SUPPORTING INFORMATION

Organosilanols as Catalysts in Asymmetric Aryl Transfer Reactions

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All ferrocenyl oxazolines **4** have been synthesized starting from ferrocene carboxylic acid following the published procedures.¹ 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 ^1H NMR at 300 MHz, for ^{13}C NMR at 75 MHz) or a Varian Inova 400 (for ^1H 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 ^1H 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 procedures² 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 $-78\text{ }^\circ\text{C}$ (by using a dry ice/acetone 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_2Cl_2 (10 mL) until getting a colourless aqueous phase. The combined organic phases were dried over Na_2SO_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,R_p*)-2-(α -dimethylhydrosilane)ferrocenyl-5-*tert*-butyloxazoline [(*S,R_p*)-5a**]**

(*S,R_p*)-**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 a 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, -C₅H₃), 4.36 (t, J = 2.5 Hz, 1H, -C₅H₃), 4.57 (dq, J = 3.5 Hz, 3.7 Hz, 1H, -SiH(CH₃)₂), 4.76-4.80 (m, 1H, -C₅H₃).

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%).

$[\alpha]_D^{25}$ -126.7 (c 3.0, CDCl₃)

HRMS for C₁₉H₂₇FeNOSi: calcd. 369.1211, found 369.1212.

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

(*S,R_p*)-**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 a 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, -C₅H₃), 4.31 (t, J = 1.6 Hz, 1H, -SiH(CH(CH₃)₂)₂), 4.47 (t, J = 2.20 Hz, 1H, -C₅H₃), 4.92 (dd, J = 1.4 Hz, 2.4 Hz, 1H, -C₅H₃).

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%).

$[\alpha]_D^{25}$ +36.0 (c 0.5, CHCl₃)

HRMS for C₂₃H₃₅FeNOSi: calcd. 425.1837, found 425.1837.

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

(*S,R_p*)-**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, -C₅H₃), 4.14 (s, 5H, C₅H₅), 4.44 (t, J = 2.20 Hz, 1H, -C₅H₃), 5.00 (bs, 1H, -C₅H₃), 5.74 (s, 1H, -SiHPh₂), 7.21-7.72 (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).

IR (KBr) ν : 734, 1113, 1145, 1659, 2152, 2955 cm^{-1} .

MS (EI): m/z 493 (M^+ , 100%), 416 (39%), 409 (32%).

$[\alpha]_D^{25}$ -52.6 (c 1.09, CHCl_3)

HRMS for $\text{C}_{29}\text{H}_{31}\text{FeNOSi}$: calcd. 493.1524, found 493.1525.

Synthesis of (*S,R_p*)-2-(α -diisopropylhydrosilane)ferrocenyl-5-phenyloxazoline [(*S,R_p*)-5d]

(*S,R_p*)-5d could be synthesized according to the general procedure A, starting from ferrocenyl-5-phenyloxazoline by using diisopropylchlorosilane with a yield of 70 % as dark orange oil. Eluent; pentane/diethyl ether: 80/20.

^1H NMR (300 MHz, CDCl_3) : δ 0.99 (d, J = 7.2 Hz, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 0.99 (d, J = 7.4 Hz, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.20 (d, J = 6.7 Hz, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.24 (d, J = 5.9 Hz, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.26-1.40 (m, 2H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 4.09 (t, J = 8.4 Hz, 1H, $-\text{CH}_2\text{O}$), 4.20 (s, 5H, C_5H_5), 4.21 (s, C_5H_5)(due to diastereomer), 4.30 (t, J = 2.1 Hz, 1H, $-\text{SiH}(\text{CH}(\text{CH}_3)_2)_2$), 4.34 (dd, J = 1.5 Hz, 2.5 Hz, $-\text{C}_5\text{H}_3$), 4.53 (t, 2.5 Hz, 1H, $-\text{C}_5\text{H}_3$), 4.62 (dd, J = 8.2 Hz, 9.9 Hz, $-\text{CH}_2\text{O}$)(due to diastereomer), 4.72 (dd, J = 8.2 Hz, 9.9 Hz, 1H, $-\text{CH}_2\text{O}$), 5.05 (dd, J = 1.2 Hz, 2.5 Hz, $-\text{C}_5\text{H}_3$), 5.11 (dd, J = 1.2 Hz, 2.5 Hz, $-\text{C}_5\text{H}_3$), 5.18-5.28 (m, 1H, $-\text{CHN-}$), 7.23-7.40 (m, 5H, $-\text{Ph}$)

^{13}C NMR (75 MHz, CDCl_3): δ 11.7 (CH), 12.36 (CH), 12.43 (CH)(due to diastereomer), 18.9 (CH_3)(due to the diastereomer), 19.0 (CH_3), 19.4 (CH_3), 19.5 (CH_3), 20.5 (CH_3), 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_2), 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, 1649, 2124, 2942 cm^{-1} .

MS (EI): m/z 445 (M^+ , 34%), 402 (100%), 285 (20%).

$[\alpha]_D^{25}$ +34.4 (c 0.61, CHCl_3)

HRMS for $\text{C}_{25}\text{H}_{31}\text{FeNOSi}$: calcd. 445.1524, found 445.1524.

Synthesis of (*S,R_p*)-2-(α -diphenylhydrosilane)ferrocenyl-5-phenyloxazoline [(*S,R_p*)-5e]

(*S,R_p*)-5e could be synthesized according to the general procedure A, starting from ferrocenyl-5-phenyloxazoline by using diphenylchlorosilane with a yield of 68 % as dark orange solid. Eluent; pentane/diethyl ether: 85/15. mp. 141-142 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) : δ 3.65-3.72 (m, 1H, $-\text{CH}_2\text{O}$), 4.10 (m, 1H, $-\text{C}_5\text{H}_3$), 4.21 (s, 5H, C_5H_5), 4.50 (bs, 1H, $-\text{C}_5\text{H}_3$), 4.54-4.62 (m, 1H, $-\text{CH}_2\text{O}$), 5.09 (bs, 2H, $-\text{C}_5\text{H}_3$, $-\text{CHN-}$), 5.76 (s, 1H, $-\text{SiHPh}_2$), 7.00-7.71 (m, 15H, $-\text{Ph}$, $-\text{SiHPh}_2$).

^{13}C NMR (100 MHz, CDCl_3): δ 66.7 (C), 70.2 (CH), 70.5 (CH), 73.0 (CH), 73.2 (CH), 74.4 (CH_2), 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^{-1} .

MS (EI): m/z 513 (M^+ , 100%), 436 (39%), 409 (28%).

$[\alpha]_D^{25}$ +77.0 (c 0.5, CHCl_3)

HRMS for $\text{C}_{31}\text{H}_{27}\text{FeNOSi}$: calcd. 513.1211, found 513.1211.

Synthesis of (*S,R_p*)-2-(α -diisopropylhydrosilane)ferrocenyl-5-iso-propyloxazoline [(*S,R_p*)-5f]

(*S,R_p*)-5f could be synthesized according to the general procedure A, starting from ferrocenyl-5-phenyloxazoline by using diisopropylchlorosilane with a yield of 81 % as dark orange oil. Eluent; pentane/diethyl ether: 80/20.

^1H NMR (300 MHz, CDCl_3) : δ 0.90-1.04 (m, 13H, $-\text{CH}(\text{CH}_3)_2$, $-\text{Si}(\text{CH}(\text{CH}_3)_2)_2$, $-\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.19 (d, J = 6.4 Hz, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.22-1.38 (m, 4H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$, -

Si(CH(CH₃)₂)₂), 1.80 (o, J = 6.7 Hz, 1H, -CH(CH₃)₂), 3.93 (dd, J = 5.9 Hz, 7.9 Hz, 1H, -CHN-), 3.96 (m, 1H, -CH₂O), 4.16 (s, 5H, C₅H₅), 4.26 (t, J = 2.0 Hz, 1H, -SiH(CH(CH₃)₂)₂), 4.32-4.35 (m, 1H, -CH₂O), 4.49 (t, J = 2.5 Hz, 1H, -C₅H₃), 4.96 (dd, J = 1.2 Hz, 2.2 Hz, -C₅H₃).

¹³C NMR (75 MHz, CDCl₃): δ 11.8 (CH), 12.3 (CH), 18.2 (CH₃), 18.9 (CH₃), 19.0 (CH₃), 19.4 (CH₃), 19.5 (CH₃), 20.5 (CH₃), 32.7 (CH), 68.1 (C), 69.5 (CH₂), 70.1 (CH), 72.3 (CH), 72.4 (CH), 72.5 (CH), 72.9 (C), 77.5 (CH).

IR (KBr) ν : 988, 1140, 1657, 2126, 2953, 3098 cm⁻¹.

MS (EI): m/z 411 (M⁺, 28%), 368 (100%), 282 (14%).

$[\alpha]_D^{25}$ +78.8 (c 0.5, CHCl₃)

HRMS for C₂₂H₃₃FeNOSi: calcd. 411.1681, found 411.1681.

Synthesis of (*S,R_p*)-2-(α -diphenylhydrosilane)ferrocenyl-5-*iso*-propyloxazoline [(*S,R_p*)-**5g**]

(*S,R_p*)-**5g** could be synthesized according to the general procedure A, starting from ferrocenyl-5-phenyloxazoline by using diphenylchlorosilane with a yield of 85 % as dark orange solid. Eluent; pentane/diethyl ether: 85/15. mp. 89-91 °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, -C₅H₃), 4.15 (s, 5H, C₅H₅), 4.16-4.22 (m, 1H, -CH₂O), 4.45 (t, J = 2.2 Hz, 1H, -C₅H₃), 5.02 (bs, -C₅H₃), 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) ν : 735, 795, 1117, 1658, 2139, 2958 cm⁻¹.

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

$[\alpha]_D^{25}$ +35.6 (c 0.5, CHCl₃)

HRMS for C₂₈H₂₉FeNOSi: 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 procedure³ for the conversion of hydrosilanes to silanols.

To a solution of ferrocenyl silane **5** (1 mmol) in acetonitrile (3 mL) was added [IrCl(C₈H₁₂)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,R_p*)-2-(α -dimethylsilanol)ferrocenyl-5-*tert*-butyloxazoline [(*S,R_p*)-**2a**]

(*S,R_p*)-**2a** could be synthesized according to the general procedure B, starting from (*S,R_p*)-**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, C₅H₅), 4.26 (dd, J = 1.4 Hz, 2.4 Hz, 1H, C₅H₃), 4.29 (dd, 8.8 Hz, 9.9 Hz, -CH₂O), 4.48 (t, 2.5 Hz, 1H, -C₅H₃), 4.82 (dd, J = 1.4 Hz, 2.5 Hz, 1H, -C₅H₃), 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%).

$[\alpha]_D^{25}$ -309.6 (c 0.5, CHCl_3)

Calcd. for $\text{C}_{19}\text{H}_{27}\text{FeNO}_2\text{Si}$: C, 59.22; H, 7.06; N, 3.63; found C, 58.90; H, 7.41; N, 3.55.

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

(*S,R_p*)-2b could be synthesized according to the general procedure B, starting from (*S,R_p*)-5b with a yield of 77 % as a dark orange oil. Eluent; pentane/diethyl ether: 90/10.

^1H NMR (400 MHz, CDCl_3) : δ 0.78 (d, J = 7.14 Hz, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 0.88 (d, J = 7.14 Hz, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 0.97 (m, 2H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.02 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.29 (m, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.35 (m, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 3.90 (m, 1H, $-\text{CHN}-$), 4.08 (m, 1H, $-\text{CH}_2\text{O}$), 4.22 (s, 5H, C_5H_5), 4.29 (dd, 8.5 Hz, 9.9 Hz, $-\text{CH}_2\text{O}$), 4.31 (m, 1H, C_5H_3), 4.50 (t, 2.5 Hz, 1H, $-\text{C}_5\text{H}_3$), 4.84 (dd, J = 1.1 Hz, 2.5 Hz, 1H, $-\text{C}_5\text{H}_3$), 7.65 (bs, 1H, $-\text{OH}$).

^{13}C NMR (100 MHz, CDCl_3): δ 13.9 (CH), 14.9 (CH), 17.86 (CH_3), 17.94 (CH_3), 18.51 (CH_3), 18.53 (CH_3), 26.5 (CH_3), 33.1 (C), 68.6 (CH_2), 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%).

$[\alpha]_D^{25}$ -165.3 (c 0.88, CHCl_3)

HRMS for $\text{C}_{23}\text{H}_{35}\text{FeNO}_2\text{Si}$: calcd. 441.1786, found 441.1786.

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

(*S,R_p*)-2c could be synthesized according to the general procedure B, starting from (*S,R_p*)-5c with a yield of 91 % as an orange solid. Eluent; pentane/diethyl ether: 95/5. mp. 104-105 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) : δ 1.04 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 3.88 (dd, 1H, J = 9.3 Hz, 10.1 Hz, $-\text{CHN}-$), 4.02 (s, 5H, C_5H_5), 4.14 (t, J = 8.8 Hz, 1H, $-\text{CH}_2\text{O}$), 4.27 (m, 2H, $-\text{CH}_2\text{O}$, $-\text{C}_5\text{H}_3$), 4.51 (t, 2.5 Hz, 1H, $-\text{C}_5\text{H}_3$), 4.89 (dd, J = 1.4 Hz, 2.5 Hz, 1H, $-\text{C}_5\text{H}_3$), 7.28 (m, 3H, $-\text{Ph}$), 7.44 (m, 3H, $-\text{Ph}$), 7.50 (m, 2H, $-\text{Ph}$), 7.88 (m, 2H, $-\text{Ph}$), 8.60 (bs, 1H, $-\text{OH}$).

^{13}C NMR (100 MHz, CDCl_3): δ 26.2 (CH_3), 33.1 (C), 68.6 (CH_2), 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%).

$[\alpha]_D^{25}$ -446.8 (c 0.5, CHCl_3)

Calcd. for $\text{C}_{29}\text{H}_{31}\text{FeNO}_2\text{Si}$: C, 68.36; H, 6.13; N, 2.75; found C, 68.23; H, 6.34; N, 2.56.

Synthesis of (*S,R_p*)-2-(α -diisopropylsilanol)ferrocenyl-5-phenyloxazoline [(*S,R_p*)-2d]

(*S,R_p*)-2d could be synthesized according to the general procedure B, starting from (*S,R_p*)-5d with a yield of 57 % as an orange solid. Eluent; pentane/diethyl ether: 80/20. mp. 99-100 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) : δ 0.81 (d, J = 7.1 Hz, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 0.89 (d, J = 7.1 Hz, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 0.93-1.04 (m, 2H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.26-1.30 (m, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.32-1.35 (m, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 4.20 (t, J = 8.5 Hz, 1H, $-\text{CH}_2\text{O}$), 4.26 (s, 5H, C_5H_5), 4.37 (dd, 1.4 Hz, 2.5 Hz, 1H, $-\text{C}_5\text{H}_3$), 4.55 (t, 2.5 Hz, 1H, $-\text{C}_5\text{H}_3$), 4.72 (dd, J = 8.5 Hz, 10.0 Hz, 1H, $-\text{CH}_2\text{O}$), 4.92 (dd, J = 1.4 Hz, 2.5 Hz, $-\text{C}_5\text{H}_3$), 5.20-5.28 (m, 1H, $-\text{CHN}-$), 7.25-7.42 (m, 5H, $-\text{Ph}$), 7.44 (bs, 1H, $-\text{OH}$).

^{13}C NMR (100 MHz, CDCl_3): δ 13.6 (CH), 14.8 (CH), 17.7 (CH_3), 18.28 (CH_3), 18.33 (CH_3), 68.9 (CH), 70.3 (CH), 72.2 (C), 72.3 (C), 72.4 (CH), 74.4 (CH_2), 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, CHCl_3)

Calcd. for $\text{C}_{25}\text{H}_{31}\text{FeNO}_2\text{Si}$: C, 65.07; H, 6.77; N, 3.04; found C, 64.80; H, 6.44; N, 2.86.

Synthesis of (S,R_p) -2-(α -diphenylsilanol)ferrocenyl-5-phenyloxazoline [(S,R_p) -2e]

(S,R_p) -2e could be synthesized according to the general procedure B, starting from (S,R_p) -5e with a yield of 91 % as an orange solid. Eluent; pentane/diethyl ether: 95/5. mp. Decompose $>150^\circ\text{C}$.

^1H NMR (300 MHz, CDCl_3): δ 4.11 (s, 5H, C_5H_5), 4.18-4.25 (m, 1H, $-\text{CH}_2\text{O}$), 4.28-4.30 (m, 1H, $-\text{C}_5\text{H}_3$), 4.56 (t, $J = 2.5$ Hz, 1H, $-\text{C}_5\text{H}_3$), 4.62-4.71 (m, 1H, $-\text{CH}_2\text{O}$), 4.99-5.01 (m, 1H, $-\text{C}_5\text{H}_3$), 5.14-5.24 (m, 1H, $-\text{CHN}-$) 7.25-7.55 (m, 13H, $-\text{Ph}$), 7.82-7.90 (m, 2H, $-\text{Ph}$), 8.26 (bs, 1H, $-\text{OH}$)

^{13}C NMR (75 MHz, CDCl_3): δ 68.9 (CH), 70.5 (CH), 71.1 (C), 72.6 (C), 73.3 (CH), 73.4 (CH), 74.8 (CH_2), 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) ν : 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, CHCl_3)

Calcd. for $\text{C}_{31}\text{H}_{27}\text{FeNO}_2\text{Si}$: C, 70.32; H, 5.14; N, 2.65; found C, 70.09; H, 5.18; N, 2.65.

Synthesis of (S,R_p) -2-(α -diisopropylsilanol)ferrocenyl-5-*iso*-propyloxazoline [(S,R_p) -2f]

(S,R_p) -2f could be synthesized according to the general procedure B, starting from (S,R_p) -5f with a yield of 65 % as an orange oil. Eluent ; pentane/diethyl ether : 85/15.

^1H NMR (400 MHz, CDCl_3): δ 0.79 (d, $J = 7.1$ Hz, 3H, $-\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 0.88 (d, $J = 7.1$ Hz, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 0.93-0.99 (m, 1H, $-\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.00 (d, $J = 6.6$ Hz, 3H, $-\text{CH}(\text{CH}_3)_2$), 1.19 (d, $J = 6.6$ Hz, 3H, $-\text{CH}(\text{CH}_3)_2$), 1.26-1.30 (m, 3H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.32-1.36 (m, 4H, $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.82 (o, $J = 6.6$ Hz, 1H, $-\text{CH}(\text{CH}_3)_2$), 3.90 (dt, $J = 6.9$ Hz, 9.3 Hz, 1H, $-\text{CHN}-$), 4.03 (t, $J = 8.5$ Hz, 1H, $-\text{CH}_2\text{O}$), 4.20 (s, 5H, C_5H_5), 4.30-4.36 (m, 2H, $-\text{C}_5\text{H}_3$, $-\text{CH}_2\text{O}$), 4.55 (t, $J = 2.5$ Hz, 1H, $-\text{C}_5\text{H}_3$), 4.84 (dd, $J = 1.4$ Hz, 2.5 Hz, $-\text{C}_5\text{H}_3$), 7.73 (bs, 1H, $-\text{OH}$).

^{13}C NMR (100 MHz, CDCl_3): δ 13.8 (CH), 14.9 (CH), 17.8 (CH_3), 17.9 (CH_3), 18.50 (CH_3), 18.53 (CH_3), 19.1 (CH_3), 19.3 (CH_3), 32.90 (CH), 70.4 (CH_2), 70.5 (CH), 72.0 (CH), 72.28 (CH), 72.30 (CH), 72.9 (C), 77.5 (CH), 168.9 (C).

IR (KBr) ν : 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, CHCl_3)

Calcd. for $\text{C}_{22}\text{H}_{33}\text{FeNO}_2\text{Si}$: C, 61.82; H, 7.78; N, 3.28; found C, 61.83; H, 7.92; N, 3.56.

Synthesis of (S,R_p) -2-(α -diphenylsilanol)ferrocenyl-5-*iso*-propyloxazoline [(S,R_p) -2g]

(S,R_p) -2g could be synthesized according to the general procedure B, starting from (S,R_p) -5g with a yield of 82 % as an orange solid. Eluent; pentane/diethyl ether: 95/5. mp. 138-139.

^1H NMR (300 MHz, CDCl_3): δ 1.03 (d, $J = 6.7$ Hz, 3H, $-\text{CH}(\text{CH}_3)_2$), 1.15 (d, $J = 6.9$ Hz, 3H, $-\text{CH}(\text{CH}_3)_2$), 1.86 (o, $J = 6.7$ Hz, 1H, $-\text{CH}(\text{CH}_3)_2$), 3.92 (ddd, $J = 6.2$ Hz, 8.2 Hz, 9.8 Hz, 1H, $-\text{CHN}-$), 4.03 (s, 5H, C_5H_5), 4.09 (dd, $J = 8.2$ Hz, 8.4 Hz, 1H, $-\text{CH}_2\text{O}$), 4.28 (dd, $J = 1.5$ Hz, 2.5 Hz, 1H, $-\text{C}_5\text{H}_3$), 4.51 (t, $J = 2.5$ Hz, 1H, $-\text{C}_5\text{H}_3$), 4.90 (dd, $J = 1.2$ Hz, 2.2 Hz, $-\text{C}_5\text{H}_3$), 7.20-7.35 (m, 3H, $-\text{Ph}$), 7.40-7.55 (m, 3H, $-\text{Ph}$), 7.80-7.85 (m, 2H, $-\text{Ph}$), 8.88 (bs, 1H, $-\text{OH}$)

^{13}C NMR (75 MHz, CDCl_3): δ 18.8. (CH_3), 18.9 (CH_3), 32.6 (CH), 70.3 (CH_2), 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) ν : 705, 736, 903, 987, 1114, 1155, 1641, 2961, 3048 cm^{-1} .

MS (EI): m/z 495 (M^+ , 100%).

$[\alpha]_D^{25} -393.6$ (c 0.5, CHCl_3)

Calcd. for $\text{C}_{28}\text{H}_{29}\text{FeNO}_2\text{Si}$: C, 67.88; H, 5.90; N, 2.83; found C, 67.83; H, 6.12; N, 2.60.

Synthesis of (*S,R_p*)-2-(α -diisopropylsilanol)ferrocenyl-5-benzyloxazoline [(*S,R_p*)-2h]

(*S,R_p*)-2h could be synthesized according to the general procedure B, starting from (*S,R_p*)-5h with a yield of 45 % as a orange oil. Eluent ; pentane/diethyl ether: 95/5.

^1H NMR (400 MHz, CDCl_3) : δ 0.81 (d, J = 6.9 Hz, 3H, -Si(CH(CH_3)₂)₂), 0.90 (d, J = 6.9 Hz, 3H, -Si(CH(CH_3)₂)₂), 0.94-1.04 (m, 1H, -Si(CH(CH_3)₂)₂), 1.28-1.31 (m, 3H, -Si(CH(CH_3)₂)₂), 1.33-1.38 (m, 3H, -Si(CH(CH_3)₂)₂), 2.79 (dd, J = 9.1 Hz, 13.7 Hz, 1H, - CH_2Ph), 3.24 (dd, J = 4.0 Hz, 13.9 Hz, 1H, - CH_2Ph), 4.08 (t, J = 8.2 Hz, 1H, - CH_2O), 4.15 (s, 5H, C_5H_5), 4.21-4.28 (m, 1H, - CH_2O), 4.30-4.33 (m, 1H, - C_5H_3), 4.38-4.47 (m, 1H, -CHN-), 4.48-4.52 (m, 1H, - C_5H_3), 4.80-4.84 (m, 1H, - C_5H_3), 7.20-7.36 (m, 5H, -Ph), 7.73 (bs, 1H, -OH).

^{13}C NMR (100 MHz, CDCl_3): 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%).

$[\alpha]_D^{25} -80.8$ (c 0.5, CHCl_3)

Calcd. for $\text{C}_{26}\text{H}_{33}\text{FeNO}_2\text{Si}$: C, 65.08; H, 7.00; N, 2.95; found C, 64.94; H, 7.08; N, 3.11.

Synthesis of (*S,R_p*)-2-(α -diphenylsilanol)ferrocenyl-5-benzyloxazoline [(*S,R_p*)-2i]

(*S,R_p*)-2i could be synthesized according to the general procedure B, starting from (*S,R_p*)-5i with a yield of 43 % as an orange oil. Eluent; pentane/diethyl ether: 95/5.

^1H NMR (300 MHz, CDCl_3) : δ 2.85 (dd, J = 8.7 Hz, 13.9 Hz, 1H, - CH_2Ph), 3.21 (dd, J = 4.5 Hz, 13.9 Hz, 1H, - CH_2Ph), 3.97 (s, 5H, C_5H_5), 4.11 (t, J = 8.2 Hz, 1H, - CH_2O), 4.21-4.28 (m, 2H, - CH_2O , - C_5H_3), 4.35-4.45 (m, 1H, -CHN-), 4.48-4.52 (m, 1H, - C_5H_3), 4.88 (dd, J = 1.2 Hz, 2.2 Hz, 1H, - C_5H_3), 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).

^{13}C NMR (75 MHz, CDCl_3): 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%).

$[\alpha]_D^{25} -378.0$ (c 0.25, CDCl_3)

HRMS for $\text{C}_{32}\text{H}_{29}\text{FeNO}_2\text{Si}$: calcd. 543.1317, found 543.1317.

2. Catalytic Asymmetric Phenyl Transfer to Aldehydes

Method 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 ZnEt_2 (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 transferred 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 transferred 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 (MgSO_4), 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). ZnEt_2 (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 ($M_w = 2000 \text{ g}\cdot\text{mol}^{-1}$, 0.5 g, 0.25 mmol) and was sealed with a septum. Freshly distilled toluene (1.5 mL) was added followed by ZnEt_2 (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 dichloromethane. 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.

^1H NMR (CDCl_3 , 300 MHz): δ 2.23 (bs, 1H, -OH), 5.78 (s, 1H, -CH), 7.23-7.45 (m, 9H, -Ph).

^{13}C NMR (CDCl_3 , 75 MHz): δ 75.7 (CH), 126.6 (2CH), 127.9 (3CH), 128.7 (2CH), 128.7 (2CH), 133.3 (C), 142.3 (C), 143.5 (C).

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.

^1H NMR (CDCl_3 , 300 MHz): δ 2.19 (bs, 1H, OH), 3.78 (s, 3H CH_3), 5.80 (s, 1H, CH), 6.84-6.89 (m, 2H, -Ph), 7.24-7.39 (m, 7H, -Ph).

^{13}C NMR (CDCl_3 , 75 MHz): δ 55.2 (CH_3), 75.6 (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).

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 μ L, 0.25 mmol) as a yellow solid.

^1H 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 $^\circ\text{C}$, 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 μ L, 0.25 mmol) as a white solid.

^1H NMR (CDCl_3 , 300 MHz): δ 2.04 (s, 1H, OH), 2.31 (s, 3H CH₃), 5.76 (s, 1H, CH), 7.08-7.37 (m, 9H, -Ph)

^{13}C NMR (CDCl_3 , 75 MHz): δ 21.2 (CH₃), 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 $^\circ\text{C}$, 230 nm, 98:2 heptane / *i*-PrOH, 0.9 mL/min; t_R = 30.3min (*S*), 33.7 min (*R*).

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Compound **5a**

Compound **5b**

Compound **5d**

plot at 604 Hz/cm : 8.00 ppm/cm

Compound **5e**

Compound **5f**

plot at 604 Hz/cm : 8.00 ppm/cm

Compound **5g**

Compound 2a

Compound **2b**

Compound 2c

Compound 2d

Compound 2e

Compound **2f**

DEPT: CH

Compound 2g

Compound **2h**

DEPT: CH

APT: C, CH2

CH, CH3

Compound 2i