SUPPORTING INFORMATION

Regio- and Stereoselective trans-Silylvinylation of Internal Alkynes

Catalyzed by RuHCl(CO)(PCy3)2

Jinbo Zhao, ShaSha Liu, Nadia Marino, and Daniel A. Clark

1-014 Center for Science and Technology, Department of Chemistry, Syracuse University,

Syracuse, NY 13244

E-mail: daclar01@syr.edu

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General Procedures: Unless otherwise indicated, all reactions were conducted in oven-(140°C) or flame-dried glassware using distilled and degassed solvents under positive pressure of dry argon (Ar) with standard Schlenk techniques. All air-sensitive reagents were stored in an MBraun labmaster glovebox containing dry argon gas. Dry tetrahydrofuran (THF), toluene (Tol), acetonitrile (CH$_3$CN), and methylene chloride (DCM) were obtained by passing commercially available pre-dried, oxygen-free formulations through two activated alumina columns using an MBraun MB-SPS solvent purification system. Dry 1,2-dichloroethane (DCE), dimethylformamide (DMF) and hexamethylphosphoramide (HMPA) were freshly distilled from calcium hydride prior to use. Dry diethyl ether (Et$_2$O) and hexanes were freshly distilled from sodium/benzophenone prior to use. Stainless steel syringes or cannulae that had been oven-dried (140°C) and cooled under argon atmosphere or in a desiccator were used to transfer anhydrous solvents and air- and moisture-sensitive liquids. Yields refer to chromatographically and spectroscopically ($^1$H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on precoated glass plates of silica gel (0.25 mm) 60 F$_{254}$ from EMD Chemicals Inc. using the indicated solvent system. Visualization was accomplished with ultraviolet light (UV 254 nm), or by shaking the plate in a sealed jar containing silica gel and Iodine. Alternatively, plates were treated with one of the following solutions (this was accomplished by holding the edge of the TLC plate with forceps or tweezers and immersing the plate into a wide-mouth jar containing the desired staining solution) and carefully heating with a hot-air gun (450°C) for approximately 1-2 min (NOTE: excess stain was removed by resting the TLC on a paper towel prior to heating): 10% phosphomolybdic acid in ethanol; 1% potassium permanganate/7% potassium carbonate/0.5% sodium hydroxide aqueous solution; and/or anisaldehyde in ethanol with 10% sulfuric acid. Flash column chromatography was performed using Silia Flash® P60 silica gel (40-63 μm) from Silicycle. All work-up and purification procedures were carried out with reagent grades solvents (purchased from VWR) in air.
**Instrumentation:** Infrared (IR) spectra were recorded on a Thermo Nicolet IR-100 spectrophotometer, $\nu_{\text{max}}$ in cm$^{-1}$. Liquid samples were prepared as thin films between two NaCl plates, and solid samples were prepared as a potassium bromide (KBr) pellet. Characteristic bands are characterized as: br (broad), s (strong 67-100%), m (medium 34-67%), and w (weak $\leq 33\%$). $^1$H NMR spectra were recorded on a Bruker Avance DPX-300 (300 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) and are calibrated using residual undeuterated solvent as an internal reference (CDCl$_3$: $\delta$ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity, coupling constants (Hz), and integration. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, at = apparent triplet, aq = apparent quartet, b = broad. $^{13}$C NMR spectra were recorded on a Bruker Avance DPX-300 (75.4 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm and are calibrated using residual undeuterated solvent as an internal reference (CDCl$_3$: $\delta$ 77.00 ppm). $^{19}$F NMR spectra were recorded on a Bruker Avance DPX-300 (282.3 MHz) spectrometer. Chemical shifts are reported in ppm and are calibrated as an external reference (0.05% trifluorotoluene in benzene from CIL: $\delta$ -63.7 ppm). $^{31}$P NMR spectra were recorded on a Bruker Avance DPX-500 (202.5 MHz) spectrometer. Chemical shifts are reported in ppm and are calibrated as an external reference (85% H$_3$PO$_4$ in water: $\delta$ 0.00 ppm). 2D NMR spectra were recorded on a Bruker Avance DPX-500 or DPX-600 spectrometer. High resolution mass spectra (HRMS) were performed at the mass spectrometry facility of CUNY Hunter College (New York, New York), SUNY Buffalo (Buffalo, New York), or Old Dominion University (Norfolk, Virginia). Optical rotations were measured at a sodium D line (589 nm) on a Rudolph Research Analytical Autopol III polarimeter and reported as follows: $[\alpha]_D^\lambda$ (c in g/100 mL), in reagent grade methylene chloride (DCM). Elemental Analyses were performed on a Costech ECS 4010 elemental analyzer with a 2 meter GC column maintained at 50°C and thermal conductivity detector using acetonilide as a standard. Single crystal X-ray diffraction data were collected at 90(2) K on a Bruker APEX DUO diffractometer coupled to a Bruker-AXS Apex II CCD detector using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å).
**Reagents and Catalysts:** Reagents and ligands were purchased at the highest commercial quality and used without further purification, unless otherwise stated.

**CuI** was purchased from Strem and used as received.

The following ruthenium complexes were prepared according to literature procedures:

- $\text{RuHCl(CO)(PPh}_3)_3^{[1]}$
- $\text{RuHCl(CO)(PCy}_3)_2^{[2]}$
- $\text{RuHCl(CO)(PrPr}_3)_2^{[3]}$
- $\text{RuHCl(CO)(PrBu}_2\text{Me)}_2^{[4]}$
- $\text{RuH(OSiPh}_3\text{(CO)(PrBu}_2\text{Me)}_2^{[5]}$
- $\text{[(PCy}_3)_2\text{(CO)ClRu=CHCH=C(CH}_3\text{)}_2\text{]}^+\text{BF}_4^-^{[6]}$
- $\text{RuH}_2\text{(CO)(PPh}_3)_3^{[7]}$

The following palladium complexes were prepared according to literature procedures:

- $\text{PdCl}_2\text{(PPh}_3)_2^{[8]}$
- $\text{Pd(PPh}_3)_4^{[9]}$

The following compounds were prepared according to literature procedures:

- 1,2-Epoxydecane $^{[10]}$
- 2-Iodo-1-octene $^{[11]}$
- L-Menthyl acrylate $^{[12]}$

**Acetophenone** was purchased from Fluka and used as received.

**Vinylidimethylchlorosilane** was purchased from Gelest and used as received.

The following reagents were purchased from Acros and used as received:

- Ethyl acrylate
- 4-Dimethyaminobenzaldehyde
- 1-Octanal

The following reagents were purchased from Aldrich and used as received:

- Acryloyl chloride
- 1-Bromo-3,5-dimethylbenzene
- 1-Bromo-4-methoxybenzene
- cyclohexanecarbaldehyde
- 1,2-Epoxy cyclohexane
1,2-Epoxypropane
Iodobenzene
1-Iodo-4-fluorobenzene
1-Iodo-4-methylbenzene
Isobornyl acrylate
Methyl acrylate
Styrene oxide
(R)-Styrene oxide
RhH(CO)(PPh₃)₃

The following reagents were purchased from Alfa and used as received:

Methyl iodide
3-Phenylpropanal

The following reagents were purchased from GFS Chemicals Company and used as received:

3-Butyne-1-ol
3,3-Dimethyl-1-butyne
4-Pentyne-1-ol
4-Pentyne-2-ol
1-Octyne
Phenylacetylene
Trimethylsilylacetylene

The following reagents were purchased from TCI and used as received:

n-Butyl acrylate
t-Butyl acrylate
Propargyl bromide

The following reagents were purchased from Impex and used as received:

4-Bromobenzaldehyde
4-Nitrobenzaldehyde

\[
\text{Ph} \quad 1) \quad \text{nBuLi, THF, } -78 \, ^\circ\text{C, 1 h} \quad \text{OH} \quad \text{Ph} \\
\text{2) Imidazole, DMAP, HMPA, } -78 \, ^\circ\text{C} \rightarrow \text{rt} \quad \text{Cl} \quad \text{Si} \quad \text{Ph} \\
\text{DCM, 0 } ^\circ\text{C} \rightarrow \text{rt} \\
\text{O} \quad \text{Si} \quad \text{Ph} \\
\]

In a typical experiment, nBuLi (2.5 M in hexanes, 8 mL, 20 mmol) was slowly added to a stirred solution of phenylacetylene (2.2 mL, 2.04 g, 20 mmol) in dry THF (40 mL) at -78 °C under Ar(g). After complete addition the solution was stirred at -78 °C for 1 h. Next a solution of 1,2-epoxypropane (4.2 mL, 3.49 g, 60 mmol) in dry HMPA (5.2 mL, 5.38 g, 30 mmol) was added and the reaction mixture was allowed to warm to rt. After being stirred at rt for 2 h, the reaction mixture was poured into water (60 mL), and extracted with Et2O (3 × 30 mL). The combined organic phases was dried over MgSO4, filtered and concentrated in vacuo to give the crude alcohol as a pale yellow oil. To a solution of the crude alcohol (3.20 g, 20 mmol), imidazole (2.72 g, 40 mmol), DMAP (488.8 mg, 4 mmol) in dry DCM (40 mL) was added vinyldimethylchlorosilane (4.1 mL, 3.62 g, 30 mmol) at 0 °C under Ar(g) and the reaction mixture was allowed to warm to rt overnight. The reaction was then quenched with sat. NH4Cl(aq) (20 mL) and extracted with DCM (3 × 20 mL). The combined organic phases was dried over MgSO4, filtered and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the silyl ether 1 4.12 g (84%) as a colorless oil.

\[
\text{TLC (hexanes:Et}_2\text{O = 60:1): R}_f = 0.33; \\
\text{Flash chromatography (2.5 cm } \phi \times 20 \text{ cm): hexanes:Et}_2\text{O = 60:1;} \\
\text{^1H NMR (300 MHz, CDCI}_3\text{): } \delta 7.42-7.37 \text{ (m, 2 H), 7.30-7.26 (m, 3 H), 6.19 (dd, } J = 20.1, 15.0 \text{ Hz, 1 H), 6.03 (dd, } J = 15.0, 4.5 \text{ Hz, 1 H), 5.81 (dd, } J = 20.1, 4.5 \text{ Hz, 1 H), 4.10-4.00 (m, 1 H), 2.60 (dd, } J = 16.5, 6.0 \text{ Hz, 1 H), 2.47 (dd, } J = 16.5, 7.2 \text{ Hz, 1 H), 1.30 (d, } J = 6.3 \text{ Hz, 3 H), 0.232 (s, 3 H), 0.229 (s, 3 H);} \\
\text{^13C NMR (75.4 MHz, CDCI}_3\text{): } \delta 137.7, 133.2, 131.5, 128.2, 127.6, 123.8, 87.4, 82.0, 67.9, 30.2, 23.4, -1.55, -1.58; \\
\text{IR (film): 2970 (s), 2235 (w), 1597 (m), 1490 (s);} \\
\text{Anal. calcd. for C}_15\text{H}_20\text{OSi: C 73.71%, H 8.25%; found: C 73.36%, H 8.34%.}
According to the general experiment, the reaction of phenylacetylene (0.27 mL, 255.4 mg, 2.5 mmol), nBuLi (2.5 M in hexanes, 1 mL, 2.5 mmol), styrene oxide (0.24 mL, 252.3 mg, 2.1 mmol) and HMPA (0.56 mL, 573.4 mg, 3.2 mmol) in THF (5 mL) afforded the crude alcohol as a pale brown oil. The reaction of the crude alcohol (466.4 mg, 2.1 mmol), imidazole (286.0 mg, 4.2 mmol), DMAP (51.3 mg, 0.42 mmol) and vinyldimethylchlorosilane (0.44 mL, 386.2 mg, 3.2 mmol) in DCM (10 mL) afforded the silyl ether 504.9 mg (78%) as a pale yellow oil.

\[ \text{TLC (hexanes:EtOAc = 60:1): } R_f = 0.25; \]

\textbf{Flash chromatography} (2.5 cm \( \phi \times 20 \) cm): hexanes:EtOAc = 60:1;

\( ^1 \text{H NMR} \) (300 MHz, CDCl\(_3\)): \( \delta \) 7.43-7.33 (m, 6 H), 7.31-7.27 (m, 4 H), 6.12 (dd, \( J = 19.8, 14.7 \) Hz, 1 H), 5.98 (dd, \( J = 14.7, 4.5 \) Hz, 1 H), 5.77 (dd, \( J = 19.8, 4.5 \) Hz, 1 H), 4.93 (dd, \( J = 7.2, 6.0 \) Hz, 1 H), 2.84 (dd, \( J = 16.8, 7.2 \) Hz, 1 H), 2.74 (dd, \( J = 16.8, 6.0 \) Hz, 1 H), 0.21 (s, 3 H), 0.16 (s, 3 H);

\( ^{13} \text{C NMR} \) (75.4 MHz, CDCl\(_3\)): \( \delta \) 143.8, 137.4, 133.3, 131.5, 128.2, 128.1, 127.6, 127.5, 125.9, 123.8, 87.4, 82.1, 73.9, 31.7, -1.5, -1.6;

\textbf{IR} (film): 2960 (s), 2230 (w), 1596 (m), 1491 (s);

\textbf{HRMS (ESI)}: calcd. for C\(_{20}\)H\(_{22}\)OSiNa\(^+\): 329.1332, found: 329.1341.
According to the general experiment, the reaction of phenylacetylene (2.64 mL, 2.46 g, 24 mmol), nBuLi (2.5 M in hexanes, 9.6 mL, 24 mmol), (R)-styrene oxide (2.28 mL, 2.40 g, 20 mmol) and HMPA (5.2 mL, 5.74 g, 30 mmol) in THF (30 mL) afforded the chiral alcohol 3.64 g (82%) as an orange oil. The reaction of the chiral alcohol (1.15 g, 5.15 mmol), imidazole (701.0 mg, 10.3 mmol), DMAP (126.0 mg, 1.03 mmol) and vinyldimethylchlorosilane (1.1 mL, 933.0 mg, 7.73 mmol) in DCM (20 mL) afforded the chiral silyl ether 990.0 mg (63%) as a pale yellow oil.

**TLC** (hexanes: Et₂O = 50:1): Rᵣ = 0.38;

**Flash chromatography** (2.5 cm φ × 15 cm): hexanes:Et₂O = 80:1 → 55:1;

[α]D²⁴ = 48.4 (c = 2.0, DCM);

**¹H NMR** (300 MHz, CDCl₃): δ 7.42-7.32 (m, 6 H), 7.30-7.25 (m, 4 H), 6.11 (dd, J = 19.8, 15.0 Hz, 1 H), 5.97 (dd, J = 15.0, 4.5 Hz, 1 H), 5.76 (dd, J = 19.8, 4.5 Hz, 1 H), 4.92 (dd, J = 7.2, 6.0 Hz, 1 H), 2.83 (dd, J = 16.8, 7.2 Hz, 1 H), 2.73 (dd, J = 16.8, 6.0 Hz, 1 H), 0.20 (s, 3 H), 0.15 (s, 3 H);

**¹³C NMR** (75.4 MHz, CDCl₃): δ 143.8, 137.4, 133.3, 131.5, 128.2, 128.1, 127.6, 127.5, 125.9, 123.8, 87.4, 82.1, 73.9, 31.6, -1.5, -1.7;

**IR** (film): 2960 (s), 2226 (w), 1597 (m), 1491 (s);

nBuLi (2.5 M in hexanes, 3 mL, 7.5 mmol) was slowly added to a stirred solution of phenylacetylene (0.82 mL, 766.1 mg, 7.5 mmol) in dry THF (40 mL) at -78 °C under Ar(g). After complete addition the solution was stirred at -78 °C for 1 h. 1,2-epoxycyclohexane (0.51 mL, 490.8 mg, 5 mmol) and boron trifluoride diethyl ether complex (0.95 mL, 1.06 g, 7.5 mmol) were successively added to the reaction mixture. After being stirred at -78 °C for 4 h, the reaction mixture was quenched with sat. NH₄Cl(aq) (20 mL), and extracted with Et₂O (3 × 30 mL). The combined organic layers was washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by flash chromatography (hexanes:EtOAc = 8:1) on silica gel to give the trans-alcohol 918.8 mg (92%) as a pale yellow oil. To a solution of the trans-alcohol (416.0 mg, 2.08 mmol) in dry Tol (20 mL) was added 2-chloro-4-nitro-benzoic acid (695.0 mg, 4.16 mmol) and triphenylphosphine (1.09 g, 4.16 mmol) at 0 °C under Ar(g). A solution of diisopropylazodicarboxylate (0.82 mL, 841.2 mg, 4.16 mmol) in dry Tol (6 mL) was added dropwise to the resulting solution. After being stirred at rt over night, the reaction was quenched with sat. NaHCO₃(aq) (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic phases was washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by flash chromatography (hexanes:Et₂O = 10:1) on silica gel to give the cis-ester 434.4 mg (84%) as a pale yellow oil. The cis-ester (368.7 mg, 1.05 mmol) was dissolved in MeOH (20 mL), and the resulting solution was treated with K₂CO₃ (583.2 mg, 4.2 mmol) at rt for 1 h. The reaction mixture was concentrated in vacuo and purified by flash chromatography (hexanes:EtOAc = 8:1) on silica gel to give the cis-alcohol 157.0 mg (74%) as a colorless oil. The reaction of the cis-alcohol (157.0 mg, 0.784 mmol), imidazole (106.8 mg, 1.568 mmol), DMAP (19.2 mg,
0.157 mmol) and vinyl(dimethyl)chlorosilane (0.16 mL, 141.9 mg, 1.176 mmol) in DCM (10 mL) afforded the silyl ether 157.5 mg (71%) as a colorless oil.

![Structure](image)

**TLC** (hexanes:EtOAc = 90:1): R<sub>f</sub> = 0.6;

**Flash chromatography** (2.5 cm φ × 10 cm): hexanes:EtOAc = 90:1;

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 7.44-7.40 (m, 2 H), 7.31-7.24 (m, 3 H), 6.20 (dd, <i>J</i> = 20.1, 15.0 Hz, 1 H), 5.99 (dd, <i>J</i> = 15.0, 4.2 Hz, 1 H), 5.81 (dd, <i>J</i> = 20.1, 4.2 Hz, 1 H), 3.87 (dt, <i>J</i> = 7.2, 3.6 Hz, 1 H), 2.84 (dt, <i>J</i> = 7.2, 3.6 Hz, 1 H), 1.97-1.87 (m, 1 H), 1.83-1.50 (m, 5 H), 1.44-1.26 (m, 2 H), 0.23 (s, 3 H), 0.22 (s, 3 H);

**<sup>13</sup>C NMR** (75.4 MHz, CDCl<sub>3</sub>): δ 138.3, 132.7, 131.6, 128.1, 127.3, 124.3, 91.7, 82.3, 71.0, 36.7, 32.3, 28.8, 22.9, 22.3, -1.26, -1.30;

**IR** (film): 2938 (s), 2231 (w), 1597 (m), 1490 (m);

**HRMS** (ESI): calcd. for C<sub>18</sub>H<sub>24</sub>OSiNa<sup>+</sup>: 307.1489, found: 307.1483.
In a typical experiment, a solution of 4-pentyne-2-ol (0.47 mL, 420.5 mg, 5 mmol), 1-bromo-3,5-dimethylbenzene (0.82 mL, 1.11 g, 6 mmol), CuI (95.2 mg, 0.5 mmol), PdCl₂(PPh₃)₂ (175.0 mg, 0.25 mmol) and piperidine (5 mL) in dry THF (10 mL) was degassed by freeze/pump/Ar (g) for 3 times and refluxed under Ar (g) over night. The reaction mixture was quenched with sat. NH₄Cl(aq) (10 mL), and extracted with Et₂O (3 × 20 mL). The combined organic layers was washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by flash chromatography (hexanes:EtOAc = 4:1) on silica gel to give the alcohol 594.0 mg (63%) as an orange oil. The reaction of the alcohol (594.0 mg, 3.15 mmol), imidazole (429.0 mg, 6.3 mmol), DMAP (77.0 mg, 0.63 mmol) and vinyldimethylchlorosilane (0.65 mL, 570.3 mg, 4.725 mmol) in DCM (20 mL) afforded the silyl ether 597.2 mg (70%) as a colorless oil.

TLC (hexanes:EtOAc = 75:1): Rf = 0.5;
Flash chromatography (2.5 cm φ× 15 cm): hexanes:EtOAc = 75:1;
¹H NMR (300 MHz, CDCl₃): δ 7.03 (s, 2 H), 6.90 (s, 1 H), 6.19 (dd, J = 20.1, 14.7 Hz, 1 H), 6.02 (dd, J = 14.7, 4.2 Hz, 1 H), 5.81 (dd, J = 20.1, 4.2 Hz, 1 H), 4.08-3.98 (m, 1 H), 2.59 (dd, J = 16.8, 6.0 Hz, 1 H), 2.45 (dd, J = 16.8, 7.2 Hz, 1 H), 2.27 (s, 6 H), 1.30 (d, J = 6.0 Hz, 3 H), 0.229 (s, 3 H), 0.225 (s, 3 H);
¹³C NMR (75.4 MHz, CDCl₃): δ 137.74, 137.70, 133.2, 129.2, 129.2, 123.4, 86.6, 82.2, 67.9, 30.2, 23.3, 21.1, -1.6;
IR (film): 2971 (s), 2235 (w), 1599 (s);
According to the general experiment, the reaction of 4-pentyne-2-ol (0.47 mL, 420.5 mg, 5 mmol), 1-bromo-4-methoxybenzene (0.75 mL, 1.12 g, 6 mmol), Cul (95.2 mg, 0.5 mmol), PdCl$_2$(PPh$_3$)$_2$ (175.0 mg, 0.25 mmol) and piperidine (5 mL) in dry THF (10 mL) afforded the alcohol 448.1 mg (47%) as a brown oil. The reaction of the alcohol (448.1 mg, 2.4 mmol), imidazole (326.9 mg, 4.8 mmol), DMAP (58.7 mg, 0.48 mmol) and vinyldimethylchlorosilane (0.5 mL, 434.5 mg, 3.6 mmol) in DCM (20 mL) afforded the silyl ether 434.5 mg (67%) as a colorless oil.

**TLC** (hexanes:Et$_2$O = 60:1): R$_f$ = 0.22;

**Flash chromatography** (2.5 cm φ × 15 cm): hexanes:Et$_2$O = 60:1;

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.36-7.31 (m, 2 H), 6.84-6.79 (m, 2 H), 6.18 (dd, $J$ = 20.1, 15.0 Hz, 1 H), 6.02 (dd, $J$ = 15.0, 4.2 Hz, 1 H), 5.80 (dd, $J$ = 20.1, 4.2 Hz, 1 H), 4.08-3.98 (m, 1 H), 3.80 (s, 3 H), 2.58 (dd, $J$ = 16.5, 6.0 Hz, 1 H), 2.45 (dd, $J$ = 16.5, 7.8 Hz, 1 H), 1.29 (d, $J$ = 6.0 Hz, 3 H), 0.23 (s, 3 H), 0.22 (s, 3 H);

$^{13}$C NMR (75.4 MHz, CDCl$_3$): δ 159.1, 137.8, 133.2, 132.9, 115.9, 113.8, 85.8, 81.7, 68.0, 55.2, 30.2, 23.4, -1.6;

**IR** (film): 2967 (s), 1608 (s), 1510 (s);

**HRMS** (EI): calcd. for C$_{16}$H$_{22}$O$_2$Si$: 274.1384$, found: 274.1384.
According to the general experiment, the reaction of 4-pentyne-2-ol (0.47 mL, 420.5 mg, 5 mmol), 1-iodo-4-fluorobenzene (0.69 mL, 1.33 g, 6 mmol), CuI (95.2 mg, 0.5 mmol), PdCl₂(PPh₃)₂ (175.0 mg, 0.25 mmol) and Et₃N (5 mL) in dry THF (10 mL) afforded the alcohol 634.8 mg (71%) as an orange oil. The reaction of the alcohol (634.0 mg, 3.6 mmol), imidazole (490.3 mg, 7.2 mmol), DMAP (88.0 mg, 0.72 mmol) and vinyldimethylchlorosilane (0.75 mL, 651.8 mg, 5.4 mmol) in DCM (20 mL) afforded the silyl ether 677.5 mg (72%) as a colorless oil.

**TLC** (hexanes:Et₂O = 35:1): Rᵣ = 0.47;

**Flash chromatography** (2.5 cm φ × 15 cm): hexanes:Et₂O = 65:1;

**¹H NMR** (300 MHz, CDCl₃): δ 7.39-7.34 (m, 2 H), 7.00-6.94 (m, 2 H), 6.18 (dd, J = 19.8, 15.0 Hz, 1 H), 6.02 (dd, J = 15.0, 4.2 Hz, 1 H), 5.80 (dd, J = 19.8, 4.2 Hz, 1 H), 4.09-3.98 (m, 1 H), 2.57 (dd, J = 16.5, 6.0 Hz, 1 H), 2.45 (dd, J = 16.5, 6.9 Hz, 1 H), 1.29 (d, J = 6.3 Hz, 3 H), 0.23 (s, 3 H), 0.22 (s, 3 H);

**¹³C NMR** (75.4 MHz, CDCl₃): δ 162.1 (d, J₂₋C = 247.9 Hz), 137.7, 133.3 (d, J₂₋C = 8.2 Hz), 133.2, 119.8, 115.4 (d, J₂₋C = 21.9 Hz), 87.1, 80.9, 67.8, 30.1, 23.4, -1.58, -1.6;

**¹⁹F NMR** (282.3 MHz, CDCl₃): δ (-112.51)-(-112.61)(m);

**IR** (film): 2971 (s), 2234 (w), 1602 (m), 1508 (s);

**HRMS** (EI): calcd. for C₁₅H₁₉FOSi⁺: 262.1184, found: 262.1182.
According to the general experiment, the reaction of 4-pentyne-2-ol (0.47 mL, 420.5 mg, 5 mmol), 1-iodo-4-methylbenzene (1.31 g, 6 mmol), Cul (95.2 mg, 0.5 mmol), PdCl₂(PPh₃)₂ (175.0 mg, 0.25 mmol) and Et₃N (5 mL) in dry THF (10 mL) afforded the alcohol 583.8 mg (67%) as a brown oil. The reaction of the alcohol (583.0 mg, 3.35 mmol), imidazole (456.3 mg, 6.7 mmol), DMAP (81.9 mg, 0.67 mmol) and vinyldimethylchlorosilane (0.69 mL, 606.5 mg, 5.025 mmol) in DCM (20 mL) afforded the silyl ether 619.5 mg (72%) as a pale yellow oil.

TLC (hexanes:Et₂O = 60:1): Rf = 0.26;

Flash chromatography (2.5 cm φ × 15 cm): hexanes:Et₂O = 60:1→50:1;

^1H NMR (300 MHz, CDCl₃): δ 7.29 (d, J = 8.1 Hz, 2 H), 7.09 (d, J = 8.1 Hz, 2 H), 6.19 (dd, J = 20.1, 15.0 Hz, 1 H), 6.02 (dd, J = 15.0, 4.2 Hz, 1 H), 5.81 (dd, J = 20.1, 4.2 Hz, 1 H), 4.09-3.99 (m, 1 H), 2.59 (dd, J = 16.5, 5.7 Hz, 1 H), 2.47 (dd, J = 16.5, 7.2 Hz, 1 H), 2.33 (s, 3 H), 1.29 (d, J = 6.0 Hz, 3 H), 0.229 (s, 3 H), 0.225 (s, 3 H);

^13C NMR (75.4 MHz, CDCl₃): δ 137.8, 137.6, 133.2, 131.4, 128.9, 120.7, 86.6, 82.0, 67.9, 30.2, 23.4, 21.4, -1.55, -1.58;

IR (film): 2970 (s), 1593 (w), 1510 (s);

In a typical experiment, a solution of Grignard reagent C₃H₃MgBr[^15] in Et₂O was prepared according to a literature procedure. To this solution of C₃H₃MgBr (7.5 mmol) in Et₂O (10 mL) at -40 °C (dry ice/CH₃CN) was added a solution of 3-phenylpropanal (0.8 mL, 805.2 mg, 6 mmol) in dry Et₂O (6 mL) dropwise. The reaction mixture was slowly allowed to warm to rt and stirred for 1 h. The reaction mixture was quenched with sat. NH₄Cl(aq) (5 mL), and extracted with Et₂O (3 × 10 mL). The combined organic layers was washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by flash chromatography (hexanes:EtOAc = 6:1) on silica gel to give the propargyl alcohol 871.2 mg (83%) as a pale yellow oil. The reaction of the propargyl alcohol (871.2 mg, 5 mmol), iodobenzene (0.67 mL, 1.22 g, 6 mmol), CuI (95.2 mg, 0.5 mmol), PdCl₂(PPh₃)₂ (175.5 mg, 0.5 mmol) and Et₃N (5 mL) in dry THF (20 mL) afforded the phenyl propargyl alcohol 825.5 mg (66%) as an orange oil. The reaction of the phenyl propargyl alcohol (825.5 mg, 3.3 mmol), imidazole (449.0 mg, 6.6 mmol), DMAP (81.0 mg, 0.66 mmol) and vinyldimethylchlorosilane (0.68 mL, 597.5 mg, 4.95 mmol) in DCM (20 mL) afforded the silyl ether 704.3 mg (64%) as a pale yellow oil.

**TLC** (hexanes:Et₂O = 60:1): Rₛ = 0.31;

**Flash chromatography** (2.5 cm ø × 15 cm): hexanes:Et₂O = 60:1;

**¹H NMR** (300 MHz, CDCl₃): δ 7.42-7.38 (m, 2 H), 7.33-7.27 (m, 5 H), 7.24-7.16 (m, 3 H), 6.21 (dd, J = 20.1, 15.0 Hz, 1 H), 6.04 (dd, J = 15.0, 4.2 Hz, 1 H), 5.82 (dd, J = 20.1, 4.2 Hz, 1 H), 4.00-3.92 (m, 1 H), 2.86-2.76 (m, 1 H), 2.69-2.53 (m, 3 H), 2.08-1.83 (m, 2 H), 0.262 (s, 3 H), 0.256 (s, 3 H);

**¹³C NMR** (75.4 MHz, CDCl₃): δ 142.1, 137.8, 133.2, 131.5, 128.4, 128.3, 128.2, 127.7, 125.7, 123.7, 87.2, 82.2, 71.1, 38.5, 31.8, 28.5, -1.4;
IR (film): 2948 (s), 2234 (w), 1598 (m), 1491 (s);
HRMS (ESI): calcd. for C_{22}H_{26}O\text{SiNa}^+: 357.1645, found: 357.1634.

According to the general experiment, the reaction of cyclohexanecarbaldehyde (1.2 mL, 1.12 g, 10 mmol) and C_{3}H_{3}MgBr^{[15]} (12 mmol) in dry Et_{2}O (20 mL) afforded the propargyl alcohol 1.14 g (75%) as a colorless oil. The reaction of the propargyl alcohol (1.14 g, 7.5 mmol), iodobenzene (1 mL, 1.84 g, 9 mmol), CuI (142.8 mg, 0.75 mmol), PdCl_{2}(PPh_{3})_{2} (263.2 mg, 0.375 mmol) and Et_{3}N (5 mL) in dry THF (20 mL) afforded the phenyl propargyl alcohol 1.29 g (75%) as a green oil. The reaction of the phenyl propargyl alcohol (1.29 g, 5.64 mmol), imidazole (768.2 mg, 11.28 mmol), DMAP (137.8 mg, 1.128 mmol) and vinylidimethylchlorosilane (1.17 mL, 1.02 g, 8.46 mmol) in DCM (20 mL) afforded the silyl ether 1.15 g (65%) as a pale green oil.

TLC (hexanes:Et_{2}O = 100:1): R_f = 0.28;
Flash chromatography (2.5 cm φ × 15 cm): hexanes:Et_{2}O = 100:1;
{\text{^1}}H NMR (300 MHz, CDCl_{3}): δ 7.42-7.39 (m, 2 H), 7.31-7.26 (m, 3 H), 6.21 (dd, J = 20.1, 14.7 Hz, 1 H), 6.00 (dd, J = 14.7, 4.2 Hz, 1 H), 5.79 (dd, J = 20.1, 4.2 Hz, 1 H), 3.71-3.65 (m, 1 H), 2.61 (dd, J = 16.8, 5.7 Hz, 1 H), 2.52 (dd, J = 16.8, 6.6 Hz, 1 H), 1.84-1.74 (m, 3 H), 1.69-1.49 (m, 2 H), 1.60-1.49 (m, 1 H), 1.33-0.95 (m, 5 H), 0.233 (s, 3 H), 0.228 (s, 3 H);
{\text{^13}}C NMR (75.4 MHz, CDCl_{3}): δ 138.2, 132.9, 131.5, 128.2, 127.5, 124.0, 88.1, 81.8, 75.7, 42.9, 29.5, 27.5, 26.5, 26.4, 26.2, 25.7, -1.3;
IR (film): 2926 (s), 2234 (w), 1596 (w), 1490 (m);
HRMS (ESI): calcd. for C_{20}H_{28}OSiNa^+: 335.1802, found: 335.1800.

According to the general experiment, the reaction of 4-nitrobenzaldehyde (3.02 g, 20 mmol) and C_3H_3MgBr^{[13]} (24 mmol) in dry Et_2O (25 mL) and dry THF (15 mL) afforded the propargyl alcohol 913 mg as a pale yellow solid. The reaction of the propargyl alcohol (540 mg, 2.82 mmol), iodobenzene (0.38 mL, 690.3 mg, 13.9 mmol), CuI (21.5 mg, 0.113 mmol), PdCl_2(PPh_3)_2 (39.6 mg, 0.0586 mmol) and Et_3N (5 mL) in dry THF (15 mL) afforded the phenyl propargyl alcohol 547.8 mg (73%) as an orange solid. The reaction of the phenyl propargyl alcohol (524.5 mg, 1.96 mmol), imidazole (267.0 mg, 3.92 mmol), DMAP (48.0 mg, 0.392 mmol) and vinyldimethylchlorosilane (0.41 mL, 354.9 mg, 2.94 mmol) in DCM (50 mL) afforded the silyl ether 535.6 mg (78%) as a pale yellow solid.

TLC (hexanes:EtOAc = 20:1): R_f = 0.35;
M.P. (43-45°C);
Flash chromatography (2.5 cm φ × 15 cm): hexanes: EtOAc = 30:1→25:1;
^1H NMR (300 MHz, CDCl_3): δ 8.23-8.19 (m, 2 H), 7.61-7.57 (m, 2 H), 7.35-7.27 (m, 5 H), 6.09 (dd, J = 18.6, 15.0 Hz, 1 H), 6.00 (dd, J = 15.0, 5.4 Hz, 1 H), 5.77 (dd, J = 18.6, 5.4 Hz, 1 H), 4.99 (dd, J = 6.9, 6.3 Hz, 1 H), 2.86 (dd, J = 16.8, 6.3 Hz, 1 H), 2.73 (dd, J = 16.8, 6.9 Hz, 1 H), 0.23 (s, 3 H), 0.17 (s, 3 H);
^13C NMR (75.4 MHz, CDCl_3): δ 151.0, 147.4, 136.7, 134.0, 131.4, 128.3, 128.0, 126.9,
123.4, 123.3, 85.8, 83.1, 73.0, 31.3, -1.6, -1.7;

**IR** (film): 1599 (m), 1490 (m);

**Anal.** calcd. for C\textsubscript{20}H\textsubscript{21}NO\textsubscript{3}Si: C 68.35%, H 6.02%; found: C 68.55%, H 6.30%.

According to the general experiment, the reaction of acetophenone (1.17 mL, 1.20 g, 10 mmol) and C\textsubscript{3}H\textsubscript{3}MgBr\textsuperscript{[13]} (12 mmol) in dry Et\textsubscript{2}O (20 mL) afforded the propargyl alcohol 1.22 g (77%) as a colorless oil. The reaction of the propargyl alcohol (1.22 g, 7.64 mmol), iodobenzene (1.02 mL, 1.87 g, 9.17 mmol), CuI (145.5 mg, 0.764 mmol), PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (268.0 mg, 0.382 mmol) and Et\textsubscript{3}N (5 mL) in dry THF (20 mL) afforded the phenyl propargyl alcohol 1.37 g (76%) as a brown oil. The reaction of the phenyl propargyl alcohol (1.37 g, 5.79 mmol), imidazole (788.6 mg, 11.58 mmol), DMAP (141.5 mg, 1.158 mmol) and vinyldimethylchlorosilane (1.2 mL, 1.05 g, 8.69 mmol) in DCM (20 mL) afforded the silyl ether 1.15 g (62%) as a colorless oil.

**TLC** (hexanes:Et\textsubscript{2}O = 60:1): R\textsubscript{f} = 0.5;

**Flash chromatography** (2.5 cm φ × 15 cm): hexanes:Et\textsubscript{2}O = 100:1;

**\textsuperscript{1}H NMR** (300 MHz, CDCl\textsubscript{3}): δ 7.53-7.49 (m, 2 H), 7.37-7.30 (m, 4 H), 7.28-7.23 (m, 4 H), 6.14 (dd, J = 20.1, 14.7 Hz, 1 H), 5.91 (dd, J = 14.7, 3.9 Hz, 1 H), 5.75 (dd, J = 20.1, 3.9 Hz, 1 H), 2.88 (d, J = 16.5 Hz, 1 H), 2.82 (d, J = 16.5 Hz, 1 H), 1.82 (s, 3 H), 0.20 (s, 3 H), 0.18 (s, 3 H);

**\textsuperscript{13}C NMR** (75.4 MHz, CDCl\textsubscript{3}): δ 147.4, 139.5, 131.9, 131.5, 128.1, 127.8, 127.6, 126.8, 125.4, 123.9, 87.3, 82.8, 77.0, 37.5, 28.1, 0.52, 0.48;

**IR** (film): 2959 (s), 2220 (w), 1597 (m), 1491 (s);
According to the general experiment, the reaction of cyclohexanone (2.07 mL, 1.96 g, 20 mmol) and C₃H₃MgBr\(^{13}\) (30 mmol) in dry Et₂O (40 mL) afforded the propargyl alcohol 2.60 g (94%) as a pale yellow oil. The reaction of the propargyl alcohol (1.60 g, 11.6 mmol), iodobenzene (1.55 mL, 2.84 g, 13.9 mmol), CuI (220.9 mg, 1.16 mmol), PdCl₂(PPh₃)₂ (407.1 mg, 0.58 mmol) and Et₃N (5 mL) in dry THF (20 mL) afforded the phenyl propargyl alcohol 2.40 g (98%) as a brown oil. The reaction of the phenyl propargyl alcohol (2.40 g, 11.2 mmol), imidazole (1.58 g, 23.2 mmol), DMAP (283.5 mg, 2.32 mmol) and vinyldimethylchlorosilane (2.4 mL, 2.10 g, 17.4 mmol) in DCM (50 mL) afforded the silyl ether 2.00 g (58%) as a pale yellow oil.

\[
\text{TLC (hexanes:Et}_2\text{O = 50:1): } R_f = 0.63;
\]

\text{Flash chromatography (2.5 cm } φ \times 15 \text{ cm): hexanes:Et}_2\text{O = 120:1} \rightarrow 100:1;
\]

\text{\(^1\)H NMR (300 MHz, CDCl\(_3\)): } \delta 7.43-7.39 \text{ (m, } 2 \text{ H), 7.32-7.27 \text{ (m, } 3 \text{ H), 6.25 (dd, } J = 20.4, 15.0 \text{ Hz, } 1 \text{ H), 5.94 (dd, } J = 15.0, 3.9 \text{ Hz, } 1 \text{ H), 5.77 (dd, } J = 20.4, 3.9 \text{ Hz, } 1 \text{ H), 2.60 (s, } 2 \text{ H), 1.73-1.18 \text{ (m, } 10 \text{ H), 0.25 (s, } 6 \text{ H);}
\]

\text{\(^{13}\)C NMR (75.4 MHz, CDCl\(_3\)): } \delta 140.1, 131.54, 131.52, 128.2, 127.5, 124.0, 87.5, 82.8, 75.3, 37.7, 33.8, 25.4, 22.3, 0.8;

\text{IR (film): 2936 (s), 1596 (m), 1490 (s);}

\text{Anal. calcd. for C}_{19}\text{H}_{26}\text{OSi: C 76.45%, H 8.78%; found: C 76.84%, H 8.30%}. 

\text{Electronic Supplementary Material (ESI) for Chemical Science}
According to the general experiment, the reaction of 1-octanal (1.56 mL, 1.28 g, 10 mmol) and C₃H₅MgBr\textsuperscript{[15]} (12 mmol) in dry Et₂O (20 mL) afforded the propargyl alcohol 1.53 g (91\%) as a pale yellow oil. The reaction of the propargyl alcohol (1.53 g, 9.08 mmol), iodobenzene (1.22 mL, 2.22 g, 10.9 mmol), Cul (172.9 mg, 0.908 mmol), PdCl₂(PPh₃)₂ (318.7 mg, 0.454 mmol) and Et₃N (10 mL) in dry THF (20 mL) afforded the phenyl propargyl alcohol 1.20 g (54\%) as a brown oil. The reaction of the phenyl propargyl alcohol (1.20 g, 4.91 mmol), imidazole (668.7 mg, 9.82 mmol), DMAP (120.0 mg, 0.982 mmol) and vinyldimethylchlorosilane (1.02 mL, 889.0 mg, 7.365 mmol) in DCM (20 mL) afforded the silyl ether 879.2 mg (55\%) as a yellow oil.

\[ \text{TLC (hexanes:Et}_2\text{O = 60:1): } R_f = 0.39; \]

\textbf{Flash chromatography} (2.5 cm φ × 15 cm): hexanes:Et₂O = 60:1;

\textbf{¹H NMR} (300 MHz, CDCl₃): δ 7.43-7.37 (m, 2 H), 7.32-7.26 (m, 3 H), 6.20 (dd, \( J = 20.4, 15.0 \) Hz, 1 H), 6.02 (dd, \( J = 15.0, 4.2 \) Hz, 1 H), 5.80 (dd, \( J = 20.4, 4.2 \) Hz, 1 H), 3.92-3.84 (m, 1 H), 2.57 (dd, \( J = 16.8, 6.3 \) Hz, 1 H), 2.51 (dd, \( J = 16.8, 6.6 \) Hz, 1 H), 1.70-1.29 (m, 12 H), 0.88 (t, \( J = 6.6 \) Hz, 3 H), 0.24 (s, 3 H), 0.23 (s, 3 H);

\textbf{¹³C NMR} (75.4 MHz, CDCl₃): δ 137.9, 133.1, 131.5, 128.2, 127.6, 123.9, 87.6, 81.9, 71.6, 36.9, 31.8, 29.5, 29.3, 28.5, 25.5, 22.7, 14.1, -1.39, -1.42;

\textbf{IR} (film): 2929 (s), 2235 (w), 1597 (m), 1491 (m);

\textbf{HRMS} (ESI): calcd. for C₂₁H₃₂OSiNa⁺: 351.2115, found: 351.2110.
According to the general experiment, the reaction of 3-phenylpropanal (3.3 mL, 3.36 g, 25 mmol) and C₃H₃MgBr[15] (30 mmol) in dry Et₂O (50 mL) afforded the crude propargyl alcohol as a pale yellow oil. To a solution of the crude propargyl alcohol (4.36 g, 25 mmol) and PPTS (628.0 mg, 2.5 mmol) in dry DCM (50 mL) was added DHP (4.5 mL, 4.21 g, 50 mmol) at 0 °C under Ar(g) and then the reaction mixture was allowed to warm to rt. After being stirred at rt for 6h, the reaction was quenched with sat. NaHCO₃(aq) (20 mL) and extracted with DCM (3 × 20 mL). The combined organic phases was washed with brine, dried over MgSO₄, filtered and concentrated *in vacuo* to give the crude ether as an orange oil. nBuLi (2.5 M in hexanes, 4 mL, 10 mmol) was slowly added to a stirred solution of the crude ether (2.19 g, 8.5 mmol) in dry THF (40 mL) at -78 °C under Ar(g). After being stirred at -78°C for 1 h, MeI (0.79 mL, 1.81 g, 12.75 mmol) was added and the reaction mixture was allowed to warm to rt. After being stirred at rt for 7 h, the reaction mixture was cooled to -78 °C again, quenched with sat. NH₄Cl(aq) (20 mL), and extracted with Et₂O (3 × 30 mL). The combined organic phases was dried over MgSO₄, filtered and concentrated *in vacuo* to give the crude product as an orange oil. To a solution of the crude product (2.32 g, 8.5 mmol) in absolute EtOH (20 mL) was added PPTS (640.8 mg, 2.55 mmol). After being stirred at 50 °C 3 h, the reaction mixture was evaporated, dissolved in DCM (30 m), washed with brine, dried over MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (hexanes:EtOAc = 7:1) on silica gel to give the alcohol 770.3 mg (48%) as a pale yellow oil. The reaction of the alcohol (770.3 mg, 4.1 mmol), imidazole (558.0 mg, 8.2 mmol), DMAP (100.2 mg, 0.82 mmol) and vinyldimethylchlorosilane (0.85 mL, 742.3 mg, 6.15 mmol) in DCM (20 mL) afforded the silyl ether 893.4 mg (81%) as a colorless oil.
TLC (hexanes:Et₂O = 60:1): Rᵣ = 0.13;

Flash chromatography (2.5 cm φ × 15 cm): hexanes:Et₂O = 50:1→40:1;

¹H NMR (300 MHz, CDCl₃): δ 7.32-7.27 (m, 2 H), 7.22-7.15 (m, 3 H), 6.19 (dd, J = 20.1, 15.0 Hz, 1 H), 6.02 (dd, J = 15.0, 4.5 Hz, 1 H), 5.80 (dd, J = 20.1, 4.5 Hz, 1 H), 3.85-3.77 (m, 1 H), 2.82-2.72 (m, 1 H), 2.63-2.53 (m, 1 H), 2.40-2.23 (m, 2 H), 2.01-1.80 (m, 2 H), 1.78 (t, J = 2.7 Hz, 3 H), 0.230 (s, 3 H), 0.225 (s, 3 H);

¹³C NMR (75.4 MHz, CDCl₃): δ 142.3, 137.8, 133.1, 128.4, 128.3, 125.7, 77.4, 76.1, 71.4, 38.3, 31.9, 27.8, 3.6, -1.4;

IR (film): 2920 (s), 1603 (w), 1496 (m);

According to the general experiment, the reaction of 4-dimethylaminobenzaldehyde (2.98 g, 20 mmol) and C₃H₇MgBr\(^{15}\) (24 mmol) in dry Et₂O (25 mL) and dry THF (15 mL) afforded the crude propargyl alcohol as a brown oil. nBuLi (2.5 M in hexanes, 9.14 mL, 22.85 mmol) was slowly added to a stirred solution of the crude propargyl alcohol (1.73 g, 9.14 mmol) in dry THF (40 mL) at -78 °C under Ar(g). After being stirred at -78 °C for 1 h, the reaction mixture was treated with MeI (1.7 mL, 3.89 g, 27.42 mmol) and then allowed to warm to rt over night. The reaction mixture was then cooled to -78 °C again, quenched with sat. NH₄Cl\(_{\text{aq}}\) (20 mL), and extracted with Et₂O (3 × 30 mL). The combined organic phases was dried over MgSO₄, filtered and concentrated \textit{in vacuo}. The residue was purified by flash chromatography (hexanes:EtOAc = 3:1) on silica gel to give the alcohol 686.0 mg (37%) as a yellow oil. The reaction of the alcohol (686.0 mg, 3.37 mmol), imidazole (459.0 mg, 6.74 mmol), DMAP (82.0 mg, 0.674 mmol) and vinyldimethylchlorosilane (0.69 mL, 603.5 mg, 5 mmol) in DCM (20 mL) afforded the silyl ether 708.1 mg (73%) as a colorless oil.

\textbf{TLC} (hexanes:Et₂O = 60:1): \(R_f = 0.13\);

\textbf{Flash chromatography} (2.5 cm \(\phi \times 15\) cm): hexanes:Et₂O = 50:1→20:1;

\textbf{\(^1H\) NMR} (300 MHz, CDCl\(_3\)): \(\delta\) 7.21 (d, \(J = 8.7\) Hz, 2 H), 6.70 (d, \(J = 8.7\) Hz, 2 H), 6.11 (dd, \(J = 19.8, 15.0\) Hz, 1 H), 5.97 (dd, \(J = 15.0, 4.5\) Hz, 1 H), 5.76 (dd, \(J = 19.8, 4.5\) Hz, 1 H), 4.73 (dd, \(J = 7.2, 6.0\) Hz, 1 H), 2.95 (s, 6 H), 2.55 (ddq, \(J = 16.5, 7.2, 2.7\) Hz, 1 H), 2.44 (ddq, \(J = 16.5, 6.0, 2.7\) Hz, 1 H), 1.77 (t, \(J = 2.7\) Hz, 3 H), 0.17 (s, 3 H), 0.13 (s, 3 H);

\textbf{\(^{13}C\) NMR} (75.4 MHz, CDCl\(_3\)): \(\delta\) 149.8, 137.9, 132.8, 132.0, 126.7, 112.1, 76.9, 76.8, 74.0, 40.6, 30.9, 3.5, -1.5, -1.6;
**IR** (film): 2919 (m), 1616 (s), 1523 (s);

**HRMS** (EI): calcd. for C_{17}H_{26}NOSi^{+}: 288.1778, found: 288.1782.
Dess-Martin reagent (1.53 g, 3.6 mmol) was added portionwise to a solution of the alcohol (486.9 mg, 3 mmol) in dry DCM (50 mL). After being stirred at rt for 3 h, the reaction mixture was quenched with sat. NaHCO₃(aq) (20 mL) and washed with sat. Na₂S₂O₃(aq) (2 × 20 mL). The organic layer was dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by flash chromatography (hexanes:EtOAc = 10:1) on silica gel to give the aldehyde 312.3 mg (65%) as a pale yellow oil. MeLi (1.6 M in Et₂O, 1.48 mL, 2.36 mmol) was slowly added to a stirred solution of the above aldehyde (312.3 mg, 1.97 mmol) in dry THF (10 mL) at -78°C under Ar(g). After being stirred at -78°C for 2 h, the reaction mixture was quenched with sat. NH₄Cl(aq) (5 mL), and extracted with Et₂O (3 × 10 mL). The combined organic layers was washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by flash chromatography (hexanes:EtOAc = 4:1) on silica gel to give the alcohol 187.1 mg (55%) as a pale yellow oil. The reaction of the alcohol (187.1 mg, 1.07 mmol), imidazole (146.3 mg, 2.148 mmol), DMAP (26.2 mg, 0.215 mmol) and vinyl(dimethyl)chlorosilane (0.22 mL, 194.4 mg, 1.611 mmol) in DCM (10 mL) afforded the silyl ether 180.0 mg (65%) as a colorless oil.

TLC (hexanes:Et₂O = 50:1): Rₜ = 0.21;

Flash chromatography (2.5 cm φ × 10 cm): hexanes:Et₂O = 50:1;

\(^1\)H NMR (300 MHz, CDCl₃): δ 7.41-7.36 (m, 2 H), 7.32-7.25 (m, 3 H), 6.29 (dd, J = 20.1, 15.0 Hz, 1 H), 6.01 (dd, J = 15.0, 4.2 Hz, 1 H), 5.79 (dd, J = 20.1, 4.2 Hz, 1 H), 4.06-3.96 (m, 1 H), 2.46 (t, J = 7.2 Hz, 2 H), 1.79-1.62 (m, 2 H), 1.19 (d, J = 6.0 Hz, 3 H), 0.228 (s, 3 H), 0.225 (s, 3 H);

\(^13\)C NMR (75.4 MHz, CDCl₃): δ 138.0, 133.0, 131.5, 128.2, 127.5, 124.0, 90.0, 80.7, 67.3, 38.1, 23.7, 15.9, -1.5, -1.6;

IR (film): 2968 (s), 1598 (m), 1491 (s);

A solution of 4-bromobenzaldehyde (3.41 g, 18.4 mmol), phenylboronic acid (2.47 g, 20.24 mmol), K₂CO₃ (3.81 g, 27.6 mmol), Pd(OAc)₂ (123.9 mg, 0.552 mmol) and PPh₃ (434.4 mg, 1.656 mmol) in Tol (30 mL) and distilled H₂O (10 mL) was degassed by freeze/pump/Arₕ for 3 times and refluxed for 5 h under Arₕ. The reaction mixture was concentrated _in vacuo_ and purified by flash chromatography on silica gel to give 4-phenylbenzaldehyde 2.42 (72%) as a white solid. According to the general experiment, the reaction of 4-phenylbenzaldehyde (1.01 g, 5.54 mmol) and C₃H₃MgBr [13] (7.2 mmol) in dry Et₂O (35 mL) afforded the propargyl alcohol 1.15 g as a yellow solid. The reaction of the propargyl alcohol (1.15 g, 5.16 mmol), iodobenzene (0.87 mL, 1.58 g, 7.73 mmol), CuI (98 mg, 0.516 mmol), PdCl₂(PPh₃)₂ (181 mg, 0.258 mmol) and Et₃N (5 mL) in dry THF (30 mL) afforded the phenyl propargyl alcohol as pale yellow solid. The reaction of the phenyl propargyl alcohol, imidazole (703 mg, 10.32 mmol), DMAP (126 mg, 10.32 mmol) and vinyl(dimethyl)silane (1.1 mL, 934 mg, 7.74 mmol) in DCM (50 mL) afforded the silyl ether 1.00 g (51%) as a pale yellow solid.

_TLC_ (hexanes:Et₂O = 60:1): _R_f = 0.37;

_M.P._ (39-41°C);

_Flash chromatography_ (2.5 cm φ × 15 cm): hexanes: Et₂O = 120:1→100:1;

₁H NMR (300 MHz, CDCl₃): δ 7.65-7.59 (m, 4 H), 7.52-7.44 (m, 4 H), 7.42-7.34 (m, 3 H), 7.32-7.28 (m, 3 H), 6.17 (dd, _J_ = 20.1, 15.0 Hz, 1 H), 6.01 (dd, _J_ = 15.0, 4.5 Hz, 1 H), 5.81
(dd, $J = 20.1$, 4.5 Hz, 1 H), 5.00 (dd, $J = 7.2$, 6.0 Hz, 1 H), 2.90 (dd, $J = 16.5$, 7.2 Hz, 1 H),
2.80 (dd, $J = 16.5$, 6.0 Hz, 1 H), 0.26 (s, 3 H), 0.21 (s, 3 H);

$^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 142.8, 140.9, 140.3, 137.4, 133.4, 131.5, 128.7, 128.2,
127.7, 127.2, 127.1, 126.8, 126.3, 123.8, 87.3, 82.3, 73.7, 31.6, -1.4, -1.6;

IR (film): 2959 (m), 1597 (m), 1488 (s);

Anal. calcd. for C$_{26}$H$_{26}$OSi: C 81.63%, H 6.85%; found: C 81.93%, H 6.90%.
The reaction of 4-phenylbenzaldehyde (911 mg, 5.0 mmol) and NaBH₄ (284 mg, 7.5 mmol) in dry MeOH (15 mL) at 0 °C afforded 4-phenylbenzyl alcohol 913 mg (100%) as a pale yellow solid. The reaction of 4-phenylbenzyl alcohol (913 mg, 5.0 mmol), Et₃N (1.05 mL, 759 mg, 7.5 mmol) and acryloyl chloride (0.49 mL, 543 mg, 6.0 mmol) in DCM (20 mL) afforded dipheylmethyl acrylate 826 mg (69%) as a white solid.

TLC (hexanes: EtOAc = 10:1): Rf = 0.3;
M.P. (29-31°C);
Flash chromatography (2.5 cm φ × 20 cm): hexanes:EtOAc = 20:1;
¹H NMR (300 MHz, CDCl₃): δ 7.62-7.58 (m, 4 H), 7.48-7.33 (m, 5 H), 6.48 (dd, J = 17.4, 1.5 Hz, 1 H), 6.19 (dd, J = 17.4, 10.5 Hz, 1 H), 5.87 (dd, J = 10.5, 1.5 Hz, 1 H), 5.25 (s, 2 H);
¹³C NMR (75.4 MHz, CDCl₃): δ 166.1, 141.3, 140.6, 134.8, 131.2, 128.8, 128.7, 128.3, 127.4, 127.3, 127.1, 66.1;
IR (film): 1724(s), 1488 (m);
Anal. calcd. for C₁₆H₁₄O₂: C 80.65%, H 5.92%; found: C 80.52%, H 6.03%.
Part 2. RuH-catalyzed intermolecular coupling reaction of Si-tethered enyne with acrylates.

In a typical experiment, RuHCl(CO)(PCy₃)₂ (18.2 mg, 0.025 mmol) was added to a 25 mL Schlenk tube in the glovebox. The vessel was sealed, removed from the glovebox and placed on a Schlenk line under Ar(g). A solution of the silyl ether (122.2 mg, 0.5 mmol) and L-menthyl acrylate (210.3 mg, 1.0 mmol) in freshly distilled DCE (1 mL, 0.5 M) was degassed by bubbling for 3 min and added to the Schlenk tube via a syringe. A cold finger condenser was attached to the Schlenk tube by removing the septum against a positive stream of Ar(g). The whole apparatus was then immersed in a preheated 85 °C oil bath. After being stirred for 9 h at 85 °C, the reaction mixture was concentrated \textit{in vacuo} and purified by flash chromatography on silica gel to give the product 2A 182.6 mg (85%, 1:1 d.r.) as a pale yellow oil.

\[ \text{TLC (pentane:Et₂O = 20:1): } R_f = 0.17; \]

\[ \text{Flash chromatography (2.5 cm } \phi \times 15 \text{ cm): pentane:Et₂O = 20:1} \rightarrow \text{18:1;} \]

\[ ^1\text{H NMR (300 MHz, CDCl₃): } \delta \ 7.78 \ (d, J = 15.6 \ Hz, 1H), 7.35-7.29 \ (m, 3H), 7.12-7.09 \ (m, 2H), 5.49 \ (d, J = 15.6 \ Hz, 1H), 4.75 \ (td, J = 10.8, 4.5 \ Hz, 1H), 4.27-4.17 \ (m, 1H), 3.08 \ (dd, J = 16.5, 5.4 \ Hz, 1H), 2.44 \ (dd, J = 16.5, 8.1 \ Hz, 0.5 \ H), 2.42 \ (dd, J = 16.5, 8.1 \ Hz, 0.5 \ H), 1.99-1.95 \ (m, 1H), 1.86-1.76 \ (m, 1H), 1.68-1.61 \ (m, 2H), 1.54-1.37 \ (m, 2H), 1.32 \ (d, J = 6.0 \ Hz, 3H), 1.10-0.92 \ (m, 3H), 0.87 \ (d, J = 7.2 \ Hz, 3H), 0.84 \ (d, J = 7.2 \ Hz, 3H), 0.73 \ (d, J = 6.9 \ Hz, 3H), -0.06 \ (s, 1.5 \ H), -0.10 \ (s, 1.5 \ H), -0.20 \ (s, 1.5 \ H), -0.23 \ (s, 1.5 \ H); \]

\[ ^{13}\text{C NMR (75.4 MHz, CDCl₃): } \delta 167.1, 153.6, 153.5, 144.9, 142.0, 140.6, 129.4, 128.1, 127.6, 122.1, 74.1, 72.4, 47.0, 41.14, 41.09, 40.9, 34.2, 31.3, 26.1, 23.9, 23.3, 22.0, 20.7, 16.2, \]
0.4, 0.2, -0.6, -0.8;

IR (film): 2958 (m), 1713 (s), 1615 (m), 1491 (w);

HRMS (ESI): calcd. for C_{26}H_{36}O_{2}SiNa^{+}-H_{2}O: 431.2377, found: 431.2391.

According to the general experiment, the reaction of the silyl ether (122.2 mg, 0.5 mmol), methyl acrylate (86.1 mg, 1.0 mmol) and RuHCl(CO)(PCy_{3})_{2} (18.2 mg, 0.025 mmol) in DCE (1.0 mL, 0.5 M) afforded the product 2B 84.4 mg (55%) as a white foam.

TLC (hexanes:EtOAc = 20:1): R_f = 0.30;

Flash chromatography (2.5 cm φ × 15 cm): hexanes:EtOAc = 20:1;

^{1}H NMR (300 MHz, CDCl_{3}): δ 7.79 (d, J = 15.6 Hz, 1 H), 7.33-7.30 (m, 3 H), 7.10-7.07 (m, 2 H), 5.51 (d, J = 15.6 Hz, 1 H), 4.28-4.17 (m, 1 H), 3.71 (s, 3 H), 3.09 (dd, J = 16.8, 5.4 Hz, 1 H), 2.43 (dd, J = 16.8, 8.4 Hz, 1 H), 1.33 (d, J = 6.3 Hz, 3 H), -0.07 (s, 3 H), -0.21 (s, 3 H);

^{13}C NMR (75.4 MHz, CDCl_{3}): δ 167.8, 154.0, 144.8, 142.4, 140.4, 129.3, 128.1, 127.7, 121.3, 72.3, 51.5, 41.2, 23.9, 0.3, -0.7;

IR (film): 2965 (m), 1720 (s), 1617 (m), 1492 (w);

HRMS (ESI): calcd. for C_{17}H_{22}O_{3}SiNa^{+}: 325.1230, found: 325.1228.
According to the general experiment, the reaction of the silyl ether (122.2 mg, 0.5 mmol), ethyl acrylate (100.1 mg, 1.0 mmol) and RuHCl(CO)(PCy₃)₂ (18.2 mg, 0.025 mmol) in DCE (1.0 mL, 0.5 M) afforded the product 2C 90.0 mg (54%) as a white foam.

TLC (hexanes:EtOAc = 20:1): Rf = 0.33;
Flash chromatography (2.5 cm φ × 15 cm): hexanes:EtOAc = 20:1;

1H NMR (300 MHz, CDCl₃): δ 7.79 (d, J = 15.6 Hz, 1 H), 7.33-7.30 (m, 3 H), 7.11-7.08 (m, 2 H), 5.50 (d, J = 15.6 Hz, 1 H), 4.28-4.17 (m, 1 H), 4.17 (q, J = 7.2 Hz, 2 H), 3.09 (dd, J = 16.5, 5.4 Hz, 1 H), 2.43 (dd, J = 16.5, 8.4 Hz, 1 H), 1.33 (d, J = 6.0 Hz, 3 H), 1.24 (t, J = 7.2 Hz, 3 H), -0.07 (s, 3 H), -0.21 (s, 3 H);

13C NMR (75.4 MHz, CDCl₃): δ 167.4, 153.7, 144.8, 142.1, 140.5, 129.3, 128.1, 127.6, 121.8, 72.3, 60.3, 41.1, 23.9, 14.2, 0.3, -0.7;

IR (film): 2967 (s), 1714 (s), 1617 (m), 1492 (w);

According to the general experiment, the reaction of the silyl ether (122.2 mg, 0.5 mmol), $n$-butyl acrylate (128.2 mg, 1.0 mmol) and RuHCl(CO)(PCy$_3$)$_2$ (18.2 mg, 0.025 mmol) in DCE (1.0 mL, 0.5 M) afforded the product 2D 89.9 mg (51%) as a pale yellow oil.

\[
\text{TLC (hexanes:EtOAc = 20:1): } R_f = 0.33;
\]

**Flash chromatography** (2.5 cm $\times$ 15 cm): hexanes:EtOAc = 20:1;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J = 15.6$ Hz, 1 H), 7.33-7.30 (m, 3 H), 7.11-7.08 (m, 2 H), 5.50 (d, $J = 15.6$ Hz, 1 H), 4.27-4.17 (m, 1 H), 4.11 (t, $J = 6.9$ Hz, 2 H), 3.08 (dd, $J = 16.8$, 5.1 Hz, 1 H), 2.43 (dd, $J = 16.8$, 8.1 Hz, 1 H), 1.60 (quint, $J = 6.9$ Hz, 2 H), 1.41-1.32 (m, 2 H), 1.33 (d, $J = 5.7$ Hz, 3 H), 0.90 (t, $J = 7.2$ Hz, 3 H), -0.07 (s, 3 H), -0.21 (s, 3 H);

$^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 167.5, 153.7, 144.8, 142.1, 140.5, 129.3, 128.1, 127.6, 121.8, 72.3, 64.3, 41.1, 30.6, 23.9, 19.1, 13.6, 0.3, -0.7;

**IR** (film): 2962 (s), 1715 (s), 1616 (m), 1493 (w);

**Anal.** calcd. for C$_{20}$H$_{28}$O$_3$Si: C 69.72%, H 8.19%; found: C 69.38%, H 8.26%.
According to the general experiment, the reaction of the silyl ether (122.2 mg, 0.5 mmol), t-butyl acrylate (128.2 mg, 1.0 mmol) and RuHCl(CO)(PCy\textsubscript{3})\textsubscript{2} (18.2 mg, 0.025 mmol) in DCE (1.0 mL, 0.5 M) afforded the product 2E 95.3 mg (58%) as a pale yellow oil.

\[ \text{TLC (hexanes:EtOAc = 20:1): } R_f = 0.33; \]

\textbf{Flash chromatography} (2.5 cm φ × 15 cm): hexanes:EtOAc = 20:1;

\textbf{\textsuperscript{1}H NMR} (300 MHz, CDCl\textsubscript{3}): \( \delta \) 7.72 (d, \( J = 15.3 \) Hz, 1 H), 7.34-7.29 (m, 3 H), 7.11-7.08 (m, 2 H), 5.43 (d, \( J = 15.3 \) Hz, 1 H), 4.24-4.18 (m, 1 H), 3.07 (dd, \( J = 16.5, 5.4 \) Hz, 1 H), 2.42 (dd, \( J = 16.5, 8.4 \) Hz, 1 H), 1.44 (s, 9 H), 1.31 (d, \( J = 6.3 \) Hz, 3 H), -0.09 (s, 3 H), -0.22 (s, 3 H);

\textbf{\textsuperscript{13}C NMR} (75.4 MHz, CDCl\textsubscript{3}): \( \delta \) 166.8, 152.9, 144.9, 141.3, 140.7, 129.3, 128.1, 127.5, 123.5, 80.4, 72.3, 41.0, 28.0, 23.9, 0.3, -0.7;

\textbf{IR} (film): 2974 (s), 1709 (s), 1615 (m), 1492 (w);

\textbf{Anal.} calcd. for C\textsubscript{20}H\textsubscript{28}O\textsubscript{3}Si: C 69.72%, H 8.19%; found: C 69.50%, H 8.33%.
According to the general experiment, the reaction of the silyl ether (122.2 mg, 0.5 mmol), isobornyl acrylate (208.3 mg, 1.0 mmol) and RuHCl(CO)(PCy₃)₂ (18.2 mg, 0.025 mmol) in DCE (1.0 mL, 0.5 M) afforded the product 2F 155.5 mg (73%) as a yellow oil.

TLC (hexanes:EtOAc = 20:1): Rf = 0.30;

Flash chromatography (2.5 cm φ × 15 cm): hexanes:EtOAc = 20:1;

$^1$H NMR (300 MHz, CDCl₃): δ 7.76 (d, $J = 15.6$ Hz, 1 H), 7.33-7.30 (m, 3 H), 7.11-7.08 (m, 2 H), 5.47 (d, $J = 15.6$ Hz, 1 H), 4.73-4.71 (m, 1 H), 4.27-4.17 (m, 1 H), 3.04 (dd, $J = 16.8$, 5.4 Hz, 1 H), 2.41 (dd, $J = 16.8$, 8.1 Hz, 1 H), 1.84-1.49 (m, 6 H), 1.32 (d, $J = 6.0$ Hz, 3 H), 1.12-1.03 (m, 1 H), 0.97 (s, 3 H), 0.822 (s, 3 H), 0.818 (s, 3 H), -0.08 (s, 3 H), -0.22 (s, 3 H);

$^{13}$C NMR (75.4 MHz, CDCl₃): δ 167.0, 153.6, 144.9, 141.8, 140.5, 129.4, 128.2, 127.7, 122.2, 81.0, 72.3, 48.9, 46.9, 45.0, 41.1, 38.8, 33.7, 27.0, 23.9, 20.1, 20.0, 11.5, 0.3, -0.7;

IR (film): 2958 (s), 1709 (s), 1616 (m), 1491 (w);

According to the general experiment, the reaction of the silyl ether (61.1 mg, 0.25 mmol), biphenylmethyl acrylate (119.2 mg, 0.5 mmol) and RuHCl(CO)(PCy₃)₂ (9.1 mg, 0.0125 mmol) in DCE (0.5 mL, 0.5 M) afforded the product 2G 90.0 mg (79%) as a white solid. Colorless needle-shaped crystals of 2G suitable for X-ray diffraction were readily obtained by evaporation of a hexane/acetonitrile solution.

\[
\text{TLC (hexanes:EtOAc = 10:1): } R_f = 0.3;
\]

\[
\text{M.P. (112-114°C);}
\]

**Flash chromatography** (2.5 cm \(\phi\times 15\) cm): hexanes:EtOAc = 12:1→10:1;

**\(^1\)H NMR** (300 MHz, CDCl₃): \(\delta\) 7.89 (d, \(J = 15.6\) Hz, 1 H), 7.60-7.58 (m, 4 H), 7.47-7.43 (m, 4 H), 7.38-7.33 (m, 4 H), 7.14-7.10 (m, 2 H), 5.61 (d, \(J = 15.6\) Hz, 1 H), 5.23 (s, 2 H), 4.31-4.20 (m, 1 H), 3.12 (dd, \(J = 16.5, 5.4\) Hz, 1 H), 2.46 (dd, \(J = 16.5, 8.4\) Hz, 1 H), 1.36 (d, \(J = 6.3\) Hz, 3 H), -0.04 (s, 3 H), -0.17 (s, 3 H);

**\(^13\)C NMR** (75.4 MHz, CDCl₃): \(\delta\) 167.3, 154.3, 144.8, 142.8, 141.2, 140.6, 140.4, 134.9, 129.3, 128.8, 128.7, 128.2, 127.7, 127.4, 127.3, 127.1, 121.3, 72.3, 66.0, 41.2, 23.9, 0.3, -0.7;

**IR** (film): 2961 (m), 1715 (s), 1617 (m), 1487 (s);

**Anal.** calcd. for C₂₉H₃₀O₃Si: C 76.61%, H 6.65%; found: C 76.38%, H 6.83%.
According to the general experiment, the reaction of the silyl ether (164.3 mg, 0.5 mmol), L-menthyl acrylate (210.3 mg, 1.0 mmol) and RuHCl(CO)(PCy3)2 (18.2 mg, 0.025 mmol) in DCE (1.0 mL, 0.5 M) afforded the product 11 196.7 mg (77%, 1:1 d.r.) as a pale yellow oil.

**TLC** (hexanes:Et2O = 25:1): Rf = 0.3;

**Flash chromatography** (2.5 cm φ × 15 cm): hexanes:Et2O = 35:1 → 25:1;

**1H NMR** (300 MHz, CDCl3): δ 7.79 (d, J = 15.6 Hz, 1 H), 7.31-7.29 (m, 3 H), 7.10-7.07 (m, 2 H), 5.48 (d, J = 15.6 Hz, 1 H), 4.74 (td, J = 10.8, 4.2 Hz, 1 H), 4.09-4.00 (m, 1 H), 3.04 (dd, J = 10.8, 5.4 Hz, 1 H), 2.50-2.40 (m, 1 H), 1.98-1.94 (m, 1 H), 1.87-1.76 (m, 1 H), 1.65-1.61 (m, 4 H), 1.53-1.26 (m, 12 H), 1.10-0.91 (m, 3 H), 0.87-0.82 (m, 9 H), 0.72 (d, J = 6.3 Hz, 3 H), -0.10 (s, 1.5 H), -0.13 (s, 1.5 H), -0.20 (s, 1.5 H), -0.24 (s, 1.5 H);

**13C NMR** (75.4 MHz, CDCl3): δ 167.0 153.53, 153.50, 144.7, 142.0, 140.6, 129.3, 128.0, 127.5, 121.9, 76.2, 73.9, 47.0, 40.9, 39.3, 39.2, 38.3, 34.1, 31.7, 31.3, 29.5, 29.2, 26.0, 25.6, 23.3, 22.6, 21.9, 20.7, 16.2, 14.0, 0.3, 0.1, -0.6, -0.8;

**IR** (film): 2928 (s), 1710 (s), 1617 (m), 1492 (w);

**HRMS** (ESI): calcd. for C32H50O3SiNa+: 533.3421, found: 533.3427.
According to the general experiment, the reaction of the silyl ether (167.3 mg, 0.5 mmol), L-menthyl acrylate (210.3 mg, 1.0 mmol) and RuHCl(CO)(PCy₃)₂ (18.2 mg, 0.025 mmol) in DCE (1.0 mL, 0.5 M) afforded the product 12 183.0 mg (72%, 1:1 d.r.) as a pale yellow oil.

TLC (hexanes:Et₂O = 15:1): R_f = 0.28;

Flash chromatography (2.5 cm φ × 15 cm): hexanes:Et₂O = 15:1;

¹H NMR (300 MHz, CDCl₃): δ 7.84 (d, J = 15.6 Hz, 1 H), 7.37-7.20 (m, 8 H), 7.16-7.13 (m, 2 H), 5.55 (d, J = 15.6 Hz, 1 H), 4.80 (td, J = 10.8, 4.2 Hz, 1 H), 4.18-4.09 (m, 1 H), 3.11 (dd, J = 16.5, 5.4 Hz, 0.5 H), 3.10 (dd, J = 16.5, 5.4 Hz, 0.5 H), 2.90-2.70 (m, 2 H), 2.58 (dd, J = 16.5, 7.5 Hz, 0.5 H), 2.56 (dd, J = 16.5, 7.5 Hz, 0.5 H), 2.04-2.00 (m, 1 H), 1.95-1.81 (m, 3 H), 1.71-1.65 (m, 2 H), 1.58-1.46 (m, 1 H), 1.43-1.34 (m, 1 H), 1.15-0.97 (m, 3 H), 0.91 (d, J = 7.2 Hz, 3 H), 0.89 (d, J = 7.2 Hz, 3 H), 0.78 (d, J = 6.9 Hz, 3 H), -0.01 (s, 1.5 H), -0.05 (s, 1.5 H), -0.11 (s, 1.5 H), -0.15 (s, 1.5 H);

¹³C NMR (75.4 MHz, CDCl₃): δ 166.9, 153.11, 153.08, 144.9, 141.9, 140.5, 129.3, 128.3, 128.2, 128.1, 127.6, 125.7, 122.1, 75.3, 74.0, 47.0, 40.9, 39.9, 39.24, 39.20, 34.1, 31.9, 31.3, 26.0, 23.3, 21.9, 20.7, 16.2, 0.3, 0.1, -0.5, -0.7;

IR (film): 2956 (s), 1708 (s), 1617 (m), 1494 (w);

HRMS (ESI): calcd. for C₃₃H₄₄O₃SiNa⁺: 539.2952, found: 539.2950.
According to the general experiment, the reaction of the silyl ether (74.0 mg, 0.24 mmol), L-menthyl acrylate (100.9 mg, 0.48 mmol) and RuHCl(CO)(PCy₃)₂ (8.7 mg, 0.012 mmol) in DCE (0.48 mL, 0.5 M) afforded the product 13 88.0 mg (75%, 1:1 d.r.) as a pale yellow oil.

TLC (hexanes:Et₂O = 35:1): Rf = 0.18;
Flash chromatography (2.5 cm φ × 15 cm): hexanes:Et₂O = 35:1 → 33:1;

¹H NMR (300 MHz, CDCl₃): δ 7.80 (d, J = 15.6 Hz, 1 H), 7.32-7.28 (m, 3 H), 7.10-7.07 (m, 2 H), 5.48 (d, J = 15.6 Hz, 1 H), 4.74 (td, J = 10.8, 4.5 Hz, 1 H), 3.81-3.74 (m, 1 H), 3.00 (dd, J = 16.8, 5.4 Hz, 0.5 H), 2.99 (dd, J = 16.8, 5.4 Hz, 0.5 H), 2.64-2.56 (m, 1 H), 2.03-1.63 (m, 12 H), 1.46-0.95 (m, 8 H), 0.87 (d, J = 6.9 Hz, 3 H), 0.86 (d, J = 6.9 Hz, 3 H), 0.72 (d, J = 6.6 Hz, 3 H), -0.08 (s, 1.5 H), -0.12 (s, 1.5 H), -0.23 (s, 1.5 H), -0.27 (s, 1.5 H);

¹³C NMR (75.4 MHz, CDCl₃): δ 167.1, 153.81, 153.78, 144.5, 142.0, 140.6, 129.3, 128.0, 127.5, 121.9, 80.4, 74.0, 47.0, 44.5, 40.9, 36.5, 36.4, 34.2, 33.3, 31.3, 29.00, 28.97, 28.5, 27.4, 26.5, 26.0, 23.3, 22.0, 20.7, 16.2, 0.1, -0.1, -0.7, -0.9;
IR (film): 2956 (s), 1710 (s), 1616 (m), 1486 (w);
HRMS (EI): calcd. for C₃₁H₄₆O₃Si⁺: 494.3211, found: 494.3199.
According to the general experiment, the reaction of the silyl ether (153.3 mg, 0.5 mmol), L-menthyl acrylate (210.3 mg, 1.0 mmol) and RuHCl(CO)(PCy$_3$)$_2$ (18.2 mg, 0.025 mmol) in Tol (1.0 mL, 0.5 M) afforded the product 14 161.4 mg (69%, 1:1 d.r.) as a pale yellow foam.

TLC (pentane:Et$_2$O = 25:1): R$_f$ = 0.24;

Flash chromatography (2.5 cm φ × 15 cm): pentane:Et$_2$O = 25:1;

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.81 (d, $J = 15.6$ Hz, 0.5 H), 7.80 (d, $J = 15.6$ Hz, 0.5 H), 7.44-7.29 (m, 8 H), 7.18-7.15 (m, 2 H), 5.55 (d, $J = 9.6$, 5.4 Hz, 1 H), 5.11 (dd, $J = 9.6$, 5.4 Hz, 1 H), 4.771 (td, $J = 10.8$, 4.2 Hz, 0.5 H), 4.767 (td, $J = 10.8$, 4.2 Hz, 0.5 H), 3.44 (dd, $J = 16.8$, 5.4 Hz, 0.5 H), 3.43 (dd, $J = 16.8$, 5.4 Hz, 0.5 H), 2.72 (dd, $J = 16.8$, 9.6 Hz, 0.5 H), 2.71 (dd, $J = 16.8$, 9.6 Hz, 0.5 H), 2.01-1.96 (m, 1 H), 1.87-1.81 (m, 1 H), 1.70-1.64 (m, 2 H), 1.53-1.32 (m, 2 H), 1.13-0.99 (m, 3 H), 0.90 (d, $J = 6.6$ Hz, 1.5 H), 0.89 (d, $J = 6.6$ Hz, 1.5 H), 0.87 (d, $J = 7.5$ Hz, 3 H), 0.75 (d, $J = 6.9$ Hz, 1.5 H), 0.74 (d, $J = 6.9$ Hz, 1.5 H), 0.12 (s, 1.5 H), 0.09 (s, 1.5 H), -0.13 (s, 1.5 H), -0.16 (s, 1.5 H);

$^{13}$C NMR (75.4 MHz, CDCl$_3$): δ 166.9, 152.72, 152.68, 145.0, 144.1, 141.7, 140.5, 129.3, 128.4, 128.2, 127.7, 127.3, 125.3, 122.5, 77.6, 74.1, 47.0, 42.4, 42.3, 40.9, 34.2, 31.3, 26.1, 23.3, 22.0, 20.7, 16.2, 0.3, 0.1, -0.8, -1.0;

IR (film): 2956 (s), 1710 (s), 1616 (m), 1495 (w);

HRMS (ESI): calcd. for C$_{31}$H$_{40}$O$_3$SiNa$: 511.2639$, found: 511.2645.
According to the general experiment, the reaction of the chiral silyl ether (153.3 mg, 0.5 mmol), L-menthyl acrylate (210.3 mg, 1.0 mmol) and RuHCl(CO)(PCy$_3$)$_2$ (18.2 mg, 0.025 mmol) in Tol (1.0 mL, 0.5 M) afforded the product 15 160.0 mg (65%) as a pale yellow foam.

TLC (hexanes: Et$_2$O = 15:1): $R_f = 0.23$;

$[\alpha]_D^{24} = -375.6$ ($c = 2.0$, DCM);

Flash chromatography (2.5 cm φ × 10 cm): hexanes:Et$_2$O = 25:1→18:1;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J = 15.6$ Hz, 1 H), 7.43-7.27 (m, 8 H), 7.17-7.14 (m, 2 H), 5.53 (d, $J = 15.6$ Hz, 1 H), 5.10 (dd, $J = 9.3$, 5.4 Hz, 1 H), 4.76 (td, $J = 10.8$, 4.5 Hz, 1 H), 3.42 (dd, $J = 16.8$, 5.4 Hz, 1 H), 2.71 (dd, $J = 16.8$, 9.3 Hz, 1 H), 2.00-1.93 (m, 1 H), 1.87-1.77 (m, 1 H), 1.68-1.62 (m, 2 H), 1.55-1.26 (m, 2 H), 1.12-0.93 (m, 3 H), 0.88 (d, $J = 6.9$ Hz, 3 H), 0.86 (d, $J = 6.9$ Hz, 3 H), 0.74 (d, $J = 7.2$ Hz, 3 H), 0.08 (s, 3 H), -0.14 (s, 3 H);

$^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 167.0, 152.7, 145.0, 144.1, 141.8, 140.5, 129.4, 128.4, 128.2, 127.7, 127.4, 125.3, 122.5, 77.6, 74.1, 47.0, 42.3, 40.9, 34.2, 31.3, 26.1, 23.3, 22.0, 20.7, 16.2, 0.1, -0.8;

IR (film): 2956 (s), 1708 (s), 1617 (m), 1496 (w);

HRMS (ESI): calcd. for C$_{31}$H$_{40}$O$_3$SiNa$: 511.2639$, found: 511.2646.
According to the general experiment, the reaction of the silyl ether (87.9 mg, 0.25 mmol), biphenylmethyl acrylate (119.2 mg, 0.5 mmol) and RuHCl(CO)(PCy₃)₂ (18.2 mg, 0.025 mmol) in Tol (0.5 mL, 0.5 M) afforded the product 16 95.0 mg (68%) as a pale yellow foam.

TLC (hexanes:EtOAc = 10:1): Rf = 0.2;

Flash chromatography (2.5 cm φ × 15 cm): hexanes:EtOAc = 12:1→6:1;

¹H NMR (300 MHz, CDCl₃): δ 8.26 (m, 2 H), 7.84 (d, J = 15.6 Hz, 1 H), 7.59-7.56 (m, 6 H), 7.47-7.34 (m, 8 H), 7.15-7.12 (m, 2 H), 5.63 (d, J = 15.6 Hz, 1 H), 5.21 (s, 2 H), 5.19 (dd, J = 9.6, 5.4 Hz, 1 H), 3.50 (dd, J = 16.8, 5.4 Hz, 1 H), 2.63 (dd, J = 16.8, 9.6 Hz, 1 H), 0.12 (s, 3 H), -0.13 (s, 3 H);

¹³C NMR (75.4 MHz, CDCl₃): δ 167.1, 151.6, 147.2, 145.6, 142.2, 141.3, 140.6, 140.1, 134.8, 129.2, 128.9, 128.8, 128.3, 128.0, 127.5, 127.3, 127.1, 125.9, 123.7, 122.3, 76.6, 66.2, 42.0, 0.1, -0.9;

IR (film): 2929 (m), 1713 (s), 1603 (m), 1512 (s), 1489 (m);

HRMS (ESI): calcd. for C₃₄H₃₁NO₅SiNa⁺: 584.1864, found: 584.1858.
According to the general experiment, the reaction of the silyl ether (95.7 mg, 0.25 mmol), biphenylmethyl acrylate (119.2 mg, 0.5 mmol) and RuHCl(CO)(PCy 3) 2 (9.1 mg, 0.0125 mmol) in Tol (0.5 mL, 0.5 M) afforded the product 17 100.0 mg (68%) as a pale yellow foam.

**TLC** (hexanes:EtOAc = 10:1): R<sub>f</sub> = 0.3;

**Flash chromatography** (2.5 cm φ × 15 cm): hexanes:EtOAc = 12:1→10:1;

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 7.92 (d, <i>J</i> = 15.6 Hz, 1 H), 7.65-7.58 (m, 8 H), 7.52-7.43 (m, 8 H), 7.40-7.37 (m, 5 H), 7.19-7.16 (m, 2 H), 5.65 (d, <i>J</i> = 15.6 Hz, 1 H), 5.23 (s, 2 H), 5.18 (dd, <i>J</i> = 9.3, 5.4 Hz, 1 H), 3.49 (dd, <i>J</i> = 16.5, 5.4 Hz, 1 H), 2.79 (dd, <i>J</i> = 16.5, 9.3 Hz, 1 H), 0.14 (s, 3 H), -0.11 (s, 3 H);

**<sup>13</sup>C NMR** (75.4 MHz, CDCl<sub>3</sub>): δ 167.2, 153.3, 145.0, 143.1, 142.5, 141.2, 140.9, 140.6, 140.34, 140.31, 134.8, 129.3, 128.8, 128.74, 128.71, 128.2, 127.8, 127.4, 127.3, 127.2, 127.1, 125.8, 121.8, 77.3, 66.1, 42.3, 0.2, -0.9;

**IR** (film): 2961 (s), 1713 (s), 1616 (s), 1488 (s);

**HRMS** (ESI): calcd. for C<sub>40</sub>H<sub>36</sub>O<sub>3</sub>SiNa<sup>+</sup>: 615.2326, found: 615.2315.
According to the general experiment, the reaction of the silyl ether (160.3 mg, 0.5 mmol), L-menthyl acrylate (210.3 mg, 1.0 mmol) and RuHCl(CO)(PCy\(_3\))\(_2\) (18.2 mg, 0.025 mmol) in DCE (1.0 mL, 0.5 M) afforded the product 18 203.0 mg (83%, 1:1 d.r.) as a white foam.

TLC (hexanes:Et\(_2\)O = 25:1): R\(_f\) = 0.26;

Flash chromatography (2.5 cm \(\phi \times 15\) cm): hexanes:Et\(_2\)O = 30:1 → 25:1;

\(^1H\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.83 (d, \(J = 15.6\) Hz, 0.5 H), 7.82 (d, \(J = 15.6\) Hz, 0.5 H), 7.50-7.46 (m, 2 H), 7.37-7.32 (m, 5 H), 7.26-7.22 (m, 1 H), 7.13-7.09 (m, 2 H), 5.522 (d, \(J = 15.6\) Hz, 0.5 H), 5.516 (d, \(J = 15.6\) Hz, 0.5 H), 4.77 (td, \(J = 10.8, 4.2\) Hz, 1 H), 3.27 (d, \(J = 16.5\) Hz, 0.5 H), 3.25 (d, \(J = 16.5\) Hz, 0.5 H), 3.13 (d, \(J = 16.5\) Hz, 0.5 H), 3.09 (d, \(J = 16.5\) Hz, 0.5 H), 2.01-1.95 (m, 1 H), 1.88-1.79 (m, 1 H), 1.70-1.65 (m, 2 H), 1.58 (s, 1.5 H), 1.57 (s, 1.5 H), 1.52-1.25 (m, 2 H), 1.13-0.92 (m, 3 H), 0.91-0.84 (m, 6 H), 0.76 (d, \(J = 6.9\) Hz, 1.5 H), 0.74 (d, \(J = 6.9\) Hz, 1.5 H), -0.05 (s, 1.5 H), -0.10 (s, 1.5 H), -0.11 (s, 1.5 H), -0.15 (s, 1.5 H);

\(^13C\) NMR (75.4 MHz, CDCl\(_3\)): \(\delta\) 167.0, 153.1, 148.8, 148.7, 145.2, 141.8, 140.5, 129.3, 128.1, 128.0, 127.6, 126.4, 124.4, 122.3, 81.4, 74.0, 47.0, 46.79, 46.76, 40.9, 34.1, 32.1, 32.0, 31.3, 26.1, 26.0, 23.3, 23.2, 22.0, 20.7, 16.25, 16.18, 0.6, 0.5, 0.4, 0.3;

IR (film): 2958 (s), 1708 (s), 1617 (m), 1493 (w);

HRMS (ESI): calcd. for C\(_{32}\)H\(_{42}\)O\(_3\)SiNa\(^+\): 525.2795, found: 525.2811.
According to the general experiment, the reaction of the silyl ether (59.7 mg, 0.2 mmol), L-menthyl acrylate (84.1 mg, 0.4 mmol) and RuHCl(CO)(PCy₃)₂ (7.3 mg, 0.01 mmol) in DCE (0.4 mL, 0.5 M) afforded the product 19 88.0 mg (92%, 1:1 d.r.) as a white foam.

\[
\text{TLC (hexanes:Et}_2\text{O = 30:1): } R_f = 0.17;
\]

**Flash chromatography** (2.5 cm φ × 15 cm): hexanes:Et₂O = 30:1 → 25:1;

**¹H NMR** (300 MHz, CDCl₃): δ 7.81 (d, J = 15.6, 1 H), 7.37-7.30 (m, 3 H), 7.13-7.10 (m, 2 H), 5.50 (d, J = 15.6, 1 H), 4.76 (td, J = 10.8, 4.5 Hz, 1 H), 2.80 (d, J = 16.8 Hz, 1 H), 2.73 (d, J = 16.8 Hz, 1 H), 2.01-1.95 (m, 1 H), 1.88-1.77 (m, 1 H), 1.69-1.63 (m, 4 H), 1.58-1.25 (m, 10 H), 1.15-0.92 (m, 3 H), 0.86 (d, J = 6.9 Hz, 3 H), 0.89 (d, J = 6.9 Hz, 3 H), 0.75 (d, J = 6.9 Hz, 3 H), -0.13 (s, 3 H), -0.17 (s, 3 H);

**¹³C NMR** (75.4 MHz, CDCl₃): δ 167.3, 154.4, 145.2, 142.2, 130.8, 129.4, 128.1, 127.5, 121.9, 79.9, 74.1, 47.1, 41.0, 39.6, 39.5, 34.2, 31.4, 26.1, 25.5, 23.4, 22.9, 22.0, 20.7, 16.3, 0.9, 0.7;

**IR** (film): 2932 (s), 1710 (s), 1617 (m);

**Anal.** calcd. for C₃₀H₄₄O₃Si: C 74.95%, H 9.22%; found: C 75.36%, H 8.90%.
According to the general experiment, the reaction of the silyl ether (131.2 mg, 0.5 mmol), L-menthyl acrylate (210.3 mg, 1.0 mmol) and RuHCl(CO)(PCy 3)2 (18.2 mg, 0.025 mmol) in DCE (1.0 mL, 0.5 M) afforded the product 20 131.6 mg (60%, 1:1 d.r.) as a colorless oil.

TLC (hexanes:Et2O = 15:1): Rf = 0.15;

Flash chromatography (2.5 cm φ× 15 cm): hexanes:Et2O = 15:1;

1H NMR (300 MHz, CDCl 3): δ 7.76 (d, J = 15.6 Hz, 1 H), 7.10-7.00 (m, 4 H), 5.43 (d, J = 15.6 Hz, 1 H), 4.74 (td, J = 10.8, 4.2 Hz, 1 H), 4.27-4.16 (m, 1 H), 3.07 (dd, J = 16.8, 5.4 Hz, 1 H), 2.42 (dd, J = 16.8, 8.4 Hz, 0.5 H), 2.41 (dd, J = 16.8, 8.4 Hz, 0.5 H), 1.98-1.94 (m, 1 H), 1.85-1.75 (m, 1 H), 1.67-1.61 (m, 2 H), 1.57-1.37 (m, 2 H), 1.32 (d, J = 6.3 Hz, 3 H), 1.11-0.92 (m, 3 H), 0.87 (d, J = 6.9 Hz, 3 H), 0.84 (d, J = 7.2 Hz, 3 H), 0.72 (d, J = 6.9 Hz, 3 H), -0.05 (s, 1.5 H), -0.08 (s, 1.5 H), -0.18 (s, 1.5 H), -0.20 (s, 1.5 H);

13C NMR (75.4 MHz, CDCl3): δ 166.9, 162.2 (d, J_{C-F} = 246.3 Hz), 154.2, 143.7, 142.0, 136.5 (d, J_{C-F} = 3.2 Hz), 131.0 (d, J_{C-F} = 7.7 Hz), 122.1, 115.1 (d, J_{C-F} = 21.3 Hz), 74.1, 72.4, 47.0, 41.2, 41.1, 40.9, 34.2, 31.3, 26.1, 23.9, 23.3, 22.0, 20.7, 16.2, 0.4, 0.2, -0.5, -0.7;

19F NMR (282.3 MHz, CDCl3): δ (-114.57)-(-114.64)(m);

IR (film): 2958 (s), 1708 (s), 1615 (m), 1507 (s);

HRMS (EI): calcd. for C_{26}H_{37}FO_{3}Si: 444.2491, found: 444.2504.
According to the general experiment, the reaction of the silyl ether (137.2 mg, 0.5 mmol), L-menthyl acrylate (210.3 mg, 1.0 mmol) and RuHCl(CO)(PCy3)2 (18.2 mg, 0.025 mmol) in DCE (1.0 mL, 0.5 M) afforded the product 21 160.7 mg (73%, 1:1 d.r.) as a white foam.

\[
\begin{align*}
&\text{TLC (hexanes:Et}_2\text{O = 15:1): } R_f = 0.15; \\
&\text{Flash chromatography (2.5 cm φ× 20 cm): hexanes:Et}_2\text{O = 15:1→8:1;}
\end{align*}
\]

\[\text{H NMR (300 MHz, CDCl}_3\text{: } \delta 7.76 (d, } J = 15.6 \text{ Hz, 1 H), 7.01 (d, } J = 8.7 \text{ Hz, 2 H), 6.85 (d, } J = 8.7 \text{ Hz, 2 H), 5.49 (d, } J = 15.6 \text{ Hz, 1 H), 4.73 (td, } J = 10.8, 4.2 \text{ Hz, 1 H), 4.25-4.15 (m, 1 H), 3.80 (s, 3 H), 3.05 (dd, } J = 16.5, 5.4 \text{ Hz, 1 H), 2.40 (dd, } J = 16.5, 8.4 \text{ Hz, 0.5 H), 2.39 (dd, } J = 16.5, 8.4 \text{ Hz, 0.5 H), 1.98-1.94 (m, 1 H), 1.85-1.76 (m, 1 H), 1.66-1.60 (m, 2 H), 1.53-1.37 (m, 2 H), 1.31 (d, } J = 6.0 \text{ Hz, 3 H), 1.10-0.91 (m, 3 H), 0.86 (d, } J = 6.6 \text{ Hz, 3 H), 0.84 (d, } J = 7.2 \text{ Hz, 3 H), 0.72 (d, } J = 6.9 \text{ Hz, 3 H), -0.05 (s, 1.5 H), -0.08 (s, 1.5 H), -0.18 (s, 1.5 H), -0.21 (s, 1.5 H);}
\]

\[\text{C NMR (75.4 MHz, CDCl}_3\text{: } \delta 167.1, 159.0, 153.5, 153.4, 144.5, 142.3, 132.9, 130.5, 121.9, 113.4, 73.9, 72.3, 55.1, 47.9, 41.1, 41.0, 40.9, 34.1, 31.3, 26.0, 23.9, 23.3, 21.9, 20.7, 16.2, 0.4, 0.2, -0.6, -0.7;}
\]

\[\text{IR (film): 2959 (s), 1709 (s), 1613 (s), 1509 (s);}
\]

\[\text{HRMS (ESI): calcd. for C}_{27}\text{H}_{40}\text{O}_4\text{SiNa}^+: 479.2588, \text{ found: 479.2577.}
\]
According to the general experiment, the reaction of the silyl ether (129.2 mg, 0.5 mmol), L-menthyl acrylate (210.3 mg, 1.0 mmol) and RuHCl(CO)(PCy 3)2 (18.2 mg, 0.025 mmol) in DCE (1.0 mL, 0.5 M) afforded the product 22 159.0 mg (74%, 1:1 d.r.) as a white foam.

**TLC** (hexanes:Et₂O = 15:1): Rf = 0.21;

**Flash chromatography** (2.5 cm φ × 20 cm): hexanes:Et₂O = 14:1→13:1;

**1H NMR** (300 MHz, CDCl₃): δ 7.77 (d, J = 15.6 Hz, 1 H), 7.11 (d, J = 7.8 Hz, 2 H), 6.97 (d, J = 7.8 Hz, 2 H), 5.50 (d, J = 15.6 Hz, 1 H), 4.73 (td, J = 10.8, 4.2 Hz, 1 H), 4.25-4.15 (m, 1 H), 3.05 (dd, J = 16.5, 5.4 Hz, 1 H), 2.41 (dd, J = 16.5, 8.1 Hz, 0.5 H), 2.39 (dd, J = 16.5, 8.1 Hz, 0.5 H), 2.33 (s, 3 H), 1.98-1.94 (m, 1 H), 1.82-1.78 (m, 1 H), 1.65-1.60 (m, 2 H), 1.52-1.35 (m, 2 H), 1.30 (d, J = 5.7 Hz, 3 H), 1.08-0.91 (m, 3 H), 0.83 (d, J = 7.2 Hz, 3 H), 0.83 (d, J = 6.9 Hz, 3 H), -0.06 (s, 1.5 H), -0.09 (s, 1.5 H), -0.20 (s, 1.5 H), -0.23 (s, 1.5 H);

**13C NMR** (75.4 MHz, CDCl₃): δ 167.0, 153.24, 153.21, 144.8, 142.1, 137.5, 137.1, 129.2, 128.7, 121.9, 73.9, 72.3, 47.0, 41.1, 41.0, 40.9, 34.1, 31.3, 26.0, 23.8, 23.2, 21.9, 21.1, 20.7, 16.2, 0.4, 0.2, -0.6, -0.8;

**IR** (film): 2957 (s), 1709 (s), 1616 (m), 1510 (w);

**HRMS** (ESI): calcd. for C₂₇H₄₀O₃SiNa⁺: 463.2639, found: 463.2645.
According to the general experiment, the reaction of the silyl ether (136.3 mg, 0.5 mmol), L-menthyl acrylate (210.3 mg, 1.0 mmol) and RuHCl(CO)(PCy₃)₂ (18.2 mg, 0.025 mmol) in DCE (1.0 mL, 0.5 M) afforded the product 23 166.4 mg (74%, 1:1 d.r.) as a pale yellow foam.

TLC (hexanes:Et₂O = 15:1): Rₓ = 0.19;

Flash chromatography (2.5 cm φ × 15 cm): hexanes:Et₂O = 15:1 →12:1;

¹H NMR (300 MHz, CDCl₃): δ 7.754 (d, J = 15.6 Hz, 0.5 H), 7.751 (d, J = 15.6 Hz, 0.5 H), 6.922 (s, 0.5 H), 6.920 (s, 0.5 H), 6.70 (s, 2 H), 5.55 (d, J = 15.6 Hz, 1 H), 4.75 (td, J = 10.8, 4.2 Hz, 1 H), 4.26-4.14 (m, 1 H), 3.05 (dd, J = 16.8, 5.4 Hz, 1 H), 2.40 (dd, J = 16.8, 8.1 Hz, 1 H), 2.28 (s, 6 H), 2.00-1.96 (m, 1 H), 1.85-1.80 (m, 1 H), 1.67-1.61 (m, 2 H), 1.53-1.35 (m, 2 H), 1.32 (d, J = 6.0 Hz, 1.5 H), 1.31 (d, J = 6.0 Hz, 1.5 H), 1.10-0.93 (m, 3 H), 0.87 (d, J = 6.9 Hz, 3 H), 0.85 (d, J = 6.9 Hz, 3 H), 0.73 (d, J = 6.9 Hz, 3 H), -0.06 (s, 1.5 H), -0.11 (s, 1.5 H), -0.20 (s, 1.5 H), -0.25 (s, 1.5 H);

¹³C NMR (75.4 MHz, CDCl₃): δ 167.1, 153.05, 152.98, 145.19, 145.15, 141.9, 140.4, 137.4, 129.0, 127.1, 122.0, 73.9, 72.3, 47.0, 41.1, 40.1, 40.9, 34.2, 31.3, 26.1, 23.9, 23.32, 23.30, 22.0, 21.2, 20.7, 16.25, 16.23, 0.4, 0.1, -0.6, -0.9;

IR (film): 2958 (s), 1710 (s), 1616 (m);

According to the general experiment, the reaction of the silyl ether (52.0 mg, 0.2 mmol), L-menthyl acrylate (84.1 mg, 0.4 mmol) and RuHCl(CO)(PCy 3)2 (7.3 mg, 0.01 mmol) in DCE (0.4 mL, 0.5 M) afforded the product 24 59.3 mg (67%, 1:1 d.r.) as a white foam.

TLC (hexanes:Et₂O = 25:1): Rf = 0.13;

Flash chromatography (2.5 cm φ × 10 cm): hexanes:Et₂O = 25:1→20:1;

¹H NMR (300 MHz, CDCl₃): δ 8.033 (d, J = 15.6 Hz, 0.5 H), 8.029 (d, J = 15.6 Hz, 0.5 H), 7.33-7.30 (m, 3 H), 7.08-7.05 (m, 2 H), 5.37 (d, J = 15.6 Hz, 1 H), 4.74 (td, J = 11.1, 4.5 Hz, 1 H), 4.14-4.03 (m, 1H), 3.27-3.20 (m, 1 H), 2.60-2.48 (m, 1 H), 1.99-1.25 (m, 8 H), 1.21 (d, J = 6.3 Hz, 1 H), 1.13-0.92 (m, 3 H), 0.88 (d, J = 7.2 Hz, 3 H), 0.853 (d, J = 7.2 Hz, 1.5 H), 0.845 (d, J = 7.2 Hz, 1.5 H), 0.74 (d, J = 6.9 Hz, 1.5 H), 0.73 (d, J = 6.9 Hz, 1.5 H), -0.09 (s, 1.5 H), -0.12 (s, 1.5 H), -0.40 (s, 1.5 H), -0.43 (s, 1.5 H);

¹³C NMR (75.4 MHz, CDCl₃): δ 167.2, 150.3, 144.7, 144.6, 140.53, 140.49, 140.4, 130.1, 128.1, 127.6, 122.4, 74.0, 70.3, 47.0, 40.9, 35.94, 35.86, 34.2, 31.3, 29.63, 29.59, 26.1, 26.0, 24.4, 23.32, 23.29, 22.0, 20.7, 16.24, 16.21, 1.0, 0.8, -0.2, -0.3;

IR (film): 2957 (s), 1708 (s), 1613 (m), 1489 (w);

According to the general experiment, the reaction of the silyl ether (56.9 mg, 0.2 mmol), L-menthyl acrylate (84.1 mg, 0.4 mmol) and RuHCl(CO)(PCy$_3$)$_2$ (14.5 mg, 0.02 mmol) in DCE (0.4 mL, 0.5 M) afforded the product 25 55.0 mg (60%, 1:1 d.r.) as a white foam.

TLC (hexanes:Et$_2$O = 13:1): R$_f$ = 0.3;

Flash chromatography (2.5 cm $\phi$ × 15 cm): hexanes:Et$_2$O = 13:1;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.80 (d, $J = 15.6$ Hz, 0.5 H), 7.79 (d, $J = 15.6$ Hz, 0.5 H), 7.34-7.31 (m, 3 H), 7.12-7.09 (m, 2 H), 5.49 (d, $J = 15.6$ Hz, 0.5 H), 5.48 (d, $J = 15.6$ Hz, 0.5 H), 4.74 (td, $J = 10.8$, 4.2 Hz, 1 H), 4.08-4.06 (m, 1 H), 3.03-2.95 (m, 1 H), 2.07-1.97 (m, 2 H), 1.88-1.78 (m, 1 H), 1.64-1.43 (m, 7 H), 1.39-1.33 (m, 4 H), 1.12-0.94 (m, 3 H), 0.89 (d, $J = 6.6$ Hz, 3 H), 0.84 (d, $J = 6.9$ Hz, 3 H), 0.76 (d, $J = 6.9$ Hz, 1.5 H), 0.73 (d, $J = 6.9$ Hz, 1.5 H), 0.19 (s, 1.5 H), 0.17 (s, 1.5 H), -0.37 (s, 1.5 H), -0.40 (s, 1.5 H);

$^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 167.2, 159.9, 159.8, 143.8, 141.9, 141.7, 141.0, 140.8, 129.5, 128.1, 127.6, 122.1, 122.0, 74.1, 73.7, 47.1, 47.0, 44.6, 40.9, 34.2, 31.3, 30.8, 26.0, 25.2, 23.3, 22.0, 20.8, 19.2, 16.5, 16.3, 1.4, 1.2, -1.5, -1.6;

IR (film): 2931 (s), 1709 (s), 1616 (m), 1491 (w);

HRMS (ESI): calcd. for C$_{29}$H$_{42}$O$_3$SiNa$: 489.2795$, found: $489.2797$. 
According to the general experiment, the reaction of the silyl ether (55.0 mg, 0.2 mmol), methyl acrylate (86.1 mg, 1.0 mmol) and RuHCl(CO)(PCy₃)₂ (14.5 mg, 0.02 mmol) in DCE (0.4 mL, 0.5 M) afforded the product 26 40.0 mg (7.4:1 by ¹H NMR of isolated material, 61%) as a white oil.

\[
\text{TLC (hexanes:Et}_2\text{O = 15:1): R}_f = 0.13;
\]

**Flash chromatography** (2.5 cm \(\phi \times 10\) cm): hexanes:Et\(_2\)O = 15:1→3:1;

¹H NMR (300 MHz, CDCl₃): \(\delta\) 7.62 (d, \(J = 15.6\) Hz, 1 H), 7.31-7.27 (m, 2 H), 7.22-7.15 (m, 3 H), 5.91 (d, \(J = 15.6\) Hz, 1 H), 4.11-4.02 (m, 1 H), 3.77 (s, 3 H), 2.98-2.90 (m, 1 H), 2.86-2.66 (m, 2 H), 2.44-2.35 (m, 1 H), 1.92 (t, \(J = 1.8\) Hz, 3 H), 1.88-1.78 (m, 2 H), 0.37 (s, 3 H), 0.32 (s, 3 H);

¹³C NMR (75.4 MHz, CDCl₃): \(\delta\) 167.9, 150.8, 142.6, 142.0, 137.1, 128.4, 128.3, 125.7, 117.9, 75.8, 51.6, 39.9, 39.0, 32.0, 20.2, 0.1, -0.4;

IR (film): 2951 (m), 1720 (s), 1619 (m), 1496 (w);

HRMS (ESI): calcd. for C\(_{19}\)H\(_{26}\)O\(_3\)SiNa⁺: 353.1543, found: 353.1542.
According to the general experiment, the reaction of the silyl ether (55.0 mg, 0.2 mmol), ethyl acrylate (100.1 mg, 1.0 mmol) and RuHCl(CO)(PCy₃)₂ (14.5 mg, 0.02 mmol) in DCE (0.4 mL, 0.5 M) afforded the product 27 52.0 mg (7.5:1 by ¹H NMR of isolated material, 75%) as a brown oil.

TLC (hexanes:Et₂O = 15:1): Rᵣ = 0.15;
Flash chromatography (2.5 cm φ × 10 cm): hexanes:Et₂O = 15:1 → 10:1;
¹H NMR (300 MHz, CDCl₃): δ 7.62 (d, J = 15.9 Hz, 1 H), 7.31-7.27 (m, 2 H), 7.23-7.15 (m, 3 H), 5.91 (d, J = 15.9 Hz, 1 H), 4.23 (q, J = 7.2 Hz, 2 H), 4.11-4.02 (m, 1 H), 2.98-2.90 (m, 1 H), 2.86-2.62 (m, 2 H), 2.44-2.35 (m, 1 H), 1.92 (t, J = 1.8 Hz, 3 H), 1.88-1.78 (m, 2 H), 1.31 (t, J = 7.2 Hz, 3 H), 0.36 (s, 3 H), 0.32 (s, 3 H);
¹³C NMR (75.4 MHz, CDCl₃): δ 167.5, 150.5, 142.4, 142.0, 137.1, 128.4, 128.3, 125.7, 118.4, 75.7, 60.4, 39.8, 38.9, 31.9, 20.2, 14.3, 0.1, -0.4;
IR (film): 2935 (m), 1713 (s), 1619 (m), 1496 (w);
HRMS (EI): calcd. for C₂₀H₂₈O₃Si⁺: 344.1802, found: 344.1790.
According to the general experiment, the reaction of the silyl ether (55.0 mg, 0.2 mmol), tert-butyl acrylate (128.2 mg, 1.0 mmol) and RuHCl(CO)(PCy₃)₂ (14.5 mg, 0.02 mmol) in DCE (0.4 mL, 0.5 M) afforded the product 28 48.0 mg (6.3:1 by ¹H NMR of isolated material, 64%) as a colorless oil.

\[
\text{TLC (hexanes:Et₂O = 20:1): R}_f = 0.15; \\
\text{Flash chromatography (2.5 cm φ × 15 cm): hexanes:Et₂O = 20:1→13:1;}
\]

¹H NMR (300 MHz, CDCl₃): \(\delta\) 7.55 (d, \(J = 15.9\) Hz, 1 H), 7.31-7.27 (m, 2 H), 7.22-7.17 (m, 3 H), 5.85 (d, \(J = 15.9\) Hz, 1 H), 4.10-4.01 (m, 1 H), 2.97-2.89 (m, 1 H), 2.85-2.65 (m, 2 H), 2.43-2.34 (m, 1 H), 1.91 (t, \(J = 1.8\) Hz, 3 H), 1.86-1.72 (m, 2 H), 1.51 (s, 9 H), 0.36 (s, 3 H), 0.31 (s, 3 H);

¹³C NMR (75.4 MHz, CDCl₃): \(\delta\) 166.9, 149.7, 142.0, 141.5, 137.3, 128.4, 128.3, 125.7, 120.2, 80.4, 75.8, 39.9, 38.8, 31.9, 28.1, 20.2, 0.1, -0.4;

IR (film): 2977 (m), 1708 (s), 1619 (m), 1496 (w);

According to the general experiment, the reaction of the silyl ether (57.5 mg, 0.2 mmol), ethyl acrylate (100.1 mg, 1.0 mmol) and RuHCl(CO)(PCy₃)₂ (14.5 mg, 0.02 mmol) in DCE (0.4 mL, 0.5 M) afforded the product 29 44.5 mg (5:1 by ¹H NMR of isolated material, 63%) as a yellow oil.

TLC (hexanes:Et₂O = 5:1): Rₜ = 0.2;

Flash chromatography (2.5 cm φ × 10 cm): hexanes:Et₂O = 10:1→3:1;

¹H NMR (300 MHz, CDCl₃): δ 7.63 (d, J = 15.9 Hz, 1 H), 7.25 (d, J = 8.7 Hz, 2 H), 6.73 (d, J = 8.7 Hz, 2 H), 5.91 (d, J = 15.9 Hz, 1 H), 4.98 ( dd, J = 9.3, 5.4 Hz, 1 H), 4.21 (q, J = 7.2 Hz, 2 H), 3.20 (ddq, J = 16.8, 5.4, 1.2 Hz, 1 H), 2.93 (s, 6 H), 2.61 (ddq, J = 16.8, 9.0, 2.1 Hz, 1 H), 1.95 (dd, J = 2.1, 1.2 Hz, 3 H), 1.29 (t, J = 7.2 Hz, 3 H), 0.393 (s, 3 H), 0.385 (s, 3 H);

¹³C NMR (75.4 MHz, CDCl₃): δ 167.5, 150.9, 147.5, 142.3, 136.9, 126.5, 118.5, 116.8, 112.7, 77.7, 60.4, 41.8, 40.8, 20.2, 14.3, -0.3, -0.4;

IR (film): 2981 (m), 1712 (s), 1617 (s), 1523 (s);


To a solution of the coupling product $2A$ (90.4 mg, 0.21 mmol) in dry THF (0.42 mL) was added TBAF (1.0 M in THF, 0.42 mL, 0.42 mmol) at rt under Ar$_{\text{(g)}}$. After being stirred overnight, the reaction mixture was concentrated in vacuo and purified by flash chromatography on silica gel to give the alcohol $30$ 59.7 mg (C4,C5) ≥20:1 isomeric purity by $^1$H NMR of isolated material, 77%, 1:1 d.r.) as a pale yellow oil.

**TLC** (hexanes:EtOAc = 3:1): $R_f = 0.36$;

**Flash chromatography** (2.5 cm $\phi \times$ 10 cm): hexanes:EtOAc = 5:1 $\rightarrow$ 4:1;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.86 (d, $J = 15.9$ Hz, 1 H), 7.39-7.30 (m, 3 H), 7.25-7.22 (m, 2 H), 5.93 (t, $J = 7.8$ Hz, 1 H), 5.75 (d, $J = 15.9$ Hz, 1 H), 4.76 (td, $J = 10.8$, 4.2 Hz, 1 H), 4.04-3.94 (m, 1 H), 2.69-2.53 (m, 2 H), 2.02-1.98 (m, 1 H), 1.89-1.80 (m, 1 H), 1.69-1.63 (m, 2 H), 1.58-1.31 (m, 2 H), 1.28 (d, $J = 6.3$ Hz, 3 H), 1.15-0.95 (m, 3 H), 0.89 (d, $J = 6.6$ Hz, 3 H), 0.87 (d, $J = 7.2$ Hz, 3 H), 0.75 (d, $J = 6.9$ Hz, 3 H);

$^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 167.0, 140.4, 140.2, 140.1, 136.1, 128.7, 128.3, 127.4, 122.2, 74.1, 67.7, 47.0, 40.9, 38.0, 34.2, 31.3, 26.1, 23.4, 23.2, 22.0, 20.7, 16.3;

IR (film): 3422 (br), 2929 (s), 2252 (w), 1708 (s), 1624 (m);

HRMS (ESI): calcd. for C$_{24}$H$_{34}$O$_3$Na$^+$: 393.2400, found: 393.2404.
To a solution of the coupling product 2A (280.9 mg, 0.658 mmol) in dry DCM (10 mL) was added ICl (1.0 M in DCM, 1.32 mL, 1.32 mmol) at -78 °C under Ar(g). After being stirred at -78 °C for 1 h in the dark, the reaction was quenched with sat. Na₂S₂O₃(aq) (5 mL) and extracted with DCM (10 mL). The organic layer was dried over MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to give the vinyl iodide 31 240.9 mg (74%, 1:1 d.r.) as a white foam.

**TLC** (hexanes:EtOAc = 10:1): Rₜ = 0.13;

**Flash chromatography** (2.5 cm φ × 15 cm): hexanes:EtOAc = 10:1→6:1;

**¹H NMR** (300 MHz, CDCl₃): δ 7.923 (d, J = 15.3 Hz, 0.5 H), 7.916 (d, J = 15.3 Hz, 0.5 H), 7.45-7.37 (m, 3 H), 7.07-7.04 (m, 2 H), 5.38 (d, J = 15.3 Hz, 1 H), 4.72 (td, J = 10.8, 4.5 Hz, 1 H), 4.33-4.24 (m, 1 H), 3.8-3.7 (m, 1 H), 3.10-3.01 (m, 1 H), 2.01-1.94 (m, 1 H), 1.87-1.74 (m, 1 H), 1.71-1.62 (m, 3 H), 1.54-1.40 (m, 1 H), 1.36 (d, J = 6.6 Hz, 3 H), 1.13-0.91 (m, 3 H), 0.88 (d, J = 6.9 Hz, 3 H), 0.86 (d, J = 7.2 Hz, 3 H), 0.73 (d, J = 6.9 Hz, 3 H);

**¹³C NMR** (75.4 MHz, CDCl₃): δ 166.9, 147.1, 143.7, 138.6, 138.5, 129.0, 128.6, 127.8, 123.8, 123.7, 116.5, 74.4, 67.8, 67.7, 50.5, 47.0, 40.9, 34.2, 31.3, 26.1, 23.3, 22.6, 22.5, 22.0, 20.7, 16.3;

**IR** (film): 3372 (br), 2927 (s), 1709 (s), 1613 (s);

To a solution of the vinyl iodide 31 (49.6 mg, 0.1 mmol), and Pd(PPh₃)₄ (5.8 mg, 0.005 mmol) in dry THF (2 mL) was added Me₂Zn (2 M in Tol, 0.15 mL, 0.3 mmol) at 0 °C under Ar(g). The reaction mixture was allowed to warm to rt and subsequently refluxed for 14.5 h. The reaction mixture was concentrated in vacuo and purified by flash chromatography on silica gel to give the product 32 28.6 mg (C₄,C₅) ≥20:1 isomeric purity by ¹H NMR of isolated material, 74%, 1:1 d.r.) as an orange oil.

TLC (hexanes:EtOAc = 3:1): R₉ = 0.36;
Flash chromatography (2.5 cm φ × 10 cm): hexanes:EtOAc = 6:1→4:1;
¹H NMR (300 MHz, CDCl₃): δ 7.99 (d, J = 15.6 Hz, 0.5 H), 7.98 (d, J = 15.6 Hz, 0.5 H), 7.40-7.27 (m, 3 H), 7.06-7.03 (m, 2 H), 5.23 (d, J = 15.6 Hz, 1 H), 4.71 (td, J = 10.8, 4.5 Hz, 1 H), 4.15-4.04 (m, 1 H), 2.81-2.70 (m, 1 H), 2.60-2.49 (m, 1 H), 2.01-1.94 (m, 1 H), 1.88-1.80 (m, 1 H), 1.67 (s, 3 H), 1.65-1.61 (m, 2 H), 1.56-1.36 (m, 2 H), 1.31 (d, J = 6.6 Hz, 3 H), 1.12-0.91 (m, 3 H), 0.87 (d, J = 6.3 Hz, 3 H), 0.85 (d, J = 7.2 Hz, 3 H), 0.73 (d, J = 6.9 Hz, 3 H);
¹³C NMR (75.4 MHz, CDCl₃): δ 167.3, 143.2, 143.1, 142.53, 142.47, 139.2, 137.03, 136.99, 129.5, 128.5, 126.9, 120.40, 120.36, 73.9, 67.3, 67.2, 47.0, 43.7, 41.0, 34.2, 31.3, 26.1, 23.42, 23.38, 22.6, 22.0, 20.7, 16.3;
IR (film): 3437 (br), 2929 (s), 2243 (w), 1703 (s), 1613 (s);
A solution of the vinyl iodide 31 (49.6 mg, 0.1 mmol), 4-methoxyphenylboronic acid (22.8 mg, 0.15 mmol), K$_2$PO$_4$ (31.8 mg, 0.15 mmol), and Pd(PPh$_3$)$_4$ (5.8 mg, 0.005 mmol) in dry Tol (2 mL) was degassed by freeze/pump/Ar(g) for 3 times and refluxed for 5 h under Ar(g). The reaction mixture was concentrated in vacuo and purified by flash chromatography on silica gel to give the product 33 41.6 mg (C4,C5 $\geq$20:1 isomeric purity by $^1$H NMR of isolated material, 90%, 1:1 d.r.) as an orange oil.

TLC (hexanes:EtOAc = 5:1): $R_f$ = 0.13;

Flash chromatography (2.5 cm $\phi$ × 10 cm): hexanes:EtOAc = 5:1→3:1;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.133 (d, $J$ = 15.3 Hz, 0.5 H), 8.129 (d, $J$ = 15.3 Hz, 0.5 H), 7.18-7.07 (m, 3 H), 6.96-6.88 (m, 4 H), 6.63-6.58 (m, 2 H), 5.52 (d, $J$ = 15.3 Hz, 1 H), 4.74 (td, $J$ = 10.8, 42 Hz, 1 H), 3.83-3.81 (m, 1 H), 3.69 (s, 3 H), 3.13-3.02 (m, 1 H), 2.97-2.86 (m, 1 H), 2.03-1.98 (m, 1 H), 1.68-1.63 (m, 2 H), 1.53-1.30 (m, 2 H), 1.24 (d, $J$ = 6.3 Hz, 3 H), 1.13-0.93 (m, 3 H), 0.89 (d, $J$ = 6.3 Hz, 3 H), 0.864 (d, $J$ = 7.2 Hz, 1.5 H), 0.856 (d, $J$ = 7.2 Hz, 1.5 H), 0.754 (d, $J$ = 6.9 Hz, 1.5 H), 0.746 (d, $J$ = 6.9 Hz, 1.5 H);

$^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 167.3, 167.2, 158.2, 145.9, 143.12, 143.07, 139.9, 137.54, 137.50, 134.0, 130.8, 130.3, 127.9, 126.5, 122.0, 121.9, 113.1, 74.0, 67.04, 66.96, 55.0, 47.0, 43.9, 40.9, 34.2, 31.3, 26.12, 26.05, 23.4, 23.3, 23.2, 23.1, 22.0, 20.7, 16.33, 16.27;

IR (film): 3436 (br), 2929 (s), 1704 (s), 1604 (s);

HRMS (ESI): calcd. for C$_{31}$H$_{40}$O$_4$Na$^+$: 499.2819, found: 499.2835.
A solution of the vinyl iodide 31 (49.6 mg, 0.1 mmol), 1-octyne (22 μL, 16.5 mg, 0.15 mmol), CuI (1.9 mg, 0.01 mmol), PdCl₂(PPh₃)₂ (3.5 mg, 0.005 mmol) in Et₂NH (2 mL) was degassed by freeze/pump/Ar (g) for 3 times and refluxed under Ar (g) overnight. The reaction mixture was concentrated in vacuo and purified by flash chromatography on silica gel to give the product 34 30.6 mg (64%, 1:1 d.r.) as a pale yellow oil.

TLC (hexanes:EtOAc = 10:1): Rᵣ = 0.3;

Flash chromatography (2.5 cm φ × 10 cm): hexanes:EtOAc = 12:1 → 8:1;

¹H NMR (300 MHz, CDCl₃): δ 7.92 (d, J = 15.3 Hz, 1 H), 7.39-7.27 (m, 3 H), 7.19-7.16 (m, 2 H), 5.46 (d, J = 15.3 Hz, 1 H), 4.73 (td, J = 10.8, 4.5 Hz, 1 H), 4.27-4.15 (m, 1 H), 2.80-2.71 (m, 1 H), 2.68-2.59 (m, 1 H), 2.12 (t, J = 6.9 Hz, 2 H), 2.00-1.96 (m, 1 H), 1.87-1.77 (m, 1 H), 1.69-1.62 (m, 2 H), 1.55-1.34 (m, 2 H), 1.31 (d, J = 6.0 Hz, 3 H), 1.27-0.92 (m, 11 H), 0.89-0.84 (m, 9 H), 0.74 (d, J = 7.2 Hz, 3 H);

¹³C NMR (75.4 MHz, CDCl₃): δ 166.8, 144.4, 140.8, 140.7, 139.0, 129.6, 128.0, 127.6, 127.3, 122.6, 101.5, 82.2, 74.1, 67.5, 67.4, 47.0, 42.03, 41.99, 40.9, 34.2, 31.4, 31.3, 28.2, 26.1, 23.4, 22.9, 22.4, 22.0, 20.7, 19.7, 16.3, 14.1;

IR (film): 3435 (br), 2930 (s), 2203 (w), 1707 (s), 1608 (s);

To an oven-dried Schlenk tube were charged vinyl iodide 31 (49.1 mg, 0.1 mmol) and Pd(PPh$_3$)$_4$ (6.0 mg, 0.005 mmol). The tube was evacuated and back-filled with Ar(g) three times and charged successfully with toluene (1 mL) and triethylamine (21 μL, 0.15 mmol). The solution was bubbled with CO(g) for 1 min. The pale yellow solution instantaneously turned red orange. The tube was then immersed in a preheated 55 °C oil bath under an atmosphere of CO(g). After TLC indicated completion (3 hrs), the reaction mixture was cooled to rt, concentrated in vacuo and purified by flash chromatography on silica gel to give the product 35 29.0 mg (74%, 1:1 d.r.) as a pale yellow oil.

TLC (hexanes:EtOAc = 4:1): R$_f$ = 0.21;

Flash chromatography (1.5 cm φ× 19 cm): hexanes:EtOAc = 6:1;

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.61 (d, $J$ = 15.3 Hz, 1 H), 7.43-7.40 (m, 3 H), 7.13-7.10 (m, 2 H), 5.69 (d, $J$ = 15.3 Hz, 1 H), 4.81-4.66 (m, 2 H), 3.45 (d, $J$ = 17.7, 7.5 Hz, 0.5 H), 3.44 (d, $J$ = 17.7, 7.8 Hz, 0.5 H), 2.85 (d, $J$ = 17.7, 6.0 Hz, 0.5 H), 2.84 (d, $J$ = 17.7, 6.3 Hz, 0.5 H), 2.01-1.95 (m, 1 H), 1.85-1.75 (m, 1 H), 1.70-1.64 (m, 2 H), 1.48 (d, $J$ = 6.0 Hz, 3 H), 1.40-1.21 (m, 2 H), 1.14-0.94 (m, 3 H), 0.90 (d, $J$ = 6.6 Hz, 3 H), 0.87 (d, $J$ = 6.9 Hz, 3 H), 0.743 (d, $J$ = 6.9 Hz, 1.5 H), 0.740 (d, $J$ = 6.9 Hz, 1.5 H);

$^{13}$C NMR (75.4 MHz, CDCl$_3$): δ 168.0, 165.8, 145.63, 145.60, 142.6, 134.7, 129.11, 129.08, 129.0, 128.6, 128.2, 128.1, 74.8, 72.7, 46.9, 40.8, 35.60, 35.56, 34.1, 31.3, 26.07, 26.05, 23.3, 23.2, 22.22, 22.19, 22.0, 20.7, 16.19, 16.17;

IR (film): 1757 (s), 1708 (s), 1616 (m), 1492 (w);

Anal. calcd. for C$_{25}$H$_{32}$O$_4$: C 75.73%, H 8.13%; found: C 75.43%, H 8.53%.

RuHCl(CO)(PCy3)2 (363.2 mg, 0.5 mmol) was added to a 100 mL Schlenk tube in the glovebox, removed from the glovebox and placed under Ar(g). A solution of the silyl ether 1 (2.444 g, 10 mmol) and L-menthyl acrylate (4.206 g, 20 mmol) in freshly distilled DCE (20 mL, 0.5 M) was degassed by bubbling for 10 min and added to the Schlenk tube via a cannulae. A cold finger condenser was attached to the Schlenk tube by removing the septum against a positive stream of Ar(g). The whole apparatus was then immersed in a preheated 85 °C oil bath. After being stirred for 18 h at 85 °C, the reaction mixture was cooled to rt, concentrated *in vacuo* and purified by flash chromatography on silica gel to give the product 2A 2.93 g (70%, 1:1 d.r.) as a pale yellow oil.
Crystal structure determination and refinement.

Colourless needle-shaped crystals of compound 2G were readily obtained by evaporation of a hexane/acetonitrile solution. Single crystal X-ray diffraction data for 2G were collected at 90(2) K on a Bruker APEX DUO diffractometer coupled to a Bruker-AXS Apex II CCD detector using graphite-monochromated Cu-Kα radiation ($\lambda = 1.54178$ Å), and processed through the SAINT1 reduction and SADABS2 absorption software. The structure was solved by direct methods using SHELXS3 and refined by the full-matrix least-squares refinements based on $F^2$ with all observed reflections (Friedel opposites not merged) using SHELXL-97.4 All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model. Similarity restraints were applied to all atoms except the terminal methyl groups (C4, C5 and C6). The compound crystallizes in the orthorhombic Pca21 space group with one target molecule per asymmetric unit (Figure S1) and Z = 4. The Flack parameter was refined by means of the TWIN and BASF instructions to yield 0.10(3). The molecule possesses one stereocenter (C3). In the final model, both the S (C3, C4) and R (C3A, C4A) enantiomers were visible, the carbon C3 as well as the attached methyl group (C4) being modelized over two positions (Figure S2). The ratio between the S and R enantiomers in the analyzed crystal was about 70:30% (refined occupancy for C3, C4 vs. C3A, C4A was 0.68696).

Crystal data for 2G (Cu-Kα): C29H30O3Si, $M_r = 454.62$, Orthorhombic, space group Pca21, $a = 25.2196(7)$, $b = 11.8584(4)$, $c = 8.5478(3)$Å, $V = 2556.3(1)$Å$^3$, $Z = 4$, $D_c = 1.181$ g cm$^{-3}$, $T = 90$ K, $F(000) = 968$, $\mu$(Mo-Kα) = 1.018 mm$^{-1}$, Refl. collected = 19289, Refl. indep. (R int) = 4450 (0.0500), Refl. obs. [$I > 2\sigma(I)$] = 3993, $R_1 [I > 2\sigma(I)] = 0.0382$, $R_1$ (all) = 0.0448, $wR_2 [I > 2\sigma(I)] = 0.0923$, $wR_2$ (all) = 0.0962, $GooF = 1.024$, $\Delta\rho_{\text{max}, \text{min}} = 0.205$ and -0.152 eÅ$^{-3}$. CCDC reference number 872200.
**Figure S1.** ORTEP plot (30% probability level) of compound 2G (S enantiomer), showing the atom labeling scheme.

**Figure S2.** View of the final model showing both the S (solid bonds) and R (dashed bonds) configurations at the C3 carbon (30% probability level ellipsoids).

**X-Ray References:**

### Summary of the crystal data

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<th>Compound</th>
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\[ R₁ = \frac{\sum|F₀| - |F₁|}{\sum|F₀|}, \quad wR² = \left( \frac{\sum[w(F₀²-FC₂²)]^2}{\sum[w(F₀²)]^2} \right)^{1/2} \text{ and } w = \frac{1}{\sum σ²(F₀²) + (mP)^2 + nP} \]

with \( P = (F₀² + 2FC₂²)/3 \), \( m = 0.0464 \) and \( n = 0.0000 \).
References:


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Diagram with chemical structures and NMR spectra.
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IN0: 0.00016600 sec
SPWCHF: 128

------- CHANNEL F1 -------

NUC1: 1H
SI: 12.20 usec
SL1: 0.00 cm
SP01: 500.120005 MHz

F1 - Acquisition parameters
NOD: 1
TD: 256
SP01: 500.122 MHz
FIDRES: 23.418764 Hz
SW: 11.387 ppm
PARAM: States-TPP1

F2 - Processing parameters
SI: 1024
AT: 500.130056 MHz
WM: Q5HRE
SBH: 2
LB: 0.00 Hz
GB: 0
FC: 0

W1 - Processing parameters
SI: 1024
MG: States-TPP1
GF: 500.1300569 MHz
NGW: Q5HRE
SSR: 2
LB: 6.00 Hz
GR: 0
S 150
Nosey

SL-2-130

\[
\begin{align*}
&\text{Ph} \\
&\text{CO}_2\text{Men}
\end{align*}
\]