Supporting Information for

Bifunctional Thiourea-Based Organocatalysts Promoted Kinetic Resolution Polymerization of Racemic Lactide to Isotactic Polylactide

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Experimental Details

Reagents, Instruments, and Methods

All synthesis and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an inert gas Ar-filled glovebox. High-performance liquid chromatography (HPLC)-grade anhydrous tetrahydrofuran (THF), toluene (TOL), chloroform ($CHCl_3$), and dichloromethane (DCM) were dried via a Vigor YJC-5 solvent purification system and stored over activated Sigma-Aldrich 4 Å molecular sieves in glovebox. Other commercial reagents were purchased from Energy Chemical and used as received without further purification.

L-Lactide (L-LA), *D*-lactide(D-LA), *rac*-lactide (*rac*-LA) were purchased from Energy Chemical and further purified by recrystallizations from dry toluene and double sublimation under vacuum. The initiators *D*-methyl lactate, *L*-methyl lactate, and benzyl alcohol (BnOH) was purchased from Energy Chemical and used as received without further purification. The initiator 4-methylbenzyl alcohol was purchased from Adamas and purified via sublimation at 55 ℃ under vacuum. Other commercial reagents were purchased from Energy Chemical and used as received.

NMR Spectroscopy

^1H and ^{13}C NMR spectra were recorded on an Agilent 400-MR DD2 or a Bruker AV II-400 MHz spectrometer (^1H: 400 MHz, ^{13}C: 100 MHz). Chemical shifts (δ) for ^1H and ^{13}C NMR spectra are given in ppm relative to $SiMe_4$. ^1H NMR chemical shifts were referenced as follows: δ 7.26 ppm for chloroform-d ($CDCl_3$), ^{13}C NMR chemical shifts were referenced as follows: δ 77.16 ppm for chloroform-d ($CDCl_3$). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiple. Tacticity of polymers was determined from the methine region of the homodecoupled ^1H NMR spectrum. P_m, the probability of forming a new isotactic dyad, was calculated utilizing methods established in the literature.[1]

High-resolution mass spectra (HRMS)

Analyses were performed on LCMS-IT-TOF (Liquid Chromatograph Mass Spectrometer, shimadzu) that combines QIT (ion trap) and TOF (time-of-flight) technologies.

X-Ray single-crystal diffraction

Data were collected on an Agilent Technologies Gemini plus single crystal diffraction.

Size exclusion chromatography (SEC)

Measurements of polymer number-average molecular weight (M_n) and molecular weight

distributions or polydispersity indices ($Đ = M_w/M_n$) were performed via 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 9 PS standards, and chromatograms were processed with Agilent OpenLab CDS Acquisition 2.5 molecular weight characterization software.

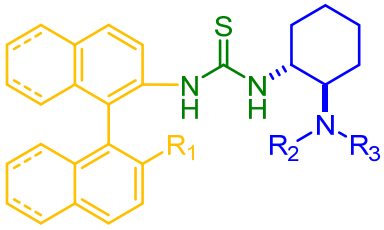
High Performance Liquid Chromatography (HPLC)

HPLC was performed on Agilent 1260 Infinity II Quaternary LC system. Enantiomeric excesses (ee) were determined by chiral HPLC analysis on Daicel chiralpak IA columns. The column employed and the respective solvent mixture are indicated for each experiment. The chromatograms were processed with Agilent OpenLab CDS software.

Differential scanning calorimetry (DSC)

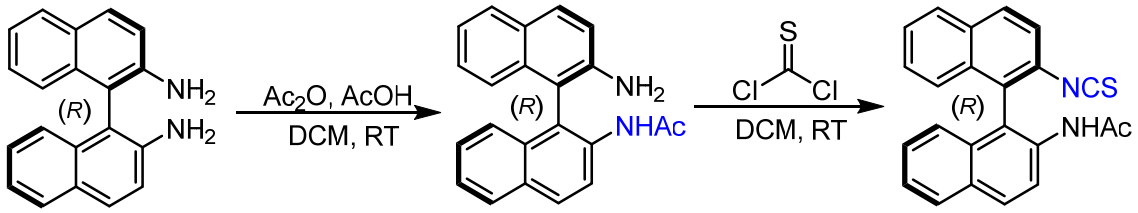
Melting-transition temperature (T_m) and glass-transition temperature (T_g) of purified and thoroughly dried polymer samples were measured by differential scanning calorimetry (DSC) on DSC25, TA Instrument. All T_m, T_c and T_g values were obtained from a second scan after the thermal history was removed from the first scan. The second heating rate was 10 °C/min and cooling rate was 10 °C/min.

Synthesis of catalysts



Scheme S1. Synthesis of catalysts.

1. Synthesis of (*R*)-BINAM-Ac-NCS



(*R*)-BINAM-Ac (*R*)-BINAM-Ac-NCS

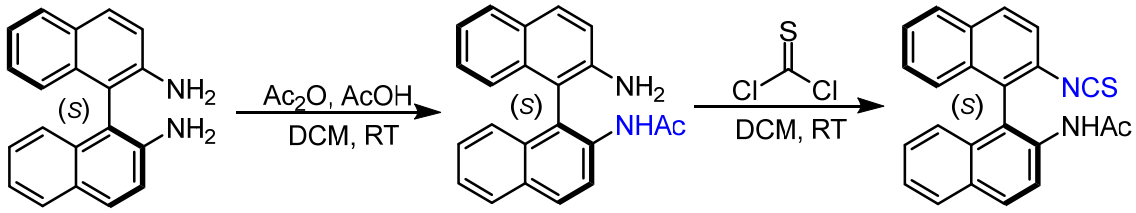
Literature procedures were modified for the preparation of (*R*)-BINAM-Ac-NCS.[2]

To a solution of (*R*)-(+)-1,1'-binaphthyl-2,2'-diamine (2.84 g, 10 mmol) and AcOH (6 mL, 100 mmol) in 70 mL of dried DCM was added acetic anhydride (1.0 mL, 10 mmol) at 0 °C under Ar. The resulting solution was stirred for overnight at room temperature, and 3 M NaOH aqueous solution (about 36 mL) was added to adjust the solution to pH = 10. The reaction mixture was extracted with DCM (3 × 20 mL) and the combined organic phases were washed with saturated brine (70 mL) and dried over anhydrous Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 4/1) to give product (*R*)-BINAM-Ac (2.25 g, 69% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J = 9.0 Hz, 1H), 8.00 (d, J = 9.0 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.9 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.43-7.39 (m, 1H), 7.29-7.14 (m, 3H), 7.04 (s, 1H), 6.92 (d, J = 8.3 Hz, 1H), 3.59 (s, 2H), 1.86 (s, 3H). The ^{1}H NMR spectrum was consistent with literature report.[2]

(*R*)-BINAM-Ac (684 mg, 2.1 mmol) was dissolved in DCM (12 mL) and sat. aq. $NaHCO_3$ (12 mL) was added. The resulting biphasic solution was cooled to 0 °C and thiophosgene (0.2 mL, 2.6 mmol) was then slowly added. The reaction mixture was allowed to warm to room temperature and stir for 12 h. The layers were separated, and the aqueous layer was extracted with DCM (3 × 10 mL). The organic layers were collected, washed with brine (30 mL), dried over anhydrous Na_2SO_4. The solution was filtered and concentrated under reduced pressure to give pure product (*R*)-BINAM-Ac-NCS (667 mg, 86% yield) as a pale-yellow solid, which was used directly in the subsequent reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 9.1

Hz, 1H), 8.07-7.93 (m, 4H), 7.56-7.35 (m, 4H),7.30-7.22 (m, 2H), 6.97 (d, J = 8.5 Hz, 1H), 6.64 (s, 1H), 1.83 (s, 3H). The ^{1}H NMR spectrum was consistent with literature report.[2]

2. Synthesis of (*S*)-BINAM-Ac-NCS



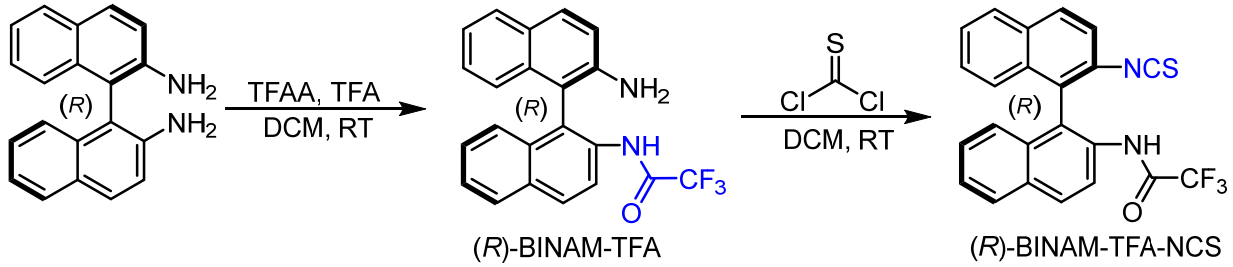
(*S*)-BINAM-Ac (*S*)-BINAM-Ac-NCS

Literature procedures were modified for the preparation of (*S*)-BINAM-Ac-NCS.[2]

To a solution of (*S*)-(−)-1,1'-binaphthyl-2,2'-diamine (2.84 g, 10 mmol) and AcOH (6 mL, 100 mmol) in 70 mL of dried DCM was added acetic anhydride (1.0 mL, 10 mmol) at 0 °C under Ar. The resulting solution was stirred for overnight at room temperature, and 3 M NaOH aqueous solution (about 36 mL) was added to adjust the solution to pH = 10. The reaction mixture was extracted with DCM (3 × 20 mL) and the combined organic phases were washed with saturated brine (70 mL) and dried over anhydrous Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 4/1) to give product (*S*)-BINAM-Ac (2.58 g, 79% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, J = 9.0 Hz, 1H), 8.00 (d, J = 9.0 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.44-7.40 (m, 1H), 7.28-7.14 (m, 3H), 7.04 (s, 1H), 6.92 (d, J = 8.3 Hz, 1H), 3.66 (s, 2H), 1.85 (s, 3H). The ^{1}H NMR spectrum was consistent with literature report.[2]

(*S*)-BINAM-Ac (684 mg, 2.1 mmol) was dissolved in DCM (12 mL) and sat. aq. $NaHCO_3$ (12 mL) was added. The resulting biphasic solution was cooled to 0 °C and thiophosgene (0.2 mL, 2.6 mmol) was then slowly added. The reaction mixture was allowed to warm to room temperature and stir for 12 h. The layers were separated, and the aqueous layer was extracted with DCM (3 × 10 mL). The organic layers were collected, washed with brine (30 mL), dried over anhydrous Na_2SO_4. The solution was filtered and concentrated under reduced pressure to give pure product BINAM-Ac-NCS (741 mg, 96% yield) as a pale-yellow solid, which was used directly in the subsequent reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, J = 9.2 Hz, 1H), 8.07-7.93 (m, 4H), 7.56-7.35 (m, 4H), 7.30-7.22 (m, 2H), 6.97 (d, J = 8.5 Hz, 1H), 6.65 (s, 1H), 1.82 (s, 3H). The ^{1}H NMR spectrum was consistent with literature report.[2]

3. Synthesis of (*R*)-BINAM-TFA-NCS

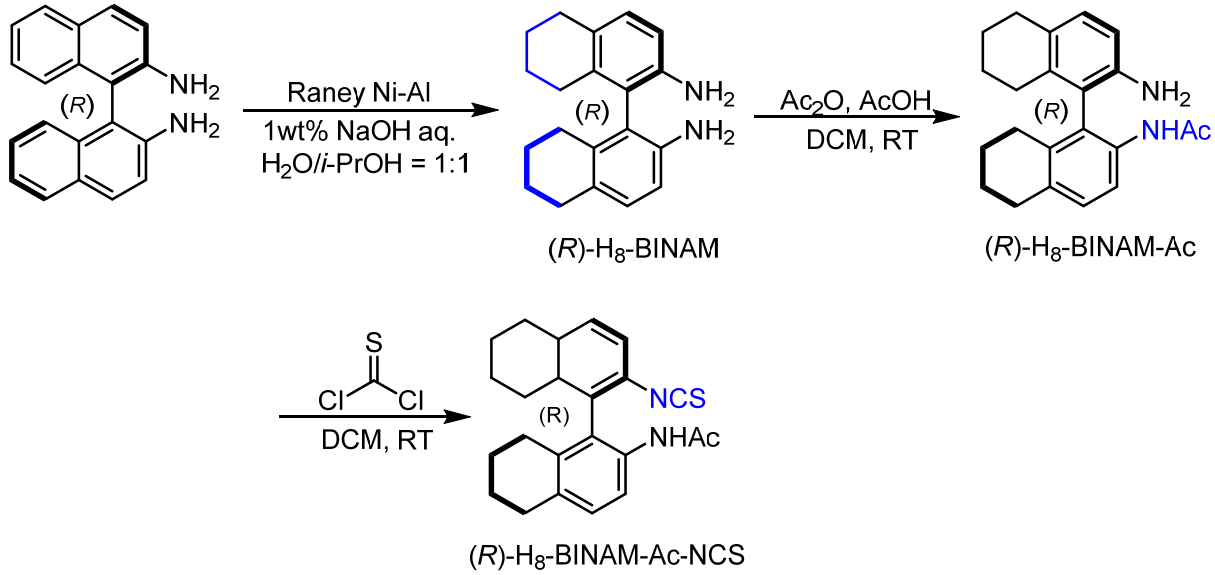


Literature procedures were modified for the preparation of (*R*)-BINAM-TFA-NCS.[2]

To a solution of (*R*)-(+)-1,1'-binaphthyl-2,2'-diamine (2.84 g, 10 mmol) and trifluoroacetic acid (TFA) (8.5 mL) in 60 mL of dried DCM was added trifluoroacetic anhydride (1.41 mL, 10 mmol) at 0 °C under Ar. The resulting solution was stirred for overnight at room temperature, and 3 M NaOH aqueous solution (about 36 mL) was added to adjust the solution to pH = 10. The reaction mixture was extracted with DCM (3 × 20 mL) and the combined organic phases were washed with saturated brine (70 mL) and dried over anhydrous Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 8/1) to give product (*R*)-BINAM-TFA (3.27 g, 86% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 9.1 Hz, 1H), 8.07 (d, J = 9.0 Hz, 1H), 7.97 (d, J = 8.6 Hz, 1H), 7.93 (s, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.52-7.48 (m, 1H), 7.36-7.14 (m, 4H), 7.16 (d, J = 8.8 Hz, 1H), 6.87-6.84 (m, 1H), 3.68 (s, 2H). The ^{1}H NMR spectrum was consistent with literature report.[2]

(*R*)-BINAM-TFA (1.75 g, 4.6 mmol) was dissolved in DCM (21 mL) and sat. aq. $NaHCO_3$ (21 mL) was added. The resulting biphasic solution was cooled to 0 °C and thiophosgene (0.45 mL, 5.6 mmol) was then slowly added. The reaction mixture was allowed to warm to room temperature and stir for 12 h. The layers were separated, and the aqueous layer was extracted with DCM (3 × 20 mL). The organic layers were collected, washed with brine (60 mL), dried over anhydrous Na_2SO_4. The solution was filtered and concentrated under reduced pressure to give pure product (*R*)-BINAM-TFA-NCS (1.67 g, 86% yield) as a pale-yellow solid, which was used directly in the subsequent reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 9.0 Hz, 1H), 8.13 (d, J = 9.3 Hz, 1H), 8.06 (d, J = 8.7 Hz, 1H), 7.99 (dd, J = 8.2, 3.4 Hz, 2H), 7.61-7.48 (m, 3H), 7.44-7.32 (m, 3H), 7.17 (d, J = 8.6 Hz, 1H), 7.11 (d, J = 8.5 Hz, 1H). The ^{1}H NMR spectrum was consistent with literature report.[2]

4. Synthesis of (*R*)-H_8-BINAM-Ac-NCS



(*R*)-H_8-BINAM (*R*)-H_8-BINAM-Ac

(*R*)-H_8-BINAM-Ac-NCS

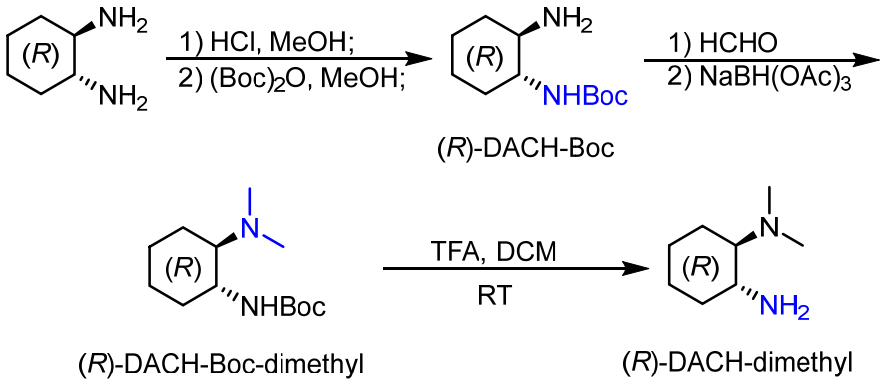
Literature procedures were modified for the preparation of (*R*)-H_8-BINAM-Ac-NCS.[3]

To a stirred mixture of (*R*)-(+)-1,1'-binaphthyl-2,2'-diamine (284 mg, 1.0 mmol) and Raney Ni-Al alloy (2.00 g) in isopropanol (100 mL) and water (100 mL) was slowly added 1.0 wt% aqueous NaOH solution (200 mL) over 2 h at 90 °C. After stirring for 30 h, the reaction mixture was cooled to room temperature. The mixture was then filtered through Celite, and the filter cake was washed with ethyl acetate (EA). The filtrates were concentrated in vacuo to remove isopropanol and then exacted with DCM, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 7/1) to give product (*R*)-H_8-BINAM (243 mg, 83% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (d, J = 8.1 Hz, 2H), 6.62 (d, J = 8.1 Hz, 2H), 2.90 (s, 4 H), 2.79-2.65 (m, 4 H), 2.33-2.12 (m, 4H), 1.78-1.61 (m, 8H).

To a solution of (*R*)-H_8-BINAM (1.21 g, 4.1 mmol) and AcOH (2.4 mL, 41.4 mmol) in 30 mL of dried DCM was added acetic anhydride (0.39 mL, 4.1 mmol) at 0 °C under Ar. The resulting solution was stirred for overnight at room temperature for 24 h, and 3 M NaOH aqueous solution was added to adjust the solution to pH = 10. The reaction mixture was extracted with DCM (3 × 20 mL) and the combined organic phases were washed with saturated brine (70 mL) and dried over anhydrous Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 4/1) to give product (*R*)-H_8-BINAM-Ac (0.98 g, 71% yield) as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.4 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.76 (s, 1H), 6.63 (d, J = 8.2 Hz, 1H), 3.32 (s, 2H), 2.78 (t, J = 6.2 Hz, 2H), 2.72 (t, J = 6.3 Hz, 2H), 2.35-2.12 (m, 2H), 2.09 (t, J = 6.3 Hz, 2H), 1.91 (s, 3H), 1.82-1.56 (m, 8H).

(*R*)-H$_8$-BINAM-Ac (983 mg, 2.9 mmol) was dissolved in DCM (15 mL) and sat. aq. NaHCO$_3$ (15 mL) was added. The resulting biphasic solution was cooled to 0 °C and thiophosgene (0.2 mL, 2.6 mmol) was then slowly added. The reaction mixture was allowed to warm to room temperature and stir for 11 h. The layers were separated, and the aqueous layer was extracted with DCM (3 × 10 mL). The organic layers were collected, washed with brine (30 mL), dried over anhydrous Na$_2$SO$_4$. The solution was filtered and concentrated under reduced pressure to give pure product (*R*)-H$_8$-BINAM-Ac-NCS (977 mg, 88% yield) as a pale-yellow solid, which was used directly in the subsequent reaction without further purification. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.99 (d, J = 8.4 Hz, 1H), 7.16 (d, J = 8.4 Hz, 1H), 7.14-7.04 (m, 2H), 6.37 (s, 1H), 3.09-2.62 (m, 4H), 2.33-1.99 (m, 4H), 1.91 (s, 3H),1.82-1.63 (m, 8H).

5. Synthesis of (*R*)-DACH-dimethyl



Literature procedures were modified for the preparation of (*R*)-DACH-dimethyl.[4, 5]

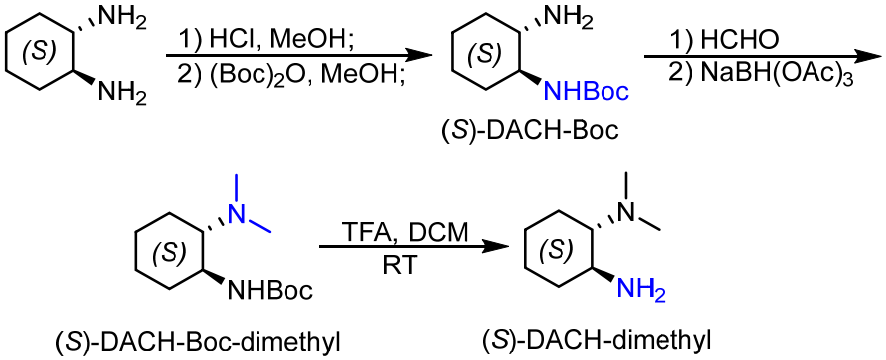
(1*R*, 2*R*)-(−)-1,2-Diaminocyclohexane (9.20 g, 80.6 mmol) was dissolved in 60 mL methanol and the solution was cooled to 0 °C. 37% HCl (6.70 mL, 80.6 mmol) was dissolved in 30 mL methanol and added dropwise to the diamine at 0 °C. The reaction mixture was allowed to warm to room temperature and further stirred at RT for 1 h. Di-*tert*-butyl dicarbonate (17.59 g, 80.6 mmol) was dissolved in 30 mL methanol and added dropwise to the reaction mixture at RT over 40 min. The solution was stirred at RT for 3 h. The solvent was removed under reduced pressure, and the resultant yellow solid was washed with diethyl ether (3 × 50 mL), yielding a white solid. The remaining residue was dissolved in 100 mL chloroform and treated with 40 mL 3.0 M NaOH. The collected organic layer was washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure to obtain (*R*)-DACH-Boc (15.58 g, 90% yield) as an off-white solid which was used directly for the next step without further purification. ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.45 (s, 1H), 3.12 (d, J = 10.8 Hz, 1H), 2.30 (td, J = 10.3 Hz, 4.0 Hz, 1H), 2.08-1.88 (m, 2H), 1.77-1.63 (m, 2H), 1.44 (s, 9H), 1.36-1.01 (m, 6H).

To a solution of (*R*)-DACH-Boc (2.14 g, 10.0 mmol) in DCM (100 mL) was added aq. HCHO

(37%, 1.5 mL, 20 mmol) and the mixture was stirred at RT for 15 min. $NaBH(OAc)_3$ (4.88 g, 23 mmol) was added and stirring was continued for 6 h at RT. Saturated $NaHCO_3$ (300 mL) was added and stirring was continued for 15 min. The layers were separated, and the aqueous phase was extracted with DCM (3 × 40 mL). The combined organic layer was dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EA/MeOH = 8/1) to give product (*R*)-DACH-Boc-dimethyl (2.21 g, 91% yield) as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.30 (s, 1H), 3.32-3.11 (m, 1H), 2.44 (d, J = 12.7 Hz, 1H), 2.22 (s, 6H), 1.98 (s, 1H), 1.84-1.74 (m, 2H), 1.69-1.60 (m, 1H), 1.44 (s, 9H), 1.29-0.98 (m, 4H).

To a solution of (*R*)-DACH-Boc-dimethyl (2.21 g, 9.1 mmol) in 100 mL DCM was added 25 mL trifluoroacetic acid. The reaction mixture was stirred at RT for 12 h. Solvent was removed under reduced pressure, 3.0 M NaOH was added until pH = 10 and the mixture was extracted with DCM (3 × 40 mL). The combined organic phases were washed with brine dried over Na_2SO_4 and concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (EA/MeOH = 4/1) to give product (*R*)-DACH-dimethyl (0.39 g, 30% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (td, J = 10.2, 4.1 Hz, 1H), 2.21 (s, 6H), 2.05-1.97 (m, 2H), 1.96 (s, 2H), 1.94-1.89 (m, 1H), 1.81-1.60 (m, 3H), 1.26-1.00 (m, 4H). The ^{1}H NMR spectrum was consistent with literature report.[5]

6. Synthesis of (*S*)-DACH-dimethyl



Literature procedures were modified for the preparation of (*S*)-DACH-dimethyl.[4, 6, 7]

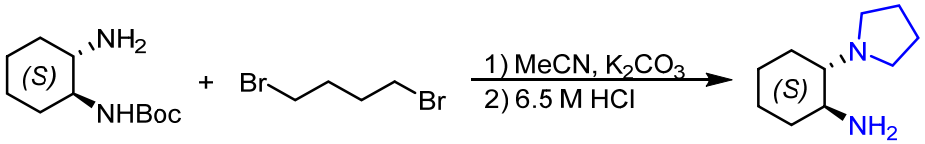
(1*S*, 2*S*)-(+)-1,2-Diaminocyclohexane (9.00 g, 78.8 mmol) was dissolved in 60 mL methanol and the solution was cooled to 0 °C. 37% HCl (6.57 mL, 78.8 mmol) was dissolved in 30 mL methanol and added dropwise to the diamine at 0 °C. The reaction mixture was allowed to warm to room temperature and further stirred at RT for 1 h. Di-*tert*-butyl dicarbonate (17.19 g, 78.7 mmol) was dissolved in 30 mL methanol and added dropwise to the reaction mixture at RT over 40 mins. The solution was stirred at RT for 3 h. The solvent was removed under reduced pressure,

and the resultant yellow solid was washed with diethyl ether (3 × 50 mL), yielding a white solid. The remaining residue was dissolved in 100 mL chloroform and treated with 40 mL 3.0 M NaOH. The collected organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to obtain (*S*)-DACH-Boc (14.57 g, 86% yield) as an off-white solid which was used directly for the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.44 (s, 1H), 3.12 (d, J = 12.2 Hz, 1H), 2.31 (td, J = 10.3, 4.0 Hz, 1H), 2.04-1.90 (m, 2H), 1.76-1.64 (m, 2H), 1.44 (s, 9H), 1.36-1.01 (m, 6H).

To a solution of (*S*)-DACH-Boc (2.14 g, 10.0 mmol) in DCM (100 mL) was added aq. HCHO (37%, 1.5 mL, 20 mmol) and the mixture was stirred at RT for 15 min. $NaBH(OAc)_3$ (4.88 g, 23 mmol) was added and stirring was continued for 6 h at RT. Saturated $NaHCO_3$ (300 mL) was added and stirring was continued for 15 min. The layers were separated, and the aqueous phase was extracted with DCM (3 × 40 mL). The combined organic layer was dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EA/MeOH = 8/1) to give product (*S*)-DACH-Boc-dimethyl (2.00 g, 83% yield) as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.25 (s, 1H), 3.33-3.06 (m, 1H), 2.45 (d, J = 12.7 Hz, 1H), 2.20 (s, 6H), 2.20-2.13 (m, 1H), 1.87-1.73 (m, 2H), 1.69-1.56 (m, 1H), 1.44 (s, 9H), 1.33-0.90 (m, 4H).

To a solution of (*S*)-DACH-Boc-dimethyl (2.00 g, 8.3 mmol) in 90 mL DCM was added 23 mL trifluoroacetic acid. The reaction mixture was stirred at RT for 12 h. Solvent was removed under reduced pressure, 3.0 M NaOH was added until pH = 10 and the mixture was extracted with DCM (3 × 40 mL). The combined organic phases were washed with brine dried over Na_2SO_4 and concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (EA/MeOH = 4/1) to give product (*S*)-DACH-dimethyl (0.87 g, 74% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (td, J = 10.2, 4.1 Hz, 1H), 2.20 (s, 6H), 2.09-1.95 (m, 2H), 1.94 (s, 2H), 1.92-1.86 (m, 1H), 1.81-1.59 (m, 3H), 1.28-0.96 (m, 4H). The ^{1}H NMR spectrum was consistent with literature report.[7]

7. Synthesis of (*S*)-DACH-pyrrolidine



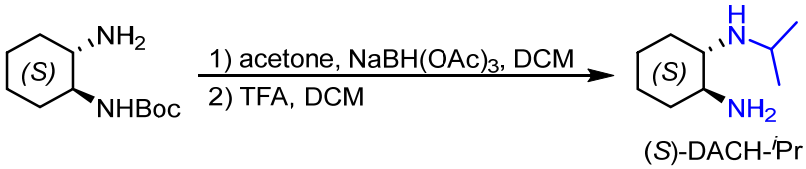
(*S*)-DACH-pyrrolidine

Literature procedures were modified for the preparation of (*S*)-DACH-pyrrolidine.[8]

(*S*)-DACH-Boc (4.28 g, 20 mmol) was dissolved in MeCN (40 mL), and K_2CO_3 (14.10 g,

102 mmol) and 1,4-dibromobutane (6.45 g, 30 mmol) were added. The suspension was stirred at RT for 24 h then at 80 °C for 22 h, and cooled to room temperature. The mixture was filtered, and the solid was washed with MeCN, and the combined filtrates were concentrated in vacuo. The residue was suspended in 6.5 M aqueous HCl (22 mL) with vigorous stirring while the evolution of gas was observed. After 12 h, the mixture was washed with diethyl ether (2 × 20 mL) to remove the excess of 1,4-dibromobutane. 3.0 M NaOH was added to the mixture until pH = 10. The aqueous phase was extracted with DCM (3 × 20 mL) and the combined organic phase was dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EA/MeOH = 4/1) to give product (*S*)-DACH-pyrrolidine (2.34 g, 70% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.67-2.61 (m, 2H), 2.56-2.50 (m, 2H), 2.29 (td, J = 10.3, 3.2 Hz, 1H), 2.11 (s, 2H), 2.00-1.89 (m, 1H), 1.88-1.54 (m, 8H), 1.35-1.03 (m, 4H). The ^{1}H NMR spectrum was consistent with literature report.[8]

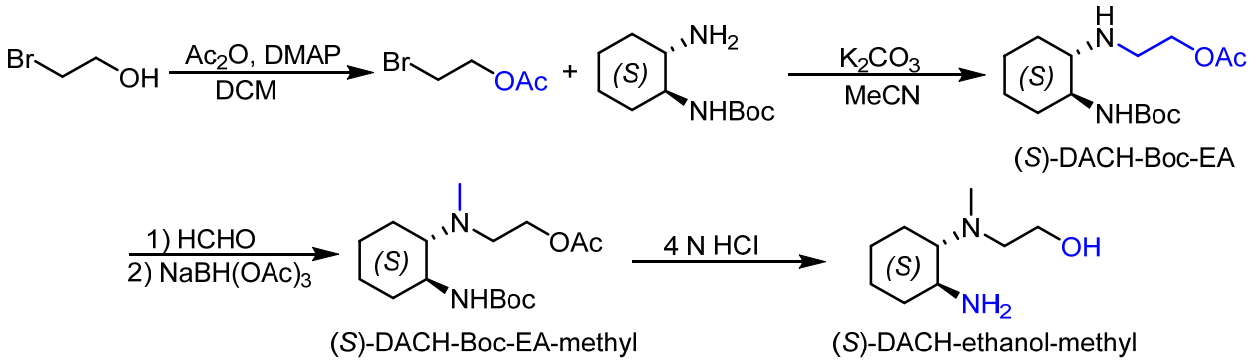
8. Synthesis of (*S*)-DACH-^{i}Pr



Literature procedures were modified for the preparation of (*S*)-DACH-^{i}Pr.[9]

To a solution of (*S*)-DACH-Boc (1.07 g, 5.0 mmol) in DCM (30 mL) was added acetone (0.88 mL, 12 mmol) and the mixture was stirred at RT for 20 min. $NaBH(OAc)_3$ (2.54 g, 12 mmol) was added and stirring was continued for 7 h at RT. Saturated $NaHCO_3$ (40 mL) was added and stirring was continued for 15 min. The layers were separated, and the aqueous phase was extracted with DCM (3 × 20 mL). The combined organic layer was dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The residue was added 15 mL DCM and 5 mL trifluoroacetic acid. The reaction mixture was stirred at RT for 11 h. Solvent was removed under reduced pressure, 3.0 M NaOH was added until pH = 10 and the mixture was extracted with DCM (3 × 20 mL). The combined organic phases were washed with brine dried over Na_2SO_4 and concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (EA/MeOH = 4/1) to give product (*S*)-DACH-^{i}Pr (0.52 g, 52% yield) as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.96-2.83 (m, J = 6.2 Hz, 1H), 2.32-2.21 (m, 1H), 2.08-1.97 (m, 2H), 1.93-1.82 (m, 1H), 1.72-1.62 (m, 2H), 1.51 (s, 3H), 1.28-1.17 (m, 2H), 1.14-1.07 (m, 1H), 1.04 (d, J = 6.3 Hz, 3H), 0.99 (d, J = 6.1 Hz, 3H), 0.95-0.81 (m, 1H). The ^{1}H NMR spectrum was consistent with literature report.[9]

9. Synthesis of (*S*)-DACH-ethanol-methyl



Literature procedures were modified for the preparation of (*S*)-DACH-ethanol-methyl.[10]

To a solution of 2-bromoethanol (4.00 g, 32.0 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (5.20 g, 42.3 mmol) in 40 mL of dried DCM was added acetic anhydride (4.0 mL, 42.3 mmol) at 0 °C under Ar. The reaction mixture was then stirred for 23 h at room temperature and 30 mL H_2O was added to quench the reaction. The layers were separated, and aqueous layer was extracted with DCM (2 × 30 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure to give product 2-bromoethyl acetate (4.71 g, 88% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.37 (t, J = 6.1 Hz, 2H), 3.50 (t, J = 6.1 Hz, 2H), 2.09 (s, 3H).

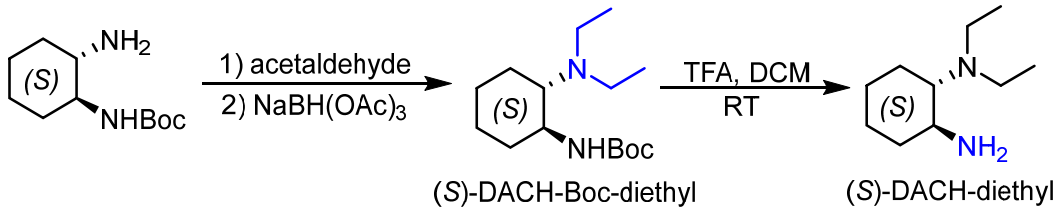
(*S*)-DACH-Boc (1.71 g, 8 mmol) was dissolved in MeCN (30 mL), and K_2CO_3 (5.53 g, 40 mmol) and 2-bromoethyl acetate (1.34 g, 8 mmol) were added. The suspension was stirred at 80 °C for 24 h and then cooled to room temperature. The mixture was filtered, and the solid was washed with MeCN, and the combined filtrates were concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EA/MeOH= 10/1) to give product (*S*)-DACH-Boc-EA (1.36 g, 57% yield) as a pale-yellow oil.

To a solution of (*S*)-DACH-Boc-EA (2.12 g, 7.1 mmol) in DCM (20 mL) was added aq. HCHO (37%, 0.63 mL, 8.5 mmol) and the mixture was stirred at RT for 20 min. $NaBH(OAc)_3$ (1.94 g, 9.2 mmol) was added and stirring was continued for 11 h at RT. Saturated $NaHCO_3$ (30 mL) was added and stirring was continued for 15 min. The layers were separated, and the aqueous phase was extracted with DCM (3 × 15 mL). The combined organic layer was dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 1/12) to give product (*S*)-DACH-Boc-EA-methyl (1.06 g, 48% yield) as a pale-yellow oil.

The residue was added 15 mL 4 N HCl and the mixture was stirred at 80 °C for 12 h. After being cooling to ambient temperature, 3.0 M NaOH was added until pH = 10. After extraction with DCM, the combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure

to obtain (*S*)-DACH-ethanol-methyl (0.55 g, 95% yield) as a pale-yellow oil, which was used directly in the subsequent reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66-3.50 (m, 2H), 2.76-2.67 (m, 1H), 2.63 (td, J = 10.2, 4.1 Hz, 1H), 2.52-2.41 (m, 1H), 2.27 (s, 5H), 2.23-2.07 (m, 1H), 1.95-1.86 (m, 1H), 1.85-1.72 (m, 2H), 1.70-1.62 (m, 1H), 1.29-0.98 (m, 5H). The ^{1}H NMR spectrum was consistent with literature report.[10]

10. Synthesis of (*S*)-DACH-diethyl



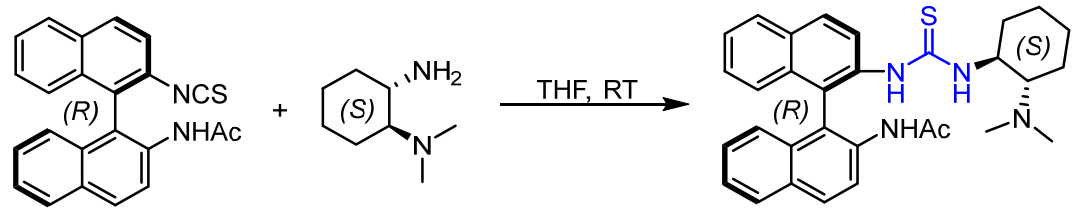
(*S*)-DACH-Boc-diethyl (*S*)-DACH-diethyl

Literature procedures were modified for the preparation of (*S*)-DACH-diethyl.[11]

To a solution of (*S*)-DACH-Boc (0.64 g, 3.0 mmol) in DCM (15 mL) was added acetaldehyde (0.32 g, 7.2 mmol) and the mixture was stirred at RT for 15 min. $NaBH(OAc)_3$ (1.53 g, 7.2 mmol) was added and stirring was continued for 6 h at RT. Saturated $NaHCO_3$ (40 mL) was added and stirring was continued for 15 min. The layers were separated, and the aqueous phase was extracted with DCM (3 × 15 mL). The combined organic layer was dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure to obtain a pale-yellow solid, which was used directly in the subsequent reaction without further purification

To a solution of (*S*)-DACH-Boc-diethyl in 15 mL DCM was added 5 mL trifluoroacetic acid. The reaction mixture was stirred at RT for 11 h. Solvent was removed under reduced pressure, 3.0 M NaOH was added until pH = 10 and the mixture was extracted with DCM (3 × 15 mL). The combined organic phases were washed with brine dried over Na_2SO_4 and concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (EA/MeOH = 8/1) to give product (*S*)-DACH-diethyl (0.37 g, 73% yield) as a dark red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.64-2.49 (m, 3H), 2.38-2.25 (m, 2H), 2.15-2.06 (m, 1H), 2.00-1.96 (m, 3H), 1.79-1.58 (m, 3H), 1.23-1.04 (m, 4H), 1.01 (t, J = 7.1 Hz, 6H). The ^{1}H NMR spectrum was consistent with literature report.[11]

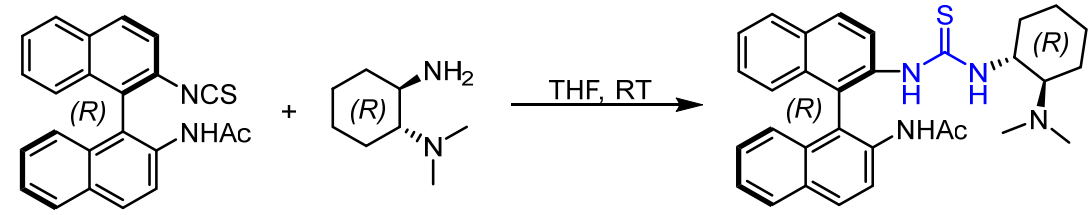
11. Synthesis of catalyst (*R*,*S*)-**1**



(*R*)-BINAM-Ac-NCS (*S*)-DACH-dimethyl (*R,S*)-**1**

To a solution of (*R*)-BINAM-Ac-NCS (1.11 g, 3.0 mmol) in THF (40 mL) was added (*S*)-DACH-dimethyl (0.43 g, 3.0 mmol) and the reaction mixture was stirred for 8 h at room temperature. The reaction mixture was concentrated, and the crude product was purified by flash chromatograph on silica gel (DCM/MeOH/$NH_3 \cdot H_2O$ = 100/3/1) to give catalyst (*R*,*S*)-**1** (1.29 g, 84% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 9.0 Hz, 1H), 8.07 (s, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.96 (d, J = 3.8 Hz, 1H), 7.94 (d, J = 2.8 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 7.53-7.44 (m, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.30-7.24 (m, 1H), 7.24-7.10 (m, 2H), 6.98 (d, J = 8.5 Hz, 1H), 6.13 (s, 1H), 2.12 (t, J = 11.1 Hz, 1H), 1.92 (s, 6H), 1.82 (s, 3H), 1.66 (d, J = 11.6 Hz, 2H), 1.48 (s, 1H), 1.10-0.72 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.07, 169.49, 136.86, 135.60, 132.99, 132.95, 132.60, 131.08, 129.24, 128.79, 128.34, 128.21, 127.50, 127.14, 126.85, 126.50, 126.10, 125.35, 125.18, 123.02, 67.23, 56.95, 40.29, 32.77, 24.73, 24.43, 24.34, 22.64. HRMS (positive ESI) calculated m/z for $C_{31}H_{35}N_4OS^+$ ($[M+H]^+$): 511.2532; found m/z: 511.2525.

12. Synthesis of catalyst (*R,R*)-**1**

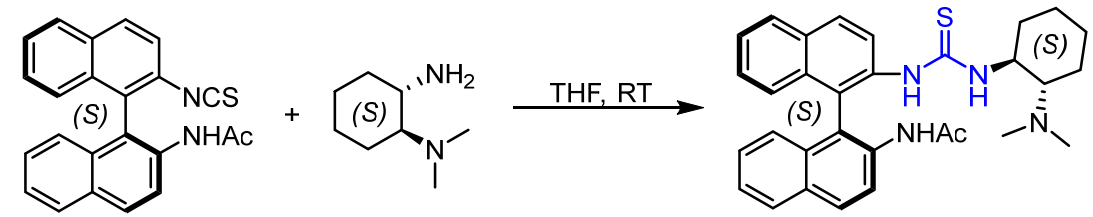


(*R*)-BINAM-Ac-NCS (*R*)-DACH-dimethyl (*R,R*)-**1**

To a solution of (*R*)-BINAM-Ac-NCS (368 mg, 1.0 mmol) in THF (25 mL) was added (*R*)-DACH-dimethyl (171 mg, 1.2 mmol) and the reaction mixture was stirred for 8 h at room temperature. The reaction mixture was concentrated, and the crude product was purified by flash chromatograph on silica gel (DCM/MeOH/$NH_3 \cdot H_2O$ = 100/3/1) to give catalyst (*R,R*)-**1** (449 mg, 88% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.60 (s, 1H), 8.77 (s, 1H), 8.38 (d, J = 9.0 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 9.1 Hz, 1H), 7.89 (t, J = 8.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.18 (t, J = 7.7 Hz, 2H), 6.96 (t, J = 8.4 Hz, 2H), 6.01 (s, 1H), 3.30 (s, 1H), 2.20-2.08 (m, 1H), 2.05-1.94 (m, 1H), 1.90 (s, 3H), 1.72-1.55 (m, 3H), 1.26 (s, 6H), 1.17-1.06 (m, 2H), 1.04-0.92 (m, 2H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 170.51, 162.64, 135.96, 133.29, 133.11, 132.37, 131.27, 129.13, 128.78, 128.31, 128.06, 128.00, 127.66, 127.00, 126.71, 126.24, 126.21, 125.74, 125.16, 123.39, 122.81, 68.31, 57.65, 39.57, 36.15, 33.51, 29.82, 24.65, 24.53, 24.34, 22.98. HRMS (positive ESI) calculated m/z for $C_{31}H_{35}N_4OS^+$ ([M+H]$^+$): 511.2532; found m/z: 511.2522.

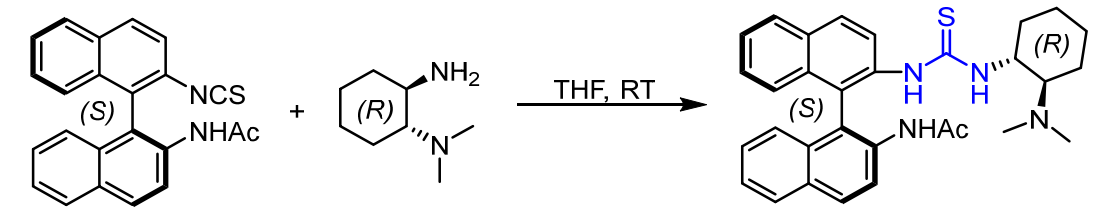
13. Synthesis of catalyst (*S,S*)-**1**



(*S*)-BINAM-Ac-NCS (*S*)-DACH-dimethyl (*S,S*)-**1**

To a solution of (*S*)-BINAM-Ac-NCS (1.00 g, 2.7 mmol) in THF (30 mL) was added (*S*)-DACH-dimethyl (0.43 g, 3.0 mmol) and the reaction mixture was stirred for 8 h at room temperature. The reaction mixture was concentrated, and the crude product was purified by flash chromatograph on silica gel (DCM/MeOH/$NH_3 \cdot H_2O$ = 100/3/1) to give catalyst (*S,S*)-**1** (1.19 g, 86% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 8.67 (s, 1H), 8.36 (d, J = 9.0 Hz, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.94 (d, J = 9.0 Hz, 1H), 7.92-7.86 (m, 2H), 7.68 (d, J = 8.8 Hz, 1H), 7.48-7.42 (m, 1H), 7.37 (t, J = 7.3 Hz, 1H), 7.24-7.15 (m, 2H), 6.99 (d, J = 8.4 Hz, 2H), 6.06 (s, 1H), 3.42 (s, 1H), 2.13 (s, 2H), 1.89 (s, 3H), 1.82-1.58 (m, 4H), 1.51-0.92 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.88, 135.93, 133.24, 133.10, 132.40, 131.28, 129.18, 128.82, 128.33, 128.08, 127.52, 127.02, 126.75, 126.27, 126.21, 125.68, 125.17, 123.38, 122.81, 68.19, 57.97, 39.55, 33.45, 29.82, 24.61, 24.51, 24.34, 22.99. HRMS (positive ESI) calculated m/z for $C_{31}H_{35}N_4OS^+$ ([M+H]$^+$): 511.2532; found m/z: 511.2523.

14. Synthesis of catalyst (*S,R*)-**1**

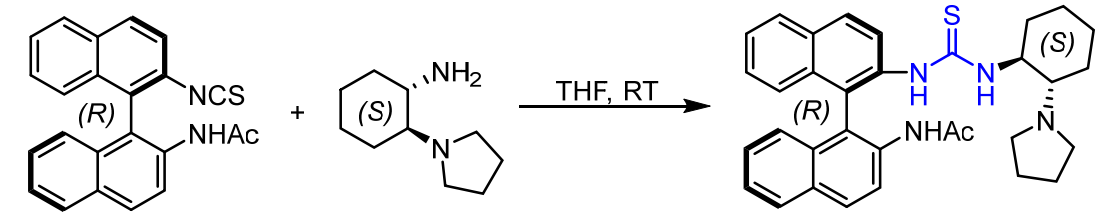


(*S*)-BINAM-Ac-NCS (*R*)-DACH-dimethyl (*S,R*)-**1**

To a solution of (*S*)-BINAM-Ac-NCS (368.5 mg, 1.0 mmol) in THF (15 mL) was added (*R*)-DACH-dimethyl (142.2 mg, 1.0 mmol) and the reaction mixture was stirred for 8 h at room temperature. The reaction mixture was concentrated, and the crude product was purified by flash chromatograph on silica gel (DCM/MeOH/$NH_3 \cdot H_2O$ = 100/3/1) to give catalyst (*S,R*)-**1** (410.2 mg,

80% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 9.0 Hz, 1H), 8.07 (s, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.96 (d, J = 3.4 Hz, 1H), 7.94 (d, J = 2.5 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.53-7.44 (m, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.30-7.25 (m, 1H), 7.25-7.14 (m, 2H), 6.98 (d, J = 8.4 Hz, 1H), 6.11 (s, 1H), 2.16-2.06 (m, 1H), 1.92 (s, 6H), 1.82 (s, 3H), 1.66 (d, J = 11.8 Hz, 2H), 1.48 (s, 1H), 1.05-0.82 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.08, 169.48, 136.85, 135.61, 132.97, 132.95, 132.61, 131.09, 129.26, 128.79, 128.35, 128.22, 127.48, 127.16, 126.85, 126.52, 126.11, 125.34, 125.19, 123.05, 67.28, 57.00, 41.04, 32.76, 24.72, 24.42, 24.33, 22.66. HRMS (positive ESI) calculated m/z for $C_{31}H_{35}N_4OS^+$ ([M+H]$^+$): 511.2532; found m/z: 511.2531.

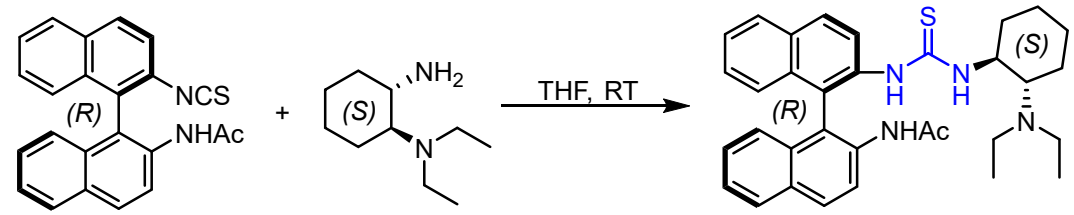
15. Synthesis of catalyst (*R,S*)-**2**



(*R*)-BINAM-Ac-NCS (*S*)-DACH-pyrrolidine (*R,S*)-**2**

To a solution of (*R*)-BINAM-Ac-NCS (1.19 g, 3.2 mmol) in THF (30 mL) was added (*S*)-DACH-pyrrolidine (0.54 g, 3.2 mmol) and the reaction mixture was stirred for 12 h at room temperature. The reaction mixture was concentrated, and the crude product was purified by flash chromatograph on silica gel (DCM/MeOH/$NH_3 \cdot H_2O$ = 100/3/1) to give catalyst (*R,S*)-**2** (1.65 g, 96% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.60 (s, 1H), 8.36 (d, J = 9.0 Hz, 1H), 8.06 (d, J = 8.8 Hz, 1H), 8.03 (s, 1H), 7.96 (d, J = 9.0 Hz, 2H), 7.91 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.54-7.45 (m, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 8.5 Hz, 1H), 5.69 (s, 1H), 3.80-3.69 (m, 3H), 2.54 (s, 2H), 2.09 (s, 3H), 1.87-1.82 (m, 6H), 1.69-1.36 (m, 4H), 1.09-0.75 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.43, 136.92, 135.51, 133.20, 132.99, 132.76, 131.10, 129.44, 128.65, 128.30, 128.24, 127.58, 127.18, 126.75, 126.59, 126.20, 125.20, 125.17, 123.18, 68.10, 32.73, 25.75, 24.77, 24.55, 23.70, 23.30. HRMS (positive ESI) calculated m/z for $C_{33}H_{37}N_4OS^+$ ([M+H]$^+$): 537.2688; found m/z: 537.2685.

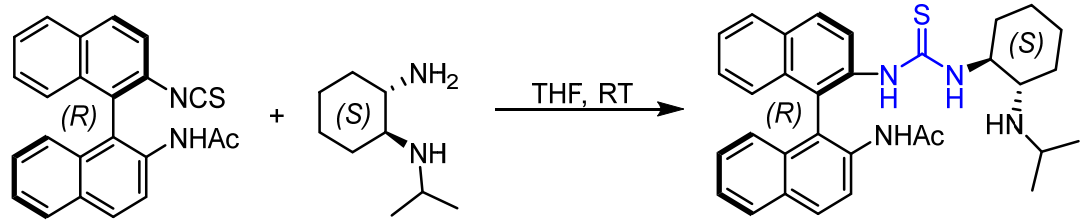
16. Synthesis of catalyst (*R,S*)-**3**



(*R*)-BINAM-Ac-NCS (*S*)-DACH-diethyl (*R,S*)-**3**

To a solution of (*R*)-BINAM-Ac-NCS (0.61 g, 1.7 mmol) in THF (15 mL) was added (*S*)-DACH-diethyl (0.37 g, 2.2 mmol) and the reaction mixture was stirred for 15 h at room temperature. The reaction mixture was concentrated, and the crude product was purified by flash chromatograph on silica gel (DCM/MeOH/$NH_3 \cdot H_2O$ = 100/3/1) to give catalyst (*R,S*)-**3** (0.51 g, 57% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 9.0 Hz, 1H), 8.11 (s, 1H), 8.05 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 8.5 Hz, 2H), 7.90 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.32-7.27 (m, 1H), 7.22 (t, J = 7.3 Hz, 2H), 7.00 (d, J = 8.4 Hz, 1H), 6.16 (s, 1H), 2.50-2.13 (m, 6H), 1.79 (s, 3H), 1.64 (t, J = 15.2 Hz, 3H), 1.48-1.37 (m, 1H), 1.05-0.92 (m, 1H), 0.91-0.65 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.08, 169.32, 136.57, 135.65, 133.36, 132.86, 132.65, 131.24, 129.52, 128.83, 128.41, 128.24, 127.29, 127.11, 126.78, 126.59, 126.10, 125.20, 125.06, 123.54, 64.66, 57.02, 42.87, 32.90, 31.72, 25.27, 24.45, 24.36, 22.79, 14.33, 14.25, 13.38. HRMS (positive ESI) calculated m/z for $C_{33}H_{39}N_4OS^+$ ($[M+H]^+$): 539.2845; found m/z: 539.2841.

17. Synthesis of catalyst (*R,S*)-**4**

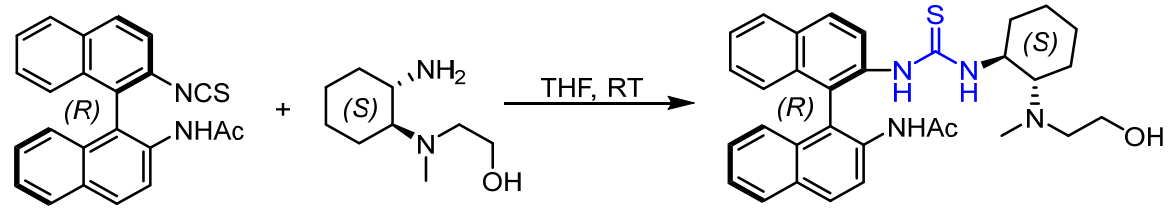


(*R*)-BINAM-Ac-NCS (*S*)-DACH-^{i}Pr (*R,S*)-**4**

To a solution of (*R*)-BINAM-Ac-NCS (0.55 g, 1.5 mmol) in THF (10 mL) was added (*S*)-DACH-^{i}Pr (0.36 g, 1.8 mmol) and the reaction mixture was stirred for 14 h at room temperature. The reaction mixture was concentrated, and the crude product was purified by flash chromatograph on silica gel (EA/MeOH = 4/1) to give catalyst (*R,S*)-**4** (0.45 g, 53% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.9 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.00-7.94 (m, 3H), 7.92 (d, J = 8.2 Hz, 1H), 7.73 (s, 1H), 7.54-7.48 (m, 1H), 7.44-7.38 (m, 1H), 7.35-7.27 (m, 2H), 7.25-7.20 (m, 1H), 7.02 (d, J = 8.5 Hz, 1H), 5.33 (s, 1H), 2.60 (p, J = 6.4 Hz, 1H), 1.85 (s, 3H), 1.83-1.74 (m, 1H), 1.68-1.60 (m, 1H), 1.56 (d, J = 12.8 Hz, 1H), 1.52-1.36 (m, 3H), 1.01-0.89 (m, 2H), 0.87 (d, J = 6.3 Hz, 3H), 0.85-0.79 (m, 1H), 0.78 (d, J = 6.2 Hz, 3H), -0.09 (t, J =

11.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.17, 169.33, 137.20, 135.36, 133.43, 132.78, 132.74, 130.92, 129.50, 129.33, 128.39, 128.26, 128.24, 127.82, 127.08, 126.49, 126.44, 125.98, 125.06, 123.89, 123.34, 62.08, 59.91, 48.28, 33.24, 32.87, 24.75, 24.55, 24.49, 23.31, 22.55. HRMS (positive ESI) calculated m/z for $C_{33}H_{39}N_4OS^+$ ([M+H]$^+$): 525.2688; found m/z: 525.2684.

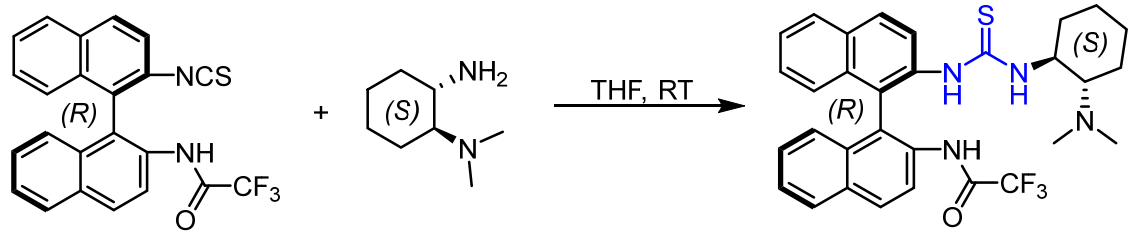
18. Synthesis of catalyst (*R,S*)-**5**



(*R*)-BINAM-Ac-NCS (*S*)-DACH-ethanol-methyl (*R,S*)-**5**

To a solution of (*R*)-BINAM-Ac-NCS (1.18 g, 3.2 mmol) in THF (30 mL) was added (*S*)-DACH-ethanol-methyl (0.55 g, 3.2 mmol) and the reaction mixture was stirred for 15 h at room temperature. The reaction mixture was concentrated, and the crude product was purified by flash chromatograph on silica gel (DCM/MeOH/$NH_3 \cdot H_2O$ = 100/3/1) to give catalyst (*R,S*)-**5** (1.51 g, 87% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 9.0 Hz, 1H), 8.02 (s, 2H), 7.97-7.91 (m, 2H), 7.89 (d, J = 8.2 Hz, 1H), 7.78 (s, 1H), 7.50-7.44 (m, 1H), 7.43-7.36 (m, 1H), 7.28-7.24 (m, 2H), 7.28-7.24 (m, 2H), 7.24-7.19 (d, J = 8.5 Hz, 1H), 7.06 (d, J = 8.5 Hz, 1H), 7.01 (d, J = 8.5 Hz, 1H), 6.65 (s, 1H), 3.26 (s, 2H), 2.45-2.24 (m, 4H), 2.18 (t, J = 11.2 Hz, 1H), 1.99 (s, 3H), 1.85 (s, 3H), 1.80-1.66 (m, 3H), 1.51 (s, 1H), 1.08 (s, 3H), 0.94-0.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.15, 169.90, 136.59, 135.33, 132.99, 132.92, 132.30, 131.13, 129.06, 128.96, 128.38, 128.31, 127.12, 126.30, 125.78, 125.42, 125.34, 122.70, 122.57, 66.75, 59.26, 55.76, 55.21, 35.60, 32.85, 25.29, 24.53, 24.49, 23.91, 21.13, 14.23. HRMS (positive ESI) calculated m/z for $C_{32}H_{37}N_4O_2S^+$ ([M+H]$^+$): 541.2637; found m/z: 541.2630.

19. Synthesis of catalyst (*R,S*)-**6**

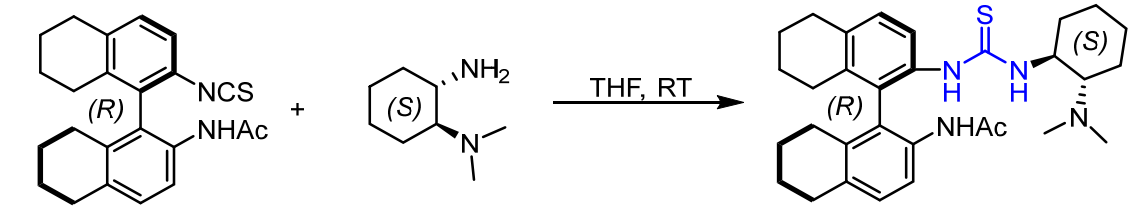


(*R*)-BINAM-TFA-NCS (*S*)-DACH-dimethyl (*R,S*)-**6**

To a solution of (*R*)-BINAM-TFA-NCS (0.63 g, 1.5 mmol) in THF (10 mL) was added (*S*)-DACH-dimethyl (0.28 g, 2.0 mmol) and the reaction mixture was stirred for 18 h at room temperature. The reaction mixture was concentrated, and the crude product was purified by flash

chromatograph on silica gel (DCM/MeOH/$NH_3 \cdot H_2O$ = 100/3/1) to give catalyst (*R,S*)-**6** (0.45 g, 53% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.86 (s, 1H), 9.28 (s, 1H), 8.07 (d, J = 8.7 Hz, 1H), 8.05-8.00 (m, 2H), 7.99-7.91 (m, 2H), 7.60 (d, J = 8.7 Hz, 1H), 7.53-7.46 (m, 2H), 7.36-7.29 (m, 2H), 7.19 (t, J = 9.4 Hz, 2H), 6.07 (s, 1H), 2.16 (s, 1H), 2.10 (s, 6H), 1.69 (t, J = 16.6 Hz, 2H), 1.47 (s, 1H), 1.09-0.66 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.50, 155.97, 136.84, 132.74, 132.71, 132.58, 132.51, 132.23, 130.32, 129.17, 128.57, 128.37, 127.61, 127.29, 126.71, 126.44, 126.35, 125.58, 125.34, 123.59, 119.99, 117.12, 114.25, 111.39, 67.64, 56.96, 40.58, 32.62, 24.66, 24.37, 22.87. HRMS (positive ESI) calculated m/z for $C_{31}H_{32}F_3N_4OS^+$ ($[M+H]^+$): 565.2249; found m/z: 565.2241.

20. Synthesis of catalyst (*R,S*)-**7**



(*R*)-H_8-BINAM-Ac-NCS (*S*)-DACH-dimethyl (*R,S*)-**7**

To a solution of (*R*)-H_8-BINAM-Ac-NCS (488.6 mg, 1.3 mmol) in THF (15 mL) was added (*S*)-DACH-dimethyl (227.6 mg, 1.6 mmol) and the reaction mixture was stirred for 6 h at room temperature. The reaction mixture was concentrated, and the crude product was purified by flash chromatograph on silica gel (DCM/MeOH/$NH_3 \cdot H_2O$ = 100/3/1) to give catalyst (*R,S*)-**7** (590.2 mg, 88% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.82 (m, 1H), 7.77 (d, J = 8.3 Hz, 1H), 7.66-7.45 (m, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.18 (d, J = 8.1 Hz, 1H), 7.08 (d, J = 8.3 Hz, 1H), 6.45 (s, 1H), 3.21 (s, 1H), 2.92-2.68 (m, 4H), 2.26-2.19 (m, 2H), 2.16 (s, 6H), 2.10 (t, J = 6.2 Hz, 3H), 1.90 (s, 3H), 1.83-1.59 (m, 12H), 1.19-1.06 (m, 3H), 1.01-0.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.28, 168.96, 136.97, 136.88, 134.83, 134.47, 134.39, 134.33, 133.63, 132.27, 129.56, 129.38, 125.41, 121.50, 66.71, 56.55, 40.45, 32.52, 29.92, 29.70, 27.70, 27.53, 27.29, 25.10, 24.69, 24.41, 23.39, 23.10, 23.03, 22.85, 22.53. HRMS (positive ESI) calculated m/z for $C_{31}H_{42}N_4OS^+$ ($[M+H]^+$): 519.3158; found m/z: 519.3152.

NMR spectra of catalysts

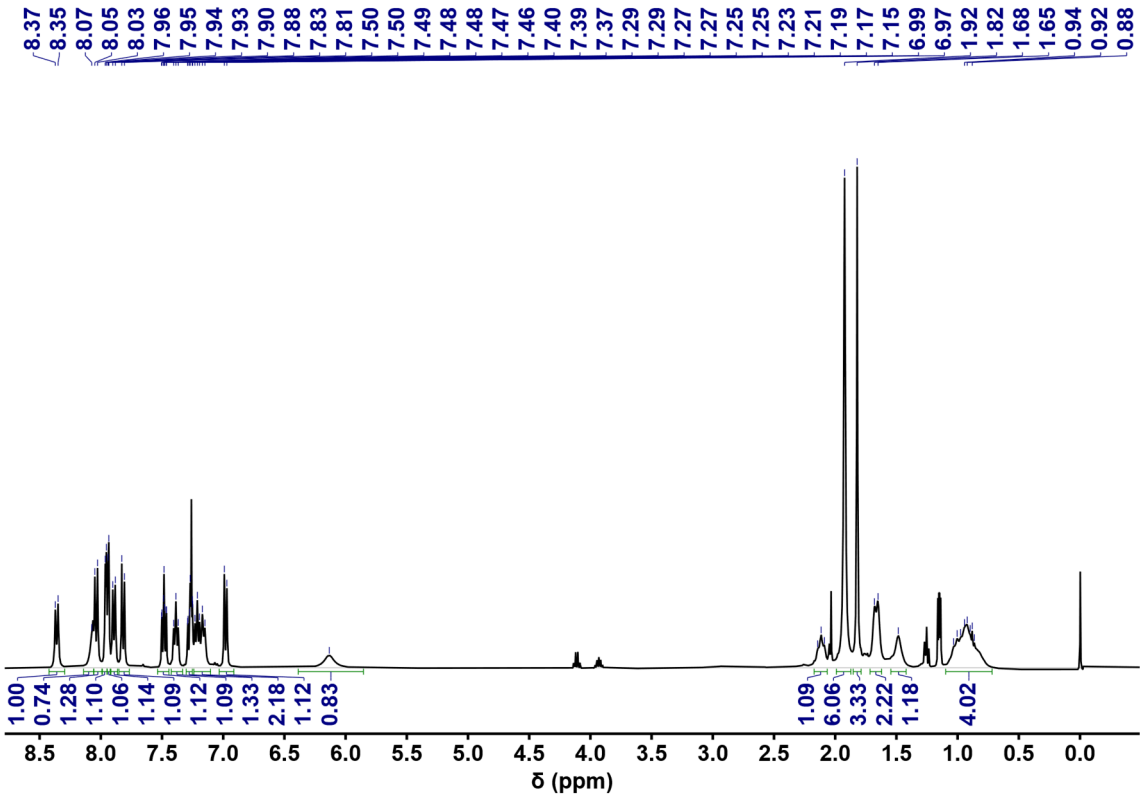


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*R,S*)-**1**.

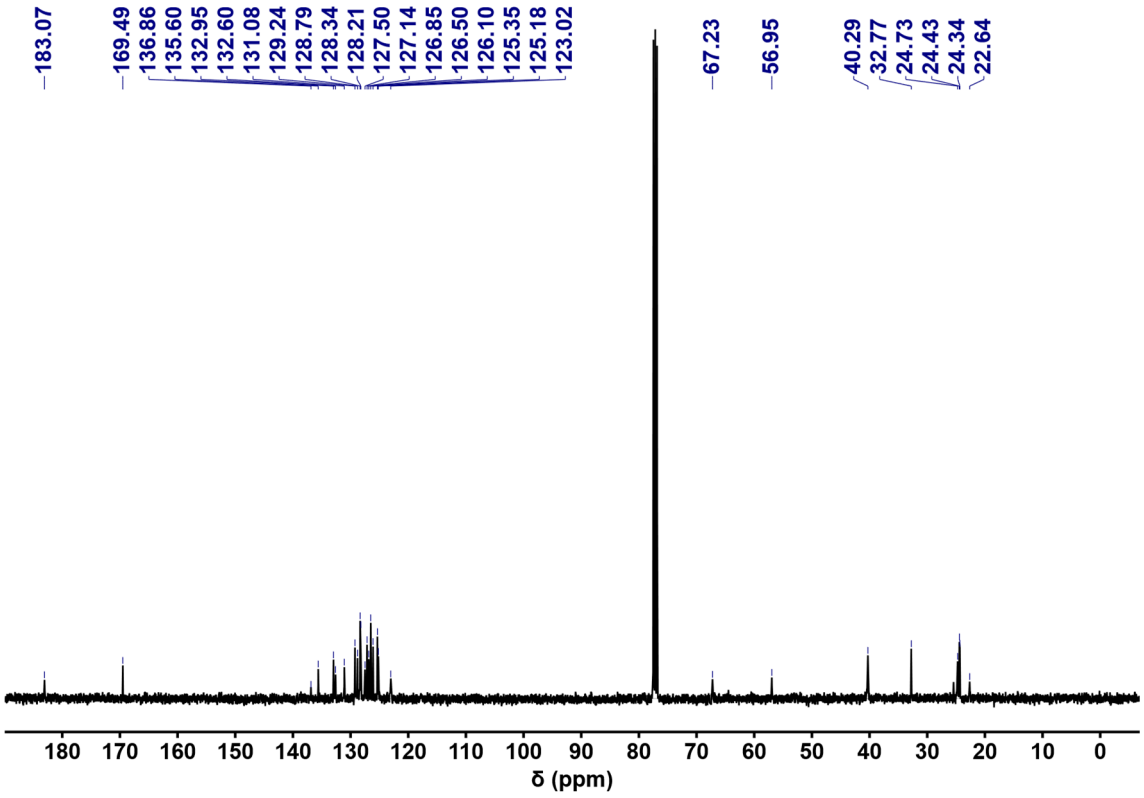


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R,S*)-**1**.

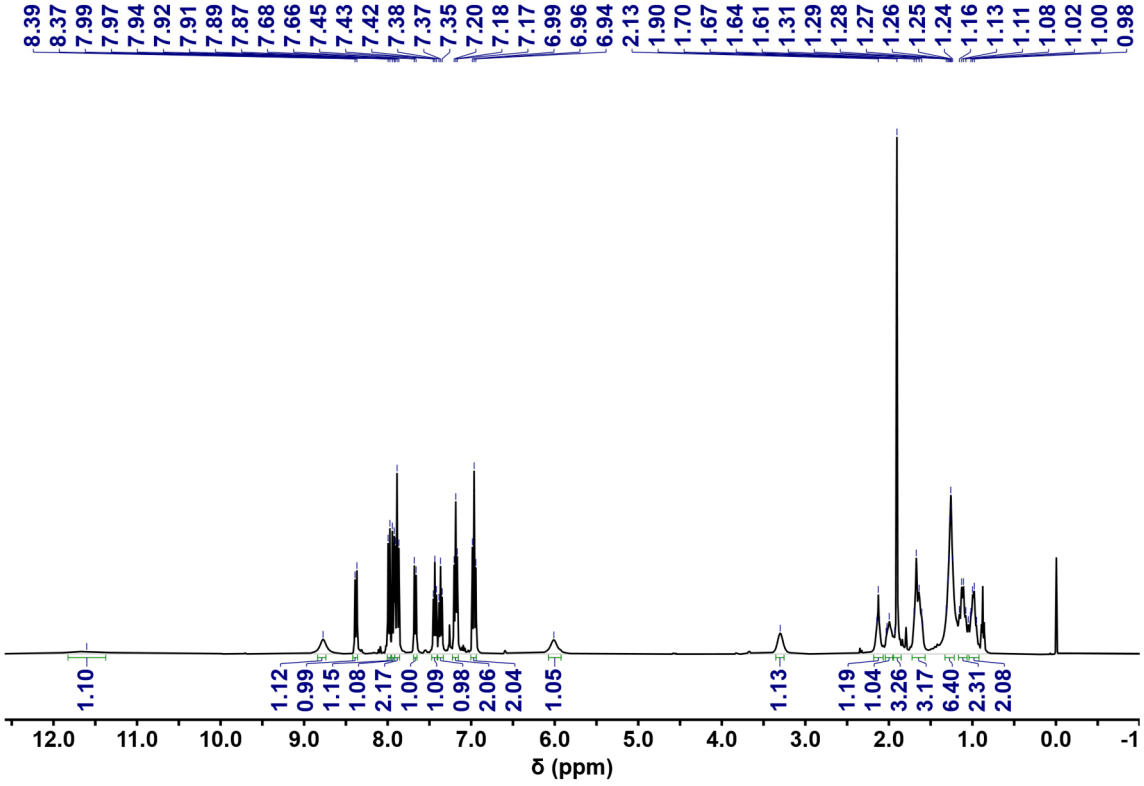


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*R,R*)-**1**.

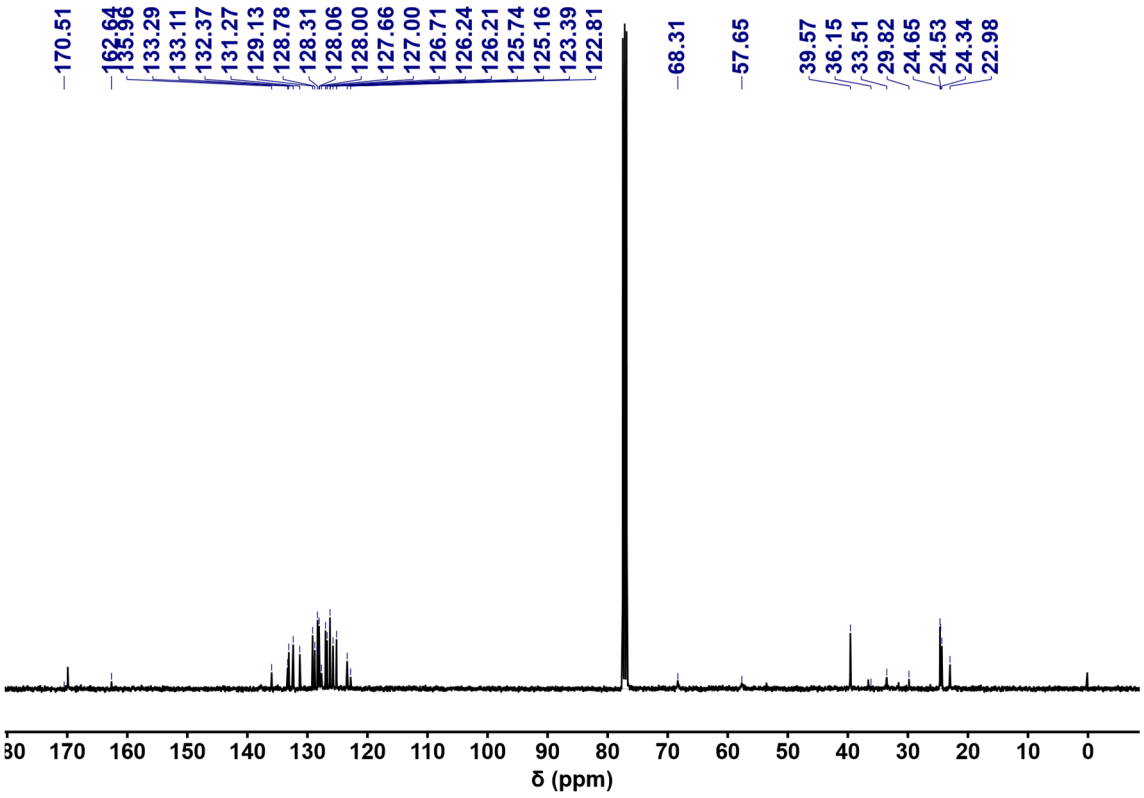


Figure S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R,R*)-**1**.

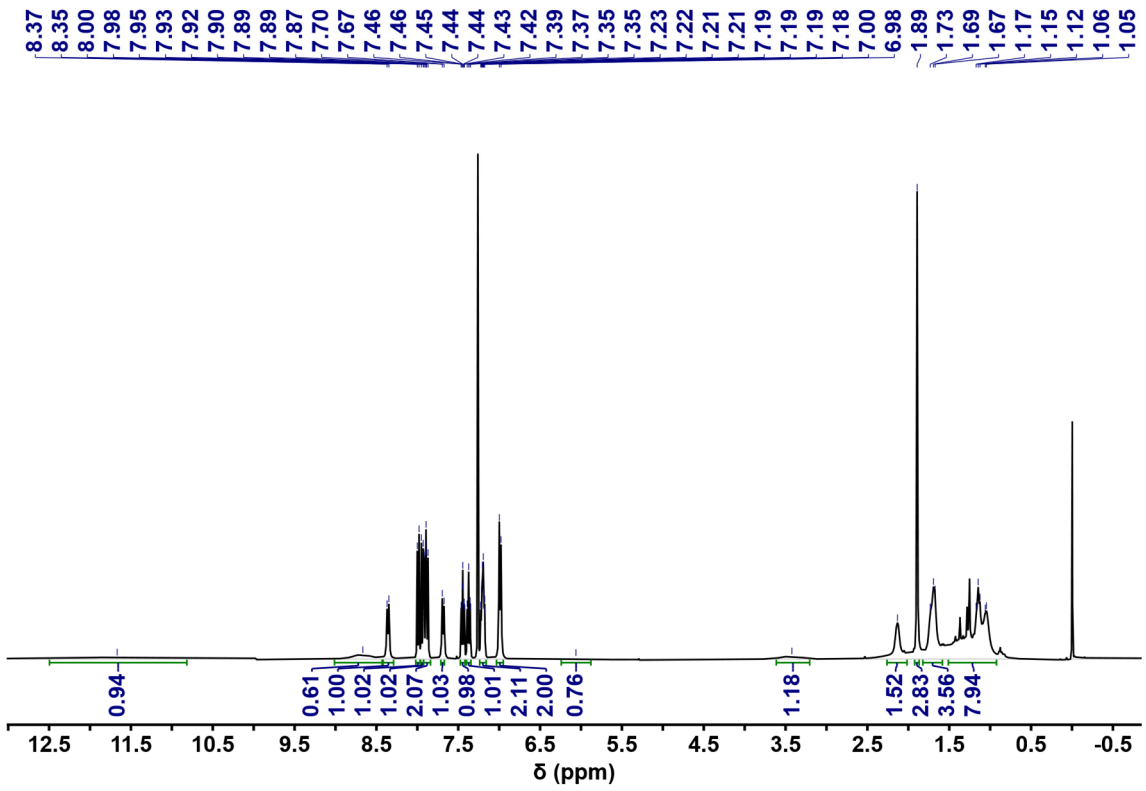


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*S,S*)-**1**.

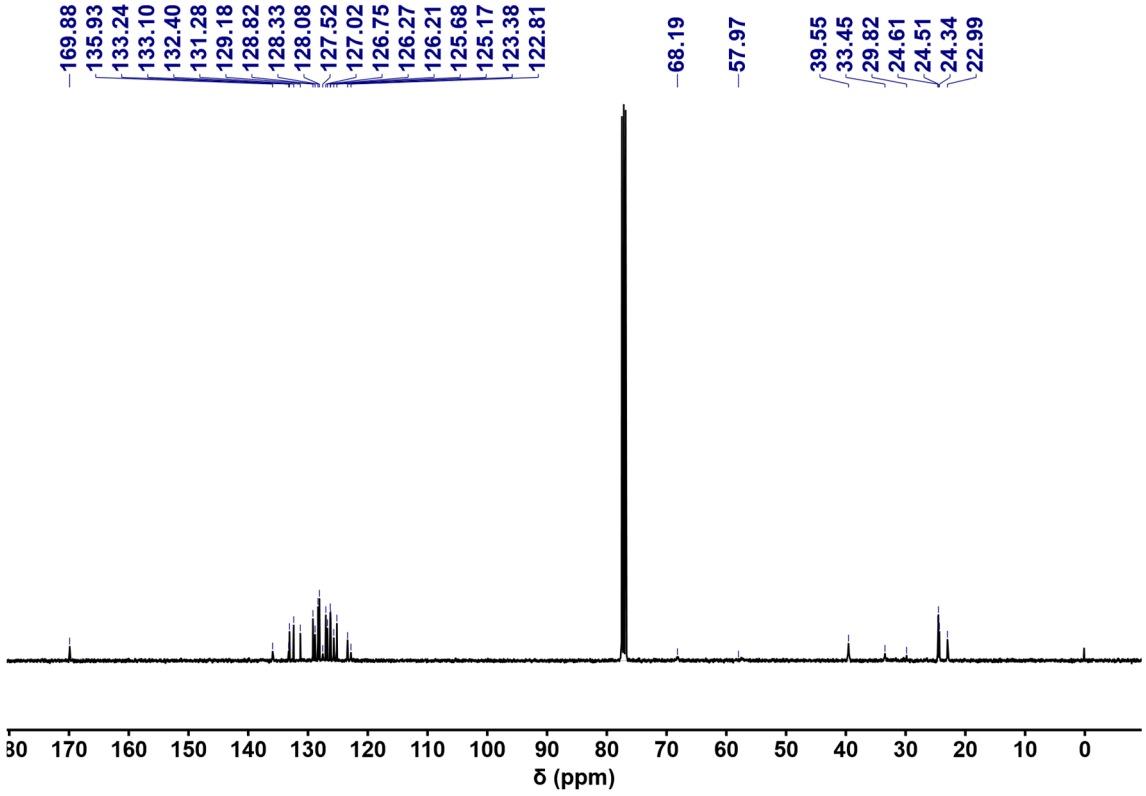


Figure S6. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*S,S*)-**1**.

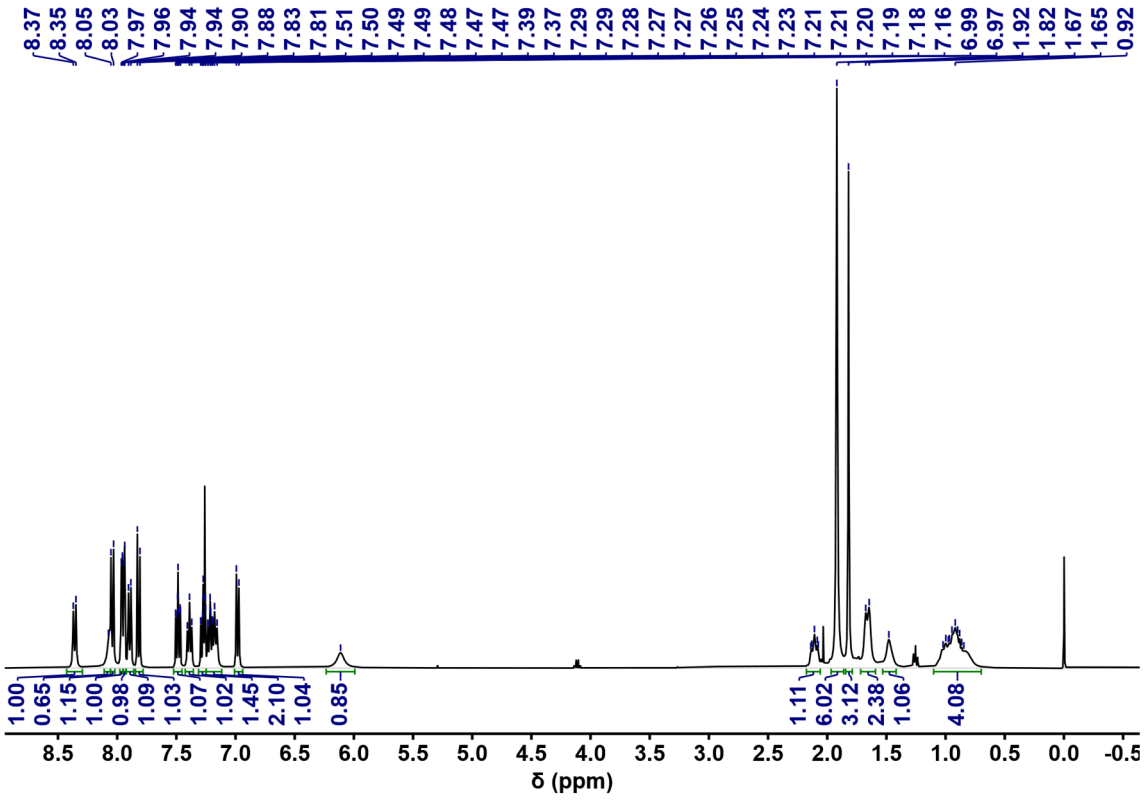


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*S,R*)-**1**.

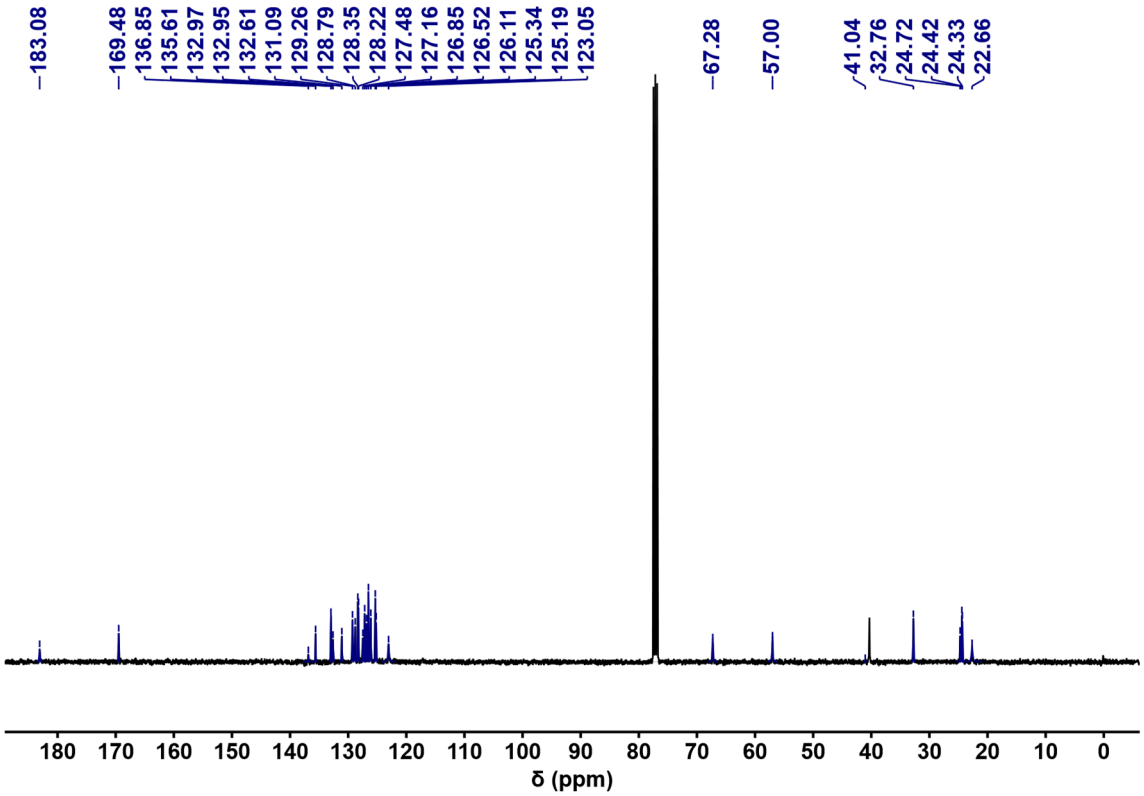


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*S,R*)-**1**.

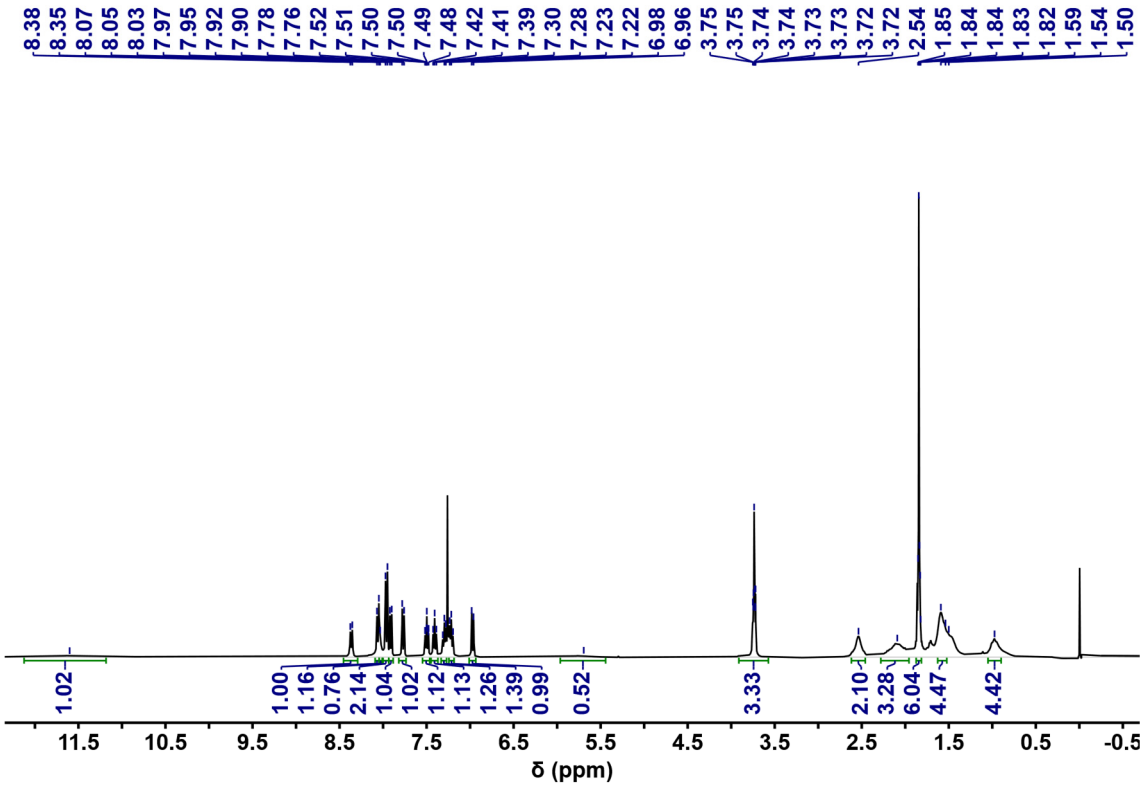


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*R,S*)-**2**.

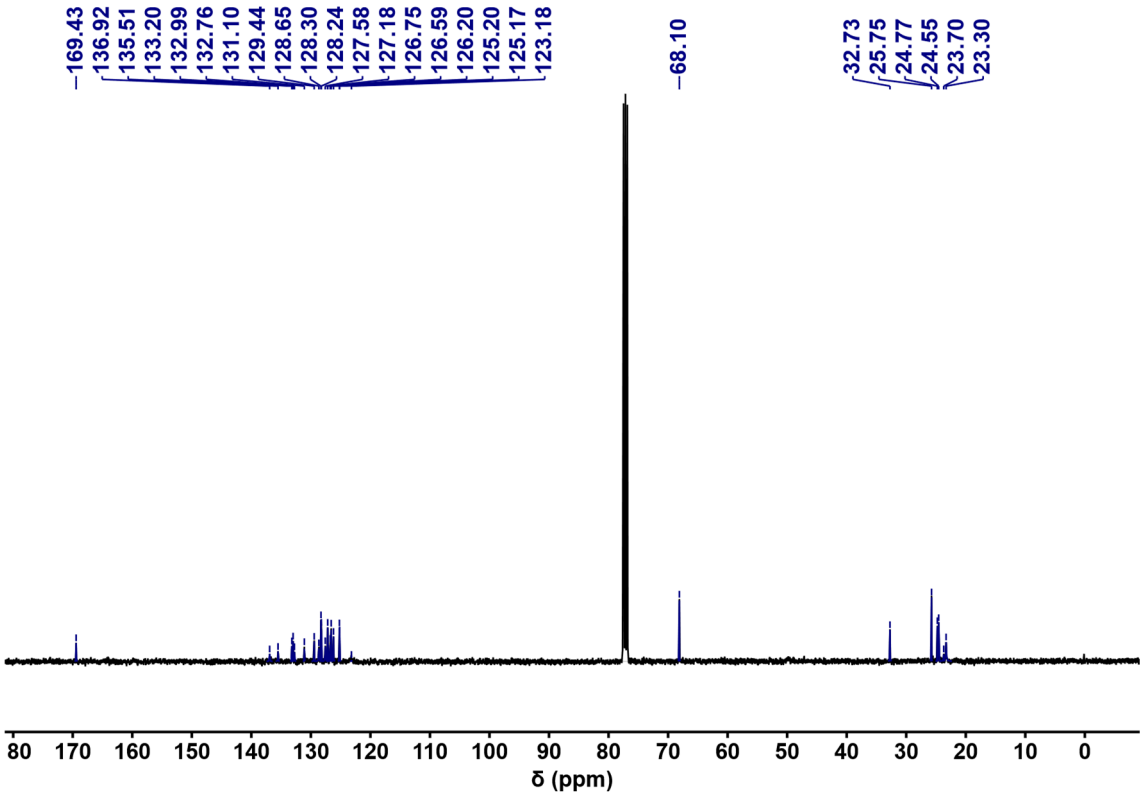


Figure S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R,S*)-**2**.

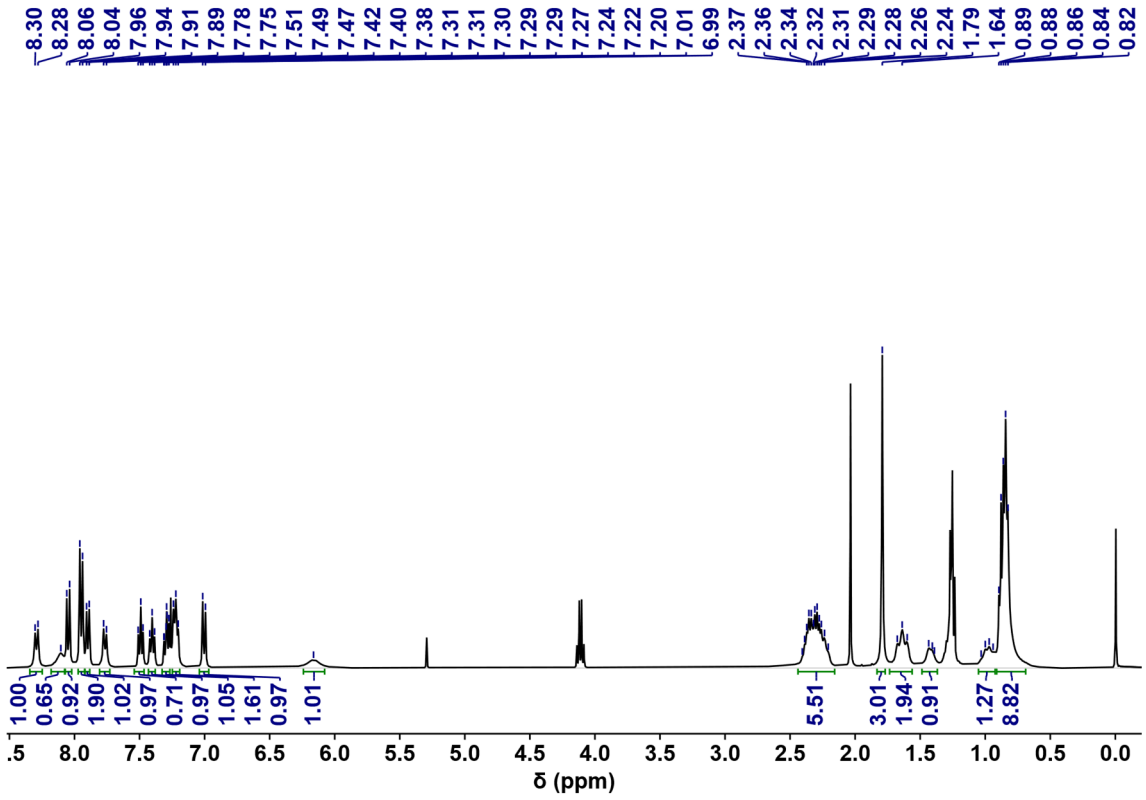


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*R,S*)-**3**.

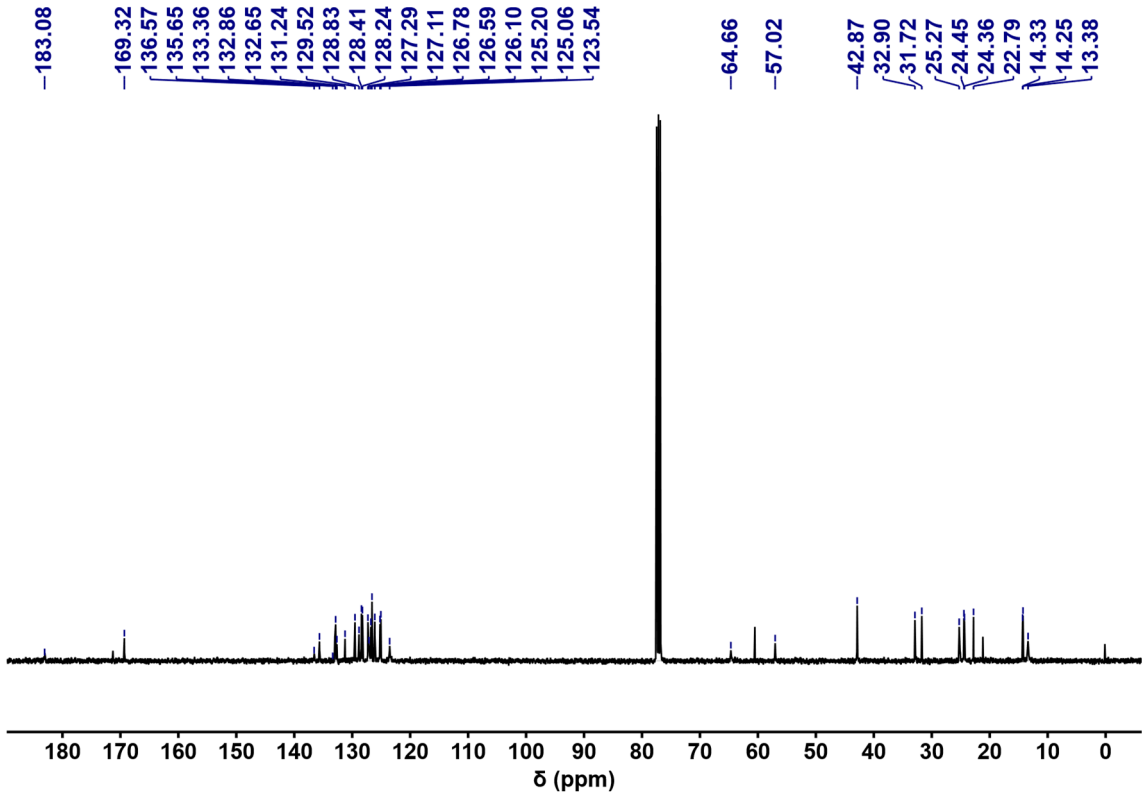


Figure S12. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R,S*)-**3**.

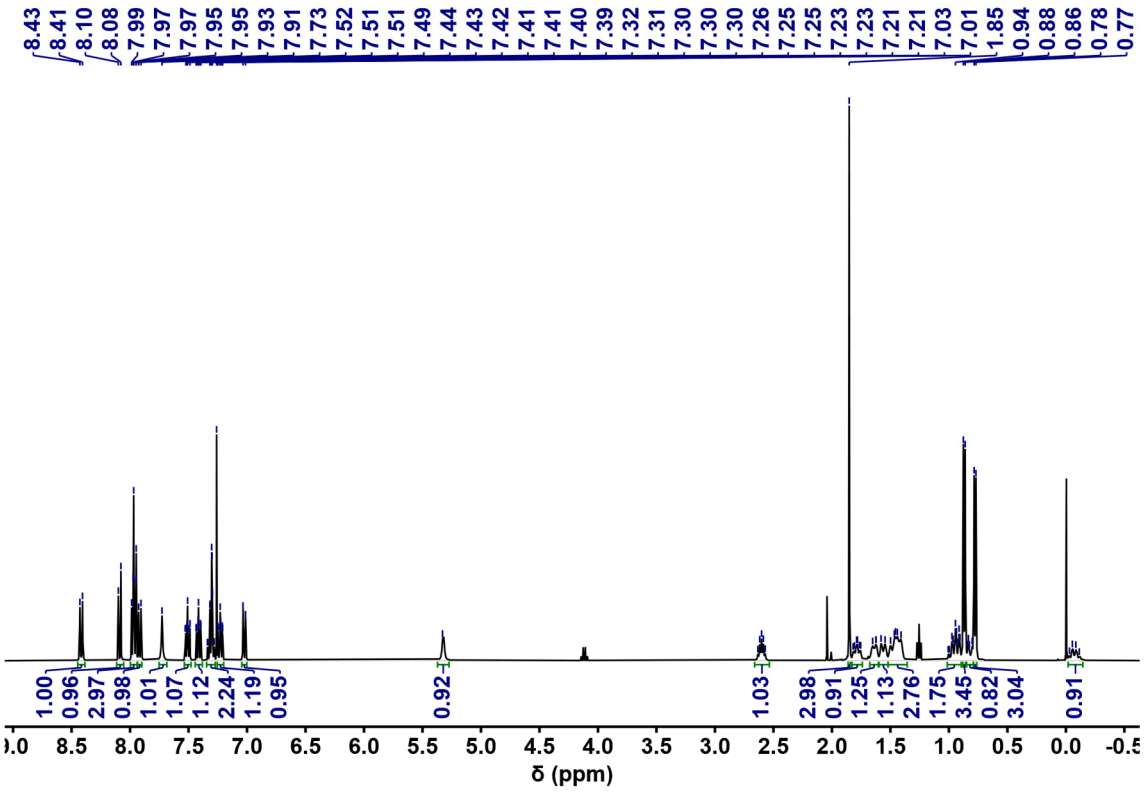


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*R,S*)-**4**.

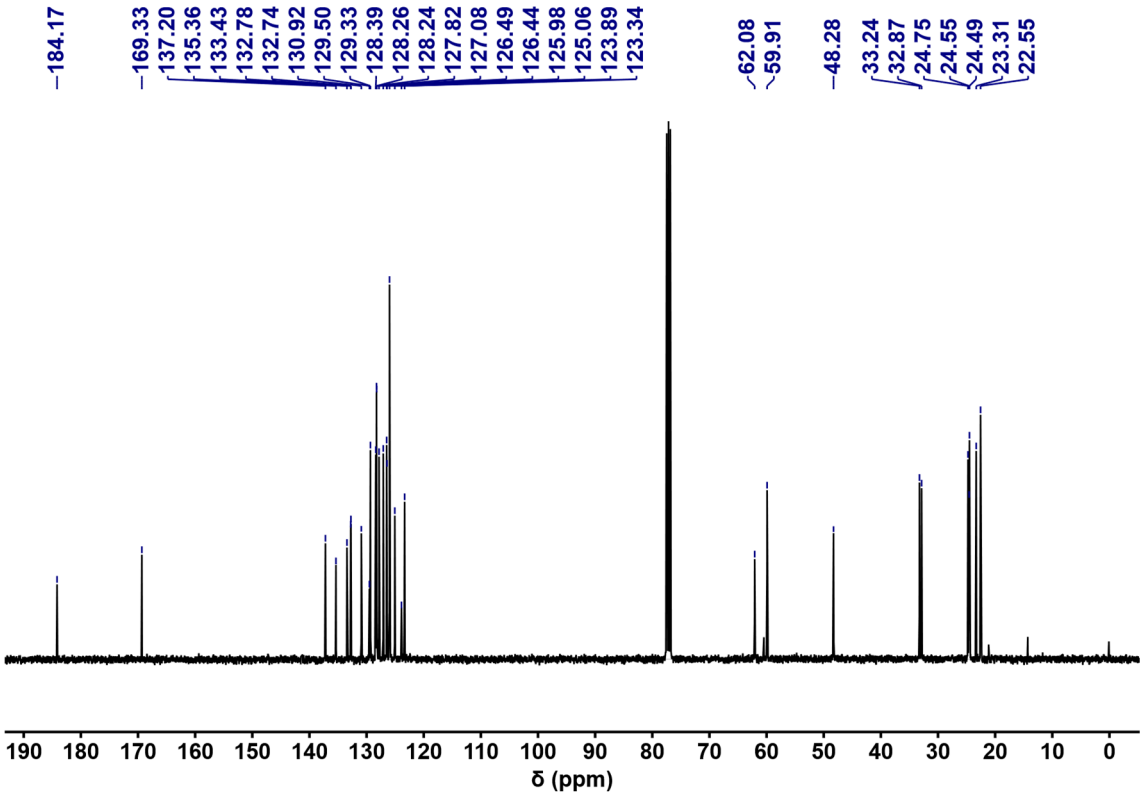


Figure S14. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R,S*)-**4**.

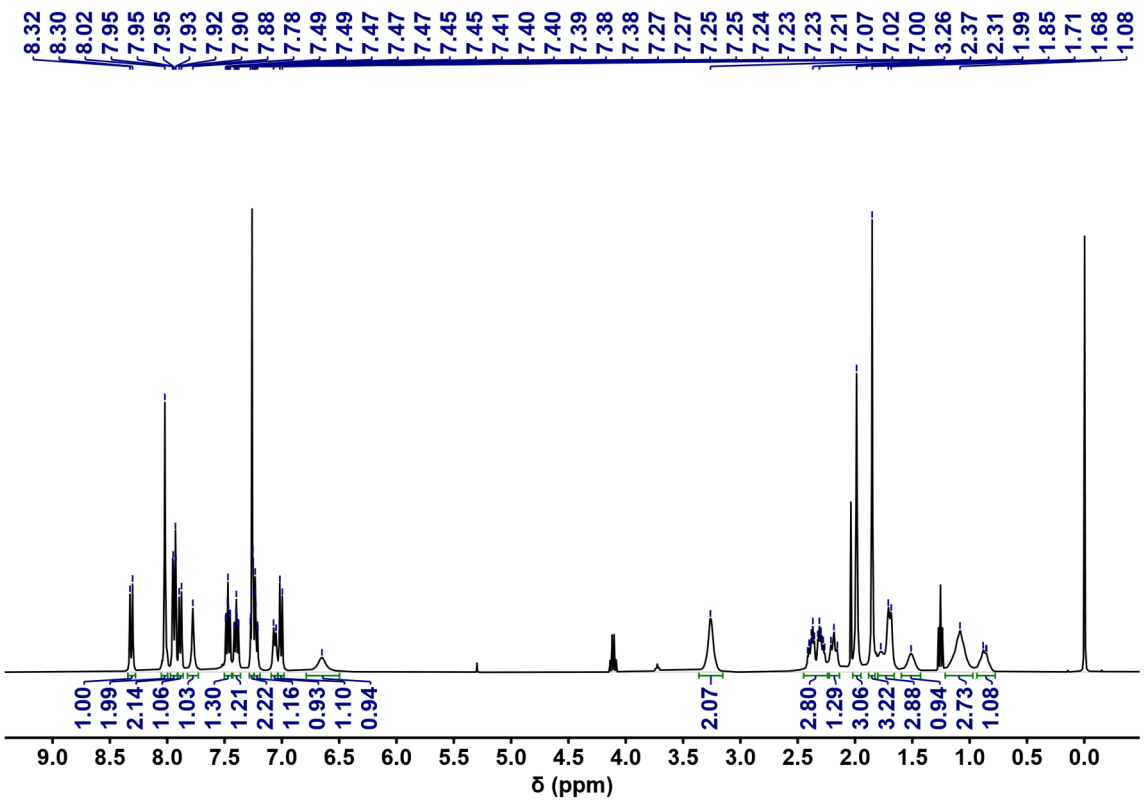


Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*R,S*)-**5**.

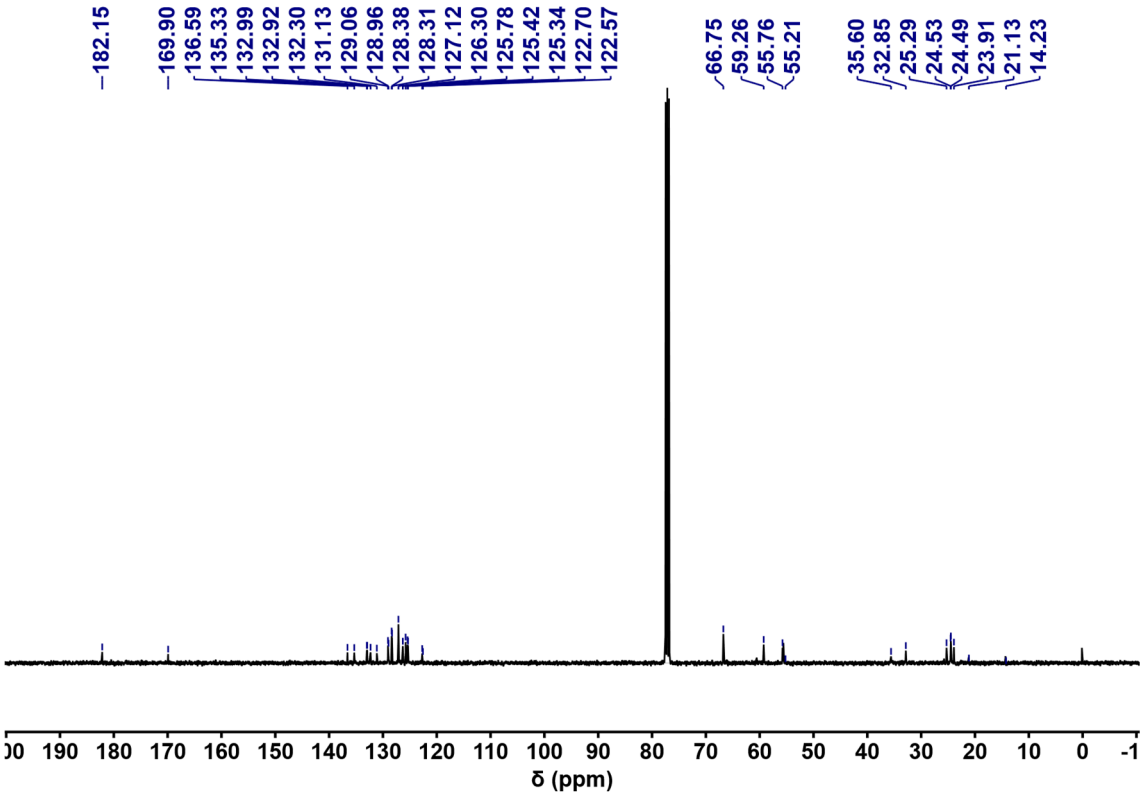


Figure S16. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R,S*)-**5**.

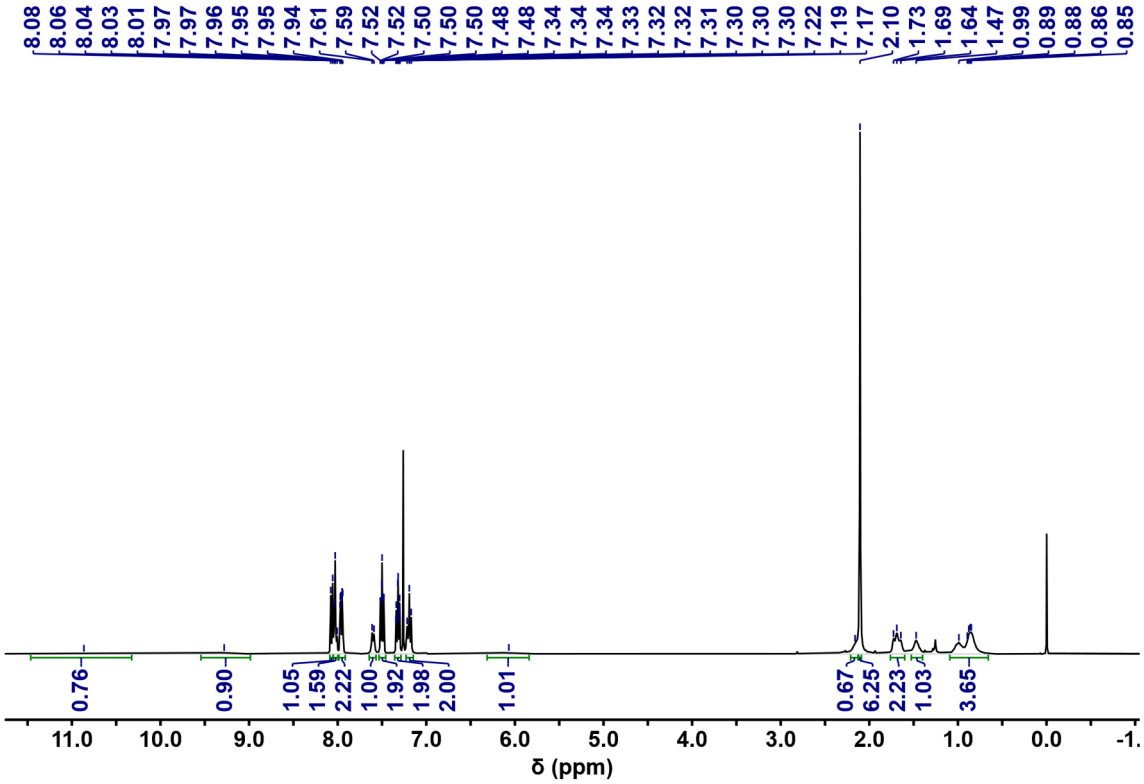


Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*R,S*)-**6**.

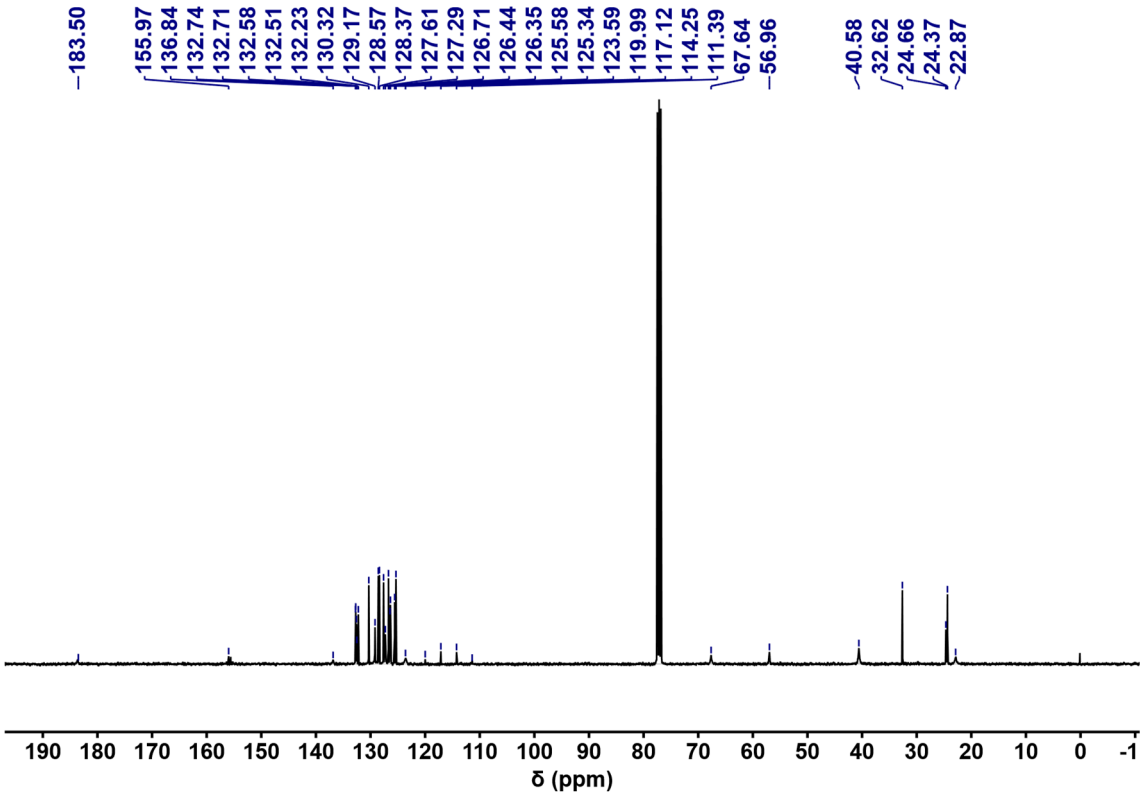


Figure S18. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R,S*)-**6**.

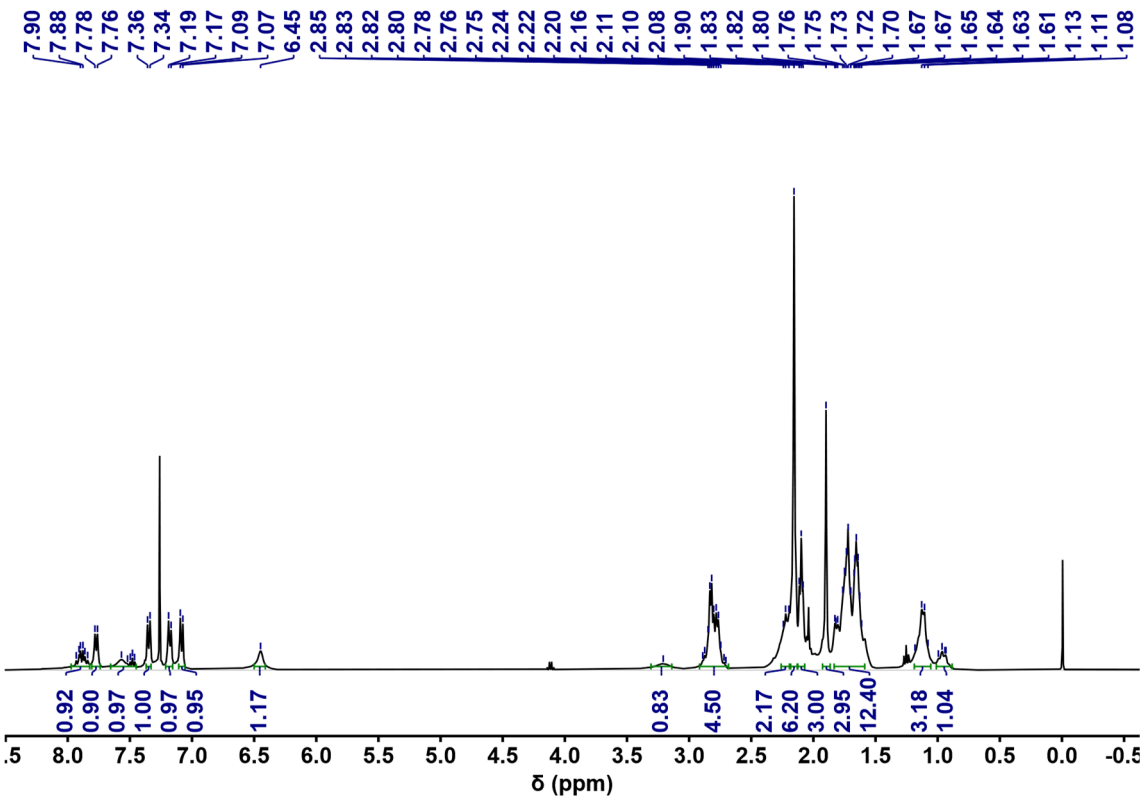


Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*R,S*)-**7**.

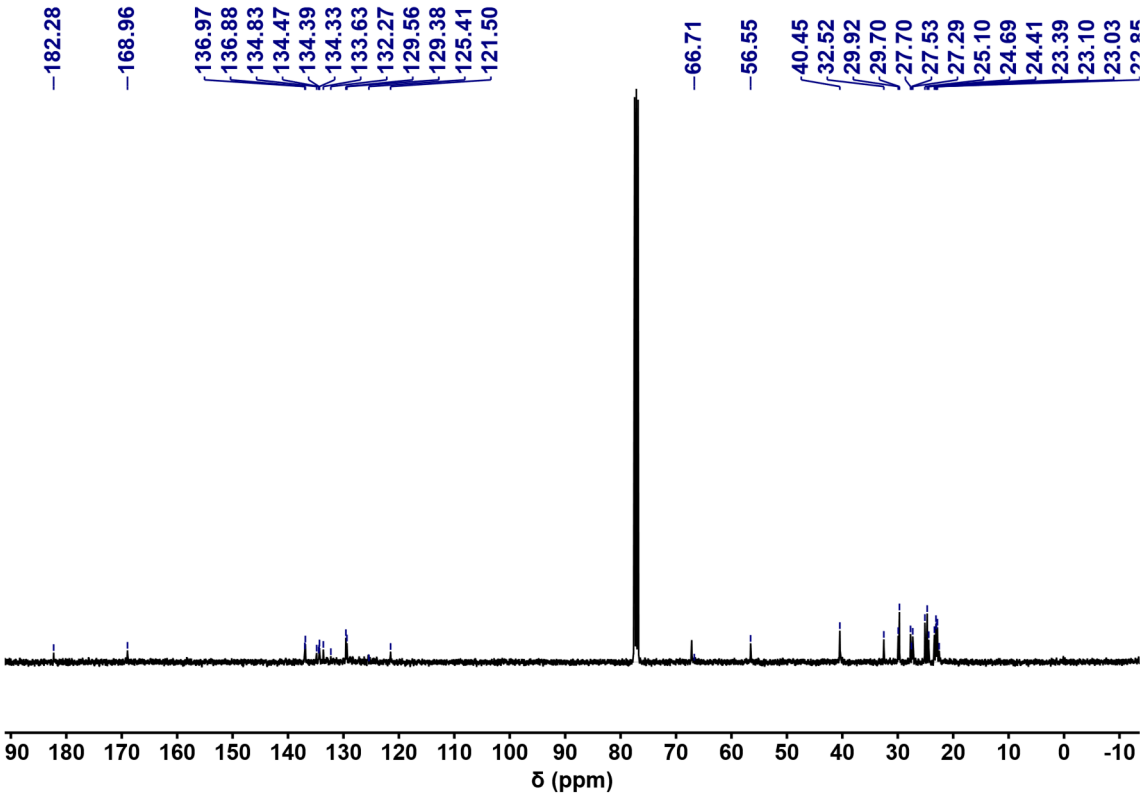


Figure S20. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R,S*)-**7**.

X-Ray crystallographic analysis

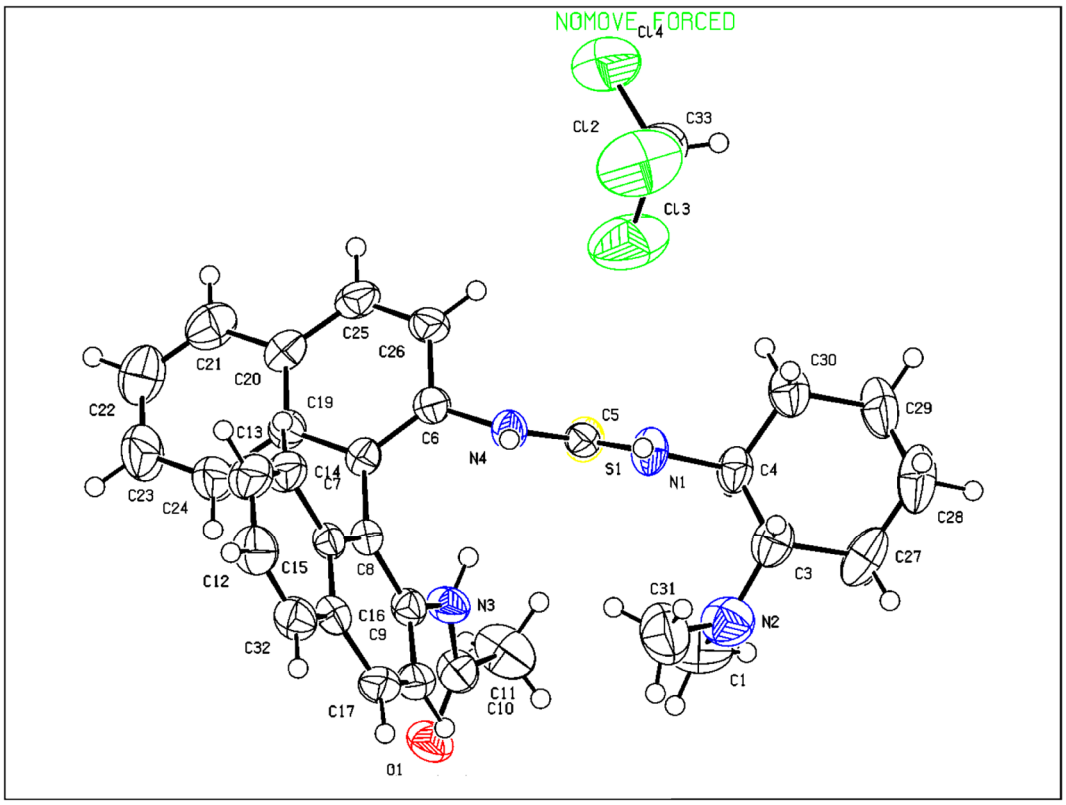


Figure S21. X-ray structure of (*R,S*)-**1**.

Table S1. Crystallographic table for (*R,S*)-**1**.

	(*R,S*)-**1**
CCDC Deposition number	2261514
Empirical formula	$C_{32}H_{35}Cl_3N_4OS$
Formula weight	630.05
Temperature (K)	290.0
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	10.4638(10)
b (Å)	13.6095(10)
c (Å)	11.5026(10)
α (°)	90
β (°)	102.123(4)
γ (°)	90
Volume ($Å^3$)	1601.5(2)
Z	2
ρ_{calc} (g/cm^3)	1.307
μ (mm^{-1})	0.383
F(000)	660.0
Crystal size (mm^3)	0.24 × 0.13 × 0.1
Radiation	MoKα (λ = 0.71073)
Theta range for data collection (°)	3.982 to 55.074
Index ranges	$-13 \leqslant h \leqslant 13$, $-17 \leqslant k \leqslant 17$, $-14 \leqslant l \leqslant 14$
Reflections collected	18095
Independent reflections	7340 [R_{int} = 0.0530, R_{sigma} = 0.0659]
Data/restraints/parameters	7340/1/373
Goodness-of-fit on F^2	1.000
Final R indexes [I>=2σ (I)]	R_1 = 0.0529, wR_2 = 0.1186
Final R indexes [all data]	R_1 = 0.0842, wR_2 = 0.1383
Largest diff. peak/hole (e $Å^{-3}$)	0.40/-0.36
Flack parameter	0.07(4)

Procedure for polymerization

Polymerizations were performed in 4 mL glass reactors inside the glovebox. In a typical polymerization reaction, catalyst (0.056 mmol, 2.0 equiv), initiator (0.028 mmol, 1.0 equiv) and *rac*-LA (200 mg, 1.39 mmol, 50 equiv) were dissolved in 1.19 mL of dichloromethane at 40 °C. At predetermined time intervals, 70 μL aliquots were withdrawn from the polymerization reaction and quickly quenched into 0.5 mL of $CDCl_3$ acidified with benzoic acid (1.0 wt%). The quenched aliquots were analyzed by ^{1}H NMR for monomer conversion.

After a desired period of time, the polymerization was quenched by addition of 2.0 mL $CHCl_3$ acidified with benzoic acid (1.0 wt%). The quenched mixture was precipitated into 50 mL of cold methanol, filtered, and washed with cold methanol to remove any catalyst residue or unreacted monomer and dried in a vacuum oven at 60 °C to a constant weight.

Table S2. Ring-opening polymerization results of LA by different catalysts.[a]

Entry	Cat.	M	Solvent	[M]:[Cat]:[I]	T (°C)	t (h)	Conv. (%)[b]	M_n[c] (kDa)	$Đ$[c]	T_m[d] (°C)	P_m[e]
1	(*R,S*)-**1**	*rac*-LA	DCM	50:2:1	40	77	39	5.5	1.09	140	0.95
2[f]	(*R,S*)-**1**	*rac*-LA	$CHCl_3$	50:2:1	40	84	48	n.d.	n.d	n.d.	n.d.
3[f]	(*R,S*)-**1**	D-LA	$CHCl_3$	50:2:1	40	84	96	12.4	1.08	163	0.99
4[f]	(*R,S*)-**1**	L-LA	$CHCl_3$	50:2:1	40	84	16	-	-	-	-
5[f]	(*S,R*)-**1**	*rac*-LA	$CHCl_3$	50:2:1	40	84	45	6.7	1.08	140	0.95
6[f]	(*S,R*)-**1**	D-LA	$CHCl_3$	50:2:1	40	84	13	-	-	-	-
7[f]	(*S,R*)-**1**	L-LA	$CHCl_3$	50:2:1	40	84	92	11.8	1.07	163	0.99
8[g]	(*R,S*)-**1**	D-LA	DCM	50:2:1	40	96	91	13.5	1.06	168	0.99
9[g]	(*R,S*)-**1**	L-LA	DCM	50:2:1	40	96	12	-	-	-	-
10[g]	(*R,S*)-**2**	*rac*-LA	DCM	50:2:1	40	120	42	7.0	1.07	131	0.91
11[g]	(*R,S*)-**2**	D-LA	DCM	50:2:1	40	120	83	12.8	1.06	163	0.99
12[g]	(*R,S*)-**2**	L-LA	DCM	50:2:1	40	120	14	-	-	-	-
13	(*R,S*)-**1**/ (*S,R*)-**1**	*rac*-LA	TOL	50:2:1	70	48	88	6.1	1.10	165	0.83
14	(*R,R*)-**1**/ (*S,S*)-**1**	*rac*-LA	TOL	50:2:1	70	48	87	6.1	1.09	n.d.	0.79

[a]Reaction conditions: concentration of monomer (M) is 1.0 M, using BnOH as initiator (I), reaction temperature (T), reaction time (t). [b]Monomer conversion measured by ^{1}H NMR of the quenched solution. [c]Number-average molecular weight (M_n) and dispersity index ($Đ = M_w/M_n$) determined by size exclusion chromatography (SEC) at 40 °C in THF. [d]T_m values were determined by DSC from the 2nd heating curve, n.d. = not detected. [e]Determined by homonuclear decoupled ^{1}H NMR and calculated based on ESC mechanism. [f]4-methylbenzyl alcohol as initiator. [g]*D*-methyl lactate as initiator.

Table S3. Ring-opening polymerization results of *rac*-LA by (*R,S*)-**1** and Base.[a]

Entry	Base	Solvent	[M]:[Cat]:[base]:[I]	*T* (°C)	*t* (min)	Conv. (%)[b]	M_n[c] (kDa)	*Đ*[c]	T_m[c] (°C)	P_m[e]
1[f]	TBD	$CHCl_3$	100:1:1:1	25	60	⩾99	20.0	1.49	n.d.	0.67
2[g]	MeOK	THF	100:3:1:0	25	5	⩾99	24.0	1.54	n.d.	0.65
3[g]	MeONa	THF	100:3:1:0	25	1	⩾99	18.6	1.46	n.d.	0.71

[a]Reaction conditions: concentration of monomer (M) is 1.0 M, reaction temperature (*T*), reaction time (*t*). [b]Monomer conversion measured by ^{1}H NMR of the quenched solution. [c]Number-average molecular weight (M_n) and dispersity index ($Đ = M_w/M_n$) determined by size exclusion chromatography (SEC) at 40 °C in THF. [d]T_m values were determined by DSC, n.d. = not detected. [e]Determined by homonuclear decoupled ^{1}H NMR and calculated based on ESC mechanism. [f]TBD = 1,5,7-[4.4.0]dec-5-ene, BnOH as initiator. [g]methoxide as initiator.

Procedure for chiral HPLC chromatograms of the unreacted monomer

Control experiment: D-LA (2.0 mg) and L-LA (5.5 mg) were dissolved in 1.5 mL of DCM/hexane = 1/2 solution for standard HPLC test.

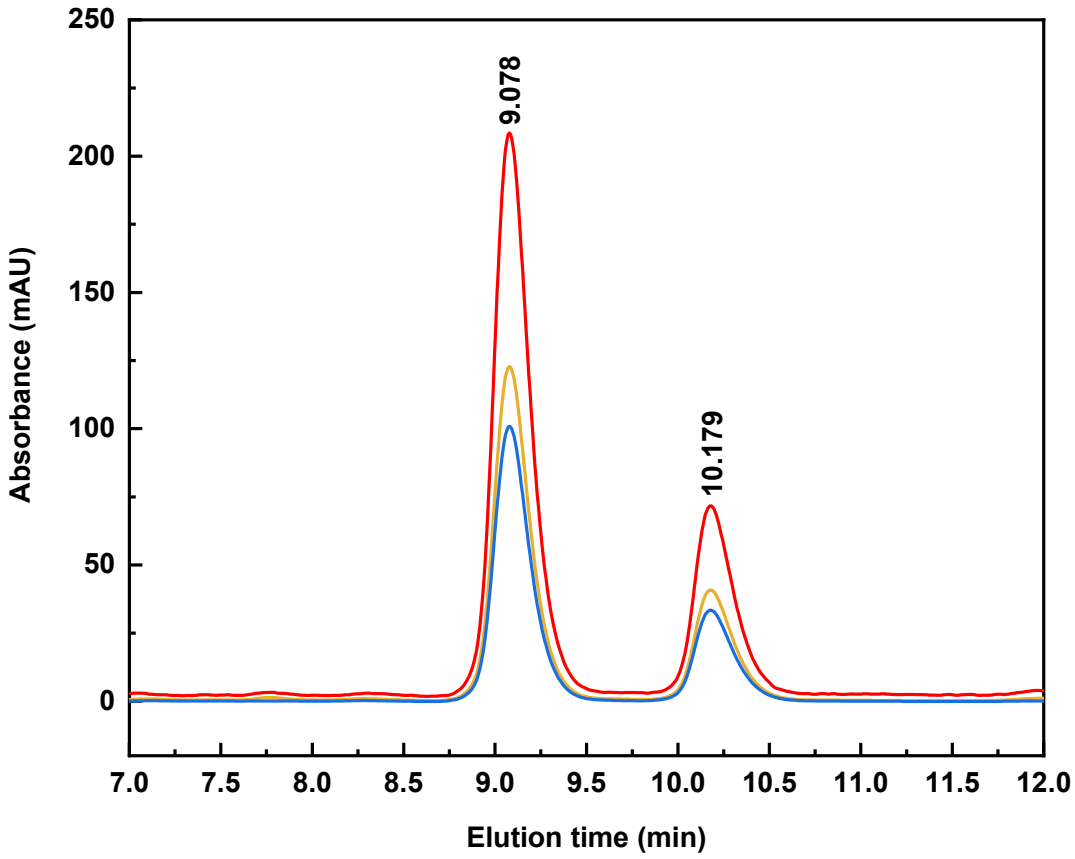


Figure S22. HPLC chromatograms of D-LA/L-LA = 4/11. Column, Chiralpak IA; flow rate, 1.0 mL/min; eluent, hexane/isopropanol = 90/10; detector, UV (230 nm; 210 nm; 202 nm); temperature, 30 °C.

signal	#	Time	Area	Height	Area%	*ee*%
210 nm	L-LA	9.079	1763.12	122.61	73.38	46.76
	D-LA	10.178	639.60	40.58	26.62	
202 nm	L-LA	9.078	2964.36	206.32	73.70	47.39
	D-LA	10.179	1058.00	68.91	26.30	
230 nm	L-LA	9.079	1444.22	100.96	73.31	46.61
	D-LA	10.178	525.91	33.48	26.69	

Procedure for chiral HPLC test of the unreacted reaction mixture: After a desired period of time, the polymerization was quenched by addition of 2.0 mL $CHCl_3$ acidified with benzoic acid (1.0 wt%). The quenched mixture was precipitated into 50 mL of cold methanol, filtered, and washed with cold methanol to remove any catalyst residue or unreacted monomer. The solution was concentrated under reduced pressure, and the residue was purified by flash chromatograph on silica gel (DCM as eluent) to obtain unreacted monomer. The unreacted monomer was dissolved in a DCM/hexane = 1/2 solution and the ee of the monomer was measured using an Agilent 1260 Series HPLC. The selectivity factor, s, was determined from the equation $s = \{\ln[(1 - c)(1 - ee)]\}/\{\ln[(1 - c)(1 + ee)]\}$, where c is the monomer conversion and ee is the enantiomeric excess of the unreacted monomer.

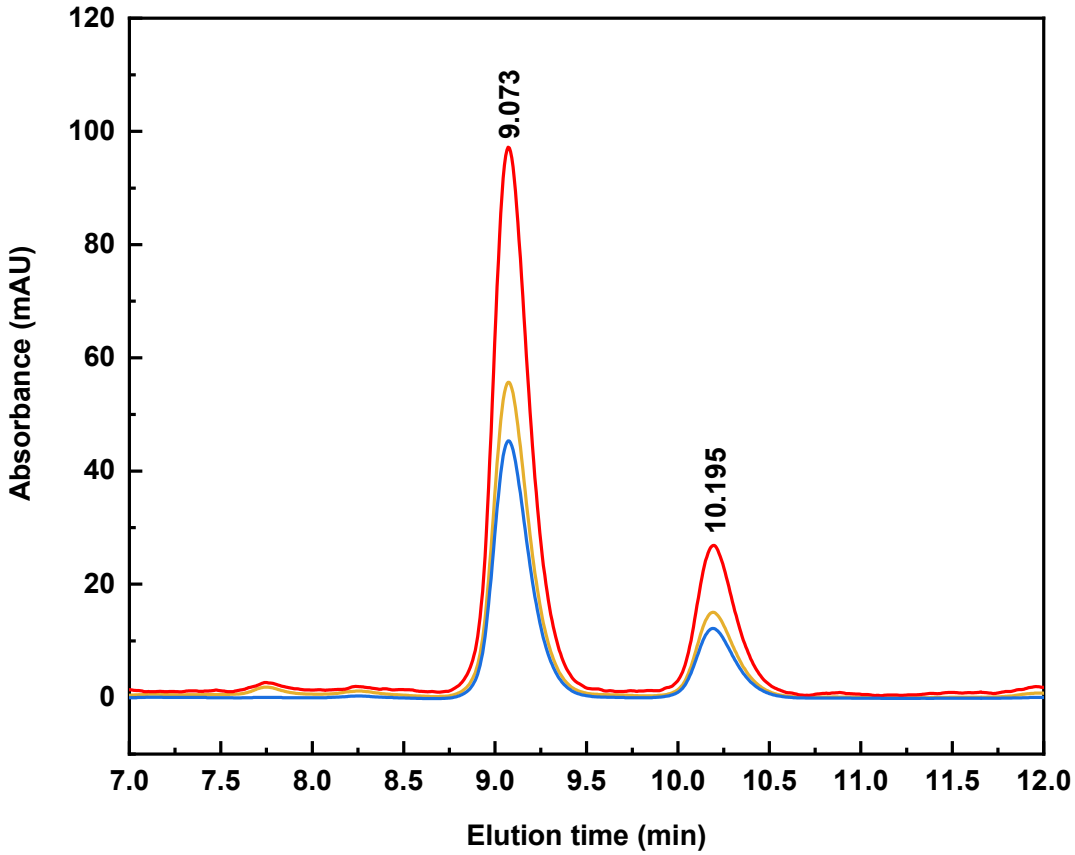


Figure S23. HPLC chromatograms of unreacted monomer obtained by (*R,S*)-**1** (**Table S2** Entry 1). Column, Chiralpak IA; flow rate, 1.0 mL·min^{-1}; eluent, hexane-isopropanol = 90/10; detector, UV (230 nm); temperature, 30 °C.

signal	#	Time	Area	Height	Area%	*ee*%
210 nm	L-LA	9.074	801.95	55.57	77.63	55.26
	D-LA	10.192	231.11	14.97	22.37	
202 nm	L-LA	9.073	1378.22	96.26	77.29	54.59
	D-LA	10.195	404.84	26.17	22.71	
230 nm	L-LA	9.074	648.81	45.50	77.54	55.09
	D-LA	10.192	187.90	12.26	22.46	

ee% = (54.98 ± 0.35)%

$s = k_D/k_L$ = {ln[(1 − c)(1 − ee)]}/{ln[(1 − c)(1 + ee)]} = 23.0

Kinetic study of the ROP of *rac*-LA, D-LA, and L-LA

Table S4. The raw date of kinetic for ROP of *rac*-LA, D-LA, and L-LA catalyzed by (*R,S*)-**1**.[a]

Entry	*t* (h)	Conv.*rac*-LA (%)	Conv.D-LA (%)	Conv.L-LA (%)
1	12	11	27	2
2	24	19	53	3
3	36	26	72	5
4	48	33	82	8
5	60	39	90	12
6	72	45	93	13
7	84	48	94	16

[a]Reaction conditions: [M]/[(*R,S*)-**1**]/[I] = 50/2/1, concentration of monomer (M) = 1.0 M, initiator (I) = 4-methylbenzyl alcohol, solvent = $CHCl_3$, reaction temperature = 40 °C.

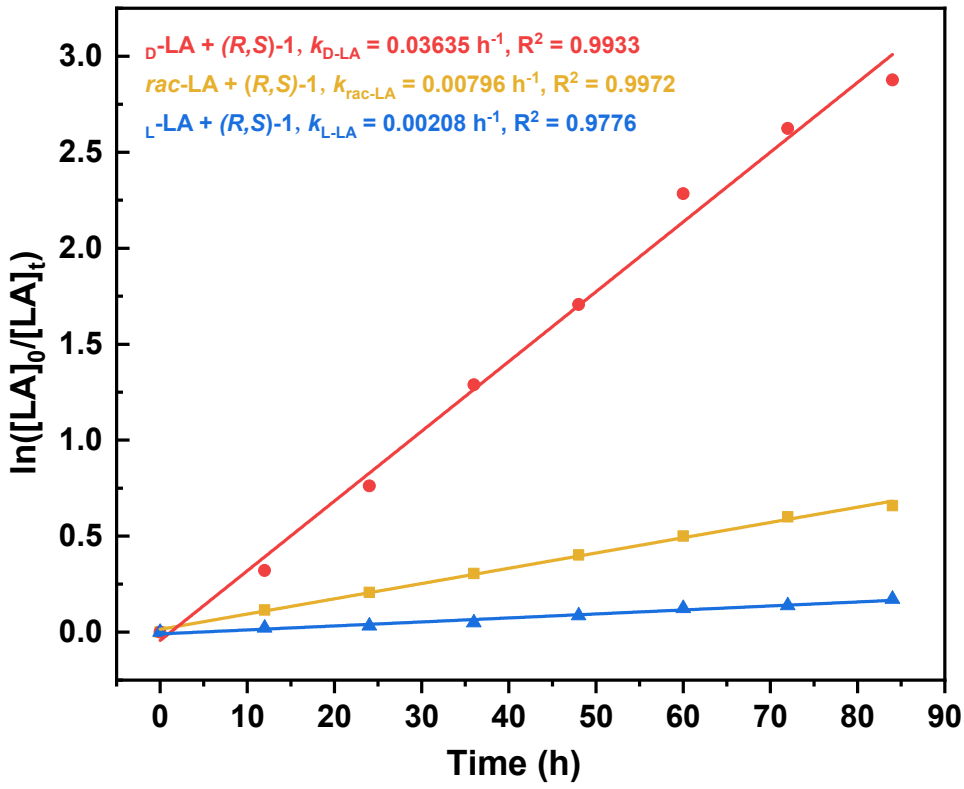


Figure S24. Plots of $\ln([LA]_0/[LA]_t)$ versus time for polymerization catalyzed by (*R,S*)-**1** ($k_{(R,S)\text{-}1/\text{D-LA}}/k_{(R,S)\text{-}1/\text{L-LA}}$ = 17.5). Red dot: ROP of D-LA, $k_{(R,S)\text{-}1/\text{D-LA}}$ = 0.03635 h^{-1}, R^2 = 0.9933. Yellow dot: ROP of *rac*-LA, $k_{(R,S)\text{-}1/rac\text{-LA}}$ = 0.00796 h^{-1}, R^2 = 0.9972. Blue dot: ROP of L-LA, $k_{(R,S)\text{-}1/\text{L-LA}}$ = 0.00208 h^{-1}, R^2 = 0.9776.

Table S5. The raw date of kinetic for ROP of *rac*-LA, D-LA, and L-LA catalyzed by (*S,R*)-**1**.[a]

Entry	*t* (h)	Conv.*rac*-LA (%)	Conv.D-LA (%)	Conv.L-LA (%)
1	12	11	2	27
2	24	19	4	49
3	36	27	5	65
4	48	32	7	77
5	60	38	10	84
6	72	44	12	89
7	84	45	13	92

[a]Reaction conditions: [M]/[(*S,R*)-**1**]/[I] = 50/2/1, concentration of monomer (M) = 1.0 M, initiator (I) = 4-methylbenzyl alcohol, solvent = $CHCl_3$, reaction temperature = 40 °C.

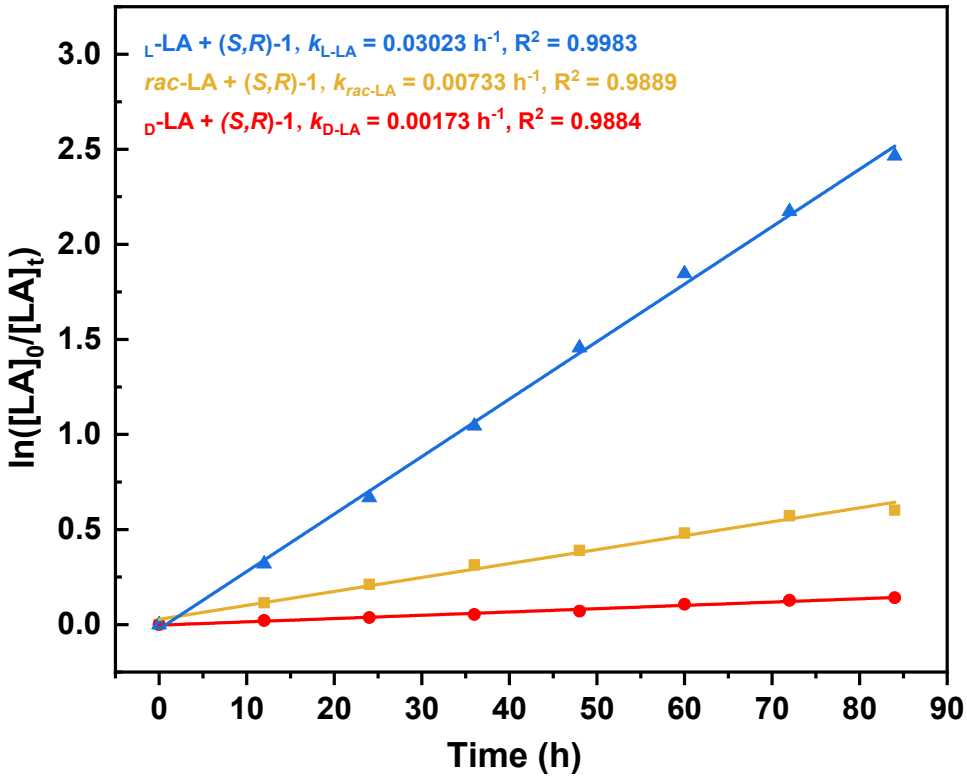


Figure S25. Plots of ln([LA]$_0$/[LA]$_t$) versus time for polymerization catalyzed by (*S,R*)-**1** ($k_{(S,R)\text{-}1/\text{L-LA}}/k_{(S,R)\text{-}1/\text{D-LA}}$ = 17.5). Red dot: ROP of D-LA, $k_{(S,R)\text{-}1/\text{D-LA}}$ = 0.00173 h^{-1}, R^2 = 0.9884. Yellow dot: ROP of *rac*-LA, $k_{(S,R)\text{-}1/rac\text{-LA}}$ = 0.00733 h^{-1}, R^2 = 0.9889. Blue dot: ROP of L-LA, $k_{(S,R)\text{-}1/\text{L-LA}}$ = 0.0302 h^{-1}, R^2 = 0.9983.

Table S6. The raw date of kinetic for ROP of *rac*-LA, D-LA, and L-LA catalyzed by (*R,S*)-**1**.[a]

Entry	*t* (h)	Conv.*rac*-LA (%)	Conv.D-LA (%)	Conv.L-LA (%)
1	12	9	20	1
2	24	16	40	2
3	36	22	54	3
4	48	27	67	5
5	60	32	74	7
6	72	36	82	9
7	84	42	87	10
8	96	45	91	12

[a]Reaction conditions: [M]/[(*R,S*)-**1**]/[I] = 50/2/1, concentration of monomer (M) = 1.0 M, initiator (I) = *D*-methyl lactate, solvent = DCM, reaction temperature = 40 °C.

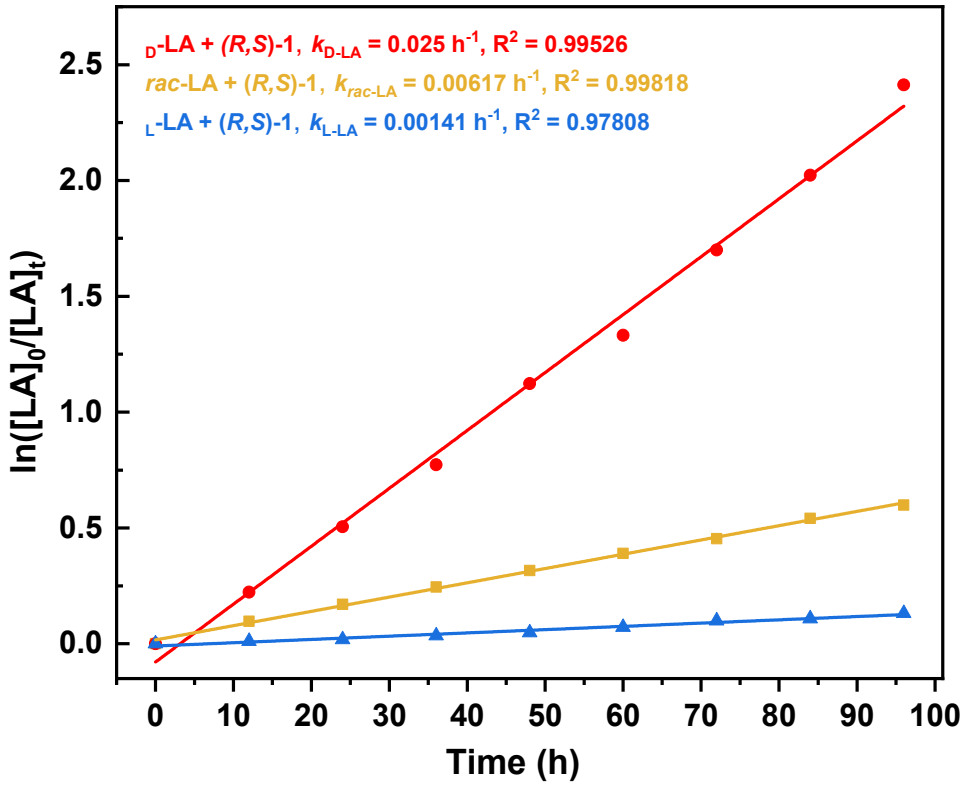


Figure S26. Plots of ln([LA]$_0$/[LA]$_t$) versus time for polymerization catalyzed by (*R,S*)-**1** ($k_{(R,S)\text{-}\mathbf{1}/\text{D-LA}}/k_{(R,S)\text{-}\mathbf{1}/\text{L-LA}}$ = 17.7). Red dot: ROP of D-LA, $k_{(R,S)\text{-}\mathbf{1}/\text{D-LA}}$ = 0.0250 h^{-1}, R^2 = 0.9953. Yellow dot: ROP of *rac*-LA, $k_{(R,S)\text{-}\mathbf{1}/rac\text{-LA}}$ = 0.00617 h^{-1}, R^2 = 0.9982. Blue dot: ROP of L-LA, $k_{(R,S)\text{-}\mathbf{1}/\text{L-LA}}$ = 0.00141 h^{-1}, R^2 = 0.9781.

Table S7. The raw date of kinetic for ROP of *rac*-LA, D-LA, and L-LA catalyzed by (*R,S*)-**2**.

Entry	*t* (h)	Conv.$_{rac\text{-LA}}$[a] (%)	Conv.$_{D\text{-LA}}$[b] (%)	Conv.$_{L\text{-LA}}$[c] (%)
1	12	6	16	1
2	24	12	30	2
3	36	18	42	5
4	48	24	55	6
5	60	30	64	8
6	72	35	73	10
7	84	39	78	12
8	96	42	83	14

[a]Reaction conditions: [M]/[(*R,S*)-**2**]/[I] = 50/2/1, concentration of monomer (M) = 1.0 M, initiator (I) = *D*-methyl lactate, solvent = DCM, reaction temperature = 40 °C.

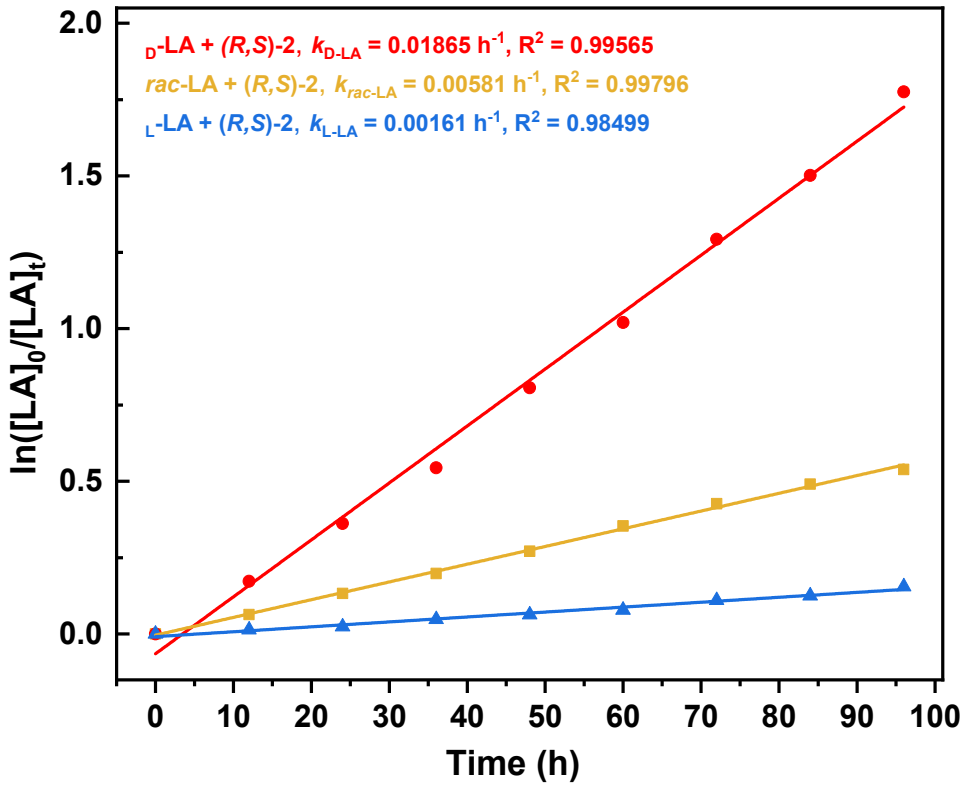


Figure S27. Plots of ln([LA]$_0$/[LA]$_t$) versus time for polymerization catalyzed by (*R,S*)-**2** ($k_{(R,S)\text{-}2/\text{D-LA}}/k_{(R,S)\text{-}2/\text{L-LA}}$ = 11.6). Red dot: ROP of D-LA, $k_{(R,S)\text{-}2/\text{D-LA}}$ = 0.0187 h^{-1}, R^2 = 0.9957. Yellow dot: ROP of *rac*-LA, $k_{(R,S)\text{-}2/rac\text{-LA}}$ = 0.00581 h^{-1}, R^2 = 0.9980. Blue dot: ROP of L-LA, $k_{(R,S)\text{-}2/\text{L-LA}}$ = 0.00161 h^{-1}, R^2 = 0.9850.

Thermal properties of polymers

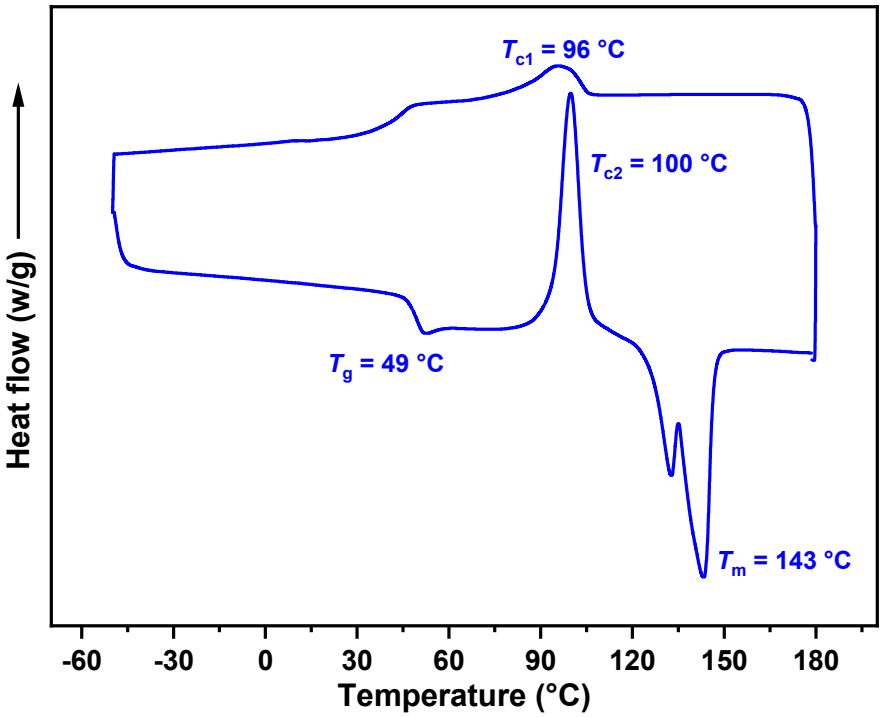


Figure S28. DSC curves of PLA obtained by [*rac*-LA]/[(*R*,*S*)-**1**]/[I] = 50/2/1, solvent = DCM.

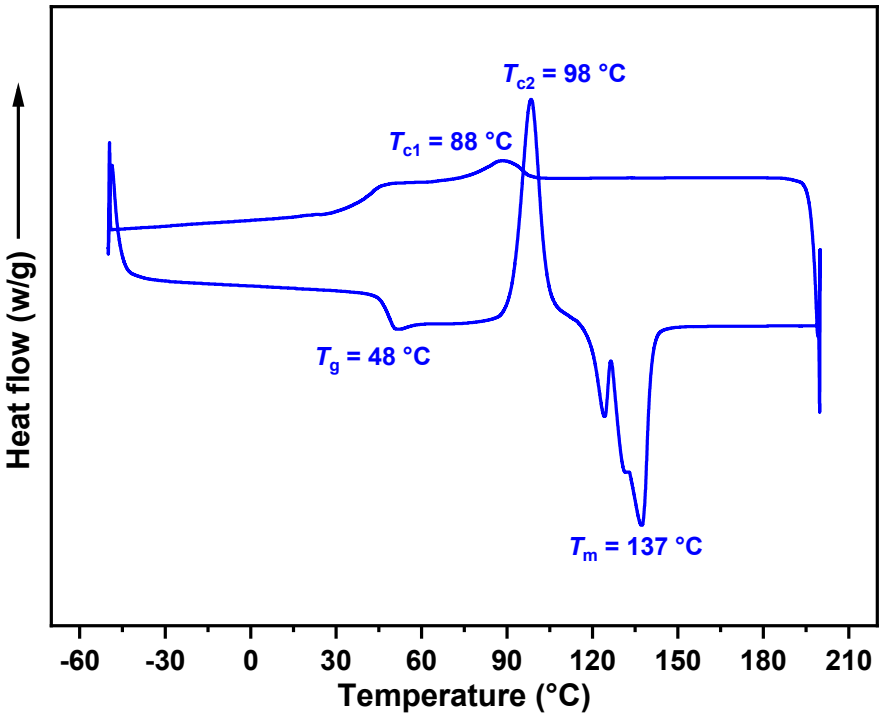


Figure S29. DSC curve of PLA obtained by [*rac*-LA]/[(*R*,*S*)-**1**]/[I] = 50/2/1, solvent = TOL.

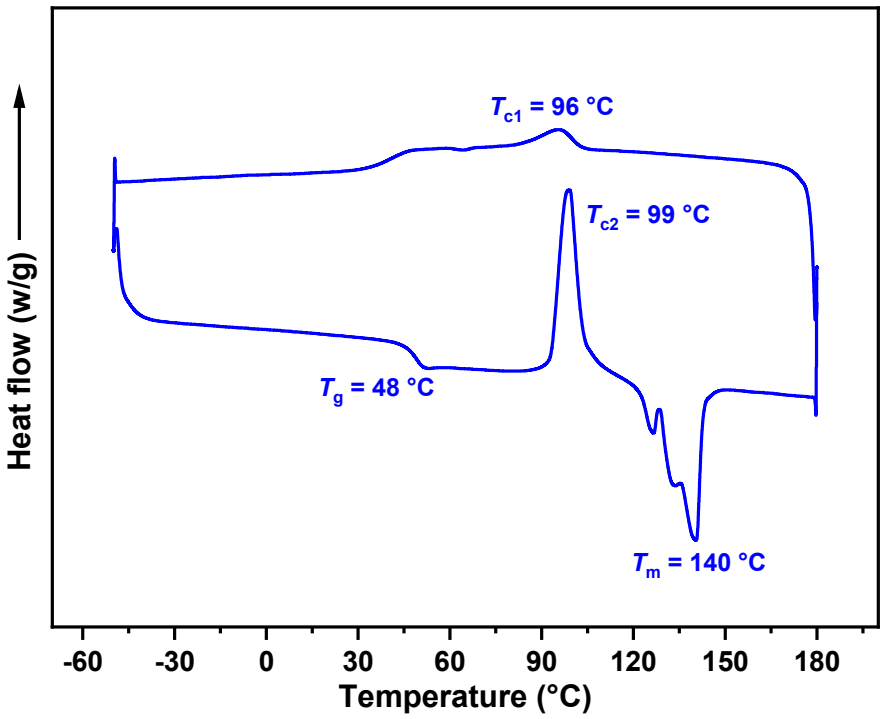


Figure S30. DSC curves of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = $CHCl_3$.

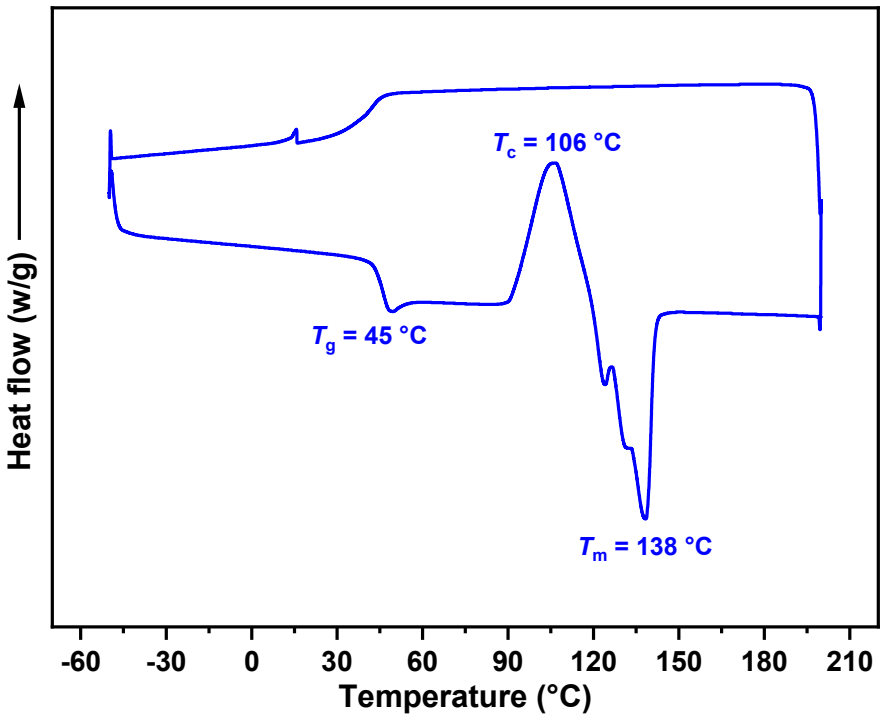


Figure S31. DSC curves of PLA obtained by [*rac*-LA]/[(*S,R*)-**1**]/[I] = 50/2/1, solvent = DCM.

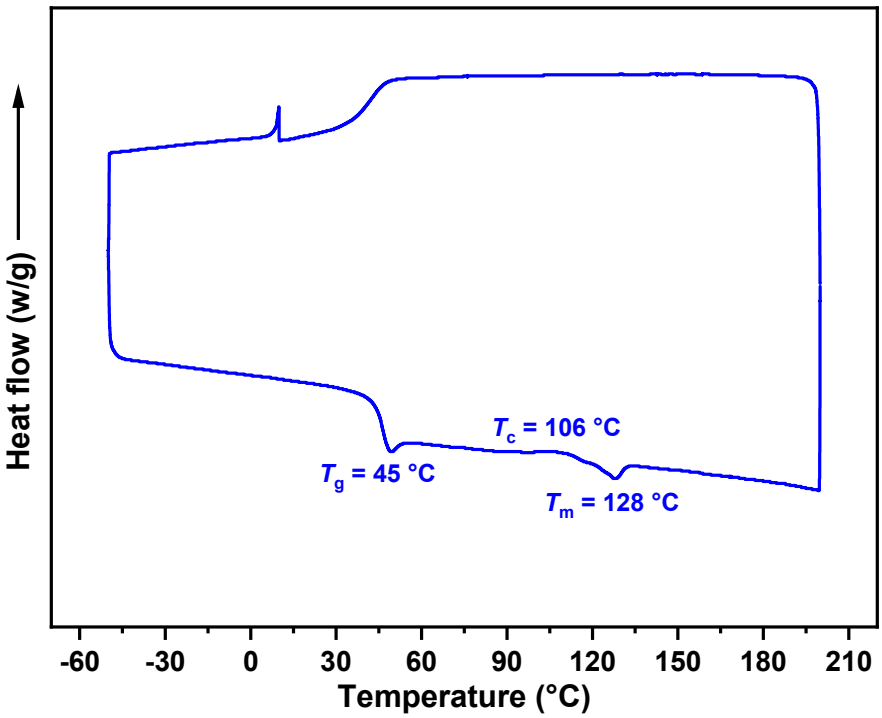


Figure S32. DSC curves of PLA obtained by [*rac*-LA]/[(*R,R*)-**1**]/[I] = 50/2/1, solvent = DCM.

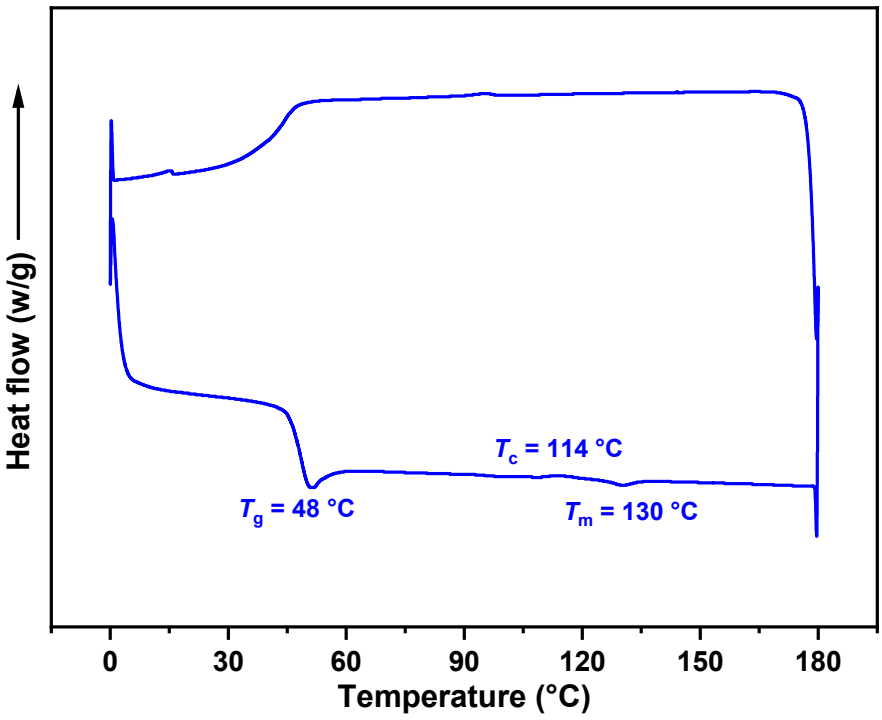


Figure S33. DSC curves of PLA obtained by [*rac*-LA]/[(*S,S*)-**1**]/[I] = 50/2/1, solvent = DCM.

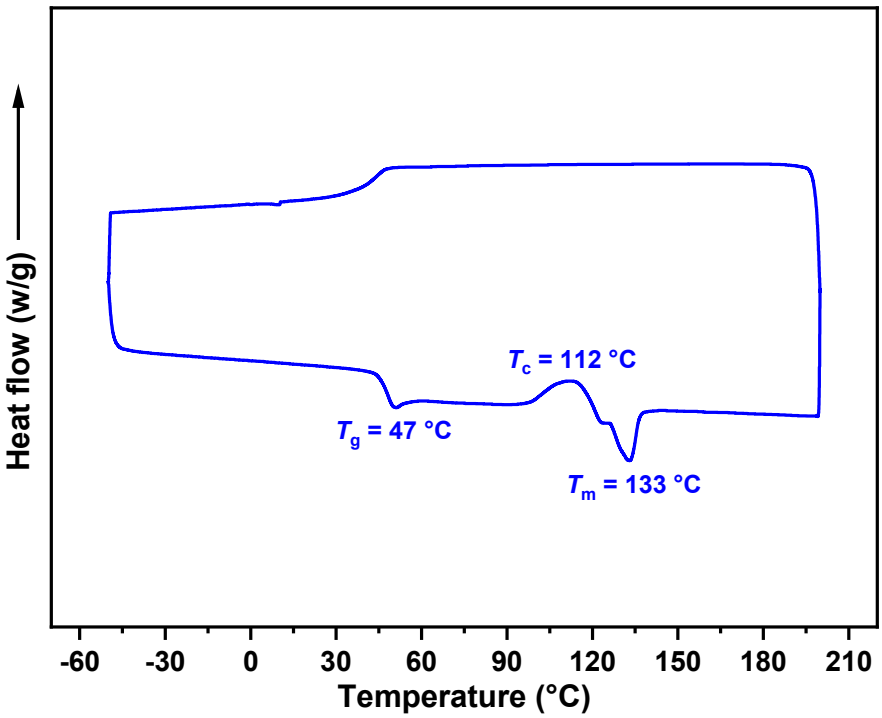


Figure S34. DSC curves of PLA obtained by [*rac*-LA]/[(*R,S*)-**2**]/[I] = 50/2/1, solvent = DCM.

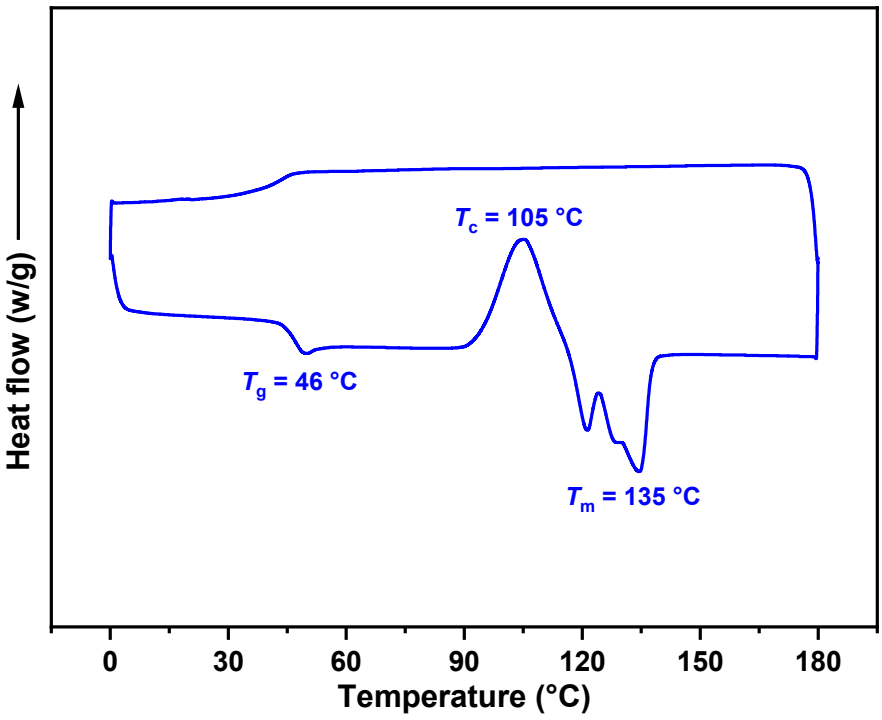


Figure S35. DSC curves of PLA obtained by [*rac*-LA]/[(*R,S*)-**3**]/[I] = 50/2/1, solvent = DCM.

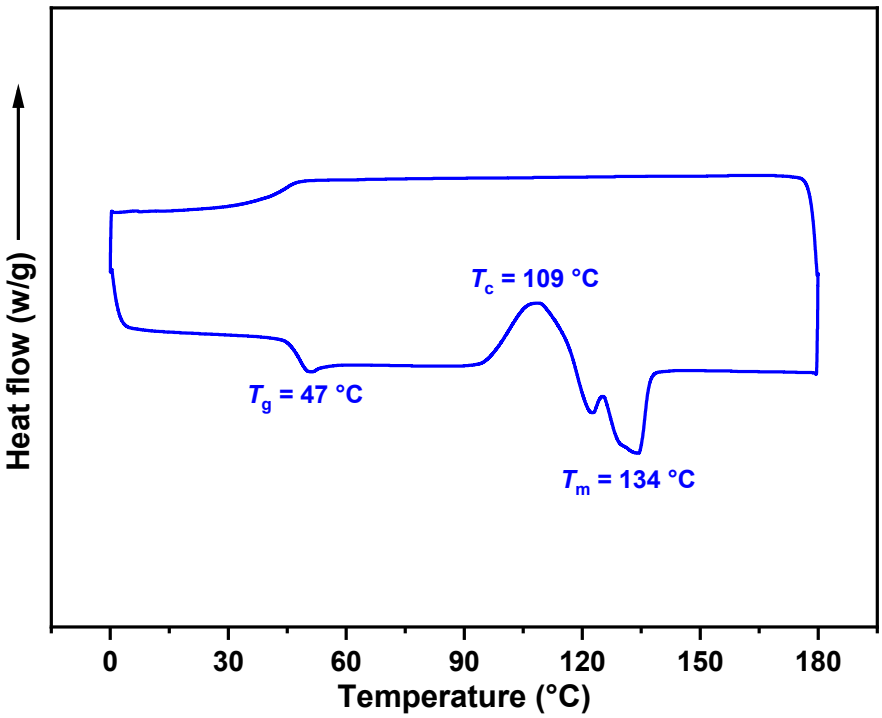


Figure S36. DSC curves of PLA obtained by [*rac*-LA]/[(*R,S*)-**6**]/[I] = 50/2/1, solvent = DCM.

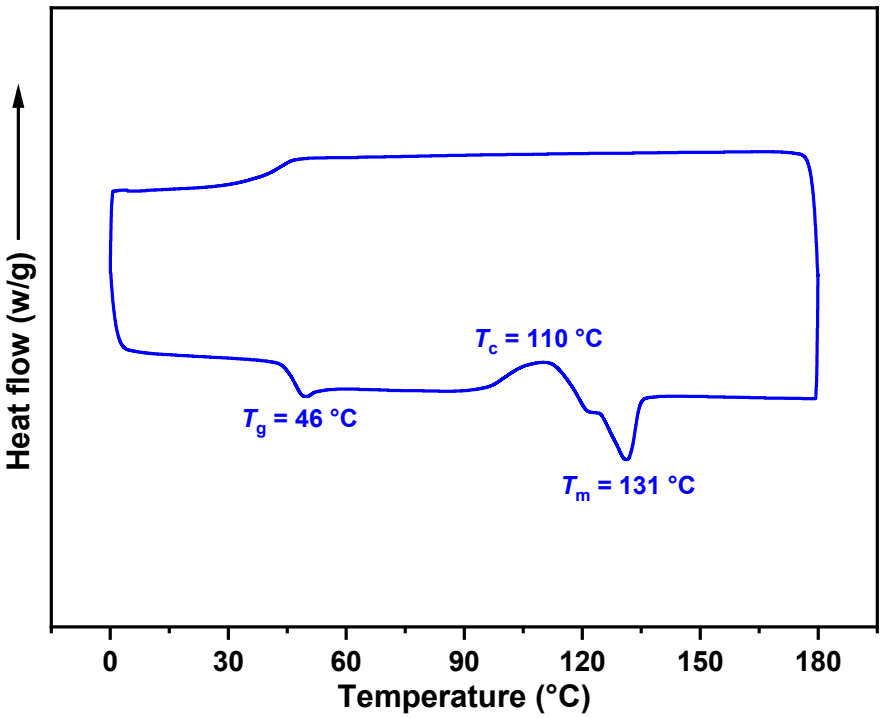


Figure S37. DSC curves of PLA obtained by [*rac*-LA]/[(*R,S*)-**7**]/[I] = 50/2/1, solvent = DCM.

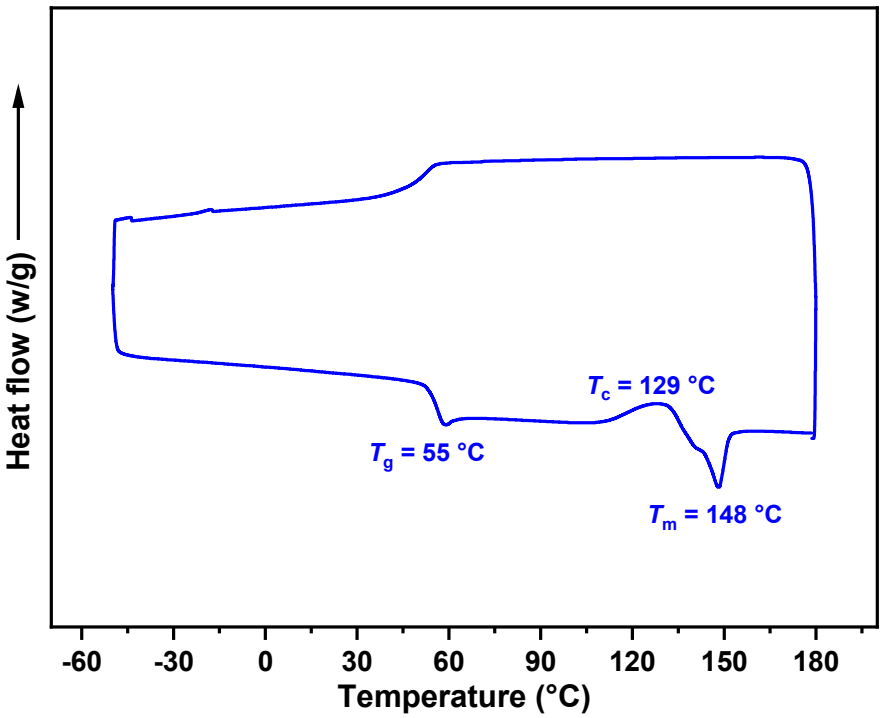


Figure S38. DSC curves of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 200/20/1, solvent = DCM.

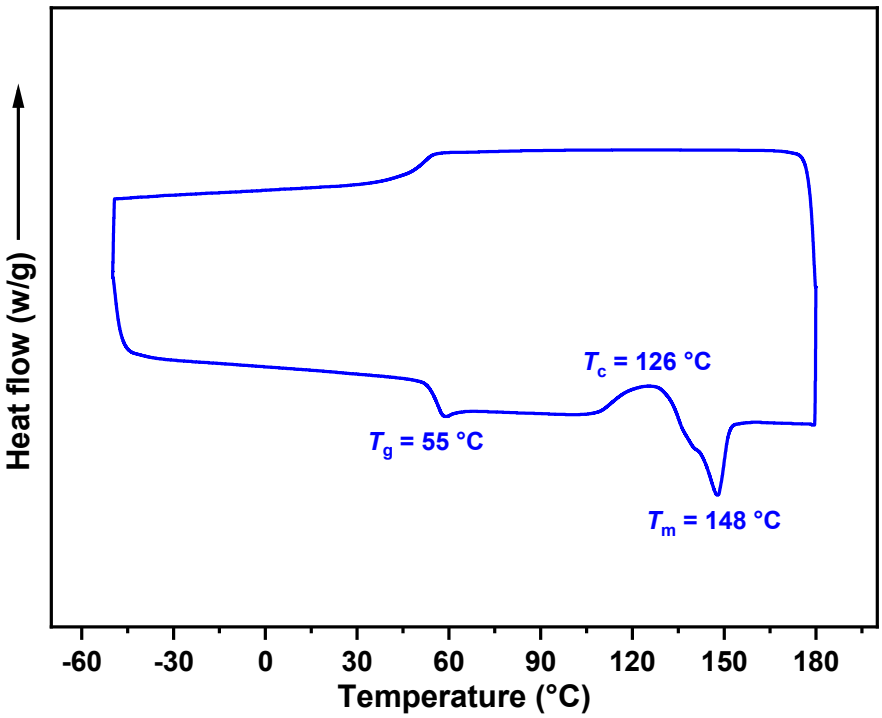


Figure S39. DSC curves of PLA obtained by [*rac*-LA]/[(*S,R*)-**1**]/[I] = 200/20/1, solvent = DCM.

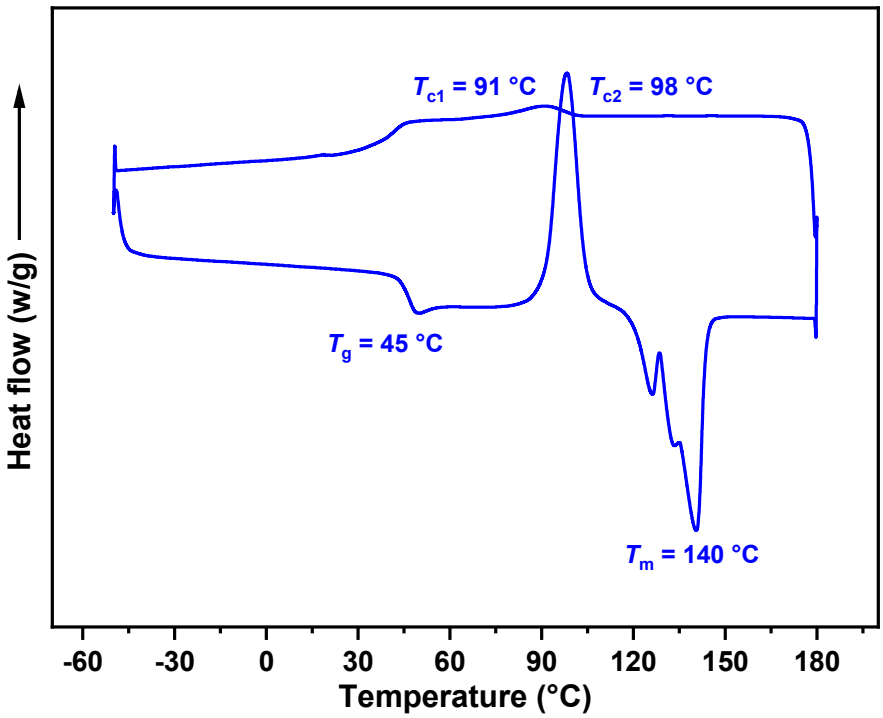


Figure S40. DSC curves of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = DCM.

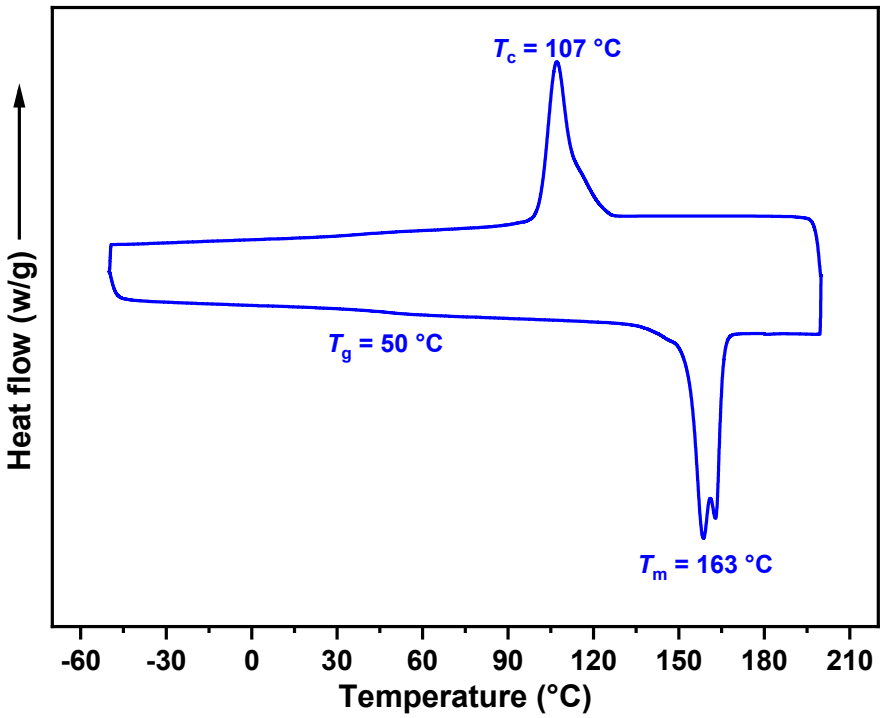


Figure S41. DSC curves of PLA obtained by [D-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = $CHCl_3$.

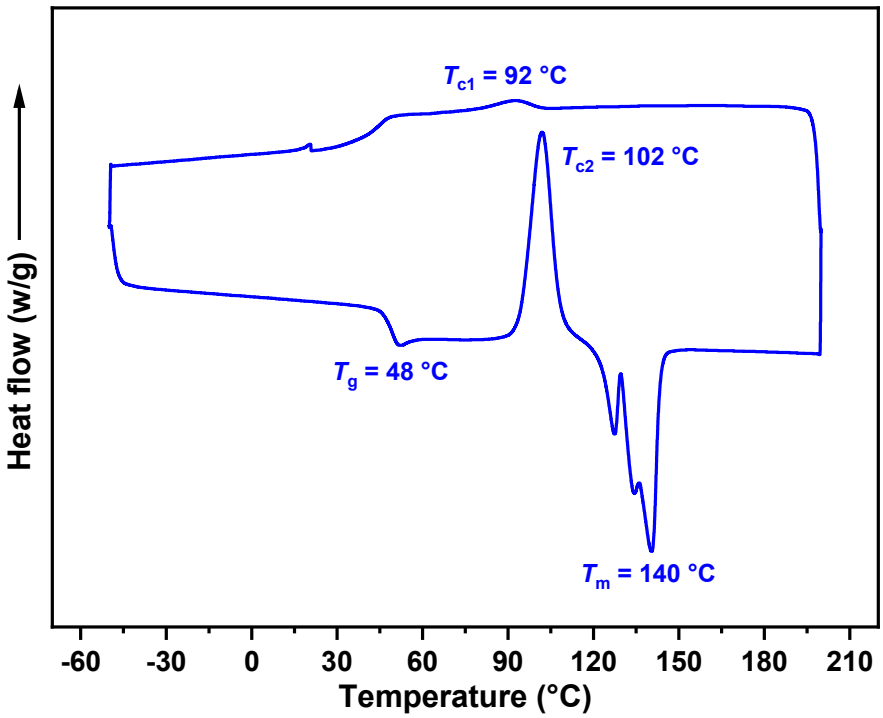


Figure S42. DSC curves of PLA obtained by [*rac*-LA]/[(*S,R*)-**1**]/[I] = 50/2/1, solvent = $CHCl_3$.

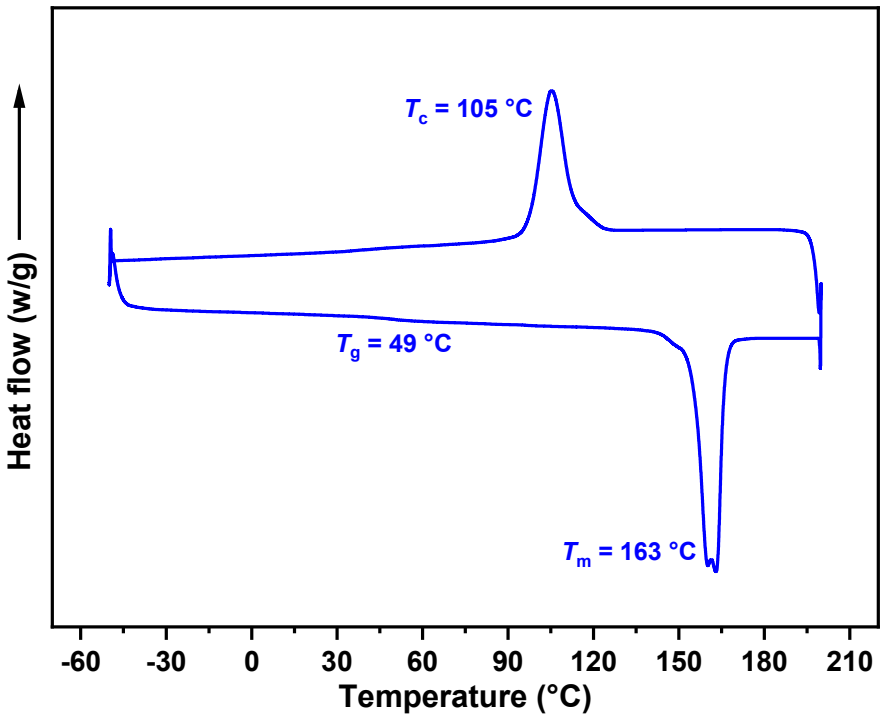


Figure S43. DSC curves of PLA obtained by [$_L$-LA]/[(*S,R*)-**1**]/[I] = 50/2/1, solvent = $CHCl_3$.

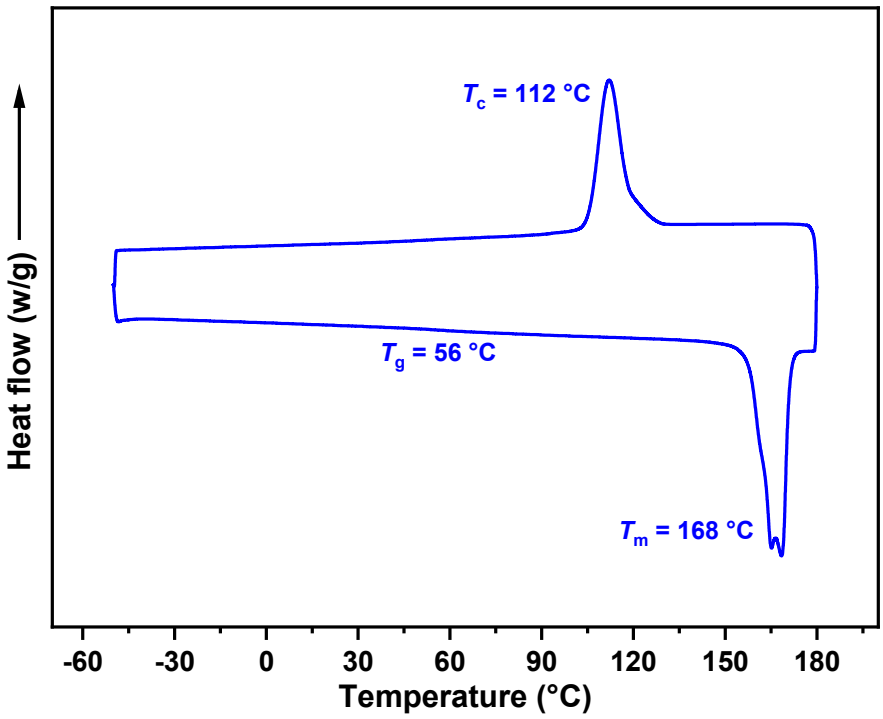


Figure S44. DSC curves of PLA obtained by [D-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = DCM.

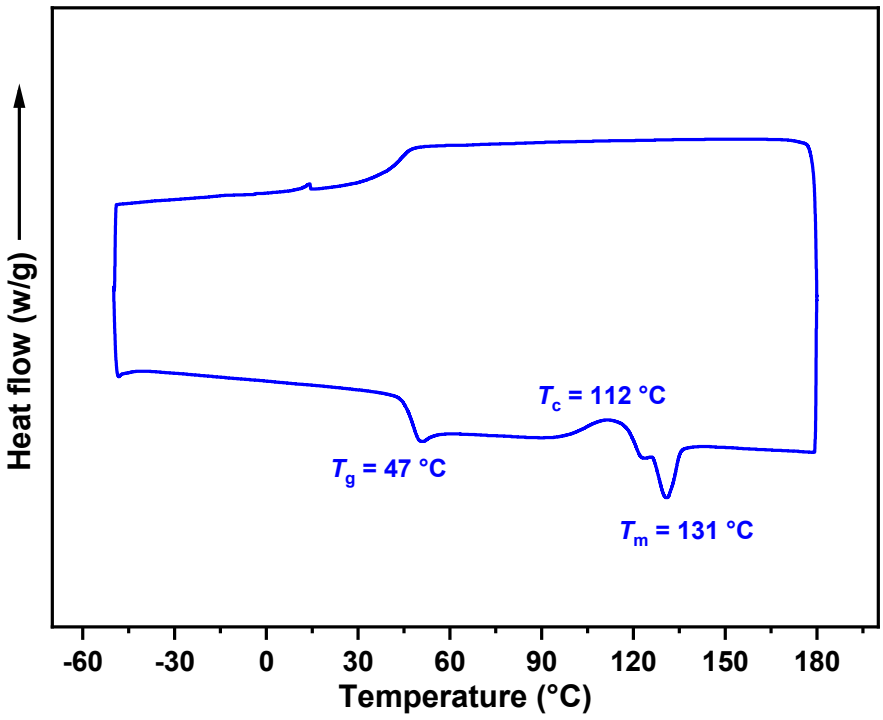


Figure S45. DSC curves of PLA obtained by [*rac*-LA]/[(*R,S*)-**2**]/[I] = 50/2/1, solvent = DCM.

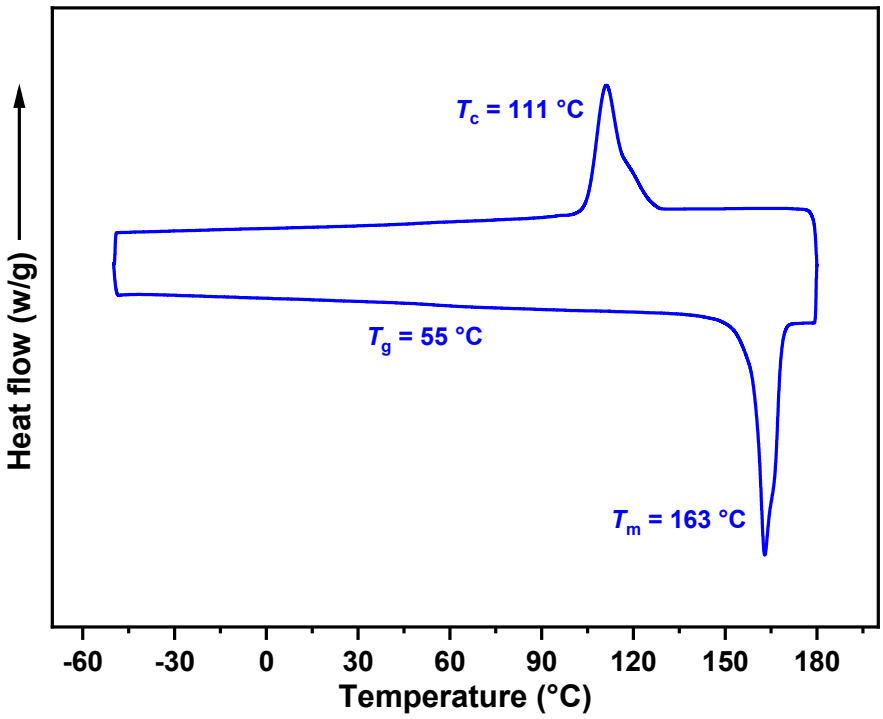


Figure S46. DSC curves of PLA obtained by [D-LA]/[(*R*,*S*)-**2**]/[I] = 50/2/1, solvent = DCM.

SEC trace of PLAs

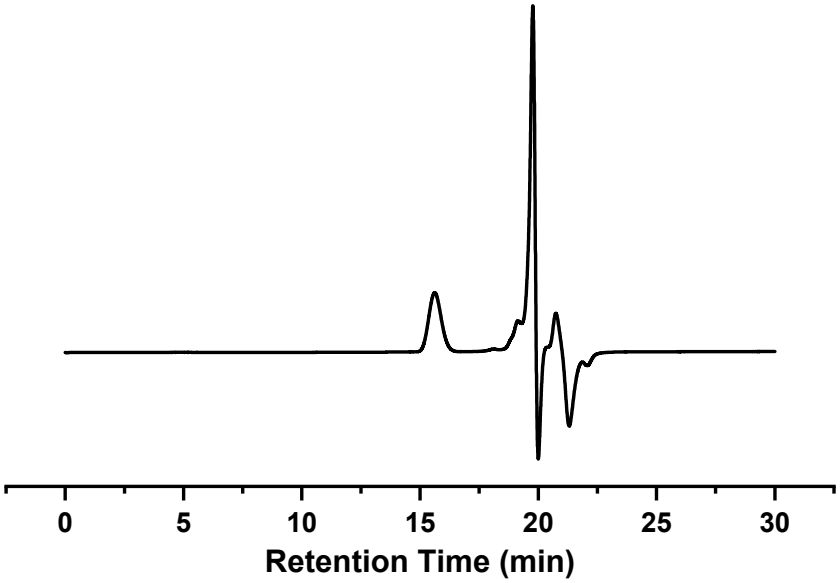


Figure S47. SEC trace of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = DCM (M_n = 6.4 kg/mol, $Đ$ = 1.08).

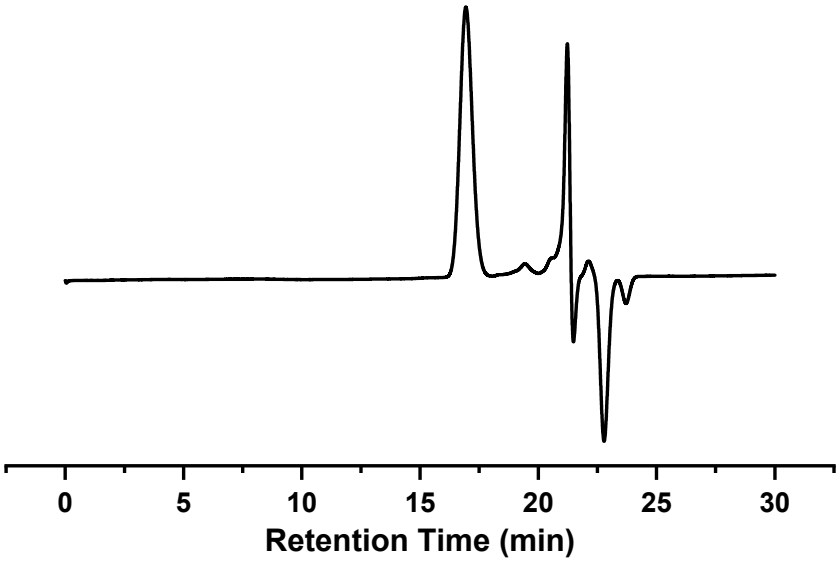


Figure S48. SEC trace of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = TOL (M_n = 5.6 kg/mol, $Đ$ = 1.08).

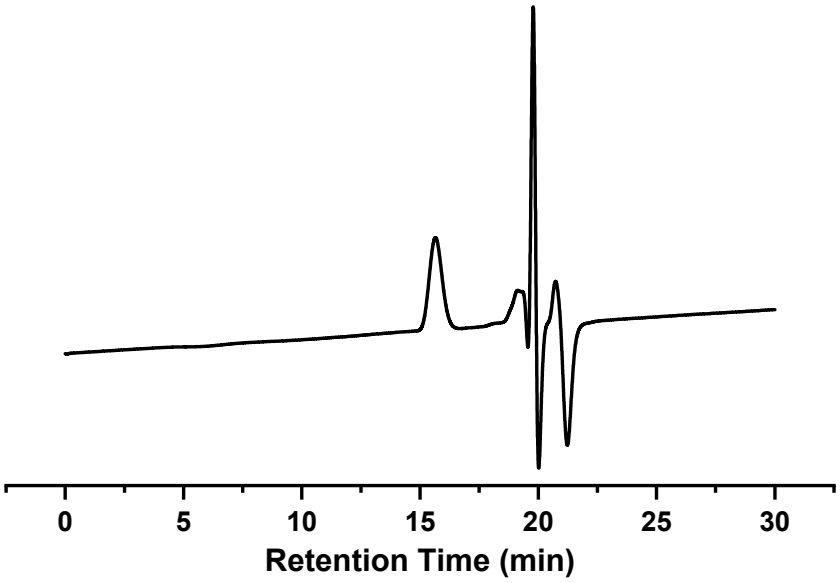


Figure S49. SEC trace of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = $CHCl_3$ (M_n = 6.2 kg/mol, $Đ$ = 1.09).

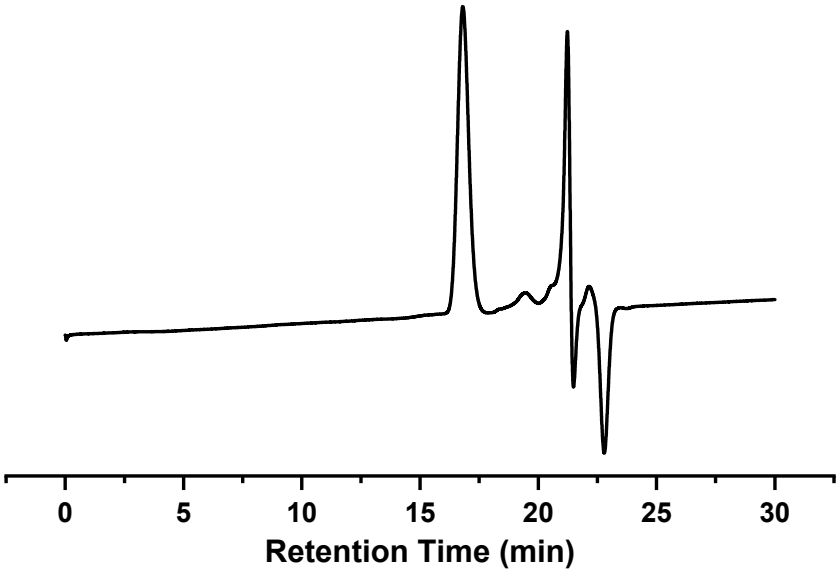


Figure S50. SEC trace of PLA obtained by [*rac*-LA]/[(*R,R*)-**1**]/[I] = 50/2/1, solvent = DCM (M_n = 6.0 kg/mol, $Đ$ = 1.06).

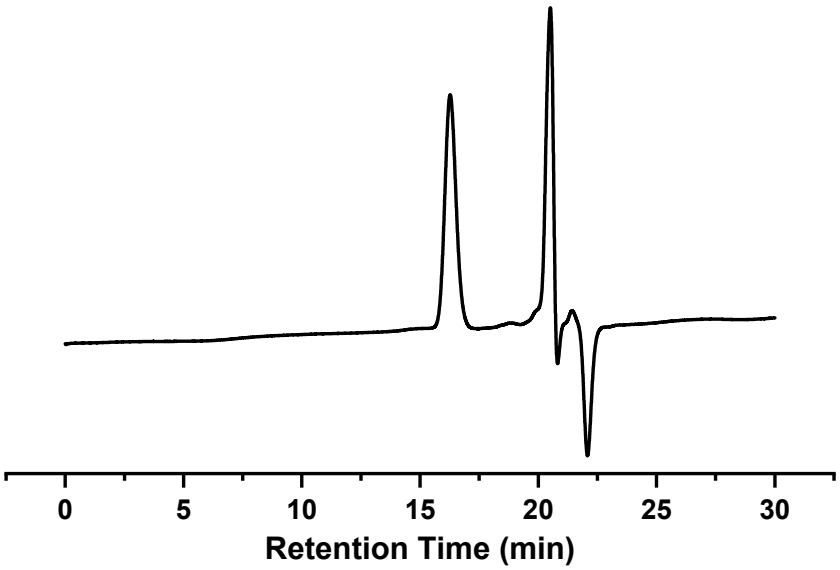


Figure S51. SEC trace of PLA obtained by [*rac*-LA]/[(*S,S*)-**1**]/[I] = 50/2/1, solent = DCM (M_n = 6.2 kg/mol, $Đ$ = 1.06).

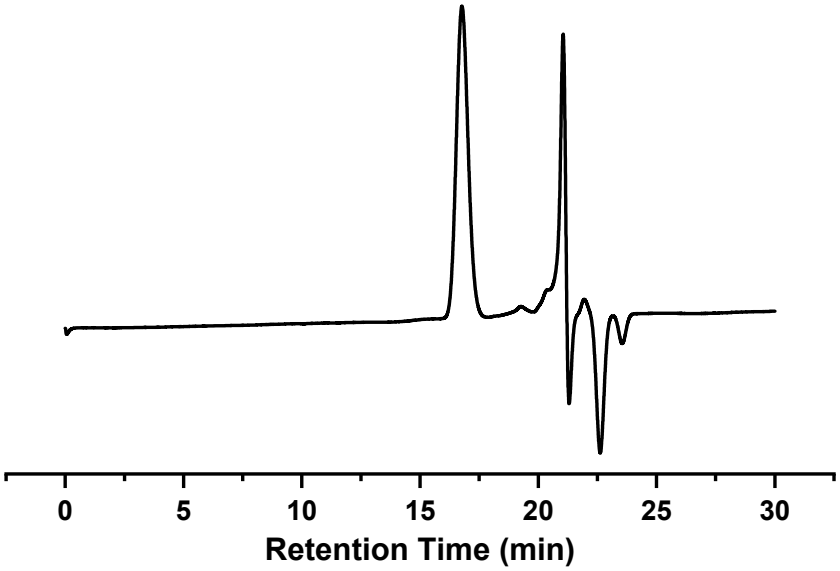


Figure S52. SEC trace of PLA obtained by [*rac*-LA]/[(*R,S*)-**2**]/[I] = 50/2/1, solvent = DCM (M_n = 5.6 kg/mol, $Đ$ = 1.07).

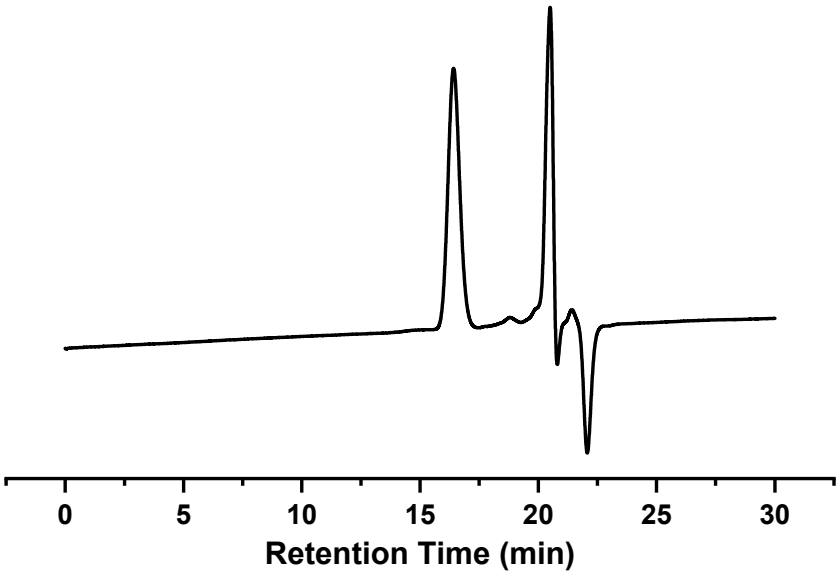


Figure S53. SEC trace of PLA obtained by [*rac*-LA]/[(*R,S*)-**3**]/[I] = 50/2/1, solvent = DCM (M_n = 5.3 kg/mol, $Đ$ = 1.07).

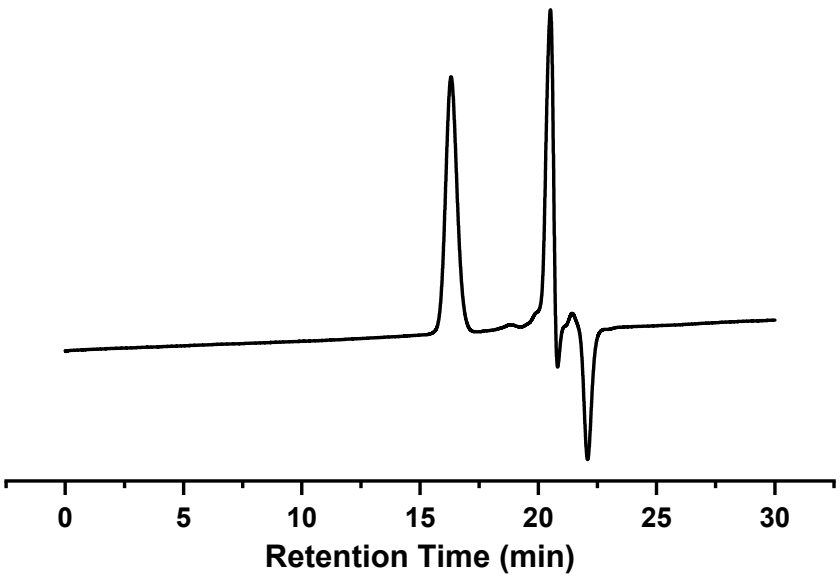


Figure S54. SEC trace of PLA obtained by [*rac*-LA]/[(*R,S*)-**6**]/[I] = 50/2/1, solvent = DCM (M_n = 6.0 kg/mol, $Đ$ = 1.07).

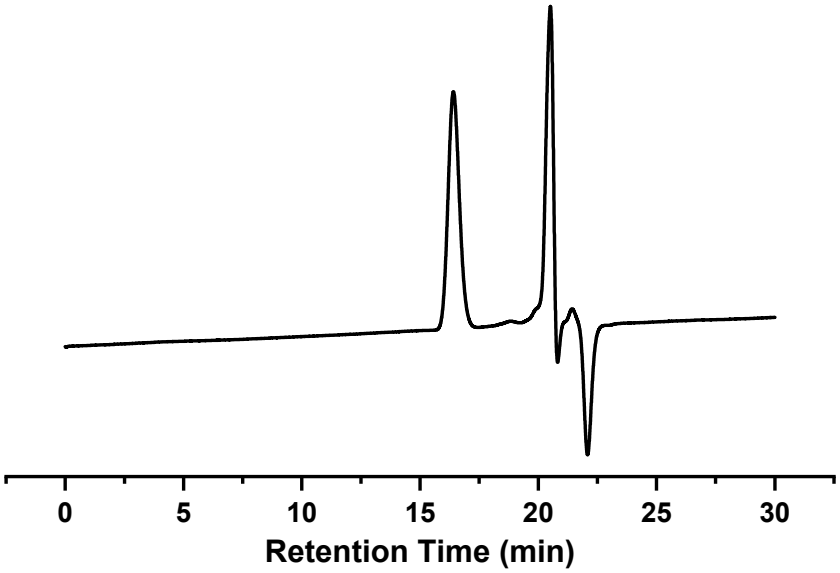


Figure S55. SEC trace of PLA obtained by [*rac*-LA]/[(*R,S*)-**7**]/[I] = 50/2/1, solent = DCM (M_n = 5.3 kg/mol, $Đ$ = 1.07).

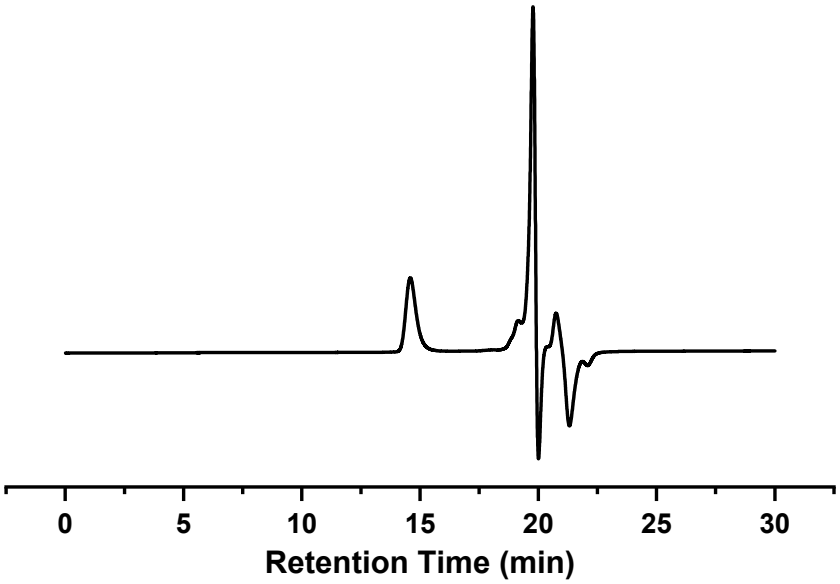


Figure S56. SEC trace of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 200/20/1, solvent = DCM (M_n = 19.7 kg/mol, $Đ$ = 1.09).

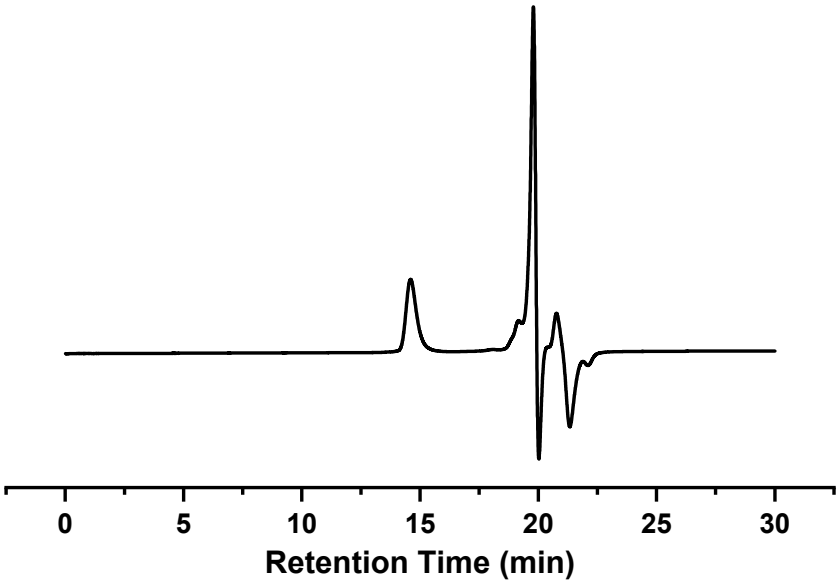


Figure S57. SEC trace of PLA obtained by [*rac*-LA]/[(*S,R*)-**1**]/[I] = 200/20/1, solvent = DCM (M_n = 19.1 kg/mol, $Đ$ = 1.10).

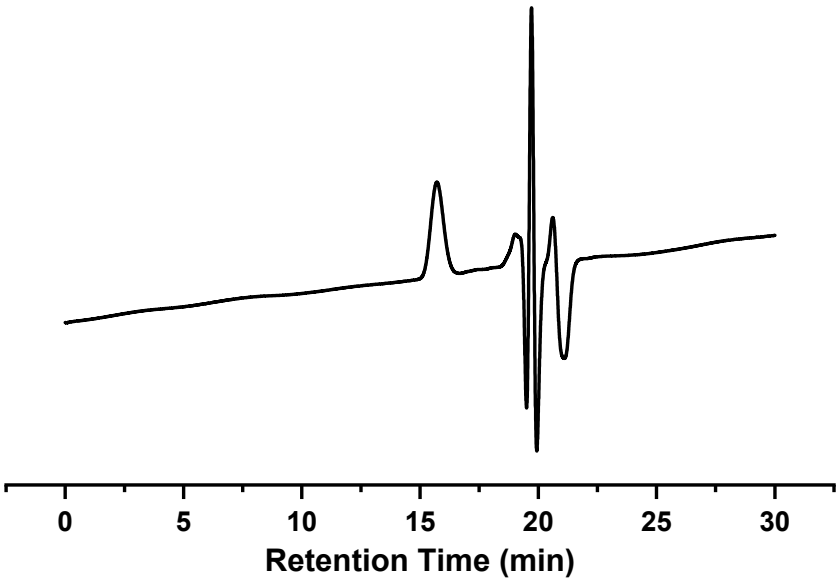


Figure S58. SEC trace of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = DCM (M_n = 5.5 kg/mol, $Đ$ = 1.09).

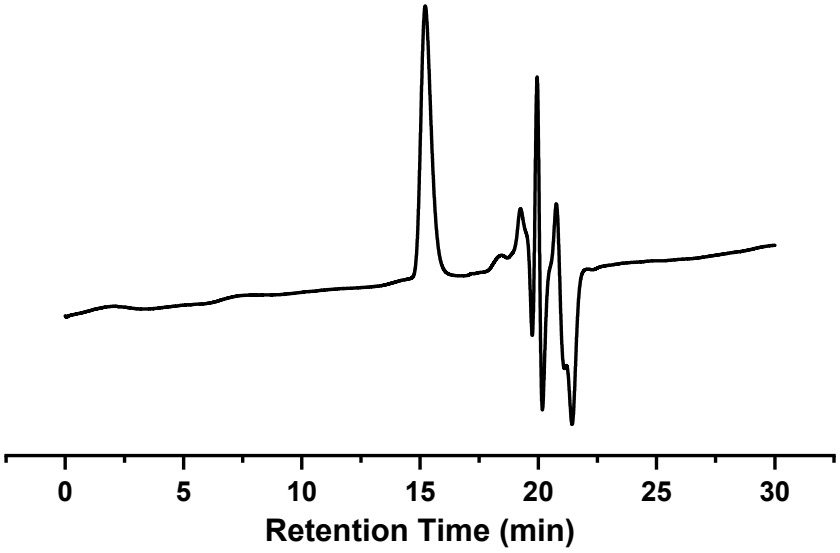


Figure S59. SEC trace of PLA obtained by [$_D$-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = $CHCl_3$ (M_n = 12.4 kg/mol, $Đ$ = 1.08).

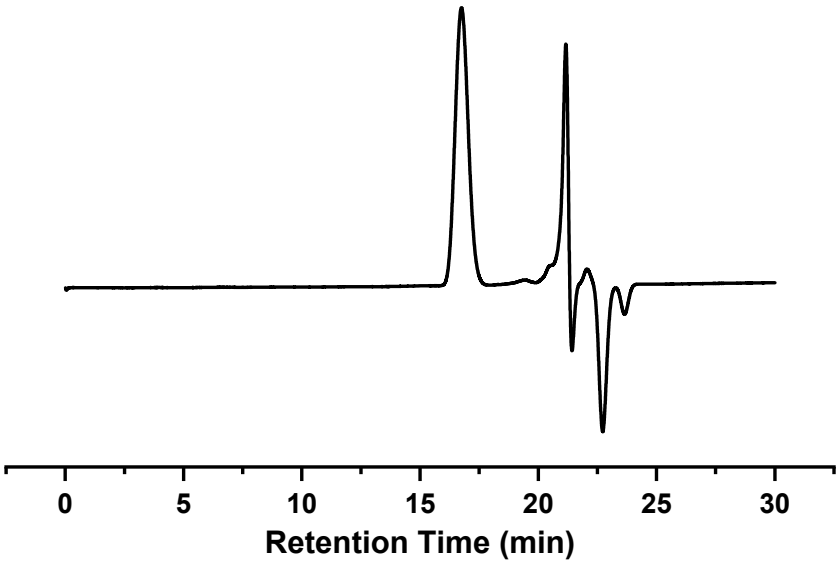


Figure S60. SEC trace of PLA obtained by [*rac*-LA]/[(*S,R*)-**1**]/[I] = 50/2/1, solvent = $CHCl_3$ (M_n = 6.7 kg/mol, $Đ$ = 1.08).

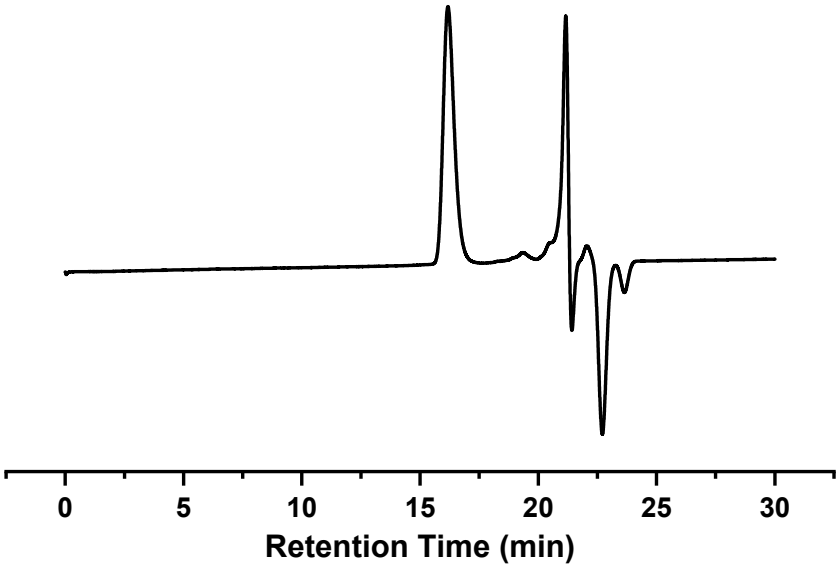


Figure S61. SEC trace of PLA obtained by [$_{L}$-LA]/[(*S,R*)-**1**]/[I] = 50/2/1, solvent = $CHCl_3$ (M_n = 11.8 kg/mol, $Đ$ = 1.07).

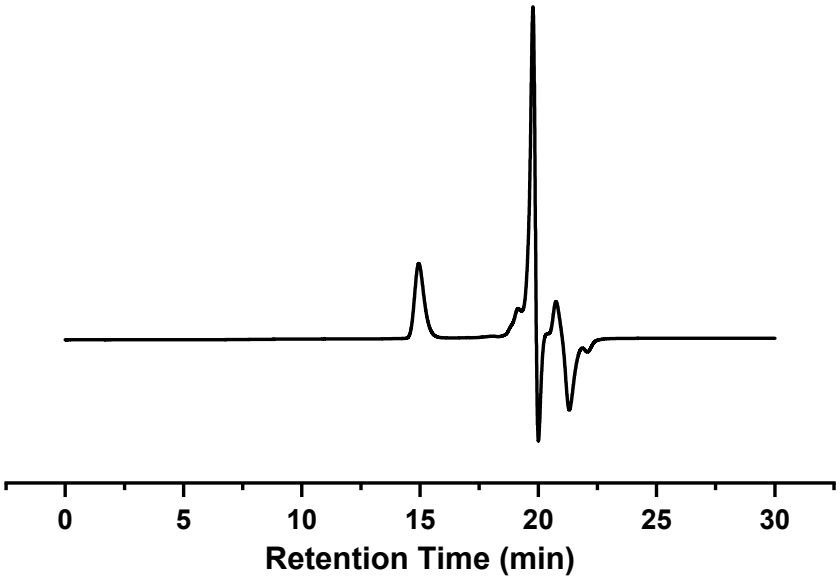


Figure S62. SEC trace of PLA obtained by [$_{D}$-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = DCM (M_n = 13.5 kg/mol, $Đ$ = 1.06).

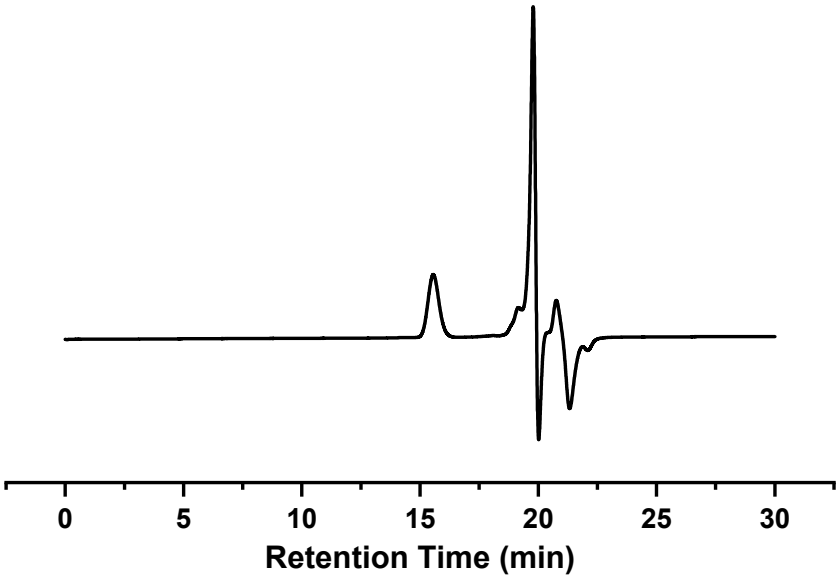


Figure S63. SEC trace of PLA obtained by [*rac*-LA]/[(*R,S*)-**2**]/[I] = 50/2/1, solvent = DCM (M_n = 7.0 kg/mol, $Đ$ = 1.07).

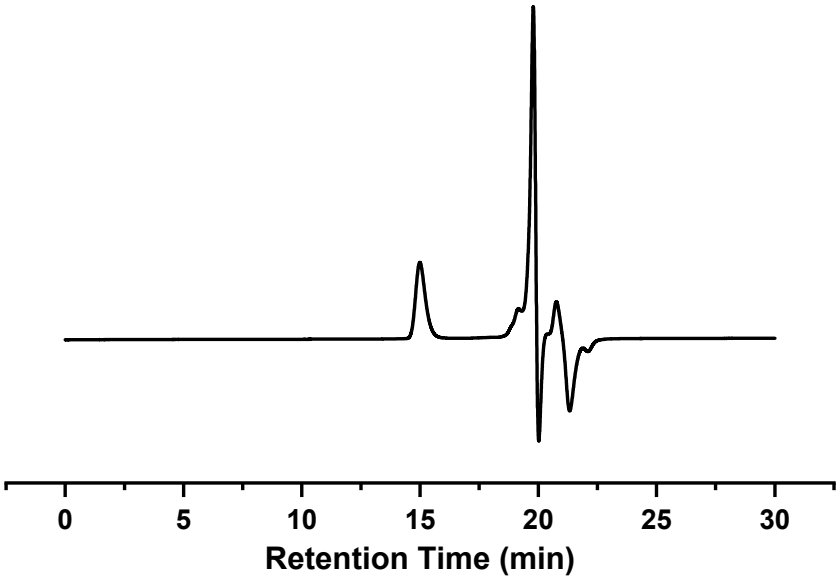


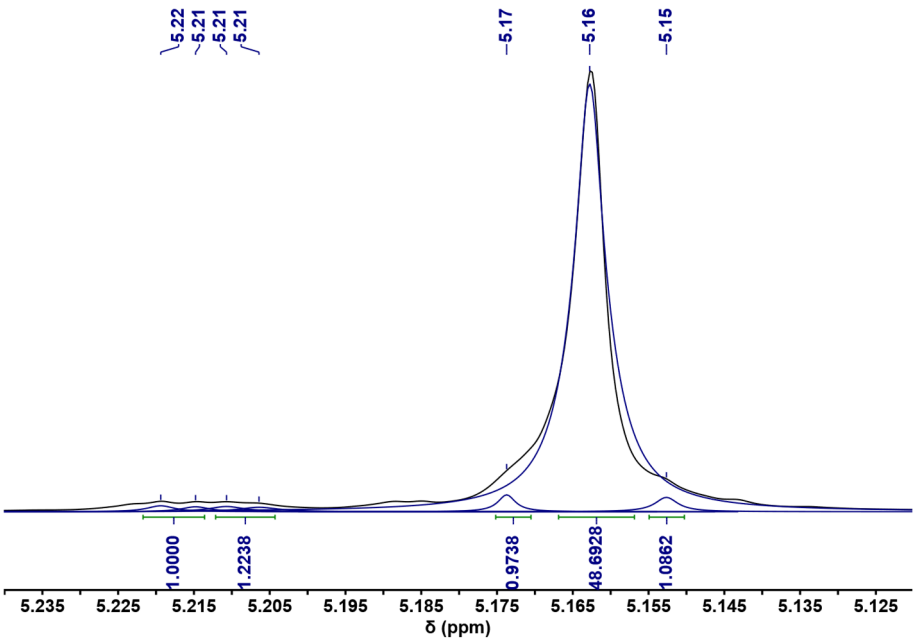
Figure S64. SEC trace of PLA obtained by [$_D$-LA]/[(*R,S*)-**2**]/[I] = 50/2/1, solvent = DCM (M_n = 12.8 kg/mol, $Đ$ = 1.06).

Homonuclear decoupled ^{1}H NMR spectra of PLAs

Homodecoupled ^{1}H NMR spectra were recorded for all the obtained PLA samples. The mechanism of this catalytic system is enantiomorphic site control mechanism (ESC). So the calculation of P_m values for each sample followed tetrad probabilities of ESC mechanisms based on non-Bernouillanin in the literature.[1]

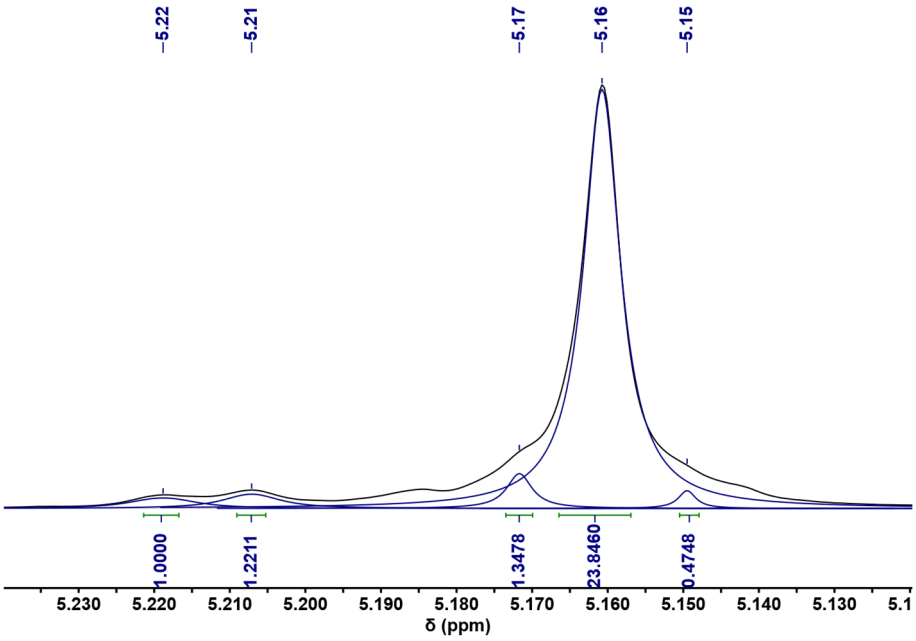
Table S8. Tetrad probabilities of ESC mechanisms based on non-Bernouillanin.

tetrad	Probability of ESC
mmm	$[P_m^2+(1-P_m)^2+P_m^3+(1-P_m)^3]/2$
mmr/rmm	$[P_m^2(1-P_m)+P_m(1-P_m)^2]/2$
rmm/mmr	$[P_m^2(1-P_m)+P_m(1-P_m)^2]/2$
rmr	$[P_m^2(1-P_m)+P_m(1-P_m)^2]/2$
mrm	$[P_m(1-P_m)]$



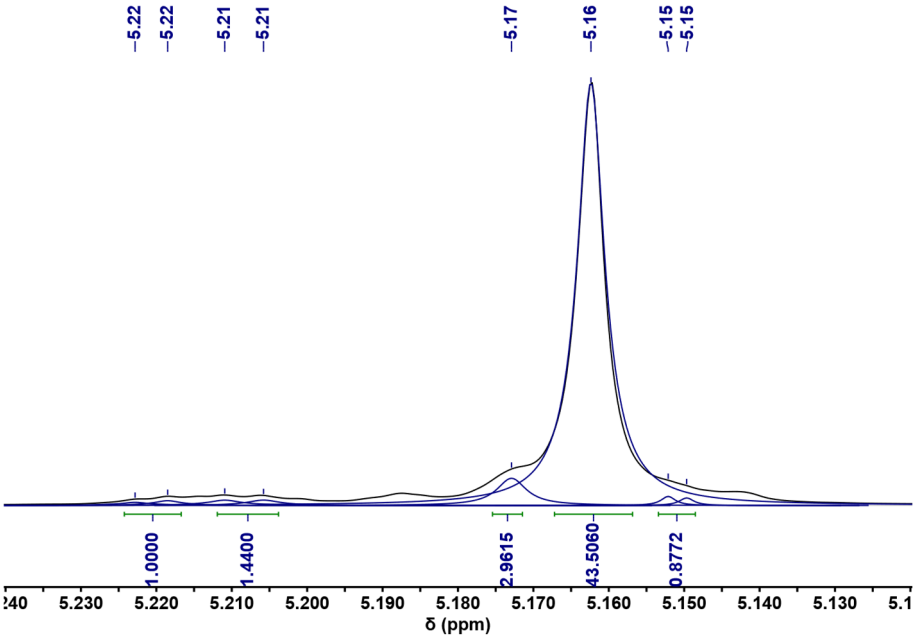
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.019	0.96
5.21	*mmr/rmm*	0.023	0.95
5.17	*rmm/mmr*	0.018	0.96
5.16	*mmm*	0.92	0.97
5.15	*mrm*	0.021	0.98
	Average		0.96

Figure S65. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = DCM (P_m = 0.96).



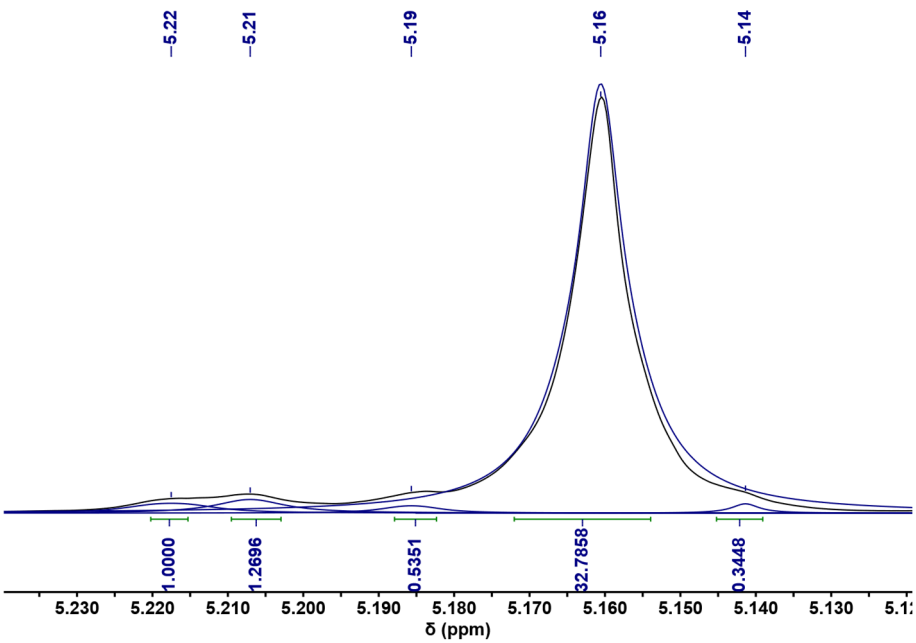
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.036	0.92
5.21	*mmr/rmm*	0.044	0.90
5.17	*rmm/mmr*	0.048	0.89
5.16	*mmm*	0.86	0.94
5.15	*mrm*	0.017	0.98
	Average		0.93

Figure S66. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = TOL (P_m = 0.93).



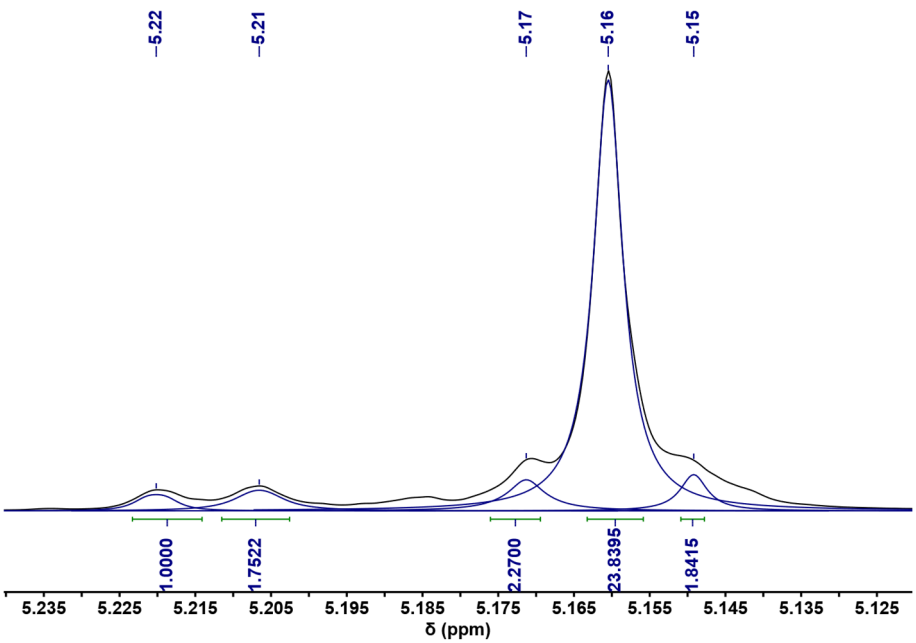
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.020	0.96
5.21	*mmr/rmm*	0.029	0.94
5.17	*rmm/mmr*	0.059	0.86
5.16	*mmm*	0.87	0.95
5.15	*mrm*	0.018	0.98
	Average		0.94

Figure S67. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = $CHCl_3$ (P_m = 0.94).



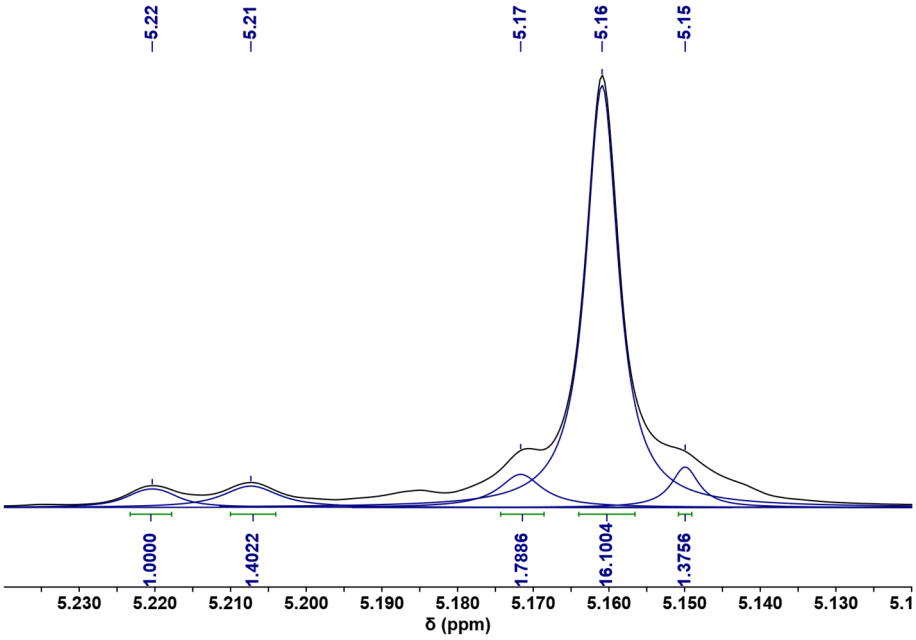
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.028	0.94
5.21	*mmr/rmm*	0.035	0.92
5.19	*rmm/mmr*	0.015	0.97
5.16	*mmm*	0.91	0.96
5.14	*mrm*	0.0096	0.99
	Average		0.96

Figure S68. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*S,R*)-**1**]/[I] = 50/2/1, solvent = DCM (P_m = 0.96).



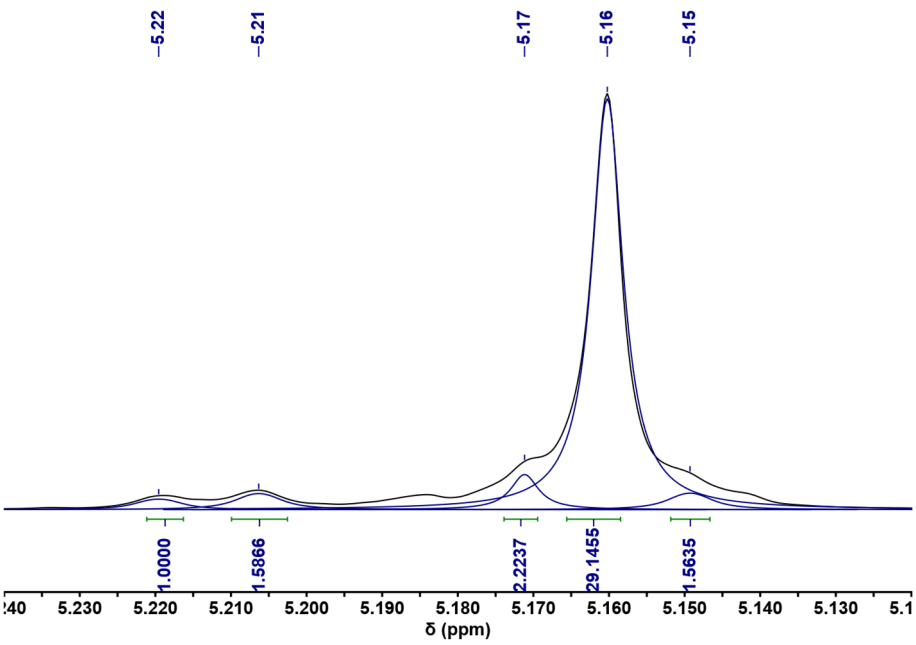
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.033	0.93
5.21	*mmr/rmm*	0.057	0.87
5.17	*rmm/mmr*	0.074	0.82
5.16	*mmm*	0.78	0.90
5.15	*mrm*	0.060	0.94
	Average		0.89

Figure S69. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*R,R*)-**1**]/[I] = 50/2/1, solvent = DCM (P_m = 0.89).



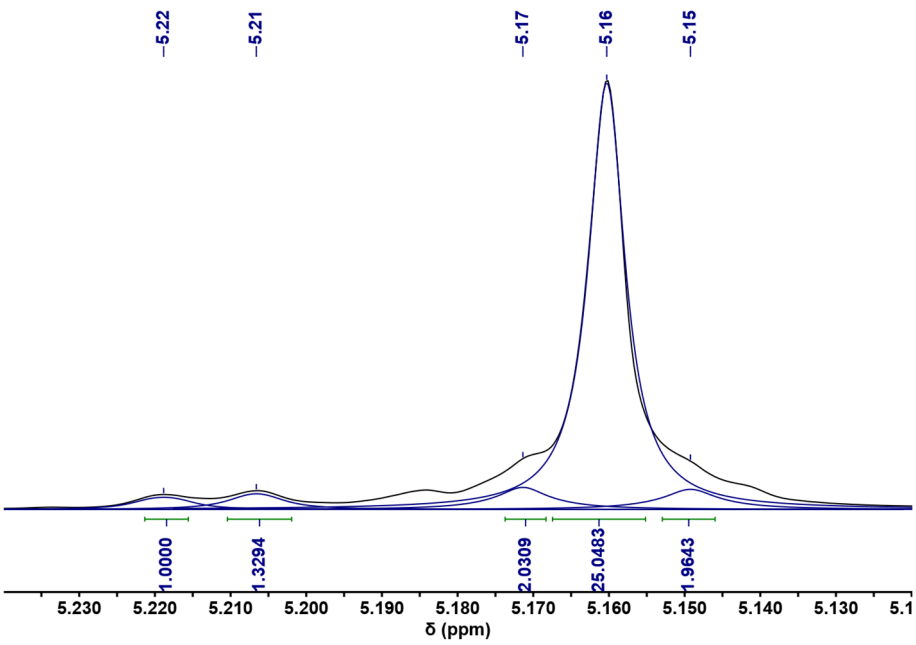
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.046	0.90
5.21	*mmr/rmm*	0.065	0.85
5.17	*rmm/mmr*	0.083	0.80
5.16	*mmm*	0.74	0.88
5.15	*mrm*	0.063	0.93
	Average		0.87

Figure S70. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*S,S*)-**1**]/[I] = 50/2/1, solvent = DCM (P_m = 0.87).



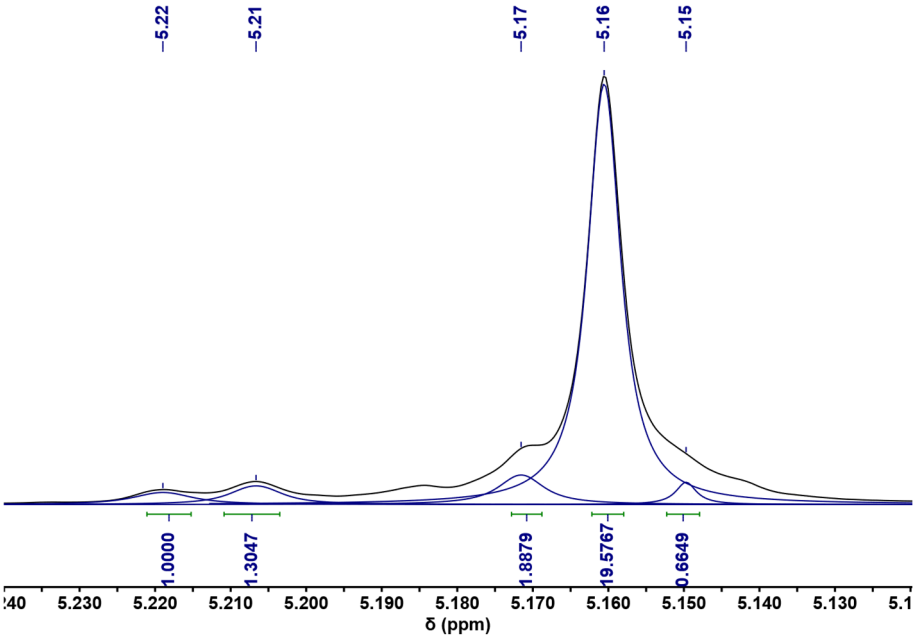
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.028	0.94
5.21	*mmr/rmm*	0.045	0.90
5.17	*rmm/mmr*	0.063	0.85
5.16	*mmm*	0.82	0.92
5.15	*mrm*	0.044	0.95
	Average		0.91

Figure S71. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*R,S*)-**2**]/[I] = 50/2/1, solvent = DCM (P_m = 0.91).



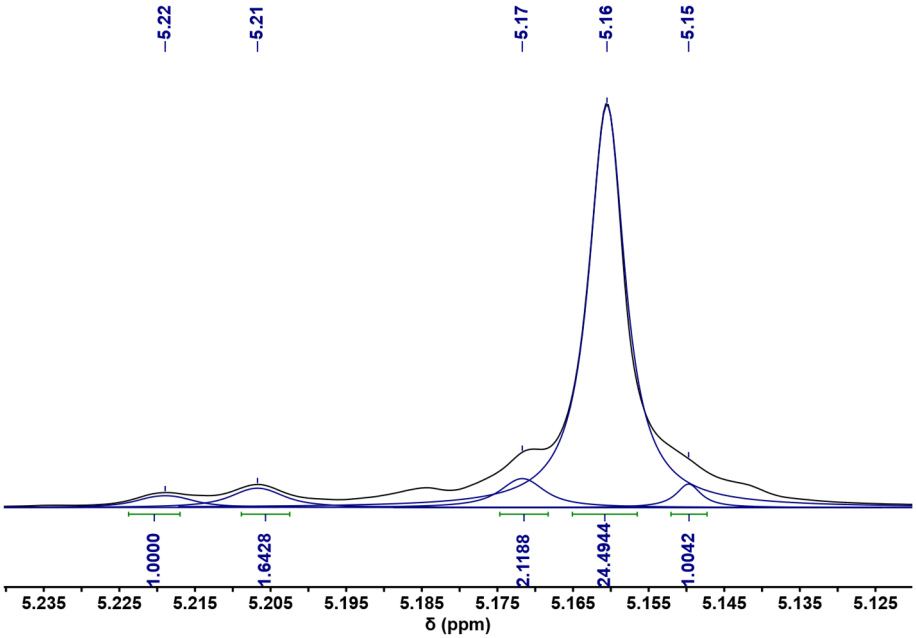
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.032	0.93
5.21	*mmr/rmm*	0.042	0.91
5.17	*rmm/mmr*	0.065	0.85
5.16	*mmm*	0.80	0.91
5.15	*mrm*	0.063	0.93
	Average		0.91

Figure S72. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*R,S*)-**3**]/[I] = 50/2/1, solvent = DCM (P_m = 0.91).



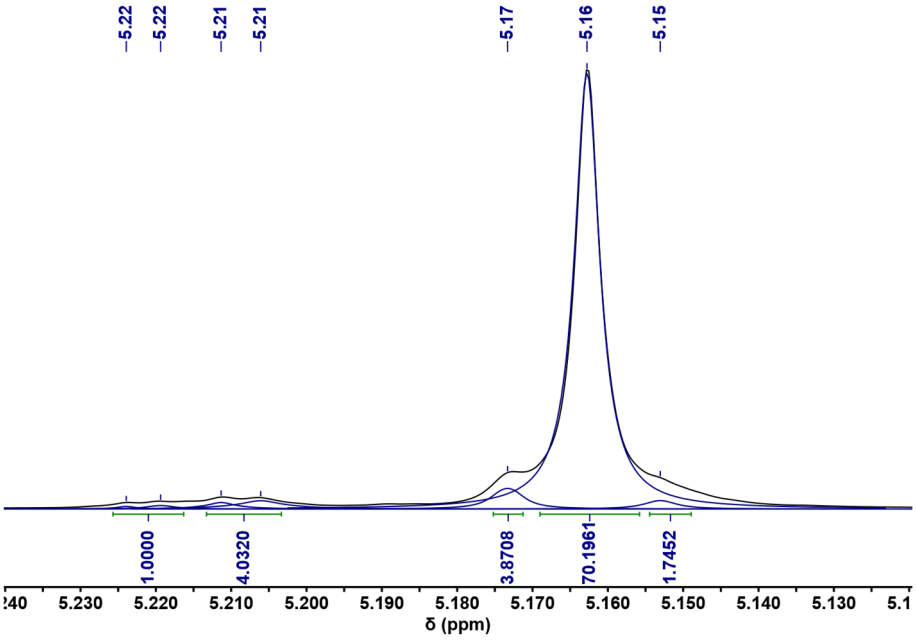
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.041	0.91
5.21	*mmr/rmm*	0.053	0.88
5.17	*rmm/mmr*	0.077	0.81
5.16	*mmm*	0.80	0.91
5.15	*mrm*	0.027	0.97
	Average		0.90

Figure S73. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*R,S*)-**6**]/[I] = 50/2/1, solvent = DCM (P_m = 0.90).



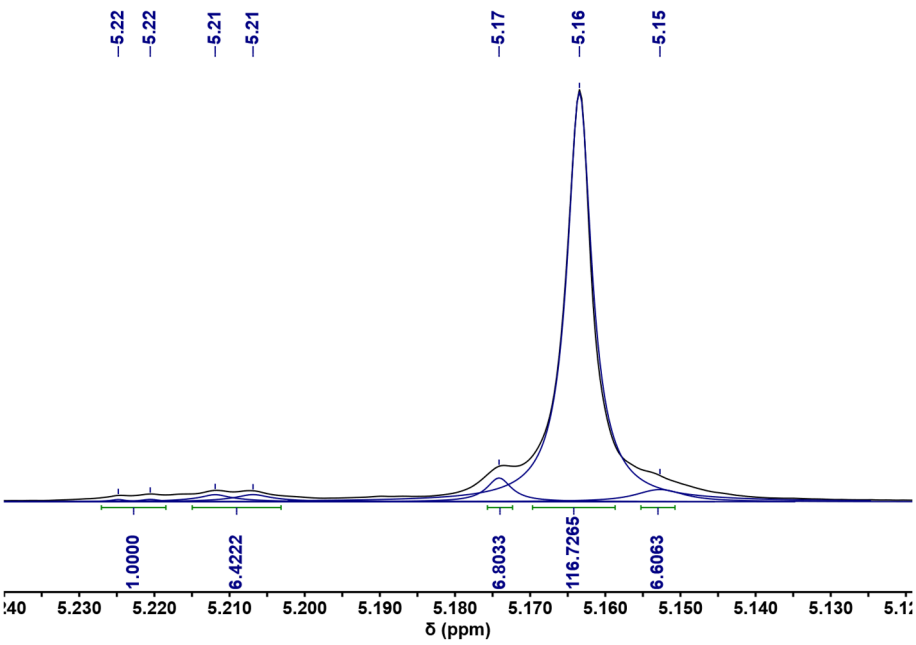
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.033	0.93
5.21	*mmr/rmm*	0.054	0.88
5.17	*rmm/mmr*	0.070	0.83
5.16	*mmm*	0.81	0.92
5.15	*mrm*	0.033	0.97
	Average		0.90

Figure S74. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*R,S*)-**7**]/[I] = 50/2/1, solvent = DCM (P_m = 0.90).



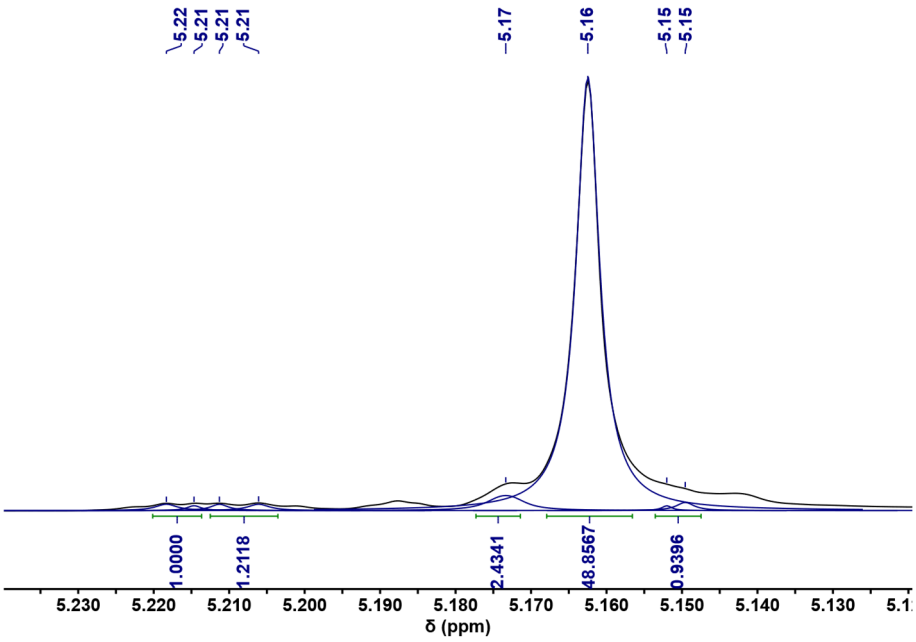
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.012	0.97
5.21	*mmr/rmm*	0.050	0.89
5.17	*rmm/mmr*	0.048	0.89
5.16	*mmm*	0.87	0.94
5.15	*mrm*	0.22	0.98
	Average		0.94

Figure S75. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 200/20/1, solvent = DCM (P_m = 0.94).



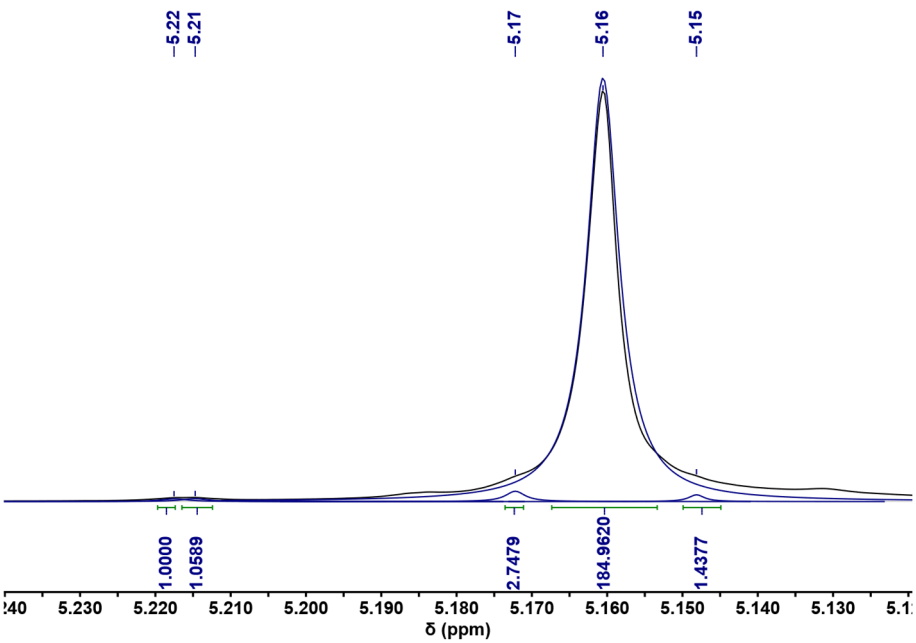
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.0073	0.99
5.21	*mmr/rmm*	0.047	0.90
5.17	*rmm/mmr*	0.049	0.89
5.16	*mmm*	0.85	0.94
5.15	*mrm*	0.048	0.95
	Average		0.93

Figure S76. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*S,R*)-**1**]/[I] = 200/20/1, solvent = DCM (P_m = 0.93).



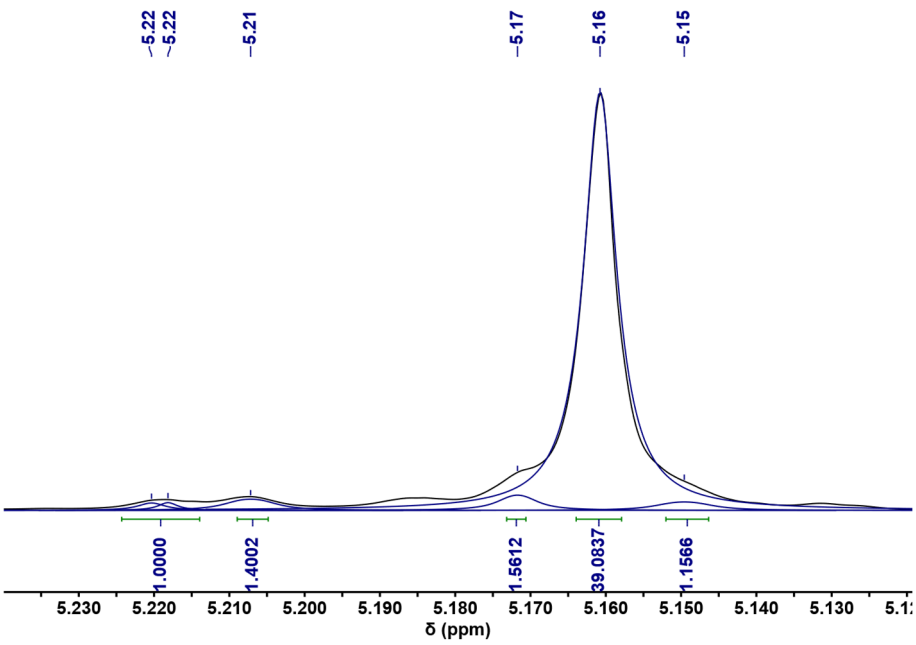
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.018	0.96
5.21	*mmr/rmm*	0.022	0.95
5.17	*rmm/mmr*	0.045	0.90
5.16	*mmm*	0.90	0.96
5.15	*mrm*	0.017	0.98
	Average		0.95

Figure S77. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = DCM (P_m = 0.95).



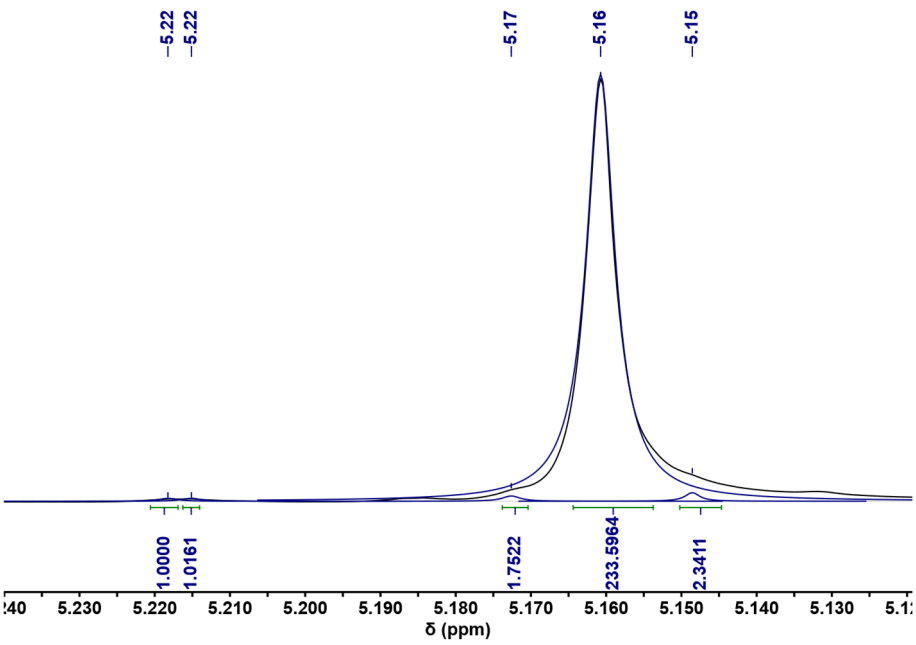
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.0052	0.99
5.21	*mmr/rmm*	0.0055	0.99
5.17	*rmm/mmr*	0.014	0.97
5.16	*mmm*	0.97	0.99
5.15	*mrm*	0.0075	0.99
	Average		0.99

Figure S78. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [$_D$-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = $CHCl_3$ (P_m = 0.99).



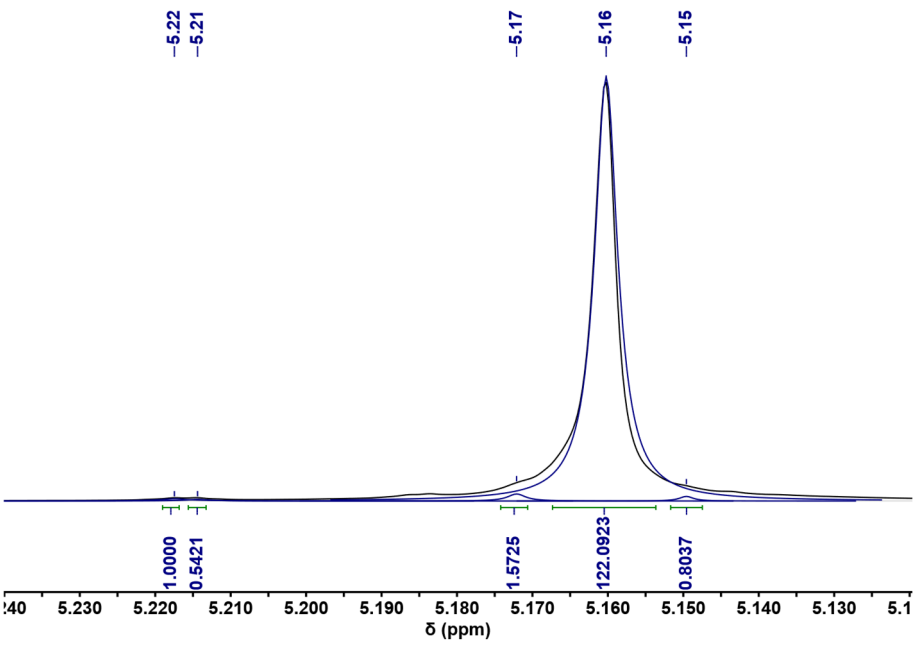
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.023	0.95
5.21	*mmr/rmm*	0.032	0.93
5.17	*rmm/mmr*	0.035	0.92
5.16	*mmm*	0.88	0.95
5.15	*mrm*	0.026	0.97
	Average		0.95

Figure S79. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*S,R*)-**1**]/[I] = 50/2/1, solvent = $CHCl_3$ (P_m = 0.95).



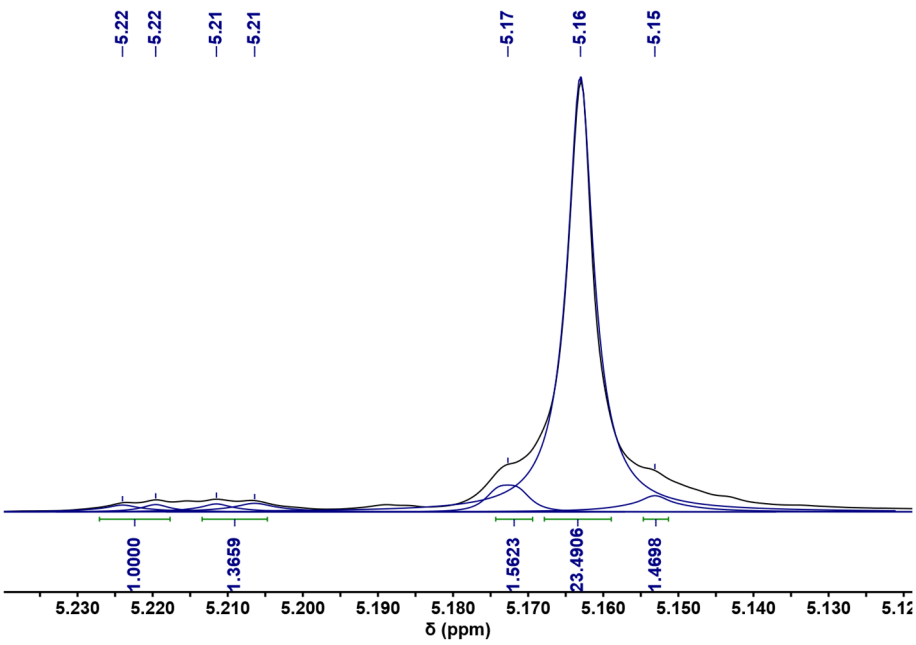
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.0042	0.99
5.21	*mmr/rmm*	0.0042	0.99
5.17	*rmm/mmr*	0.0073	0.99
5.16	*mmm*	0.97	0.99
5.15	*mrm*	0.0098	0.99
	Average		0.99

Figure S80. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [L-LA]/[(*S,R*)-**1**]/[I] = 50/2/1, solvent = $CHCl_3$ (P_m = 0.99).



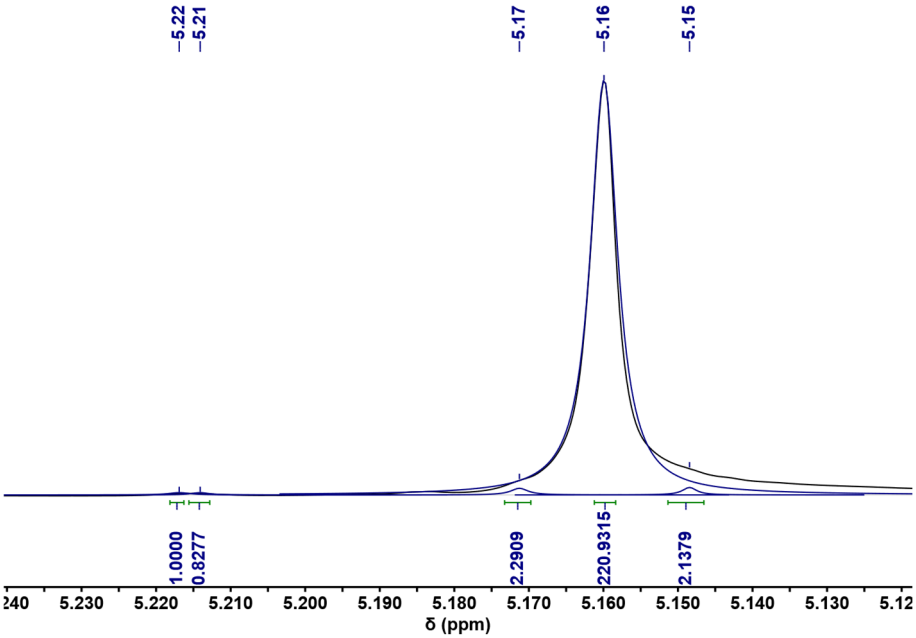
ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.0079	0.98
5.21	*mmr/rmm*	0.0043	0.99
5.17	*rmm/mmr*	0.012	0.97
5.16	*mmm*	0.97	0.99
5.15	*mrm*	0.0064	0.99
	Average		0.99

Figure S81. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [$_D$-LA]/[(*R,S*)-**1**]/[I] = 50/2/1, solvent = DCM (P_m = 0.99).



ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.035	0.93
5.21	*mmr/rmm*	0.047	0.89
5.17	*rmm/mmr*	0.054	0.88
5.16	*mmm*	0.81	0.92
5.15	*mrm*	0.051	0.95
	Average		0.91

Figure S82. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [*rac*-LA]/[(*R,S*)-**2**]/[I] = 50/2/1, solvent = DCM (P_m = 0.91).



ppm	tetrad	ratio	$P_{m,ESC}$
5.22	*rmr*	0.0044	0.99
5.21	*mmr/rmm*	0.0036	0.99
5.17	*rmm/mmr*	0.010	0.98
5.16	*mmm*	0.97	0.99
5.15	*mrm*	0.0094	0.99
	Average		0.99

Figure S83. Homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PLA obtained by [$_D$-LA]/[(*R,S*)-**2**]/[I] = 50/2/1, solvent = DCM (P_m = 0.99).

References

1. Orhan, B.; Tschan, M. J.-L.; Wirotius, A.-L.; Dove, A. P.; Coulembier, O.; Taton, D. Isoselective Ring-Opening Polymerization of *rac*-Lactide from Chiral Takemoto's Organocatalysts: Elucidation of Stereocontrol. *ACS Macro Lett.* **2018,** *7*, 1413-1419.

2. Zhu, J.-B.; Chen, E. Y.-X. From *meso*-Lactide to Isotactic Polylactide: Epimerization by B/N Lewis Pairs and Kinetic Resolution by Organic Catalysts. *J. Am. Chem. Soc.* **2015,** *137*, 12506-12509.

3. Masson, G.; Bekkaye, M. Synthesis of New Axially Chiral Iodoarenes. *Synthesis* **2015,** *48*, 302-312.

4. Kulkarni, C.; Berrocal, J. A.; Lutz, M.; Palmans, A. R. A.; Meijer, E. W. Directing the Solid-State Organization of Racemates via Structural Mutation and Solution-State Assembly Processes. *J. Am. Chem. Soc.* **2019,** *141*, 6302-6309.

5. Amarasinghe, N. R.; Turner, P.; Todd, M. H. The First Catalytic, Enantioselective Aza-Henry Reaction of an Unactivated Cyclic Imine. *Adv. Synth. Catal.* **2012,** *354*, 2954-2958.

6. Tiffner, M.; Novacek, J.; Busillo, A.; Gratzer, K.; Massa, A.; Waser, M. Design of chiral urea-quaternary ammonium salt hybrid catalysts for asymmetric reactions of glycine Schiff bases. *RSC Adv.* **2015,** *5*, 78941-78949.

7. Bulman Page, P.; Farah, M.; Buckley, B.; Chan, Y.; Blacker, A. Preparation of C_2-Symmetric Biaryl Bisiminium Salts and Their Use as Organocatalysts for Asymmetric Epoxidation. *Synlett* **2015,** *27*, 126-130.

8. Yan, L.; Huang, G.; Wang, H.; Xiong, F.; Peng, H.; Chen, F. Squaramide-Linked Chloramphenicol Base Hybrid Catalysts for the Asymmetric Michael Addition of 2,3-Dihydrobenzofuran-2-carboxylates to Nitroolefins. *Eur. J. Org. Chem.* **2018,** *2018*, 99-103.

9. Liu, F.; Gou, S.; Li, L. Asymmetric Henry reactions of aldehydes with various nitroalkanes catalyzed by copper(II) complexes of novel chiral *N*-monoalkyl cyclohexane-1,2-diamines. *Appl. Organometal. Chem.* **2014,** *28*, 186-193.

10. Yamaoka, Y.; Miyabe, H.; Takemoto, Y. Catalytic enantioselective petasis-type reaction of quinolines catalyzed by a newly designed thiourea catalyst. *J. Am. Chem. Soc.* **2007,** *129*, 6686-6687.

11. Suez, G.; Bloch, V.; Nisnevich, G.; Gandelman, M. Design and Development of Bioinspired Guanine-Based Organic Catalyst for Asymmetric Catalysis. *Eur. J. Org. Chem.* **2012,** *2012*, 2118-2122.