SUPPORTING INFORMATION

Organosilanols as Catalysts in Asymmetric Aryl Transfer Reactions

Salih Özçubukçu, Frank Schmidt, and Carsten Bolm*

Institut für Organische Chemie der RWTH Aachen, Landoltweg 1, D-52074 Aachen, Germany
Carsten.Bolm@oc.rwth-aachen.de

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All ferrocenyl oxazolines 4 have been synthesized starting from ferrocene carboxylic acid following the published procedures. THF was distilled from sodium/benzophenone ketyl radical under argon. Sec-Butyllithium was purchased from Fluka (1.3 M in cyclohexane).

All the NMR spectra were measured in CDCl$_3$ on a Varian Mercury 300 (for $^1$H NMR at 300MHz, for $^{13}$C NMR at 75 MHz) or a Varian Inova 400 (for $^1$H NMR at 400 MHz, for $^{13}$C NMR at 100 MHz) spectrometer using TMS as internal standard or residual solvent peaks (at 7.26 ppm for $^1$H NMR or 77 ppm for $^{13}$C NMR). Chemical shifts were given in ppm and coupling constants $J$, are given in Hz. Infrared spectra were measured as KBr discs.

1. Synthesis of Organosilanols

General Procedure A

Ferrocenyl silanes 5 could be synthesized according to the following general procedure, which is slightly modified to published procedures for the synthesis of diastereomerically pure ortho-substituted ferrocenyl oxazolines.

A solution of ferrocenyl oxazoline 4 (1 mmol) in dry THF (20 mL) at room temperature under argon atmosphere were prepared and cooled to −78 °C (by using a dry ice/aceton mixture). After being treated dropwise with sec-BuLi (1 mL, 1.3 mmol, 1.3 M in cyclohexane) solution, it was stirred for 2 hours at the same temperature. Addition of sec-BuLi changed the colour of the solution from orange to red. Chlorosilane (1.5 mmol) was added dropwise and the solution was allowed to warm up to room temperature overnight. It was washed with water (20 mL) and the aqueous phase was extracted with CH$_2$Cl$_2$ (10 mL) until getting a colourless aqueous phase. The combined organic phases were dried over Na$_2$SO$_4$, filtered and concentrated under
reduced pressure. Flash column chromatography was used to purify the corresponding ferrocenyl silanes 5 with a suitable solvent system of pentane and diethyl ether.

**Synthesis of (S,Rp)-2-(α-dimethylhydroxilane)ferrocenyl-5-tert-butyloxazoline [(S,Rp)-5a]**

(S,Rp)-5a could be synthesized according to the general procedure A, starting from ferrocenyl-5-tert-butyloxazoline by using dimethylchlorosilane with a yield of 64% as an orange oil. Eluent; pentane/diethyl ether: 85/15.

^1H NMR (300 MHz, CDCl3): δ 0.29 (d, J = 3.5 Hz, 3H, -SiH(CH3)2), 0.31 (d, J = 3.7 Hz, 3H, -SiH(CH3)2), 0.89 (s, 9H, -(C(CH3)3)), 3.81 (dd, J = 7.4 Hz, 8.7 Hz, 1H, -CHN-), 4.04-4.10 (m, 1H, -CH2O), 4.08 (s, 5H, C5H5), 4.15 (dd, J = 8.7 Hz, 9.3 Hz, 1H, -CH2O), 4.21 (dd, J = 1.2 Hz, 1.9 Hz, 1H, -C3H5), 4.36 (t, J = 2.5 Hz, 1H, -C3H5), 4.57 (dq, J = 3.5 Hz, 3.7 Hz, 1H, -SiH(CH3)2), 4.76-4.80 (m, 1H, -C5H5).

^13C NMR (75 MHz, CDCl3): δ -3.2 (CH3), -1.7 (CH3), 36.0 (CH3), 33.7 (C), 68.3 (CH2), 69.5 (C), 69.9 (CH), 72.0 (CH), 73.0 (CH), 76.4 (CH).

IR (KBr) ν: 759, 1657, 2140, 2957 cm⁻¹.

MS (EI): m/z 369 (M⁺,100%), 354 (28%), 312 (30%), 195 (21%), 121 (12%).

[a]D²⁵ +126.7 (c 3.0, CDCl3)

HRMS for C13H27FeNOSi: calcd. 369.1211, found 369.1212.

**Synthesis of (S,Rp)-2-(α-diisopropylhydroxilane)ferrocenyl-5-tert-butyloxazoline [(S,Rp)-5b]**

(S,Rp)-5b could be synthesized according to the general procedure A, starting from ferrocenyl-5-tert-butyloxazoline by using diisopropylchlorosilane with a yield of 64% as an orange oil. Eluent; pentane/diethyl ether: 85/15.

^1H NMR (400 MHz, CDCl3): δ 0.95 (s, 9H, -(C(CH3)3)), 0.97 (d, J = 7.7 Hz, 3H, -CH(CH3)2), 1.01 (d, J = 7.7 Hz, 1H, -CH(CH3)2), 1.20 (d, J = 6.9 Hz, 3H, -CH(CH3)2), 1.25 (d, J = 6.6 Hz, 3H, -CH(CH3)2), 1.30-1.40 (m, 2H, -CH(CH3)2), 3.88 (dd, 1H, J = 8.0 Hz, 10.0 Hz, -CHN-), 4.09 (t, J = 8.2 Hz, 1H, -CH2O), 4.15 (s, 5H, C5H5), 4.23 (dd, J = 8.5 Hz, 10.1 Hz, 1H, -CH2O), 4.29 (dd, J = 1.4 Hz, 2.4 Hz, 1H, -C5H5), 4.31 (t, J = 1.6 Hz, 1H, -SiH(CH(CH3)2)2), 4.47 (t, J = 2.20 Hz, 1H, -C5H5), 4.92 (dd, J = 1.4 Hz, 2.4 Hz, 1H, -C5H5).

^13C NMR (100 MHz, CDCl3): δ 11.8 (CH), 12.3 (CH), 18.8 (CH3), 19.3 (CH3), 19.6 (CH3), 20.7 (CH3), 26.0 (CH3), 33.5 (C), 68.0 (CH2), 68.1 (C), 69.7 (C), 70.0 (CH), 72.0 (CH), 72.3 (CH), 76.2 (CH), 77.3 (CH), 165.4 (C).

IR (KBr) ν: 788, 998, 1657, 2125, 2951 cm⁻¹.

MS (EI): m/z 425 (M⁺,41%), 382 (100%), 2822 (22%).

[a]D²⁵ +36.0 (c 0.5, CHCl3)

HRMS for C25H35FeNOSi: calcd. 425.1837, found 425.1837.

**Synthesis of (S,Rp)-2-(α-diphenylhydroxilane)ferrocenyl-5-tert-butyloxazoline [(S,Rp)-5c]**

(S,Rp)-5c could be synthesized according to the general procedure A, starting from ferrocenyl-5-tert-butyloxazoline by using diphenylchlorosilane with a yield of 91% as a dark orange solid. Eluent; pentane/diethyl ether: 85/15. mp. 118-120°C.

^1H NMR (300 MHz, CDCl3): δ 0.82 (s, 9H, -(C(CH3)3)), 3.72 (dd, 1H, J = 8.2 Hz, 9.7 Hz, -CHN-), 4.09 (t, J = 8.2 Hz, 1H, -CH2O), 4.02-4.05 (m, 1H, -CH2O), 4.10-4.15 (m, 1H, -C5H5), 4.14 (s, 5H, C5H5), 4.44 (t, J = 2.20 Hz, 1H, -C5H5), 5.00 (bs, 1H, -C5H5), 5.74 (s, 1H, -SiHPh2), 7.17-7.27 (m, 10H, -SiHPh2).

^13C NMR (75 MHz, CDCl3): δ 25.7 (CH3), 33.4 (C), 66.2 (C), 68.3 (CH2), 70.2 (CH), 72.7 (CH), 72.8 (CH), 75.8 (C), 76.1 (CH), 78.8 (CH), 127.4 (CH), 127.8 (CH), 128.8 (CH), 129.3 (CH), 135.0 (CH), 135.7 (CH), 135.8 (C), 136.0 (C), 165.3 (C).
**Synthesis of (**S,R**)<sub>p</sub>-2-(α-diisopropylhydroxilane)ferroceny-5-phenylcyloazoline ([**S,R**]<sub>p</sub>-5d)**

(S,R)<sub>p</sub>-5d could be synthesized according to the general procedure A, starting from ferroceny-5-phenylcyloazoline by using diisopropylchlorosilane with a yield of 70 % as dark orange oil. Eluent: pentane/diethyl ether: 80/20.

1H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.99 (d, <i>J</i> = 7.2 Hz, 3H, -CH<sub>2</sub>O), 4.10 (m, 1H, -CH<sub>2</sub>), 4.21 (s, 2H, -Si(CH<sub>3</sub>)), 4.53 (t, <i>J</i> = 2.5 Hz, 1H, -C<H><sub>3</sub>H<sub>3</sub>), 4.62 (dd, <i>J</i> = 8.2 Hz, 9.9 Hz, 1H, -CH<sub>2</sub>O) (due to diastereomer), 4.72 (dd, <i>J</i> = 8.2 Hz, 9.9 Hz, 1H, -CH<sub>2</sub>O), 5.05 (dd, <i>J</i> = 1.2 Hz, 2.5 Hz, -C<H><sub>2</sub>H<sub>3</sub>), 5.11 (dd, <i>J</i> = 1.2 Hz, 2.5 Hz, -C<H><sub>2</sub>H<sub>3</sub>), 5.18–5.28 (m, 1H, -CHN-), 7.23–7.40 (m, 5H, -Ph)

13C NMR (75 MHz, CDCl<sub>3</sub>): δ 11.7 (CH), 12.36 (CH), 12.43 (CH) (due to diastereomer), 18.9 (CH)(due to the diastereomer), 19.0 (CH), 13.4 (CH), 19.4 (CH), 20.5 (CH), 68.3 (CH), 68.4 (CH) (due to the diastereomer), 69.7 (CH), 70.0 (CH)(due to the diastereomer), 70.2 (CH), 72.6 (CH), 72.7 (CH) (due to the diastereomer), 74.4 (CH), 77.8 (CH), 126.6 (CH) (due to the diastereomer), 126.7 (CH), 127.39 (CH), 127.44 (CH) (due to the diastereomer), 128.65 (CH), 128.69 (CH) (due to the diastereomer), 142.8 (C), 168.0 (C).

IR (KBr) ν : 997, 1139, 1458, 2146, 3064 cm<sup>-1</sup>.

MS (EI): <i>m/z</i> 445 (M<sup>+</sup>,34%), 402 (100%), 285 (20%).

[α]<sub>D</sub><sup>25</sup> +34.4 (c 0.61, CHCl<sub>3</sub>)

HRMS for C<sub>25</sub>H<sub>31</sub>FeNOSi: calcd. 445.1524, found 445.1524.

**Synthesis of (**S,R**)<sub>p</sub>-2-(α-diisopropylhydroxilane)ferroceny-5-phenylcyloazoline ([**S,R**]<sub>p</sub>-5e)**

(S,R)<sub>p</sub>-5e could be synthesized according to the general procedure A, starting from ferroceny-5-phenylcyloazoline by using diphenylchlorosilane with a yield of 68 % as dark orange solid. Eluent; pentane/diethyl ether: 85/15. mp. 141-142 °C.

1H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.65-3.72 (m, 1H, -CH<sub>2</sub>O), 4.10 (m, 1H, -C<H><sub>3</sub>H<sub>3</sub>), 4.21 (s, 2H, -Si(CH<sub>3</sub>)), 4.54-4.62 (m, 1H, -C<H><sub>2</sub>O), 5.09 (bs, 2H, -C<H><sub>2</sub>H<sub>3</sub>, -CHN-), 5.76 (s, 1H, -SiHPPh<sub>2</sub>), 7.00-7.71 (m, 15H, -Ph, -SiHPPh<sub>2</sub>).

13C NMR (100 MHz, CDCl<sub>3</sub>): δ 66.7 (C), 70.2 (CH), 70.5 (CH), 73.0 (CH), 73.2 (CH), 74.4 (CH), 75.1 (C), 79.2 (CH), 126.9 (CH), 127.4 (CH), 127.6 (CH), 127.9 (CH) 129.1 (CH), 129.5 (CH), 135.1 (CH), 135.3 (C), 135.5 (C), 135.6 (CH), 142.3 (C), 167.3 (C).

IR (KBr) ν : 697, 731, 812, 1151, 1642, 2146, 3064 cm<sup>-1</sup>.

MS (EI): <i>m/z</i> 513 (M<sup>+</sup>,100%), 436 (39%), 409 (28%).

[α]<sub>D</sub><sup>25</sup> +77.0 (c 0.5, CHCl<sub>3</sub>)

HRMS for C<sub>31</sub>H<sub>27</sub>FeNOSi: calcd. 513.1211, found 513.1211.

**Synthesis of (**S,R**)<sub>p</sub>-2-(α-diisopropylhydroxilane)ferroceny-5-iso-propylcyloazoline ([**S,R**]<sub>p</sub>-5f)**

(S,R)<sub>p</sub>-5f could be synthesized according to the general procedure A, starting from ferroceny-5-phenylcyloazoline by using diisopropylchlorosilane with a yield of 81 % as dark orange oil. Eluent: pentane/diethyl ether: 80/20.

1H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.90-1.04 (m, 13H, -CH(CH<sub>3</sub>)<sub>2</sub>, -Si(CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (d, <i>J</i> = 6.4 Hz, 3H, Si(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>, 1.22-1.38 (m, 4H, Si(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>,
Synthesis of (S,R)-2-(α-diphenylhydrosilane)ferroceny1-5-iso-propyloxazoline [(S,Rp)-5g]

(S,Rp)-5g could be synthesized according to the general procedure A, starting from ferroceny1-5-phenyloxazoline by using diphenylchlorosilane with a yield of 85 % as dark orange solid. Eluent: pentane/diethyl ether: 90/10. mp. 104-105 °C.

1H NMR (400 MHz, CDCl3) : δ 0.76 (d, J = 6.9 Hz, 3H, -CH(CH3)2), 0.89 (d, J = 6.9 Hz, 3H, -CH(CH3)2), 1.66 (o, J = 6.6 Hz, 1H, -CH(CH3)2), 3.57 (t, J = 8.3 Hz, 1H, -CH2O), 3.82 (dt, J = 6.0 Hz, 8.8 Hz, -CHN), 4.03-4.06 (m, 1H, -C2H5), 4.15 (s, 5H, C5H15), 4.16-4.22 (m, 1H, -CH2O), 4.45 (t, J = 2.2 Hz, 1H, -C2H5), 5.02 (bs, -C2H5), 5.71 (s, 1H, -SiHPh2), 7.25-7.70 (m, 10H, -SiHPh2).

13C NMR (100 MHz, CDCl3): δ 18.1 (CH3), 19.0 (CH3), 32.5 (CH), 66.2 (C), 69.6 (CH2), 70.3 (CH), 72.5 (CH), 72.7 (CH), 72.9 (CH), 75.8 (C), 78.9 (CH), 127. 5 (CH), 127.8 (CH), 128.9 (CH), 129.3 (CH), 135.0 (CH), 135.6 (CH), 135.70 (C), 135.74 (C), 165.5 (C).

IR (KBr) v : 735, 795, 1117, 1658, 2139, 2953, 3098 cm\(^{-1}\).

MS (EI): m/z 479 (M\(^+\),100%), 408 (54%), 402 (83%).

[α]D\(^{25}\) +35.6 (c 0.5, CHCl3)

HRMS for C\(_{22}\)H\(_{20}\)FeNOSi: calcd. 479.1368, found 479.1268.

General Procedure B

Organosilanols 2 could be synthesized according to the following General Procedure B, which is slightly modified to the published procedure\(^5\) for the conversion of hydrosilanes to silanols.

To a solution of ferrocenyl silane 5 (1 mmol) in acetonitrile (3 mL) was added [IrCl(C\(_5\)H\(_{12}\))]\(_2\) (7 mg, 0.01 mmol) and water (36 mg, 2.0 mmol). The reaction mixture was stirred open air at room temperature. The reaction was monitored by TLC. Column chromatography or preparative TLC plates were used to purify the diastereomerically and enantiomerically enriched organosilanols by using suitable solvent system of pentane and diethyl ether.

Synthesis of (S,Rp)-2-(α-dimethylsilanol)ferroceny1-5-tert-butyloxazoline [(S,Rp)-2a]

(S,Rp)-2a could be synthesized according to the general procedure B, starting from (S,Rp)-5a with a yield of 91 % as an orange solid. Eluent: pentane/diethyl ether: 90/10. mp. 104-105 °C.

1H NMR (400 MHz, CDCl3) : δ 0.21 (s, 3H, Si(CH3)2), 0.49 (s, 3H, Si(CH3)2), 1.01 (s, 9H, -C(CH3)3), 3.93 (dd, 1H, J = 9.4 Hz, 9.9 Hz, -CHN), 4.14 (t, J = 8.8 Hz, 1H, -CH2O), 4.23 (s, 5H, C5H15), 4.26 (dd, J = 1.4 Hz, 2.4 Hz, 1H, C1H1), 4.29 (dd, 8.8 Hz, 9.9 Hz, -CH2O), 4.48 (t, 2.5 Hz, 1H, -C3H3), 4.82 (dd, J = 1.4 Hz, 2.5 Hz, 1H, -C3H3), 7.83 (bs, 1H, -OH)

13C NMR (100 MHz, CDCl3): δ 0.0 (CH3), 2.91 (CH3), 25.98 (CH3), 33.0 (C), 68.4 (CH2), 69.8 (CH), 72.1 (CH), 72.5 (CH), 72.8 (C), 73.9 (C), 75.2 (CH), 76.3 (CH), 168.7 (C).
IR (KBr) ν : 1149, 1643, 2858, 3441 cm⁻¹.
MS (EI): m/z 385 (M⁺,100%), 328 (27%).
[α]D²⁵ −309.6 (c 0.5, CHCl₃)
Calcd. for C₁₉H₂₇FeNO₂Si: C, 59.22; H, 7.06; N, 3.63; found C, 58.90; H, 7.41; N, 3.55.

Synthesis of (S,Rp)-2-(α-diiisopropylsilanol)ferrocenyl-5-tert-butyloxazoline [(S,Rp)-2b]
(S,Rp)-2b could be synthesized according to the general procedure B, starting from (S,Rp)-5b with a yield of 77% as a dark orange oil. Eluent: pentane/diethyl ether: 90/10.

¹H NMR (400 MHz, CDCl₃): δ 0.78 (d, J = 7.14 Hz, 3H, Si(CH(CH₃)₂)₂), 0.88 (d, J = 7.14 Hz, 3H, Si(CH(CH₃)₂)₂), 0.97 (m, 2H, Si(CH(CH₃)₂)₂), 1.02 (s, 9H, -C(CH₃)₃), 1.29 (m, 3H, Si(CH(CH₃)₂)₂), 1.35 (m, 3H, Si(CH(CH₃)₂)₂), 3.90 (m, 1H, -CH₂O), 4.08 (m, 1H, -CH₂O), 4.22 (s, 5H, C₂H₅), 4.29 (dd, 8.5 Hz, 9.9 Hz, -CH₂O), 4.31 (m, 1H, C₂H₅), 4.50 (t, 2.5 Hz, 1H, -C₆H₅), 4.84 (dd, J = 1.1 Hz, 2.5 Hz, 1H, -C₆H₅), 7.65 (bs, 1H, -OH).

¹³C NMR (100 MHz, CDCl₃): δ 13.9 (CH), 14.9 (CH), 17.86 (CH₃), 17.94 (CH₃), 18.51 (CH₃), 26.5 (CH₃), 33.1 (C), 68.6 (CH₂), 70.3 (CH), 72.0 (C), 72.2 (CH), 72.3 (CH), 73.1 (C), 75.7 (CH), 76.8 (CH), 169.0 (C).
IR (KBr) ν : 890, 990, 1149, 1642, 2863, 3444 cm⁻¹.
MS (EI): m/z 441 (M⁺,57%), 398 (100%), 298 (37%).
[α]D²⁵ −165.3 (c 0.88, CHCl₃)
HRMS for C₂₃H₁₅FeNO₂Si: calcd. 441.1786, found 441.1786.

Synthesis of (S,Rp)-2-(α-diphenylsilanol)ferrocenyl-5-tert-butyloxazoline [(S,Rp)-2c]
(S,Rp)-2c could be synthesized according to the general procedure B, starting from (S,Rp)-5c with a yield of 91% as an orange solid. Eluent: pentane/diethyl ether: 95/5. mp. 104-105 °C.

¹H NMR (400 MHz, CDCl₃): δ 1.04 (s, 9H, -C(CH₃)₃), 3.88 (dd, 1H, J = 9.3 Hz, 10.1 Hz, -CH₂O), 4.02 (s, 5H, C₂H₅), 4.14 (t, J = 8.8 Hz, 1H, -CH₂O), 4.27 (m, 2H, -CH₂O, -C₆H₅), 4.51 (t, 2.5 Hz, 1H, -C₆H₅), 4.89 (dd, J = 1.4 Hz, 2.5 Hz, 1H, -C₆H₅), 7.28 (m, 3H, -Ph), 7.44 (m, 3H, -Ph), 7.50 (m, 2H, -Ph), 7.88 (m, 2H, -Ph), 8.60 (bs, 1H, -OH).

¹³C NMR (100 MHz, CDCl₃): δ 26.2 (CH₂), 33.1 (C), 68.6 (CH₂), 70.1 (CH), 70.5 (C), 72.9 (CH), 72.9 (C), 75.1 (CH), 78.1 (CH), 127.3 (CH), 127.4 (CH), 129.0 (CH), 129.5 (CH), 134.4 (CH), 134.7 (CH), 136.0 (C), 138.6 (C), 168.8 (C).
IR (KBr) ν : 702, 901, 1113, 1150, 1638, 2955 cm⁻¹.
MS (EI): m/z 509 (M⁺,100%).
[α]D²⁵ −446.8 (c 0.5, CHCl₃)
Calcd. for C₂₉H₂₃FeNO₂Si: C, 68.36; H, 6.13; N, 2.75; found C, 68.23; H, 6.34; N, 2.56.

Synthesis of (S,Rp)-2-(α-diiisopropylsilanol)ferrocenyl-5-phenyloxazoline [(S,Rp)-2d]
(S,Rp)-2d could be synthesized according to the general procedure B, starting from (S,Rp)-5d with a yield of 57% as an orange solid. Eluent: pentane/diethyl ether: 80/20. mp. 99-100 °C.

¹H NMR (400 MHz, CDCl₃): δ 0.81 (d, J = 7.1 Hz, 3H, Si(CH(CH₃)₂)₂), 0.89 (d, J = 7.1 Hz, 3H, Si(CH(CH₃)₂)₂), 0.93-1.04 (m, 2H, Si(CH(CH₃)₂)₂), 1.26-1.30 (m, 3H, Si(CH(CH₃)₂)₂), 1.30-1.35 (m, 3H, Si(CH(CH₃)₂)₂), 4.20 (t, J = 8.5 Hz, 1H, -CH₂O), 4.26 (s, 5H, C₆H₅), 4.37 (dd, 1.4 Hz, 2.5 Hz, 1H, -C₆H₅), 4.55 (t, 2.5 Hz, 1H, -C₆H₅), 4.72 (dd, J = 8.5 Hz, 10.0 Hz, 1H, -CH₂O), 4.92 (dd, J = 1.4 Hz, 2.5 Hz, -C₆H₅), 5.20-5.28 (m, 1H, -CH₂O), 7.25-7.42 (m, 5H, -Ph), 7.44 (bs, 1H, -OH).

¹³C NMR (100 MHz, CDCl₃): δ 13.6 (CH), 14.8 (CH), 17.7 (CH₃), 18.28 (CH₃), 18.33 (CH₃), 68.9 (CH), 70.3 (CH), 72.2 (C), 72.3 (C), 72.4 (CH), 74.4 (CH₂), 77.4 (CH), 126.1 (CH), 127.5 (CH), 128.8 (CH), 141.6 (C), 170.3 (C).
IR (KBr) ν : 890, 989, 1148, 1633, 2860, 2940 cm⁻¹.
MS (EI): m/z 461 (M⁺,59%), 418 (100%).
\[ \alpha \] D 25° -227.2 (c 0.5, CHCl₃)
Calcd. for C₅H₃FeNO₃Si: C, 65.07; H, 6.77; N, 3.04; found C, 64.80; H, 6.44; N, 2.86.

Synthesis of \((S,R)\)-2-(\(\alpha\)-diphenylsilanol)ferrocenyl-5-phenyloxazoline \([(S,R)\)-2e]
\((S,R)\)-2e could be synthesized according to the general procedure B, starting from \((S,R)\)-5e with a yield of 91 % as an orange solid. Eluent; pentane/diethyl ether: 95/5. mp. Decompose >150 °C.
1H NMR (300 MHz, CDCl₃) : δ 4.11 (s, 5H, C₅H₅), 4.18-4.25 (m, 1H, -CH₂O), 4.28-4.30 (m, 1H, -C₆H₅), 4.56 (t, J = 2.5 Hz, 1H, -C₆H₅), 4.62-4.71 (m, 1H, -CH₂O), 4.99-5.01 (m, 1H, -C₆H₅), 5.14-5.24 (m, 1H, -CHN), 7.25-7.55 (m, 13H, -Ph), 7.82-7.90 (m, 2H, -Ph), 8.26 (bs, 1H, -OH)
13C NMR (75 MHz, CDCl₃): δ 68.9 (CH), 70.5 (CH), 71.1 (C), 72.6 (C), 73.3 (CH), 73.4 (CH), 74.8 (CH₂), 78.8 (CH), 126.3 (CH), 127.6 (CH), 127.7 (CH), 127.8 (CH) 129.1 (CH), 129.4 (CH), 129.8 (CH), 134.7. (CH), 135.0 (CH), 136.0 (C), 138.6 (C), 142.0 (C), 170.5 (C).
IR (KBr) v: 698, 1115, 1157, 1626 cm⁻¹.
MS (EI): m/z 529 (M⁺,100%), 452 (30%), 344 (27%).
\[ \alpha \] D 25° -307.2 (c 0.5, CHCl₃)
Calcd. for C₅H₃FeNO₃Si: C, 70.32; H, 5.14; N, 2.65; found C, 70.09; H, 5.18; N, 2.65.

Synthesis of \((S,R)\)-2-(\(\alpha\)-diisopropylsilanol)ferrocenyl-5-iso-propyloxazoline \([(S,R)\)-2f]
\((S,R)\)-2f could be synthesized according to the general procedure B, starting from \((S,R)\)-5f with a yield of 65 % as an orange oil. Eluent; pentane/diethyl ether : 85/15.
1H NMR (400 MHz, CDCl₃) : δ 0.79 (d, J = 7.1 Hz, 3H,-Si(CH(CH₃)₂)₂), 0.88 (d, J = 7.1 Hz, 3H, Si(CH(CH₃)₂)₂), 0.93-0.99 (m, 1H, -Si(CH(CH₃)₂)₂), 1.00 (d, J = 6.6 Hz, 3H, -CH(CH₃)₂), 1.19 (d, J = 6.6 Hz, 3H, -CH(CH₃)₂), 1.26-1.30 (m, 3H, Si(CH(CH₃)₂)₂), 1.32-1.36 (m, 4H, Si(CH(CH₃)₂)₂, -Si(CH(CH₃)₂)₂), 1.82 (o, J = 6.6 Hz, 1H, -CH(CH₃)₂), 3.90 (dt, J = 6.9 Hz, 9.3 Hz, 1H, -CHN), 4.03 (t, J = 8.5 Hz, 1H, -CH₂O), 4.20 (s, 5H, C₅H₅), 4.30-4.36 (m, 2H, -C₆H₅, -CH₂O), 4.55 (t, J = 2.5 Hz, 1H, -C₆H₅), 4.84 (dd, J = 1.4 Hz, 2.5 Hz, -C₆H₅), 7.23 (bs, 1H, -OH)
13C NMR (100 MHz, CDCl₃): δ 13.8 (CH), 14.9 (CH), 17.8 (CH₂), 17.9 (CH₃), 18.50 (CH₃), 18.53 (CH₃), 19.1 (CH₃), 19.3 (CH₃), 32.90 (CH), 70.4 (CH₂), 70.5 (CH), 72.0 (CH), 72.28 (CH), 72.30 (CH), 72.9 (C), 77.5 (CH), 168.9 (C).
IR (KBr) v: 888, 987, 1151, 1643, 2865, 2957, 3098 cm⁻¹.
MS (EI): m/z 427 (M⁺,47%), 384 (100%), 298 (25%).
\[ \alpha \] D 25° -312.1 (c 0.95, CHCl₃)
Calcd. for C₅H₃FeNO₃Si: C, 61.82; H, 7.78; N, 3.28; found C, 61.83; H, 7.92; N, 3.56.

Synthesis of \((S,R)\)-2-(\(\alpha\)-diphenylsilanol)ferrocenyl-5-iso-propyloxazoline \([(S,R)\)-2g]
\((S,R)\)-2g could be synthesized according to the general procedure B, starting from \((S,R)\)-5g with a yield of 82 % as an orange solid. Eluent; pentane/diethyl ether: 95/5. mp. 138-139.
1H NMR (300 MHz, CDCl₃) : δ 1.03 (d, J = 6.7 Hz, 3H, -CH(CH₃)₂), 1.15 (d, J = 6.9 Hz, 3H, -CH(CH₃)₂), 1.86 (o, J = 6.7 Hz, 1H, -CH(CH₃)₂), 3.92 (dd, J = 6.2 Hz, 8.2 Hz, 9.8 Hz, 1H, -CHN), 4.03 (s, 5H, C₅H₅), 4.09 (dd, J = 8.2 Hz, 8.4 Hz, 1H,-CH₂O), 4.28 (dd, J = 1.5 Hz, 2.5 Hz, 1H, -C₆H₅), 4.51 (t, J = 2.5 Hz, 1H, -C₆H₅), 4.90 (dd, J = 1.2 Hz, 2.2 Hz, -C₆H₅), 7.20-7.35 (m, 3H, -Ph), 7.40-7.55 (m, 3H, -Ph), 7.80-7.85 (m, 2H, -Ph), 8.88 (bs, 1H, -OH)
13C NMR (75 MHz, CDCl₃): δ 18.8. (CH₃), 18.9 (CH₃), 32.6 (CH), 70.3 (CH₂), 70.4 (CH), 70.7 (C), 71.4 (CH), 73.0 (CH), 73.1 (CH), 78.3 (CH), 127.5 (CH), 127.6 (CH), 129.3 (CH), 129.7 (CH), 134.6 (CH), 134.9 (CH), 136.1 (C), 138.8 (C), 169.1 (C).
IR (KBr) v: 705, 736, 903, 987, 1114, 1155, 1641, 2961, 3048 cm⁻¹.
MS (EI): m/z 495 (M⁺,100%).
[α]D<sup>25</sup> -393.6 (c 0.5, CHCl₃)
Caled. for C<sub>28</sub>H₂₉FeNO₃Si: C, 67.88; H, 5.90; N, 2.83; found C, 67.83; H, 6.12; N, 2.60.

Synthesis of (S,R<sub>p</sub>)-2-(α-diisopropylsilanol)ferrocenyl-5-benzoxazoline [(S,R<sub>p</sub>)-2h]
(S,R<sub>p</sub>)-2h could be synthesized according to the general procedure B, starting from (S,R<sub>p</sub>)-5h with a yield of 45 % as a orange oil. Eluent: pentane/diethyl ether: 95/5.

1H NMR (400 MHz, CDCl₃): δ 8.01 (d, J = 6.9 Hz, 3H, -Si(CH(CH₃)₂)), 0.90 (d, J = 6.9 Hz, 3H, -Si(CH(CH₃)₂)), 0.94-1.04 (m, 1H, -Si(CH(CH₃)₂)), 1.28-1.31 (m, 3H, -Si(CH(CH₃)₂)), 1.33-1.38 (m, 3H, -Si(CH(CH₃)₂)), 2.79 (dd, J = 9.1 Hz, 13.7 Hz, 1H, -CH₂Ph), 3.24 (dd, J = 4.0 Hz, 13.9 Hz, 1H, -CH₂Ph), 4.08 (t, J = 8.2 Hz, 1H, -CH₂O), 4.15 (s, 5H, C₆H₅), 4.21-4.28 (m, 1H, -CH₂O), 4.30-4.33 (m, 1H, -C₃H₃), 4.38-4.47 (m, 1H, -CHN-), 4.48-4.52 (m, 1H, -C₅H₃), 4.80-4.84 (m, 1H, -C₅H₃), 7.20-7.36 (m, 5H, -Ph), 7.73 (bs, 1H, -OH).

13C NMR (100 MHz, CDCl₃): δ 14.0 (CH), 15.0 (CH), 17.8 (CH₃), 17.9 (CH₃), 18.49 (CH₃), 18.53 (CH₃), 41.5 (CH₂), 66.8 (CH), 70.6 (CH), 71.3 (CH₂), 72.0 (C), 72.4 (CH), 72.5 (CH), 126.7 (CH), 128.7 (CH), 129.5 (CH), 137.3 (C), 169.6 (C).

IR (KBr) ν: 888, 988, 1147, 1640, 2863, 2940, 3090 cm⁻¹.

MS (EI): m/z 495 (M⁺,54%), 432 (100%).
[α]D<sup>25</sup> -80.8 (c 0.5, CHCl₃)
Caled. for C<sub>26</sub>H₃₃FeNO₃Si: C, 65.08; H, 7.00; N, 2.95; found C, 64.94; H, 7.08; N, 3.11.

Synthesis of (S,R<sub>p</sub>)-2-(α-diphenylsilanol)ferrocenyl-5-benzoxazoline [(S,R<sub>p</sub>)-2i]
(S,R<sub>p</sub>)-2i could be synthesized according to the general procedure B, starting from (S,R<sub>p</sub>)-5i with a yield of 43 % as an orange oil. Eluent: pentane/diethyl ether: 95/5.

1H NMR (300 MHz, CDCl₃): δ 2.85 (dd, J = 8.7 Hz, 13.9 Hz, 1H, -CH₂Ph), 3.21 (dd, J = 4.5 Hz, 13.9 Hz, 1H, -CH₂Ph), 3.97 (s, 5H, C₆H₅), 4.11 (t, J = 8.2 Hz, 1H, -CH₂O), 4.21-4.28 (m, 2H, -CH₂O, -C₅H₃), 4.35-4.45 (m, 1H, -CHN-), 4.48-4.52 (m, 1H, -C₃H₃), 4.88 (dd, J = 1.2 Hz, 2.2 Hz, 1H, -C₃H₃), 7.20-7.39 (m, 8H, -Ph), 7.41-7.53 (m, 5H, -Ph), 7.86-7.90 (m, 2H, -Ph) 8.62 (bs, 1H, -OH).

13C NMR (75 MHz, CDCl₃): δ 41.4 (CH₂), 66.5 (CH), 70.5 (CH), 71.4 (CH₂), 72.6 (C), 73.1 (CH), 73.2 (CH), 78.6 (CH), 126.8 (CH), 127.6 (CH), 127.7 (CH), 128.8 (CH), 129.4 (CH), 129.7 (CH), 129.8 (CH), 134.7 (CH), 135.0 (CH), 136.1 (C), 137.3 (C), 138.8 (C), 169.7 (C).

IR (KBr) ν: 756, 1114, 1151, 1638, 2923, 3008 cm⁻¹.

MS (EI): m/z 543 (M⁺,100%), 466 (28%), 344 (24%).
[α]D<sup>25</sup> -378.0 (c 0.25, CDCl₃)
HRMS for C<sub>32</sub>H₂₉FeNO₃Si: calcd. 543.1317, found 543.1317.

2. Catalytic Asymmetric Phenyl Transfer to Aldehydes

**Methode A:** In a glovebox a 10 mL vial was charged with diphenylzinc (35.5 mg, 0.16 mmol). The vial was sealed with a septum and removed from the glovebox. Freshly distilled toluene was added (1.25 mL). After the addition of ZnEt₂ (1 M in heptane, 0.33 mL, 0.33 mmol), the mixture was stirred for 45 min at room temperature. Another vial was charged with catalyst 2 (10 mol%, 0.025 mmol), sealed with a septum, and flushed with argon. Toluene (1 mL) was added to dissolve 2 and the solution was transfered via syringe into the first vial. The resulting mixture was stirred for 30 min at room temperature, then cooled to 10 °C and stirred for an additional 10 min at this temperature. A third vial was charged with aldehyde 6 (0.25 mmol), closed with a septum, flushed with argon, and the substrate was dissolved in toluene (1 mL). After cooling to 10 °C the solution was transfered via syringe into the other reaction vial. The resulting mixture was stirred for 12 h at 10 °C. Then the
reaction was quenched with water. Diluted acetic acid (20% in water, 30 mL) was added and the mixture extracted with dichloromethane. The organic layer was washed with water, dried (MgSO₄), filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, eluents: pentane / diethyl ether 8:2) to give the desired alcohol 7.

**Methode B:** The protocol was identical to the one described for *methode A* with the following exceptions: A 10 mL vial was charged with triphenylborane (60.5 mg, 0.25 mmol). ZnEt₂ (1 M in heptane, 0.75 mL, 0.75 mmol) in toluene (0.4 mL) and catalyst 2c (13.5 mg, 0.025 mmol) in toluene (1 mL) were used. After the 12 h reaction time (at 0 °C) the mixture was quenched with water and acetic acid (20% in water, 30 mL) was added. The subsequent work-up was performed as described above.

**Methode C:** A well dried Schlenk tube was charged with phenyl boronic acid (73 mg, 0.6 mmol) and dimethyl-polyethylenglycol (Mₘ = 2000 g•mol⁻¹, 0.5 g, 0.25 mmol) and was sealed with a septum. Freshly distilled toluene (1.5 mL) was added followed by ZnEt₂ (148 µL, 1.8 mmol). The mixture was heated to 60 °C, stirred for 12 h at this temperature and afterwards cooled to room temperature. A 10 mL vial was charged with catalyst 2c (13.5 mg, 0.025 mmol), sealed with a septum, flushed with argon, and dissolved in toluene (1 mL). The solution was transferred via syringe to the first solution. The mixture was stirred for 30 min at room temperature and then also cooled to 10 °C. Stirring was continued for additional 10 min at this temperature. Another vial was charged with *p*-chlorobenzaldehyde (*6a*) (35 mg, 0.25 mmol) and dissolved in toluene (1 mL). After cooling to 10 °C the solution was transferred via syringe into the other solution. The reaction was stirred for 12 h at 10 °C. Then the reaction was quenched with water. Subsequently it was filtered through a pad of celite and washed with dichloromethan. Acetic acid (20% in water, 30 mL) was added. The subsequent work-up was performed as described above.

**Synthesis of (R)-(4-chlorophenyl)phenylmethanol (7a)**
According to the different methods (A, B or C), it was obtained from *p*-chlorobenzaldehyde (*6a*) as a white solid.

\[
\begin{align*}
\text{H NMR (CDCl₃, 300 MHz): } & \delta 2.23 \text{ (bs, 1H, -OH)}, 5.78 \text{ (s, 1H, -CH)}, 7.23-7.45 \text{ (m, 9H, -Ph).} \\
\text{C NMR (CDCl₃, 75 MHz): } & \delta 75.7 \text{ (CH), 126.6 (2CH), 127.9 (3CH), 128.7 (2CH), 128.7 (2CH), 133.3 (C), 142.3 (C), 143.5 (C).}
\end{align*}
\]

HPLC – separation conditions:
Chiralcel OB-H, 30 °C, 230 nm, 90:10 heptane / *i*-PrOH, 0.5 mL/min; \( t_R = 25.7 \) min (R), 33.6 min (S).

**Synthesis of (R)-(4-methoxyphenyl)phenylmethanol (7b)**
According to method A, it was obtained from *p*-methoxybenzaldehyde (*6b*) (34 mg, 0.25 mmol) as a clear liquid.

\[
\begin{align*}
\text{H NMR (CDCl₃, 300 MHz): } & \delta 2.19 \text{ (bs, 1H, -OH)}, 3.78 \text{ (s, 3H CH₃)}, 5.80 \text{ (s, 1H, -CH)}, 6.84-6.89 \text{ (m, 2H, -Ph)}, 7.24-7.39 \text{ (m, 7H, -Ph).} \\
\text{C NMR (CDCl₃, 75 MHz): } & \delta 55.2 \text{ (CH₃)}, 75.6 \text{ (CH), 113.7 (2CH), 126.2 (2CH), 127.2 (CH), 127.7 (2CH), 128.2 (2CH), 136.0 (C), 143.8 (C), 158.8 (C).}
\end{align*}
\]

HPLC – separation conditions:
Chiralcel OJ, 25 °C, 254 nm, 90:10 heptane / *i*-PrOH, 1.0 mL/min; \( t_R = 39.7 \) min (R), 45.4 min (S).
Synthesis of (R)-(2-bromophenyl)phenylmethanol (7c)
According to method A, it was obtained from o-bromobenzaldehyde (6c) (29 µL, 0.25 mmol) as a yellow solid.
$^1$H NMR (CDCl$_3$, 300 MHz): δ 2.47 (s, 1H, OH), 6.17 (s, 1H, CH), 7.20-7.42-6.89 (m, 7H, -Ph), 7.50-7.59 (m, 2H, -Ph).
$^{13}$C NMR (CDCl$_3$, 75 MHz): δ 74.9 (CH), 122.9 (C), 127.1 (2CH), 127.8 (CH), 127.9 (CH), 128.6 (2CH), 129.2 (CH), 129.7 (CH), 132.9 (CH), 142.2 (C), 142.6 (C).
HPLC – separation conditions:
Chiralcel OD, 25 °C, 220 nm, 90:10 heptane / i-PrOH, 1.0 mL/min; $t_R = 10.4$ min (R), 14.2 min (S).

Synthesis of (R)-(4-methylphenyl)phenylmethanol (7d)
According to method A, it was obtained from p-methylbenzaldehyde (6d) (29 µL, 0.25 mmol) as a white solid.
$^1$H NMR (CDCl$_3$, 300 MHz): δ 2.04 (s, 1H, OH), 2.31 (s, 3H CH$_3$), 5.76 (s, 1H, CH), 7.08-7.37 (m, 9H, -Ph)
$^{13}$C NMR (CDCl$_3$, 75 MHz): δ 21.2 (CH$_3$), 76.2 (CH), 126.6 (2CH), 126.7 (2CH), 127.5 (CH), 128.5 (2CH), 129.3 (2CH), 137.3 (C), 141.0 (C), 144.0 (C).
HPLC – separation conditions:
Chiralcel OD, 30 °C, 230 nm, 98:2 heptane / i-PrOH, 0.9 mL/min; $t_R = 30.3$min (S), 33.7 min (R).

References:
Compound 5a
Compound 5b
Compound 5c
Compound 5d
Compound 5e
Compound 5f
Compound 5g
Compound 2a
Compound 2c
Compound 2d
Compound 2f
Compound 2g
Compound 2h
Compound 2i