**Supporting Information**

**Regio-selective and Stereo-selective Hydrosilylation of Internal Alkynes Catalyzed by Ruthenium Complexes**

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(A) General Methods

Analytical thin layer chromatography (TLC) was HSGF 254 (0.15-0.2 mm thickness). Preparative thin layer chromatography (PTLC) was HSGF 254 (0.4-0.5 mm thickness). The reagents (chemicals) were purchased from commercial sources (J&K, TCI, Sigma-Aldrich, Adamas-beta, TCI, etc.), and used without further purification. Analytical all products were characterized by their NMR and MS spectra. $^{1}$H and $^{13}$C NMR spectra were recorded on a 400 MHz, 500 MHz or 600 MHz instrument. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet(t), quartet (q), multiplet (m), doublet of doublets (dd) and broad (br). High-resolution mass spectra (HRMS) were measured on Micromass Ultra Q-TOF spectrometer. All propargyl alcohols were prepared by following the same procedure as described in the literature$^1$.

(B) Typical Synthesis Procedure and Characterization of 3
To a reaction tube was added propargyl alcohols 2 (0.2 mmol), silanes 1 (0.24 mmol), CpRu(Ph3P)2Cl (2 mol%) and dichloromethane (2.0 mL). Then the reaction tube was evacuated and purged with argon three times. The solution was kept at room temperature for 12h. The crude mixture was purified by silica gel column chromatography (EA/PE=1/20 v/v) to give the corresponding product 3.

1. Characterization of 3

\((Z)-2-\text{(dimethyl(phenyl)silyl)}-1-(4\text{-nitrophenyl})\text{but-2-en-1-ol (3a)}\)

Following general procedure B, 3a was obtained as colorless oil (61.4 mg, yield 94%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.18 – 8.12 (m, 2H), 7.46 (d, \(J = 8.3\) Hz, 2H), 7.43 – 7.40 (m, 2H), 7.36 – 7.28 (m, 3H), 6.44 (m, \(J = 7.0, 0.8\) Hz, 1H), 5.37 (s, 1H), 2.11 – 1.98 (m, 1H), 1.76 (t, \(J = 6.3\) Hz, 3H), 0.33 – 0.28 (m, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 150.8, 147.0, 142.7, 140.9, 138.6, 133.7, 129.0, 127.9, 127.3, 123.2, 79.3, 19.0, -0.7, -0.8. HRMS (ESI) m/z: calculated for C\(_{18}\)H\(_{20}\)NO\(_3\)Si-\([\text{M - H}]^+\): 326.1218, found: 326.1224.

\((Z)-2-\text{(dimethyl(phenyl)silyl)}-1-\text{phenylbut-2-en-1-ol (3b)}\)

Following general procedure B, 3b was obtained as colorless oil (49.0 mg, yield 87%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.39 (dd, \(J = 7.5, 1.7\) Hz, 2H), 7.30 – 7.18 (m, 8H), 6.46 – 6.38 (m, 1H), 5.29 (d, \(J = 3.0\) Hz, 1H), 1.81 (d, \(J = 4.4\) Hz, 1H), 1.66 (d, \(J = 7.0\) Hz, 3H), 0.24 (s, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 142.7, 140.3, 139.6, 138.8, 133.3, 128.2, 127.6, 127.2, 126.7, 126.4, 78.4, 17.4, -1.3, -1.4. HRMS (ESI) m/z: calculated for C\(_{18}\)H\(_{22}\)NaOSi\(^+\) [M+Na]\(^+\): 305.1332, found: 305.1332.

\((Z)-2-\text{(dimethyl(phenyl)silyl)}-1-(4\text{-methoxyphenyl})\text{but-2-en-1-ol (3c)}\)

Following general procedure B, 3c was obtained as colorless oil (58.0 mg, yield 89%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.40 (d, \(J = 7.6\) Hz, 2H), 7.32 – 7.21 (m, 8H), 6.44 – 6.36 (m, 1H), 5.25 (d, \(J = 3.0\) Hz, 1H), 1.82 (d, \(J = 4.3\) Hz, 1H), 1.67 (d, \(J = 7.0\) Hz, 3H), 0.24 (s, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 142.6, 140.3, 139.7, 138.8, 133.4, 128.2, 127.6, 127.3, 126.8, 126.4, 78.4, 17.4, -1.4. HRMS (ESI) m/z: calculated for C\(_{18}\)H\(_{22}\)O\(_2\)Si\(^+\) [M+H]\(^+\): 319.1380, found: 319.1381.
en-1-ol (3c)
Following general procedure B, 3c was obtained as colorless oil (44.3 mg, yield 71%).\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 7.44 (dd, \(J = 6.3, 2.9\) Hz, 2H), 7.33 – 7.28 (m, 3H), 7.21 (d, \(J = 8.6\) Hz, 2H), 6.87 (d, \(J = 8.6\) Hz, 2H), 6.32 (q, \(J = 6.9\) Hz, 1H), 5.33 (d, \(J = 4.4\) Hz, 1H), 5.16 (d, \(J = 4.2\) Hz, 1H), 3.73 (s, 3H), 1.55 (d, \(J = 7.0\) Hz, 3H), 0.17 (d, \(J = 6.9\) Hz, 6H).\(^1\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 158.4, 142.2, 140.2, 138.1, 137.0, 134.0, 129.0, 128.4, 128.0, 113.5, 77.6, 55.4, 18.0, -0.21, -0.23. HRMS (ESI) m/z: calculated for C\(_{19}\)H\(_{24}\)NaO\(_2\)Si\(^+\) [M+Na]\(^+\): 335.1438, found: 335.1434.

\((Z)-2-\text{(dimethyl(phenyl)silyl)-1-}(\text{p-tolyl})\text{but-2-en-1-ol (3d)}\)

Following general procedure C, 3d was obtained as colorless oil (49.7 mg, yield 84%).\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.48 – 7.42 (m, 2H), 7.35 – 7.27 (m, 3H), 7.22 – 7.16 (m, 2H), 7.13 (d, \(J = 6.6\) Hz, 2H), 6.48 (q, \(J = 6.8\) Hz, 1H), 5.31 (s, 1H), 2.35 (d, \(J = 1.5\) Hz, 3H), 1.87 – 1.80 (m, 1H), 1.70 (dd, \(J = 7.0, 1.4\) Hz, 3H), 0.28 (t, \(J = 2.4\) Hz, 6H).\(^1\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 140.2, 139.7, 139.1, 138.9, 136.3, 133.3, 128.3, 128.2, 127.2, 126.4, 78.1, 20.6, 17.4, -1.3, -1.4. HRMS (EI) m/z: calculated for C\(_{19}\)H\(_{24}\)OSi: 296.1591, found 296.1597.

\((Z)-2-\text{(dimethyl(phenyl)silyl)-1-}(\text{o-tolyl})\text{but-2-en-1-ol (3e)}\)

Following general procedure B, 3e was obtained as colorless oil (45 mg, yield 76%).\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 7.51 – 7.44 (m, 2H), 7.36 (d, \(J = 6.8\) Hz, 1H), 7.34 – 7.27 (m, 3H), 7.19 – 7.05 (m, 3H), 6.06 – 5.99 (m, 1H), 5.33 (s, 1H), 2.14 (s, 3H), 1.52 (d, \(J = 7.0\) Hz, 3H), 0.34 (d, \(J = 5.5\) Hz, 3H), 0.24 (d, \(J = 10.0\) Hz, 3H).\(^1\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 142.7, 140.7, 139.8, 137.6, 135.6, 134.0, 130.3, 129.1, 128.1, 127.6, 127.1, 125.7, 72.4, 19.2, 18.0, -0.7, -0.8. HRMS (ESI) m/z: calculated for C\(_{19}\)H\(_{24}\)NaOSi\(^+\) [M+Na]\(^+\): 319.1489, found: 319.149.

\((Z)-1-\text{(2-chlorophenyl)-2-}(\text{dimethyl(phenyl)silyl})\text{but-2-en-1-ol}\)
Following general procedure B, 3f was obtained as colorless oil (51.8mg, yield 82%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.61 – 7.56 (m, 2H), 7.56 – 7.52 (m, 1H), 7.35 (m, $J$ = 8.5, 4.7, 2.0 Hz, 4H), 7.30 (m, $J$ = 7.4, 1.2 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.16 (qd, $J$ = 7.0, 1.1 Hz, 1H), 5.72 (s, 1H), 1.94 (dd, $J$ = 15.5, 1.9 Hz, 1H), 1.67 (dd, $J$ = 7.1, 0.9 Hz, 3H), 0.49 (d, $J$ = 3.3 Hz, 3H), 0.46 (d, $J$ = 3.2 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.8, 140.2, 139.4, 139.0, 133.9, 133.0, 129.5, 128.9, 128.6, 128.5, 127.8, 126.6, 73.2, 18.1, -1.2, -1.3. HRMS (ESI) m/z: calculated for C$_{18}$H$_{21}$ClNaOSi$^+$ [M +Na]$^+$: 339.0942, found: 339.0948.

(Z)-1-(3-chlorophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3g)

Following general procedure B, 3g was obtained as colorless oil (53.7mg, yield 85%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.48 (dd, $J$ = 7.6, 1.7 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.32 (s, 1H), 7.29 – 7.26 (m, 2H), 7.22 (dt, $J$ = 5.3, 3.8 Hz, 1H), 6.48 (dd, $J$ = 6.9, 3.5 Hz, 1H), 5.31 (s, 1H), 2.05 (s, 1H), 1.78 (d, $J$ = 7.1 Hz, 3H), 0.36 (s, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 145.4, 141.1, 140.7, 139.4, 139.0, 134.1, 133.8, 129.4, 128.9, 127.9, 127.2, 127.0, 125.0, 78.8, 18.0, -0.8, -0.9. HRMS (ESI) m/z: calculated for C$_{18}$H$_{20}$ClOSi$^-$ [M-H]$^-$: 315.0977, found: 315.0971.

(Z)-1-(4-chlorophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3h)

Following general procedure B, 3h was obtained as colorless oil (56.8mg, yield 90%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.41 – 7.37 (m, 2H), 7.32 – 7.26 (m, 3H), 7.24 (t, $J$ = 3.5 Hz, 2H), 7.19 (d, $J$ = 8.4 Hz, 2H), 6.42 (dd, $J$ = 7.0, 3.5 Hz, 1H), 5.25 (d, $J$ = 4.1 Hz, 1H), 1.85 (d, $J$ = 4.5 Hz, 1H), 1.69 (d, $J$ = 7.0 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 141.2, 140.3, 140.2, 138.5, 133.3, 132.4, 128.4, 127.7, 127.7, 127.3, 78.1, 17.4, -1.3, -1.4. HRMS (ESI) m/z: calculated for C$_{18}$H$_{20}$ClOSi$^-$ [M-H]$^-$: 315.0977, found: 315.0973.
Following general procedure B, 3i was obtained as colorless oil (52.4mg, yield 91%). $^1$H NMR (600 MHz, CDCl$_3$) δ 7.50 – 7.45 (m, 2H), 7.38 – 7.31 (m, 3H), 7.29 (dd, $J = 4.8$, 2.8 Hz, 1H), 7.12 – 7.08 (m, 1H), 6.98 (d, $J = 5.0$ Hz, 1H), 6.56 – 6.50 (m, 1H), 5.37 (s, 1H), 1.94 (s, 1H), 1.74 (d, $J = 7.1$ Hz, 3H), 0.35 (s, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 145.3, 140.9, 139.6, 139.2, 133.8, 128.8, 127.8, 126.9, 125.6, 121.5, 76.1, 17.9, -0.9, -1.0. HRMS (EI) m/z: calculated for C$_{16}$H$_{20}$OSSi: 288.0999, found 288.0998.

Following general procedure B, 3j was obtained as colorless oil (48mg, yield 80%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.44 – 7.40 (m, 2H), 7.35 – 7.28 (m, 3H), 7.26 – 7.22 (m, 2H), 7.03 – 6.96 (m, 2H), 6.48 (qd, $J = 7.0$, 1.1 Hz, 1H), 5.30 (s, 1H), 1.85 – 1.76 (m, 1H), 1.73 (dd, $J = 7.1$, 0.7 Hz, 3H), 0.28 (dd, $J = 6.3$, 3.1 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 161.6 (d, $J = 252$ Hz), 140.4, 139.6, 138.7, 138.5 (d, $J = 2.5$ Hz), 133.4, 128.4, 128.2 (d, $J = 7.5$ Hz), 127.36, 114.4 (d, $J = 20$ Hz), 78.0, 17.5, -1.3, -1.4. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -115.78 (s). HRMS (ESI) m/z: calculated for C$_{18}$H$_{21}$FNOSi$^+$ [M +Na$^+$]: 323.1238, found: 323.1246.

Following general procedure B, 3k was obtained as white solid (71mg, yield 87%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.66 – 7.61 (m, 2H), 7.45 – 7.41 (m, 2H), 7.36 – 7.28 (m, 3H), 7.04 (d, $J = 8.2$ Hz, 2H), 6.43 (tt, $J = 7.0$, 3.5 Hz, 1H), 5.25 (s, 1H), 1.90 (m, 1H), 1.72 (d, $J = 7.0$ Hz, 3H), 0.30 (s, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 143.0, 140.9, 140.8, 139.0, 137.1, 133.8, 128.9, 127.8, 92.7, 78.8,
18.0, -0.7, -0.8. HRMS (ESI) m/z: calculated for C_{18}H_{20}IOSi \text{ [M-H]}^{-}: 407.0334, found: 407.0333.

(Z)-1-(4-bromophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3l)

Following general procedure B, 3l was obtained as colorless oil (57.6mg, yield 80%).^1H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.42 (ddd, \(J = 11.4, 7.0, 5.4\) Hz, 4H), 7.34 – 7.28 (m, 3H), 7.16 (t, \(J = 7.4\) Hz, 2H), 6.49 – 6.40 (m, 1H), 5.27 (s, 1H), 1.75 – 1.69 (m, 3H), 0.29 (d, \(J = 3.3\) Hz, 6H).^13C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 142.2, 140.8, 140.7, 139.0, 133.8, 131.2, 128.9, 128.6, 127.8, 121.0, 78.7, 17.9, -0.8,-0.9. HRMS (ESI) m/z: calculated for C_{18}H_{20}BrOSi \text{ [M-H]}^{-}: 359.0472, found: 359.0467.

(Z)-methyl-4-(2-(dimethyl(phenyl)silyl)-1-hydroxybut-2-en-1-yl)benzoate (3m)

Following general procedure B, 3m was obtained as white solid (43.5mg, yield 63%).^1H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.98 (d, \(J = 8.3\) Hz, 2H), 7.42 (dd, \(J = 7.8, 1.5\) Hz, 2H), 7.38 (d, \(J = 8.1\) Hz, 2H), 7.35 – 7.27 (m, 3H), 6.46 – 6.40 (m, 1H), 5.35 (s, 1H), 3.92 (s, 3H), 2.02 (m, 1H), 1.71 (d, \(J = 7.0\) Hz, 3H), 0.28 (d, \(J = 2.9\) Hz, 6H).^13C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 166.7, 148.1, 141.1, 140.4, 138.5, 133.3, 129.0, 128.4, 128.4, 127.4, 126.2, 78.8, 51.7, 17.5, -1.2, -1.3. HRMS (ESI) m/z: calculated for C_{20}H_{23}O_{3}Si \text{ [M-H]}^{-}: 339.1422, found: 339.1416.

(Z)-1-[(1,1'-biphenyl)-2-yl]-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3n)

Following general procedure B, 3n was obtained as colorless oil (56.5mg, yield 79%).^1H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.59 (dd, \(J = 7.7, 1.3\) Hz, 1H), 7.43 – 7.26 (m, 13H), 6.27 (qd, \(J = 7.0, 1.4\) Hz, 1H), 5.41 (s, 1H), 1.80 (m, 1H), 1.69 – 1.64 (m, 3H), 0.26 (d, \(J = 3.3\) Hz, 3H), 0.20 (d, \(J = 3.2\) Hz, 3H).
\[ ^{13}\text{C NMR (126 MHz, CDCl}_3 \] \( \delta \) 141.5, 141.1, 140.8, 140.2, 139.6, 139.3, 133.8, 130.2, 129.4, 128.7, 128.0, 127.7, 127.3, 127.2, 127.1, 73.4, 18.1, -1.4, -1.5. HRMS (ESI) m/z: calculated for C_{24}H_{26}NaOSi^{+} [M +Na]^{+}: 381.1645, found: 381.1647.

\[ (Z)-2-(\text{dimethyl(phenyl)silyl})-1-(\text{naphthalen-2-yl})\text{but-2-en-1-ol (3o)} \]

Following general procedure B, 3o was obtained as colorless oil (59.1mg, yield 89%).\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \( \delta \) 7.90 – 7.84 (m, 3H), 7.82 (s, 1H), 7.54 – 7.44 (m, 5H), 7.34 – 7.26 (m, 3H), 6.42 – 6.34 (m, 1H), 5.63 (d, \( J = 4.4 \) Hz, 1H), 5.39 (d, \( J = 4.3 \) Hz, 1H), 1.60 (d, \( J = 7.0 \) Hz, 3H), 0.19 (dd, \( J = 13.9, 3.2 \) Hz, 6H). \(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \( \delta \) 142.6, 142.0, 140.1, 139.3, 134.0, 133.2, 132.5, 129.0, 128.2, 128.1, 127.9, 127.5, 126.4, 126.1, 125.9, 125.3, 78.3, 18.1, -0.1, -0.2. HRMS (ESI) m/z: calculated for C_{22}H_{24}NaOSi^{+} [M +Na]^{+}: 355.1489, found: 355.1499.

\[ (Z)-1-(\text{benzofuran-3-yl})-2-(\text{dimethyl(phenyl)silyl})\text{but-2-en-1-ol (3p)} \]

Following general procedure B, 3p was obtained as colorless oil (52.8mg, yield 82%).\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \( \delta \) 7.57 (d, \( J = 7.4 \) Hz, 1H), 7.52 – 7.45 (m, 3H), 7.33 – 7.25 (m, 3H), 7.25 – 7.16 (m, 2H), 6.45 (q, \( J = 6.9 \) Hz, 1H), 5.79 (d, \( J = 5.1 \) Hz, 1H), 5.31 (d, \( J = 5.0 \) Hz, 1H), 1.58 (d, \( J = 7.0 \) Hz, 3H), 0.30 (s, 3H), 0.25 (s, 3H). \(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \( \delta \) 161.2, 154.6, 139.9, 139.6, 138.9, 134.0, 129.1, 128.6, 128.1, 124.2, 123.1, 121.4, 111.4, 103.5, 72.25, 18.1, -0.5, -0.6. HRMS (ESI) m/z: calculated for C_{20}H_{22}NaO_{2}Si^{+} [M +Na]^{+}: 345.1281, found: 345.1284.

\[ (Z)-4-(\text{dimethyl(phenyl)silyl})\text{-2-methylhexa-1,4-dien-3-ol (3q)} \]

Following general procedure B, 3q was obtained as colorless oil (36.9mg, yield 75%).\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.60 – 7.51 (m,
(Z)-3-(dimethyl(phenyl)silyl)-1-phenylpent-3-en-2-ol (3r)

Following general procedure B, 3r was obtained as colorless oil (50.3 mg, yield 85%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.62 – 7.56 (m, 2H), 7.41 – 7.36 (m, 3H), 7.29 (t, \(J = 7.4\) Hz, 2H), 7.22 (t, \(J = 7.3\) Hz, 1H), 7.10 (d, \(J = 7.3\) Hz, 2H), 6.63 – 6.57 (m, 1H), 4.41 (dd, \(J = 9.4, 3.1\) Hz, 1H), 2.91 (dd, \(J = 13.7, 3.3\) Hz, 1H), 2.62 (dd, \(J = 13.7, 9.5\) Hz, 1H), 1.72 (d, \(J = 7.1\) Hz, 3H), 1.57 (s, 1H) 0.52 (s, 6H). \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 140.8, 140.1, 139.3, 139.0, 138.1, 133.9, 129.4, 128.9, 128.5, 127.9, 126.4, 76.7, 45.0, 18.0, -0.5, -0.6. HRMS (ESI) m/z: calculated for C\(_{19}\)H\(_{24}\)NaOSi\(^+[M+Na]^+\): 319.1489, found: 319.1487.

(Z)-benzyl-4-(2-(dimethyl(phenyl)silyl)-1-hydroxybut-2-en-1-yl)piperidine-1-carboxylate (3s)

Following general procedure B, 3s was obtained as colorless oil (71.1 mg, yield 84%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.55 – 7.51 (m, 2H), 7.38 – 7.33 (m, 7H), 7.33 – 7.29 (m, 1H), 6.36 (q, \(J = 7.0\) Hz, 1H), 5.12 (s, 2H), 4.20 (s, 2H), 3.89 (d, \(J = 7.2\) Hz, 1H), 2.66 (s, 2H), 1.94 – 1.83 (m, 1H), 1.69 (d, \(J = 7.1\) Hz, 3H), 1.55 (m, \(J = 14.8, 11.0, 7.4, 4.0\) Hz, 2H), 1.45 (s, 1H), 1.17 (d, \(J = 10.7\) Hz, 2H), 0.46 (d, \(J = 2.2\) Hz, 6H). \(^13\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 155.2, 140.3, 140.1, 139.3, 137.0, 133.7, 128.9, 128.4, 127.9, 127.8, 81.8, 66.9, 44.1, 44.0, 41.0, 18.0, -0.41, -0.42. HRMS (ESI) m/z: calculated for C\(_{25}\)H\(_{33}\)NNaO\(_3\)Si\(^+[M+Na]^+\): 446.2122, found: 446.2122.
Following general procedure B, 3t was obtained as colorless oil (33.7mg, yield 72%). 

\[^{1}H\text{ NMR (600 MHz, CDCl}_{3}\] \(\delta\) 7.57 – 7.52 (m, 2H), 7.35 (dd, \(J = 9.3, 6.3\) Hz, 3H), 6.44 (qd, \(J = 7.0, 0.8\) Hz, 1H), 4.16 – 4.09 (m, 1H), 1.64 (d, \(J = 7.0\) Hz, 3H), 1.61 (ddd, \(J = 14.9, 7.0, 5.2\) Hz, 1H), 1.51 (m, 2H), 0.90 (q, \(J = 7.4\) Hz, 3H), 0.44 (s, 6H).

\[^{13}C\text{ NMR (151 MHz, CDCl}_{3}\] \(\delta\) 141.0, 139.1, 137.5, 133.3, 128.3, 127.4, 78.1, 30.2, 17.5, 10.2, -0.9, -1.0. HRMS (ESI) m/z: calculated for C\(_{14}\)H\(_{22}\)NaOSi\(^{+}\) [M +Na\(^{+}\)]: 257.1332, found: 257.1331.

\(\text{(E)-2-(dimethyl(phenyl)silyl)-4,4-dimethyl-1-phenylpent-2-en-1-ol (3u)}\)

Following general procedure B, 3u was obtained as colorless oil (57mg, yield 88%). \[^{1}H\text{ NMR (500 MHz, CDCl}_{3}\] \(\delta\) 7.45 – 7.41 (m, 2H), 7.37 – 7.20 (m, 8H), 6.20 (d, \(J = 4.5\) Hz, 1H), 6.07 (d, \(J = 1.0\) Hz, 1H), 1.71 (d, \(J = 4.8\) Hz, 1H), 1.18 (s, 9H), 0.20 (d, \(J = 3.1\) Hz, 3H), 0.10 – 0.06 (m, 3H).\[^{13}C\text{ NMR (126 MHz, CDCl}_{3}\] \(\delta\) 153.3, 142.4, 140.0, 139.7, 133.4, 128.2, 127.4, 127.3, 126.3, 125.8, 71.0, 34.6, 31.2, -1.1, -1.6. LRMS (APCI\(^{−}\)) m/z calculated for (M-H)\[^{−}\][C\(_{21}\)H\(_{27}\)OSi] \(^{−}\): 323.2, found 323.7. HRMS (EI) m/z: calculated for C\(_{21}\)H\(_{28}\)O\(_{2}\)Si: 324.1908, found: 324.1910

\(\text{(Z)-2-(dimethyl(phenyl)silyl)-1-phenylhex-2-en-1-ol (3v)}\)

Following general procedure B, 3v was obtained as colorless oil (54mg, yield 87%). \[^{1}H\text{ NMR (500 MHz, CDCl}_{3}\] \(\delta\) 7.47 – 7.42 (m, 2H), 7.38 – 7.26 (m, 8H), 6.41 (td, \(J = 7.5, 0.9\) Hz, 1H), 5.36 (s, 1H), 2.12 – 2.04 (m, 2H), 1.38 – 1.28 (m, 2H), 0.81 (t, \(J = 7.4\) Hz, 3H), 0.30 (d, \(J = 2.0\) Hz, 6H).\[^{13}C\text{ NMR (126 MHz, CDCl}_{3}\] \(\delta\) 145.8, 143.1, 139.6, 139.6, 133.8, 128.7, 128.1, 127.7, 127.2, 127.0, 79.0, 34.0, 22.7, 13.8, -0.6, -0.7. LRMS (APCI\(^{−}\)) m/z calculated for (M-H)\[^{−}\][C\(_{20}\)H\(_{25}\)OSi] \(^{−}\): 309.2, found 309.0. HRMS (ESI) m/z: calculated for C\(_{20}\)H\(_{26}\)NaOSi\(^{+}\) [M +Na\(^{+}\)]: 333.1645, found: 333.1638

\(\text{(E)-2-(dimethyl(phenyl)silyl)-1,3-diphenylprop-2-en-1-ol (3w)}\)
Following general procedure B, 3w was obtained as colorless oil (46mg, yield 67%). 

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.59 – 7.54 (m, 2H), 7.43 – 7.39 (m, 2H), 7.39 – 7.33 (m, 5H), 7.33 – 7.25 (m, 6H), 7.13 (s, 1H), 6.02 (s, 1H), 0.33 (d, $J = 3.3$ Hz, 3H), 0.29 (d, $J = 3.4$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 144.91, 142.75, 141.86, 139.35, 137.26, 134.05, 128.97, 128.61, 128.23, 127.87, 127.46, 127.05, 126.29, 72.75, -1.12, -1.44. HRMS (ESI) m/z: calculated for C$_{23}$H$_{24}$OSi$^+$ [M +H]$^+$: 344.1597, found: 344.1596.

(Z)-3-cyclohexyl-2-(dimethyl(phenyl)silyl)-1-phenylprop-2-en-1-ol (3x)

Following general procedure B, 3x was obtained as colorless oil (67mg, yield 64%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (m, 2H), 7.35 – 7.26 (m, 8H), 6.18 (d, $J = 10.0$ Hz, 1H), 5.31 (s, 1H), 2.24 – 2.11 (m, 1H), 1.88 (s, 1H), 1.60 (d, $J = 9.0$ Hz, 2H), 1.56 (s, 1H), 1.41 (s, 2H), 1.04 (m, 5H), 0.25 (m, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 150.9, 143.19, 139.89, 137.59, 133.89, 128.7, 128.1, 127.6, 127.2, 127.0, 78.9, 40.8, 32.6, 32.5, 25.9, 25.6, 25.5, -0.59, -0.68. HRMS (ESI) m/z: calculated for C$_{23}$H$_{31}$OSi$^+$ [M+Na]$^+$: 350.2101, found: 350.2100

(Z)-1-(4-nitrophenyl)-2-(triethylsilyl)but-2-en-1-ol (4a)

Following general procedure B, 4a was obtained as colorless oil (57.7mg, yield 94%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.18 (dd, $J = 8.5$, 6.7 Hz, 2H), 7.53 (t, $J = 10.1$ Hz, 2H), 6.37 (tt, $J = 7.1$, 3.5 Hz, 1H), 5.33 (d, $J = 3.5$ Hz, 1H), 1.89 (d, $J = 4.1$ Hz, 1H), 1.87 (d, $J = 7.1$ Hz, 3H), 0.86 (dd, $J = 9.5$, 6.2 Hz, 9H), 0.69 – 0.50 (m, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 150.6, 146.4, 142.0, 139.9, 126.9, 122.7, 78.3, 17.1, 7.1, 3.6. HRMS (ESI) m/z: calculated for C$_{16}$H$_{25}$NNaO$_3$Si$^+$ [M+Na]$^+$: 330.1496, found: 330.1488.

(Z)-1-(4-nitrophenyl)-2-(triethoxysilyl)but-2-en-1-ol (4b)

Following general procedure B, 4b was obtained as colorless oil (23.4mg, yield 61%). $^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$
8.20 – 8.15 (m, 2H), 7.56 (d, J = 8.5 Hz, 2H), 6.61 (m, J = 7.0, 1.0 Hz, 1H), 5.59 (d, J = 4.6 Hz, 1H), 5.27 (d, J = 4.5 Hz, 1H), 3.61 (q, J = 7.0 Hz, 6H), 1.90 – 1.85 (m, 3H), 1.05 (t, J = 7.0 Hz, 9H).\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 153.5, 146.6, 142.0, 137.1, 128.3, 123.3, 75.4, 58.0, 18.4, 17.8. HRMS (ESI) m/z: calculated for \(\text{C}_{16}\text{H}_{24}\text{NO}_{6}\text{Si}^-\) [M -H]: 354.1378, found: 354.1379.

\(\text{(Z)-2-(tert-butyldimethylsilyl)-1-(4-nitrophenyl)but-2-en-1-ol (4c)}\)

Following general procedure B, \(4c\) was obtained as colorless oil (36.8 mg, yield 60%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.21 – 8.14 (m, 2H), 7.53 (t, J = 9.8 Hz, 2H), 6.36 (tt, J = 7.0, 3.5 Hz, 1H), 5.40 (d, J = 6.6 Hz, 1H), 1.91 (s, 1H), 1.87 (d, J = 7.2 Hz, 3H), 0.93 (d, J = 3.0 Hz, 9H), 0.12 (d, J = 3.1 Hz, 3H), 0.09 – 0.04 (m, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 151.5, 147.0, 143.4, 141.0, 127.6, 123.3, 77.6, 27.4, 18.9, 18.6, -2.9, -3.3. HRMS (ESI) m/z: calculated for \(\text{C}_{16}\text{H}_{24}\text{NO}_{3}\text{Si}^-\) [M -H]: 306.1531, found: 306.1534.

**C** The NOE analysis

a) The NOE analysis of 3j
b) The NOE analysis of 3s

c) The NOE analysis of 3t
d) The NOE analysis of 3u

e) The NOE analysis of 3v
f) The NOE analysis of 3x
g) The NOE analysis of 4a

h) The NOE analysis of 4c
(D) Gram-scale preparation of 3a and synthetic applications of
**vinylsilane**

**a) Gram-scale preparation of 3a**

The dry sealed tube was charged with propargyl alcohol 2a (1 g, 5.2 mmol, 1 equiv), 1a (6.2 mmol, 1.2 equiv), CpRu(Ph₃P)₂Cl (5 mol%) (0.26 mmol, 0.05 equiv) and 50 mL dry DCM. The mixture was kept at room temperature for 12 h under Argon atmosphere. The resulting mixture was diluted with dichloromethane and washed by water. The combined organic layers were dried with Na₂SO₄, filtered, concentrated and purified by column chromatography on silica gel (PE/EA = 20/1, v/v) to give the desired product 3a (1.22 g, 75% yield).

**b) The coupling reaction of vinylsilane 3za**

To a 25 mL of Schlenk tube were added Pd(OAc)₂ (2.3 mg, 0.01 mmol, 5 mol%), Xantphos (12 mg, 0.02 mmol, 10 mol%), K₂CO₃ (66 mg, 0.48 mmol), and AgF (61 mg, 0.48 mmol) under air. The mixture was then evacuated and backfilled with Argon (3 times). 3za (75 mg, 0.24 mmol), Phenylacetylene (20.5 mg, 0.2 mmol), and dry MeCN (2 mL) were added subsequently. The Schlenk tube was screw capped and stirred under room temperature for 12 h. After this time, the reaction mixture was diluted with EtOAc, filtered through a pad of celite, and concentrated. The residue was purified with silica gel chromatography (PE/EA) to give product 5a as colorless oil (34 mg, 68% yield).

(Z)-1-phenyl-2-(triethoxysilyl)but-2-en-1-ol(3za)
The product 3za was obtained as colorless oil (55mg, yield 60%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (d, $J = 7.2$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.20 (t, $J = 7.1$ Hz, 1H), 6.48 – 6.40 (m, 1H), 5.19 (d, $J = 9.5$ Hz, 1H), 3.96 (d, $J = 9.5$ Hz, 1H), 3.69 – 3.60 (m, 6H), 1.93 (d, $J = 7.0$ Hz, 3H), 1.13 (t, $J = 7.0$ Hz, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 144.1, 143.3, 137.0, 127.8, 126.6, 126.0, 79.6, 58.3, 17.9, 17.6. HRMS (EI) m/z: calculated for C$_{16}$H$_{26}$O$_2$Si: 310.1595, found: 310.1600

(E)-1-phenyl-2-(phenylethynyl)but-2-en-1-ol (5a)

The product 5a was a colorless oil (34mg, yield 68%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (d, $J = 7.5$ Hz, 2H), 7.41 – 7.33 (m, 4H), 7.30 (dd, $J = 8.2$, 5.1 Hz, 4H), 6.21 – 6.13 (m, 1H), 5.30 (d, $J = 4.2$ Hz, 1H), 2.28 (d, $J = 4.8$ Hz, 1H), 1.98 (d, $J = 6.8$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 141.6133, 130.9, 127.8, 127.8, 127.3, 126.8, 126.0, 122.7, 96.0, 84.6, 76.3, 15.6. HRMS (EI) m/z: calculated for C$_{18}$H$_{16}$O: 248.1196, found: 248.1199

c) The epoxidation reaction of vinylsilane 3a

Preparation of silicane epoxide 5b: Vinylsilane 3a (65.4 mg, 0.2mmol) was taken up in CH$_2$Cl$_2$ (4 mL) and treated with mCPBA (662 mg, 3.07 mmol assuming 80% purity) at 0°C. After the reaction mixture had been stirred for 14 h, saturated aqueous sodium bicarbonate (10mL) and solid Na$_2$S$_2$O$_3$ (ca. 2 g) were added. The mixture was extracted with ether (3×30 mL), and the combined organic layers were dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Silica gel chromatography (petroleum ether/ethyl acetate(v/v,20/1) as eluent) afforded the desired epoxyalcohol as a single isomer (51.5 mg, 75% yield).
The product 5b was obtained as colorless oil (51.5 mg, 75% yield). 1H NMR (500 MHz, CDCl3) δ 8.11 – 8.06 (m, 2H), 7.41 – 7.37 (m, 1H), 7.36 – 7.30 (m, 4H), 7.24 (dd, J = 6.4, 4.7 Hz, 2H), 4.76 (s, 1H), 3.54 (q, J = 5.7 Hz, 1H), 2.67 (s, 1H), 1.40 (d, J = 5.8 Hz, 3H), 0.36 – 0.33 (m, 3H), 0.18 – 0.15 (m, 3H). 13C NMR (126 MHz, CDCl3) δ 147.8, 147.0, 135.8, 134.2, 129.8, 129.0, 128.0, 123.4, 72.5, 58.4, 54.3, 15.8, -1.6, -3.0. HRMS (ESI) m/z: calculated for C18H20NO4Si [M-H]−: 342.1167, found: 342.1165

d) The protodesilylation reaction of vinylsilane 3a

Preparation of protodesilylation 5c: Vinylsilane 3a (65.4 mg, 0.2 mmol) was dissolved in THF (4 mL) and treated with TBAF (0.24 mmol, 1 M in THF) at room temperature. After the reaction mixture was stirred for 30 min, saturated aqueous sodium bicarbonate was added, the mixture was extracted with ether (3 × 30 mL), and the combined organic layers were dried over Na2SO4 and concentrated under reduced pressure. Silica gel chromatography (eluent: petroleum ether/ethyl acetate (v/v, 20/1) as eluent) afforded the desired product (27.1 mg, 70% yield).

1-hydroxy-1-(4-nitrophenyl)butan-2-one (5c)

The product 5c was obtained as colorless oil (27.1 mg, 70% yield). 1H NMR (500 MHz, CDCl3) δ 8.23 – 8.14 (m, 2H), 7.54 (d, J = 8.4 Hz, 2H), 5.89 – 5.78 (m, 1H), 5.66 – 5.57 (m, 1H), 5.26 (d, J = 7.4 Hz, 1H), 2.03 (s, 1H), 1.74 (dd, J = 6.5, 1.1 Hz, 3H). 13C NMR (126 MHz, CDCl3) δ 150.4, 147.2, 132.6, 129.4, 126.8, 123.6, 74.4, 17.7. LRMS (APCI-) m/z calculated for (M-H)- [C10H11NO3]−: 192.0, found 192.1. HRMS (ESI) m/z: calculated for C10H11NNaO3+ [M+Na]+: 216.0637, found: 216.0640
(E) Copies of $^1$H NMR and $^{13}$C NMR Spectra for the Products

(Z)-2-(dimethyl(phenyl)silyl)-1-(4-nitrophenyl)but-2-en-1-ol (3a)
(Z)-2-(dimethyl(phenyl)silyl)-1-phenylbut-2-en-1-ol (3b)
(Z)-2-(dimethyl(phenyl)silyl)-1-(4-methoxyphenyl)but-2-en-1-ol (3c)
(Z)-2-(dimethyl(phenyl)silyl)-1-(p-tolyl)but-2-en-1-ol (3d)
(Z)-2-(dimethyl(phenyl)silyl)-1-(o-tolyl)but-2-en-1-ol (3e)
(Z)-1-(2-chlorophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3f)
(Z)-1-(3-chlorophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3g)
(Z)-1-(4-chlorophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3h)
(Z)-2-(dimethyl(phenyl)silyl)-1-(thiophen-3-yl)but-2-en-1-ol (3i)
(Z)-2-(dimethyl(phenyl)silyl)-1-(4-fluorophenyl)but-2-en-1-ol (3j)
(Z)-2-(dimethyl(phenyl)silyl)-1-(4-iodophenyl)but-2-en-1-ol (3k)
(Z)-1-(4-bromophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3l)
(Z)-methyl-4-(2-(dimethyl(phenyl)silyl)-1-hydroxybut-2-en-1-yl)benzoate (3m)
(Z)-1-((1,1'-biphenyl)-2-yl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3n)
(Z)-2-(dimethyl(phenyl)silyl)-1-(naphthalen-2-yl)but-2-en-1-ol (3o)
(Z)-1-(benzofuran-3-yl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3p)
(Z)-4-(dimethyl(phenyl)silyl)-2-methylhexa-1,4-dien-3-ol (3q)
(Z)-3-(dimethyl(phenyl)silyl)-1-phenylpent-3-en-2-ol (3r)
(Z)-benzyl-4-(2-(dimethyl(phenyl)silyl)-1-hydroxybut-2-en-1-yl)piperidine-1-
carboxylate (3s)

(Z)-4-(dimethyl(phenyl)silyl)hex-4-en-3-ol (3t)
(E)-2-(dimethyl(phenyl)silyl)-4,4-dimethyl-1-phenylpent-2-en-1-ol (3u)
(Z)-2-(dimethyl(phenyl)silyl)-1-phenylhex-2-en-1-ol (3v)
(E)-2-(dimethyl(phenyl)silyl)-1,3-diphenylprop-2-en-1-ol (3w)
(Z)-3-cyclohexyl-2-(dimethyl(phenyl)silyl)-1-phenylprop-2-en-1-ol (3x)
(Z)-1-(4-nitrophenyl)-2-(triethylsilyl)but-2-en-1-ol (4a)
(Z)-1-(4-nitrophenyl)-2-(triethoxysilyl)but-2-en-1-ol (4b)
(Z)-2-(tert-butyldimethylsilyl)-1-(4-nitrophenyl)but-2-en-1-ol (4c)
(Z)-1-phenyl-2-(triethoxysilyl)but-2-en-1-ol (3za)
(E)-1-phenyl-2-(phenylethynyl)but-2-en-1-ol (5a)
(2-(dimethyl(phenyl)silyl)-3-methyloxiran-2-yl)(4-nitrophenyl)methanol (5b)
1-hydroxy-1-(4-nitrophenyl)butan-2-one (5c)
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