Supporting Information

Overcoming aggregation in indium salen catalysts for isoselective lactide polymerization

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Contents

Experimental Section

General considerations. Unless otherwise indicated, all air- and/or water-sensitive reactions (synthesis and reactions involving metal complexes) were carried out under dry nitrogen using either an MBraun glove box or standard Schlenk line techniques. Proligands, unless stated otherwise were synthesized without employing air-sensitive techniques. NMR spectra were recorded on a Bruker Avance 400 MHz or 600 MHz spectrometer. ^{1}H NMR chemical shifts are reported in ppm versus residual protons in deuterated chloroform; δ 7.27 $CDCl_3$. $^{13}C\{^{1}H\}$ NMR chemical shifts are reported in ppm versus residual ^{13}C in the solvent; δ 77.2 $CDCl_3$. Diffraction measurements for X-ray crystallography were made on a Bruker APEX DUO diffractometer with graphite monochromated Mo-Kα radiation. The structures (Table S2) were solved by direct methods and refined by full-matrix least-squares using the SHELXTL crystallographic software of Bruker-AXS. Unless specified, all non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were constrained to geometrically calculated positions but were not refined. Elemental analysis (C, H, and N) was performed using a Carlo Erba EA1108 elemental analyzer. The elemental composition of unknown samples was determined by using a calibration factor. The calibration factor was determined by analyzing a suitable certified organic standard (OAS) of a known elemental composition. Molecular weights were determined by triple detection gel permeation chromatography (GPC-LLS) using a Waters liquid chromatograph equipped with a Water 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 × 300 mm) HR5E, HR4 and HR2, Water 2410 differential refractometer, Wyatt tristar miniDAWN (laser light scattering detector) and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min^{-1} was used and samples were dissolved in THF (2 mg mL^{-1}). Narrow molecular weight polystyrene standards were used for calibration purposes. The molar mass was calculated with ASTRA© 5 software using the Mark-Houwink parameters, laser light scattering detector data, and concentration detector. Distribution and moment procedures of ASTRA© 5 was used to calculate molar mass moments M_n, M_w and M_z. Differential scanning calorimetry (DSC) was carried out using a Shimadzu DSC 60 calorimeter.

Materials. Solvents (tetrahydrofuran, toluene, hexanes and diethyl ether) were collected from an MBraun solvent purification system whose columns are packed with activated alumina. CD_2Cl_2, $CDCl_3$, ethyl acetate, and pyridine were dried over CaH_2, and degassed through a series of three freeze-pump-thaw cycles. Where dry solvents were not required (i.e. ligand synthesis) solvents were used as received from the manufacturer. 1,3,5-Trimethoxybenzene, tetrakis(trimethylsilyl) silane, KOtBu, and NaOEt were purchased from Aldrich and used as received after drying overnight under vacuum. $InCl_3$ was purchased from Strem chemicals and used as received. (±)/(*R,R*)-**1** and (±)/(*R,R*)-**6**[18] as well as (*R,R*)-H_2(ONNO$_{Br}$),[19b] (*R,R*)-H_2(ONNO$_{Me}$),[19c] (*R,R*)-H_2(ONNO$_{Cm}$)[19d] and KCH_2Ph[30] were synthesized according to previously reported procedures. Racemic, D, L-lactide were a gift from PURAC America Inc. and recrystallized twice from hot dried toluene.

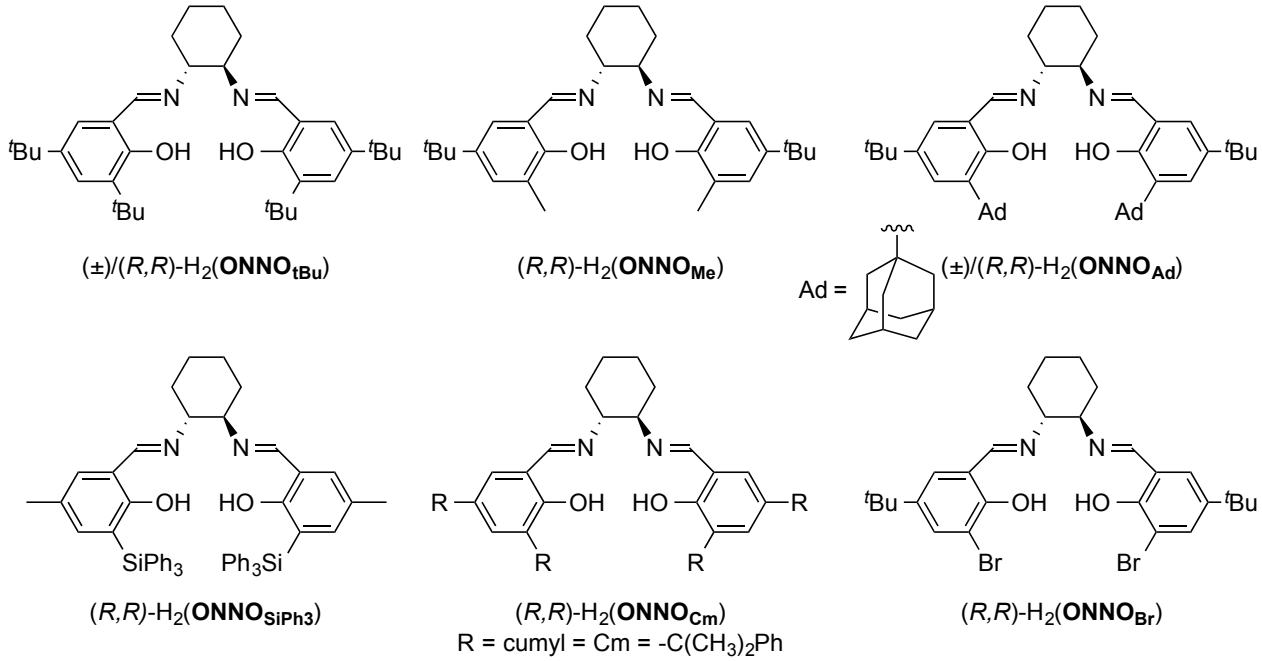


Chart S1. Enantiopure and racemic H2(ONNOR) proligands: R=t-Bu,[19a] Br,[19b] Me,[19c] Cm[19d], Ad and SiPh3 (this work).

Synthesis of (*R,R*)-H_2(ONNO$_{Ad}$). A 250 mL round-bottom flask was charged with a teflon stir bar, (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate (0.390 g, 1.48 mmol) and anhydrous K_2CO_3 (0.102 g, 0.739 mmol). To this mixture 15 mL of water was added and stirred until complete dissolution was achieved. 3-Adamantan-1-yl-5-*tert*-butyl-2-hydroxybenzaldehyde (0.920 g, 294 mmol) was suspended in 50 mL of ethanol in a 250 mL Erlenmeyer flask. This was stirred and CH_2Cl_2 was added drop-wise until complete dissolution of the salicylaldehyde was achieved. This solution was then added at once to the stirring aqueous solution in the 250 mL round-bottom flask. Upon mixing a bright yellow solution is observed immediately. A reflux condenser was attached to the round bottom flask and the reaction was heated to reflux (~90 °C) and allowed to stir for 4h. The reaction was then allowed to cool down to room temperature and reaction was concentrated using rotary evaporation until the volume decreased by ~25%. This mixture was then cooled down to ~5 °C in a refrigerator for 30 minutes and filtered using suction filtration. The bright yellow solid isolated was repeatedly washed with water. The solid was then dissolved in 25 mL of CH_2Cl_2 and washed successively with two 25 mL portions of water and 25 mL of a saturated NaCl solution. The organic phase was subsequently dried over anhydrous $MgSO_4$, filtered and the solvent was removed using rotary evaporation to yield a yellow powder. This was left under dynamic vacuum overnight prior to use (yield: 0.960 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) : δ 8.30 (2H, s, N=C*H*), 7.25 (2H, s, Ar*H*), 6.98 (2H, s, Ar*H*), 3.35-3.30 (2H, s, -C*H*- of DACH), 2.16 (12H, br s, -CH_2- of Ad), 2.08 (6H, br s, -C*H*- of Ad), 1.80 (12H, br s, -CH_2- of Ad), 1.92-1.30 (8H, *overlapping* m, -CH_2- of DACH), 1.24 (18 H, br s, Ar-C(CH_3)$_3$). ^{13}C NMR (100.63 MHz, $CDCl_3$, 25 °C): δ 166.0, 158.2, 139.9, 136.6, 126.7, 126.0, 117.8, 72.4, 40.3, 37.2, 34.1, 33.3, 31.4, 29.1, 24.4. Anal. calcd (found) for $C_{48}H_{66}N_2O_2$: 82.00 (81.42), H 9.68 (9.46), N 3.98 (3.60).

Synthesis of (±)-H_2(ONNO$_{Ad}$). The racemic ligand was prepared and purified in an analogous manner to (±)-H_2(ONNO$_{tBu}$)[19a] from (±)-1,2-diaminocyclohexane (0.055 g, 0.48 mmol) and 3-adamantan-1-yl-5-*tert*-butyl-2-hydroxybenzaldehyde (0.300 g, 9.6 mmol) (yield: 0.210 g, 62%). The compound has an NMR signature similar to that of (*R,R*)-(ONNO$_{Ad}$)H_2. Anal. calcd (found) for $C_{48}H_{66}N_2O_2$: C 82.00 (82.20), H 9.68 (9.53), N 3.98 (3.00).

Synthesis of (*R,R*)-H_2(ONNO$_{SiPh3}$). This was synthesized in a manner analogous to (*R,R*)-H_2(ONNO$_{Ad}$) from (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate (0.044 g, 0.16 mmol) and 3-triphenylsilyl-5-methyl-2-hydroxybenzaldehyde (0.130 g, 0.33 mmol) and isolated as a yellow solid (yield: 0.126 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) : δ 8.13 (2H, s, N=C*H*), 7.25 (2H, s, Ar*H*), 7.62-6.92 (34 H, *overlapping* m, -$SiPh_3$, Ar*H*), 3.24-3.18 (2H, s, -C*H*- of DACH), 2.18 (6H, s, $ArCH_3$), 1.93-1.75 (4H, *overlapping* m, -CH_2- of DACH), 1.73-1.51 (2H, m, -CH_2-), 1.49-1.25 (2H, m, -CH_2-). ^{13}C{^{1}H} NMR (100.63 MHz, $CDCl_3$, 25 °C): δ 164.6, 164.0, 141.8, 136.3, 134.8, 134.2, 129.2, 127.6, 127.2, 121.0, 117.7, 72.8, 33.0, 24.2, 20.4. Anal. calcd (found) for $C_{58}H_{54}N_2O_2Si_2$: C 80.33 (79.74), H 6.28 (6.03), N 3.28 (3.16).

Synthesis of (*R,R*)-(ONNO$_{Me}$)InCl (*R,R*)-2. Complex (*R,R*)-**2** was prepared and purified in an analogous manner to (*R,R*)-**1** from (*R,R*)-H_2(ONNO$_{Me}$) (0.400 g, 0.86 mmol) as a yellow solid (yield: 0.432 g, 82%). X-ray quality crystals were grown by slow evaporation in acetonitrile. ^{1}H NMR (600 MHz, CDCl3, 25 °C): δ 8.36 (1H, s, N=C*H*), 8.18 (1H, s, N=C*H*), 7.34 (2H, s, Ar*H*), 6.95 (1H, s, Ar*H*), 6.90 (1H, s, Ar*H*), 3.70-3.66 (1H, m, -C*H*-), 3.11-3.08 (1H, m, -C*H*-), 2.61-2.57 (1H, m, -CH_2-), 2.48-3.44 (1H, m, -CH_2-), 2.30 (6H, s, Ar-CH_3), 2.09-2.06 (2H, m, -CH_2-), 1.57-1.41 (m, 4H, -CH_2-), 1.28 (18H, br s, Ar-C(CH_3)$_3$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C): δ 170.6, 167.0, 166.7, 138.5, 138.3, 134.3, 133.9, 132.1, 129.1, 125.7, 116.5, 116.3, 65.2, 63.4, 33.8, 31.5, 31.5, 31.5, 27.2, 24.3, 23.9, 17.2, 17.2, 2.1. Anal. Calcd (found) for $C_{30}H_{40}ClInN_2O_2$: C, 59.98(59.71); H, 6.60(6.74); N, 4.59(4.84).

Synthesis of (*R,R*)-(ONNO$_{Ad}$)InCl (*R,R*)-3. Complex (*R,R*)-**3** was prepared and purified in an analogous manner (*R,R*)-**1** from (*R,R*)-H_2(ONNO$_{Ad}$) (0.103 g, 0.146 mmol) as a yellow solid (yield: 0.099g, 79%). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) : δ 8.43 (1H, s, N=C*H*), 8.18 (1H, s, N=C*H*), 7.45 (2H, s, Ar*H*), 6.98 (1H, s, Ar*H*), 6.92 (1H, s, Ar*H*), 3.64-3.60 (1H, m, -C*H*- of DACH), 3.24-3.20 (1H, m, -C*H*- of DACH), 2.64-2.61 (1H, m, -CH_2- of DACH), 2.48-2.44 (1H, m, -CH_2- of DACH), 2.26-2.24 (12H, d (J^3 = 6.0 Hz), -CH_2- of Ad), 2.16-1.69 (20H, overlapping -C*H*- and –CH_2- resonances of Ad and DACH), 1.52-1.42 (m, 4H, -CH_2- of DACH), 1.31 (18H, br s, Ar-C(CH_3)$_3$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C): δ 171.9, 168.6, 167.8, 166.7, 142.6, 137.9, 137.9, 131.0, 130.5, 129.8, 129.6, 117.5, 68.0, 64.9, 63.2, 40.6, 40.5, 37.3, 37.2, 34.0, 31.3, 29.1, 27.0, 25.3, 24.2, 23.6. Anal. Calcd (found) for $C_{48}H_{64}ClInN_2O_2$: C, 67.72(67.79); H, 7.58(7.75); N, 3.29(3.17).

Synthesis of (±)-(ONNO$_{Ad}$)InCl (±)-3. The racemic complex (±)-**3** was prepared and purified in an analogous manner to (*R,R*)-**1** from (±)-H_2(ONNO$_{Ad}$) (0.060 g, 0.085 mmol) as a yellow solid (yield: 0.054 g, 74%). X-ray quality single crystals were obtained by crystalizing in diethyl ether for four days at –30 °C. The complex has an

identical NMR signature to that of (*R,R*)-**3**. Anal. calcd (found) for $C_{48}H_{64}ClInN_2O_2$: C, 67.72(67.62); H, 7.58(7.44); N, 3.29(3.51).

Synthesis of (*R,R*)-(ONNO$_{Cm}$)InCl (*R,R*)-4. This complex (*R,R*)-**4** was prepared and purified in an analogous manner to (*R,R*)-**1** from (*R,R*)-H_2(ONNO$_{Cm}$) (0.482 g, 0.606 mmol) as a yellow solid (yield: 0.423 g, 74%). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) : δ 8.23 (1H, s, N=C*H*), 8.02 (1H, s, N=C*H*), 7.32-7.15 (20H, overlapping peaks, Ar*H*), 7.10 (2H, s, Ar*H*), 6.88 (1H, s, Ar*H*), 6.85 (1H, s, Ar*H*), 3.49-3.46 (1H, m, -C*H*-), 3.09-3.06 (1H, m,-C*H*-), 2.53-2.49 (1H, m, -CH_2-), 2.34-2.31 (1H, m, -CH_2-), 2.04-2.00 (2H, m, -CH_2-), 1.76 (3H, s, -CH_3), 1.76 (3H, br s, -CH_3), 1.75 (3H, br s, -CH_3), 1.72 (3H, br s, -CH_3), 1.70 (3H, br s, -CH_3), 1.64 (12H, br s, -CH_3), 1.41-1.37 (4H, m, -CH_2-). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C): δ 170.5, 166.7, 150.7, 150.6, 133.1, 132.8, 131.5, 128.0, 126.7, 126.7, 126.0, 125.6, 124.9, 124.8, 65.9, 63.1, 42.9, 42.2, 31.0, 30.8, 30.7, 29.4, 28.2, 26.9, 24.1, 23.6, 15.3. Anal. calcd (found) for $C_{56}H_{60}ClInN_2O_2$: C, 71.30(70.94); H, 6.41(6.78); N, 2.97(3.18).

Synthesis of (*R,R*)-(ONNO$_{SiPh3}$)InCl (*R,R*)-5. This complex (*R,R*)-**5** was prepared and purified in an analogous manner to (*R,R*)-**1** from (*R,R*)-H_2(ONNO$_{SiPh3}$) (0.148 g, 0.171 mmol) as a yellow solid (yield: 0.139 g, 80%). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) : δ 8.30 (1H, s, N=C*H*), 8.06 (1H, s, N=C*H*), 7.40-6.98 (H, overlapping peaks, Ar*H*), 3.70-3.64 (1H, m, -C*H*-), 3.13-3.11 (1H, m,-C*H*-), 2.45-2.41 (1H, m, -CH_2-), 2.40-2.35 (1H, m, -CH_2-), 2.11(3H, s, ArCH_3), 2.09(3H, s, ArCH_3), 2.06-2.02 (2H, m, -CH_2-), 2.01 (2H, m, -CH_2-), 1.53-1.40 (m, 4H, -CH_2-). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C): δ 165.7, 147.4, 136.2, 136.1, 135.9, 134.6, 129.5, 128.2, 127.7, 121.5, 126.9, 126.9, 67.8, 62.4, 51.4, 30.7, 25.0, 23.2, 21.1, 20.2, 19.5. Anal. calcd (found) for $C_{58}H_{62}ClInN_2O_2Si_2$: C, 68.60(68.25); H, 5.16(5.42); N, 2.76(2.10).

One-pot synthesis of (*R,R*)-[(ONNO$_{Me}$)InOEt]$_2$ (*R,R*)-7 (Representative procedure). A 20 mL scintillation vial was charged with the proligand (*R,R*)-H_2(ONNO$_{Me}$) (0.100 g, 0.216 mmol), $InCl_3$ (0.048 g, 0.216 mmol), 3 mL toluene, and a magnetic stir bar. The mixture was stirred for 30 minutes and a suspension of 6 equiv. NaOEt (0.088 mg, 1.3 mmol) in 4 mL of toluene was added to the reaction. The mixture was allowed to stir at room temperature overnight, and filtered using glass filter paper. The solvent was removed under vacuum to yield a yellow solid (0.087 g, 65%). Salt metathesis of (*R,R*)-**2** (0.110 g, 0.180 mmol), analogous to the synthesis of *(R,R)*-**6** was also used in the synthesis of this complex (yield: 0.088 g, 78%). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.22 (1H, s, N=C*H*), 7.97 (1H, m, N=C*H*), 7.27 (1H, s, Ar*H*), 7.21 (1H, s, Ar*H*), 6.85 (1H, s, Ar*H*), 6.78 (1H, s, Ar*H*), 3.62 (1H, m, -CH_2-), 3.37-3.28 (2H, m, -CH_2- of -OCH_2CH$_3$), 2.82-2.79 (1H, m, -C*H*-), 2.26 (3H, s, ArCH_3), 2.14 (3H, m, ArCH_3), 1.93-1.91 (1H, -CH_2-), 1.85-1.83 (1H, m, -CH_2-), 1.77 (1H, -CH_2-), 1.44–1.42 (1H, m, -CH_2-), 1.33-1.20 (3H, m, -CH_2-) 1.32 (3H, t(J^3 = 6.7 Hz), -OCH$_2$CH_3), 1.27 (9H, s, ArC(CH_3)$_3$), 1.27 (9H, s, ArC(CH_3)$_3$), 1.07–1.03 (1H, m, -CH_2-).^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C): δ 170.5, 168.2, 167.3, 163.0, 135.9, 135.7, 132.7, 132.2, 131.7, 131.6, 129.2, 128.6, 128.4, 126.9, 125.4, 117.6, 116.4, 68.5, 62.8, 59.9, 33.7, 31.6, 31.6, 27.2, 24.8, 24.7, 20.6, 17.8, 17.2. Anal. Calcd (found) for $C_{32}H_{45}InN_2O_3$: C 61.94(61.33); H 7.31(7.36); N 4.51(4.54).

Synthesis of (*R,R*)-[(ONNO$_{Ad}$)InOEt]$_2$ (*R,R*)-8. (*R,R*)-**8** was synthesized via the salt metathesis (analogous to the synthesis of *(R,R)*-**6**) of (*R,R*)-**3** (0.182 g, 0.214 mmol) as a yellow solid (yield: 0.142 g, 77%) and the one pot synthesis (analogous to the one-pot synthesis of *(R,R)*-**7**) with (*R,R*)-H_2(ONNO$_{Ad}$) (0.141 g, 0.200 mmol) (yield: 0.097 g, 56%). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.13 (1H, s, N=C*H*), 8.03 (1H, m, N=C*H*), 7.43 (1H, s, Ar*H*), 7.31 (1H, s, Ar*H*), 6.90 (1H, s, Ar*H*), 6.78 (1H, s, Ar*H*), 3.88-3.77 (1H, m, -C*H*-), 3.76-3.61 (2H, m, -CH_2- of -OCH_2CH$_3$), 2.74-2.68 (1H, m, -C*H*-), 2.36-1.15 (38H overlapping signals Ad and –CH_2- of DACH), 1.31 (9H, s, Ar(CH_3)$_3$), 1.27 (9H, s, ArC(CH_3)$_3$), 1.07 (3H, t(J^3 = 6.3 Hz), -OCH$_2$CH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C): δ 171.6, 169.3, 168.7, 162.5, 142.3, 141.8, 135.7, 134.5, 130.0, 129.5, 129.0, 128.2, 127.8, 125.3, 118.1, 118.0, 69.8, 62.6, 60.3, 40.6, 40.4, 37.2, 37.1, 33.9, 31.3, 29.1, 27.5, 24.7, 20.7. Anal. calcd (found) for $C_{50}H_{69}InN_2O_3$: C 69.76(70.07); H 8.08(7.95); N 3.39(3.42).

Synthesis of (*R,R*)-[(ONNO$_{Cm}$)InOEt]$_2$ (*R,R*)-9. (*R,R*)-**9** was synthesized via the salt metathesis (analogous to the synthesis of *(R,R)*-**6**) of (*R,R*)-**4** (0.338 g, 0.358 mmol) as a yellow solid (yield: 0.256 g, 75%) and the one pot synthesis with (*R,R*)-H_2(ONNO$_{cumyl}$) (0.266 g, 0.335 mmol)(yield: 0.189 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.86 (1H, s, N=C*H*), 7.82 (1H, m, N=C*H*), 7.38-7.34 (2H, m, Ar*H*), 7.28-7.05 (14H, overlapping signals, Ar*H*), 6.98-6.94 (2H, m, Ar*H*), 6.71 (1H, s, Ar*H*), 6.70-6.64 (2H, m, Ar*H*), 6.62 (1H, s, Ar*H*), 6.54-6.50 (2H, m, Ar*H*), 3.81-3.73 (1H, m, -C*H*-), 3.51 (2H, q, -CH_2- of -OCH_2CH$_3$), 2.46-2.42 (1H, m, -C*H*-), 2.13 (3H, s, -CH_3), 2.05-2.01 (1H, m, -CH_2-), 1.93 (3H, s, -CH_3), 1.88-1.83 (1H, m, -CH_2-), 1.70 (3H, s, -CH_3), 1.64 (3H, s, -CH_3), 1.64 (3H, s, -CH_3), 1.51 (3H, s, -CH_3), 1.50 (3H, s, -CH_3), 1.45 (3H, s, -CH_3) 1.75-1.19 (6H, overlapping signals -CH_2-

of DACH) , 1.09 (3H, t(J^3 = 3.2 Hz), -OCH_2CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 25 °C): δ 171.4, 168.5, 167.7, 161.8, 151.6, 151.2, 150.7, 150.2, 141.8, 141.6, 134.7, 133.7, 131.6, 131.5, 129.4, 127.8, 127.8, 126.6, 126.5, 125.2, 123.6, 118.2, 118.0, 68.9, 62.6, 59.3, 44.2, 42.2, 42.0, 41.7, 31.6, 30.9, 30.7, 30.4, 27.7, 26.4, 24.5, 24.4, 21.1. Anal. calcd (found) for $C_{58}H_{65}InN_2O_3$: C 73.10(72.92); H 6.88(6.49); N 2.94 (2.83).

Synthesis of (*R,R*)-[($ONN_{Br}O_{tBu}$)InOEt]$_2$ (*R,R*)-10. (*R,R*)-**10** was synthesized using the one pot synthesis with (*R,R*)-$H_2(ONNO_{Br})$ (0.204 g, 0.344 mmol) as a yellow solid (0.178 g, 69%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.23 (1H, s, N=C*H*), 7.94 (1H, m, N=C*H*), 7.72 (1H, s, Ar*H*), 7.68 (1H, s, Ar*H*), 7.01 (1H, s, Ar*H*), 6.91 (1H, s, Ar*H*), 3.67-3.65 (1H, m, -CH_2-), 3.66-3.41 (2H, m, -CH_2- of -OCH_2CH_3), 2.89-2.85 (1H, m, -C*H*-), 2.33-2.29 (1H, -CH_2-), 1.89-1.83 (3H, m, -CH_2-), 1.50-1.19 (4H, overlapping peaks, -CH_2-), 1.48 (3H, t (J^3 = 3.6 Hz), -OCH_2CH_3), 1.29 (9H, s, ArC(CH_3)$_3$), 1.26 (9H, s, ArC(CH_3)$_3$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 25 °C): δ 170.4, 164.2, 163.6, 162.8, 137.7, 137.4, 135.3, 130.7, 128.9, 128.2, 119.3, 118.8, 118.4, 117.7, 68.5, 62.8, 60.7, 33.7, 31.3, 31.0, 28.1, 24.5, 24.4, 20.8. Anal. calcd (found) for $C_{30}H_{39}Br_2InN_2O_3$: C 48.03 (48.39); H 5.24 (5.16); N 3.73 (3.73).

Synthesis of potassium pyridin-2-ylmethoxide ($KOCH_2Pyr$). A 20 mL scintillation vial was charged with 2-pyridine methanol (0.629 g, 5.76 mmol), 7 mL of THF and a Teflon stir bar. In a separate 20 mL vial KOtBu (0.647 g, 5.76 mmol) was dissolved in 7 mL of THF. The KOtBu solution was added slowly to the stirring 2-pyridine methanol solution. After ~10 min of stirring, a light grey precipitate can be observed. The reaction was allowed to stir for 16 h. The reaction was allowed to settle, and the dark green solution was decanted to isolate a grey colored solid. This solid was repeatedly washed with hexanes, until the washings were colorless. Then the solid was dried *in vacuo* to give $KOCH_2Pyr$ a white powder (yield: 0.780 g, 92%). ^1H NMR (600 MHz, THF-d_8, 25 °C): δ 8.35 (1H, br s, Ar*H*(Pyr)), 7.52 (1H, t(J^3 = 5.6 Hz), Ar*H*(Pyr)), 7.38-7.35 (1H, m, Ar*H*(Pyr)), 6.99-6.97 (1H, m, Ar*H*(Pyr)), 6.98 (1H, br s, -CH_2-). While the compound was sufficiently soluble to obtain a ^1H NMR spectrum, we were unable to get $^{13}C\{H\}$ data for the compound due to poor solubility in common solvents. Anal. calcd (found) for C_6H_6NOK: C 48.95(48.61); H 4.11(4.86); N 9.51(8.78).

Synthesis of (*R,R*)-[($ONNO_{tBu}$)InOCH$_2$Pyr (*R,R*)-11. Complex (*R,R*)-**1** (0.124 g, 0.178 mmol) was dissolved in toluene (2 mL) and added to a slurry of potassium pyridin-2-ylmethoxide (0.027 g, 0.183 mmol) in toluene (2 mL). The mixture was stirred at room temperature for 16 h. The resulting mixture was filtered and the solution evaporated under vacuum to afford a yellow solid (yield: 0.105 g, 77%). Yellow coloured X-ray quality crystals were obtained by crystallizing from hexanes at ambient temperature. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.66-8.65 (1H, d, Ar*H*(pyr)), 8.31 (1H, s, N=C*H*), 8.14 (1H, s, N=C*H*), 7.70-7.67 (1H, m, Ar*H*(pyr)), 7.46 (1H, s, ArH), 7.30 (1H, s, ArH), 7.21-7.18 (1H, m, Ar*H*(pyr)), 7.15-7.11 (1H, m, Ar*H*(pyr)), 5.02(2H, s, -CH_2- of –OCH_2Pyr), 4.29-4.24(1H, m, -C*H*-), 3.03-2.98(1H, m, -C*H*-), 2.54-2.49 (1H, m, -CH_2- of DACH), 2.24-2.21 (1H, m, -CH_2- of DACH), 2.05-1.98 (2H, m, -CH_2- of DACH), 1.74-1.69 (1H, m, -CH_2- of DACH), 1.60-1.56 (2H, m, -CH_2- of DACH), 1.49 (9H, s, Ar-C(CH_3)$_3$), 1.42-1.35 (1H, m, -CH_2- of DACH), 1.30 (9H, s, Ar-C(CH_3)$_3$), 1.27 (9H, s, Ar-C(CH_3)$_3$), 1.19 (9H, s, Ar-C(CH_3)$_3$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 169.1, 168.7, 168.1, 165.5, 164.6, 147.6, 141.2, 141.1, 138.1, 135.4, 135.0, 129.9, 129.3, 128.8, 128.5, 121.8, 121.4, 118.2, 117.8, 67.4, 64.9, 63.9, 35.8, 35.2, 33.0, 31.4, 30.0, 29.6, 29.3, 27.2, 24.8, 23.8. Anal. calcd (found) for $C_{42}H_{58}N_3O_3In$: C 65.71 (66.02), H 7.61(7.78), N 5.47(5.83).

Synthesis of (*R,R*)-[($ONNO_{SiPh3}$)InOCH$_2$Pyr (*R,R*)-12. Complex (*R,R*)-**12** was synthesized via the salt metathesis of (*R,R*)-**5** (0.126 g, 0.124 mmol) (yield: 0.069 g, 51%, 25 °C). The red solid obtained was further purified by washing with acetonitrile and dried under vacuum. However, minor impurities could still be observed in the ^1H NMR spectrum. . ^1H NMR (600 MHz, $CDCl_3$): δ 8.26 (1H, s, N=C*H*), 7.94 (1H, s, N=C*H*), 7.80-6.74 (37H, overlapping peaks, Ar*H*(pyr) and Ar*H* (-$SiPh_3$)), 6.22-6.19 (1H, m, Ar*H*(pyr)), 4.56 (1H, d (J^2 = 20 Hz), -CH_2- of –OCH_2Pyr), 4.38-4.34(1H, m, -C*H*-), 4.03 (1H, d (J^2 = 20 Hz), -CH_2- of –OCH_2Pyr), 2.92-2.85(1H, m, -C*H*-), 2.30-1.28.49 (8H, overlapping multiplets , -CH_2- of DACH), 2.17 (3H, s, ArCH_3), 2.05 (3H, s, ArCH_3), ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): 165.2, 164.0, 159.0, 148.1, 145.8, 141.1, 139.3, 138.0, 137.4, 135.1, 135.9, 135.7, 134.6, 134.4, 128.6, 127.8, 127.2, 126.7, 124.8, 122.0, 121.6, 120.8, 120.4, 120.0, 65.4, 63.6, 32.6, 30.8, 24.4, 23.4, 21.0, 20.1, 20.0, 19.7, 13.7. $^{13}C\{^1H\}$ resonances cannot be identified with great confidence due to the presence of impurities and overlapping signals. X-ray quality crystal were not obtained in sufficient yield for further reactivity.

Synthesis of (*R,R*)-[($ONNO_{Br}$)InOCH$_2$Pyr (*R,R*)-13. A 20 mL scintillation vial was charged with the proligand $H_2(ONNO_{Br})$ (0.037 g, 0.063 mmol), anhydrous $InCl_3$ (0.019 g, 0.094 mmol), 2 mL toluene and a magnetic stir bar. This was allowed to stir for 30 min and a suspension of 5 equiv of potassium pyridin-2-ylmethoxide (0.047 g, 0.31 mmol) in 2 mL toluene was added to the reaction. The mixture was stirred at room temperature for 16 h, and the

remaining salt was filtered off using a glass filter paper. The solution was then evaporated under vacuum to afford a yellow solid. This was further purified with successive washings with hexanes to remove any residual 2-pyridinemethanol and dried *in vacuo*. (yield: 0.026 g, 51%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 9.50-9.48 (1H, d, Ar*H*(pyr)), 8.58-8.57 (1H, d, Ar*H*(pyr)) 8.33 (1H, s, N=C*H*), 8.13 (1H, s, N=C*H*), 7.75-7.68 (2H, m, Ar*H*(pyr)), 7.65 (1H, s, Ar*H*), 7.57 (1H, s, ArH), 7.04 (1H, s, Ar*H*), 6.99 (1H, s, ArH), 4.77(2H, s, -CH_2- of –OCH_2Pyr), 4.41-4.35(1H, m, -C*H*- of DACH), 3.12-3.08(1H, m, -C*H*- of DACH), 2.37-2.30 (1H, m, -CH_2- of DACH), 2.09-2.02 (1H, m, -CH_2- of DACH), 1.84-1.77 (2H, m, -CH_2- of DACH), 1.71-1.44 (4H, m (overlapping), -CH_2- of DACH), 1.25(9H, s, ArC(CH_3)$_3$), 1.23 (9H, s, ArC(CH_3)$_3$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C): δ 169.1, 164.1, 163.7, 163.2, 148.6, 138.2, 137.9, 137.6, 134.7, 134.5, 130.7, 130.2, 122.3, 120.7, 118.8, 118.2, 117.8, 67.4, 64.5, 63.7, 33.7, 31.3, 29.9, 27.4, 24.7, 23.7. Anal. calcd (found) for $C_{34}H_{40}Br_2InN_3O_3$: C 50.21(50.38); H 4.96 (5.00); N 5.17(5.51).

Representative procedure for ROP of lactide: Large scale samples for GPC and ^{1}H{^{1}H} NMR studies. In a 20 mL scintillation vial charged with a stir bar, *rac*-**6** (5.0 mg, 0.035 mmol) was dissolved in 2 mL of CH_2Cl_2. *rac*-lactide (0.205 g, 1.42 mmol) in 2 mL of CH_2Cl_2 was added to the stirring solution. The reaction was allowed to proceed for 4 h after which time the reaction was quenched with a few drops of HCl (1.5 M) in diethyl ether. A 0.5 mL sample of the reaction mixture was evaporated under vacuum for 3 hours and was dissolved in $CDCl_3$. ^{1}H{^{1}H} NMR spectrum of the methine region was obtained on a Bruker 600 MHz spectrometer. An analogous procedure was followed for the polymerization of *rac*-LA with other catalysts. Thereafter, the mixture was evaporated under vacuum and the polymer was isolated by washing three times with cold methanol. The isolated polymer was subsequently dried under vacuum for 4 h prior to GPC analysis.

Representative procedure for crossover experiment. In two 20 mL scintillation vials (*R,R*)-**6** (5.2 mg, 3.7×10^{-3} mmol) and (*R,R*)-**8** (6.3 mg, 3.7×10^{-3} mmol) were weighed separately. A volume of 0.3 mL of CD_2Cl_2 was added to each vial and the contents were mixed inside Teflon sealed J-young tube and taken to the NMR spectrometer immediately to acquire spectra.

Procedure for reaction of pyridine with (*R,R*)-6. In a 20 mL scintillation vial, (*R,R*)-**6** (10 mg, 7 10^{-3} mmol) was dissolved in neat pyridine (5 mL) and the solution was transferred to Teflon capped flask with a stir bar. The Teflon sealed flask was taken out of the glove box, stirred under reflux for 16 h. Thereafter the reaction was dried under vacuum and a NMR sample was prepared of the contents in $CDCl_3$ and a ^{1}H NMR spectrum was acquired.

Procedure for reaction of ethyl acetate with (*R,R*)-6. A 20 mL scintillation vial was charged with (*R,R*)-**6** (10 mg, 7×10^{-3} mmol), ethyl acetate (5 mL) and a Teflon stir bar. The reaction was allowed to stir at room temperature for 16 h. Thereafter the reaction was dried under vacuum and a NMR sample was prepared of the contents in $CDCl_3$ and a ^{1}H NMR spectrum was acquired.

Representative procedure for sample preparation for PGSE NMR spectroscopy (±)-6. In a 1.00 mL volumetric flask 6.2 mg of (±)-**6** (0.0044 mmol, 0.0044 M) was dissolved and made up to the line with a standard solution of tetrakis(trimethylsilyl)silane (TMSS) (0.94 mM in CD_2Cl_2) which was previously prepared. TMSS was used as an internal standard. A 0.5 mL volume of this solution of (±)-**6** in TMSS was transferred into a NMR tube, which was sealed with a Teflon cap for spectroscopy.

Representative procedure for determination of glass transition temperature (T_g) of polymers. Approximately 2–3 mg of the samples were weighed and sealed in an aluminum pan. The experiments were carried out under a nitrogen atmosphere. The samples were heated at a rate of 10 °C /min from 40 to 200 °C and then held isothermally for 5 min to destroy any residual crystal nuclei before cooling at 5 °C /min. The transition and melting temperatures were obtained from a second heating sequence, performed at 10 °C /min.

A. Characterization of compounds in solution

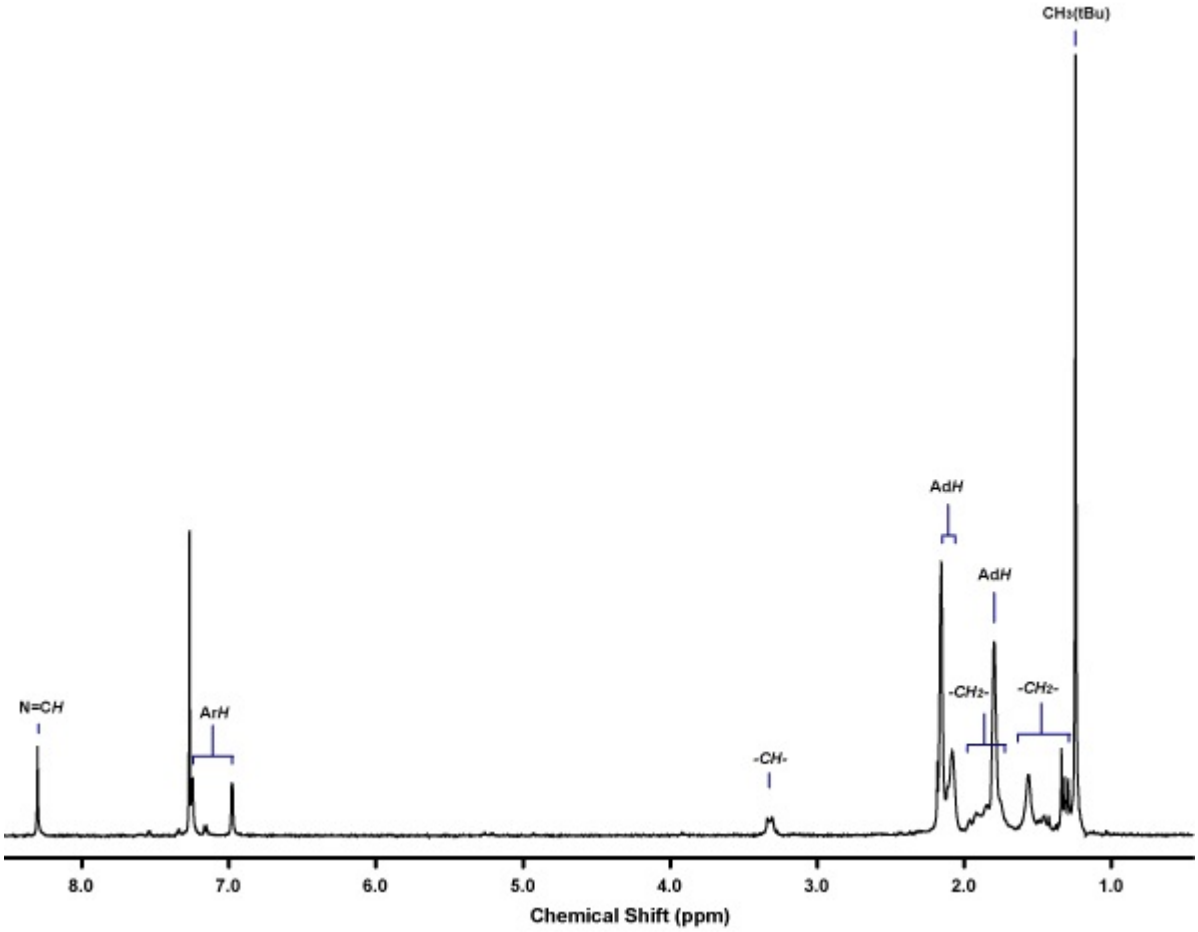


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-$H_2(ONNO_{Ad})$.

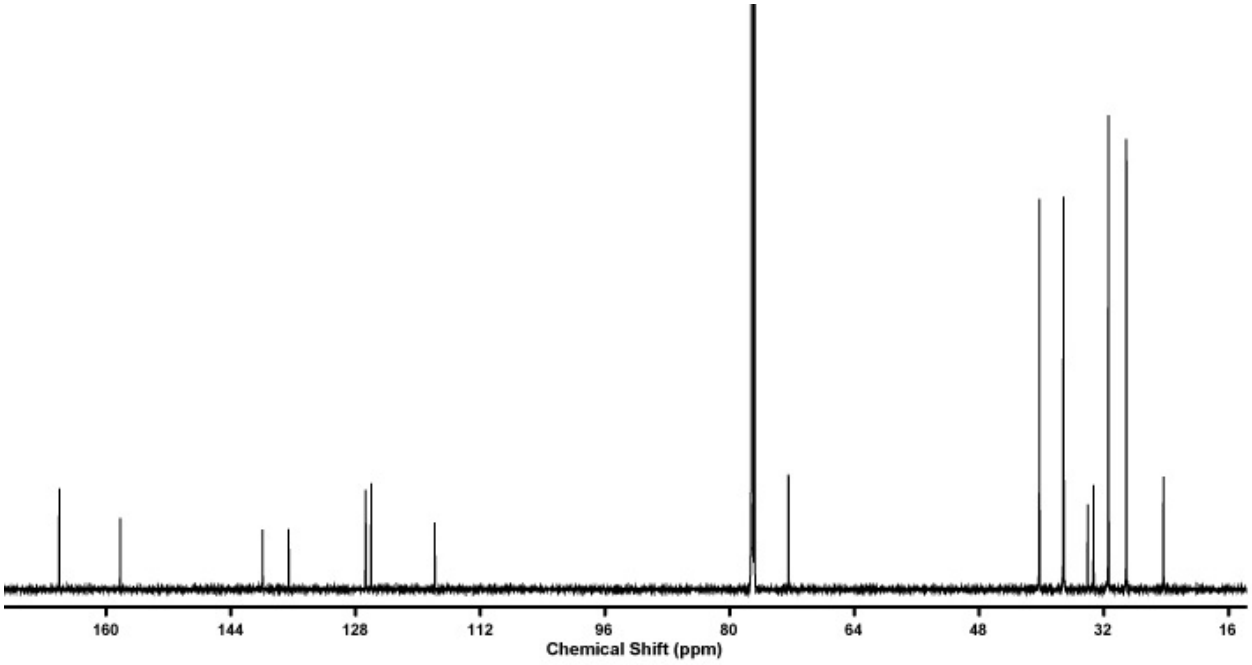


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-$H_2(ONNO_{Ad})$.

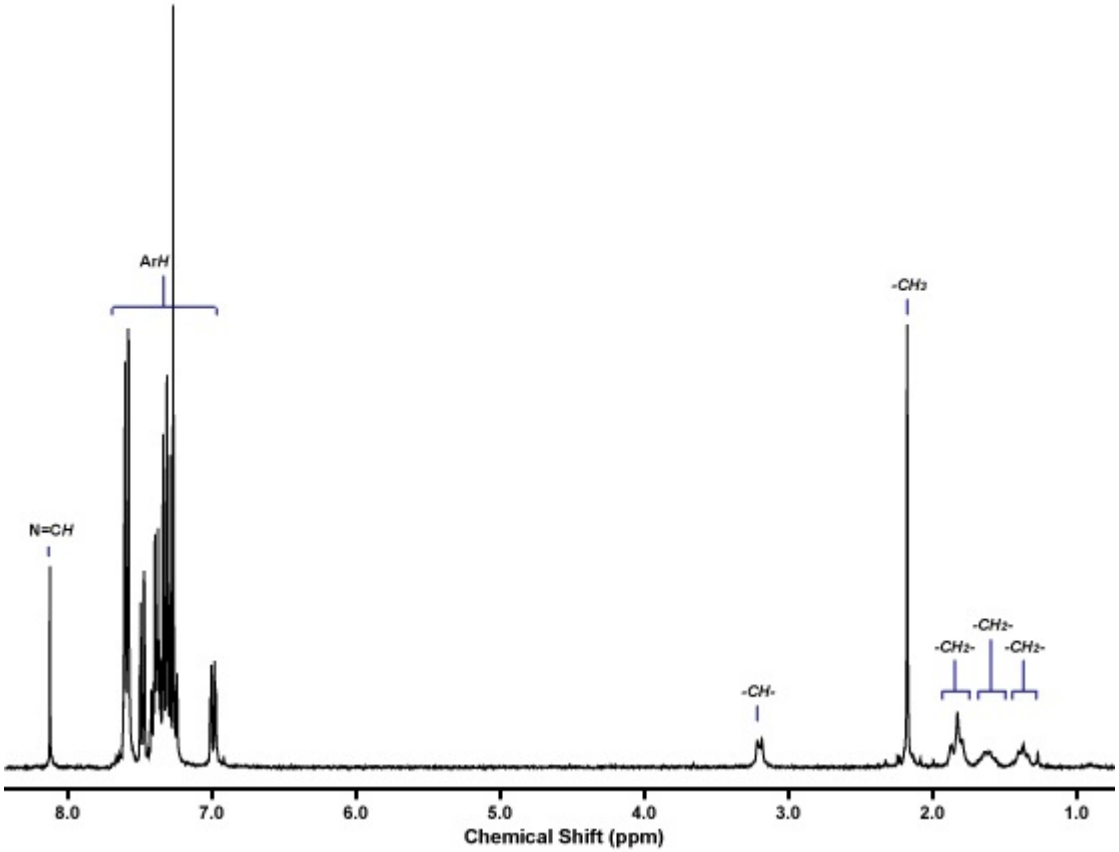


Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-(ONNO $_{SiPh3}$)H_2

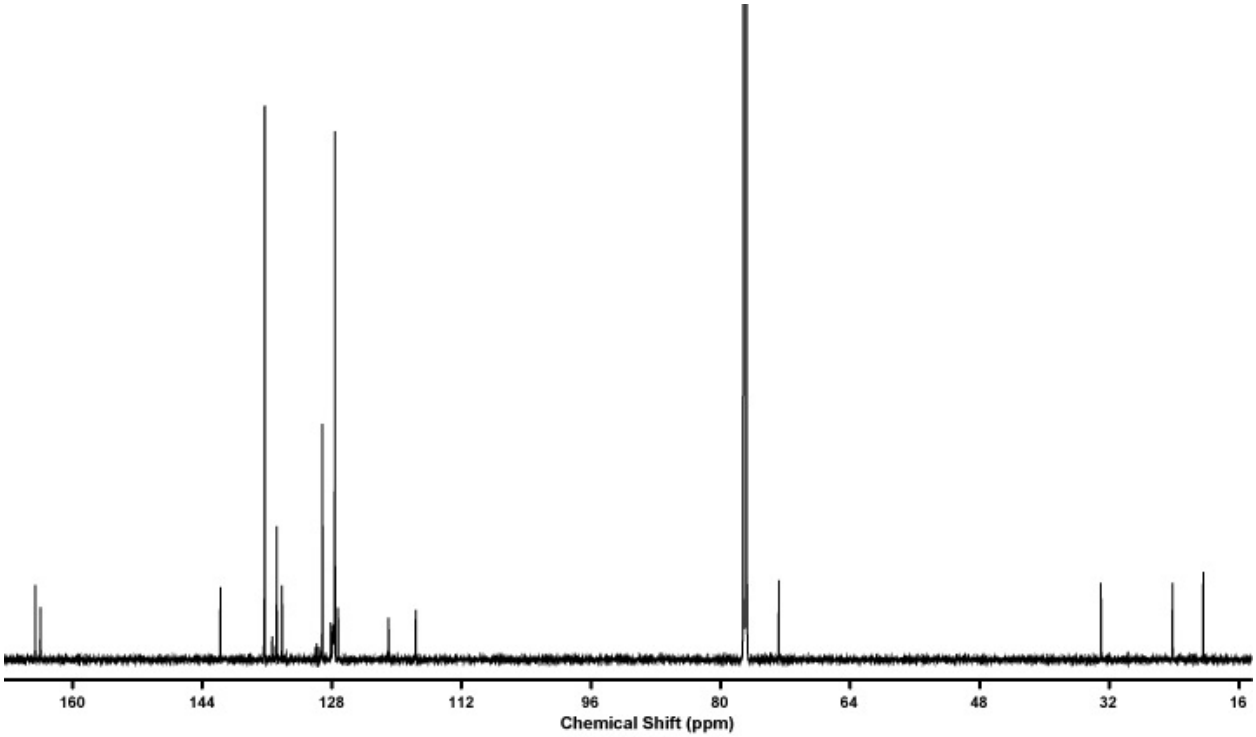


Figure S4. $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 25 °C) of (*R,R*)-(ONNO $_{SiPh3}$)H_2

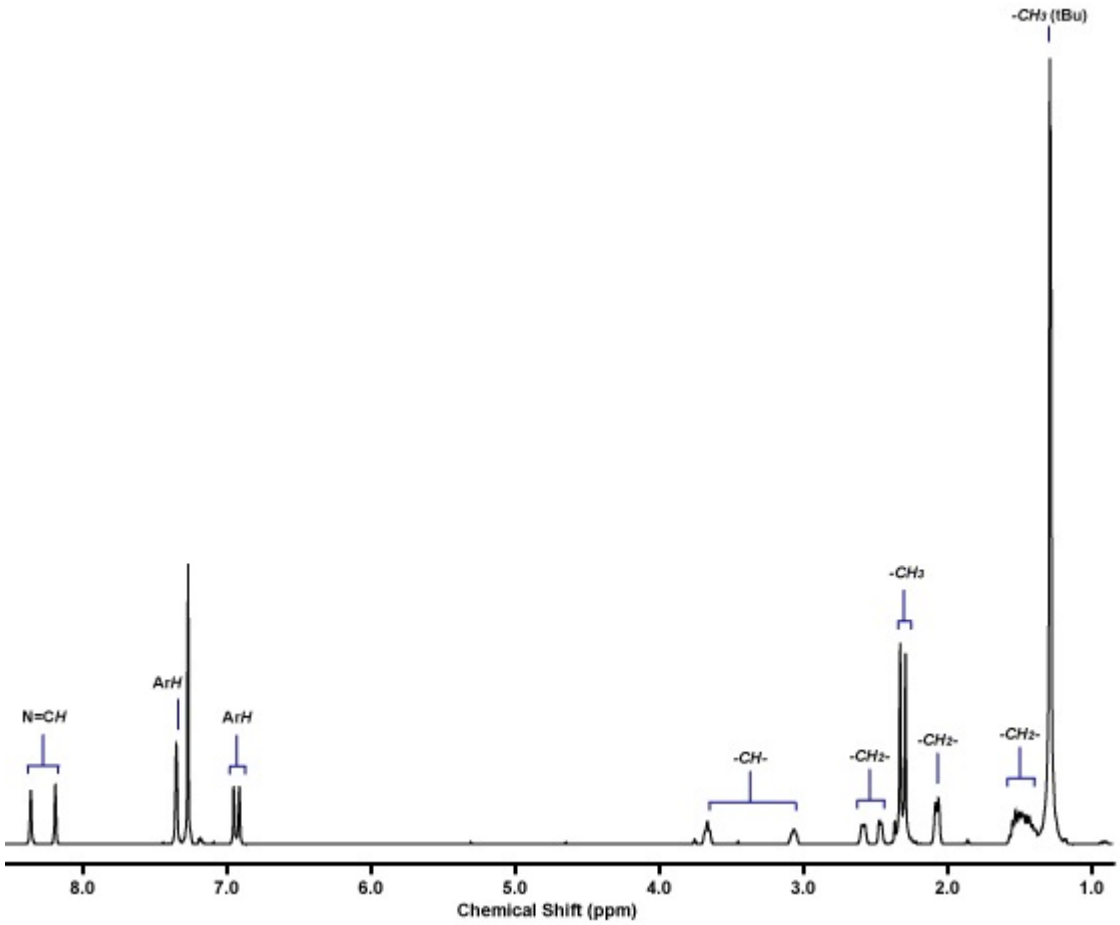


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**2**

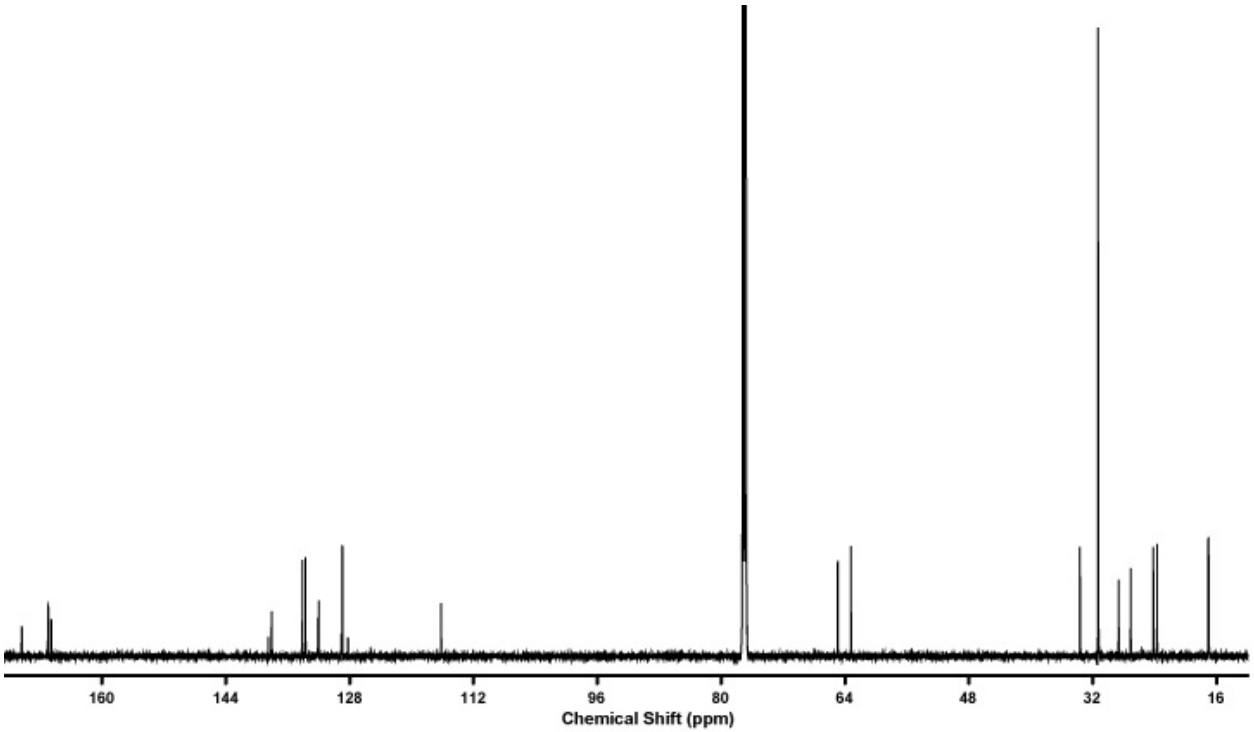


Figure S6. $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**2**

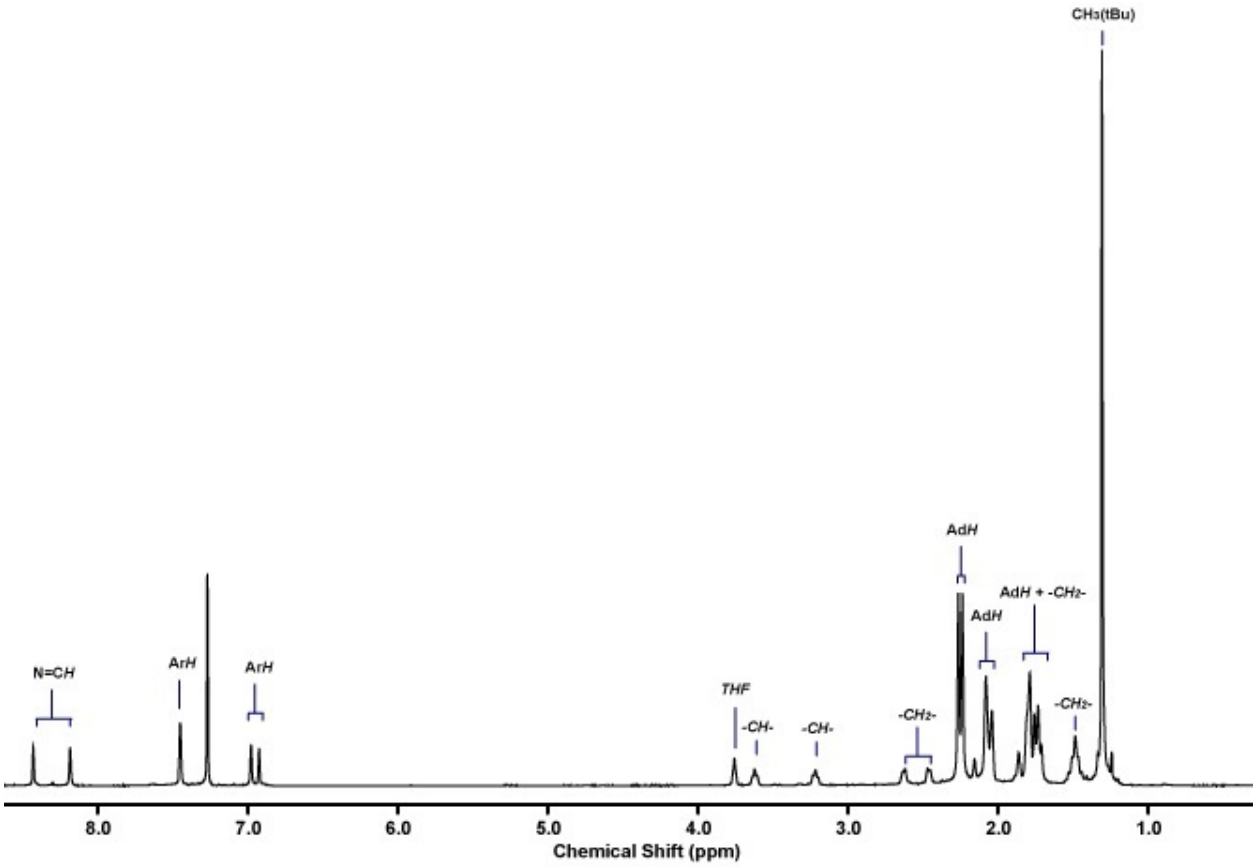


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**3**

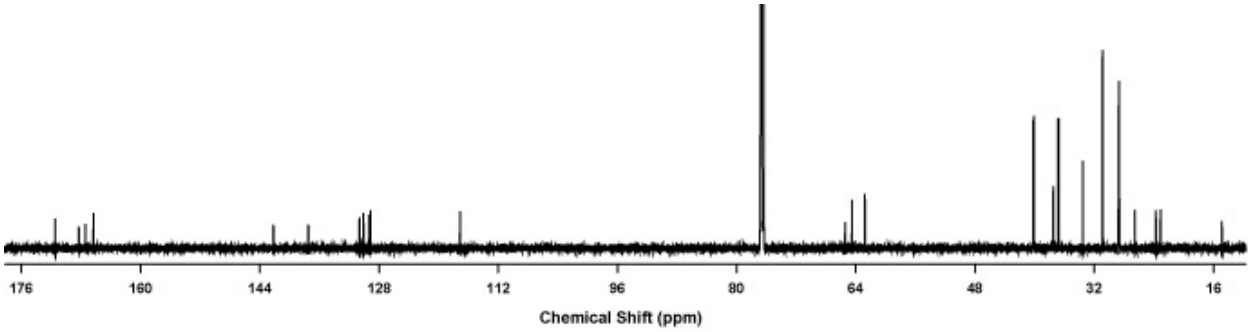


Figure S8. $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**3**

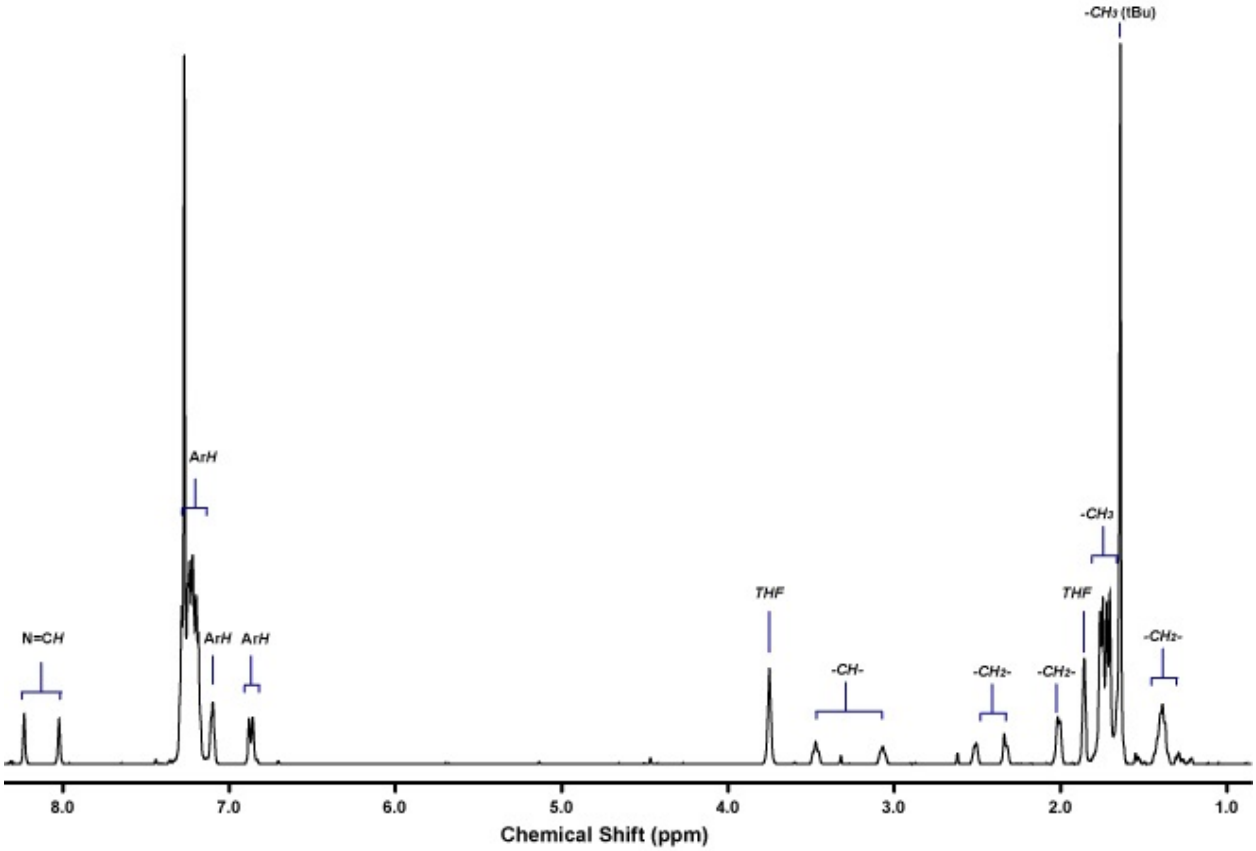


Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**4**

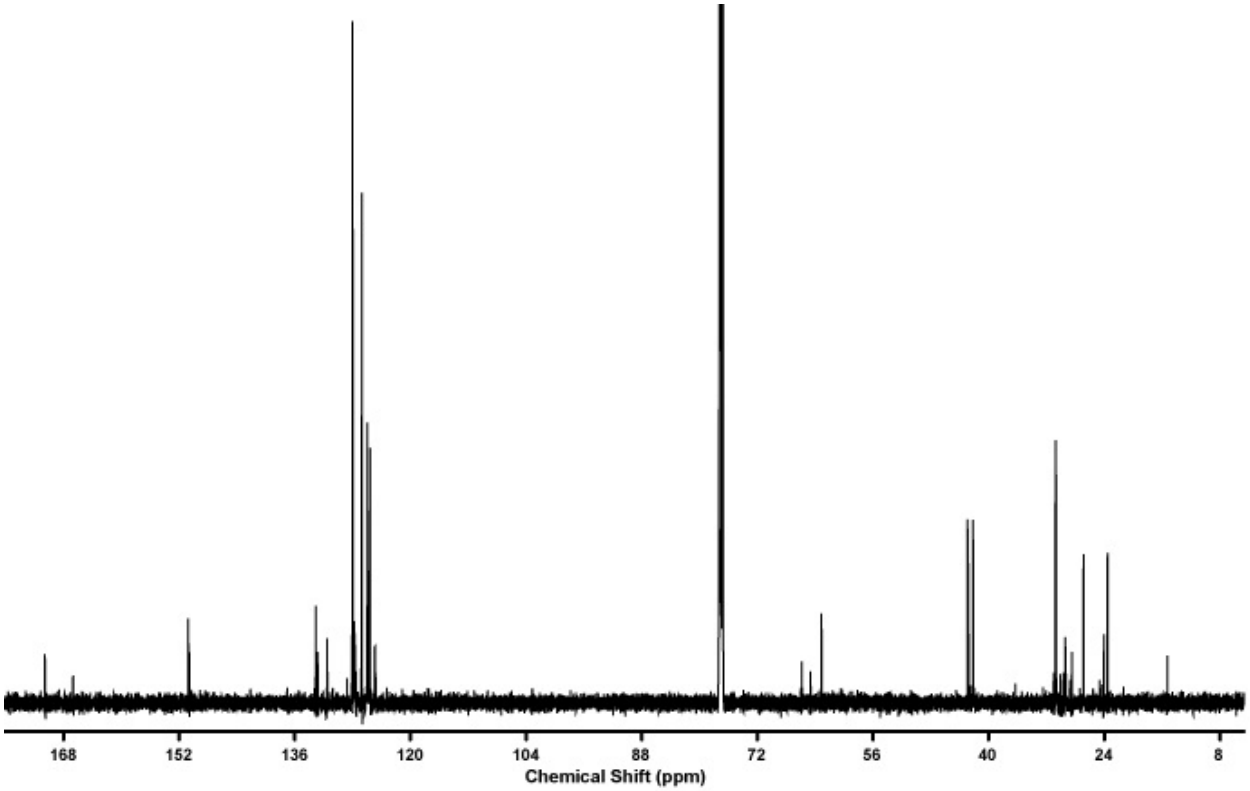


Figure S10. $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**4**

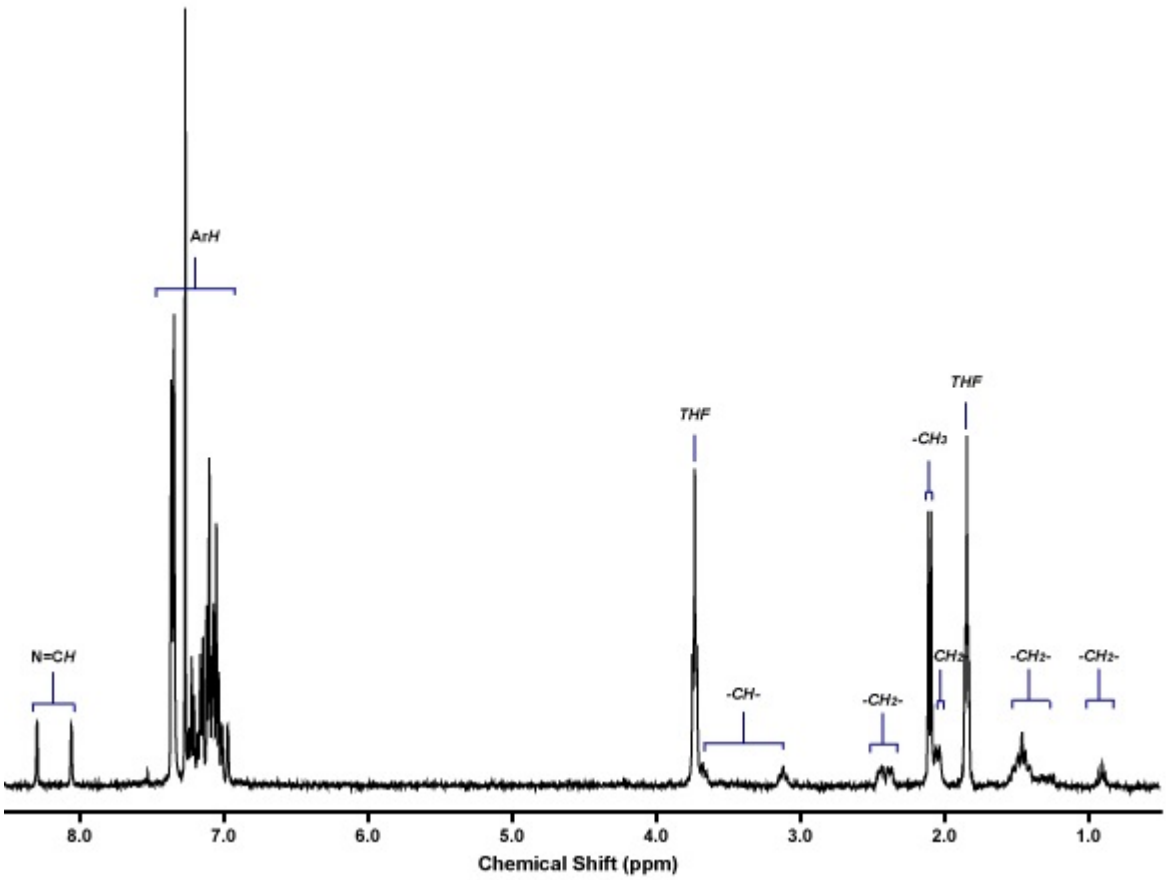


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**5**

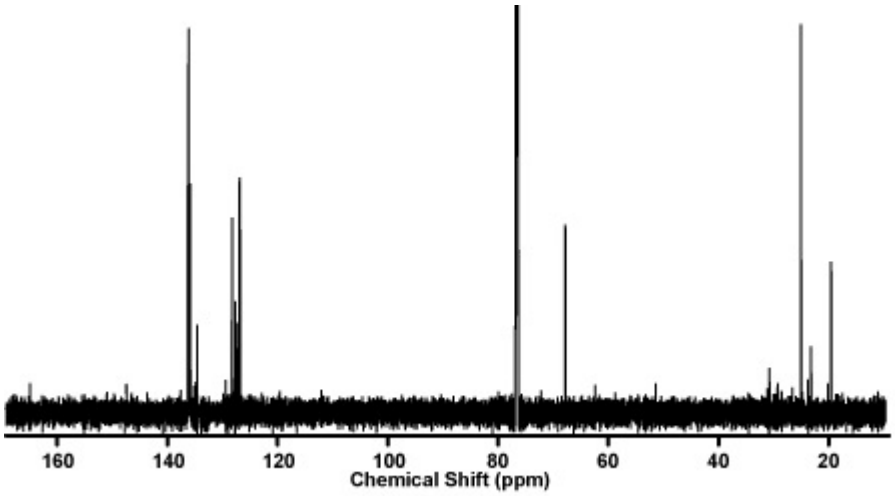


Figure S12. $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**5**

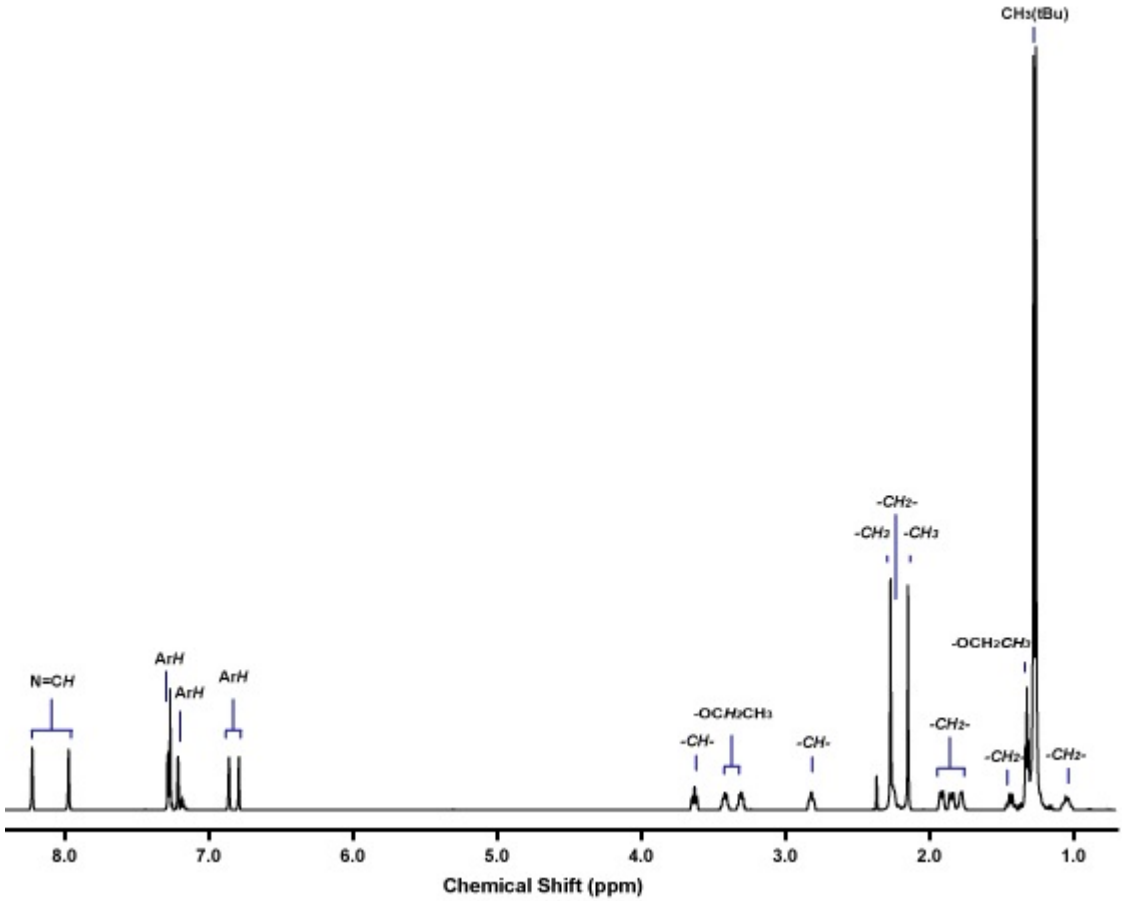


Figure S13. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**7**

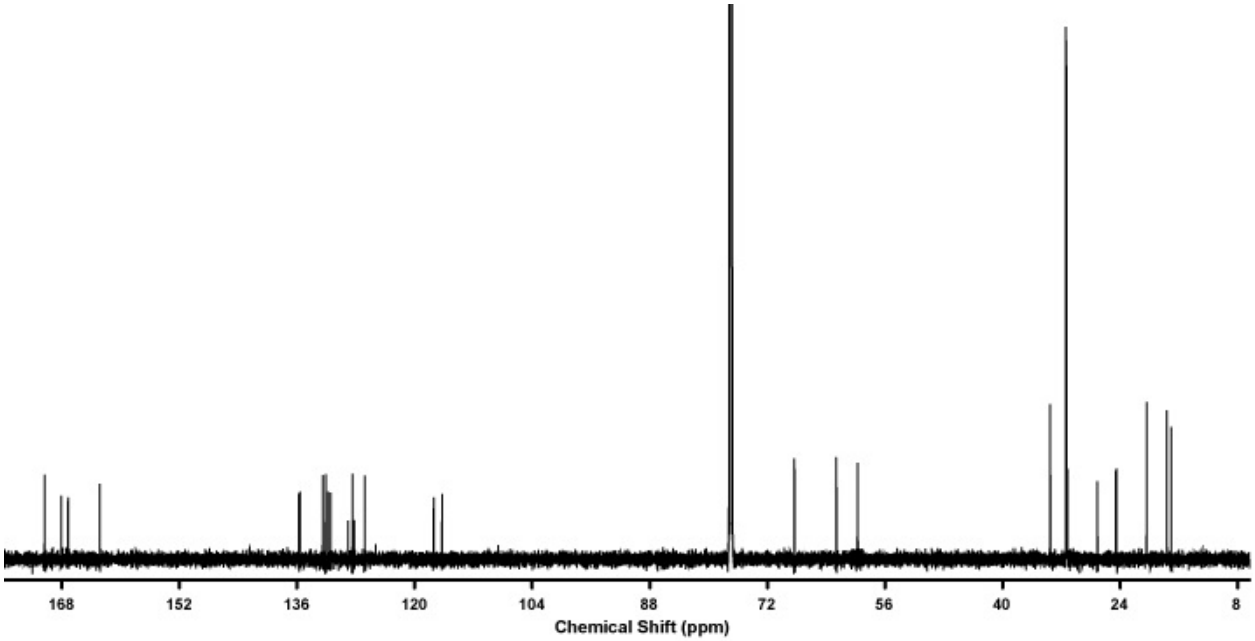


Figure S14. $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**7**

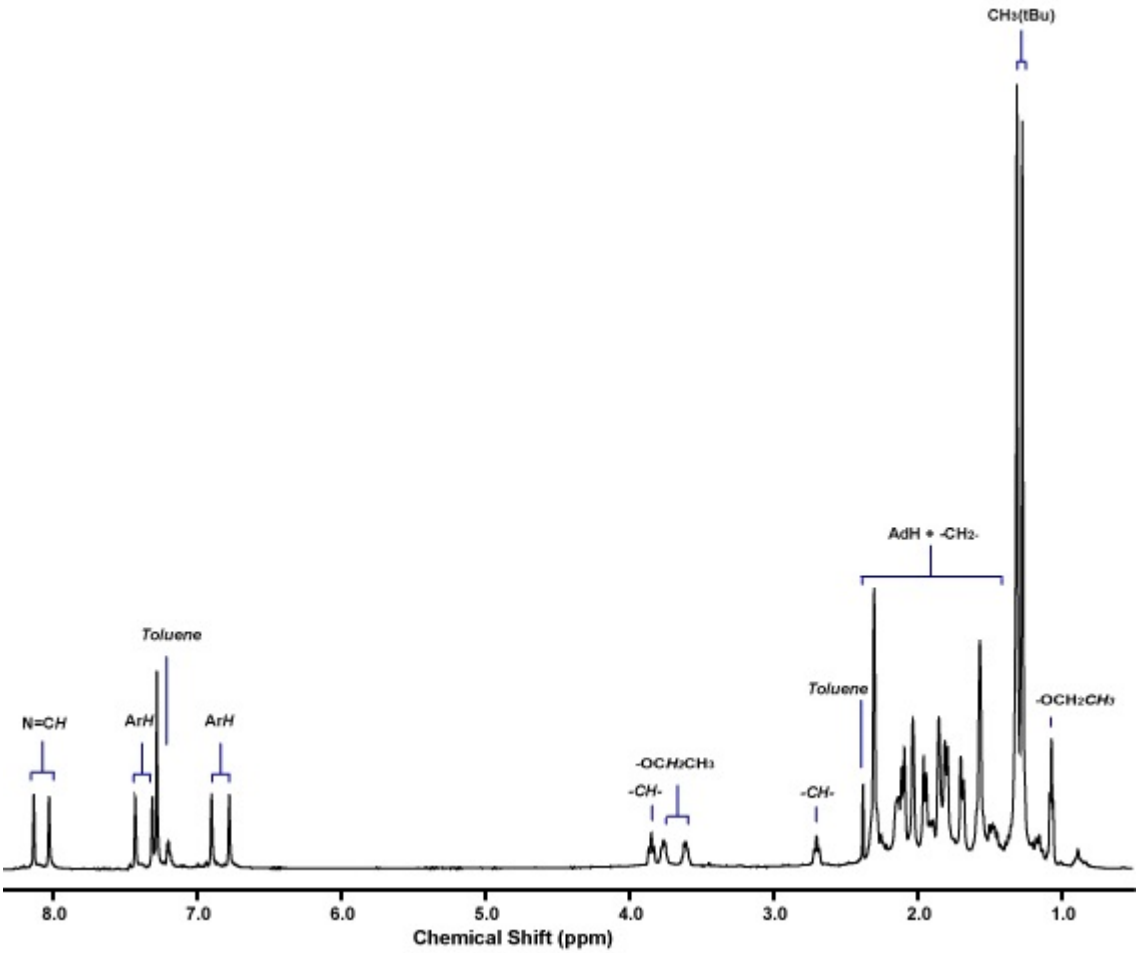


Figure S15. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**8**

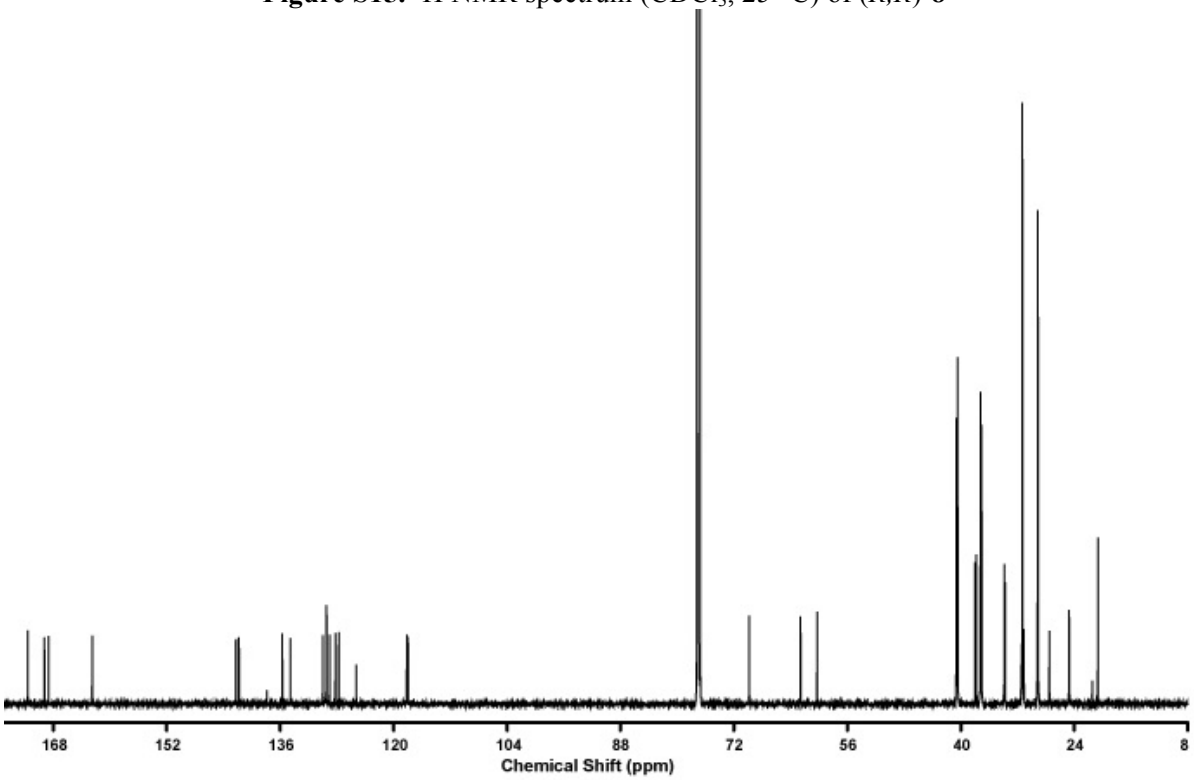


Figure S16. $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**8**

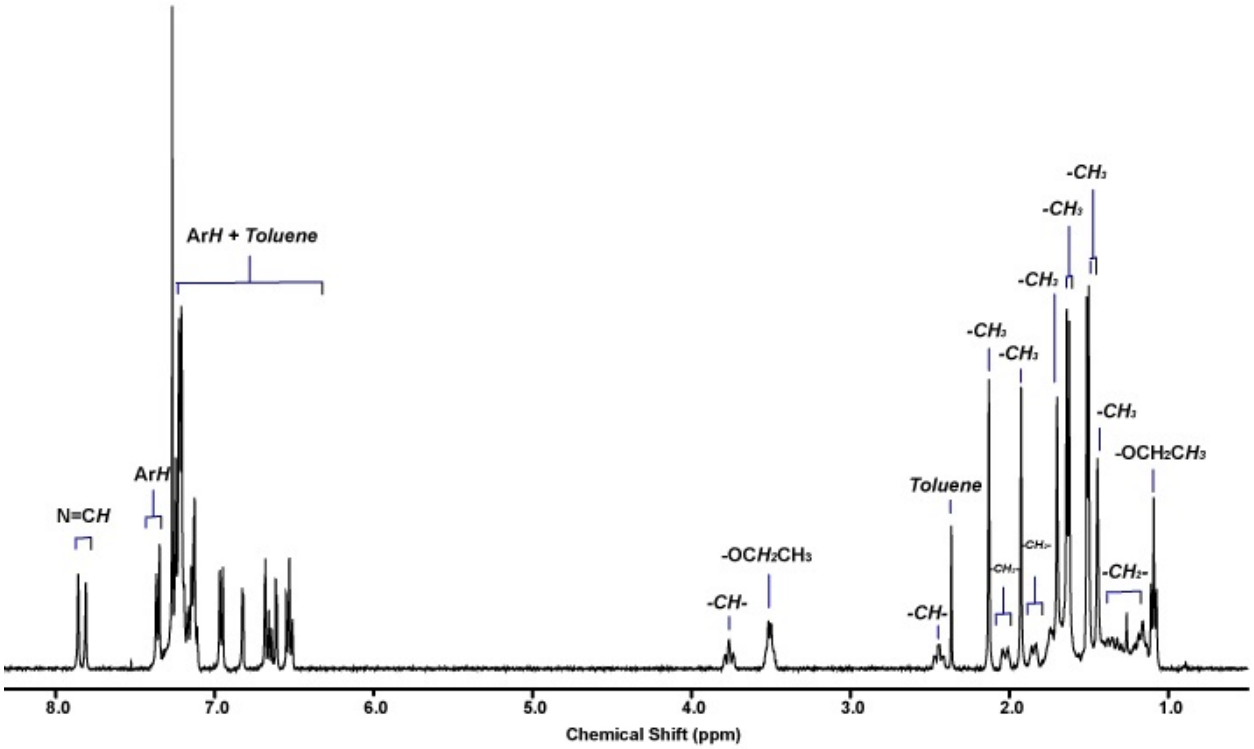


Figure S17. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**9**

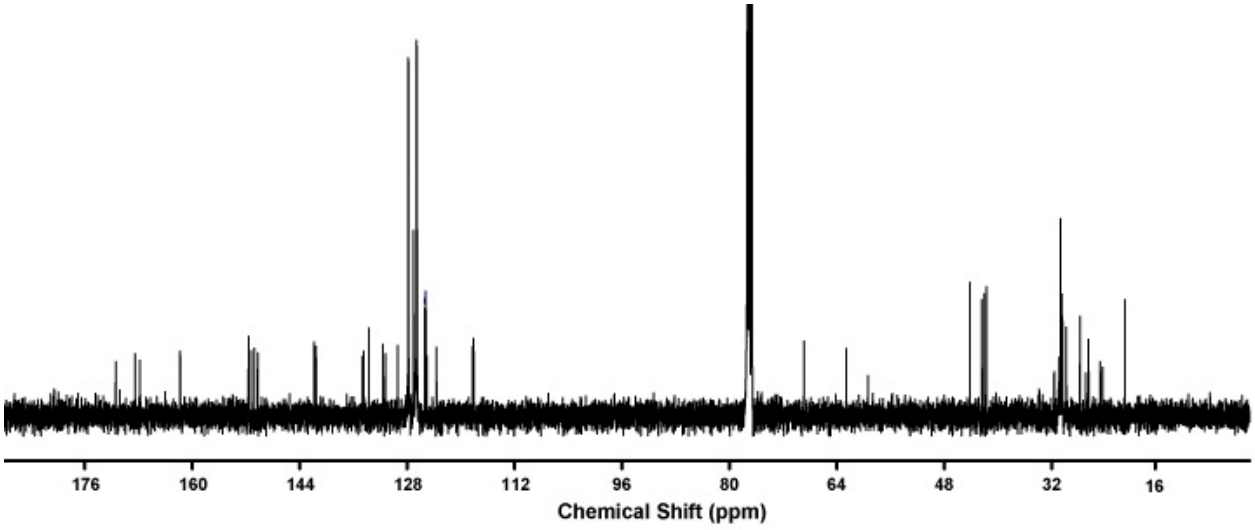


Figure S18. $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**9**

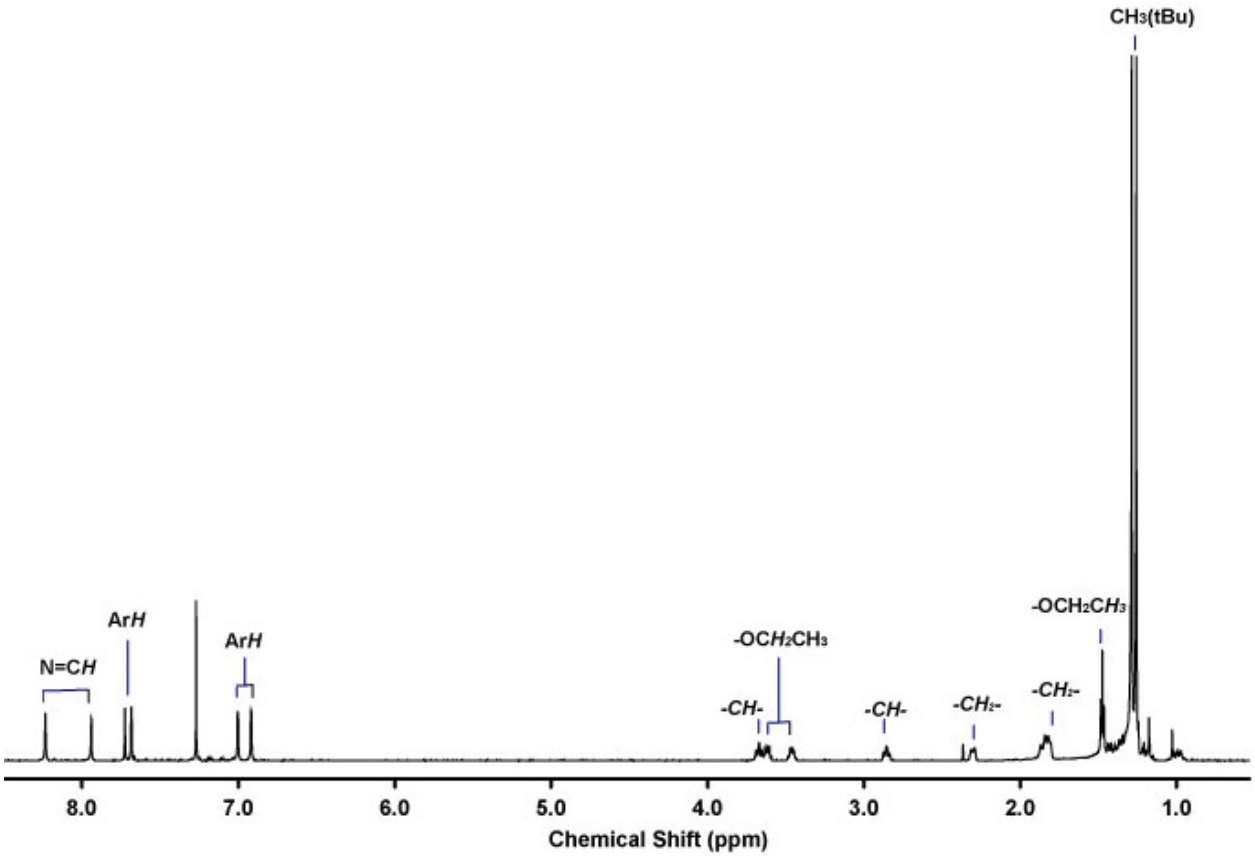


Figure S19. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**10**

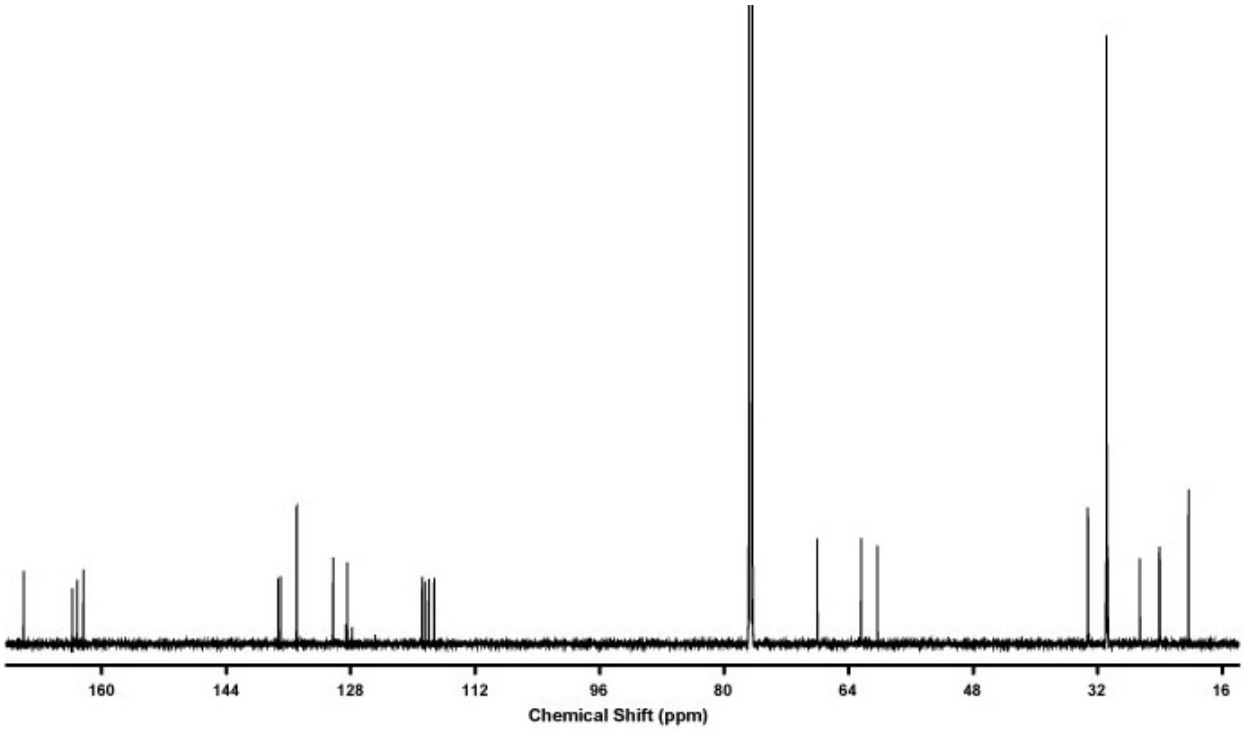


Figure S20. $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**10**

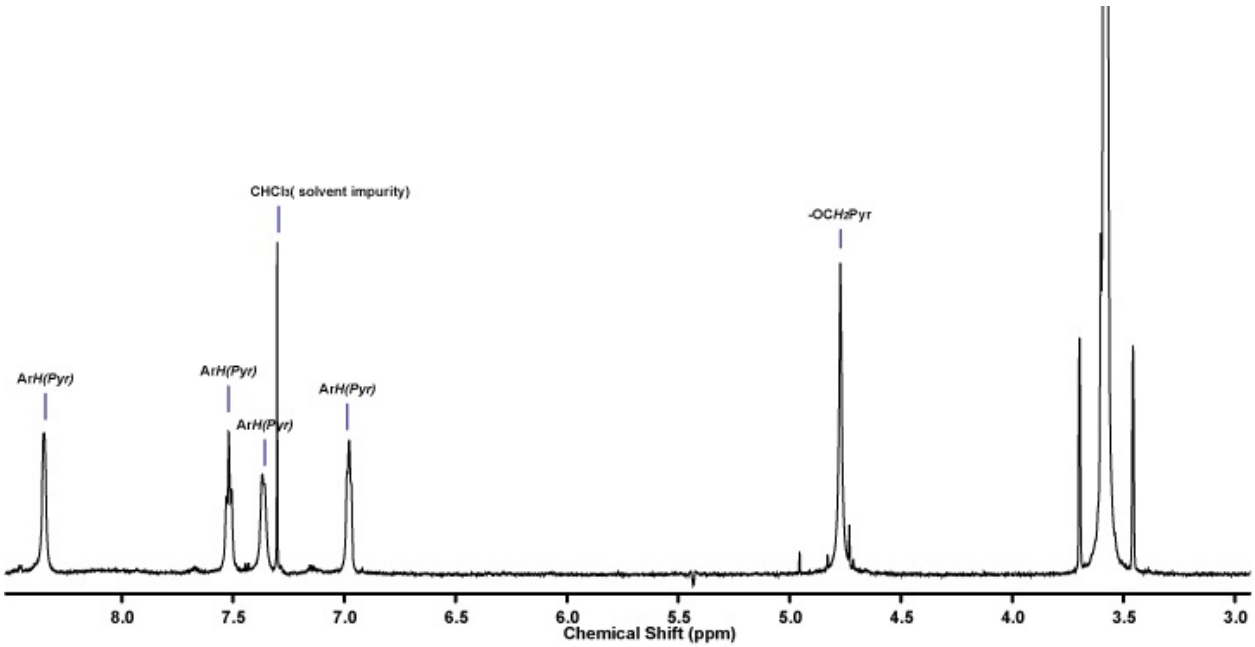


Figure S21. ^{1}H NMR spectrum (THF-d_8, 25 °C) of $KOCH_2Pyr$

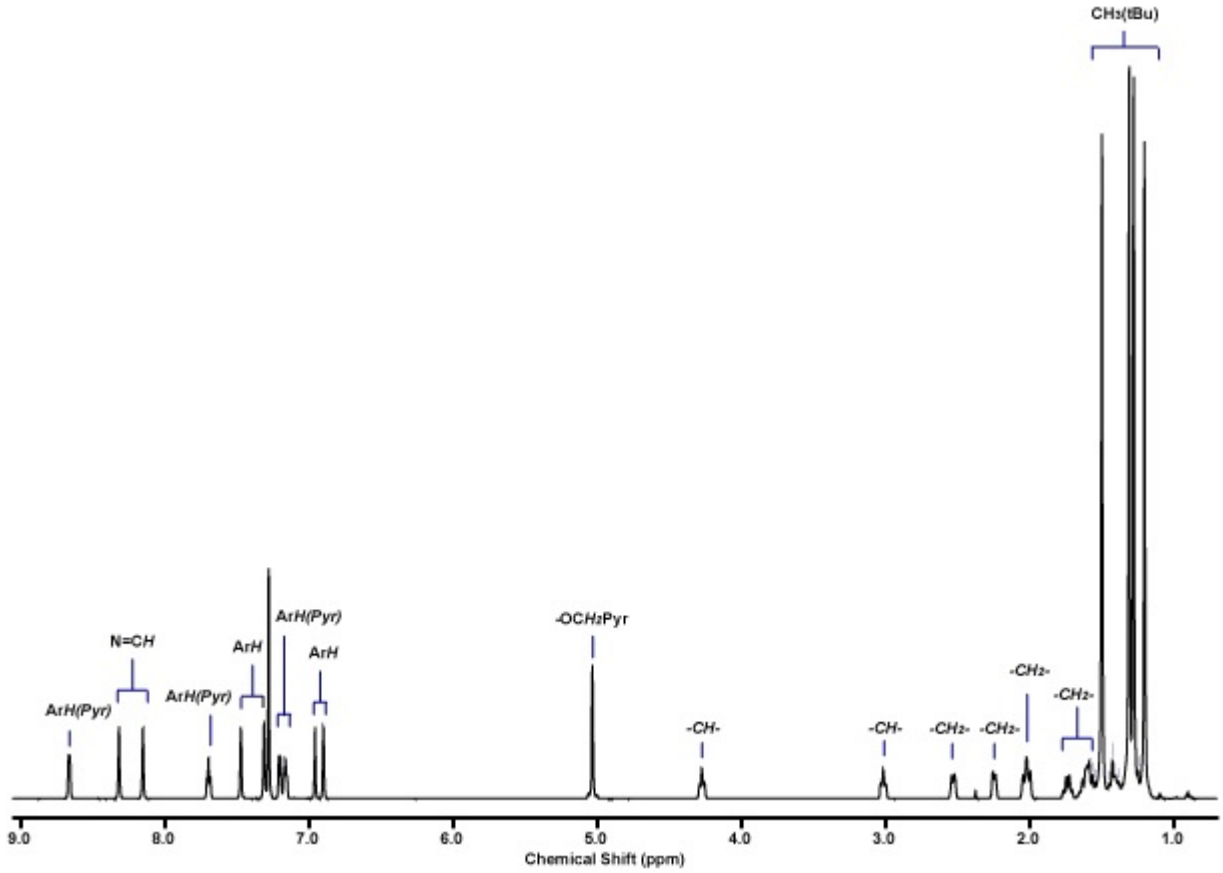


Figure S22. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**11**

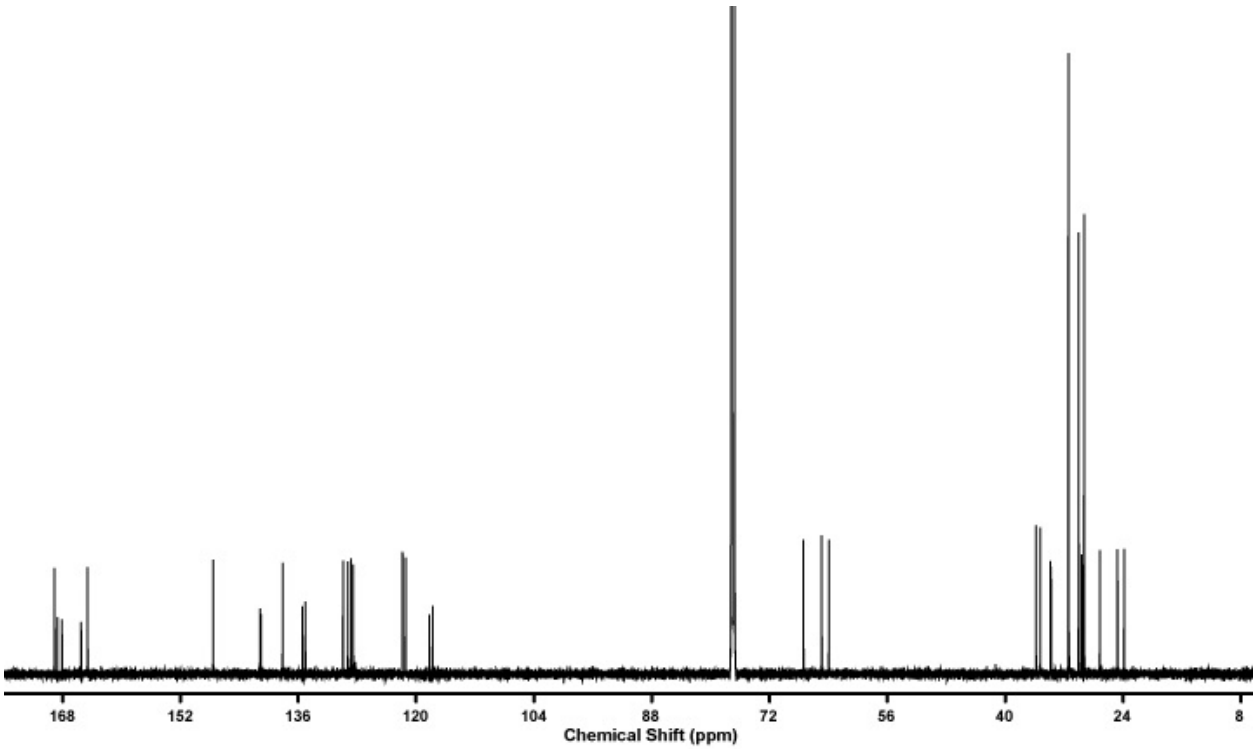


Figure S23. $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**11**

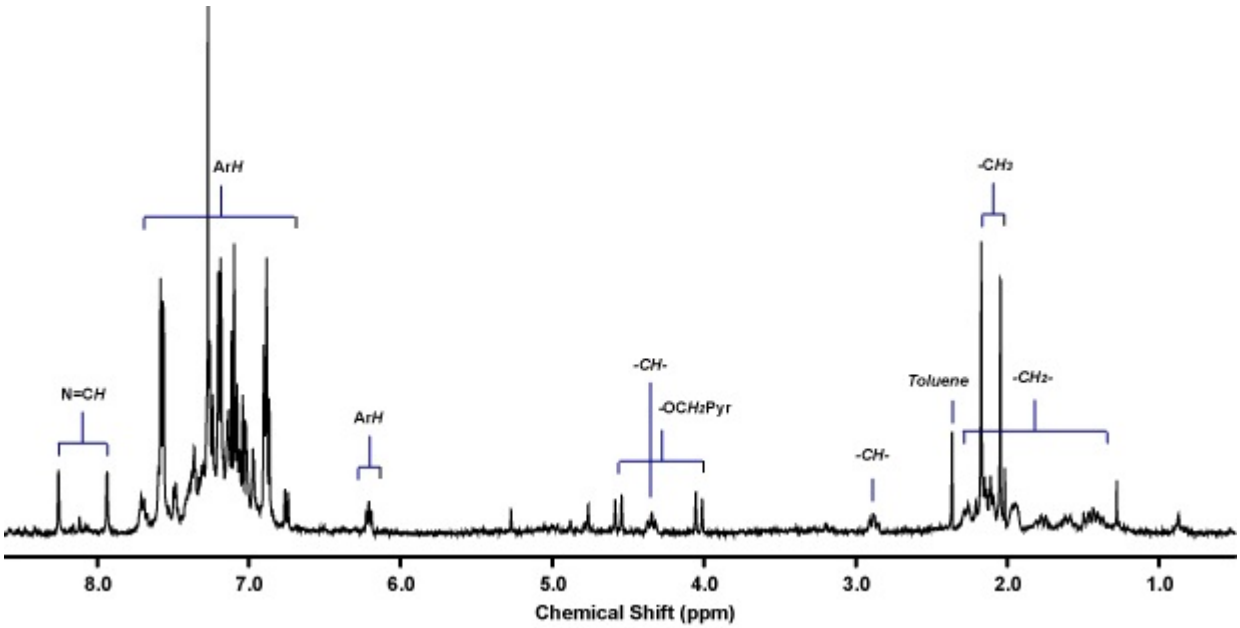


Figure S24. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**12**

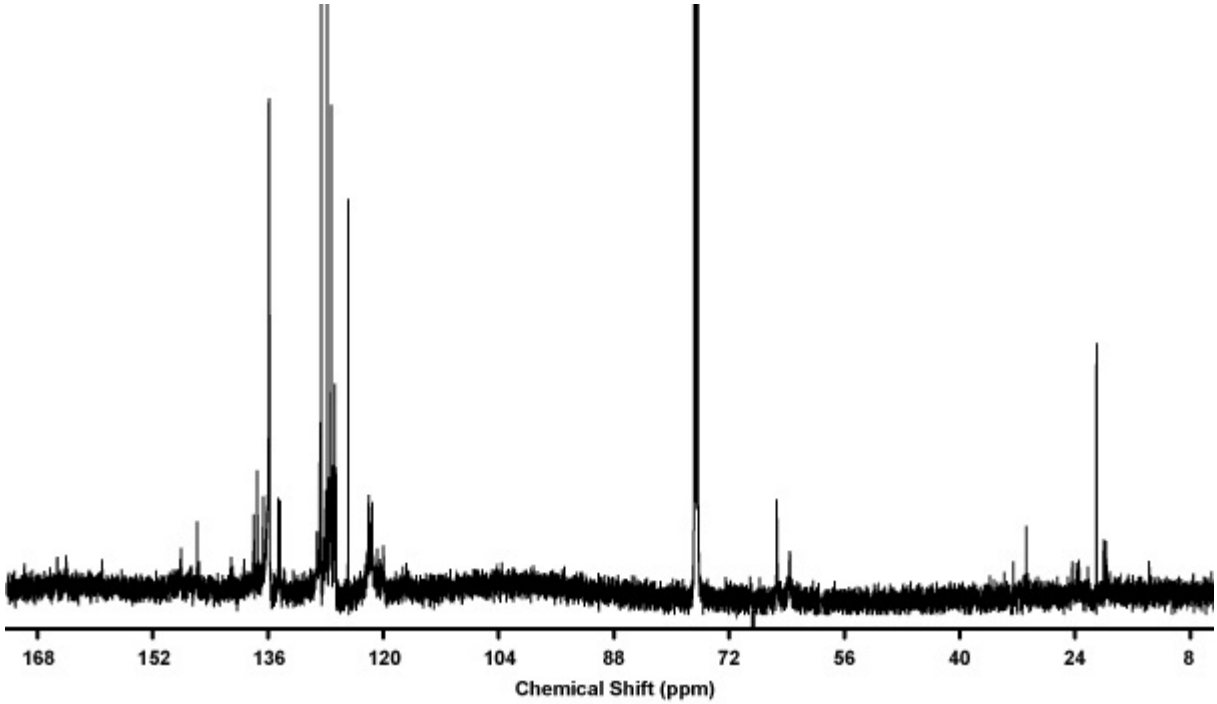


Figure S25. $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**12**

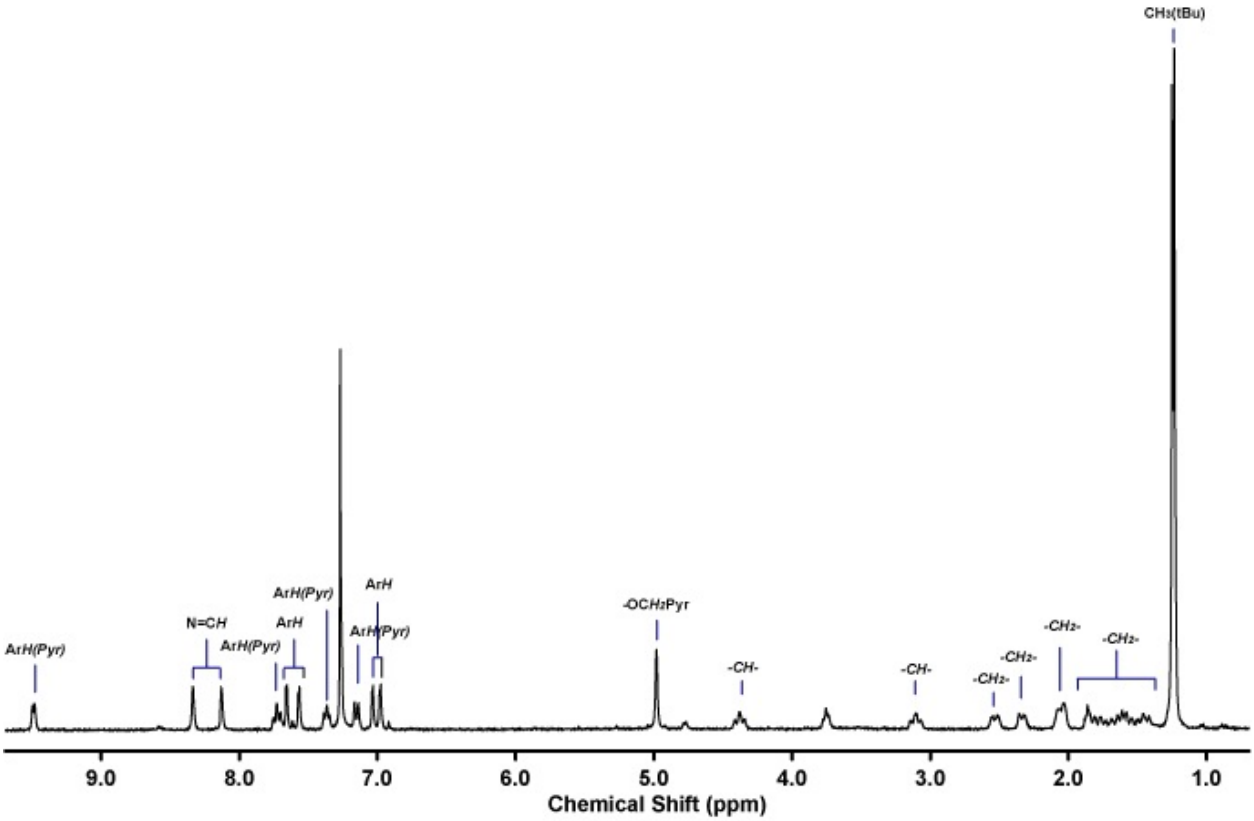


Figure S26. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**13**

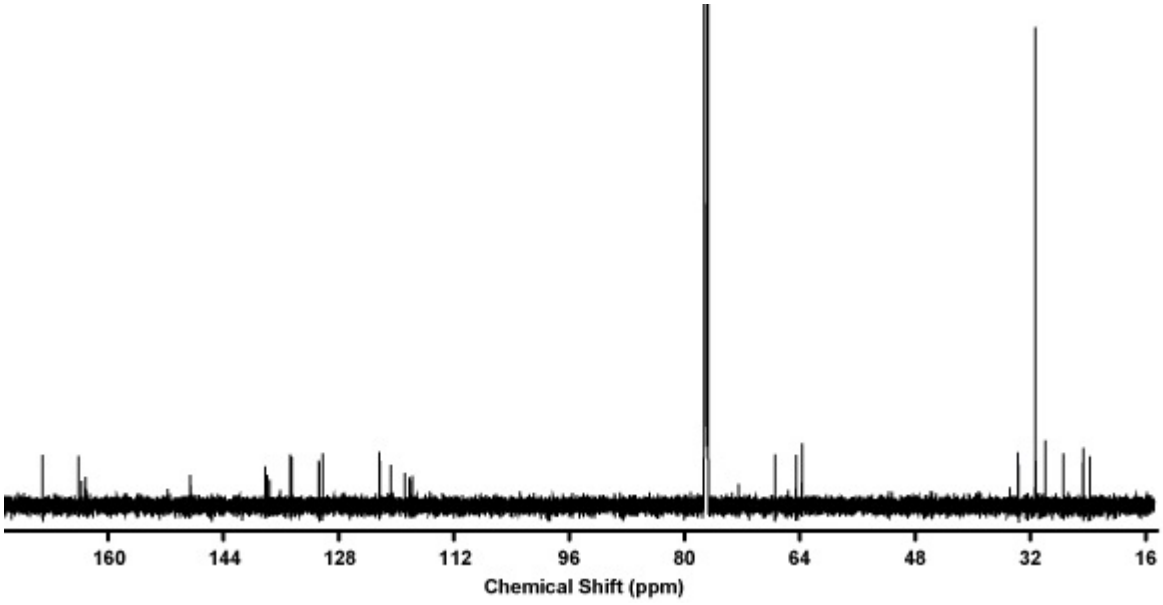


Figure S27. $^{13}C\{^{1}H\}$ spectrum ($CDCl_3$, 25 °C) of (*R,R*)-**13**

B. Reactivity, crossover and variable temperature experiments

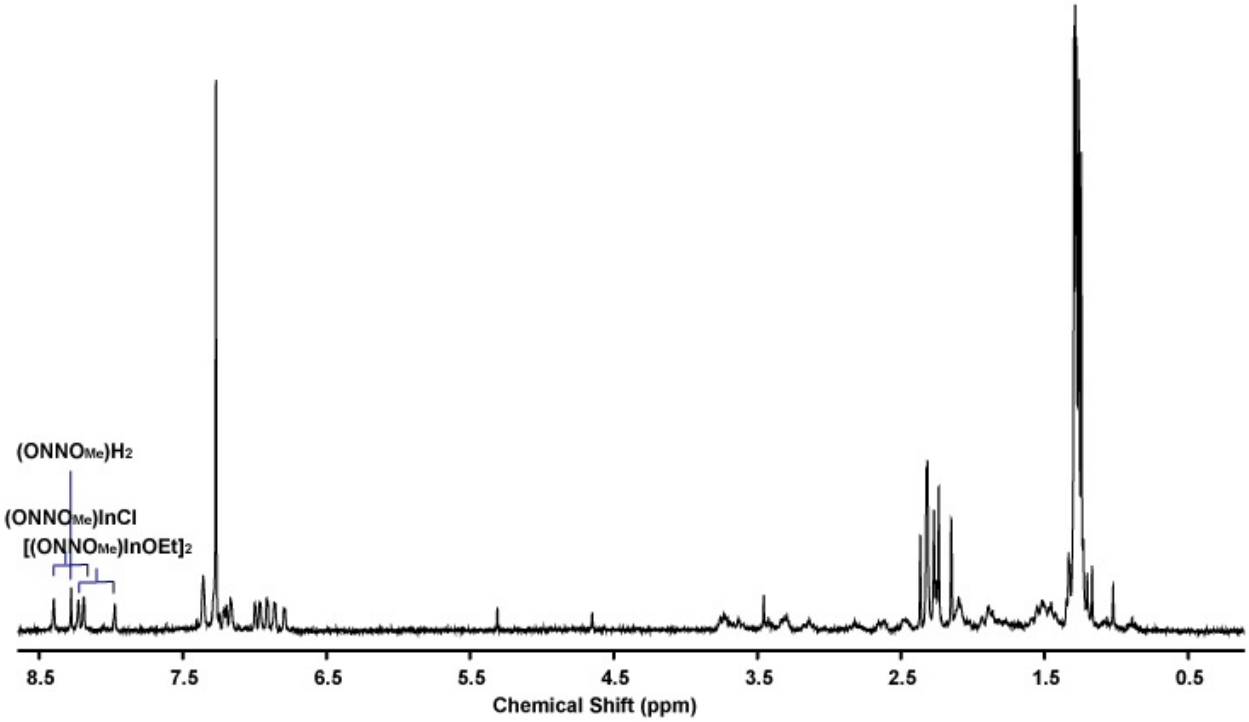


Figure S28. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of a one pot synthesis of (*R,R*)-**7** after 24 h when only 3.5 equiv of NaOEt was used

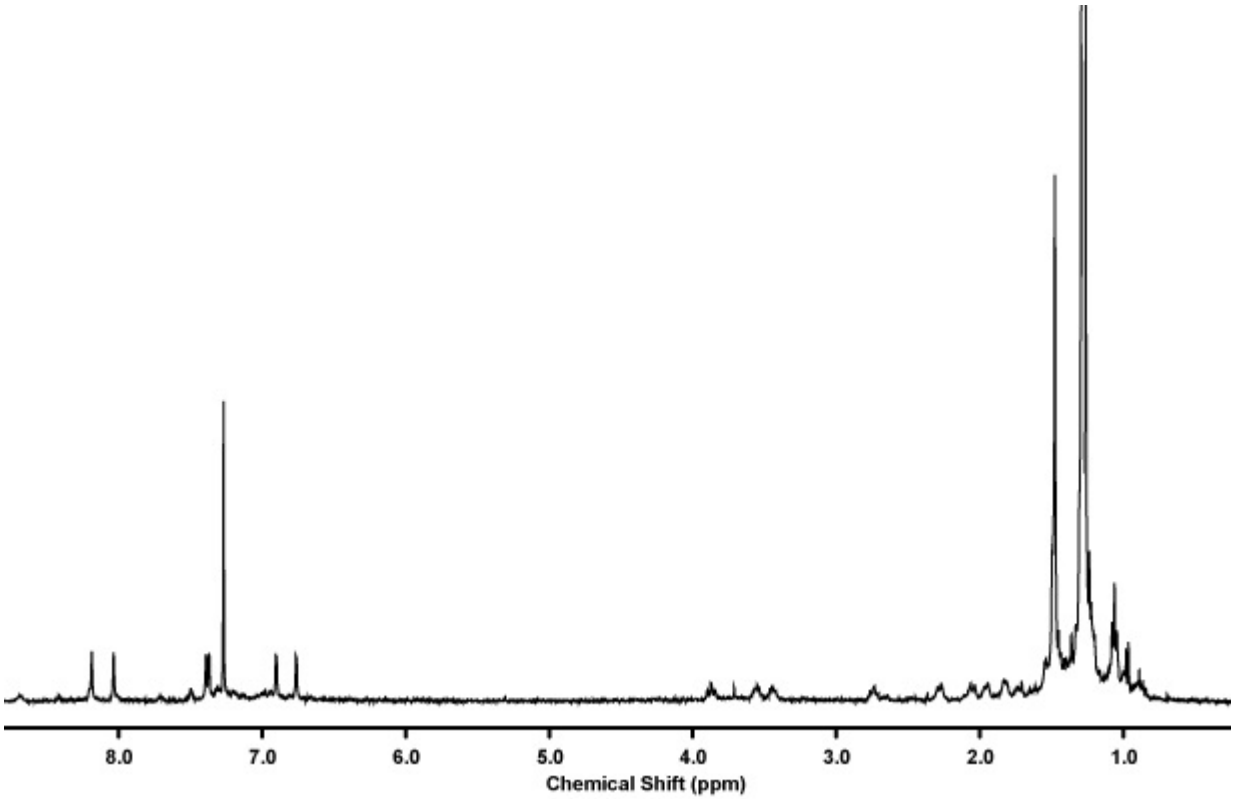


Figure S29. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the reaction between (*R,R*)-**6** and pyridine

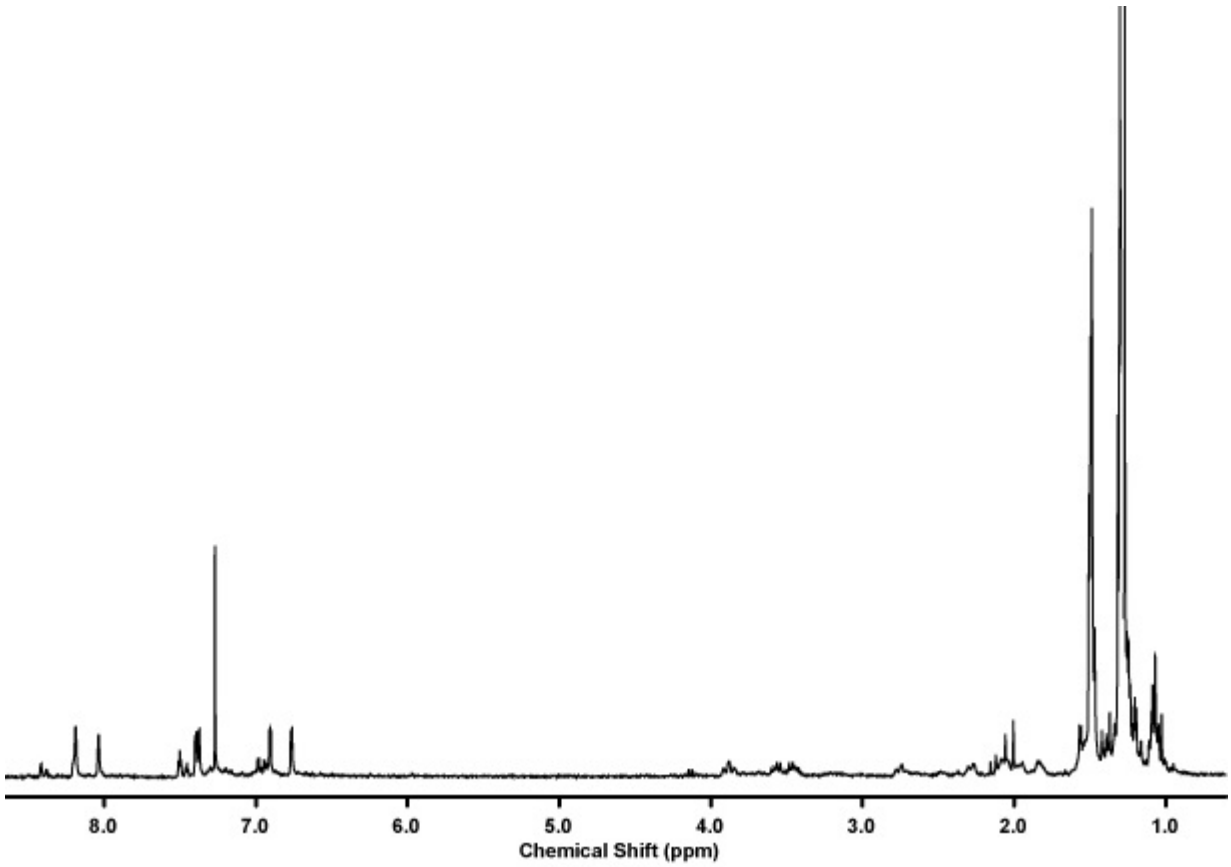


Figure S30. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the reaction between (*R,R*)-**6** and ethyl acetate

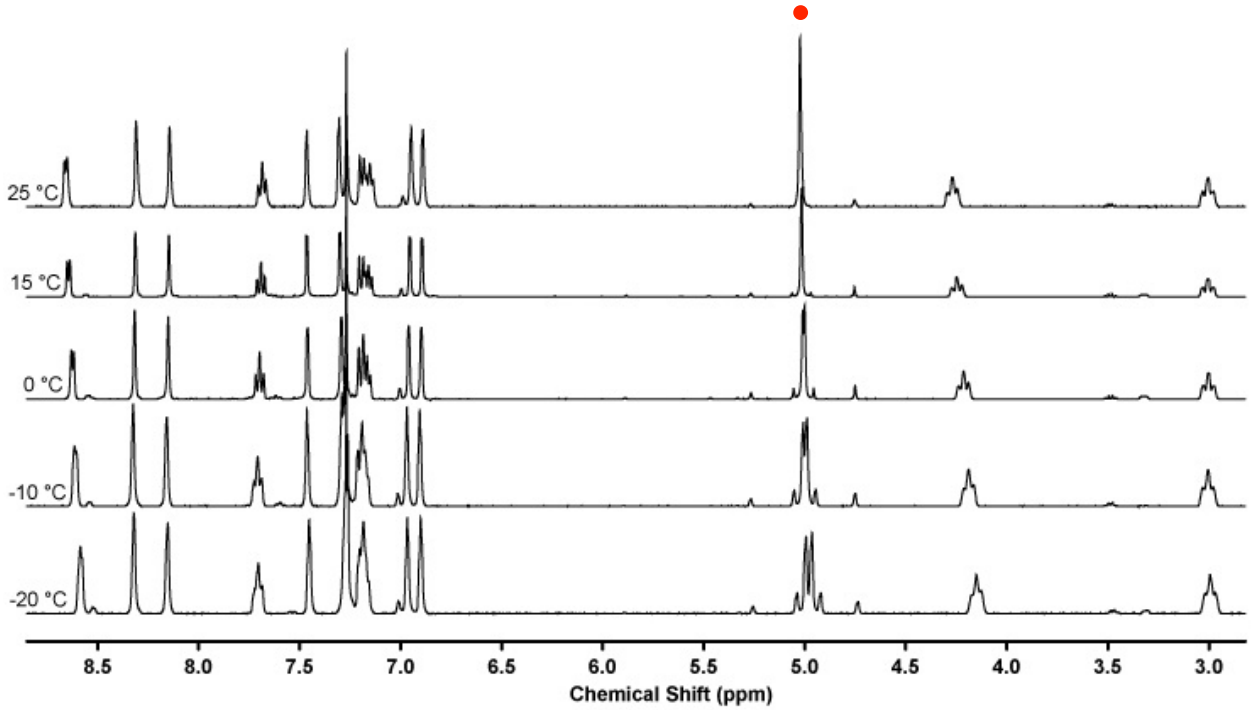
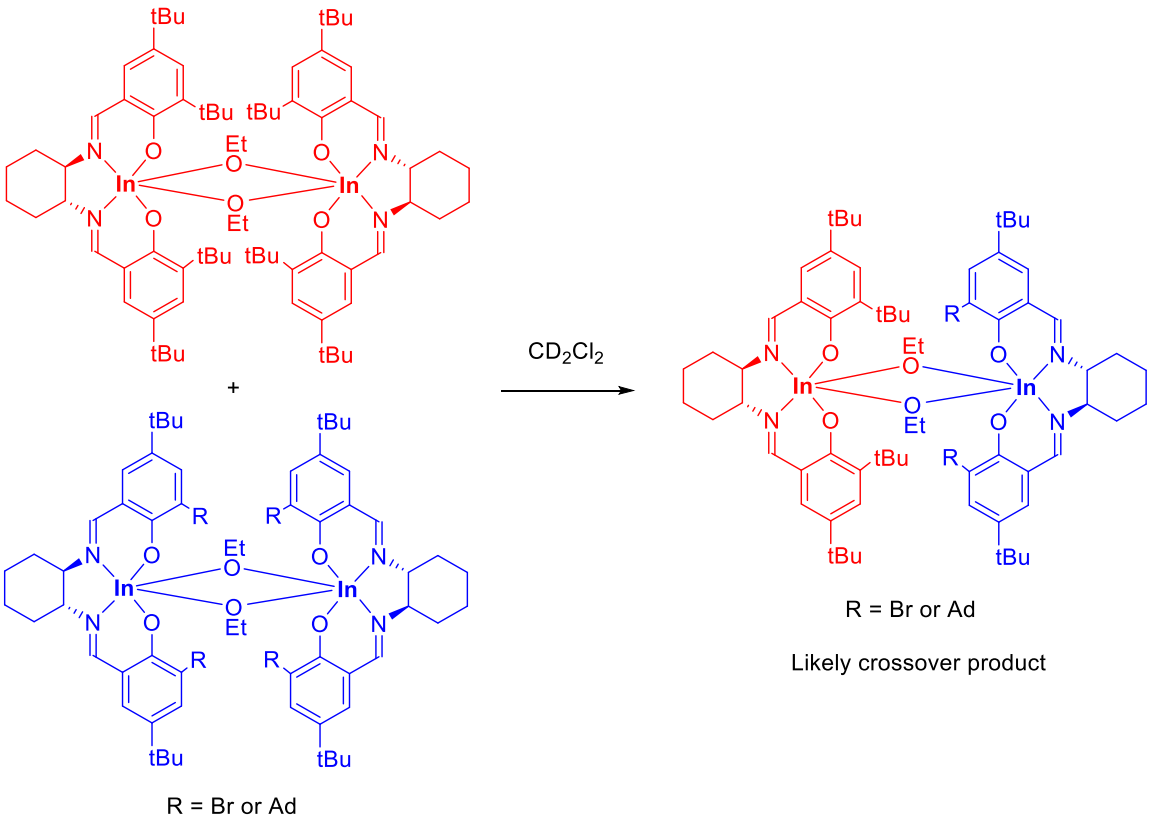


Figure S31. ^{1}H NMR spectra of *(R,R)*-**11** in $CDCl_3$ at temperatures from −20 °C to 25 °C. The methylene resonance of the alkoxide is labelled with (●).



Scheme S1. Crossover experiment of *(R,R)*-**6** with (*R,R*)-**8** or (*R,R*)-**10**

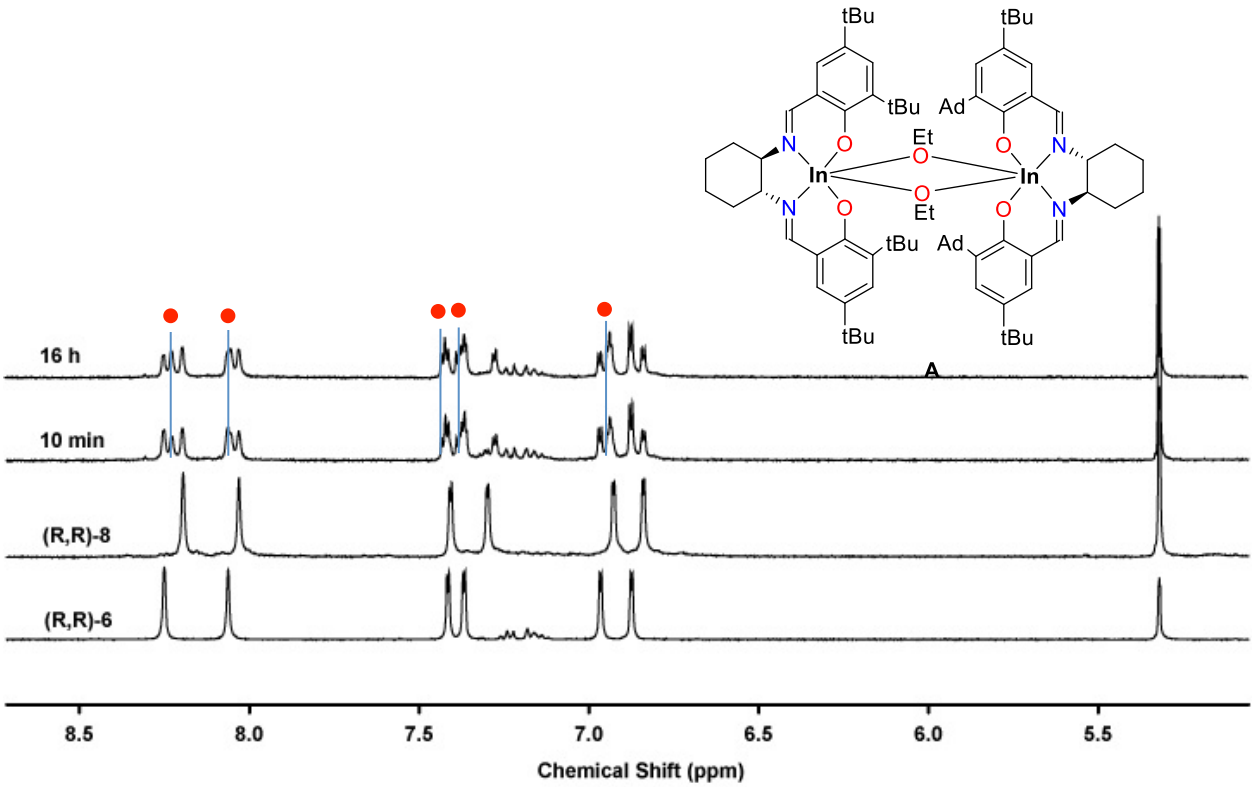


Figure S32. Crossover reaction between *(R,R)*-**6** and *(R,R)*-**8** at in CD_2Cl_2 at 25 °C. The resonances for the likely crossover product (**A**) are labelled with (●)

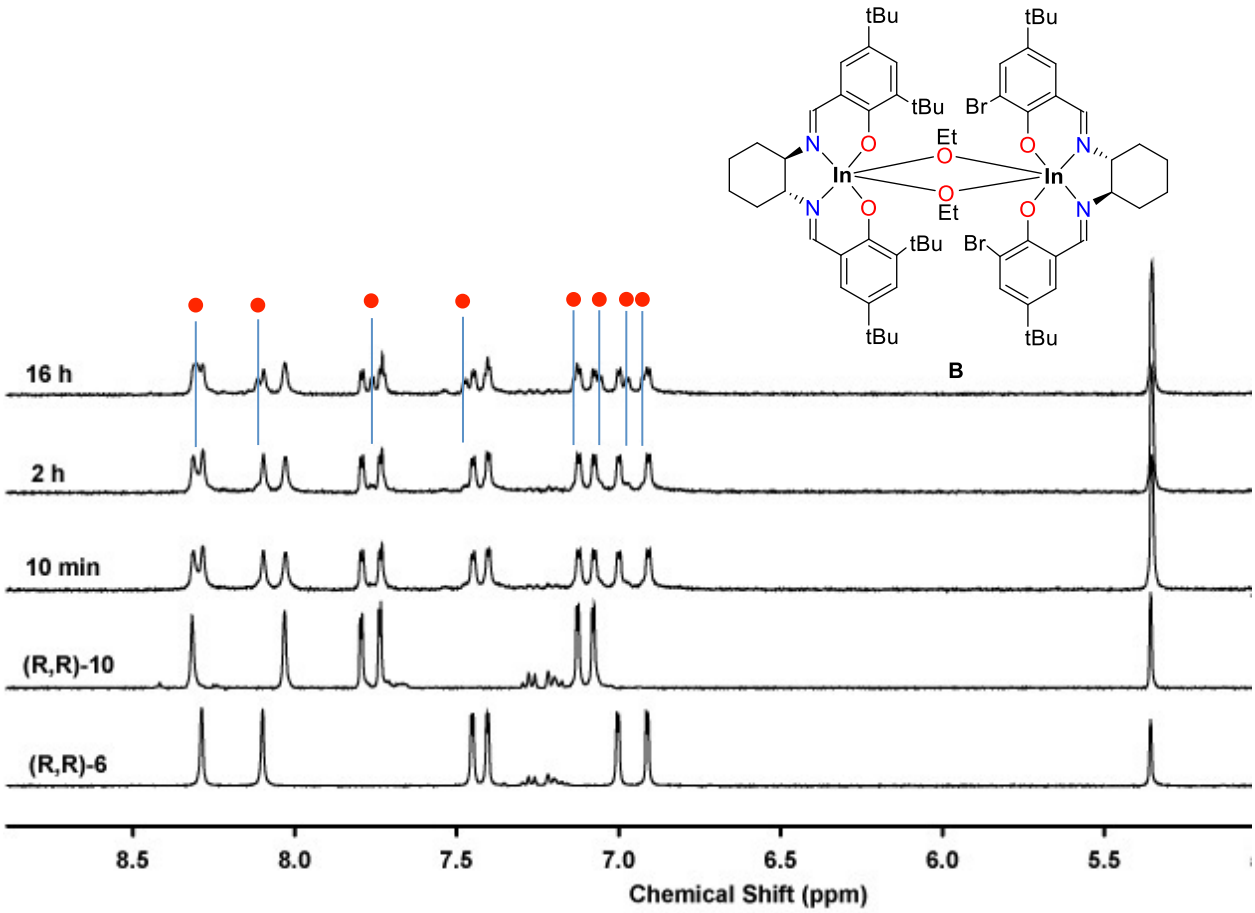


Figure S33. Crossover reaction between *(R,R)*-**6** and *(R,R)*-**10** at in CD_2Cl_2 at 25 °C. The resonances for the likely crossover product (**B**) are labelled with (●)

C. Analysis of polymers

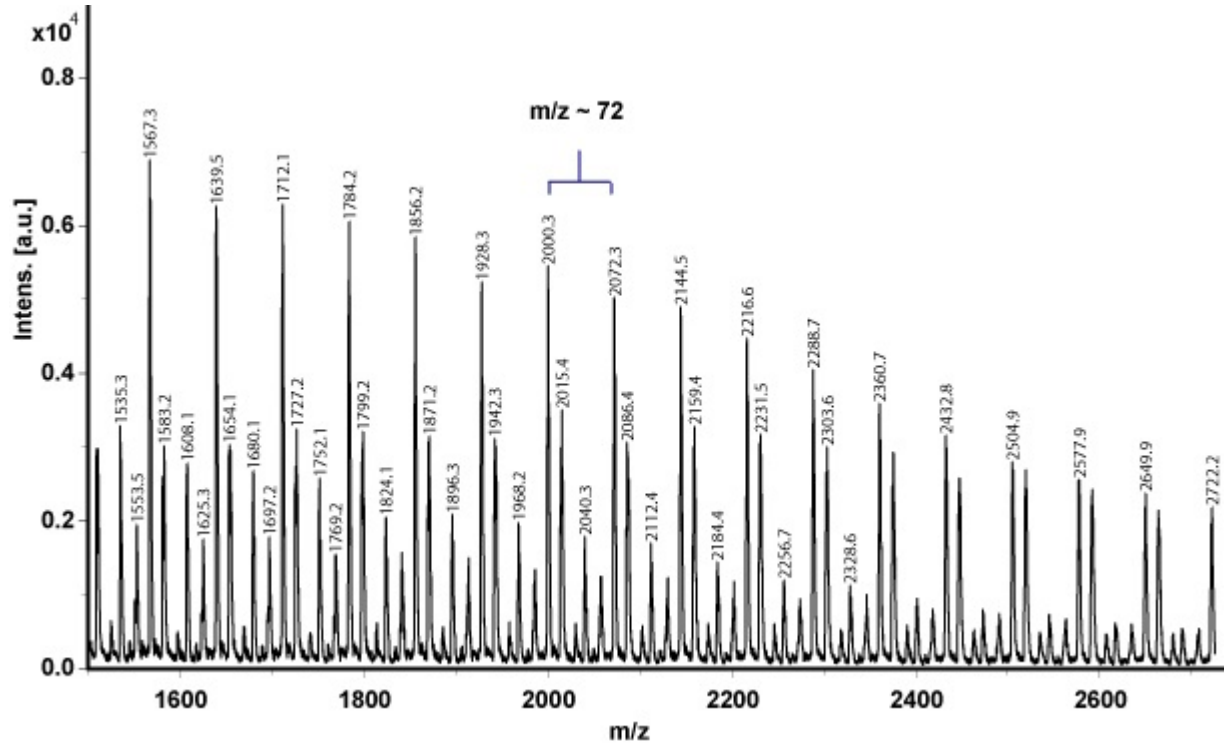


Figure S34. MALDI-TOF mass spectrum of a PLA oligomer grown with (*R,R*)-**6**.

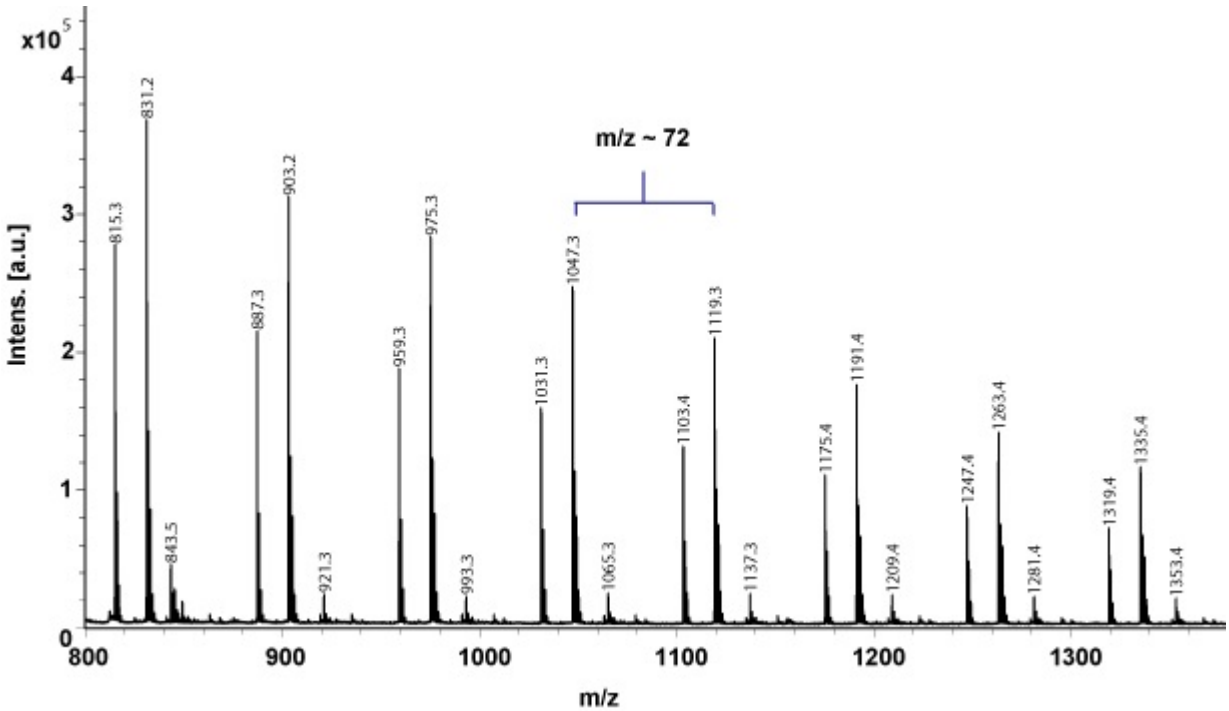


Figure S35. MALDI-TOF mass spectrum of a PLA oligomer grown with *(R,R)*-**11**.

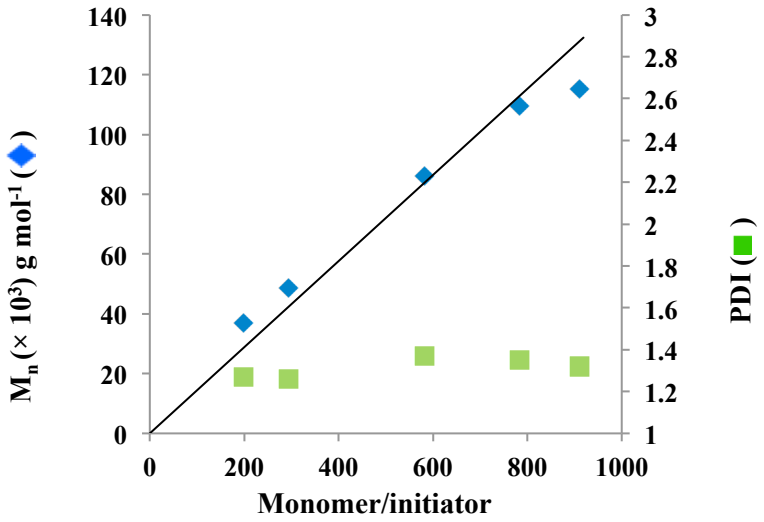


Figure S36. Plot of observed PLA M_n (◆) and molecular weight distribution (■) as functions of lactide:ethoxide in polymerizations with *(R,R)*-**11** (M_n = number averaged molecular weight, PDI = polydispersity index). The line indicates calculated M_n values based on the lactide:ethoxide ratio. All reactions were carried out at room temperature in CH_2Cl_2 and polymer samples obtained at >90% conversion.

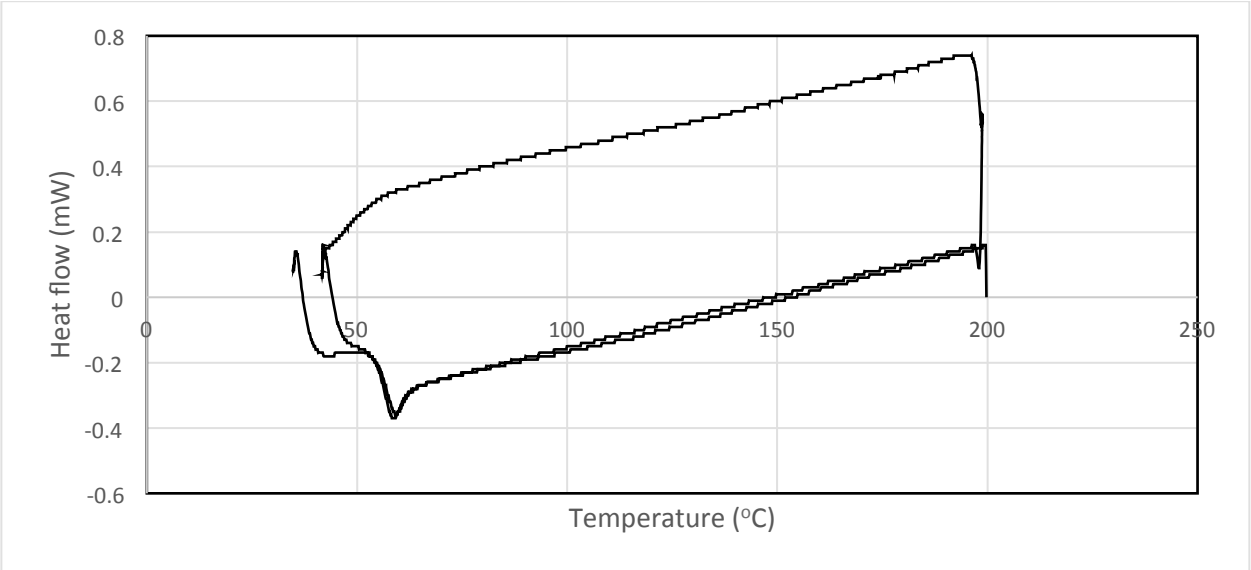


Figure S37. Heat flow vs. temperature curve for PLA formed from the polymerization of *rac*-LA with (*R,R*)-**6** at a monomer:initiator ratio of 400 at 25 °C in CH_2Cl_2 (P_m = 0.77). The curve shows a glass transition temperature of 55 °C and no melting point.

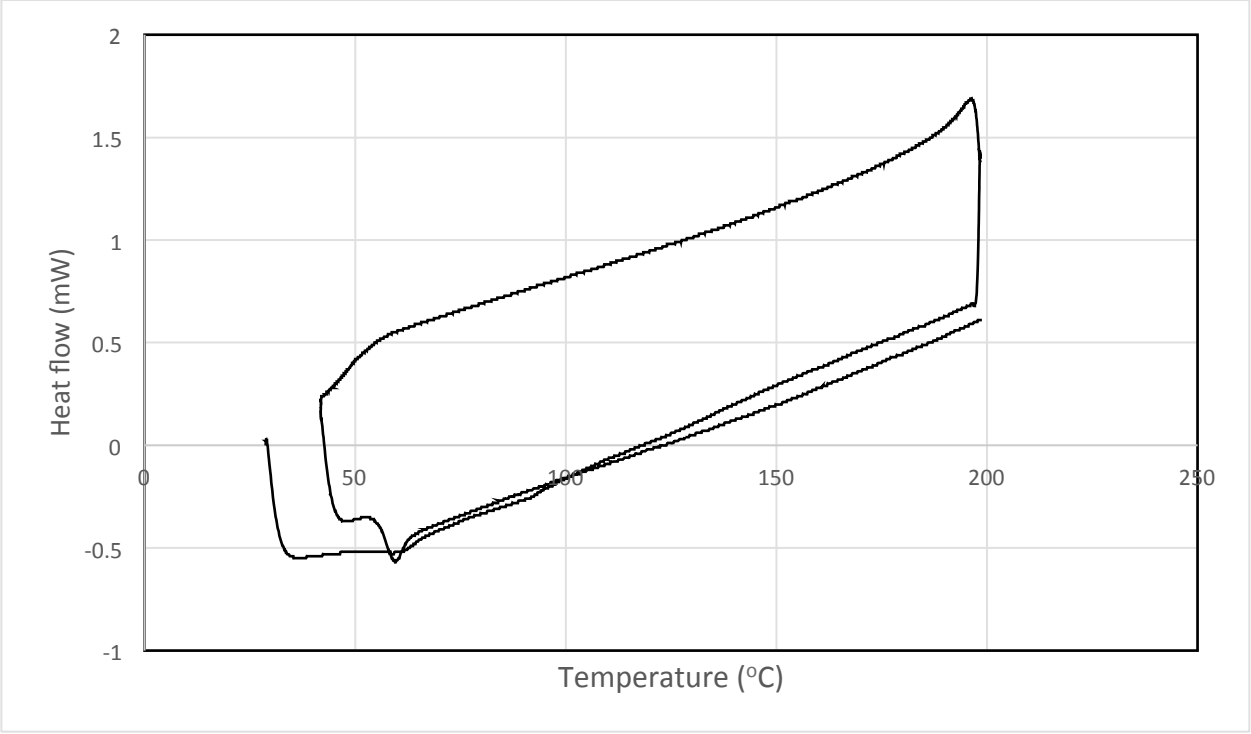


Figure S38. Heat flow vs. temperature curve for PLA formed polymerizing *rac*-LA with (*R,R*)-**8** at a monomer:initiator ratio of 400 at 25 °C in CH_2Cl_2 (P_m = 0.76). The curve shows a glass transition temperature of 55 °C and no melting point.

D. Depolymerization Experiments

Experimental

In the glovebox, a 200 mg sample of isolated, dry poly(lactic acid) (synthesized using (*R,R*)-**6**, Table S1, entry1) was dissolved in 3 mL of CH_2Cl_2. To this stirring solution, (*R,R*)-**6** (5 mg, 0.004 mmol) dissolved in 1 mL CH_2Cl_2 was added. ([(*R,R*)-**6**)] ~1 mM to replicate polymerization conditions.) A control experiment was setup simultaneously, without addition of (*R,R*)-**6**. The total volume was kept the same in both reactions. After 16 h the reactions were quenched with a drop of HCl (1.5 M in Et_2O) and the polymer samples were isolated through the addition of cold methanol. The polymers were dried under vacuum for 8 h prior to GPC analysis.

Table S1. GPC data for depolymerisation experiments

Entry	Description	M_{nGPC} ($\times 10^5$)[a]	PDI
1	Polymer prior to reaction	1.70	1.10
2	Polymer isolated after reaction with (*R,R*)-**6**	1.14	1.14
3	Polymer isolated from control experiment	1.79	1.09

[a]In THF (2 mg mL^{-1}) and molecular weights were determined by GPC-LLS (flow rate = 0.5 mL min^{-1}.) Universal calibration was carried out with polystyrene standards, laser light scattering detector data, and concentration detector. Each experiment is duplicated to ensure accuracy.

E. Characterization of complexes in the solid state

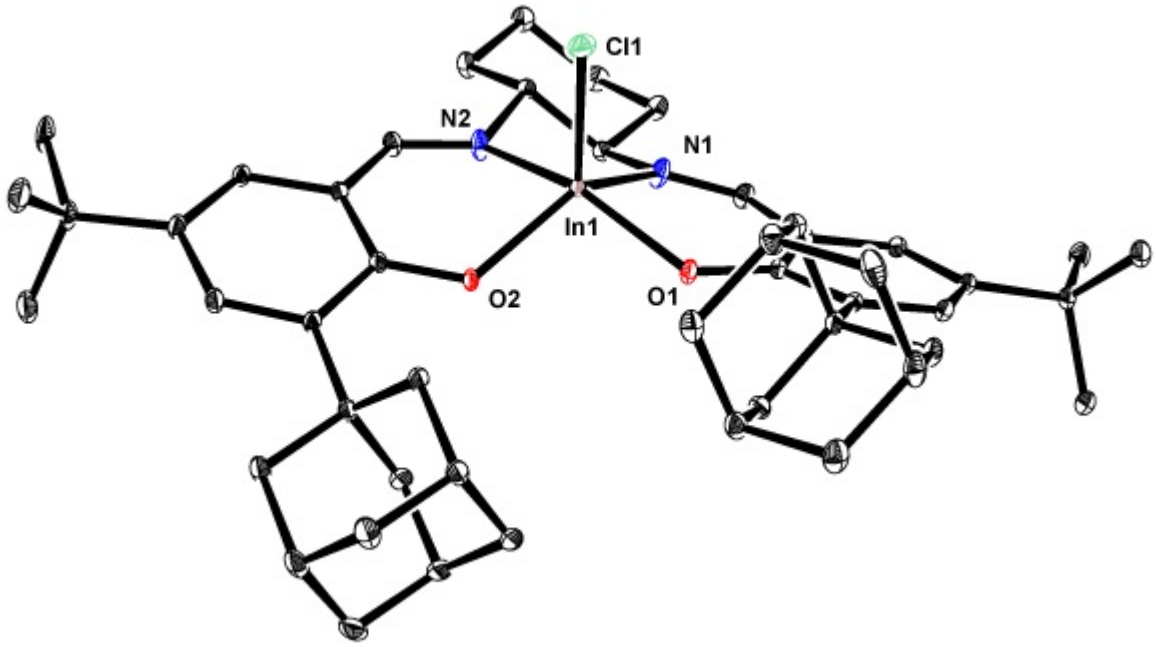


Figure S39. Molecular structures of ±-**3** depicted with ellipsoids at 50% probability (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°) for ±-**3**: In1-Cl1 2.3704(7), In1-N1 2.194(2), In1-O1 2.0661(16), In1-N2 2.194(2), In1-O2 2.0648(16), O2-In1-Cl1 112.57(6), O2-In1-N1 133.07(9), N1-In1-Cl1 100.29(7), O1-In1-N1 85.27(7), N2-In1-Cl1 112.57(6), O2-In1-N2 83.93(7), O2-In1-O1 95.88(7), O1-In1-N2 151.87(8).

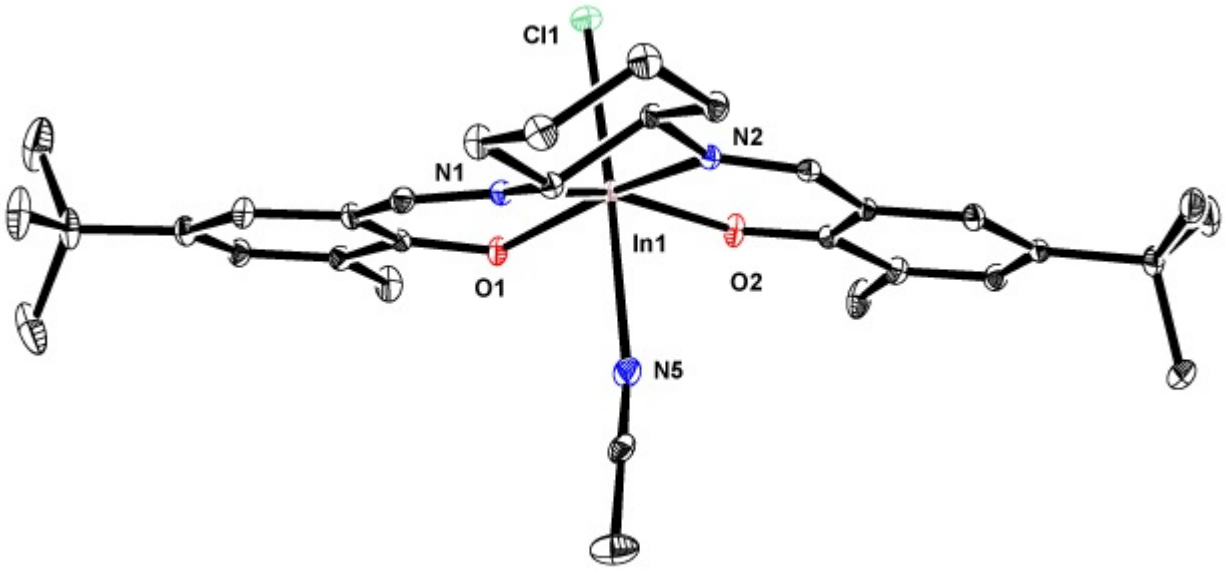


Figure S40. Molecular structures of *(R,R)*-**2**•CH_3CN depicted with ellipsoids at 50% probability (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°) for *(R,R)*-**2**: In1-Cl1 2.470(1), In1-N1 2.213(3), In1-O1 2.066(3), In1-N2 2.181(3), In1-O2 2.071(3), In1-N5 2.521(4), O1-In1-Cl1 95.41(8), O2-In1-N1 157.36(11), O2-In1-Cl1 100.68(8), O1-In1-N1 87.62(11), N1-In1-Cl1 98.59(8), O2-In1-N2 89.52(12), N2-In1-Cl1 96.93(9), O1-In1-N2 161.07(11), O2-In1-O1 102.24(11), N1-In1-N2 76.40(12), Cl1-In1-N5 175.44(9), O1-In1-N5 84.85(11).

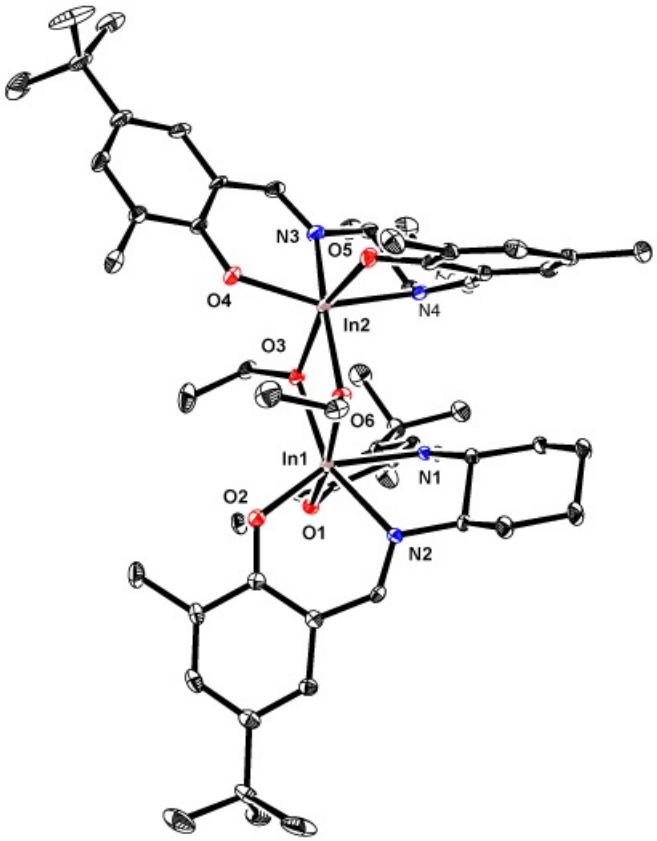


Figure S41. Molecular structures of *(R,R)*-**7** depicted with ellipsoids at 50% probability (H atoms and solvent molecules omitted for clarity). Selected bond lengths (Å) and angles (°) for *(R,R)*-**7**: In1-O1 2.105(3), In1-N1 2.250(3), In1-O2 2.092(3), In1-N2 2.291(3), In1-O3 2.147(3), O1-In1-O3 89.73(10), O1-In1-N1 83.33(11), O1-In1-O2 93.90(10), O3-In1-N1 92.75(10), O3-In1-O2 115.12(10), O2-In1-N1 152.03(10), N2-In1-O1.

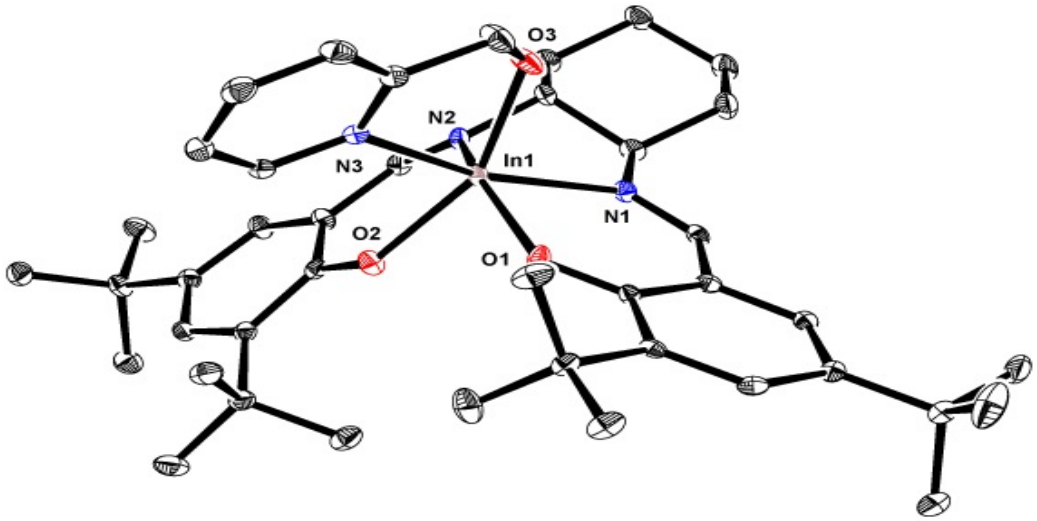


Figure S42. Molecular structures of *(R,R)*-**11** depicted with ellipsoids at 50% probability (H atoms and solvent molecules omitted for clarity). Selected bond lengths (Å) and angles (°) for ±-**11**: In1-O1 2.0957(16), In1-N1 2.2582(17), In1-O2 2.1244(15), In1-N2 2.2277(19), In1-O3 2.0855(15), In1-N3 2.2962(16), O1-In1-O3 105.32(6), O1-In1-N1 83.77(6), O1-In1-O2 88.61(6), O3-In1-N1 89.09(6), O3-In1-O2 155.18(6), O2-In1-N1 113.16(6), O1-In1-N2 72.62(6), N2-In1-N1 72.62(6), O3-In1-N2 94.54(6), O2-In1-N2 82.54(6), O1-In1-N3 90.13(6), O2-In1-N3 84.97(6).

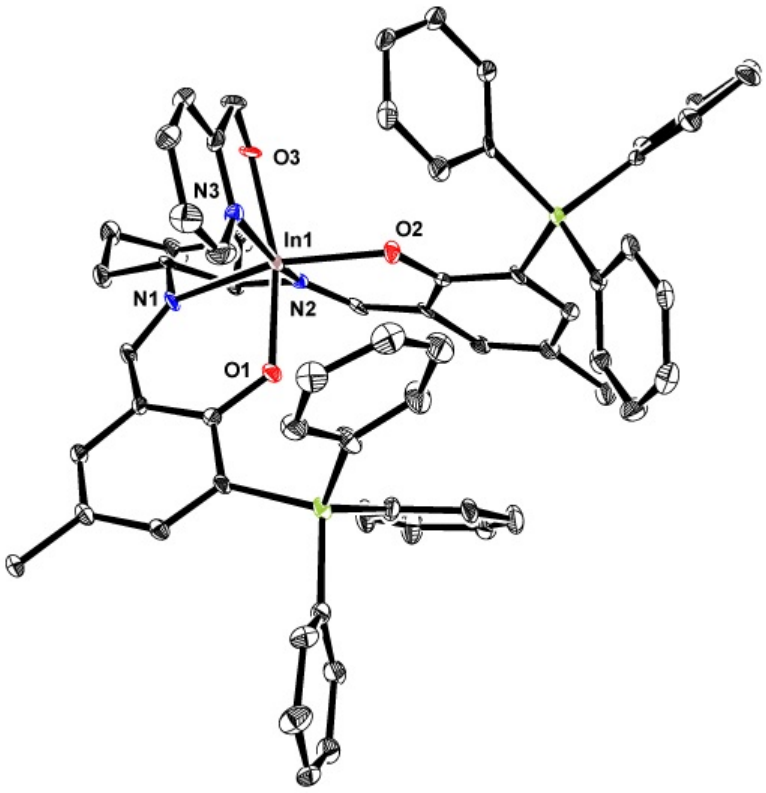


Figure S43. Molecular structures of *(R,R)*-**12** depicted with ellipsoids at 50% probability (H atoms and solvent molecules omitted for clarity). Selected bond lengths (Å) and angles (°) for *(R,R)*-**12**: In1-O1 2.106(6), In1-N1 2.234(6), In1-O2 2.091(5), In1-N2 2.233(7), In1-O3 2.084(5), In1-N3 2.242(7), O1-In1-O3 162.0(2), O1-In1-N1 81.6(2), O1-In1-O2 94.9(2), O3-In1-N1 91.6(2), O3-In1-O2 98.4(2), O2-In1-N1 153.6(2), O1-In1-N2 103.7(2), N2-In1-N1 71.9(2), O3-In1-N2 89.8(2), O2-In1-N2 83.8(2), O1-In1-N3 89.9(3), O2-In1-N3 102.7(2).

Table S2. Selected crystallographic parameters of X-ray structures

	(*R*,*R*)-2.CH_3CN	**(±)-3**	**(*R*,*R*)-7**	**(*R*,*R*)-11**	**(*R*,*R*)-12**
empirical formula	$C_{34}H_{46}N_4O_2InCl$	$C_{48}H_{64}N_2O_2InCl$	$C_{73}H_{103.50}N_{8.5}O_6In_2$	$C_{42}H_{58}N_3O_3In$	$C_{64}H_{58}N_3O_3Si_2In$
Fw	693.02	851.28	1425.78	767.73	1088.13
T (K)	90	90	90	90	90
a (Å)	36.780(4)	11.7715(13)	15.0752(9)	9.192(2)	12.019(5)
b (Å)	8.3688(8)	12.7462(15)	22.4148(14)	16.465(4)	20.066(9)
c (Å)	24.188(2)	15.4167(17)	23.2893(13)	25.858(6)	23.278(11)
α (deg)	90	105.421(2)	90	90	90
β (deg)	115.260(2)	96.436(2)	90	90	90
γ (deg)	90	103.430(2)	90	90	90
volume ($Å^3$)	6733.3(11)	2131.3(4)	7869.6(8)	3913.6(15)	5614(4)
Z	8	2	4	4	4
crystal system	monoclinic	triclinic	orthorhombic	orthorhombic	orthorhombic
space group	*C 2* (#5)	*P -1*(#2)	*P 21 21 21*	*P 21 21 21*	*P 21 21 21*
d_{calc} (g/cm^3)	1.367	1.327	1.203	1.303	1.287
μ (MoKα) (cm^{-1})	8.16	6.57	6.37	6.44	5.11
2θmax (deg)	60.2	60.3	60	58.6	51
absorption correction (T_{min}, T_{max})	0.8152, 0.8705	0.857, 0.900	0.518, 0.846	0.8356, 0.9256	0.7981, 0.8231
total no. of reflections	133172	141946	42732	48390	46482
no. of indep reflections (R_{int})	9766 (0.0322)	12569 (0.0310)	21833 (0.0437)	10690 (0.0511)	10262 (0.067)
residuals (refined on F^2, all data): R_1; wR_2	0.0228; 0.0487	0.0357; 0.0913	0.1120; 0.0670	0.0572: 0.0388	0.1458: 0.0647
GOF	1.026	1.392	1.02	1.023	0.722
no. observations [I > 2s(I)]	18669	12105	8453	9566	8759
residuals (refined on F^2): R_1[a]; wR_2[b]	0.0202;0.0473	0.0343;0.0908	0.1033; 0.0469	0.0550; 0.0307	0.1324; 0.0497

[a] $R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$; [b] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma \, w(F_o^2)^2]^{1/2}$.

F. Determination of polymer tacticity

Representative analysis of homonuclear decoupled $^{1}H\{^{1}H\}$ NMR spectra to determine tacticity

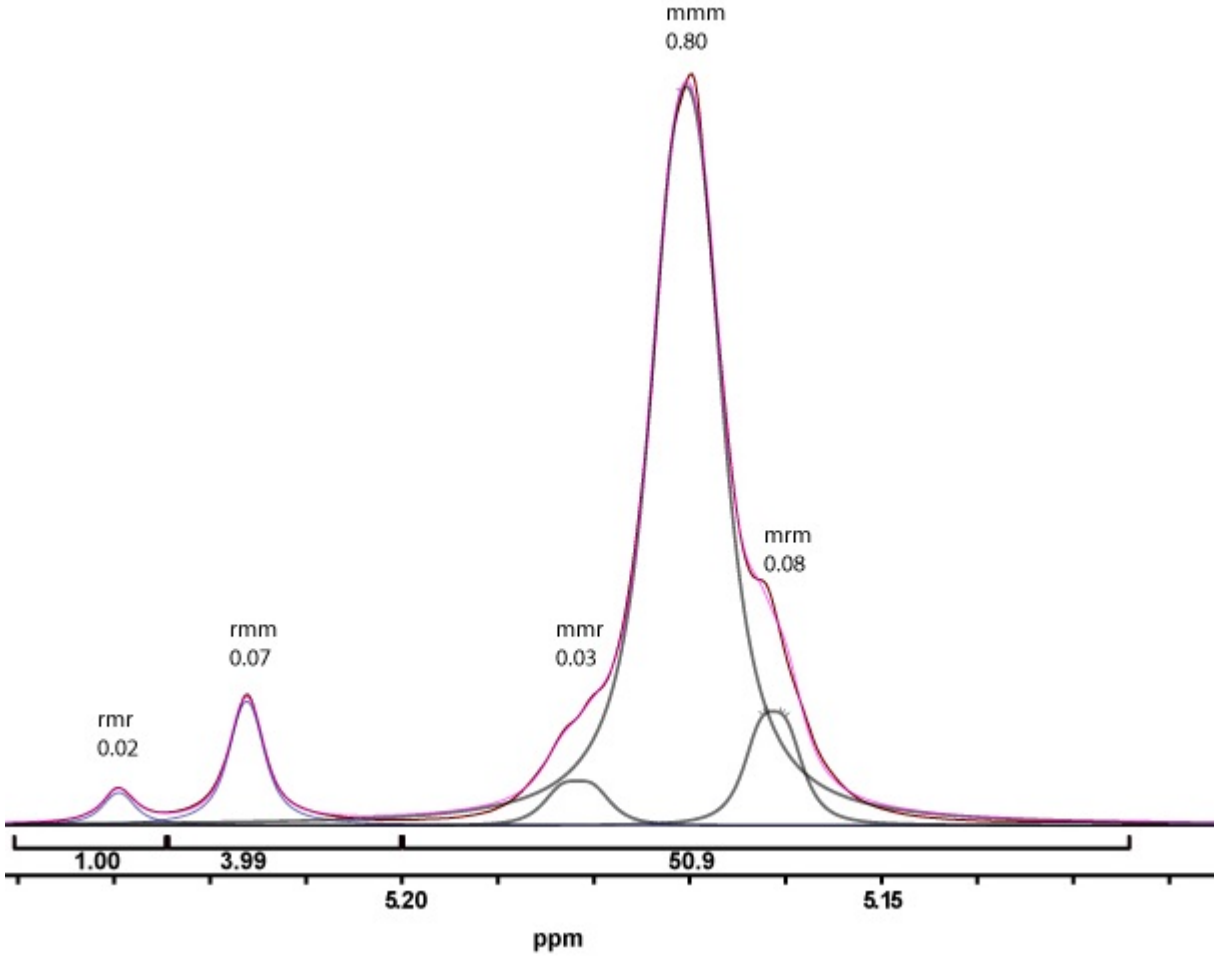


Figure S44. $^{1}H\{H\}$ NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of the methine region of PLA generated with (*R,R*)-**6** (Table 2, entry 1 in publication)

1. Analysis A.[1]

Equations used:

$[mmm] = (P_m)^2 + P_r P_m/2$

$[mmr] = P_r P_m/2$

$[rmm]^* = P_r P_m/2$

$[rmr]^* = (P_r)^2/2$

$[mrm] = ((P_r)^2 + P_r P_m)/2$

$P_r = \sqrt{(2/1.00+3.99+50.9)} = 0.189$

$P_m = 2\ (3.99/55.89) / 0.189 = 0.76$

*Effectively only these two equations are used in the calculations as the other peaks cannot be accurately integrated.

2. Analysis B.[2]

$[mmm] = P_m(P_m+1)/2$

$[mmr] = P_m(1 - P_m)/2$

$[rmm] = P_m(1 - P_m)/2$

$[rmr] = (1 - P_m)^2/2$

$[mrm] = (1 - P_m)/2$

Peak	Integration	P_m
rmr	0.02	0.80
rmm	0.07	0.83
mmr	0.03	0.93
mmm	0.80	0.86
mrm	0.08	0.84
Average		**0.85**

All five peaks are used in the calculations. Spectral deconvolution is used in the integration of all 5 peaks. All deconvolutions were computed using the NMR processing software MesRenoVa 10.0.1 with generalized Lorentzian line fitting. Efforts were made to minimize the residual error ~1%.

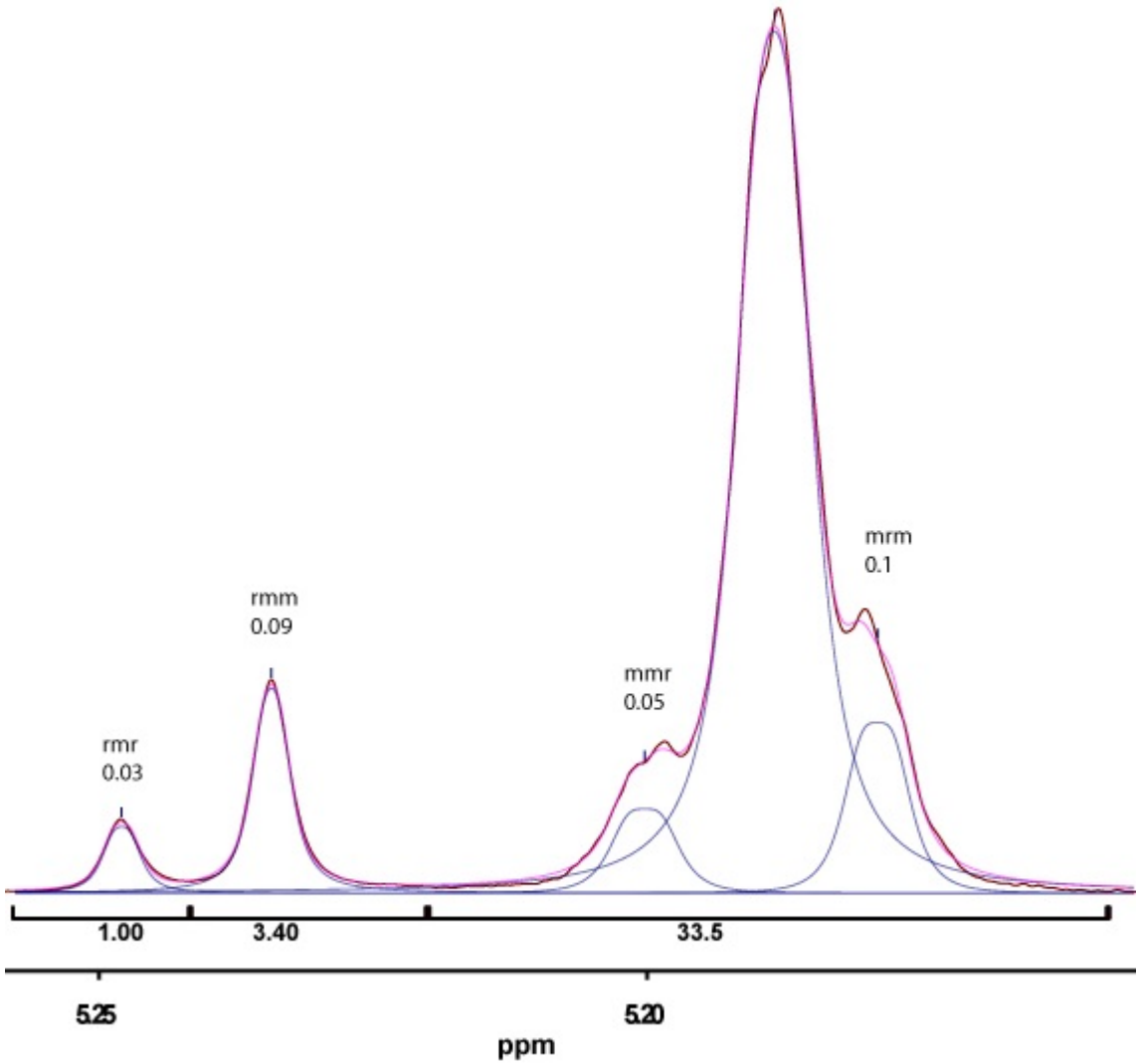


Figure S45. $^{1}H\{H\}$ NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of the methine region of PLA generated with *(R,R)*-**8** (Table 2, entry 3 in publication).

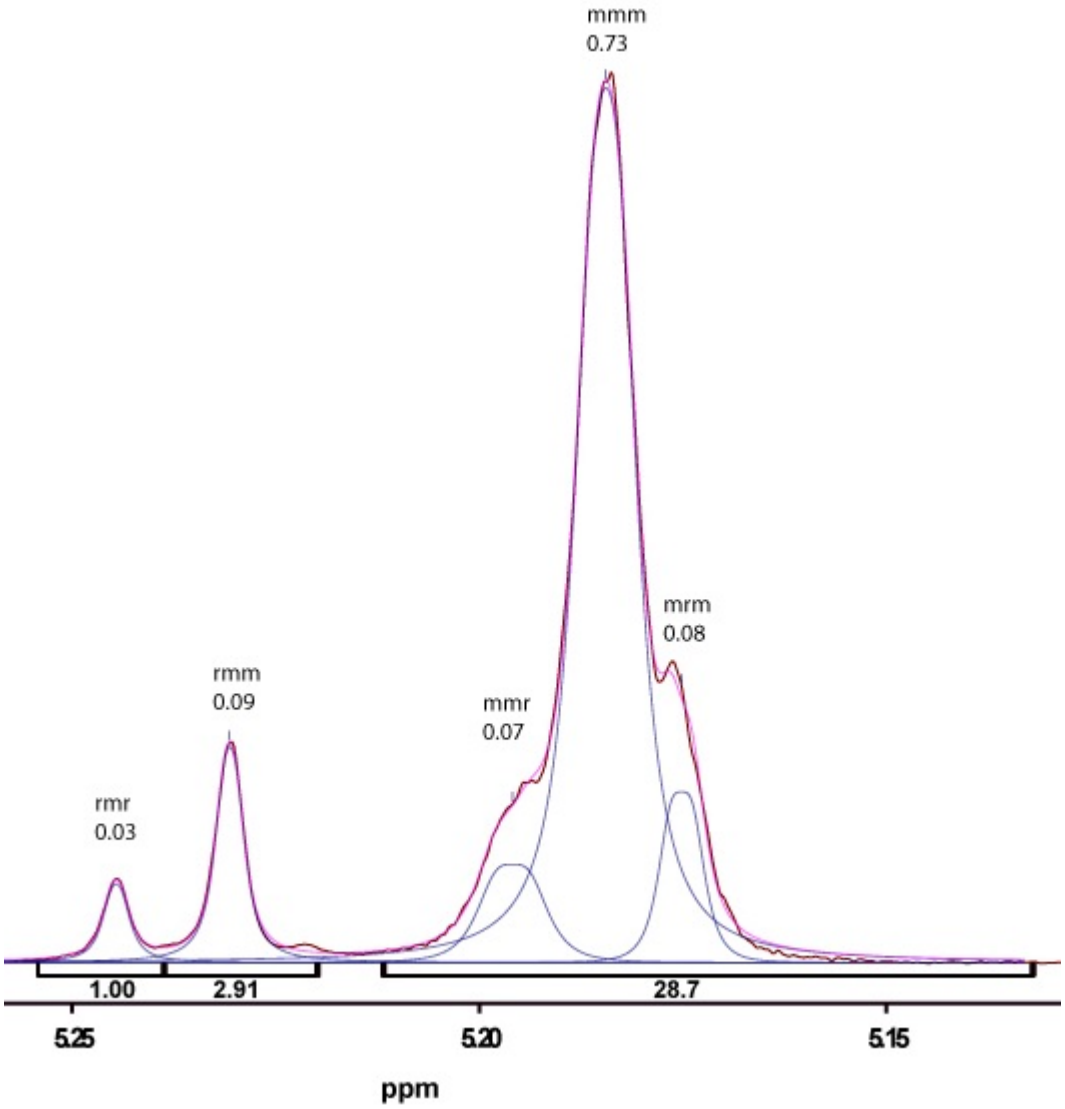


Figure S46. $^{1}H\{H\}$ NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of the methine region of PLA generated with *(R,R)*-**9** (Table 2, entry 6 in publication).

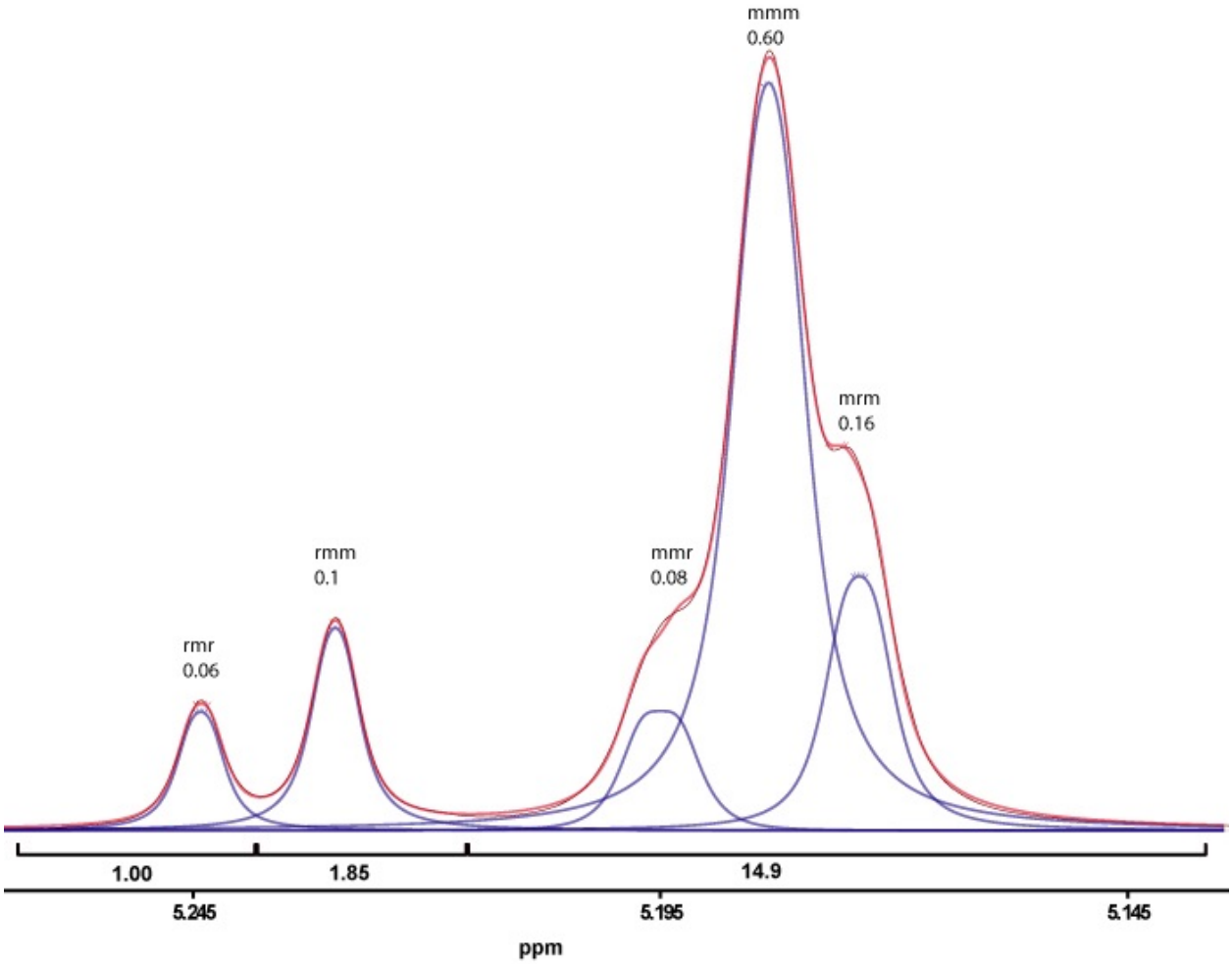


Figure S47. $^{1}H\{H\}$ NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of the methine region of PLA generated with *(R,R)*-**7** (Table 2, entry 10 in publication).

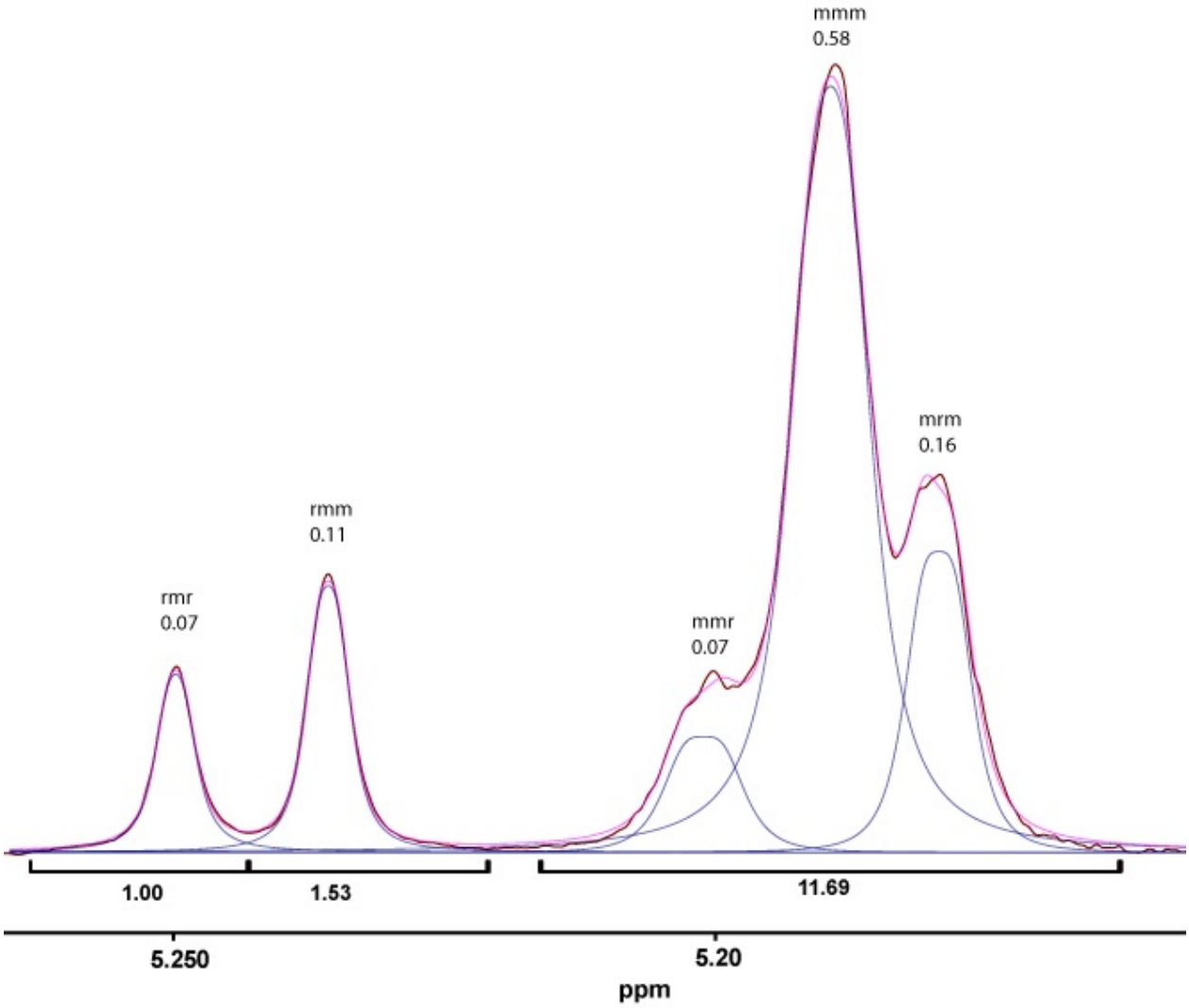


Figure S48. $^{1}H\{H\}$ NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of the methine region of PLA generated with *(R,R)*-**10** (Table 2, entry 8 in publication).

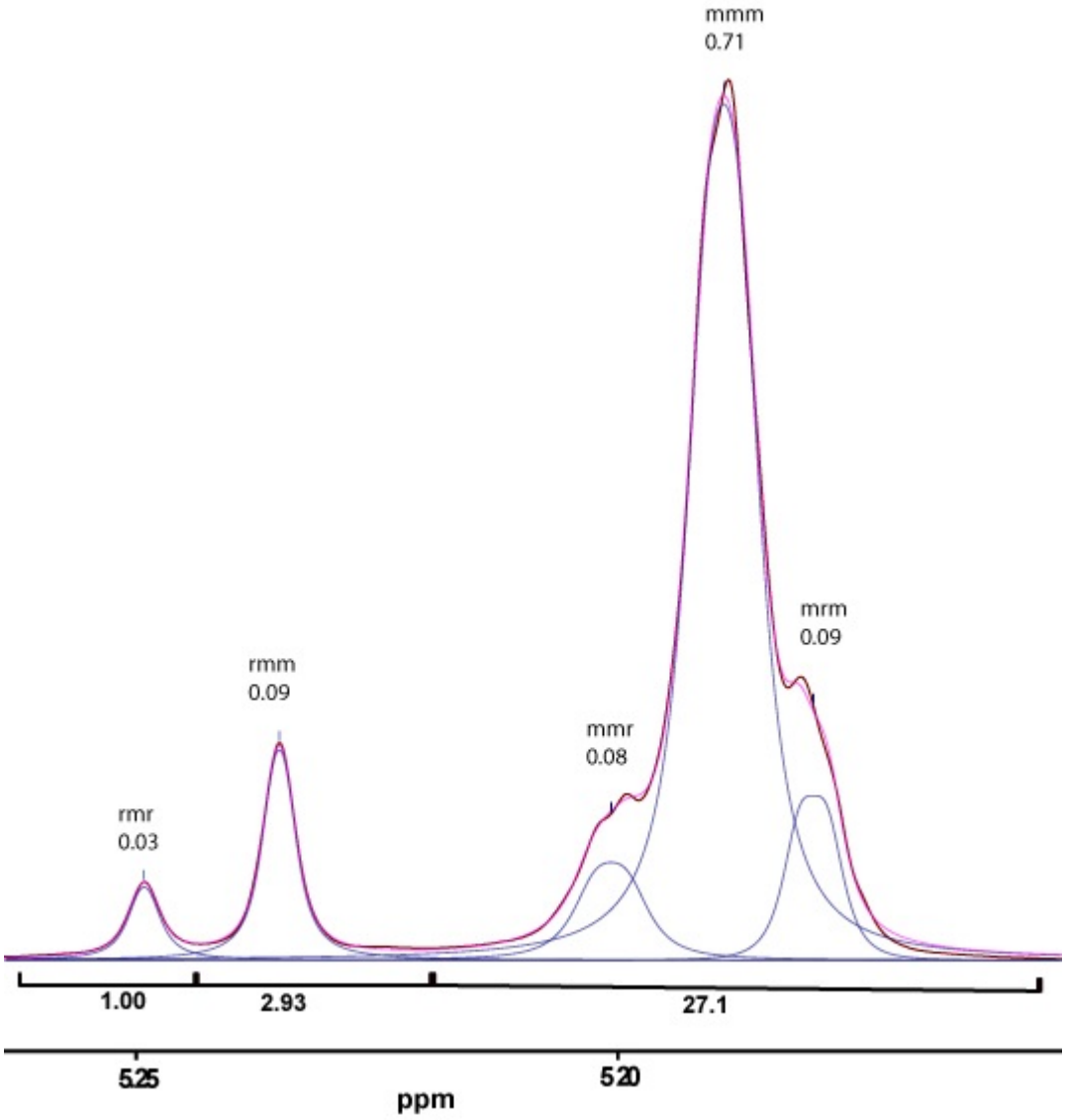


Figure S49. $^{1}H\{H\}$ NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of the methine region of PLA generated with *(R,R)*-**11** (Table 2, entry 11 in publication).

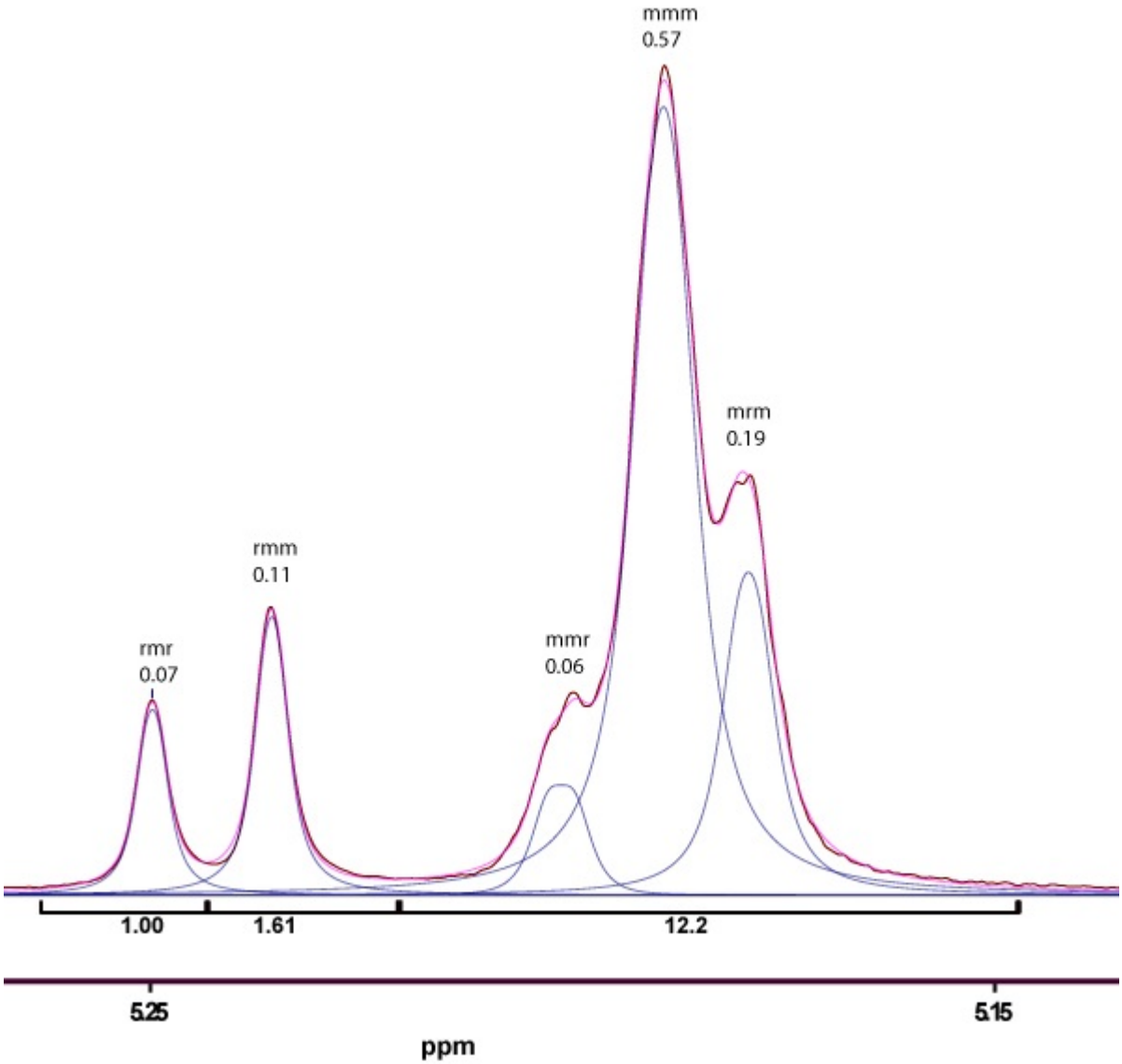


Figure S50. $^{1}H\{H\}$ NMR spectrum ($CDCl_3$, 25 °C, 600 MHz) of the methine region of PLA generated with *(R,R)*-**13** (Table 2, entry 13 in publication).

G. PGSE and hydrodynamic radii

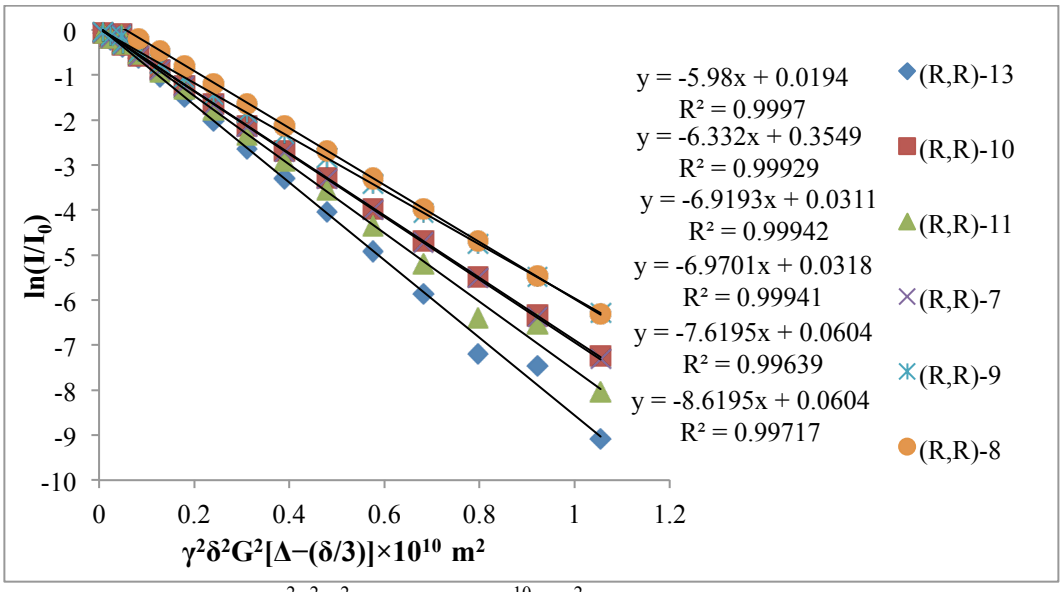


Figure S51. Plot of $\ln(I/I_0)$ vs. $\gamma^2\delta^2G^2[\Delta-(\delta/3)]\times10^{-10}$ (m^2 s) from PGSE experiment for compounds *(R,R)*-**7-11, 13** in CD_2Cl_2 at 25 °C. Intensities of four well separated peaks were individually plotted to obtain the above trend lines. The slopes from the trend line for each peak were averaged to obtain the translational diffusion coefficient (D_t). I = observed spin echo intensity, I_0 = intensity in the absence of a gradient, G = gradient strength, γ = gyromagnetic ratio, δ = length of gradient pulse, Δ = delay between gradient midpoints.

Procedure for calculating the diffusion coefficient and radii of a compound from PGSE NMR and X-ray data:

The translational diffusion coefficients (D_t) were calculated from the plots of $\ln(I/I_0)$ vs. $\gamma^2\delta^2G^2[\Delta-(\delta/3)]\times10^{-10}$ (m^2 s) as indicated above. A modified Stokes-Einstein equation (1) was used to calculate the $c^{sa}r_H^{sa}$ value.[3] Equation **2** was used to determine f_s. A plot of c^{sa} r_H^{sa} vs. r_H^{sa} based on equation **3** reported by Chen *et al.* was used to r_H^{sa}.[4]

$$c^{sa}r_H^{sa} = \frac{D_t^{st}c^{st}f_s^{st}r_H^{st}}{D_t^{sa}f_s^{sa}} \quad \textbf{(1)}$$

D_t^{st} = translational diffusion coefficient of internal standard (TMSS, $D_t^{st} \approx 14.2 \times 10^{-10}$ m^2 s^{-1}, CD_2Cl_2, 25 °C)
c^{st} = internal standard size correction factor (TMSS, $c^{st} = 5.1$)
f_s^{st} = internal standard size and shape correction factor (TMSS, $f_s^{st} = 1$)
r_H^{st} = internal standard hydrodynamic radius (TMSS, 4.51 Å)
D_t^{sa} = translational diffusion coefficient of sample (CD_2Cl_2, 25 °C)
c^{sa} = sample size correction factor
f_s^{sa} = sample size and shape correction factor calculated from eq (2)
r_H^{sa} = sample hydrodynamic radius

$$f_s = \frac{\sqrt{1-\left(\frac{b}{a}\right)^2}}{\left(\frac{b}{a}\right)^{\frac{2}{3}} \ln \frac{1+\sqrt{1-\left(\frac{b}{a}\right)^2}}{\left(\frac{b}{a}\right)}} \quad \textbf{(2)}$$

a = major semiaxes of a prolate ellipsoid estimated from X-ray crystal structure
b = minor semiaxes of a prolate ellipsoid estimated from X-ray crystal structure

$$cr_H = \frac{6r_H}{1+0.695\left(\frac{r_{solv}}{r_H}\right)^{2.234}} \quad \textbf{(3)}$$

r_{solv} = hydrodynamic radius of the solvent (CH_2Cl_2 = 2.49 Å)
r_H = hydrodynamic radius of sample

H. In situ polymerization studies

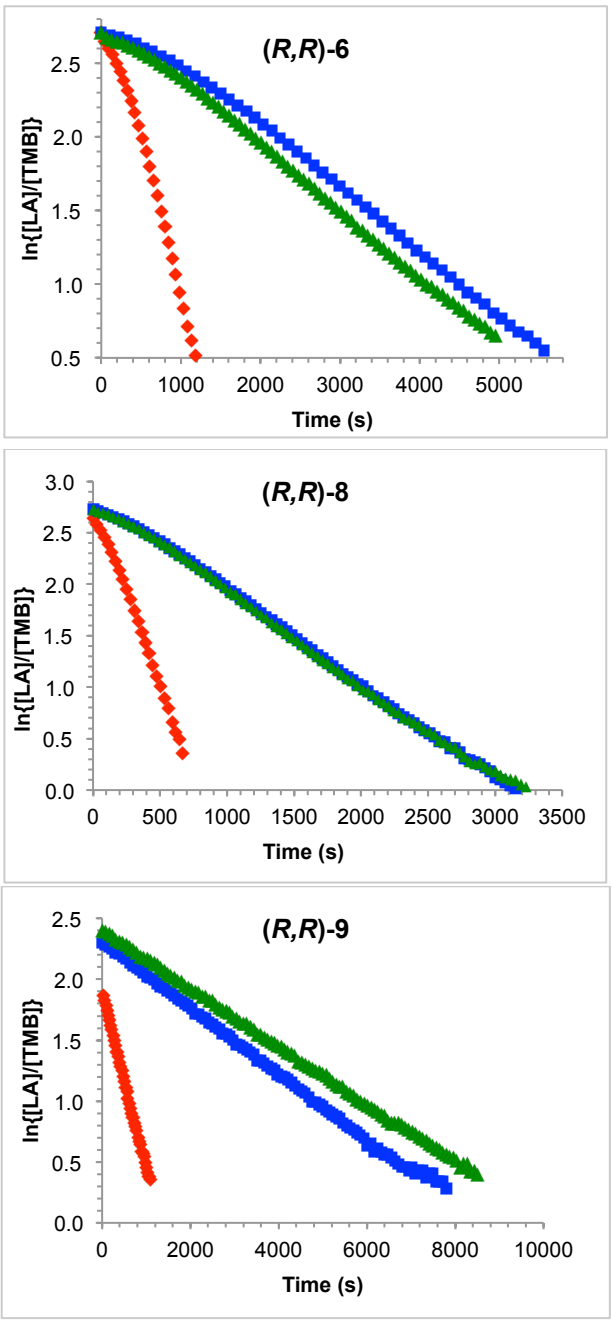


Figure S52. Plots for the ROP of 200 equiv L-LA (u), D-LA (n) and *rac*-LA (▲) vs. time for (*R,R*)-**6** (a, top) (*R,R*)-**8** (b, middle) and (*R,R*)-**9** (c, bottom). All reactions were carried out in CD_2Cl_2 at 25 °C and followed to 90% conversion. [Catalyst] = 0.0011 M, [LA] = 0.45 M. k_{obs} was determined from the slope of the plots of ln([LA]/[TMB]) vs. time (TMB = 1,3,5-trimethoxybenzene).

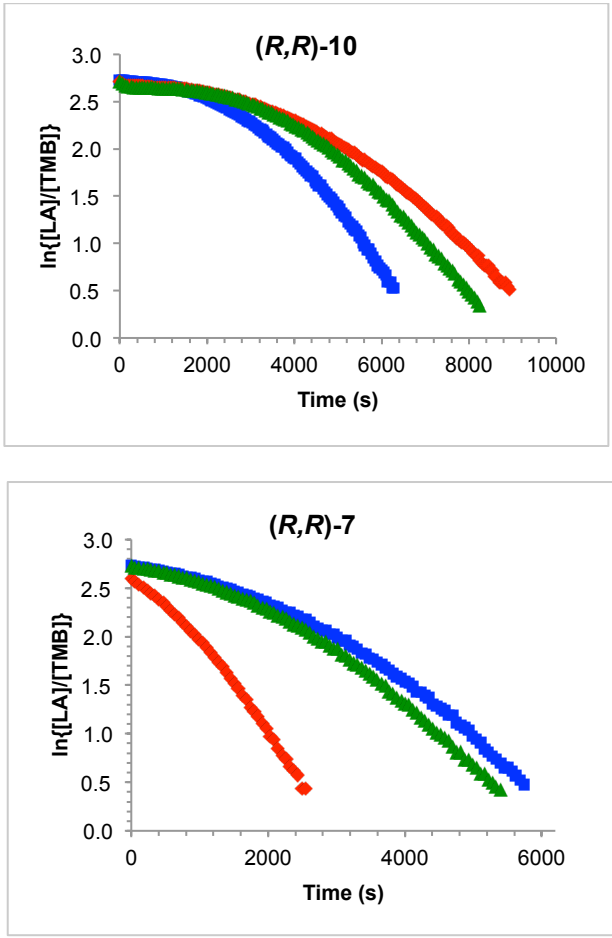


Figure S53. Plots for the ROP of 200 equiv L-LA (◆), D-LA (■) and *rac*-LA (▲) vs. time for $[(ONNO_{Br})InOEt]_2$ (*R,R*)-**10** (a, top) and $[(ONNO_{Me})InOEt]_2$ (*R,R*)-**7** (b, bottom). All reactions were carried out in CD_2Cl_2 at 25 °C and followed to 90% conversion by ^1H NMR spectroscopy. [Catalyst] = 0.0011 M, [LA] = 0.45 M. The value of k_{obs} was determined from the slope of the plots of ln([LA]/[TMB]) vs. time (TMB = 1,3,5-trimethoxybenzene).

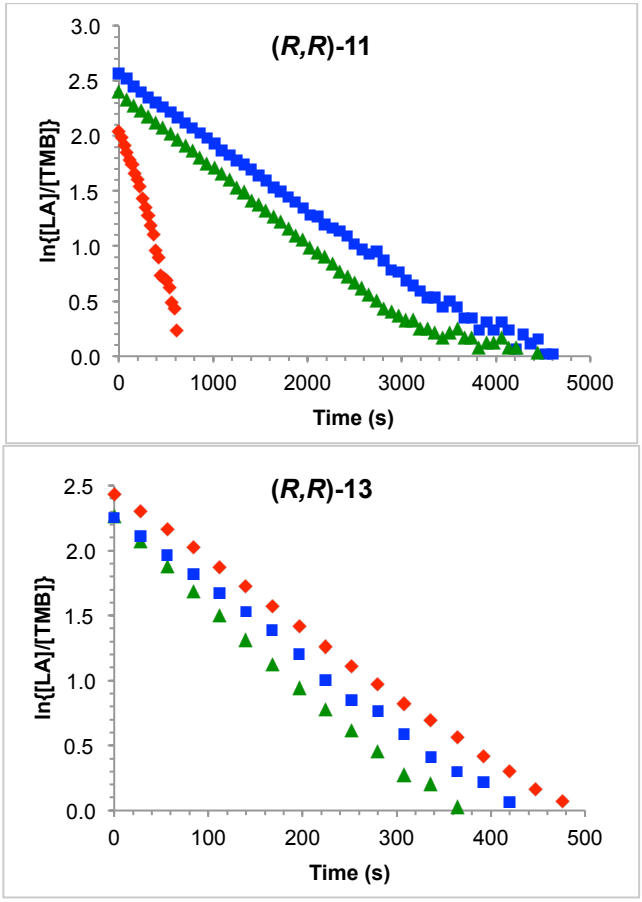


Figure S54. Plots for the ROP of 200 equiv L-LA (◆), D-LA (■) and *rac*-LA (▲) vs. time for ($ONNO_{tBu}$)$InOCH_2Pyr$ (*R,R*)-**11** (a, top) and ($ONNO_{Br}$)$InOCH_2Pyr$ (*R,R*)-**13** (b, bottom). All reactions were carried out in CD_2Cl_2 at 25 °C and followed to 90% conversion by ^1H NMR spectroscopy. [Catalyst] = 0.0011 M, [LA] = 0.45 M. The k_{obs} determined from the slope of the plots of ln([LA]/[TMB]) vs. time (TMB = 1,3,5-Trimethoxybenzene).

I. References

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