Title: "Total Synthesis of (±)-Cameroonanol"

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Supporting Information

Contents: Experimental procedures together with analytical and spectral data for all compounds.

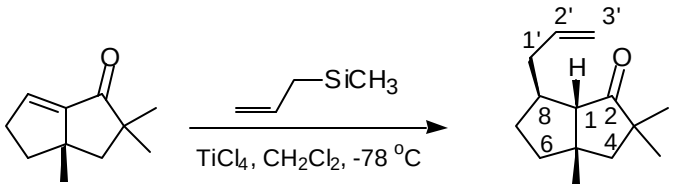
General Experimental

All reactions were performed under N_2 using oven dried glassware. Et_2O, THF, and benzene were distilled from sodium / benzophenone ketyl before use. CH_2Cl_2 and Et_3N were distilled from CaH_2 before use. Anhydrous HBr vapor was used directly from the compressed gas cyclinder. $TiCl_4$ was distilled (bp 135-136) under nitrogen and stored in the freezer at -33 °C as a 1.0 **M** solution in anhydrous CH_2Cl_2. Solutions of reactive hydrides were titrated by measuring hydrogen evolution with a gas burette upon hydrolysis. Ozone was generated as a dilute stream in oxygen by a Wellsbach T-816 ozonator. Solvents used for chromatography were distilled prior to use. All other reagents and solvents used were reagent grade.

Column chromatography was performed according to Still's[1] procedure using 100-700 times excess Woelm 32-64 μm grade silica gel. HPLC separations were performed using a Waters Associates M6000 pump and Waters 2410 Refractive Index Detector with the following solvents and columns: Method A = Acetonitrile:H_2O (80:20) at 16 mL/min and Phenomenex Luna 5μ C8(2) semi-preparative scale column, Method B = Et_2O:hexane (5:95) at 16 mL/min using a Dynamax®-60A semi-preparative scale column. TLC anaylsis was performed using Merck glass TLC plates (0.25 mm 60 F-254 silica gel). Visualization of the developed plates was accomplished by staining with ethanolic phosphomolybdic acid, ceric ammonium molybdate, or p-anisaldehyde followed by heating on a hotplate (ca. 120°C). GC was conducted using a Shimadzu Model 14A-GC on a Rt_x-200 300 mm fused silica capillary column (split ratio~ 100:1) and the following temperature programs: Method A = 75 °C for 2.0 min, ramp 12 °C/min to 270 °C, and hold for 20 min; Method B = 125 °C for 2.0 min, ramp 12°C/min to 270 °C, and hold for 10 min. The standard operating conditions were 300 °C injector temperature and 310 °C detector temperature. A Hewlett-Packard 3395 integrator was used to integrate the FID detector signal. GC-MS was performed with a Hewlett-Packard HP 5890A on a HP-1® column (100% dimethlypolysiloxane; ID 0.22 mm, 0.33 μm film thickness) with the method A temperature profile. Electron impact (EI) mass spectral ion

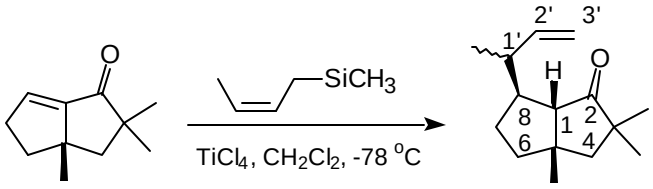
analysis of the raw column effluent was performed with the attached HP 5970 quadrapole MS and related data station.

NMR spectral data were collected in the University of Illinois Varian-Oxford Instruments Center for Excellence in NMR (V.O.I.C.E.) using the Unity 400, Unity 500 Unity-Inova 500 NB, and Keck 750 MHz spectrometers. The following solvents and reference values (ppm) were used: $CDCl_3$ (^{1}H: 7.26, ^{13}C: 77.0), C_6D_6 (^{1}H: 7.15, ^{13}C: 128.0), C_5D_5N (^{1}H: 7.19, ^{13}C: 123.5). In some cases, chloroform-*d*, was passed through a pipette filled with basic alumina immediately before use. In the NMR spectral data, a forward slash indicates that the designated assignment is ambiguous. IR spectra were collected using a Mattson Galaxy Series Model 5000 FTIR. Samples for IR analysis were prepared as either dilute solutions in CCl_4 or neat films on NaCl plates. Melting points were determined in open capillary tubes and are uncorrected. Microanalysis and mass spectral data were collected by the University of Illinois Microanalysis and Mass Spectroscopy Laboratories, respectively.



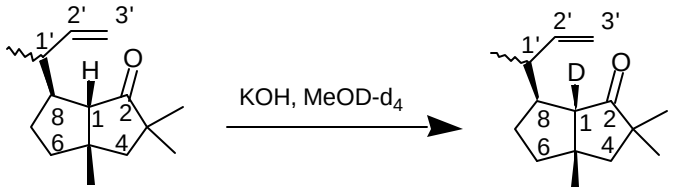
(1*S,5*S**,8*S**)-3,3,5-Trimethyl-8-(2-propenyl)bicyclo[3.3.0]octan-2-one (7).** This preparation is based on a procedure described by Hosomi and Sakurai.[2] A 1.00 **M** solution of $TiCl_4$ in CH_2Cl_2 (2.44 mL, 2.44 mmol) was added dropwise over 5 min to a stirred solution of enone **6** (400 mg, 2.44 mmol) in CH_2Cl_2 (8 mL) at -78 °C (dry ice / 2-propanol). The resulting dark yellow solution was stirred at -78 °C for 10 min before the dropwise addition allyltrimethysilane (306 mg, 2.68 mmol) in CH_2Cl_2 (3 mL). An opaque purple color developed immediately. The purple solution was stirred at -78 °C for 20 min and then at 0 °C for 10 min. During this time, aliquots were spotted directly onto TLC plates. Although fast, the disappearance of the bicyclic enone at -78 °C could be followed by TLC. The solution was stirred and cooled at 0 °C as water (10 mL) was added to hydrolyze the $TiCl_4$. After 5 min the entire heterogeneous mixture was diluted with ether (60 mL). The organic layer was washed

with 10% HCl (25 mL), satd. $NaHCO_3$ (25 mL), satd. NaCl (20 mL); dried ($MgSO_4$); and concentrated under reduced pressure to afford 468 mg of crude **7**. Purification by flash chromatography (32 g SiO_2; ether:pentane, 15:85) afforded 409 mg (82%) of **7** as a clear, colorless oil: TLC R_f = 0.65 (EtOAc:hexane, 15:85), t_R = 11.62 min (GC Method A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddt, 1H, *J* = 17.0, 10.3, 6.7 Hz, C2'-H), 5.04 (ddt, 1H, *J* = 17.0, 2.2, 1.7 Hz, C3'-H), 5.00 (ddt, 1H, *J* = 9.6, 2.2, 1.2 Hz, C3'-H), 2.23 (m, 2H), 2.14 (d, 1H, *J* = 3.6 Hz, C1-H), 2.10 (m, 1H), 1.77 (d, 1H, *J* = 13.7 Hz, C4-H), 1.72 (d, 1H, *J* = 13.7 Hz, C4-H), 1.60-1.69 (m, 2H), 1.40-1.56 (m, 2H), 1.27 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.07 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 225.88 (C_q, C2), 137.29 (CH, C2'), 115.97 (CH_2, C1'), 63.82 (CH, C1), 50.78 (CH_2), 47.15 (C_q), 44.11 (C_q), 43.65 (CH), 41.89 (CH_2), 40.04 (CH_2), 31.33 (CH_2), 29.93 (CH_3), 27.55 (CH_3), 26.05 (CH_3); IR (neat film) ν_{max} 2956 (C-H), 2936 (C-H), 2867 (C-H), 1732 (C=O), 1641, 1456, 912 cm^{-1}. Distillation of a small sample in a Kugelrohr apparatus (ot 100-110 °C at 0.8 Torr) gave the analytical sample: Anal. Calcd for $C_{14}H_{22}O$ (206.33): C, 81.51; H, 10.74. Found: C, 81.52; H, 10.82.

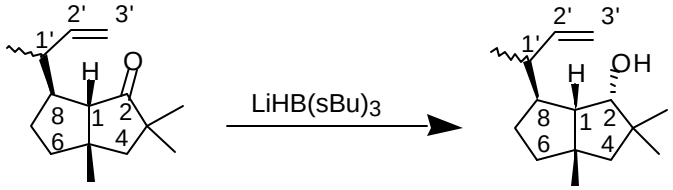


(1S*,5S*,8S*)-3,3,5-Trimethyl-8-[(1'R and 1'S)-(1'-methyl-2'-propen-1-yl)]bicyclo[3.3.0]octan-2-ones (8a,8b). This preparation is based on a procedure described by Sakurai.[2,3] A solution of bicyclic enone **6** (1.49 g, 9.0 mmol) in CH_2Cl_2 (72 mL) was stirred and cooled at -78 °C as an aliquot of 1.00 **M** $TiCl_4$ in CH_2Cl_2 (9.0 mL, 9.0 mmol) was added dropwise over 7 min. After 10 min, a solution of (*Z*)-crotyltrimethysilane (1.50 g, 11.7 mmol, *Z*:*E* = 5:1) in CH_2Cl_2 (27 mL) was added dropwise over 10 min. The purple solution was stirred at -78 °C for 5 min and at 0 °C for 5 min. During this time, aliquots were spotted directly onto TLC plates. The $TiCl_4$ was hydrolyzed by adding water (24 mL). After 5 min,

the heterogeneous mixture was diluted with ether (2 x 70 mL). The combined organic layers were washed with 10% HCl (60 mL), satd. $NaHCO_3$ (60 mL), satd. NaCl (60 mL); dried ($MgSO_4$); and evaporated to give 1.88 g of crude. Purification by flash chromatography (Et_2O:hexane, 5:95) afforded 1.73 g (87%) of a 1:1 mixture of 1'α (anti) and 1'β (syn) methyl isomers (GC) as a clear, colorless oil: TLC R_f = 0.65 (15:85, Et_2O:hexane); The following data were obtained by analyses and spectra of the isomer mixture: GC t_R = 12.08 (1'α), 12.16 min (1'β) (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) (1'α-isomer) δ 1.01 (d, 3H, *J* = 6.4 Hz, 1'-CH_3), 1.08 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.207 (s, 3H, CH_3), 1.41-1.81 (m, 8H, α + β isomer), 1.74 and 1.79 (ABq, 2H, J_{AB} = 13.4 Hz, C4), 1.96-2.11 (m, 3H, α + β isomer), 2.21 (d, 1H, *J* = 4.9 Hz, C1), 4.95-5.01 (m, 4H, C3', α + β isomers), 5.67 (ddd, 1H, *J* = 17.1, 10.3, 8.5 Hz, C2'); (1'β-isomer) δ 1.06 (d, 3H, *J* = 6.8 Hz, 1'-CH_3), 1.06 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.211 (s, 3H, CH_3), 1.41-1.81 (m, 8H, α + β isomer), 1.72 and 1.76 (ABq, 2H, J_{AB} = 13.6 Hz, C4), 1.96-2.11 (m, 3H, α + β isomers), 2.14 (sext, 1H, *J* = 7.3 Hz), 2.29 (d, 1H, *J* = 3.66 Hz, C1), 4.95-5.01 (m, 4H, C3', α+β isomer), 5.74 (9-line symm m, 1H, C2'); ^{13}C NMR (126 MHz, $CDCl_3$) (1'β isomer) δ 19.5, 26.6, 27.9, 29.2, 29.4, 41.7, 42.8, 44.4, 47.1, 49.6, 50.3, 62.4, 114.1, 142.4, 226.2 (C2); (1'α-isomer) δ 18.8, 26.4, 28.1, 28.9, 29.8, 41.6, 43.2, 44.3, 46.8, 48.8, 50.1, 61.8, 113.9, 143.8, 226.1 (C2); IR (CCl_4) 2962, 2931, 2869, 1734 (C=O), 1466, 1376 cm^{-1}; MS (EI, 70 eV) *m/z* (rel intensity %): 220 (20), 192 (4), 165 (4), 136 (43), 125 (10), 108 (8), 93 (6), 81 (100). Kugelrohr distillation at 60-65°C (0.30 torr) gave an analytical sample: Anal. Calcd for $C_{15}H_{24}O$ (220.34): C, 81.76; H, 10.98. Found: C, 81.78; H, 11.06. A subsequent reaction carried out as described above using bicyclic enone **6** (0.50 g, 3.0 mmol) and *(E)*-crotyltrimethylsilane (0.50 g, 3.9 mmol) proceded to give 0.57g (86%) of a 1:1.8 (1'α-Me:1'β-Me) mixture of keto-olefins. In a similar reaction, a solution of (*Z*)-crotyltrimethysilane (82 mg, 0.64 mmol, *Z*:*E* = 6:1) in CH_2Cl_2 (3 mL) was added to a solution of enone **6** (100 mg, 0.61 mmol) and $TiCl_4$ (0.61 mmol) in CH_2Cl_2 (9 mL) at -78 °C and allowed to stir at -78 °C for 20 min and then at 0 °C for 10 min. Workup gave 118 mg of of a 1.2:1 (GC) mixture of **8a,b**. Purification by flash chromatography (13 g SiO_2; EtOAc:hexane, 5:95) afforded 81 mg (61%) of **8a,b** as a clear, colorless oil.

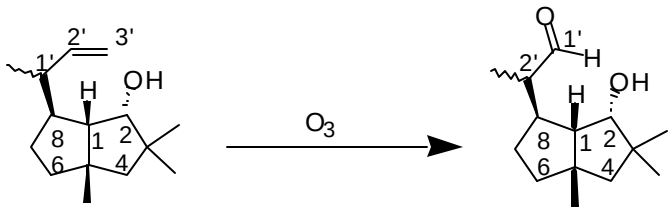


(1S*,5S*,8S*)-3,3,5-Trimethyl-8-[(1'R and 1'S)-(1-deuterio-1'-methyl-2'-propen-1-yl)]bicyclo[3.3.0]octan-2-ones. A solution of ketones **8a,8b** (40 mg, 0.18 mmol, 1:1 isomer ratio) and KOH (8 mg, 0.14 mmol) in CD_3OD (0.18 mL) was stirred and heated at 50 °C for 2 hr. After cooling to rt., Et_2O (4 mL) and 5% HCl (1 mL) were added. The organic layer was washed with satd. $NaHCO_3$ (1 mL) and satd. NaCl (1 mL), dried ($MgSO_4$), and evaporated to afford 23 mg of crude ketone. ^1H NMR spectral analysis indicated 90% deuterium incorporation at C1. Purification by column chromatography (Et_2O:hexane, 10:90) afforded 20 mg (50%) of a 1:1 mixture of 1'α and 1'β isomers (GC) as a clear, colorless oil: TLC R_f = 0.65 (15:85, Et_2O:hexane); The following data were obtained by analyses and spectra of the isomer mixture. GC t_R = 11.41 (1'α), 11.49 min (1'β) (Method A); ^1H and ^{13}C NMR (500 and 125 MHz, $CDCl_3$) spectra were identical to those of the starting ketone except for the following: absence of the δ = 2.21 and 2.29 signals (C1-H) in the ^1H spectrum and δ = 61.8 and 62.4 (C1) in the ^{13}C spectrum.



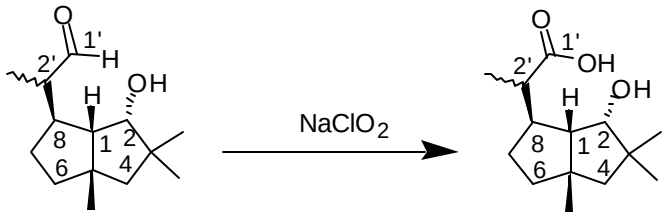
(1*S,2*S**,5*S**,8*S**)-8-[(1'*R* and 1'*S*)-(1'-Methyl-2'-propen-1-yl)]-3,3,5-trimethylbicyclo-[3.3.0]octan-2-ols (9a,b).** A solution of ketones **8a,b** (800 mg, 3.63 mmol) in THF (6 mL) was stirred and cooled at 0 °C in an ice water bath under N_2 as a solution of L-Selectride® (lithium tri-*sec*-butylborohydride) in THF (Aldrich; 7.26 mL, 7.26 mmol) was added dropwise over 3 min. The resulting solution was stirred at 0 °C for 4 h. The reaction was stopped and excess hydride was destroyed by the careful addition of 3 **M** NaOH (5 mL).

The flask was fitted with an efficient reflux condenser, and 30% H_2O_2 (4 mL) was added dropwise over 30 min *(Caution! Vigorous reaction)*. After the solution had stirred at rt for 30 min, ether (100 mL) and water (20 mL) were added. The organic layer was washed with 3 **M** NaOH (20 mL), water (20 mL), and satd. NaCl (20 mL); dried ($MgSO_4$); and concentrated under reduced pressure to afford 1.28 g of crude **9a,b** as a clear, colorless oil. GC analysis of the crude product showed an 1:1.76 ratio of methyl isomers. Flash chromatography (80 g SiO_2; ether:hexane, 1:9) of the crude oil gave 782 mg (97%) of **9a,b** as a clear colorless oil. The GC ratio of methyl isomers was 1:1.74. Data taken from mixture: **Minor isomer (1'$_a$-Me isomer):** t_R = 10.86 min. (Method A); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.55 (CH), 112.92 (CH_2), 82.64 (CH), 60.16 (CH), 52.19 (CH_2), 50.09 (C_q), 47.04 (C_q), 44.97 (CH), 44.08 (CH), 43.71 (CH_2), 33.07 (CH_2), 30.36 (CH_3), 27.94 (CH_3), 24.12 (CH_3), 19.05 (CH_3); GC-MS (CI, 130 eV) *m/z* (relative intensity %): 223 (5, MH^+), 221 (12), 205 (47), 149 (100), 135 (36), 109 (36). **Major isomer (1'$_b$-Me isomer):** t_R = 11.08 min (Method A); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.77 (CH), 112.78 (CH_2), 82.89 (CH), 59.96 (CH), 52.11 (CH_2), 50.16 (C_q), 47.19 (C_q), 44.15 (CH), 43.87 (CH), 43.67 (CH_2), 32.77 (CH_2), 30.32 (CH_3), 27.90 (CH_3), 24.17 (CH_3), 19.14 (CH_3); GC-MS (CI, 130 eV) *m/z* (relative intensity %): 223 (4, MH^+), 221 (11), 205 (48), 149 (100), 135 (37), 109 (36).

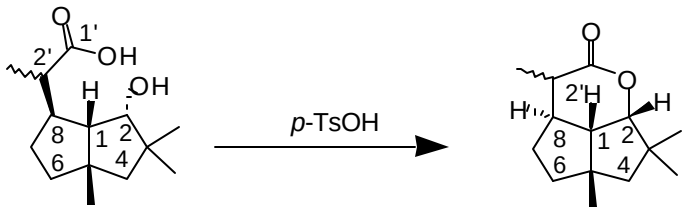


(1*S,2*S**,5*S**,8*S**)-8-[(2'*R* and 2'*S*)-(2'-Methyl-1'-ethanal)]-3,3,5-trimethylbicyclo-[3.3.0]octan-2-ols.** A solution of olefin **9a,b** (318 mg, 1.430 mmol) in anhydrous MeOH (20 mL) was stirred and cooled at -78 °C (dry ice / 2-propanol) while purging with O_2 (1.0 L/min) for 5 min. Oxygen containing O_3 (~1.8 mmol / min) was passed

through the solution until the KI trap darkened. O_3 generation was stopped, the solution was purged with O_2 for 10 min, and Me_2S (1.5 mL, ~20 mmol) was added in a single portion. The solution was stirred at -10 °C (ice / water / salt) for 2 h under N_2 and at rt for another 2 h. The solvents were removed under reduced pressure, and the residue was partitioned between hexane (40 mL) and water (10 mL). The organic layer was washed with H_2O (2 × 10 mL) and satd. NaCl (10 mL), dried (Na_2SO_4), and carefully concentrated under reduced pressure to afford (279 mg, 87%) of a clear, slightly yellow oil. GC of the crude product showed a methyl isomer ratio of 1:1.34, but a ^1H NMR analysis of same material showed 1:1.83. Product mixture: IR (neat film) ν_{max} 3503 br. s (OH), 2947, 2866, 2718, 1721 (C=O), 1716 (C=O), 1456, 1376, 1075 cm^{-1}; Minor product: t_R = 12.32 min (Method A); GC-MS (CI, 130 eV) *m/z* (relative intensity %): 223 (MH^+) (3), 209 (31), 189 (28), 149 (100), 109 (76). Major product: t_R = 12.53 min (Method A); GC-MS (CI, 130 eV) *m/z* (relative intensity %): 223 (MH^+) (3), 209 (31), 189 (27), 149 (100), 109 (54).



(1*S,2*S**,5*S**,8*S**)-8-[(2'*R* and 2'*S*)-(2'-Methyl-1'-ethanoyl]-3,3,5-trimethylbicyclo-[3.3.0]octan-2-ols.** The selective oxidation of the aldehyde in the presence of the secondary alcohol was performed by a procedure of Lindgren[4] and Kraus[5] with isoprene as the Cl_2 scavenger. A suspension of aldehyde (287 mg, 1.28 mmol) in *t*-butyl alcohol (15 mL), isoprene (12.8 mmol), and aqueous phosphate buffer (1 **M**, pH = ~3.5) (15 mL) was stirred at rt as $NaClO_2$ (159 mg, 1.41 mmol) in H_2O (2 mL) was added in one portion. The suspension rapidly turned light green. After 15 min at rt ether (150 mL), water (30 mL), and 10% HCl (5 mL) were added. The organic layer was washed with H_2O (20 mL) and extracted with 3 **M** NaOH (2 × 20 mL). The organic layer was washed with satd. NaCl (20 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give 117 mg of neutral products. The basic aqueous layer was acidified with 6 **M** HCl and extracted with ether (2 × 25 mL). This ether layer was dried ($MgSO_4$) and concentrated under reduced pressure to give 263 mg (86 %) of acid mixture as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.52 (d, 1H, *J* = 5.4 Hz, major), 3.50 (d, 1H, *J* = 5.6 Hz, minor), 2.55 (app. quintet, 1H, *J* = 7.1 Hz), 2.30-2.46 (m, 3H), 2.04 (t, 1H, *J* = 6.1 Hz), 2.00 (t, 1H, *J* = 5.9 Hz), 1.85-1.95 (m, 2H), 1.66 (d, 2H, *J* = 12.9 Hz), 1.53-1.62 (m, 1H), 1.51 (d, 1H, *J* = 12.9 Hz), 1.40-1.51 (m, 4H), 1.33 (d, 1H, *J* = 12.9 Hz, major), 1.32 (d, 1H, *J* = 12.9 Hz, minor), 1.21 (d, 3H, *J* = 6.8 Hz, CH_3, minor), 1.19 (d, 3H, *J* = 6.8 Hz, CH_3, major), 1.10 (s, 6H, $(CH_3)_2$), 1.02 (s, 3H, CH_3, major), 1.01 (s, 6H, $(CH_3)_2$), 0.99 (s, 3H, CH_3, minor); ^{13}C NMR (100 MHz, $CDCl_3$) (major) δ 182.37, 82.49, 59.01, 51.99, 50.39, 49.12, 44.54, 43.30, 41.18, 32.81, 30.32, 27.98, 24.17, 15.11; (minor) δ 182.78, 81.74, 61.15, 52.19, 50.42, 46.80, 46.30, 43.03, 41.62, 32.76, 30.57, 28.25, 16.50.

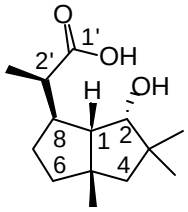


(1*S,2*S**,5*S**,8*S**)-8-[(2'*R* and 2'*S*)-(2'-Methyl-1'-ethanoic acid)]-3,3,5-trimethylbicyclo-[3.3.0]octan-2-ol Lactones (10a,10b).** A solution of acid mixture (197 mg, 0.820 mmol) and crystalline *p*-TsOH•H_2O (3 mg, 0.015 mmol) in benzene (25 mL) was stirred and heated at reflux for 45 min. The reaction progress was monitored by directly spotting aliquots onto TLC plates and observing the appearance of the lactones. A second portion of *p*-TsOH•H_2O (3 mg, 0.015 mmol) was added after 45 min, and the refluxing was continued for ~ 30 min. The solution was rapidly cooled to rt, and ether (20 mL), water (10 mL), and 10% HCl (2 dps) were added. The ethereal solution was extracted with 3 **M** NaOH (2 × 10 mL), water (10 mL), and satd. NaCl (20 mL); and dried ($MgSO_4$). Evaporation of the solvents at reduced pressure to provided 75 mg (41%) of an oil. Purification by flash chromatography (12 g SiO_2; ether:hexane, 1:9) afforded pure **10b** (27 mg, 15%), a mixture of α + β secondary methyl isomers (20 mg, 11%), and **10a** (18 mg, 10%) were obtained (total yield 36%; α/β ratio 1.8:1). The combined aqueous base extractions were acidified to pH ~1 with 10% HCl and extracted with ether (2 × 10 mL). The organic layer was dried ($MgSO_4$) and evaporated to give nearly pure 1'β-Me starting acid (37 mg, 19%) that contained a small amount (~ 5 % by ^{1}H NMR) of the 1'α-Me isomer.

(1*S,2*S**,5*S**,8*S**)-8-[(2'S)-(2-Methyl-1-ethanoic acid)]-3,3,5-trimethylbicyclo-[3.3.0]octan-2-ol Lactone (10a):** t_R = 13.36 min (GC Method A); TLC R_f = 0.28 (EtOAc:hexane, 15:85); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.59 (d, 1H, *J* = 6.3 Hz, C1-H), 2.24 (dq, 1H, *J* = 12.2, 7.1 Hz, C8-H), 1.82-1.96 (m, 4H), 1.65-1.73 (m, 2H), 1.60 (s, 2H, C3-H_2), 1.27 (d, 3H, *J* = 7.1 Hz, C8-CH_3), 1.18 (s, 3H), 1.17 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.02 (C-9), 90.84 (C-1), 59.49, 57.02, 45.91, 45.03, 43.30,

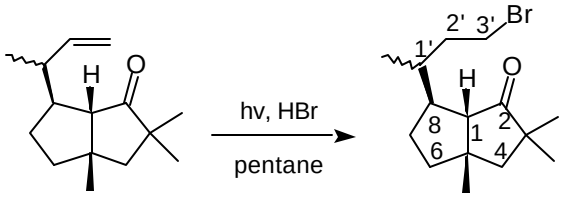
42.54, 41.95, 33.06, 29.79, 28.56, 28.14, 15.25; IR (CCl_4 soln.) ν_{max} 2956, 2929, 2870, 2856, 1736 (C=0), 1460, 1376, 1182, 1169, 1149, 1115, 1050, 908 cm^{-1}; MS (CI, 130 eV) *m/z* (relative intensity %): 223 (27, MH^+), 205 (47), 177 (42), 163 (16), 149 (100); HRCIMS Calcd for $C_{14}H_{23}O_2$: 223.1698. Found: 223.1702 (Δ = 1.8 ppm).

(1*S,2*S**,5*S**,8*S**)-8-[(2'*R*)-(2'-Methyl-1'-ethanoic acid)]-3,3,5-trimethylbicyclo-[3.3.0]octan-2-ol Lactones (10b):** t_R = 13.66 min (GC Method A); TLC R_f = 0.25 (EtOAc:hexane, 15:85); ^1H NMR (400 MHz, $CDCl_3$) δ 4.58 (d, 1H, *J* = 6.8 Hz, C1-H), 2.88 (qd, 1H, *J* = 7.6, 5.0 Hz, C8-H), 2.29 (tt, 1H, *J* = 12.9, 5.2 Hz), 2.05 (dd, 1H, *J* = 13.2, 6.8 Hz), 1.84-1.93 (m, 2H), 1.66-1.74 (m, 1H), 1.60 (s, 2H), 1.42-1.53 (m, 1H), 1.19 (d, 3H, *J* = 7.6 Hz, C8-CH_3), 1.19 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.11 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.47, 91.19, 57.00, 51.89, 45.50, 43.30, 41.84, 41.53, 38.18, 33.10, 28.59, 28.41, 27.15, 10.71; IR (CCl_4 soln.) ν_{max} 2955, 2872, 2856, 1736 (C=O), 1462, 1377, 1040, 908 cm^{-1}; MS (CI, 130 eV) *m/z* (relative intensity %): 223 (82, MH^+), 205 (47), 177 (47), 149 (100), 79 (45); HRCIMS Calcd for $C_{14}H_{23}O_2$: 223.1698. Found: 223.1699 (Δ = 0.4 ppm).



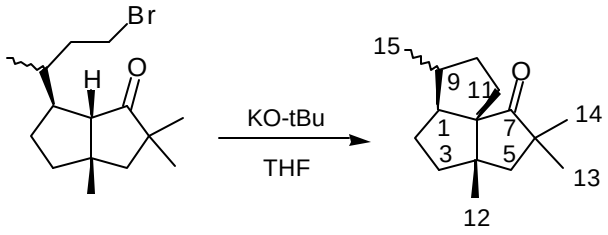
(1*S,2*S**,5*S**,8*S**)-8-[(2'*R*)-(2'-Methyl-1'-ethanoic acid)]-3,3,5-trimethylbicyclo-[3.3.0]octan-2-ol.** ^1H NMR (400 MHz, $CDCl_3$) δ 5.0 (br. s, 1H, -COOH), 3.51 (d, 1H, *J* = 5.4 Hz, C2-H), 2.55 (app. quintet of d, 1H, *J* = 6.8, 2.5 Hz), 2.44 (app. quintet, 1H, *J* = 6.8 Hz), 2.04 (t, 1H, *J* = 6.0 Hz), 1.86-1.94 (m, 1H), 1.65 (d, 1H, *J* = 12.9 Hz, C4-H α or β), 1.46-1.60 (m, 2H), 1.52 (s, 1H), 1.33 (d, 1H, *J* = 12.9 Hz, C4-H β or α), 1.20 (d, 3H, *J* = 6.8 Hz, C1'-CH_3), 1.10 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.01 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.47 (C_q, C2'), 82.49 (CH, C2), 59.03 (CH, C2'),

51.98 (CH_2), 50.38 (C_q), 47.13 (C_q), 44.57 (CH), 43.30 (CH_2), 41.16 (CH), 32.81 (CH_2), 30.32 (CH_3), 27.97 (CH_3), 24.16 (CH_3), 15.15 (CH_3). Attempts to obtain MS data with EI and CI ionization failed to give a molecular ion.



(1S*,5S*,8S*)-3,3,5,Trimethyl-8-[1R' and 1S')-(1'-methyl-3'-bromopropyl)]bicyclo[3.3.0]octan-2-ones (11). The radical hydrobromination was based on a procedure described by Molander.[6] A solution of olefin (100 mg, 0.45 mmol, 1:1 isomer ratio) in HPLC grade pentane (30 mL, Aldrich) was placed in a 300-mL round bottomed quartz flask. The flask was fitted with a gas-dispersion tube (5 mm OD, 25-50 micron porosity) and sealed with a gas outlet connected to a trap followed by a satd. $NaHCO_3$ bath. The gas dispersion tube was lowered below the solution level and the solution was purged with N_2 for 5 min. The flask was lowered into the Rayonnet photochemical reactor equipped with 8 254-nm bulbs symmetrically positioned around the flask. The gas dispersion tube was raised above the liquid level, and HBr flow was initiated (ca. 5 cm^3/min). Once HBr was observed to reach the neutralization bath, the gas-dispersion tube was lowered below the solution level, magnetic stirring was initiated, and the lamps were energized. After 13 min, the irradiation and HBr flow were terminated. The solution was purged with N_2 for 5 min, washed with satd. $NaHCO_3$ (4 mL) and satd. NaCl (4 mL), dried ($MgSO_4$), and evaporated to give 120 mg of crude bromo ketone. Purification by flash chromatography (2:98, EtOAc:hexane) afforded 105 mg (73%) (Purity: 95%, 1:1 isomer ratio by GC) as a clear, colorless oil: The NMR assignments for the individual isomers were made by comparison with spectra of the 1:1.8 isomer mixture; TLC R_f = 0.64 (15:85, Et_2O:hexane); t_R = 15.64 (1'α), 15.74 min (1'β) (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (d, 3H, *J* = 6.6 Hz, 1'-CH_3, 1'α), 0.94 (d, 3H, *J* = 6.2 Hz, 1'-CH_3, 1'β), 1.08 (s, 6H, CH_3, 1'α + 1'β), 1.101 (s, 3H, CH_3, 1'β), 1.104 (s, 3H, CH_3, 1'α), δ1.21 (s, 3H, CH_3, 1'β), 1.22 (s, 3H, CH_3, 1'α), 1.43-1.79 (m, 12H), 1.74 and 1.81 (ABq, 2H, J_{AB} = 13.6 Hz, C4, 1'α), 1.74 and 1.82 (ABq, 2H, J_{AB} = 13.6 Hz, C4, 1'β), 1.93 (qd, 1H, *J* = 8.0, 5.3 Hz, 1'α), 2.00 (m, 2H), 2.07 (dddd, 1H, *J* = 14.0, 8.9, 8.0, 3.2 Hz,

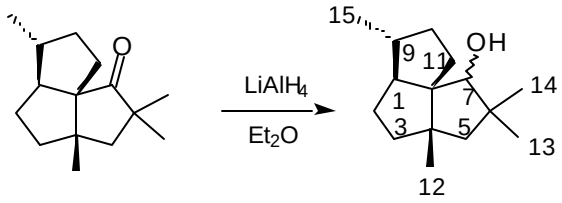
1'α), 2.19 (d, 1H, *J* = 5.3 Hz, 1'β), 2.21 (d, 1H, *J* = 5.3 Hz, 1'α), 3.40 (m, 2H), 3.56 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (1'α–isomer) δ 16.3, 26.7, 28.08, 29.1, 29.8, 32.3, 36.5, 38.7, 41.7, 44.5, 47.1, 49.4, 50.1, 62.5, 226.1 (C2); (1'β–isomer) δ 17.0, 26.8, 28.12, 28.9, 30.4, 32.4, 36.0, 38.0, 41.6, 44.6, 47.0, 48.9, 50.0, 61.4, 226.3 (C2); IR (CCl_4) 2958, 2867, 1731 (C=O), 1458, 1380, 1088 cm^{-1}; MS (EI, 70 eV) *m/z* (rel intensity %): 302 (4), 300 (4), 221 (62), 203 (5), 165 (36), 137 (55), 125 (63), 109 (29), 95 (15), 81 (100), 67 (13); Kugelrohr distillation at 130-135°C (0.09 torr) gave a sample for elemental analysis: Anal. Calcd for $C_{15}H_{24}O$ (301.27): C, 60.00; H, 8.36. Found: C, 59.52; H, 8.25. HRMS (EI, 70 eV) Calcd for $C_{15}H_{25}OBr$: 300.1089. Found: 300.1097 (Δ = -2.7 ppm). A subsequent reaction carried out as described about using a 1:1.8 (1'α-Me:1'β-Me) mixture of keto-olefins (150 mg, 0.68 mmol) gave 148 mg (72%) of a 1:1.8 mixture of bromo ketones.



(±)-Cameroonanone and (±)-9-epi-Cameroonanone. (1S*,5S*,8S*,9R*)-and-(1S*,5S*,8S*,9S*)-3,3,5,9-Tetramethyl-tricyclo[6.3.0.0]undecan-2-ones (12,13). The cyclization was based on a procedure described by Piers.[7] An aliquot of 1.0 **M** KO-tBu (2.79 mL, 2.79 mmol) in THF was added dropwise over 4 min to a stirred solution of 613 mg (560 mg pure ketone, 1.86 mmol, 1:1 1'α:β isomer ratio) of bromo ketone in THF (42 mL). After 10 min, the excess base was neutralized by adding 10% HCl (6 mL). The solution was diluted with hexane (35 mL). The organic layer was washed with satd. $NaHCO_3$ (17 mL), satd. NaCl (17 mL), dried ($MgSO_4$), and evaporated to give 387 mg (93% crude yield) of pale-yellow oil that was 99% pure by GC. Purification by column chromatography (57 g SiO_2; 0.75:99.25, Et_2O:hexane) afforded 152 mg of clear, colorless oil **12** that was >98% pure by GC. Two additional column chromatographies (25 g SiO_2 and 32 g SiO_2 respectively; 0.75:99.25,

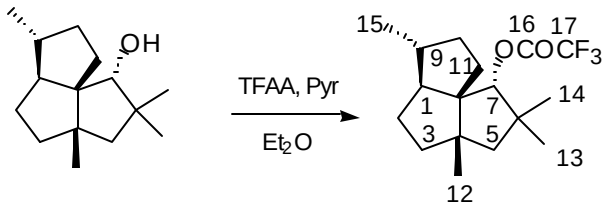
Et_2O:hexane) of fractions containing a mixture of epimeric ketones afforded 15 mg (GC Purity: 100%) of **12** in addition to 16 mg (GC Purity: 100%) and 82 mg (GC Purity: 98%) of **13**. HPLC purification (Method A) gave an analytical sample of **13** (68 mg, GC Purity: 100%). The nmr spectral data were identical to those previously reported for **12**.[4] **(±)-12**: TLC R_f = 0.78 (15:85, Et_2O:hexane); t_R = 12.11 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (d, 3H, *J* = 5.9 Hz, C15), 1.06 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.39-1.61 (m, 6H), 1.64 and 1.72 (ABq, 2H, J_{AB} = 13.9 Hz, C5), 1.72-1.84 (m, 3H), 1.90 (t, 1H, *J* = 7.7 Hz, C1); ^{13}C NMR (126 MHz, $CDCl_3$) δ 18.8, 24.6, 27.4, 27.7, 28.8, 31.7, 36.6, 40.8, 43.3, 45.0, 47.6, 48.4, 61.2, 70.7, 229.3 (C7); ^{1}H NMR (750 MHz, C_5D_5N) δ 0.90 (d, 3H, *J* = 6.6 Hz, C15), 0.99 (s, 3H, C12), 1.04 (s, 3H, C14), 1.09 (s, 3H, C13), 1.27 (ddt, 1H, *J* = 13.1, 6.6, 1.8 Hz, C2-βH), 1.37 (m, 1H, C9), 1.38 (ddd, 1H, *J* = 12.7, 10.9, 6.3 Hz, C11-βH), 1.46 (m, 1H, C3), 1.47 (m, 1H, C3), 1.51 and 1.60 (ABq, 2H, J_{AB} = 13.8 Hz, C5-βH and αH), 1.57 (qd, 1H, *J* = 11.2, 6.5 Hz, C10-αH), 1.69 (m, 1H, C10-βH), 1.70 (m, 2H, C2-αH), 1.81 (ddd, 1H, *J* = 12.7, 6.5, 2.9 Hz, C11-αH), 1.90 (td, 1H, *J* = 8.3, 1.7 Hz, C1); ^{13}C NMR (189 MHz, C_5D_5N) δ 19.5 (C15), 25.0 (C12), 27.9 (C14), 28.3 (C13), 29.5 (C2), 32.3 (C11), 37.3 (C10), 41.4 (C3), 43.8 (C9), 45.4 (C6), 48.2 (C4), 48.7 (C5), 61.8 (C1), 71.2 (C8), 228.4 (C7); IR (CCl_4) 2954, 2870, 1727 (C=O), 1549, 1468 cm^{-1}; MS (EI, 70 eV) *m/z* (rel intensity %): 220 (27), 205 (3), 192 (6), 177 (4), 165 (100), 149 (5), 136 (30), 121 (56), 110 (42), 94 (34), 79 (58), 67 (16). Kugelrohr distillation at 40-45°C (0.30 torr) gave an analytical sample: Anal. Calcd for $C_{15}H_{24}O$ (220.34): C, 81.76; H, 10.98. Found: C, 81.46; H, 11.22. **(±)-13**: TLC R_f = 0.74 (15:85, Et_2O:hexane); t_R = 12.67 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (d, 3H, *J* = 6.8 Hz, C15), 1.06 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.14 (m, 1H), 1.15 (s, 3H, CH_3), 1.46 (m, 1H), 1.56-1.82 (m, 6H), 1.65 and 1.76 (ABq, 2H, J_{AB} = 13.6 Hz, C5), 2.05 (m, 1H), 2.40 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.2 (CH_3), 24.5 (CH_3), 24.6 (CH_2), 27.4 (CH_3), 28.6 (CH_3), 29.9 (CH_2), 34.8 (CH_2), 37.9 (CH), 43.1 (CH_2), 45.2 (C), 48.5 (C), 49.2 (CH_2), 57.1 (CH_2), 71.5 (C), 228.1 (C7); ^{1}H NMR (750 MHz, C_5D_5N) δ 0.83 (d, 3H, *J* = 6.9 Hz, C15), 0.98 (s, 3H, C12), 1.04 (s, 3H, C13/14), 1.06 (qd, 3H, *J* = 12.2, 7.1 Hz, C10-βH), 1.15 (s, 3H, C13/14), 1.34 (dt, 1H, *J* = 12.2, 8.1 Hz, C3), 1.42 (m, 1H, C2), 1.50 (m, 1H, C2), 1.52 and 1.64 (ABq, 2H, J_{AB} = 13.6

Hz, C5), 1.56 (m, 1H, C3), 1.58 (m, 1H, C11-βH), 1.63 (dt, 1H, *J* = 12.5, 6.2 Hz, C10), 1.92 (ddd, 1H, *J* = 13.2, 12.5, 7.0 Hz, C11-αH), 2.00 (dsext, 1H, *J* = 12.8, 6.5 Hz, C9), 2.39 (ddd, 1H, *J* = 9.4, 7.7, 5.7 Hz, C1); ^{13}C NMR (189 MHz, C_5D_5N) δ 15.3 (C15), 24.5 (C12), 24.7 (C2), 27.5 (C13/14), 28.7 (C13/14), 30.0 (C11), 34.9 (C10), 38.2 (C9), 43.0 (C3), 45.0 (C6), 49.00 (C4), 49.01 (C5), 57.2 (C1), 71.6 (C8), 226.6 (C7); IR (CCl_4) 2960, 2929, 2862, 1728 (C=O), 1460, 1380 cm^{-1}; MS (EI, 70 eV) *m/z* (rel intensity %): 220 (100), 205 (47), 192 (29), 178 (38), 165 (56), 149 (12), 135 (42), 121 (82), 107 (49), 93 (56), 79 (90), 67 (25). Kugelrohr distillation at 45-50°C (0.65 torr) gave an analytical sample: Anal. Calcd for $C_{15}H_{24}O$ (220.34): C, 81.76; H, 10.98. Found: C, 81.41; H, 11.06. A subsequent reaction carried out as described above using a 1:1.8 (1'α-Me:1'β-Me) mixture of bromo ketones (65mg, 0.22 mmol) gave 37 mg (77%) of a 1:1.6 mixture of ketones **12** and **13**.

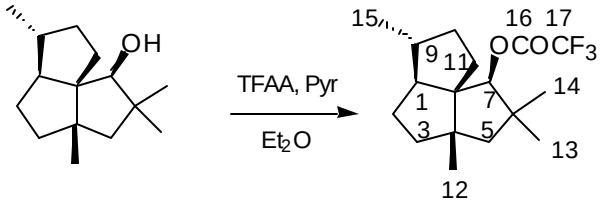


(±)-Cameroonan-7a and 7b-ols. (1S*,5S*,7R*,8S*,9S*)-and-(1S*,5S*, 7S*,8S*,9S*)-3,3,5,9-Tetramethyl-tricyclo[6.3.0.0]undecan-2-ols (1,14). The reduction was performed according to the procedure described by Weyerstahl.[8] A suspension of $LiAlH_4$ (22mg, 0.579 mmol) in ether (3 mL) was stirred and cooled at 0 °C as a solution of **(±)-12** (85 mg, 0.386 mmol) in ether (2 mL) was added dropwise over 1 min. After 30 min at 0 °C, the excess hydride was consumed by the sequential addition of water (22 μL), 15% NaOH (22 μL), and water (66 μL) at 1 min intervals according to standard procedures[5] and the suspended salts were allowed to stir at 0 °C for 30 min and rt for 15 min. The ethereal supernatent was pipetted from the white salts, and the salts were washed with ether (2x4 mL). The ethereal solution and washes were combined, dried ($MgSO_4$), and evaporated to give a white solid residue (79 mg) that was a 1.4:1 mixture of α:β isomers by GC. Purification by column chromatography (8:92, Et_2O:pentane) gave 74 mg (86%) (isomer ratio of 1.4:1 by GC). Further column chromatography (2:98, Et_2O:pentane) followed by HPLC purification (Method B) of fractions containing a mixture of α:β alcohols afforded 34 mg (GC Purity: 100%) of **1** and 24 mg (GC Purity: 99%) of **14** as crystalline solids. The spectral data were identical to those previously reported[4] except for coupling observed in the present case between the hydroxyl proton and the carbinol proton. **1**: mp = 48-49 °C; TLC R_f = 0.47 (15:85, Et_2O:hexane); t_R = 7.52 min (Method B); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.00 (d, 3H, *J* = 6.6 Hz, C15), 1.04 (s, 3H, CH_3), 1.24 (m, 1H), 1.32 (dddd, 1H, *J* = 12.6, 6.0, 2.2, 1.4 Hz), 1.34 (d, 1H, *J* = 8.1 Hz, OH, Ex D_2O), 1.39-1.47 (m, 3H), 1.41 and 1.55 (ABq, 2H, J_{AB} = 14.3 Hz, C5), 1.53 (m, 1H), 1.58-1.68 (m, 2H), 1.78 (ddt, 1H, *J* = 12.4, 10.6, 8.4 Hz), 1.91 (t, 1H, *J* = 8.2 Hz), 3.69 (d, 1H, *J* = 7.9 Hz, C7; exch D_2O s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.4 (CH_3), 23.8 (CH_3), 25.7 (CH_3), 29.0 (CH_2), 32.4 (CH_3), 35.3

(CH_2), 36.1 (CH_2/C), 38.6 (CH_2/C), 40.0 (CH_2/C), 43.8 (CH), 47.6 (CH_2/C), 51.4 (CH), 52.6 (CH_2/C), 67.1 (CH_2/C), 89.7 (C7); ^{1}H NMR (500 MHz, C_6D_6) δ 0.91 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.05 (d, 3H, *J* = 6.3 Hz, C15), 1.27 (dddd, 1H, *J* = 12.7, 5.2, 3.2, 1.4 Hz), 1.33 and 1.48 (ABq, 2H, J_{AB} = 14.2 Hz, C5), 1.33-1.42 (m, 4H), 1.37 (d, 1H, *J* = 5.2, OH), 1.44-1.49 (m, 1H), 1.54-1.62 (m, 2H), 1.76 (ddt, 1H, *J* = 12.9, 9.6, 8.9 Hz), 2.08 (t, 1H, *J* = 7.8 Hz), 3.50 (d, 1H, *J* = 5.5 Hz, C7); ^{13}C NMR (126 MHz, C_6D_6) δ 19.5, 24.1, 25.8, 29.3, 32.5, 35.6, 36.5, 38.9, 40.3, 44.2, 47.6, 51.5, 52.9, 67.4, 89.4 (C7); IR (CCl_4) 3634 (OH), 2949, 2866, 1549, 1464 cm^{-1}; MS (EI, 70 eV) *m/z* (rel intensity %): 222 (5), 204 (22), 189 (15), 166 (36), 148 (34), 135 (100), 124 (46), 109 (29), 96 (42), 81 (32), 67 (17). **14**: mp = 62-63 °C; TLC R_f = 0.43 (15:85, Et_2O:hexane); t_R = 7.81 min (Method B); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (s, 3H, CH_3), 0.92 (d, 3H, *J* = 6.6 Hz, C15), 0.97 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 1.18 (ddt, 1H, *J* = 12.1, 9.7, 9.4 Hz), 1.34-1.55 (m, 5H), 1.37 and 1.38 (ABq, 2H, J_{AB} = 13.4 Hz, C5), 1.42 (d, 1H, *J* = 6.8 Hz, OH, Ex D_2O), 1.59-1.70 (m, 2H), 1.79 (dddd, 1H, *J* = 12.0, 7.5, 6.3, 3.5 Hz), 1.88 (ddd, 1H, *J* = 13.7, 8.8, 3.6 Hz), 3.36 (d, 1H, *J* = 6.8 Hz, C7, Ex D_2O s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.0 (CH_3), 21.5 (CH_3), 25.7 (CH_2), 26.4 (CH_2), 28.4 (CH_3), 28.5 (CH_3), 36.7 (CH_2), 38.1 (CH), 41.7 (CH_2/C), 43.5 (CH_2/C), 48.4 (CH_2/C), 52.7 (CH_2/C), 62.7 (CH), 65.7 (CH_2/C), 88.2 (C7); ^{1}H NMR (500 MHz, C_6D_6) 0.85 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 0.95 (dd, 3H, *J* = 6.5, 0.8 Hz, C15), 1.00 (s, 3H, CH_3), 1.22 (dtd, 1H, *J* = 11.7, 9.2, 8.9 Hz), 1.27-1.34 (m, 1H), 1.27 and 1.30 (ABq, 2H, J_{AB} = 13.0 Hz, C5), 1.35-1.48 (m, 5H), 1.51-1.62 (m, 2H), 1.76 (m, 1H), 2.09 (ddd, 1H, *J* = 12.7, 8.5, 3.4 Hz), 3.14 (d, 1H, *J* = 5.16 Hz, C7); ^{13}C NMR (126 MHz, C_6D_6) δ 19.2, 21.8, 25.9, 26.8, 28.5, 28.7, 37.1, 38.5, 42.0, 43.8, 48.4, 53.0, 62.9, 66.2, 87.9 (C7); IR (CCl_4) 3630 (OH), 2949, 2934, 2866, 1454, 1374, 1085 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity %): 222 (11), 204 (19), 189 (14), 176 (10), 166 (63), 148 (32), 135 (100), 124 (61), 109 (38), 96 (63), 81 (43), 67 (22).



(±)-Cameroonan-7a-yl Trifluoroacetate. (1S*,5S*,7R*,8S*,9R*)-3,3,5,9-Tetramethyl-Tricyclo[6.3.0.0]undecan-2-yl Trifluoroacetate. The procedure was based on one described by Ho.[9] A solution of cameroonan-7α-ol (15 mg, 0.067 mmol) and pyridine (7 μL) in ether (0.4 mL) was stirred and cooled at 0 °C as trifluoroacetic anhydride (10 μL, 0.074 mmol) was added dropwise over 10 s. The reaction was stirred for 20 min at 0 °C, during this time aliquots were removed and spotted directly onto TLC plates. After 20 min, the reaction was diluted with pentane (5 mL). The pentane solution was washed with 10% HCl (2 mL), satd. $NaHCO_3$ (2 mL), H_2O (2 mL), and satd. NaCl (2 mL); dried ($MgSO_4$); and evaporated to afford 15 mg of crude trifluoroacetate. The spectral data were similar to those previously reported[11], except for the presence of a mutliplet at δ = 1.00 in the ^{1}H NMR and a signal (δ = 67.0) in the ^{13}C NMR previously reported as 77.2. Purification by column chromatography (pentane) gave 14 mg (67%) of a clear cololess oil. TLC R_f = 0.40 (pentane); t_R = 11.69 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (s, 3H, CH_3), 0.98 (d, 3H, *J* = 6.6 Hz, C15), 1.00 (m, 1H), 1.06 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 1.35 (dddd, 1H, *J* = 13.1, 5.3, 3.2, 1.6 Hz), 1.42-1.48 (m, 3H), 1.50 and 1.71 (ABq, 2H, J_{AB} = 14.1 Hz, C5), 1.53-1.56 (m, 1H), 1.60-1.68 (m, 2H), 1.87 (ddt, 1H, *J* = 13.1, 10.1, 8.6, Hz), 2.11 (td, 1H, *J* = 8.4, 1.3 Hz), 5.17 (s, 1H, C7); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.1, 24.9, 25.2, 29.0, 31.8, 35.2, 35.5, 39.66, 39.69, 43.6, 49.3, 52.6, 53.0, 67.0, 95.1 (C7) (The signals for the trifluoromethyl and carbonyl carbons were too weak to detect); IR (neat) 2949, 2872, 1780 (C=O), 1464, 1382, 1345, 1223, 1166, 981 cm^{-1}; MS (EI, 70 eV) *m/z* (rel intensity %): 318 (2), 303 (18), 272 (2), 247 (9), 229 (4), 220 (2), 204 (28), 189 (16), 176 (9), 161 (13), 148 (42), 135 (100), 121 (13), 107 (15), 93 (19); HRMS (EI, 70 eV) Calcd for $C_{17}H_{25}O_2F_3$: 318.1807. Found: 318.1808 (Δ = -0.5 ppm).



(±)-Cameroonan-7b-yl Trifluoroacetate. (1S*,5S*,7S*,8S*,9R*)-3,3,5,9-Tetramethyltricyclo[6.3.0.0]undecan-2-yl trifluoroacetate. Esterification as described above of cameroonan-7β-ol (10 mg, 0.045 mmol) with trifluoroacetic anhydride (7 μL, 0.05 mmol) and pyridine (4 μL) in ether (0.4 mL) afforded 9 mg of crude trifluoroacetate. Purification by column chromatography (pentane) gave 7 mg (49%) of a clear cololess oil. TLC R_f = 0.43 (pentane); t_R = 11.59 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (d, 3H, *J* = 6.6 Hz, C15), 0.97 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.39-1.60 (m, 8H), 1.71-1.85 (m, 4H), 4.95 (s, 1H, C7); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.2, 24.2, 26.8, 27.6, 28.0, 29.1, 36.0, 40.5, 42.0, 42.1, 50.9, 52.7, 61.0, 66.4, 93.4 (C7) (The signals for the trifluoromethyl and carbonyl carbons were too weak to detect); IR (CCl_4) 2953, 2872, 1781 (C=O), 1225, 1162; MS (EI, 70 eV) *m/z* (rel intensity %): 318 (3), 303 (4), 275 (2), 220 (3), 204 (32), 189 (16), 176 (8), 161 (15), 148 (25), 135 (100); HRMS (EI, 70 eV) Calcd for $C_{17}H_{25}O_2F_3$: 318.1807. Found: 318.1814 (Δ = -2.3 ppm).

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