Supporting Information
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Supporting Information

A Highly Diastereoselective Access to Silicon-containing Oxazines via the TMSOTf-promoted Reaction of N-Benzoyl-N,O-acetals with Allyl Silanes

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General methods S2
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Spectral data for 13 S2-S9
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General Methods.

IR spectra were recorded with FT-IR as a thin film or using Neat pellets and are expressed in cm\(^{-1}\). \(^1\)H (400 or 600 MHz) and \(^{13}\)C (100 or 150 MHz) NMR spectra were recorded using CDCl\(_3\) as a solvent, and the ratio of the compounds were determined by \(^1\)H NMR. Chemical shifts are reported in ppm downfield to tetramethylsilane. Coupling constants are reported and expressed in Hz; splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (double doublet), dt (double triplet). All reactions were carried out using freshly distilled and dry solvents. Column chromatography was performed over silica gel (100-200 Mesh) using petroleum ether and ethyl acetate as eluent. Mass spectra were obtained from high resolution ESI mass spectrometer.

General procedure for the reaction of 11 with allylsilanes:

To the mixture of \(N\)-acyl, \(O\)-acetal 11 (1 mmol), allyl silane (1 mmol) in anhydrous dichloromethane (10 ml) under nitrogen was added at -78 °C TMSOTf (0.16 mL, 1 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO\(_3\) solution, and then extracted with dichloromethane. The combined organic extracts were dried over Na\(_2\)SO\(_4\). After concentration in \textit{vacuo}, the residue was purified by flash chromatography afforded the product 13.

\(\text{Trans-2,4-diphenyl-6-trimethylsilylmethyl-5,6-dihydro-4H-[1,3]oxazine (trans-13a)}\) yield: 74%; colorless liquid; IR (neat): 2937, 1644, 1511, 1251, 1036, 919, 850, 739, 702 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.90-7.88\) (m, 2H), 7.28-7.19 (m, 7H), 7.16-7.09 (m, 1H), 4.58 (dd, \(J = 11.6\) Hz, 4.8 Hz, 1H), 4.43-4.36 (m, 1H), 2.14
(ddd, $J = 13.6$ Hz, 4.8 Hz, 2.4 Hz, 1H), 1.47-1.38 (m, 1H), 1.05-0.99 (m, 1H), 0.86-0.81 (m, 1H), 0.00 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 157.0, 145.3, 134.7, 130.9, 129.0, 128.5, 127.9, 127.3, 127.0, 74.6, 57.6, 41.1, 25.2, 0.0; Anal. Calcd for C$_{20}$H$_{25}$NOSi: C, 74.25; H, 7.79; N, 4.33. Found: C, 74.47; H, 7.60; N, 4.43.

Selected data for *cis*-13a: $^1$H NMR (400 MHz, CDCl$_3$): δ 8.00-7.98 (m, 2H), 7.39-7.18 (m, 8H), 4.84 (t, 10Hz, 1H), 4.26-4.22 (m, 1H), 2.00-1.92 (m, 2H), 1.16-1.21 (m, 1H), 0.92-0.87 (m, 1H), 0.00 (s, 9H).

**Trans-6-[(tert-butyl-dimethyl-silanyl)-methyl]-2,4-diphenyl-5,6-dihydro-4H-[1,3]-oxazine (trans-13b):** yield 78%, colorless liquid; IR (neat): 2942, 1648, 1517, 1252, 1040, 917, 846, 742, 695 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.94 (d, $J = 8.0$ Hz, 2H), 7.34 - 7.13 (m, 8H), 4.63 (dd, $J = 11.6$ Hz 4.8 Hz, 1H), 4.47-4.40 (m, 1H), 2.23-2.18 (m, 1H), 1.47 (dd, $J = 24.4$ Hz, 11.6 Hz, 1H), 1.05 (dd, $J = 14.8$ Hz, 8.0 Hz, 1H), 0.87 (dd, $J = 14.8$ Hz, 6.0 Hz, 1H), 0.81 (s, 9H), 0.05 (s, 3H), 0.00 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 156.4, 144.7, 134.2, 130.4, 128.4, 128.0, 127.4, 126.7, 126.4, 74.2, 57.1, 40.6, 26.4, 20.3, 16.5, -4.8, -5.3; Anal. Calcd for C$_{23}$H$_{31}$NO$_2$Si: C, 75.56; H, 8.55; N, 3.83. Found: C, 75.64; H, 8.62; N, 3.94.
**cis-13b:** colorless liquid; IR (neat): 2937, 1644, 1510, 1253, 1035, 737, 701 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 (d, $J = 8.0$ Hz, 2H), 7.41 – 7.20 (m, 8H), 4.88 (t, $J = 4.8$ Hz, 1H), 4.29 - 4.23 (m, 1H), 2.06 – 1.95 (m, 2H), 1.17 (dd, $J = 14.4$ Hz, 8.0 Hz, 1H), 0.89 (dd, $J = 14.8$ Hz, 6.8 Hz, 1H), 0.82 (s, 9H), 0.00 (s, 3H), -0.05 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 156.5, 144.5, 134.2, 130.4, 128.3, 128.0, 127.3, 126.8, 126.6, 70.2, 54.3, 37.6, 26.3, 19.8, 16.5, -5.1, -5.31; Anal. Calcd for C$_{23}$H$_{31}$NOSi: C, 75.56; H, 8.55; N, 3.83. Found: C, 75.47; H, 8.46; N, 3.76.

**trans-13c:** yield: 70%, colorless liquid; IR (neat): 2939, 1635, 1521, 1248, 1032, 928, 817, 732, 703 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.71 (t, $J = 7.6$Hz, 4H), 7.58 (d, $J = 7.6$Hz, 2H), 7.45-7.12 (m, 14H), 4.47 (dd, $J = 11.2$ Hz, 4.8 Hz, 1H), 4.42-4.36 (m, 1H), 2.06-2.01 (m, 1H), 1.82 (dd, $J = 14.8$ Hz, 8.0 Hz, 1H), 1.53-1.46 (m, 2H), 1.09 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 156.0, 144.6, 136.2, 136.1, 134.2, 133.9, 133.7, 130.1, 129.4, 129.3, 128.3, 127.9, 127.8, 127.7, 127.3, 126.5, 126.3, 73.5, 56.8, 40.2, 27.8, 18.1; Anal. Calcd for C$_{33}$H$_{35}$NOSi: C, 80.93; H, 7.20; N, 2.86. Found: C, 80.78; H, 7.32; N, 3.01.
2-Phenyl-4-p-tolyl-6-trimethylsilanylmethyl-5,6-dihydro-4H-[1,3]oxazine (trans-13d): yield (88%), colorless oil; IR (neat): 2932, 1630, 1517, 1244, 1025, 931, 817, 722, 698 cm\(^{-1}\); ¹H NMR (CDCl\(_3\), 400 MHz) δ 7.89 (d, \(J = 6.8\) Hz, 2H), 7.28-7.20 (m, 2H), 7.13 (d, \(J = 7.6\) Hz, 2H), 7.05-7.01 (m, 2H), 4.54 (dd, \(J = 11.2\) Hz, 4.4 Hz, 1H), 4.39-4.34 (m, 1H), 2.19 (s, 3H), 2.11 (ddd, \(J = 13.2\) Hz, 4.4 Hz, 2.0 Hz, 1H), 1.46-1.37 (m, 1H), 1.01 (dd, \(J = 14.8\) Hz, 8.4 Hz, 1H), 0.82 (dd, \(J = 14.8\) Hz, 6.0 Hz, 1H), 0.00 (s, 9H); ¹³C NMR (CDCl\(_3\), 100 MHz) δ 158.8, 142.4, 136.7, 134.8, 130.9, 129.9, 128.5, 128.0, 126.9, 74.6, 57.4, 41.1, 25.2, 21.7, 0.00; Anal. Calcd for C\(_{21}\)H\(_{27}\)NOSi: C, 74.73; H, 8.06; N, 4.15. Found: C, 74.82; H, 7.99; N, 4.17.

Selected data for cis-13d: ¹H NMR (CDCl\(_3\), 400 MHz) δ 4.72 (t, \(J = 4.4\) Hz, 1H), 4.19-4.12 (m, 1H), 2.18 (s, 3H), -0.08 (s, 3H); ¹³C NMR (CDCl\(_3\), 100 MHz) δ 129.5, 128.6, 127.9, 127.3, 70.6, 54.6, 38.2, 24.6, -0.10.

2-Phenyl-4-m-tolyl-6-trimethylsilanyloxymethyl-5,6-dihydro-4H-[1,3]oxazine (trans-13e): yield 80%, colorless oil; IR (neat): 2936, 1634, 1524, 1246, 1037, 925, 822, 728, 700 cm\(^{-1}\); ¹H NMR (CDCl\(_3\), 400 MHz) δ 8.12-8.10 (m, 2H), 7.50-7.42 (m, 3H), 7.36-7.19 (m, 4H), 4.76 (dd, \(J = 11.6\) Hz, 4.8 Hz, 1H), 4.63-4.56 (m, 1H), 2.41 (s, 3H), 2.33 (ddd, \(J = 13.6\) Hz, 4.8 Hz, 2.4 Hz, 1H), 1.68-1.59 (m, 1H), 1.24 (dd, \(J = 18.4\) Hz, 8.4 Hz, 1H), 1.03 (dd, \(J = 14.8\) Hz, 6.0 Hz, 1H), 0.22 (s, 9H); ¹³C NMR (CDCl\(_3\), 100 MHz) δ 156.8, 142.4, 136.7, 134.8, 130.9, 129.7, 128.5, 128.0, 126.9, 74.6, 57.4, 41.1, 25.3, 21.7, 0.02; Anal. Calcd for C\(_{21}\)H\(_{27}\)NOSi: C, 74.73; H, 8.06; N, 4.15. Found: C,
74.60; H, 7.92; N, 4.22.

Selected data for the cis-13e: ¹H NMR (CDCl₃, 400 MHz) δ 4.93 (t, J = 4.8 Hz, 1H), 4.40-4.34 (m, 1H), 2.10-2.05 (m, 1H), 0.13 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz) δ 142.1, 136.7, 134.9, 130.9, 129.6, 128.6, 127.9, 127.3, 70.6, 54.6, 38.2, 24.7, 21.6, -0.09.

4-(4-Chloro-phenyl)-2-phenyl-6-trimethylsilanylmethyl-5,6-dihydro-4H-[1,3]oxazine (trans-13f): yield: 75%, colorless liquid; IR (Neat): 2941, 1630, 1526, 1242, 1035, 931, 825, 730, 704 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.87 (d, J = 7.6 Hz, 2H), 7.30-7.17 (m, 7H), 4.55 (dd, J = 11.2 Hz, 4.8 Hz, 1H), 4.42-4.35 (m, 1H), 2.13-2.09 (m, 1H), 1.37 (dd, J = 24.4 Hz, 11.6 Hz, 1H), 1.02 (dd, J = 14.4 Hz, 8.0 Hz, 1H), 0.83 (dd, J = 14.8 Hz, 6.0 Hz, 1H), 0.00 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 157.2, 143.9, 134.6, 132.9, 131.1, 129.1, 128.6, 128.4, 127.9, 74.6, 56.9, 40.9, 25.2, 0.0; Anal. Calcd for C₂₀H₂₄ClNOSi: C, 67.11; H, 6.76; N, 3.91. Found: C, 67.22; H, 6.85; N, 3.82.

4-(2-Chloro-phenyl)-2-phenyl-6-trimethylsilanylmethyl-5,6-dihydro-4H-[1,3]oxazine (trans-13g): yield: 84%, colorless liquid; IR (Neat): 2938, 1637, 1519, 1235, 1031, 927, 821, 735, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.03 (d, J = 7.6 Hz, 2H), 7.43-7.35 (m, 3H), 705 (t, J = 8.4 Hz, 2H), 4.72 (dd, J = 11.2 Hz, 4.4 Hz, 1H), 4.59-4.55 (m, 1H), 2.28 (dt, J = 13.6 Hz, 1.5 Hz, 1H), 1.59-1.50 (m, 1H), 1.18 (dd, J =
4-(4-Fluoro-phenyl)-2-phenyl-6-trimethylsilanylmethyl-5,6-dihydro-4H-[1,3]oxazine (trans-13h): yield 66%, colorless liquid; IR (Neat): 2940, 1647, 1532, 1244, 1020, 931, 845, 733, 701 cm\(^{-1}\); H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 8.0\) Hz, 2H), 7.35-7.04 (m, 8H), 4.95 (dd, \(J = 11.2\) Hz, 4.4 Hz, 1H), 4.46-4.39 (m, 1H), 2.38 (dt, \(J = 13.6\) Hz, 2.0 Hz, 1H), 1.21-1.10 (m, 1H), 1.02 (dd, \(J = 14.4\) Hz, 8.0 Hz, 1H), 0.84 (dd, \(J = 14.8\) Hz, 6.0 Hz, 1H), 0.00 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.8, 142.7, 134.7, 132.9, 131.1, 129.7, 128.7, 128.6, 128.5, 127.9, 75.0, 55.0, 38.4, 25.2, -0.00. HRMS calcd for C\(_{20}\)H\(_{25}\)NFOSi [M + H]\(^+\) 342.1689, found: 342.1685.

4-(4-Bromo-phenyl)-2-phenyl-6-trimethylsilanylmethyl-5,6-dihydro-4H-[1,3]oxazine (trans-13i): yield 79%; colorless oil; IR (Neat): 2938, 1635, 1530, 1239, 1034, 928, 830, 725, 702 cm\(^{-1}\); H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.87 (d, \(J = 6.8\) Hz, 2H), 7.33 – 7.21 (m, 5H), 7.12 – 7.00 (d, \(J = 8.4\) Hz, 2H), 4.53 (dd, \(J = 11.6\) Hz, 4.8 Hz, 1H), 4.41 – 4.34 (m, 1H), 2.10 (ddd, \(J = 13.6\) Hz, 4.8 Hz, 2.0 Hz, 1H), 1.41 – 1.32 (m, 1H), 1.01 (dd, \(J = 14.4\) Hz, 8.0 Hz, 1H), 0.82 (dd, \(J = 14.4\) Hz, 8.0 Hz, 1H), 0.00 (s, 9H);
\[13\text{C NMR (CDCl}_3, 100 \text{ MHz}) \delta 157.2, 144.4, 134.6, 132.0, 131.1, 128.8, 128.6, 127.9, 121.0, 74.6, 57.0, 40.8, 25.2, 0.00; \text{Anal. Calcd for C}_{20}\text{H}_{24}\text{BrNOSi: C, 59.70; H, 6.01; N, 3.48. Found: C, 59.62; H, 6.07; N, 3.55.}\]

Selected data for the \textit{cis}\textsuperscript{13i}: \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta 7.01 \text{ (d, } J = 8.4 \text{ Hz, } 2\text{H}), 4.89 \text{ (t, } J = 4.8 \text{ Hz, } 1\text{H}), 4.16-4.09 \text{ (m, } 1\text{H}), 1.92-1.85 \text{ (m, } 1\text{H}), 1.79 \text{ (dt, } J = 14.0 \text{ Hz, } 4.0 \text{ Hz, } 1\text{H}), -0.08 \text{ (s, } 9\text{H}); \text{\textsuperscript{13}C NMR (CDCl}_3, 100 \text{ MHz}) \delta 128.2, 70.7, 54.1, 37.9, 24.6.\]

\[\text{NO}_2\]
\[\text{Ph}\]
\[\text{TMS}\]
\[\text{trans-13j}\]

\textbf{4-(4-Nitro-phenyl)-2-phenyl-6-trimethylsilanylmethyl-5,6-dihydro-4H-[1,3]-oxazine (\textit{trans}\textsuperscript{13j})}: yield: 40%, colorless liquid; IR (Neat): 2942, 1630, 1534, 1242, 1028, 931, 828, 731, 698 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 8.24 \text{ (d, } J = 8.4 \text{ Hz, } 2\text{H}), 8.07 \text{ (d, } J = 7.2 \text{ Hz, } 2\text{H}), 7.60 \text{ (d, } J = 8.4 \text{ Hz, } 2\text{H}), 7.51-7.42 \text{ (m, } 3\text{H}), 4.86 \text{ (dd, } J = 11.2 \text{ Hz, } 4.4 \text{ Hz, } 1\text{H}), 4.64-4.58 \text{ (m, } 1\text{H}), 2.36-2.33 \text{ (m, } 1\text{H}), 1.56 \text{ (dd, } J = 24.8 \text{ Hz, } 11.6 \text{ Hz, } 1\text{H}), 1.22 \text{ (dd, } J = 14.8 \text{ Hz, } 8.4 \text{ Hz, } 1\text{H}), 1.04 \text{ (dd, } J = 14.8 \text{ Hz, } 6.0 \text{ Hz, } 1\text{H}), 0.20 \text{ (s, } 9\text{H}); \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3): \delta 157.7, 152.7, 147.5, 131.3, 128.7, 127.9, 127.9, 124.4, 74.6, 57.1, 40.5, 25.2, 0.0; \text{Anal. Calcd for C}_{20}\text{H}_{24}\text{BrN}_2\text{O}_3\text{Si: C, 65.19; H, 6.56; N, 7.60. Found: C, 65.24; H, 6.43; N, 7.72.}\]

\[\text{NO}_2\]
\[\text{Ph}\]
\[\text{TMS}\]
\[\text{trans-13k}\]

\textbf{4-(3-Nitro-phenyl)-2-phenyl-6-trimethylsilanylmethyl-5,6-dihydro-4H-[1,3]-Oxazine (\textit{trans}\textsuperscript{13k})}: yield 25%, colorless liquid; IR (Neat): 2944, 1645, 1538, 1249, 1024,
921, 840, 729, 705 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.12 (s, 1H), 7.96 (d, \(J = 8.0\) Hz, 1H), 7.87 (d, \(J = 7.2\) Hz, 2H), 7.60 (d, \(J = 7.6\) Hz, 1H), 7.36 (t, \(J = 8.0\) Hz, 1H), 7.29-7.22 (m, 3H), 4.68 (dd, \(J = 11.2\) Hz 4.4 Hz, 1H), 4.45-4.39 (m, 1H), 2.20-2.16(m, 1H), 1.40 (dd, \(J = 24.4\) Hz, 12.0 Hz, 1H), 1.03 (dd, \(J = 14.8\) Hz, 8.4 Hz, 1H), 0.84 (dd, \(J = 14.8\)Hz, 6.0 Hz, 1H), 0.00 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 157.8, 149.1, 147.5, 134.3, 133.3, 131.3, 129.9, 128.7, 127.9, 122.4, 122.1, 74.6, 56.9, 40.5, 25.2, 0.0; Anal. Calcd for C\(_{20}\)H\(_{24}\)BrN\(_2\)O\(_3\)Si: C, 65.19; H, 6.56; N, 7.60. Found: C, 65.33; H, 6.62; N, 7.46.

2-Phenyl-4-(4-trifluoromethyl-phenyl)-6-trimethylsilyloxymethyl-5,6-dihydro-4H-[1,3]oxazine (trans-13l): yield 57%, colorless liquid; IR (Neat): 2941, 1635, 1532, 1244, 1021, 923, 841, 733, 702 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.04-8.03 (m, 2H), 7.62 (d, \(J = 8.4\) Hz, 2H), 7.52 (d, \(J = 8.4\) Hz, 2H), 7.46-7.43 (m, 1H), 7.41-7.38 (m, 2H), 4.80 (dd, \(J = 11.4\) Hz, 4.8 Hz, 1H), 4.59-4.54 (m, 1H), 2.31 (ddd, \(J = 13.8\) Hz, 4.8 Hz, 2.4 Hz, 1H), 1.58-1.51 (m, 1H), 1.18 (dd, \(J = 14.4\) Hz, 7.8 Hz, 1H), 1.00 (dd, \(J = 14.4\) Hz, 6.0 Hz, 1H), 0.16 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 156.8, 142.4, 136.7, 134.9, 130.9, 129.7, 128.5, 128.0, 126.9, 74.6, 57.4, 41.1, 25.3, 21.7; \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 156.8, 142.4, 136.7, 134.8, 130.9, 129.7, 128.5, 128.0, 126.9, 74.6, 57.4, 41.1, 25.3, 21.7, 0.02; Anal. Calcd for C\(_{21}\)H\(_{24}\)F\(_3\)NOSi: C, 64.42; H, 6.18; N, 3.58. Found: C, 64.57; H, 6.42; N, 3.69.

Selected data for the cis isomer: \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 142.1, 136.6, 134.9, 129.6, 128.6, 127.9, 127.3, 70.6, 54.6, 38.2, 24.7, 14.8, -0.09.
$^1$H NMR spectrum of trans-13a

$^{13}$C NMR spectrum of trans-13a
$\text{H NMR spectrum of } \textit{cis-13a}$
$^1$H NMR spectrum of trans-13b

$^{13}$C NMR spectrum of trans-13b
$^1$H NMR spectrum of cis-$13b$

$^{13}$C NMR spectrum of cis-$13b$
$^1$H NMR spectrum of trans-13c

$^{13}$C NMR spectrum of trans-13c
$^1$H NMR spectrum of trans-13d

$^{13}$C NMR spectrum of trans-13d
$^{1}H$ NMR spectrum of \textit{trans-$13e$}

$^{13}C$ NMR spectrum of \textit{trans-$13e$}
$^1$H NMR spectrum of trans-13f

$^{13}$C NMR spectrum of trans-13f
$^1$H NMR spectrum of trans-13g

$^{13}$C NMR spectrum of trans-13g
$^1$H NMR spectrum of trans-13h

$^{13}$C NMR spectrum of trans-13h
$^1$H NMR spectrum of *trans-13i*

$^{13}$C NMR spectrum of *trans-13i*
$^1$H NMR spectrum of trans-13j

$^{13}$C NMR spectrum of trans-13j
$^1$H NMR spectrum of trans-13k

$^{13}$C NMR spectrum of trans-13k
$^1$H NMR spectrum of trans-13l

$^{13}$C NMR spectrum of trans-13l