Supporting Information
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EXPERIMENTAL PROCEDURES

General Methods

Reactions which required the use of anhydrous, inert atmosphere techniques were carried out under an atmosphere of nitrogen. In most cases, solvents were obtained by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. All other solvents were purchased as “anhydrous” grade from Fisher Scientifics. “petrol ether” refers to petroleum spirit b.pt. 40-60 °C. TLC was performed using aluminium backed plates precoated with Alugram™ SIL G/UV 254nm. Visualisation was accomplished by UV light and/or KMnO₄ followed by gentle warming. Organic layers were routinely dried with anhydrous MgSO₄ and evaporated using a Büchi rotary evaporator. When necessary, further drying was facilitated by high vacuum. Flash column chromatography was carried out using Davisil LC 60Å silica gel (35-70 micron) purchased from Fisher Scientifics.

IR spectra were recorded on Perkin-Elmer 1600 FT IR spectrometer with only selected absorbances quoted as ν in cm⁻¹. NMR spectra were run in CDCl₃ (unless otherwise specified) on either a Brüker Avance 250, 300, 400 or 500 MHz instruments at 298 K. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dq, doublet of quartets; td, triplet of doublets; m, multiplet and br, broad.

A micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Brüker Daltonik GmbH, Bremen, Germany) was used; this was coupled to an Agilent 1200 LC system (Agilent Technologies, Waldbronn, Germany). The LC system was used as an autosampler only. 10μl of sample was injected into a 30:70 flow of water:acetonitrile at 0.6mL/min to the mass spectrometer. For each acquisition 10μL of calibrant of 5mM sodium formate was injected after the sample. The observed mass and isotope pattern matched the corresponding theoretical values as calculated from the expected elemental formula.

X-Ray crystallography was recorded on a Nonius Kappa CCD diffractometer with Mo-Kα radiation (λ=0.71074Å). All structures were solvent by direct methods and refined on all F² data using SHELX-97 suite of programmes.
This was performed in accordance with a literature procedure.\textsuperscript{3c} Acetyl chloride (85.45 mL, 1.197 mol, 2.40 equiv) was gradually added with stirring to a cooled (<25 °C) mixture of aluminium chloride (100.0 g, 0.75 mol, 1.50 equiv) in DCM (225 mL). The resulting yellow-brown solution was decanted into a flask, cooled to <10 °C, and decalin 3 (80.9 mL, 0.51 mol, 1.00 equiv) was gradually added over 30 min with stirring and cooling to keep the temperature of the reaction mixture below 10 °C. After a further 2 h at 10-15°C, the mixture was gradually added to a vigorously stirred slurry of crushed ice (1 kg) and water. The lower organic layer was separated and, together with DCM extracts of the aqueous layer, washed several times with ice-cold water and dried over MgSO\textsubscript{4}, then filtered. The filtrate was concentrated under reduced pressure. Fractional distillation of the residual brown oil gave (1S*,4aR*,8aR*)-9-methyleneoctahydro-1H-1,4a-(epoxymethano)naphthalene 4 (b.p. 82-85 °C / 5.8 Torr) which was then further purified by refluxing with LiAlH\textsubscript{4} (0.5 g) in dry diethyl ether (30 mL) for 30 min. Excess of hydride was destroyed by cautious addition of ethyl acetate (5 mL), and ice-cold dilute sulphuric acid (50 mL, 0.5 N) was gradually added to the cooled mixture. The ethereal layer was rapidly separated and, with further ethereal extracts of aqueous layer, was washed with water (2 × 50 mL) and dried over MgSO\textsubscript{4}, then filtered. The filtrate was concentrated under reduced pressure. Further distillation afforded pure (1S*,4aR*,8aR*)-9-methyleneoctahydro-1H-1,4a-(epoxymethano)naphthalene 4 (22.81 g, 25%) as a pale yellow oil; b.pt. 65 °C / 1.5 Torr; δ\textsubscript{H} (250 MHz, CDCl\textsubscript{3}) 4.22 (1H, dt, J = 1.0, 0.5 Hz, >CH-O-), 4.03 (1H, d, J = 4.5 Hz, =CH\textsubscript{2}), 3.66 (1H, d, J = 1.5 Hz, =CH\textsubscript{2}), 1.88-1.07 (15H, m, cy-CH); δ\textsubscript{C} (75 MHz, CDCl\textsubscript{3}) 166.0 (>C=CH\textsubscript{2}), 80.4 (>CH-O-), 76.9 (=CH\textsubscript{2}), 50.0 (3\textdegree), 46.2 (4\textdegree), 39.5 (2\textdegree), 31.3 (2\textdegree), 30.2 (2\textdegree), 26.5 (2\textdegree), 24.9 (2\textdegree), 22.1 (2\textdegree), 18.9 (2\textdegree); ν\textsubscript{max} (film) 2927, 2860, 1679, 1455, 1369, 1198, 1106, cm\textsuperscript{-1}; TOF-ESI+ m/z calculated for (C\textsubscript{12}H\textsubscript{18}O + H\textsuperscript{+})\textsuperscript{+}, 179.1435, found, 179.1422.
This was performed in accordance with a literature procedure.\textsuperscript{10} A mixture of vinyl ether 4 (20.18 g, 113.2 mmol, 1.00 equiv) in diethyl ether (150 mL) and dilute sulphuric acid (1 N, 290 mL) was stirred and gently refluxed for 2.5 h. The ether layer was separated and, with the ether extracts of aqueous layer, was dried over MgSO\textsubscript{4} and filtered. The filtrate was concentrated under reduced pressure. The residue was washed with cold light petroleum to give required 1-((1\textsuperscript{S},4a\textsuperscript{R},8a\textsuperscript{R})\textsuperscript{-1-Hydroxydecahydronaphthalen-4a-yl})ethanone 6 (11.26 g, 51%), which crystallised from petroleum ether; m.pt. 60-61 °C; R\textsubscript{f} 0.54 (50% EtOAc in petroleum ether); δ\textsubscript{H} (300 MHz, CDCl\textsubscript{3}) 5.46 (1H, d, J 8.5 Hz, -OH), 3.70 (1H, dq, J 8.5, 3.0 Hz, >CH-OH), 2.17 (3H, s, CH\textsubscript{3}), 2.13-1.47 (6H, m, cy-CH), 1.13-0.99 (9H, m, cy-CH); δ\textsubscript{C} (75 MHz, CDCl\textsubscript{3}) 217.5 (>C=O), 68.9 (>CH-OH), 56.1 (3\textsuperscript{o}), 48.8 (4\textsuperscript{o}), 39.5 (2\textsuperscript{o}), 36.9 (2\textsuperscript{o}), 35.0 (2\textsuperscript{o}), 26.9 (CH\textsubscript{3}), 26.4 (2\textsuperscript{o}), 25.7 (2\textsuperscript{o}), 24.2 (2\textsuperscript{o}), 17.2 (2\textsuperscript{o}); ν\textsubscript{max} (film), 3751, 3649, 3351, 2927, 2860, 2554, 2350, 2159, 2032, 1977, 1679, 1455, 1369, 1253, 1198, 1177, 1137, 1106, 1066, 1041, 1009, 981, 947, 915, 884, 778, 720, 644, 618 cm\textsuperscript{-1}; TOF-ESI+ m/z calculated for (C\textsubscript{12}H\textsubscript{20}O\textsubscript{2} + H)+, 197.1541, found, 197.1514; calculated for (C\textsubscript{12}H\textsubscript{20}O\textsubscript{2} + Na)+, 219.1361, found, 219.1327.
1-((1S*,4aR*)-1-(tert-Butyldimethylsilyloxy)decahydronaphthalen-4a-yl)ethanone (7)

tert-Butyldimethylsilyl chloride (0.37 g, 2.46 mmol, 1.25 equiv) was slowly added to a solution of hydroxyketone 6 (0.387 g, 1.97 mmol, 1.00 equiv) and imidazole (0.537 g, 7.89 mmol, 4.00 equiv) in dry DMF (6 mL) with stirring at 0 °C. The reaction mixture was allowed to warm to rt, stirred for 17 h, and poured into iced LiCl(aq) solution (20 mL). The aqueous mixture was extracted with ethyl acetate (3 × 15 mL), then the organic layer was washed with brine (3 × 10 mL), dried over MgSO₄ and filtered. The filtrate was concentrated under reduced pressure to furnish the crude product which was purified by column chromatography (1% to 5% EtOAc in petroleum ether) to give 1-((1S*,4aR*)-1-(tert-butyldimethylsilyloxy)decahydro-naphthalen-4a-yl)ethanone 7 (0.58 g, 95%) as a colourless oil; Rf 0.53 (5% EtOAc in petroleum ether); δH (300 MHz, CDCl₃) 3.74 (1H, br s, >CH-OSi-), 2.16 (3H, s, CH₃), 1.85-1.03 (15H, m, cy-CH), 0.85 (9H, s, -Si(CH₃)₂-C(CH₃)₃), 0.01 (3H, s, -Si(CH₃)₂-C(CH₃)₃); δC (75 MHz, CDCl₃) 210.4 (>C=O), 71.8 (>CH-OSi), 52.2 (3°), 48.7 (4°), 38.9 (2°), 38.1 (2°), 35.1 (2°), 28.2 (>Si(CH₃)₂-C(CH₃)₃), 27.1 (2°), 26.5 (CH₃), 25.7 (>Si(CH₃)₂-C(CH₃)₃), 21.3, 18.8, 18.0, -4.8 (>Si(CH₃)₂-C(CH₃)₃); νmax (film), 2929, 2855, 1702, 1461, 1445, 1361, 1344, 1251, 1202, 1158, 1069, 1049, 1017, 983, 954, 925, 900, 866, 837, 807, 774, 650 cm⁻¹; TOF-ESI+ m/z calculated for (C₁₈H₃₄O₃Si + H)⁺, 311.2406, found, 311.2406; calculated for (C₁₈H₃₄O₃Si + Na)⁺, 333.2225, found, 333.2236.
R\textsuperscript{*}-1-((1S\textsuperscript{*},4aR\textsuperscript{*},8aR\textsuperscript{*})-1-(tert-Butyldimethylsilyloxy)decahydronaphthalen-4a-yl)ethanol (8)

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To a solution of ketone 7 (1.65 g, 5.31 mmol, 1.00 equiv) in dry DCM (20 mL) at -78 °C was added DIBAL-H (1.0 M in DCM; 7.97 mL, 7.97 mmol, 1.50 equiv). The reaction mixture was stirred at -78 °C for 5 min, then at rt for 1.5 h. The reaction mixture was diluted with EtOAc (150 mL) and poured onto saturated aq. sodium potassium tartrate (150 mL) and water (150 mL). The reaction mixture was stirred vigorously for 30 min. The aqueous phase was washed with EtOAc (2 × 50 mL). The combined organic layers were washed with saturated aq. NaCl (2 × 50 mL), dried over MgSO\textsubscript{4} and filtered. The filtrate was concentrated under reduced pressure and purified by chromatography (25% EtOAc-petroleum ether) to give R\textsuperscript{*}-1-((1S\textsuperscript{*},4aR\textsuperscript{*},8aR\textsuperscript{*})-1-(tert-butyldimethylsilyloxy)-decahydronaphthalen-4a-yl)ethanol 8 (1.15 g, 70%) as an colourless oil; R\textsubscript{F} 0.88 (25% EtOAc in petroleum ether); δ\textsubscript{H} (300 MHz, CDCl\textsubscript{3}) 5.38 (1H, app s, OH), 4.26 (1H, q, J 6.0 Hz, -CHCH\textsubscript{3}-OH), 3.81 (1H, q, J 3.0 Hz >CH-OH), 2.28-1.21 (14H, m, cy-CH), 1.12 (3H, dd, J 6.0, 1.0 Hz, -CH\textsubscript{3}), 0.89 (9H, s, >Si(CH\textsubscript{3})\textsubscript{3}-C(CH\textsubscript{3})\textsubscript{3}), 0.86-0.68 (1H, m, cy-CH), 0.08 (6H, s, >Si(CH\textsubscript{3})\textsubscript{2}-C(CH\textsubscript{3})\textsubscript{3}); δ\textsubscript{C} (75 MHz, CDCl\textsubscript{3}) 72.6 (>CH-O-), 65.7 (-CHCH\textsubscript{3}-OH), 50.7 (HO-CHCH\textsubscript{3}-C(4\textsuperscript{*})-CH<), 41.8 (2\textsuperscript{*}), 39.6 (HO-CHCH\textsubscript{3}-C(4\textsuperscript{*})-CH<), 34.1 (2\textsuperscript{*}), 33.8 (2\textsuperscript{*}), 27.1 (>Si(CH\textsubscript{3})\textsubscript{2}-C(CH\textsubscript{3})\textsubscript{3}), 25.88 (2\textsuperscript{*}), 25.82 (>Si(CH\textsubscript{3})\textsubscript{2}-C(CH\textsubscript{3})\textsubscript{3}), 21.3 (2\textsuperscript{*}), 19.0 (2\textsuperscript{*}), 18.5 (2\textsuperscript{*}), 16.4 (CH\textsubscript{3}), -4.84 (>Si(CH\textsubscript{3})\textsubscript{3}); ν\textsubscript{max} (film), 3402, 2928, 2857, 2094, 1462, 1385, 1364, 1307, 1252, 1199, 1163, 1137, 1124, 1094, 1071, 1051, 1018, 998, 981, 939, 900, 890, 863, 837, 822, 803, 776, 732, 687, 644 cm\textsuperscript{-1}; TOF-ESI+ m/z calculated for (C\textsubscript{18}H\textsubscript{36}O\textsubscript{3}Si + H\textsuperscript{+}), 313.2562, found, 313.2547; calculated for (C\textsubscript{18}H\textsubscript{36}O\textsubscript{3}Si + Na\textsuperscript{+}), 335.2382, found, 335.2374.
(1S*,4aR*,8aR*)-4a-((R*)1-hydroxyethyl)decahydronaphthalen-1-ol (11)

A solution of silyl ether 7 (0.55 g, 1.77 mmol, 1.00 equiv) in dry ether (10 mL) was added under N₂ to a suspension of LiAlH₄ (0.100 g, 2.65 mmol, 1.50 equiv) in dry ether (10 mL). The mixture was stirred at rt for 17 h. Water was added until effervescence ceased, followed by 1 M aqueous HCl until all unreacted LiAlH₄ was consumed. After extraction with ether (3 x 15 mL), the combined organic extracts were dried over MgSO₄ and filtered. The filtrate was purified by column chromatography (25% to 50% EtOAc in petroleum ether) to give two diastereomers 11 and 12.

(1S*,4aR*,8aR*)-4a-((R*)1-hydroxyethyl)decahydronaphthalen-1-ol 11 (270 mg, 77%) white solid; m.pt. 120-121 °C; Rf 0.14 (25% EtOAc in petroleum ether); δH (300 MHz, CDCl₃) 5.46 (2H, s, OH), 4.28 (1H, q, J 6.0 Hz, -CH(CH₃)OH), 3.69-3.66 (1H, m, (>CH-OH), 2.16-1.77 (5H, m, cy-CH), 1.55-1.28 (8H, m, cy-CH), 1.14 (3H, d, J 6.0 Hz, -CH3), 0.93-0.72 (2H, m, cy-CH); δC (75 MHz, CDCl₃) 69.9 (-CHCH₃-OH), 66.3 (>CH-OH), 50.4 (HO-CHCH₂-C(4°)-CH<), 41.5 (HO-CH(CH₃)-C(4°)-CH<), 39.5 (2°), 37.6 (2°), 34.4 (2°), 33.9 (2°), 27.1 (2°), 25.2 (2°), 18.9 (2°), 17.1 (CH₃); νmax (film), 3152, 2921, 2867, 1456, 16374, 1319, 1261, 1196, 1155, 1123, 1088, 1051, 1013, 987, 956, 934, 903, 885, 866, 843, 798, 774, 731, 667 cm⁻¹; TOF-ESI+ m/z calculated for (C₁₃H₂₂O₂ + H)⁺, 199.1698, found, 199.1684; calculated for (C₁₃H₂₂O₂ + Na)⁺, 221.1517, found, 221.1507.

(1S*,4aR*,8aR*)-4a-((S*)1-hydroxyethyl)decahydronaphthalen-1-ol 12 (22 mg, 6%) as a white solid; Rf 0.37 (25% EtOAc in petroleum ether); δH (250 MHz, CDCl₃) 4.45 (1H, q, J 6.5 Hz, -CH(CH₃)OH), 3.91-3.88 (1H, m, (>CH-OH), 2.72 (2H, s, OH), 2.36-2.16 (1H, m, HO-CHCH₂-C(4°)-CH<), 1.89-1.24 (12H, m, cy-CH), 1.17 (3H, d, J 6.5 Hz, -CH₃), 0.96-0.71 (2H, m, cy-CH); δC (75 MHz, CDCl₃) 72.2 (-CH(CH₃)OH), 71.8 (>CH-OH), 50.7 (HO-CHCH₂-C(4°)-CH<), 39.1 (HO-CHCH₂-C(4°)-CH<), 38.3 (2°), 37.6 (2°), 34.6 (2°), 28.5 (2°), 27.4 (2°), 22.9 (2°), 18.4 (2°), 17.2 (CH₃); νmax (film), 3298, 2924, 2850, 1452, 1370, 1335, 1307, 1261, 1195, 1152, 1126, 1092, 1068, 1042, 1030, 1008, 9889, 976, 953, 928,
903, 881, 845, 803, 779, 731, 674, 631 cm$^{-1}$; TOF-ESI+ m/z calculated for (C$_{12}$H$_{22}$O$_2$ + H)$^+$, 199.1698, found, 199.1683; calculated for (C$_{13}$H$_{22}$O$_2$ + Na)$^+$, 221.1517, found, 221.1499.
(E)-N’-(1-((1S*,4aR*,8aR*)-1-Hydroxydecahydro-naphthalen-4a-yl)ethylidene)-2,4,6-trimethylbenzenesulfonohydrazide (13)

To a solution of hydroxyketone 6 (5.00 g, 25.49 mmol, 1.00 equiv) in ethanol (125 mL) was added 2,4,6-trimethylbenzenesulfonohydrazide (5.46 g, 25.49 mmol, 1.00 equiv), p-TSA (5 mol%, 1.27 mmol, 242 mg) and 4Å molecular sieves. The reaction mixture was refluxed for 3 h under nitrogen atmosphere. The reaction mixture was left to cool over 16 h, during which time the product crystallised. The precipitate was then filtered and washed with cold ethanol (2 × 50 mL), to give the desired (E)-N’-(1-((1S*,4aR*,8aR*)-1-hydroxydecahydro-naphthalen-4a-yl)ethylidene)-2,4,6-trimethylbenzenesulfonohydrazide 13 (8.58 g, 86%) as a white solid; m.pt. 173-175 °C; Rf 0.47 (40% EtOAc in petroleum ether); δH (300 MHz, CDCl₃) 6.97 (2H, s, Ar-H), 5.33 (1H, br s, -NH-), 3.60 (1H, br s, -OH), 2.69 (6H, s, Ar-CH₃), 2.29 (3H, s, Ar-p-CH₃), 1.79 (3H, s, -CH₃), 1.82-1.76 (3H, m), 1.43-0.99 (12H, m) 0.65-0.52 (1H, m); δC (75 MHz, CDCl₃) 161.2 (CH₃-C=N-), 143.0 (Ar-C), 139.8 (Ar-C), 132.4 (Ar-C), 131.9 (Ar-C), 69.4 (>C-OH), 49.6 (3°), 49.0 (4°), 39.4 (2°), 37.5 (2°), 35.4 (2°), 27.3 (2°), 25.2 (2°), 23.0 (2°), 22.6 (1°), 20.9 (2°), 17.2 (1°), 12.6 (1°); v_max (film) 3360, 3261, 2938, 2857, 1636, 1604, 1446, 1380, 1338, 1161, 1110, 950, 891 cm⁻¹; TOF-ESI+ m/z calculated for (C₂₁H₂₂N₂O₃S + H)⁺, 393.2211, found, 393.2205; calculated for (C₂₁H₂₂N₂O₃S + Na)⁺, 415.2031, found, 415.2018.
(1S*,4aS*,8aR*)-4a-Vinyldecahydronaphthalen-1-ol (14)

To a solution of hydrazide 13 (2.42 g, 6.17 mmol, 1.00 equiv) in Et₂O (40 mL) was added n-BuLi (1.74 M, 10.8 mL, 18.82 mmol, 3.09 equiv), dropwise within 10 min at -78 °C. The bright yellow reaction mixture was warmed up to rt and the resulting orange solution then stirred under N₂ atmosphere for 1.5 h. The reaction mixture then was washed with aqueous NH₄Cl solution (3 × 20 mL), water (2 × 20 mL), brine (2 × 20 mL). The combined organic extracts were dried over MgSO₄ and filtered. The filtrate was concentrated under reduced pressure to give the crude. Purification by column chromatography (10% EtOAc in petroleum ether) gave (1S*,4aS*,8aR*)-4a-vinyldecahydronaphthalen-1-ol 14 (1.10 g, 99%) as a colourless oil; Rf 0.50 (25% EtOAc in petroleum ether); δH (300 MHz, CDCl₃) 6.55 (1H, dd, J 18.0, 11.0 Hz, CH=CH₂), 5.08 (1H, dd, Jcis 11.0, 1.5 Hz, -CH=CH₂), 5.01 (1H, dd, Jtrans 18.0, 1.5 Hz, -CH=CH₂), 3.66 (1H, q, J 2.5 Hz, -O-CH), 1.86-1.66 (6H, m), 1.55-1.02 (10H, m); δC (75 MHz, CDCl₃) 142.8 (-CH=CH₂), 112.2 (-CH=CH₂), 72.0 (-CH-OH), 49.6 (2°), 43.1 (3°), 39.6 (4°), 38.3 (2°), 33.9 (2°), 26.9 (2°), 25.6 (2°), 21.8 (2°), 16.6 (2°); νmax (film) 3416, 2925, 2849, 1629, 1450, 12.43, 1153, 927, 903 cm⁻¹; TOF-ESI+ m/z calculated for (C₁₂H₂₀O + H)⁺, 181.1592, found, 181.1583; (C₁₂H₂₀O + Na)⁺, 203.1411, found, 203.1398.
(4aS*,8aR*)-4a-Vinloyctahydronaphthalen-1(2H)-one (2)

![Chemical Structure](image)

To a stirred solution of oxalyl chloride (1.59 mL, 18.54 mmol, 1.10 equiv) in dichloromethane (80 mL) at – 78 °C under nitrogen was added dimethyl sulfoxide (2.57 mL, 36.25 mmol, 2.15 equiv). The solution was stirred for 10 min, then vinyl alcohol 14 (3.04 mg, 16.86 mmol, 1.00 equiv) in dry DCM (20 mL) was added. The reaction mixture was stirred for 90 min at -78 °C under nitrogen, and then triethylamine (11.83 mL, 84.31 mmol, 5.00 equiv) was added. After 15 min the solution was allowed to warm to rt over 30 min, then water (100 mL) was added and the reaction mixture was transferred to a separating funnel. The mixture extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with brine (2 × 50 mL) and dried over MgSO₄, then filtered. The filtrate was concentrated under reduced pressure and purified by column chromatography (10% EtOAc in petroleum ether) to give (4aR*,8aR*)-octahydronaphthalen-1(2H)-one 2 (2.98 g, 99%) as a pale yellow oil; Rf 0.58 (25% EtOAc-petroleum ether); δν (300 MHz, CDCl₃) 5.48 (1H, dd, J 18.0, 11.0 Hz, -CH₂), 5.12 (1H, dd, J cis 11.0, 1.0 Hz, -CH=CH₂), 4.93 (1H, dd, J trans 18.0, 1.0 Hz, -CH=CH₂), 2.29-2.23 (2H, m), 2.15 (1H, dd, J 12.0, 3.0 Hz) 1.87-1.59 (7H, m), 1.47-1.07 (5H, m); δν (75 MHz, CDCl₃) 212.2 (C=O), 140.5 (-CH=CH₂), 116.4 (-CH=CH₂), 57.1 (3°), 46.0 (4°), 41.1 (2°), 39.8 (2°), 39.7 (2°), 25.4 (2°), 22.0 (2°), 21.3 (2°), 20.9 (2°); νmax (film) 2931, 2851, 1708, 1638, 1449, 1366, 1311, 1206, 1089, 999, 918, 838 cm⁻¹; TOF-ESI+ m/z calculated for (C₁₂H₁₈O + H)⁺, 179.1435, found, 179.1428; (C₁₂H₁₈O + Na)⁺, 201.1255, found, 201.1246.
To a stirred solution of vinyl ketone 2 (0.580 g, 3.25 mmol, 1.00 equiv) in anhydrous THF (30 mL), was added a 0.5 M THF solution of 9-BBN (9.76 mL, 4.88 mmol, 1.50 equiv) dropwise under N₂ at 0 °C and the resulting mixture was then stirred at rt for 4 h. H₂O (1 mL) was added followed by aq 3N NaOH (8 mL) and aq 30% H₂O₂ (6 mL). The reaction mixture was heated to 60 °C and stirred for 2 h under nitrogen atmosphere, then extracted with EtOAc (2 × 15 mL). The combined extracts were washed with water (2 × 15 mL) and brine (2 × 15 mL), dried over MgSO₄ and filtered. The filtrate was concentrated under reduced pressure to give the crude. Purification by column chromatography (25% EtOAc in petroleum ether) gave two diastereomers. The major diastereomer was (1R*,4aS*,8aR*)-4a-vinyldecahydronaphthalen-1-ol 14 (210 mg, 35%) as a colourless oil, data as reported on page S9. The minor diastereomer was (1R*,4aS*,8aR*)-4a-vinyldecahydronaphthalen-1-ol 15 (61.4 mg, 11%), a white solid; m.pt. 54-56 °C; Rₚ 0.46 (30% EtOAc in petroleum ether); δH (250 MHz, CDCl₃) 6.01 (1H, dd, J₁₈.₀, 13.5 Hz, -CH=CH₂), 5.16 (1H, dd, J₁₈.₀, 0.5 Hz, -CH=CH₂), 5.01 (1H, dd, J₁₈.₀, 1.0 Hz, -CH=CH₂), 3.44 (1H, td, J 10.5, 4.5 Hz, -O-CH<), 2.01-1.03 (16H, m); δC (62.5 MHz, CDCl₃) 142.0 (-CH=CH₂), 114.1 (-CH=CH₂), 70.4 (>CH-OH), 52.9 (2°), 41.6 (3°), 41.5 (4°), 40.0 (2°), 36.5 (2°), 26.4 (2°), 22.8 (2°), 21.8 (2°), 20.3 (2°); νmax (film) 3416, 2925, 2849, 1629, 1450, 1243, 1153, 927, 903 cm⁻¹; TOF-ESI+ m/z calculated for (C₁₂H₂₀O + H)⁺, 181.1592, found, 181.1583; (C₁₂H₂₀O + Na)⁺, 203.1411, found, 203.1398.
(4aS*,8aS*)-1-methylene-4a-vinyldecahydronaphthalene (16)

A solution of methyltriphenylphosphonium bromide (25.05 g, 70.11 mmol, 2.50 equiv) and potassium tert-butoxide (1.0 M in THF, 56.09 mL, 56.09 mmol, 2.00 equiv) in THF (150 mL) was stirred at reflux under N₂ for 3 h. Vinyl ketone 2 (5.0 g, 28.04 mmol, 1.00 equiv) in toluene (15 mL) was then added dropwise to the above solution and the resulting mixture was stirred at reflux for 16 h. The reaction was carefully quenched by the addition of acetone (100 mL) and stirring at 100 °C for 30 min. The reaction mixture was then allowed to cool to rt and water (100 mL) was added. The reaction mixture was extracted with Et₂O (3 x 120 mL) and the combined organic layers were washed with brine (2 x 150 mL), dried over MgSO₄ and filtered. The filtrate was concentrated under reduced pressure to give the crude. Purification by column chromatography (100% hexane) gave (4aS*,8aS*)-1-methylene-4a-vinyldecahydronaphthalene 16 (4.55 g, 92%) as an oily liquid; b.pt. 233-235 °C / 760 Torr; Rᵣ 0.73 (100% pentane); δH (500 MHz, CDCl₃) 5.86 (1H, dd, J₁₁ 18.0, 11.0 Hz, vinyl -CH=CH₂), 5.13 (1H, dd, J₁₁ 11.0, 1.0 Hz, vinyl -CH=CH₂), 5.01 (1H, dd, J₁₂ 18.0, 1.5 Hz, vinyl -CH=CH₂), 4.76 (1H, q, J 1.5 Hz, >C=CH₂), 4.52 (1H, q, J 1.5 Hz, >C=CH₂), 2.37-2.28 (1H, m), 2.11-1.99 (1H, m), 1.85-1.74 (3H, m), 1.62-1.51 (4H, m), 1.45-1.24 (6H, m); δc (125 MHz, CDCl₃) 150.6 (>C=CH₂), 142.1 (>C=CH₂), 113.6 (>C=CH₂), 106.1 (>C=CH₂), 50.2 (4°), 42.7 (2°), 42.6 (4°), 39.5 (2°), 36.8 (2°), 26.7 (2°), 25.1 (2°), 23.5 (2°), 21.9 (2°); νmax (film) 2926, 2845, 1644, 1145, 1140, 1230, 1151, 997, 858, 785 cm⁻¹; TOF-ESI+ m/z calculated for (C₁₃H₂₀ + H)⁺, 177.1638, found, 177.1634.
To a stirred solution of bis-alkene 16 (4.05 g, 22.97 mmol, 1.00 equiv) in anhydrous THF (50 mL) was added 9-BBN (0.5 M THF solution, 68.92 mL, 34.46 mmol, 1.50 equiv) dropwise under N₂ at -15 °C and the resulting mixture was stirred for 15 min. The reaction mixture was allowed to warm up to rt and stirred for 96 h. Aqueous 3N NaOH (25 mL) following by aqueous 30% H₂O₂ (25 mL) was added and the exothermic reaction mixture was left to cool to rt with stirring over 3 h. The reaction mixture was then diluted with aq. NH₄Cl (50 mL) and extracted with Et₂O (2 × 50 mL). The combined organic extracts were washed with water (50 mL) and saturated brine (2 × 25 mL), dried over MgSO₄ and filtered. The filtrate was concentrated under reduced pressure to give the crude. Purification by column chromatography (25% EtOAc in petroleum ether) gave ((1S*,4aS*,8aS*)-4a-vinyldecahydronaphthalen-1-yl)methanol 1 (2.54 g, 79%) a colourless oil; Rf 0.39 (25% EtOAc in petroleum ether); δH (250 MHz, CDCl₃) 6.05 (1H, dd, J 17.5, 11.0 Hz, CH-CH₂), 5.00 (1H, dd, Jcis 9.5, 1.0 Hz, -CH=CH₂), 4.95 (1H, dd, Jtrans 16.0, 1.5 Hz, -CH=CH₂), 3.66-3.56 (2H, m, -CH₃-OH), 2.42 (1H, s, -CH₂-OH), 1.89-0.97 (16H, m); δC (62.5 MHz, CDCl₃) 142.5 (-CH=CH₂), 111.9 (-CH=CH₂), 60.4 (>CH-CH₂-OH), 48.1 (3°), 44.9 (3°), 32.9 (2°), 40.0 (4°), 38.5 (2°), 28.0 (2°), 27.4 (2°), 26.5 (2°), 22.0 (2°), 17.4 (2°); νmax (film) 3311, 2923, 2859, 1448, 1410, 1223, 1149, 1069, 1020, 995, 974, 827, 756, 650 cm⁻¹; TOF-ESI+ m/z calculated for (C₁₃H₂₂O₁ + H)⁺, 195.1748, found, 195.1729.
**$(1S^*,4aS^*,8aS^*)$-4a-vinylecahydronaphthalene-1-carbaldehyde (17)**

![Chemical Structure](image)

To a stirred solution of oxalyl chloride (1.38 mL, 16.13 mmol, 1.10 equiv) in dichloromethane (80 mL) at -78 °C under nitrogen was added DMSO (2.23 mL, 31.53 mmol, 2.15 equiv). The solution was stirred for 20 min, then $((1S^*,4aS^*,8aS^*)$-4a-vinylecahydronaphthalene-1-yl)methanol 1 (2.85 g, 14.66 mmol, 1.00 equiv) in dry DCM (20 mL) was added. The reaction mixture was stirred at -78 °C under nitrogen for 2.5 h, and then triethylamine (10.26 mL, 73.33 mmol, 5.00 equiv) was added at the same temperature. After 20 min the solution allowed to warm to rt over 30 min, then water (100 mL) was added and the reaction mixture was extracted with Et$_2$O (2 × 75 mL). The combined organic extracts were washed with brine (2 × 50 mL) and dried over MgSO$_4$, then filtered. The filtrate was concentrated under reduced pressure and purified by column chromatography (10% EtOAc in petroleum ether) to give $(1S^*,4aS^*,8aS^*)$-4a-vinylecahydronaphthalene-1-carbaldehyde 17 (2.45 g, 87%) as a pale yellow oil; $R_f$ 0.64 (20% EtOAc-petroleum ether); $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 9.89 (1H, s, -CHO), 5.99 (1H, dd, $J$ 17.5, 11.0 Hz, -CH=CH$_2$), 5.14 (1H, d, $J_{\text{cis}}$ 11.0 Hz, -CH=CH$_2$), 5.06 (1H, d, $J_{\text{trans}}$ 17.5 Hz, -CH=CH$_2$), 2.22-2.20 (2H, m), 1.95-0.84 (14H, m); $\delta_{\text{C}}$ (100 MHz, CDCl$_3$) 204.7 (-CHO), 140.2 (-CH=CH$_2$), 115.1 (-CH=CH$_2$), 51.9 (3°), 48.2 (3°), 43.0 (2°), 40.6 (4°), 38.9 (2°), 27.5 (2°), 26.4 (2°), 26.0 (2°), 22.0 (2°), 18.6 (2°); $\nu_{\text{max}}$ (film) 2923, 2854, 1723, 1448, 1236, 1074, 911 cm$^{-1}$; TOF-ESI+ m/z calculated for $(C_{12}H_{20}O + H)^+$, 193.1593, found, 193.1587; $(C_{12}H_{20}O + Na)^+$, 215.1413, found, 215.1404.