Supporting Information

Rhodium-catalyzed synthesis of Si-stereogenic alkoxysilanes and silyl enol ethers via hydrosilylation of carbonyl compounds

Yang Ding,^{‡a} Jie Ke,^{‡a} Wenbin Zhang,^c Bin Li,^{*b} and Chuan He^{*a}

^aShenzhen Grubbs Institute and Department of Chemistry, Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen, Guangdong 518055, China. ^bSchool of Environmental and Chemical Engineering, Wuyi University, Jiangmen, Guangdong 529020, China.

^cGuangdong Wamo New Material Technology CO., LTD, Jiangmen, Guangdong 529020, China. E-mail: <u>hec@sustech.edu.cn</u>; <u>andonlee@163.com</u>.

Table of Contents

| 1. | General Information | |
|----|---|-----|
| 2. | Reaction Optimization | S4 |
| 3. | General Procedure for the Hydrosilylation of Carbonyl Compounds | |
| 4. | Characterization of Products | |
| 5. | Gram-Scale Reaction and Synthetic Application | S21 |
| 6. | Single Crystal X-Ray Diffraction | S25 |
| 7. | References | S27 |
| 8. | NMR Spectra | S28 |
| 9. | HPLC Chromatography | |

1. General Information

Regular reactions were carried out under an argon atmosphere with magnetic stirring. Catalytic reactions were performed in a colorless 10 mL microwave reaction tube under an inert argon atmosphere. Unless otherwise noted, anhydrous solvents were obtained from the Inert Pure Solv solvent purification system (THF and toluene). Flash chromatography was performed using GENERAL-REAGENT silica gel (200-300 mech). Unless otherwise specified, all reagents were purchased from commercial suppliers (Adamas, Bide Pharmatech, Energy Chemical, TCI, Aldrich, Alfa, and J&K) and directly used without further purification. Tert-butyl(phenyl)silane **1a** or other dihydrosilanes **1b-1d**¹ and mono- α -arylation of ketones² are known compounds and synthesized according to the reported literature.

NMR spectra were recorded on Bruker DRX-400 or DPX-600 spectrometers at 400 MHz for ¹H NMR, 101 MHz for ¹³C NMR, and 376 MHz for ¹⁹F NMR or 600 MHz for ¹H NMR, 151 MHz for ¹³C NMR, and 565 MHz for ¹⁹F NMR, respectively, at ambient temperature. NMR standards were used as follows: $(^{1}H NMR) TMS = 0 ppm$; $(^{13}C NMR) CDCl_3 = 77.23 ppm$. Chemical shifts (δ) were reported in ppm and coupling constants (J) were quoted in Hertz (Hz). ¹H NMR data were recorded as follows: Chemical shifts (δ , ppm), multiplicities (s = singlet; d = doublet; dd = doublet of doublets; t = triplet; td = triplet of doublets; q = quartet; m = multiplet), coupling constant (Hz), integration. ¹³C NMR data were reported in terms of chemical shift (δ , ppm). High-resolution mass spectra (HRMS) were performed on an Agilent Technologies 6230 TOF LC/MS spectrometer by electrospray ionization (ESI). X-ray single-crystal diffraction data were collected on Bruker D8 VENTURE. HPLC analyses were performed on Agilent 1260 Infinity II. Chiral columns OD-3, OJ-3, OD-H and OJ-H were purchased from Daicel®. Optical rotation was measured on Rudolph Automatic Polarimeter at 589 nm and 25.2 °C. Data are reported as follows: [a]_D^{temp}, concentration (c in g/100 mL), and solvent.

2. Reaction Optimization

Table S1. Optimization of the reaction time^a



| Entry | Time (h) | 3a Yield [%] ^b | 3a er ^c |
|-------|----------|----------------------------------|---------------------------|
| 1 | 1 | 25 | 94:6 |
| 2 | 2 | 36 | 94:6 |
| 3 | 4 | 43 | 94:6 |
| 4 | 6 | 63 | 94:6 |
| 5 | 12 | 94 | 94:6 |
| 6 | 18 | 93 | 94:6 |
| 7 | 24 | 43 | 94:6 |
| 8 | 48 | 43 | 94:6 |

^{*a*}Reaction conditions: **1a** (0.11 mmol), **2a** (0.1 mmol), [Rh(cod)Cl]₂ (1 mol%), **L6** (2.2 mol%) in toluene (1.0 mL) at room temperature under argon for different time; ^{*b*}NMR yield with 1,1,2,2-tetrachloroethane as standard; ^{*c*}The enantiomeric ratio was determined by chiral HPLC.

3. General Procedure for the Hydrosilylation of Carbonyl Compounds

General procedure for the synthesis of Si-stereogenic alkoxysilanes



Procedure A: Inside an argon-filled glovebox, an oven-dried 10 mL microwave reaction tube was charged with $[Rh(cod)Cl]_2$ (1 mol%), L6 (2.2 mol%) and anhydrous toluene (2.0 mL). After being stirred at room temperature for 10 min, followed by the addition of dihydrosilane substrates 1 (0.22 mmol, 1.1 equiv). The solution was allowed to stir at room temperature for 10 min, and the aldehyde or ketone 2 (0.2 mmol) was added. The tube was capped and taken outside of the glovebox. Then, the resulting mixture was stirred at room temperature for 12 h. After the reaction was completed, the reaction mixture was filtered through a short silica gel pad and evaporated under reduced pressure, then purified by flash chromatography on silica gel to afford the target product. The enantiomeric ratio was determined by chiral HPLC analysis. Corresponding racemic samples were obtained by carrying out the reactions at identical conditions with racemic BINAP.

General procedure for the synthesis of Si-stereogenic silyl enol ethers



Procedure B: Inside an argon-filled glovebox, an oven-dried 10 mL microwave reaction tube was charged with [Rh(cod)Cl]₂ (1 mol%), **L6** (2.2 mol%) and anhydrous tetrahydrofuran (2.0 mL). After being stirred at room temperature for 10 min, followed

by the addition of *tert*-butyl(phenyl)silane **1a** (0.22 mmol, 1.1 equiv). The solution was allowed to stir at room temperature for 10 min, and α,β -unsaturated ketones **2o-2r** (0.2 mmol) was added. The tube was capped and taken outside of the glovebox. Then the resulting mixture was stirred at room temperature for 12 h. After the reaction was completed, the reaction mixture was filtered through a short silica gel pad and evaporated under reduced pressure, then purified by flash chromatography on silica gel to afford the target product. The enantiomeric ratio was determined by chiral HPLC analysis. Corresponding racemic samples were obtained by carrying out the reactions at identical conditions with (\pm)-L6.

4. Characterization of Products

(S)-(Benzyloxy)(tert-butyl)(phenyl)silane (3a)

Ph, H tBu Si O

The reaction was performed according to **Procedure A** with the corresponding aldehyde (21.2 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3a** as a colorless oil (49.5 mg, 92% yield). The enantiomeric ratio was established as 94:6 *er* by HPLC analysis using a Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 100:0, 0.4 mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (major) = 12.89 min, tr (minor) = 13.59 min. [α] $\rho^{25.2}$ = -27.1 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.59 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.43-7.35 (m, 3H), 7.32 (d, *J* = 4.4 Hz, 4H), 7.27-7.23 (m, 1H), 4.83-4.74 (m, 3H), 1.00 (s, 9H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 140.8, 134.8, 133.7, 130.3, 128.4, 128.0, 127.3, 126.5, 67.0, 25.9, 18.3 ppm.

HRMS (ESI, m/z) [M - H]⁻ calcd for [C₂₈H₂₅Si]⁻: 269.1367; found: 269.1365.

(S)-tert-Butyl((4-methylbenzyl)oxy)(phenyl)silane (3b)



The reaction was performed according to **Procedure A** with the corresponding aldehyde (24.0 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3b** as a colorless oil

(52.3 mg, 92% yield). The enantiomeric ratio was established as 90:10 *er* by HPLC analysis using a Daicel Chiralpak OJ-H column (*n*-hexane/isopropanol = 98:2, 0.6 mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (minor) = 7.35 min, tr (major) = 11.40 min. [α]_D^{25.2} = -40.4 (c = 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃): δ 7.61-7.57 (m, 2H), 7.45-7.35 (m, 3H), 7.23-7.19 (m, 2H), 7.14-7.12 (m, 2H), 4.74 (d, *J* = 4.9 Hz, 3H), 2.33 (s, 3H), 0.98 (s, 9H) ppm.
¹³C NMR (101 MHz, CDCl₃): δ 137.8, 136.9, 134.8, 133.8, 130.2, 129.1, 128.0, 126.7, 66.9, 25.9, 21.4, 18.3 ppm.

HRMS (ESI, m/z) [M - H]⁻ calcd for [C₁₈H₂₃OSi]⁻: 283.1524.; found: 283.1519.

(S)-tert-Butyl((4-(methylthio)benzyl)oxy)(phenyl)silane (3c)



The reaction was performed according to **Procedure A** with the corresponding aldehyde (30.4 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3c** as a colorless oil (50.6 mg, 80% yield). The enantiomeric ratio was established as 94:6 *er* by HPLC analysis using a Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 100:0, 1 mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (minor) = 9.45 min, tr (major) = 10.97 min. [α]p^{25.2} = -35.5 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.61-7.55 (m, 2H), 7.45-7.35 (m, 3H), 7.23 (d, *J* = 0.9 Hz, 4H), 4.76-4.69 (m, 3H), 2.47 (s, 3H), 0.99 (s, 9H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 137.8, 137.2, 134.8, 133.6, 130.3, 128.0, 127.2, 127.0, 66.6, 25.9, 18.3, 16.3 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{18}H_{25}OSSi]^+$: 317.1390; found: 317.1386.

(S)-tert-Butyl(phenyl)((4-(trifluoromethyl)benzyl)oxy)silane (3d)

Ph, H tBu CF₃

The reaction was performed according to **Procedure A** with the corresponding aldehyde (34.8 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3d** as a colorless oil (58.8 mg, 87% yield). The enantiomeric ratio was established as 93:7 *er* by HPLC analysis using a Daicel Chiralpak OJ-H column (*n*-hexane/isopropanol = 98:2, 0.6 mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (minor) = 6.69 min, tr (major) = 14.33 min. [α] $p^{25.2}$ = -33.2 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.60-7.56 (m, 4H), 7.46-7.36 (m, 5H), 4.82 (s, 2H), 4.77 (s, 1H), 1.01 (s, 9H) ppm.

¹³**C NMR** (101 MHz, CDCl₃): δ 144.8, 134.7, 133.3, 130.5, 129.5 (q, *J* = 32.3 Hz), 128.1, 126.5, 125.8, 125.4 (q, *J* = 3.9 Hz), 66.3, 25.8, 18.3 ppm.

¹⁹**F NMR** of **3d** (565 MHz, CDCl₃) δ -62.5 ppm

HRMS (ESI, m/z) [M - H]⁻ calcd for [C₁₈H₂₀F₃OSi]⁻: 337.1241; found: 337.1245.

(S)-4-(((tert-Butyl(phenyl)silyl)oxy)methyl)benzonitrile (3e)

Ph, H tBu Si O

The reaction was performed according to **Procedure A** with the corresponding aldehyde (26.2 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford product **3e** as a colorless oil (38.4 mg, 65% yield). The enantiomeric ratio was established as 94:6 *er* by HPLC analysis using a Daicel Chiralpak OD-3 column (*n*-

hexane/isopropanol = 100:0, 1 mL/min), λ = 220 nm, temperature = 28 °C, tr (minor) = 25.54 min, tr (major) = 28.00 min. [α]_D^{25.2} = -6.1 (c = 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 7.64-7.55 (m, 4H), 7.45-7.36 (m, 5H), 4.81 (s, 2H), 4.76 (s, 1H), 1.01 (s, 9H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 146.3, 134.7, 133.0, 132.3, 130.5, 128.2, 126.7, 119.2, 111.0, 66.1, 25.8, 18.3 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{18}H_{22}NOSi]^+$: 296.1465; found: 296.1462.

(S)-tert-Butyl(phenyl)((3-(trifluoromethoxy)benzyl)oxy)silane (3f)



The reaction was performed according to **Procedure A** with the corresponding aldehyde (38.0 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3f** as a colorless oil (50.6 mg, 70% yield). The enantiomeric ratio was established as 93:7 *er* by HPLC analysis using a Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 100:0, 0.4 mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (minor) = 11.50 min, tr (major) = 11.80 min. [α] $p^{25.2} = -43.2$ (c = 1.0, CHCl₃).

¹**H NMR** (600 MHz, CDCl₃): δ 7.59-7.56 (m, 2H), 7.45-7.42 (m, 1H), 7.40-7.36 (m, 2H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.24-7.20 (m, 2H), 7.10-7.07 (m, 1H), 4.81-4.75 (m, 3H), 1.01 (s, 9H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ 149.6 (q, J = 15.1 Hz), 143.3, 134.7, 133.3, 130.4, 129.8, 128.1, 124.5, 120.7 (q, J = 256.7 Hz), 119.6, 118.8, 66.1, 25.8, 18.3 ppm.
¹⁹F NMR (565 MHz, CDCl₃): δ -57.7 ppm.

HRMS (ESI, m/z) [M - H]⁻ calcd for [C₁₈H₂₀F₃O₂Si]⁻: 353.1190; found: 353.1196.

(S)-tert-Butyl((2-methylbenzyl)oxy)(phenyl)silane (3g)



The reaction was performed according to **Procedure A** with the corresponding aldehyde (24.0 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3g** as a white solid (52.4 mg, 94% yield). The enantiomeric ratio was established as 97:3 *er* by HPLC analysis using a Daicel Chiralpak OJ-H column (*n*-hexane/isopropanol = 98:2, 0.6 mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (minor) = 6.97 min, tr (major) = 16.22 min. [α]p^{25.2} = -41.7 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.59 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.45-7.34 (m, 4H), 7.21-7.10 (m, 3H), 4.79-4.71 (m, 3H), 2.24 (s, 3H), 0.99 (s, 9H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 138.6, 135.6, 134.8, 133.7, 130.3, 130.1, 128.0, 127.4, 127.0, 126.0, 65.4, 25.9, 18.8, 18.3 ppm.

HRMS (ESI, m/z) [M - H]⁻ calcd for [C₁₈H₂₃OSi]⁻: 283.1524.; found: 283.1518.

(S)-tert-Butyl((2-chlorobenzyl)oxy)(phenyl)silane (3h)



The reaction was performed according to **Procedure A** with the corresponding aldehyde (28.0 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3h** as a white solid (49.3 mg, 81% yield). The enantiomeric ratio was established as 95:5 *er* by HPLC analysis using a Daicel Chiralpak OJ-H column (*n*-hexane/isopropanol = 96:4, 1

mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (minor) = 3.37 min, tr (major) = 3.82 min. $[\alpha]_D^{25.2} = -51.5$ (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.64-7.57 (m, 3H), 7.46-7.36 (m, 3H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.22-7.16 (m, 1H), 4.86 (s, 2H), 4.80 (s, 1H), 1.02 (s, 9H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 138.3, 134.7, 133.4, 131.8, 130.4, 129.1, 128.3, 128.1, 127.7, 126.9, 64.4, 25.9, 18.4 ppm.

HRMS (ESI, m/z) [M - H]⁻ calcd for [C₁₇H₂₀OClSi]⁻: 303.0977.; found: 303.0971.

(S)-((2-Bromobenzyl)oxy)(tert-butyl)(phenyl)silane (3i)



The reaction was performed according to **Procedure A** with the corresponding aldehyde (36.8 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3i** as a white solid (60.6 mg, 87% yield). The enantiomeric ratio was established as 96:4 *er* by HPLC analysis using a Daicel Chiralpak OJ-H column (*n*-hexane/isopropanol = 96:4, 1 mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (minor) = 3.43 min, tr (major) = 3.95 min. [α] $p^{25.2}$ = -54.3 (c = 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃): δ 7.63-7.57 (m, 3H), 7.48 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.44-7.36 (m, 3H), 7.36-7.31 (m, 1H), 7.15-7.09 (m, 1H), 4.81 (s, 3H), 1.02 (s, 9H) ppm.
¹³C NMR (101 MHz, CDCl₃): δ 139.8, 134.7, 133.4, 132.4, 130.4, 128.6, 128.1, 127.9, 127.5, 121.5, 66.7, 25.9, 18.4 ppm.

HRMS (ESI, m/z) [M - H]⁻ calcd for [C₁₇H₂₀OBrSi]⁻: 347.0472; found: 347.0468.

(S)-tert-Butyl(naphthalen-1-ylmethoxy)(phenyl)silane (3j)

Ph, H tBu O

The reaction was performed according to **Procedure A** with the corresponding aldehyde (31.2 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3j** as a colorless oil (38.4 mg, 88% yield). The enantiomeric ratio was established as 95:5 *er* by HPLC analysis using a Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 100:0, 1 mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (major) = 17.35 min, tr (minor) = 18.86 min. [α] $_{D}^{25.2}$ = -55.8 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 8.00-7.94 (m, 1H), 7.86-7.82 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.62-7.58 (m, 2H), 7.56-7.53 (m, 1H), 7.49-7.33 (m, 6H), 5.28-5.19 (m, 2H), 4.79 (s, 1H), 0.99 (s, 9H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 136.0, 134.8, 133.7(4), 133.6(8), 131.1, 130.3, 128.8, 128.1, 128.0, 126.1, 125.8, 125.6, 124.5, 123.7, 65.5, 25.9, 18.3 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{21}H_{25}OSi]^+$: 369.1669; found: 369.1667.

(S)-(Benzo[b]thiophen-3-ylmethoxy)(tert-butyl)(phenyl)silane (3k)

The reaction was performed according to **Procedure A** with the corresponding aldehyde (32.4 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3k** as a white solid (58.7 mg, 90% yield). The enantiomeric ratio was established as 93:7 *er* by HPLC analysis using a Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 100:0, 1 mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (major) = 13.60 min, tr (minor) = 14.60 min. [α] $\rho^{25.2}$ = -44.3 (c = 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃): δ 7.85-7.80 (m, 1H), 7.76-7.72 (m, 1H), 7.61-7.56 (m, 2H), 7.45-7.29 (m, 6H), 5.05-4.95 (m, 2H), 4.76 (s, 1H), 0.98 (s, 9H) ppm.
¹³C NMR (101 MHz, CDCl₃): δ 140.9, 137.9, 135.8, 134.8, 133.5, 130.3, 128.1, 124.5, 124.1, 123.2, 123.0, 122.2, 62.4, 25.9, 18.3 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{19}H_{23}OSSi]^+$: 327.1233; found: 327.1233.

(S)-tert-Butyl((2,2-difluorobenzo[d][1,3]dioxol-5-yl)methoxy)(phenyl)silane (3l)



The reaction was performed according to **Procedure A** with the corresponding aldehyde (37.2 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3l** as a colorless oil (57.4 mg, 82% yield). The enantiomeric ratio was established as 94:6 *er* by HPLC analysis using a Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 100:0, 1 mL/min), $\lambda = 280$ nm, temperature = 28 °C, tr (minor) = 5.76 min, tr (major) = 5.92 min. [α] $p^{25.2} = -27.4$ (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.59-7.54 (m, 2H), 7.46-7.35 (m, 3H), 7.07 (t, *J* = 1.0 Hz, 1H), 6.96 (d, *J* = 1.1 Hz, 2H), 4.76-4.69 (m, 3H), 1.00 (s, 9H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ 144.1, 143.0, 137.1, 134.7, 133.3, 131.9 (t, *J* = 255.2 Hz), 130.5, 128.1, 121.5, 109.2, 108.2, 66.5, 25.8, 18.3 ppm.

¹⁹**F NMR** (565 MHz, CDCl₃) δ -50.0 ppm

HRMS (ESI, m/z) [M - H]⁻ calcd for [C₁₈H₁₉F₂O₃Si]⁻: 349.1077; found: 349.1074.

(S)-(Benzhydryloxy)(tert-butyl)(phenyl)silane (3m)

Ph, H PII tBu Si O

The reaction was performed according to **Procedure A** with the corresponding ketone (91.0 mg, 0.5 mmol), **1a** (90.3 mg, 0.55 mmol), [Rh(cod)Cl]₂ (2.5 mg, 1 mol%), **L6** (5.8 mg, 2.2 mol%) in anhydrous toluene (5.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3m** as a colorless oil (147.1 mg, 85% yield). The enantiomeric ratio was established as 95:5 *er* by HPLC analysis using a Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 100:0, 0.4 mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (major) = 14.23 min, tr (minor) = 16.11 min. [α] $p^{25.2} = -23.6$ (c = 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃): δ 7.49-7.45 (m, 2H), 7.42-7.36 (m, 1H), 7.35-7.27 (m, 8H), 7.26-7.24 (m, 2H), 7.23-7.16 (m, 2H), 5.75 (s, 1H), 4.61 (s, 1H), 0.98 (s, 9H) ppm.
¹³C NMR (101 MHz, CDCl₃): δ 144.6, 144.1, 134.9, 133.5, 130.2, 128.5, 128.4, 127.9, 127.5, 127.2, 127.0, 126.5, 78.2, 25.9, 18.3 ppm.

HRMS (ESI, m/z) [M - H]⁻ calcd for [C₂₃H₂₅OSi]⁻: 345.1680; found: 345.1674.

(1S)-tert-Butyl(1,2-diphenylethoxy)(phenyl)silane (3n)



The reaction was performed according to **Procedure A** with the corresponding ketone (39.2 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (2.0 mg, 2 mol%), **L6** (4.6 mg, 4.4 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3n** as a colorless oil (59.8 mg, 83% yield). The enantiomeric ratio of major configuration was established as 99:1 *er* by HPLC analysis using a Daicel Chiralpak OD-H+OD-3 column (*n*-hexane/isopropanol = 100:0, 0.4 mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (minor) = 25.98 min, tr (major) = 27.23 min. [α] $\rho^{25.2} = -93.0$ (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.32 (dd, *J* = 24.7, 6.9 Hz, 4H), 7.25-7.19 (m, 7H), 7.14-7.07 (m, 4H), 4.74 (dd, *J* = 8.4, 4.4 Hz, 1H), 4.36 (s, 1H), 3.04-2.87 (m, 2H), 0.88 (s, 9H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 143.9, 138.9, 134.9, 133.4, 130.3, 129.9, 128.3, 128.2, 127.7, 127.5, 126.4, 126.3, 77.9, 47.7, 25.8, 18.1 ppm.

HRMS (ESI, m/z) [M - H]⁻ calcd for [C₂₄H₂₇OSi]⁻: 359.1837; found: 359.1837.

(S)-tert-Butyl(cyclopent-1-en-1-yloxy)(phenyl)silane (30)

Ph, H tBu Si O

The reaction was performed according to **Procedure B** with the corresponding α,β unsaturated ketone (16.4 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (2.0 mg, 2 mol%), **L6** (4.6 mg, 4.4 mol%) in anhydrous tetrahydrofuran (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3o** as a colorless oil (30.0 mg, 61% yield). The enantiomeric ratio was established as 97:3 *er* by HPLC analysis using a Daicel Chiralpak OJ-3 column (*n*-hexane/isopropanol = 100:0, 0.15 mL/min), λ = 220 nm, temperature = 28 °C, tr (minor) = 23.91 min, tr (major) = 25.11 min. [α]_D^{25.2} = -45.6 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.58 (m, 2H), 7.42-7.34 (m, 3H), 4.85 (s, 1H), 4.60 (p, *J* = 2.1 Hz, 1H), 2.34-2.27 (m, 2H), 2.22-2.16 (m, 2H), 1.82 (p, *J* = 7.4 Hz, 2H), 0.98 (s, 9H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 156.0, 134.5, 133.4, 130.3, 128.0, 102.5, 33.0, 28.8, 25.7, 21.5, 18.1 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{15}H_{23}OSi]^+$: 247.1513; found: 247.1513.

(S)-tert-Butyl(cyclohex-1-en-1-yloxy)(phenyl)silane (3p)

Ph, H tBu Si

The reaction was performed according to **Procedure B** with the corresponding α,β unsaturated ketone (19.2 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (2.0 mg, 2 mol%), **L6** (4.6 mg, 4.4 mol%) in anhydrous tetrahydrofuran (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3p** as a colorless oil (46.3 mg, 89% yield). The enantiomeric ratio was established as 97.5:2.5 *er* by HPLC analysis using a Daicel Chiralpak OJ-3 column (*n*-hexane/isopropanol = 100:0, 0.15 mL/min), $\lambda = 220$ nm, temperature = 28 °C, tr (minor) = 23.98 min, tr (major) = 25.46 min. [α] $p^{25.2} = -47.6$ (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.60-7.56 (m, 2H), 7.44-7.34 (m, 3H), 4.89-4.86 (m, 1H), 4.83 (s, 1H), 2.10-2.04 (m, 2H), 1.97-1.90 (m, 2H), 1.67-1.60 (m, 2H), 1.50-1.43 (m, 2H), 0.97 (s, 9H) ppm.

¹³**C NMR** (101 MHz, CDCl₃): δ 151.4, 134.5, 134.0, 130.2, 127.9, 104.0, 29.4, 25.7, 23.9, 23.2, 22.4, 18.1 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{16}H_{25}OSi]^+$: 261.1669; found: 261.1668.

(S)-((1,4-Dioxaspiro[4.5]dec-7-en-8-yl)oxy)(tert-butyl)(phenyl)silane (3q)



The reaction was performed according to **Procedure B** with the corresponding α,β unsaturated ketone (30.8 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (2.0 mg, 2 mol%), **L6** (4.6 mg, 4.4 mol%) in anhydrous tetrahydrofuran (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford product **3q** as a colorless oil (39.5 mg, 62% yield). The enantiomeric ratio was established as 96.5:3.5 *er* by HPLC analysis using a Daicel Chiralpak OJ-H column (*n*hexane/isopropanol = 98:2, 0.4 mL/min), λ = 220 nm, temperature = 28 °C, tr (major) = 12.04 min, tr (minor) = 14.31 min. [α] ρ ^{25.2} = -8.5 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.60-7.56 (m, 2H), 7.44-7.34 (m, 3H), 4.85 (s, 1H), 4.75-4.70 (m, 1H), 3.97-3.93 (m, 4H), 2.34-2.28 (m, 2H), 2.22-2.17 (m, 2H), 1.83-1.76 (m, 2H), 0.96 (s, 9H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 150.8, 134.5, 133.6, 130.2, 127.9, 107.9, 100.4, 64.6(1), 64.5(9), 34.0, 31.3, 28.1, 25.7, 18.1 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{18}H_{27}O_3Si]^+$: 319.1724; found: 319.1723.

(1*S*)-*tert*-Butyl(((*S*)-3-methylcyclohex-1-en-1-yl)oxy)(phenyl)silane (3r)

Ph, H tBu Si O Me

The reaction was performed according to **Procedure B** with the corresponding α, β unsaturated ketone (22.0 mg, 0.2 mmol), **1a** (36.1 mg, 0.22 mmol), [Rh(cod)Cl]₂ (2.0 mg, 2 mol%), **L6** (4.6 mg, 4.4 mol%) in anhydrous tetrahydrofuran (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford product **3r** as a colorless oil (36.7 mg, 67% yield). The enantiomeric ratio was established as 96:4 *er* by HPLC analysis using a Daicel Chiralpak OJ-H+OJ-3 column (*n*hexane/isopropanol = 100:0, 0.3 mL/min), λ = 220 nm, temperature = 28 °C, tr (minor) = 23.98 min, tr (major) = 25.23 min. [α] ρ ^{25.2} = -18.7 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.60-7.56 (m, 2H), 7.44-7.34 (m, 3H), 4.84 (s, 1H), 4.76-4.74 (m, 1H), 2.20-2.12 (m, 1H), 2.06-2.01 (m, 2H), 1.78-1.69 (m, 1H), 1.68-1.60 (m, 1H), 1.54-1.46 (m, 1H), 0.97 (s, 9H), 0.89 (d, *J* = 6.9 Hz, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 151.1, 134.6, 133.9 130.1, 127.9, 110.6, 31.2, 29.6, 29.3, 25.8, 22.5, 21.9, 18.2 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{17}H_{27}OSi]^+$: 275.1826; found: 275.1822.

(S)-Cyclohexyl((2-methylbenzyl)oxy)(phenyl)silane (3s)



The reaction was performed according to **Procedure A** with 2-methylbenzaldehyde (24.0 mg, 0.2 mmol), cyclohexyl(phenyl)silane (41.8 mg, 0.22 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was

purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 30:1) to afford product **3s** as a colorless oil (42.2 mg, 68% yield). The enantiomeric ratio was established as 98:2 *er* by HPLC analysis using a Daicel Chiralpak OD-3 column (*n*hexane/isopropanol = 100:0, 1 mL/min), λ = 250 nm, temperature = 28 °C, tr (minor) = 13.76 min, tr (major) = 15.31 min. [α]p^{25.2} = -10.1 (c = 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 7.60-7.56 (m, 2H), 7.44-7.33 (m, 4H), 7.19-7.15 (m, 2H), 7.14-7.09 (m, 1H), 4.82 (d, *J* = 2.0 Hz, 1H), 4.73 (s, 2H), 2.24 (s, 3H), 1.89-1.83 (m, 1H), 1.77-1.62 (m, 6H), 1.29-1.23 (m, 3H), 1.12-1.02 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 138.4, 135.7, 134.6, 134.2, 130.2, 130.1, 128.1, 127.5, 127.2, 126.0, 65.3, 27.7(6), 27.7(4), 27.0, 26.9, 26.8, 25.3, 18.8 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{20}H_{27}OSi]^+$: 311.1826; found: 311.1826.

(S)-Cyclohexyl(2-methoxyphenyl)((2-methylbenzyl)oxy)silane (3t)



The reaction was performed according to **Procedure A** with the 2-methylbenzaldehyde aldehyde (24.0 mg, 0.2 mmol), cyclohexyl(2-methoxyphenyl)silane (48.4 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 30:1) to afford product **3t** as a colorless oil (57.8 mg, 85% yield). The enantiomeric ratio was established as 90:10 *er* by HPLC analysis using a Daicel Chiralpak OD-H+OD-3 column (*n*-hexane/isopropanol = 99.5:0.5, 1 mL/min), λ = 220 nm, temperature = 28 °C, tr (major) = 23.96 min, tr (minor) = 24.90 min. [α]p^{25.2} = -12.8 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.50-7.47 (m, 1H), 7.43-7.36 (m, 2H), 7.21-7.13 (m, 2H), 7.12-7.09 (m, 1H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 4.85 (d, *J* =

1.8 Hz, 1H), 4.75 (s, 2H), 3.77 (s, 3H), 2.24 (s, 3H), 1.84 (d, J = 11.7 Hz, 1H), 1.741.63 (m, 5H), 1.26-1.20 (m, 5H) ppm.
¹³C NMR (101 MHz, CDCl₃): δ 164.4, 138.8, 136.6, 135.5, 132.0, 130.0, 127.2, 127.1, 125.9, 122.5, 120.8, 109.7, 65.3, 55.2, 27.8(8), 27.8(6), 27.3, 27.1, 27.0, 25.1, 18.8 ppm.
HRMS (ESI, m/z) [M + H]⁺ calcd for [C₂₁H₂₉O₂Si]⁺: 341.1931; found: 341.1931.

(S)-Cyclohexyl((2-methylbenzyl)oxy)(naphthalen-1-yl)silane (3u)



The reaction was performed according to **Procedure A** with the 2-methylbenzaldehyde aldehyde (24.0 mg, 0.2 mmol), cyclohexyl(naphthalen-2-yl)silane (52.8 mg, 0.22 mmol), [Rh(cod)Cl]₂ (1.0 mg, 1 mol%), **L6** (2.3 mg, 2.2 mol%) in anhydrous toluene (2.0 mL) at room temperature for 12 h. After the solvent was removed under vacuum, the residue was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 30:1) to afford product **3u** as a colorless oil (53.3 mg, 73% yield). The enantiomeric ratio was established as 90:10 *er* by HPLC analysis using a Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 100:0, 1 mL/min), λ = 220 nm, temperature = 28 °C, tr (major) = 23.96 min, tr (minor) = 24.90 min. [α] $p^{25.2}$ = -12.8 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 8.27-8.21 (m, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.88-7.84 (m, 1H), 7.79 (dd, *J* = 6.7, 1.3 Hz, 1H), 7.52-7.47 (m, 3H), 7.39-7.35 (m, 1H), 7.19-7.14 (m, 2H), 7.12-7.08 (m, 1H), 5.13 (d, *J* = 1.8 Hz, 1H), 4.73 (s, 2H), 2.22 (s, 3H), 1.93 (d, *J* = 13.5 Hz, 1H), 1.6-1.69 (m, 1H), 1.66-1.57 (m, 3H), 1.28-1.13 (m, 6H) ppm. ¹³**C NMR** (101 MHz, CDCl₃): δ 138.4, 137.4, 135.8, 135.2, 133.4, 132.7, 130.9, 130.1, 129.0, 128.2, 127.5, 127.4, 126.4, 126.0, 125.9, 125.3, 65.4, 27.8, 27.7, 27.5, 27.1, 26.9, 25.8, 18.9 ppm.

HRMS (ESI, m/z) [M - H]⁻ calcd for [C₂₄H₂₇OSi]⁻: 359.1837; found: 359.1836.

5. Gram-Scale Reaction and Synthetic Application



Procedure for Gram-Scale reaction: Inside an argon-filled glovebox, a 200 mL oneneck round bottom flask was charged with $[Rh(cod)Cl]_2$ (22.2 mg, 1 mol%), L6 (53.0 mg, 2.2 mol%) and anhydrous toluene (45 mL). After being stirred at room temperature for 10 min, followed by the addition of *tert*-butyl(phenyl)silane (812.3 mg, 4.95 mmol). The solution was allowed to stir at room temperature for 10 min, and the 2methylbenzaldehyde (540 mg, 4.5 mmol) was added. Sealed the round bottom and took it outside of the glove box. Then, the resulting mixture was stirred at room temperature for 12 h. After the reaction was completed, the reaction mixture was evaporated under reduced pressure. the residue was purified by flash chromatography on silica gel (petroleum ether) to afford the target product **3g** as a white solid (1.12 g, 87% yield, 99:1 *er*).

Synthetic application:



Procedure for the synthesis of 4³: To a solution of methyltrioxorhenium (MTO, 5 mg, 10 mol%) in dichloromethane (1.0 mL) was added urea/hydrogen peroxide adduct (UHP, 188 mg, 0.2 mmol). The resulting mixture was stirred for 10 minutes before adding **3g** (56.8 mg, 0.2 mmol). After stirring at ambient temperature overnight, the mixture was filtered through a short silica gel pad. After concentration, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 20:1) to afford **4** as a white solid (58.2 mg, 97% yield). The enantiomeric ratio was established as 95:5 *er* by HPLC analysis using a Daicel Chiralpak OJ-H column (*n*-

hexane/isopropanol = 95:5, 1 mL/min), λ = 220 nm, temperature = 28 °C, tr (minor) = 5.47 min, tr (major) = 12.35 min. [α]_D^{25.2} = -18.9 (c = 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 7.69-7.64 (m, 2H), 7.48-7.40 (m, 2H), 7.40-7.35 (m, 2H), 7.23-7.15 (m, 2H), 7.15-7.10 (m, 1H), 4.82 (d, *J* = 2.8 Hz, 2H), 2.24 (s, 3H), 1.62 (br, 1H), 1.01 (s, 9H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 138.9, 135.5, 135.2, 132.6, 130.3, 123.1, 128.0, 127.3, 126.6, 126.1, 63.1, 26.1, 18.8, 18.6 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{18}H_{25}O_2Si]^+$: 301.1618; found: 301.1614.



Procedure for the synthesis of 5⁴: Inside an argon-filled glovebox, an oven-dried 5 mL reaction tube was charged with 3g (56.8 mg, 0.2 mmol), allyl acetate (40 mg, 0.4 mmol), Karstedt catalyst (100 μ L, 0.01 mmol, 0.1 M in xylene) and anhydrous cyclohexane (1.0 mL). The tube was capped and taken outside of the glovebox. The resulting mixture was stirred at 40 °C for 12 h. After removing the solvent under vacuum, the residues were purified by flash chromatography (petroleum ether) to afford 5 as a colorless oil (53.8 mg, 70% yield). The enantiomeric ratio was established as 95:5 *er* by HPLC analysis using a Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 95:5, 1 mL/min), λ = 220 nm, temperature = 28 °C, tr (major) = 5.23 min, tr (minor) = 9.11 min. [α]D^{25.2} = -8.5 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.57-7.51 (m, 3H), 7.38 (q, *J* = 7.8, 6.6 Hz, 3H), 7.25-7.10 (m, 3H), 4.83 (s, 2H), 4.01 (t, *J* = 6.7 Hz, 2H), 2.25 (s, 3H), 2.03 (s, 3H), 1.80-1.68 (m, 2H), 1.15-1.01 (m, 2H), 0.98 (s, 9H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 171.4, 139.1, 135.1, 134.9, 134.3, 130.0, 129.8, 128.0, 127.2, 126.2, 126.1, 67.2, 63.9, 26.7, 23.2, 21.2, 19.3, 18.8, 7.2 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{23}H_{33}O_3Si]^+$: 385.2193; found: 385.2198.

$$Ph \longrightarrow \frac{nBuLi}{Et_2O, r.t., 1 h} \left[Ph \longrightarrow Li\right] \xrightarrow{3g} tBu \xrightarrow{Ph} tBu \xrightarrow{H} tBu \xrightarrow{Ph} tBu$$

Procedure for the synthesis of 6⁴: To a solution of ethynylbenzene (102.1 mg, 1.0 mmol) in anhydrous Et₂O (1.0 mL) was added *n*BuLi (320 µL, 0.8 mmol, 2.5 M in *n*-hexane) dropwise under argon at room temperature. The mixture was stirred at room temperature for 1 h and then was added into another 10 mL reaction tube containing **3g** (56.8 mg, 0.2 mmol) via a syringe. After stirring for another 12 h at room temperature, the reaction mixture was quenched with water and extracted with EtOAc. The combined organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated. The residues were purified by flash chromatography (petroleum ether) to afford **6** as a colorless oil (44.4 mg, 84% yield). The enantiomeric ratio was established as 96:4 *er* by HPLC analysis using a Daicel Chiralpak OJ-3 column (*n*-hexane/isopropanol = 100:0, 0.1 mL/min), λ = 250 nm, temperature = 28 °C, tr (major) = 51.39 min, tr (minor) = 65.68 min. [α]p^{25.2} = 3.6 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.73-7.68 (m, 2H), 7.56-7.51 (m, 2H), 7.46-7.37 (m, 3H), 7.36-7.30 (m, 3H), 4.50 (s, 1H), 1.06 (s, 9H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 135.6, 132.4, 132.3, 130.1, 129.1, 128.5, 128.0, 123.0, 108.9, 87.6, 26.7, 17.7 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{18}H_{21}Si]^+$: 265.1407; found: 265.1407.



Procedure for the synthesis of 7⁴: To a solution of 1-bromo-2-methoxybenzene (149.6 mg, 0.8 mmol) in anhydrous Et₂O (1.0 mL) was added *n*BuLi (400 μ L, 1.0 mmol, 2.5 M in *n*-hexane) dropwise under argon at room temperature. The mixture was stirred at room temperature for 1 h and then was added into another 10 mL reaction tube containing **3g** (56.8 mg, 0.2 mmol) via a syringe. After stirring for another 12 h at room

temperature, the reaction mixture was quenched with water and extracted with EtOAc. The combined organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated. The residues were purified by flash chromatography (petroleum ether) to afford **7** as a colorless oil (40.0 mg, 74% yield). The enantiomeric ratio was established as 93:7 *er* by HPLC analysis using a Daicel Chiralpak OJ-H column (*n*-hexane/isopropanol = 99:1, 0.6 mL/min), λ = 220 nm, temperature = 28 °C, tr (minor) = 7.50 min, tr (major) = 8.11 min. [α]p^{25.2} = 39.8 (c = 1.0, CHCl₃).

¹**H NMR** (400 MHz, CDCl₃): δ 7.74-7.68 (m, 2H), 7.57-7.51 (m, 1H), 7.39-7.29 (m, 4H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 4.60 (s, 1H), 3.79 (s, 3H), 1.06 (s, 9H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ 164.0, 138.4, 136.1, 135.1, 131.7, 129.3, 127.7, 123.0, 120.8, 109.8, 54.9, 28.4, 18.4 ppm.

HRMS (ESI, m/z) $[M + H]^+$ calcd for $[C_{171}H_{23}OSi]^+$: 271.1513; found: 271.1515.

6. Single Crystal X-Ray Diffraction

Single crystal suitable for X-ray diffraction of compound **3k** was obtained from a solution of the compound **3k** (93:7 *er*) in *n*-hexane. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre under reference number CCDC 2360226. Diffraction Data were collected on a BrukerD8 venture employing Cu-K α radiation ($\lambda = 1.54178$ Å).



| Identification code | DY240602_0m | |
|-------------------------------------|--|--|
| Empirical formula | C19H22OSSi | |
| Formula weight | 326.51 | |
| Temperature/K | 100.0(2) | |
| Crystal system | orthorhombic | |
| Space group | P212121 | |
| a/Å | 6.0130(2) | |
| b/Å | 16.5709(4) | |
| c/Å | 17.6278(4) | |
| <i>α</i> /° | 90 | |
| β/° | 90 | |
| γ/° | 90 | |
| Volume/Å ³ | 1756.45(8) | |
| Z | 4 | |
| p _{calc} g/cm ³ | 1.235 | |
| µ/mm ⁻¹ | 2.270 | |
| F(000) | 696.0 | |
| Crystal size/mm ³ | $0.36 \times 0.25 \times 0.1$ | |
| Radiation | $CuK\alpha (\lambda = 1.54178)$ | |
| 20 range for data collection/° | 7.322 to 136.944 | |
| Index ranges | $-6 \le h \le 7, -19 \le k \le 19, -20 \le l \le 21$ | |
| Reflections collected | 15680 | |
| Independent reflections | 3213 [Rint = 0.0555, Rsigma = 0.0403] | |
| Data/restraints/parameters | 3213/0/202 | |
| Goodness-of-fit on F ² | 1.125 | |
| Final R indexes [I>=2 σ (I)] | R1 = 0.0293, WR2 = 0.0758 | |
| Final R indexes [all data] | R1 = 0.0295, WR2 = 0.0759 | |
| Largest diff. peak/hole / e Å-3 | 0.45/-0.33 | |
| Flack parameter | 0.077(6) | |

Table S2. Crystallographic data and structure refinement for compound 3k

7. References

- 1. Z.-Z. Zhu, K. Chen, L.-Z. Yu, X.-Y. Tang and M. Shi, *Org. Lett.*, 2015, **17**, 5994-5997.
- 2. Z. Li, Y. Peng and T. Wu, Org. Lett., 2021, 23, 881-885.
- G. Zhan, H.-L. Teng, Y. Luo, S.-J. Lou, M. Nishiura, and Z. Hou, *Angew. Chem. Int. Ed.*, 2018, 57, 12342-12346.
- 4. W. Yuan, X. Zhu, Y. Xu and C. He, Angew. Chem. Int. Ed., 2022, 61, e202204912.

8. NMR Spectra









¹³C NMR spectrum of **3d** (101 MHz, CDCl₃)





10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)







- 10 - 10 - 20 - 30 - 40 - 50 - 60 - 70 - 80 - 90 - 100 - 110 - 120 - 130 - 140 - 150 - 160 - 170 - 180 - 190 - 200 - 210 Γ1 (ppm)












210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 F1 (ppm)





















210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)







210 200 190 180 170 160 150 140 130 120 110 100 90 fl (ppm) -10



¹³C NMR spectrum of **5** (101 MHz, CDCl₃)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ſ1 (ppm)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)





9. HPLC Chromatography






































































| reak | Retitme | TAbe | WIGCH | Area | nergiic | Area |
|------|---------|------|--------|------------|-----------|---------|
| # | [min] | | [min] | [mAU*s] | [mAU] | 00 |
| | | | | | | |
| 1 | 24.242 | BV | 0.5485 | 5662.32129 | 151.35031 | 48.3052 |
| 2 | 25.251 | VB | 0.5875 | 6059.64941 | 139.84288 | 51.6948 |



2 25.225 FM R 0.7096 7037.72168 165.30736 95.9027







23.90170 51.0624



2 23.848 VB 0.3652 567.80792

| Peak | RetTime | Туре | Width | Area | Height | Area |
|------|---------|------|--------|------------|-----------|---------|
| # | [min] | | [min] | [mAU*s] | [mAU] | 8 |
| | | | | | | |
| 1 | 23.964 | MF R | 0.4101 | 4913.20947 | 199.67773 | 89.9018 |
| 2 | 24.895 | FM R | 0.4400 | 551.87347 | 20.90639 | 10.0982 |















| # | [min] | | [min] | [mAU*s] | [mAU] | 8 |
|---|-------|------|--------|------------|-----------|---------|
| | | | | | | |
| 1 | 5.335 | VB | 0.0907 | 1472.22205 | 249.98006 | 50.3352 |
| 2 | 9.488 | VV R | 0.1925 | 1452.61108 | 114.12514 | 49.6648 |









8.174 VV R 0.2627 3475.88330 204.12251 50.5211

2

