Supporting Information for

Leveraging the monomer structure for high-performance chemically recyclable semiaromatic polyesters

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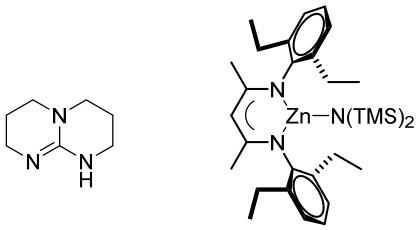
Materials and Methods

All synthesis and manipulations of air- and moisture-sensitive materials were carried out in an argon-filled glovebox. All reagents from Adamas-beta and Energy Chemical were used as received unless otherwise stated. High-performance liquid chromatography (HPLC)-grade organic solvents were dried by *Vigor* YJC-5 and then stored over activated 4 Å molecular sieves. The initiator *p*-tolylmethanol was purchased from adamas and sublimed at 55 °C prior to use. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was sublimed under vacuum at 60 °C prior to use. 2,6-diethylphenyl substituted *β*-diiminate zinc trimethylsilyl complex **Zn1** was prepared according to literature procedures.[1]



TBD **Zn1**

NMR ^{1}H and ^{13}C NMR spectra were recorded on an Agilent 400-MR DD2 or a Brüker Advance 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz). Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Size Exclusion Chromatography (SEC) Measurements of polymer absolute weight-average molecular weight (M_w), number average molecular weight (M_n), and molecular weight distributions or dispersity indices ($Đ$ = M_w/M_n) were performed via size exclusion chromatography (SEC). The SEC instrument consisted of an Agilent LC system equipped with one guard column and two PL gel 5 μm mixed-C gel permeation columns and coupled with an Agilent G7162A 1260 Infinity II RI detector. The analysis was performed at 40 °C using THF as the eluent at a flow rate of 1.0 mL/min. The instrument was calibrated with nine polystyrene standards, and chromatograms were processed with Agilent OpenLab CDS Acquisition 2.5 molecular weight characterization software.

Differential scanning calorimetry (DSC) Melting-transition temperature (T_m) and glass-transition temperature (T_g) of purified and thoroughly dried polymer samples were measured by differential scanning calorimetry (DSC) on a TRIOS DSC25, TA Instrument. All T_g values were obtained from a second scan after the thermal history was removed from the first scan.

Thermo-gravimetric analysis (TGA) Decomposition onset temperatures (T_{onset}) and maximum rate decomposition temperatures (T_{max}) of the polymers were measured by thermal gravimetric analysis (TGA) on a TGA55 Analyzer, TA Instrument. Polymer samples were heated from ambient temperature to 600 °C at a heating rate of 10 °C/min. Values of T_{max} were obtained from derivative (wt%/°C) vs. temperature (°C) plots and defined by the peak values, while T_{onset} values were obtained from wt% vs. temperature (°C) plots and defined by the temperature of 5% weight loss.

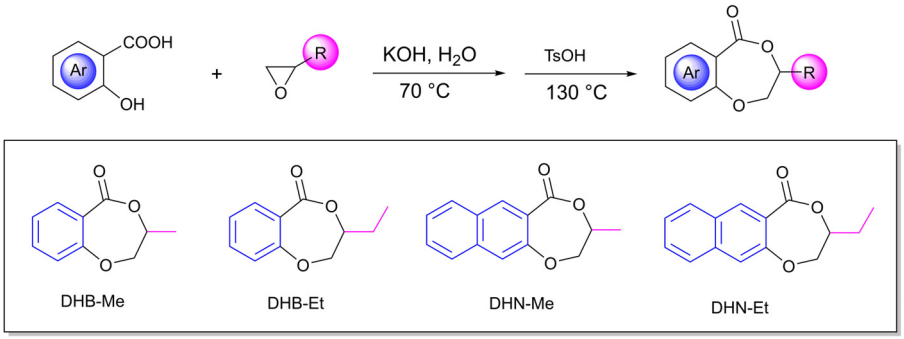
Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy

(MALDI−TOF MS). An AXIMA performance instrument was used in reflection mode with dithranol as the matrix. A thin layer of a 1% NaI solution was first deposited on the target plate, followed by the solutions of matrix (5 μL, 5 mg/mL in dichloromethane) and polymer (2 μL, 5 mg/mL in dichloromethane) were mixed together. The mixed solution was spotted on the MALDI sample plate and air-dried. The raw data was processed in the Shimadzu Biotech MALDI-MS software.

Wide angle X-ray diffraction (WXRD) Powder X-ray diffraction data were obtained using a Bruker D2 Phaser diffractometer with Cu-Kα radiation (λ = 1.5416 A) at 30 kV and 10 mA (scan of 2θ = 5–30° with a speed of 2°/min).

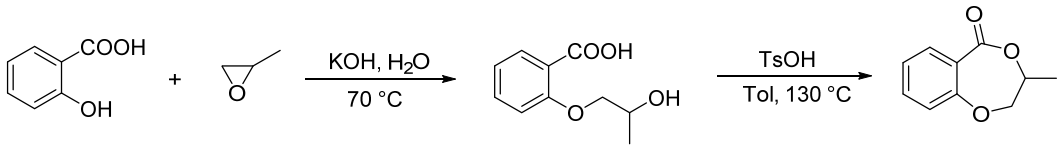
Mechanical Analysis. Tensile stress/strain testing was performed by an Instron 34SC-1 universal testing system. Samples were made by melt press in a steel mold (50 × 4 × 0.4 mm^3) and were stretched at a strain rate of 10 mm/min at ambient temperature until break. The measurements were performed 3-5 times for each test, and the values reported are averaged from the measured data.

General Monomer Preparations



Scheme S1. Synthesis of monomers.

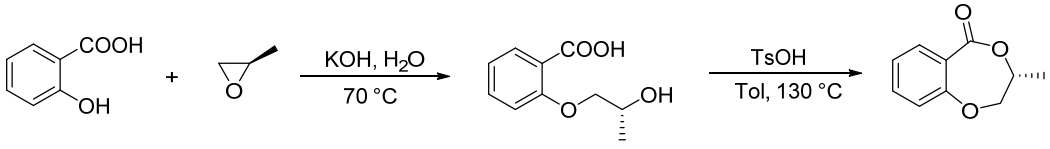
Synthesis of DHB-Me



A 75 mL pressure tube equipped with a stir bar was charged with salicylic acid (6.9 g, 0.05 mol), KOH (5.6 g, 0.1 mol), H_2O (3.6 mL, 0.2 mol) and propylene oxide (14.0 mL, 0.2 mol). After stirring for 12 h at 70 °C, the reaction was quenched by the addition of 12 M HCl (9 mL) slowly and diluted with water (30 mL), then the mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude product was directly used for the next step.

In a 500 mL flask which connected to a Dean-Stark trap, the above crude product was dissolved in 300 mL toluene and 1.9 g TsOH was used as catalyst. After refluxing for 12 h at 130 °C, the reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 20: 1) to afford DHB-Me as white solid (5.0 g, 56% for two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.00 (dd, *J* = 8.3, 1.3 Hz, 1H), 4.75 – 4.68 (m, 1H), 4.36 – 4.26 (m, 2H), 1.40 (d, *J* = 6.7 Hz, 3H).

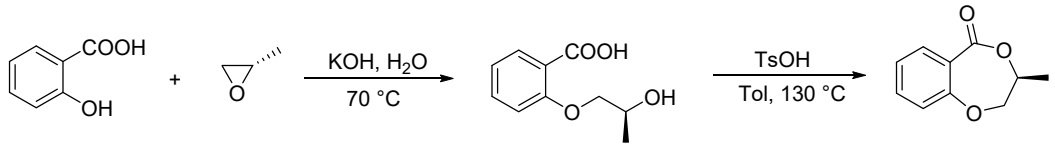
Synthesis of (*R*)-DHB-Me



A 75 mL pressure tube equipped with a stir bar was charged with salicylic acid (6.9 g, 0.05 mol), KOH (5.6 g, 0.1 mol), H_2O (3.6 mL, 0.2 mol) and (*R*)-propylene oxide (12.9 mL, 0.2 mol). After stirring for 12 h at 70 °C, the reaction was quenched by the addition of 12 M HCl (9 mL) slowly and diluted with water (30 mL), then the mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude product was directly used for the next step.

In a 500 mL flask which connected to a Dean-Stark trap, the above crude product was dissolved in 300 mL toluene and 1.9 g TsOH was used as catalyst. After refluxing for 12 h at 130 °C, the reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 20: 1) to afford (*R*)-DHB-Me as white solid (4.4 g, 49% for two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, J = 7.9, 1.8 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.14 – 7.10 (m, 1H), 7.00 (d, J = 8.3 Hz, 1H), 4.76 – 4.68 (m, 1H), 4.36 – 4.26 (m, 2H), 1.40 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 155.0, 134.7, 133.2, 122.9, 120.9, 120.4, 75.6, 72.4, 16.3. ESI-MS: calculated m/z 179.0708; found m/z 179.0706 $[M + H]^+$.

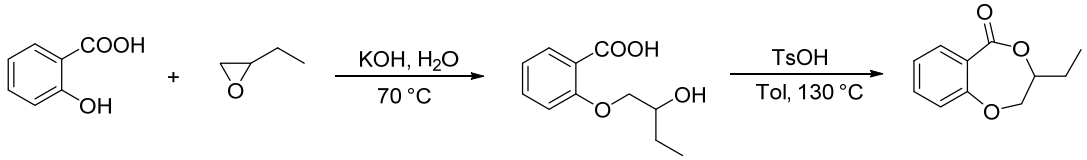
Synthesis of (*S*)-DHB-Me



A 75 mL pressure tube equipped with a stir bar was charged with salicylic acid (6.9 g, 0.05 mol), KOH (5.6 g, 0.1 mol), H_2O (3.6 mL, 0.2 mol) and (*S*)-propylene oxide (12.9 mL, 0.2 mol). After stirring for 12 h at 70 °C, the reaction was quenched by the addition of 12 M HCl (9 mL) slowly and diluted with water (30 mL), then the mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude product was directly used for the next step.

In a 500 mL flask which connected to a Dean-Stark trap, the above crude product was dissolved in 300 mL toluene and 1.9 g TsOH was used as catalyst. After refluxing for 12 h at 130 °C, the reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 20: 1) to afford (*S*)-DHB-Me as white solid (3.8 g, 43% for two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, J = 8.0, 1.6 Hz, 1H), 7.51-7.46 (m, 1H), 7.12 (dd, J = 8.1, 7.1 Hz, 1H), 7.01 (d, J = 8.3 Hz, 1H), 4.76-4.69 (m, 1H), 4.37-4.27 (m, 2H), 1.41 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 155.1, 134.8, 133.3, 122.9, 120.9, 120.4, 75.6, 72.4, 16.3. ESI-MS: calculated m/z 179.0708; found m/z 179.0706 $[M + H]^+$.

Synthesis of DHB-Et

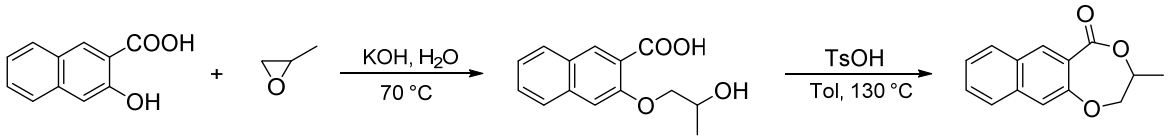


A 75 mL pressure tube equipped with a stir bar was charged with salicylic acid (6.9 g, 0.05 mol), KOH (5.6 g, 0.1 mol), H_2O (3.6 mL, 0.2 mol) and 1,2-epoxybutane (16.4 mL, 0.2 mol). After stirring for 24 h at 70 °C, the reaction was quenched by the addition of 12 M HCl (9 mL) slowly and diluted with water (30 mL), then the mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude product was directly used for the next step.

In a 500 mL flask which connected to a Dean-Stark trap, the above crude product was dissolved in 300 mL toluene, and 1.9 g TsOH was used as catalyst. After refluxing for 24 h at

130 °C, the reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 20: 1) to afford DHB-Et as white solid (4.4 g, 46% for two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.50-7.46 (m, 1H), 7.14-7.10 (m, 1H), 7.00 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.47-4.43 (m, 1H), 4.38-4.33 (m, 2H), 1.84-1.62 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 155.2, 134.7, 133.4, 122.7, 120.8, 120.1, 77.4, 74.4, 24.0, 9.7. ESI-MS: calculated m/z 193.0865; found m/z 193.0862 $[M + H]^+$.

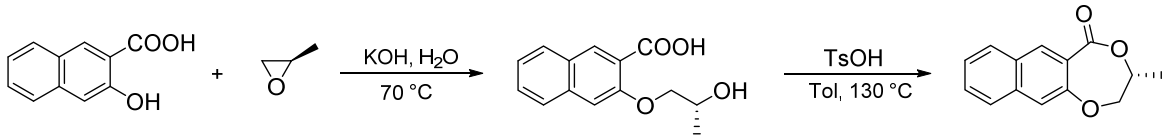
Synthesis of DHN-Me



A 75 mL pressure tube equipped with a stir bar was charged with 3-Hydroxy-2-naphthoic acid (9.4 g, 0.05 mol), KOH (5.6 g, 0.1 mol), H_2O (10 mL) and propylene oxide (14.0 mL, 0.2 mol). After stirring for 12 h at 70 °C, the reaction was quenched by the addition of 12 M HCl (9 mL) slowly and diluted with water (30 mL), then the mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude product was directly used for the next step.

In a 500 mL flask which connected to a Dean-Stark trap, the above crude product was dissolved in 300 mL toluene, and 1.9 g TsOH was used as catalyst. After refluxing for 12 h at 130 °C, the reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 20: 1) to afford DHN-Me as white solid (7.4 g, 65% for two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.56-7.53 (m, 1H), 7.46 (d, *J* = 7.9 Hz, 2H), 4.70-4.62 (m, 1H), 4.33-4.17 (m, 2H), 1.37 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 150.4, 136.4, 133.4, 129.9, 128.8, 128.7, 126.8, 125.8, 124.6, 118.0, 76.3, 71.8, 15.6. ESI-MS: calculated m/z 229.0865; found m/z 229.0855 $[M + H]^+$.

Synthesis of (*R*)-DHN-Me

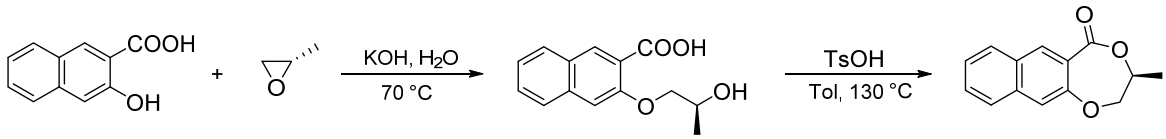


A 75 mL pressure tube equipped with a stir bar was charged with 3-Hydroxy-2-naphthoic acid (9.4 g, 0.05 mol), KOH (5.6 g, 0.1 mol), H_2O (15 mL) and (*R*)-propylene oxide (12.9 mL, 0.2 mol). After stirring for 12 h at 70 °C, the reaction was quenched by the addition of 12 M HCl (9 mL) slowly and diluted with water (30 mL), then the mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude product was directly used for the next step.

In a 500 mL flask which connected to a Dean-Stark trap, the above crude product was dissolved in 300 mL toluene, and 1.9 g TsOH was used as catalyst. After refluxing for 24 h at 130 °C, the reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 20: 1) to

afford (*R*)-DHN-Me as white solid (5.0 g, 44% for two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.58-7.54 (m, 1H), 7.49-7.45 (m, 2H), 4.72-4.64 (m, 1H), 4.32 (t, *J* = 11.1 Hz, 1H), 4.19 (dd, *J* = 11.5, 3.1 Hz, 1H), 1.39 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 150.5, 136.5, 133.4, 130.0, 128.9, 128.7, 126.9, 125.9, 124.6, 118.0, 76.4, 71.8, 15.7. ESI-MS: calculated m/z 229.0865; found m/z 229.0883 $[M + H]^+$.

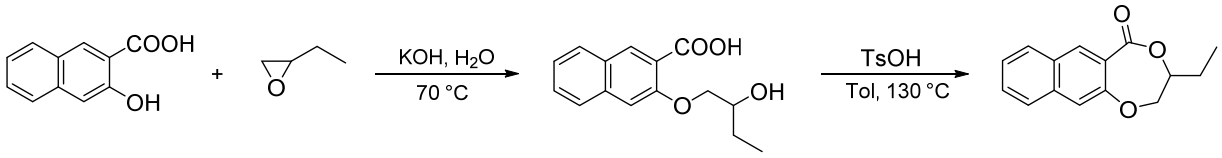
Synthesis of (*S*)-DHN-Me



A 75 mL pressure tube equipped with a stir bar was charged with 3-Hydroxy-2-naphthoic acid (9.4 g, 0.05 mol), KOH (5.6 g, 0.1 mol), H_2O (15 mL) and (*S*)-propylene oxide (12.9 mL, 0.2 mol). After stirring for 12 h at 70 °C, the reaction was quenched by the addition of 12 M HCl (9 mL) slowly and diluted with water (30 mL), then the mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude product was directly used for the next step.

In a 500 mL flask which connected to a Dean-Stark trap, the above crude product was dissolved in 300 mL toluene, and 1.9 g TsOH was used as catalyst. After refluxing for 24 h at 130 °C, the reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 20: 1) to afford (*S*)-DHN-Me as white solid (6.3 g, 55% for two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.89 (dd, J = 8.2, 1.2 Hz, 1H), 7.77 (dd, J = 8.4, 1.1 Hz, 1H), 7.58-7.54 (m, 1H), 7.49-7.45 (m, 2H), 4.72-4.64 (m, 1H), 4.32 (t, J = 11.1 Hz, 1H), 4.19 (dd, J = 11.5, 3.1 Hz, 1H), 1.39 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 150.5, 136.5, 133.4, 130.0, 128.9, 128.7, 126.9, 125.9, 124.6, 118.0, 76.4, 71.8, 15.7. ESI-MS: calculated m/z 229.0865; found m/z 229.0880 $[M + H]^+$.

Synthesis of DHN-Et



A 75 mL pressure tube equipped with a stir bar was charged with 3-hydroxy-2-naphthoic Acid (9.4 g, 0.05 mol), KOH (5.6 g, 0.1 mol), H_2O (3.6 mL, 0.2 mol) and 1,2-epoxybutane (16.4 mL, 0.2 mol). After stirring for 24 h at 70 °C, the reaction was quenched by the addition of 12 M HCl (9 mL) slowly and diluted with water (30 mL), then the mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude product was directly used for the next step.

In a 500 mL flask which connected to a Dean-Stark trap, the above crude product was dissolved in 300 mL toluene, and 1.9 g TsOH was used as catalyst. After refluxing for 24 h at 130 °C, the reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 20:1) to

afford DHN-Et as white solid (4.1 g, 34% for two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.49 – 7.45 (m, 2H), 4.45 – 4.40 (m, 1H), 4.36 (t, *J* = 10.8 Hz, 1H), 4.24 – 4.20 (m, 1H), 1.82 – 1.60 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 150.5, 136.4, 133.4, 129.9, 128.9, 128.7, 126.8, 125.8, 124.6, 118.0, 76.7, 75.1, 23.4, 9.8. ESI-MS: calculated m/z 243.1021; found m/z 243.1012 $[M + H]^+$.

NMR spectra of monomers

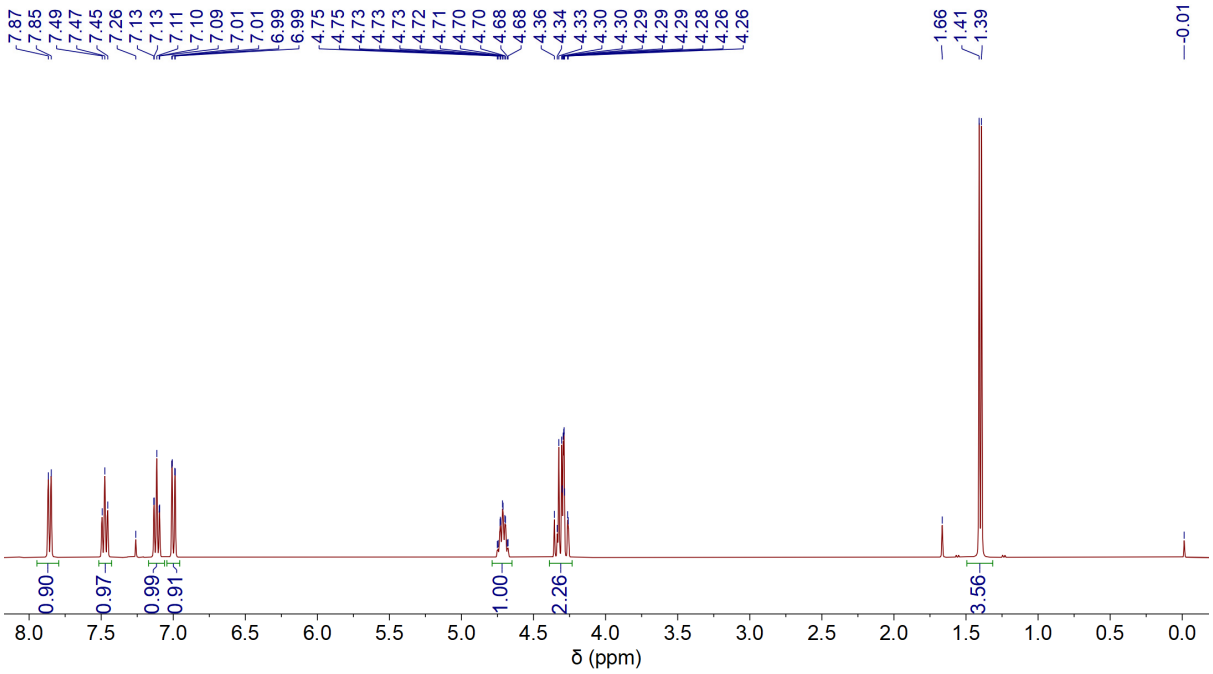


Fig. S1. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of DHB-Me. Residual solvent peaks at 7.26 ppm and 1.66 ppm for $CHCl_3$ and H_2O, respectively.

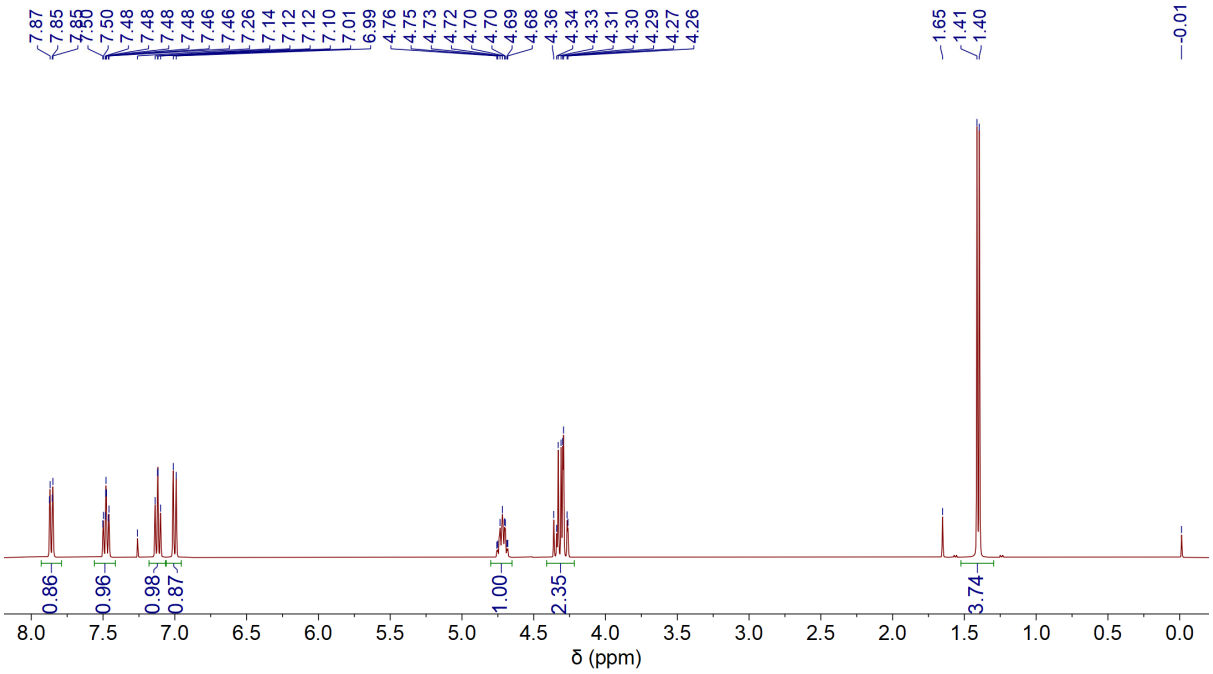


Fig. S2. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of (*R*)-DHB-Me. Residual solvent peaks at 7.26 ppm and 1.65 ppm for $CHCl_3$ and H_2O, respectively.

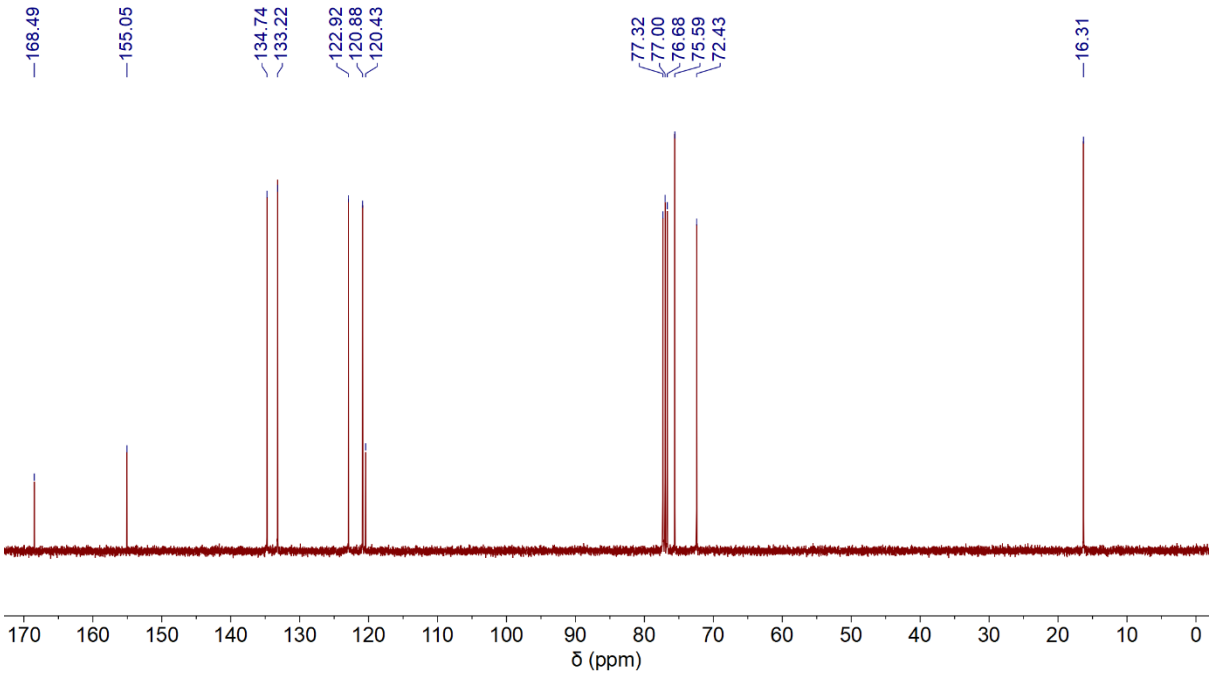


Fig. S3. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of (*R*)-DHB-Me.

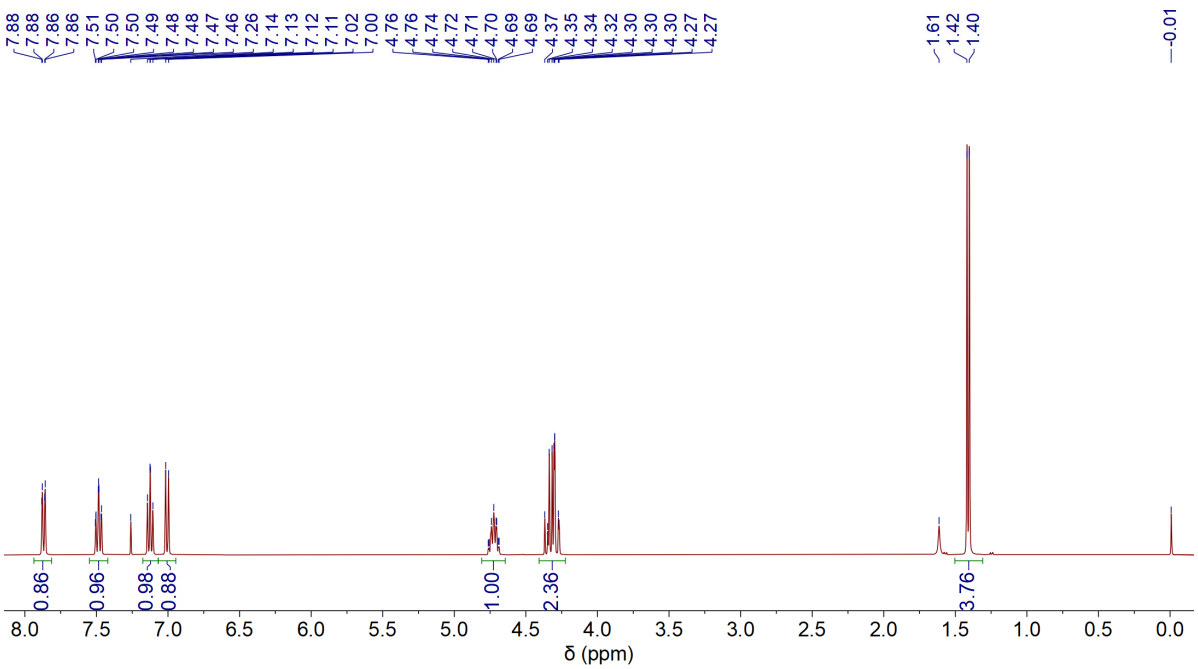


Fig. S4. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of (*S*)-DHB-Me. Residual solvent peaks at 7.26 ppm and 1.61 ppm for $CHCl_3$ and H_2O, respectively.

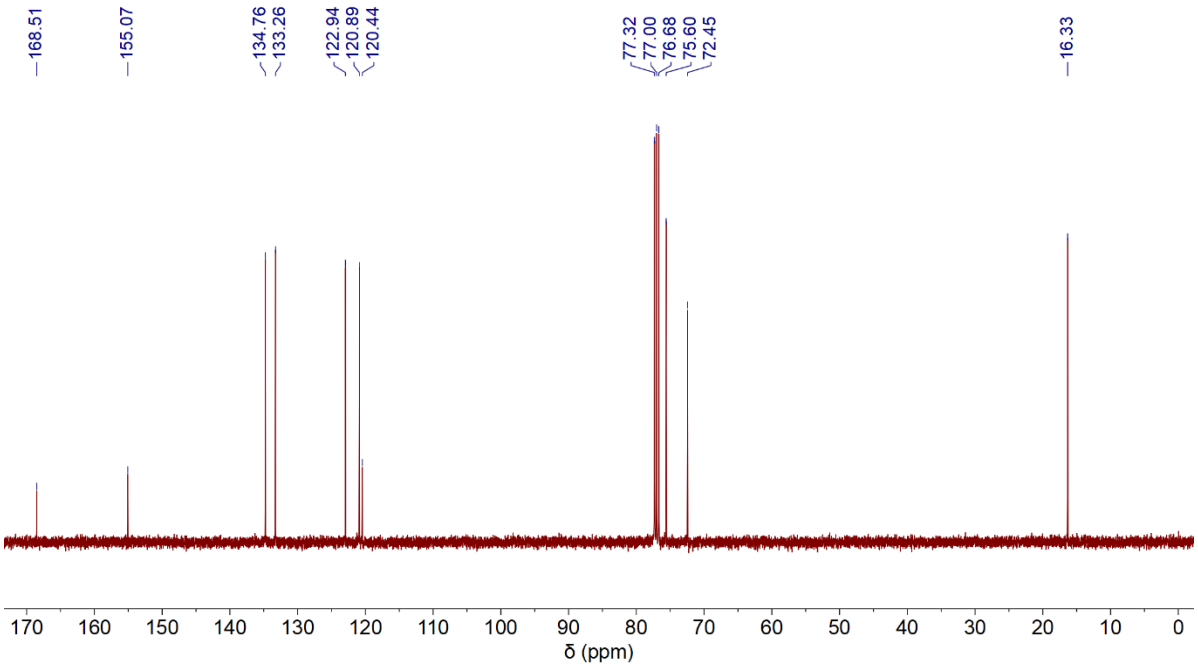


Fig. S5. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of (*S*)-DHB-Me.

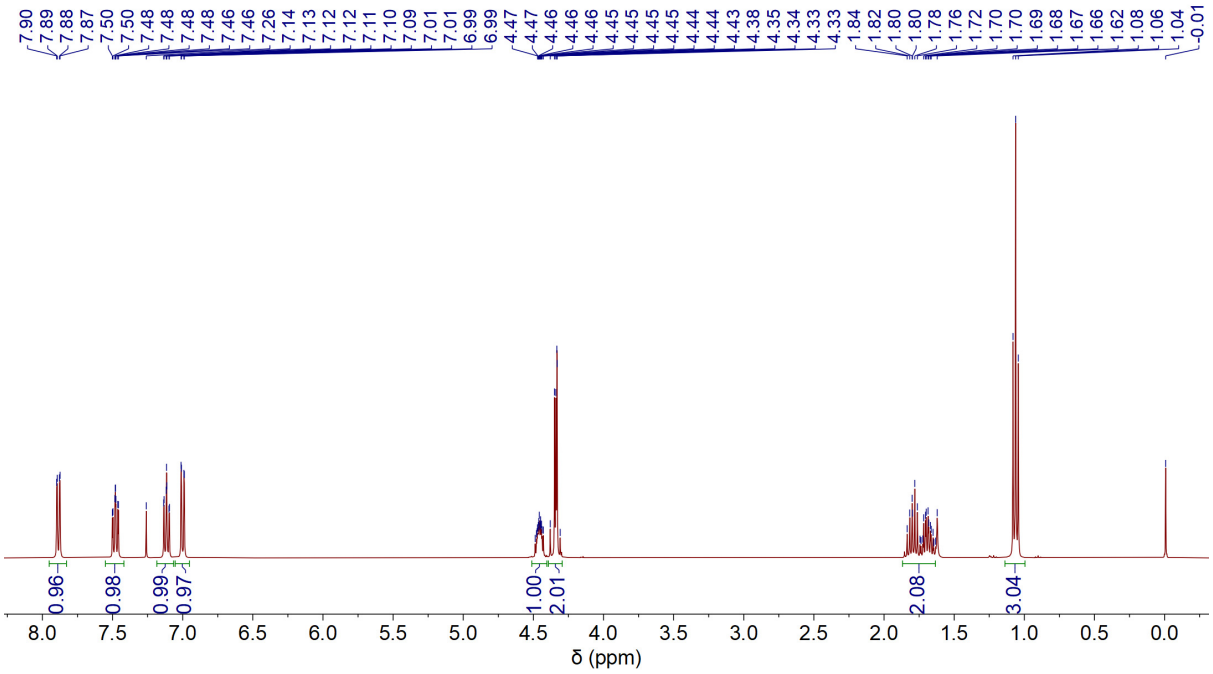


Fig. S6. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of DHB-Et. Residual solvent peaks at 7.26 ppm and 1.62 ppm for $CHCl_3$ and H_2O, respectively.

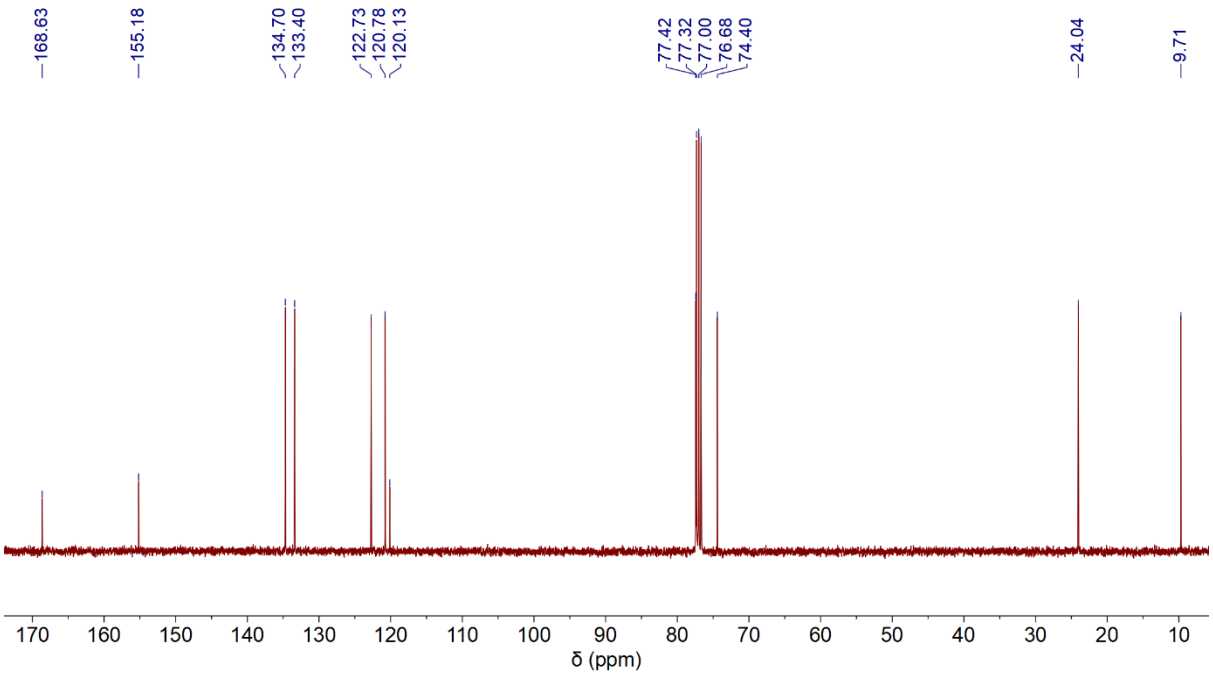


Fig. S7. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of DHB-Et.

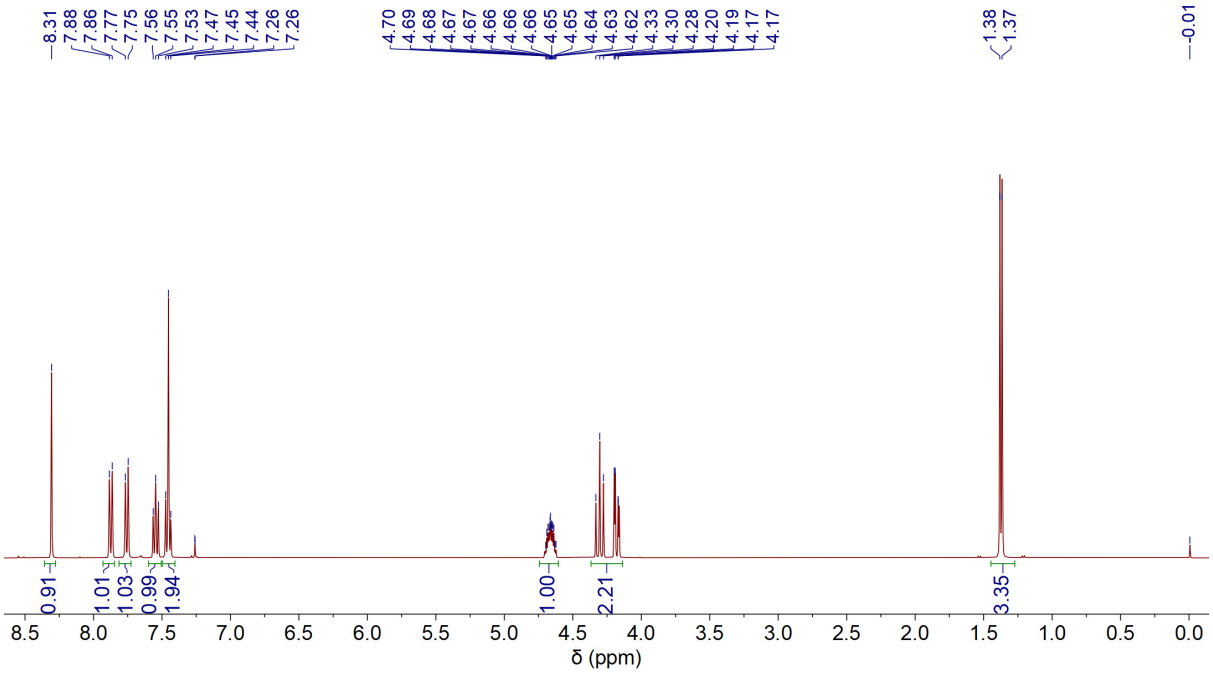


Fig. S8. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of DHN-Me. Residual solvent peaks at 7.26 ppm for $CHCl_3$.

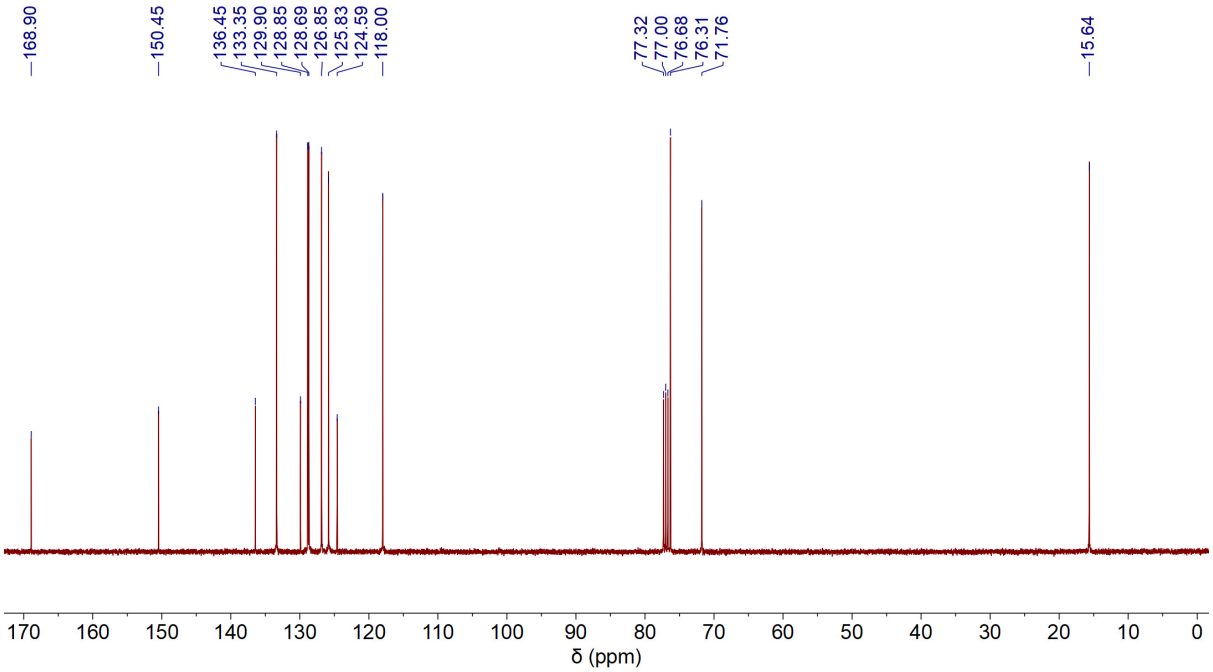


Fig. S9. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of DHN-Me.

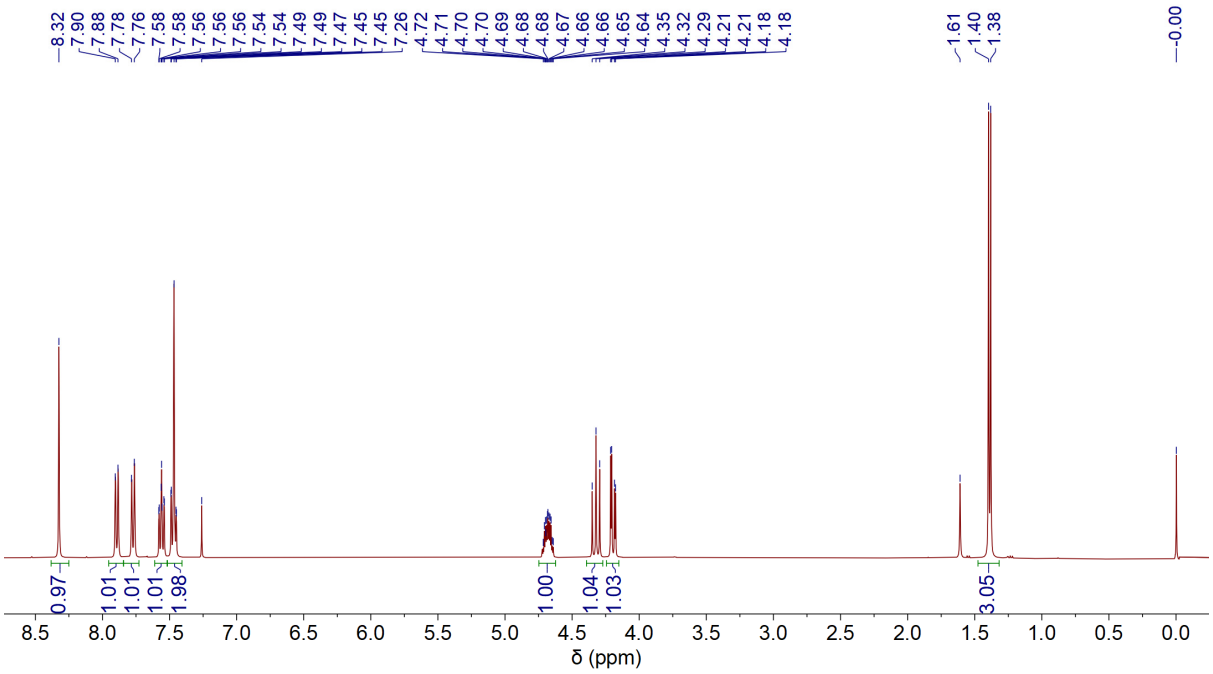


Fig. S10. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of (*R*)-DHN-Me. Residual solvent peaks at 7.26 ppm and 1.61 ppm for $CHCl_3$ and H_2O, respectively.

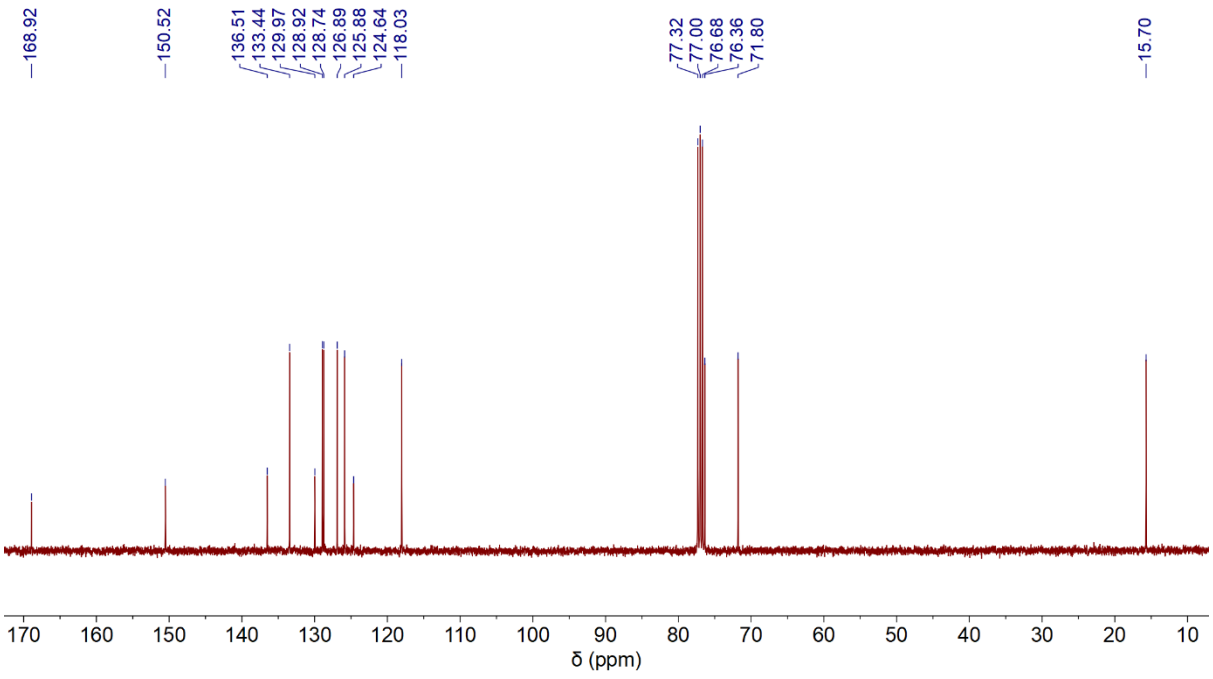


Fig. S11. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of (*R*)-DHN-Me.

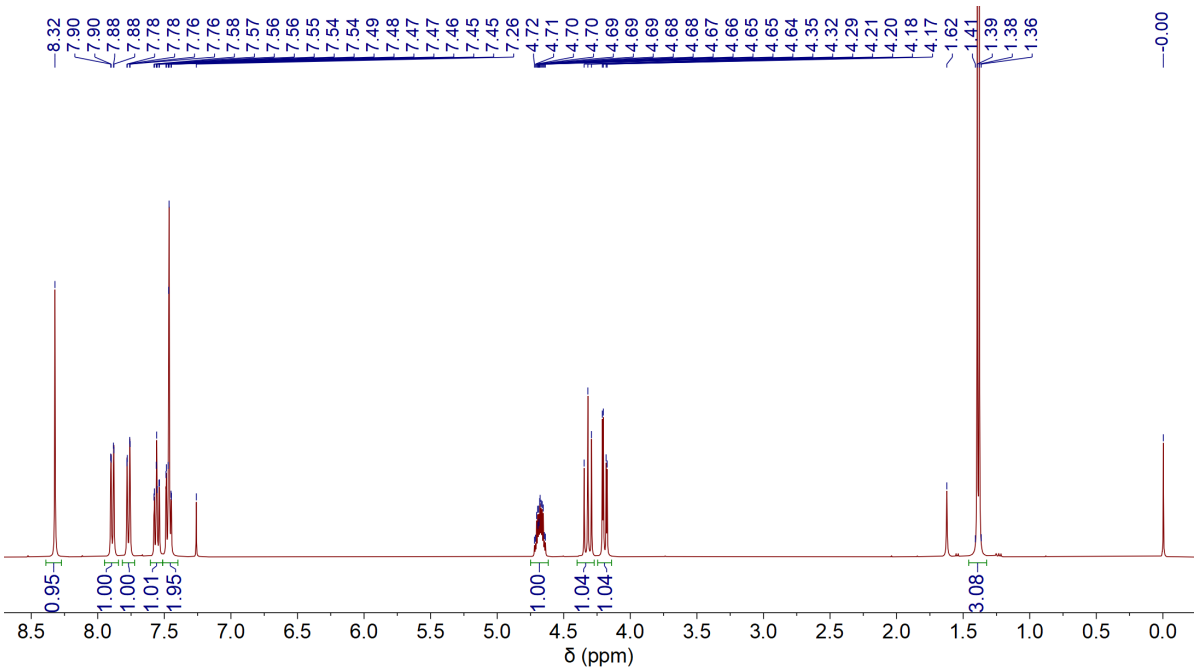


Fig. S12. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of (*S*)-DHN-Me. Residual solvent peaks at 7.26 ppm and 1.62 ppm for $CHCl_3$ and H_2O, respectively.

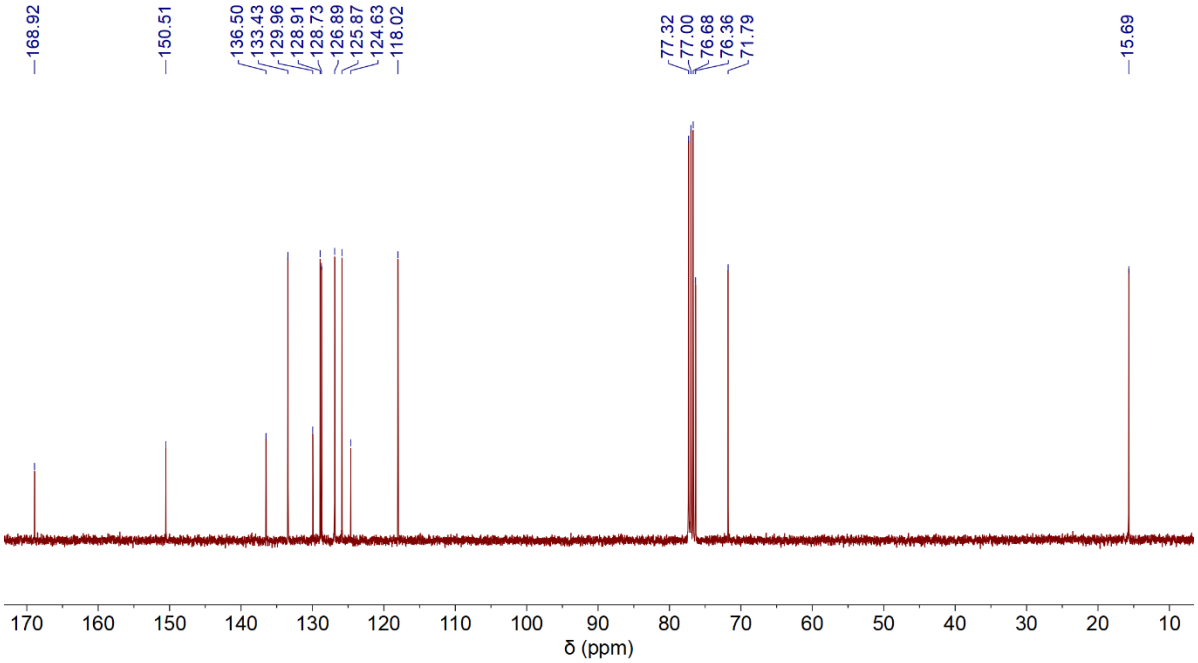


Fig. S13. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of (*S*)-DHN-Me.

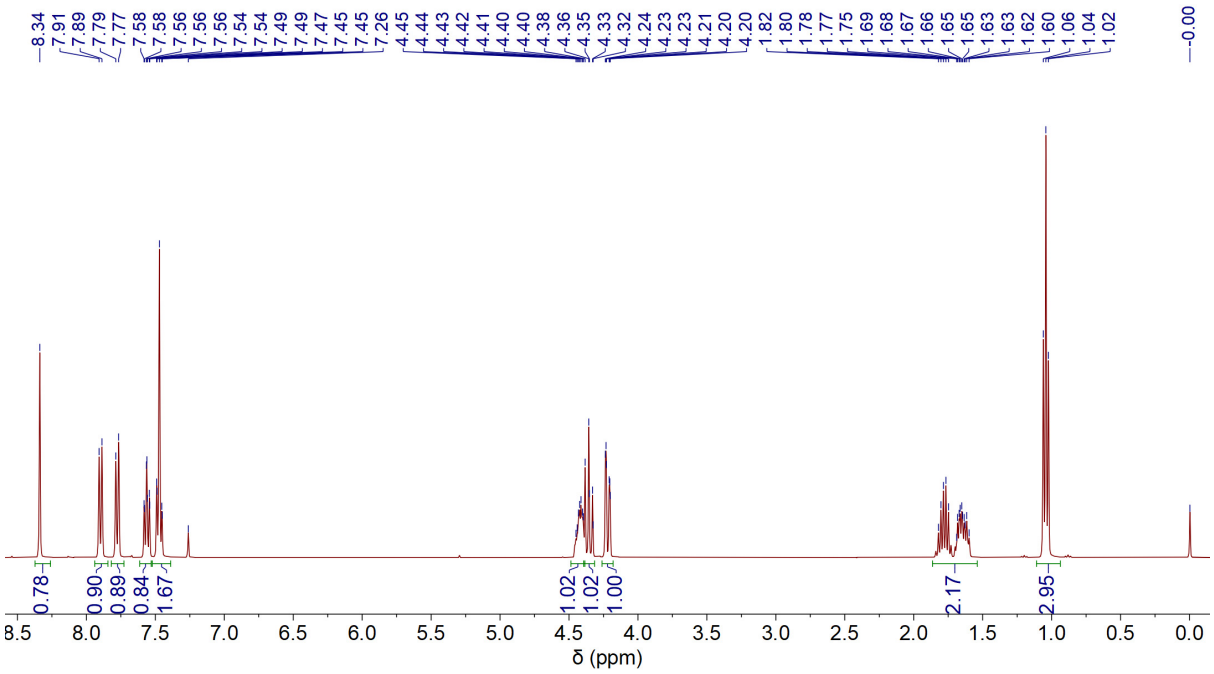


Fig. S14. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of DHN-Et. Residual solvent peak at 7.26 ppm for $CHCl_3$.

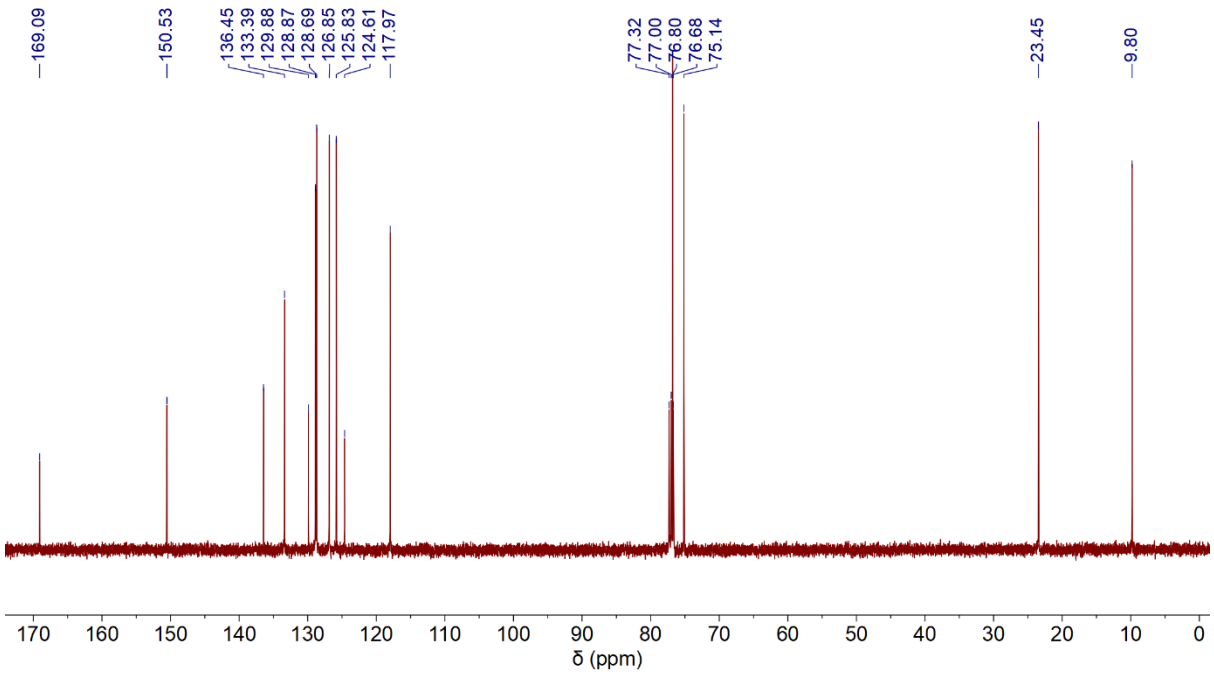


Fig. S15. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of DHN-Et.

General Polymerization Procedures

Note: Prior to polymerization, DHB-Me, (*R*)-DHB-Me and DHB-Et were further purified via recrystallization from ethanol and sublimation at 100 °C twice. DHN-Me, (*R*)-DHN-Me and DHN-Et were further purified via recrystallization from ethanol twice, dried in a vacuum oven at 60 °C for 24 h and washed with extra dry *n*-hexane in glovebox.

Polymerizations were performed in 4 mL vials at 70 °C or 100 °C inside the glovebox, or in 25 mL Schlenk flasks interfaced to a dual-manifold Schlenk line with oil bath for runs. As for DHB-Me and DHB-Et, the catalyst was added to the vigorously stirred prepared monomer and initiator (*p*-tolylmethanol) under bulk condition. As for DHN-Me and DHN-Et, the solution of catalyst in toluene was added to the vigorously stirred prepared monomer and initiator (*p*-tolylmethanol) solution (toluene). After a desired period of time, the polymerization was quenched by addition of 0.5 mL $CHCl_3$ containing benzoic acid (1 *wt* %). The quenched mixture was dissolved in $CHCl_3$ and precipitated into 100 mL of cold methanol, filtered, and washed with cold methanol; then the polymer was dissolved in $CHCl_3$ and precipitated into 100 mL cold *n*-hexane to ensure any catalyst residue or unreacted monomer was removed. All polymers were dried in a vacuum oven at 60 °C to a constant weight.

Table S1. Results for the copolymerization of DHB-Me and DHB-Et.[a]

Entry	[DHB-Me]/[DHB-Et]/[**Zn1**]/[I]	**Conv.** [b] **(%)**		**DHB-Me content**[b] **(%)**	M_n[c] (kDa)	$Đ$[c]	T_g[d] (℃)	T_d[e] (℃)
		DHB-Me	**DHB-Et**					
1	50:1000:1:1	76	58	7	57.5	1.13	50	342

[a]Reaction conditions: Initiator (I) = *p*-tolylmethanol, bulk condition, 70 °C, reaction time = 6 h. [b]Monomer conversion measured by ^{1}H NMR of the quenched solution, DHB-Me content measured by ^{1}H NMR of resulting polymers. [c]Number-average molecular weight (M_n) and dispersity index ($Đ = M_w/M_n$) determined by SEC at 40 °C in THF. [d]T_g measured by differential scanning calorimetry (DSC) from the second heating-scan curves with the cooling and second heating rate of 10 °C min^{-1}. [e]T_d measured by thermal gravimetric analysis (TGA) at a heating rate of 10 °C min^{-1}.

Polymer Characterizations

P(DHB-Me):

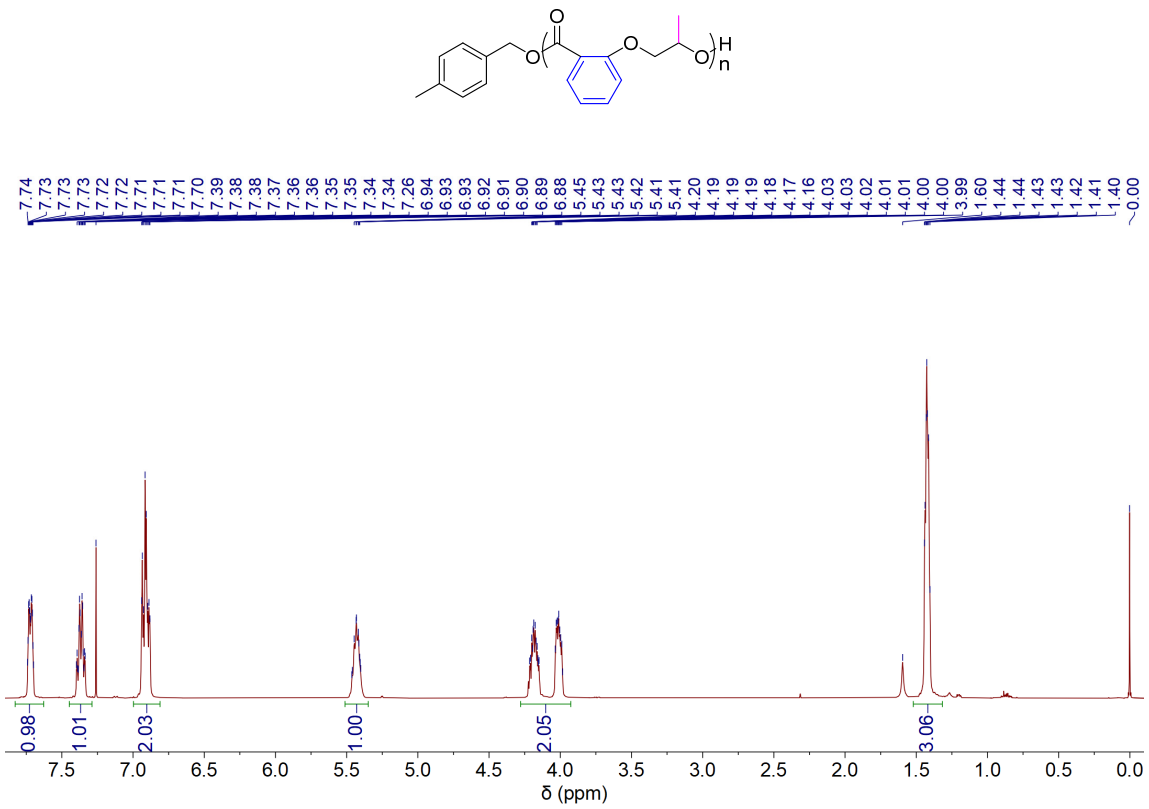


Fig. S16. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P(DHB-Me) obtained by [DHB-Me]/[TBD]/[I] = 100/1/1.

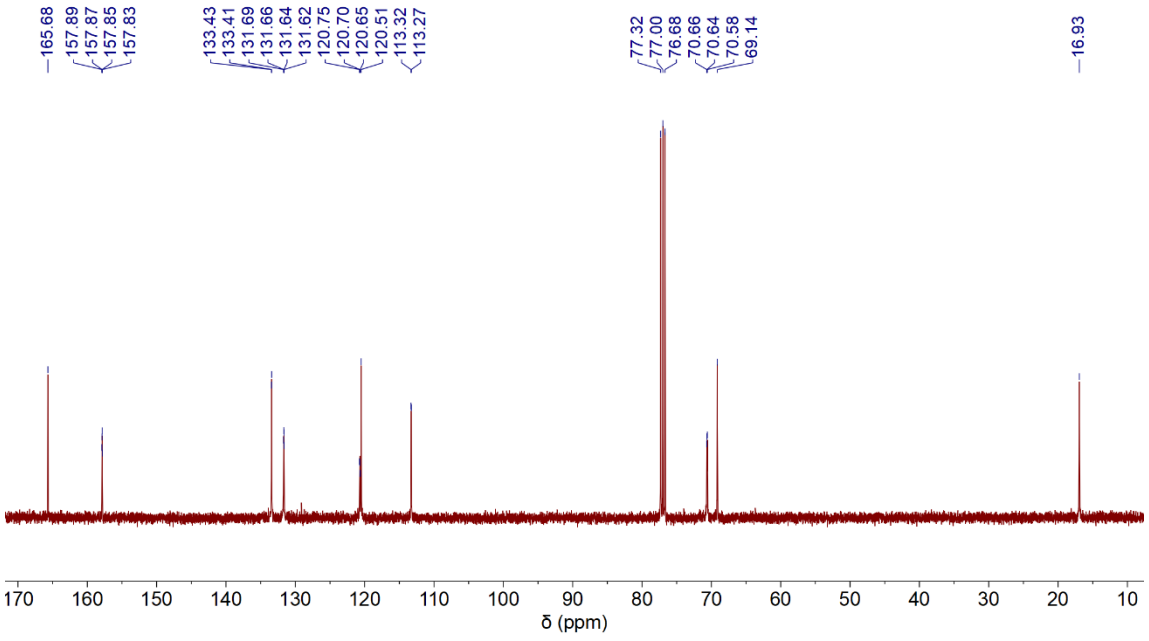


Fig. S17. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P(DHB-Me) obtained by [DHB-Me]/[TBD]/[I] = 100/1/1.

P[(*R*)-DHB-Me]:

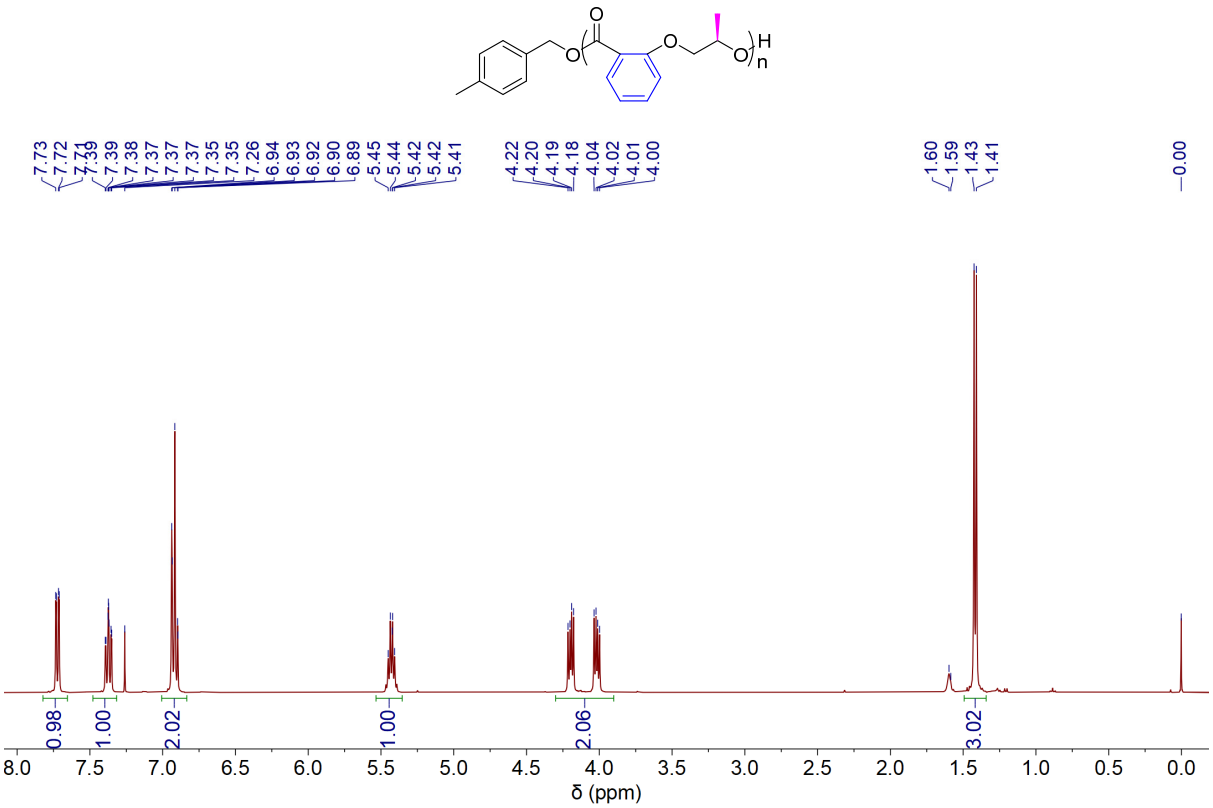


Fig. S18. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P[(*R*)-DHB-Me] obtained by [(*R*)-DHB-Me]/[**Zn1**]/[I] = 500/1/1.

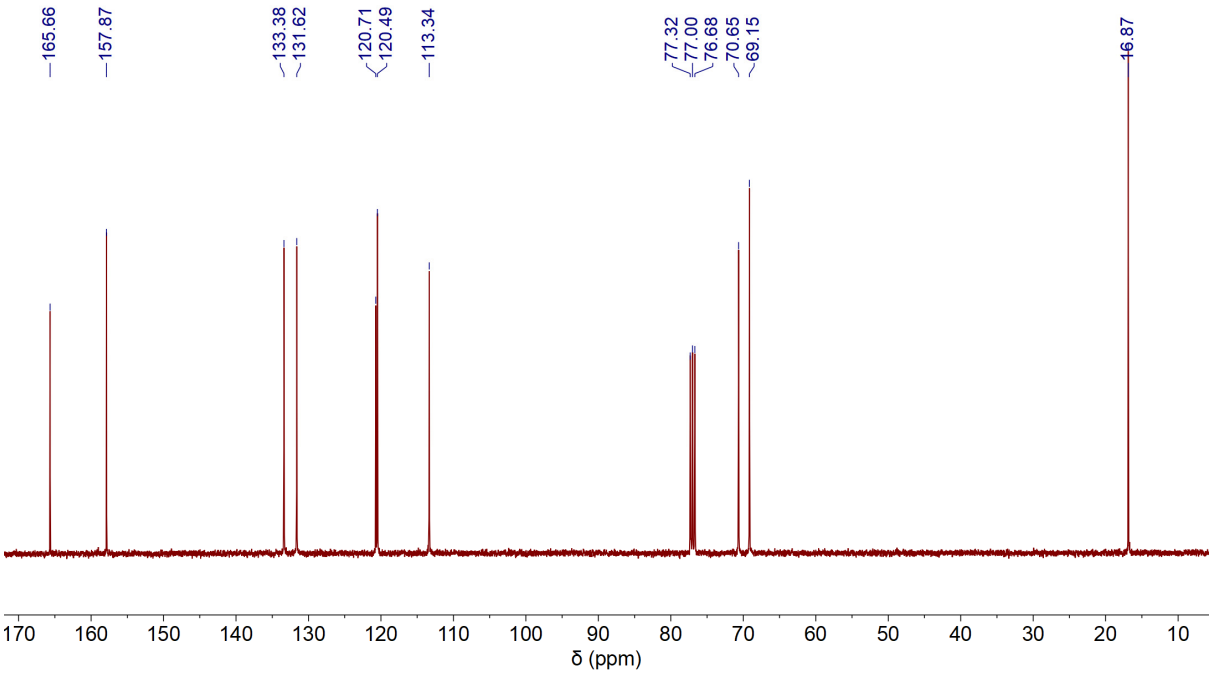


Fig. S19. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P[(*R*)-DHB-Me] obtained by [(*R*)-DHB-Me]/[**Zn1**]/[I] = 500/1/1.

P[(*S*)-DHB-Me]:

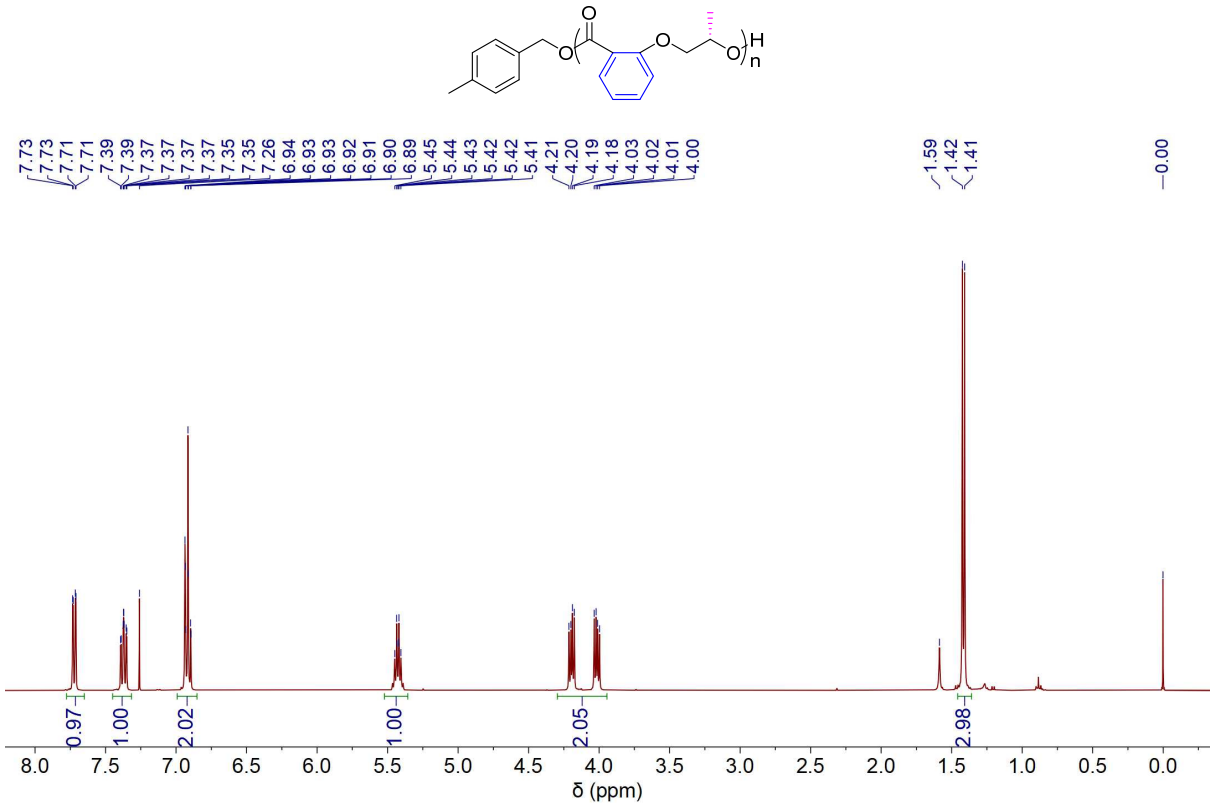


Fig. S20. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P[(*S*)-DHB-Me] obtained by [(*S*)-DHB-Me]/[TBD]/[I] = 500/1/1.

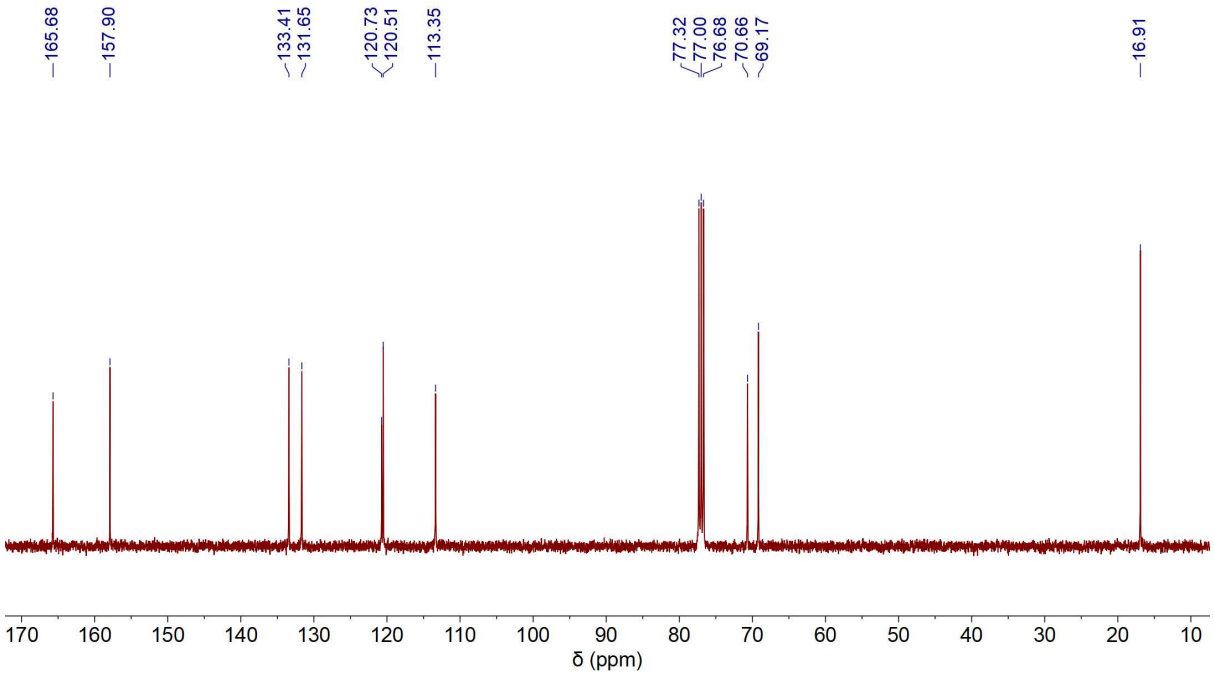


Fig. S21. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P[(*S*)-DHB-Me] obtained by [(*S*)-DHB-Me]/[TBD]/[I] = 500/1/1.

P(DHB-Et):

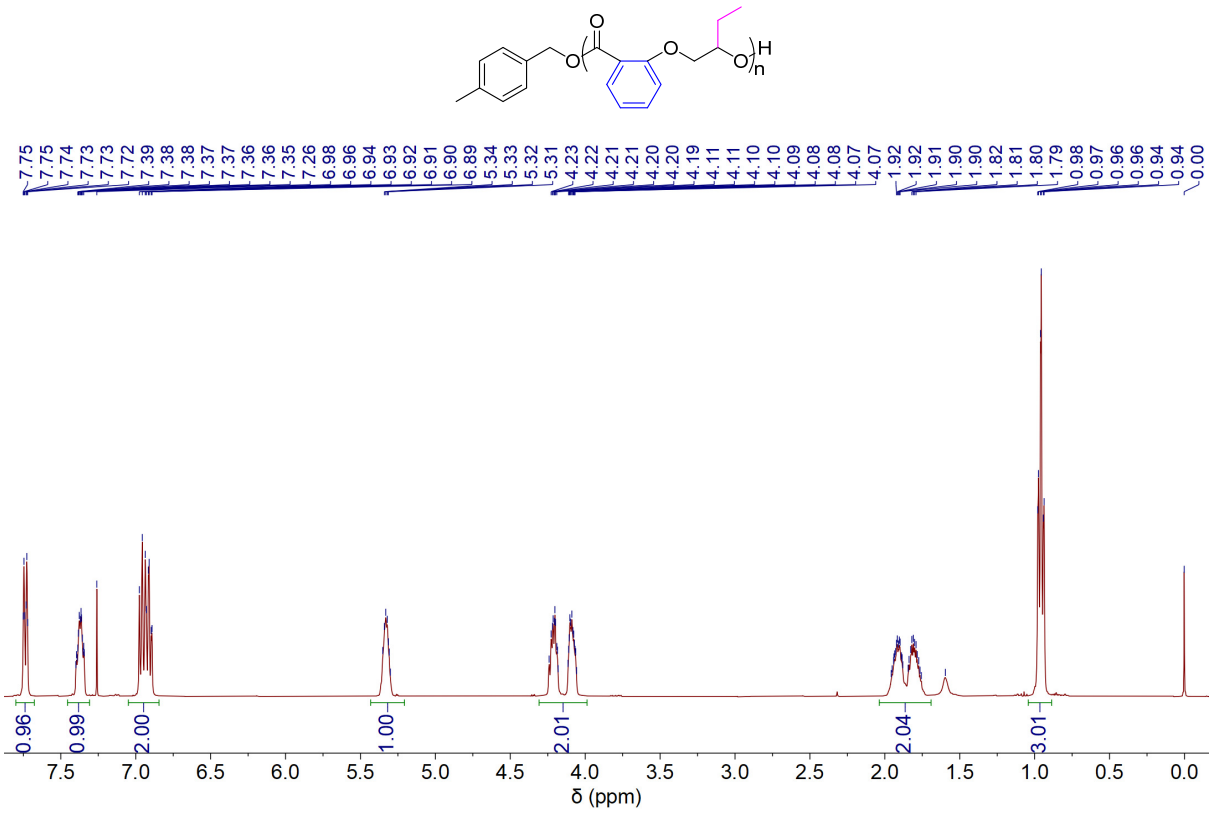


Fig. S22. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P(DHB-Et) obtained by [DHB-Et]/[TBD]/[I] = 500/1/1.

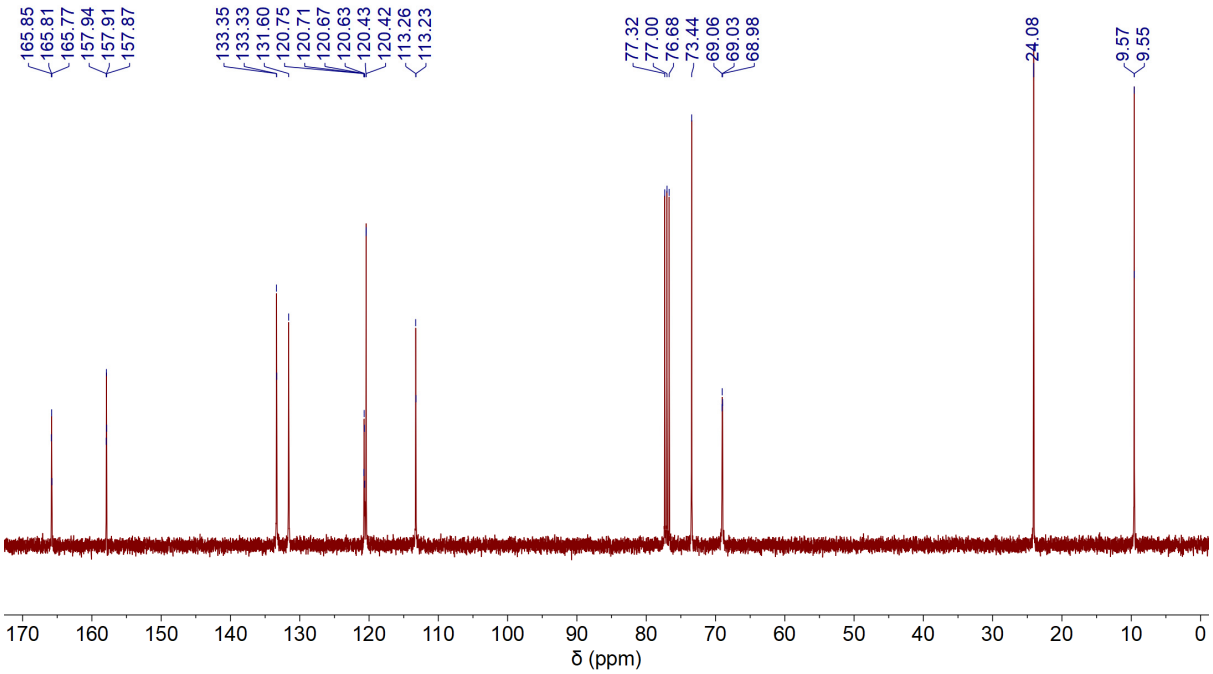


Fig. S23. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P(DHB-Et) obtained by [DHB-Et]/[TBD]/[I] = 500/1/1.

P(DHN-Me):

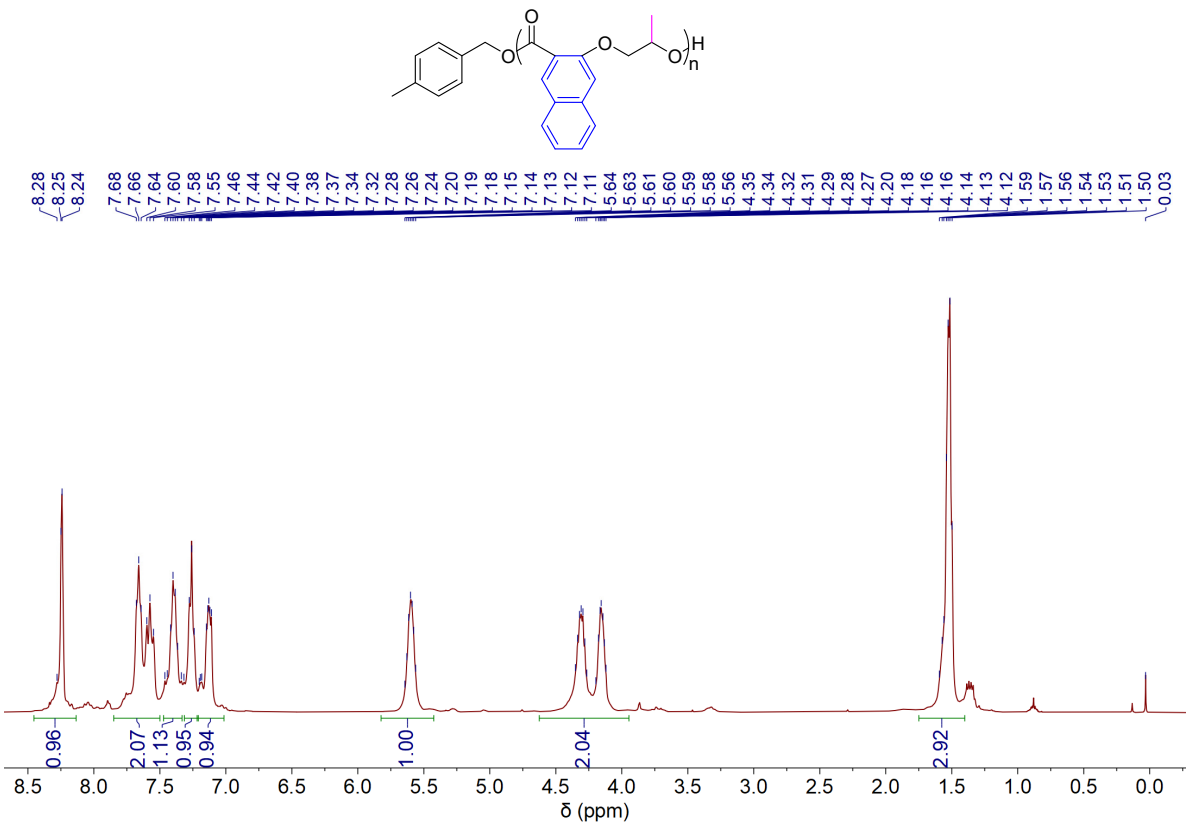


Fig. S24. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P(DHN-Me) obtained by [DHN-Me]/[**Zn1**]/[I] = 1000/1/1.

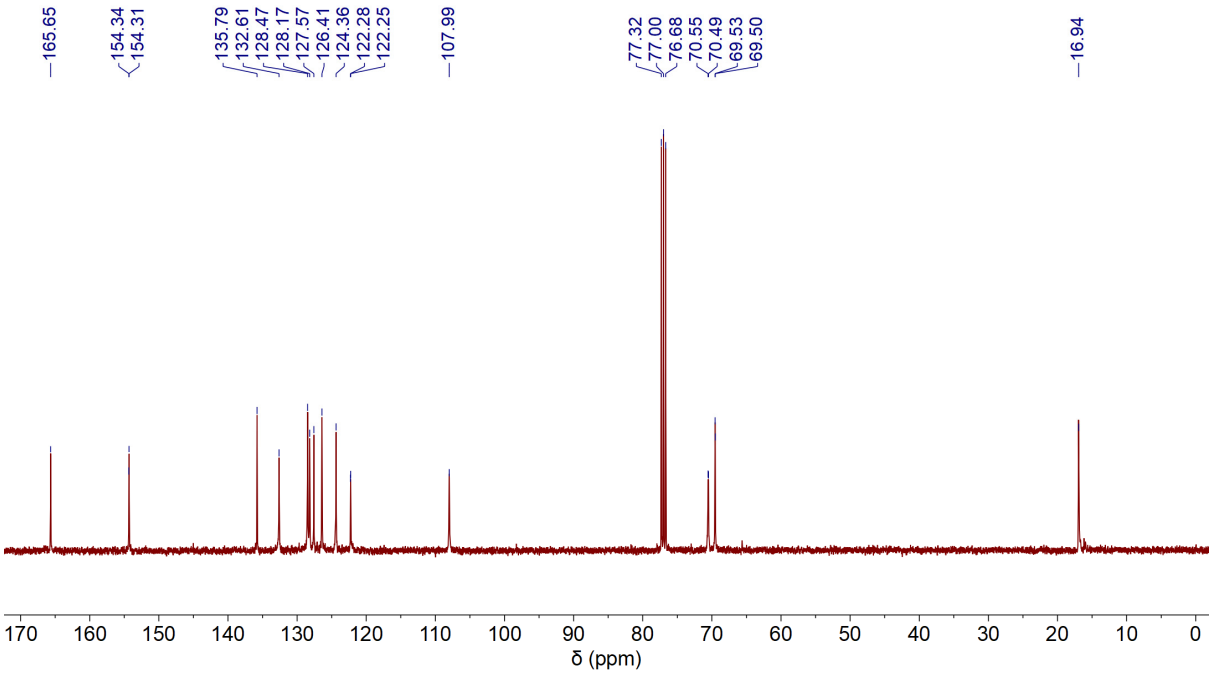


Fig. S25. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P(DHN-Me) obtained by [DHN-Me]/[**Zn1**]/[I] = 1000/1/1.

P[(*R*)-DHN-Me]:

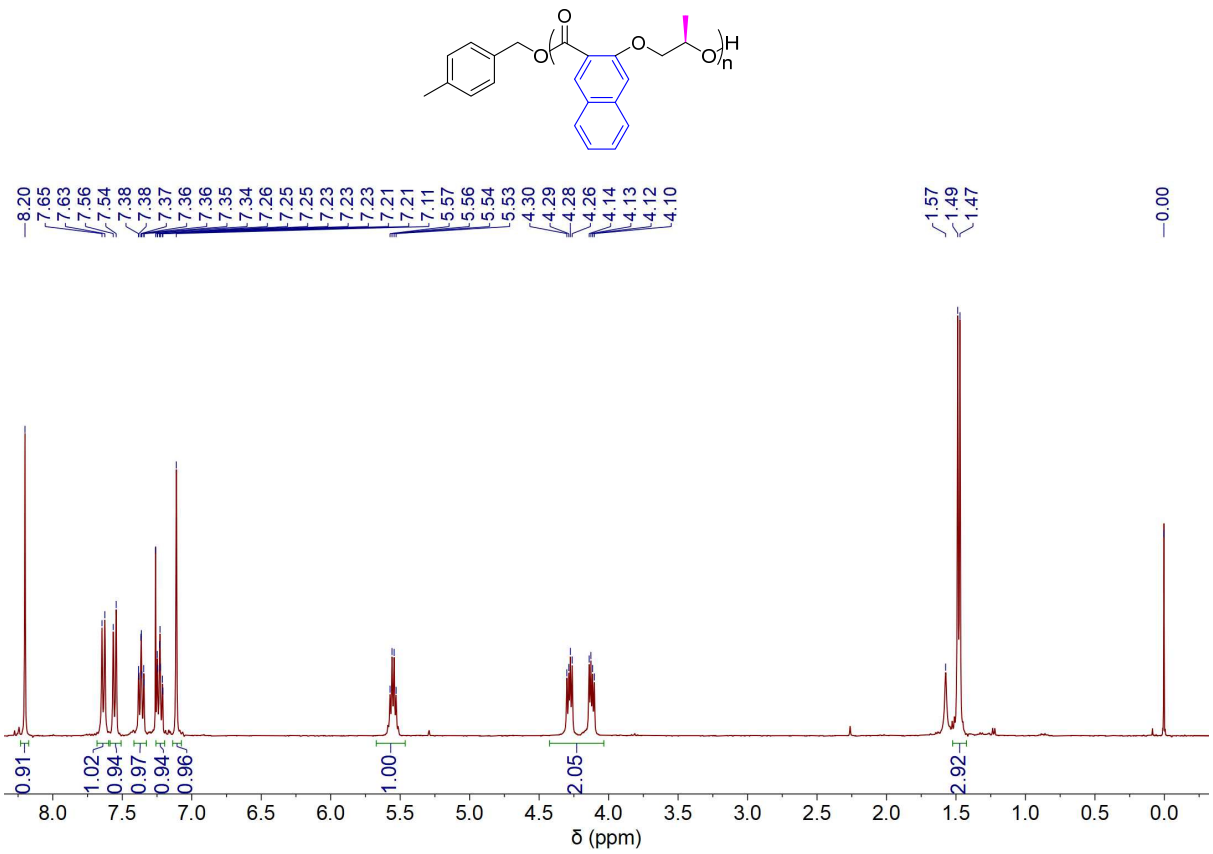


Fig. S26. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P[(*R*)-DHN-Me] obtained by [(*R*)-DHN-Me]/[**Zn1**]/[I] = 100/1/1.

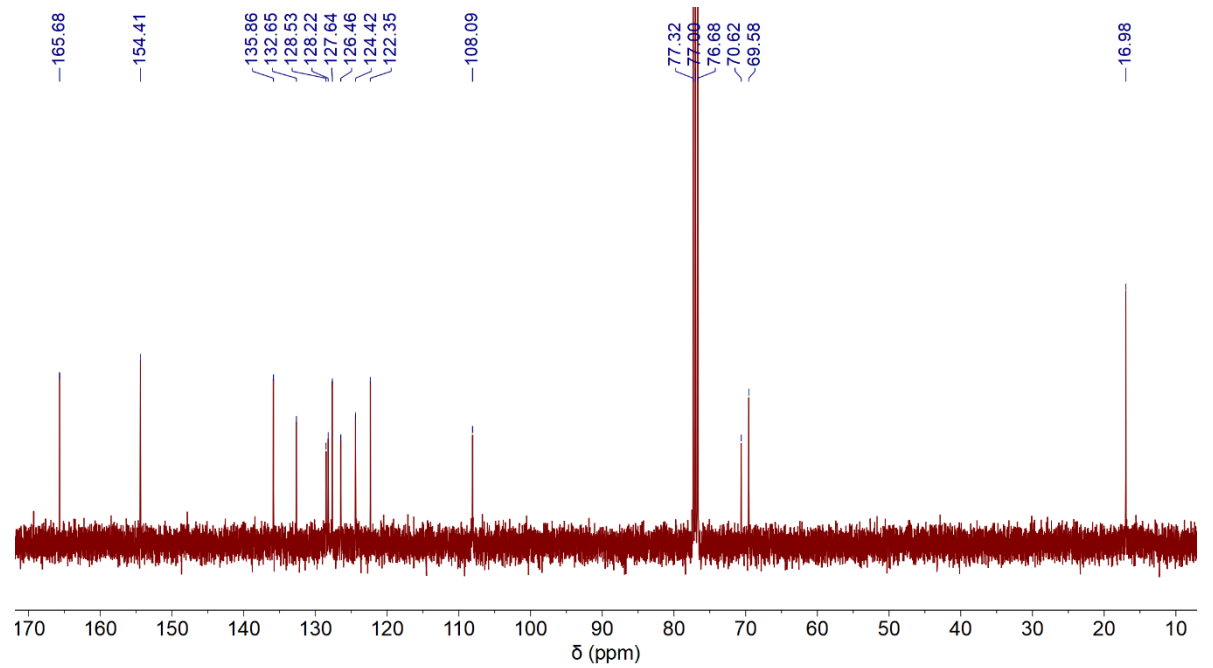


Fig. S27. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P[(*R*)-DHN-Me] obtained by [(*R*)-DHN-Me]/[**Zn1**]/[I] = 100/1/1.

P[(*S*)-DHN-Me]:

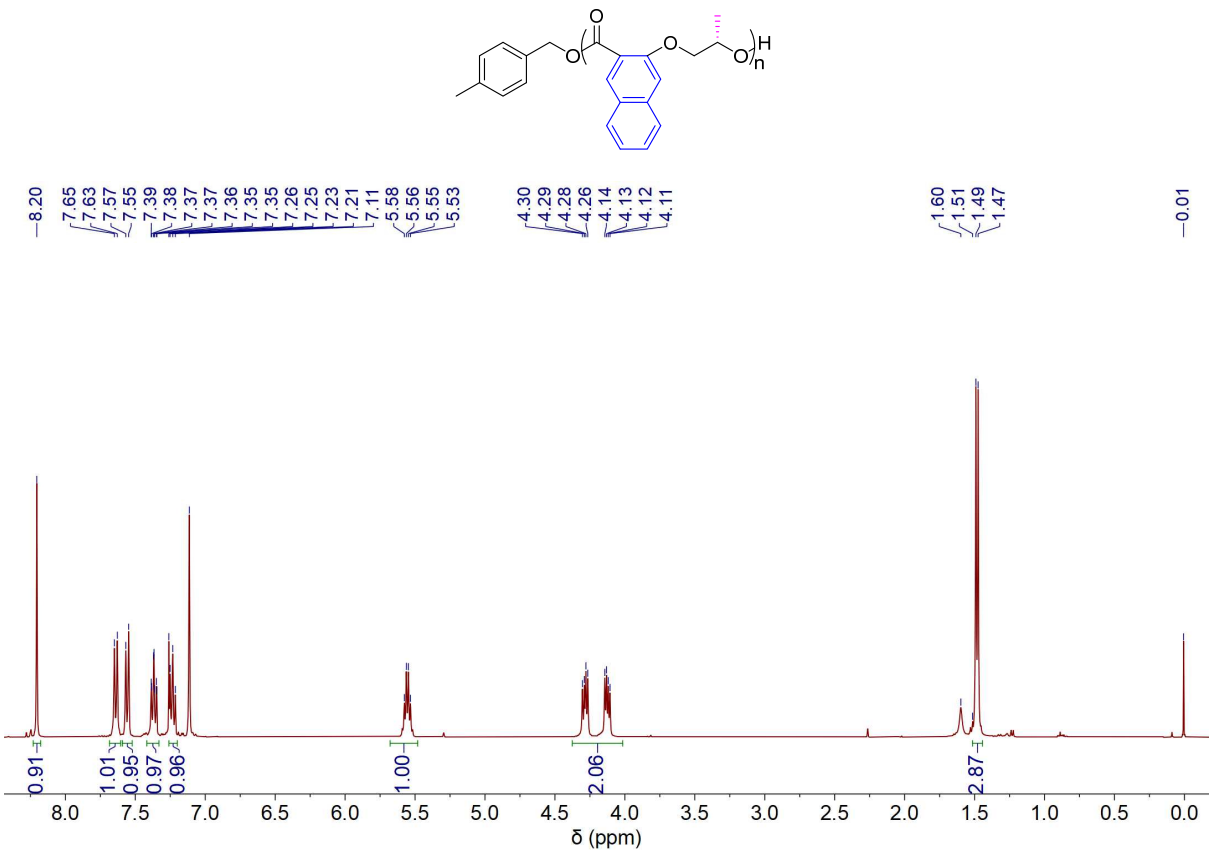


Fig. S28. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P[(*S*)-DHN-Me] obtained by [(*S*)-DHN-Me]/[**Zn1**]/[I] = 100/1/1.

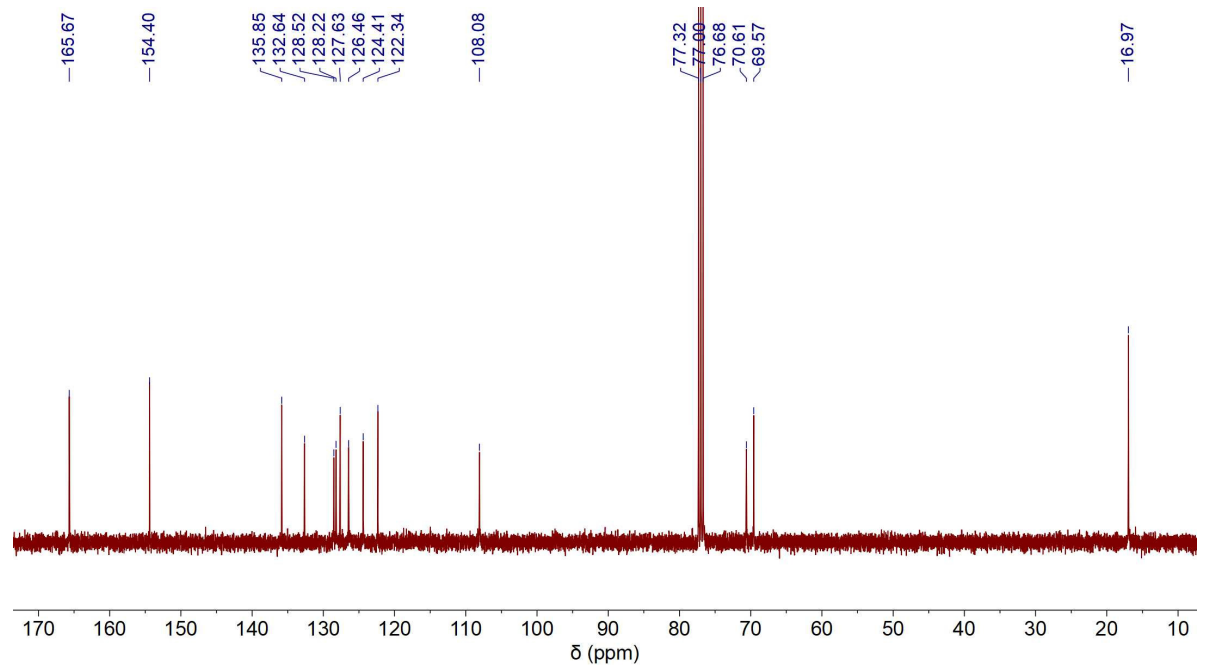


Fig. S29. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P[(*S*)-DHN-Me] obtained by [(*S*)-DHN-Me]/[**Zn1**]/[I] = 100/1/1.

P(DHN-Et):

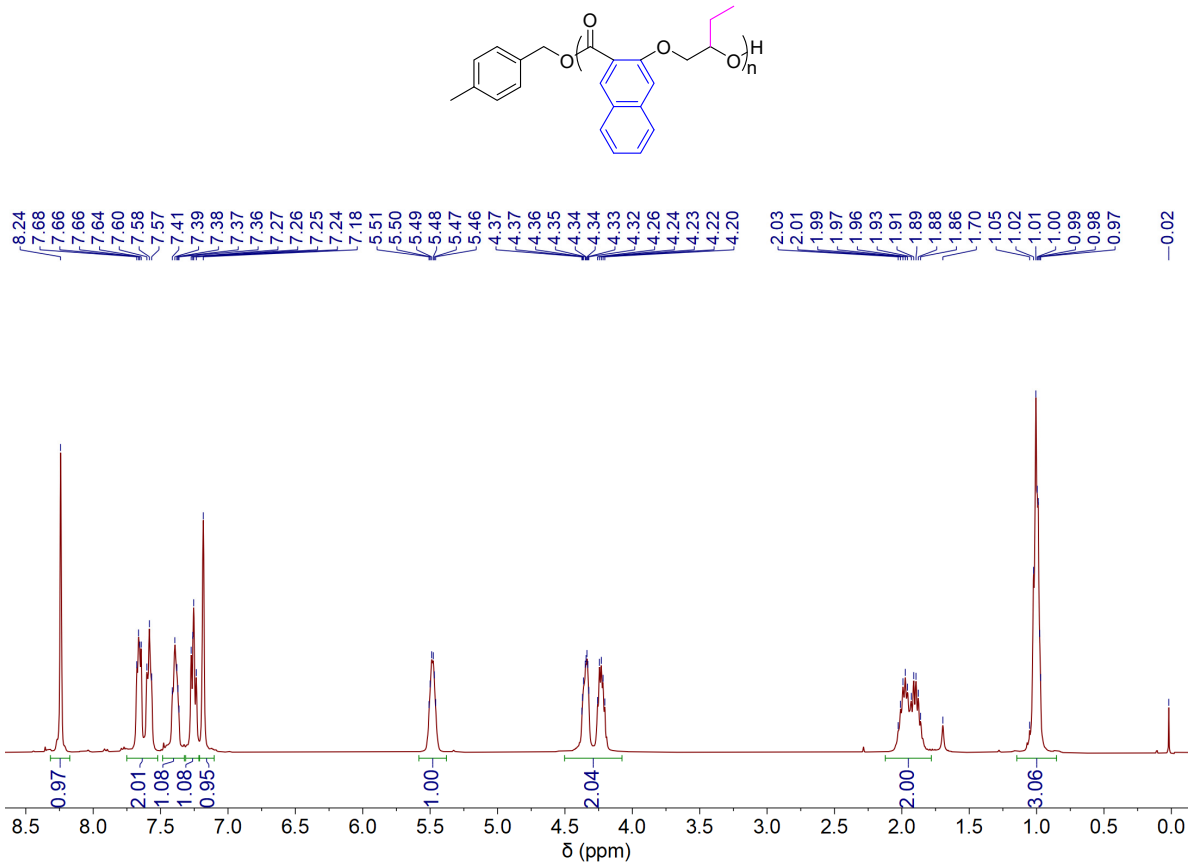


Fig. S30. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P(DHN-Et) obtained by [DHN-Et]/[**Zn1**]/[I] = 500/1/1.

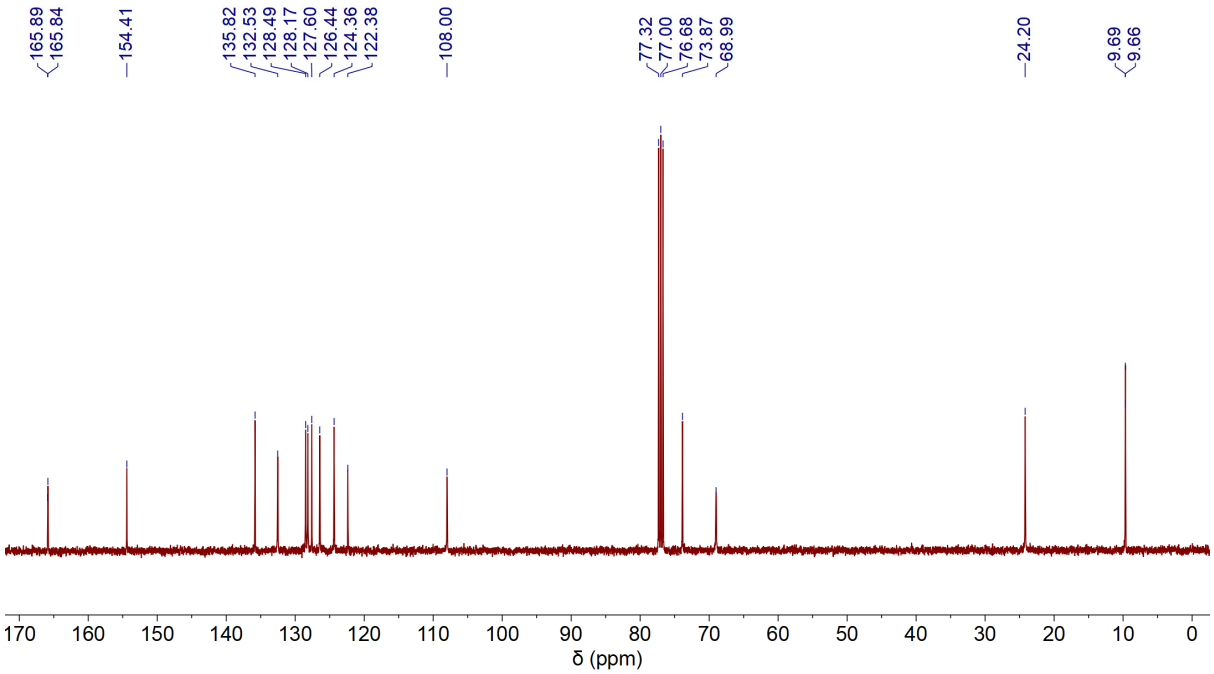


Fig. S31. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P(DHN-Et) obtained by [DHN-Et]/[**Zn1**]/[I] = 500/1/1.

P(DHB-Me-*co*-DHB-Et):

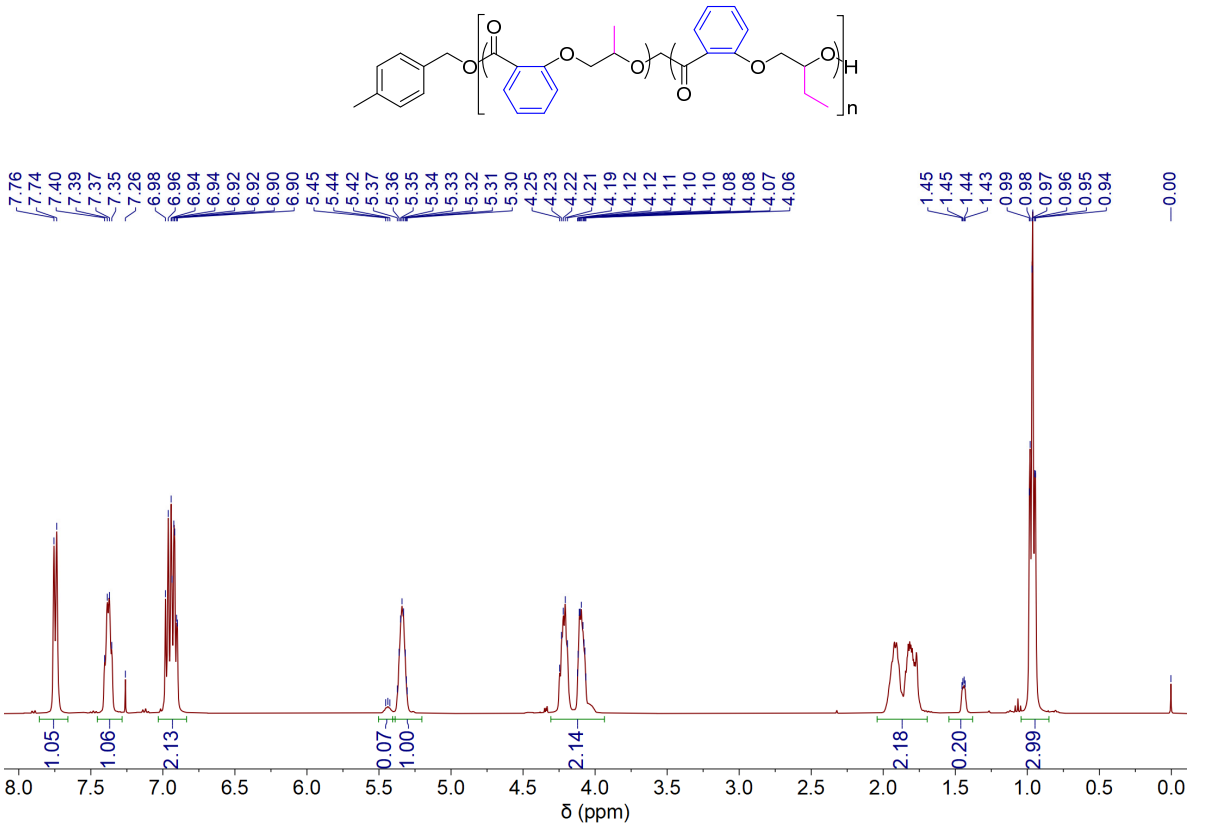


Fig. S32. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P(DHB-Me-*co*-DHB-Et) obtained by [DHB-Me]/[DHB-Et]/[**Zn1**]/[I] = 50/1000/1/1.

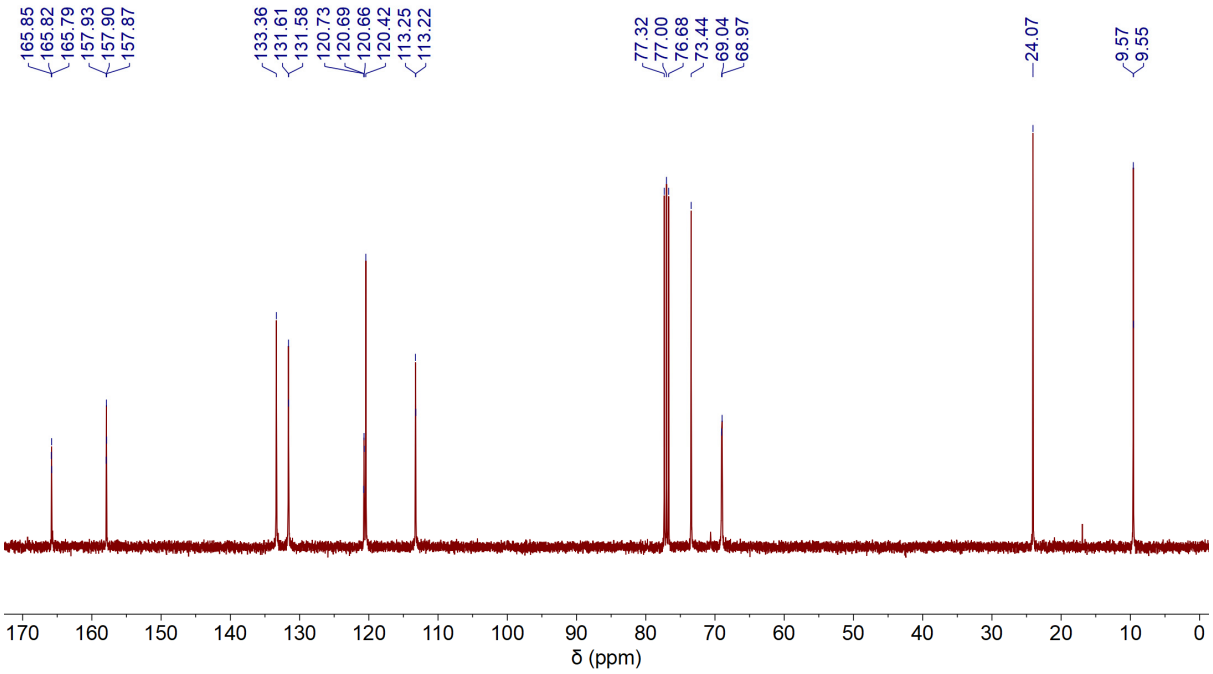


Fig. S33. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P(DHB-Me-*co*-DHB-Et) obtained by [DHB-Me]/[DHB-Et]/[**Zn1**]/[I] = 50/1000/1/1.

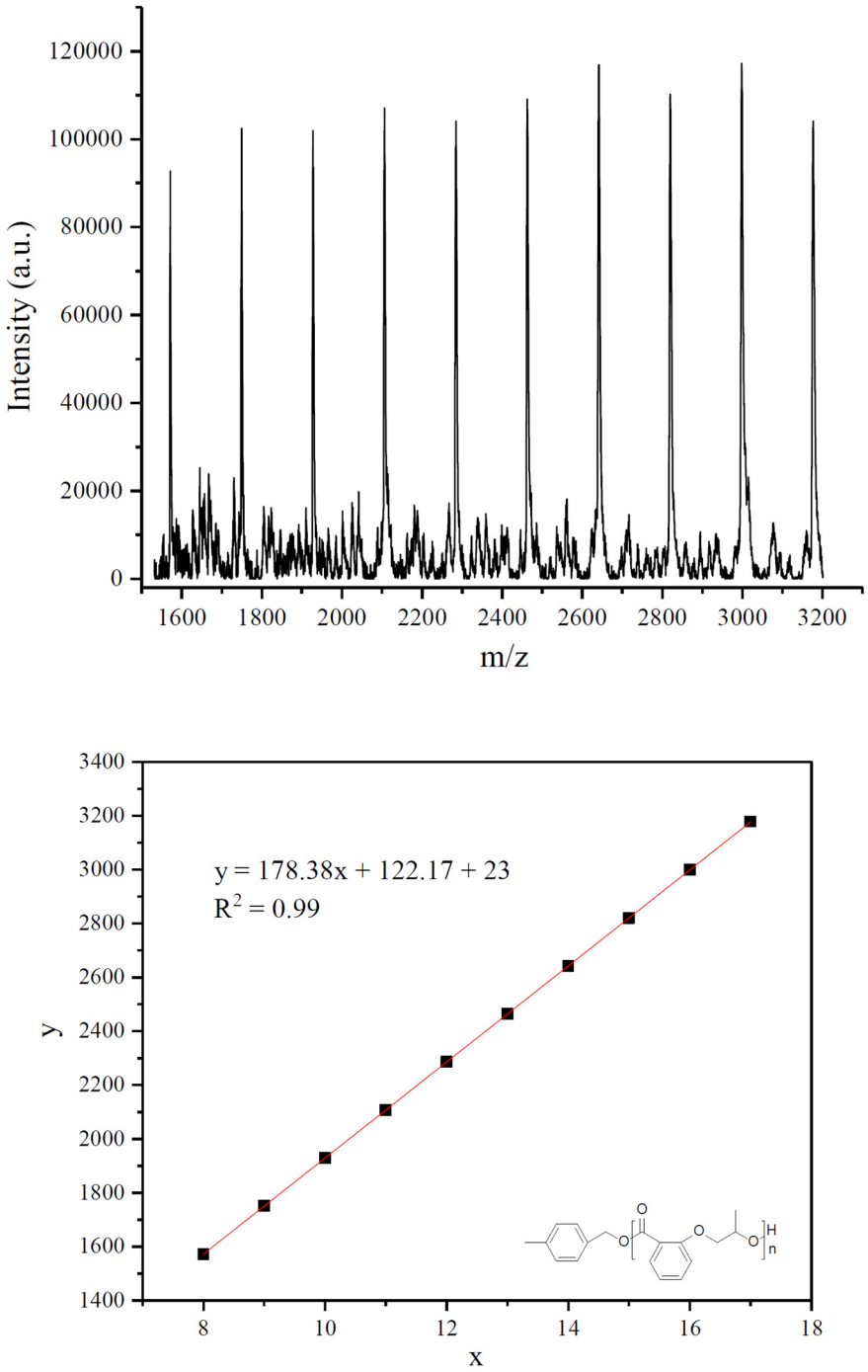


Figure S34. a) MALDI-TOF MS spectrum of the low-molecular-weight P(DHB-Me) produced by [DHB-Me]/[**Zn1**]/[I] = 50/1/1. b) linear plot of m/z values (y) *vs* the number of DHB-Me repeat units (x).

The spacing between the two neighboring molecular ion peaks corresponding to the exact molar mass of the repeat unit, DHB-Me [mass/charge ratio (m/z) = 178.06], as shown by the slope of the linear plot of *m/z* values (y axis) versus the number of DHB-Me repeat units (x axis). The intercept of the plot, 122.17 + 23, represents the total mass of chain ends plus the mass of Na^+ [Mend = 122.17 ($CH_3C_6H_4CH_2OH$) g/mol + 23 (Na^+) g/mol], corresponding to linear structure $CH_3C_6H_4CH_2O$–[DHB-Me]$_n$–H.

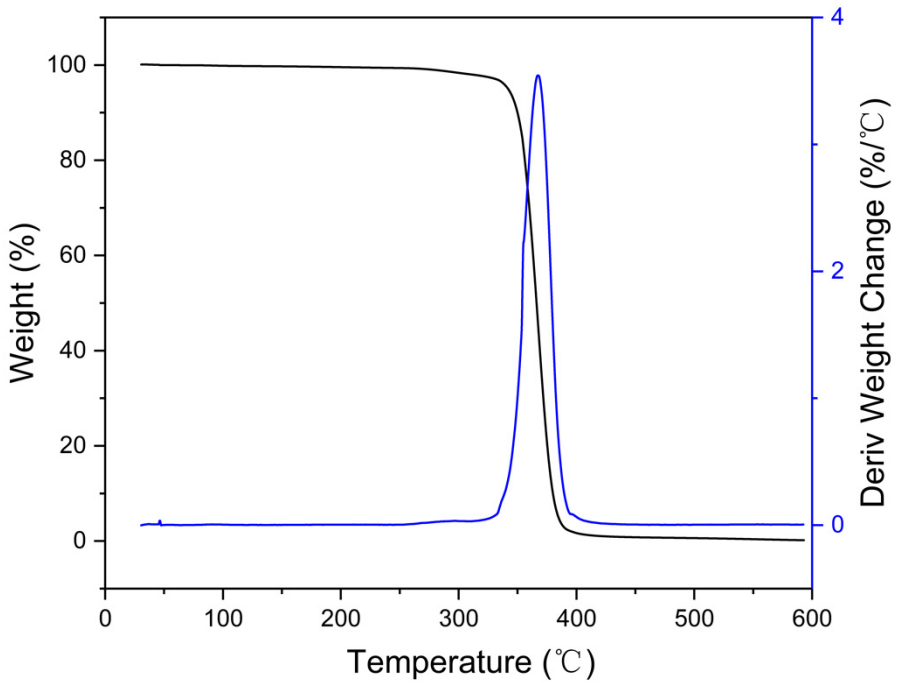


Fig. S35. TGA and DTG curves for P(DHB-Me) obtained by [DHB-Me]/[**Zn1**]/[I] = 500/1/1, T_d = 342 °C, T_{max} = 367 °C.

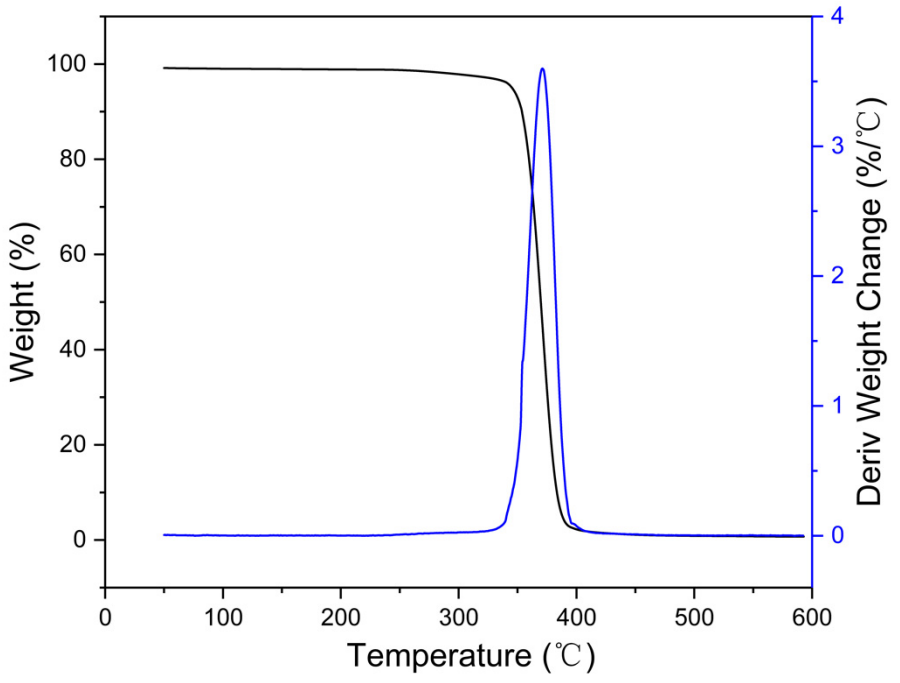


Fig. S36. TGA and DTG curves for P[(*R*)-DHB-Me] obtained by [(*R*)-DHB-Me]/[**Zn1**]/[I] = 500/1/1, T_d = 345 °C, T_{max} = 371 °C.

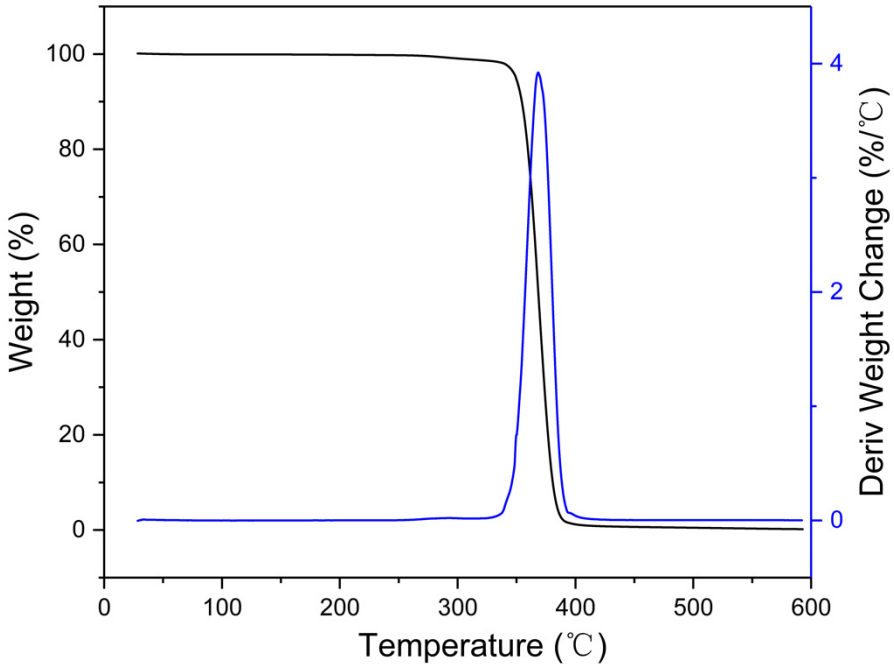


Fig. S37. TGA and DTG curves for P(DHB-Et) obtained by [DHB-Et]/[**Zn1**]/[I] = 500/1/1, T_d = 349 °C, T_{max} = 368 °C.

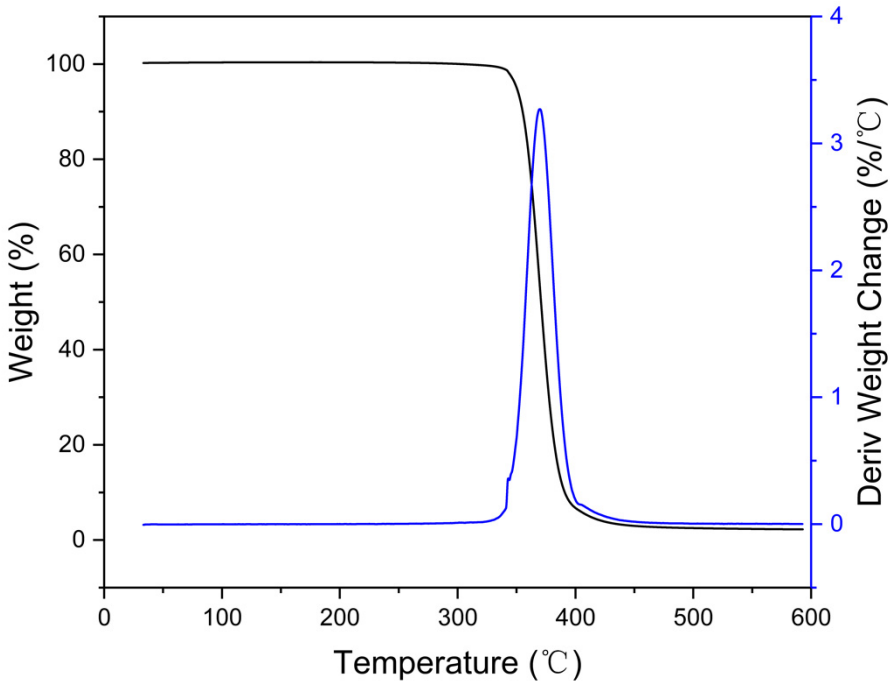


Fig. S38. TGA and DTG curves for P(DHN-Me) obtained by [DHN-Me]/[**Zn1**]/[I] = 500/1/1, T_d = 336 °C, T_{max} = 369 °C.

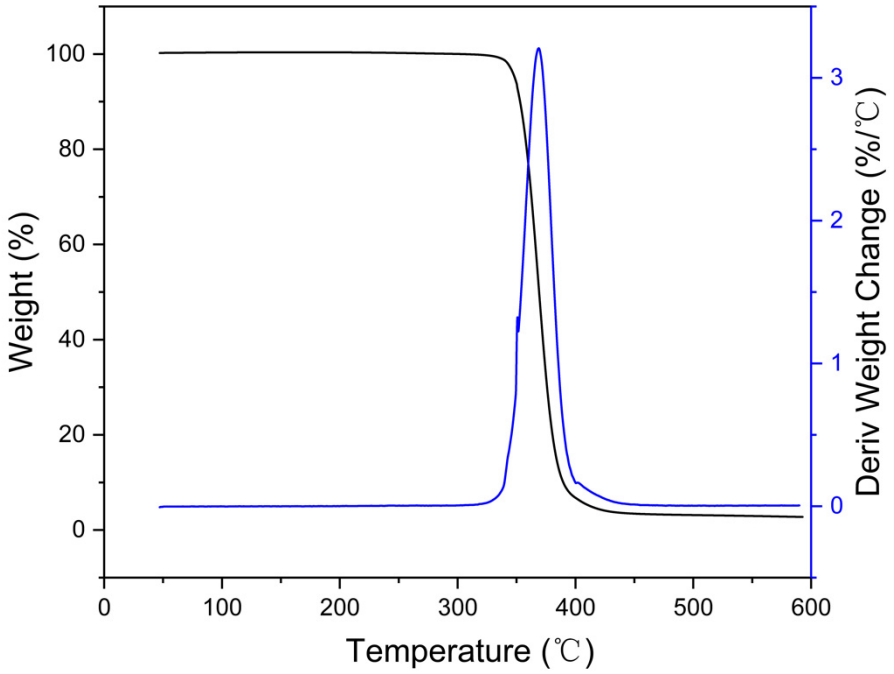


Fig. S39. TGA and DTG curves for P[(*R*)-DHN-Me] obtained by [(*R*)-DHN-Me]/[**Zn1**]/[I] = 500/1/1, T_d = 349 °C, T_{max} = 369 °C.

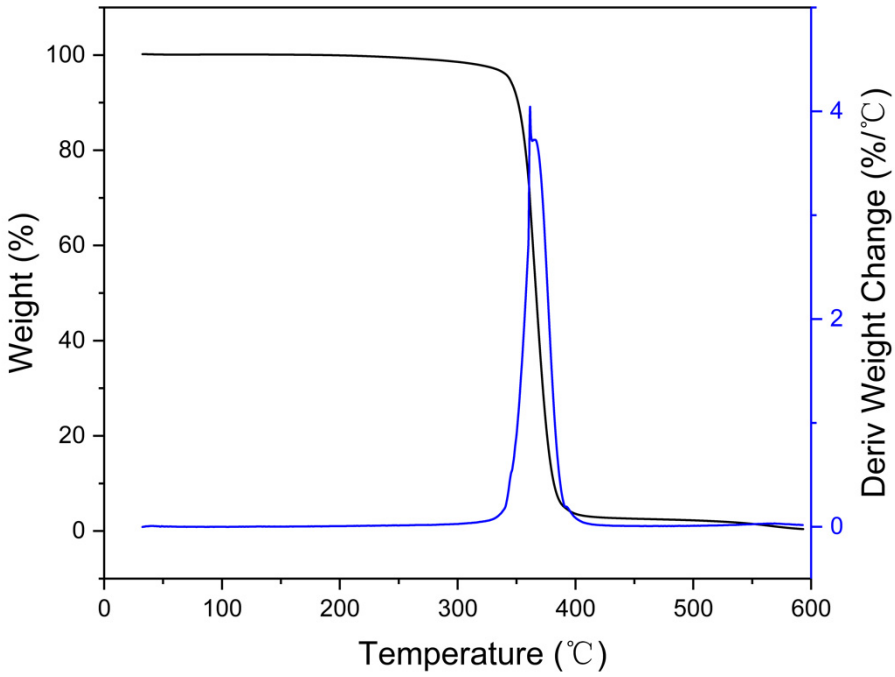


Fig. S40. TGA and DTG curves for P(DHN-Et) obtained by [DHN-Et]/[**Zn1**]/[I] = 500/1/1, T_d = 344 °C, T_{max} = 361 °C.

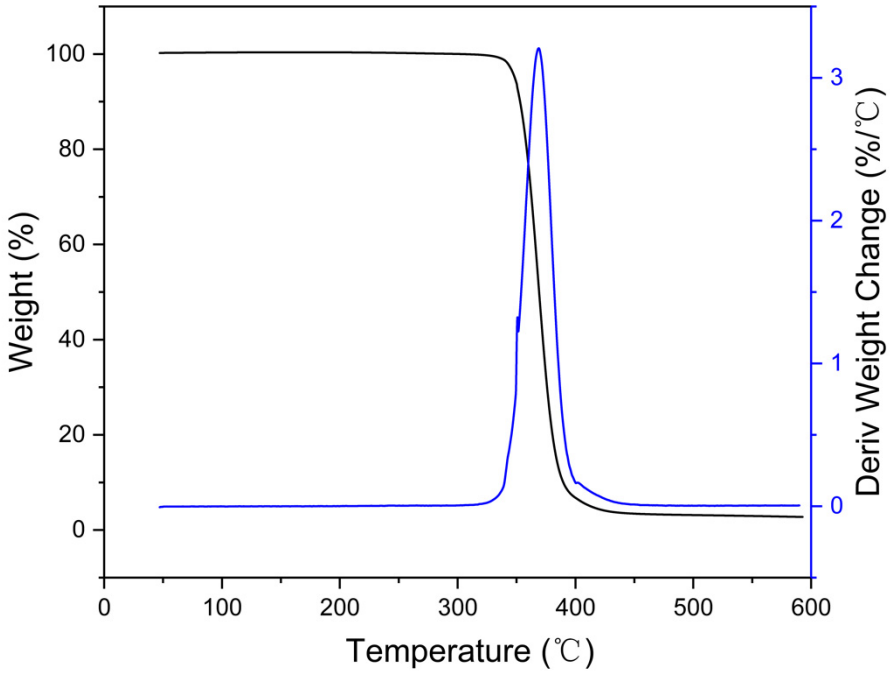


Fig. S41. TGA and DTG curves for P(DHB-Me-*co*-DHB-Et) obtained by [DHB-Me]/[DHB-Et]/[**Zn1**]/[I] = 50/1000/1/1, T_d = 342 °C, T_{max} = 366 °C.

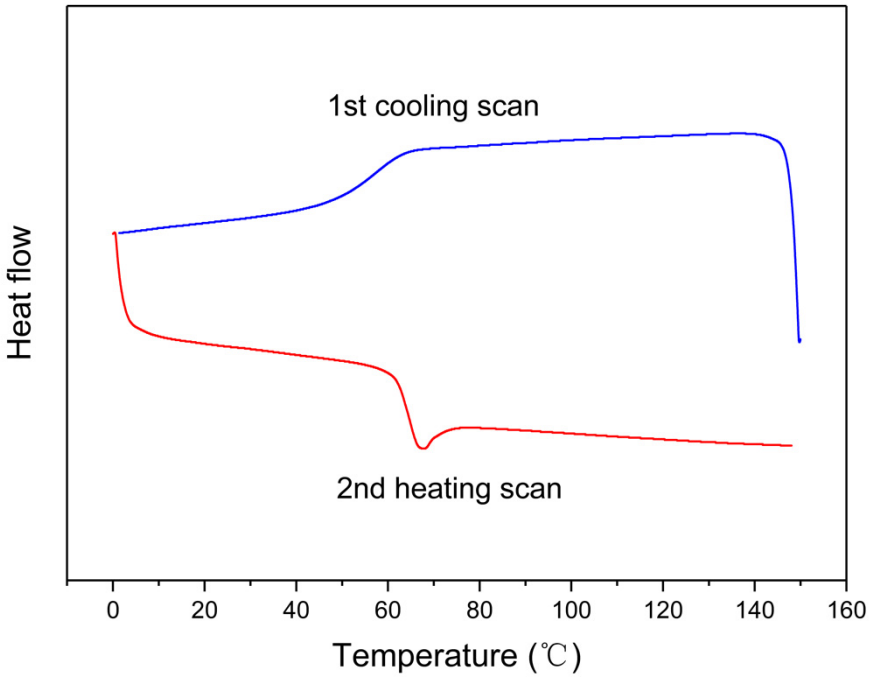


Fig. S42. DSC curves for P(DHB-Me) obtained by [DHB-Me]/[**Zn1**]/[I] = 500/1/1, T_g = 65 °C.

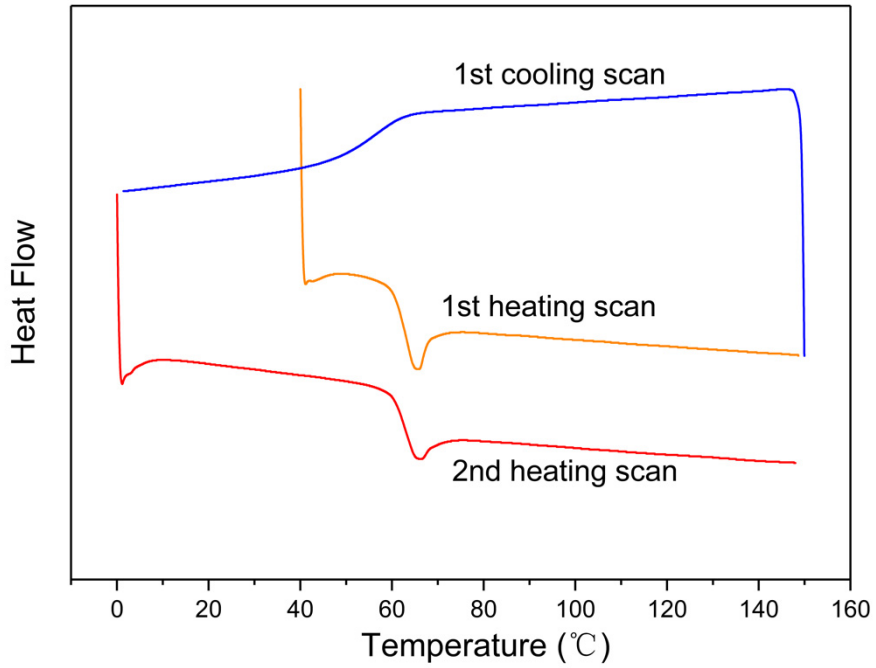


Fig. S43. DSC curves for P[(*R*)-DHB-Me] obtained by [(*R*)-DHB-Me]/[**Zn1**]/[I] = 500/1/1, T_g = 63 °C.

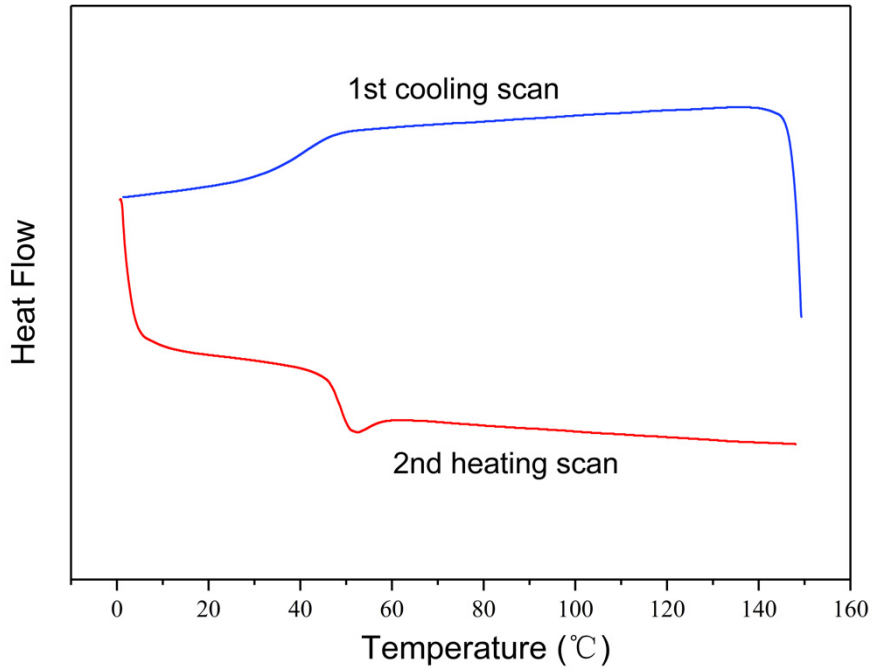


Fig. S44. DSC curves for P(DHB-Et) obtained by [DHB-Et]/[**Zn1**]/[I] = 500/1/1, T_g = 49 °C.

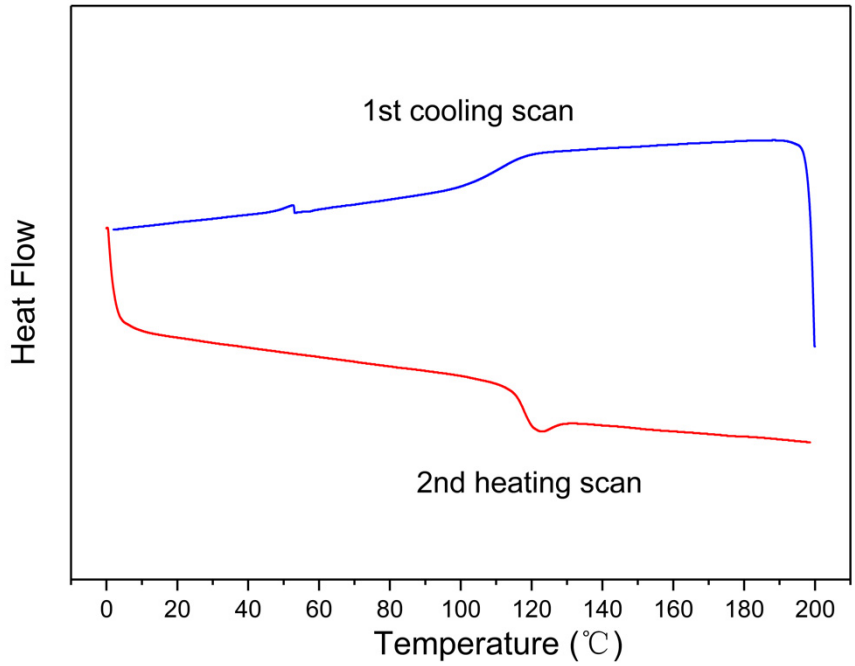


Fig. S45. DSC curves for P(DHN-Me) obtained by [DHN-Me]/[**Zn1**]/[I] = 500/1/1, T_g = 118 °C.

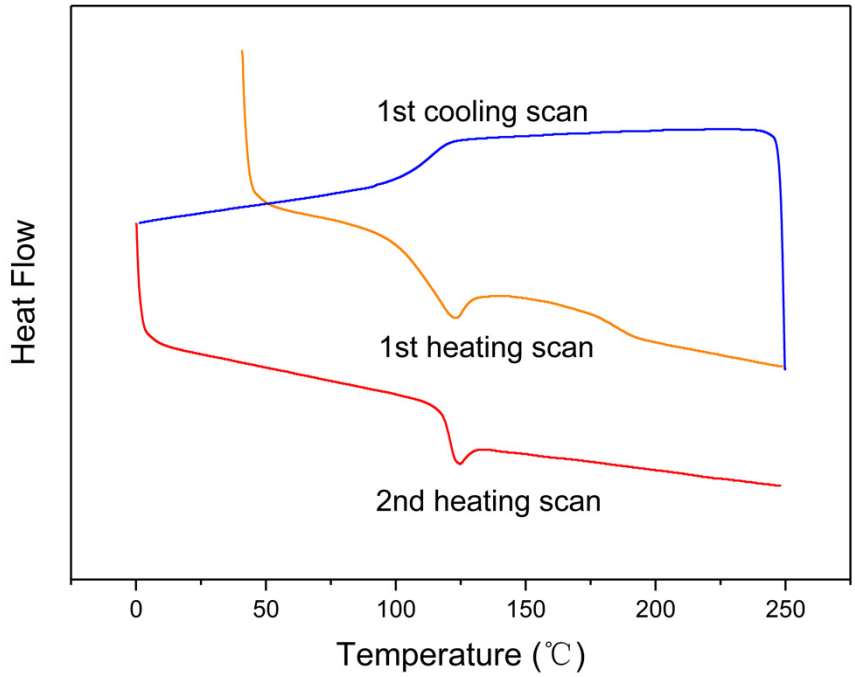


Fig. S46. DSC curves for P[(*R*)-DHN-Me] obtained by [(*R*)-DHN-Me]/[**Zn1**]/[I] = 500/1/1, T_g = 121 °C.

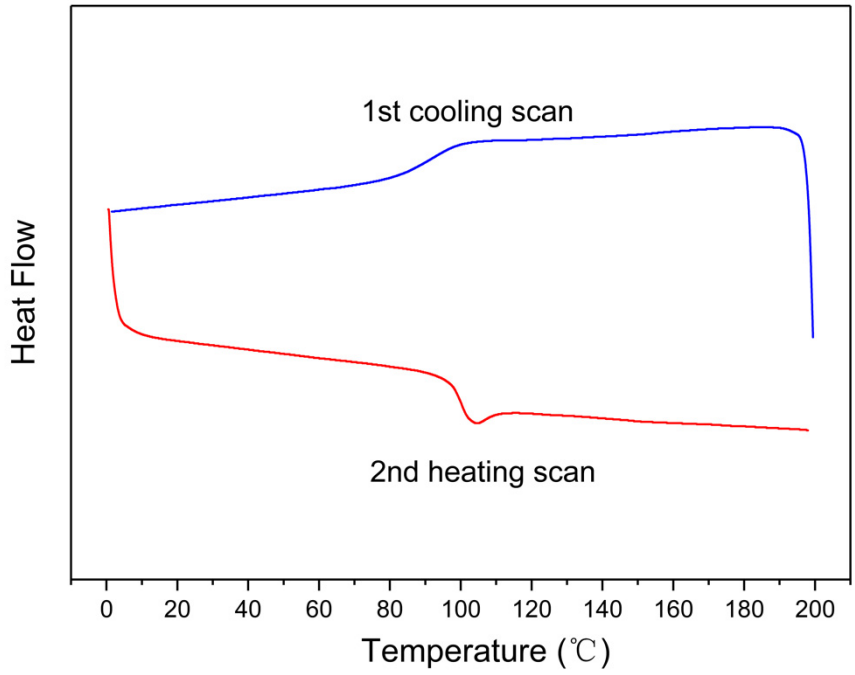


Fig. S47. DSC curves for P(DHN-Et) obtained by [DHN-Et]/[**Zn1**]/[I] = 500/1/1, T_g = 100 °C.

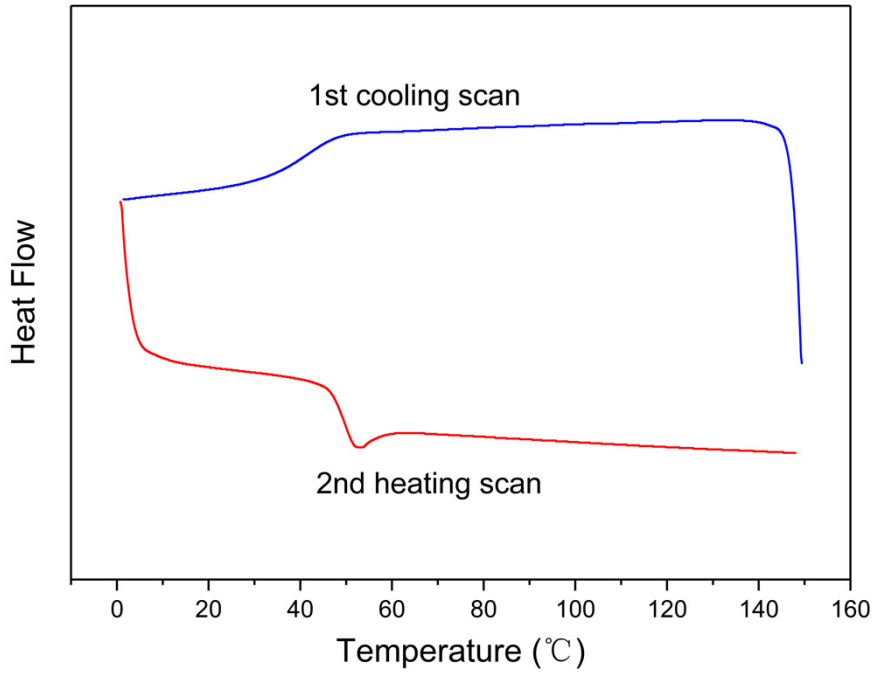


Fig. S48. DSC curves for P(DHB-Me-*co*-DHB-Et) obtained by [DHB-Me]/[DHB-Et]/[**Zn1**]/[I] = 50/1000/1/1, T_g = 50 °C.

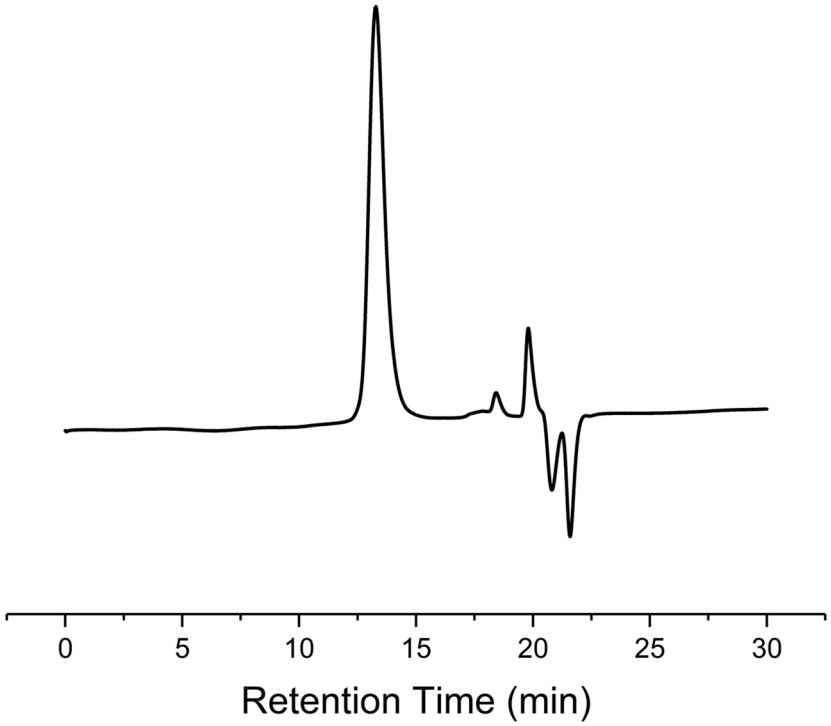


Fig. S49. GPC trace of P(DHB-Me) obtained by [DHB-Me]/[**Zn1**]/[I] = 1000/1/1, M_n = 97.6 kg. mol^{-1}, $Đ$ = 1.19 (Table 1, entry 4).

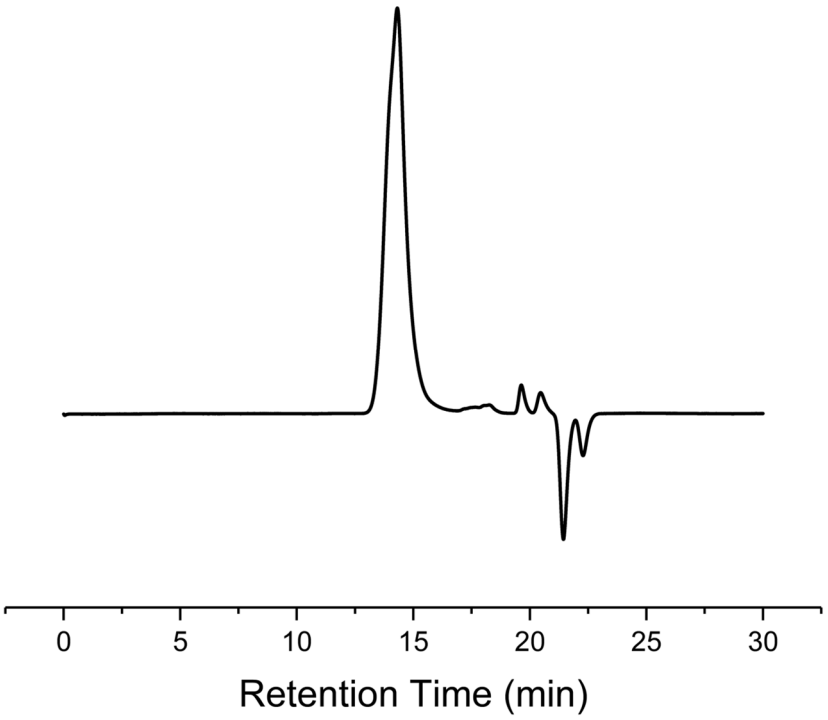


Fig. S50. GPC trace of P[(*R*)-DHB-Me] obtained by [(*R*)-DHB-Me]/[**Zn1**]/[I] = 500/1/1, M_n = 36.6 kg. mol^{-1}, $Đ$ = 1.25 (Table 1, entry 6).

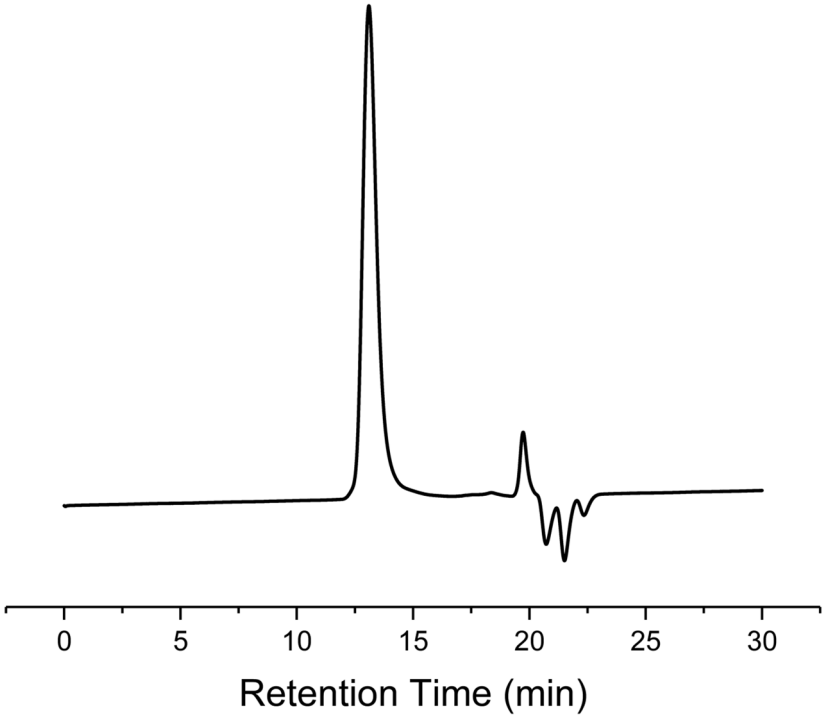


Fig. S51. GPC trace of P(DHB-Et) obtained by [DHB-Et]/[**Zn1**]/[I] = 1000/1/1, M_n = 123 kg. mol^{-1}, $Đ$ = 1.17 (Table 1, entry 12).

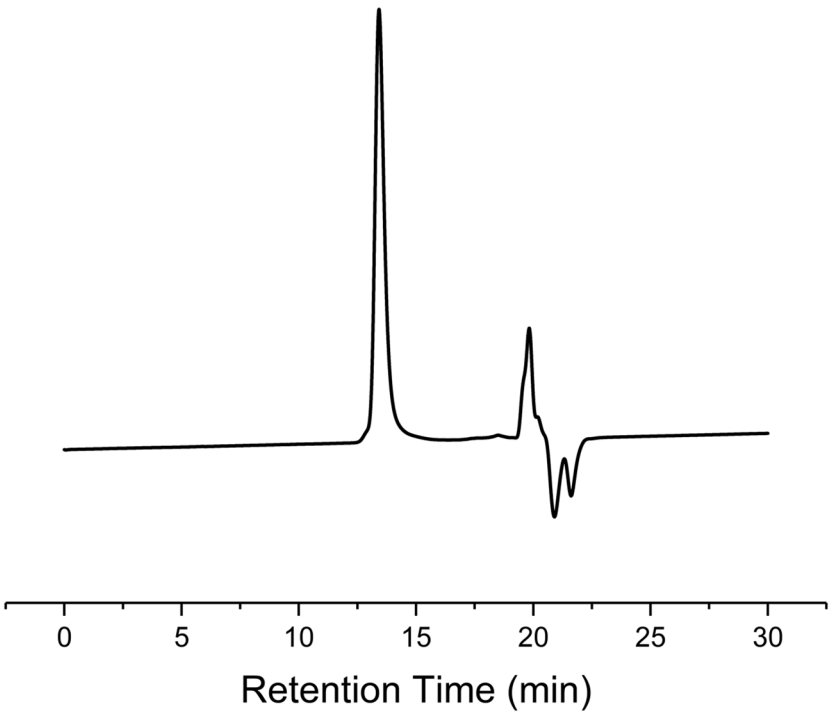


Fig. S52. GPC trace of P(DHN-Me) obtained by [DHN-Me]/[**Zn1**]/[I] = 500/1/1, M_n = 66.0 kg. mol^{-1}, $Đ$ = 1.13 (Table 1, entry 14).

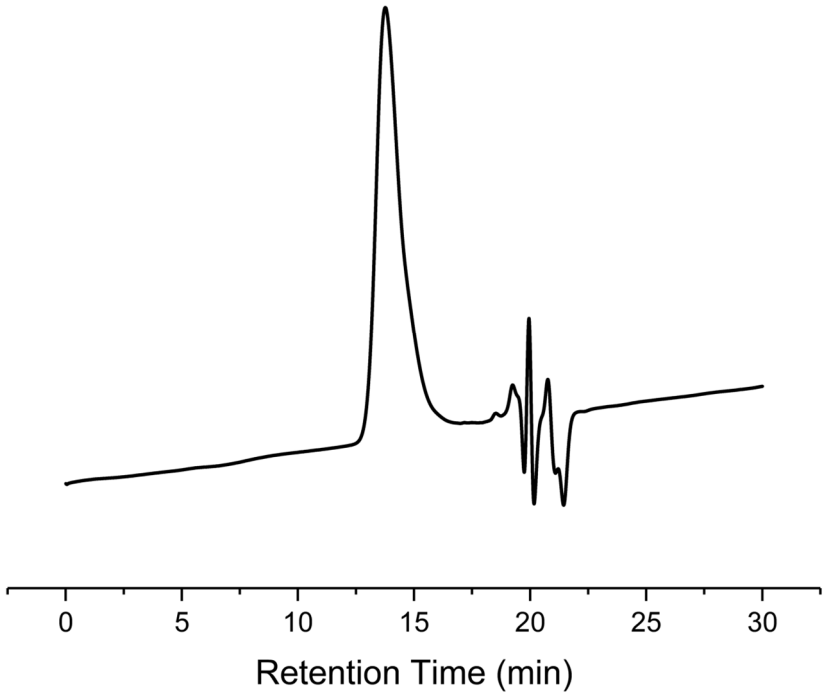


Fig. S53. GPC trace of P[(*R*)-DHN-Me] obtained by [(*R*)-DHN-Me]/[**Zn1**]/[I] = 500/1/1, M_n = 42.5 kg. mol^{-1}, $Đ$ = 1.57 (Table 1, entry 17).

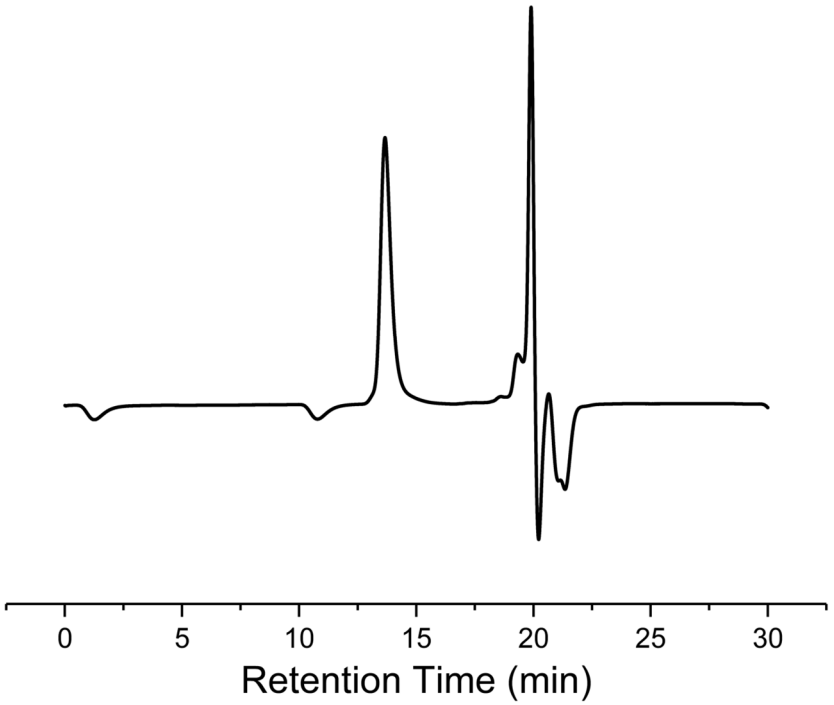


Fig. S54. GPC trace of P(DHN-Et) obtained by [DHN-Et]/[**Zn1**]/[I] = 1000/1/1, M_n = 66.7 kg mol^{-1}, $Đ$ = 1.10 (Table 1, entry 21).

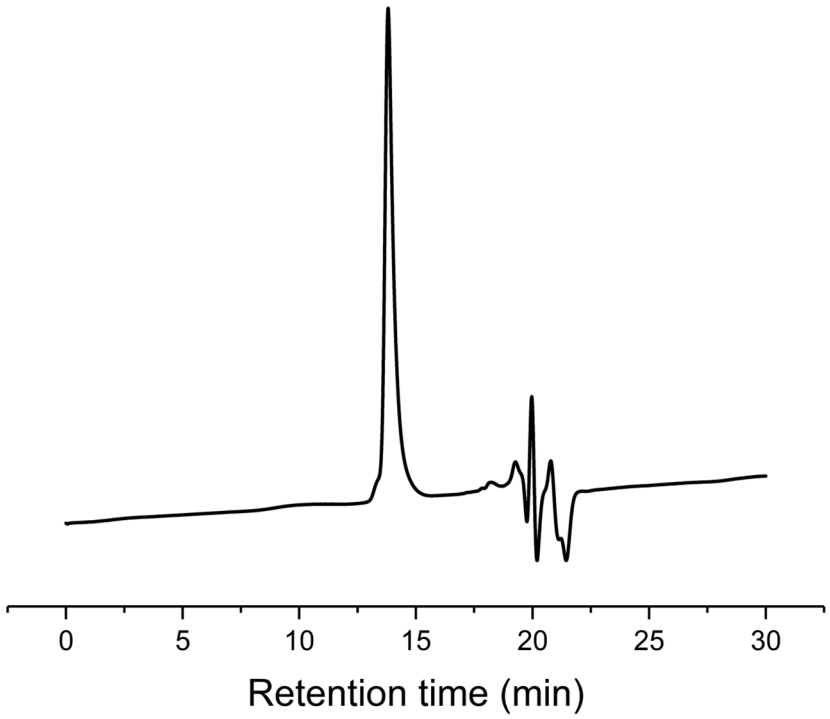


Fig. S55. GPC trace of P(DHB-Me-*co*-DHB-Et) obtained by [DHB-Me]/[DHB-Et]/[**Zn1**]/[I] = 50/1000/1/1, M_n = 57.5 kg mol^{-1}, $Đ$ = 1.13 (Table S1, entry 1).

General Stereocomplexation Procedures

Stereocomplexes were prepared from a mixture of isotactic (*R*)-polymer and (*S*)-polymer in a 1:1 molar ratio (approximately 100 mg total). The solid polymer sample was dissolved in $CHCl_3$ (20 mg mL^{-1}), filtered through a plastic frit (0.22 μm pore size nylon filter), and allowed to evaporate slowly and undisturbedly for 3–7 days. The obtained crystalline solid was collected and dried in a vacuum oven at 60 °C to a constant weight.

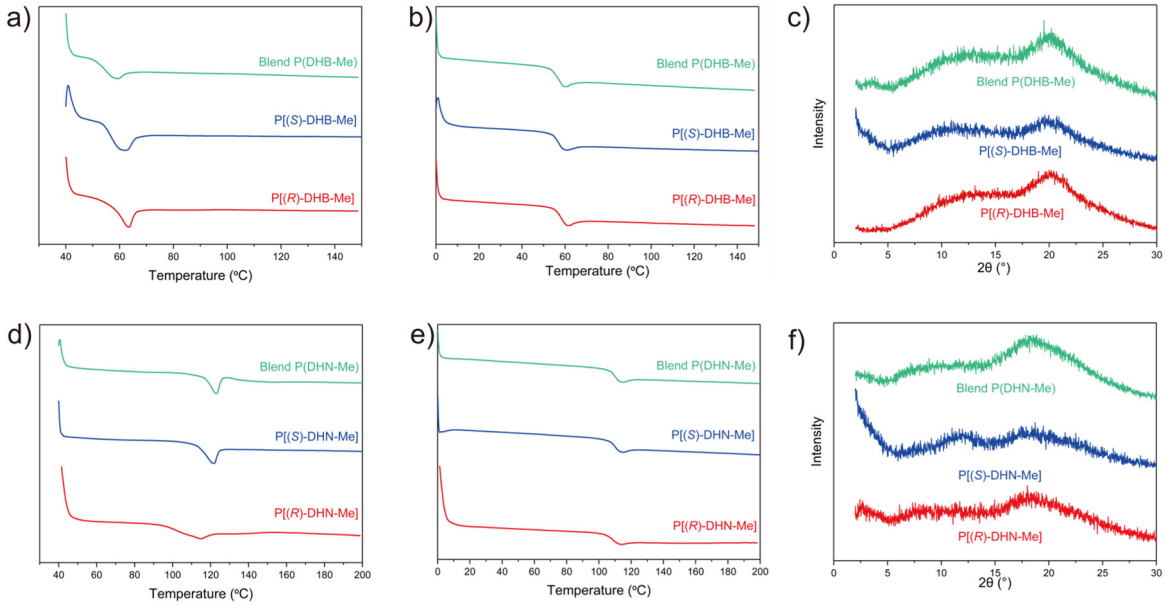


Fig. S56. a) DSC curves for P(DHB-Me)s (first heating, 10°C min^{-1}); b) DSC curves for P(DHB-Me)s (second heating, 10°C min^{-1}); c) PXRD spectra of P(DHB-Me)s; d) DSC curves for P(DHN-Me)s (first heating, 10°C min^{-1}); e) DSC curves for P(DHN-Me)s (second heating, 10°C min^{-1}); f) PXRD spectra of P(DHN-Me)s.

Mechanical Property

Table S2. Summary of mechanical properties of polymers. [a]

Polymer	M_n/KDa	E/GPa	σ_Y/MPa	σ_B/MPa	Elongation/%
P(DHB-Me)	97.6	2.17 ± 0.36	-	33.69 ± 5.39	10.91 ± 2.15
P(DHB-Et)	123	0.74 ± 0.17	5.78 ± 2.91	3.16 ± 0.57	762.63 ± 94.40
P(DHN-Me)	88.7	2.11 ± 0.34	-	45.35 ± 1.94	3.10 ± 0.45
P(DHN-Et)	66.7	0.98 ± 0.11	-	35.18 ± 1.58	4.30 ± 0.62
P(DHB-Me-*co*-DHB-Et)	57.5	0.82 ± 0.11	-	38.16 ± 3.56	5.86 ± 0.56

[a]Condition: Tested by uniaxial tensile tests. Strain rate of 10 mm/min, E: Tensile modulus, σ_Y: yield strength, σ_B: break strength.

Table S3. Summary of mechanical properties of P(DHB-Me).[a]

Sample	E/MPa	σ_B/MPa	Elongation/%
1	1832.32	33.61	14.25
2	2889.78	44.42	11.84
3	1806.38	33.36	9.97
4	2195.33	34.68	9.41
5	2104.90	33.76	9.08

[a]Condition: Tested by uniaxial tensile tests. Strain rate of 10 mm/min, E: Tensile modulus, σ_B: break strength.

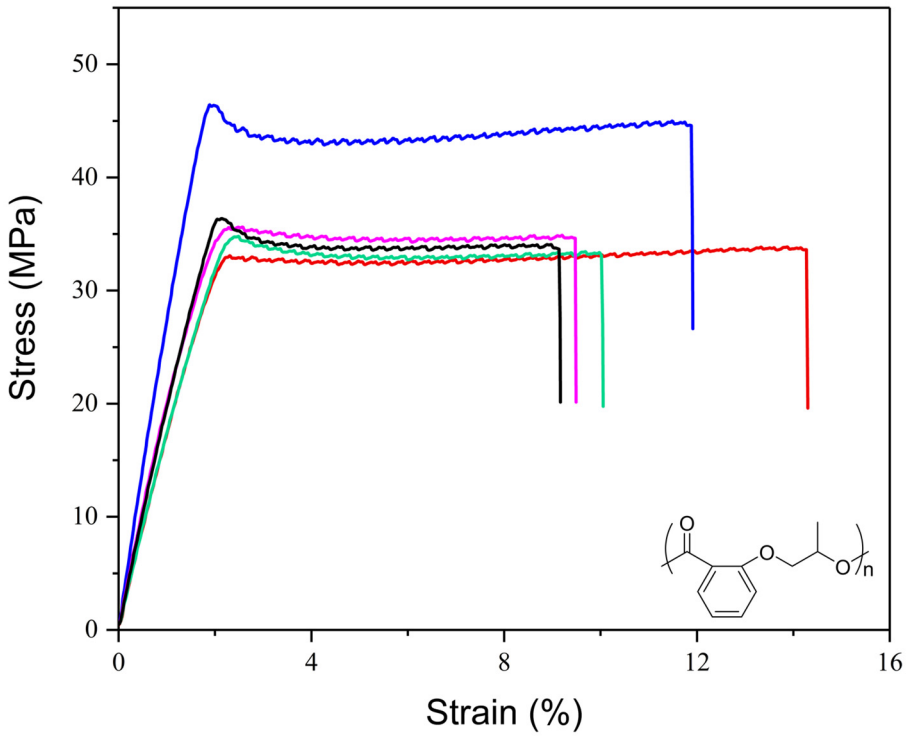


Figure S57. Stress-strain curves of P(DHB-Me).

Table S4. Summary of mechanical properties of P(DHB-Me)s.

Polymer	M_n/KDa	E/GPa	σ_b/MPa	Elongation/%
P(DHB-Me)	35.0	2.28 ± 0.20	39.30 ± 1.31	2.89 ± 0.27
P[(*R*)-DHB-Me]	36.6	2.40 ± 0.14	31.30 ± 1.82	1.73 ± 0.24
P[(*S*)-DHB-Me]	36.6	2.51 ± 0.14	35.69 ± 4.27	1.96 ± 0.21

[a] Condition: Tested by uniaxial tensile tests. Strain rate of 5 mm/min, E: Tensile modulus, σ_Y: yield strength, σ_B: break strength.

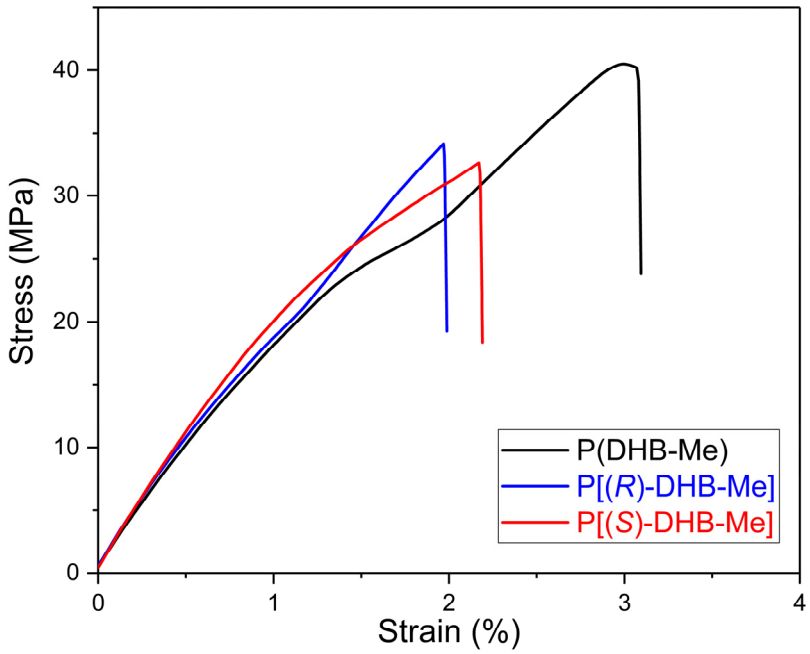


Fig S58. Stress-Strain curves of P(DHB-Me)s.

Table S5. Summary of mechanical properties of P(DHB-Et).[a]

Sample	E/MPa	σ_Y/MPa	σ_B/MPa	Elongation/%
1	719.29	7.66	2.87	719.29
2	498.07	2.41	2.43	885.31
3	702.43	3.51	3.16	852.97
4	977.22	9.50	3.97	680.84
5	803.47	5.80	2.99	700.44

[a]Condition: Tested by uniaxial tensile tests. Strain rate of 10 mm/min, E: Tensile modulus, σ_Y: yield strength, σ_B: break strength.

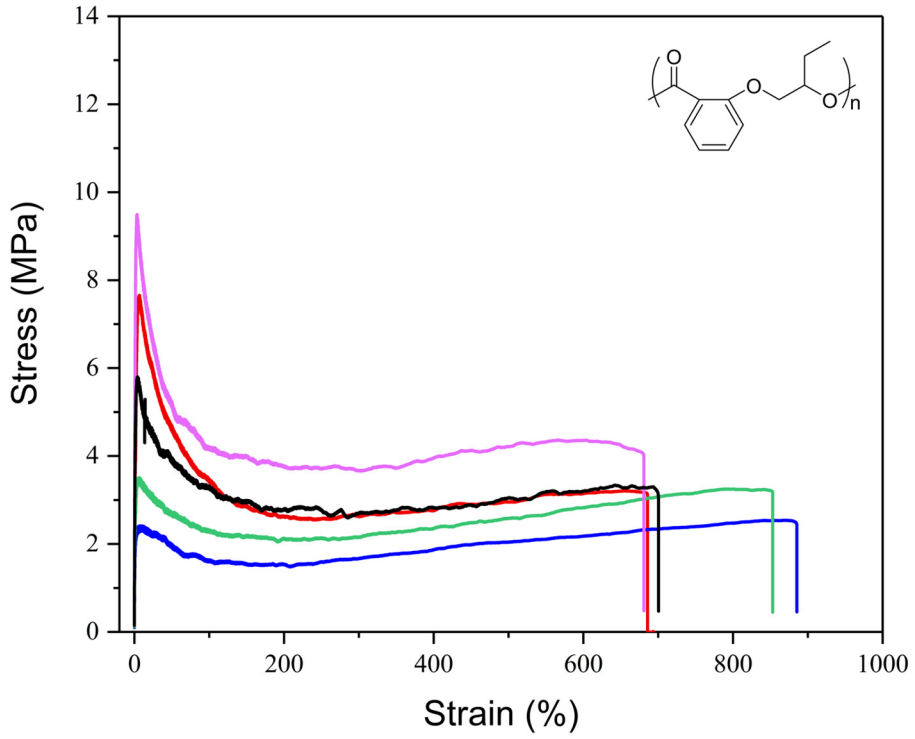


Figure S59. Stress-strain curves of P(DHB-Et).

Table S6. Summary of mechanical properties of P(DHN-Me).[a]

Sample	E/MPa	σ_B/MPa	Elongation/%
1	1948.34	42.23	3.66
2	2014.98	46.11	2.74
3	2338.01	46.48	2.66
4	2074.36	44.80	3.47
5	2176.40	47.13	2.95

[a]Condition: Tested by uniaxial tensile tests. Strain rate of 10 mm/min, E: Tensile modulus, σ_B: break strength.

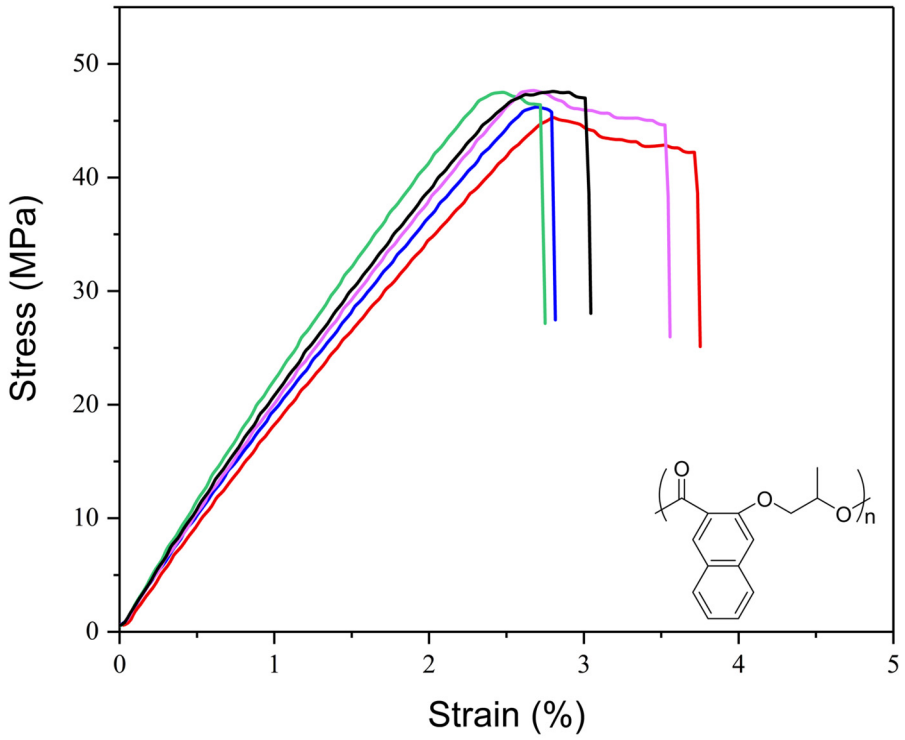


Figure S60. Stress-strain curves of P(DHN-Me).

Table S7. Summary of mechanical properties of P(DHN-Et).[a]

Sample	E/MPa	σ_B/MPa	Elongation/%
1	947.96	36.69	4.93
2	841.30	34.79	4.78
3	961.53	33.67	3.99
4	1017.85	36.98	4.40
5	1135.20	33.77	3.40

[a]Condition: Tested by uniaxial tensile tests. Strain rate of 10 mm/min, E: Tensile modulus, σ_B: break strength.

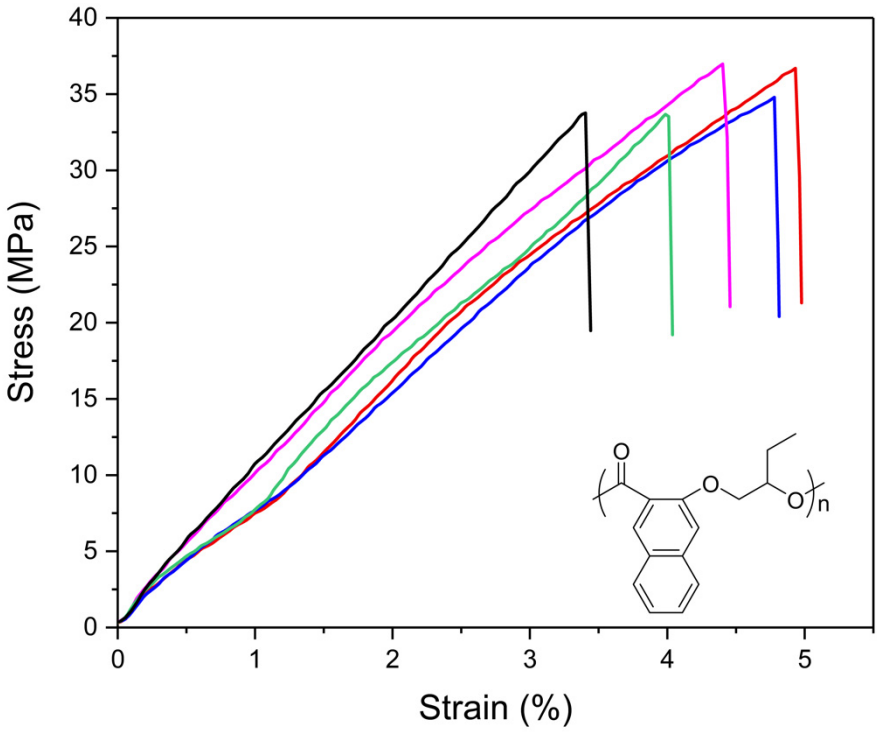


Figure S61. Stress-strain curves of P(DHN-Et).

Table S8. Summary of mechanical properties of P(DHB-Me-*co*-DHB-Et).[a]

Sample	E/MPa	σ_B/MPa	Elongation/%
1	881.97	41.55	5.70
2	635.25	32.10	6.64
3	931.03	38.88	5.19
4	837.59	39.14	5.59
5	810.76	39.11	6.17

[a]Condition: Tested by uniaxial tensile tests. Strain rate of 10 mm/min, E: Tensile modulus, σ_B: break strength.

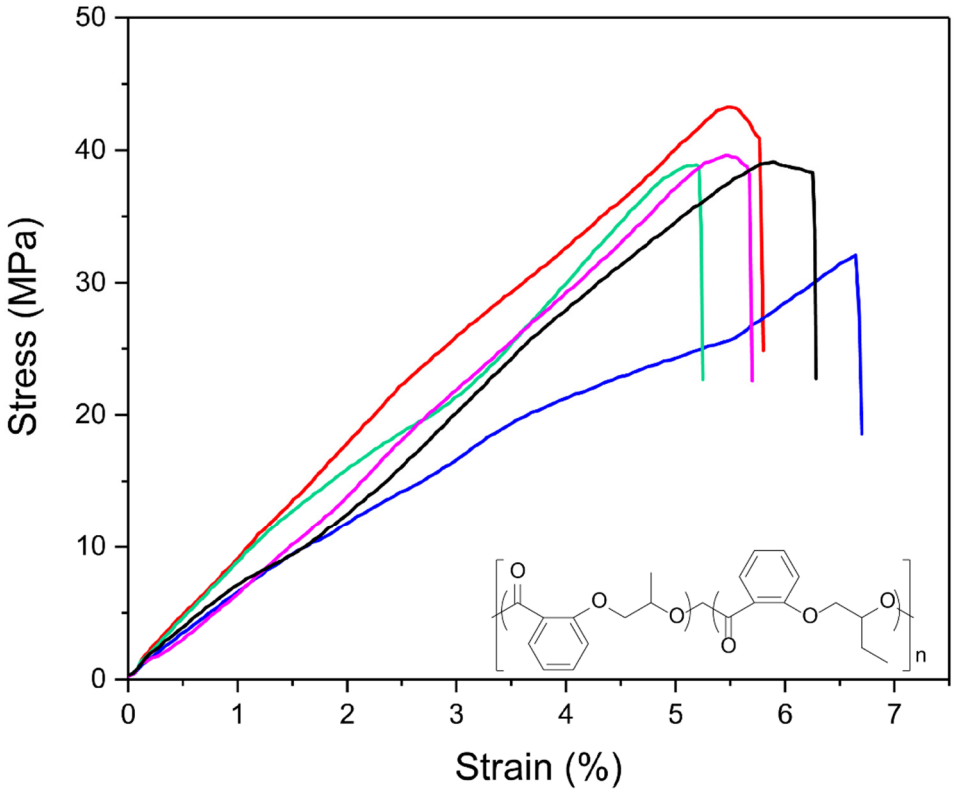


Figure S62. Stress-strain curves of P(DHB-Me-*co*-DHB-Et).

Thermodynamic study

In an argon-filled glovebox, a toluene stock solution of DHB-Me (712.2 mg, 4 mmol), *p*-tolylmethanol (4.9 mg, 0.04 mmol) and **Zn1** (23.6 mg, 0.04 mmol) was prepared in a 2 mL volumetric flask. The stock solution was divided equally to 4 vials (2 mL). Then the vials were sealed and brought outside of glovebox. After stirring at specific temperature for 5 h, the reaction was quenched by addition of 0.3 mL $CDCl_3$ containing benzoic acid (1 *wt*%). The polymerization reaction reached equilibrium at 45−75 °C and the conversion of DHB-Me was monitored by ^{1}H NMR. The equilibrium monomer concentration, $[DHB\text{-}Me]_{eq}$, was measured to be 0.68, 0.80, 0.94 and 1.10 mol. L^{-1} for 45 °C, 55 °C, 65 °C and 75 °C. The Van't Hoff plot of $\ln[DHB\text{-}Me]_{eq}$ versus $1/T \times 10^3$ gave a linear fitting with a slope of –1.78 and an intercept of 5.21, from which the thermodynamic parameters were calculated to be ΔH_p° = –14.8 kJ. mol^{-1} and ΔS_p° = –43.3 J. mol^{-1}. K^{-1}, based on the equation $\ln[DHB\text{-}Me]_{eq} = \Delta H_p^\circ/RT - \Delta S_p^\circ/R$, where R is the molar gas constant. T_c was calculated to be 69 °C at $[DHB\text{-}Me]_0$ = 1 mol/L, based on the equation $T_c = \Delta H_p^\circ/(\Delta S_p^\circ + R\ln [DHB\text{-}Me]_0)$.

Table S9. Raw data over equilibrium conversion at various temperatures for DHB-Me.[a]

Entry	T (K)	Conv. [b] (%)	M_0 (mol/L)	$T^{-1} \times 10^3$ (K^{-1})	$[M]_{eq}$ (mol/L)	$\ln[M_{eq}]$ (mol/L)
1	318.3	66	2.0	3.14	0.68	-0.3857
2	328.3	60	2.0	3.05	0.80	-0.2231
3	338.3	53	2.0	2.96	0.94	-0.0619
4	348.3	45	2.0	2.87	1.10	0.0953

[a]Reaction conditions: Catalyst = **Zn1**, initiator (I) = *p*-tolylmethanol, toluene, [DHB-Me]/[**Zn1**]/[I] = 100/1/1, $[M]_0$ = 2 mol. L^{-1}. [b]Monomer conversion measured by ^{1}H NMR of the quenched solution.

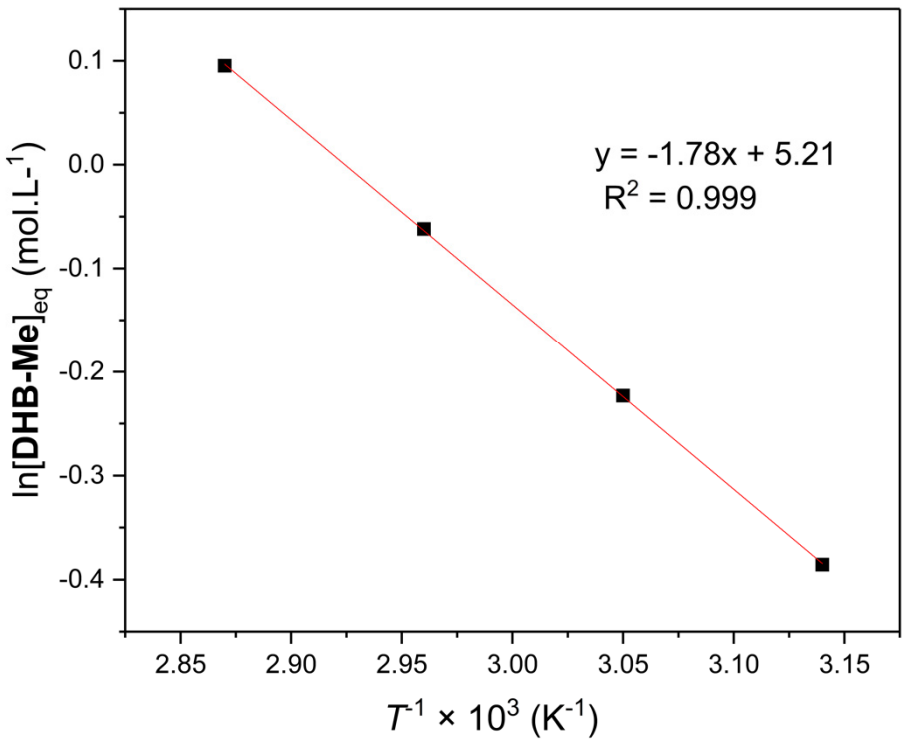


Fig. S63. Van't Hoff plot of $\ln[DHB\text{-}Me]_{eq}$ *vs.* reciprocal of the absolute temperature (T^{-1}).

General procedure for the depolymerization of polymers in dilute solutions

The depolymerization was conducted at 120 °C or 140 °C with **Zn1** or TBD as the catalyst. Depolymerization of P(DHB-Me) was used as an example. Inside an argon-filled glovebox, a 15 mL pressure tube was charged with the purified P(DHB-Me) (18 mg), **Zn1** (5 mol%) and toluene (5 mL). The reactor was sealed, taken out of the glovebox, and immersed in the oil bath. The mixture was stirred at 120 °C for 0.5 h. The reaction mixture (3 mL) was withdrawn and concentrated under reduced pressure to determine the conversion by ^{1}H NMR spectroscopy.

Table S10. Results for depolymerization of polymers in dilute solutions.[a]

Entry	Polymer	Catalyst	Catalyst loading (mol %)	Temperature (°C)	Time (h)	Conv.[b] (%)
1	**P(DHB-Me)**	**Zn1**	5	120	0.5	96
2	**P(DHB-Me)**	TBD	10	120	12	63
3	**P(DHB-Et)**	**Zn1**	5	120	0.5	94
4	**P(DHB-Et)**	TBD	10	120	12	74
5	**P(DHN-Me)**	**Zn1**	5	140	0.5	80
6	**P(DHN-Me)**	TBD	10	140	12	93
7	**P(DHN-Et)**	**Zn1**	5	140	0.5	83
8	**P(DHN-Et)**	TBD	10	140	12	98

[a]Reaction conditions: [M] = 0.2 M, toluene. [b]Polymer conversion measured by ^{1}H NMR of the solution.

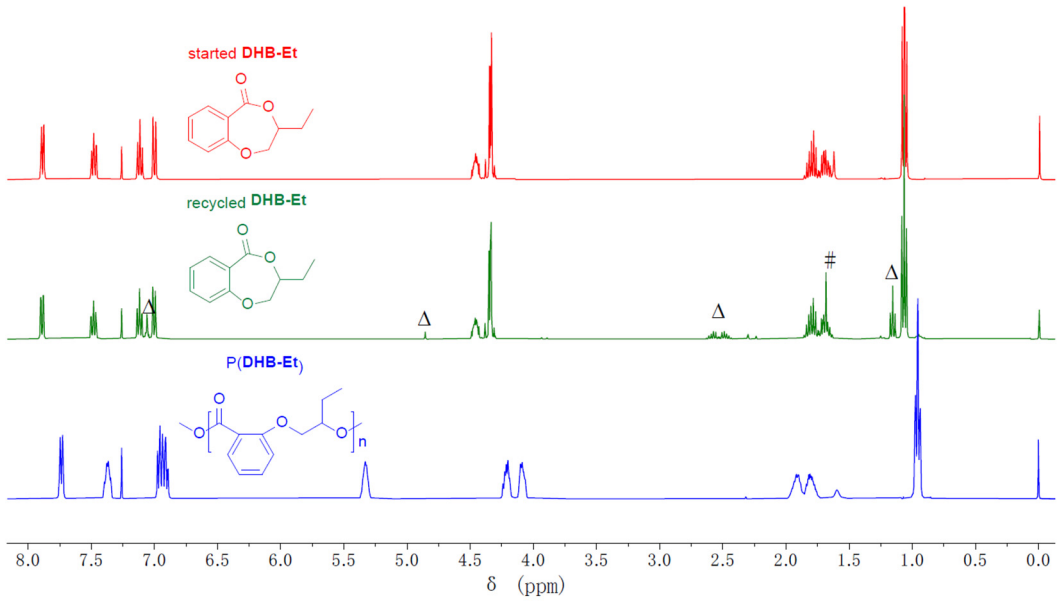


Fig. S64. ^{1}H NMR spectra of P(DHB-Et) prepared by [DHB-Et]/[**Zn1**]/[I] = 100/1/1 (bottom), recycled DHB-Et after depolymerization (middle) and clean starting DHB-Et for comparison (top). (*solvent toluene impurity, Δ catalyst **Zn1** residual, # H_2O)

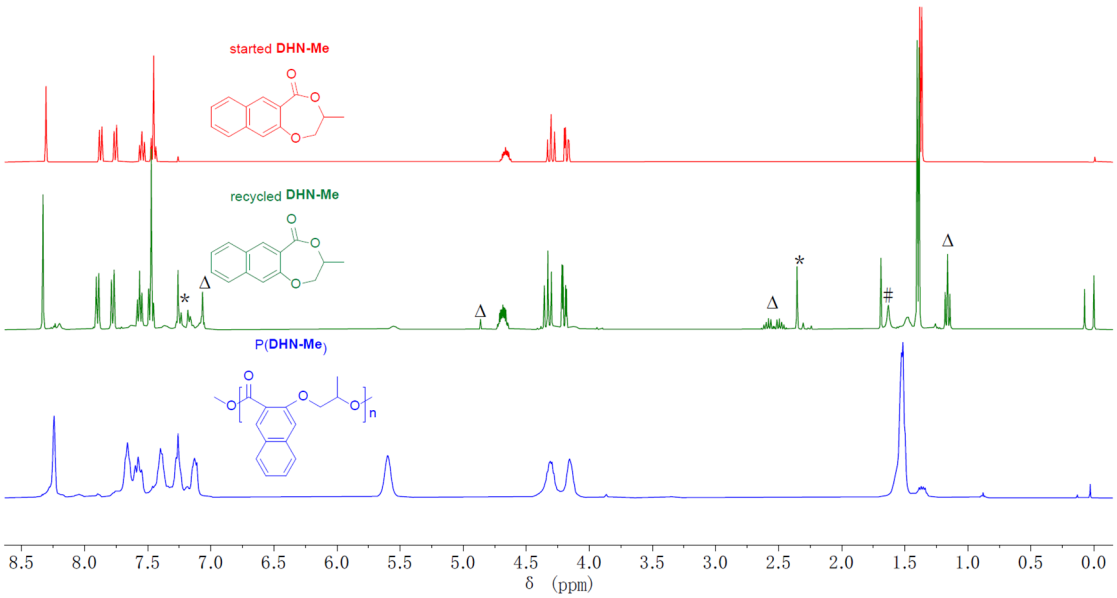


Fig. S65. ^{1}H NMR spectra of P(DHN-Me) prepared by [DHN-Me]/[**Zn1**]/[I] = 100/1/1 (bottom), recycled DHN-Me after depolymerization (middle) and clean starting DHN-Me for comparison (top). (*solvent toluene impurity, Δ catalyst **Zn1** residual, # H_2O)

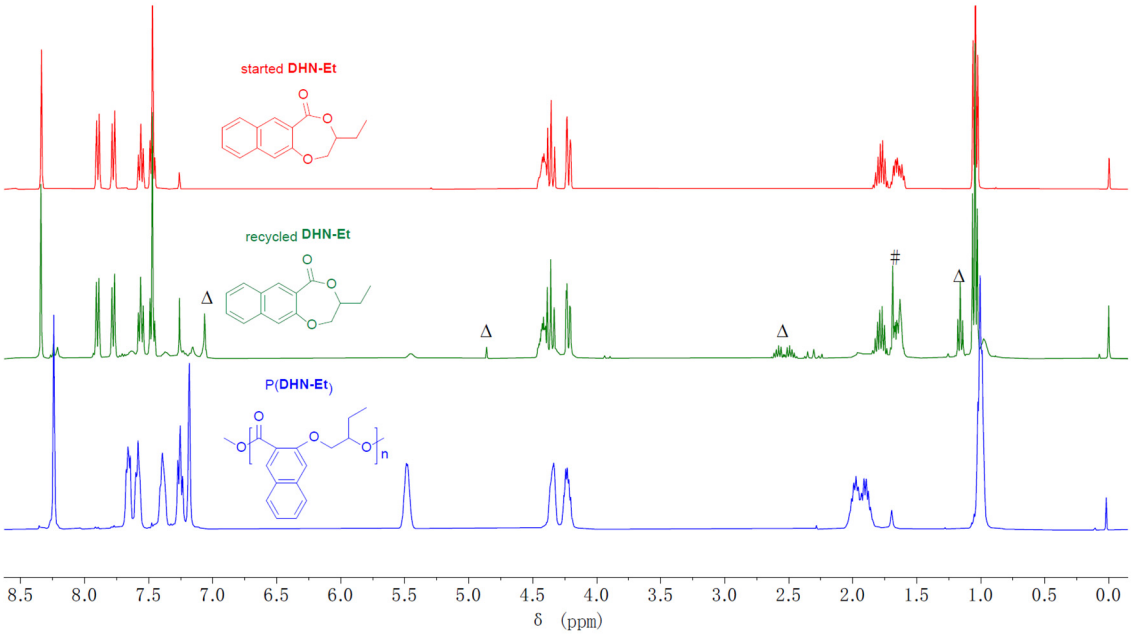


Fig. S66. ^{1}H NMR spectra of P(DHN-Et) prepared by [DHN-Et]/[**Zn1**]/[I] = 100/1/1 (bottom), recycled DHN-Et after depolymerization (middle) and clean starting DHN-Et for comparison (top). (Δ catalyst **Zn1** residual, # H_2O)

Reference

[1] M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123,* 8738-8749.