Total synthesis based on the originally claimed structure of mucosin

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General Information

All commercially available reagents and solvents were used in the form they were supplied without any further purification. (+)-Bis[(R)-1-phenylethyl]amine hydrochloride (optical purity ≥ 99% ee by GLC) was purchased from Sigma-Aldrich. The stated yields are based on isolated material. The melting points are uncorrected. Thin layer chromatography was performed on silica gel 60 F 254 aluminum-backed plates fabricated by Merck. Flash column chromatography was performed on silica gel 60 (40-63 µm) fabricated by Merck. NMR spectra were recorded on a Bruker AscendTM 400 at 400 MHz for 1H NMR and at 100 MHz for 13C NMR. Coupling constants (J) are reported in hertz and chemical shifts are reported in parts per million (δ) relative to the central residual protium solvent resonance in 1H NMR (CDCl3 = δ 7.27) and the central carbon solvent resonance in 13C NMR (CDCl3 = δ 77.00 ppm). Mass spectra were recorded at 70 eV on Waters Prospec Q spectrometer using EI as the method of ionization. IR spectra (4000–600 cm⁻¹) were recorded on a Perkin-Elmer Spectrum BX series FT-IR spectrophotometer using a reflectance cell (HATR). Optical rotations were measured using a 1 mL cell with a 1.0 dm path length on a Perkin Elmer 341 polarimeter using the stated solvents. Determination of enantiomeric excess was performed by GLC on an Agilent Technologies 7820A GC instrument with split (1:30) injection, FID
detector and equipped with a chiral stationary phase (Agilent J&W GC columns, CP-Chirasil-DEX CB, 25 m, 0.25 mm, 0.25 μm) applying the conditions stated. X-ray crystallography was performed on a Bruker D8 Venture diffractometer with InCoatec ImuS Microfocus radiation source and Photon 100 CMOS detector. Data collection with Apex2,¹ data integration and cell refinement with SAINT,¹ absorption correction by SADABS,¹ structure solution with SHELXT,² structure refinement with SHELXL.³ Molecular graphics from Mercury.⁴
Preparation of *meso*-ketone (4):

**Step 1:**

![Chemical structure](image)

1,4-Cyclohexadiene 9 (5 g, 62.5 mmol, 1.0 equiv.) was added to a suspension of zinc powder (8.2 g, 125 mmol, 2.0 equiv.) in dry Et<sub>2</sub>O (100 mL) and sonicated at 0 °C for 15 min. Then trichloroacetyl chloride (22.8 g, 125 mmol, 2.0 equiv.) in dry Et<sub>2</sub>O (100 mL) was added dropwise over 2 h while the reaction mixture was still sonicating. After complete addition the reaction mixture was sonicated for a further 2 h at 0-10 °C. The colour changed from colourless to dark yellow. The sonication was then stopped and the reaction mixture filtered and concentrated in vacuo. The resulting orange slurry was diluted in Et<sub>2</sub>O (400 mL) and washed with H<sub>2</sub>O (2 x 400 mL) and sat. aq. NaHCO<sub>3</sub> (1 x 400 mL). The organic layer was dried (MgSO<sub>4</sub>) and filtered and concentrated from colourless to dark yellow. The resulting crude dark yellow oil was purified by column chromatography on silica (hexane/EtOAc 99:1) to afford the title compound as a colourless oil. All spectroscopic and physical data were in full agreement with those reported in the literature.<sup>5</sup> Yield: 2.25 g (47%); 1H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.90-5.81 (m, 2H), 4.07-4.01 (m, 1H), 3.32 (ddt, <i>J</i> = 2.0, 7.9, 10.4 Hz, 1H), 2.63-2.50 (m, 2H), 2.39-2.32 (m, 1H), 2.17-2.10 (m, 1H); 13C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.3, 127.3, 126.3, 88.5, 53.7, 45.2, 23.1, 21.3; IR (neat, cm<sup>-1</sup>) 3041 (w), 2939 (w), 2895 (w), 2841 (w) 1799 (s), 1644 (w), 1433 (m); HRMS (El+): Exact mass calculated for C<sub>8</sub>H<sub>10</sub>OCl<sub>2</sub> [M]<sup>+</sup>: 189.9952, found 189.9953; TLC (hexane/EtOAc 4:1, KMnO<sub>4</sub> stain): <i>R</i><sub>t</sub> = 0.65.

**rac-(1R,6S)-8,8-Dichlorobicyclo[4.2.0]oct-3-en-7-one (10).**

![Chemical structure](image)

To a stirring solution of *rac-(1R,6S)-8,8-dichlorobicyclo[4.2.0]oct-3-en-7-one* 10 (2.0 g, 10.5 mmol, 1.0 equiv.) in dry Et<sub>2</sub>O (50 mL), at 0 °C, was added diazomethane (2.5 g, 58.8 mmol, 5.6 equiv.) in dry Et<sub>2</sub>O (50 mL) dropwise over 15 min. The reaction mixture bubbled and turned a deep golden yellow colour. After 30 min the reaction was warmed to room temperature and left to stir for 2 h. The reaction was then quenched with glacial AcOH (5 mL) dropwise until there was no more gas evolution and the colour changed from golden yellow to almost colourless. The resulting mixture was then washed with H<sub>2</sub>O (2 x 300 mL), sat. aq. NaHCO<sub>3</sub> (1 x 300 mL), brine (1 x 300 mL), dried with MgSO<sub>4</sub>, filtered and concentrated in vacuo. The resulting dark yellow oil was purified by column chromatography on silica (hexane/EtOAc 9:1) to afford the title compound as a colourless oil. Yield: 1.6 g (75%); 1H NMR (400 MHz, CDCl<sub>3</sub>) δ; 5.64-5.57 (m, 2H), 2.86-2.80 (m, 1H), 2.74-2.69 (m, 1H), 2.54 (dd, <i>J</i> = 7.5, 19.2 Hz, 1H), 2.38-2.29 (m, 2H), 2.07-2.00 (m, 2H), 1.72-1.64 (m, 1H); 13C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.7, 123.9, 123.1, 89.5, 46.7, 36.6, 28.1, 25.8, 23.5; IR (neat, cm<sup>-1</sup>) 3033 (m), 2916 (m), 2842 (m), 1764 (s) 1662 (w) 1434
(m), 1402 (m); HRMS (EI+): Exact mass calculated for C₉H₁₀OCl₂ [M]⁺: 204.0109, found 204.0103; TLC (hexane/EtOAc 4:1, KMnO₄ stain): Rₓ = 0.60.

*meso-(1S,6R)-Bicyclo[4.3.0]non-3-ene-8-one (4).*

To a stirring suspension of zinc powder (1.71 g, 26.3 mmol, 2.0 equiv.) in glacial AcOH (50 mL) was added *rac-(1R,6R)-7,7-dichlorobicyclo[4.2.0]oct-3-en-7-one (11)* (2.7 g, 13.2 mmol, 1.0 equiv.) in glacial AcOH (30 mL) dropwise. The resulting reaction mixture was stirred for 16 h at 70 °C. The reaction mixture was then cooled to room temperature and filtered to remove the resulting solid. The filtrate was diluted with CH₂Cl₂ (200 mL) and washed with H₂O (2 x 300 mL), sat. aq. NaHCO₃ (1 x 300 mL), brine (1 x 300 mL), dried with MgSO₄, filtered and concentrated in vacuo. The resulting crude pale yellow oil was purified by column chromatography on silica (hexane/EtOAc 95:5) to give the *meso* compound as a colourless oil. All spectroscopic and physical data were in full agreement with those reported in the literature.⁶ Yield: 2.45 g (72%); ¹H NMR (400 MHz, CDCl₃) δ 5.70-5.69 (m, 2H), 2.46-2.41 (m, 2H), 2.34-2.25 (m, 4H), 2.10 (dd, J = 6.4, 18.6 Hz, 2H) 1.89-1.83 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 219.6 124.6 (2C), 44.6 (2C), 32.3 (2C), 26.2 (2C); IR (neat, cm⁻¹) 3024 (m), 2834 (m), 1744 (s), 1655 (w), 1439 (m), 1407 (s); HRMS (EI+): Exact mass calculated for C₉H₁₂O [M]⁺: 136.0888, found 136.0983; TLC (hexane/EtOAc 4:1, KMnO₄ stain): Rₓ = 0.51.
Figure S-1 $^1$H-NMR spectrum of compound 10.

Figure S-2 $^{13}$C-NMR spectrum of compound 10.
Figure S-3 $^1$H-NMR spectrum of compound 11.

Figure S-4 $^{13}$C-NMR spectrum of compound 11.
Figure S-5 $^1$H-NMR spectrum of compound 4.

Figure S-6 $^{13}$C-NMR spectrum of compound 4.
Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
44 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Sample 1 C8H8Cl2 MW 191
DEHS2016021901 540 (6.602)

Minimum:  187.0
Maximum:  197.0

Mass  Calc. Mass  mDa  PPM  DBE  Score  Formula
189.9953  189.9952  0.1  0.4  4.0  1  C8 H8 O Cl2

Figure S-7 HRMS of compound 10.

Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
48 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Sample 2 C9H10OCl2 MW 205
DEHS2016021902 515 (12.982)

Minimum:  160.0
Maximum:  240.0

Mass  Calc. Mass  mDa  PPM  DBE  Score  Formula
204.0103  204.0109  -0.6  -2.8  4.0  1  C9 H10 O Cl2

Figure S-8 HRMS of compound 11.
Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

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Figure S-9 HRMS of compound 4.
Figure S-10 IR of compound 10.

Figure S-11 IR of compound 11.
Figure S-12 IR of compound 4.
Preparation of mucosin (1) and the methyl ester (2):

**Scheme S-2** Synthetic route to mucosin (1) and its methyl ester 2.
Methyl (15,65,7R)-8-oxobicyclo[4.3.0]non-3-ene-7-carboxylate (12).\(^7\)

(+)-Bis[(R)-1-phenylethyl]amine hydrochloride (2.5 g, 9.60 mmol, 1.6 equiv.) was added in one portion to dry THF (10 mL) at room temperature and stirred for 5 min. The stirring suspension was then cooled to -78 °C and BuLi (2.5 M in hexane, 7.67 mL, 19.2 mmol, 3.2 equiv.) was added dropwise. The suspension changed colour from cloudy white to pale orange. After stirring at -78 °C for 15 min the suspension was warmed to room temperature whereby a transparent yellow solution was formed. This was then cooled to -78 °C again and meso-(15,6R)-bicyclo[4.3.0]non-3-ene-8-one 4 (826 mg, 6.07 mmol, 1.0 equiv.) was added dropwise over 10 min in dry THF (10 mL). This mixture was then stirred for 45 min whereby a purple colour evolved. Methyl cyanoformate (0.96 mL, 12.1 mmol, 2.0 equiv.) was then added dropwise over 5 min and the mixture immediately turned bright yellow in colour. This mixture was left stirring for 2.5 h and then quenched by addition of H\(_2\)O (2 mL) at -78 °C. The mixture was then warmed to room temperature and extracted with EtOAc (2 x 50 mL). The resulting organic layer was then washed with H\(_2\)O (2 x 100 mL), 0.5 M HCl (1 x 100 mL) and brine (1 x 100 mL). The organic layer was then dried over MgSO\(_4\), filtered and concentrated in vacuo. The resulting crude keto-ester was purified by column chromatography (hexane/EtOAc 5:1) to form a colourless oil. This oil was then recrystallised from hexane at 0°C, filtered and air dried to obtain the title compound as white crystals. All spectroscopic and physical data were in full agreement with those reported in the literature.\(^7\) Yield: 812 mg (69%); [\(\alpha\)]\(^D\)\(_{589}\) -161.2 (c = 1.0, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.73-5.66 (m, 2H), 3.76 (s, 3H), 3.04 (d, \(J = 11.1 \) Hz, 1H), 2.88-2.83 (m, 1H), 2.52-2.38 (m, 3H), 2.33-2.21 (m, 2H), 2.04 (dd, \(J = 19.8, 18.2\) Hz, 1H), 1.67-1.61 (m, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 211.6, 169.7, 124.9, 123.9, 57.7, 52.4, 46.6, 37.3, 29.7, 26.8, 25.3; IR (neat, cm\(^{-1}\)) 3034 (w), 2945 (m), 2908 (m), 2837 (w), 1751 (s), 1718 (s) 1656 (w) 1433 (s) 1404 (m); HRMS (EI+): Exact mass calculated for C\(_{11}\)H\(_{14}\)O\(_3\): [M\(^+\)]: 194.0933, found 194.0943; m.p.: 59-61 °C; TLC (hexane/EtOAc 4:1, K\(_2\)MnO\(_4\) stain): \(R_\text{f}\) = 0.42.

racc-Methyl (15,65,7R)-8-oxobicyclo[4.3.0]non-3-ene-7-carboxylate (12).

LDA (1M in THF/Hexanes, 1.65 mL, 1.65 mmol, 1.5 equiv.) was added dropwise to dry THF (5 mL) at -78 °C and stirred for 30 min. Then meso-(15,6R)-bicyclo[4.3.0]non-3-ene-8-one 4 (150 mg, 1.10 mmol, 1.0 equiv.) was added dropwise in dry THF (5 mL) over 5 min and left to stir for 45 min. To the resulting yellow solution was added methyl cyanoformate (0.174 mL, 2.2 mmol, 2.0 equiv.) dropwise over 5 min and the reaction changed from yellow to colourless. After 30 min and monitoring the reaction via TLC the reaction was quenched at -78 °C by sat. aq. NH\(_4\)Cl (2 mL) and the reaction mixture was left to slowly warm to room temperature. The reaction mixture was then poured over H\(_2\)O (1 x 20 mL) and the organic phase separated. The aqueous phase was then extracted with EtOAc (2 x 20 mL). The organic phases were then combined, washed with H\(_2\)O (2 x 50 mL), brine (1 x 50 mL), dried over MgSO\(_4\), filtered and concentrated in vacuo to from a crude yellow oil. This yellow oil was purified by column chromatography on silica (hexane/EtOAc, 5:1) to afford the racemic keto-ester. This was recrystallised in the same fashion as the optically active ketoester to afford pure white crystals. Yield: 166 mg, (78%).

The material was used in the preparation of racemic reference material for chiral GLC analysis.
Methyl (15S,6S)-8-(((trifluoromethyl)sulfonyl)oxy)bicyclo[4.3.0]non-3,7-diene-7-carboxylate (13).

NaH (60% disp. in min. oil, 148 mg, 3.71 mmol, 1.8 equiv.) was added to dry toluene (10 mL). The suspension was stirred for 5 min and then methyl (15S,6S,7R)-8-oxobicyclo[4.3.0]non-3-ene-7-carboxylate 12 (400 mg, 2.06 mmol, 1.0 equiv.), dissolved in dry toluene (7 mL), was added dropwise over 10 min during which bubbling occurred. After the full addition of 12 the reaction mixture was heated to 85 °C for 1.5 h during which time the mixture turned to a brown colour. The reaction mixture was then cooled to 0 °C and the triflic anhydride (0.52 mL, 3.09 mmol, 1.5 equiv.), was added dropwise. The reaction mixture changed colour from brown to a pale yellow/white slurry. After stirring at 0 °C for 1 h and monitoring by TLC the reaction mixture was quenched carefully with H2O (10 mL). The resulting mixture was extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with H2O (1 x 150 mL), brine (1 x 150 mL), dried over MgSO4, filtered and concentrated in vacuo. This afforded a brown oil, which was purified by column chromatography on silica (hexane/EtOAc 95:5) to afford the unsaturated triflate as a colourless oil. Yield: 527 mg (83%); [α]26D +100.8 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 5.95-5.89 (m, 1H), 5.86-5.81 (m, 1H), 3.81 (s, 3H), 3.10 (q, J = 6.7 Hz, 1H), 2.84-2.77 (m, 1H), 2.72-2.63 (m, 1H), 2.57-2.42 (m, 2H), 2.34-2.26 (m, 1H), 2.05-1.96 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 162.6, 153.9, 127.9, 127.3, 126.6, 118.3 (q, JCF = 320 Hz), 51.8, 39.5, 38.9, 32.0, 27.3, 26.2; IR (neat, cm-1) 3036 (w), 2953 (m), 2845 (w), 1723 (s), 1425 (s); HRMS (EI+): Exact mass calculated for C12H13O5S3 [M]+: 326.0436, found 326.0438; TLC (hexane/EtOAc 4:1, KMnO4 stain): Rf = 0.75.

Following the same procedure as above, racemic synthesis was performed to obtain reference material for chiral GLC analysis.

Methyl (15S,6S)-8-butylbicyclo[4.3.0]non-3,7-diene-7-carboxylate (14).

Solid Cu(I)CN (1.45 g, 16.18 mmol, 2.5 equiv.) was added to dry Et2O (5 mL) at room temperature. This was stirred for 5 min, cooled to -50 °C and then BuLi (2.5 M in hexane, 6.47 mL, 16.18 mmol, 2.5 equiv.) was added dropwise over 5 min. This mixture was stirred for 1 h at -50 °C and a dark brown suspension occurred. Methyl (15S,6S)-8-(((trifluoromethyl)sulfonyl)oxy)bicyclo[4.3.0]non-3,7-diene-7-carboxylate 13 (1.98 g, 6.47 mmol, 1.0 equiv.) was then added via cannula at -50 °C in dry Et2O (5 mL). The reaction changed from a dark brown suspension to black slurry and was left to stir for 1 h whilst monitoring by TLC. Once the reaction was finished sat. aq. NH4Cl (5 mL) was added dropwise. The reaction turned from black to dark purple and was left to warm to room temperature. The subsequent ethereal slurry was filtered through celite and the celite filter washed with EtOAc (3 x 15 mL). The organic layer was then separated and the aqueous layer extracted with EtOAc (2 x 15 mL). The organic layers were then combined, washed with H2O (1 x 100 mL), brine (1 x 100 mL), dried over MgSO4, filtered and concentrated in vacuo. This afforded a crude yellow oil, which was purified by column chromatography in silica (hexane/EtOAc 98:2) to afford the unsaturated butyl diene as a colourless oil. Yield: 1.33 g (88%); [α]D26 +124.5 (c = 3.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 5.88-5.83 (m, 1H), 5.79-5.73 (m, 1H), 3.72 (s, 3H), 2.94 (q, J = 7.6 Hz, 1H), 2.64-2.54 (m, 1H), 2.52-2.38 (m, 4H) 2.32-2.23 (m, 2H), 1.97-1.90 (m, 1H), 1.84-1.77 (m, 1H), 1.46-1.28 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 166.6, 159.9, 132.5, 127.9, 126.4, 50.8, 43.7, 42.3, 34.2, 30.1, 29.8, 27.5, 27.2, 22.7, 13.9; IR (neat, cm-1) 3025 (w), 2926 (s), 1709 (s), 1630
GLC analysis.

Following the same procedure as above, racemic synthesis was performed to obtain reference material for chiral GLC analysis.

Methyl (15,65,75,8R)-8-butylbicyclo[4.3.0]non-3-ene-7-carboxylate (15).

1) Methyl (15,65)-8-butylbicyclo[4.3.0]non-3,7-diene-7-carboxylate 14 (1.33 g, 5.68 mmol, 1.0 equiv.) was dissolved in MeOH (5 mL) at room temperature. This was stirred for 5 min then magnesium turnings (3.75 g, 156 mmol, 28 equiv.) were added in one portion. The turnings were stirred at room temperature for 10 min and then heated to 40 °C. A violent reaction occurs with lots of bubbling. After all the magnesium turnings had been consumed the addition of 27.5 equiv. of magnesium turnings in one portion was repeated at 40 °C. After 3 h the reaction was then cooled to room temperature to give a white cloudy mixture. Glacial AcOH (5mL) was added dropwise until the cloudy suspension had dissolved to leave a colourless solution. The reaction mixture was then concentrated in vacuo to leave a white slurry, which was poured over EtOAc/H2O 1:1 (100 mL). The organic phase was separated and the aqueous layer was extracted again with EtOAc (2 x 50 mL). The organic phases were combined and washed with sat. aq. NaHCO3 (1 x 100 mL), brine (1 x 100 mL), dried over MgSO4, filtered and concentrated in vacuo, to give a crude product. This crude product was analysed by 1H and 13C NMR to show the reaction had gone to completion by the formation of two unconjugated diastereomeric esters in a 2:1 ratio, no further purification was carried out. The crude diastereomeric esters were then equilibrated with NaOMe as shown below.

2) To MeOH (10 mL) at room temperature was added sodium metal (760 mg, 33.1 mmol, 6.0 equiv.). This was left to stir until all the sodium metal had dissolved. The crude diastereomeric esters were then added dropwise in MeOH (5 mL) and the reaction mixture was heated to 70 °C and monitored by TLC. After 3 h the reaction had gone to completion, was cooled to room temperature and concentrated in vacuo but not to dryness. The crude mixture was then poured over Et2O (50 mL) and H2O (50 mL). The organic layer was separated and the aqueous layer was extracted with Et2O (2 x 50 mL). The organic layers were then combined, washed with H2O (1 x 50 mL), brine (1 x 50 mL), dried over MgSO4, filtered and concentrated in vacuo to form a crude yellow oil. This crude yellow oil was purified by column chromatography on silica (hexane/EtOAc 98:2) to give the title compound as a colourless oil. Yield: 1.24 g (93%); [α]D26 = -4.32 (c = 2.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 5.73-5.66 (m, 2H), 3.69 (s, 3H), 2.32-2.22 (m, 1H) 2.22-2.14 (m, 5H), 2.09-2.02 (m, 1H), 1.91-1.77 (m, 2H), 1.54-1.49 (m, 1H), 1.36-1.21 (m, 5H), 1.15-1.09 (m, 1H), 0.87 (t, J = 6.8 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 177.2, 126.3, 125.5, 55.5, 51.5, 42.7, 41.2, 38.3, 36.9, 35.4, 30.6, 28.0, 26.5, 22.8, 14.0; IR (neat, cm⁻¹) 3024 (m), 2927 (s), 2856 (s), 1726 (s), 1657 (w), 1628 (w), 1541 (w), 1520 (w), 1458 (m), 1434 (s); HRMS (EI+): Exact mass calculated for C15H22O2 [M]+: 236.1776, found 236.1783; TLC (hexane/EtOAc 9:1, KMnO4 stain): Rf = 0.85.

Following the same procedure as above, racemic synthesis was performed to obtain reference material for chiral GLC analysis.
Methyl (15,6S,7S,8R)-8-butylbicyclo[4.3.0]non-3-ene-7-carboxylate 15 (1.24 g, 5.25 mmol, 1.0 equiv.) was dissolved in hexane (20 mL) at room temperature and stirred for 5 min. The solution was then cooled to 0 °C and DIBAL-H (1 M in hexane, 10.5 mL, 10.51 mmol, 2.0 equiv.) was added dropwise over 5 min. The reaction was then left to warm to room temperature. After 30 min the reaction was cooled back to 0 °C and quenched with sat. aq. NH₄Cl (6 mL). The reaction mixture was allowed to warm to room temperature whereby a cloudy suspension occurred. This suspension was poured over sat. aq. NH₄Cl (30 mL) and the organic layer separated. The aqueous layer was extracted with EtOAc (2 x 50 mL) and the organic layers combined, washed with H₂O (1 x 100 mL), brine (1 x 100 mL), dried over MgSO₄, filtered and concentrated in vacuo to give a crude cloudy oil. This was then purified by column chromatography on silica (hexane/EtOAc 95:5) to afford the title compound as a colourless oil. Yield: 1.01 g, (93%); [α]°D = -10.33 (c = 8.0, CHCl₃); 1H NMR (400 MHz, CDCl₃) δ 5.70-5.64 (m, 2H), 3.61-3.52 (m, 2H), 2.24-2.03 (m, 3H), 1.92-1.81 (m, 4H), 1.57-1.42 (m, 4H), 1.33-1.22 (m, 5H), 1.18-1.11 (m, 1H), 0.89 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl₃) δ 126.0, 125.8, 65.7, 54.0, 41.0, 37.8, 37.7, 37.4, 35.0, 31.0, 27.7, 27.3, 22.9, 14.1; IR (neat, cm⁻¹) 3316 (br.), 3020 (m), 2918 (s), 1657 (m), 1464 (m), 1433 (m); HRMS (EI⁺): Exact mass calculated for C₁₄H₂₀O [M-H₂O]+: 190.1722, found 190.1723; TLC (hexane/EtOAc 4:1, KMnO₄ stain): Rf = 0.35. The enantiomeric excess was determined by chiral GLC analysis (CP-Chirasil-DEX CB, using the following program: 80 °C (30 min) - 3 degrees/min to 150 °C - 150 °C (5 min)): t₁(e₁, major) = 38.97 min and t₁(e₂, minor) = 39.95 min; ee > 99%.

Following the same procedure as above, racemic synthesis was made to obtain reference material for chiral GLC analysis.

(15,6S,7S,8R)-8-Butyl-7-((methylsulfonyl)oxymethyl)bicyclo[4.3.0]non-3-ene (pre-17a).

To a stirring solution of (15,6S,7S,8R)-8-butyl-7-(hydroxymethyl)bicyclo[4.3.0]non-3-ene 16 (1.01 g, 4.81 mmol, 1.0 equiv.) in dry CH₂Cl₂ (10 mL) at room temperature, was added Et₃N (1.34 mL, 9.62 mmol, 2.0 equiv.) dropwise. This solution was left stirring for 5 min then cooled to 0 °C. Then methanesulfonyl chloride (1.12 mL, 14.43 mmol, 3.0 equiv.) was added dropwise and the reaction was left at 0 °C for 10 min then warmed to room temperature and left for 2 h. The reaction mixture turned colourless to yellow. After 2 h brine (5 mL) was added dropwise and the volatiles concentrated in vacuo to afford a yellow liquid. This was poured over EtOAc (50 mL) and sat. aq. NaHCO₃ (50 mL) was added. The organic layers were combined and washed with brine (1 x 50 mL), dried over MgSO₄, filtered and concentrated in vacuo to afford a crude yellow oil. This was then purified by column chromatography on silica (hexane/EtOAc 95:5) to afford the title compound as a colourless oil. Yield: 1.30 g, (94%); [α]°D = -11.65 (c = 8.0, CHCl₃); 1H NMR (400 MHz, CDCl₃) δ 5.69-5.62 (m, 2H), 4.18-4.10 (m, 2H), 2.99 (s, 3H), 2.24-2.07 (m, 3H), 1.94-1.79 (m, 4H), 1.68-1.50 (m, 3H), 1.33-1.22 (m, 5H), 1.19-1.12 (m, 1H), 0.88 (t, J = 6.6 Hz, 3H); 13C NMR (100 MHz, CDCl₃) δ 126.0, 125.2, 72.0, 50.3, 40.9, 38.0, 37.5, 37.2, 36.8, 34.9, 30.7, 27.2, 27.1, 22.7, 14.0; IR (neat, cm⁻¹) 3024 (w), 2926 (s), 1657 (w), 1464 (m) 1435 (w); HRMS (EI⁺): Exact mass calculated for C₁₅H₂₆O₃S₂ [M]+: 286.1603, found 286.1606; TLC (hexane/EtOAc 4:1, KMnO₄ stain): Rf = 0.45.
(15,6S,7S,8R)-8-Butyl-7-(cyanomethyl)bicyclo[4.3.0]non-3-ene (17).

A stirring solution of (15,6S,7S,8R)-8-butyl-7-(cyanomethyl)bicyclo[4.3.0]non-3-ene **pre-17b** (906 mg, 4.18 mmol, 1.0 equiv.) in hexane (10 mL) was cooled to -78 °C. Then Dibal-H (1 M in hexane, 6.26 mL, 6.26 mmol, 1.5 equiv.) was added dropwise over 5 min and the reaction left to stir for 20 min. Then sat. aq. Rochelle salt (5 mL) was added dropwise to the reaction mixture and then left to warm to room temperature. The resulting cloudy suspension was poured over EtOAc (20 mL) and sat. aq. Rochelle salt (20 mL). The organic layer was separated and the aqueous phase extracted with EtOAc (2 x 20 mL). The organic phases were combined and washed with brine (1 x 50 mL), dried over MgSO₄, filtered and concentrated *in vacuo* to afford a cloudy brown oil. This was then purified by column chromatography on silica (hexane/EtOAc 95:5) to afford the aldehyde as a colourless oil. Yield: 813 mg, (88%); [α]₂⁰° _D_ = -4.40 (c = 8.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 9.77 (t, J = 2.5 Hz, 1H), 5.71-5.64 (m, 2H), 2.44 (dd, J = 2.5, 6.5 Hz, 2H), 2.22-2.08 (m, 3H), 1.96-1.91 (m, 1H), 1.89-1.67 (m, 4H), 1.55-1.49 (m, 2H), 1.33-1.15 (m, 5H), 1.13-1.08 (m, 1H), 0.88 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 203.0, 126.3, 125.6, 49.5, 45.3, 45.0, 41.8, 37.9, 36.4, 34.9, 30.8, 27.7, 27.1, 22.8, 14.0; IR (neat, cm⁻¹) 3024 (m), 2923 (s), 2718 (m), 1720 (s), 1657 (w), 1465 (m), 1434 (m); HRMS (EI+): Exact mass calculated for C₁₅H₂₈O [M]+: 220.1827, found 220.1828; TLC (hexane/EtOAc 4:1, KMnO₄ stain): Rₜ = 0.82.

(15,6S,7S,8R)-8-Butyl-7-(formylmethyl)bicyclo[4.3.0]non-3-ene (pre-17a) (1.30 g, 4.55 mmol, 1.0 equiv.) in dry DMSO (10 mL) was added solid KCN (1.77 g, 27.3 mmol, 6.0 equiv.) in one portion. The reaction mixture was then heated to 70 °C for 2 h. The reaction mixture changed from colourless to yellow. After 2 h the reaction was cooled to room temperature and H₂O (5 mL) was added dropwise. The reaction mixture turned from yellow to colourless. This was then poured over EtOAc (20 mL) and the organic layer separated. The aqueous layer was then extracted with EtOAc (2 x 20 mL) and the organic layers combined. They were then washed with brine (1 x 50 mL), dried over MgSO₄, filtered and concentrated *in vacuo* to afford a crude brown oil. This was then purified by column chromatography on silica (hexane/EtOAc 98:2) to give the title compound as a colourless oil. Yield: 906 mg, (92%); [α]₂⁰° _D_ = -19.15 (c = 8.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 5.73-5.65 (m, 2H), 2.41 (d, J = 6.7 Hz, 2H), 2.27-2.14 (m, 3H), 2.04-1.96 (m, 1H), 1.93-1.76 (m, 3H), 1.67-1.49 (m, 3H), 1.36-1.19 (m, 5H), 1.15-1.08 (m, 1H), 0.90 (t, J = 6.8 Hz, 3H) ¹³C NMR (100 MHz, CDCl₃) δ 126.5, 125.4, 119.0, 46.4, 43.9, 41.3, 37.9, 36.0, 34.6, 30.6, 27.9, 26.3, 22.8, 21.0, 14.0; IR (neat, cm⁻¹) 3024 (m), 2921 (s), 1658 (w), 1465 (m) 1436 (m); HRMS (EI+): Exact mass calculated for C₁₅H₂₉N [M]+: 217.1830, found 217.1827; TLC (hexane/EtOAc 4:1, KMnO₄ stain): Rₜ = 0.82.

(15,6S,7S,8R)-8-Butyl-7-((methylsulfonyl)oxymethyl)bicyclo[4.3.0]non-3-ene (pre-17b) (813 mg, 4.49 mmol, 1.0 equiv.) in hexane/EtOAc (95:5) to give the title compound as a colourless oil. Yield: 906 mg, (92%); [α]₂⁰° _D_ = -19.15 (c = 8.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 5.73-5.65 (m, 2H), 2.41 (d, J = 6.7 Hz, 2H), 2.27-2.14 (m, 3H), 2.04-1.96 (m, 1H), 1.93-1.76 (m, 3H), 1.67-1.49 (m, 3H), 1.36-1.19 (m, 5H), 1.15-1.08 (m, 1H), 0.90 (t, J = 6.8 Hz, 3H) ¹³C NMR (100 MHz, CDCl₃) δ 126.5, 125.4, 119.0, 46.4, 43.9, 41.3, 37.9, 36.0, 34.6, 30.6, 27.9, 26.3, 22.8, 21.0, 14.0; IR (neat, cm⁻¹) 3024 (m), 2921 (s), 1658 (w), 1465 (m) 1436 (m); HRMS (EI+): Exact mass calculated for C₁₅H₂₉S [M]+: 233.1848, found 233.1846; TLC (hexane/EtOAc 4:1, KMnO₄ stain): Rₜ = 0.82.
(15,6S,7S,8R)-8-Butyl-7-(prop-2'-yn-1'-yl)bicyclo[4.3.0]non-3-ene (18).

To a stirring solution of (15,6S,7S,8R)-8-Butyl-7-(formylmethyl)bicyclo[4.3.0]non-3-ene 17 (300 mg, 1.36 mmol, 1.0 equiv.) in dry MeOH (15 mL) at 0 °C was added solid K₂CO₃ (451 mg, 3.27 mmol, 2.4 equiv.) in one portion and Ohira-Bestmann reagent (10% w/w in MeCN, 4.9 mL, 3.9 g, 2.05 mmol, 1.5 equiv.). The suspension was then warmed to room temperature and left stirring overnight. After analysis by TLC the mixture was treated with sat. aq. NaHCO₃ (20 mL), and the resulting mixture poured over CH₂Cl₂ (20 mL). The organic phase was separated and the aqueous phase was washed with CH₂Cl₂ (3 x 10 mL). The organic phases were then combined, dried over Na₂SO₄, filtered and concentrated in vacuo to afford a crude oil. This was purified by column chromatography on silica (hexane/EtOAc, 95:5) to afford title compound as a colourless oil. Yield: 253 mg, (86%); [α]D²⁶ -16.95 (c = 8.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 5.73-5.66 (m, 2H), 2.28 (dd, J = 2.6, 5.9 Hz, 2H), 2.23-2.08 (m, 3H), 1.97-1.79 (m, 5H), 1.70-1.53 (m, 2H), 1.44-1.38 (m, 1H), 1.36-1.16 (m, 5H), 1.13-1.06 (m, 1H), 0.90 (t, J = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ; 126.4, 126.0, 83.6, 68.6, 49.0, 43.5, 40.6, 38.2, 36.6, 34.8, 30.9, 28.1, 27.0, 22.9, 22.3, 14.1; IR (neat, cm⁻¹) 3310 (m), 3021 (m), 2954 (s), 2915 (s), 1657 (w), 1465 (m), 1435 (m); HRMS (EI⁺): Exact mass calculated for C₃6H₂₆ [M]⁺: 216.1878, found 216.1870; TLC (hexane, KMO₃ stain and anisaldehyde dip): Rf = 0.24.

(15,6S,7S,8R)-8-Butyl-7-(E)-7'-ethoxy-7'-oxohept-2'-eny)bicyclo[4.3.0]non-3-ene (19).

To a stirring solution of Cp₂ZrCl₂ (95 mg, 0.324 mmol, 2.0 equiv.) in dry THF (2 ml) at 0 °C was added DIBAL-H (1M in hexane, 0.32 mL, 0.324 mmol, 2.0 equiv.) via dropwise addition. The resulting homogenous mixture was then protected from light and stirred at 0 °C for 1 h after which time a colourless heterogeneous mixture formed. Then (15,6S,7S,8R)-8-butyl-7-(prop-2'-yn-1'-yl)bicyclo[4.3.0]non-3-ene 18 (35 mg, 0.162 mmol, 1.0 equiv.) dissolved in dry THF (2 mL) was added dropwise to the reaction mixture at 0 °C. After 1 h at 0 °C iodine (63 mg, 0.248 mmol, 1.5 equiv.) was added in one portion to the homogeneous yellow reaction mixture. The reaction mixture was then warmed to room temperature and stirred for 1 h. To the preformed vinyl iodide was successively added 4-ethoxy-4-oxobutylzinc bromide solution (0.5M in THF) (0.648 mL, 0.324 mmol, 2.0 equiv.) dropwise and (Ph₃P)₄Pd (19 mg, 0.016 mmol, 0.01 equiv.) in one portion. The resulting tea brown mixture was stirred at room temperature for 1 h and monitored by TLC. Once the reaction had gone to completion 1M HCl (10 mL) was added dropwise and the reaction poured over Et₂O (15 mL). The aqueous phase was extracted with Et₂O (3 x 15 mL) and the organic phases combined, dried over MgSO₄, filtered and concentrated in vacuo to form a crude brown oily mixture. This oily mixture was purified by column chromatography on silica (hexane/EtOAc, 95:5) to afford the title compound as a colourless oil. Yield: 27 mg, (51%); [α]D²⁶ -11.15 (c = 2.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 5.70-5.64 (m, 2H), 5.47-5.33 (m, 2H), 4.13 (q, J = 7.1 Hz, 2 H), 2.29 (t, J = 7.5 Hz, 2H), 2.22-2.15 (m, 1H), 2.12-2.01 (m, 6H), 1.89-1.76 (m, 3H), 1.73-1.66 (m, 3H), 1.53-1.47 (m, 2H), 1.34-1.16 (m, 9H), 1.12-1.04 (m, 1H), 0.88 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.8, 130.3, 129.9, 126.2, 126.1, 126.0, 126.1, 126.0, 50.1, 44.0, 40.3, 38.1, 37.7, 37.1, 34.9, 33.7, 31.9, 31.0, 27.8, 27.7, 24.8, 22.9, 14.2, 14.1; IR (neat, cm⁻¹) 3021 (m), 2920 (s), 1734 (s), 1657 (w), 1438 (m); HRMS (EI⁺): Exact mass calculated for C₂₂H₃₆O₂ [M]⁺: 332.2715, found 332.2722; TLC (hexane/EtOAc 95:5, KMO₃ stain): Rf = 0.65.
(15,6S,7S,8R)-8-Butyl-7-((E)-7'-hydroxy-7'-oxohept-2'-enyl)bicyclo[4.3.0]non-3-ene (1).

To a stirring solution of the (15,6S,7S,8R)-8-butyl-7-((E)-7'-ethoxy-7'-oxohept-2'-enyl)bicyclo[4.3.0]non-3-ene 18 (27 mg, 0.081 mmol, 1.0 equiv.) in THF/MeOH/H₂O (2:2:1) (5 mL) at room temperature was added lithium hydroxide monohydrate (119 mg, 2.84 mmol, 35.0 equiv.) in one portion. The reaction mixture was left stirring and monitored by TLC. After 3 h the reaction had gone to completion and was acidified to pH 2 by 1M HCl (5 mL). The reaction mixture was then poured over EtOAc (5 mL) and the aqueous phase extracted with EtOAc (3 x 5 mL). The organic phases were then combined and washed with brine (1 x 20 mL), dried over MgSO₄, filtered and concentrated in vacuo to form a colourless oil. This was then purified by column chromatography on silica (hexane/EtOAc, 3:2) to afford the title compound as a colourless oil. Yield: 24 mg, (97%); [α]ᵢ²⁰ -10.19 (c = 2.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 11.24 (br, 1H), 5.71-5.64 (m, 2H), 5.48-5.33 (m, 2H), 2.35 (t, J = 7.5 Hz, 2H), 2.23-2.14 (m, 1H), 2.13-2.02 (m, 6H), 1.89-1.75 (m, 3H), 1.73-1.65 (m, 3H), 1.55-1.44 (m, 2H), 1.36-1.15 (m, 6H), 1.12-1.05 (m, 1H), 0.89 (t, J = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 180.3, 130.6, 129.7, 126.2, 126.0, 126.0, 51.4, 51.0, 44.0, 40.3, 38.1, 37.7, 37.1, 34.9, 33.3, 31.8, 31.0, 27.8, 27.7, 24.4, 22.9, 14.1; IR (neat, cm⁻¹) 3021 (m), 2920 (s), 1708 (s), 1457 (m), 1436 (m), 1412 (m); HRMS (EI⁺): Exact mass calculated for C₂₀H₂₂O₂ [M⁺]: 304.2402, found 304.2391; TLC (hexane/EtOAc 3:2, KMnO₄ stain): Rf = 0.40.

(15,6S,7S,8R)-8-Butyl-7-((E)-7'-methoxy-7'-oxohept-2'-enyl)bicyclo[4.3.0]non-3-ene (2).

To a stirring solution of (15,6S,7S,8R)-8-butyl-7-((E)-7'-hydroxy-7'-oxohept-2'-enyl)bicyclo[4.3.0]non-3-ene 1 (24 mg, 0.079 mmol, 1.0 equiv.) in toluene/MeOH (3:2) (5 mL) at room temperature was added TMS diazomethane solution (2M in hexane) (0.06 mL, 0.119 mmol, 1.5 equiv.) dropwise over 2 min. The reaction mixture bubbled and turned transparent yellow. The reaction was monitored by TLC and after 1 h had gone to completion. The reaction mixture was then concentrated in vacuo and directly purified by column chromatography on silica (hexane/EtOAc, 95:5) to afford the title compound as a colourless oil. Yield: 23 mg, (92%); [α]ᵢ²⁰ -9.8 (c = 0.8, hexane); ¹H NMR (400 MHz, CDCl₃) δ 5.70-5.64 (m, 2H), 5.46-5.33 (m, 2H), 3.67 (s, 3H), 2.31 (t, J = 7.6 Hz, 2H), 2.22-2.15 (m, 1H), 2.12-2.01 (m, 6H), 1.89-1.75 (m, 3H), 1.73-1.65 (m, 3H), 1.54-1.44 (m, 2H), 1.34-1.16 (m, 6H), 1.12-1.04 (m, 1H), 0.88 (t, J = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 174.2, 130.4, 129.9, 126.3, 126.1, 51.4, 51.0, 44.0, 40.3, 38.1, 37.7, 37.1, 34.9, 33.4, 31.9, 31.0, 27.8, 27.7, 24.8, 22.9, 14.1; IR (neat, cm⁻¹) 3020 (w), 2952 (m), 2923 (s), 1741 (s), 1657 (w), 1603 (w), 1541 (w), 1508 (w), 1458 (m), 1436 (m); HRMS (EI⁺): Exact mass calculated for C₂₁H₂₃O₂ [M⁺]: 318.2559, found 318.2544; TLC (hexane/EtOAc 95:5, KMnO₄ stain): Rf = 0.65.
Figure S-13 $^1$H-NMR spectrum of compound 12.

Figure S-14 $^{13}$C-NMR spectrum of compound 12.
Figure S-15 $^1$H-NMR spectrum of compound 13.

Figure S-16 $^{13}$C-NMR spectrum of compound 13.
Figure S-17 $^1$H-NMR spectrum of compound 14.

Figure S-18 $^{13}$C-NMR spectrum of compound 14.
Figure S-19 $^1$H-NMR spectrum of compound 15.

Figure S-20 $^{13}$C-NMR spectrum of compound 15.
Figure S-21 $^1$H-NMR spectrum of compound 16.

Figure S-16 $^{13}$C-NMR spectrum of compound 22.
Figure S-23 $^1$H-NMR spectrum of compound \textit{pre-17a}.

Figure S-24 $^{13}$C-NMR spectrum of compound \textit{pre-17a}.
Figure S-25 $^1$H-NMR spectrum of compound pre-17b.

Figure S-26 $^{13}$C-NMR spectrum of compound pre-17b.
Figure S-27 $^1$H-NMR spectrum of compound 17.

Figure S-28 $^{13}$C-NMR spectrum of compound 17.
Figure S-29 $^1$H-NMR spectrum of compound 18.

Figure S-30 $^{13}$C-NMR spectrum of compound 18.
Figure S-31 $^1$H-NMR spectrum of compound 19.

Figure S-32 $^{13}$C-NMR spectrum of compound 19.
Figure S-33 $^1$H-NMR spectrum of compound 1.

Figure S-34 $^{13}$C-NMR spectrum of compound 1.
Figure S-35 $^{1}$H-NMR spectrum of compound 2.

Figure S-36 $^{13}$C-NMR spectrum of compound 2.
Figure S-37 HRMS of compound 12.

Figure S-38 HRMS of compound 13.
Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
30 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

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Figure S-39 HRMS of compound 14.

Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
31 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

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<th>Mass</th>
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Figure S-40 HRMS of compound 15.
**Figure S-41** HRMS of compound 16.

**Figure S-42** HRMS of compound pre-17a.
Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
51 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

C15H23N  HRMS MW 217  pr 4
DEHarv201604040160 (3.247)

Voltage El+
5.31e3

Minimum: 200.0 100.0

Maximum: 211.9874 216.0

Mass  Calc. Mass  mDa  PPM  DBE  Score  Formula
217.1827  217.1830  -0.3  -1.6  5.0  1  C15 H23 N

Figure S-43 HRMS of compound pre-17b.

Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
53 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

C15H24O  HRMS MW 220  pr 5
DEHarv201604040160 (5.601)

Voltage El+
1.66e4

Minimum: 200.0 100.0

Maximum: 222.2903 220.0

Mass  Calc. Mass  mDa  PPM  DBE  Score  Formula
220.1828  220.1827  0.1  0.4  4.0  1  C15 H24 O

Figure S-44 HRMS of compound 17.
Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Minimum:               200.0  10.0  50.0
Maximum:               202.1632
Mass        Calc. Mass  mDa    PPM    DBE    Score    Formula
216.1870     216.1878      -0.8   -3.7  5.0     1    C16 H24

Figure S-45 HRMS of compound 18.

Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
32 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Minimum:               200.0  10.0  50.0
Maximum:               230.9881
Mass        Calc. Mass  mDa    PPM    DBE    Score    Formula
332.2722     332.2715      0.7   2.0   5.0     1    C22 H36 O2

Figure S-46 HRMS of compound 19.
## Elemental Composition Report

### Single Mass Analysis

**Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0**

**Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%**

Monoisotopic Mass, Odd and Even Electron Ions

29 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

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<th>PPM</th>
<th>DBE</th>
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<td>304.2391</td>
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<td>5.0</td>
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<td>C20 H32 O2</td>
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</table>

**Figure S-47 HRMS of compound 1.**

## Elemental Composition Report

### Single Mass Analysis

**Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0**

**Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%**

Monoisotopic Mass, Odd and Even Electron Ions

31 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

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<th>PPM</th>
<th>DBE</th>
<th>Score</th>
<th>Formula</th>
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</thead>
<tbody>
<tr>
<td>318.2544</td>
<td>318.2559</td>
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<td>-4.7</td>
<td>5.0</td>
<td>1</td>
<td>C21 H34 O2</td>
</tr>
</tbody>
</table>

**Figure S-48 HRMS of compound 2.**
Figure S-49 IR of compound 12.

Figure S-50 IR of compound 13.
Figure S-51 IR of compound 14.

Figure S-52 IR of compound 15.
Figure S-53 IR of compound 16.

Figure S-54 IR of compound pre-17a.
Figure S-55 IR of compound pre-17b.

Figure S-56 IR of compound 17.
Figure S-57 IR of compound 18.

Figure S-58 IR of compound 19.
Figure S-59 IR of compound 1.

Figure S-60 IR of compound 2.
Acq. Operator : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 7820 GC
Injection Date  : 5/2/2016 15:28:06
Injection Volume: Manually
Method          : C:\CHEM32\1\METHODS\CP7502\CP7502.M
Last changed    : 5/2/2016 14:05:55 by SYSTEM
Sample Info     : 80 grader 30 min, 3 grader/min til 150 grader, 5 min hold time

Additional Info : Peak(s) manually integrated

Signal 1: FID1 B, Back Signal

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<tr>
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<td>-</td>
<td>pentadekan</td>
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</tr>
<tr>
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<td>-</td>
<td>-</td>
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<td>-</td>
<td>hexadekan</td>
<td></td>
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</tbody>
</table>

Totals : 0.00000

Figure S-61 Chiral GLC of compound 16.
Figure S-62 Report from chiral GLC of compound 16.

Warning : Calibrated compound(s) not found
Data File C:\CHEM32\1\DATA\TEST\STD TEST309.D
Sample Name: Rac fort 1:5

Acq. Operator : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 7820 GC Location : Vial 1
Injection Date  : 5/10/2016 14:46:51
Inj Volume : Manually
Method : C:\CHEM32\1\METHODS\CP7502\CP7502.M
Last changed : 5/2/2016 14:05:55 by SYSTEM
Sample Info : 80 grader 30 min, 3 grader/min til 150 grader, 5 min hold time
Additional Info : Peak(s) manually integrated

External Standard Report

Sorted By : Signal
Calib. Data Modified : Tuesday, August 20, 2013 11:04:49
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 B, Back Signal

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</table>

Figure S-63 Chiral GLC of compound rac-16.
Figure S-64 Report from chiral GLC of compound rac-16.

**Warning:** Calibrated compound(s) not found.

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### Area Percent Report

**Sorted By:** Signal

**Calib. Data Modified:** Tuesday, August 20, 2013 11:04:49

**Multiplier:** 1.0000

**Dilution:** 1.0000

*Do not use Multiplier & Dilution Factor with ISTDs*

**Signal 1: FID1 B, Back Signal**

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<td>hexadekan</td>
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<td>3572.11621</td>
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<tr>
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<td>39.949 MM</td>
<td>0.5835</td>
<td>3581.17065</td>
<td>50.06329</td>
<td>?</td>
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</table>

**Totals:** 7153.28687

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**Warning:** Calibrated compound(s) not found.

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*** End of Report ***
Preparation 3,5-dinitrobenzoate derivative of (16).

Scheme S-3 Derivatization of advanced intermediate 16 to 2,5-dinitrobenzoate 16-DNB.

(15,6S,7S,8R)-8-Butyl-7-((3,5-dinitrobenzoyl)oxymethyl)bicyclo[4.3.0]non-3-ene (16-DNB).

A stirring solution of (1S,6S,7S,8R)-8-butyl-7-(hydroxymethyl)bicyclo[4.3.0]non-3-ene 16 (120 mg, 0.577 mmol, 1.0 equiv.) in dry DCM (10 mL) was added Et₃N (0.241 mL, 1.73 mmol, 3.0 equiv.) dropwise. The solution was then cooled to 0 °C and 3,5-dinitrobenzoyl chloride (173 mg, 0.75 mmol, 1.3 equiv.) was added in one portion. The reaction was slowly warmed to room temperature and monitored by TLC until completion. After 2h, the reaction mixture was poured over H₂O (10 mL) and the organic layer separated. The aqueous layer was then extracted with DCM (2 x 10 mL) and the organic layers combined. The organic layers were then washed with H₂O (1 x 30 mL), brine (1 x 30 mL), dried with MgSO₄, filtered and concentrated in vacuo to form a crude orange oil. This was purified by column chromatography on silica (hexane/EtOAc, 95:5) to afford the title compound as a slightly off-white powder. Yield: 185 mg, (82%), [α]D²⁶ -3.67 (c = 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 9.25-9.24 (m, 1H), 9.16-9.15 (m, 2H), 5.74-5.67 (m, 2H), 4.45-4.37 (m, 2H), 2.27-2.14 (m, 3H), 1.85-1.79 (m, 1H), 1.74-1.68 (m, 1H), 1.66-1.60 (m, 1H), 1.42-1.19 (m, 6H), 0.89-0.88 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.6, 148.6, 134.1, 129.3 (2C), 126.2, 125.2, 122.3, 69.7, 50.0, 41.8, 38.7, 37.7, 37.2, 35.1, 30.9, 27.4, 27.3, 22.8, 14.0; IR (neat, cm⁻¹) 3012 (m), 3022 (m), 2922 (s), 1728 (s), 1628 (m), 1597 (w), 1540 (s); HRMS (EI⁺): Exact mass calculated for C₂₁H₂₆N₂O₆ [M⁺]: 402.1791, found 402.1788; m.p.: 45-47 °C; TLC (hexane/EtOAc 9:1, KMnO₄ stain): Rf = 0.55.
Figure S-65 ¹H-NMR spectrum of compound 16-DNB.

Figure S-66 ¹³C-NMR spectrum of compound 16-DNB.
Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
23 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Figure S-67 HRMS spectrum of compound 16-DNB.
Figure S-68 IR spectrum of compound 16-DNB.
X-ray crystallography on compound (16-DNB):

Figure S-69 Single crystal X-ray structure of the 3,5-dinitrobenzoate of alcohol 16 at 110 K. The disordered n-butyl group (H-atoms omitted) has a major orientation [occupancy 0.74(3)] with trans,trans,gauche+ torsion angles along C9-C10-C18-C19-C20-C21, while the minor orientation (atoms in lighter tone) is trans,gauche–,gauche–.

Table S-1 Crystal data for 3,5-dinitrobenzoate of alcohol 16.*

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>Table S-1 Crystal data for 3,5-dinitrobenzoate of alcohol 16.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C_{21}H_{26}N_{2}O_{6}</td>
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<td>M_r</td>
<td>402.44</td>
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<td>Crystal system, space group</td>
<td>Monoclinic, P2_1</td>
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<td>a (Å)</td>
<td>10.866(5)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>5.196(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>18.617(10)</td>
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<tr>
<td>β (°)</td>
<td>106.703(11)</td>
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<tr>
<td>V (Å³)</td>
<td>1006.8(9)</td>
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<td>µ (mm⁻¹)</td>
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<tr>
<td>Temperature (K)</td>
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<td>Crystal size (mm)</td>
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<td>T_{min}, T_{max}</td>
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<td>No. of measured, independent and observed [I &gt; 2σ(I)] reflections</td>
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<td>Refinement</td>
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<tr>
<td>No. of parameters</td>
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<tr>
<td>Δρ_{max}, Δρ_{min} (e Å⁻³)</td>
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<td>CCDC</td>
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* Bruker D8 Venture diffractometer with InCoatec ImuS Microfocus radiation source and Photon 100 CMOS detector. Data collection with Apex2, data integration and cell refinement with SAINT, absorption correction by SADABS, structure solution with SHELXT, structure refinement with SHELXL. Molecular graphics from Mercury.
First total synthesis of mucosin based on its structural assignment

Harrison C. Gallantree-Smith, Simen G Antonsen, Carl Henrik Görbitz,* Trond V. Hansen, Jens M. J. Nolsoe and Yngve H. Stenström

Experimental
Very fragile, small platelets were obtained by slow evaporation from a methanol/pentane mixture.

Refinement
Two disorder positions, with occupancies 0.74 (3) and 0.26 (3) were refined for the C18—C21 n-butyl group attached to C10. Their covalent geometries were restrained by a SHELXL SAME 0.004 0.008 command, additional restraints were imposed on the C—C bond lengths in this substituent. Corresponding atoms in the two conformations shared the same displacement parameters, except that a fixed value was used for C20H, which is separated from C20 by 1.38 Å.

name

Crystal data

\[ \text{C}_8\text{H}_7\text{N}_6\text{O}_4 \]

\[ M_0 = 402.44 \]

Monoclinic, \( P2_1 \)

\[ a = 10.866 (5) \text{ Å} \]

\[ b = 5.196 (2) \text{ Å} \]

\[ c = 18.617 (10) \text{ Å} \]

\[ \beta = 106.703 (11) ^\circ \]

\[ V = 1006.8 (9) \text{ Å}^3 \]

\[ Z = 2 \]

\[ F(000) = 428 \]

\[ D_x = 1.327 \text{ Mg m}^{-3} \]

Mo Ka radiation, \( \lambda = 0.71073 \text{ Å} \)

Cell parameters from 2295 reflections

\[ \mu = 0.10 \text{ mm}^{-1} \]

\[ T = 110 \text{ K} \]

Plate, colourless

\[ 0.21 \times 0.19 \times 0.01 \text{ mm} \]

Data collection

Bruker D8 Venture with Photon 100 CMOS detector
diffactometer

Radiation source: InCotec ImuS Microfocus

Graphite monochromator

Detector resolution: 8.3 pixels \text{ mm}^{-1}

Sets of exposures each taken over 0.5° rotation scans

Absorption correction: multi-scan

\( SADABS \) (Bruker, 2014)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\[ R[F^2 > 2 \sigma(F^2)] = 0.085 \]

\[ wR(F^2) = 0.225 \]

\[ S = 1.03 \]

2089 reflections

278 parameters

77 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\[ w = 1/[\sigma^2(F^2) + (0.0936P)^2 + 2.6032P] \]

where \( P = (F^2 + 2F_C)/3 \)
**Supporting Information**

$\sigma_{\text{max}} < 0.001$

$\Delta \rho_{\text{max}} = -0.28$ e Å$^{-3}$

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Two disorder positions refined for n-butyl group attached to C10. Occupancies 0.74 (3) and 0.26 (3).

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)**

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<th>z</th>
<th>$U_{\text{iso}}$/Å$^2$</th>
<th>Occ. (&lt;1)</th>
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<td>C1</td>
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<td>0.6594 (5)</td>
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YS.cif sup-2

S54
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YS.cif

sup-3
supporting information

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