Supporting Information

Compound 19: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.387 (d, *J* = 2 Hz, 1 H), 5.132 (d, *J* = 2.8 Hz, 1 H), 5.033 (dd, *J* = 1.6, 5.2 Hz, 1 H), 4.991 (d, *J* = 10.8 Hz, 1 H), 4.384 (dd, *J* = 2.0, 8.4 Hz, 1 H), 4.261 (ddd, *J* =9.6, 6.8, 2.8, 1 H), 3.799 (s, 3 H), 3.349 (s, 3 H), 3.017 (dddd, *J* = 10.8, 6.4, 6.4, 6.4 Hz, 1 H), 3.017 (1 H), 2.077 (dd, *J* =2, 7.6 Hz, 1 H), 2.043 (dd, *J* =2, 8 Hz, 1 H), 1.866-1.785 (m, 3 H), 1.631 (dddd, *J* = 3.2, 8, 9.6, 17.6, 1 H), 1.546 (dd, *J* = 2.8, 8.4 Hz, 1 H), 1.510 (dd, *J* = 2.8, 8.8 Hz, 1 H), 1.163-1.131 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.00, 146.70, 128.29, 115.96, 103.99, 94.38, 76.29, 68.71, 54.94, 52.49, 40.64, 39.43, 35.68, 21.44, 21.08.

Compounds 20α and **20**β, major isomers from atom transfer reaction: **Isomer 20**α: mp = 120-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.407 (bt, *J* = 2.4 Hz, 1 H), 4.930 (d, *J* = 4.8 Hz, 1 H), 4.589 (ddd, *J* = 8.8, 2.8, 11.6 Hz, 1 H), 3.750 (s, 3 H), 3.316 (s, 3 H), 2.925 (bm, 1 H), 2.705-2.516 (m, 2 H), 2.295 (dd, *J* = 12, 14 Hz, 1 H), 2.234-2.074 (m, 6 H), 1.947 (dd, *J* = 2.8, 14 Hz, 1 H), 1.581 (ddd, *J* = 4.4, 9.6, 12.8 Hz, 1 H), 1.392 (dddd, *J* = 7.2, 10, 14, 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 176.22, 140.57, 126.39, 103.29, 77.80, 74.91, 54.54, 54.14, 52.69, 39.69, 39.18, 38.50, , 30.78, 30.52, 25.86; HRMS for $C_{14}H_{19}O_4$ $(M\text{-}OCH_3)^+$ calcd 251.1283, found 251.1287. **Isomer 20**β: mp = 96-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 (bs, 1 H), 4.96 (apparent d, *J* = 5.2, 1 Hz), 4.36 (ddd, *J* = 5.6, 7.2, 10.8, 1 H), 3.80 (s, 3 H), 3.28 (s, 3 H), 3.16 (bs, 1 H), 3.00-2.96 (m, 1 H), 2.52-2.46 (m, 1 H), 2.45-2.41 (dd, *J* = 3.6, 13.2 Hz, 1 H) 2.35-2.25, (m, 6 H), 1.82-1.73 (m, 1 H), 1.68-1.61 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 173.05, 137.28, 124.63, 99.57, 71.82, 71.09, 52.68, 50.03, 48.84, 36.90, 35.49, 33.57, 29.17, 27.09, 20.41. HRMS for $C_{14}H_{22}O_4$, Mr = 254.32, $(M\text{-}OCH_3)^+$ calcd 251.1283, found 251.1284.

Compound 30: ^{1}H NMR (400MHz, $CDCl_3$) δ 5.05 (dd, *J* = 2.4, 5.6 Hz, 1H), 4.82 (d, *J* = 10.0 Hz, 2H) 4.05 (m, 2H), 3.54 (d, *J* = 10.0 Hz, 1H), 3.36 (s, 3H), 3.34 (d, *J* = 10.0 Hz, 1H), 2.88 (m, 1H), 2.63 (dd, *J* = 6, 12.4 Hz, 1H), 3.32 (bm, 1H), 2.22-2.08 (m, 3H), 1.95-1.82 (m, 2H), 1.72-1.54 (m, 2H), 1.3 (m, 1H), 1.16 (dd, *J* = 14.8 Hz, 1H), 0.906 (s, 9H), 0.865 (s, 9H), 0.042 (s, 3H), 0.038 (s, 3H), 0.009 (s, 3H), 0.003 (s, 3H); ^{13}C NMR (100 MHz) 146.96, 111.22, 104.75, 78.61, 74.35, 67.06, 54.85, 51.20, 47.69, 41.91, 36.73, 34.49, 33.84, 31.17, 25.97, 25.91, 25.73, 24.51, 18.29, 17.93, -4.34, -5.11, -5.48, -5.52: exact mass calcd for $C_{23}H_{43}O_4Si_2$ $(M - C_4H_9)^+$ [HRMS (EI)]; 439.269992, observed; 439.270837.

Compound 32β: ^{1}H NMR (400MHz, $CDCl_3$) major isomer; δ 4.58 (app. p, *J* = 5.6 Hz, 1H), 4.14 (bt, *J* = 10.0 Hz, 1H) 3.94 (d, *J* = 10.8 Hz, 1H), 3.29 (d, *J* = 10.8 Hz, 1H), 2.91 (dd, *J* = 17.6, 8.8 Hz, 1H), 2.77-2.72 (bm, 1H), 2.32 (dd, *J* = 17.6, 2.4, 1H), 2.06-1.98 (m, 2H), 1.92-1.88 (m, 2H), 1.76-1.62 (m, 3H), 1.29-1.18 (bm, 2H), 1.05 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz) 176.86, 81.90, 76.69, 70.45, 49.42, 48.80, 37.77, 36.29, 36.13, 32.62, 31.90, 30.51, 26.99, 23.04: exact mass calcd for $C_{14}H_{23}O_4$; 255.159634, observed [HRMS (FAB)] $(M+H)^+$; 255.158630. X-ray crystal structure data of **32**β; two milligrams of the major isomer was recrystalized from chloroform-hexane

to provide colorless, orthororhombic crystals (0.20 x 0.13 x 0.067 mm), $C_{14}H_{22}O_4$, M_r = 254.32, space group $Pca2_1$, a = 10.940(2) Å, b = 8.3561(12) Å, c = 28.903(4) Å, V = 2642.2(6) $Å^3$, Z = 8, D_{calcd} = 1.279 Mg/m^3, T = 150 °K, F(000) = 1104, μ(Mo Kα) = 0.092 mm^{-1}. Data were collected on a Bruker SMART CCD diffractometer with monchromatic Mo Kα radiation (λ = 0.71071 Å) by the ω/2θ at final convergence method in the range of $1.41 \leq \theta \leq 23.37°$. $R_1[I > 2\sigma(I)] = 0.0476$, $\omega R_2 = 0.0913$ for 331 parameters, GOF = 0.877, $\Delta\rho_{max} = 0.256$, $\Delta\rho_{min} = -0.216$ e $Å^{-3}$. The structure was solved using direct methods and refined by full matrix least-square on F^2 with all non-H atoms anisotropic and H atoms isotropic. Due to the presence of ~15% of the minor isomer within the 2 mg sample, a second crystal was obtained from ether-hexane-chloroform and data collected of the monocinic system (0.40 x 0.40 x 0.039 mm), using the similar parameters and methods for solving the structure as described above; $C_{14}H_{22}O_4$, M_r = 254.32, space group $P2_{1/c}$, a = 29.250(3) Å, b = 8.3635(8) Å, c = 10.9490(11) Å, V = 2643.7(5) $Å^3$, Z = 8, D_{calcd} = 1.278 Mg/m^3, T = 150 °K, F(000) = 1104, μ(Mo Kα) = 0.092 mm^{-1}. Data were collected using monchromatic Mo Kα radiation (λ = 0.71073 Å) by the ω/2θ at final convergence method in the range of $1.41 \leq \theta \leq 23.30°$. $R_1[I > 2\sigma(I)] = 0.0421$, $\omega R_2 = 0.0938$ for 331 parameters, GOF = 0.924, $\Delta\rho_{max} = 0.261$, $\Delta\rho_{min} = -0.196$ e $Å^{-3}$. Relative configurations obtained for both crystals were identical.

Minor isomer of **32**β (epimer of major isomer at pro-C10); ^{1}H NMR (400MHz, $CDCl_3$) δ 4.58 (app. p, J = 6.4 Hz, 1H), 4.14 (bt, J = 8.4 Hz, 1H) 3.80 (d, J = 11.2 Hz, 1H), 3.20 (d, J = 11.2 Hz, 1H), 2.91 (dd, J = 16.8, 6.8 Hz, 1H), 2.80-2.67 (bm, 1H), 2.25 (d, J = 16.8, 1H), 2.19 (bm, 1H), 2.10-1.40 (bm, 6H), 1.38-1.14 (bm, 2H), 0.88 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz) 177.06, 81.49, 77.94, 69.36, 47.94, 47.20, 39.95, 33.21, 32.29, 31.742, 31.02, 26.32, 22.145, 20.74.