Oxyallyl Cation Capture via Electrophilic Deborylation of Organoboronates: Access to $\alpha,\alpha'$-Substituted Cyclic Ketones

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Supporting Information

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1. General considerations

All reactions were carried out in oven- or flame-dried glassware under an argon atmosphere. THF, Et$_2$O, toluene, and CH$_2$Cl$_2$ were purged with argon and dried over activated alumina columns. Flash chromatography was performed on 60 Å silica gel (EMD Chemicals Inc.). Analytical thin layer chromatography was performed on EMD silica gel/TLC plates with fluorescent detector 254 nm. The $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded on a JEOL ECA-600, ECA-500, or ECX-400P spectrometer using residual solvent peak as an internal standard (CDCl$_3$: 7.26 ppm for $^1$H NMR and 77.2 ppm for $^{13}$C NMR). Analysis by HPLC was performed on a Shimadzu Prominence LC (LC-20AB) equipped with a SPD-20A UV-Vis detector and a Chiralpak or Chiralcel (250 mm x 4.6 mm) column. HRMS were acquired from the Mass Spectroscopy Laboratory of University of Houston using electrospray ionization (ESI-TOF) or electron impact (EI). Commercially available compounds were purchased from Aldrich, Acros, Ark Pharm, and Alfa Aesar and were used without further purification. Chemical names were generated using Cambridgesoft ChemBioDraw Ultra 12.0.
2. Reaction optimization

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\[\begin{array}{|c|c|c|c|}
\hline
\text{entry} & \text{catalyst} & \text{equiv} & \text{solvent} & \text{yield}^a \\
\hline
1 & Py\cdot\text{TfOH} & 1 & \text{CH}_2\text{Cl}_2 & - \\
2 & Py\cdot\text{TfOH} & 1 & \text{MeCN} & - \\
3 & \text{BA}^b & 1 & \text{CH}_2\text{Cl}_2 & <10 \\
4 & (n\text{-Bu})_4\text{NHSO}_4 & 0.5 & \text{CH}_2\text{Cl}_2 & - \\
5 & (n\text{-Bu})_4\text{NHSO}_4 & 0.5 & \text{PhMe} & - \\
6 & (n\text{-Bu})_4\text{NHSO}_4 & 0.5 & \text{MeCN} & 41 \\
7^c & (n\text{-Bu})_4\text{NHSO}_4 & 0.5 & \text{MeCN} & \text{trace} \\
8 & (n\text{-Bu})_4\text{NHSO}_4 & 0.5 & \text{MeOH} & 20 \\
9 & (n\text{-Bu})_4\text{NHSO}_4 & 0.5 & \text{HFIP} & 32 \\
10 & (n\text{-Bu})_4\text{NHSO}_4 & 0.5 & \text{THF} & - \\
11 & \text{Sc(OTf)}_3 & 0.2 & \text{MeCN} & 65 \\
12 & \text{Sc(OTf)}_3 & 0.5 & \text{MeCN} & 61 \\
13 & \text{Bi(OTf)}_3 & 0.2 & \text{MeCN} & 46 \\
14 & \text{Cu(OTf)}_2 & 0.2 & \text{MeCN} & 17 \\
15 & \text{La(OTf)}_3 & 0.2 & \text{MeCN} & 65 \\
16 & \text{LiBr} & 0.5 & \text{MeCN} & <5 \\
17 & \text{LiCl} & 0.5 & \text{MeCN} & 23 \\
18 & \text{LiOTf} & 0.5 & \text{MeCN} & 67 \\
19 & \text{LiClO}_4 & 0.5 & \text{MeCN} & 71 \\
20 & \text{LiPF}_6 & 0.5 & \text{MeCN} & 79 \\
21 & \text{LiPF}_6 & 0.5 & \text{HFIP} & \text{trace} \\
22 & \text{LiPF}_6 & 0.2 & \text{MeCN} & 26 \\
23 & \text{LiPF}_6\text{ and 4 Å MS} & 0.2 & \text{MeCN} & - \\
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\end{array}\]
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\(^a\text{Via }^1\text{H NMR integration relative to an internal standard. }^b\text{BA = TFAA, TfOH, and CSA. }^c\text{4-methoxylboronic acid was used.}\)
3. Starting material syntheses

3.1 General procedure A to synthesize cyclohexyl silyl enol ethers

According to a reported procedure,\(^1\) to a flame-dried flask equipped with a stir bar was subsequently added 1,2-cyclohexanedione (1.12 g, 10.0 mmol, 1.0 equiv), CH\(_2\)Cl\(_2\) (15 mL), TBSCI (1.66 g, 11.0 mmol, 1.1 equiv), and imidazole (885 mg, 13 mmol, 1.3 equiv) under argon atmosphere. The reaction was allowed to stir at room temperature for 24 hours. After the reaction completion as monitored by TLC, aqueous HCl (1 M, 5 mL) was added to quench the reaction. The organic layer was then extracted with CH\(_2\)Cl\(_2\) (50 mL x 2), washed with brine, dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The crude product was purified via column chromatography on silica gel with 5% diethyl ether in hexanes as eluent to give the ketone SI-2 (2.21 g, 98% yield) as a colorless liquid. Spectral data matched those reported in literature.\(^2\)

To a flame-dried flask equipped with a stir bar was added ketone SI-2 (678 mg, 3 mmol, 1 equiv) and CH\(_2\)Cl\(_2\) (25 mL). The reaction flask was then cooled to 0 °C before an appropriate solution of Grignard reagent was added dropwise over a period of 30 minutes. The reaction was allowed to warm to room temperature. After the reaction completion as monitored by TLC, the reaction was cooled to 0 °C, and water (5 mL) was added to quench the reaction. The crude mixture was passed through a Celite pad, extracted with CH\(_2\)Cl\(_2\) (50 mL x 2), washed with brine, dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The crude product was purified via column chromatography on silica gel with 5% diethyl ether in hexanes as eluent.

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6-((tert-butyldimethylsilyl)oxy)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-1-ol (1a)

The title compound was synthesized from phenylmagnesium bromide (4.5 mL, 4.5 mmol, 1.5 equiv) following general procedure A. After purification via flash column chromatography, the product was obtained in 82% yield (748 mg, 2.46 mmol) as a colorless liquid. \(^1\)H NMR: (500 MHz, CDCl\(_3\)): \(\delta 7.48\) (d, \(J = 7.5\) Hz, 2H), 7.30 (dd, \(J = 7.5, 7.5\) Hz, 2H), 7.23 – 7.20 (m, 1H), 5.07 (t, \(J = 4.0\) Hz, 1H), 2.78 (s, 1H), 2.26 – 2.10 (m, 2H), 2.09 – 2.00 (m, 1H), 1.95 – 1.90 (m, 1H), 1.68 – 1.59 (m, 1H), 1.49 – 1.45 (m, 1H), 0.70 (s, 9H), 0.18 (s, 3H), 0.06 (s, 3H). \(^13\)C NMR: (126 MHz, CDCl\(_3\)): \(\delta 150.7, 146.8, 127.8, 126.8, 126.2, 105.1, 75.5, 39.6, 25.5, 24.5, 19.2, 18.0, -4.2, -5.0\). IR (neat): 3449 (br), 2929, 2857, 1660, 1441, 1176, 917, 837 cm\(^{-1}\). HRMS-ESI m/z: [M+Na], calculated for C\(_{18}\)H\(_{28}\)NaO\(_2\)Si: 327.1756; found: 327.1749. \(R_f\) = 0.33 (silica gel, 5% EtOAc/hexane, UV).

6-((tert-butyldimethylsilyl)oxy)-4'-methoxy-1,2,3,4-tetrahydro-[1,1'-biphenyl]-1-ol (SI-4)

The title compound was synthesized from 4-methoxyphenylmagnesium bromide (4.5 mL, 4.5 mmol, 1.5 equiv) following general procedure A. After purification via flash column chromatography, the product was obtained in 89% yield (893 mg, 2.67 mmol) as a colorless liquid. Spectral data matched those reported in literature.\(^3\)

2-((tert-butyldimethylsilyl)oxy)-1-vinylcyclohex-2-enol (SI-5)

The title compound was synthesized from vinylmagnesium bromide (4.5 mL, 4.5 mmol, 1.5 equiv) following general procedure A. After purification via flash column chromatography, the product was obtained in 65% yield (495 mg, 1.95 mmol) as a colorless liquid. \textsuperscript{1}H NMR: (500 MHz, CDCl\textsubscript{3}): \(\delta\) 5.91 (dd, \(J = 17.3, 10.6\) Hz, 1H), 5.24 – 5.23 (m, 1H), 5.14 – 5.08 (m, 1H), 4.87 (dd, \(J = 3.9, 3.9\) Hz, 1H), 2.59 (s, 1H), 2.15 – 1.94 (m, 2H), 1.84 – 1.73 (m, 2H), 1.71 – 1.60 (m, 1H), 1.60 – 1.48 (m, 1H), 0.89 (s, 9H), 0.18 (s, 3H), 0.14 (s, 3H). \textsuperscript{13}C NMR: (126 MHz, CDCl\textsubscript{3}): \(\delta\) 150.4, 142.9, 113.6, 104.2, 73.6, 36.1, 25.8, 24.3, 19.3, 18.2, -4.3, -4.6. IR (neat): 3459 (br), 2930, 2858, 1662, 1242, 1174, 918, 828, 778 cm\textsuperscript{-1}. HRMS-ESI m/z: [M+H], calculated for C\textsubscript{14}H\textsubscript{27}O\textsubscript{2}Si: 255.1780; found: 255.1779.

R\textsubscript{f} = 0.33 (silica gel, 5% EtOAc/hexane, UV).

1-allyl-2-((tert-butyldimethylsilyl)oxy)cyclohex-2-enol (SI-6)

The title compound was synthesized from allylmagnesium bromide (4.5 mL, 4.5 mmol, 1.5 equiv) following general procedure A. After purification via flash column chromatography, the product was obtained in 76% yield (566 mg, 2.28 mmol) as a colorless liquid. Spectral data matched those reported in literature.\textsuperscript{3}

2-((tert-butyldimethylsilyl)oxy)-1-(phenylethynyl)cyclohex-2-enol (SI-7)

The title compound was synthesized from phenylethynylmagnesium bromide (4.5 mL, 4.5 mmol, 1.5 equiv) following general procedure A. After purification via flash column chromatography, the product was obtained in 92% yield (905 g, 2.76 mmol) as a colorless liquid. \textsuperscript{1}H NMR: (500 MHz, CDCl\textsubscript{3}): \(\delta\) 7.42 – 7.37 (m, 2H), 7.31 – 7.27 (m, 3H), 4.88 (t, \(J = 4.0\) Hz, 1H), 3.15 (s, 1H), 2.28 – 2.25 (m, 1H), 2.20 – 2.03 (m, 2H), 2.01 – 1.91 (m, 1H), 1.86 – 1.72 (m, 2H), 0.97 (s, 9H), 0.23 (s, 3H), 0.22 (s, 3H). \textsuperscript{13}C NMR: (126 MHz, CDCl\textsubscript{3}): \(\delta\) 149.6, 131.7, 128.3, 128.2, 123.1, 104.3, 92.4, 83.1, 68.3, 37.6, 25.9, 24.2, 19.9, 18.3, -4.1, -4.9. IR (neat): 3448 (br), 2928, 2857, 1664, 1250, 1171, 921, 830, 754 cm\textsuperscript{-1}. HRMS-ESI m/z: [M+H], calculated for C\textsubscript{20}H\textsubscript{29}O\textsubscript{2}Si: 329.1937; found: 329.1938. R\textsubscript{f} = 0.30 (silica gel, 5% EtOAc/hexane, UV).
2-((tert-butyldimethylsilyl)oxy)-1-isobutylcyclohex-2-enol (SI-8)

The title compound was synthesized from isobutylmagnesium bromide (4.5 mL, 4.5 mmol, 1.5 equiv) following general procedure A. After purification via flash column chromatography, the product was obtained in 85% yield (724 mg, 2.55 mmol) as a colorless liquid. Spectral data matched those reported in literature.3

2-((tert-butyldimethylsilyl)oxy)-1-methylcyclohex-2-enol (SI-9)

The title compound was synthesized from methylmagnesium bromide (4.5 mL, 4.5 mmol, 1.5 equiv) following general procedure A. After purification via flash column chromatography, the product was obtained in 90% yield (653 g, 2.7 mmol) as a colorless liquid. Spectral data matched those reported in literature.3

3.2. General procedure B to synthesize cyclopentyl silyl enol ethers

Synthesis of SI-12: According to a reported procedure,4 to a 100 mL round bottom flask equipped with a stir bar was added SI-10 (2.0 mL, 20 mmol, 1.0 equiv) and water (35 mL). After the mixture was heated to 100 °C, a solution of FeCl3 (6.49 g, 40 mmol, 2.0 equiv) in water (35 mL, preheated at 90 °C) was added dropwise over a period of 20 minutes to the reaction mixture. Then, the reaction was allowed to stir at 100 °C under reflux conditions for another 50 minutes. After the reaction was allowed to cool to room temperature, saturated aq. (NH4)2SO4 was added to quench the reaction. The organic layer was extracted with Et2O (100 mL x 3), washed with brine, dried over Na2SO4, and concentrated under reduced

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pressure, yielding SI-11 in approximately 50% yield (0.98 g, 10 mmol) as a brown oil. The crude product was used for the next step without further purification.

To the round bottom flask containing SI-11 of the previous step was subsequently added TBSCl (2.0 g, 13.0 mmol, 1.3 equiv), imidazole (1.02 g, 15.0 mmol, 1.5 equiv), and CH₂Cl₂ (15 mL). The reaction was allowed to stir at room temperature for 3 hours. After the reaction completion as monitored by TLC, HCl (1 M, 2 mL) was added to quench the reaction. The organic layer was extracted with CH₂Cl₂ (50 mL x 2), washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was purified via column chromatography on silica gel with 30% CH₂Cl₂ in hexanes as eluent to give SI-12 (1.93 g, 91%) as a colorless liquid. Spectral data matched those reported in literature.⁵

Synthesis of SI-13: To a flame-dried round bottom flask was added SI-12 (212 mg, 1.0 mmol, 1 equiv) and CH₂Cl₂ (8 mL). The reaction was cooled to 0 °C, and a solution of Grignard reagent (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise under argon atmosphere. The reaction was allowed to stir for 5 hours. After the reaction was completed as monitored by TLC, the reaction was cooled to 0 °C before water was added to quench the reaction. The crude mixture was passed through a Celite pad, extracted with CH₂Cl₂ (30 mL x 3), washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was purified via column chromatography on silica gel with 5% diethyl ether in hexanes as eluent.

2-((tert-butyldimethylsilyl)oxy)-1-methylcyclopent-2-enol (SI-14)

The title compound was synthesized from methylmagnesium bromide following general procedure B. After purification via flash column chromatography, the product was obtained in 84% yield (192 mg, 0.84 mmol) as a colorless liquid. Spectral data matched those reported in literature.⁵

2-((tert-butyldimethylsilyl)oxy)-1-phenylcyclopent-2-enol (SI-15)

The title compound was synthesized from phenylmagnesium bromide following general procedure B. After purification via flash column chromatography, the product was obtained in 70% yield (203 mg, 0.70 mmol) as a brown liquid. Spectral data matched those reported in literature.⁵

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The title compound was synthesized from phenylethynylmagnesium bromide following general procedure B. After purification via flash column chromatography, the product was obtained in 56% yield (176 mg, 0.56 mmol) as a colorless liquid. $^1$H NMR: (500 MHz, CDCl$_3$): 7.40 (dd, $J = 6.6$, 2.9 Hz, 2H), 7.32 – 7.27 (m, 3H), 4.80 (t, $J = 2.4$ Hz, 1H), 2.58 (s, 1H), 2.53 – 2.49 (m, 1H), 2.36 – 2.30 (m, 2H), 2.24 – 2.20 (m, 1H), (0.97 (s, 9H), 0.23 (s, 3H), 2.22 (s, 3H). $^{13}$C NMR: (126 MHz, CDCl$_3$): 154.3, 131.7, 128.3, 123.0, 103.9, 90.9, 84.1, 76.4, 38.51, 25.8, 24.7, 18.3, -4.6, -4.9. IR (neat): 3413 (br), 2930, 2857, 1651, 1329, 1253, 1043, 1002, 837, 755 cm$^{-1}$. HRMS-ESI m/z: [M+Na], calculated for C$_{20}$H$_{28}$NaO$_2$Si: 337.1600; found: 337.1601. $R_f$ = 0.33 (silica gel, 20% Et$_2$O/hexane, UV).

The title compound was synthesized from p-tolylmagnesium bromide following general procedure B in a 3.0 mmol scale. After purification via flash column chromatography, the product was obtained in 38% yield (343 mg, 1.14 mmol) as a brown liquid. Spectral data matched those reported in literature.$^5$

4. General procedure C for the addition of organoboronates to $\alpha$-hydroxyl silyl enol ethers

To a flame-dried vial equipped with a stir bar was added $\alpha$-hydroxyl silyl enol ether (0.2 mmol, 1 equiv), an appropriate trifluoroborate salt (2 equiv), and MeCN (2 mL) under argon atmosphere. Then, LiPF$_6$ (15.2 mg, 0.1 mmol, 0.5 equiv) was quickly added to the reaction vial. (Note: The reaction should run in the glovebox if the atmospheric humidity is high since LiPF$_6$ is very hygroscopic). The reaction was allowed to stir at room temperature for 3 to 6 hours with cyclohexyl substrates and about 5 minutes with cyclopentyl substrates. After the reaction completion as monitored by TLC, the crude mixture was absorbed onto silica gel via rotary evaporation. The product was purified via flash column on silica gel with an appropriate gradient of dichloromethane in hexanes as eluent. For a larger scale synthesis, the above
procedure was also applied using a round-bottom flask instead of a vial. Note: reaction products are generally stable under atmospheric conditions. However, the degradation of products were observed at room temperature, especially with alkyne substituted products. All products should be stored at low temperature.

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\text{tert-butyl}((4\text{-methoxy-1',4',5',6'-tetrahydro-[1,1':3',1''-terphenyl]-2'-yl)}\text{oxy})\text{dimethylsilane (3a)}
\]

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium trifluoro(4-methoxyphenyl)borate (85.6 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with a 10% dichloromethane in hexanes as eluent, the product was obtained in 78% yield (61.5 mg, 0.156 mmol) as a colorless oil. \[^1\text{H NMR} (500 \text{ MHz, CDCl}_3)\]: \(\delta 7.40 – 7.37 (m, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.21 (m, 2H), 7.19 – 7.14 (m, 1H), 6.89 – 6.85 (m, 2H), 3.81 (s, 3H), 3.42 (t, \(J = 5.6 \text{ Hz}, 1H\)), 2.63 – 2.57 (m, 1H), 2.28 (ddd, \(J = 11.2, 5.6, 4.7 \text{ Hz}, 1H\)), 2.13 – 2.04 (m, 1H), 1.77 – 1.63 (m, 2H), 1.63 – 1.56 (m, 1H), 0.53(s, 9H), -0.18 (s, 3H), -0.50 (s, 3H). \[^{13}\text{C NMR} (126 \text{ MHz, CDCl}_3)\]: \(\delta 157.9, 145.9, 141.8, 136.9, 129.5, 129.2, 127.8, 125.9, 119.7, 113.5, 55.3, 45.8, 34.1, 30.6, 25.5, 19.8, 18.0, -4.2, -4.5. \ IR (neat): 2927, 2855, 1598, 1470, 1192, 1104, 962, 826, 778, 686 \text{ cm}^{-1}\). HRMS-ESI m/z: [M+H], calculated for C_{25}H_{35}O_{2}Si: 395.2406; found: 395.2403. \(R_f = 0.33\) (silica gel, 5% EtOAc/hexanes, UV).

\[
(E)\text{-tert-butyl}(3\text{-styryl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2'-yl)}\text{oxy})\text{silane (3b)}
\]

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(styryl)borate (84 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 10% dichloromethane in hexanes as eluent, the product was obtained in 95% yield (74.2 mg, 0.19 mmol) as a colorless oil. \[^1\text{H NMR} (500 \text{ MHz, CDCl}_3)\]: \(\delta 7.46 – 7.41 (m, 2H), 7.40 – 7.28 (m, 6H), 7.26 – 7.22 (m, 1H), 7.20 – 7.17 (m, 1H), 6.54 (d, \(J = 16.0 \text{ Hz}, 1H\)), 6.37 (dd, \(J = 16.0, 7.0 \text{ Hz}, 1H\)), 3.05 – 3.03 (m, 1H), 2.64 – 2.54 (m, 1H), 2.30 – 2.20 (m, 1H), 2.04 – 1.94 (m, 1H), 1.88 – 1.76 (m, 2H), 1.74 – 1.63 (m, 1H), 0.74 (s, 9H), -0.01 (s, 3H), -0.43 (s, 3H). \[^{13}\text{C NMR} (126 \text{ MHz, CDCl}_3)\]: \(\delta 146.3, 141.8, 138.0, 133.2, 130.7, 129.2, 128.6, 127.9, 127.0, 126.2, 126.0, 118.4, 43.6, 30.6, 30.5, 25.8, 20.2, 18.2, -3.9, -4.5. \ IR (neat): 2927, 2855, 1598, 1470, 1192, 1104, 962, 826, 749 \text{ cm}^{-1}\). HRMS-ESI m/z:
(E)-*tert*-butyl((4'-methoxy-3-styryl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)dimethylsilane (3c)

The title compound was synthesized from SI-4 (66.9 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(styryl)borate (84 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 10% dichloromethane in hexanes as eluent, the product was obtained in 92% yield (77.3 mg, 0.184 mmol) as a colorless oil. ¹H NMR: (500 MHz, CDCl₃): δ 7.40 (d, J = 7.5 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.22 (t, J = 7.3 Hz, 1H), 6.88 – 6.81 (m, 2H), 6.50 (d, J = 15.9 Hz, 1H), 6.34 (dd, J = 15.9, 7.2 Hz, 1H), 3.81 (s, 3H), 3.02 – 3.00 (m, 1H), 2.59 – 2.50 (m, 1H), 2.22 – 2.16 (m, 1H), 2.00 – 1.90 (m, 1H), 1.85 – 1.71 (m, 2H), 1.71 – 1.60 (m, 1H), 0.74 (s, 9H), -0.03 (s, 3H), -0.42 (s, 3H). ¹³C NMR: (126 MHz, CDCl₃): δ 157.8, 145.9, 138.0, 134.2, 133.4, 130.6, 130.2, 128.6, 127.0, 126.2, 117.7, 113.2, 55.4, 43.7, 30.7, 30.6, 25.9, 20.3, 18.2, -3.9, -4.3. IR (neat): 2953, 2930, 1677, 1600, 1511, 1418, 1249, 1029, 970, 831, 738 cm⁻¹. HRMS-ESI m/z: [M+H], calculated for C₂₇H₃₅O₂Si: 421.2563; found: 421.2560. Rf = 0.50 (silica gel, 5% EtOAc/hexanes, UV).

(E)-*tert*-butyldimethyl((6-styryl-2-vinylcyclohex-1-en-1-yl)oxy)silane (3d)

The title compound was synthesized from SI-5 (50.9 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(styryl)borate (84 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 10% dichloromethane in hexanes as eluent, the product was obtained in 88% yield (60.0 mg, 0.176 mmol) as a colorless oil. ¹H NMR: (500 MHz, CDCl₃): δ 7.34 (d, J = 7.5 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 17.7, 11.0 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 6.22 (dd, J = 16.0, 7.2 Hz, 1H), 5.00 (d, J = 17.7 Hz, 1H), 4.89 (d, J = 11.1 Hz, 1H), 3.03 – 3.01 (m, 1H), 2.25 – 2.17 (m, 2H), 1.93 – 1.80 (m, 1H), 1.78 – 1.64 (m, 2H), 1.64 – 1.52 (m, 1H), 0.92 (s, 9H), 0.13 (s, 6H). ¹³C NMR: (126 MHz, CDCl₃): δ 149.3, 137.8, 133.5, 132.5, 131.0, 128.5, 127.0, 126.2, 116.3, 109.0, 43.7, 30.5, 26.0, 24.1, 19.3, 18.5, -3.4, -3.6. IR (neat): 2952, 2929, 2557, 1701, 1470, 1193, 1252, 1100, 835, 737 cm⁻¹. HRMS-ESI m/z: [M+H], calculated for C₂₅H₃₇O₂Si: 340.2222 ; found: 340.2197. Rf = 0.43 (silica gel, 5% EtOAc/hexanes, UV).
The title compound was synthesized from SI-6 (53.7 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(styryl)borate (84 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 10% dichloromethane in hexanes as eluent, the product was obtained in 83% yield (58.9 mg, 0.166 mmol) as a colorless oil. ^1H NMR: (500 MHz, CDCl₃): δ 7.37 (d, \( J = 7.4 \) Hz, 2H), 7.30 (t, \( J = 7.6 \) Hz, 2H), 7.20 (t, \( J = 7.3 \) Hz, 1H), 6.41 (d, \( J = 16.0 \) Hz, 1H), 6.24 (dd, \( J = 16.0, 6.9 \) Hz, 1H), 5.78 (ddt, \( J = 16.7, 10.0, 6.6 \) Hz, 1H), 5.08 – 4.99 (m, 2H), 2.99 – 2.88 (m, 2H), 2.84 – 2.80 (m, 1H), 2.07 – 1.93 (m, 2H), 1.87 – 1.81 (m, 1H), 1.73 – 1.58 (m, 2H), 1.57 – 1.49 (m, 1H), 0.92 (s, 9H), 0.13 (d, \( J = 1.1 \) Hz, 6H). ^13C NMR: (126 MHz, CDCl₃): δ 144.6, 138.0, 137.1, 133.2, 130.7, 128.5, 126.9, 126.2, 115.1, 114.9, 42.9, 35.1, 30.8, 28.0, 26.0, 19.5, 18.5, -3.3, -3.7. IR (neat): 2954, 2931, 2858, 1706, 1463, 1202, 1264, 1097, 837, 734 cm⁻¹. HRMS-ESI m/z: [M+H], calculated for C₂₃H₃₅OSi: 355.2457; found: 355.2457. Rf = 0.47 (silica gel, 5% EtOAc/hexanes, UV).

The title compound was synthesized from SI-7 (65.6 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(styryl)borate (84 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 85% yield (70.5 mg, 0.17 mmol) as a colorless oil. ^1H NMR: (500 MHz, CDCl₃): δ 7.45 (d, \( J = 7.0 \) Hz, 2H), 7.37 (d, \( J = 7.5 \) Hz, 2H), 7.35 – 7.26 (m, 5H), 7.22 (t, \( J = 7.2 \) Hz, 1H), 6.46 (d, \( J = 15.9 \) Hz, 1H), 6.25 (dd, \( J = 15.9, 7.4 \) Hz, 1H), 3.07 – 2.06 (m, 1H), 2.36 (t, \( J = 5.7 \) Hz, 2H), 1.97 – 1.85 (m, 1H), 1.80 – 1.68 (m, 2H), 1.68 – 1.55 (m, 1H), 0.96 (s, 9H), 0.29 (s, 3H), 0.23 (s, 3H). ^13C NMR: (126 MHz, CDCl₃): δ 156.3, 137.6, 131.8, 131.3, 128.6, 128.3, 127.6, 127.2, 126.2, 124.5, 101.3, 92.1, 89.8, 43.9, 30.3, 29.7, 25.9, 19.7, 18.5, -3.3, -3.6. IR (neat): 2929, 2856, 1626, 1595, 1253, 1142, 928, 834, 737 cm⁻¹. HRMS-ESI m/z: [M+Na], calculated for C₂₈H₃₄NaOSi: 437.2277; found: 437.2273. Rf = 0.40 (silica gel, 5% EtOAc/hexanes, UV).
The title compound was synthesized from SI-8 (56.8 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(styryl)borate (84 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 10% dichloromethane in hexanes as eluent, the product was obtained in 87% yield (64.5 mg, 0.174 mmol) as a colorless oil. $^1$H NMR: (600 MHz, CDCl$_3$): $\delta$ 7.35 – 7.34 (m, 2H), 7.30 – 7.28 (m, 2H), 7.19 (t, $J$ = 7.4 Hz, 1H), 6.41 (d, $J$ = 16.0 Hz, 1H), 6.19 (dd, $J$ = 16.0, 6.5 Hz, 1H), 2.94 – 2.93 (m, 1H), 2.24 (dd, $J$ = 12.9, 8.5 Hz, 1H), 2.03 – 1.97 (m, 1H), 1.96 – 1.94 (m, 1H), 1.82 – 1.77 (m, 2H), 1.69 – 1.64 (m, 2H), 1.63 – 1.56 (m, 1H), 1.51 – 1.49 (m, 1H), 0.92 – 0.89 (m, 15H), 0.10 (s, 3H), 0.10 (s, 3H). $^{13}$C NMR: (151 MHz, CDCl$_3$): $\delta$ 144.4, 138.1, 133.7, 130.6, 128.5, 126.8, 126.1, 116.5, 42.8, 39.5, 30.6, 28.7, 26.6, 26.1, 23.1, 22.3, 19.5, 18.4, -3.1, -3.7. IR (neat): 2954, 2930, 2857, 1705, 1463, 1194, 1103, 966, 837 cm$^{-1}$. HRMS-ESI m/z: [M+H], calculated for C$_{24}$H$_{39}$OSi: 371.2770; found: 371.2773. 

**RF** = 0.43 (silica gel, 5% CH$_2$Cl$_2$/hexanes, UV).

The title compound was synthesized from SI-9 (48.5 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(styryl)borate (84 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 10% dichloromethane in hexanes as eluent, the product was obtained in 79% yield (51.9 mg, 0.158 mmol) as a colorless oil. $^1$H NMR: (500 MHz, CDCl$_3$): $\delta$ 7.36 (d, $J$ = 7.5 Hz, 2H), 7.29 (t, $J$ = 7.6 Hz, 2H), 7.19 (t, $J$ = 7.2 Hz, 1H), 6.40 (d, $J$ = 15.9 Hz, 1H), 6.24 (dd, $J$ = 15.9, 7.3 Hz, 1H), 2.93 – 2.92 (m, 1H), 2.07 – 1.94 (m, 2H), 1.90 – 1.79 (m, 1H), 1.72 – 1.61 (m, 5H), 1.55 – 1.52 (m, 1H), 0.92 (s, 9H), 0.12 (s, 6H). $^{13}$C NMR: (126 MHz, CDCl$_3$): $\delta$ 144.0, 138.0, 133.5, 130.4, 128.5, 126.9, 126.2, 113.3, 43.2, 31.1, 30.8, 26.0, 20.0, 18.4, 17.1, -3.4, -3.6. IR (neat): 2953, 2930, 2857, 1705, 1463, 1194, 1103, 966, 837 cm$^{-1}$. HRMS-ESI m/z: [M+H], calculated for C$_{21}$H$_{33}$OSi: 329.2301; found: 329.2303. 

**RF** = 0.27 (silica gel, 5% CH$_2$Cl$_2$/hexanes, UV).
The title compound was synthesized from SI-14 (45.6 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(styryl)borate (84 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 85% yield (53.5 mg, 0.17 mmol) as a colorless oil. $^{1}$H NMR: (500 MHz, CDCl$_3$): δ 7.37 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.7 Hz, 2H), 7.16 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 16.0 Hz, 1H), 6.21 (d, J = 16.0 Hz, 1H), 2.67 – 2.63 (m, 1H), 2.54 – 2.35 (m, 2H), 2.20 – 2.05 (m, 1H), 1.50 – 1.46 (m, 1H), 1.10 (d, J = 6.9 Hz, 3H), 1.02 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H). $^{13}$C NMR: (126 MHz, CDCl$_3$): δ 157.3, 138.7, 128.7, 126.5, 125.9, 125.3, 122.5, 116.9, 40.6, 28.9, 26.8, 25.9, 18.9, 18.5, -3.83, -3.95. IR (neat): 2955, 2930, 2857, 1718, 1463, 1389, 1252, 1105, 964, 838 cm$^{-1}$. HRMS-ESI m/z: [M+H]+, calculated for C$_{20}$H$_{31}$OSi: 315.2144; found: 315.2140. R$_f$ = 0.45 (silica gel, 5% Et$_2$O/hexanes, UV).

The title compound was synthesized from SI-15 (58.0 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(styryl)borate (84 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 10% dichloromethane in hexanes as eluent, the product was obtained in 82% yield (61.7 mg, 0.164 mmol) as a colorless oil. $^{1}$H NMR: (600 MHz, CDCl$_3$): δ 7.62 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 7.6 Hz, 2H), 7.31 (td, J = 7.6, 2.7 Hz, 4H), 7.23 – 7.20 (m, 1H), 7.16 (t, J = 7.3 Hz, 1H), 6.46 (d, J = 15.9 Hz, 1H), 6.29 (dd, J = 15.9, 8.0 Hz, 1H), 3.54 – 3.44 (m, 1H), 2.78 – 2.73 (m, 1H), 2.70 – 2.56 (m, 1H), 2.31 – 2.19 (m, 1H), 1.83 – 1.80 (m, 1H), 0.92 (s, 9H), 0.13 (s, 3H), 0.02 (s, 3H). $^{13}$C NMR: (126 MHz, CDCl$_3$): δ 151.5, 137.7, 136.7, 132.7, 130.4, 128.6, 127.9, 127.1, 127.1, 126.2, 125.7, 116.2, 50.6, 29.9, 28.3, 25.9, 18.3, -3.3, -3.5. IR (neat): 2930, 2856, 1688, 1634, 1448, 1255, 1067, 967, 838, 751, 694 cm$^{-1}$. HRMS-ESI m/z: [M+H]+, calculated for C$_{25}$H$_{33}$OSi: 377.2301; found: 377.2301. R$_f$ = 0.60 (silica gel, 5% Et$_2$O/hexanes, UV). Note: The reaction time is about 5 minutes. Giving additional time afforded a mixture of 2 diastereomers.
(E)-tert-butyldimethyl(2-(phenylethynyl)-5-styrylcyclopent-1-en-1-yl)oxy)silane (3k)

The title compound was synthesized from SI-16 (62.8 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(styryl)borate (84 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 10% dichloromethane in hexanes as eluent, the product was obtained in 86% yield (68.8 mg, 0.17 mmol) as a colorless oil. 1H NMR: (600 MHz, CDCl3): δ 7.41 (d, J = 7.0 Hz, 2H), 7.34 (d, J = 7.5 Hz, 2H), 7.31 – 7.26 (m, 4H), 7.25 – 7.24 (m, 1H), 7.20 (t, J = 7.3 Hz, 1H), 6.42 (d, J = 15.8 Hz, 1H), 6.14 (dd, J = 15.8, 8.4 Hz, 1H), 3.37 – 3.35 (m, 1H), 2.62 – 2.53 (m, 1H), 2.51 – 2.48 (m, 1H), 2.27 – 2.16 (m, 1H), 1.84 – 1.72 (m, 1H), 0.92 (s, 9H), 0.27 (s, 3H), 0.25 (s, 3H). 13C NMR: (151 MHz, CDCl3): δ 161.1, 137.5, 131.4, 131.2, 131.1, 128.9, 128.3, 127.6, 127.2, 126.2, 124.2, 120.6, 86.5, 50.0, 31.3, 28.6, 25.7, 18.3 , -3.5, -3.6. IR (neat): 2928, 2856, 2198, 1628, 1594, 1490, 1350, 1251, 837, 752 cm⁻¹. HRMS-ESI m/z: [M+H], calculated for C27H33OSi: 401.2301; found: 401.2300. Rf = 0.53 (silica gel, 5% Et2O/hexanes, UV).

(E)-tert-butyl(3-(4-fluorostyryl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)dimethylsilane (4a)

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(4-fluorostyryl)borate (91.2 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 85% yield (69.4 mg, 0.17 mmol) as a colorless oil. 1H NMR: (600 MHz, CDCl3): δ 7.37 – 7.31 (m, 4H), 7.27 (t, J = 7.7 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.03 – 6.95 (m, 2H), 6.46 (d, J = 15.9 Hz, 1H), 6.24 (dd, J = 15.9, 7.1 Hz, 1H), 3.04 – 2.92 (m, 1H), 2.62 – 2.47 (m, 1H), 2.24 – 2.14 (m, 1H), 2.00 – 1.88 (m, 1H), 1.84 – 1.71 (m, 2H), 1.70 – 1.60 (m, 1H), 0.70 (s, 9H), -0.05 (s, 3H), -0.48 (s, 3H). 13C NMR: (126 MHz, CDCl3): δ 162.1 (d, J = 245.4 Hz), 146.1, 141.7, 134.1 (d, J = 2.6 Hz), 133.0, 129.5, 129.2, 127.9, 127.6 (d, J = 7.6 Hz), 126.0, 118.5, 115.4 (d, J = 21.4 Hz), 43.6, 30.6, 30.5, 25.8, 20.2, 18.2, -3.9, -4.5. 19F NMR: (470 MHz, CDCl3) δ -115.6 (m). IR (neat): 2928, 2856, 1646, 1601, 1508, 1224, 1190, 1102, 963, 827, 778, 760 cm⁻¹. HRMS-ESI m/z: [M+H], calculated for C26H34FOSi: 409.2363; found: 409.2362. Rf = 0.50 (silica gel, 5% EtOAc/hexane, UV).
(E)-*tert*-butyldimethyl((3-(4-methylstyryl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)silane (4b)

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(4-methylstyryl)borate (89.6 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 96% yield (77.7 mg, 0.192 mmol) as a colorless oil. $^1$H NMR: (500 MHz, CDCl$_3$): δ 7.39 – 7.35 (m, 2H), 7.33 – 7.29 (m, 4H), 7.19 (d, $J$ = 7.3 Hz, 1H), 7.15 (d, $J$ = 8.0 Hz, 2H), 6.50 (d, $J$ = 15.9 Hz, 1H), 6.31 (dd, $J$ = 15.9, 7.1 Hz, 1H), 3.03 – 3.02 (m, 1H), 2.60 – 2.57 (m, 1H), 2.37 (s, 3H), 2.25 – 2.22 (m, 1H), 2.04 – 1.91 (m, 1H), 1.88 – 1.74 (m, 2H), 1.74 – 1.61 (m, 1H), 0.74 (s, 9H), -0.02 (s, 3H), -0.43 (s, 3H). $^{13}$C NMR: (126 MHz, CDCl$_3$): δ 146.4, 141.8, 136.7, 135.3, 132.2, 130.5 , 129.3, 129.2 127.8, 126.1, 125.9, 118.3, 43.6, 30.7, 30.5, 25.8, 21.3, 20.2, 18.2, -3.9, -4.5. IR (neat): 2952, 2928, 2856, 1685, 1604, 1471, 1253, 1178, 1104, 835, 752, 737 cm$^{-1}$. HRMS-ESI m/z: [M+H], calculated for C$_{27}$H$_{37}$OSi: 405.2614; found: 405.2613. R$_f$ = 0.47 (silica gel, 5% EtOAc/hexanes, UV).

(E)-*tert*-butyldimethyl((3-(pent-1-en-1-yl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)silane (4c)

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium (E)-trifluoro(pent-1-en-1-yl)borate (70.4 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 51% yield (36.4 mg, 0.102 mmol) as a colorless oil. $^1$H NMR: (600 MHz, CDCl$_3$): δ 7.29 (d, $J$ = 7.4 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.12 (t, $J$ = 7.3 Hz, 1H), 5.52 – 5.50 (m, 2H), 2.76 – 2.75 (m, 1H), 2.56 – 2.43 (m, 1H), 2.19 – 2.10 (m, 1H), 2.06 – 1.95 (m, 2H), 1.87 – 1.76 (m, 1H), 1.74 – 1.70 m, 1H), 1.65 – 1.57 (m, 2H), 1.47 – 1.34 (m, 2H), 0.91 (t, $J$ = 7.3 Hz, 3H), 0.71 (s, 9H), -0.07 (s, 3H), -0.49 (s, 3H). $^{13}$C NMR: (151 MHz, CDCl$_3$): δ 147.0, 142.0, 132.6, 131.2, 129.2, 127.7, 125.7, 117.7, 43.1, 34.9, 30.9, 30.5, 25.8, 22.8, 20.0, 18.2, 13.8, -4.0, -4.5. IR (neat): 2956, 2928, 2856, 1647, 1600, 1464, 1251, 1194, 1054, 964, 828, 757 cm$^{-1}$. HRMS-ESI m/z: [M+H], calculated for C$_{23}$H$_{37}$OSi: 357.2614; found: 357.2616. R$_f$ = 0.47 (silica gel, 5% EtOAc/hexanes, UV).
The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium trifluoro(phenylethynyl)borate (83.2 mg, 0.2 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 90% yield (69.8 mg, 0.18 mmol) as a colorless oil. $^1$H NMR: (500 MHz, CDCl$_3$): $\delta$ 7.47 – 7.44 (m, 2H), 7.34 – 7.27 (m, 7H), 7.21 – 7.16 (m, 1H), 3.36 (t, $J = 4.7$ Hz, 1H), 2.51 – 2.40 (m, 1H), 2.36 – 2.26 (m, 1H), 2.10 – 1.96 (m, 3H), 1.81 – 1.69 (m, 1H), 0.79 (s, 9H), -0.06 (s, 3H), -0.19 (m, 3H). $^{13}$C NMR: (126 MHz, CDCl$_3$): $\delta$ 143.4, 141.4, 131.7, 129.3, 128.3, 127.9, 127.7, 126.2, 124.2, 117.9, 92.3, 81.2, 34.0, 30.8, 30.5, 25.8, 20.7, 18.3, -4.3, -4.4. IR (neat): 2928, 2856, 1598, 1471, 1193, 1105, 983, 827, 753 cm$^{-1}$. HRMS-ESI m/z: [M+H$^+$], calculated for C$_{26}$H$_{33}$OSi: 389.2301; found: 389.2305. RF = 0.50 (silica gel, 5% EtOAc/hexanes, UV).

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium trifluoro(4-methoxyphenylethynyl)borate (95.2 mg, 0.4 mmol, 1.5 equiv) following general procedure C. After purification via flash column chromatography with 10% dichloromethane in hexanes as eluent, the product was obtained in 72% yield (60.3 mg, 0.144 mmol) as a colorless oil. $^1$H NMR: (500 MHz, CDCl$_3$): $\delta$ 7.36 (d, $J = 8.7$ Hz, 2H), 7.31 – 7.27 (m, 4H), 7.16 (t, $J = 7.0$ Hz, 1H), 6.82 (d, $J = 8.6$ Hz, 2H), 3.80 (s, 3H), 3.32 – 3.31 (m, 1H), 2.44 – 2.41 (m, 1H), 2.30 – 2.27 (m, 1H), 2.06 – 1.91 (m, 3H), 1.80 – 1.65 (m, 1H), 0.76 (s, 9H), -0.08 (s, 3H), -0.22 (s, 3H). $^{13}$C NMR: (126 MHz, CDCl$_3$): $\delta$ 159.1, 143.5, 141.4, 133.0, 129.3, 127.9, 126.1, 117.7, 116.4, 113.9, 90.6, 80.9, 55.4, 33.9, 30.9, 25.8, 20.6, 18.3, -4.3, -4.4. IR (neat): 2930, 2856, 1607, 1465, 1194, 1028, 973, 830, 750 cm$^{-1}$. HRMS-ESI m/z: [M+H$^+$], calculated for C$_{27}$H$_{35}$O$_2$Si: 419.2406; found: 419.2403. RF = 0.33 (silica gel, 5% EtOAc/hexanes, UV).
**tert-butyl((3-((4-fluorophenyl)ethynyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)dimethylsilane (5c)**

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium trifluoro((4-fluorophenyl)ethynyl)borate (90.4 mg, 0.2 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 95% yield (77.3 mg, 0.19 mmol) as a colorless oil. ¹H NMR: (500 MHz, CDCl₃): δ 7.44 – 7.39 (m, 2H), 7.34 – 7.27 (m, 4H), 7.21 – 7.16 (m, 1H), 7.03 – 6.97 (m, 2H), 3.34 (t, J = 5.0 Hz, 1H), 2.51 – 2.39 (m, 1H), 2.35 – 2.25 (m, 1H), 2.09 – 1.92 (m, 3H), 1.82 – 1.69 (m, 1H), 0.78 (s, 9H), -0.07 (s, 3H), -0.22 (s, 3H). ¹³C NMR: (126 MHz, CDCl₃): δ 162.2 (d, J = 248.6 Hz), 143.2, 141.3, 133.49 (d, J = 8.1 Hz), 129.2, 128.0, 126.2, 120.2 (d, J = 3.3 Hz), 118.0, 115.5 (d, J = 22.2 Hz), 91.9, 80.1, 34.0, 30.8, 30.5, 25.8, 20.7, 18.3, -4.3, -4.4. ¹⁹F NMR: (470 MHz, CDCl₃) δ -112.1 (m). IR (neat): 2930, 2857, 1601, 1470, 1193, 1092, 738 cm⁻¹. HRMS-ESI m/z: [M+H], calculated for C₂₆H₃₂FOSi: 407.2206; found: 407.2206. Rᵣ = 0.53 (silica gel, 5% EtOAc/hexanes, UV).

**tert-butyldimethyl((3-((trimethylsilyl)ethynyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)silane (5d)**

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium trifluoro(((trimethylsilyl)ethynyl)borate (81.6 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 61% yield (46.9 mg, 0.122 mmol) as a colorless oil. ¹H NMR: (500 MHz, CDCl₃): δ 7.30 – 7.24 (m, 4H), 7.19 – 7.12 (m, 1H), 3.14 – 3.13 (m, 1H), 2.43 – 2.33 (m, 1H), 2.28 – 2.23 (m, 1H), 1.98 – 1.82 (m, 3H), 1.73 – 1.60 (m, 1H), 0.75 (s, 9H), 0.16 (s, 9H), -0.11 (s, 3H), -0.25 (s, 3H). ¹³C NMR: (126 MHz, CDCl₃): δ 143.2, 141.4, 129.2, 127.9, 126.1, 117.7, 108.9, 84.9, 34.4, 30.8, 30.5, 25.8, 20.6, 18.3, 0.2, -4.3, -4.5. IR (neat): 2955, 2929, 2857, 2168, 1662, 1560, 1471, 1249, 1194, 836, 757 cm⁻¹. HRMS-ESI m/z: [M+H], calculated for C₂₃H₃₇OSi₂: 385.2383; found:385.2383. Rᵣ = 0.50 (silica gel, 5% EtOAc/hexanes, UV).
**tert-butyl((3-(3,3-dimethylbut-1-yn-1-yl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)dimethylsilane**  
(5e)

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium (3,3-dimethylbut-1-yn-1-yl)trifluoroborate (75.2 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 45% yield (33.2 mg, 0.09 mmol) as a colorless oil.  

**1H NMR:** (500 MHz, CDCl$_3$): $\delta$ 7.30 – 7.24 (m, 4H), 7.18 – 7.13 (m, 1H), 3.06 – 3.03 (m, 1H), 2.42 – 2.33 (m, 1H), 2.23 (dt, $J = 8.3, 4.8$ Hz, 1H), 1.95 – 1.82 (m, 3H), 1.70 – 1.58 (m, 1H), 1.22 (s, 9H), 0.74 (s, 9H), -0.09 (s, 3H), -0.23 (s, 3H).  

**13C NMR:** (126 MHz, CDCl$_3$): $\delta$ 144.3, 141.6, 129.2, 127.8, 125.9, 117.1, 89.2, 80.6, 33.2, 31.4, 31.3, 30.6, 27.5, 25.8, 20.5, 18.2, -4.3, -4.5. **IR (neat):** 2958, 2930, 2858, 1685, 1599, 1464, 1252, 1202, 1101, 958, 836, 757 cm$^{-1}$.  

**HRMS-ESI m/z:** [M+H$^+$], calculated for C$_{24}$H$_{37}$OSi: 369.2614; found: 369.2610. **Rf** = 0.53 (silica gel, 5% EtOAc/hexanes, UV).

**tert-butyl((3-(cyclopropylethynyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)dimethylsilane**  
(5f)

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium (cyclopropylethynyl)trifluoroborate (68.8 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 37% yield (26.1 mg, 0.074 mmol) as a colorless oil.  

**1H NMR:** (500 MHz, CDCl$_3$): $\delta$ 7.29 – 7.23 (m, 4H), 7.17 – 7.12 (m, 1H), 3.06 – 3.01 (m, 1H), 2.42 – 2.30 (m, 1H), 2.25 – 2.20 (m, 1H), 1.95 – 1.80 (m, 3H), 1.72 – 1.59 (m, 1H), 1.31 – 1.16 (m, 1H), 0.79 – 0.67 (m, 11H), 0.67 – 0.58 (m, 2H), -0.11 (s, 3H), -0.27 (s, 3H).  

**13C NMR:** (126 MHz, CDCl$_3$): $\delta$ 143.9, 141.5, 129.2, 127.8, 126.0, 117.3, 83.9, 77.4, 33.3, 31.1, 30.5, 25.8, 20.6, 18.3, 8.0, 8.0, -0.11, -4.3, -4.5. **IR (neat):** 2958, 2930, 2858, 1685, 1599, 1464, 1252, 1202, 1101, 958, 836, 757 cm$^{-1}$. **HRMS-ESI m/z:** [M+H$^+$], calculated for C$_{23}$H$_{33}$OSi: 353.2301; found: 353.2300. **Rf** = 0.43 (silica gel, 5% EtOAc/hexanes, UV).
**tert-butyl(dimethyl)((4-(methylthio)-1',4',5',6'-tetrahydro-[1,1':3',1''-terphenyl]-2'-yl)oxy)silane (6a)**

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium trifluoro(4-(methylthio)phenyl)borate (92.0 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with a gradient of 5 – 10% dichloromethane in hexanes as eluent, the product was obtained in 75% yield (61.5 mg, 0.15 mmol) as a colorless oil. **1H NMR**: (500 MHz, CDCl$_3$): δ 7.38 (d, $J = 7.4$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.25 (s, 4H), 7.18 (t, $J = 7.3$ Hz, 1H), 3.43 (t, $J = 5.7$ Hz, 1H), 2.67 – 2.53 (m, 1H), 2.49 (s, 3H), 2.31 – 2.262 (m, 1H), 2.14 – 2.04 (m, 1H), 1.79 – 1.56 (m, 3H), 0.53 (s, 9H), -0.17 (s, 3H), -0.51 (s, 3H). **13C NMR**: (126 MHz, CDCl$_3$): δ 145.54, 142.1, 141.7, 135.3, 129.1, 127.9, 126.9, 126.0, 120.0, 46.2, 34.0, 30.6, 25.5, 19.9, 18.0, 16.5, -4.2, -4.52. **IR (neat)**: 2919, 2851, 1654, 1489, 1207, 1177, 1129, 828, 776, 756, 699 cm$^{-1}$. **HRMS-ESI m/z**: [M+H], calculated for C$_{25}$H$_{35}$OSSi: 411.2178; found: 411.2174.  

**((3-(benzo[d][1,3]dioxol-5-yl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)(tert-butyl)dimethylsilane (6b)**

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium benzo[d][1,3]dioxol-5-yltrifluoroborate (91.2 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% Et$_2$O in hexanes as eluent, the product was obtained in 75% yield (61.3 mg, 0.15 mmol) as a colorless oil. **1H NMR**: (500 MHz, CDCl$_3$): δ 7.38 (d, $J = 7.5$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.17 (t, $J = 7.3$ Hz, 1H), 6.85 (s, 1H), 6.78 (s, 2H), 5.95 (s, 2H), 3.39 (t, $J = 5.5$ Hz, 1H), 2.64 – 2.55 (m, 1H), 2.28 (dt, $J = 16.4, 5.3$ Hz, 1H), 2.13 – 2.04 (m, 1H), 1.76 – 1.64 (m, 2H), 1.64 – 1.60 (m, 1H), 0.56 (s, 9H), -0.15 (s, 3H), -0.49 (s, 3H). **13C NMR**: (126 MHz, CDCl$_3$): δ 147.4, 145.7, 145.7, 141.7, 138.9, 129.1, 127.9, 126.0, 121.7, 119.9, 109.0, 108.0, 100.8, 46.4, 34.1, 30.6, 25.5, 19.8, 18.0, -4.2, -4.5. **IR (neat)**: 2929, 2856, 1647, 1599, 1485, 1437, 1248, 1195, 1040, 829, 736 cm$^{-1}$. **HRMS-ESI m/z**: [M+H], calculated for C$_{25}$H$_{33}$O$_3$Si: 409.2199; found: 409.2196. **R$_f$** = 0.37 (silica gel, 5% EtOAc/hexanes, UV).
The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium trifluoro(mesityl)borate (90.4 mg, 0.2 mmol, 12 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 59% yield (48.0 mg, 0.12 mmol) as a colorless oil. 

**1H NMR:** (500 MHz, CDCl3): δ 7.35 (d, J = 7.4 Hz, 2H), 7.28 (t, J = 7.7 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 6.79 (d, J = 13.6 Hz, 2H), 3.80 – 3.78 (m, 1H), 2.63 – 2.60 (m, 1H), 2.39 – 2.33 (m, 1H), 2.31 (s, 3H), 2.23 (s, 3H), 2.02 – 1.94 (m, 2H), 1.84 – 1.67 (m, 2H), 0.42 (s, 9H), -0.23 (s, 3H), -0.71 (s, 3H). 

**13C NMR:** (126 MHz, CDCl3): δ 147.0, 141.8, 137.1, 137.1, 136.2, 135.0, 130.5, 129.3, 128.9, 127.9, 125.9, 116.9, 43.0, 31.1, 30.4, 25.3, 24.0, 20.8, 20.6, 20.4, 17.8, -4.6, -5.0. **IR (neat):** 2926, 2855, 1646, 1470, 1178, 1122, 918, 826, 777 cm⁻¹. **HRMS - ESI m/z:** [M+H], calculated for C27H39OSi: 407.2770; found: 407.2766. **Rf** = 0.36 (silica gel, 5% EtOAc/hexanes, UV).

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium trifluoro(thiophen-2-yl)borate (76.5 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with a gradient of 5 – 10% dichloromethane in hexanes as eluent, the product was obtained in 43% yield (31.8 mg, 0.086 mmol) as a colorless oil. 

**1H NMR:** (400 MHz, CDCl3): δ 7.41 – 7.33 (m, 2H), 7.28 (t, J = 7.3, 2H), 7.18 – 7.16 (m, 2H), 6.96 – 6.95 (m, 2H), 3.71 – 3.70 (m, 1H), 2.63 – 2.55 (m, 1H), 2.27 – 2.20 (m, 1H), 2.16 – 2.01 (m, 1H), 1.94 – 1.91 (m, 1H), 1.82 – 1.72 (m, 1H), 1.69 – 1.64 (m, 1H), 0.61 (s, 9H), -0.01 (s, 3H), -0.49 (s, 1H). **13C NMR:** (101 MHz, CDCl3): δ 148.6, 145.7, 141.6, 129.0, 127.9, 126.3, 126.0, 124.9, 123.2, 119.0, 41.8, 33.6, 30.3, 25.6, 19.4, 18.0, -4.3, -4.8. **IR (neat):** 2927, 2855, 1648, 1315, 1251, 1192, 918, 826, 776, 691 cm⁻¹. **HRMS - ESI m/z:** [M+H], calculated for C22H31OSSi: 371.1865; found: 371.1868. **Rf** = 0.53 (silica gel, 5% EtOAc/hexanes, UV).
*tert*-butyl(3-(furan-2-yl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)dimethylsilane (6e)

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium trifluorofuran(2-y1)borate (69.6 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 55% yield (39.0 mg, 0.11 mmol) as a colorless oil. $^1$H NMR: (500 MHz, CDCl$_3$): δ 7.33 (d, $J$ = 7.3 Hz, 3H), 7.28 (d, $J$ = 7.4 Hz, 2H), 7.16 (t, $J$ = 7.2 Hz, 1H), 6.32 – 6.31 (m, 1H), 6.17 (d, $J$ = 3.0 Hz, 1H), 3.53 – 3.51 (m, 1H), 2.60 – 2.49 (m, 1H), 2.25 – 2.20 (m, 1H), 1.99 – 1.96 (m, 1H), 1.75 – 1.59 (m, 2H), 0.62 (s, 9H), -0.14 (s, 3H), -0.48 (s, 3H). $^{13}$C NMR: (126 MHz, CDCl$_3$): δ 157.3, 144.1, 141.6, 140.8, 129.0, 127.8, 126.0, 119.0, 110.1, 114.5, 40.5, 30.2, 29.8, 25.6, 19.7, 18.0, -4.4, -4.6. IR (neat): 2929, 2857, 1590, 1464, 1399, 1198, 1104, 755 cm$^{-1}$. HRMS-ESI m/z: [M+H], calculated for C$_{22}$H$_{31}$O$_2$Si: 355.2093; found: 355.2091. $R_f$ = 0.50 (silica gel, 5% EtOAc/hexanes, UV).

((3-(benzo[b]thiophen-2-yl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)oxy)(tert-butyl)dimethylsilane (6f)

The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium benzo[b]thiophen-2-yltrifluoroborate (96.0 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 85% yield (71.5 mg, 0.17 mmol) as a colorless oil. $^1$H NMR: (500 MHz, CDCl$_3$): δ 7.88 (dd, $J$ = 13.8, 7.9 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.38 – 7.31 (m, 3H), 7.29 (s, 1H), 7.22 – 7.19 (m, 1H), 3.90 – 3.89 (m, 1H), 2.74 – 2.61 (m, 1H), 2.41 – 2.27 (m, 1H), 2.21 – 2.08 (m, 1H), 2.00 – 1.97 (m, 1H), 1.80 – 1.62 (m, 2H), 0.52 (s, 9H), -0.18 (s, 3H), -0.46 (s, 3H). $^{13}$C NMR: (126 MHz, CDCl$_3$): δ 145.2, 141.7, 140.9, 138.5, 138.3, 129.1, 127.9, 126.1, 124.0, 123.9, 123.5, 123.1, 121.7, 119.3, 40.9, 30.4, 30.3, 25.5, 20.0, 18.0, -4.2, -4.5. IR (neat): 2929, 2855, 1647, 1470, 1196, 1105, 964, 921, 827, 730 cm$^{-1}$. HRMS-ESI m/z: [M+H], calculated for C$_{26}$H$_{33}$OSSi: 421.2021; found: 421.2021. $R_f$ = 0.50 (silica gel, 5% EtOAc/hexanes, UV).
The title compound was synthesized from 1a (60.9 mg, 0.2 mmol, 1 equiv) and potassium trifluoro(1-(phenylsulfonyl)-1H-indol-3-yl)borate (145 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 10% dichloromethane in hexanes as eluent, the product was obtained in 82% yield (89.2 mg, 0.164 mmol) as a colorless oil. 

\[ \text{IR (neat): 2928, 2855, 1652, 1446, 1369, 1174, 1118, 745 cm}^{-1} \]

HRMS-ESI m/z: [M+H] calculated for C_{26}H_{33}OSSi: 544.2342; found: 544.2336.

The title compound was synthesized from SI-14 (45.7 mg, 0.2 mmol, 1 equiv) and potassium trifluoro(phenylethynyl)borate (83.2 mg, 0.4 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 5% dichloromethane in hexanes as eluent, the product was obtained in 87% yield (54.4 mg, 0.174 mmol) as a colorless oil. 

\[ \text{IR (neat): 2956, 2857, 2806, 1629, 1594, 1465, 1200, 1090, 974, 839, 751 cm}^{-1} \]

HRMS-ESI m/z: [M+H] calculated for C_{20}H_{29}OSi: 313.1988; found: 313.1985.

\[ \text{IR (neat): 2956, 2928, 2857, 2806, 1629, 1594, 1465, 1200, 1090, 974, 839, 751 cm}^{-1} \]

HRMS-ESI m/z: [M+H] calculated for C_{20}H_{29}OSi: 313.1988; found: 313.1985.

\[ \text{IR (neat): 2956, 2928, 2857, 2806, 1629, 1594, 1465, 1200, 1090, 974, 839, 751 cm}^{-1} \]

HRMS-ESI m/z: [M+H] calculated for C_{20}H_{29}OSi: 313.1988; found: 313.1985.
tert-butyl((2-(4-methoxyphenyl)-5-methylcyclopent-1-en-1-yl)oxy)dimethylsilane (7b)

The title compound was synthesized from SI-14 (45.7 mg, 0.2 mmol, 1 equiv) and potassium trifluoro(4-methoxyphenyl)borate (85.6 mg, 0.2 mmol, 2 equiv) following general procedure C. After purification via flash column chromatography with 10% dichloromethane in hexanes as eluent, the product was obtained in 69% yield (40.0 mg, 0.138 mmol) as a colorless oil. $^1$H NMR: (500 MHz, CDCl$_3$): δ 7.52 – 7.48 (m, 2H), 6.84 – 6.82 (m, 2H), 3.80 (s, 3H), 2.74 – 2.59 (m, 2H), 2.54 – 2.43 (m, 1H), 2.19 – 2.06 (m, 1H), 1.53 – 1.39 (m, 1H), 1.12 (d, $J = 6.8$ Hz, 3H), 0.94 (s, 9H), 0.11 (s, 3H), -0.02 (s, 3H). $^{13}$C NMR: (126 MHz, CDCl$_3$): δ 157.3, 152.9, 128.8, 128.0, 113.8, 113.2, 55.3, 41.2, 29.8, 28.6, 25.97, 19.2, 18.4, -3.6, -3.9. IR (neat): 2955, 2929, 2857, 1637, 1607, 1511, 1463, 1246, 1214, 1178, 1100, 1032, 972, 836, 749 cm$^{-1}$. HRMS-ESI m/z: [M+H], calculated for C$_{19}$H$_{31}$O$_2$Si: 319.2093; found: 319.2093. R$_f$ = 0.33 (silica gel, 5% EtOAc/hexanes, UV).

5. Control experiments

5.1. Role of borate nucleophiles

To a flame-dried vial equipped with a stir bar was subsequently added 1a (60.8 mg, 0.2 mmol, 1 equiv), styrene or phenylacetylene (3 equiv), and MeCN (2 mL). LiPF$_6$ (15.2 mg, 0.1 mmol, 0.5 equiv) was then added to the reaction vial. Based on TLC and NMR analysis, product 3b or 5a was not observed in the crude mixture. Additionally, the loss of 1a was observed.
5.2. Probing the reaction mechanism

Synthesis of 8: According to a reported procedure, to a flame-dried vial was subsequently added 1a (243 mg, 0.8 mmol, 1 equiv), Pd catalyst (7.4 mg, 0.04 mmol, 5 mol %), and PPh3 (21 mg, 0.08 mmol, 10 mol %), DMA (1 mL), and hexamethyldisilane (0.1 mL, 0.48 mmol, 0.6 equiv). The reaction was allowed to heat at 80 °C for 3 hours. After the reaction was completed as monitored by TLC, the reaction was extracted with Et2O, washed with brine, dried over Na2SO4, and concentrated under reduced pressure. The crude product was purified via column chromatography on silica gel with 5% diethyl ether in hexanes as eluent, yielding 8 in 56% (0.45 mmol, 169 mg) as a colorless oil. 1H NMR: (600 MHz, CDCl3): δ 7.36 (d, J = 7.9 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.16 – 7.14 (m, 1H), 4.97 (t, J = 4.0 Hz, 1H), 2.22 – 2.09 (m, 2H), 1.98 – 1.95 (m, 1H), 1.92 – 1.81 (m, 1H), 1.75 – 1.68 (m, 1H), 1.62 – 1.54 (m, 1H), 0.65 (s, 9H), 0.17 (s, 9H), 0.10 (s, 3H), -0.21 (s, 3H). 13C NMR: (151 MHz, CDCl3): δ 151.5, 147.6, 127.4, 126.1, 126.1, 107.0, 78.1, 42.9, 25.6, 24.8, 19.3, 18.1, 22, -4.3, -5.4. IR (neat): 2929, 2857, 1653, 1472, 1243, 1176, 1121, 1043, 825, 755 cm⁻¹. HRMS-ESI m/z: [M+Na], calculated for C21H36NaO2Si2: 399.2152; found: 399.2151. Rf = 0.67 (silica gel, 5% EtOAc/hexane, UV).

The reaction between protected substrate 8 and potassium (E)-trifluorostyryl)borate under the standard conditions as general procedure C provided 3b in 81% yield (63.2 mg, 0.16 mmol).

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6. Procedure for one-pot synthesis cyclic ketones

To a flame-dried 100 mL round-bottom flask equipped with a stir bar was added 1a (1.52 g, 5.0 mmol, 1 equiv), potassium 4-methoxynaphthyltrifluoroborate (2.1 g, 10.0 mmol, 2 equiv), and MeCN (40 mL) under argon atmosphere. LiPF$_6$ (380 mg, 2.5 mmol, 0.5 equiv) was then quickly added as one portion at room temperature. The reaction was allowed to stir for 3 hours at the same temperature. After 1a was completely consumed as monitored by TLC, the reaction was cooled to 0 °C. 4 N HCl (2.5 mL, 10 mmol, 2 equiv) was added slowly to the reaction mixture. The reaction was allowed to warm to room temperature for 12 hours. After the reaction completion, the reaction mixture was concentrated under reduced pressure, then absorbed onto silica gel via rotary evaporation. The crude product was purified via column chromatography on silica gel with 10% Et$_2$O in hexanes as eluent, yielding cis-disubstituted ketone 9 in 75% (1.05 g, 3.75 mmol) as the major diastereomer over 2 steps. The relative configuration was determined by X-ray crystallography of its single crystal, which was grown by slow solvent (CH$_2$Cl$_2$) evaporation technique. $^1$H NMR: (400 MHz, CDCl$_3$): δ 7.34 – 7.30 (m, 2H), 7.25 (d, J = 6.3 Hz, 1H), 7.17 (d, J = 7.5 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 3.87 – 3.66 (m, 5H), 2.41 – 2.33 (m, 2H), 2.23 – 1.98 (m, 4H). $^{13}$C NMR: (101 MHz, CDCl$_3$): δ 208.7, 158.5, 138.6, 130.7, 129.8, 128.9, 128.3, 127.0, 113.7, 58.0, 57.2, 55.3, 36.6, 36.4, 26.2. IR (neat): 2953, 2857, 2361, 1706, 1514, 1274, 1242, 1177, 1029, 830, 758 cm$^{-1}$. HRMS-ESI m/z: [M+H], calculated for C$_{19}$H$_{21}$O$_2$: 281.1542; found: 281.1541. Rf = 0.23 (silica gel, 15% EtOAc/hexane, UV).

To a flame-dried 50 mL round-bottom flask equipped with a stir bar was added 1a (395 mg, 1.3 mmol, 1 equiv), potassium (E)-trifluoro(styryl)borate (546 mg, 2.6 mmol, 2 equiv), and MeCN (12 mL) under argon atmosphere. LiPF$_6$ (99 mg, 0.65 mmol, 0.5 equiv) was then quickly added as one portion at room temperature. The reaction was allowed to stir for 3 hours at the same temperature. After the reaction completion as monitored by TLC, the reaction was cooled to 0 °C. 4 N HCl (0.65 mL, 2.6 mmol, 2 equiv) was added slowly to the reaction mixture. The reaction was allowed to warm to room temperature for 12 hours. After the reaction completion, the reaction mixture was concentrated under reduced pressure, then
absorbed onto silica gel via rotary evaporation. The crude product was purified via column chromatography on silica gel with 10% Et₂O in hexanes as eluent, yielding a mixture of 2 diastereomers of 10 (280 mg, 1.01 mmol, 78% yield) with the ratio of cis/trans = 5:1 based on NMR analysis of the crude mixture. The major diastereomer was purified by recrystallization from EtOAc and hexanes, and its relative configuration was determined by NOE experiments. 

**¹H NMR:** (500 MHz, CDCl₃): δ 7.43 – 7.32 (m, 4H), 7.32 – 7.27 (m, 3H), 7.22 (t, J = 7.3 Hz, 1H), 7.17 (d, J = 7.5 Hz, 2H), 6.52 (dd, J = 16.2, 7.3 Hz, 1H), 6.41 (d, J = 16.2 Hz, 1H), 3.71 (dd, J = 12.1, 4.7 Hz, 1H), 3.38 (dt, J = 12.5, 6.2 Hz, 1H), 2.43 – 2.27 (m, 2H), 2.10 – 1.99 (m, 3H), 1.91 – 1.83 (m, 1H). 

**¹³C NMR:** (126 MHz, CDCl₃): δ 209.3, 138.5, 137.4, 131.2, 128.8, 128.6, 128.4, 127.7, 127.4, 127.0, 126.4, 57.9, 54.5, 36.2, 35.9, 25.7, 25.7. 

**IR (neat):** 3027, 2935, 2860, 1711, 1494, 1448, 1041, 965, 752, 696 cm⁻¹. 

**HRMS-ESI m/z:** [M+H], calculated for C₂₀H₂₁O: 277.1592; found: 277.1589. 

**Rf** = 0.37 (silica gel, 20% Et₂O/hexane, UV).

To a flame-dried 50 mL round-bottom flask equipped with a stir bar was added 1b (644 mg, 2.66 mmol, 1 equiv), potassium 4-methoxylphenyltrifluoroborate (1.12 g, 5.32 mmol, 2 equiv), and MeCN (20 mL) under argon atmosphere. LiPF₆ (205 mg, 1.33 mmol, 0.5 equiv) was then quickly added as one portion at room temperature. The reaction was allowed to stir for 6 hours at the same temperature. After the reaction completion as monitored by TLC, the reaction was cooled to 0 °C. 4 N HCl (1.3 mL, 5.32 mmol, 2 equiv) was added slowly to the reaction mixture. The reaction was allowed to warm to room temperature for 12 hours. After the reaction completion, the reaction mixture was concentrated under reduced pressure, then absorbed onto silica gel via rotary evaporation. The crude product was purified via column chromatography on silica gel with 10% Et₂O in hexanes as eluent, yielding cis-11 in 67% (388 mg, 1.78 mmol) with the ratio of cis/trans = 11:1 based on NMR analysis of the crude mixture. 

**¹H NMR:** (600 MHz, CDCl₃): δ 7.05 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 3.78 (s, 3H), 3.58 (dd, J = 11.9, 4.9 Hz, 1H), 2.63 – 2.49 (m, 1H), 2.30 – 2.23 (m, 1H), 2.19 (dd, J = 13.1, 2.7 Hz, 1H), 2.02 – 1.87 (m, 3H), 1.56 – 1.46 (m, 1H), 1.05 (d, J = 6.4 Hz, 3H). 

**¹³C NMR:** (151 MHz, CDCl₃): δ 211.8, 158.5, 131.1, 129.7, 113.7, 57.0, 55.3, 45.9, 37.3, 36.7, 25.9, 14.9. 

**IR (neat):** 2969, 2929, 2850, 1709, 1614, 1515, 1248, 1181, 1040, 1027, 815 cm⁻¹. 

**HRMS-ESI m/z:** [M+H], calculated for C₁₄H₁₉O₂: 219.1385; found: 219.1382. 

**Rf** = 0.37 (silica gel, 20% EtOAc/hexane, UV).
To a flame-dried 7 mL vial equipped with a stir bar was added 1a (120 mg, 0.4 mmol, 1 equiv), potassium trifluoro(phenylethynyl)borate (166 mg, 0.8 mmol, 2 equiv), and MeCN (4 mL) under argon atmosphere. LiPF$_6$ (30 mg, 0.2 mmol, 0.5 equiv) was then quickly added as one portion at room temperature. The reaction was allowed to stir for 3 hours at the same temperature. After the reaction completion as monitored by TLC, the reaction mixture was passed through a short silica plug and washed with Et$_2$O. The reaction crude was concentrated under reduced pressure. MeCN (3 mL) was added to the vial containing the crude mixture, followed by PMA/SiO$_2$ (200 mg, 2 mol %) as one portion. The reaction was allowed to stir at room temperature for 2 hours. After the reaction completion, the reaction mixture was concentrated under reduced pressure, then absorbed onto silica gel via rotary evaporation. The crude product was purified via column chromatography on silica gel with 5% Et$_2$O in hexanes as eluent, yielding cis-12 (47 mg, 0.17 mmol, 43% yield) with the ratio of cis/trans > 10:1 based on NMR analysis of the crude mixture. $^1$H NMR: (600 MHz, CDCl$_3$): $\delta$ 7.50 – 7.43 (m, 2H), 7.35 – 7.32 (m, 4H), 7.29 – 7.23 (m, 2H), 7.18 (d, $J = 7.5$ Hz, 2H), 4.32 (dd, $J = 12.2, 5.1$ Hz, 1H), 3.71 – 3.65 (m, 1H), 2.36 – 2.26 (m, 3H), 2.12 – 2.01 (m, 2H), 1.91 (dd, $J = 10.1, 3.8$ Hz, 1H). $^{13}$C NMR: (151 MHz, CDCl$_3$): $\delta$ 206.5, 138.0, 131.8, 128.6, 128.5, 128.4, 128.4, 127.2, 123.0, 87.0, 85.7, 53.4, 44.6, 35.5, 34.4, 21.9. IR (neat): 2930, 2862, 1720, 1599, 1490, 1444, 1264, 1086, 1027, 895, 733 cm$^{-1}$. HRMS-ESI m/z: [M+H], calculated for C$_{20}$H$_{19}$O: 275.1436; found: 275.1435. R$_f$ = 0.47 (silica gel, 20% EtOAc/hexane, UV).

To a flame-dried 50 mL round-bottom flask equipped with a stir bar was added 1c (578 mg, 1.9 mmol, 1 equiv), potassium trifluoro(4-(methylthio)phenyl)borate (874 mg, 3.8 mmol, 2 equiv), and MeCN (15 mL) under argon atmosphere. LiPF$_6$ (144 mg, 0.95 mmol, 0.5 equiv) was then quickly added as one portion at room temperature. The reaction was allowed to stir for 1 hour at the same temperature. After the reaction completion as monitored by TLC, the reaction was cooled to 0 °C. 4 N HCl (0.95 mL, 3.8 mmol, 38 equiv) was then added slowly. The reaction mixture was stirred at room temperature for 30 min. After the reaction completion, the reaction mixture was concentrated under reduced pressure, then absorbed onto silica gel via rotary evaporation. The crude product was purified via column chromatography on silica gel with 5% Et$_2$O in hexanes as eluent, yielding trans-13 (65% yield) with the ratio of cis/trans > 10:1 based on NMR analysis of the crude mixture. $^1$H NMR: (600 MHz, CDCl$_3$): $\delta$ 7.40 – 7.30 (m, 2H), 7.25 – 7.10 (m, 4H), 7.10 – 7.00 (m, 2H), 5.50 (s, 1H), 4.10 (dd, $J = 12.2, 5.1$ Hz, 1H), 3.10 – 3.00 (m, 1H), 2.30 – 2.20 (m, 3H), 2.10 – 2.00 (m, 2H), 1.90 (dd, $J = 10.1, 3.8$ Hz, 1H). $^{13}$C NMR: (151 MHz, CDCl$_3$): $\delta$ 206.5, 138.0, 131.8, 128.6, 128.5, 128.4, 128.4, 127.2, 123.0, 87.0, 85.7, 53.4, 44.6, 35.5, 34.4, 21.9. IR (neat): 2930, 2850, 1720, 1599, 1490, 1444, 1264, 1086, 1027, 895, 733 cm$^{-1}$. HRMS-ESI m/z: [M+H], calculated for C$_{20}$H$_{19}$O: 275.1436; found: 275.1435. R$_f$ = 0.47 (silica gel, 20% EtOAc/hexane, UV).

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2 equiv) was added slowly to the reaction mixture. The reaction was allowed to warm to room temperature for 90 minutes. After the reaction completion, the reaction mixture was concentrated under reduced pressure, then absorbed onto silica gel via rotary evaporation. The crude product was purified via column chromatography on silica gel with 5% Et₂O in hexanes as eluent, yielding 2 diastereomers of 13 in 65% (366 mg, 1.24 mmol, 65% yield) with the ratio of cis/trans = 1:6 based on NMR analysis of the crude mixture. The major diastereomer was purified by recrystallization from EtOAc and hexanes at −20 °C, and its relative configuration was determined by X-ray crystallography of its single crystal, which was grown by vapor diffusion technique from chloroform and pentanes. 

**1H NMR:** (600 MHz, CDCl₃): δ 7.26 – 7.21 (m, 2H), 7.18 – 7.13 (m, 4H), 7.12 (d, J = 7.9 Hz, 2H), 7.08 – 7.04 (m, 2H), 3.40 (dd, J = 11.4, 8.7 Hz, 2H), 2.63 – 2.52 (m, 2H), 2.46 (s, 3H), 2.32 (s, 3H), 2.20 – 2.04 (m, 2H). 

**13C NMR:** (151 MHz, CDCl₃): δ 215.5, 137.0, 136.7, 135.4, 129.4, 128.7, 128.1, 127.1, 55.5, 55.4, 29.7, 29.5, 21.2, 16.1. 

**IR (neat):** 2961, 2934, 2872, 2837, 1736, 1676, 1600, 1512, 1087, 1003, 840, 807 cm⁻¹. 

**HRMS-ESI m/z:** [M+H], calculated for C₁₉H₂₁O₅S: 297.1313; found: 297.1310. 

**Rf** = 0.43 (silica gel, 20% Et₂O/hexane, UV).

To a flame-dried 25 mL round-bottom flask equipped with a stir bar was added 1d (290 mg, 1.3 mmol, 1 equiv), potassium 4-methoxyphenyltrifluoroborate (546 mg, 2.6 mmol, 2 equiv), and MeCN (10 mL) under argon atmosphere. LiPF₆ (95 mg, 0.65 mmol, 0.5 equiv) was then quickly added as one portion at room temperature. The reaction was allowed to stir for 1 hour at the same temperature. After the reaction completion as monitored by TLC, the reaction was cooled to 0 °C. 4 N HCl (0.65 mL, 2.6 mmol, 2 equiv) was added slowly to the reaction mixture. The reaction was allowed to warm to room temperature for 90 minutes. After the reaction completion, the reaction mixture was concentrated under reduced pressure, then absorbed onto silica gel via rotary evaporation. The crude product was purified via column chromatography on silica gel with 10% Et₂O in hexanes as eluent, yielding 2 inseparable diastereomers of 14 in 61% (162 mg, 0.79 mmol, 61% yield) with the ratio of cis/trans = 3.4:1 based on NMR analysis of the crude mixture. 

**1H NMR:** (600 MHz, CDCl₃): δ 7.12 – 7.08 (m, 4H), 6.86 (d, J = 8.5 Hz, 4H), 3.78 (s, 6H), 3.40 (dd, J = 8.7, 8.7 Hz, 1H), 3.23 (dd, J = 12.2, 8.3 Hz, 1H), 2.46 – 2.15 (m, 6H), 2.00 – 1.92 (m, 1H), 1.77 – 1.74 (m, 1H), 1.56 – 1.48 (m, 2H), 1.19 (d, J = 6.9 Hz, 3H), 1.15 (d, J = 7.4 Hz, 3H). 

**13C NMR:** (151 MHz, CDCl₃): δ 220.7, 219.9, 158.5, 158.5, 131.2, 131.1, 129.1, 125.91, 114.1, 141.1, 55.3, 54.3, 53.8, 44.9, 42.5, 30.1, 29.9, 29.2, 29.1, 15.6, 14.7. 

**IR (neat):** 2961, 2934, 2872, 2837, 1736, 1676, 1600, 1512, 1455, 1244, 1177,
1151, 1031, 827 cm\(^{-1}\). **HRMS-ESI** m/z: [M+H], calculated for C\(_{13}\)H\(_{17}\)O\(_2\): 205.1229; found: 205, 1227. \(R_f\) = 0.26 (silica gel, 20% EtOAc/hexane, UV).

7. **X-ray crystallographic information**

![Chemical Structure]

**Table 1. Crystal data and structure refinement for 9**

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<tr>
<th>Identification code</th>
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<tbody>
<tr>
<td>Empirical formula</td>
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<td>Formula weight</td>
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<tr>
<td>Temperature</td>
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<tr>
<td>Wavelength</td>
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<td>Crystal system, space group</td>
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| Unit cell dimensions | a = 13.1167(7) Å  alpha = 90 deg.  
b = 12.2561(7) Å  beta = 111.247(2) deg.  
c = 9.8996(6) Å  gamma = 90 deg. |
| Volume              | 1483.28(15) Å\(^3\) |
| Z, Calculated density | 4,  1.255 Mg/m\(^3\) |
| Absorption coefficient | 0.628 mm\(^{-1}\) |
| F(000)              | 600 |
| Crystal color and shape | Colorless flat column |
| Crystal size        | 0.40 x 0.30 x 0.15 mm |
| Theta range for data collection | 3.62 to 66.49 deg. |
| Limiting indices    | -15\(<=\)h\(<=\)15, -14\(<=\)k\(<=\)14, -11\(<=\)l\(<=\)10 |
| Reflections collected / unique | 10058 / 2512 [R(int) = 0.0318] |
| Completeness to theta = 66.49 | 97.0 % |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.7528 and 0.6275 |
| Refinement method   | Full-matrix least-squares on F\(^2\) |
Table 2. Crystal data and structure refinement 13

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<td>Max. and min. transmission</td>
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<tr>
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<tr>
<td>R indices (all data)</td>
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1a

X : parts per Million : Carbon13
X: parts per Million: Carbon13
X : parts per Million : Carbon13
SI-16

X : parts per Million : Proton
MeO

OTBS

Ph

3c

X : parts per Million : Carbon13

S45
OTBS

3g

X: parts per Million: Proton
3g

X: parts per Million: Carbon13
OTBS
Me

3h

X: parts per Million: Carbon13
3i

OTBS

Me

Ph

$X$: parts per Million : Proton
OTBS

Ph

3j

X : parts per Million : Carbon13

abundance

0 0.1 0.2 0.3 0.4 0.5 0.6

190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 0 -10.0


S59
X : parts per Million : Fluorine19
4b

X: parts per Million: Proton

abundance

0.738
-0.017
-0.426

S65
4b

X : parts per Million : Carbon13
$5c$

$X : \text{parts per Million : Carbon13}$
5e

X : parts per Million : Carbon13
0
10.0
20.0
30.0
40.0
50.0

X : parts per Million : Carbon13

S81
6a
abundance

X : parts per Million : Carbon13

6a
6b
6d
$6e$
7a

X: parts per Million: Proton

Me

OTBS

Ph

S96
7b

abundance

X : parts per Million : Proton

S98
X : parts per Million : Carbon13
9

Ph

OMe

X : parts per Million : Proton

abundance

9

S102
X : parts per Million : Carbon13

S103
X : parts per Million : Proton

S110
abundance

X : parts per Million : Carbon13

S111
The diagram shows a molecular structure with chemical shifts labeled as follows:

- $H^a$ (major)
- $H^b$ (minor)
- Me (major)
- Me (minor)

The graph plots abundance against parts per million (ppm) for protons. The molecule 14 is represented with the chemical shifts and labels indicated.
abundance

X : parts per Million : Carbon13

S113