Electronic Supplementary Information

Enantiodivergent Asymmetric Catalysis with Tropos BIPHEP Ligand and a Proline Derivative as Chiral Selector

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Experimental Section

General: All reactions were carried out under a dry argon atmosphere either with Schlenk technique or in a glovebox. Multinuclear NMR spectra were recorded with a Bruker AV III 400 or AV 600 spectrometer. The operation frequencies for the spectrometers are 400.2 MHz for $^1$H, 100.6 MHz for $^{13}$C, 376.4 MHz for $^{19}$F and 162.0 MHz for $^{31}$P with the AV III 400 spectrometer and 600.1 MHz for $^1$H, 150.9 MHz for $^{13}$C, 564.6 MHz for $^{19}$F and 242.9 MHz for $^{31}$P with the AV 600 spectrometer. Various temperature NMR experiments were exclusively recorded with the AV 600 spectrometer. Chemical shifts ($\delta$) of $^1$H and $^{13}$C($^1$H) NMR-spectroscopy are given in ppm using the residual solvent signal as internal standards. For $^{31}$P($^1$H) NMR spectroscopy chemical shifts are given relative to 85 % phosphoric acid as external standard. Coupling constants $J$ are given in Hertz (Hz) and for the characterization of the multiplicity the following symbols are used: $s = $ singlet, $d = $ doublet, $t = $ triplet, $dd = $ doublet of a doublet, $m = $ multiplet, $br = $ broad. The assignment of the signals was made on the basis of 2D-NMR spectroscopy ($^1$H-$^{13}$C HSQC, $^1$H-$^{13}$C HMBC, $^1$H-$^1$H COSY, $^1$H-$^{31}$P HMBC). HR-MS-ESI data was recorded with a Thermo Fisher Scientific LTQ Orbitrap XL (ESI) and ESI-MS measurements were performed with a 500-MS from Varian. The mass of the standard. Coupling constants $J$ are given in Hertz (Hz) and for the characterization of the multiplicity the following symbols are used: $s = $ singlet, $d = $ doublet, $t = $ triplet, $dd = $ doublet of a doublet, $m = $ multiplet, $br = $ broad. The assignment of the signals was made on the basis of 2D-NMR spectroscopy ($^1$H-$^{13}$C HSQC, $^1$H-$^{13}$C HMBC, $^1$H-$^1$H COSY, $^1$H-$^{31}$P HMBC). HR-MS-ESI data was recorded with a Thermo Fisher Scientific LTQ Orbitrap XL (ESI) and ESI-MS measurements were performed with a 500-MS from Varian. The mass of the molecular ion is given. Reagents were purchased from ABCR, Aldrich, Heraeus, io-li-tec and were used without further purification. Anhydrous solvents were obtained from a solvent drying system of Innovative Technologies. Methanol was delivered from Acros in anhydrous grade and was purified and degased by freeze-pump-thaw cycles as well as stored under argon atmosphere. Water was degassed by purging argon through a frit for 2 h. Deuterated solvents (1,2-Dichloroethane-d$_2$ from Euriso-top and were degassed with freeze-pump-thaw cycles. ($^5$-Prolinium-methylester-bis[trifluoromethyl]sulfonyl)-amide (2) was prepared following a literature procedure, $^2$ degassed, and dried under high vacuum (1x10$^{-3}$ mbar) at 60 °C overnight prior to use. NMR-spectra of air-sensitive species were recorded using screw-cap NMR-tubes filled under argon. Hydrogenation reactions were performed in 10 ml (experiments in Table 1) or 20 ml stainless steel reactors build at the ITMC and equipped with a 6 ml glass liner (10 ml reactor) or a 12 ml glass liner (20 ml reactor).

Synthesis of complexes and catalyst precursors

Synthesis of [Rh(BIPHEP)(acac)] (3): [Rh(CO)$_2$(acac)] (206 mg, 800 µmol) and 2,2'-bis(diphenylphosphanyl)-1,1'-biphenyl 1 (BIPHEP, 418 mg, 800 µmol, 1.00 eq.) were placed in a Schlenk tube and dissolved in CH$_2$Cl$_2$ (20 mL). The red reaction mixture was allowed to stir for 1 h at room temperature. All volatiles were removed in vacuo resulting in a red to orange solid (580 mg, quant.). $^1$H-NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 7.98-6.79$ (m, 26H, $^1$H), 5.25 (s, 1H, CH$_2$), 1.44 (s, 6H, C$_3$H$_6$). $^{31}$P($^1$H)-NMR (161 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 51.49$ (d, $^{31}$P,$^1$H$_{ab} = 189.2$ Hz). HR-MS (ESI) (+): $m/z = 724.11841$ (7) [M] calculated for C$_{42}$H$_{31}$P$_2$O$_2$Rh: 724.11618.

Preparation of [{(Rh($^{31}$P,BIPHEP)($^{31}$P-3-acac)($^{31}$P-3-ProLOMe)])[NTf$_2$]} (4): (S$_5$)-Prolinium-methylester-bis(trifluoromethyl)sulfonylamide 2 (33 mg, 80 µmol, 1.7 eq.) was added to a solution of [Rh(BIPHEP)(acac)] (29 mg, 40 µmol) in CH$_2$Cl$_2$ (0.4 mL) at -50 °C. The resulting red mixture was stirred for 10 min at -30 °C. At constant temperature of -30 °C both diastereomers [Rh([[S$_5$]-BIPHEP)][[[S$_5$]-ProLOMe]][NTf$_2$]$_2$ and [Rh([[R$_5$]-BIPHEP)][[[S$_5$]-ProLOMe]][NTf$_2$]$_2$ ([S$_5$]/[R$_5$]-4) were detected by NMR (> 93 % by $^{31}$P-NMR). Diastereomer A: $^1$H-NMR (600 MHz, CD$_2$Cl$_2$, -30 °C): $\delta = 8.17-5.87$ (m, H$_{ab}$), 5.08 (s, 1H, H-2), 3.61 (s, 3H, H-4), 2.11 (s, 3H, H-1), 0.91 (s, 3H, H-3), -16.57 (dt, 1H, $^{31}$P$_{ab} = 15.1$ Hz, $^{31}$P$_{ab} = 23.4$ Hz, H-5). $^{31}$P($^1$H)-NMR (243 MHz, CD$_2$Cl$_2$, -30 °C): $\delta = 43.06$ (dd, $^{31}$P,$^1$H$_{ab} = 130.3$ Hz, $^{31}$P$_{ab} = 38.5$ Hz), 32.59 (dd, $^{31}$P$_{ab} = 124.1$ Hz, $^{31}$P$_{ab} = 39.6$ Hz). Diastereomer B: $^1$H-NMR (600 MHz, CD$_2$Cl$_2$, -30 °C): $\delta = 8.17-5.87$ (m, H$_{ab}$), 5.03 (s, 1H, H-2), 3.54 (s, 3H, H-4), 2.10 (s, 3H, H-1), 0.90 (s, 3H, H-3), -16.88 (dt, 1H, $^{31}$P$_{ab} = 16.4$ Hz, $^{31}$P$_{ab} = 23.5$ Hz, H-5). $^{31}$P($^1$H)-NMR (243 MHz, CD$_2$Cl$_2$, -30 °C): $\delta = 41.16$ (dd, $^{31}$P$_{ab} = 130.0$ Hz, $^{31}$P$_{ab} = 35.7$ Hz), 33.37 (dd, $^{31}$P$_{ab} = 123.8$ Hz, $^{31}$P$_{ab} = 36.5$ Hz).

$^a$ signals of coordinated ProLOMe are not listed as they overlap with the corresponding signals of 2 present in excess.

$^b$ signal integration is not possible due to overlapping with signals of 2 in the same region.

$c$ in the spectra an additional coupling was observed because of insufficient broadband proton-decoupling of the strongly upfield shifted hydride signal.
Preparation of the diastereomeric mixture \((S,S)\)/\((R,S)\)-[Rh(BIPHEP)][(S)-ProLOMe]]\([\text{NTf}_2] \) \((S,S)\)/\((R,S)\)-5:

\((S,S)\)-Prolinyl-methylene-bis[(trifluoromethyl)sulfonylamide (230 mg, 561 µmol, 14 eq.) was added to a solution of [Rh(BIPHEP)][acac] (29 mg, 40 µmol) in CHCl\(_3\) (0.4 mL) at -10 °C. The resulting dark red mixture was stirred for 10 min at 0 °C. At constant temperature of 0 °C both diastereomers \([Rh(\{S\})-\text{BIPHEP}\][(S)-\text{ProLOMe}]]\([\text{NTf}_2] \) and \([Rh(\{R\})-\text{BIPHEP}\][(S)-\text{ProLOMe}]]\([\text{NTf}_2] \) \((S,S)\)/\((R,S)\)-5 were formed in a 1:1 ratio (NMR). \((S,S)\)-[Rh(BIPHEP)][(S)-ProLOMe]]\([\text{NTf}_2] \) \((S,S)\)/\((R,S)\)-5: \(1^H\)-NMR (400 MHz, CDCl\(_3\), 25 °C): \( \delta \) = 8.02-6.86 (m, H\(P-Rh\)), 6.50-6.41 (m, 2H, H\(Ar\)), 6.36-6.29 (m, 2H, H\(Ar\)). \(31^p\)-[\(d\)H]-NMR (161 MHz, CDCl\(_3\), 25 °C): \( \delta \) = 52.08 (dd, \(J_{p-Rh} = 205.9 \) Hz, \(J_{p-P} = 65.8\)), 45.84 (dd, \(J_{p-Rh} = 170.5 \) Hz, \(J_{p-P} = 65.8\)).

\(a\) signals of coordinated ProLOMe are not listed as they overlap with the corresponding signals of 2 present in excess.

\(b\) signal integration is not possible due to overlapping with signals of 2 in the same region.

Catalytic procedures

Typical procedure for R-selective catalytic hydrogenations reported in Table 1 and figure 3:

The substrate (1.75 mmol, 175 eq.) and HNTf\(_2\) (7.0 mg, 25 µmol, 2.5 eq.) were dissolved in methanol (2 mL) (substrate 12) or methanol (1 mL) and water (1 mL) (substrates 6, 8, 10, 14) and were combined with a solution freshly prepared solution of [Rh(\{R\})-BIPHEP][(S)-ProLOMe]] \((R,S)\)-5 which was formed in situ as described above (c = 0.1 mol L\(^{-1}\), 0.1 mL, 10 µmol). After stirring for 10 min, the red solution was transferred into a 10 mL stainless steel reactor equipped with a 6 mL glass vial and a stirring bar which was tempered to 0 °C through a cryostat. The reactor was pressurized with hydrogen (40 bar). The mixture was continuously stirred at 0 °C for 16 h. Then, the pressure was released carefully and the resulting homogeneous solution was diluted with methanol, filtered through a SiO\(_2\) pad, and analyzed by GC or HPLC.

Typical procedure for S-selective catalytic hydrogenations reported in figure 3:

The substrate (1.75 mmol, 175 eq.) and [Rh(BIPHEP)][acac] (7.2 mg, 10 µmol) were dissolved in CHCl\(_3\) (1 mL) and stirred for 10 min. The solution was transferred into a 10 mL stirred stainless steel reactor equipped with a 6 mL glass vial and a stirring bar which was previously tempered at 0 °C through a cryostat. A cold solution (0 °C) of \((S,S)\)-prolinyl-methylene-bis[(trifluoromethyl)sulfonylamide (2) (57 mg, 140 µmol, 14 eq.) in CHCl\(_3\) (1 mL) was transferred into a 10 mL stainless steel reactor equipped with a 6 mL glass vial and a stirring bar. After stirring for 10 min, the reactor was pressurized with hydrogen (40 bar). The mixture was continuously stirred at 0 °C for 16 h. Then, the pressure was released carefully and the resulting homogeneous solution was diluted with CH\(_2\)Cl\(_2\) or CH\(_3\)OH, filtered through a SiO\(_2\) pad, and analyzed by GC or HPLC.

Procedure for R-selective hydrogenation of 6 at 0.025 mol-% catalyst loading:

Methyl 2-acetamidoacrylate (6) (573 mg, 4.00 mmol, 4000 eq.) was dissolved in CH\(_2\)Cl\(_2\) (4 mL) and combined with a freshly prepared solution of [Rh(\{R\})-BIPHEP][(S)-ProLOMe]] \((R,S)\)-5 (c = 0.001 mol L\(^{-1}\), 1.0 mL, 1 µmol) in CH\(_2\)Cl\(_2\) (see above). After stirring for 10 min, the slightly red solution was transferred into a 20 mL stainless steel reactor tempered to 0 °C through a cryostat and equipped with a 12 mL glass liner and a stirring bar. The stirrer was switched off and the reactor pressurized with hydrogen (40 bar). Afterwards the stirrer was started with a stirring speed of 700 rpm. The pressure drop was monitored with a digital pressure transducer (±0.1 bar). After 75 minutes the pressure was constant. Then, the pressure was carefully released and the resulting homogeneous solution was diluted with CH\(_2\)Cl\(_2\) filtered through a SiO\(_2\) pad and analyzed by GC.

Procedure for S-selective hydrogenation of 6 at 0.025 mol-% catalyst loading:

Methyl 2-acetamidoacrylate (6) (573 mg, 4.00 mmol, 4000 eq.) was dissolved in CH\(_2\)Cl\(_2\) (4 mL) and cooled to -10 °C. The substrate solution was combined with a freshly prepared solution of [Rh(\{oc\}-BIPHEP][(S)-ProLOMe]] \((R,S)\)/\((S,S)\)-5 (c = 0.001 mol L\(^{-1}\), 1.0 mL, 1 µmol) in CH\(_2\)Cl\(_2\) (see above). After stirring for 10 min, the slightly red solution was transferred into a 20 mL stainless steel reactor tempered to 0 °C through a cryostat and equipped with a 12 mL glass liner and a stirring bar. The stirrer was switched off and the reactor pressurized with hydrogen (40 bar). Afterwards the stirrer was switched on with a stirring speed of 700 rpm. The pressure drop was monitored with a digital pressure transducer (±0.1 bar). After 75 minutes the pressure was constant. Then, the pressure was released carefully and the resulting homogeneous solution was diluted with CH\(_2\)Cl\(_2\) filtered through a SiO\(_2\) pad and analyzed by GC.
**Typical procedure for the catalytic hydroboration of styrene:**

The solvent of a freshly prepared $[\text{Rh}((R\_a-\text{BIPHEP})[\text{S}\_c-\text{ProlOMe}]) \text{]} \ (R\_aS\_c)$-5 ($c = 0.1 \text{ mol L}^{-1}, 0.1 \text{ mL}, 10 \mu\text{mol}$) in $\text{CH}_2\text{Cl}_2$ (prepared by procedure A) was evaporated with a high vacuum pump. The Schlenk was introduced in a Glovebox, styrene (16) (170.0 µl, 1.48 mmol, 148 eq) was added and diluted with the appropriate solvent (2.0 mL). The red solution was tempered to the reaction temperature through a cryostat and catecholborane (250 µl, 2.35 mmol, 235 eq) was slowly added to the solution. The reaction mixture was kept at constant temperature during the reaction time ($rt = 1 \text{ h}, 0 \degree \text{C} = 3 \text{ h}, <0 \degree \text{C} = 12 \text{ h}$). After the reaction time, ethanol (2.5 mL), hydrogen peroxide (2.5 mL, 30% aqueous solution), and sodium hydroxide (2.5 mL, 2M aqueous solution) were added to the solution. The reaction mixture was allowed to warm to room temperature and stirred for 3 h at ambient pressure. The reaction mixture was then extracted with diethylether (50 mL). The organic phase was separated and washed with sodium hydroxide (25 mL, 2M aqueous solution), deionized water (25 mL) and sodium chloride (2 x 25 mL). The organic phase was dried with sodium sulfate and volatiles were evaporated at 40 °C and 800 mbar. A part of the residue was dissolved in methylene chloride (1 mL) and 1-hexanol (app. 10 mg) as an external standard for GC-analysis was added. Selectivity and enantioselectivity were determined by GC-analysis.
Kinetic of the diastereomerisation of ($\{S_aS_c\}/\{R_aS_c\}$-5) to $\{R_aS_c\}$-5 at different temperatures

Rate constants (first reaction order) of the diastereomerisation of ($\{S_aS_c\}/\{R_aS_c\}$-5) to $\{R_aS_c\}$-5 at different temperatures. Ratios ($\{S_aS_c\}$-5/$\{R_aS_c\}$-5) determined by $^{31}\text{P}\{^1\text{H}\}$-NMR spectroscopy (CD$_2$ClCD$_2$Cl).

Arrhenius Plot for the diastereomerisation of ($\{S_aS_c\}/\{R_aS_c\}$-5) to $\{R_aS_c\}$-5 at different temperatures

$E_A = 12258 \times 8.314 / 4,1868 / 1000 = 24.3$ kcal/mol; $\alpha(\%) = 1-R^2 = 4.2\%$  => $E_A = 24.3 \pm 1.0$ kcal/mol
NMR-data:

(S)-Prolinium-methylester-bis[(trifluoromethyl)sulfonyl]-amide (2):
[Rh(BiPHEP)(acac)] (3):
[(H)Rh(κ²-BIPHEP)(η²-acac)(κ²-ProOMe)][NTf₂] (4):
\{(S,S)}/\{(R,S)\}-[Rh(BIPHEP)]\{(S)\}-ProlOMe\}[[NTf_2] \{(S,S)\}/\{(R,S)\}-5]
[Rh([(R)-BIPHEP][(S)-ProlOMe]][NTf₂] \((R,S)_5\) - 5
$^{31}$P($^1$H)-NMR spectra of (R,Sc)-5 before and after hydrogenation of methyl 2-acetamidoacrylate (6)

$^{31}$P($^1$H)-NMR spectra of the crude reaction mixture before (CD$_2$Cl$_2$, 0 °C, 162 MHz (upper spectrum)) and after 243 MHz (lower spectrum) hydrogenation of 6 using (R,Sc)-5.

$^{31}$P($^1$H)-NMR spectra of (R,Sc)/(S,aSc)-5 before and after hydrogenation of methyl 2-acetamidoacrylate (6)

$^{31}$P($^1$H)-NMR spectra of the crude reaction mixture before (CD$_2$Cl$_2$, 0 °C, 243 MHz (upper spectrum)) and after 243 MHz (lower spectrum) hydrogenation of 6 using the diastereomeric mixture (S,aSc)/(R,Sc)-5 as catalyst.
GC/HPLC-data of the hydrogenation products:

Methyl 2-acetamidoacrylate (6):

\[
\begin{align*}
\text{cat, } H_2 & \rightarrow \\
\text{solvent, } 0 \, ^\circ C
\end{align*}
\]

Chiral GC analysis: *Ivadex* 7 (25 m), hydrogen flow (2 mL / min), film thickness (0.25 µm), inner diameter (0.25 mm), injector temperature = 250 °C, temperature program = 90 °C isotherm (10 min), 90 °C – 160 °C (5 °C / min), 160 °C isotherm (10 min), \( t_r = (R)-7: 12.88 \text{ min}, (S)-7: 11.46 \text{ min}, 6: 9.40 \text{ min}. \)

Hydrogenation of Methyl 2-acetamidoacrylate (6) – resulting in \( (R) \)-selectivity (Table 1, entry 1).
Hydrogenation of Methyl 2-acetamidoacrylate (6) – resulting in $(R)$-selectivity (Table 1, entry 2).

Hydrogenation of Methyl 2-acetamidoacrylate (6) – resulting in $(R)$-selectivity (Table 1, entry 3).
Hydrogenation of Methyl 2-acetamidoacrylate (6) – resulting in (R)-selectivity (Table 1, entry 4).

Hydrogenation of Methyl 2-acetamidoacrylate (6) – resulting in (R)-selectivity (Table 1, entry 5).
Hydrogenation of Methyl 2-acetamidoacrylate (6) – resulting in (R)-selectivity (Table 1, entry 6).

| Retention Time | Area         | Area % | Substance |
|----------------|--------------|--------|-----------|
| 12.701         | 334819       | 77.401 | 74.924    |

Hydrogenation of Methyl 2-acetamidoacrylate (6) – resulting in (R)-selectivity (Table 1, entry 7).

| Retention Time | Area         | Area % | Substance |
|----------------|--------------|--------|-----------|
| 11.234         | 875871       | 22.568 | 74.924    |
Hydrogenation of Methyl 2-acetamidoacrylate (6) – resulting in (R)-selectivity (Table 1, entry 8).

Hydrogenation of Methyl 2-acetamidoacrylate (6) – resulting in (R)-selectivity (Table 1, entry 9 and Fig. 3).
Hydrogenation of Methyl 2-acetamidoacrylate (6) – resulting in (S)-selectivity (Fig. 3).
Dimethyl itaconate (8):

\[ \text{8} \quad \xrightarrow{\text{cat, H}_2, \text{solvent, 0 °C}} \quad \text{9} \]

**Chiral GC analysis:** Lipodex E (25 m), hydrogen pressure (0.6 bar), injector temperature = 250 °C, temperature program = 80 °C isotherm, \( t_r = 8: 19.76, (S)-9: 14.90, (R)-9: 14.44. \)

Hydrogenation of Dimethyl itaconate (8) resulting in (R)-selectivity (Fig. 3).

Hydrogenation of Dimethyl itaconate (8) resulting in (S)-selectivity (Fig. 3).
Methyl 2-(trifluoromethyl)acrylate (10):

\[
\begin{array}{c}
\text{cat. } H_2 \quad \text{solvent, } 0 \degree C \\
\end{array}
\]

The product solution was diluted with toluene to prevent signal overlapping of the enantiomere and substrate signals. **Chiral GC analysis:** Chiralsil-DEX (25 m), hydrogen flow (2 mL / min), film thickness (0.25 µm), inner diameter (0.25 mm), injector temperature = 250 °C, temperature program = 50 °C isotherm (4.5 min), 50 °C – 160 °C (10 °C /min), 160 °C isotherm (4.5 min), \( t_r = (R)-11: 3.48, (S)-11: 3.11, 10: 3.01 \) min.

Hydrogenation of Methyl 2-(trifluoromethyl)acrylate (10) resulting in (R)-selectivity (Fig. 3).
tion of Methyl 2-(trifluoromethyl)acrylate (10) resulting in (S)-selectivity (Fig. 3).
Methyl 2-acetamido-3-phenylacrylate (12):

\[
\begin{align*}
\text{Ph} \quad \overset{\text{cat. H}_2}{\longrightarrow} \quad \overset{\text{solvent, 0 °C}}{\longrightarrow} \quad \text{Ph} \\
\overset{\text{HN}}{\text{O}} & \quad \text{O} \quad \text{Ph} \\
\overset{\text{HN}}{\text{O}} & \quad \text{O} \quad \text{Ph}
\end{align*}
\]

**Chiral HPLC analysis:** *Chiralpak IB* (250 mm), eluent flow (0.5 mL / min), particle size (5.0 µm), inner diameter (4.6 mm), eluent: n-heptane : 2-propanol (95:5), DAD: 220 nm, \( t_r = 12 \): 132.23 min, (S)-13: 56.98 min, (R)-13: 52.68 min.

Hydrogenation of Methyl 2-acetamido-3-phenylacrylate (12) resulting in (R)-selectivity (Fig. 3).
Hydrogenation of Methyl 2-acetamido-3-phenylacrylate (12) resulting in (S)-selectivity (Fig. 3).
(Z)-2-Benzamido-3-phenylacrylic acid (14):

![Chemical Structure](image)

The product solution was diluted with methanol to prevent 1:25 (V:V) before HPLC analysis. **Chiral HPLC analysis:** *Chiralpak-AD-H* (250 mm), eluent flow (0.5 mL / min), particle size (5.0 µm), inner diameter (4.6 mm), eluent: *n*-heptane : 2-propanol (95:5) – acidified with 0.1 % trifluoroacetic acid, DAD: 220 nm, *t*₁₅ = (R)-15: 103.03 min, (S)-15: 87.88 min.

Hydrogenation of (Z)-2-Benzamido-3-phenylacrylic acid (14) resulting in (R)-selectivity (Fig. 3).
Hydrogenation of (Z)-2-Benzamido-3-phenylacrylic acid (14) resulting in (S)-selectivity (Fig. 3).
GC-data of the hydroboration of styrene (16):

\[
\begin{align*}
1. & \quad (R,S)_\text{sc}-5 (0.75 \text{ mol\%}), \text{catecholborane} \\
2. & \quad \text{H}_2\text{O}_2, \text{NaOH}
\end{align*}
\]

Yield determination by GC: Hp-Wax (30 m), nitrogen pressure (1 bar), evaporating temperature = 250 °C, temperature program = 50 °C isotherm (5 min), 50 °C – 180 °C (8 °C / min), 180 °C isotherm (15 min), \( t_r \), = 2-Phenylethanol (18): 25.93 min, 1-Phenylethanol (17): 23.78 min, 1-Hexanol (Standard): 12.17 min, 16: 8.63 min.

Hydroboration of styrene (16) – n/iso-ratio and conversion (Table 2, entry 2).
Hydroboration of styrene (16) – n/iso-ratio and conversion (Table 2, entry 3).
Hydroboration of styrene (16) – n/iso-ratio and conversion (Table 2, entry 4).
Hydroboration of styrene (16) – \( n/\text{iso} \)-ratio and conversion (Table 2, entry 5).
Hydroboration of styrene (16) – n/iso-ratio and conversion (Table 2, entry 6).

| #  | RetTime | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|----|---------|------|-------------|-------------|-------------|--------|
| 1  | 0.873   | PB   | 0.0206      | 1.41738e4   | 9370.81934  | 10.33677|
| 2  | 0.984   | BB   | 0.0125      | 1.46533     | 1.95812     | 0.00107 |
| 3  | 1.223   | BB   | 0.0419      | 35.64670    | 5.37836     | 0.01141 |
| 4  | 1.442   | BP   | 0.0427      | 1.39631e4   | 4433.43848  | 9.89139 |
| 5  | 1.596   | VB   | 0.0561      | 9.3642e4    | 2.95120e4   | 72.44999|
| 6  | 1.752   | BB   | 0.0368      | 436.72949   | 165.57539   | 3.1850  |
| 7  | 2.207   | PB   | 0.0490      | 13.75633    | 4.46289     | 0.01003 |
| 8  | 4.604   | PB   | 0.0772      | 14.15342    | 2.88723     | 0.01032 |
| 9  | 5.458   | BB   | 0.0811      | 15.44831    | 2.94988     | 0.01127 |
| 10 | 12.171  | BB   | 0.0757      | 4000.44629  | 769.13171   | 2.91747 |
| 11 | 17.830  | PP   | 0.0730      | 18.16029    | 3.71980     | 0.01325 |
| 12 | 23.775  | BB   | 0.0675      | 5455.21289  | 1235.76721  | 3.93842 |
| 13 | 25.910  | BB   | 0.0765      | 48.14921    | 9.13800     | 0.03511 |
**Chiral GC analysis:** *Chiral-DEX* (25 m), hydrogen flow (2 mL/min), film thickness (0.25 µm), inner diameter (0.25 mm), injector temperature = 250 °C, temperature program = 50 °C – 160 °C (3 °C/min), 160 °C isotherm (10 min), $t_r = 2$-Phenylethanol (18): 11.98 min, (S)-17: 11.48 min, (R)-17: 10.73 min.

Hydroboration of styrene (16) – determination of enantioselectivity (Table 2, entry 2).
Hydroboration of styrene (16) – determination of enantioselectivity (Table 2, entry 3).

Hydroboration of styrene (16) – determination of enantioselectivity (Table 2, entry 4).
Hydroboration of styrene (16) – determination of enantioselectivity (Table 2, entry 5).

Hydroboration of styrene (16) – determination of enantioselectivity (Table 2, entry 6).
HR-MS (ESI)(+): [Rh(BIPHEP)(acac)] (3):

References

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