Supporting Information

Gold-Catalyzed Rearrangement of (Silylecyclopropenyl)methyl Ethers into (Silylmethylene)cyclopropanes

Florence Hiault, Alexis Archambeau, Frédéric Miege, Christophe Meyer* and Janine Cossy*
Laboratory of Organic Chemistry, Institute of Chemistry, Biology and Innovation (CBI)
ESPCI Paris, CNRS (UMR8231), PSL Research University, 10 rue Vauquelin 75231 Paris Cedex 05 - France

Table of Content

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. General methods</td>
<td>SI-2</td>
</tr>
<tr>
<td>2. Preparation of trimethylsilylcyclopropanes 1a, 1b, and 1b’</td>
<td>SI-2</td>
</tr>
<tr>
<td>3. Preparation of (dimethylphenylsilyl)cyclopropenyl carbinols 8a-8j/j’</td>
<td>SI-6</td>
</tr>
<tr>
<td>4. Preparation of MOM ethers 9a-9j/9j’</td>
<td>SI-13</td>
</tr>
<tr>
<td>5. Determination of the optical purities of (R)-8a and 10a generated by gold-catalyzed rearrangement of (R)-9a</td>
<td>SI-19</td>
</tr>
<tr>
<td>5. Copies of the $^1$H and $^{13}$C NMR spectra of new compounds</td>
<td>SI-20</td>
</tr>
<tr>
<td>6. Relevant correlations in the NOESY spectra of compounds 10a, 10b, 10c</td>
<td>SI-102</td>
</tr>
</tbody>
</table>
1. General methods

Reactions involving air- and moisture-sensitive organometallic reagents were carried out under argon in flame-dried glassware with a magnetic stirring bar and sealed with a rubber septum.

THF was distilled from sodium-benzophenone. \( \text{iPr}_2\text{NH}, \text{iPr}_2\text{NEt}, \text{CH}_2\text{Cl}_2 \) and \( \text{iPrOH} \) were distilled from \( \text{CaH}_2 \). Reagents were obtained from commercial suppliers and used as received without further purification.

Flash column chromatography was performed on silica gel (230-400 mesh).

TLC was performed on silica gel plates visualized either with a UV lamp (254 nm), or using solutions of \( p \)-anisaldehyde-sulfuric acid-acetic acid in EtOH or \( \text{KMnO}_4-\text{K}_2\text{CO}_3 \) in water followed by heating.

Infrared spectra were recorded with a Bruker TENSOR 27 instrument (IR-FT) with attenuated total reflectance (ATR).

NMR spectra were recorded with a Bruker AVANCE 400 instrument. \(^1\text{H} \) NMR spectra were recorded at 400 MHz and data are reported as follows: chemical shift relative to tetramethylsilane, multiplicity, coupling constant, integration. \(^{13}\text{C} \) NMR spectra were recorded at 100 MHz and data are reported as follows: chemical shift referenced to the solvent signal (\( \delta \) 77.16 ppm for CDCl₃) and carbon environment (deduced from DEPT experiments).

HRMS (ESI) were obtained with an orbitrap mass analyzer.

Enantiomeric purities were determined by supercritical fluid chromatography (SFC) on a Minigram Berger SFC-Mettler Toledo apparatus equipped with a chiral stationary phase.
2. Preparation of trimethylsilylcyclopropenes 1a, 1b, and 1b’

2.1. Preparation of 1a

![Chemical Reaction Diagram]

\[
\text{Me} \quad \text{Me} \\
H \quad O \quad \text{OBn} \\
\text{13} \\
\text{Me} \quad \text{Me} \\
O \quad \text{OBn} \\
\text{1a}
\]

{2-[2-(Benzyloxy)-1-(prop-2-en-1-yloxy)ethyl]-3,3-dimethylcycloprop-1-en-1-yl}trimethylsilane (1a).

To a solution of cyclopropene 13\(^1\) (71 mg, 0.27 mmol) and Me\(_3\)SiCl (70 µL, 0.55 mmol, 2 equiv) in THF (2.7 mL) at –50 °C, was added dropwise a solution of LDA [0.60 mL, 0.5 M (stock solution prepared by treatment of iPr\(_2\)NH in THF and n-BuLi in hexanes), 0.30 mmol, 1.1 equiv]. The reaction mixture was warmed to rt and stirred for further 10 min but incomplete conversion was observed by TLC analysis. The reaction mixture was cooled to –50 °C and more LDA was added (0.16 mL, 0.5 M in THF/hexanes, 0.080 mmol, 0.3 equiv). After warming to rt, the reaction mixture was hydrolyzed with saturated aqueous solution of NH\(_4\)Cl. The mixture was extracted with Et\(_2\)O and the combined organic phases were washed with brine, dried over MgSO\(_4\), filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/EtOAc, 98:2 to 95:5) to afford 55 mg (60%) of 1a as a colorless oil.

IR (neat): 1776, 1453, 1363, 1248, 1195, 1095, 993, 923, 838, 734, 696 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.37–7.26 (m, 5H), 5.95 (m, 1H), 5.31 (dm, apparent br d, \(J = 17.2 \text{ Hz}, 1H\)), 5.18 (dm, apparent br d, \(J = 10.4 \text{ Hz}, 1H\)), 4.67 (apparent t, \(J = 5.5 \text{ Hz}, 1H\)), 4.66 (d, AB syst, \(J = 12.0 \text{ Hz}, 1H\)), 4.57 (d, AB syst, \(J = 12.0 \text{ Hz}, 1H\)), 4.19 (dd, \(J = 12.7, 5.2 \text{ m, 1H}\)), 4.00 (apparent dd, \(J = 12.7, 6.0 \text{ Hz}, 1H\)), 3.64 (d, \(J = 5.5 \text{ Hz}, 2H\)), 1.14 (s, 6H), 0.14 (s, 9H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 145.0 (C), 138.5 (C), 135.0 (CH), 128.5 (2 \times CH), 127.8 (2 \times CH), 127.7 (CH), 126.8 (C), 117.0 (CH\(_2\)), 76.1 (CH), 73.6 (CH\(_2\)), 72.3 (CH\(_2\)), 70.4 (CH\(_2\)), 28.0 (CH\(_3\)), 27.9 (CH\(_3\)), 21.0 (C), –0.5 (3 \times CH\(_3\)).

HRMS (ESI): \(m/z\) calcd for C\(_{20}\)H\(_{30}\)O\(_2\)NaSi [M + Na\(^+\)]: 353.19029; found: 353.19073.

---

2.2. Preparation of 1b

{[2-(Benzyloxy)-1-(3,3-dimethylcycloprop-1-en-1-yl)ethoxy]methyl}benzene (15).

To a solution of cyclopropenyl carbinol 14 (151 mg, 0.692 mmol), n-Bu₄NI (25.5 mg, 0.069 mmol, 10 mol %) and benzyl bromide (120 μL, 1.01 mmol, 1.5 equiv) in THF (2.5 mL) at 0 °C was added t-BuOK (93 mg, 0.83 mmol, 1.2 equiv). The reaction mixture was warmed to rt, stirred for 0.5 h and then hydrolyzed with a saturated aqueous solution of NH₄Cl. The resulting mixture was extracted with Et₂O, the combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/EtOAc, 92:8 to 94:6) to afford 204 mg (96%) of 15 as a yellow oil.

IR (neat): 1751, 1496, 1454, 1364, 1205, 1094, 733, 695, 606 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.40–7.25 (m, 10H), 7.17 (m, apparent br s, 1H), 4.76 (dd, J = 12.0, 2.9 Hz, 1H), 4.68 (m, 1H), 4.62 (dd, J = 12.0, 2.9 Hz, 1H), 4.59–4.54 (m, 2H), 3.74–3.65 (m, 2H), 1.19 (d, J = 3.1 Hz, 3H), 1.18 (d, J = 3.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 138.4 (C), 138.3 (C), 132.4 (C), 128.5 (4 x CH), 127.9 (2 x CH), 127.8 (2 x CH), 127.7 (2 x CH), 117.7 (CH), 74.9 (CH), 73.6 (CH₂), 72.0 (CH₂), 71.3 (CH₂), 27.9 (CH₃), 27.8 (CH₃), 20.0 (C).

HRMS (ESI): m/z calcd for C₂₁H₂₄O₂Na [M + Na⁺]: 331.16697; found: 331.16685.

{2-[1,2-Bis(benzyloxy)ethyl]-3,3-dimethylcyclo-prop-1-en-1-yl]trimethylsilane (1b).

This compound was prepared by silylation of cyclopropene 15 using LDA (1.4 equiv) and TMSCl (2 equiv) in THF (−50 °C to rt), as described for the preparation of 1a from 13, and purified by flash column chromatography (petroleum ether/EtOAc, 92:8 to 94:6).

Yield: 97 mg (77%); colorless oil.

IR (neat): 1776, 1454, 1363, 1248, 1094, 1028, 837, 732, 695, 632 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.42–7.27 (m, 10H), 4.77 (d, AB syst, J = 12.0 Hz, 1H), 4.73 (br dd, J = 6.8, 4.2 Hz, 1H), 4.64 (d, AB syst, J = 12.0 Hz, 1H), 4.57 (d, AB syst, J =
12.0 Hz, 1H), 4.55 (d, AB syst, \(J = 12.0\) Hz, 1H), 3.74–3.67 (m, 2H), 1.19 (s, 3H), 1.18 (s, 3H), 0.17 (s, 9H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 144.9\) (C), 138.6 (C), 138.5 (C), 128.4 (4 x CH), 127.9 (2 x CH), 127.8 (2 x CH), 127.6 (2 x CH), 127.0 (C), 76.0 (CH), 73.5 (CH\(_2\)), 72.4 (CH\(_2\)), 71.3 (CH\(_2\)), 28.0 (2 x CH\(_3\)), 21.0 (C), –0.5 (3 x CH\(_3\)).

HRMS (ESI): \(m/z\) calcld for C\(_{24}\)H\(_{32}\)O\(_2\)SiNa [M + Na\(^+\)]: 403.20674; found: 403.20638.

### 2.3. Preparation of 1'b

{(2-(Benzyloxy)-1-(3,3-dimethylcycloprop-1-en-1-yl)ethoxy)(2H\(_2\))methyl}benzene (15').

This compound was prepared by benzylolation of cyclopropenylcarbinol 14 with PhCD\(_2\)Br, as described for the preparation of 15.

Yield: 207 mg (94%); yellow oil.

IR (neat): 1750, 1496, 1450, 1364, 1257, 1096, 1026, 717, 696, 603 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.39–7.25\) (m, 10H), 7.16 (m, 1H), 4.67 (m, 1H), 4.62 (d, AB syst, \(J = 12.1\) Hz, 1H), 4.56 (d, AB syst, \(J = 12.1\) Hz, 1H), 3.73–3.65 (m, 2H), 1.19 (s, 3H), 1.18 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 138.3\) (C), 132.4 (C), 128.5 (4 x CH), 128.0 (2 x CH), 127.8 (2 x CH), 127.73 (CH), 127.69 (CH), 117.7 (CH), 74.8 (CH), 73.6 (CH\(_2\)), 72.0 (CH\(_2\)), 70.5 (CD\(_2\), weak intensity), 27.9 (CH\(_3\)), 27.8 (CH\(_3\)), 20.0 (C).

HRMS (ESI): \(m/z\) calcld for C\(_{21}\)H\(_{22}\)D\(_2\)O\(_2\)Na [M + Na\(^+\)]: 333.17947; found: 333.17940.

{2-[2-(Benzyloxy)-1-[phenyl(2H\(_2\))methoxyethyl]-3,3-dimethylcycloprop-1-en-1-yl]-trimethylsilane (1'b).

This compound was prepared by silylation of cyclopropene 15' using LDA (1.2 equiv) and TMSCl (2 equiv) in THF (~50 °C to rt), as described for the preparation of 1b from 15, and purified by flash column chromatography (petroleum ether/EtOAc, 98:2 to 96:4).

Yield: 98 mg (75%); colorless oil.

IR (neat): 1776, 1450, 1363, 1248, 1096, 1027, 838, 732, 716, 696, 632 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.40–7.25\) (m, 10H), 4.71 (dd, \(J = 6.8, 4.3\) Hz, 1H), 4.63 (d, AB syst, \(J = 12.0\) Hz, 1H), 4.55 (d, AB syst, \(J = 12.0\) Hz, 1H), 3.73–3.64 (m, 2H), 1.175 (s, 3H), 1.169 (s, 3H), 0.16 (s, 9H).
13C NMR (100 MHz, CDCl3): δ = 145.0 (C), 138.5 (2 × C), 128.4 (4 × CH), 127.9 (2 × CH), 127.8 (2 × CH), 127.6 (2 × CH), 127.0 (C), 75.9 (CH), 73.5 (CH2), 72.4 (CH2), 70.5 (CD2, quintet, 1J_C-D = 21Hz), 28.0 (2 × CH3), 21.0 (C), –0.5 (3 × CH3).

HRMS (ESI): m/z calcd for C24H30D2O2SiNa [M + Na+]: 405.21937; found: 405.21893.

3. Preparation of (dimethylphenylsilyl)cyclopropenyl carbinols 8a-8j/j’

2-(Benzyloxy)-1-[2-(dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]ethan-1-ol (8a) (Representative procedure).

To a solution of cyclopropenylsilane 62 (1.29 g, 6.39 mmol, 1.6 equiv) in THF (20 mL) at −78 °C was added dropwise n-BuLi (2.4 mL, 2.5 M solution in hexanes, 6.0 mmol, 1.5 equiv). After 1 h stirring from −78 °C to −10 °C, the reaction mixture was cooled to −50 °C and benzyloxyacetaldehyde (561 µL, 4.00 mmol) was added. The reaction mixture was allowed to warm to −10 °C within 1 h, stirred for a further 1 h at that temperature and then hydrolyzed with a saturated aqueous solution of NH4Cl. The layers were separated and the aqueous phase was extracted with Et2O. The combined organic phases were washed with brine, dried over MgSO4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (petroleum ether/Et2O, 100:0 to 93:7) afforded 977 mg (70%) of alcohol 8a as a yellow oil.

IR (neat): 3448 (br), 1777, 1454, 1428, 1363, 1248, 1113, 818, 778, 731, 697, 655 cm−1.

1H NMR (400 MHz, CDCl3): δ = 7.58–7.55 (m, 2H), 7.40–7.27 (m, 8H), 4.91 (m, 1H), 4.56 (d, AB syst, J = 12.1 Hz, 1H), 4.53 (d, AB syst, J = 12.1 Hz, 1H), 3.63 (dd, J = 9.6, 3.5 Hz, 1H), 3.49 (dd, J = 9.6, 6.9 Hz, 1H), 2.24 (d, J = 5.1 Hz, 1H, OH), 1.18 (s, 3H), 1.17 (s, 3H), 0.424 (s, 3H), 0.419 (s, 3H).

13C NMR (100 MHz, CDCl3): δ = 149.0 (C), 138.1 (C), 138.0 (C), 133.8 (2 × CH), 129.4 (CH), 128.6 (2 × CH), 128.0 (2 × CH), 127.9 (3 × CH), 124.6 (C), 73.6 (CH2), 73.2 (CH2), 69.8 (CH), 27.93 (CH3), 27.85 (CH3), 22.6 (C), –1.6 (2 × CH3).

HRMS (ESI): m/z calcd for C22H28O2SiNa [M + Na+]: 375.17508; found: 375.17532.

4-[(tert-Butyldimethylsilyl)oxy]-1-[2-(dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]butan-1-ol (8b).

Prepared from 4-[(tert-butyldimethylsilyl)oxy]butanal \(^3\) and purified by flash column chromatography (petroleum ether/Et\(_2\)O, 90:10).

Yield: 920 mg (63%); yellow oil.

IR (neat): 3426 (br), 1776, 1249, 1112, 833, 818, 775, 730, 699, 656 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.60–7.56\) (m, 2H), \(7.39–7.35\) (m, 3H), \(4.71\) (dt, \(J = 6.5, 5.2\) Hz, 1H), \(3.68–3.60\) (m, 2H), \(2.07\) (d, \(J = 5.2\) Hz, 1H, OH), \(1.81–1.71\) (m, 1H), \(1.68–1.62\) (m, 3H), \(1.20\) (s, 3H), \(1.19\) (s, 3H), \(0.89\) (s, 9H), \(0.44\) (s, 6H), \(0.05\) (s, 6H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 152.4\) (C), \(138.3\) (C), \(133.8\) (2 \(\times\) CH), \(129.4\) (CH), \(128.0\) (2 \(\times\) CH), \(122.1\) (C), \(70.2\) (CH), \(63.2\) (CH\(_2\)), \(33.1\) (CH\(_2\)), \(28.7\) (CH\(_2\)), \(28.1\) (CH\(_3\)), \(27.9\) (CH\(_3\)), \(26.1\) (3 \(\times\) CH\(_3\)), \(22.9\) (C), \(18.5\) (C), \(−1.51\) (CH\(_3\)), \(−1.49\) (CH\(_3\)), \(−5.2\) (2 \(\times\) CH\(_3\)).

HRMS (ESI): \(m/z\) calcd for C\(_{23}\)H\(_{40}\)O\(_2\)Si\(_2\)Na [M + Na\(^+\)]: 427.24590; found: 427.24660.

1-[2-(Dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]-3-phenylpropan-1-ol (8c).

Prepared from 3-phenylpropionaldehyde and purified by flash column chromatography (petroleum ether/Et\(_2\)O: 80:20).

Yield: 407 mg (81%); colorless oil.

IR (neat): 3424 (br), 1775, 1248, 1113, 1057, 1029, 833, 817, 777, 731, 697, 655 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.64–7.61\) (m, 2H), \(7.43–7.40\) (m, 3H), \(7.33–7.30\) (m, 2H), \(7.24–7.21\) (m, 3H), \(4.75\) (m, 1H), \(2.77\) (t, \(J = 7.9\) Hz, 2H), \(2.04–1.88\) (m, 2H), \(1.57\) (br s, 1H, OH), \(1.28\) (s, 3H), \(1.25\) (s, 3H), \(0.49\) (s, 6H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 152.1\) (C), \(141.9\) (C), \(138.1\) (C), \(133.7\) (2 \(\times\) CH), \(129.5\) (CH), \(128.6\) (2 \(\times\) CH), \(128.5\) (2 \(\times\) CH), \(128.1\) (2 \(\times\) CH), \(126.0\) (CH), \(122.8\) (C), \(69.9\) (CH), \(37.8\) (CH\(_2\)), \(31.6\) (CH\(_2\)), \(28.3\) (CH\(_3\)), \(27.9\) (CH\(_3\)), \(23.3\) (C), \(−1.6\) (2 \(\times\) CH\(_3\)).

HRMS (ESI): \(m/z\) calcd for C\(_{23}\)H\(_{40}\)O\(_2\)Si\(_2\)Na [M + Na\(^+\)]: 359.18016; found: 359.18042.

1-[2-(Dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]hex-5-en-1-ol (8d).

Prepared from hex-5-enal\(^4\) and purified by flash column chromatography (petroleum ether/Et\(_2\)O, 100:0 to 95:5).

Yield: 217 mg (77%); colorless oil.

IR (neat): 3412, 1775, 1641, 1428, 1364, 1248, 1113, 910, 834, 817, 777, 731, 699, 655 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.60–7.55\) (m, 2H), 7.39–7.36 (m, 3H), 5.79 (ddt, \(J = 17.0, 10.2, 6.7\) Hz, 1H), 5.03–4.93 (m, 2H), 4.68 (m, 1H), 2.09–2.04 (m, 2H), 1.67–1.58 (m, 2H), 1.53–1.45 (m, 2H), 1.41 (d, \(J = 5.2\) Hz, 1H, OH), 1.20 (s, 3H), 1.19 (s, 3H), 0.44 (s, 6H).

\(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 152.3\) (C), 138.7 (CH), 138.2 (C), 133.7 (2 \(\times CH\)), 129.5 (CH), 128.1 (2 \(\times CH\)), 122.4 (C), 114.8 (CH\(_2\)), 70.3 (CH), 35.6 (CH\(_2\)), 33.7 (CH\(_2\)), 28.2 (CH\(_3\)), 27.8 (CH\(_3\)), 24.6 (CH\(_2\)), 23.1 (C), –1.57 (CH\(_3\)), –1.59 (CH\(_3\)).

HRMS (ESI): \(m/z\) calcd for C\(_{19}\)H\(_{28}\)OSiNa \([M + Na^+]\): 323.18016; found: 323.18009.

1-[2-(Dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]-5-(trimethylsilyl)pent-4-yn-1-ol (8e).

Prepared from 5-trimethylsilyl-4-pentynal\(^5\) and purified by flash column chromatography (petroleum ether/Et\(_2\)O, 80:20).

Yield: 406 mg (88%); colorless oil.

IR (neat): 3426 (br), 2175, 1776, 1249, 1113, 1067, 1036, 836, 817, 778, 759, 731, 699, 655, 640 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.59–7.56\) (m, 2H), 7.39–7.36 (m, 3H), 4.82 (apparent dt, \(J = 7.8, 5.1\) Hz, 1H), 2.43–2.28 (m, 2H), 1.91–1.73 (m, 2H), 1.62 (d, \(J = 5.4\) Hz, 1H, OH), 1.21 (s, 3H), 1.19 (s, 3H), 0.45 (s, 6H), 0.15 (s, 9H).

\(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 151.6\) (C), 138.0 (C), 133.7 (2 \(\times CH\)), 129.5 (CH), 128.1 (2 \(\times CH\)), 123.2 (C), 106.6 (C), 85.4 (C), 69.4 (CH), 34.8 (CH\(_2\)), 28.2 (CH\(_3\)), 27.8 (CH\(_3\)), 23.2 (C), 16.2 (CH\(_2\)), 0.2 (3 \(\times CH_3\)), –1.6 (2 \(\times CH_3\)).

HRMS (ESI): \(m/z\) calcd for C\(_{21}\)H\(_{32}\)OSi\(_2\)Na \([M + Na^+]\): 379.18839; found: 379.18889.

---


Prepared from freshly distilled benzaldehyde and purified by flash column chromatography (petroleum ether/Et₂O, 90:10).

Yield: 548 mg (95%); yellow oil.

IR (neat): 3414 (br), 1773, 1453, 1364, 1248, 1113, 1064, 1013, 816, 777, 729, 697, 655 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.62–7.58 (m, 2H), 7.43–7.30 (m, 8H), 5.78 (d, J = 4.4 Hz, 1H), 2.05 (br d, J = 4.4 Hz, 1H, OH), 1.26 (s, 3H), 1.08 (s, 3H), 0.44 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ = 151.9 (C), 141.4 (C), 138.0 (C), 133.8 (2 x CH), 129.5 (CH), 128.6 (2 x CH), 128.1 (2 x CH), 127.9 (CH), 126.5 (2 x CH), 123.2 (C), 72.5 (CH), 27.8 (CH₃), 27.5 (CH₃), 23.9 (C), −1.7 (2 x CH₃).

HRMS (ESI): m/z calcd for C₂₀H₂₄O₂SiNa [M + Na⁺]: 331.14886; found: 331.14868.

[2-(Dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl](4-methoxyphenyl)methanol (8g).

Prepared from p-methoxybenzaldehyde and purified by flash column chromatography (petroleum ether/Et₂O: 80:20).

Yield: 273 mg (70%); yellow oil.

IR (neat): 3425 (br), 1774, 1611, 1511, 1249, 1171, 1114, 836, 822, 780, 732, 700 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.56–7.54 (m, 2H), 7.37–7.26 (m, 3H), 7.25 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.68 (s, 1H), 3.79 (s, 3H), 1.92 (br s, 1H, OH), 1.20 (s, 3H), 1.04 (s, 3H), 0.4 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ = 159.4 (C), 152.0 (C), 138.1 (C), 133.8 (2 x CH), 133.6 (C), 129.4 (CH), 128.1 (2 x CH), 127.9 (2 x CH), 122.9 (C), 114.0 (2 x CH), 72.2 (CH), 55.4 (CH₃), 27.8 (CH₃), 27.5 (CH₃), 23.8 (C), −1.64 (CH₃), −1.61 (CH₃).

HRMS (ESI): m/z calcd for C₂₁H₂₆O₂SiNa [M + Na⁺]: 361.15943; found: 361.15928.

[2-(Dimethylphenylsilyl)-3,3-dimethylcycloprop-1-enyl](2-fluorophenyl)methanol (8h).

Prepared from 2-fluorobenzaldehyde and purified by flash column chromatography (petroleum ether/Et₂O, 90:10).
Yield: 443 mg (84%), colorless oil.

IR (neat): 3431 (br), 1774, 1589, 1488, 1456, 1248, 1226, 1113, 1019, 985, 834, 819, 777, 755, 731, 699, 655 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.56–7.52 (m, 2H), 7.41–7.35 (m, 4H), 7.28–7.23 (m, 1H), 7.12 (td, J = 7.5, 1.2 Hz, 1H), 7.02 (ddd, J = 10.4, 8.2, 1.2 Hz, 1H), 6.00 (d, J = 5.6 Hz, 1H), 2.06 (dd, J = 5.6, 1.0 Hz, OH), 1.20 (s, 3H), 1.01 (s, 3H), 0.38 (s, 3H), 0.37 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 160.0 (C, ¹JC-F = 246.7 Hz), 151.0 (C), 138.0 (C), 133.8 (2 × CH), 129.5 (CH), 129.4 (CH, ³JC-F = 8.7 Hz), 128.6 (C, ²JC-F = 13.1 Hz), 128.1 (2 × CH), 127.9 (CH, ³JC-F = 4.3 Hz), 124.4 (CH, ⁴JC-F = 3.5 Hz), 123.7 (C), 115.5 (CH, ²JC-F = 21.2 Hz), 67.0 (CH, ³JC-F = 3.3 Hz), 27.7 (CH₃), 27.1 (CH₃), 24.2 (C), −1.78 (CH₃), −1.76 (CH₃).

HRMS (ESI): m/z calcd for C₂₀H₂₃FOSiNa [M + Na⁺]: 349.13944; found: 349.13950.

1-[2-(Dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]-2-methylpropan-1-ol (8i).

Prepared from freshly distilled isobutyraldehyde and purified by flash column chromatography (petroleum ether/Et₂O, 100:0 to 90:10).

Yield: 141 mg (35%); yellow oil.

IR (neat): 3468 (br), 1771, 1248, 1113, 1024, 998, 833, 817, 777, 730, 699, 656 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.61–7.57 (m, 2H), 7.40–7.37 (m, 3H), 4.49 (br t, J = 4.9 Hz, 1H), 1.88 (m, 1H), 1.41 (m, 1H, OH), 1.23 (s, 3H), 1.19 (s, 3H), 0.94 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H), 0.46 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ = 151.8 (C), 138.2 (C), 133.7 (2 × CH), 129.5 (CH), 128.1 (2 × CH), 123.7 (C), 75.8 (CH), 33.0 (CH), 28.4 (CH₃), 27.8 (CH₃), 23.4 (C), 18.4 (CH₃), 17.5 (CH₃), −1.6 (CH₃), −1.7 (CH₃).

HRMS (ESI): m/z calcd for C₁₇H₂₆OSiNa [M + Na⁺]: 297.16451; found: 297.16463.
(1R*,2S*)-1-[2-(Dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]-2-phenylpropan-1-ol (8j) and (1S*,2R*)-1-[2-(dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]-2-phenylpropan-1-ol (8j').

Prepared from 2-phenylpropionaldehyde (201 mg, 1.50 mmol) and purified by flash column chromatography (petroleum ether/Et₂O, 100:0 to 95:5).

Yield: 405 mg (82%), 8j/8j' (syn/anti) = 90:10.

IR (neat): 3579, 3457, 1770, 1248, 1113, 1018, 833, 818, 777, 760, 731, 698, 655 cm⁻¹.

HRMS (ESI): m/z calcd for C₂₂H₂₈OSiNa [M + Na⁺]: 359.18016; found: 359.18076.

Diastereomer (8j):

\[ \delta = 7.51–7.47 (m, 2H), 7.37–7.33 (m, 3H), 7.30–7.26 (m, 2H), 
7.23–7.18 (m, 3H), 4.85 \text{(apparent t, } J = 5.9 \text{ Hz, 1H), 2.94 \text{(apparent quintet, } J = 7.0 \text{ Hz, 1H),}} 
1.47 \text{(d, } J = 5.8 \text{ Hz, 1H, OH), 1.30 \text{(d, } J = 7.0 \text{ Hz, 3H), 1.03 \text{(s, 3H), 1.02 \text{(s, 3H), 0.38 \text{(s, 3H),)}}} 
0.37 \text{(s, 3H).}}

\[ \delta = 151.7 \text{(C), 143.9 \text{(C), 138.1 \text{(C), 133.7 \text{(2 × CH), 129.4 \text{(CH), 128.4 \text{(2 × CH), 128.08 \text{(2 × CH), 128.05 \text{(2 × CH), 126.6 \text{(CH), 124.3 \text{(C), 74.9 \text{(CH),}}}}}}}
44.9 \text{(CH), 28.0 \text{(CH₃), 27.5 \text{(CH₃), 23.7 \text{(C), 16.9 \text{(CH₃),} −1.7 \text{(CH₃), −1.8 \text{(CH₃).}}}$

Diastereomer (8j'):

\[ \delta = 7.50–7.47 (m, 2H), 7.37–7.29 (m, 5H), 7.25–7.21 (m, 3H), 
4.80 \text{(dd, } J = 7.0 \text{, 5.1 Hz, 1H), 2.95 \text{(apparent quintet, } J = 7.0 \text{ Hz, 1H), 1.44 \text{(d, } J = 5.1 \text{ Hz,}} 
1H, OH), 1.30 \text{(d, } J = 7.0 \text{ Hz, 3H), 1.20 \text{(s, 3H), 1.12 \text{(s, 3H), 0.39 \text{(s, 3H), 0.37 \text{(s, 3H).}}}$

\[ \delta = 151.0 \text{(C), 142.9 \text{(C), 138.0 \text{(C), 133.8 \text{(2 × CH), 129.4 \text{(CH), 128.5 \text{(2 × CH), 128.3 \text{(2 × CH), 128.1 \text{(2 × CH), 126.8 \text{(CH), 124.7 \text{(C), 75.2 \text{(CH),}}}}}}}
45.0 \text{(CH), 28.5 \text{(CH₃), 27.7 \text{(CH₃), 23.4 \text{(C), 18.0 \text{(CH₃),} −1.7 \text{(CH₃), −1.8 \text{(CH₃).}}}$

A diastereomeric mixture of alcohols 8j/8j' with an inverted ratio was also prepared by an oxidation/reduction sequence.
1-[(3,3-Dimethyl-2-(phenyldimethylsilyl)cycloprop-1-en-1-yl)-2-phenylpropan-1-one (16).

To a solution of a diastereomeric mixture of alcohols 8j/8j’ (syn/anti = 90:10) (60 mg, 0.18 mmol) in CH₂Cl₂ (2 mL) at 0 °C, was added Dess-Martin periodinane (111 mg, 0.262 mmol, 1.2 equiv). After 10 min, the reaction mixture was warmed to rt, stirred for 10 min and then hydrolyzed with a saturated aqueous solution of NaHCO₃. The resulting mixture was extracted with Et₂O and the combined organic phases were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/Et₂O, 80:20) to afford 57 mg (96%) of ketone 16 as a yellow oil.

IR (neat): 1739, 1670, 1249, 1147, 1114, 835, 818, 778, 732, 698, 655 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.54–7.51 (m, 2H), 7.40–7.34 (m, 3H), 7.30–7.20 (m, 3H), 7.11–7.09 (m, 2H), 3.87 (q, J = 7.0 Hz, 1H), 1.41 (d, J = 7.0 Hz, 3H), 1.06 (s, 3H), 0.88 (s, 3H), 0.444 (s, 3H), 0.438 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 196.4 (C), 146.6 (C), 145.4 (C), 140.2 (C), 136.3 (C), 133.9 (2 × CH), 129.7 (CH), 128.9 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.1 (CH), 53.0 (CH), 27.1 (CH₃), 26.7 (CH₃), 26.2 (C), 17.7 (CH₃), −2.0 (CH₃), −2.3 (CH₃).

HRMS (ESI): m/z calcd for C₂₂H₂₆OSiNa [M + Na⁺]: 357.16451; found: 357.16460.

Reduction of ketone 13 with DIBAL-H

DIBAL-H (0.13 mmol, 1M solution in CH₂Cl₂, 0.13 mmol, 1.2 equiv) was added to a solution of ketone 16 (35.0 mg, 0.105 mmol) in CH₂Cl₂ (3 mL) at −78 °C. After 20 min, the reaction was quenched with MeOH (1 mL) and the resulting mixture was poured into a saturated aqueous solution of Rochelle’s salt overlaid with Et₂O. After 1 h stirring, the layers were separated and the aqueous phase was extracted with Et₂O. The combined organic extracts were dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether/Et₂O, 90:10) afforded 25 mg (70%) of a diastereomeric mixture of alcohols 8j/8j’ (syn/anti = 23:77) as a colorless oil.
4. Preparation of MOM ethers 9a-9j/9j’

\[ {2-[2-(Benzyloxy)-1-(methoxymethoxy)ethyl]-3,3-dimethylcycloprop-1-en-1-yl}dimethylphenylsilane (9a) \]

(Representative procedure).

To a solution of alcohol 8a (507 mg, 1.44 mmol) in CH₂Cl₂ (15 mL) at 0 °C were successively added \( p \)-Pr₂NEt (1.25 mL, 7.18 mmol, 5 equiv) and MOMCl (0.55 mL, 7.2 mmol, 5 equiv) dropwise. After stirring for 12 h at rt, the reaction mixture was hydrolyzed with a saturated aqueous solution of NH₄Cl. The layers were separated and the aqueous phase was extracted with CH₂Cl₂. The combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/Et₂O, 90:10) to afford 508 mg (89%) of 9a as a yellow oil.

IR (neat): 1776, 1364, 1248, 1153, 1113, 1028, 919, 817, 778, 731, 697, 655 cm⁻¹.

\(^1\)H NMR (400 MHz, CDCl₃): \( \delta = 7.56–7.53 \) (m, 2H), 7.36–7.25 (m, 8H), 4.98 (apparent t, \( J = 5.6 \) Hz, 1H), 4.72 (d, AB syst, \( J = 6.6 \) Hz, 1H), 4.61 (d, AB syst, \( J = 6.6 \) Hz, 1H), 4.57 (d, AB syst, \( J = 12.0 \) Hz, 1H), 4.53 (d, AB syst, \( J = 12.0 \) Hz, 1H), 3.62 (d, \( J = 5.6 \) Hz, 2H), 3.38 (s, 3H), 1.153 (s, 3H), 1.148 (s, 3H), 0.41 (s, 6H).

\(^13\)C NMR (100 MHz, CDCl₃): \( \delta = 146.9 \) (C), 138.3 (C), 137.9 (C), 133.9 (2 x CH), 129.3 (CH), 128.4 (2 x CH), 127.9 (3 x CH), 127.7 (2 x CH), 125.3 (C), 94.7 (CH₂), 73.4 (CH₂), 72.5 (CH), 72.2 (CH₂), 55.5 (CH₃), 27.92 (CH₃), 27.90 (CH₃), 21.6 (C), -1.6 (2 x CH₃).

HRMS (ESI): \( m/z \) calcd for C₂₄H₃₂O₃SiNa [M + Na⁺]: 419.20129; found: 419.20175.

5-[2-(Dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]-10,10,11,11-tetramethyl-2,4,9-trioxa-10-siladodecane (9b).

Purified by flash column chromatography (petroleum ether/Et₂O, 95:5).

Yield: 441 mg (80%); colorless oil.

IR (neat): 1776, 1249, 1152, 1096, 1034, 832, 817, 775, 731, 699, 656 cm⁻¹.

\(^1\)H NMR (400 MHz, CDCl₃): \( \delta = 7.59–7.54 \) (m, 2H), 7.38–7.32 (m, 3H), 4.72 (dd, \( J = 6.9 \), 5.1 Hz, 1H), 4.68 (d, AB syst, \( J = 6.8 \) Hz, 1H), 4.47 (d, AB syst, \( J = 6.8 \) Hz, 1H), 3.67–3.57 (m, 2H), 3.36 (s, 3H), 1.79–1.59 (m, 4H), 1.17 (s, 3H), 1.16 (s, 3H), 0.89 (s, 9H), 0.42 (s, 6H), 0.04 (s, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 149.4 (C), 138.0 (C), 133.9 (2 x CH), 129.3 (CH), 127.9 (2 x CH), 123.1 (C), 94.5 (CH$_2$), 72.8 (CH), 62.9 (CH$_2$), 55.6 (CH$_3$), 30.8 (CH$_2$), 29.0 (CH$_2$), 27.95 (CH$_3$), 27.88 (CH$_3$), 26.1 (3 x CH$_3$), 21.6 (C), 18.5 (C), -1.4 (CH$_3$), -1.5 (CH$_3$), -5.2 (2 x CH$_3$).

HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{44}$O$_3$Si$_2$Na [M + Na$^+$]: 471.27212; found: 471.27202.

{2-[1-(Methoxymethoxy)-3-phenylpropyl]-3,3-dimethylcycloprop-1-en-yl}dimethylphenylsilane (9c).

Purified by flash column chromatography (petroleum ether/Et$_2$O, 80:20).

Yield: 291 mg (94%); colorless oil.

IR (neat): 1775, 1248, 1147, 1113, 1099, 920, 833, 817, 777, 731, 698, 655 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.57–7.55 (m, 2H), 7.36–7.34 (m, 3H), 7.29–7.25 (m, 2H), 7.20–7.15 (m, 3H), 4.75 (apparent t, $J$ = 6.2 Hz, 1H), 4.70 (d, AB syst, $J$ = 6.8 Hz, 1H), 4.50 (d, AB syst, $J$ = 6.8 Hz, 1H), 3.39 (s, 3H), 2.83–2.65 (m, 2H), 1.99–1.93 (m, 2H), 1.19 (s, 3H), 1.18 (s, 3H), 0.42 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 149.1 (C), 142.1 (C), 138.0 (C), 133.9 (2 x CH), 129.3 (CH), 128.5 (4 x CH), 128.0 (2 x CH), 126.0 (CH), 123.7 (C), 94.6 (CH$_2$), 72.7 (CH), 55.8 (CH$_3$), 36.3 (CH$_2$), 32.0 (CH$_2$), 28.05 (CH$_3$), 27.97 (CH$_3$), 21.7 (C), -1.45 (CH$_3$), -1.51 (CH$_3$).

HRMS (ESI): $m/z$ calcd for C$_{24}$H$_{32}$O$_2$SiNa [M + Na$^+$]: 403.20638; found: 403.20684.

{2-[1-(Methoxymethoxy)hex-5-en-1-yl]-3,3-dimethylcycloprop-1-en-1-yl}dimethylphenylsilane (9d).

Purified by flash column chromatography (petroleum ether/EtOAc, 98:2 to 95:5).

Yield: 167 mg (97%); colorless oil.

IR (neat): 1775, 1641, 1248, 1151, 1113, 1099, 1032, 993, 913, 833, 817, 777, 655 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.59–7.57 (m, 2H), 7.38–7.35 (m, 3H), 5.80 (ddt, $J$ = 16.9, 10.2, 6.7 Hz, 1H), 5.05–4.95 (m, 2H), 4.72 (apparent t, $J$ = 6.3 Hz, 1H), 4.70 (d, AB syst, $J$ = 6.8 Hz, 1H), 4.49 (d, AB syst, $J$ = 6.8 Hz, 1H), 3.38 (s, 3H), 2.11–2.05 (m, 2H), 1.72–1.64 (m, 2H), 1.62–1.47 (m, 2H), 1.19 (s, 3H), 1.18 (s, 3H), 0.44 (s, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 149.4$ (C), 138.6 (CH), 138.0 (C), 133.8 ($2 \times$ CH), 129.3 (CH), 127.9 ($2 \times$ CH), 123.2 (C), 114.8 (CH$_2$), 94.4 (CH$_2$), 72.7 (CH), 55.6 (CH$_3$), 33.8 (CH$_2$), 33.6 (CH$_2$), 27.94 (CH$_3$), 27.88 (CH$_3$), 24.9 (CH$_2$), 21.6 (C), $-1.47$ (CH$_3$), $-1.54$ (CH$_3$).

HRMS (ESI): $m/z$ calcd for C$_{21}$H$_{32}$O$_2$SiNa [M + Na$^+$]: 367.20638; found: 367.20645.

{5-[2-(Dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]-5-(methoxymethoxy)pent-1-yn-1-yl]trimethylsilane (9e).

Purified by flash column chromatography (petroleum ether/Et$_2$O, 90:10).

Yield: 280 mg (99%); colorless oil.

IR (neat): 2175, 1775, 1249, 1149, 1113, 1100, 1023, 917, 837, 816, 778, 759, 731, 699, 654, 639 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.59$–7.56 (m, 2H), 7.39–7.35 (m, 3H), 4.87 (t, $J = 6.4$ Hz, 1H), 4.69 (d, AB syst, $J = 6.7$ Hz, 1H), 4.48 (d, AB syst, $J = 6.7$ Hz, 1H), 3.39 (s, 3H), 2.47–2.31 (m, 2H), 1.90–1.85 (m, 2H), 1.20 (s, 3H), 1.18 (s, 3H), 0.44 (s, 6H), 0.17 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 148.8$ (C), 137.9 (C), 133.8 ($2 \times$ CH), 129.3 (CH), 128.0 ($2 \times$ CH), 124.0 (C), 106.6 (C), 94.4 (CH$_2$), 85.2 (C), 71.3 (CH), 55.7 (CH$_3$), 33.4 (CH$_2$), 27.95 (CH$_3$), 27.87 (CH$_3$), 21.7 (C), 16.3 (CH$_2$), 0.3 ($3 \times$ CH$_3$), $-1.48$ (CH$_3$), $-1.55$ (CH$_3$).

HRMS (ESI): $m/z$ calcd for C$_{23}$H$_{36}$O$_2$Si$_2$Na [M + Na$^+$]: 423.21460; found: 423.21503.

{2-[(Methoxymethoxy)phenylmethyl]-3,3-dimethylcycloprop-1-en-1-yl]dimethylphenylsilane (9f).

Purification by flash column chromatography (petroleum ether/Et$_2$O, 95:5).

Yield: 271 mg (95%); colorless oil.

IR (neat): 1775, 1454, 1428, 1248, 1149, 1113, 1098, 1034, 1026, 918, 816, 778, 730, 697, 655 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.55$–7.53 (m, 2H), 7.40–7.28 (m, 8H), 5.71 (s, 1H), 4.78 (d, AB syst, $J = 6.7$ Hz, 1H), 4.62 (d, AB syst, $J = 6.7$ Hz, 1H), 3.39 (s, 3H), 1.20 (s, 3H), 1.08 (s, 3H), 0.35 (s, 3H), 0.34 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 149.7$ (C), 139.6 (C), 138.0 (C), 133.8 (2 x CH), 129.2 (CH), 128.5 (2 x CH), 128.0 (CH), 127.9 (2 x CH), 127.5 (2 x CH), 123.9 (C), 94.0 (CH$_2$), 74.5 (CH), 55.5 (CH$_3$), 27.9 (CH$_3$), 27.4 (CH$_3$), 22.7 (C), –1.6 (CH$_3$), –1.7 (CH$_3$).

HRMS (ESI): $m/z$ calcd for C$_{22}$H$_{28}$O$_2$SiNa [M + Na$^+$]: 375.17508; found: 375.17565.

{2-[(Methoxymethoxy)(4-methoxyphenyl)methyl]-3,3-dimethylcycloprop-1-en-1-yl]-dimethylphenylsilane (9g).}

Purified by flash column chromatography (petroleum ether/EtOAc, 100:0 to 95:5).

Yield: 179 mg (41%); yellow oil.

IR (neat): 1775, 1611, 1511, 1246, 1172, 1148, 1113, 1096, 1029, 817, 778, 731, 699, 655 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.52$–7.50 (m, 2H), 7.35–7.31 (m, 3H), 7.25 (br d, $J = 8.6$ Hz, 2H), 6.84 (br d, $J = 8.6$ Hz, 2H), 5.62 (s, 1H), 4.72 (d, AB syst, $J = 6.7$ Hz, 1H), 4.56 (d, AB syst, $J = 6.7$ Hz, 1H), 3.79 (s, 3H), 3.35 (s, 3H), 1.16 (s, 3H), 1.05 (s, 3H), 0.34 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 159.5$ (C), 149.8 (C), 138.1 (C), 133.9 (2 x CH), 131.7 (C), 129.2 (CH), 128.9 (2 x CH), 127.8 (2 x CH), 123.6 (C), 113.9 (2 x CH), 93.8 (CH$_2$), 74.1 (CH), 55.5 (CH$_3$), 55.4 (CH$_3$), 27.9 (CH$_3$), 27.4 (CH$_3$), 22.6 (C), –1.60 (CH$_3$), –1.55 (CH$_3$).

HRMS (ESI): $m/z$ calcd for C$_{23}$H$_{30}$O$_3$SiNa [M + Na$^+$]: 405.18564; found: 405.18651.

{2-[(2-Fluorophenyl)(methoxymethoxy)methyl]-3,3-dimethylcycloprop-1-en-1-yl]dimethylphenylsilane (9h).}

Purified by flash column chromatography (petroleum ether/Et$_2$O, 90:10).

Yield: 200 mg (88%); colorless oil.

IR (neat): 1776, 1589, 1488, 1456, 1428, 1249, 1229, 1150, 1113, 1093, 1027, 834, 816, 778, 756, 731, 699, 655 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.54$–7.52 (m, 2H), 7.46 (apparent br t, $J = 7.4$ Hz, 1H), 7.38–7.32 (m, 3H), 7.30–7.25 (m, 1H), 7.13 (apparent br t, $J = 7.4$ Hz, 1H), 7.04 (m, 1H), 6.08 (s, 1H), 4.80 (d, AB syst, $J = 6.7$ Hz, 1H), 4.62 (d, AB syst, $J = 6.7$ Hz, 1H), 3.38 (s, 3H), 1.20 (s, 3H), 1.07 (s, 3H), 0.345 (s, 3H), 0.338 (s, 3H).
\[ ^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3): \delta = 160.1 (\text{C}, J_{C,F} = 247.2 \text{ Hz}), 148.8 (\text{C}), 137.9 (\text{C}), 133.8 (2 \times \text{CH}), 129.5 (\text{CH}, J_{C,F} = 8.1 \text{ Hz}), 129.2 (\text{CH}), 129.0 (\text{CH}, J_{C,F} = 3.6 \text{ Hz}), 127.9 (2 \times \text{CH}), 127.0 (\text{C}, J_{C,F} = 14.0 \text{ Hz}), 124.4 (\text{C}), 124.3 (\text{CH}, J_{C,F} = 3.2 \text{ Hz}), 115.4 (\text{CH}, J_{C,F} = 21.9 \text{ Hz}), 94.3 (\text{CH}_2), 67.9 (\text{CH}, J_{C,F} = 3.2 \text{ Hz}), 55.6 (\text{CH}_3), 27.8 (\text{CH}_3), 27.2 (\text{CH}_3), 22.9 (\text{C}), -1.71 (\text{CH}_3), -1.69 (\text{CH}_3). \]

HRMS (ESI): m/z calcd for C\(_{22}\)H\(_{27}\)FO\(_2\)SiNa [M + Na\(^+\): 393.16566; found: 393.16625.

\(\{2\text{-[1-(Methoxymethoxy)-2-methylpropyl]-3,3-dimethylcycloprop-1-en-1-yl]}\text{dimethylphenylsilane (9i).}\)

Purified by flash column chromatography (petroleum ether/Et\(_2\)O, 95:5).

Yield: 34 mg (42%); colorless oil.

IR (neat): 1771, 1248, 1154, 1113, 1098, 1034, 1001, 922, 833, 816, 777, 731, 699, 655 cm\(^{-1}\).

\[^1\text{H} \text{ NMR (400 MHz, CDCl}_3): \delta = 7.58–7.55 (\text{m, 2H}), 7.37–7.34 (\text{m, 3H}), 4.64 (d, AB syst, J = 6.8 \text{ Hz}, 1\text{H}), 4.51 (d, J = 5.1 \text{ Hz}, 1\text{H}), 4.44 (d, AB syst, J = 6.8 \text{ Hz}, 1\text{H}), 3.36 (s, 3\text{H}), 1.94 (m, 1\text{H}), 1.17 (s, 3\text{H}), 1.15 (s, 3\text{H}), 0.97 (d, J = 6.2 \text{ Hz}, 3\text{H}), 0.96 (d, J = 6.2 \text{ Hz}, 3\text{H}), 0.42 (s, 6\text{H}).\]

\[^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3): \delta = 148.6 (\text{C}), 138.1 (\text{C}), 133.9 (2 \times \text{CH}), 129.3 (\text{CH}), 127.9 (2 \times \text{CH}), 124.6 (\text{C}), 94.5 (\text{CH}_2), 78.2 (\text{CH}), 55.7 (\text{CH}_3), 31.9 (\text{CH}), 28.1 (\text{CH}_3), 27.9 (\text{CH}_3), 21.5 (\text{C}), 19.1 (\text{CH}_3), 18.0 (\text{CH}_3), -1.47 (\text{CH}_3), -1.52 (\text{CH}_3).\]

HRMS (ESI): m/z calcd for C\(_{19}\)H\(_{30}\)O\(_2\)SiNa [M + Na\(^+\): 341.19073; found: 341.19116.

\((1R^*,2S^*)\)-\(\{2\text{-[1-Methoxymethoxy-2-phenylpropyl]-3,3-dimethylcycloprop-1-en-1-yl]}\text{dimethylphenylsilane (9j) and (1S^*,2S^*)}\)-\(\{2\text{-[1-methoxymethoxy-2-phenylpropyl]-3,3-dimethylcycloprop-1-en-1-yl]}\text{dimethylphenylsilane (9j').}\)

Synthesized from a diastereomeric mixture of \(8j/8j'\) (\(8j/8j' = 90:10\) or 23:77) and purified by flash column chromatography on silica gel (petroleum ether/Et\(_2\)O, 95:5).

Yield: 171 mg (92%) (\(9j/9j' = 90:10\)) or 13 mg (46%) (\(9j/9j' = 23:77\)); colorless oils.

IR (neat): 1771, 1452, 1364, 1248, 1152, 1113, 1097, 1026, 919, 816, 777, 761, 731, 698, 655 cm\(^{-1}\).
Diastereomer (9j):

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.52$–7.49 (m, 2H), 7.37–7.32 (m, 3H), 7.28–7.15 (m, 5H), 4.88 (d, $J = 5.8$ Hz, 1H), 4.61 (d, AB syst, $J = 6.8$ Hz, 1H), 4.36 (d, AB syst, $J = 6.8$ Hz, 1H), 3.07 (s, 3H), 3.01 (m, 1H), 1.34 (d, $J = 7.1$ Hz, 3H), 1.05 (s, 3H), 1.00 (s, 3H), 0.36 (s, 3H), 0.35 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 148.7$ (C), 144.2 (C), 138.0 (C), 133.9 (2 x CH), 129.3 (CH), 128.3 (2 x CH), 128.2 (2 x CH), 127.9 (2 x CH), 126.4 (CH), 124.8 (C), 94.4 (CH$_2$), 77.3 (CH), 55.6 (CH$_3$), 43.5 (CH), 27.7 (CH$_3$), 27.6 (CH$_3$), 21.9 (C), 16.7 (CH$_3$), –1.6 (CH$_3$), –1.7 (CH$_3$).

Diastereomer (9j$^*$):

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.53$–7.49 (m, 2H), 7.37–7.33 (m, 3H), 7.28–7.15 (m, 5H), 4.82 (d, $J = 7.8$ Hz, 1H), 4.54 (d, AB syst, $J = 6.9$ Hz, 1H), 4.29 (d, AB syst, $J = 6.9$ Hz, 1H), 3.01 (apparent quintet, $J = 7.1$ Hz, 1H), 2.92 (s, 3H), 1.27 (d, $J = 7.1$ Hz, 3H), 1.13 (s, 3H), 1.11 (s, 3H), 0.374 (s, 3H), 0.371 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 148.3$ (C), 144.1 (C), 137.9 (C), 133.9 (2 x CH), 129.3 (CH), 128.3 (2 x CH), 128.2 (2 x CH), 127.9 (2 x CH), 126.4 (CH), 126.2 (C), 94.4 (CH$_2$), 78.0 (CH), 55.4 (CH$_3$), 43.7 (CH), 28.2 (CH$_3$), 27.7 (CH$_3$), 21.8 (C), 18.6 (CH$_3$), –1.6 (2 x CH$_3$).

HRMS (ESI): $m/z$ calcd for C$_{24}$H$_{32}$O$_2$SiNa [M + Na$^+$]: 403.2063; found: 403.20674.
5. Determination of the optical purities of \((R)-8a\) and \(10a\) generated by gold-catalyzed rearrangement of \((R)-9a\)

The enantiomeric excess of \((R)-8a\) was determined by SFC [Daicel Chiralpak OD-H, 100 bar, sc \(\text{CO}_2/\text{MeOH}\) (97:3), flow rate 5.0 mL/min, \(\lambda = 210\) nm] after calibration with a racemic sample.

\[ (\pm)-8a \] \[ (R)-8a \text{ (ee = 75\%)} \]

\[ t_R = 5.38 \text{ min (minor) and 5.74 min (major)} \]

The gold-catalyzed rearrangement of optically active \((R)-9a\) (ee = 75\%) led to compound \(10a\) which was analyzed by SFC [Daicel Chiralpak OJ-H, 100 bar, sc \(\text{CO}_2/\text{MeOH}\) (95:5), flow rate 5.0 mL/min, \(\lambda = 220\) nm] after calibration with an authentic sample of \((\pm)-10a\) (arising from the gold-catalyzed rearrangement of \((\pm)-9a\)).

\[ (\pm)-10a \text{ by gold-catalyzed rearrangement of (±)-9a.} \] \[ 10a \text{ by gold-catalyzed rearrangement of optically active (R)-9a (ee = 75\%)} \]

Racemic \(10a\) was obtained by gold-catalyzed rearrangement of optically enriched \((R)-9a\), \(t_R = 2.99\) min (minor) and 3.85 min (major).
8ψ8γ
(syn'α=90.10)

SI-53
9j9 (syn/anti = 23/77)
$^{10J(}^{10J')}$

(dr = 65.35)
(NOESY)

SI-102

PhMe₂Si

nOe

10a