Endo Selective Pd-Catalyzed Silyl Methyl Heck Reaction

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General Information

NMR spectra were recorded on BrukerAvance DRX-500 (500 MHz) or DPX-400 (400 MHz) instrument. LRMS and HRMS analyses were performed on Micromass 70 VSE mass spectrometer. GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle Silica-P flash silica gel (40-63 µm) and/or Florisil® (60-100 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. All manipulations with transition metal catalysts were conducted in oven-dried glassware under inert atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous solvents purchased from Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system and/or stored over calcium hydride. All other starting materials were purchased from Strem Chemicals, Aldrich, Gelest Inc., Alfa Aesar, or TCI.
Part I: Synthesis of Starting Materials

Synthesis of vinyl phenols:

\[
\begin{align*}
\text{R} & \quad \text{OH} \quad \text{H} \\
\text{R} & \quad \text{OH} \quad \text{H}
\end{align*}
\]

To a suspension of MePPh\(_3\)Br (2.2 equiv) (EtPPh\(_3\)Br for \(1\)n and PrPPh\(_3\)I for \(1\)o) in THF (50 mL) was added tBuOK in one portion (2.2 equiv) and the resulting mixture was stirred at room temperature 2 h. The reaction mixture was cooled to -78 °C and salicylaldehyde derivatives (1.0 equiv) was added over 10 min. The mixture was stirred overnight at room temperature. A saturated ammonium chloride solution was added and the aqueous phase was extracted with ether (3 x 50 mL). The organic phase was dried over Na\(_2\)SO\(_4\), filtered and concentrated. The compound was purified by flash (20:1 Hex:EtOAc) to give a clear/yellow oil. Identity and purity were assessed by \(^1\)H NMR and were compared to the literature reports.

Synthesis of complex phenols and alcohols:

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{B(Pin)} & \quad \text{Ph} \quad \text{Ph}
\end{align*}
\]

In a V-vial charged with 2-bromophenol (34 \(\mu\)L, 1 equiv, 0.3 mmol), vinyl-B(Pin)\(^2\) (0.184 g, 2 equiv, 0.6 mmol), Pd(OAc)\(_2\) (6.8 mg, 0.1 equiv, 0.03mmol), dpf (33 mg, 0.2 equiv, 0.06mmol), K\(_3\)PO\(_4\) (0.191 g, 3 equiv, 0.9 mmol) under N\(_2\) atmosphere (glove box). Dry dioxane was added via syringe and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 110 °C for 12 h. The resulting mixture was cooled down to room temperature and filtered through a short layer of silica gel over celite plug with the aid of DCM. The filtrate was concentrated under reduced pressure and purified by column chromatography 2:1 Hex:EtOAc.

Isolated yield = 88%, 72 mg. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.30-7.39 (m, 7H), 7.21 (s, 1H), 7.17-7.19 (m, 3H) 7.08-7.12 (m, 3H) 6.94-6.98 (t, 2H), 5.06 (s, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 115.9, 121.1, 125.9, 127.1, 127.8, 128.2, 128.4,128.6, 128.9, 129.7, 130.5, 131.0, 136.2, 136.4, 141.7, 153.8. HRMS (EI) calcd. for C\(_{20}\)H\(_{16}\)O [M]^+: 272.1201, found: 272.1201.
The standard procedure for Wittig olefination was used (see above), full conversion after 24 h at 55 °C. SM was obtained by a publish procedure. Isolated yield = 28%, 180 mg (4 mmol scale). 

$^1$H NMR (500 MHz, CDCl$_3$) δ ppm 7.19 (dt, J = 7.3, 1.5 Hz, 1 H), 7.14 (dd, J = 7.6, 1.8 Hz, 1 H), 6.93 (dd, J = 8.2, 0.6 Hz, 1 H), 7.14 (dt, J = 7.3, 1.2 Hz, 1 H), 5.63 (s, 1 H), 5.30 (s, 1 H), 5.05 (d, J = 1.2 Hz, 1 H), 1.68 - 1.59 (m, 1 H), 0.82 - 0.77 (m, 2 H), 0.56 - 0.52 (m, 2 H). 

$^{13}$C NMR (126 MHz, CDCl$_3$) δ ppm 152.4, 147.3, 128.9, 128.8, 119.9, 115.3, 112.8, 17.1, 6.81.

HRMS (ESI) calcd. for C$_{17}$H$_{29}$OSi [M]+: 277.1988, found: 277.1984.

To a 100 mL flask equipped with a magnetic stir bar, argon inlet, and septum, NaH (1.06 g, 44 mmol) and trimethylsulfoxonium iodide (9.68 g, 44 mmol) was added. Followed by slow addition of DMSO (30 mL) and stirred at r.t. for 30 min. After H$_2$ evolution, $^{2'}$Hydroxychalcone in 10 mL DMSO was added slowly. The reaction was stirred overnight at r.t. Then, the reaction was quenched by addition of 50 mL H$_2$O and extracted 3x with 30 mL Et$_2$O. The organic phase was dried over Na$_2$SO$_4$, filtered and concentrated. The compound was purified by column chromatography (20:1 Hex:EtOAc) to give cp3 as a clear/yellow oil (44%, 2.72 g).

$^1$H NMR (500 MHz, CDCl$_3$) δ ppm 7.88 - 7.90 (d, 1 H), 7.46 - 7.49 (t, 1 H), 7.31 - 7.34 (t, 2 H), 7.25 - 7.27 (t, 1 H), 7.18 - 7.20 (d, 2 H), 6.99 - 7.01 (d, 1 H), 6.89 - 6.91 (t, 1 H), 2.89 - 2.93 (m, 1 H), 2.75 - 2.78 (m, 1 H), 1.96 - 2.05 (m, 1 H), 1.61 - 1.65 (m, 1 H). 

$^{13}$C NMR (126 MHz, CDCl$_3$) δ ppm 203.3, 162.3, 139.9, 136.2, 130.0, 128.6, 126.8, 126.3, 119.9, 118.9, 118.4, 30.5, 28.5, 19.4.

HRMS (ESI) calcd. for C$_{16}$H$_{14}$O$_2$ [M]+H: 239.1072, found: 239.1075

To a suspension of MePPh$_3$Br (2.2 equiv, 7.2 g, 20.1 mmol) in THF (30 mL) was added $^t$BuOK in one portion (2.2 equiv, 2.26 g, 20.1) and the resulting mixture was stirred at room temperature 2 h. The reaction mixture was cooled to 0 °C and cp3 (1.0 equiv, 2.72 g, 8.76 mmol) in 10 mL THF was added over 10 min. The mixture was stirred overnight at 55 °C. A saturated ammonium chloride solution was added and the aqueous phase was extracted with ether (3 x 50 mL). The organic phase was dried over Na$_2$SO$_4$, filtered and concentrated. The compound was purified by flash (20:1 Hex:EtOAc) to give cp3' clear/yellow oil (41%, 857 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ ppm 7.27 - 7.30 (t, 2 H), 7.10 - 7.22 (m, 6 H), 6.94 - 6.96 (d, 1 H), 6.88 - 6.91 (t, 1 H), 5.54 (s, 1 H), 5.40 (s, 1 H), 5.14 (s, 1 H), 2.00 - 2.03 (m, 1 H), 1.93 - 1.97 (m, 1 H), 1.96 - 2.05 (m, 1 H), 1.24 - 1.29 (m, 2 H). 

$^{13}$C NMR (126 MHz, CDCl$_3$) δ ppm 152.41, 146.1, 141.8, 129.0, 128.9, 128.5, 125.9, 125.8, 120.1, 115.5, 113.5, 29.3, 25.6, 15.9.

HRMS (ESI) calcd. for C$_{17}$H$_{16}$OSi [M]+H: 237.1279, found: 237.1278.
To a 100 mL flask equipped with a stirring bar, argon inlet, and septum, reduced estrone substrate\(^4\)(1.35 g, 1 equiv, 5.27 mmol), In(OTf)\(_3\) (296 mg, 0.1 equiv, 0.527 mmol), NIS (1.3 g, 1.1 equiv, 5.8 mmol) and MeCN (10 mL) was added. The reaction was then stirred at room temperature for 8 h. Upon completion, the reaction was filtered through celite and concentrated. The residue was purified by column chromatography 9:1 Hex: EtOAc. The iodination intermediate was obtained as white crystals (59%, 118 g). In a V-vial charged with iodinated steroid (0.77 g, 1 equiv, 2.01 mmol), vinyltributlytin (1.17 mL, 2 equiv, 4.02 mmol), Pd(P\(^t\)Bu\(_2\))\(_2\) (52 mg, 0.05 equiv, 0.1 mmol), under N\(_2\) atmosphere (glove box). Dry THF (10 mL) was added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 110 °C for 12 h. The resulting mixture was cooled down to room temperature and filtered through a short layer of silica gel over celite plug with the aid of DCM. The filtrate was concentrated under reduced pressure and purified by column chromatography (9:1 Hex:EtOAc) to yield \(\text{cp4}\) as white crystals (86%, 490 mg).

Overall yield = 48% over two steps.

\(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.33 (s, 1H), 6.89-6.95 (dd, 1H), 6.53 (s, 1H), 5.69-5.73 (dd, 1H), 5.30-5.32 (dd, 1H), 4.99 (s, 1H), 2.80-2.84 (m, 2H), 2.31-2.35 (m, 1H), 2.18-2.21 (m, 1H), 1.89-1.92 (m, 2H), 1.69-1.80 (4H), 1.52-1.54 (m, 2H), 1.13-1.40, (m, 10H), 0.94-0.97, (t, 1H), 0.77 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 13.6, 17.6, 20.6, 25.3, 26.8, 28.1, 29.5, 38.8, 39.2, 41.1, 43.9, 53.6, 114.7, 115.8, 124.3, 131.9, 133.4, 138.1, 150.6.

A 25 mL Schlenk flask under argon was charged with 2-bromostyrene (0.62 mL, 1 equiv, 5 mmol) and THF (10 mL). The solution was cool to -78 °C. \(^n\)BuLi (2.12 mL, 1.1 equiv, 2.6 M, 5.5 mmol) was added dropwise. After stirring at -78 °C for 1 h, 3-methyl-buten-2-one (0.54 mL, 1.1 equiv, 5.5 mmol) in 5 mL THF was added to the reaction pot. The reaction was allowed to stir for 1h at -78 °C. A saturated ammonium chloride solution was added and the aqueous phase was extracted with DCM (3 x 50 mL). The organic phase was dried over Na\(_2\)SO\(_4\), filtered and concentrated. The compound was purified by column chromatography (10:1 Hex:EtOAc) to give a clear oil (72%, 683 mg).
S

H NMR (500 MHz, CDCl₃): δ ppm 7.54-7.56 (m, 1H), 7.44-7.46 (m, 1H), 7.25-7.31 (m, 3H), 5.51-5.55 (d, 1H), 5.21-5.23 (d, 1H), 5.12 (s, 1H), 4.97 (s, 1H), 2.07 (s, 1H), 1.74 (s, 3H), 1.65 (s, 3H).

13C NMR (126 MHz, CDCl₃): δ ppm 19.6, 28.9, 20.6, 111.3, 115.5, 125.9, 127.4, 127.4, 127.8, 142.4, 150.3.

Synthesis of chloro(iodomethyl)diisopropylsilane:

\[
\begin{align*}
\text{Si}^\text{Pr}_2\text{Si} \quad \text{ICH}_2\text{Cl}, \text{MeLi} \\
\text{THF, -78 °C, 2h} \\
\text{Si}^\text{Pr}_2\text{Si} \quad \text{NaI} \\
\text{Acetone} \\
\text{85 °C, 1h} \\
\text{Si}^\text{Pr}_2\text{Si} \quad \text{TCCA} \\
\text{DCM, 0 °C, 1h} \\
\text{Cl}^\text{Si} \quad \text{I}
\end{align*}
\]

To a solution of dichlorodiisopropylsilane (6.8 mL, 1 equiv, 40 mmol) and chloroiodomethane (4.4 mL, 1.5 equiv, 60 mmol) in THF (50 mL) was added a solution of MeLi-LiBr complex (1.5 M in ether, 40 mL, 60 mmol) dropwise at -78 °C. The reaction mixture was stirred at -78 °C for 1 h and then allowed to warm to room temperature before quenching with saturated ammonium chloride solution. The aqueous layer was extracted with hexane. The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product, (chloromethyl)diisopropylsilane, was used for the next step without further purification.

To a solution of NaI (18 g, 3 equiv, 120 mmol) in ACS standard acetone (40 mL) was added crude (chloromethyl)diisopropylsilane in acetone (5mL). The reaction mixture was refluxed at 85 °C for 1h. The reaction allowed to cool to room temperature before quenching with saturated solution of Na₂S₂O₃. The aqueous layer was extracted with hexane. The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product, 5.1g, (50% yield) (iodomethyl)diisopropylsilane, was used for the next step without further purification.

To a solution of TCCA (1.67 g, 0.36 equiv, 7.2 mmol) in dry DCM (40 mL) under argon was added crude (chloromethyl)diisopropylsilane (5.1 g, 1 equiv, 20 mmol) in DCM(5mL) dropwise at 0 °C for 1 h. The mixture was allowed to warm to r.t.and was then filtered through celite and concentrated. The residue was then dissolved in hexanes and re-filtered through celite and then concentrated to yield chloro(iodomethyl)diisopropylsilane (quantitative, 5.8 g) as a pink/purple oil. The crude product, >95% purity, chloro(iodomethyl)diisopropylsilane, was used for the next step without further purification.

Yield = 50% over three steps.

1H NMR (500 MHz, CDCl₃): δ ppm 2.22 (s, 2H), 1.41-1.47 (m, 2H), 1.12 -1.14 (dd, 12H).

13C NMR (126 MHz, CDCl₃): δ ppm 13.4, 16.9, 17.3. HRMS (EI) calcd. for C₇H₁₆SiCl [M]+: 289.9755, found: 289.9759.
Synthesis of secondary chloro(bromomethyl)diisopropylsilane:

\[
\begin{array}{c}
\text{H-Si-Pr} \\
\text{Cl}
\end{array}
\xrightarrow{1)} \text{LDA, BnBr, THF, -78 °C to r.t.}
\begin{array}{c}
\text{Si-Pr}
\end{array}
\xrightarrow{2)} \text{TCCA, DCM, r.t.}
\begin{array}{c}
\text{Cl-Si-Pr-Br Ph}
\end{array}
\]

To a solution of diisopropylamine (0.7 mL, 1 equiv, 5 mmol) in THF (10 mL) was added a solution of n-BuLi (2.63 M in hexanes, 1.9 mL, 5 mmol) dropwise at -78 °C. The reaction mixture was stirred at 0 °C for 0.5 h and then allowed to warm to room temperature for 0.5 h. The reaction mixture was then cooled down to -100 °C (EtOH and Liquid N₂), followed by addition of BnBr (0.6 mL, 1 equiv, 5 mmol) and chlorodiisopropylsilane (1.02 mL, 1.1 equiv, 6 mmol) in THF:Hex -1:1 (14 mL). The reaction was stirred overnight at -100 °C to r.t. before quenching with saturated ammonium chloride solution. The aqueous layer was extracted with hexane. The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product, (bromomethyl)diisopropylsilane (52% yield, 830 mg), was used for the next step without further purification.

To a solution of TCCA (0.15 g, 0.36 equiv, 0.64 mmol) in dry DCM (10 mL) under argon was added crude (chloromethyl)diisopropylsilane (0.513 g, 1 equiv, 1.8 mmol) in DCM (5 mL) dropwise at 0 °C for 1 h. The mixture was allowed to warm to r.t. and was then filtered through celite and concentrated. The residue was then dissolved in hexanes and re-filtered through celite and then concentrated to yield chloro(bromomethyl)diisopropylsilane (quantitative) as a white solid. The crude product, chloro(bromomethyl)diisopropylsilane (>95% purity, quantitative), was used for the next step without further purification.
Part II: Synthesis of silyl tethered phenols, 1a-1r, and alcohols, 3a-3j:

Method A: To a stirred mixture of imidazole (450 mg, 6.6 mmol, 2.2 equiv) and THF (20 mL), chloro(iodomethyl)diisopropylsilane (872 mg, 3 mmol, 1 equiv) was added at r.t. under argon atmosphere. To this mixture, phenol/alcohol (3.3 mmol, 1.1 equiv) in 5 mL of THF was added. The mixture was stirred until completion of the reaction (3 h) as judged by GC/MS. To this mixture, hexane (20 mL) was added and filtered. The filtrate was then concentrated under reduced pressure. The residue was purified by column chromatography in hexanes.

Method B: To a stirred mixture of DMAP (18.3 mg, 0.15 mmol, 5 mol %), chloro(iodomethyl)diisopropylsilane (872 mg, 3 mmol, 1 equiv), triethylamine (0.3 mL, 3 mmol, 1 equiv) DCM (10 mL), phenol/alcohol (3.3 mmol, 1.1 equiv) in 5 mL of DCM was added at 0 °C under argon atmosphere. The mixture was stirred until completion of the reaction (1 h) as judged by GC/MS. After completion the mixture was quenched with saturated ammonium chloride solution and extracted with DCM (3 x 50 mL). The combined organic layer was washed with brine. The organic layer was dried with Na₂SO₄, filtered, and then evaporated by rotary evaporator under reduced pressure. The residue was purified by column chromatography in hexanes.

Method C: To a stirred mixture of phenol/alcohol (3.3 mmol, 1.1 equiv) and THF (10 mL), MeLi (2.06 mL, 1.5 M, 3.3 mmol, 1.1 equiv) was added dropwise at 0 °C under argon atmosphere. To this mixture, chloro(iodomethyl)diisopropylsilane (872 mg, 3 mmol, 1 equiv) in 5 mL of THF was added at 0 °C. The mixture was stirred until completion of the reaction (1 h) as judged by GC/MS. After completion the mixture was quenched with saturated ammonium chloride solution and extracted with DCM (3 x 50 mL). The combined organic layer was washed with brine. The organic layer was dried with Na₂SO₄, filtered, and then evaporated by rotary evaporator under reduced pressure. The residue was purified by column chromatography in hexanes.

Method D: To a stirred mixture of phenol/alcohol (3.3 mmol, 1.1 equiv) and THF (10 mL), MeLi (2.06 mL, 1.5 M, 3.3 mmol, 1.1 equiv) was added dropwise at 0 °C under argon atmosphere. To this mixture, HMPA (0.57 mL, 3.3 mmol, 1.1 equiv) was added, followed by, chloro(iodomethyl)diisopropylsilane (872 mg, 3 mmol, 1 equiv) in 5 mL of THF was added at 0 °C. The mixture was stirred until completion of the reaction by (1 h) GC/MS. After completion the mixture was quenched with saturated ammonium chloride solution and extracted with DCM (3 x 50 mL). The combined organic layer was washed with brine. The organic layer was dried with Na₂SO₄, filtered, and then evaporated by rotary evaporator under reduced pressure. The residue was purified by column chromatography in hexanes.
Benzene tethered substrates, 1a-1r:

(iodomethyl)diisopropyl(2-vinylphenoxy)silane, 1a:

\[
\begin{align*}
\text{Coupling of 2-vinyl-phenol}^1 \text{ with chloro(iodomethyl)diisopropylsilane using Method A. Isolated yield = 84\%, 943 mg.}
\text{\( \text{H NMR (500 MHz, CDCl}_3\): \( \delta \) ppm 7.51-7.53 (d, 1H), 7.08-7.17 (m, 2H), 6.96-6.99 (t, 1H), 6.85-6.86 (d, 1H), 5.68-5.73 (dd, 1H), 5.53-5.56 (dd, 1H), 2.26 (s, 2H), 1.42-1.39 (m, 2H), 1.10-1.18 (m, 12H).} \\
\text{\( \text{C NMR (126 MHz, CDCl}_3\): \( \delta \) ppm 12.7, 17.4, 17.7, 114.1, 119.3, 121.8, 126.2, 128.7, 128.9, 131.8, 152.3.} \\
\text{HRMS (ESI) calcd. for C}_{15}\text{H}_{23}\text{IOSi [M]+H: 375.0641, found: 375.0647}}
\end{align*}
\]

(iodomethyl)diisopropyl(5-methoxy-2-vinylphenoxy)silane, 1b:

\[
\begin{align*}
\text{Coupling of 5-methoxy-2-vinylphenol}^5 \text{ with chloro(iodomethyl)diisopropylsilane using Method A. Isolated yield = 62\%, 752 mg.}
\text{\( \text{H NMR (500 MHz, CDCl}_3\): \( \delta \) ppm 7.42-7.44 (d, 1H), 6.96-7.03 (dd, 1H), 6.53-6.56 (d, 1H), 6.43-6.44 (s, 1H), 5.53-5.60 (dd, 1H), 5.13-5.16 (dd, 1H), 3.79 (s, 3H), 2.25 (s, 2H), 1.42-1.47 (m, 2H), 1.13-1.16 (m, 12H).} \\
\text{\( \text{C NMR (126 MHz, CDCl}_3\): \( \delta \) ppm 12.7, 17.4, 17.7, 114.1, 119.3, 121.8, 126.8, 131.3, 151.2, 160.1.} \\
\text{HRMS (ESI) calcd. for C}_{16}\text{H}_{25}\text{IO}_2\text{Si [M]+H: 405.0747, found: 405.0751}}
\end{align*}
\]

(5-fluoro-2-vinylphenoxy)(iodomethyl)diisopropylsilane, 1c:

\[
\begin{align*}
\text{Coupling of 5-fluoro-2-vinylphenol}^1 \text{ with chloro(iodomethyl)diisopropylsilane using Method A. Isolated yield = 69\%, 812 mg.}
\text{\( \text{H NMR (500 MHz, CDCl}_3\): \( \delta \) ppm 7.42-7.46 (t, 1H), 6.95-7.02 (dd, 1H), 6.66-6.71 (t, 1H), 6.55-6.59 (d, 1H), 5.59-5.64 (d, 1H), 5.21-5.24 (d, 1H), 2.23 (s, 2H), 1.37-1.46 (m, 2H), 1.13-1.16 (m, 12H).} \\
\text{\( \text{C NMR (126 MHz, CDCl}_3\): \( \delta \) ppm 12.7, 17.3, 17.6, 106.7, 106.9, 108.8, 108.9,}
\end{align*}
\]
113.7, 125.4, 127.1, 127.1, 130.9, 153.1, 161.7, 163.6. HRMS (ESI) calcd. for \(C_{15}H_{22}FIOSi\) [M]+H: 393.0547, found: 393.0551.

(iodomethyl)diisopropyl(4-methyl-2-vinylphenoxy)silane, 1d:

\[
\text{Coupling of 4-methyl-2-vinylphenol}^6\text{ with chloro(iodomethyl)diisopropylsilane using Method A.}
\]

Isolated yield = 68\%, 792 mg.

\(^{1}H\) NMR (500 MHz, CDCl\(3\)): \(\delta\) ppm 7.30 (s, 1H), 7.03-7.09 (dd, 1H), 6.93-6.94 (d, 1H), 6.72-6.74 (d, 1H), 5.66-5.69 (d, 1H), 5.22-5.24 (d, 1H), 2.29 (s, 3H), 2.23 (s, 3H), 1.37-1.45 (m, 2H), 1.05 -1.18 (m, 12H). \(^{13}C\) NMR (126 MHz, CDCl\(3\)): \(\delta\) ppm 12.7, 17.4, 17.7, 20.7, 113.7, 119.1, 126.6, 128.4, 129.3, 130.9, 131.9, 150.1. HRMS (EI) calcd. for \(C_{16}H_{25}IOSi\) [M]+: 388.0719, found: 388.0716.

(4-chloro-2-vinylphenoxy)(iodomethyl)diisopropylsilane, 1e:

\[
\text{Coupling of 4-chloro-2-vinylphenol}^6\text{ with chloro(iodomethyl)diisopropylsilane using Method A.}
\]

Isolated yield = 84\%, 1.03 g.

\(^{1}H\) NMR (500 MHz, CDCl\(3\)): \(\delta\) ppm 7.49-7.51 (d, 1H), 7.05-7.15 (m, 2H), 6.94-6.98 (t, 1H), 6.82-6.84 (d, 1H), 5.67-5.71 (d, 1H), 5.24-5.27 (d, 1H), 2.24 (s, 2H), 1.39-1.46 (m, 2H), 1.11 -1.15 (m, 12H). \(^{13}C\) NMR (126 MHz, CDCl\(3\)): \(\delta\) ppm 12.7, 17.4, 17.7, 115.4, 120.5, 126.1, 126.8, 128.4, 130.5, 130.8, 150.6. HRMS (EI) calcd. for \(C_{15}H_{22}ClOSi\) [M]+: 408.0173, found: 408.0172.

(iodomethyl)diisopropyl(4-nitro-2-vinylphenoxy)silane, 1f:

\[
\text{Coupling of 4-nitro-2-vinylphenol}^4\text{ with chloro(iodomethyl)diisopropylsilane using Method A.}
\]

Isolated yield = 48\%, 603 mg.

\(^{1}H\) NMR (500 MHz, CDCl\(3\)): \(\delta\) ppm 8.39-8.40 (d, 1H), 8.03-8.06 (dd, 1H), 7.00-7.07 (dd, 1H), 6.91-6.93 (d, 1H), 5.83-5.87 (dd, 1H), 5.43-5.46 (dd, 1H), 2.26 (s, 2H), 1.41-1.49 (m, 2H), 1.13 -1.17 (m, 12H). \(^{13}C\) NMR (126 MHz, CDCl\(3\)): \(\delta\) ppm 12.7, 17.3, 17.5, 117.2, 119.3, 122.2, 124.2,
129.9, 130.0, 142.4, 157.6. HRMS (ESI) calcd. for C_{15}H_{22}INO_{3}Si [M]+H: 420.0492, found: 420.0489.

(iodomethyl)diisopropyl(2-methoxy-6-vinylphenoxy)silane, 1g:

Coupling of 2-methoxy-6-vinylphenol\(^7\) with chloro(iodomethyl)diisopropylsilane using Method A. Isolated yield = 43%, 521 mg.
\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ ppm 7.09-7.17 (m, 2H), 6.87-6.91 (t, 1H), 6.75-6.77 (dd, 1H), 5.65-5.69 (dd, 1H), 5.24-5.28 (dd, 1H), 3.80 (s, 3H), 2.26 (s, 2H), 1.36-1.44 (m, 2H), 1.08 -1.13 (m, 12H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ ppm 13.3, 17.6, 17.8, 55.1, 110.5, 114.2, 117.8, 121.2, 129.6, 131.9, 142.0, 150.0. HRMS (EI) calcd. f or C_{16}H_{25}IO_{2}Si [M]+: 404.0669, found: 404.0671.

(2-fluoro-6-vinylphenoxy)(iodomethyl)diisopropylsilane, 1h:

Coupling of 2-fluoro-6-vinylphenol\(^8\) with chloro(iodomethyl)diisopropylsilane using Method A. Isolated yield = 61%, 717 mg.
\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ ppm 7.25-7.27 (d, 1H), 7.03-7.11 (dd, 1H), 6.64-6.99 (t, 1H), 6.89-6.1 (m, 1H), 5.69-5.74 (dd, 1H), 5.31-5.34 (dd, 1H), 2.27 (s, 2H), 1.41-1.49 (m, 2H), 1.11 -1.17 (m, 12H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ ppm 12.9, 17.3, 17.6, 106.7, 106.9, 108.8, 108.9, 113.7, 125.4, 127.0, 127.1, 130.1, 153.1, 161.67, 163.6. HRMS (EI) calcd. for C_{15}H_{23}IO_{2}Si [M]+: 392.0469, found: 392.0467.

(iodomethyl)diisopropyl(2-vinylbenzyloxy)silane, 1i:

Coupling of 2-vinylbenzylol\(^6\) with chloro(iodomethyl)diisopropylsilane using Method B. Isolated yield = 70%, 815 mg.
\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ ppm 7.48-7.51 (t, 2H), 7.28-7.29 (m, 2H), 6.94-6.99 (dd, 1H), 5.85-5.68 (d, 1H), 5.34-5.32 (d, 1H), 4.95 (s, 2H), 2.13 (s, 2H), 1.24-1.34 (m, 2H), 1.11 -1.12 (m,
\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 12.4, 17.5, 17.7, 63.7, 116.0, 125.6, 126.9, 127.4, 127.7, 133.9, 135.8, 137.6. HRMS (EI) calcd. for C\(_{16}\)H\(_{25}\)OSi [M]+: 388.0719, found: 388.0720.

(iodomethyl)diisopropyl(2-vinylphenethoxy)silane, 1j:

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \text{Si} \text{iPr} \text{iPr} \text{I}
\end{array}
\]

Coupling of 2-vinylphenethanol\(^1\) with chloro(iodomethyl)diisopropylsilane using Method B. Isolated yield = 70\%, 845 mg.
\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.48-7.50 (t, 1H), 7.20-7.22 (m, 3H), 7.02-7.06 (dd, 1H), 5.63-5.67 (d, 1H), 5.30-5.32 (d, 1H), 3.88-3.91 (t, 2H), 2.97-3.00 (t, 2H), 2.00 (s, 2H), 1.17-1.21 (m, 2H), 1.03 -1.05 (m, 12H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 12.2, 17.4, 17.6, 36.7, 64.3, 115.7, 125.7, 126.7, 127.7, 130.5, 134.7, 136.0, 137.0. HRMS (ESI) calcd. for C\(_{17}\)H\(_{27}\)OSi [M]+H: 403.0954, found: 403.0958.

(bromo(phenyl)methyl)diisopropyl(2-vinylphenoxy)silane, 1k:

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \text{Si} \text{iPr} \text{iPr} \text{Br}
\end{array}
\]

Coupling of 2-vinylphenol\(^1\) with chloro(bromomethyl)diisopropylsilane using Method A. Isolated yield = 68\%, 823 mg.
\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.52-7.54 (dd, 1H), 7.44-7.46 (d, 2H), 7.20-7.30 (m, 3H), 7.08-7.16 (m, 2H), 6.95-6.99 (t, 1H), 6.83-6.85 (d, 1H), 5.67-5.71 (dd, 1H), 5.23-5.26 (dd, 1H), 4.62 (s, 1H), 1.55-1.62 (m, 1H), 1.39-1.45 (m, 1H), 1.15-1.21 (m, 6H) 0.99-1.07 (m, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 13.1, 13.2, 17.4, 17.5, 17.6, 17.7, 17.8, 18.0, 38.2,113.9, 119.4, 121.7, 126.6, 127.4, 128.5, 128.6, 128.7, 129.3, 131.9, 139.6,152.1. HRMS (ESI) calcd. for C\(_{21}\)H\(_{28}\)BrOSi [M]+H: 403.1093, found: 403.1088.

(iodomethyl)diisopropyl(2-(1-phenylvinyl)phenoxy)silane, 1l:

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \text{Si} \text{iPr} \text{iPr} \text{I}
\end{array}
\]
Coupling of 2-(1-phenylvinyl)phenol\(^9\) with chloro(iodomethyl)diisopropylsilane using Method A. Isolated yield = 87\%, 1.17 g.
\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.22-7.33 (m, 7H), 6.99-7.03 (t, 1H), 6.86-6.88 (d, 1H), 5.75 (s, 1H), 5.32 (s, 1H), 2.03 (s, 2H), 1.19-1.25 (m, 2H), 0.91-0.97 (m, 12H). \(^13\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 12.5, 17.1, 17.5, 115.7, 119.0, 121.4, 126.6, 127.4, 128.1, 128.8, 131.7, 133.0, 140.5, 147.4, 152.5. HRMS (ESI) calcd. for C\(_{21}\)H\(_{27}\)IOSi [M]+H: 451.0954, found: 451.0947.

\((E)-(2-(1,2-diphenylvinyl)phenoxy)(iodomethyl)diisopropylsilane, 1m:\)

\[
\begin{array}{c}
\text{O} \\
\text{Ph} \\
\text{Si} \\
\text{Pr} \\
\text{Pr}
\end{array}
\]

Coupling of phenol \(\text{cp1}\) with chloro(iodomethyl)diisopropylsilane using Method D. Isolated yield = 76\%, 1.2 g.
\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.41-7.43 (m, 2H), 7.28-7.35 (m, 4H), 7.13-7.19 (m, 7H), 6.92-7.01 (m, 2H), 2.05 (dd, 2H), 1.15-1.27 (m, 2H), 0.91-0.97 (m, 12H). \(^13\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 12.7, 17.3, 17.5, 118.7, 121.7, 127.3, 128.0, 128.2, 128.8, 129.9, 131.0, 132.4, 137.6, 139.4, 142.5. HRMS (ESI) calcd. for C\(_{27}\)H\(_{31}\)IOSi [M]+H: 527.1267, found: 527.1262.

\((Z)-(iodomethyl)diisopropyl(2-(prop-1-enyl)phenoxy)silane, 1n:\)

\[
\begin{array}{c}
\text{O} \\
\text{Me} \\
\text{Si} \\
\text{Pr} \\
\text{Pr}
\end{array}
\]

Coupling of (Z)-2-(prop-1-enyl)phenol\(^10\) with chloro(iodomethyl)diisopropylsilane using Method A. Isolated yield = 58\%, 675 mg.
\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.25-7.26 (d, 1H), 7.10-7.14 (t, 1H), 6.93-6.97 (t, 1H), 6.85-6.88 (d, 1H), 6.53-6.56 (dd, 1H), 5.77-5.85 (m, 1H) 2.23 (s, 2H), 1.81-1.84 (dd, 3H) 1.36-1.43 (m, 2H), 1.09-1.15 (m, 12H). \(^13\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 12.7, 14.6, 17.3, 17.7, 119.4, 121.2, 126.2, 126.8, 127.8, 128.7, 130.5, 152.8. HRMS (EI) calcd. for C\(_{16}\)H\(_{25}\)IOSi [M]+: 388.0709, found 388.0708

\((iodomethyl)diisopropyl(2-(2-methylprop-1-enyl)phenoxy)silane, 1o:\)

\[
\begin{array}{c}
\text{O} \\
\text{Me} \\
\text{Si} \\
\text{Pr} \\
\text{Pr}
\end{array}
\]
Coupling of 2-(2-methylprop-1-enyl)phenol<sup>6</sup> with chloro(iodomethyl)diisopropylsilane using Method A. Isolated yield = 72%, 869 mg.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ ppm 7.17-7.19 (d, 1H), 7.08-7.11 (t, 1H), 6.94-6.97 (t, 1H), 6.85-6.87 (d, 1H), 6.33 (s, 1H), 2.20 (s, 2H) 1.92 (s, 3H), 1.79 (s, 3H) 1.37-1.42 (m, 2H), 1.10-1.15 (m, 12H). 13<sup>C</sup>NMR (126 MHz, CDCl<sub>3</sub>): δ ppm 12.6, 17.3, 17.6, 19.4, 26.4, 119.4, 121.3, 121.7, 127.2, 130.13, 130.6, 135.14, 152.7. HRMS (ESI) calcd. for C<sub>17</sub>H<sub>27</sub>IOSi [M]+: 403.0954, found: 403.0954.

(iodomethyl)diisopropyl(3-methyl-2-(2-vinylphenyl)but-3-en-2-yloxy)silane, 1p:

Coupling of ca1 with chloro(iodomethyl)diisopropylsilane using Method D. Isolated yield = 48%, 637 mg.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ ppm 7.55-7.49 (m, 2H), 7.32-7.38 (dd, 1H), 7.23-7.26 (m, 2H), 5.48-5.52 (dd, 1H), 5.20 (s,1H), 5.10-5.13 (dd, 1H), 4.93 (t, 1H), 1.94-2.01 (m, 2H) 1.83 (s, 3H) 1.56 (s, 3H) 1.21-1.28 (m, 1H) 1.11-1.16 (m, 1H) 1.07-1.08 (dd, 6H) 0.94-0.99 (t, 6H). 13<sup>C</sup>NMR (500 MHz, CDCl<sub>3</sub>): δ ppm 13.5, 13.6, 17.7, 17.8, 17.9, 18.1, 19.8, 29.3, 79.9, 113.8, 126.1, 127.1, 127.2, 127.6, 137.0, 137.2, 142.4, 150.9. HRMS (ESI) calcd. for C<sub>20</sub>H<sub>31</sub>IOSi [M]+: 442.1189, found: 442.1192.

(iodomethyl)diisopropyl(((8S,9S,13S,14S)-(8S,9S,13S,14S)-13-methyl-2-vinyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)silane, 1q:

Coupling of cp4 with chloro(iodomethyl)diisopropylsilane using Method A. Isolated yield = 66%, 1.06 g.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ ppm 7.41 (s, 1H), 7.00-7.06 (dd, 1H), 6.52 (s, 1H), 5.61-5.65 (d, 1H), 5.16-5.18 (d,1H), 2.74-2.81, (m, 2H), 2.31-2.34 (dd, 1H) 2.23 (s, 2H) 2.18-2.19 (m, 1H), 1.87-1.92 (m, 2H) 1.64-1.69 (m, 3H) 1.49-1.58 (m, 2H), 1.22-1.45 (m, 9H), 1.07-1.16 (m, 16H), 0.75 (s, 3H). 13<sup>C</sup>NMR (126 MHz, CDCl<sub>3</sub>): δ ppm 12.3, 12.7, 17.4, 17.6, 17.7, 18.7, 20.6, 25.2, 26.7, 28.1, 29.6, 31.6, 39.1, 40.5, 41.1, 44.1, 53.6, 59.5, 112.7, 119.1, 122.9, 125.9, 132.2, 134.0, 137.7, 149.9. HRMS (ESI) calcd. for C<sub>27</sub>H<sub>44</sub>IOSi [M]+H: 537.2050, found: 537.2054.
Silyl-tethered aliphatic alkenols, 3a-3k:

(hept-1-en-4-yloxy)(iodomethyl)diisopropylsilane, 3a:

\[
\begin{align*}
\text{O} & \quad \text{Pr} \\
\text{\&} & \quad \text{Pr} \\
\text{Si} & \quad 1
\end{align*}
\]

Coupling of 1-heptene-4-ol with chloro(iodomethyl)diisopropylsilane using Method B. Isolated yield = 79%, 873 mg.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 5.79-5.87 (m, 1 H), 5.04-5.08 (m, 2 H), 3.90-3.95 (m, 1 H), 2.22-2.32 (m, 2 H), 2.08 (s, 2 H), 1.43-1.50 (m, 2 H), 1.31-1.40 (m, 2 H), 1.18-1.25 (m, 2 H), 1.07-1.10 (t, 12 H), 0.89-0.92 (t, 3 H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 12.6, 14.3, 17.5, 17.8, 18.3, 38.9, 41.6, 72.5, 116.9, 134.9, HRMS (CI) calcd. for C\(_{14}\)H\(_{29}\)IOSi [M]+H: 369.1111, found: 369.1108.

(iodomethyl)diisopropyl(non-1-en-4-yloxy)ilane, 3b:

\[
\begin{align*}
\text{O} & \quad \text{Pr} \\
\text{\&} & \quad \text{Pr} \\
\text{Si} & \quad 1
\end{align*}
\]

Coupling of 1-nonen-4-ol with chloro(iodomethyl)diisopropylsilane using Method B. Isolated yield = 77%, 915 mg.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 5.87 - 5.79 (m, 1 H), 5.08 - 5.03 (m, 2 H), 3.94 - 3.89 (m, 1 H), 2.32 - 2.22 (m, 2 H), 2.08 (s, 2 H), 1.51 - 1.44 (m, 2 H), 1.36 - 1.12 (m, 8 H), 1.09 (t, \(J = 7.7\) Hz, 12 H), 0.89 (t, \(J = 6.6\) Hz, 3 H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 12.6, 14.0, 17.5, 17.8, 22.6, 24.7, 32.0, 36.6, 41.5, 72.7, 116.9, 135.0. HRMS (CI) calcd. for C\(_{16}\)H\(_{34}\)OISi [M]+H: 397.14240, found: 397.14168.

(iodomethyl)diisopropyl((1-phenylbut-3-en-1-yl)oxy)silane, 3c:

\[
\begin{align*}
\text{Ph} & \quad \text{Pr} \\
\text{\&} & \quad \text{Pr} \\
\text{Si} & \quad 1
\end{align*}
\]

Coupling of 4-phenyl-1-butene-4-ol with chloro(iodomethyl)diisopropylsilane using Method B. Isolated yield = 79%, 953 mg.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.30-7.32 (m, 3 H), 7.23-7.28 (m, 1 H), 5.71-5.80 (m, 1 H), 5.02-5.04 (m, 2 H), 5.00 (s, 1 H), 4.85-4.88, (t, 3 H), 2.52-2.58 (m, 1 H), 2.42-2.47 (m, 1 H), 1.94 (d, 2 H), 1.20-1.27 (m, 1 H), 1.14-1.18 (m, 1 H), 1.07-1.11 (dd, 6 H) 0.94-1.00 (dd, 6 H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 12.4, 12.5, 17.3, 17.5, 17.6, 17.9, 45.5, 75.5, 117.3, 126.0, 127.3, 128.1, 134.6, 144.5. HRMS (CI) calcd. for C\(_{17}\)H\(_{27}\)IOSi [M]+H: 403.09545, found: 403.09531.
(iodomethyl)diisopropyl(4-propylhept-1-en-4-yl)oxy)silane, 3d:

Coupling 4-n-propyl-1-heptene-4-ol with chloro(iodomethyl)diisopropylsilane using Method D. Isolated yield = 58%, 739 mg.

$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 5.79-5.88 (m, 1H), 5.02-5.06 (m, 2H), 2.27-2.28 (d, 2H), 2.10 (s, 2H), 1.44-1.55 (m, 4H), 1.32-1.36 (m, 4H), 1.14-1.26 (m, 2H), 1.07-1.10, (t, 14H), 0.88-0.91 (t, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 13.7, 14.7, 17.1, 17.5, 17.9, 18.2, 42.7, 44.8, 78.6, 117.0, 134.9. HRMS (CI) calcd. for C$_{17}$H$_{35}$IOSi [M]+H: 411.15805, found: 411.15814.

((1-allylcyclohexyl)oxy)(iodomethyl)diisopropylsilane, 3e:

Coupling of 1-allyl-cyclohexanol with chloro(iodomethyl)diisopropylsilane using Method D. Isolated yield = 44%, 520 mg.

$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 5.82-5.91 (m, 1H), 5.02-5.07 (m, 2H), 2.33-2.34 (d, 2H), 2.12 (s, 2H), 1.59-1.65 (m, 4H), 1.47-1.50 (m, 2H), 1.15-1.25 (m, 2H), 1.08-1.10, (t, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 13.7, 17.1, 17.5, 17.9, 18.2, 22.8, 25.5, 38.1, 75.9, 117.0, 134.7. HRMS (EI) calcd. for C$_{16}$H$_{31}$IOSi [M]+H: 394.1189 found: 394.1189.

(iodomethyl)diisopropyl((1R,2S)-2-vinylcyclohexyloxy)silane, 3f:

Coupling of (1R,2S)-2-vinylcyclohexanol$^{11}$ with chloro(iodomethyl)diisopropylsilane using Method B. Isolated yield = 65%, 741 mg.

$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 5.81-5.90 (m, 1H), 4.98-5.05 (m, 2H), 3.50-3.56 (m, 1H), 2.07 (s, 2H), 1.73-2.00 (m, 2H), 1.54-1.75 (m, 3H), 1.30-1.43 (m, 1H) 1.14-1.30 (m, 5H), 1.05-1.09, (dd, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 13.0, 13.1, 17.9, 18.0, 18.2, 18.4, 24.9, 25.1, 30.8, 36.1, 50.2, 75.7, 114.6, 142.1. HRMS (CI) calcd. for C$_{15}$H$_{29}$IOSi [M]+H: 381.11110, found: 381.11144.

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(iodomethyl)diisopropyl(3-phenylbut-3-enyloxy)silane, 3g:

\[
\text{Ph} \text{Pr} \text{Pr} \text{O} \text{Si} \text{I}
\]

Coupling of 3-phenylbut-3-en-1-ol\(^{12}\) with chloro(iodomethyl)diisopropylsilane using Method B. Isolated yield = 72%, 869 mg.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.41-7.44 (m, 2H), 7.32-7.35 (t, 2H), 7.26-7.29 (m, 1H), 5.36-5.36 (d, 1H), 5.13-5.13 (d, 1H), 3.84-3.87 (t, 2H), 2.79-2.82 (t, 2H), 2.03 (s, 2H), 1.17-1.21 (m, 2H), 1.04-1.06, (dd, 12H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 12.2, 17.4, 17.7, 38.7, 62.9, 114.1, 126.1, 127.4, 128.3, 140.9, 145.1. HRMS (EI) calcd. for C\(_{17}\)H\(_{27}\)IOSi [M]+: 402.0876, found: 402.0880.

(iodomethyl)diisopropyl(4-phenylpent-4-enyloxy)silane, 3h:

\[
\text{Ph} \text{Pr} \text{Pr} \text{Pr} \text{Pr} \text{O} \text{Si} \text{I}
\]

Coupling of 4-phenylpent-4-en-1-ol\(^{13}\) with chloro(iodomethyl)diisopropylsilane using Method B. Isolated yield = 74%, 924 mg.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.42-7.44 (d, 2H), 7.31-7.35 (t, 2H), 7.26-7.28 (d, 1H), 5.31 (s, 1H), 5.09 (s, 1H), 3.76-3.78 (t, 2H), 2.60-2.63 (t, 2H), 2.07 (s, 2H), 1.70-1.74 (m, 2H), 1.19-1.25 (m, 2H), 1.05-1.09, (dd, 12H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 12.3, 17.5, 17.7, 31.4, 31.5, 63.2, 112.4, 126.1, 127.4, 128.3, 141.1, 148.1. HRMS (EI) calcd. for C\(_{18}\)H\(_{29}\)IOSi [M]+: 416.1032, found: 416.1040.

(iodomethyl)diisopropyl((5-phenylhex-5-en-1-yl)oxy)silane, 3i:

\[
\text{Ph} \text{Pr} \text{Pr} \text{Pr} \text{Pr} \text{Pr} \text{Pr} \text{O} \text{Si} \text{I}
\]

Coupling of 5-phenylhex-5-en-1-ol\(^{14}\) with chloro(iodomethyl)diisopropylsilane using Method B. Isolated yield = 69%, 891 mg.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.40-7.42 (d, 2H), 7.31-7.34 (t, 2H), 7.26-7.28 (d, 1H), 5.27-5.28 (dd, 1H), 5.07-5.07 (dd, 1H), 3.72-3.75 (t, 2H), 2.52-2.55 (t, 2H), 2.06 (s, 2H), 1.52-1.62 (m, 4H), 1.17-1.25 (m, 2H), 1.03-1.09, (dd, 12H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 12.3, 17.4, 17.7, 24.4, 32.4, 35.0, 63.6, 112.3, 126.1, 127.3, 128.3, 141.3, 148.5. HRMS (ESI) calcd. for C\(_{19}\)H\(_{31}\)IOSi [M]+H: 431.1267, found: 431.1268.
(iodomethyl)diisopropyl((1S,2R,5S)-5-methyl-2-(prop-1-en-2-yl)cyclohexyl)oxy)silane, 3j:

Coupling of Isopulegol with chloro(iodomethyl)diisopropylsilane using Method C.
Isolated yield = 68%, 833 mg.
$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 4.75-4.77 (d, 2H), 3.70-3.76 (m, 1H), 3.72-3.75 (t, 2H), 2.05-2.06 (d, 2H), 1.88-1.97 (m, 2H), 1.72 (s, 3H), 1.59-1.64 (m, 2H), 1.41-1.48 (m, 1H), 1.26-1.35 (m, 1H), 1.11-1.23 (m, 2H), 1.04-1.09 (m, 12H), 0.87-0.94 (m, 4H).$^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 12.7, 12.9, 17.5, 17.6, 17.8, 17.9, 20.9, 22.3, 30.6, 31.6, 34.3, 45.4, 53.6, 73.8, 111.2, 126.1, 147.8. HRMS (ESI) calcd. for C$_{17}$H$_{33}$IOSi [M]+H: 409.1424, found: 409.1421
Part III: Table S1: Optimization of the Silyl Methyl Heck Reaction

![Optimization Diagram]

| Entry | Catalyst | Ligand | Base | Additive | T  | h  | A : B | GC Yield, %, of A<sup>a,b</sup> |
|-------|----------|--------|------|----------|----|----|-------|----------------------------------|
| 1     | Pd(PPh₃)<sub>3</sub> | -      | PMP  | -        | 110| 24 | -     | NR<sup>c</sup>                  |
| 2     | Pd₂(4OMe-dba)<sub>3</sub> | SIMesHBF₄ | Cs₂CO₃ | KOtBu   | 65 | 24 | 1 : 1 | 10<sup>d</sup> Decomp<sup>de</sup> |
| 3     | Pd₂dba<sub>3</sub> | BuPPh₂ | Pr₂NEt | -       | 120| 24 | 1 : 2.3 | 23                              |
| 4     | Pd(OAc)<sub>2</sub> | P(Pr<sub>2</sub>NH)₂ | Pr₂NEt | -       | 120| 24 | 1 : 1 | 5                               |
| 5     | Pd(OAc)<sub>2</sub> | [P(dp)][Pr<sub>2</sub>N] | Pr₂NEt | -       | 120| 24 | 40 : 1 | 24                              |
| 6     | Pd(OAc)<sub>2</sub> | dpff   | Pr₂NEt | -       | 120| 24 | >50 : 1 | 60                              |
| 7     | Pd(OAc)<sub>2</sub> | dpff   | Pr₂NEt | Ag(OTf) | 120| 24 | >50 : 1 | 20                              |
| 8     | Pd(OAc)<sub>2</sub> | dpff   | Pr₂NEt | Ag(OTf) | 120| 24 | >50 : 1 | 11                              |
| 9     | Pd(OAc)<sub>2</sub> | dpff   | Pr₂NEt | Ag(OTf) | 120| 24 | >50 : 1 | 11                              |
| 10    | Pd(OAc)<sub>2</sub> | L      | Pr₂NEt | Ag(OTf) | 120| 24 | >50 : 1 | 40                              |
| 11    | Pd(OAc)<sub>2</sub> | L      | Pr₂NEt | Ag(OTf) | 85 | 24 | -     | NR                              |
| 12    | Pd(OAc)<sub>2</sub> | L      | Pr₂NEt | Ag(OTf) | 85 | 24 | >50 : 1 | 76 (68)                         |
| 13    | Pd(OAc)<sub>2</sub> | L      | NEt₃  | Ag(OTf) | 85 | 24 | >50 : 1 | 71                              |
| 14    | Pd(OAc)<sub>2</sub> | L      | PMP   | Ag(OTf) | 85 | 24 | >50 : 1 | 75                              |
| 15    | Pd(OAc)<sub>2</sub> | L      | Ag₂CO₃| Ag(OTf) | 85 | 24 | >50 : 1 | 75                              |
| 16    | Pd(OAc)<sub>2</sub> | L      | Cs₂CO₃| Ag(OTf) | 85 | 24 | >50 : 1 | 78                              |
| 17    | Pd(OAc)<sub>2</sub> | L      | Cs₂CO₃| -       | 85 | 24 | 15 : 1 | 76                              |
| 18    | Pd(OAc)<sub>2</sub> | L      | Cs₂CO₃| -       | 85 | 3  | 30 : 1 | 83                              |
| 19    | Pd(OAc)<sub>2</sub> | L      | Pr₂NEt| -       | 85 | 3  | 40 : 1 | 89 (73)                         |
| 20    | Pd(OAc)<sub>2</sub> | L      | Pr₂NEt| -       | 75 | 12 | 40 : 1 | 92 (79)                         |
| 21    | Pd(OAc)<sub>2</sub> | L      | Pr₂NEt| -       | 65 | 24 | -     | 50%. conv                       |
| 22    | -        | -      | Pr₂NEt| -       | 75 | 12 | <2    |                                  |

<sup>a</sup>GC was calibrated using tetradecane as an internal standard. <sup>b</sup>Isolated yields are in parentheses. <sup>c</sup>Reaction was conducted under 10 atm of CO. <sup>d</sup>5 mol % catalyst was used. <sup>e</sup>MeCN was used as solvent.
Part IV: Endo-Selective Silyl Methyl Heck Reaction

An oven dried 2.5 mL Wheaton V-vial, containing a stirring bar, was charged with phenol/alcohol-derived iodomethylsilanes (0.2 mmol), Pd(OAc)$_2$ (4.5 mg, 0.01 mmol), Ligand L (20.6 mg, 0.02 mmol), and Ag(OTf) 51.2 mg, 0.2 mmol for 1m, 3a-c and 3f-i under N$_2$ atmosphere (glove box). 2 mL of dry toluene (5 mL toluene for 1j-k, 3i) and iPr$_2$NEt (76 µL, 0.44 mmol) (DABCO instead of iPr$_2$NEt, 50 mg, 0.44 mmol for 3d-c) were added via syringes and the reaction vessel was capped with pressure screw cap. The reaction mixture was heated at 75 °C for 5 - 20 h (extended time (36 h) and higher temperature (110 – 130 °C) are required for 1i, 1j-k, 1m, 3i). The resulting mixture was cooled down to room temperature and filtered through a short layer of silica gel over celite plug with the aid of DCM. The filtrate was concentrated under reduced pressure and purified by column chromatography (Hexanes - 2i-2j, 3a-f. Hexanes: EtOAc = 50:1 – 2i, 2l, 2p, 2r, 4f, 4j. Hexanes: EtOAc = 50:1 → 35:1 – 2j-k, 2m, 4g-i.)

Silyl Methyl Heck of Benzene Tethered Systems, 2a-2o:

2,2-diisopropyl-2,3-dihydrobenzo[f][1,2]oxasilepine, 2a:

![Structure of 2a]

0.2 mmol scale: Isolated yield = 79%, 38.9 mg. Endo : Exo = 33: 1 (NMR Ratio)
3.8 mmol scale: Isolated yield = 72%, 674 mg. Endo : Exo = 33 : 1 (NMR Ratio)

$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 7.13-7.18 (t, 1H), 7.07-7.10 (d, 1H), 6.93-7.00 (m, 2H), 6.28-6.30 (d, J = 10.8 Hz, 1H), 6.06-6.13 (m, J = 10.8, J = 7.6,1H), 1.63-1.64 (d, J = 7.6 Hz, 2H), 1.08-1.23 (m, 14H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 12.4, 13.6, 17.5, 17.7, 120.9, 121.6, 126.1, 127.8, 128.1, 130.9, 154.2. HRMS (ESI) calcd. for C$_{15}$H$_{22}$OSi [M]+H: 247.1518, found: 247.1520.

2,2-diisopropyl-8-methoxy-2,3-dihydrobenzo[f][1,2]oxasilepine, 2b:

![Structure of 2b]
Isolated yield = 87%, 48.1 mg. Endo : Exo = 99: 1 (NMR Ratio)
$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 6.96-6.99 (d, 1H), 6.53-6.55 (m, 2H), 6.20-6.22 (d, $J = 11$ Hz, 1H), 5.96-5.99 (m, $J = 11$, $J = 7.3$, 1H), 3.79(s, 3H), 1.60-1.62 (d, $J = 7.3$ Hz, 2H), 1.06-1.19 (m, 14H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 12.1, 13.6, 17.4, 17.7, 55.3, 106.6, 107.5, 121.0, 125.8, 126.3, 131.6, 155.1, 159.5. HRMS (ESI) calcd. for C$_{16}$H$_{24}$O$_2$Si [M]+H:277.1624, found: 277.1622.

8-fluoro-2,2-diisopropyl-2,3-dihydrobenzo[f][1,2]oxasilepine, 2c:

Isolated yield = 74%, 39.1 mg. Endo : Exo = 99 : 1 (NMR Ratio)
$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 6.99-7.00 (m, 1H), 6.65-6.70 (m, 2H), 6.20-6.22 (d, $J = 10.6$, 1H), 6.01-6.07 (m, $J = 10.6$, $J = 7.7$, 1H), 1.61-1.62 (d, $J = 7.7$ Hz, 2H), 1.06-1.20 (m, 14H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 12.4, 13.6, 17.4, 17.6, 108.2, 108.3, 108.5, 108.6, 124.4, 125.3, 127.7, 131.6, 131.7, 155.0. HRMS (ESI) calcd. for C$_{15}$H$_{21}$FOSi [M]+H: 265.1413, found: 265.1419.

2,2-diisopropyl-7-methyl-2,3-dihydrobenzo[f][1,2]oxasilepine, 2d:

Isolated yield = 76%, 39.5 mg. Endo : Exo = 25: 1 (NMR Ratio)
$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 6.95-6.97 (m, 1H), 6.88-6.90 (m, 2H), 6.24-6.26 (d, $J = 11$ Hz, 1H), 6.06-6.12 (m, $J = 11$, $J = 7.4$, 1H), 2.30 (s, 3H), 1.61-1.62 (d, $J = 7.4$ Hz, 2H), 1.08-1.20 (m, 14H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 12.3, 13.6, 17.5, 17.7, 20.5, 121.4, 127.9, 128.0, 128.5, 130.1, 131.2, 151.9. HRMS (ESI) calcd. for C$_{16}$H$_{24}$OSi [M]+H: 261.1675, found: 261.1668.

7-chloro-2,2-diisopropyl-2,3-dihydrobenzo[f][1,2]oxasilepine, 2e:

Isolated yield = 72%, 40.4 mg. Endo : Exo = 25: 1 (NMR Ratio)
$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 7.07-7.09 (dd, 1H), 7.04 (s, 1H), 6.88-6.90 (d, 1H), 6.17-6.19 (d, $J = 11$ Hz, 1H), 6.09-6.14 (m, $J = 10.6$, $J = 7.3$, 1H), 1.61-1.63 (d, $J = 7.3$ Hz, 2H), 1.05-1.18 (m, 14H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 12.4, 13.6, 17.4, 17.7, 122.9, 124.9, 125.7,
127.6, 129.5, 130.2, 152.7. HRMS (ESI) calcd. for C_{15}H_{21}ClOSi [M]+H: 281.1128, found: 281.1132.

2,2-diisopropyl-7-nitro-2,3-dihydrobenzo[f][1,2]oxasilepine, 2f:

![2,2-diisopropyl-7-nitro-2,3-dihydrobenzo[f][1,2]oxasilepine](image)

Isolated yield = 33%, 19.2 mg. Endo : Exo = 32 : 1 (NMR Ratio)

$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 8.01-8.03 (m, 2H), 7.01-7.03 (d, 1H), 6.26-6.28 (d, $J = 11$, 1H), 6.18-6.23 (m, $J = 11$, $J = 7.3$, 1H), 1.66-1.67 (d, $J = 7.3$ Hz, 2H), 1.16-1.23 (m, 2H), 1.06-1.10 (dd, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 12.6, 13.6, 17.3, 17.5, 122.2, 123.4, 124.5, 127.1, 128.8, 130.5, 141.7, 159.6. HRMS (ESI) calcd. for C$_{15}$H$_{21}$NO$_3$Si [M]+$^+$:292.1369, found: 292.1372.

2,2-diisopropyl-9-methoxy-2,3-dihydrobenzo[f][1,2]oxasilepine, 2g:

![2,2-diisopropyl-9-methoxy-2,3-dihydrobenzo[f][1,2]oxasilepine](image)

Isolated yield = 90%, 49.7 mg. Endo : Exo = 99: 1 (NMR Ratio)

$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 6.87-6.90 (t, 1H), 6.76-6.78 (d, 2H), 6.25-6.27 (d, $J = 10.6$, 1H), 6.09-6.13 (m, $J = 11$, $J = 7.7$, 1H), 3.85 (s, 3H), 1.60-1.62 (d, $J = 7.3$ Hz, 2H), 1.07-1.20 (m, 14H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 12.1, 13.6, 17.4, 17.7, 55.8, 110.2, 120.7, 122.5, 125.7, 128.7, 129.4, 143.6, 151.5. HRMS (ESI) calcd. for C$_{16}$H$_{24}$O$_2$Si [M]+$^+$: 277.1624, found: 277.1629.

9-fluoro-2,2-diisopropyl-2,3-dihydrobenzo[f][1,2]oxasilepine, 2h:

![9-fluoro-2,2-diisopropyl-2,3-dihydrobenzo[f][1,2]oxasilepine](image)

Isolated yield = 74%, 39.1 mg. Endo : Exo = 99: 1 (NMR Ratio)

$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 6.93-6.97 (dt, 1H), 6.82-6.87 (m, 2H), 6.25-6.27 (d, $J = 10.6$, 1H), 6.10-6.15 (m, $J = 10.6$, $J = 7.3$, 1H), 1.64-1.65 (d, $J = 7.34$ Hz, 2H), 1.07-1.23 (m, 14H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 12.4, 13.6, 17.2, 17.4, 114.0, 114.2, 120.5, 120.6, 125.1, 125.2, 125.63, 125.66, 129.2, 130.8, 142.2, 142.3, 153.8, 155.8. HRMS (ESI) calcd. for C$_{15}$H$_{21}$FOSi [M]+$^+$: 265.1424, found: 261.1424.
(Z)-3,3-diisopropyl-3,4-dihydro-1H-benzo[f][1,2]oxasilocine, 2i:

\[
\text{Isolated yield } = 60\%, 31.2 \text{ mg. Endo : Exo : Dehal = 92 : 0 : 8 (GC Ratio)}
\]

\[\text{1}^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta \text{ ppm } 7.47-7.49 (d, 1H), 7.28-7.32 (m, 2H), 7.15-7.16 (d, 1H), 6.49-6.51 (d, } J = 11.0 \text{ Hz, 1H), 6.06-6.11 (m, } J = 10.8, J = 8.4, 1H), 4.71 (s, 2H), 1.39-1.41 (d, } J = 8.4 \text{ Hz, 2H), 0.99-1.1 (m, 14H).} \]

\[\text{1}^3\text{C NMR (126 MHz, CDCl}_3\text{): } \delta \text{ ppm } 126.1, 126.9, 127.2, 127.9, 128.0, 130.1, 131.1, 137.8.} \]

HRMS (ESI) calcd. for C\textsubscript{16}H\textsubscript{24}OSi[M]+H: 261.1675, found: 261.1677.

(Z)-4,4-diisopropyl-1,2,4,5-tetrahydrobenzo[f][1,2]oxasilonine and diisopropyl(methyl)(2-vinylphenethoxy)silane, 2j:

\[
\text{Isolated yield } = 33\% \text{ of compound A, 18 mg. Total yield } = 53\%, 29 \text{ mg.}
\]

Endo: Exo: Dehal = 1.6 : 0 : 1 (NMR Ratio)

\[\text{1}^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta \text{ ppm } 7.00-7.35 (m, 4H), 6.43-6.46 (d, } J = 10.8 \text{ Hz, 1H), 6.06-6.11 (m, } J = 10.8, J = 8.4, 1H), 4.10-4.13 (t, 2H), 2.83-2.87 (t, 2H), 1.37-1.40 (t, 2H), 0.93-1.1 (m, 14H).} \]

\[\text{1}^3\text{C NMR (126 MHz, CDCl}_3\text{): } \delta \text{ ppm } 12.9, 15.7, 17.5, 17.7, 65.1, 126.1, 126.9, 127.2, 128.6, 129.4, 130.0, 131.5, 139.3.} \]

HRMS (EI) calcd. for C\textsubscript{17}H\textsubscript{26}OSi[M]+H: 275.1831, found: 275.1829.

2,2-diisopropyl-3-phenyl-2,3-dihydrobenzo[f][1,2]oxasilepine, 2k

\[
\text{Isolated yield } = 67\%, 43.2 \text{ mg. Endo : Exo = } >99 : 1 \text{ (NMR Ratio)}.
\]

\[\text{1}^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta \text{ ppm } 7.29-7.32 (t, 2H), 7.13-7.25 (m, 4H), 6.98-7.06 (m, 3H), 6.33-6.36 (dd, 1H), 6.25-6.30 (m, 1H), 3.41-3.43 (dd, 1H), 1.07-1.37 (m, 14H).} \]

\[\text{1}^3\text{C NMR (126 MHz, CDCl}_3\text{): } \delta \text{ ppm } 12.4, 14.3, 17.3, 17.5, 18.0, 18.8, 36.9, 121.1, 121.6, 123.9, 125.3, 127.7, 127.8, 128.2, 128.3, 128.7, 130.9, 134.3, 140.7, 154.1.} \]

HRMS (EI) calcd. for C\textsubscript{21}H\textsubscript{26}OSi[M]+: 322.1753, found: 322.1756.
2,2-diisopropyl-5-phenyl-2,3-dihydrobenzo[f][1,2]oxasilepine, 2i:

\[
\text{Isolated yield } = 96\%, 62 \text{ mg. Endo: Exo} = 100:0 \text{ (NMR Ratio)} \]

1H NMR (500 MHz, CDCl\textsubscript{3}): δ ppm 7.20-7.30 (m, 6H), 7.06-7.07 (d, 1H), 6.91-6.96 (m, 2H), 6.33-6.36 (t, J = 8.1, 1H), 1.73-1.75 (d, J = 8.1 Hz, 2H), 1.16-1.24 (m, 2H), 1.09-1.11 (d, 12H).

13C NMR (126 MHz, CDCl\textsubscript{3}): δ ppm 13.4, 13.5, 17.5, 17.8, 121.3, 121.6, 126.0, 126.5, 128.0, 128.3, 130.7, 131.9, 137.1, 143.9 154.9. HRMS (ESI) calcd. for C\textsubscript{21}H\textsubscript{26}OSi[M]+H: 323.1831, found: 323.1830.

2,2-diisopropyl-4,5-diphenyl-2,3-dihydrobenzo[f][1,2]oxasilepine, 2m:

\[
\text{Isolated yield } = 64\%, 51 \text{ mg. Endo: Exo} = 100:0 \text{ (NMR Ratio)} \]

1H NMR (500 MHz, CDCl\textsubscript{3}): δ ppm 6.84-7.34 (m, 14H), 0.88-1.33 (m, 16H).

13C NMR (126 MHz, CDCl\textsubscript{3}): δ ppm 17.5, 17.8, 21.3, 121.9, 122.1, 125.8, 126.2,127.5, 127.7, 128.1, 128.4, 129.7, 130.1, 131.7, 132.6, 133.6, 133.9, 137.3, 143.9, 144.1. HRMS (ESI) calcd. for C\textsubscript{27}H\textsubscript{30}OSi [M]+H: 398.2066, found: 398.2071.

2,2-diisopropyl-4-vinyl-3,4-dihydro-2H-benzo[e][1,2]oxasiline, 2n, and other isomers, 2n’, 2n”, 2n”’.

\[
\text{Isolated yield } = 78\%, 40.6 \text{ mg. Ratio } = 4.8 : 3.8 : 1.4 : 1 \]

1H NMR (500 MHz, CDCl\textsubscript{3}): δ ppm only olefinic proton were analyzed: 2n’ = 6.10 (s, 3.8H), 2n”’= 5.66-5.71 (q, 1H), 2n”’=5.50 – 5.55 (q, 1.4H), 2n= 5.08-5.17 (dd, 4.8H). 13C NMR (500 MHz, CDCl\textsubscript{3}): δ ppm – See below. HRMS (ESI) calcd. for C\textsubscript{16}H\textsubscript{24}OSi [M]+H: 261.165, found: 261.1672
2,2-diisopropyl-4-(prop-1-en-2-yl)-3,4-dihydro-2H-benzo[e][1,2]oxasiline, 2o:

\[\text{O} \quad \text{Pr}\]
\[
\begin{array}{c}
\text{Me} \\
\end{array}
\]

Isolated yield = 76%, 41.7 mg. Endo : Exo = 0 : 100 (NMR Ratio)

\[^1\text{H} \text{NMR (500 MHz, CDCl}_3\]): \delta \text{ppm 7.11-7.14(t, 1H), 6.99-7.01 (d, 1H), 6.90-6.92 (d, 1H), 6.84-6.88 (t, 1H), 4.87-5.02 (d, 2H), 3.62-3.65 (dd, 1H), 1.85 (s, 3H) 0.99-1.24 (m, 16H).} \]

\[^{13}\text{C} \text{NMR (126 MHz, CDCl}_3\): \delta \text{ppm 11.1, 12.8, 13.2, 16.9, 17.1, 17.3, 19.8, 43.5,112.9, 119.6, 120.5, 127.6, 127.9, 130.9, 147.9, 155.4.} \]

HRMS (ESI) calcd. for C\(_{17}\)H\(_{26}\)OSi [M]+H: 275.1831, found: 275.1828

2-diisopropyl-4a,9b-dimethyl-5-methylene-2,3,4,4a,5,9b-hexahydroindeno[2,1-e][1,2]oxasiline, 2p:

\[\text{O} \quad \text{Pr}\]
\[
\begin{array}{c}
\text{Me} \\
\end{array}
\]

Isolated yield = 87%, 54.7 mg.

\[^1\text{H} \text{NMR (500 MHz, CDCl}_3\]): \delta \text{ppm 7.44-7.46 (d, 2H), 7.23-7.32 (m, 2H), 5.47 (s, 1H), 4.89 (s, 1H), 1.78- 1.86 (m, 1H), 1.68-1.75 (m, 1H), 1.31 (s, 3H), 1.25 (s, 3H), 1.09 -1.11 (d, 3H), 1.02-1.03 (d, 3H), 0.76-0.80 (m, 7H), 0.64-0.73 (m, 2H), 0.54-0.61 (m, 1H).} \]

\[^{13}\text{C} \text{NMR (126 MHz, CDCl}_3\): \delta \text{ppm 1.4, 13.2, 13.4, 16.9, 17.1, 17.3, 17.5, 20.7, 28.0, 33.3, 51.2, 84.32, 102.2, 120.5, 123.4, 127.6, 128.6, 137.5, 150.6.} \]

HRMS (EI) calcd. for C\(_{20}\)H\(_{30}\)O\(_2\)Si [M]+: 315.2144, found: 315.2145.

Steroid, 2q.

\[\text{O} \quad \text{Pr}\]
\[
\begin{array}{c}
\text{Me} \\
\end{array}
\]

Isolated yield = 82%, 67 mg. Endo : Exo = 99 : 1 (NMR Ratio)

\[^1\text{H} \text{NMR (500 MHz, CDCl}_3\): \delta \text{ppm 6.99 (s, 1H), 6.70 (s, 1H), 6.23-6.25 (d, J=11 Hz, 1H), 5.98-6.03 (m, J=11 Hz, J=7.7 Hz, 1H), 2.82 (t,2H), 2.19-2.29, (m, 2H), 1.86-1.93 (m, 2H), 1.65- 1.78 (m, 3H) 1.61-1.62 (d, J= 7.7 Hz, 2H), 1.49-1.56 (m, 3H), 1.31-1.40 (m, 3H), 1.21-1.30 (m, 3H),} \]

s25
1.06-1.18 (m, 14H) 0.75 (s, 3H). $^{13}$C NMR (126MHz, CDCl$_3$): δ ppm 12.4, 13.6, 13.7, 17.5, 17.6, 17.7, 20.6, 25.2, 26.7, 28.2, 29.4, 38.9, 39.1, 40.5, 41.1, 44.0, 53.6, 121.2, 125.3, 126.5, 127.1, 127.8, 133.3, 136.8, 151.8. HRMS (EI) calcd. for C$_{27}$H$_{40}$OSi [M]+H: 408.2848, found: 408.2854.

**Silyl Methyl Heck reaction of aliphatic systems, 4a-4j:**

2,2-diisopropyl-7-propyl-2,3,4,7-tetrahydro-1,2-oxasilepine, 4a:

![Structural diagram of 4a](image)

Isolated yield = 65%, 31.2 mg. Endo : Exo = >50 : 1 (NMR Ratio).

$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 5.81-5.85 (m, J = 10.6 Hz, 1H), 5.47-5.52 (m, J = 10.6, 1H), 3.91-3.94 (m, 1H), 2.17-2.32 (m, 2H), 1.57-1.64 (m, 2H), 1.42-1.53 (m, 2H), 1.30-1.39 (m, 2H), 0.98-1.09 (m, 12H), 0.88-0.92 (t, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 11.6, 12.9, 13.1, 14.1, 17.5, 17.7, 19.1, 36.9, 40.9, 72.3, 126.0, 127.5. HRMS (ESI) calcd. for C$_{14}$H$_{28}$OSi [M]+: 241.1988, found 241.1991.

2,2-diisopropyl-7-pentyl-2,3,4,7-tetrahydro-1,2-oxasilepine, 4b:

![Structural diagram of 4b](image)

Isolated yield = 76% 40.8 mg. Endo : Exo = 36 : 1 (NMR Ratio) $^1$H NMR (500 MHz, CDCl$_3$): δ ppm 5.81-5.85 (m, J = 10.6 Hz, 1H), 5.47-5.51 (m, J = 10.6, 1H), 3.89-3.93 (m, 1H), 2.19-2.31 (m, 2H), 1.58-1.63 (m, 2H), 1.41-1.52 (dd, 2H), 1.26-1.38 (m, 10H), 0.98-1.09 (m, 14H), 0.87-0.92 (m, 5H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 11.6, 12.9, 13.2, 14.1, 17.5, 17.6, 17.7, 22.7, 25.6, 29.7, 31.8, 36.9, 38.7, 72.6, 126.0, 127.6. HRMS (ESI) calcd. for C$_{16}$H$_{32}$OSi [M]+: 269.2301, found: 269.2302.

2,2-diisopropyl-7-phenyl-2,3,4,7-tetrahydro-1,2-oxasilepine, 4c:

![Structural diagram of 4c](image)

Isolated yield = 83%, 45.5 mg, isomers are separable.

$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 7.40-7.41 (t, 2H), 7.32-7.36 (t, 2H), 7.23-7.26 (t, 1H), 5.92-5.97 (d, J = 11 Hz, 1H), 5.53-5.58 (m, J = 11, 1H), 5.11-5.12 (d, 1H), 2.56-2.62 (m, 1H), 2.45-2.50 (m, 1H), 1.75-1.80 (dd, 1H), 1.66-1.71 (dd, 1H), 0.99-1.21 (m, 14H). $^{13}$C NMR (126 MHz,
CDCl$_3$; δ ppm 11.6, 12.9, 13.1, 17.6, 17.7, 17.8, 40.1, 74.3, 125.3, 125.8, 126.7, 128.0, 128.2, 145.8. HRMS (ESI) calcd. for C$_{17}$H$_{26}$OSi [M]+H: 275.1831, found: 275.1825.

2,2-diisopropyl-7,7-dipropyl-2,3,6,7-tetrahydro-1,2-oxasilepine, 4d:

Isolated yield = 80%, 45.2 mg. Endo : Exo = 25 : 1 (NMR Ratio) 
$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 5.90-5.95 (m, $J = 10.6$ Hz, 1H), 5.44-5.50 (m, $J = 11$, 1H), 2.26-2.27 (d, 2H), 1.58-1.59 (d, 2H), 1.43-1.47 (m, 1H), 1.20-1.47 (m, 6H), 1.07-1.11 (t, 4H), 0.99-0.98 (m, 12H), 0.85-0.91 (t, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm: 12.0, 13.1, 13.9, 14.8, 17.3, 17.4, 17.70, 17.73, 74.3, 38.0, 42.0, 77.2, 124.5, 129.3. HRMS (ESI) calcd. for C$_{17}$H$_{34}$OSi [M]+H: 283.2457, found: 283.2461.

8,8-diisopropyl-7-oxa-8-silaspiro[5.6]dodec-10-ene, 4e:

Isolated yield = 75%, 39 mg. Endo : Exo = 16 : 1 (NMR Ratio) 
$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 5.90-5.95 (m, $J = 10.6$ Hz, 1H), 5.47-5.52 (m, $J = 10.6$, 1H), 2.26-2.27 (d, 2H), 1.58-1.68 (m, 6H), 1.16-1.42 (m, 6H), 0.99-1.01 (dd, 12H), 0.86-0.91 (m, 2H), 1.04-1.21 (m, 14H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm: 11.8, 13.9, 13.1, 17.4, 17.5, 17.7, 17.8, 22.3, 26.2, 38.8, 40.1, 73.6, 124.2, 129.1. HRMS (ESI) calcd. for C$_{16}$H$_{30}$OSi [M]+H: 267.2144, found: 267.2146.

8,8-diisopropyl-7-oxa-8-silaspiro[5.6]dodec-10-ene, 4f:

Isolated yield = 71%, 35.8 mg. Endo : Exo = 50 : 1 (NMR Ratio) 
$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 5.72-5.77 (m, $J = 10.6$ Hz, 1H), 5.11-5.14 (m, $J = 10.6$, 1H), 3.58-3.62 (m, 1H), 2.22-2.23 (d, 1H), 1.98-2.01 (m, 1H), 1.50-1.74 (m, 5H), 1.09-1.35 (m, 4H) 0.88-1.02 (m, 14H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm: 11.3, 12.2, 13.23, 13.8, 17.5, 17.7, 17.8, 25.1, 25.5, 32.6, 36.4, 46.4, 75.2, 125.2, 132.5. HRMS (ESI) calcd. for C$_{15}$H$_{28}$OSi [M]+H: 253.1988, found: 253.1990.
2,2-diisopropyl-5-phenyl-2,3,6,7-tetrahydro-1,2-oxasiline, 4g and 2,2-diisopropyl-5-phenyl-2,3,4,7-tetrahydro-1,2-oxasiline, 4g'.

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\text{4g} \quad : \quad \text{4g'}

Isolated yield = 80%, 44 mg. 4g : 4g' = 7 : 1 (NMR Ratio)

\( { }^1 \text{H NMR (500 MHz, CDCl}_3 \text{)}: \delta \text{ ppm 7.29-7.36 (m, 5H), 6.21-6.24 (t, 1H), 4.05-4.08 (t, 2H), 2.86-2.88 (t, 2H), 1.82-1.85 (d, 2H), 0.98-1.07 (m, 14H).} \)

\( { }^{13} \text{C NMR (126 MHz, CDCl}_3 \text{)}: \delta \text{ ppm 13.1, 17.6, 17.7, 34.9, 63.6, 125.5, 126.1, 126.3, 128.3, 137.4, 143.5. HRMS (ESI) calcd. for C}_{17}H_{26}OSi [M]+H: 275.1831, \text{found: } 274.1833. \)

(E)-2,2-diisopropyl-5-phenyl-3,6,7,8-tetrahydro-2H-1,2-oxasiloline, 4h and (E)-2,2-diisopropyl-5-phenyl-3,4,7,8-tetrahydro-2H-1,2-oxasiloline, 4h'.

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\text{4h} \quad : \quad \text{4h'}

Isolated yield = 85%, 49 mg. 4h : 4h' = 17 : 1 (NMR Ratio)

\( { }^1 \text{H NMR (500 MHz, CDCl}_3 \text{)}: \delta \text{ ppm 7.38-7.40 (d, 2H), 7.29-7.34 (t, 2H), 7.20-7.23 (t, 1H), 6.18-6.22 (t, 1H), 3.71-3.74 (t, 2H), 2.71-2.74 (t, 2H), 1.80-1.82 (d, 2H), 1.72-1.78 (m, 2H), 1.08-1.15 (m, 12H), 0.94-1.04 (m, 2H).} \)

\( { }^{13} \text{C NMR (126 MHz, CDCl}_3 \text{)}: \delta \text{ ppm 12.6, 14.85, 17.6, 17.8, 24.5, 30.2, 60.6, 124.9, 125.6, 126.3, 128.4, 135.9, 142.1. HRMS (EI) calcd. for C}_{18}H_{28}OSi [M]+: 289.1988, \text{found: } 289.1992. \)

E)-2,2-diisopropyl-5-phenyl-2,3,6,7,8,9-hexahydro-1,2-oxasilonine, 4i, and diisopropyl(methyl)(5-phenylhex-5-enyloxy)silane, 4i'.
Total yield = 88%, 53.2 mg. 4i : 4i' = 1 : 1 (NMR Ratio), Yield of 4i = 44%, 26.6 mg.

1H NMR (500 MHz, CDCl3): δ ppm -only olefinic proton were analyzed: 4i = 5.59-5.63 (t, 1H), 4i' = 5.28 (s, 1H), 4i'' = 5.07 (s, 1H). 13C NMR (126 MHz, CDCl3): δ ppm – See below. HRMS (ESI) calcd. for C_{19}H_{30}OSi [M]+: 303.2144, found: 303.2142.

(5aR,8S,9aS)-2,2-diisopropyl-5,8-dimethyl-2,3,5a,6,7,8,9,9a-octahydrobenzo[f][1,2]oxasilepine, 4j, and (5aR,8S,9aS)-2,2-diisopropyl-8-methyl-5-methylenedecahydrobenzo[f][1,2]oxasilepine, 4j'.

Total yield = 90%, 50 mg. 4j : 4j' = 3.5 : 1 (NMR Ratio). Isomers are separable. Yield of 4j = 45%, 25.2 mg.

1H NMR (500 MHz, CDCl3): δ ppm of 4j = 4.80-4.84 (d, 2H), 3.51-3.56 (m, 1H), 2.33-2.39 (m, 1H), 2.21-2.26 (m, 1H), 1.93-2.05 (m, 2H) 1.55-1.64 (m, 2H), 1.42-1.46 (m, 1H), 1.26-1.36 (m, 1H), 0.91-1.11 (m, 19H), 0.76-0.83 (m, 2H). 13C NMR (126 MHz, CDCl3): δ ppm 11.8, 12.8, 13.7, 17.3, 17.5, 17.9, 22.1, 29.5, 31.7, 31.8, 34.5, 44.7, 53.3, 74.9, 111.7, 155.4. HRMS (ESI) calcd. for C_{17}H_{32}OSi [M]+H: 281.2301, found: 281.2302.
Part V: Synthetic Utility of the Silyl Methyl Heck reaction.

Ring opening:

(Z)-2-(3-(diisopropyl(methyl)silyl)prop-1-en-1-yl)phenol, 11:

![Chemical structure](image)

A 50 mL Schlenk flask equipped with a magnetic stir bar under Ar atmosphere was charged with compound 2a (0.611 g, 2.48 mmol, 1 eq) and 14 mL of dry THF. The mixture was cooled to -78 °C and 4.65 mL (7.44 mmol, 3 eq) methyllithium in diethylether (1.6 mol/L in Et₂O) was added drop-wise via syringe. Then, the reaction mixture was stirred at r.t. Upon completion (monitored by GC), the reaction was quenched with NH₄Cl solution (20 mL) at 0 °C and 35 mL of CH₂Cl₂ was added. The aqueous layer was extracted 3x with 30 mL of CH₂Cl₂. The combined extracts were washed with brine and then dried with Na₂SO₄. The organic layer was concentrated in vacuo and the crude product was purified by silica gel column chromatography (EA: Hexanes – 1:50) to produce compound 11 as a clear and colorless oil (70%, 456 mg).

¹H NMR (500 MHz, CDCl₃): δ ppm 7.16 (t, J = 7.3 Hz, 1 H), 7.09 (d, J = 7.3 Hz, 1 H), 6.92 - 6.87 (m, 2 H), 6.21 (d, J = 11.2 Hz, 1 H), 6.05 - 6.00 (m, 1 H), 5.16 (s, 1 H), 4.98 (d, J = 1.1 Hz, 2 H), 0.91 - 0.88 (m, 12 H), 0.12 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ ppm 9.2, 11.8, 14.3, 17.9, 114.9, 120.7, 128.4, 129.7, 134.3. HRMS (EI) calcd. for C₁₆H₂₇OSi [M]+: 263.1831, found: 263.1833.

Intramolecular Hosomi-Sakurai Reaction:

3-vinyl-3H-spiro[benzofuran-2,1'-cyclohexane], 12:

![Chemical structure](image)

A 2 mL vial equipped with a magnetic stir bar under Ar atmosphere was charged with compound 11 (100 mg, 0.38 mmol) and 1,1-dimethoxycyclohexane (66 mg, 0.46 mmol) with 1 mL of CH₂Cl₂. The reaction mixture was cooled to -78 °C, followed by addition of boron trifluoride diethyletherate (108 mg, 0.76 mmol). The reaction mixture was stirred at r.t. for 60-90 min. Upon the completion (monitored by GC), the reaction was quenched with 5% NaHCO₃ solution (2 mL). The aqueous layer was extracted 3x with 3 mL of CH₂Cl₂. The combined organic layers
was then washed with brine and dried with Na$_2$SO$_4$. The organic layer was concentrated \textit{in vacuo} and the crude product was purified by silica gel column chromatography (EA: Hexanes = 1 : 100) to produce 12 as a clear and colorless oil (91%, 74 mg).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ ppm 7.13 (t, $J = 7.7$ Hz, 1 H), 7.05 (d, $J = 7.4$ Hz, 1 H), 6.83 (dt, $J = 7.3$, 0.7 Hz, 1 H), 6.78 (d, $J = 7.7$ Hz, 1 H), 5.88 - 5.81 (m, 1 H), 5.21 - 5.17 (m, 2 H), 3.62 (d, $J = 9.5$ Hz, 1 H), 1.89 - 1.26 (m, 10 H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ ppm 22.2, 22.7, 25.4, 32.1, 37.1, 56.8, 90.6, 109.8, 117.4, 120.0, 125.4, 128.4, 130.0, 136.0, 158.3. HRMS (EI) calcd. for C$_{15}$H$_{19}$O [M]$^+$: 215.1436, found: 215.1434.

Oxidation:

Tamao oxidation of 2a and 2q: A 10 mL flask, containing a stirring bar, was charged with 2a (24.6 mg, 0.1 mmol) or 2r (40.8 mg, 0.1 mmol), KHCO$_3$ (100 mg, 1 mmol), and DMF (1 mL) and 50%. H$_2$O$_2$ (80 µL) was added via syringes under argon atmosphere. The reaction mixture was heated at 70 °C for 6h. The reaction was then cooled to room temperature, followed by addition of KF on Al$_2$O$_3$ (36.5 mg, 0.3 mmol). The reaction mixture was stirred for another 4h at room temperature. The product was purified by silica gel column chromatography (eluent: hexanes/AcOEt 4:1 – 1:1) to give 10 or 14 as white solids.

Z)-2-(3-hydroxyprop-1-en-1-yl)phenol, 10:

\[
\begin{align*}
&\text{ HO} \\
&\text{ HO} \\
&\text{ HO} \\
&\text{ HO}
\end{align*}
\]

Isolated yield = 87%, 13 mg.

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ ppm 9.46 (s, 1 H), 7.07 (t, $J = 7.7$ Hz, 1 H), 7.01 (d, $J = 7.4$ Hz, 1 H), 6.81 (d, $J = 8.0$ Hz, 1 H), 6.75 (t, $J = 7.3$ Hz, 1 H), 6.51 (d, $J = 12.2$ Hz, 1 H), 5.74 - 5.69 (m, 1 H), 4.76 (t, $J = 5.2$ Hz, 1 H), 4.15 - 4.12 (m, 2 H). $^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ ppm 58.7, 115.6, 118.9, 123.9, 124.9, 128.9, 130.4, 132.5, 155.4. HRMS (EI) calcd. for C$_9$H$_{10}$O$_2$ [M]$^+$: 150.0681, found: 150.0679. (Ele- loss of water) HRMS (EI) calcd. for C$_9$H$_9$O [M]$^+$: 133.0653, found: 133.0655.

(8S,9S,13S,14S)-2-((Z)-3-hydroxyprop-1-enyl)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-ol, 14:

\[
\begin{align*}
&\text{ HO} \\
&\text{ HO} \\
&\text{ HO} \\
&\text{ HO}
\end{align*}
\]

Yield after extraction = 80%, 25 mg. A small portion was recrystallized in DCM for NMR spectra.
1H NMR (500 MHz, DMSO-d6): δ ppm 9.12 (s, 1H), 6.90 (s, 1H), 6.48 (s, 1H), 5.62-5.67 (m, 1H), 4.72-4.74 (t, 1H), 4.13-4.15 (t, 3H), 2.65-2.71 (m, 2H), 2.49 (s, 2H), 2.20-2.23 (d, 1H), 2.09-2.12 (t, 1H), 1.79-1.81 (d, 2H), 1.59-1.71 (m, 3H), 1.43-1.47 (t, 1H), 1.26-1.37 (m, 3H), 1.16-1.26 (m, 4H), 1.06-1.12 (m, 1H), 0.7 (s, 3H).

13C NMR (126 MHz, DMSO-d6): δ ppm 17.9, 20.6, 25.2, 26.9, 28.1, 29.4, 30.9, 38.8, 39.3, 41.1, 43.8, 53.4, 58.8, 115.3, 121.4, 125.2, 125.4, 127.2, 130.5, 131.5, 131.9, 136.9, 153.0.

HRMS (ESI) calcd. for C21H28O2 [M]+Na: 325.1987, found: 325.1986.

Woerpel oxidation of 2p. To an ice-cooled (0 °C) stirred solution of KH (57.8 mg, 1.44 mmol, dry powder, 95%) in 1.5 mL of NMP was added tert-butyl hydroperoxide (0.22 mL, 5.0 ~ 6.0 M in decane) dropwise. The mixture was allowed to warm up to room temperature and kept for 10 min, then was added a solution of 2p (38 mg, 0.12 mmol) in 1.2 mL of NMP. The mixture was stirred overnight and then 1.5 mL TBAF (0.6 mmol, 1.0 M solution in THF) was added. The mixture was stirred for another 3h and cooled to 0°C. 1.0 g of Na2S2O3•5H2O and 5.0 mL of water were added. The mixture was stirred at 0°C for 30 min and neutralized of addition of NH4Cl. The mixture was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with H2O (4 × 10 mL) and brine (10 mL), dried (Na2SO4), and concentrated. Flash silica gel column chromatography (1:2 – 1:1 EtOAc/hexanes) purification of the residue gave 13 as a white solid.

(1S,2S)-2-(2-hydroxyethyl)-1,2-dimethyl-3-methylene-2,3-dihydro-1H-inden-1-ol, 13:

Isolated yield = 82%, 22 mg.

1H NMR (500 MHz, CDCl3): δ ppm 7.42-7.46 (dd, 2H), 7.25-7.32 (m, 2H), 5.55 (s, 1H), 4.94 (s, 1H), 3.54-3.58 (m, 1H), 3.31-3.36 (m, 1H), 2.00-2.06 (m, 1H), 1.71 (bs, 1H), 1.59-1.63 (m, 1H), 1.32 (s, 3H), 1.26 (bs, 1H), 1.24 (s, 3H).

13C NMR (126 MHz, CDCl3): δ ppm 21.9, 26.9, 41.7, 59.3, 81.8, 103.4, 120.2, 122.9, 128.1, 129.1, 150.6, 154.9 HRMS (APCG) calcd. for C14H28O2 [M]-H2O: 200.1201, found 200.1207.
Part VI: Mechanistic Studies:

Table S2: Radical Traps Studies

![Chemical structure diagram]

| Additive       | GC Yield Endo | Endo : Exo Ratio |
|----------------|---------------|-----------------|
| - None         | 92%           | 40 : 1          |
| - BHT          | 92%           | 40 : 1          |
| - Galvinyloxy  | 68%           | 19 : 1          |
| - TEMPO        | NR            | -               |

Radical Clock Experiments:

(2-(1-cyclopropylvinyl)phenoxy)(iodomethyl)diisopropylsilane, 5a:

![Chemical structure diagram]

Coupling of cp2 with chloro(iodomethyl)diisopropylsilane using Method A. Isolated yield = 70%, 870 mg.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ ppm 7.18 - 7.15 (m, 2 H), 6.95 (t, $J$ = 7.3 Hz, 1 H), 6.87 (d, $J$ = 8.5 Hz, 1 H), 5.08 (s, 1 H), 4.96 (s, 1 H), 2.26 (s, 2H), 1.78 - 1.75 (m, 1 H), 1.46 - 1.40 (m, 2 H), 1.17 (d, $J$ = 7.3 Hz, 6 H), 1.13 (d, $J$ = 7.3 Hz, 6 H), 0.73 - 0.70 (m, 2 H), 0.52 – 0.48 (m, 2 H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ ppm 7.0, 12.6, 16.9, 17.4, 17.7, 111.3, 119.3, 121.4, 128.1, 130.5, 133.7, 149.6, 152.0. HRMS (ESI) calcd. for C$_{18}$H$_{27}$OISi [M]+H: 414.0954, found: 414.0952
(iodomethyl)diisopropyl(2-(1-(2-phenylcyclopropyl)vinyl)phenoxy)silane, 5b:

Coupling of cp3' with chloro(iodomethyl)diisopropylsilane using Method C. Isolated yield = 47%, 691 mg.

$^1$H NMR (500 MHz, CDCl$_3$) δ ppm 7.23-7.26 (t, 2H), 7.12-7.16 (m, 3H), 7.06-7.08 (d, 2H), 6.92-6.95 (t, 1H), 6.83-6.85 (d, 1H), 5.15 (s, 1H), 5.02 (s, 1H), 2.19 (s, 2H), 2.02-2.06 (m, 1H), 1.93-1.97 (m, 1H), 1.35-1.41 (m, 2H), 1.15-1.22 (m, 2H), 1.06-1.12 (m, 14H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ ppm 12.6, 17.3, 17.7, 25.7, 29.1, 111.9, 119.3, 121.4, 125.5, 125.8, 128.2, 128.3, 130.5, 133.3, 142.8, 148.2, 152.1. HRMS (ESI) calcd. for C$_{24}$H$_{31}$OISi [M]+H: 491.1268, found: 491.1267.

(E)-2,2-diisopropyl-5-(prop-1-en-1-yl)-2,3-dihydrobenzo[f][1,2]oxasilepine, 7a, 9a:

Isolated yield = 58%, 33.2 mg. Endo : Exo = >99 : 1 (NMR Ratio), 7a : 9a = 1 : 1, Isomers are separable. Reaction run at 110°C for 36h. Isolated yield = 68%, 38.9 mg, 7a : 9a = 0 : 100

7a
$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 7.13-7.19 (m, 2H), 6.88-7.00 (m, 2H), 6.70-6.78 (m, 1H), 6.14-6.20 (m, 1H), 4.91-5.32 (m, 2H), 2.67-2.74 (m, 2H), 0.97-1.22 (m, 16H). HRMS (EI) calcd. for C$_{17}$H$_{26}$OSi [M]+H: 286.1753, found: 286.1750.

9a
$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 7.16-7.19 (t, 1H), 6.96-7.01 (d, 1H), 6.15-6.19 (d, 1H), 5.97-5.99 (t, 1H), 5.44-5.48 (m, 1H), 1.72-1.74 (d, 3H), 1.56-1.57 (d, 1H), 1.06-1.17 (m, 14H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 12.6, 13.3, 17.5, 17.7, 18.2, 120.9, 121.8, 124.3, 125.7, 128.1, 128.7, 131.3, 133.9, 135.1, 154.1. HRMS (EI) calcd. for C$_{18}$H$_{26}$OSi [M]+H: 286.1753, found: 286.1753.
(5E/Z)-2,2-diisopropyl-5-(3-phenylallylidene)-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepine, 7b:

\[
\begin{align*}
&\text{O} \quad \text{Si} \quad \text{Pr} \\
&\text{Ph} \quad \text{Si} \quad \text{Pr}
\end{align*}
\]

Isolated yield = 91%, 66 mg. Trans : Cis = 7 : 1

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.51-7.53 (d, 2H), 7.37-7.40 (t, 2H), 7.19-7.30 (m, 5H), 6.95-6.98 (m, 2H), 6.68-6.71 (d, 1H), 6.37-6.39 (d, 1H), 2.87-2.90 (m, 2H), 1.15-1.18 (m, 2H), 1.04-1.14 (m, 14H). \(^1^3\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm 10.4, 13.2, 17.1, 17.2, 26.1, 120.9, 121.2, 124.7, 126.4, 126.5, 127.5, 128.6, 128.7, 129.1, 129.9, 133.3, 153.6. HRMS (ESI) calcd. for C\(_{24}\)H\(_{30}\)O\(_5\)Si [M]+H: 363.2144, found: 363.2139.

**Deuterium Labeled Study:**

\[
\begin{align*}
&\text{OH} \\
&\text{D} \\
\end{align*}
\]

Coupling of (Z)-2-(vinyl-2-d)phenol\(^{15}\) with chloro(iodomethyl)diisopropylsilane using Method A. Isolated yield = 51%, 574 mg. 88% D-incorporation.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.50 (dd, J = 7.7, 1.5 Hz, 1 H), 7.12-7.15 (m, 1 H), 7.07-7.09 (m, 1H), 6.96 (t, J = 7.3 Hz, 1 H), 6.84 (d, J = 8.1 Hz, 1 H), 5.68 (d, J = 17.7 Hz, 0.1 H), 5.25 (d, J = 11.0 Hz, 0.9 H), 2.24 (s, 2 H), 1.40-1.46 (m, 2 H), 1.16 (s, 3 H), 1.15 (s, 3 H), 1.14 (s, 3H), 1.12 (s, 3H). \(^1^3\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) ppm -21.3, 12.7, 17.4, 17.7, 113.6, 114.0, 119.4, 121.8, 126.3, 128.7, 129.0, 131.8, 152.3. \(^2\)H NMR (500 MHz, CCl\(_4\)): \(\delta\) ppm 5.99-6.02. HRMS (EI) calcd. for C\(_{15}\)H\(_{22}\)DOSi [M]+: 376.0704, found: 376.0704
**Rationale for Deuterium labeled study:**

In order to verify whether the cyclization step follows the classical Heck or radical pathway, we performed the following studies. Thus, 1ad, possessing a Z-deuterium moiety was tested in the endo-selective cyclization reaction. In the event that the cyclization occurs via a classical migratory insertion (carbopalladation) path, it would produce a stereo defined alkyl palladium species, which will undergo a β-hydride elimination with complete preservation of the deuterium label. In contrast, upon radical cyclization, the recombination of an alkyl radical with Pd(I) could occur from either face, thus producing non-stereodefined alkyl palladium intermediate, which in turn, upon a subsequent β-hydride elimination would produce a product with scrambled deuterium label at the alkene moiety. The experiments completely confirmed the latter scenario and hence are in agreement with the radical path for this cyclization reaction.

**Scheme S1: Rationale for Deuterium labeled study. Mechanism of Pd-mediated pathway (above) and radical hybrid pathway (below)**

**Result:**

Isolated yield = 74%, 36.5 mg. Endo : Exo = 28 : 1.

$^1$H NMR (500 MHz, CDCl$_3$): δ ppm 7.13-7.16 (t, 1H), 7.07-7.09 (d, 2H), 6.93-6.99 (m, 2H), 6.27-6.29 (m, 1H), 6.06-6.11 (m, 0.53H), 1.62-1.63 (m, 2H), 1.15-1.23 (m, 2H), 1.07-1.14 (m, 14H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ ppm 12.2, 12.3, 13.6, 17.4, 17.7, 120.9, 121.6, 125.9,
128.1, 128.4, 130.9, 154.1. $^2$H NMR (500 MHz, CCl$_4$): $\delta$ ppm 6.36. LRMS calcd. for C$_{15}$H$_{21}$DOSi[M]+: 247.1503, found: 247.1500.

**Hydro-Dehalogenation Side Product Studies:**
Since cyclization of 3i produced substantial amounts of hydro-dehalogenated by-product, in order to verify the nature of this side reaction, we performed it in PhMe-$d_8$. The $^2$H NMR and GC/MS analyses indicated a substantial incorporation of deuterium into a silyl methyl moiety, thus confirming a radical nature of the hydro-dehalogenation process.

![Reaction Scheme](image)

**Applying our Conditions to Substrates Possessing β-Hydrogens:**
We also verified whether this endo-selective method could be applied to simple substrates possessing β-Hydrogens. Thus, we applied our optimized conditions to cyclization of haloalkene 15. However, in the cyclization of alkenyl bromide, formation of an exo-cyclization product was observed in low overall yield, whereas the products of premature beta hydride elimination as a major byproduct were formed in the case of alkenyl iodide. This study entails that the silane moiety is required for the observed endo-selectivity.

![Reaction Scheme](image)
Part VII: Spectral Data

Spectral Data of the Starting Materials:

$^1$H Spectrum of cp1

[Graph showing $^1$H Spectrum of cp1]

$^{13}$C Spectrum of cp1

[Graph showing $^{13}$C Spectrum of cp1]
$^1$H Spectrum of cp2

$^{13}$C Spectrum of cp2
$^1$H Spectrum of cp3

$^{13}$C Spectrum of cp3
$^1$H Spectrum of cp3’

$^{13}$C Spectrum of cp3’
$^1$H Spectrum of cp4

$^{13}$C Spectrum of cp4
$^1$H Spectrum of ca1

$^{13}$C Spectrum of ca1
$^1$H Spectrum of ClSi($^i$Pr)$_2$CH$_2$I

$^1$C Spectrum of ClSi($^i$Pr)$_2$CH$_2$I
$^1$H Spectrum of 1a

$^{13}$C Spectrum of 1a
$^1$H Spectrum of 1b

$^{13}$C Spectrum of 1b
$^1$H Spectrum of 1c

$^{13}$C Spectrum of 1c
$^1$H Spectrum of 1d

$^{13}$C Spectrum of 1d
$^1$H Spectrum of 1e

$^1$C Spectrum of 1e
$^1$H Spectrum of 1f

$^{13}$C Spectrum of 1f
1H Spectrum of 1g

13C Spectrum of 1g
$^1$H Spectrum of $1h$

$^{13}$C Spectrum of $1h$
**$^1$H Spectrum of 1i**

![$^1$H Spectrum of 1i](image1)

**$^{13}$C Spectrum of 1i**

![$^{13}$C Spectrum of 1i](image2)

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S53
$^1$H Spectrum of 1j

$^{13}$C Spectrum of 1j
$^1$H Spectrum of 1k

$^{13}$C Spectrum of 1k
$^1$H Spectrum of 11

$^{13}$C Spectrum of 11
$^1$H Spectrum of 1m

$^{13}$C Spectrum of 1m
$^1$H Spectrum of 1n

$^{13}$C Spectrum of 1n
$^1$H Spectrum of 1o

$^{13}$C Spectrum of 1o
$^1$H Spectrum of 1p

$^{13}$C Spectrum of 1p
$^1$H Spectrum of 1q

$^{13}$C Spectrum of 1q
$^1$H Spectrum of 3a

$^{13}$C Spectrum of 3a
$^1$H Spectrum of 3b

$^{13}$C Spectrum of 3b
$^1$H Spectrum of 3c

$^{13}$C Spectrum of 3c
$^1$H Spectrum of 3d

$^{13}$C Spectrum of 3d
$^1$H Spectrum of 3e

$^{13}$C Spectrum of 3e
$^1$H Spectrum of 3g

$^{13}$C Spectrum of 3g
$^{1}H$ Spectrum of 3h

$^{13}C$ Spectrum of 3h
$^1$H Spectrum of 3i

$^{13}$C Spectrum of 3i
$^1$H Spectrum of 3j

$^{13}$C Spectrum of 3j
Spectral Data of the Products:

$^1$H Spectrum of 2a

$^{13}$C Spectrum of 2a

$^{13}$C DEPT Spectrum of 2a
$^1$H Spectrum of 2f

$^{13}$C Spectrum of 2f

$^{13}$C DEPT Spectrum of 2f
$^1$H Spectrum of 2j and 2j'

$^{13}$C Spectrum of 2j and 2j'
$^1$H Spectrum of 2k

$^1$C Spectrum of 2k

$^{13}$C DEPT Spectrum of 2k
$^1$H Spectrum of 2m

$^{13}$C Spectrum of 2m

$^{13}$C DEPT Spectrum of 2m
$^1$H Spectrum of $2n$, $2n'$, $2n''$, $2n'''$

$^{13}$C Spectrum of $2n$, $2n'$, $2n''$, $2n'''$
\(^1\)H Spectrum of \(2o\)

\(^{13}\)C Spectrum of \(2o\)

\(^{13}\)C DEPT Spectrum of \(2o\)
\(^1\)H Spectrum of 4a

\(^1\)C Spectrum of 4a

\(^1\)C DEPT Spectrum of 4a
\(^1\)H Spectrum of 4f

\(^{13}\)C Spectrum of 4f

\(^{13}\)C DEPT Spectrum of 4f
$^1$H Spectrum of 4g

$^{13}$C Spectrum of 4g

$^{13}$CDEPT Spectrum of 4g
$^1$H Spectrum of 4h

$^{13}$C Spectrum of 4h

$^{13}$C DEPT Spectrum of 4h
$^1$H Spectrum of 4i and 4'i

$^{13}$C Spectrum of 4i and 4'i

$^{13}$C Spectrum of 4i and 4'i
**$^1$H Spectrum of 5a**

![1H Spectrum of 5a](image1)

**$^1$H Spectrum of 5a**

![1H Spectrum of 5a](image2)
$^1$H Spectrum of 5b

$^{13}$C Spectrum of 5b
$^1$H Spectrum of 7a

$^1$H Spectrum of 9a
$^{13}\text{C}$ Spectrum of 9a

$^{13}\text{C}$ DEPT Spectrum of 9a
$^1$H Spectrum of 7b

$^{13}$C Spectrum of 7b

$^{13}$C DEPT Spectrum of 7b
\(^{1}H\) Spectrum of 11

\(^{13}C\) Spectrum of 11
\(^1\)H Spectrum of 12

\[^{13}\]C Spectrum of 12
$^1$H Spectrum of 13

$^{13}$C Spectrum of 13
$^1\text{H}$ Spectrum of 14

$^1\text{C}$ Spectrum of 14
$^1$H Spectrum of 2ad

$^{13}$C Spectrum of 2ad
$^{13}\text{C}$ DEPT Spectrum of 2ad

$^2\text{H}$ Spectrum of 2ad
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