Supporting Information

Desymmetrization of 1,4-Cyclohexadienyltriisopropoxysilane using Cu-catalysis

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Table of Contents:

General, Experimental Procedures, and References..........................................................S2-S11

Confirmation of Absolute Configuration of Compounds 2 (R = Ph)..................................... S12

$^1$H NMR Spectra and GC or HPLC Chromatograms of Compounds 2..................................S13-S30

$^1$H and $^{13}$C NMR Spectra of New Compounds 2 (R = 4-i-PrC$_6$H$_4$, 4-t-BuC$_6$H$_4$, 4-FC$_6$H$_4$, 4-ClC$_6$H$_4$, 3-MeC$_6$H$_4$, 3-BrC$_6$H$_4$, 5-Br-2-furyl, 2-thienyl, and 5-Br-2-thienyl) ..................................................S31-S39
General

$^1$H NMR spectra were recorded at 300 or 400 MHz and $^{13}$C NMR spectra at 75 or 100 MHz on a Bruker AMX 400, DPX300 or ARX 300. Chemical shifts δ in ppm relative to CDCl$_3$ (δ = 7.26 and δ = 77.0 ppm) as internal standard. The multiplicity in the $^{13}$C NMR spectra was determined by DEPT spectra and was indicated by (s), (d), (t), and (q) for quaternary, tertiary, secondary, and primary carbons, respectively. Flash chromatography: silica gel 60 (40 – 63 µm, Merck). FT-IR spectra were recorded on a Bruker IFS28. Mass spectra were recorded on a Varian CH7 (EI), Finnigan MAT95S, a Bruker Daltonics Micro Tof, a Waters-Micromass Quatro LCZ (ESI). The enantiomeric ratio (er) of the syn-isomer and the isomer ratio were determined by GC (Hewlett Packard 6890 or Shimadzu GC-2014) equipped with a Chiraldex G-TA column or a Supelco γ-DEX column and by HPLC (KNAUSER instrument, High Precision KNAUSER HPLC Pump, Eurochrom V3.05 software) equipped with a Chiralcel OD-H column. In general, reactions were carried out in dry THF, which had been distilled from potassium, under an argon atmosphere.

Materials

Chiral ligands were purchased from Acros, Sigma-Aldrich, and Strem and used as received. The following ligands were generously provided by Solvias (JOSIPHOS, WALPHOS, MANDYPHOS, and TANIAPHOS).

General Procedure for the Desymmetrization of 3 (GP1).

A 10 mL Schlenk tube was charged with a stir bar and flushed with Ar. (S)-DIFLUORPHOS (6.8 mg, 0.01 mmol, 10 mol%), Cu(OTf)$_2$ (3.6 mg, 0.01 mmol, 10 mol%) and THF (0.15 mL) were added. The mixture was stirred under Ar at room temperature for 10 minutes followed by the addition of CF$_3$CH$_2$OH (22 µL, 0.31 mmol, 300 mol%). After cooling to -25 °C, a solution of cyclohexadiene 3 (85 mg, 0.30 mmol, 300 mol%) and an aldehyde (0.1 mmol, 100 mol%) in THF (0.2 mL) were added followed by dropwise addition of TBAF (1M in THF; 0.1 mL, 100 mol%). After being stirred for 20 h at -25 °C, the mixture was diluted with pentane. The resulting suspension was purified by flash chromatography over silica gel to afford the corresponding homoallylic alcohol (9:1, pentane:MTBE).

General Procedure for the Synthesis of Racemic Products (GP2).

$s$BuLi (0.60 mL, 0.72 mmol, 1.2 equiv, 1.26M in hexanes) and TMEDA (110 µL, 729 µmol, 1.2 equiv) were added to a solution of 1,4-cyclohexadiene (60 µL, 51 mg, 0.64 mmol, 1.1 equiv) in THF (3.0 mL) at -78 °C. The resulting yellow solution was stirred for 90–120 min at this temperature. Titanium(IV)tetraisopropoxide (0.25 mL, 0.83 mmol, 1.4 equiv) was added at -78 °C. The resulting reaction mixture was stirred for 30 min at this temperature. An aldehyde (0.58 mmol, 1.0 equiv) was then added. The brown reaction mixture was stirred for 1h at -78 °C. The mixture was allowed to slowly warm up to room temperature and was then stirred overnight. Water and MTBE were added and a white precipitate formed. The mixture was stirred for 15 min at room temperature. After removal of the white precipitate by filtration over Celite, the organic layer was separated and the aqueous phase was extracted with MTBE. The combined organic layers were washed with brine and dried over MgSO$_4$. The solvents were removed in vacuo. The racemic alcohols were purified by flash chromatography over silica gel (9:1, pentane:MTBE).
Cyclohexa-2,4-dien-1-yl-(phenyl)methanol (2; R = Ph)\(^1\)

Homoallylic alcohol 2 (R = Ph) was obtained using PhCHO (11 mg, 0.10 mmol) by applying GP1 in 83\% yield as a colorless oil.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.41−7.25\) (m, 5H; Ph-H), 6.07−5.70 (m, 3H; vinyl-H), 5.42−5.35 (m, 1H; vinyl-H), 4.66 (d, \(J = 7.4\) Hz, 1H; CH-OH), 2.70−2.59 (m, 1H), 2.51−2.38 (m, 1H), 2.36−2.24 (m, 1H), 1.90 (brs, 1H) ppm.

\(\text{syn} : \text{anti} : 4 = 90.1 : 8.4 : 1.5; \text{e.r. of syn} = 94.2 : 5.8\) (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C \((T_0)\) then a temperature gradient (rate, 0.5 °C min\(^{-1}\), final temperature 180 °C \((T_F)\)). Retention times: \text{syn}-isomer (enantiomer 1: 88.78 min, enantiomer 2: 89.58 min), \text{anti}-isomer (92.45 min), 4 (91.48 min).

Cyclohexa-2,4-dien-1-yl-(4-methylphenyl)methanol (2; R = 4-MeC\(_6\)H\(_4\))\(^1\)

Homoallylic alcohol 2 (R = 4-MeC\(_6\)H\(_4\)) was obtained using 4-MeC\(_6\)H\(_4\)CHO (13 mg, 0.11 mmol) by applying GP1 in 60\% yield as a colorless oil.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.22\) and 7.16 (AA’BB’; \(J_{AB} = 8.1\) Hz, 4H; Ar-H), 6.03−5.70 (m, 3H; vinyl-H), 5.41−5.34 (m, 1H; vinyl-H), 4.62 (d, \(J = 7.5\) Hz, 1H; CH-OH), 2.72−2.58 (m, 1H), 2.50−2.25 (m, 2H), 2.35 (s, 3H; CH\(_3\)), 1.84 (brs, 1H) ppm.

\(\text{syn} : \text{anti} : 4 = 93.1 : 6.3 : 0.6; \text{e.r. of syn-isomer} = 96.6 : 3.4\) (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C \((T_0)\) then a temperature gradient (rate, 0.3 °C min\(^{-1}\), final temperature 180 °C \((T_F)\)). Retention times: \text{syn}-isomer (enantiomer 1: 148.44 min, enantiomer 2: 149.75 min), \text{anti}-isomer (154.28 min), 4 (152.49 min).

Cyclohexa-2,4-dien-1-yl-(4-methoxyphenyl)methanol (2; R = 4-OMeC\(_6\)H\(_4\))\(^1\)

Homoallylic alcohol 2 (R = 4-OMeC\(_6\)H\(_4\)) was obtained using 4-OMeC\(_6\)H\(_4\)CHO (13 mg, 0.11 mmol) by applying GP1 in 59\% yield as a colorless solid.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.25\) and 6.88 (AA’BB’; \(J_{AB} = 8.6\) Hz, 4H; Ar-H), 6.02−5.69 (m, 3H; vinyl-H), 5.39−5.32 (m, 1H; vinyl-H), 4.60 (d, \(J = 7.7\) Hz, 1H; CH-OH), 3.81 (s, 3H; OCH\(_3\)), 2.70−2.56 (m, 1H), 2.50−2.28 (m, 2H), 1.83 (brs, 1H) ppm.

\(\text{syn} : \text{anti} : 4 = 95.5 : 3.3 : 1.2; \text{e.r. of syn-isomer} = 97.2 : 2.8\) (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C \((T_0)\) then a temperature gradient (rate, 0.3 °C min\(^{-1}\), final temperature 180 °C \((T_F)\)). Retention times: \text{syn}-isomer (enantiomer 1: 269.97 min, enantiomer 2: 271.35 min), \text{anti}-isomer (278.25 min), 4 (275.97 min).
(4-Bromophenyl)(cyclohexa-2,4-dien-1-yl)methanol (2; R = 4-BrC₆H₄)

Homoallylic alcohol 2 (R = 4-BrC₆H₄) was obtained using 4-BrC₆H₄CHO (18 mg, 0.10 mmol) by applying GP1 in 85% yield as a colorless oil.

\(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.47\) and \(7.21\) (AA’BB’; \(J_{AB} = 8.3\) Hz, 4H; Ar-H), \(6.09 – 5.70\) (m, 3H; vinyl-H), \(5.41 – 5.33\) (m, 1H; vinyl-H), \(4.64\) (d, \(J = 7.1\) Hz, 1H; CH-OH), \(2.65 – 2.52\) (m, 1H), \(2.48 – 2.35\) (m, 1H), \(2.34 – 2.20\) (m, 1H), \(1.92\) (brs, 1H) ppm.

\(\text{syn : anti} = 92.4 : 7.6\); e.r. of \(\text{syn-isomer} = 92.4 : 7.6\) (determined by GC analysis using Chiraldex G-TA).

Temperature program: 0 min at 100 °C (\(T_0\)) then a temperature gradient (rate, \(0.3\) °C min\(^{-1}\), final temperature \(180\) °C (\(T_E\))). Retention times: \(\text{syn-isomer} (\text{enantiomer 1: 221.73 min, enantiomer 2: 223.28 min}), \text{anti-isomer (227.00 min).}\)

Cyclohexa-2,4-dien-1-yl-(2-methylphenyl)methanol(2; R = 2-MeC₆H₄)

Homoallylic alcohol 2 (R = 2-MeC₆H₄) was obtained using 2-MeC₆H₄CHO (13 mg, 0.11 mmol) by applying GP1 in 83% yield as a colorless oil.

\(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.50 – 7.44\) (m, 1H; Ar-H), \(7.27 – 7.11\) (m, 3H; Ar-H), \(6.06 – 5.70\) (m, 3H; vinyl-H), \(5.37 – 5.30\) (m, 1H; vinyl-H), \(4.96\) (d, \(J = 7.5\) Hz, 1H; CH-OH), \(2.71 – 2.46\) (m, 1H), \(2.40 – 2.20\) (m, 2H), \(2.31\) (s, 3H; CH\(_3\)), \(1.67\) (brs, 1H) ppm.

\(\text{syn : anti} = 90.7 : 9.3\); e.r. of \(\text{syn-isomer} = 91.7 : 8.3\) (determined by GC analysis using Chiraldex G-TA).

Temperature program: 5 min at 100 °C (\(T_0\)) then a temperature gradient (rate, \(2.0\) °C min\(^{-1}\), final temperature \(180\) °C (\(T_E\))). Retention times: \(\text{syn-isomer} (\text{enantiomer 1: 49.63 min, enantiomer 2: 50.13 min}), \text{anti-isomer (52.35 min).}\)

Cyclohexa-2,4-dien-1-yl-(2-methoxyphenyl)methanol (2; R = 2-OMeC₆H₄)

Homoallylic alcohol 2 (R = 2-OMeC₆H₄) was obtained using 2-OMeC₆H₄CHO (14 mg, 0.10 mmol) by applying GP1 in 68% yield as a colorless oil.

\(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.28 – 7.21\) (m, 2H; Ar-H), \(6.99 – 6.92\) (m, 1H; Ar-H), \(6.91 – 6.86\) (m, 1H; Ar-H), \(6.10 – 5.70\) (m, 3H; vinyl-H), \(5.43 – 5.34\) (m, 1H; vinyl-H), \(4.82 – 4.74\) (m, 1H; CH-OH), \(3.85\) (s, 3H; OCH\(_3\)), \(2.86 – 2.74\) (m, 1H), \(2.68 – 2.62\) (m, 1H), \(2.54 – 2.40\) (m, 1H), \(2.36 – 2.24\) (m, 1H) ppm.

\(\text{syn : anti} = 94.6 : 5.4\); e.r. of \(\text{syn-isomer} = 95.6 : 4.4\) (determined by GC analysis using Supelco \(\gamma\)-DEX).

Temperature program: 5 min at 100 °C (\(T_0\)) then a temperature gradient (rate, \(0.5\) °C min\(^{-1}\), final temperature \(200\) °C (\(T_E\))). Retention times: \(\text{syn-isomer (enantiomer 1: 199.57 min, enantiomer 2: 200.92 min}), \text{anti-isomer (206.89 min).}\)
Cyclohexa-2,4-dien-1-yl-(3-methoxyphenyl)methanol (2; $R = 3$-OMeC$_6$H$_4$)

Homoallylic alcohol 2 ($R = 3$-OMeC$_6$H$_4$) was obtained using 3-OMeC$_6$H$_4$CHO (15 mg, 0.11 mmol) by applying GP1 in 59% yield as a colorless solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.30–7.22 (m, 1H; Ar-H), 6.93–6.88 (m, 2H; Ar-H), 6.85–6.80 (m, 1H; Ar-H), 6.06–5.70 (m, 3H; vinyl-H), 5.45–5.37 (m, 1H; vinyl-H), 4.64 (d, $J = 7.5$ Hz, 1H; CH-OH), 3.81 (s, 3H; OCH$_3$), 2.70–2.58 (m, 1H), 2.50–2.20 (m, 2H), 1.80 (brs, 1H ppm).

$^s$yn : $^a$nti = 82.4 : 13.6 : 4.0; e.r. of $^s$yn = 94.2 : 5.8 (determined by GC analysis using Chiraldex G-TA).

Retention times: syn-isomer (enantiomer 1: 261.37 min, enantiomer 2: 263.07 min), anti-isomer (269.38 min), 4 (265.96 min).

Cyclohexa-2,4-dien-1-yl-(2-naphthyl)methanol (2; $R = 2$-naphtyl)

Homoallylic alcohol 2 ($R = 2$-naphtyl) was obtained using 2-naphthaldehyde (16 mg, 0.10 mmol) by applying GP1 in 79% yield as a colorless solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.86–7.77 (m, 4H; Ar-H), 7.52–7.43 (m, 3H; Ar-H), 6.10–5.69 (m, 3H; vinyl-H), 5.45–5.37 (m, 1H; vinyl-H), 4.84 (d, $J = 7.5$ Hz, 1H; CH-OH), 2.80–2.70 (m, 1H), 2.55–2.44 (m, 1H), 2.40–2.27 (m, 1H), 2.20–1.90 (m, 1H) ppm.

$^s$yn : $^a$nti = 86.5 : 13.5; e.r. of $^s$yn-isomer = 92.8 : 7.2 (determined by HPLC analysis using Chiralcel OD-H).

Eluent: 1 % $i$-PrOH in cyclohexane (1 mL/min). Retention times: $^s$yn-isomer (enantiomer 1: 28.92 min, enantiomer 2: 38.09 min), anti-isomer (41.00 min).

Cyclohexa-2,4-dien-1-yl-(2-furyl)methanol (2; $R = 2$-furyl)

Homoallylic alcohol 2 ($R = 2$-furyl) was obtained using 2-furaldehyde (10 mg, 0.10 mmol) by applying GP1 in 71% yield as a colorless oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.39–7.37 (m, 1H; Ar-H), 6.37–6.33 (m, 1H; Ar-H), 6.28–6.25 (m, 1H; Ar-H), 6.06–5.70 (m, 3H; vinyl-H), 5.50–5.44 (m, 1H; vinyl-H), 4.64 (d, $J = 7.7$ Hz, 1H; CH-OH), 2.88–2.74 (m, 1H), 2.50–2.30 (m, 2H), 1.87 (brs, 1H ppm).

$^s$yn : $^a$nti = 72.4 : 27.6; e.r. of $^s$yn-isomer = 94.3 : 5.7 (determined by GC analysis using Chiraldex G-TA).

Retention times: $^s$yn-isomer (enantiomer 1: 70.83 min, enantiomer 2: 71.39 min), anti-isomer (73.30 min).
rac-Cyclohexa-2,4-dien-1-yl-(4-isopropylphenyl)methanol (2; R = 4-i-PrC₆H₄)
Homoallylic alcohol 2 (R = 4-i-PrC₆H₄) was obtained using 4-i-PrC₆H₄CHO (85 µl, 0.56 mmol) by applying GP2 in 80% yield as a colorless oil.
IR (neat) 3391 (brs), 3038 (s), 2960 (s), 2871 (m), 1510 (m), 1462 (m), 1418 (m), 1054 (m), 1015 (m), 828 (s), 682 (s) cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δsyn and anti = 7.16–7.08 (m, 4H; Ar-H), 5.95–5.54 (m, 3.1H; vinyl-H), 5.31–5.23 (m, 0.9H for syn; vinyl-H), 4.49 (d, J = 7.7 Hz, 1H; CH-OH), 2.80 (sept, J = 6.9 Hz, 1H), 2.58–2.46 (m, 1H), 2.39–2.15 (m, 2H), 1.91 (brs, 1H), 1.15 (d, J = 6.9 Hz, 6H) ppm. ¹³C NMR (75 MHz, CDCl₃) δsyn = 148.2 (s), 140.3 (s), 127.1 (d), 126.6 (d), 126.3 (d), 125.9 (d), 125.3 (d), 123.8 (d), 75.4 (d), 40.2 (d), 33.8 (d), 24.2 (t), 24.0 (q) ppm. MS (ESI): 251 ([M + Na]⁺). HRMS: ([M + Na]⁺) calcd for C₁₆H₂₀Na: 251.1463; found: 251.1396.
syn : anti = 94.3 : 5.7 (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C (T₀) then a temperature gradient (rate, 0.3 °C min⁻¹, final temperature 180 °C (Tₑ)). Retention times: syn-isomer (enantiomer 1: 187.71 min, enantiomer 2: 188.83 min), anti-isomer (enantiomer 1: 193.43 min, enantiomer 2: 194.25 min).

Cyclohexa-2,4-dien-1-yl-(4-isopropylphenyl)methanol (2; R = 4-i-PrC₆H₄)
Homoallylic alcohol 2 (R = 4-i-PrC₆H₄) was obtained using 4-i-PrC₆H₄CHO (15, 0.10 mmol) by applying GP1 in 78% yield as a colorless oil.
¹H NMR (300 MHz, CDCl₃) δ = 7.16–7.08 (m, 4H; Ar-H), 5.95–5.54 (m, 3H; vinyl-H), 5.31–5.23 (m, 1H; vinyl-H), 4.49 (d, J = 7.7 Hz, 1H; CH-OH), 2.80 (sept, J = 6.9 Hz, 1H), 2.58–2.46 (m, 1H), 2.39–2.15 (m, 2H), 1.77 (brs, 1H), 1.15 (d, J = 6.9 Hz, 6H) ppm.
syn : anti : 4 = 91.5 : 6.5 : 2.0; e.r. of syn-isomer = 96.1 : 3.9 (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C (T₀) then a temperature gradient (rate, 0.3 °C min⁻¹, final temperature 180 °C (Tₑ)). Retention times: syn-isomer (enantiomer 1: 187.58 min, enantiomer 2: 188.88 min), anti-isomer (193.41 min), 4 (191.50 min).

rac-(4-tert-Butylphenyl)-[cyclohexa-2,4-dien-1-yl]methanol (2; R = 4-t-BuC₆H₄)
Homoallylic alcohol 2 (R = 4-t-BuC₆H₄) was obtained using 4-t-BuC₆H₄CHO (90 µl, 0.54 mmol) by applying GP2 in 81% yield as a colorless oil.
IR (neat) 3391 (brs), 3038 (s), 2963 (s), 2905 (m), 2868 (m), 1511 (m), 1463 (m), 1409 (m), 1364 (m), 1270 (m), 1109 (m), 1014 (m), 826 (m), 735 (m), 681 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δsyn and anti = 7.37 and 7.25 (AA′BB′); JAB = 8.4 Hz, 4H; Ar-H), 6.06–5.70 (m, 3.1H; vinyl-H), 5.44–5.38 (m, 0.9H for syn; vinyl-H), 4.62 (d, J = 7.7 Hz, 1H; CH-OH), 2.71–2.60 (m, 1H), 2.50–2.30 (m, 2H), 2.00 (brs, 1H), 1.32 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃) δsyn = 150.5 (s), 139.9 (s), 127.2 (d), 126.4 (d), 126.0 (d), 125.3 (d), 125.2 (d), 123.8 (d), 76.9 (s), 75.4 (d), 40.3 (d), 31.4 (q), 24.3 (t) ppm. MS (ESI): 265 ([M + Na]⁺). HRMS: ([M + Na]⁺) calcd for C₁₇H₂₂ONa: 265.1563; found: 265.1554.
syn : anti = 91.5 : 8.5 (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C (T₀) then a temperature gradient (rate, 0.3 °C min⁻¹, final temperature 180 °C (Tₑ)). Retention times: syn-isomer (enantiomer 1: 207.36 min, enantiomer 2: 208.43 min), anti-isomer (enantiomer 1: 213.05 min, enantiomer 2: 213.88 min).
(4-tert-Butylphenyl)-[cyclohexa-2,4-dien-1-yl]methanol (2; R = 4-t-BuC₆H₄)
Homoallylic alcohol 2 (R = 4-t-BuC₆H₄) was obtained using 4-t-BuC₆H₄CHO (16 mg, 0.10 mmol) by applying GP1 in 84% yield as a colorless oil.

1H NMR (300 MHz, CDCl₃) δ = 7.37 and 7.25 (AA'BB'; J_{AB} = 8.4 Hz, 4H; Ar-H), 6.06–5.70 (m, 3H; vinyl-H), 5.44–5.38 (m, 1H; vinyl-H), 4.62 (d, J = 7.7 Hz, 1H; CH-OH), 2.71–2.60 (m, 1H), 2.50–2.30 (m, 2H), 1.84 (brs, 1H), 1.32 (s, 9H) ppm.

\textit{syn} : \textit{anti} = 93.9 : 3.9 : 2.2; e.r. of \textit{syn}-isomer = 97.2 : 2.8 (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C (T₀) then a temperature gradient (rate, 0.3 °C min⁻¹, final temperature 180 °C (Tₑ)). Retention times: \textit{syn}-isomer (enantiomer 1: 207.29 min, enantiomer 2: 208.51 min), \textit{anti}-isomer (213.06 min), 4 (210.98 min).

\begin{center}
\includegraphics[width=0.2\textwidth]{cyclohexa-2,4-dien-1-yl-(4-fluorophenyl)methanol.png}
\end{center}

\textbf{rac-Cyclohexa-2,4-dien-1-yl-(4-fluorophenyl)methanol (2; R = 4-FC₆H₄)}
Homoallylic alcohol 2 (R = 4-FC₆H₄) was obtained using 4-FC₆H₄CHO (60 µl, 0.57 mmol) by applying GP2 in 78% yield as a colorless oil.

IR (neat) 3391 (brs), 3039 (s), 2874 (brs), 1894 (w), 1682 (m), 1604 (s), 1512 (s), 1224 (s), 1157 (m), 838 (s), 684 (s) cm⁻¹. 1H NMR (400 MHz, CDCl₃) δ_{\textit{syn}} and δ_{\textit{anti}} = 7.33–7.26 (m, 2H; Ar-H), 7.07–6.99 (m, 2H; Ar-H), 6.08–5.68 (m, 3H; vinyl-H), 5.38–5.32 (m, 0.9H for \textit{syn}; vinyl-H), 4.65 (d, J = 7.4 Hz, 1H; CH-OH), 2.63–2.53 (m, 1H), 2.46–2.37 (m, 1H), 2.34–2.24 (m, 1H), 2.15 (s, 1H) ppm. 13C NMR (100 MHz, CDCl₃) δ_{\textit{syn}} = 162.2 (J = 245.5 Hz, s), 138.7 (J = 3.2 Hz, s), 128.2 (J = 8.0 Hz, d), 126.6 (d), 125.8 (d), 125.6 (d), 123.8 (d), 115.0 (J = 21.3 Hz, d), 74.8 (d), 40.4 (d), 24.1 (t) ppm. MS (ESI): 227 ([M + Na]⁺).

HRMS: ([M + Na]⁺) calcd for C_{13}H_{13}FONa: 227.0843; found: 227.0846.

\textit{syn} : \textit{anti} = 93.1 : 6.9 (determined by GC analysis using Chiraldex G-TA). Temperature program: 5 min at 100 °C (T₀) then a temperature gradient (rate, 1.0 °C min⁻¹, final temperature 180 °C (Tₑ)). Retention times: \textit{syn}-isomer (enantiomer 1: 44.95 min, enantiomer 2: 45.83 min), \textit{anti}-isomer (enantiomer 1: 46.99 min, enantiomer 2: 47.62 min).

\textbf{Cyclohexa-2,4-dien-1-yl-(4-fluorophenyl)methanol (2; R = 4-FC₆H₄)}
Homoallylic alcohol 2 (R = 4-FC₆H₄) was obtained using 4-FC₆H₄CHO (12, 0.10 mmol) by applying GP1 in 91% yield as a colorless oil.

1H NMR (300 MHz, CDCl₃) δ = 7.33–7.26 (m, 2H; Ar-H), 7.07–6.99 (m, 2H; Ar-H), 6.08–5.68 (m, 3H; vinyl-H), 5.38–5.32 (m, 1H; vinyl-H), 4.65 (d, J = 7.4 Hz, 1H; CH-OH), 2.65–2.34 (m, 1H), 2.34–2.24 (m, 1H), 1.73 (brs, 1H) ppm.

\textit{syn} : \textit{anti} = 88.7 : 11.3; e.r. of \textit{syn}-isomer = 94.0 : 6.0 (determined by GC analysis using Chiraldex G-TA). Temperature program: 5 min at 100 °C (T₀) then a temperature gradient (rate, 1.0 °C min⁻¹, final temperature 180 °C (Tₑ)). Retention times: \textit{syn}-isomer (enantiomer 1: 44.91 min, enantiomer 2: 45.70 min), \textit{anti}-isomer (46.92 min).
**rac**-(4-Chlorophenyl)-[cyclohexa-2,4-dien-1-yl]methanol (2; **R** = 4-ClC₆H₄)

Homoallylic alcohol 2 (**R** = 4-ClC₆H₄) was obtained using 4-ClC₆H₄CHO (80 mg, 0.57 mmol) by applying GP2 in 63% yield as a colorless oil.

IR (neat) 3387 (brs), 3038 (s), 2869 (m), 2824 (w), 1596 (w), 1491 (s), 1410 (w), 1091 (s), 1013 (s), 824 (s), 753 (s), 679 (s) cm⁻¹.  

¹H NMR (400 MHz, CDCl₃) δ syn and anti 7.35−7.24 (m, 4H; Ar-H), 6.08−5.70 (m, 3.3H; vinyl-H), 5.38−5.33 (m, 0.7H for syn; vinyl-H), 4.65−4.58 (m, 1H; CH-OH), 2.65−2.52 (m, 1H), 2.48−2.35 (m, 1H), 2.33−2.21 (m, 1H), 2.15−1.95 (m, 1H) ppm.  

¹³C NMR (100 MHz, CDCl₃) δ syn = 141.38 (s), 133.20 (s), 128.37 (d), 127.99 (d), 126.47 (d), 125.85 (d), 125.79 (d), 123.78 (d), 74.75 (d), 40.29 (d), 23.89 (t) ppm.  

δ anti = 141.39 (s), 133.28 (s), 128.47 (d), 127.71 (d), 126.19 (d), 125.73 (d), 125.70 (d), 124.11 (d), 76.46 (d), 40.26 (d), 25.81 (t) ppm.  


**syn** : **anti** = 76.7 : 23.3 (determined by GC analysis using Chiraldex G-TA). Temperature program: 5 min at 100 °C (**T₀**) then a temperature gradient (rate, 1.0 °C min⁻¹, final temperature 180 °C (**Tₜ**)). Retention times: **syn**-isomer (enantiomer 1: 64.87 min, enantiomer 2: 65.48 min), **anti**-isomer (enantiomer 1: 66.63 min, enantiomer 2: 67.06 min).

(4-Chlorophenyl)-[cyclohexa-2,4-dien-1-yl]methanol (2; **R** = 4-ClC₆H₄)

Homoallylic alcohol 2 (**R** = 4-ClC₆H₄) was obtained using 3-MeC₆H₄CHO (65 µl, 0.55 mmol) by applying GP1 in 82% yield as a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ = 7.35−7.24 (m, 4H; Ar-H), 6.08−5.70 (m, 3H; vinyl-H), 5.40−5.33 (m, 1H; vinyl-H), 4.61 (d, **J** = 7.5 Hz, 1H; CH-OH), 2.65−2.52 (m, 1H), 2.48−2.35 (m, 1H), 2.33−2.21 (m, 1H), 1.93 (brs, 1H) ppm  

**syn** : **anti** = 83.5 : 16.5; c.e. of **syn**-isomer = 95.0 : 5.0 (determined by GC analysis using Chiraldex G-TA). Temperature program: 5 min at 100 °C (**T₀**) then a temperature gradient (rate, 1.0 °C min⁻¹, final temperature 180 °C (**Tₜ**)). Retention times: **syn**-isomer (enantiomer 1: 64.92 min, enantiomer 2: 65.54 min), **anti**-isomer (66.67 min).

**rac**-Cyclohexa-2,4-dien-1-yl-(3-methylphenyl)methanol (2; **R** = 3-MeC₆H₄)

Homoallylic alcohol 2 (**R** = 3-MeC₆H₄) was obtained using 3-MeC₆H₄CHO (65 µl, 0.55 mmol) by applying GP2 in 78% yield as a colorless oil.

IR (neat) 3396 (brs), 3037 (s), 2918 (m), 2867 (m), 1608 (m), 1488 (w), 153 (w), 1029 (m), 785 (m), 707 (s), 683 (s) cm⁻¹.  

¹H NMR (300 MHz, CDCl₃) δ = 7.35−7.24 (m, 4H; Ar-H), 6.08−5.70 (m, 3H; vinyl-H), 5.40−5.33 (m, 1H; vinyl-H), 4.65 (d, **J** = 7.1 Hz, 1H; CH-OH), 2.65−2.52 (m, 1H), 2.48−2.35 (m, 1H), 2.33−2.21 (m, 1H), 1.93 (brs, 1H) ppm  

**syn** : **anti** = 90.2 : 9.8 (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C (**T₀**) then a temperature gradient (rate, 0.3 °C min⁻¹, final temperature 180 °C (**Tₜ**)). Retention times: **syn**-isomer (enantiomer 1: 143.41 min, enantiomer 2: 144.43 min), **anti**-isomer (149.33 min).
Cyclohexa-2,4-dien-1-yl-(3-methylphenyl)methanol (2; R = 3-MeC₆H₄)
Homoallylic alcohol 2 (R = 3-MeC₆H₄) was obtained using 3-MeC₆H₄CHO (21 mg, 0.10 mmol) by applying GP1 in 55% yield as a colorless oil.

1H NMR (300 MHz, CDCl₃) δ = 7.24 (dd, J = 7.2, 7.2 Hz, 1H; Ar-H), 7.17–7.07 (m, 3H; Ar-H), 6.07–5.70 (m, 3H; vinyl-H), 5.43–5.35 (m, 1H; vinyl-H), 4.61 (d, J = 7.5 Hz, 1H; CH-OH), 2.71–2.57 (m, 1H), 2.50–2.25 (m, 2H), 2.36 (s, 3H; CH₃), 1.86 (brs, 1H) ppm.

syn : anti = 89.1 : 10.2 : 0.7; e.r. of syn-isomer = 96.0 : 4.0 (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C (T₀) then a temperature gradient (rate, 0.3 °C min⁻¹, final temperature 180 °C (Tₑ)). Retention times: syn-isomer (enantiomer 1: 143.14 min, enantiomer 2: 144.57 min), anti-isomer (146.38 min).

rac-(3-Bromophenyl)-[cyclohexa-2,4-dien-1-yl]methanol (2; R = 3-BrC₆H₄)
Homoallylic alcohol 2 (R = 3-BrC₆H₄) was obtained using 3-BrC₆H₄CHO (75 µl, 0.64 mmol) by applying GP2 in 62% yield as a colorless oil.

IR (neat) 3385 (brs), 3037 (s), 2870 (m), 2822 (w), 1594 (m), 1570 (s), 1474 (m), 1427 (s), 1190 (m), 1070 (m), 1025 (w), 785 (m), 700 (s) cm⁻¹. 1H NMR (300 MHz, CDCl₃) δ = 7.50−7.47 (m, 1H; Ar-H), 7.44−7.38 (m, 1H; Ar-H), 7.26−7.17 (m, 1H; Ar-H), 6.08−5.69 (m, 3.4H; vinyl-H), 5.42−5.34 (m, 0.6H for syn; vinyl-H), 4.64−4.56 (m, 1H; CH-OH), 2.65−2.52 (m, 1H), 2.47−1.95 (m, 3H) ppm.

13C NMR (75 MHz, CDCl₃) δ = 145.2 (s), 130.6 (d), 130.5 (d), 129.9 (d), 129.8 (d), 129.7 (d), 129.4 (d), 126.4 (d), 125.9 (d), 125.8 (d), 125.2 (d), 125.0 (d), 124.1 (d), 123.8 (d), 122.6 (s), 122.4 (s), 76.4 (d), 74.7 (d), 40.2 (d), 40.1 (d), 25.8 (t), 23.7 (t) ppm (six peaks were overlapped.). MS (ESI): 335 [(M + Na)+]. HRMS: [(M + Na)+] C₁₃H₁₃⁷⁸BrONa and C₁₃H₁₃⁸⁰BrONa: 287.0042 and 289.0022; found: 287.0031 and 289.0023.

syn : anti = 56.0 : 44.0 (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C (T₀) then a temperature gradient (rate, 0.3 °C min⁻¹, final temperature 180 °C (Tₑ)). Retention times: syn-isomer (enantiomer 1: 215.20 min, enantiomer 2: 216.60 min), anti-isomer (enantiomer 1: 219.71 min, enantiomer 2: 220.36 min).

(3-Bromophenyl)-[cyclohexa-2,4-dien-1-yl]methanol (2; R = 3-BrC₆H₄)
Homoallylic alcohol 2 (R = 3-BrC₆H₄) was obtained using 3-BrC₆H₄CHO (18 mg, 0.10 mmol) by applying GP1 in 78% yield as a colorless oil.

1H NMR (300 MHz, CDCl₃) δ = 7.51−7.47 (m, 1H; Ar-H), 7.44−7.38 (m, 1H; Ar-H), 7.26−7.17 (m, 1H; Ar-H), 6.08−5.69 (m, 3H; vinyl-H), 5.42−5.34 (m, 1H; vinyl-H), 4.64 (d, J = 7.1 Hz, 1H; CH-OH), 2.65−2.52 (m, 1H), 2.49−2.35 (m, 1H), 2.33−2.20 (m, 1H), 1.96 (brs, 1H) ppm. 13C NMR (75 MHz, CDCl₃) δ = 145.3 (s), 130.6 (d), 129.8 (d), 129.7 (d), 126.4 (d), 125.9 (d), 125.8 (d), 125.2 (d), 125.0 (d), 124.1 (d), 123.8 (d), 122.6 (s), 122.4 (s), 76.4 (d), 74.7 (d), 40.2 (d), 40.1 (d), 25.8 (t), 23.7 (t) ppm.

syn : anti = 87.5 : 12.5; e.r. of syn-isomer = 93.8 : 6.2 (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C (T₀) then a temperature gradient (rate, 0.3 °C min⁻¹, final temperature 180 °C (Tₑ)). Retention times: syn-isomer (enantiomer 1: 215.16 min, enantiomer 2: 216.58 min), anti-isomer (219.73 min).
**rac-(5-Bromo-2-furyl)-[cyclohexa-2,4-dien-1-yl]methanol (2; R = 5-Br-2-furyl)**

Homoallylic alcohol 2 (R = 5-Br-2-furyl) was obtained using 5-bromofuran-2-carboxaldehyde (102 mg, 0.583 mmol) by applying GP2 in 75% yield as a colorless oil. The compound turned out to be unstable. Some decomposition occurred during NMR analysis.

**IR (neat)** 3383 (brs), 3039 (s), 2925 (s), 2869 (s), 1680 (w), 1501 (s), 1201 (m), 1124 (s), 1011 (s), 946 (m), 923 (m), 785 (s), 679 (s) cm⁻¹. **¹H NMR (300 MHz, CDCl₃)** δ<sub>syn</sub> and δ<sub>anti</sub> = 6.27−6.22 (m, 2H; Ar-H), 6.07−5.68 (m, 3.6H; vinyl-H), 5.51−5.44 (m, 0.4H for syn; vinyl-H), 4.67−4.55 (m, 1H; CH₂-OH), 2.89−2.71 (m, 1H), 2.46−2.33 (m, 1H), 2.28−1.90 (m, 2H) ppm.

**¹³C NMR (75 MHz, CDCl₃)** δ<sub>syn</sub> and δ<sub>anti</sub> = 157.5 (s), 157.4 (s), 125.93 (d), 125.84 (d), 125.78 (d), 125.7 (d), 125.4 (d), 123.91 (d), 123.90 (d), 121.3 (s), 121.2 (s), 111.84 (d), 111.83 (d), 110.0 (d), 109.8 (d), 70.6 (d), 68.8 (d), 37.8 (d), 37.7 (d), 25.5 (t), 24.1 (t) ppm (one peak was overlapped.). **MS (ESI):** 277 ([M + Na]+). **HRMS:** ([M + Na]+) calcd for C₁₁H₁₁BrO₂Na and C₁₁H₁₁BrO₂Na: 276.9835 and 276.9815; found: 276.9826 and 278.9837.

**syn : anti = 4 : 6 (determined by ¹H NMR analysis).**

**[5-Bromo-2-furyl]-[cyclohexa-2,4-dien-1-yl]methanol (2; R = 5-Br-2-furyl)**

Homoallylic alcohol 2 (R = 5-Br-2-furyl) was obtained using thiophen-2-carboxaldehyde (60 µl, 0.65 mmol) by applying GP2 in 66% yield as a colorless oil. The compound turned out to be unstable. Some decomposition occurred during NMR analysis.

**¹H NMR (300 MHz, CDCl₃)** δ = 6.27−6.22 (m, 2H; Ar-H), 6.07−5.68 (m, 3H; vinyl-H), 5.51−5.44 (m, 1H; vinyl-H), 4.67−4.55 (m, 1H; CH₂-OH), 2.89−2.71 (m, 1H), 2.46−2.30 (m, 2H), 1.91−1.88 (m, 1H) ppm.

The enantiomeric ratio was determined after debromination (sBuLi, THF, -78 °C, then H₂O) leading to the formation of 2 (R = 2-furyl).

**syn : anti = 77.1 : 22.9; e.r. of syn-isomer = 94.1 : 5.9 (determined by GC analysis using Chiraldex G-TA).**

**Temperature program:** 0 min at 100 °C (T₀) then a temperature gradient (rate, 0.3 °C min⁻¹, final temperature 180 °C (Tₑ)). **Retention times:** syn-isomer (enantiomer 1: 70.87 min, enantiomer 2: 71.42 min), anti-isomer (73.35 min).

**rac-Cyclohexa-2,4-dien-1-yl-(thien-2-yl)methanol (2; R = 2-thienyl)**

Homoallylic alcohol 2 (R = 2-thienyl) was obtained using thiophen-2-carboxaldehyde (60 µl, 0.65 mmol) by applying GP2 in 66% yield as a colorless oil. The compound turned out to be unstable. Some decomposition occurred during NMR analysis.

**IR (neat)** 3393 (brs), 3037 (s), 2927 (s), 2871 (s), 1670 (m), 1410 (m), 1306 (m), 1232 (d), 1014 (s), 854 (m), 755 (w), 699 (s) cm⁻¹. **¹H NMR (300 MHz, CDCl₃)** δ<sub>syn</sub> and δ<sub>anti</sub> = 7.28−7.25 (m, 1H; Ar-H), 6.98−6.96 (m, 2H; Ar-H), 6.08−5.72 (m, 3.2H; vinyl-H), 5.52−5.46 (m, 0.8H for syn; vinyl-H), 4.89 (d, J = 7.8 Hz, 1H; CH₂-OH), 2.74−2.65 (m, 1H), 2.49−2.33 (m, 2H), 2.23−2.02 (m, 1H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ<sub>syn</sub> = 146.9 (s), 126.5 (d), 126.4 (d), 125.9 (d), 125.6 (d), 124.84 (d), 124.79 (d), 123.9 (d), 71.6 (d), 40.9 (d), 24.5 (t) ppm. **MS (ESI):** 215 ([M+ Na]+). **HRMS:** ([M + Na]+) calcd for C₁₁H₁₂OSNa: 215.0501; found: 215.0507.

**syn : anti = 85.6 : 14.4 (determined by GC analysis using Chiraldex G-TA).** **Temperature program:** 0 min at 100 °C (T₀) then a temperature gradient (rate, 0.3 °C min⁻¹, final temperature 180 °C (Tₑ)). **Retention

**Cyclohexa-2,4-dien-1-yl-(thien-2-yl)methanol (2; R = 2-thienyl)**

Homallyl alcohol 2 (R = 2-thienyl) was obtained using thiophen-2-carboxaldehyde (11 mg, 0.10 mmol) by applying GP1 in 63% yield as a colorless oil. The compound turned out to be unstable. Some decomposition occurred during NMR analysis.

\[ \text{H NMR (300 MHz, CDCl}_3 \text{)} \delta = 7.28-7.25 \ (m, 1H; Ar-H), 6.98-6.96 \ (m, 2H; Ar-H), 6.08-5.72 \ (m, 3H; vinyl-H), 5.52-5.46 \ (m, 1H; vinyl-H), 4.89 \ (d, J = 7.8 Hz, 1H; CH-OH), 2.75-2.63 \ (m, 1H), 2.49-2.33 \ (m, 2H), 2.10-1.98 \ (m, 1H) ppm. \]

\[ \text{syn : anti : 4} = 90.4 : 8.4 : 1.2; \text{ e.r. of syn-isomer = 96.4 : 3.6 (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C (T}_0 \text{) then a temperature gradient (rate, 0.3 °C min}^{-1}, \text{ final temperature 180 °C (T}_E \text{)). Retention times: syn-isomer (enantiomer 1: 124.22 min, enantiomer 2: 125.03 min), anti-isomer (128.48 min), 4 (129.90 min).} \]

\[ \text{IR (neat) 3386 (brs), 3037 (s), 2921 (s), 2875 (s), 1440 (s), 1046 (m), 1012 (m), 968 (m), 854 (w), 797 (w), 694 (s) cm}^{-1}. \text{ H NMR (300 MHz, CDCl}_3 \text{)} \delta_{\text{syn and anti}} = 6.92-6.88 \ (m, 2H; Ar-H), 6.71-6.67 \ (m, 2H; Ar-H), 6.06-5.70 \ (m, 3.3H; vinyl-H), 5.52-5.45 \ (m, 0.7H for syn; vinyl-H), 4.81-4.74 \ (m, 1H; CH-OH), 2.68-2.54 \ (m, 1H), 2.48-2.28 \ (m, 2H), 2.27-2.00 \ (m, 1H) ppm. \text{ C NMR (75 MHz, CDCl}_3 \text{)} \delta_{\text{syn}} = 148.5 \ (s), 129.2 \ (d), 125.84 \ (d), 125.82 \ (d), 125.76 \ (d), 125.0 \ (d), 123.9 \ (d), 111.7 \ (d), 71.6 \ (d), 40.4 \ (d), 24.3 \ (t) ppm. \delta_{\text{anti}} = 148.7 \ (s), 129.3 \ (d), 125.9 \ (d), 125.6 \ (d), 124.6 \ (d), 124.0 \ (d), 111.6 \ (d), 73.2 \ (d), 40.6 \ (d), 25.6 \ (t) ppm (one peak was overlapped.). MS (EI) 268 (<1, [M – H}_2^+), 191 (100\%\). \]

\[ \text{syn : anti = 8 : 2 (determined by H NMR analysis).} \]

**rac-(5-Bromothien-2-yl)-[cyclohexa-2,4-dien-1-yl]methanol (2; R = 5-Br-2-thienyl)**

Homallyl alcohol 2 (R = 5-Br-2-thienyl) was obtained using 5-bromothiophen-2-carboxaldehyde (70 µl, 0.59 mmol) by applying GP2 in 66% yield as colorless oil. The compound turned out to be unstable. Some decomposition occurred during NMR analysis.

IR (neat) 3386 (brs), 3037 (s), 2921 (s), 2875 (s), 1440 (s), 1046 (m), 1012 (m), 968 (m), 854 (w), 797 (w), 694 (s) cm\(^{-1}\). 1H NMR (300 MHz, CDCl\(_3\)) \(\delta_{\text{syn and anti}} = 6.92-6.88 \ (m, 2H; Ar-H), 6.71-6.67 \ (m, 2H; Ar-H), 6.06-5.70 \ (m, 3.3H; vinyl-H), 5.52-5.45 \ (m, 0.7H for syn; vinyl-H), 4.81-4.74 \ (m, 1H; CH-OH), 2.68-2.54 \ (m, 1H), 2.48-2.28 \ (m, 2H), 2.27-2.00 \ (m, 1H) ppm. 13C NMR (75 MHz, CDCl\(_3\)) \(\delta_{\text{syn}} = 148.5 \ (s), 129.2 \ (d), 125.84 \ (d), 125.82 \ (d), 125.76 \ (d), 125.0 \ (d), 123.9 \ (d), 111.7 \ (d), 71.6 \ (d), 40.4 \ (d), 24.3 \ (t) ppm. \delta_{\text{anti}} = 148.7 \ (s), 129.3 \ (d), 125.9 \ (d), 125.6 \ (d), 124.6 \ (d), 124.0 \ (d), 111.6 \ (d), 73.2 \ (d), 40.6 \ (d), 25.6 \ (t) ppm (one peak was overlapped.). MS (EI) 268 (<1, [M – H\(_2^+\)], 191 (100\%). \]

\[ \text{syn : anti = 8 : 2 (determined by H NMR analysis).} \]

**Cyclohexa-2,4-dien-1-yl-[cyclohexa-2,4-dien-1-yl]methanol (2; R = 5-Br-2-thienyl)**

Homallyl alcohol 2 (R = 5-Br-2-thienyl) was obtained using 5-bromothiophen-2-carboxaldehyde (19 mg, 0.10 mmol) by applying GP1 in 44% yield as colorless oil. The compound turned out to be unstable. Some decomposition occurred during NMR analysis.

1H NMR (300 MHz, CDCl\(_3\)) \(\delta = 6.92-6.88 \ (m, 2H; Ar-H), 6.72-6.68 \ (m, 2H; Ar-H), 6.06-5.70 \ (m, 3H; vinyl-H), 5.52-5.45 \ (m, 1H; vinyl-H), 4.81-4.74 \ (m, 1H; CH-OH), 2.68-2.54 \ (m, 1H), 2.48-2.28 \ (m, 2H), 2.27-2.00 \ (m, 1H) ppm. The enantiomeric ratio was determined after debromination (sBuLi, THF, -78 °C, then H\(_2\)O) leading to the formation of 2 (R = 2-thienyl).

\[ \text{syn : anti = 71.1 : 28.9; e.r. of syn-isomer = 95.4 : 4.6 (determined by GC analysis using Chiraldex G-TA). Temperature program: 0 min at 100 °C (T}_0 \text{) then a temperature gradient (rate, 0.3 °C min}^{-1}, \text{ final temperature 180 °C (T}_E \text{)). Retention times: syn-isomer (enantiomer 1: 124.33 min, enantiomer 2: 125.11 min), anti-isomer (128.50 min).} \]

**References**

Confirmation of Absolute Configuration of Compounds 2 (R = Ph)

Figure S1. GC Chromatograms of a) rac-2 (R = Ph), b) syn-2 (R = Ph) prepared from (R,R)-TADDOL derivative 1, c) syn-2 (R = Ph) prepared from (R,R)-TADDOL derivative 1, and d) 2 and 4 (R = Ph) prepared by GP1 (Cu-(S)-DIFLUORPHOS cat.).

Absolute configuration of 2 (R = Ph) prepared by GP1 (Figure S1d) was determined by comparison to our previous work.\textsuperscript{1} Reaction of (R,R)-1 with PhCHO provides the syn-2 isomer as unambiguously proved before.\textsuperscript{1} The reaction of 3 with Cu-(S)-DIFLUORPHOS provided the same isomer as major compound as clearly proved by GC analysis. The absolute configuration of all other products were assigned in analogy.
Figure S2A. GC chromatograms of a) rac-2 (R = Ph), b) 2 (R = Ph) prepared by GP1.

Figure S2B. $^1$H NMR (300 MHz) spectrum of 2 (R = Ph) prepared by GP1 in CDCl$_3$. 
2 (R = 4-MeC₆H₄)

Figure S3A. GC chromatograms of a) rac-2 (R = 4-MeC₆H₄), b) 2 (R = 4-MeC₆H₄) prepared by GP1.

Figure S3B. ¹H NMR (300 MHz) spectrum of 2 (R = 4-MeC₆H₄) prepared by GP1 in CDCl₃.
Figure S4A. GC chromatograms of a) rac-2 (R = 4-\text{PrC}_6\text{H}_4), b) 2 (R = 4-\text{PrC}_6\text{H}_4) prepared by GP1.

Figure S4B. $^1$H NMR (300 MHz) spectrum of 2 (R = 4-\text{PrC}_6\text{H}_4) prepared by GP1 in CDCl$_3$. 
Figure S5A. GC chromatograms of a) rac-2 (R = 4-\text{tBuC}_6\text{H}_4), b) 2 (R = 4-\text{tBuC}_6\text{H}_4) prepared by GP1.

Figure S5B. $^1$H NMR (300 MHz) spectrum of 2 (R = 4-\text{tBuC}_6\text{H}_4) prepared by GP1 in CDCl$_3$. 
Figure S6A. GC chromatograms of a) rac-2 (R = 4-OMeC$_6$H$_4$), b) 2 (R = 4-OMeC$_6$H$_4$) prepared by GP1.

Figure S6B. $^1$H NMR (300 MHz) spectrum of 2 (R = 4-OMeC$_6$H$_4$) prepared by GP1 in CDCl$_3$.  

2 (R = 4-OMeC$_6$H$_4$)
Figure S7A. GC chromatograms of a) rac-2 (R = 4-BrC₆H₄), b) 2 (R = 4-BrC₆H₄) prepared by GP1.

Figure S7B. ¹H NMR (300 MHz) spectrum of 2 (R = 4-BrC₆H₄) prepared by GP1 in CDCl₃.
Figure S8A. GC chromatograms of a) rac-2 (R = 4-ClC₆H₄), b) 2 (R = 4-ClC₆H₄) prepared by GP1.

Figure S8B. ¹H NMR (300 MHz) spectrum of 2 (R = 4-ClC₆H₄) prepared by GP1 in CDCl₃.
**Figure S9B.** $^1$H NMR (300 MHz) spectrum of 2 (R = 4-FC$_6$H$_4$) prepared by GP1 in CDCl$_3$. 

**Figure S9A.** GC chromatograms of a) rac-2 (R = R = 4-FC$_6$H$_4$), b) 2 (R = R = 4-FC$_6$H$_4$) prepared by GP1.
**Figure S10A.** GC chromatograms of a) rac-2 (R = 2-MeC₆H₄), b) 2 (R = 2-MeC₆H₄) prepared by GP1.

**Figure S10B.** $^1$H NMR (300 MHz) spectrum of 2 (R = 2-MeC₆H₄) prepared by GP1 in CDCl₃.
Figure S11A. GC chromatograms of a) rac-2 (R = 2-OMeC₆H₄), b) 2 (R = 2-OMeC₆H₄) prepared by GP1.

Figure S11B. $^1$H NMR (300 MHz) spectrum of 2 (R = 2-OMeC₆H₄) prepared by GP1 in CDCl₃.
Figure S12A. GC chromatograms of a) rac-2 (R = 3-MeC₆H₄), b) 2 (R = 3-MeC₆H₄) prepared by GP1.

Figure S12B. ¹H NMR (300 MHz) spectrum of 2 (R = 3-MeC₆H₄) prepared by GP1 in CDCl₃.
Figure S13A. GC chromatograms of a) rac-2 (R = 3-OMeC₆H₄), b) 2 (R = 3-OMeC₆H₄) prepared by GP1.

Figure S13B. ¹H NMR (300 MHz) spectrum of 2 (R = 3-OMeC₆H₄) prepared by GP1 in CDCl₃.
Figure S14A. GC chromatograms of a) rac-2 (R = 3-BrC₆H₄), b) 2 (R = 3-BrC₆H₄) prepared by GP1.

Figure S14B. ¹H NMR (300 MHz) spectrum of 2 (R = 3-BrC₆H₄) prepared by GP1 in CDCl₃.
Figure S15A. GC chromatograms of a) rac-2 (R = 2-furyl), b) 2 (R = 2-furyl) prepared by GP1.

Figure S15B. $^1$H NMR (300 MHz) spectrum of 2 (R = 2-furyl) prepared by GP1 in CDCl$_3$. 

S26
**Figure S16A.** GC chromatograms of a) rac-2 (R = 2-furyl), b) 2 (R = 2-furyl) after protonation of 2 (R = 5-Br-2-furyl) by sec-BuLi.

**Figure S16B.** $^1$H NMR (300 MHz) spectrum of 2 (R = 5-Br-2-furyl) prepared by GP1 in CDCl$_3$. 

S27
Figure S17A. GC chromatograms of a) rac-2 (R = 2-thienyl), b) 2 (R = 2-thienyl) prepared by GP1.

Figure S17B. $^1$H NMR (300 MHz) spectrum of 2 (R = 2-thienyl) prepared by GP1 in CDCl$_3$. 
Figure S18A. GC chromatograms of a) rac-2 (R = 2-thienyl), b) 2 (R = 2-thienyl) after protonation of 2 (R = 5-Br-2-thienyl) by sec-BuLi.

Figure S18B. $^1$H NMR (300 MHz) spectrum of 2 (R = 5-Br-2-thienyl) prepared by GP1 in CDCl$_3$. 
Figure S19A. HPLC chromatograms of a) rac-2 (R = 2-naphtyl), b) 2 (R = 2-naphtyl) prepared by GP1.

Figure S19B. $^1$H NMR (300 MHz) spectrum of 2 (R = 2-naphtyl) prepared by GP1 in CDCl$_3$. 
Figure S20. $^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) spectra of rac-2 ($R = 4$-$i$-PrC$_6$H$_4$) prepared by GP2 in CDCl$_3$. 
Figure S21. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra of rac-2 (R = 4-\text{-}BuC$_6$H$_4$) prepared by GP2 in CDCl$_3$. 
Figure S22. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra of rac-2 ($R = 4$-FC$_6$H$_4$) prepared by GP2 in CDCl$_3$. 

S33
**Figure S23.** $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra of rac-2 (R = 4-ClC$_6$H$_4$) prepared by GP2 in CDCl$_3$
**Figure S24.** \(^1\)H NMR (300 MHz) and \(^{13}\)C NMR (75 MHz) spectra of rac-2 (R = 3-MeC\(_6\)H\(_4\)) prepared by GP2 in CDCl\(_3\).
Figure S25. $^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) spectra of rac-2 (R = 3-BrC$_6$H$_4$) prepared by GP2 in CDCl$_3$. 
Figure S26. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra of rac-2 (R = 5-Br-2-furyl) prepared by GP2 in CDCl$_3$. 
Figure S27. $^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) spectra of rac-2 (R = 2-thienyl) prepared by GP2 in CDCl$_3$. 
Figure S28. $^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) spectra of rac-2 ($R = 5$-Br-2-thienyl) prepared by GP2 in CDCl$_3$. 