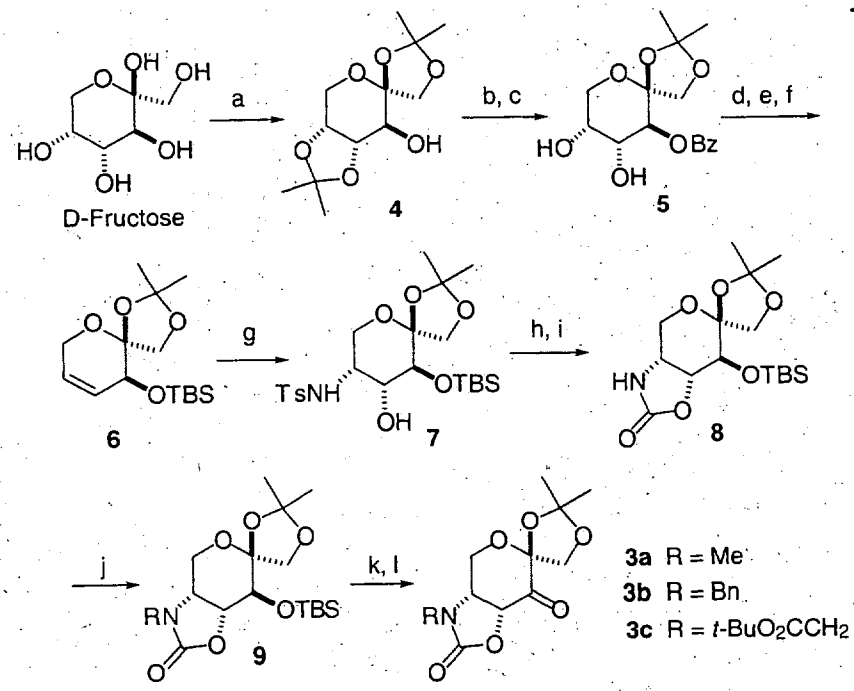

Reaction Conditions: **a**: 2,2-dimethoxypropane, acetone, $HClO_4$, 0 °C, 53%. **b**: PhCOCl, Et_3N, CH_2Cl_2, rt, 93%. **c**: DDQ (0.1 eq.), CH_3CN-H_2O, rt, 24 h, 92%. **d**: PPh_3, imidazole, I_2, Zn, 79%. **e**: K_2CO_3, MeOH, rt, 12 h, 68%. **f**: TBSCl, Et_3N, DMAP, CH_2Cl_2, rt, 24 h, 100%. **g**: $K_2OsO_6H_4$, chloramine-T trihydrate, CH_3CN-H_2O, rt, overnight, 91%. **h**: triphosgene, pyridine, CH_2Cl_2, 0 °C, 84%. **i**: Li, NH_3(l), THF, -78 °C, overnight, 64%. **j**: (i) for **9a** NaH, MeI, THF, rt, 2 h, 93%; (ii) for **9b** NaH, BnBr, THF, rt, 2 h, 70%; (iii) for **9c** NaH, t-BuO_2CCH_2Br, THF, rt, 96%. **k**: TBAF, THF, rt, 91-96% **l**: PCC, 3 Å MS, CH_2Cl_2, rt, 3-12 h, 73-93%.

Preparation of Compound 7. To a solution of alcohol **4**[1] (2.6 g, 10.0 mmol) in CH_2Cl_2 (15 mL) were added Et_3N (5.0 mL, 30.0 mmol) and PhCOCl (1.7 g, 12.0 mmol). Upon stirring at rt until no starting material was left as judged by TLC, the reaction mixture was poured into water, extracted with Et_2O, washed with brine, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give the benzoate as a colorless oil (3.39 g, 93 %). ^{1}H NMR ($CDCl_3$, 300Mz) δ 8.11-8.08 (m, 2H), 7.60-7.54 (m, 1H), 7.47-7.42 (m, 2H), 5.39 (d, J = 7.8 Hz, 1H), 4.46 (dd, J = 7.8, 5.1 Hz, 1H), 4.29 (dd, J = 5.1, 2.4 Hz, 1H), 4.21 (dd, J = 13.2, 2.4 Hz, 1H), 4.14 (d, J = 13.2 Hz, 1H), 4.01 (d, J = 9.2 Hz, 1H), 3.90 (d, J = 9.2 Hz, 1H), 1.61 (s, 3H), 1.51 (s, 3H), 1.41 (s, 3H), 1.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.1, 133.5, 130.0, 129.6, 128.6, 112.3, 109.8, 104.0, 75.2, 73.9, 71.8, 70.7, 60.6, 28.0, 26.6, 26.5, 26.3.

To a solution of the above benzoate (0.364 g, 1.0 mmol) in CH_3CN/H_2O (3.4 mL, 10/1) was added DDQ (0.23 g, 0.10 mmol).[2] Upon stirring at rt for 24 h, the reaction mixture was concentrated and purified by flash chromatography to give diol **5** as a colorless oil (0.297 g, 92%). IR (KBr, film) 3465, 1718, 1700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.11-8.08 (m, 2H), 7.60-7.54 (m, 1H), 7.47-7.42 (m, 2H), 5.40 (d, J = 9.9 Hz, 1H), 4.18-3.83 (m, 6H), 3.10-2.68 (br s, 2H), 1.52 (s, 3H), 1.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.7, 133.8, 130.2, 129.4, 128.7, 112.3, 104.7, 72.2, 71.4, 70.4, 69.8, 64.2, 26.7, 26.6.

To a refluxing mixture of diol **5** (2.5 g, 7.72 mmol), PPh_3 (7.69 g, 29.32 mmol), imidazole (3.78 g, 55.56 mmol) and zinc (0.031 g) in toluene (37 mL) was added I_2 (3.92 g, 15.43 mmol) over 45 min.[2] After the reaction mixture was stirred at reflux for 1 h, another batch of zinc (0.031 g) was added. Upon stirring for an additional 3.5 h, the reaction mixture was cooled, filtered, concentrated, and purified by flash chromatography to give the olefin as a colorless oil (1.77 g, 79%). ^1H NMR ($CDCl_3$, 300 MHz) δ 8.12-8.08 (m, 2H), 7.61-7.55 (m, 1H), 7.47-7.42 (m, 2H), 6.01-5.95 (m, 1H), 5.79-5.73 (m, 2H), 4.51-4.43 (m, 1H), 4.25-4.18 (m, 1H), 4.04 (m, 2H), 1.60 (s, 3H), 1.50 (s, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 166.3, 133.4, 129.9, 129.7, 128.7, 128.6, 123.6, 112.1, 101.6, 72.1, 65.9, 61.7, 27.0, 26.3.

To a solution of the above olefin (24.56 g, 84.69 mmol) in methanol (423 mL) was added K_2CO_3 (23.41 g, 169.0 mmol). Upon stirring at rt for 12h, the reaction mixture was filtered, concentrated, and purified by flash chromatography to give the alcohol as a colorless oil (10.78 g, 68%). $[\alpha]^{20}_D$ = -71.6 (*c* 0.75, $CHCl_3$); IR (KBr, film) 3443, 1221, 1057, cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.87-5.81 (m, 1H), 5.76-5.71 (m, 1H), 4.36-4.27 (m, 1H), 4.17 (d, J = 8.4 Hz, 1H), 4.15-4.06 (m, 2H), 4.01 (d, J = 8.4 Hz, 1H), 2.10 (s, 1H), 1.54 (s, 3H), 1.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 127.3, 127.0, 111.9, 103.1, 72.3, 64.0, 61.4, 27.1, 26.3.

To a solution of the above alcohol (0.052 g, 0.28 mmol) in CH_2Cl_2 (1.5 mL) were added Et_3N (0.283 g, 2.8 mmol), DMAP (0.0034 g, 0.028 mmol), and TBDMSCl (0.063 g, 0.42 mmol) at rt. Upon stirring at rt for 24 h, the reaction mixture was quenched with water, extracted with Et_2O, washed with brine, dried (Na_2SO_4), filtered, concentrated, and purified by flash

chromatography to give compound **6** as a colorless oil (0.084 g, 100%). $[\alpha]^{20}_D$ = 2.7 (*c* 0.45, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.75 (m, 1H), 5.62 (m, 1H), 4.35-4.26 (m, 2H), 4.09-4.00 (m, 1H), 4.02 (d, *J* = 8.4 Hz, 1H), 3.89 (d, *J* = 8.4 Hz, 1H), 1.50 (s, 3H), 1.40 (s, 3H), 0.89 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 127.8, 126.8, 112.1, 103.2, 71.8, 65.0, 61.8, 27.5, 26.3, 26.0, 18.2, -4.0, -4.7.

To a solution of **6** (2.16 g, 7.2 mmol) in CH_3CN/H_2O (14 mL, v/v 1/1) were added chloramine-T trihydrate (2.44 g, 8.64 mmol) and $K_2OsO_6H_4$ (0.018 g, 0.036 mmol).[3] After the mixture was stirred at rt overnight, Na_2SO_3 and EtOAc were added. Upon stirring for an additional 1 h, the layers were separated. The organic layer was dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **7** as a white solid (3.09 g, 91%). mp 62-65 °C; $[\alpha]^{20}_D$ = -60.7 (*c* 0.23, $CHCl_3$); IR (KBr, film) 3532, 3271 cm^{-1}; ^1H NMR ($CDCl_3$+D_2O, 300 MHz) δ 7.78-7.75 (m, 2H), 7.34-7.33 (m, 2H), 5.23 (d, *J* = 7.2 Hz, 1H), 4.03 (d, *J* = 8.4 Hz, 1H), 3.88 (d, *J* = 8.4 Hz, 1H), 3.82 (dd, *J* = 12.6, 2.1 Hz, 1H), 3.76 (dd, *J* = 9.5, 4.5 Hz, 1H), 3.54 (d, *J* = 9.5 Hz, 1H), 3.50-3.48 (m, 1H), 3.29 (dd, *J* = 12.6, 2.4 Hz, 1H), 2.43 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H), 0.89 (s, 9H), 0.136 (s, 3H), 0.092 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 130.0, 127.3, 112.2, 105.8, 71.8, 71.1, 70.1, 61.9, 55.1, 27.1, 26.4, 26.1, 21.8, 18.6, -3.6, -4.5; Anal. Calcd for $C_{22}H_{37}NO_7SSi$: C, 54.18; H, 7.65; N, 2.87. Found: C, 53.96; H, 7.66; N, 2.61.

Preparation of compound 8. To a solution of compound **7** (0.50 g, 1.06 mmol) and pyridine (0.84 g, 10.6 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added triphosgene (0.315 g, 1.06 mmol). Upon stirring at 0 °C until no starting material was left as judged by TLC, the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give the carbamate as a white solid (0.442 g, 84%). mp 118-120 °C; $[\alpha]^{20}_D$ = -84.1 (*c* 0.29, $CHCl_3$); IR (KBr, film) 1792, 1373, 1175 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 4.56 (dd, *J* = 7.8, 6.6 Hz, 1H), 4.47 (dd, *J* = 13.2, 1.5 Hz, 1H), 4.42 (m, 1H), 4.25 (dd, *J* = 13.2, 2.4 Hz, 1H), 4.01 (d, *J* =

8.7 Hz, 1H), 3.90 (d, J = 8.7 Hz, 1H), 3.79 (d, J = 6.6 Hz, 1H), 2.45 (s, 3H), 1.49 (s, 3H), 1.42 (s, 3H), 0.89 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.1, 145.9, 134.1, 129.9, 128.6, 112.1, 103.9, 76.0, 72.7, 70.2, 60.0, 57.2, 26.5. 26.4, 25.8, 21.9, 18.2, -4.4, -4.9; Anal. Calcd for $C_{23}H_{35}NO_8SSi$: C, 53.78; H, 6.87; N, 2.73. Found: C, 54.00; H, 7.05; N, 2.60.

To a solution of the above carbamate (26.57 g, 51.79 mmol) in THF (52 mL) and liquid ammonia (450 mL) at -78 °C was added Li (3.60 g, 518.0 mmol). Upon stirring at -78 °C overnight, the reaction mixture was quenched with solid NH_4Cl and warmed to rt. The resulting mixture was diluted with MeOH, filtered, concentrated, and purified by flash chromatography to give compound **8** as a white solid (11.91 g, 64%). mp 124-126 °C; $[\alpha]^{20}_D$ = -114.2 (*c* 0.33 $CHCl_3$); IR (KBr, film) 3255, 1769, 1718, 1125 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.45 (s, 1H, NH), 4.58 (dd, J = 7.2, 6.9 Hz, 1H), 4.13-4.06 (m, 3H), 3.94 (d, J = 8.7, 1H), 3.86 (d, J = 6.9 Hz, 1H), 3.80 (m, 1H), 1.49 (s, 3H), 1.43 (s, 3H), 0.92 (s, 9H), 0.19 (s, 3H), 0.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 159.8, 112.4, 104.3, 78.9, 72.1, 70.3, 60.0, 53.0, 26.8, 26.4, 25.9, 18.3, -4.1, -5.0; Anal. Calcd for $C_{16}H_{29}NO_6Si$: C, 53.46; H, 8.13; N, 3.90. Found: C, 53.49; H, 8.24; N, 3.88.

Preparation of ketone 3a

To a solution of compound **8** (1.077 g, 3.0 mmol) in THF (15 mL) was added NaH (0.18 g, 4.5 mmol) at 0 °C under N_2. After the reaction mixture was stirred at 0 °C for 0.5 h, MeI (1.3 g, 9.0 mmol) was added. Upon stirring at rt for an additional 2 h, the reaction was quenched with water, extracted with EtOAc, washed with brine, dried (Na_2SO_4), filtered, concentrated, purified by flash chromatography to give compound **9a** as a white solid (1.04 g, 93%). mp 116.5-118 °C; $[\alpha]^{20}_D$ = -109.6 (*c* 0.36, $CHCl_3$); IR (KBr, film) 1767 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.51 (dd, J = 7.2, 6.9 Hz, 1H), 4.10 (dd, J = 13.5, 2.7 Hz, 1H), 4.10 (d, J = 9.0 Hz, 1H), 3.91 (d, J = 9.0 Hz, 1H), 3.86 (d, J = 13.5 Hz, 1H), 3.74 (d, J = 6.9 Hz, 1H), 3.70 (dd, J = 7.5, 2.7 Hz, 1H), 2.84 (s, 3H), 1.50 (s, 3H), 1.44 (s, 3H), 0.92 (s, 9H), 0.20 (s, 3H), 0.12 (s, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.4, 112.5, 104.6, 76.2, 72.1, 70.5, 57.7, 57.2, 29.2, 26.9, 26.4, 25.9, 18.3, -4.1, -5.0; Anal. Calcd for $C_{17}H_{31}NO_6Si$: C, 54.66; H, 8.37; N, 3.75. Found: C, 54.87; H, 8.50; N, 3.77.

To a solution of **9a** (0.315 g, 0.845 mmol) in THF (10 mL) was added TBAF (0.85 mL, 0.85 mmol, 1.0 M in THF) at rt under N_2. Upon stirring until no starting material was left as judged by TLC, the reaction mixture was concentrated and purified by flash chromatography to give the alcohol as a white solid (0.199 g, 91%). mp 119-121 °C; $[\alpha]^{20}_D$ = -145.5 (*c* 0.17, $CHCl_3$); IR (KBr, film) 3244, 1765 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.64 (dd, *J* = 7.2, 5.7 Hz, 1H), 4.17 (d, *J* = 9.0 Hz, 1H), 4.10 (dd, *J* = 13.5, 2.1 Hz, 1H), 3.96 (d, *J* = 9.0 Hz, 1H), 3.88 (d, *J* = 13.5 Hz, 1H), 3.81 (d, *J* = 5.7 Hz, 1H), 3.75 (dd, *J* = 7.2, 2.1 Hz, 1H), 3.02 (s, 1H), 2.86 (s, 3H), 1.52 (s, 3H), 1.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.3, 112.2, 103.8, 74.7, 72.7, 69.1, 57.5, 56.7, 29.0, 26.5, 26.4. Anal. Calcd for $C_{11}H_{17}NO_6$: C, 50.96; H, 6.61; N, 5.40. Found: C, 51.16; H, 6.82; N, 5.36.

To a mixture of the above alcohol (0.199 g, 0.77 mmol) and powdered 3 Å MS (0.72 g) in CH_2Cl_2 (3.8 mL) was added PCC (0.385 g, 1.79 mmol) portionwise over 15 min. Upon stirring at rt under N_2 for 3 h, the reaction mixture was filtered through celite and washed with Et_2O. The filtrate was concentrated and purified by flash chromatography to give ketone **3a** as a white solid (0.183 g, 93%). mp 168-169 °C; $[\alpha]^{20}_D$ = -110.1 (*c* 0.32, $CHCl_3$); IR (KBr, film) 3387 (hydrate), 1750 cm^{-1}; **Ketone**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.00 (d, *J* = 7.5 Hz, 1H), 4.50 (d, *J* = 10 Hz, 1H), 4.29 (d, *J* = 13.8 Hz, 1H), 4.17 (d, *J* = 7.5 Hz, 1H), 4.03 (m, 2H), 2.88 (s, 3H), 1.55 (s, 3H), 1.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 194.4, 157.4, 114.4, 104.2, 72.8, 70.9, 61.2, 57.8, 29.1, 26.6, 26.0. **Hydrate**: ^{1}H NMR (CD_3CN-D_2O, v/v 1.5/1, 400 MHz) δ 4.59 (d, *J* = 8.6 Hz, 1H), 4.30 (d, *J* = 9.2 Hz, 1H), 4.00 (d, *J* = 14.0 Hz, 1H), 3.89 (d, *J* = 8.6 Hz, 1H), 3.78 (d, *J* = 14.0 Hz, 1H), 3.72 (d, *J* = 9.2 Hz, 1H), 2.72 (s, 3H), 1.41 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (CD_3CN-D_2O, v/v 1.5/1, 100 MHz) δ 160.3, 113.0, 106.2, 91.4, 75.7, 72.3, 58.5, 57.7, 29.1, 26.4, 26.3. Anal. Calcd for $C_{11}H_{15}NO_6$: C, 51.36; H, 5.88; N, 5.45. Found: C, 51.54; H, 5.83; N, 5.27.

Preparation of ketone 3b

To a solution of **8** (0.718 g, 2.0 mmol) in THF (10 mL) was added NaH (0.12 g, 3.0 mmol) at 0 °C under N_2. After the reaction mixture was stirred at 0 °C for 0.5 h, BnBr (0.513 g, 3 mmol) was added. Upon stirring at rt for another 2 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **9b** as a white solid (0.631 g, 70%). mp 126-128 °C; $[\alpha]^{20}_D$ = -54.8 (*c* 0.16, $CHCl_3$); IR (KBr, film) 1758, 1252, 1123 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.37-7.25 (m, 5H), 4.89 (d, *J* = 15.6 Hz, 1H), 4.47 (dd, *J* = 7.2, 6.9 Hz, 1H), 4.13 (d, *J* = 15.6 Hz, 1H), 4.12 (d, *J* = 9.0 Hz, 1H), 3.97 (dd, *J* = 13.5, 3.0 Hz, 1H), 3.92 (d, *J* = 9.0 Hz, 1H), 3.84 (d, *J* = 13.5 Hz, 1H), 3.79 (d, *J* = 6.9 Hz, 1H), 3.64 (dd, *J* = 7.2, 3.0 Hz, 1H), 1.47 (s, 3H), 1.42 (s, 3H), 0.93 (s, 9H), 0.23 (s, 3H), 0.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.2, 134.9, 129.0, 128.2, 112.4, 104.5, 76.3, 72.0, 70.5, 56.8, 54.6, 46.1, 26.8, 26.3, 25.9, -4.1, -5.0; Anal. Calcd for $C_{23}H_{35}NO_6Si$: C, 61.44; H, 7.85; N, 3.12. Found: C, 61.54; H, 7.67; N, 3.10.

To a solution of **9b** (0.598 g, 1.33 mmol) in THF (15 mL) was added TBAF (1.4 mL, 1.4 mmol, 1.0 M in THF) at rt under N_2. Upon stirring until no starting material was left as judged by TLC, the reaction mixture was concentrated and purified by flash chromatography to give the alcohol as a white solid (0.409 g, 92%). mp 145-146 °C; $[\alpha]^{20}_D$ = -88.1 (*c* 0.13, $CHCl_3$); IR (KBr, film) 3416, 1755 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40-7.28 (m, 5H), 4.89 (d, *J* = 15.3 Hz, 1H), 4.63 (t, *J* = 7.2 Hz, 1H), 4.24 (d, *J* = 9.0 Hz, 1H), 4.19 (d, *J* = 15.3 Hz, 1H), 4.03-3.99 (m, 2H), 3.90-3.85 (m, 2H), 3.71 (dd, *J* = 7.2, 2.0 Hz, 1H), 3.20 (m, 1H), 1.52 (s, 3H), 1.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.3, 134.9, 129.0, 128.1, 112.2, 103.8, 75.1, 72.6, 69.1, 57.2, 54.0, 46.1, 26.4; Anal. Calcd for $C_{17}H_{21}NO_6$: C, 60.89; H, 6.31; N, 4.18. Found: C, 60.66; H, 6.24; N, 4.15.

To a mixture of the above alcohol (0.409 g, 1.22 mmol) and powdered 3Å MS (1.12 g) in CH_2Cl_2 (5.3 mL) was added PCC (0.605 g, 2.807 mmol) portionwise over 15 min. Upon

stirring under N_2 for 3 h, the reaction mixture was filtered through celite and washed with Et_2O. The filtrate was concentrated and purified by flash chromatography to give ketone **3b** as a white solid (0.298 g, 73%). mp 130.0-131.5 °C; $[\alpha]^{20}_D$ = -95.2 (*c* 0.24, $CHCl_3$); IR (KBr, film) 3394 (hydrate), 1754 cm^{-1}; **Hydrate**: ^1H NMR (CD_3CN-D_2O, v/v 1.5/1, 400 MHz) δ 7.30 (m, 5H), 4.58 (d, *J* = 8.4 Hz, 1H), 4.52 (d, *J* = 16.0 Hz, 1H), 4.32 (d, *J* = 9.4 Hz, 1H), 4.24 (d, *J* =16.0 Hz, 1H), 3.92 (d, *J* = 13.2 Hz, 1H), 3.84 (d, *J* = 8.4 Hz, 1H), 3.77 (d, *J* = 9.4 Hz, 1H), 3.68 (d, *J* = 13.2 Hz, 1H), 1.39 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (CD_3CN-D_2O, v/v 1.5/1, 100 MHz) δ 160.1, 136.9, 129.8, 128.8, 128.7, 112.9, 106.2, 91.4, 75.9, 72.3, 58.6, 55.8, 46.4, 26.4, 26.3. Anal. Calcd for $C_{17}H_{19}O_6N$•0.7 H_2O: C, 59.02; H, 5.94; N, 4.05. Found: C, 59.01; H, 6.10; N, 4.00.

Preparation of ketone 3c

To a solution of compound **8** (1.0 g, 2.79 mmol) in THF (20 mL) was added NaH (0.134 g, 3.3 mmol) at 0 °C under N_2. After the reaction mixture was stirred at 0 °C for 0.5 h, $BrCH_2CO_2{}^tBu$ (0.652 g, 3.3 mmol) was added. Upon stirring at rt until no starting material was left as judged by TLC, the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **9c** as a colorless oil (1.26 g, 96%). $[\alpha]^{20}_D$ = -96.0 (*c* 0.93, $CHCl_3$), IR (KBr) 1772, 1739 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.54 (dd, *J* = 7.5, 7.2 Hz, 1H), 4.17 (d, *J* = 18.0 Hz, 1H), 4.13-4.06 (m, 2H), 4.08 (d, *J* = 8.7 Hz, 1H), 3.89 (d, *J* = 8.7 Hz, 1H), 3.77-3.72 (m, 2H), 3.63 (d, *J* = 18.0 Hz, 1H), 1.47 (s, 3H), 1.44 (s, 9H), 1.42 (s, 3H), 0.90 (s, 9H), 0.19 (s, 3H), 0.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.2, 158.2, 112.5, 104.6, 82.9, 76.8, 72.0, 70.4, 57.1, 55.7, 43.8, 28.2, 26.8, 26.3, 25.9, 18.3, -4.0, -5.0; Anal. Calcd for $C_{22}H_{39}NO_8Si$: C, 55.79; H, 8.30; N, 2.96. Found: C, 55.83; H, 8.04; N, 2.89.

To a solution of **9c** (1.2 g, 2.54 mmol) in THF (25 mL) was added TBAF (2.55 mL, 2.55 mmol, 1.0 M in THF). Upon stirring at rt until no starting material was left as judged by TLC, the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered,

concentrated, and purified by flash chromatography to give the alcohol as a white solid (0.876 g, 96%). mp 104.0-106.0 °C; $[\alpha]^{20}_D$ = -128.3 (*c* 0.27, $CHCl_3$); IR (KBr) 3442, 1763, 1738 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.67 (dd, *J* = 7.2, 6.9 Hz, 1H), 4.20 (d, *J* = 18.0 Hz, 1H), 4.17 (d, *J* = 8.7 Hz, 1H), 4.14-4.05 (m, 2H), 3.94 (d, *J* = 8.7 Hz, 1H), 3.81-3.75 (m, 2H), 3.64 (d, *J* = 18.0 Hz, 1H), 1.50 (s, 3H), 1.45 (s, 9H), 1.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.2, 158.2, 112.3, 103.9, 83.0, 75.6, 72.4, 69.0, 57.4, 55.0, 43.8, 28.2, 26.44. 26.39; Anal. Calcd for $C_{16}H_{25}NO_8$: C, 53.47; H, 7.01; N, 3.90. Found: C, 53.57; H, 6.93; N, 3.95.

To a solution of the alcohol (0.85 g, 2.37 mmol) in CH_2Cl_2 (10 mL) were added 3Å MS (2.2 g) and PCC (1.2 g, 5.57 mmol). Upon stirring at rt for 12 h, the reaction mixture was passed through a short silica gel column. The filtrate was concentrated and purified by flash chromatography to give ketone **3c** as a white solid (0.755 g, 89%). mp 175.0-177.0 °C; $[\alpha]^{20}_D$ = -114.8 (*c* 0.27 $CHCl_3$); IR (KBr) 1774, 1736, 1215 cm^{-1}; **Hydrate**: ^1H NMR (CD_3CN-D_2O, v/v 1.5/1, 300 MHz) δ 4.63 (d, *J* = 8.0 Hz, 1H), 4.30 (d, *J* = 9.2 Hz, 1H), 4.03-3.97 (m, 2H), 3.94 (d, *J* = 18.2 Hz, 1H), 3.77 (d, *J* = 9.2 Hz, 1H), 3.76 (d, *J* = 18.2 Hz, 1H), 3.72 (d, *J* = 13.6 Hz, 1H), 1.41 (s, 3H), 1.39 (s, 9H), 1.36 (s, 3H); ^{13}C NMR (CD_3CN-D_2O, v/v 1.5/1, 100 MHz) δ 169.5, 160.3, 113.2, 106.3, 91.4, 84.1, 76.3, 72.0, 58.7, 56.5, 44.8, 28.2, 26.5, 26.3. Anal. Calcd for $C_{16}H_{23}NO_8$: C, 53.78; H, 6.49; N, 3.92. Found: C, 53.69; H, 6.62; N, 3.79.

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