Supporting Information

Route to Hexadiene 3. A solution of *t*-BuLi (pentane, 3.4 mL, 4.55 mmol, Aldrich) was added to a cold stirred solution (-98 °C) of dry THF (40 mL). The resulting yellow mixture was stirred at –98 °C for 5 min and the vinyl iodide (726 mg, 2.62 mmol) in dry THF (6 mL) was added very slowly (dropwise). The reaction was stirred at –98 °C for 10 min and the aceal aldehyde (494.4 mg, 1.75 mmol) in dry THF (6 mL) was added. Stirring was continued for 30 min at –78 °C and 30 min at room temperature (21 °C). Saturated aqueous NH_4Cl (20 mL) and ether (20 mL) were added to the stirred reaction. The organic layer was separated, the aqueous layer extracted with additional ether, and the combined organic layers were dried ($MgSO_4$), filtered, concentrated, and chromatographed (4:1, petroleum ether/Et_2O) to afford the secondary alcohol (74.5%, 753 mg) as a colorless oil.

Diastereoisomer 1 50.9%, IR (neat) 3458, 3081, 2929, 1636, 1445, 1374, 1228, 1158, 1054, 909, 870, 802 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.30 (s, 3H), 1.38 (s, 3H), 1.65 (s, 3H), 1.67 (s, 3H), 1.75 (t, 3H, *J* = 1.0 Hz), 2.23-2.31 (m, 2H), 2.24-2.30 (m, 2H), 3.36 (s, 3H), 3.48 (d, 1H, *J* = 3.8 Hz), 4.19 (dd, 1H, *J* = 5.9, 9.3 Hz), 4.30 (dd, 1H, *J* = 3.9, 5.9 Hz), 4.50 (dd, 1H, *J* = 3.9, 9.3 Hz), 4.55 (dd, 1H, *J* = 0.9, 1.9 Hz), 4.55 (half of d of ABq, 1H, *J* = 6.3 Hz), 4.62 (half of d of ABq, 1H, *J* = 6.3 Hz), 4.90 (dd, 1H, *J* = 1.4, 2.8 Hz), 4.93 (dd, 1H, *J* = 3.8, 10.2 Hz), 5.01 (d, 1H, *J* = 1.4 Hz), 5.15 (brs, 1H), 5.15 (dd, 1H, *J* = 1.3, 10.7 Hz), 5.35 (brs, 1H), 5.35-5.39 (m, 2H), 5.71 (brd, 1H, *J* = 10.2 Hz), 6.41 (ddd, 1H, *J* = 0.5, 10.2, 17.4 Hz), 6.49 (dd, 1H, *J* = 10.7, 18.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.5. 21.6, 22.7, 25.2, 26.6, 30.0, 55.8, 71.2, 72.2, 79.1, 79.4, 93.9, 108.8, 111.7, 113.0, 116.6, 119.6, 119 .6, 125.2, 126.8, 131.2, 136.3, 137.1, 142.1, 146.5, 149.9; EIMS: *m/z* 417.3 (1.1, M^+- CH_3OCH_2), 295.2 (0.9), 279.2 (0.5), 249.2 (1.6), 233.2 (1.4), 223.1 (1.3), 219.1 (1.4), 205.1 (1.4), 203.1 (7.8), 193.1 (2.5), 191.1 (3.8), 189.1 (1.9), 187.1 (1.3), 179.1 (25.5), 177.1 (10.2), 173.1 (2.6), 163.1 (11.4), 159.1 (7.5), 150.1 (17.1), 149.1 (19.0), 135.1 (16.1), 133.1 (9.8), 121.1 (17.0), 109.1 (27.3), 105.1 (26.4), 93.1 (23.6), 91.1 (26.1), 81.1 (17.8), 79.1 (22.7), 67.1 (26.4), 59.0 (20.7), 55.1 (212.6), 45 (100), 43.1 (10.3), 32.0 (14.2).

Diastereoisomer 2: 23.6%, $[\alpha]^{27}_D$=+11.6 (c 1.69, $CHCl_3$); IR (neat) 3493, 3081, 2930, 1635, 144, 1374, 1247, 1215, 1071, 908 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.54 (s, 3H), 1.61 (s, 3H), 1.62 (s, 3H), 1.71 (q, 3H, *J* = 0.9 Hz), 1.87-1.95 (m, 1H), 2.02-2.12 (m, 1H), 2.12-2.21 (m, 2H), 2.60 (d, 1H, *J* = 6.6 Hz), 3.37 (s, 3H), 4.09 (brd, 1H, *J* = 6.0 Hz), 4.14 (dd, 1H, *J* = 2.2, 6.6 Hz), 4.26 (t, 1H, *J*~6.6 Hz), 4.50 (dd, 1H, *J* = 0.9, 2.7 Hz), 4.59 (d, 1H, *J* = 6.7 Hz), 4.66 (d, 1H, *J* = 6.7 Hz), 4.86-4.90 (m, 1H, *J* = 1.5 Hz), 4.94 (brs, 1H), 4.95 (dd, 1H, *J* = 6.6, 10.2 Hz), 5.06 (brs, 1H), 5.15 (dd, 1H, *J* = 1.5, 10.7 Hz), 5.34-5.41 (m, 3H, *J* = 1.5, 10.3, 17.3 Hz), 5.48 (d, 1H, *J* = 10.2 Hz), 6.41 (ddd, 1H, *J* = 0.8, 10.7, 17.3 Hz), 6.65 (dd, 1H, *J* = 10.3, 17.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.5, 21.6, 22.6, 24.7, 26.4, 29.9, 31.4, 55.6, 69.3, 71.6, 77.3, 79.5, 93.4, 108.6, 110.7, 113.1, 117.1, 119. 8, 125.27, 125.31, 131.3, 136.0, 136.4, 142.5, 146.3, 149.0; EIMS: *m/z* 417.3 (2.3, M^+- CH_3), 342.3 (2.6), 295.2 (1.2), 279.2 (1.2), 249.2 (3.3), 223.1 (1.7), 219.1 (1.6), 205.1 (1.7), 201.1 (1.7), 193.1 (2.1), 191.1 (5.5), 189.1 (3.0), 187.1 (2.3), 179.1 (62.1), 177.1 (21.1), 173.1 (4.7), 163.1 (17.4), 159.1 (16.7), 150.1 (23.7), 149.1 (21.3), 135.1 (30.0), 133.1 (16.7), 121.1 (23.5), 109.1 (31.2), 105.1 (39.6), 93.1 (40.9), 91.1 (39.9), 81.1 (24.0), 79.1 (40.4), 67.1 (35.5), 59.0 (25.8), 55.1 (22.9), 45 (100), 43.1 (27.6), 32.0 (18.1); HRMS calcd for $C_{25}H_{37}O_5$ (M^+-CH_3) 417.26939, found 417.26578; Anal. Calcd. for $C_{26}H_{40}O_5$: C, 72.19; H, 9.32. Found: C, 72.29; H, 9.16.

Cis-Acetal Adduct 4. Neat oxalyl chloride (39 µL, 0.445 mmol) was added dropwise over a period of 1 min to a cold (-78 °C) stirred solution of DMSO (63 µL, 0.890 mmol) in dry CH_2Cl_2 (6 mL). The was stirred for 5 min at –78 °C and a solution of alcohol above (128.4 mg, 0.297 mmol) in dry CH_2Cl_2 (4 mL) was added dropwise. Stirring was continued at –78 °C for 1 h, freshly distilled Et_3N (281 µL, 2.018 mmol) was added, and the resulting mixture was stirred for 1 h at 0 °C. Saturated aqueous NH_4Cl (4 mL) was added, the resulting phases were separated,, and the aqueous layer was extracted with additional CH_2Cl_2. The combined extracts were dried ($MgS\ O_4$), filtered, filtered, concentrated, and chromatographed (2:1 petroleum ether/ether) to afford adduct **4** (67%, 86.4) as a colorless oil: $[\alpha]^{31}_D$= –75.81 (c 2.92, $CHCl_3$); IR (neat) 3079, 2931, 1728, 1635, 1449, 1376, 1217, 1155, 1110, 1082, 1033, 903 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.21-1.34 (m, 2H), 1.36 (s, 3H), 1.46 (s, 3H), 1.51-1.60 (m, 1H), 1.52 (s, 3H), 1.57 (s, 3H),

1.62 (q, 3H, *J* = 0.9 Hz), 1.90 (brdd, 2H, *J*~7.9, 9.9 Hz), 1.98-2.04 (m, 1H), 2.11-2.27 (m, 2H), 2.77 (d, 1H, *J* = 11.5 Hz), 3.26 (s, 3H), 3.60 (dd, 1H, *J* = 6.9, 11.5 Hz), 4.42 (ddd, 1H, *J* = 0.9, 1.7, 1.8 Hz), 4.50 (half of d of ABq, 1H, *J* = 6.6 Hz), 4.60 (d, 1H, *J* = 6.9 Hz), 4.61 (half of d of ABq, 1H, *J* = 6.6 Hz), 4.62 (d, 1H, *J* = 6.9 Hz), 4.74 (d, 1H, *J* = 8.6 Hz), 4.81 (dd, 1H, 1H, *J* = 0.9, 2.7 Hz), 4.94 (d, 1H, *J* = 11.0 Hz), 5.23 (d, 1H, *J* = 17.4 Hz), 5.88 (t, 1H, *J* = 3.7 Hz), 6.33 (dd, 1H, *J* = 11.0, 17.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4, 21.6, 22.1, 22.5, 22.7, 25.3, 25.4, 27.0, 32.5, 40.8, 48.2, 55.3, 77.9, 78.1, 81.3, 95.3, 111.3, 111.5, 1 13.3, 125.8, 129.2, 133.5, 135.2, 140.0, 145.9, 210.7; EIMS: *m/z* 415 (1.9, M^+- CH_3), 385 (0.6, M^+-CH_3OCH_2), 368 (0.8), 310 (5.4), 249 (6.1), 188 (79.7), 145 (46.0), 117 (39.0), 91 (33.5); HRMS calcd for $C_{26}H_{38}O_5$ 430.27204, found 430.26903.

Trans-Acetal Adduct 5. A stirred solution of enone **6** (192 mg, 0.345 mmol) in dry toluene (35 mL) was heated at reflux for 17 h. The mixture was allowed to cool to 21 °C, the reaction concentrated, chromatographed (3:2, petroleum ether/Et_2O) to afford the single diasteromer **5** (97%, 186 mg) as a colorless oil. IR (neat): 1733, 1613, 1588, 1514, 1451, 1374, 1302, 1237, 915, 826, 759 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.13-1.22 (m, 1H), 1.39 (s, 3H), 1.40 (s, 3H), 1.50-1.60 (m, 1H), 1.57 (s, 3H), 1.59 (s, 3H), 1.67 (s, 3H), 1.69-1.76 (m, 1H), 1.84-1.93 (s, 1H), 2.04-2.22 (m, 3H), 2.26-2.33 (m, 1H), 2.89 (broad s, 1H, $w_{1/2}$= 9 Hz), 3.36 (s, 3H), 3.54 (d, 1H, *J* = 11 Hz), 3.74 (s, 3H), 3.79 (d, 1H, *J* = 11 Hz), 4.03 (d, 1H, *J* = 11 Hz), 4.35 (d, 1H, *J* = 11 Hz), 4.41 (d, 1H, *J* = 11 Hz), 4.47 (broad s, 1H, $w_{1/2}$= 6 Hz), 4.72-4.79 (m, 3H), 4.85 (broad s, 1H, $w_{1/2}$= 7 Hz), 4.90 (d, 1H, *J* = 11 Hz), 5.74-5.78 (broad m, 1H), 6.82 (d, 2H, *J* = 8.5 Hz), 7.23 (d, 2H, *J* = 8.5 Hz). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 19.2, 21.6, 21.7, 22.5, 25.5, 26.6, 27.8, 39.3, 47.5, 52.1, 55.1, 55.5, 71.3, 72.0, 73.1, 76.9, 78.5, 95.9, 111. 4, 113.0, 113.6, 125.3, 129.4, 130.0, 130.6, 132.5, 135.4, 146.2, 159.1, 206.1. MS (electrospray, 1 : 1 CH_3CN-H_2O) *m/z* 555 ($M + H^+$), 577 ($M + Na^+$), 654 ($M + 2H_2O + CH_3CN + Na^+$).

Pentadiene 6. Dess-Martin periodinane (250 mg, 0.607 mmol) was added to a stirred solution of the corresponding alcohol (257 mg, 0.462 mmol) in dry CH_2Cl_2 (10 mL). The reaction was stirred at 21 °C for 45 min. Et_2O (30 mL) was added, followed by saturated aqueous $NaHCO_3$ (1.0 M, 10 mL) and stirring continued for 30 min. The layers were separated and extacted with Et_2O (3 x 10 mL). The combined organic extracts were washed with brine (30 mL), dried ($MgSO_4$), filyered, concentrated, and chromatographed (2:1 petroleum ether/Et_2O). High vacuum drying 21 °C for 20 min yielded enone **6** (75%,192 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.30 (s, 3H), 1.41 (s, 3H), 1.64 (s, 6H), 1.74 (s, 3H), 2.06-2.36 (m, 4H), 3.32 (s, 3H), 3.76 (s, 3H), 4.10 (s, 2H), 4.36 (s, 2H), 4.48-4.77 (m, 6H), 4.87-4.94 (m, 1H), 5.11 (d, 1H, *J* = 11 Hz), 5.33 (d, 1H, *J* = 17.5 Hz), 5.64 (d, 1H, *J* = 10 Hz), 5.85 (br s, 1H, $w_{1/2}$ = 3 Hz), 6.20 (br s, 1H, $w_{1/2}$ = 2.5 Hz), 6.32 (dd, 1H, *J* = 17.5, 11 Hz), 6.82 (d, 2H, *J* = 8.5 Hz), 7.19 (d, 2H, *J* = 8.5 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 19.6, 21.6, 22.6, 26.0, 26.6, 29.8, 30.1, 55.1, 55.4, 63.6, 70.8, 72.2, 77.9, 79.2, 93.5, 110.9, 113.4, 113.6, 115.2, 125.8, 127.6, 129.4, 129.6, 129.8, 135.5, 137.9, 140.5, 146.0, 146.9, 159.1, 198.3.

Triene 17. Dess-Martin periodinane (150.3 mg, 0.354 mmol) was added to a stirred solution of the corresponding alcohol (66.0 mg, 0.177 mmol) in dry CH_2Cl_2 (1.5 mL) at 0 °C . The reaction was stirred at 21 °C for 4 h. Et_2O (10 mL) was added, followed by saturated aqueous $NaHCO_3$ (1.0 M, 10 mL) and stirring continued for 30 min. The layers were separated and extacted with Et_2O (3 x 10 mL). The combined organic extracts were washed with brine (30 mL), dried ($MgSO_4$), filtered, concentrated, and chromatographed (8:1 to 1:1 petroleum ether/Et_2O) to afford the trienone **17** (65%, 62 mg) as a colorless oil. ^{1}H NMR (C_6D_6, 500 MHz): δ 1.11 (s, 3H), 1.57 (s, 3H), 2.03 (s, 3H), 3.13 (s, 3H), 3.31 (s, 3H), 4.30–4.45 (m, 5H), 4.57-4.65 (m, 3H), 4.90 (s, 1H), 5.12 (d, 1H, *J* = 11.9 Hz), 5.23 (d, 1H, *J* = 11.9 Hz), 5.50 (d, 1H, *J* = 18..4 Hz), 6.24 (d, 1H, *J* = 17.8 Hz), 6.73 (dd, 1H, *J* = 11.9, 18.4 Hz) 7.09 (dd, 1H, *J* = 11.9, 17.8 Hz). ^{13}C NMR (C_6D_6, 125MHz) : δ 24.8, 26.5, 55.2, 56.7, 62..1, 73.3, 81.2, 83.3, 95.8, 96..4, 110..3, 114.6, 126.7, 128.3, 131.9, 132.9, 134.8, 139.4, 197.8. IR (neat) 2933, 1694, 1380, 1152, 1095, 1030 cm^{-1}. HRMS calcd for $C_{18}H_{27}O_7$ (M^+-CH_3OCH_2) 355.1757, found 355.1761.

Adduct 23. A stirred solution of enone **17** (28.3 mg, 0.076 mmol) in dry dichloromethane (1 mL) was heated at 40 °C for 4 h. The reaction concentrated and chromatographed (3:1 to 1:5, petroleum ether/Et_2O)

to afford the adduct **23** (87%, 24.6 mg) as a colorless oil. ^{1}H NMR (C_6D_6, 500 MHz): δ 1.23 (s, 3H), 1.29 (s, 3H), 1.30 (s, 3H), 1.53-1.59 (m, 1H), 1.83-1.89 (m, 1H), 2.20-2.26 (m, 1H), 2.40 (t, 1H, *J* =4.0 Hz), 2.42-2.46 (m, 1H), 3.07 (s, 3H), 3.20 (s, 3H), 4.11 (d, 1H, *J* = 12.3 Hz), 4.21 (d, 1H, *J* = 5.7 Hz), 4.31 (d, 1H, *J* =3.6 Hz) 4.39-4.42 (m, 2H), 4.45-4.49 (m, 3H), 4.56 (d, 1H, *J* = 6.4 Hz), 5.56 (t, 1H, *J* = 3.5 Hz). ^{13}C NMR (C_6D_6, 125 MHz): δ 18.2, 22.4, 26.2, 27.0, 42.8, 49.5, 55.0, 55.9, 69.9, 77.6, 77.7, 78.2, 95.4, 97.8, 110.7, 126.2, 128.3, 137.8, 206.3. IR (neat) 2928, 1722, 1151, 1099, 1036 cm^{-1}. HRMS calcd for $C_{19}H_{30}O_7$ (M^+) 370.1992, found 370.1993.

Triene 18. The corresponding alcohol (317 mg, 0.857 mmol) was dissolved in dry CH_2Cl_2 (3 mL) and added to a solution of Dess-Martin periodinane (750 mg, 1.769 mmol) and $NaHCO_3$ (750 mg) in dry CH_2Cl_2 (40 mL) at 0 °C. The reaction was stirred at 21 °C for 2 h. Et_2O (100 mL) was added, followed by saturated aqueous $NaHCO_3$ (1.0 M, 30 mL) and stirring continued for 30 min. The layers were separated and extacted with Et_2O (3 x 30 mL). The combined organic extracts were washed with brine (50 mL), dried ($MgSO_4$), filtered, concentrated, and chromatographed (4:1 petroleum ether/Et_2O) to afford enone **18** (85%, 268 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 3H), 1.60 (s, 3H), 1.79 (s, 3H), 1.91 (s, 3H), 3.41 (s, 3H), 4.32 (s, 2H), 4.66-4.71 (m, 2H), 5.17 (d, *J* = 11.2 Hz, 1H), 5.39 (d, *J* = 17.4 Hz, 1H), 5.60 (s, 1H), 5.72 (d, *J* = 10.5 Hz, 1H), 6.33 (d, *J* = 17.5 Hz, 1H), 6.63 (dd, *J* = 17.4, 11.2 Hz, 1H), 6.90 (dd, *J* = 17.5, 10.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 20.7, 24.9, 26.3, 55.5, 62.2, 70.6, 80.8, 81.3, 96.0, 110.5, 115.0, 128.8, 131.2, 131.5, 133.9, 136.8, 169.2, 197.0.

Adduct 24. A stirred solution of enone **18** (260 mg, 0.707 mmol) in dry acetonitrile (30 mL) was heated at 40 °C for 4 h. The reaction was concentrated and chromatographed (3:2, petroleum ether/Et_2O) to afford the adduct **24** (95%, 224 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 3H), 1.28 (s, 3H), 1.30 (s, 3H), 1.68-1.78 (m, 1H), 1.99-2.06 (m, 1H), 2.13 (s, 3H), 2.18-2.24 (m, 1H), 2.27-2.39 (m, 1H), 2.60-2.62 (m, 1H), 3.36 (s, 3H), 3.95 (d, *J* = 12.3 Hz, 1H), 4.27 (d, *J* = 5.7 Hz, 1H), 4.29-4.33 (m, 2H), 4.59 (s, 2H), 5.59-5.61 (m, 1H), 5.79 (d, *J* = 3.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 17.2, 20.8, 21.7, 25.9, 26.5, 26.7, 41.7, 49.1, 55.3, 69.4, 71.5, 76.6, 76.9, 95.5, 111.0, 127.0, 136.4, 169.6, 206.8.

Lactol 19. The diol from alcohol **15** (240 mg, 0.73 mmol) was dissolved in methylene chloride (10 mL) and treated with activated manganese dioxide (300 mg). After 4 h the solution was filtered and concentrated to furnish the lactol **19** (238 mg, 99%) as a clear oil. ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.43 (s, 3H), 1.95 (s, 3H), 2.45 (s, 1H), 3.36 (s, 3H), 4.24 (d, *J* = 11.4 Hz, 1H), 4.32 (d, *J* = 11.4 Hz, 1H), 4.49 (d, *J* = 5.8 Hz, 1H), 4.59 (d, *J* = 6.7 Hz, 1H), 4.61 (d, *J* = 6.7 Hz, 1H), 4.85 (dd, *J* = 5.8, 4.1 Hz, 1H), 5.16 (d, *J* = 11.2 Hz, 1H), 5.35 (d, *J* = 10.7 Hz, 1H), 5.38 (d, *J* = 17.5 Hz, 1H), 5.59 (d, *J* = 17.5 Hz, 1H), 6.10 (dd, *J* = 17.5, 10.7 Hz, 1H), 6.75 (dd, *J* = 17.5, 11.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.1, 23.9, 25.5, 55.5, 61.9, 78.4, 83.3, 86.2, 95.3, 103.8, 112.4, 114.4, 117.3, 130.1, 134.1, 136.5, 136.7.

Adduct 25. A solution of lactol **19** (40 mg, 0.12 mmol) in acetonitrile (5 mL) was heated at 70 °C for 72 h. The solution was concentrated and chromatographed (2:1, petroleum ether/ethyl acetate to afford the adduct **25** (25 mg, 62 %) as a clear oil, along with recovered starting material (12 mg, 30 %). ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 3H), 1.35 (s, 3H), 1.45 (s, 3H), 1.72-1.76 (m, 1H), 2.04-2.13 (m, 2H), 2.30-2.39 (m, 1H), 2.45 (dd, *J* = 8.5, 4.0 Hz, 1H), 3.37 (s, 3H), 3.93 (dd, *J* = 6.4, 2.4 Hz, 1H), 3.99 (d, *J* = 11.4 Hz, 1H), 4.08 (br s, 1H), 4.15 (d, *J* = 11.4 Hz, 1H), 4.42 (m, 2H), 4.61 (d, *J* = 6.6 Hz, 1H), 4.65 (d, *J* = 6.6 Hz, 1H), 5.85 (t, *J* = 3.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.7, 21.6, 24.0, 25.3, 27.2, 42.2, 52.9, 55.7, 60.3, 74.5, 77.3, 79.2, 95.3, 110.7, 131.8, 137.3, 207.7.

Triene 22. Dess-Martin periodinane (486.2 mg, 1.146 mmol) was added to a stirred solution of the corresponding alcohol **21** (142.3 mg, 382.1 mmol) in dry CH_2Cl_2 (3.30 mL) at 0 °C. The reaction was stirred at 21 °C for 4 h. Et_2O (10 mL) was added, followed by saturated aqueous $NaHCO_3$ (1.0 M, 10 mL) and stirring continued for 30 min. The layers were separated and extacted with Et_2O (3 x 10 mL). The combined organic extracts were washed with brine (30 mL), dried ($MgSO_4$), filtered, concentrated, and chromatographed (6:1 to 3:1, petroleum ether/Et_2O) to afford the enone **22** (80%, 114 mg) as a colorless

oil. ^{1}H NMR (C_6D_6, 500 MHz): δ 1.24 (s, 3H), 1.83 (s, 3H), 3.12 (s, 3H), 3.22(2) (s, 3H), 3.22(3) (s, 3H), 4.29 (d, 1H, *J* = 6.5), 4.40 (d, 1H, *J* = 11.6), 4.51-4.58 (m, 4H), 4.73-4.78 (m, 2H), 5.02 (d, 1H, *J* = 6.7 Hz), 5.14 (d, 1H, *J* = 11.2 Hz), 5.33 (d, 1H, *J* = 10.6 Hz), 5.56 (d, 1H, *J* =17.4 Hz), 6.33 (d, 1H, *J* = 17.5 Hz), 6.67 (dd, 1H, *J* = 11.2, 17.4 Hz), 6.69 (dd, 1H, *J* = 10.6, 17.5 Hz). ^{13}C NMR (C_6D_6, 125 MHz) : δ 10.3, 23.2, 24.0, 52.2, 52.6, 58.9, 73.3, 75.2, 79.7, 91.1, 92.6, 108.4, 112.5, 126.5, 129.7, 131.6, 133.0, 13 8.8, 193.7. IR (neat) 2936, 1700, 1212, 1151, 1099, 1031 $cm^{-1.}$; Anal. Calcd. for $C_{19}H_{30}O_7$: % C 61.60, % H 8.16; Found: % C 61.39, % H 7.93.

Adduct 26. A stirred solution of enone **22** (35.0 mg, 0.094 mmol) in dry toluene (1 mL) was placed in a pressure tube equipped with an expansion side arm and sealed with a threaded Teflon cap. The reaction was heated at 220 ^{o}C for 24 h. The solution was allowed to cool to 21 ^{o}C, the reaction concentrated, chromatographed (3:2, petroleum ether/Et_2O) to afford the adduct **26** (72%, 25.2 mg) as a colorless oil. ^{1}H NMR (C_6D_6, 500 MHz): δ 1.28 (s, 3H), 1.31 (s, 3H), 1.32 (s, 3H), 1.35-1.44 (m, 1H), 1.66-1.73 (m, 1H), 2.15-2.23 (m, 2H), 2.49-2.56 (m, 1H), 3.18 (s, 3H), 3.26 (s, 3H), 3.82-3.86 (m, 2H), 4.01 (d, 1H, *J* = 11.0 Hz), 4.37 (s, 2H), 4.61 (d, 1H, *J* = 6.65 Hz) 4.67 (s, 1H), 4.74 (d, 1H, *J* = 11.0), 5.03 (d, 1H, *J* = 6.7 Hz), 5.42-5.44 (m, 1H). ^{13}C NMR (C_6D_6, 125MHz) δ 17.1, 22.1, 26.7(1), 26.7(5), 27.0, 45.6, 49.2, 55.3, 56.1, 69.2, 75.2, 78.7, 80.0, 95.6, 97.8, 111.0, 131.1, 1 36.3, 201.1. IR (neat) 2933, 1737, 1152, 1031, 750 $cm^{-1.}$ HRMS calcd for $C_{19}H_{30}O_7$ (M^+) 370.1992, found 370.1994.