Template-Directed C-H Insertion: Synthesis of the Dioxabicyclo[3.2.1]octane Core of the Zaragozic Acids

(Supporting Information)

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MATERIALS AND GENERAL PROCEDURES All reactions were carried out in oven- or flame-dried glassware under a nitrogen atmosphere, unless otherwise noted. All solvents were reagent grade. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone under argon. Methanol (MeOH) was dried from magnesium methoxide, prepared from magnesium turnings and iodine. Triethylamine (Et_3N) was distilled from calcium hydride, under nitrogen, and stored over potassium hydroxide. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride under nitrogen. *N*,*N*-dimethylformamide (DMF) was purchased from Aldrich and dried over freshly activated 4 Å molecular sieves prior to use. *N*,*N*-dimethylformamide dimethyl acetal (DMF-DMA) was purchased from Aldrich and used without further purification. Potassium hexamethyldisilazide solution (KHMDS) was purchased from Aldrich and standardized by titration with diphenylacetic acid prior to use. BF_3•Et_2O was distilled from calcium hydride, under reduced pressure, and stored under a nitrogen atmosphere. Diazomethane (CH_2N_2) was prepared according to the method of Hudlicky[i] and standardized by titration with an ethereal solution of benzoic acid prior use. Rhodium (II) acetate was prepared according to the method of Wilkinson.[ii] Except as otherwise indicated, all reactions were magnetically stirred and monitored by thin-layer chromatography with Merck Kieselgel 60-F_{254}. Visualization was accomplished by UV light, potassium permanganate and/or phosphomolybdic acid. Flash column chromatography was performed according to the method of Still[iii] using silica gel 60 (mesh 230-400) supplied by E. Merck. Yields refer to chromatographically and spectrographically pure compounds, unless otherwise stated. Melting points were determined in a open capillary on a Thomas Hoover capillary melting point apparatus or Fisher Johns melting point apparatus and are uncorrected.

Infrared spectra were recorded on an ATI Mattson genesis series FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 MHz ^{1}H, 100 MHz ^{13}C), a Bruker Avance 500 (500 MHz ^{1}H, 125 MHz, ^{13}C) and a Bruker AM-400 (400 MHz, ^{1}H, 100 MHz, ^{13}C) spectrometer. Chemical shift values (δ) are reported relative to internal tetramethylsilane (TMS) (δ 0.00 ppm), pyridine (δ 8.74, 7.58 and 7.22 ppm), chloroform (δ 7.27 ppm) for ^{1}H and pyridine (δ 150.35, 135.91 and 123.87 ppm) chloroform (δ 77.23 ppm) for ^{13}C. High-resolution electron impact (EI) mass spectra were obtained on a Kratos Concept 1H spectrometer at the University of Illinois Research Resources Center with a typical ionization voltage of 70 eV. High-resolution chemical ionization (CI) mass spectra were obtained on a FINNIGAN MAT 95 and high-resolution fast atom bombardment (FAB) spectra were obtained on a VG 7070-HF at the Mass Spectrometry Service Laboratory, University of Minnesota. Elemental analyses were performed by the Midwestern Microlab, Indianapolis, IN.

Representative Procedure for the Preparation of Pyruvate Ester Acetals (9):

2-Carboxymethyl-2,5,5-trimethyl-1,3-dioxane (9a): $BF_3 \bullet Et_2O$ (21.70 g, 153.8 mmol) was added dropwise to a stirred solution of 2,2-dimethyl-1,3-propanediol (**8a**) (8.00 g, 76.9 mmol) and methyl pyruvate (15.70 g, 153.8 mmol) in MeCN (200 mL). The reaction was stirred for 16 h then quenched with saturated aqueous $NaHCO_3$ (60 mL) and allowed to stir for an additional 20 min. The resulting mixture was concentrated under reduced pressure to one third its original volume. The concentrate was then extracted with CH_2Cl_2 (4 x 30 mL) and the combined organic extracts dried (Na_2SO_4) and concentrated. The resulting residue was purified by flash chromatography on silica gel (EtOAc/hexanes, 1:1) to give **9a** (10.40 g, 72%): yellow oil; R_f 0.66 (EtOAc/hexanes, 1:1); IR (film) 2955, 2871, 1744, 1471, 1369, 1121, 1079, 1015, 882, 807, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3 H), 3.46 (s, 4 H), 1.49 (s, 3 H), 1.16 (s, 3 H), 0.68 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 98.1, 73.4 (2 C), 52.5, 29.4, 25.8, 22.6, 21.8; high-resolution mass spectrum (CI) *m/z* 189.1132 [$(M+H)^+$; calcd for $C_9H_{17}O_4$ 189.1127].

2-Carboxymethyl-5,5-diethyl-2-methyl-1,3-dioxane (9b): (1.06 g, 70%): yellow oil; R_f 0.24 (EtOAc/hexanes, 1:3); IR (film) 2966, 2877, 1745, 1460, 1376, 1265, 1118, 1031, 892, 805, 658 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.83 (s, 3 H), 3.68 (d, *J* = 11.7 Hz, 2 H), 3.45 (d, *J* = 11.7 Hz, 2 H), 1.70 (q, *J* = 7.5 Hz, 2 H), 1.51 (s, 3 H), 1.04 (q, *J* = 7.5 Hz, 2 H), 0.86 (t, *J* = 7.5, 3 H), 0.75 (t, *J* = 7.5, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 98.4, 70.7 (2 C), 52.5, 34.1, 25.8, 24.3, 22.3, 7.6, 6.5; high-resolution mass spectrum (CI) *m/z* 217.1445 [$(M+H)^+$; calcd for $C_{11}H_{21}O_4$ 217.1440].

8-Carboxymethyl-8-methyl-7,9-dioxaspiro[4.5]decane (9c): (1.14 g, 80%): yellow oil; R_f 0.38 (EtOAc/hexanes, 1:1); IR (film) 2962, 2807, 2103, 1724, 1647, 1334, 1280, 1192, 1132, 886, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3 H), 3.59-3.49 (m, 4 H), 1.84-1.77 (m, 2 H), 1.66-1.58 (m, 2 H), 1.55-1.52 (m, 4 H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 98.3, 72.4 (2 C), 52.6, 41.2, 34.5, 32.0, 26.0, 25.4, 24.7; high-resolution mass spectrum (CI) *m/z* 232.1538 $[(M+NH_4)^+$; calcd for $C_{11}H_{22}NO_4$ 232.1549].

***trans*-2-Carboxymethyl-*cis*-2,4,6-trimethyl-1,3-dioxane (9d):** (800 mg, 88%): yellow oil; R_f 0.18 (EtOAc/hexanes, 1:9); IR (film) 2974, 2938, 1745, 1440, 1385, 1266, 1112, 1052, 978, 817, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.81-3.73 (m, 2 H), 3.72 (s, 3 H), 1.45 (s, 3 H), 1.41-1.40 (m, 1 H) 1.23-1.20 (m, 1 H), 1.15 (d, *J* = 6.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 98.8, 68.9 (2 C), 52.4, 39.4, 26.7 (2 C), 21.8; high-resolution mass spectrum (CI) *m/z* 189.1127 $[(M+H)^+$; calcd for $C_9H_{17}O_4$ 189.1127].

Procedure for the Preparation of Pyruvate Acid Acetals (10) (Method A):

2-Carboxy-2,5,5-trimethyl-1,3-dioxane (10a): A solution of ester **9a** (10.40 g, 0.06 mol) and NaOH (11.60 g, 0.27 mol) in a mixture of THF (100 mL) and H_2O (100 mL) was stirred at room temperature for 5 h. After cooling to 0 °C, the reaction mixture was then acidified to pH 1 with ice cold 6 M aqueous H_3PO_4 (20 mL) and quickly extracted with EtOAc (5 x 20 mL). The combined organic extracts were then dried (Na_2SO_4), and concentrated to provide **10a** (8.20 g, 85%): white solid; mp 115-116 °C ; IR (KBr) 3503, 3957, 2871, 1719, 1198, 1138, 1073, 1011, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.56 (s, 1 H), 3.54 (m, 4 H), 1.58 (s, 3 H), 1.18 (s, 3 H), 0.73 (s, 3 H); ^{13}C (100 MHz, $CDCl_3$) δ 175.9, 98.0, 73.7 (2 C), 29.6, 25.8, 22.7, 22.0; high-resolution mass spectrum (EI) *m/z* 129.0916 $[(M-CO_2H)^+$; calcd for $C_7H_{13}O_2$ 129.0916].

2-Carboxy-5,5-diethyl-2-methyl-1,3-dioxane (10b): (930 mg, 99%): white solid; mp 122-23 °C; IR (KBr) 3476, 2961, 1674, 1470, 1353, 1279, 1141, 1014, 952, 773 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (d, *J* = 11.6 Hz, 2 H), 3.52 (d, *J* = 11.6 Hz, 2 H), 1.71 (q, *J* = 7.5 Hz, 2 H), 1.59 (s, 3 H), 1.10 (q, *J* = 7.5 Hz, 2 H), 0.86 (t, *J* = 7.5 Hz, 3 H), 0.75 (q, *J* = 7.5 Hz, 3 H); ^{13}C (100 MHz, $CDCl_3$) δ 176.1, 98.2, 71.0 (2 C), 34.4, 25.7, 24.4, 22.4, 7.7, 6.7; high-resolution mass spectrum (CI) *m/z* 203.1285 [$(M+H)^+$; calcd for $C_{10}H_{19}O_4$ 203.1283].

8-Carboxy-8-methyl-7,9-dioxaspiro[4.5]decane (10c): (550 mg, 86%): white solid; mp 127-28 °C; IR (KBr) 2996, 2880, 1747, 1461, 1265, 1189, 1124, 1034, 879, 807 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (bs, 1 H), 3.69 (d, *J* = 11.2 Hz, 2 H), 3.62 (d, *J* = 11.2 Hz, 2 H), 1.84 (m, 2 H), 1.70-1.63 (m, 2 H), 1.59 (s, 3 H), 1.58-1.54 (m, 2 H) 1.16 (m, 2 H); ^{13}C (100 MHz, $CDCl_3$) δ 175.9, 99.0, 72.3 (2 C), 41.1, 34.3, 31.9, 25.7, 25.3, 24.6; high-resolution mass spectrum (CI) *m/z* 218.1402 [$(M+NH_4)^+$; calcd for $C_{10}H_{20}NO_4$ 218.1392].

***trans*-2-Carboxy-*cis*-2,4,6-trimethyl-1,3-dioxane (10d):** (550 mg, 96%): white solid; mp 117-118 °C; IR (KBr) 3058, 2982, 1733, 1320, 1207, 1152, 1098, 976, 912, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95-3.87 (m, 2 H), 1.60 (s, 3 H), 1.51 (d, *J* = 13.2 Hz, 1 H), 1.33-1.31 (m, 1 H), 1.26 (d, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 98.7, 69.3 (2 C), 39.35, 26.8, 21.9; high-resolution mass spectrum (CI) *m/z* 175.0981 [$(M+H)^+$; calcd for $C_8H_{15}O_4$ 175.0970].

Procedure for the Preparation of 2-Carboxy-2-methyl-1,3-dioxane (10e) (Method B): A mixture of 1,3-propanediol (**8e**) (2.00 g, 26.3 mmol), pyruvic acid (1.54 g, 17.5 mmol) and Amberlite IR-120 (plus) resin (200 mg, ~10 mol%) in benzene (CAUTION!)

(50 mL) were heated at reflux in a Dean-Stark apparatus for 16 h. After cooling to room temperature, the reaction mixture was filtered, concentrated and the resulting residue dissolved in 2 M aqueous NaOH (20 mL). The reaction mixture was then heated at reflux for 2 h, cooled to room temperature, acidified to pH 1 with ice cold 6 M aqueous H_3PO_4 (25 mL) and rapidly extracted with EtOAc (4 x 10 mL). The combined organic extracts were then dried (Na_2SO_4), concentrated and the resulting residue purified by flash chromatography on silica gel (EtOAc/hexanes, 3:1) to provide **10e** (1.87 g, 73%): white solid; mp 94-95 °C; R_f 0.65 (EtOAc/hexanes, 3:1); IR (KBr) 3501, 2924, 1735, 1208, 1153, 910, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.06-4.02 (m, 2 H), 3.96-3.89 (m, 2 H), 2.15-2.10 (m, 1 H), 1.59 (s, 3 H), 1.44-1.41 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 174.8, 98.3, 63.4, 26.1, 24.6; high-resolution mass spectrum (EI) *m/z* 101.0602 [$(M-CO_2H)^+$; calcd for $C_6H_{10}O_4$ 101.0602].

Representative Procedure for the Preparation of α–Diazo Ketones (11):

2-Diazoacetyl-2,5,5-trimethyl-1,3-dioxane (11a): A solution of acid **10a** (500 mg, 2.8 mmol) and Et_3N (48 μL, 3.4 mmol) in anhydrous CH_2Cl_2 (10 mL) was cooled to –20 °C and isobutyl chloroformate (38 μL, 3.0 mmol) was added dropwise via syringe. After stirring for 5 min, an ethereal solution of diazomethane (CAUTION!) (0.1 M, 43 mL, 4.3 mmol) was added via a flame-polished pipette and the reaction mixture allowed to warm to room temperature over 16 h. The mixture was then concentrated and the resulting residue purified by flash chromatography on silica gel (EtOAc/hexanes, 2:5) to provide **11a** (550 mg, 99%): yellow solid; mp 65-66 °C; R_f 0.48 (EtOAc/hexanes, 2:5); IR (KBr) 2952, 2867, 2106, 1645, 1336, 1193, 909, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.73 (s, 1 H), 3.52 (d, *J* = 11.1 Hz, 2 H), 3.49 (d, *J* = 11.1 Hz, 2 H), 1.45 (s, 3 H), 1.18 (s, 3

H), 0.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 100.4, 73.2 (2 C), 53.7, 29.7, 25.3, 22.6, 22.0; high-resolution mass spectrum (CI) *m/z* 199.1079 [$(M+H)^+$; calcd for $C_9H_{15}N_2O_3$ 199.1083].

2-Diazoacetyl-5,5-diethyl-2-methyl-1,3-dioxane (11b): (660 mg, 87%): white solid; mp 70-71 °C; R_f 0.38 (EtOAc/hexanes, 3:1); IR (KBr) 2965, 2875, 2106, 1647, 1460, 1336, 1196, 1087, 1030, 888, 832, 656; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (s, 1 H), 3.60 (d, *J* = 11.3 Hz, 2 H), 3.49 (d, *J* = 11.3 Hz, 2 H), 1.68 (q, *J* = 7.5 Hz, 2 H), 1.44 (s, 3 H), 1.06 (q, *J* = 7.5 Hz, 2 H), 0.85 (t, *J* = 7.5 Hz, 3 H), 0.75 (t, *J*= 7.5 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 194.3, 100.3, 70.1 (2 C), 53.2, 34.2, 25.2, 24.1, 22.1, 7.4, 6.3; high-resolution mass spectrum (CI) *m/z* 227.1391 [$(M+H)^+$; calcd for $C_{11}H_{19}N_2O_3$ 227.1396].

2-Diazoacetyl-8-methyl-7,9-dioxaspiro[4.5]decane (11c): (670 mg, 99%): white solid; mp 62-63 °C; R_f 0.17 (EtOAc/hexanes, 1:9); IR (KBr) 3123, 3084, 2953, 2864, 2106, 1647, 1336, 1194, 1032, 893, 831 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 5.73 (s, 1 H), 3.61 (d, *J* = 11.0 Hz, 2 H), 3.52 (d, *J* = 11.0 Hz, 2 H), 1.79 (t, *J* = 6.9 Hz, 2 H), 1.68-1.60 (m, 2 H), 1.58-1.51 (m, 2 H), 1.42 (s, 3 H), 1.11 (t, *J* = 6.9 Hz, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 194.3, 100.1, 71.6 (2 C), 53.4, 41.0, 33.9, 31.9, 25.3, 25.1, 24.4; high-resolution mass spectrum (CI) *m/z* 225.1259 [$(M+H)^+$; calcd for $C_{11}H_{17}N_2O_3$ 225.1239].

***trans*-2-Diazoacetyl-*cis*-2,4,6-trimethyl-1,3-dioxane (11d):** (540 mg, 95%): yellow oil; R_f 0.28 (EtOAc/hexanes, 3:1); IR (film) 3123, 2973, 2934, 2106, 1646, 1330, 1199, 1175, 1109, 972, 911, 743, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (s, 1 H), 3.91-3.77 (m, 2 H), 1.52-1.48 (m, 1 H), 1.48 (s, 3 H), 1.27-1.24 (m, 1 H), 1.22 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 101.4, 68.7 (2 C), 53.4, 39.5, 26.9 (2 C), 21.9; high-resolution mass spectrum (CI) *m/z* 199.1078 [$(M+H)^+$; calcd for $C_{10}H_{17}N_2O_3$ 199.1083].

2-Diazoacetyl-2-methyl-1,3-dioxane (11e): (620 mg, 67%): yellow solid; mp 38-39 °C ; R_f 0.25 (EtOAc/hexanes, 2:5); IR (KBr) 3086, 2968, 2873, 2100, 1635, 1345, 1196, 1145, 976, 869, 821, 656 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.73 (s, 1 H), 3.97-3.83 (m, 4 H), 2.09-1.98 (m, 2 H), 1.42 (s, 3 H); ^{13}C (100 MHz, $CDCl_3$) δ 194.1, 100.4, 62.6 (2 C), 53.4, 25.8, 24.5; high-resolution mass spectrum (CI) *m/z* 171.0769 [$(M+H)^+$; calcd for $C_7H_{11}N_2O_3$ 171.0770].

Representative Procedure for C-H Insertion:

Substrate 11a (Table 2, entry 1): To a flame dried flask, under nitrogen, was added $Rh_2(OAc)_4$ (12.0 mg, 2 mol%) and anhydrous CH_2Cl_2 (48 mL). A solution of α-diazo ketone **11a** (250 mg, 1.28 mmol) in CH_2Cl_2 (8 mL) was then added to the reaction mixture over 20 h via syringe pump. The reaction was then filtered, concentrated and the resulting residue purified by flash chromatography on silica gel (EtOAc/hexanes, 1:9) to give ketone **12a** (110 mg, 52%) and enol ether **13a** (8 mg, 4%):

1,4,4-Trimethyl-2,8-dioxabicyclo[3.2.1]octan-7-one (12a): yellow oil; R_f 0.37 (EtOAc/hexanes, 2:5); IR (film) 2957, 2870, 1787, 1469, 1389, 1176, 1028, 921, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.20 (d, *J* = 7.5 Hz, 1 H), 3.62 (d, *J* = 12.1 Hz, 1 H), 3.47 (d, *J* = 12.1 Hz, 1 H), 2.60 (dd, *J* = 18.4, 7.5 Hz, 1 H), 2.40 (d, *J* = 18.4 Hz, 1 H), 1.37 (s, 3 H), 1.33 (s, 3 H), 0.76 (s, 3 H); ^{13}C (100 MHz, $CDCl_3$) δ 211.5, 98.0, 80.4, 71.8, 37.6, 33.2, 24.7, 22.0, 18.2; high-resolution mass spectrum (CI) *m/z* 171.1015 [$(M+H)^+$; calcd for $C_9H_{15}O_3$ 171.1021].

1,4,4-Trimethyl-7-methylene-2,6,8-trioxabicyclo[3.2.1]octane (13a): white solid; readily sublimes; R_f 0.82 (EtOAc/hexanes, 2:5); IR (film) 3049, 2986, 2350, 1437, 895, 737, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.16 (s, 1 H), 4.45 (d, *J* = 2.9 Hz, 1 H), 4.12

(d, *J* = 2.9 Hz, 1 H), 3.76 (d, *J* = 11.6 Hz, 1 H), 3.43 (d, *J* = 11.6 Hz, 1 H), 1.58 (s, 3 H), 1.19 (s, 3 H), 0.83 (s, 3 H); ^{13}C (100 MHz, $CDCl_3$) δ 156.9, 107.7, 101.8, 80.2, 71.23, 35.2, 22.6, 21.4, 20.6; high-resolution mass spectrum (CI) *m/z* 188.1287 [$(M+NH_4)^+$; calcd for $C_9H_{18}NO_3$ 188.1287].

4,4-Diethyl-1-methyl-2,8-dioxabicyclo[3.2.1]octan-7-one (12b): (71 mg, 42%): colorless oil; R_f 0.27 (EtOAc/hexanes, 1:9); IR (film) 2968, 2877, 1767, 1463, 1384, 1089, 863, 802, 711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.41 (d, *J* = 7.5 Hz, 1 H), 3.62 (d, *J* = 12.3 Hz, 1 H), 3.50 (d, *J* = 12.3 Hz, 1 H), 2.61 (dd, *J* = 18.2, 7.5 Hz, 1 H), 2.61 (d, *J* = 7.5 Hz, 1 H), 2.45 (d, *J* = 18.2 Hz, 1 H), 1.94 (q, *J* = 7.6 Hz, 2 H), 1.35 (s, 3 H), 1.09 (q, *J* = 7.6 Hz, 2 H), 0.91 (t, *J* = 7.6 Hz, 3 H), 0.77 (t, *J* = 7.6 Hz, 3 H); ^{13}C (100 MHz, $CDCl_3$) δ 211.6, 128.3, 98.0, 69.4, 37.5, 37.1, 23.3, 22.8, 18.0, 7.5, 6.4; high-resolution mass spectrum (CI) *m/z* 199.1333 [$(M+H)^+$; calcd for $C_{11}H_{19}O_3$ 199.1334].

4,4-Diethyl-1-methyl-7-methylene-2,6,8-trioxabicyclo[3.2.1]octane (13b): (20 mg, 12%) colorless oil; R_f 0.51 (EtOAc/hexanes, 1:9); IR (film) 2966, 2876, 1689, 1390, 1336, 1201, 1125, 958, 911, 855, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (s, 1 H), 4.44 (d, *J* = 2.4 Hz, 1 H), 4.11 (d, *J* = 2.4 Hz, 1 H), 3.62 (d, *J* = 11.5 Hz, 1 H) 3.58 (d, *J* = 11.5 Hz, 1 H), 1.74 (q, *J* = 7.6 Hz, 2 H), 1.55 (s, 3 H), 1.34 (q, *J* = 7.6 Hz, 2 H), 0.88 (t, *J* = 7.6 Hz, 3 H), 0.80 (t, *J* = 7.6 Hz, 3 H); ^{13}C (100 MHz, $CDCl_3$) δ 157.1, 105.8, 101.9, 80.0, 69.5, 40.0, 29.9, 22.8, 20.6, 7.8, 6.6; high-resolution mass spectrum (CI) *m/z* 199.1334 [$(M+H)^+$; calcd for $C_{11}H_{19}O_3$ 199.1334].

1-Methyl-2,8-dioxaspiro[4.5]bicyclo[3.2.1]octan-7-one (12c): (90 mg, 50%): white solid; mp 65-66 °C; R_f 0.30 (EtOAc/hexanes, 2:5); IR (KBr) 2952, 2864, 1765, 1448, 1179, 1102, 864 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (d, *J* = 7.4 Hz, 1 H), 3.65 (d, *J*

= 13.2 Hz, 1 H), 3.57 (d, *J* = 13.2 Hz, 1 H), 2.66 (dd, *J* = 18.2, 7.4 Hz, 1 H), 2.29 (d, *J* = 18.2 Hz, 1 H), 2.16-2.06 (m, 1 H), 1.89-1.87 (m, 1 H), 1.78-1.74 (m, 1 H), 1.66-1.56 (m, 3 H), 1.40 (s, 3 H), 1.38-1.25 (m, 1 H), 1.08-1.03 (m, 1 H); ^{13}C (100 MHz, $CDCl_3$) δ 211.6, 98.2, 80.1, 70.67, 45.0, 38.9, 36.5, 32.5, 25.6, 25.1, 18.2; high-resolution mass spectrum (CI) *m/z* 197.1162 [$(M+H)^+$; calcd for $C_{11}H_{17}O_3$ 197.1178].

4-Spiro[4.5]-1-methyl-7-methylene-2,6,8-trioxabicyclo[3.2.1]octane (13c): (20 mg, 11%): colorless oil; R_f 0.66 (EtOAc/hexanes, 2:5); IR (film) 2955, 2866, 1688, 1453, 1369, 1333, 1198, 1122, 1022, 959, 910, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25 (s, 1 H), 4.56 (d, *J* = 4.2 Hz, 1 H), 4.13 (d, *J* = 4.2 Hz, 1 H), 3.79 (d, *J* = 11.2 Hz, 1H), 3.51 (d, *J* = 11.2 Hz, 1 H), 1.72-1.63 (m, 1 H), 1.61-1.58 (m, 2 H), 1.52 (s, 3 H), 1.49-1.48 (m, 2 H), 1.28-1.26 (m, 1 H), 1.06-0.90 (m, 1 H), 0.89-0.86 (m, 1 H); ^{13}C (100 MHz, $CDCl_3$) δ 157.2, 107.4, 101.7, 80.2, 70.6, 46.5, 34.0, 32.1, 25.6, 25.2, 20.6; high-resolution mass spectrum (CI) *m/z* 197.1165 [$(M+H)^+$; calcd for $C_{11}H_{17}O_3$ 197.1178].

(1α,3α,5αβ)-1,3,5-Trimethyl-2,8-dioxabicyclo[3.2.1]octan-7-one (12d): (51 mg, 43%): colorless oil; R_f 0.05 (EtOAc/hexanes, 1:9); IR (film) 2972, 1762, 1445, 1375, 1170, 908, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97-3.93 (m, 1 H), 2.35 (s, 2 H), 1.68 (d, *J* = 11.2 Hz, 1 H), 1.59 (dd, *J* = 11.2, 3.8 Hz, 1 H), 1.48 (s, 3 H), 1.39 (s, 3 H), 1.24 (d, *J* = 6.0 Hz, 3 H); ^{13}C (100 MHz, DMSO) δ 212.5, 99.7, 77.2, 67.1, 45.1, 42.1, 25.6, 21.8, 18.5; high-resolution mass spectrum (CI) *m/z* 171.1019 [$(M+H)^+$; calcd for $C_9H_{15}O_3$ 171.1021].

1-Methyl-2,8-dioxabicyclo[3.2.1]octan-7-one (12e): (70 mg, 44%): clear oil; R_f 0.33 (EtOAc/hexanes, 2:5); IR (film) 2977, 2939, 1760, 1383, 1181, 1092, 919, 842, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (m, 1 H), 4.00-3.93 (m, 2 H), 2.71 (dd, *J* = 18.3, 7.8,

Hz, 1 H), 2.51-2.47 (m, 1 H), 2.27 (d, *J* = 18.3 Hz, 1 H), 1.43 (m, 1 H), 1.29 (s, 3 H); ^{13}C (100 MHz, $CDCl_3$) δ 211.2, 98.4, 71.7, 60.9, 39.7, 29.3, 18.7; high-resolution mass spectrum (CI) *m/z* 143.0715 [$(M+H)^+$; calcd for $C_7H_{11}O_3$ 143.0708].

2,4-*O*-Benzylidene xylitol (17): A suspension of 2,4-*O*-benzylidene-D-sorbitol (13.50 g, 50.00 mmol) in H_2O (50 mL) and EtOH (10 mL) was treated with 0.59 M aqueous sodium periodate (90.0 mL, 53.1 mmol). The reaction mixture was stirred at rt for 2 h then 1.0 M aqueous barium chloride (25 mL, 25.0 mmol) was added. A white solid rapidly precipitated from the clear reaction mixture and after stirring for 5 min this solid was removed by filtration. The filter cake was washed with a mixture of H_2O and EtOH (120 mL, 5:1) and the combined filtrates placed in a thick-walled glass Parr hydrogenation flask together with freshly prepared Ra-Ni (~ 3 g). The hydrogenation flask was placed in a Parr hydrogenation apparatus (H_2, 50 psi) and the mixture agitated at room temperature for 30 h, filtered through Celite 521 and the filtrates concentrated to dryness in vacuo. The resulting residue was then recrystallized from a mixture of *i*-PrOH and $CHCl_3$ to yield **17** (7.80 g, 65% yield): white powder; mp 138-141 °C (lit.[12] 142-144 °C); IR (KBr) 3435, 3371, 3304, 2944, 2881, 1413, 1365, 1302, 992 cm^{-1}; ^{1}H NMR (400 MHz, pyridine-d_5) δ 7.71 (m, 2 H), 7.33 (m, 3 H), 5.96 (s, 1 H), 4.44 (m, 5 H), 4.33 (s, 2 H; ^{13}C NMR (100 MHz, pyridine-d_5) δ 139.6, 129.1, 128.3 127.4, 101.9, 82.5, 64.6, 62.6 ; high resolution mass spectrum (EI) *m/z* 240.0996 [$(M)^+$; calcd for $C_{12}H_{16}O_5$ 240.0998.

***cis*-5-Benzyloxy-4,6-bis(benzyloxymethyl)-2-phenyl-1,3-dioxane**: To a stirred suspension of NaH (60% dispersion in mineral oil, 1.00 g, 25 mmol) in DMF (25 mL), at 0 °C, was added a solution of 2,4-*O*-benzylidene xylitol (**17**) (1.00 g, 4.16 mmol) in DMF

(20 mL). After 20 min, tetrabutylammonium iodide (77 mg, 0.208 mmol) and benzyl bromide (2.50 mL, 20.8 mmol) were then added and the mixture stirred at room temperature for 20 h before being quenched by the addition of MeOH (1 mL). Concentration in vacuo gave a residue which was taken up in EtOAc (200 mL), washed with H_2O (3 x 75 mL) then brine (3 x 75 mL), dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified by flash chromatography on silica gel (hexanes/EtOAc, 12:1) to give the title compound (1.08 g, 51% yield): white solid; mp 84-88 °C (hexanes/EtOAc); R_f 0.36 (hexanes/EtOAc, 5:1); IR (film) 3028, 2909, 1497, 1396 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.25 (m, 20 H), 5.63 (s, 1 H), 4.64 (s, 2 H), 3.88 (q, J = 9.4 Hz, 4 Hz), 4.16-4.13 (dt, J = 1.1, 5.2 Hz, 2 H), 3.67 (d, J = 5.2 Hz, 4 H), 1.56 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 138.1, 129.0, 128.6, 128.4, 128.3, 128.1, 127.9, 127.8, 126.5, 101.2, 78.9, 74.5, 73.7, 70.4, 69.2; high resolution mass spectrum (EI) *m/z* 510.2406 [$(M)^+$; calcd for $C_{33}H_{34}O_5$ 510.2406]. Anal. Calcd for $C_{33}H_{34}O_5$: C, 77.62; H, 6.71. Found: C, 77.59; H, 6.74.

1,3,5-Tri-*O*-benzyl xylitol (7): A solution of *cis*-5-benzyloxy-4,6-bis(benzyloxymethyl)-2-phenyl-1,3-dioxane (8.25 g, 16.10 mmol), ethanethiol (4.78 mL, 64.60 mmol) and *p*-toluenesulfonic acid monohydrate (400 mg, 2.10 mmol) in $CHCl_3$ (200 mL) was stirred at room temperature for 48 h. The reaction mixture was then washed with saturated aqueous Na_2CO_3 (2 x 100 mL), brine (2 x 100 mL), the organic phase dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc, 1:1) to afford **7** (5.31 g, 78% yield): colorless oil; R_f 0.35 (hexanes/EtOAc, 1:1); IR (film) 3436, 3029, 2864, 1496, 1453, 1204, 729 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.35-7.32 (m, 15 H), 4.65 (s, 2 H), 4.53 (s,

4 H), 4.04 (m, 2 H), 3.70 (m, 1 H), 3.58 (m, 4 H), 2.94 (d, J = 5.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 137.9, 128.5, 128.3, 128.0, 127.9, 127.8, 78.3, 74.7, 73.4, 71.1, 70.9 ; high resolution mass spectrum (EI) *m/z* 331.1541 [$(M-C_7H_7)^+$; calcd for $C_{19}H_{23}O_5$ 331.1546].

***trans*-Carboxyamide-*cis*-5-benzyloxy-4,6-bis(benzyloxymethyl)-2-methyl-1,3-dioxane (20):** Trimethyl orthoacetate (2.23 mL, 17.55 mmol) and *p*-toluenesulfonic acid monohydrate (99 mg, 0.52 mmol) were added to a mixture of diol **7** (4.94 g, 11.70 mmol) and freshly activated 4 Å molecular sieves (5.00 g) in CH_2Cl_2 (180 mL). The reaction mixture was then stirred at room temperature for 30 min before being quenched with powdered anhydrous Na_2CO_3 (2.50 g). After stirring for a further 20 min, the reaction mixture was decanted and concentrated to provide **18**. This residue was then dissolved in CH_2Cl_2 (180 mL) and freshly activated 4 Å molecular sieves (5.00 g) added. This mixture was then treated with trimethylsilyl cyanide (4.68 mL, 35.10 mmol) (CAUTION!) and $SnCl_2$ (400 mg, 0.47 mmol). The reaction mixture was heated at reflux for 1.5 h, cooled to room temperature and quenched with powdered anhydrous K_2CO_3 (2.50 g). After stirring for 20 min, the reaction mixture was decanted from the solids and concentrated to provide nitrile **19** (2.34 g) which was used directly in the following procedure:

A mixture of **19**, NaOH (2.34 g, 18.4 mmol) and hydrogen peroxide (30%, 1.8 mL, 58.5 mmol) in EtOH (180 mL) was heated at reflux for 1 h. The reaction mixture was then cooled to 0 °C, quenched with powdered $Na_2S_2O_5$ (2.00 g), stirred for 20 min, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc, 5:1 then 1:2) to afford **20** (4.19 g, 73% yield from **7**): white solid; mp

105-107 °C; R_f 0.30 (hexanes/EtOAc, 1:2); IR (KBr) 3409, 3207, 3029, 2874, 1679, 1584, 1452, 1349, 1210, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 15 H), 6.27 (s, 1 H), 5.37 (s, 1 H), 4.56 (s, 2 H), 4.50 (d, *J* = 11.7 Hz, 2 H), 4.43 (d, *J* = 11.7 Hz, 2 H), 4.04-4.01 (m, 2 H), 3.63-3.59 (m, 2 H), 3.49-3.45 (m, 3 H), 1.57 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 138.1, 137.9, 128.6, 128.5, 128.1, 128.0, 99.5, 74.5, 74.4, 73.6, 69.3, 69.2, 26.8; high resolution mass spectrum (EI) *m/z* 491.2306 [$(M)^+$; calcd for $C_{29}H_{33}NO_6$ 491.2308]. Anal. Calcd for $C_{29}H_{33}NO_6$: C, 70.86; H, 6.77. Found: C, 70.62; H, 6.84.

***trans*-Carboxymethyl-*cis*-5-benzyloxy-4,6-bis(benzyloxymethyl)-2-methyl-1,3-dioxane (21):** A solution of amide **20** (860 mg, 1.74 mmol) and DMF-DMA (830 μL, 6.24 mmol) in anhydrous MeOH (60 mL) was placed in a pressure tube. The reaction mixture was then subjected to 3 cycles of freeze-thawing under nitrogen, sealed and heated at 100 °C for 72 h. After cooling to 0 °C, the pressure tube was cautiously opened and the reaction mixture quenched with 2 M aqueous HCl (1 mL), diluted with EtOAc (120 mL), washed with H_2O (2 x 60 mL) then brine (60 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc, 2:1) to give ester **21** (650 mg, 73% yield): pale yellow oil; R_f 0.75 (hexanes/EtOAc, 1:2); IR (film) 3061, 3030, 2919, 2863, 1745, 1496, 1454, 1213, 1145, 948 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 15 H), 4.58 (s, 2 H), 4.53 (d, *J* = 11.7 Hz, 2 H), 4.45 (d, *J* = 11.7 Hz, 2 H), 4.01-3.99 (m, 2 H), 3.79 (s, 3 H), 3.60 (d, *J* = 6.6 Hz, 4 H), 3.55 (d, *J* = 1.5 Hz, 1 H), 1.56 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 138.4, 138.0, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 99.0, 74.6, 74.4, 73.6,

69.5, 68.7, 52.8, 26.0; high resolution mass spectrum (EI) *m/z* 506.2304 [$(M)^+$; calcd for $C_{30}H_{34}O_7$ 506.2305].

***trans*-2-Carboxy-*cis*-5-benzyloxy-4,6-bis(benzyloxymethyl)-2-methyl-1,3-dioxane:** A mixture of ester **21** (2.10 g, 4.15 mmol) and LiOH (1.80 g, 42.90 mmol) in THF (125 mL) and H_2O (50 mL) was heated at reflux for 4 h, cooled to room temperature and concentrated to 1/3 its original volume under reduced pressure. The concentrate was acidified to pH 6 with 5 M aqueous HCl then to pH 2 with 2 M aqueous H_3PO_4 and extracted with $CHCl_3$ (5 x 20 mL), Et_2O (2 x 20 mL) and $CHCl_3$ (5 x 20 mL). The combined organic extracts were then dried over $MgSO_4$ and concentrated to the title compound (1.94 g) which was used directly in the following procedure:

***trans*-2-Diazoacetyl-*cis*-5-benzyloxy-4,6-bis(benzyloxymethyl)-2-methyl-1,3-dioxane (4):** A mixture of *trans*-2-carboxy-*cis*-5-benzyloxy-4,6-*bis*-benzyloxymethyl-2-methyl-1,3-dioxane (1.94 g) and Et_3N (655 μL, 4.73 mmol) in CH_2Cl_2 (32 mL) was stirred at room temperature for 30 min then cooled to -30 °C and treated with isobutyl chloroformate (539 μL, 4.14 mmol). After stirring at this temperature for 45 min, the reaction mixture was warmed to 0 °C and treated with an ethereal solution of diazomethane (0.1 M, 59.0 mL, 59.0 mmol) (CAUTION!). The reaction mixture was stirred at 0 °C for 1 h, concentrated under reduced pressure (using a safety screen) and the resulting yellow residue purified by flash chromatography on silica gel (hexanes/EtOAc, 2:1) to give α–diazo ketone **4** (1.89 g, 88% yield from **21**): yellow crystals; mp 89-90 °C; R_f 0.23 (hexanes/EtOAc, 2:1); IR (film) 2865, 2106, 1646, 14.56, 1338, 1201, 1105 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 15 H), 5.76 (bs, 1 H), 4.61 (s, 2 H), 4.56 (d, J = 11.8 Hz, 2 H), 4.47 (d, J = 11.8 Hz, 2 H), 4.06 (m, 2 H),

3.67-3.52 (m, 5 H), 1.53, (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 138.2, 137.9, 128.6, 128.5, 128.4, 128.0, 127.9, 101.3, 74.4, 74.2, 73.6, 69.5, 69.1, 53.7, 26.0; high resolution mass spectrum (CI, NH_3) *m/z* 517.2313 [$(M+H)^+$; calcd for $C_{30}H_{33}N_2O_6$ 517.2338]; high resolution mass spectrum (EI) *m/z* 488.2191 [$(M)^+$; calcd for $C_{30}H_{32}O_4$ 488.2199]. Anal. Calcd for $C_{30}H_{32}N_2O_6$: C, 69.75; H, 6.24 , N, 5.42. Found: C, 69.71; H, 6.32, N, 5.21.

(1α,3β,4β,5αβ)-4-Benzyloxy-3,5-bis(benzyloxymethyl)-1-methyl-2,8-dioxabicyclo[3.2.1]octan-7-one (22): A solution of α–diazo ketone **4** (250 mg, 0.48 mmol) in CH_2Cl_2 (10 mL) was added over 8 h, via syringe pump, to a stirred solution of $Rh_2(OAc)_4$ (4 mg, 9 μmol) in CH_2Cl_2 (38 mL). The reaction mixture was then concentrated and the residue purified by flash chromatography on silica gel (hexanes/EtOAc, 5:1) to afford bicyclic furanone **22** (116 mg, 49% yield): colorless oil; R_f 0.52 (hexanes/EtOAc, 2:1); IR (film) 3063, 3030, 2919, 2869 1767, 1496, 1454, 1386, 1266, 1100 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 15 H), 4.68 (d, *J* = 11.4 Hz, 1 H), 4.57 (d, *J* = 11.4 Hz, 1 H), 4.48-4.42 (m, 4 H), 4.08-4.11 (dt, *J* = 2.2, 6.3 Hz, 1 H), 3.67-3.63 (m, 2 H), 3.53-3.48 (m, 3 H), 2.66 (d , *J* = 18.6 Hz, 1 H), 2.28 (d, *J* = 18.6 Hz, 1 H), 1.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 137.7, 137.6, 128.9, 128.7, 128.6, 128.2, 128.16, 128.10 128.07, 100.0, 82.0, 75.0, 73.8, 73.7, 73.2, 72.7, 71.0, 68.8, 42.3, 18.2; high resolution mass spectrum (EI) *m/z* 488.2197 [$(M)^+$; calcd for $C_{30}H_{32}O_6$ 488.2199].

(1α,3β,4β,5αβ)-(4-Benzyloxy-3,5-bis(benzyloxymethyl)-1-methyl-2,8-dioxabicyclo[3.2.1]oct-6-en-7-yloxy)-triisopropylsilane (23): A solution of KHMDS (0.5 M in THF, 600 μL, 0.3 mmol) in THF (3 mL) was cooled to -78 °C and a solution of

ketone **22** (118 mg, 0.24 mmol) in THF (2 mL) was added dropwise. After stirring at -78 °C for 40 min, triisopropylsilyl chloride (77 μL, 0.36 mmol) was added via syringe and the resulting mixture removed from the cold bath and allowed to warm to room temperature over 30 min. The reaction was quenched with powdered anhydrous K_2CO_3 (200 mg), stirred for 20 min, filtered through a plug of Celite 521 and concentrated. The resulting residue was purified by flash column chromatography over silica gel (hexanes/EtOAc, 8:1) to provide enol ether **23** (125 mg, 80% yield): colorless oil; R_f 0.16 (hexanes/EtOAc, 8:1); IR (film) 2934, 2863, 1640, 1454, 1385, 1340, 1294, 1250, 1098 1015 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.34-7.26 (m, 15 H), 5.20 (s, 1 H), 4.62 (d, *J* = 11.5 Hz, 1 H), 4.55 (d, *J* = 11.5 Hz, 1 H), 4.49 (d, *J* = 4.2 Hz, 2 H), 4.44 (s, 2 H), 4.42-4.39 (m, 1 H), 3.72 (d, *J* = 8.8 Hz, 1 H), 3.69-3.66 (m, 1 H), 3.62-3.59 (m, 1 H), 3.57 (d, *J* = 3.4 Hz, 1 H), 3.34 (d, *J* = 8.8 Hz, 1 H), 1.48 (s, 3 H), 1.48-1.06 (m, 21 H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.7, 138.4, 138.1, 128.8, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 105.7, 102.0, 85.8, 74.8, 73.7, 73.6, 73.4, 73.2, 70.3, 69.8, 19.9, 17.9, 12.4; high resolution mass spectrum (FAB) *m/z* 645.3587 [$(M+H)^+$; calcd for $C_{39}H_{52}O_6Si$ 644.3611].

(1α,3β,4β,5αβ,6β,7α)–4-Benzyloxy-3,5-bis(benzyloxymethyl)-6-hydroxy-1-methyl-7-(triisopropylsilanyloxy)-2,8-dioxabicyclo[3.2.1]octan-6-ol (24): A solution of enol ether **23** (18 mg, 0.028 mmol) in THF (2 mL) was treated with BH_3•Me_2S (2 M in THF, 40 μL, 0.08 mmol) and then heated at reflux for 5 h. The reaction mixture was then cooled to room temperature, quenched with 0.6 M aqueous NaOH (2 mL) and H_2O_2 (30%, 2.00 mL, 65.00 mmol) and stirred at room temperature for 48 h. The reaction mixture was extracted with Et_2O (4 x 10 mL) and the combined organic extracts washed with brine (40 mL), dried ($MgSO_4$), filtered and concentrated. The resulting residue was

purified by column chromatography on silica gel (hexanes/EtOAc, 9:1) to provide **24** (15.0 mg, 81% yield): colorless oil; R_f 0.25 (hexanes/EtOAc, 9:1); IR (film): 3647, 3027, 2921, 2861, 1487, 1383, 1183, 1126, 1089, 1020, 910 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36-7.25 (m, 15 H), 4.66 (d, *J* = 11.5 Hz, 1 H), 4.51 (d, *J* = 11.5 Hz, 1 H), 4.47 (s, 2 H), 4.40-4.36 (m, 1 H), 4.30 (d, *J* = 11.6 Hz, 1 H), 4.25 (d, *J* = 11.6 Hz, 1 H), 4.06 (d, *J* = 2.2 Hz, 1 H), 4.00-3.99 (m, 1 H), 3.72-3.64 (m, 2 H), 3.55-3.50 (m, 3 H), 2.76 (d, *J* = 2.5 Hz, 1 H), 1.46 (s, 3 H), 1.15-1.05 (m, 21 H); ^{1}H-NMR (400 MHz, CD_3OD) δ 7.36-7.18 (m, 15 H), 4.60 (d, *J* = 11.7 Hz, 1 H), 4.53 (s, 2 H), 4.48 (s, 2 H), 4.49-4.44 (m, 2 H) 4.08 (d, *J* = 2.3 Hz, 1 H), 3.97 (d, *J* = 2.3 Hz, 1 H), 3.66 (d, *J* = 8.1 Hz, 1 H), 3.61-3.58 (m, 3 H), 3.47 (m 1 H), 1.34 (s, 3 H), 1.15-1.11 (m, 21 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.4, 137.3, 128.8, 128.5, 128.4, 128.0, 127.9, 127.8, 104.5, 85.2 (2 C), 80.6, 74.9, 73.9, 73.4, 72.6, 71.1, 69.2, 67.7, 22.9, 18.2, 12.5; high resolution mass spectrum (EI) *m/z* 662.3649 [$(M)^+$; calcd for $C_{39}H_{54}O_7Si$ 662.3639].

^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.3, 137.2, 128.8, 128.5, 128.4, 128.0, 127.5, 104.5, 85.2, 80.6, 74.8, 73.9, 73.4, 72.4, 71.0, 69.1, 67.6, 22.9, 18.2, 12.5.

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