Supplementary Information for

Stereospecific polymerization of donor-acceptor cyclopropanes with C(sp3)–H bond as the dormant species

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1. Materials and Methods

1.1 Materials

All Chemicals were purchased from TCI, J&K, Energy Chemical, and Adamas-beta, and were used as received without further purification.

Deuterated chloroform was purchased from Cambridge Isotope Laboratories.

All anhydrous solvents were purchased from J&K and were used as received.

1.2 Methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 Hz (100 Hz for ^{13}C) spectrometer at ambient temperature. All ^{1}H and ^{13}C NMR spectra were referenced δ 7.26 ppm and δ 77.16 ppm for $CDCl_3$.

The number average molecular weight (M_n), weight-average molecular weight (M_w), and dispersity ($Đ = M_w/M_n$) were measured by gel permeation chromatography (GPC) using an Agilent 1200 infinity system with one guard column and two MZ-Gel LS columns (300×8.0 mm, 5 um) and coupled with a Wyatt Optilab refractive index detector. The analyses were carried out at 35 °C using $CHCl_3$ as the eluent at a flow rate of 1.0 mL/min.

High performance liquid chromatography (HPLC) analysis was performed on Waters e2695 system equipped with Chiralpak IC or OD-H column (Daicel Chemical Industries, LTD).

TGA analyses were recorded on a TA Q50 TGA instrument by heating the polymer samples from 20 °C to 700 °C at the rate of 10 °C/min. DSC analyses were recorded on a TA Q20 DSC instrument at a rate of 10 °C/min.

MALDI-TOF-MS analyses of low MW polymer was performed on a Bruker Autoflex Speed TOF/TOF instrument. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as the matrix and CF_3CO_2Na was used as the cationic reagent. High resolution mass (HRMS) analyses were performed on a ThermoFisher LTQ-Orbitrap XL instrument.

Specific optical rotations were recorded on a Polarimeter 341 plus instrument at 20 °C, using sodium lamp (λ= 589 nm, 20 W). The specific rotation $[\alpha]_D^{20}$were calculated as follows: $[\alpha]_D^{20} = (100\times a)/(c\times d)$, α, optical rotation; conc, concentration in $CHCl_3$ (1 g/100 mL); d, optical tube length (dm). The circular dichroism (CD) spectra were measured in a 2.0 mm quartz cell on a JASCO J-1700 spectropolarimeter.

2. Synthesis of Monomers

M1–**M4**, **M6**, (*R*)-**M1**–(*R*)-**M4**, (*R*)-**M6**, (*S*)-**M1**–(*S*)-**M4**, and (*S*)-**M6** were synthesized according to literature procedures. [1–3] **M5** was synthesized according to previous report.[4] All data are in consistent with literatures.

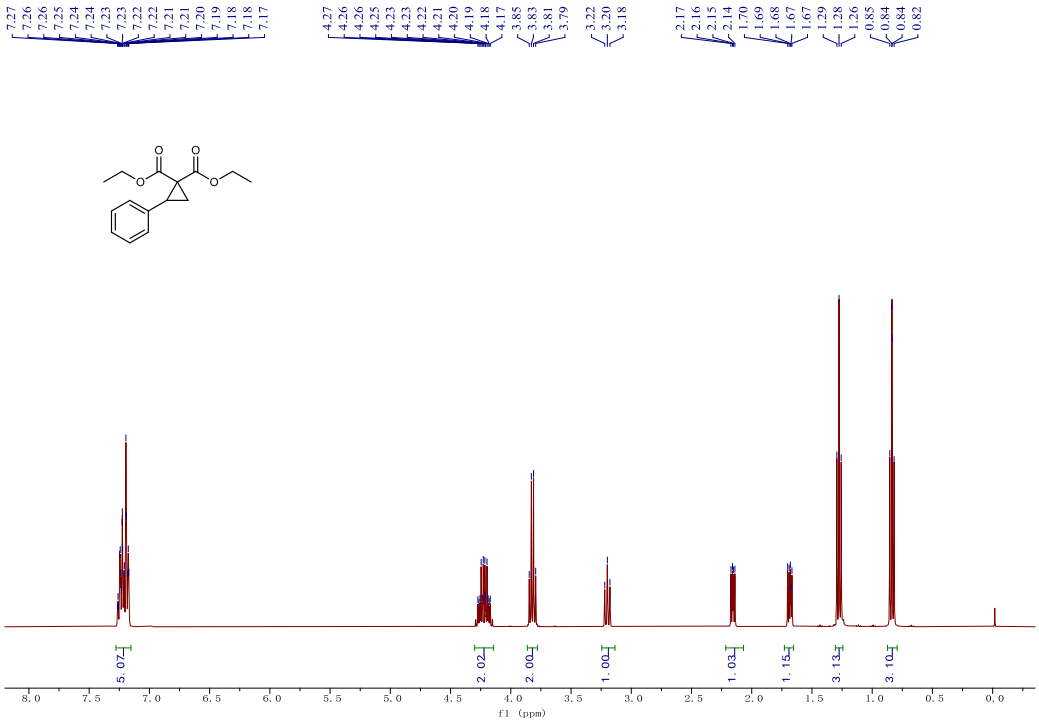


Fig. S1 ^{1}H NMR spectrum of **M1** in $CDCl_3$

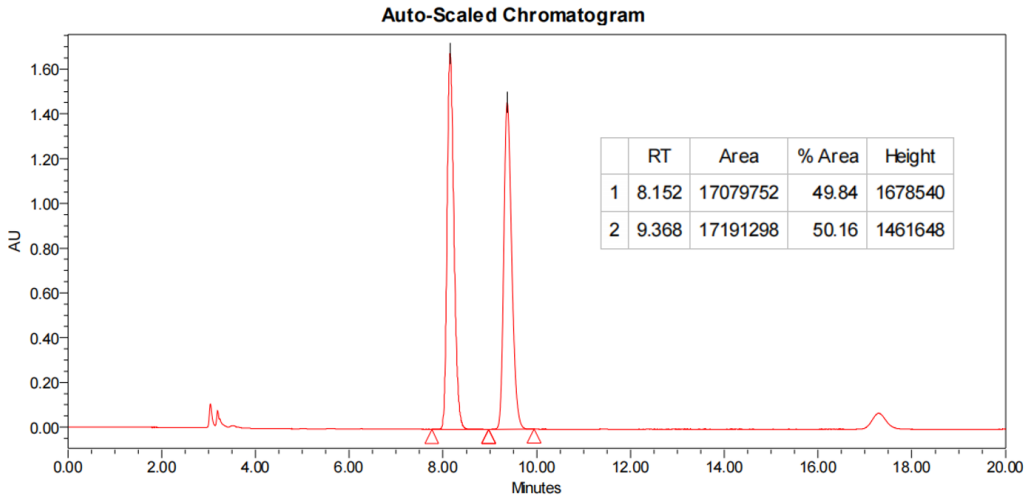
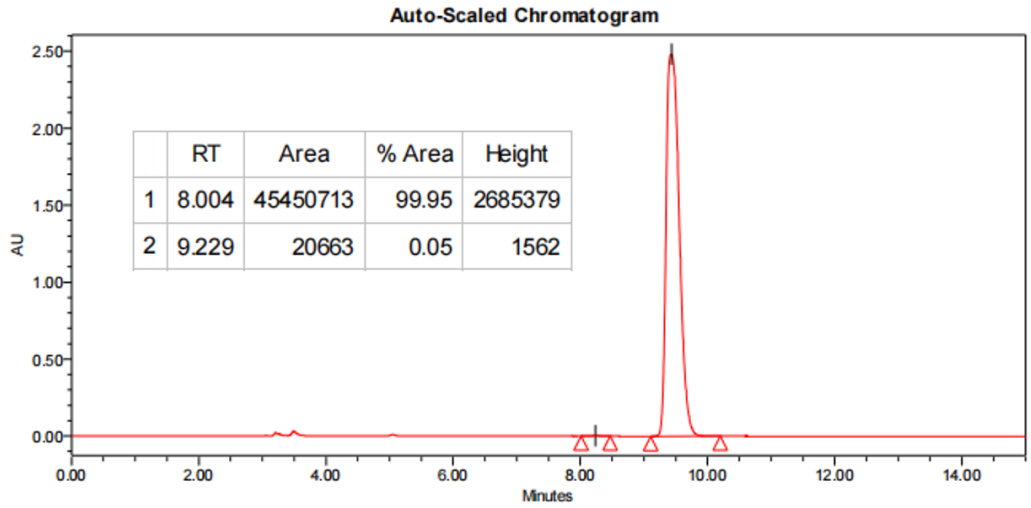
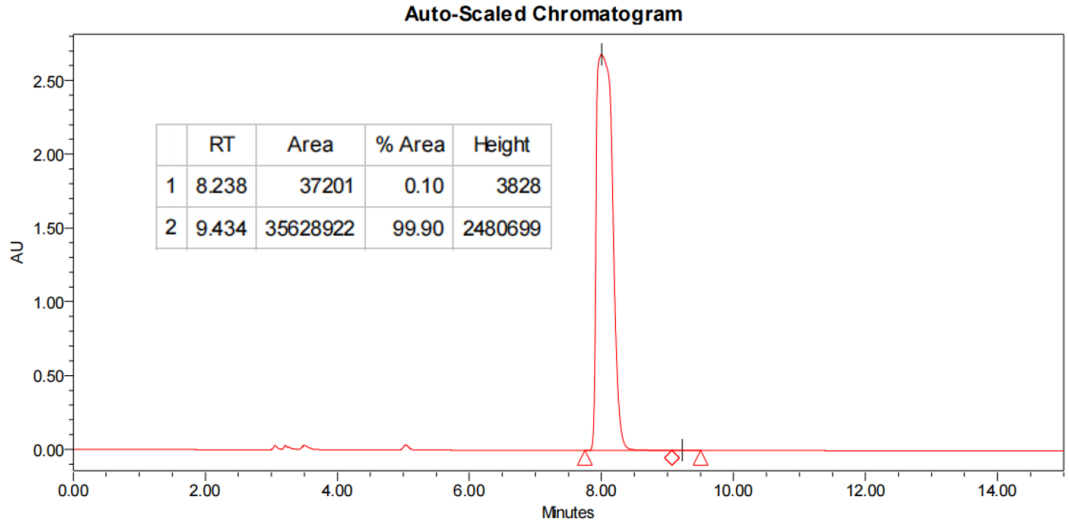


Fig. S2 HPLC spectrum of **M1.** Chiralpak IC, hexane/isopropanol = 95/5, 1 mL/min, 30 °C, 220 nm



	RT	Area	% Area	Height
1	8.004	45450713	99.95	2685379
2	9.229	20663	0.05	1562

Fig. S3 HPLC spectrum of (*R*)-**M1.** Chiralpak IC, hexane/isopropanol = 95/5, 1 mL/min, 30 °C, 220 nm



	RT	Area	% Area	Height
1	8.238	37201	0.10	3828
2	9.434	35628922	99.90	2480699

Fig. S4 HPLC spectrum of (*S*)-**M1.** Chiralpak IC, hexane/isopropanol = 95/5, 1 mL/min, 30 °C, 220 nm

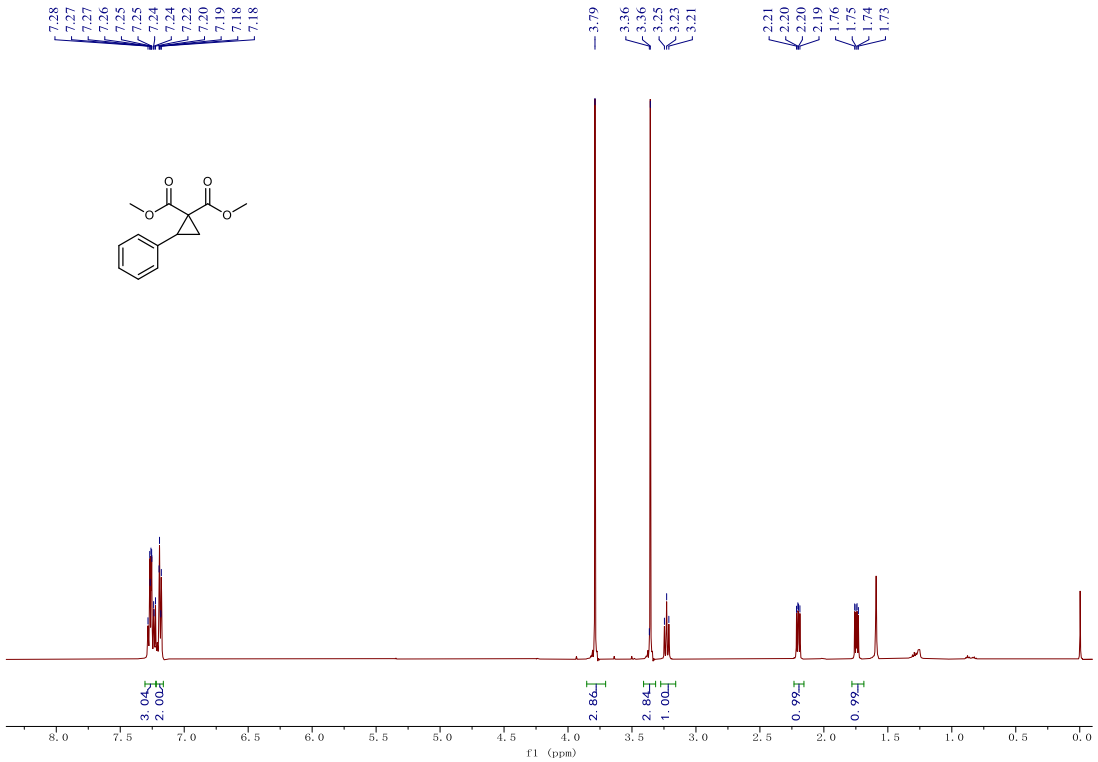


Fig. S5 ^{1}H NMR spectrum of **M2** in $CDCl_3$

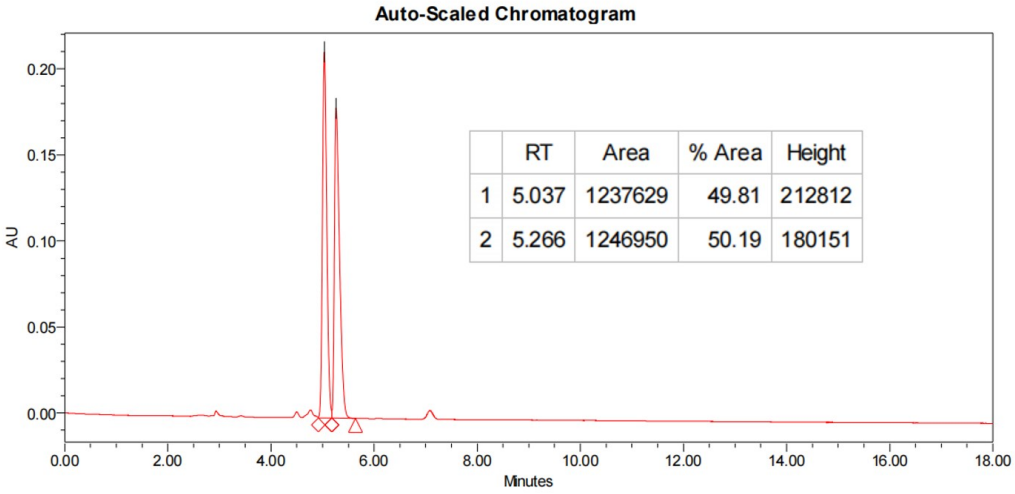


Fig. S6 HPLC spectrum of **M2.** Chiralpak OD, hexane/isopropanol = 90/10, 1 mL/min, 30 °C, 254 nm

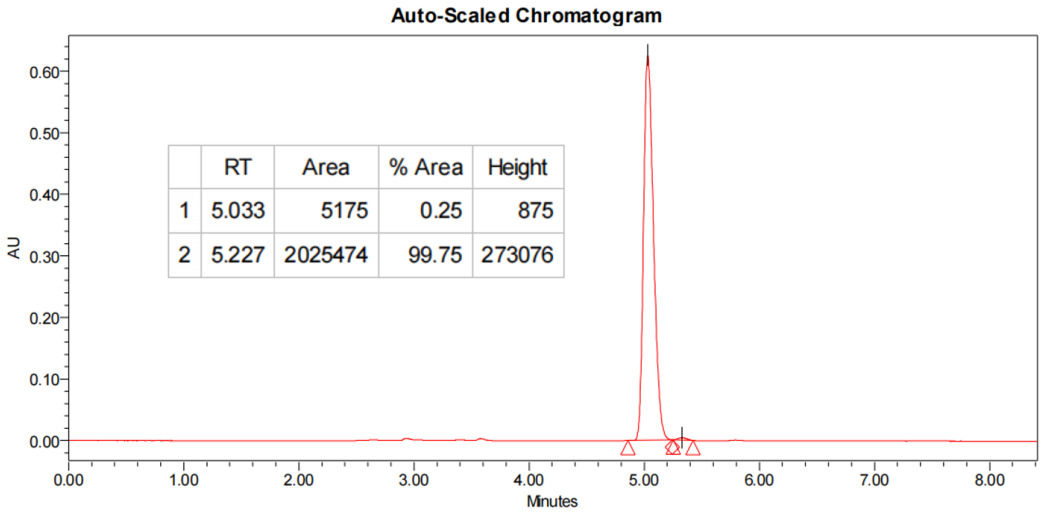


Fig. S7 HPLC spectrum of (*R*)-**M2.** Chiralpak OD, hexane/isopropanol = 90/10, 1 mL/min, 30 °C, 254 nm

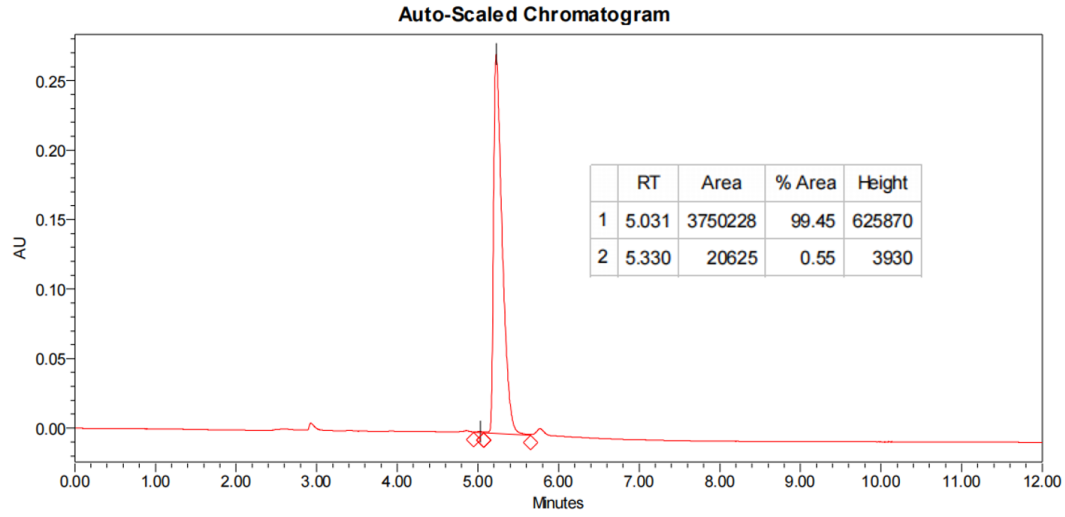


Fig. S8 HPLC spectrum of (*S*)-**M2.** Chiralpak OD, hexane/isopropanol = 90/10, 1 mL/min, 30 °C, 254 nm

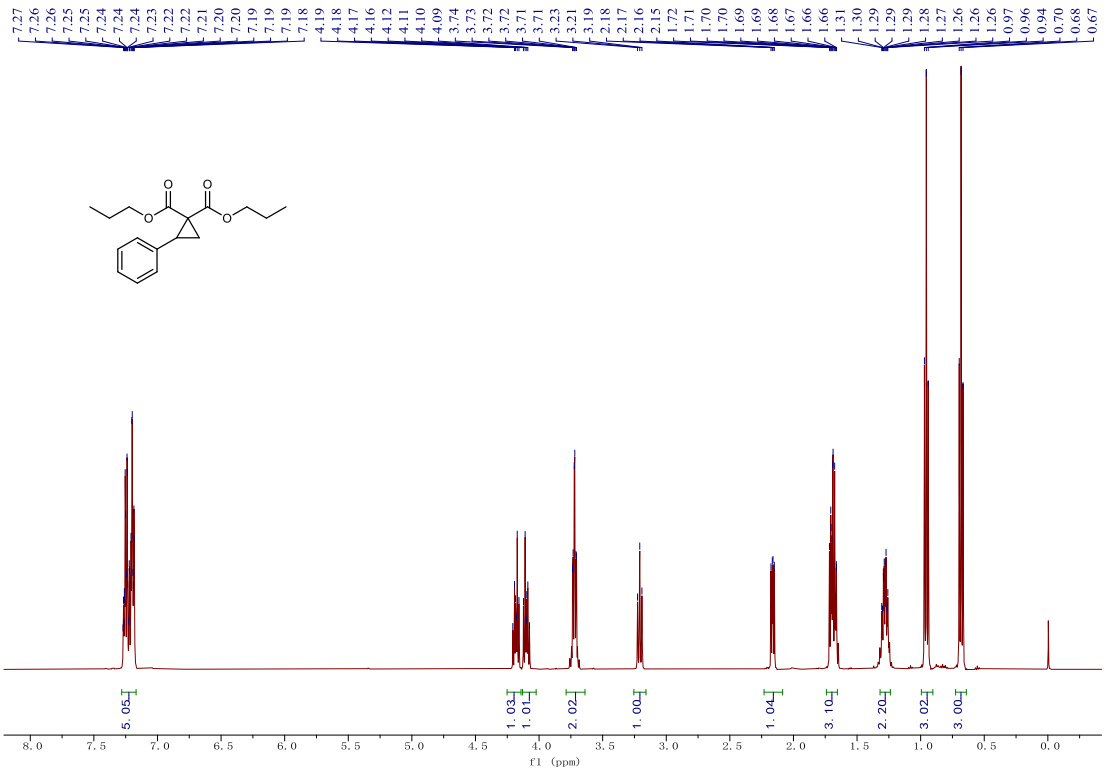


Fig. S9 ^{1}H NMR spectrum of **M3** in $CDCl_3$

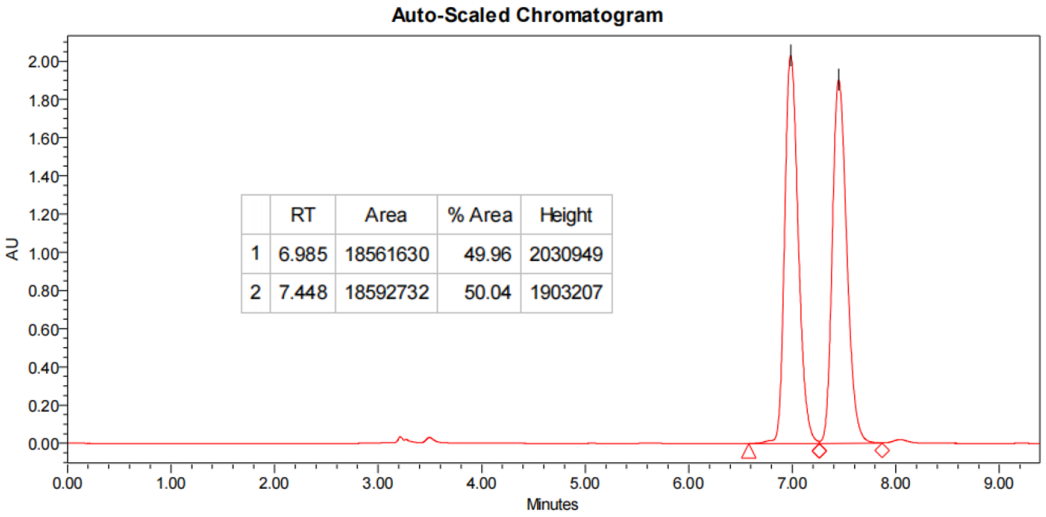


Fig. S10 HPLC spectrum of **M3.** Chiralpak IC, hexane/isopropanol = 95/5, 1 mL/min, 30 °C, 220 nm

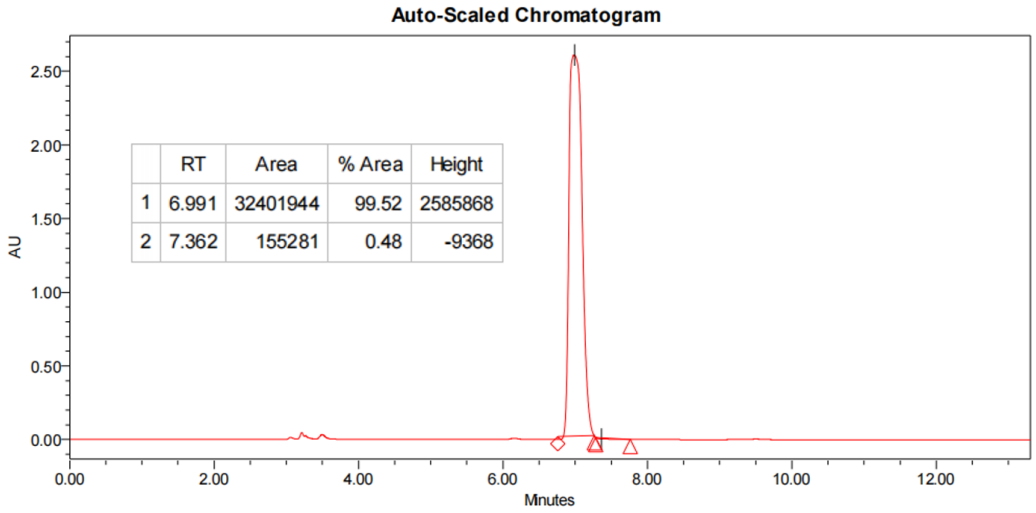


Fig. S11 HPLC spectrum of (*R*)-**M3.** Chiralpak IC, hexane/isopropanol = 95/5, 1 mL/min, 30 °C, 220 nm

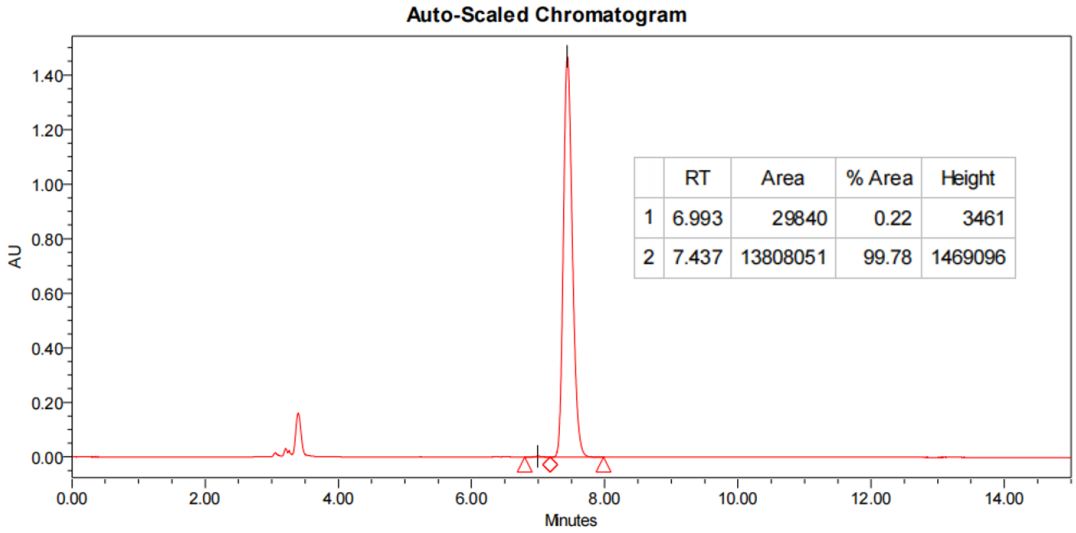


Fig. S12 HPLC spectrum of (*S*)-**M3.** Chiralpak IC, hexane/isopropanol = 95/5, 1 mL/min, 30 °C, 220 nm

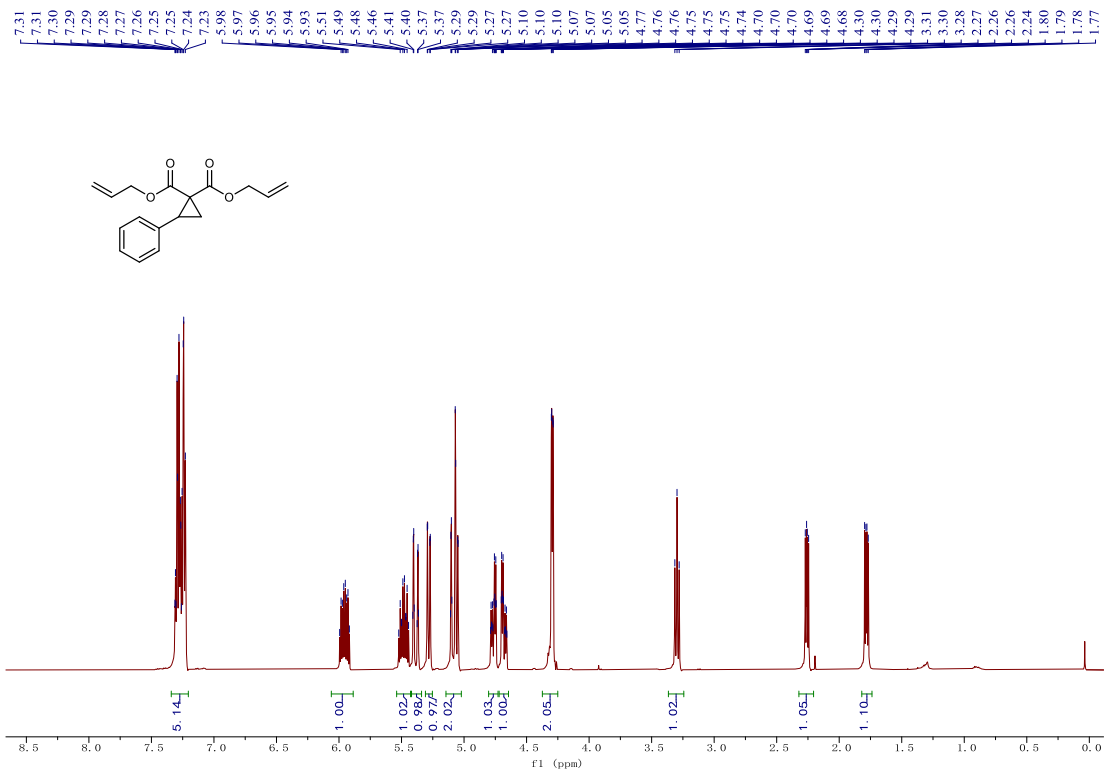


Fig. S13 ^{1}H NMR spectrum of **M4** in $CDCl_3$

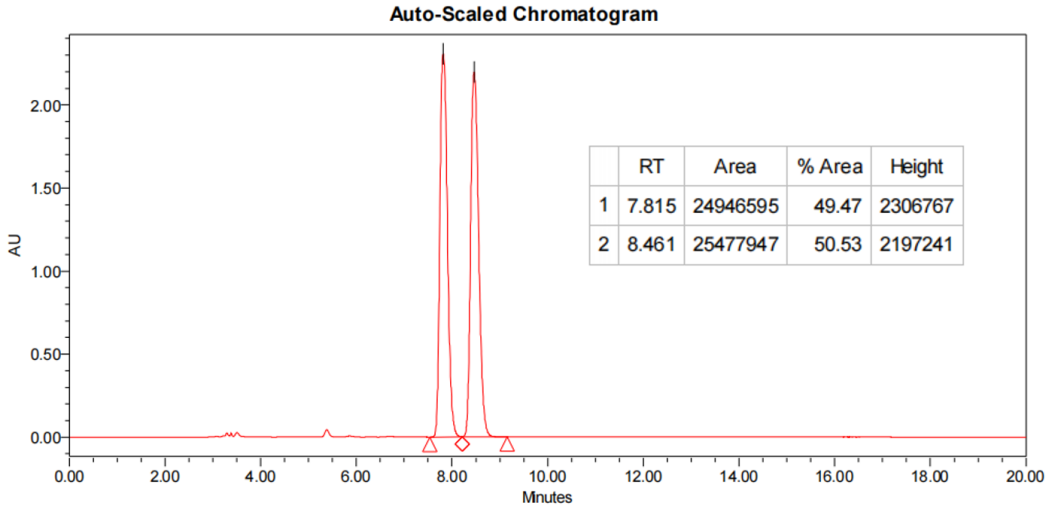
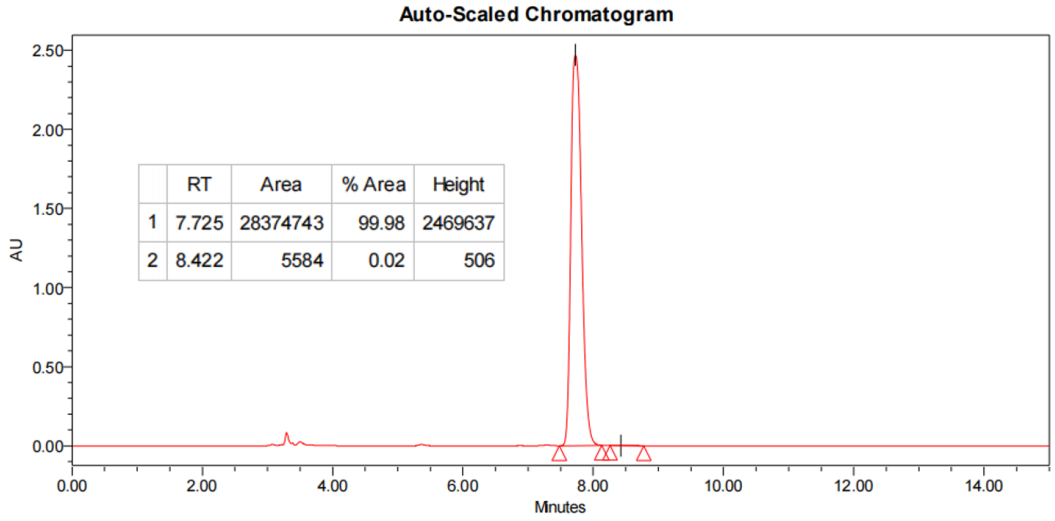
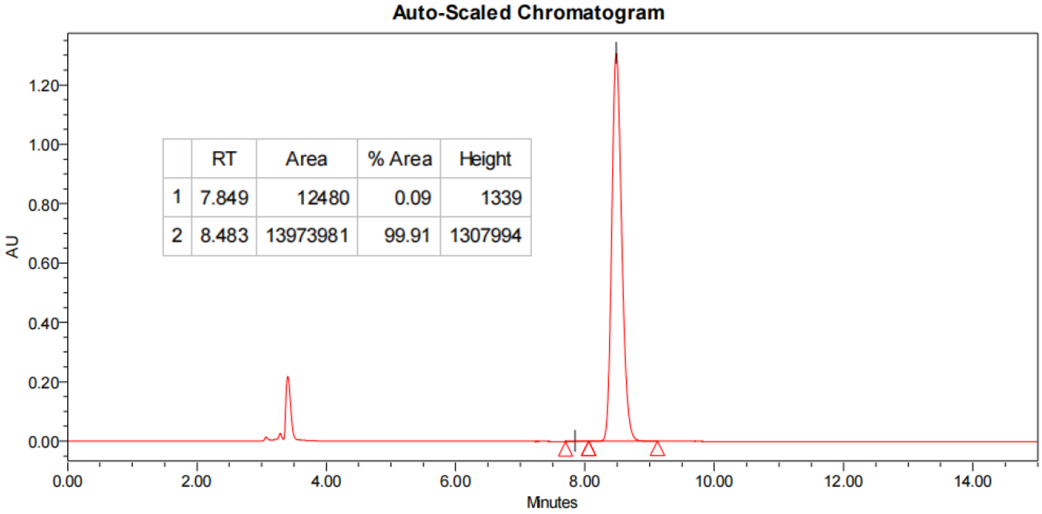


Fig. S14 HPLC spectrum of **M4.** Chiralpak IC, hexane/isopropanol = 97/3, 1 mL/min, 30 °C, 220 nm



	RT	Area	% Area	Height
1	7.725	28374743	99.98	2469637
2	8.422	5584	0.02	506

Fig. S15 HPLC spectrum of (*R*)-**M4.** Chiralpak IC, hexane/isopropanol = 97/3, 1 mL/min, 30 °C, 220 nm



	RT	Area	% Area	Height
1	7.849	12480	0.09	1339
2	8.483	13973981	99.91	1307994

Fig. S16 HPLC spectrum of (*S*)-**M4.** Chiralpak IC, hexane/isopropanol = 97/3, 1 mL/min, 30 °C, 220 nm

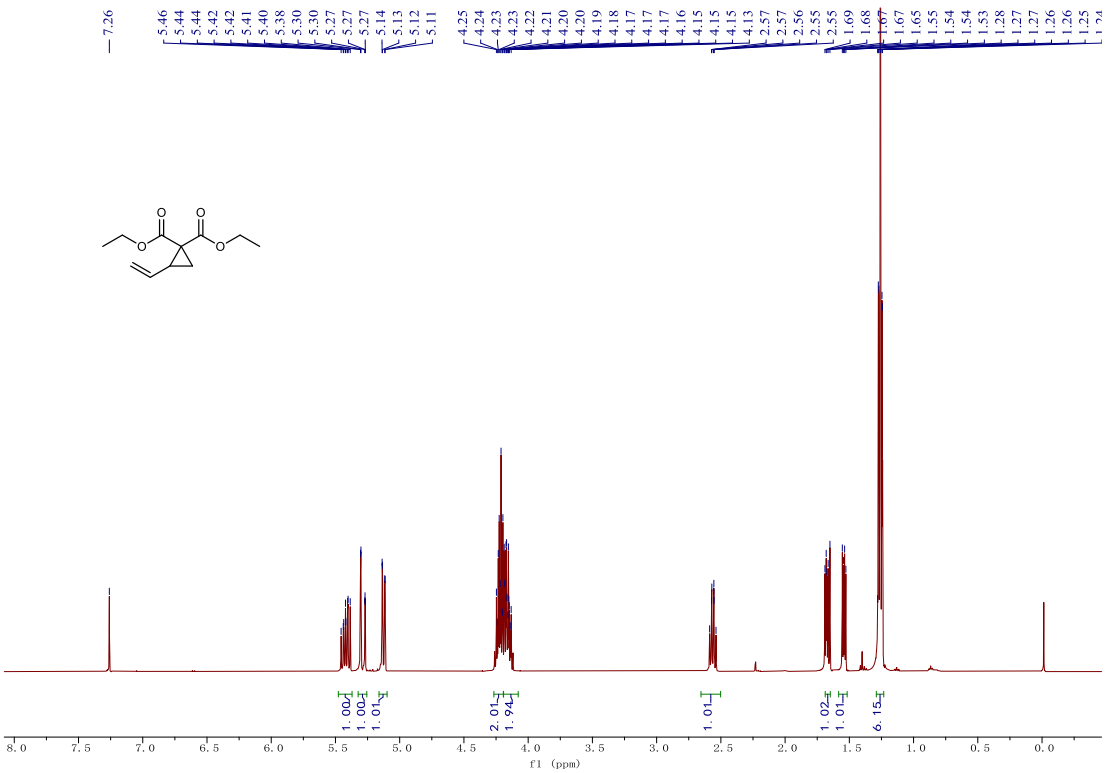


Fig. S17 ^{1}H NMR spectrum of **M6** in $CDCl_3$

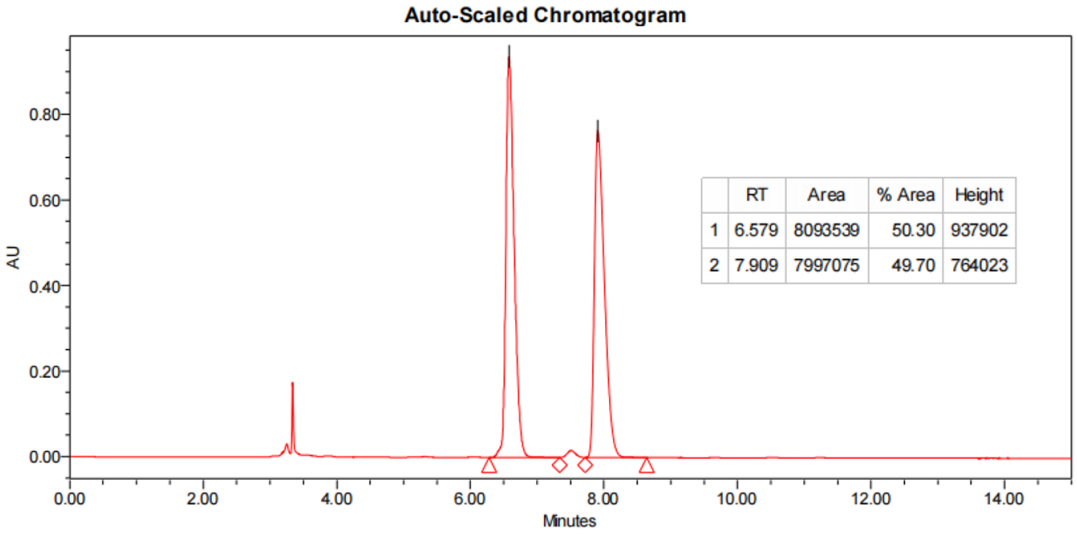


Fig. S18 HPLC spectrum of **M6.** Chiralpak IC, hexane/isopropanol = 97/3, 1 mL/min, 30 °C, 220 nm

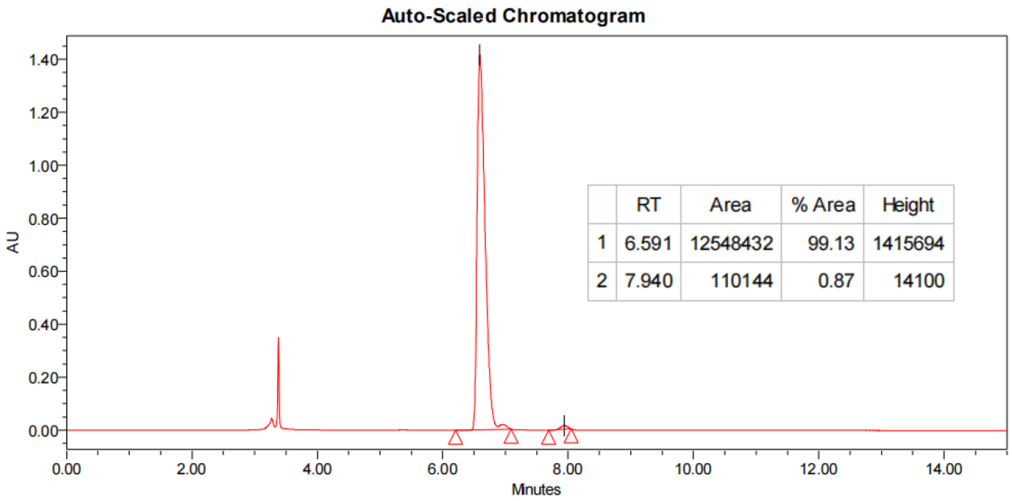


Fig. S19 HPLC spectrum of (*R*)-**M6.** Chiralpak IC, hexane/isopropanol = 97/3, 1 mL/min, 30 °C, 220 nm

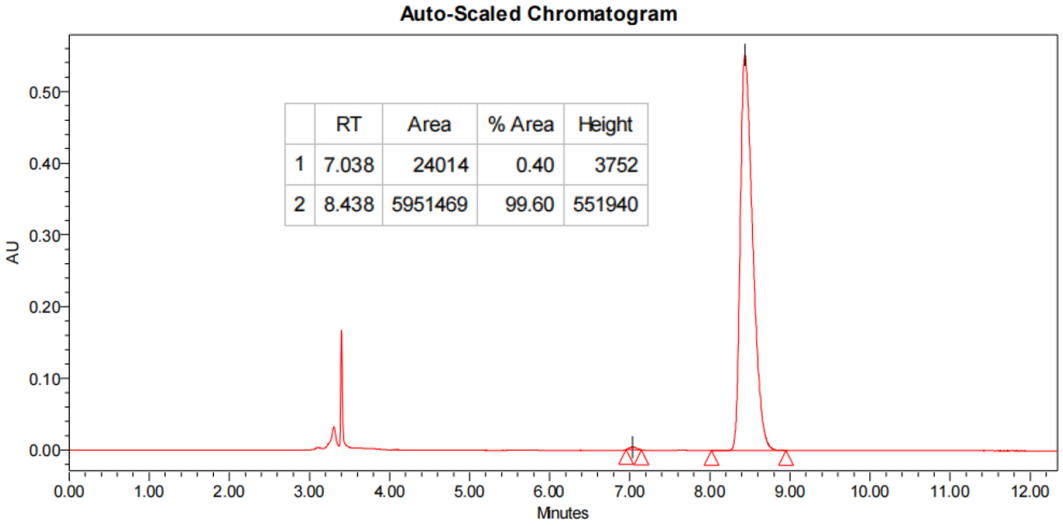


Fig. S20 HPLC spectrum of (*S*)-**M6.** Chiralpak IC, hexane/isopropanol = 97/3, 1 mL/min, 30 °C, 220 nm

3. Stereospecific ROP of DACs

3.1 General Polymerization Procedure

In a N_2-filled glove box, to an oven-dried 10 mL Schlenk tube containing a magnetic stir bar were added monomer (0.4 mmol), anhydrous MeCN (0.4 mL), dry $MgBr_2$ (0.02 mmol), DBU (0.02 mmol), and initiator (0.02 mmol). The reaction was stirred at 50 °C for 24 h. An aliquot was taken for ^{1}H NMR analysis to determine the monomer conversion, then dried under vacuum for direct GPC analysis to obtain the M_n and $Đ$. For further purification, the reaction mixture was slowly added into 10.0 mL of hexane while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with hexane (5.0 mL × 2) and dried overnight under vacuum at 50 °C to a constant weight.

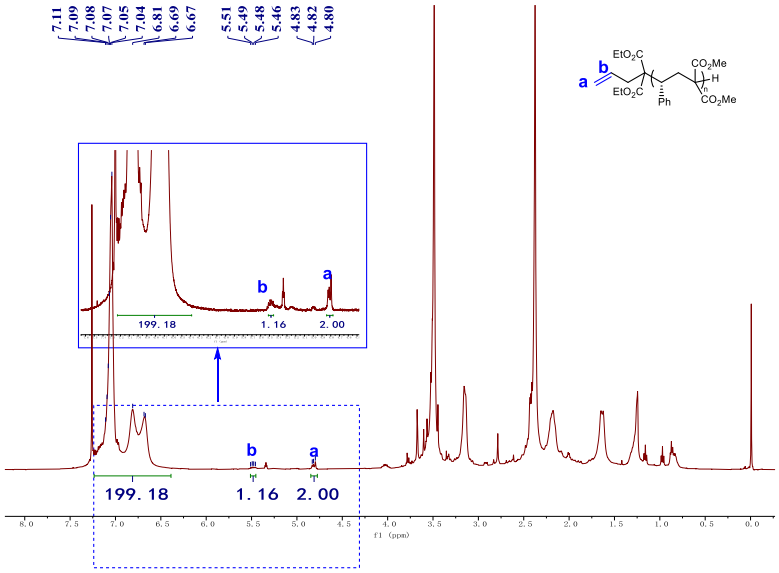


Fig. S21 ^{1}H NMR of P[(*S*)-**M2**] ($CDCl_3$). $M_{n,NMR}$ = 199.18/5*234.25 + 220.23 = 9.6 kDa

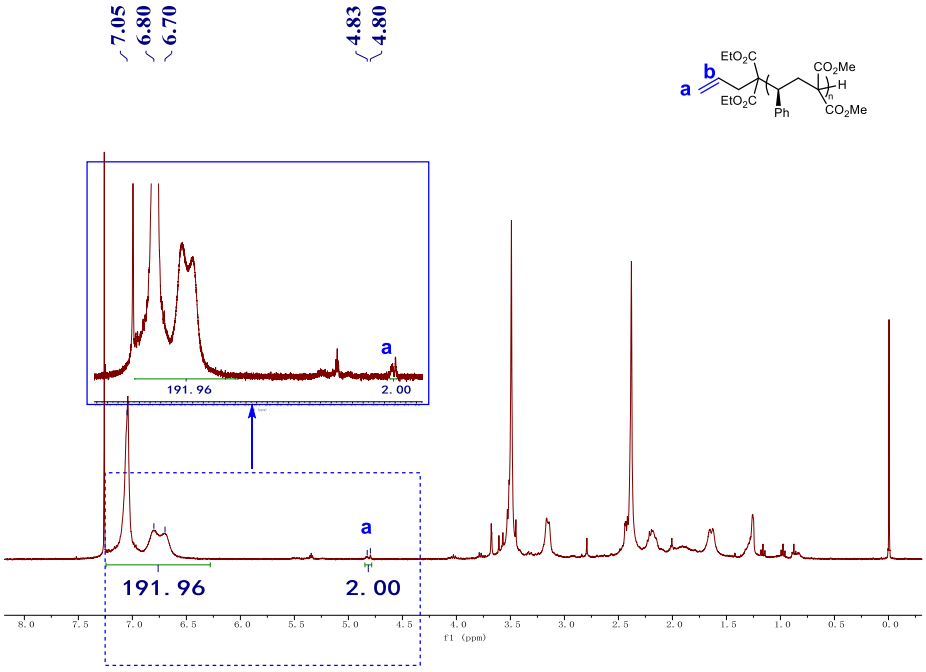


Fig. S22 ^{1}H NMR of P[(*R*)-**M2**] in $CDCl_3$, $M_{n,NMR}$ = 191.96/5 * 234.25 + 220.23 = 9.1 kDa

Table S1. Monomer Racemization

entry	monomer (ee%)	time (min)	conv. (%)	*ee*% of recovered monomer
1	(*S*)-**M1** (>99)	150	48	>99
2	(*S*)-**M2** (>99)	110	74	>99
3	(*S*)-**M3** (>99)	180	36	>99
4	(*S*)-**M4** (>99)	120	62	>99
5	(*S*)-**M6** (>99)	90	45	38

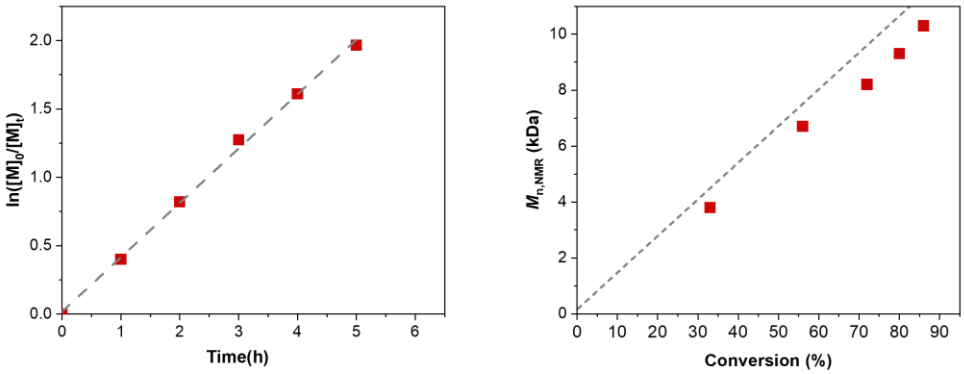
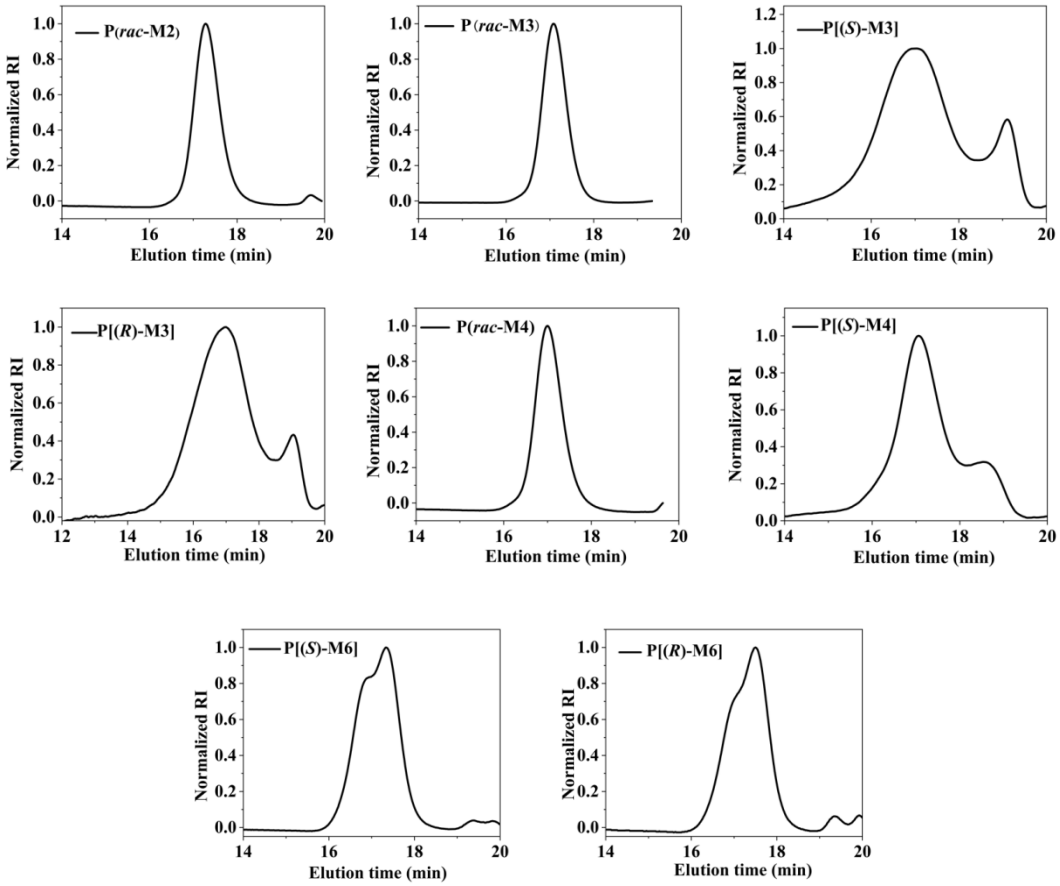
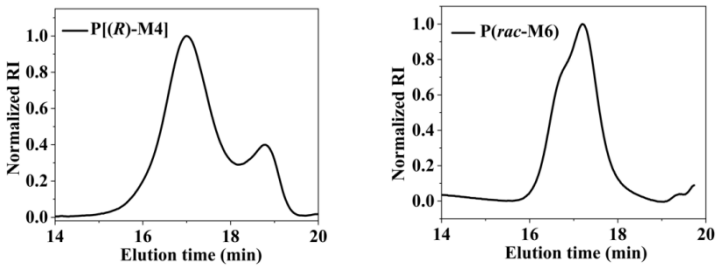


Fig. S23 Progress analysis for the polymerization of (*S*)-M1 under conditions of [(*S*)-**M1**]/[diethyl 2-allylmalonate]/[$MgBr_2$]/[DBU] = 100/2/5/5 in MeCN at 50°C.

3.2 GPC traces for PM2–PM6





The low-MW tail (M_n ~ 3 kDa) of **P**[(*S*)-**M1**] was separated via diffusion dialysis in dichloromethane. The mass cutoff was 3.5 kDa. The obtained low-MW polymer was characterized by MALDI-TOF mass spectrometry, which showed a major set of peaks that supported the high fidelity of diethyl malonate chain ends, and a minor set of peaks that corresponded to water-initiation and Dieckmann condensation-type backbiting.

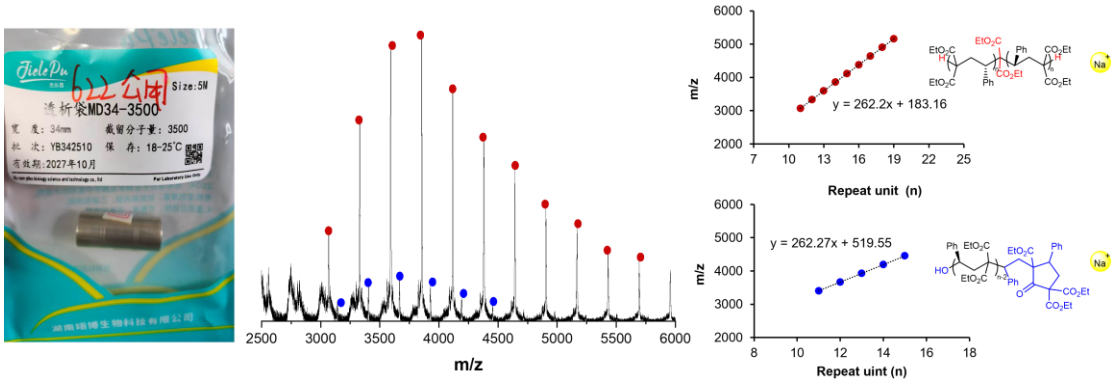


Fig. S24 Separation and characterization of low-MW **P**[(*S*)-**M1**].

Although the MALDI-TOF mass analysis for the high-MW (>15 kDa) polymer was unsuccessful, major peaks in their ^{1}H NMR spectra were almost identical—at least the repeating units remain the same.

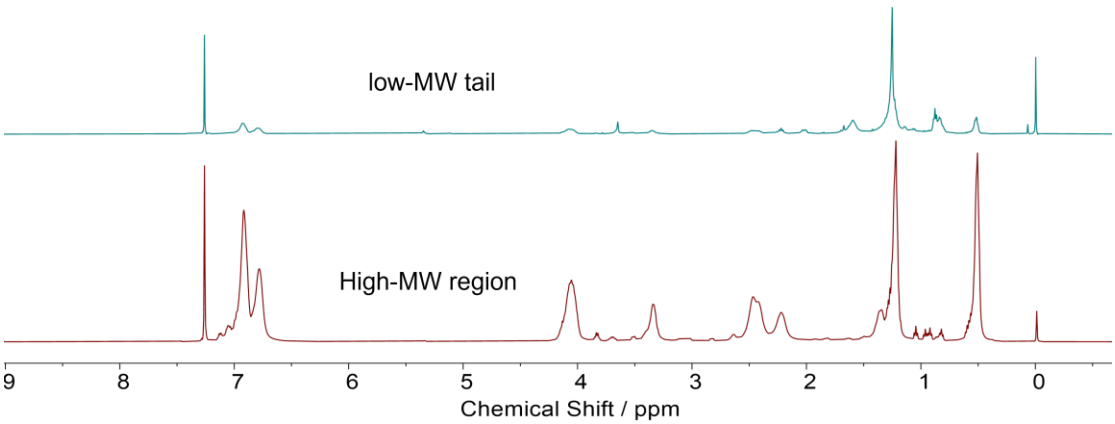
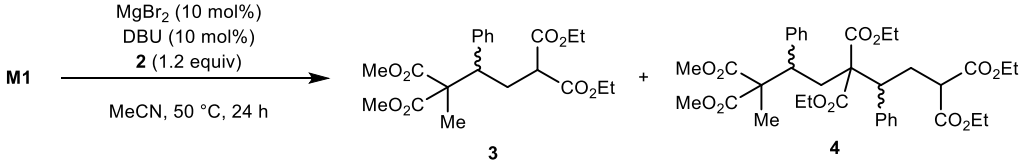
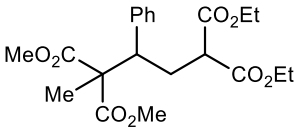


Fig. S25 Comparison of the ^{1}H NMR spectra of low- and high-MW **P**[(*S*)-**M1**].

4. Small-Molecule Model Reaction

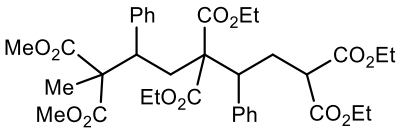


To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar in a N_2-filled glove box, **M1** (1.0 equiv, 0.3 mmol), $MgBr_2$ (0.1 equiv, 0.03 mmol), DBU (0.1 equiv, 0.03 mmol), diethyl methylmalonate (1.2 equiv, 0.36 mmol) and anhydrous MeCN (1.0 mL) were sequentially added. The tube was stirred at 50 ℃ for 24 h. Then the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (*n*-pentane/EtOAc = 5:1) to give **3** as a colorless liquid (88mg, 72% yield) and **4** as a colorless liquid (28mg, 14% yield).



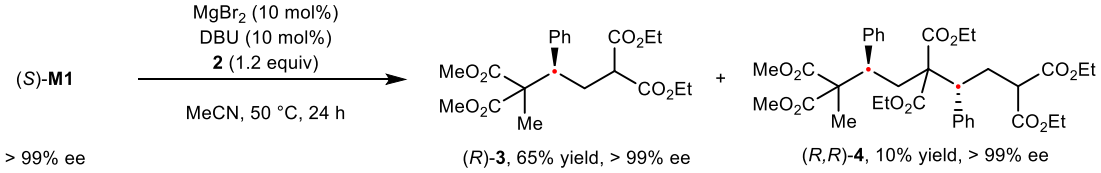
Tetraethyl 3-phenylpentane-1,1,4,4-tetracarboxylate (3)

Colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 3H), 7.20 (dd, *J* = 7.9, 1.7 Hz, 2H), 4.27 (qd, *J* = 7.1, 2.2 Hz, 2H), 4.01 (p, *J* = 7.0 Hz, 2H), 3.79 (s, 3H), 3.61 (s, 3H), 3.51 (dd, *J* = 12.1, 2.9 Hz, 1H), 3.06 (dd, *J* = 10.2, 4.6 Hz, 1H), 2.59 – 2.39 (m, 2H), 1.44 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.3, 169.1, 168.9, 137.4, 129.5, 128.3, 127.6, 61.2, 61.2, 58.3, 52.4, 52.3, 50.5, 47.8, 30.2, 17.7, 14.0, 13.8. **HRMS:** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{29}O_8$ 409.1857, found 409.1858.

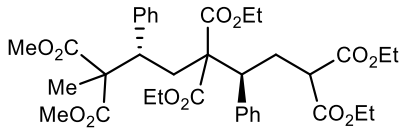


Hexaethyl 3,6-diphenyloctane-1,1,4,4,7,7-hexacarboxylate (4)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 6.99 (m, 10H), 4.36 – 4.10 (m, 3H), 4.01 – 3.83 (m, 3H), 3.62 – 3.54 (m, 4H), 3.43 (d, *J* = 52.7 Hz, 4H), 3.33 – 3.02 (m, 2H), 2.92 (ddd, *J* = 9.9, 4.8, 2.0 Hz, 1H), 2.73 – 2.45 (m, 2H), 2.39 – 2.11 (m, 2H), 1.31 (dd, *J* = 25.4, 7.1 Hz, 3H), 1.27 – 1.22 (m, 3H), 1.20 (d, *J* = 7.2 Hz, 3H), 1.10 (td, *J* = 7.1, 3.4 Hz, 3H), 0.98 (q, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.5, 171.5, 171.4, 171.2, 169.9, 169.8, 169.7, 169.5, 169.2, 169.1, 169.0, 138.3, 138.2, 138.1, 137.6, 128.2, 128.0, 127.5, 127.5, 127.4, 127.1, 127.0, 61.2, 61.2, 61.2, 61.1, 61.0, 60.8, 60.7, 60.6, 59.6, 59.6, 52.3, 52.2, 52.0, 52.0, 51.0, 50.8, 50.7, 48.9, 47.3, 46.6, 37.5, 34.7, 31.5, 31.3, 20.0, 19.3, 14.1, 13.8, 13.5, 13.4.**HRMS:** (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{47}O_{12}$ 671.3062, found 671.3063.

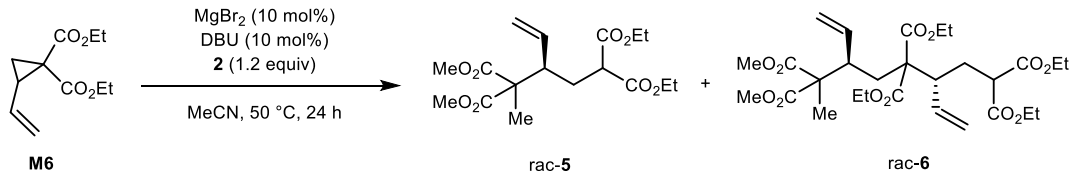


To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar in a N_2-filled glove box, *(S)*-**M1** (1.0 equiv, 0.3 mmol), $MgBr_2$ (0.1 equiv, 0.03 mmol), DBU (0.1 equiv, 0.03 mmol), dimethyl methylmalonate (1.2 equiv, 0.36 mmol) and anhydrous MeCN (1.0 mL) were sequentially added. TThe tube was stirred at 50 ℃ for 24 h. Then the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (*n*-pentane/EtOAc = 5:1) to give (*R*)-**3** as a colorless liquid (80 mg, 65% yield, 99% ee) and (*R,R*)-**4** as a colorless liquid (21 mg, 10% yield).



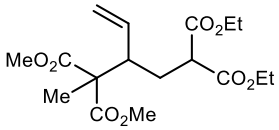
Hexaethyl (3S,6S)-3,6-diphenyloctane-1,1,4,4,7,7-hexacarboxylate (*R,R*)-**4**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.03 (m, 10H), 4.31 – 4.09 (m, 4H), 3.90 (qd, *J* = 7.1, 1.3 Hz, 2H), 3.49 (s, 4H), 3.38 (s, 3H), 3.27 – 3.16 (m, 2H), 3.07 (dd, *J* = 10.7, 7.2 Hz, 1H), 2.93 (dd, *J* = 9.9, 4.7 Hz, 1H), 2.60 (ddd, *J* = 14.2, 12.2, 4.8 Hz, 1H), 2.50 (dd, *J* = 14.8, 11.0 Hz, 1H), 2.34 (ddd, *J* = 14.2, 9.9, 2.5 Hz, 1H), 2.15 (dd, *J* = 14.8, 1.3 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.18 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.5, 171.2, 169.9, 169.5, 169.2, 169.0, 138.3, 137.7, 128.2, 127.5, 127.4, 127.1, 61.2, 61.2, 61.0, 60.8, 59.6, 52.0, 52.0, 51.0, 50.8, 47.3, 37.5, 31.3, 20.0, 14.1, 13.8, 13.4. **HRMS:** (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{47}O_{12}$ 671.3062, found 671.3063.



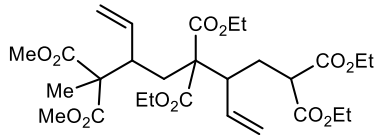
M6 rac-**5** rac-**6**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar in a N_2-filled glove box, **M6** (1.0 equiv, 0.3 mmol), $MgBr_2$ (0.1 equiv, 0.03 mmol), DBU (0.1 equiv, 0.03 mmol), diethyl methylmalonate (1.2 equiv, 0.36 mmol) and anhydrous MeCN (1.0 mL) were sequentially added. The tube was stirred at 50 ℃ for 24 h. Then the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (*n*-pentane/EtOAc = 5:1) to give rac-**5** as a colorless liquid (43 mg, 40% yield) and rac-**6** as a colorless liquid (19 mg, 11% yield).



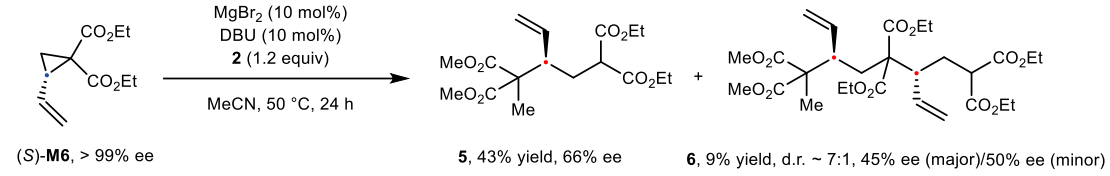
Tetraethyl 3-vinylpentane-1,1,4,4-tetracarboxylate (rac-5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (dt, *J* = 16.9, 10.0 Hz, 1H), 5.19 – 5.02 (m, 2H), 4.21 (qd, *J* = 7.1, 1.1 Hz, 2H), 4.12 (tq, *J* = 7.1, 3.5 Hz, 2H), 3.67 (d, *J* = 11.1 Hz, 6H), 3.32 (dd, *J* = 10.4, 4.3 Hz, 1H), 2.68 (ddd, *J* = 12.0, 9.9, 2.3 Hz, 1H), 2.11 (ddd, *J* = 13.7, 10.5, 2.3 Hz, 1H), 1.89 (ddd, *J* = 13.7, 11.7, 4.3 Hz, 1H), 1.39 (s, 3H), 1.24 (dt, *J* = 19.2, 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.3, 171.2, 169.3, 168.9, 135.5, 120.1, 61.4, 61.3, 57.4, 52.4, 52.4, 50.1, 47.2, 28.9, 17.4, 14.0, 13.9. **HRMS:** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{27}O_8$ 359.1700, found 359.1701.



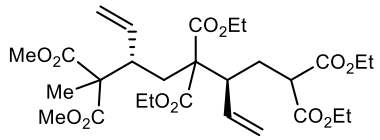
Hexaethyl 3,6-divinyloctane-1,1,4,4,7,7-hexacarboxylate (rac-6)

^{1}H NMR (500 MHz, CDCl3) δ 5.72 – 5.34 (m, 2H), 5.19 (td, *J* = 10.1, 1.9 Hz, 1H), 5.09 (ddd, *J* = 16.7, 14.4, 1.9 Hz, 1H), 5.02 – 4.83 (m, 2H), 4.28 – 3.99 (m, 8H), 3.65 (d, *J* = 4.5 Hz, 6H), 3.35 – 3.25 (m, 1H), 2.97 – 2.76 (m, 1H), 2.61 (dddd, *J* = 21.6, 12.1, 9.9, 2.2 Hz, 1H), 2.27 (dddd, *J* = 44.7, 14.0, 10.3, 2.2 Hz, 1H), 2.17 – 2.03 (m, 1H), 1.96 (dddd, *J* = 32.3, 14.0, 10.5, 5.8 Hz, 2H), 1.62 (ddd, *J* = 13.9, 11.7, 4.5 Hz, 1H), 1.38 (d, *J* = 2.9 Hz, 3H), 1.31 – 1.18 (m, 12H). **^{13}C NMR** (126 MHz, CDCl3) δ 171.4, 171.4, 171.3, 171.2, 169.7, 169.6, 169.6, 169.4, 169.3, 169.0, 137.2, 136.5, 135.5, 135.4, 120.6, 120.0, 118.7, 61.3, 61.2, 61.2, 60.9, 60.9, 60.9, 60.9, 59.8, 59.1, 58.9, 58.7, 52.2, 52.2, 50.3, 50.1, 47.6, 47.2, 45.8, 45.4, 34.8, 34.1, 29.6, 29.4, 18.2, 18.1, 14.0, 13.9, 13.9, 13.9, 13.7. **HRMS:** (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{43}O_{12}$ 571.2749, found 571.2750.



To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar in a N_2-filled glove box, (*S*)-**M6** (1.0 equiv, 0.3 mmol), $MgBr_2$ (0.1 equiv, 0.03 mmol), DBU (0.1 equiv, 0.03 mmol), diethyl methylmalonate (1.2 equiv, 0.36 mmol) and anhydrous MeCN (1.0 mL) were sequentially added. The tube was stirred at 50 ℃ for 24 h. Then the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (*n*-pentane/EtOAc = 5:1) to give **5** as a colorless liquid (46 mg, 43% yield, 66% ee) and **6** as a colorless liquid (15 mg, 9% yield).

Hexaethyl (3S,6S)-3,6-divinyloctane-1,1,4,4,7,7-hexacarboxylate (5)



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 – 5.55 (m, 1H), 5.53 – 5.28 (m, 1H), 5.20 (ddd, *J* = 10.1, 8.1, 1.9 Hz, 1H), 5.10 (ddd, *J* = 17.0, 11.5, 1.9 Hz, 1H), 5.04 – 4.89 (m, 2H), 4.29 – 4.05 (m, 8H), 3.67 (d, *J* = 3.4 Hz, 6H), 3.32 (ddd, *J* = 10.3, 7.2, 4.4 Hz, 1H), 2.92 (qd, *J* = 10.5, 2.1 Hz, 1H), 2.72 – 2.51 (m, 1H), 2.38 – 1.87 (m, 4H), 1.40 (d, *J* = 2.4 Hz, 3H), 1.31 – 1.20 (m, 12H). **13C NMR for major**(126 MHz, CDCl3) δ 171.5, 171.4, 169.8, 169.7, 169.5, 169.1, 137.2, 135.5, 120.7, 118.7, 61.3, 61.2, 61.0, 61.0, 59.8, 59.0, 52.3, 52.3, 50.4, 47.7, 45.9, 34.8, 29.6, 18.2, 14.1, 14.0, 13.8. **^{13}C NMR for minor** (126 MHz, $CDCl_3$) δ 169.7, 169.4, 136.5, 129.9, 120.1, 60.9, 59.1, 58.8, 50.2, 47.3, 45.5, 35.9, 34.1, 31.9, 29.7, 29.4, 29.3, 29.2, 27.2, 25.5, 22.7, 18.3, 13.9. **HRMS:** (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{43}O_{12}$ 571.2749, found 571.2750.

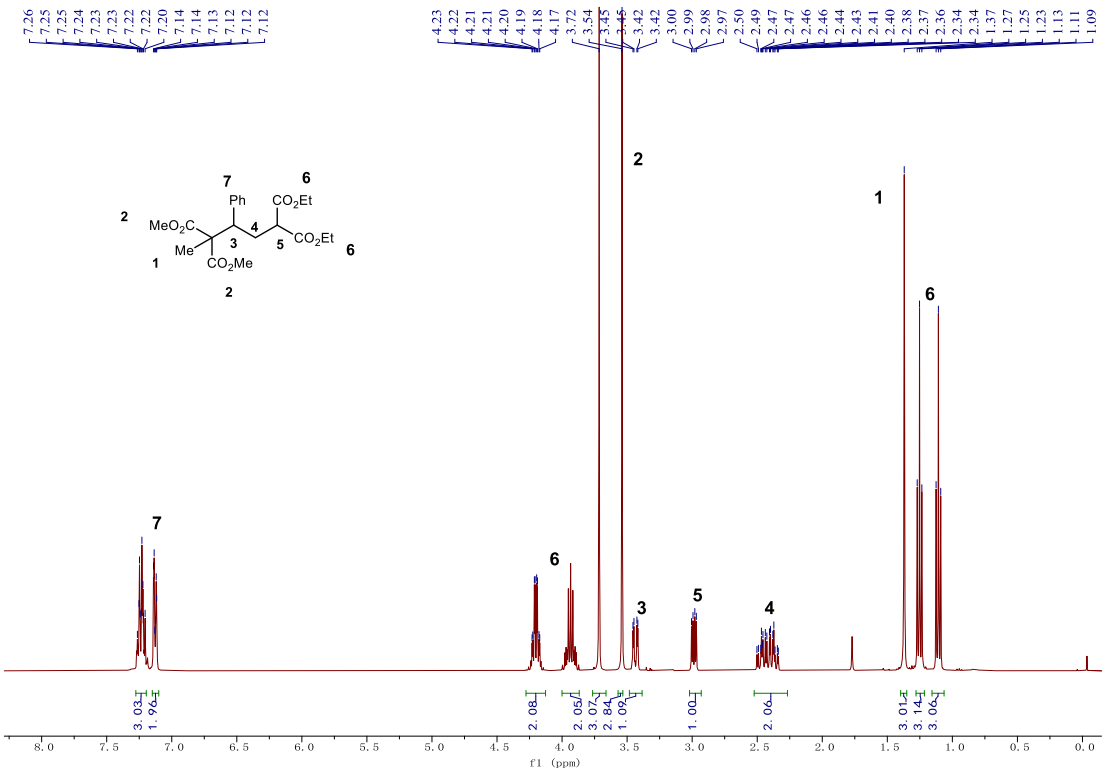


Fig. S26 ^{1}H NMR spectrum of **3** in $CDCl_3$

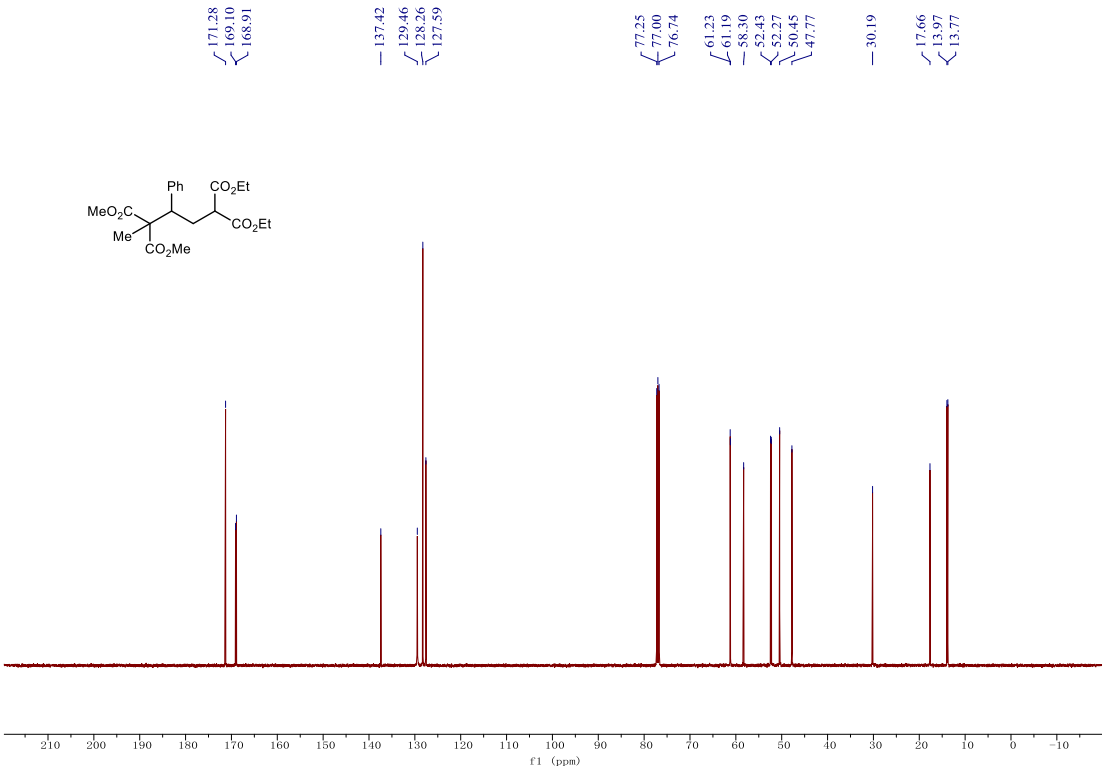
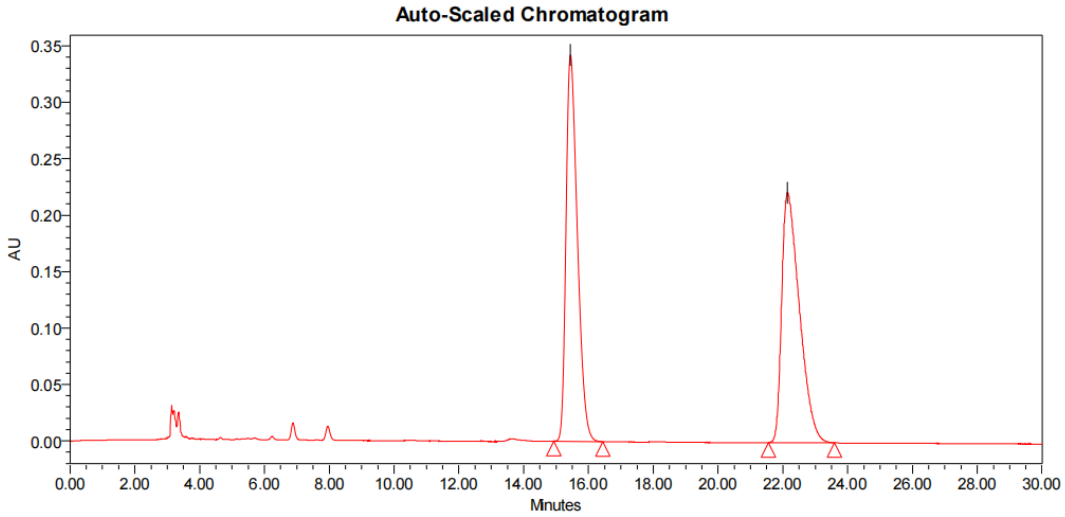
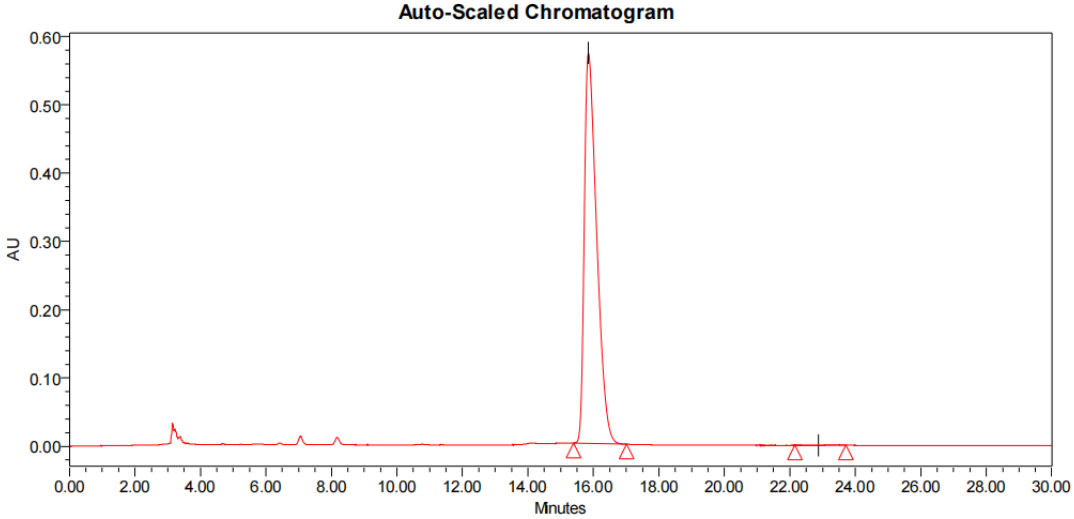


Fig. S27 ^{13}C NMR spectrum of **3** in $CDCl_3$



	RT	Area	% Area	Height
1	15.442	8329653	49.71	342337
2	22.143	8426674	50.29	221491

Fig. S28 HPLC spectrum of **3.** Chiralpak IC, hexane/isopropanol = 90/10, 1 mL/min, 30 °C, 220 nm



	RT	Area	% Area	Height
1	15.848	15025002	99.90	571768
2	22.867	15195	0.10	-303

Fig. S29 HPLC spectrum of (*R*)-**3.** Chiralpak IC, hexane/isopropanol = 90/10, 1 mL/min, 30 °C, 220 nm

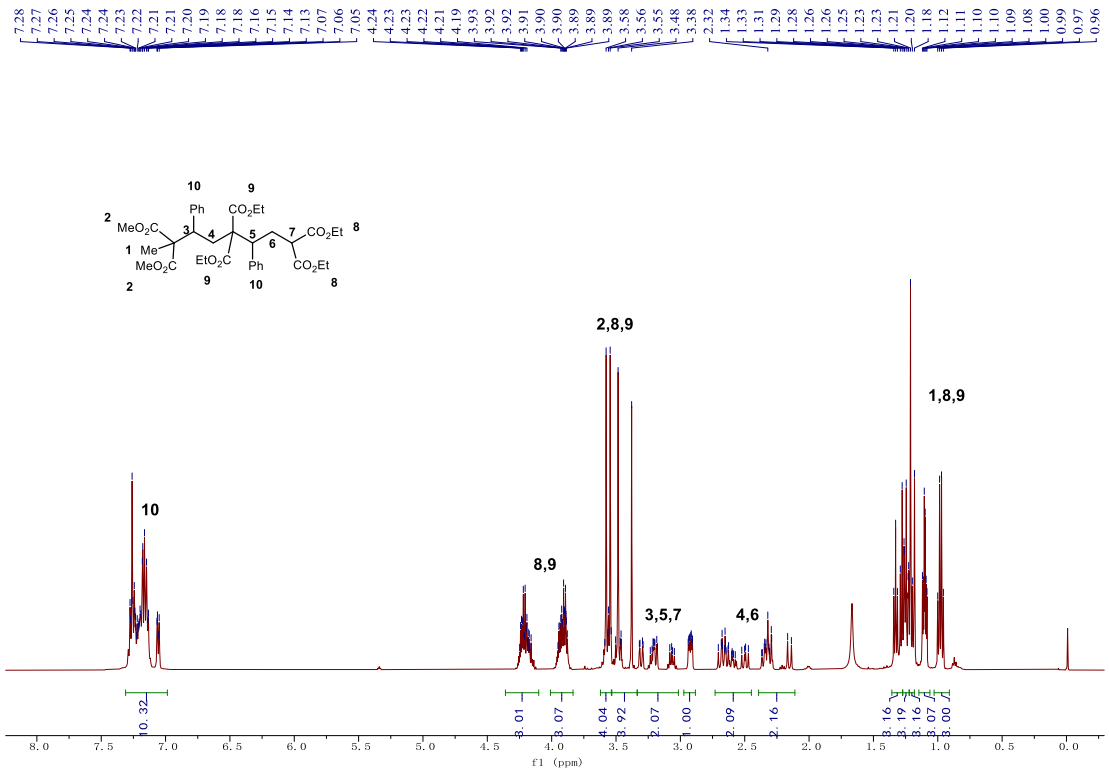


Fig. S30 ^{1}H NMR spectrum of **4** in $CDCl_3$

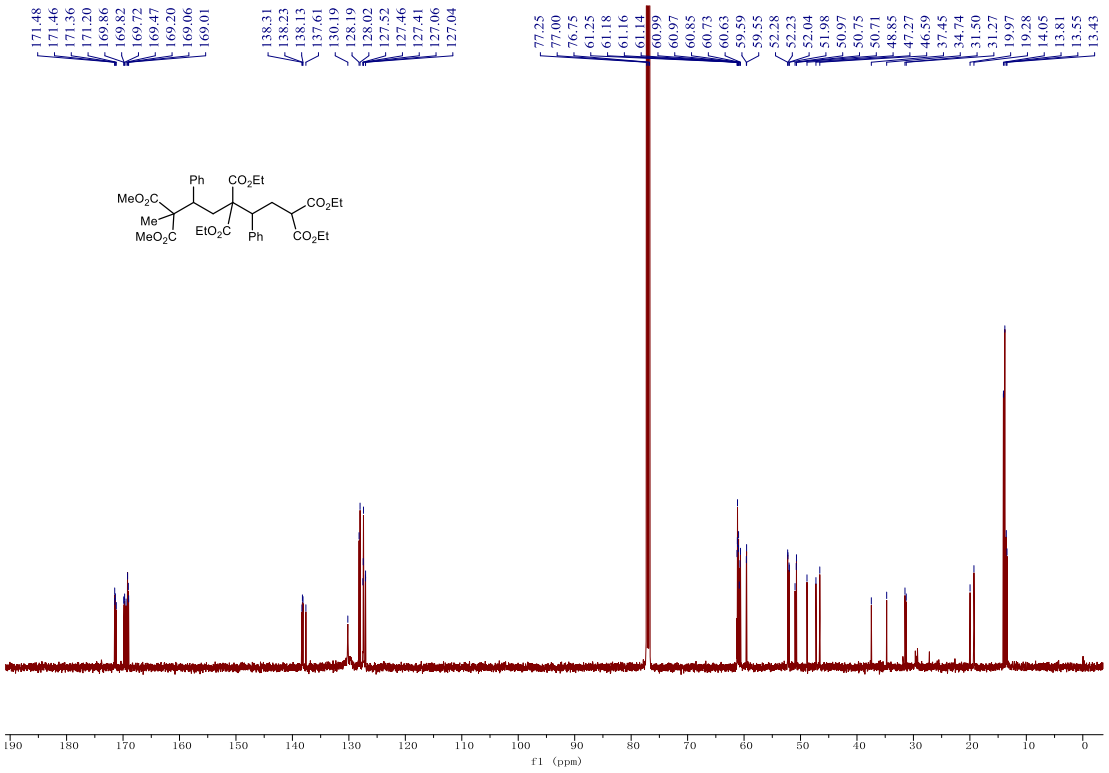


Fig. S31 ^{13}C NMR spectrum of **4** in $CDCl_3$

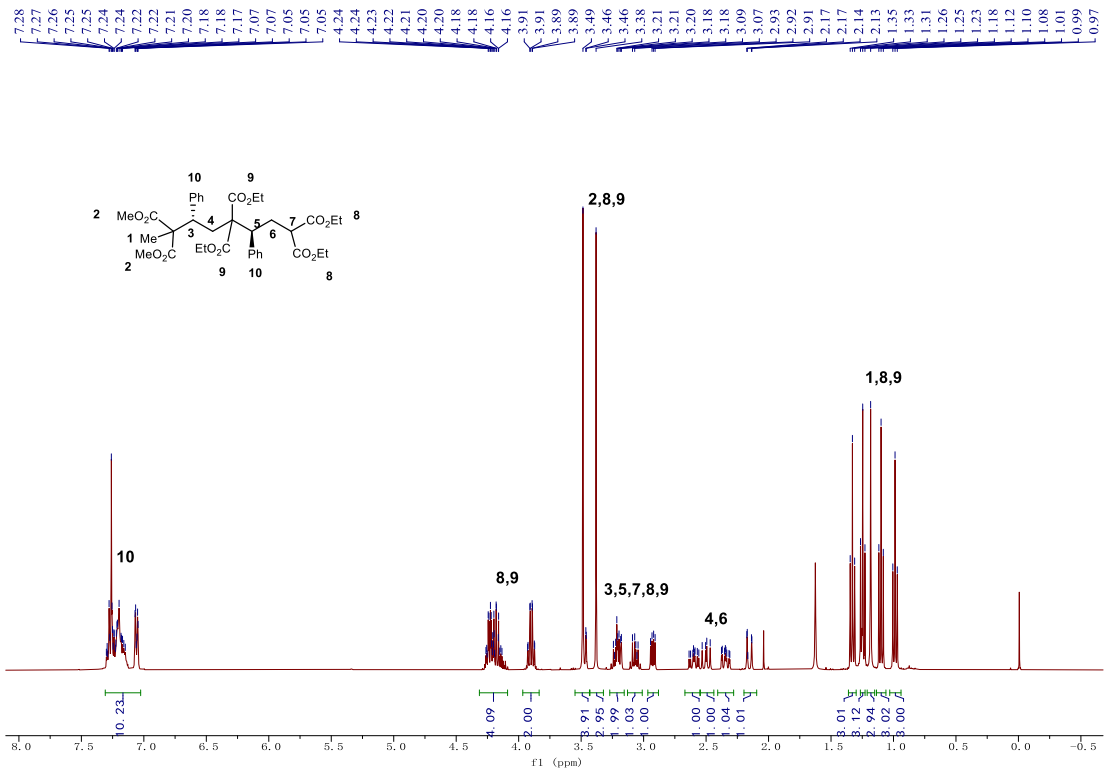


Fig. S32 ^{1}H NMR spectrum of (*R,R*)-**4** in $CDCl_3$

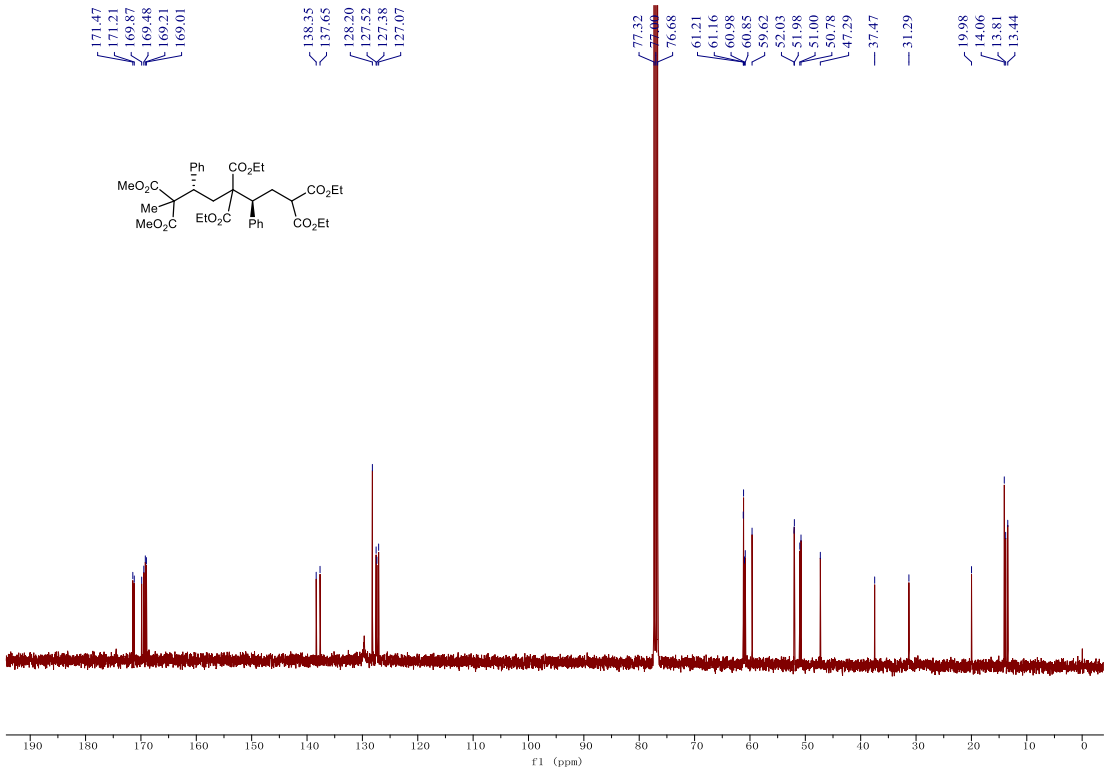
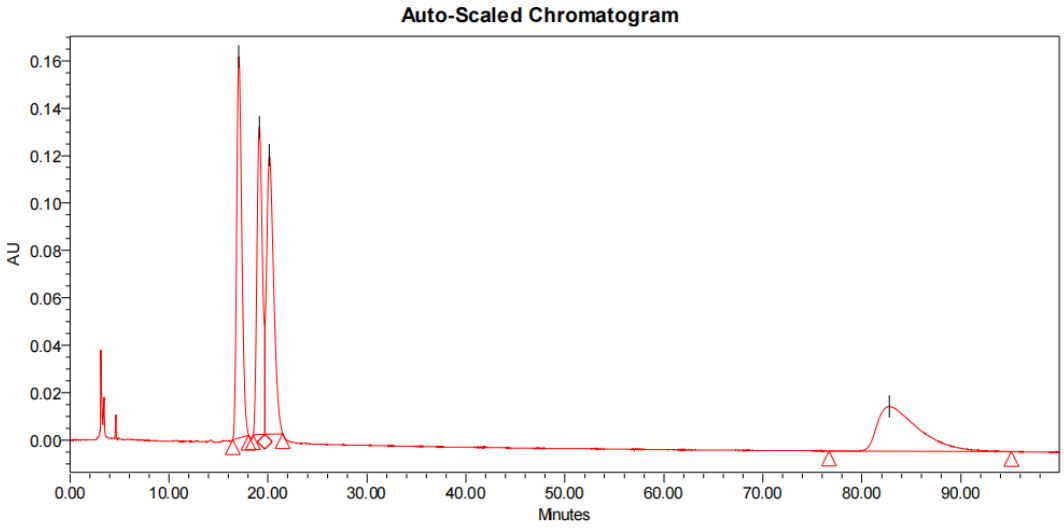
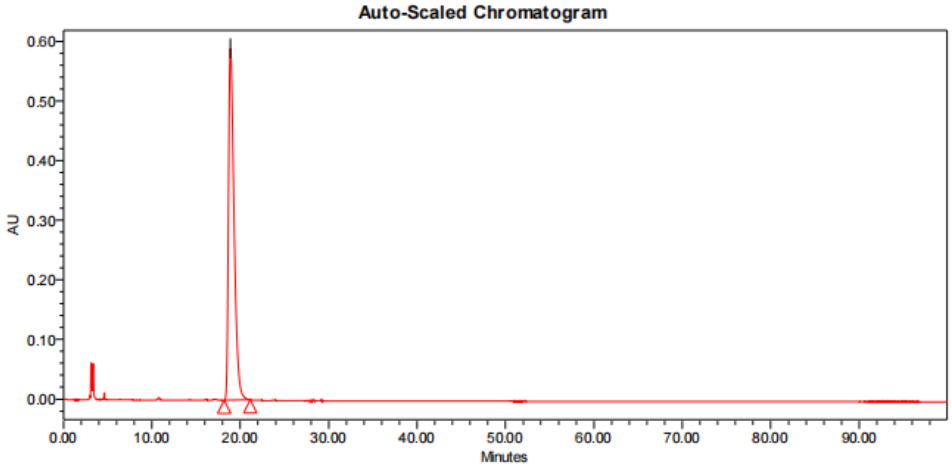


Fig. S33 ^{13}C NMR spectrum of (*R,R*)-**4** in $CDCl_3$



	RT	Area	% Area	Height
1	17.047	5769474	26.04	160976
2	19.119	4982597	22.48	129711
3	20.140	5924686	26.74	117625
4	82.790	5483313	24.74	18823

Fig. S34 HPLC spectrum of **4.** Chiralpak IC, hexane/isopropanol = 90/10, 1 mL/min, 30 °C, 220 nm



	RT	Area	% Area	Height
1	18.879	25848769	100.00	590150

Fig. S35 HPLC spectrum of (*R,R*)-**4.** Chiralpak IC, hexane/isopropanol = 90/10, 1 mL/min, 30 °C, 220 nm

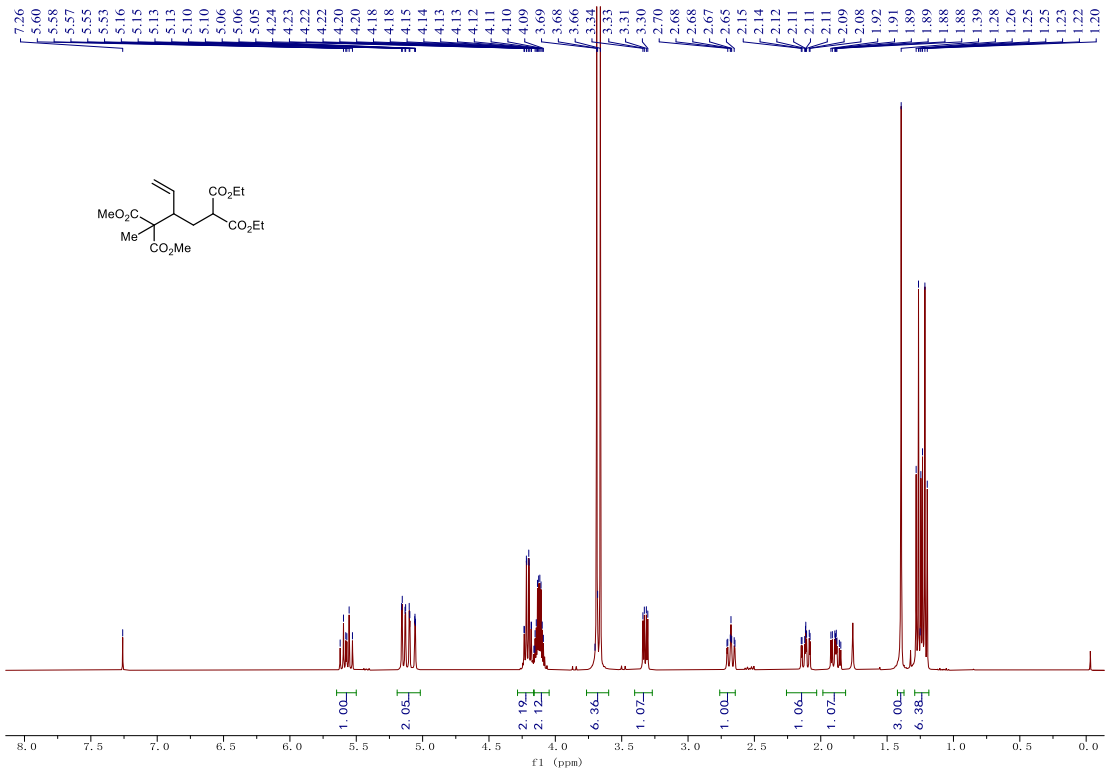


Fig. S36 ^{1}H NMR spectrum of *rac*-**5** in $CDCl_3$

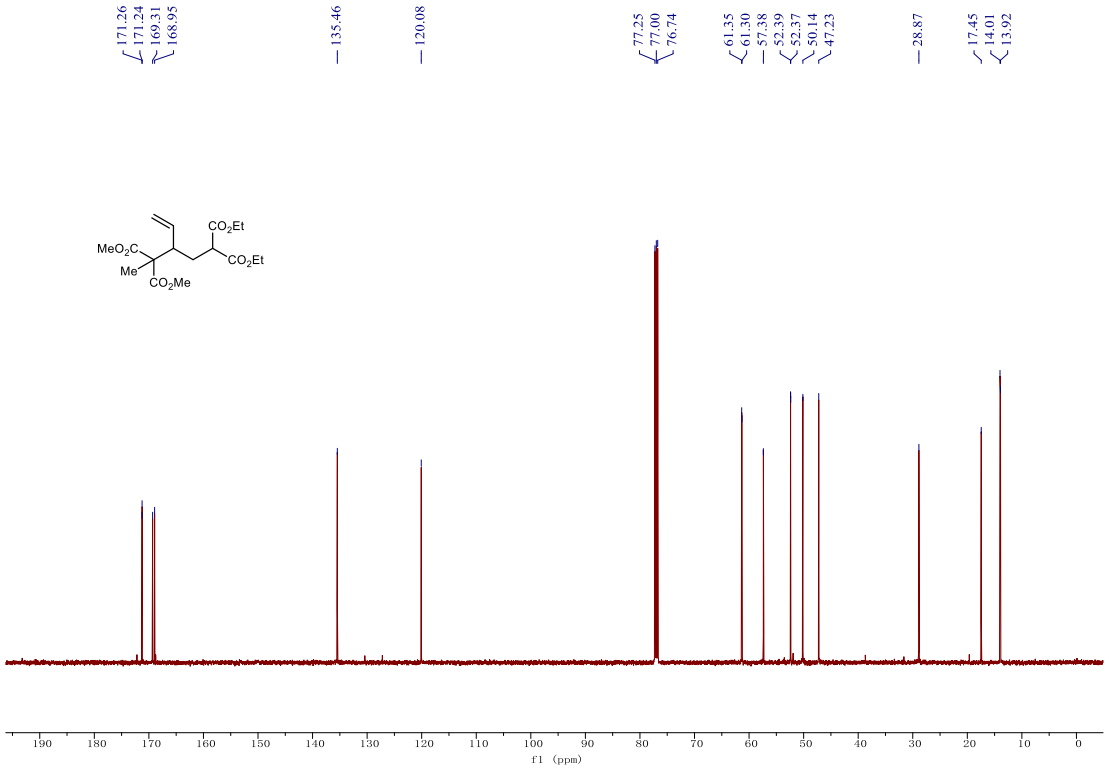
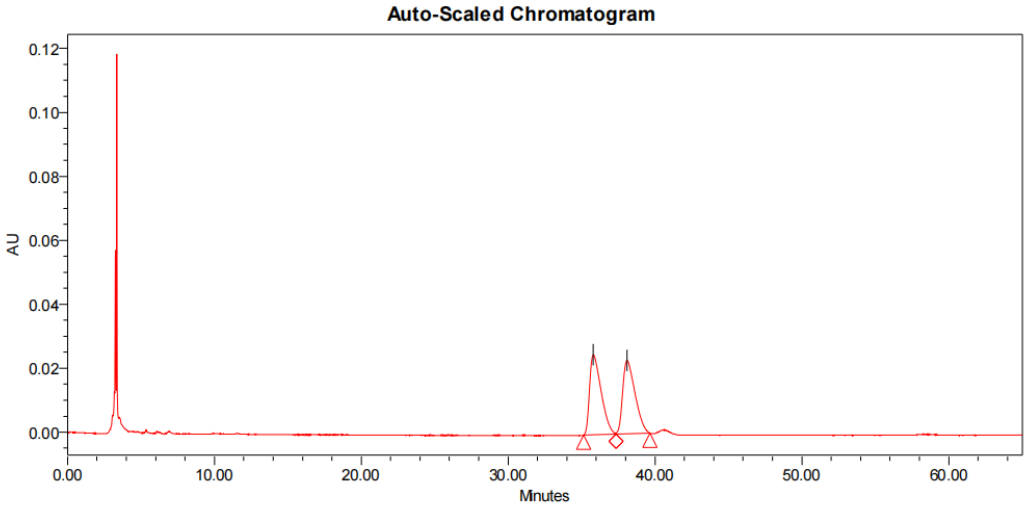
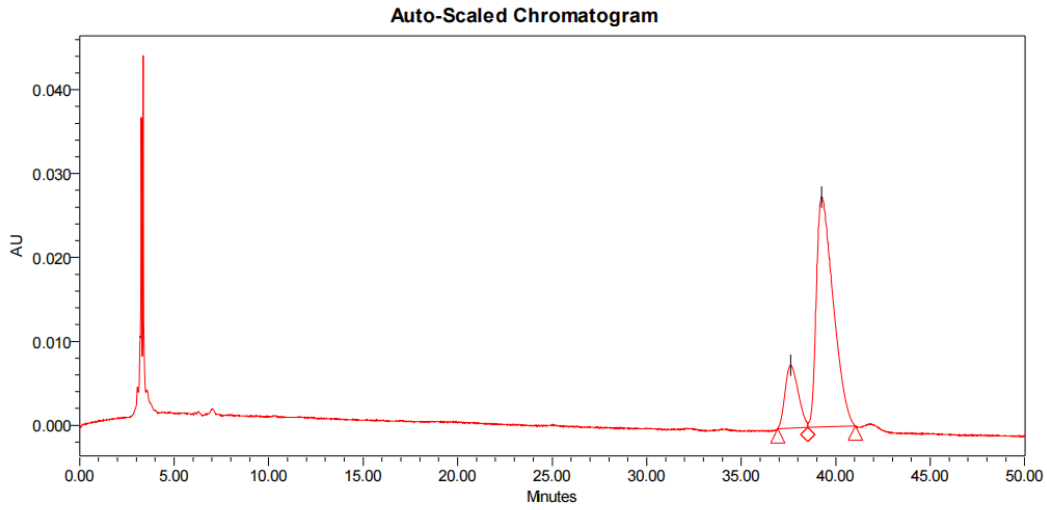


Fig. S37 ^{13}C NMR spectrum of *rac*-**5** in $CDCl_3$



	RT	Area	% Area	Height
1	35.794	1369264	50.54	25040
2	38.101	1339861	49.46	22916

Fig. S38 HPLC spectrum of *rac*-**5.** Chiralpak IC, hexane/isopropanol = 97/3, 1 mL/min, 30 °C, 220 nm



	RT	Area	% Area	Height
1	37.607	358868	17.24	7526
2	39.251	1723166	82.76	27431

Fig. S39 HPLC spectrum of **5.** Chiralpak IC, hexane/isopropanol = 97/3, 1 mL/min, 30 °C, 220 nm

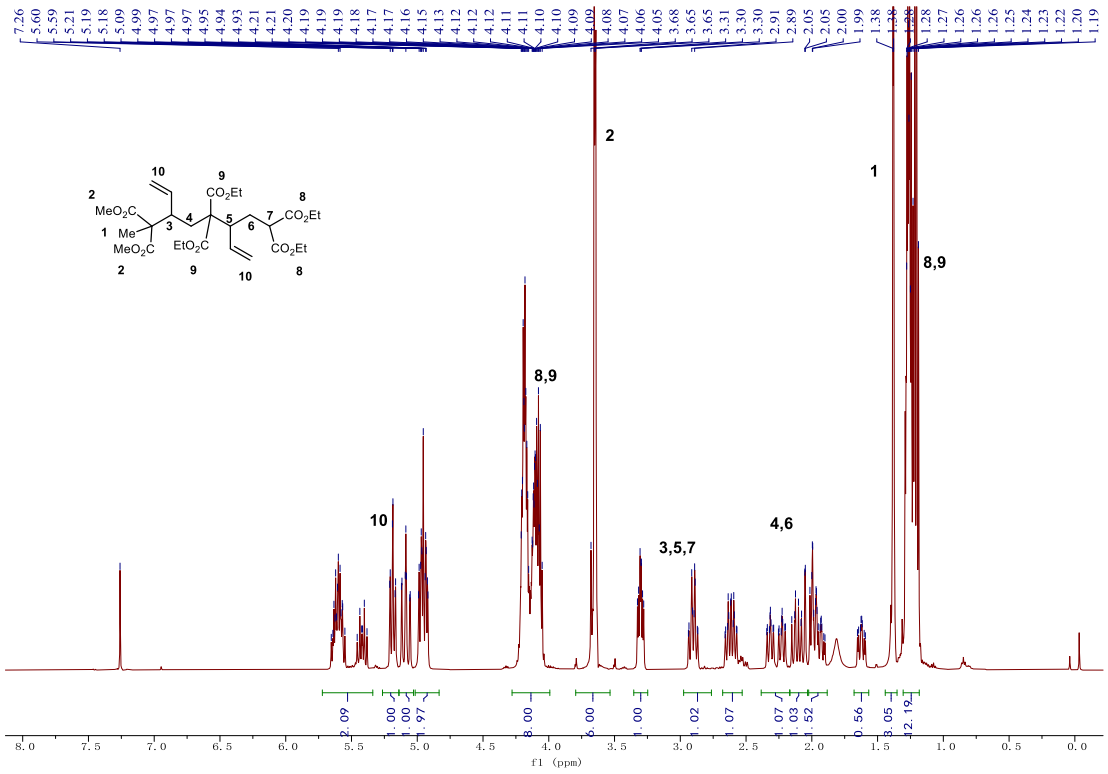


Fig. S40 ^{1}H NMR spectrum of *rac*-**6** in $CDCl_3$

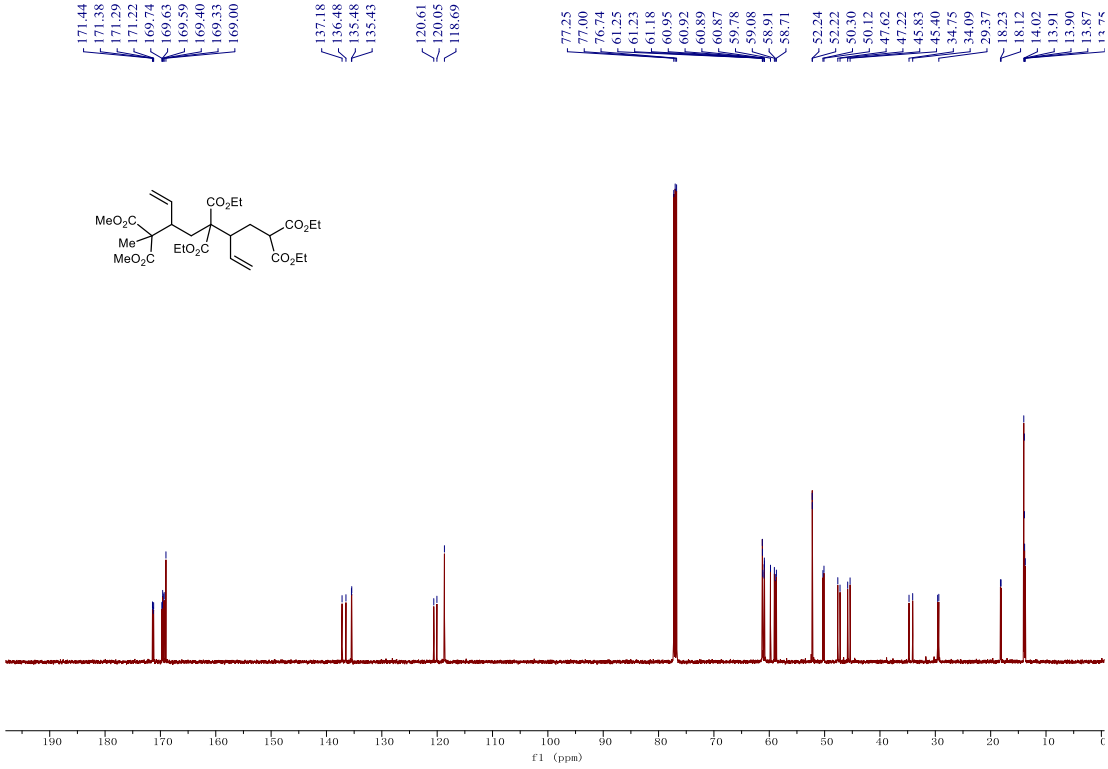


Fig. S41 ^{13}C NMR spectrum of *rac*-**6** in $CDCl_3$

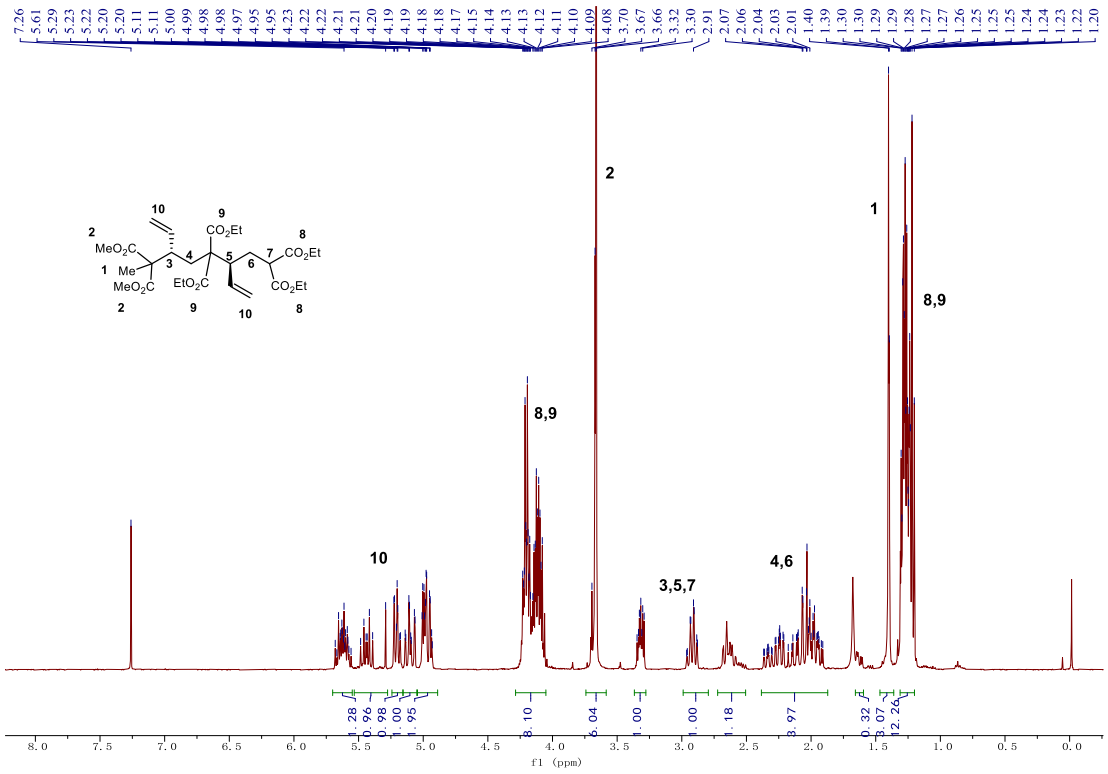


Fig. S42 ^{1}H NMR spectrum of **6** in $CDCl_3$

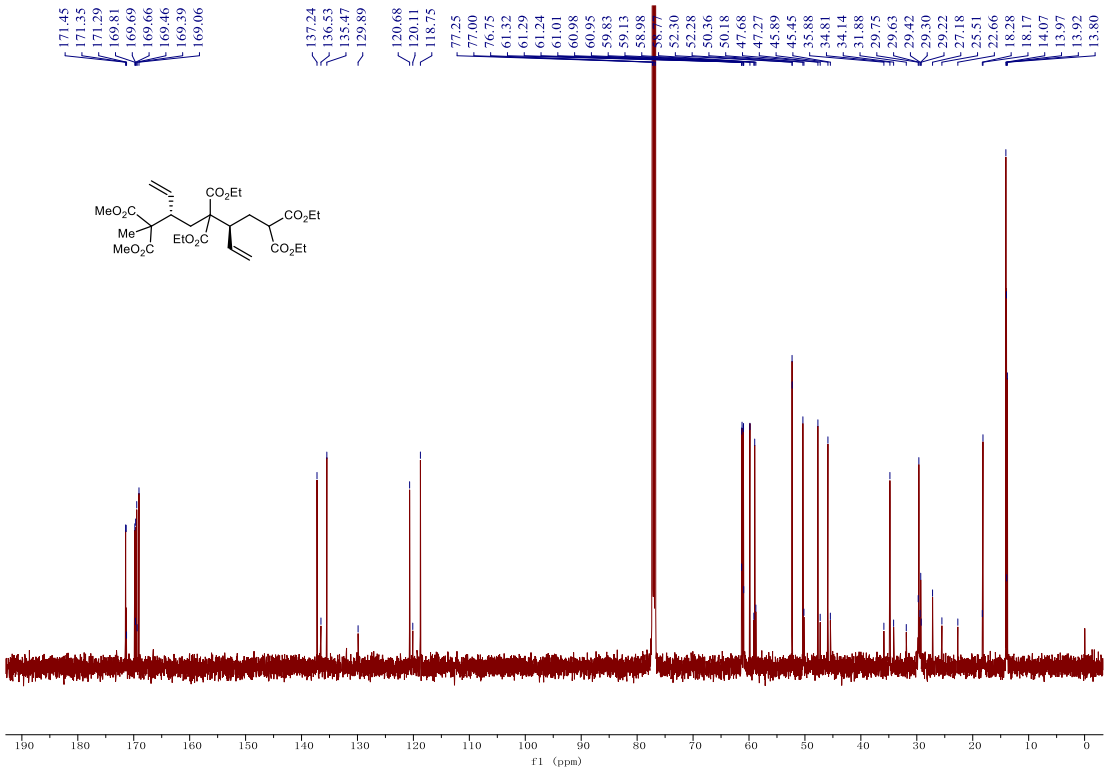
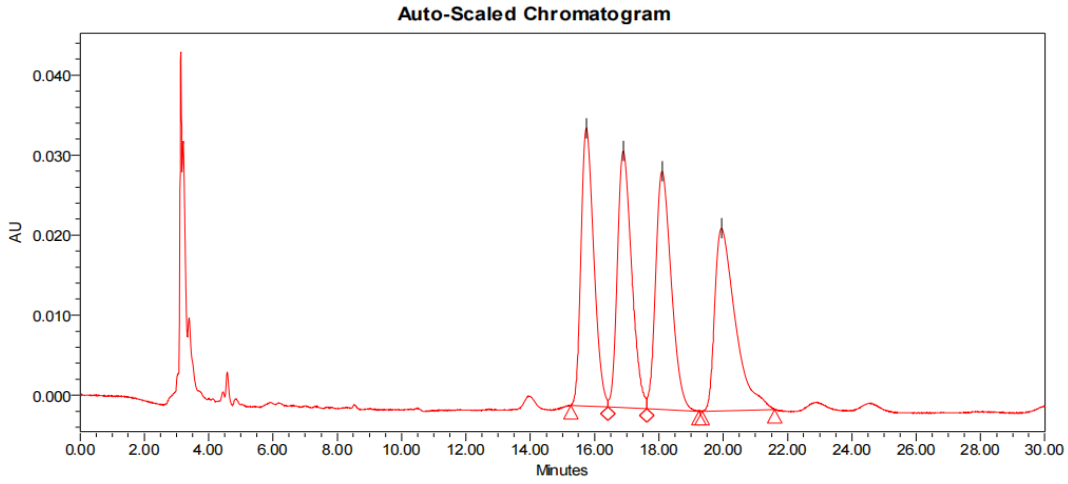
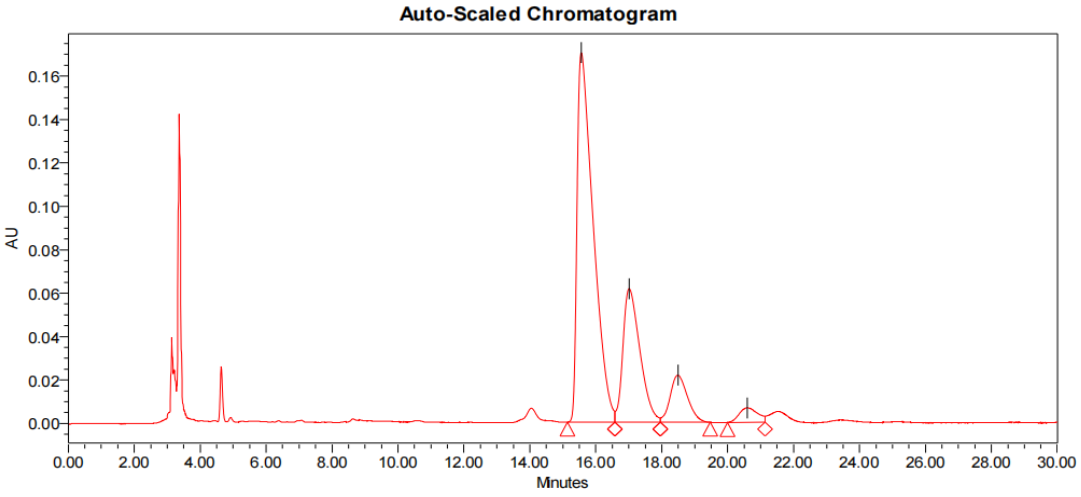


Fig. S43 ^{13}C NMR spectrum of **6** in $CDCl_3$



	RT	Area	% Area	Height
1	15.747	954091	24.15	34727
2	16.895	987007	24.99	32089
3	18.109	1000403	25.33	29768
4	19.947	1008488	25.53	22814

Fig. S44 HPLC spectrum of *rac*-**6.** Chiralpak IC, hexane/isopropanol = 90/10, 1 mL/min, 30 °C, 220 nm



	RT	Area	% Area	Height
1	15.558	5803542	63.94	170218
2	17.017	2213355	24.39	61480
3	18.500	795935	8.77	21697
4	20.588	263696	2.91	6714

Fig. S45 HPLC spectrum of **6.** Chiralpak IC, hexane/isopropanol = 90/10, 1 mL/min, 30 °C, 220 nm

5. Chain-Extension Experiment

P[(*S*)-M1] macroinitiator: an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was transferred into a N_2-filled glove box. To this tube, (*S*)-**M1** (0.4 mmol), anhydrous MeCN (0.4 mL), $MgBr_2$ (0.02 mmol), DBU (0.02 mmol) and diethyl 2-allylmalonate (0.016 mmol) were sequentially added. The tube was taken out of the glove box and stirred at 50 ℃ for 24 h. The reaction mixture was slowly added into 20.0 mL of hexane while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with hexane and dried overnight under vacuum at 50 °C to a constant weight. 90 mg, $M_{n,GPC}$ = 7.0 kDa, $Đ$ = 1.19, $[\alpha]_D^{20}$ = + 15.31.

PM5 macroinitiator: an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was transferred into a N_2-filled glove box. To this tube, $La(OTf)_3$ (0.2 mmol), DBU (0.2 mmol), diethyl 2-allylmalonate (0.16 mmol), anhydrous MeCN (4.0 mL) and **M5** (4.0 mmol), were sequentially added. The tube was taken out of the glove box and stirred at 50 ℃ for 24 h. The reaction mixture was slowly added into 20.0 mL of hexane while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with hexane and dried overnight under vacuum at 50 °C to a constant weight. $M_{n,GPC}$ = 5.4 kDa, $Đ$ = 1.09.

P[(*S*)-M1]-b-P[(*R*)-M1]: an oven-dried 10 mL Schlenk tube equipped with a stirring bar was transferred into a N_2-filled glove box. To this tube, **P**[(*S*)-**M1**] macroinitiator (0.002 mmol), (*R*)-**M1** (0.2 mmol), dry $MgBr_2$ (0.02 mmol), DBU (0.02 mmol) and anhydrous MeCN (0.4 mL) were quickly added. The tube was taken out of the glove box and stirred at 50 ℃. After 24 h, an aliquot was taken for ^{1}H NMR analysis to determine the monomer conversion (86%) and for GPC analysis to obtain polymer MW and its distribution ($M_{n,GPC}$ = 15.7 kDa, $Đ$ = 1.20, $[\alpha]_D^{20}$ = + 1.29). For further purification, the reaction mixture was slowly added into 10.0 mL of hexane while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with hexane and dried overnight under vacuum at 50 °C to a constant weight.

P[(*S*)-M1]-b-PM5-b-P[(*S*)-M1]: an oven-dried 10 mL Schlenk tube equipped with a stirring bar was transferred into a N_2-filled glove box. To this tube, **PM5** macroinitiator (0.008 mmol), (*S*)-**M1** (0.2 mmol), dry $MgBr_2$ (0.02 mmol), DBU (0.02 mmol) and anhydrous MeCN (0.4 mL) were quickly added. The tube was taken out of the glove box and stirred at 50 ℃. After 24 h, an aliquot was taken for ^{1}H NMR analysis to determine the monomer conversion (98%) and for GPC analysis to obtain polymer MW and its distribution ($M_{n,GPC}$ = 12.3 kDa, $Đ$ = 1.05, $[\alpha]_D^{20}$ = + 10.54). For further purification, the reaction mixture was slowly added into 10.0 mL of hexane while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with hexane and dried overnight under vacuum at 50 °C to a constant weight.

P[(*R*)-M1]-b-P[(*S*)-M1]-b-PM5-b-P[(*S*)-M1]-b-P[(*R*)-M1]: an oven-dried 10 mL Schlenk tube equipped with a stirring bar was transferred into a N_2-filled glove box. To this tube, P[(*S*)-M1]-b-PM7-b-P[(*S*)-M1] macroinitiator (0.008 mmol), (*R*)-**M1** (0.2 mmol), dry $MgBr_2$ (0.02 mmol), DBU (0.02 mmol) and anhydrous MeCN (0.4 mL) were quickly added. The tube was taken out of the glove box and stirred at 50 ℃. After 24 h, an aliquot was taken for ^{1}H NMR analysis to determine the monomer conversion (98%) and for GPC analysis to obtain polymer MW and its distribution ($M_{n,GPC}$ = 18.2 kDa, $Đ$ = 1.07, $[\alpha]_D^{20}$ = + 1.61). For further purification, the reaction mixture was slowly added into 10.0 mL of hexane while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with hexane and dried overnight under vacuum at 50 °C to a constant weight.

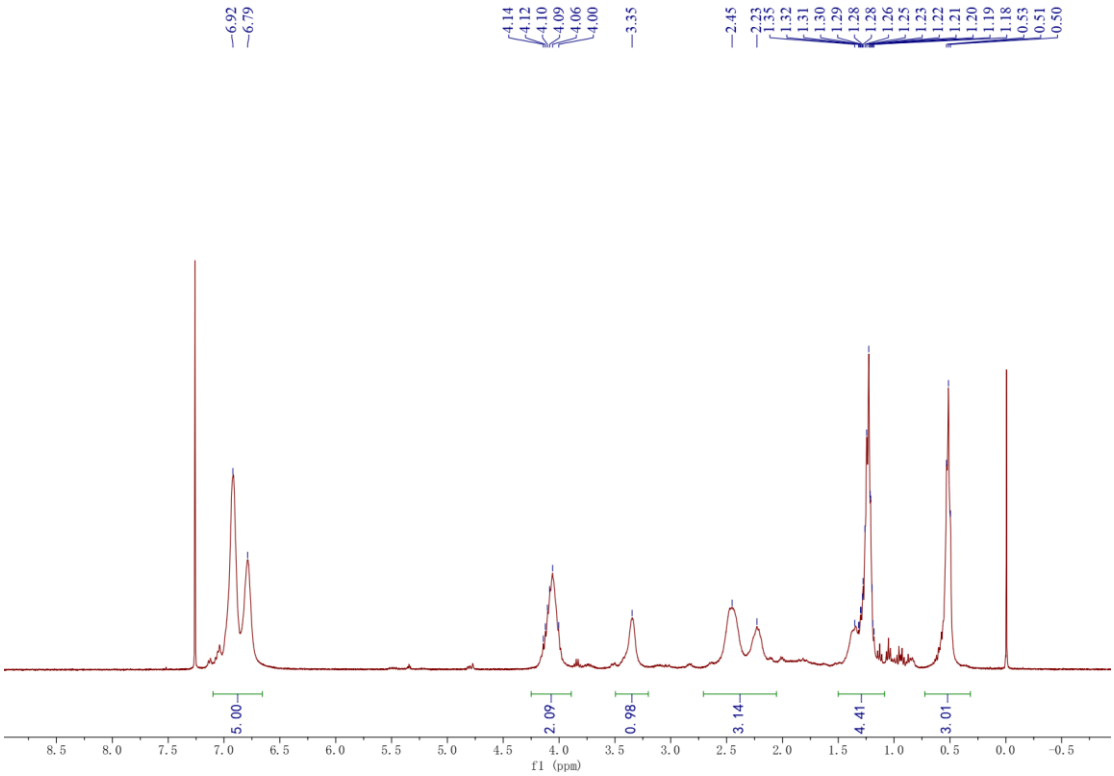


Fig. S46 ^{1}H NMR spectrum of P[(*S*)-**M1**]-b-P[(*R*)-**M1**] in $CDCl_3$

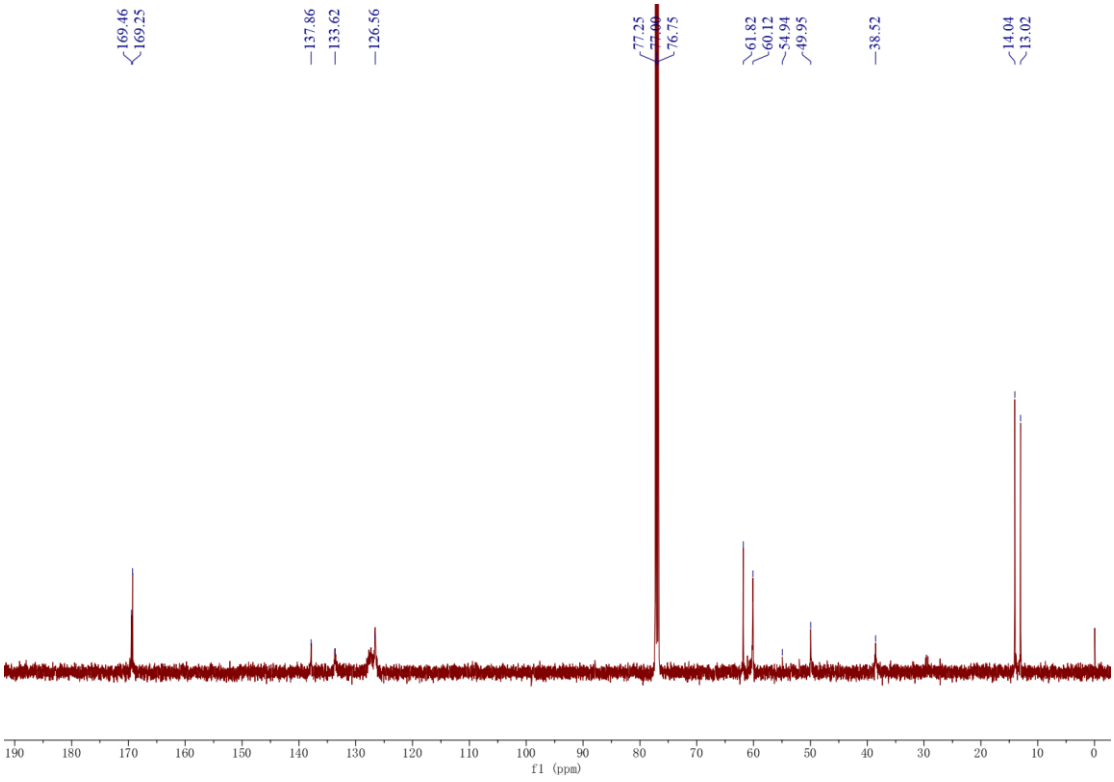


Fig. S47 ^{13}C NMR spectrum of P[(*S*)-**M1**]-b-P[(*R*)-**M1**] in $CDCl_3$

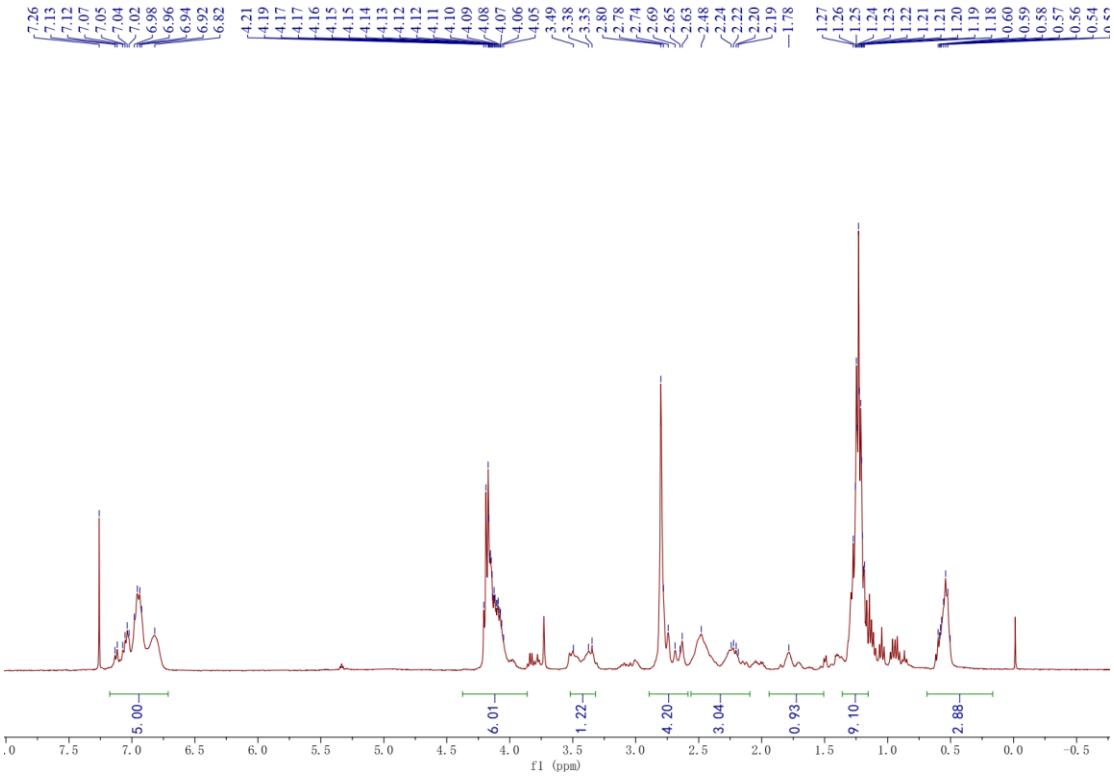


Fig. S48 ^{1}H NMR spectrum of P[(*S*)-**M1**]-b-**PM5**-b-P[(*S*)-**M1**] in $CDCl_3$

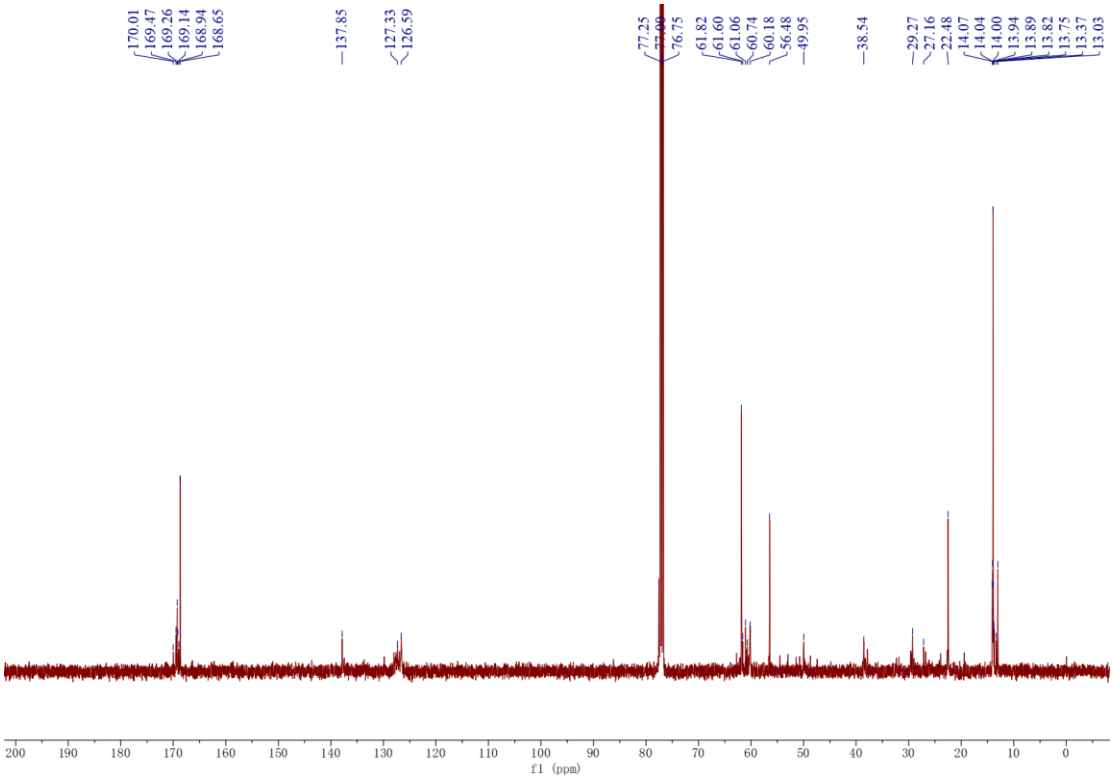


Fig. S49 ^{13}C NMR spectrum of P[(*S*)-**M1**]-b-**PM5**-b-P[(*S*)-**M1**] in $CDCl_3$

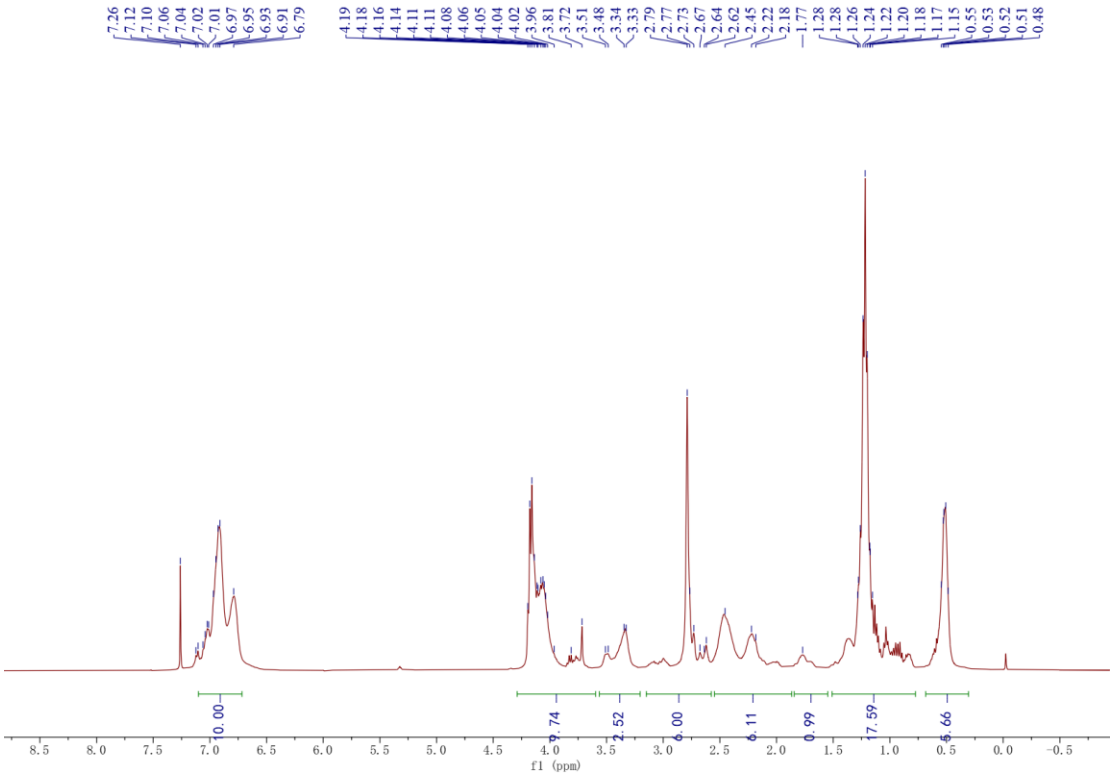


Fig. S50 ^{1}H NMR spectrum of P[(*R*)-**M1**]-b-P[(*S*)-**M1**]-b-**PM5**-b-P[(*S*)-**M1**]-b-P[(*R*)-**M1**] in $CDCl_3$

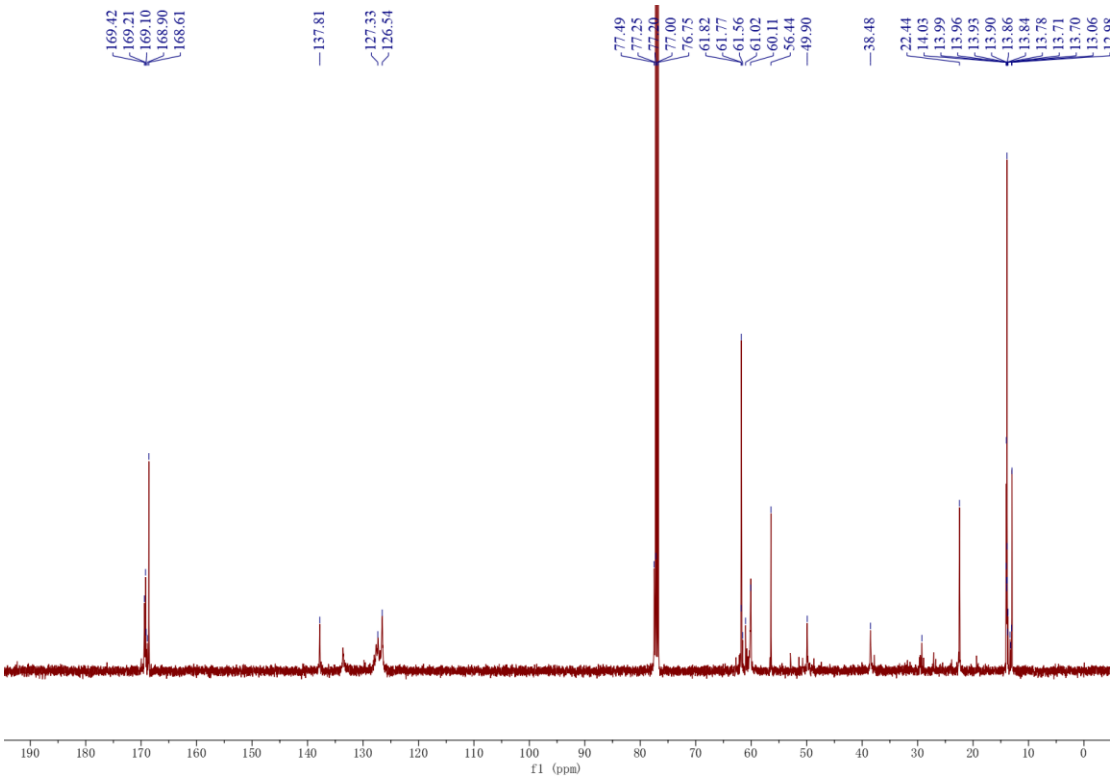


Fig. S51 ^{13}C NMR spectrum of P[(*R*)-**M1**]-b-P[(*S*)-**M1**]-b-**PM5**-b-P[(*S*)-**M1**]-b-P[(*R*)-**M1**] in $CDCl_3$

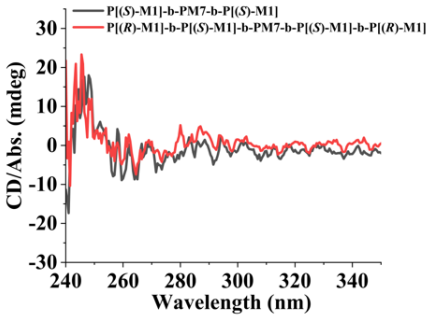


Fig. S52 CD spectra of P[(*S*)-**M1**]-b-**PM5**-b-P[(*S*)-**M1**] and P[(*R*)-**M1**]-b-P[(*S*)-**M1**]-b-**PM5**-b-P[(*S*)-**M1**]-b-P[(*R*)-**M1**]in $CHCl_3$ at 1×10^{-5} M.

6. Thermal Analysis

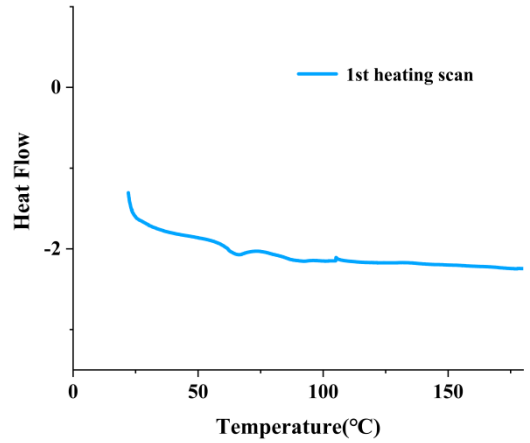


Fig. S53 DSC curves of **PM1** (12.2 kDa, $Đ$ = 1.05). T_g = 66 °C (1st heating scan).

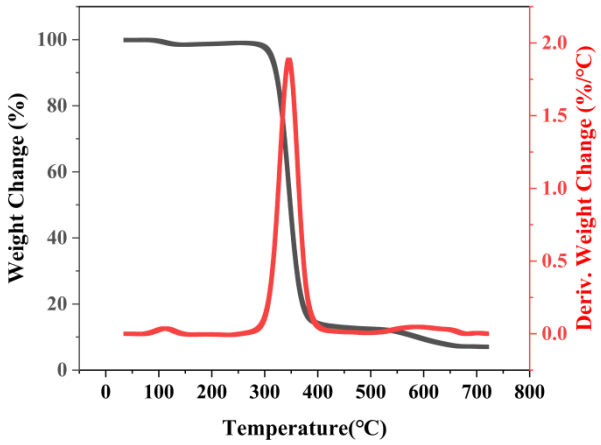


Fig. S54 TGA and DTG curves of **PM1** (12.2 kDa, $Đ$ = 1.05). $T_d^{5\%}$ = 311 °C, $T_{max,}$ = 336 °C.

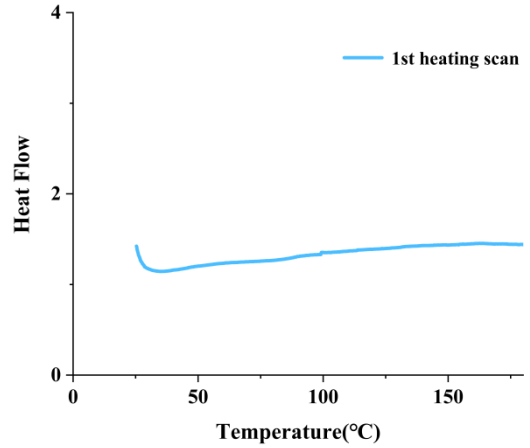


Fig. S55 DSC curves of **P[(*S*)-M1]** (13.9 kDa, $Đ$ = 1.36). (1st heating scan).

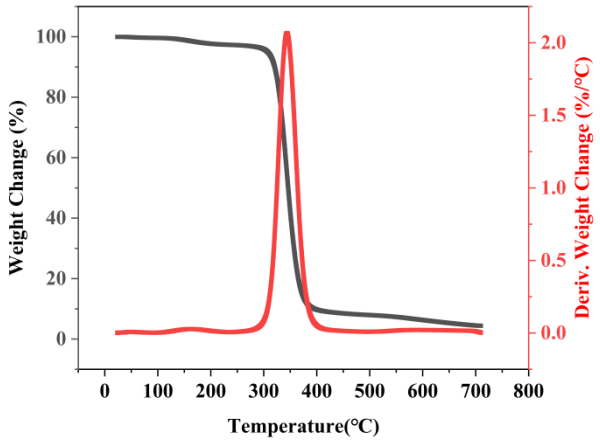


Fig. S56 TGA and DTG curves of P[(*S*)-**M1**] (13.9 kDa, $Đ$ = 1.36). $T_d^{5\%}$ = 307 °C, T_{max} = 344 °C.

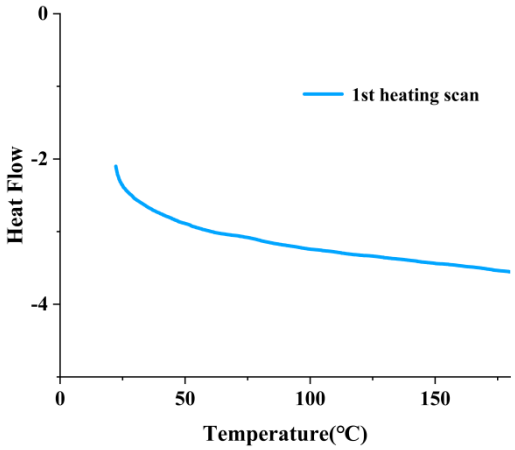


Fig. S57 DSC curves of **P**[(*R*)-**M1**] (14.2 kDa, $Đ$ = 1.30). (1st heating scan).

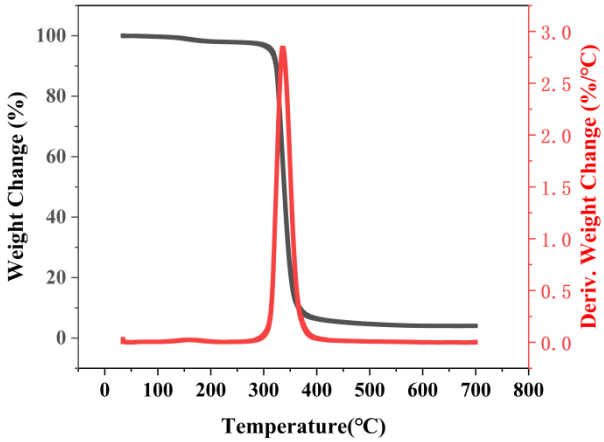


Fig. S58 TGA and DTG curves of **P**[(*R*)-**M1**] (14.2 kDa, $Đ$ = 1.30). $T_d^{5\%}$ = 314 °C, T_{max}= 337 °C.

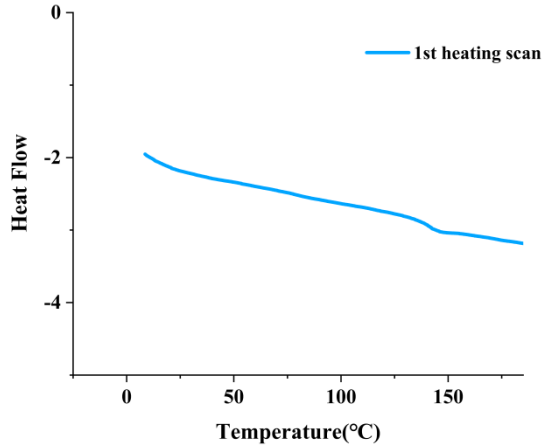


Fig. S59 DSC curves of **PM2** (9.6 kDa, $Đ$ = 1.07). T_g = 140 °C (2nd heating scan)

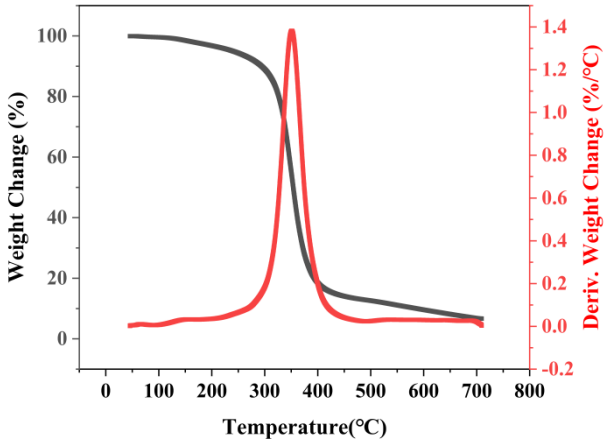


Fig. S60 TGA and DTG curves of **PM2** (9.6 kDa, $Đ$ = 1.07). $T_d^{5\%}$ = 240 °C, T_{max} = 351 °C.

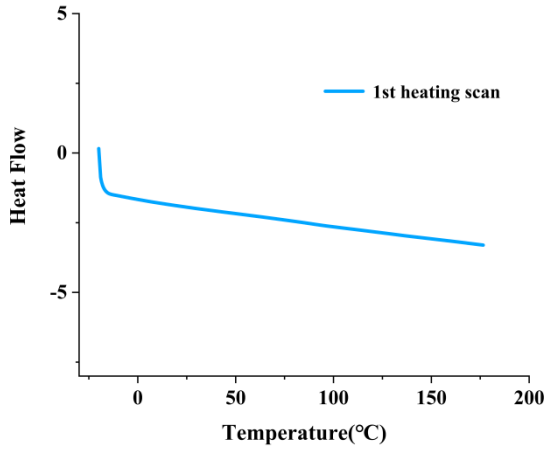


Fig. S61 DSC curves of **P[(*S*)-M2]** (1st heating scan).

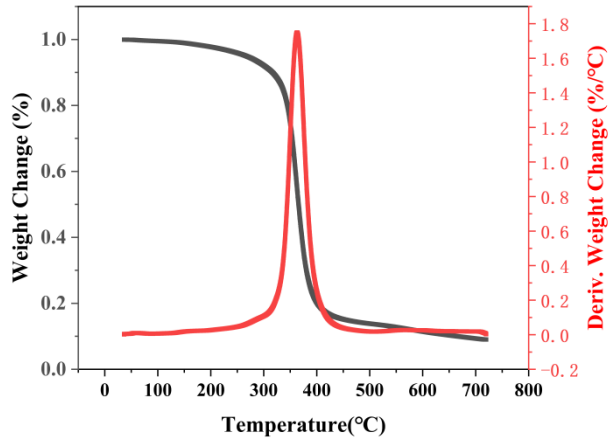


Fig. S62 TGA and DTG curves of **P[(*S*)-M2]**. $T_d^{5\%}$ = 251 °C, T_{max} = 362 °C.

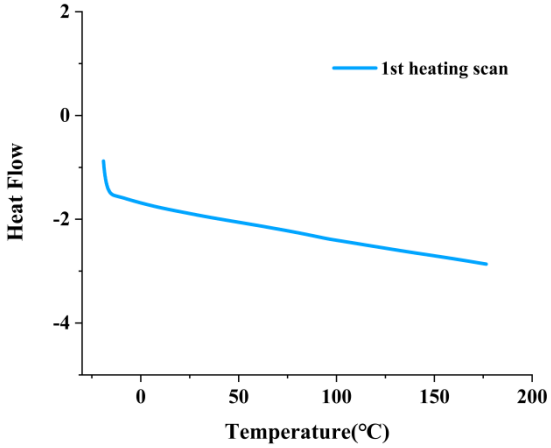


Fig. S63 DSC curves of **P[(*R*)-M2]** (1st heating scan).

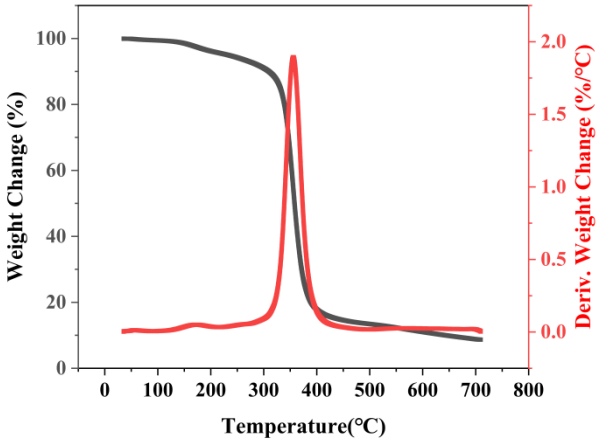


Fig. S64 TGA and DTG curves of **P[(*R*)-M2]**. $T_d^{5\%}$ = 232 °C, T_{max} = 355 °C.

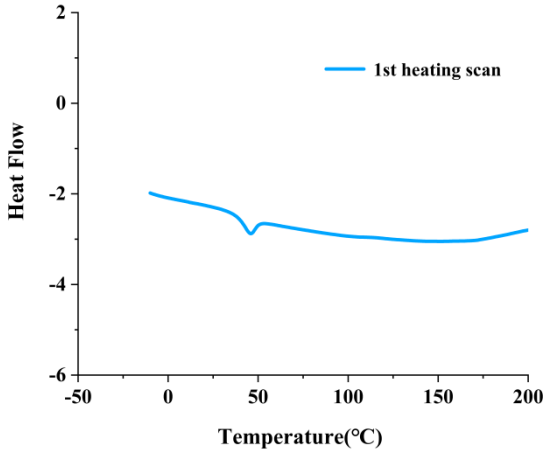


Fig. S65 DSC curves of **PM3** (11.5 kDa, $Đ$ = 1.07). T_g = 35 °C (1st heating scan)

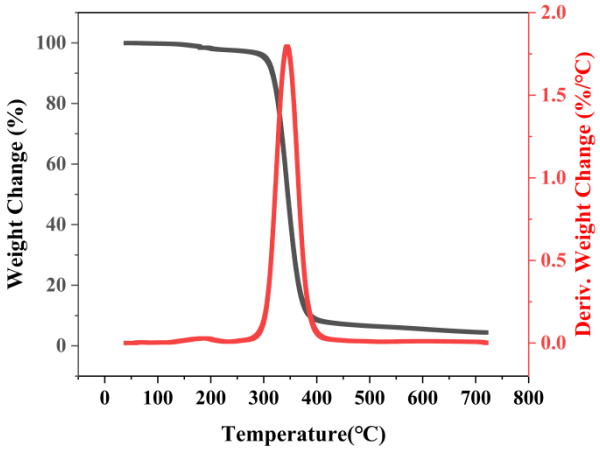


Fig. S66 TGA and DTG curves of **PM3** (11.5 kDa, $Đ$ = 1.07). $T_d^{5\%}$ = 293 °C, T_{max} = 337 °C.

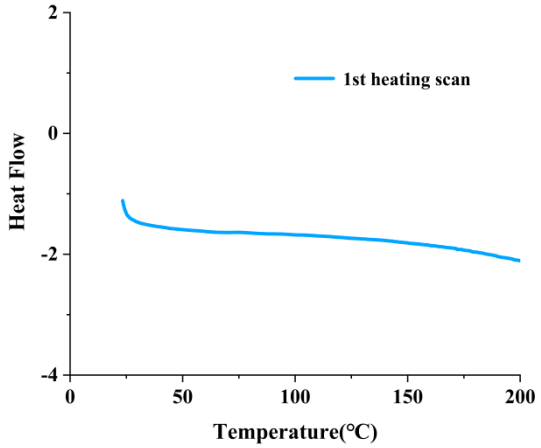


Fig. S67 DSC curves of P[(*S*)-**M3**] (15.0 kDa, $Đ$ = 1.35) (1st heating scan).

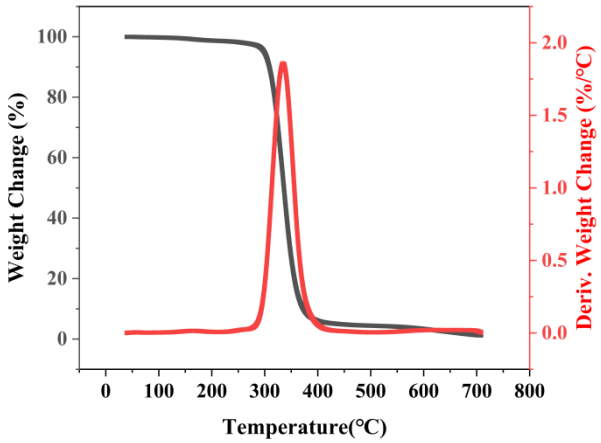


Fig. S68 TGA and DTG curves of **P[(*S*)-M3]** (15.0 kDa, $Đ$ = 1.35). $T_d^{5\%}$ = 297 °C, T_{max} = 334 °C.

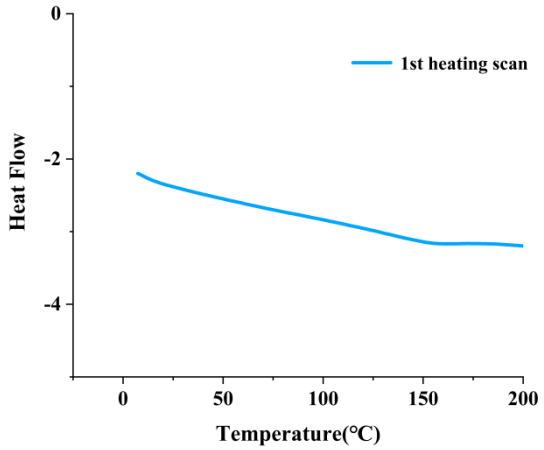


Fig. S69 DSC curves of **P[(*R*)-M3]** (16.0 kDa, $Đ$ = 1.37) (1st heating scan).

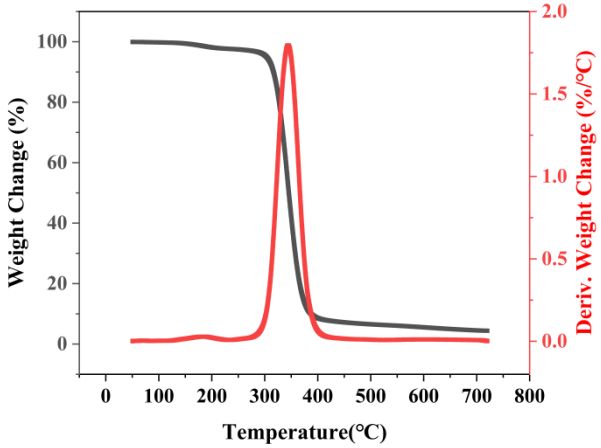


Fig. S70 TGA and DTG curves of **P[(*R*)-M3]** (16.0 kDa, $Đ$ = 1.37). $T_d^{5\%}$ = 299 °C, T_{max} = 343 °C.

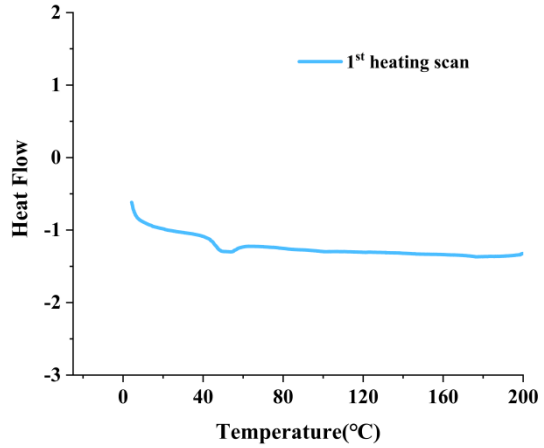


Fig. S71 DSC curves of **PM4)** (12.1 kDa, $Đ$ = 1.07). T_g = 45 °C (1st heating scan)

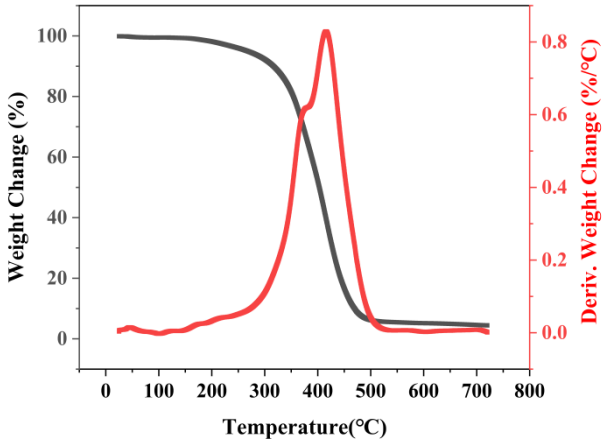


Fig. S72 TGA and DTG curves of **PM4)** (12.1 kDa, $Đ$ = 1.07). $T_d^{5\%}$ = 267 °C, T_{max} = 418 °C.

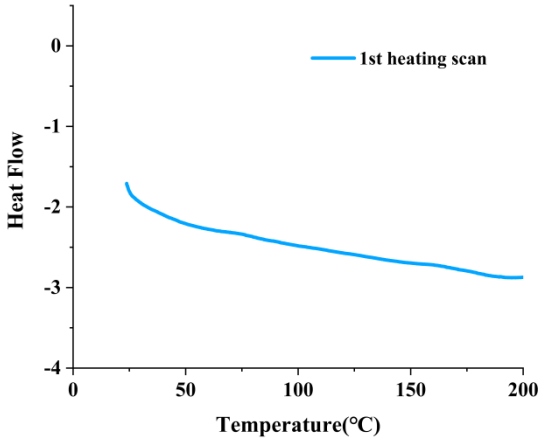


Fig. S73 DSC curves of **P**[(*S*)-**M4**] (14.8 kDa, $Đ$ = 1.19). (1st heating scan)

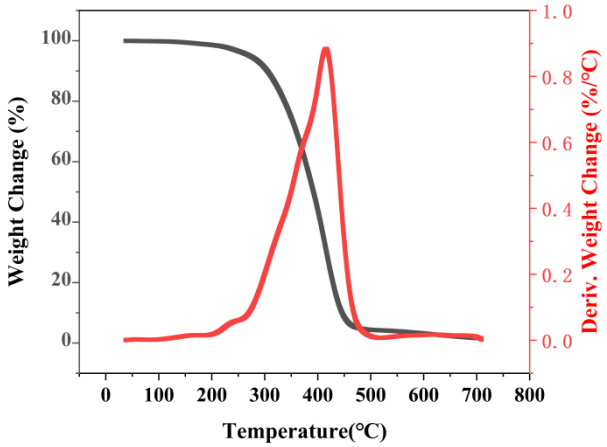


Fig. S74 TGA and DTG curves of **P[(*S*)-M4]** (14.8 kDa, $Đ$ = 1.19). $T_d^{5\%}$ = 271 °C, T_{max} = 414 °C.

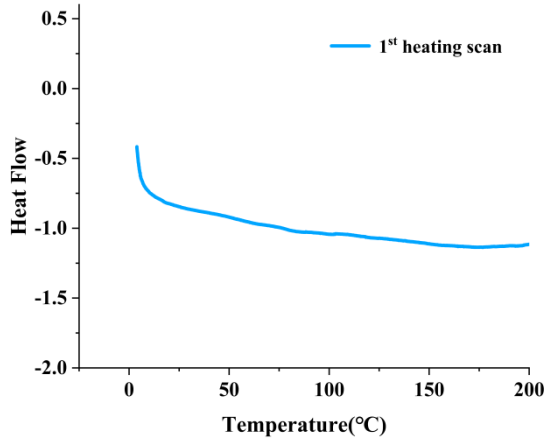


Fig. S75 DSC curves of **P[(*R*)-M4]** (15.0 kDa, $Đ$ = 1.19). (1st heating scan)

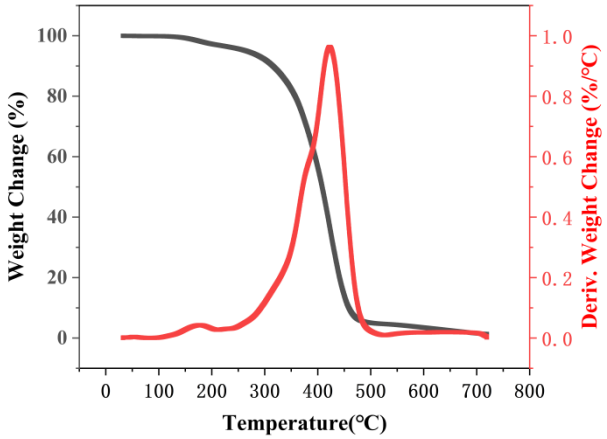


Fig. S76 TGA and DTG curves of **P[(*R*)-M4]** (15.0 kDa, $Đ$ = 1.19). $T_d^{5\%}$ = 264 °C, T_{max} = 424 °C.

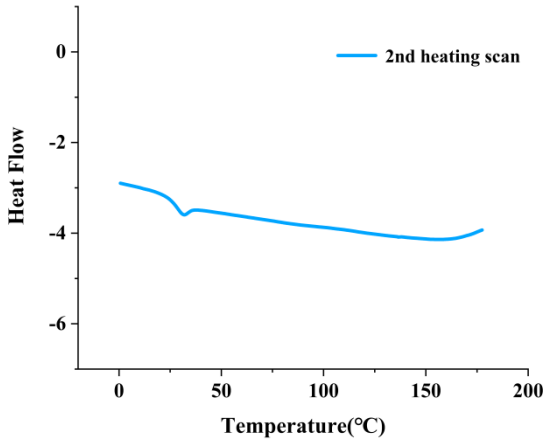


Fig. S77 DSC curves of **PM6** (9.4 kDa, $Đ$ = 1.15). T_g = 22 °C (2nd heating scan)

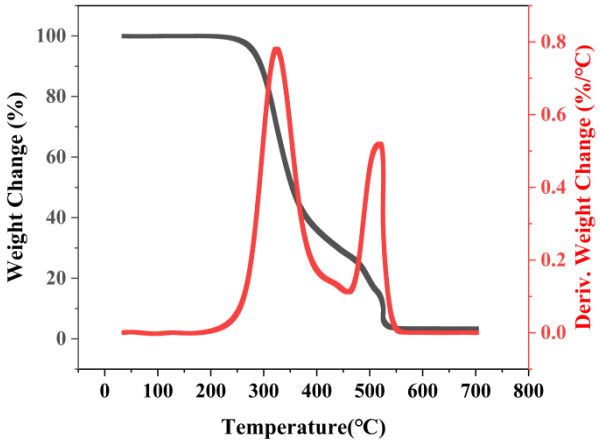


Fig. S78 TGA and DTG curves of **PM6** (9.4 kDa, $Đ$ = 1.15). $T_d^{5\%}$ = 280 °C, T_{max} = 323 °C.

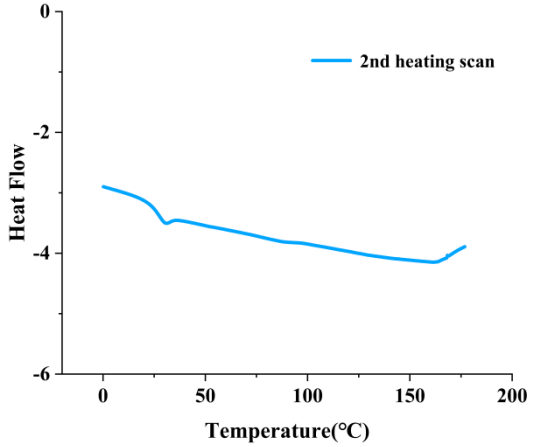


Fig. S79 DSC curves of **P**[*(S)*-**M6**] (10.8 kDa, $Đ$ = 1.16). T_g = 22 °C (2nd heating scan)

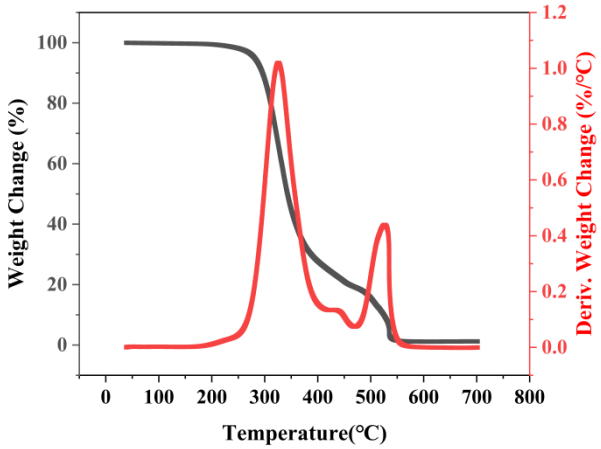


Fig. S80 TGA and DTG curves of **P**[(*S*)-**M6**] (10.8 kDa, $Đ$ = 1.16). $T_d^{5\%}$ = 282 °C, T_{max} = 325 °C.

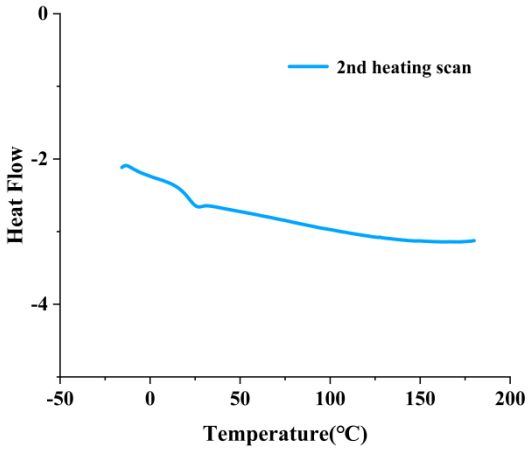


Fig. S81 DSC curves of **P**[(*R*)-**M6**] (11.3 kDa, $Đ$ = 1.14). T_g = 22 °C (2nd heating scan)

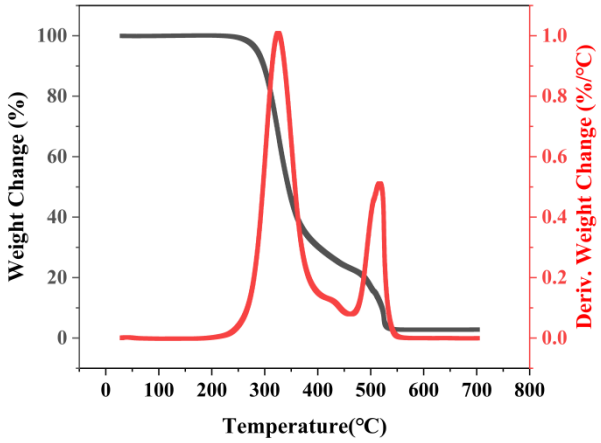


Fig. S82 TGA and DTG curves of **P**[(*R*)-**M6**] (11.3 kDa, $Đ$ = 1.14). $T_d^{5\%}$ = 281 °C, T_{max} = 323 °C.

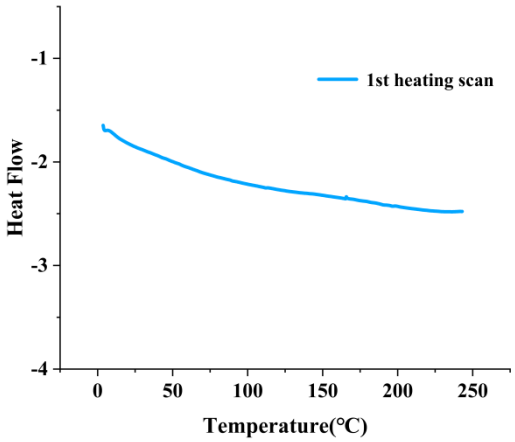


Fig. S83 DSC curves of **P**[(*S*)-**M1**]-*b*-**P**[(*R*)-**M1**] (15.7 kDa, $Đ$ = 1.20). (1st heating scan)

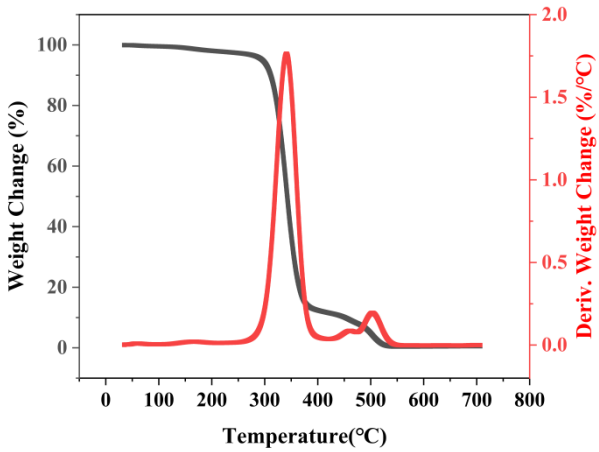


Fig. S84 TGA and DTG curves of **P**[(*S*)-**M1**]-*b*-**P**[(*R*)-**M1**] (15.7 kDa, $Đ$ = 1.20). $T_d^{5\%}$ = 295 °C, T_{max}= 341 °C.

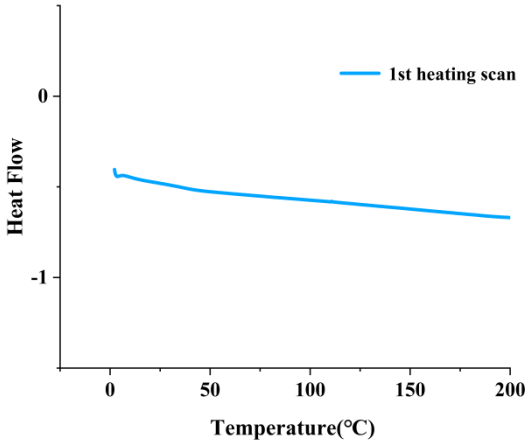


Fig. S85 DSC curves of **P**[(*S*)-**M1**]-*b*-**PM5**-*b*-**P**[(*S*)-**M1**] (12.3 kDa, $Đ$ = 1.05). (1st heating scan)

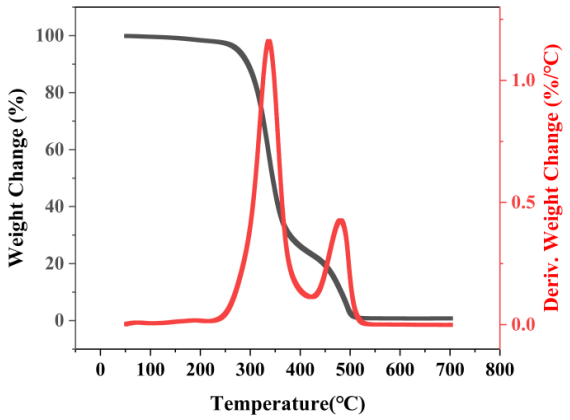


Fig. S86 TGA and DTG curves of **P**[(*S*)-**M1**]-*b*-**PM5**-*b*-**P**[(*S*)-**M1**] (12.3 kDa, *Đ* = 1.05). $T_d^{5\%}$ = 274 °C, T_{max}= 336 °C.

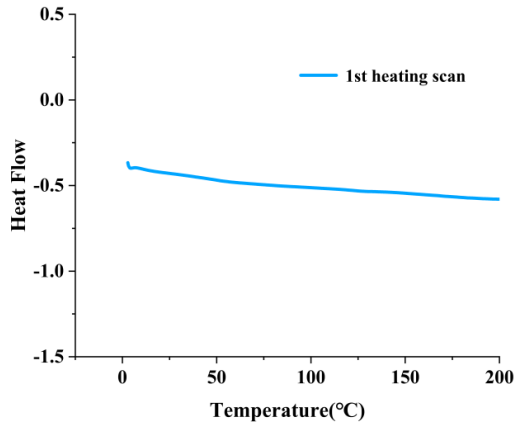


Fig. S87 DSC curves of **P**[(*R*)-**M1**]-*b*-**P**[(*S*)-**M1**]-*b*-**PM5**-*b*-**P**[(*S*)-**M1**]-*b*-**P**[(*R*)-**M1**] (18.2 kDa, *Đ* = 1.07). (1st heating scan)

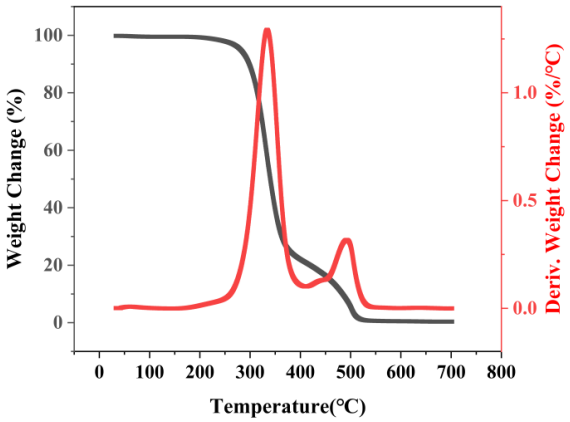


Fig. S88 TGA and DTG curves of **P**[(*R*)-**M1**]-*b*-**P**[(*S*)-**M1**]-*b*-**PM5**-*b*-**P**[(*S*)-**M1**]-*b*-**P**[(*R*)-**M1**] (18.2 kDa, *Đ* = 1.07). $T_d^{5\%}$ = 280 °C, T_{max}= 333 °C.

7. NMR Spectra of Homopolymers

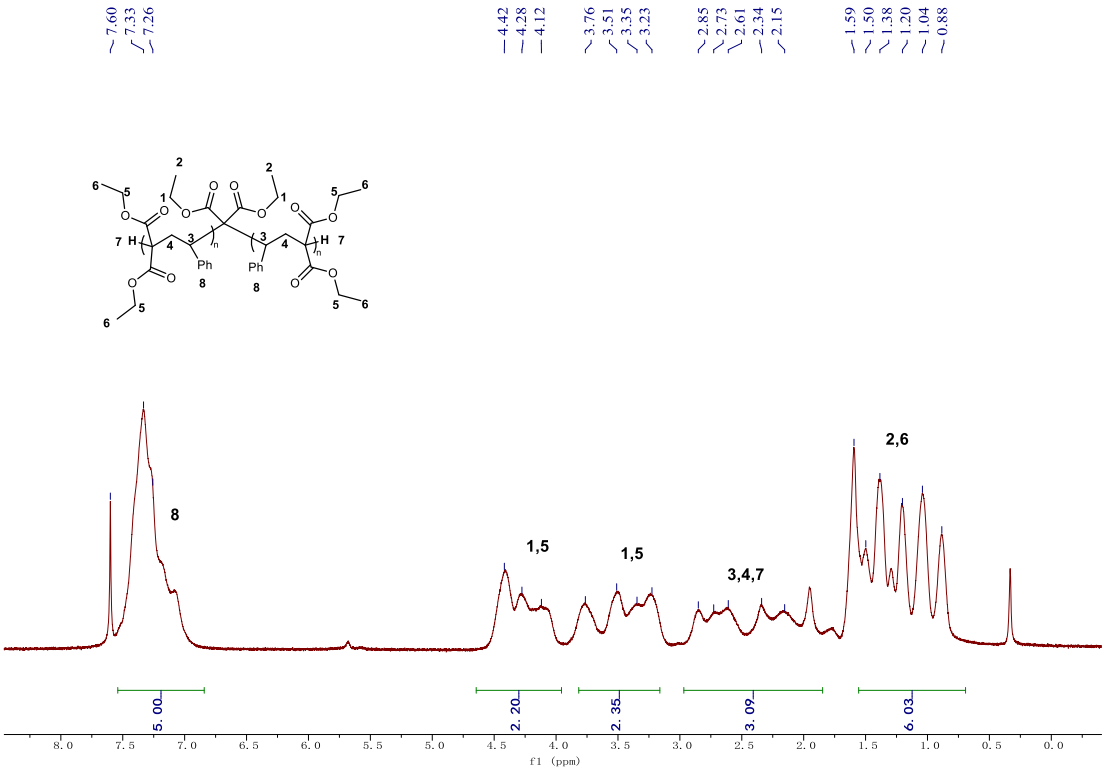


Fig. S89 ^{1}H NMR spectrum of **PM1** in $CDCl_3$

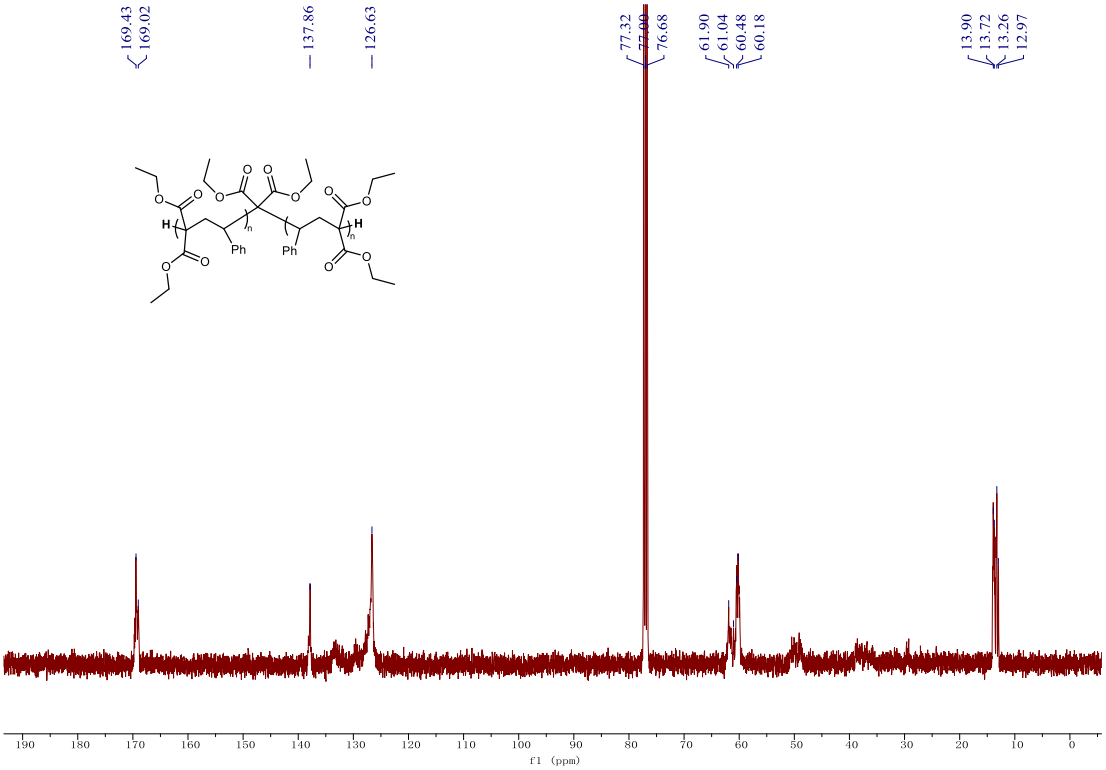


Fig. S90 ^{13}C NMR spectrum of **PM1** in $CDCl_3$

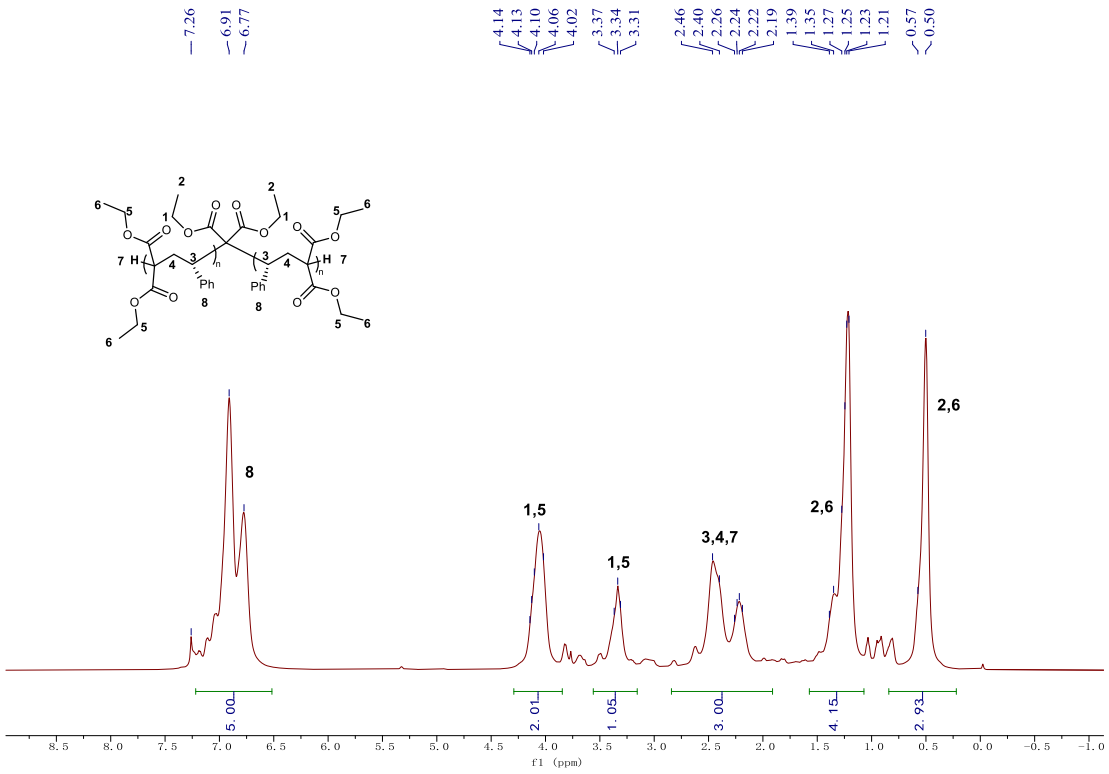


Fig. S91 ^{1}H NMR spectrum of **P**[(S)-**M1**] in $CDCl_3$

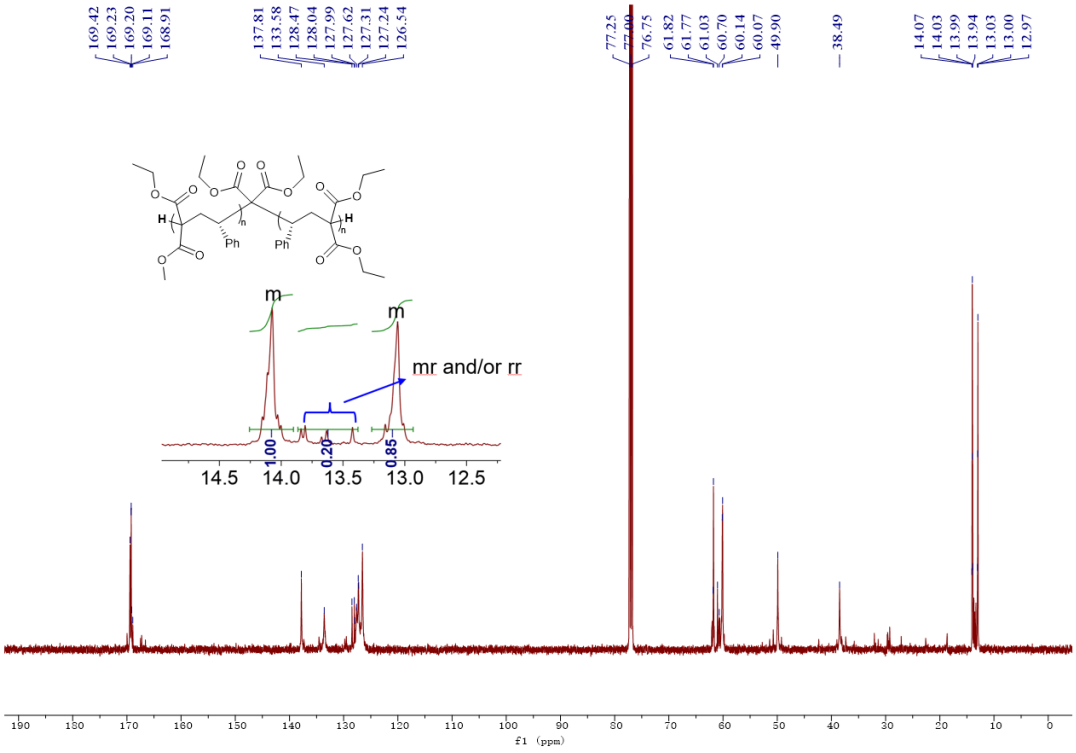


Fig. S92 ^{13}C NMR spectrum of **P**[(S)-**M1**] in $CDCl_3$. The tacticity was determined to be > 90%m.

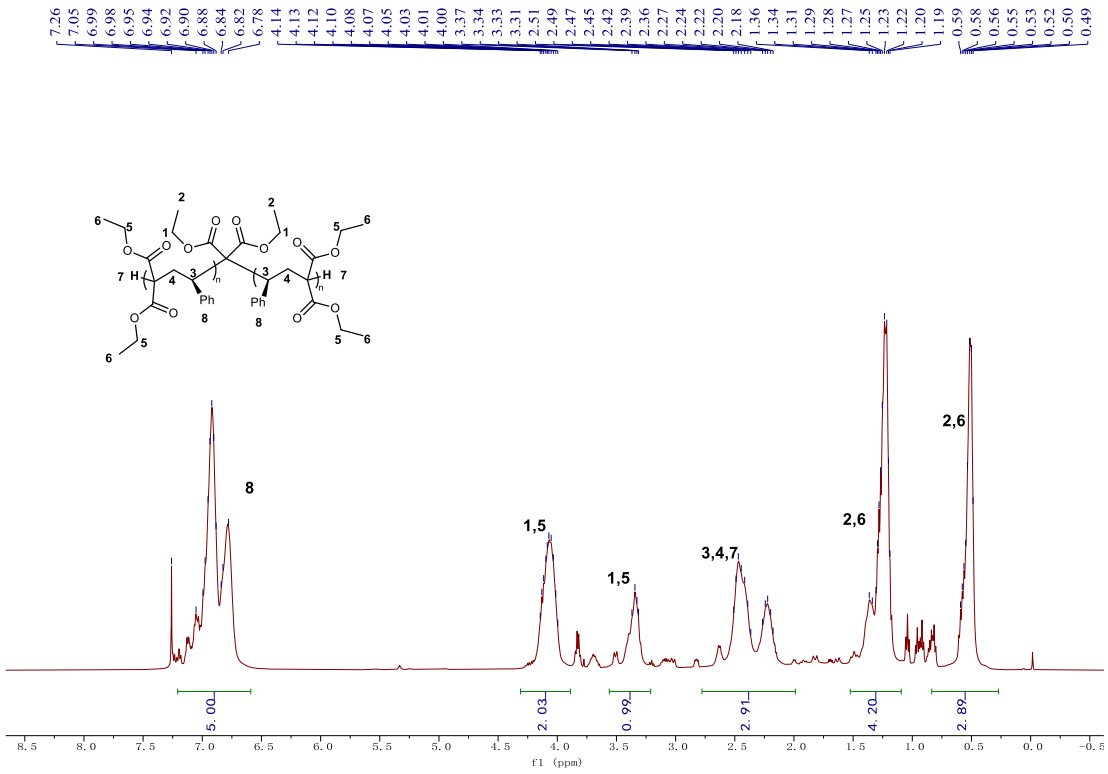


Fig. S93 ^{1}H NMR spectrum of **P**[(*R*)-**M1**] in $CDCl_3$

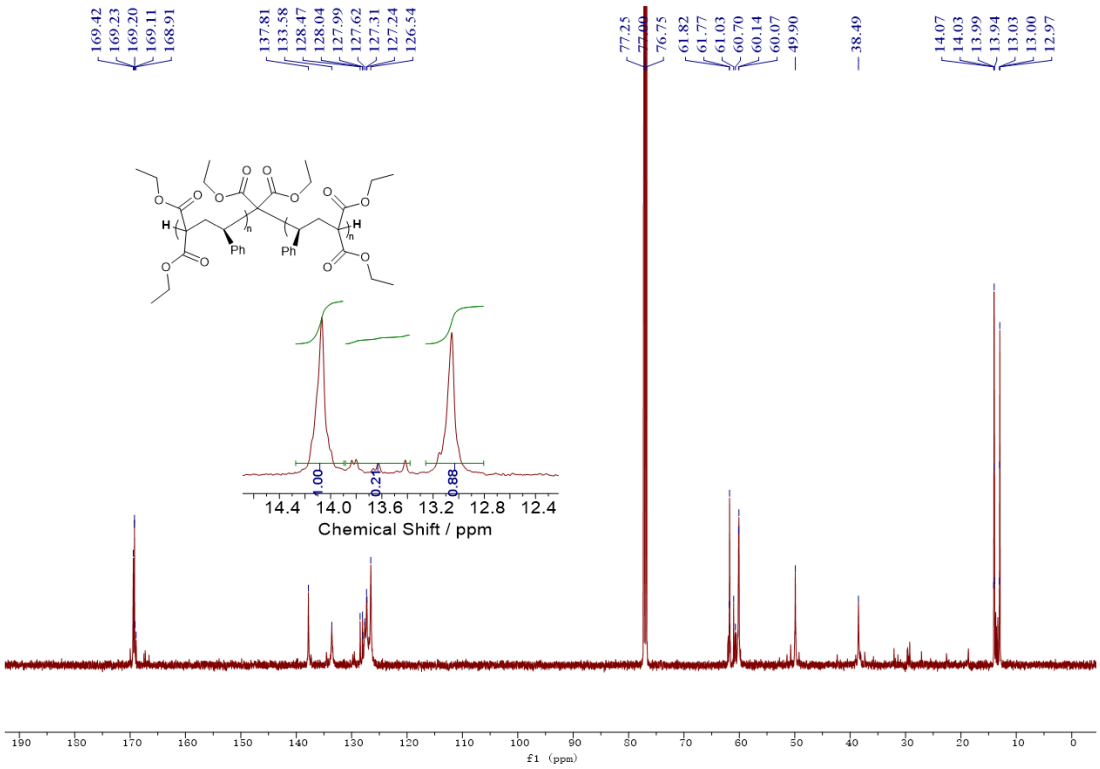


Fig. S94 ^{13}C NMR spectrum of **P**[(*R*)-**M1**] in $CDCl_3$. The tacticity was determined to be > 90%m.

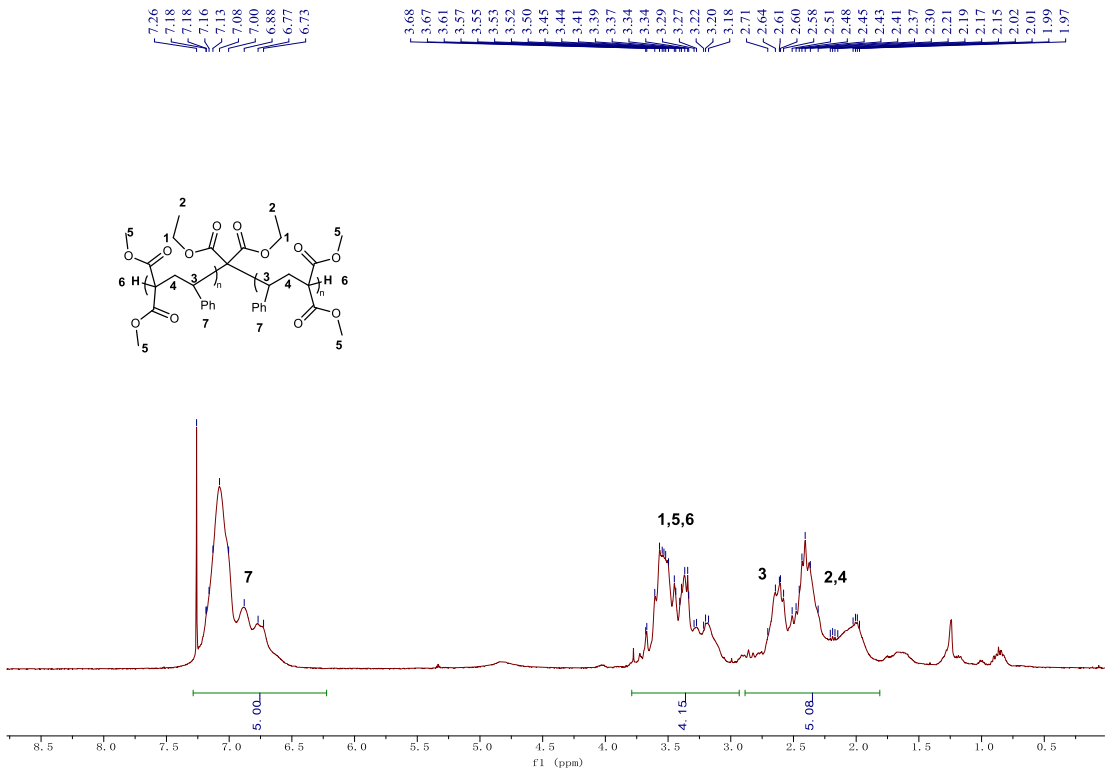


Fig. S95 ^{1}H NMR spectrum of **PM2** in $CDCl_3$

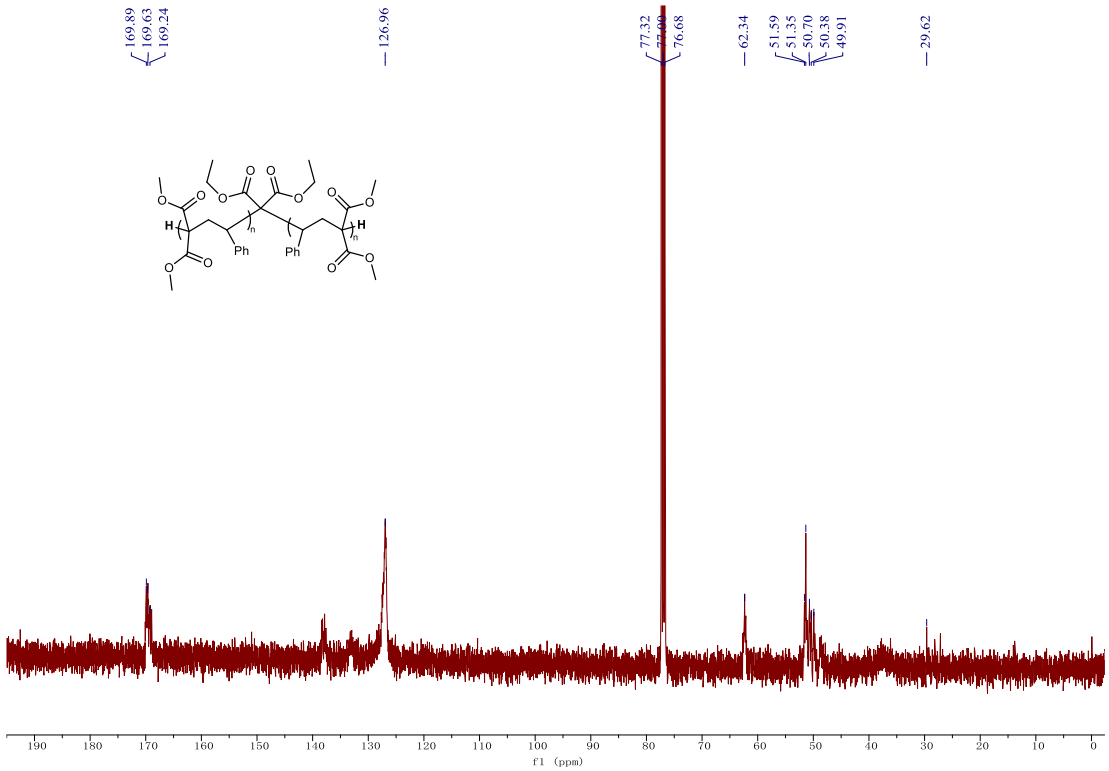


Fig. S96 ^{13}C NMR spectrum of **PM2** in $CDCl_3$

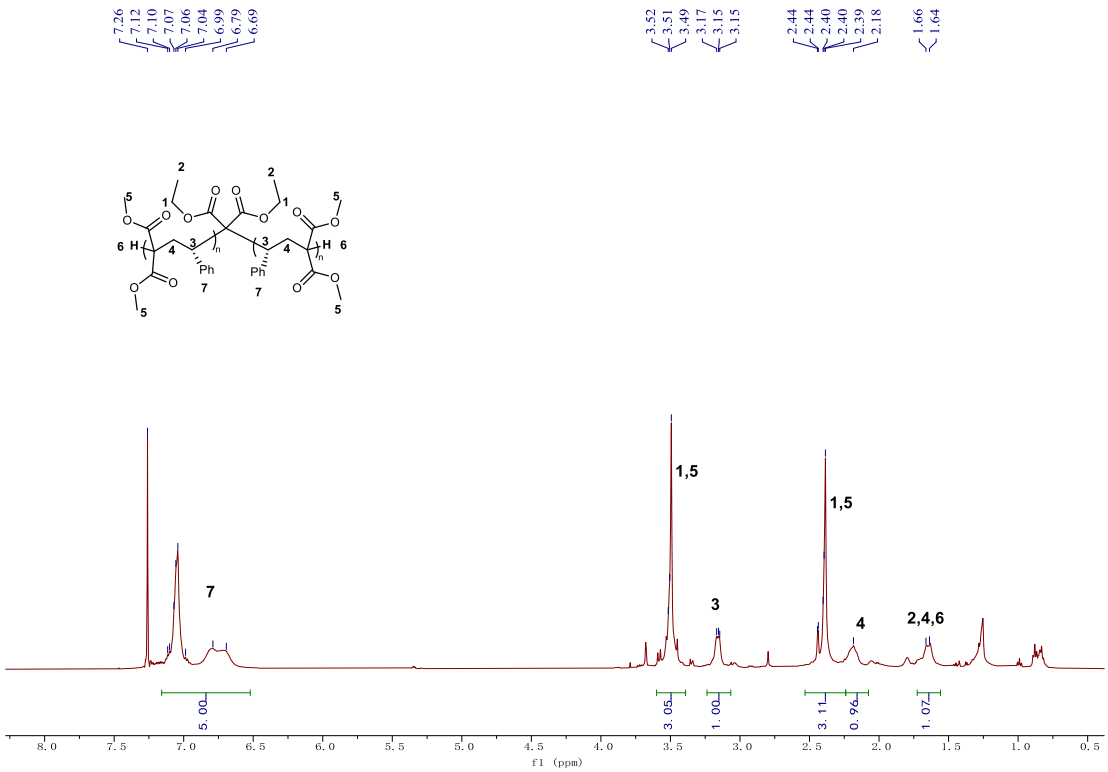


Fig. S97 ^{1}H NMR spectrum of **P**[(*S*)-**M2**] in $CDCl_3$

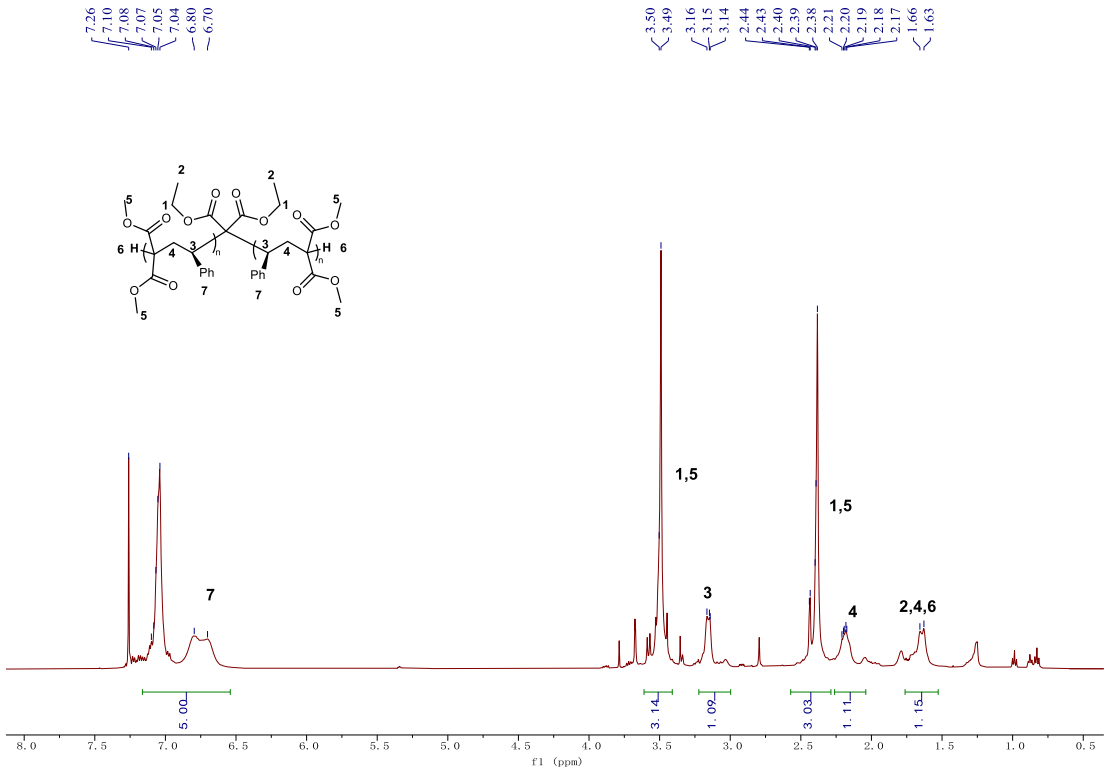


Fig. S98 ^{1}H NMR spectrum of **P**[(*R*)-**M2**] in $CDCl_3$

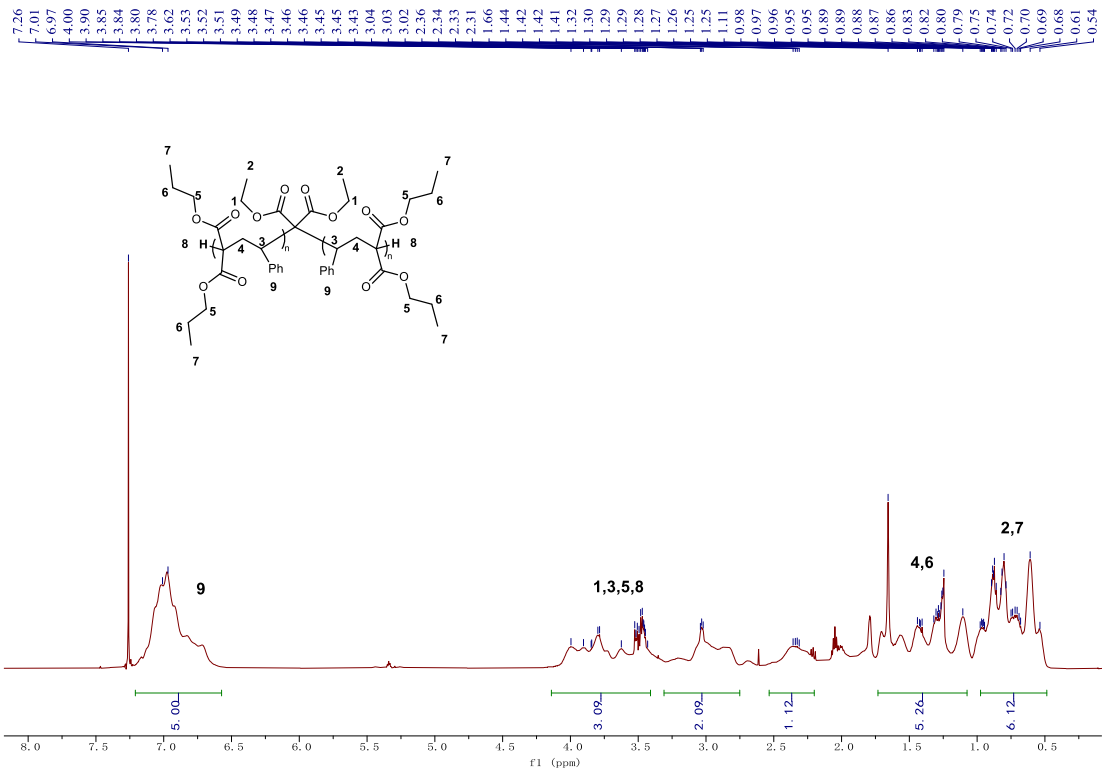


Fig. S99 ^{1}H NMR spectrum of **PM3** in $CDCl_3$

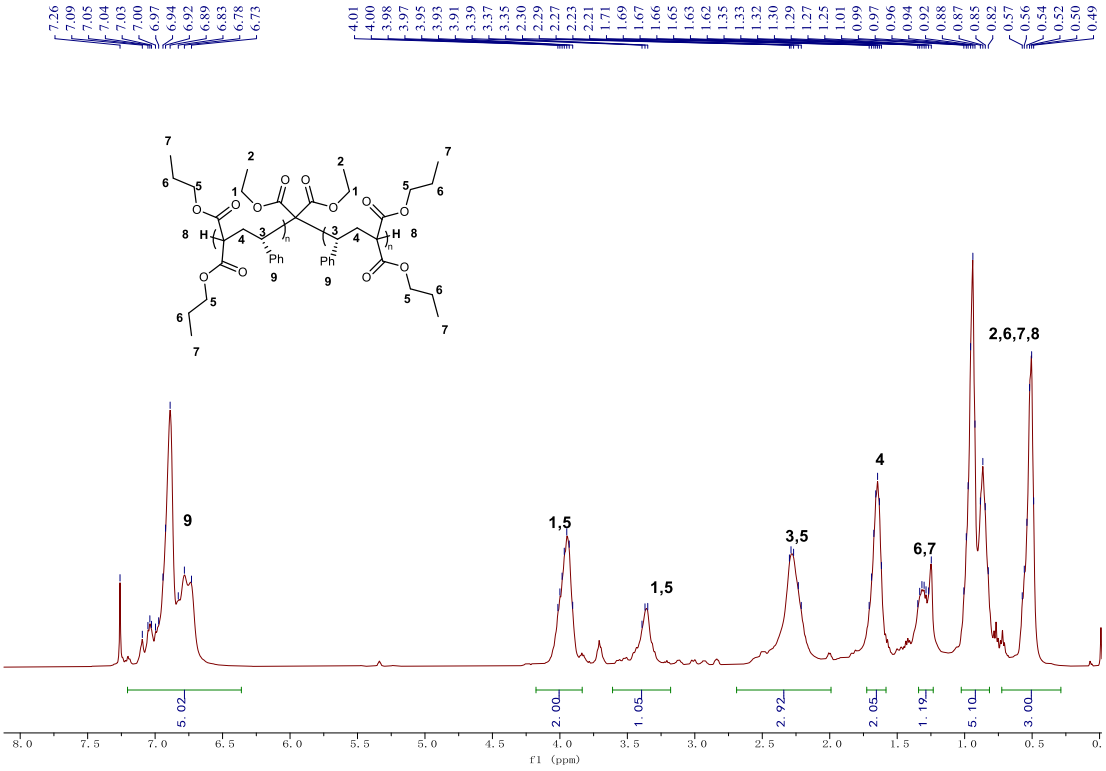


Fig. S100 ^{1}H NMR spectrum of **P[(*S*)-M3]** in $CDCl_3$

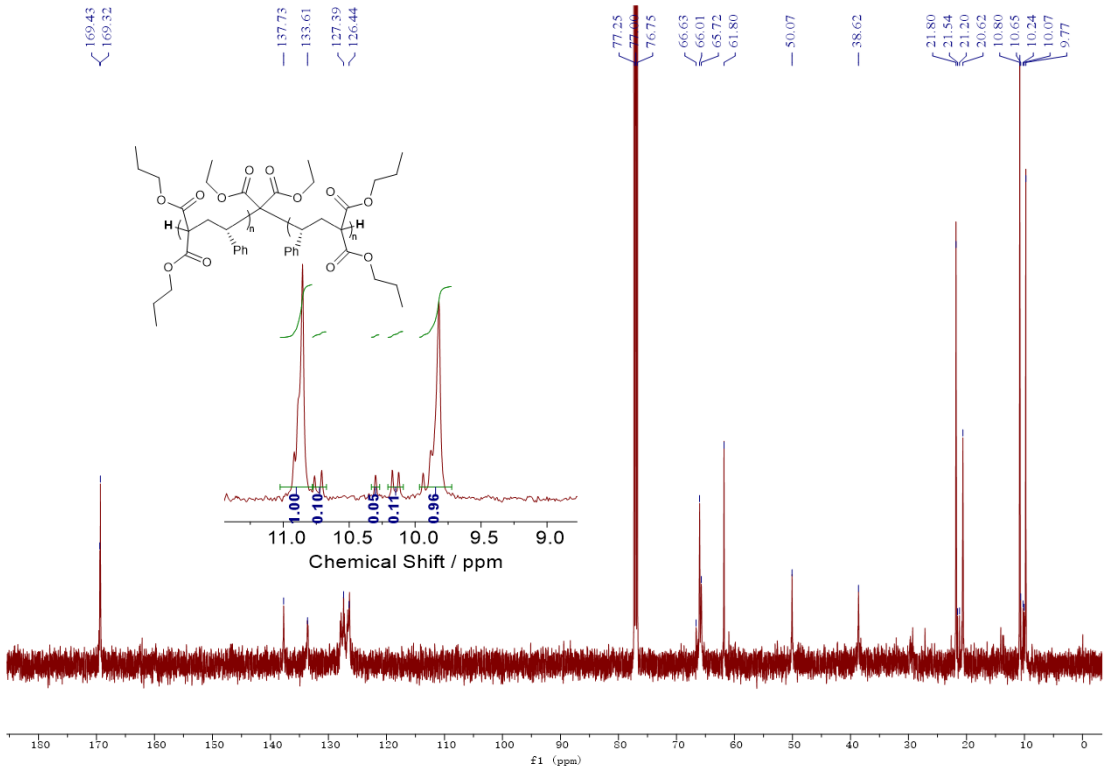


Fig. S101 ^{13}C NMR spectrum of **P**[(*S*)-**M3]** in $CDCl_3$. The tacticity was determined to be > 90%m.

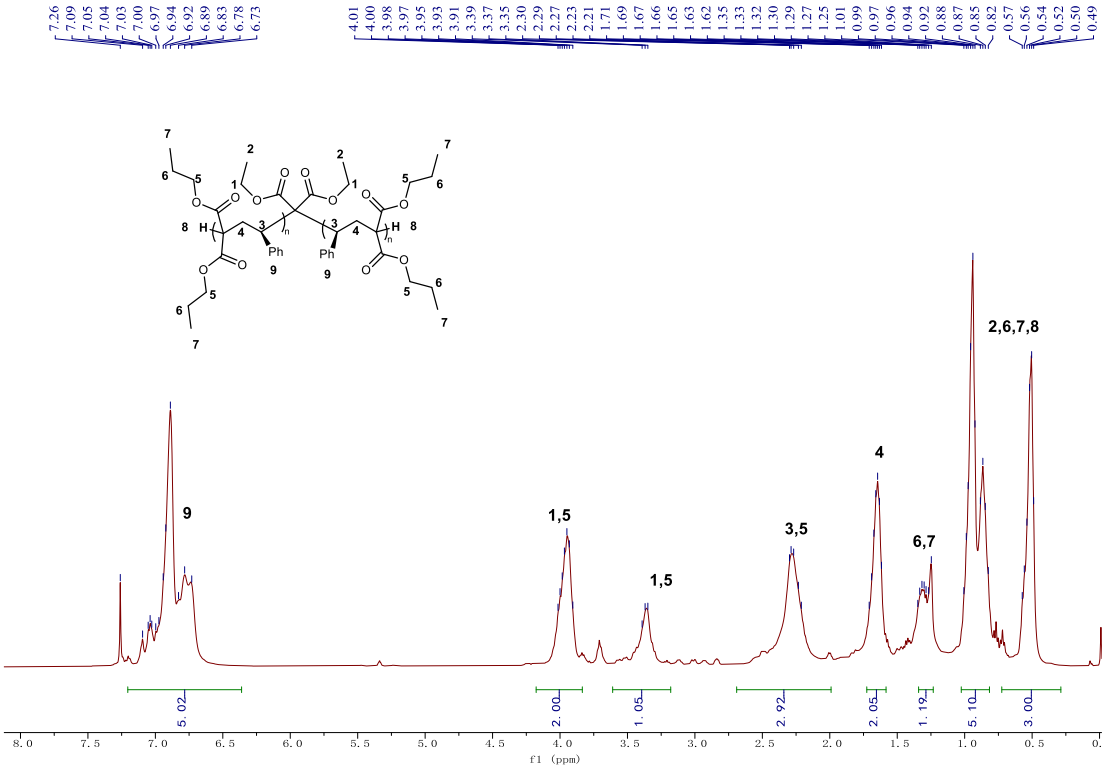


Fig. S102 ^{1}H NMR spectrum of **P**[(*R*)-**M3**] in $CDCl_3$

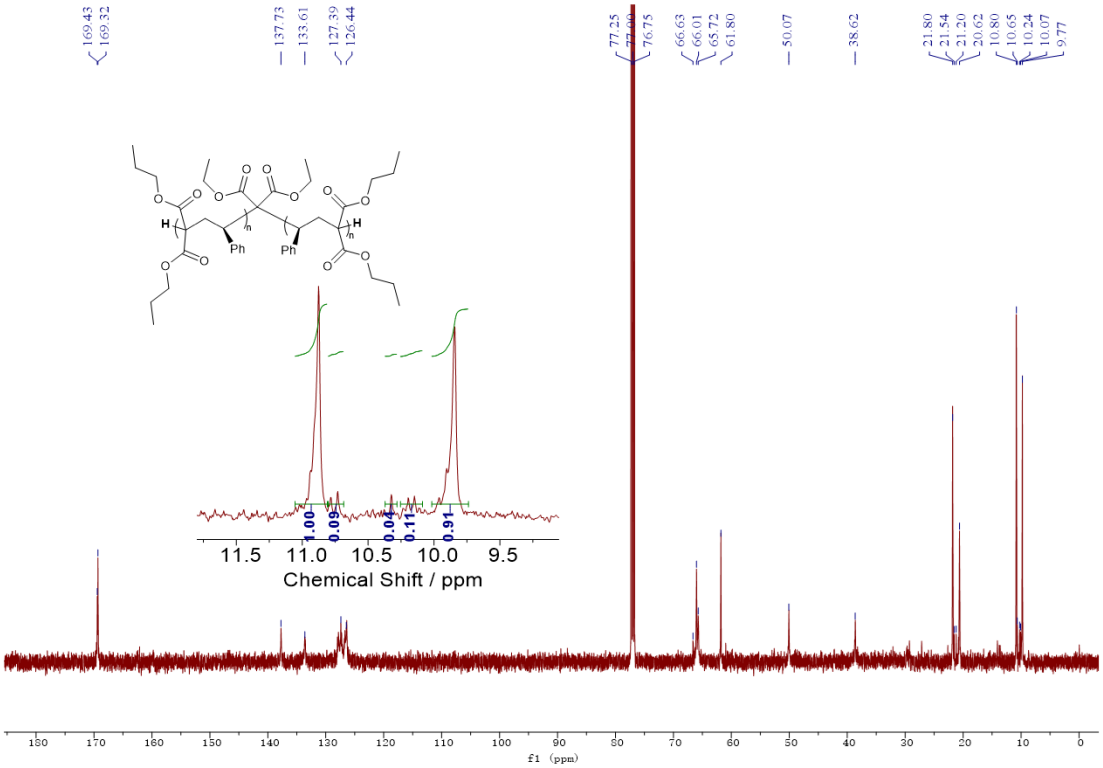


Fig. S103 ^{13}C NMR spectrum of **P**[(*R*)-**M3**] in $CDCl_3$. The tacticity was determined to be > 90%m.

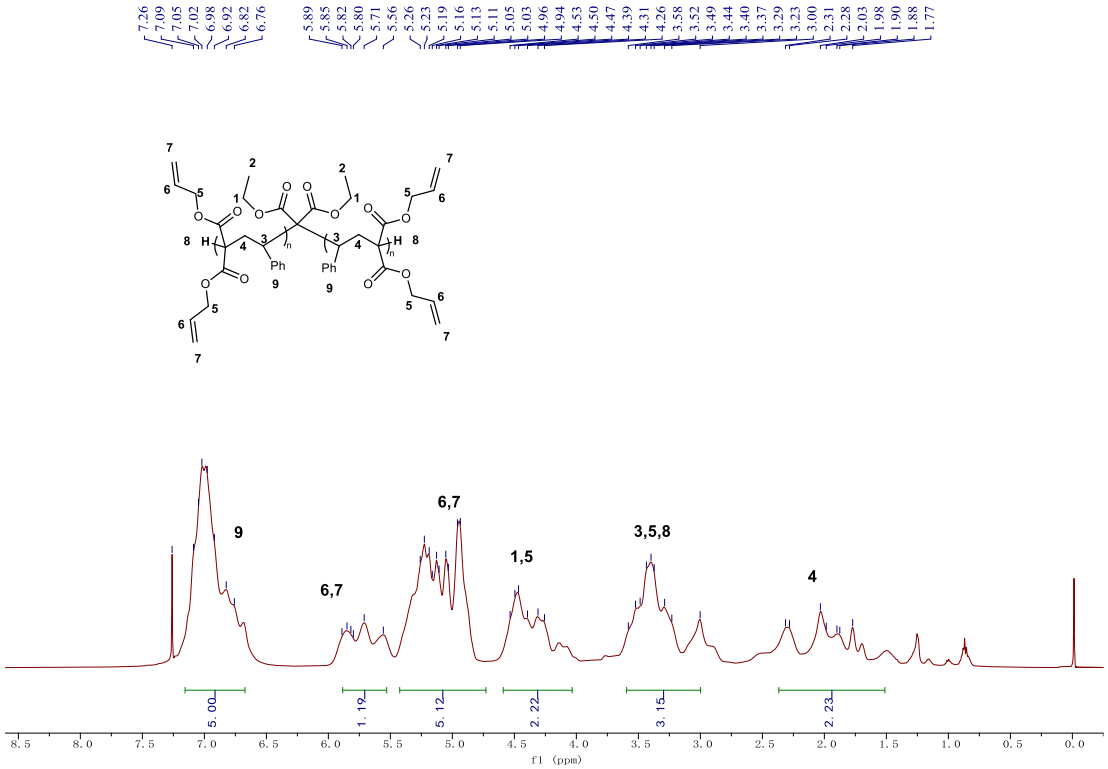


Fig. S104 ^{1}H NMR spectrum of **PM4** in $CDCl_3$

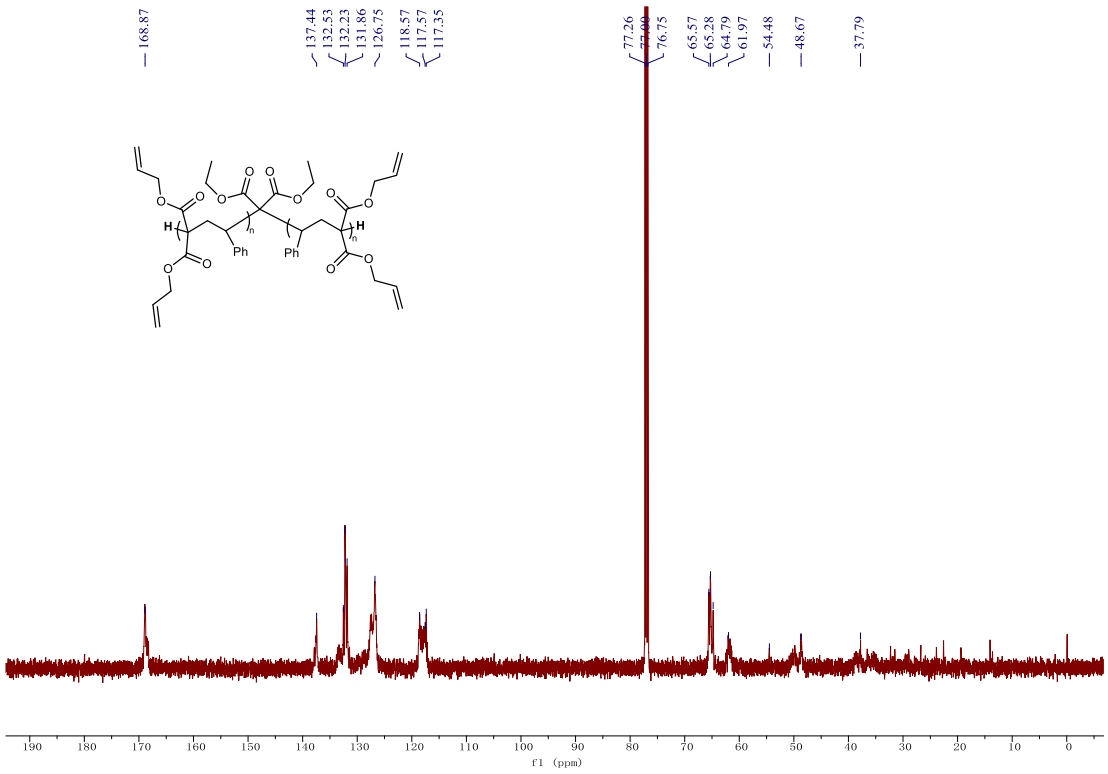


Fig. S105 ^{13}C NMR spectrum of **PM4** in $CDCl_3$

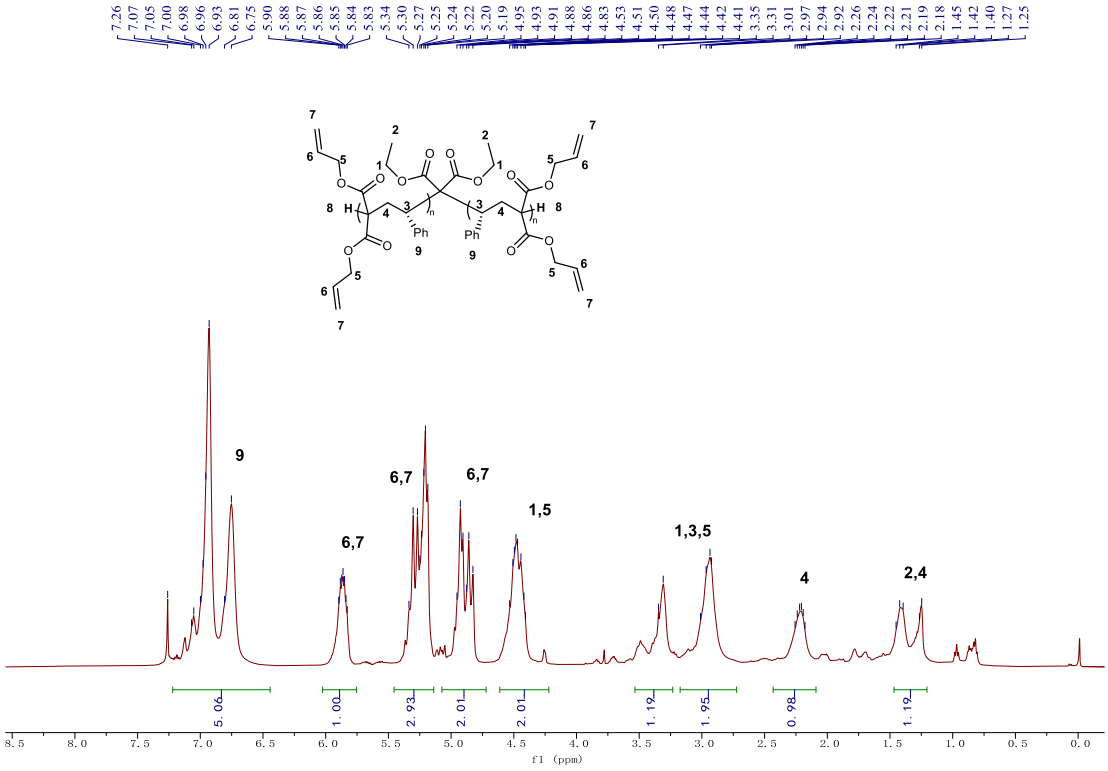


Fig. S106 ^{1}H NMR spectrum of **P**[(*S*)-**M4**] in $CDCl_3$

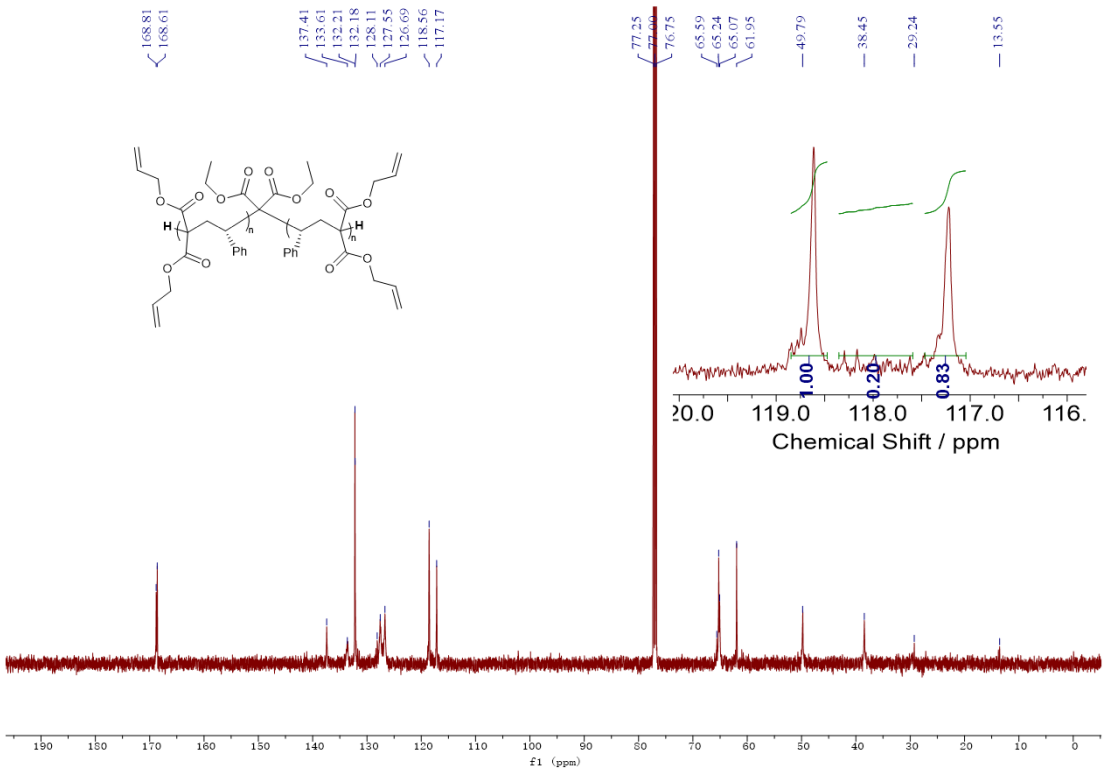


Fig. S107 ^{13}C NMR spectrum of **P**[(*S*)-**M4**] in $CDCl_3$. The tacticity was determined to be > 90%m.

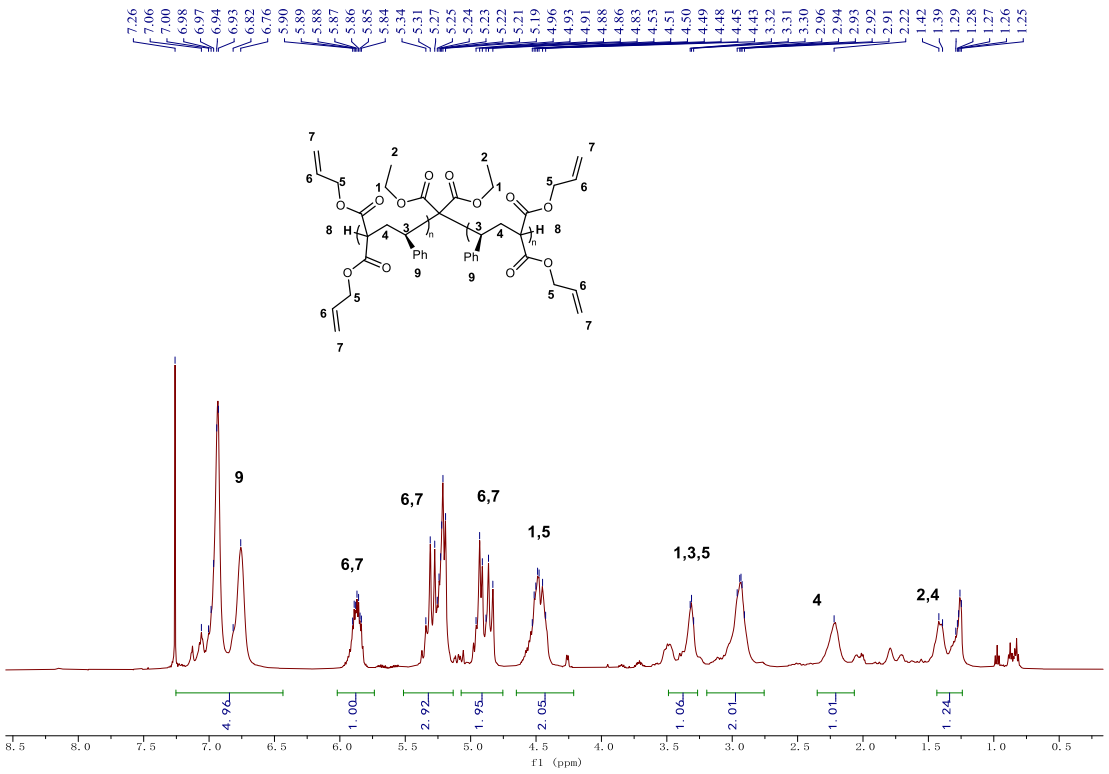


Fig. S108 ^{1}H NMR spectrum of **P**[(*R*)-**M4**] in $CDCl_3$

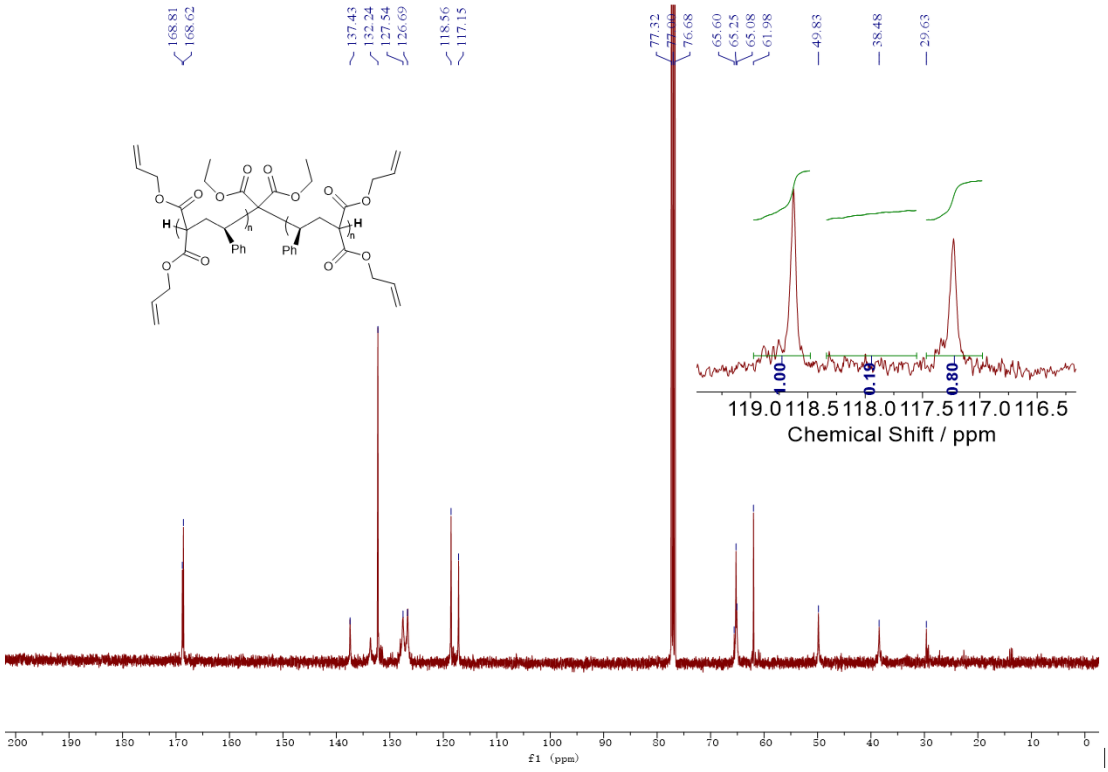


Fig. S109 ^{13}C NMR spectrum of **P[(*R*)-M4]** in $CDCl_3$. The tacticity was determined to be > 90%m.

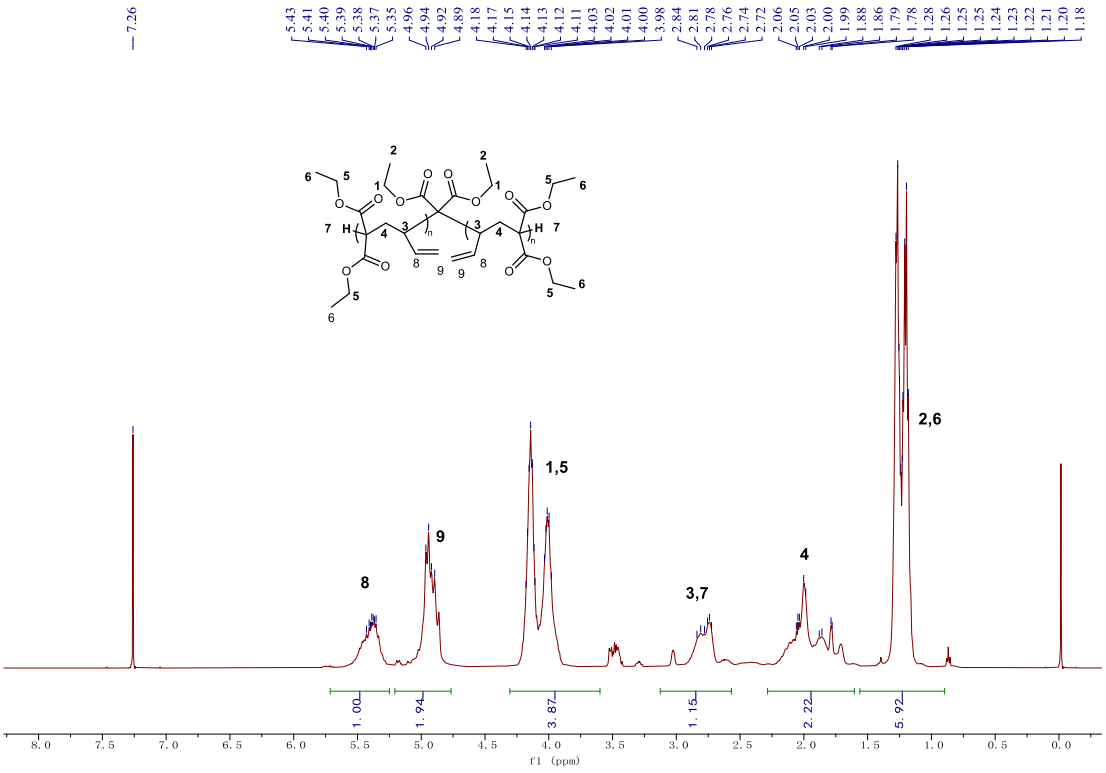


Fig. S110 ^{1}H NMR spectrum of **PM6** in $CDCl_3$

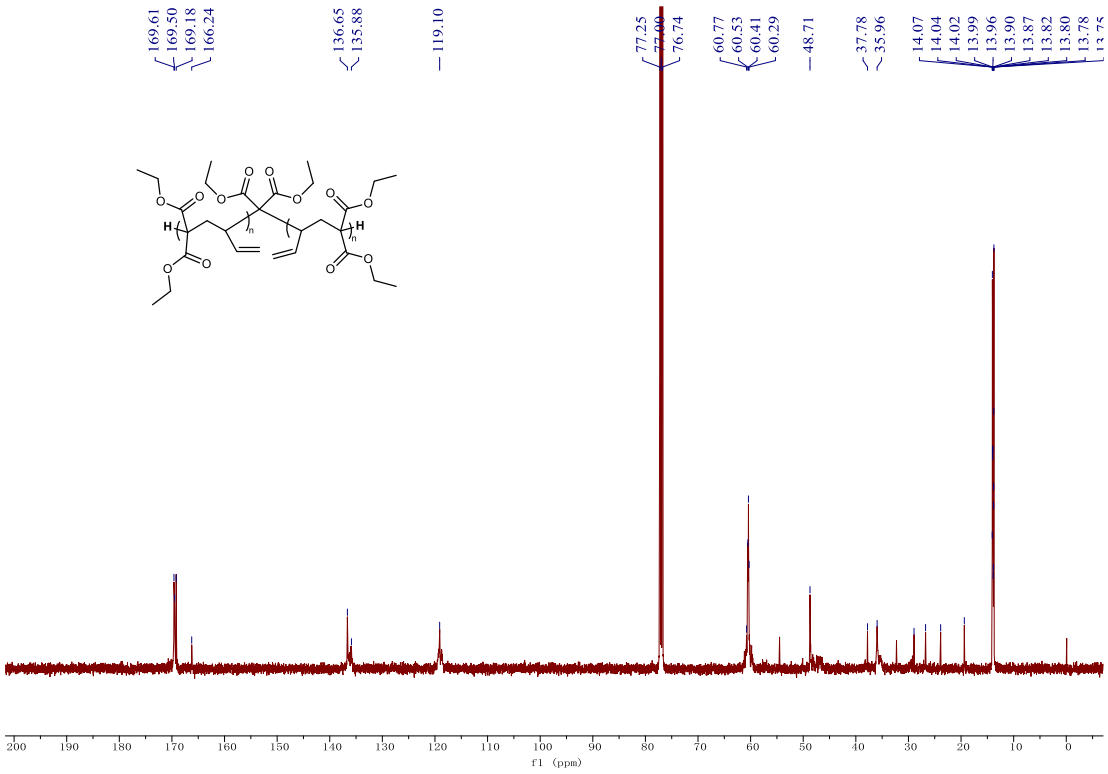


Fig. S111 ^{13}C NMR spectrum of **PM6** in $CDCl_3$

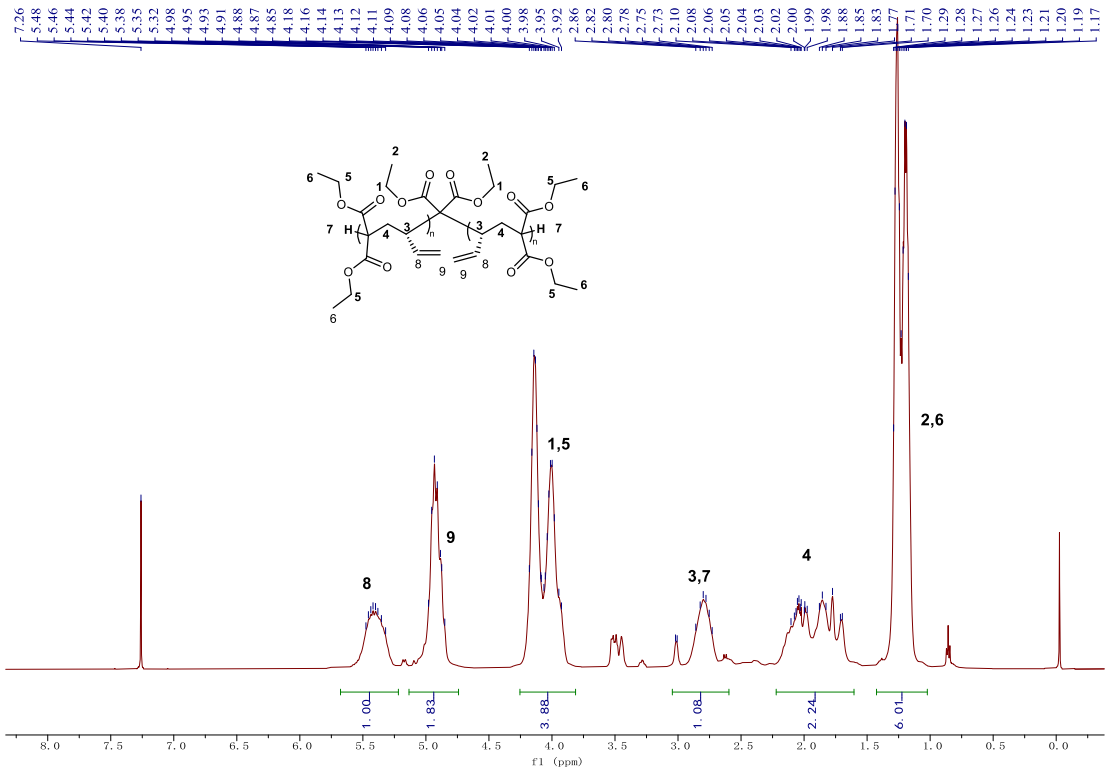


Fig. S112 ^{1}H NMR spectrum of **P[(*S*)-M6]** in $CDCl_3$

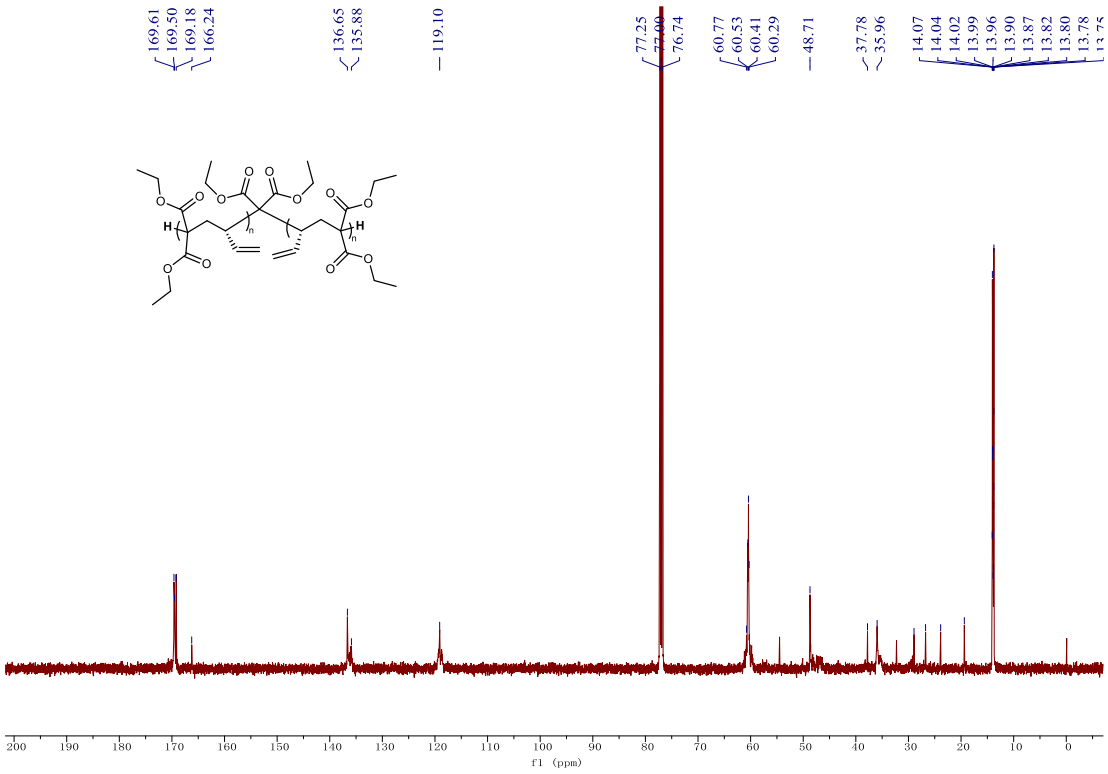


Fig. S113 ^{13}C NMR spectrum of **P[(*S*)-M6]** in $CDCl_3$

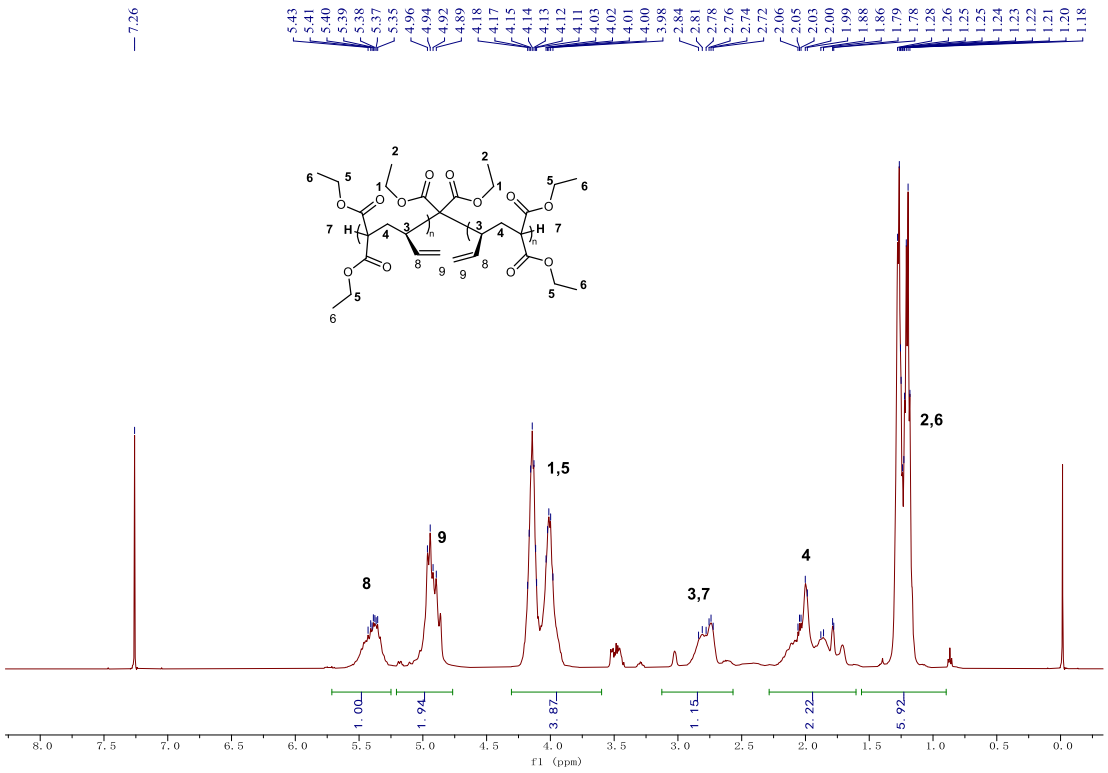


Fig. S114 ^{1}H NMR spectrum of **P[(*R*)-M6]** in $CDCl_3$

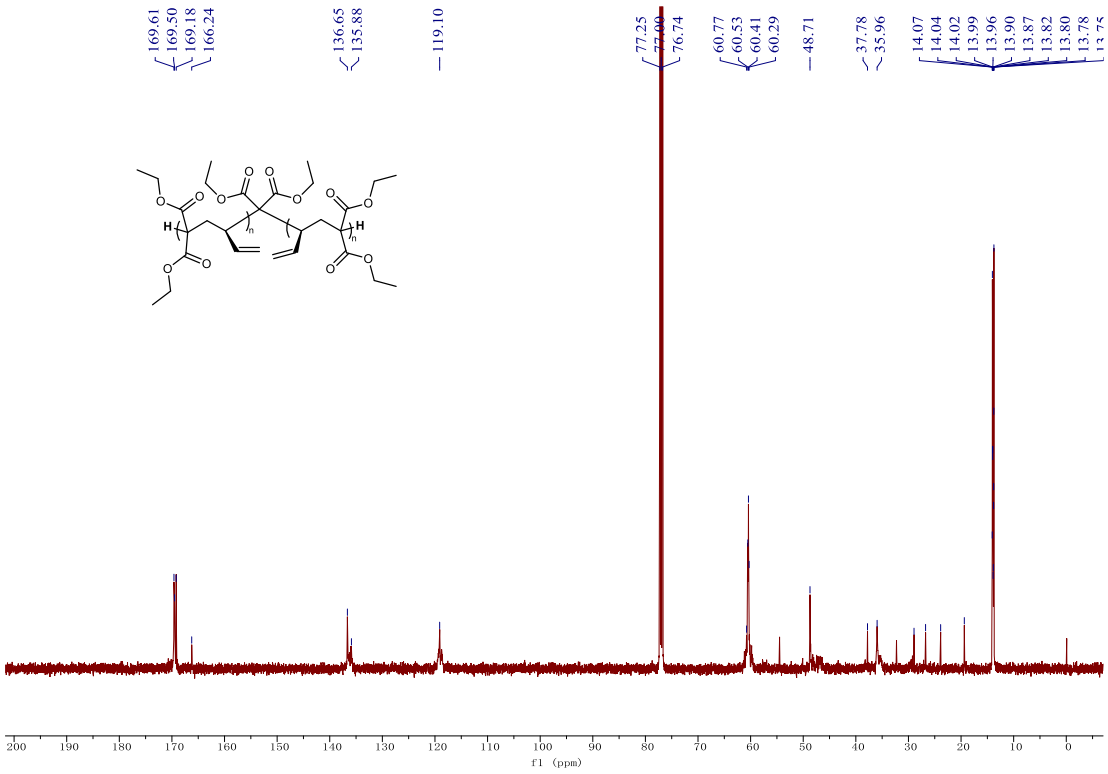


Fig. S115 ^{13}C NMR spectrum of **P[(*R*)-M6]** in $CDCl_3$

8. Specific Rotation and CD Spectra of Homopolymer

Table S2. Specific rotations

monomer	conc. (g/100 mL) in $CHCl_3$	$[\alpha]_D^{20}$
P[(*S*)-M1]	0.428	+17.92
P[(R)-M1]	0.330	-16.67
P[(*S*)-M2]	0.270	+21.63
P[(R)-M2]	0.312	-17.92
P[(*S*)-M3]	0.380	+6.32
P[(R)-M3]	0.298	-4.97
P[(*S*)-M4]	1.135	+10.12
P[(R)-M4]	0.360	-9.81
P[(*S*)-M6]	1.980	-1.23
P[(R)-M6]	1.930	+1.18

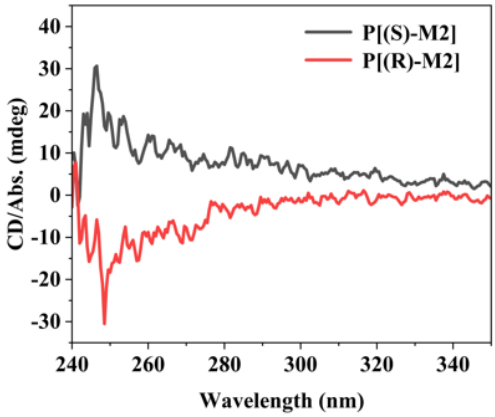


Fig. S116 CD spectra of **P[(*S*)-M2]** and **P[(*R*)-M2]**.in $CHCl_3$ at 1×10^{-5} M.

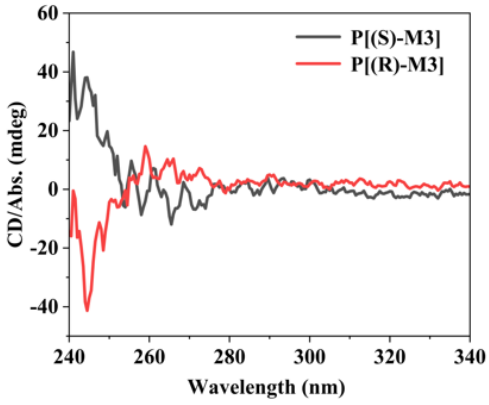


Fig. S117 CD spectra of **P[(*S*)-M3]** and **P[(*R*)-M3]** in $CHCl_3$ at 1×10^{-5} M.

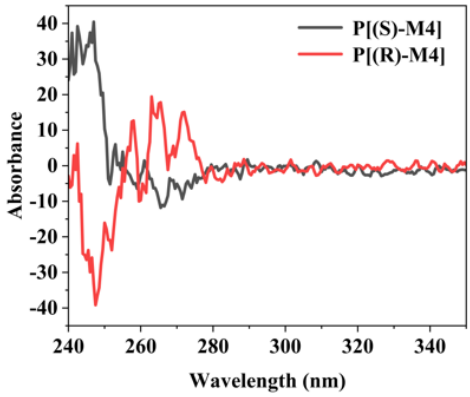


Fig. S118 CD spectra of **P[(*S*)-M4]** and **P[(*R*)-M4]** in $CHCl_3$ at 1×10^{-5} M.

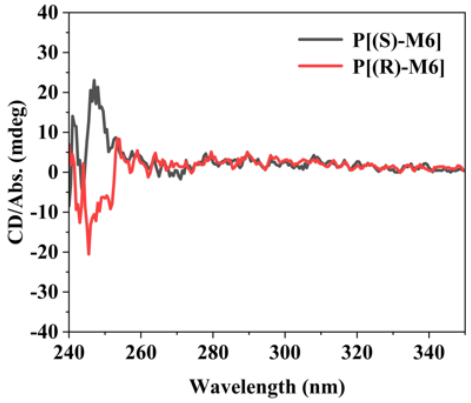


Fig. S119 CD spectra of **P[(*S*)-M6]** and **P[(*R*)-M6]** in $CHCl_3$ at 1×10^{-5} M.

9. Computational Details

9.1 Computational Methods

All calculations were performed using Gaussian16[5] unless otherwise specified. Geometry optimizations were carried out with the M06-2X[6] functional with D3[7] dispersion correction. Optimizations used the Def2-SV(P)[8] basis set for all atoms. Vibrational frequencies were calculated to verify stationary points as minima or first-order saddle points (transition states). Enthalpies reported are the sum of $E_{(large)} + \Delta E_{ZPE(small)} + \Delta U_{(small)} + nRT$. E is the SCF energy. $\Delta E_{ZPE(small)}$ is the zero-point energy correction. $\Delta U_{(small)}$ is the thermal energy vibrational, rotational, and translational corrections. R is the gas constant. T is the temperature at 298 K unless otherwise specified. Small = M06-2X-D3/Def2-SV(P). Large = PWPB95-D3(BJ)[9]/Def2-TZVPP. Calculations correspond to 1 atm with no concentration corrections. Gibbs free energies reported in the table below are the sum of $E_{(large)} + \Delta E_{ZPE(small)} + \Delta U_{(small)} + nRT + T\Delta S_{(small)}$. PWPB95-D3(BJ)/Def2-TZVPP is computed using Orca 6.1[10] based on the optimized structures to obtain single point energies for the $E_{(large)}$. The SMD[11] model with acetonitrile parameters was utilized as the implicit solvent model unless otherwise specified.

9.2 Confirmation of Reference Point (Starting Material)

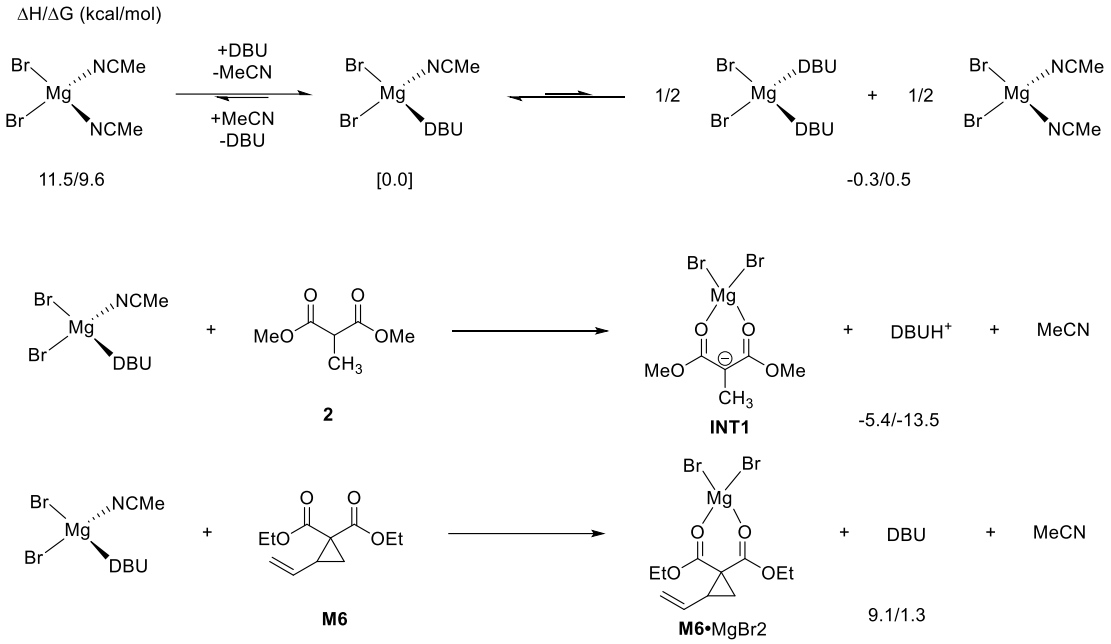


Fig. S120 Computed energy profile for the ground state of Mg^{2+} and the formation of intermediates **INT1** and **M6•**$MgBr_2$, energy shown in kcal/mol.

We investigated the ground state of the $MgBr_2$ catalyst (**Fig. S117**). In the presence of MeCN and DBU, $MgBr_2$ can form three potential coordination complexes: $MgBr_2(MeCN)_2$, $MgBr_2(DBU)_2$, and $MgBr_2(MeCN)(DBU)$. Given that DBU is present in stoichiometric equivalence to $MgBr_2$, the transformation from $MgBr_2(MeCN)_2$ to $MgBr_2(MeCN)(DBU)$ is exergonic by 9.6 kcal/mol. Conversely, the further transformation to the bis-DBU species is endergonic by 0.5 kcal/mol. Thus, the predominant species under reaction conditions is $MgBr_2(MeCN)(DBU)$. Upon the introduction of initiator **2** and monomer **M6**, **2** is rapidly converted into **INT1** with a Gibbs energy decrease of 13.5 kcal/mol, driven by the Lewis acid-enhanced acidity of the α-H in **2**. In contrast, monomer **M6** remains structurally uncoordinated, as the transformation is endergonic by 1.3 kcal/mol (**Fig. S117**).

9.3 Absolute and Relative Energies

SMD(MeCN)-M06-2X-D3/Def2-SV(P)						
Species	EE	H	G	ΔEE	ΔH	ΔG
DBU	-461.514705	-461.256717	-461.302558			
DBUH+	-461.996478	-461.723684	-461.769707			
MeCN	-132.592936	-132.542833	-132.571348			
MgBr2(DBU)(MeCN)	-5942.153937	-5941.83324	-5941.910756	0.0	0.0	0.0
MgBr2(DBU)2	-6271.099295	-6270.569759	-6270.659132	-0.2	-0.2	0.6
MgBr2(MeCN)2	-5613.209103	-5613.097402	-5613.160511	14.5	13.8	11.9
S3	-534.937016	-534.761115	-534.811711			
INT1	-5882.508751	-5882.336599	-5882.40307	-4.5	-5.5	-13.6
M6	-728.809559	-728.532832	-728.596163			

M6•MgBr2	-6076.837641	-6076.551023	-6076.63011	11.4	9.7	1.8
TS1	-11959.33841	-11958.87901	-11958.99952	16.4	15.1	22.9
INT2&INT4	-11959.38806	-11958.92628	-11959.04375	-14.7	-14.5	-4.8
TS2	-6076.788301	-6076.504046	-6076.582496	42.4	39.2	31.7
INT3	-6076.789075	-6076.504342	-6076.585078	41.9	39.0	30.1
M1	-882.300585	-881.972983	-882.04137			
M1•MgBr2	-6230.329708	-6229.992339	-6230.07678	10.8	9.0	0.9
TS3	-12112.83361	-12112.32304	-12112.44681	13.8	12.7	21.6
SMD(MeCN)-PWPB95-D3(BJ)/Def2-TZVPP						
Species	EE	H	G	ΔEE	ΔH	ΔG
DBU	-461.9144324	-461.6564444	-461.7022854			
DBUH+	-462.4029509	-462.1301569	-462.1761799			
MeCN	-132.7182203	-132.6681173	-132.6966323			
MgBr2(DBU)(MeCN)	-5943.195768	-5942.875071	-5942.952587	0.0	0.0	0.0
MgBr2(DBU)2	-6272.412239	-6271.882703	-6271.972076	-0.3	-0.3	0.5
MgBr2(MeCN)2	-5613.980173	-5613.868472	-5613.931581	12.2	11.5	9.6
S3	-535.4483614	-535.2724604	-535.3230564			
INT1	-5883.530011	-5883.357859	-5883.42433	-4.4	-5.4	-13.5
M6	-729.4778835	-729.2011565	-729.2644875			
M6•MgBr2	-6078.023611	-6077.736993	-6077.81608	10.9	9.2	1.3
TS1	-11961.54388	-11961.08448	-11961.20499	17.0	15.7	23.5
INT2&INT4	-11961.58844	-11961.12666	-11961.24412	-10.9	-10.7	-1.0
TS2	-6077.981513	-6077.697258	-6077.775708	37.3	34.1	26.6
INT3	-6077.981976	-6077.697243	-6077.777979	37.0	34.1	25.2
M1	-883.0827607	-882.7551587	-882.8235457			
M1•MgBr2	-6231.629608	-6231.292239	-6231.37668	10.2	8.4	0.3
TS3	-12115.15422	-12114.64365	-12114.76742	13.6	12.5	21.4

DBU

C	-0.92672000	-1.47749900	-0.38698900
C	0.36826500	-0.72356300	-0.12595800
C	-2.08818300	-1.15208800	0.55906700
C	-0.85039400	1.46049600	0.26713800
C	-2.94850300	0.00612300	0.05305200
C	-2.10412700	1.13456400	-0.54172000
H	-1.24115800	-1.31551100	-1.43408700
H	-1.08591600	1.43915200	1.35133500
H	-1.68474100	-0.91618600	1.55963100
H	-3.56237600	0.39778700	0.88276600
H	-0.64568500	-2.53553400	-0.30164000
H	-2.71556100	-2.04937400	0.68653700
H	-0.55695600	2.49592500	0.03673400
H	-3.65157900	-0.35995600	-0.71550700
H	-2.71492600	2.05013000	-0.60537700
H	-1.79668500	0.89521900	-1.57375100

C	1.58401200	1.34445200	0.30207400
H	1.51711700	2.36839000	-0.09973300
H	1.70583400	1.43189400	1.40090900
C	2.77235800	0.61570600	-0.29692700
H	3.71025500	1.10345100	0.01261700
H	2.71204300	0.66443700	-1.39831800
C	2.72301000	-0.83491900	0.15631900
H	3.48838300	-1.43104400	-0.37024000
H	2.97571500	-0.89599300	1.23288300
N	1.42871300	-1.45145400	-0.06545800
N	0.33813400	0.65396700	-0.01755400

DBUH$^+$

C	0.93561700	1.50156100	-0.25659800
C	-0.30767800	0.66579500	-0.05948300
C	2.13472900	1.10162600	0.60584400
C	0.90418300	-1.50120600	0.21867900
C	2.96519700	-0.00804300	-0.03576000
C	2.08403400	-1.09228800	-0.65441300
H	1.19834000	1.47226900	-1.32872700
H	1.20495200	-1.58288500	1.27852200
H	1.77707100	0.78851300	1.60160900
H	3.62833300	-0.45312100	0.72509200
H	0.64349400	2.53838600	-0.03817700
H	2.75902500	1.99382400	0.76801300
H	0.56245400	-2.49552700	-0.09776700
H	3.61485900	0.41718200	-0.81957300
H	2.68507800	-1.99780900	-0.83461200
H	1.69990900	-0.77800000	-1.63977600
C	-1.56417400	-1.33464000	0.43550200
H	-1.44265800	-2.38661300	0.14730800
H	-1.73782400	-1.29470700	1.52501700
C	-2.71968100	-0.70550900	-0.32121400
H	-3.65893700	-1.20356900	-0.04116300
H	-2.56634400	-0.84148900	-1.40434300
C	-2.78933900	0.76951900	0.01625500
H	-3.44084400	1.31505600	-0.68088200
H	-3.16967500	0.92430900	1.03927500
N	-1.45010800	1.33904500	-0.08734500
N	-0.29735100	-0.64511500	0.13349800
H	-1.38233900	2.34578900	-0.21575800

MeCN

N	-1.43377600	-0.00002400	-0.00002100
C	-0.28030500	0.00005500	0.00004100
C	1.17873600	-0.00001300	-0.00003500
H	1.54858500	-0.97472300	-0.35257700
H	1.54868500	0.79273800	-0.66763800

H	1.54857400	0.18189900	1.02033100

$MgBr_2(DBU)(MeCN)$

Mg	-1.28319900	-0.26696200	-0.10433000
N	0.53666200	0.70553000	-0.33098700
C	1.77104000	0.30588400	-0.14248800
C	0.28788200	2.10672800	-0.66750200
C	1.96220900	-1.17715400	0.11507200
N	2.83623600	1.14001000	-0.14284500
C	1.25119900	3.01754900	0.06587000
H	-0.75723400	2.35423500	-0.42192100
H	0.39383500	2.24224600	-1.75977400
C	3.09733800	-1.85783600	-0.65853400
H	2.09601300	-1.33242500	1.20089700
H	1.00994200	-1.65802500	-0.14134500
C	4.25059700	0.73410200	-0.19587000
C	2.65896400	2.58993500	-0.28995300
H	1.10124800	4.07024500	-0.21761100
H	1.08877300	2.92723600	1.15394000
C	4.43064600	-1.79621700	0.08440000
H	3.19122300	-1.39183600	-1.65460500
H	2.81915000	-2.90869100	-0.83742800
C	4.66349800	-0.42156800	0.71147300
H	4.53512600	0.52105800	-1.24325000
H	4.81326700	1.62817900	0.10553400
H	3.38934900	3.07991100	0.37209500
H	2.90241400	2.88306500	-1.32751100
H	5.25132700	-2.03246000	-0.61460400
H	4.45328700	-2.56505900	0.87589200
H	5.73324000	-0.29967500	0.94683100
H	4.12280000	-0.32524200	1.66805400
N	-2.02521800	1.03226900	1.42598300
C	-2.44773600	1.70837800	2.25622800
C	-2.98206400	2.56401400	3.30175600
H	-2.85349700	3.61682500	3.00792500
H	-4.05173300	2.34272400	3.43670900
H	-2.44025600	2.36976400	4.23984100
Br	-2.65108200	0.24905500	-2.09498900
Br	-1.47734900	-2.50922900	0.90397600

$MgBr_2(DBU)_2$

Mg	-0.03717800	0.69650700	0.24615500
N	-1.35131900	-0.68393100	-0.63522700
C	-2.65530800	-0.63354300	-0.52021000
C	-0.75734600	-1.83352600	-1.30880000
C	-3.22557700	0.65067700	0.05790200
N	-3.47817900	-1.65233400	-0.86796100
C	-1.48410900	-3.11049000	-0.93484300

H	0.31012200	-1.88446600	-1.04949900
H	-0.81464800	-1.68160600	-2.40370700
C	-4.44791300	1.23365300	-0.66088500
H	-3.44355900	0.49548200	1.12910600
H	-2.41446100	1.39064100	0.01633400
C	-4.94109900	-1.57153900	-1.00380700
C	-2.94061600	-2.94408100	-1.31447100
H	-1.06365600	-3.98311000	-1.45777600
H	-1.38890100	-3.28246500	0.15152800
C	-5.76481200	0.67654500	-0.12430700
H	-4.36271800	1.04049700	-1.74410900
H	-4.43221500	2.32913000	-0.54397100
C	-5.68463900	-0.83253900	0.10601400
H	-5.20096200	-1.14523000	-1.99084000
H	-5.28395900	-2.61518400	-1.01499900
H	-3.55152900	-3.73431500	-0.85031900
H	-3.06626300	-3.02858700	-2.40933500
H	-6.57658900	0.90384500	-0.83671100
H	-6.02296100	1.17655900	0.82513000
H	-6.70194700	-1.25143800	0.17129300
H	-5.19233100	-1.05991100	1.06667300
N	1.66356400	-0.51778000	0.46990800
C	2.88735100	-0.45186200	0.01093700
C	1.29191200	-1.58706700	1.39728900
C	3.17974000	0.68203100	-0.95195300
N	3.85833400	-1.34904100	0.31481000
C	2.09806800	-2.84517500	1.14881200
H	0.21036200	-1.78304300	1.28951500
H	1.43619800	-1.23341200	2.43358200
C	4.46881800	1.47141500	-0.69701200
H	3.18474700	0.27116300	-1.97786700
H	2.31894400	1.36107000	-0.90090400
C	5.29641000	-1.18483000	0.04798700
C	3.56635000	-2.47961800	1.20100900
H	1.87693800	-3.61148500	1.90715300
H	1.85180600	-3.26215600	0.15638300
C	5.67359700	0.87186300	-1.42050100
H	4.65921200	1.51789500	0.38924700
H	4.31607000	2.51224100	-1.02507200
C	5.68356200	-0.65437700	-1.32992500
H	5.75265300	-0.56124700	0.84013400
H	5.72174900	-2.19175000	0.15934300
H	4.18575100	-3.32809000	0.87296300
H	3.86608000	-2.22864100	2.23553600
H	6.60323300	1.27862700	-0.98655500
H	5.65924300	1.17149500	-2.48269700
H	6.69324000	-1.03038700	-1.56210700
H	5.00752200	-1.10050700	-2.07849800

Br	-0.62968700	1.15640100	2.63674200
Br	0.00099600	2.75407500	-1.16454000

$MgBr_2(MeCN)_2$

Mg	-0.18562500	0.00416300	0.00589100
N	1.24835600	1.51353400	0.33756500
C	2.01739000	2.35085700	0.51661100
N	1.20259700	-1.51395300	-0.45780000
C	1.93935500	-2.36434000	-0.69991700
C	2.98911100	3.40544500	0.74212100
H	3.92426800	2.95900900	1.11331700
H	3.17639200	3.93149400	-0.20626100
H	2.58961900	4.10969100	1.48760700
C	2.86877300	-3.43710100	-1.00432200
H	3.76550100	-3.01196700	-1.48042600
H	3.14774700	-3.94759700	-0.07005500
H	2.38423000	-4.14949700	-1.68922300
Br	-1.22477700	-0.55677900	2.14440000
Br	-1.42678600	0.56628300	-2.02185600

2

C	-0.04539000	0.84749900	-0.49907100
C	-1.09362800	-0.22671900	-0.25642700
O	-0.90200700	-1.40364600	-0.42345300
O	-2.25690800	0.28208400	0.13000300
C	-3.31705400	-0.64895400	0.33343900
C	1.31446800	0.17615100	-0.47084500
O	2.01197400	-0.01611200	-1.43065100
O	1.65455300	-0.17274500	0.76823500
C	2.90234300	-0.84140700	0.91541300
H	-3.53569100	-1.19068900	-0.59970100
H	-3.04779100	-1.36985700	1.12047200
H	2.90270000	-1.78237600	0.34347300
H	3.72670800	-0.20135800	0.56467700
C	-0.13715100	2.02311100	0.47421600
H	-1.09792000	2.54328200	0.34850900
H	-0.05585000	1.67511500	1.51569900
H	0.67702400	2.73876800	0.27719500
H	-4.18753400	-0.05638200	0.64194000
H	3.01356700	-1.04957300	1.98724000
H	-0.19763600	1.19834500	-1.53293000

INT1

C	2.53496600	-0.01922700	-0.01932200
C	1.81432700	-1.23535900	-0.04064300
O	0.56453100	-1.37813000	-0.05536400
O	2.56455000	-2.34501000	-0.04663600
C	1.88837800	-3.59210700	-0.05613700

C	1.82258600	1.20278600	-0.04447000
O	0.57787500	1.37579000	-0.06027500
O	2.60599000	2.28864000	-0.05329600
C	1.96800000	3.55616800	-0.06895100
H	1.25534600	-3.70583600	0.83784800
H	1.26355800	-3.69653800	-0.95689200
H	1.34863200	3.67523800	-0.97164800
H	1.33676900	3.69135600	0.82327200
Mg	-0.83781900	0.00417700	-0.00691700
C	4.04323900	0.01323700	-0.00124700
H	4.44940700	-1.00121700	0.11194800
H	4.46180500	0.44384300	-0.92929200
H	4.42420400	0.62784100	0.83272300
H	2.67426100	-4.35946200	-0.05652800
H	2.77654400	4.29954700	-0.07031100
Br	-2.03502900	0.01644000	2.15512400
Br	-2.21837700	0.00903900	-2.05309400

M6

C	-0.06775600	0.62691600	1.52017900
C	-0.11405000	-0.06172600	0.17859600
C	-1.35816300	-0.82449900	-0.16025300
O	-1.37321200	-1.93196600	-0.62950100
O	-2.46012400	-0.15155900	0.16960100
C	-4.81300600	0.11254600	0.40198900
C	-3.71114000	-0.81871400	-0.04252100
C	1.13611200	-0.60511800	-0.45436900
O	1.20417000	-0.95894000	-1.60105100
O	2.17697900	-0.59613400	0.37604800
C	4.48354000	-0.84303800	0.90610300
C	3.44353100	-0.97396700	-0.18030600
H	-0.94959400	0.50705100	2.15471700
H	0.90026300	0.61749700	2.02789300
H	-5.78982200	-0.37361400	0.25056600
H	-4.70731100	0.35986700	1.47076800
H	-4.79337200	1.04679300	-0.18237100
H	-3.79692700	-1.07434600	-1.11052100
H	-3.71146700	-1.75833500	0.53262600
H	5.46906600	-1.13607800	0.51078400
H	4.54594200	0.19761000	1.26413900
H	4.24024400	-1.49745100	1.75881800
H	3.36878700	-2.00748900	-0.55392700
H	3.66011600	-0.31763600	-1.03873300
C	-0.20058000	1.46905900	0.29740900
H	-1.19496600	1.86751100	0.07902300
C	0.93182300	2.29912600	-0.17937400
C	0.77350600	3.43483000	-0.86303500
H	-0.22461000	3.81077200	-1.11843000

H	1.63718800	4.02606800	-1.18412800
H	1.94105000	1.94807200	0.07150300

M6•$MgBr_2$

C	-3.16030600	0.58475100	-1.01036100
C	-1.71924300	0.34337000	-0.60887500
C	-0.76242100	1.48180900	-0.66630800
O	0.45445800	1.38162000	-0.53136800
O	-1.33867200	2.63416000	-0.84721600
C	-1.42544400	5.00975800	-1.02537900
C	-0.51268700	3.82523300	-0.83759300
C	-1.14700500	-1.02698700	-0.72584200
O	0.02783100	-1.30913300	-0.50684800
O	-2.01521600	-1.93376700	-1.06400600
C	-2.78894500	-4.15796000	-1.43794700
C	-1.58298500	-3.31695200	-1.10623700
H	-3.36112600	1.55073900	-1.47796600
H	-3.66658000	-0.28092900	-1.44462600
H	-0.82163200	5.93072900	-1.02581000
H	-1.96179100	4.94211600	-1.98529300
H	-2.15919700	5.07228900	-0.20595800
H	0.02271300	3.85697700	0.12318200
H	0.22261900	3.73096300	-1.65046100
H	-2.48549300	-5.21552300	-1.48555300
H	-3.56655900	-4.05192200	-0.66441500
H	-3.21030200	-3.87059300	-2.41443200
H	-0.79306100	-3.39799700	-1.86763300
H	-1.15535100	-3.56658400	-0.12364400
Mg	1.56595000	-0.16797300	0.11739600
C	-2.87394500	0.55114500	0.43769700
H	-2.77904100	1.51730800	0.94385200
C	-3.29339500	-0.56506900	1.31822300
C	-3.39632300	-0.42608900	2.64207200
H	-3.15314200	0.52227200	3.13616400
H	-3.73315900	-1.25643600	3.27097200
H	-3.54951000	-1.51618000	0.83926900
Br	1.47918000	-0.12393700	2.55701300
Br	3.55819700	-0.50328100	-1.23294400

TS1

C	-0.19152200	0.21757100	-1.02567400
C	1.30310700	-0.02922900	-1.01048800
C	2.18744000	1.08124900	-1.21459300
O	3.43315600	1.05953300	-1.16343300
O	1.56253700	2.21797100	-1.48653700
C	1.40040000	4.52605100	-2.01190300
C	2.34894300	3.40644300	-1.65618900
C	1.83750800	-1.33228200	-0.73717500

O	3.04125300	-1.60568100	-0.55869900
O	0.93320500	-2.29243900	-0.67611800
C	0.16000300	-4.50533600	-0.26454600
C	1.37010600	-3.60394400	-0.28867700
H	-0.45000300	1.06189500	-1.67258200
H	-0.78071300	-0.68315200	-1.24524700
H	1.96810800	5.46128200	-2.14028900
H	0.87524300	4.30320700	-2.95484600
H	0.65349400	4.67449500	-1.21521500
H	2.88918300	3.60702900	-0.71726000
H	3.09018100	3.23110900	-2.45060500
H	0.47124700	-5.52130900	0.02786500
H	-0.58992800	-4.13948800	0.45462300
H	-0.31298400	-4.54987100	-1.25828400
H	2.12471600	-3.95190100	-1.01082900
H	1.84953900	-3.53425600	0.70104800
Mg	4.43895300	-0.27367700	-0.07876700
C	-0.10896700	0.53328900	0.41368700
H	0.40086800	1.45646600	0.70050300
C	-0.24212200	-0.50869800	1.42275500
C	0.26519000	-0.35834600	2.65675200
H	0.83301200	0.53885700	2.92783100
H	0.14422400	-1.13584700	3.41901800
H	-0.79176100	-1.41174800	1.13133600
C	-2.01029900	1.88168200	1.00609000
C	-2.45622500	1.98472900	-0.35186300
O	-3.20033400	1.18524400	-0.95658700
O	-1.96743000	3.02817100	-1.00926900
C	-2.31895900	3.17086800	-2.38255800
C	-2.68522500	0.95511200	1.87021900
O	-3.45993100	0.03774600	1.53244600
O	-2.39677500	1.11136600	3.15281300
C	-2.95271200	0.17547300	4.07201500
H	-1.94037800	2.32065000	-2.97126400
H	-3.41135400	3.23846200	-2.49610300
H	-4.04993600	0.26143400	4.09136400
H	-2.66949200	-0.85210400	3.79879300
Mg	-4.10898800	-0.44198400	-0.27536100
C	-1.23447400	3.01084700	1.63473500
H	-0.59193300	3.50094400	0.88853900
H	-1.89788200	3.78018700	2.07086400
H	-0.59524900	2.62814900	2.44694700
H	-1.84649600	4.10313800	-2.71638800
H	-2.53599900	0.43757200	5.05297400
Br	6.68340300	-0.80817800	-0.86984500
Br	-2.95064500	-2.48437700	-1.02214400
Br	-6.54800900	-0.28542700	-0.47635100
Br	3.94685300	0.38354100	2.25160500

INT2&INT4

C	-0.36533900	0.34391800	-0.01170700
C	1.11693700	0.07602800	-0.06959300
C	1.91754000	0.79537000	-0.98723100
O	3.16234000	0.72919700	-1.13750200
O	1.23109000	1.63766200	-1.77043800
C	0.96947800	3.29585800	-3.44572300
C	1.96237200	2.42535600	-2.71173200
C	1.73294400	-0.79485100	0.86089200
O	2.95410000	-1.07577600	0.94545500
O	0.89499500	-1.36723600	1.73154100
C	0.27391500	-2.81726900	3.49868000
C	1.43084900	-2.28594500	2.68432300
H	-0.75717400	0.39029900	-1.04227400
H	-0.86539300	-0.50234600	0.48409200
H	1.50022700	3.92992200	-4.17398100
H	0.23713200	2.67766200	-3.98954200
H	0.42966900	3.94970800	-2.74083700
H	2.70921500	3.03031100	-2.17319700
H	2.50169000	1.75772400	-3.40235300
H	0.64282200	-3.54341000	4.24046600
H	-0.23608200	-1.99948300	4.03430600
H	-0.45799900	-3.32238300	2.84697300
H	1.95440000	-3.09585200	2.15200600
H	2.16699300	-1.76468300	3.31726200
Mg	4.45416100	-0.36469300	-0.12220900
C	-0.70517500	1.66124000	0.71802900
H	-0.25526500	2.49462500	0.15358200
C	-0.14702000	1.67093100	2.11532900
C	0.68049300	2.60927900	2.57811300
H	0.98276600	3.45742500	1.95070700
H	1.08768600	2.55986200	3.59401600
H	-0.41752400	0.82174100	2.75695100
C	-2.25842400	1.97461000	0.70947400
C	-2.72107700	1.82324100	-0.73539400
O	-3.40085300	0.91058100	-1.19072000
O	-2.28373400	2.78377700	-1.49421500
C	-2.60044000	2.72670300	-2.89431700
C	-2.94485300	0.96996400	1.62318400
O	-3.32996100	-0.14673700	1.29169500
O	-3.03517400	1.37677400	2.85401200
C	-3.56737900	0.46179500	3.82530500
H	-2.16592000	1.81723100	-3.33427100
H	-3.69191900	2.72808200	-3.02659100
H	-4.59950100	0.19489200	3.55654200
H	-2.93923300	-0.44007500	3.86671300
Mg	-3.97413400	-0.88108000	-0.46874600

C	-2.51105400	3.41364000	1.18177800
H	-1.97492900	4.11210600	0.52369300
H	-3.58738900	3.65027700	1.15775600
H	-2.14095600	3.53872300	2.20830900
H	-2.15558100	3.62600400	-3.33423800
H	-3.53992500	0.99984100	4.77958500
Br	-6.40924000	-0.98577600	-0.41154300
Br	-2.55755200	-2.66537600	-1.32369300
Br	5.95315700	1.04084100	1.24548300
Br	5.49040100	-2.10409000	-1.53279900

TS2

C	-2.92726200	1.09302700	-0.65601200
C	-1.49969400	0.68147700	-0.37522100
C	-0.48318500	1.65231700	-0.16339200
O	0.73173700	1.41955100	0.02011500
O	-0.90017500	2.91563000	-0.17107100
C	-0.64785600	5.27365800	-0.04328300
C	0.07572300	3.94936200	0.01262300
C	-1.17861600	-0.70138300	-0.37778100
O	-0.05039300	-1.21871400	-0.23731600
O	-2.23630600	-1.49762100	-0.55449900
C	-3.38287100	-3.57210300	-0.70026900
C	-2.02840500	-2.91562300	-0.57396300
H	-2.99501600	2.19080500	-0.51363400
H	-3.27534300	0.85523700	-1.67423800
H	0.07486100	6.09352500	0.09404400
H	-1.14542500	5.40544400	-1.01781300
H	-1.40585200	5.33839600	0.75418600
H	0.57536300	3.79911000	0.98241300
H	0.83575300	3.86728100	-0.78008200
H	-3.25757000	-4.66577600	-0.74228100
H	-4.01959200	-3.32721400	0.16578400
H	-3.89210500	-3.24318200	-1.62095500
H	-1.37331600	-3.16609600	-1.42327000
H	-1.51690700	-3.21380000	0.35417800
Mg	1.68939500	-0.31418600	0.07067300
C	-3.80784600	0.50923300	0.35460700
H	-3.51986400	0.65650500	1.40444100
C	-4.97461000	-0.22561800	0.09192500
C	-5.69290100	-0.69021800	1.15140400
H	-5.35194300	-0.51051700	2.17800400
H	-6.62324200	-1.25094900	1.00934600
H	-5.28563800	-0.40371600	-0.94164900
Br	2.55145400	-0.79313400	2.32569000
Br	3.18652700	-0.57630500	-1.86449600

INT3

C	-2.90107000	1.14917300	-0.40946300
C	-1.46871100	0.71973100	-0.23388100
C	-0.42609500	1.67479700	-0.12393200
O	0.79717000	1.42786000	-0.03180800
O	-0.82991900	2.94313500	-0.12413000
C	-0.54653400	5.29890800	-0.02435100
C	0.16541600	3.96722000	-0.00390200
C	-1.16956400	-0.66107600	-0.30780900
O	-0.04738500	-1.20792900	-0.25708200
O	-2.25816400	-1.43222100	-0.44446200
C	-3.47322100	-3.46944900	-0.56615600
C	-2.09504600	-2.85602900	-0.48916000
H	-3.02704600	2.15623700	0.05271000
H	-3.23308100	1.24562000	-1.45841100
H	0.19115100	6.11203200	0.06541200
H	-1.09974500	5.43079200	-0.96838300
H	-1.25535800	5.37534700	0.81618400
H	0.72016300	3.81718400	0.93565100
H	0.87655900	3.87371200	-0.83953900
H	-3.38248100	-4.56596400	-0.62059500
H	-4.06794000	-3.21288100	0.32622600
H	-4.00807800	-3.11851100	-1.46394000
H	-1.48429100	-3.11354600	-1.36845800
H	-1.55469100	-3.17988200	0.41379100
Mg	1.71130700	-0.32994500	0.03435900
C	-3.83743400	0.32900200	0.35315200
H	-3.53824300	0.03806300	1.36867700
C	-5.12088300	-0.04547700	-0.08478300
C	-5.90497400	-0.75887600	0.76713400
H	-5.53782100	-1.03714900	1.76203000
H	-6.91525800	-1.07505600	0.48546500
H	-5.45800500	0.23372500	-1.08720100
Br	2.54228500	-0.80274700	2.30442200
Br	3.21810100	-0.65310100	-1.88251200

M1

C	-0.67234700	0.08104000	-1.68275600
C	-0.86438200	0.47702700	-0.23319300
C	-2.26541300	0.66535900	0.25710300
O	-2.64023400	1.59543400	0.92151800
O	-3.07588900	-0.30118300	-0.17557800
C	-5.19187500	-1.35496100	-0.44234300
C	-4.46296100	-0.18016700	0.16410800
C	0.17840900	1.28787100	0.47831100
O	0.18538400	1.47606200	1.66630300
O	1.14662300	1.69642900	-0.33775000
C	3.30812200	2.56896400	-0.81247900
C	2.31789800	2.24298400	0.27967600

H	-1.58742000	-0.03317300	-2.26890600
H	0.17048500	0.55362500	-2.19204900
H	-6.26409600	-1.28980400	-0.19836500
H	-5.08226600	-1.35782300	-1.53900800
H	-4.79982700	-2.30493300	-0.04415800
H	-4.55695200	-0.16228500	1.26149000
H	-4.83838200	0.78007600	-0.22404800
H	4.22030500	2.99786300	-0.36804900
H	3.58563300	1.66068900	-1.37229000
H	2.88348000	3.30356700	-1.51595400
H	2.03240000	3.13845500	0.85407000
H	2.71808800	1.49828100	0.98842600
C	-0.39499100	-0.93066800	-0.63620700
H	-1.16746500	-1.68862200	-0.47586400
C	0.99277300	-1.35354100	-0.26238200
C	2.06588400	-1.26089400	-1.15461000
C	1.22708100	-1.83679500	1.03264700
C	3.35011100	-1.64326800	-0.76069100
H	1.89863400	-0.88650800	-2.16817400
C	2.50844100	-2.21901200	1.42797400
H	0.39286900	-1.90461400	1.73766700
C	3.57517000	-2.12103200	0.53107000
H	4.17908400	-1.56613000	-1.46914800
H	2.67599100	-2.59200900	2.44167700
H	4.58086900	-2.41803200	0.83937600

M1•$MgBr_2$

C	-1.89404700	2.18646000	-1.24041200
C	-0.74933000	1.29699300	-0.78599300
C	0.54579300	1.91934400	-0.40181600
O	1.58184700	1.29737400	-0.17943800
O	0.48363400	3.21301000	-0.28485000
C	1.32272000	5.38789500	0.21517400
C	1.66494300	3.92092200	0.16765500
C	-0.72201300	-0.12793100	-1.21900400
O	0.17409300	-0.92010400	-0.93697400
O	-1.77173600	-0.49142500	-1.89032100
C	-3.26036400	-2.05086100	-2.90877000
C	-1.94745100	-1.89893900	-2.18402400
H	-1.63460600	3.23498800	-1.39743600
H	-2.55683600	1.73359600	-1.98163000
H	2.20585400	5.95064600	0.55599900
H	1.03719100	5.75543000	-0.78339200
H	0.49542900	5.57463500	0.91831700
H	1.93807100	3.52210300	1.15612900
H	2.47879000	3.70403700	-0.53961900
H	-3.41614400	-3.11473800	-3.14725300
H	-4.09721300	-1.70652600	-2.27998200

H	-3.25626600	-1.47817500	-3.84997400
H	-1.09261600	-2.22801700	-2.79320200
H	-1.93179400	-2.44347800	-1.22682200
Mg	1.88125200	-0.67527000	0.09891900
C	-1.94822700	1.68011200	0.14121800
H	-1.63205500	2.37429300	0.92809200
C	-2.88419600	0.60086500	0.58857800
C	-4.16910900	0.48888200	0.05021100
C	-2.45951200	-0.31883300	1.55681300
C	-5.02322100	-0.53012600	0.47652800
H	-4.50353800	1.20152700	-0.70878800
C	-3.31014400	-1.34152600	1.97549700
H	-1.44910800	-0.24143400	1.97451800
C	-4.59439000	-1.44883100	1.43580300
H	-6.02707100	-0.60930700	0.05150000
H	-2.96649200	-2.05900700	2.72503300
H	-5.26126800	-2.25026700	1.76369900
Br	1.38360400	-1.13475600	2.45054800
Br	3.81420300	-1.49937200	-1.11981400

TS3

C	-0.23167700	0.58895600	-0.88049500
C	1.27032700	0.41379100	-0.96517600
C	2.12230500	1.55956900	-0.83036900
O	3.36831900	1.55676900	-0.81700300
O	1.46780100	2.70597400	-0.71660200
C	1.25679300	5.05350900	-0.42626000
C	2.23137800	3.90361600	-0.50375700
C	1.84702900	-0.88716300	-1.16106500
O	3.05567900	-1.17503500	-1.06732200
O	0.97012100	-1.82468600	-1.46539500
C	0.25493700	-4.02831300	-1.99805500
C	1.41889400	-3.18629600	-1.53378400
H	-0.54498900	1.57425600	-1.24041700
H	-0.79408100	-0.22103200	-1.36259900
H	1.80895300	5.98981800	-0.24714300
H	0.69798100	5.15199500	-1.37084600
H	0.54051100	4.90349800	0.39790900
H	2.80863000	3.78990200	0.42740600
H	2.94038400	4.02373000	-1.33688700
H	0.57246900	-5.08114900	-2.06749400
H	-0.59110100	-3.95874800	-1.29574000
H	-0.08994900	-3.69700400	-2.99059200
H	2.26733200	-3.24478800	-2.23200700
H	1.77356600	-3.48589400	-0.53318800
Mg	4.50566500	-0.01057900	-0.35595500
C	-0.09883600	0.49163700	0.58658700
H	0.35174900	1.35411600	1.08404500

C	-2.06921600	1.45247500	1.57829200
C	-2.44950100	2.10956600	0.36268300
O	-3.16634200	1.64242400	-0.54679900
O	-1.92750200	3.31921400	0.20702400
C	-2.22417800	4.01972900	-0.99770700
C	-2.76480600	0.24892900	1.93799600
O	-3.52104400	-0.43018200	1.21385000
O	-2.52173000	-0.15795900	3.17339700
C	-3.14821300	-1.35823100	3.61507500
H	-1.76436900	3.51641900	-1.86312900
H	-3.31196600	4.08677600	-1.14727100
H	-4.23760500	-1.21378000	3.68984500
H	-2.93290400	-2.18704200	2.92516400
Mg	-4.15648700	-0.07188200	-0.62952100
C	-1.36225800	2.22339900	2.66483300
H	-0.72139400	3.00534900	2.23184800
H	-2.07432600	2.71222900	3.35487700
H	-0.73163000	1.54990400	3.26732700
H	-1.79809800	5.02284500	-0.87340100
H	-2.72705200	-1.56702500	4.60715900
C	-0.07251500	-0.76789500	1.32931000
C	-0.74789800	-1.91349900	0.86947800
C	0.63327200	-0.82353300	2.54392900
C	-0.70356400	-3.09092400	1.61152100
H	-1.31339700	-1.87983500	-0.06679800
C	0.67423900	-2.00380400	3.28127600
H	1.17632500	0.06014900	2.88895300
C	0.00672500	-3.13892800	2.81514500
H	-1.23273400	-3.97751400	1.25247700
H	1.23816000	-2.04194200	4.21622700
H	0.03967500	-4.06680600	3.39212100
Br	4.47579100	-0.16284000	2.10346100
Br	6.58484900	-0.16076800	-1.63315000
Br	-3.11712300	-1.64297300	-2.22617900
Br	-6.58357700	0.26884900	-0.71636300

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