

Supporting Information

Bimetallic mechanism operating in the copolymerization of propylene oxide with carbon dioxide catalyzed by cobalt-salen complexes

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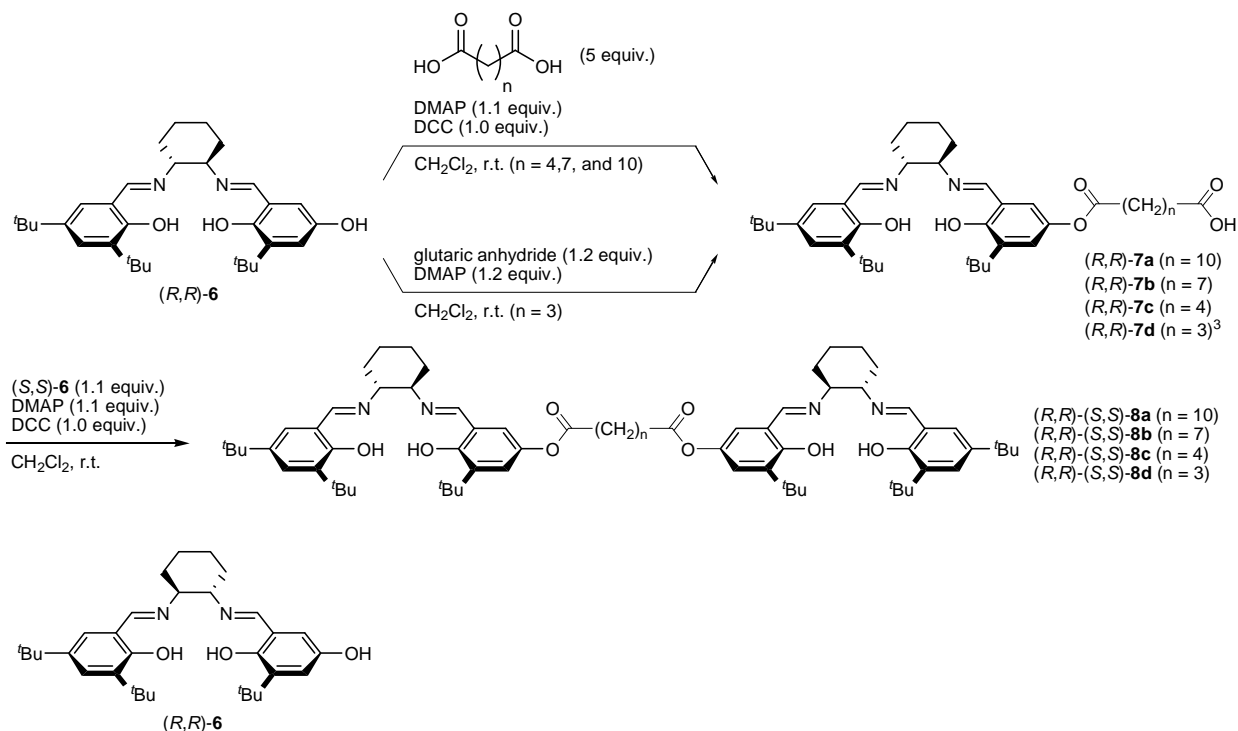
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General Methods and Materials. All manipulations involving air- and/or moisture-sensitive compounds were carried out in a glove box under argon or with the standard Schlenk technique under argon purified by passing through a hot column packed with BASF catalyst R3-11. Analytical thin-layer chromatography was performed on glass plates coated with 0.25-mm 230–400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). For silica-gel column chromatography, Silica gel 60N (spherical neutral, particle size 63–210 μm , Kanto Kagaku Co., Ltd.) was used. NMR spectra were recorded on a 500 MHz (^1H 500 MHz; ^{13}C 125 MHz) spectrometer. Chemical shifts are reported in ppm relative to the residual protiated solvent peak (7.26 ppm for CHCl_3) for ^1H and deuteriochloroform (77.16 ppm) for ^{13}C . Data are presented in the following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, quint = quintet, m = multiplet and/or multiplet resonances), coupling constant in hertz (Hz), and signal area integration in natural numbers. Mass spectra are taken with FAB method by using *m*-nitrobenzylalcohol as a matrix. The recycling preparative gel-permeation-chromatography (GPC) was performed with JAI GEL-1H and -2H columns (chloroform as an eluent). Gel-permeation-chromatography (GPC) analyses for evaluating molecular weight were carried with two columns (Shodex KF-804L) using tetrahydrofuran as an eluent at 40 °C at 1 mL/min. The molecular weight was calibrated against standard polystyrene samples.

All the solvents used for reactions were distilled under argon after drying over an appropriate drying reagent or passed through solvent purification columns. Most of reagents were used without further purification unless otherwise specified. Carbon dioxide (>99.99%) was purchased from Showa tansan Co., LTD. Propylene oxide was refluxed over a mixture of CaH_2 and fractionally distilled under argon. The compounds *rac*-**5**,¹ (*R,R*)- and (*S,S*)-**6**,² (*R,R*)-**7d**,³ (*R,R*)-(*R,R*)-**8a**⁴ were synthesized according to the literatures.

Synthetic Procedures



Synthesis of (R,R)-7a. A round-bottom flask containing magnetic stirring bar was charged with dodecanedioic acid (230 mg, 1.0 mmol), **(R,R)-6** (101 mg, 0.20 mmol), 4-(dimethylamino)pyridine (DMAP, 27 mg, 0.22 mmol), and dichloromethane (4 mL). *N,N'*-Dicyclohexylcarbodiimide (41 mg, 0.20 mmol) in dichloromethane (1 mL) was added, and the mixture was stirred at room temperature for 4 h. The resulting suspension was filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography [silica gel; AcOEt/hexane (1/2) as an eluent, $R_f = 0.38$] to provide the title compound **(R,R)-7a** (104 mg, 72% yield) as a yellow solid: ^1H NMR (500 MHz, CDCl_3) $\delta = 8.30$ (s, 1H), 8.23 (s, 1H), 7.31 (d, $J = 2.4$ Hz, 1H), 6.98 (d, $J = 2.4$ Hz, 1H), 6.91 (d, $J = 2.7$ Hz, 1H), 6.75 (d, $J = 2.7$ Hz, 1H), 3.34–3.32 (m, 2H), 2.49 (t, $J = 7.5$ Hz, 2H), 2.35 (t, $J = 7.5$ Hz, 2H), 1.96–1.92 (m, 2H), 1.88–1.87 (m, 2H), 1.77–1.68 (m, 4H), 1.65–1.60 (m, 2H), 1.49–1.44 (m, 2H), 1.41–1.29 (m, 30H), 1.24 (s, 9H); ^{13}C NMR (500 MHz, CDCl_3) $\delta = 180.1, 172.9, 166.0, 164.8, 158.2, 158.1, 141.7, 140.1, 138.6, 136.5, 127.0, 126.1, 122.9, 121.5, 118.3, 117.9, 72.6, 72.3, 35.1, 35.0,$

34.4, 34.18, 34.15, 33.31, 33.25, 31.5, 29.6, 29.5, 29.34, 29.27, 29.22, 29.17, 25.1, 24.8, 24.4. Anal. Calcd for $C_{44}H_{66}N_2O_6$ (%): C, 73.50; H, 9.25; N, 3.90. Found: C, 73.22; H, 9.18; N, 3.63. LRMS-FAB⁺ m/z (relative intensity, ion) 720 (100%, $[M + H]^+$), 719 (83%, M^+), 506 (22%, $[M - C_{12}H_{21}O_3$ (dodecanedioate unit) + $H]^+$), 505 (21%, $[M - C_{12}H_{21}O_3$ (dodecanedioate unit)]⁺).

Synthesis of (R,R)-7b. The crude product was obtained from nonanedioic acid (188 mg, 1.0 mmol) and (R,R)-6 (101 mg, 0.20 mmol) according to the procedure described for the synthesis of (R,R)-7a. Purification by column chromatography [silica gel; AcOEt/hexane (1/2) as an eluent, R_f = 0.38] gave the title compound (R,R)-7b (114 mg, 84% yield) as a yellow solid: ¹H NMR (500 MHz, CDCl₃) δ = 8.32 (s, 1H), 8.25 (s, 1H), 7.34 (d, J = 2.3 Hz, 1H), 7.00 (d, J = 2.3 Hz, 1H), 6.94 (d, J = 2.7 Hz, 1H), 6.78 (d, J = 2.7 Hz, 1H), 3.35–3.33 (m, 2H), 2.51 (t, J = 7.6 Hz, 2H), 2.37 (t, J = 7.6 Hz, 2H), 1.97–1.91 (m, 2H), 1.89–1.87 (m, 2H), 1.76–1.70 (m, 4H), 1.68–1.63 (m, 2H), 1.49–1.45 (m, 2H), 1.43–1.39 (m, 24H), 1.26 (s, 9H); ¹³C NMR (500 MHz, CDCl₃) δ = 180.1, 172.8, 166.0, 164.8, 158.2, 158.1, 141.6, 140.1, 138.6, 136.5, 127.0, 126.1, 122.9, 121.5, 118.3, 117.9, 72.5, 72.3, 35.1, 35.0, 34.4, 34.14, 34.12, 33.3, 33.2, 31.5, 29.6, 29.3, 29.00, 28.97, 25.0, 24.7, 24.4. Anal. Calcd for $C_{41}H_{60}N_2O_6$ (%): C, 72.75; H, 8.93; N, 4.14. Found: C, 72.51; H, 9.02; N, 3.91. LRMS-FAB⁺ m/z (relative intensity, ion) 677 (100%, $[M + H]^+$), 676 (83%, M^+), 506 (18%, $[M - C_9H_{15}O_3$ (nonanedioate unit) + $H]^+$), 505 (19%, $[M - C_9H_{15}O_3$ (nonanedioate unit)]⁺).

Synthesis of (R,R)-7c. The crude product was obtained from hexanedioic acid (120 mg, 0.82 mmol) and (R,R)-6 (83 mg, 0.16 mmol) according to the procedure described for the synthesis of (R,R)-7a. Purification by column chromatography [silica gel; AcOEt/hexane (1/1) as an eluent, R_f = 0.35] gave the title compound (R,R)-7c (79 mg, 78% yield) as a yellow solid: ¹H NMR (500 MHz, CDCl₃) δ = 8.32 (s, 1H), 8.24 (s, 1H), 7.33 (d, J = 2.5 Hz, 1H), 7.00 (d, J = 2.5 Hz, 1H), 6.94 (d, J = 2.8 Hz, 1H), 6.78 (d, J = 2.8 Hz, 1H), 3.35–3.33 (m, 2H), 2.55 (t, J = 7.0 Hz, 2H), 2.43 (t, J = 7.0 Hz,

2H), 1.97–1.93 (m, 2H), 1.89–1.87 (m, 2H), 1.81–1.74 (m, 6H), 1.49–1.45 (m, 2H), 1.42 (s, 9H), 1.40 (s, 9H), 1.25 (s, 9H); ^{13}C NMR (500 MHz, CDCl_3) δ = 179.5, 172.3, 166.0, 164.8, 158.3, 158.1, 141.6, 140.1, 138.7, 136.5, 127.0, 126.1, 122.9, 121.5, 118.3, 117.9, 72.6, 72.3, 35.1, 35.0, 34.2, 34.0, 33.7, 33.3, 33.2, 31.5, 29.6, 29.3, 24.39, 24.37, 24.15. Anal. Calcd for $\text{C}_{38}\text{H}_{54}\text{N}_2\text{O}_6$ (%): C, 71.89; H, 8.57; N, 4.41. Found: C, 71.68; H, 8.75; N, 4.16. LRMS-FAB $^+$ m/z (relative intensity, ion) 635 (100%, $[\text{M} + \text{H}]^+$), 634 (88%, M^+), 506 (15%, $[\text{M} - \text{C}_6\text{H}_9\text{O}_3$ (hexanedioate unit) + $\text{H}]^+$), 505 (19%, $[\text{M} - \text{C}_6\text{H}_9\text{O}_3$ (hexanedioate unit)] $^+$).

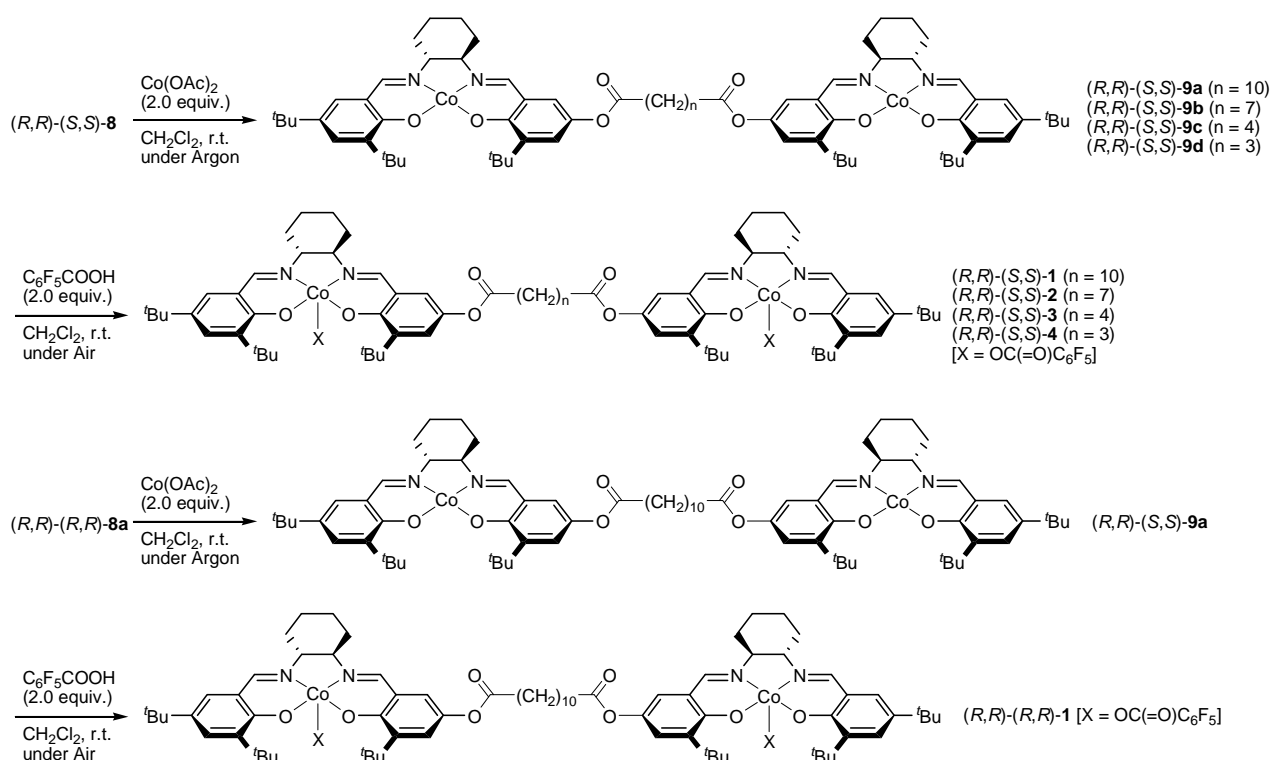
Synthesis of (*R,R*)-(*S,S*)-8a**.** A round-bottom flask containing magnetic stirring bar was charged with (*R,R*)-**7a** (206 mg, 0.29 mmol), 4-(dimethylamino)pyridine (DMAP, 39 mg, 0.32 mmol), (*S,S*)-**6** (145 mg, 0.29 mmol), and dichloromethane (15 mL). *N,N'*-Dicyclohexylcarbodiimide (59 mg, 0.29 mmol) in dichloromethane (3 mL) was added, and the mixture was stirred at room temperature for 3.5 h. The resulting suspension was filtrated through a pad of Celite $^{\text{®}}$ and silica-gel, and concentrated under reduced pressure. This crude product was purified by the recycling preparative GPC (chloroform as an eluent) to provide the title compound (*R,R*)-(*S,S*)-**8a** (254 mg, 70% yield) as a yellow solid: ^1H NMR (500 MHz, CDCl_3) δ = 13.86 (s, 2H), 13.62 (s, 2H), 8.31 (s, 2H), 8.23 (s, 2H), 7.31 (d, J = 2.3 Hz, 2H), 6.98 (d, J = 2.3 Hz, 2H), 6.92 (d, J = 2.9 Hz, 2H), 6.75 (d, J = 2.9 Hz, 2H), 3.35–3.30 (m, 4H), 2.49 (t, J = 7.5 Hz, 4H), 1.97–1.92 (m, 4H), 1.88–1.87 (m, 4H), 1.74–1.68 (m, 8H), 1.48–1.44 (m, 4H), 1.41–1.28 (m, 48H), 1.31 (m, 10H), 1.24 (s, 18H); ^{13}C NMR (125 MHz, CDCl_3) δ = 172.9, 166.0, 164.8, 158.2, 158.1, 141.7, 140.1, 138.6, 136.5, 127.0, 126.1, 122.9, 121.5, 118.3, 117.9, 72.6, 72.4, 35.1, 35.0, 34.5, 34.2, 33.34, 33.27, 31.6, 29.6, 29.4, 29.3, 25.1, 24.4. Anal. Calcd for $\text{C}_{76}\text{H}_{110}\text{N}_4\text{O}_8$ (%): C, 75.58; H, 9.18; N, 4.64. Found: C, 75.70; H, 9.43; N, 4.12. LRMS-FAB $^+$ m/z (relative intensity, ion) 1208 (41%, $[\text{M} + \text{H}]^+$), 506 (20%, $[\text{M} - \text{C}_{44}\text{H}_{65}\text{N}_2\text{O}_5$ (dodecanedioate unit + salen unit) + $\text{H}]^+$), 505 (21%, $[\text{M} - \text{C}_{44}\text{H}_{65}\text{N}_2\text{O}_5$ (dodecanedioate unit + salen unit)] $^+$).

Synthesis of (R,R)-(S,S)-8b. The crude product was obtained from (R,R)-7b (140 mg, 0.21 mmol) and (R,R)-6 (104 mg, 0.21 mmol) according to the procedure described for the synthesis of (R,R)-(S,S)-8a (reaction time: 2.5 h). Purification by the recycling preparative GPC (chloroform as an eluent) gave the title compound (R,R)-(S,S)-8b (169 mg, 70% yield) as a yellow solid: ¹H NMR (500 MHz, CDCl₃) δ = 13.87 (s, 2H), 13.62 (s, 2H), 8.30 (s, 2H), 8.23 (s, 2H), 7.31 (d, *J* = 2.4 Hz, 2H), 6.98 (d, *J* = 2.4 Hz, 2H), 6.91 (d, *J* = 2.7 Hz, 2H), 6.75 (d, *J* = 2.7 Hz, 2H), 3.33–3.31 (m, 4H), 2.50 (t, *J* = 7.6 Hz, 4H), 1.96–1.91 (m, 4H), 1.88–1.86 (m, 4H), 1.73–1.69 (m, 8H), 1.47–1.38 (m, 46H), 1.23 (s, 18H); ¹³C NMR (125 MHz, CDCl₃) δ = 172.8, 166.0, 164.8, 158.2, 158.1, 141.7, 140.1, 138.6, 136.5, 127.0, 126.1, 122.9, 121.5, 118.3, 117.9, 72.6, 72.3, 35.1, 35.0, 34.4, 34.2, 33.3, 31.5, 29.6, 29.3, 29.1, 25.0, 24.4. Anal. Calcd for C₇₃H₁₀₄N₄O₈ (%): C, 75.22; H, 8.99; N, 4.81. Found: C, 75.25; H, 9.16; N, 4.56. LRMS-FAB⁺ *m/z* (relative intensity, ion) 1166 (51%, [M + H]⁺), 1165 (34%, M⁺), 506 (21%, [M – C₄₁H₅₉N₂O₅ (nonanedioate unit + salen unit) + H]⁺), 505 (25%, [M – C₄₁H₅₉N₂O₅ (nonanedioate unit + salen unit)]⁺).

Synthesis of (R,R)-(S,S)-8c. The crude product was obtained from (R,R)-7c (223 mg, 0.35 mmol) and (R,R)-6 (177 mg, 0.35 mmol) according to the procedure described for the synthesis of (R,R)-(S,S)-8a (reaction time: 3 h). Purification by the recycling preparative GPC (chloroform as an eluent) gave the title compound (R,R)-(S,S)-8c (137 mg, 35% yield) as a yellow solid: ¹H NMR (500 MHz, CDCl₃) δ = 13.88 (s, 2H), 13.61 (s, 2H), 8.30 (s, 2H), 8.21 (s, 2H), 7.31 (d, *J* = 2.4 Hz, 2H), 6.98 (d, *J* = 2.4 Hz, 2H), 6.92 (d, *J* = 2.7 Hz, 2H), 6.76 (d, *J* = 2.7 Hz, 2H), 3.33–3.31 (m, 4H), 2.57–2.55 (m, 4H), 1.96–1.91 (m, 4H), 1.89–1.87 (m, 4H), 1.83–1.81 (m, 4H), 1.75–1.70 (m, 4H), 1.48–1.44 (m, 4H), 1.40 (s, 18H), 1.37 (s, 18H), 1.23 (s, 18H); ¹³C NMR (125 MHz, CDCl₃) δ = 172.3, 166.0, 164.8, 158.3, 158.1, 141.6, 140.1, 138.7, 136.5, 127.0, 126.1, 122.9, 121.5, 118.3, 117.9, 72.6, 72.4, 35.1, 35.0, 34.2, 34.0, 33.34, 33.26, 31.6, 29.6, 29.3, 24.44, 24.42. Anal. Calcd for C₇₀H₉₈N₄O₈ (%): C, 74.83; H, 8.79; N, 4.99. Found: C, 74.60; H, 8.88; N, 4.80. LRMS-FAB⁺ *m/z* (relative intensity, ion) 1124 (62%,

$[M + H]^+$, 1123 (37%, M^+), 506 (20%, $[M - C_{38}H_{53}N_2O_5$ (hexanedioate unit + salen unit) + $H]^+$), 505 (25%, $[M - C_{38}H_{53}N_2O_5$ (hexanedioate unit + salen unit)] $^+$).

Synthesis of (R,R)-(S,S)-8d. The crude product was obtained from (R,R)-7d (271 mg, 0.44 mmol) and (R,R)-6 (222 mg, 0.44 mmol) according to the procedure described for the synthesis of (R,R)-(S,S)-8a (reaction time: 2 h). Purification by the recycling preparative GPC (chloroform as an eluent) gave the title compound (R,R)-(S,S)-8d (139 mg, 29% yield) as a yellow solid: 1H NMR (500 MHz, $CDCl_3$) δ = 13.89 (s, 2H), 13.61 (s, 2H), 8.31 (s, 2H), 8.22 (s, 2H), 7.31 (d, J = 2.6 Hz, 2H), 6.98 (d, J = 2.6 Hz, 2H), 6.93 (d, J = 2.9 Hz, 2H), 6.77 (d, J = 2.9 Hz, 2H), 3.36-3.30 (m, 4H), 2.65 (t, J = 7.3 Hz, 4H), 2.13 (quintet, J = 7.3 Hz, 2H), 1.97-1.92 (m, 4H), 1.89-1.87 (m, 4H), 1.75-1.71 (m, 4H), 1.49-1.45 (m, 4H), 1.40 (s, 18H), 1.38 (s, 18H), 1.24 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.9, 166.0, 164.8, 158.3, 158.1, 141.5, 140.1, 138.7, 136.5, 127.0, 126.1, 122.9, 121.5, 118.3, 117.9, 72.6, 72.4, 35.1, 35.0, 34.2, 33.34, 33.26, 31.6, 29.6, 29.3, 24.4. LRMS-FAB $^+$ m/z (relative intensity, ion) 1110 (43%, $[M + H]^+$), 1109 (28%, M^+), 506 (18%, $[M - C_{37}H_{51}N_2O_5$ (pentanedioate unit + salen unit) + $H]^+$), 505 (20%, $[M - C_{37}H_{51}N_2O_5$ (pentanedioate unit + salen unit)] $^+$). HRMS-ESI (m/z): calcd for $C_{69}H_{96}N_4O_8Na$ ($[M+Na]^+$) 1131.7126, Found 1131.7106.



Synthesis of dimeric cobalt(III) complex $(R,R)-(S,S)-1$. A 20 mL Schlenk tube containing a stirring bar was charged with cobalt(II) acetate (32 mg, 0.18 mmol), $(R,R)-(S,S)-8a$ (109 mg, 0.09 mmol), and EtOH (5 mL) under argon. After stirring at room temperature for 2 h, the resulting red precipitation was collected via filtration, washed with cold EtOH, and dried under reduced pressure to give dinuclear cobalt(II) complex $(R,R)-(S,S)-9a$ (99 mg).

A round-bottom flask containing a stirring bar was charged with the obtained cobalt complex $(R,R)-(S,S)-9a$ (99 mg, 0.08 mmol), pentafluorobenzoic acid (32 mg, 0.15 mmol), and dichloromethane (5 mL). After stirring at room temperature for 12 h, the reaction mixture was concentrated and dried under reduced pressure to provide the title complex $(R,R)-(S,S)-1$ as a green powder (127 mg, 81% for two steps): ^1H NMR (d -DMSO, 500 MHz) δ = 7.92 (s, 2H), 7.89 (s, 2H), 7.52 (s, 2H), 7.49 (s, 2H), 7.33 (s \times 2, 2H), 7.10 (s \times 2, 2H), 3.63-3.62 (m, 4H), 3.12-3.05 (m, 4H), 2.60 (t, J = 7.3 Hz, 4H), 2.05-2.03 (m, 4H), 1.97-1.95 (m, 4H), 1.78-1.60 (m, 50H), 1.43-1.34 (m, 26H). LRMS-FAB⁺ m/z

(relative intensity, ion) 1321 (42%, M^+), 563 (100%, $[M - C_{44}H_{63}CoN_2O_5$ (dodecanedioate unit + Co-salen unit) + $H]^+$), 562 (75%, $[M - C_{44}H_{63}CoN_2O_5$ (dodecanedioate unit + Co-salen unit)] $^+$).

Synthesis of dimeric cobalt(III) complex (*R,R*)-(*S,S*)-2. The title complex (*R,R*)-(*S,S*)-2 was obtained from cobalt(II) acetate (22 mg, 0.13 mmol), (*R,R*)-(*S,S*)-8b (73 mg, 0.063 mmol), and pentafluorobenzoic acid (14 mg, 0.068 mmol) as a green powder (51 mg, 48% for two steps) according to the procedure described for the synthesis of (*R,R*)-(*S,S*)-1 (reaction time: 3.5 h for the first step and 18 h for the second step): 1H NMR (*d*-DMSO, 500 MHz) δ = 7.93 (s, 2H), 7.89 (s, 2H), 7.52 (s, 2H), 7.49 (s, 2H), 7.34 (s, 2H), 7.11 (s, 2H), 3.66-3.60 (m, 4H), 3.12-3.06 (m, 4H), 2.62 (t, J = 7.7 Hz, 4H), 2.06-2.02 (m, 4H), 1.97-1.89 (m, 4H), 1.78-1.60 (m, 46H), 1.46-1.43 (m, 4H), 1.34 (s, 18H). LRMS-FAB $^+$ m/z (relative intensity, ion) 1279 (55%, M^+), 563 (100%, $[M - C_{41}H_{57}CoN_2O_5$ (nonanedioate unit + Co-salen unit) + $H]^+$), 562 (90%, $[M - C_{41}H_{57}CoN_2O_5$ (nonanedioate unit + Co-salen unit)] $^+$).

Synthesis of dimeric cobalt(III) complex (*R,R*)-(*S,S*)-3. The title complex (*R,R*)-(*S,S*)-3 was obtained from cobalt(II) acetate (36 mg, 0.21 mmol), (*R,R*)-(*S,S*)-8c (115 mg, 0.10 mmol), and pentafluorobenzoic acid (33 mg, 0.16 mmol) as a green powder (127 mg, 74% for two steps) according to the procedure described for the synthesis of (*R,R*)-(*S,S*)-1 (reaction time: 1.5 h for the first step and 18 h for the second step): 1H NMR (*d*-DMSO, 500 MHz) δ = 7.93 (s, 2H), 7.90 (s, 2H), 7.52 (s, 2H), 7.49 (s, 2H), 7.35 (s, 2H), 7.13 (s, 2H), 3.64-3.62 (m, 4H), 3.12-3.05 (m, 4H), 2.70-2.67 (m, 4H), 2.05-2.03 (m, 4H), 1.97-1.91 (m, 4H), 1.80-1.75 (m, 40H), 1.64-1.61 (m, 4H), 1.34 (s, 18H). LRMS-FAB $^+$ m/z (relative intensity, ion) 1237 (70%, M^+), 563 (100%, $[M - C_{38}H_{51}CoN_2O_5$ (hexanedioate unit + Co-salen unit) + $H]^+$), 562 (95%, $[M - C_{38}H_{51}CoN_2O_5$ (hexanedioate unit + Co-salen unit)] $^+$).

Synthesis of dimeric cobalt(III) complex (R,R)-(S,S)-4. The title complex (R,R)-(S,S)-4 was obtained from cobalt(II) acetate (38 mg, 0.22 mmol), (R,R)-(S,S)-8d (119 mg, 0.11 mmol), and pentafluorobenzoic acid (9 mg, 0.04 mmol) as a green powder (36 mg, 20% for two steps) according to the procedure described for the synthesis of (R,R)-(S,S)-1 (reaction time: 1.5 h for the first step and 6 h for the second step). ¹H NMR (*d*-DMSO, 500 MHz) δ = 7.93 (s, 2H), 7.89 (s, 2H), 7.52 (s, 2H), 7.49 (s, 2H), 7.37 (s, 2H), 7.16 (s, 2H), 3.64–3.62 (m, 4H), 3.12–3.06 (m, 4H), 2.78–2.74 (m, 6H), 2.06–2.01 (m, 4H), 1.97–1.89 (m, 4H), 1.78 (s, 18H), 1.75 (s, 18H), 1.34 (s, 18H). LRMS-FAB⁺ *m/z* (relative intensity, ion) 1223 (83%, M⁺), 563 (100%, [M – C₃₇H₄₉CoN₂O₅ (pentanedioate unit + Co–salen unit) + H]⁺), 562 (95%, [M – C₃₇H₄₉CoN₂O₅ (pentanedioate unit + Co–salen unit)]⁺).

Synthesis of dimeric cobalt(III) complex (R,R)-(R,R)-1. The title complex (R,R)-(R,R)-1 was obtained from cobalt(II) acetate (27 mg, 0.22 mmol), (R,R)-(R,R)-8a (94 mg, 0.11 mmol), and pentafluorobenzoic acid (29 mg, 0.14 mmol) as a green powder (113 mg, 83% for two steps) according to the procedure described for the synthesis of (R,R)-(S,S)-1 (reaction time: 1.5 h for the first step and 18 h for the second step). ¹H NMR (*d*-DMSO, 500 MHz) δ = 7.92 (s, 2H), 7.89 (s, 2H), 7.52 (s, 2H), 7.49 (s, 2H), 7.33 (s, 2H), 7.10 (s, 2H), 3.64–3.62 (m, 4H), 3.12–3.05 (m, 4H), 2.60 (t, *J* = 7.1 Hz, 4H), 2.05–2.03 (m, 4H), 1.97–1.95 (m, 4H), 1.78–1.60 (m, 50H), 1.43–1.34 (m, 26H).

Representative procedure for the copolymerization of propylene oxide with carbon dioxide. A 50 mL autoclave containing a magnetic stirring bar was charged with propylene oxide (2.0 mL, 29 mmol) and cobalt complex (1.4×10^{-2} mmol) under argon. After CO₂ (5.0 MPa) was introduced, the reaction mixture was stirred at 25 °C for 2 h. The CO₂ pressure was released, and the polymerization mixture was transferred into a round-bottom flask with dichloromethane. To the mixture was added phenanthrene as an internal standard. A small aliquot of the mixture was picked up and concentrated.

Analyses of the residue by ^1H and ^{13}C NMR spectroscopy and GPC gave the yield of copolymer and cyclic propylene carbonate, carbonate linkage, [rr]/[mm] ratio, molecular weight, and molecular-weight distribution.

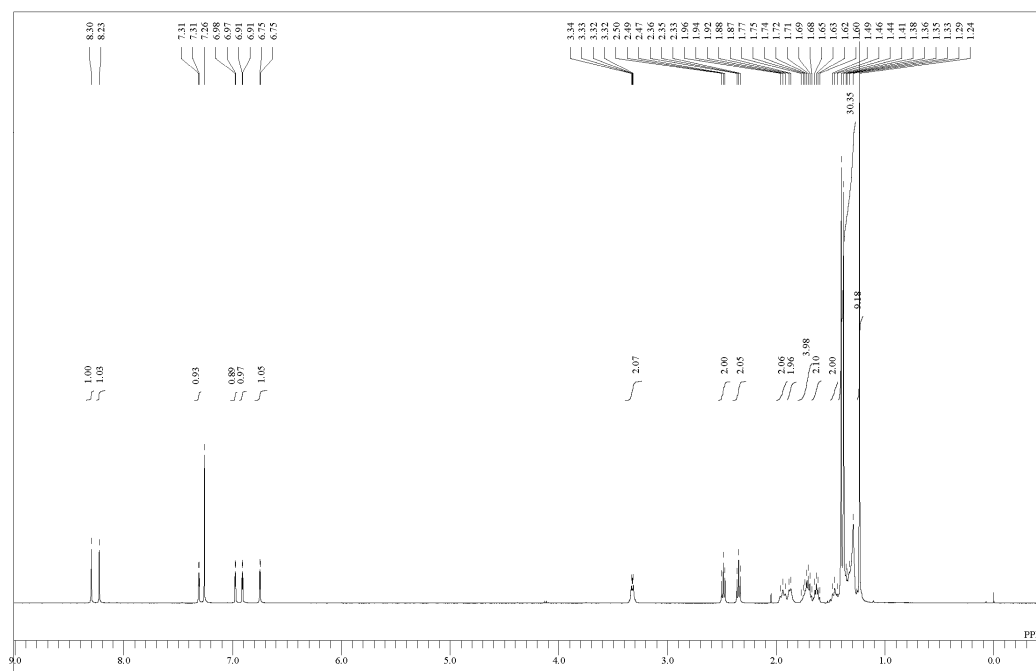


Figure S1. ¹H NMR spectrum of (R,R)-7a (CDCl₃).

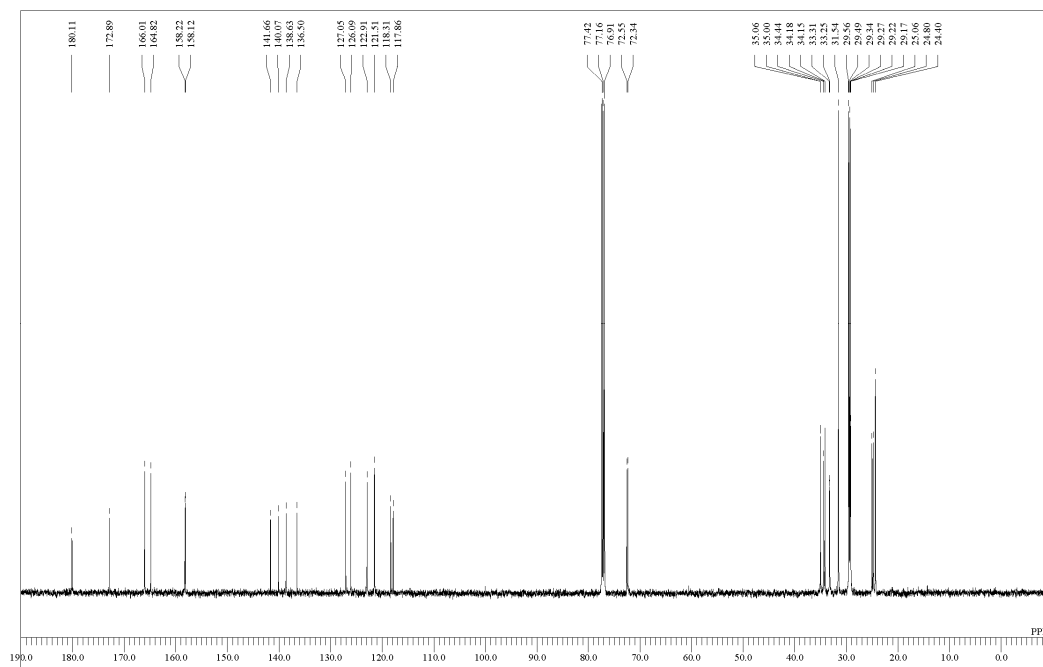


Figure S2. ¹³C NMR spectrum of (R,R)-7a (CDCl₃).

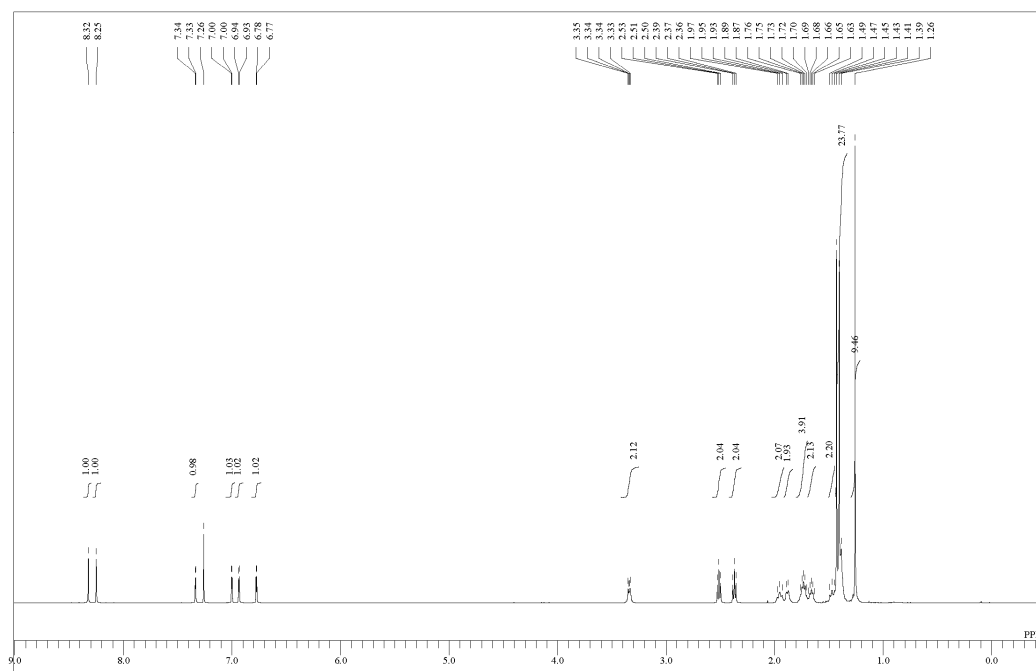


Figure S3. ^1H NMR spectrum of (*R,R*)-**7b** (CDCl_3).

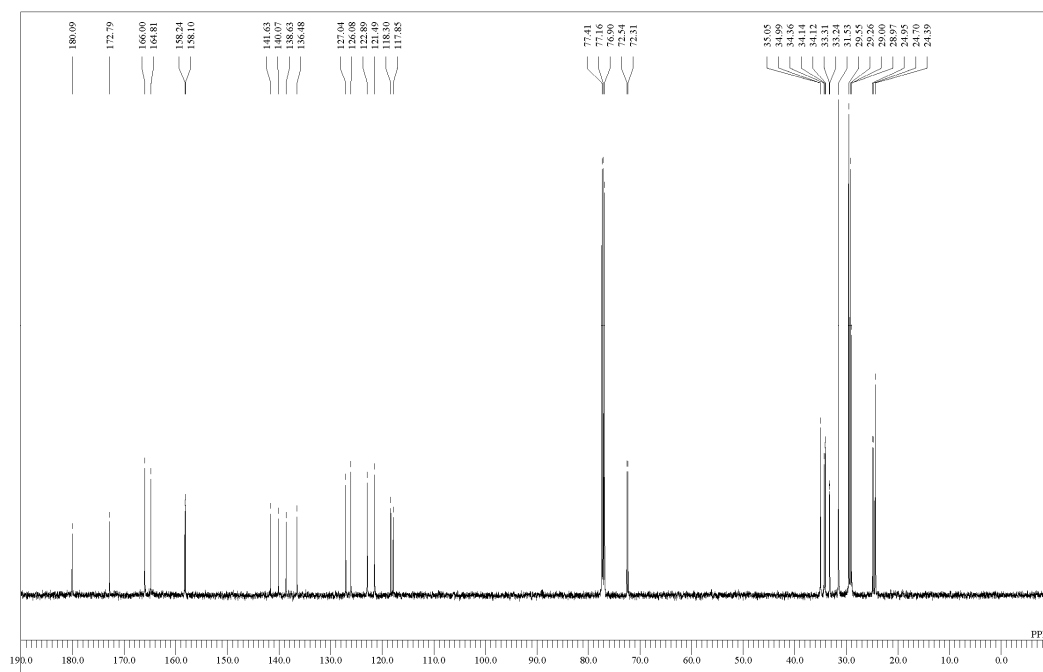


Figure S4. ^{13}C NMR spectrum of (*R,R*)-**7b** (CDCl_3).

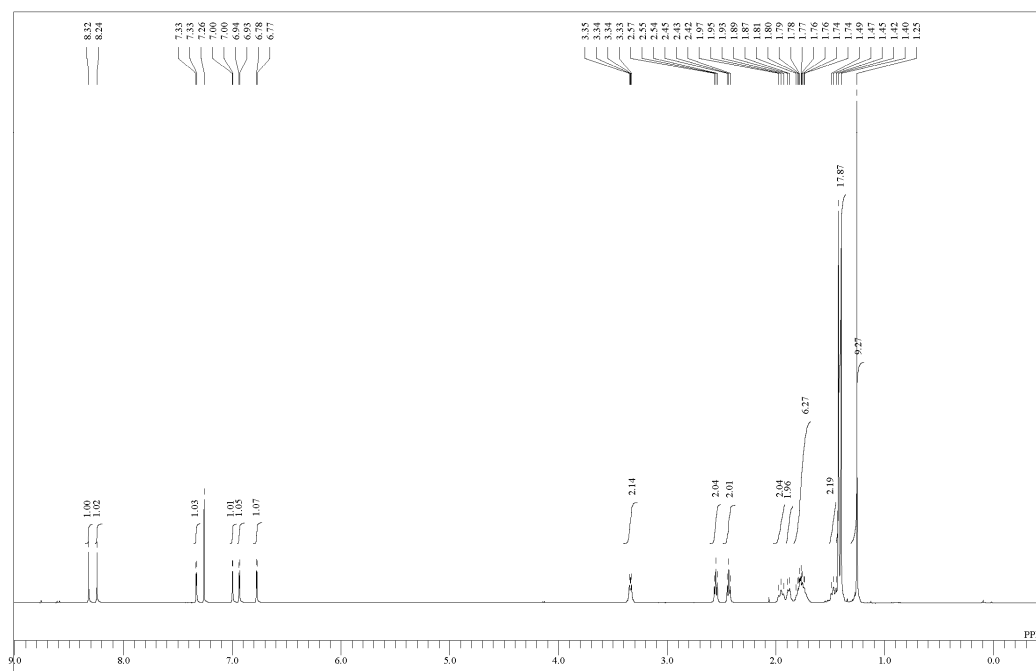


Figure S5. ¹H NMR spectrum of (R,R)-7c (CDCl₃).

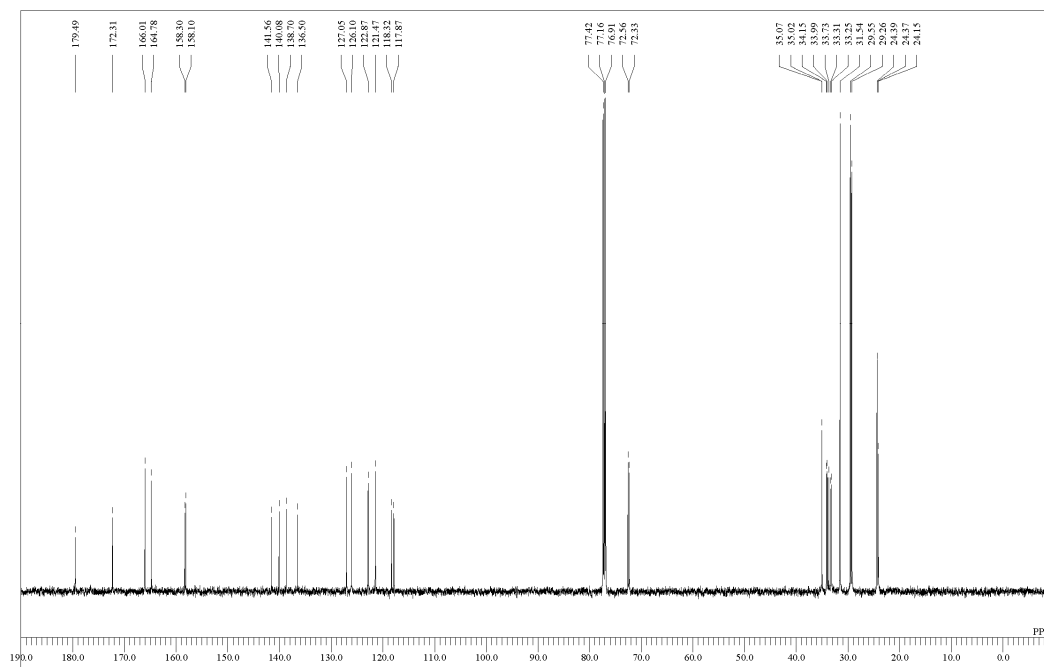


Figure S6. ¹³C NMR spectrum of (R,R)-7c (CDCl₃).

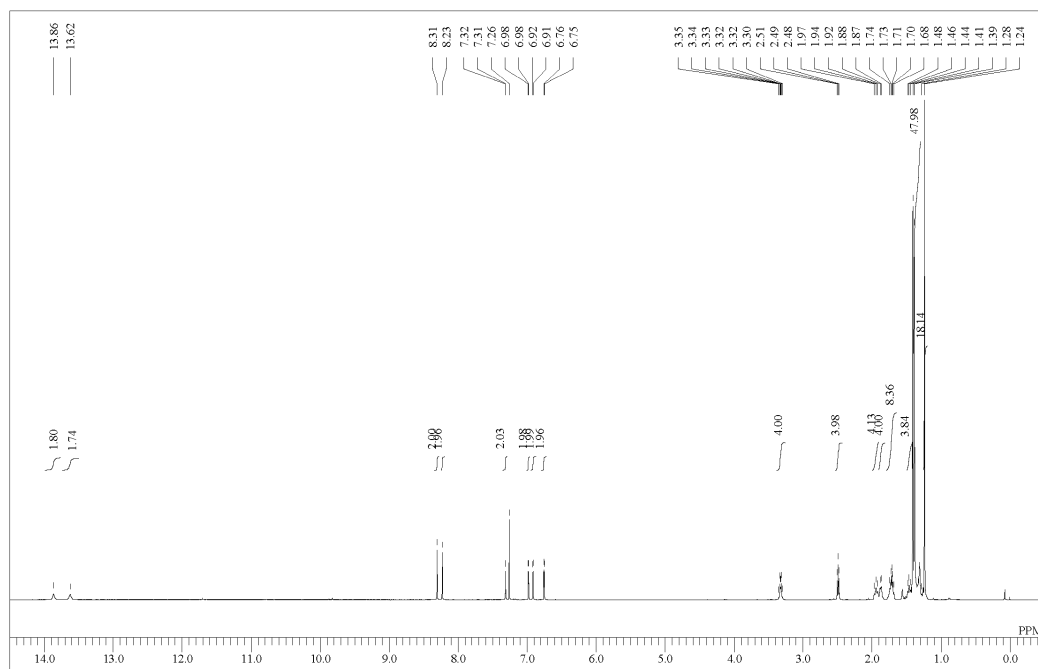


Figure S7. ¹H NMR spectrum of (R,R)-(S,S)-8a (CDCl₃).

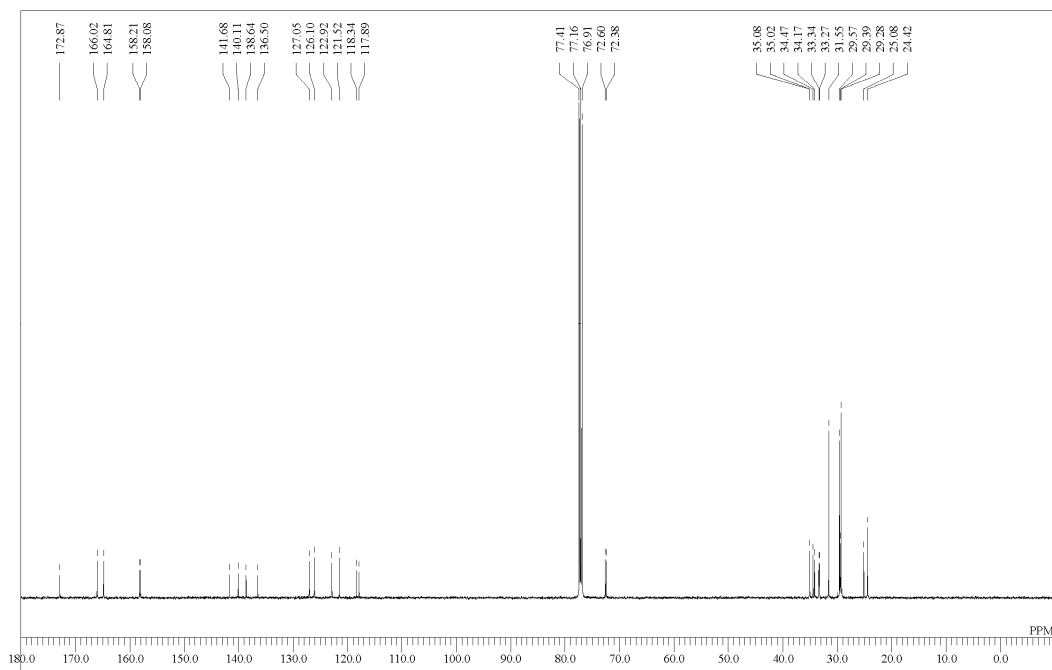


Figure S8. ¹³C NMR spectrum of (R,R)-(S,S)-8a (CDCl₃).

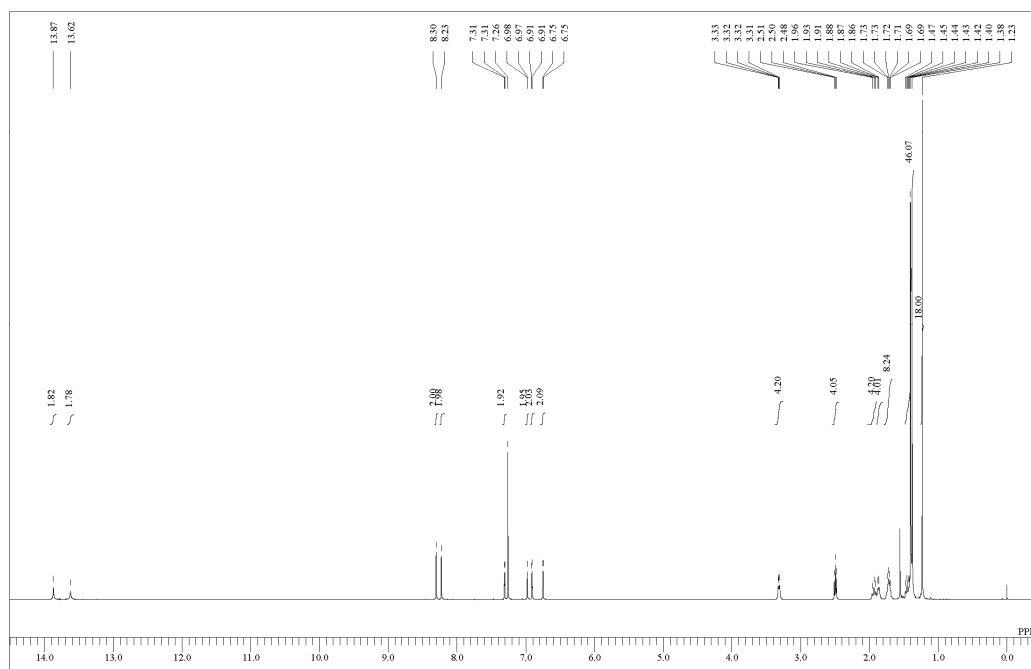


Figure S9. ¹H NMR spectrum of (R,R)-(S,S)-8b (CDCl₃).

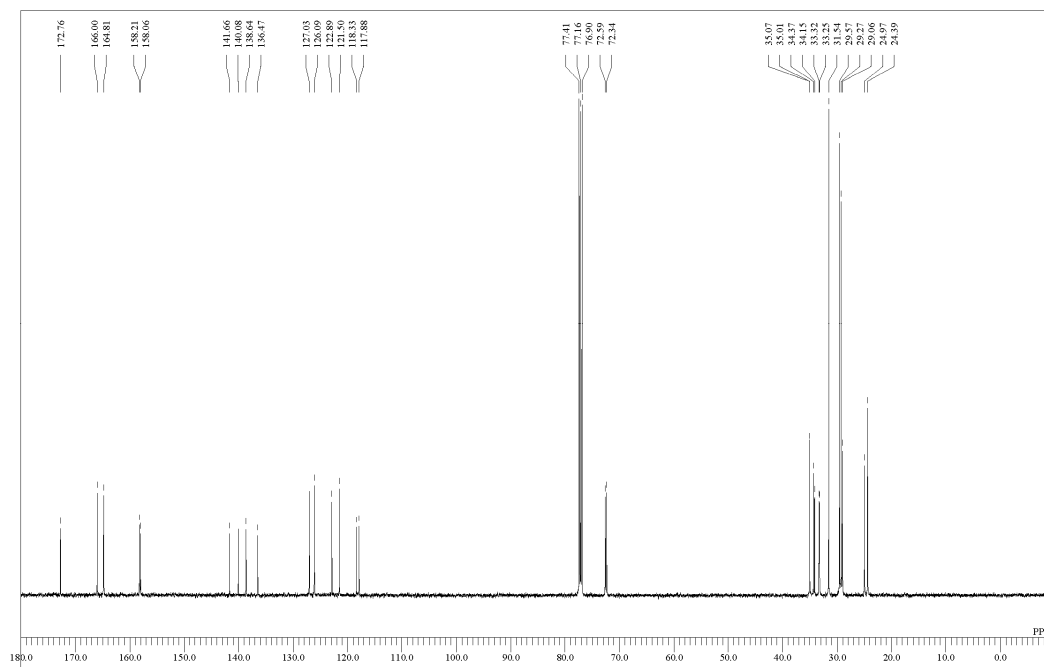


Figure S10. ¹³C NMR spectrum of (R,R)-(S,S)-8b (CDCl₃).

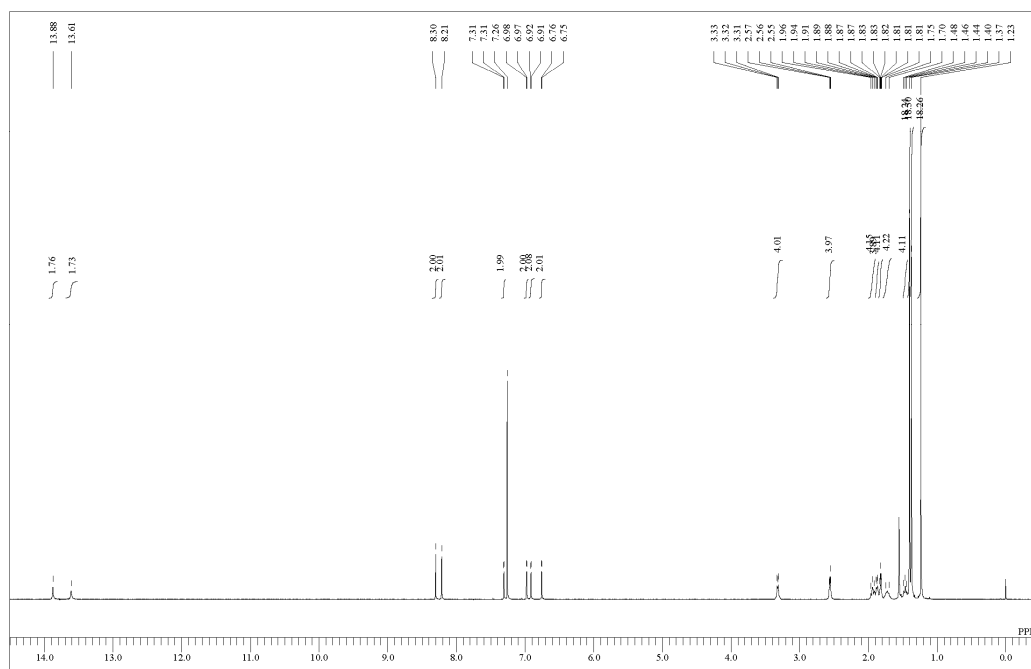


Figure S11. ¹H NMR spectrum of (R,R)-(S,S)-8c (CDCl₃).

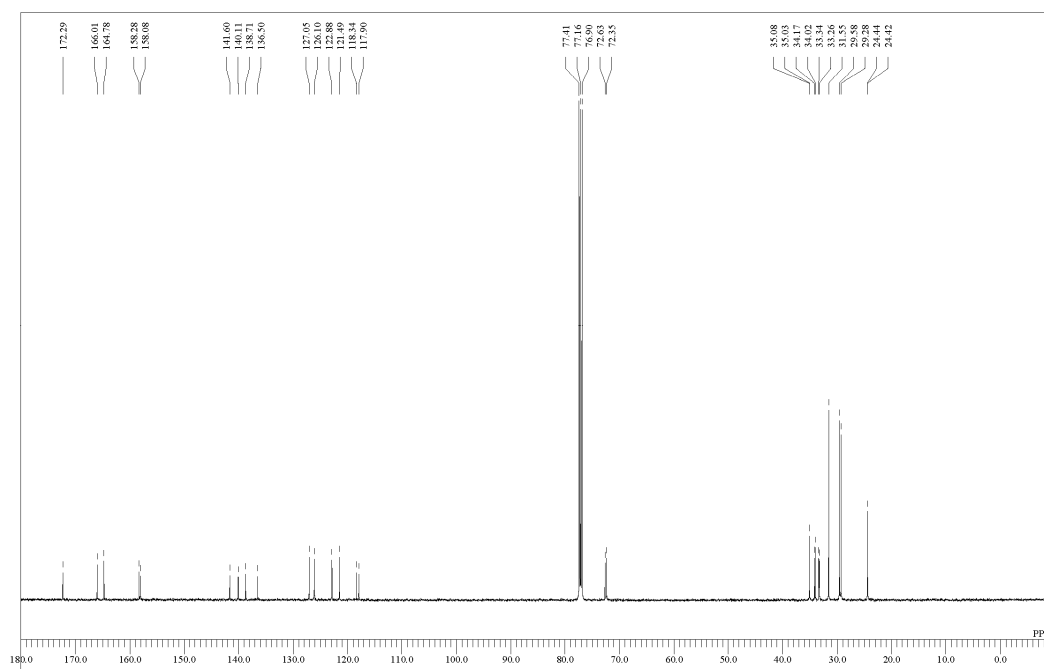


Figure S12. ¹³C NMR spectrum of (R,R)-(S,S)-8c (CDCl₃).

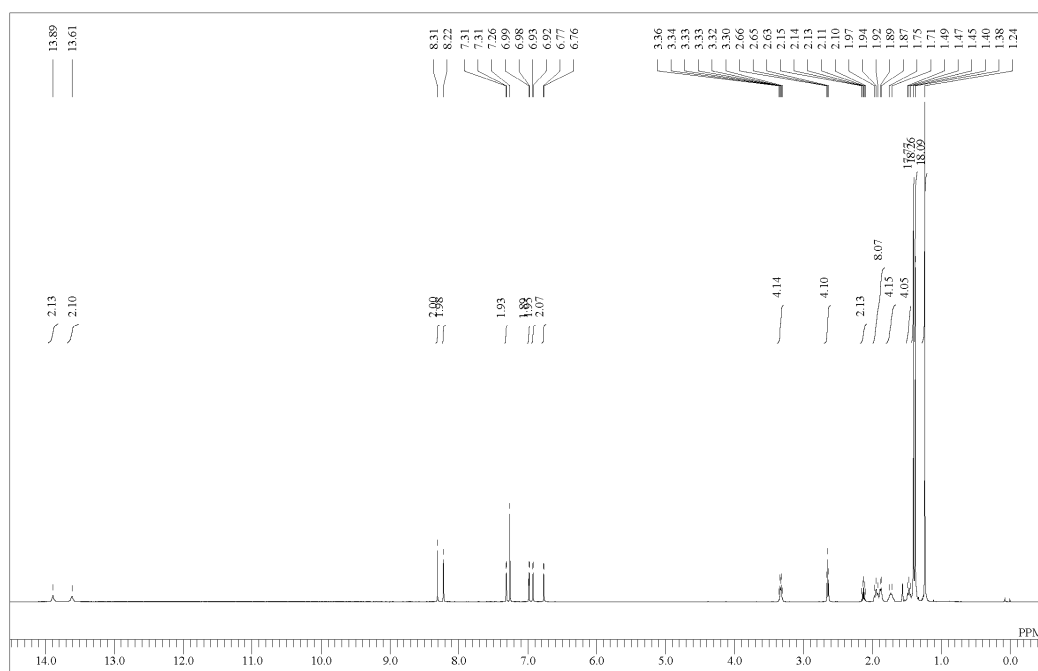


Figure S13. ¹H NMR spectrum of (R,R)-(S,S)-8d (CDCl₃).

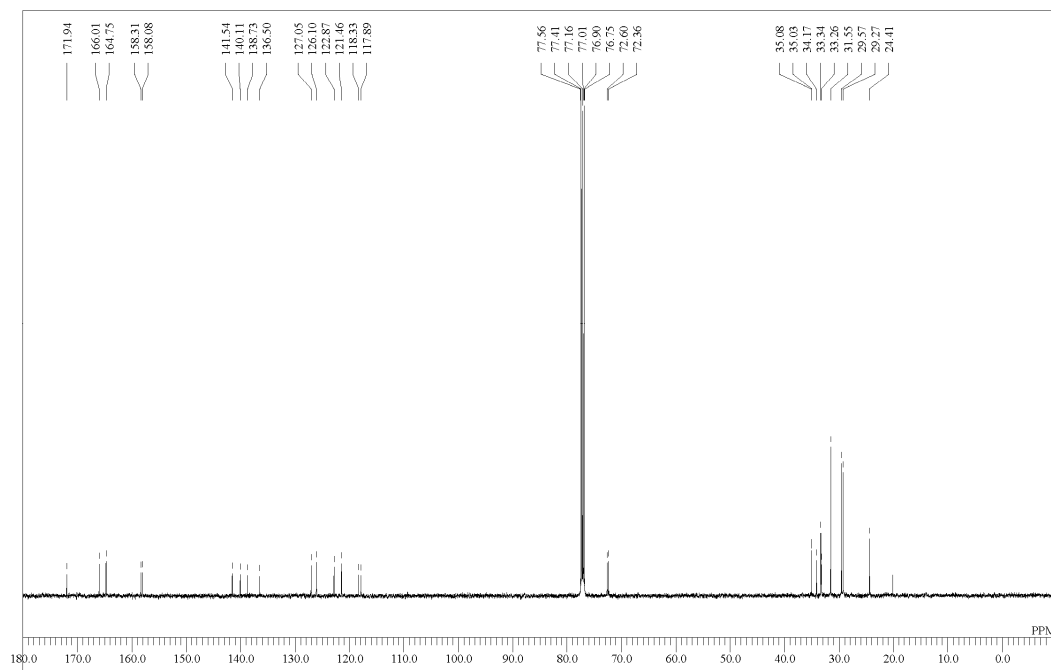


Figure S14. ¹³C NMR spectrum of (R,R)-(S,S)-8d (CDCl₃).

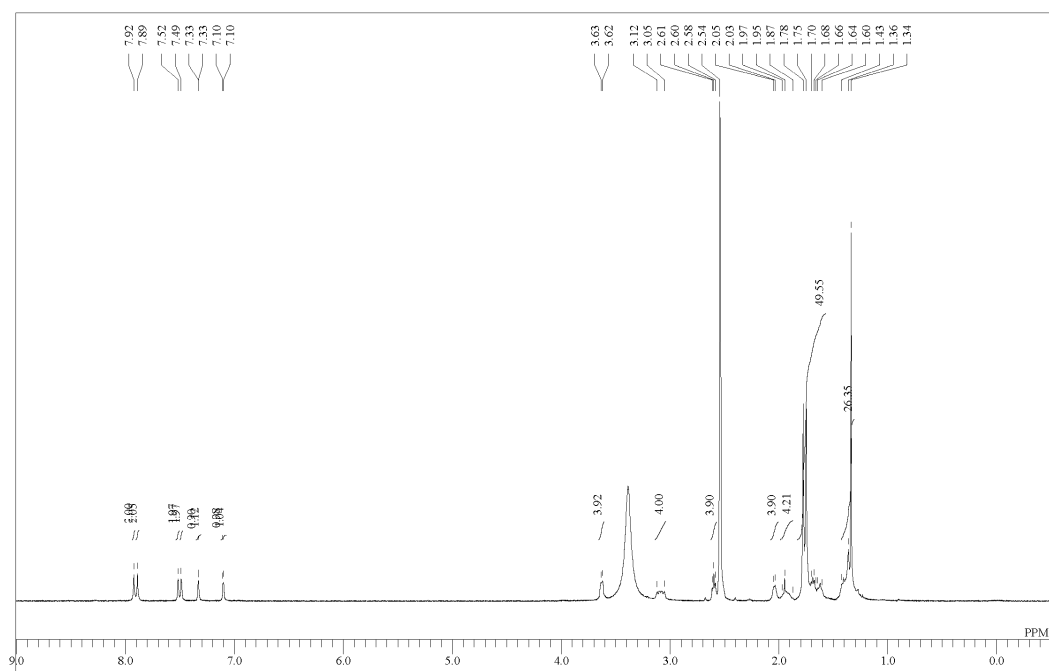


Figure S15. ¹H NMR spectrum of (R,R)-(S,S)-1 (DMSO-d₆).

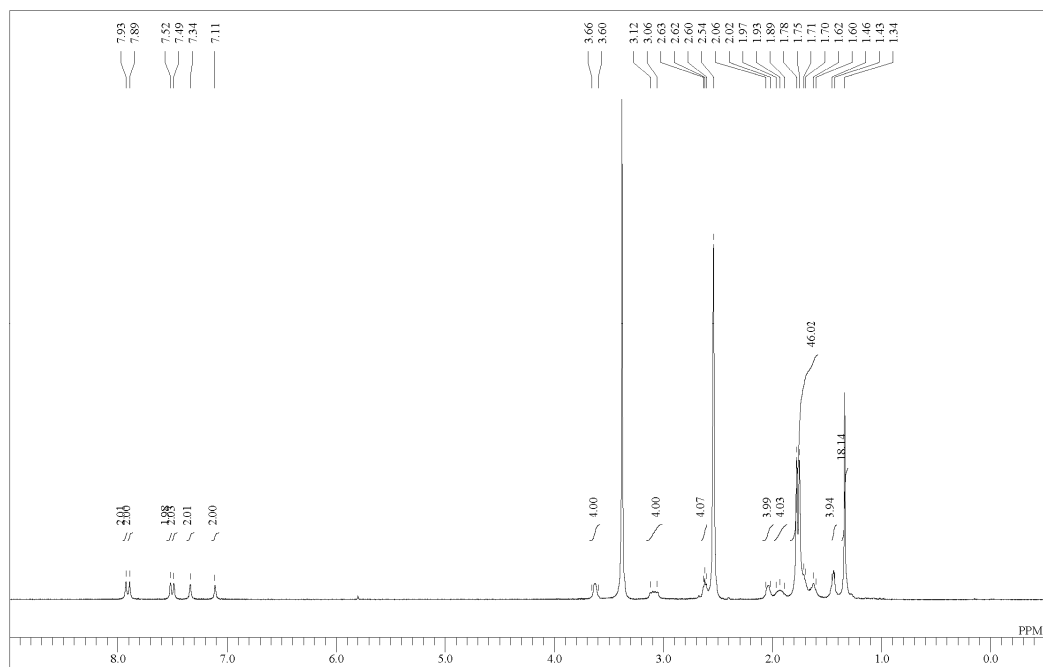


Figure S16. ¹H NMR spectrum of (R,R)-(S,S)-2 (DMSO-d₆).

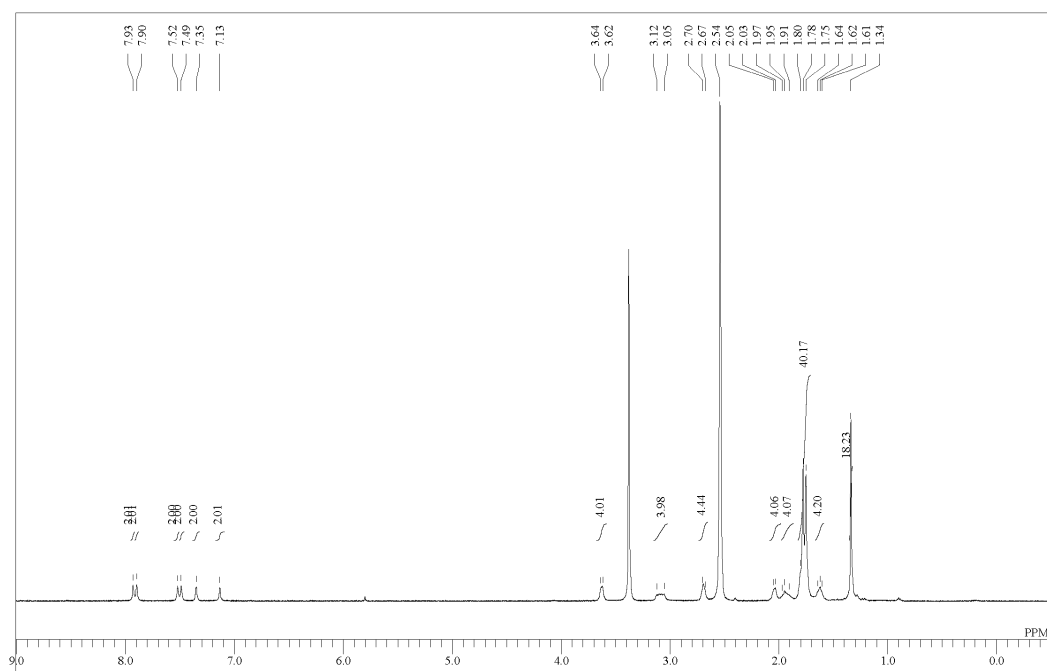


Figure S17. ¹H NMR spectrum of (R,R)-(S,S)-3 (DMSO-d₆).

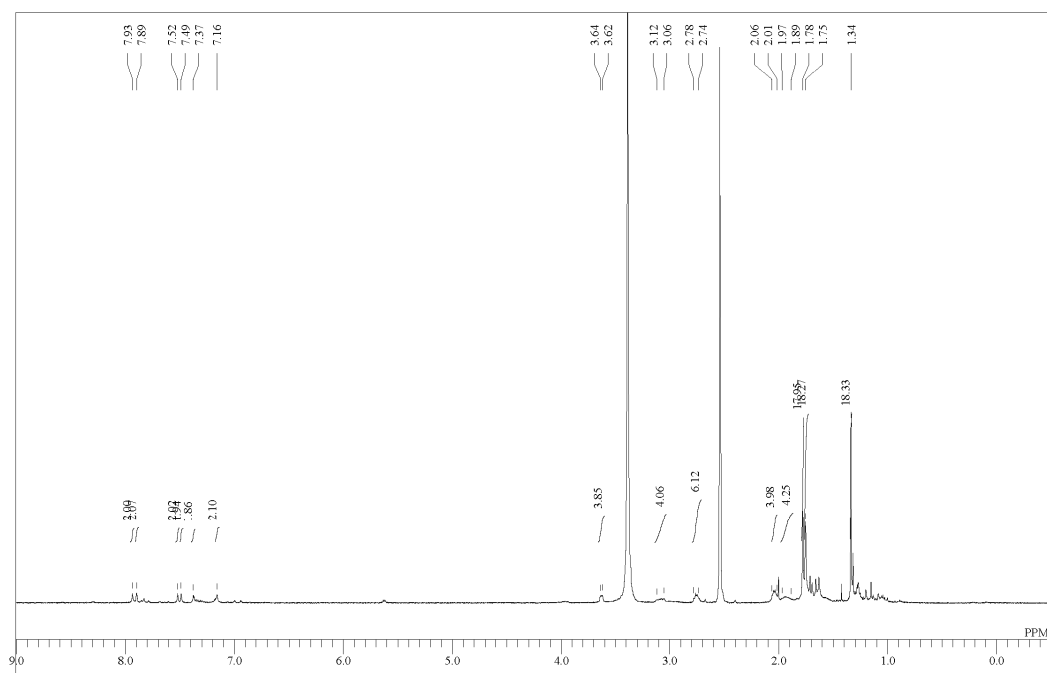


Figure S18. ¹H NMR spectrum of (R,R)-(S,S)-4 (DMSO-d₆).

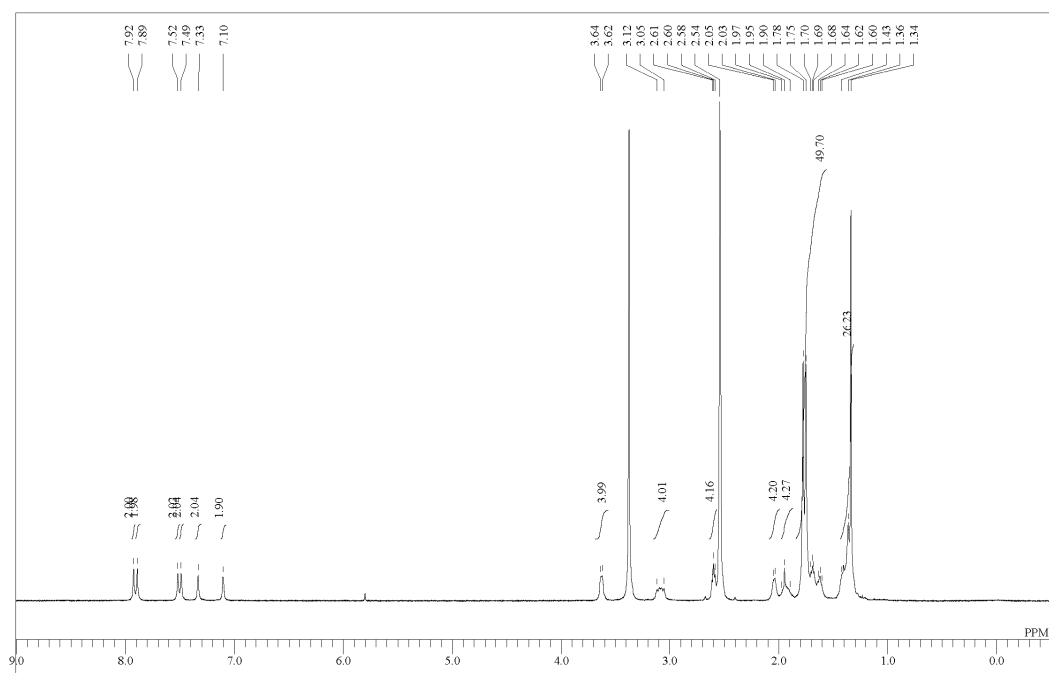


Figure S19. ^1H NMR spectrum of (R,R) -(R,R)-**1** (DMSO-d_6).

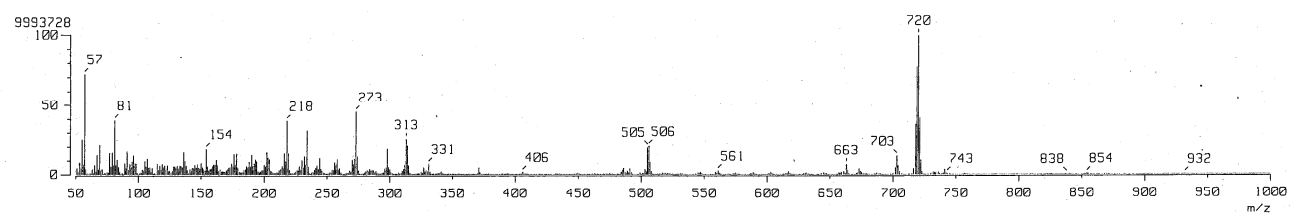


Figure S20. Mass spectrum (FAB) of (*R,R*)-**7a**.

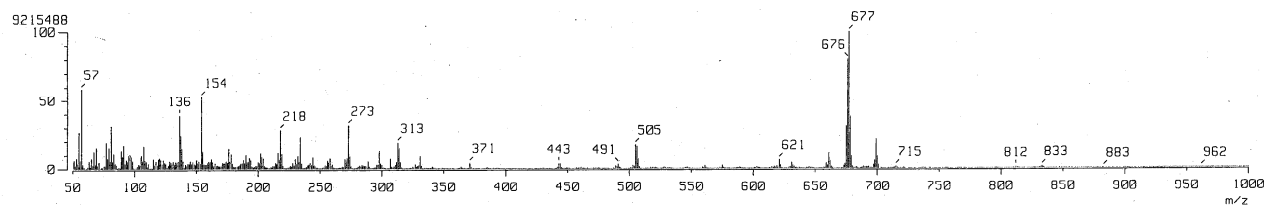
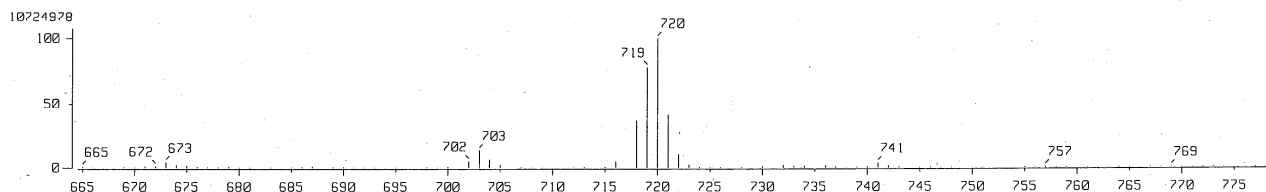


Figure S21. Mass spectrum (FAB) of (*R,R*)-**7b**.

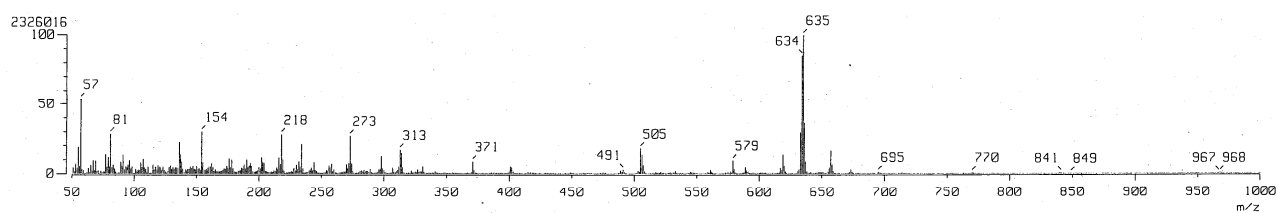
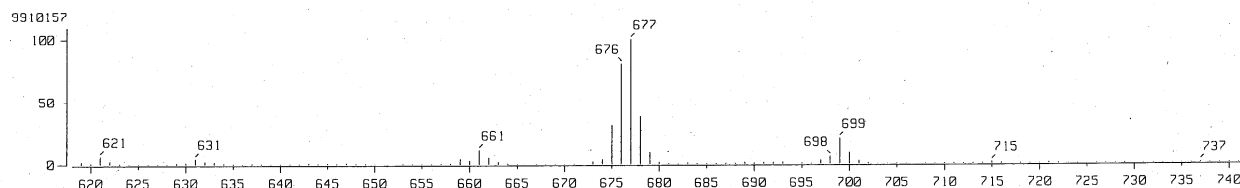
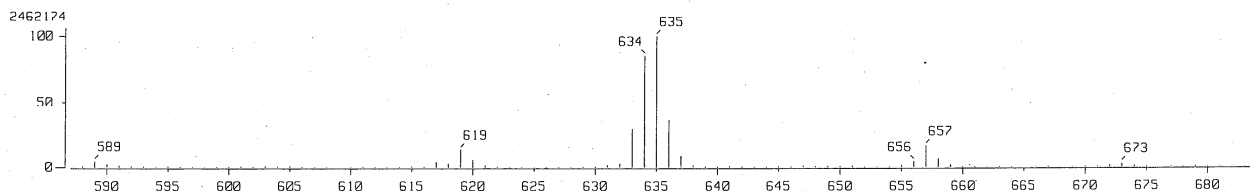


Figure S22. Mass spectrum (FAB) of (*R,R*)-**7c**.



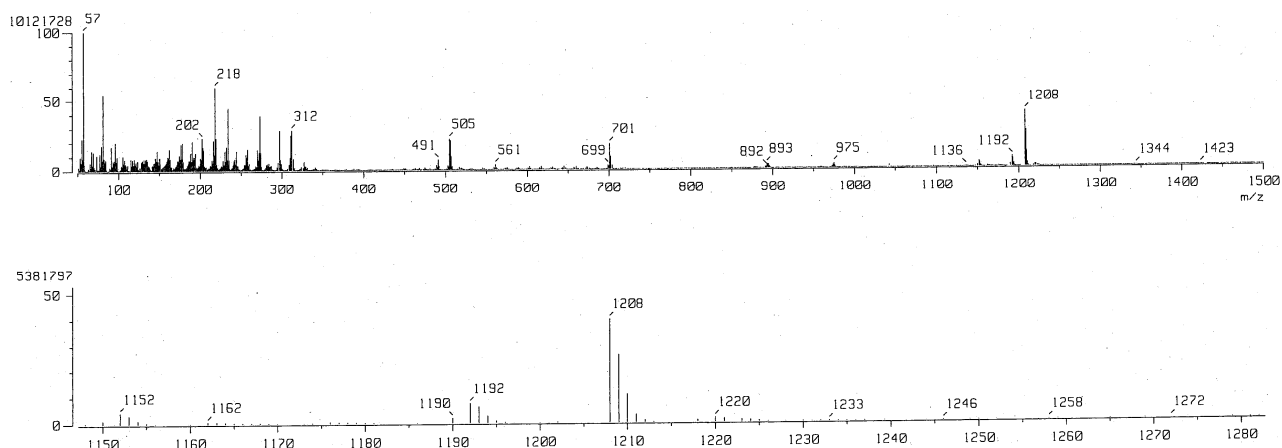


Figure S23. Mass spectrum (FAB) of (R,R)-(S,S)-8a.

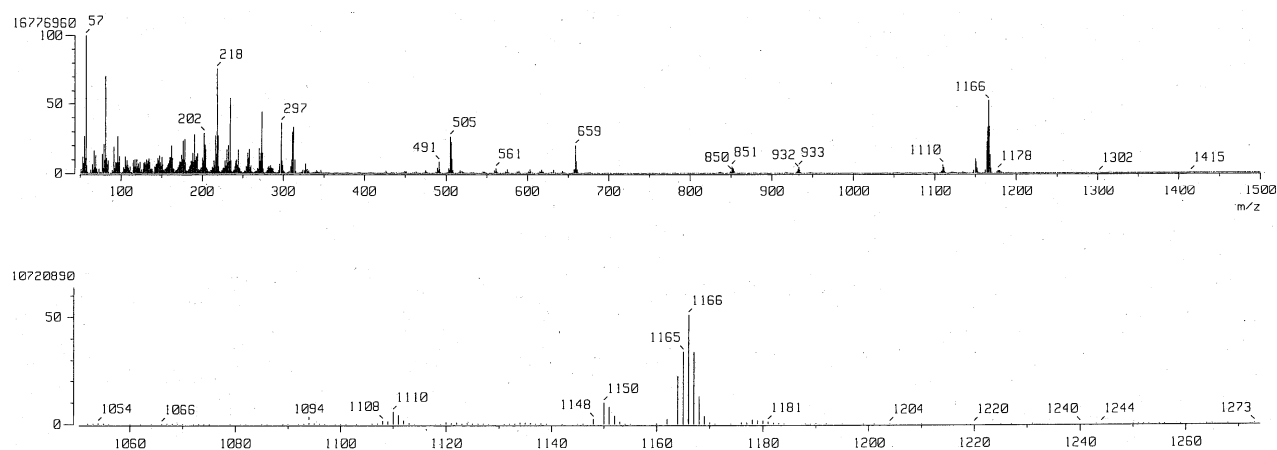


Figure S24. Mass spectrum (FAB) of (R,R)-(S,S)-8b.

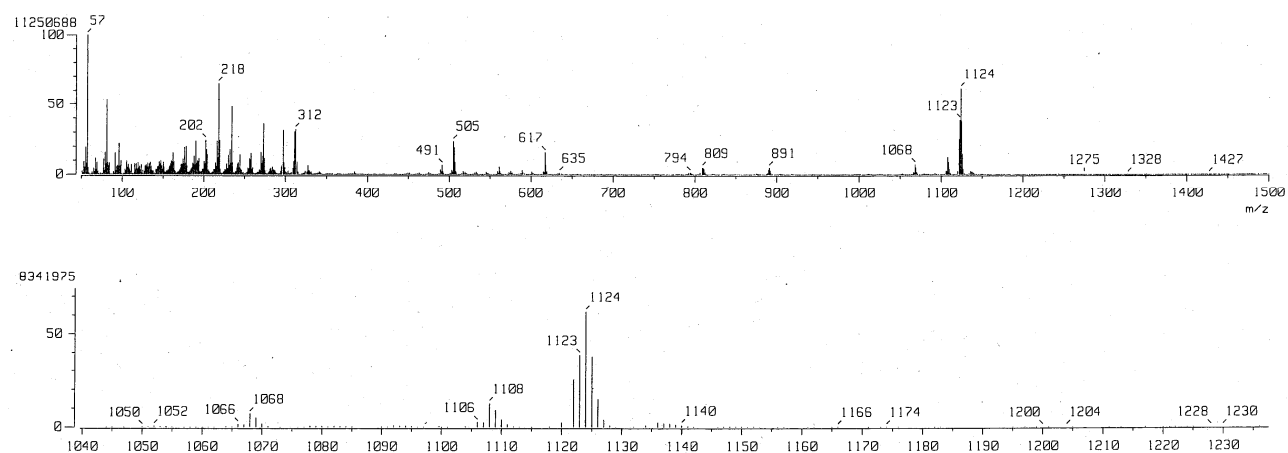


Figure S25. Mass spectrum (FAB) of (R,R)-(S,S)-8c.

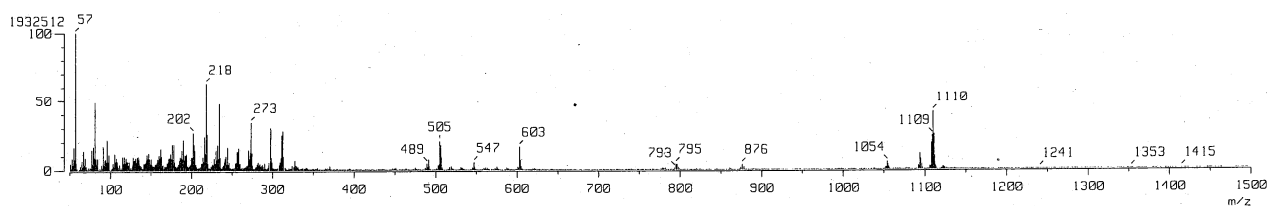


Figure S26. Mass spectrum (FAB) of *(R,R)-(S,S)*-8d.

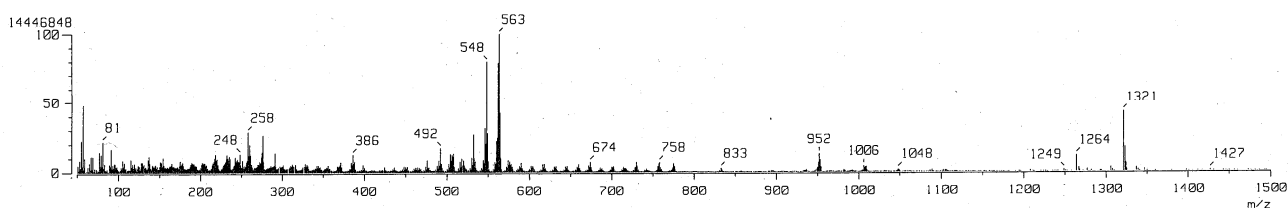
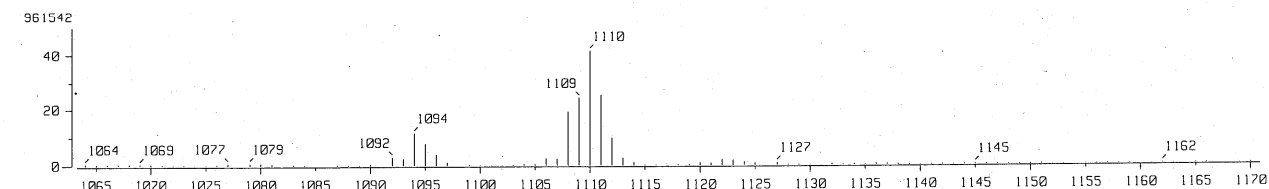


Figure S27. Mass spectrum (FAB) of *(R,R)-(S,S)*-1.

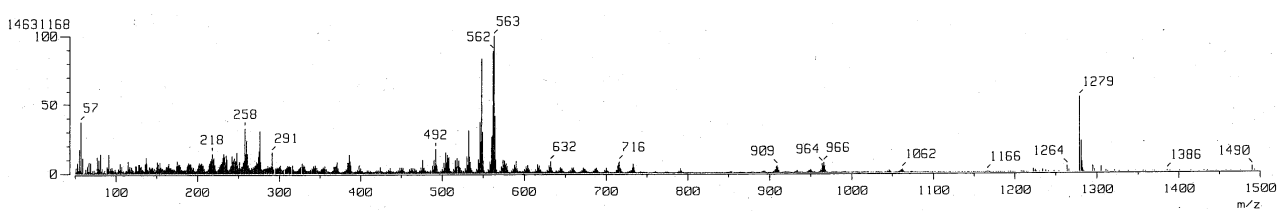
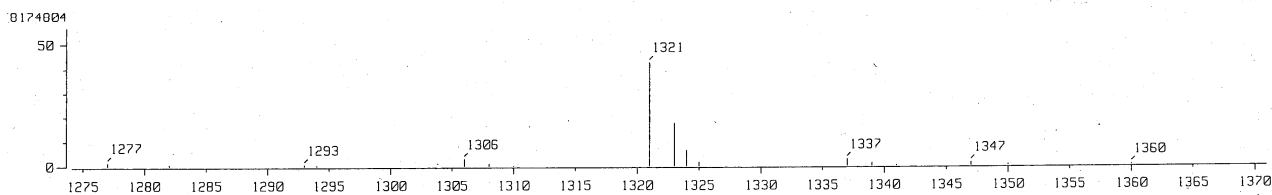
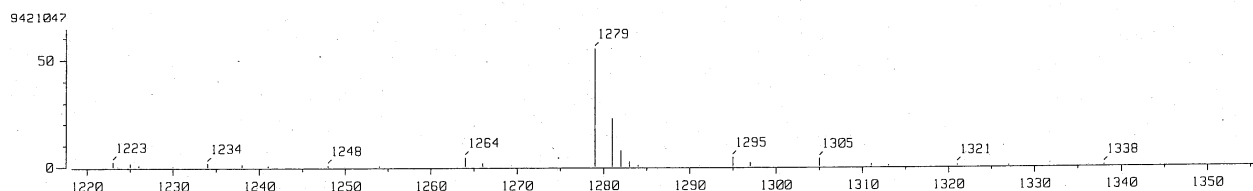


Figure S28. Mass spectrum (FAB) of *(R,R)-(S,S)*-2.



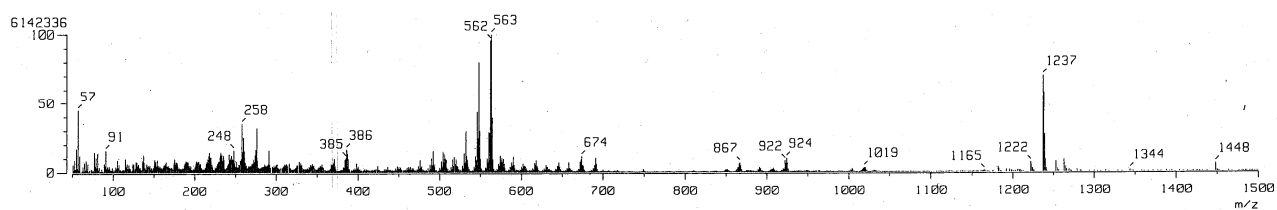


Figure S29. Mass spectrum (FAB) of (R,R)-(S,S)-3.

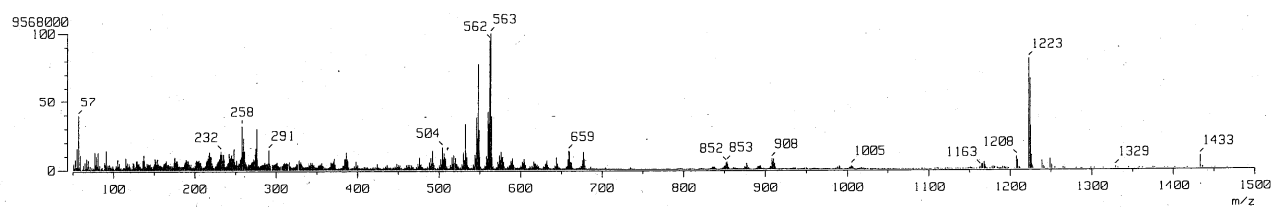
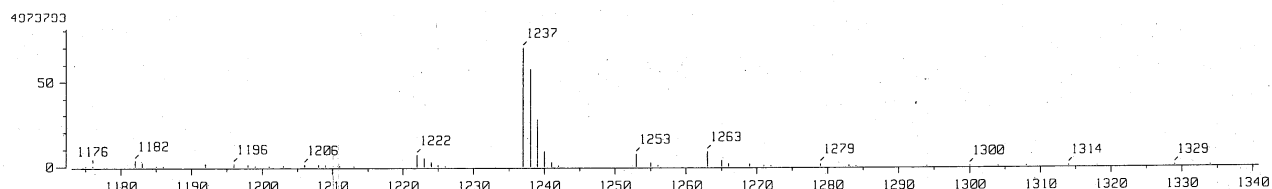
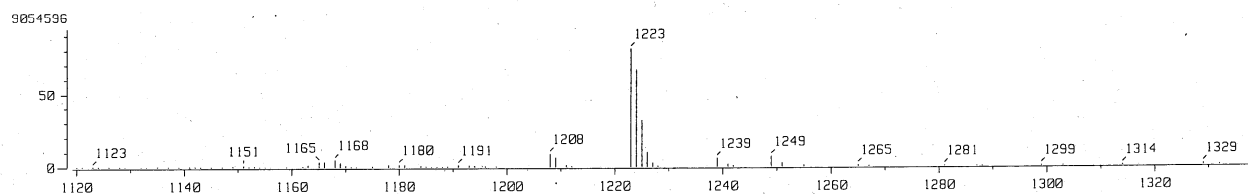


Figure S30. Mass spectrum (FAB) of (R,R)-(S,S)-4.



References

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- 2) Madhavan, N.; Takatani, T.; Sherrill, C. D.; Weck, M. *Chem. Eur. J.* **2009**, *15*, 1186.
- 3) Reger, T. S.; Janda, K. D. *J. Am. Chem. Soc.* **2000**, *122*, 6929.
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