Supporting information

1. Experimental Section

1.1 Materials, Reagents, and Methods

1.1.1 General information

2-methylbenzenethiol, 3-methylbenzenethiol, 4-methylbenzenethiol, 2,6-dimethylbenzenethiol, 2,4-dimethylbenzenethiol, 4-methoxybenzenethiol, *p*-cresol, 4-bromo-1-butene, 5-bromo-1-penten were purchased from Energy Chemical and used as received without further purification. NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer, or a Varian Inova 400 MHz spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts were referred to $SiMe_4$ (TMS).

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an argon-filled glovebox. Toluene and tetrahydrofuran (THF) were distilled from sodium/benzophenone under nitrogen, degassed and stored over fresh Na chips. C_6D_6 was dried over sodium. CD_2Cl_2, $CDCl_3$ was dried over CaH_2, then degassed and stored over 4 Å molecular sieves. All monomers were dried over CaH_2 overnight, vacuum distillated, and stored over activated Davison 4 Å molecular sieves in the glovebox for further use. Monomers **S1**[1], **S2**[2], **S7**[1], **S8**[1], **S9**[3], **S10**[2], **S11**[1], **S12**[1], and **S14**[1] were prepared according to the literature procedures. Sc-1 and Sc-2 were prepared according to the literature procedures.[4]

1.1.2 Typical polymerization procedure

In the glove box, a toluene solution (0.5 mL) of $[Ph_3C][B(C_6F_5)_4]$ (18.5 mg, 20 μmol) was added to a toluene solution (0.5 mL) of scandium complex (5.8 mg, 10 μmol) in a 10-mL flask. The mixture was stirred at room temperature for 5 minutes. The monomer was then added by syringe. The polymerization was immediately quenched by addition of 1 mL methanol. The quenched mixture was precipitated into 20 mL of methanol, stirred for 1 h, filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight.

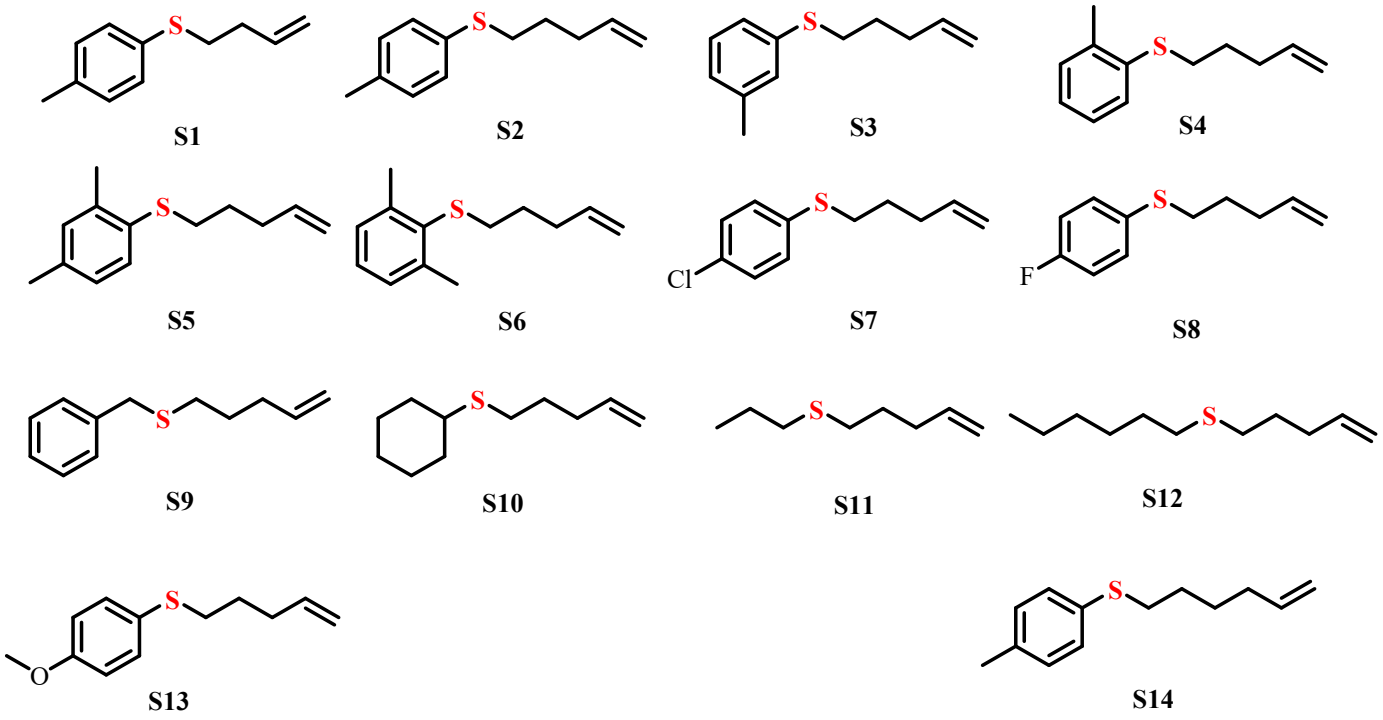
1.1.3 Polymer characterizations.

Polymer number (M_n) and weight (M_w) average molecular weights and polydispersity index (PDI = M_w/M_n) were measured by gel permeation chromatography (GPC) analyses carried out at 28 ºC and a flow rate of 1.0 mL/min with CH_2Cl_2 as the eluent, on a Agilent 1260 GPC instrument equipped with four PLgel 5 µm mixed-C columns.

Thermal properties were determined using a TA DSC Q20 at rate of 10 K/min and Mettler-Toledo TGA/SDTA 851.

Power X-ray diffraction data were collected on an EMPYREAN diffractometer with Cu KR radiation (λ = 1.54056 Å) over the 2θ range of 5-40° with a scan speed of 0.3333 °/s and a step size of 0.01° at room temperature.

1.2 Synthesis and Characterization of α-olefin monomers



Scheme S1. Structures of α-olefin monomers(**S1-S14**)

S3: In a flame dried equipped under argon, 5.00 g of 3-methylbenzenethiol (40.3 mmol, 1.0 equiv) was dissolved in 45 mL dimethylformamide and cooled to 0 °C. 1.4 g (60.4 mmol, 1.5 equiv) of NaH (available as a 60% oil dispersion) was added and the slurry was allowed to stir for 5 min. 6.6 g 5-bromo-1-penten (44.3 mmol, 1.1 equiv) was then added via syringe. The reaction was allowed to warm to room temperature over 12h, at

which point full conversion was observed by TLC analysis. The reaction mixture was cooled to 0 ℃, carefully quenched via the dropwise addition of H_2O. Then diluted with ~ 500 mL H_2O. The aqueous phase was extracted three times with diethyl ether. The combined organics were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness in vacuo. **S3** was obtained as a colorless oil (91%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.11 (m, 3H), 7.01 (d, *J* = 7.2 Hz, 1H), 5.82 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.07 (d, *J* = 17.2 Hz, 1H), 5.02 (d, *J* = 10.3 Hz, 1H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.35 (s, 3H), 2.22 (dd, *J* = 14.1, 7.0 Hz, 2H), 1.83 – 1.72 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.48, 137.58, 136.54, 129.66, 128.67, 126.62, 125.97, 115.36, 32.87, 32.72, 28.33, 21.34. HRMS (EI^+) m/z calcd for $C_{12}H_{16}S^+$ $[M]^+$ 192.3214, found 192.0945.

S4: In a flame dried equipped under argon, 5.00 g of 2-methylbenzenethiol (40.3 mmol, 1.0 equiv) was dissolved in 45 mL dimethylformamide and cooled to 0 ℃. 1.40 g (60.4 mmol, 1.5 equiv) of NaH (available as a 60% oil dispersion) was added and the slurry was allowed to stir for 5 min. 6.6 g 5-bromo-1-penten (44.3 mmol, 1.1 equiv) was then added via syringe. The reaction was allowed to warm to room temperature over 12h, at which point full conversion was observed by TLC analysis. The reaction mixture was cooled to 0 ℃, carefully quenched via the dropwise addition of H_2O. Then diluted with ~ 500 mL H_2O. The aqueous phase was extracted three times with diethyl ether. The combined organics were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness in vacuo. **S4** was obtained as a colorless oil (95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 1H), 7.21 – 7.15 (m, 2H), 7.10 (td, *J* = 7.2, 1.3 Hz, 1H), 5.81 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.07 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.02 (d, *J* = 10.1 Hz, 1H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.39 (s, 3H), 2.29 – 2.17 (m, 2H), 1.84 – 1.72 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.68, 137.41, 136.17, 130.18, 127.70, 126.49, 125.52, 115.55, 33.01, 32.29, 28.30, 20.51. HRMS (EI^+) m/z calcd for $C_{12}H_{16}S^+$ $[M]^+$ 192.3214, found 192.0965.

S5: In a flame dried equipped under argon, 5.00 g of 2,4-dimethylbenzenethiol (36.2 mmol, 1.0 equiv) was dissolved in 45 mL dimethylformamide and cooled to 0 ℃. 1.30 g (54.3 mmol, 1.5 equiv) of NaH (available as a 60% oil dispersion) was added and the slurry was allowed to stir for 5 min. 5.9 g 5-bromo-1-penten (39.8 mmol, 1.1 equiv) was then added via syringe. The reaction was allowed to warm to room temperature over 12h,

at which point full conversion was observed by TLC analysis. The reaction mixture was cooled to 0 °C, carefully quenched via the dropwise addition of H_2O. Then diluted with ~ 500 mL H_2O. The aqueous phase was extracted three times with diethyl ether. The combined organics were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness in vacuo. **S5** was obtained as a colorless oil (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.9 Hz, 1H), 7.06 – 6.94 (m, 2H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.06 (dq, *J* = 17.1, 1.8 Hz, 1H), 5.02 (d, *J* = 10.1 Hz, 1H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H), 2.27 – 2.16 (m, 2H), 1.80 – 1.70 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.00, 137.67, 135.62, 132.25, 131.05, 129.19, 127.12, 115.33, 32.95, 32.87, 28.32, 20.89, 20.42. HRMS (EI$^+$) m/z calcd for $C_{13}H_{18}S^+$ $[M]^+$ 206.3480, found 206.1122.

S6: In a flame dried equipped under argon, 5.00 g of 2,6-dimethylbenzenethiol (36.2 mmol, 1.0 equiv) was dissolved in 45 mL dimethylformamide and cooled to 0 °C. 1.30 g (54.3 mmol, 1.5 equiv) of NaH (available as a 60% oil dispersion) was added and the slurry was allowed to stir for 5 min. 5.9 g 5-bromo-1-penten (39.8 mmol, 1.1 equiv) was then added via syringe. The reaction was allowed to warm to room temperature over 12h, at which point full conversion was observed by TLC analysis. The reaction mixture was cooled to 0 °C, carefully quenched via the dropwise addition of H_2O. Then diluted with ~ 500 mL H_2O. The aqueous phase was extracted three times with diethyl ether. The combined organics were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness in vacuo. **S6** was obtained as a colorless oil (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.05 (m, 3H), 5.76 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.00 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.96 (d, *J* = 10.2 Hz, 1H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.55 (s, 6H), 2.20 – 2.12 (m, 2H), 1.68 – 1.58 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.11, 137.82, 133.86, 128.10, 115.25, 34.78, 32.99, 29.11, 22.17. HRMS (EI$^+$) m/z calcd for $C_{13}H_{18}S^+$ $[M]^+$ 206.3480, found 206.1121.

S13: In a flame dried equipped under argon, 5.00 g of 4-methoxybenzenethiol (35.7 mmol, 1.0 equiv) was dissolved in 45 mL dimethylformamide and cooled to 0 °C. 1.3 g (53.5 mmol, 1.5 equiv) of NaH (available as a 60% oil dispersion) was added and the slurry was allowed to stir for 5 min. 5.8 g 5-bromo-1-penten (39.3 mmol, 1.1 equiv) was then added via syringe. The reaction was allowed to warm to room temperature over 12h, at

which point full conversion was observed by TLC analysis. The reaction mixture was cooled to 0 °C, carefully quenched via the dropwise addition of H_2O. Then diluted with ~ 500 mL H_2O. The aqueous phase was extracted three times with diethyl ether. The combined organics were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness in vacuo. **S13** was obtained as a colorless oil (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.77 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.02 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.97 (d, *J* = 10.1 Hz, 1H), 3.79 (s, 3H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.23 – 2.09 (m, 2H), 1.74 – 1.61 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.71, 137.60, 132.95, 126.60, 115.14, 114.42, 55.12, 35.03, 32.51, 28.40. HRMS (EI$^+$) m/z calcd for $C_{12}H_{16}OS^+$ $[M]^+$ 208.3208, found 208.0915.

Table S1 Oxidation of **PS2** by mCPBA[a]

Entry	**PS2**	**mCPBA**	[S2]/mCPBA	t(h)	Yield(%)[b]		
					-S-	-SO-	$-SO_2-$
1	100mg	89.9mg	1/1	12	30.4	69.6	0
2	100mg	98.8mg	1/1.1	12	12.6	87.4	0
3	100mg	107.8mg	1/1.2	12	0	95.8	4.2
4	100mg	134.8mg	1/1.5	12	0	73.1	26.9
5	100mg	179.7mg	1/2	12	0	0	100
6[c]	100mg	108mg	1/0.2	12	82.6	11.5	5.9

[a] Conditions：100mg **PS2** (M_n = 44 kg/mol, PDI = 1.53), in 20mL CH_2Cl_2, 25℃, mCPBA= m-chloro-perbenzoic acid; [b] Determined by ^{1}H NMR spectroscopy in $CDCl_3$; [c] Oxidation by oxone, 60℃, in 20mL EtOH

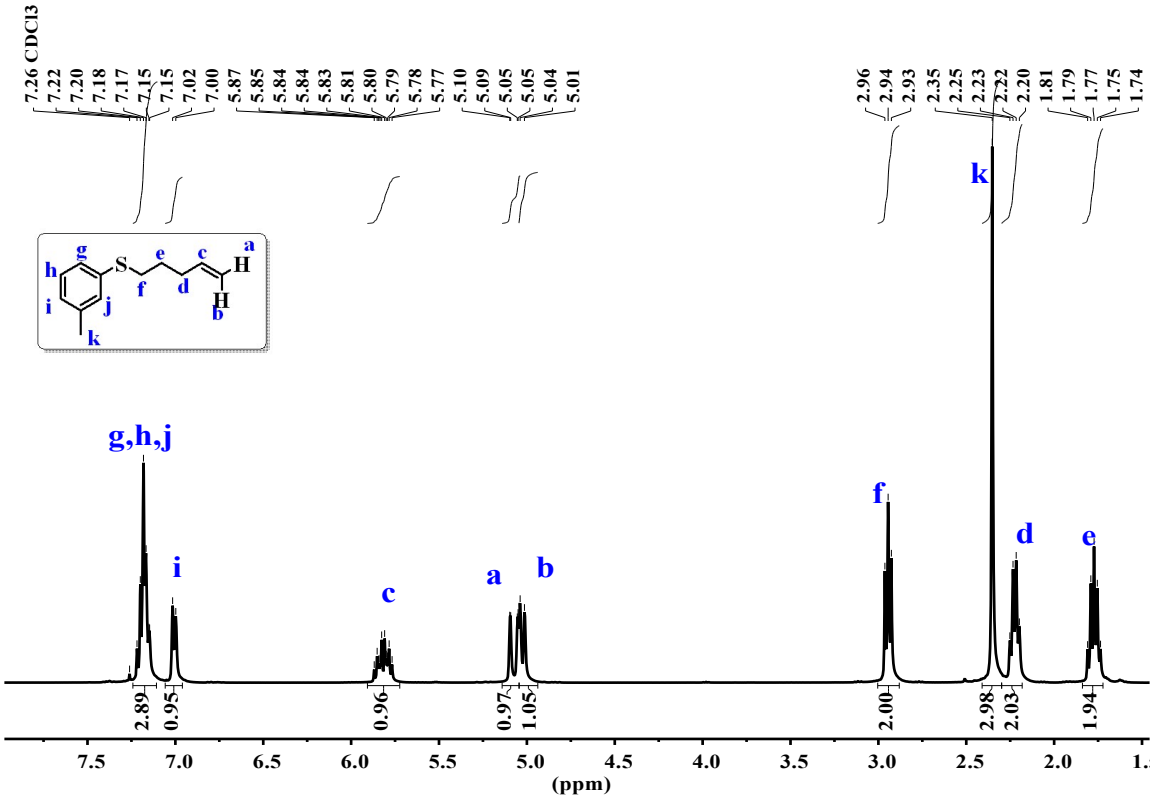


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **S3.**

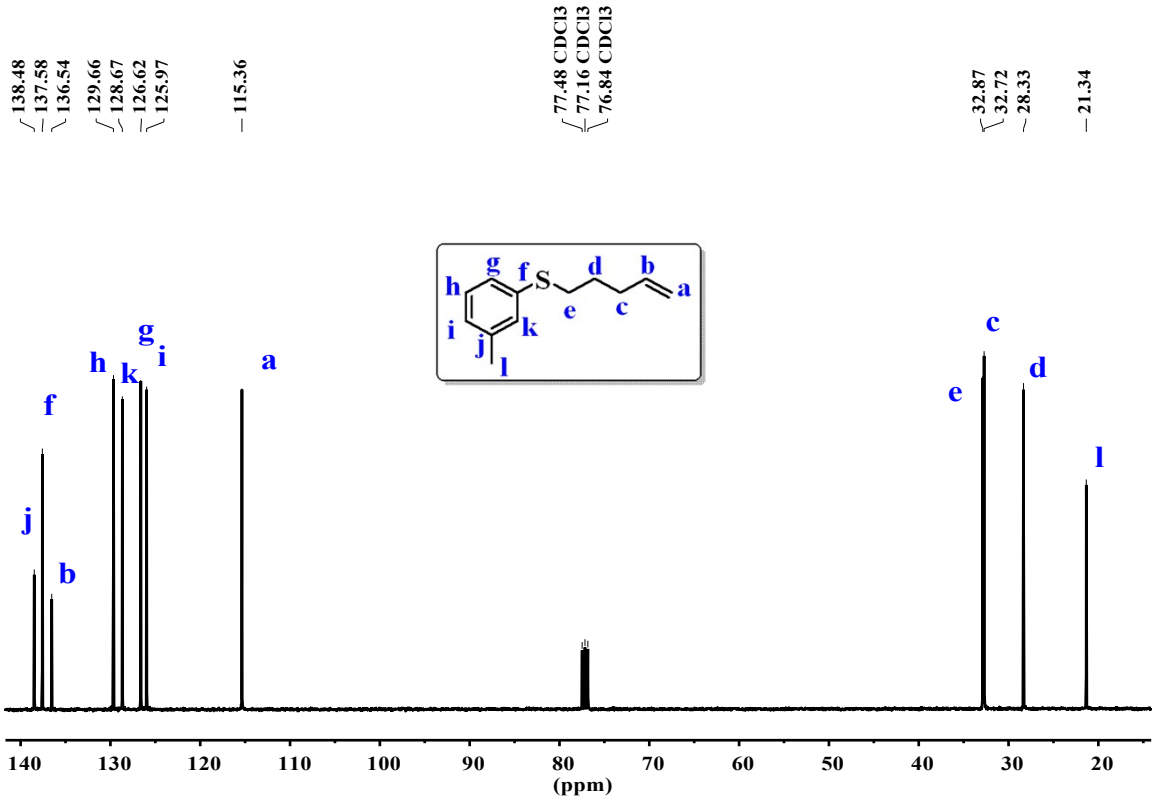


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of **S3**.

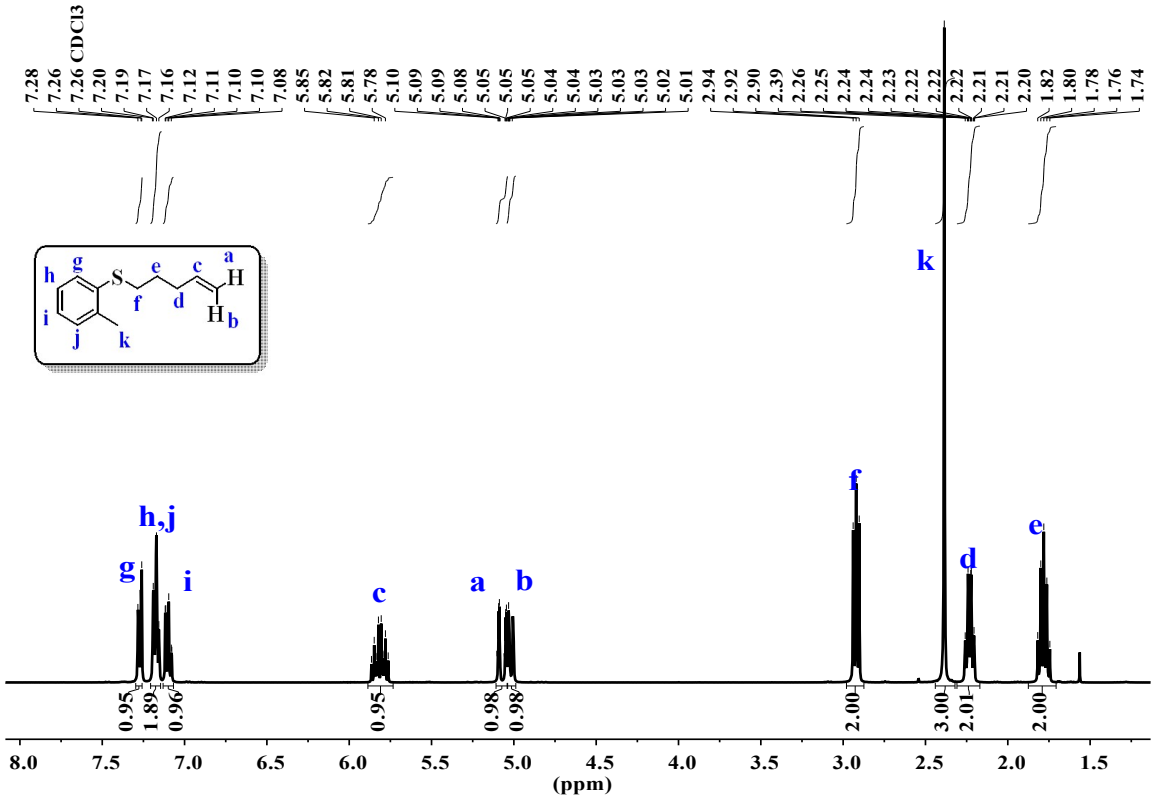


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **S4.**

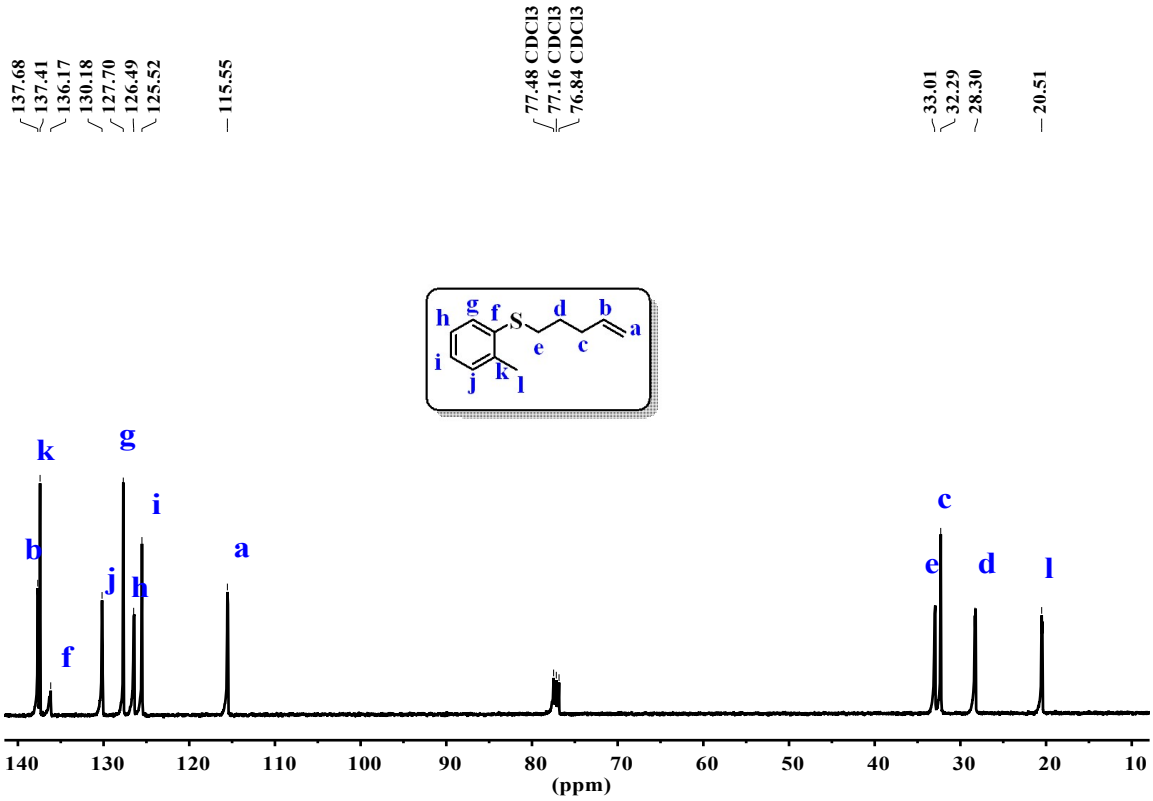


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of **S4**.

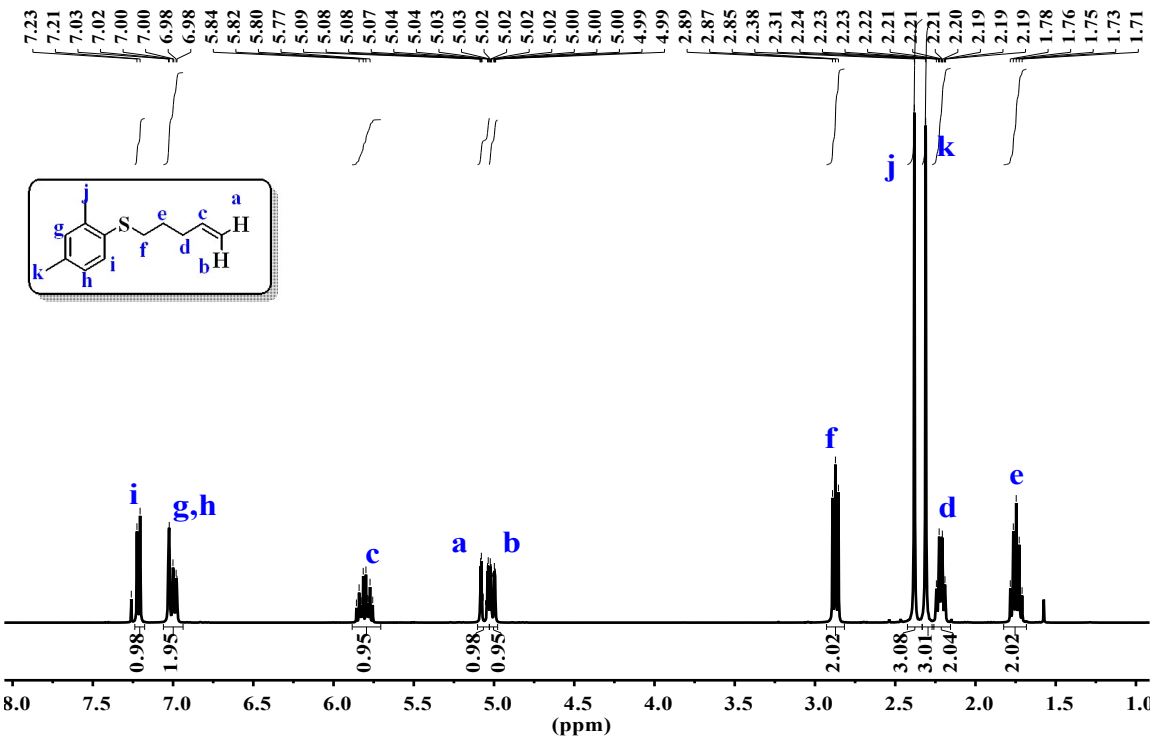


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of the **S5.**

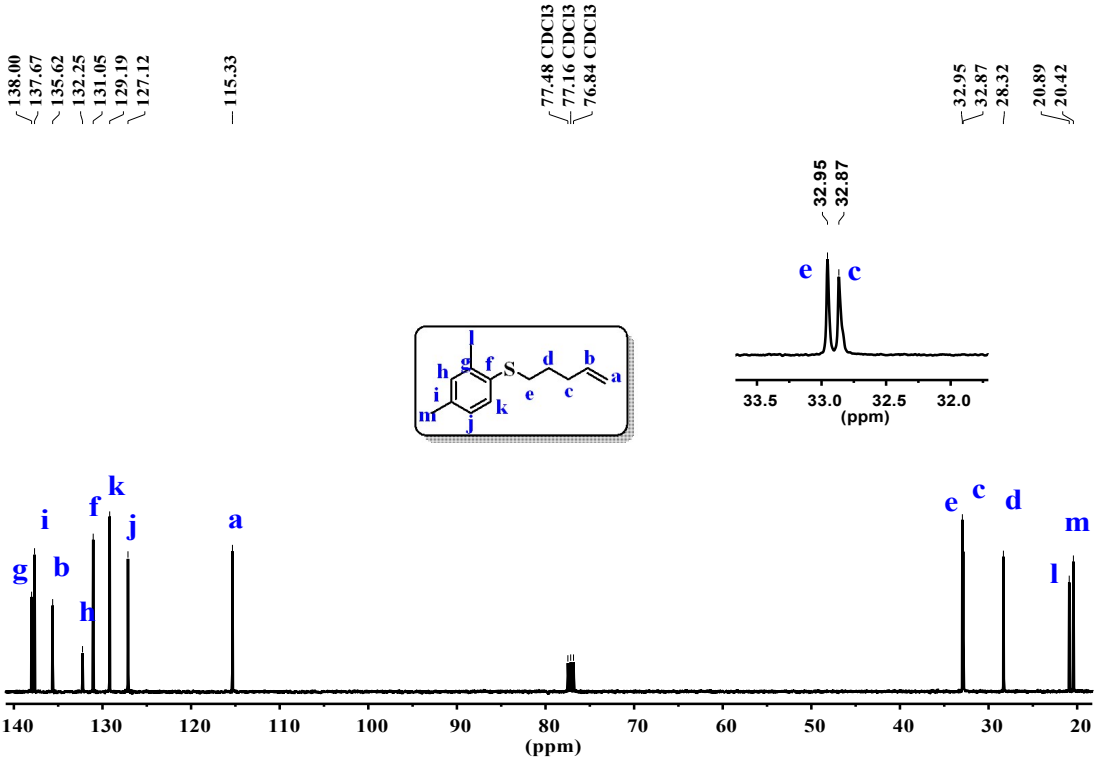


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of **S5**.

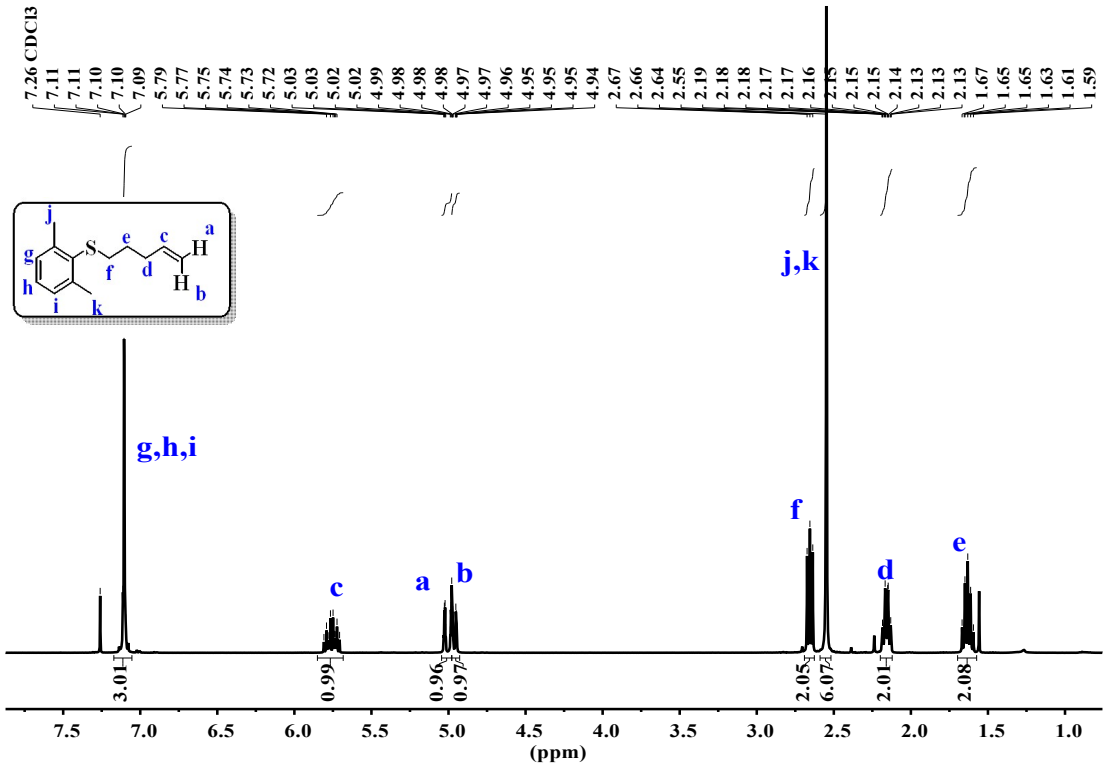


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of the **S6.**

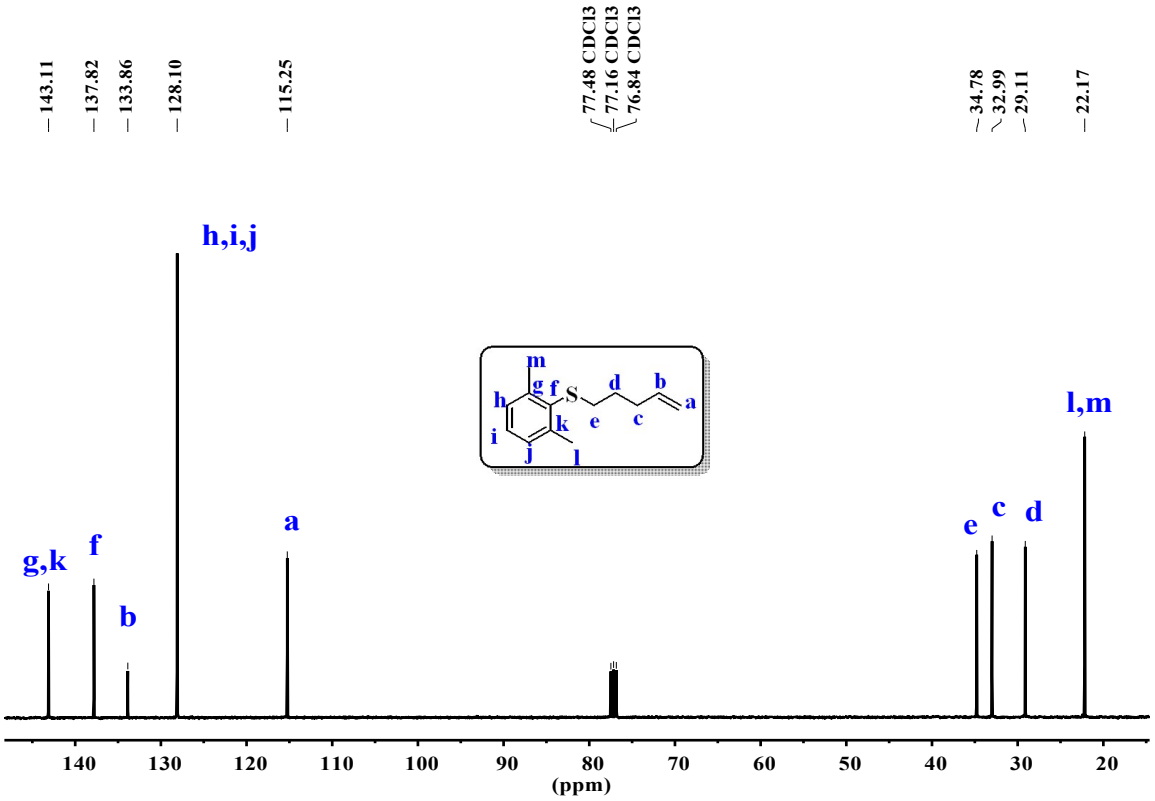


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of **S6**.

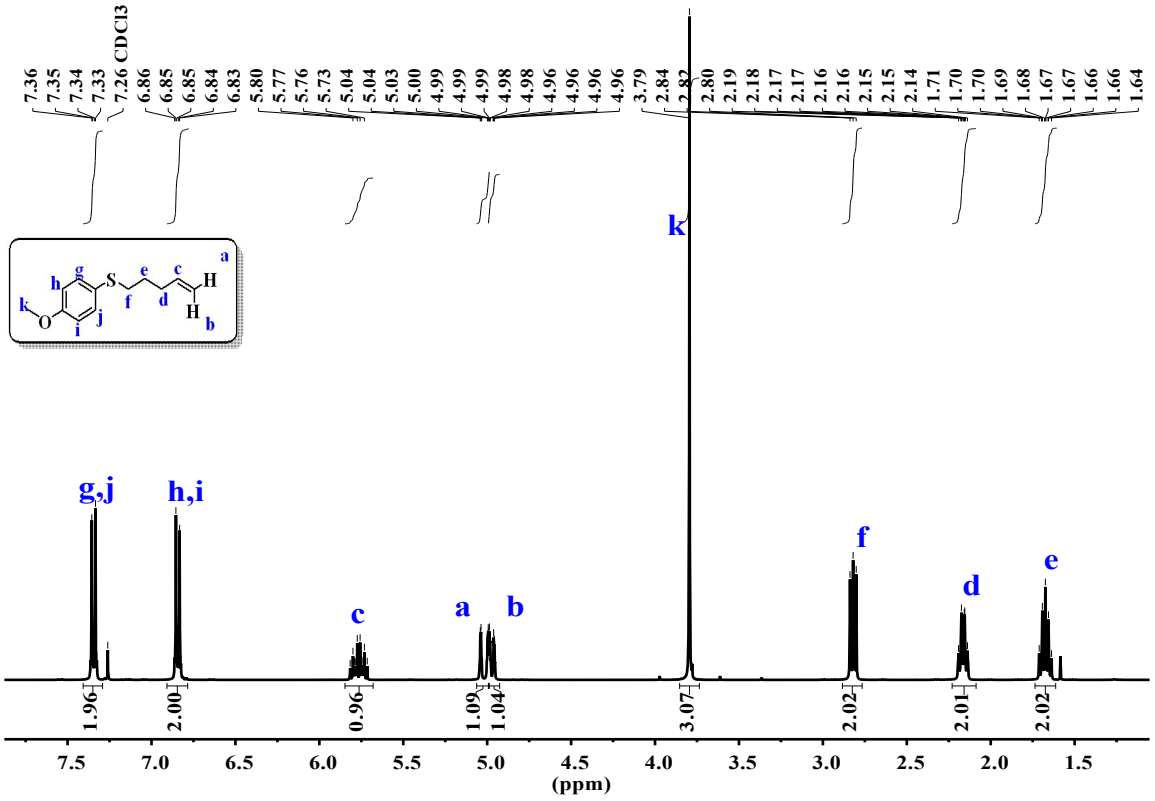


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of the **S13.**

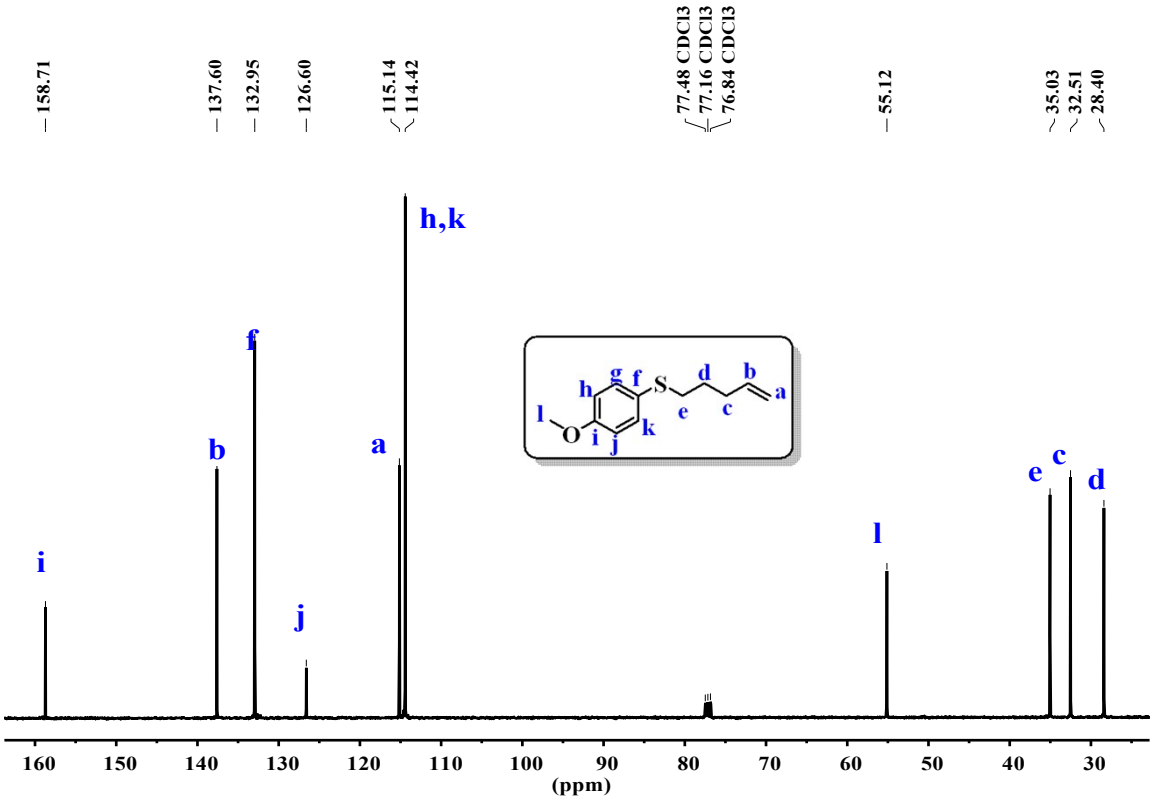


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C) of **S13**.

2 Microstructure analysis of polymers

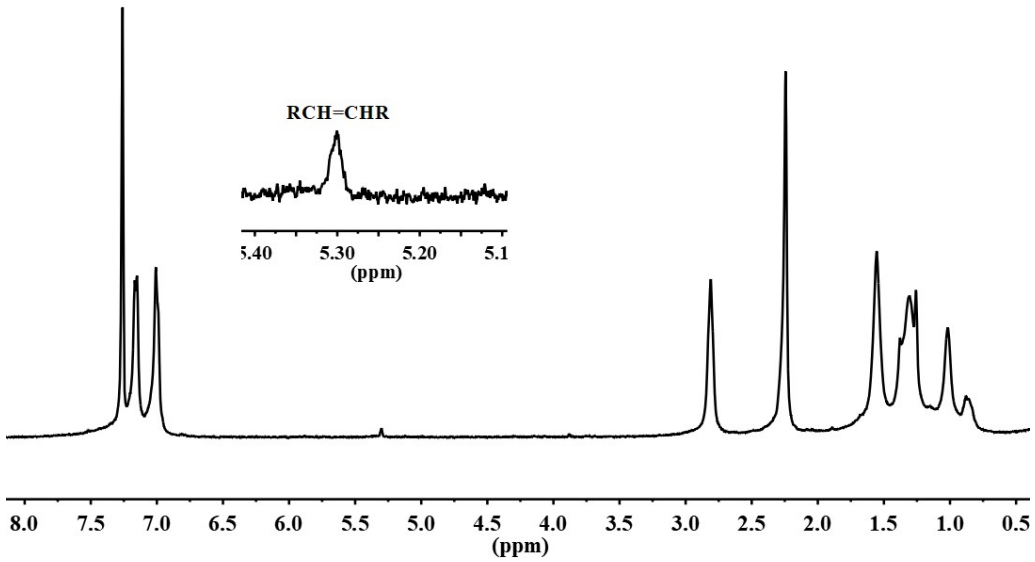


Figure S11. ^{1}H NMR of poly-S2 oligomer.

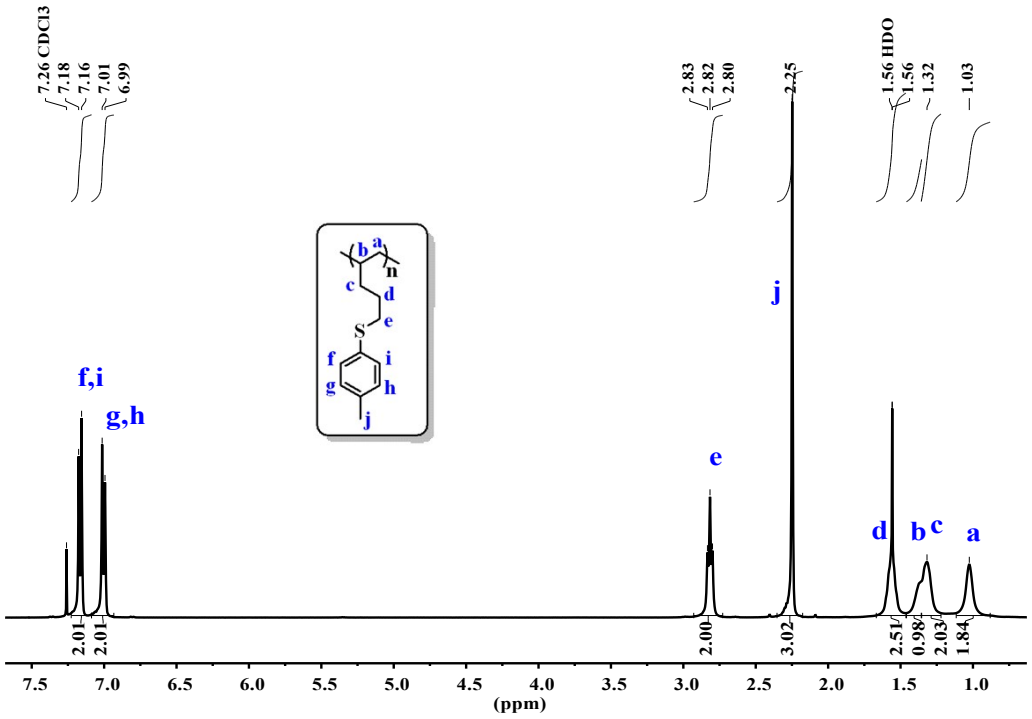


Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the poly-S2 produced by Sc-1 as catalyst in toluene at R. T., [S2]/[Sc-1] = 500/1(Table 1, entry 3).

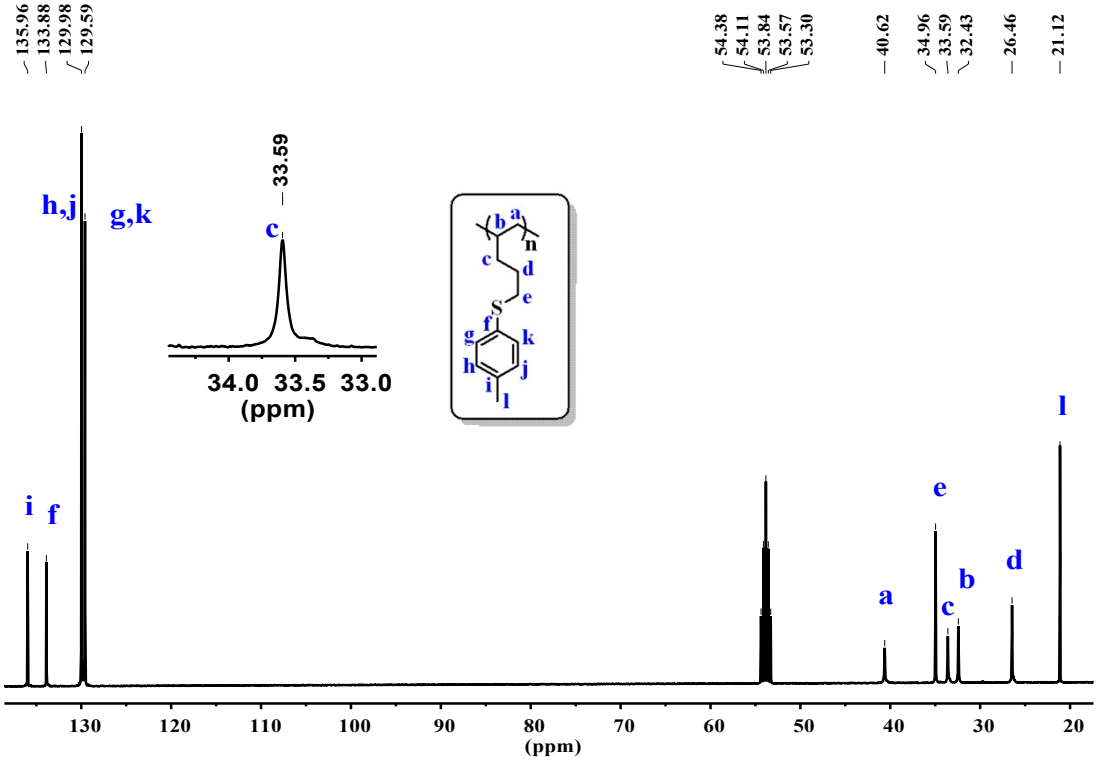


Figure 13. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 25 °C) of the poly-S2 produced by Sc-1 as catalyst in toluene at R. T., [S2]/[Sc-1] = 500/1, rrrr = 86% (Table 1, entry 3).

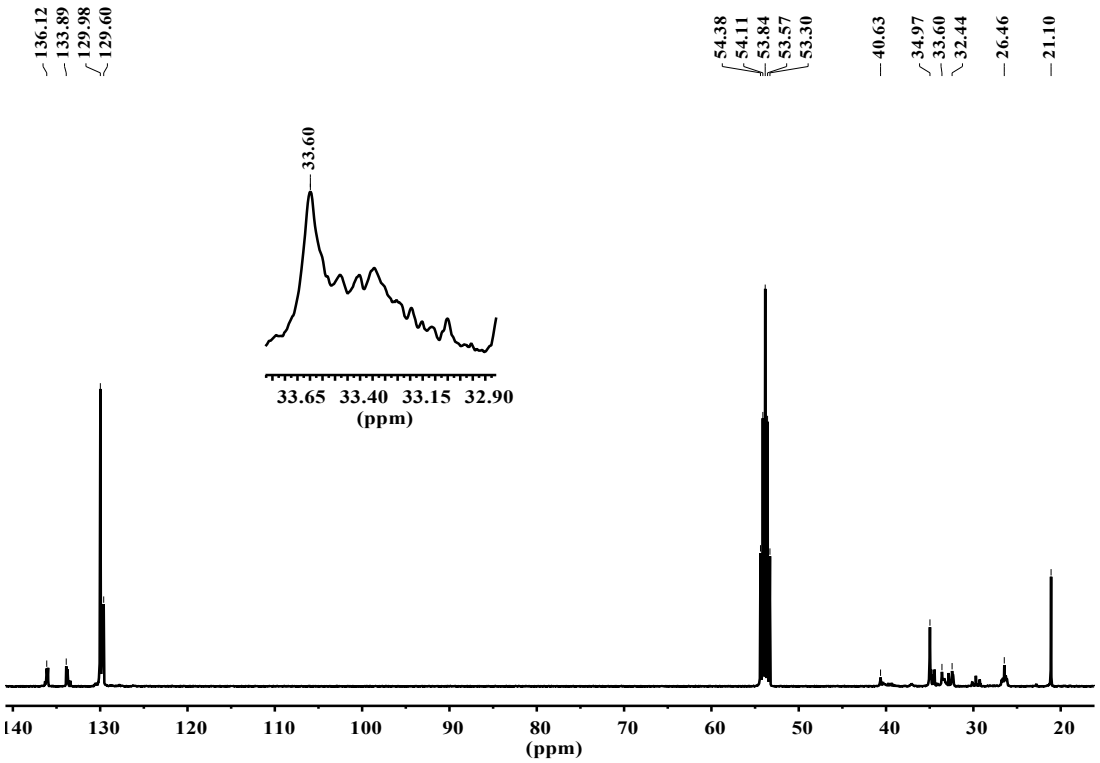


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 25 °C) of the atactic poly-S2 produced by adding Et_2O, [S2]/[Sc-1]/[Et_2O] = 100/1/2, *rrrr* = 38% (Table 1, entry 6).

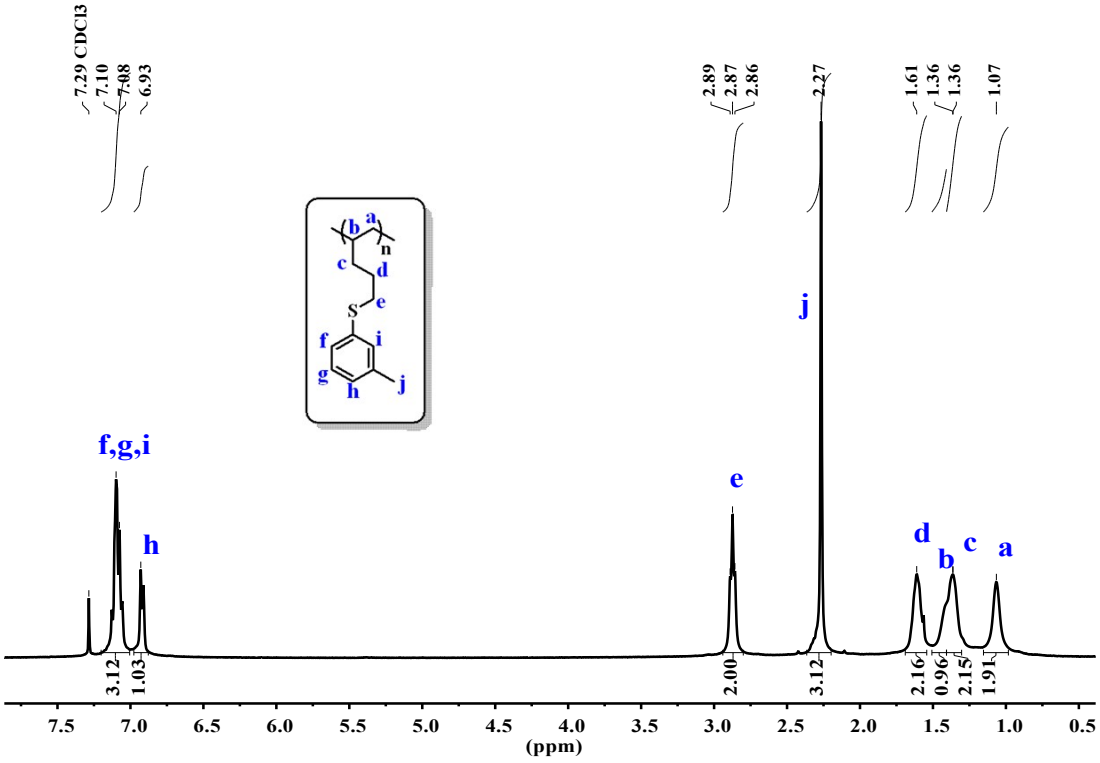


Figure S15. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the poly-S3 produced by Sc-1 as catalyst in toluene at R. T., [S3]/[Sc-1]= 500/1 (Table 1, entry 8).

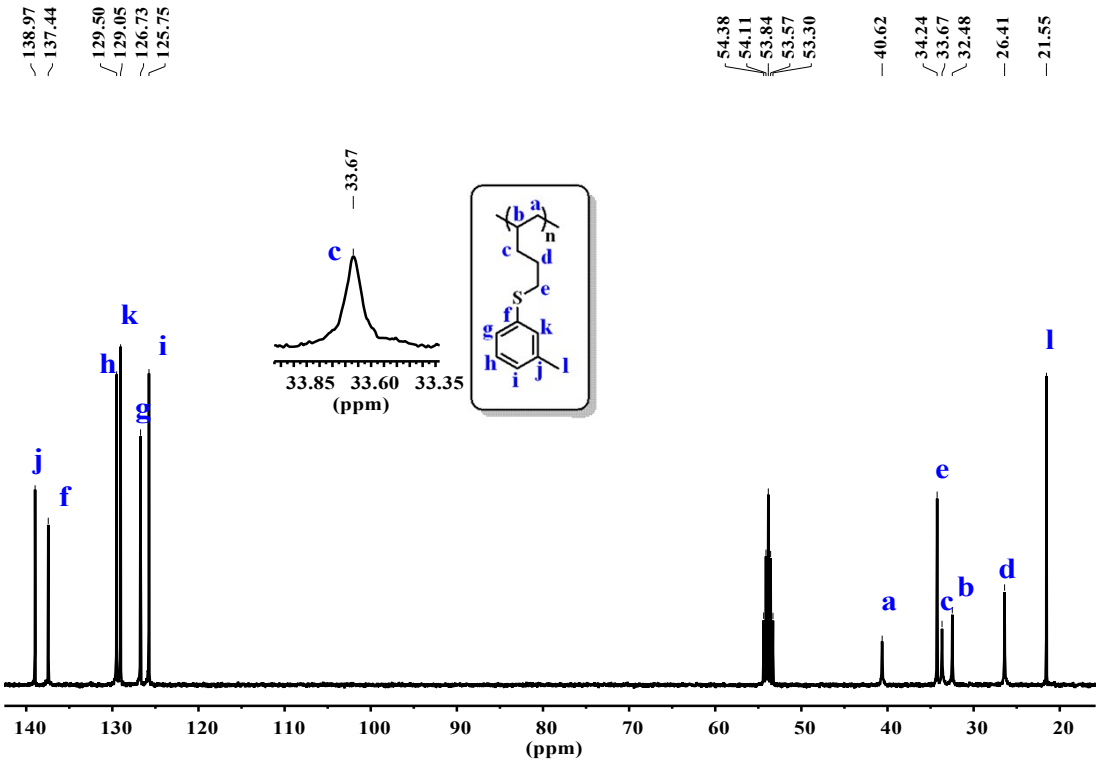


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 25 °C) of the poly-S3 produced by Sc-1 as catalyst in toluene at R. T., [S3]/[Sc-1] = 500/1, *rrrr* > 95% (Table 1, entry 8).

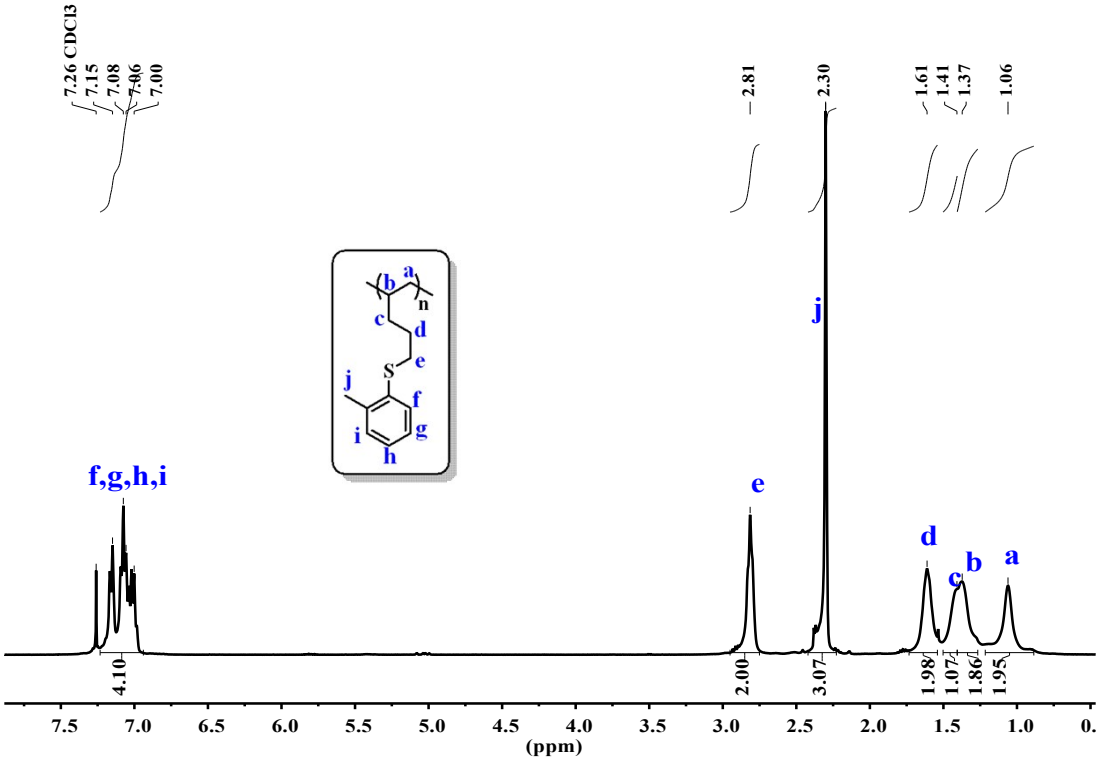


Figure S17. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the poly-S4 produced by Sc-1 as catalyst in toluene at R. T., [S4]/[Sc-1] = 500/1 (Table 1, entry 9).

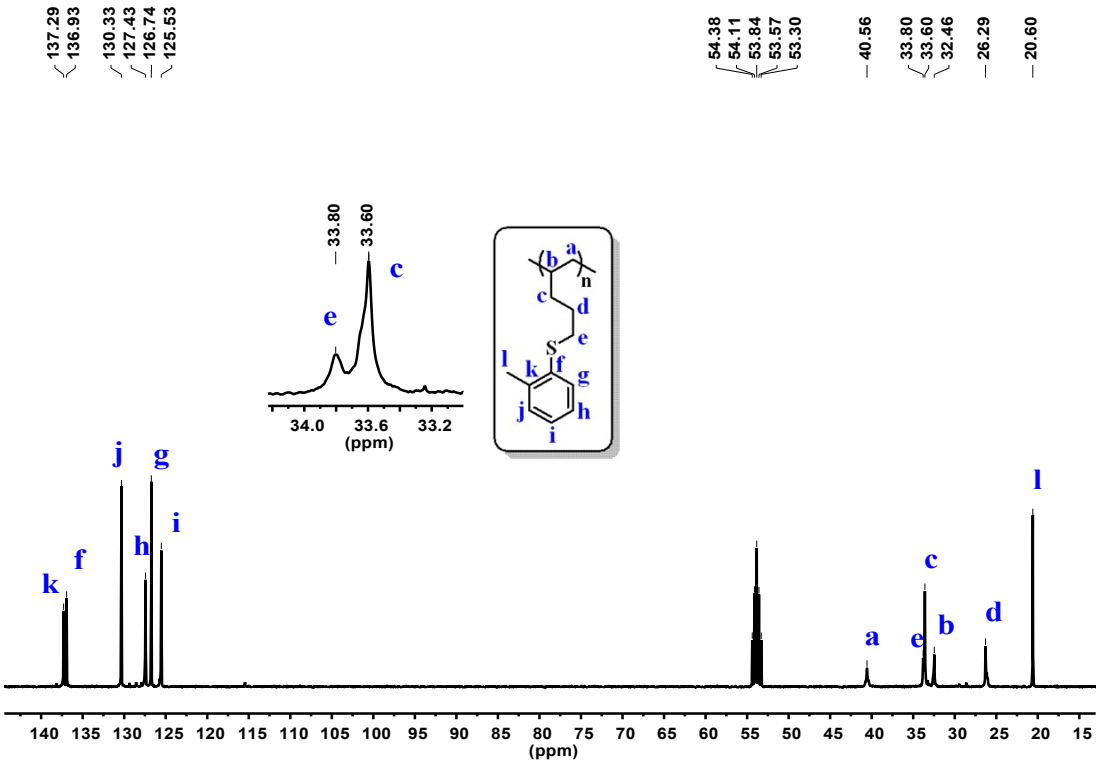


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 25 °C) of the poly-S4 produced by Sc-1 as catalyst in toluene at R. T., [S4]/[Sc-1] = 500/1, *rrrr* = 50% (Table 1, entry 9).

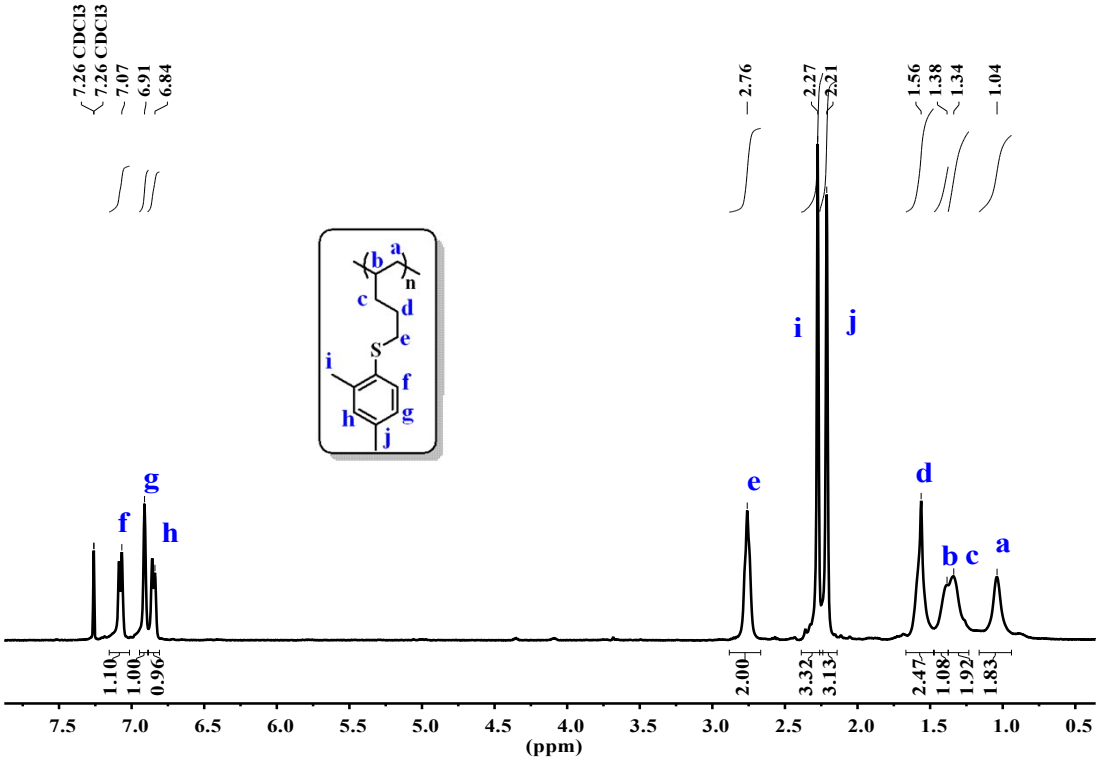


Figure S19. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the poly-S5 produced by Sc-1 as catalyst in toluene at R. T., [S5]/[Sc-1] = 500/1 (Table 1, entry 10).

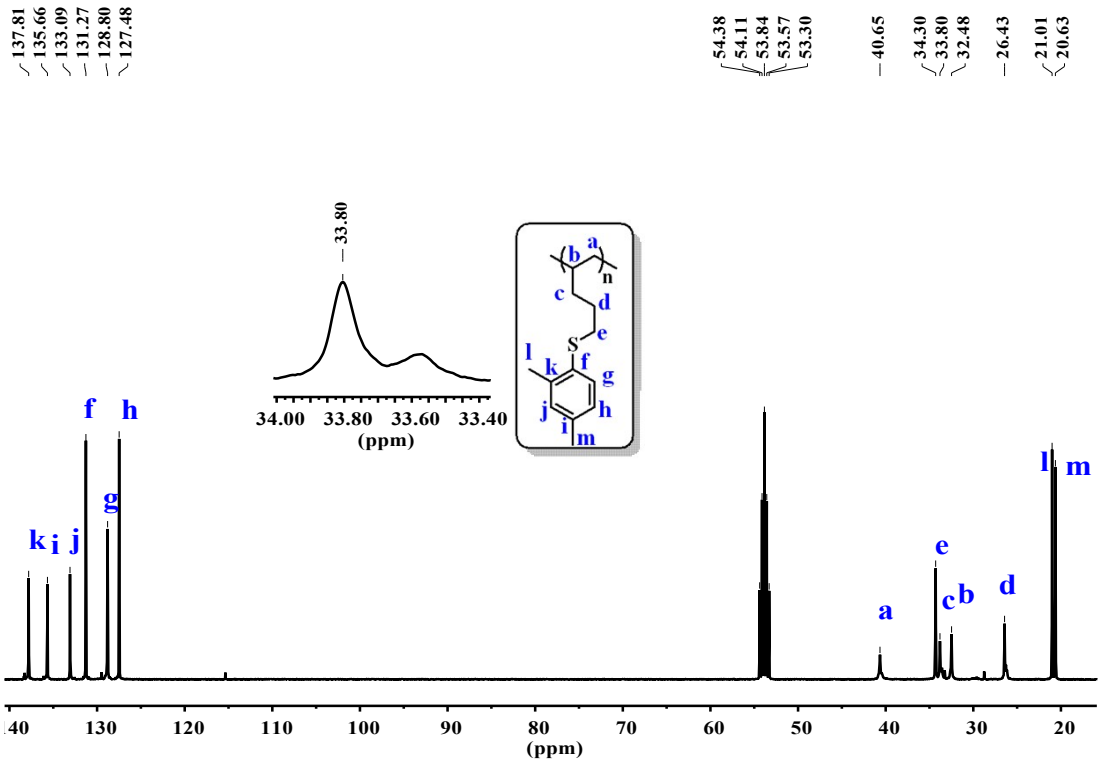


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 25 °C) the poly-S5 produced by Sc-1 as catalyst in toluene at R. T., [S5]/[Sc-1] = 500/1, *rrrr* = 70% (Table 1, entry 10).

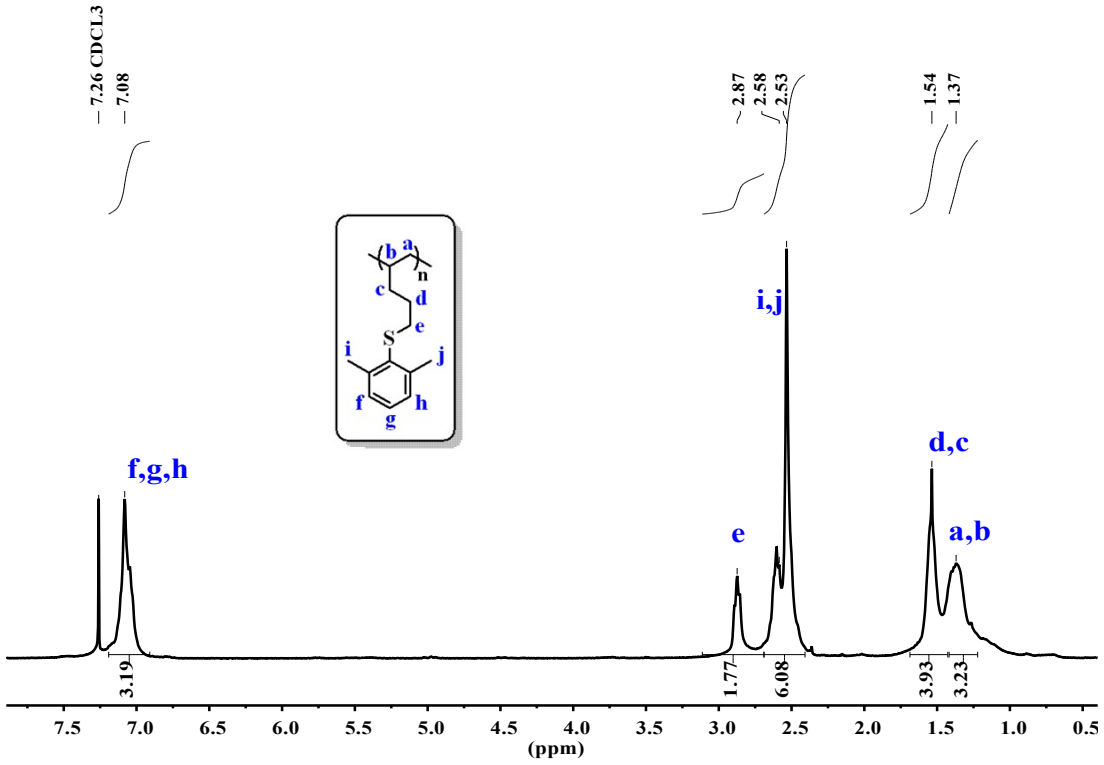


Figure S21. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the poly-S6 produced by Sc-1 as catalyst in toluene at R. T., [S6]/[Sc-1] = 500/1 (Table 1, entry 11).

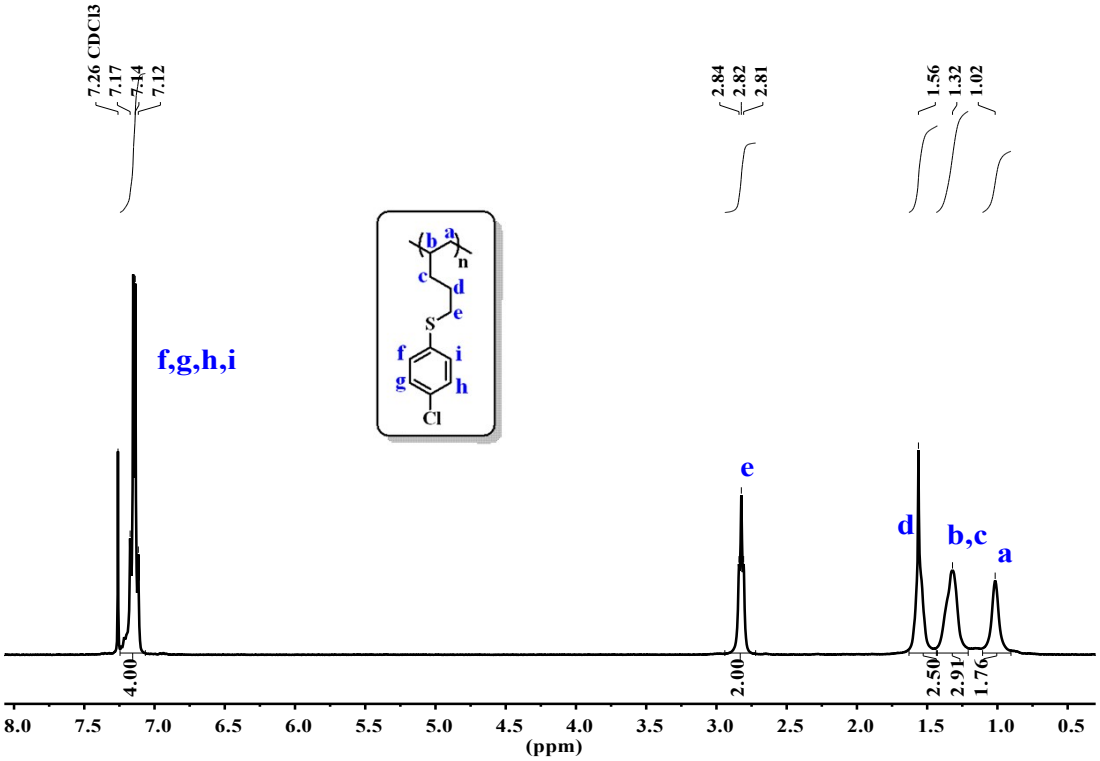


Figure S22. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the poly-S7 produced by Sc-1 as catalyst in toluene at R. T., [S7]/[Sc-1] = 500/1 (Table 1, entry 12).

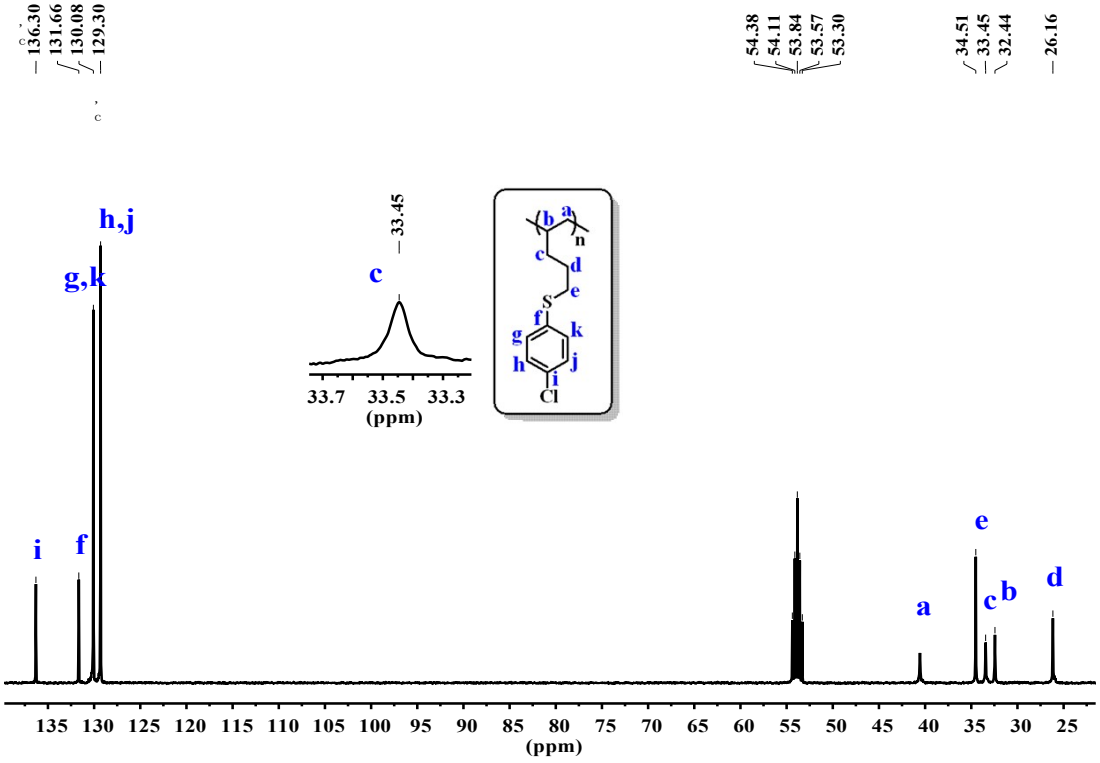


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 25 °C) of the poly-S7 produced by Sc-1 as catalyst in toluene at R. T., [S7]/[Sc-1] = 500/1, *rrrr* > 95% (Table 1, entry 12).

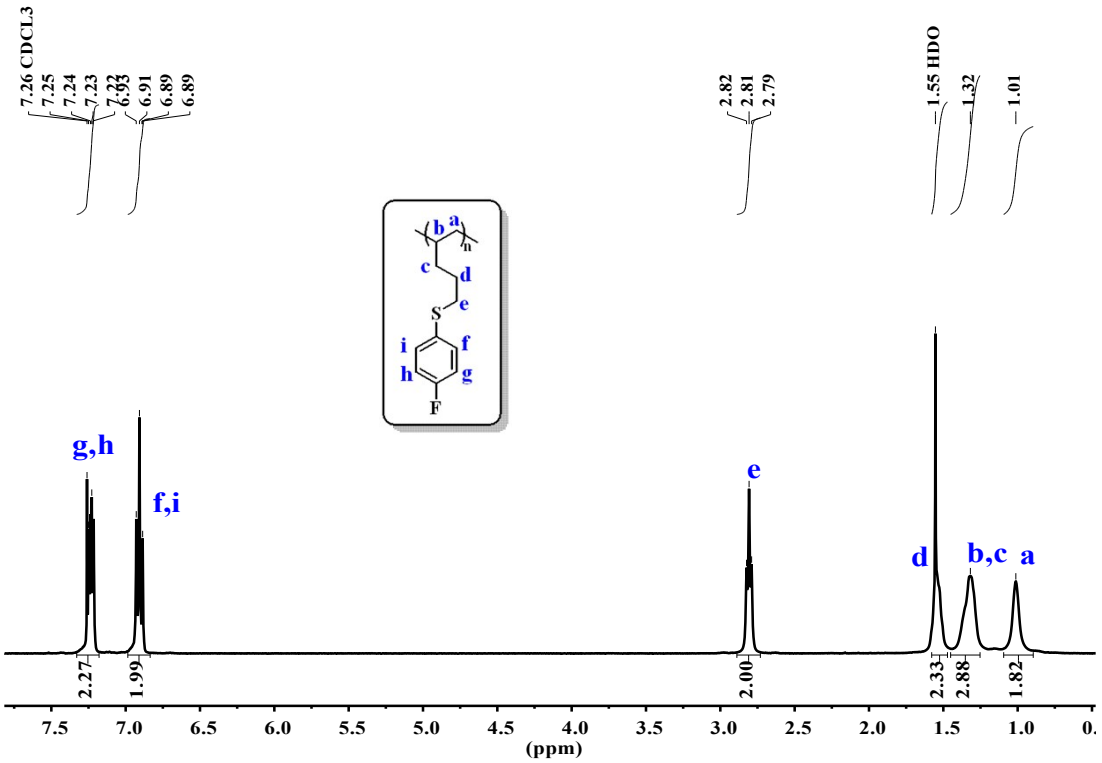


Figure S24. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the poly-S8 produced by Sc-1 as catalyst in toluene at R. T., [S8]/[Sc-1] = 500/1 (Table 1, entry 13).

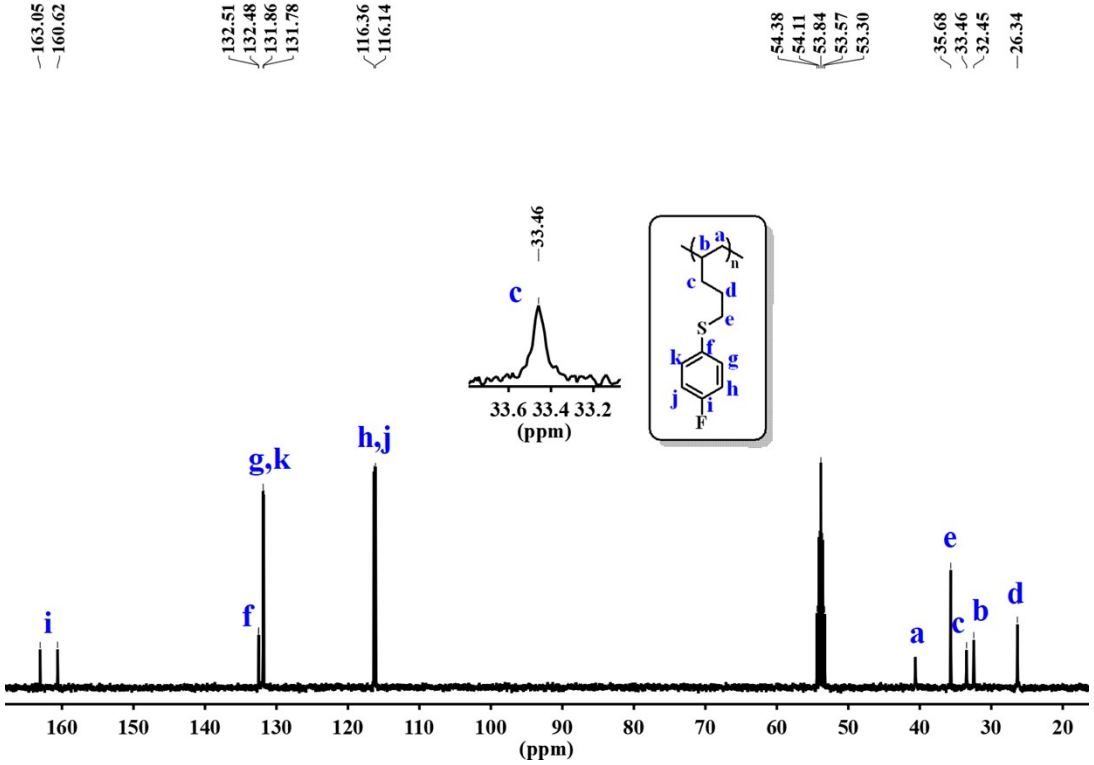


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 25 °C) of the poly-S8 produced by Sc-1 as catalyst in toluene at R. T., [S8]/[Sc-1] = 500/1, *rrrr* > 95% (Table 1, entry 13).

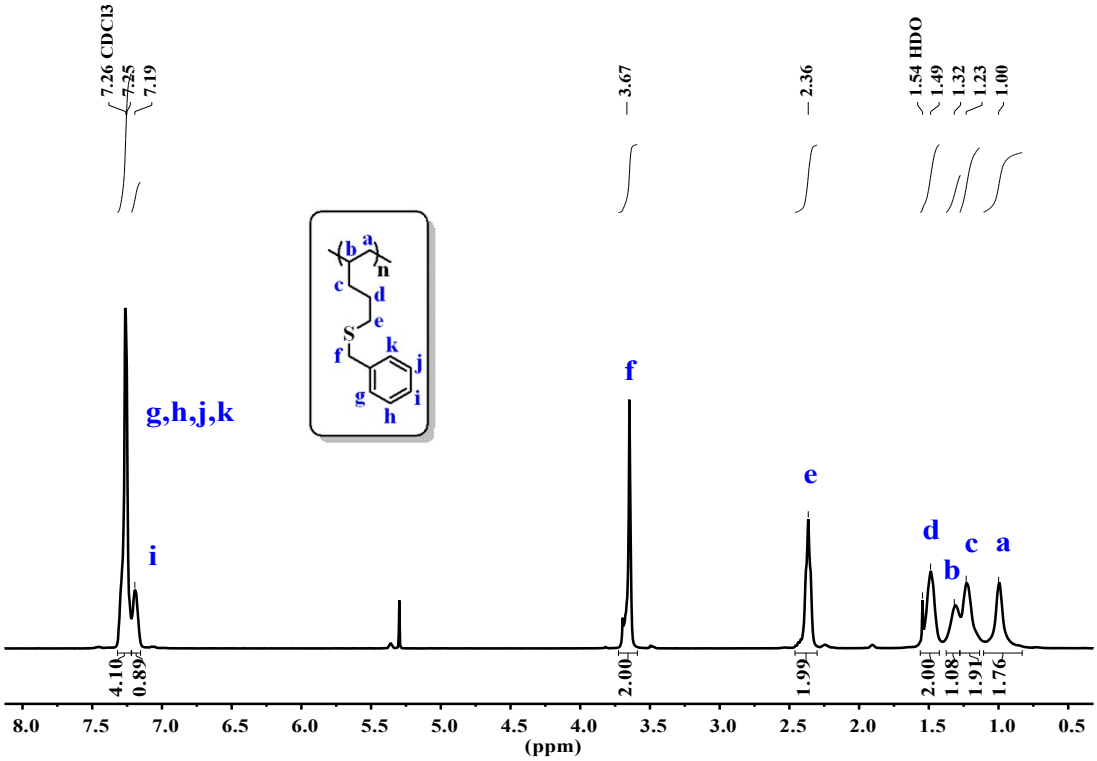


Figure S26. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the poly-S9 produced by Sc-1 as catalyst in toluene at R. T., [S9]/[Sc-1] = 500/1 (Table 1, entry 14).

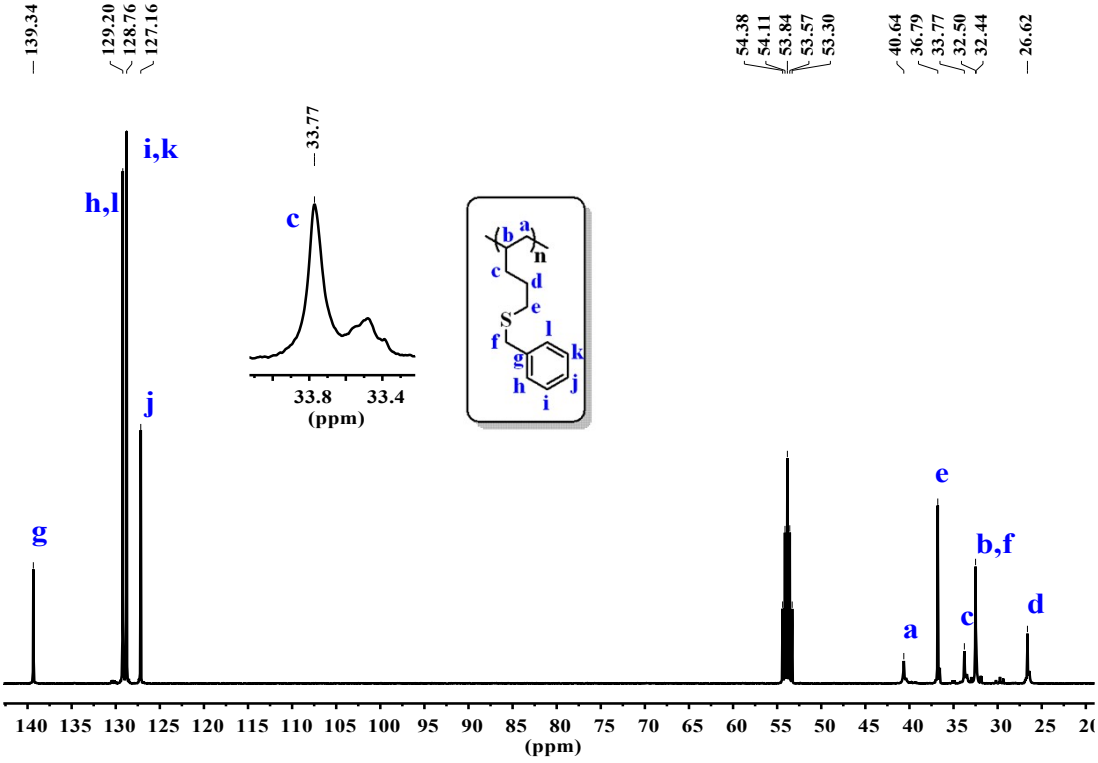


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 25 °C) of the poly-S9 produced by Sc-1 as catalyst in toluene at R. T., [S9]/[Sc-1] = 500/1, *rrrr* = 70% (Table 1, entry 14).

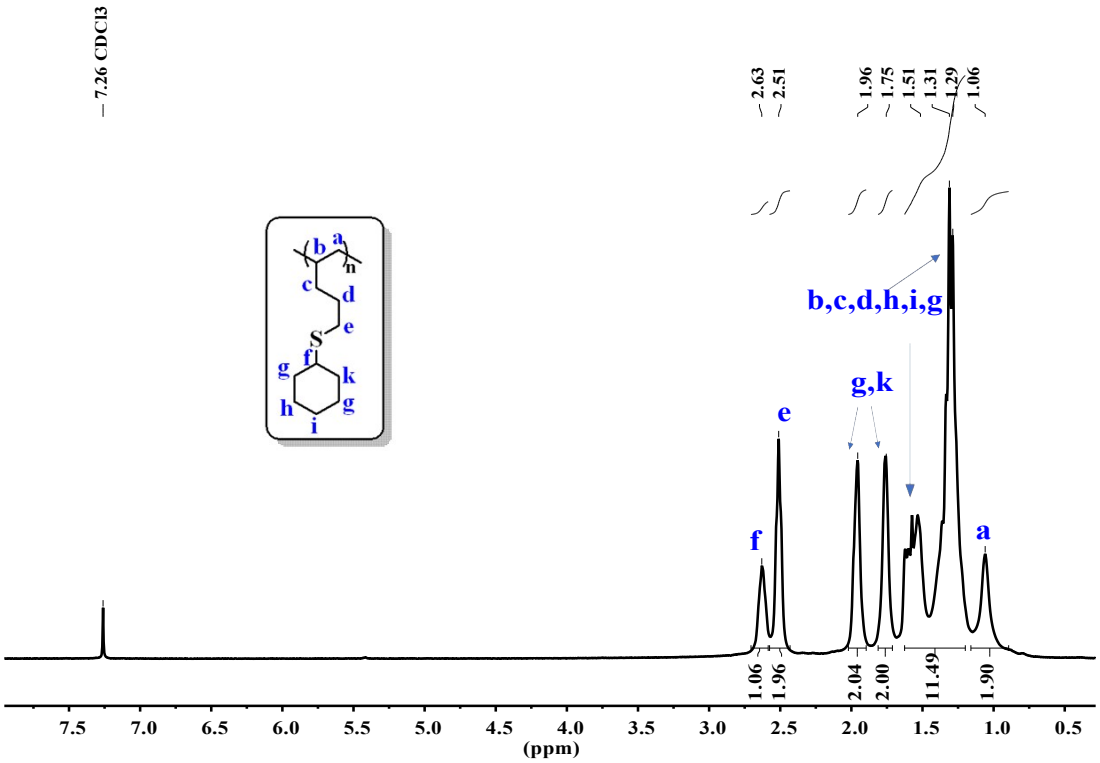


Figure S28. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the Poly-S10 produced by Sc-1 as catalyst in toluene at R. T., [S10]/[Sc-1] = 500/1 (Table 1, entry 15).

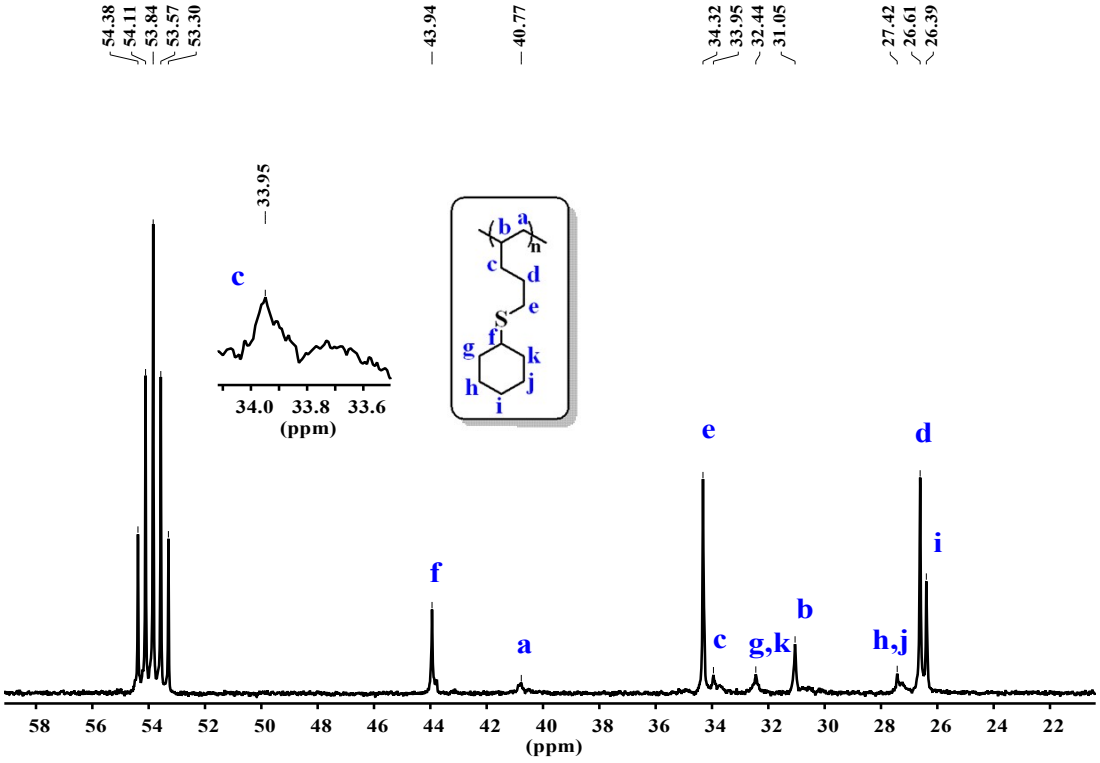


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 25 °C) of the poly-S10 produced by Sc-1 as catalyst in toluene at R. T., [S10]/[Sc-1] = 500/1, *rrrr* = 69% (Table 1, entry 15).

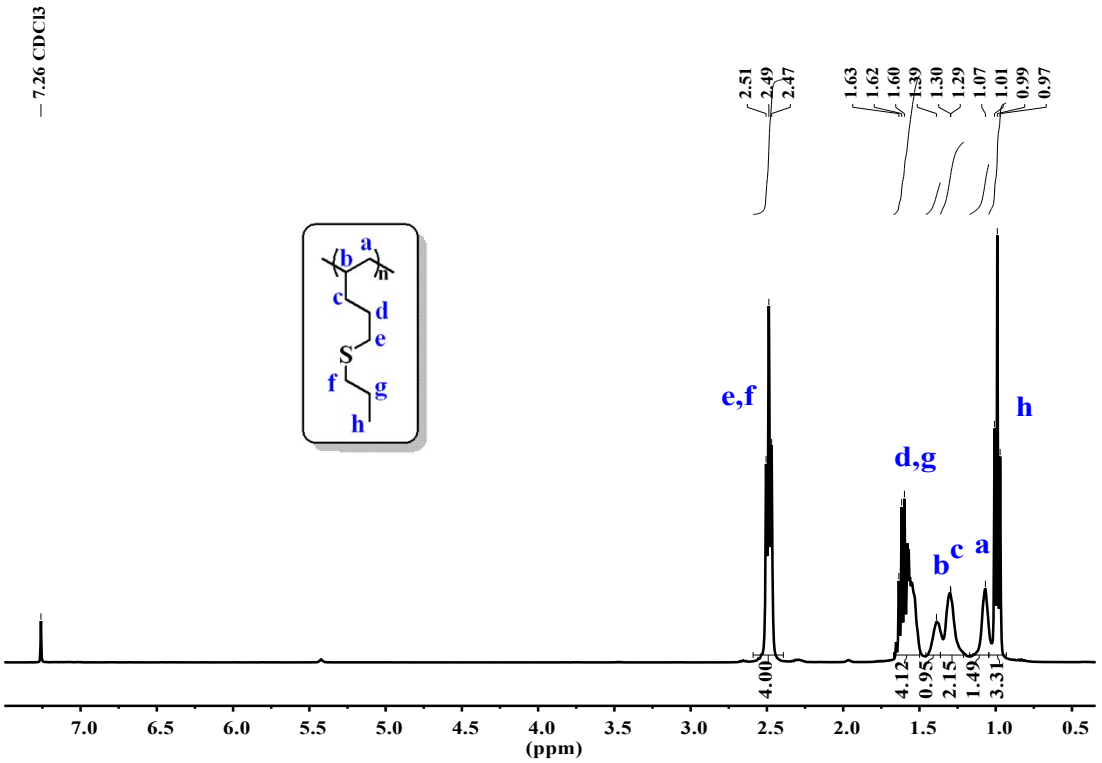


Figure S30. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the poly-S11 produced by Sc-1 as catalyst in toluene at R. T., [S11]/[Sc-1] = 500/1 (Table 1, entry 16).

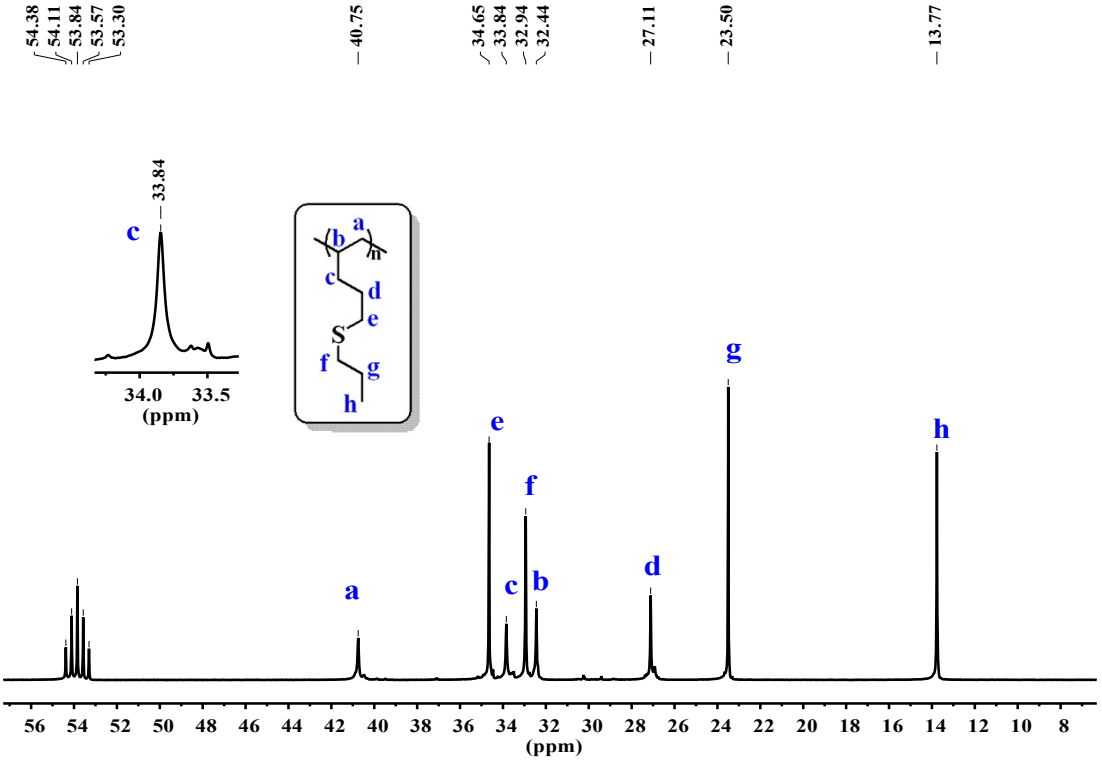


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 25 °C) of the poly-S11 produced by Sc-1 as catalyst in toluene at R. T., [S11]/[Cat] = 500/1, *rrrr* = 82% (Table 1, entry 16).

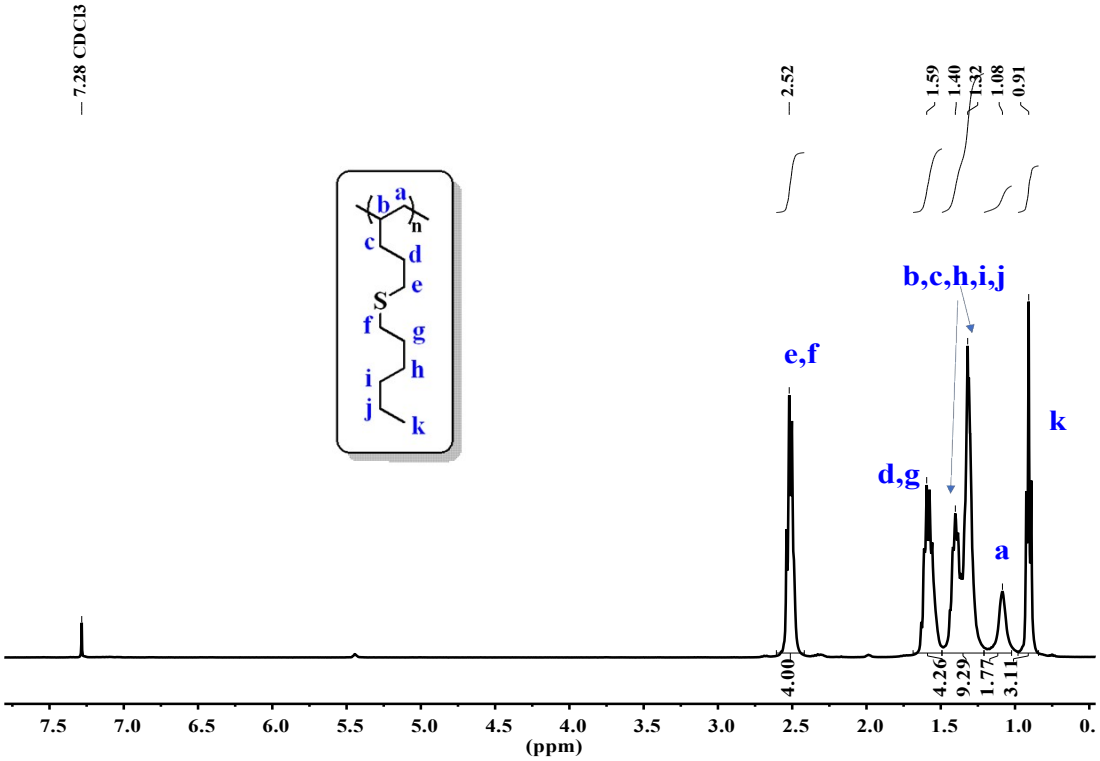


Figure S32. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the poly-S12 produced by Sc-1 as catalyst in toluene at R. T., [S12]/[Sc-1] = 500/1 (Table 1, entry 17).

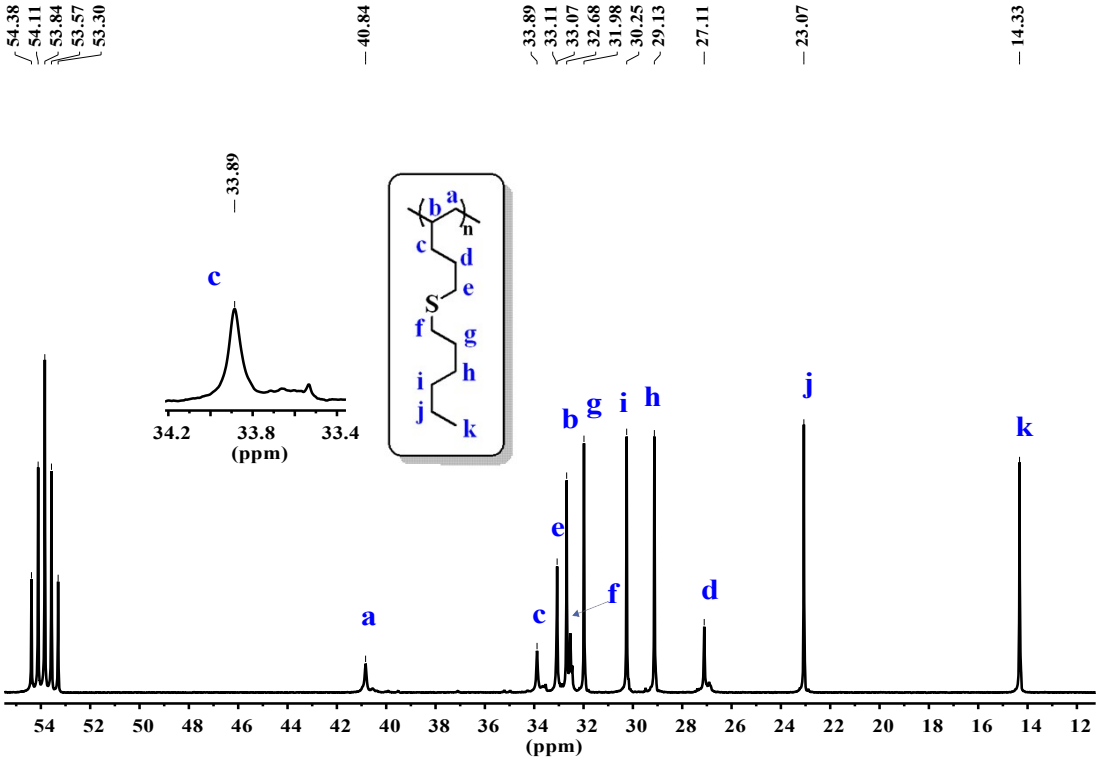


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 25 °C) of the poly-S12 produced by Sc-1 as catalyst in toluene at R. T., [S12]/[Cat] = 500/1, *rrrr* = 61% (Table 1, entry 17).

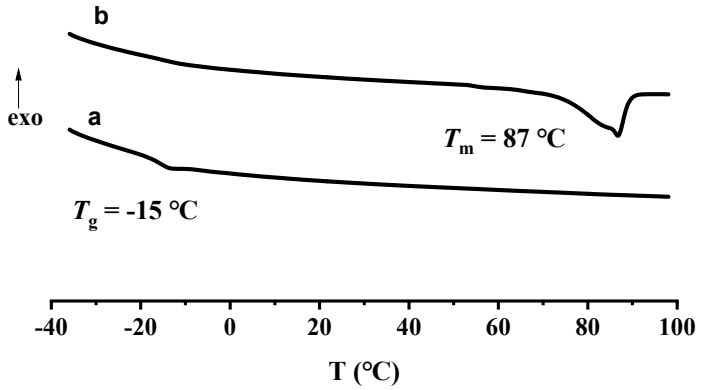


Figure S34. DSC profiles of atactic poly-S2 (Table 1, entry 6) (a) and syndiotactic poly-S2 (Table 1, entry 3) (b).

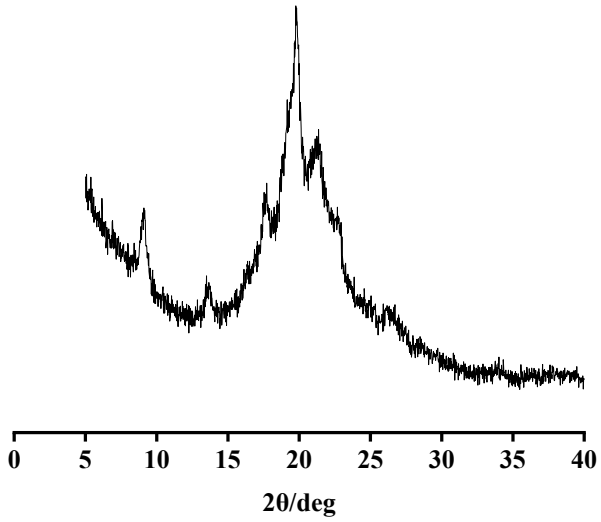


Figure S35. Wide-angle X-ray diffraction profiles of syndiotactic poly-S2 (Table 1, entry 3).

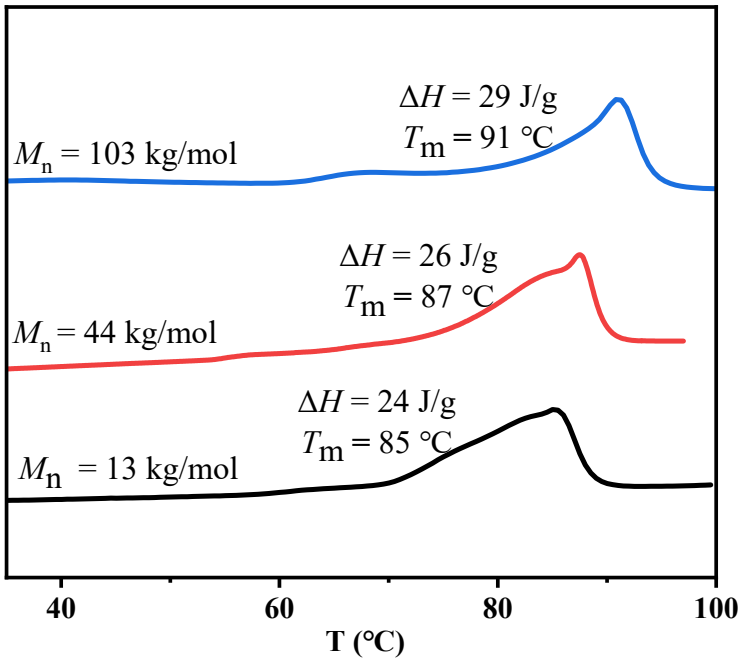


Figure S36. DSC curves of poly-S2 with different molecular weight (Table 1, entries 2,3, and 5).

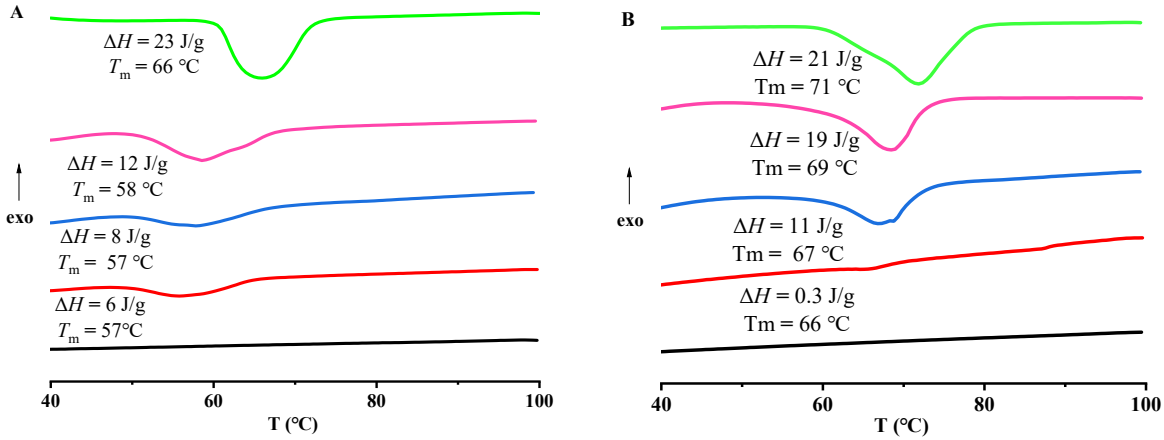


Figure S37. DSC profiles of syndiotactic poly-S7 (M_n = 30 kg/mol, $Đ$ = 2.34) (A) and poly-S8 (M_n = 25 kg/mol, $Đ$ = 1.68) (B) that were crystallized isothermally at room temperature for various time after first melting: 4 hours (black line), 24 hours (red line), 48 hours (blue line); 72 hours (pink line); the first heating ramp as reference (green line).

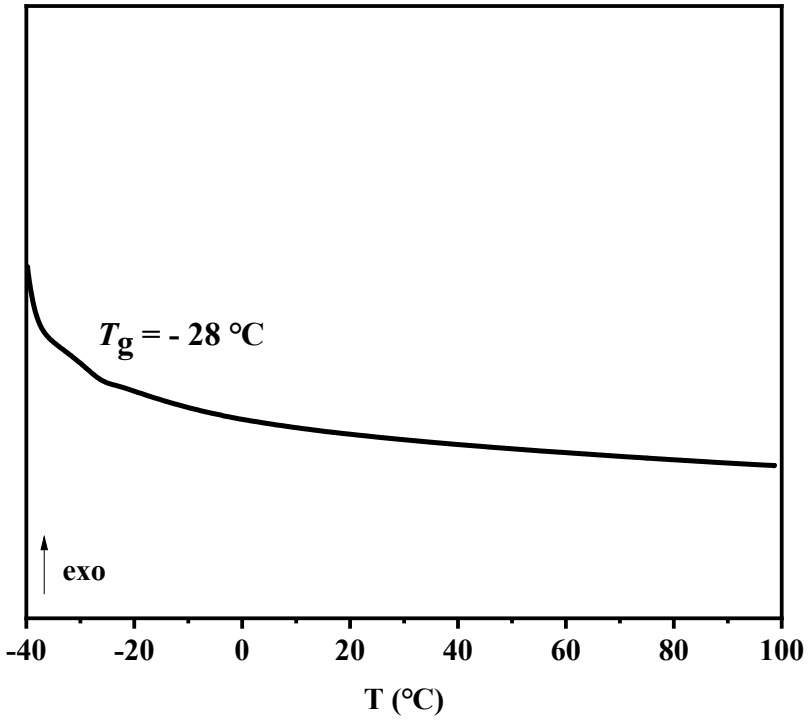


Figure S38. DSC curves of poly-S3 produced by Sc-1 as catalyst in toluene at R. T., [S3]/[Cat.] = 500/1 with the cooling and heating rate of 10 °C/min (Table 1, entry 8).

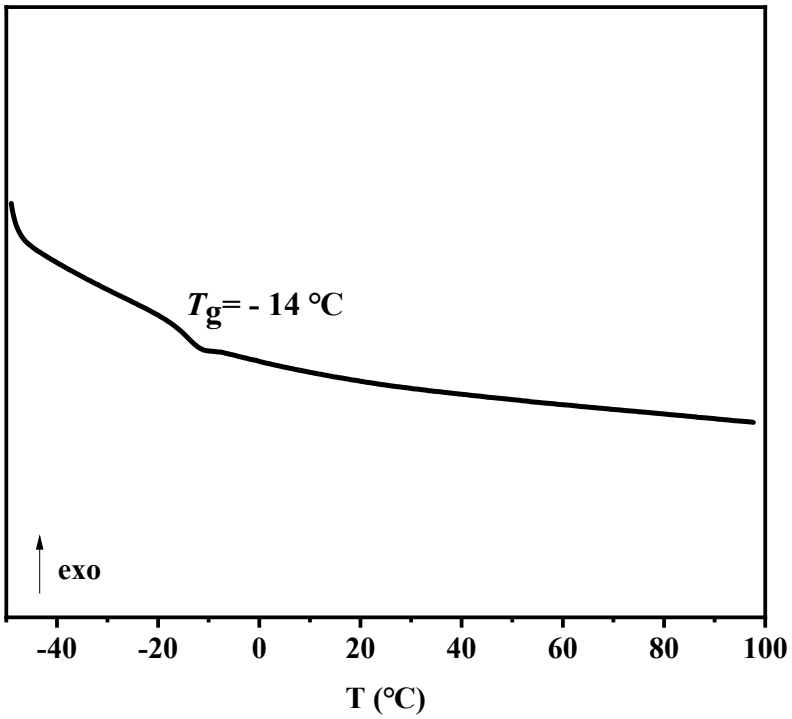


Figure S39. DSC curves of poly-S4 produced by Sc-1 as catalyst in toluene at R. T., [S4]/[Cat.] = 500/1 with the cooling and heating rate of 10 °C/min (Table 1, entry 9).

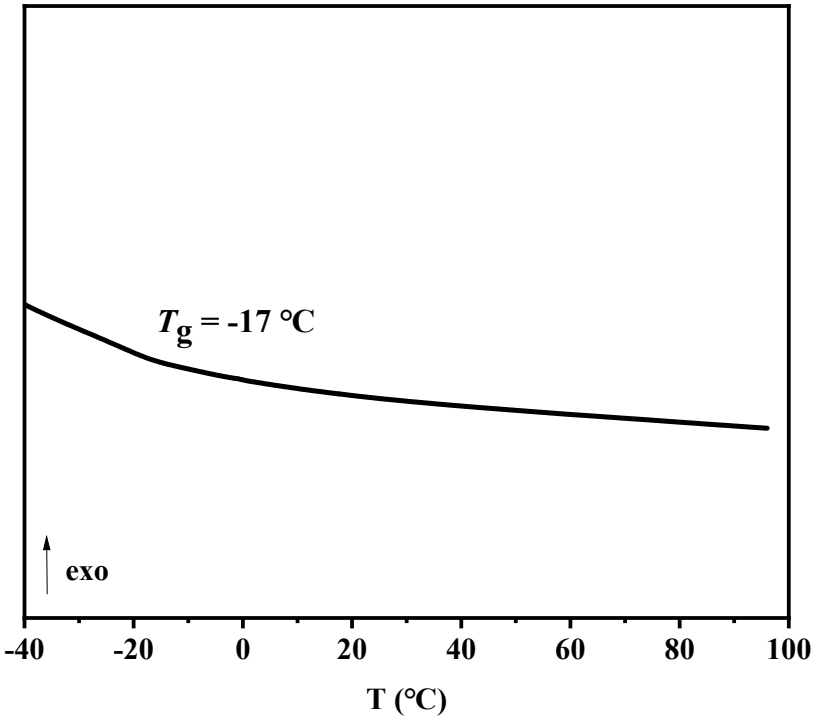


Figure S40. DSC curves of poly-S5 produced by Sc-1 as catalyst in toluene at R. T., [S5]/[Cat.] = 500/1 with the cooling and heating rate of 10 °C/min (Table 1, entry 10).

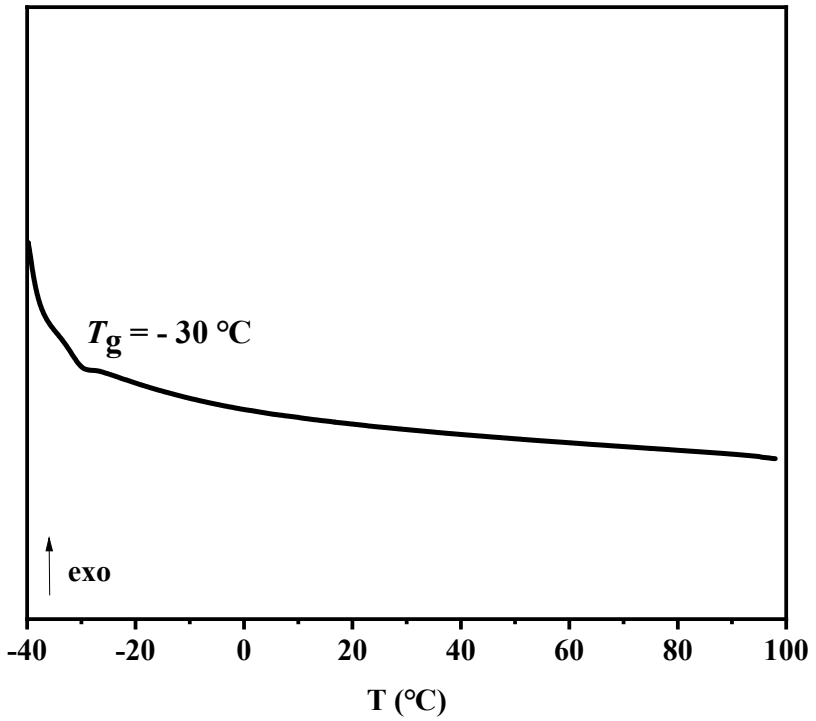


Figure S41. DSC curves of poly-S9 produced by Cat.1 as catalyst in toluene at R. T., [S9]/[Cat.] = 500/1 with the cooling and heating rate of 10 °C/min (Table 1, entry 14).

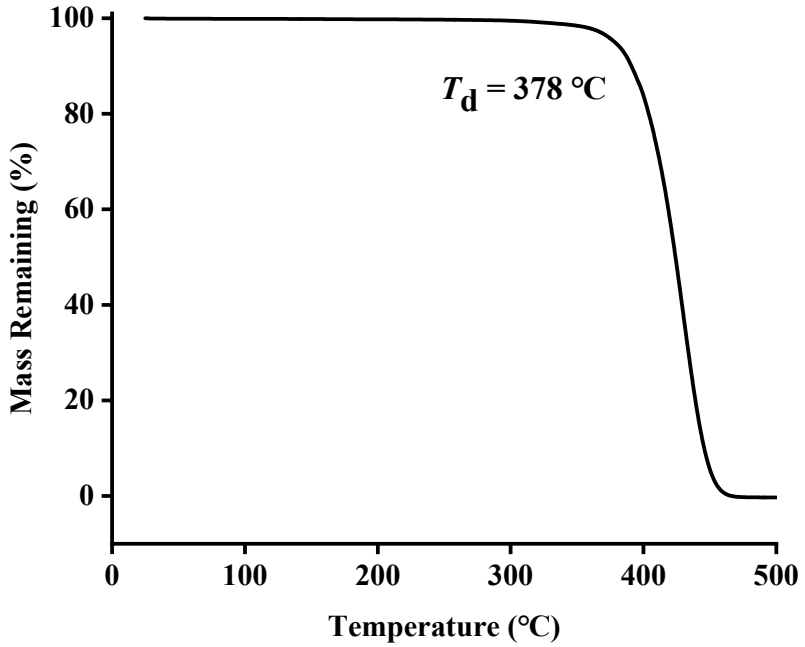


Figure S42. TGA curves for poly-S2 produced by Sc-1 as catalyst in toluene at R. T., [S2]/[Cat.] = 500/1 (Table 1, entry 3).

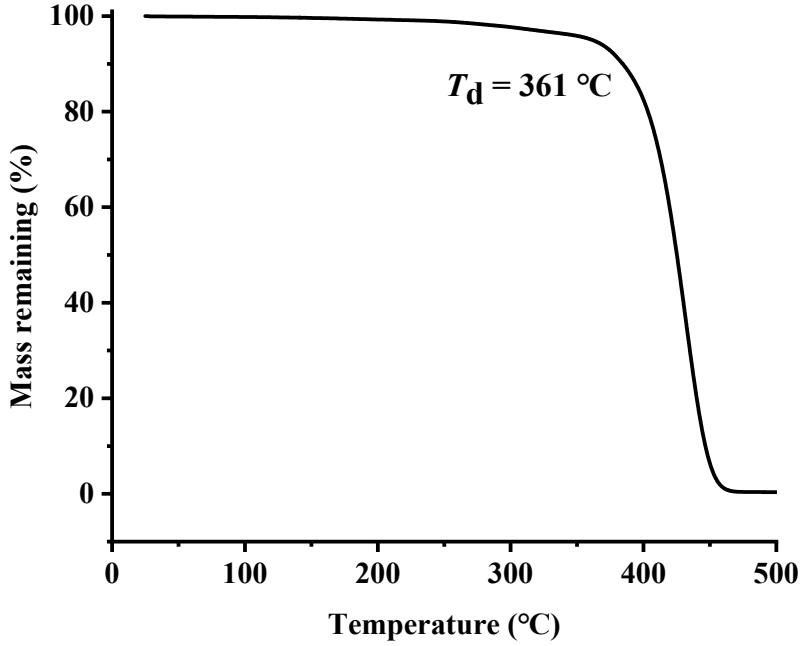


Figure S43. TGA curves for poly-S7 produced by Sc-1 as catalyst in toluene at R. T., [S7]/[Cat.] = 500/1 (Table 1, entry 12).

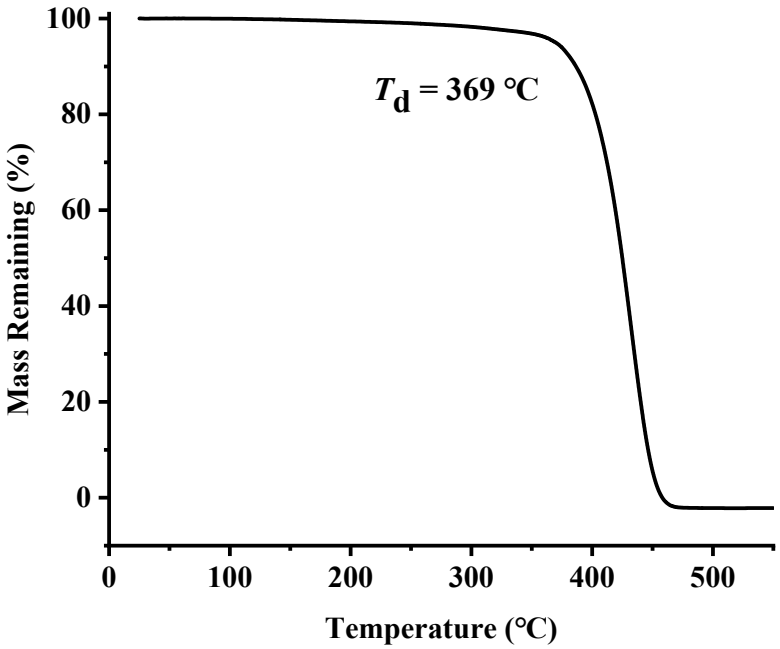


Figure S44. TGA curves for poly-S8 produced by Sc-1 as catalyst in toluene at R. T., [S8]/[Cat.] = 500/1 (Table 1, entry 13).

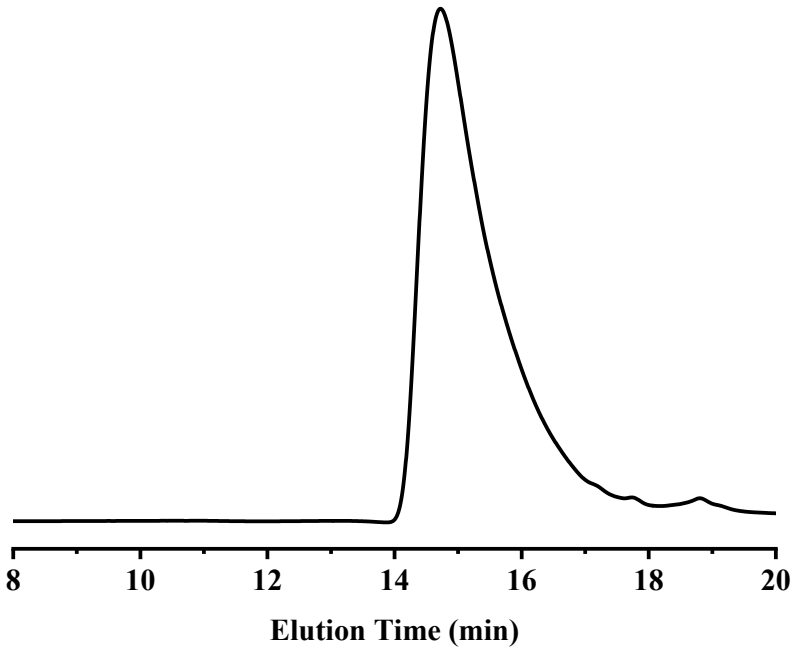


Figure S45. The GPC trace of the poly-S2 produced by Sc-1 as catalyst in toluene at R. T., [S2]/[Sc-1] = 100/1, M_n = 13 kg/mol, $Đ$ = 2.23 (Table 1, entry 2).

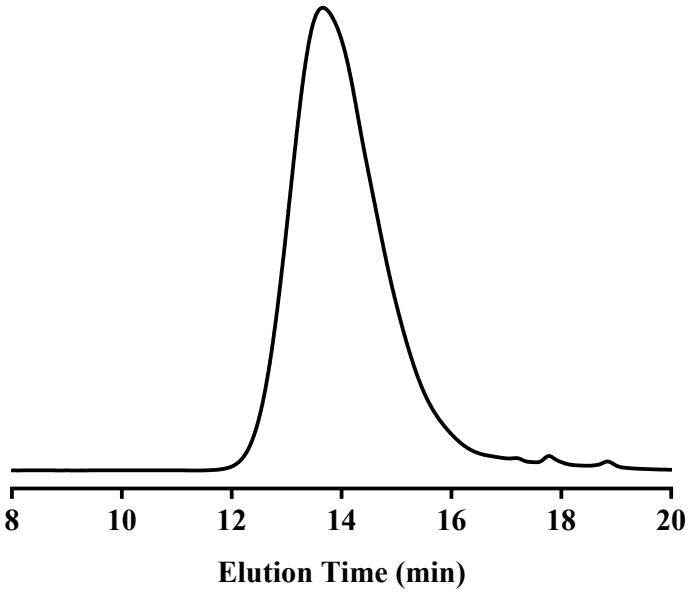


Figure S46. The GPC trace of the poly-S2 produced by Sc-1 as catalyst in toluene at R. T., [S2]/[Sc-1] = 500/1, M_n = 44 kg/mol, $Đ$ = 1.53 (Table 1, entry 3).

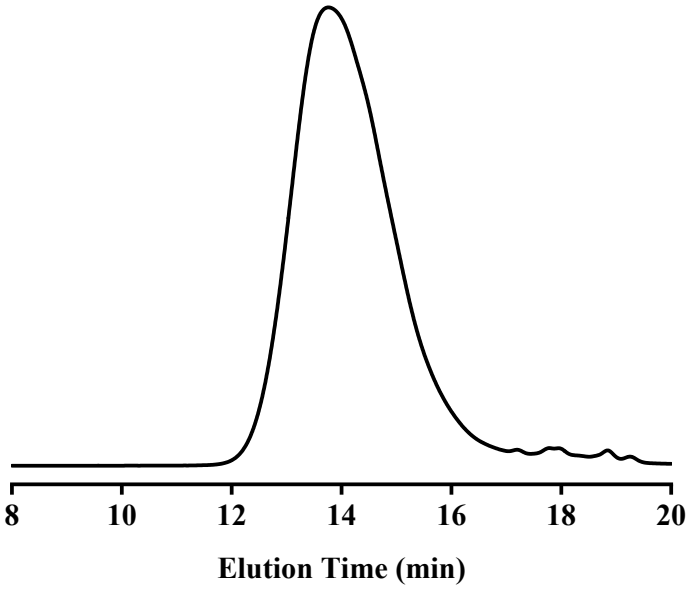


Figure S47. The GPC trace of the poly-S2 produced by Sc-1 as catalyst in toluene at R. T., [S2]/[Sc-1] = 1000/1, M_n = 34 kg/mol, $Đ$ = 1.73 (Table 1, entry 4).

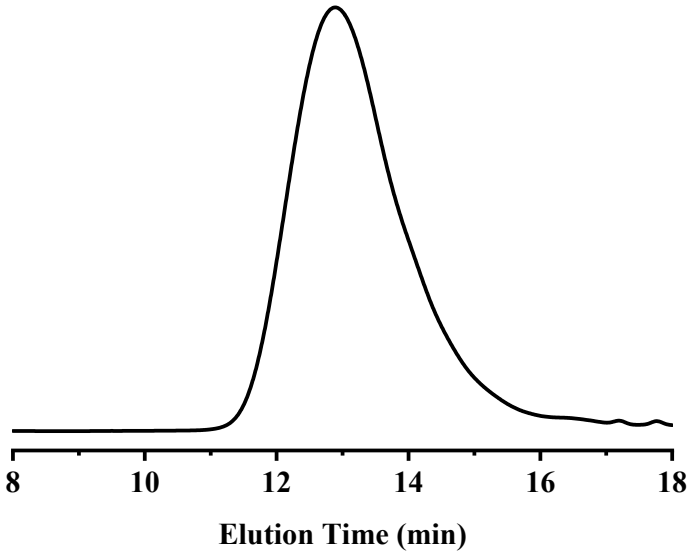


Figure S48. The GPC trace of the poly-S2 produced by Sc-1 as catalyst in toluene at -20 ℃, [S2]/[Sc-1] = 1000/1, M_n = 103 kg/mol, $Đ$ = 1.91 (Table 1, entry 5).

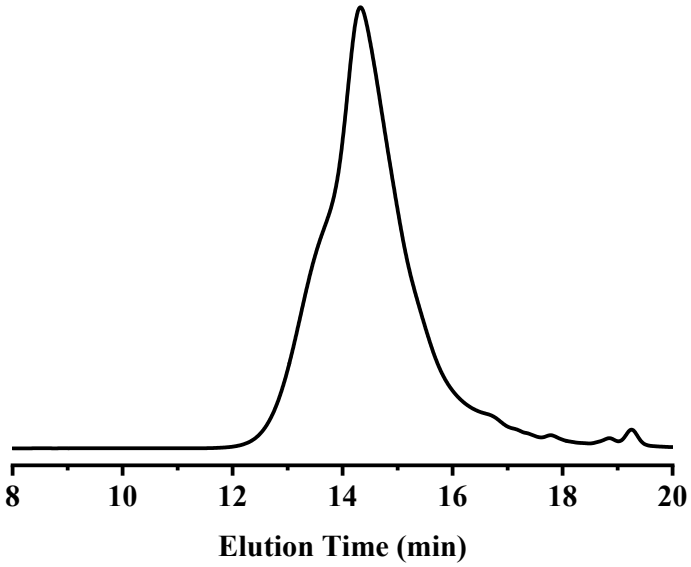


Figure S49. The GPC trace of the poly-S3 produced by Sc-1 as catalyst in toluene at R. T., [S3]/[Sc] = 500/1, M_n = 24 kg/mol, $Đ$ = 1.97 (Table 1, entry 8).

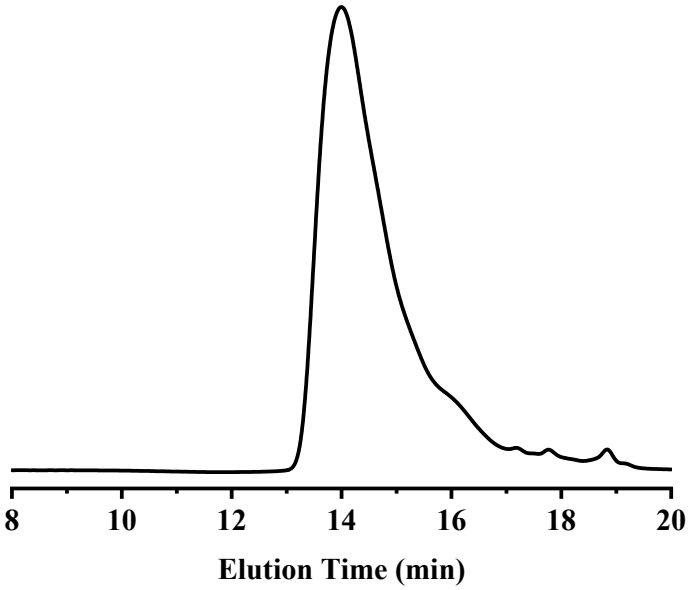


Figure S50. The GPC trace of the poly-S4 produced by Sc-1 as catalyst in toluene at R. T., [S4]/[Sc-1] = 500/1, M_n = 19 kg/mol, $Đ$ = 2.53 (Table 1, entry 9).

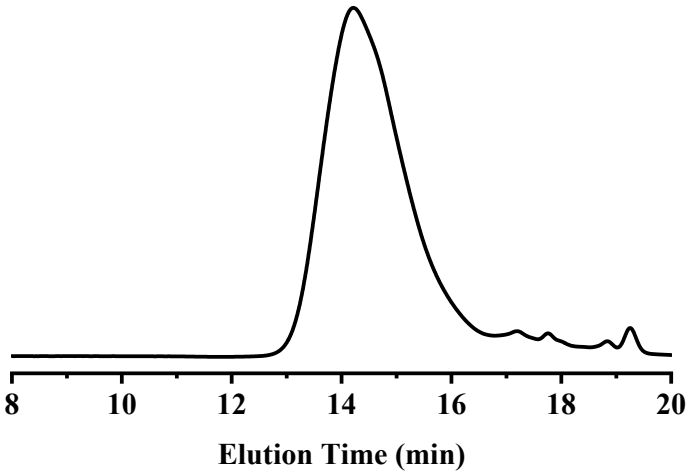


Figure 51. The GPC trace of the poly-S5 produced by Sc-1 as catalyst in toluene at R. T., [S5]/[Sc-1] = 500/1, M_n = 21 kg/mol, $Đ$ = 1.81 (Table 1, entry 10).

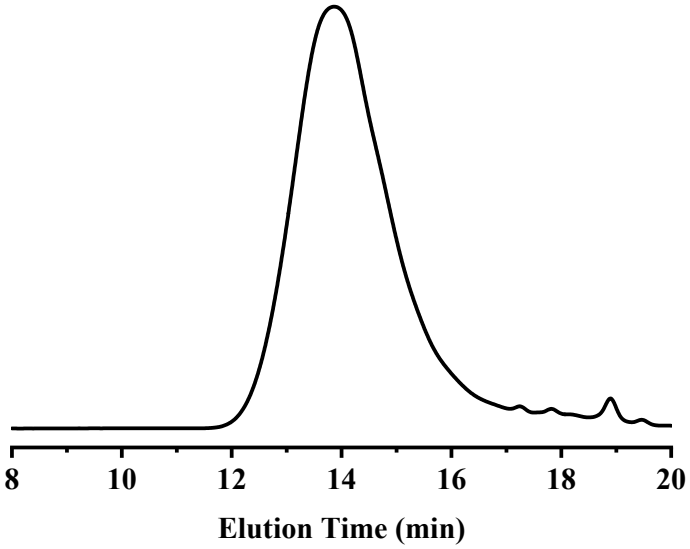


Figure S52. The GPC trace of the poly-S7 produced by Sc-1 as catalyst in toluene at R. T., [S7]/[Sc-1] = 500/1, M_n = 30 kg/mol, $Đ$ = 2.34 (Table 1, entry 12).

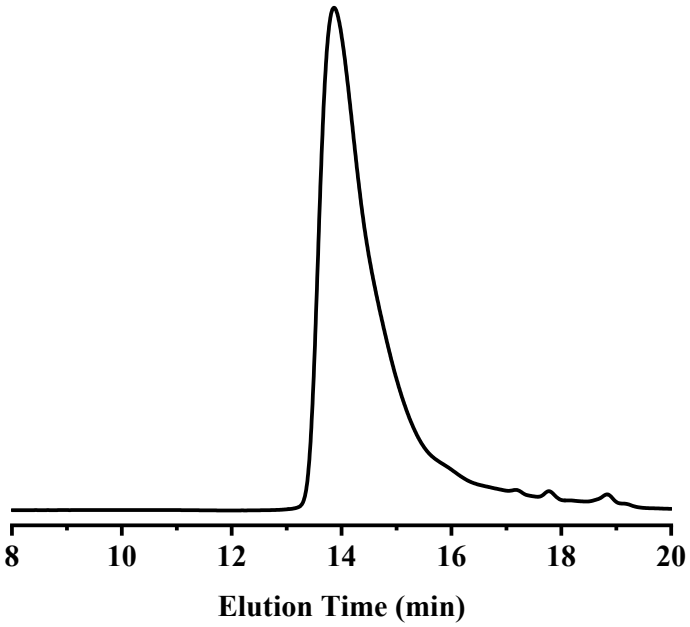


Figure S53. The GPC trace of the poly-S8 produced by Sc-1 as catalyst in toluene at R. T., [S8]/[Cat] = 500/1, M_n = 25 kg/mol, $Đ$ = 1.68 (Table 1, entry 13).

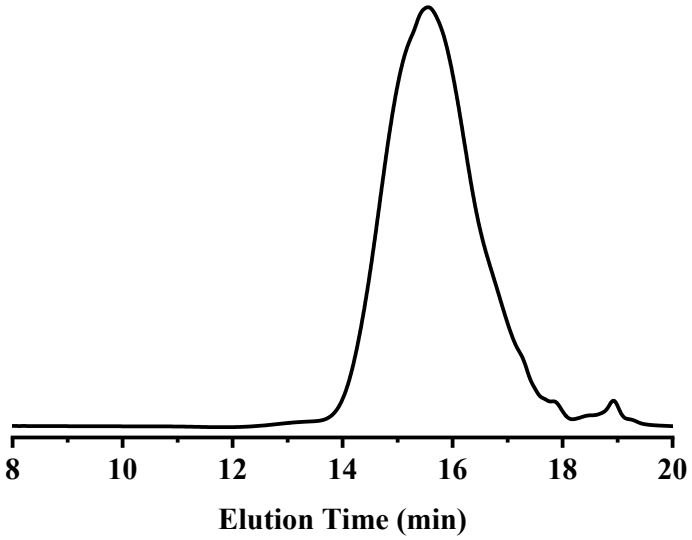


Figure S54. The GPC trace of the poly-S9 produced by Sc-1 as catalyst in toluene at R. T., [S9]/[Sc] = 500/1, M_n = 5.2 kg/mol, $Đ$ = 2.11 (Table 1, entry 14).

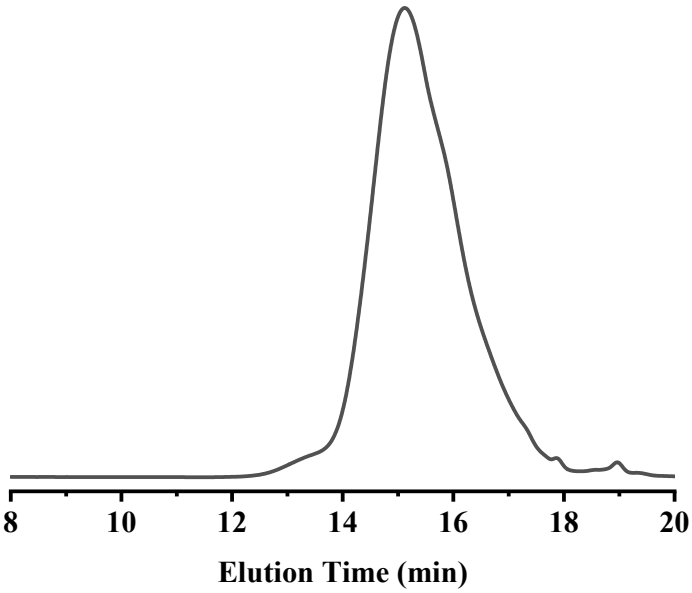


Figure S55. The GPC trace of the poly-S11 produced by Cat.1 as catalyst in toluene at R. T., [S11]/[Sc-1] = 500/1. M_n = 6.1 kg/mol, Đ = 2.41 (Table 1, entry 16).

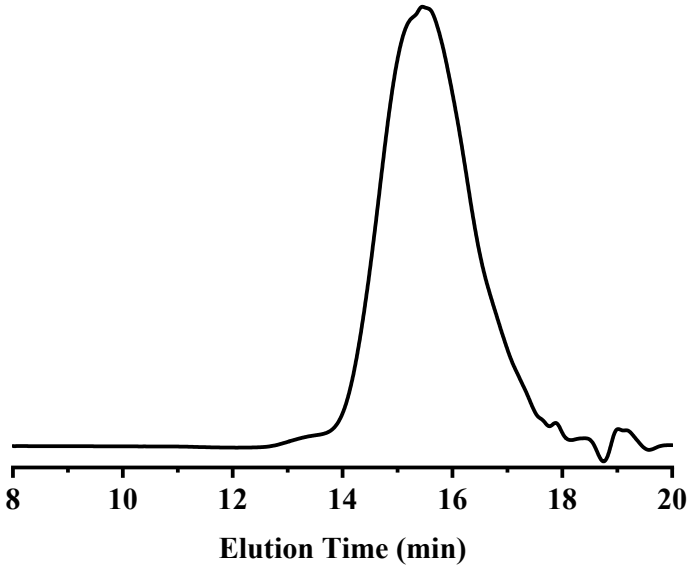


Figure 56. The GPC trace of the poly-S12 produced by Sc-1 as catalyst in toluene at R. T., [S12]/[Cat] = 500/1, M_n = 5.3 kg/mol, $Đ$ = 2.12 (Table 1, entry 17).

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(1) Wang, C.*, et al.*, Heteroatom-assisted olefin polymerization by rare-earth metal catalysts. *Sci. Adv.* **2017,** *3*.

(2) Wang, H.*, et al.*, Halocyclizations of Unsaturated Sulfoximines. *Org Lett* **2016,** *18*, 2431-2434.

(3) Lin, Y. A.*, et al.*, Allyl Sulfides Are Privileged Substrates in Aqueous Cross-Metathesis: Application to Site-Selective Protein Modification. *J. Am. Chem. Soc.* **2008,** *130*, 9642-9643.

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