Electronic Supplementary Information for:

Salan ligands assembled around chiral bipyrrolidine: predetermination of chirality around octahedral Ti and Zr centres

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General

All experiments employing metal complexes were performed under an atmosphere of dry nitrogen in a nitrogen-filled glovebox. Ether was purified by reflux and distillation under dry argon atmosphere from Na/benzophenone. Pentane was washed with HNO_3/H_2SO_4 prior to distillation from Na/benzophenone/tetraglyme. Toluene was refluxed over Na and distilled. Titanium tetra(isopropoxide) and Zirconium tetra(*tert*-butoxide) were purchased from Aldrich. 2-(bromomethyl)-4,6-di-*tert*-butylphenol,[1] 2-(bromomethyl)-4,6-dichlorophenol,[2] and tetrabenzylzirconium[3] were prepared according to literature procedures. (*S,S*)-bipyrrolidine and (*R,R*)-bipyrrolidine were prepared according to a literature procedure,[4] in addition to some (*S,S*)-bipyrrolidine obtained as a gift from Prof. Alexandre Alexakis (Geneve). NMR data for the metal complexes were recorded on a Bruker AC-200 and AC-400 spectrometers and referenced to protio impurities in benzene-d_6 (δ 7.15) and to ^{13}C chemical shift of benzene (δ 128.70). The molecular weights of poly(1-hexene) were determined by gel permeation chromatography (GPC) using TSKgel GMHHR-M, TSKgel and G 4000 HHR columns set on a Jasco instrument equipped with a refractive index detector. Molecular weight determination was carried out relative to polystyrene standards using tetrahydrofuran (HPLC grade, distilled and filtered under vacuum prior to use) as the eluting solvent. X-ray diffraction measurements of (*S,S*)-Lig^{1}Zr(O-t-Bu)$_2$ were performed on a Nonius Kappa CCD diffractometer system, using MoKα (λ=0.7107 Å) radiation. The analyzed crystal grown from a cold pentane solution was embedded within a drop of viscous oil and freeze-cooled to *ca*. 110 K. The structure was solved by a combination of direct methods and Fourier techniques using SIR-97[5] software, and was refined by full-matrix least squares with SHELXL-97.[6] Elemental analyses were performed in the microanalytical laboratory in the Hebrew University of Jerusalem. CD spectra in diethyl ether were measured on an Aviv model 202 circular dichroism spectrometer.

(*S*,*S*)-Lig^{1}H$_2$. Et_3N (0.2 mL, 2 equiv) was added dropwise to a solution of (*S*,*S*)-bipyrrolidine (210 mg, 1.50 mmol) and 2-(bromomethyl)-4,6-di-*tert*-buthylphenol (920 mg, 3 mmol) in 50 mL of THF. The mixture was stirred for 24 h at RT, producing a white precipitate of $Et_3N{\cdot}HBr$, which was filtered off and extracted with cold THF. The filtrate was washed twice with water and dried under vacuum. The resulting solid was recrystallized from methanol, yielding 420 mg (49%) of Lig^{1}H$_2$. The (*R*,*R*) isomer was obtained analogously in 60% (520 mg) using 890 mg (2.90 mmol) of (*R*,*R*)- bipyrrolidine. MS (DCI): [MH^+] 576.9. $[\alpha]_D$ (for (*S*,*S*)-Lig^{1}H$_2$) = - 26º (8.1 mg/2 mL of CH_2Cl_2, *d* = 0.5). $[\alpha]_D$ (for (*R*,*R*)-Lig^{1}H$_2$) = + 26º (14.5 mg/10 mL of CH_2Cl_2, *d* = 1). Anal. calcd. for $C_{38}H_{60}N_2O_2$: C, 79.11; H, 10.48; N, 4.86. Found: C, 78.85; H, 10.62; N, 4.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 2.2 Hz, 2H), 6.80 (d, *J* = 2.2 Hz, 2H), 3.98 (d, *J* = 13.4 Hz, 2H, AB system), 2.57 (d, *J* = 13.4 Hz, 2H, AB system), 3.06 (m, 2H), 2.77 (m, 2H), 2.23 (m, 2H), 2.00 (m, 2H), 1.78 (m, 6H), 1.41 (s, 18H), 1.28 (s, 18H). ^{13}C NMR (100.66 MHz, $CDCl_3$) δ 154.3 (*C*), 140.9 (*C*), 135.7 (*C*), 123.1 (*C*H), 122.9 (*C*H), 122.4 (*C*), 65.8 (*C*H), 59.6 (CH_2), 55.3 (CH_2), 32.0 ($C(CH_3)_3$), 29.9 ($C(CH_3)_3$), 25.9 (CH_2), 24.2 (CH_2).

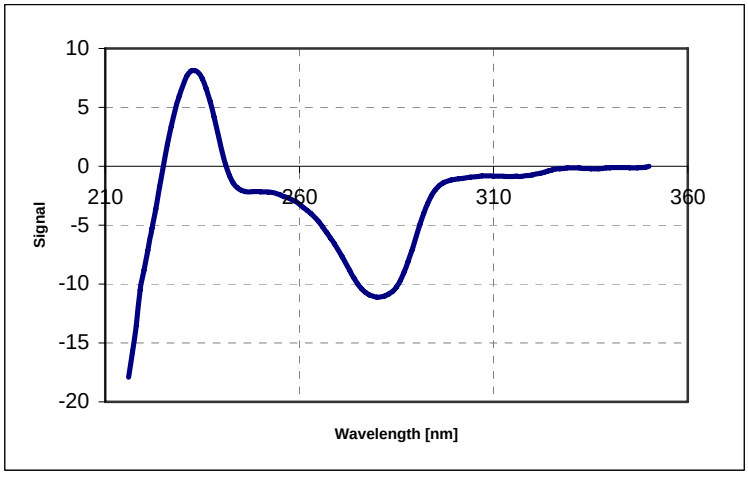

Fig. 1. CD spectrum of (*R*,*R*)-Lig^{1}H$_2$ (*c* = 1.25 μM, *l* = 1 mm).

(*S*,*S*)-Lig^{2}H$_2$. Et_3N (0.2 mL, 2 equiv) was added dropwise to a solution of (*S*,*S*)-bipyrrolidine (180 mg, 1.28 mmol) and 2-(bromomethyl)-4,6-dichlorophenol (600 mg, 2.56 mmol) in 50 mL of THF. The mixture was stirred for 24 h at RT, producing a white precipitate of Et_3N·HBr, which was filtered off and extracted with cold THF. The filtrate was washed twice with water and dried under vacuum. The resulting solid was recrystallized from methanol, yielding 59% (370 mg) of Lig^{2}H$_2$. The (*R*,*R*) isomer was obtained analogously in 61% (320 mg) using 150 mg (1.07 mmol) of (*R*,*R*)-bipyrrolidine. MS (DCI): [MH+] 489.0. $[\alpha]_D$ (for (*S*,*S*)-Lig^{2}H$_2$) = -71º (15.5 mg/10 mL of CH_2Cl_2, *d* = 0.5). $[\alpha]_D$ (for (*R*,*R*)-Lig^{2}H$_2$) = +71º (17.5 mg/10 mL of CH_2Cl_2, *d* = 1). ^{1}H NMR (400 MHz, C_6D_6) δ 11.3 (br s, 2H), 7.27 (d, *J* = 2.4 Hz, 2H), 6.66 (d, *J* = 2.4 Hz, 2H), 3.43 (d, *J* = 14.0 Hz, 2H, AB system), 2.57 (d, *J* = 14.0 Hz, 2H, AB system), 2.41 (m, 2H), 2.13 (m, 2H), 1.53 (m, 4H), 1.21 (m, 4H), 1.13 (m, 4H), 0.92 (m, 2H). ^{13}C NMR (100.66 MHz, C_6D_6) δ 153.4 (*C*), 129.3 (*C*H), 126.4 (*C*H), 124.8 (*C*), 123.7 (*C*), 122.3 (*C*), 64.5 (*C*H), 57.4 (*C*H$_2$), 54.5 (*C*H$_2$), 25.1 (*C*H$_2$), 23.6(*C*H$_2$).

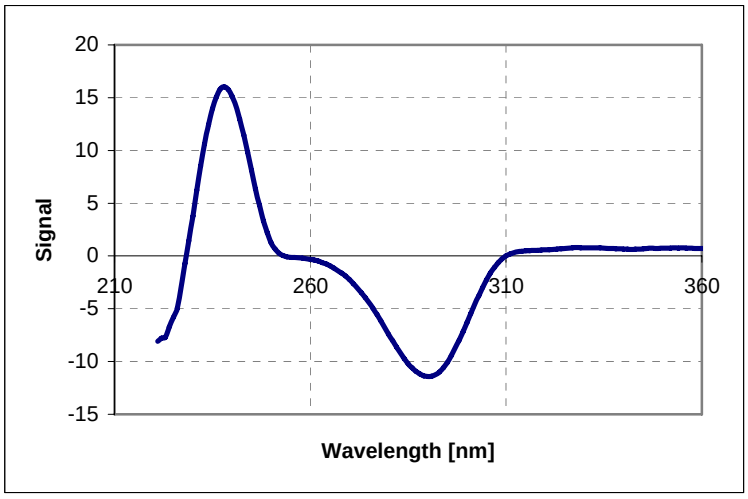

Fig. 2. CD spectrum of (*R*,*R*)-Lig^{2}H$_2$ (*c* = 1.22 μM, *l* = 1 mm).

(*S*,*S*)-Lig^{1}Ti(O-i-Pr)$_2$. (*S*,*S*)-Lig^{1}H$_2$ (37.6 mg, 0.065 mmol) was dissolved in *ca*. 2 mL of ether and added dropwise to a solution of Ti(O-i-Pr)$_4$ (18.9 mg, 0.065 mmol) in ether. The reaction mixture turned yellow in seconds, and the solution was stirred at RT for 24 h. The

solvent was removed under vacuum, and the resulting yellow solid was washed with pentane (*ca*. 2 mL). The final yield was 88% (42.3 mg). The (*R*,*R*) complex was obtained analogously in 90% using 43.0 mg (0.075 mmol) of (*R*,*R*)-Lig^{1}H$_2$. $[\alpha]_D$ (for (*S*,*S*)-Lig^{1}Ti(O-i-Pr)$_2$) = +254º (4.2 mg/2 mL of CH_2Cl_2, *d* = 0.5). $[\alpha]_D$ (for (*R*,*R*)-Lig^{1}Ti(O-i-Pr)$_2$) = -270º (4.0 mg/2 mL of CH_2Cl_2, *d* = 0.5). Anal. calcd. for $C_{44}H_{72}N_2O_4Ti{\cdot}Et_2O$: C, 70.73; H, 10.14; N, 3.44. Found: C, 70.09; H, 9.52; N, 3.39. ^{1}H NMR (400 MHz, C_6D_6) δ 7.57 (d, *J* = 2.3 Hz, 2H), 6.89 (d, *J* = 2.3 Hz, 2H), 4.95 (sept, 2H), 4.40 (d, *J* = 13.3 Hz, 2H, AB system), 3.39 (m, 2H), 3.06 (d, *J* = 13.3 Hz, 2H, AB system), 2.54 (m, 2H), 2.73 (m, 2H), 1.84 (s, 18H), 1.47 (m, 4H), 1.37 (d, 6H), 1.32 (s, 18H), 1.20 (d, 6H), 0.90 (m, 2H), 0.71 (m, 2H); ^{13}C NMR (100.66 MHz, C_6D_6), δ 160.1 (*C*), 138.8 (*C*), 136.3 (*C*), 124.2 (*C*H), 124.1 (*C*), 124.0 (*C*H), 77.4 (*C*H), 63.9 (*C*H), 60.6 (CH_2), 55.7 (CH_2), 32.1 ($C(CH_3)_3$), 30.8 ($C(CH_3)_3$), 27.1 (CH_3), 26.7 (CH_3), 24.3 (CH_2), 20.6 (CH_2).

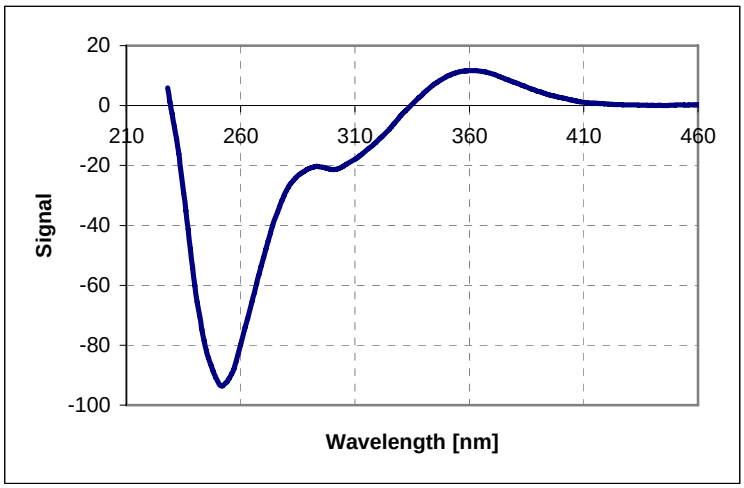

Fig. 3. CD spectrum of (*R*,*R*)-Lig^{1}Ti(O-i-Pr) (*c* = 1.28 μM, *l* = 1 mm).

(*S*,*S*)-Lig^{1}Zr(O-t-Bu)$_2$. (*S*,*S*)-Lig^{1}H$_2$ (33.0 mg, 0.057 mmol) was dissolved in *ca*. 2 mL of ether and added dropwise to a solution of Zr(O-t-Bu)$_4$ (22.1 mg, 0.057 mmol) in ether. The reaction mixture turned yellow in seconds, and the solution was stirred at RT for 24 h. The solvent was removed under vacuum, and the resulting yellow solid was washed with pentane (*ca*. 2 mL). The final yield was 92% (42.6 mg). The (*R*,*R*) complex was obtained analogously in

100% using 25.8 mg (0.045 mmol) of (*R*,*R*)-Lig^{1}H$_2$. $[\alpha]_D$ (for (*R*,*R*)-Lig^{1}Zr(O-t-Bu)$_2$) = -172º (10.3 mg/5 mL of CH_2Cl_2, *d* = 0.5). ^{1}H NMR (400 MHz, C_6D_6), δ 7.58 (d, *J* = 1.8 Hz, 2H), 6.87 (d, *J* = 1.8 Hz, 2H), 4.62 (d, *J* = 13.0 Hz, 2H, AB system), 3.25 (m, 2H), 2.95 (d, *J* = 13.0 Hz, 2H, AB system), 2.83 (m, 2H), 2.75 (m, 2H), 1.82 (s, $C(CH_3)_3$, 18H), 1.45 (s, $C(CH_3)_3$, 18H), 1.40 (m, 6H), 1.31 (s, $C(CH_3)_3$, 18H), 0.79 (m, 2H), 0.70 (m, 2H); ^{13}C NMR (100.66 MHz, C_6D_6), δ 159.1 (*C*), 138.3 (*C*), 137.0 (*C*), 124.6 (*C*H), 124.3 (*C*H), 124.0 (C), 75.7 ($C(CH_3)_3$), 63.2 (*C*H), 60.0 (CH_2), 54.1 (CH_2), 35.8 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 33.6 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$), 24.3 (CH_2), 20.2 (CH_2).

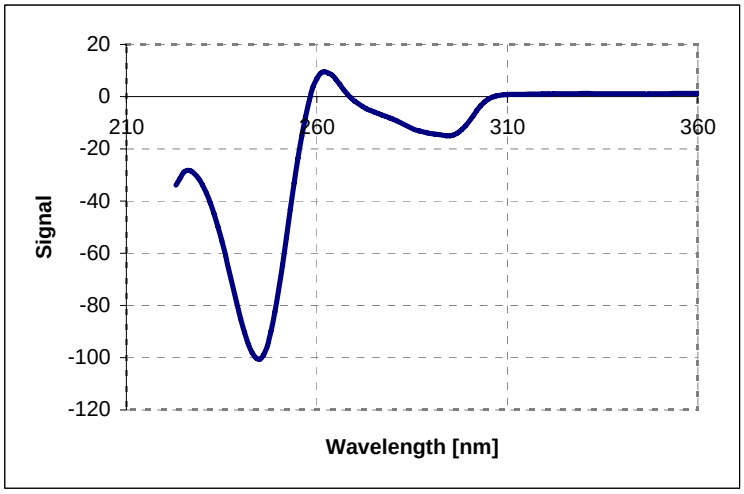

Fig. 4. CD spectrum of (*R*,*R*)-Lig^{1}Zr(O-t-Bu)$_2$ (*c* = 1.11 μM, *l* = 1 mm).

(*S*,*S*)-Lig^{1}ZrBn$_2$. (*S*,*S*)-Lig^{1}H$_2$ (49.9 mg, 0.086 mmol) was dissolved in *ca*. 2 mL of ether and added dropwise to a solution of $ZrBn_4$ (39.9 mg, 0.086 mmol) in ether. The reaction mixture turned yellow in seconds, and the solution was stirred at RT for 24 h. The solvent was removed under vacuum, and the resulting yellow solid was washed with pentane (*ca*. 2 mL). The final yield was 100% (70.8 mg). The (*R*,*R*) complex was obtained analogously in 100% using 34.6 mg (0.060 mmol) of (*R*,*R*)-Lig^{1}H$_2$. ^{1}H NMR (400 MHz, C_6D_6), δ 7.59 (d, *J* = 2.4 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 4H), 6.92 (t, *J* = 7.5 Hz, 4H), 6.78 (t, *J* = 7.3 Hz, 2H), 6.72 (d, *J* = 2.4

Hz, 2H), 3.78 (d, *J* = 13.6 Hz, 2H, AB system), 2.94 (d, *J* = 10.4, 2H, AB system), 2.89 (m, 2H), 2.67 (m, 2H), 2.61 (d, *J* = 13.6 Hz, 2H, AB system), 2.55 (d, *J* = 13.9 Hz, 2H, AB system), 2.45 (m, 2H), 1.85 (s, C(*C*H$_3$)$_3$, 18H), 1.39 (m, 4H), 1.27(s, C(*C*H$_3$)$_3$, 18H), 0.69 (m, 2H), 0.54 (m,2H); ^{13}C NMR (100.66 MHz, C_6D_6), δ 157.5 (*C*), 149.1 (*C*), 141.0 (*C*), 137.4 (*C*), 128.7 (*C*H), 127.3 (*C*H), 125.8 (*C*), 124.9 (*C*H), 124.6 (*C*H), 121.4 (*C*H), 68.7 (*C*H$_2$), 64.8 (*C*H), 58.4 (*C*H$_2$), 53.3 (*C*H$_2$), 35.7 (*C*(CH$_3$)$_3$), 34.4 (*C*(CH$_3$)$_3$), 31.9 (C(*C*H$_3$)$_3$), 30.6 (C(*C*H$_3$)$_3$), 23.9 (*C*H$_2$), 20.1 (*C*H$_2$).

(*S*,*S*)-Lig^{2}Ti(O-i-Pr)$_2$. (*S*,*S*)-Lig^{2}H$_2$ (35.5 mg, 0.072 mmol) was dissolved in *ca*. 2 mL of ether and added dropwise to a solution of Ti(O-i-Pr)$_4$ (21.6 mg, 0.072 mmol) in ether. The reaction mixture turned yellow in seconds, and the solution was stirred at RT for 24 h. The solvent was removed under vacuum, and the resulting yellow solid was washed with pentane (*ca*. 2 mL). The final yield was 91% (43.6 mg). The (*R*,*R*) complex was obtained analogously in 92% using 64.2 mg (0.13 mmol) of (*R*,*R*)-Lig^{1}H$_2$. $[\alpha]_D$ (for (*R*,*R*)-Lig^2(Ti(O-i-Pr)$_2$) = - 824º (5.1 mg/2 mL of CH_2Cl_2, *d* = 0.5). Anal. calcd. for $C_{28}H_{36}Cl_4N_2O_4Ti$: C, 51.40; H, 5.55; N, 4.28. Found: C, 51.51; H, 5.05; N, 3.66. ^{1}H NMR (400 MHz, C_6D_6), δ 7.33 (d, *J* = 2.2 Hz, 2H), 6.55 (d, *J* = 2.2 Hz, 2H), 5.44 (sept, 2H), 4.43 (d, *J* = 13.6 Hz, 2H, AB system), 3.23 (m, 2H), 2.59 (m, 2H), 2.56 (d, *J* = 13.6 Hz, 2H, AB system), 2.35 (m, 2H), 1.48 (d, 6H), 1.34 (d, 6H), 1.04 (m, 4H), 0.93 (m, 4H), 0.53 (m, 2H); ^{13}C NMR (100.66 MHz, C_6D_6), δ 156.9 (C), 129.7 (2C, *C*H), 127.0 (*C*), 123.1 (C), 121.3 (C), 79.1 (*C*H), 63.6 (*C*H), 59.5 (*C*H$_2$), 54.7 (*C*H$_2$), 26.4 (*C*(*C*H$_3$)$_3$), 26.1 (*C*(*C*H$_3$)$_3$), 24.1 (*C*H$_3$), 20.6 (*C*H$_3$).

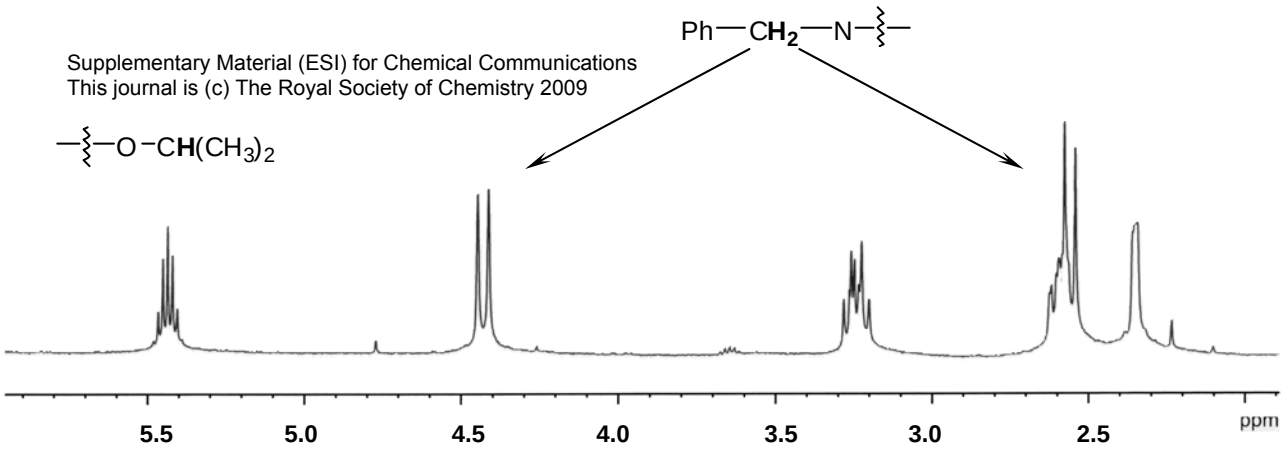

Fig. 5. ^{1}H NMR spectrum of (*R*,*R*)-Lig^{2}Ti(O-i-Pr)$_2$ in C_6D_6 (selected region) demonstrating the formation of a single stereoisomer.

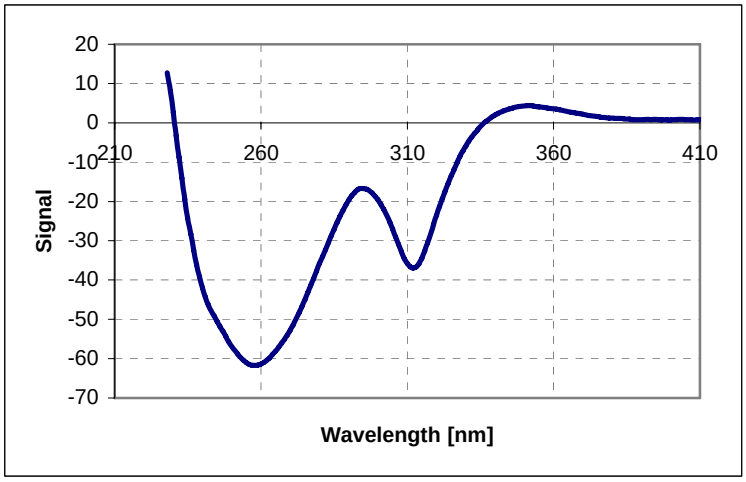

Fig. 6. CD spectrum of (*R*,*R*)-Lig^{2}Ti(O-i-Pr)$_2$ (*c* = 1.09 μM, *l* = 1 mm).

(*S*,*S*)-Lig^{2}Zr(O-t-Bu)$_2$. (*S*,*S*)-Lig^{2}H$_2$ (14.2 mg, 0.030 mmol) was dissolved in *ca*. 2 mL of ether and added dropwise to a solution of Zr(O-t-Bu)$_4$ (10.9 mg, 0.030 mmol) in ether. The reaction mixture turned yellow in seconds, and the solution was stirred at RT for 24 h. The solvent was removed under vacuum, and the resulting yellow solid was washed with pentane (*ca*. 2 mL). The final yield was 100% (23.7 mg). The (*R*,*R*) complex was obtained analogously in 100% using 25.6 mg (0.052 mmol) of (*R*,*R*)-Lig^{1}H$_2$. $[\alpha]_D$ (for (*R*,*R*)-Lig^{2}Zr(O-t-Bu)$_2$) = -204º (2.7 mg/2 mL of CH_2Cl_2, *d* = 0.5). Anal. calcd. for $C_{30}H_{40}Cl_4N_2O_4Zr{\cdot}Et_2O$: C, 51.06; H, 6.30; N, 3.50;. Found: C, 51.38; H, 5.98; N, 3.50. ^{1}H NMR (400 MHz, C_6D_6), δ 7.33 (d, *J* = 2.6 Hz, 2H), 6.54 (d, *J* = 2.6 Hz, 2H), 4.43 (d, *J* = 13.4 Hz, 2H, AB system), 3.19 (m, 2H), 2.63 (m,

2H), 2.47 (d, J = 13.4 Hz, 2H, AB system), 2.29 (m, 2H), 1.59 (m, 4H), 1.52 (s, 18H), 1.25 (m, 4H), 0.45 (m, 2H); ^{13}C NMR (100.66 MHz, C_6D_6), δ 156.3 (C), 130.1 (2C, *C*H), 126.7 (C), 126.7 (C), 126.7 (C), 124.3 (C), 120.9 (C), 76.8 (*C*$(CH_3)_3$), 63.1 (*C*H), 58.7 (*C*H_2), 53.5 (*C*H_2), 33.4 (C(*C*$H_3)_3$), 24.2 (*C*H_2), 20.4 (*C*H_2).

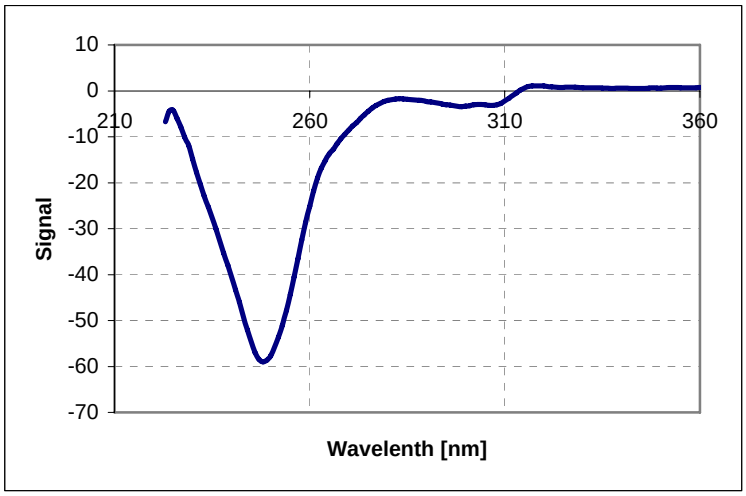

Fig.7 CD spectrum of (*R*,*R*)-Lig^{2}Zr(O-t-Bu)$_2$ (c = 1.05 μM, l = 1 mm).

(*S*,*S*)-Lig^{2}ZrBn$_2$. (*S*,*S*)-Lig^{2}H$_2$ (21.1 mg, 0.043 mmol) was dissolved in *ca*. 2 mL of ether and added dropwise to a solution of ZrBn$_4$ (19.4 mg, 0.043 mmol) in ether. The reaction mixture turned yellow in seconds, and the solution was stirred at RT for 24 h. The solvent was removed under vacuum, and the resulting yellow solid was washed with pentane (*ca*. 2 mL). The final yield was 95% (31.1 mg). The (*R*,*R*) complex was obtained analogously in 92% using 22.8 mg (0.047 mmol) of (*R*,*R*)-Lig^{1}H$_2$. ^{1}H NMR (400 MHz, C_6D_6), δ 7.31 (d, J = 2.4 Hz, 2H), 7.28 (br s, 2H), 7.26 (br s, 2H), 7.13 (br s, 2H), 7.11 (br s, 2H), 6.92 (t, J = 7.3 Hz, 2H), 6.40 (d, J = 2.4 Hz, 2H), 3.67 (d, J = 13.9 Hz, 2H, AB system), 2.69 (m, 2H), 2.37 (m, 2H), 2.34 (d, J = 9.3 Hz, 2H), 2.22 (d, J = 13.9 Hz, 2H, AB system), 2.18 (m, 2H), 2.08 (d, J = 9.3 Hz, 2H), 1.09 (m, 2H), 0.71(m, 2H), 0.37 (m, 2H); ^{13}C NMR (100.66 MHz, CD_2Cl_2), δ 155.0 (*C*), 145.2 (*C*),

130.0 (*C*H), 129.5 (*C*H), 128.6 (*C*H), 126.2 (*C*), 125.7 (*C*), 123.9 (*C*), 123.4 (*C*H), 123.2 (*C*), 65.1 (*C*H), 62.3 (*C*H_2), 57.2 (*C*H_2), 52.7 (*C*H_2), 23.8 (*C*H_2), 19.9 (*C*H_2).

General procedure of polymerization of 1-hexene.

$B(C_6F_5)_3$ (1.2 – 1.5 equiv, 12 – 15 μmol) was dissolved in *ca*. 1 mL of 1-hexene and added to a stirred solution of Lig^1ZrBn_2 or Lig^2ZrBn_2 (10 μmol) in 4 mL of 1-hexene. The resulting mixture was stirred at RT under a nitrogen atmosphere until a viscous polymer mixture had formed. The remaining olefin was removed under vacuum yielding poly(1-hexene) as a colorless sticky oil.

No.	Cat.	1-Hexene (g)	Polymerization Time (h)	Polymer Obtained (g)	Activity (g $mmol^{-1}$ h^{-1})	Mw (g/mol)	PDI
3	*(S,S)* – Lig^1ZrBn_2	3.4	24	0.17	low	21,500	1.2
6	*(S,S)* – Lig^2ZrBn_2	3.4	1	1.27	150	9,500	1. 6

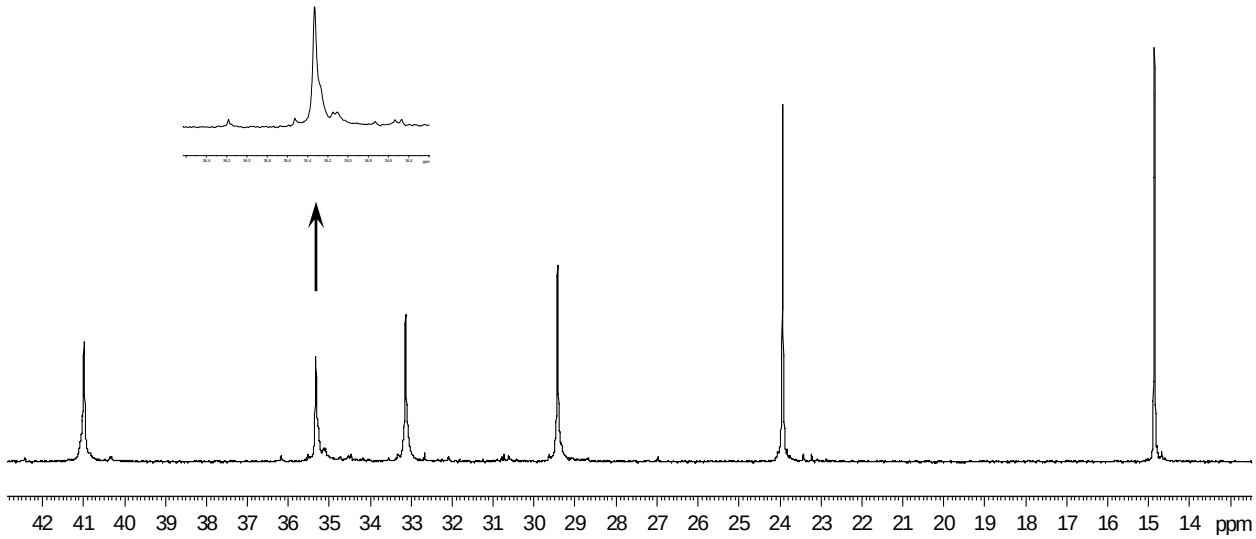

Fig. 8. ^{13}C NMR spectrum of poly(1-hexene) synthesized with (*S*,*S*)-$Lig^1ZrBn_2/B(C_6F_5)_3$.

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