

Alkyne 8. To a stirred solution of potassium *tert*-butoxide (0.27 mL, 1.0 M THF solution) in THF (0.5 mL) at $-78\text{ }^{\circ}\text{C}$ was added a solution of (diazomethyl)phosphonate (40.2 mg, 1.25 mmol) in THF (0.5 mL). After 5 min, a solution of **5** (110 mg, 0.21 mmol) in THF (0.5 mL) was added dropwise, and the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 12 h. The mixture was then warmed to room temperature and was quenched with satd. aqueous NH_4Cl . The aqueous layer was extracted with 3 x 5 mL portions of Et_2O , and the combined organic extracts were dried (MgSO_4), concentrated *in vacuo*, and purified by chromatography (SiO_2 , 5% Et_2O /hexane) to give **8** (85 mg, 80%) as colorless crystals: $[\alpha]_{\text{D}}^{24} -24.1$ (c 1.12, CHCl_3); mp $52\text{-}54\text{ }^{\circ}\text{C}$; IR (film) 3310 2951, 2927, 2883, 2854, 1743, 1691, 1472, 1254, 1089, 990, 837, 775 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 4.45 (1H, dd, $J = 3.1, 7.5$ Hz), 3.76 (1H dd; $J = 2.1, 6.4$ Hz), 3.65 (1H, s), 3.33 (1H, qn, $J = 7.5$) 2.40-2.26 (3H, m), 2.06 (1H, s), 1.24 (3H, s), 1.18 (3H, d, $J = 6.9$ Hz), 1.17 (3H, 3H), 1.07 (3H, d, $J = 7.0$ Hz), 0.92 (9H, s), 0.86 (9H, s), 0.08 (3H, s), 0.07 (3H, s), 0.00 (3H, s); ^{13}C NMR (CDCl_3 , 75 MHz) δ 218.6, 172.3, 85.6, 75.7, 73.3, 70.8, 53.9, 46.5, 32.1, 26.1, 23.7, 18.7, 18.5, 18.2, 15.8, -3.3, -3.9, -4.5, -4.7; HRMS (CI) calcd. for $\text{C}_{27}\text{H}_{52}\text{Si}_2\text{O}_5$ ($\text{M}+\text{H}^+$) 512.3353, found 512.3342.

Enyne 9. To a stirred solution of **8** (70.0 mg, 0.135 mmol) in Et_2O (1.0 mL) and DMF (0.4 mL) at room temperature was added Et_3N (18.8 μL , 0.135 mmol) and CuI (25.7 mg, 0.135 mmol). After the mixture turned clear (approximately 5 min), a solution of **7** (29.1 mg, 0.068 mmol) in Et_2O (1.0 mL) was added, and the mixture was stirred for 18 h. The reaction mixture was quenched with satd aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (5 mL) and was extracted with Et_2O (3 x 2 mL). The combined organic extracts were dried (MgSO_4), concentrated *in vacuo*, and purified by flash chromatography over silica gel (50-60% CH_2Cl_2 /hexanes) to give **9** (35.6 mg, 60%) as a colorless oil: $[\alpha]_{\text{D}}^{23} -16.7$ (c 1.01); IR (film) 2927, 2857, 2371, 2341, 1743, 1683, 1648, 1482, 1251, 991, 837 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 6.91(1H, s), 6.46 (1H, s), 5.36 (1H, t, $J = 4.7$ Hz), 4.45 (1H, dd, $J = 3.1, 6.9$), 4.11 (1H, t, $J = 6.6$), 3.76-3.72 (1H, m), 3.74-3.67 (1H, m), 3.67 (3H, s), 3.36-3.31 (1H, qn, $J = 6.8$), 2.71 (3H, s), 2.41-2.25 (7H, m), 2.01 (3H, s), 1.80 (3H, s), 1.24 (3H, s), 1.16 (3H, s), 1.12 (3H, d, $J = 7.0$), 1.05 (3H, d, $J = 6.8$), 0.92 (9H, s), 0.88 (9H, s), 0.87 (9H, s), 0.09 (3H, s), 0.06 (6H, s), 0.04 (3H, s), 0.01 (3H, s), -0.00 (3H, s); ^{13}C NMR (CDCl_3 , 75 MHz): δ 218.0, 172.4, 164.3, 153.2, 142.5, 132.2, 122.2, 118.6, 118.9, 83.1, 80.2, 78.6, 75.9, 73.5, 53.7, 51.6, 46.3, 40.4, 35.7, 32.6, 29.7, 29.2, 26.1, 26.0, 25.8, 23.8, 21.7, 19.2, 18.9, 18.4, 18.2, 16.2, 15.7,

13.9, -3.3, -3.9, -4.4, -4.6, -4.7, -4.9; HRMS (CI) calcd. for $C_{46}H_{34}O_6Si_3SN$ ($M+H^+$) 862.5327, found 862.5325.

Triene 6. A suspension of **9** (10 mg, 0.011 mmol) and Lindlar catalyst (1.35 mg, 5% Pd) was stirred at room temperature under an atmosphere of H_2 for 28 h. The suspension was filtered through silica gel (Et_2O rinse), concentrated *in vacuo*, and purified by flash chromatography over silica gel (40-60% CH_2Cl_2 /hexane) to give **6** (6.8 mg, 68%) as a colorless oil: $[\alpha]_D^{23} + 3.6$ (c 1.00, $CHCl_3$); IR (film) 1743, 1699 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 6.91 (1H, s), 6.45 (1H, s), 5.58 (1H, t, $J = 9.2$ Hz), 5.2 - 5.35 (1H, m), 5.16 (1H, t, $J = 6.6$ Hz), 4.39 (1H, dd, $J = 3.1, 6.9$ Hz), 4.09 (1H, t, $J = 6.6$ Hz), 3.8 - 3.9 (1H, m), 3.6 - 3.7 (1H, m); 3.66 (3H, s), 3.03 (1H, qn, $J = 6.7$ Hz), 2.70 (3H, s), 2.65 - 2.75 (2H, m), 2.3 - 2.5 (2H, m), 2.15 - 2.35 (3H, m), 1.99 (3H, s), 1.64 (3H, s), 1.19 (3H, s), 1.06 (3H, s), 1.03 (3H, d, $J = 7.1$ Hz), 1.00 (3H, d, $J = 7.0$ Hz), 0.92 (9H, s), 0.88 (9H, s), 0.86 (9H, s), 0.08 (3H, s), 0.07 (6H, s), 0.04 (3H, s), 0.00 (3H, s), -0.01 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 218.0, 172.6, 164.5, 153.4, 142.5, 135.5, 131.7, 128.7, 122.2, 119.0, 115.2, 79.1, 76.1, 74.2, 53.5, 51.8, 46.4, 40.4, 37.9, 35.6, 30.9, 26.4, 26.2, 26.0, 24.0, 23.9, 19.4, 19.3, 18.7, 18.4, 14.9, 14.1, -3.3, -3.7, -4.3, -4.4, -4.7; HRMS (CI) calcd. for $C_{46}H_{86}O_6Si_3SN$ ($M+H^+$) 864.5484, found 864.5510.