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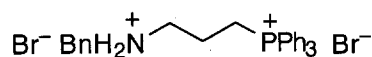
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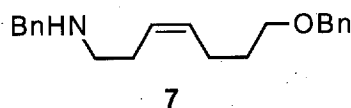
## Synthesis of the Tricyclic Core of Sarain A. Use of Formaldehyde in an Intramolecular Grigg Azomethine Ylide Cyclization.

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### Supporting Information



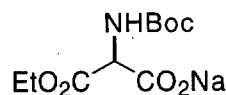
**N-(Phenylmethyl)-3-aminopropyltriphenylphosphonium bromide hydrobromide.** To a rapidly stirring suspension of 3-bromopropyltriphenylphosphonium bromide<sup>1</sup> (21.0 g, 45.3 mmol) in ethanol (210 mL) was added benzylamine (12.4 mL, 113 mmol). After one week the reaction mixture was concentrated under reduced pressure and then recrystallized from ethanol to afford the ammonium hydrobromide (21.7 g, 84%) as colorless crystals: mp 291–292 °C; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 7.95–7.75 (m, 15H), 7.58–7.50 (m, 2H), 7.47–7.40 (m, 3H), 4.24 (s, 2H), 3.75–3.65 (m, 2H), 3.38 (t, *J* = 6.9 Hz, 2H), 2.17–2.08 (m, 2H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 136.5, 136.4, 135.0, 134.9, 132.2, 131.8, 131.6, 131.2, 130.7, 130.2, 119.6, 118.7, 52.5, 48.2, 20.8; Anal. Calc'd for C<sub>28</sub>H<sub>30</sub>Br<sub>2</sub>NP: C, 58.86; H, 5.29; N, 2.45; Found: C, 59.03; H, 5.49; N, 2.53.



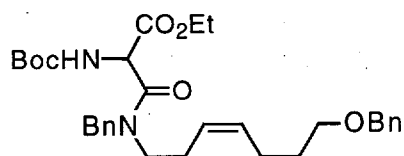
**Olefin 7:** To a 0° solution of 61.2 mL (290 mmol) of bis(trimethylsilyl)amine in THF (500mL) was slowly added 92 mL (277 mmol) of *n*-butyllithium. After stirring at 0 °C for 30 min, this solution was slowly cannulated into a -78 °C suspension of N-(phenylmethyl)-3-aminopropyltriphenylphosphonium bromide hydrobromide (79.1g; 138 mmol) in THF (1300mL). This suspension was allowed to warm slowly to room temperature and stirred until the solid had dissolved (ca. 2 hours). This solution was then recooled to -78 °C and into it was cannulated a solution of aldehyde **6** (23.5 g; 130 mmol) in THF (200 mL). The reaction mixture was stirred at -78 °C for 1 h, and then allowed to warm to ambient temperature and stirred for 12 h. The mixture was concentrated *in vacuo*, redissolved in CH<sub>2</sub>Cl<sub>2</sub> and treated with 300 g of silica gel. This mixture was evaporated to a fine powder and loaded on a column of silica gel. The desired olefin was eluted with 30% to 60% EtOAc/Hexane solvent system to give 32.59 g (81%) of the desired olefin in a *Z:E* ratio of 76:24. The purified *Z* isomer **7** could be isolated as a pale yellow syrup: IR (CHCl<sub>3</sub>) 3420, 1540 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 1.68 (pentet, *J* = 6.7 Hz, 2H), 2.17 (q, *J* = 7.4 Hz, 2H), 2.27 (q, *J* = 7.0 Hz, 2H), 2.67 (t, *J* = 7.0 Hz, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 3.79 (s, 2H), 4.49 (s, 2H), 5.38 (dt, *J* = 10.8, 7.1 Hz, 1H), 5.48 (dt, *J* = 10.8, 7.2 Hz, 1H), 7.11–7.37 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 23.8, 27.7, 29.5, 48.8, 53.7, 69.5, 72.6, 126.6, 127.2, 127.3, 127.4.

1 Maryanoff, B. E.; Reitz, A. B.; Duhl-Emsweiler, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 217.

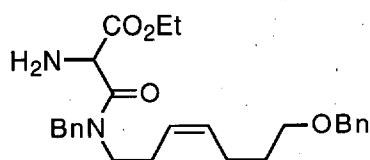
127.8, 128.1 (2C), 130.8, 138.4, 140.2; Anal. Calcd for  $C_{21}H_{27}NO$ : C, 81.51; H, 8.79; N, 4.53. Found: C, 81.63; H, 8.88; N, 5.04.

**10**

**Carboxylate salt 10:** Diester **9** (2.747 g; 9.98 mmol) was stirred with NaOH (10.48 mmol) in absolute EtOH (200 mL) for 24 h. The solvent was removed *in vacuo* and the material was azeotroped 3 times from benzene to obtain 2.65 g (99%) of a white non-crystalline solid that could be crushed into a powder. This material was not purified for analysis but was dried under vacuum for several days and used in this condition.

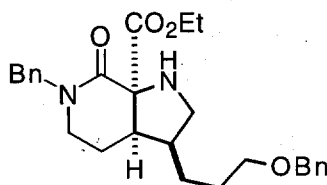
**11**

**Amide 11:** To a 0 °C suspension of carboxylate salt **10** (10.83 g; 40.2 mmol) in  $CH_2Cl_2$  (100 mL) was added pivaloyl chloride (4.46 mL; 36.2 mmol) and the solution was stirred 2 h at 0 °C. Then  $Et_3N$  (11.2 mL; 80.4 mmol) was added and the solution stirred another 10 min. Olefin **7** (6.1 g; 20.1 mmol) was then cannulated in as a solution in  $CH_2Cl_2$  (5 mL), and DMAP was added to the reaction (1.83 g; 8.0 mmol). The reaction mixture was allowed to warm to ambient temperature and stir for 16 h. To the reaction mixture was added 50 mL  $H_2O$  and 50 mL saturated aqueous  $NaHCO_3$ , and the mixture was extracted with 2x 50 mL  $CH_2Cl_2$ . The combined organic layers were dried ( $MgSO_4$ ) and concentrated *in vacuo*. The crude material was purified by chromatography on silica gel, eluting with 10% to 15% EtOAc/Hexane to obtain 8.98 g (83%) of the desired amide **11** as a colorless syrup: IR ( $CHCl_3$ ) 3431, 1753, 1706, 1653  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  1.18-1.30 (m, 3H), 1.42 (s, 2.3 H), 1.45 (s, 5.7 H), 1.50 (s, 1H), 1.66 (pentet,  $J = 6.6$  Hz, 2H), 2.09 (app sextet,  $J = 7.5$  Hz, 2H), 2.27 (q,  $J = 7.6$  Hz, 1H), 2.38 (q,  $J = 7.2$  Hz, 1H), 3.20-3.50 (m, 1.5H), 3.45 (q,  $J = 6.5$  Hz, 2H), 3.62 (pentet,  $J = 7.5$  Hz, 0.5H), 4.12-4.27 (m, 2H), 4.29-4.98 (m, 2H), 4.48 (s, 0.4H), 4.49 (s, 0.6H), 5.28 (s, 2H), 5.28-5.55 (m, 2H), 5.84 (d,  $J = 8.8$  Hz, 0.6H), 5.88 (d,  $J = 8.6$  Hz, 0.4H), 7.15-7.38 (m, 10H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$  13.9, 14.1, 23.7, 23.8, 24.9, 26.5, 27.0, 27.6, 28.1(2C), 29.4, 45.6, 46.0, 47.0, 48.8, 51.6, 53.3, 54.2, 54.6, 61.2, 62.1(2C), 69.5, 72.8, 80.2, 84.9, 124.9, 125.7, 126.8, 127.3, 127.4, 127.5, 127.6, 127.7, 128.2, 128.3, 128.5, 128.7, 131.6, 132.5, 135.9, 136.7, 138.5, 155.0(2C), 166.4, 166.7, 167.5, 167.6; Anal. Calcd for  $C_{31}H_{42}N_2O_6$ : C, 69.12; H, 7.86; N, 5.20. Found: C, 68.77; H, 7.89; N, 5.36.



12

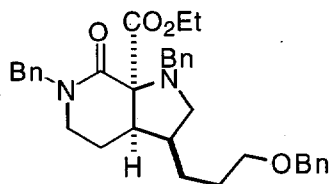
**Amine 12:** To a 0 °C solution of amide **11** (8.98 g; 16.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was added 10 mL TFA dropwise. The reaction mixture was stirred 1.5 h at 0 °C, another 10 mL of TFA was added, and the reaction mixture was stirred a further 2.5 h. The reaction mixture was brought to neutrality by careful addition at 0 °C of 50% aqueous NaOH. Phenolphthalein can be used to warn of the approaching endpoint. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x20 mL) and the combined organic layers were dried (MgSO<sub>4</sub>) and concentrated *in vacuo* to give the crude product. The material was purified by chromatography on silica gel with 30% EtOAc/hexane to 80% EtOAc/hexane. To obtain completely acid free material for the next step, this chromatographed material was passed through another column of silica gel and was eluted with EtOAc containing 5% Et<sub>3</sub>N. The product amine **12** was obtained as a light yellow syrup in a yield of 6.16 g (84%): IR (CHCl<sub>3</sub>) 3414, 1744, 1655 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 1.25 (td, *J* = 7.2, 4.0 Hz, 3H), 1.65 (pentet, *J* = 6.4 Hz, 2H), 1.80 (br s, 2H), 2.10 (pentet, *J* = 7.9 Hz, 2H), 2.32 (sextet, *J* = 7.2 Hz, 2H), 3.23 (m, 1H), 3.45 (td, *J* = 6.4, 1.6 Hz, 2H), 3.45-3.58 (m, 1H), 4.10-4.28 (m, 2H), 4.32 (d, *J* = 15.0 Hz, 0.5H), 4.38 (s, 0.5H), 4.48, 4.49, 4.49 (3 singlets, total 1.5H), 4.59 (d, *J* = 17.2 Hz, 0.5H), 4.81 (d, *J* = 17.1 Hz, 0.5H), 4.98 (d, *J* = 15.0 Hz, 0.5 H), 5.31 (m, 1H), 5.38-5.54 (m, 1H), 7.16-7.40 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 14.0, 23.8, 23.9, 25.1, 26.5, 29.5(2C), 46.4, 46.6, 48.7, 51.3, 55.5, 56.0, 61.8(2C), 69.4, 69.6, 72.8(2C), 125.0, 125.9, 126.4, 127.3, 127.4, 127.5(2C), 127.7(2C), 128.3(2C), 128.5, 128.9, 131.6, 132.6, 136.3, 137.0, 138.4, 138.5, 169.2, 170.7(2C); Anal. Calcd for C<sub>26</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.16; H, 8.09; N, 6.31.



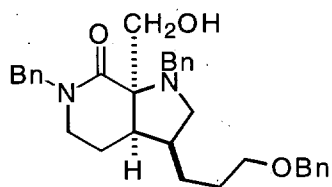
13

**Amine 13:** A solution of amine **12** (7.64 g; 17.4 mmol) in toluene was heated to reflux. Paraformaldehyde was then added (543 mg; 18.1 mmol) and the reaction mixture was refluxed for 12 h. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel; elution by 50% EtOAc/hexane removed less polar impurities, and 5% MeOH/EtOAc was then used to elute the product. The desired cyclized compound **13** was obtained as a light yellow syrup in a yield of 6.02 g (78%): IR (CHCl<sub>3</sub>) 3461, 3356, 1737, 1644 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 1.28 (t, *J* = 7.2 Hz, 3H), 1.31-1.52 (m, 2H), 1.56 (app pentet, *J* = 7.1 Hz, 2H), 1.61-1.77 (m, 2H), 2.14 (m, 2H), 2.57 (dt, *J* = 12.3, 6.3 Hz, 1H), 2.66 (t, *J* = 10.2 Hz, 1H), 3.22 (dt, *J* = 12.4, 4.3 Hz, 1H), 3.28-3.40 (m, 2H), 3.41-3.49 (m, 2H), 4.23 (m, 2H), 4.29 (d, *J* = 14.8 Hz, 1H), 4.47 (s, 2H), 4.98 (d, *J* = 14.8 Hz, 1H), 7.24-7.33 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 13.8, 21.4, 24.7, 28.4, 41.2, 44.7, 46.3, 48.9, 50.3, 61.7, 69.9,

72.6, 127.1; 127.3, 127.6(2C), 128.1, 128.3, 136.5, 138.2, 168.6, 173.5; Anal. Calcd for  $C_{27}H_{36}N_2O_4$ : C, 71.97; H, 8.05; N, 6.22. Found: C, 71.84; H, 7.67; N, 6.19.

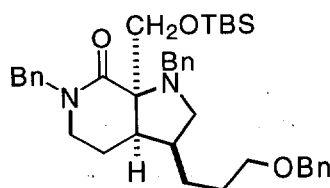


**N-Benzyl derivative of amine 13:** A mixture of amine **13** (6.02 g; 13.3 mmol), benzyl bromide (2.38 mL; 20.0 mmol) and sodium carbonate monohydrate (4.97 g; 40.0 mmol) in a solvent system of 8:2:1  $CH_2Cl_2/H_2O/EtOH$  (55 mL total volume) was heated at reflux for 24 h. Saturated aqueous sodium chloride (30 mL) was added and the reaction mixture was extracted with  $CH_2Cl_2$  (3x20 mL). The combined organic layers were dried ( $MgSO_4$ ) and concentrated *in vacuo*. The crude product was purified by chromatography on silica gel with 15% EtOAc/hexane. The product was obtained as a colorless syrup in a yield of 6.87 g (95%): IR ( $CHCl_3$ ) 1736, 1703, 1640,  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  1.32 (t,  $J = 7.1$  Hz, 3H), 1.37-1.54 (m, 4H), 1.67 (m, 1H), 1.88 (ddd,  $J = 25.4, 12.9, 5.2$  Hz, 1H), 2.28 (m, 1H), 2.56 (ddd,  $J = 12.6, 6.2, 4.3$  Hz, 1H), 2.76 (t,  $J = 8.7$  Hz, 1H), 2.94 (t,  $J = 9.1$  Hz, 1H), 3.29 (ddd,  $J = 12.3, 4.9, 2.3$  Hz, 1H), 3.30-3.44 (m, 3H), 4.08 (d,  $J = 15.0$  Hz, 1H), 4.26 (m, 2H), 4.41 (d,  $J = 14.8$  Hz, 1H), 4.45 (s, 2H), 4.86 (d,  $J = 14.7$  Hz, 1H), 4.86 (d,  $J = 15.1$  Hz, 1H), 7.18-7.34 (m, 15 H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$  14.2, 21.2, 25.8, 28.5, 38.1, 46.2, 46.6, 49.8, 53.9, 55.9, 61.0, 70.1, 72.8, 75.2, 126.1, 127.3, 127.5(2C), 127.7, 127.9, 128.0, 128.3, 128.5, 137.0, 138.4, 141.7, 167.4, 173.3; Anal. Calcd for  $C_{34}H_{42}N_2O_4$ : C, 75.53; H, 7.83; N, 5.18. Found: C, 75.14; H, 7.52; N, 4.99.



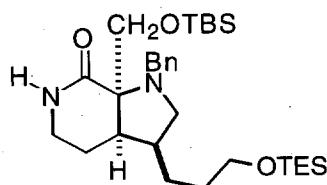
**Reduction of the angular ester group:** The foregoing ester (4.02g; 7.4 mmol) was dissolved in ether (125 mL) and cooled to  $-78^\circ C$ . DIBAL-H (2.65 mL; 14.9 mmol) was then added dropwise over a period of 15 min. The reaction mixture was stirred for 45 min at  $-78^\circ C$  and was then removed from the cold bath and quenched by addition of  $H_2O$  (10 mL). The reaction mixture was stirred 30 min with 1M aqueous sodium/potassium tartrate salt (100 mL) and 1M NaOH (100 mL). The reaction mixture was extracted with EtOAc (5x20 mL), dried ( $MgSO_4$ ) and concentrated *in vacuo*. The residue was filtered through a short plug of silica gel, eluting with 50% EtOAc/hexane until all product had been obtained. The solvent was removed *in vacuo* to give a mixture of aldehyde and alcohol as a thick syrup. This mixture was then dissolved in EtOH (100 mL) and treated with  $NaBH_4$  (0.56 g; 15 mmol). The mixture was stirred 1 h then quenched by addition of  $H_2O$  (10 mL). Most of the EtOH was removed *in vacuo*, and an additional 10 mL of  $H_2O$  was added. The reaction mixture was then extracted with  $CH_2Cl_2$  (3x20 mL), dried ( $MgSO_4$ ), and concentrated *in vacuo*. The material was purified by chromatography on silica gel with 2:2:1 EtOAc/Hexane/ $CH_2Cl_2$  to give the product alcohol (2.83 g; 76%) as a thick syrup which

solidified to a waxy solid on standing: IR (CHCl<sub>3</sub>) 3420, 1626 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 1.28-1.38 (m, 1H), 1.41-1.62 (m, 3H), 1.64-1.72 (m, 1H), 1.78-1.90 (m, 1H), 2.38 (m, 1H), 2.52 (t, *J* = 9.4 Hz, 1H), 2.54 (m, buried, 1H), 2.73 (m, buried, 1H), 2.78 (t, *J* = 8.8 Hz, 1H), 3.30 (m, 2H), 3.42 (m, 2H), 3.62 (d, *J* = 10.8 Hz, 1H), 3.96 (d, *J* = 13.9 Hz, 1H), 4.16 (d, *J* = 10.8 Hz, 1H), 4.38 (d, *J* = 14.7 Hz, 1H), 4.46 (s, 2H), 4.93 (d, *J* = 14.7 Hz, 1H), 7.18-7.37 (m, 15H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 22.0, 25.8, 28.7, 38.5, 41.7, 46.4, 50.3, 53.6, 56.3, 63.5, 70.1, 70.2, 72.8, 126.4, 127.4, 127.5(2C), 127.9(2C), 128.1, 128.3, 128.6, 137.0, 138.4, 140.9, 171.6; Anal. Calcd for C<sub>32</sub>H<sub>38</sub>N<sub>2</sub>O<sub>3</sub>: C, 77.08; H, 7.68; N, 5.62. Found: C, 76.78; H, 7.83; N, 5.66.



14

**Silyl ether 14:** The foregoing alcohol (2.83 g; 5.7 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (60 mL) and treated with Et<sub>3</sub>N (1.58 mL; 1.4 mmol), DMAP (140 mg; 1.14 mmol), and *t*-butyldimethylsilyl chloride (1.28 g; 8.5 mmol). The reaction mixture was stirred 16 h and was then worked up by addition of H<sub>2</sub>O (20 mL) and extraction with CH<sub>2</sub>Cl<sub>2</sub> (2x20 mL). The organic layers were dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The material was purified by chromatography on silica gel with 8% EtOAc/hexane to give 2.94 g (84%) of silyl ether **14** as a colorless syrup: IR (CHCl<sub>3</sub>) 1632 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.07 (s, 6H), 0.89 (s, 9H), 1.22-1.78 (m, 6H), 2.38 (m, 1H), 2.55 (m, buried, 1H), 2.57 (t, *J* = 8.8 Hz, 1H), 2.69 (t, *J* = 9.1 Hz, 1H), 3.15-3.25 (m, 2H), 3.41 (m, 2H), 3.57 (d, *J* = 8.9 Hz, 1H), 3.80 (d, *J* = 13.8 Hz, 1H), 4.26 (d, *J* = 9.0 Hz, 1H), 4.34 (d, *J* = 14.8 Hz, 1H), 4.45 (s, 2H), 4.60 (d, *J* = 13.8 Hz, 1H), 4.86 (d, *J* = 14.8 Hz, 1H), 7.13-7.33 (m, 15H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ -5.4, 18.1, 21.6, 25.8(2C), 28.7, 37.8, 41.9, 46.3, 50.1, 53.5, 56.4, 63.3, 70.2, 70.3, 72.8, 126.1, 127.0, 127.4, 127.5, 127.8, 127.9(2C), 128.3, 128.4, 137.5, 138.4, 141.6, 170.8; Anal. Calcd for C<sub>38</sub>H<sub>52</sub>N<sub>2</sub>SiO<sub>3</sub>: C, 74.46; H, 8.55; N, 4.57. Found: C, 74.19; H, 8.58; N, 4.51.

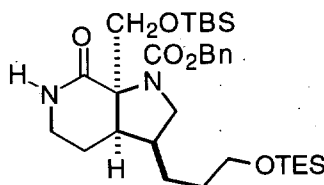


15

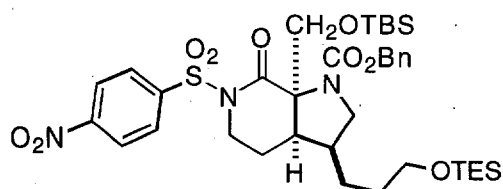
**Amide 15:** Pieces of sodium metal totalling 1.49 g (65 mmol) were washed briefly in EtOH and then added to a mixture of liquid ammonia (150 mL) and *t*-butyl alcohol (3.11 mL; 32 mmol) at -78 °C. The blue solution was stirred 45 min at -78 °C or until all sodium had dissolved. A solution of tribenzyl compound **14** (3.98 g; 6.5 mmol) in ether (50 mL) was cannulated in and the cold bath was removed. The reaction mixture was allowed to stir at refluxing NH<sub>3</sub> temperature for 1.5 h. and was then quenched by the addition of solid NH<sub>4</sub>Cl until the blue color disappeared. After the NH<sub>3</sub> had boiled off, H<sub>2</sub>O

(30mL) was added and the reaction mixture was extracted with EtOAc (3x30mL). The organic layers were dried (MgSO<sub>4</sub>) and the solvent was removed *in vacuo* to give a yellow syrup.

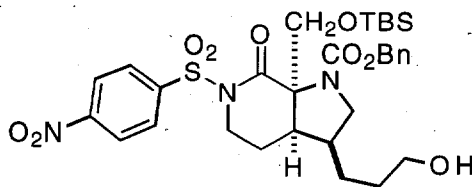
This residue was stirred in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) with Et<sub>3</sub>N (1.81 mL; 13.0 mmol) and triethylsilyl chloride (1.64 mL; 9.75 mmol) for 2 h. The solvent was evaporated and the residue was worked up by addition of H<sub>2</sub>O (10 mL) and extraction with EtOAc (3x10 mL). The organic layers were dried (MgSO<sub>4</sub>) and the solvent was evaporated to give the crude product. This product was purified by chromatography on silica gel with 25% EtOAc/hexane to give 3.04 g (86%) of **15** as a colorless syrup: IR (CHCl<sub>3</sub>) 3406, 3300, 1698, 1662 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.08 (s, 3H), 0.08 (s, 3H), 0.59 (q, *J* = 7.9 Hz, 6H), 0.90 (s, 9H), 0.95 (t, *J* = 8.0 Hz, 9H), 1.30 (m, 1H), 1.37-1.51 (m, 3H), 1.63-1.81 (m, 2H), 2.41 (m, 1H), 2.54 (t, *J* = 9.2 Hz, 1H), 2.55 (m, buried, 1H), 2.71 (t, *J* = 8.8 Hz, 1H), 3.19-3.31 (m, 2H), 3.45-3.63 (m, 2H), 3.57 (d, *J* = 9.1 Hz, 1H), 3.89 (d, *J* = 13.8 Hz, 1H), 4.16 (d, *J* = 9.1 Hz, 1H), 4.42 (d, *J* = 13.8 Hz, 1H), 6.07 (br s, 1H), 7.14-7.30 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ -5.5, 4.3, 6.7, 18.1, 21.8, 25.4, 25.8, 31.7, 37.8, 41.1, 41.8, 53.6, 56.4, 62.7, 63.5, 69.9, 126.1, 127.8, 128.3, 141.5, 173.3; Anal. Calcd for C<sub>30</sub>H<sub>54</sub>N<sub>2</sub>Si<sub>2</sub>O<sub>3</sub>: C, 65.88; H, 9.95; N, 5.12. Found: C, 65.54; H, 9.93; N, 4.96.

**16**

**Benzyl carbamate 16:** Benzyl compound **15** (151 mg; 0.28 mmol) and palladium(II) hydroxide (20% on carbon; 30 mg) were stirred in EtOH (10 mL) under an H<sub>2</sub> atmosphere for 2 h. The reaction was filtered through celite and the solvent was removed *in vacuo*. The residue was dissolved in 4:1:1 CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O/EtOH (4 mL) and to this solution was added sodium carbonate hydrate (171 mg; 1.38 mmol) and benzyl chloroformate (.079 mL; 0.55 mmol). The reaction was stirred for 24 h, and then the solvent was removed *in vacuo*. To the residue was added H<sub>2</sub>O (5 mL) and the reaction was then extracted with EtOAc (3x5 mL). The organic layers were dried (MgSO<sub>4</sub>), and the solvent was removed *in vacuo*. The material was purified by chromatography on silica gel with 50% EtOAc/hexane to give 147 mg (90%) of **16** as a colorless syrup: IR (CHCl<sub>3</sub>) 3416, 3218, 1689 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ -0.03 (s, 3H), 0.01 (s, 3H), 0.59 (q, *J* = 7.9 Hz, 6H), 0.85 (s, 9H), 0.95 (t, *J* = 7.9 Hz, 9H), 1.32-1.54 (m, 4H), 1.63-1.83 (m, 2H), 2.69 (m, 2H), 3.07 (t, *J* = 10.8 Hz, 1H), 3.17 (m, 2H), 3.61 (m, 2H), 3.82 (app t, *J* = 8.2 Hz, 1H), 4.14 (AB, *J* = 6.4 Hz, Δ*v* = 16.7 Hz, 2H), 5.12 (AB, *J* = 5.2 Hz, Δ*v* = 17.7 Hz, 2H), 5.83 (br s, 1H), 7.26-7.40 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ -5.6, 4.2, 6.6, 17.9, 23.9, 25.0, 25.7, 31.3, 38.6, 40.1, 43.8, 53.2, 62.4, 64.1, 66.7, 69.2, 127.5, 127.7, 128.1, 136.6, 154.8, 172.7; Anal. Calcd for C<sub>31</sub>H<sub>54</sub>N<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>: C, 63.01; H, 9.21; N, 4.74. Found: C, 63.07; H, 9.26; N, 4.61.



**N-Nosyl Lactam:** Lactam **16** (147 mg; 0.25 mmol) was dissolved in THF (3 mL) and cooled to 0 °C. Lithium bis(trimethylsilyl)amide (0.32 mL of a 1M solution in hexane; 0.32 mmol) was added dropwise and the reaction was stirred 15 min at 0 °C. Solid 4-nitrobenzenesulfonyl chloride (83 mg; 0.37 mmol) was added, and the reaction was stirred at 0 °C for 5 min. The reaction was then warmed to ambient temperature and stirred for 1.5 h. The reaction was worked up by adding saturated aqueous sodium chloride (5 mL) and then extracting with EtOAc (4x5 mL). The organic layers were dried (MgSO<sub>4</sub>) and the solvent was removed *in vacuo*. The material was partially purified by chromatography on a short silica gel column with 12% EtOAc /hexane which gave a mixture of desired product plus unreacted sulfonyl chloride. This material was usually carried into the next step, but a small amount of the product was purified for analysis as a colorless syrup: IR (CHCl<sub>3</sub>) 1722, 1703 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ -0.10 (s, 3H), -0.08 (s, 3H), 0.59 (q, *J* = 7.8 Hz, 9H), 0.78 (s, 9H), 0.95 (t, *J* = 8.0 Hz, 9H), 1.37-1.52 (m, 4H), 1.64 (m, 1H), 2.06 (br d, *J* = 14.5 Hz, 1H), 2.64 (t, *J* = 7.6 Hz, 1H), 2.80 (m, 1H), 3.10 (t, *J* = 10.7 Hz, 1H), 3.52-3.66 (m, 3H), 3.83 (t, *J* = 9.3 Hz, 1H), 3.92 (d, *J* = 10.5 Hz, 1H), 4.01 (m, 1H), 4.21 (dt *J* = 14.1, 4.0 Hz, 1H), 4.92 (br s, 1H), 5.17 (br s, 1H), 7.27-7.39 (m, 5H), 8.15 (d, *J* = 8.8 Hz, 2H), 8.26 (d, *J* = 8.9 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ -5.8(2C), 4.3, 6.7, 18.0, 24.7, 25.6, 25.7, 31.4, 38.8, 44.3, 45.1, 54.2, 62.3, 63.9, 67.2, 71.1, 123.8, 127.8, 128.0, 128.4, 129.9, 132.1, 144.5, 150.5, 153.5, 170.6; Anal. Calcd for C<sub>37</sub>H<sub>57</sub>N<sub>3</sub>SSi<sub>2</sub>O<sub>4</sub>: C, 57.26; H, 7.40; N, 5.41. Found: C, 57.33; H, 7.61; N, 5.23.

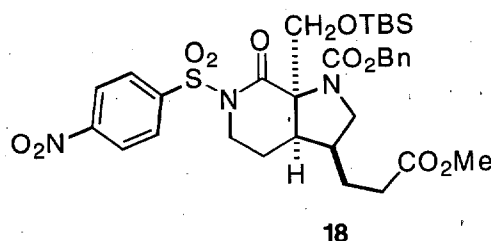


**17**

**Alcohol 17:** This mixture was dissolved in 20:1 THF/H<sub>2</sub>O (3 mL) and treated with camphor-sulfonic acid (5 mg). The reaction was stirred 2 h and then the solvent was removed *in vacuo*. The residue was purified by chromatography on silica gel with 40% EtOAc/hexane to give 121 mg (73%) of the product alcohol **17** as a colorless syrup: IR (CHCl<sub>3</sub>) 3625, 3482, 1722, 1702 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ -0.11 (s, 3H), -0.08 (s, 3H), 0.78 (s, 9H), 1.43-1.70 (m, 6H), 2.07 (br d, *J* = 15.0 Hz, 1H), 2.65 (t, *J* = 7.1 Hz, 1H), 2.83 (m, 1H), 3.11 (t, *J* = 10.5 Hz, 1H), 3.57-3.72 (m, 3H), 3.85 (t, *J* = 9.2 Hz, 1H), 3.91 (d, *J* = 10.5 Hz, 1H), 4.03 (br s, 1H), 4.21 (dt, *J* = 13.9, 4.0 Hz, 1H), 4.94 (br s, 1H), 5.17 (br s, 1H), 7.26-7.42 (m, 5H), 8.15 (d, *J* = 8.7 Hz, 2H), 8.26 (d, *J* = 9.1 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ -5.9(2C), 17.6, 17.9, 24.6, 25.6(2C), 31.0, 38.8, 44.3, 45.1, 54.1, 62.2, 63.8, 67.2, 71.1, 123.8, 127.7, 127.9, 128.4, 129.8, 136.0, 144.4, 150.4, 153.4, 170.6; Anal. Calcd for C<sub>31</sub>H<sub>43</sub>N<sub>3</sub>SSiO<sub>9</sub>: C, 56.26; H,



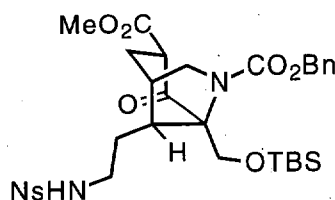
6.55; N, 6.35. Found: C, 56.44; H, 6.64; N, 6.04.



**Methyl Ester 18:** Oxalyl chloride (0.188 mL; 2.15 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) was cooled to  $-78^\circ\text{C}$ . DMSO (0.173 mL; 2.44 mmol) was added dropwise over 10 min. The reaction was stirred for 15 min and then a solution of alcohol **17** (950 mg; 1.44 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added dropwise over 10 min. The reaction was stirred for 20 min and then  $\text{Et}_3\text{N}$  (1.1 mL; 7.89 mmol) was added dropwise. The reaction was stirred a further 10 min at  $-78^\circ\text{C}$  and was then removed from the cold bath and allowed to slowly warm to ambient temperature. After stirring for 30 min at ambient temperature,  $\text{H}_2\text{O}$  (30 mL) was added and the reaction was extracted with  $\text{CH}_2\text{Cl}_2$  (3x10 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ) and the solvent was removed *in vacuo* to obtain a sticky solid. This material was dissolved in  $\text{Et}_2\text{O}$  and filtered to remove the solid. The filtrate was concentrated *in vacuo* to give crude aldehyde as a yellow syrup. This material was generally used directly in the next step.

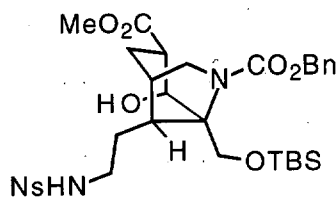
The crude aldehyde was dissolved in 1:1 *t*-butyl alcohol/ $\text{H}_2\text{O}$  (4 mL) and cooled to  $0^\circ\text{C}$ . To this stirred solution was added 2-methyl-2-butene (0.5 mL), monobasic sodium phosphate hydrate (1.5 g; 10.9 mmol), and finally sodium chlorite (1.5 g; 16.6 mmol). The reaction was stirred at ambient temperature for 4 h. The reaction was diluted with  $\text{H}_2\text{O}$  (20 mL) and  $\text{CH}_2\text{Cl}_2$  (20 mL) and was then extracted with  $\text{CH}_2\text{Cl}_2$  (3x10 mL). The organic layers were dried ( $\text{MgSO}_4$ ) and the solvent was removed *in vacuo* to give carboxylic acid as a yellow syrup. This material was generally used directly in the next step.

The crude acid was dissolved in DMF (2 mL) with potassium carbonate (800 mg; 5.79 mmol) and iodomethane (0.20 mL; 3.21 mmol) and was stirred for 12 h. Upon completion,  $\text{H}_2\text{O}$  (40 mL) was added, the solution was saturated with NaCl, and then extracted with  $\text{Et}_2\text{O}$  (5x10 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ) and the solvent was removed *in vacuo*. The residue was purified by chromatography on silica gel with 20% to 25%  $\text{EtOAc}$ /hexane to obtain 837 mg (85%) of methyl ester **18** as a colorless syrup: IR ( $\text{CHCl}_3$ )  $1723\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  -0.11 (s, 3H), -0.08 (s, 3H), 0.77 (s, 9H), 1.60-1.89 (m, 3H), 2.04 (br d,  $J = 15.0\text{ Hz}$ , 1H), 2.29 (app t,  $J = 8.2\text{ Hz}$ , 2H), 2.65 (t,  $J = 6.5\text{ Hz}$ , 1H), 2.82 (m, 1H), 3.11 (t,  $J = 10.7\text{ Hz}$ , 1H), 3.62 (t,  $J = 13.5\text{ Hz}$ , 1H), 3.67 (s, 3H), 3.83 (t,  $J = 9.3\text{ Hz}$ , 1H), 3.90 (d,  $J = 10.6\text{ Hz}$ , 1H), 4.08 (br s, 1H), 4.21 (dt,  $J = 13.9, 3.7\text{ Hz}$ , 1H), 4.91 (br s, 1H), 5.12 (br s, 1H), 7.25-7.39 (m, 5H), 8.15 (d,  $J = 8.7\text{ Hz}$ , 2H), 8.27 (d,  $J = 8.9\text{ Hz}$ , 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  -6.2, -5.9, 14.1, 17.9, 20.9, 24.4, 24.7, 25.6, 32.4, 38.4, 44.3, 44.9, 51.7, 53.7, 60.3, 63.9, 67.2, 71.0, 123.8, 127.8, 128.0, 128.4, 129.9, 136.0, 144.4, 150.4, 153.3, 170.4, 172.8; Anal. Calcd for  $\text{C}_{32}\text{H}_{43}\text{N}_3\text{SSiO}_{10}$ : C, 55.71; H, 6.28; N, 6.09. Found: C, 55.37; H, 6.42; N, 5.80.



19

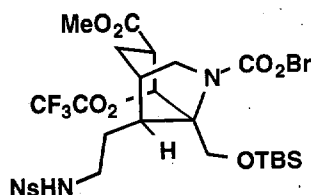
**Keto Ester 19:** Ester **18** (738 mg; 1.06 mmol) was dissolved in THF (4 mL) and cooled to -78 °C. Lithium bis(trimethylsilyl)amide (3.42 mL of a 1M solution in hexane; 3.42 mmol) was added over 2 min (reaction turns dark brown during the addition). The cold bath was removed immediately and the reaction was allowed to warm up to ambient temperature. After 15 min the reaction was quenched by adding H<sub>2</sub>O (20 mL). The water layer was saturated with NaCl and was then extracted with EtOAc (4x5 mL). The organic layers were dried (MgSO<sub>4</sub>) and the solvent was removed *in vacuo*. The residue was purified by chromatography on silica gel with 25% to 30% EtOAc/hexane to provide rearranged ester **19** (515 mg; 70%) as a colorless syrup: IR (CHCl<sub>3</sub>) 3673, 3385, 3284, 1721 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ -0.09 (s, 1H), -0.07 (s, 1H), -0.03 (s, 2H), -0.01 (s, 2H), 0.82 (s, 4H), 0.84 (s, 5H), 1.35-1.61 (m, 3H), 2.05 (app q, *J* = 8.8 Hz, 1H), 2.29 (t, *J* = 11.6 Hz, 1H), 2.38 (m, 1H), 2.82 (m, 1H), 3.02-3.15 (m, 2H), 3.42 (dd, *J* = 10.9, 9.2 Hz, 1H), 3.46-3.90 (m, 3H), (2 singlets totalling 3H at 3.73, 3.74), 4.26 (d, *J* = 12.3 Hz, 0.3H), 4.54 (d, *J* = 12.4 Hz, 0.4H), 4.84-5.19 (m, 3H), 7.22-7.40 (m, 5H), 8.02 (d, *J* = 8.7 Hz, 2H), 8.37 (d, *J* = 9.0 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ -5.7(2C), -5.6, 14.0, 17.9(2C), 24.5, 24.6, 25.2, 25.6(2C), 28.8, 28.9, 33.4, 34.0, 41.5, 42.2, 44.2, 44.7, 45.3, 51.3, 51.4, 51.6, 52.2, 52.3, 52.9, 53.2, 53.9, 56.5, 57.4, 66.7, 67.2, 67.6, 73.0, 73.3, 73.5, 124.3(2C), 124.4, 127.6, 127.9(2C), 128.0, 128.1, 128.3(2C), 128.4, 135.5, 136.1, 145.8, 149.9, 153.6, 154.1, 154.5, 167.9, 170.6, 170.7; Anal. Calcd for C<sub>32</sub>H<sub>43</sub>N<sub>3</sub>SSiO<sub>10</sub>: C, 55.71; H, 6.28; N, 6.09. Found: C, 55.55; H, 6.39; N, 5.71.



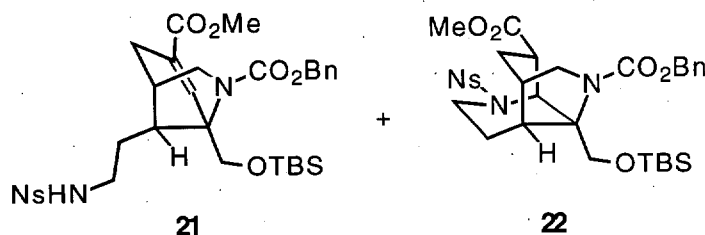
20

**Hydroxy Ester 20:** Keto ester **19** (515 mg; 0.75 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) and then MeOH (12 mL) was added and the reaction was cooled to 0 °C. Sodium borohydride was added in 10 mg portions every 20 min and the reaction was followed by TLC. When the starting material was consumed, the reaction mixture was quenched by addition of saturated aqueous NH<sub>4</sub>Cl (10 mL). The solvent was removed *in vacuo* and 10 mL of H<sub>2</sub>O was added. The aqueous layer was saturated with NaCl and then was extracted with EtOAc (3x10 mL). The organic layers were dried (MgSO<sub>4</sub>) and the solvent was removed *in vacuo*. The residue was purified by chromatography on silica gel with 10 % Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> to afford 344 mg (67%) of hydroxy ester **20** as a colorless syrup: IR (CHCl<sub>3</sub>) 3484, 3386, 3282, 1694 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ -0.07 (s, 1H), -0.02 (s, 1H), 0.02 (s, 2H), 0.02 (s, 2H), 0.81 (s, 2H), 0.83 (s, 7H), 1.70 (m, 1H), 1.83-2.05 (m, 3H), 2.09-2.22 (m, 2H), 2.42 (m, 0.2H), 2.61 (m, 1H), 2.88-3.16 (m, 2H), 3.31 (d, *J* = 10.6 Hz, 0.5H), 3.39 (m, 1H), (2 singlets totalling 3H at 3.69, 3.70),

3.83-4.00 (m, 0.2H), 4.01 (d,  $J = 11.0$  Hz, 0.5H), 4.18-4.26 (m, 0.2H), 4.45 (m, 0.6H), 4.54 (d,  $J = 9.5$  Hz, 0.2H), 4.63 (d,  $J = 10.9$  Hz, 0.6H), 4.72-4.84 (m, 0.2H), 4.94-5.24 (m, 3H), 7.26-7.41 (m, 5H), 8.03 (d,  $J = 8.9$  Hz, 2H), 8.35 (d,  $J = 8.9$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  -5.7, -5.6(2C), 17.9, 18.0, 22.9, 25.1, 25.6, 25.7, 26.1, 27.6, 31.7, 32.6, 33.2, 40.5, 41.3, 41.6, 41.8, 42.0, 42.8, 47.7, 51.7, 52.1, 58.4, 60.2, 66.3, 67.0, 67.2, 67.4, 68.4, 69.5, 69.9, 72.9, 124.2, 124.3, 127.5, 127.8(2C), 127.9, 128.1(2C), 128.3, 128.4, 136.0, 136.6, 145.8, 146.1, 149.8, 149.9, 153.3, 157.0, 174.3, 174.9; Anal. Calcd for  $\text{C}_{32}\text{H}_{45}\text{N}_3\text{SSiO}_{10}$ : C, 55.55; H, 6.56; N, 6.07. Found: C, 55.90; H, 6.87; N, 6.09.



**Trifluoroacetate of Hydroxy Ester 20:** Hydroxy ester **20** (350 mg; 0.50 mmol) was dissolved in pyridine (3 mL) and cooled to  $0^\circ\text{C}$ . Trifluoroacetic anhydride (0.216 mL; 1.52 mmol) was added dropwise, and the reaction mixture was stirred at  $0^\circ\text{C}$  for 4 h. The reaction mixture was quenched by dropwise addition of saturated aqueous sodium bicarbonate (6 mL). The reaction mixture was then extracted with  $\text{CH}_2\text{Cl}_2$  (4x5 mL), dried ( $\text{MgSO}_4$ ), and the solvent was removed *in vacuo*. The residue was partially purified by rapid chromatography on a short column of silica gel, eluting with 50% EtOAc/hexane. This gives a mixture of product trifluoroacetate plus starting alcohol **20**. The mixture is best carried on to the next step, but a small amount of the trifluoroacetate was purified for analysis: IR ( $\text{CHCl}_3$ ) 3386, 3287, 1795, 1739, 1702  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  -0.13 (s, 1H), -0.09 (s, 1H), -0.02 (s, 2H), 0.00 (s, 2H), 0.81 (s, 9H), 1.60-1.80 (m, 2H), 1.88 (m, 1H), 1.99 (t,  $J = 13.6$  Hz, 1H), 2.29-2.38 (m, 2H), 2.86 (m, 1H), 2.94-3.11 (m, 2H), 3.31-3.44 (m, 2H), 3.46 (dd,  $J = 10.6, 3.9$  Hz, 1H), 3.60 (s, 3H), 4.28 (m, 0.2H), 4.71 (d,  $J = 10.9$  Hz, 1H), 4.78 (br s, 1H), 5.04-5.41 (m, 2H), 5.75 (m, 0.2H), 5.81 (d,  $J = 4.0$  Hz, 0.8H), 7.26-7.44 (m, 5H), 8.03 (d,  $J = 8.9$  Hz, 2H), 8.37 (d,  $J = 8.9$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  -5.8, 17.9, 22.8, 25.0, 25.5, 29.4, 31.6, 39.8, 40.0, 41.0, 42.4, 51.6, 51.8, 52.2, 58.4, 66.6, 67.5, 72.3, 72.8, 114.1 (q,  $J = 286$  Hz), 124.3, 127.7, 128.0, 128.1, 128.3, 136.2, 145.8, 149.9, 153.3, 155.5 (q,  $J = 43$  Hz), 170.9; Anal. Calcd for  $\text{C}_{34}\text{H}_{44}\text{N}_3\text{F}_3\text{SSiO}_{11}$ : C, 51.83; H, 5.63; N, 5.33. Found: C, 51.50; H, 5.77; N, 5.43.

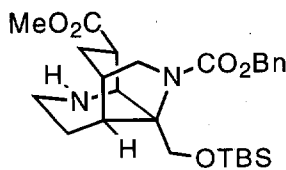


**Unsaturated Ester 21 and Cyclization Product 22:** The mixture from the trifluoroacetylation was dissolved in THF (3 mL) and DBU (0.30 mL; 2.0 mmol) was added. The reaction mixture was stirred at ambient temperature for 3 h and the solvent was then removed *in vacuo*. The residue was purified by chromatography on silica gel with elution by 20% to 25% to 30% EtOAc/hexane to obtain

112 mg (33%) of the desired  $\alpha,\beta$  unsaturated ester **21**, 106 mg (31%) of the already cyclized **22**, and 116 mg (33%) of the starting alcohol **20**.

The unsaturated ester **21** was isolated as a colorless syrup and gave the following analysis: IR ( $\text{CHCl}_3$ ) 3387, 3277, 1694  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  -0.08 (br s, 2H), 0.01 (s, 2H), 0.03 (s, 2H), 0.84 (s, 9H), 1.44 (m, 1H), 1.60 (m, 1H), 2.27-2.41 (m, 3H), 2.54 (br d,  $J = 18.4$  Hz, 1H), 3.10 (app q,  $J = 6.5$  Hz, 2H), 3.36 (d,  $J = 10.5$  Hz, 0.6H), 3.52 (m, 1H), 3.70 (buried, 1H), 3.71 (s, 3H), 4.35 (m, 0.3H), 4.76 (d,  $J = 11.4$  Hz, 0.7H), 4.92-5.21 (m, 3.3H), 6.77 (s, 0.2H), 6.89 (s, 0.8H), 7.25-7.41 (m, 5H), 8.02 (d,  $J = 8.9$  Hz, 2H), 8.35 (d,  $J = 8.9$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  -5.6, -5.5, 18.0, 25.7, 30.3, 32.8, 40.1, 42.3, 51.7, 55.3, 60.7, 63.9, 66.4, 124.3, 127.7, 127.8, 128.1, 128.3, 130.5, 136.6, 140.2, 146.0, 149.9, 154.2, 166.6; Anal. Calcd for  $\text{C}_{32}\text{H}_{43}\text{N}_3\text{SSiO}_9$ : C, 57.04; H, 6.43; N, 6.24. Found: C, 57.42; H, 6.44; N, 6.13.

The cyclized material **22** was isolated as a colorless syrup and had the following characteristics: IR ( $\text{CHCl}_3$ ) 1731, 1695  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (6 singlets totalling 6H at -0.23, -0.23, -0.19, -0.16, -0.05, -0.02), (3 singlets totalling 9H at 0.74, 0.78, 0.80), 1.74 (td,  $J = 13.4, 7.3$  Hz, 1H), 1.81-2.07 (m, 2.5 H), 2.10-2.25 (m, 0.5H), 2.32-2.43 (m, 2.5H), 2.46 (m, 1H), 2.93 (m, 1H), 3.07 (d,  $J = 10.5$  Hz, 0.7H), 3.14 (d,  $J = 10.3$  Hz, 0.7H), 3.20-3.56 (m, 3H), (3 singlets totalling 3H at 3.52, 3.54, 3.55), 3.67-3.89 (m, 2H), 4.26 (d,  $J = 10.3$  Hz, 0.6H), 4.48 (m, 0.6H), 4.66 (d,  $J = 5.2$  Hz, 0.6H), 4.92-5.37 (m, 2H), 7.27-7.52 (m, 5H), 7.65 (d,  $J = 8.8$  Hz, 0.6H), 7.96 (d,  $J = 8.8$  Hz, 1.2H), 8.03 (d,  $J = 8.8$  Hz, 0.2H), 8.16 (d,  $J = 8.8$  Hz, 0.6H), 8.33 (d,  $J = 8.8$  Hz, 0.1H), 8.34 (d,  $J = 8.8$  Hz, 1.3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  -5.9(2C), -5.8(2C), -5.7, -5.6, 17.8, 17.9(2C), 21.6, 21.7, 21.9, 25.5(2C), 25.6, 26.7, 29.3, 29.5, 29.6, 34.1(2C), 35.1, 35.5, 35.6, 35.8, 39.4, 40.2, 40.3, 41.0, 41.6(2C), 51.9(2C), 52.1, 52.3, 52.9, 53.1, 53.9, 54.2, 54.4, 58.0, 59.0, 62.5, 63.0, 63.6, 63.9, 66.2, 66.4, 67.5, 124.1, 124.2, 127.6, 127.7(2C), 127.8(2C), 127.9, 128.0, 128.3(2C), 128.4, 128.5(2C), 128.7, 129.4, 136.0, 136.6, 144.8, 146.9, 147.0, 149.5, 149.7, 150.0, 153.2, 154.3, 172.3, 172.6, 172.8; Anal. Calcd for  $\text{C}_{32}\text{H}_{43}\text{N}_3\text{SSiO}_9$ : C, 57.04; H, 6.43; N, 6.24. Found: C, 56.80; H, 6.53; N, 5.87.

**23**

**Compound 23:** A mixture of nosyl substrates **21** and **22** (230 mg; 0.34 mmol) was stirred in DMF (1 mL) with potassium carbonate (236 mg; 1.71 mmol) and thiophenol (0.105 mL; 1.02 mmol) for 4h. To the reaction mixture was added  $\text{H}_2\text{O}$  (10 mL) which was then saturated with NaCl. The aqueous layer was extracted with EtOAc (5x5 mL), dried ( $\text{MgSO}_4$ ), and the solvent was removed *in vacuo*. The material was purified by chromatography on silica gel with 30% EtOAc/hexane to provide 72 mg (48%) of **23** as a syrup which readily crystallized: mp 95  $^\circ\text{C}$ ; IR ( $\text{CHCl}_3$ ) 3372, 1724, 1690  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  -0.06 s, 1H), -0.02 (s, 1H), 0.00 (s, 2H), 0.03 (s, 2H), 0.84 (s, 9H), 1.78 (m, 1H), 1.86 (dd,  $J = 13.9, 7.8$  Hz, 1H), 2.07 (m, 1H), 2.37 (m, 2H), 2.44 (m, 1H), 2.66 (dt,  $J = 12.5, 8.2$  Hz,

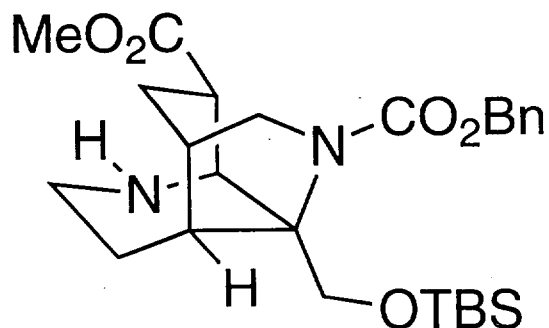
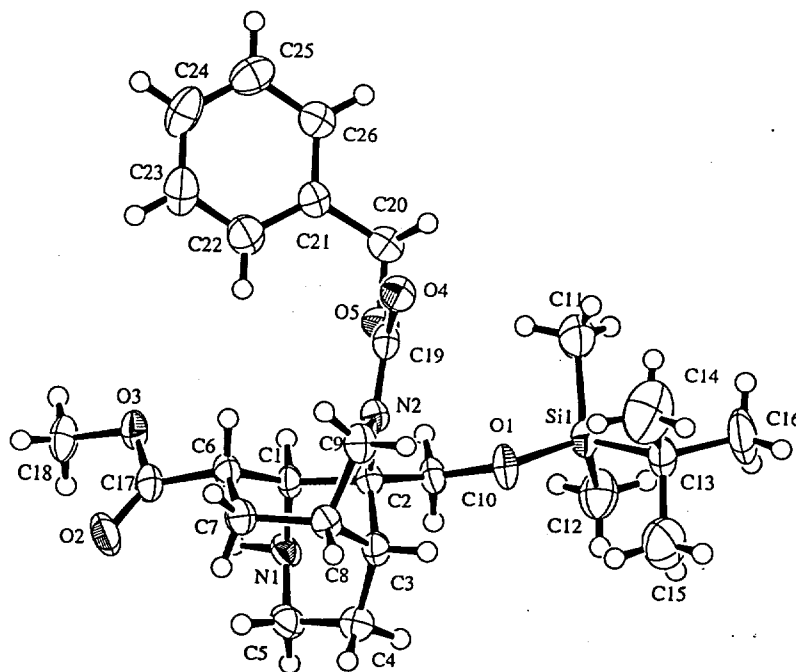
1H), 2.81 (ddd,  $J = 11.2, 7.4, 4.8$  Hz, 1H), 3.16 (tt,  $J = 12.6, 5.0$  Hz, 1H), 3.34 (d,  $J = 10.2$  Hz, 1H), 3.37-3.55 (m, 2H), 3.63 (d,  $J = 4.8$  Hz, 1H), (2 singlets totalling 3H at 3.70, 3.71), 4.16 (d,  $J = 6.0$  Hz, 1H), 4.21 (d,  $J = 10.3$  Hz, 1H), 4.50 (d,  $J = 10.3$  Hz, 1H), 4.88-5.27 (m, 3H), 7.25-7.37 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  -5.5(2C), 18.0, 18.1, 22.7, 22.9, 25.8(2C), 30.5, 30.7, 35.4, 36.5, 36.9, 38.7, 38.9, 42.9, 43.0, 51.7(2C), 52.3, 53.6, 54.3, 54.8, 59.6, 60.9, 63.8, 64.2, 66.1, 67.0, 127.7(2C), 127.9(2C), 128.4(2C), 136.7, 137.1, 153.4, 154.9, 174.6, 174.8; MS (FAB) 489 (M+H); Anal. Calcd for  $\text{C}_{26}\text{H}_{40}\text{N}_2\text{SiO}_5$ : C, 63.90; H, 8.25; N, 5.73. Found: C, 63.51; H, 8.15; N, 5.51.

**X-ray structure of compound 23:**

The compound crystallizes as a racemic mixture in the triclinic space group  $P\bar{1}$  with a single molecule in the asymmetric unit. The connectivity and relative chirality of the five chiral centers in the compound were the same as the predicted structure. There were no apparent unusual bond lengths or angles in the structure.

All hydrogen atoms were placed in predicted positions except for the amine proton H(1). This hydrogen was assigned to the largest peak in the Fourier map after all other hydrogens had been assigned. None of the hydrogen positions were refined.

A relatively weak hydrogen bond from the amine hydrogen H(1) to the benzyl ester carbonyl oxygen O(4) links molecules of the same chirality into infinite chains along the *a* axis. (See figure). The O(4)-N(1) and O(4)-H(1) distances are 3.108(4) Å and 2.033 Å respectively. The N(1)-H(1)-O(4) angle is 161.4°.

**23**

*Experimental*Data Collection

A fragment of a colorless plate shaped crystal of  $C_{26}N_2SiO_5H_{40}$  having approximate dimensions of 0.40 x 0.22 x 0.18 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on an Siemens SMART<sup>10</sup> diffractometer with graphite monochromated Mo-K $\alpha$  radiation.

Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 3159 reflections with  $I > 10\sigma$  in the range  $3.00 < 2\theta < 45.00^\circ$  corresponded to a primitive triclinic cell with dimensions:

$$\begin{aligned} a &= 8.1689(2) \text{ \AA} & \alpha &= 99.215(1)^\circ \\ b &= 11.5150(3) \text{ \AA} & \beta &= 104.032(1)^\circ \\ c &= 15.1496(1) \text{ \AA} & \gamma &= 97.506(1)^\circ \\ V &= 1343.14(5) \text{ \AA}^3 \end{aligned}$$

For  $Z = 2$  and F.W. = 488.70, the calculated density is 1.21 g/cm<sup>3</sup>. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$$P\bar{1} (\#2)$$

The data were collected at a temperature of  $-90 \pm 1^\circ\text{C}$ . Frames corresponding to an arbitrary hemisphere of data were collected using  $\omega$  scans of  $0.30^\circ$  counted for a total of 10 seconds each.

Data Reduction

Data were integrated using the program SAINT<sup>11</sup> with box parameters of 1.6 x 1.6 x 0.6 to a maximum  $2\theta$  value of  $52.3^\circ$ . No decay correction was applied. The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on comparison of redundant and equivalent data was applied using the program SADABS<sup>13</sup> ( $T_{\max} = 0.928$ ,  $T_{\min} = 0.486$ ). The 7173 integrated and corrected reflections were averaged to yield 4528 unique data ( $R_{\text{int}} = 0.032$ ).

Structure Solution and Refinement

The structure was solved by direct methods<sup>1</sup> and expanded using Fourier techniques<sup>2</sup>. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement<sup>3</sup> was based on 2564 observed reflections ( $I > 3.00\sigma(I)$ ) and 307 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.052$$

$$R_w = \sqrt{(\Sigma w(|Fo| - |Fc|)^2 / \Sigma w Fo^2)} = 0.057$$

The standard deviation of an observation of unit weight<sup>4</sup> was 1.52. The weighting scheme was based on counting statistics and included a factor ( $p = 0.030$ ) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.24 and -0.38 e<sup>-</sup>/Å<sup>3</sup>, respectively.

Neutral atom scattering factors were taken from Cromer and Waber<sup>5</sup>. Anomalous dispersion effects were included in Fcalc<sup>6</sup>; the values for  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley<sup>7</sup>. The values for the mass attenuation coefficients are those of Creagh and Hubbel<sup>8</sup>. All calculations were performed using the teXsan<sup>9</sup> crystallographic software package of Molecular Structure Corporation.

#### References

(1) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G. (1994). J. Appl. Cryst., in preparation.

(2) DIRDIF92: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., Garcia-Granda, S., Gould, R.O., Smits, J.M.M. and Smykalla, C. (1992). The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized:  $\sum w(|Fo| - |Fc|)^2$

where  $w = \frac{1}{\sigma^2(Fo)} = \frac{4Fo^2}{\sigma^2(Fo^2)}$

(4) Standard deviation of an observation of unit weight:

$$\sqrt{\sum w(|Fo| - |Fc|)^2 / (No - Nv)}$$

where: No = number of observations

Nv = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

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(7) Creagh, D. C. & McAuley, W.J. ; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

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(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

(10) SMART Area-Detector Software Package; Siemens Industrial Automation, Inc.: Madison, WI, (1995)



(11) SAINT: SAX Area-Dectector Integration Program; V4.024; Siemens Industrial Automation, Inc.: Madison, WI, (1995)

(12) XPREP (v 5.03) Part of the SHELXTL Crystal Structure Determination Package; Siemens Industrial Automation, Inc.: Madison, WI, (1995)

(13) SADABS - Siemens Area Detector ABSorption correction program, George Sheldrick, (1996). Advance copy, private communication.

## EXPERIMENTAL DETAILS

## A. Crystal Data

Empirical Formula	$C_{26}N_2SiO_5H_{40}$
Formula Weight	488.70
Crystal Color, Habit	colorless, plate
Crystal Dimensions	0.40 X 0.22 X 0.18 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination ( $2\theta$ range)	3159 ( 3.0 - 45.0° )
Lattice Parameters	$a = 8.1689(2) \text{ \AA}$ $b = 11.5150(3) \text{ \AA}$ $c = 15.1496(1) \text{ \AA}$ $\alpha = 99.215(1)^\circ$ $\beta = 104.032(1)^\circ$ $\gamma = 97.506(1)^\circ$ $V = 1343.14(5) \text{ \AA}^3$
Space Group	$P\bar{1}$ (#2)
Z value	2
$D_{calc}$	1.208 g/cm <sup>3</sup>
$F_{000}$	528.00
$\mu(MoK\alpha)$	1.24 cm <sup>-1</sup>

## B. Intensity Measurements

Diffractometer	SMART
Radiation	MoK $\alpha$ ( $\lambda = 0.71069 \text{ \AA}$ ) graphite monochromated
Crystal to Detector Distance	60 mm

Temperature	-90°C
Scan Type	$\omega(0.3^\circ/\text{frame})$
Scan Rate	10.0 sec./frame
$2\theta_{\text{max}}$	52.3°
No. of Reflections Measured	Total: 7173 Unique: 4528 ( $R_{\text{int}} = 0.032$ )
Corrections	Lorentz-polarization  Absorption ( $T_{\text{max}} = 0.928$ , $T_{\text{min}} = 0.486$ )

## C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w( F_o  -  F_c )^2$
Least Squares Weights	$\frac{1}{\sigma^2(F_o)} = \frac{4F_o^2}{\sigma^2(F_o^2)}$
p-factor	0.030
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ( $I > 3.00\sigma(I)$ )	2564
No. Variables	307
Reflection/Parameter Ratio	8.35
Residuals: R; Rw; Rall	0.052 ; 0.057 ; 0.105
Goodness of Fit Indicator	1.52
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	$0.24 \text{ e}^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	$-0.38 \text{ e}^-/\text{\AA}^3$

Table 1. Atomic coordinates and  $B_{iso}/B_{eq}$ 

atom	x	y	z	$B_{eq}$
Si(1)	0.5171(1)	0.48658(9)	0.74016(8)	2.64(3)
O(1)	0.5797(3)	0.3811(2)	0.7941(2)	2.82(7)
O(2)	0.9910(4)	-0.1167(2)	0.8527(2)	3.94(8)
O(3)	0.8603(3)	-0.1179(2)	0.7039(2)	3.17(7)
O(4)	0.2325(3)	0.0685(2)	0.7133(2)	3.31(7)
O(5)	0.4406(3)	0.1213(2)	0.6447(2)	2.81(6)
N(1)	0.9754(4)	0.1734(3)	0.8111(2)	2.65(7)
N(2)	0.5072(4)	0.1373(2)	0.7984(2)	2.15(7)
C(1)	0.7972(5)	0.1113(3)	0.7820(2)	2.26(8)
C(2)	0.6863(4)	0.1985(3)	0.8144(2)	2.05(8)
C(3)	0.7448(5)	0.2304(3)	0.9203(2)	2.31(9)
C(4)	0.9381(5)	0.2733(3)	0.9592(3)	3.30(10)
C(5)	1.0490(5)	0.2032(3)	0.9120(3)	3.03(10)
C(6)	0.7570(5)	-0.0078(3)	0.8161(2)	2.10(8)
C(7)	0.7457(5)	0.0090(3)	0.9167(3)	2.48(9)
C(8)	0.6623(5)	0.1162(3)	0.9437(2)	2.59(9)
C(9)	0.4792(5)	0.1014(3)	0.8833(3)	2.65(10)
C(10)	0.6965(5)	0.3082(3)	0.7697(3)	2.57(9)
C(11)	0.3737(6)	0.4183(4)	0.6227(3)	4.9(1)
C(12)	0.7028(6)	0.5826(4)	0.7253(3)	4.2(1)
C(13)	0.4050(5)	0.5701(3)	0.8172(3)	2.8(1)
C(14)	0.2562(7)	0.4879(5)	0.8308(4)	6.6(2)
C(15)	0.5369(7)	0.6219(5)	0.9119(3)	6.0(2)
C(16)	0.3409(7)	0.6754(4)	0.7785(3)	5.4(2)
C(17)	0.8829(5)	-0.0865(3)	0.7961(3)	2.95(10)
C(18)	0.9818(5)	-0.1861(4)	0.6742(3)	3.6(1)
C(19)	0.3820(5)	0.1076(3)	0.7196(3)	2.54(9)
C(20)	0.3168(5)	0.0823(4)	0.5566(3)	2.62(10)
C(21)	0.2725(5)	-0.0517(3)	0.5250(3)	2.67(9)
C(22)	0.3676(6)	-0.1268(4)	0.5688(3)	4.0(1)
C(23)	0.3226(7)	-0.2501(4)	0.5372(3)	4.3(1)
C(24)	0.1854(7)	-0.2982(4)	0.4616(3)	4.4(1)
C(25)	0.0918(6)	-0.2228(4)	0.4165(3)	4.1(1)
C(26)	0.1358(5)	-0.1000(4)	0.4487(3)	2.8(1)

Table 1. Atomic coordinates and  $B_{iso}/B_{eq}$  (continued)

atom	x	y	z	$B_{eq}$
H(1)	1.0489	0.1177	0.7738	4.4122
H(2)	0.7630	0.0935	0.7160	2.7137
H(3)	0.6893	0.2932	0.9401	2.7743
H(4)	0.9629	0.3542	0.9534	3.9554
H(5)	0.9680	0.2687	1.0230	3.9554
H(6)	1.0572	0.1314	0.9349	3.6404
H(7)	1.1602	0.2499	0.9258	3.6404
H(8)	0.6471	-0.0475	0.7782	2.5231
H(9)	0.8584	0.0209	0.9567	2.9795
H(10)	0.6798	-0.0612	0.9242	2.9795
H(11)	0.6651	0.1281	1.0077	3.1100
H(12)	0.4218	0.0209	0.8709	3.1756
H(13)	0.4156	0.1523	0.9115	3.1756
H(14)	0.6676	0.2832	0.7041	3.0865
H(15)	0.8098	0.3528	0.7912	3.0865
H(16)	0.4118	0.3487	0.5983	5.9273
H(17)	0.2599	0.3973	0.6270	5.9273
H(18)	0.3763	0.4741	0.5829	5.9273
H(19)	0.7565	0.5369	0.6865	5.0460
H(20)	0.7823	0.6142	0.7842	5.0460
H(21)	0.6657	0.6464	0.6976	5.0460
H(22)	0.1696	0.4627	0.7736	7.9169
H(23)	0.2950	0.4201	0.8513	7.9169
H(24)	0.2104	0.5295	0.8760	7.9169
H(25)	0.5823	0.5588	0.9371	7.2575
H(26)	0.4823	0.6624	0.9531	7.2575
H(27)	0.6272	0.6764	0.9037	7.2575
H(28)	0.2933	0.7195	0.8216	6.4580
H(29)	0.2556	0.6464	0.7213	6.4580
H(30)	0.4339	0.7258	0.7688	6.4580
H(31)	1.0937	-0.1392	0.6959	4.3421
H(32)	0.9804	-0.2568	0.6990	4.3421
H(33)	0.9509	-0.2068	0.6084	4.3421
H(34)	0.2149	0.1117	0.5606	3.1392
H(35)	0.3611	0.1150	0.5116	3.1392
H(36)	0.4638	-0.0945	0.6206	4.7729
H(37)	0.3875	-0.3015	0.5682	5.1100
H(38)	0.1550	-0.3823	0.4405	5.2474
H(39)	-0.0024	-0.2551	0.3636	4.8619
H(40)	0.0708	-0.0486	0.4177	3.3626

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Si(1)	0.0400(7)	0.0269(6)	0.0464(7)	0.0118(5)	0.0161(6)	0.0122(5)
O(1)	0.047(2)	0.034(2)	0.052(2)	0.024(1)	0.027(1)	0.020(1)
O(2)	0.059(2)	0.055(2)	0.051(2)	0.038(2)	0.008(2)	0.013(2)
O(3)	0.048(2)	0.036(2)	0.044(2)	0.023(1)	0.020(1)	0.009(1)
O(4)	0.029(2)	0.042(2)	0.049(2)	0.005(1)	0.016(1)	0.008(1)
O(5)	0.030(2)	0.046(2)	0.034(2)	0.005(1)	0.010(1)	0.009(1)
N(1)	0.023(2)	0.035(2)	0.041(2)	0.009(1)	0.008(2)	0.010(2)
N(2)	0.027(2)	0.029(2)	0.033(2)	0.007(1)	0.013(2)	0.009(1)
C(1)	0.031(2)	0.026(2)	0.031(2)	0.013(2)	0.011(2)	0.006(2)
C(2)	0.026(2)	0.025(2)	0.031(2)	0.007(2)	0.010(2)	0.008(2)
C(3)	0.034(2)	0.030(2)	0.032(2)	0.012(2)	0.011(2)	0.007(2)
C(4)	0.040(3)	0.039(3)	0.039(2)	0.010(2)	0.009(2)	0.005(2)
C(5)	0.028(2)	0.038(3)	0.051(3)	0.005(2)	0.005(2)	0.012(2)
C(6)	0.028(2)	0.025(2)	0.034(2)	0.007(2)	0.009(2)	0.009(2)
C(7)	0.039(2)	0.033(2)	0.039(2)	0.010(2)	0.014(2)	0.013(2)
C(8)	0.037(2)	0.038(2)	0.027(2)	0.014(2)	0.013(2)	0.008(2)
C(9)	0.041(3)	0.040(2)	0.041(2)	0.013(2)	0.023(2)	0.012(2)
C(10)	0.027(2)	0.028(2)	0.045(2)	0.011(2)	0.013(2)	0.012(2)
C(11)	0.074(4)	0.049(3)	0.061(3)	0.024(3)	0.010(3)	0.011(2)
C(12)	0.063(3)	0.044(3)	0.081(4)	0.011(2)	0.033(3)	0.020(3)
C(13)	0.051(3)	0.036(2)	0.045(3)	0.022(2)	0.018(2)	0.009(2)
C(14)	0.083(4)	0.079(4)	0.130(5)	0.014(3)	0.069(4)	0.013(4)
C(15)	0.097(4)	0.082(4)	0.057(3)	0.040(3)	0.025(3)	0.004(3)
C(16)	0.101(4)	0.069(4)	0.075(4)	0.064(3)	0.027(3)	0.018(3)
C(17)	0.040(3)	0.025(2)	0.046(3)	0.010(2)	0.015(2)	0.013(2)
C(18)	0.051(3)	0.037(3)	0.067(3)	0.021(2)	0.034(2)	0.009(2)
C(19)	0.034(2)	0.024(2)	0.041(3)	0.009(2)	0.015(2)	0.009(2)
C(20)	0.033(2)	0.045(3)	0.037(2)	0.008(2)	0.012(2)	0.012(2)
C(21)	0.036(2)	0.039(2)	0.031(2)	0.012(2)	0.017(2)	0.010(2)
C(22)	0.055(3)	0.053(3)	0.037(2)	0.020(2)	0.014(2)	0.007(2)
C(23)	0.081(4)	0.048(3)	0.050(3)	0.028(3)	0.028(3)	0.016(2)
C(24)	0.090(4)	0.038(3)	0.050(3)	0.013(3)	0.037(3)	0.002(2)
C(25)	0.054(3)	0.052(3)	0.042(3)	-0.001(2)	0.018(2)	-0.002(2)
C(26)	0.036(2)	0.048(3)	0.036(2)	0.010(2)	0.015(2)	0.009(2)

The general temperature factor expression:

$$\exp(-2\pi^2(a^*U_{11}h^2 + b^*U_{22}k^2 + c^*U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Si(1)	O(1)	1.638(2)	Si(1)	C(11)	1.859(5)
Si(1)	C(12)	1.839(4)	Si(1)	C(13)	1.874(4)
O(1)	C(10)	1.426(4)	O(2)	C(17)	1.202(4)
O(3)	C(17)	1.345(4)	O(3)	C(18)	1.453(4)
O(4)	C(19)	1.220(4)	O(5)	C(19)	1.357(4)
O(5)	C(20)	1.428(4)	N(1)	C(1)	1.462(4)
N(1)	C(5)	1.466(4)	N(2)	C(2)	1.483(4)
N(2)	C(9)	1.472(4)	N(2)	C(19)	1.332(4)
C(1)	C(2)	1.538(4)	C(1)	C(6)	1.564(4)
C(2)	C(3)	1.527(5)	C(2)	C(10)	1.527(4)
C(3)	C(4)	1.528(5)	C(3)	C(8)	1.530(5)
C(4)	C(5)	1.518(5)	C(6)	C(7)	1.532(5)
C(6)	C(17)	1.509(5)	C(7)	C(8)	1.533(5)
C(8)	C(9)	1.525(5)	C(13)	C(14)	1.517(6)
C(13)	C(15)	1.544(6)	C(13)	C(16)	1.527(5)
C(20)	C(21)	1.509(5)	C(21)	C(22)	1.379(5)
C(21)	C(26)	1.378(5)	C(22)	C(23)	1.393(6)
C(23)	C(24)	1.373(6)	C(24)	C(25)	1.383(6)
C(25)	C(26)	1.389(5)			

Table 4. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
N(1)	H(1)	1.11	C(1)	H(2)	0.95
C(3)	H(3)	0.95	C(4)	H(4)	0.95
C(4)	H(5)	0.95	C(5)	H(6)	0.95
C(5)	H(7)	0.95	C(6)	H(8)	0.95
C(7)	H(9)	0.95	C(7)	H(10)	0.95
C(8)	H(11)	0.95	C(9)	H(12)	0.95
C(9)	H(13)	0.95	C(10)	H(14)	0.95
C(10)	H(15)	0.95	C(11)	H(16)	0.95
C(11)	H(17)	0.95	C(11)	H(18)	0.95
C(12)	H(19)	0.95	C(12)	H(20)	0.95
C(12)	H(21)	0.95	C(14)	H(22)	0.95
C(14)	H(23)	0.95	C(14)	H(24)	0.95
C(15)	H(25)	0.95	C(15)	H(26)	0.95
C(15)	H(27)	0.95	C(16)	H(28)	0.95
C(16)	H(29)	0.95	C(16)	H(30)	0.95
C(18)	H(31)	0.95	C(18)	H(32)	0.95
C(18)	H(33)	0.95	C(20)	H(34)	0.95
C(20)	H(35)	0.95	C(22)	H(36)	0.95
C(23)	H(37)	0.95	C(24)	H(38)	0.95
C(25)	H(39)	0.95	C(26)	H(40)	0.95

Table 5. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	Si(1)	C(11)	109.6(2)	O(1)	Si(1)	C(12)	110.3(2)
O(1)	Si(1)	C(13)	104.2(1)	C(11)	Si(1)	C(12)	107.8(2)
C(11)	Si(1)	C(13)	112.8(2)	C(12)	Si(1)	C(13)	112.1(2)
Si(1)	O(1)	C(10)	124.1(2)	C(17)	O(3)	C(18)	116.5(3)
C(19)	O(5)	C(20)	115.6(3)	C(1)	N(1)	C(5)	114.0(3)
C(2)	N(2)	C(9)	111.1(3)	C(2)	N(2)	C(19)	128.7(3)
C(9)	N(2)	C(19)	120.0(3)	N(1)	C(1)	C(2)	108.0(3)
N(1)	C(1)	C(6)	117.3(3)	C(2)	C(1)	C(6)	108.6(3)
N(2)	C(2)	C(1)	111.1(3)	N(2)	C(2)	C(3)	101.2(3)
N(2)	C(2)	C(10)	112.4(3)	C(1)	C(2)	C(3)	107.6(3)
C(1)	C(2)	C(10)	111.2(3)	C(3)	C(2)	C(10)	112.8(3)
C(2)	C(3)	C(4)	113.5(3)	C(2)	C(3)	C(8)	100.3(3)
C(4)	C(3)	C(8)	119.0(3)	C(3)	C(4)	C(5)	115.4(3)
N(1)	C(5)	C(4)	111.0(3)	C(1)	C(6)	C(7)	114.5(3)
C(1)	C(6)	C(17)	108.5(3)	C(7)	C(6)	C(17)	113.6(3)
C(6)	C(7)	C(8)	112.7(3)	C(3)	C(8)	C(7)	112.1(3)
C(3)	C(8)	C(9)	100.7(3)	C(7)	C(8)	C(9)	111.3(3)
N(2)	C(9)	C(8)	101.8(3)	O(1)	C(10)	C(2)	109.6(3)
Si(1)	C(13)	C(14)	111.0(3)	Si(1)	C(13)	C(15)	107.7(3)
Si(1)	C(13)	C(16)	111.6(3)	C(14)	C(13)	C(15)	109.5(4)
C(14)	C(13)	C(16)	109.7(4)	C(15)	C(13)	C(16)	107.2(4)
O(2)	C(17)	O(3)	123.5(4)	O(2)	C(17)	C(6)	126.3(4)
O(3)	C(17)	C(6)	110.2(3)	O(4)	C(19)	O(5)	122.9(3)
O(4)	C(19)	N(2)	125.1(3)	O(5)	C(19)	N(2)	112.0(3)
O(5)	C(20)	C(21)	113.9(3)	C(20)	C(21)	C(22)	121.9(4)
C(20)	C(21)	C(26)	118.9(3)	C(22)	C(21)	C(26)	119.2(4)
C(21)	C(22)	C(23)	120.0(4)	C(22)	C(23)	C(24)	120.7(4)
C(23)	C(24)	C(25)	119.3(4)	C(24)	C(25)	C(26)	119.9(4)
C(21)	C(26)	C(25)	120.8(4)				



Table 6. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	N(1)	H(1)	107.1	C(5)	N(1)	H(1)	113.5
N(1)	C(1)	H(2)	107.5	C(2)	C(1)	H(2)	107.5
C(6)	C(1)	H(2)	107.5	C(2)	C(3)	H(3)	107.8
C(4)	C(3)	H(3)	107.8	C(8)	C(3)	H(3)	107.8
C(3)	C(4)	H(4)	108.0	C(3)	C(4)	H(5)	108.0
C(5)	C(4)	H(4)	108.0	C(5)	C(4)	H(5)	108.0
H(4)	C(4)	H(5)	109.5	N(1)	C(5)	H(6)	109.1
N(1)	C(5)	H(7)	109.1	C(4)	C(5)	H(6)	109.1
C(4)	C(5)	H(7)	109.1	H(6)	C(5)	H(7)	109.5
C(1)	C(6)	H(8)	106.6	C(7)	C(6)	H(8)	106.5
C(17)	C(6)	H(8)	106.6	C(6)	C(7)	H(9)	108.7
C(6)	C(7)	H(10)	108.7	C(8)	C(7)	H(9)	108.7
C(8)	C(7)	H(10)	108.7	H(9)	C(7)	H(10)	109.4
C(3)	C(8)	H(11)	110.8	C(7)	C(8)	H(11)	110.8
C(9)	C(8)	H(11)	110.8	N(2)	C(9)	H(12)	111.4
N(2)	C(9)	H(13)	111.4	C(8)	C(9)	H(12)	111.3
C(8)	C(9)	H(13)	111.3	H(12)	C(9)	H(13)	109.5
O(1)	C(10)	H(14)	109.4	O(1)	C(10)	H(15)	109.4
C(2)	C(10)	H(14)	109.4	C(2)	C(10)	H(15)	109.5
H(14)	C(10)	H(15)	109.5	Si(1)	C(11)	H(16)	109.4
Si(1)	C(11)	H(17)	109.5	Si(1)	C(11)	H(18)	109.5
H(16)	C(11)	H(17)	109.5	H(16)	C(11)	H(18)	109.5
H(17)	C(11)	H(18)	109.5	Si(1)	C(12)	H(19)	109.5
Si(1)	C(12)	H(20)	109.5	Si(1)	C(12)	H(21)	109.5
H(19)	C(12)	H(20)	109.5	H(19)	C(12)	H(21)	109.5
H(20)	C(12)	H(21)	109.5	C(13)	C(14)	H(22)	109.4
C(13)	C(14)	H(23)	109.5	C(13)	C(14)	H(24)	109.5
H(22)	C(14)	H(23)	109.5	H(22)	C(14)	H(24)	109.4
H(23)	C(14)	H(24)	109.5	C(13)	C(15)	H(25)	109.5
C(13)	C(15)	H(26)	109.4	C(13)	C(15)	H(27)	109.4
H(25)	C(15)	H(26)	109.5	H(25)	C(15)	H(27)	109.5
H(26)	C(15)	H(27)	109.5	C(13)	C(16)	H(28)	109.4
C(13)	C(16)	H(29)	109.5	C(13)	C(16)	H(30)	109.5
H(28)	C(16)	H(29)	109.5	H(28)	C(16)	H(30)	109.5
H(29)	C(16)	H(30)	109.5	O(3)	C(18)	H(31)	109.5
O(3)	C(18)	H(32)	109.5	O(3)	C(18)	H(33)	109.5
H(31)	C(18)	H(32)	109.5	H(31)	C(18)	H(33)	109.5
H(32)	C(18)	H(33)	109.5	O(5)	C(20)	H(34)	108.4
O(5)	C(20)	H(35)	108.4	C(21)	C(20)	H(34)	108.3
C(21)	C(20)	H(35)	108.4	H(34)	C(20)	H(35)	109.5
C(21)	C(22)	H(36)	120.0	C(23)	C(22)	H(36)	120.0
C(22)	C(23)	H(37)	119.6	C(24)	C(23)	H(37)	119.6
C(23)	C(24)	H(38)	120.3	C(25)	C(24)	H(38)	120.3
C(24)	C(25)	H(39)	120.1	C(26)	C(25)	H(39)	120.1
C(21)	C(26)	H(40)	119.6	C(25)	C(26)	H(40)	119.6
N(1)	H(1)	O(4)	161.4				

Table 7. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Si(1)	O(1)	C(10)	C(2)	-163.8(2)	O(1)	Si(1)	C(13)	C(14)	-58.8(4)
O(1)	Si(1)	C(13)	C(15)	61.1(3)	O(1)	Si(1)	C(13)	C(16)	178.5(3)
O(1)	C(10)	C(2)	N(2)	49.1(4)	O(1)	C(10)	C(2)	C(1)	174.4(3)
O(1)	C(10)	C(2)	C(3)	-64.6(4)	O(2)	C(17)	O(3)	C(18)	-3.6(5)
O(2)	C(17)	C(6)	C(1)	114.4(4)	O(2)	C(17)	C(6)	C(7)	-14.2(5)
O(3)	C(17)	C(6)	C(1)	-64.4(4)	O(3)	C(17)	C(6)	C(7)	167.0(3)
O(4)	C(19)	O(5)	C(20)	-2.4(5)	O(4)	C(19)	N(2)	C(2)	-171.9(3)
O(4)	C(19)	N(2)	C(9)	12.5(5)	O(5)	C(19)	N(2)	C(2)	10.6(5)
O(5)	C(19)	N(2)	C(9)	-165.0(3)	O(5)	C(20)	C(21)	C(22)	-11.9(5)
O(5)	C(20)	C(21)	C(26)	169.9(3)	N(1)	C(1)	C(2)	N(2)	-172.5(3)
N(1)	C(1)	C(2)	C(3)	-62.6(3)	N(1)	C(1)	C(2)	C(10)	61.5(4)
N(1)	C(1)	C(6)	C(7)	78.6(4)	N(1)	C(1)	C(6)	C(17)	-49.5(4)
N(1)	C(5)	C(4)	C(3)	40.8(4)	N(2)	C(2)	C(1)	C(6)	-44.4(4)
N(2)	C(2)	C(3)	C(4)	168.5(3)	N(2)	C(2)	C(3)	C(8)	40.4(3)
N(2)	C(9)	C(8)	C(3)	38.8(3)	N(2)	C(9)	C(8)	C(7)	-80.2(3)
N(2)	C(19)	O(5)	C(20)	175.2(3)	C(1)	N(1)	C(5)	C(4)	-54.1(4)
C(1)	C(2)	N(2)	C(9)	97.2(3)	C(1)	C(2)	N(2)	C(19)	-78.7(4)
C(1)	C(2)	C(3)	C(4)	51.8(4)	C(1)	C(2)	C(3)	C(8)	-76.3(3)
C(1)	C(6)	C(7)	C(8)	37.2(4)	C(2)	N(2)	C(9)	C(8)	-13.8(4)
C(2)	C(1)	N(1)	C(5)	66.4(3)	C(2)	C(1)	C(6)	C(7)	-44.1(4)
C(2)	C(1)	C(6)	C(17)	-172.2(3)	C(2)	C(3)	C(4)	C(5)	-42.3(4)
C(2)	C(3)	C(8)	C(7)	68.7(3)	C(2)	C(3)	C(8)	C(9)	-49.7(3)
C(3)	C(2)	N(2)	C(9)	-16.9(3)	C(3)	C(2)	N(2)	C(19)	167.2(3)
C(3)	C(2)	C(1)	C(6)	65.6(3)	C(3)	C(8)	C(7)	C(6)	-51.1(4)
C(4)	C(3)	C(2)	C(10)	-71.2(4)	C(4)	C(3)	C(8)	C(7)	-55.6(4)
C(4)	C(3)	C(8)	C(9)	-174.0(3)	C(5)	N(1)	C(1)	C(6)	-56.6(4)
C(5)	C(4)	C(3)	C(8)	75.3(4)	C(6)	C(1)	C(2)	C(10)	-170.4(3)
C(6)	C(7)	C(8)	C(9)	60.8(4)	C(6)	C(17)	O(3)	C(18)	175.2(3)
C(8)	C(3)	C(2)	C(10)	160.7(3)	C(8)	C(7)	C(6)	C(17)	162.6(3)
C(8)	C(9)	N(2)	C(19)	162.5(3)	C(9)	N(2)	C(2)	C(10)	-137.5(3)
C(10)	O(1)	Si(1)	C(11)	70.5(3)	C(10)	O(1)	Si(1)	C(12)	-48.0(3)
C(10)	O(1)	Si(1)	C(13)	-168.5(3)	C(10)	C(2)	N(2)	C(19)	46.6(5)
C(11)	Si(1)	C(13)	C(14)	60.0(4)	C(11)	Si(1)	C(13)	C(15)	179.9(3)
C(11)	Si(1)	C(13)	C(16)	-62.6(4)	C(12)	Si(1)	C(13)	C(14)	-178.1(3)
C(12)	Si(1)	C(13)	C(15)	-58.2(3)	C(12)	Si(1)	C(13)	C(16)	59.2(4)
C(19)	O(5)	C(20)	C(21)	-74.9(4)	C(20)	C(21)	C(22)	C(23)	-179.8(4)
C(20)	C(21)	C(26)	C(25)	179.2(3)	C(21)	C(22)	C(23)	C(24)	1.0(7)
C(21)	C(26)	C(25)	C(24)	0.3(6)	C(22)	C(21)	C(26)	C(25)	0.9(6)
C(22)	C(23)	C(24)	C(25)	0.3(7)	C(23)	C(22)	C(21)	C(26)	-1.5(6)
C(23)	C(24)	C(25)	C(26)	-0.9(7)					

Table 8. Non-bonded Contacts out to 3.80 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
O(2)	C(7)	3.555(5)	75702	O(2)	C(4)	3.582(4)	75702
O(2)	C(8)	3.645(4)	75702	O(3)	O(4)	3.444(4)	65501
O(3)	C(12)	3.612(5)	54501	O(3)	C(26)	3.676(4)	65602
O(4)	N(1)	3.108(4)	45501	O(4)	C(18)	3.229(5)	45501
O(4)	C(26)	3.492(5)	55602	O(4)	C(25)	3.724(5)	55602
O(4)	C(17)	3.747(4)	45501	N(1)	C(25)	3.508(5)	65602
N(1)	C(26)	3.745(5)	65602	C(1)	C(26)	3.651(5)	65602
C(1)	C(25)	3.710(5)	65602	C(10)	C(25)	3.720(6)	65602
C(12)	C(18)	3.580(6)	56501	C(12)	C(17)	3.780(5)	56501
C(16)	C(18)	3.664(6)	46501	C(20)	C(22)	3.586(5)	65602
C(20)	C(26)	3.711(5)	55602				

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one-digit numbers and one two-digit number: TA (first digit) + TB (second digit) + TC (third digit) + SN (last two digits). TA, TB and TC are the crystal lattice translation digits along cell edges a, b and c. A translation digit of 5 indicates the origin unit cell. If TA = 4, this indicates a translation of one unit cell length along the a-axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus  $\pm 4$  lattice translations from the origin (TA=5, TB=5, TC=5) can be represented.

The SN, or symmetry operator number, refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of symmetry operators relevant to this structure are given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of the atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through symmetry operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (eg. cation and anion) that reside in the same asymmetric unit.

## Symmetry Operators:

(1) X, Y, Z (2) -X, -Y, -Z