TOWARD THE TOTAL SYNTHESIS OF VARIECOLIN

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General: NMR spectra were recorded in $CDCl_3$ at 500 MHz for ^1H and 125 MHz for ^{13}C. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel plates using *p*-anisaldehyde for visualization. Flash chromatography was performed using silica gel purchased from ASI (Flash Silica Gel 32-63). All reactions were performed under a dry atmosphere of nitrogen using oven- and/or heat gun-dried glassware unless otherwise stated. Dess-Martin periodinane was purchased from Lancaster. Porcine pancreas lipase was purchased from Sigma-Aldrich (L 3126, EC 3.1.1.3). Other reagents were purchased from Aldrich and Fisher, and were used as received.

***cis*-1-Iodomethyl-2-(methoxymethyl)cyclopentane (12):** Treatment of the known lactone **5** (2.20 g, 15.7 mmol) with $LiAlH_4$ (596 mg, 15.7 mmol, 1 equiv) under standard conditions yielded diol **11** (1.86 g, 14.4 mmol, 92%) which, without purification, was treated with NaH (60% dispersion in oil, 605 mg, 15.1 mmol, 1.05 equiv) in THF (70 mL) followed by alkylation with MeI (1.17 mL, 18.7 mmol, 1.3 equiv) to afford the mono-protected alcohol (1.90 g, 13.5 mmol) as a clear oil. The alcohol (1.95 g, 13.5 mmol) was dissolved in toluene/ THF (5:1, 120 mL), to which was added PPh_3 (10.39 g, 40.5 mmol, 3 equiv), imidazole (1.80 g, 27 mmol, 2 equiv), and iodine (6.7 g, 27 mmol, 2 equiv). The mixture was stirred in the absence of light for 72 h before solvent was removed *in vacuo*. The resultant solid was taken up in Et_2O and filtered through Celite. The solvent was removed *in vacuo*. Flash column chromatography of the oil (silica gel, hexanes) gave the iodo methyl ether **12** as a pale yellow oil (2.41 g, 9.5 mmol, 66% from **11**): IR (thin film) 2954, 2867, 1448, 1181, 1111 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.18 (m, 6H), 2.99-3.17 (apparent t, J=9.5 Hz, 1H), 2.29 (dd, J=15.0, 7.6 Hz, 1H), 2.12 (dd, J=13.5, 6.9 Hz, 1H), 1.81 (apparent d, J=7.6 Hz, 1H), 1.14-1.68 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.73, 58.64, 45.28, 42.08, 32.78, 28.39, 22.91, 9.47; HRMS (CI^+): *m/z* calcd for $C_8H_{16}OI$ $(M+H)^+$ 255.0245, found 255.0247.

(1*R,2*S**)-2-(2-Chloroethyl)-1-[(8*R**,12R*)-(12-methoxymethyl)cyclopent-8-ylmethyl]cyclohexan-1-ol (13):** A solution of SmI_2 in THF (200 mL) was prepared from samarium metal (6.04 g, 40 mmol, 2.55 equiv) and diiodomethane (2.54 mL, 31.5 mmol, 2.5 equiv). The resultant solution was stirred at 0 °C. NiI_2 (10 mg, cat. amount) was added followed 30 min later by a mixture of iodo ether **12** (4.01 g, 15.78 mmol) and chloro ketone **9** (2.5 g, 15.78 mmol, 1 equiv) in THF (40 mL). The reaction was allowed to warm to rt, stirred for a further 16 h and then quenched by the addition of saturated Rochelle's salt solution (20 mL). The aqueous layer was washed with Et_2O (3 x 100 mL) and the combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to yield the crude coupled compound **13** as a 1:1 mixture of diastereomers (3.2 g, 72%). Separation of the diastereomers was achieved by column chromatography (silica gel, Et_2O: hexanes, 1:3): IR (thin film, both diastereomers) 2936, 1724, 1214 cm^{-1}.

First eluted diastereomer, colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 3.85 (broad singlet, 1H), 3.57 (m, 1H), 3.44 (m, 1H), 3.28 (dd, *J*=10.4, 5.9 Hz, 1H), 3.25 (s, 3H), 3.08 (dd, *J*=9.3, 3.7 Hz, 1H), 2.30 (m, 1H), 2.03 (m, 2H), 1.77-1.88 (m, 2H), 1.72 (m, 1H), 1.05-1.61 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 74.23, 71.99, 58.47, 44.38, 43.68, 40.92, 38.44, 36.81, 36.38, 32.69, 32.61, 29.67, 27.19, 25.32, 21.87, 21.85; HRMS (CI^+): *m/z* calcd for $C_{16}H_{30}O_2Cl$ $(M+H)^+$ 289.1934, found 289.1934; LRMS *m/z* (CI^+) 289 (100). Second eluted diastereomer; colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 3.49-3.65 (m, 2H), 3.31 (apparent t, *J*=8.3 Hz, 1H), 3.28 (s, 3H), 3.15 (dd, *J*=9.3, 6.3 Hz, 1H), 2.01-2.21 (m, 4H), 1.15-1.77 (m, 17H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.80, 73.16, 58.64, 44.48, 42.53, 41.20, 39.77, 37.75, 36.96, 32.85, 32.19, 28.66, 26.90, 24.13, 23.00, 22.23; HRMS (CI^+): *m/z* calcd for $C_{16}H_{30}O_2Cl$ $(M+H)^+$ 289.1934, found 289.1931; LRMS *m/z* (CI^+) 289 (100).

(1*R,10*S**)-(*R**,*R**-3,4-Cyclopentyl)-1-[10-(2'-chloroethyl)]oxaspiro[5.5]undecan-2-one (10): 13** (300 mg, 0.1 mmol, first eluted diastereomer) was dissolved in a mixture of MeCN (4 mL), carbon tetrachloride (4 mL) and water (6 mL) to which was added sodium periodate (670 mg, 0.3 mmol, 3 equiv). This was stirred at 0 °C for 15 min before $RuCl_3$•(H_2O)n (25 mg, 10 mol%) was added. The reaction immediately turned black and was allowed to warm to rt. After 2 h a further crystal of $RuCl_3$•(H_2O)n (~10 mg) was added. Further amounts of $RuCl_3$•(H_2O)n (~10 mg) were added every 3 h until the starting material had been consumed as indicated by tlc and GC. Once reaction was complete, the solution was added to 7% aqueous HCl (50 mL) and washed with Et_2O (5 x 50 mL). The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed *in vacuo*. Flash chromatography (silica gel, Et_2O: hexanes, 1:2) yielded the lactone **10** as a colorless oil (180 mg, 65%): IR (thin film) 2936, 1724, 1214 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.57 (apparent t, *J*=7.2 Hz, 1H), 3.46 (m, 1H), 2.78 (dd, *J*=7.2 Hz, 1H), 2.41 (m, 1H), 1.23-2.03 (m, 19H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.25, 83.55, 43.58, 42.19, 42.18, 36.78, 34.58, 34.00, 32.29, 32.02, 30.66, 26.05, 24.76, 24.62, 21.28; HRMS (CI^+): *m/z* calcd for $C_{15}H_{24}O_2Cl$ $(M+H)^+$ 293.1284, found 293.1298; LRMS *m/z* (CI^+) 293 (100) .

(4*R,6a*S**,10a*R**)-Tridecahydro-4-hydroxy-10a-epoxydibenzo[a,d]cyclooctene-1*H*-4 (14)**: SmI_2 was prepared from samarium metal (135 mg, 0.9 mmol, 3 equiv) and diiodomethane (0.06 mL, 0.75 mmol, 2.5 equiv) in THF (20 mL) and stirred at –10 °C. To this was added NiI_2 (5 mg, cat amount) and subsequently lactone **10** (80 mg, 0.3 mmol) in THF (10 mL). The reaction mixture was irradiated and stirred at 0 °C for 9 h after which **10** had been consumed. The reaction mixture was poured into saturated Rochelle's salt solution (10 mL) and washed with Et_2O (3 x 50 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo*. Purification by flash column chromatography (silica gel, Et_2O:hexanes, 1:3) gave a yellow oil (49 mg, 63%), a fraction of which crystallised as a pale yellow crystalline solid: IR (thin film) 3405, 2930, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.65 (broad s, 1H), 2.21-2.31 (m, 1H), 2.05 (ddd, *J*=19.5, 14.2, 8.8 Hz, 1H), 1.13-1.92 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 98.70, 74.57, 51.42, 47.16, 40.69, 38.85, 38.41, 33.63, 31.56, 30.20, 26.30, 26.18, 25.16, 24.49, 21.98; HRMS (CI^+): *m/z* calcd for $C_{15}H_{24}O_2Na$ $(M+Na)^+$ 259.1674, found 259.1675; LRMS (CI^+) *m/z* 259 (89).

Dimethyl *cis*-Cyclohex-4-ene-1,2-dicarboxylate (16): The dimethyl ester **16** was prepared according to a literature procedure[1] using *cis*-1,2,3,6-tetrahydrophthalic anhydride **15** (152 g, 1.0 mol) and methanol. The title compound **16** was obtained in 90% yield (178.3 g).

***meso*-3,4-Bis(methoxycarbonyl)hexanedioic Acid (17):** This material was prepared according to a literature procedure[2] using **16** (80 g, 0.4 mol). The crude diacid **17** was obtained in 90% yield (94.5 g) and was directly used for the next step without any further purification.

Dimethyl *cis*-4-Oxocyclopentane-1,2-dicarboxylate (18): Prepared according to a modified literature procedure.[2] A suspension of the dicarboxylic acid **17** (50 g, 0.19 mol), anhydrous NaOAc (12.5 g, 0.15 mol) and acetic anhydride were heated at reflux for 5 h during which time the reaction mixture turned black. After the reaction mixture had reached rt the formed acetic acid and remaining acetic anhydride were removed on a rotary evaporator (bath temperature 40 °C) and then under high vacuum. The residue was then dissolved in ethyl acetate

(500 mL), filtered through a plug of Celite to remove the precipitate NaOAc, and concentrated *in vacuo*. The resultant black oil was purified by flash chromatography (ethyl acetate:hexanes, 1:1, R_f 0.5) and afforded **18** as white needles after recrystallization from diethyl ether (37 g, 97%); mp 58 °C, lit. 58 °C.[2]

Dimethyl *cis*-6,10-Dioxaspiro[5.4]decane-2,3-dicarboxylate (19): The ketone **18** (37 g, 0.18 mol), 1,3-propanediol (21 g, 0.27 mol) and *p*-toluenesulfonic acid (200 mg) were dissolved in benzene (250 mL) and heated at reflux using a Dean Stark Trap. After 5 h no starting material could be detected by GC and the reaction mixture was allowed to reach rt, diluted with ethyl ether (500 mL) and washed (5 x 200 mL) with saturated aqueous $NaHCO_3$, water (200 mL) and brine (200 mL). After drying the combined organic fractions over Na_2SO_4 and filtering, the solvent was removed on a rotary evaporator to yield **19** as a yellow oil (44.2 g, 95%) which solidified upon standing at 0 ^oC; mp 51 °C, lit 52 °C.[2] Analytical data for **19** was consistent with that previously reported.[2]

***cis*-3,4-Bis(hydroxylmethyl)-6,10-dioxaspiro[4.5]decane (20):** A solution of the diester **19** (45 g, 0.17 mol) in tetrahydrofuran (250 mL) was added dropwise via canula to a mechanically stirred solution of $LiAlH_4$ (18 g, 0.47 mol) in tetrahydrofuran at 0 °C. After the addition was completed the reaction mixture was allowed to warm to rt and was stirred for another 5 h at that temperature. The reaction mixture was then diluted with ethyl ether (300 mL), cooled to 0 °C, and carefully hydrolyzed with water (18 mL), 15% sodium hydroxide solution (18 mL) and water (54 mL) again. The precipitate was filtered off, washed with ethyl ether (5 x 200 mL) and the combined filtrates were dried over Na_2SO_4 and filtered. Evaporation of the solvent gave **20** (30 g, 85%) as a pale yellow oil. Further purification was unnecessary: IR (neat) 3386, 2935, 2872, 1475, 1433, 1369, 1327, 1292, 1251, 1216, 1148, 1106, 1025, 964, 933 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.86 (m, 4H), 3.74-3.68 (m, 4H), 3.28-3.03 (br, 2H), 2.14 (m, 2H), 2.04 (m, 2H), 1.75-1.25 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 108.2, 63.0, 61.7, 61.4, 41.1, 38.2, 25.6; HRMS (CI^+): *m/z* calcd for $C_{10}H_{19}O_4$ $(M+H)^+$ 203.1283, found 203.1277.

***cis*-3,4-Bis(acetoxymethyl)-6,10-dioxaspiro[4.5]decane (21):** To a stirred solution of the diol **20** (10 g, 0.05 mol) in dry pyridine (30 mL) was slowly added acetic anhydride (22 mL, 0.23 mol) at 0 °C. The reaction mixture was kept 1 h at this temperature, then stirred for another 24 h at rt followed by cooling the reaction mixture again to 0 °C. Methanol (10 mL) was then slowly added to the reaction mixture which was stirred for 1 h. Evaporation of the solvent under reduced pressure and drying of the residue under high vacuum for 12 h furnished crude diacetate **21** (14.3

g, 98%). Further purification was not required: IR (neat) 2964, 2864, 1738, 1434, 1369, 1328, 1248, 1153, 1110, 1035 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.14 (dd, *J*=6.8, 11.2 Hz, 2H), 4.04 (dd, *J*=6.8, 11.2 Hz, 2H), 3.89-3.83 (m, 4H), 2.50-2.48 (m, 2H), 2.21-2.17 (m, 2H), 2.04 (s, 6H), 1.83-1.79 (m, 2H), 1.71-1.69 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 171.0, 108.0, 64.4, 61.8, 61.3, 38.5, 37.9, 25.5, 21.0; HRMS (CI$^+$): *m/z* calcd for $C_{14}H_{23}O_6$ $(M+H)^+$ 287.1500, found 287.1495.

***cis*-3,4-Bis(hydroxymethyl)cyclopentanone (22):** The diacetate **21** (9 g, 0.03 mol) was dissolved in wet acetone (400 mL) and pyridinium *p*-toluenesulfonate was added. The mixture was heated at reflux for 5 h before being concentrated on a rotary evaporator. The crude product was dissolved in dichloromethane and washed with saturated aqueous $NaHCO_3$ solution. The organic phase was dried over Na_2SO_4 and filtered, and the solvent was removed *in vacuo* to furnish crude **22**. This material was subsequently stirred in methanol (250 mL) with potassium carbonate (2.0 g, 0.014 mol). After the starting material had been consumed, the reaction mixture was carefully quenched with 15% $KHSO_4$ to pH 6 followed by extraction with dichloromethane (5 x 200 mL). Flash chromatography (silica gel, ethyl acetate, R_f 0.1) furnished **22** (3 g, 80%): IR (neat) 3382, 2934, 2223, 1731, 1659, 1402, 1259, 1171, 1029 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.85-3.78 (m, 4H), 3.12 (br, 2H), 2.66-2.64 (m, 2H), 2.35 (dd, *J*=9.0, 19.1 Hz, 2H); 2.22 (dd, *J*=7.1, 19.2Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 217.9, 62.6, 40.8, 40.0; HRMS (CI$^+$): *m/z* calcd for $C_7H_{13}O_3$ $(M+H)^+$ 145.0865, found 145.0872.

Immobilisation of crude PPL on Kieselgur: Crude PPL (porcine pancreas lipase, purchased from Sigma-Aldrich L 3126, EC 3.1.1.3) (10 g) was added to a magnetically stirred buffer solution (100 mL, pH=7, 0.1 M, Fluka 82637) at rt. After the addition had been completed the mixture was stirred another 30 min at rt followed by dividing the mixture into two equal amounts (weight) and centrifugation (3000 U/min, rt) for 30 min. The supernatant, slightly cloudy liquid was carefully decanted off, poured into a three neck round bottom flask equipped with an overhead stirrer and thermometer, and cooled to 0 °C. To this solution was slowly added, under stirring, Hyflo Super Cel (Fluka, 56678), followed by 150 mL of acetone (HPLC-grade) at 0 °C (approximately 30 min). After the addition was completed the mixture was stirred another 30 min at 0 °C and then filtered through a glass frit. The immobilized enzyme was then dried for 4 d under high vacuum (0.03 mm Hg) to remove water. This important drying procedure was repeated until no mass loss was observed. Immobilized crude PPL was stored in a tightly closed container at rt. No loss of activity was observed over a period of 3 months.

(3*R*,4*S*)-3-Acetoxymethyl-4-(hydroxymethyl)cyclopentanone (23): A round bottom flask equipped with a magnetic stirrer bar was charged with the diol **22**, dry vinyl acetate (90 mL) and immobilized PPL (4 g). The reaction mixture was vigorously stirred until all the diol had been consumed and approximately 30% diacetate had been formed. The catalyst was then filtered off through a glass frit and washed with diethyl ether (3 x 200 mL). The combined filtrates were evaporated and the residue was purified by flash chromatography yielding **23** as a colorless oil (0.66 g, 48%). The enantiomeric excess (ee = 96%) was determined using a chiral GC column (Supelco β-Dex 120, 15 m, 160 °C isothermal, Inj. 250 °C, Det. 250 °C) R_t = 18.5 min (3*R*, 4*S*); R_t = 19.5 min (3*S*, 4*R*): $[\alpha]_D^{20}$ =+16.60; (*c* = 1.25, $CHCl_3$); IR (neat) 3453, 2901, 1732, 1370, 1246, 1169, 1035 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.25 (dd, *J*=6.4, 11.4 Hz, 1H), 4.19 (dd, *J*=6.6, 11.4 Hz, 1H), 3.77 (dd, *J*=5.5, 10.8 Hz, 1H), 3.73 (dd, *J*=6.0, 10.8 Hz, 1H), 2.75-2.73 (m, 1H), 2.60-2.58 (m, 1H), 2.39-2.33 (m, 3H), 2.25-2.20 (m, 2H), 2.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.3, 170.9, 64.6, 62.5, 41.6, 41.4, 39.4, 36.8; 20.7; HRMS (CI^+): *m/z* calcd for $C_9H_{15}O_4$ $(M+H)^+$ 187.0970, found 187.0970.

(3*R*,4*S*)-3-(Methylxanthyloxy)methyl-4-(hydroxymethyl)cyclopentanone (24): A solution of the monoacetate **23** (2 g, 10.7 mmol) and carbon disulfide (7 mL, 116 mmol) in dry DMF (50 mL) was stirred at rt, to which was added DBN (3.5 mL, 28.0 mmol). The red-orange mixture was stirred at rt for 30 min. To this was added dropwise methyl iodide (13.7 mL, 210 mmol) and stirring was continued for 45 min. The reaction mixture was concentrated *in vacuo* and taken up in dichloromethane (200 mL). The organic solution was washed with water (3 x 100 mL), 15% $KHSO_4$ (10 mL), brine (100 mL), dried over Na_2SO_4, and filtered. Concentration *in vacuo* gave crude **24**. Flash chromatography (silica gel, hexanes:ethyl acetate, 3:1, R_f 0.3) furnished pure **24** (2.1 g, 71%) as a yellow oil. The enantiomeric purity was checked by chiral HPLC (column: Chiralpak AD, eluent: hexanes:iso-propanol, 95:5, 1.0 mL/min, R_t 13.9 min, 15.2 min for the racemate). No racemization occurred during this transformation: $[\alpha]_D^{20}$ = -4.5 (*c* = 1.43, $CHCl_3$); IR (neat) 2956, 1741, 1404, 1367, 1239, 1066 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.66 (d, *J*=6.4 Hz, 2H), 4.18-4.14 (m, 2H), 2.94-2.90 (m, 1H), 2.79-2.76 (m, 1H), 2.54 (s, 3H), 2.46-2.39 (m, 2H), 2.26-2.22 (m, 2H), 2.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.8, 215.3, 170.7, 73.1, 64.0, 41.3, 40.9, 36.7, 36.6, 20.8, 19.2; HRMS (CI^+): *m/z* calcd for $C_{11}H_{17}O_4S_2$ $(M+H)^+$ 277.0568, found 277.0571.

(3*R*,4*R*)-3-Acetoxymethyl-4-methylcyclopentanone (25): A solution containing the xanthate **24** (2 g, 7.2 mmol), triethylsilane (3.3 g, 28.7 mmol), di-*tert*-butyl peroxide (0.2 g, 1.36

mmol), and *tert*-dodecanethiol (57 μL, 0.24 mmol) in octane (200 mL) was stirred and heated at reflux for 24 h. The mixture was allowed to cool and excess silane and octane were removed on a rotary evaporator. The residual oil was purified by flash chromatography (silica gel, hexanes:ethyl acetate, 3:1, R_f 0.4) to give **25** (0.9 g, 75%) as a slightly yellow oil: $[\alpha]_D^{20}$ = +25.1 (c = 1.12, $CHCl_3$); IR (neat) 2962, 1740, 1405, 1369, 1240, 1162 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.13 (dd, J=6.1, 11.4 Hz, 1H), 4.10 (dd, J=6.4, 11.0 Hz, 1H), 2.56-2.53 (m, 2H), 2.34-2.31 (m, 2H), 2.11-1.97 (m, 5H), 1.0 (d, J=6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.7, 170.9, 64.6, 46.3, 40.5, 38.2, 31.9, 20.8, 15.0; HRMS (CI^+): m/z calcd for $C_9H_{15}O_3$ $(M+H)^+$ 171.1021, found 171.1027.

(3*R*,4*R*)-3-Hydroxymethyl-4-methylcyclopentanone (26): To a stirred solution of **25** (0.7 g, 4.11 mmol) in methanol (150 mL) was added potassium carbonate (0.22 g, 1.6 mol). After all the starting material had been consumed the reaction mixture was quenched with saturated aqueous NH_4Cl solution, carefully acidified with a 15% $KHSO_4$ solution to pH6, and extracted with dichloromethane (3 x 150 mL). The organic phase was separated, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give pure **26** (0.5 g, 95%) as a colorless liquid: $[\alpha]_D^{20}$ = +29.9 (c = 1.01, $CHCl_3$); IR (neat) 3408, 2960, 1731, 1402, 1165, 1025 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.73-3.69 (m, 2H), 2.53-2.03 (m, 6H), 1.85 (br, 1H), 1.01 (d, J=7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 219.4, 62.9, 46.6, 41.4, 40.5, 31.9, 14.9; HRMS (CI^+): m/z calcd for $C_7H_{13}O_2$ $(M+H)^+$ 129.0915, found 129.0914.

(3*R*,4*R*)-3-Hydroxymethyl(carboxyethyl)-4-methylcyclopentanone (27): To a solution of **26** (0.6 g, 4.68 mmol), DMAP (0.1 g, 0.8 mmol) and pyridine (0.8 g, 9.50 mmol) in tetrahydrofuran (30 mL) was added ethyl chloroformate (0.56 g, 5.22 mmol) dropwise. The reaction mixture was stirred for 18 h at rt. The mixture was diluted with ethyl acetate (200 mL), then washed with a 2 M solution of HCl and brine. The organic phase was dried over Na_2SO_4 and filtered. The solvent was removed *in vacuo* to furnish crude **27**. Flash chromatography (silica gel, hexanes:ethyl acetate, 1:1, R_f 0.8) gave **27** (0.8 g, 85%) as a colorless oil: $[\alpha]_D^{20}$ = +36.4 (c = 1.13, $CHCl_3$); IR (neat) 2964, 1743, 1465, 1406, 1369, 1259, 1161, 1011, 873 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.22-4.15 (m, 4H), 2.62-2.54 (m, 2H), 2.42-2.31 (m, 2H), 2.14-2.00 (m, 2H), 1.30 (t, J=6.6 Hz, 3H), 1.01 (d, J=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.4, 155.0, 67.8, 64.1, 46.5, 39.8, 38.4, 31.7, 14.8, 14.2; HRMS (CI^+): m/z calcd for $C_{10}H_{17}O_4$ $(M+H)^+$ 201.1126, found 201.1124; Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.97; H, 8.06. Found: C, 59.52; H, 8.0.

(3a*R*,4*R*,6a*R*)-4-Methyltetrahydrocyclopenta[c]furan-1,6-dione (29): To a solution of **27** (0.67 g, 3.35 mmol) in tetrahydrofuran was added dropwise a solution of KO-*t*-Bu in THF (3.35 mL, 1.0 M solution) at -60 °C. The reaction was stirred for 1 h before quenching with saturated aqueous NH_4Cl solution. Extraction of the reaction mixture with ethyl acetate (200 mL), drying over Na_2SO_4, filtering, and evaporation of the solvent furnished a 1:1 mixture of the lactone **29** and **28**. The crude product was dissolved in benzene (100 mL) with *p*-toluenesulfonic acid (10 mg) and heated at reflux for 1 h. The reaction was allowed to cool, diluted with ethyl ether (200 mL), and washed with saturated aqueous $NaHCO_3$ solution (50 mL) and water (100 mL). The organic phase was dried over Na_2SO_4 and filtered. The solvent was removed *in vacuo* to give crude **29**. This was purified by flash chromatography (silica gel, hexanes:ethyl acetate, 1.1, R_f 0.2) yielding pure **29** (0.5 g, 96%) as a white solid: mp 82 - 84 °C; $[\alpha]_D^{20}$ = -170.2 (*c* = 1.04, $CHCl_3$); IR (neat) 2974, 1780, 1737, 1182, 1137 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.48 (t, *J*=9.9 Hz, 1H), 4.26 (dd, *J*=7.4, 9.9 Hz, 1H), 3.46-3.43 (m, 1H), 3.34 (d, *J*=9.2 Hz, 1H), 2.63-2.57 (m, 2H), 2.16-2.14 (m,1H), 1.15 (d, *J*=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 170.2, 67.3, 55.0, 44.0, 42.2, 30.6, 15.2; HRMS (CI^+): *m/z* calcd for $C_8H_{11}O_3$ $(M+H)^+$ 155.0708, found 155.0706; Anal. Calcd for $C_8H_{10}O_3$: C, 62.31; H, 6.54. Found: C, 62.03; H, 6.60.

(7a*R*,1*R*)-7a-Methyl-5-oxo-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-ol, Pivaloate Ester (32): To a stirred solution of the Hajos-Parrish ketone **31** (30.5 g, 0.186 mol) in absolute ethanol (300 mL) at –78 °C was added $NaBH_4$ (1.8 g, 48 mmol) over a period of 1 h using a powder addition funnel. The reaction mixture was allowed to warm to 5 °C and then cooled to –10 °C at which temperature the pH was adjusted to between 5 and 7 with 1.2 N HCl. The mixture was concentrated under reduced pressure. Ethyl acetate and water were added to the residue. The aqueous phase was extracted twice with ethyl acetate and the combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure affording the alcohol as a yellow solid, which was used in the next step without purification. To a stirred solution of the alcohol and of DMAP (0.170 g, 1.39 mmol) in anhydrous pyridine (190 mL) was added at 0 °C trimethylacetyl chloride (29.2 g, 29.8 mL, 0.242 mol) over a period of 15 min. The mixture was stirred 15 min at 0 °C and 17 h at rt. The reaction was quenched with water and the mixture was extracted three times with ether. The organic phase was successively washed with 1 M HCl, saturated aqueous $CuSO_4$ (twice), saturated aqueous NH_4Cl (twice) and brine. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, gradient elution, 20 to 30% EtOAc in petroleum ether) affording the ester **32** (37.8 g, 0.151 mmol, 81% from **31**) as a pale yellow oil: $[\alpha]_D^{25}$ = –31.2 (*c* = 1.34, $CHCl_3$); IR (film) 2976, 1728, 1674, 1282, 1205, 1153 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.75 (s, 1H), 4.75-4.71 (m, 1H), 2.72-2.68 (m, 1H), 2.45-2.20 (m, 4H), 1.95-1.93 (m, 1H), 1.84-1.78 (m, 2H), 1.17 (s, 9H), 1.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 177.9, 172.8, 123.4, 80.5, 44.7, 38.8, 34.2, 33.1, 27.1, 26.5, 26.2, 16.5; Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: 71.75; H, 9.01.

(7a*R*,1*R*)-4-(2-Benzyloxyethyl)-7a-methyl-5-oxo-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-ol, Pivaloate Ester: (33): A mixture of NaH (0.19 g, 4.84 mmol, 60% in mineral oil, washed 3 times with anhydrous hexanes) in anhydrous DMSO (4 mL) was stirred at 55 °C until evolution of hydrogen gas ceased (ca. 2 h). To the resulting solution was added anhydrous THF (15 mL) and the mixture was cooled to –78 °C. A solution of the indanone **32** (1.01 g, 4.04 mmol) in anhydrous DMSO (4 mL) was added to the mixture. The mixture was allowed to warm to rt and was stirred for 1.5 h. A solution of benzyl 2-iodoethyl ether (1.16 g, 4.44 mmol) in anhydrous DMSO (2 mL) was added to the mixture. The mixture was stirred for 6 h at the same temperature and quenched with a mixture of saturated aqueous NH_4Cl and ice. The mixture was extracted three times with ether and the combined organic phase was washed with brine and dried with $MgSO_4$. The solvent was removed under reduced pressure to give a residue that was purified by flash chromatography (silica gel, 20% EtOAc in petroleum ether) affording the alkylated indanone **33** (0.946 g, 2.46 mmol, 61%) as a viscous pale yellow oil: $[\alpha]^{25}_D$ = –11.6 (*c* = 1.03, $CHCl_3$); IR (film) 2971, 1731, 1660, 1282, 1156, 1104 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34-7.27 (m, 5H), 4.78 (t, *J*=8.8 Hz, 1H), 4.46 (s, 2H), 3.47 (t, *J*=6.7 Hz, 2H), 2.69-2.49 (m, 5H), 2.39 (dd, *J*=18.0, 3.55 Hz, 1H), 2.25-2.22 (m, 1H), 1.96-1.79 (m, 3H), 1.23 (s, 9H), 1.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 178.0, 168.3, 138.6, 130.3, 128.2, 127.4, 127.3, 80.7, 72.7, 68.8, 44.8, 38.9, 33.8, 33.2, 27.1, 26.44, 26.36, 25.6, 16.8; HRMS (CI^+): *m/z* calcd for $C_{24}H_{33}O_4$ $(M+H)^+$ 385.2378, found 385.2367.

(1*R*,3a*S*,5a*R*,6*R*,8a*R*)-3a-Methoxy-5a-methyl-3-oxoinden-6-ol, Pivaloate Ester: (34): To a stirred green solution of $NiCl_2•6H_2O$ (2.38 g, 10.0 mmol), and alkylated indanone **33** (0.771 g, 2.01 mmol) in MeOH (50 mL) at –78 °C was added $NaBH_4$ (0.76 g, 20.1 mmol) over a period of 20 min using a powder addition funnel. The cooling bath was removed and the mixture was stirred for 10 min. Then, silica gel (10 g) was added and the mixture was stirred for 20 min. The mixture was filtered through a silica gel pad. The solvent was removed *in vacuo* and the crude product was used without further purification. [Analytical data for purified (silica gel, 30%

EtOAc in petroleum ether) *trans*-fused ketone; colorless oil: $[\alpha]_D^{25} = -7.4$ ($c = 1.24$, $CHCl_3$); IR (film) 2971, 1726, 1284, 1162 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35-7.26 (m, 4H), 4.63 (t, *J*=8.5 Hz, 1H), 4.47 (dd, *J*=12.0, 16.2 Hz, 2H), 3.61-3.56 (m, 1H), 3.51-3.46 (m, 1H), 2.51-2.28 (m, 4H), 1.93-1.86 (m, 2H), 1.74-1.52 (m, 7H), 1.21 (s, 9H), 1.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.7, 178.3, 138.6, 128.3, 127.6, 127.5, 80.7, 72.7, 68.4, 49.8, 47.2, 43.1, 38.8, 37.6, 35.6, 28.1, 27.2, 26.8, 24.4, 11.6.] To a stirred solution of the crude *trans*-fused ketone in anhydrous methanol (15 mL) was added 10% palladium on charcoal (105 mg). The mixture was stirred for 1.5 h under 1 atm of hydrogen and then filtered through Celite. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica gel, 20% EtOAc in petroleum ether) affording the ketal **34** (0.325 g, 1.05 mmol, 52%) as a colorless oil: $[\alpha]^{25}_D = +18.4$ ($c = 1.72$, $CHCl_3$); IR (film) 2971, 1729, 1164 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.55 (t, *J*=8.0 Hz, 1H), 3.89 (dd, *J*=8.1, 16.2 Hz, 1H), 3.82-3.78 (m, 1H), 3.20 (s, 3H), 2.20-2.17 (m, 2H), 2.00-1.97 (m, 1H), 1.71-1.20 (m, 9H), 1.18 (s, 9H), 0.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4, 107.8, 81.5, 65.1, 48.0, 45.8, 45.2, 42.5, 38.9, 33.2, 27.8, 27.3, 27.2, 26.7, 24.0, 10.7; HRMS (CI^+): *m/z* calcd for $C_{18}H_{30}O_4$ $(M)^+$ 310.2144, found 310.2131.

(1*R*,3a*S*,5a*R*,8a*R*)-3a-Methoxyl-5a-methyldecahydro-3-oxa-*as*-indacen-6-one (35): To a stirred solution of the ketal **34** (0.395 g, 1.27 mmol) in anhydrous THF (15 mL) at 0 °C was added a solution of $LiAlH_4$ in ether (1 M, 1.3 mL, 1.3 mmol). The mixture was stirred at 0 °C for 70 min and then sodium potassium tartrate solution was added and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (30% EtOAc in petroleum ether) affording the alcohol (0.188 g, 0.831 mmol, 65%) as a white solid: $[\alpha]_D^{25} = +33.8$ ($c = 1.12$, $CHCl_3$); IR ($CHCl_3$) 3024, 2957, 1207, 1107, 1028, 792, 666 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.85 (dd, *J*=8.0, 16.1 Hz, 1H), 3.79-3.76 (m, 1H), 3.60 (t, *J*=8.4 Hz, 1H), 3.18 (s, 3H), 2.19-1.92 (m, 5H), 1.71-1.4 (m, 5H), 1.27-1.06 (m, 3H), 0.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.9, 80.8, 65.1, 47.9, 45.9, 45.3, 42.6, 32.9, 30.4, 27.1, 26.7, 23.6, 9.6; Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: 68.59; H, 9.89. To a stirred solution of the alcohol (0.188 g, 0.831 mmol) in CH_2Cl_2 (3 mL) was added the Dess-Martin periodinane (0.39 g, 1.821 mmol). The mixture was stirred at rt for 50 min. Saturated aqueous $NaHCO_3$ and 10% aqueous $Na_2S_2O_3$ were added. The aqueous phase was extracted three times with ether. The organic extracts were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica gel, gradient elution, 30 to 40% EtOAc in petroleum ether) affording the ketone **35** (0.161 g, 0.72 mmol, 57% from **34**) as a white crystalline solid: mp 59-60 °C; $[\alpha]_D^{25}$ = –27.8 (*c* = 1.48, $CHCl_3$); IR ($CHCl_3$) 1736 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.90 (dd, *J*=8.2, 16.2 Hz, 1H), 3.84-3.80 (m, 1H), 3.20 (s, 3H), 2.45 (dd, *J*=11.1, 19.4 Hz, 1H), 2.28-2.23 (m, 2H), 2.12-2.09 (m, 2H), 1.96-1.91 (m, 1H), 1.75-1.69 (m, 3H), 1.6-1.5 (m, 1H), 1.40-1.32 (m, 2H), 0.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 219.6, 107.7, 65.0, 48.0, 47.4, 46.3, 44.9, 36.0, 28.0, 26.6, 26.4, 22.1, 12.3; HRMS (CI^+): *m/z* calcd for $C_{13}H_{20}O_3$ $(M+H)^+$ 224.1412, found 224.1404.

(1*R*,3a*S*,5a*R*,8a*R*)-3a*S*-Methoxy-5a-methyl-1,2,3a,4,5,5a,8,8a,8b-octahydro-3-oxa-*as*-indacen-6-one (36): To a solution of diisopropylamine (2.07 mL, 1.49 g, 14.7 mmol) in THF (20 mL) at –78 °C was added *n*-BuLi (1.6 M in hexanes, 9.2 mL, 14.7 mmol). The mixture was stirred at –78 °C for 35 min. A solution of the ketone **35** (1.04 g, 4.62 mmol) in THF (5 mL) was added dropwise over a period of 5 min and the reaction mixture was stirred at –78 °C for 45 min. Then, triethylamine (2.7 mL, 19.7 mmol) and TMSCl (1.7 mL, 13.3 mmol) were added. The mixture was allowed to warm to rt, stirred for 35 min, and quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted twice with ether and the combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude enol ether was then dissolved in CH_2Cl_2 (21 mL) and CH_3CN (7 mL). Palladium(II) acetate (1.3 g, 5.9 mmol) was added in one portion. The reaction mixture was stirred for 4.5 h at 35-40 °C. After filtration through a silica gel pad (silica gel, 50% EtOAc in petroleum ether), the solvent was removed under reduced pressure. Purification of the residue by flash chromatography (30% EtOAc in petroleum ether) provided **36** (0.806 g, 3.55 mmol, 77% yield) as a pale yellow oil: $[\alpha]_D^{25}$ = +114.8 (*c* = 1.17, $CHCl_3$); IR (film) 2940, 1714, 1076, 1023 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J*=5.2 Hz, 1H), 6.09 (dd, *J*=2.5, 5.2 Hz, 1H), 3.95-3.86 (m, 2H), 3.25 (s, 3H), 2.41-2.33 (m, 4H), 1.91-1.58 (m, 4H), 1.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.8, 158.4, 132.5, 108.3, 64.7, 52.0, 50.7, 48.1, 42.6, 27.4, 26.6, 26.1, 18.8; HRMS (CI^+): *m/z* calcd for $C_{13}H_{18}O_3$ $(M)^+$ 222.1256, found 222.1258.

(1*R*,3a*S*,5a*R*,8*S*,8a*R*)-8-Isopropenyl-3a-methoxy-5a-methyldecahydro-3-oxa-*as*-indacen-6-one (37): To a stirred solution of 2-bromopropene (0.120 g, 0.996 mmol) in THF (1 mL) at –78 °C was added *n*-BuLi (1.6 M in hexanes, 1.25 mL, 2.0 mmol). The solution was stirred at –78 °C for 45 min. CuCN (0.0446 g, 0.498 mmol) was added. The mixture was warmed to 0 °C and stirred until the CuCN dissolved (15 min). The solution was cooled to –78 °C and a solution of the enone **36** (0.0982 g, 0.442 mmol) in THF (1 mL) was added. The solution was stirred at –78 °C for 2 h and then quenched with aqueous NH_4Cl. The aqueous phase was extracted three times with ether. The organic extracts were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. Purification of the residue by flash chromatography (silica gel, 30% EtOAc in petroleum ether) gave the ketone **37** (0.0961 g, 0.364 mmol, 82% yield) as a white solid: mp 92 °C; $[\alpha]_D^{25} = -25.4$ (c = 0.56, $CHCl_3$); IR ($CHCl_3$) 1730, 734, 675 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.00 (s, 1H), 4.84 (s, 1H), 3.97-3.92 (m, 1H), 3.87-3.84 (m, 1H), 3.22 (s, 3H), 2.94 (t, J=7.5 Hz, 1H), 2.74 (d, J=19.5 Hz, 1H), 2.50-2.34 (m, 4H), 2.0-1.6 (m, 4H), 1.85 (s, 3H), 1.33-1.26 (m, 1H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.9, 145.8, 113.6, 108.1, 64.7, 50.3, 48.0, 47.1, 43.8, 43.4, 40.1, 30.8, 27.7, 26.5, 25.1, 15.8; HRMS (CI^+): m/z calcd for $C_{16}H_{24}O_3$ $(M)^+$ 264.1725, found 264.1732; Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: 72.74; H, 8.92.

(1*R*,3a*S*,5a*R*,8a*R*,8*S*)-8-Isopropenyl-3a-methoxy-5a-methyldecahydro-3-oxa-*as*-indacene (38): To a stirred solution of the ketone **37** (0.121 g, 0.458 mmol) in diethylene glycol (5 mL) was added hydrazine hydrate (0.75 mL, 4.58 mmol) and potassium carbonate (0.60 g, 4.58 mmol). The mixture was heated to 150 °C for 1 h. The condenser was removed and the temperature was increased to 200 °C. After the excess of hydrazine and water had boiled off (40 min), the condenser was replaced and the bath temperature was maintained at 205 °C for 1.5 h. The mixture was cooled and partitioned between hexanes and 10% hydrochloric acid. The organic layer was separated, washed with another portion of 10% hydrochloric acid, with water, and with saturated aqueous $NaHCO_3$. The mixture was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 15% EtOAc in petroleum ether) affording the ketal **38** (0.0602 g, 0.240 mmol, 52%) as a colorless oil: $[\alpha]_D^{25} = +64.5$ (c = 1.05, $CHCl_3$); IR (film) 2952, 1107, 1084, 1057, 1028, 897 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.79 (s, 1H), 4.77 (s, 1H), 3.91 (dd, J=8.1, 14.9 Hz, 1H), 3.80-3.76 (m, 1H), 3.20 (s, 3H), 2.84 (dd, J=9.5, 17.1 Hz, 1H), 2.29-2.14 (m, 3H), 2.0-1.5 (m, 7H), 1.75 (s, 3H), 1.24-1.20 (m, 2H), 0.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 113.1, 108.6, 65.0, 52.8, 47.9, 45.5, 43.5, 41.1, 40.3, 37.0, 29.5, 28.4, 27.3, 23.7, 18.7; HRMS (CI^+): m/z calcd for $C_{16}H_{26}O_2$ $(M)^+$ 250.1933, found 250.1926.

(1*R*,3a*S*,5a*R*,8a*R*,8*S*)-8-Acetyl-3a-methoxy-5a-methyldecahydro-3-oxa-*as*-indacene (39): Ketal **38** (0.670 g, 2.676 mmol) was dissolved in dichloromethane (42 mL), methanol (14mL) and pyridine (1mL). The solution was cooled to –78 °C and ozone was bubbled through the solution until the starting material was consumed (40 min). Dimethyl sulfide was added (1 mL) and the solution was warmed slowly to room temperature. After stirring at room temperature overnight, the volatiles were evaporated. The residue was purified by chromatography (silica gel treated with 2.5% v/v of triethylamine, 10% ethyl acetate in hexanes) to obtain ketone **39** (0.585 g, 2.318 mmol, 87%) as a colorless oil. $[\alpha]_D^{22}$ = +104.2 (*c* = 1.0, $CHCl_3$); IR (film) 2941, 1707, 1452, 1352, 1251, 1167, 1110, 1086, 1055, 1024, 937, 896 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.90-4.00 (m, 1H), 3.75-3.85 (m, 1H), 3.19 (s, 3H), 3.0-3.1 (m, 1H), 2.45-2.55 (m, 1H), 2.30-2.40 (m, 1H), 2.05-2.15 (m, 1H), 2.12 (s, 3H), 1.90-2.10 (m, 1H), 1.55-1.80 (m, 2H), 1.55-1.65 (m, 2H), 1.40-1.50 (m, 1H), 1.15-1.30 (m, 3H), 0.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.5 (C), 108.3 (C), 64.8 (CH_2), 53.3 (CH), 50.2 (CH), 47.9 (CH_3), 42.6 (CH), 41.3 (C), 40.1 (CH_2), 35.9 (CH_2), 31.2 (CH_3), 29.0 (CH_2), 26.8 (CH_2), 25.9 (CH_2), 17.1 (CH_3); HRMS (CI^+): *m/z* calcd for $C_{15}H_{23}O_3$ $(M - H)^+$ 251.1646, found 251.1627.

(1*R*,3a*S*,5a*R*,8a*R*,8*R*)-8-Acetyl-3a-methoxy-5a-methyldecahydro-3-oxa-*as*-indacene (40): To a stirred solution of ketone **39** (0.560 g, 2.219 mmol) in methanol (10 mL) was added sodium methoxide (97 mg, 1.80 mmol). After overnight stirring, water was added and the resulting mixture was extracted twice with dichloromethane. The solution was dried with magnesium sulfate and the solvents were removed at reduced pressure to afford ketone **40** (0.560 g, 2.219 mmol, 100%) as a colorless oil. $[\alpha]_D^{22}$ = -8.4 (*c* = 1.0, $CHCl_3$); IR (film) 2941, 1707, 1452, 1352, 1251, 1167, 1110, 1086, 1055, 1024, 937, 896 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.90 (q, J = 8.5 Hz 1H), 3.75-3.85 (m, 1H), 3.19 (s, 3H), 2.71 (td, J_1 = 6.0 Hz, J_2 = 11.0 Hz, 1H), 2.05-2.25 (m, 3H), 2.18 (s, 3H), 1.93 (dd, J_1 = 6.5 Hz, J_2 = 11.0 Hz, 1H), 1.65-1.80 (m, 2H), 1.55-1.65 (m, 2H), 1.45-1.55 (m, 1H), 1.30-1.45 (m, 3H), 0.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.8 (C), 108.1 (C), 65.2 (CH_2), 53.5 (CH), 50.5 (CH), 48.0 (CH_3), 45.5 (CH), 42.3 (C), 38.8 (CH_2), 34.5 (CH_2), 29.9 (CH_3), 28.0 (CH_2), 27.5 (CH_2), 27.0 (CH_2), 16.8 (CH_3); HRMS (CI^+): *m/z* calcd for $C_{15}H_{23}O_3$ $(M - H)^+$ 251.1646, found 251.1645.

(1*R*,3a*S*,5a*R*,8a*R*,8*R*)-8-Isopropenyl-3a-methoxy-5a-methyldecahydro-3-oxa-*as*-indacene (41): To a stirred suspension of methyltriphenylphosphonium bromide (1.146 g, 3.21 mmol) in ethyl ether (25 mL) under a nitrogen atmosphere was added potassium *tert*-butoxide (0.360 g, 3.21 mmol). The yellow suspension was stirred at room temperature for 40 minutes. After this time, a solution of ketone **40** (0.450 g, 1.783 mmol) in ether (10 mL) was added. The reaction mixture was stirred at room temperature for 6 h. About two thirds of the solvent were removed at reduced pressure and the contents of the flask were purified by flash chromatography (silica gel treated with 2.5% v/v of triethylamine, 10% ethyl ether in petroleum ether) to obtain ketal **41** (0.440 g, 1.758 mmol, 99%) as a colorless oil. $[\alpha]_D^{22}$ = +68.72 (*c* = 1.25, $CHCl_3$); IR (film) 1372, 1351, 1277, 1151, 1079, 1051, 1005, 909 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.79 (d, *J* = 2.5 Hz, 1H), 4.64 (d, *J* = 2.5 Hz, 1H), 3.84 (q, *J* = 8.5 Hz 1H), 3.75-3.80 (m, 1H), 3.19 (s, 3H), 2.46 (td, J_1 = 6.0 Hz, J_2 = 11.0 Hz, 1H), 2.12-2.20 (m, 1H), 2.05-2.10 (m, 1H), 1.85-2.00 (m, 3H), 1.70-1.80 (m, 1H), 1.71 (s, 3H), 1.55-1.65 (m, 1H), 1.40-1.65 (m, 2H), 1.15-1.35 (m, 3H), 0.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0 (C), 111.1 (CH_2), 108.3 (C), 65.8 (CH_2), 49.6 (CH), 49.5 (CH), 48.0 (CH_3), 46.0 (CH), 41.8 (C), 38.9 (CH_2), 35.1 (CH_2), 28.9 (CH_2), 27.1 (CH_2), 26.4 (CH_2), 18.3 (CH_3), 16.8 (CH_3); HRMS (CI$^+$): *m/z* calcd for $C_{16}H_{25}O_2$ (M - H)$^+$ 249.1854, found 249.1840.

(1*R*,3a*S*,5a*R*,8a*R*,8*R*)-8-Isopropenyl-5a-methyldecahydro-3-oxa-*as*-indacen-3a-ol (42): To a stirred solution of the ketal **41** (0.410 g, 1.638 mmol) in MeCN/H_2O (10 mL, 9:1) was added $PdCl_2(MeCN)_2$ (22.5 mg). The solution was stirred for 24 h and then concentrated under reduced pressure. Ether was added and the organic phase was separated. This extraction was repeated twice. The combined ethereal extracts were dried with magnesium sulfate, the solvents were removed and the crude product was purified by flash chromatography (silica gel, 30% EtOAc in petroleum ether) to give the hemiketal **42** (0.330 g, 1.39 mmol, 85% yield) as a white solid: m.p. 94 °C; $[\alpha]_D^{22}$ = +42.4 (*c* = 1.00, $CHCl_3$); IR (film) 3386, 2980, 1638, 1047, 1020, 885 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.80 (d, *J* = 2 Hz, 1H), 4.65 (d, *J* = 2 Hz, 1H), 3.97 (td, J_1 = 8.4 Hz, J_2 = 2.3 Hz, 1H), 3.85 (q, *J* = 13.5 Hz, 1H), 2.45-2.55 (m, 1H), 2.15-2.25 (m, 2H), 1.90-2.10 (m, 5H), 1.69 (s, 3H),1.40-1.60 (m, 3H), 1.33 (td, J_1 = 5.5 Hz, J_2 = 11.0 Hz, 1H), 1.15-1.25 (m, 2H), 0.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0 (C), 111.2 (CH_2), 106.1 (C), 65.9 (CH_2), 49.5 (CH), 49.2 (CH), 45.6 (CH_2), 41.9 (C), 38.9 (CH_2), 35.3 (CH_2), 35.3 (CH_2), 29.0 (CH_2), 26.2 (CH_2), 18.2 (CH_3), 16.9 (CH_3); HRMS (CI$^+$): *m/z* calcd for $C_{15}H_{23}O$ (M-OH)$^+$ 219.1749, found 219.1748; Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: 76.48; H, 10.67. Crystals of **42** suitable for X-ray analysis were grown by cooling an ethereal solution of the compound to 0 °C.

(3*R*,3a*R*,4*R*,7a*R*)-4-(2-Chloroethyl)-3-isopropenyl-7a-methyloctahydroinden-5-one (*ent*-4): To a stirred solution of the hemiketal **42** (18.0 mg, 0.076 mmol) in CCl_4 (0.63 mL) and CH_3CN (2.1 mL) was added PPh_3 (0.199 g, 0.76 mmol). The mixture was stirred for 36 h and purified through a flash column chromatography (silica gel, 10% EtOAc in petroleum ether) affording unreacted starting material (4 mg, 0.017 mmol, 22%) and the chloro ketone *ent*-**4** (14.0 mg, 0.055 mmol, 72%) as a colorless oil: $[\alpha]_D^{22}$ = +18.4 (*c* = 0.50, $CDCl_3$); IR (film) 2956, 1704, 1642, 1453, 1383, 1288, 1156, 1108, 889 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.78 (s, 1H), 4.69

(s, 1H), 3.60-3.7 (m, 1H), 3.52 (td, J_1 = 5.4 Hz, J_2 = 9.8 Hz, 1H), 2.60-2.70 (m, 2H), 2.52 (td, J_1 = 7.0 Hz, J_2 = 14.0 Hz, 1H), 2.34 (ddd, J_1 = 1.9 Hz, J_2 = 5.4 Hz, J_3 = 15.1 Hz, 1H), 2.10-2.22 (m, 1H), 2.00-2.10 (m, 1H), 1.87-1.97 (m, 2H), 1.67 (s, 3H), 1.50-1.65 (m, 4H), 1.25-1.32 (m, 1H), 1.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.3 (C), 148.4 (C), 111.3 (CH_2), 53.9 (CH), 48.9 (CH), 48.8 (CH), 44.6 (CH_2), 42.8 (C), 38.8 (CH_2), 38.3 (CH_2), 37.5 (CH_2), 31.0 (CH_2), 29.0 (CH_2), 19.0 (CH_3), 18.0 (CH_3); LRMS (CI^+): *m/z* 220 (100%), 255 ($M+H^+$, 65%), 257 ($M+H^+$, 22%) HRMS (CI^+): *m/z* calcd for $C_{15}H_{24}ClO$ $(M+H)^+$ 255.1516, found 255.1527.

Table S1. Summary of Structure Determination of Compound 35.

Formula:	$C_{13}H_{20}O_3$
Formula weight:	224.29
Crystal class:	orthorhombic
Space group:	$P2_12_12_1$ (#19)
Z	4
Cell constants:	
a	10.7967(12)Å
b	15.5753(11)Å
c	7.2427(14)Å
V	1217.9(3)$Å^3$
μ	6.88 cm^{-1}
crystal size, mm	0.38 x 0.22 x 0.04
D_{calc}	1.223 g/cm^3
F(000)	488
Radiation:	Cu-K_α (λ=1.54178Å)
2θ range	9.96 – 120.04 °
hkl collected:	$0\leq h \leq 12$; $0\leq k \leq 17$; $0\leq l \leq 7$
No. reflections measured:	890
No. unique reflections:	890
No. observed reflections	806 (F>4σ)
No. reflections used in refinement	890
No. parameters	148
R indices (F>4σ)	R_1=0.0411
	wR_2=0.1008
R indices (all data)	R_1=0.0514
	wR_2=0.1351
GOF:	1.225
Final Difference Peaks, e/$Å^3$	+0.188, -0.173

Table S2. Refined Positional Parameters for Compound 35.

Atom	x	y	z	U_{eq}, Å^2
C1	0.2450(4)	0.8316(3)	0.2887(7)	0.0540(13)
C2	0.1660(5)	0.8306(3)	0.1167(7)	0.063(2)
H2a	0.1645(5)	0.8880(3)	0.0647(7)	0.084
H2b	0.0818(5)	0.8158(3)	0.1511(7)	0.084
C3	0.2095(5)	0.7684(3)	-0.0310(8)	0.0619(14)
H3a	0.2855(5)	0.7894(3)	-0.0865(8)	0.082
H3b	0.1473(5)	0.7639(3)	-0.1271(8)	0.082
C4	0.2319(4)	0.6807(3)	0.0547(7)	0.0491(12)
C5	0.2915(5)	0.6138(3)	-0.0716(9)	0.067(2)
C6	0.3703(5)	0.5561(3)	0.0477(9)	0.077(2)
H6a	0.4534(5)	0.5518(3)	-0.0023(9)	0.103
H6b	0.3347(5)	0.4990(3)	0.0538(9)	0.103
C7	0.3733(5)	0.5973(3)	0.2409(9)	0.077(2)
H7a	0.3177(5)	0.5679(3)	0.3249(9)	0.102
H7b	0.4563(5)	0.5965(3)	0.2920(9)	0.102
C8	0.3300(4)	0.6891(3)	0.2045(7)	0.0544(13)
H8	0.4003(4)	0.7185(3)	0.1466(7)	0.072
C9	0.2905(5)	0.7454(3)	0.3634(7)	0.0543(13)
H9	0.2265(5)	0.7173(3)	0.4380(7)	0.072
C10	0.4006(5)	0.7723(4)	0.4824(9)	0.078(2)
H10a	0.3758(5)	0.7797(4)	0.6102(9)	0.104
H10b	0.4663(5)	0.7300(4)	0.4764(9)	0.104
C11	0.4424(5)	0.8572(4)	0.3996(8)	0.075(2)
H11a	0.4415(5)	0.9020(4)	0.4925(8)	0.099
H11b	0.5259(5)	0.8522(4)	0.3511(8)	0.099
C12	0.1452(8)	0.9582(4)	0.4120(11)	0.105(2)
H12a	0.135(5)	0.9863(11)	0.5290(11)	0.158
H12b	0.068(3)	0.9598(4)	0.346(7)	0.158
H12c	0.208(3)	0.9870(11)	0.341(7)	0.158
C13	0.1106(4)	0.6387(4)	0.1216(9)	0.073(2)
H13a	0.057(2)	0.628(2)	0.0179(11)	0.109
H13b	0.070(2)	0.6762(12)	0.207(4)	0.109
H13c	0.1292(5)	0.5852(13)	0.181(5)	0.109
O1	0.3556(3)	0.8771(2)	0.2519(5)	0.0633(10)
O2	0.1811(3)	0.8708(2)	0.4412(6)	0.0745(12)
O3	0.2802(5)	0.6084(3)	-0.2388(6)	0.0914(14)

$U_{eq}={}^{1}/_{3}[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*cos\gamma+2U_{13}aa^*cc^*cos\beta+2U_{23}bb^*cc^*c$

Table S3. Bond Distances in Compound 35, Å

C1-O1	1.414(6)	C1-O2	1.439(6)	C1-C2	1.510(7)
C1-C9	1.530(7)	C2-C3	1.518(7)	C3-C4	1.519(7)
C4-C8	1.522(7)	C4-C5	1.528(7)	C4-C13	1.542(6)
C5-O3	1.220(7)	C5-C6	1.509(8)	C6-C7	1.539(9)
C7-C8	1.528(7)	C8-C9	1.508(7)	C9-C10	1.527(7)
C10-C11	1.520(8)	C11-O1	1.456(6)	C12-O2	1.430(7)

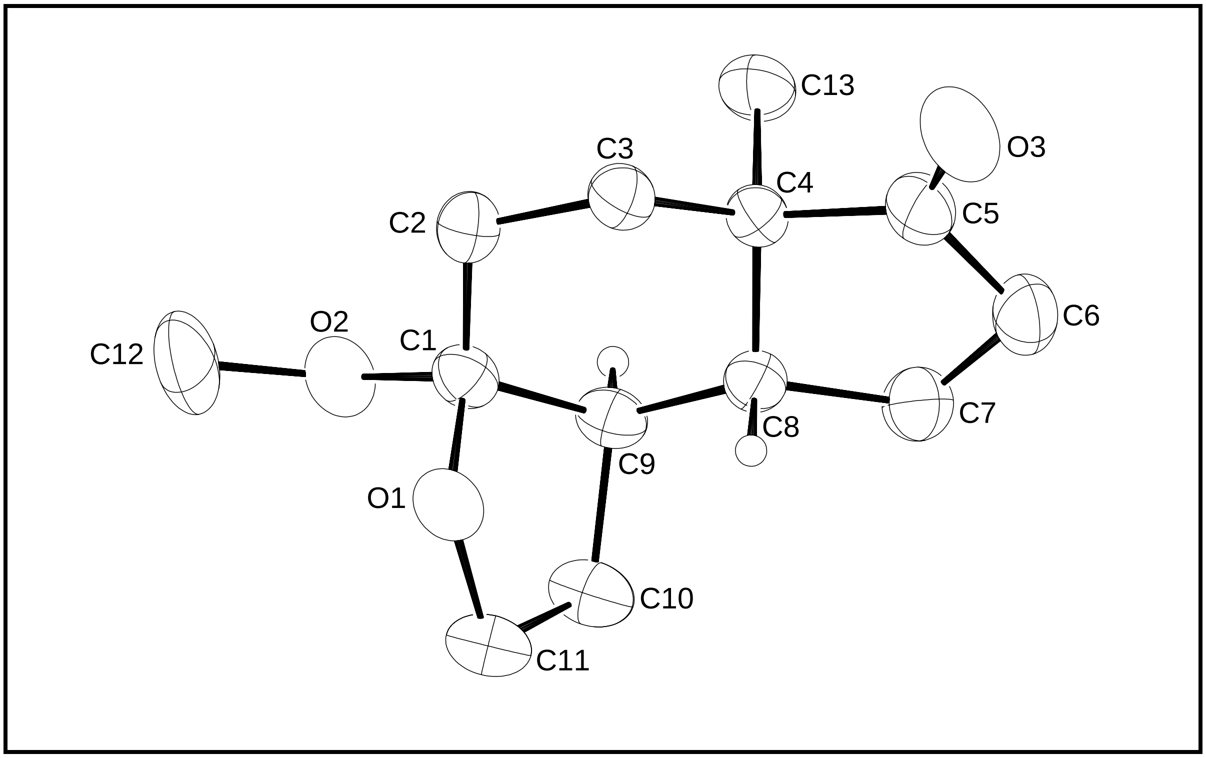
Table S4. Bond Angles in Compound 35, °

O1-C1-O2	109.7(4)	O1-C1-C2	109.1(4)	O2-C1-C2	111.5(4)
O1-C1-C9	103.6(4)	O2-C1-C9	104.8(4)	C2-C1-C9	117.7(4)
C1-C2-C3	114.4(4)	C2-C3-C4	109.6(4)	C3-C4-C8	108.9(4)
C3-C4-C5	115.8(4)	C8-C4-C5	101.1(4)	C3-C4-C13	112.0(4)
C8-C4-C13	113.8(4)	C5-C4-C13	104.8(4)	O3-C5-C6	125.7(6)
O3-C5-C4	126.8(6)	C6-C5-C4	107.5(5)	C5-C6-C7	106.5(5)
C8-C7-C6	103.1(5)	C9-C8-C4	113.4(4)	C9-C8-C7	119.9(5)
C4-C8-C7	104.8(4)	C8-C9-C10	111.8(4)	C8-C9-C1	109.3(4)
C10-C9-C1	102.0(4)	C11-C10-C9	104.3(5)	O1-C11-C10	106.5(4)
C1-O1-C11	107.4(4)	C12-O2-C1	114.8(5)		

Table S5. Refined Thermal Parameters (U's) for Compound 35.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.054(3)	0.055(3)	0.053(3)	-0.004(3)	0.004(3)	-0.009(2)
C2	0.066(3)	0.053(3)	0.070(4)	0.000(3)	-0.003(3)	0.006(3)
C3	0.066(3)	0.059(3)	0.061(3)	-0.005(3)	-0.009(3)	0.002(3)
C4	0.050(2)	0.049(2)	0.048(3)	-0.001(3)	0.004(3)	-0.004(2)
C5	0.065(3)	0.050(3)	0.085(5)	0.004(4)	0.006(4)	-0.012(3)
C6	0.071(3)	0.052(3)	0.109(5)	-0.003(4)	0.012(4)	-0.001(3)
C7	0.074(4)	0.055(3)	0.100(5)	0.007(4)	-0.012(4)	0.001(3)
C8	0.047(2)	0.048(2)	0.068(3)	0.001(3)	0.000(3)	-0.003(2)
C9	0.057(3)	0.059(3)	0.048(3)	0.003(3)	-0.005(3)	-0.010(2)
C10	0.076(4)	0.083(4)	0.075(4)	-0.003(4)	-0.014(4)	-0.018(3)
C11	0.066(3)	0.085(4)	0.072(4)	-0.004(4)	-0.013(4)	-0.019(3)
C12	0.123(5)	0.075(4)	0.118(6)	-0.041(4)	0.033(6)	0.005(4)
C13	0.055(3)	0.072(3)	0.091(4)	-0.008(4)	0.002(3)	-0.014(3)
O1	0.065(2)	0.057(2)	0.067(2)	-0.003(2)	0.011(2)	-0.013(2)
O2	0.074(2)	0.073(2)	0.076(3)	-0.020(2)	0.019(2)	-0.005(2)
O3	0.129(4)	0.078(3)	0.067(3)	-0.012(3)	0.009(3)	-0.007(3)

The form of the anisotropic displacement parameter is:
$\exp[-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+ 2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$.



ORTEP drawing of compound **35** with 30% probability thermal ellipsoids.

Table S6. Summary of Structure Determination of Compound 37.

Formula:	$C_{16}H_{22}O_3$
Formula weight:	262.34
Crystal class:	monoclinic
Space group:	$P2_1$ (#4)
Z	2
Cell constants:	
a	8.7020(2)Å
b	6.1931(1)Å
c	13.3767(3)Å
β	91.685(1)°
V	720.59(3)$Å^3$
μ	0.82 cm^{-1}
crystal size, mm	0.42 x 0.25 x 0.07
D_{calc}	1.209 g/cm^3
F(000)	284
Radiation:	Mo-K_α (λ=0.71069Å)
2θ range	5.52 – 54.96 °
hkl collected:	$-11 \leq h \leq 11$; $-8 \leq k \leq 8$; $-17 \leq l \leq 17$
No. reflections measured:	7585
No. unique reflections:	2877 (R_{int}=0.0214)
No. observed reflections	2735 (F>4σ)
No. reflections used in refinement	2877
No. parameters	176
R indices (F>4σ)	R_1=0.0375
	wR_2=0.0894
R indices (all data)	R_1=0.0398
	wR_2=0.0912
GOF:	1.080
Final Difference Peaks, e/$Å^3$	+0.152, -0.149

Table S7. Refined Positional Parameters for Compound 37

Atom	x	y	z	U_{eq}, Å^2
C1	0.2177(2)	0.8060(3)	0.90237(12)	0.0332(3)
C2	0.0470(2)	0.7557(3)	0.88567(12)	0.0386(4)
H2a	-0.0121(2)	0.8472(3)	0.92918(12)	0.051
H2b	0.0285(2)	0.6070(3)	0.90455(12)	0.051
C3	-0.0108(2)	0.7894(3)	0.77739(13)	0.0381(4)
H3a	-0.1150(2)	0.7352(3)	0.76934(13)	0.051
H3b	-0.0117(2)	0.9423(3)	0.76170(13)	0.051
C4	0.0936(2)	0.6708(3)	0.70650(12)	0.0320(3)
C5	0.0610(2)	0.7056(3)	0.59552(12)	0.0367(4)
C6	0.2107(2)	0.7193(3)	0.54204(11)	0.0388(4)
H6a	0.2173(2)	0.8554(3)	0.50660(11)	0.052
H6b	0.2177(2)	0.6027(3)	0.49392(11)	0.052
C7	0.3431(2)	0.7015(3)	0.62183(11)	0.0330(3)
H7	0.4157(2)	0.8183(3)	0.60847(11)	0.044
C8	0.2563(2)	0.7659(3)	0.71765(11)	0.0309(3)
H8	0.2413(2)	0.9223(3)	0.71154(11)	0.041
C9	0.3290(2)	0.7350(3)	0.82183(10)	0.0305(3)
H9	0.3609(2)	0.5847(3)	0.83212(10)	0.041
C10	0.4644(2)	0.8902(3)	0.84234(13)	0.0385(4)
H10a	0.5400(2)	0.8260(3)	0.88800(13)	0.051
H10b	0.5138(2)	0.9285(3)	0.78076(13)	0.051
C11	0.3905(2)	1.0858(3)	0.8889(2)	0.0604(6)
H11a	0.4442(2)	1.1233(3)	0.9510(2)	0.080
H11b	0.3952(2)	1.2083(3)	0.8438(2)	0.080
C12	0.2110(2)	0.7776(4)	1.08167(12)	0.0509(5)
H12a	0.2631(12)	0.710(2)	1.13761(14)	0.076
H12b	0.1040(5)	0.740(2)	1.0812(5)	0.076
H12c	0.222(2)	0.9315(5)	1.0871(6)	0.076
C13	0.0829(2)	0.4240(3)	0.72242(13)	0.0355(3)
H13a	0.1303(13)	0.3867(4)	0.7858(4)	0.053
H13b	0.1350(12)	0.3510(3)	0.6699(5)	0.053
H13c	-0.0231(2)	0.3810(4)	0.7214(9)	0.053
C14	0.4340(2)	0.4933(3)	0.62327(11)	0.0336(4)
C15	0.3935(2)	0.3146(3)	0.57501(14)	0.0429(4)
H15a	0.4600(2)	0.1971(3)	0.57458(14)	0.057
H15b	0.2984(2)	0.3065(3)	0.54154(14)	0.057
C16	0.5886(2)	0.5037(4)	0.67718(13)	0.0449(4)
H16a	0.6497(7)	0.615(2)	0.6481(8)	0.067
H16b	0.6399(8)	0.3672(9)	0.6712(10)	0.067
H16c	0.5745(2)	0.535(3)	0.7466(3)	0.067
O1	0.23314(13)	1.0326(2)	0.90742(9)	0.0415(3)
O2	0.27679(13)	0.7062(2)	0.99143(8)	0.0402(3)
O3	-0.06593(14)	0.7223(3)	0.55636(9)	0.0530(4)

$U_{eq}={}^{1}/_{3}[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*cos\gamma+2U_{13}aa^*cc^*cos\beta+2U_{23}bb^*cc^*c$

Table S8. Bond Distances in Compound 37, Å

C1-O1	1.411(2)	C1-O2	1.425(2)	C1-C2	1.528(2)
C1-C9	1.534(2)	C2-C3	1.533(2)	C3-C4	1.521(2)
C4-C5	1.518(2)	C4-C8	1.537(2)	C4-C13	1.547(2)
C5-O3	1.213(2)	C5-C6	1.507(2)	C6-C7	1.551(2)
C7-C14	1.513(2)	C7-C8	1.559(2)	C8-C9	1.526(2)
C9-C10	1.539(2)	C10-C11	1.514(3)	C11-O1	1.437(2)
C12-O2	1.422(2)	C14-C15	1.324(3)	C14-C16	1.509(2)

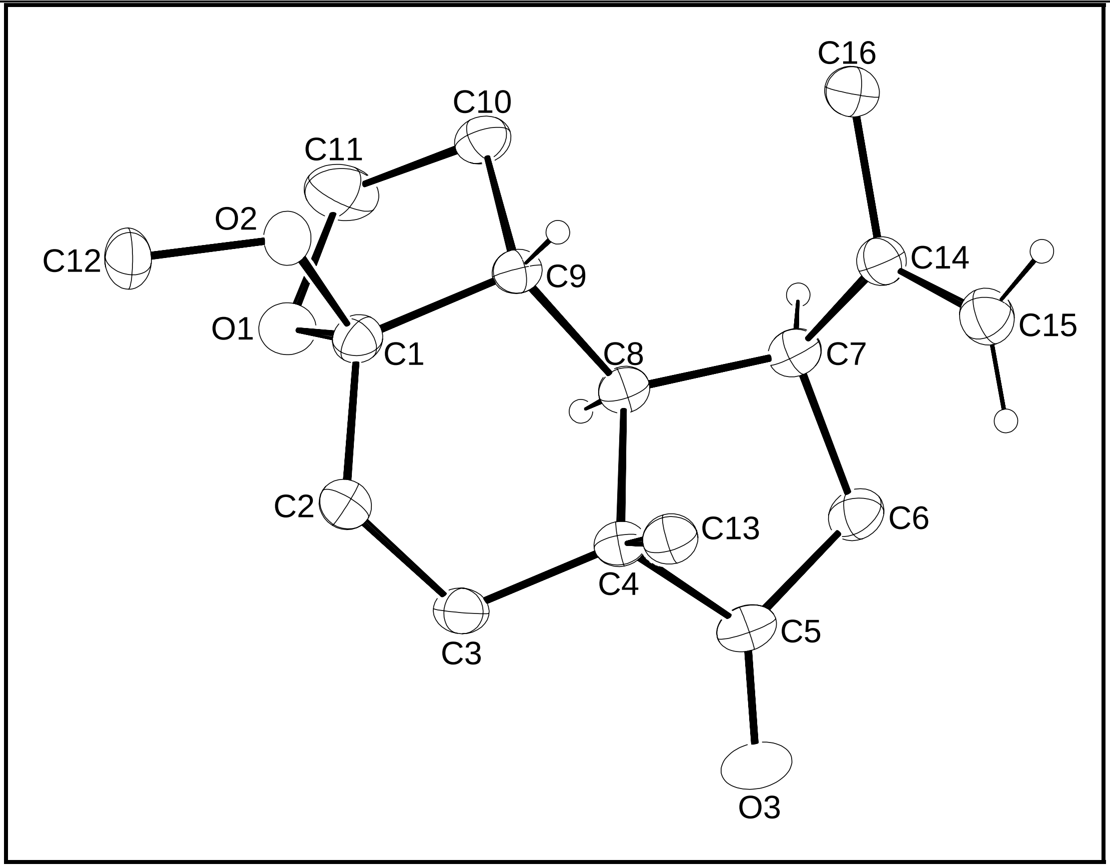
Table S9. Bond Angles in Compound 37, °

O1-C1-O2	111.10(13)	O1-C1-C2	107.49(13)	O2-C1-C2	111.06(14)
O1-C1-C9	104.92(14)	O2-C1-C9	104.06(12)	C2-C1-C9	118.05(13)
C1-C2-C3	113.62(14)	C4-C3-C2	109.78(13)	C5-C4-C3	116.33(13)
C5-C4-C8	100.68(12)	C3-C4-C8	108.66(13)	C5-C4-C13	105.35(14)
C3-C4-C13	110.60(14)	C8-C4-C13	115.10(13)	O3-C5-C6	125.4(2)
O3-C5-C4	125.1(2)	C6-C5-C4	109.46(12)	C5-C6-C7	107.71(13)
C14-C7-C6	116.52(14)	C14-C7-C8	118.27(12)	C6-C7-C8	100.34(12)
C9-C8-C4	113.38(13)	C9-C8-C7	121.39(13)	C4-C8-C7	106.84(12)
C8-C9-C1	110.61(12)	C8-C9-C10	112.30(13)	C1-C9-C10	101.05(13)
C11-C10-C9	103.96(14)	O1-C11-C10	107.81(14)	C15-C14-C16	119.3(2)
C15-C14-C7	125.1(2)	C16-C14-C7	115.4(2)	C1-O1-C11	108.03(14)
C12-O2-C1	115.50(13)				

Table S10. Refined Thermal Parameters (U's) for Compound 37

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0347(8)	0.0309(8)	0.0337(7)	-0.0005(6)	-0.0034(6)	0.0027(7)
C2	0.0325(7)	0.0446(10)	0.0388(8)	-0.0016(7)	0.0029(6)	-0.0005(8)
C3	0.0295(7)	0.0417(9)	0.0427(9)	-0.0011(8)	-0.0034(6)	0.0022(7)
C4	0.0290(7)	0.0321(8)	0.0346(7)	0.0021(6)	-0.0024(6)	-0.0027(6)
C5	0.0356(8)	0.0343(8)	0.0396(8)	0.0053(8)	-0.0093(6)	-0.0038(7)
C6	0.0405(8)	0.0436(10)	0.0321(7)	0.0060(8)	-0.0038(6)	-0.0012(8)
C7	0.0329(7)	0.0338(8)	0.0320(7)	0.0051(7)	-0.0013(6)	-0.0058(7)
C8	0.0313(7)	0.0280(8)	0.0333(7)	0.0021(6)	-0.0019(6)	-0.0027(6)
C9	0.0282(6)	0.0302(8)	0.0328(7)	0.0000(7)	-0.0030(6)	-0.0007(6)
C10	0.0327(8)	0.0417(10)	0.0407(8)	-0.0016(7)	-0.0042(7)	-0.0061(7)
C11	0.0393(10)	0.0417(11)	0.100(2)	-0.0200(11)	-0.0049(11)	-0.0082(8)
C12	0.0531(11)	0.0674(14)	0.0322(8)	-0.0077(9)	0.0029(7)	0.0165(10)
C13	0.0343(8)	0.0335(8)	0.0385(8)	0.0032(7)	0.0000(6)	-0.0053(7)
C14	0.0308(7)	0.0400(9)	0.0302(7)	0.0026(7)	0.0029(6)	-0.0030(7)
C15	0.0422(9)	0.0416(10)	0.0451(9)	-0.0030(8)	0.0034(7)	0.0005(8)
C16	0.0352(8)	0.0600(12)	0.0393(8)	-0.0023(9)	-0.0004(7)	0.0053(9)
O1	0.0390(6)	0.0321(6)	0.0530(7)	-0.0082(6)	-0.0054(5)	0.0036(5)
O2	0.0429(6)	0.0482(7)	0.0292(5)	-0.0013(6)	-0.0007(4)	0.0130(6)
O3	0.0391(6)	0.0695(10)	0.0493(7)	0.0099(7)	-0.0155(5)	-0.0011(7)

The form of the anisotropic displacement parameter is:
$\exp[-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$.



ORTEP drawing of compound **37** with 30% probability thermal ellipsoids.

Table S11. Summary of Structure Determination of Compound 42.

Formula:	$C_{15}H_{24}O_2$
Formula weight:	236.34
Crystal class:	orthorhombic
Space group:	$P2_12_12_1$ (#19)
Z	4
Cell constants:	
a	13.8574(1)Å
b	6.1093(1)Å
c	15.9407(1)Å
V	1349.52(3)$Å^3$
μ	0.75 cm^{-1}
crystal size, mm	0.40 x 0.12 x 0.10
D_{calc}	1.163 g/cm^3
F(000)	520
Radiation:	Mo-K_α (λ=0.71069Å)
2θ range	5.12 – 50.68 °
hkl collected:	$-16 \leq h \leq 16$; $-7 \leq k \leq 7$; $-19 \leq l \leq 19$
No. reflections measured:	8732
No. unique reflections:	2466 (R_{int}=0.0321)
No. observed reflections	2338 ($F>4\sigma$)
No. reflections used in refinement	2466
No. parameters	158
R indices ($F>4\sigma$)	R_1=0.0380
	wR_2=0.0867
R indices (all data)	R_1=0.0411
	wR_2=0.0886
GOF:	1.101
Final Difference Peaks, $e/Å^3$	+0.151, -0.119

Table S12. Refined Positional Parameters for Compound 42.

Atom	x	y	z	U_{eq}, Å^2
C1	0.52389(12)	0.5157(3)	0.35462(10)	0.0310(4)
C2	0.41655(12)	0.5667(3)	0.35149(11)	0.0353(4)
H2a	0.38782(12)	0.4870(3)	0.30515(11)	0.047
H2b	0.40809(12)	0.7217(3)	0.34065(11)	0.047
C3	0.36328(12)	0.5072(3)	0.43226(11)	0.0354(4)
H3a	0.29806(12)	0.5645(3)	0.43003(11)	0.047
H3b	0.35933(12)	0.3492(3)	0.43726(11)	0.047
C4	0.41502(12)	0.6003(3)	0.50847(10)	0.0311(4)
C5	0.37526(13)	0.5283(3)	0.59354(11)	0.0389(4)
H5a	0.35499(13)	0.3763(3)	0.59188(11)	0.052
H5b	0.32072(13)	0.6182(3)	0.60986(11)	0.052
C6	0.46008(13)	0.5591(3)	0.65471(11)	0.0425(4)
H6a	0.46230(13)	0.4396(3)	0.69471(11)	0.056
H6b	0.45317(13)	0.6955(3)	0.68531(11)	0.056
C7	0.55385(12)	0.5628(3)	0.60046(10)	0.0319(4)
H7	0.57704(12)	0.7142(3)	0.59838(10)	0.042
C8	0.51723(11)	0.5018(3)	0.51219(9)	0.0264(3)
H8	0.50962(11)	0.3424(3)	0.51131(9)	0.035
C9	0.57902(11)	0.5621(3)	0.43642(9)	0.0266(3)
H9	0.59803(11)	0.7164(3)	0.43912(9)	0.035
C10	0.66781(12)	0.4166(3)	0.42380(10)	0.0308(4)
H10a	0.71689(12)	0.4917(3)	0.39130(10)	0.041
H10b	0.69514(12)	0.3726(3)	0.47721(10)	0.041
C11	0.62808(13)	0.2197(3)	0.37610(11)	0.0383(4)
H11a	0.67018(13)	0.1824(3)	0.32964(11)	0.051
H11b	0.62310(13)	0.0939(3)	0.41297(11)	0.051
C12	0.41518(14)	0.8526(3)	0.50456(12)	0.0415(4)
H12a	0.4555(7)	0.9001(3)	0.4591(5)	0.062
H12b	0.4396(9)	0.9104(3)	0.5564(3)	0.062
H12c	0.3505(2)	0.9044(3)	0.4958(8)	0.062
C13	0.63245(12)	0.4247(3)	0.63870(10)	0.0333(4)
C14	0.7072(2)	0.5148(4)	0.67700(13)	0.0528(6)
H14a	0.7533(2)	0.4267(4)	0.70256(13)	0.070
H14b	0.7136(2)	0.6663(4)	0.67839(13)	0.070
C15	0.62031(14)	0.1821(3)	0.63548(11)	0.0413(4)
H15a	0.6304(9)	0.1319(4)	0.5791(2)	0.062
H15b	0.5563(3)	0.1443(3)	0.6532(8)	0.062
H15c	0.6665(6)	0.1142(3)	0.6720(6)	0.062
O1	0.53420(8)	0.2818(2)	0.34570(7)	0.0350(3)
O2	0.57424(9)	0.6215(2)	0.28941(7)	0.0439(3)
H2	0.5374(4)	0.644(3)	0.2501(6)	0.066

$$U_{eq}={}^{1}/_{3}[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*cos\_+2U_{13}aa^*cc^*cos\_+2U_{23}bb^*cc^*c$$

Table S13. Bond Distances in Compound 42, Å

C1-O2	1.409(2)	C1-O1	1.443(2)	C1-C2	1.520(2)
C1-C9	1.537(2)	C2-C3	1.528(2)	C3-C4	1.521(2)
C4-C5	1.528(2)	C4-C8	1.540(2)	C4-C12	1.543(2)
C5-C6	1.539(2)	C6-C7	1.561(2)	C7-C13	1.507(2)
C7-C8	1.541(2)	C8-C9	1.526(2)	C9-C10	1.531(2)
C10-C11	1.526(2)	C11-O1	1.439(2)	C13-C14	1.322(3)
C13-C15	1.492(2)				

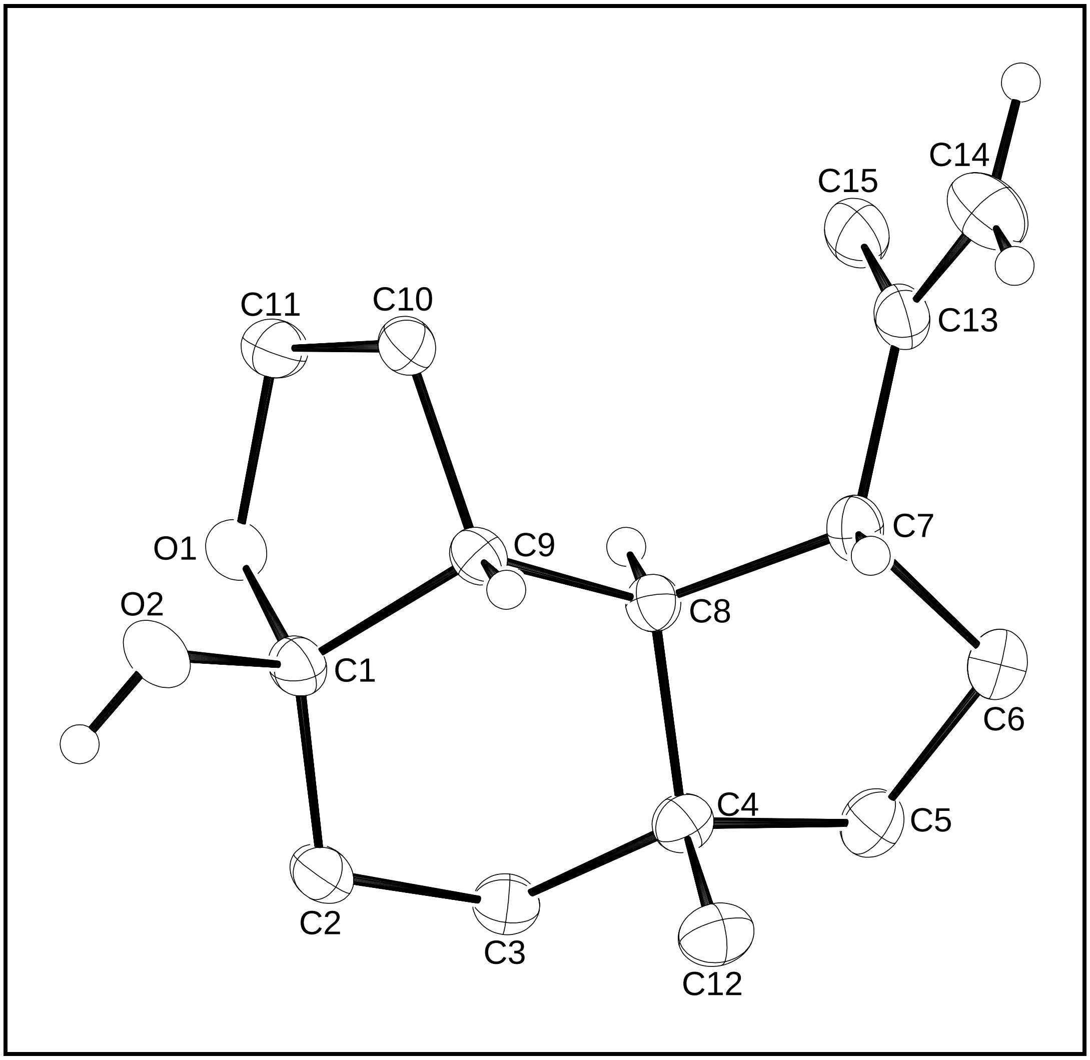
Table S14. Bond Angles in Compound 42, °

O2-C1-O1	109.41(13)	O2-C1-C2	111.50(13)	O1-C1-C2	107.23(14)
O2-C1-C9	107.17(13)	O1-C1-C9	102.51(12)	C2-C1-C9	118.45(14)
C1-C2-C3	113.34(14)	C4-C3-C2	110.87(14)	C3-C4-C5	115.53(14)
C3-C4-C8	108.55(13)	C5-C4-C8	100.65(13)	C3-C4-C12	110.0(2)
C5-C4-C12	108.9(2)	C8-C4-C12	112.99(14)	C4-C5-C6	104.57(14)
C5-C6-C7	106.65(13)	C13-C7-C8	118.17(14)	C13-C7-C6	111.70(14)
C8-C7-C6	103.20(13)	C9-C8-C4	113.04(12)	C9-C8-C7	118.67(12)
C4-C8-C7	104.10(13)	C8-C9-C10	114.52(13)	C8-C9-C1	110.37(12)
C10-C9-C1	100.43(12)	C11-C10-C9	103.47(13)	O1-C11-C10	106.63(14)
C14-C13-C15	121.2(2)	C14-C13-C7	121.3(2)	C15-C13-C7	117.4(2)
C11-O1-C1	108.50(13)				

Table S15. Refined Thermal Parameters (U's) for Compound 42.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0303(8)	0.0368(9)	0.0260(8)	0.0051(7)	0.0000(7)	0.0010(7)
C2	0.0305(8)	0.0445(9)	0.0309(8)	0.0036(8)	-0.0057(7)	0.0027(8)
C3	0.0274(8)	0.0413(10)	0.0373(9)	-0.0009(8)	-0.0025(7)	-0.0004(8)
C4	0.0277(8)	0.0336(8)	0.0320(9)	0.0003(7)	0.0016(7)	0.0009(7)
C5	0.0344(9)	0.0473(12)	0.0351(9)	0.0004(8)	0.0069(8)	0.0007(8)
C6	0.0438(10)	0.0524(11)	0.0313(9)	-0.0030(9)	0.0039(8)	0.0074(9)
C7	0.0372(9)	0.0309(9)	0.0277(8)	-0.0032(7)	-0.0006(7)	-0.0016(7)
C8	0.0267(8)	0.0268(7)	0.0256(8)	-0.0004(7)	-0.0003(6)	-0.0009(6)
C9	0.0259(8)	0.0272(8)	0.0268(8)	0.0013(7)	-0.0026(6)	-0.0031(7)
C10	0.0274(8)	0.0380(9)	0.0270(8)	-0.0005(8)	-0.0020(6)	0.0007(7)
C11	0.0360(9)	0.0409(10)	0.0380(9)	-0.0059(8)	-0.0086(8)	0.0082(8)
C12	0.0394(10)	0.0358(9)	0.0493(11)	-0.0016(8)	0.0003(9)	0.0069(8)
C13	0.0344(9)	0.0408(9)	0.0247(8)	0.0013(8)	-0.0003(7)	-0.0006(8)
C14	0.0478(12)	0.0616(13)	0.0490(12)	0.0049(10)	-0.0141(9)	-0.0045(10)
C15	0.0506(11)	0.0406(10)	0.0326(9)	0.0041(8)	-0.0020(8)	0.0071(9)
O1	0.0339(6)	0.0391(6)	0.0320(6)	-0.0072(5)	-0.0082(5)	0.0041(5)
O2	0.0356(6)	0.0672(9)	0.0291(6)	0.0187(6)	-0.0003(5)	0.0022(7)

The form of the anisotropic displacement parameter is:
$\exp[-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+ 2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$.



ORTEP drawing of compound **42** with 30% probability thermal ellipsoids.

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[2] Gais, H.-J.; Bülow, G., Zatorski, A., Jentsch, M., Maidonis, P., Hemmerle, H. *J. Org. Chem.* **1989**, *54*, 5115.