Silylmethyl Substituted Aziridine and Azetidene as Masked 1,3- and 1,4-Dipoles for Formal [3 + 2] and [4 + 2] Cycloaddition Reactions

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SUPPLEMENTARY INFORMATION

Experimental details and characterization data (15 pages).
General. $^1$H and $^{13}$C spectra were recorded on JEOL JNM-LA400 instrument using solutions in CDCl$_3$. The $^1$H and $^{13}$C spectra are referred, respectively, to TMS used as an internal standard and the central line for CDCl$_3$ respectively. Elemental (C, H and N) analyses were performed on a ThermoQuest EA 1110 elemental analyzer. All the reactions were carried out using freshly distilled dry solvents. Column chromatography was performed over silica gel (100-200 mesh) obtained from Acme Chemicals using mixtures of hexanes and EtOAc. The separation of isomers was achieved by radial chromatography using plates coated with silica gel PF$_{254}$ (E-Merck). Solvents were removed under reduced pressure on a rotovap. Organic extracts were dried with anhydrous Na$_2$SO$_4$.

Procedure for the preparation of aziridine 1a. A solution of N,N-dichloro-p-toluenesulfonylamine (2.900 g, 12.08 mmol) in CCl$_4$ (10 mL) was added to a solution of allyl tert-butyldiphenylsilane (3.382 g, 12.08 mmol) in CCl$_4$ (12 mL) at 0-5 °C under stirring. The stirring was continued for 4h at room temperature. After the solvent was removed under reduced pressure, the residue was dissolved in benzene (12 mL), cooled to 5-10 °C, and treated with 20% aqueous solution of Na$_2$SO$_3$ (12 mL). After stirring for 4h at room temperature, the reaction mixture was diluted with EtOAc. The organic layer was separated, dried, and concentrated. The residual solid material was dissolved in acetonitrile (74 mL), mixed with tetrabutylammonium bromide (408 mg, 1.26 mmol) and NaOH (506 mg, 12.6 mmol), and stirred for 2h at room temperature. The solvent was removed and the residue was purified by column chromatography to obtain the pure product 1a as a colorless dense liquid (2.897 g, 53%).

1a. $^1$H NMR: δ 7.67-7.64 (2H, m), 7.53-7.48 (4H, m), 7.39-7.20 (8H, m), 2.80-2.74 (1H, m), 2.37 (3H, s), 2.24-2.22 (1H, m), 1.87-1.81 (1H, dd, $J = 14.6$, 3.2 Hz), 1.61-1.60 (1H, m), 1.00-0.94 (1H, m), 0.97 (9H, s). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 144.2, 135.8, 135.7, 135.2, 133.4, 133.0, 129.6, 129.5, 127.9, 127.8, 127.7, 38.5, 35.8, 27.6, 21.6, 17.9, 14.3. Anal Calcd for C$_{26}$H$_{31}$NO$_2$Si: C, 69.44; H, 6.95; N, 3.11. Found: C, 69.38; H, 6.89; N, 3.12.

1b. Following the procedure outlined above for the preparation of 1a, crotyl tert-butyldiphenylsilane afforded a mixture of diastereomers 1b (cis:trans = 1.1:1) as a colorless dense liquid (2.908 g, 52%).
cis-1b. \(^1\)H NMR: δ 7.70-7.68 (2H, m), 7.58-7.51 (4H, m), 7.44-7.25 (8H, m), 2.93-2.88 (1H, m), 2.65-2.56 (1H, m), 2.42 (3H, s), 1.66-1.62 (1H, dd, \(J = 14.6, 2.9\) Hz), 1.04-1.02 (1H, m), 1.03 (9H, s), 0.64 (3H, d, \(J = 5.9\) Hz). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 144.0, 135.9, 135.87, 135.6, 135.5, 133.0, 129.5, 129.46, 127.8, 127.76, 127.6, 43.2, 41.6, 27.6, 21.6, 17.9, 11.5, 8.8. Anal Calcd for C\(_{27}\)H\(_{33}\)NO\(_2\)Si: C, 69.93; H, 7.17; N, 3.02. Found: C, 69.85; H, 7.10; N, 3.05.

trans-1b. \(^1\)H NMR: δ 7.80-7.77 (2H, m), 7.64-7.58 (4H, m), 7.44-7.25 (8H, m), 2.64-2.61 (1H, m), 2.42 (3H, s), 2.10-2.06 (1H, m), 1.53-1.46 (1H, m), 1.29-1.25 (1H, m), 1.05 (9H, s), 0.75 (3H, d, \(J = 5.8\) Hz). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 143.6, 138.5, 135.8, 133.6, 132.9, 129.5, 127.9, 127.8, 127.0, 48.9, 46.8, 27.6, 21.5, 18.0, 15.0, 12.3. Anal Calcd for C\(_{27}\)H\(_{33}\)NO\(_2\)Si: C, 69.93; H, 7.17; N, 3.02. Found: C, 69.87; H, 7.10; N, 3.00.

**General procedure for the BF\(_3\)·Et\(_2\)O-assisted cycloaddition reactions of aziridines 1a, 1b with nitriles:** BF\(_3\)·Et\(_2\)O (0.18 mmol) was added to a stirred solution of the aziridine (0.18 mmol) and nitrile (0.18 mmol) in CH\(_2\)Cl\(_2\) (1.3 mL) at 25 °C under nitrogen. After 5 min, the reaction was quenched by saturated aqueous NaHCO\(_3\) and the stirring was continued until the organic layer had become clear (1h). The aqueous phase was extracted with CH\(_2\)Cl\(_2\) (2 x 5 mL) and dried. The crude material was purified by column chromatography over silica gel. The separation of the cis- and trans-isomers was achieved by radial chromatography over silica gel.

2. Following the general procedure outlined above, the aziridine 1a reacted with acetonitrile to afford the product 2 as a colorless dense liquid (0.080 g, 90%).

![TBDPS](image)

\(^1\)H NMR: δ 7.60-7.58 (2H, m), 7.54-7.49 (4H, m), 7.47-7.28 (8H, m), 3.90-3.86 (1H, m), 3.06-3.01 (1H, m), 2.68-2.63 (1H, dd, \(J = 10.0, 7.6\) Hz), 2.43 (3H, s), 2.21 (3H, s), 1.76-1.72 (1H, dd, \(J = 14.9, 3.2\) Hz), 0.98 (9H, s), 0.93-0.86 (1H, dd, \(J = 14.9, 11.5\) Hz). \(^{13}\)C NMR: δ 154.3, 144.4, 136.0, 135.9, 134.9, 134.2, 133.1, 129.8, 129.5, 129.4, 127.8, 127.1, 60.7, 54.4,
27.6, 21.5, 18.7, 17.8, 16.8. Anal Calcd for C_{28}H_{34}N_{2}O_{2}SSi: C, 68.53; H, 6.98; N, 5.71. Found: C, 68.45; H, 6.92; N, 5.67.

3. Following the general procedure outlined above, the aziridine 1a reacted with 3-bromopropionitrile to afford the product 3 as a colorless dense liquid (0.087 g, 85%).

![TBDPS](image)

1H NMR: δ 7.52-7.45 (6H, m), 7.41-7.15 (8H, m), 4.34-4.23 (2H, m), 3.94-3.86 (1H, m), 3.00-2.94 (1H, m), 2.64-2.60 (1H, dd, J = 10.0, 7.3 Hz), 2.37 (3H, s), 1.70-1.66 (1H, dd, J = 14.9, 3.2 Hz), 0.92 (9H, s), 0.87-0.80 (1H, dd, J = 14.9, 11.5 Hz). 13C NMR: δ 153.4, 144.7, 136.0, 135.9, 134.4, 134.1, 132.9, 129.8, 129.5, 129.4, 127.5, 127.6, 61.5, 54.5, 27.6, 23.3, 21.6, 18.3, 18.0. Anal Calcd for C_{28}H_{33}BrN_{2}O_{2}SSi: C, 59.04; H, 5.84; N, 4.92. Found: C, 58.95; H, 5.78; N, 4.95.

4. Following the general procedure outlined above, the aziridine 1a reacted with benzonitrile to afford the product 4 as a colorless dense liquid (0.086 g, 87%).

![TBDPS](image)

1H NMR: δ 7.64-7.19 (19H, m), 3.83-3.75 (1H, m), 3.39-3.33 (1H, dd, J = 12.0, 8.8 Hz), 3.00-2.94 (1H, dd, J = 12.0, 7.3 Hz), 2.38 (3H, s), 1.59-1.54 (1H, dd, J = 14.9, 3.9 Hz), 0.96 (9H, s), 0.76-0.70 (1H, dd, J = 14.9, 10.7 Hz). 13C NMR: δ 157.6, 144.4, 136.0, 135.9, 134.3, 134.0, 133.3, 130.8, 130.5, 129.6, 129.3, 127.8, 127.6, 62.5, 55.8, 27.6, 21.6, 18.5, 18.0. Anal Calcd for C_{33}H_{36}N_{2}O_{2}SSi: C, 71.70; H, 6.56; N, 5.07. Found: C, 71.64; H, 6.54; N, 5.05.

5. Following the general procedure outlined above, the aziridine 1a reacted with phenylacetonitrile and afforded the product 5 as a colorless dense liquid (0.092 g, 90%).
\[^1\text{H NMR:}\ \delta\ 7.58-7.50\ (6\text{H, m}),\ 7.45-7.09\ (13\text{H, m}),\ 4.07-3.87\ (3\text{H, m}),\ 3.04-2.99\ (1\text{H, m}),\ 2.67-2.63\ (1\text{H, dd, } J = 10.0, 7.3\ \text{Hz}),\ 2.37\ (3\text{H, s}),\ 1.78-1.74\ (1\text{H, dd, } J = 14.9, 3.2\ \text{Hz}),\ 1.00\ (9\text{H, s}),\ 0.91-0.84\ (1\text{H, dd, } J = 14.9, 11.2\ \text{Hz}).\ \[^{13}\text{C NMR:}\ \delta\ 155.9,\ 144.0,\ 136.0,\ 135.96,\ 135.6,\ 134.7,\ 134.2,\ 133.2,\ 129.6,\ 129.2,\ 128.3,\ 127.7,\ 127.1,\ 61.0,\ 54.3,\ 35.6,\ 27.6,\ 21.5,\ 18.7,\ 17.9.\ \text{Anal Calcd for C}_{34}\text{H}_{38}\text{N}_{2}\text{O}_{2}\text{SSi: C, 72.04; H, 6.76; N, 4.94. Found: C, 72.00; H, 6.80; H, 4.95.}\n\]

**6.** Following the general procedure outlined above, the aziridine 1\(^a\) reacted with trans-cinnamonicnitrile and afforded the product 6 as a colorless dense liquid (0.088 g, 84%).

\[^1\text{H NMR:}\ \delta\ 7.58-7.50\ (8\text{H, m}),\ 7.46-7.32\ (10\text{H, m}),\ 7.28-7.23\ (3\text{H, m}),\ 4.00-3.92\ (1\text{H, m}),\ 3.27-3.22\ (1\text{H, m}),\ 2.85-2.81\ (1\text{H, dd, } J = 10.7, 6.8\ \text{Hz}),\ 2.38\ (3\text{H, s}),\ 1.57-1.53\ (1\text{H, dd, } J = 14.7, 4.6\ \text{Hz}), 0.97\ (9\text{H, s}), 0.87-0.81\ (1\text{H, dd, } J = 14.7, 10.2\ \text{Hz}).\ \[^{13}\text{C NMR:}\ \delta\ 153.8,\ 144.4,\ 139.8,\ 136.1,\ 136.0,\ 135.5,\ 134.4,\ 134.1,\ 133.6,\ 129.8,\ 129.5,\ 129.4,\ 129.3,\ 128.7,\ 127.8,\ 127.7,\ 127.66,\ 127.4,\ 115.6,\ 61.3,\ 54.7,\ 27.6,\ 21.5,\ 19.1,\ 18.0.\ \text{Anal Calcd for C}_{35}\text{H}_{38}\text{N}_{2}\text{O}_{2}\text{SSi: C, 72.62; H, 6.62; N, 4.84. Found: C, 72.65; H, 6.65; N, 4.80.}\n\]

**7.** Following the general procedure outlined above, the aziridine 1\(^a\) reacted with the TBDPS protected 3-hydroxy propionitrile and afforded the product 7 as a colorless dense liquid (0.112 g, 82%).

\[^1\text{H NMR:}\ \delta\ 7.71-7.21\ (24\text{H, m}),\ 3.94\ (2\text{H, t, } J = 7.1\ \text{Hz}),\ 3.84-3.74\ (1\text{H, m}),\ 3.06-3.01\ (1\text{H, m}),\ 2.92\ (2\text{H, t, } J = 7.1\ \text{Hz}),\ 2.69-2.64\ (1\text{H, dd, } J = 10.2, 7.1\ \text{Hz}),\ 2.4\ (3\text{H, s}),\ 1.64-1.59\ (1\text{H, m}).\}
\[ dd, J = 14.9, 3.9 \text{ Hz}), \ 1.04 \ (9H, s), \ 0.95 \ (9H, s), \ 0.85-0.78 \ (1H, dd, J = 14.9, 10.7 \text{ Hz}). \]

\[^{13}\text{C} \text{ NMR: } \delta 154.6, 144.2, 135.9, 135.91, 135.5, 135.2, 134.9, 134.2, 133.7, 133.6, 133.3, 129.8, 129.5, 129.4, 129.3, 127.7, 127.5, 127.2, 61.1, 60.9, 54.1, 33.0, 27.6, 26.7, 21.5, 19.1, 18.7, 17.9. \] Anal Calcd for \( \text{C}_{45}\text{H}_{54}\text{N}_{2}\text{O}_{3}\text{SSi}^2 \): C, 71.19; H, 7.17; N, 3.69. Found: C, 71.12; H, 7.12; N, 3.70.

8. Following the general procedure outlined above, the aziridine 1a reacted with 2-furonitrile and afforded the product 8 as a colorless dense liquid (0.082 g, 84%).

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8 \\
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\[^{1}\text{H} \text{ NMR: } \delta 7.57-7.28 \ (14H, m), \ 7.19-7.15 \ (2H, m), \ 6.52-6.50 \ (1H, dd, J = 3.5, 1.8 \text{ Hz}), \ 3.76-3.68 \ (1H, m), \ 3.25-3.19 \ (1H, dd, J = 12.0, 8.6 \text{ Hz}), \ 2.90-2.83 \ (1H, dd, J = 12.0, 8.1 \text{ Hz}), \ 2.36 \ (3H, s), \ 1.81-1.77 \ (1H, dd, J = 14.9, 2.7 \text{ Hz}), \ 0.95 \ (9H, s), \ 0.77-.70 \ (1H, dd, J = 14.9, 11.5 \text{ Hz}). \] \[^{13}\text{C} \text{ NMR: } \delta 157.6, 144.4, 136.0, 135.9, 134.3, 134.0, 133.3, 130.8, 130.5, 129.6, 129.3, 127.8, 127.7, 127.6, 65.5, 55.8, 27.6, 21.5, 18.5, 18.0. \] Anal Calcd for \( \text{C}_{31}\text{H}_{34}\text{N}_{2}\text{O}_{3}\text{SSi}^2 \): C, 68.60; H, 6.31; N, 5.16. Found: C, 68.54; H, 6.30; N, 5.18.

9. Following the general procedure outlined above, the aziridine 1b reacted with acetonitrile to afford a mixture of diastereomers 9 as a colorless dense liquid (0.083 g, 92%).

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\text{N} \\
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8 \ (cis) \\
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\[^{1}\text{H} \text{ NMR: } \delta 7.54-7.20 \ (14H, m), \ 3.66-3.59 \ (1H, m), \ 3.27-3.20 \ (1H, m), \ 2.39 \ (3H, s), \ 2.19 \ (3H, s) 1.78-1.73 \ (1H, dd, J = 15.1, 4.2 \text{ Hz}), \ 1.40-1.33 \ (1H, dd, J = 15.1, 11.0 \text{ Hz}), \ 1.02 \ (9H, s), \ 0.90 \ (3H, d, J = 6.6 \text{ Hz}). \] \[^{13}\text{C} \text{ NMR: } \delta 154.2, 144.0, 136.1, 136.0, 134.4, 133.7, 129.8, 129.5, 129.2, 127.7, 127.5, 126.6, 64.4, 60.2, 27.7, 21.5, 18.1, 17.4, 16.1, 10.7. \] Anal Calcd for \( \text{C}_{29}\text{H}_{36}\text{N}_{2}\text{O}_{2}\text{SSi}^2 \): C, 69.01; H, 7.19; N, 5.55. Found: C, 68.95; H, 7.16; N, 5.50.
1H NMR: δ 7.64-7.62 (2H, m), 7.55-7.31 (12H, m), 3.45-3.42 (1H, m), 3.04-2.99 (1H, m), 2.43 (3H, s), 2.29 (3H, s), 1.18-1.13 (1H, dd, J = 14.9, 3.2 Hz), 0.86 (9H, s), 0.67 (3H, d, J = 6.4 Hz), 0.23-0.16 (1H, dd, J = 14.9, 10.5 Hz). 13C NMR: δ 153.5, 144.3, 136.0, 135.9, 134.0, 132.9, 129.9, 129.86, 129.6, 129.3, 127.7, 127.2, 68.5, 62.6, 27.5, 21.5, 21.0, 18.4, 18.0, 17.4. Anal Calcd for C29H36N2O2Si: C, 69.01; H, 7.19; N, 5.55. Found: C, 68.95; H, 7.20; N, 5.53.

10. Following the general procedure outlined above, reaction of the aziridine 1b with trans-cinnamonicitrile afforded a mixture of diastereomers 10 (cis:trans = 67:33) as a colorless dense liquid (0.091 g, 86%).

1H NMR: δ 7.68-7.65 (m), 7.58-7.31 (m), 7.24-7.23 (m), 7.15-7.11 (m), 3.61-3.50 (m), 3.46-3.39 (m, major), 3.32-3.27 (m, minor), 2.38 (s, minor), 2.32 (s, major), 1.80-1.75 (dd, J = 15.1, 5.6 Hz), 1.42-1.33 (m), 1.02 (s), 0.99 (d, J = 6.6 Hz), 0.92 (d, J = 6.6 Hz), 0.87 (s), 0.40-0.35 (dd, J = 14.8, 10.4 Hz). 13C NMR: δ 153.8, 152.8, 144.4, 144.0, 139.8, 139.6, 136.4, 136.2, 136.0, 135.99, 135.5, 135.3, 134.4, 133.9, 133.8, 129.8, 129.7, 129.4, 129.1, 128.7, 127.7, 127.6, 127.45, 127.4, 126.6, 116.6, 116.4, 69.0, 64.8, 63.7, 60.3, 27.7, 26.8, 21.5, 19.1, 18.1, 17.9, 16.1, 10.9. Anal Calcd for C36H40N2O2Si: C, 72.93; H, 6.80; N, 4.73. Found: C, 72.88; H, 6.76; N, 4.75.

General procedure for the BF₃·Et₂O-assisted cycloaddition reaction of aziridines 1a, 1b with carbonyl substrates: BF₃·Et₂O (0.18 mmol) was added to a stirred solution of the aziridine (0.18 mmol) and a carbonyl substrate (0.18 mmol) in CH₂Cl₂ (1.3 mL) at 25 °C under nitrogen. After 5 min, the reaction was quenched by saturated aqueous NaHCO₃ and the stirring was continued until the organic layer had become clear (1h). The aqueous phase was extracted with CH₂Cl₂ (2 x 5 mL) and dried. The crude material was purified by column
chromatography over silica gel. The separation of the cis- and trans-isomers was achieved by radial chromatography over silica gel.

11. Following the general procedure outlined above, the aziridine 1a reacted with propionaldehyde and afforded a mixture of diastereomers 11 (cis:trans = 67:33) as a colorless dense liquid (0.082 g, 90%).

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11 \quad (cis + trans)
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^1H NMR: δ 7.59-7.57 (m), 7.52-7.30 (m), 7.07-7.05 (m), 4.93-4.90 (dd, \( J = 7.3, 4.2 \) Hz, minor), 4.79-4.77 (dd, \( J = 5.6, 3.6 \) Hz, major), 4.19-4.12 (m, minor), 3.08-3.00 (m, major), 2.96-2.92 (dd, \( J = 10.0, 5.9 \) Hz, minor), 2.87-2.83 (dd, \( J = 12.2, 4.9 \) Hz, major), 2.51-2.45 (dd, \( J = 12.2, 10.2 \) Hz), 2.44-2.39 (dd, \( J = 10.0, 7.6 \) Hz), 2.43 (s, minor), 2.29 (s, major), 1.82-1.46 (m), 1.41-1.35 (m), 1.24-1.16 (m), 0.93 (s), 0.91 (t, \( J = 7.3 \) Hz, major), 0.81 (t, \( J = 7.3 \) Hz, minor). ^13C NMR: δ 143.8, 143.6, 135.9, 135.8, 135.7, 134.5, 133.9, 133.8, 133.7, 133.1, 132.9, 129.7, 129.6, 129.5, 129.4, 129.38, 128.0, 127.7, 127.6, 127.4, 91.8, 91.3, 75.1, 74.1, 53.5, 52.9, 29.3, 28.4, 27.6, 27.5, 21.6, 21.5, 17.95, 17.9, 16.0, 15.1, 8.8, 7.9. Anal Calcd for C\(_{29}\)H\(_{37}\)NO\(_3\)SSi: C, 68.60; H, 7.34; N, 2.76. Found: C, 68.54; H, 7.30; N, 2.76.

12. Following the general procedure outlined above, the aziridine 1a reacted with benzaldehyde and afforded a mixture of diastereomers 12 (cis:trans = 57:43) as a colorless dense liquid (0.087 g, 87%).

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12 \quad (cis)
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^1H NMR: δ 7.52-7.30 (17H, m), 7.09-7.07 (2H, m), 5.89 (1H, s), 3.38-3.31 (1H, m), 2.98-2.94 (1H, dd, \( J = 12.2, 4.9 \) Hz), 2.59-2.54 (1H, dd, \( J = 12.2, 10.2 \) Hz), 2.32 (3H, s), 1.84-1.79 (1H, dd, \( J = 14.7, 3.9 \) Hz), 1.31-1.25 (1H, dd, \( J = 14.7, 10.5 \) Hz), 0.95 (9H, s). ^13C NMR: δ 143.8, 139.0, 135.8, 134.8, 133.7, 132.7, 129.8, 129.6, 129.5, 128.7, 128.2, 127.8, 127.6,
127.4, 126.7, 90.4, 76.2, 53.1, 27.5, 21.5, 18.0, 15.5. Anal Calcd for C$_{33}$H$_{37}$NO$_3$SSi: C, 71.31; H, 6.71; N, 2.52. Found: C, 71.26; H, 6.67; N, 2.54.

![Diagram](image)

12 (trans)

$^1$H NMR: $\delta$ 7.70-7.67 (2H, m), 7.47-7.25 (17H, m), 6.16 (1H, s), 4.08-4.02 (1H, m), 3.03-2.99 (1H, dd, $J = 10.5$, 6.3 Hz), 2.69-2.65 (1H, dd, $J = 10.5$, 7.3 Hz), 2.47 (3H, s), 1.41-1.35 (1H, dd, $J = 14.6$, 6.3 Hz), 1.00-0.95 (1H, dd, $J = 14.6$, 7.8 Hz), 0.93 (9H, s). $^{13}$C NMR: $\delta$ 144.1, 138.2, 135.9, 135.8, 134.1, 129.8, 129.5, 129.4, 128.3, 128.2, 127.7, 127.6, 126.3, 90.2, 74.5, 52.9, 27.5, 21.6, 17.9, 16.3. Anal Calcd for C$_{33}$H$_{37}$NO$_3$SSi: C, 71.31; H, 6.71; N, 2.52. Found: C, 71.25; H, 6.72; N, 2.53.

13. Following the general procedure outlined above, the aziridine 1a reacted with trans-cinnamaldehyde and afforded a mixture of diastereomers 13 (cis:trans = 57:43) as a colorless dense liquid (0.099 g, 95%).

![Diagram](image)

13 (cis)

$^1$H NMR: $\delta$ 7.54-7.24 (17H, m), 7.10-7.08 (2H, m), 6.71 (1H, d, $J = 15.9$ Hz), 6.11-6.06 (1H, dd, $J = 15.9$, 5.6 Hz), 5.42 (1H, d, $J = 5.6$ Hz), 3.33-3.28 (1H, m), 2.95-2.91 (1H, dd, $J = 12.2$, 5.1 Hz), 2.61-2.56 (1H, m), 2.32 (3H, s), 1.82-1.77 (1H, dd, $J = 14.6$, 3.9 Hz) 1.33-1.26 (1H, dd, $J = 14.6$, 10.5 Hz) 0.96 (9H, s). $^{13}$C NMR: $\delta$ 143.8, 135.8, 135.78, 134.8, 134.2, 133.7, 133.2, 132.8, 129.8, 129.6, 129.5, 128.48, 128.1, 128.8, 127.76, 127.5, 126.9, 126.3, 89.8, 75.8, 52.9, 27.5, 21.5, 18.0, 15.5. Anal Calcd for C$_{35}$H$_{39}$NO$_5$SSi: C, 72.25; H, 6.76; N, 2.41. Found: C, 72.21; H, 6.80; N, 2.44.
$^1$H NMR: $\delta$ 7.64-7.61 (2H, m), 7.54-7.22 (17H, m), 6.54 (1H, d, $J = 15.9$ Hz), 5.97-5.92 (1H, dd, $J = 15.9$, 4.6 Hz), 5.62 (1H, d, $J = 4.6$ Hz), 4.23-4.19 (1H, m), 3.00-2.96 (1H, dd, $J = 10.0$, 5.8 Hz), 2.55-2.51 (1H, dd, $J = 10.0$, 8.1 Hz), 2.45 (3H, s), 1.53-1.48 (1H, dd, $J = 14.6$, 5.8 Hz), 1.08-1.02 (1H, dd, $J = 14.6$, 8.5 Hz), 0.96 (9H, s). $^{13}$C NMR: $\delta$ 143.9, 136.0, 135.9, 135.8, 134.5, 134.0, 133.8, 133.1, 132.7, 129.7, 129.6, 129.5, 128.4, 128.0, 127.8, 127.7, 126.9, 125.9, 89.4, 74.8, 52.8, 27.6, 21.5, 18.0, 15.9. Anal Calcd for C$_{35}$H$_{39}$NO$_3$Si: C, 72.25; H, 6.76; N, 2.41. Found: C, 72.20; H, 6.70; N, 2.42.

14. Following the general procedure outlined above, the aziridine 1a reacted with 2-furaldehyde and afforded a mixture of diastereomers 14 (cis:trans = 52:48) as a colorless dense liquid (0.091 g, 93%).

\[
\text{TBDPS} \quad \text{O} \quad \text{O} \quad \text{N} \quad \text{Ts}
\]

14 (cis)

$^1$H NMR: $\delta$ 7.55-7.34 (13H, m), 7.10-7.08 (2H, m), 6.42 (1H, d, $J = 3.2$ Hz), 6.33-6.31 (1H, dd, $J = 3.2$, 2.0 Hz), 5.91 (1H, s), 3.41-3.33 (1H, m), 2.99-2.94 (1H, dd, $J = 12.0$, 5.2 Hz), 2.74-2.68 (1H, dd, $J = 12.0$, 9.6 Hz), 2.32 (3H, s), 1.84-1.80 (1H, dd, $J = 14.4$, 3.6 Hz), 1.34-1.28 (1H, dd, $J = 14.4$, 10.4 Hz), 0.95 (9H, s). $^{13}$C NMR: $\delta$ 151.3, 143.8, 143.1, 135.83, 135.8, 134.6, 133.7, 132.7, 129.7, 129.6, 129.5, 127.8, 127.7, 127.3, 110.2, 108.8, 84.1, 76.4, 52.9, 27.5, 21.5, 18.0, 15.5. Anal Calcd for C$_{31}$H$_{35}$NO$_4$Si: C, 68.22; H, 6.46; N, 2.57. Found: C, 68.17; H, 6.42; N, 2.55.

\[
\text{TBDPS} \quad \text{O} \quad \text{O} \quad \text{N} \quad \text{Ts}
\]

14 (trans)

$^1$H NMR: $\delta$ 7.57-7.28 (15H, m), 6.26-6.24 (2H, m), 6.03 (1H, s), 4.31-4.24 (1H, m), 3.00-2.96 (1H, dd, $J = 9.5$, 5.8 Hz), 2.52-2.48 (1H, dd, $J = 9.5$, 8.0 Hz), 2.45 (3H, s), 1.61-1.57 (1H, dd, $J = 14.4$, 5.4 Hz), 1.09-1.03 (1H, dd, $J = 14.4$, 9.3 Hz), 0.96 (9H, s). $^{13}$C NMR: $\delta$ 151.3, 144.0, 143.0, 135.9, 135.87, 133.8, 133.7, 133.0, 129.7, 129.6, 129.5, 127.9, 127.7, 127.68, 110.1, 109.1, 84.1, 75.4, 52.6, 27.6, 21.6, 18.0, 15.8. Anal Calcd for C$_{31}$H$_{35}$NO$_4$Si: C, 68.22; H, 6.46; N, 2.57. Found: C, 68.15; H, 6.40; N, 2.58.
15. Following the general procedure outlined above with aziridine 1a and cyclohexanone afforded the product 15 as a colorless dense liquid (0.082 g, 80%).

\[
\begin{align*}
\text{TBDPS} & \quad \text{O} & \quad \text{N} & \quad \text{Ts} \\
\text{15}
\end{align*}
\]

\(^1\)H NMR: \(\delta\) 7.63-7.54 (4H, m), 7.52-7.49 (2H, m), 7.43-7.30 (6H, m), 7.22-7.20 (2H, m), 4.09-4.02 (1H, m), 3.08-3.04 (1H, dd, \(J = 8.5, 5.1\) Hz), 2.57-2.52 (1H, m), 2.41 (3H, s), 2.23-2.15 (1H, m), 1.95-1.86 (1H, m), 1.71-1.66 (1H, dd, \(J = 14.6, 6.6\) Hz), 1.59-1.09 (9H, m), 1.02 (9H, s). \(^1\)C NMR: \(\delta\) 142.8, 137.7, 136.0, 135.9, 134.2, 133.5, 129.3, 129.29, 127.6, 127.57, 127.2, 98.2, 72.2, 53.9, 36.2, 35.0, 27.7, 24.5, 23.5, 23.3, 21.5, 18.0, 15.4. Anal Calcd for C\(_{32}\)H\(_{41}\)NO\(_3\)SSi: C, 70.16; H, 7.54; N, 2.56. Found: C, 70.15; H, 7.50; N, 2.55.

16 and 17. Following the general procedure outlined above, the aziridine 1b reacted with propionaldehyde and afforded a mixture of diastereomers 16 and 17 (cis:trans) as a colorless dense liquid (0.083 g, 92%).

\[
\begin{align*}
\text{TBDPS} & \quad \text{O} & \quad \text{N} & \quad \text{Et} & \quad \text{Ts} \\
\text{16}
\end{align*}
\]

\(^1\)H NMR: \(\delta\) 7.48-7.28 (12 H, m), 7.13-7.11 (2H, m), 4.51-4.49 (1H, dd, \(J = 7.08, 2.7\) Hz), 3.18-3.12 (1H, m), 3.09-3.04 (1H, m), 2.33 (3H, s) 1.94-1.87 (1H, m), 1.71-1.64 (1H, m), 1.53-1.47 (1H, dd, \(J = 14.9, 6.6\) Hz), 1.15-1.10 (1H, dd, \(J = 14.9, 7.6\) Hz), 0.96 (9H, s), 0.95 (3H, d, \(J = 6.6\) Hz), 0.89 (3H, t, \(J = 7.3\) Hz). \(^1\)C NMR: \(\delta\) 143.4, 136.0, 135.9, 135.8, 134.6, 134.1, 129.5, 129.4, 129.2, 127.6, 127.5, 127.4, 91.0, 77.2, 57.6, 29.8, 27.7, 21.5, 17.9, 16.3, 10.9, 8.4. Anal Calcd for C\(_{30}\)H\(_{39}\)NO\(_3\)SSi: C, 69.06; H, 7.53; N, 2.68. Found: C, 69.00; H, 7.55; N, 2.70.
**H NMR:** δ 7.72-7.70 (2H, m), 7.48-7.28 (12H, m), 4.92-4.90 (1H, dd, J = 7.1, 3.9 Hz), 3.77-3.72 (1H, m), 3.08-3.04 (1H, m), 2.43 (3H, s), 1.72-1.63 (2H, m), 1.58-1.53 (1H, dd, J = 14.4, 7.3 Hz), 1.04 (3H, d, J = 6.6 Hz), 0.92-0.86 (1H, m), 0.89 (9H, s), 0.77 (3H, t, J = 7.3 Hz).

**13C NMR:** δ 143.8, 136.0, 135.96, 135.9, 134.1, 133.4, 129.7, 129.3, 129.2, 127.9, 127.6, 127.4, 91.8, 80.6, 62.3, 28.6, 27.6, 20.5, 17.9, 15.4, 10.9, 8.5. Anal Calcd for C₃₀H₃₉NO₃SSi: C, 69.06; H, 7.53; N, 2.68. Found: C, 69.01; H, 7.50; N, 2.65.

18. Following the general procedure outlined above, the aziridine 1b reacted with cyclohexanone and afforded a mixture of diastereomers 18 (cis:trans = 57:43) as a colorless dense liquid (0.083 g, 82%).

![18 (cis + trans)](image)

**H NMR:** δ 7.68-7.52 (m), 7.40-7.25 (m), 7.17-7.15 (m), 3.78-3.73 (m, minor), 3.70-3.65 (m, major), 3.34-3.29 (m, minor), 3.12-3.07 (m, major), 2.42 (s, major), 2.39 (s, minor), 2.36-2.15 (m), 1.91-1.78 (m), 1.66-1.12 (m), 1.17 (d, J = 6.6 Hz), 1.09 (d, J = 6.6 Hz), 1.03 (s), 1.00 (s).

**13C NMR:** δ 142.7, 142.6, 138.9, 139.0, 136.1, 135.9, 135.8, 134.3, 133.9, 133.8, 129.4, 129.3, 129.2, 129.1, 129.06, 127.7, 127.6, 127.5, 127.3, 127.2, 127.0, 99.2, 97.7, 79.0, 74.6, 62.7, 58.4, 40.0, 37.5, 35.4, 32.5, 27.7, 24.5, 24.4, 23.5, 23.3, 23.2, 23.17, 21.4, 19.5, 18.1, 18.0, 16.2, 15.5, 10.6. Anal. Calcd. for C₃₃H₄₃NO₃SSi: C, 70.54; H, 7.71; N, 2.49. Found: C, 70.47; H, 7.74; N, 2.50.

**Procedure for the preparation of azetidine 19.** Trimethylsulfoxonium iodide (0.132 mg, 0.6 mmol) was added slowly under N₂ to a stirred suspension of 55% NaH (0.044 mg, 1 mmol) in THF/DMF (6 mL, 5:1) at 0 °C. After stirring for 0.5 h at 0 °C, a solution of aziridine 1a (0.224 g, 0.5 mmol) in THF (1 mL) was added dropwise followed by further stirring at 110 °C for 7h. The reaction was quenched with saturated aqueous ammonium chloride and extracted with EtOAc (2 x 5 mL). The organic layer was dried and concentrated. Purification of the residue by silica gel column chromatography furnished the pure product 19 as a colorless dense liquid (0.093 g, 40%).
**General procedure for the BF$_3$·Et$_2$O-assisted cycloaddition reaction of azetidine 19 with nitriles:** BF$_3$·Et$_2$O (0.18 mmol) was added to a stirred solution of the azetidine (0.18 mmol) and nitrile (0.18 mmol) in CH$_2$Cl$_2$ (1.3 mL) at 25 °C under nitrogen. After 1h, the reaction was quenched with saturated aqueous NaHCO$_3$ and the stirring was continued until the organic layer had become clear (1h). The aqueous phase was extracted with CH$_2$Cl$_2$ (2 x 5 mL) and dried. The crude material was purified by column chromatography over silica gel.

**20.** Following the general procedure outlined above, the azetidine 19 reacted with acetonitrile and afforded the product 20 as a colorless dense liquid (0.059 g, 65%).

**21.** Following the general procedure outlined above, the azetidine 19 reacted with trans-cinnamonitrile and afforded the product 21 as a colorless dense liquid (0.064 g, 60%).
\[ \text{TBDPS-} \text{NTs} \]

\[ \text{NTs} \text{N} \text{TBDPS} \]

\( ^1 \text{H NMR: } \delta 7.60-7.51 (6H, m), 7.42-7.18 (13H, m), 7.06 (1H, d, } J = 15.6 \text{ Hz), 6.89 (1H, d, } J = 15.6 \text{ Hz), 3.68-3.62 (1H, m), 3.27-3.20 (2H, m), 2.39 (3H, s), 1.65-1.60 (1H, dd, } J = 14.9, 6.1 \text{ Hz), 1.48-1.42 (1H, m), 1.15-1.09 (1H, dd, } J = 14.9, 8.6 \text{ Hz), 1.19-1.12 (1H, m), 0.99 (9H, s). } \]

\( ^{13} \text{C NMR: } \delta 147.5, 144.1, 136.6, 136.2, 136.1, 136.0, 135.7, 134.7, 134.3, 129.7, 129.1, 129.0, 128.6, 128.5, 127.5, 127.1, 124.2, 117.9, 51.8, 44.2, 30.3, 27.8, 21.6, 18.7, 18.1. \]

Anal Calcd for C\(_{36}\)H\(_{40}\)N\(_2\)O\(_2\)SSi: C, 72.93; H, 6.80; N, 4.73. Found: C, 72.85; H, 6.75; N, 4.75.

22. Following the general procedure outlined above, the azetidine 19 reacted with 2-furonitrile and afforded 22 as a colorless dense liquid (0.062 g, 62%).

\[ \text{TBDPS-} \text{NTs} \]

\[ \text{NTs} \text{O} \text{NTs} \]

\( ^1 \text{H NMR: } \delta 7.59-7.54 (4H, m), 7.44-7.24 (9H, s), 7.16-7.14 (2H, m), 6.66 (1H, d, } J = 3.4 \text{ Hz), 6.42-6.41 (1H, dd, } J = 3.4, 1.7 \text{ Hz), 3.50-3.44 (1H, m), 3.14-3.05 (2H, m), 2.36 (3H, s), 1.87-1.83 (1H, dd, } J = 15.1, 4.1 \text{ Hz), 1.28-1.22 (1H, m), 1.17-1.11 (1H, dd, } J = 15.1, 10.0 \text{ Hz), 1.13-1.07 (1H, m), 0.97 (9H, s). } \]

\( ^{13} \text{C NMR: } \delta 149.4, 144.1, 143.4, 142.7, 136.2, 136.1, 135.9, 134.7, 133.9, 129.6, 129.1, 127.6, 127.5, 127.46, 113.2, 111.3, 52.3, 44.0, 31.2, 27.7, 21.6, 18.7, 18.1. \)

Anal Calcd for C\(_{32}\)H\(_{36}\)N\(_2\)O\(_3\)SSi: C, 69.03; H, 6.52; N, 5.03. Found: C, 68.94; H, 6.55; N, 5.05.

**Procedure for the preparation of 23.** BF\(_3\)Et\(_2\)O (0.014 mL, 0.114 mmol) was added to a stirred solution of the azetidine 19 (0.053 mg, 0.114 mmol) in CH\(_2\)Cl\(_2\) (1.3 mL) at 25 °C under nitrogen. After 1h, the reaction was quenched by saturated aqueous NaHCO\(_3\) and the stirring was continued until the organic layer had become clear (1 h). The aqueous phase was extracted with CH\(_2\)Cl\(_2\) (2 x 5 mL) and dried. The crude material was purified by column chromatography over silica gel to obtain the pure product 23 as a colorless dense liquid (0.049 g, 92%).
\[ \text{TBDPS} \]

\[ 23 \]

\[^1\text{H NMR: } \delta 7.50-7.47 (2H, m), 7.40-7.12 (12H, m), 3.64-3.60 (1H, dd, } J = 10.2, 8.6 \text{ Hz), 3.12-3.01 (2H, m), 2.93-2.88 (1H, dd, } J = 11.7, 10.2 \text{ Hz), 2.34 (3H, s), 1.96-1.90 (1H, m), 1.83-1.73 (1H, m), 1.41-1.31 (1H, m), 0.94 (9H, s). \]

\[^{13}\text{C NMR: } \delta 143.0, 136.1, 133.8, 132.8, 132.6, 129.5, 129.4, 129.3, 127.7, 127.6, 127.3, 51.0, 48.6, 28.6, 28.1, 22.6, 21.5, 18.4. \]

Anal Calcd for C\(_{27}\)H\(_{33}\)NO\(_2\)SSi: C, 69.93; H, 7.17; N, 3.02. Found: C, 69.95; H, 7.20; N, 3.05.

**Trasformation of TBDPS function into hydroxy group via oxidative cleavage of carbon–silicon bond in 11.** To an ice-cold suspension of KH (164 mg, 1.23 mmol, 30% dispersion in mineral oil, washed with 3 x 2 mL of hexanes) in DMF (1 mL) was added \( t\)-BuOOH (70%, 162 \( \mu \)L, 1.18 mmol) dropwise. After 10 min, a solution of the oxazolildine \( 11 \) (\( cis + trans \)) (97 mg, 0.191 mmol) in DMF (1 mL) was added. The mixture was stirred at 25 °C for 40 h and quenched by adding solid Na\(_2\)S\(_2\)O\(_3\) (300 mg). The reaction mixture was stirred for 30 min and partitioned between water and diethyl ether. The aqueous layer was extracted with ether (3 x 10 mL) and dried. The crude material was purified by column chromatography over silica gel to obtain the pure product \( 24 \) (\( cis + trans \)) as a colorless dense liquid (32 mg, 60%).

\[ \text{HO} \]

\[ \text{O} \]

\[ \text{Et} \]

\[ 24 \text{ (cis + trans)} \]

\[^1\text{H NMR: } \delta 7.76-7.74 (m), 7.36-7.35 (m), 5.19-5.16 (dd, } J = 6.8, 4.9 \text{ Hz, minor), 5.14-5.11 (m, major), 4.29-4.23 (m, minor), 3.67-3.61 (m), 3.53-3.44 (m), 3.34-3.17 (m), 2.45 (s), 1.87-1.68 (m), 0.98 (t, } J = 7.3 \text{ Hz, major), 0.97 (t, } J = 7.3 \text{ Hz, minor). }^{13}\text{C NMR: } \delta 144.3, 144.2, 134.6, 133.9, 130.0, 129.8, 127.9, 127.6, 93.0, 92.6, 76.9, 76.6, 61.9, 61.8, 47.6, 46.8, 29.2, 28.3, 21.5, 8.8, 8.2. \]

Anal Calcd for C\(_{13}\)H\(_{15}\)NO\(_4\)S: C, 54.72; H, 6.71; N, 4.91. Found: C, 54.62; H, 6.75; N, 4.95.