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Supporting Information

Stereoselective Alcohol Silylation by Dehydrogenative Si–O Coupling: Scope, Limitations, and Mechanism of the Cu–H-Catalyzed Non-Enzymatic Kinetic Resolution with Silicon-Stereogenic Silanes

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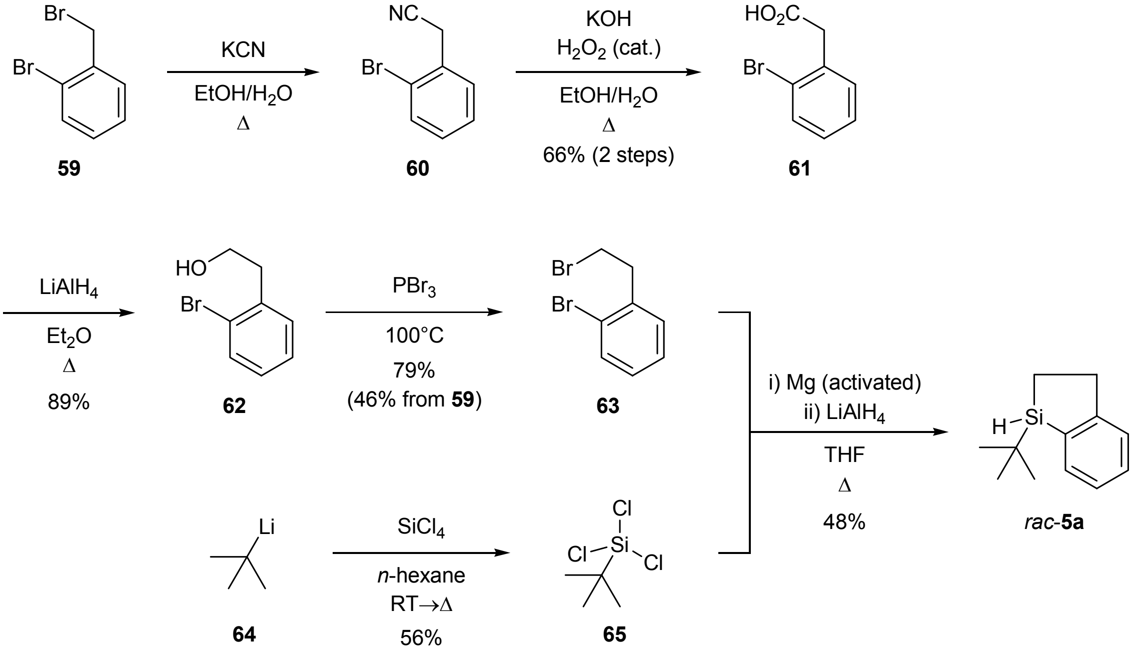
1 General Information

Reagents for starting material syntheses, CuCl as well as ligands **L1a**, **L1g** and **L2** were purchased from commercial sources. NaO*t*Bu was freshly prepared and stored under argon atmosphere. Silanes *rac*-**1**,[S1] *rac*-**2**,[S2] *rac*-**3**,[S3] **4a**,[S4] *rac*-**4b**,[S5] *rac*-**5b**,[S6] ligands **L1b**–**L1f**,[S7–S10] as well as **L3a**[S11] and **L3b**[S12] were prepared according to known procedures. All reactions were performed in flame-dried glassware under a static pressure of argon. Liquids and solutions were transferred with syringes or double-ended needles. Toluene (Na/benzophenone), THF (K/benzophenone), CH_2Cl_2, Et_2O and *i*Pr_2NH (all CaH_2) were dried by continuous distillation from the indicated drying reagent prior to use. Analytical thin-layer chromatography (TLC) was performed on silica gel SIL G-25 glass plates by Macherey-Nagel/Germany; for flash column chromatography silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by Merck (Germany), cyclohexane and *tert*-butyl methyl ether as solvent were used. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker AM 400, AV 400, DRX 500, Varian INOVA 500 and Unity plus 600 spectrometers. HPLC analyses were performed with an Agilent 1200 or a Merck-Hitachi LaChrom 7100 instrument using chiral stationary phases (Daicel Chiralcel OD-H, AD-H, OJ-R, OJ-RH or Chiralpak IA, IB columns). Mass spectra were recorded with Finnigan MAT TSQ 7000 (EI, CI) or Bruker MicroTOF (ESI) instruments. IR spectra were recorded on Perkin-Elmer Paragon 1000 or Varian 3100 FT-IR instruments. Optical rotations were measured in a 1 dm cuvette on a Perkin-Elmer 341 polarimeter. Elemental analyses were conducted on a Vario EL instrument from Elementaranalysensysteme GmbH.

2 Synthesis and Resolution of 1-*tert*-Butyl-1-silaindane (5a)

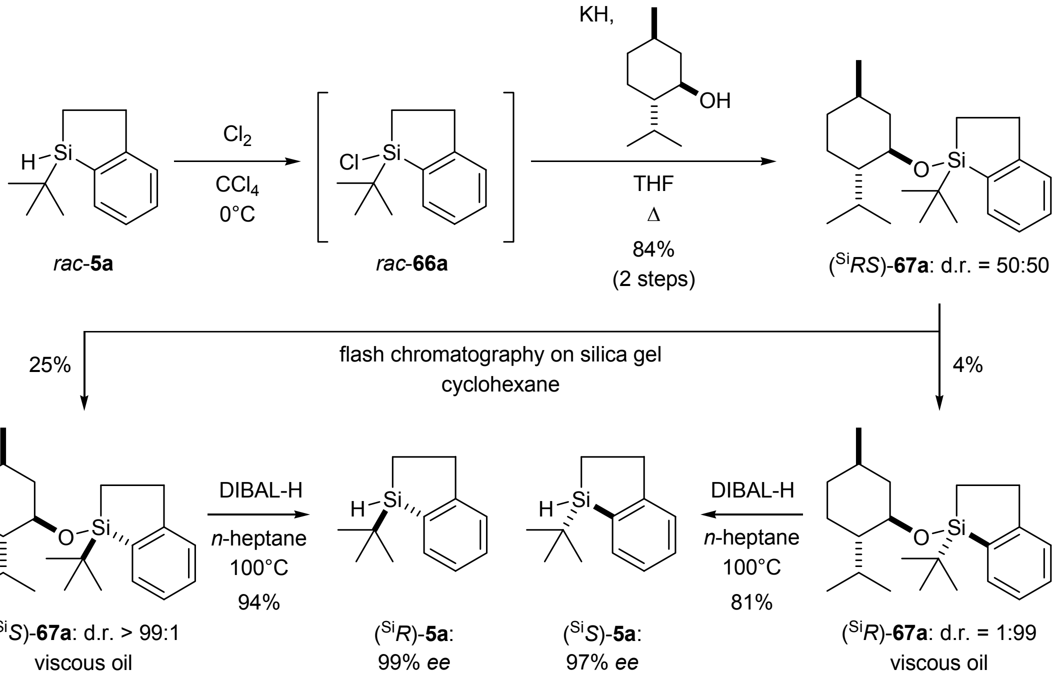
2.1 Results and Discussion

The cyclization precursors were prepared according to modified literature procedures (Scheme S1): For dibromide **63** a four-step synthesis by Adamczyk[S13] was adapted at larger scale (**59**[S3a]→**63**).[S6] Cyclization with Sommer´s trichlorosilane **65**[S14] occurred cleanly under the conditions developed earlier by our group (**63**→*rac*-**5a**).[S4]



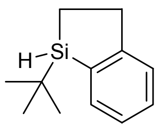
Scheme S1. Synthesis of silaindane *rac*-**5a**.

In our hands, the well-established classical resolution strategy[S15] using (–)-menthol again proved as synthetically most efficient (Scheme S2). Following a protocol developed earlier for a related cyclic silane,[S4] racemic silane *rac*-**5a** was converted into chlorosilane *rac*-**66a**; the latter was directly subjected to silyl ether formation with the potassium salt of (–)-menthol (>99% *ee*) to form (^{Si}*RS*)-**67a** as a 1:1-mixture of diastereomers. Until today, fractional crystallization notoriously failed; for this reason, repeated flash chromatography on silica gel using cyclohexane as a solvent was the method of choice for the separation of diastereomers. Both diastereomers, (^{Si}*S*)-**67a** and (^{Si}*R*)-**67a**, were made available in virtually diastereopure form, although only the less polar diastereomer (^{Si}*S*)-**67a** was obtained in a synthetically useful yield of 25% (based on both diastereomers). If, however, a slightly diminished diastereomeric purity (d.r. = 95:5) is accepted, a yield of 12% for (^{Si}*R*)-**67a** was available by a single flash column chromatography. Finally, both diastereomers readily underwent reductive cleavage with DIBAL-H with complete retention of configuration at the silicon atom under the previously established reaction conditions[S4,S5] to give the desired highly enantioenriched silaindanes (^{Si}*R*)-**5a** and (^{Si}*S*)-**5a** [(^{Si}*S*)-**67a**→(^{Si}*R*)-**5a** and (^{Si}*R*)-**67a**→(^{Si}*S*)-**5a**]. Devoid of an X-ray crystallographic proof of absolute and relative configurations for one of the silyl ethers **67a**, an assignment was made based on retention times of **5a** in the HPLC analysis on a chiral stationary phase as well as the sign of optical rotation by comparison to related silane **4a**. This was later confirmed by X-ray crystallography in a related study.[S16] Moreover, identical signs of optical rotation of recovered alcohol in kinetic resolution with either (^{Si}*R*)-**4a** or (^{Si}*R*)-**5a** further substantiated these conclusions.



Scheme S2. Resolution of silaindane *rac*-**5a**: Access to highly enantioenriched (^{Si}*R*)-**5a**.

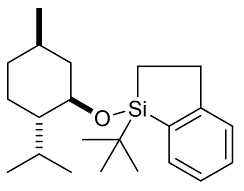
2.2 Experimental Details



rac-**5a**

$C_{12}H_{18}Si$
190.36 g/mol

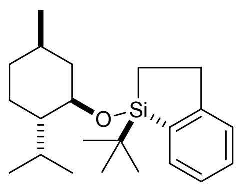
***rac*-1-*tert*-Butyl-1-silaindane (*rac*-5a):** A 1-L three-necked flask equipped with a reflux condenser, a 500-mL pressure-equalizing dropping funnel, an argon-inlet and a magnetic stirring bar was charged with magnesium turnings (24.3 g, 1.00 mol, 10.0 equiv). The flask was subsequently flame dried in vacuo (3 times) with vigorous stirring, backfilled with argon and stirring was continued for 12 h. Then, the magnesium turnings were suspended in THF (150 mL) and a solution of 1,2-dibromoethane (8.80 mL, 18.8 g, 100 mmol, 1.00 equiv) in THF (50 mL) was added dropwise. After complete addition, the mixture was heated to reflux and a solution of dibromide **63** (26.4 g, 100 mmol, 1.00 equiv) and trichlorosilane **65** (19.6 g, 100 mmol, 1.00 equiv) in THF (400 mL) was added slowly over a period of 4 h. The reaction mixture was maintained for a further 12 h at reflux. The resulting solution was transferred to another 1-L three-necked flask equipped with a reflux condenser, an argon-inlet and a magnetic stirring bar, containing a suspension of $LiAlH_4$ (6.83 g, 180 mmol, 1.80 equiv) in THF (100 mL). Heating at reflux for 8 h was followed by careful quenching of the resulting mixture at 0°C with acetone (50 mL), water (400 mL) and finally, conc. HCl (100 mL) until pH 4 was reached. The organic layer was separated and the aqueous phase was extracted with *tert*-butyl methyl ether (4 × 150 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4), filtered and volatiles were evaporated under reduced pressure. The crude product was distilled in vacuo (b.p. 79°C at 4 mbar) affording the silane *rac*-**5a** (9.14 g, 48%) as a colorless liquid. For analytical data, see "Experimental Section" of this Full Paper.



(^{Si}*RS*)-**67a**
$C_{22}H_{36}OSi$
344.61 g/mol

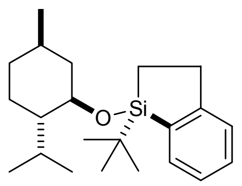
(^{Si}*RS*)-1-*tert*-Butyl-1-[(1*R*,2*S*,5*R*)-1-menthyloxy]-1-silaindane [(^{Si}*RS*)-67a]: A saturated solution of Cl_2 in CCl_4 (30 mL) was added to a solution of *rac*-**5a** (5.68 g, 30.0 mmol, 1.00 equiv) in CCl_4 (15 mL) at 0°C until a permanent pale yellow color appeared. After 4 min the reaction mixture was purged with argon. Evaporation of the solvent under reduced pressure provided crude *rac*-**66a** as a yellowish oil which was used in the subsequent etherification without further purification.

A solution of (–)-menthol (7.04 g, 45.0 mmol, 1.50 equiv, >99% *ee*) in THF (60 mL) was added to a suspension of oil-free potassium hydride (2.10 g, 52.5 mmol, 1.75 equiv) in THF (20 mL) at room temperature. To ensure complete deprotonation, the mixture was heated at reflux for 1 h. Subsequently, the mixture was treated portionwise with a solution of freshly prepared chlorosilane *rac*-**67a** in THF (50 mL) at ambient temperature. Heating at reflux for 4 h was followed by cooling to ambient temperature, quenching with water (100 mL) and then 2M HCl until pH 7 was reached. The organic layer was separated and the aqueous phase was extracted with *tert*-butyl methyl ether (4 × 100 mL). The combined organic layers were washed with brine (50 mL), dried (Na_2SO_4), filtered and the volatiles were evaporated under reduced pressure. The crude product was optionally distilled under high vacuum (b.p. 120–130°C at 10^{-6} mbar) to remove excess (–)-menthol furnishing a diastereomeric mixture of (–)-menthyl silyl ethers (^{Si}*RS*)-**67a** (8.68 g, 84%, d.r. = 50:50) as a colorless, viscous oil. Separation of diastereomers by repeated flash column chromatography on silica gel with cyclohexane as eluent (e.g., for 4 g of diastereomers: ∅ 8 cm, length 35 cm) delivered highly diastereomerically enriched (^{Si}*S*)-**67a** [2.13 g, 25% based on (^{Si}*RS*)-**67a** or 21% based on *rac*-**5a**, d.r. > 99:1] as a highly viscous oil. The second diastereomer (^{Si}*R*)-**67a** [310 mg, 4% based on (^{Si}*RS*)-**67a** or 3% based on *rac*-**5a**, d.r. = 1:99] was obtained by the same procedure. Synthetically useful amounts of (^{Si}*S*)-**67a** [1.04 g, 12% based on (^{Si}*RS*)-**67a** or 10% based on *rac*-**5a**, d.r. = 5:95] were accessible in slightly reduced diastereomeric ratio. Analytical data for (^{Si}*RS*)-**67a**: HPLC (Daicel Chiralcel OJ-R, 40°C, EtOH/water 60:40, flow rate 0.80 mL·min^{-1}, λ = 230 nm): t_R = 23.0 min [(^{Si}*S*)-**67a**], 26.0 min [(^{Si}*R*)-**67a**]; IR (film): $\tilde{\nu}$ = 3056 (m), 2925 (s), 1592 (s), 1463 (s), 1066 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 345 [$(M+H)^+$]; HRMS (EI): *m/z*: calcd for $C_{22}H_{36}OSi$ [$(M-C_4H_9)^+$]: 287.1831, found: 287.1832; elemental analysis calcd (%) for $C_{22}H_{36}OSi$ (344.6): C 76.68, H 10.53; found: C 76.79, H 10.61.



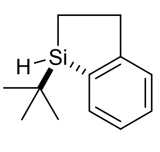
(${}^{\mathrm{Si}}$*S*)-**67a**
$C_{22}H_{36}OSi$
344.61 g/mol

Analytical data for (${}^{\mathrm{Si}}$*S*)-**67a**: R$_f$ = 0.49 (cyclohexane); $[\alpha]^{20}_{\mathrm{D}}$ = –83.1 (*c* = 1.33, $CHCl_3$), $[\alpha]^{20}_{578}$ = –87.0, $[\alpha]^{20}_{546}$ = –99.0, $[\alpha]^{20}_{436}$ = –171, $[\alpha]^{20}_{365}$ = –281; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.45 (d, *J* = 6.9 Hz, 3H), 0.75–0.86 (m, 2H), 0.83 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H), 0.93–1.03 (m, 1H), 0.95 (ddd, *J* = 15.5 Hz, *J* = 9.5 Hz, *J* = 6.0 Hz, 1H), 0.97 (s, 9H), 1.03 (ddd, *J* = 15.5 Hz, *J* = 9.3 Hz, *J* = 5.0 Hz, 1H), 1.11–1.23 (m, 2H), 1.49–1.59 (m, 2H), 1.75 (dddd, *J* = 12.2 Hz, *J* = 4.4 Hz, *J* = 3.4 Hz, *J* = 2.0 Hz, 1H), 2.27 (qqd, *J* = *J* = 7.0 Hz, *J* = 2.5 Hz, 1H), 2.95 (ddd, *J* = 17.0 Hz, *J* = 9.3 Hz, *J* = 6.0 Hz, 1H), 3.09 (ddd, *J* = 17.0 Hz, *J* = 9.6 Hz, *J* = 4.9 Hz, 1H), 3.27 (ddd, *J* = *J* = 10.3 Hz, *J* = 4.4 Hz, 1H), 7.17 (m$_c$, 1H), 7.23 (m$_c$, 1H), 7.31 (ddd, *J* = 7.6 Hz, *J* = 7.2 Hz, *J* = 1.4 Hz, 1H), 7.57 (ddd, *J* = 7.2 Hz, *J* = 1.3 Hz, *J* = 0.7, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.2, 15.8, 18.7, 21.5, 22.4, 22.8, 25.2, 26.1, 30.3, 31.6, 34.6, 45.3, 50.4, 72.8, 125.4, 126.2, 129.9, 133.3, 134.9, 154.3 ppm.



(${}^{\mathrm{Si}}$*R*)-**67a**
$C_{22}H_{36}OSi$
344.61 g/mol

Analytical data for (${}^{\mathrm{Si}}$*R*)-**67a**: R$_f$ = 0.45 (cyclohexane); $[\alpha]^{20}_{\mathrm{D}}$ = –29.7 (*c* = 1.00, $CHCl_3$), $[\alpha]^{20}_{578}$ = –30.8, $[\alpha]^{20}_{546}$ = –34.5, $[\alpha]^{20}_{436}$ = –52.8, $[\alpha]^{20}_{365}$ = –65.8; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.64 (d, *J* = 6.9 Hz, 3H), 0.73–1.05 (m, 5H), 0.78 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 7.1 Hz, 3H), 0.96 (s, 9H), 1.11–1.25 (m, 2H), 1.51–1.56 (m, 2H), 1.73 (dddd, *J* = 12.3 Hz, *J* = 4.4 Hz, *J* = 3.5 Hz, *J* = 2.0 Hz, 1H), 2.21 (qqd, *J* = *J* = 7.0, *J* = 2.5 Hz, 1H), 2.93 (ddd, *J* = 16.6 Hz, *J* = 8.7 Hz, *J* = 7.2 Hz, 1H), 3.08 (ddd, *J* = 16.9 Hz, *J* = 8.8 Hz, *J* = 5.4 Hz, 1H), 3.32 (ddd, *J* = *J* = 10.3 Hz, *J* = 4.4 Hz, 1H), 7.18 (m$_c$, 1H), 7.23 (m$_c$, 1H), 7.32 (ddd, *J* = 7.6 Hz, *J* = 7.2 Hz, *J* = 1.4 Hz, 1H), 7.60 (ddd, *J* = 7.2 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.2, 15.9, 18.7, 21.5, 22.4, 22.8, 25.3, 26.0, 30.4, 31.6, 34.6, 45.2, 50.3, 72.9, 125.5, 126.2, 129.8, 133.1, 135.7, 154.1 ppm.



(${}^{\mathrm{Si}}$*R*)-**5a**
$C_{12}H_{18}Si$
190.36 g/mol

(${}^{\mathrm{Si}}$*R*)-1-*tert*-Butyl-1-silaindane [(${}^{\mathrm{Si}}$*R*)-5a]: A 25-mL Schlenk flask equipped with a magnetic stirring bar and a reflux condenser was charged with a solution of (${}^{\mathrm{Si}}$*S*)-**67a** (2.13 g, 6.19 mmol, 1.00 equiv, d.r. > 99:1) in *n*-heptane (50 mL). DIBAL-H (25.0 mL, 25.0 mmol, 4.00 equiv, 1.0M in *n*-hexane) was added in one portion at ambient temperature. The reaction mixture was subsequently heated to reflux and maintained at this temperature for 20 h. The reaction was quenched at ambient temperature by careful addition of water (100 mL) followed by 2M HCl until pH 7 was reached. The organic layer was separated and the aqueous phase extracted with *tert*-butyl methyl ether (4 × 40 mL). The combined organic layers were washed with brine (30 mL), dried (Na_2SO_4), filtered and volatiles were evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with cyclohexane as eluent, furnishing the analytically pure, highly enantiomerically enriched silane (${}^{\mathrm{Si}}$*R*)-**5a** (1.11 g, 94%, 99% *ee*) as a colorless liquid. For analytical data, see "Experimental Section" of this Full Paper.

Analogously, starting from (${}^{\mathrm{Si}}$*R*)-**67a** (310 mg, 0.900 mmol, 1.00 equiv, d.r. = 1:99), the second enantiomer (${}^{\mathrm{Si}}$*S*)-**5a** (139 mg, 81%, 97% *ee*) was available. Analytical data for (${}^{\mathrm{Si}}$*S*)-**5a**: $[\alpha]^{20}_{\mathrm{D}}$ = –42.0 (*c* = 1.01, $CHCl_3$), $[\alpha]^{20}_{578}$ = –43.5, $[\alpha]^{20}_{546}$ = –48.1, $[\alpha]^{20}_{436}$ = –72.1, $[\alpha]^{20}_{365}$ = –84.6.

3 Syntheses of Racemic Alcohols

For the preparation of racemic alcohols, the addition of metalated *ortho*-methylhetarenes to commercially available aldehydes provided a straightforward access to the desired donor-functionalized secondary alcohols. Compared to the parent organolithium derivatives that were prepared by deprotonation with *n*BuLi or LDA, organocerium reagents[S17] derived therof led in a number of examples to improved results. This procedure diminished the formation of undesired byproducts that were usually difficult to separate by flash chromatography. Organocerium reagents were prepared analogously to a procedure developed by Imamoto.[S18]

3.1 General Procedures

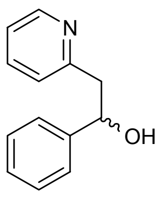
3.1.1 Cerium(III)/*n*BuLi-mediated Synthesis of Racemic Alcohols (GP 2)

A 100-mL Schlenk flask equipped with a magnetic stirring bar was charged with Cerium(III) chloride ($CeCl_3 \cdot 7H_2O$) (3.73 g, 10.0 mmol, 1.00 equiv). The solid was heated to 140°C in vacuo (0.1 mbar) using an oil bath with slow stirring for 3 h.[S18b] After backfilling with argon, anhydrous THF (50 mL) was added at −78°C and strirring of the white suspension was continued for 1 h. At this temperature a solution of the respective lithiated hetarene in THF—prepared by slow addition of *n*BuLi (4.00 mL, 10.0 mmol, 1.00 equiv, 2.5M solution in hexanes) to a solution of the required methyl substituted hetarene (10.0 mmol, 1.0 equiv) in THF (20 mL) at −20°C and stirring for 1 h—was added in one portion and maintained for 1 h at this temperature. Subsequently, the respective aldehyde (12.0 mmol, 1.20 equiv) was added dropwise to the orange-colored suspension that decolorized immediately. After 10 min at −78°C, the reaction was quenched with water (50 mL) and *tert*-butyl methyl ether (20 mL). The pH was adjusted to 7–8 by addition of 2M HCl and the organic phase was separated. The aqueous phase was extracted with *tert*-butyl methyl ether (4 × 40 mL), washed with brine (30 mL) and dried (Na_2SO_4). Evaporation of the solvents under reduced pressure was followed by purification of the residual by flash chromatography on silica gel or recrystallization furnishing the analytically pure racemic alcohol.

3.1.2 LDA-mediated Synthesis of Racemic Alcohols (GP 3)

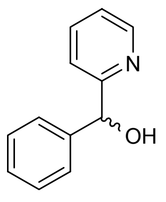
In a 100-mL Schlenk flask equipped with a magnetic stirring bar, a solution of freshly distilled *i*Pr_2NH (1.82 mL, 1.32 g, 13.0 mmol, 1.30 equiv) in THF (40 mL) was cooled to −78°C followed by slow addition of *n*BuLi (4.80 mL, 12.0 mmol, 1.20 equiv, 2.5M solution in hexanes). The reaction was then allowed to warm to room temperature and maintained for further 30 min at this temperature. After recooling to −78°C a solution of the respective methyl substituted hetarene (10.0 mmol, 1.00 equiv) in anhydrous THF (10 mL) was added in one portion and maintained at this temperature for further 30 min. Subsequently, the respective aldehyde (12.0 mmol, 1.20 equiv) was added dropwise to the deep colored mixture upon which decolorized immediately. The mixture was maintained at at –78°C for further 30 min; then the reaction mixture was quenched with water (20 mL) and *tert*-butyl methyl ether (10 mL). The pH was adjusted to 7–8 by addition of 2M HCl and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL), washed with brine (20 mL) and dried (Na_2SO_4). Evaporation of the solvents under reduced pressure was followed by purification of the residual by flash chromatography on silica gel or recrystallization furnishing the analytically pure racemic alcohol.

3.2 Experimental Details and Characterization Data



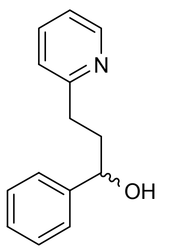
rac-**6**
$C_{13}H_{13}NO$
199.25 g/mol

***rac*-1-Phenyl-2-(pyridin-2-yl)ethanol (*rac*-6):**[S19,S20] According to GP 2, starting from $CeCl_3{\cdot}7H_2O$ (3.73 g, 10.0 mmol, 1.00 equiv), *n*BuLi (4.00 mL, 10.0 mmol, 1.00 equiv, 2.5M solution in hexanes), 2-picoline (0.99 mL, 0.93 g, 10 mmol, 1.0 equiv) and benzaldehyde (1.21 mL, 1.27 g, 12.0 mmol, 1.20 equiv), recrystallization from *tert*-butyl methyl ether/CH_2Cl_2 furnished analytically pure *rac*-**6** (1.74 g, 74%) as a white solid (m.p. 107°C). For further analytical data, see compound (*S*)-**6** in the "Experimental Section" of this Full Paper.

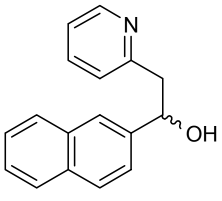


rac-**8**
$C_{12}H_{11}NO$
185.22 g/mol

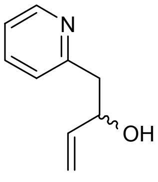
***rac*-1-Phenyl-2-(pyridin-2-yl)methanol (*rac*-8):**[S21] According to a procedure developed by Gilman, a flame-dried 100-mL Schlenk flask equipped with a magnetic stirring bar was charged with a solution of 2-bromopyridine (4.8 mL, 7.9 g, 50 mmol, 1.0 equiv) in Et_2O (40 mL). After cooling to –40°C *n*BuLi (20 mL, 50 mmol, 1.0 equiv, 2.5M solution in hexanes) was added dropwise within 15 min. The mixture was maintained at this temperature for further 15 min and then warmed to –20°C followed by dropwise addition of benzaldehyde (5.1 mL, 5.3 g, 50 mmol, 1.0 equiv). After 30 min at –20°C, the reaction mixture was quenched with water (50 mL) and 2M HCl (30 mL). The pH was adjusted to 7–8 and the aqueous phase was separated and extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined organic layers were washed with brine (30 mL), dried (Na_2SO_4) and volatiles were evaporated under reduced pressure. Purification by vacuum distillation followed by flash chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether 3:1→3:2) furnished *rac*-**8** (4.50 g, 49%) as a yellow oil that crystallized upon storage at 4°C. B.p. 135–142°C at 0.5 mbar; m.p. 76°C (cyclohexane/*tert*-butyl methyl ether); R_f = 0.13 (cyclohexane/*tert*-butyl methyl ether 2:1); HPLC (Daicel Chiralpak IA, 20°C, *n*-heptane/*i*PrOH 90:10, flow rate 0.80 $mL{\cdot}min^{-1}$, λ = 230 nm): t_R = 13.6 min [(*S*)-**8**], 15.7 min [(*R*)-**8**]; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.17 (br s, 1H), 5.66 (s, 1H), 7.04–7.31 (m, 7H), 7.52 (br dd, *J* = *J* = 7.6 Hz, 1H), 8.47 (br d, *J* = 4.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 75.1, 121.5, 122.5, 127.2, 127.9, 128.7, 136.9, 143.3, 147.9, 160.9 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3373 (s), 3066 (s), 3032 (s), 2977 (m), 2890 (w), 1594 (s), 1573 (s), 1493 (m), 1473 (s), 1455 (s), 1436 (s), 1402 (s), 1367 (w), 1342 (w), 1307 (w), 1228 (w), 1199 (s), 1149 (w), 1180 (m), 1053 (s), 1026 (s), 1041 (s), 999 (m), 967 (w), 849 (w) cm^{-1}; LRMS (EI): *m/z*: 185 [M$^+$]; HRMS (ESI): *m/z*: calcd for $C_{12}H_{11}NO$ [(M+H)$^+$]: 186.0913, found: 186.0903.


rac-**9**
$C_{14}H_{15}NO$
213.28 g/mol

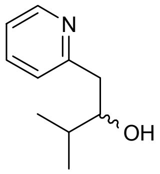
***rac*-1-Phenyl-3-(pyridin-2-yl)propanol (*rac*-9):**[S22] According to GP 2, lithiation with *n*BuLi (4.00 mL, 10.0 mmol, 1.00 equiv, 2.5M solution in hexanes) and subsequent transmetalation with $CeCl_3 \cdot 7H_2O$ (3.73 g, 10.0 mmol, 1.00 equiv) of 2-picoline (0.99 mL, 0.93 g, 10 mmol, 1.0 equiv) was conducted. To this reagent racemic epoxystyrene (1.37 mL, 1.44 g, 12.0 mmol, 1.20 equiv) was added at −78°C After further 30 min at −78°C, the reaction was quenched with water (50 mL) and *tert*-butyl methyl ether (20 mL). The usual workup (see GP 2) was followed by purification of the crude product (85:15 mixture of regioisomers) by flash chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether 1:2) to give analytically pure *rac*-**9** (784 mg, 37%) as a white solid. M.p. 70°C (cyclohexane/*tert*-butyl methyl ether); R_f = 0.14 (cyclohexane/*tert*-butyl methyl ether 1:2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.13–2.23 (m, 2H), 2.97 (m, 2H), 4.81 (dd, *J* = 7.9 Hz, *J* = 4.2 Hz, 1H), 5.39 (br s, 1H), 7.12 (ddd, *J* = 7.2 Hz, *J* = 4.8 Hz, *J* = 0.8 Hz, 1H), 7.16 (br d, *J* = 7.8 Hz, 1H), 7.21–7.25 (m, 1H), 7.30–7.34 (m, 2H), 7.38–7.41 (m, 2H), 7.60 (ddd, *J* = *J* = 7.4 Hz, *J* = 1.9 Hz, 1H), 8.48 (br d, *J* = 4.7 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 34.4, 38.1, 73.6, 121.3, 123.3, 125.9, 127.0, 128.3, 137.0, 145.3, 148.5, 161.4 ppm; IR (ATR): $\tilde{\nu}$ = 3191 (s), 3081 (w), 3056 (w), 2974 (w), 2954 (w), 2938 (m), 2925 (s), 2846 (s), 1593 (s), 1568 (s), 1474 (S), 1444 (s), 1343 (m), 1321 (m), 1304 (m), 1278 (w), 1243 (w), 1196 (s), 1150 (s), 1007 (w), 1081 (s), 1061 (s), 1052 (s), 1005 (s), 950 (m), 911 (m), 872 (m), 807 (w), 774 (m), 739 (s), 699 (s) cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{14}H_{15}NO$ [(M+H)$^+$]: 214.1226, found: 214.1211; elemental analysis calcd (%) for $C_{14}H_{15}NO$ (213.3): C 78.84, H 7.09, N 6.57; found: C 78.73, H 6.99, N 6.29.


rac-**16**
$C_{17}H_{15}NO$
249.31 g/mol

***rac*-1-(Naphth-2-yl)-2-(pyridin-2-yl)ethan-2-ol (*rac*-16):** According to GP 2, starting from $CeCl_3 \cdot 7H_2O$ (3.73 g, 10.0 mmol, 1.00 equiv), *n*BuLi (4.00 mL, 10.0 mmol, 1.00 equiv, 2.5M solution in hexanes), 2-picoline (0.99 mL, 0.93 g, 10 mmol, 1.0 equiv) and 2-naphthaldehyde (1.36 mL, 1.56 g, 10.0 mmol, 1.00 equiv), purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 1:2) furnished analytically pure *rac*-**16** (1.52 g, 61%) as a white solid. For analytical data, see compound (*R*)-**16** in the "Experimental Section" of this Full Paper.


rac-**17**
$C_9H_{11}NO$
149.19 g/mol

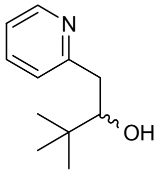
***rac*-1-(Pyridin-2-yl)but-3-en-2-ol (*rac*-17):**[S23] According to GP 2, starting from $CeCl_3 \cdot 7H_2O$ (1.65 g, 4.43 mmol, 1.00 equiv), *n*BuLi (1.77 mL, 4.43 mmol, 1.00 equiv, 2.5M solution in hexanes), 2-picoline (0.43 mL, 0.41 g, 4.4 mmol, 1.0 equiv) and acroleine (0.36 mL, 300 mg, 5.3 mmol, 1.2 equiv), purification by flash chromatography (CH_2Cl_2/MeOH 97:3) furnished analytically pure *rac*-**17** (280 mg, 56%) as a low-melting white solid (m.p. 46°C). For further analytical data, see compound (*S*)-**17** in the "Experimental Section" of this Full Paper.



rac-**18**

$C_{10}H_{15}NO$
165.23 g/mol

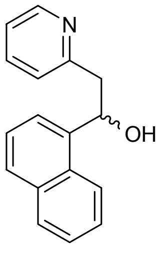
***rac*-3-Methyl-1-(pyridin-2-yl)butan-2-ol (*rac*-18):**[S23] According to GP 2, starting from $CeCl_3\cdot 7H_2O$ (3.73 g, 10.0 mmol, 1.00 equiv), *n*BuLi (4.00 mL, 10.0 mmol, 1.00 equiv, 2.5M solution in hexanes), 2-picoline (0.99 mL, 0.93 g, 10 mmol, 1.0 equiv) and isobutyraldehyde (1.09 mL, 864 mg, 12.0 mmol, 1.20 equiv), purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 2:1→1:1) furnished analytically pure *rac*-**18** (991 mg, 60%) as a colorless oil. For analytical data, see compound (*S*)-**18** in the "Experimental Section" of this Full Paper.



rac-**19**

$C_{11}H_{17}NO$
179.26 g/mol

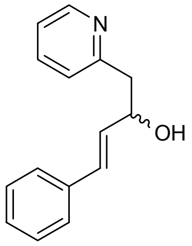
***rac*-3,3-Dimethyl-1-(pyridin-2-yl)butan-2-ol (*rac*-19):** According to GP 2, starting from $CeCl_3\cdot 7H_2O$ (1.86 g, 5.00 mmol, 1.00 equiv), *n*BuLi (2.00 mL, 5.00 mmol, 1.00 equiv, 2.5M solution in hexanes), 2-picoline (0.49 mL, 0.47 g, 5.0 mmol, 1.0 equiv) and pivalaldehyde (0.65 mL, 0.52 g, 6.0 mmol, 1.2 equiv), purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 1:1) furnished analytically pure *rac*-**19** (601 mg, 67%) as a colorless oil that solidified upon storage at 4°C. M.p. 39°C (cyclohexane/*tert*-butyl methyl ether). For further analytical data, see compound (*S*)-**19** in the "Experimental Section" of this Full Paper.



rac-**24**

$C_{17}H_{15}NO$
249.31 g/mol

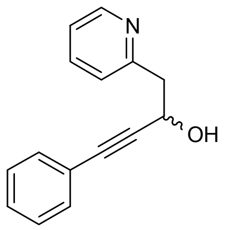
***rac*-1-(Naphth-1-yl)-2-(pyridin-2-yl)ethan-2-ol (*rac*-24):** According to GP 2, starting from $CeCl_3\cdot 7H_2O$ (3.73 g, 10.0 mmol, 1.00 equiv), *n*BuLi (4.00 mL, 10.0 mmol, 1.00 equiv, 2.5M solution in hexanes), 2-picoline (0.99 mL, 0.93 g, 10 mmol, 1.0 equiv) and 1-naphthaldehyde (1.36 mL, 1.56 g, 10.0 mmol, 1.00 equiv), purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 1:1) furnished analytically pure *rac*-**24** (1.23 g, 49%) as a white solid. M.p. 114°C (cyclohexane/*tert*-butyl methyl ether). For further analytical data, see compound (*R*)-**24** in the "Experimental Section" of this Full Paper.



rac-**25**

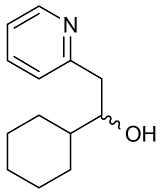
$C_{15}H_{15}NO$
225.29 g/mol

***rac*-(*E*)-4-Phenyl-1-(pyridin-2-yl)but-3-en-2-ol (*rac*-25):**[S23] According to GP 2, starting from $CeCl_3\cdot 7H_2O$ (1.86 g, 5.00 mmol, 1.00 equiv), *n*BuLi (2.00 mL, 5.00 mmol, 1.00 equiv, 2.5M solution in hexanes), 2-picoline (0.49 mL, 0.47 g, 5.0 mmol, 1.0 equiv) and cinnamic aldehyde (0.77 mL, 0.79 g, 6.0 mmol, 1.2 equiv), purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 1:2) furnished analytically pure *rac*-**25** (1.04 g, 91%) as a white solid. For analytical data, see compound (*R*)-**25** in the "Experimental Section" of this Full Paper.



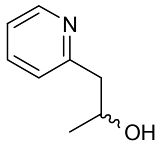
rac-**26**
$C_{15}H_{13}NO$
223.27 g/mol

***rac*-4-Phenyl-1-(pyridin-2-yl)but-3-in-2-ol (*rac*-26):**[S24] According to GP 2, starting from $CeCl_3{\cdot}7H_2O$ (2.67 g, 7.70 mmol, 1.00 equiv), *n*BuLi (3.10 mL, 7.70 mmol, 1.00 equiv, 2.5M solution in hexanes), 2-picoline (0.76 mL, 0.72 g, 7.7 mmol, 1.0 equiv) and a solution of 3-phenylpropinal[S25] (1.00 g, 7.70 mmol, 1.00 equiv) in THF (2 mL), purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 1:1) furnished analytically pure *rac*-**26** (1.06 g, 62%) as a yellowish oil. For analytical data, see compound (*R*)-**26** in the "Experimental Section" of this Full Paper.



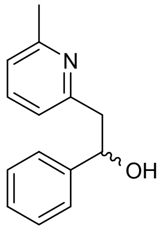
rac-**27**
$C_{13}H_{19}NO$
205.30 g/mol

***rac*-1-Cyclohexyl-2-(pyridin-2-yl)ethanol (*rac*-27):** According to GP 2, starting from $CeCl_3{\cdot}7H_2O$ (3.73 g, 10.0 mmol, 1.00 equiv), *n*BuLi (4.00 mL, 10.0 mmol, 1.00 equiv, 2.5M solution in hexanes), 2-picoline (0.99 mL, 0.93 g, 10 mmol, 1.0 equiv) and cyclohexylcarbaldehyde (1.45 g, 1.35 mmol, 1.20 equiv), purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 1:1) furnished analytically pure *rac*-**27** (1.47 g, 72%) as a colorless oil that solidified upon storage at 4°C. For analytical data, see compound (*R*)-**27** in the "Experimental Section" of this Full Paper.



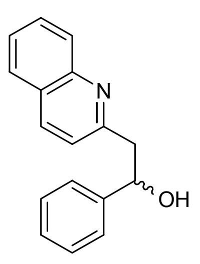
rac-**28**
$C_8H_{11}NO$
137.18 g/mol

***rac*-1-(Pyridin-2-yl)propan-2-ol (*rac*-28):**[S26] According to GP 2, starting from $CeCl_3{\cdot}7H_2O$ (1.65 g, 4.43 mmol, 1.00 equiv), *n*BuLi (1.77 mL, 4.43 mmol, 1.00 equiv, 2.5M solution in hexanes), 2-picoline (0.43 mL, 0.41 g, 4.4 mmol, 1.0 equiv) and acetaldehyde (0.300 mL, 234 mg, 5.31 mmol, 1.20 equiv), purification by flash chromatography (CH_2Cl_2/MeOH 97:3) furnished analytically pure *rac*-**28** (275 mg, 60%) as a colorless oil. For analytical data, see compound (*S*)-**28** in the "Experimental Section" of this Full Paper.



rac-**34**
$C_{14}H_{15}NO$
213.28 g/mol

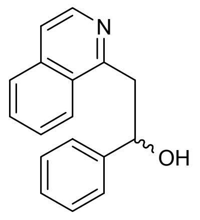
***rac*-1-Phenyl-2-(6-methylpyridin-2-yl)ethanol (*rac*-34):**[S27] According to GP 3, starting from *i*Pr_2NH (1.82 mL, 1.32 g, 13.0 mmol, 1.10 equiv), *n*BuLi (4.80 mL, 12.0 mmol, 1.00 equiv, 2.5M solution in hexanes), 2,6-lutidine (1.29 g, 12.0 mmol, 1.00 equiv) and benzaldehyde (1.21 mL, 1.28 g, 12.0 mmol, 1.20 equiv), purification by flash chromatography (CH_2Cl_2/MeOH 95:5) furnished analytically pure *rac*-**34** (2.41 g, 94%) as a colorless oil. For analytical data, see compound (*S*)-**34** in the "Experimental Section" of this Full Paper.



rac-**35**

$C_{17}H_{15}NO$
249.31 g/mol

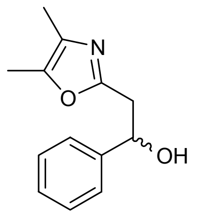
***rac*-1-Phenyl-2-(quinolin-2-yl)ethanol (*rac*-35):**[S28] According to GP 2, starting from $CeCl_3\cdot 7H_2O$ (3.73 g, 10.0 mmol, 1.00 equiv), *n*BuLi (4.00 mL, 10.0 mmol, 1.00 equiv, 2.5M solution in hexanes), 2-methylquinoline (1.43 g, 10.0 mmol, 1.00 equiv) and benzaldehyde (1.21 mL, 1.27 g, 12.0 mmol, 1.20 equiv), purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 2:3) furnished analytically pure *rac*-**35** (1.37 g, 55%) as a white solid. For analytical data, see compound (*S*)-**35** in the "Experimental Section" of this Full Paper.



rac-**36**

$C_{17}H_{15}NO$
249.31 g/mol

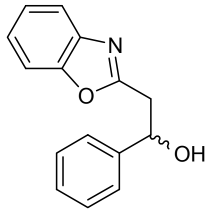
***rac*-2-(Isoquinolin-1-yl)-1-phenylethan-2-ol (*rac*-36):**[S29] According to GP 2, starting from $CeCl_3\cdot 7H_2O$ (1.88 g, 5.43 mmol, 1.00 equiv), *n*BuLi (2.17 mL, 5.43 mmol, 1.00 equiv, 2.5M solution in hexanes), 1-methylisoquinoline[S30,S31] (776 mg, 5.43 mmol, 1.00 equiv) and benzaldehyde (0.66 mL, 0.69 g, 6.5 mmol, 1.2 equiv), purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 3:2) furnished analytically pure *rac*-**36** (1.18 g, 87%) as yellowish solid. For analytical data, see compound (*S*)-**36** in the "Experimental Section" of this Full Paper.



rac-**37**

$C_{13}H_{15}NO_2$
217.26 g/mol

***rac*-2-(4,5-Dimethyloxazol-2-yl)-1-phenylethan-2-ol (*rac*-37):**[S32] According to GP 3, starting from *i*Pr_2NH (557 mg, 5.50 mmol, 1.10 equiv), *n*BuLi (2.20 mL, 5.50 mmol, 1.10 equiv, 2.5M solution in hexanes), 2,3,5-trimethyloxazole (556 mg, 5.00 mmol, 1.00 equiv) and benzaldehyde (584 mg, 5.50 mmol, 1.10 equiv), purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 1:1) furnished analytically pure *rac*-**37** (667 g, 61%) as a colorless oil. For analytical data, see compound (*S*)-**37** in the "Experimental Section" of this Full Paper.

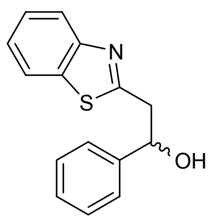


rac-**38**

$C_{15}H_{13}NO_2$
239.27 g/mol

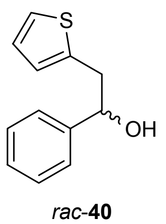
***rac*-2-(Benzoxazol-2-yl)-1-phenylethanol (*rac*-38):**[S33] A flame-dried 100-mL Schlenk flask equipped with a magnetic stirring bar was charged with a solution of 2-methylbenzoxazole (1.33 g, 10.0 mmol, 1.00 equiv) in THF (30 mL). After cooling to –78°C *n*BuLi (4.0 mL, 10 mmol, 1.0 equiv, 2.5M solution in hexanes) was added dropwise within 10 min. The mixture was maintained at this temperature for further 1 h, then a solution of benzaldehyde (1.21 mL, 1.27 g, 12.0 mmol, 1.20 equiv) in THF (20 mL) was added within 20 min. After further 1 h at –78°C, the reaction was allowed to warm to ambient temperature and quenched with saturated NH_4Cl (20 mL) and water (30 mL). The organic phase was separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 30 mL), washed with brine (20 mL) and dried (Na_2SO_4). Evaporation of the solvents under reduced pressure was followed by recrystallization from ethanol to furnish analytically pure *rac*-**38** (933 mg, 39%) as a white solid. M.p. 143–145°C (ethanol); $R_f = 0.26$ (cyclohexane/*tert*-butyl methyl ether 2:1); HPLC (Daicel Chiralcel OD-H, 20°C, *n*-heptane/*i*PrOH 92:8, flow rate 0.80 $mL\cdot min^{-1}$, $\lambda = 230$ nm): $t_R = 15.9$ min and 17.4 min; ^1H NMR (400

MHz, $CDCl_3$): δ = 3.31 (dd, *J* = 16.3 Hz, *J* = 4.7 Hz, 1H), 3.34 (dd, *J* = 16.3 Hz, *J* = 8.1 Hz, 1H), 3.86 (br s, 1H), 5.36 (dd, *J* = 8.1 Hz, *J* = 4.7 Hz, 1H), 7.29–7.36 (m, 3H), 7.36–7.41 (m, 2H), 7.45–7.49 (m, 2H), 7.49–7.53 (m, 1H), 7.67–7.72 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.2, 71.3, 110.6, 119.8, 124.5, 125.0, 125.8, 128.1, 128.8, 140.9, 142.6, 150.6, 164.9 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3412 (m), 3065 (w), 1613 (s), 1495 (s), 1455 (s), 1057 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 240 [$(M+H)^+$]; elemental analysis calcd (%) for $C_{15}H_{13}NO_2$ (239.3): C 75.30, H 5.48, N 5.85; found: C 75.05, H 5.38, N 5.82.



rac-**39**
$C_{15}H_{13}NOS$
255.33 g/mol

***rac*-2-(Benzothiazol-2-yl)-1-phenylethanol (*rac*-39):**[S34] A flame-dried 100-mL Schlenk flask equipped with a magnetic stirring bar was charged with a solution of 2-methylbenzothiazole (1.49 g, 10.0 mmol, 1.00 equiv) in THF (30 mL). After cooling to –78°C *n*BuLi (4.0 mL, 10 mmol, 1.0 equiv, 2.5M solution in hexanes) was added dropwise within 15 min. The mixture was maintained at this temperature for further 60 min, then a solution of benzaldehyde (1.21 mL, 1.27 g, 12.0 mmol, 1.20 equiv) in THF (20 mL) was added within 20 min. After further 1 h at –30°C, the reaction was allowed to warm to ambient temperature and quenched with saturated NH_4Cl (20 mL) and water (30 mL). The organic phase was separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 30 mL), washed with brine (20 mL) and dried (Na_2SO_4). Evaporation of the solvents under reduced pressure was followed by recrystallization from ethanol to furnish analytically pure *rac*-**39** (1.80 g, 70%) as a white solid. M.p. 139–141°C (ethanol); R_f = 0.31 (cyclohexane/*tert*-butyl methyl ether 2:1); HPLC (Daicel Chiralcel OD-H, 20°C, *n*-heptane/*i*PrOH 80:20, flow rate 0.80 mL·min^{-1}, λ = 230 nm): t_R = 10.8 min and 12.4 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.46 (dd, *J* = 15.8 Hz, *J* = 6.9 Hz, 1H), 3.47 (dd, *J* = 15.8 Hz, *J* = 5.5 Hz, 1H), 4.27 (br s, 1H), 5.31 (dd, *J* = 6.7 Hz, *J* = 5.7 Hz, 1H), 7.31 (m_c, 1H), 7.35–7.41 (m, 2H), 7.39 (ddd, *J* = 8.0 Hz, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.45–7.49 (m, 2H), 7.49 (ddd, *J* = 8.2 Hz, *J* = 7.1 Hz, *J* = 1.2 Hz, 1H), 7.85 (ddd, *J* = 8.0 Hz, *J* = 1.3 Hz, *J* = 0.6 Hz, 1H), 8.01 (ddd, *J* = 8.2 Hz, *J* = 1.2 Hz, *J* = 0.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.1, 72.8, 121.6, 122.8, 125.2, 125.9, 126.2, 127.9, 128.7, 134.8, 142.8, 152.9, 168.9 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3399 (m), 3066 (w), 1603 (s), 1456 (s), 1437 (s), 1062 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 256 [$(M+H)^+$]; elemental analysis calcd (%) for $C_{15}H_{13}NOS$ (255.3): C 70.56, H 5.13, N 5.49, S 12.56; found: C 70.41, H 5.14, N 5.46, S 12.77.

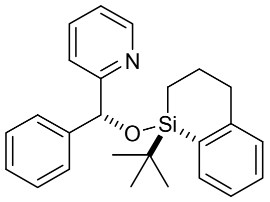


rac-**40**
$C_{12}H_{12}OS$
204.29 g/mol

***rac*-1-Phenyl-2-(thiophen-2-yl)ethanol (*rac*-40):**[S35] A flame-dried 100-mL Schlenk flask equipped with a magnetic stirring bar was charged with a solution of 2-bromothiophene (1.64 g, 10.0 mmol, 1.00 equiv) in THF (15 mL). After cooling to –30°C *n*BuLi (4.0 mL, 10 mmol, 1.0 equiv, 2.5M solution in hexanes) was added dropwise within 10 min. The mixture was maintained at this temperature for further 45 min and then a solution of racemic epoxystyrene (1.21 g, 10.0 mmol, 1.00 equiv) in THF (15 mL) was added within 20 min. After further 30 min at –30°C, the reaction was allowed to warm to ambient temperature and quenched with saturated NH_4Cl (20 mL) and water (30 mL). The organic phase was separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 30 mL), washed with brine (20 mL) and dried (Na_2SO_4). Evaporation of the solvents under reduced pressure was followed by flash chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether 4:1) furnished analytically pure *rac*-**40** (175 mg, 8%) as a colorless oil. R_f = 0.26 (cyclohexane/*tert*-butyl methyl ether 2:1); HPLC (Daicel Chiralcel OD-H, 20°C, *n*-heptane/*i*PrOH 99:1, flow rate 1.00 $mL\cdot min^{-1}$, λ = 230 nm): t_R = 42.7 min and 48.5 min; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.14 (d, *J* = 3.2 Hz, 1H), 3.23 (ddd, *J* = 14.9 Hz, *J* = 7.5 Hz, *J* = 0.8 Hz, 1H), 3.24 (ddd, *J* = 14.8 Hz, *J* = 5.4 Hz, *J* = 0.9 Hz, 1H), 4.90 (ddd, *J* = 7.6 Hz, *J* = 5.4 Hz, *J* = 3.1 Hz, 1H), 6.84 (dddd, *J* = 3.4 Hz, *J* = *J* = *J* = 1.0 Hz. 1H), 6.94 (dd, *J* = 5.1 Hz, *J* = 3.4 Hz, 1H), 7.17 (dd, *J* = 5.1 Hz, *J* = 1.2 Hz, 1H), 7.27–7.31 (m, 1H), 7.32–7.40 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.1, 75.1, 124.5, 126.0, 126.4, 127.0, 127.9, 128.6, 140.2, 143.3 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3418 (m), 3066 (w), 2917 (s), 1603 (s), 1494 (s), 1438 (s), 1048 (s) cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{12}H_{12}OS$ [M^+]: 204.0609, found: 204.0611; elemental analysis calcd (%) for $C_{12}H_{12}OS$ (204.3): C 70.55, H 5.92, S 15.70; found: C 70.23, H 5.84, S 15.68.

4 Experimental Details and Characterization Data for New Silyl Ethers

4.1 Chelate Ring Size and Diastereoselectivity (Table 2)



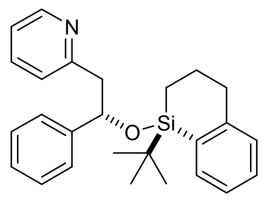
(^{Si}S*,*R**)-**10a**

$C_{25}H_{29}NOSi$
387.59 g/mol

(^{Si}*S,*R**)-2-[1-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-1-phenylmethyl]-pyridine [(^{Si}*S**,*R**)-10a] (Table 2, Entry 1):** According to GP 1, the reaction mixture consisting of *rac*-**8** (74.1 mg, 0.400 mmol, 1.00 equiv), *rac*-**4a** (45.0 mg, 0.220 mmol, 0.550 equiv), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 24 h at 20°C, after which a conversion of 51% was detected by ^1H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 93:7→3:2) furnished analytically pure silyl ether (^{Si}*S**,*R**)-**10a** (58 mg, 37%, d.r. = 81:19) and alcohol *rac*-**8** (32 mg, 43%).

Analytical data for (^{Si}*S**,*R**)-**10a**: R_f = 0.09 (cyclohexane/*tert*-butyl methyl ether 93:7); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.71 (dddd, *J* = 15.2 Hz, *J* = 5.6 Hz, *J* = 4.3 Hz, *J* = 1.4 Hz, 1H), 0.84 (ddd, *J* = 15.2 Hz, *J* = 12.0 Hz, *J* = 5.4 Hz, 1H), 1.07 (s, 9H), 1.48 (m_c, 1H), 1.92 (m_c, 1H), 2.55 (ddd, *J* = 15.8 Hz, *J* = 11.1 Hz, *J* = 2.6 Hz, 1H), 2.69 (br dd, *J* = 15.0 Hz, *J* = 5.8 Hz, 1H), 5.80 (s, 1H), 7.05–7.15 (m, 3H), 7.16–7.33 (m, 4H), 7.38–7.46 (m, 3H), 7.67 (ddd, *J* = *J* = 7.4 Hz, *J* = 1.6 Hz, 1H), 7.74 (br d, *J* = 8.1 Hz, 1H), 8.40 (ddd, *J* = 4.9 Hz, *J* = 1.9 Hz, *J* = 1.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.6, 18.8, 22.6, 26.2, 35.6, 78.1, 119.9, 121.8, 125.1, 126.6, 127.4, 128.3, 128.6, 129.6, 130.4, 135.0, 136.7, 143.8, 148.5, 150.7, 164.1 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3060 (m), 3032 (w), 3003 (w), 2930 (s), 2890 (s), 2858 (s), 1590 (s), 1572 (m), 1493 (m), 1472 (s), 1452 (m), 1435 (s), 1390 (w), 1362 (m), 1293 (w), 1271 (w), 1192 (m), 1144 (m), 1101 (s), 1077 (s), 1069 (s), 1029 (m), 996 (m), 973 (m), 847 (m), 825 (m), 810 (w) cm^{-1}; LRMS (CI/NH$_3$): *m/z*: 388 [(M+H)$^+$]; elemental analysis calcd (%) for $C_{25}H_{29}NOSi$ (387.6): C 77.47, H 7.54, N 3.61; found: C 77.23, H 7.74, N 3.40.

NMR spectroscopic data for (^{Si}*S**,*S**)-**10a** (minor diastereomer): ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.66–0.74 (m, 1H), 0.85 (ddd, *J* = 15.2 Hz, *J* = 12.3 Hz, *J* = 5.3 Hz, 1H), 1.06 (s, 9H), 1.58 (m$_c$, 1H), 1.88–2.01 (m, 1H), 2.51–2.60 (m, 1H), 2.70–2.88 (m, 1H), 5.80 (s, 1H), 7.05–7.15 (m, 3H), 7.16–7.33 (m, 4H), 7.38–7.46 (m, 3H), 7.61–7.66 (m, 1H), 7.68 (ddd, *J* = *J* = 7.5 Hz, *J* = 1.8 Hz, 1H), 8.47 (ddd, *J* = 4.9 Hz, *J* = 1.7 Hz, *J* = 0.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 9.7, 18.8, 22.6, 26.2, 35.6, 78.2, 120.4, 122.1, 125.1, 126.2, 127.1, 128.1, 128.5, 129.6, 130.3, 135.2, 136.8, 143.8, 148.6, 150.7, 164.1 ppm.



(^{Si}*S**,*S**)-**7a**

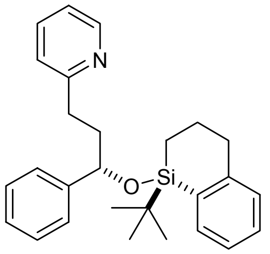
$C_{26}H_{31}NOSi$

401.62 g/mol

(^{Si}*S,*S**)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-2-phenylethyl]pyridine [(^{Si}*S**,*S**)-7a] (Table 2, Entry 2):**[S20,S36] According to GP 1, the reaction mixture consisting of *rac*-**6** (79.7 mg, 0.400 mmol, 1.00 equiv), *rac*-**4a** (40.9 mg, 0.200 mmol, 0.500 equiv), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 24 h at 20°C, after which a conversion of 47% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 95:5→1:1) furnished analytically pure silyl ether (^{Si}*S**,*S**)-**7a** (71 mg, 44%, d.r. = 92:8) and alcohol *rac*-**6** (40 mg, 50%).

Analytical data for (^{Si}*S**,*S**)-**7a**: R$_f$ = 0.15 (cyclohexane/*tert*-butyl methyl ether 9:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.33 (dddd, *J* = 15.0 Hz, *J* = 6.2 Hz, *J* = 3.9 Hz, *J* = 1.2 Hz, 1H), 0.56 (ddd, *J* = 15.1 Hz, *J* = 12.1 Hz, *J* = 5.2 Hz, 1H), 0.84 (s, 9H), 1.24 (m$_c$, 1H), 1.70 (m$_c$, 1H), 2.39 (ddd, *J* = 16.0 Hz, *J* = 11.0 Hz, *J* = 2.7 Hz, 1H), 2.52 (dddd, *J* = 15.9 Hz, *J* = 5.6 Hz, *J* = *J* = 1.8 Hz, 1H), 3.01 (dd, *J* = 13.2 Hz, *J* = 3.4 Hz, 1H), 3.12 (dd, *J* = 13.0 Hz, *J* = 9.6 Hz, 1H), 4.96 (dd, *J* = 9.6 Hz, *J* = 3.2 Hz, 1H), 6.72 (dd, *J* = 7.3 Hz, *J* = 1.5 Hz, 1H), 6.93–7.05 (m, 2H), 7.10–7.38 (m, 8H), 7.57 (ddd, *J* = *J* = 7.5 Hz, *J* = 1.2 Hz, 1H), 8.50 (br d, *J* = 4.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 9.7, 18.6, 22.6, 26.1, 35.5, 50.2, 75.6, 121.4, 125.0, 125.3, 126.2, 127.3, 128.2, 128.3, 129.7, 130.5, 135.0, 136.0, 145.2, 149.2, 150.6, 159.1 ppm; IR (cuvette/CDCl$_3$): $\tilde{\nu}$ = 3060 (w), 3031 (w), 3004(w), 2953 (m), 2929 (s), 2891 (m), 2858 (s), 1594 (s), 1570 (m), 1493 (w), 1474 (s), 1463 (m), 1453 (m), 1437 (s), 1402 (w), 1362 (m), 1293 (m), 1269 (m), 1206 (m), 1143 (m), 1128 (m), 1078 (s), 1068 (s), 1012 (m), 975 (m), 843 (m), 825 (s), 797 (s) cm^{-1}; LRMS (CI/NH$_3$): *m/z*: 402 [(M+H)$^+$]; elemental analysis calcd (%) for $C_{26}H_{31}NOSi$ (401.6): C 77.76, H 7.78, N 3.49; found: C 77.47, H 8.06, N 3.28.

NMR spectroscopic data for (^{Si}*S**,*R**)-**7a** (minor diastereomer): ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.19 (dddd, *J* = 15.1 Hz, *J* = 6.2 Hz, *J* = 4.0 Hz, *J* = 1.5 Hz, 1H), 0.54 (ddd, *J* = 15.0 Hz, *J* = 12.0 Hz, *J* = 5.3 Hz, 1H), 0.81 (s, 9H), 1.40 (m$_c$, 1H), 1.80 (m$_c$, 1H), 2.37–2.47 (m, 1H), 2.53–2.63 (m, 1H), 3.00–3.08 (m, 1H), 3.08–3.16 (m, 1H), 5.05 (dd, *J* = 9.0 Hz, *J* = 4.0 Hz, 1H), 6.84 (dd, *J* = *J* = 7.3 Hz, 1H), 6.93–7.05 (m, 2H), 7.10–7.38 (m, 8H), 7.54–7.61 (m, 1H), 8.55 (br d, *J* = 5.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 9.4, 18.7, 23.0, 26.1, 35.6, 50.2, 78.0, 121.5, 124.6, 125.4, 126.2, 127.1, 128.0, 128.2, 129.1, 130.9, 134.6, 136.0, 144.9, 149.2, 150.2, 159.1 ppm.



($^{Si}S^*$,S^*)-**11a**

$C_{27}H_{33}NOSi$

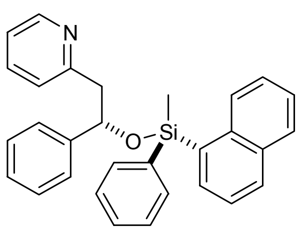
415.64 g/mol

($^{Si}S^*$,S^*)-2-[3-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-3-phenylpropyl]pyridine [($^{Si}S^*$,S^*)-11a] (Table 2, Entry 3): According to GP 1, the reaction mixture consisting of *rac*-**9** (85.3 mg, 0.400 mmol, 1.00 equiv), *rac*-**4a** (45.0 mg, 0.220 mmol, 0.550 equiv), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 62 h at 50°C, after which a conversion of 45% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→1:2) furnished analytically pure silyl ether ($^{Si}S^*$,S^*)-**11a** (57 mg, 37%, d.r. = 79:21) and alcohol *rac*-**9** (34 mg, 40%).

Analytical data for ($^{Si}S^*$,S^*)-**11a**: R_f = 0.37 (cyclohexane/*tert*-butyl methyl ether 6:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.49 (dddd, J = 15.1 Hz, J = 6.0 Hz, J = 3.8 Hz, J = 1.4 Hz, 1H), 0.67 (ddd, J = 15.3 Hz, J = 12.0 Hz, J = 5.4 Hz, 1H), 1.00 (s, 9H), 1.33 (m_c, 1H), 1.80 (m_c, 1H), 2.00–2.23 (m, 2H), 2.63 (ddd, J = 15.5 Hz, J = 10.8 Hz, J = 2.7 Hz, 1H), 2.62–2.68 (m, 1H), 2.75 (ddd, J = 13.8 Hz, J = 10.9 Hz, J = 5.0 Hz, 1H), 2.89 (ddd, J = 14.1 Hz, J = 10.9 Hz, J = 5.4 Hz, 1H), 4.64 (dd, J = 7.0 Hz, J = 5.0 Hz, 1H), 6.99 (br d, J = 8.0 Hz, 1H), 7.05 (dd, J = 7.4 Hz, J = 4.7 Hz, 1H), 7.10 (br d, J = 7.4 Hz, 1H), 7.15–7.30 (m, 6H), 7.30 (ddd, J = J = 7.7 Hz, J = 1.7 Hz, 1H), 7.52 (ddd, J = J = 7.6 Hz, J = 1.4 Hz, 1H), 7.72 (dd, J = 7.3 Hz, J = 1.3 Hz, 1H), 8.46 (br d, J = 4.3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.7, 18.7, 22.8, 26.2, 34.1, 35.6, 40.5, 74.8, 121.0, 122.9, 125.2, 126.2, 127.1, 128.1, 128.6, 129.5, 131.2, 135.2, 136.6, 145.0, 148.8, 150.8, 162.0 ppm; IR (ATR): $\tilde{\nu}$ = 3058 (w), 2927 (s), 2855 (s), 1590 (s), 1569 (w), 1549 (w), 1513 (w), 1472 (s), 1433 (s), 1360 (m), 1293 (w), 1205 (w), 1142 (m), 1086 (s), 1074 (s), 1049 (s), 1027 (m), 1005 (m), 976 (m), 916 (w), 866 (m), 823 (s), 739 (s), 699 (s) cm^{-1}; LRMS (EI): *m/z*: 358 [$(M-C_4H_9)^+$]; HRMS (ESI): *m/z*: calcd for $C_{27}H_{33}NOSi$ [$(M+H)^+$]: 416.2404, found: 416.2406.

NMR spectroscopic data for ($^{Si}S^*$,R^*)-**11a** (minor diastereomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91–1.28 (m, 2H), 0.96 (s, 9H), 1.62 (m_c, 1H), 1.73 (m_c, 1H), 2.00–2.23 (m, 2H), 2.50–2.90 (m, 4H), 4.74 (dd, J = J = 5.7 Hz, 1H), 6.93 (dd, J = J = 7.4 Hz, 1H), 7.04–7.08 (m, 1H), 7.12 (br d, J = 7.5 Hz, 1H), 7.15–7.30 (m, 7H), 7.54 (ddd, J = J = 7.7 Hz, J = 1.7 Hz, 1H), 7.64 (dd, J = 7.3 Hz, J = 1.3 Hz, 1H), 8.46 (br d, J = 4.3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.2, 18.6, 22.7, 26.1, 34.0, 35.7, 40.3, 75.1, 121.0, 122.9, 124.7, 126.2, 126.9, 127.9, 128.6, 129.6, 130.9, 134.6, 136.6, 144.6, 148.9, 150.2, 161.9 ppm.

4.2 Silane Substitution Pattern and Diastereoselectivity (Table 3)



(${}^{Si}S^*,S^*$)-**12**

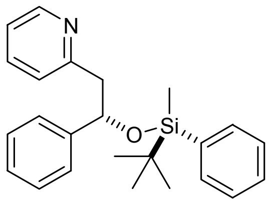
$C_{30}H_{27}NOSi$

445.63 g/mol

(${}^{Si}S^*,S^*$)-2-[2-(Methyl(naphth-1-yl)phenylsilyl-1-oxy)-2-phenylethyl]pyridine [(${}^{Si}S^*,S^*$)-12] (Table 3, Entry 1):[S36] According to GP 1, the reaction mixture consisting of *rac*-**6** (79.7 mg, 0.400 mmol, 1.00 equiv), *rac*-**1** (58.2 mg, 0.220 mmol, 0.550 equiv), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 3 h at 20°C, after which a conversion of 51% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→3:2) furnished analytically pure silyl ether (${}^{Si}S^*,S^*$)-**12** (90 mg, 51%, d.r. = 57:43) and alcohol *rac*-**6** (34 mg, 47%).

Analytical data for (${}^{Si}S^*,S^*$)-**12**: R_f = 0.18 (cyclohexane/*tert*-butyl methyl ether 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.41 (s, 3H), 3.12 (dd, *J* = 13.4 Hz, *J* = 4.2 Hz, 1H), 3.30 (dd, *J* = 13.3 Hz, *J* = 9.1 Hz, 1H), 5.27 (dd, *J* = 9.1 Hz, *J* = 4.4 Hz, 1H), 7.06–7.12 (m, 2H), 7.16–7.41 (m, 13H), 7.48 (ddd, *J* = *J* = 7.4 Hz, *J* = 1.7 Hz, 1H), 7.66 (dd, *J* = 6.6 Hz, *J* = 1.4 Hz, 1H), 7.76–7.82 (m, 1H), 7.83–7.90 (m, 2H), 8.49 (ddd, *J* = 4.9 Hz, *J* = 2.0 Hz, *J* = 1.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.5, 49.7, 76.3, 121.4, 124.9, 124.9, 125.3, 125.4, 126.4, 127.3, 127.8, 128.1, 128.6, 128.9, 129.6, 130.6, 133.3, 134.2, 134.3, 134.9, 136.0, 136.8, 137.2, 144.2, 149.3, 158.9 ppm; IR (ATR): $\tilde{\nu}$ = 3060 (s), 2976 (s), 1593 (s), 1570 (m), 1505 (m), 1476 (s), 1454 (m), 1438 (s), 1429 (m), 1388 (w), 1367 (m), 1320 (w), 1258 (s), 1225 (s), 1211 (m), 1147 (m), 1113 (s), 1089 (s), 1068 (s), 1015 (m), 997 (w), 985 (w), 893 (m), 827 (s), 805 (s) cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{30}H_{27}NOSi$ [$(M+H)^+$]: 446.1935, found: 446.1932; elemental analysis calcd (%) for $C_{30}H_{27}NOSi$ (445.6): C 80.86, H 6.11, N 3.14; found: C 80.61, H 6.41, N 2.92.

NMR spectroscopic data for (${}^{Si}S^*,R^*$)-**12** (minor diastereomer): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.38 (s, 3H), 3.10 (dd, *J* = 13.4 Hz, *J* = 4.2 Hz, 1H), 3.26 (dd, *J* = 13.4 Hz, *J* = 9.0 Hz, 1H), 5.31 (dd, *J* = 9.0 Hz, *J* = 4.3 Hz, 1H), 6.93–6.98 (m, 2H), 7.16–7.41 (m, 14H), 7.59 (dd, *J* = 6.9 Hz, *J* = 1.4 Hz, 1H), 7.76–7.82 (m, 1H), 7.83–7.90 (m, 2H), 8.40 (m_c, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.7, 49.5, 76.3, 121.3, 124.8, 124.9, 125.4, 125.7, 126.4, 127.4, 127.7, 128.2, 128.6, 129.0, 129.5, 130.6, 133.4, 134.2, 134.3, 134.9, 135.7, 136.8, 136.9, 144.4, 149.1, 158.7 ppm.



(${}^{Si}S^*,S^*$)-**13**

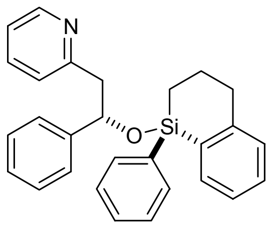
$C_{24}H_{29}NOSi$

375.58 g/mol

(${}^{Si}S^*,S^*$)-2-[2-(*tert*-Butylmethylphenylsilyl-1-oxy)-2-phenylethyl]pyridine [(${}^{Si}S^*,S^*$)-13] (Table 3, Entry 2):[S20,S36] According to GP 1, the reaction mixture consisting of *rac*-**6** (199 mg, 1.00 mmol, 1.00 equiv), *rac*-**2** (98.1 mg, 0.550 mmol, 0.550 equiv), CuCl (5.0 mg, 0.050 mmol, 0.050 equiv), **L1d** (34.6 mg, 0.100 mmol, 0.100 equiv) and NaO*t*Bu (4.8 mg, 0.050 mmol, 0.050 equiv) in toluene (10 mL) was stirred for 12 h at 20°C, after which a conversion of 52% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 94:6→1:1) furnished analytically pure silyl ether (${}^{Si}S^*,S^*$)-**13** (192 mg, 51%, d.r. = 59:41) and alcohol *rac*-**6** (67 mg, 34%).

Analytical data for (^{Si}*S**,*S**)-**13**: R$_f$ = 0.15 (cyclohexane/*tert*-butyl methyl ether 6:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.04 (s, 3H), 0.81 (s, 9H), 3.14 (dd, *J* = 12.8 Hz, *J* = 4.1 Hz, 1H), 3.24 (dd, *J* = 12.6 Hz, *J* = 8.8 Hz, 1H), 5.21 (dd, *J* = 9.0 Hz, *J* = 4.2 Hz, 1H), 7.10–7.41 (m, 12H), 7.59 (ddd, *J* = *J* = 7.8 Hz, *J* = 1.8 Hz, 1H), 8.57–8.61 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = –7.1, 18.6, 26.0, 50.2, 76.0, 121.5, 125.2, 126.1, 127.1, 127.3, 128.1, 129.1, 134.7, 135.7, 136.1, 144.9, 149.2, 158.9 ppm; IR (ATR): $\tilde{\nu}$ = 3069 (w), 3019 (w), 2958 (s), 2928 (s), 2856 (m), 1647 (s), 1468 (s), 1426 (m), 1361 (w), 1254 (m), 1105 (m), 778 (m), 752 (s), 735 (s) cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{24}H_{29}NOSi$ [(M+H)$^+$]: 376.2091, found: 376.2096; elemental analysis calcd (%) for $C_{24}H_{29}NOSi$ (375.6): C 76.75, H 7.78, N 3.73; found: C 76.63, H 7.76, N 3.50.

NMR spectroscopic data for (^{Si}*S**,*R**)-**13** (minor diastereomer): ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.10 (s, 3H), 0.82 (s, 9H), 3.12 (dd, *J* = 13.0 Hz, *J* = 8.9 Hz, 1H), 3.23 (dd, *J* = 13.0 Hz, *J* = 8.9 Hz, 1H), 5.14 (dd, *J* = 9.0 Hz, *J* = 4.2 Hz, 1H), 7.10–7.41 (m, 12 H), 7.54 (ddd, *J* = *J* = 7.6 Hz, *J* = 2.0 Hz, 1H), 8.55–8.59 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = –6.8, 18.5, 26.0, 50.2, 75.8, 121.4, 125.3, 126.2, 127.3, 127.4, 128.2, 129.2, 134.5, 135.6, 136.1, 145.0, 149.1, 158.9 ppm.



(^{Si}*S**,*S**)-**14**

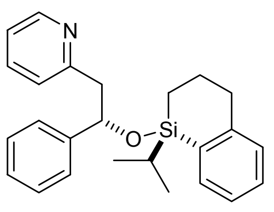
$C_{28}H_{27}NOSi$

M = 421.61 g/mol

(^{Si}*S,*S**)-2-[2-(1-Phenyl-1-silatetralinyl-1-oxy)-2-phenylethyl]pyridine [(^{Si}*S**,*S**)-14] (Table 3, Entry 3):**[S36] According to GP 1, the reaction mixture consisting of *rac*-**6** (79.7 mg, 0.400 mmol, 1.00 equiv), *rac*-**3** (49.4 mg, 0.220 mmol, 0.550 equiv), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4 mL) was stirred for 4 h at 20°C, after which a conversion of 52% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→3:2) furnished analytically pure silyl ether (^{Si}*S**,*S**)-**14** (87 mg, 51%, d.r. = 66:34) and alcohol *rac*-**6** (36 mg, 45%).

Analytical data for (^{Si}*S**,*S**)-**14**: R$_f$ = 0.48 (cyclohexane/*tert*-butyl methyl ether 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.66 (ddd, *J* = 15.0 Hz, *J* = 9.5 Hz, *J* = 4.2 Hz, 1H), 0.86 (ddd, *J* = 15.0 Hz, *J* = 9.5 Hz, *J* = 4.2 Hz, 1H), 1.59–1.83 (m, 2H), 2.57–2.73 (m, 2H), 3.08 (dd, *J* = 13.2 Hz, *J* = 3.9 Hz, 1H), 3.20 (dd, *J* = 13.2 Hz, *J* = 9.3 Hz, 1H), 5.17 (dd, *J* = 9.2 Hz, *J* = 3.8 Hz, 1H), 6.84 (dd, *J* = 7.2 Hz, *J* = 1.1 Hz, 1H), 6.97 (ddd, *J* = *J* = 7.2 Hz, *J* = 1.0 Hz, 1H), 7.04 (br d, *J* = 3.7 Hz, 1H), 7.07–7.35 (m, 12H), 7.38–7.41 (m, 1H), 7.51 (ddd, *J* = *J* = 7.5 Hz, *J* = 2.0 Hz, 1H), 8.50 (ddd, *J* = 4.9 Hz, *J* = 2.0 Hz, *J* = 1.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8, 22.6, 35.1, 49.9, 75.8, 121.4, 125.1, 125.4, 126.3, 127.4, 127.7, 128.3, 128.5, 129.5, 129.7, 131.0, 134.4, 135.2, 136.0, 136.7, 144.7, 149.3, 150.0, 159.0 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3056 (w), 3030 (w), 3001 (w), 2956 (s), 2926 (s), 2870 (s), 1593 (s), 1570 (m), 1476 (s), 1454 (s), 1437 (s), 1378 (m), 1366 (m), 1310 (w), 1292 (w), 1268 (w), 1202 (m), 1140 (m), 1112 (s), 1077 (s), 1068 (s), 1013 (m), 974 (m), 880 (m), 810 (w) cm^{-1}; LRMS (EI): *m/z*: 421 [M$^+$]; elemental analysis calcd (%) for $C_{28}H_{27}NOSi$ (421.6): C 79.77, H 6.45, N 3.32; found: C 79.45, H 6.46, N 3.23.

NMR spectroscopic data for (^{Si}*S**,*R**)-**14** (minor diastereomer): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.55–0.64 (m, 1H), 0.81 (ddd, *J* = 14.5 Hz, *J* = 8.6 Hz, *J* = 4.2 Hz, 1H), 1.59–1.83 (m, 2H), 2.57–2.73 (m, 2H), 3.10 (dd, *J* = 13.1 Hz, *J* = 4.0 Hz, 1H), 3.21 (dd, *J* = 13.0 Hz, *J* = 9.6 Hz, 1H), 5.20 (dd, *J* = 9.3 Hz, *J* = 4.0 Hz, 1H), 6.94 (ddd, *J* = *J* = 7.3 Hz, *J* = 1.2 Hz, 1H), 7.02 (br d, *J* = 4.1 Hz, 1H), 7.07–7.35 (m, 13H), 7.38–7.41 (m, 1H), 7.56 (ddd, *J* = *J* = 7.8 Hz, *J* = 2.0 Hz, 1H), 8.55 (ddd, *J* = 4.9 Hz, *J* = 1.8 Hz, *J* = 1.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.4, 22.6, 35.1, 49.8, 76.1, 121.5, 125.0, 125.1, 126.3, 127.3, 127.7, 128.1, 128.4, 129.5, 129.6, 131.3, 134.4, 135.4, 136.0, 136.4, 144.5, 149.4, 149.7, 159.1 ppm.



(^{Si}*S**,*S**)-**7b**

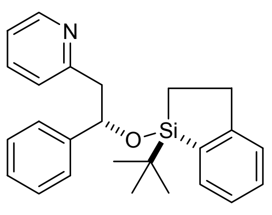
C$_{25}$H$_{29}$NOSi

387.59 g/mol

(^{Si}*S,*S**)-2-[2-(1-Isopropyl-1-silatetralinyl-1-oxy)-2-phenylethyl]pyridine [(^{Si}*S**,*S**)-7b] (Table 3, Entry 5):** According to GP 1, the reaction mixture consisting of *rac*-**6** (79.7 mg, 0.400 mmol, 1.00 equiv), *rac*-**4b** (91.4 mg, 0.480 mmol, 1.20 equiv), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4 mL) was stirred for 24 h at 20°C, after which full conversion was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1) furnished analytically pure silyl ether (^{Si}*S**,*S**)-**7b** (145 mg, 94%, d.r. = 83:17).

Analytical data for (^{Si}*S**,*S**)-**7b**: R$_f$ = 0.33 (cyclohexane/*tert*-butyl methyl ether 4:1); ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.38 (dddd, *J* = 14.9 Hz, *J* = 8.2 Hz, *J* = 4.2 Hz, *J* = 0.8 Hz, 1H), 0.59 (ddd, *J* = 14.9 Hz, *J* = 10.6 Hz, *J* = 4.4 Hz, 1H), 0.80–0.96 (m, 7H), 1.42 (m$_c$, 1H), 1.65 (m$_c$, 1H), 2.47 (ddd, *J* = 15.9 Hz, *J* = 9.5 Hz, *J* = 2.7 Hz, 1H), 2.53 (br ddd, *J* = 15.7 Hz, *J* = 7.2 Hz, *J* = 3.0 Hz, 1H), 3.04 (dd, *J* = 12.9 Hz, *J* = 3.8 Hz, 1H), 3.11 (dd, *J* = 12.9 Hz, *J* = 9.0 Hz, 1H), 4.99 (dd, *J* = 9.2 Hz, *J* = 4.0 Hz, 1H), 6.77 (dd, *J* = 7.1 Hz, *J* = 1.2 Hz, 1H), 6.97 (br d, *J* = 7.2 Hz, 1H), 6.99 (dd, *J* = *J* = 7.7 Hz, 1H), 7.10–7.18 (m, 2H), 7.18–7.21 (m, 1H), 7.23–7.26 (m, 1H), 7.27–7.31 (m, 2H), 7.31–7.35 (m, 2H), 7.57 (ddd, *J* = *J* = 7.7 Hz, *J* = 1.9 Hz, 1H), 8.50 (ddd, *J* = 4.8 Hz, *J* = 1.8 Hz, *J* = 0.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ = 9.9, 14.0, 16.9, 17.1, 22.6, 35.3, 49.9, 75.4, 121.4, 125.1, 125.2, 126.1, 127.3, 128.2, 128.3, 129.3, 131.0, 134.5, 136.1, 145.0, 148.9, 150.1, 159.0 ppm; IR (ATR): $\tilde{\nu}$ = 3056 (w), 3004 (w), 2922 (s), 2862 (s), 1591 (s), 1569 (w), 1494 (w), 1473 (s), 1454 (m), 1435 (s), 1365 (w), 1293 (w), 1269 (w), 1207 (w), 1142 (m), 1128 (m), 1077 (s), 1064 (s), 1015 (w), 996 (m), 971 (w), 938 (m), 915 (w), 882 (s), 786 (s), 776 (s), 739 (s), 699 (s) cm^{-1}; HRMS (ESI): *m/z*: calcd for C$_{25}$H$_{29}$NOSi [(M+H)$^+$]: 388.2091, found: 388.2091; elemental analysis calcd (%) for C$_{25}$H$_{29}$NOSi (387.6): C 77.47, H 7.54, N 3.61; found: C 77.08 H 7.54, N 3.39.

NMR spectroscopic data for (^{Si}*S**,*R**)-**7b** (minor diastereomer): ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.32 (dddd, *J* = 14.8 Hz, *J* = 8.1 Hz, *J* = 4.1 Hz, *J* = 0.8 Hz, 1H), 0.56 (ddd, *J* = 14.9 Hz, *J* = 10.6 Hz, *J* = 4.5 Hz, 1H), 0.80–0.96 (m, 7H), 1.57 (m$_c$, 1H), 1.72 (m$_c$, 1H), 2.45–2.60 (m, 2H), 3.04–3.09 (m, 1H), 3.12 (dd, *J* = 13.3 Hz, *J* = 9.4 Hz, 1H), 5.10 (dd, *J* = 9.2 Hz, *J* = 3.2 Hz, 1H), 6.92 (br dd, *J* = *J* = 7.4 Hz, 1H), 6.98 (br d, *J* = 7.6 Hz, 1H), 7.05 (dd, *J* = 7.3 Hz, *J* = 1.2 Hz, 1H), 7.10–7.18 (m, 2H), 7.18–7.21 (m, 1H), 7.23–7.26 (m, 1H), 7.27–7.31 (m, 2H), 7.31–7.35 (m, 2H), 7.55 (ddd, *J* = *J* = 7.7 Hz, *J* = 1.9 Hz, 1H), 8.52 (ddd, *J* = 4.8 Hz, *J* = 1.8 Hz, *J* = 0.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ = 9.5, 13.8, 16.9, 17.1, 22.8, 35.3, 49.8, 75.7, 121.5, 124.8, 125.2, 126.1, 127.1, 128.0, 128.3, 129.2, 131.2, 134.9, 136.1, 144.8, 148.9, 149.7, 159.0 ppm.



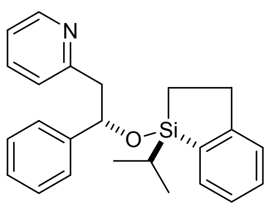
$(^{\mathrm{Si}}S^{*},S^{*})$-**15a**

$C_{25}H_{29}NOSi$

387.59 g/mol

$(^{\mathrm{Si}}S^{*},S^{*})$-2-[2-(1-*tert*-Butyl-1-silaindanyl-1-oxy)-2-phenylethyl]pyridine [$(^{\mathrm{Si}}S^{*},S^{*})$-15a] (Table 3, Entry 6): According to GP 1, the reaction mixture consisting of *rac*-**6** (79.7 mg, 0.400 mmol, 1.00 equiv), *rac*-**5a** (41.9 mg, 0.220 mmol, 0.550 equiv), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4 mL) was stirred for 1 h at 20°C, after which a conversion of 52% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*t*-butyl methyl ether 95:5→3:2) furnished analytically pure silyl ether $(^{\mathrm{Si}}S^{*},S^{*})$-**15a** (76 mg, 49%, d.r. = 86:14) and alcohol *rac*-**6** (37 mg, 47%).

Analytical data for $(^{\mathrm{Si}}S^{*},S^{*})$-**15a**: R_f = 0.32 (cyclohexane/*tert*-butyl methyl ether 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.35 (ddd, *J* = 15.5 Hz, *J* = 9.5 Hz, *J* = 6.0 Hz, 1H), 0.67 (ddd, *J* = 15.5 Hz, *J* = 9.1 Hz, *J* = 5.0 Hz, 1H), 0.88 (s, 9H), 2.63 (ddd, *J* = 16.8 Hz, *J* = 9.4 Hz, *J* = 5.0 Hz, 1H), 2.69 (ddd, *J* = 17.1 Hz, *J* = 9.0 Hz, *J* = 6.0 Hz, 1H), 3.02 (dd, *J* = 13.2 Hz, *J* = 3.8 Hz, 1H), 3.09 (dd, *J* = 13.2 Hz, *J* = 9.3 Hz, 1H), 4.90 (dd, *J* = 9.3 Hz, *J* = 3.8 Hz, 1H), 6.87 (ddd, *J* = 7.2 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz, 1H), 7.01–7.28 (m, 10H), 7.55 (ddd, *J* = *J* = 7.6 Hz, *J* = 1.8 Hz, 1H), 8.47 (ddd, *J* = 4.9 Hz, *J* = 1.8 Hz, *J* = 0.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.1, 18.5, 25.9, 30.0, 49.9, 75.5, 121.3, 125.1, 125.3, 125.9, 126.0, 127.2, 128.2, 130.0, 132.9, 133.6, 136.0, 144.9, 149.1, 154.5, 159.1 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3060 (w), 2928 (s), 2855 (s), 1592 (s), 1471 (s), 1438 (s), 1068 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 388 [$(M+H)^+$]; HRMS (EI): *m/z*: calcd for $C_{25}H_{29}NOSi$ [$(M-C_4H_9)^+$]: 330.1314, found: 330.1319; elemental analysis calcd (%) for $C_{25}H_{29}NOSi$ (387.6): C 77.47, H 7.54, N 3.61; found: C 77.59, H 7.46, N 3.33.



$(^{\mathrm{Si}}S^{*},S^{*})$-**15b**

$C_{24}H_{27}NOSi$

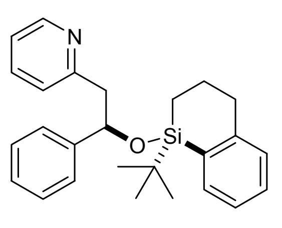
373.56 g/mol

$(^{\mathrm{Si}}S^{*},S^{*})$-2-[2-(1-Isopropyl-1-silaindanyl-1-oxy)-2-phenylethyl]pyridine [$(^{\mathrm{Si}}S^{*},S^{*})$-15b] (Table 3, Entry 7): According to GP 1, the catalyst was prepared from CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (2.0 mL). To this pale yellow solution activated, powdered molecular sieves 4Å (200 mg) were added followed by the addition of *rac*-**6** (79.7 mg, 0.400 mmol, 1.00 equiv) in toluene (1.5 mL) and *rac*-**5b** (84.6 mg, 0.480 mmol, 1.20 equiv) in toluene (0.5 mL). After stirring for 4 h at 20°C, full conversion was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 95:5→9:1) furnished analytically pure silyl ether $(^{\mathrm{Si}}S^{*},S^{*})$-**15b** (127 mg, 85%, d.r. = 52:48).

Analytical data for $(^{\mathrm{Si}}S^{*},S^{*})$-**15b**: R_f = 0.28 (cyclohexane/*tert*-butyl methyl ether 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.41 (ddd, *J* = 15.4 Hz, *J* = 9.5 Hz, *J* = 5.3 Hz, 1H), 0.65 (ddd, *J* = 15.4 Hz, *J* = 9.5 Hz, *J* = 5.2 Hz, 1H), 0.90–0.95 (m, 6H), 0.95–1.05 (m, 1H), 2.64 (ddd, *J* = 16.8 Hz, *J* = 9.4 Hz, *J* = 5.4 Hz, 1H), 2.73 (ddd, *J* = 16.8 Hz, *J* = 9.1 Hz, *J* = 5.4 Hz, 1H), 3.04–3.13 (m, 2H), 4.95 (dd, *J* = 9.2 Hz, *J* = 4.0 Hz, 1H), 6.92 (br d, *J* = 6.8 Hz, 1H), 7.05 (ddd, *J* = *J* = 7.3 Hz, *J* = 1.0 Hz, 1H), 7.08–7.32 (m, 9H), 7.59 (ddd, *J* = *J* = 7.3 Hz, *J* = 1.7 Hz, 1H), 8.48 (ddd, *J* = 4.7 Hz, *J* = 1.7 Hz, *J* = 1.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.0, 13.8, 16.9, 17.1, 30.1, 49.4, 75.4, 121.5, 125.2, 125.4, 125.9, 126.0, 127.3, 128.2, 130.0, 133.1, 134.2, 136.3, 144.7, 148.7, 154.1, 158.9 ppm; IR (ATR): $\tilde{\nu}$ = 3059 (w), 2941 (s), 2923 (s), 2863 (s), 1592 (s), 1570 (w), 1438 (s), 1255 (w), 1206 (w), 1120 (m), 1128 (m), 1082 (s), 1062 (s), 1015 (w), 995 (m), 940 (m), 881 (s), 785 (s), 742 (s), 699 (s) cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{24}H_{27}NOSi$ [$(M+H)^+$]: 374.1940, found: 374.1929; elemental analysis calcd (%) for $C_{24}H_{27}NOSi$ (373.6): C 77.16, H 7.29, N 3.75; found: C 76.89 H 7.46, N 3.71.

NMR spectroscopic data for (^{Si}*S**,*R**)-**15b** (minor diastereomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.28 (ddd, *J* = 15.4 Hz, *J* = 9.1 Hz, *J* = 6.1 Hz, 1H), 0.59 (ddd, *J* = 15.4 Hz, *J* = 8.7 Hz, *J* = 5.4 Hz, 1H), 0.90–0.95 (m, 6H), 0.95–1.05 (m, 1H), 2.73–2.82 (m, 2H), 3.04–3.13 (m, 2H), 5.00 (dd, *J* = *J* = 6.5 Hz, 1H), 6.94 (ddd, *J* = *J* = 7.3 Hz, *J* = 0.8 Hz, 1H), 7.01 (br d, *J* = 7.0 Hz, 1H), 7.08–7.32 (m, 9H), 7.57 (ddd, *J* = *J* = 7.5 Hz, *J* = 1.8 Hz, 1H), 8.52 (ddd, *J* = 4.7 Hz, *J* = 1.7 Hz, *J* = 1.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 6.9, 13.9, 16.9, 17.0, 30.2, 49.5, 75.5, 121.6, 125.1, 125.2, 125.9, 125.9, 127.2, 128.1, 129.8, 132.8, 134.4, 136.3, 144.6, 148.7, 154.4, 158.9 ppm.

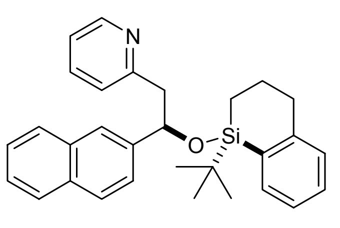
4.3 Kinetic Resolution of 2-(Pyridin-2-yl)ethanols with Silatetraline 4a (Tables 4 & 5)



(^{Si}*R*,*R*)-**7a**
$C_{26}H_{31}NOSi$
401.62 g/mol

(^{Si}*R*,*R*)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-2-phenylethyl]pyridine [(^{Si}*R*,*R*)-7a] (Table 4, Entry 1):[S36] According to GP 1, the reaction mixture consisting of *rac*-**6** (79.7 mg, 0.400 mmol, 1.00 equiv), (^{Si}*S*)-**4a** (49.1 mg, 0.240 mmol, 0.600 equiv, 94% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 24 h at 20°C, after which a conversion of 58% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→1:1) furnished analytically pure silyl ether (^{Si}*R*,*R*)-**7a** (92 mg, 57%, d.r. = 84:16) and alcohol (*S*)-**6** (33 mg, 42%, 88 % *ee*).

Analytical data for (^{Si}*R*,*R*)-**7a** agreed with those of (^{Si}*S**,*S**)-**7a** (see above); $[\alpha]^{20}_{D}$ = +64.4 (*c* = 0.590, $CHCl_3$), $[\alpha]^{20}_{578}$ = +67.5, $[\alpha]^{20}_{546}$ = +77.6, $[\alpha]^{20}_{436}$ = +142; $[\alpha]^{20}_{365}$ = +256.

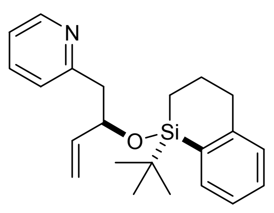


(^{Si}*R*,*R*)-**20a**
$C_{30}H_{33}NOSi$
451.67 g/mol

(^{Si}*R*,*R*)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-2-(naphth-2-yl)-ethyl]pyridine [(^{Si}*R*,*R*)-20a] (Table 4, Entry 2): According to GP 1, the reaction mixture consisting of *rac*-**16** (99.7 mg, 0.400 mmol, 1.00 equiv), (^{Si}*S*)-**4a** (49.1 mg, 0.240 mmol, 0.600 equiv, 99% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 14 h at 20°C, after which a conversion of 54% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 14:1→1:1) furnished analytically pure silyl ether (^{Si}*R*,*R*)-**20a** (90 mg, 50%, d.r. = 85:15) and alcohol (*S*)-**16** (42 mg, 42%, 75% *ee*).

Analytical data for (^{Si}*R*,*R*)-**20a**: R_f = 0.30 (cyclohexane/*tert*-butyl methyl ether 5:1); $[\alpha]^{20}_{D}$ = +91.2 (*c* = 1.06, $CHCl_3$), $[\alpha]^{20}_{578}$ = +95.4, $[\alpha]^{20}_{546}$ = +110, $[\alpha]^{20}_{436}$ = +206; $[\alpha]^{20}_{365}$ = +371; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.31 (dddd, *J* = 15.1 Hz, *J* = 6.2 Hz, *J* = 4.0 Hz, *J* = 1.5 Hz, 1H), 0.54 (ddd, *J* = 15.0 Hz, *J*

= 12.1 Hz, *J* = 5.1 Hz, 1H), 0.86 (s, 9H), 1.19 (ddddd, *J* = 13.3 Hz, *J* = 12.0 Hz, *J* = 10.9 Hz, *J* = 3.9 Hz, *J* = 2.8 Hz, 1H), 1.83 (ddddd, *J* = 13.2 Hz, *J* = *J* = 6.3 Hz, *J* = 5.2 Hz, *J* = 2.8 Hz, 1H), 2.36 (ddd, *J* = 15.7 Hz, *J* = 10.9 Hz, *J* = 2.8 Hz, 1H), 2.48 (dd, *J* = 15.6 Hz, *J* = 5.8 Hz, 1H), 3.06 (dd, *J* = 13.1 Hz, *J* = 3.7 Hz, 1H), 3.19 (dd, *J* = 13.1 Hz, *J* = 9.3 Hz, 1H), 5.13 (dd, *J* = 9.3 Hz, *J* = 3.7 Hz, 1H), 6.75 (dd, *J* = 7.3 Hz, *J* = 1.5 Hz, 1H), 6.94–7.02 (m, 2H), 7.14 (ddd, *J* = 7.5 Hz, *J* = 4.8 Hz, *J* = 1.2 Hz, 1H), 7.18 (ddd, *J* = 7.8 Hz, *J* = *J* = 1.1 Hz, 1H), 7.21 (ddd, *J* = *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.43–7.47 (m, 2H), 7.55 (ddd, *J* = *J* = 7.6 Hz, *J* = 1.9 Hz, 1H), 7.55 (dd, *J* = 8.5 Hz, *J* = 1.8 Hz, 1H), 7.65–7.67 (m, 1H), 7.73–7.77 (m, 1H), 7.80–7.84 (m, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 8.51 (ddd, *J* = 4.9 Hz, *J* = 1.8 Hz, *J* = 0.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7, 18.7, 22.6, 26.1, 35.5, 50.2, 75.7, 121.4, 124.5, 124.8, 125.0, 125.2, 125.7, 126.0, 127.8, 128.1, 128.3, 129.3, 130.5, 133.0, 133.3, 135.0, 135.9, 142.7, 149.4, 150.6, 159.1 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3057 (w), 2926 (s), 1590 (s), 1473 (s), 1436 (s), 1071 (s) cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{30}H_{33}NOSi$ [M^+]: 451.2331, found: 451.2323; elemental analysis calcd (%) for $C_{30}H_{33}NOSi$ (451.7): C 79.77, H 7.36, N 3.10; found: C 79.43, H 7.54, N 2.83.



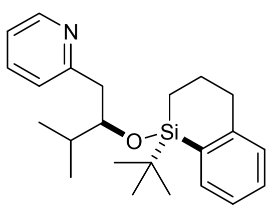
(^{Si}*R*,*R*)-**21a**

$C_{22}H_{29}NOSi$
351.56 g/mol

(^{Si}*R*,*R*)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-but-3-enyl]pyridine [(^{Si}*R*,*R*)-21a] (Table 4, Entry 3):[S36] According to GP 1, the reaction mixture consisting of *rac*-**17** (59.7 mg, 0.400 mmol, 1.00 equiv), (^{Si}*S*)-**4a** (49.1 mg, 0.240 mmol, 0.600 equiv, 94% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 40 h at 20°C, after which a conversion of 50% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→ CH_2Cl_2/MeOH 97:3) furnished analytically pure silyl ether (^{Si}*R*,*R*)-**21a** (67 mg, 48%, d.r. = 88:12) and alcohol (*S*)-**17** (30 mg, 50%, 69% *ee*).

Analytical data for (^{Si}*R*,*R*)-**21a**: R_f = 0.27 (cyclohexane/*tert*-butyl methyl ether 4:1); $[\alpha]^{20}_{D}$ = +1.05 (*c* = 0.190, $CHCl_3$), $[\alpha]^{20}_{578}$ = +1.58, $[\alpha]^{20}_{546}$ = +2.11, $[\alpha]^{20}_{436}$ = +11.6; $[\alpha]^{20}_{365}$ = +37.4; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (ddd, *J* = 14.8 Hz, *J* = 12.0 Hz, *J* = 5.3 Hz, 1H), 0.85 (s, 9H), 0.96 (dddd, *J* = 15.1 Hz, *J* = 6.0 Hz, *J* = 4.0 Hz, *J* = 1.6 Hz, 1H), 1.61 (m_c. 1H), 1.96 (m_c, 1H), 2.51 (ddd, *J* = 15.7 Hz, *J* = 11.0 Hz, *J* = 2.5 Hz, 1H), 2.68 (br dd, *J* = 14.8 Hz, *J* = 6.0 Hz, 1H), 2.89–2.96 (m, 2H), 4.47 (m_c, 1H), 5.00 (ddd, *J* = 10.7 Hz, *J* = *J* = 1.6 Hz, 1H), 5.08 (ddd, *J* = 17.3 Hz, *J* = *J* = 1.6 Hz, 1H), 5.90 (ddd, *J* = 17.0 Hz, *J* = 10.4 Hz, *J* = 6.3 Hz, 1H), 6.92 (dd, *J* = 7.2 Hz, *J* = 1.6 Hz, 1H), 6.99 (br dd, *J* = *J* = 7.2 Hz, 1H), 7.04 (br d, *J* = 7.8 Hz, 1H), 7.11 (ddd, *J* = 7.6 Hz, *J* = 5.0 Hz, *J* = 0.9 Hz, 1H), 7.15 (br d, *J* = 7.8 Hz, 1H), 7.21 (ddd, *J* = *J* = 7.5 Hz, *J* = 1.6 Hz, 1H), 7.54 (ddd, *J* = *J* = 7.9 Hz, *J* = 1.9 Hz, 1H), 8.47 (ddd, *J* = 4.7 Hz, *J* = 1.9 Hz, *J* = 0.9 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.0, 18.7, 22.8, 26.1, 35.6, 47.4, 74.3, 114.4, 121.3, 124.9, 125.0, 128.4, 129.2, 131.0, 134.9, 135.9, 141.2, 149.2, 150.4, 158.9 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3058 (m), 3003 (m), 2930 (s), 2891 (s), 2858 (s), 1643 (w), 1592 (s), 1570 (m), 1474 (s), 1463 (m), 1436 (m), 1389 (w), 1362 (w), 1345 (w), 1294 (w), 1269 (w), 1233 (w), 1196 (w), 1143 (s), 1128 (s), 1115 (s), 1075 (s), 1030 (s), 975 (s), 929 (m), 825 (s), 801 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 352 [$(M+H)^+$]; elemental analysis calcd (%) for $C_{22}H_{29}NOSi$ (351.6): C 75.16, H 8.31, N 3.98; found: C 74.88, H 8.36, N 3.68.

NMR spectroscopic data for ($^{\text{Si}}$*R*,*S*)-**21a** (minor diastereomer): ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.49 (dddd, *J* = 15.1 Hz, *J* = 6.0 Hz, *J* = 4.0 Hz, *J* = 1.6 Hz, 1H), 0.65 (ddd, *J* = 15.1 Hz, *J* = 12.0 Hz, *J* = 5.0 Hz, 1H), 0.84 (s, 9H), 1.75 (m$_c$. 1H), 2.09 (m$_c$, 1H), 2.66 (ddd, *J* = 15.5 Hz, *J* = 11.0 Hz, *J* = 2.8 Hz, 1H), 2.78 (br dd, *J* = 14.8 Hz, *J* = 6.0 Hz, 1H), 2.89–2.96 (m, 2H), 4.59 (m$_c$, 1H), 4.91 (ddd, *J* = 10.7 Hz, *J* = *J* = 1.6 Hz, 1H), 5.06 (ddd, *J* = 17.0 Hz, *J* = *J* = 1.6 Hz, 1H), 5.78 (ddd, *J* = 17.0 Hz, *J* = 10.4 Hz, *J* = 6.0 Hz, 1H), 7.04 (br d, *J* = 7.8 Hz, 1H), 7.10–7.18 (m, 1H), 7.16 (br d, *J* = 7.8 Hz, 1H), 7.23 (ddd, *J* = *J* = 7.2 Hz, *J* = 1.6 Hz, 1H), 7.29 (ddd, *J* = *J* = 7.5 Hz, *J* = 1.6 Hz, 1H), 7.57 (ddd, *J* = *J* = 7.6 Hz, *J* = 1.9 Hz, 1H), 7.63 (dd, *J* = 7.5 Hz, *J* = 1.3 Hz, 1H), 8.52 (ddd, *J* = 4.7 Hz, *J* = 1.9 Hz, *J* = 0.9 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ = 9.4, 18.7, 22.7, 26.1, 35.7, 47.3, 74.3, 114.3, 121.4, 124.8, 125.4, 128.3, 129.3, 131.6, 134.6, 136.0, 140.8, 149.2, 150.2, 158.9 ppm.



($^{\text{Si}}$*R*,*R*)-**22a**

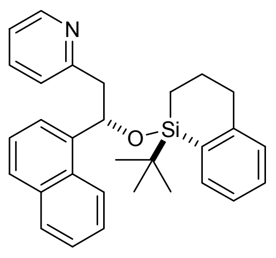
$C_{23}H_{33}NOSi$

367.60 g/mol

($^{\text{Si}}$*R*,*R*)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-3-methylpropyl]pyridine [($^{\text{Si}}$*R*,*R*)-22a] (Table 4, Entry 4): According to GP 1, the reaction mixture consisting of *rac*-**18** (66.1 mg, 0.400 mmol, 1.00 equiv), ($^{\text{Si}}$*S*)-**4a** (49.1 mg, 0.240 mmol, 0.600 equiv, 93% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 48 h at 60°C, after which a conversion of 51% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→1:1) furnished analytically pure silyl ether ($^{\text{Si}}$*R*,*R*)-**22a** (69 mg, 47%, d.r. = 80:20) and alcohol (*S*)-**18** (25 mg, 38%, 47% *ee*).

Analytical data for ($^{\text{Si}}$*R*,*R*)-**22a**: R$_f$ = 0.49 (cyclohexane/*tert*-butyl methyl ether 4:1); $[\alpha]^{20}_{D}$ = +33.9 (*c* = 0.330, CHCl$_3$), $[\alpha]^{20}_{578}$ = +35.2, $[\alpha]^{20}_{546}$ = +41.5, $[\alpha]^{20}_{436}$ = +84.5; $[\alpha]^{20}_{365}$ = +176; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.80–1.03 (m, 2H), 0.87 (s, 9H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H), 1.60 (m$_c$, 1H), 1.75 (qqd, *J* = *J* = 6.9 Hz, *J* = 3.2 Hz, 1H), 2.02 (m$_c$, 1H), 2.52 (ddd, *J* = 15.7 Hz, *J* = 11.0 Hz, *J* = 2.8 Hz, 1H), 2.68 (br dd, *J* = 15.7 Hz, *J* = 6.0 Hz, 1H), 2.75 (dd, *J* = 13.3 Hz, *J* = 7.8 Hz, 1H), 2.80 (dd, *J* = 13.5 Hz, *J* = 5.2 Hz, 1H), 4.07 (ddd, *J* = 7.8 Hz, *J* = 5.2 Hz, *J* = 3.4 Hz, 1H), 6.95–7.25 (m, 6H), 7.40 (ddd, *J* = *J* = 7.7 Hz, *J* = 1.9 Hz, 1H), 8.43 (ddd, *J* = 4.9 Hz, *J* = 1.9 Hz, *J* = 1.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 9.9, 17.5, 18.9, 23.1, 26.2, 33.2, 35.7, 41.6, 77.5, 121.0, 124.6, 124.9, 128.3, 129.1, 132.0, 135.2, 135.8, 149.2, 149.9, 160.2 ppm; IR (cuvette/CDCl$_3$): $\tilde{\nu}$ = 3057 (m), 2960 (s), 2930 (s), 2858 (s), 1590 (s), 1570 (m), 1474 (s), 1435 (s), 1394 (m), 1362 (m), 1294 (w), 1270 (w), 1257 (w), 1214 (w), 1181 (w), 1143 (m), 1129 (m), 1076 (s), 1054 (s), 1030 (m), 1007 (m), 976 (w), 884 (w), 877 (w), 824 (s), 722 (s), 710 (s), 698 (m) cm^{-1}; LRMS (CI/NH$_3$): *m/z*: 368 [(M+H)$^+$]; elemental analysis calcd (%) for $C_{23}H_{33}NOSi$ (367.6): C 75.15, H 9.05, N 3.81; found: C 75.00, H 9.13, N 3.39.

NMR spectroscopic data for ($^{\text{Si}}$*R*,*S*)-**22a** (minor diastereomer): ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.40 (dddd, *J* = 15.3 Hz, *J* = 6.4 Hz, *J* = 3.9 Hz, *J* = 1.8 Hz, 1H), 0.56 (ddd, *J* = 15.0 Hz, *J* = 11.9 Hz, *J* = 4.9 Hz, 1H), 0.81 (s, 9H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 1.51–1.64 (m, 1H), 1.66–1.79 (m, 1H), 1.91 (m$_c$, 1H), 2.45–2.55 (m, 1H), 2.65–2.73 (m, 1H), 2.80 (dd, *J* = 13.1 Hz, *J* = 8.6 Hz, 1H), 2.87 (dd, *J* = 13.0 Hz, *J* = 4.3 Hz, 1H), 4.07 (ddd, *J* = 8.5 Hz, *J* = 4.3 Hz, *J* = 3.4 Hz, 1H), 6.95–7.25 (m, 5H), 7.55 (ddd, *J* = *J* = 7.7 Hz, *J* = 1.8 Hz, 1H), 7.60 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 8.53 (ddd, *J* = 4.9 Hz, *J* = 1.9 Hz, *J* = 0.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 9.3, 16.8, 18.8, 23.3, 26.1, 33.0, 35.8, 41.0, 77.4, 121.1, 124.8, 124.9, 128.5, 129.2, 131.9, 135.3, 135.9, 149.3, 150.2, 160.5 ppm.

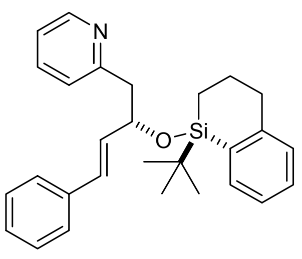


(^{Si}S,S)-**29a**
$C_{30}H_{33}NOSi$
451.67 g/mol

(^{Si}S,S)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-2-(naphth-1-yl)-ethyl]-pyridine [(^{Si}S,S)-29a] (Table 5, Entry 1):[S36] According to GP 1, the reaction mixture consisting of *rac*-**24** (99.7 mg, 0.400 mmol, 1.00 equiv), (^{Si}R)-**4a** (49.1 mg, 0.240 mmol, 0.600 equiv, 93% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 48 h at 20°C, after which a conversion of 57% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→1:1) furnished analytically pure silyl ether (^{Si}S,S)-**29a** (102 mg, 57%, d.r. = 84:16) and alcohol (R)-**24** (43 mg, 43%, 80% *ee*).

Analytical data for (^{Si}S,S)-**29a**: R_f = 0.48 (cyclohexane/*t*-butyl methyl ether 4:1); $[\alpha]^{20}_D = -50.6$ (c = 0.681, $CHCl_3$), $[\alpha]^{20}_{578} = -52.9$, $[\alpha]^{20}_{546} = -60.7$, $[\alpha]^{20}_{436} = -114$; $[\alpha]^{20}_{365} = -218$; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.21 (br d, J = 14.7 Hz, 1H), 0.49 (ddd, J = 15.2 Hz, J = 12.0 Hz, J = 4.8 Hz, 1H), 0.86 (s, 9H), 1.07 (m_c, 1H), 1.56 (m_c, 1H), 2.33 (ddd, J = 16.2 Hz, J = 10.5 Hz, J = 2.9 Hz, 1H), 2.44 (br dd, J = 15.3 Hz, J = 5.3 Hz, 1H), 3.20–3.39 (m, 2H), 5.69 (m_c, 1H), 6.72 (br d, J = 7.5 Hz, 1H), 6.96 (dd, $J = J$ = 7.4 Hz, 1H), 6.99 (d, J = 7.3 Hz, 1H), 7.18 (dd, J = 7.4 Hz, J = 5.0 Hz, 1H), 7.21 (ddd, $J = J$ = 7.4 Hz, J = 1.4 Hz, 1H), 7.22 (dd, J = 7.6 Hz, J = 1.3 Hz, 1H), 7.42–7.52 (m, 3H), 7.61 (ddd, $J = J$ = 7.6 Hz, J = 1.5 Hz, 1H), 7.62–7.70 (m, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.84–7.88 (m, 1H), 8.34 (m_c, 1H), 8.55 (ddd, J = 4.8 Hz, J = 1.8 Hz, J = 0.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.6, 18.7, 22.6, 26.2, 35.4, 48.7, 73.7, 121.6, 124.2, 125.0, 125.3, 125.5, 126.0, 127.9, 128.3, 128.8, 129.3, 130.3, 130.4, 133.9, 134.9, 136.5, 140.6, 148.8, 150.6, 159.1 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3057 (m), 2930 (s), 2858 (s), 1597 (s), 1570 (w), 1510 (w), 1473 (m), 1437 (m), 1389 (w), 1362 (w), 1293 (w), 1269 (w), 1230 (w), 1201 (w), 1143 (m), 1128 (m), 1076 (s), 999 (m), 976 (w), 825 (m), 803 (m) cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{30}H_{33}NOSi$ [$(M+H)^+$]: 452.2404, found: 452.2403; elemental analysis calcd (%) for $C_{30}H_{33}NOSi$ (451.7): C 79.77, H 7.36, N 3.10; found: C 79.66, H 7.65, N 2.68.

NMR spectroscopic data for (^{Si}S,R)-**29a** (minor diastereomer): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.21 (m, 1H), 0.56 (ddd, J = 15.2 Hz, J = 12.0 Hz, J = 5.2 Hz, 1H), 0.81 (s, 9H), 1.01–1.13 (m_c, 1H), 1.71–1.82 (m, 1H), 2.40–2.48 (m, 1H), 2.55 (br dd, J = 15.6 Hz, J = 5.9 Hz, 1H), 3.20–3.39 (m, 2H), 5.82 (m_c, 1H), 6.66 (dd, $J = J$ = 7.5 Hz, 1H), 6.90–7.06 (m, 2H), 7.12–7.35 (m, 3H), 7.42–7.51 (m, 3H), 7.58–7.72 (m, 2H), 7.80–7.89 (m, 2H), 8.34 (m_c, 1H), 8.61 (ddd, J = 4.9 Hz, J = 1.6 Hz, J = 0.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.3, 18.8, 23.1, 26.1, 35.6, 48.7, 73.9, 121.7, 124.1, 124.4, 125.2, 125.4, 125.5, 125.8, 127.7, 128.1, 128.7, 129.0, 130.3, 130.4, 133.7, 135.3, 136.5, 140.6, 148.8, 150.0, 159.1 ppm.



(^{Si}S,S)-**30a**

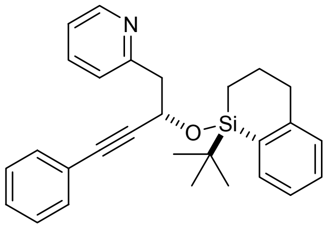
$C_{28}H_{33}NOSi$

427.65 g/mol

(^{Si}S,S,E)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-4-phenylbut-3-enyl]-pyridine [(^{Si}S,S)-30a] (Table 5, Entry 2):[S36] According to GP 1, the reaction mixture consisting of *rac*-**25** (90.1 mg, 0.400 mmol, 1.00 equiv), (^{Si}R)-**4a** (49.1 mg, 0.240 mmol, 0.600 equiv, 93% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 24 h at 20°C, after which a conversion of 57% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→2:3) furnished analytically pure silyl ether (^{Si}S,S)-**30a** (97 mg, 56%, d.r. = 87:13) and alcohol (R)-**25** (38 mg, 43%, 74% *ee*).

Analytical data for (^{Si}S,S)-**30a**: R_f = 0.48 (cyclohexane/*tert*-butyl methyl ether 4:1); $[\alpha]^{20}_{D}$ = –67.5 (*c* = 0.440, $CHCl_3$), $[\alpha]^{20}_{578}$ = –71.4, $[\alpha]^{20}_{546}$ = –82.5, $[\alpha]^{20}_{436}$ = –163; $[\alpha]^{20}_{365}$ = –326; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84 (ddd, *J* = 15.1 Hz, *J* = 11.5 Hz, *J* = 5.1 Hz, 1H), 0.87 (s, 9H), 0.93 (dddd, *J* = 15.3 Hz, *J* = 6.3 Hz, *J* = 4.0 Hz, *J* = 1.2 Hz, 1H), 1.69 (m_c. 1H), 1.88 (m_c, 1H), 2.49 (ddd, *J* = 15.7 Hz, *J* = 11.0 Hz, *J* = 2.5 Hz, 1H), 2.62 (br dd, *J* = 15.1 Hz, *J* = 6.3 Hz, 1H), 2.96 (dd, *J* = 13.2 Hz, *J* = 4.7 Hz, 1H), 3.03 (dd, *J* = 13.2 Hz, *J* = 7.8 Hz, 1H), 4.65 (m_c, 1H), 6.25 (dd, *J* = 15.8 Hz, *J* = 6.9 Hz, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 6.94 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.01–7.05 (m, 2H), 7.08–7.14 (m, 2H), 7.18–7.25 (m, 3H), 7.28–7.30 (m, 3H), 7.56 (ddd, *J* = *J* = 7.7 Hz, *J* = 1.8 Hz, 1H), 8.50 (ddd, *J* = 4.8 Hz, *J* = 1.8 Hz, *J* = 0.9 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.3, 18.7, 22.7, 26.1, 35.6, 47.6, 74.2, 121.3, 125.0, 126.5, 127.5, 128.4, 128.6, 129.3, 129.9, 130.9, 132.8, 135.0, 135.9, 137.0, 149.3, 150.5, 158.9 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3060 (m), 3028 (m), 3002 (m), 2930 (s), 2858 (s), 1592 (s), 1570 (m), 1494 (m), 1474 (s), 1463 (m), 1437 (m), 1404 (w), 1362 (m), 1294 (w), 1270 (w), 1201 (w), 1143 (s), 1108 (s), 1075 (s), 1005 (m), 968 (s), 938 (s), 825 (s), 799 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 428 [$(M+H)^+$]; elemental analysis calcd (%) for $C_{28}H_{33}NOSi$ (427.7): C 78.64, H 7.78, N 3.28; found: C 78.65, H 8.05, N 2.98.

NMR spectroscopic data for (^{Si}S,R)-**30a** (minor diastereomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.53 (dddd, *J* = 15.0 Hz, *J* = 6.3 Hz, *J* = 4.1 Hz, *J* = 1.3 Hz, 1H), 0.68 (ddd, *J* = 15.0 Hz, *J* = 11.9 Hz, *J* = 5.1 Hz, 1H), 0.85 (s, 9H), 1.75 (m_c. 1H), 2.09 (m_c, 1H), 2.59–2.69 (m, 1H), 2.79 (br dd, *J* = 15.9 Hz, *J* = 6.0 Hz, 1H), 2.96–3.07 (m, 2H), 4.75 (m_c, 1H), 6.08 (dd, *J* = 15.9 Hz, *J* = 6.7 Hz, 1H), 6.32 (d, *J* = 15.9 Hz, 1H), 7.01–7.05 (m, 1H), 7.08–7.14 (m, 2H), 7.18–7.25 (m, 3H), 7.28–7.30 (m, 3H), 7.54–7.60 (m, 1H), 7.58 (ddd, *J* = *J* = 7.7 Hz, *J* = 2.0 Hz, 1H), 7.64 (dd, *J* = 7.3 Hz, *J* = 1.4 Hz, 1H), 8.55 (ddd, *J* = 4.9 Hz, *J* = 1.8 Hz, *J* = 0.9 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.2, 18.6, 23.0, 26.1, 35.7, 47.6, 74.3, 121.4, 124.9, 125.1, 126.5, 127.3, 128.4, 128.5, 129.3, 129.8, 131.9, 132.7, 135.6, 136.0, 137.1, 149.3, 150.2, 159.0 ppm.



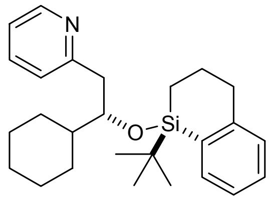
(^{Si}S,S)-**31a**
$C_{28}H_{31}NOSi$
425.64 g/mol

(^{Si}*S*,*S*)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-4-phenylbut-3-inyl]-pyridine [(^{Si}*S*,*S*)-31a] (Table 5, Entry 3):[S36] According to GP 1, the reaction mixture consisting of *rac*-**26** (89.3 mg, 0.400 mmol, 1.00 equiv), (^{Si}R)-**4a** (53.1 mg, 0.260 mmol, 0.650 equiv, 93% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 48 h at 20°C, after which a conversion of 63% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→1:1) furnished analytically pure silyl ether (^{Si}S,S)-**31a** (87 mg, 51%, d.r. = 74:26) and alcohol (R)-**26** (38 mg, 31%, 89% *ee*). Silyl ether (^{Si}S,S)-**31a** was contaminated with 7% of the silyl ether of *Z*-alkene [≡(^{Si}S,S,Z)-**30a**, Z:E = 93:7, d.r. (Z) = 90:10]; (R)-**26** contained 21% of *Z*-alkene [≡(R,Z)-**25**, 57% *ee*] as revealed by ^{1}H NMR spectroscopy.

Analytical data for (^{Si}S,S)-**31a**: R_f = 0.50 (cyclohexane/*tert*-butyl methyl ether 4:1); $[\alpha]^{20}_{D}$ = –82.3 (c = 1.00, $CHCl_3$), $[\alpha]^{20}_{578}$ = –87.2, $[\alpha]^{20}_{546}$ = –99.2, $[\alpha]^{20}_{436}$ = –188; $[\alpha]^{20}_{365}$ = –338; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (s, 9H), 0.91 (ddd, J = 14.9 Hz, J = 11.9 Hz, J = 5.0 Hz, 1H), 1.32 (dddd, J = 14.9 Hz, J = 5.3 Hz, J = 4.1 Hz, J = 1.6 Hz, 1H), 1.83 (m_c. 1H), 2.04 (m_c, 1H), 2.54 (ddd, J = 15.8 Hz, J = 11.0 Hz, J = 2.8 Hz, 1H), 2.73 (dddd, J = 15.7 Hz, J = 6.0 Hz, J = J = 1.9 Hz, 1H), 3.19–3.30 (m, 2H), 4.91 (dd, J = 8.2 Hz, J = 5.0 Hz, 1H), 6.98 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.03–7.33 (m, 10H), 7.60 (ddd, J = J = 7.8 Hz, J = 1.8 Hz, 1H), 8.53 (ddd, J = 4.9 Hz, J = 1.9 Hz, J = 0.9 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.6, 18.7, 22.6, 26.2, 35.5, 49.0, 72.9, 83.5, 86.1, 121.4, 124.2, 125.0, 125.5, 126.0, 127.9, 128.3, 128.8, 129.3, 130.4, 135.0, 136.0, 149.3, 150.6, 159.3 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3058 (m), 3003 (m), 2930 (s), 2891 (s), 2858 (s), 1592 (s), 1570 (m), 1490 (m), 1474 (s), 1463 (m), 1437 (s), 1404 (w), 1390 (w), 1361 (m), 1346 (m), 1294 (w), 1270 (w), 1256 (w), 1187 (w), 1144 (m), 1128 (m), 1075 (s), 1033 (m), 1000 (m), 976 (m), 936 (s), 928 (m), 898 (w), 887 (w), 825 (s), 809 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 426 [$(M+H)^+$]; HRMS (EI): *m/z*: calcd for $C_{28}H_{31}NOSi$ [M^+]: 425.2175, found: 425.2158.

NMR spectroscopic data for (^{Si}S,R)-**30a** (minor diastereomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.70–0.76 (m, 1H), 0.86 (s, 9H), 1.29–1.42 (m, 1H), 1.68 (m_c. 1H), 1.97 (m_c, 1H), 2.38–2.81 (m, 2H), 3.19–3.30 (m, 2H), 5.05 (dd, J = 8.2 Hz, J = 5.7 Hz, 1H), 6.93–7.00 (m, 1H), 7.03–7.33 (m, 10H), 7.57–7.63 (m, 1H), 8.52–8.55 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.3, 18.8, 23.1, 26.1, 35.6, 49.6, 72.9, 83.5, 86.1, 121.6, 124.5, 125.2, 125.3, 125.8, 127.6, 128.1, 128.7, 129.0, 130.3, 135.4, 136.0, 149.3, 150.6, 159.3 ppm.

Analytical data for for silyl ethers of *Z*-alkene: Selected NMR spectroscopic signals for (^{Si}S,S,Z)-**30a** (major diastereomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.00–3.12 (m, 2H), 5.00–5.07 (m, 1H), 5.71 (dd, J = 12.0 Hz, J = 8.8 Hz, 1H), 6.35 (d, J = 12.0 Hz, 1H), 8.49 (ddd, J = 5.0 Hz, J = 1.9 Hz, J = 1.0 Hz, 1H) ppm. Selected NMR spectroscopic signals for (^{Si}S,R,Z)-**30a** (minor diastereomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.00–3.12 (m, 2H), 5.00–5.07 (m, 1H), 5.61 (dd, J = 11.0 Hz, J = 9.5 Hz, 1H), 6.19 (d, J = 11.7 Hz, 1H) ppm. Selected NMR spectroscopic signals for (^{Si}S,S,E)-**30a** (major diastereomer of minor *E*-alkene component): (^{Si}*S*,*S*,*E*)-**30a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.24 (dd, *J* = 16.1 Hz, *J* = 6.6 Hz, 1H), 6.34 (d, *J* = 16.7 Hz, 1H) ppm. LRMS (CI/NH_3): *m/z*: 428 [$(M+H)^+$].



(^{Si}*S*,*S*)-**32a**

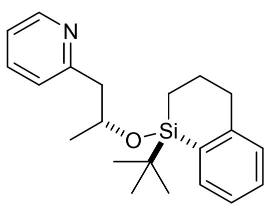
$C_{26}H_{37}NOSi$

407.66 g/mol

(^{Si}*S*,*S*)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-2-(cyclohexyl)ethyl]-pyridine [(^{Si}*S*,*S*)-32a] (Table 5, Entry 4): According to GP 1, the reaction mixture consisting of *rac*-**27** (82.1 mg, 0.400 mmol, 1.00 equiv), (^{Si}*R*)-**4a** (53.1 mg, 0.260 mmol, 0.650 equiv, 93% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 48 h at 60°C, after which a conversion of 56% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→1:1) furnished analytically pure silyl ether (^{Si}*S*,*S*)-**32a** (90 mg, 55%, d.r. = 73:27) and alcohol (*R*)-**27** (35 mg, 43%, 42% *ee*).

Analytical data for (^{Si}*S*,*S*)-**32a**: R_f = 0.51 (cyclohexane/*tert*-butyl methyl ether 4:1); $[\alpha]^{20}_{D}$ = −10.4 (*c* = 0.240, $CHCl_3$), $[\alpha]^{20}_{578}$ = −11.7, $[\alpha]^{20}_{546}$ = −13.3, $[\alpha]^{20}_{436}$ = −25.8; $[\alpha]^{20}_{365}$ = −54.6; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80–0.90 (m, 1H), 0.86 (s, 9H), 0.94–1.08 (m, 4H), 1.13–1.24 (m, 2H), 1.27–1.41 (m, 1H), 1.52–1.84 (m, 6H), 2.02 (m_c, 1H), 2.53 (ddd, *J* = 15.7 Hz, *J* = 10.9 Hz, *J* = 2.8 Hz, 1H), 2.69 (br dd, *J* = 16.0 Hz, *J* = 5.7 Hz, 1H), 2.78 (dd, *J* = 13.4 Hz, *J* = 7.8 Hz, 1H), 2.82 (dd, *J* = 13.4 Hz, *J* = 5.0 Hz, 1H), 4.04 (ddd, *J* = 7.8 Hz, *J* = 5.0 Hz, *J* = 3.4 Hz, 1H), 6.95–7.25 (m, 6H), 7.40 (ddd, *J* = *J* = 7.6 Hz, *J* = 1.9 Hz, 1H), 8.43 (ddd, *J* = 4.9 Hz, *J* = 2.0 Hz, *J* = 0.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.9, 18.9, 23.1, 26.1, 26.2, 26.6, 26.7, 28.1, 28.2, 35.8, 42.8, 43.8, 77.3, 121.0, 124.6, 124.9, 128.3, 129.1, 132.0, 135.2, 135.8, 149.1, 149.9, 160.2 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3058 (w), 3003 (w), 2930 (s), 2856 (s), 1593 (m), 1570 (w), 1474 (m), 1463 (m), 1450 (m), 1435 (m), 1361 (w), 1294 (w), 1269 (w), 1198 (w), 1142 (m), 1128 (w), 1086 (s), 1064 (m), 1006 (w), 938 (s), 910 (s), 874 (m), 825 (m), 728 (m), 713 (w), 705 (w) cm^{-1}; LRMS (CI/NH_3): *m/z*: 408 [$(M+H)^+$]; HRMS (EI): *m/z*: calcd for $C_{26}H_{37}NOSi$ [$(M-C_4H_9)^+$]: 350.1940, found: 350.1940; elemental analysis calcd (%) for $C_{26}H_{37}NOSi$ (407.7): C 76.60, H 9.15, N 3.44; found: C 76.28, H 9.15, N 3.02.

NMR spectroscopic data for (^{Si}*S*,*R*)-**32a** (minor diastereomer): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.44 (dddd, *J* = 15.4 Hz, *J* = 6.6 Hz, *J* = 4.2 Hz, *J* = 1.4 Hz, 1H), 0.57 (ddd, *J* = 15.2 Hz, *J* = 11.9 Hz, *J* = 5.2 Hz, 1H), 0.81 (s, 9H), 0.94–1.08 (m, 3H), 1.13–1.24 (m, 2H), 1.27–1.41 (m, 1H), 1.52–1.84 (m, 6H), 1.92 (m_c, 1H), 2.47–2.70 (m, 2H), 2.72–2.91 (m, 2H), 4.01–4.06 (m, 1H), 6.95–7.25 (m, 5H), 7.54 (ddd, *J* = *J* = 7.7 Hz, *J* = 1.9 Hz, 1H), 7.60 (dd, *J* = 7.7 Hz, *J* = 1.5 Hz, 1H), 8.53 (ddd, *J* = 4.9 Hz, *J* = 2.0 Hz, *J* = 0.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.3, 18.8, 23.3, 26.1, 26.2, 26.5, 26.9, 27.4, 28.8, 35.8, 41.9, 43.7, 77.2, 121.1, 124.8, 125.4, 128.5, 129.2, 132.5, 135.4, 135.9, 149.3, 150.2, 160.6 ppm.



(^{Si}*S*,*R*)-**33a**

$C_{21}H_{29}NOSi$

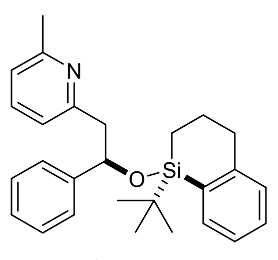
339.55 g/mol

(^{Si}*S*,*R*)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)propyl]pyridine [(^{Si}*S*,*R*)-33a] (Table 5, Entry 5):[S36] According to GP 1, the reaction mixture consisting of *rac*-**28** (54.9 mg, 0.400 mmol, 1.00 equiv), (^{Si}*R*)-**4a** (49.1 mg, 0.240 mmol, 0.600 equiv, 93% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 48 h at 20°C, after which a conversion of 58% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→ CH_2Cl_2/MeOH 97:3) furnished analytically pure silyl ether (^{Si}*S*,*R*)-**33a** (77 mg, 57%, d.r. = 76:24) and alcohol (*S*)-**28** (23 mg, 42%, 73% *ee*).

Analytical data for (^{Si}*S*,*R*)-**33a**: R_f = 0.29 (cyclohexane/*tert*-butyl methyl ether 4:1); $[\alpha]^{20}_{D} = -4.12$ (*c* = 0.850, $CHCl_3$), $[\alpha]^{20}_{578} = -4.35$, $[\alpha]^{20}_{546} = -5.41$, $[\alpha]^{20}_{436} = -13.2$; $[\alpha]^{20}_{365} = -33.6$; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84 (s, 9H), 0.89 (ddd, *J* = 15.1 Hz, *J* = 12.0 Hz, *J* = 5.2 Hz, 1H), 0.95 (dddd, *J* = 15.2 Hz, *J* = 5.8 Hz, *J* = 4.5 Hz, *J* = 1.6 Hz, 1H), 1.19 (d, *J* = 6.1 Hz, 3H), 1.64 (m_c, 1H), 2.04 (m_c, 1H), 2.54 (ddd, *J* = 15.7 Hz, *J* = 11.3 Hz, *J* = 2.8 Hz, 1H), 2.71 (br dd, *J* = 15.7 Hz, *J* = 6.0 Hz, 1H), 2.83–2.91 (m, 2H), 4.20–4.27 (m, 1H), 7.01–7.26 (m, 6H), 7.51 (ddd, *J* = *J* = 7.7 Hz, *J* = 1.8 Hz, 1H), 8.47 (br d, *J* = 4.3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.4, 18.6, 22.9, 24.0, 26.0, 35.7, 48.5, 69.4, 121.2, 124.8, 125.0, 128.4, 129.2, 131.3, 135.0, 136.0, 149.0, 150.2, 159.6 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3058 (m), 3002 (m), 2930 (s), 2858 (s), 1592 (s), 1570 (m), 1474 (s), 1463 (m), 1436 (s), 1405 (w), 1389 (w), 1376 (m), 1362 (m), 1294 (w), 1270 (w), 1200 (w), 1142 (s), 1128 (s), 1091 (s), 1076 (s), 1053 (s), 992 (s), 936 (m), 930 (m), 923 (m), 825 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 340 $[(M+H)^+]$; elemental analysis calcd (%) for $C_{21}H_{29}NOSi$ (339.6): C 74.28, H 8.61, N 4.13; found: C 74.17, H 8.66, N 3.85.

NMR spectroscopic data for (^{Si}*S*,*S*)-**33a** (minor diastereomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.47 (dddd, *J* = 15.1 Hz, *J* = 6.1 Hz, *J* = 4.0 Hz, *J* = 1.5 Hz, 1H), 0.62 (ddd, *J* = 15.1 Hz, *J* = 12.1 Hz, *J* = 5.1 Hz, 1H), 0.83 (s, 9H), 1.09 (d, *J* = 6.1 Hz, 3H), 1.60 (m_c, 1H), 1.95 (m_c, 1H), 2.48–2.57 (m, 1H), 2.68–2.74 (m, 1H), 2.83–2.91 (m, 2H), 4.20–4.27 (m, 1H), 7.01–7.26 (m, 5H), 7.57 (ddd, *J* = *J* = 7.6 Hz, *J* = 1.8 Hz, 1H), 7.60 (dd, *J* = 7.3 Hz, *J* = 1.5 Hz, 1H), 8.53 (br d, *J* = 4.2 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.2, 18.5, 23.3, 23.9, 26.0, 35.7, 48.7, 69.5, 121.3, 124.9, 125.4, 128.5, 129.3, 132.3, 135.6, 135.3, 149.1, 150.3, 159.7 ppm.

4.4 Variation of the Donor in the Kinetic Resolution with Silatetraline 4a (Table 6)



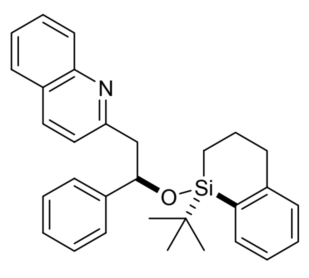
($^{Si}R,R$)-**41a**

$C_{27}H_{33}NOSi$

415.64 g/mol

(^{Si}*R*,*R*)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-2-phenylethyl]-6-methylpyridine [(^{Si}*R*,*R*)-41a] (Table 6, Entry 1): According to GP 1, the reaction mixture consisting of *rac*-**34** (85.3 mg, 0.400 mmol, 1.00 equiv), (^{Si}*S*)-**4a** (49.1 mg, 0.240 mmol, 0.600 equiv, 98% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 24 h at 20°C, after which a conversion of 60% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→1:1) furnished analytically pure silyl ether (^{Si}*R*,*R*)-**41a** (94 mg, 57%, d.r. = 77:23) and alcohol (*S*)-**34** (27 mg, 32%, 89% *ee*).

Analytical data for (^{Si}*R*,*R*)-**41a**: = 0.76 (cyclohexane/*tert*-butyl methyl ether 1:1); $[\alpha]^{20}_{D}$ = +69.3 (*c* = 0.720, $CHCl_3$), $[\alpha]^{20}_{578}$ = +73.4, $[\alpha]^{20}_{546}$ = +84.0, $[\alpha]^{20}_{436}$ = +153.7, $[\alpha]^{20}_{365}$ = +273.3; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.31 (ddd, *J* = 15.1 Hz, *J* = 6.3 Hz, *J* = 3.9 Hz, 1H), 0.56 (ddd, *J* = 15.1 Hz, *J* = 12.2 Hz, *J* = 5.1 Hz, 1H), 0.83 (s, 9H), 1.22 (m_c, 1H), 1.70 (m_c, 1H), 2.39 (ddd, *J* = 15.5 Hz, *J* = 11.3 Hz, *J* = 2.6 Hz, 1H), 2.54 (br dd, *J* = 15.5 Hz, *J* = 6.1 Hz, 1H), 2.51 (s, 3H), 2.99 (dd, *J* = 13.1 Hz, *J* = 3.4 Hz, 1H), 3.08 (dd, *J* = 13.1 Hz, *J* = 9.6 Hz, 1H), 4.95 (dd, *J* = 9.6 Hz, *J* = 3.4 Hz, 1H), 6.63 (d, *J* = 7.4 Hz, 1H), 6.93 (dd, *J* = *J* = 7.4 Hz, 1H), 7.00–7.05 (m, 3H), 7.21 (ddd, *J* = *J* = 7.5 Hz, *J* = 1.3 Hz, 1H), 7.22–7.32 (m, 3H), 7.34–7.38 (m, 2H), 7.49 (dd, *J* = *J* = 7.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.6, 18.5, 22.5, 24.4, 25.9, 35.4, 49.9, 75.3, 120.8, 122.2, 124.7, 126.1, 127.2, 128.0, 128.1, 129.0, 130.4, 134.9, 136.2, 145.3, 150.5, 157.5, 158.3 ppm; IR (film): $\tilde{\nu}$ = 2927 (s), 2856 (s), 1593 (w), 1458 (s), 1076 (s) cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{27}H_{34}NOSi$ [$(M+H)^+$]: 416.2404, found: 416.2400; elemental analysis calcd (%) for $C_{27}H_{33}NOSi$ (415.6): C 78.02, H 8.00, N 3.37; found: C 77.90, H 8.18, N 3.25.



($^{Si}R,R$)-**42a**

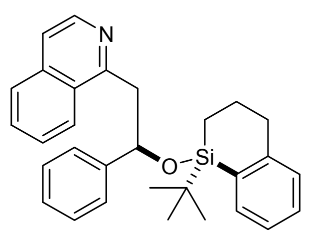
$C_{30}H_{33}NOSi$

451.67 g/mol

(^{Si}*R*,*R*)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-2-phenylethyl]quinoline [(^{Si}*R*,*R*)-42a] (Table 6, Entry 2): According to GP 1, the reaction mixture consisting of *rac*-**35** (99.7 mg, 0.400 mmol, 1.00 equiv), (^{Si}*S*)-**4a** (50.8 mg, 0.250 mmol, 0.625 equiv, 99% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 24 h at 20°C, after which a conversion of 57% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 95:5→2:1) furnished analytically pure silyl ether (^{Si}*R*,*R*)-**42a** (95 mg, 52%, d.r. = 81:19) and alcohol (*S*)-**35** (36 mg, 36%, 82% *ee*).

Analytical data for (^{Si}*R*,*R*)-**42a**: R_f = 0.51 (cyclohexane/*tert*-butyl methyl ether 5:1); $[\alpha]^{20}_{D}$ = +31.9 (*c* = 1.13, $CHCl_3$), $[\alpha]^{20}_{578}$ = +32.8, $[\alpha]^{20}_{546}$ = +37.8, $[\alpha]^{20}_{436}$ = +71.9; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.32 (dddd, *J* = 15.1 Hz, *J* = 6.1 Hz, *J* = 4.0 Hz, *J* = 1.5, 1H), 0.54 (ddd, *J* = 15.1 Hz, *J* = 12.1 Hz, *J* = 5.1 Hz, 1H), 0.80 (s, 9H), 1.22 (ddddd, *J* = 13.3 Hz, *J* = 12.1 Hz, *J* = 11.0 Hz, *J* = 3.9 Hz, *J* = 2.8 Hz, 1H), 1.67 (ddddd, *J* = 13.2 Hz, *J* = *J* = 6.2 Hz, *J* = 5.2 Hz, *J* = 2.8 Hz, 1H), 2.34 (ddd, *J* = 15.7 Hz, *J* = 11.0

Hz, *J* = 2.8 Hz, 1H), 2.48 (dd, *J* = 15.7 Hz, *J* = 5.9 Hz, 1H), 3.18 (dd, *J* = 13.1 Hz, *J* = 3.7 Hz, 1H), 3.30 (dd, *J* = 13.1 Hz, *J* = 9.5 Hz, 1H), 5.06 (dd, *J* = 9.5 Hz, *J* = 3.6 Hz, 1H), 6.33 (m$_c$, 1H), 6.39 (dd, *J* = 7.3 Hz, *J* = 1.6 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 7.03 (ddd, *J* = *J* = 7.4 Hz, *J* = 1.6 Hz, 1H), 7.23–7.27 (m, 1H), 7.28–7.33 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.36–7.40 (m, 2H), 7.52 (ddd, *J* = 8.1 Hz, *J* = 6.9 Hz, *J* = 1.2 Hz, 1H), 7.70 (ddd, *J* = 8.5 Hz, *J* = 6.9 Hz, *J* = 1.5 Hz, 1H), 7.82 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 1H), 7.99 (ddd, *J* = 8.5 Hz, *J* = 1.9 Hz, *J* = 0.8 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 9.7, 18.5, 22.6, 26.1, 35.5, 50.9, 75.8, 123.8, 124.6, 125.8, 126.2, 127.1, 127.4, 127.6, 128.1, 128.3, 129.1, 129.2, 130.3, 134.9, 135.6, 145.3, 148.2, 150.4, 159.9 ppm; IR (cuvette/CHCl$_3$): $\tilde{\nu}$ = 3060 (w), 2929 (s), 1600 (s), 1472 (s), 1431 (s), 1067 (s) cm^{-1}; LRMS (CI/NH$_3$): *m/z*: 452 [(M+H)$^+$]; elemental analysis calcd (%) for C$_{30}$H$_{33}$NOSi (451.7): C 79.77, H 7.36, N 3.10; found: C 79.51, H 7.43, N 2.91.



(^{Si}*R*,*R*)-**43a**

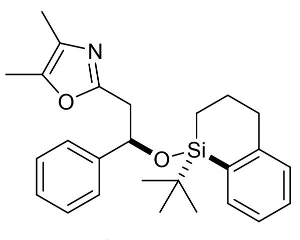
C$_{30}$H$_{33}$NOSi
451.67 g/mol

(^{Si}*R*,*R*)-1-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-2-phenylethyl]isoquinoline [(^{Si}*R*,*R*)-43a] (Table 6, Entry 3): According to GP 1, the reaction mixture consisting of *rac*-**36** (99.7 mg, 0.400 mmol, 1.00 equiv), (^{Si}*S*)-**4a** (45.0 mg, 0.220 mmol, 0.550 equiv, 97% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 48 h at 40°C, after which a conversion of 52% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 9:1→1:1) furnished analytically pure silyl ether (^{Si}*R*,*R*)-**43a** (83 mg, 46%, d.r. = 83:17) and alcohol (*S*)-**36** (47 mg, 47%, 54% *ee*).

Analogously, racemic (^{Si}*R**,*R**)-**43a** (148 mg, 82%) was obtained from *rac*-**36** (99.7 mg, 0.400 mmol, 1.00 equiv) and *rac*-**4a** (89.9 mg, 0.440 mmol, 1.10 equiv) in presence of CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) after 24 h at 20°C. Flash chromatography and recrystallization from hexanes furnished single crystals of the major diastereomer suitable for X-ray crystallography.

Analytical data for (^{Si}*R*,*R*)-**43a**: M.p. 103°C (cyclohexane/*tert*-butyl methyl ether); R$_f$ = 0.25 (cyclohexane/*tert*-butyl methyl ether 6:1); $[\alpha]^{20}_{D}$ = +73.9 (*c* = 0.805, CHCl$_3$), $[\alpha]^{20}_{578}$ = +77.5, $[\alpha]^{20}_{546}$ = +89.7, $[\alpha]^{20}_{436}$ = +175; $[\alpha]^{20}_{365}$ = −122; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 0.29 (dddd, *J* = 14.9 Hz, *J* = 6.1 Hz, *J* = 3.6 Hz, *J* = 1.3 Hz, 1H), 0.29 (ddd, *J* = 15.0 Hz, *J* = 12.0 Hz, *J* = 5.2 Hz, 1H), 0.85 (s, 9H), 1.82 (m$_c$, 1H), 1.66 (m$_c$, 1H), 2.34 (ddd, *J* = 15.8 Hz, *J* = 11.0 Hz, *J* = 2.3 Hz, 1H), 2.47 (br dd, *J* = 15.6 Hz, *J* = 6.3 Hz, 1H), 3.31 (dd, *J* = 13.5 Hz, *J* = 4.1 Hz, 1H), 3.88 (dd, *J* = 13.3 Hz, *J* = 9.3 Hz, 1H), 5.12 (dd, *J* = 9.7 Hz, *J* = 4.1 Hz, 1H), 6.27 (dd, *J* = 7.4 Hz, *J* = 1.3 Hz, 1H), 6.76 (dd, *J* = *J* = 7.2 Hz, 1H), 6.96 (br d, *J* = 7.8 Hz, 1H), 7.14 (ddd, *J* = *J* = 7.4 Hz, *J* = 1.4 Hz, 1H), 7.24–7.29 (m, 1H), 7.30–7.35 (m, 2H), 7.40–7.43 (m, 2H), 7.53 (ddd, *J* = 8.2 Hz, *J* = 6.9 Hz, *J* = 1.0 Hz, 1H), 7.56 (d, *J* = 5.7 Hz, 1H), 7.66 (ddd, *J* = *J* = 7.8 Hz, *J* = 0.9 Hz, 1H), 7.83 (br d, *J* = 8.3 Hz, 1H), 8.24 (br d, *J* = 8.5 Hz, 1H), 8.42 (d, *J* = 5.5 Hz, 1H) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 9.6, 18.3, 22.6, 25.8, 35.4, 46.4, 76.1, 119.5, 124.8, 126.1, 128.5, 126.9, 127.0, 127.4, 128.2, 128.3, 128.4,129.1, 129.9, 130.2, 134.7, 136.4, 141.8, 145.3, 150.4, 159.4 ppm; IR (ATR): $\tilde{\nu}$ = 3053 (w), 3001 (w), 2997 (w), 2960 (m), 2949 (m), 2928 (s), 2907 (s), 2887 (m), 2853 (s), 1622 (m), 1587 (s), 1562 (s), 1471 (m), 1433 (s), 1388 (m), 1359 (m), 1345 (w), 1293 m), 1260 (s), 1142 (m), 1064 (s), 1051 (s), 1011 (s), 943 (m), 911 (m), 869 (m), 849 (m), 831 (s), 798 (s), 758 (s), 742 (s), 698 (s) cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{30}H_{33}NOSi$ $[(M+H)^+]$: 452.2404, found: 452.2413; elemental analysis calcd (%) for $C_{30}H_{33}NOSi$ (451.7): C 79.77, H 7.36, N 3.10; found: C 79.53, H 7.27, N 2.87.

NMR spectroscopic data for (^{Si}R,*S*)-**43a** (minor diastereomer): ^1H NMR (600 MHz, $CDCl_3$): δ = 0.22–0.30 (m, 1H), 0.51–0.56 (m, 1H), 0.62 (s, 9H), 1.13–1.23 (m, 1H), 1.60 (m_c, 1H), 2.29–2.38 (m, 1H), 2.45–2.52 (m, 1H), 3.29–3.34 (m, 1H), 3.84–3.91 (m, 1H), 5.22 (dd, *J* = 10.2 Hz, *J* = 3.6 Hz, 1H), 6.82 (dd, *J* = *J* = 7.5 Hz, 1H), 6.93–6.96 (m, 2H), 7.12 (ddd, *J* = *J* = 7.5 Hz, *J* = 1.6 Hz, 1H), 7.24–7.29 (m, 3H), 7.35–7,38 (m, 2H), 7.51–7.55 (m, 1H), 7.59 (ddd, *J* = 8.4 Hz, *J* = 7.0 Hz, *J* = 1.0 Hz, 1H), 7.64–7.69 (m, 1H), 7.80–7.84 (m, 1H), 8.33 (br d, *J* = 8.5 Hz, 1H), 8.48 (d, *J* = 5.5 Hz, 1H) ppm.



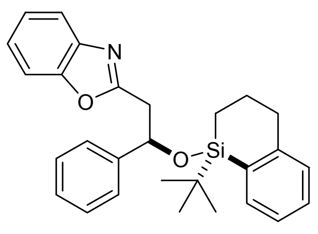
(^{Si}R,*R*)-**44a**

$C_{26}H_{33}NO_2Si$

419.63 g/mol

(^{Si}*R*,*R*)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-2-phenylethyl]-4,5-dimethyloxazole [(^{Si}*R*,*R*)-44a] (Table 6, Entry 4): According to GP 1, the reaction mixture consisting of *rac*-**37** (86.9 mg, 0.400 mmol, 1.00 equiv), (^{Si}S)-**4a** (46.0 mg, 0.225 mmol, 0.560 equiv, 99% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 21 h at 20°C, after which a conversion of 55% was detected by ^1H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 14:1→1:1) furnished analytically pure silyl ether (^{Si}R,*R*)-**44a** (83 mg, 50%, d.r. = 79:21) and alcohol (*S*)-**37** (36 mg, 41%, 65% *ee*).

Analytical data for (^{Si}R,*R*)-**44a**: R_f = 0.40 (cyclohexane/*tert*-butyl methyl ether 5:1); $[\alpha]^{20}_D$ = +38.6 (*c* = 1.42, $CHCl_3$), $[\alpha]^{20}_{578}$ = +40.4, $[\alpha]^{20}_{546}$ = +45.9, $[\alpha]^{20}_{436}$ = +80.8; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.42 (dddd, *J* = 15.1 Hz, *J* = 6.1 Hz, *J* = 4.0 Hz, *J* = 1.5 Hz, 1H), 0.62 (ddd, *J* = 15.1 Hz, *J* = 12.2 Hz, *J* = 5.1 Hz, 1H), 0.88 (s, 9H), 1.27 (ddddd, *J* = 13.3 Hz, *J* = 12.2 Hz, *J* = 11.0 Hz, *J* = 3.9 Hz, *J* = 2.7 Hz, 1H), 1.74 (ddddd, *J* = 13.3 Hz, *J* = *J* = 6.1 Hz, *J* = 5.2 Hz, *J* = 2.8 Hz, 1H), 2.05 (s, 3H), 2.16 (s, 3H), 2.43 (ddd, *J* = 15.7 Hz, *J* = 11.1 Hz, *J* = 2.9 Hz, 1H), 2.57 (dd, *J* = 15.7 Hz, *J* = 5.9 Hz, 1H), 2.84 (dd, *J* = 14.4 Hz, *J* = 3.7 Hz, 1H), 3.09 (dd, *J* = 14.4 Hz, *J* = 9.6 Hz, 1H), 4.95 (dd, *J* = 9.6 Hz, *J* = 3.7 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.09 (dd, *J* = *J* = 7.2 Hz, 1H), 7.19 (dd, *J* = 7.1 Hz, *J* = 1.6 Hz, 1H), 7.20–7.31 (m, 5H), 7.25 (ddd, *J* = 7.6 Hz, *J* = 7.4 Hz, *J* = 1.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7, 9.9, 11.2, 18.6, 22.6, 25.9, 35.6, 40.0, 74.0, 124.9, 126.1, 127.7, 128.3, 128.5, 129.4, 130.2, 130.5, 135.0, 142.6, 144.3, 150.6, 159.6 ppm; IR (cuvette/$CHCl_3$): $\tilde{\nu}$ = 3058 (w), 2928 (s), 1595 (s), 1472 (s), 1433 (s), 1088 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 420 $[(M+H)^+]$; elemental analysis calcd (%) for $C_{26}H_{33}NO_2Si$ (419.6): C 74.42, H 7.93, N 3.34; found: C 74.09, H 8.07, N 2.96.



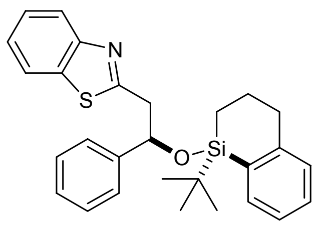
($^{\text{Si}}R^*,R^*$)-**45a**

$C_{28}H_{31}NO_2Si$

441.64 g/mol

($^{\text{Si}}R^*,R^*$)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-2-phenylethyl]-benzoxazole [($^{\text{Si}}R^*,R^*$)-45a] (Table 6, Entry 5): According to GP 1, the reaction mixture consisting of *rac*-**38** (95.7 mg, 0.400 mmol, 1.00 equiv), *rac*-**4a** (45.0 mg, 0.220 mmol, 0.550 equiv), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in benzene (4.0 mL) was stirred for 20 h at 20°C, after which a conversion of 18% was detected by ^1H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 15:1→1:1) furnished analytically pure silyl ether ($^{\text{Si}}R^*,R^*$)-**45a** (14 mg, 8%, d.r. = 83:17). Alcohol *rac*-**38** was not recovered; ^1H NMR spectroscopy of the crude reaction mixture indicated decomposition of the latter.

Analytical data for ($^{\text{Si}}R^*,R^*$)-**45a**: R_f = 0.60 (cyclohexane/*tert*-butyl methyl ether 5:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.41 (dddd, *J* = 15.3 Hz, *J* = 6.2 Hz, *J* = 4.0 Hz, *J* = 1.5 Hz, 1H), 0.61 (ddd, *J* = 15.1 Hz, *J* = 12.2 Hz, *J* = 5.1 Hz, 1H), 0.85 (s, 9H), 1.25–1.36 (m, 1H), 1.69–1.79 (m, 1H), 2.37–2.45 (m, 1H), 2.52–2.60 (m, 1H), 3.11 (dd, *J* = 14.4 Hz, *J* = 3.8 Hz, 1H), 3.35 (dd, *J* = 14.4 Hz, *J* = 9.4 Hz, 1H), 5.12 (dd, *J* = 9.4 Hz, *J* = 3.8 Hz, 1H), 6.69 (dd, *J* = *J* = 7.3 Hz, 1H), 6.93 (dd, *J* = 7.3 Hz, *J* = 1.3 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 7.13 (ddd, *J* = *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.17–7.38 (m, 7H), 7.43–7.46 (m, 1H), 7.64–7.69 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7, 18.5, 22.7, 25.9, 35.5, 40.7, 73.7, 110.5, 119.8, 124.1, 124.6, 124.9, 126.0, 127.9, 128.4, 128.5, 129.5, 130.2, 134.8, 141.6, 144.0, 150.5, 150.9, 164.4 ppm; IR (cuvette/$CHCl_3$): $\tilde{\nu}$ = 3057 (w), 2926 (s), 2854 (s), 1615 (s), 1494 (s), 1455 (s), 1087 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 442 [$(M+H)^+$]; HRMS (EI): *m/z*: calcd for $C_{28}H_{31}NO_2Si$ [$(M-C_4H_9)^+$]: 384.1420, found: 384.1420.



($^{\text{Si}}R^*,R^*$)-**46a**

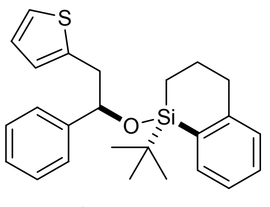
$C_{28}H_{31}NOSSi$

457.70 g/mol

($^{\text{Si}}R^*,R^*$)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-2-phenylethyl]-benzothiazole [($^{\text{Si}}R^*,R^*$)-46a] (Table 6, Entry 6): According to GP 1, the reaction mixture consisting of *rac*-**39** (102 mg, 0.400 mmol, 1.00 equiv), *rac*-**4a** (45.0 mg, 0.220 mmol, 0.550 equiv), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in benzene (4.0 mL) was stirred for 20 h at 20°C, after which a conversion of 48% was detected by ^1H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 15:1→1:1) furnished analytically pure silyl ether ($^{\text{Si}}R^*,R^*$)-**46a** (50 mg, 28%, d.r. = 92:8) and alcohol *rac*-**39** (4 mg, 4%); ^1H NMR spectroscopy of the crude reaction mixture indicated decomposition of the latter.

Analytical data for ($^{\text{Si}}R^*,R^*$)-**46a**: R_f = 0.65 (cyclohexane/*tert*-butyl methyl ether 5:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.41 (dddd, *J* = 15.1 Hz, *J* = 6.2 Hz, *J* = 4.0 Hz, *J* = 1.5 Hz, 1H), 0.63 (ddd, *J* = 15.2 Hz, *J* = 12.0 Hz, *J* = 5.1 Hz, 1H), 0.91 (s, 9H), 1.32 (ddddd, *J* = 13.5 Hz, *J* = 12.1 Hz, *J* = 11.1 Hz, *J* = 4.0 Hz, *J* = 2.8 Hz, 1H), 1.75 (ddddd, *J* = 13.2 Hz, *J* = *J* = 6.2 Hz, *J* = 5.2 Hz, *J* = 2.8 Hz, 1H), 2.42 (ddd, *J* = 15.7 Hz, *J* = 11.0 Hz, *J* = 2.8 Hz, 1H), 2.56 (dd, *J* = 15.8 Hz, *J* = 5.4 Hz, 1H), 3.33 (dd, *J* = 14.2 Hz, *J* = 4.0 Hz, 1H), 3.47 (dd, *J* = 14.2 Hz, *J* = 8.3 Hz, 1H), 5.08 (dd, *J* = 8.3 Hz, *J* = 4.0, 1H), 6.65–6.70 (m, 1H), 6.98–7.02 (m, 2H), 7.14 (m_c, 1H), 7.24–7.35 (m, 5H), 7.37 (ddd, *J* = 7.9 Hz, *J* = 7.2

Hz, *J* = 1.2 Hz, 1H), 7.46 (ddd, *J* = 8.1 Hz, *J* = 7.2 Hz, *J* = 1.3 Hz, 1H), 7.85 (ddd, *J* = 8.0 Hz, *J* = 1.3 Hz, *J* = 0.6 Hz, 1H), 7.93 (ddd, *J* = 8.1 Hz, *J* = 1.2 Hz, *J* = 0.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7, 18.6, 22.8, 26.1, 35.5, 45.4, 74.8, 121.5, 122.8, 124.7, 124.9, 125.8, 126.2, 127.7, 128.4, 129.4, 130.3, 134.9, 135.7, 143.9, 150.5, 153.3, 168.1 ppm; IR (cuvette/$CHCl_3$): $\tilde{\nu}$ = 3057 (w), 2926 (s), 2854 (s), 1589 (m), 1455 (m), 1066 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 458 [(M+H)$^+$]; elemental analysis calcd (%) for $C_{28}H_{31}NOSSi$ (457.7): C 73.48, H 6.83, N 3.06, S 7.01; found: C 73.69, H 6.62, N 3.28, 7.24.



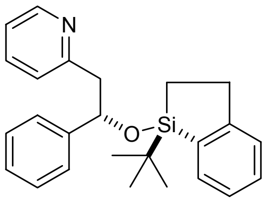
(^{Si}*R**,*R**)-**47a**

$C_{25}H_{30}OSSi$
406.66 g/mol

(^{Si}*R,*R**)-2-[2-(1-*tert*-Butyl-1-silatetralinyl-1-oxy)-2-phenylethyl]thiophene [(^{Si}*R**,*R**)-47a] (Table 6, Entry 7):** According to GP 1, the reaction mixture consisting of *rac*-**40** (81.7 mg, 0.400 mmol, 1.00 equiv), *rac*-**4a** (45.0 mg, 0.220 mmol, 0.550 equiv), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in benzene (4.0 mL) was stirred for 20 h at 20°C, after which a conversion of 27% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane→cyclohexane/*tert*-butyl methyl ether 15:1→4:1) furnished analytically pure silyl ether (^{Si}*R**,*R**)-**47a** (39 mg, 24%, d.r. = 65:35) and alcohol *rac*-**40** (57 mg, 70%).

Analytical data for (^{Si}*R**,*R**)-**47a**: R$_f$ = 0.26 (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.39 (dddd, *J* = 15.1 Hz, *J* = 5.9 Hz, *J* = 4.1 Hz, *J* = 1.7 Hz, 1H), 0.64 (ddd, *J* = 15.1 Hz, *J* = 12.2 Hz, *J* = 5.2 Hz, 1H), 0.95 (s, 9H), 1.30 (ddddd, *J* = 13.3 Hz, *J* = 12.2 Hz, *J* = 11.1 Hz, *J* = 3.9 Hz, *J* = 2.7 Hz, 1H), 1.77 (ddddd, *J* = 13.4 Hz, *J* = *J* = 6.1 Hz, *J* = 5.3 Hz, *J* = 2.8 Hz, 1H), 2.45 (ddd, *J* = 15.7 Hz, *J* = 11.2 Hz, *J* = 2.8 Hz, 1H), 2.57 (dd, *J* = 15.5 Hz, *J* = 6.0 Hz, 1H), 3.07 (ddd, *J* = 14.5 Hz, *J* = 4.9 Hz, *J* = 0.8 Hz, 1H), 3.16 (dd, *J* = 14.5 Hz, *J* = 6.7 Hz, 1H), 4.68 (dd, *J* = 7.0 Hz, *J* = 4.9 Hz, 1H), 6.62 (ddd, *J* = 3.4 Hz, *J* = 1.2 Hz, *J* = 0.8 Hz, 1H), 6.87 (dd, *J* = 5.1 Hz, *J* = 3.4 Hz, 1H), 7.05–7.29 (m, 9H), 7.11 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7, 18.6, 22.9, 26.1, 35.6, 41.3, 76.1, 123.8, 125.2, 126.2, 126.5, 127.9, 128.1, 128.4, 129.4, 130.8, 135.2, 140.3, 144.3, 150.8 ppm; IR (cuvette/$CHCl_3$): $\tilde{\nu}$ = 3057 (w), 2926 (s), 2855 (s), 1589 (m), 1066 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 407 [(M+H)$^+$]; HRMS (EI): *m/z*: calcd for $C_{25}H_{30}NOSSi$ [(M–C_4H_9)$^+$]: 349.1082, found: 349.1077.

4.5 Kinetic Resolution with Silaindane 5a (Table 7)

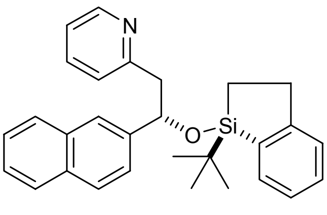


(^{Si}*S*,*S*)-**15a**

$C_{25}H_{29}NOSi$
387.59 g/mol

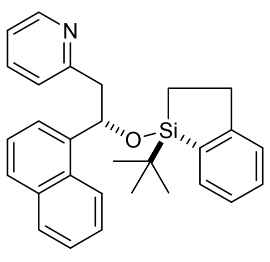
(^{Si}*S*,*S*)-2-[2-(1-*tert*-Butyl-1-silaindanyl-1-oxy)-2-phenylethyl]pyridine [(^{Si}*S*,*S*)-15a] (Table 7, Entry 1): According to GP 1, the reaction mixture consisting of *rac*-**6** (79.7 mg, 0.400 mmol, 1.00 equiv), (^{Si}*R*)-**5a** (43.5 mg, 0.230 mmol, 0.570 equiv, 99% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 4 h at 0°C, after which a conversion of 53% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 14:1→1:1) furnished analytically pure silyl ether (${}^{\mathrm{Si}}$*S*,*S*)-**15a** (79 mg, 51%, d.r. = 77:23) and alcohol (*S*)-**6** (36 mg, 45%, 83 % *ee*)

Analytical data for (${}^{\mathrm{Si}}$*S*,*S*)-**15a** agreed with those of (${}^{\mathrm{Si}}$*S**,*S**)-**15a** (see above); $[\alpha]^{20}_{\mathrm{D}}$ = –70.8 (*c* = 1.69, $CHCl_3$), $[\alpha]^{20}_{578}$ = –73.3, $[\alpha]^{20}_{546}$ = –84.1, $[\alpha]^{20}_{436}$ = –155; $[\alpha]^{20}_{365}$ = –277.


(${}^{\mathrm{Si}}$*S*,*S*)-**48a**
$C_{29}H_{31}NOSi$
437.65 g/mol

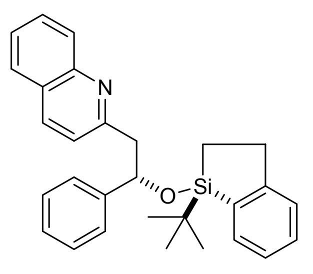
(${}^{\mathrm{Si}}$*S*,*S*)-2-[2-(1-*tert*-Butyl-1-silaindanyl-1-oxy)-2-(naphthalin-2-yl)-ethyl]pyridine [(${}^{\mathrm{Si}}$*S*,*S*)-48a] (Table 7, Entry 2): According to GP 1, the reaction mixture consisting of *rac*-**16** (99.7 mg, 0.400 mmol, 1.00 equiv), (${}^{\mathrm{Si}}$*R*)-**5a** (48.0 mg, 0.250 mmol, 0.630 equiv, 99% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 2 h at 20°C, after which a conversion of 58% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 14:1→2:3) furnished analytically pure silyl ether (${}^{\mathrm{Si}}$*S*,*S*)-**48a** (96 mg, 57%, d.r. = 76:24) and alcohol (*R*)-**16** (38 mg, 38%, 69% *ee*).

Analytical data for (${}^{\mathrm{Si}}$*S*,*S*)-**48a**: R_f = 0.30 (cyclohexane/*tert*-butyl methyl ether 5:1); $[\alpha]^{20}_{\mathrm{D}}$ = –89.3 (*c* = 1.60, $CHCl_3$), $[\alpha]^{20}_{578}$ = –93.5, $[\alpha]^{20}_{546}$ = –107, $[\alpha]^{20}_{436}$ = –202; $[\alpha]^{20}_{365}$ = –366; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.31 (ddd, *J* = 15.5 Hz, *J* = 9.7 Hz, *J* = 5.9 Hz, 1H), 0.63 (ddd, *J* = 15.6 Hz, *J* = 9.3 Hz, *J* = 4.8 Hz, 1H), 0.90 (s, 9H), 2.55 (ddd, *J* = 16.9 Hz, *J* = 9.7 Hz, *J* = 4.8 Hz, 1H), 2.64 (ddd, *J* = 16.9 Hz, *J* = 9.3 Hz, *J* = 5.8 Hz, 1H), 3.08 (dd, *J* = 13.3 Hz, *J* = 3.7 Hz, 1H), 3.16 (dd, *J* = 13.2 Hz, *J* = 9.4 Hz, 1H), 5.07 (dd, *J* = 9.4 Hz, *J* = 3.7 Hz, 1H), 6.90 (ddd, *J* = 7.2 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz, 1H), 7.05 (m_c, 1H), 7.08 (m_c, 1H), 7.13 (ddd, *J* = 7.6 Hz, *J* = 4.9, *J* = 1.1 Hz, 1H), 7.18 (ddd, *J* = 7.7 Hz, *J* = *J* = 1.1 Hz, 1H), 7.26 (ddd, *J* = 7.6 Hz, *J* = 7.3 Hz, *J* = 1.4 Hz, 1H), 7.42–7.48 (m, 2H), 7.51 (dd, *J* = 8.5 Hz, *J* = 1.7 Hz, 1H), 7.55 (ddd, *J* = *J* = 7.6 Hz, *J* = 1.9 Hz, 1H), 7.62–7.64 (m, 1H), 7.72–7.83 (m, 2H), 7.79 (d, *J* = 8.5 Hz, 1H), 8.48 (ddd, *J* = 4.9 Hz, *J* = 1.8 Hz, *J* = 0.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.1, 18.6, 26.0, 30.0, 49.9, 75.7, 121.3, 124.3, 124.6, 125.0, 125.3, 125.7, 126.0, 126.1, 127.7, 128.0, 128.1, 130.0, 132.9, 133.0, 133.3, 133.6, 135.9, 142.4, 149.3, 154.5, 159.0 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3017 (w), 2928 (s), 2855 (s), 1591 (s), 1436 (s), 1046 (s) cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{29}H_{31}NOSi$ [M^+]: 437.2175, found: 437.2184; elemental analysis calcd (%) for $C_{29}H_{31}NOSi$ (437.7): C 79.59, H 7.14, N 3.20; found: C 79.38, H 7.27, N 3.01.


(${}^{\mathrm{Si}}$*S*,*S*)-**49a**
$C_{29}H_{31}NOSi$
437.65 g/mol

(${}^{\mathrm{Si}}$*S*,*S*)-2-[2-(1-*tert*-Butyl-1-silaindanyl-1-oxy)-2-(naphth-1-yl)ethyl]-pyridine [(${}^{\mathrm{Si}}$*S*,*S*)-49a] (Table 7, Entry 3): According to GP 1, the reaction mixture consisting of *rac*-**24** (99.7 mg, 0.400 mmol, 1.00 equiv), (${}^{\mathrm{Si}}$*R*)-**5a** (48.0 mg, 0.250 mmol, 0.630 equiv, 99% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 2 h at 20°C, after which a conversion of 56% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 95:5→1:1) furnished analytically pure silyl ether (${}^{\mathrm{Si}}$*S*,*S*)-**49a** (96 mg, 55%, d.r. = 77:23) and alcohol (*R*)-**24** (41 mg, 41%, 75% *ee*).

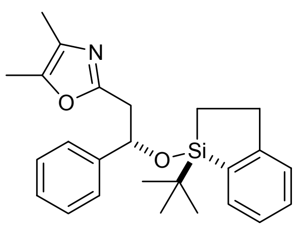
Analytical data for (^{Si}*S*,*S*)-**49a**: R$_f$ = 0.40 (cyclohexane/*tert*-butyl methyl ether 5:1); $[\alpha]^{20}_{D}$ = –56.4 (*c* = 1.49, CHCl$_3$), $[\alpha]^{20}_{578}$ = –59.1, $[\alpha]^{20}_{546}$ = –68.0, $[\alpha]^{20}_{436}$ = –129, $[\alpha]^{20}_{365}$ = –246; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.21 (ddd, *J* = 15.5 Hz, *J* = 9.8 Hz, *J* = 5.7 Hz, 1H), 0.63 (ddd, *J* = 15.6 Hz, *J* = 9.4 Hz, *J* = 4.7 Hz, 1H), 0.91 (s, 9H), 2.47 (ddd, *J* = 16.8 Hz, *J* = 9.7 Hz, *J* = 4.7 Hz, 1H), 2.60 (ddd, *J* = 16.9 Hz, *J* = 9.4 Hz, *J* = 5.8 Hz, 1H), 3.18 (dd, *J* = 13.5 Hz, *J* = 9.1 Hz, 1H) 3.23 (dd, *J* = 13.5 Hz, *J* = 3.9 Hz, 1H), 5.62 (dd, *J* = 8.9 Hz, *J* = 3.7 Hz, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 7.00–7.06 (m, 2H), 7.15 (ddd, *J* = 7.5 Hz, *J* = 4.9 Hz, *J* = 1.2 Hz, 1H), 7.20 (ddd, *J* = 7.7 Hz, *J* = *J* = 1.0 Hz, 1H), 7.24 (ddd, *J* = 7.7 Hz, *J* = 7.2 Hz, *J* = 1.4 Hz, 1H), 7.41–7.47 (m, 3H), 7.57 (ddd, *J* = *J* = 7.6 Hz, *J* = 1.9 Hz, 1H), 7.60–7.65 (m, 1H), 7.73–7.77 (m, 1H), 7.82–7.87 (m, 1H), 8.17–8.25 (m, 1H), 8.51 (ddd, *J* = 4.9 Hz, *J* = 1.8 Hz, *J* = 0.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 6.1, 18.6, 26.0, 30.0, 48.9, 73.5, 121.3, 123.6, 123.8, 125.0, 125.3, 125.4, 125.5, 126.0, 126.1, 127.8, 128.8, 129.9, 130.2, 133.0, 133.5, 133.8, 135.8, 140.6, 149.5, 154.5, 159.5 ppm; IR (cuvette/CDCl$_3$): $\tilde{\nu}$ = 3013 (w), 2928 (s), 2856 (s), 1593 (s), 1471 (s), 1438 (s), 1047 (s) cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{29}H_{31}NOSi$ [M$^+$]: 437.2175, found: 437.2175; elemental analysis calcd (%) for $C_{29}H_{31}NOSi$ (437.7): C 79.59, H 7.14, N 3.20; found: C 79.38, H 7.18, N 3.01.



(^{Si}*S*,*S*)-**50a**
$C_{29}H_{31}NOSi$
437.65 g/mol

(^{Si}*S*,*S*)-2-[2-(1-*tert*-Butyl-1-silaindanyl-1-oxy)-2-phenylethyl]quinoline [(^{Si}*S*,*S*)-50a] (Table 7, Entry 4): According to GP 1, the reaction mixture consisting of *rac*-**35** (99.7 mg, 0.400 mmol, 1.00 equiv), (^{Si}*R*)-**5a** (48.0 mg, 0.250 mmol, 0.630 equiv, 99% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 2 h at 20°C, after which a conversion of 58% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 95:5→1:1) furnished analytically pure silyl ether (^{Si}*S*,*S*)-**50a** (100 mg, 57%, d.r. = 75:25) and alcohol (*R*)-**35** (40 mg, 40%, 74% *ee*).

Analytical data for (^{Si}*S*,*S*)-**50a**: R$_f$ = 0.49 (cyclohexane/*tert*-butyl methyl ether 5:1); $[\alpha]^{20}_{D}$ = –35.2 (*c* = 1.45, CHCl$_3$), $[\alpha]^{20}_{578}$ = –37.1, $[\alpha]^{20}_{546}$ = –42.7, $[\alpha]^{20}_{436}$ = –80.9, $[\alpha]^{20}_{365}$ = –169; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.35 (ddd, *J* = 15.5 Hz, *J* = 9.2 Hz, *J* = 6.3 Hz, 1H), 0.64 (ddd, *J* = 15.5 Hz, *J* = 8.7 Hz, *J* = 5.3 Hz, 1H), 0.84 (s, 9H), 2.55–2.70 (m, 2H), 3.19 (dd, *J* = 13.2 Hz, *J* = 3.7 Hz, 1H), 3.27 (dd, *J* = 13.2 Hz, *J* = 9.5 Hz, 1H), 5.01 (dd, *J* = 9.5 Hz, *J* = 3.7 Hz, 1H), 6.51 (ddd, *J* = 7.2 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz, 1H), 6.60 (m$_c$, 1H), 7.02 (m$_c$, 1H), 7.12 (ddd, *J* = 7.6 Hz, *J* = 7.3 Hz, *J* = 1.4 Hz, 1H), 7.21–7.27 (m, 1H), 7.27–7.33 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.34–7.37 (m, 2H), 7.52 (ddd, *J* = 8.1 Hz, *J* = 6.9 Hz, *J* = 1.2 Hz, 1H), 7.69 (ddd, *J* = 8.4, *J* = 6.9 Hz, *J* = 1.5 Hz, 1H), 7.81 (dd, *J* = 8.1 Hz, *J* = 1.5 Hz, 1H), 7.97 (ddd, *J* = 8.5 Hz, *J* = 1.9 Hz, *J* = 0.8 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 6.0, 18.5, 25.9, 30.0, 50.6, 75.7, 123.6, 125.0, 125.8, 125.9, 126.0, 127.1, 127.3, 127.5, 128.3, 129.1, 129.2, 129.8, 132.8, 133.4, 135.6, 145.0, 148.1, 154.3, 159.8 ppm; IR (cuvette/CDCl$_3$): $\tilde{\nu}$ = 3012 (w), 2928 (s), 2856 (s), 1600 (s), 1471 (s), 1067 (s) cm^{-1}; LRMS (CI/NH$_3$): *m/z*: 438 [(M+H)$^+$]; elemental analysis calcd (%) for $C_{29}H_{31}NOSi$ (437.7): C 79.59, H 7.14, N 3.20; found: C 79.33, H 7.13, N 3.02.



(^{Si}*S*,*S*)-**51a**
$C_{25}H_{31}NO_2Si$
405.60 g/mol

(^{Si}*S*,*S*)-2-[2-(1-*tert*-Butyl-1-silaindanyl-1-oxy)-2-phenylethyl]-4,5-dimethyloxazole [(^{Si}*S*,*S*)-51a] (Table 7, Entry 5): According to GP 1, the reaction mixture consisting of *rac*-**37** (86.9 mg, 0.400 mmol, 1.00 equiv), (^{Si}*R*)-**5a** (48.0 mg, 0.250 mmol, 0.630 equiv, 99% *ee*), CuCl (2.0 mg, 0.020 mmol, 0.050 equiv), **L1d** (13.9 mg, 0.0400 mmol, 0.100 equiv) and NaO*t*Bu (1.9 mg, 0.020 mmol, 0.050 equiv) in toluene (4.0 mL) was stirred for 2 h at 20°C, after which a conversion of 57% was detected by ^{1}H NMR spectroscopy. Purification by flash chromatography (cyclohexane/*tert*-butyl methyl ether 14:1→1:1) furnished analytically pure silyl ether (^{Si}*S*,*S*)-**51a** (89 mg, 55%, d.r. = 74:26) and alcohol (*R*)-**37** (36 mg, 41%, 65% *ee*).

Analytical data for (^{Si}*S*,*S*)-**50a**: R_f = 0.33 (cyclohexane/*tert*-butyl methyl ether 5:1); $[\alpha]^{20}_{D} = -46.0$ (*c* = 1.62, $CHCl_3$), $[\alpha]^{20}_{578} = -48.0$, $[\alpha]^{20}_{546} = -54.8$, $[\alpha]^{20}_{436} = -98.1$, $[\alpha]^{20}_{365} = -165$; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.40 (ddd, *J* = 15.5 Hz, *J* = 9.5 Hz, *J* = 5.9 Hz, 1H), 0.72 (ddd, *J* = 15.6 Hz, *J* = 9.2 Hz, *J* = 5.0 Hz, 1H), 0.93 (s, 9H), 2.05 (s, 3H), 2.17 (s, 3H), 2.64 (ddd, *J* = 17.2 Hz, *J* = 9.6 Hz, *J* = 5.1 Hz, 1H), 2.66 (ddd, *J* = 17.0 Hz, *J* = 9.2 Hz, *J* = 5.9 Hz, 1H), 2.84 (dd, *J* = 14.5 Hz, *J* = 3.7 Hz, 1H), 3.05 (dd, *J* = 14.5 Hz, *J* = 9.8 Hz, 1H), 4.89 (dd, *J* = 9.8 Hz, *J* = 3.7 Hz, 1H), 7.11–7.33 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.1, 10.0, 11.2, 18.5, 25.8, 30.0, 39.9, 74.0, 125.3, 125.8, 126.1, 127.6, 128.3, 130.1, 130.3, 133.0, 133.5, 142.6, 144.0, 154.7, 159.5 ppm; IR (cuvette/$CDCl_3$): $\tilde{\nu}$ = 3012 (w), 2927 (s), 2856 (s), 1591 (s), 1471 (s), 1438 (s), 1046 (s) cm^{-1}; LRMS (CI/NH_3): *m/z*: 406 $[(M+H)^+]$; elemental analysis calcd (%) for $C_{25}H_{31}NO_2Si$ (405.6): C 74.03, H 7.70, N 3.45; found: C 73.97, H 7.80, N 3.23.

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6 Quantumchemical Calculations

Table S1: Cartesian coordinates and energies of structures reported in the text (reaction of $(H_3P)_2CuOCH_3$).

Table S2: Cartesian coordinates and energies of structures reported in the text (reaction of $(H_3P)_2CuOC(CH_3)_3$).

Figure S1: Optimized structures (PBE/TZVPP) in the reaction of $(H_3P)_2CuOCH_3$ with $(H_3C)_3SiH$

Figure S2: Optimized structures (PBE/TZVPP) of reactant and product complexes in the reaction of $(H_3P)_2CuOC(CH_3)_3$ with $(H_3C)_3SiH$

Figure S3: Two calculated (PBE/TZVPP) paths of the reaction of $(H_3P)_2CuOC(CH_3)_3$ with $(H_3C)_3SiH$.

Table S1. Cartesian coordinates and energies of structures reported in the text (reaction of $(H_3P)_2CuOCH_3$). All quantities are given in atomic units (Hartree, Bohr). The geometries were optimized at the PBE level of theory, SCSMP2- and B3LYP energies were calculated at these geometries without further optimization. The TZVPP AO basis was used in all calculations.

$(H_3P)_2CuH$			
Energies: SCSMP2 : -2325.4396665, B3LYP : -2327.277160801, PBE : -2326.865904439			
0.00191044341150	1.07069594382307	-0.00147572972022	cu
3.70801424206121	-1.02045058501083	-0.00107972517314	p
-3.71071548493265	-1.01991950955031	-0.00053030944027	p
-0.01749944691139	3.98691118258146	0.03433488403084	h
5.33625602439031	-0.44547175746895	2.06875535877882	h
4.32747299020515	-3.66231563538687	-0.07934788601296	h
5.45284599185390	-0.30000448148702	-1.92508229012863	h
-4.35108278664509	-3.65777084803452	-0.05822279792447	h
-5.35228071488244	-0.41129089195665	2.04904791208838	h
-5.43313561021473	-0.30584021614359	-1.94698415745654	h

$(H_3P)_2CuOCH_3$			
Energies: SCSMP2 : -2439.7986656, B3LYP : -2441.819981839, PBE : -2441.337637366			
0.07666797472318	0.01183599016125	-0.00599156757966	cu
3.13971473358186	-0.00244818049716	2.76089702457175	p
-4.08049456232762	-0.01316926294541	1.11811368727213	p
-0.15962996327214	0.04437502424657	-3.49363967529801	o
2.91890066976167	0.85783524198537	5.31395145288104	h
4.32657667518770	-2.34898088358406	3.36779617569914	h
5.42858774818452	1.32748139773740	2.23181245664077	h
-5.27677446523650	-2.05932435769198	2.41054242167481	h
-5.31810977182320	1.93025142582515	2.52686501147677	h
-5.74965329728555	0.02994188957792	-0.99470980382770	h
1.90853191728052	-0.04230072077887	-5.13960571609121	c
1.36810496029004	0.70482745790144	-7.02254090746960	h
3.55954862893613	1.08841322914084	-4.50167395363730	h
2.61035820516722	-1.99694808022948	-5.45341944669620	h

$(H_3C)_3SiH$			
Energies: SCSMP2 : -409.1948542, B3LYP : -409.7926152161, PBE : -409.5797118675			
0.25665467235863	0.45375772355411	-3.38031296486457	c
0.00006044351390	-0.67891771449090	-0.00029218025092	si
-3.05497721660603	0.45355907496589	1.46804818835768	c
2.79832163970455	0.45346534291876	1.91273319073785	c
2.00113272477691	-0.23635508773082	-4.27175261992790	h
-1.34561715879877	-0.21787463839184	-4.51878809431409	h
0.27454600511853	2.53015472474225	-3.47041019240178	h
-0.00069456804995	-3.52524074577105	-0.00044278210212	h
-3.14044494171018	2.52991637820436	1.50152592567226	h
-3.24085824078153	-0.22140608777640	3.42359766698346	h
-4.69918450687871	-0.23333502928068	0.40088232308531	h
2.87570722459523	2.52996231854316	1.95990281221878	h
2.68868556379887	-0.22296468902282	3.87353612139059	h
4.58505448311418	-0.23086749000529	1.10450842047147	h

Table S1 (continued)

$(H_3C)_3SiOCH_3$

Energies: SCSMP2 : -523.5771010, B3LYP : -524.3572256822, PBE : -524.0708029454

-2.90246007277188	1.02663988687773	-2.09607607881365	c
-0.00064389783256	0.73861756215039	-0.03686135021904	si
-0.03160744479184	3.14719030764427	2.57036867398639	c
2.92863315171970	1.05790079983804	-2.05177871939972	c
0.00420985949138	-2.05994477504251	1.47899110475371	o
-2.90951786495550	-0.38161922969234	-3.62405649899853	h
-4.63680304825309	0.77107622634177	-0.98169727083440	h
-2.98900900110362	2.90418750365423	-2.98432825072954	h
0.02342343872094	5.07789426968381	1.80479257284064	h
1.61081100732897	2.90356792102800	3.81741352198594	h
-1.74584019385959	2.96370061780591	3.72777431396685	h
2.97445159975571	2.91091604686878	-2.99279355629933	h
4.64949023565041	0.88656679388784	-0.90101598319842	h
3.00567873140425	-0.39222136695771	-3.53829897582885	h
0.00222298910889	-4.41653352833119	0.20063643234996	c
-1.72018895968729	-4.68064739187388	-0.94746946301479	h
1.66097600086693	-4.63379388915857	-1.04715880628480	h
0.06591426230398	-5.92716657599776	1.62485875160809	h

$[(H_3P)_2CuOCH_3 \cdot (H_3C)_3SiH]$ (intermediate, INT)

Energies: SCSMP2 : -2849.0030653, B3LYP : -2851.606537453, PBE : -2850.920055247

-2.98809039041528	-0.37871243883473	-5.59331013136483	c
-0.17070538200247	0.62253008091228	-3.58201648556920	si
0.20207445887339	4.05430902263549	-4.88828512631465	c
-0.03127450904911	0.23885582220136	1.71615204980618	cu
3.90972830679033	0.12786234253784	3.23443216444921	p
-3.27051210056001	0.61574581513582	4.43284829442428	p
3.06666640968124	-0.64092946957980	-4.55363652298253	c
-0.85949317396047	-2.11851401529526	-1.19878796098653	o
-3.31729793439463	-2.42658771838502	-5.62551995657631	h
-4.70994865276462	0.51420017553440	-4.84071025885049	h
-2.75348797396103	0.29722051924922	-7.54495067431613	h
-0.48088268050467	2.11380745421454	-0.84076915018469	h
0.52830741301205	4.05944997092012	-6.94667890546382	h
1.80068929403500	5.03441117635397	-3.98381974579940	h
-1.50598133711950	5.18497534251227	-4.51640261284724	h
4.48090660495290	0.22532064655993	5.87056850385904	h
5.50191151975544	-1.98137242617804	2.69027788101474	h
5.69223682274552	2.01310561323849	2.50131174088985	h
-3.07622531421543	0.28226861534590	7.10606308889847	h
-4.64969505212286	2.92860317211225	4.55971885602125	h
-5.42194389174629	-0.97775819809298	4.10810663217767	h
3.41908216061230	-0.13865855070110	-6.54007676397239	h
4.55473165416640	0.29334796677252	-3.43761294918468	h
3.30903121271599	-2.69028336601945	-4.34739887582547	h
-0.42294562567673	-4.71200902947667	-1.58733078510100	c
-1.00429123204733	-5.29618654140976	-3.50709831440983	h
1.58996712899541	-5.23836293382209	-1.35573366231183	h
-1.53326559578875	-5.83633011708072	-0.22370288481808	h

Table S1 (continued)

$(H_3P)_2CuOCH_3{\cdot}(H_3C)_3SiH$ (r-complex)

Energies: SCSMP2 : -2849.0033788, B3LYP : -2851.615050996, PBE : -2850.925067708

-2.43301958292738	4.51489384563271	-2.07267460454900	c
-0.01420308497753	4.20964411242729	0.51171918311399	si
-0.62279243107229	6.52559800521659	3.17662331705177	c
-0.03512850428370	-1.65507250620295	0.05855179233171	cu
2.86045582110941	-3.39331245071667	2.54264816265249	p
-4.17576950508776	-2.78438048506224	0.43992272597087	p
3.30999366970304	4.54215118254252	-0.71564765448731	c
0.35659022704450	-0.80880017693126	-3.41312863718210	o
-2.08823934571707	2.99960126357148	-3.45453009488473	h
-4.37000682748209	4.35133890530072	-1.33909022201194	h
-2.26610289450864	6.35533733127435	-3.02459206785715	h
-0.27766376244920	1.57015744173707	1.72581479045988	h
-0.46903496594128	8.48197235289400	2.48844110982048	h
0.74856810839489	6.28768049953233	4.71843672293313	h
-2.52724859781677	6.28310849289470	3.96948909135616	h
2.51219860883785	-4.11351620564820	5.12494513893443	h
3.96937920924964	-5.73100563710041	1.77630100215367	h
5.20017794420683	-2.11207533227598	2.95071377096846	h
-4.78601323520774	-5.33426702834418	-0.18813367474101	h
-5.85083847711450	-2.64670488810854	2.56100520672597	h
-5.86963390434095	-1.65644615051763	-1.32785499580993	h
3.60163356407805	6.42996376112789	-1.53567189171299	h
4.71480791796423	4.28130510817982	0.79211893841151	h
3.64233934187404	3.12546801852895	-2.19478488879997	h
2.45097519614493	-1.59976468128534	-4.80986604371885	c
2.30509039757244	-0.92448413454992	-6.79049420231428	h
4.28889702220323	-0.87353907585331	-4.07303877974509	h
2.65474107035921	-3.69013609032118	-4.91525703864704	h

Table S1 (continued)

$[(H_3P)_2CuH{\cdot}(H_3C)_3SiOCH_3]$ (p-complex)

Energies: SCSMP2 : -2849.0284086, B3LYP : -2851.636898786, PBE : -2850.943694571

0.03050039845218	-1.48978059493809	-7.43410775413937	c
0.05136599001433	0.37515052875700	-4.38658631501619	si
-2.83063590723490	2.41122525089129	-4.09261126509916	c
-0.19249099725116	1.09766247698865	2.50845395973690	cu
3.41806087867965	-0.33489539364013	4.27022972593184	p
-3.83079892523172	-1.00733990645233	3.16409383698967	p
3.04406594667793	2.28069596221732	-4.11847856685262	c
-0.13703242876566	-1.67610438741668	-1.90887036148569	o
1.70390927360799	-2.70575051619399	-7.62882720971135	h
-1.66007787903670	-2.68912581461088	-7.57807058858936	h
0.02077963893497	-0.19168670268665	-9.05809074445739	h
-0.10674447278421	3.91265565858454	1.69508631748441	h
-2.86324911444265	3.85943565378809	-5.58285525646615	h
-2.80738821884232	3.36893914288191	-2.24810577581669	h
-4.57101363858235	1.28841182388679	-4.24985443721407	h
3.99042830533017	0.94639137981860	6.57215230321267	h
4.28454896518353	-2.76341574747008	5.13624712169865	h
5.73465153073252	0.29720520982095	3.04025802385995	h
-4.24521997278334	-3.67708749636263	3.39474211307956	h
-5.27481543745018	-0.35049293954187	5.34667740293758	h
-5.82216702106339	-0.60905882603779	1.39226113791564	h
3.18113992091108	3.66254674958955	-5.66548834198871	h
3.03514906641809	3.31624304523653	-2.31657627254582	h
4.74424416917760	1.08776931035219	-4.19540589653544	h
1.47644527637467	-3.81646783576001	-1.73576410730471	c
1.16693993897623	-5.14421549986525	-3.31273242209162	h
3.49392315548986	-3.28020267699893	-1.71790518344666	h
1.05565244215853	-4.80526533161887	0.04251742565974	h

Table S1 (continued)

TS [$(H_3P)_2CuH{\cdot}(H_3C)_3SiOCH_3$] (r-complex -> INT)
lowest normal vibration (mainly along Si-O bond) : -90.3 cm^{-1}

Energies: SCSMP2 : -2848.9997460, B3LYP : -2851.606091451, PBE : -2850.918673118

4.01983328489931	3.11515215771061	-0.57771796982338	c
2.41914273242748	0.28872124642809	0.91365202915959	si
4.01285153032166	0.07478479264945	4.18420573921943	c
-2.96268153635844	0.14216936143483	0.20324664259778	cu
-4.43573779588615	-3.78084491728392	0.67319580879278	p
-5.60943167213359	3.38050364510323	1.02988701111715	p
3.10238344890173	-2.95138968661464	-0.45091183586580	c
-0.46654919383746	0.95038247749867	-2.39998943536002	o
3.99759173504332	3.00823668214582	-2.64570929270319	h
3.02750111675076	4.85760658762732	-0.03634967806919	h
5.98218397674155	3.26462158326764	0.09402888592845	h
-0.27171884282146	0.71245149723721	2.11934810830297	h
6.05862483300205	-0.26873590320778	4.00380562874466	h
3.21581354550580	-1.46632981553871	5.33233882279887	h
3.76978628935382	1.84069151534404	5.25717258114948	h
-7.06268229733746	-4.32148485419514	0.97228135780386	h
-4.01000076871464	-5.60086123762152	-1.27351654237867	h
-3.60361595335746	-5.35443238682020	2.69995831783736	h
-8.29870672749026	3.14047122514774	1.01321632531208	h
-5.49110748738134	4.76022423530528	3.34582189065478	h
-5.51308589106484	5.53970666523567	-0.58369505607729	h
5.15144613265805	-3.29669127368787	-0.34149984215499	h
2.19074414230142	-4.42362979696834	0.70123594711157	h
2.49918310499171	-3.18312176773484	-2.41741038400959	h
-0.44335008436896	0.07822012037213	-4.88674160091370	c
1.32460334938790	0.64562049333974	-5.86375497378908	h
-0.57335292910789	-2.01620422503134	-5.05448570629090	h
-2.02966804242661	0.86416157885692	-6.01161277909498	h

Table S2. Cartesian coordinates and energies of structures reported in the text (reaction of $(H_3P)_2CuOC(CH_3)_3$). All quantities are given in atomic units (Hartree, Bohr). The geometries were optimized at the PBE level of theory, SCSMP2- and B3LYP energies were calculated at these geometries without further optimization. The TZVPP AO basis was used in all calculations.

$(H_3P)_2CuOC(CH_3)_3$			
Energies: SCSMP2 : -2557.4891466, B3LYP : -2559.733956954, PBE : -2559.166625354			
0.06142644149677	0.01408717058175	1.26694609206363	cu
3.70307179654792	-0.00496562213653	3.21312331806244	p
-3.64955216810336	-0.00884984982964	3.54541794097011	p
-1.39225651607197	-0.02396794862211	-1.92681197751887	o
4.08443397463879	1.01992736213693	5.68522927217998	h
4.87383205856795	-2.38350736133314	3.71699238419873	h
5.88234236174951	1.14457918530476	2.11107350927025	h
-4.47054464063414	-2.02490876363858	5.14329242944450	h
-4.46278908808688	1.96310124396000	5.20145584745267	h
-5.81211275739199	0.01669240001773	1.94338679928584	h
-0.07507926921324	-0.00279226237056	-4.24528698453186	c
1.49781032248171	2.43184981429425	-4.49929641145150	c
2.48298674361491	2.55211164592802	-6.32852961989861	h
2.92391037600684	2.50619387282790	-2.98481457489179	h
0.26196424450709	4.08987524855179	-4.30185366794596	h
-2.06893421323280	-0.09988389379768	-6.36309959119474	c
-3.21144843923326	-1.82383537538267	-6.17163745472059	h
-1.20158279302278	-0.08514812399214	-8.25312442714540	h
-3.33990124251657	1.53502371783572	-6.20431072031846	h
1.67335023948140	-2.31872972124852	-4.45244783237101	c
2.65447740550846	-2.40984510285989	-6.28557860366062	h
0.56687383069203	-4.05958584305789	-4.20583531561599	h
3.11025556461552	-2.24817239337091	-2.94736841822973	h

$(H_3C)_3SiOC(CH_3)_3$			
Energies: SCSMP2 : -641.2599742, B3LYP : -642.2641297908, PBE : -641.8925998625			
-3.28085364381386	3.28808507268799	-0.96416853515470	c
0.00705549288816	2.35336465979574	0.07699334860519	si
0.98593070619270	4.34920923659732	2.85291914675116	c
2.27628878378293	2.85578762127115	-2.64147203359816	c
0.07863661774350	-0.59890157300911	1.23235118501427	o
-3.90145841897975	2.25126289309576	-2.65199431960691	h
-4.66172127932894	2.93768318671214	0.54801105331549	h
-3.33974218957259	5.31739972126855	-1.41558252880675	h
0.94821198210153	6.37018808012062	2.37006781412859	h
2.90953994923230	3.87008178915728	3.47130220608094	h
-0.29343385915439	4.04950337674398	4.46116109254916	h
2.28916541975273	4.86522508847685	-3.17888763436690	h
4.21655446518577	2.33101444594276	-2.11846469783292	h
1.74739272133440	1.76796067230548	-4.33045232034882	h
-0.00057838866292	-3.07118411505815	0.10052158017489	c
-0.78891016219055	-4.87209368293822	2.22671576868136	c
0.56193316960881	-4.75361769841171	3.79788857034929	h
-0.85219062911081	-6.83603508646332	1.55384440438210	h
-2.66726215910928	-4.35795608416661	2.94539923590702	h
2.64576486207047	-3.76406102848857	-0.86048453155428	c
4.02577671743913	-3.60835229358612	0.68221598327064	h
3.23651563257126	-2.50080556383892	-2.39763491650474	h
2.68256603814653	-5.71341898617799	-1.57856875063835	h
-1.92938029696544	-3.18273012029252	-2.05963441572880	c
-2.04255481924300	-5.10779749242358	-2.83213725510741	h
-1.39424396758498	-1.91137025965173	-3.61378237046773	h
-3.81666511096337	-2.64336021347928	-1.38425578031964	h

Table S2 (continued)

$(H_3P)_2CuOC(CH_3)_3{\cdot}(H_3C)_3SiH$ (r-complex)			
Energies: SCSMP2 : -2966.6926564, B3LYP : -2969.526743006, PBE : -2968.752048155			
-3.03560939832759	4.09355990694619	-2.78161500354556	c
0.17262385296500	4.69725380668578	-1.37909255562505	si
0.51434828785740	8.07093653848754	-0.23129214704367	c
0.08809249131904	-0.46806213948702	1.49231570174941	cu
3.45960969381345	-1.05837538549760	3.92748615023446	p
-3.80708939829675	-0.44968623520601	3.45792055514782	p
2.78995171430877	3.82252722829845	-3.62090008241376	c
-0.70525365660728	-1.60451300437679	-1.84615318886467	o
-3.18869920077545	2.06101779163136	-3.19093081885001	h
-4.56015368483709	4.64438052311085	-1.48211927706957	h
-3.28423748709776	5.16317149595798	-4.54642058260578	h
0.44833156298371	3.05947605967520	1.02284196197313	h
0.34005758553962	9.39931509415742	-1.82157703734495	h
2.36577738082714	8.38510839814330	0.65616201413468	h
-0.95318861425032	8.55233951601866	1.15737680997268	h
3.95997857045936	0.27867699333445	6.22532410205789	h
3.89134344721377	-3.51167020022399	4.96461721633557	h
5.94131621701059	-0.75646698851871	2.91218216286864	h
-4.65992097039661	-2.88471126969294	4.23986926351186	h
-4.80479424731155	0.85739503156884	5.61266682766931	h
-5.90004895680458	0.05986239434698	1.83822080333091	h
2.69571235689029	4.97263501733911	-5.34970047451937	h
4.66336149280006	4.09695150921840	-2.76790223725547	h
2.57184663184669	1.82374433610061	-4.13597608566865	h
-0.03184833736602	-3.97481633487329	-2.83785394166584	c
-1.23703901609285	-6.12128102941527	-1.27618048405360	c
-0.53210864098165	-6.04114466317448	0.68165515528088	h
-0.80867923659165	-8.00783216998457	-2.04437879547098	h
-3.30098658347115	-5.88181301395571	-1.23199553648894	h
2.85963084656586	-4.33750088027342	-2.87433089549741	c
3.41750037213602	-6.15597550101563	-3.71848075383966	h
3.60481459080497	-4.27635826840700	-0.93118649932999	h
3.75986974050724	-2.80954919347924	-3.95700417312115	h
-1.04112335186902	-4.09521057011360	-5.56798678870582	c
-3.10011122775250	-3.82127855516714	-5.56326425480915	h
-0.61608957042186	-5.91413618323672	-6.48271724529929	h
-0.19306273805138	-2.57386584043830	-6.70052550104562	h

Table S2 (continued)

$[(H_3P)_2CuH\cdot(H_3C)_3SiOC(CH_3)_3]$ (p-complex)

Energies: SCSMP2 : -2966.7098461, B3LYP : -2969.542472976, PBE : -2968.763757597

0.76082187640073	2.31510433556589	-7.48868098395333	c
0.58077494650540	2.17667556561383	-3.91599629510955	si
-1.47895356027461	4.79986991108266	-2.69643046230183	c
0.23339967138409	1.13397093996326	4.00287377786137	cu
2.97994854262010	-1.95852515305130	5.04211255393592	p
-3.95215762898185	0.38208217700960	3.74067343879329	p
3.85593317125631	2.51312625020506	-2.54838844109273	c
-0.87675512955574	-0.46689575617084	-2.87340778242543	o
1.97830469796220	0.83524787152374	-8.29115077560528	h
-1.11765211460606	2.14870818417804	-8.35885344724275	h
1.56109725880450	4.14737859305057	-8.06260365969783	h
1.29890144298032	3.84160446948562	3.71971367828264	h
-0.79070959672927	6.64350845208788	-3.36601738006342	h
-1.43422284566200	4.82577005932540	-0.61841595271215	h
-3.44476038674666	4.57911342247403	-3.32951607013356	h
4.18695906714037	-1.58104690349088	7.42317236985315	h
2.73199331875399	-4.64941211015677	5.31201155846055	h
5.25395037195394	-2.06982029247728	3.59854815671570	h
-5.36088925281146	-1.92798323711262	3.90698104923009	h
-5.50646337228080	1.75452428403772	5.46430243232256	h
-5.14156956048685	1.26242911099785	1.49257544002191	h
4.67514330195592	4.33433210163059	-3.13154801554956	h
3.75414819154626	2.51506775012702	-0.47071910631952	h
5.15219526892081	1.01320572600973	-3.16388119030336	h
-0.60866831059833	-3.09474328358554	-3.51843416276300	c
-1.86341186717828	-4.56296539682127	-1.35920762465984	c
-3.86347896183980	-4.02761609006645	-1.20023293468497	h
-0.92570791707978	-4.12848418010304	0.44291925168313	h
-1.75775566293077	-6.61095972235468	-1.68808377346427	h
-2.00193970536547	-3.63216048986075	-6.00556827684394	c
-1.98727544012073	-5.66564725044441	-6.43283890481226	h
-1.11386433302435	-2.63485540591153	-7.59244978027316	h
-3.97663831684398	-3.00809105444135	-5.86304820481816	h
2.18055583341065	-3.85332200094469	-3.73376967623825	c
3.19220526875438	-3.42931438676413	-1.97073732215090	h
3.11749873681805	-2.84036069283025	-5.28625409035611	h
2.35324061426360	-5.88868514397887	-4.11315726167196	h

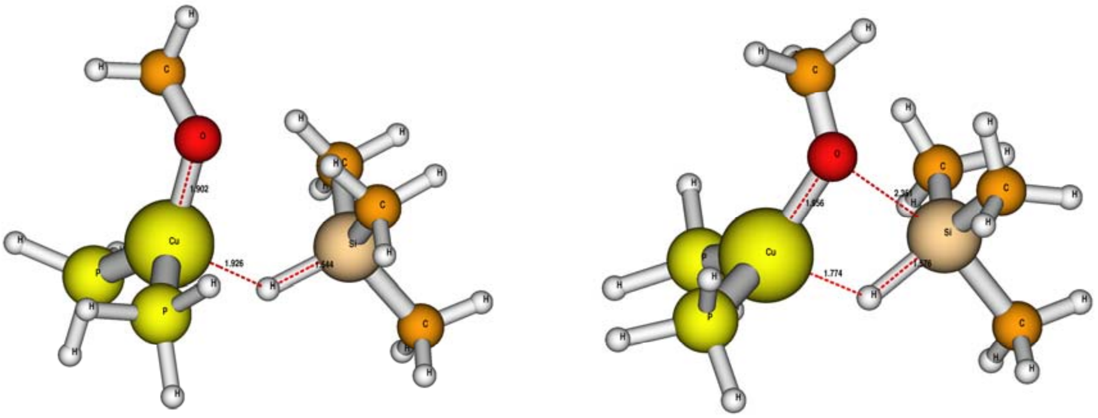
Table S2 (continued)

TS (highest point of Si-O reaction coordinate [r(Si-O) = 1.89 Å])

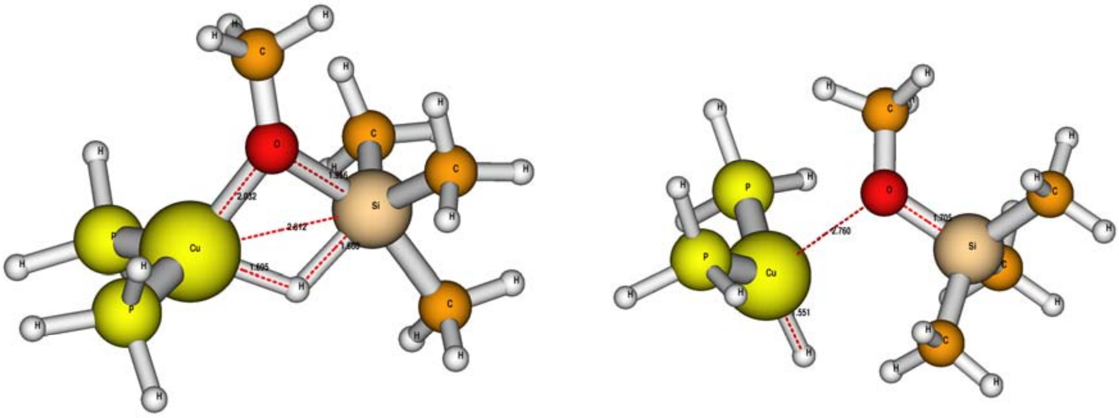
Energies: SCSMP2 : -2966.6841041, B3LYP : -2969.508147897, PBE : -2968.738233945

-3.17980170270270	0.34182708108108	-0.47207235135135	si
0.58075329729730	0.34182708108108	-0.47207235135135	o
2.68815329729730	2.04324008108108	-0.47207235135135	c
3.26407529729730	2.95654708108108	2.22857564864865	c
4.97600729729730	0.56350808108108	-1.47577035135135	c
2.20600829729730	4.31862908108108	-2.21354035135135	c
0.53675529729730	5.39517208108108	-1.61864835135135	h
1.91119829729730	3.68975908108108	-4.16880635135135	h
3.83884629729730	5.60294408108108	-2.19124235135135	h
6.69119229729730	1.73694408108108	-1.51498135135135	h
5.34570429729730	-1.08267591891892	-0.25639735135135	h
4.59749029729730	-0.11772591891892	-3.40097235135135	h
4.97695529729730	4.13242008108108	2.27993764864865	h
3.57448029729730	1.31680308108108	3.46988664864865	h
1.68987729729730	4.06203408108108	3.00183664864865	h
-3.43498870270270	3.17353808108108	1.73868064864865	c
-3.33516670270270	0.89359708108108	-4.02026135135135	c
-6.64837370270270	-0.87474591891892	-0.00707835135135	c
-3.18427670270270	2.54420508108108	3.70677164864865	h
-2.05596670270270	4.67939208108108	1.38637264864865	h
-5.34642870270270	3.97610008108108	1.60051264864865	h
-1.80815670270270	2.07421008108108	-4.76799835135135	h
-3.24407070270270	-0.94573791891892	-4.99037235135135	h
-5.16327070270270	1.75075008108108	-4.51504535135135	h
-8.04976370270270	0.57066008108108	-0.54742835135135	h
-7.00963670270270	-2.57197391891892	-1.15979635135135	h
-7.00796570270270	-1.38739491891892	1.98014564864865	h
-2.50623970270270	-2.52185491891892	0.49400064864865	h
0.54114429729730	-3.17388591891892	1.06756764864865	cu
1.35779529729730	-3.79875691891892	5.15717764864865	p
1.83561129729730	-6.19690791891892	-1.64777235135135	p
0.20901629729730	-2.21592991891892	7.01659964864865	h
3.85376429729730	-3.63276691891892	6.17617064864865	h
0.74372329729730	-6.13225591891892	6.36362764864865	h
4.33407129729730	-7.22440891891892	-1.74295935135135	h
1.64398929729730	-5.70462891891892	-4.29384435135135	h
0.57749429729730	-8.58245691891892	-1.71873135135135	h

Figure S1. Optimized structures (PBE/TZVPP) in the reaction of $(H_3P)_2CuOCH_3$ with $(H_3C)_3SiH$.

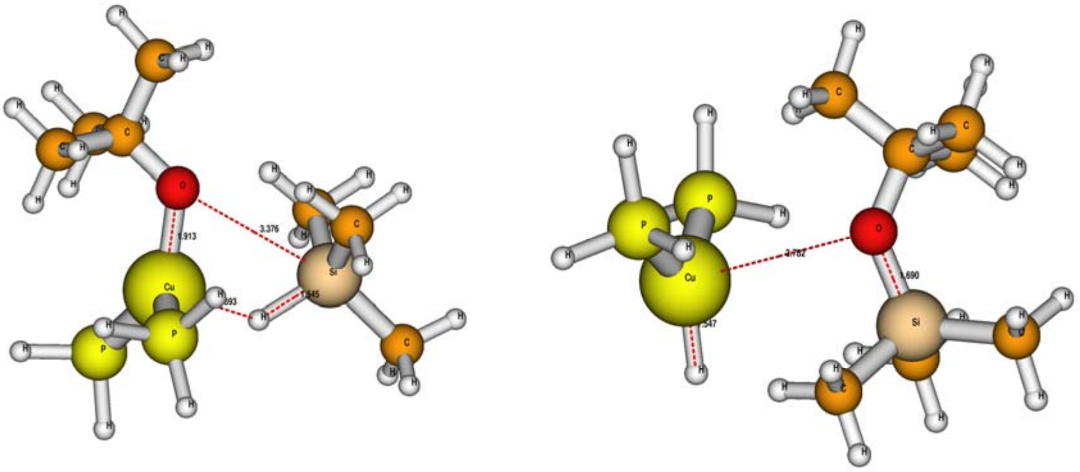


r-Complex TS



INT p-Complex

Figure S2. Optimized structures (PBE/TZVPP) of reactant and product complexes in the reaction of $(H_3P)_2CuOC(CH_3)_3$ with $(H_3C)_3SiH$.

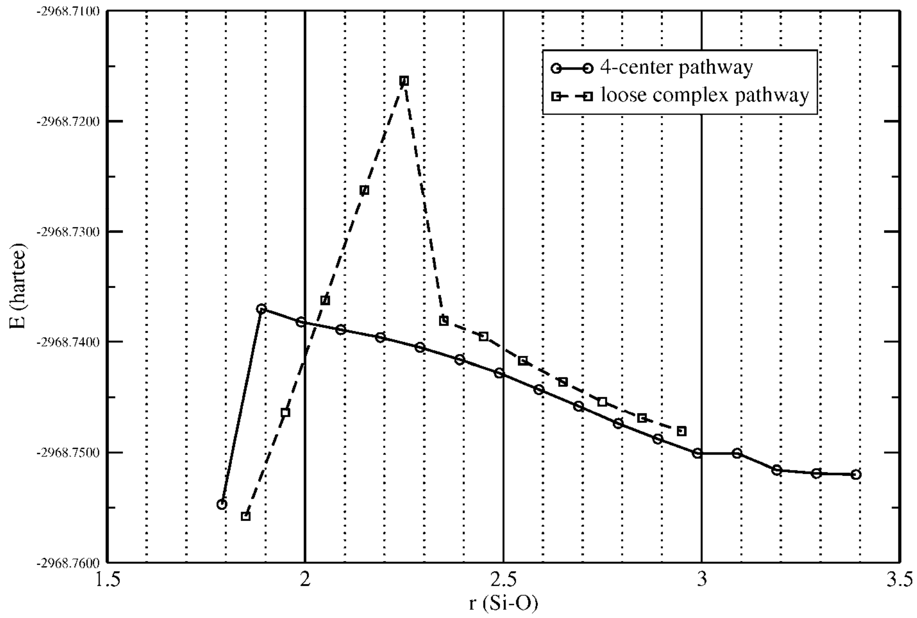


r-Complex

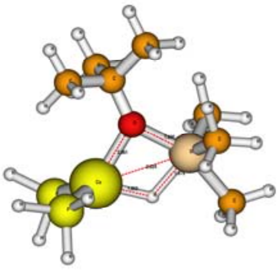
p-Complex

Figure S3. Two calculated (PBE/TZVPP) paths of the reaction of $(H_3P)_2CuOC(CH_3)_3$ with $(CH_3)_3SiH$. At each point, r(Si-O) was kept fixed and all other coordinates were fully optimized.

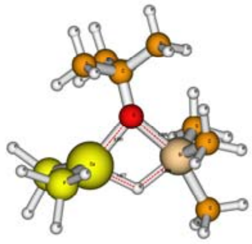
In the *4-center pathway*, the dihedral angle ($Cu-H-Si-CH_3$) is ≈ 0°. This allows the close approach of the CuH moiety. In the *loose complex pathway* (($Cu-H-Si-CH_3$) ≈ 180°), energies are lower at short Si-O distances due to less steric interactions, but there is also no short Si-H contact. This explains the high energies at r(Si-O) ≈ 2.2 Å. At longer Si-O distances, the $(H_3C)_3Si$ and *tert*-butyl group are rotated (($Cu-H-Si-CH_3$) ≈ 0°) and the system follows the 4-center pathway.



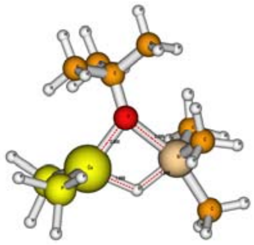
Selected structures on the 4-center pathway:



r(Si-O) = 1.89 Å

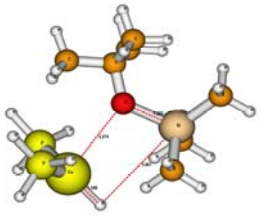


r(Si-O) = 1.99 Å

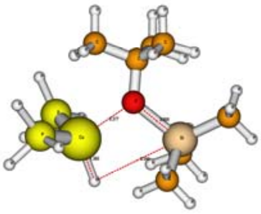


r(Si-O) = 2.09 Å

Selected structures on the loose complex pathway:



r(Si-O) = 1.95 Å



r(Si-O) = 2.05 Å