Supporting Information

New Strategy for convergent steroid synthesis

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1) General Remarks: Reactions were performed under a nitrogen atmosphere unless otherwise specified. Tetrahydrofuran was distilled on sodium benzophenone ketyl, dichloromethane, diisopropylamine, triethylamine from calcium hydride, and methanol from magnesium. Anhydrous DMF was purchased from Aldrich Chemicals Co. in Sure Seal bottles and used as such. All other reagents were purchased from Aldrich Chemicals Co. and used with no further purification unless otherwise specified. Melting points are uncorrected.

2) Experimental details

Trifluoro-methanesulfonic acid [1S-(1 β ,7 $\alpha\beta$)]-1-(tert-butyl-dimethyl-silanyloxy)-7 α -methyl-2,6,7,7 α -tetrahydro-1H-inden-4-yl ester **S1:** 1.56 M n-butyllithium (0.860 mL, 1.34 mmol, 1.9 equiv.) was added to diisopropylamine (0.185 mL, 1.41 mmol, 2 equiv.) at 0°C. The solution was stirred 10 min at 0°C, THF (9 mL) was added and the solution was again stirred 10 min at 0°C. The mixture was cooled to -78°C and the ketone **10** (198 mg, 0.706 mmol, 1 equiv.) in THF (9 mL) was added *via cannula*. The solution was stirred 2 h at -78°C and the Comins' reagent (599 mg, 1.41 mmol, 2 equiv.) in THF (9 mL) was added *via cannula*. The mixture was stirred 3 h at -30°C and then quenched by the addition of an aqueous saturated solution of NH₄Cl. The mixture was extracted with EtOAc (3 X 20 mL). The combined organic phases were dried with MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography (100% Hex to 10/90 : EtOAc/Hex) to afford 212 mg of **S1** (73 %, colorless oil). **IR** (neat, ν cm⁻¹) : 2932, 2858, 1421, 1249, 1211, 1142; **¹H NMR** (300 MHz, CDCl₃, δ ppm) : 5.75 (1H, m, HC=COTf); 5.66 (1H, s, C=CH); 4.01 (1H, t, J=8.1 Hz, CH-OTBS); 2.55-2.32 (3H, m); 1.79 (1H, dd, J=13.7, 4.5 Hz); 1.37-1.25 (1H, m); 1.08 (1H, d, J=6.7 Hz); 0.94 (3H, s, C-CH₃); 0.90 (9H, s, SiC-(CH₃)₃); 0.05 (6H, s, Si-(CH₃)₂); **¹³C NMR** (75 MHz, CDCl₃, δ ppm) : 144.1; 139.0; 120.6; 119.0; 81.5; 48.3; 38.3; 32.7; 25.7; 23.1; 18.0; 15.0; -4.6; -4.9; **MS** : (EI)

355 (M-C₄H₉)⁺; **HRMS** : (EI) Calcd for C₁₃H₁₈F₃O₄SSi (M-C₄H₉) = 355.0647; found = 355.0655 ± 0.0011; [α]_D²⁵ : +5.8 (C=1.00, CHCl₃).

[1S-(1 β ,7 α β)]-1-(tert-Butyl-dimethyl-silanyloxy)-7a-methyl-2,6,7,7a-tetrahydro-1H-indene-4-carboxylic acid methyl ester **11**: A mixture of K₂CO₃ (200 mg, 1.46 mmol, 3 equiv.), methanol (0.785 mL, 19.4 mmol, 40 equiv.) and bis(triphenylphosphine)palladium(II) chloride (20 mg, 0.03 mmol, 0.06 equiv.) in DMF (30 mL) was purged with carbon monoxide at room temperature for 5 min. A solution of vinyl triflate **S1** (200 mg, 0.485 mmol, 1 equiv.) in DMF (10 mL) was added *via cannula* and the purging was continued for an additional 10 min. The mixture was stirred at room temperature under an atmosphere of carbon monoxide for 40 h. The mixture was then quenched by the addition of a saturated aqueous solution of NH₄Cl. The mixture was extracted with 2/1 Hex/Et₂O (3 X 40 mL). The combined organic phases were dried with MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography (3/97 : EtOAc/Hex) to afford 94 mg of **11** (60 %, colorless oil). **IR** (neat, ν cm⁻¹) : 2929, 1724, 1254, 1133; **¹H NMR** (300 MHz, CDCl₃, δ ppm) : 6.89-6.87 (1H, m, CH=C-CO₂Me); 6.10 (1H, s, C=CH); 3.94 (1H, t, J=7.6 Hz, CH-OTBS); 3.76 (3H, s, CO₂-CH₃); 2.54-2.30 (4H, m); 1.85-1.78 (1H, m); 1.34-1.24 (1H, m); 0.90 (9H, s, SiC-(CH₃)₃); 0.88 (3H, s, C-CH₃); 0.05 (6H, s, Si-(CH₃)₂); **¹³C NMR** (75 MHz, CDCl₃, δ ppm) : 166.9; 139.9; 139.6; 126.8; 122.8; 81.6; 51.5; 46.3; 38.4; 33.0; 25.8; 24.2; 18.0; 15.2; -4.5; -4.9; **MS** : (EI) 322 M⁺, 265 (M-C₄H₉)⁺; **HRMS** : (EI) Calcd for C₁₈H₃₀O₃Si = 322.1964; found = 322.1958 ± 0.0010; [α]_D²⁵ : -31.6 (C=1.00, CHCl₃).

[1S-(1 β ,7 α β)]-[1-(tert-Butyl-dimethyl-silanyloxy)-7a-methyl-2,6,7,7a-tetrahydro-1H-inden-4-yl]-methanol **S2**: A 1M solution of diisobutylaluminum hydride in CH₂Cl₂ (0.977 mL, 0.977 mmol, 3 equiv.) was slowly added to a solution of ester **11** (105 mg, 0.326 mmol, 1 equiv.) in CH₂Cl₂ (20 mL) at -78°C. The mixture was stirred 2 h at -78°C and then quenched with acetone. Sodium sulfate decahydrate was added and the mixture was stirred 1 h at room temperature. The mixture was filtered through silica gel and concentrated. The residue was purified by flash chromatography (30/70 : EtOAc/Hex) to afford 86 mg of **S2** (86 %, colorless oil). **IR** (neat, ν cm⁻¹) : 3336, 2928, 2856, 1472, 1373, 1251, 1119; **¹H NMR** (300 MHz, CDCl₃, δ ppm) : 5.80 (1H, d, J=4.6 Hz, CH=C-CH₂OH); 5.46 (1H, s, C=CH); 4.23 (1H, dd, J=14.2, 13.0 Hz, CH₂-OH); 3.95 (1H, t, J=8.1 Hz, CH-OTBS); 2.44-2.11 (3H, m); 1.80 (1H, dd, J=11.8, 5.0 Hz); 1.41 (1H, br, OH); 1.33-1.25 (1H, m); 0.90 (9H, s, SiC-(CH₃)₃); 0.89 (3H, s, C-CH₃); 0.04 (6H, s, Si-(CH₃)₂); **¹³C NMR** (75 MHz, CDCl₃, δ ppm) : 144.1; 133.2; 126.6; 117.2; 82.0; 63.7;

45.8; 38.1; 33.9; 25.8; 23.3; 18.1; 15.1; -4.5; -4.9; **MS** : (EI) 237 (M-C₄H₉)⁺; **HRMS** : (EI) Calcd for C₁₃H₂₁O₂Si (M-C₄H₉) = 237.1311; found = 237.1315 ± 0.0007; [α]_D²⁵ : -50.0 (c=1.00, CHCl₃).

[1S-(1 β ,7 $\alpha\beta$)]-1-(tert-Butyl-dimethyl-silanyloxy)-7a-methyl-2,6,7,7a-tetrahydro-1H-indene-4-carbaldehyde **12**: Dess-Martin reagent (575 mg, 1.35 mmol, 3 equiv.) was added to a solution of alcohol **S2** (133 mg, 0.452 mmol, 1 equiv.) in CH₂Cl₂ (30 mL) at 0°C. The mixture was stirred 1 h at room temperature and then concentrated. The residue was purified by flash chromatography on florisil (20/80 : EtOAc/Hex) to afford 114 mg of **12** (86 %, colorless oil). **IR** (neat, ν cm⁻¹) : 2928, 2856, 1698, 1253, 1120; **¹H NMR** (300 MHz, CDCl₃, δ ppm) : 9.52 (1H, CHO); 6.69 (1H, t, J=4.0 Hz, CH=CCHO); 6.38 (1H, t, J=2.4 Hz, C=CH); 3.98 (1H, t, J=7.7 Hz, CH-OTBS); 2.56-2.35 (3H, m); 1.92-1.85 (1H, m); 1.37-1.22 (2H, m); 0.90 (9H, s, SiC-(CH₃)₃); 0.87 (3H, s, C-CH₃); 0.05 (6H, s, Si-(CH₃)₂); **¹³C NMR** (75 MHz, CDCl₃, δ ppm) : 193.4; 150.6; 138.1; 135.1; 124.1; 81.5; 46.0; 38.9; 33.2; 25.8; 24.9; 18.1; 15.2; -4.5; -4.9; **MS** : (EI) 235 (M-C₄H₉)⁺; **HRMS** : (EI) Calcd for C₁₃H₁₉O₂Si (M-C₄H₉) = 235.1154; found = 235.1161 ± 0.0007; [α]_D²⁵ : -3.5 (c=0.80, CHCl₃).

[1S-(1 β ,7 $\alpha\beta$)]-3-[1-(tert-Butyl-dimethyl-silanyloxy)-7a-methyl-2,6,7,7a-tetrahydro-1H-inden-4-yl]-3-hydroxy-propionic acid allyl ester **S3**: 1.56 M n-butyllithium (1.45 mL, 2.26 mmol, 5.8 equiv.) was added to diisopropylamine (0.308 mL, 2.35 mmol, 6 equiv.) at 0°C. The solution was stirred 10 min at 0°C, THF (20 mL) was added and the solution was again stirred 10 min at 0°C. The mixture was cooled to -78°C and the allyl acetate (0.259 mL, 2.40 mmol, 6.1 equiv.) was added. The solution was stirred 10 min at -78°C and the aldehyde **12** (114 mg, 0.39 mmol, 1 equiv.) in THF (15 mL) was added *via cannula*. The solution was stirred 30 min at -78°C and then quenched by the addition of a saturated aqueous solution of NH₄Cl. The mixture was extracted with EtOAc (3 X 20 mL) and the combined organic phases were dried with MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography (20/80 : EtOAc/Hex) to afford 137 mg of **S3** (89 %, colorless oil). **IR** (neat, ν cm⁻¹) : 3470, 2928, 2856, 1738, 1251, 1156, 1118; **¹H NMR** (300 MHz, CDCl₃, δ ppm) : 5.98-5.85 (2H, m); 5.50-5.23 (3H, m); 4.84-4.72 (1H, m); 4.62 (2H, d, J=5.68 Hz, CO₂-CH₂-CH=CH₂); 3.93 (1H, t, J=8.1 Hz, CH-OTBS), 2.93-2.12 (6H, m); 1.82-1.73 (1H, m); 1.34-1.16 (1H, m); 0.90 (9H, s, SiC-(CH₃)₃); 0.87 (1.5H, s, C-CH₃); 0.84 (1.5H, s, C-CH₃); 0.04 (6H, s, Si-(CH₃)₂); **¹³C NMR** (75 MHz, CDCl₃, δ ppm) : (presence of overlapping signals) 172.6; 172.5; 143.4; 143.0; 134.5;

131.9; 131.8; 126.0; 124.3; 118.6; 118.5; 118.0; 117.0; 81.8; 69.2; 66.9; 65.4; 65.3; 46.1; 41.4; 38.2; 33.8; 33.6; 25.8; 23.3; 23.2; 18.1; 15.1; 15.0; -4.5; -4.9; **MS** : (EI) 392 M⁺, 335 (M-C₄H₉)⁺; **HRMS** : (EI) Calcd for C₂₂H₃₆O₄Si = 392.2383; found = 392.2392 ± 0.0011; [α]_D²⁵ : -46.5 (c=1.20, CHCl₃).

[1S-(1 β ,7 $\alpha\beta$)]-3-[1-(tert-Butyl-dimethyl-silanyloxy)-7 α -methyl-2,6,7,7a-tetrahydro-1H-inden-4-yl]-3-oxo-propionic acid allyl ester **13**: Dess-Martin reagent (39 mg, 0.09 mmol, 3 equiv.) was added to a solution of alcohol **S3** (12 mg, 0.03 mmol, 1 equiv.) in CH₂Cl₂ (3 mL) at 0°C. The mixture was stirred 1 h at room temperature and then concentrated. The residue was purified by flash chromatography (15/85 : EtOAc/Hex) to afford 12 mg of **13** (100 %, colorless oil). **IR** (neat, ν cm⁻¹) : 2929, 1748, 1684, 1252, 1122; **¹H NMR** (300 MHz, CDCl₃, δ ppm) : 6.72 (1H, t, J=3.9, CH=C-C=O); 6.25 (1H, s, C=CH); 5.97-5.84 (1H, m, CO₂-CH₂-CH=CH₂); 5.39-5.21 (2H, m, CO₂-CH₂-CH=CH₂); 4.64 (2H, td, J=1.4, 6.1 Hz, CO₂-CH₂-CH=CH₂); 3.93 (1H, t, J=8.2 Hz, CH-OTBS); 3.76 (2H, s, CO-CH₂-CO); 2.50-2.30 (4H, m); 1.89-1.78 (1H, m); 0.90 (9H, s, SiC-(CH₃)₃); 0.86 (3H, s, C-CH₃); 0.04 (6H, s, Si-(CH₃)₂); **¹³C NMR** (75 MHz, CDCl₃, δ ppm) : 193.2; 167.5; 141.1; 134.2; 132.9; 131.7; 124.7; 118.6; 81.5; 65.9; 46.3; 38.7; 32.9; 25.8; 24.6; 18.1; 15.1; -4.5; -4.9; **MS** : (EI) 390 M⁺, 333 (M-C₄H₉)⁺; **HRMS** : (EI) Calcd for C₂₂H₃₄O₄Si = 390.2226; found = 390.2231 ± 0.0011; [α]_D²⁵ : -19.8 (c=0.80, CHCl₃).

[1S-(1 β ,4 $\alpha\beta$,5 β)]-5-Methoxymethoxy-4 α -methyl-octahydro-1-oxa-cyclopropa[d]indene **S4**: Dimethyldioxirane in acetone (20.4 mL, 2.04 mmol, 1 equiv.) was added to a solution of alkene **14** (546 mg, 2.04 mmol, 1 equiv.) in dry CH₂Cl₂ (15 mL) at -78 °C. The mixture was stirred at -78°C for 1 h, concentrated, and the residue was purified by flash chromatography (20/80 : EtOAc/Hex) to afford 400 mg of **S4** (71 %, colorless oil). **IR** (neat, ν cm⁻¹) : 2939, 1461, 1440, 1377, 1216, 1150, 1113, 1046, 917; **¹H NMR** (300 MHz, CDCl₃, δ ppm) : 4.68 (1H, d, J=6.7 Hz, O-CHH-O); 4.62 (1H, d, J=6.7 Hz, O-CHH-O); 3.75-3.70 (1H, m, CH-OMOM); 3.35 (3H, s, CH₂-O-CH₃); 3.05 (1H, s, CH-O-C); 2.04-1.71 (5H, m); 1.68-1.52 (2H, m); 1.39-1.27 (2H, m); 1.01-0.97 (1H, m); 0.97 (3H, s, C-CH₃); **¹³C NMR** (75 MHz, CDCl₃, δ ppm) : 95.6; 86.0; 66.0; 60.4; 55.1; 40.1; 34.9; 27.5; 26.6; 25.9; 15.3; 14.7; **MS** : (EI) 212 M⁺; **HRMS** : (EI) Calcd for C₁₂H₂₀O₃ = 212.1412; found = 212.1411 ± 0.0006; [α]_D²⁵ : +52.6 (c=1.00, CHCl₃).

[1S-(1 β ,3 $\alpha\beta$,4, α ,7 $\alpha\beta$)]-1-Methoxymethoxy-7a-methyl-octahydro-indene-3a,4-diol **15:**

A solution of KOH (5.7 g, 102 mmol, 50 equiv.) in water (35 mL) was added to a solution of **S4** (433 mg, 2.04 mmol, 1 equiv.) in DMSO (35 mL). The mixture was heated to 120°C for 16 h and quenched by the addition of brine (100 mL). The mixture was extracted with Et₂O (3 X 60 mL). The combined organic phases were dried with MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography (100% EtOAc) to afford 380 mg of **15** (81 %, white solid). **IR** (neat, ν cm⁻¹) : 3495, 2940, 2870, 1468, 1454, 1347, 1140, 1071, 1029; **¹H NMR** (300 MHz, CDCl₃, δ ppm) : 4.66 (1H, d, J=6.8 Hz, O-CHH-O); 4.54 (1H, d, J=6.8 Hz, O-CHH-O); 3.76-3.69 (2H, m, CH-OH + CH-OMOM); 3.35 (3H, s, CH₂-O-CH₃); 2.98 (2H, br, CH-OH + C-OH); 2.35-1.94 (2H, m); 1.92-1.77 (3H, m); 1.60-1.45 (2H, m); 1.35-1.21 (2H, m) 1.06 (3H, s, C-CH₃); 1.06-0.94 (1H, m); **¹³C NMR** (75 MHz, CDCl₃, δ ppm) : 94.6; 87.1; 85.7; 72.6; 55.6; 50.1; 33.9; 30.8; 30.1; 26.9; 19.7; 14.1; **MS** : (CI) 248 (M+NH₄)⁺, 231 (M+H)⁺; **HRMS** : (CI) Calcd for C₁₂H₂₃O₄ (M+H) = 231.1596; found = 231.1600 $\pm$ 0.0007; [α]_D²⁵ : +61.7 (c=1.00, CHCl₃); **MP** : 67-69°C.

[1S-(1 β ,3 $\alpha\beta$,4, α ,7 $\alpha\beta$)]-(1,3a-Bis-methoxymethoxy-7a-methyl-octahydro-inden-4-yloxy)-trimethyl-silane **S5:**

Trimethylsilyl chloride (2.09 mL, 16.5 mmol, 10 equiv.) was added to a solution of diol **15** (380 mg, 1.65 mmol, 1 equiv.) and triethylamine (3.46 mL, 24.8 mmol, 15 equiv.) in dry THF (15 mL). The solution was stirred 2 h at room temperature and then quenched by the addition of a saturated aqueous solution of NaHCO₃. The mixture was extracted with EtOAc (3 X 15 mL) and the combined organic phases were dried with MgSO₄, filtered, and concentrated. The residue was dissolved in dry CH₂Cl₂ (20 mL) and N,N-diisopropylethylamine (7.2 mL, 41.3 mmol, 25 equiv.) and 4-dimethylaminopyridine (21 mg, 0.17 mmol, 0.1 equiv.) was added. At 0°C chloromethyl methyl ether (2.5 mL, 33.0 mmol, 20 equiv.) was added. The solution was stirred 10 min at 0°C and 72 h at room temperature and then quenched by the addition of a saturated aqueous solution of NaHCO₃. The mixture was extracted with CH₂Cl₂ (3 X 15 mL) and the combined organic phases were dried with MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography (40/58/2 : EtOAc/ Hex/Et₃N) to afford 591 mg of **S5** (100 %, yellow oil). **IR** (neat, ν cm⁻¹) : 2946, 2880, 1251, 1154, 1101, 1034; **¹H NMR** (300 MHz, CDCl₃, δ ppm) : 4.86 (1H, d, J=6.8 Hz, O-CHH-O); 4.54 (1H, d, J=6.8 Hz, O-CHH-O); 4.62 (2H, m, O-CH₂-O); 4.11 (1H, dd, J=5.5, 8.2 Hz, CH-OTMS); 3.78 (1H, dd, J=3.0, 6.1 Hz, CH-OMOM); 3.38 (3H, s, CH₂-O-CH₃); 3.37 (3H, s, CH₂-O-CH₃); 2.14-1.97 (2H, m); 1.75-1.55 (4H, m); 1.45-1.15 (4H, m); 0.97 (3H, s, C-CH₃); 0.10 (9H, s, Si(CH₃)₃); **¹³C NMR** (75 MHz, CDCl₃, δ ppm) : 96.1; 92.6; 86.5;

80.8; 73.6; 55.3; 55.0; 48.6; 32.4; 30.6; 28.7; 27.4; 17.0; 16.8; 0.2; **MS** : (EI) 301 (M-C₂H₅O)⁺; **HRMS** : (EI) Calcd for C₁₅H₂₉O₄Si (M- C₂H₅O) = 301.1835; found = 301.1833 ± 0.0009; [α]_D²⁵ : +2.8 (c=1.00, CHCl₃).

[1S-(1 β ,3 $\alpha\beta$,4, α ,7 $\alpha\beta$)]-1,3a-Bis-methoxymethoxy-7a-methyl-octahydro-inden-4-ol 16:

Tetrabutylammonium fluoride 1 M in THF (3.4 mL, 3.4 mmol, 2 equiv.) was added to a solution of compound **S5** (591 mg, 1.7 mmol, 1 equiv.) in dry THF (20 mL) at 0°C. The solution was stirred 10 min at room temperature and then quenched by the addition of a saturated aqueous solution of NH₄Cl. The mixture was extracted with EtOAc (3 X 20 mL) and the combined organic phases were dried with MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography (30/70 : EtOAc/Hex) to afford 400 mg of **16** (86 %, colorless oil). **IR** (neat, ν cm⁻¹) : 3449, 2937, 1468, 1145, 1097, 1032; **¹H NMR** (300 MHz, CDCl₃, δ ppm) : 4.91 (1H, d, J=7.6 Hz, O-CHH-O); 4.64 (1H, d, J=7.6 Hz, O-CHH-O); 4.63 (1H, d, J=6.8 Hz, O-CHH-O); 4.54 (1H, d, J=6.8 Hz, O-CHH-O); 4.40 (1H, d, J=2.3 Hz, CH-OH); 3.72 (1H, ddd, J=2.2, 5.4, 11.5 Hz, CH-OH); 3.63 (1H, dd, J=3.6, 7.7 Hz, CH-OMOM); 3.45 (3H, s, CH₂-O-CH₃); 3.33 (3H, s, CH₂-O-CH₃); 2.28-2.15 (1H, m); 2.06 (1H, ddd, J=1.6, 9.1, 15.4 Hz); 1.94-1.73 (2H, m); 1.65-1.47 (3H, m); 1.40-1.25 (2H, m); 1.18-1.08 (1H, m); 1.08 (3H, s, C-CH₃); **¹³C NMR** (75 MHz, CDCl₃, δ ppm) : 95.8; 91.7; 90.5; 85.7; 71.9; 55.1; 55.0; 51.0; 37.3; 30.8; 29.0; 23.6; 19.7; 14.5; **MS** : (EI) 242 (M-CH₃-OH)⁺, 229 (M-C₂H₅O)⁺; **HRMS** : (EI) Calcd for C₁₃H₂₂O₄ (M- C₃OH) = 242.1518; found = 242.1512 ± 0.0007; [α]_D²⁵ : -66.5 (c=1.00, CHCl₃).

[1S-(1 β ,3 $\alpha\beta$,7 $\alpha\beta$)]-1,3a-Bis-methoxymethoxy-7a-methyl-octahydro-inden-4-one S6:

Tetrapropylammonium perruthenate (VII) was added to a solution of alcohol **16** (68 mg, 0.25 mmol, 1 equiv.), 4-methylmorpholine N-oxide (44 mg, 0.375 mmol, 1.5 equiv) and 4A molecular sieves (125 mg) in dry CH₂Cl₂ (8 mL). The mixture was stirred 1 h at room temperature, filtered through silica gel (100% EtOAc) and concentrated to afford 69 mg of **S6** (100 %, colorless oil). **IR** (neat, ν cm⁻¹) : 2943, 2890, 1715, 1465, 1441, 1310, 1217, 1153, 1111, 1038, 919; **¹H NMR** (300 MHz, CDCl₃, δ ppm) : 4.56-4.46 (4H, m, 2 x O-CH₂-O); 3.71-3.64 (1H, m, CH-OMOM); 3.33 (3H, s, CH₂-O-CH₃); 3.28 (3H, s, CH₂-O-CH₃); 2.84-2.73 (1H, m); 2.53-2.40 (1H, m); 2.27-2.18 (1H, m); 2.07-1.92 (1H, m); 1.91-1.55 (6H, m); 1.03 (3H, s, C-CH₃); **¹³C NMR** (75 MHz, CDCl₃, δ ppm) : 210.7; 95.6; 93.2; 87.6; 75.3; 56.1; 55.1; 52.6; 37.5; 29.5; 26.2; 23.6; 22.7; 16.5; **MS** : (EI) 272 M⁺; **HRMS** : (EI) Calcd for C₁₄H₂₄O₅ = 272.1624; found = 272.1631 ± 0.0008; [α]_D²⁵ : +13.3 (c=1.00, CHCl₃).

Trifluoro-methanesulfonic acid [1S-(1 β ,3a β ,7a β)]-1,3a-bis-methoxymethoxy-7a-methyl-2,3,3a,6,7,7a-hexahydro-1H-inden-4-yl ester 17: 1.0 M LiHMDS in THF (1.9 mL, 1.90 mmol, 4 equiv.) was added to THF (3 mL) at -78°C and the ketone **S6** (129 mg, 0.474 mmol, 1 equiv.) in THF (3 mL) was added *via cannula* to the solution. The solution was stirred 2 h at -78°C and the Comins' reagent (804 mg, 1.90 mmol, 4 equiv.) in THF (3 mL) was added *via cannula*. The mixture was stirred 2 h at -30°C and then quenched by the addition of an aqueous saturated solution of NH_4Cl . The mixture was extracted with EtOAc (3 X 15 mL). The combined organic phases were dried with MgSO_4 , filtered, and concentrated. The residue was purified by flash chromatography (20/80 : EtOAc/Hex) to afford 176 mg of **17** (92 %, colorless oil). **IR** (neat, ν cm^{-1}) : 2938, 1415, 1213, 1144, 1025; **^1H NMR** (300 MHz, CDCl_3 , δ ppm) : 5.95 (1H, t, $J=3.9$ Hz, $\text{CH}=\text{C}$); 4.77 (1H, d, $J=7.4$ Hz, O- CHH -O); 4.70 (1H, d, $J=7.4$ Hz, O- CHH -O); 4.65 (1H, d, $J=6.8$ Hz, O- CHH -O); 4.56 (1H, d, $J=6.8$ Hz, O- CHH -O); 3.82 (1H, t, $J=8.3$ Hz, CH-OMOM); 3.39 (3H, s, $\text{CH}_2\text{-O-CH}_3$); 3.35 (3H, s, $\text{CH}_2\text{-O-CH}_3$); 2.32-2.25 (2H, m); 2.18-1.95 (3H, m); 1.78-1.57 (3H, m); 1.06 (3H, s, C- CH_3); **^{13}C NMR** (75 MHz, CDCl_3 , δ ppm) : 148.7; 121.3; 95.8; 92.8; 82.7; 77.0; 55.9; 55.3; 48.9; 28.3; 25.8; 25.4; 21.0; 16.1; **MS** : (EI) 343 ($\text{M-C}_2\text{H}_5\text{O}_2$) $^+$; **HRMS** : (EI) Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_5\text{SF}_3$ ($\text{M-C}_2\text{H}_5\text{O}_2$) = 343.0827; found = 343.0835 ± 0.0010 ; $[\alpha]_D^{25}$: +38.0 ($c=1.00$, CHCl_3).

[1S-(1 β ,3a β ,7a β)]-1-(1,3a-Bis-methoxymethoxy-7a-methyl-2,3,3a,6,7,7a-hexahydro-1H-inden-4-yl)-ethanone 18: A solution of vinyl triflate **17** (316 mg, 0.781 mmol, 1 equiv.), $\text{CH}_2=\text{C}(\text{SnBu}_3)\text{OEt}$ (644 mg, 1.78 mmol, 2.3 equiv.) and LiCl (278 mg, 6.56 mmol, 8.4 equiv.) in DMF (30 mL) was purged with argon 5 min at room temperature. Bis(triphenylphosphine)palladium(II) chloride (18 mg, 0.026 mmol, 0.03 equiv.) was added and the mixture was stirred at 60°C under an atmosphere of argon for 18 h. The mixture was then quenched by the addition of a saturated aqueous solution of oxalic acid (6 mL) and stirred at room temperature for 2 h. The mixture was quenched by the addition of a saturated aqueous solution of NaHCO_3 and extracted with Et_2O (3 X 25 mL). The combined organic phases were dried with MgSO_4 , filtered, and concentrated. The residue was purified by flash chromatography (15/83/2 : EtOAc/Hex/ Et_3N) to afford 117 mg of **18** (50 %, colorless oil). **IR** (neat, ν cm^{-1}) : 2930, 2887, 2822, 1681, 1628, 1373, 1225, 1154, 1030; **^1H NMR** (300 MHz, CDCl_3 , δ ppm) : 7.00 (1H, dd, $J=3.3, 4.7$ Hz, $\text{CH}=\text{C}$); 4.73 (1H, d, $J=7.3$ Hz, O- CHH -O); 4.66 (1H, d, $J=6.7$ Hz, O- CHH -O); 4.57 (1H, d, $J=6.7$ Hz, O- CHH -O); 4.55 (1H, d, $J=7.3$ Hz, O- CHH -O); 3.67 (1H, t, $J=8.5$ Hz, CH-OMOM); 3.36 (3H, s, $\text{CH}_2\text{-O-CH}_3$); 3.31 (3H, s, $\text{CH}_2\text{-O-CH}_3$); 2.35-2.20 (3H, m); 2.92 (3H, s, CO CH_3); 1.91-1.77 (1H, m); 1.75-1.49 (4H, m); 1.02 (3H, s, C- CH_3); **^{13}C**

NMR (75 MHz, CDCl₃, δ ppm) : 198.4; 143.3; 141.32; 95.6; 92.9; 82.0; 77.3; 55.5; 55.2; 47.4; 32.4; 27.9; 26.3; 26.2; 22.5; 16.7; **MS** : (CI) 316 (M+NH₄)⁺, 267 (M-OCH₃)⁺; **HRMS** : (CI) Calcd for C₁₆H₃₀NO₅ (M+NH₄) = 316.2124; found = 316.2119 $\pm$ 0.0009; [α]_D²⁵ : +111 (c=1.10, CHCl₃).

[1S-(1 β ,3 $\alpha\beta$,7 $\alpha\beta$)]-3-(1,3a-Bis-methoxymethoxy-7 α -methyl-2,3,3a,6,7,7a-hexahydro-1H-inden-4-yl)-3-oxo-propionic acid allyl ester **19**: 1.0 M LiHMDS in THF (1.20 mL, 1.20 mmol, 2.9 equiv.) was added to THF (10 mL) at -78°C and the ketone **18** (125 mg, 0.419 mmol, 1 equiv.) in THF (10 mL) was added *via cannula* to the solution. The solution was stirred 2 h at -78°C and allylcyanofornate (300 mg, 2.70 mmol, 6.4 equiv.) was added. The mixture was stirred 15 min at -78°C and then quenched by the addition of an aqueous saturated solution of NH₄Cl. The mixture was extracted with EtOAc (3 X 15 mL). The combined organic phases were dried with MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography (20/78/2 : EtOAc/Hex/Et₃N) to afford 140 mg of **19** (87 %, colorless oil). **IR** (neat, ν cm⁻¹) : 2932, 2887, 1743, 1681, 1151, 1027; **¹H NMR** (300 MHz, CDCl₃, δ ppm) : 6.98-6.93 (1H, m, CH=C); 5.98-5.81 (1H, m, CO₂-CH₂-CH=CH₂); 5.46-5.19 (2H, m, CO₂-CH₂-CH=CH₂); 4.78-4.43 (6H, m, 2 x O-CH₂-O + CO₂-CH₂-CH=CH₂); 3.78-3.58 (3H, m, CO-CH₂-CO + CH-OMOM); 3.32 (3H, s, CH₂-O-CH₃); 3.24 (3H, s, CH₂-O-CH₃); 2.43-2.04 (4H, m); 1.90-1.75 (1H, m); 1.74-1.45 (3H, m); 0.98 (3H, s, C-CH₃); enol form: 12.24 (0.1H, s, HO-C=CH-CO); 3.37 (0.3H, s, CH₂-O-CH₃); 3.26 (0.3H, s, CH₂-O-CH₃); **¹³C NMR** (75 MHz, CDCl₃, δ ppm) : 192.2; 167.6; 144.2; 143.3; 140.7; 139.0; 131.7; 118.6; 118.3; 95.6; 92.9; 90.0; 81.9; 77.4; 65.8; 64.8; 56.4; 55.6; 55.5; 55.2; 47.6; 46.7; 33.5; 32.7; 27.9; 26.5; 26.2; 16.8; 16.4; **MS** : (CI) 400 (M+NH₄)⁺; **HRMS** : (CI) Calcd for C₂₀H₃₄NO₇ (M+NH₄) = 400.2335; found = 400.2331 $\pm$ 0.0012; [α]_D²⁵ : +97.9 (c=1.10, CHCl₃).

[5R-(5 α ,9 β ,10 α ,13 β ,17 β)]-17-(tert-Butyl-dimethyl-silanyloxy)-13-methyl-1,7-dioxo-1,2,3,4,5,6,7,9,11,12,13,15,16,17-tetradecahydro-cyclopenta[a]phenanthrene-10-carboxylic acid methyl ester **20**: Cesium carbonate (29 mg, 0.09 mmol, 5 equiv.) was added to a solution of Nazarov reagent **13** (7 mg, 0.018 mmol, 1 equiv.) and cyclohexenone **1** (14 mg, 0.09 mmol, 5 equiv.) in dry CH₂Cl₂ (5 mL). The mixture was stirred 16 h at room temperature, filtered through silica gel and concentrated. The residue was dissolved in THF (5 mL) and tetrakis(triphenylphosphine)palladium(0) (3 mg, 0.002 mmol, 0.1 equiv.) and morpholine (0.02 mL, 0.2 mmol, 10 equiv.) were added. The

mixture was stirred 3 h at room temperature and concentrated. The residue was purified by flash chromatography (15/85 : EtOAc/Hex) to afford 5 mg of **20** (60 %, 2 steps, colorless oil). **IR** (neat, ν cm^{-1}) : 2954, 1712, 1248, 1126; **^1H NMR** (300 MHz, CDCl_3 , δ ppm) : 3.75 (3H, s, $\text{CO}_2\text{-CH}_3$); 3.53 (1H, dd, $J=7.7, 10.0$ Hz, CH-OTBS); 3.35-3.25 (1H, m); 3.01-2.83 (2H, m); 2.70-2.43 (3H, m); 2.33 (1H, dd, $J=11.7, 16.1$ Hz); 2.14 (1H, dd, $J=3.6, 16.2$ Hz); 1.97-1.46 (10H, m); 0.93 (3H, s, C-CH_3); 0.88 (9H, s, $\text{SiC-(CH}_3)_3$); 0.02 (3H, s, Si-CH_3); 0.01 (3H, s, Si-CH_3); **^{13}C NMR** (75 MHz, CDCl_3 , δ ppm) : 207.6; 200.3; 171.6; 125.3; 80.8; 64.3; 52.5; 46.0; 42.3; 40.1; 39.4; 33.2; 30.0; 29.7; 28.4; 28.1; 25.8; 23.0; 20.5; 18.0; 16.6; -4.4; -4.9; **MS** : (EI) 460 M^+ , 403 ($\text{M-C}_4\text{H}_9$) $^+$; **HRMS** : (EI) Calcd for $\text{C}_{26}\text{H}_{40}\text{O}_5\text{Si}$ = 460.2645; found = 460.2651 ± 0.0014 ; $[\alpha]_{\text{D}}^{25}$: +28.4 ($c=0.50$, CHCl_3).

[5R-(5 α ,9 β ,10 α ,13 β ,17 β)]-17-Hydroxy-13-methyl-1,7-dioxo-1,2,3,4,5,6,7,9,11,12,13,15,16,17-tetradecahydro-cyclopenta[a]phenanthrene-10-carboxylic acid methyl ester **21**: A catalytic amount of *p*-toluenesulfonic acid was added to a solution of **20** (2 mg, 0.004 mmol) in MeOH (2 mL) and the mixture was heated 2 h at reflux. The mixture was then quenched by the addition of a saturated aqueous solution of NaHCO_3 . The MeOH was removed in vacuo and the mixture was extracted with EtOAc (3 X 2 mL). The combined organic phases were dried with MgSO_4 , filtered, and concentrated. The residue was purified by flash chromatography (60/40 : EtOAc/Hex) to afford 2 mg of **21** (100 %, colorless oil). The reaction was only done once so the yield may be not precise. **IR** (neat, ν cm^{-1}) : 3436, 2929, 2865, 1709, 1620, 1460, 1431, 1244; **^1H NMR** (300 MHz, CDCl_3 , δ ppm) : 3.75 (3H, s, $\text{CO}_2\text{-CH}_3$); 3.64 (1H, dd, $J=7.8, 10.2$ Hz); 3.34-3.31 (1H, m); 3.00-2.87 (2H, m); 2.72-2.45 (3H, m); 2.36 (1H, dd, $J=11.7, 16.2$ Hz); 2.18-1.55 (9H, m); 1.29-1.22 (1H, m); 1.10-0.85 (2H, m); 0.96 (3H, s, C-CH_3); **^{13}C NMR** (75 MHz, CDCl_3 , δ ppm) : 207.6; 199.0; 171.6; 162.9; 125.7; 80.9; 64.3; 52.6; 45.5; 42.2; 40.1; 39.4; 33.0; 29.7; 29.4; 28.3; 28.1; 23.0; 20.5; 16.3; **MS** : (EI) 346 M^+ ; **HRMS** : (EI) Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_5$ = 346.1782; found = 346.1782 ± 0.0010 ; $[\alpha]_{\text{D}}^{25}$: +30.0 ($c=0.10$, CHCl_3).

[5R-(5 α ,9 β ,10 α ,13 β)]-13-Methyl-1,7,17-trioxo-1,2,3,4,5,6,7,9,11,12,13,15,16,17-tetradecahydro-cyclopenta[a]phenanthrene-10-carboxylic acid methyl ester **22**: Dess-Martin reagent (11 mg, 0.025 mmol, 5 equiv.) was added to a solution of alcohol **21** (2 mg, 0.005 mmol, 1 equiv.) in CH_2Cl_2 (2 mL) at 0°C . The mixture was stirred 1 h at room temperature and then concentrated. The residue was purified by flash chromatography (50/50 : EtOAc/Hex) to afford 1 mg of **22** (50 %, colorless oil). The reaction was only done once so the yield may be not precise. **IR** (neat, ν cm^{-1}) : 2933,

2859, 1741, 1710, 1624, 1452, 1245, 1218; $^1\text{H NMR}$ (300 MHz, CDCl_3 , δ ppm) : 3.75-3.57 (1H, m); 3.74 (3H, s, $\text{CO}_2\text{-CH}_3$); 3.36-3.23 (2H, m); 3.07-2.92 (2H, m); 2.77-2.15 (6H, m); 1.95-1.80 (4H, m); 1.70-0.8 (3H, m); 1.17 (3H, s, C-CH_3); **MS** : (EI) 346 M^+ ; **HRMS** : (EI) Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_5$ = 344.1624; found = 344.1618 ± 0.0010 ; **MP** : 163-164°C.

[4S-(4 β ,5 β ,9 α ,10 β ,13 β ,17 β)]-17-(tert-Butyl-dimethyl-silanyloxy)-4-(tert-butyl-diphenyl-silanyloxy)-13-methyl-1,7-dioxo-1,2,3,4,5,6,7,9,11,12,13,15,16,17-tetradecahydro-cyclopenta[a]phenanthrene-10-carboxylic acid methyl ester 23:

Cesium carbonate (17 mg, 0.05 mmol, 1.5 equiv.) was added to a solution of Nazarov reagent **13** (13 mg, 0.03 mmol, 1 equiv.) and cyclohexenone **4** (8 mg, 0.05 mmol, 1.5 equiv.) in dry CH_2Cl_2 (3 mL). The mixture was stirred 16 h at room temperature, filtered through silica gel and concentrated. The residue was dissolved in THF (5 mL) and tetrakis(triphenylphosphine)palladium(0) (4 mg, 0.003 mmol, 0.1 equiv.) and morpholine (0.03 mL, 0.3 mmol, 10 equiv.) were added. The mixture was stirred 3 h at room temperature and concentrated. The residue was purified by flash chromatography (5/95 : EtOAc/Hex) to afford 4 mg of **23** (17%, 2 steps, colorless oil). **IR** (neat, ν cm^{-1}) : 2954, 2856, 1714, 1690, 1613, 1428, 1251, 1113; $^1\text{H NMR}$ (300 MHz, CDCl_3 , δ ppm) : 7.65 (4H, td, $J=8.3, 1.5$ Hz, Si-(Ph)₂ (meta)); 7.42-7.35 (6H, m, Si-(Ph)₂ (para, ortho)); 3.86-3.83 (1H, m, CH-OTBDPS); 3.73 (3H, s, $\text{CO}_2\text{-CH}_3$); 3.59 (1H, dd, $J=7.2, 10.31$ Hz, CH-OTBS); 3.33-3.05 (3H, m); 3.04-2.86 (1H, m); 2.85-2.70 (1H, m); 2.25-1.20 (11H, m); 1.07 (9H, s, Si-(Ph)₂-C(CH₃)₃); 0.96 (3H, s, C-CH_3); 0.88 (9H, s, Si-(CH₃)₂-C(CH₃)₃); 0.03 (3H, s, Si-CH₃); 0.02 (3H, s, Si-CH₃); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , δ ppm) : 207.9; 198.4; 171.9; 165.7; 135.8; 135.7; 133.6; 132.9; 130.0; 127.8; 127.7; 124.6; 80.8; 71.4; 61.9; 52.1; 47.6; 46.2; 41.2; 38.9; 35.4; 33.9; 30.2; 30.0; 29.0; 27.0; 25.8; 22.1; 19.2; 18.2; 18.0; -4.5; -4.9; **MS** : (EI) 714 M^+ , 657 ($\text{M-C}_4\text{H}_9$)⁺; **HRMS** : (EI) Calcd for $\text{C}_{42}\text{H}_{58}\text{O}_6\text{Si}_2$ = 714.3772; found = 714.3766 ± 0.0021 ; $[\alpha]_{\text{D}}^{25}$: -26.7 ($c=0.30$, CHCl_3).

[4S-(4 β ,5 β ,9 α ,10 β ,13 β ,17 β)]-4-(tert-Butyl-diphenyl-silanyloxy)-17-methoxymethoxy-13-methyl-1,7-dioxo-1,2,3,4,5,6,7,9,11,12,13,15,16,17-tetradecahydro-cyclopenta[a]phenanthrene-10-carboxylic acid methyl ester 26: Cesium carbonate (194 mg, 0.596 mmol, 2 equiv.) was added to a solution of Nazarov reagent **19** (114 mg, 0.298 mmol, 1 equiv.) and cyclohexenone **4** (244 mg, 0.596 mmol, 2 equiv.) in dry CH_2Cl_2 (10 mL). The mixture was stirred 16 h at room temperature, filtered through

silica gel and concentrated. The residue was dissolved in THF (10 mL) and tetrakis(triphenylphosphine)palladium(0) (17 mg, 0.015 mmol, 0.05 equiv.) and morpholine (0.2 mL, 2 mmol, 7 equiv.) were added. The mixture was stirred 3 h at room temperature and concentrated. The residue was purified by flash chromatography (25/75 : EtOAc/Hex) to afford 106 mg of **26** (55%, 2 steps, colorless oil). **IR** (neat, ν cm^{-1}) : 2954, 2890, 2858, 1713, 1690, 1613, 1428, 1218, 1113, 1055; **^1H NMR** (300 MHz, CDCl_3 , δ ppm) : 7.67-7.63 (4H, m, Si-(Ph) $_2$ -*t*-Bu (meta)); 7.47-7.35 (6H, m, Si-(Ph) $_2$ -*t*-Bu (para, ortho)); 4.69 (1H, d, $J=6.6$ Hz, O-CHH-O); 4.64 (1H, d, $J=6.6$ Hz, O-CHH-O); 4.85 (1H, dd, $J=3.7, 6.65$ Hz, CH-OTBDPS); 3.74 (3H, s, CO_2 -CH $_3$); 3.55 (1H, dd, $J=7.1, 10.6$ Hz, CH-OMOM); 3.36 (3H, s, CH $_2$ -O-CH $_3$); 3.31-3.08 (3H, m); 3.03-2.75 (2H, m); 2.28-1.78 (7H, m); 1.68-1.56 (2H, m); 1.44-1.35 (2H, m); 1.08 (9H, s, Si-C(CH $_3$) $_3$); 1.04 (3H, s, C-CH $_3$); **^{13}C NMR** (75 MHz, CDCl_3 , δ ppm) : 207.7; 198.3; 171.8; 164.7; 135.8; 135.8; 133.6; 132.8; 130.0; 127.8; 127.7; 124.7; 96.0; 85.5; 71.3; 61.9; 55.2; 52.1; 47.6; 45.4; 41.1; 38.8; 35.4; 34.0; 30.2; 28.9; 27.3; 27.0; 22.0; 19.2; 18.7; **MS** : (EI) 644 M^+ , 587 ($\text{M}-\text{C}_4\text{H}_9$) $^+$; **HRMS** : (EI) Calcd for $\text{C}_{38}\text{H}_{48}\text{O}_7\text{Si}$ = 644.3169; found = 644.3181 $\pm$ 0.0019; $[\alpha]_{\text{D}}^{25}$: -16.0 ($c=1.10$, CHCl_3).

[4S-(4 β ,5 β ,9 α ,10 β ,13 β ,17 β)]-4-(tert-Butyl-diphenyl-silanyloxy)-17-hydroxy-13-methyl-1-oxo-1,2,3,4,5,6,7,9,11,12,13,15,16,17-tetradecahydro-cyclopenta[a]phenanthrene-10-carboxylic acid methyl ester **27:** The alcohol **24** (28 mg, 0.047 mmol) was dissolved in EtOH (5 mL). Palladium on activated carbon was added and the mixture was purged with hydrogen at room temperature for 10 min. The mixture was stirred at room temperature under an atmosphere of hydrogen for 18 h. The solution was filtered through silica gel and concentrated. The residue was purified by flash chromatography (30/70 : EtOAc/Hex) to afford 21 mg of **27** (76 %, colorless oil). **IR** (neat, ν cm^{-1}) : 3430, 2952, 2861, 1741, 1709, 1428, 1220, 1111; **^1H NMR** (300 MHz, CDCl_3 , δ ppm) : 7.73-7.66 (4H, m, Si-(Ph) $_2$ -*t*-Bu (meta)); 7.49-7.36 (6H, m, Si-(Ph) $_2$ -*t*-Bu (para, ortho)); 4.22 (1H, td, J =8.6, 3.7 Hz, $\underline{\text{CH}}$ -OTBDPS); 3.70 (3H, s, CO_2 - $\underline{\text{CH}}_3$); 3.54 (1H, dd, J =7.1, 10.48 Hz, $\underline{\text{CH}}$ -OH); 2.75-2.68 (1H, m, $\underline{\text{CH}}$ -CH-OTBDPS); 2.55-2.42 (2H, m); 2.38-1.50 (13H, m); 1.36-1.13 (2H, m); 1.07 (9H, s, Si-C($\underline{\text{CH}}_3$) $_3$); 1.02 (3H, s, C- $\underline{\text{CH}}_3$); **^{13}C NMR** (75 MHz, CDCl_3 , δ ppm) : 207.7; 171.1; 138.2; 135.9; 135.8; 134.2; 133.4; 129.9; 129.8; 127.8; 127.6; 125.6; 82.3; 68.7; 65.4; 51.8; 48.4; 42.9; 38.5; 36.4; 34.6; 32.7; 29.6; 27.0; 24.6; 23.6; 23.3; 21.2; 19.4; 16.3; **MS** : (EI) 586 M^+ , 529 ($\text{M}-\text{C}_4\text{H}_9$) $^+$; **HRMS** : (EI) Calcd for $\text{C}_{36}\text{H}_{46}\text{O}_5\text{Si}$ = 586.3114; found = 586.3105 $\pm$ 0.0017; **$[\alpha]_D^{25}$** : -105 (c =1.00, CHCl_3).

[4S-(4 β ,5 β ,9 α ,10 β ,13 β ,17 β)]-4-(tert-Butyl-diphenyl-silanyloxy)-13-methyl-17-(4-nitro-benzoyloxy)-1-oxo-1,2,3,4,5,6,7,9,11,12,13,15,16,17-tetradecahydro-cyclopenta[a]phenanthrene-10-carboxylic acid methyl ester **28:** 4-nitrobenzoyl chloride (66 mg, 0.358 mmol, 10 equiv.) was added to a solution of **27** (21 mg, 0.036 mmol, 1 equiv.), pyridine (3 mL) and 4-dimethylaminopyridine (1 mg, 0.006 mmol, 0.2 equiv.) in dry CH_2Cl_2 (3 mL) at room temperature. The mixture was stirred at room temperature 4 h and then quenched by the addition of an 1 M aqueous solution of HCl. The mixture was extracted with CH_2Cl_2 (3 X 3 mL). The combined organic phases were dried with MgSO_4 , filtered, and concentrated. The residue was purified by flash chromatography (20/80 : EtOAc/Hex) to afford 25 mg of **28** (94 %, colorless oil). **IR** (neat, ν cm^{-1}) : 2930, 2855, 1723, 1529, 1275, 1104; **^1H NMR** (300 MHz, CDCl_3 , δ ppm) : 8.29 (2H, d, J =8.6 Hz, NO_2 -Ph (ortho)); 8.20 (2H, d, J =8.6 Hz, NO_2 -Ph (meta)); 7.74-7.68 (4H, m, Si-(Ph) $_2$ (meta)); 7.51-7.37 (6H, Si-(Ph) $_2$ (para, ortho)); 4.83 (1H, dd, J =6.7, 10.0 Hz, $\underline{\text{CH}}$ -OCOPh); 4.24 (1H, td, J =8.9, 3.7 Hz, $\underline{\text{CH}}$ -OTBDPS); 3.72 (3H, s, CO_2 - $\underline{\text{CH}}_3$); 2.76-2.70 (1H, m); 2.52-2.39 (3H, m); 2.30-1.60 (10H, m); 1.34-1.15 (4H, m);

1.23 (3H, s, C-CH₃); 1.08 (9H, s, Si-C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃, δ ppm) : 207.5; 171.0; 164.5; 150.5; 136.1; 135.9; 134.1; 133.3; 130.7; 127.6; 126.6; 123.5; 84.3; 68.4; 65.5; 51.9; 48.2; 43.0; 38.4; 36.5; 34.7; 32.9; 27.0; 26.4; 24.5; 23.8; 23.2; 21.0; 19.4; 17.8; **MS** : (EI) 735 M⁺, 678 (M-C₄H₉)⁺; **HRMS** : (EI) Calcd for C₄₃H₄₉O₈NSi = 735.3227; found = 735.3218 ± 0.0022; [α]_D²⁵ : -50.9 (c=1.00, CHCl₃).

[4S-(4β,5β,9α,10β,13β,17β)]-4-Hydroxy-13-methyl-17-(4-nitro-benzoyloxy)-1-oxo-1,2,3,4,5,6,7,9,11,12,13,15,16,17-tetradecahydro-cyclopenta[a]phenanthrene-10-carboxylic acid methyl ester 29: Pyridine hydrofluoride (0.2 ml, excess) was added to a solution of **28** (25 mg, 0.034 mmol, 1 equiv.) in THF (3 ml). The mixture was heated at 90°C for 8 h in a sealed polypropylene bottle. The mixture was added to a saturated aqueous solution of NaHCO₃. The mixture was extracted with EtOAc (3 X 3 ml). The combined organic phases were dried with MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography (60/40 : EtOAc/Hex) to afford 11 mg of **29** (65 %, colorless oil). **IR** (neat, ν cm⁻¹) : 3502, 2928, 1742, 1722, 1528, 1276; ¹H NMR (300 MHz, CDCl₃, δ ppm) : 8.31-8.19 (4H, m, NO₂-Ph); 4.85 (1H, dd, J=7.0, 10.7 Hz, CH-OCOPh); 4.32 (1H, td, J=9.3, 3.8 Hz, CH-OH); 3.72 (3H, s, CO₂-CH₃); 2.75-1.60 (14H, m); 1.26 (3H, s, C-CH₃); ¹³C NMR (75 MHz, CDCl₃, δ ppm) : 207.1; 171.0; 164.5; 150.5; 136.7; 135.9; 130.7; 126.4; 123.5; 84.3; 66.1; 65.6; 52.0; 47.7; 43.1; 38.3; 36.7; 34.8; 33.0; 26.4; 24.3; 23.8; 22.9; 20.9; 17.8; **MS** : (EI) 497 M⁺; **HRMS** : (EI) Calcd for C₂₇H₃₁O₈N = 497.2049; found = 497.2033 ± 0.0015; [α]_D²⁵ : -23.7 (c=1.00, CHCl₃); **MP** : 203-208°C.

[5S-(5β,9α,10β,13β,17β)]-13-Methyl-17-(4-nitro-benzoyloxy)-1,4-dioxo-1,2,3,4,5,6,7,9,11,12,13,15,16,17-tetradecahydro-cyclopenta[a]phenanthrene-10-carboxylic acid methyl ester 30: Dess-Martin reagent (22 mg, 0.050 mmol, 5 equiv.) was added to a solution of alcohol **29** (5 mg, 0.010 mmol, 1 equiv.) in CH₂Cl₂ (2 mL) at 0°C. The mixture was stirred 1 h at room temperature and then concentrated. The residue was purified by flash chromatography (50/50 : EtOAc/Hex) to afford 4 mg of **30** (81 %, colorless oil). **IR** (neat, ν cm⁻¹) : 2926, 2854, 1751, 1720, 1528, 1276; ¹H NMR (300 MHz, CDCl₃, δ ppm) : 8.29 (2H, d, J=8.7 Hz, NO₂-Ph (ortho)); 8.20 (2H, d, J=8.7 Hz, NO₂-Ph (meta)); 4.82 (1H, dd, J=6.9, 10.4 Hz, CH-OCOPh); 3.74 (3H, s, CO₂-CH₃); 1.51-1.49 (1H, m); 2.97-2.55 (4H, m); 2.54-2.40 (1H, m); 2.37-1.78 (8H, m); 1.43-1.20 (5H, m); 1.29 (3H, s, C-CH₃); ¹³C NMR (75 MHz, CDCl₃, δ ppm) : 206.6; 204.7; 169.1;

164.4; 138.4; 137.3; 135.9; 130.7; 125.6; 123.5; 84.1; 65.4; 52.3; 50.9; 43.0; 40.4; 37.0; 36.8; 34.5; 26.3; 24.2; 23.9; 21.5; 21.0; 17.5; **MS** : (EI) 495 M⁺; **HRMS** : (EI) Calcd for C₂₇H₂₉O₈N = 495.1893; found = 495.1885 ± 0.0015; [α]_D²⁵ : +49.0 (c=1.00, CHCl₃); **MP** : 195-200°C.

3) X-Ray data

Figure S1. Ortep of compound 22

Figure S2. Ortep of the enantiomer of compound 30

Table S 1.1. Crystal data and structure refinement for compound **22**.

Identification code	PD021097	
Empirical formula	C ₂₀ H ₂₄ O ₅	
Formula weight	344.39	
Temperature	173(1) K	
Wavelength	0.71073 Å	
Diffractometer used	Bruker AXS P4/SMART 1000	
Detector distance	5 cm	
Monochromator used	Graphite	
Crystal size	0.2 x 0.4 x 0.6 mm ³	
Colour and habit	Colourless, irregular	
Crystal system	Monoclinic	
Space group	P2	
Unit cell dimensions	a = 7.0129(8) Å	$\alpha = 90^\circ$
	b = 16.4800(16) Å	$\beta = 99.319(2)^\circ$
	c = 7.4762(8) Å	$\gamma = 90^\circ$
Volume	852.64(16) Å ³	
Z	2	
Density (calculated)	1.341 Mg/m ³	
Absorption coefficient	0.096 mm ⁻¹	
F(000)	368	
Theta range for data collection	2.47 to 27.50°	
Completeness to theta = 27.50°	98.3 %	
Scan type	ω and ϕ	
Scan range	0.3°	
Exposure time	30s	
Index ranges	$-9 \leq h \leq 8, -21 \leq k \leq 21, -9 \leq l \leq 8$	
Standard reflections collection	50 frames at beginning and end of data collection	

Crystal stability	no decay
Reflections collected	6113
Independent reflections	3428 [R(int) = 0.0161]
System used	SHELXL 5.1
Solution	Direct methods
Hydrogen atoms	Found, refined isotropically
Absorption correction	SADABS
Min./Max. transmission ratio	0.927
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3428 / 1 / 323
Goodness-of-fit on F ²	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0794
R indices (all data)	R1 = 0.0301, wR2 = 0.0796
Largest/mean shift/esd	0.001/0.000
Absolute structure parameter	0.1(6)
Largest diff. peak and hole	0.261 and -0.145 e.Å ⁻³

$$wR2 = (\sum[w(F_o^2 - F_c^2)^2] / \sum[F_o^4])^{1/2}$$

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$\text{Weight} = 1 / [\sigma^2(F_o^2) + (0.0583 * P)^2 + (0.0475 * P)]$$

$$\text{where } P = (\max(F_o^2, 0) + 2 * F_c^2) / 3$$

Table S 1.2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for compound **22**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7458(2)	8262(1)	1899(1)	25(1)
C(2)	5776(2)	7728(1)	1151(2)	29(1)

C(3)	4133(2)	8274(1)	232(2)	31(1)
C(4)	3534(2)	8831(1)	1658(2)	31(1)
C(5)	5168(2)	9381(1)	2547(2)	26(1)
C(6)	5582(2)	10082(1)	1331(2)	31(1)
C(7)	6738(2)	10714(1)	2489(2)	30(1)
C(8)	8188(2)	10369(1)	3959(2)	25(1)
C(9)	8834(2)	9518(1)	3594(2)	23(1)
C(10)	7068(2)	8917(1)	3269(1)	22(1)
C(11)	10557(2)	9234(1)	4991(2)	28(1)
C(12)	10498(2)	9531(1)	6909(2)	29(1)
C(13)	10411(2)	10454(1)	6919(2)	26(1)
C(14)	8862(2)	10782(1)	5460(2)	27(1)
C(15)	8181(2)	11587(1)	6087(2)	33(1)
C(16)	8459(2)	11503(1)	8160(2)	36(1)
C(17)	9865(2)	10811(1)	8644(2)	31(1)
O(18)	8991(1)	8213(1)	1387(1)	36(1)
O(19)	6459(2)	11434(1)	2257(2)	43(1)
C(20)	6812(2)	8503(1)	5044(2)	27(1)
O(21)	5889(2)	8770(1)	6116(1)	40(1)
O(22)	7819(2)	7812(1)	5278(1)	34(1)
C(23)	7830(3)	7403(1)	6993(2)	46(1)
C(24)	12368(2)	10837(1)	6694(2)	36(1)
O(25)	10465(2)	10580(1)	10153(1)	47(1)

Table S 1.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for compound **22**.

C(1)-O(18)	1.2010(15)
C(1)-C(2)	1.5048(15)
C(1)-C(10)	1.5426(15)
C(2)-C(3)	1.5335(17)
C(2)-H(2A)	0.967(19)

C(2)-H(2B)	0.972(19)
C(3)-C(4)	1.5166(19)
C(3)-H(3A)	0.981(18)
C(3)-H(3B)	1.007(18)
C(4)-C(5)	1.5273(16)
C(4)-H(4A)	0.954(18)
C(4)-H(4B)	0.998(18)
C(5)-C(6)	1.5263(17)
C(5)-C(10)	1.5551(14)
C(5)-H(5)	0.957(16)
C(6)-C(7)	1.5045(17)
C(6)-H(6A)	0.932(19)
C(6)-H(6B)	1.01(2)
C(7)-O(19)	1.2103(16)
C(7)-C(8)	1.4838(15)
C(8)-C(14)	1.3325(16)
C(8)-C(9)	1.5121(15)
C(9)-C(11)	1.5368(15)
C(9)-C(10)	1.5737(15)
C(9)-H(9)	0.963(15)
C(10)-C(20)	1.5279(15)
C(11)-C(12)	1.5219(17)
C(11)-H(11A)	0.94(2)
C(11)-H(11B)	0.963(18)
C(12)-C(13)	1.5226(15)
C(12)-H(12A)	0.950(18)
C(12)-H(12B)	0.953(19)
C(13)-C(14)	1.5095(15)
C(13)-C(17)	1.5217(16)
C(13)-C(24)	1.5441(17)
C(14)-C(15)	1.5091(16)

C(15)-C(16)	1.5369(19)
C(15)-H(15A)	1.03(2)
C(15)-H(15B)	0.986(16)
C(16)-C(17)	1.5116(18)
C(16)-H(16A)	0.93(3)
C(16)-H(16B)	0.96(2)
C(17)-O(25)	1.2009(17)
C(20)-O(21)	1.1927(16)
C(20)-O(22)	1.3373(15)
O(22)-C(23)	1.4472(15)
C(23)-H(23A)	0.95(2)
C(23)-H(23B)	0.91(3)
C(23)-H(23C)	1.00(3)
C(24)-H(24A)	0.94(2)
C(24)-H(24B)	0.97(2)
C(24)-H(24C)	1.01(2)
O(18)-C(1)-C(2)	122.01(11)
O(18)-C(1)-C(10)	121.56(10)
C(2)-C(1)-C(10)	116.32(9)
C(1)-C(2)-C(3)	108.07(10)
C(1)-C(2)-H(2A)	108.4(10)
C(3)-C(2)-H(2A)	108.6(10)
C(1)-C(2)-H(2B)	110.2(11)
C(3)-C(2)-H(2B)	111.8(11)
H(2A)-C(2)-H(2B)	109.6(15)
C(4)-C(3)-C(2)	108.28(10)
C(4)-C(3)-H(3A)	110.3(10)
C(2)-C(3)-H(3A)	107.1(11)
C(4)-C(3)-H(3B)	112.0(10)
C(2)-C(3)-H(3B)	108.4(10)
H(3A)-C(3)-H(3B)	110.7(14)

C(3)-C(4)-C(5)	113.05(10)
C(3)-C(4)-H(4A)	106.6(10)
C(5)-C(4)-H(4A)	108.8(10)
C(3)-C(4)-H(4B)	110.7(10)
C(5)-C(4)-H(4B)	109.1(10)
H(4A)-C(4)-H(4B)	108.4(14)
C(6)-C(5)-C(4)	113.08(10)
C(6)-C(5)-C(10)	110.13(9)
C(4)-C(5)-C(10)	113.53(10)
C(6)-C(5)-H(5)	103.1(9)
C(4)-C(5)-H(5)	109.3(9)
C(10)-C(5)-H(5)	106.9(9)
C(7)-C(6)-C(5)	108.52(10)
C(7)-C(6)-H(6A)	108.0(12)
C(5)-C(6)-H(6A)	110.3(11)
C(7)-C(6)-H(6B)	107.2(11)
C(5)-C(6)-H(6B)	110.2(11)
H(6A)-C(6)-H(6B)	112.5(15)
O(19)-C(7)-C(8)	123.85(12)
O(19)-C(7)-C(6)	122.44(11)
C(8)-C(7)-C(6)	113.68(10)
C(14)-C(8)-C(7)	122.34(11)
C(14)-C(8)-C(9)	123.38(10)
C(7)-C(8)-C(9)	114.28(10)
C(8)-C(9)-C(11)	112.66(9)
C(8)-C(9)-C(10)	111.11(9)
C(11)-C(9)-C(10)	115.22(9)
C(8)-C(9)-H(9)	105.8(9)
C(11)-C(9)-H(9)	107.9(9)
C(10)-C(9)-H(9)	103.2(9)
C(20)-C(10)-C(1)	108.85(9)

C(20)-C(10)-C(5)	107.86(9)
C(1)-C(10)-C(5)	110.33(9)
C(20)-C(10)-C(9)	110.31(8)
C(1)-C(10)-C(9)	108.84(9)
C(5)-C(10)-C(9)	110.63(9)
C(12)-C(11)-C(9)	113.82(10)
C(12)-C(11)-H(11A)	110.1(11)
C(9)-C(11)-H(11A)	108.9(11)
C(12)-C(11)-H(11B)	107.2(10)
C(9)-C(11)-H(11B)	106.7(10)
H(11A)-C(11)-H(11B)	110.1(16)
C(11)-C(12)-C(13)	109.48(10)
C(11)-C(12)-H(12A)	112.2(10)
C(13)-C(12)-H(12A)	108.9(11)
C(11)-C(12)-H(12B)	112.2(11)
C(13)-C(12)-H(12B)	108.2(12)
H(12A)-C(12)-H(12B)	105.7(14)
C(14)-C(13)-C(17)	102.92(9)
C(14)-C(13)-C(12)	112.25(9)
C(17)-C(13)-C(12)	113.98(10)
C(14)-C(13)-C(24)	108.86(10)
C(17)-C(13)-C(24)	106.51(10)
C(12)-C(13)-C(24)	111.77(11)
C(8)-C(14)-C(15)	128.57(11)
C(8)-C(14)-C(13)	122.79(10)
C(15)-C(14)-C(13)	108.48(10)
C(14)-C(15)-C(16)	103.83(10)
C(14)-C(15)-H(15A)	107.0(11)
C(16)-C(15)-H(15A)	109.4(11)
C(14)-C(15)-H(15B)	111.1(9)
C(16)-C(15)-H(15B)	112.0(9)

H(15A)-C(15)-H(15B)	112.9(14)
C(17)-C(16)-C(15)	106.30(10)
C(17)-C(16)-H(16A)	106.0(16)
C(15)-C(16)-H(16A)	112.6(16)
C(17)-C(16)-H(16B)	107.8(13)
C(15)-C(16)-H(16B)	110.9(12)
H(16A)-C(16)-H(16B)	113(2)
O(25)-C(17)-C(16)	125.45(12)
O(25)-C(17)-C(13)	125.13(12)
C(16)-C(17)-C(13)	109.42(10)
O(21)-C(20)-O(22)	124.02(11)
O(21)-C(20)-C(10)	124.86(11)
O(22)-C(20)-C(10)	111.09(9)
C(20)-O(22)-C(23)	116.02(11)
O(22)-C(23)-H(23A)	107.5(13)
O(22)-C(23)-H(23B)	105.9(15)
H(23A)-C(23)-H(23B)	109(2)
O(22)-C(23)-H(23C)	107.5(16)
H(23A)-C(23)-H(23C)	110(2)
H(23B)-C(23)-H(23C)	117(2)
C(13)-C(24)-H(24A)	109.7(12)
C(13)-C(24)-H(24B)	111.5(12)
H(24A)-C(24)-H(24B)	111.5(17)
C(13)-C(24)-H(24C)	110.3(12)
H(24A)-C(24)-H(24C)	110.2(17)
H(24B)-C(24)-H(24C)	103.5(17)

Symmetry transformations used to generate equivalent atoms:

Table S 1.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for OLE-1048. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	27(1)	26(1)	21(1)	1(1)	4(1)	2(1)
C(2)	32(1)	28(1)	26(1)	-3(1)	5(1)	-3(1)
C(3)	28(1)	36(1)	28(1)	0(1)	1(1)	-4(1)
C(4)	22(1)	39(1)	33(1)	-2(1)	4(1)	-2(1)
C(5)	22(1)	30(1)	26(1)	-1(1)	4(1)	2(1)
C(6)	30(1)	33(1)	28(1)	3(1)	-2(1)	3(1)
C(7)	32(1)	29(1)	28(1)	4(1)	3(1)	3(1)
C(8)	26(1)	23(1)	27(1)	2(1)	4(1)	1(1)
C(9)	21(1)	24(1)	25(1)	0(1)	4(1)	1(1)
C(10)	22(1)	24(1)	21(1)	1(1)	4(1)	1(1)
C(11)	23(1)	27(1)	33(1)	-3(1)	1(1)	4(1)
C(12)	29(1)	26(1)	29(1)	1(1)	-1(1)	3(1)
C(13)	27(1)	25(1)	27(1)	-1(1)	3(1)	-1(1)
C(14)	27(1)	22(1)	30(1)	2(1)	5(1)	0(1)
C(15)	41(1)	23(1)	35(1)	-2(1)	4(1)	3(1)
C(16)	44(1)	30(1)	35(1)	-4(1)	9(1)	5(1)
C(17)	35(1)	29(1)	30(1)	-3(1)	5(1)	-1(1)
O(18)	29(1)	41(1)	39(1)	-12(1)	10(1)	1(1)
O(19)	53(1)	29(1)	42(1)	7(1)	-3(1)	6(1)
C(20)	28(1)	30(1)	22(1)	-1(1)	5(1)	-4(1)
O(21)	46(1)	48(1)	30(1)	1(1)	19(1)	3(1)
O(22)	49(1)	30(1)	23(1)	4(1)	6(1)	3(1)
C(23)	72(1)	39(1)	26(1)	9(1)	6(1)	-3(1)
C(24)	31(1)	39(1)	35(1)	-1(1)	2(1)	-7(1)
O(25)	62(1)	51(1)	28(1)	1(1)	4(1)	14(1)

Table S 1.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **22**.

	x	y	z	U(eq)
H(2A)	5340(20)	7448(11)	2150(30)	36(4)
H(2B)	6160(30)	7334(11)	310(30)	34(4)
H(3A)	3060(20)	7916(11)	-270(20)	38(4)
H(3B)	4610(20)	8586(11)	-760(20)	33(4)
H(4A)	3140(20)	8489(11)	2560(20)	33(4)
H(4B)	2410(30)	9172(11)	1130(20)	33(4)
H(5)	4780(20)	9651(9)	3560(20)	22(3)
H(6A)	4430(30)	10320(12)	780(20)	38(4)
H(6B)	6400(30)	9887(12)	420(30)	41(5)
H(9)	9250(20)	9539(9)	2430(20)	21(3)
H(11A)	10610(20)	8662(13)	4970(20)	37(4)
H(11B)	11700(30)	9459(12)	4620(20)	36(4)
H(12A)	9420(30)	9323(11)	7380(20)	31(4)
H(12B)	11610(30)	9366(12)	7740(20)	41(5)
H(15A)	9100(30)	12023(13)	5740(30)	47(5)
H(15B)	6820(20)	11689(9)	5560(20)	25(4)
H(16A)	7330(40)	11351(16)	8570(30)	69(7)
H(16B)	9030(30)	11985(13)	8740(30)	48(5)
H(23A)	8300(30)	7778(14)	7930(30)	50(5)
H(23B)	8690(40)	6985(17)	7010(30)	61(6)
H(23C)	6470(40)	7254(18)	7070(40)	79(8)
H(24A)	13320(30)	10685(13)	7670(30)	50(5)
H(24B)	12740(30)	10693(13)	5550(30)	50(5)
H(24C)	12250(30)	11450(14)	6630(30)	47(5)

Table S 2.1. Crystal data and structure refinement for compound **30**

Identification code	PD020769	
Empirical formula	C ₂₇ H ₂₉ N O ₈	
Formula weight	495.51	
Temperature	198(2) K	
Wavelength	0.71073 Å	
Diffractometer used	Bruker AXS P4/SMART 1000	
Detector distance	6 cm	
Monochromator used	Graphite	
Crystal size	0.125 x 0.35 x 0.525 mm ³	
Colour and habit	Colourless, plate	
Crystal system	Tetragonal	
Space group	P4(3)2(1)2	
Unit cell dimensions	a = 8.1945(5) Å	α = 90°
	b = 8.1945(5) Å	β = 90°
	c = 72.014(7) Å	γ = 90°
Volume	4835.7(6) Å ³	
Z	8	
Density (calculated)	1.361 Mg/m ³	
Absorption coefficient	0.101 mm ⁻¹	
F(000)	2096	
Theta range for data collection	2.26 to 25.00°	
Completeness to theta = 25.00°	99.9 %	
Scan type	ω and φ	
Scan range	0.3°	
Exposure time	30s	

Index ranges	-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -85 ≤ l ≤ 81
Standard reflections collection	50 frames at beginning and end of data
Crystal stability	no decay
Reflections collected	24753
Independent reflections	4207 [R(int) = 0.0391]
System used	SHELXL 5.1
Solution	Direct methods
Hydrogen atoms	Found, refined isotropically
Absorption correction	SADABS
Min./Max. transmission ratio	0.663
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4207 / 0 / 442
Goodness-of-fit on F ²	1.191
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1082
R indices (all data)	R1 = 0.0524, wR2 = 0.1092
Largest/mean shift/esd	0.000/0.000
Absolute structure parameter	0.7(16)
Largest diff. peak and hole	0.159 and -0.146 e.Å ⁻³

$$wR2 = (\sum[w(F_o^2 - F_c^2)^2] / \sum[F_o^4])^{1/2}$$

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$\text{Weight} = 1 / [\sigma^2(F_o^2) + (0.0232 * P)^2 + (3.07 * P)]$$

$$\text{where } P = (\max(F_o^2, 0) + 2 * F_c^2) / 3$$

Table S 2.2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for compound **30**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
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C(1)	9365(4)	6314(3)	1015(1)	41(1)
C(2)	9717(5)	4880(4)	1139(1)	55(1)
C(3)	8402(5)	4560(4)	1281(1)	61(1)
C(4)	6691(4)	4696(3)	1208(1)	46(1)
C(5)	6335(4)	6185(3)	1089(1)	39(1)
C(6)	4641(4)	6203(4)	1008(1)	46(1)
C(7)	4383(4)	4919(4)	857(1)	49(1)
C(8)	5737(4)	4867(3)	715(1)	38(1)
C(9)	7439(4)	4983(3)	791(1)	36(1)
C(10)	7630(4)	6396(3)	935(1)	35(1)
C(11)	8800(4)	4917(4)	646(1)	44(1)
C(12)	8363(4)	3761(4)	490(1)	50(1)
C(13)	6803(4)	4317(4)	395(1)	48(1)
C(14)	5456(4)	4560(3)	538(1)	44(1)
C(15)	3833(5)	4181(5)	449(1)	61(1)
C(16)	4229(6)	3456(6)	258(1)	74(1)
C(17)	6013(6)	3016(4)	273(1)	62(1)
O(18)	10391(3)	7308(3)	975(1)	55(1)
O(19)	5629(3)	3736(3)	1249(1)	64(1)
C(20)	7453(3)	8085(3)	847(1)	35(1)
O(21)	7390(3)	8390(2)	685(1)	45(1)
O(22)	7361(3)	9195(2)	982(1)	44(1)
C(23)	7361(5)	10874(3)	925(1)	48(1)
C(24)	7073(5)	5876(4)	282(1)	51(1)
O(25)	6803(4)	2979(3)	91(1)	73(1)
C(26)	7263(4)	1569(4)	21(1)	50(1)
O(27)	6998(3)	279(3)	89(1)	72(1)
C(28)	8135(4)	1796(4)	-162(1)	45(1)
C(29)	8653(4)	429(4)	-254(1)	52(1)
C(30)	9408(4)	593(4)	-426(1)	54(1)

C(31)	9589(4)	2126(4)	-501(1)	46(1)
C(32)	9089(5)	3498(4)	-409(1)	57(1)
C(33)	8385(5)	3330(4)	-236(1)	56(1)
N(32)	10382(4)	2298(4)	-681(1)	58(1)
O(33)	11143(4)	1152(3)	-743(1)	80(1)
O(34)	10261(4)	3606(4)	-760(1)	89(1)

Table S 2.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for compound **30**.

C(1)-O(18)	1.206(4)
C(1)-C(2)	1.502(4)
C(1)-C(10)	1.537(4)
C(2)-C(3)	1.508(5)
C(3)-C(4)	1.501(5)
C(4)-O(19)	1.210(4)
C(4)-C(5)	1.518(4)
C(5)-C(6)	1.505(4)
C(5)-C(10)	1.548(4)
C(6)-C(7)	1.532(4)
C(7)-C(8)	1.508(4)
C(8)-C(14)	1.320(4)
C(8)-C(9)	1.502(4)
C(9)-C(11)	1.531(4)
C(9)-C(10)	1.559(3)
C(10)-C(20)	1.527(3)
C(11)-C(12)	1.514(4)
C(12)-C(13)	1.517(5)
C(13)-C(14)	1.520(4)
C(13)-C(17)	1.529(4)
C(13)-C(24)	1.534(4)
C(14)-C(15)	1.507(5)

C(15)-C(16)	1.536(5)
C(16)-C(17)	1.509(6)
C(17)-O(25)	1.457(4)
C(20)-O(21)	1.194(3)
C(20)-O(22)	1.332(3)
O(22)-C(23)	1.436(3)
O(25)-C(26)	1.317(4)
C(26)-O(27)	1.185(4)
C(26)-C(28)	1.510(4)
C(28)-C(29)	1.369(4)
C(28)-C(33)	1.380(4)
C(29)-C(30)	1.392(5)
C(30)-C(31)	1.374(4)
C(31)-C(32)	1.367(4)
C(31)-N(32)	1.461(4)
C(32)-C(33)	1.382(5)
N(32)-O(33)	1.212(4)
N(32)-O(34)	1.215(4)
O(18)-C(1)-C(2)	122.4(3)
O(18)-C(1)-C(10)	121.7(2)
C(2)-C(1)-C(10)	115.8(3)
C(1)-C(2)-C(3)	113.6(3)
C(4)-C(3)-C(2)	114.7(3)
O(19)-C(4)-C(3)	122.5(3)
O(19)-C(4)-C(5)	121.6(3)
C(3)-C(4)-C(5)	115.8(3)
C(6)-C(5)-C(4)	113.8(3)
C(6)-C(5)-C(10)	110.7(2)
C(4)-C(5)-C(10)	111.3(2)
C(5)-C(6)-C(7)	113.4(3)
C(8)-C(7)-C(6)	113.6(3)

C(14)-C(8)-C(9)	121.9(3)
C(14)-C(8)-C(7)	122.0(3)
C(9)-C(8)-C(7)	115.7(2)
C(8)-C(9)-C(11)	115.1(2)
C(8)-C(9)-C(10)	112.5(2)
C(11)-C(9)-C(10)	113.9(2)
C(20)-C(10)-C(1)	106.5(2)
C(20)-C(10)-C(5)	109.4(2)
C(1)-C(10)-C(5)	111.0(2)
C(20)-C(10)-C(9)	113.0(2)
C(1)-C(10)-C(9)	108.1(2)
C(5)-C(10)-C(9)	108.9(2)
C(12)-C(11)-C(9)	111.0(3)
C(11)-C(12)-C(13)	110.2(3)
C(12)-C(13)-C(14)	110.4(2)
C(12)-C(13)-C(17)	114.0(3)
C(14)-C(13)-C(17)	100.0(3)
C(12)-C(13)-C(24)	111.6(3)
C(14)-C(13)-C(24)	110.9(3)
C(17)-C(13)-C(24)	109.4(2)
C(8)-C(14)-C(15)	127.0(3)
C(8)-C(14)-C(13)	123.4(3)
C(15)-C(14)-C(13)	109.2(2)
C(14)-C(15)-C(16)	105.8(3)
C(17)-C(16)-C(15)	103.5(3)
O(25)-C(17)-C(16)	111.9(3)
O(25)-C(17)-C(13)	110.1(3)
C(16)-C(17)-C(13)	106.5(3)
O(21)-C(20)-O(22)	124.5(2)
O(21)-C(20)-C(10)	126.6(2)
O(22)-C(20)-C(10)	108.9(2)

C(20)-O(22)-C(23)	116.4(2)
C(26)-O(25)-C(17)	119.3(3)
O(27)-C(26)-O(25)	124.8(3)
O(27)-C(26)-C(28)	123.9(3)
O(25)-C(26)-C(28)	111.2(3)
C(29)-C(28)-C(33)	120.8(3)
C(29)-C(28)-C(26)	117.9(3)
C(33)-C(28)-C(26)	121.3(3)
C(28)-C(29)-C(30)	119.4(3)
C(31)-C(30)-C(29)	119.0(3)
C(32)-C(31)-C(30)	122.0(3)
C(32)-C(31)-N(32)	119.0(3)
C(30)-C(31)-N(32)	119.0(3)
C(31)-C(32)-C(33)	118.7(3)
O(33)-N(32)-O(34)	123.7(3)
O(33)-N(32)-C(31)	118.7(3)
O(34)-N(32)-C(31)	117.5(3)
C(28)-C(33)-C(32)	120.1(3)

Symmetry transformations used to generate equivalent atoms:

Table S 2.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **30**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	61(2)	30(1)	32(1)	-6(1)	-4(1)	3(1)
C(2)	73(2)	35(2)	58(2)	2(2)	-23(2)	-3(2)
C(3)	103(3)	40(2)	39(2)	9(2)	-14(2)	-2(2)
C(4)	84(2)	25(1)	29(1)	-6(1)	7(1)	-5(2)

C(5)	64(2)	25(1)	29(1)	-2(1)	8(1)	-1(1)
C(6)	61(2)	36(2)	42(2)	3(1)	17(2)	-1(1)
C(7)	55(2)	47(2)	44(2)	-3(1)	10(2)	-10(2)
C(8)	55(2)	27(1)	31(1)	2(1)	4(1)	-2(1)
C(9)	54(2)	27(1)	29(1)	-2(1)	3(1)	6(1)
C(10)	54(2)	23(1)	28(1)	0(1)	2(1)	2(1)
C(11)	52(2)	39(2)	41(2)	-4(1)	3(1)	9(1)
C(12)	74(2)	38(2)	37(1)	-3(1)	12(2)	9(2)
C(13)	73(2)	38(2)	34(1)	-2(1)	7(1)	-6(2)
C(14)	60(2)	34(2)	37(1)	2(1)	3(1)	-7(1)
C(15)	74(3)	71(3)	37(2)	4(2)	-6(2)	-21(2)
C(16)	101(3)	79(3)	41(2)	-3(2)	-13(2)	-28(3)
C(17)	111(3)	47(2)	29(1)	-2(1)	4(2)	-14(2)
O(18)	62(1)	42(1)	62(1)	3(1)	-6(1)	-7(1)
O(19)	106(2)	37(1)	48(1)	6(1)	14(1)	-17(1)
C(20)	42(2)	27(1)	36(1)	1(1)	6(1)	3(1)
O(21)	68(1)	34(1)	32(1)	6(1)	7(1)	6(1)
O(22)	73(1)	22(1)	36(1)	0(1)	12(1)	0(1)
C(23)	66(2)	21(1)	56(2)	3(1)	11(2)	2(1)
C(24)	73(2)	45(2)	36(2)	-1(1)	9(2)	3(2)
O(25)	136(2)	46(1)	37(1)	-8(1)	16(1)	-9(1)
C(26)	53(2)	47(2)	49(2)	-7(2)	-9(2)	-2(2)
O(27)	87(2)	49(1)	81(2)	3(1)	23(1)	-3(1)
C(28)	49(2)	45(2)	40(1)	-7(1)	-12(1)	-1(1)
C(29)	53(2)	40(2)	64(2)	-3(2)	0(2)	-2(2)
C(30)	56(2)	47(2)	60(2)	-13(2)	2(2)	3(2)
C(31)	49(2)	55(2)	36(1)	-7(1)	-5(1)	1(1)
C(32)	78(2)	45(2)	48(2)	0(2)	0(2)	3(2)
N(32)	62(2)	63(2)	49(2)	-7(2)	-3(1)	1(2)
C(33)	85(3)	45(2)	39(2)	-10(1)	-2(2)	4(2)
O(33)	85(2)	75(2)	79(2)	-17(1)	27(2)	8(2)

O(34) 127(3) 81(2) 57(2) 11(2) 18(2) 21(2)

Table S 2.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **30**.

	x	y	z	U(eq)
H(2A)	10760(40)	5120(30)	1195(4)	39(8)
H(2B)	9810(30)	3920(40)	1060(3)	35(7)
H(3A)	8510(40)	3530(50)	1342(5)	69(11)
H(3B)	8410(40)	5330(50)	1382(5)	68(11)
H(5)	6440(30)	7140(40)	1172(4)	43(8)
H(6A)	4440(40)	7280(40)	944(4)	51(8)
H(6B)	3840(30)	6030(30)	1110(4)	38(7)
H(7A)	3350(40)	5010(40)	803(4)	58(10)
H(7B)	4260(40)	3800(40)	917(4)	51(8)
H(9)	7520(30)	4010(40)	871(4)	41(7)
H(12A)	9240(40)	3810(40)	384(4)	42(8)
H(12B)	8200(40)	2610(40)	544(4)	65(10)
H(14A)	9850(50)	4610(40)	706(5)	68(11)
H(14B)	8950(40)	5940(40)	592(4)	43(8)
H(15A)	3040(50)	5050(50)	444(5)	80(13)
H(15B)	3270(40)	3300(40)	526(4)	49(8)
H(16A)	4140(40)	4360(50)	166(5)	71(11)
H(16B)	3530(50)	2620(50)	207(5)	93(13)
H(17)	6180(40)	2000(40)	335(4)	60(10)
H(23A)	8430(50)	11110(40)	884(5)	66(11)
H(23B)	6560(40)	11050(40)	831(5)	70(12)
H(23C)	7120(40)	11490(40)	1035(4)	59(10)
H(24A)	6140(40)	6190(40)	201(4)	57(9)

H(24B)	8060(40)	5750(40)	200(4)	48(8)
H(24C)	7280(40)	6800(40)	366(4)	56(9)
H(29)	8510(40)	-610(40)	-200(4)	47(8)
H(30)	9820(40)	-260(40)	-492(4)	50(9)
H(32)	9280(40)	4590(40)	-468(4)	61(10)
H(33)	8120(40)	4240(40)	-158(5)	69(11)

4) ^1H NMR spectra