Electronic Supplementary Information

Construction of fused bis(pyran) units from enones via a hydrosilylation/dihydroxylation/acetalization/reduction sequence†

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General. Reactions were carried out in oven dried glassware under a positive argon atmosphere unless otherwise stated. Transfer of anhydrous solvents and reagents was accomplished with oven dried glass syringes with stainless steel needles or stainless steel cannulae. Solvents were distilled before use: methylene chloride from calcium hydride, THF, benzene, and diethyl ether from sodium/benzophenone ketyl, and toluene from sodium metal. Thin layer chromatography was performed on glass plates precoated with 0.25 mm Kieselgel 60 F_{254} (Merck). Flash chromatography columns were packed with 230-400 mesh silica gel (Merck). Gas chromatograms were obtained on a Hewlett-Packard 5890 series II capillary gas chromatograph with a 30 m HP-5 column and a flame ionization detector. ^{1}H NMR spectra were recorded on Varian instruments at 300 MHz, 400 MHz, or 500 MHz and coupling constants (J) are reported in Hertz (Hz), chemical shifts are reported (ppm) relative to chloroform-*d* or benzene-*d*. ^{13}C NMR spectra were recorded at 100 MHz or 125 MHz. HPLC analysis were performed on a Gilson HPLC with an UV detector. Chiral columns include Chiralpak AD-H, AS-H, OJ-H, and OD-H.

Methyl 1,3-dioxolane-3-propanoate. THF (90 mL) and one crystal of iodine were added to 1.5 g (62.5 mmol) of flame-dried magnesium turnings in a three-neck flask (250 mL) under Ar. A solution of 6.0 g (33 mmol) of 2-(2-bromoethyl)-1,3-dioxolane (Aldrich) in 30 mL of THF was placed in an addition funnel, and 5 mL of this solution was added to the magnesium turnings. Then several drops of 1,2-dibromoethane was added to the reaction mixture. The reaction was initiated and the solution began to boil. The remainder of alkyl halide was added at a rate such as to maintain the solvent at reflux. After completing the addition of the halide, the reaction was stirred for 1 h.

The mixture was then cooled to -78 °C and methyl chloroformate (3.4 mL, 44 mmol) in THF (30 mL) was added dropwise to maintain a reaction temperature below -70 °C. The mixture was stirred for another 1 h at -78 °C, and then allowed to warm to room temperature. The resulting solution was decanted from the excess magnesium and quenched with the addition of saturated aqueous ammonium chloride (10 mL). THF was evaporated at room temperature and the residue was diluted with water (30 mL), and then the mixture was extracted with ether (3 x 50 mL). The combined organic layers were dried with potassium carbonate. After evaporation, the residue was subjected to the silica gel column (3.5 x 20 cm), using hexane and ethyl acetate (6:1) as the eluent. 3.4 g (yield 65%) of methyl 1,3-dioxolane-3-propanoate was obtained. R_f 0.59

(hexane:EtOAc = 2:1); IR (neat) 2953, 2887, 1739, 1438, 1139 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (t, J = 4.3 Hz, 1H), 3.97-3.83 (m, 4H), 3.67 (s, 3H), 2.44 (t, J = 7.4 Hz, 2H), 2.01 (td, J = 7.4, 4.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 103.1, 65.0, 51.6, 28.8, 28.1.

Dimethyl 2-oxo-5-(1,3-dioxolane)pentylphosphonate 4. To a hexane solution of *n*-BuLi (7.5 mL, 1.6 M, 12 mmol) in THF (15 mL) was added dimethyl methyl phosphonate (1.62 mL, 15 mmol) at -78 °C under Ar. After 1 h, methyl 1,3-dioxolane-propanoate (0.96 g, 6.0 mmol) was added dropwise. The mixture was stirred at -78 °C under Ar for 3 h, and then poured into saturated aqueous ammonium chloride (10 mL). The mixture was extracted with chloroform (3 x 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated at room temperature under vacuum. After dimethyl methyl phosphonate was removed at room temperature under high vacuum, the crude product (0.98 g, yield 65%) was used in the following reaction without farther purification. R_f 0.41 (CH_2Cl_2:MeOH = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (t, J = 4.2 Hz, 1H), 3.96–3.82 (m, 4H), 3.78 (d, J = 11.3 Hz, 6H), 3.11 (d, J = 22.6 Hz, 2H), 2.73 (t, J = 7.2 Hz, 2H), 1.99 (td, J = 7.2, 4.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.0 (d, J = 6.1 Hz), 103.0, 65.0 (2C), 53.0 (d, J = 6.5 Hz), 41.2 (d, J = 128 Hz), 37.9 (d, J = 1.6 Hz), 27.4 .

7-(*tert*-Butyldimethylsilanyloxy)-1-[1,3]dioxolan-2-yl-hept-4-en-3-one 5a. To a mixture of dimethyl 2-oxo-5-(1,3-dioxolane)pentylphosphonate **4** (0.91 g, 3.6 mmol) and LiCl (0.46 g, 11 mmol, very hygroscopic, flame-dried) in anhydrous CH_3CN (15 mL) in a flame-dried flask was added diisopropylethylamine (3.74 mL, 20.2 mmol), followed by the addition of a solution of 3-(*tert*-butyldimethylsiloxy)-propanal **3a** (0.651 g, 3.5 mmol) in 3 mL of CH_3CN under an argon atmosphere. The mixture was stirred overnight. The reaction was quenched by addition into saturated aqueous $NaHCO_3$ (10 mL), and the enone product was extracted with dichloromethane (3 x 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under vacuum. Purification of the residue by flash chromatography (hexane/*t*-BuOMe 10:1) gave 0.792 g (72%) of **5a:** R_f 0.47 (Hexane:EtOAc = 2:1); IR (neat) 2954, 2929, 2884, 2857, 1740, 1699, 1676, 1633, 1472, 1261, 1099 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (dt, J = 16.0, 7.0 Hz, 1H), 6.13 (dt, J = 16.0, 1.4 Hz, 1H), 4.91 (t, J = 4.4 Hz, 1H), 3.97-3.83 (m, 4H), 3.72 (t, J = 6.4 Hz, 2H), 2.67 (t, J = 7.3 Hz, 2H), 2.41 (qd, J = 6.4, 1.5 Hz, 2H), 1.98 (td, J = 7.0, 4.4 Hz, 2H), 0.85 (s, 9H) 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 144.0, 131.7, 103.4, 65.0, 61.6, 35.9, 33.7, 27.8, 25.8, 18.2, -5.4. HRMS (EI) [M^+] for $C_{16}H_{30}O_4Si$ calcd 314.19135, found: m/z 314.19030.

7-(*tert*-Butyldimethylsilanyloxy)-1-[1,3]dioxolan-2-yl-4-hydroxyheptan-3-one 6a. To a mixture of tris(triphenylphosphine) rhodium chloride (4.8 mg, 5.1 μmol) and triethylsilane (1.2 mL, 16 mmol) under Ar was added enone **5a** (154 mg, 0.49 mmol). The mixture was heated in 80 °C oil bath. After cooling to rt, the mixture was filtered through a short Al_2O_3 plug with ether and hexane (1:10). After excess triethylsilane was removed under vacuum, the residue was used in the next step without further purification.

A mixture of this resulting silyl enol ether (0.49 mmol) and *N*-methylmorpholine *N*-oxide (102 mg, 0.75 mmol) in 10 mL of acetone and water (9:1) was treated with 0.40 mL of OsO_4 solution (0.05 mmol/mL in 2-propanol, 0.02 mmol). The reaction mixture was stirred at room temperature overnight. Solid sodium sulfite (0.5 g) was added to the reaction mixture at 0 °C and the mixture was stirred for 1 h. Dichloromethane (10 mL) was added to the reaction mixture. After the organic layer was separated, the aqueous layer was further extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated to give an dark yellow oil, which was purified by flash chromatography with ethyl acetate and hexane (6:1) to afford 90 mg (55%) of **6a** as a colorless oil: R_f 0.37 (hexane:EtOAc = 2:1); IR (neat) 3472, 2955, 2930, 2857, 2832, 1712, 1472, 1361 cm $^{-1}$; ^{1}H NMR (400 MHz, C_6D_6) δ 4.74 (t, *J* = 4.4 Hz, 1H), 3.96 (dd, *J* = 7.9, 3.7 Hz, 1H), 3.47-3.27 (m, 6H), 2.45 (ddd, *J* = 17.6, 7.8, 6.8 Hz, 1H), 2.28 (ddd, *J* = 17.6, 7.2, 7.2 Hz, 1H), 2.03-1.98 (m, 2H), 2.04 (td, *J* = 7.2, 4.1 Hz, 2H), 2.02-1.95 (m, 1H), 1.80 (dddd, *J* = 13.2, 9.6, 6.1, 3.7 Hz, 1H), 1.67-1.54 (m, 2H), 1.43 (dddd, *J* = 13.0, 9.4, 7.8, 4.9 Hz, 1H), 0.95 (s, 9H), 0.021 (s, 3H), 0.019 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 211.3, 103.3, 76.3, 64.8, 62.8, 31.9, 30.6, 28.5, 28.0, 26.1, 18.4, -5.3. HRMS (EI) $[M]^+$for $C_{26}H_{36}O_5Si$ calcd 332.20190, found: m/z 332.20139.

2-(3,3-Dimethoxy-propyl)2,4-dimethoxy-tetrahydropyran 7. A round-bottom flask was charged with hydroxy ketone **6a** (150 mg, 0.45 mmol), camphorsulfonic acid (120 mg, 0.52 mmol) and trimethyl orthoformate (1 mL) in anhydrous methanol (10 mL). The mixture was heated at reflux for 16 h. Then the reaction mixture was neutralized to pH 8–10 and extracted with dichloromethane (3 x 15 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified through flash column chromatography (2 x 20 cm), using ethyl acetate and hexane (1:8) as the eluent to afford 66 mg (60%) of the title product: R_f 0.55 (hexane:EtOAc = 1:1); IR (neat) 2955, 2932, 2857, 1161cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 4.21-4.28 (m, 1H), 3.62 (dddd, *J* = 11.0, 11.0, 4.6, 4.6 Hz, 1H), 3.53 (ddd, *J* = 11.4, 5.3, 1.8 Hz, 1H), 3.41 (ddd, *J* = 12.9, 11.4, 2.4 Hz, 1H), 3.12 (s, 3H), 3.11 (s, 3H), 3.10 (s, 3H), 3.04 (s, 3H), 2.27 (ddd, *J* = 17.6, 7.2 Hz, 1H), 1.93-1.88 (m, 1H), 1.80-1.67 (m, 4H), 1.40 (dddd, *J* = 12.7, 12.7, 11.1, 5.1 Hz, 1H), 1.34 (dd, *J* = 12.4, 10.9 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 104.5, 101.3, 73.5, 59.6, 55.0, 52.6, 52.0, 47.0, 39.6, 32.2, 31.4, 27.2. HRMS (EI) $[M-OCH_3]^+$ for $C_{11}H_{21}O_4$ calcd 217.14398, found: m/z 217.14426; MS (ESI) $[M+Na]^+$ for $C_{12}H_{24}O_5Na$ m/z 271.1.

Tricyclic Acetal 9. A round-bottom flask was charged with hydroxy ketone **6a** (84 mg, 0.25 mmol), camphorsulfonic acid (186 mg, 0.80 mmol) and trimethyl orthoformate (0.88 mL, 4.0 mmol) in anhydrous methanol (10 mL). The mixture was heated at reflux overnight. Then the reaction mixture was neutralized to pH 8–10 and extracted with dichloromethane (3 x 10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified through flash column chromatography (1.5 x 20 cm), using ethyl acetate and hexane (1:5) as the eluent to afford 17 mg (61%) of the title product: R_f 0.29 (hexane:EtOAc = 1:1); IR (CH_2Cl_2 cast film) 2929, 2890, 2820, 1338, 1176 cm $^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03-3.91 (m, 5H), 3.81-3.73 (m, 2H), 3.53-3.51 (m, 1H), 3.35 (s, 3H), 2.24-2.22 (m, 1H), 2.16-1.90 (m, 4H), 1.90-1.81 (m, 1H), 1.75-1.64 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 108.0, 79.0, 70.4, 64.4, 63.9, 61.2, 55.6, 38.6, 27.0, 26.0, 23.3. HRMS (EI) $[M]^+$ for $C_{11}H_{18}O_4$ calcd 214.12051, found: m/z 214.12056.

Dimethoxyoctahydropyrano[3,2]pyrans 11a, 13a and 14a. In a 100 mL rb flask, hydroxy ketone **6a** (157 mg, 0.50 mmol) was dissolved in 25 mL of anhydrous dichloromethane and 10 mL of methanol and trimethyl orthoformate (1:9), then camphorsulfonic acid (58 mg, 0.25 mmol) was added. The mixture was stirred at room temperature for 3 h and then was heated in the oil bath (50 °C) for 48 h. When the starting material was consumed based on TLC, the mixture was neutralized with 2 N NaOH until a pH of 8-10 was reached. The aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under vacuum to give 61 mg (61%) of three isomeric bis(acetals) **11a**, **13a** and **14a** in a ratio of 10:1:20 (measured by integration of OMe signals in ^1H NMR spectrum). The mixture was purified with flash column chromatography (hexane:*t*-BuOMe, gradient of 10:1 □ 5:1) to each isomer in pure form:

Bis(acetal) **13a**: R_f 0.71 (hexane:EtOAc = 1:1); ^1H NMR (400 MHz, C_6D_6) □ 4.17 (dd, *J* = 9.7, 2.0 Hz, 1H), 3.55-3.52 (m, 2H), 3.36 (s, 3H), 3.34 (dd, *J* = 2.9, 2.9 Hz, 1H), 3.03 (s, 3H), 2.19-2.02 (m, 3H), 1.89 (ddd, *J* = 13.1, 4.6, 2.7 Hz, 1H),1.74-1.70 (m, 1H), 1.59 (dddd, *J* = 12.9, 4.8, 2.7, 2.1 Hz, 1H), 1.15 (ddd, *J* = 14.0, 13.1, 4.6 Hz, 1H), 0.96-0.92 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) □ 103.3, 93.9, 72.2, 61.0, 55.8, 47.0, 30.9, 29.1, 24.8, 19.8.

Bis(acetal) **14a**: R_f 0.75 (hexane:EtOAc = 1:1); IR (film) 2955, 2932, 2857, 1361, 1101 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) □ 4.60 (dd, *J* = 3.4, 1.0 Hz, 1H), 3.81 (dd, *J* = 2.5, 2.5 Hz, 1H), 3.64-3.52 (m, 2H), 3.14 (s, 3H), 3.08 (s, 3H), 2.17-2.10 (m, 2H), 2.01 (dddd, *J* = 12.8, 12.8, 6.0, 3.4 Hz, 1H), 1.84 (ddd, *J* = 12.5, 12.5, 4.3 Hz, 1H), 1.81-1.76 (m, 1H), 1.66-1.63 (m, 1H), 1.62 (dddd, *J* = 12.9, 4.2, 2.7, 1.3 Hz, 1H), 1.05-0.94 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) □ 98.0, 94.2, 65.5, 60.9, 54.2, 46.5, 27.7, 26.8, 24.4, 19.7. HRMS (EI) $[M]^+$ for $C_{10}H_{18}O_4$ calcd 202.12051, found: m/z 202.12009.

Bis(acetal) **11a**: R_f 0.46 (hexane:EtOAc = 1:1); IR (film) 2955, 2932, 2857, 1361, 1101 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) □ 4.57 (dd, *J* = 3.7, 0.5 Hz, 1H), 3.83 (dd, *J* = 12.1, 4.0 Hz, 1H), 3.50-3.45 (m, 1H), 3.34 (dddd, *J* = 11.0, 5.1, 1.2, 1.2 Hz, 1H), 3.18 (s, 3H), 3.02 (s, 3H), 2.15-2.10 (m, 2H), 1.92 (ddd, *J* = 12.8, 12.8, 6.0, 3.4 Hz, 1H), 1.84 (ddd, *J* = 12.5, 12.5, 4.3 Hz, 1H), 1.82-1.71 (m, 2H), 1.58-1.48 (m, 3H), 1.33-1.26 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) □ 98.1, 95.4, 70.8, 60.4, 54.3, 46.6, 28.1, 26.1, 24.7, 23.8. HRMS (EI) $[M]^+$ for $C_{10}H_{18}O_4$ calcd 202.12051, found: m/z 202.12036.

Bis(pyrans) 15a and 16a. To a mixture of the bisacetal (61 mg, 0.30 mmol) and Et_3SiH (0.48 mL, 3.0 mmol) in dichloromethane (15 mL) at 0 °C was added TMSOTf (260 μL, 1.5 mmol). The mixture was stirred at room temperature for 24 h. Then the mixture was poured into a $NaHCO_3$ (solid)/ice mixture. The aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered, concentrated, and purified by flash chromatography (2 x 20 cm; pentane/Et_2O, gradient of 20:1 □ 10:1) to yield ca. 26 mg (51%) of the volatile bispyran products in a ratio of 10:1 **15a**:**16a** (measured via integration of bridgehead protons in ^1H NMR spectrum). Spectral data of major product **15a**: IR (neat) 2953, 2834, 1093 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) □ 3.70 (dddd, *J* = 11.2, 4.7, 1.5, 1.5 Hz, 1H), 3.10 (ddd, *J* = 11.8, 11.3, 2.4 Hz, 1H), 2.91-2.84 (m, 1H), 1.95-1.89 (m, 1H), 1.54-1.44 (m, 1H), 1.42-1.34 (m, 1H), 1.21 (ddddd, *J* = 13.4, 4.2, 2.8, 2.8, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6) □ 79.1, 67.8, 30.3, 26.3. HRMS (EI) $[M^+]$ for $C_{10}H_{18}O_2$ calcd 170.13068, found: m/z 170.13067.

2,2-Dimethyl-3-(*tert*-butyldimethylsiloxy)-1-propanol. A 250 mL three-neck flask was charged with NaH (2.1 g, 60% wt % in mineral oil, 53 mmol) in 120 mL of anhydrous THF. To this suspension was added 2,2-dimethyl-1,3-propanediol (5.0 g, 48 mmol) in three portions over 5 min. The resulting thick slurry was stirred at room temperature for 1 h. TBSiOTf (11.0 mL, 48 mmol) was added to the above suspension and the mixture was stirred for 3 h. The mixture was diluted with 100 mL of methyl *tert*-butyl ether and washed with 10% K_2CO_3, brine, and dried over Na_2SO_4. The residue was purified by flash column chromatography (3.5 x 20 cm; hexane/EtOAc 8:1) to provide 5.2 g (50%) of the title compound as a colorless oil: R_f 0.61 (hexane/EtOAc = 5:1); IR (neat) 3385, 2955, 2930, 2858, 1472, 1097 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 3.47 (d, *J* = 5.8 Hz, 2H), 3.47 (s, 2H), 2.80 (br, t, *J* = 5.8 Hz, 1H), 0.90 (s, 9H), 0.89 (s, 6H) 0.07 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 72.7, 72.2, 36.4, 25.8, 21.4, 18.2, -5.7. HRMS (EI) $[M–tBu]^+$ for $C_7H_{17}O_2Si$ calcd 161.09978, found: m/z 161.09947.

3-(*tert*-Butyldimethylsiloxy)-2,2-dimethylpropanal 3b. A solution of DMSO (3.3 mL, 42 mmol) in anhydrous dichloromethane (5 mL) was added dropwise at -78 °C to a solution of oxalyl chloride (2.1 mL, 24 mmol) in anhydrous dichloromethane (40 mL) and the mixture was stirred for 30 min. The alcohol (4.35 g, 20 mmol) in dichloromethane (5 mL) was added slowly to the reaction mixture, which was stirred for 1 h. Then the mixture was treated with triethylamine (12.2 mL, 88 mmol) and the reaction mixture was stirred for 1 h at -78 °C and allowed to warm to room temperature. The mixture was partitioned between water and dichloromethane, and the organic layer was washed with 5% HCl (20 mL) and saturated $NaHCO_3$ (20 mL), dried over $MgSO_4$, then filtered, and concentrated. The residue was filtered through a short plug of silica gel using diethyl ether as the eluent. The crude product (3.7 g, 85%) was used without the purification (The pure product underwent air oxidation to the acid).

7-(*tert*-Butyldimethylsilanyloxy)-1-[1,3]dioxolan-2-yl-6,6-dimethyl-hept-4-en-3-one 5b. To a solution of phosphonate **4** (2.38 g, 10.6 mmol) and LiCl (1.35 g, 31.8 mmol, very hygroscopic, flame-dried) in anhydrous CH_3CN (50 mL) in a flame-dried flask was added diisopropylethylamine (11.1 mL, 63.6 mmol), followed by the addition of a solution of crude aldehyde **3b** (1.9 g, 9.5 mmol) in 10 mL of CH_3CN under an argon atmosphere. The mixture was stirred overnight. Another portion of the aldehyde (0.20 g, 1.0 mmol) was added and the reaction mixture was stirred for 3h. The reaction was quenched by addition into saturated aqueous $NaHCO_3$, and the enone product was extracted with dichloromethane. The organic layer was dried with $MgSO_4$ and concentrated under vacuum. Purification of the residue by flash chromatography (hexane/*t*-BuOMe, gradient from 10:1 □ 8:1) gave 2.58 g (72%) of enone **5b** as a colorless oil: R_f 0.55 (hexane:EtOAc = 4:1); IR (neat) 2956, 2930, 2885, 2857, 1699, 1676, 1628, 1472, 1101 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 6.84 (d, *J* = 16.3 Hz, 1H), 6.04 (d, *J* = 16.3 Hz, 1H), 4.93 (t, *J* = 4.4 Hz, 1H), 3.95-3.83 (m, 4H), 3.36 (s, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 1.99 (td, *J* = 7.4, 4.4 Hz, 2H), 1.03 (s, 6H), 0.88 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 200.0, 154.0, 127.4, 103.5, 71.1, 65.0, 39.1, 33.7, 27.9, 25.8, 23.3, 18.2, -5.5. HRMS (EI) $[M^+]$ for $C_{18}H_{34}O_4Si$ calcd 342.22263, found: m/z 342.22206.

7-(*tert*-Butyldimethylsilanyloxy)-1-[1,3]dioxolan-2-yl-6,6-dimethyl-4-hydroxy-heptan-3-one 6b. *tert*-Butyldimethyl silane (TBSiH, 470 μL, 2.0 mmol) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt's catalyst, 20 μL, 0.1 M, xylenes solution) were added into a 15 mL round bottom flask, which was flushed with argon. Then enone **5b** (342 mg, 1.0 mmol) was introduced via a syringe, and the mixture was stirred at room temperature for 1 h. The reaction mixture was filtered through a short silica plug, using 10:1 hexane/*tert*-butyl methyl ether as the eluent. After the solvent and excess TBSiH were evaporated under vacuum, the residue was directly used in the next reaction.

To a well-stirred mixture of AD-mix-□ (1.4 g, Aldrich) and $CH_3SO_2NH_2$ (85 mg, 1.0 mmol) in 1:1 *t*-BuOH/H_2O (10 mL) at 0 °C was added the crude silyl enol ether. The reaction mixture was stirred for 4 h at 0 °C and slowly warmed up to room temperature overnight. Solid sodium sulfite (1.0 g) was added to the reaction mixture at 0 °C. Dichloromethane (30 mL) was added to the reaction mixture. After the organic layer was separated, the aqueous layer was further extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated, and the residue was purified by flash chromatography (2 x 20 cm; hexane/EtOAc, gradient of 6:1 □ 4:1) to afford 198 mg (55%) of the desired **6b** as a colorless oil: R_f 0.30 (hexane:EtOAc = 1:1); IR (neat) 3473, 2955, 2930, 2885, 2857, 1714, 1472, 1093cm $^{-1}$; ^1H NMR (500 MHz, C_6D_6) □4.79 (t, *J* = 4.4 Hz, 1H), 4.12 (ddd, *J* = 10.3, 4.2, 1.9 Hz, 1H), 3.96 (d, *J* = 4.2 Hz, 1H), 3.50-3.36 (m, 4H), 3.34 (d, *J* = 9.7 Hz, 1H), 3.23 (t, *J* = 9.7 Hz, 1H), 2.66 (ddd, *J* = 14.7, 7.9, 6.8 Hz, 1H), 2.50 (ddd, *J* = 14.7, 7.9, 6.8 Hz, 1H), 1.98-2.10 (m, 2H), 1.76 (dd, *J* = 14.3, 1.9 Hz, 1H), 1.25 (dd, *J* = 14.3, 10.3 Hz, 1H), 0.94 (s, 9H), 0.93 (s, 3H), 0.90 (s, 3H), 0.08 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) □212.9, 103.3, 74.9, 71.2, 65.0, 64.9, 43.8, 35.4, 31.8, 27.4, 26.0, 25.9, 24.0, 18.3, -5.5. HRMS (EI) [M^+] for $C_{18}H_{36}O_5Si$ calcd 360.23382, found: m/z 360.23322. Anal. Calcd for $C_{18}H_{36}O_5Si$: C, 59.96; H, 10.06. Found C 59.99; H, 10.43.

2,4-Dimethoxy-7,7-dimethyloctahydropyrano[3,2]pyrans 11b, 12b and 14b. Hydroxyketone **6b** (180 mg, 0.50 mmol) and camphorsulfonic acid (58 mg, 0.25 mmol) were dissolved in a mixture of CH_2Cl_2 (25 mL) and trimethyl orthoformate in methanol (10 mL of 1:9 mixture), and stirred at room temperature for 3 h, then heated at reflux for 2 days. The cooled mixture was neutralized to pH 8-10 with 2N NaOH. After the layers were separated, the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous $MgSO_4$, and concentrated under vacuum to give three isomeric bis(acetals) **11b**, **12b** and **14b** in a ratio of 20:1:10 (measured by integration of OMe signals in ^1H NMR spectrum). The mixture was purified with the flash chromatography (*t*-BuOMe/hexane, gradient of 1:10 □ 1:6) to give 50 mg (43%) of **11b** and 24 mg (21 %) of **14b**. (The minor isomer, tentatively assigned as **12b**, could not be obtained in sufficient quantity to allow full characterization.)

Bis(acetal) **14b**: R_f 0.70 (Hexane:EtOAc = 1:1); IR ($CHCl_3$ cast film) 2955, 2930, 2885, 2857, 1472, 1093 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) □4.54 (br, d, *J* = 1.8 Hz, 1H), 3.87 (dd, *J* = 3.9, 2.3, Hz 1H), 3.50 (dd, *J* = 10.8, 0.6 Hz, 1H), 3.21 (dd, *J* = 10.8, 2.6 Hz, 1H), 3.14 (s, 9H), 3.05 (s, 9H), 1.98 (dd, *J* = 14.0, 4.0 Hz, 1H), 1.95-1.78 (m, 2H), 1.66-1.76 (m, 1H), 1.51 (dt, *J* = 14.0, 2.4 Hz, 1H), 1.38 (s, 3H), 0.69 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) □ 97.5, 94.1, 70.8, 66.8, 54.3, 46.5, 37.2, 28.5, 28.2, 27.6, 27.1, 26.3. HRMS (ESI) $[M+Na]^+$ for $C_{12}H_{22}O_4Na$ calcd 253.14103, found: m/z 253.14150.

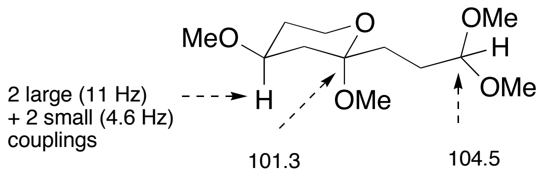
Bis(acetal) **11b**: R_f 0.49 (Hexane:EtOAc = 1:1); IR ($CHCl_3$ cast film) 2953, 2870, 2829, 1470, 1049 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) □4.60 (dd, *J* = 3.8, 0.6, Hz 1H), 4.10 (ddd, *J* = 12.6, 4.6, 0.6 Hz, 1H), 3.43 (dd, *J* = 10.8, 0.7 Hz, 1H), 3.20 (s, 9H), 3.02 (s, 9H), 3.00 (dd, *J* =10.8, 2.1 Hz, 1H), 2.06 (ddd, *J* = 12.5, 12.0, 0.6 Hz, 1H), 1.95 (ddd, *J* = 13.7, 13.7, 4.4 Hz, 1H), 1.86 (ddd, *J* = 13.6, 4.6, 2.6 Hz, 1H), 1.76 (dddd, *J* = 13.6, 13.4, 4.6, 3.8 Hz, 1H), 1.59 (dddd, *J* = 13.3, 3.8, 2.6, 1.1 Hz, 1H), 1.38 (ddd, *J* = 12.0, 4.6, 2.1 Hz, 1H), 1.03 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (125

MHz, C_6D_6) □ 98.2, 95.2, 70.4, 67.7, 54.3, 46.8, 37.0, 34.2, 28.2, 27.5, 25.2, 24.7; HRMS (ESI) $[M+Na]^+$ for $C_{12}H_{22}O_4Na$ calcd 253.14103, found: m/z 253.14121.

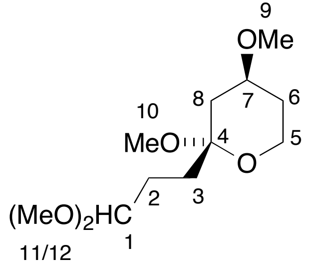
Bis(pyrans) 15b and 16b. To a mixture of bis(acetals) **11b** and **14b** (50 mg, 0.22 mmol), Et_3SiH (350 *μ*L, 2.2 mmol) in dichloromethane (10 mL) was added TMSOTf (189 *μ*L, 1.1 mmol) at 0 °C. The mixture was stirred at room temperature for 24 h. Then the mixture was poured into a $NaHCO_3$ (solid)/ice mixture. The aqueous layer was extracted with dichloromethane (3 x 15 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered, concentrated, and purified by flash chromatography (2 x 20 cm; pentane/Et_2O, gradient of 20:1 □ 10:1) to yield 24 mg (64%) of the bispyran products in a ratio of 15:1 **15b**:**16b** (measured via integration of methyl singlets in the ^{1}H NMR spectrum). Spectral data of major product **15b**: IR (neat) 2953, 1093 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) □ 3.72 (dddd, *J* = 11.4, 4.8,1.6, 1.6 Hz, 1H), 3.33 (dd, *J* = 11.1, 2.4 Hz, 1H), 3.14-3.09 (m, 2H), 3.01 (dd, *J* = 11.0, 0.6 Hz, 1H), 2.80 (ddd, *J* = 11.0, 9.0, 4.4 Hz, 1H), 1.97-1.94 (m, 1H), 1.75 (ddd, *J* = 12.3, 4.5, 2.4 Hz, 1H), 1.54-1.36 (m, 2H), 1.30 (dd, *J* = 11.8, 11.8 Hz, 1H), 0.99 (s, 3H), 0.60 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) □ 79.6, 78.1, 76.4, 67.9, 43.3, 33.1, 30.0, 27.2, 26.3, 25.2; HRMS (EI) $[M^+]$ for $C_{10}H_{18}O_2$ calcd 170.13068, found: m/z 170.13067.

Structural Assignment for Pyran 7:

Key Chemical Shifts and Couplings



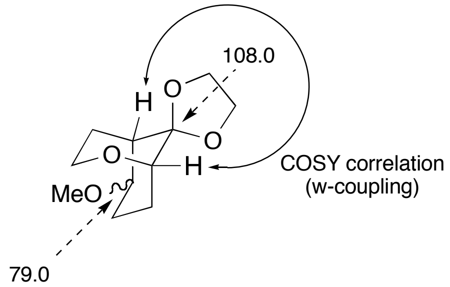
Key HMBC Correlations



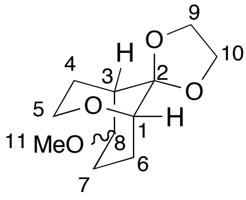
carbon	hydrogens
1	2,3
4	3,5,9,10
7	6,8
9	7
11,12	1

Structural Assignment for Bridged Bicyclic Product 9:

Key Chemical Shifts and Couplings



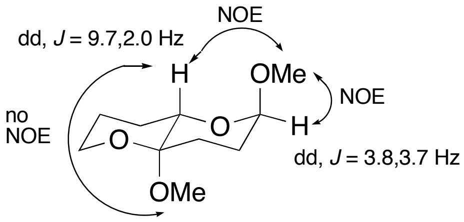
Key HMBC Correlations



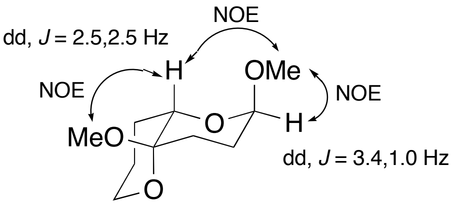
carbon	hydrogens
1	5,6
2	9,10
3	4,5,7
5	1,3,4
11	8

Structural Assignments for Bis(acetals) 11a/14a:

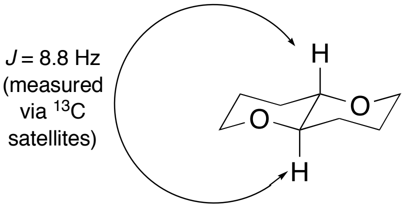
11a:



14a:



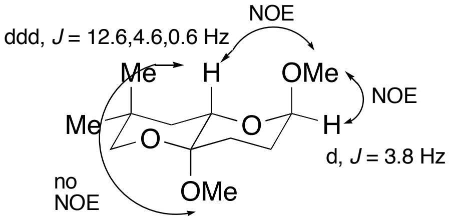
Structural Assignment for Bis(pyran) 15a:



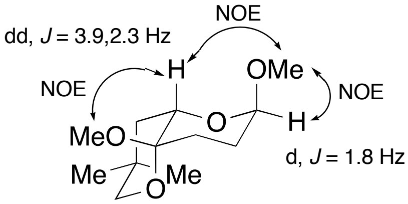
Note: this product showed high symmetry (only 4 carbon resonances), and its spectral data were different from those of the known[1] **16a**.

Structural Assignments for Bis(acetals) 11b/14b:

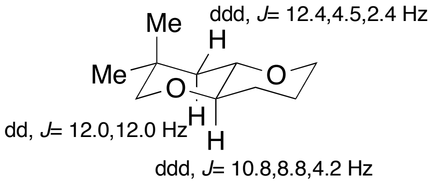
11b:



14b



Structural Assignment for Bis(pyran) 15b:



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[1] Hoffmann, R. W.; Münster, I. *Liebigs Ann. Recl.* **1997**, *6*, 1143–1150.