Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information-I

Direct Organocatalytic Stereoselective Transfer Hydrogenation of Conjugated Olefins of Steroids

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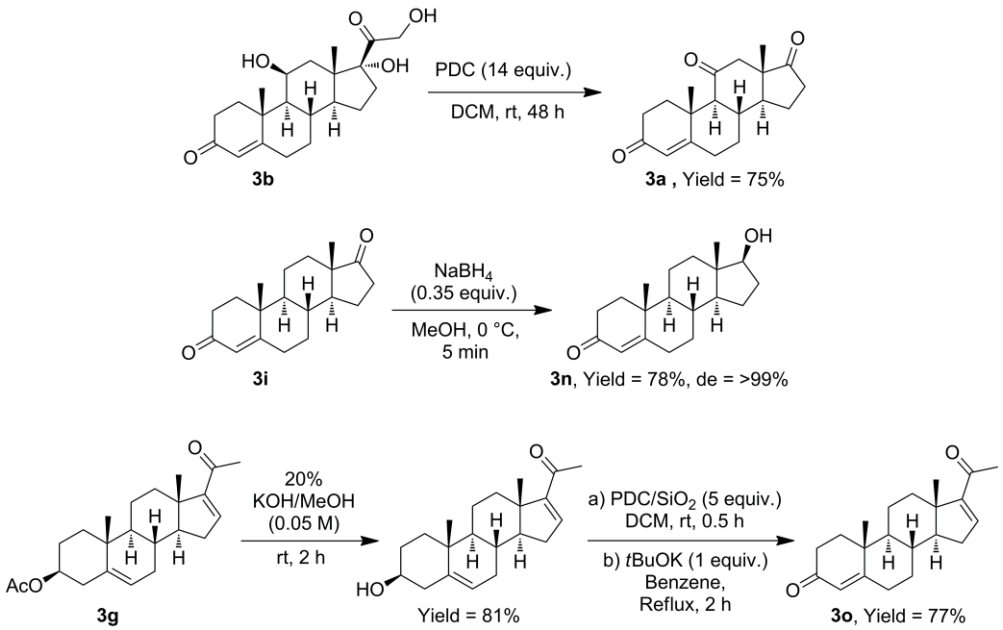
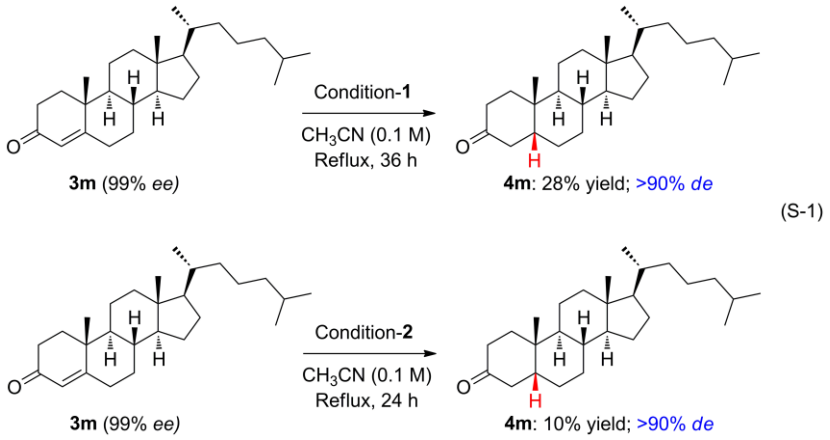
General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra (HRMS) were recorded on ESI-TOF maXis. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα (λ = 0.71073 Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received. All steroid starting materials were used as received generous gift from Dr. C. S. Venkatesan, Gland Pharma Limited, Hyderabad, India. Starting materials **3a**,[1] **3n** (Procedure **H**, See SI), and **3o** (Procedure **I**, See SI) were prepared following the literature or modified procedures (see Scheme S1).



Scheme S1: Synthesis of steroid starting materials **3a**, **3n** and **3o**.



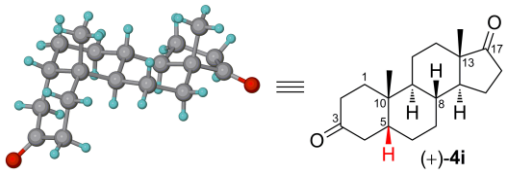


Figure S1: X-ray crystal structure of (+)-5β-androstane-3,17-dione (**4i**).

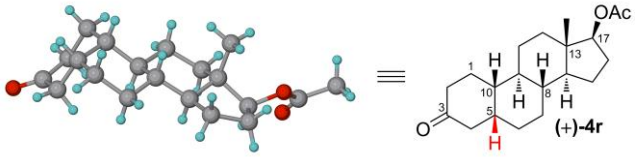


Figure S2: X-ray crystal structure of (+)-17β-acetoxy-5β-estran-3-one (**4r**).

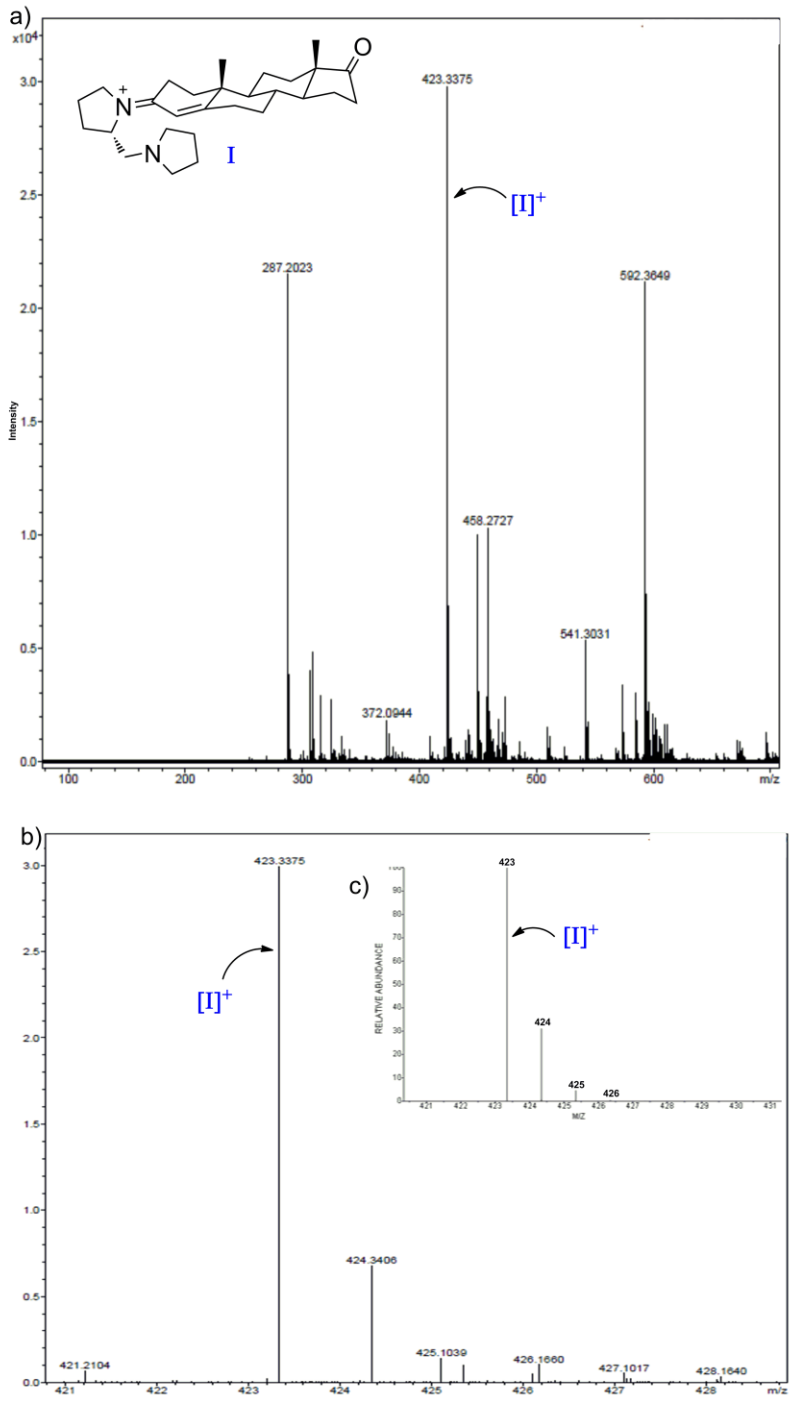


Figure S3: [a] ESI-HRMS (positive mode) spectrum of the reaction after 5 min of **3i** and **1b** in CD_3CN at rt. [b] The observed ESI-HRMS isotopic pattern of *pre*-transition state intermediate $[\mathbf{I}]^+$. [c] The simulated ESI-HRMS isotopic pattern of *pre*-transition state intermediate $[\mathbf{I}]^+$.

General Experimental Procedures:

Procedure A: ***General procedure for organocatalytic hydrogenation***: (*S*)-(+)-1-(2-Pyrrolidinylmethyl)pyrrolidine **1b** (12 mg, 0.075 mmol) and D-camphor sulphonic acid (17 mg, 0.075 mmol) in dry CH_3CN (3.0 mL, 0.1 M) were stirred at rt for 5 min, then added chiral enone **3** (0.3 mmol) and stirring was continued at the same temperature for another 5 min. To this, added Hantzsch ester **2a** (152 mg, 0.6 mmol) and refluxed for the time indicated in Tables 1-4. The crude reaction mixture was purified with or without aqueous work-up. Pure hydrogenated products **4** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure B: ***General procedure for palladium/charcoal catalyzed hydrogenation***: The mixture of 5% Pd/C (5 mol-%), Hantzsch ester **2a** (152 mg, 0.9 mmol) and the enone **3** (0.3 mmol) in EtOH (3.0 mL, 0.1 M) was heated to 80 °C for the time indicated in Table 3. Crude mixture was then passed through a pad of celite. Pure hydrogenated products **4** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure C: ***General procedure for acyclic amine salt catalyzed hydrogenation***: The mixture of acyclic amine salt **1c** (13 mg, 0.04 mmol), Hantzsch ester **2a** (101 mg, 0.4 mmol) and the enone **3** (0.2 mmol) in CH_3CN (0.1 M) was heated to 80 °C for 6-24 h. Then the crude reaction mixture was worked up with NH_4Cl solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure hydrogenated products **4** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure D: ***General procedure for reduction of hydrogenated product*.** To the pure hydrogenated product **4m** (38 mg, 0.1 mmol) in ethanol (0.04 M), was added sodium borohydride (6 mg, 0.15 mmol) at 0 °C under nitrogen atmosphere and the reaction mixture was stirred at same temperature for 5 min. Then the crude reaction mixture was worked up with 1N HCl solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure alcohol (+)-**5m** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure E: ***General procedure for oxidation of hydrogenated products***. To the pure hydrogenated product **4b** or **4c** (0.1 mmol) in DCM (0.05 M) was added pyridinium dichromate (526 mg, 1.4 mmol) under nitrogen atmosphere and the reaction mixture was stirred at rt for 48 h. Then the crude reaction mixture was worked up with 1N HCl solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. The crude

mixture was purified by column chromatography (silica gel, mixture of hexane/ethyl acetate) to obtain the oxidized product *cis*-(+)-**4a** or (+)-**4t** respectively as solids.

Procedure F: ***General procedure for deacetylation of hydrogenated product.*** To the mixture of hydrogenated product **4g** and pyridine byproduct (50 mg, 0.1 mmol) was added 2 mL of 20% methanolic KOH and the mixture was stirred at rt for 2 h. Then the crude reaction mixture was worked up with 1N HCl solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. The mixture was then purified by column chromatography (silica gel, mixture of hexane/ethyl acetate) to obtain pure deacetylated product (+)-**5g**.

Procedure G: ***General procedure for Pd/C catalyzed hydrogenation under hydrogen atmosphere*.** The mixture of 5% Pd/C (5 mol%) and the enone **3e** (0.2 mmol) in EtOH (0.1 M) was stirred at rt under hydrogen atmosphere for 2 h. Crude mixture was then passed through a pad of celite. The hydrogenated product *trans*-**4e** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure H: ***General procedure for synthesis of testosterone*.** To the pure androstan-4-ene-3,17-dione **3i** (143 mg, 0.5 mmol) in methanol (0.3 M), was added sodium borohydride (7 mg, 0.17 mmol) at 0 °C under nitrogen atmosphere and the reaction mixture was stirred at same temperature for 5 min. Then the crude reaction mixture was worked up with 1N HCl solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure testosterone **3n** (112 mg, 78% yield, >99% de) was isolated as a solid through column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure I: ***General procedure for synthesis of dehydroprogesterone***

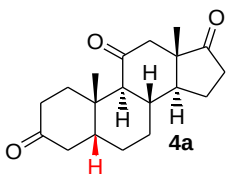
Step 1: The mixture of 16-dehydro pregnenolone-3-acetate **3g** (122 mg, 0.4 mmol) and 10 mL of 20% methanolic KOH was stirred for 0.5 h at rt. Then the crude reaction mixture was worked up with 1N HCl solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure deacetylated product (82 mg, 78% yield) was isolated by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Step 2: To the above deacetylated product (100 mg, 0.38 mmol) was added pyridinium chlorochromate (488 mg, 1.9 mmol) over SiO_2 (500 mg) in DCM (0.1 M) and the mixture was stirred at rt for 0.5 h. Then the crude reaction mixture was worked up with 1N HCl solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and

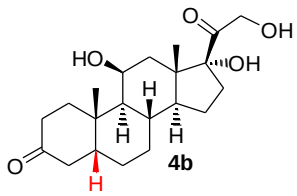
concentrated. Pure oxidized product (77 mg, 77% yield) was isolated by column chromatography (silica gel, mixture of hexane/ethyl acetate)

Step 3: To the above oxidized product (77 mg, 0.29 mmol) was added *t*BuOK (32 mg, 0.29 mmol) and dry benzene (0.1 M) and refluxed for 2 h, then the crude reaction mixture was worked up with 1N HCl solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure isomerized dienone product **3o** was isolated as a solid by column chromatography (silica gel, mixture of hexane/ethyl acetate).

(+)-5β-Androstane-3,11,17-trione (4a): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 176 °C; **$[\alpha]_D^{25}$ = +148.1° (*c* = 0.5 g/100 mL, CH_3OH, 74% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 2924, 2857, 1744 (*C*=O), 1705 (*C*=O), 1653 (*C*=O), 1462, 1377, 1163, 1014 and 723 cm^{-1}; ^1H NMR ($CDCl_3$, major *cis*-isomer) δ 2.77-2.73 (1H, m), 2.58-2.49 (2H, m), 2.46-2.23 (4H, m), 2.18-1.91 (6H, m), 1.81-1.63 (3H, m), 1.54-1.27 (4H, m), 1.25 (3H, s, C*H*$_3$), 0.85 (3H, s, C*H*$_3$); ^1H NMR ($CDCl_3$, minor *trans*-isomer) δ 2.77-2.73 (1H, m), 2.58-2.49 (2H, m), 2.46-2.23 (4H, m), 2.18-1.91 (6H, m), 1.81-1.63 (3H, m), 1.54-1.27 (4H, m), 1.23 (3H, s, C*H*$_3$), 0.85 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135, major *cis*-isomer) δ 217.2 (C, *C*=O), 212.2 (C, *C*=O), 208.6 (C, *C*=O), 52.6 (CH), 50.5 (C), 50.4 (CH_2), 50.3 (CH), 44.7 (CH), 42.2 (CH_2), 37.4 (CH_2), 36.2 (CH_2), 36.2 (CH), 36.0 (CH_2), 34.5 (C), 25.8 (CH_2), 25.2 (CH_2), 22.5 (CH_3), 21.6 (CH_2), 14.7 (CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135, minor *trans*-isomer) δ 217.2 (C, *C*=O), 211.1 (C, *C*=O), 208.6 (C, *C*=O), 64.3 (CH), 50.5 (C), 50.3 (CH), 50.3 (CH_2), 46.8 (CH), 44.2 (CH_2), 37.9 (CH_2), 36.9 (CH_2), 36.2 (CH), 36.0 (CH_2), 35.3 (C), 31.0 (CH_2), 27.9 (CH_2), 22.5 (CH_3), 21.6 (CH_2), 11.1 (CH_3); LRMS m/z 302.95 (M + H^+), calcd for $C_{19}H_{26}O_3$ 302.1882; HRMS m/z 325.1783 (M + Na), calcd for $C_{19}H_{26}O_3Na$ 325.1780; Anal. calcd for $C_{19}H_{26}O_3$ (302.1882): C, 75.46; H, 8.67. Found: C, 75.32; H, 8.61%.

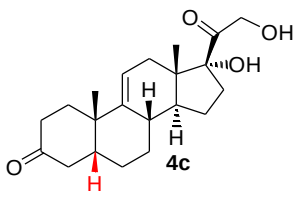


(+)-5β-Dihydrocortisol (4b): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 196 °C; **$[\alpha]_D^{25}$ = +61.5° (*c* = 1.0 g/100 mL, CH_3OH, 72% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 3449 (O*H*), 2924, 1722 (*C*=O), 1691 (*C*=O), 1462, 1373, 1257, 1090, 1034, 845, 794 and 744 cm^{-1}; ^1H NMR ($CDCl_3$ + CD_3OD (4 drops), major *cis*-isomer) δ 4.64 (1H, d, *J* = 16.0 Hz), 4.40-4.35 (1H, m), 4.27 (1H, d, *J* = 16.0 Hz), 2.70 (2H, t, *J* = 16.0



Hz), 2.34-2.23 (3H, m), 2.11-1.68 (9H, m), 1.62-1.38 (6H, m), 1.26 (3H, s, C*H*$_3$), 0.87 (3H, s, C*H*$_3$); ^{1}H NMR ($CDCl_3$ + CD_3OD (4 drops), minor *trans*-isomer) δ 4.63 (1H, d, *J* = 16.0 Hz), 4.40-4.35 (1H, m), 4.26 (1H, d, *J* = 16.0 Hz), 2.70 (2H, t, *J* = 16.0 Hz), 2.34-2.23 (3H, m), 2.11-1.68 (9H, m), 1.62-1.38 (6H, m), 1.23 (3H, s, C*H*$_3$), 0.87 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$ + CD_3OD (4 drops), DEPT-135, major *cis*-isomer) δ 214.4 (C, *C*=O), 212.2 (C, *C*=O), 88.7 (C), 67.6 (CH), 66.7 (CH_2), 52.2 (CH), 47.3 (C), 46.5 (CH), 43.3 (CH), 42.0 (CH_2), 39.4 (CH_2), 37.4 (CH_2), 36.5 (CH_2), 34.8 (C), 33.6 (CH_2), 31.1 (CH), 26.2 (CH_2), 25.5 (CH_3), 25.5 (CH_2), 23.5 (CH_2), 17.1 (CH_3); ^{13}C NMR ($CDCl_3$ + CD_3OD (4 drops), DEPT-135, minor *trans*-isomer) δ 213.5 (C, *C*=O), 212.2 (C, *C*=O), 88.7 (C), 67.7 (CH), 66.7 (CH_2), 56.8 (CH), 52.0 (CH), 47.6 (CH), 47.3 (C), 43.8 (CH_2), 39.2 (CH_2), 37.9 (CH_2), 37.7 (CH_2), 35.6 (C), 33.6 (CH_2), 32.0 (CH_2), 31.1 (CH), 28.1 (CH_2), 25.5 (CH_3), 25.5 (CH_2), 13.7 (CH_3); LRMS m/z 365.30 (M + H^+), calcd for $C_{21}H_{32}O_5$ 364.2250; HRMS m/z 387.2149 (M + Na), calcd for $C_{21}H_{32}O_5Na$ 387.2148; Anal. calcd for $C_{21}H_{32}O_5$ (364.2250): C, 69.20; H, 8.85. Found: C, 69.32; H, 8.76%.

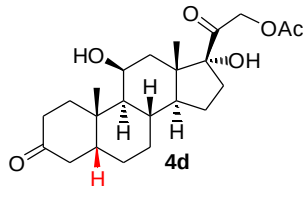
(+)-17α,21-Dihydroxy-5β-pregn-9(11)-ene-3,20-dione (4c): Prepared following the procedure **B** and



4c

purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 228 °C; **$[\alpha]_D^{25}$ = +59.2° (*c* = 0.5 g/100 mL, CH_3OH, 87% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 3449 (O*H*), 2924, 2857, 1693 (*C*=O), 1643, 1454, 1377, 1263, 1103 and 1039 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (4 drops)] δ 5.58 (1H, d, *J* = 4.8 Hz), 4.69 (1H, d, *J* = 19.6 Hz), 4.26 (1H, d, *J* = 19.6 Hz), 2.78-2.66 (2H, m), 2.56 (1H, dt, *J* = 14.4, 5.6 Hz), 2.45 (1H, t, *J* = 14.0 Hz), 2.35-2.30 (1H, m), 2.19-1.91 (7H, m), 1.76-1.73 (1H, m), 1.66-1.54 (3H, m), 1.40-1.23 (3H, m), 1.15 (3H, s, C*H*$_3$), 0.56 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$ + CD_3OD (4 drops), DEPT-135) δ 214.8 (C, *C*=O), 212.2 (C, *C*=O), 138.5 (C), 119.1 (CH), 88.5 (C), 66.4 (CH_2), 47.8 (CH), 46.3 (C), 44.4 (CH), 43.2 (CH_2), 38.5 (C), 37.7 (CH_2), 37.0 (CH_2), 36.2 (CH), 33.5 (CH_2), 31.8 (CH_2), 28.3 (CH_3), 26.2 (CH_2), 25.9 (CH_2), 24.0 (CH_2), 14.3 (CH_3); LRMS m/z 347.30 (M + H^+), calcd for $C_{21}H_{30}O_4$ 346.2144; HRMS m/z 369.2047 (M + Na), calcd for $C_{21}H_{30}O_4Na$ 369.2042; Anal. calcd for $C_{21}H_{30}O_4$ (346.2144): C, 72.80; H, 8.73. Found: C, 72.68; H, 8.81%.

(+)-5β-Dihydrocortisol-21-acetate (4d): Prepared following the procedure **A** and purified by column

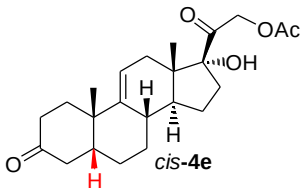


4d

chromatography using EtOAc/hexane and isolated as solid. Mp 214 °C; **$[\alpha]_D^{25}$ = +74.7° (*c* = 0.67 g/100 mL, CH_3OH, 66% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 3424 (O*H*), 2920, 2579, 1742 (*C*=O), 1722 (*C*=O), 1695 (*C*=O), 1454, 1375, 1227, 1153, 1039, 895, 846 and 785 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (4 drops)] δ 5.06 (1H, d, *J* = 16.0 Hz), 4.84 (1H, d, *J* =

16.0 Hz), 4.45-4.40 (1H, m), 2.78-2.60 (3H, m), 2.33-2.20 (3H, m), 2.18 (3H, s, C*H*$_3$), 2.15-1.91 (5H, m), 1.89-1.68 (5H, m), 1.60 (1H, dd, *J* = 12.0, 4.0 Hz), 1.54-1.30 (3H, m), 1.26 (3H, s, C*H*$_3$), 0.93 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$ + CD_3OD (4 drops), DEPT-135) δ 213.0 (C, *C*=O), 205.0 (C, *C*=O), 170.8 (C, O-*C*=O), 89.8 (C), 68.1 (CH), 67.9 (CH_2), 52.5 (CH), 47.7 (C), 46.5 (CH), 43.6 (CH), 42.3 (CH_2), 39.7 (CH_2), 37.7 (CH_2), 36.7 (CH_2), 35.0 (C), 34.6 (CH_2), 31.3 (CH), 26.5 (CH_2), 25.9 (CH_3), 25.7 (CH_2), 23.6 (CH_2), 20.5 (CH_3), 17.1 (CH_3); LRMS m/z 407.25 (M + H^+), calcd for $C_{23}H_{34}O_6$ 406.2355; HRMS m/z 429.2253 (M + Na), calcd for $C_{23}H_{34}O_6Na$ 429.2253; Anal. calcd for $C_{23}H_{34}O_6$ (406.2355): C, 67.96; H, 8.43. Found: C, 67.85; H, 8.51%.

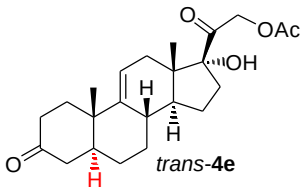
(+)-21-Acetoxy-17α-hydroxy-5β-9(11)-pregnene-3,20-dione (*cis*-4e): Prepared following the procedure



cis-**4e**

A and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 216 °C; **$[\alpha]_D^{25}$ = +49.8° (*c* = 0.7 g/100 mL, CH_3OH, 71% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 3428 (O*H*), 2924, 2856, 1738 (*C*=O), 1715 (*C*=O), 1635, 1462, 1377, 1269, 1230, 1144, 1047, 777 and 731 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CD_3OD (4 drops), major *cis*-isomer) δ 5.60 (1H, s, olefinic-H), 5.16 (1H, d, *J* = 15.0 Hz), 4.83 (1H, d, *J* = 19.0 Hz), 2.81 (1H, d, *J* = 15.0 Hz), 2.71 (1H, t, *J* = 10.0 Hz), 2.58 (1H, dt, *J* = 10.0, 2.0 Hz), 2.45 (1H, t, *J* = 15.0 Hz), 2.32 (1H, br d, *J* = 15.0 Hz), 2.18 (3H, s, C*H*$_3$), 2.05-1.73 (9H, m), 1.60-1.56 (2H, m), 1.35-1.24 (3H, m), 1.15 (3H, s, C*H*$_3$), 0.58 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$ + CD_3OD (4 drops), DEPT-135, major *cis*-isomer) δ 214.3 (C, *C*=O), 205.7 (C, *C*=O), 170.9 (C, O-*C*=O), 138.8 (C), 119.3 (CH), 89.3 (C), 67.9 (CH_2), 48.3 (CH), 46.6 (C), 44.5 (CH), 43.5 (CH_2), 38.7 (C), 38.0 (CH_2), 37.3 (CH_2), 36.5 (CH), 34.0 (CH_2), 31.9 (CH_2), 28.7 (CH_3), 26.5 (CH_2), 26.2 (CH_2), 24.2 (CH_2), 20.3 (CH_3), 14.3 (CH_3); LRMS m/z 389.35 (M + H^+), calcd for $C_{23}H_{32}O_5$ 388.2250; HRMS m/z 411.2148 (M + Na), calcd for $C_{23}H_{32}O_5Na$ 411.2148; Anal. calcd for $C_{23}H_{32}O_5$ (388.2250): C, 71.11; H, 8.30. Found: C, 71.23; H, 8.26%.

(+)-21-Acetoxy-17α-hydroxy-5α-9(11)-pregnene-3,20-dione (*trans*-4e): Prepared following the procedure

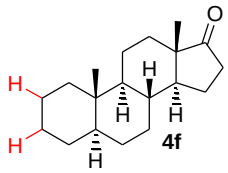


trans-**4e**

G and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 240 °C; **$[\alpha]_D^{25}$ = +60.6° (*c* = 0.57 g/100 mL, CH_3OH, 41% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 3428 (O*H*), 2924, 2856, 1738 (*C*=O), 1715 (*C*=O), 1635, 1462, 1377, 1269, 1230, 1144, 1047, 777 and 731 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CD_3OD (4 drops), major *trans*-isomer) δ 5.35 (1H, d, *J* = 4.8 Hz), 5.02 (1H, d, *J* = 14.0 Hz), 4.77 (1H, d, *J* = 14.8 Hz), 2.73-2.61 (2H, m), 2.59-2.55 (1H, m), 2.53-2.37 (1H, m), 2.35-2.30 (1H, m), 2.25-2.20 (2H, m), 2.17-2.16 (1H, m), 2.10 (3H, s, *CH*$_3$), 2.05-1.73 (7H, m), 1.60-1.56

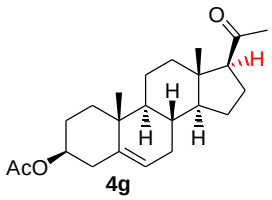
(2H, m), 1.35-1.24 (2H, m), 1.08 (3H, s, C*H*$_3$), 0.55 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$ + CD_3OD (4 drops), DEPT-135, major *trans*-isomer) δ 211.5 (C, *C*=O), 204.8 (C, *C*=O), 170.5 (C, O-*C*=O), 145.4 (C), 116.8 (CH), 89.9 (C), 67.7 (CH_2), 48.7 (CH), 47.0 (C), 45.0 (CH), 44.6 (CH_2), 38.1 (CH_2), 37.8 (C), 37.02 (CH), 37.0 (CH_2), 34.8 (CH_2), 32.8 (CH_2), 31.8 (CH_2), 28.7 (CH_2), 24.4 (CH_2), 20.5 (CH_3), 17.3 (CH_3), 14.2 (CH_3); LRMS m/z 389.35 (M + H^+), calcd for $C_{23}H_{32}O_5$ 388.2250; HRMS m/z 411.2148 (M + Na), calcd for $C_{23}H_{32}O_5Na$ 411.2148; Anal. calcd for $C_{23}H_{32}O_5$ (388.2250): C, 71.11; H, 8.30. Found: C, 71.23; H, 8.26%.

(+)-5α-Androstan-17-one (4f): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 128 °C; **$[\alpha]_D^{25}$ = +96.2° (*c* = 0.78 g/100 mL, $CHCl_3$, 99% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 2924, 1745 (*C*=O), 1464, 1377, 1257, 1201, 1122, 1057, 1009, 831 and 723 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.42 (1H, dd, *J* = 19.6, 8.0 Hz), 2.06 (1H, td, *J* = 18.0, 8.8 Hz), 1.93-1.88 (1H, m), 1.83-1.74 (2H, m), 1.66-1.63 (3H, m), 1.56-1.33 (4H, m), 1.30-1.15 (8H, m), 1.07-0.85 (3H, m), 0.83 (3H, s, C*H*$_3$), 0.78 (3H, s, C*H*$_3$), 0.73-0.69 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 221.4 (C, *C*=O), 54.8 (CH), 51.5 (CH), 47.7 (C), 46.9 (CH), 38.5 (CH_2), 36.3 (C), 35.8 (CH_2), 35.0 (CH), 31.5 (CH_2), 30.9 (CH_2), 28.9 (CH_2), 28.7 (CH_2), 26.6 (CH_2), 22.0 (CH_2), 21.7 (CH_2), 20.0 (CH_2), 13.7 (CH_3), 12.1 (CH_3); LRMS m/z 275.00 (M + H^+), calcd for $C_{19}H_{30}O$ 274.2297; HRMS m/z 297.2195 (M + Na), calcd for $C_{19}H_{30}ONa$ 297.2195; Anal. calcd for $C_{19}H_{30}O$ (274.2297): C, 83.15; H, 11.02. Found: C, 83.25; H, 11.09%.



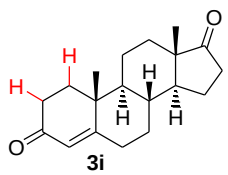
4f

(+)-3β-Acetoxy-5-pregnene-20-one (4g): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 190 °C**; $[\alpha]_D^{25}$ = +33.7° (*c* = 0.68 g/100 mL, $CHCl_3$, >99% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 2924, 2855, 1728, 1708, 1454, 1373, 1219, 1105, 1032 and 766 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.36 (1H, d, *J* = 5.0 Hz), 4.64-4.57 (1H, m), 2.53 (1H, t, *J* = 9.0 Hz), 2.36-2.31 (2H, m), 2.21-2.15 (1H, m), 2.13 (3H, s, COC*H*$_3$), 2.04 (3H, s, COC*H*$_3$), 2.06-1.98 (2H, m), 1.91-1.85 (2H, m), 1.72-1.55 (5H, m), 1.50-1.45 (3H, m), 1.29-1.13 (3H, m), 1.05-0.95 (1H, m), 1.02 (3H, s, C*H*$_3$), 0.63 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 209.2 (C, *C*=O), 170.3 (C, O-*C*=O), 139.6 (C), 122.2 (CH), 73.7 (CH), 63.5 (CH), 56.7 (CH), 49.8 (CH), 43.8 (C), 38.7 (CH_2), 38.0 (CH_2), 36.9 (CH_2), 36.5 (C), 31.7 (CH), 31.6 (CH_2), 31.3 (CH_3), 27.6 (CH_2), 24.3 (CH_2), 22.7 (CH_2), 21.2 (CH_3), 20.9 (CH_2), 19.2 (CH_3), 13.1 (CH_3); LRMS m/z 358.55 (M^+), calcd for $C_{23}H_{34}O_3$ 358.2508; HRMS m/z 381.2400 (M + Na), calcd for $C_{23}H_{34}O_3Na$ 381.2406.



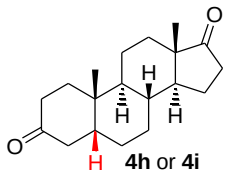
4g

(+)-4-Androstene-3,17-dione (3i): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 176 °C; **$[\alpha]_D^{25}$ = +195.2° (*c* = 0.25 g/100 mL, $CHCl_3$, 99% *ee*)**; IR (Nujol): ν_{max} 2924, 2858, 1724 (*C*=O), 1641, 1597, 1454, 1373, 1219, 1111, 1032 and 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.76 (1H, s, olefinic-*H*), 2.52-2.35 (5H, m), 2.14-1.97 (4H, m), 1.89-1.86 (1H, m), 1.77-1.70 (3H, m), 1.69-1.42 (2H, m), 1.33-1.27 (2H, m), 1.22 (3H, s, C*H*$_3$), 1.19-0.98 (2H, m), 0.93 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 220.3 (C, *C*=O), 199.3 (C, *C*=O), 170.3 (C), 124.1 (CH), 53.8 (CH), 50.8 (CH), 47.5 (C), 38.6 (C), 35.7 (2 x CH_2), 35.1 (CH), 33.9 (CH_2), 32.5 (CH_2), 31.3 (CH_2), 30.7 (CH_2), 21.7 (CH_2) , 20.3 (CH_2), 17.4 (CH_3), 13.7 (CH_3); LRMS m/z 287.15 (M + H^+), calcd for $C_{19}H_{26}O_2$ 286.1933; HRMS m/z 287.2011 (M + H^+), calcd for $C_{19}H_{26}O_2H$ 287.2011; Anal. calcd for $C_{19}H_{26}O_2$ (286.1933): C, 79.68; H, 9.15. Found: C, 79.56; H, 9.21%.



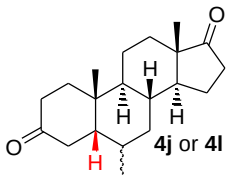
3i

(+)-5β-Androstane-3,17-dione (4h or **4i):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 134 °C; **$[\alpha]_D^{25}$ = +119.1° (*c* = 0.75 g/100 mL, $CHCl_3$, 86% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 2920, 2855, 1738 (*C*=O), 1707 (*C*=O), 1462, 1375 and 1014 cm^{-1}; ^1H NMR ($CDCl_3$) 2.67 (1H, t, *J* = 14.4 Hz), 2.50-2.43 (1H, m), 2.34-2.27 (1H, m), 2.23-2.14 (1H, m), 2.12-2.00 (2H, m), 1.98-1.84 (4H, m), 1.71-1.50 (4H, m), 1.49-1.18 (8H, m), 1.05 (3H, s, C*H*$_3$), 0.89 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 220.8 (C, *C*=O), 212.7 (C, *C*=O), 51.4 (CH), 47.8 (C), 44.1 (CH), 42.2 (CH_2), 41.0 (CH), 37.1 (CH_2), 36.9 (CH_2), 35.8 (CH_2), 35.1 (CH), 35.0 (C), 31.6 (CH_2), 26.3 (CH_2), 24.7 (CH_2), 22.6 (CH_3), 21.7 (CH_2), 20.4 (CH_2), 13.8 (CH_3); LRMS m/z 289.20 (M + H^+), calcd for $C_{19}H_{28}O_2$ 288.2089; HRMS m/z 311.1987 (M + Na), calcd for $C_{19}H_{28}O_2Na$ 311.1987; Anal. calcd for $C_{19}H_{28}O_2$ (288.2089): C, 79.12; H, 9.78. Found: C, 79.26; H, 9.65%.



4h or **4i**

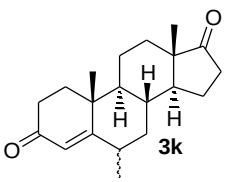
(+)-6-Methyl-5β-androstane-3,17-dione (4j or **4l):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 144 °C; **$[\alpha]_D^{25}$ = +69.2° (*c* = 0.33 g/100 mL, $CHCl_3$, 59% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 2924, 2860, 1730, 1713, 1454, 1377, 1246, 1055 and 1014 cm^{-1}; ^1H NMR ($CDCl_3$, major isomer) δ 2.61 (1H, t, *J* = 14.5 Hz), 2.46 (1H, dd, *J* = 19.5, 9.0 Hz), 2.37 (1H, dd, *J* = 14.5, 6.0 Hz), 2.32-2.30 (1H, m), 2.13-1.94 (5H, m), 1.86-1.69 (6H, m), 1.57-1.22 (6H, m),1.22 (3H, s, C*H*$_3$), 0.96 (3H, d, *J* = 7.5 Hz, CHC*H*$_3$), 0.92 (3H, s, C*H*$_3$); ^1H NMR ($CDCl_3$, minor isomer) δ 2.61 (1H, t, *J* = 14.5 Hz), 2.46 (1H, dd, *J* = 19.5, 9.0 Hz), 2.39-2.35 (1H, m), 2.32-2.30 (1H, m), 2.13-1.94 (5H, m), 1.86-1.69 (6H, m), 1.57-1.22 (6H, m),1.05 (3H, s, C*H*$_3$), 0.89 (3H, s, C*H*$_3$), 0.82 (3H, d, *J* = 7.0 Hz,



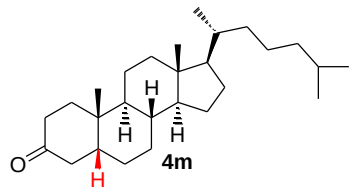
4j or **4l**

C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 220.7 (C, *C*=O), 212.1 (C, *C*=O), 54.5 (CH), 51.0 (CH), 48.4 (CH), 47.7 (C), 43.3 (CH_2), 41.1 (CH_2), 38.1 (CH_2), 37.7 (CH_2), 36.3 (C), 35.8 (CH_2), 32.9 (CH), 31.5 (CH_2), 30.2 (CH), 21.9 (CH_2), 20.6 (CH_2), 15.7 (CH_3), 14.9 (CH_3), 13.8 (CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 220.5 (C, *C*=O), 212.7 (C, *C*=O), 51.3 (CH), 49.6 (CH), 47.8 (C), 43.3 (CH_2), 40.7 (CH), 37.01 (CH_2), 36.98 (C), 36.7 (CH_2), 35.8 (CH_2), 35.2 (CH), 32.7 (CH_2), 31.7 (CH_2), 29.4 (CH), 22.7 (CH_3), 21.7 (CH_2), 20.5 (CH_2), 19.2 (CH_3), 13.8 (CH_3); LRMS m/z 302.95 (M + H^+), calcd for $C_{20}H_{30}O_2$ 302.2246; HRMS m/z 303.2324 (M + H^+), calcd for $C_{20}H_{30}O_2H$ 303.2324; Anal. calcd for $C_{20}H_{30}O_2$ (302.2246): C, 79.42; H, 10.00; Found: C, 79.32; H, 10.11%.

(+)-6-Methyl-4-androstene-3,17-dione (3k): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 198 °C; **$[\alpha]_D^{25}$ = +114.2° (*c* = 0.13 g/100 mL, $CHCl_3$, 18-23% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 2924, 2862, 1738, 1666, 1604, 1462, 1377, 1265, 1190, 1093, 1016, 812 and 715 cm^{-1}; ^{1}H NMR ($CDCl_3$, major isomer) δ 5.78 (1H, br s, olefinic-H), 2.74-2.68 (1H, m), 2.54-2.32 (3H, m), 2.17-2.02 (3H, m), 2.01-1.93 (1H, m), 1.92-1.85 (2H, m), 1.82-1.79 (1H, m), 1.76-1.69 (4H, m), 1.63-1.36 (3H, m), 1.29 (3H, s, C*H*$_3$), 1.27 (3H, d, *J* = 7.6 Hz, C*H*$_3$), 0.94 (3H, s, C*H*$_3$); ^{1}H NMR ($CDCl_3$, minor isomer) δ 5.81 (1H, d, *J* = 1.25 Hz, olefinic-H), 2.74-2.68 (1H, m), 2.54-2.32 (3H, m), 2.17-2.02 (3H, m), 2.01-1.93 (1H, m), 1.92-1.85 (2H, m), 1.82-1.79 (1H, m), 1.76-1.69 (4H, m), 1.63-1.36 (3H, m), 1.21 (3H, s, C*H*$_3$), 1.10 (3H, d, *J* = 6.5 Hz, C*H*$_3$), 0.92 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 220.2 (C, *C*=O), 199.6 (C, *C*=O), 173.4 (C), 121.5 (CH), 53.4 (CH), 51.0 (CH), 47.5 (C), 38.9 (C), 38.1 (CH), 37.7 (CH_2), 36.3 (CH_2), 35.7 (CH_2), 34.0 (CH_2), 33.7 (CH), 31.3 (CH_2), 23.0 (CH_3), 21.8 (CH_2), 20.4 (CH_2), 18.3 (CH_3), 13.8 (CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 220.1 (C, *C*=O), 199.5 (C, *C*=O), 174.5 (C), 125.4 (CH), 54.1 (CH), 50.7 (CH), 47.5 (C), 39.7 (CH_2), 38.4 (C), 38.1 (CH), 35.9 (CH_2), 35.0 (CH_2), 33.6 (CH_2), 31.3 (CH_2), 30.0 (CH), 23.0 (CH_3), 21.7 (CH_2), 20.5 (CH_2), 18.3 (CH_3), 13.7 (CH_3); LRMS m/z 301.20 (M + H^+), calcd for $C_{20}H_{28}O_2$ 300.2089; Anal. calcd for $C_{20}H_{28}O_2$ (300.2089): C, 79.96; H, 9.39; Found: C, 79.85; H, 9.28%.

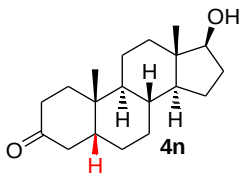


(+)-5β-Cholestan-3-one (4m): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 62 °C; **$[\alpha]_D^{25}$ = +38.2° (*c* = 1.0 g/100 mL, $CHCl_3$, 86% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 2918, 2727, 1716 (*C*=O), 1464, 1379, 1263 and 723 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.70 (1H, t, *J* = 14.5 Hz), 2.34 (1H, dt, *J* = 15.0, 5.5 Hz), 2.16 (1H, qd, *J* = 14.5, 4.0 Hz), 2.06-2.00 (3H, m), 1.92-1.79 (3H, m), 1.61-1.59 (1H, m), 1.54-1.44



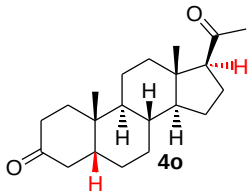
(5H, m), 1.42-1.32 (6H, m), 1.28-1.20 (3H, m), 1.18-1.05 (7H, m), 1.02 (3H, s, C*H*$_3$), 0.92 (3H, d, *J* = 10.0 Hz, CHC*H*$_3$), 0.87 (3H, d, *J* = 6.5 Hz, CHC*H*$_3$), 0.87 (3H, d, *J* = 6.5 Hz, CHC*H*$_3$), 0.69 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 213.2 (C, *C*=O), 56.5 (CH), 56.3 (CH), 44.3 (CH), 42.7 (C), 42.3 (CH_2), 40.8 (CH), 40.1 (CH_2), 39.5 (CH_2), 37.1 (CH_2), 37.0 (CH_2), 36.1 (CH_2), 35.7 (CH), 35.5 (CH), 34.8 (C), 28.2 (CH_2), 27.9 (CH), 26.6 (CH_2), 25.8 (CH_2), 24.1 (CH_2), 23.8 (CH_2), 22.7 (CH_3), 22.6 (CH_3), 22.5 (CH_3), 21.2 (CH_2), 18.6 (CH_3), 12.0 (CH_3); LRMS m/z 387.30 (M + H^+), calcd for $C_{27}H_{46}OH$ 387.3549; HRMS m/z 409.3444 (M + Na), calcd for $C_{27}H_{46}ONa$ 409.3447; Anal. calcd for $C_{27}H_{46}O$ (386.3549): C, 83.87; H, 11.99. Found: C, 83.75; H, 11.89%.

(+)-17β-Hydroxy-5β-androstan-3-one (4n): Prepared following the procedure **A** and purified by column



chromatography using EtOAc/hexane and isolated as solid. Mp 140 °C; **[α]$_D^{25}$ = +32.1° (*c* = 0.6 g/100 mL, CH_3OH, 94% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 3420 (O*H*), 2924, 2858, 1705 (*C*=O), 1635, 1446, 1375, 1261, 1128 and 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.66 (1H, t, *J* = 8.5 Hz), 2.68 (1H, t, *J* = 14.0 Hz), 2.35-2.29 (1H, m), 2.19-2.15 (1H, m), 2.14-2.00 (3H, m), 1.92-1.80 (4H, m), 1.74-1.72 (1H, m), 1.65-1.58 (1H, m), 1.56-1.41 (4H, m), 1.40-1.34 (2H, m), 1.33-1.22 (3H, m), 1.16-1.04 (2H, m), 1.03 (3H, s, C*H*$_3$), 0.76 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 213.1 (C, *C*=O), 81.8 (CH), 51.0 (CH), 44.2 (CH), 43.1 (C), 42.2 (CH_2), 40.9 (CH), 37.1 (CH_2), 37.0 (CH_2), 36.8 (CH_2), 35.6 (CH), 34.9 (C), 30.5 (CH_2), 26.4 (CH_2), 25.3 (CH_2), 23.3 (CH_2), 22.6 (CH_3), 20.7 (CH_2), 11.1 (CH_3); LRMS m/z 291.00 (M + H^+), calcd for $C_{19}H_{30}O_2$ 290.2246; HRMS m/z 313.2147 (M + Na), calcd for $C_{19}H_{30}O_2Na$ 313.2144; Anal. calcd for $C_{19}H_{30}O_2$ (290.2246): C, 78.57; H, 10.41. Found: C, 78.45; H, 10.48%.

(+)-5β-Dihydroprogesterone (4o): Prepared following the procedure **A** and purified by column



chromatography using EtOAc/hexane and isolated as solid. Mp 116 °C; **[α]$_D^{25}$ = +96.1° (*c* = 0.47 g/100 mL, $CHCl_3$, 86% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 2924, 2858, 1728 (*C*=O), 1709, 1462, 1377, 1261, 1101, 1049, 1016, 821 and 723 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.69 (1H, t, *J* = 14.0 Hz), 2.55 (1H, t, *J* = 9.5 Hz), 2.34 (1H, dt, *J* = 15.0, 5.0 Hz), 2.21-2.16 (2H, m), 2.13 (3H, s, COC*H*$_3$), 2.09-2.02 (3H, m), 1.95-1.81 (2H, m), 1.73-1.65 (2H, m), 1.58-1.46 (5H, m), 1.47-1.37 (2H, m), 1.32-1.22 (4H, m), 1.03 (3H, s, C*H*$_3$), 0.64 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 212.9 (C, *C*=O), 209.3 (C, *C*=O), 63.7 (CH), 56.6 (CH), 44.2 (C), 44.1 (CH), 42.3 (CH_2), 40.8 (CH), 39.1 (CH_2), 37.1 (CH_2), 36.9 (CH_2), 35.5 (CH), 34.9 (C), 31.5 (CH_3), 26.5 (CH_2), 25.7 (CH_2), 24.4 (CH_2), 22.9 (CH_2), 22.6 (CH_3), 21.2 (CH_2), 13.4 (CH_3); LRMS m/z

314.75 (M - H^+), calcd for $C_{21}H_{32}O_2$ 316.2402; HRMS m/z 339.2305 (M + Na), calcd for $C_{21}H_{32}O_2Na$ 339.2300; Anal. calcd for $C_{21}H_{32}O_2$ (316.2402): C, 79.70; H, 10.19. Found: C, 79.65; H, 10.24%.

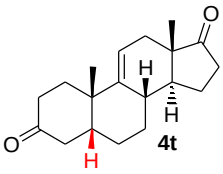
(+)-19-Hydroxy-5β-androstane-3,17-dione (4p): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 202 °C; **$[\alpha]_D^{25}$ = +108.7° (*c* = 0.68 g/100 mL, CH_3OH, 79% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 3453 (O*H*), 2924, 2855, 1730 (*C*=O), 1693 (*C*=O), 1462, 1377, 1261, 1092, 1043, 1014, 802 and 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.95 (1H, d, *J* = 11.0 Hz), 3.68 (1H, d, *J* = 10.5 Hz), 2.66 (1H, t, *J* = 14.5 Hz), 2.47 (1H, dd, *J* = 19.2, 8.5 Hz), 2.39-2.29 (3H, m), 2.14-2.02 (3H, m), 2.00-1.86 (5H, m), 1.74-1.50 (5H, m), 1.47-1.16 (5H, m), 0.88 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 220.6 (C, *C*=O), 212.7 (C, *C*=O), 64.6 (CH_2), 51.8 (CH), 47.7 (C), 41.9 (CH_2), 41.3 (CH), 39.1 (C), 36.7 (CH_2), 36.2 (CH), 35.8 (CH_2), 35.0 (CH), 32.1 (CH_2), 30.7 (CH_2), 25.9 (CH_2), 24.4 (CH_2), 21.7 (CH_2), 20.5 (CH_2), 13.8 (CH_3); LRMS m/z 305.25 (M + H^+), calcd for $C_{19}H_{28}O_3$ 304.2038; HRMS m/z 327.1939 (M + Na), calcd for $C_{19}H_{28}O_3Na$ 327.1936; Anal. calcd for $C_{19}H_{28}O_3$ (304.2038): C, 74.96; H, 9.27. Found: C, 74.85; H, 9.21%.

(+)-17β-Hydroxy-19-nor-5β-androstan-3-one or 17β-Hydroxy-5β-estran-3-one (4q): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 110 °C; **$[\alpha]_D^{25}$ = +28.3° (*c* = 0.67 g/100 mL, $CHCl_3$, 82% *de* and 99% *ee*)**; IR (Neat): ν_{max} 3500 (O*H*), 2926, 2855, 1709 (*C*=O), 1462, 1377 and 1016 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.68 (1H, t, *J* = 8.5 Hz), 2.59 (1H, t, *J* = 14.0 Hz), 2.28-2.16 (4H, m), 2.10-2.05 (2H, m), 1.88-1.85 (1H, m), 1.78-1.59 (6H, m), 1.53-1.42 (3H, m), 1.35-1.07 (7H, m), 0.79 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 212.8 (C, *C*=O), 81.9 (CH), 50.0 (CH), 43.2 (C), 42.9 (CH_2), 41.5 (CH), 39.8 (CH), 38.5 (CH), 38.3 (CH), 36.7 (CH_2), 36.4 (CH_2), 30.55 (CH_2), 30.51 (CH_2), 27.7 (CH_2), 25.5 (CH_2), 25.0 (CH_2), 23.2 (CH_2), 11.0 (CH_3); LRMS m/z 277.15 (M + H^+), calcd for $C_{18}H_{28}O_2$ 276.2089; HRMS m/z 299.1988 (M + Na), calcd for $C_{18}H_{28}O_2Na$ 299.1987; Anal. calcd for $C_{18}H_{28}O_2$ (276.2089): C, 78.21; H, 10.21. Found: C, 78.15; H, 10.26%.

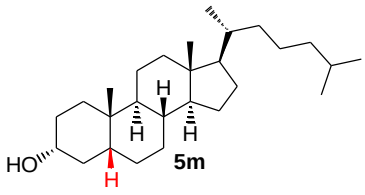
(+)-17β-Acetoxy-5β-estran-3-one (4r or **4s):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 130 °C; **$[\alpha]_D^{25}$ = +50.6° (*c* = 0.83 g/100 mL, $CHCl_3$, 96% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 2930, 2849, 1740 (*C*=O), 1703 (*C*=O), 1454, 1373, 1238, 1099 and 1022

cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.62 (1H, t, *J* = 8.0 Hz), 2.59 (1H, t, *J* = 14.0 Hz), 2.27-2.09 (6H, m), 2.04 (3H, s, COC*H*$_3$), 1.81-1.58 (6H, m), 1.55-1.46 (3H, m), 1.37-1.28 (2H, m), 1.25-1.10 (5H, m), 0.83 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 212.7 (C, *C*=O), 171.1 (C, O-*C*=O), 82.8 (CH), 49.7 (CH), 42.9 (CH_2), 42.8 (C), 41.2 (CH), 39.8 (CH), 38.32 (CH), 38.3 (CH), 36.8 (CH_2), 36.4 (CH_2), 30.5 (CH_2), 27.7 (CH_2), 27.5 (CH_2), 25.4 (CH_2), 25.0 (CH_2), 23.3 (CH_2), 21.1 (CH_3), 12.1 (CH_3); LRMS m/z 319.15 (M + H^+), calcd for $C_{20}H_{30}O_3$ 318.2195; HRMS m/z 341.2093 (M + Na), calcd for $C_{20}H_{30}O_3Na$ 341.2093; Anal. calcd for $C_{20}H_{30}O_3$ (318.2195): C, 75.43; H, 9.50. Found: C, 75.28; H, 9.41%.

(+)-5β-Androst-9(11)-ene-3,17-dione (4t): Prepared following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 144 °C; **$[\alpha]_D^{25}$ = +139.1° (*c* = 0.4 g/100 mL, CH_3OH, >99% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 2924, 2855, 1736 (*C*=O), 1707 (*C*=O), 1462, 1377, 1267, 1205, 1072, 1034, 1010, 914, 819 and 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.61 (1H, d, *J* = 5.5 Hz), 2.55-2.44 (2H, m), 2.42-2.35 (1H, m), 2.34-2.24 (2H, m), 2.20-2.14 (2H, m), 2.12-2.05 (4H, m), 1.99-1.93 (2H, m), 1.87-1.84 (1H, m), 1.63-1.56 (3H, m), 1.41-1.37 (1H, m), 1.27 (1H, dq, *J* = 8.25, 4.5 Hz), 1.18 (3H, s, C*H*$_3$), 0.85 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 221.3 (C, *C*=O), 212.7 (C, *C*=O), 140.3 (C), 118.6 (CH), 48.6 (CH), 46.0 (C), 44.4 (CH), 43.6 (CH_2), 39.2 (C), 38.1 (CH_2), 37.4 (CH_2), 36.2 (CH_2), 35.9 (CH), 33.5 (CH_2), 28.9 (CH_3), 26.1 (CH_2), 25.6 (CH_2), 22.7 (CH_2), 14.0 (CH_3); LRMS m/z 287.05 (M + H^+), calcd for $C_{19}H_{26}O_2$ 286.1933; HRMS m/z 309.1833 (M + Na), calcd for $C_{19}H_{26}O_2Na$ 309.1831; Anal. calcd for $C_{19}H_{26}O_2$ (286.1933): C, 79.68; H, 9.15. Found: C, 79.55; H, 9.23%.

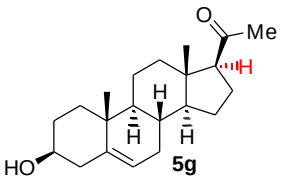


(+)-5β,3α-Cholestan-3-ol (5m): Prepared following the procedure **D** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 110 °C; **$[\alpha]_D^{25}$ = +29.5° (*c* = 0.45 g/100 mL, $CHCl_3$, 78% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 3244 (O*H*), 2924, 2855, 1643, 1462, 1377, 1261, 1163, 1082, 1045, 800 and 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.62 (1H, tt, *J* = 12.0, 4.0 Hz), 1.97 (1H, td, *J* = 12.0, 7.0 Hz), 1.85-1.72 (4H, m), 1.72-1.64 (1H, m), 1.58-1.48 (5H, m), 1.43-1.32 (8H, m), 1.27-1.21 (4H, m), 1.17-1.07 (6H, m), 1.05-0.99 (2H, m), 0.92 (3H, s, C*H*$_3$), 0.90 (3H, d, *J* = 6.5 Hz, CHC*H*$_3$), 0.87 (3H, d, *J* = 6.5 Hz, CHC*H*$_3$), 0.86 (3H, d, *J* = 6.5 Hz, CHC*H*$_3$), 0.64 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 71.9 (CH), 56.5 (CH), 56.4 (CH), 42.7 (C), 42.1 (CH), 40.5 (CH), 40.2 (CH_2), 39.5 (CH_2), 36.5 (CH_2), 36.2 (CH_2), 35.9 (CH), 35.8 (CH), 35.4 (CH_2), 34.6 (C), 30.6 (CH_2), 28.3 (CH_2), 28.0 (CH), 27.2 (CH_2), 26.4 (CH_2), 24.2 (CH_2), 23.8 (CH_2), 23.4 (CH_3), 22.8 (CH_3), 22.5 (CH_3), 20.8 (CH_2), 18.7 (CH_3), 12.0 (CH_3); LRMS m/z 389.35 (M + H^+), calcd for $C_{27}H_{48}O$ 388.3705;



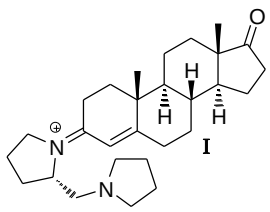
HRMS m/z 411.3604 (M + Na), calcd for $C_{27}H_{48}ONa$ 411.3603; Anal. calcd for $C_{27}H_{48}O$ (388.3705): C, 83.44; H, 12.45. Found: C, 83.28; H, 12.41%.

(+)-3β-Hydroxy-5-pregnene-20-one (5g): Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 190 °C; **$[\alpha]_D^{25}$ = +26.6° (*c* = 0.46 g/100 mL, $CHCl_3$, >99% *de* and 99% *ee*)**; IR (Nujol): ν_{max} 3501 (O*H*), 2924, 2855, 1682 (*C*=O), 1462, 1377, 1165, 1053, 1016, 949, 800 and 737 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.35 (1H, d, *J* = 5.0 Hz), 3.53 (1H, tt, *J* = 11.0, 4.5 Hz), 2.53 (1H, t, *J* = 9.5 Hz), 2.30-2.23 (1H, m), 2.19-2.17 (2H, m), 2.12 (3H, s, COC*H*$_3$), 2.06-1.97 (2H, m), 1.87-1.84 (2H, m), 1.70-1.61 (5H, m), 1.54-1.44 (4H, m), 1.30-0.95 (4H, m), 1.01 (3H, s, C*H*$_3$), 0.63 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 209.4 (C, *C*=O), 140.8 (C), 121.3 (CH), 71.6 (CH), 63.7 (CH), 56.9 (CH), 50.0 (CH), 43.9 (C), 42.2 (CH_2), 38.8 (CH_2), 37.2 (CH_2), 36.5 (C), 31.8 (CH_3), 31.7 (CH_2), 31.6 (CH_2), 31.4 (CH), 24.4 (CH_2), 22.8 (CH_2), 21.0 (CH_2), 19.3 (CH_3), 13.2 (CH_3); LRMS m/z 317.25 ($M + H^+$), calcd for $C_{21}H_{32}O_2$ 316.2402; HRMS m/z 339.2299 (M + Na), calcd for $C_{21}H_{32}O_2Na$ 339.2300; Anal. calcd for $C_{21}H_{32}O_2$ (316.2402): C, 79.70; H, 10.19. Found: C, 79.58; H, 10.25%.



5g

(*S*,*Z*)-1-((8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-1*H*-cyclopenta[*a*]phenanthren-3(2*H*,6*H*,10*H*)-ylidene)-2-(pyrrolidin-1-ylmethyl)pyrrolidin-1-ium (I): ^1H NMR (CD_3CN) δ 5.86 (1H, s, olefinic-H), 4.00-3.99 (1H, m), 3.83-3.64 (3H, m), 3.57-3.43 (3H, m), 3.27-3.10 (2H, m), 2.61-2.35 (6H, m), 2.14-1.89 (11H, m), 1.83-1.81 (2H, m), 1.72-1.55 (4H, m), 1.47-1.29 (2H, m), 1.20 (3H, s, C*H*$_3$), 1.09-0.98 (2H, m), 0.88 (3H, s, C*H*$_3$); ^{13}C NMR (CD_3CN, DEPT-135) δ 224.7 (C, *C*=O), 205.7 (C, *C*=N), 181.8 (C, *C*=CH), 123.0 (CH, C=*C*H), 57.9 (CH), 56.6 (CH_2), 56.3 (CH_2), 55.7 (CH_2), 54.3 (CH), 51.1 (CH), 48.6 (C), 48.2 (CH_2), 40.1 (C), 36.4 (CH_2), 35.3 (CH), 35.3 (CH_2), 33.7 (CH_2), 33.4 (CH_2), 31.8 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 23.7 (CH_2), 23.5 (2 x CH_2), 22.2 (CH_2), 20.9 (CH_2), 17.5 (CH_3), 14.0 (CH_3); HRMS m/z 423.3375 (M^+), calcd for $C_{28}H_{43}N_2O$ 423.3375.



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References:

1. Lokman, P. M.; Irwin, J. L.; Biackwell, L. F.; Davie, P. S.; Thomas, M.; Young, G. *Steroids* **1997**, *62*, 655-658.

Data block for Product-(+)-4r:

Bond precision: C-C = 0.0033 A Wavelength=1.54180

Cell: a=6.77744(12) b=14.0740(3) c=19.0348(4)
alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1815.65(6)	1815.64(6)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C20 H30 O3	?
Sum formula	C20 H30 O3	C20 H30 O3
Mr	318.44	318.44
Dx,g cm-3	1.165	1.165
Z	4	4
Mu (mm-1)	0.601	0.601
F000	696.0	696.0
F000'	697.96	
h,k,lmax	8,17,23	8,16,23
Nref	2071[3577]	2870
Tmin,Tmax	0.817,0.860	0.844,1.000
Tmin'	0.796	

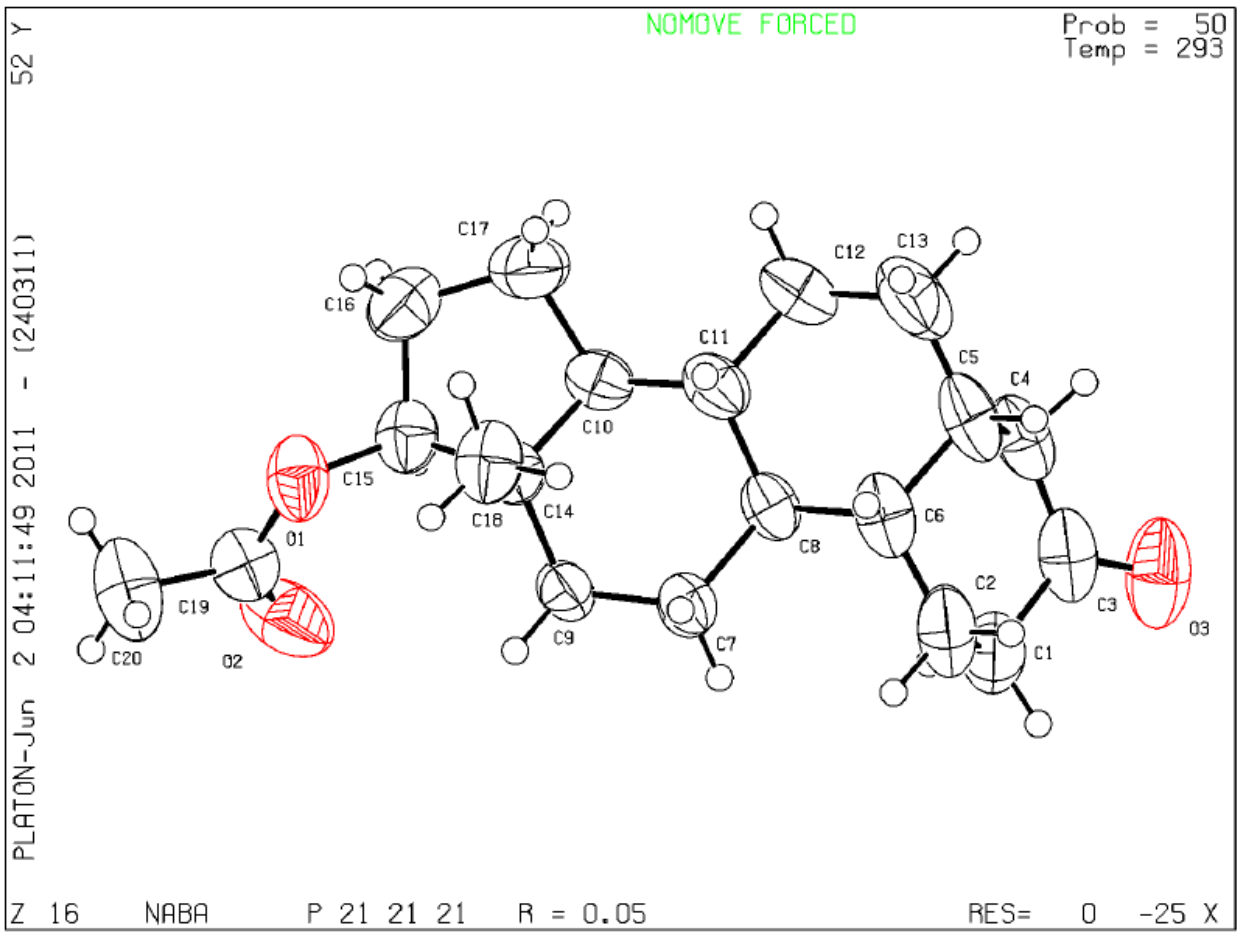
Correction method= MULTI-SCAN

Data completeness= 1.39/0.80 Theta(max)= 72.060

R(reflections)= 0.0466(2627) wR2(reflections)= 0.1336(2870)

S = 1.061 Npar= 210

Data block for Product-(+)-4r - ellipsoid plot



Data block for Product-(+)-4i:

Bond precision: C-C = 0.0040 A Wavelength=0.71073

Cell: a=7.9253(18) b=8.4074(17) c=25.074(5)
alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1670.7(6)	1670.7(6)
Space group	P 21 21 21	P2(1)2(1)2(
Hall group	P 2ac 2ab	?
Moiety formula	C19 H28 O2	?
Sum formula	C19 H28 O2	C19 H28 O2
Mr	288.41	288.41
Dx,g cm-3	1.147	1.147
Z	4	4
Mu (mm-1)	0.072	0.072
F000	632.0	632.0
F000'	632.26	
h,k,lmax	9,10,31	9,10,31
Nref	1991[3424]	3097
Tmin,Tmax	0.983,0.989	0.983,0.989
Tmin'	0.972	

Correction method= MULTI-SCAN

Data completeness= 1.56/0.90 Theta(max)= 26.350

R(reflections)= 0.0588(2166) wR2(reflections)= 0.1356(3097)

S = 1.024 Npar= 192

Data block for Product-(+)-4i - ellipsoid plot