Copper-Catalyzed Enantio- and Diastereoselective Addition of Silicon Nucleophiles to 3,3-Disubstituted Cyclopropenes

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Supporting Information

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1. General Information

All reactions were performed in flame-dried glassware using conventional Schlenk techniques under a static pressure of nitrogen unless stated otherwise. Liquids and solutions were transferred with syringes. All metal salts were purchased from commercial suppliers and used as received. All solvents (CH₂Cl₂, toluene, Et₂O, and THF) were dried and purified following standard procedures. Technical grade solvents for extraction or chromatography (cyclohexane, CH₂Cl₂, ethanol, ethyl acetate, and n-pentane) were distilled prior to use. All ligands were directly purchased from TCI, ABCR, Sigma Aldrich, and Solvias. Racemic products were obtained using rac-BINAP as ligand under the standard conditions. Analytical thin layer chromatography (TLC) was performed on ALUGRAM® Xtra SIL G/UV₂₅₄ TLC-Sheets by Macherey-Nagel. Flash column chromatography was performed on silica gel 60 (40-63 µm, 230-400 mesh, ASTM) by Grace using the indicated solvents. ¹H, ¹³C, ¹⁹F and ²⁹Si NMR spectra were recorded in CDCl₃ or C₆D₆ on Bruker AV400 or AV500 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (CHCl₃: δ = 7.26 ppm for ¹H NMR and CDCl₃: δ = 77.16 ppm for ¹³C NMR, C₆D₅H: δ = 7.15 ppm for ¹H NMR and C₆D₆: δ = 128.62 ppm for ¹³C NMR). Data are reported as follows: chemical shift, multiplicity (br = broad signal, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, mc = centrosymmetric multiplet), coupling constants (Hz), and integration. Gas liquid chromatography (GLC) was performed on an Agilent Technologies 7820A gas chromatograph equipped with a HP-5 capillary column (30 m × 0.32 mm, 0.25 µm film thickness) by Agilent Technologies/CS-Chromatographie Service using the following program: N₂ carrier gas, injection temperature 250 °C, detector temperature 300 °C, flow rate: 1.7 mL/min; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min. Infrared (IR) spectra were recorded on an Agilent Technologies Cary 630 FT-IR spectrometer equipped with an ATR unit and the signals are reported in wave-numbers (cm⁻¹). Melting points (m.p.) were determined with a Stuart Scientific SMP20 melting point apparatus and are not corrected. High resolution mass spectrometry (HRMS) analysis was performed by the Analytical Facility at the Institut für Chemie, Technische Universität Berlin. Optical rotations were measured on a Schmidt & Haensch Polartronic H532 polarimeter with [α]₀ values reported in 10⁻¹ (° cm² g⁻¹); concentration c is in g/100 mL and λ as indicated. Enantiomeric excesses were determined by analytical high performance liquid chromatography (HPLC) analysis on an Agilent Technologies 1290 Infinity instrument with a chiral stationary phase using a Daicel Chiralcel OD-H column, or a Daicel Chiralcel OJ-H column (n-heptane/iso-propanol mixtures as solvent), or on an Agilent Technologies 1200 Infinity instrument with a stationary phase using a Daicel Chiralcel OJ-RH column or a Daicel Chiralcel OD-RH column (acetonitrile/water mixtures as solvent). Data for the single crystal structure determination were collected with an Agilent SuperNova diffractometer equipped with a CCD area Atlas detector and a mirror monochromator by utilizing Cu-Kα radiation (λ = 1.5418 Å). Software packages used: CrysAlis PRO for data collection, cell
2. Optimization Study

General Procedure for the Optimization Reactions

An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar was charged with the copper salt (10.0 mol%) and the ligand (12.0 mol%). The tube was placed under vacuum and backfilled with N₂ (3 times). The solvent (1 mL) was added, and the resulting suspension was stirred for 1 h at room temperature. Then, Me₂PhSiBpin (2a, 0.300 mmol, 1.50 equiv) was added and the mixture was stirred for 10 min. A NaOttBu solution (0.3 M in THF, 50.0 mol%) was added dropwise and the reaction mixture was stirred for 15 min. The mixture was then cooled to −78 °C for 10 min, and (1-methylcycloprop-2-en-1-yl)benzene (1a, 0.200 mmol, 1.00 equiv) and methanol (0.600 mmol, 3.00 equiv) were added sequentially. The resulting suspension was warmed to 0 °C and maintained at this temperature for 10 h. After the indicated reaction time, the reaction mixture was filtered through a short plug of silica gel, and the filter cake was washed with 10 mL EtOAc. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel using the indicated mixture of cyclohexane and EtOAc. The diastereoselectivity was determined by ¹H NMR spectroscopy and the enantiomeric excess was determined by HPLC analysis on a chiral stationary phase.

Table S1: Detailed Optimizations of Hydrosilylation of Cyclopropene 1a.

<table>
<thead>
<tr>
<th>Entry[a]</th>
<th>Copper</th>
<th>Ligand</th>
<th>Solvent</th>
<th>Yield [%]</th>
<th>d.r.[b]</th>
<th>ee [%][c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(CH₃CN)₄PF₆</td>
<td>L₁</td>
<td>THF</td>
<td>70</td>
<td>96:4</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>Cu(CH₃CN)₄PF₆</td>
<td>L₂</td>
<td>THF</td>
<td>78</td>
<td>97:3</td>
<td>72</td>
</tr>
<tr>
<td>Reaction</td>
<td>Cu Complex</td>
<td>Ligand</td>
<td>Solvent</td>
<td>Yield (%)</td>
<td>Product Ratio</td>
<td>Isolated Yield (%)</td>
</tr>
<tr>
<td>----------</td>
<td>------------</td>
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<td>-----------</td>
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</tr>
<tr>
<td>3</td>
<td>Cu(CH$_3$CN)$_4$PF$_6$</td>
<td>L3</td>
<td>THF</td>
<td>58</td>
<td>86:14</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>Cu(CH$_3$CN)$_4$PF$_6$</td>
<td>L4</td>
<td>THF</td>
<td>71</td>
<td>$\geq$ 98:2</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>Cu(CH$_3$CN)$_4$PF$_6$</td>
<td>L5</td>
<td>THF</td>
<td>73</td>
<td>$\geq$ 98:2</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>Cu(CH$_3$CN)$_4$PF$_6$</td>
<td>L6</td>
<td>THF</td>
<td>73</td>
<td>$\geq$ 98:2</td>
<td>96</td>
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<tr>
<td>7</td>
<td>Cu(CH$_3$CN)$_4$PF$_6$</td>
<td>L6</td>
<td>Toluene</td>
<td>81</td>
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<td>Cu(CH$_3$CN)$_4$PF$_6$</td>
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<td>DCM</td>
<td>79</td>
<td>97:3</td>
<td>82</td>
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<tr>
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<td>L6</td>
<td>Et$_2$O</td>
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<tr>
<td>10</td>
<td>Cu(OAc)$_2$</td>
<td>L6</td>
<td>THF</td>
<td>62</td>
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<td>70</td>
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<td>11$^{[d]}$</td>
<td>Cu(CH$_3$CN)$_4$PF$_6$</td>
<td>L6</td>
<td>THF</td>
<td>74</td>
<td>$\geq$ 98:2</td>
<td>92</td>
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<td>12</td>
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<td>L7</td>
<td>THF</td>
<td>73</td>
<td>97:3</td>
<td>92</td>
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<tr>
<td>13</td>
<td>Cu(CH$_3$CN)$_4$PF$_6$</td>
<td>L8</td>
<td>THF</td>
<td>74</td>
<td>$\geq$ 98:2</td>
<td>97</td>
</tr>
</tbody>
</table>

[a] All reactions were performed on a 0.20 mmol scale with isolated yield after flash chromatography on silica gel. [b] Determined by $^1$H NMR analysis. [c] Determined by HPLC on a chiral stationary phase. [d] Run at -20
3. General Procedures

3.1 General Procedures for the Preparation of Cyclopropenes (GP1)

An oven-dried 250-mL Schlenk flask equipped with a magnetic stir bar was charged with methyltriphenylphosphonium bromide (36.0 mmol, 1.20 equiv) suspended in Et₂O (100 mL) under the atmosphere of nitrogen, potassium tert-butoxide (36.0 mmol, 1.20 equiv) was added and the reaction mixture was stirred for 1 h at room temperature. Then, a solution of the ketone (SI-1, 30.0 mmol, 1.00 eq) in Et₂O was added dropwise. The reaction was monitored by TLC. After full conversion, H₂O (100 mL) was added and the aqueous phase was extracted with Et₂O (2 × 50 mL). The combined organic layers were concentrated under reduced pressure and the alkene SI-2 was obtained by flash column chromatography with n-pentane as the eluent.

A 500-mL flask equipped with a magnetic stir bar was charged with alkene (SI-2, 1.00 equiv), TEBAC (0.85 mol%), bromoform (1.60 equiv) suspended in CH₂Cl₂ (4 mL/mmol), a solution of 50% NaOH (2.86 mL/mmol) was added and the reaction mixture was then stirred for 12-36 h at 35 °C. The reaction was monitored by TLC. After full conversion, H₂O (100 mL) was slowly added and the aqueous phase was extracted with CH₂Cl₂ (2 × 50 mL). The combined organic layers were concentrated under reduced pressure and the dibromo cyclopropane SI-3 was obtained by flash column chromatography with n-pentane as the eluent.

An oven-dried 250-mL Schlenk flask equipped with a magnetic stir bar was charged with dibromocyclopropanes (SI-3, 1.00 equiv), Ti(OiPr)₄ (0.10 equiv) suspended in Et₂O (100 mL) under the atmosphere of nitrogen, EtMgBr (3.0 M in Et₂O, 1.30 equiv) was added dropwise at 0 °C (ice bath) and the reaction mixture was then stirred for 3 h at room temperature. The reaction was monitored by TLC and quenched with 10% aq. HCl after full conversion. The aqueous phase was extracted with Et₂O (2 × 50 mL) and the combined organic layers were concentrated under reduced pressure and the monobromocyclopropane SI-4 was obtained as a mixture of diastereomers by flash column chromatography with n-pentane as the eluent.

An oven-dried 25-mL Schlenk flask equipped with a magnetic stir bar was charged with monobromocyclopropanes (SI-4, 1.00 equiv) suspended in DMSO (0.55 mL/mmol) under the...
atmosphere of nitrogen, potassium tert-butoxide (1.30 equiv) was added and the reaction mixture was then stirred overnight at room temperature. The reaction was monitored by TLC. After full conversion, H₂O (100 mL) was added and the aqueous phase was extracted with Et₂O (2 × 50 mL). The combined organic layers were concentrated under reduced pressure and the cyclopropene 1 was obtained by flash column chromatography with n-pentane as the eluent.

1a–i, 1k–o, 1q–s were synthesized following GP1 according to the reported procedure. All spectroscopic data were in agreement with those reported.

3.2 General Procedures for the Preparation of R₃SiBpin (GP2)

Method A:

\[
\begin{align*}
\text{R₃SiCl} & \quad \xrightarrow{\text{Li (4.00 equiv)}} \quad \text{THF} \quad \text{R₃SiLi} \\
\text{SI-5} & \quad \text{0 °C, overnight} \quad \text{SI-6} \\
\text{1.00 equiv} & \quad (\sim 1.0 \text{ M in THF}) \quad \text{HBpin or iPrOBpin} \\
\text{2.00 equiv} & \quad \xrightarrow{\text{R₃SiBpin}}
\end{align*}
\]

An oven-dried 100 mL Schlenk flask equipped with a magnetic stir bar was charged with activated lithium chunks (999 mg, 144 mmol, 4.00 equiv) suspended in THF (30 mL) under the atmosphere of nitrogen, the corresponding chlorosilane (SI-5, 36.0 mmol, 1.00 equiv) was then added and stirred overnight at 0 °C to give R₃SiLi SI-6. Next, to a solution of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane or 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (72.0 mmol, 2.00 equiv) in hexane (40 mL) was added freshly prepared R₃SiLi (SI-6, ~1.0 M in THF) dropwise at 0 °C over 30 min under N₂. After the addition, the mixture was stirred overnight at room temperature. Then the mixture was filtered through Celite to remove white residual solid, and the filtrate was concentrated under reduced pressure. Products R₃SiBpin 2 were obtained by fractional distillation or recrystallized.

2a–d were synthesized following Method A according to the reported procedure. All spectroscopic data were in agreement with those reported.

Method B

\[
\begin{align*}
\text{R₃SiH} & \quad \xrightarrow{\text{[Ir(cod)OMe]₂ (0.5 mol%)}} \quad \text{dtbpy (1.0 mol%)} \\
\text{SI-7} & \quad \text{B₂pin₂ (1.00 equiv)} \quad \text{cyclohexane} \quad \text{80 °C, 12-36 h} \\
\text{2} & \quad \text{R₃SiBpin}
\end{align*}
\]

An oven-dried 50-mL Schlenk flask equipped with a magnetic stir bar was charged with [Ir(cod)OMe]₂ (6.60 mg, 0.5 mol%), dtbpy (1.0 mg, 1.00 mol%), B₂pin₂ (0.51 g, 2.00 mmol, 1.00 equiv), dtbpy (5.40 mg, 1.0 mol%) under the atmosphere of nitrogen, cyclohexane (2 mL) and hydrosilane (SI-7, 8.00 mmol, 4.00 equiv) were then added and the resulting dark brown solution was heated at 80 °C for 12–36 h. The reaction was monitored by TLC. After full conversion, the reaction mixture was cooled to
room temperature and concentrated under reduced pressure. The corresponding R₃SiBpin 2 was obtained as colorless oil or white solid by flash column chromatography with cyclohexane/EtOAc as the eluent.

2e–g were synthesized following Method B according to the reported procedure.[S7] All spectroscopic data were in agreement with those reported.

3.3 General Procedures for the Enantioselective Formal Hydrosilylation of Cyclopropenes (GP3)

An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar was charged with the Cu(CH₃CN)₄PF₆ (7.50 mg, 10.0 mol%) and the chiral ligand (R)-DM-Segphos (17.3 mg, 12.0 mol%). The tube was placed under vacuum and backfilled with N₂ (3 times). THF (1 mL) was added, and the resulting suspension was stirred for 1 h at room temperature. Then, R₃SiBpin (2, 0.300 mmol, 1.50 equiv) was added and the mixture was stirred for 10 min. A NaOtBu solution (9.60 mg, 0.3 M in THF, 50.0 mol%) was added dropwise and the reaction mixture was stirred for 15 min. The mixture was then cooled to –78 °C for 10 min, and the corresponding cyclopropene (1, 0.200 mmol, 1.00 equiv) and methanol (0.600 mmol, 3.00 equiv) were added sequentially. The resulting suspension was warmed to 0 °C and maintained at this temperature for 10 h. After the indicated reaction time, the reaction mixture was filtered through a short plug of silica gel, and the filter cake was washed with 10 mL EtOAc. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel using the indicated mixture of cyclohexane and EtOAc. The diastereoselectivity was determined by 1H NMR spectroscopy and the enantiomeric excess was determined by HPLC analysis on a chiral stationary phase.

4. Experimental Details for the Preparation of R₃SiBpin

4.1 tert-Butyl(methyl)(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2c)
Prepared from tert-butylchloro(methyl)(phenyl)silane (7.63 g, 36.0 mmol, 1.00 equiv), lithium chunks (999 mg, 144 mmol, 4.00 equiv) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13.4 g, 72.0 mmol, 2.00 equiv) following the Method A of GP2. The product 2c was obtained as colorless oil (3.28 g, 30% yield).

IR (ATR): \( \tilde{\nu} = 2977, 2928, 2855, 1426, 1371, 1304, 1240, 1136, 1106, 955, 848, 821, 782, 698, 676 \text{ cm}^{-1} \). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 0.34 (s, 3H), 0.92 (s, 9H), 1.28 (d, \( J = 3.0 \text{ Hz} \), 12H), 7.32–7.37 (m, 3H), 7.61–7.65 (m, 2H) ppm. \(^{13}\)C\(^{1}\)H NMR (125 MHz, CD\(_2\)Cl\(_2\)): \( \delta \) -8.2, 17.3, 25.2, 27.3, 83.4, 127.5, 128.7, 135.5, 137.0 ppm. HRMS (APCI) exact mass for [M+H]^+ C\(_{17}\)H\(_{30}\)BO\(_2\)Si+: calculated 305.2103, found 305.2107.

5. Experimental Details for the Preparation of Cyclopropenes

5.1 5-(2,2-Dibromo-1-methylcyclopropyl)benzo[d][1,3]dioxole (SI-3j)

Prepared from 5-(prop-1-en-2-yl)benzo[d][1,3]dioxole (4.86 g, 30.0 mmol, 1.00 equiv), TEBAC (58.1 mg, 0.85 mol%), bromoform (12.1 g, 48.0 mmol, 1.60 equiv), 85.8 mL 50% NaOH solution following the GP1. The product SI-3j was obtained as brown oil (7.47 g, 75% yield).

\( R_f = 0.30 \) (n-pentane). IR (ATR): \( \tilde{\nu} = 2982, 2923, 2891, 1504, 1487, 1435, 1225, 1039, 936, 860, 811, 696 \text{ cm}^{-1} \). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 1.68 (s, 3H), 1.75 (d, \( J = 7.6 \text{ Hz} \), 1H), 2.09 (d, \( J = 7.6 \text{ Hz} \), 1H), 5.96–5.97 (m, 2H), 6.72–6.81 (m, 3H) ppm. \(^{13}\)C\(^{1}\)H NMR (125 MHz, CD\(_2\)Cl\(_2\)): \( \delta \) 27.9, 34.2, 35.6, 37.1, 101.2, 108.2, 109.2, 121.7, 136.4, 146.8, 147.6 ppm. HRMS (APCI) exact mass for [M-Br]^+ C\(_{11}\)H\(_{11}\)BrO\(_2\): calculated 252.9864, found 252.9862.

5.2 5-(1-Methylcycloprop-2-en-1-yl)benzo[d][1,3]dioxole (1j)

Prepared from 5-(prop-1-en-2-yl)benzo[d][1,3]dioxole (4.86 g, 30.0 mmol, 1.00 equiv), TEBAC (58.1 mg, 0.85 mol%), bromoform (12.1 g, 48.0 mmol, 1.60 equiv), 85.8 mL 50% NaOH solution following the GP1. The product 1j was obtained as brown oil (7.47 g, 75% yield).

\( R_f = 0.30 \) (n-pentane). IR (ATR): \( \tilde{\nu} = 2982, 2923, 2891, 1504, 1487, 1435, 1225, 1039, 936, 860, 811, 696 \text{ cm}^{-1} \). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 0.34 (s, 3H), 0.92 (s, 9H), 1.28 (d, \( J = 3.0 \text{ Hz} \), 12H), 7.32–7.37 (m, 3H), 7.61–7.65 (m, 2H) ppm. \(^{13}\)C\(^{1}\)H NMR (125 MHz, CD\(_2\)Cl\(_2\)): \( \delta \) 27.9, 34.2, 35.6, 37.1, 101.2, 108.2, 109.2, 121.7, 136.4, 146.8, 147.6 ppm. HRMS (APCI) exact mass for [M-Br]^+ C\(_{11}\)H\(_{11}\)BrO\(_2\): calculated 252.9864, found 252.9862.
Prepared from 5-(2-bromo-1-methylcyclopropyl)benzo[d][1,3]dioxole (5.08 g, 20.0 mmol, 1.00 equiv) and potassium tert-butoxide (2.92 g, 26.0 mmol, 1.30 equiv) following the GP1. The product 1j was obtained as colorless oil (2.44 g, 70% yield).

\[ \text{RF} = 0.35 \ (n\text{-pentane). IR (ATR): } \tilde{\nu} = 2964, 2885, 1635, 1503, 1484, 1434, 1242, 1103, 936, 862, 813, 768 \text{ cm}^{-1}. \]

\[ \text{IR (ATR): } \tilde{\nu} = 2964, 2885, 1635, 1503, 1484, 1434, 1242, 1103, 936, 862, 813, 768 \text{ cm}^{-1}. \]

\[ \text{IR (ATR): } \tilde{\nu} = 3079, 3058, 3024, 3004, 1600, 1492, 1445, 1442, 1050, 1016, 925, 818, 758, 696, 670 \text{ cm}^{-1}. \]

\[ \text{IR (ATR): } \tilde{\nu} = 3079, 3058, 3024, 3004, 1600, 1492, 1445, 1442, 1050, 1016, 925, 818, 758, 696, 670 \text{ cm}^{-1}. \]

\[ \text{IR (ATR): } \tilde{\nu} = 3079, 3058, 3024, 3004, 1600, 1492, 1445, 1442, 1050, 1016, 925, 818, 758, 696, 670 \text{ cm}^{-1}. \]

\[ \text{IR (ATR): } \tilde{\nu} = 3079, 3058, 3024, 3004, 1600, 1492, 1445, 1442, 1050, 1016, 925, 818, 758, 696, 670 \text{ cm}^{-1}. \]

\[ \text{IR (ATR): } \tilde{\nu} = 3079, 3058, 3024, 3004, 1600, 1492, 1445, 1442, 1050, 1016, 925, 818, 758, 696, 670 \text{ cm}^{-1}. \]

\[ \text{IR (ATR): } \tilde{\nu} = 3079, 3058, 3024, 3004, 1600, 1492, 1445, 1442, 1050, 1016, 925, 818, 758, 696, 670 \text{ cm}^{-1}. \]

\[ \text{IR (ATR): } \tilde{\nu} = 3079, 3058, 3024, 3004, 1600, 1492, 1445, 1442, 1050, 1016, 925, 818, 758, 696, 670 \text{ cm}^{-1}. \]

\[ \text{IR (ATR): } \tilde{\nu} = 3079, 3058, 3024, 3004, 1600, 1492, 1445, 1442, 1050, 1016, 925, 818, 758, 696, 670 \text{ cm}^{-1}. \]

\[ \text{IR (ATR): } \tilde{\nu} = 3079, 3058, 3024, 3004, 1600, 1492, 1445, 1442, 1050, 1016, 925, 818, 758, 696, 670 \text{ cm}^{-1}. \]

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\[ \text{IR (ATR): } \tilde{\nu} = 3079, 3058, 3024, 3004, 1600, 1492, 1445, 1442, 1050, 1016, 925, 818, 758, 696, 670 \text{ cm}^{-1}. \]
7.40–7.43 (m, 2H) ppm. $^{13}$C$^{{}^1}$H NMR (125 MHz, CD$_2$Cl$_2$): δ 4.7, 16.4, 19.6, 29.1, 111.5, 125.3, 126.5, 127.9, 149.5 ppm. HRMS (APCI) exact mass for [M]$^+$ C$_{12}$H$_{22}$+: calculated 157.1012, found 157.1012.
6. Experimental Details for the Hydrosilylation of Cyclopropanes

6.1 Dimethyl((1R,2S)-2-methyl-2-phenylcyclopropyl)(phenyl)silane (3aa)

Prepared from (1-methylcycloprop-2-en-1-yl)benzene (1a, 26.0 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3aa as a colorless oil (39.4 mg, 74% yield, d.r. ≥ 98:2, 97% ee).

IR (ATR): \(\tilde{\nu} = 3064, 2953, 2921, 2851, 2359, 2328, 1601, 1494, 1446, 1427, 1249, 1112, 1023, 831, 813, 764, 699 \text{ cm}^{-1}\).

\(\text{IR } (\text{A}) \text{TR} : v = 3064, 2953, 2921, 2851, 2359, 2328, 1601, 1494, 1446, 1427, 1249, 1112, 1023, 831, 813, 764, 699 \text{ cm}^{-1}\).

\(1^H \text{NMR} (500 \text{ MHz, CDCl}_3): \delta 0.29 (dd, J = 10.5 \text{ Hz, J} = 7.7 \text{ Hz, 1H}), 0.39 (s, 3H), 0.41 (s, 3H), 0.80 (dd, J = 7.7 \text{ Hz, J} = 3.6 \text{ Hz, 1H}), 1.31 (dd, J = 10.5 \text{ Hz, J} = 3.7 \text{ Hz, 1H}), 1.38 (s, 3H), 7.15–7.19 (m, 1H), 7.28–7.29 (m, 4H), 7.37–7.39 (m, 3H), 7.61–7.63 (m, 2H) \text{ ppm}. \)

\(1^C\{^1H\} \text{NMR} (125 \text{ MHz, CDCl}_3): \delta –1.4, –1.3, 14.2, 19.3, 23.9, 25.6, 125.6, 126.9, 127.9, 128.3, 129.0, 134.0, 140.0, 149.0 \text{ ppm}. \)

\(2^9\text{Si}\{^1H\} \text{DEPT NMR} (99 \text{ MHz, CDCl}_3): \delta –3.9 \text{ ppm}. \)

HRMS (EI) exact mass for [M]+ C_{18}H_{22}Si+: calculated 266.1485, found 266.1481.

Optical rotation: \(\left[\alpha\right]_D^\circ = –63.7 (c 1.0, \text{CH}_2\text{Cl}_2, 97\% \text{ ee}). \)

The enantiomeric excess of 3aa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane/iPrOH = 99.9:0.1, flow rate 0.4 mL/min): \(t_R = 13.4 \text{ min (major)}, t_s = 14.5 \text{ min (minor)}. \)

6.2 ((1R,2S)-2-(4-Fluorophenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ba)

Prepared from 1-fluoro-4-(1-methylcycloprop-2-en-1-yl)benzene (1b, 29.6 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol,
1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3ba as a colorless oil (40.9 mg, 72% yield, d.r. ≥ 98:2, 97% ee).

**Rf** = 0.65 (cyclohexane/EtOAc = 150/1). IR (ATR): ν = 3062, 2955, 2367, 2340, 2185, 2143, 1510, 1427, 1255, 1228, 1112, 1017, 833, 773, 732, 701 cm⁻¹. **1H NMR** (500 MHz, CDCl₃): δ 0.22 (dd, J = 10.5 Hz, J = 7.7 Hz, 1H), 0.38 (s, 3H), 0.40 (s, 3H), 0.77 (dd, J = 7.7 Hz, J = 3.7 Hz, 1H), 1.31 (dd, J = 10.7 Hz, J = 3.8 Hz, 1H), 1.33 (s, 3H), 6.91–6.97 (m, 2H), 7.19–7.26 (m, 2H), 7.36–7.40 (m, 3H), 7.58–7.63 (m, 2H) ppm. **13C{1H} NMR** (125 MHz, CDCl₃): δ –1.4, –1.3, 13.9, 19.1, 24.3, 25.3, 114.9 (d, J = 20.9 Hz), 127.9, 128.6 (d, J = 2.9 Hz), 129.0, 133.9, 139.8, 144.7 (d, J = 46.2 Hz), 161.1 (d, J = 243.7 Hz) ppm. **19F NMR** (471 MHz, CDCl₃): δ –117.9 ppm. **29Si{1H} DEPT NMR** (99 MHz, CDCl₃): δ –3.9 ppm. **HRMS** (APCI) exact mass for [M+H]+ C₁₈H₂₂FSi+: calculated 285.1469, found 285.1469.

Optical rotation: [α]D = –56.7 (c 0.5, CH₂Cl₂, 97% ee). The enantiomeric excess of 3ba was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-RH column, column temperature 20 °C, solvent MeCN:H₂O = 80:20, flow rate 0.3 mL/min): tR = 18.2 min (major), tR = 21.8 min (minor).

### 6.3 ((1R,2S)-2-(4-Chlorophenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ca)

![Chemical Structure](image)

**3ca**

C₁₈H₂₂ClSi

M = 300.90 g/mol

Prepared from 1-chloro-4-(1-methylcycloprop-2-en-1-yl)benzene (**1c**, 32.8 mg, 0.200 mmol, 1.00 equiv), according to **GP3** with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (**2a**, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3ca as a colorless oil (43.8 mg, 73% yield, d.r. ≥ 98:2, 90% ee).

**Rf** = 0.60 (cyclohexane/EtOAc = 150/1). IR (ATR): ν = 3066, 2953, 1493, 1447, 1427, 1399, 1344, 1249, 1114, 1013, 887, 829, 774, 730, 701 cm⁻¹. **1H NMR** (500 MHz, CDCl₃): δ 0.24 (dd, J = 10.5 Hz, J = 7.8 Hz, 1H), 0.39 (s, 3H), 0.41 (s, 3H), 0.80 (dd, J = 7.8 Hz, J = 3.8 Hz, 1H), 1.27 (dd, J = 10.6 Hz, J = 3.9 Hz, 1H), 1.34 (s, 3H), 7.17–7.20 (m, 2H), 7.22–7.26 (m, 2H), 7.37–7.39 (m, 3H), 7.59–7.62 (m, 2H) ppm. **13C{1H} NMR** (125 MHz, CDCl₃): δ –1.4, –1.3, 14.4, 19.3, 23.8, 25.1, 127.9, 128.3, 128.4, 129.1, 131.3, 133.9, 139.7, 147.5 ppm. **29Si{1H} DEPT NMR** (99 MHz, CDCl₃): δ –3.9 ppm. **HRMS** (APCI) exact mass for [M+H]+ C₁₉H₂₃ClSi+: calculated 301.1174, found 301.1175.
Optical rotation: $\delta^{\text{d}} = -73.2$ (c 0.5, CH$_2$Cl$_2$, 90% ee). The enantiomeric excess of 3ca was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.2 mL/min): $t_R = 30.9$ min (major), $t_S = 33.1$ min (minor).

6.4 ((1R,2S)-2-(4-Bromophenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3da)

Prepared from 1-bromo-4-(1-methylcycloprop-2-en-1-yl)benzene (1d, 41.6 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3da as a colorless oil (43.8 mg, 74% yield, d.r. ≥ 98:2, 94% ee).

$R_f = 0.60$ (cyclohexane/EtOAc = 150/1). IR (ATR): $\tilde{\nu} = 3064, 2952, 1489, 1448, 1426, 1394, 1342, 1248, 1112, 1074, 1008, 905, 888, 867, 811, 773, 731, 700$ cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.23 (dd, $J = 10.4$ Hz, $J = 7.8$ Hz, 1H), 0.38 (s, 3H), 0.80 (dd, $J = 7.8$ Hz, $J = 3.8$ Hz, 1H), 1.24 (dd, $J = 10.5$ Hz, $J = 3.8$ Hz, 1H), 1.33 (s, 3H), 7.11–7.14 (m, 2H), 7.36–7.39 (m, 5H), 7.57–7.62 (m, 2H) ppm. $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$): $\delta$ –1.5, –1.3, 14.4, 19.3, 23.7, 25.1, 119.3, 127.9, 128.7, 129.1, 131.3, 133.9, 139.7, 148.0 ppm. $^{29}$Si($^1$H) DEPT NMR (99 MHz, CDCl$_3$): $\delta$ –3.9 ppm. HRMS (APCI) exact mass for [M-Ph]$^+$ C$_{12}$H$_{16}$BrSi$: calculated 267.0205, found 267.0204.

Optical rotation: $\delta^{\text{d}} = -72.0$ (c 2.0, CH$_2$Cl$_2$, 94% ee). The enantiomeric excess of 3da was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.3 mL/min): $t_R = 22.2$ min (major), $t_S = 23.5$ min (minor).
6.5 Dimethyl((1R,2S)-2-methyl-2-(4-(trifluoromethyl)phenyl)cyclopropyl)(phenyl)silane (3ea)

![Structural formula of 3ea](image)

**C_{19}H_{21}F_{3}Si**

**M = 334.45 g/mol**

Prepared from 1-(1-methylcycloprop-2-en-1-yl)-4-(trifluoromethyl)benzene (1e, 39.6 mg, 0.200 mmol, 1.00 equiv), according to **GP3** with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3ea as a colorless oil (50.1 mg, 75% yield, d.r. ≥ 98:2, 91% ee). 

**R_f = 0.60** (cyclohexane/EtOAc = 150/1). **IR** (ATR): ∩ = 3067, 2956, 1617, 1410, 1324, 1250, 1164, 1120, 1070, 1015, 841, 814, 775, 732, 700 cm⁻¹. **^1H NMR** (500 MHz, CDCl₃): δ 0.29 (dd, J = 10.6 Hz, J = 7.8 Hz, 1H), 0.40 (s, 3H), 0.41 (s, 3H), 0.86 (dd, J = 7.9 Hz, J = 3.9 Hz, 1H), 1.34 (dd, J = 10.6 Hz, J = 3.9 Hz, 1H), 1.37 (s, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.37–7.40 (m, 3H), 7.52 (d, J = 8.0 Hz, 2H), 7.57–7.62 (m, 2H) ppm. **^13C{^1H} NMR** (125 MHz, CDCl₃): δ –1.5, –1.3, 15.2, 19.8, 23.3, 25.3, 124.5 (d, J = 271.6 Hz), 125.3 (q, J = 3.7 Hz), 127.0, 127.7, 128.0, 129.1, 133.9, 139.5, 153.0 ppm. **^19F NMR** (471 MHz, CDCl₃): δ –62.3 ppm. **^{29}Si{^1H} DEPT NMR** (99 MHz, CDCl₃): δ –3.9 ppm. **HRMS** (EI) exact mass for [M-F]⁺ C_{19}H_{21}F_{2}Si⁺: calculated 315.1375, found 315.1374.

Optical rotation: [α]D²⁵ = –63.2 (c 0.5, CH₂Cl₂, 91% ee). The enantiomeric excess of 3ea was determined by HPLC analysis on a chiral stationary phase (Daice Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.2 mL/min): tᵣ = 25.5 min (major), tᵣ = 27.2 min (minor).

6.6 Dimethyl((1R,2S)-2-methyl-2-(p-tolyl)cyclopropyl)(phenyl)silane (3fa)

![Structural formula of 3fa](image)

**C_{19}F_{24}Si**

**M = 280.48 g/mol**
Prepared from 1-methyl-4-(1-methylcyclopent-2-en-1-yl)benzene (1f, 28.8 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3fa as a colorless oil (45.9 mg, 82% yield, d.r. ≥ 98:2, 92% ee).

**Rf** = 0.65 (cyclohexane/EtOAc = 150/1). **IR** (ATR): $\tilde{\nu}$ = 3049, 2952, 1515, 1427, 1248, 1112, 1083, 1019, 887, 815, 773, 730, 701 cm$^{-1}$. **$^1$H NMR** (500 MHz, CDCl$_3$): δ 0.26 (dd, $J = 10.5$ Hz, $J = 7.8$ Hz, 1H), 0.38 (s, 3H), 0.40 (s, 3H), 0.77 (dd, $J = 7.7$ Hz, $J = 3.7$ Hz, 1H), 1.28 (dd, $J = 10.5$ Hz, $J = 3.7$ Hz, 1H), 1.36 (s, 3H), 2.32 (s, 3H), 7.08–7.10 (m, 2H), 7.16–7.19 (m, 2H), 7.36–7.39 (m, 3H), 7.60–7.63 (m, 2H) ppm. **$^{13}$C($^1$H) NMR** (125 MHz, CDCl$_3$): δ –1.4, –1.3, 14.0, 19.2, 21.1, 24.0, 25.3, 126.8, 127.9, 128.9, 129.0, 134.0, 135.1, 140.0, 146.1 ppm. **$^{29}$Si($^1$H) DEPT NMR** (99 MHz, CDCl$_3$): δ −3.9 ppm. **HRMS** (APCI) exact mass for [M+H]$^+$ C$_{19}$H$_{25}$Si$:\text{calculated} 281.1720, \text{found} 281.1720.$

Optical rotation: [α]$^\circ$ = –69.3 (c 1.0, CH$_2$Cl$_2$, 92% ee). The enantiomeric excess of 3fa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-RH column, column temperature 20 °C, solvent MeCN:H$_2$O = 60:40, flow rate 0.3 mL/min): t$_R$ = 116.9 min (minor), t$_R$ = 121.8 min (major).

### 6.7 (1R,2S)-2-((1,1'-Biphenyl)-4-yl)-2-methylcyclopropyl(dimethylphenyl)silane (3ga)

Prepared from 4-(1-methylcyclopent-2-en-1-yl)-1,1'-biphenyl (1g, 41.2 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3ga as a waxy solid (56.1 mg, 82% yield, d.r. ≥ 98:2, 95% ee).

**Rf** = 0.50 (cyclohexane/EtOAc = 150/1). **IR** (ATR): $\tilde{\nu}$ = 3053, 3026, 2953, 1601, 1520, 1486, 1447, 1407, 1249, 1113, 1080, 887, 835, 813, 766, 731, 698 cm$^{-1}$. **$^1$H NMR** (500 MHz, CDCl$_3$): δ 0.33 (dd, $J = 10.6$ Hz, $J = 7.8$ Hz, 1H), 0.40 (s, 3H), 0.42 (s, 3H), 0.83 (dd, $J = 7.8$ Hz, $J = 3.8$ Hz, 1H), 1.34 (dd, $J = 10.4$ Hz, $J = 3.7$ Hz, 1H), 1.41 (s, 3H), 7.30–7.34 (m, 3H), 7.37–7.44 (m, 5H), 7.49–7.52 (m, 2H), 7.56–7.63 (m, 4H) ppm. **$^{13}$C($^1$H) NMR** (125 MHz, CDCl$_3$): δ –1.34, –1.26, 14.6, 19.6, 23.8, 25.2, 127.07, 127.13 (2C), 127.2, 127.9, 128.8, 129.0, 134.0, 138.6, 139.9, 141.2,
148.1 ppm. $^{29}$Si{$^1$H} DEPT NMR (99 MHz, CDCl$_3$): $\delta$ –3.9 ppm. HRMS (APCI) exact mass for [M+H]$^+$ C$_{24}$H$_{27}$Si$: calculated 343.1877, found 343.1877.

Optical rotation: $[\alpha]_D^2 = –76.0$ (c 0.5, CH$_2$Cl$_2$, 95% ee). The enantiomeric excess of 3ga was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99:1, flow rate 0.4 mL/min): $t_R = 13.4$ min (minor), $t_R = 16.8$ min (major).

6.8 ((1R,2S)-2-(4-Methoxyphenyl)-2-methylcyclopropyl)dimethyl(phenyl) silane (3ha)

Prepared from 1-methoxy-4-(1-methylcycloprop-2-en-1-yl)benzene (1h, 32.0 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3ha as a colorless oil (45.0 mg, 76% yield, d.r. ≥ 98:2, 94% ee).

$R_f = 0.20$ (cyclohexane/EtOAc = 150/1). IR (ATR): $\tilde{\nu} = 3064, 2993, 2952, 2833, 1610, 1461,$ 1427, 1245, 1179, 1111, 1036, 887, 830, 814, 773, 731, 701 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.23 (dd, $J = 10.5$ Hz, $J = 7.6$ Hz, 1H), 0.38 (s, 3H), 0.40 (s, 3H), 0.75 (dd, $J = 7.7$ Hz, $J = 3.6$ Hz, 1H), 1.24 (dd, $J = 10.4$ Hz, $J = 3.6$ Hz, 1H), 1.34 (s, 3H), 3.79 (s, 3H), 6.80–6.84 (m, 2H), 7.18–7.21 (m, 2H), 7.36–7.39 (m, 3H), 7.60–7.63 (m, 2H) ppm. $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ –1.4, –1.3, 13.7, 19.0, 24.4, 25.2, 55.4, 113.7, 127.9, 128.1, 128.9, 133.9, 140.1, 141.3, 157.7 ppm. $^{29}$Si{$^1$H} DEPT NMR (99 MHz, CDCl$_3$): $\delta$ –3.9 ppm. HRMS (APCI) exact mass for [M+H]$^+$ C$_{19}$H$_{25}$OSi$: calculated 297.1669, found 297.1666.

Optical rotation: $[\alpha]_D^2 = –72.0$ (c 0.6, CH$_2$Cl$_2$, 94% ee). The enantiomeric excess of 3ha was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.4 mL/min): $t_R = 30.4$ min (minor), $t_R = 32.8$ min (major).
**6.9 ((1R,2S)-2-(3-Methoxyphenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ia)**

![Chemical structure of 3ia]

C<sub>19</sub>H<sub>24</sub>OSi  
M = 296.48 g/mol

Prepared from 1-methoxy-3-(1-methylcycloprop-2-en-1-yl)benzene (1i, 32.0 mg, 0.200 mmol, 1.0 equiv), according to **GP3** with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.0 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3ia as a colorless oil (50.3 mg, 85% yield, d.r. ≥ 98:2, 93% ee).  

**R<sub>f</sub>** = 0.20 (cyclohexane/EtOAc = 150/1). **IR** (ATR): \( \tilde{\nu} \) = 3066, 2994, 2953, 2833, 1604, 1581, 1488, 1461, 1427, 1345, 1283, 1249, 1216, 1179, 1111, 1048, 903, 831, 813, 774, 732, 701 cm<sup>-1</sup>.  

**1H NMR** (500 MHz, CDCl<sub>3</sub>): \( \delta \) 0.28 (dd, \( J = 10.6 \) Hz, \( J = 7.8 \) Hz, 1H), 0.38 (s, 3H), 0.40 (s, 3H), 0.77 (dd, \( J = 7.8 \) Hz, \( J = 3.6 \) Hz, 1H), 1.30 (dd, \( J = 10.5 \) Hz, \( J = 3.8 \) Hz, 1H), 1.35 (s, 3H), 3.80 (s, 3H), 6.69–6.72 (m, 1H), 6.82–6.88 (m, 2H), 7.20 (t, \( J = 8.1 \) Hz, 1H), 7.36–7.39 (m, 3H), 7.58–7.63 (m, 2H) ppm. **13C<sup>1H</sup> NMR** (125 MHz, CDCl<sub>3</sub>): \( \delta \) –1.4, –1.3, 14.3, 19.4, 23.8, 25.6, 55.3, 110.5, 113.2, 119.3, 127.9, 129.0, 129.3, 133.9, 139.9, 150.7, 159.6 ppm. **29Si<sup>1H</sup> DEPT NMR** (99 MHz, CDCl<sub>3</sub>): \( \delta \) –3.9 ppm. **HRMS** (APCI) exact mass for [M+H]<sup>+</sup> C<sub>19</sub>H<sub>25</sub>OSi<sup>+</sup>: calculated 297.1669, found 297.1666.  

Optical rotation: [\( \alpha \)]<sub>D</sub> = −74.6 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>, 93% ee). The enantiomeric excess of 3ia was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99:1, flow rate 0.3 mL/min): \( t_<R> \) = 17.8 min (major), \( t_<R> \) = 20.1 min (minor).

**6.10 ((1R,2S)-2-(Benzo[d][1,3]dioxol-5-yl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ja)**

![Chemical structure of 3ja]

C<sub>19</sub>H<sub>22</sub>O<sub>2</sub>Si  
M = 310.46 g/mol

Prepared from 5-(1-methylcycloprop-2-en-1-yl)benzo[d][1,3]dioxole (1j, 34.8 mg, 0.200 mmol, 1.00 equiv), according to **GP3** with
dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3ja as a colorless oil (52.1 mg, 84% yield, d.r. ≥ 98:2, 94% ee).

Rf = 0.20 (cyclohexane/EtOAc = 150/1). IR (ATR): ν = 3066, 2953, 2890, 1607, 1504, 1487, 1431, 1345, 1238, 1220, 1111, 1085, 938, 916, 812, 773, 731, 702 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 0.21 (dd, J = 10.6 Hz, J = 7.8 Hz, 1H), 0.37 (s, 3H), 0.39 (s, 3H), 0.72 (dd, J = 7.7 Hz, J = 3.7 Hz, 1H), 1.21 (dd, J = 10.6 Hz, J = 3.7 Hz, 1H), 1.31 (s, 3H), 5.91 (s, 2H), 6.69–6.79 (m, 3H), 7.35–7.39 (m, 3H), 7.58–7.62 (m, 2H) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ −1.4, −1.3, 13.7, 19.0, 24.6, 25.9, 100.9, 107.9, 108.2, 120.1, 127.9, 129.0, 133.9, 139.9, 143.4, 145.5, 147.5 ppm. ²⁹Si{¹H} DEPT NMR (99 MHz, CDCl₃): δ −4.0 ppm. HRMS (APCI) exact mass for [M+H]+ C₁₉H₂₃O₂Si+: calculated 311.1462, found 311.1465.

Optical rotation: [α]D² = −72.0 (c 2.0, CH₂Cl₂, 94% ee). The enantiomeric excess of 3ja was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:iPrOH = 95:5, flow rate 0.6 mL/min): tR = 10.6 min (major), tR = 18.1 min (minor).

6.11 Dimethyl((1R,2R)-2-methyl-2-(thiophen-2-yl)cyclopropyl)(phenyl)silane (3ka)

Prepared from 2-(1-methylcycloprop-2-en-1-yl)thiophene (1k, 27.2 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3ka as a colorless oil (45.2 mg, 83% yield, d.r. ≥ 98:2, 90% ee).

Rf = 0.60 (cyclohexane/EtOAc = 150/1). IR (ATR): ν = 3066, 2953, 2890, 1443, 1426, 1312, 1249, 1111, 1081, 1006, 939, 906, 814, 774, 730, 696 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 0.38 (s, 3H), 0.40 (s, 3H), 0.45 (dd, J = 10.7 Hz, J = 8.1 Hz, 1H), 0.92 (dd, J = 8.1 Hz, J = 3.8 Hz, 1H), 1.37 (dd, J = 10.8 Hz, J = 3.8 Hz, 1H), 1.45 (s, 3H), 6.79 (dd, J = 3.5 Hz, J = 1.3 Hz, 1H), 6.89 (dd, J = 5.2 Hz, J = 3.6 Hz, 1H), 7.05 (dd, J = 5.2 Hz, J = 1.2 Hz, 1H), 7.37–7.40 (m, 3H), 7.59–7.63 (m, 2H) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ −1.5, −1.3, 13.7, 19.0, 24.6, 25.9, 100.9, 107.9, 108.2, 120.1, 127.9, 129.0, 133.9, 139.9, 141.8, 121.9, 126.7, 127.9, 129.1, 134.0, 139.5, 155.3 ppm. ²⁹Si{¹H} DEPT NMR (99 MHz, CDCl₃): δ −4.1 ppm. HRMS (APCI) exact mass for [M+H]+ C₁₆H₂₁SSi+: calculated 273.1128, found 273.1127.
Optical rotation: $[\alpha]_{D}^{20} = -76.2$ (c 2.0, CH$_2$Cl$_2$, 90% ee). The enantiomeric excess of 3ka was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.3 mL/min): $t_R = 24.3$ min (major), $t_R = 26.8$ min (minor).

6.12 Dimethyl((1R,2S)-2-methyl-2-(naphthalen-1-yl)cyclopropyl)(phenyl)silane (3la)

\[
\text{IR (ATR): } \tilde{\nu} = 3046, 2953, 1593, 1506, 1447, 1427, 1334, 1250, 1111, 1086, 999, 889, 831, 777, 734, 701 \text{ cm}^{-1}.
\]

\[
\text{H NMR (500 MHz, CDCl$_3$): } \delta = 0.37 (dd, J = 10.4 Hz, J = 7.8 Hz, 1H), 0.48 (s, 3H), 0.53 (s, 3H), 0.97 (dd, J = 7.5 Hz, J = 3.4 Hz, 1H), 1.34 (dd, J = 10.8 Hz, J = 3.7 Hz, 1H), 1.48 (s, 3H), 7.36–7.47 (m, 7H), 7.66–7.71 (m, 3H), 7.82–7.85 (m, 1H), 8.30 ppm.
\]

\[
\text{C$_{22}$H$_{24}$Si NMR (125 MHz, CDCl$_3$): } \delta = -1.39, -1.36, 11.8, 18.7, 24.6, 25.7, 125.3, 125.4, 125.5, 125.6, 126.3, 127.0, 128.0, 128.8, 129.1, 131.9, 134.0, 134.1, 139.8, 145.3 ppm.
\]

\[
\text{Si$^{29}$ NMR (99 MHz, CDCl$_3$): } \delta = -3.8 \text{ ppm.}
\]

Optical rotation: $[\alpha]_{D}^{20} = -53.4$ (c 0.9, CH$_2$Cl$_2$, 94% ee). The enantiomeric excess of 3la was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-RH column, column temperature 20 °C, solvent MeCN:H$_2$O = 70:30, flow rate 0.3 mL/min): $t_R = 63.7$ min (major), $t_R = 70.0$ min (minor).
6.13 Dimethyl((1R,2S)-2-methyl-2-(naphthalen-2-yl)cyclopropyl)(phenyl)silane (3ma)

Prepared from 2-(1-methylcycloprop-2-en-1-yl)naphthalene (1m, 36.0 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3ma as a colorless oil (44.9 mg, 71% yield, d.r. ≥ 98:2, 95% ee).

Rf = 0.50 (cyclohexane/EtOAc = 150/1). IR (ATR): \( \tilde{\nu} = 3051, 2953, 1631, 1599, 1505, 1447, 1421, 1333, 1248, 1111, 950, 892, 815, 773, 746, 701 \) cm\(^{-1}\). \( ^1\)H NMR (500 MHz, CDCl\(_3\)): δ 0.38 (dd, J = 10.5 Hz, J = 7.8 Hz, 1H), 0.41 (s, 3H), 0.44 (s, 3H), 0.87 (dd, J = 7.8 Hz, J = 3.8 Hz, 1H), 1.42 (dd, J = 10.6 Hz, J = 3.8 Hz, 1H), 1.46 (s, 3H), 7.37–7.46 (m, 6H), 7.62–7.64 (m, 2H), 7.69 (d, J = 1.8 Hz, 1H), 7.74–7.79 (m, 3H) ppm. \( ^{13}\)C\{\( ^1\)H\} NMR (125 MHz, CDCl\(_3\)): δ –1.3, –1.2, 14.2, 19.3, 23.8, 25.8, 124.9, 125.3, 125.8, 126.0, 127.6, 127.7, 127.9 (2C), 129.0, 131.9, 133.6, 134.0, 140.0, 146.4 ppm. \( ^{29}\)Si\{\( ^1\)H\} DEPT NMR (99 MHz, CDCl\(_3\)): δ –3.8 ppm. HRMS (APCI) exact mass for [M+H]\(^+\) \( \text{C}_{22}\text{H}_{25}\text{Si}^+\): calculated 317.1720, found 317.1723.

Optical rotation: \([\alpha]_D^2 = –56.0 \) (c 1.0, CH\(_2\)Cl\(_2\), 95% ee). The enantiomeric excess of 3ma was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-RH column, column temperature 20 °C, solvent MeCN:H\(_2\)O = 80:20, flow rate 0.3 mL/min): t\(_R\) = 32.4 min (major), t\(_R\) = 42.8 min (minor).

6.14 ((1R,2S)-2-Ethyl-2-phenylcyclopropyl)dimethyl(phenyl)silane (3na)

Prepared from (1-ethylcycloprop-2-en-1-yl)benzene (1n, 28.8 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3na as a colorless oil (38.1 mg, 68% yield, d.r. = 97:3, 90% ee).
$R_f = 0.60$ (cyclohexane/EtOAc = 150/1). **IR** (ATR): $\bar{\nu} = 3054, 3022, 2972, 1601, 1492, 1447, 1427, 1362, 1249, 1111, 1026, 988, 935, 918, 830, 813, 762, 731, 700 $ cm$^{-1}$. **$^1$H NMR** (500 MHz, CDCl$_3$): $\delta$ 0.22 (dd, $J = 10.3$ Hz, $J = 7.7$ Hz, 1H), 0.40 (s, 3H), 0.44 (s, 3H), 0.70 (dd, $J = 7.7$ Hz, $J = 3.7$ Hz, 1H), 0.77 (t, $J = 7.3$ Hz, 3H), 1.28–1.39 (m, 2H), 1.76–1.85 (m, 1H), 7.16–7.22 (m, 1H), 7.26–7.30 (m, 4H), 7.38–7.41 (m, 2H) ppm. **$^{13}$C{$^1$H} NMR** (125 MHz, CDCl$_3$): $\delta$ –1.4, –1.1, 12.2, 13.4, 16.3, 30.2, 32.7, 125.8, 127.9, 128.1, 128.9, 129.0, 133.9, 140.1, 146.7 ppm. **$^{29}$Si{$^1$H} DEPT NMR** (99 MHz, CDCl$_3$): $\delta$ –6.1 ppm.

**HRMS** (APCI) exact mass for $[M+H]^+$ C$_{19}$H$_{25}$Si+: calculated 281.1720, found 281.1726.

Optical rotation: $[\alpha]_D^0 = –50.5$ (c 0.5, CH$_2$Cl$_2$, 90% ee). The enantiomeric excess of 3na was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:PrOH = 99:1, flow rate 0.3 mL/min): $t_R = 18.5$ min (major), $t_R = 20.4$ min (minor).

### 6.15 ((1R,2R)-2-Isopropyl-2-phenylcyclopropyl)dimethyl(phenyl)silane (3oa)

Prepared from (1-isopropylcycloprop-2-en-1-yl)benzene (1o, 31.6 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3oa as a colorless oil (28.2 mg, 48% yield, d.r. = 84:16, 93% ee with a bad separation). $R_f = 0.60$ (cyclohexane/EtOAc = 150/1). **IR** (ATR): $\bar{\nu} = 3052, 3023, 2978, 2870, 1600, 1492, 1444, 1427, 1364, 1302, 1250, 1161, 1112, 1018, 965, 917, 830, 811, 770, 731, 702 $ cm$^{-1}$. **$^1$H NMR** (500 MHz, CDCl$_3$): $\delta$ 0.28 (dd, $J = 10.3$ Hz, $J = 7.7$ Hz, 1H), 0.39 (s, 3H), 0.48 (s, 3H), 0.70 (dd, $J = 7.8$ Hz, $J = 3.5$ Hz, 1H), 0.78 (d, $J = 6.8$ Hz, 3H), 0.87 (d, $J = 6.8$ Hz, 3H), 1.18 (dd, $J = 10.3$ Hz, $J = 3.5$ Hz, 1H), 1.22–1.29 (m, 1H), 7.18–7.23 (m, 1H), 7.24–7.29 (m, 4H), 7.35–7.43 (m, 3H), 7.64–7.68 (m, 2H) ppm. **$^{13}$C{$^1$H} NMR** (125 MHz, CDCl$_3$): $\delta$ –1.3, –0.9, 13.0, 17.0, 21.1, 21.0, 34.8, 38.5, 126.2, 127.3, 127.9, 128.9, 131.7, 133.8, 140.3, 144.7 ppm. **$^{29}$Si{$^1$H} DEPT NMR** (99 MHz, CDCl$_3$): $\delta$ –4.8 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ C$_{20}$H$_{26}$Si+: calculated 295.1877, found 295.1887.

Optical rotation: $[\alpha]_D^0 = –37.5$ (c 1.0, CH$_2$Cl$_2$, 93% ee). The enantiomeric excess of 3oa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-RH column, column temperature 20 °C, solvent MeCN:H$_2$O = 70:30, flow rate 0.3 mL/min): $t_R = 38.8$ min (major), $t_R = 41.8$ min (minor).
6.16 Dimethyl(phenyl)((1R,2R)-1-phenyl-[1,1'-bi(cyclopropan)]-2-yl)silane (3pa)

Prepared from [1,1'-bi(cyclopropan)]-2-en-1-ylbenzene (1p, 31.2 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3pa as a colorless oil (40.9 mg, 76% yield, d.r. = 90:10, 93% ee). 

Rf = 0.60 (cyclohexane/EtOAc = 150/1). IR (ATR): ν = 3066, 3001, 2953, 1599, 1492, 1445, 1426, 1248, 1111, 1021, 963, 920, 831, 812, 771, 731, 700 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 0.05–0.16 (m, 2H), 0.29–0.35 (m, 1H), 0.36 (dd, J = 10.8 Hz, J = 7.8 Hz, 1H), 0.41–0.45 (m, 1H), 0.46 (s, 3H), 0.50 (s, 3H), 0.81 (dd, J = 7.8 Hz, J = 4.0 Hz, 1H), 1.00–1.05 (m, 1H), 1.18–1.21 (m, 1H), 1.19–1.22 (m, 1H), 7.19–7.22 (m, 1H), 7.28–7.33 (m, 4H), 7.40–7.43 (m, 3H), 7.67–7.70 (m, 2H) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ –1.29, –1.27, 4.8, 5.4, 14.0, 15.5, 16.8, 31.7, 125.9, 127.8, 128.0, 128.9, 129.0, 133.9, 140.4, 147.0 ppm. ²⁹Si{¹H} DEPT NMR (99 MHz, CDCl₃): δ –4.1 ppm. HRMS (APCI) exact mass for [M+H]+ C₂₀H₂₅Si+: calculated 293.1720, found 293.1721. Optical rotation: [α]D² = –80.8 (c 2.0, CH₂Cl₂, 93% ee). The enantiomeric excess of 3pa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane/iPrOH = 99.9:0.1, flow rate 0.3 mL/min): tR = 22.0 min (major), tR = 24.4 min (minor).

6.17 ((1R,2R)-2-Benzyl-2-methylcyclopropyl)dimethyl(phenyl)silane (3qa)

Prepared from ((1-methylcycloprop-2-en-1-yl)methyl)benzene (1q, 28.8 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3qa as a colorless oil (31.9 mg, 57% yield, d.r. > 98:2, 94% ee).
$R_f$ = 0.65 (cyclohexane/EtOAc = 150/1). IR (ATR): $\tilde{\nu}$ = 3064, 3025, 2952, 2903, 1602, 1494, 1452, 1427, 1248, 1111, 1084, 1030, 934, 831, 813, 773, 730, 701 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ -0.03 (dd, $J$ = 10.2 Hz, $J$ = 7.3 Hz, 1H), 0.27 (s, 6H), 0.47 (dd, $J$ = 7.3 Hz, $J$ = 3.5 Hz, 1H), 0.87 (dd, $J$ = 10.3 Hz, $J$ = 3.7 Hz, 1H), 0.97 (s, 3H), 2.54 (d, $J$ = 13.9 Hz, 1H), 2.71 (d, $J$ = 13.9 Hz, 1H), 2.70–2.75 (m, 3H), 7.26–7.28 (m, 2H), 7.30–7.40 (m, 3H), 7.48–7.52 (m, 2H) ppm. $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$): $\delta$ –1.5, –1.2, 10.5, 17.6, 20.9, 22.3, 48.5, 126.1, 127.8, 128.2, 128.8, 129.5, 133.9, 140.3, 140.7 ppm.

Optical rotation: $[\alpha]_D^2$ = $–20.3$ (c 0.5, CH$_2$Cl$_2$, 94% ee). The enantiomeric excess of 3qa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:PrOH = 99.9:0.1, flow rate 0.2 mL/min): $t_R$ = 36.2 min (major), $t_R$ = 39.3 min (minor).

6.18

6.18

$((1S,2R)-3',4'-Dihydro-2'H-spirocyclopropene-1,1'-napthalene)-2'-yl)dimethyl(phenyl)silane (3ra)$

Prepared from 3',4'-dihydro-2'H-spirocyclopropene-1,1'-napthalene (1r, 31.2 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3ra as a colorless oil (9.9 mg, 17% yield, d.r. $\geq$ 98:2, 81% ee). $R_f$ = 0.55 (cyclohexane/EtOAc = 150/1). IR (ATR): $\tilde{\nu}$ = 3064, 3025, 2952, 2903, 1602, 1494, 1452, 1427, 1248, 1111, 1084, 1030, 934, 831, 813, 773, 730, 701 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.35 (s, 3H), 0.37 (s, 3H), 0.46 (dd, $J$ = 10.5 Hz, $J$ = 8.0 Hz, 1H), 0.86 (dd, $J$ = 8.1 Hz, $J$ = 3.8 Hz, 1H), 1.26 (dd, $J$ = 10.3 Hz, $J$ = 3.9 Hz, 1H), 1.59–1.81 (m, 4H), 2.82 (t, $J$ = 5.9 Hz, 2H), 6.77 (d, $J$ = 7.9 Hz, 1H), 7.02–7.10 (m, 3H), 7.33–7.37 (m, 3H), 7.54–7.58 (m, 2H) ppm. $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$): $\delta$ –1.4, –1.2, 18.5, 22.7, 23.6, 24.4, 30.9, 32.8, 121.9, 124.8, 126.2, 127.9, 128.9, 129.0, 134.0, 137.6, 139.8, 142.9 ppm. $^1$H–$^{29}$Si HMOC NMR (99 MHz, CDCl$_3$): $\delta$ –4.5 ppm. HRMS (APCI) exact mass for [M+H]$^+$ C$_{20}$H$_{25}$Si$: calculated 281.1721, found 281.1725.

Optical rotation: $[\alpha]_D^2$ = $–58.5$ (c 0.2, CH$_2$Cl$_2$, 81% ee). The enantiomeric excess of 3ra was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column,
column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.3 mL/min): t_R = 27.3 min (minor), t_R = 29.8 min (major).

6.19 (R)-(2,2-diphenylcyclopropyl)dimethyl(phenyl)silane (3sa)

Prepared from cycloprop-2-ene-1,1-diyl dibenzene (1s, 38.4 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3sa as a colorless oil (40.0 mg, 61% yield, 94% ee).

R_f = 0.50 (cyclohexane/EtOAc = 150/1). IR (ATR): ν = 3057, 3020, 2953, 1597, 1493, 1445, 1426, 1248, 1111, 1017, 941, 829, 812, 775, 731, 699 cm^{-1}. ^1H NMR (500 MHz, CDCl_3): δ = –0.18 (s, 3H), –0.03 (s, 3H), 0.99 (dd, J = 10.5 Hz, J = 7.8 Hz, 1H), 1.38 (dd, J = 10.6 Hz, J = 3.8 Hz, 1H), 1.58 (dd, J = 7.9 Hz, J = 3.9 Hz, 1H), 7.10–7.14 (m, 1H), 7.17–7.23 (m, 7H), 7.27–7.29 (m, 2H), 7.31–7.37 (m, 3H), 7.47–7.49 (m, 2H) ppm. ^13C{^1H} NMR (125 MHz, CDCl_3): δ = –3.4, –2.8, 14.4, 18.1, 35.8, 125.8, 126.6, 127.6, 127.8, 128.20, 128.23, 128.9, 130.8, 133.8, 139.8, 143.1, 148.0 ppm. ^29Si{^1H} DEPT NMR (99 MHz, CDCl_3): δ = –4.2 ppm. HRMS (APCI) exact mass for [M+H]^+ C_{23}H_{25}Si+: calculated 329.1720, found 329.1723.

Optical rotation: [α]_D^28 = –132.7 (c 0.66, CH_2Cl_2, 94% ee). The enantiomeric excess of 3sa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99:1, flow rate 0.4 mL/min): t_R = 28.0 min (major), t_R = 33.7 min (minor).

6.20 Methyl(1R,2S)-2-methyl-2-phenylcyclopropyl)diphenylsilane (3ab)

Prepared from (1-methylcycloprop-2-ene-1-yl)benzene (1a, 26.0 mg, 0.200 mmol, 1.00 equiv), according to GP3 with methyldiphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2b, 97.3 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3ab as a colorless oil (42.7 mg, 65% yield, d.r. ≥ 98:2, 97% ee).
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R_f = 0.50 (cyclohexane/EtOAc = 150/1). IR (ATR): υ = 3066, 3021, 2996, 2952, 1492, 1427, 1252, 1110, 1027, 886, 787, 725, 698 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 0.59 (dd, J = 10.5 Hz, J = 7.7 Hz, 1H), 0.67 (s, 3H), 0.89 (dd, J = 7.8 Hz, J = 3.8 Hz, 1H), 1.29 (s, 3H), 1.42 (dd, J = 10.7 Hz, J = 3.9 Hz, 1H), 7.15–7.21 (m, 1H), 7.29–7.32 (m, 4H), 7.34–7.40 (m, 6H), 7.59–7.64 (m, 4H) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ –26.2, 13.0, 19.4, 23.8, 25.7, 125.7, 126.9, 128.0, 128.4, 129.3, 134.87, 134.94, 137.9, 138.0, 148.7 ppm. ²⁹Si{¹H} DEPT NMR (99 MHz, CDCl₃): δ –8.2 ppm. HRMS (APCI) exact mass for [M+H]^+ C₂₃H₂₅Si+: calculated 329.1720, found 329.1725.

Optical rotation: [α]D² = −89.1 (c 0.7, CH₂Cl₂, 97% ee). The enantiomeric excess of 3ab was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99:1, flow rate 0.3 mL/min): t_R = 21.0 min (major), t_R = 23.8 min (minor).

**6.21 ((1R,2S)-2-(4-bromophenyl)-2-methylcyclopropyl)(methyl)diphenylsilane (3db)**

![Structure of 3db](image)

Prepared from 1-bromo-4-(1-methylcycloprop-2-en-1-yl)benzene (1d, 41.6 mg, 0.200 mmol, 1.00 equiv), according to GP3 with methylidiphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2b, 97.3 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3db as a colorless oil (43.8 mg, 54% yield, d.r. ≥ 98:2, 98% ee).

R_f = 0.50 (cyclohexane/EtOAc = 150/1). IR (ATR): υ = 3066, 3021, 2996, 2952, 1492, 1427, 1252, 1110, 1027, 886, 787, 725, 698 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 0.53 (dd, J = 10.5 Hz, J = 7.8 Hz, 1H), 0.66 (s, 3H), 0.89 (dd, J = 7.8 Hz, J = 3.9 Hz, 1H), 1.25 (s, 3H), 1.38 (dd, J = 10.5 Hz, J = 3.9 Hz, 1H), 7.13–7.17 (m, 2H), 7.33–7.42 (m, 8H), 7.56–7.62 (m, 4H) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ –26.7, 13.4, 19.5, 23.5, 25.2, 119.4, 128.0, 128.6, 129.3, 129.4, 131.4, 134.8, 134.9, 137.6, 137.7, 141.8 ppm. ²⁹Si{¹H} DEPT NMR (99 MHz, CDCl₃): δ –8.3 ppm. HRMS (APCI) exact mass for [M-Br]^+ C₂₃H₂₃SiBr: calculated 327.1569, found 327.1569.

Optical rotation: [α]D² = −81.5 (c 1.0, CH₂Cl₂, 98% ee). The enantiomeric excess of 3db was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.4 mL/min): t_R = 22.5 min (major), t_R = 27.4 min (minor).
6.22 ((1R,2S)-2-[[1,1'-Biphenyl]-4-yl]-2-methylcyclopropyl)(methyl)diphenylsilane (3gb)

Prepared from 4-(1-methylcyclopent-2-en-1-yl)-1,1'-biphenyl (1g, 41.2 mg, 0.200 mmol, 1.00 equiv), according to GP3 with methyldiphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2b, 97.3 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3gb as a waxy solid (57.4 mg, 71% yield, d.r. ≥ 98:2, 98% ee).

\[ R_f = 0.40 \text{ (cyclohexane/EtOAc = 150/1).} \]

IR (ATR): \[ \tilde{\nu} = 3066, 3049, 3024, 2994, 2955, 1601, 1486, 1446, 1427, 1252, 1111, 1081, 1024, 904, 885, 868, 838, 787, 766, 728, 698 \text{ cm}^{-1}. \]

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\]): \delta \text{ 0.64 (dd, } J = 10.5 \text{ Hz, } J = 7.8 \text{ Hz, 1H), 0.69 (s, 3H), 0.94 (dd, } J = 7.8 \text{ Hz, } J = 3.8 \text{ Hz, 1H), 1.33 (s, 3H), 1.48 (dd, } J = 10.4 \text{ Hz, } J = 3.8 \text{ Hz, 1H), 7.31–7.45 (m, 11H), 7.51–7.55 (m, 2H), 7.57–7.67 (m, 6H) ppm.} \]

\[ ^{13}C\{^1H\} \text{ NMR (125 MHz, CDCl}_3\): } \delta \text{ –2.6, 13.4, 19.7, 23.6, 25.3, 127.1, 127.9, 128.0, 128.9, 129.27, 129.32, 129.7, 134.1, 134.88, 134.94, 137.8, 137.9, 138.7, 141.2, 147.9 ppm.} \]

\[ ^{29}Si\{^1H\} \text{ DEPT NMR (99 MHz, CDCl}_3\): } \delta \text{ –8.2 ppm.} \]

HRMS (APCI) exact mass for \([\text{M+H}^+\) C\text{29H}_{29}\text{Si}^+\): calculated 405.2033, found 405.2033.

Optical rotation: \[ [\alpha]_D = -105.4 (c 1.0, \text{ CH}_2\text{Cl}_2, 98\% \text{ ee}). \] The enantiomeric excess of 3gb was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralsel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99:1, flow rate 0.4 mL/min): \( t_R = 14.8 \text{ min (minor), } t_R = 24.4 \text{ min (major).} \)

6.23 Triethyl((1R,2S)-2-methyl-2-phenylcyclopropyl)silane (3ae)

Prepared from (1-methylcyclopent-2-en-1-yl)benzene (1a, 26.0 mg, 0.200 mmol, 1.00 equiv), according to GP3 with triethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2e, 72.7 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3ae as a colorless oil (14.8 mg, 30% yield, d.r. ≥ 98:2, 99% ee).
$R_f = 0.80$ (cyclohexane/EtOAc = 150/1).  IR (ATR): $\tilde{\nu} = 3056, 3024, 2952, 2910, 2874, 1602, 1494, 1456, 1416, 1378, 1240, 1120, 1015, 886, 763, 735, 698 \text{ cm}^{-1}$.  $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.02 (dd, $J = 10.7$ Hz, $J = 8.0$ Hz, 1H), 0.59-0.67 (m, 6H), 0.71 (dd, $J = 7.9$ Hz, $J = 3.6$ Hz, 1H), 1.02 (t, $J = 7.9$ Hz, 9H), 1.12 (dd, $J = 10.7$ Hz, $J = 3.7$ Hz, 1H), 1.43 (s, 3H), 7.14–7.17 (m, 1H), 7.25–7.30 (m, 4H) ppm.  $^{13}$C$^\{1\}$H NMR (125 MHz, CDCl$_3$): $\delta$ 4.6, 7.8, 11.6, 19.0, 24.5, 24.9, 125.5, 127.0, 128.3, 149.3 ppm.  $^1$H$^{29}$Si HMQC NMR (99 MHz, CDCl$_3$): $\delta$ 6.8 ppm.  HRMS (EI) exact mass for [M$^+$]$: C_{16}H_{26}Si$: calculated 246.1798, found 246.1798.

Optical rotation: $[\alpha]_D = -73.2$ (c 0.3, CH$_2$Cl$_2$, 99% ee).  The enantiomeric excess of 3ae was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.2 mL/min): $t_R = 13.7$ min (major), $t_R = 14.5$ min (minor).

6.24 ((1R,2S)-2-Methyl-2-phenylcyclopropyl)tripropylsilane (3af)

Prepared from (1-methylcycloprop-2-en-1-yl)benzene (1a, 26.0 mg, 0.200 mmol, 1.00 equiv), according to GP3 with tripropyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2f, 85.3 mg, 0.300 mmol, 1.50 equiv) at 0 °C in THF for 10 h.  Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3af as a colorless oil (15.0 mg, 26% yield, d.r. ≥ 98:2, 95% ee).

$R_f = 0.80$ (cyclohexane/EtOAc = 150/1).  IR (ATR): $\tilde{\nu} = 3057, 3024, 2953, 2924, 2867, 1602, 1494, 1451, 1410, 1375, 1332, 1200, 1120, 1066, 1028, 1003, 889, 811, 762, 698 \text{ cm}^{-1}$.  $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.01 (dd, $J = 10.6$ Hz, $J = 7.9$ Hz, 1H), 0.55-0.66 (m, 6H), 0.70 (dd, $J = 7.9$ Hz, $J = 3.6$ Hz, 1H), 1.18 (dd, $J = 10.6$ Hz, $J = 3.7$ Hz, 1H), 1.37-1.40 (m, 9H), 7.13–7.18 (m, 1H), 7.26–7.28 (m, 4H) ppm.  $^{13}$C$^\{1\}$H NMR (125 MHz, CDCl$_3$): $\delta$ 12.5, 16.7, 17.8, 18.9, 19.2, 24.4, 25.1, 125.5, 126.9, 128.3, 149.4 ppm.  $^1$H$^{29}$Si HMQC NMR (99 MHz, CDCl$_3$): $\delta$ 1.4 ppm.  HRMS (APCI) exact mass for [M+H$^+$]$: C_{19}H_{32}Si$: calculated 289.2346, found 289.2358.

Optical rotation: $[\alpha]_D = -55.8$ (c 1.1, CH$_2$Cl$_2$, 95% ee).  The enantiomeric excess of 3af was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-RH column, column temperature 20 °C, solvent MeCN:H$_2$O = 75:25, flow rate 0.3 mL/min): $t_R = 42.0$ min (major), $t_R = 47.4$ min (minor).
6.25 tert-Butyldimethyl((1R,2S)-2-methyl-2-phenylcyclopropyl)silane (3ag)

Prepared from (1-methylcyclopent-2-en-1-yl)benzene (1a, 26.0 mg, 0.200 mmol, 1.0 equiv), according to GP3 with tert-butyldimethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2g, 72.7 mg, 0.300 mmol, 1.0 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 5fa as a colorless oil (11.3 mg, 23% yield, d.r. ≥ 98:2, 93% ee with a bad separation).

\[ R_f = 0.80 \] (cyclohexane/EtOAc = 150/1). IR (ATR): \( \tilde{\nu} = 3057, 3025, 2952, 2928, 2855, 1602, 1494, 1464, 1445, 1361, 1250, 1120, 1073, 1025, 937, 888, 830, 805, 763, 698 \) cm\(^{-1}\). \( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 0.05 \) (d, \( J = 34.7 \) Hz, 6H), 0.08 (dd, \( J = 10.6 \) Hz, \( J = 8.6 \) Hz, 1H), 0.68 (dd, \( J = 7.8 \) Hz, \( J = 3.5 \) Hz, 1H), 0.95 (s, 9H), 1.20 (dd, \( J = 10.6 \) Hz, \( J = 3.7 \) Hz, 1H), 1.41 (s, 3H), 7.13–7.19 (m, 1H), 7.25–7.30 (m, 4H) ppm. \( ^{13}\)C\{\(^1\)H\} NMR (125 MHz, CDCl\(_3\)): \( \delta = -4.9 \) (d, \( J = 14.8 \) Hz), 11.4, 17.3, 18.7, 24.3, 25.2, 26.8, 125.6, 127.2, 128.3, 149.5 ppm. \( ^1\)H-\(^{29}\)Si HMQC NMR (99 MHz, CDCl\(_3\)): \( \delta = 7.9 \) ppm. HRMS (APCI) exact mass for \([M+H]^+\) \( C_{16}H_{27}Si^+: \) calculated 247.1877, found 247.1884.

Optical rotation: \[ [\alpha]_D^2 = -50.8 \] (c 1.0, CH\(_2\)Cl\(_2\), 93% ee). The enantiomeric excess of 5fa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-RH column, column temperature 20 °C, solvent MeCN:H\(_2\)O = 60:40, flow rate 0.4 mL/min): \( t_R = 58.0 \) min (major), \( t_R = 63.8 \) min (minor).

6.26 Dimethyl((1R,2S,3R)-2-methyl-2-phenylcyclopropyl-3-d)(phenyl)silane (3aa-d\(_d\))

Prepared from (1-methylcyclopent-2-en-1-yl)benzene (1a, 26.0 mg, 0.200 mmol, 1.0 equiv), according to GP3 (CD\(_3\)OD instead of CH\(_3\)OH) with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.0 equiv) at 0 °C in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3aa-d\(_d\) as a colorless oil (38.0 mg, 71% yield, d.r. ≥ 98:2, 90% ee).

\[ R_f = 0.60 \] (cyclohexane/EtOAc = 150/1). IR (ATR): \( \tilde{\nu} = 3065, 3023, 2954, 1601, 1494, 1445, 1427, 1249, 1112, 1022, 857, 812, 765, 731, 699 \) cm\(^{-1}\). \( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 0.28 \) (d, \( J = 10.4 \) Hz, 1H), 0.39 (s, 3H), 0.41 (s, 3H), 1.30 (d, \( J = 10.5 \) Hz, 1H), 1.37 (s, 3H), 7.15–7.18 (m,
1H), 7.27–7.28 (m, 4H), 7.37–7.39 (m, 3H), 7.61–7.63 (m, 2H) ppm. $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): δ –1.4, –1.3, 14.1, 18.9 (t, $J = 24.0$ Hz), 23.9, 25.5, 125.6, 126.9, 127.9, 128.3, 129.0, 134.0, 140.0, 149.0 ppm. $^{29}$Si{$^1$H} DEPT NMR (99 MHz, CDCl$_3$): δ –3.9 ppm. HRMS (APCI) exact mass for [M+H]$^+$ C$_{18}$H$_{22}$DSi$: calculated 268.1626, found 268.1626.

Optical rotation: [α]$_D^2$ = –65.8 (c 0.8, CH$_2$Cl$_2$, 90% ee). The enantiomeric excess of 3aa-$d_1$ was determined by HPLC analysis on a chiral stationary phase (Daicel Chiracel OD-H column, column temperature 20 ºC, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.3 mL/min): $t_R$ = 22.5 min (major), $t_R$ = 23.4 min (minor).

6.27 Dimethyl((1R,2S,3S)-2-methyl-2-phenylcyclopropyl-1,3-$d_2$)(phenyl)silane(3aa-$d_2$)

![Chemical Structure](image)

Prepared from (1-methylcycloprop-2-en-1-yl-2,3-$d_2$)benzene (1t, 26.4 mg, 0.200 mmol, 1.00 equiv), according to GP3 with dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a, 78.6 mg, 0.300 mmol, 1.50 equiv) at 0 ºC in THF for 10 h. Purification by flash column chromatography on silica gel using cyclohexane/EtOAc = 150/1 afforded 3aa-$d_2$ as a colorless oil (38.7 mg, 72% yield, d.r. ≥ 98:2, 96% ee). $R_f$ = 0.60 (cyclohexane/EtOAc = 150/1). IR (ATR): $\tilde{\nu}$ = 3065, 3021, 2954, 1601, 1493, 1445, 1427, 1249, 1113, 1071, 1017, 950, 883, 832, 814, 768, 732, 698 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): δ 0.40 (s, 3H), 0.43 (s, 3H), 0.79 (s, 1H), 1.39 (s, 3H), 7.16–7.21 (m, 1H), 7.28–7.32 (m, 4H), 7.38–7.41 (m, 3H), 7.61–7.65 (m, 2H) ppm. $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): δ –1.4, –1.3, 13.8 (t, $J = 21.5$ Hz), 18.9 (t, $J = 24.5$ Hz), 23.9, 25.4, 125.6, 126.9, 127.9, 128.3, 129.0, 133.9, 140.0, 148.9 ppm. $^{29}$Si{$^1$H} DEPT NMR (99 MHz, CDCl$_3$): δ –3.9 ppm. HRMS (APCI) exact mass for [M+H]$^+$ C$_{18}$H$_{20}$D$_2$Si$: calculated 269.1689, found 269.1697.

Optical rotation: [α]$_D^2$ = –78.2 (c 2.0, CH$_2$Cl$_2$, 96% ee). The enantiomeric excess of 3aa-$d_2$ was determined by HPLC analysis on a chiral stationary phase (Daicel Chiracel OD-H column, column temperature 20 ºC, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.3 mL/min): $t_R$ = 21.0 min (major), $t_R$ = 22.2 min (minor).
7. Tamao–Fleming Oxidation of the Cyclopropysilane 3ga

HBF₄•OEt₂ (230 mg, 2.50 mmol, 2.50 equiv) was added dropwise to a solution of ((1R,2S)-2-[(1,1'-biphenyl]-4-yl)-2-methylcyclopropyl)dimethyl(phenyl)silane [3ga, 171 mg, 0.500 mmol, 1.00 equiv, d.r. ≥ 98:2, 93% ee] in CH₂Cl₂ (2.5 mL) at 0 °C. The mixture stirred for 5 hour at 0 °C. Then the solvent was removed under vacuum and MeOH (2.5 mL) and THF (2.5 mL) were added. KF (58.0 mg, 1.00 mmol, 2.00 equiv) and KHCO₃ (503 mg, 2.00 mmol, 10.0 equiv) were added to the solution at 0 °C and the mixture was stirred for 15 minutes at 0 °C. H₂O₂ (680 mg, 6.50 mmol, 13.0 equiv, 30% in water) was added, and the mixture was stirred overnight at room temperature. The reaction was quenched with Na₂S₂O₃ (10 mL, 2M aqueous) and poured into HCl (0.5M aqueous). The mixture was then extracted with Et₂O and the combined organic phases were dried over anhydrous MgSO₄, filtered and evaporated under reduced pressure. Purification of the residue by flash column chromatography on silica gel using cyclohexane/EtOAc = 3/1 as eluent afforded the corresponding alcohol SI-8 as a white solid (6.70 mg, 6% yield, d.r. ≥ 98:2, 92% ee, unstable).

Rᶠ = 0.35 (cyclohexane/EtOAc = 3/1). IR (ATR): ν = 3459, 3029, 2978, 2930, 1713, 1601, 1486, 1447, 1401, 1266, 1159, 1106, 948, 841, 766, 733, 697 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ 0.84 (dd, J = 6.0 Hz, J = 3.7 Hz, 1H), 1.23 (t, J = 6.5 Hz, 1H), 1.55 (s, 3H), 2.18 (s, 1H), 3.66 (dd, J = 7.0 Hz, J = 3.8 Hz, 1H), 7.22–7.26 (m, 2H), 7.29–7.34 (m, 1H), 7.39–7.44 (m, 1H), 7.49–7.52 (m, 2H), 7.54–7.58 (m, 2H) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 18.4, 22.6, 25.7, 58.3, 127.0, 127.1, 127.20, 127.22, 128.9, 138.8, 141.0, 145.1 ppm. HRMS (APCI) exact mass for [M-H]⁺ C₁₆H₁₅O⁺: calculated 223.1123, found 223.1118.

The enantiomeric excess of SI-8 was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IA column, column temperature 20 °C, solvent Heptane:iPrOH = 97:3, flow rate 0.5 mL/min): tᵣ = 37.2 min (minor), tᵣ = 44.4 min (major).
8. HPLC Traces

Dimethyl((1R,2S)-2-methyl-2-phenylocyclopropyl)(phenyl)silane (3aa): The enantiomeric excess of 3aa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.4 mL/min): $t_R = 13.4$ min (major), $t_R = 14.5$ min (minor).

rac-3aa

(R,S)-3aa
**3ba**

**((1R,2S)-2-(4-Fluorophenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ba):** The enantiomeric excess of 3ba was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-RH column, column temperature 20 °C, solvent MeCN:H2O = 80:20, flow rate 0.3 mL/min): tR = 18.2 min (major), tR = 21.8 min (minor).

**rac-3ba**

**(_R,S_)-3ba**

**(_R,S_)-3ba**
((1R,2S)-2-(4-Chlorophenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ca): The enantiomeric excess of 3ca was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.2 mL/min): $t_R = 30.9$ min (major), $t_R = 33.1$ min (minor).

rac-3ca

(R,S)-3ca
**3da**

((1R,2S)-2-(4-Bromophenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3da): The enantiomeric excess of 3da was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.3 mL/min): tR = 22.2 min (major), tR = 23.5 min (minor).

**rac-3da**

![ rac-3da HPLC chromatogram ]

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**(R,S)-3da**

![ (R,S)-3da HPLC chromatogram ]

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Dimethyl((1R,2S)-2-methyl-2-(4-(trifluoromethyl)phenyl)cyclopropyl)(phenyl)silane (3ea): The enantiomeric excess of 3ea was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.2 mL/min): $t_R = 25.5$ min (major), $t_R = 27.2$ min (minor).

rac-3ea

(R,S)-3ea
Dimethyl((1\text{R},2\text{S})-2-methyl-2-(p-tolyl)cyclopropyl)(phenyl)silane (3fa): The enantiomeric excess of 3fa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-RH column, column temperature 20 °C, solvent MeCN:H\text{2}O = 60:40, flow rate 0.3 mL/min): \(t_R = 116.9\) min (minor), \(t_R = 121.8\) min (major).

\(\text{rac-}3\text{fa}\)

\(\text{(R,S)-}3\text{fa}\)
((1R,2S)-2-[(1,1'-Biphenyl]-4-yl]-2-methylcyclopropyl)dimethyl(phenyl)silane (3ga): The enantiomeric excess of 3ga was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane/iPrOH = 99:1, flow rate 0.4 mL/min): \( t_R = 13.4 \) min (minor), \( t_R = 16.8 \) min (major).
((1R,2S)-2-(4-Methoxyphenyl)-2-methylecyclopropyl)dimethyl(phenyl)silane (3ha): The enantiomeric excess of 3ha was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.4 mL/min): $t_R = 30.4$ min (minor), $t_R = 32.8$ min (major).

**rac-3ha**

**(*R,S*)-3ha**
((1R,2S)-2-(3-Methoxyphenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ia): The enantiomeric excess of 3ia was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralecel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99:1, flow rate 0.3 mL/min): $t_R = 17.8$ min (major), $t_R = 20.1$ min (minor).

$\textit{rac-3ia}$

$\textit{(R,S)-3ia}$
((1R,2S)-2-(Benzo[d][1,3]dioxol-5-yl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ja): The enantiomeric excess of 3ja was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane:iPrOH = 95:5, flow rate 0.6 mL/min): t_R = 10.6 min (major), t_R = 18.1 min (minor).

rac-3ja

(R,S)-3ja
Dimethyl((1R,2R)-2-methyl-2-(thiophen-2-yl)cyclopropyl)(phenyl)silane (3ka): The enantiomeric excess of 3ka was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.3 mL/min): t\text{R} = 24.3 min (major), t\text{R} = 26.8 min (minor).

\textit{rac-3ka}

\textit{(R,R)-3ka}
Dimethyl((1R,2S)-2-methyl-2-(naphthalen-1-yl)cyclopropyl)(phenyl)silane (3la): The enantiomeric excess of 3la was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-RH column, column temperature 20 °C, solvent MeCN:H₂O = 70:30, flow rate 0.3 mL/min): tᵣ = 63.7 min (major), tᵣ = 70.0 min (minor).

rac-3la

(R,S)-3la
Dimethyl((1R,2S)-2-methyl-2-(naphthalen-2-yl)cyclopropyl)(phenyl)silane (3ma): The enantiomeric excess of 3ma was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-RH column, column temperature 20 °C, solvent MeCN:H2O = 80:20, flow rate 0.3 mL/min): t_R = 32.4 min (major), t_R = 42.8 min (minor).

rac-3ma

(\(R,S\))-3ma

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(\(R,S\))-3ma

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</table>
((1R,2S)-2-Ethyl-2-phenylcyclopropyl)dimethyl(phenyl)silane (3na): The enantiomeric excess of 3na was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.3 mL/min): $t_R = 18.5$ min (major), $t_R = 20.4$ min (minor).

rac-3na

(R,S)-3na
((1R,2R)-2-Isopropyl-2-phenylcyclopropyl)dimethyl(phenyl)silane (3oa): The enantiomeric excess of 3oa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-RH column, column temperature 20 °C, solvent MeCN:H₂O = 70:30, flow rate 0.3 mL/min): tᵣ = 38.8 min (major), tᵣ = 41.8 min (minor) with a bad separation.

rac-3oa

(R,R)-3oa
Dimethyl(phenyl)((1R,2R)-1-phenyl-[1,1'-bi(cyclopropan)]-2-yl)silane (3pa): The enantiomeric excess of 3pa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.3 mL/min): t_R = 22.0 min (major), t_R = 24.4 min (minor).

rac-3pa

(R,R)-3pa
The enantiomeric excess of 3qa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.2 mL/min): $t_R = 36.2$ min (major), $t_R = 39.3$ min (minor).

**rac-3qa**

**($R,R$)-3qa**
((1S,2R)-3',4'-Dihydro-2'H-spiro[cyclopropane-1,1'-napthalen]-2-yl)dimethyl(phenyl)silane (3ra): The enantiomeric excess of 3ra was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.3 mL/min): \( t_R = 27.3 \) min (minor), \( t_R = 29.8 \) min (major).

\textit{rac-3ra}

\textit{(S,R)-3ra}
**3sa**

(R)-(2,2-diphenylcyclopropyl)dimethyl(phenyl)silane (3sa): The enantiomeric excess of 3sa was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent Heptane/iPrOH = 99:1, flow rate 0.4 mL/min): $t_R = 28.0$ min (major), $t_R = 33.7$ min (minor)

**rac-3sa**

![HPLC chromatogram of rac-3sa](image)

**(+)-3sa**

![HPLC chromatogram of (+)-3sa](image)
Methyl((1R,2S)-2-methyl-2-phenylcyclopropyl)diphenylsilane (3ab): The enantiomeric excess of 3ab was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99:1, flow rate 0.3 mL/min): \( t_R = 21.0 \text{ min (major)} \), \( t_R = 23.8 \text{ min (minor)} \).
((1R,2S)-2-(4-Bromophenyl)-2-methylcyclopropyl)(methyl)diphenylsilane (3db): The enantiomeric excess of 3db was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.4 mL/min): t_R = 22.5 min (major), t_R = 27.4 min (minor).

rac-3db

(rac)-3db

(Signal 4: DAD1 D, Sig=230.4 Ref=360.100 (ZLU/H-PH2MESi-BPMP-RAC.D)

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(R.S)-3db

(Signal 4: DAD1 D, Sig=230.4 Ref=360.100 (ZLU/H-PH2MESi-BPMP-CHIRAL.D)

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<tr>
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</tbody>
</table>
((1R,2S)-2-([1,1'-Biphenyl]-4-yl)-2-methylcyclopropyl)(methyl)diphenylsilane (3gb): The enantiomeric excess of 3gb was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99:1, flow rate 0.4 mL/min): t\textsubscript{R} = 14.8 min (minor), t\textsubscript{R} = 24.4 min (major).

\textit{rac-3gb}

\begin{table}
\centering
\begin{tabular}{cccccc}
\hline
\textbf{Peak} & \textbf{RetTime} & \textbf{Type} & \textbf{Width} & \textbf{Area} & \textbf{Height} & \textbf{Area} \\
\textbf{#} & [min] & & [min] & [mAU*s] & [mAU] & \% \\
\hline
1 & 14.562 & W & 0.3815 & 2.32556e4 & 918.31066 & 49.8629 \\
2 & 23.552 & B & 0.9163 & 2.33836e4 & 342.59732 & 58.1371 \\
\hline
\end{tabular}
\end{table}

\textit{(R,S)-3gb}

\begin{table}
\centering
\begin{tabular}{cccccc}
\hline
\textbf{Peak} & \textbf{RetTime} & \textbf{Type} & \textbf{Width} & \textbf{Area} & \textbf{Height} & \textbf{Area} \\
\textbf{#} & [min] & & [min] & [mAU*s] & [mAU] & \% \\
\hline
\textit{rac-3gb} & 1 & 14.792 & W & 0.4242 & 133.35529 & 5.24009 & 1.2345 \\
2 & 24.435 & W & 1.0978 & 1.06686e4 & 161.96240 & 98.7655 \\
\hline
\end{tabular}
\end{table}
Triethyl((1R,2S)-2-methyl-2-phenylcyclopropyl)silane (3ae): The enantiomeric excess of 3ae was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.2 mL/min): $t_R = 13.7$ min (major), $t_R = 14.5$ min (minor).

rac-3ae

(R,S)-3ae
(1R,2S)-2-Methyl-2-phenylcyclopropyl)tripropylsilane (3af): The enantiomeric excess of 3af was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-RH column, column temperature 20 °C, solvent MeCN:H$_2$O = 75:25, flow rate 0.3 mL/min): $t_R = 42.0$ min (major), $t_R = 47.3$ min (minor).

**rac-3af**

![DAD1 D, Sig=230.4 Ref=360,100 (ZI/ZL-H-NPRESHIR-RAC-2D)](image)

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<tbody>
<tr>
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**(R,S)-3af**

![DAD1 D, Sig=230.4 Ref=360,100 (ZI/ZL-H-NPRESHIR-CHIRAL D)](image)

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<thead>
<tr>
<th>Peak RetTime Type</th>
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<th>Area %</th>
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</thead>
<tbody>
<tr>
<td># [min]</td>
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<td>[mAU*s]</td>
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<td>2 47.326 BB</td>
<td>1.1933</td>
<td>1462.29834</td>
<td>18.39735</td>
<td>2.6390</td>
</tr>
</tbody>
</table>
Tert-butyldimethyl((1\textit{R},2\textit{S})-2-methyl-2-phenylcyclopropyl)silane (3ag): The enantiomeric excess of 3ag was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-RH column, column temperature 20 °C, solvent MeCN:H\textsubscript{2}O = 60:40, flow rate 0.4 mL/min): \( t_R = 58.0 \text{ min (major), } t_R = 63.8 \text{ min (minor) with a bad separation.} 

\textit{rac}-3ag

\begin{center}
\includegraphics[width=\textwidth]{image1}
\end{center}

\begin{center}
\begin{tabular}{lllll}
Peak & RetTime & Type & Width & Area & Height & Area & \%\\
\hline
1 & 57.720 & MM & 2.0027 & 1.5919e4 & 132.47739 & 49.0899 & \\
2 & 63.368 & MM & 2.0534 & 1.6509e4 & 134.00111 & 50.9101 & \\
\end{tabular}
\end{center}

\textit{(R,S)}-3ag

\begin{center}
\includegraphics[width=\textwidth]{image2}
\end{center}

\begin{center}
\begin{tabular}{lllll}
Peak & RetTime & Type & Width & Area & Height & Area & \%\\
\hline
1 & 57.961 & MM & 2.1696 & 3.8373e4 & 294.78568 & 96.2744 & \\
\end{tabular}
\end{center}
Dimethyl((1R,2S,3R)-2-methyl-2-phenylcyclopropyl-3-d)(phenyl)silane (3aa-d1): The enantiomeric excess of 3aa-d1 was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.3 mL/min): tR = 22.5 min (major), tR = 23.4 min (minor).

rac-3aa-d1

(R,S,R)- 3aa-d1
Dimethyl((1R,2S,3S)-2-methyl-2-phenylcyclopropyl-1,3-d2)(phenyl)silane (3aa-d2): The enantiomeric excess of 3aa-d2 was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent Heptane:iPrOH = 99.9:0.1, flow rate 0.3 mL/min): tR = 21.0 min (major), tR = 22.2 min (minor).

rac-3aa-d2

(R,S,S)- 3aa-d2
(1R,2S)-2-((1,1'-biphenyl)-4-yl)-2-methylcyclopropan-1-ol (SI-8): The enantiomeric excess of SI-8 was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel IA column, column temperature 20 °C, solvent Heptane:iPrOH = 97:3, flow rate 0.5 mL/min): t<sub>R</sub> = 37.2 min (minor), t<sub>R</sub> = 44.4 min (major).
9. Determination of the Absolute Configurations of the Products

A solution of (R,S)-3ga (d.r. ≥ 98:2, 95% ee) in EtOH/Et₂O was left standing at room temperature to grow single crystals. The absolute configuration of 3ga was confirmed unambiguously by X-ray diffraction analysis, and the other compounds were assigned the same stereochemistry. CCDC 1935247 contains the supplementary crystallographic data for (R,S)-3ga.

(((1R,2S)-2-([1,1'-Biphenyl]-4-yl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ga)

![3ga](image)

Table S2. Crystal data and structure refinement for cu-3488a.

<table>
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<th>Identification code</th>
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</tr>
<tr>
<td>Temperature</td>
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<td>Wavelength</td>
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<td>Crystal system</td>
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<td>Space group</td>
<td>P2₁</td>
</tr>
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<td>Unit cell dimensions</td>
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<td>a = 11.1006(6) Å</td>
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<tr>
<td>b = 7.9444(4) Å</td>
<td>β = 93.722(5)°</td>
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<tr>
<td>c = 22.0823(15) Å</td>
<td>γ = 90°</td>
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<td>Z</td>
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<td>Density (calculated)</td>
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<td>F(000)</td>
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<tr>
<td>Crystal size</td>
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<td>Parameter</td>
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<tr>
<td>Theta range for data collection</td>
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<td>Absorption correction</td>
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<td>Full-matrix least-squares on F²</td>
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<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on F²</td>
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<td>Final R indices [I&gt;2sigma(I)]</td>
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<td>R indices (all data)</td>
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<td>Absolute structure parameter</td>
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<td>Largest diff. peak and hole</td>
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</tr>
</tbody>
</table>
10. NOE interactions for representative compounds
11. NMR Spectra

tert-Butyl(methyl)(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2c) $^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$):
5-(2,2-Dibromo-1-methylcyclopropyl)benzo[1,3]dioxole (SI-3j) $^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$):
5-(1-Methylcycloprop-2-en-1-yl)benzo[d][1,3]dioxole (1j): $^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$):

![NMR Spectra Image]
(2,2-Dibromo-[1,1′-bi(cyclopropan)]-1-yl)benzene (SI-3p): $^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$):
[1,1'-Bi(cyclopropan)]-2-en-1-ylbenzene (1p): $^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$):
Dimethyl((1R,2S)-2-methyl-2-phenylcyclopropyl)(phenyl)silane (3aa) \(^1\)H NMR (500 MHz, CDCl₃)
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}\text{Si}^{[\text{H}]} \text{ DEPT NMR (99 MHz, CDCl}_3\text{):}
((1R,2S)-2-(4-Fluorophenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ba): $^1$H NMR (500 MHz, CDCl$_3$)  

$\#$ = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^29$Si$^1$H DEPT NMR (99 MHz, CDCl$_3$):
$^{19}\text{F NMR}$ (471 MHz, CDCl$_3$):
((1R,2S)-2-(4-Chlorophenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ca): $^1$H NMR (500 MHz, CDCl$_3$) # = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}$Si$^1$H \textit{DEPT NMR} (99 MHz, CDCl$_3$):
(1R,2S)-2-(4-Bromophenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3da): 

\[ ^1H \text{NMR (500 MHz, CDCl}_3 \] 

\[ \# = H_2O \]
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}$Si{$^1$H} DEPT NMR (99 MHz, CDCl₃):
Dimethyl((1R,2S)-2-methyl-2-(4-(trifluoromethyl)phenyl)cyclopropyl)(phenyl)silane (3ea): $^1$H NMR (500 MHz, CDCl$_3$)  

# = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}\text{Si}^{1}\text{H}_{}$ DEPT NMR (99 MHz, CDCl$_3$):
$^{19}\text{F NMR}$ (471 MHz, CDCl$_3$):
Dimethyl((1R,2S)-2-methyl-2-(p-tolyl)cyclopropyl)(phenyl)silane (3fa): $^1$H NMR (500 MHz, CDCl$_3$) $#$ = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}$Si–$^1$H DEPT NMR (99 MHz, CDCl$_3$):
((1R,2S)-2-((1,1'-Biphenyl)-4-yl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ga): \(^1\)H NMR (500 MHz, CDCl\(_3\))
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl$_3$)
((1R,2S)-2-(4-Methoxyphenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ha): $^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}\text{Si}^{[1\text{H}]}$ DEPT NMR (99 MHz, CDCl$_3$)
((1R,2S)-2-(3-Methoxyphenyl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ia) $^1$H NMR (500 MHz, CDCl$_3$)  

# = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}\text{Si}^{1\text{H}}\text{ DEPT NMR (99 MHz, CDCl}_3\text{)}$
((1R,2S)-2-(Benzo[d][1,3]dioxol-5-yl)-2-methylcyclopropyl)dimethyl(phenyl)silane (3ja): $^1$H NMR (500 MHz, CDCl$_3$)  

# = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}$Si-$^1$H DEPT NMR (99 MHz, CDCl$_3$):
Dimethyl((1R,2R)-2-methyl-2-(thiophen-2-yl)cyclopropyl)(phenyl)silane (3ka): \(^{1}H\) NMR (500 MHz, CDCl\(_3\))
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}\text{Si}^{1\text{H}}$ DEPT NMR (99 MHz, CDCl$_3$):
Dimethyl(1R,2S)-2-methyl-2-(naphthalen-1-yl)cyclopropyl)(phenyl)silane (3la): $^1$H NMR (500 MHz, CDCl$_3$)  # = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}\text{Si}^{1\text{H}}$ DEPT NMR (99 MHz, CDCl$_3$):
Dimethyl((1R,2S)-2-methyl-2-(naphthen-2-yl)cyclopropyl)(phenyl)silane (3ma): $^1$H NMR (500 MHz, CDCl$_3$)  # = H$_2$O
$^{13}$C NMR (125 MHz, CDCl₃):
$^{29}\text{Si}^{1}\text{H} \text{ DEPT NMR} (99 \text{ MHz, CDCl}_3)$:
((1R,2S)-2-Ethyl-2-phenylcyclopropyl)dimethyl(phenyl)silane (3na): $^1$H NMR (500 MHz, CDCl$_3$)  

# = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}$Si$^{1}$H DEPT NMR (99 MHz, CDCl$_3$):
((1R,2R)-2-Isopropyl-2-phenylcyclopropyl)dimethyl(phenyl)silane (3a): $^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl$_3$):
Dimethyl(phenyl)((1R,2R)-1-phenyl-[1,1'-bi(cyclopropan)]-2-yl)silane (3pa): $^1$H NMR (500 MHz, CDCl$_3$)   $\#$ = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl$_3$):
((1R,2R)-2-Benzyl-2-methylcyclopropyl)dimethyl(phenyl)silane (3qa) $^1$H NMR (500 MHz, CDCl$_3$) $\# = \text{H}_2\text{O}$
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^29$Si$^1$H DEPT NMR (99 MHz, CDCl$_3$):
((15S,2R)-3',4'-Dihydro-2'H-spiro[cyclopropane-1,1'-naphthalen]-2-yl)dimethyl(phenyl)silane (3ra) $^1$H NMR (500 MHz, CDCl$_3$) $\# = H_2O$
$^{13}$C NMR (125 MHz, CDCl$_3$):
\(^{1}H-^{29}\text{Si}\) HMQC NMR (99 MHz, CDCl\(_3\)):
(R)-(2,2-diphenylcyclopropyl)dimethyl(phenyl)silane (3sa): $^1$H NMR (500 MHz, CDCl$_3$) \( \# = \text{H}_2\text{O} \)
13C NMR (125 MHz, CDCl3):
$^{29}\text{Si}^{1\text{H}}$ DEPT NMR (99 MHz, CDCl$_3$):
Methyl((1R,2S)-2-methyl-2-phenylcyclopropyl)diphenylsilane (3ab): $^1$H NMR (500 MHz, CDCl$_3$) \# = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}$Si$^1$H DEPT NMR (99 MHz, CDCl$_3$):
\[(1R,2S)-2-(4\text{-bromophenyl})-2\text{-methylcyclopropyl})(methyl)diphenylsilane (3db) \text{ } ^1\text{H NMR (500 MHz, CDCl}_3) \quad \# = \text{H}_2\text{O}\]
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}$Si-$^1$H DEPT NMR (99 MHz, CDCl$_3$):
((1R,2S)-2-([1,1'-biphenyl]-4-yl)-2-methylcyclopropyl)(methyl)diphenylsilane (3gb):) $^1$H NMR (500 MHz, CDCl$_3$)  # = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}$Si$^1$H DEPT NMR (99 MHz, CDCl$_3$):
Triethyl((1R,2S)-2-methyl-2-phenylcyclopropyl)silane (3ae) $^1$H NMR (500 MHz, CDCl$_3$)  

# = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^1$H-$^{29}$Si HMQC NMR (99 MHz, CDCl$_3$):
((1R,2S)-2-Methyl-2-phenylcyclopropyl)tripropylsilane (3af) $^1$H NMR (500 MHz, CDCl$_3$)
\(^{13}\)C NMR (125 MHz, CDCl\(_3\)):
$^1\text{H}-^{29}\text{Si HMQC NMR}$ (99 MHz, CDCl$_3$):
tert-Butyldimethyl((1R,2S)-2-methyl-2-phenycyclopropyl)silane (3ag) $^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^1$H-$^{29}$Si HMQC NMR (99 MHz, CDCl$_3$):
Dimethyl((1R,2S,3R)-2-methyl-2-phenylcyclopropyl-3-d)(phenyl)silane (3aa-d) $^1$H NMR (500 MHz, CDCl$_3$) # = H$_2$O
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}$Si$^1$H DEPT NMR (99 MHz, CDCl$_3$):
Dimethyl((1R,2S,3S)-2-methyl-2-phenylcyclopropyl-1,3-\textit{d}_2)(phenyl)silane (3aa-\textit{d}_2) \textit{^1}H NMR (500 MHz, CDCl\textsubscript{3})
$^{13}$C NMR (125 MHz, CDCl$_3$):
$^{29}\text{Si}^{[1\text{H}]} \text{ DEPT NMR (99 MHz, CDCl}_3\text{):} \quad$
(1R,2S)-2-((1,1'-biphenyl)-4-yl)-2-methylcyclopropan-1-ol (SI-8) $^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$):
12. References

[S4] Cambridge Crystallographic Data Centre:
   http://www.ccdc.cam.ac.uk/Solutions/CSDSystem/Pages/Mercury.aspx.