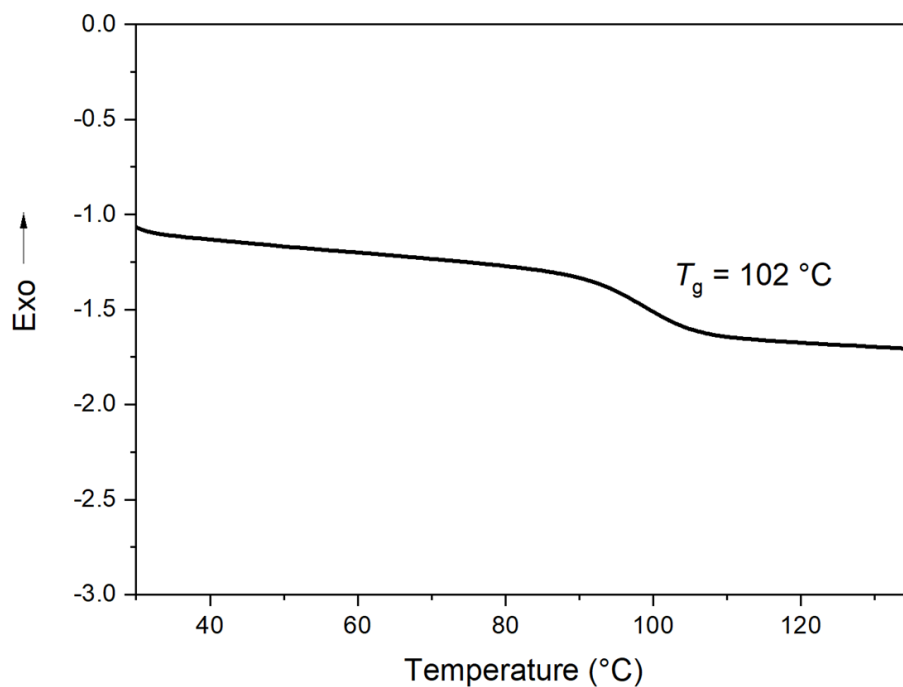


Fig. S12 The DSC curve of **P5**.

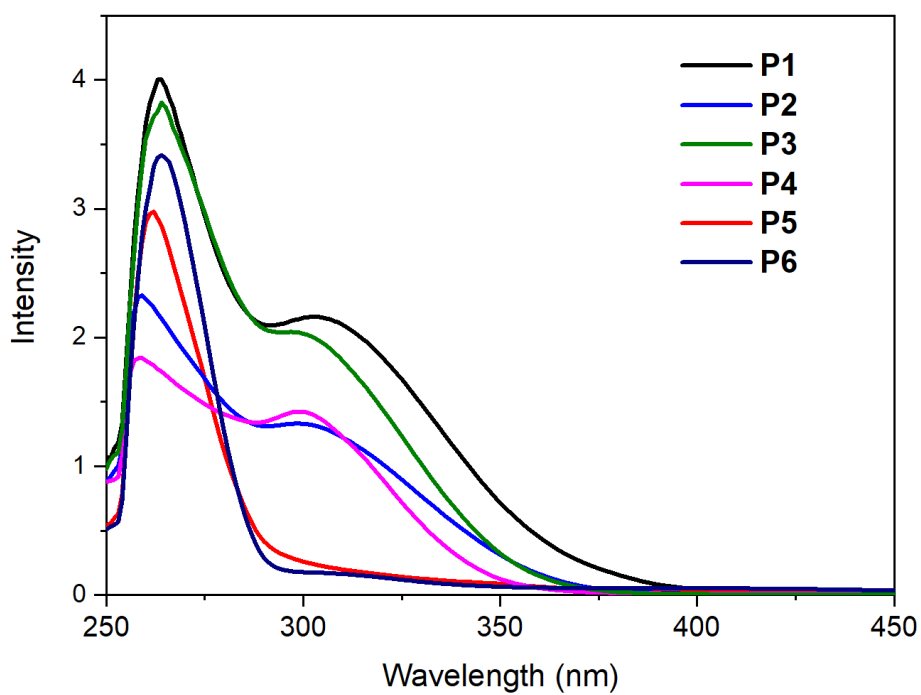


Fig. S13 The UV-vis spectra of **P1-P6**.

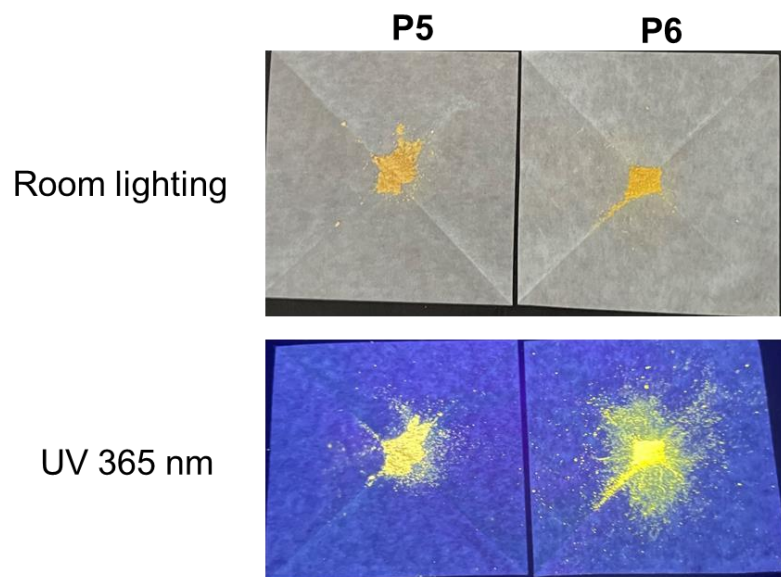


Fig. S14 The photos of **P5** and **P6** powders taken under room lighting and irradiated with a UV lamp (365 nm).

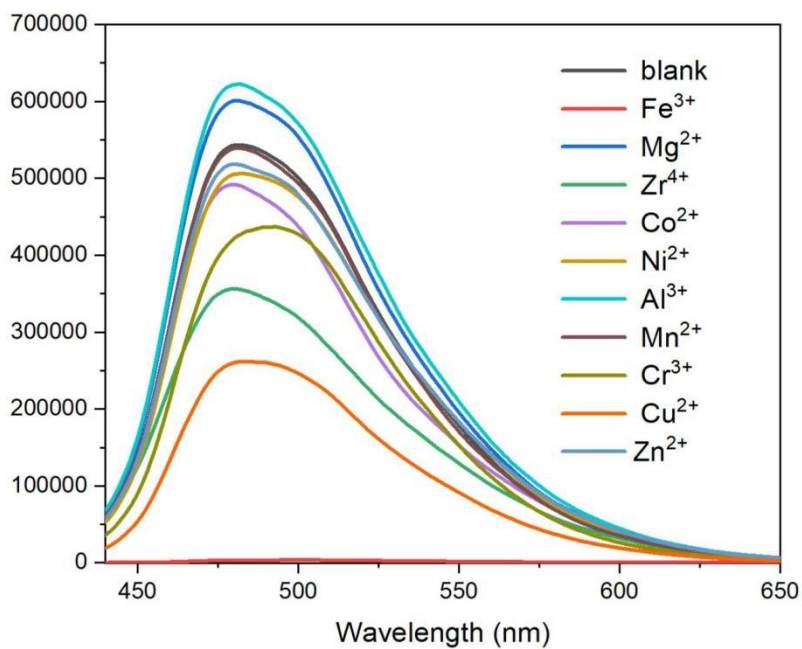
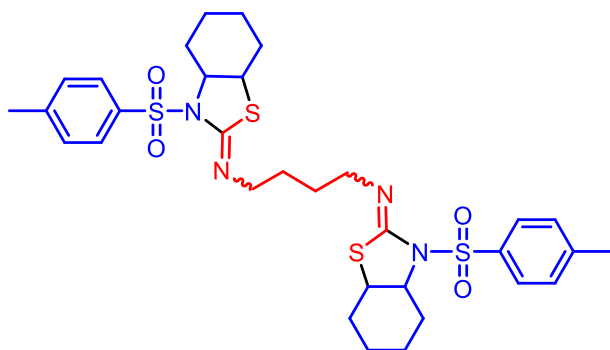


Fig. S15 PL spectra of **P6** in DMSO/water mixtures with different metal ions.

2. Characterization Data

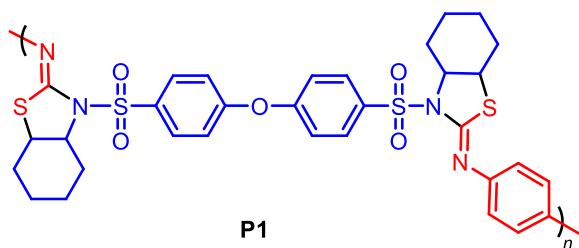


FT-IR (neat): 2924 , 2853, 1635, 1447, 1347, 1179, 1083, 1018, 805, 699, 654, 543 cm^{-1} ;

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 0.68-2.06 (20H, m), 2.26-2.45 (6H, m), 2.73-3.20 (6H, m), 3.49-4.24 (2H, m), 7.02-8.04 (8H, m).

^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): 130.4, 123.0, 129.6 , 128.8 , 127.7 , 126.9 , 27.3 , 25.1 , 24.3 , 24.2 , 24.1, 23.9 , 22.7 , 21.6 , 21.5 , 19.5.

HRMS $[\text{M} + \text{H}^+]$: Calcd. for $\text{C}_{38}\text{H}_{38}\text{N}_4\text{O}_5\text{S}_4$: 675.2122, found: 675.2155.

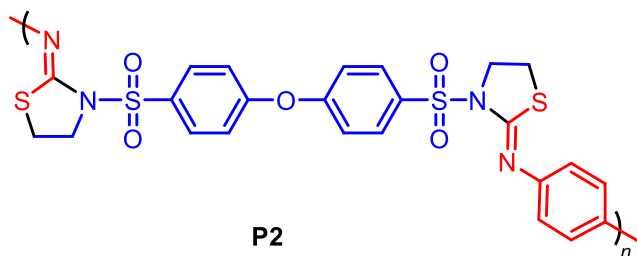


P1

FT-IR (neat): 2935 , 2864, 1619, 1566, 1483, 1354, 1237, 1153, 1081, 1036, 829 cm^{-1} ;

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 1.07-2.07 (16H, m), 2.93 (2H, br), 3.80 (2H, br), 6.19-6.67 (4H, m), 7.05-7.42 (4H, m), 7.74-8.17 (4H, m).

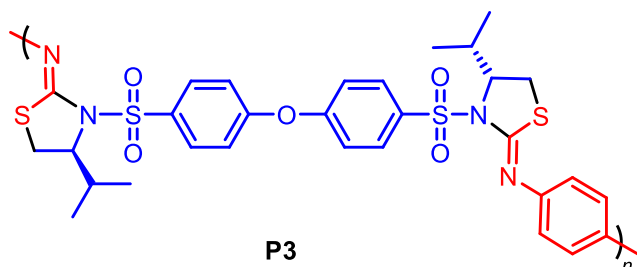
^{13}C NMR (125 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 159.5, 154.5, 145.8, 133.3, 131.3, 120.8, 118.9, 69.9, 48.4, 32.2, 28.6, 24.6, 23.7.



FT-IR (neat): 2930, 1627, 1573, 1337, 1253, 1157, 1085, 836, 692, 550 cm^{-1} ;

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 4.04-4.29 (4H, m), 6.50-6.74 (4H, m), 7.26-7.45 (4H, m), 8.00-8.19(4H, m).

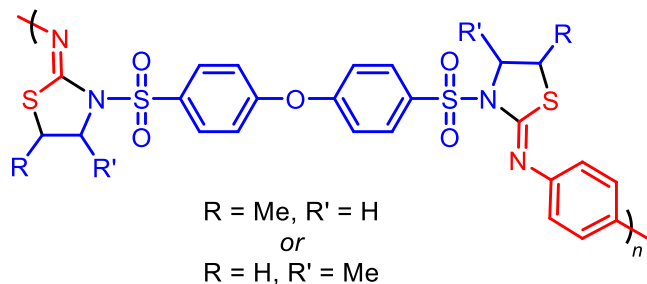
^{13}C NMR (125 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 132.1, 125.1, 122.2, 121.5, 120.8, 119.7, 119.6, 50.6, 27.3.



FT-IR (neat): 2962, 1618, 1570, 1491, 1347, 1244, 1157, 1085, 839 cm^{-1} ;

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 0.6-1.31 (10H, m), 2.03-2.34 (2H, m), 3.03-3.27 (2H, m), 3.41-3.53 (2H, m), 4.50-4.87 (2H, m), 6.09-6.84 (4H, m), 6.92-7.49 (4H, m), 7.77-8.37(4H, m);

^{13}C NMR (125 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 159.5, 154.2, 146.2, 134.0, 131.5, 120.9, 119.0, 66.4, 32.0, 29.01, 19.0, 17.8.

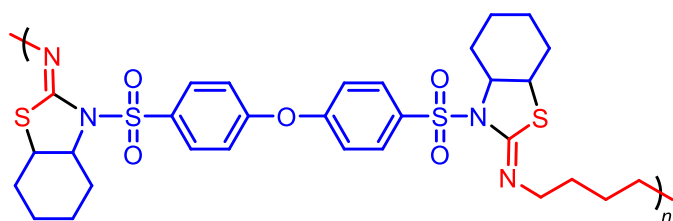


P4

FT-IR (neat): 2974, 1626, 1578, 1487, 1352, 1243, 1152, 1082, 833, 693, 553 cm^{-1} ;

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 1.19-1.65 (6H, br), 2.88-3.19 (2H, m), 3.47-3.65 (1H, m), 3.77-4.00 (1H, m), 4.23-4.40 (1H, m), 4.90-5.11 (1H, m), 6.40-6.81 (4H, m), 6.99-6.54 (4H, m), 7.77-8.23 (4H, m).

^{13}C NMR (125 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 159.7, 159.4, 153.3, 152.0, 149.0, 145.8, 120.9, 131.5, 126.9, 125.5, 121.9, 121.2, 119.1, 57.9, 57.5, 34.0, 33.8, 19.8, 19.5.

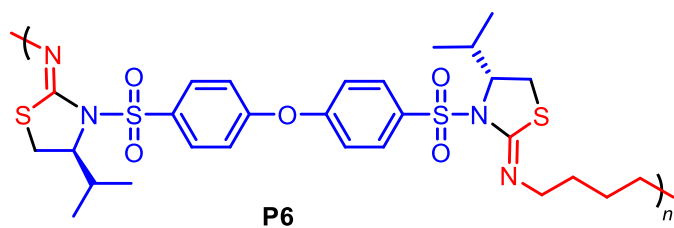


P5

FT-IR (neat): 2930, 2858, 1657, 1578, 1483, 1244, 1149, 1085, 696, 560 cm^{-1} ;

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 0.93-2.23 (20H, m), 2.63-3.26 (6H, m), 3.54-3.72 (2H, m), 7.01-7.46 (4H, m), 7.71-8.03 (4H, m).

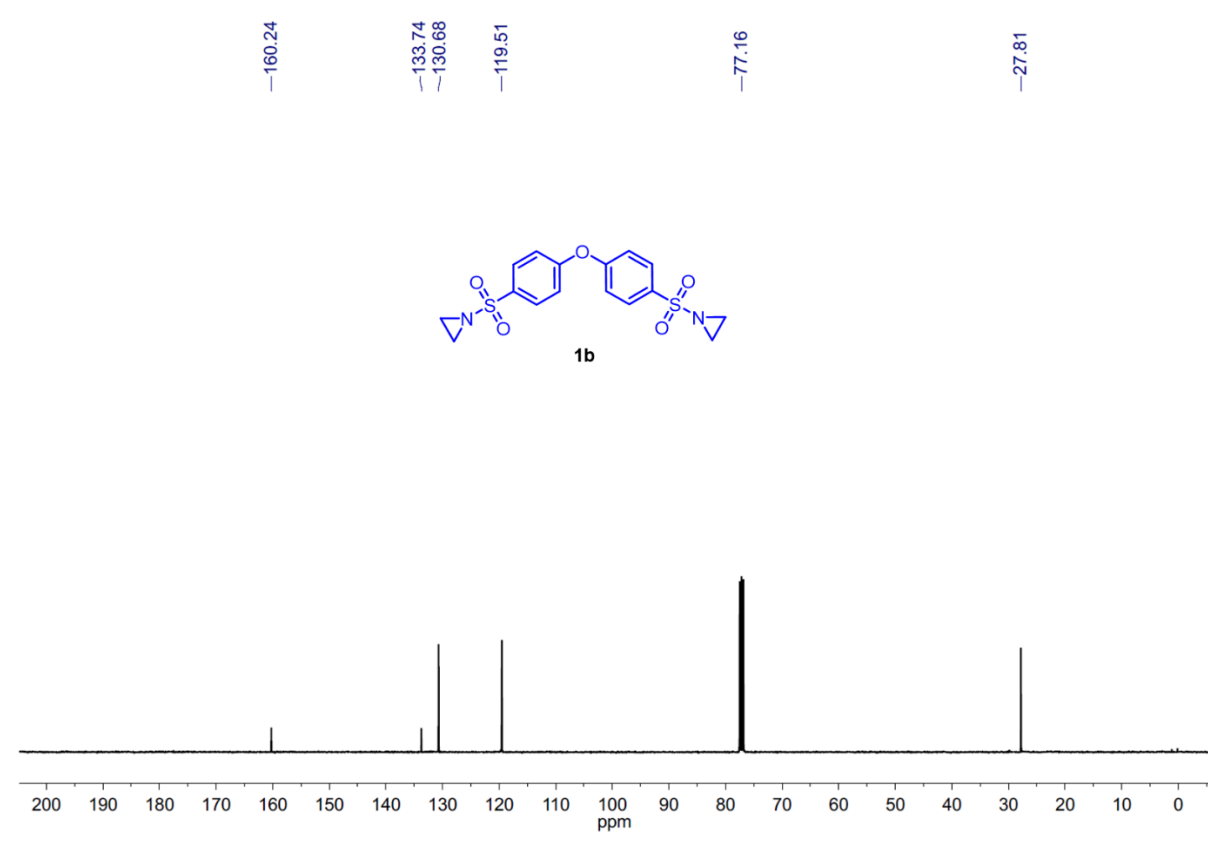
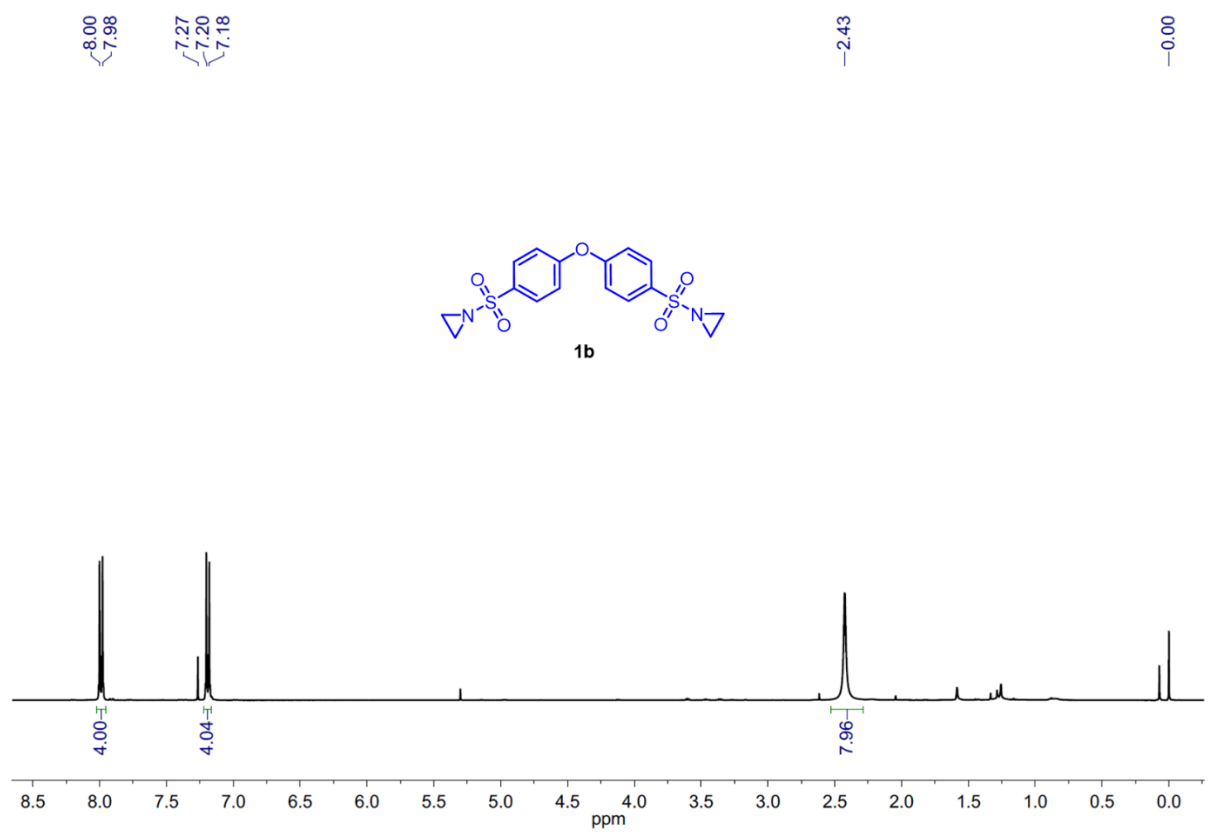
^{13}C NMR (125 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 159.6, 152.5, 151.9, 134.3, 131.6, 129.5, 119.1, 69.5, 55.2, 54.6, 48.7, 45.0, 32.5, 29.4, 28.1, 27.8, 27.3, 25.1, 24.2.

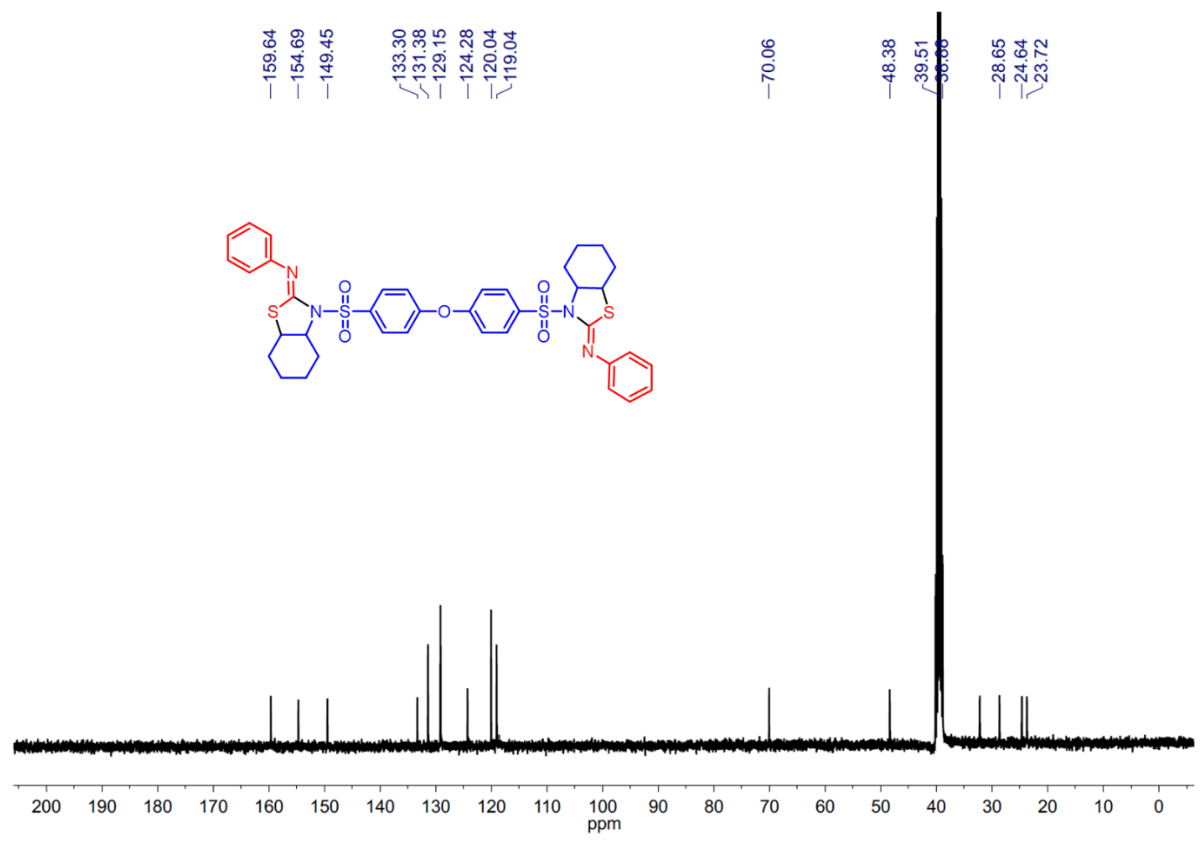
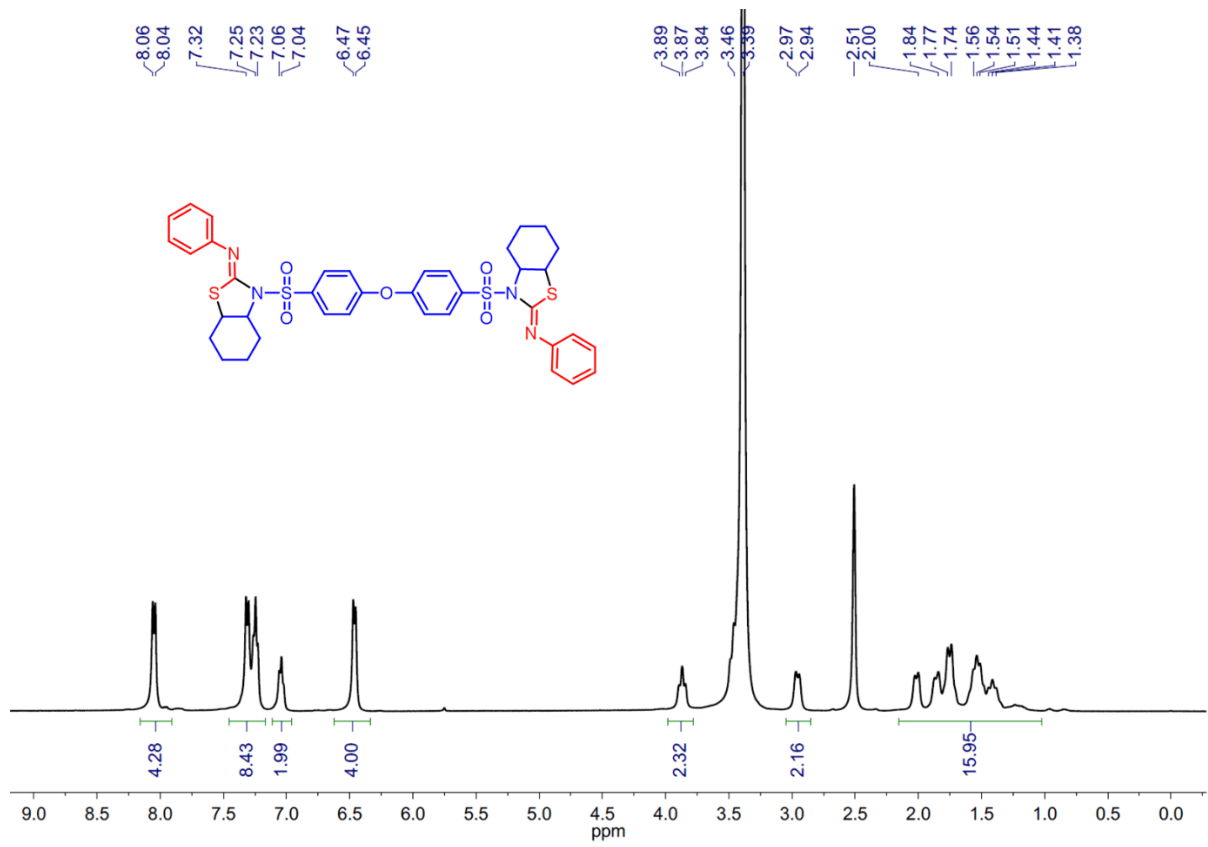


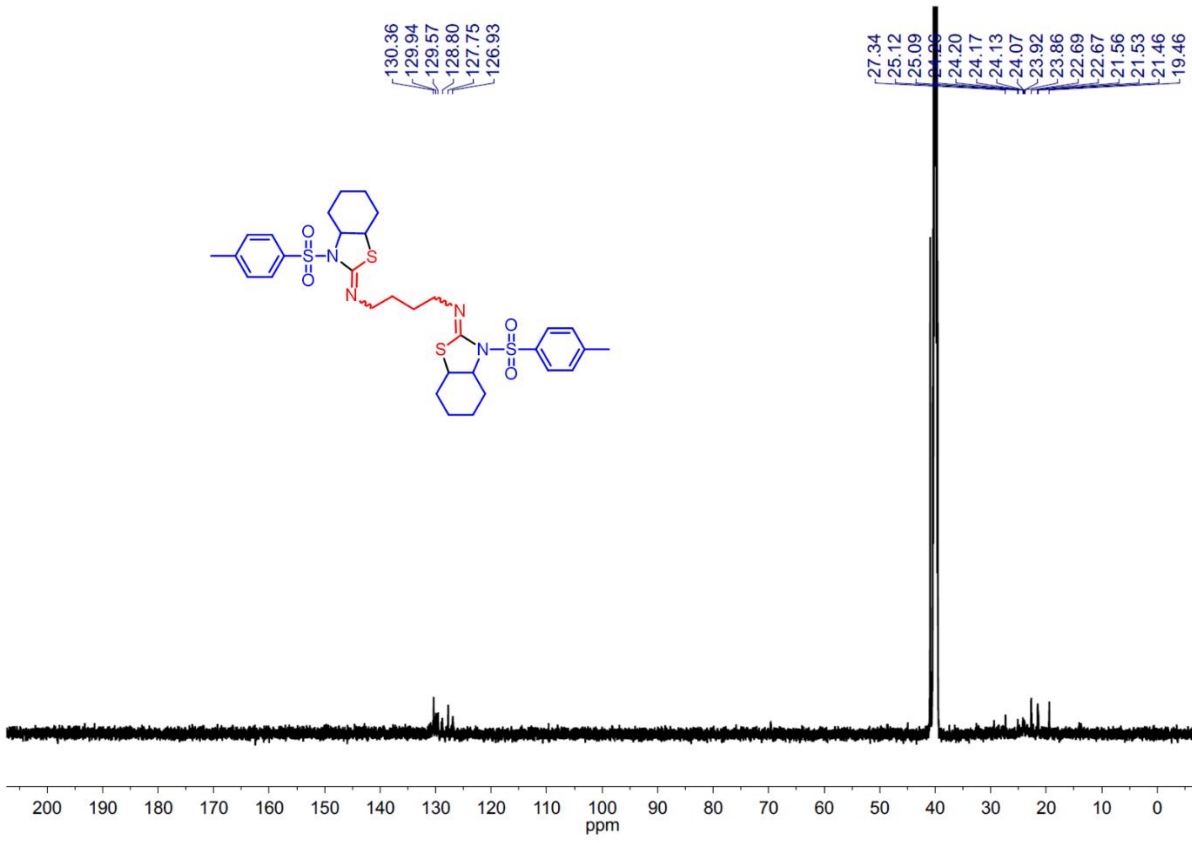
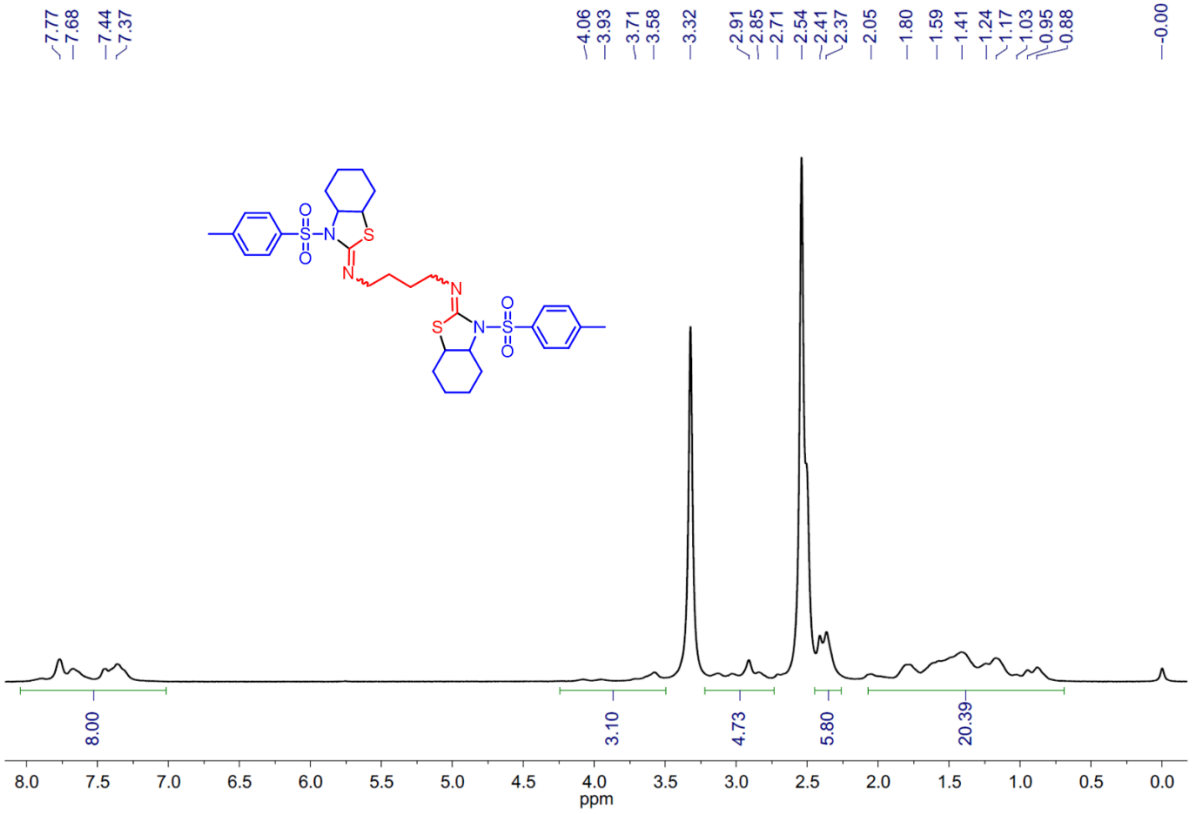
FT-IR (neat): 2965, 2098, 1580, 1480, 1320, 1237, 1150, 1087, 875, 688, 557 cm^{-1} ;

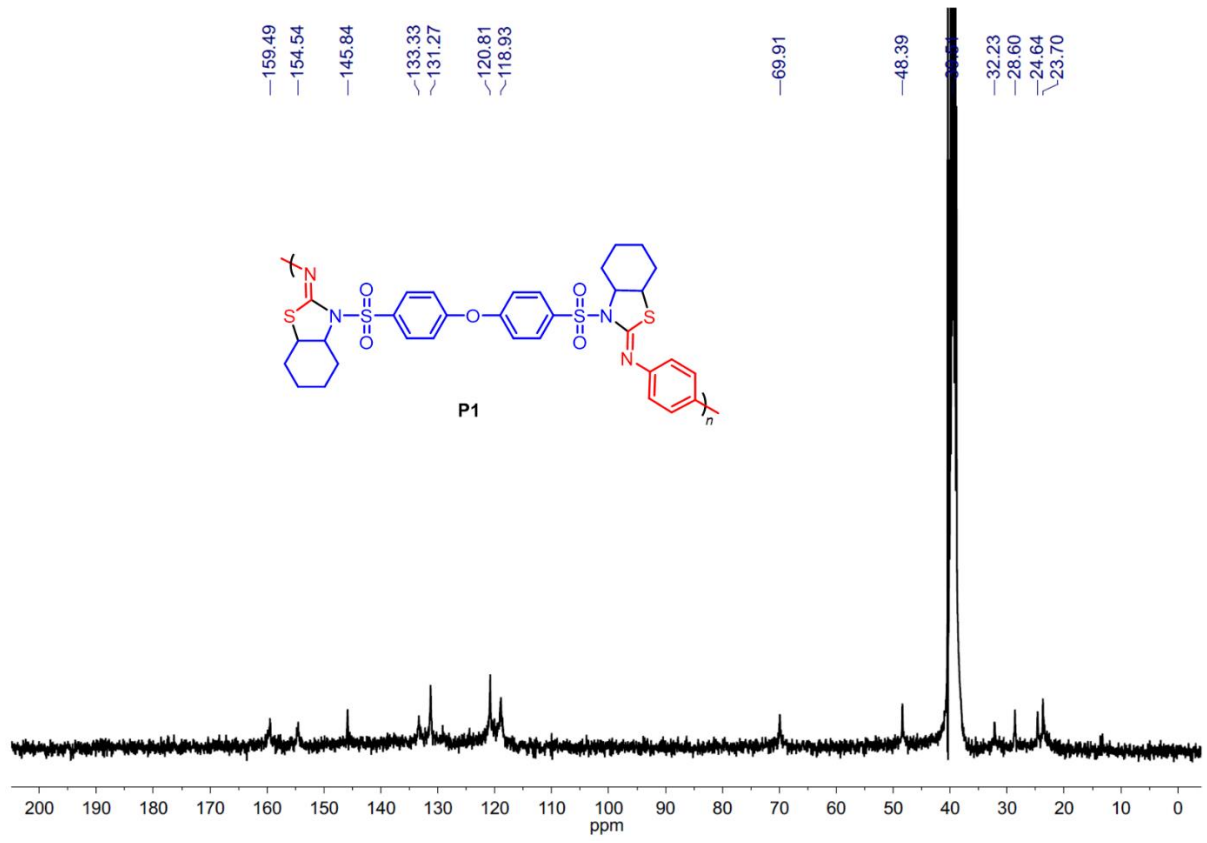
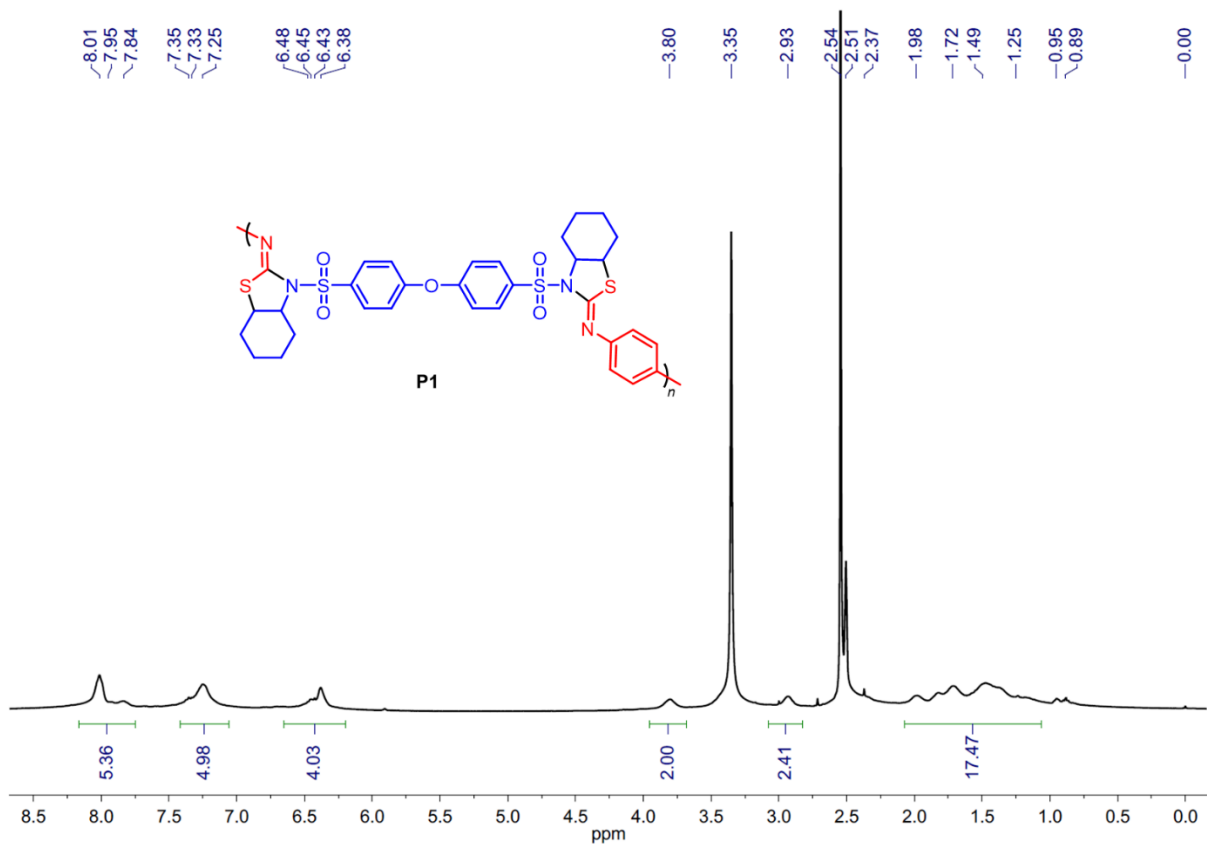
^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 0.14-1.90 (16H, m), 3.51-3.89 (2H, m), 4.23-4.75 (2H, m), 6.80-7.57 (4H, m), 7.61-8.40 (4H, m).

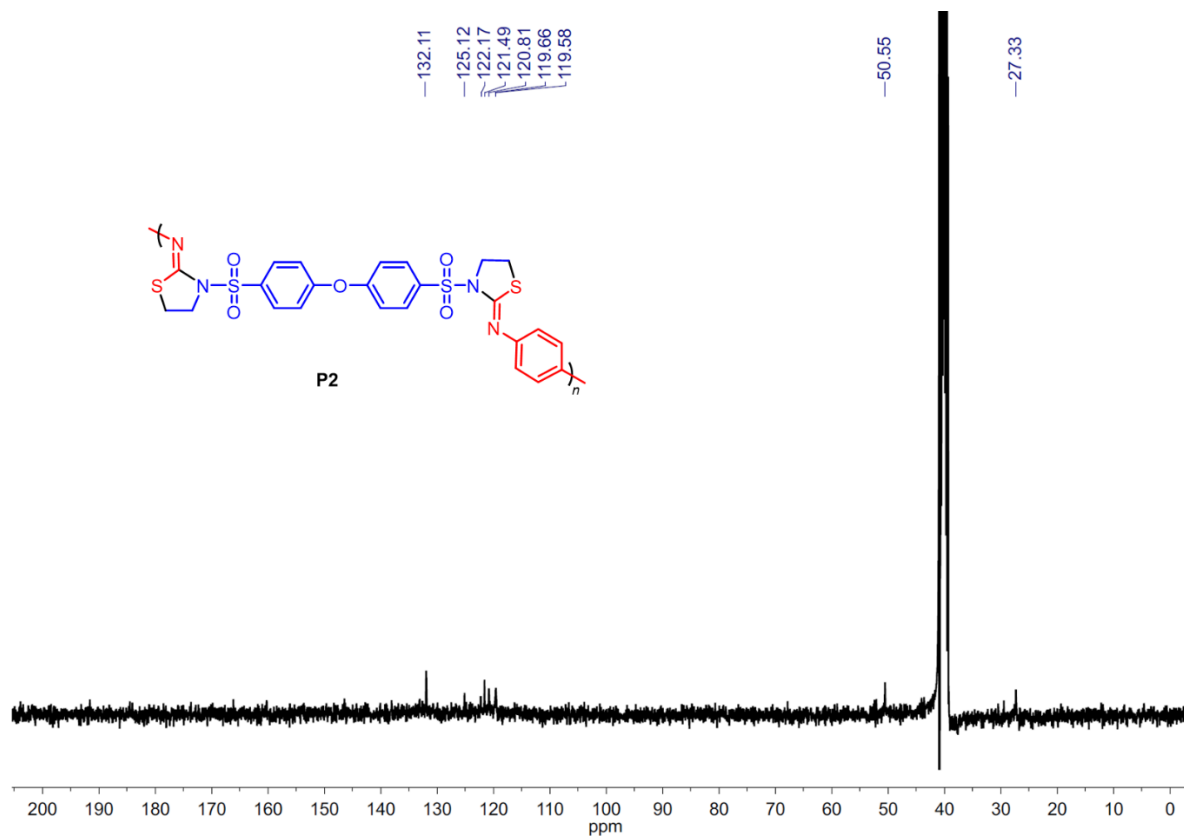
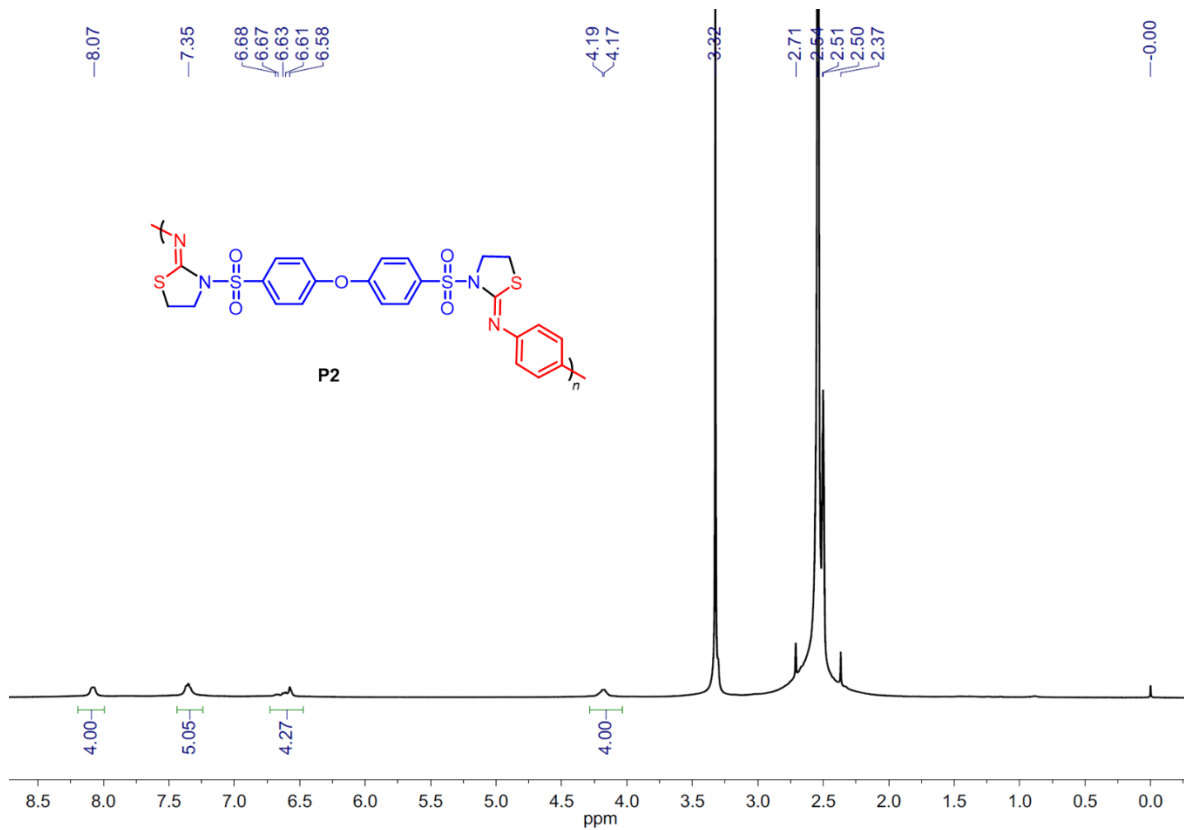
^{13}C NMR (125 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 130.61 , 121.35 , 45.85 , 44.5 , 32.6 , 29.4 , 19.1, 18.8.

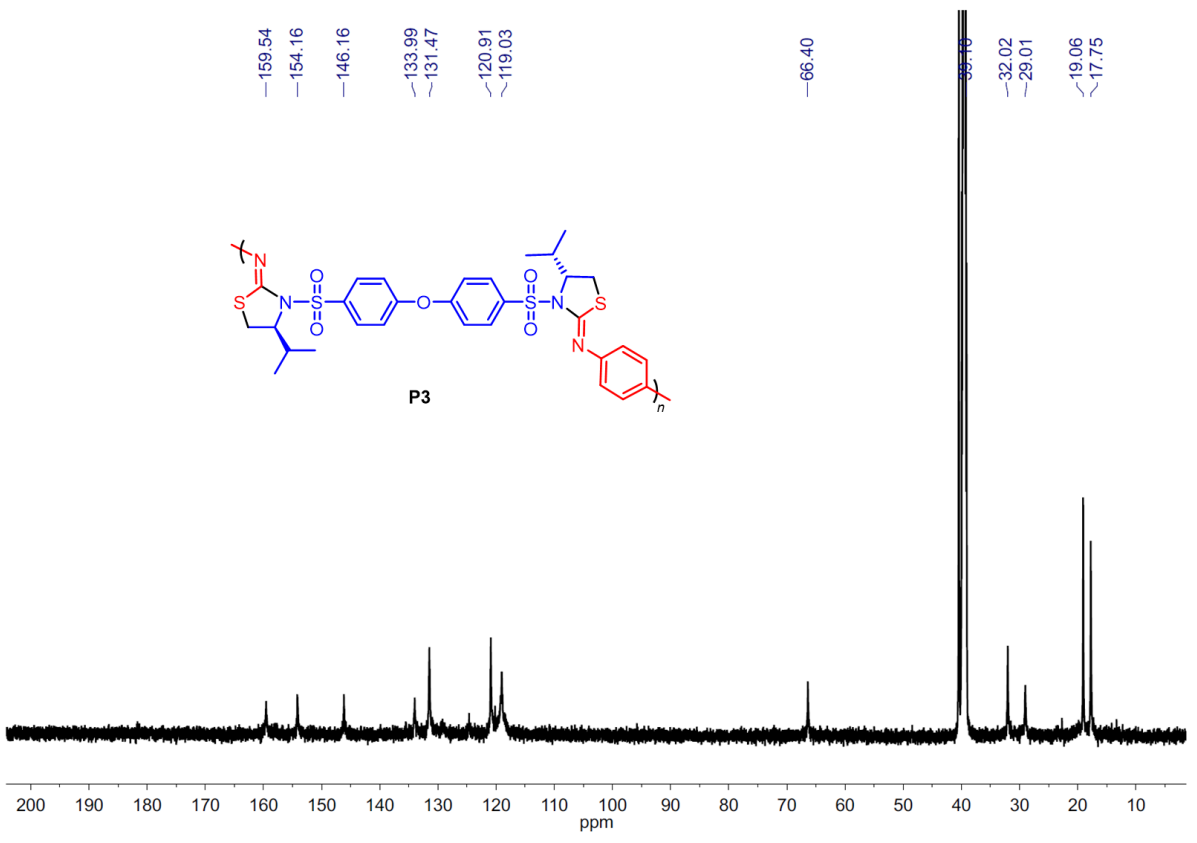
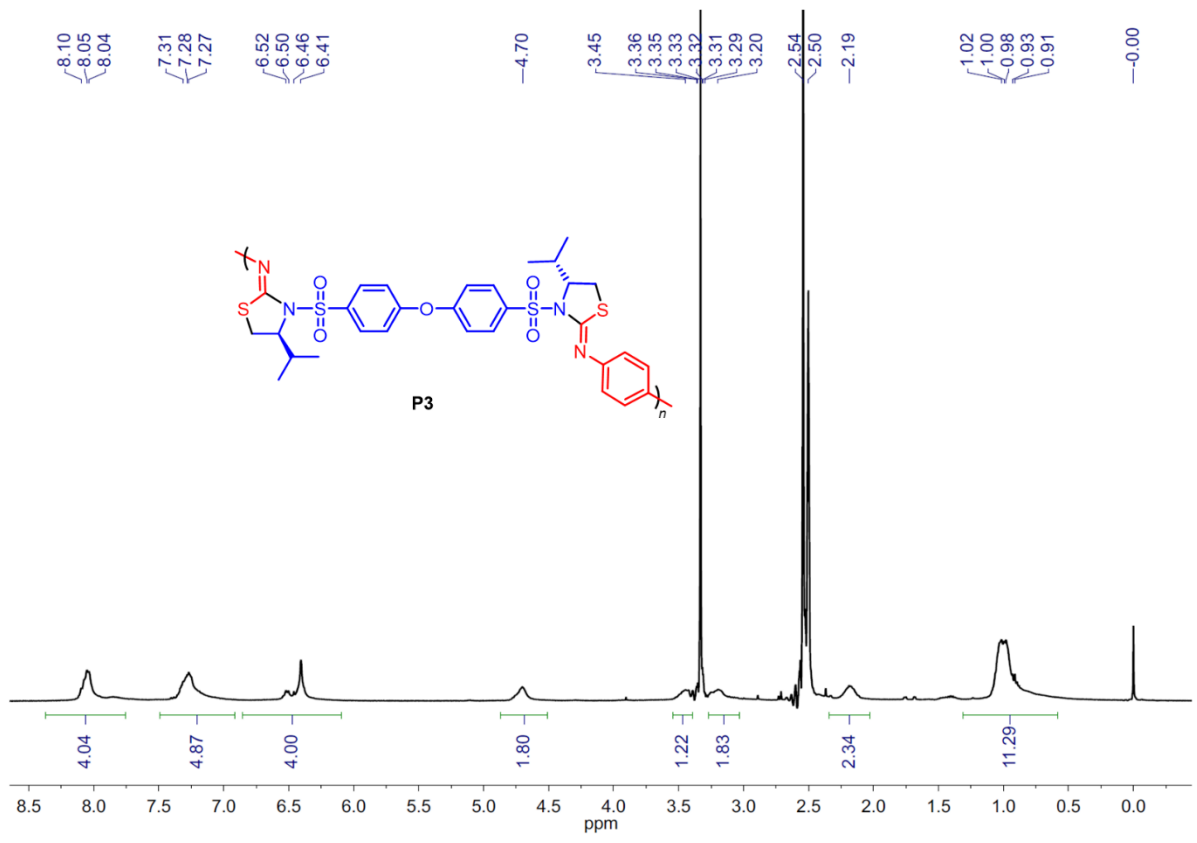


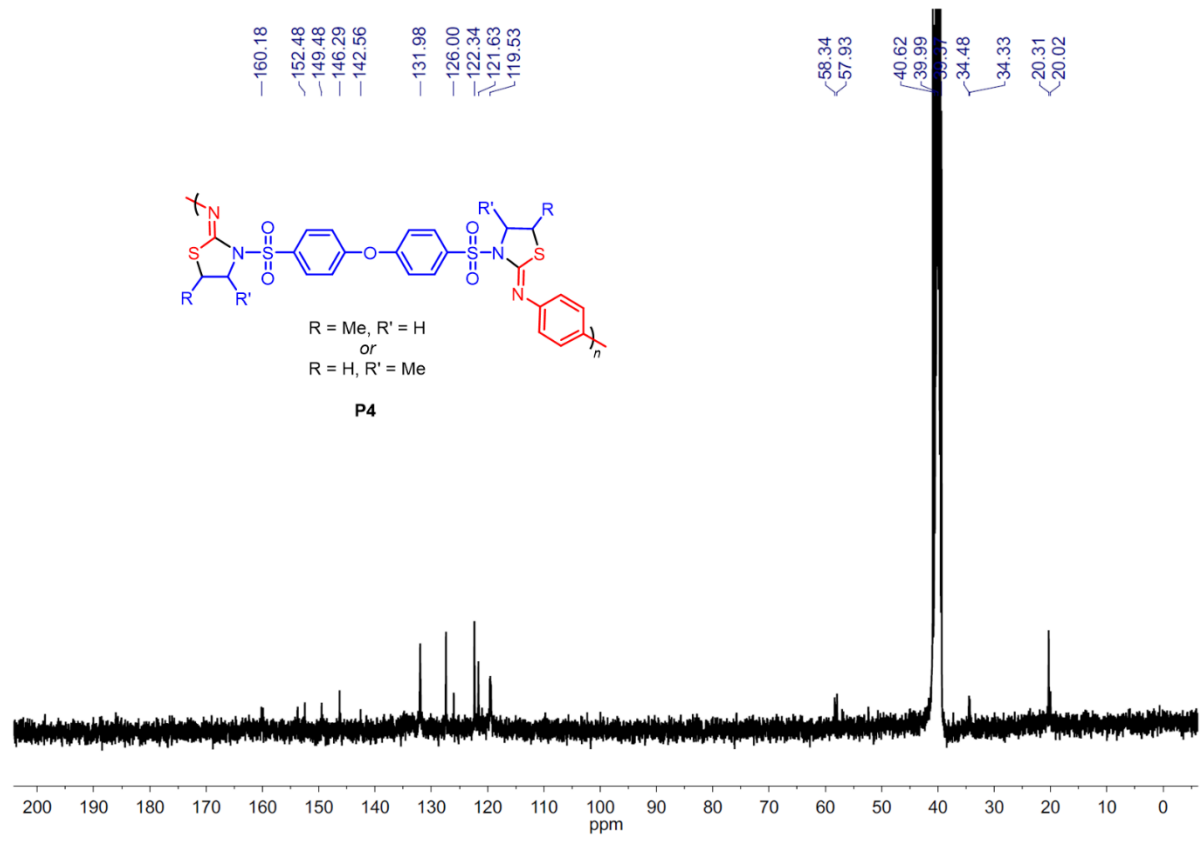
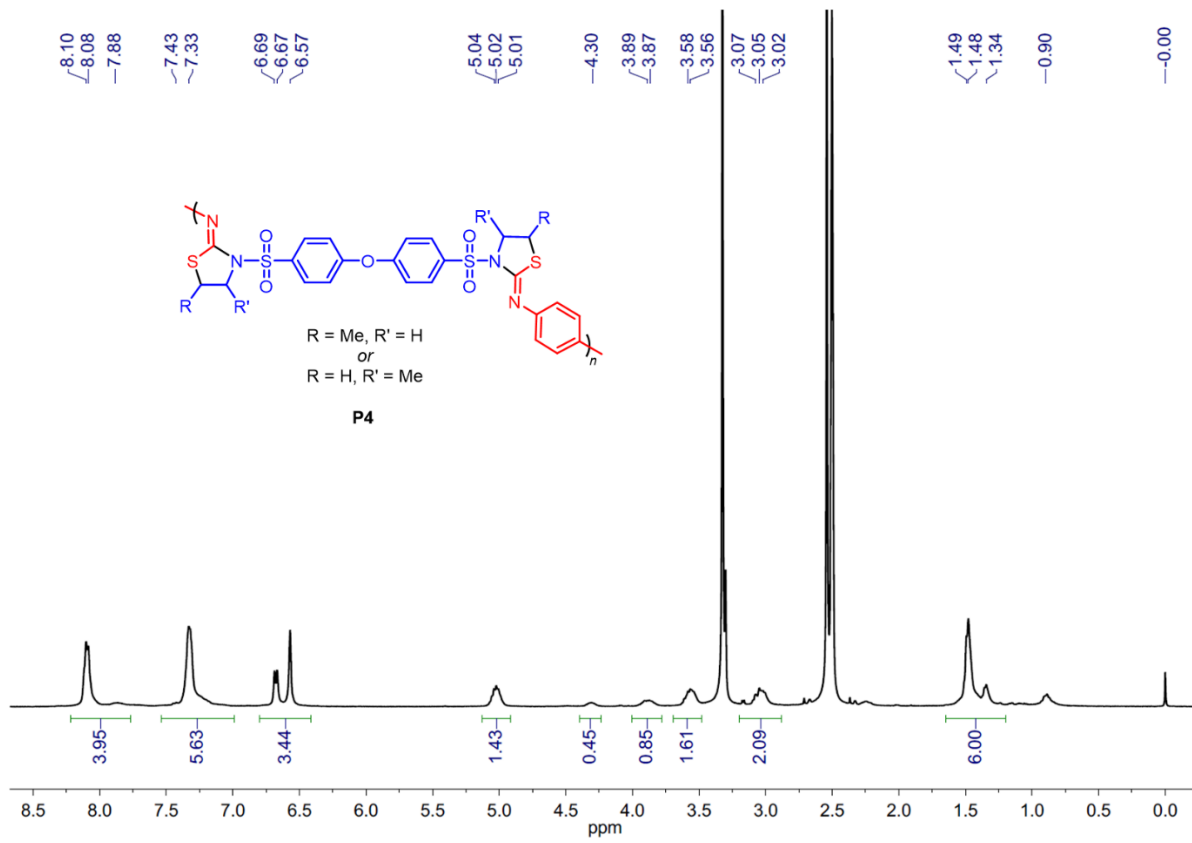


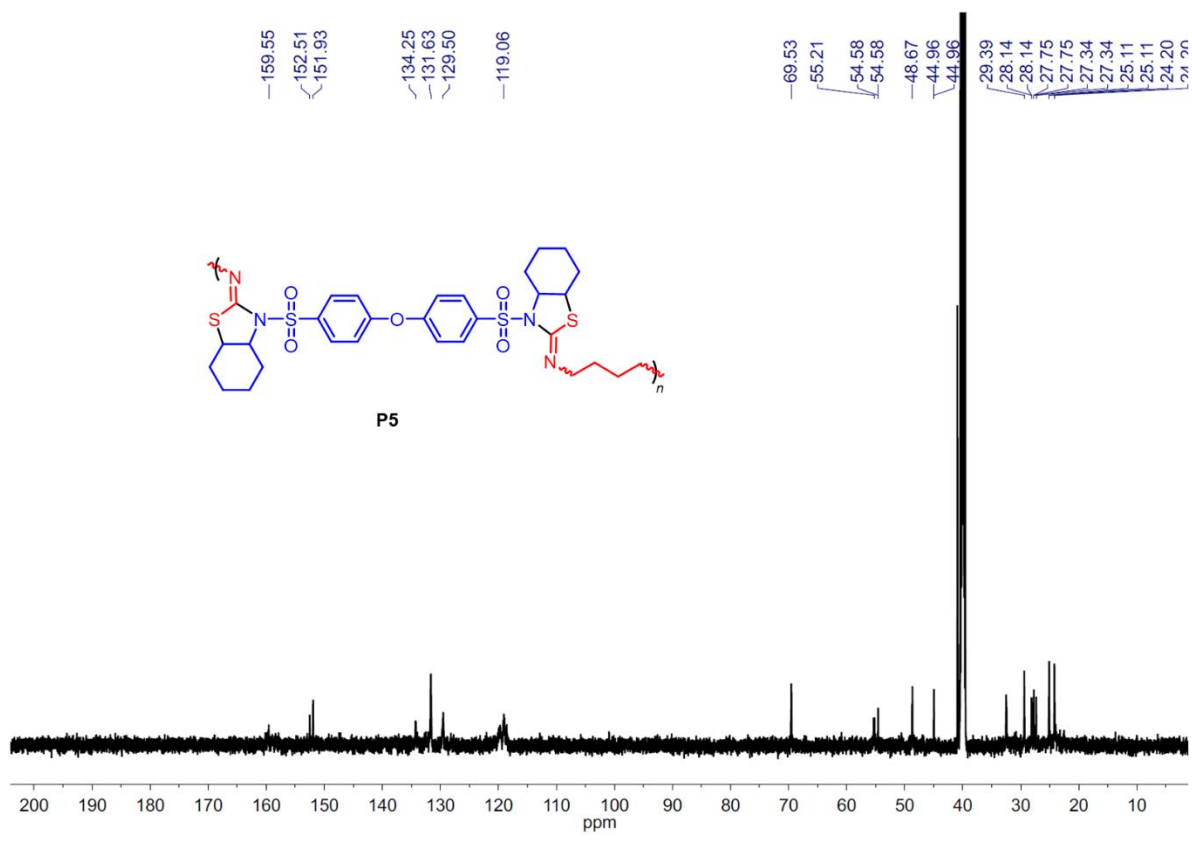
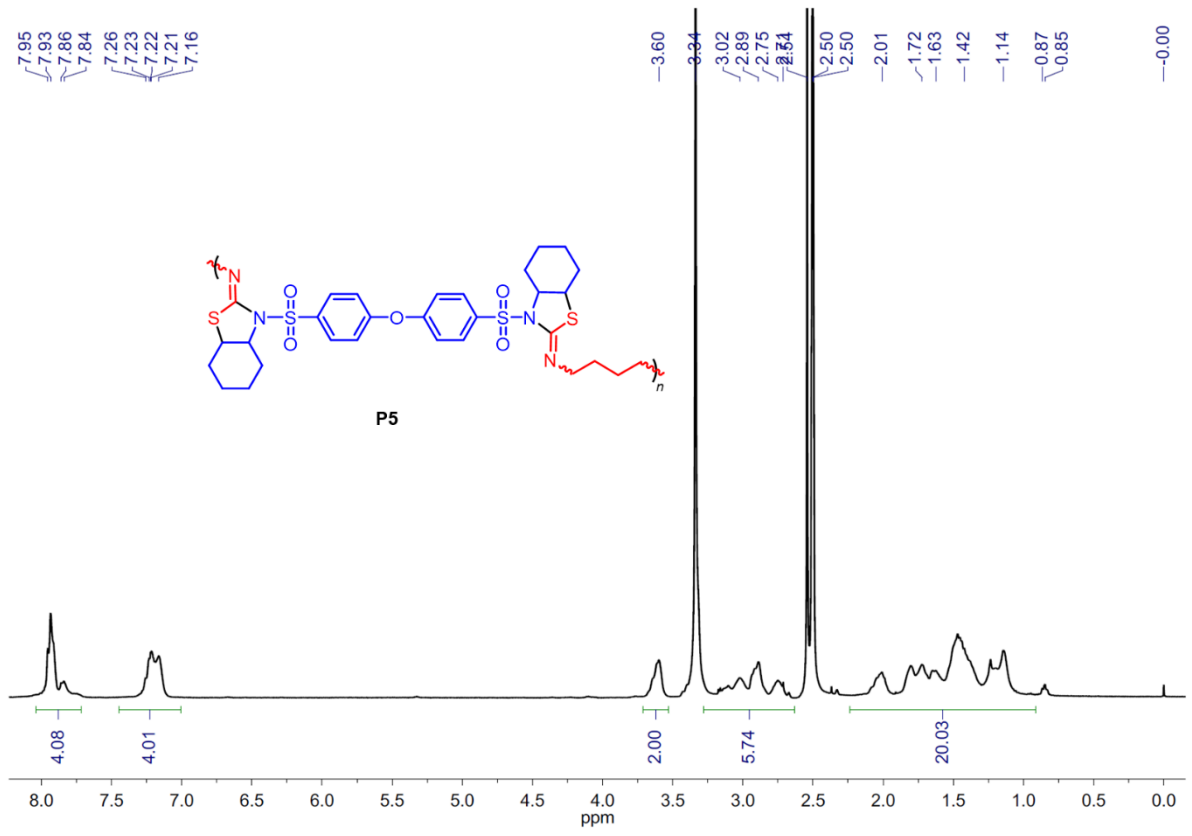


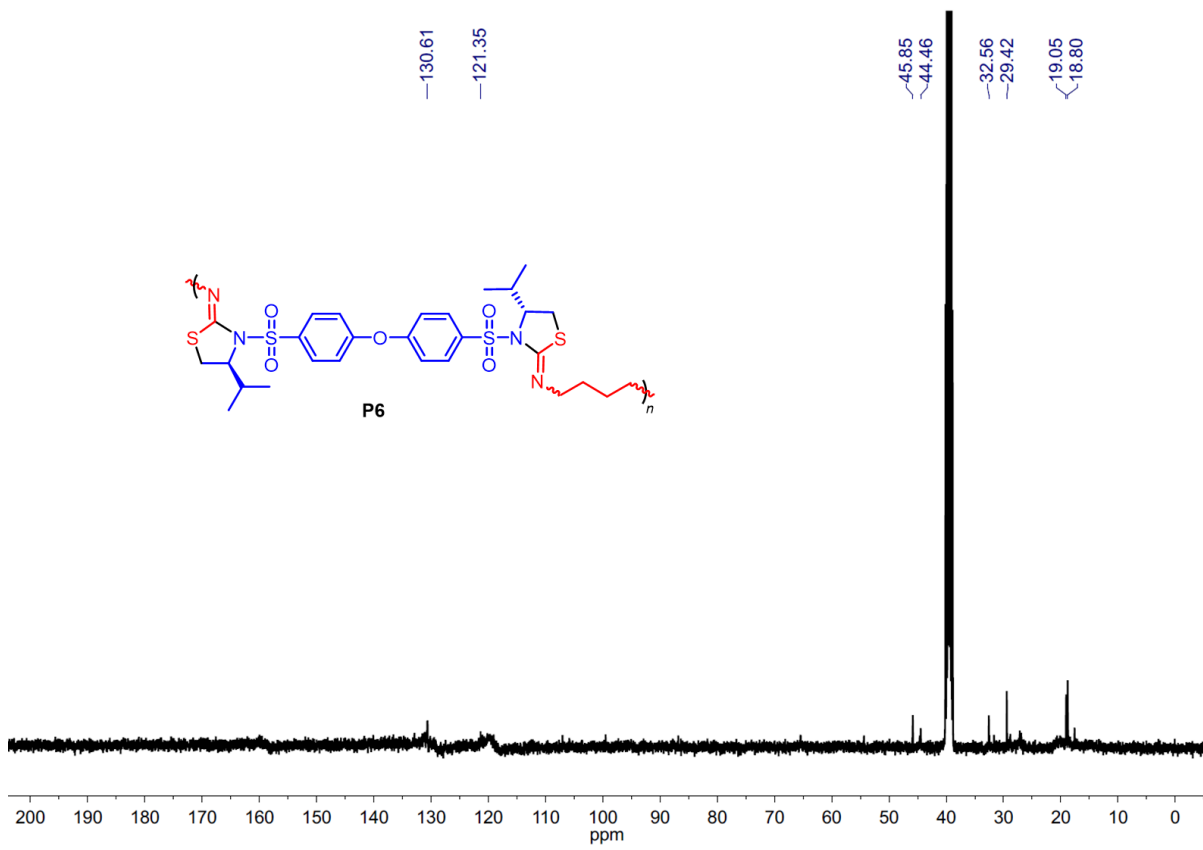
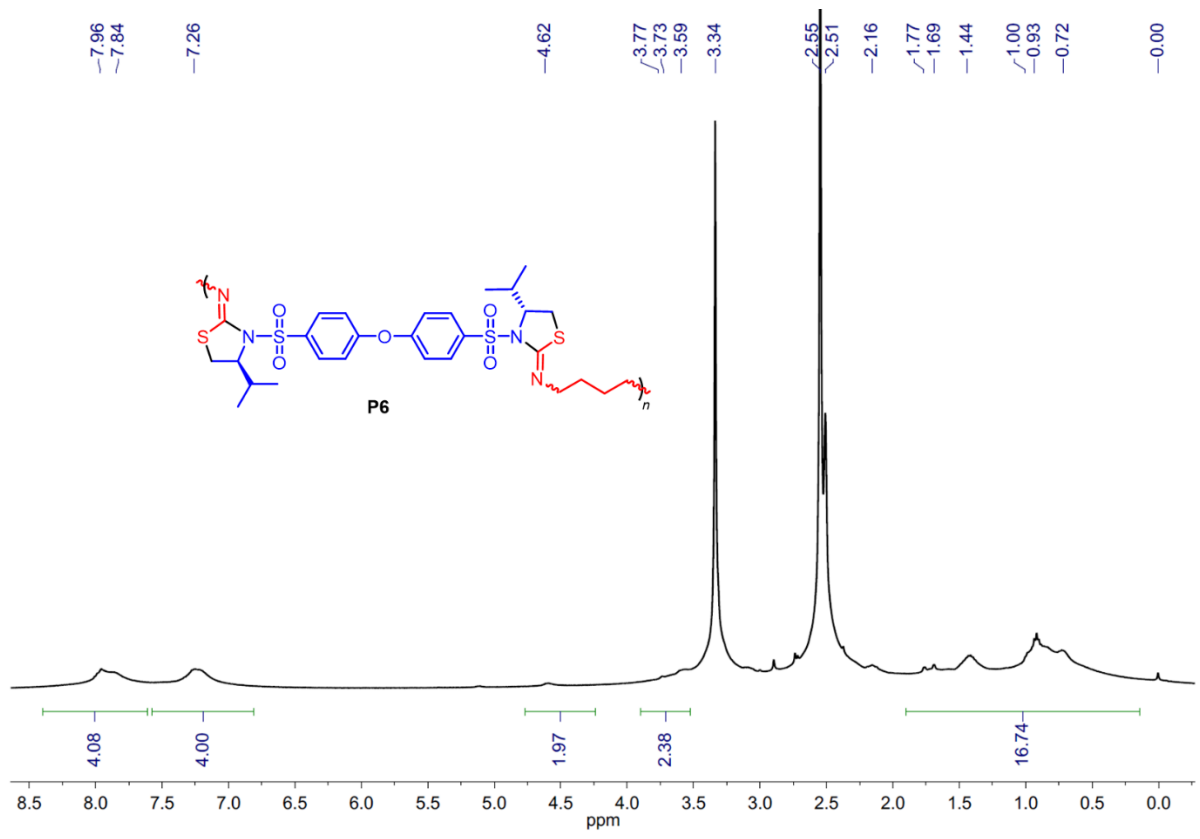






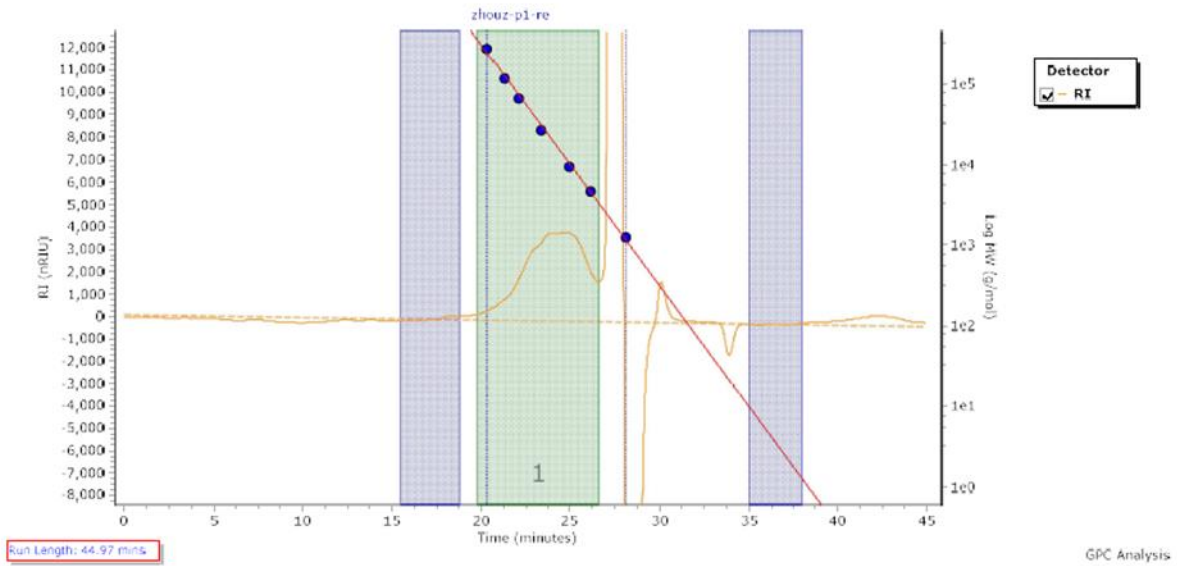




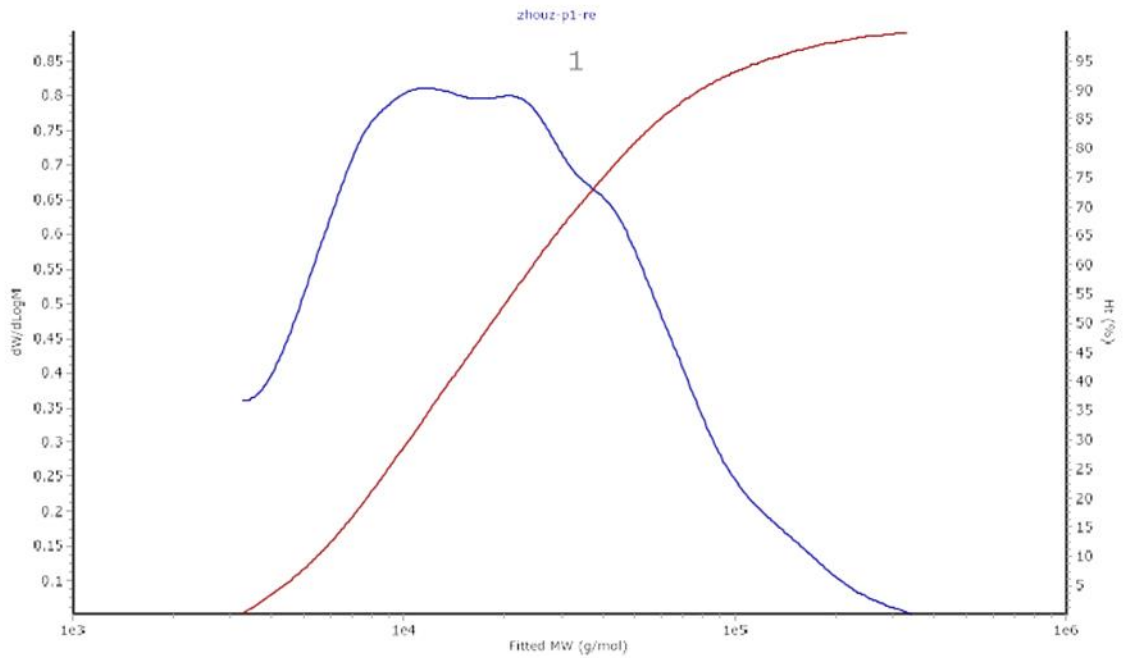


Chromatogram Plot

P1



Distribution Plot



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	11527	12821	34250	92782	167000	82563	2.671

Peak Information

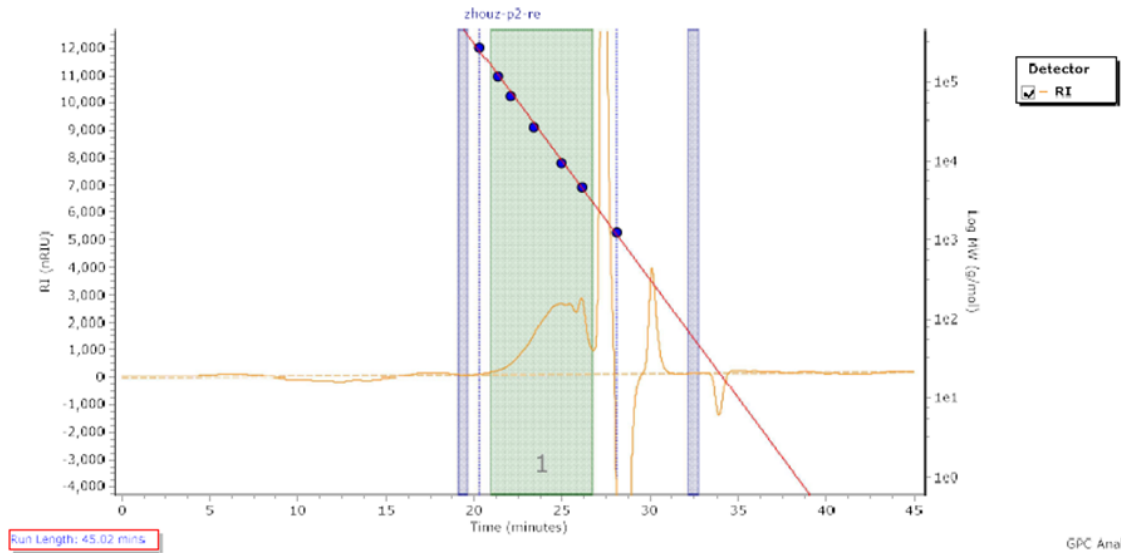
	Start (mins)	End (mins)
Baseline region 1	15.55833	18.87500
Baseline region 2	35.04167	38.07500
Peak 1	19.85000	26.61667

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	24.76667	978371.738	3962.823

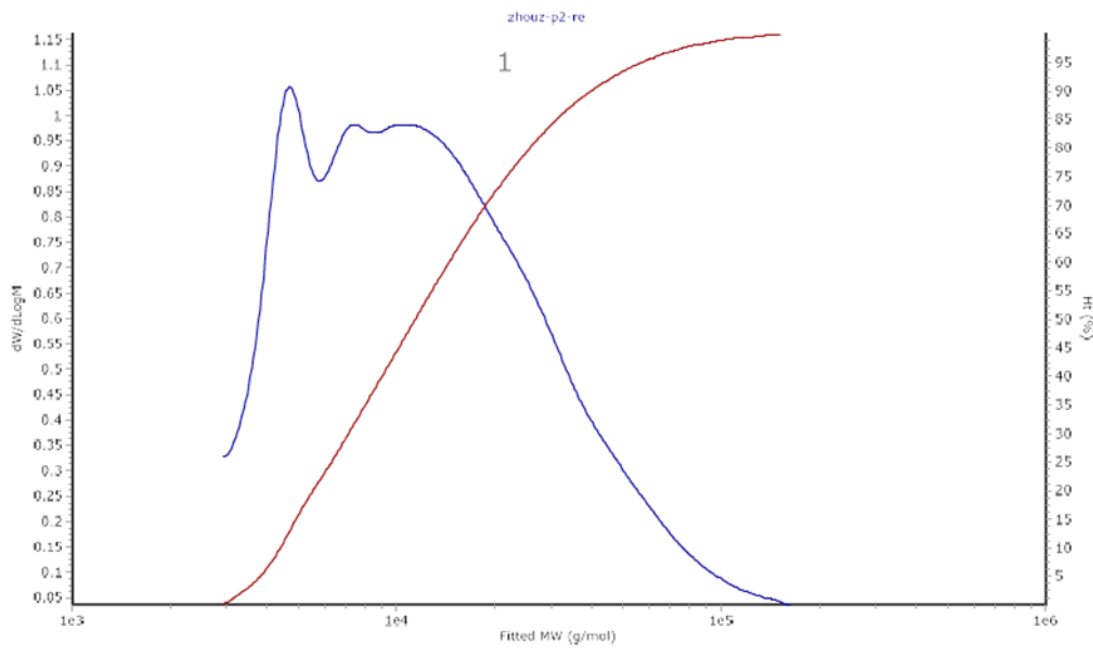
Chromatogram Plot

P2



GPC Analysis

Distribution Plot



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	4672	9167	18262	39929	70065	36000	1.992

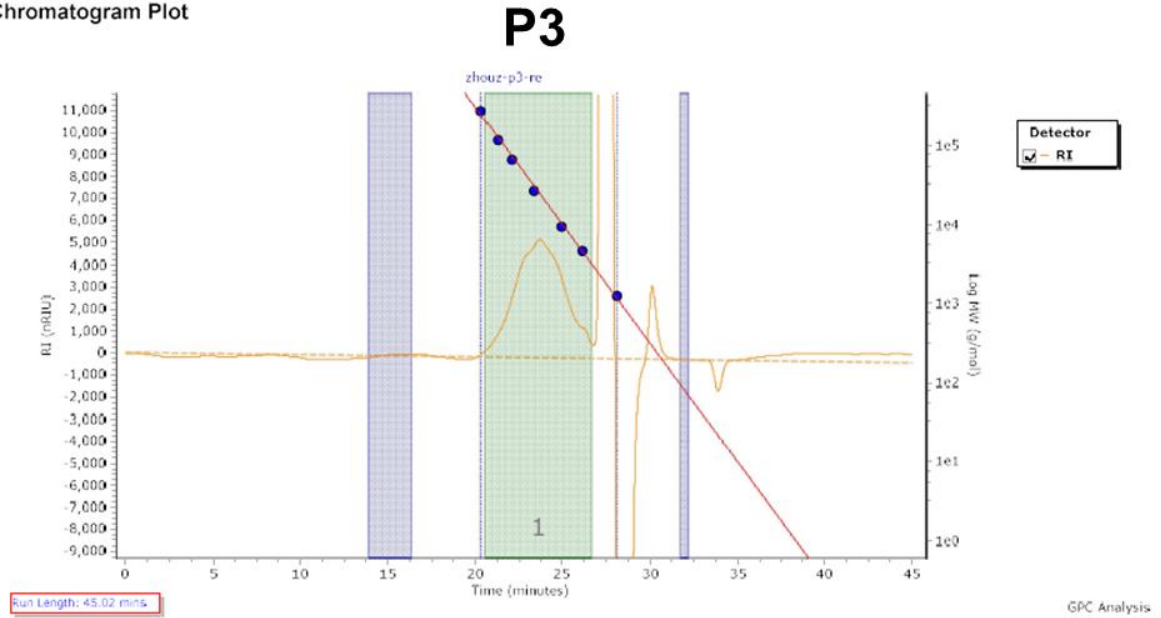
Peak Information

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Baseline region 1	19.15833	19.74167
Baseline region 2	32.16667	32.80833
Peak 1	20.94167	26.76667

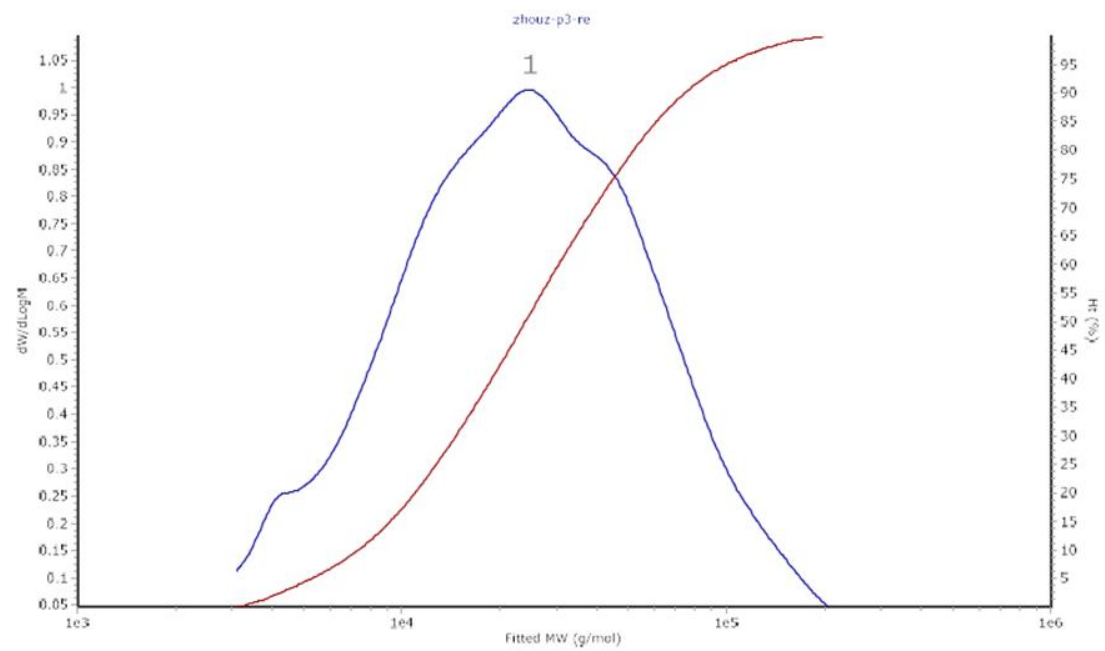
Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	26.07500	522116.458	2752.718

Chromatogram Plot



Distribution Plot



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	24628	16343	34281	63284	94720	58794	2.098

Peak Information

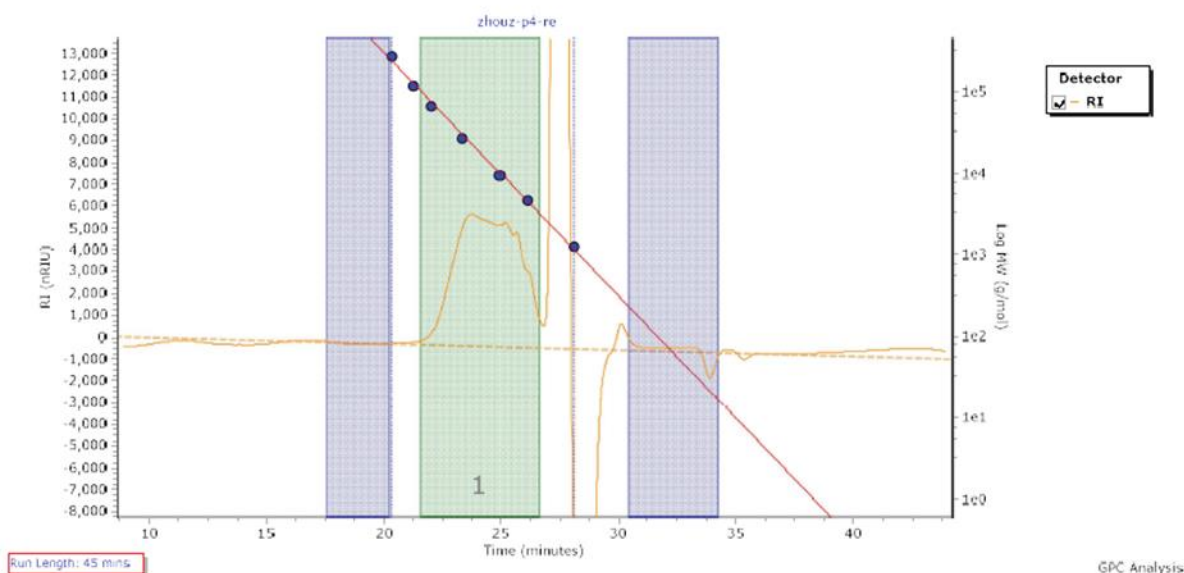
	Start (mins)	End (mins)
Baseline region 1	13.95833	16.48333
Baseline region 2	31.70000	32.27500
Peak 1	20.59167	26.69167

Peak Trace Information

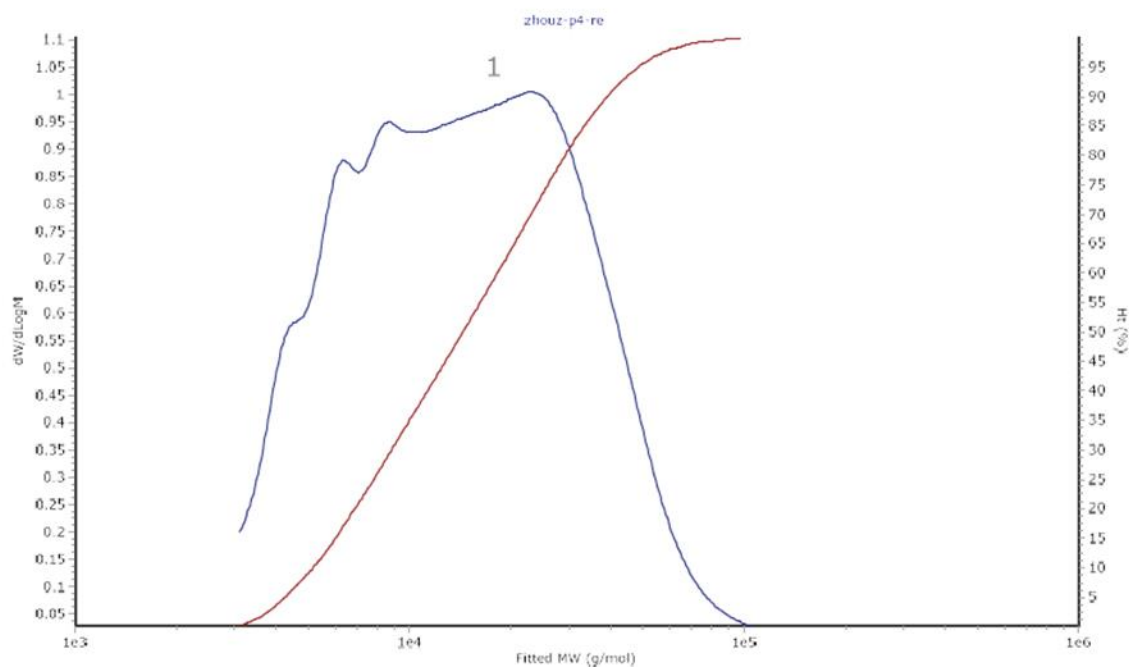
Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	23.66667	1070403.998	5323.044

Chromatogram Plot

P4



Distribution Plot



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	22986	10931	18994	30645	42767	28898	1.738

Peak Information

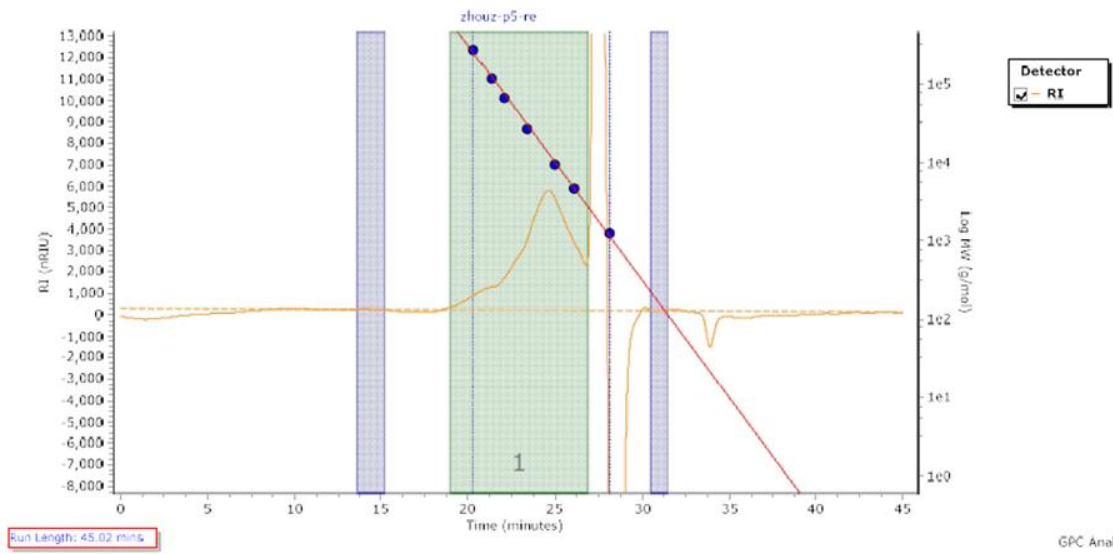
	Start (mins)	End (mins)
Baseline region 1	17.55833	20.30000
Baseline region 2	30.43333	34.25833
Peak 1	21.56667	26.68333

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	23.76667	1200180.833	6022.847

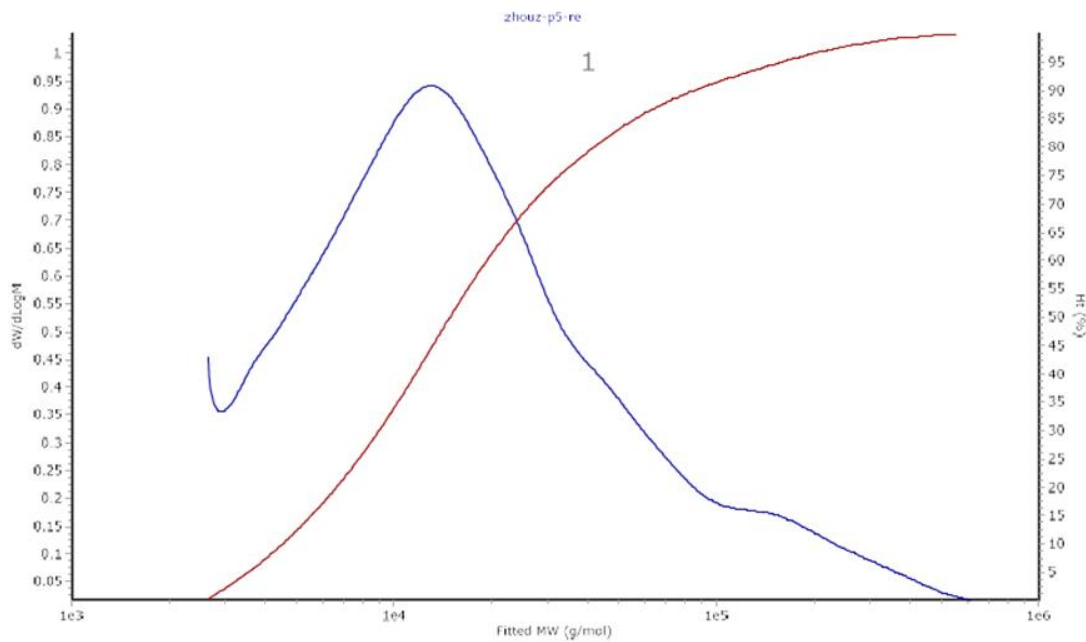
Chromatogram Plot

P5



GPC Analysis

Distribution Plot



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	13006	10710	36666	150299	290874	129868	3.424

Peak Information

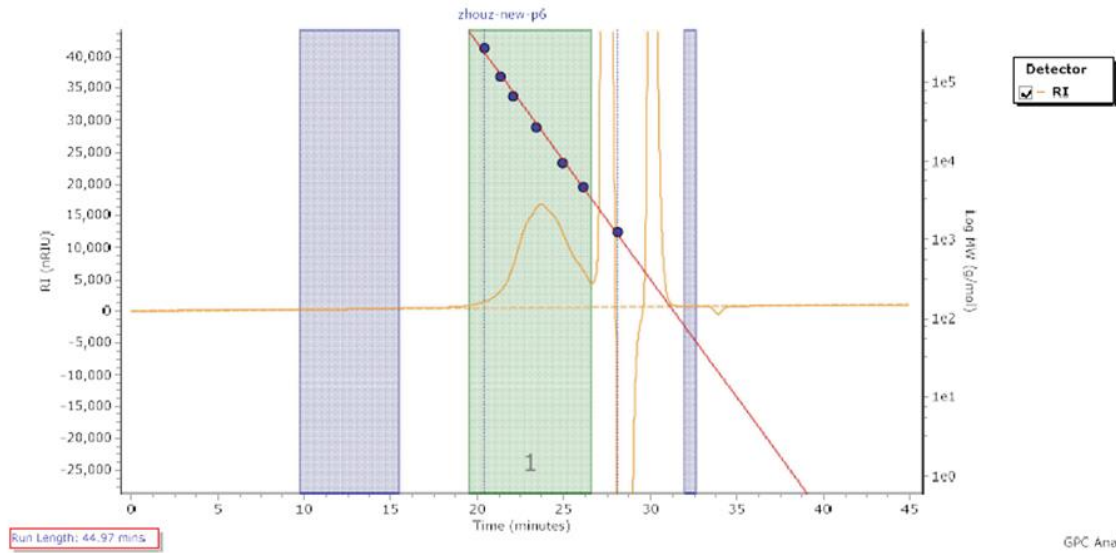
	Start (mins)	End (mins)
Baseline region 1	13.63333	15.32500
Baseline region 2	30.47500	31.55833
Peak 1	19.00000	26.91667

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	24.60000	1188274.838	5591.342

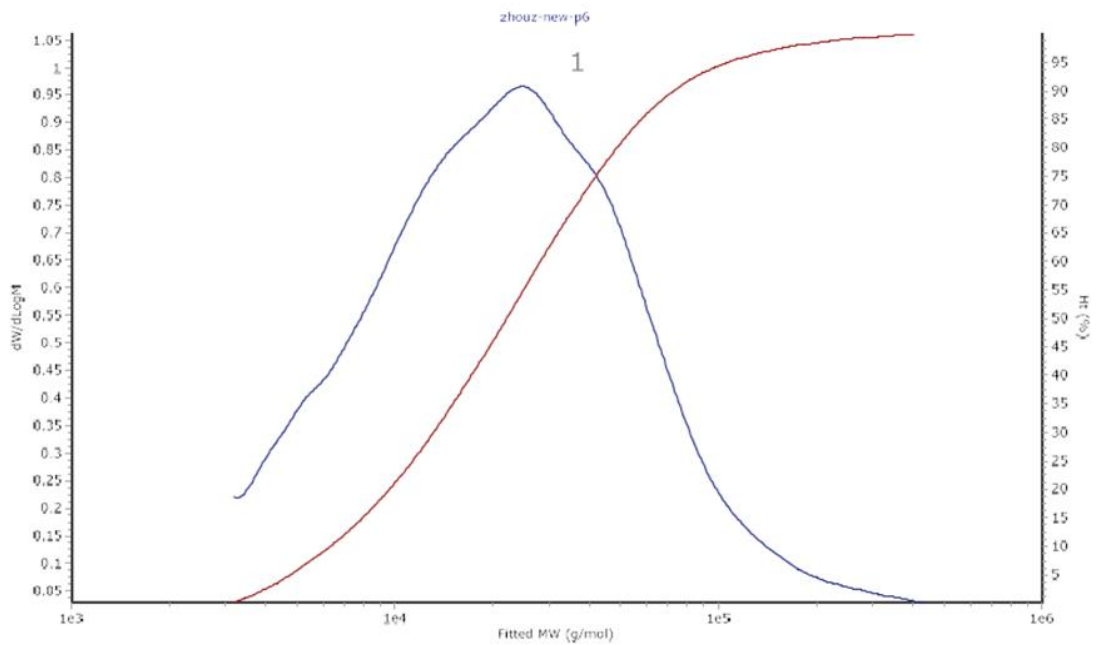
Chromatogram Plot

P6



GPC Analysis

Distribution Plot



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	24770	14846	35405	91101	186452	79880	2.385

Peak Information

	Start (mins)	End (mins)
Baseline region 1	9.81667	15.60000
Baseline region 2	31.98333	32.68333
Peak 1	19.51667	26.65000

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	23.66667	3389098.338	16343.035