Supporting Information

Pd-mediated cross-coupling of C-17 lithiated androst-16-en-3-ol – An access to functionalized arylated steroid derivatives

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2.1. General Remarks

NMR spectra were recorded on a *Bruker* Avance 300, *Bruker* Avance 400, *Bruker* Avance 500 DRX 500 or *Bruker* Avance 600 spectrometer as solutions at room temperature. Chemical shifts δ are expressed in parts per million (ppm) downfield from tetramethylsilane (TMS). References for ^{1}H NMR and ^{13}C NMR were the residual solvent peaks of chloroform (^{1}H: δ = 7.26 ppm) and D_1-chloroform (^{13}C: δ = 77.0 ppm). All coupling constants (*J*) are absolute values and are expressed in Hertz (Hz). The description of signals includes: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, dd = doublet of doublets and ddd = double doublet of doublets and so forth. The spectra were analyzed according to first order. The assignments of the signal structure in ^{1}H NMR were made by the multiplicity and for ^{13}C NMR by DEPT 90- and DEPT 135-spectra (DEPT = distortionless enhancement by polarization transfer) and are described as follows: + = primary or tertiary C-atom (positive DEPT-signal), – = secondary C-atom (negative signal) and C_q = quaternary C-atom (no signal). Due to OH at C-3 of the steroidal framework not being visible in the ^{1}H NMR spectra, the sum of H-atoms does not add up to the number of H atoms in the sum formula.

IR spectra were recorded on a FT-IR *Bruker* IFS 88 spectrometer. The compoands were measured either between KBr plates or as pure substances by ATR technique (ATR = attenuated total reflection). The position of the absorption band is given in wave numbers $\tilde{\nu}$ in cm^{-1}. The intensities of the bands were characterized as follows: vs = very strong (0-20% T), s = strong (21-40% T), m = medium (41-60% T), w = weak (61-80% T), vw = very weak (81-100% T).

Mass spectra were measured by EI-MS (electron impact mass spectrometry) and were recorded on a *Finnigan MAT 95*. The peaks are given as mass-to-charge-ratio (*m*/*z*). The molecule peak is given as $[M]^+$ and characteristic fragment peaks are given as [M – fragment]$^+$ or [fragment]$^+$. The signal intensities are given in percent, relatively to the intensity of the base signal (100%). For the high resolution mass, the following abbreviations were used: calc. = calculated data, found = measured data.

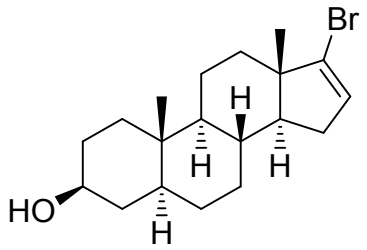
Analytical thin layer chromatography (TLC) was carried out on Merck silica gel coated aluminum plates (silica gel 60, F_{254}), detected under UV-light at 254 nm or stained with "Seebach staining solution" (mixture of molybdato phosphoric acid, cerium(IV)-sulfate tetrahydrate, sulfuric acid and water) or basic potassium permanganate solution. Solvent mixtures are understood as volume/volume. Solvents, reagents and chemicals were purchased from *Sigma-Aldrich*, *ABCR, Thermo Fisher, TCI, ChemPur* and *Acros Organics*. All solvents, reagents and chemicals were used as purchased unless stated otherwise.

Air- or moisture-sensitive reactions were carried out under argon atmosphere in oven-dried and previously evacuated glass ware. Liquids were transferred with plastic syringes and steel cannula. Reaction control was performed by thin layer chromatography. If not stated otherwise, crude products were purified by flash chromatography by the procedure of Still.[1] Silica gel 60 (0.040 × 0.063 mm, Geduran®, Merck) was used as stationary phase and as mobile phase, solvents of p.a. quality were used.

2.2. Experimental Procedures and Analytical Data

2.2.1 Synthesis of the steroidal substrates

(3*β*, 5*α*)-17-Bromoandrost-16-en-3-ol (**2-Br**)

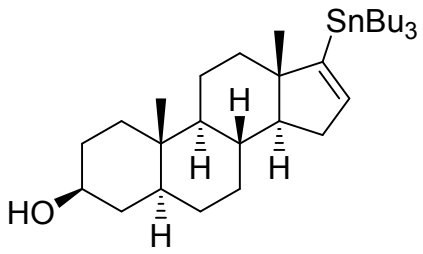


The synthesis of (3*β*, 5*α*)-17-Bromoandrost-16-en-3-ol (**2-Br**) followed a modified, reported procedure.[2] A solution of e*pi*-androsterone (500 mg, 1.72 mmol, 1.00 equiv.), hydrazine monohydrate (1.10 mL, 34.4 mmol, 20.0 equiv.) and triethylamine (4.80 mL, 34.4 mmol, 20.0 equiv.) in ethanol (25 mL) was heated in an argon atmosphere for 16 hours to 50 °C. After cooling, the solvents were totally removed and the obtained colourless powder was dissolved in dry pyridine (7.0 mL) in an argon atmosphere. *N*-Bromosuccinimide (918 mg, 5.16 mmol, 3.00 equiv.) in dry pyridine (7.0 mL) was then added slowly while cooling the mixture with an ice bath. The mixture was stirred for 1 hour at room temperature and afterwards quenched with 1 M aqueous HCl solution. The product was extracted with ethyl acetate (3 × 50 mL) and the combined organic layers were washed with saturated aqueous solution of $NaHCO_3$ (40 mL) and brine (40 mL). The organic phase was dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography (CH/EtOAc, 5:1) to afford vinylbromide **1a-Br** (461 mg, 1.30 mmol, 76%) as a colourless powder.

***R**_f* = 0.22 (*c*Hex/EtOAc, 3:1) – **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 5.81 (dd, ^3J = 3.3, 1.7 Hz, 1H, =C*H*), 3.59 (tt, ^3J = 15.9, 11.1, 4.8 Hz, 1H, C*H*OH), 2.11 (ddd, ^3J = 14.8, 6.2, 3.3 Hz, 1H, =CHCH_2^b), 1.87 (ddd, ^3J = 14.8. 11.1, 1.8 Hz, 1H, =CHCH_2^a), 1.83 – 1.77 (m, 1H, CH_2), 1.73 – 1.21 (m, 13H, 8-C*H,* C*H* and 7 different CH_2), 1.18 – 1.06 (m, 1H, 5-C*H*), 1.02 – 0.88 (m, 2H, 2 different CH_2), 0.83 (s, 3H, CH_3), 0.82 (s, 3H, CH_3), 0.72 (ddd, ^3J = 12.3, 10.0, 4.6 Hz, 1 H, C*H*) ppm. – **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 135.6 (=*C*H), 128.8 (C_qBr), 71.1 (+, *C*HOH), 55.3 (+, *C*H), 54.5 (+, *C*H), 48.6 (13-C_q), 44.9 (+, 5-*C*H), 38.0 (–, *C*H_2), 36.6 (–, *C*H_2), 35.5 (10-C_q), 34.4 (–, *C*H_2), 34.1 (+, 8-*C*H), 31.6 (–, *C*H_2), 31.3 (–, *C*H_2), 31.2 (–, *C*H_2), 28.3 (–, 6-*C*H_2), 21.1 (–, 11-*C*H_2), 15.1 (+,

18-*C*H$_3$), 12.1 (+, 19-*C*H$_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3271 (br), 2921 (w), 2841 (w), 1588 (vw), 1450 (w), 1368 (w), 1245 (vw), 1178 (vw), 1134 (vw), 1079 (vw), 1060 (w) 1040 (w), 996 (w), 949 (vw), 919 (vw), 873 (vw), 851 (vw), 834 (vw), 820 (vw), 802 (w), 740 (vw), 708 (vw), 656 (w), 609 (vw), 587 (vw), 565 (vw), 520 (vw), 495 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 354 (17) + 352 (17) $[M]^{\bullet+}$, 339 (38) + 337 (40) $[M - CH_3]^+$, 321 (17) + 319 (18), 273 (100) $[M - Br]^+$, 255 (23), 239 (28). – **HRMS** (EI, $C_{19}H_{29}O^{79}Br$): calc. = 352.1396; found = 352.1398.

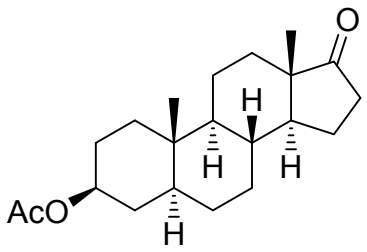
(3*β*, 5*α*)-17-Tributyltinandrost-16-en-3-ol (**2-SnBu$_3$**)



At -78 °C *tert*-Buthyllithium in *n*-pentane (1.9 M, 1.7 mL, 3.17 mmol, 3.50 equiv) was added to a solution of the vinylbromide **2-Br** (320 mg, 906 µmol, 1.00 equiv.) in dry THF (15.0 mL) in an argon atmosphere. The solution turned yellow and after 30 minutes stirring at -78 °C tributyltin chloride (0.37 mL, 1.36 mmol, 1.50 equiv.) was added. The solution was allowed to warm to room temperature and was stirred for an additional hour. Then a saturated aqueous solution of NH_4Cl (10 mL) was added and the product was extracted with dichloromethane (2 × 15 mL). The combined organic phases were washed with brine (10 mL), dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography (CH/EtOAc, 5:1) to afford the product **2-SnBu$_3$** (411 mg, 729 µmol, 80%) as a colourless oil.

***R**$_f$* = 0.41 (EtOAc/CH, 1:3) – **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 5.84 (dd, *J* = 3.0, 1.4, 36.9 Hz, 1H, =C*H*), 3.59 (tt, *J* = 10.6, 4.2 Hz, 1H), 2.12 (ddd, *J* = 15.1, 6.6, 3.1 Hz, 1H, =CH_2^a), 1.96 (ddd, *J* = 15.1, 11.5, 1.5 Hz, 1H, =CH_2^b), 1.83 – 1.65 (m, 4H, 3 different CH_2), 1.61 – 1.22 (m, 19H, different CH_2 + C*H* + 8-C*H*), 1.18 – 1.05 (m, 1H, 5-C*H*), 1.04 – 0.93 (m, 2H, 2 different CH_2), 0.91 – 0.85 (m, 9H, 3 × CH_3), 0.84 (s, 3H, 18-CH_3), 0.77 – 0.70 (m, 1H, C*H*), 0.69 (s, 3H, 19-CH_3) ppm. – **^{13}C-NMR** (100 MHz, $CDCl_3$): δ = 158.0 (C_qSnBu$_3$), 139.8 (+, s d, SnC_q=*C*H, $^2J_{SnC}$ = 34.8 Hz), 71.2 (+, *C*HOH), 56.4 (+, *C*H), 54.9 (+, *C*H), 50.7(13-C_q), 44.9 (+, 5-*C*H), 38.1 (–, *C*H$_2$), 37.2 (–, *C*H$_2$), 36.7 (–, *C*H$_2$), 35.6 (10-C_q), 34.5 (+, 8-*C*H), 33.9 (–, *C*H$_2$), 32.3 (–, *C*H$_2$), 31.4 (*C*H$_2$), 29.1 (–, s d, 3 × SnCH$_2$*C*H$_2$, $^2J_{SnC}$ = 19.3 Hz), 28.6 (–, *C*H$_2$), 27.3 (– , 3 × SnCH$_2$CH$_2$*C*H$_2$), 21.3 (–, *C*H$_2$), 17.1 (+, 18-*C*H$_3$), 13.5 (+, 3 × SnCH$_2$CH$_2$*C*H$_3$), 12.2 (+, 19-*C*H$_3$), 9.42 (–, s d+d, 3 × Sn*C*H$_2$, $^1J_{SnC}$ = 337.4 + 322.4 Hz) ppm. – **MS** (EI, eV): *m/z* (%) = 507 (100) [M – Bu]$^+$, 449 (11) [M – 2Bu]$^+$, 393 (16) [M – 3Bu]$^+$. – **HRMS** (EI, [M – Bu]$^+$, $C_{27}H_{47}OSn$): calc. = 507.2643; found = 507.2640.

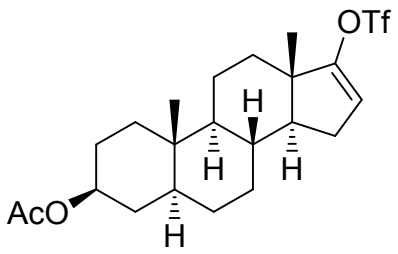
3*β*-Acetyloxy-5*α*-androstan-17-on



Epi-androsterone (662 mg, 2.28 mmol, 1.00 equiv.) was dissolved in acetic anhydride (2.0 mL) and dry pyridine (0.37 mL, 4.56 mmol, 2.00 equiv.) in an argon atmosphere. The suspension was stirred overnight at room temperature while the suspension cleared off. The mixture was carefully poured into a saturated aqueous solution of $NaHCO_3$ (50 mL), ethyl acetate (50 mL) was added and the mixture was stirred for 30 minutes. The phases were separated and the aqueous phase was extracted with ethyl acetate (2 × 50 mL). The combined organic layers were washed with brine (50 mL) and then dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography (CH/EtOAc, 3:1) to afford the acetyl protected *epi*-androsterone (745 mg, 2.24 mmol, 98%) as a colourless solid.

***R**_f* = 0.35 (CH/EtOAc, 5:1) – **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 4.67 (tt, ^3J = 11.0, 4.9 Hz, 1H, 3*α*-C*H*OAc), 2.41 (dd, ^3J = 19.3, 8.8 Hz, 1H, 16-CH_2^a), 2.05 (dd, ^3J = 19.3, 8.8 Hz, 1H, 16-CH_2^b), 2.00 (s, 3H, OCH_3), 1.91 (m, 1H, CH_2), 1.82 – 1.66 (m, 4H, 3 different CH_2), 1.62 (tdd, 2H, CH_2), 1.57 – 1.47 (m, 3H, 2 different C*H*2 + 8-C*H*), 1.41 – 1.19 (m, 7H, 4 different CH_2 and C*H* and 5-C*H*), 1.06 – 0.91 (m, 2H, *C*H_2) 0.84 (s, 3H, CH_3), 0.83 (s, 3H, CH_3), 0.72 (td, ^3J = 11.4, 4.1 Hz, 1H, C*H*). – **^{13}C-NMR** (151 MHz, $CDCl_3$) δ = 221.3 (17-C_qO). 170.8 (C_qOOCH$_3$), 73.6 (+, 3-*C*HOAc), 54.4 (+, *C*H), 51.5 (+, *C*H), 47.9 (13-C_q), 44.8 (+, 5-*C*H), 36.8 (–, *C*H_2), 36.0 (–, 16-*C*H_2), 35.8 (10-C_q), 35.2 (+, 8-*C*H), 34.1 (–, *C*H_2), 31.7 (–, *C*H_2), 30.9 (–, *C*H_2), 28.4 (–, *C*H_2), 27.5 (–, *C*H_2), 21.9 (–, *C*H_2), 21.6 (+, CO*C*H$_3$), 20.6 (–, *C*H_2), 13.9 (+, 18-*C*H$_3$), 12.3 (+, 19-*C*H$_3$). – **IR (ATR)**: $\tilde{\nu}$ = 2920 (w), 2840 (vw), 1723 (*ν*-C=O, m), 1450 (vw), 1366 (w), 1233 (*ν*-C-O, m), 1130 (vw) 1060 (w), 965 (vw) cm^{-1}. – **MS** (EI, 70 eV): m/z (%) = 332 (55) $[M]^+$, 272 (100) $[M – AcO]^+$, 257 (28), 218 (40), 201 (29), 107 (23). – **HRMS** ($C_{21}H_{32}O_3$): calc. = 332.2346, found = 332.2345.

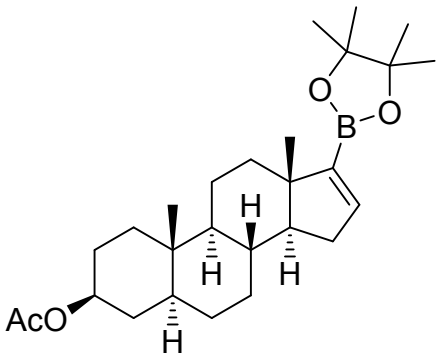
3*β*-Acetyloxy-5*α*-androst-16-en-17-triflate (**2-OTf**)



The synthesis of 3*β*-Acetyloxy-5*α*-androst-16-en-17-triflate (**2-OTf**) followed a modified, reported procedure.[3] Acetylated *epi*-androsterone (1.10 g, 3.31 mmol, 1.00 equiv.) and $PhNTf_2$ (1.42 g, 3.97 mmol, 1.20 equiv.) were dissolved in dry THF (10 mL) under argon atmosphere. At -78 °C KHMDS (0.7 M, 4.8 mL, 3.31 mmol, 1.00 equiv.) in dry toluene was added slowly to the reaction and stirred for 15 minutes. Then the mixture was allowed to warm to room temperature for 1 – 3 hours (TLC control). Upon completion, the solution was quenched with acetic acid. Then ethyl acetate (50 mL) and saturated aqueous solution of NH_4Cl (50 mL) and brine (50 mL) were added. After phase separation the organic layer was dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography (CH/EtOAc, 10:1) to afford the vinyltriflate **2-OTf** (1.35 g, 2.91 mmol, 88%) as a colourless solid.

R_f = 0.77 (EtOAc/CH, 1:4). – **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 5.58 (dd, ^3J = 3.4, 1.7 Hz, 1H, =C*H*), 4.72 (tt, ^3J = 11.4, 4.9 Hz, 1H, C*H*OAc), 2.23 (ddd, J = 14.9, 5.7, 3.3 Hz, 1H, =CHCH_2^a), 2.05 (s, 3H, OCH_3), 1.99 (ddd, J = 14.8, 10.9, 1.7 Hz, 1H, =CHCH_2^b), 1.90 – 1.80 (m, 1H, CH_2), 1.78 – 1.47 (m, 9H,different CH_2 + 8-C*H* + C*H*), 1.17 – 1.45 (m, 5H, different CH_2), 1.05 (td, J = 16.7, 3.9 Hz, 1H, 5-C*H*), 0.99 (s, 3H, CH_3), 0.95 – 1.01 (m, 1H, CH_2), 0.88 (s, 3H, CH_3), 0.96 – 0.77 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 170.6 (C_qO), 159.2 (C_q=CH), 118.5 (q, ^1J = 320.5 Hz, *C*F_3), 114.3 (+, *C*H=C_q), 73.4 (+, 3-*C*HOH), 54.5 (+, *C*H), 54.0 (+, *C*H), 44.7 (13-C_q), 44.7 (+, 5-CH) 36.4 (–, *C*H_2), 35.6 (10-C_q), 33.8 (–, *C*H_2), 33.3 (+, 8-*C*H), 32.5 (–, *C*H_2), 30.6 (–, *C*H_2), 28.4 (–, *C*H_2), 28.1 (–, *C*H_2), 27.3 (–, *C*H_2), 21.3 (+, O*C*H_3), 20.4 (–, *C*H_2), 15.2 (+, 18-*C*H_3), 12.0 (+, 19-*C*H_3) ppm. – **IR** (ATR): $\tilde{\nu}$ = 2913 (w), 2852 (vw), 1734 (w), 1440 (w), 1416 (w), 1244 (vw), 1206 (w), 1142 (w), 1120 (w), 1073 (vw),1045 (w), 949 (w), 913 (vw), 889 (vw), 867 (w), 822 (vw), 693 (w), 620 (w), 600 (w), 568 (vw), 518 (w), 433 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 464 (10) $[M]^{\bullet+}$, 404 (81), 389 (100), 357 (61), 314 (22), 196 (40), 107 (19). – **HRMS** (EI, $C_{22}H_{31}O_5F_3{}^{32}S_1$): calc. = 464.1839; found = 464.1838.

3*β*-Acetyloxy-17-(4',4',5',5'-Tetramethyl-1',3',2'-dioxaborolan-2-yl)-5*α*-androst-16-en (**2-Pin$_2$**)

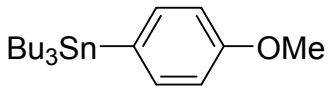


Vinyltriflate **2-OTf** (570 mg, 1.23 mmol, 1.00 equiv.), bis(pinacolato)diboron (784 mg, 3.09 mmol, 2.51 equiv.), triphenylphosphine (32.3 mg, 123 µmol, 0.10 equiv.) and potassium *tert* butoxide (207 mg, 1.85 mmol, 1.50 equiv) were dissolved in dry toluene (20 mL) under argon atmosphere and degassed (2 freeze-pump-thaw cycles). Afterwards bis(triphenylphosphine)-palladium(II)dichloride (43.2 g, 61.5 µmol, 5 mol%) was added and the mixture was heated to 50 °C for 2 hours. Then water (50 mL) was added and the product was extracted with diethylether (3 × 40 mL). The combined organic phases were washed with brine (50 mL), then dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography (CH/EtOAc, 10:1) to afford the vinyltriflate **2-Pin$_2$** (400 mg, 904 µmol, 74%) as a colourless solid.

***R*$_f$** = 0.83 (EtOAc/CH, 1:4) – **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 6.47 (dd, ^3J = 3.1, 1.6 Hz, 1H, C*H*=CH_2), 4.68 (tt, ^3J = 11.3, 4.9 Hz, 1H, C*H*OAc), 2.14 (ddd, ^3J = 16.1, 6.7, 3.1 Hz, 1H, =CHCH_2), 2.08 – 2.00 (m, 1H, =CHCH_2), 2.01 (s, 3H, OCH_3), 1.97 – 1.18 (m, 15H, CH_2 and C*H*), 1.24 (s, 12H, 4 × CH_3), 0.85 (s, 3H, CH_3), 1.06 – 0,91 (m, 2H, 2 different CH_2), 0.75 (s, 3H, CH_3), 0.68 – 0.76 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (100 MHz, $CDCl_3$): δ = 170.8 (C_qO + C_qBPin$_2$), 146.0 (+, =*C*H), 82.8 (2 × OC_qMe$_2$), 73.9 (+, *C*HOAc), 56.8 (+, *C*H), 55.1 (+, *C*H), 48.1 (13-C_q), 45.0 (+, 5-*C*H), 36.7 (–, *C*H$_2$), 36.0 (–, *C*H$_2$), 35.9 (10-C_q), 34.5 (+, 8-*C*H), 34.2 (–, *C*H$_2$), 33.7 (–, *C*H$_2$), 32.5 (–, *C*H$_2$), 28.8 (–, *C*H$_2$), 27.7 (–, *C*H$_2$), 25.0 (+, 2 × OC*C*H$_3$), 24.9 (+, 2 × OC*C*H$_3$), 21.6 (+, OCH_3), 21.4 (–, *C*H$_2$), 17.0 (+, 18-*C*H$_3$), 12.4 (+, 19-*C*H$_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 2923 (w), 2855 (w), 1729 (w), 1595 (w), 1438 (w), 1358 (w), 1310 (w), 1244 (m), 1136 (w), 1021 (w), 948 (w), 887 (w), 855 (w), 712 (w), 696 (w), 670 (vw), 604 (w), 517 (w), 433 (w) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 442 (100) $[M]^{\bullet+}$, 427 (58) $[M - CH_3]^+$, 314 (39) $[M - HBPin_2]^+$. – **HRMS** (EI, $C_{27}H_{43}O_4{}^{11}B_1$): calc. = 442.3249; found = 442.3247.

2.2.2 Synthesis of the tributyltin compoand

4-(Tributylstannyl)ansiole



The synthesis of 4-(tributylstannyl)anisole followed a modified, reported procedure.[4] In a Schlenk flask under argon atmosphere, 4-bromoanisole (250 mg, 1.34 mmol, 1.00 equiv.) was dissolved in dry THF (6.0 mL). After cooling to –78 °C, *tert*-BuLi in *n*-pentane (1.9 M, 1.3 mL, 3.34 mmol, 2.50 equiv.) was added dropwise and the resulting yellow solution was stirred for 30 minutes at –78 °C. Then tributyltin chloride (0.40 mL, 1.47 µmol, 1.10 equiv.) was added and the solution was allowed to warm to room temperature. Stirring was continued for further 30 minutes and then the reaction was quenched with a saturated aqueous NH_4Cl solution (15 mL) and extracted with dichloromethane (2 × 25 mL). The combined organic phases were washed with brine and dried over Na_2SO_4. After evaporation the crude product was obtained as colourless liquid and was used for Stille coupling without further purification.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.92 (d, J = 8.5 Hz, 2H, C*H*CSnBu$_3$), 6.92 (d, J = 7.6 Hz, 2H, C*H*COMe), 3.81 (s, 3H, OC*H*$_3$), 1.42 – 1.64 (m, 6H, SnCH$_2$C*H*$_2$), 1.26 – 1.41 (m, 6H, C*H*$_2$CH$_3$), 0.98 – 1.10 (m, 3H, SnC*H*$_2$), 0.86 – 0.94 (m, 9H, C*H*$_3$), 0.80 – 0.86 (m, 3H, SnC*H*$_2$) ppm. – **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 159.4 (*C*OMe), 137.2 (2 × *C*H$_{Ar}$CSnBu$_3$), 129.2 (*C*BuSn$_3$), 113.6 (2 × *C*H$_{Ar}$COMe), 54.7 (CO*C*H$_3$), 29.2 (3 × SnCH$_2$CH$_2$*C*H$_2$), 27.4 (3 × SnCH$_2$*C*H$_2$), 13.4 (3 × *C*H$_3$), 9.3 (3 × Sn*C*H$_2$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 2953 (w), 2921 (m), 2870 (w), 2841 (w), 1586 (m), 1565 (vw), 1494 (w), 1461 (w), 1417 (vw), 1375 (w), 1339 (vw), 1275 (w), 1242 (m), 1179 (w), 1072 (w), 1036 (w), 959 (vw), 873 (w), 820 (w), 806 (w), 788 (w), 685 (w), 659 (w), 592 (w), 515 (w) cm^{-1}. – **MS** (EI, 70 eV): *m/z* (%) = 398 (20) $[M]^{\bullet+}$, 325 (100) $[M - Bu]^+$, 291 (75) $[M - 2Bu]^+$, 227 (56) $[M - 3Bu]^+$. – **HRMS** (EI, $C_{19}H_{34}O^{120}Sn$): calc. 398.1626; found = 398.1625.

The analytical and spectral properties match those reported in the literature.[4]

Cross-coupling reactions

General procedure for the lithiation and the "Feringa" cross-coupling (Table 2), GP-1

A flame-dried Schlenk tube was charged with the vinylbromide **2-Br** (1.00 equiv.) and diluted with dry THF under argon atmosphere. After cooling to -78 °C, ^{t}BuLi in *n*-pentane (1.9 M, 3.10 equiv.) was slowly added and then stirred at -78 °C for 30 minutes. In a dry vial $Pd_2(dba)_3$ (5 mol%), XPhos (20 mol%) and the aryl bromide (1.30 equiv.) were solved in dry toluene and stirred at room temperature for 10 minutes. Afterwards the lithium organyl was slowly (30 minutes) cannulated to the toluene solution charged with the bromide and the catalytic system. After addition, the reaction was stirred overnight at room temperature and then quenched with a saturated solution of aqueous NH_4Cl. The mixture was extracted twice with DCM. The combined organic phases were washed with brine, then dried over Na_2SO_4 and the solvents were removed under reduced pressure. The crude product was purified by column chromatography.

General procedure for the Stille coupling reaction (Scheme 2), GP-2:

A Schlenk tube was charged with the vinylstannane **2-SnBu$_3$** (1.00 equiv.), the bromide (1.10 equiv.), LiCl (10.0 equiv.) and CuCl (10.0 equiv.). Dry DMF was added under argon atmosphere and the reaction mixture was degassed using three freeze-pump-thaw cycles. Then $Pd(PPh_3)_4$ (10 mol%) was added and the reaction mixture was stirred at 60 °C. After cooling to room temperature, an aqueous solution of KF (3 M, 4.00 equiv.) was added to the reaction mixture and stirred for 30 min, followed by filtration over Celite®. An aqueous saturated NH_4Cl solution was added and twice extracted with dichloromethane. The organic layers were washed with brine and were then dried over Na_2SO_4 and the solvents were removed under reduced pressure. The crude product was purified by column chromatography.

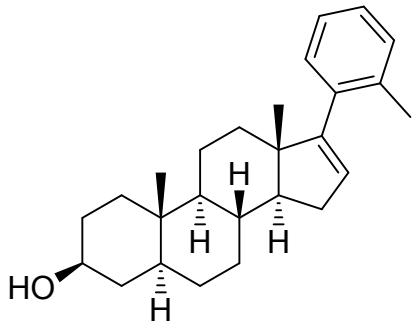
General procedure for the Suzuki coupling reactions (Scheme 2), GP-3:

A Schlenk tube was charged with the vinylpinacolatoborane **2-BPin$_2$** (1.00 equiv.) and the bromide (1.10 equiv.). A benzene, MeOH and a 2M Na_2CO_3 solution in water were added and the mixture

was degassed applying three freeze-pump-thaw cycles. Then $Pd(PPh_3)_4$ (10 mol%) was added and the reaction mixture was refluxed. After cooling to room temperature, H_2O was added to the mixture and extracted three times with dichloromethane. The organic layers were washed with brine and were dried over Na_2SO_4 and the solvents were removed under reduced pressure. The crude product was purified by column chromatography.

Compoands of the Scope of Substrate (Table 2)

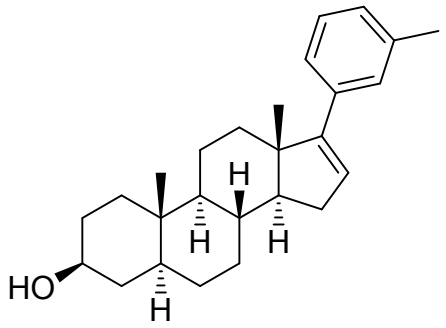
(3*β*, 5*α*)-17-(2'-Methylphenyl)-5*a*-androst-16-en-3-ol (**4a**)



The synthesis followed the **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), ^{t}BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and *ortho*-bromotoluene (31 µL, 44 mg, 257 µmol, 1.30 equiv.). After column chromatography (silica gel, CH/EtOAc, 4:1) the product **4a** was obtained as a colourless solid[a] (22 mg, 60.3 µmol, 31%).

R_f = 0.34 (EtOAc/CH, 1:3) – **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.25 – 6.94 (m, 4H, CH_{Ar}), 5.55 (dd, *J* = 3.2, 1.6 Hz, 1H, =C*H*), 3.60 (tt, *J* = 11.2, 4.8 Hz, 1H, C*H*OH), 2.29 (s, 3H, $C_{q,Ar}CH_3$), 2.30 – 2.20 (m, 1H, =CHCH_2[a]), 2.04 (ddd, *J* = 15.2, 11.0, 1.6 Hz, 1H, =CHCH_2[b]), 1.83 – 1.44 (m, 7H, 5 different CH_2 + 8-C*H* + C*H*), 1.40 – 1.24 (m, 7H, 5 different CH_2), 1.15 (dddd, *J* = 12.3, 9.1, 6.3, 2.9 Hz, 1H, 5-C*H*), 1.09 – 0.93 (m, 2H, 2 different CH_2), 0.91 (s, 3H, CH_3), 0.85 (s, 3H, CH_3), 0.82 – 0.71 (m, 1H, C*H*) ppm. - **^{13}C-NMR** (101 MHz, $CDCl_3$): *δ* = 153.7 (C_q=CH), 137.4 (C_q), 136.1 (C_q), 129.9 (+, =CH_{Ar}), 128.7 (+, =CH_{Ar}), 127.8 (+, C_q=C*H*), 126.3 (+, =CH_{Ar}), 124.6 (+, =CH_{Ar}), 71.1 (+, *C*HOH), 57.0 (+, *C*H), 54.7 (+, *C*H), 49.4 (13-C_q), 45.0 (+, 5-*C*H), 38.1 (–, *C*H_2), 36.7 (–, *C*H_2), 35.6 (10-C_q), 35.0 (–, *C*H_2), 34.3 (+, 8-*C*H), 31.9 (–, *C*H_2), 31.8 (–, *C*H_2), 31.4 (–, *C*H_2), 28.6 (–, *C*H_2), 21.0 (–, *C*H_2), 20.7 (+, $C_{q,Ar}CH_3$), 16.3 (+, 18-*C*H_3), 12.2 (+, 19-*C*H_3) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3323 (br), 2968 (w), 2920 (w), 2846 (w), 1624 (vw). 1450 (w), 1372 (w), 1179 (vw), 1157 (vw), 1135 (vw), 1114 (vw), 1079 (w), 1061 (w), 1036 (m), 999 (w), 957 (vw), 924 (vw), 858 (vw), 820 (vw), 760 (m), 724 (w), 678 (w), 678 (w), 661 (w), 606 (w), 591 (w), 448 (w) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 364 (79) $[M]^{\bullet+}$, 349 (100) $[M - CH_3]^+$, 274 (73), 259 (37). – **HRMS** (EI, $C_{26}H_{36}O$): calc. = 364.2761; found = 364.2759.

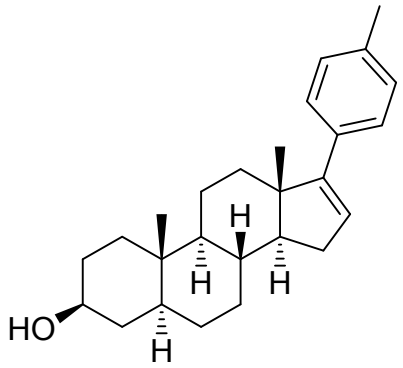
(3*β*, 5*α*)-17-(3'-Methylphenyl)-5*a*-androst-16-en-3-ol (**4b**)



The synthesis followed the **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), ^{t}BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and *meta*-bromotoluene (31 µL, 44 mg, 257 µmol, 1.30 equiv.). After column chromatography (silica gel, CH/EtOAc, 4:1) the product **4b** was obtained as a colourless solid[a] (42 mg, impurities of **5**, 44%).

***R**f* = 0.18 (EtOAc/CH, 1:3) – **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.13 – 7.06 (m, 3H, 3 × CH_{Ar}), 7.00 – 6.96 (m, 1H, CH_{Ar}), 5.80 (dd, *J* = 3.0, 1.7 Hz, 1H, =C*H*), 3.53 (tt, *J* = 10.7, 4.7 Hz, 1H, C*H*OH), 2.27 (s, 3H, $C_{q,Ar}$ H_3), 2.12 (ddd, *J* = 15.5, 6.5, 3.3 Hz, 1H, =CHCH_2^b), 1.98 – 1.88 (m, 2H, =CHCH_2^a + CH_2), 1.78 – 1.72 (m, 1H, CH_2), 1.69 – 1.43 (m, 6H, 4 different CH_2, 8-C*H* and C*H*), 1.39 – 1.18 (m, 6H, 5 different CH_2), 1.05 – 1.12 (m, 1H, 5-C*H*), 0.94 (s, 3H, CH_3), 0.99 – 0.89 (m, 2H, 2 different CH_2), 0.79 (s, 3H, CH_3), 0.75 – 0.65 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (100 MHz, $CDCl_3$): δ = 154.6 (C_q=CH), 137.4 ($C_{q,Ar}$), 137.2 ($C_{q,Ar}$), 127.8 (+, *C*H$_{Ar}$), 127.3 (+, *C*H$_{Ar}$), 127.2 (+, *C*H$_{Ar}$), 126.8 (+, =*C*H), 123.6 (+, *C*H$_{Ar}$), 71.2 (+, *C*HOH), 57.4 (+, *C*H), 54.6 (+, *C*H), 47.3 (13-C_q), 44.9 (+, 5-*C*H), 38.1 (–, *C*H$_2$), 36.7 (–, *C*H$_2$), 35.5 (10-C_q), 35.4 (–, *C*H$_2$), 33.9 (+, 8-*C*H), 31.8 (–, *C*H$_2$), 31.4 (–,*C*H$_2$), 31.3 (–,*C*H$_2$), 28.5 (–, *C*H$_2$), 21.4 (+, $C_{q,Ar}$*C*H$_3$), 21.1(–, *C*H$_2$), 16.6 (+, 18-*C*H$_3$), 12.2 (+, 19-*C*H$_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3365 (br), 2931 (w), 2838 (w), 1605 (w), 1582 (w), 1449 (w), 1338 (w), 1202 (w), 1176 (w), 1162 (w), 1073 (w), 1037 (w), 1015 (w), 940 (w), 849 (w), 829 (w), 817 (w), 735 (vw), 692 (w), 675 (vw), 612 (vw), 543 (vw), 487 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 364 (100) $[M]^{\bullet+}$, 349 (84) $[M - CH_3]^+$, 331 (18). – **HRMS** (EI, $C_{26}H_{36}O_1$): calc. = 364.2761, found = 364.2762.

(3*β*, 5*α*)-17-(4'-Methylphenyl)-5*a*-androst-16-en-3-ol (**4c**)

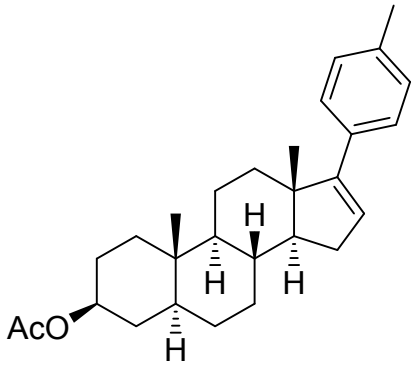


The synthesis followed the **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), ^{t}BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and *para*-bromotoluene (44 mg, 257 µmol, 1.30 equiv.). After column chromatography (silica gel, CH/EtOAc, 4:1) the product **4c** was obtained as a colourless solid (35 mg, 94.9 µmol, 48%).

According to the **GP-2**, synthesis acquires the vinylstannane **2a-SnBu$_3$** (70 mg, 124 µmol, 1.00 equiv.), 4-bromotoluene (32 mg, 186 µmol, 1.50 equiv.), LiCl (53 mg, 1.25 mmol, 10.0 equiv.), CuCl (124 mg, 1.25 mmol, 10.0 equiv.) and $Pd(PPh_3)_4$ (16 mg, 12.4 µmol, 10 mol%) in dry DMF (3.0 mL). After column chromatography (silica gel, CH/EE, 4:1) the product **4c** was obtained as colourless solid (31 mg, 84.9 µmol, 58%).

***R**$_f$* = 0.23 (EtOAc/CH, 1:3) – **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.19 (d, ^3J = 8.2 Hz, 2H, =C*H*$_{Ar}$), 7.02 (d, ^3J = 7.6 Hz, 2H, C*H*$_{Ar}$), 5.77 (dd, ^3J = 3.3, 1.8 Hz, 1H, =C*H*), 3.52 (tt, ^3J = 9.6, 4.7 Hz, 1H, C*H*OH), 2.25 (s, 3H, $C_{q,Ar}CH_3$), 2.10 (ddd, *J* = 15.5, 6.5, 3.3 Hz, 1H, =CHC*H*$_2$), 2.00 – 1.84 (m, 2H, =CHC*H*$_2$ + C*H*$_2$), 1.74 – 1.42 (m, 7H, 8-C*H* + C*H*+ 5 different C*H*$_2$), 1.33 – 1.18 (m, 6H, 5 different C*H*$_2$), 1.13 – 1.00 (m, 1H, 5-C*H*), 0.98 – 0.88 (m, 2H, 2 different C*H*$_2$), 0.93 (s, 3H, C*H*$_3$), 0.78 (s, 3H, C*H*$_3$), 0.61 – 0.77 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (100 MHz, $CDCl_3$): δ = 154.6 (C_q=CH), 136.1 (C_q=CH$_{Ar}$), 134.3 (C_q=CH$_{Ar}$), 128.6 (+, 2 × *C*H$_{Ph}$), 126.4 (+, 2 × *C*H$_{Ph}$), 126.2 (+, =*C*H), 71.2(+, *C*HOH), 57.4 (+, *C*H), 54.5 (+, *C*H), 47.2 (13-*C*$_q$), 44.9 (+, 5-*C*H), 38.1 (–, *C*H$_2$), 36.7 (–, *C*H$_2$), 35.5 (10-*C*$_q$), 35.4 (–, *C*H$_2$), 33.9 (+, 8-*C*H), 31.8 (–, *C*H$_2$), 31.4 (–, *C*H$_2$), 31.3 (–, *C*H$_2$), 28.5 (–, *C*H$_2$), 21.1 (–, *C*H$_2$), 20.9, (+, $C_{q.Ar}CH_3$), 16.6 (+,18-*C*H$_3$), 12.2 (+, *C*H$_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3267 (br), 2921 (m), 2851 (w), 1508 (vw), 1448 (w), 1367 (vw), 1078 (w), 717 (vw), 623 (vw), 584 (vw), 516 (vw), 489 (w), 463 (w) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 364 (100) $[M]^{\bullet+}$, 349 (56) $[M - CH_3]^+$. – **HRMS** (EI, $C_{26}H_{36}O$): calc. = 364.2761; found = 364.2762.

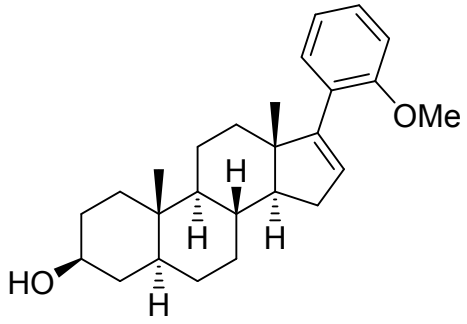
3*β*-Acetyloxy-17-(4'-methyphenyl)-5*α*-androst-16-en (**4c-Ac**)



According to **GP-3** vinylpinacolatoborane **1b-BPin$_2$** (60 mg, 136 µmol, 1.00 equiv.), 4-tolylbromide (26 mg, 149 µmol, 1.10 equiv.) and $Pd(PPh_3)_4$ (16 mg, 13.6 µmol, 10 mol%) were used in a mixture of benzene (3.0 mL), MeOH (0.7 mL) and 2M Na_2CO_3 solution in water (0.2 mL). After column chromatography (silica gel, CH/EE, 10:1) the product **4c** was obtained as a colourless powder in mixture with the defunctionalized product (36 mg, containing according to ^{1}H NMR analysis 84.4 µmol, 62% of **4b**).

***R**$_f$* = 0.74 (EE/CH, 1:3) – **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.26 (d, ^3J = 8.2 Hz, 2H, =C*H*$_{Ar}$), 7.10 (d, ^3J = 7.8 Hz, 2H, C*H*$_{Ar}$), 5.84 (dd, ^3J = 3.3, 1.8 Hz, 1H, =C*H*), 4.70 (tt, ^3J = 11.4, 4.9 Hz, 1H, C*H*OH), 2.33 (s, 3H, $C_{q,Ar}CH_3$), 2.18 (ddd, J = 15.4, 6.5, 3.3 Hz, 1H, =CHC*H*$_2$), 2.06 – 1.81 (m, 2H, =CHC*H*$_2$ + C*H*$_2$), 2.03 (s, 3H, OC*H*$_3$), 1.79 – 1.49 (m, 7H, 8-C*H* + C*H*+ 5 different C*H*$_2$), 1.38 – 1.17 (m, 6H, 5 different C*H*$_2$), 1.13 – 1.00 (m, 1H, 5-C*H*), 0.98 – 0.88 (m, 2H, 2 different C*H*$_2$), 1.01 (s, 3H, C*H*$_3$), 0.88 (s, 3H, C*H*$_3$), 0.79 – 0.73 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 170.1 (*C*$_q$O), 154.5 (*C*$_q$=CH), 136.1 (*C*$_q$=CH$_{Ar}$), 134.3 (*C*$_q$=CH$_{Ar}$), 128.6 (+, 2 × *C*H$_{Ph}$), 126.4 (+, 2 × *C*H$_{Ph}$), 126.2 (+, =*C*H), 73.5 (+, *C*HOH), 57.3 (+, *C*H), 54.3 (+, *C*H), 47.2 (13-*C*$_q$), 44.7 (+, 5-*C*H), 36.4 (–, *C*H$_2$), 35.5 (10-*C*$_q$), 35.3 (–, *C*H$_2$), 33.9 (+, 8-*C*H), 33.9 (–, *C*H$_2$), 31.7 (–, *C*H$_2$), 31.3 (–, *C*H$_2$), 28.4 (–, *C*H$_2$), 27.3 (–, *C*H$_2$), 21.3 (+, *C*$_{q.Ar}$CH$_3$), 21.0 (–, 11-*C*H$_2$), 20.9 (+, O*C*H$_3$), 16.5 (+,18-*C*H$_3$), 12.1 (+, *C*H$_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 2923 (m), 2854 (w), 1729 (m), 1438 (w), 1359 (m), 1310 (m), 1244 (s), 1143 (m), 1064 (w), 1022 (m), 963 (m), 949 (w), 926 (w), 887 (w), 854 (m), 801 (w), 766 (vw), 712 (vw), 697 (m), 671 (m), 612 (vw), 579 (vw), 529 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 406 (11) [M]$^{\bullet+}$, 316 (100) [defunctionalized steroid]$^{\bullet+}$, 301 (34) [defunctionalized steroid – Me]$^{\bullet+}$, 272 (20), 256 (22), 241 (64). – **HRMS** (EI, $C_{28}H_{38}O_2$): calc. = 406.2866; found = 406.2866. –

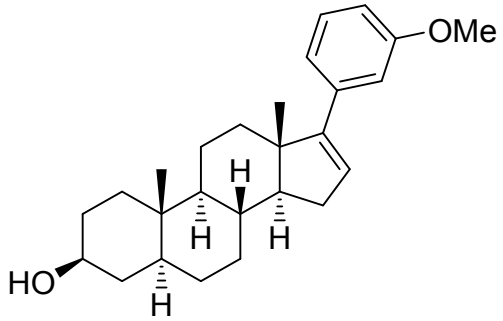
(3*β*, 5*α*)-17-(2‘-Methoxyphenyl)androst-16-en-3-ol (**4d**)



The synthesis followed the **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), ^{t}BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and *ortho*-bromoanisole (32 µL, 48 mg, 257 µmol, 1.30 equiv.). After column chromatography (silica gel, CH/EtOAc, 4:1) the product **4d** was obtained as a colourless solid (27 mg, 71.0 µmol, 36%).

***R**f* = 0.30 (EtOAc/CH, 1:3). – **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.22 (d, *J* = 7.8, 1.8 Hz, 1H, C*H*$_{Ar}$), 7.09 (dd, *J* = 7.4, 1.8 Hz, 1H, C*H*$_{Ar}$), 6.86 – 6.93 (m, 2H, C*H*$_{Ar}$), 5.76 (dd, ^3J = 3.2, 1.6 Hz, 1H, C*H*=CH$_2$), 3.78 (s, 3H, OC*H*$_3$), 3.61 (tt, ^3J = 10.9, 5.5 Hz, 1H, C*H*OH), 2.25 (ddd, *J* = 15.2, 6.1, 3.2 Hz, 1H, CH=C*H*$_2^a$), 2.02 (ddd, *J* = 15.2, 11.2, 1.7 Hz, 1H, CH=C*H*$_2^b$), 1.87 – 1.19 (m, 14H, 7 different C*H*$_2$ + 8-C*H* + C*H*), 1.21 – 1.11 (m, 1H, 5-C*H*), 1.07 – 0.96 (m, 2H, 2 different C*H*$_2$), 0.90 (s, 3H, C*H*$_3$), 0.85 (s, 3H, C*H*$_3$), 0.84 – 0.72 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 157.2 (*C*$_q$), 119.8 (+, *C*H$_{Ar}$), 152.4 (*C*$_q$), 130.3 (+, *C*H$_{Ar}$), 128.5 (+, *C*H=C$_q$), 127.7 (+, *C*H$_{Ar}$), 126.9 (+, *C*$_q$=CH$_{Ar}$), 110.5 (+, *C*H$_{Ar}$), 71.2 (+, *C*HOH), 56.8 (+, *C*H), 55.2 (+, O*C*H$_3$), 54.7 (+, *C*H), 48.8 (13-*C*$_q$), 45.0 (+, 5-*C*H), 38.1 (–, *C*H$_2$), 36.7 (–, *C*H$_2$), 35.5 (10-*C*$_q$), 34.8 (–, *C*H$_2$), 34.3 (+, 8-*C*H), 31.9 (–, *C*H$_2$), 31.4 (–, 2 × *C*H$_2$), 28.6 (–, *C*H$_2$), 21.1 (–, *C*H$_2$), 16.2 (+, 18-*C*H$_3$), 12.2 (+, 19-*C*H$_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3280 (br, vw), 2924 (w), 2844 (vw), 1592 (vw), 1488 (vw), 1450 (vw), 1432 (w), 1370 (vw), 1296 (vw), 1240 (w), 1179 (vw), 1111 (vw), 1079 (vw), 1029 (w), 956 (vw), 922 (vw), 817 (vw), 784 (vw), 748 (w), 656 (vw), 606 (vw), 569 (vw), 449 (vw) cm^{-1}. **MS** (EI, eV): *m/z* (%) = 380 [M]$^{\bullet+}$, 365 (38) [M – CH$_3$]$^+$, 257(24). – **HRMS** (EI, $C_{26}H_{36}O_2$): calc. = 380.2710; found = 380.2710.

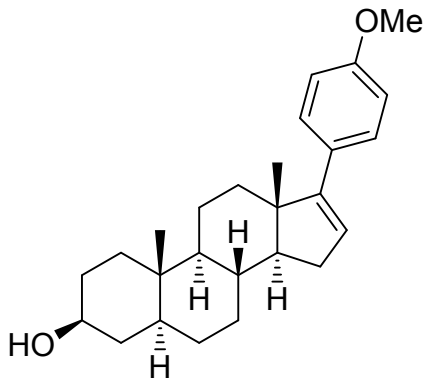
VKO-209: (3*β*, 5*α* 17-(3‘-Methoxyphenyl)androst-16-en-3-ol (**4e**)



The synthesis followed the **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), *t*BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and *ortho*-bromoanisole (32 µL, 48 mg, 257 µmol, 1.30 equiv.). After column chromatography (silica gel, CH/EtOAc, 4:1) the product **4e** was obtained as a colourless solid (24 mg, 63.9 µmol, 32%).

***R**_f* = 0.23 (EtOAc/CH, 1:3). – **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.21 (dd, *J* = 8.0 Hz, 1H, C*H*$_{Ar}$), 7.01 – 6.86 (m, 2H, 2 different C*H*$_{Ar}$), 6.83 – 6.72 (m, 1H, C*H*$_{Ar}$), 5.90 (dd, *J* = 3.3, 1.8 Hz, 1H, C*H*=CH_2), 3.80 (s, 3H, OC*H*$_3$), 3.60 (tt, *J* = 10.2, 4.6 Hz, 1H, C*H*OH), 2.20 (ddd, *J* = 15.5, 60.3, 3.3 Hz, 1H, CH=C*H*$_2^a$), 2.10 – 1.94 (m, 2H, C*H*$_2$ + CH=C*H*$_2^b$), 1.83 – 1.25 (m, 13H 7 different C*H*$_2$ + 8-C*H* + C*H*) 1.22 – 1.10 (m, 1H, 5-C*H*), 1.07 – 0.89 (m, 2H, 2 different C*H*$_2$), 1.01 (s, 3H, C*H*$_3$), 0.86 (s, 3H, C*H*$_3$), 0.84 – 0.67 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 159.1 (*C*$_q$OMe), 154.6 (*C*$_q$=CH), 138.6 (*C*$_q$=CH$_{Ar}$), 128.8 (+, *C*H$_{Ar}$), 127.3 (+, *C*H=C$_q$), 119.1 (+, *C*H$_{Ar}$), 112.4 (+, *C*H$_{Ar}$), 111.7 (+, *C*H$_{Ar}$), 71.1 (+, *C*HOH), 57.4 (+, *C*H), 55.0 (+, O*C*H$_3$), 54.6 (+, *C*H), 47.3 (13-*C*$_q$), 45.0 (+, 5-*C*H), 38.1 (–, *C*H$_2$), 36.7 (–, *C*H$_2$), 35.5 (10-*C*$_q$), 35.4 (–, *C*H$_2$), 34.0 (+, 8-*C*H), 31.8 (–, *C*H$_2$), 31.4 (–, 2 × *C*H$_2$), 28.5 (–, *C*H$_2$), 21.1 (–, *C*H$_2$), 16.6 (+, 18-*C*H$_3$), 12.2 (+, 19-*C*H$_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3330 (vw), 2926 (w), 2840 (vw), 1602 (vw), 1572 (w), 1486 (w), 1435 (w), 1371 (w), 1299 (w), 1264 (w), 1249 (vw), 1206 (w), 1176 (w), 1080 (w), 1047 (w), 1030 (w), 1006 (vw), 953 (vw), 903 (vw), 870 (vw), 830 (vw), 783 (w), 764 (w), 696 (w), 666 (w), 563 (vw), 444 (vw)– **MS** (EI, eV): *m/z* (%) = 380 $[M]^{\bullet+}$, 365 (40) $[M - CH_3]^+$, 257 (31).– **HRMS** (EI, $C_{26}H_{36}O_2$): calc. = 380.2710; found = 380.2710

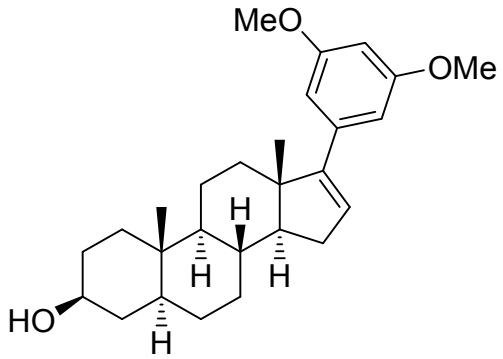
(3*β*, 5*α*)-17-(4'-Methoxyphenyl)androst-16-en-3-ol (**4f**)



The synthesis followed the **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), ^{t}BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and *para*-bromoanisole (32 µL, 48 mg, 257 µmol, 1.30 equiv.). After column chromatography (silica gel, CH/EtOAc, 4:1) the product **4f** was obtained as a colourless solid (41 mg, 108 µmol, 55%).

***R**$_f$* =0.27 (EtOAc/CH, 1:3) – **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.7 Hz, 2H, C*H*=CH–COMe), 6.83 (d, *J* = 8.7 Hz, 2H, C*H*=COMe), 5.79 (dd, ^3J = 3.3 Hz, ^3J = 1.8 Hz, 1H, C*H*=CH_2), 3.80 (s, 3H, OCH_3), 3.60 (ddd, ^3J = 15.8 , 10.7, 4.5 Hz, 1H, C*H*OH), 2.17 (ddd, ^3J = 15.4, 6.4, 3.2 Hz, 1H, CH=CH_2^a), 2.07 – 1.91 (m, 2H, CH=CH_2^b + CH_2), 1.90 – 1.75 (m, 1H, CH_2), 1.74 – 1.48 (m, 7H, -C*H* + C*H* + 5 different CH_2), 1.47 – 1.24 (m, 5H, 4 different CH_2), 1.19 – 1.10 (m, 1H, 5-C*H*), 1.08 – 0.92 (m, 2H, 2 different CH_2), 0.99 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 0.81 – 0.68 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (100 MHz, $CDCl_3$): δ = 158.3 (C_qOMe), 154.2 (C_q=CH), 129.9 (C_q=CH_{Ar}), 127.6 (+,2 × CH_{Ar}), 125.4 (+, *C*H=C_q), 113.3 (+, 2 × CH_{Ar}), 71.1 (+, *C*HOH), 57.4 (+, *C*H), 55.1 (+, OCH_3), 54.4 (+, *C*H), 47.2 (13-C_q), 44.9 (+, 5-*C*H), 38.1 (–, *C*H_2), 36.7 (–, *C*H_2), 35.5 (10-C_q), 35.5 (–, *C*H_2), 33.9 (+, 8-*C*H), 31.4 (–, *C*H_2), 31.4 (–, *C*H_2), 31.3 (–, *C*H_2), 28.5 (–, *C*H_2), 21.1 (–, 11-*C*H_2), 16.5 (+, 18-*C*H_3), 12.2 (+, 19-*C*H_3) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3232 (vw, br), 2927 (w), 2852 (w), 1601 (vw), 1508 (w), 1451 (vw), 1366 (vw), 1242 (w), 1176 (w), 1106 (vw), 1079 (vw), 1038 (w), 958 (vw), 833 (vw), 810 (w), 800 (w), 710 (vw), 625 (vw), 584 (vw), 507 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 380 (100) $[M]^{\bullet+}$, 365 $[M - CH_3]^+$. – **HRMS** (EI, $C_{26}H_{36}O_2$): calc. = 380.2710; found = 380.2711.

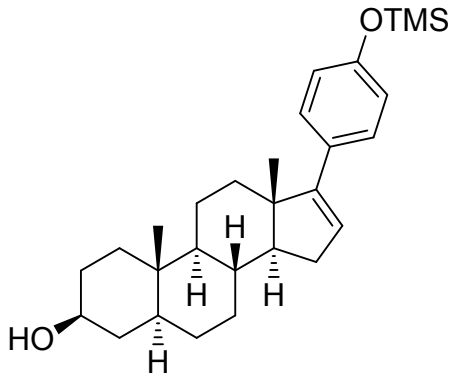
(3*β*, 5*α*)-17-(3',5'-Dimethoxyphenyl)-5*a*-androst-16-en-3-ol (**4g**)



The synthesis followed **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), ^{t}BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and 1-bromo-3,5-dimethoxybenzene (56 mg, 257 µmol, 1.30 equiv.). After column chromatography (silica gel, CH/EtOAc, 4:1) the product **4g** was obtained as a colourless solid (39 mg, 93.8 µmol, 47%).

***R**$_f$* = 0.18 (EtOAc/CH, 1:3). – **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 6.54 (d, ^4J = 2.3 Hz, 2H, 2'- and 6'-C*H*$_{Ar}$), 6.37 (dd, ^4J = 2.3 Hz, 1H, 4'-C*H*$_{Ar}$), 5.92 (dd, J = 3.0, 1.7 Hz, 1H, =C*H*), 3.80 (s, 6H, 2 × O*C*H$_3$), 3.61 (tt, J = 11.0, 4.7 Hz, 1H, C*H*OH), 2.20 (ddd, J = 15.6, 6.4, 3.3 Hz, 1H, =CHC*H*$_2^a$), 2.08 – 1.91 (m, 2H, =CHC*H*$_2^b$ + C*H*$_2$), 1.82 – 1.35 (m, 13H, 7 different C*H*$_2$ + 8-C*H* + C*H*), 1.20 – 1.07 (m, 1H, 5-C*H*), 1.02 – 0.98 (m, 2H, 2 different C*H*$_2$), 0.99 (s, 3H, C*H*$_3$), 0.85 (s, 3H, C*H*$_3$), 0.78 – 0.67 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 160.2 (2 × *C*$_q$OMe), 154.6 (*C*$_q$=CH), 127.5 (+, =*C*H), 139.1 (*C*$_{q,Ar}$), 104.8 (+,2' + 6'-*C*H$_{Ar}$), 98.5 (+, 4'-*C*H$_{Ar}$), 71.1 (+, *C*HOH), 57.4 (+, *C*H), 55.1 (+, 2 × O*C*H$_3$), 54.5 (+, *C*H), 47.3 (13-*C*$_q$), 44.9 (+, 5-*C*H), 38.0 (–, *C*H$_2$), 36.6 (–, *C*H$_2$), 35.5 (–, *C*H$_2$), 35.4 (10-*C*$_q$), 33.9 (+, 8-*C*H), 31.7 (–, *C*H$_2$), 31.3 (–,2 × *C*H$_2$), 28.5 (–, *C*H$_2$), 21.1(–, *C*H$_2$), 16.7 (+, *C*H$_3$), 12.2 (+, *C*H$_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3365 (br), 2931 (w), 2838 (w), 1605 (w), 1582 (w), 1449 (w), 1338 (w), 1202 (w), 1176 (w), 1162 (w), 1073 (w), 1037 (w), 1015 (w), 940 (w), 849 (w), 829 (w), 817 (w), 735 (vw), 692 (w), 675 (vw), 612 (vw), 543 (vw), 487 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 410 (35) $[M]^{\bullet+}$, 395 (16) $[M - CH_3]^+$, 278 (63), 214 (100). – **HRMS** (EI, $C_{27}H_{38}O_3$): calc. = 410.2815 found = 410.2813.

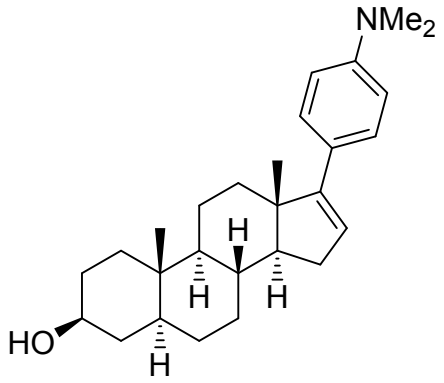
(3*β*, 5*α*)-17-(4‘-Trimethylsilylphenyl)androst-16-en-3-ol (**4h**)



The synthesis followed the **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), ^{t}BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and 1-bromo-4-(trimethylsiloxy)benzene (50 µL, 63 mg, 257 µmol, 1.30 equiv.). After column chromatography (silica gel, CH/EtOAc, 4:1) the product **4h** was obtained as a colourless solid (24 mg, 55.2 µmol, 28%).

***R*$_f$** = 0.57 (EtOAc/CH, 1:4). – **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.6 Hz, 2H, 3‘,5‘-C*H*), 6.76 (d, *J* = 8.4 Hz, 1H, 2‘,6‘-C*H*), 5.78 (dd, *J* = 3.3, 1.8 Hz, 1H, =C*H*), 3.57 (tt, *J* = 11.1, 4.7 Hz, 1H, C*H*OH), 2.17 (ddd, *J* = 15.8, 6.5, 3.3 Hz, 1H, =CHCH_2^a), 2.06 – 1.91 (m, 2H, =CHCH_2^b, CH_2), 1.75 – 1.58 (m, 5H, 4 different CH_2 + 5-C*H*), 1.53 – 1.25 (m, 8H, 5 different CH_2 + C*H*), 1.17 – 1.07 (m, 1H, 5-C*H*), 1.03 – 0.94 (m, 2H, 2 different CH_2), 0.98 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 0.73 – 0.68 (m, 1H, C*H*), 0.12 (s, 9H, Si(CH_3)$_3$) ppm. – **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 154.4 (C_q=CH, $C_{q,Ar}$), 154.2 ($C_{q,Ar}$), 129.9 ($C_{q,Ar}$), 127.8 (+, 2‘,6‘-*C*H$_{Ar}$), 125.4 (+, C_q=*C*H), 114.9 (+, 3‘,4‘-*C*H$_{Ar}$), 72.0 (+, *C*HOH), 57.5 (+, *C*H), 54.7 (+, *C*H), 47.2 (13-C_q), 45.2 (+, *C*H), 38.4 (–, *C*H$_2$), 36.9 (–, *C*H$_2$), 35.6 (10-C_q), 35.5 (–, *C*H$_2$), 34.0 (+, 5-*C*H), 31.9 (–, *C*H$_2$), 31.7 (–, *C*H$_2$), 31.3 (–, *C*H$_2$), 28.6 (–, *C*H$_2$), 21.1 (–, *C*H$_2$), 16.6 (+, 18-*C*H$_3$), 12.2 (+, 19-*C*H$_3$), 0.17 (Si(*C*H$_3$)$_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 2924 (w), 2851 (vw), 1560 (vw), 1509 (vw), 1444 (vw), 1377 (w), 1249 (w), 1174 (vw), 1092 (w), 1067 (w), 901 (vw), 882 (w), 835 (m), 749 (w), 694 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 439 (100) $[M]^{\bullet+}$, 423 (14) $[M - CH_3]^+$, 181 (25). – **HRMS** (EI, $C_{28}H_{42}O_2Si$): calc. = 438.3949; found = 438.2949.

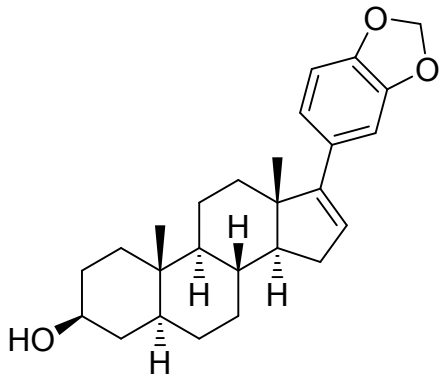
(3*β*, 5*α*) 17-(4'-(Dimethylamino)phenyl)-5*a*-androst-16-en-3-ol (**4i**)



The synthesis followed **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), ^{t}BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and 4-bromo-*N,N*-dimethylaniline (51 mg, 257 µmol, 1.30 equiv.). After column chromate-graphy (silica gel, CH/EtOAc, 4:1) the product **4i** was obtained as a colourless solid (28 mg, 70.6 µmol, 36%).

***R**$_f$* = 0.23 (EtOAc/CH, 1:3) – **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.9 Hz, 2',6'-C*H*$_{Ar}$), 6.68 (d, *J* = 8.8 Hz, 3',5'-C*H*$_{Ar}$), 5.75 (dd, *J* = 3.3, 1.8 Hz, 1H, =C*H*), 3.60 (tt, *J* = 10.7, 4.8 Hz, 1H, C*H*OH), 2.94 (s, 6H, N(C*H*$_3$)$_2$), 2.16 (ddd, *J* = 15.4, 6.5, 3.3 Hz, 1H, =CHC*H*$_2^a$), 2.09 (dd, *J* = 7.7, 2.5 Hz, 1H, C*H*$_2$), 1.96 (ddd, *J* = 15.4, 11.3, 1.8 Hz, 1H, =CHC*H*$_2^b$), 1.82 – 1.43 (m, 10H, C*H* + 8-C*H* + 6 different C*H*$_2$) , 1.35 – 1.26 (m, 3H, 2 different C*H*$_2$), 1.18 – 1.10 (m, 1H, 5-C*H*), 1.05 – 0.95 (m, 2H, 2 different C*H*$_2$), 1.00 (s, 3H, C*H*$_3$), 0.86 (s, 3H, C*H*$_3$), 0.78 – 0.72 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 154.4 (*C*$_q$N), 149.3 (*C*$_q$=CH), 127.2 (+, 3',5'-*C*H$_{Ar}$ + *C*$_q$C=CH), 123.7 (+, =*C*H), 112.1 (+, 2',6'-*C*H$_{Ar}$), 71.2 (+, *C*HOH), 57.4 (+, *C*H), 54.6 (+, *C*H), 47.1 (13-*C*$_q$), 44.9 (+, 5-*C*H), 40.4 (+, 2 × N*C*H$_3$), 38.1(–, *C*H$_2$), 36.7 (–, *C*H$_2$), 35.6 (–, *C*H$_2$), 35.5 (10-*C*$_q$), 33.9 (+, 8-*C*H), 31.8 (–, *C*H$_2$), 31.4 (–, *C*H$_2$), 31.2 (–, *C*H$_2$), 28.6 (–, *C*H$_2$), 21.2(–, *C*H$_2$), 16.6 (+, 18-*C*H$_3$), 12.2 (+, 19-*C*H$_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3262 (vw), 2919 (w), 2847 (w), 1609 (w), 1518 (w), 1444 (w), 1348 (w), 1224 (w), 1197 (w), 1158 (w), 1138 (w), 1080 (w), 1039 (w), 945 (w), 858 (vw), 824 (w), 797 (w), 709 (vw), 627 (vw), 569 (vw), 533 (vw), 510 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 393 (100) [M]$^{\bullet+}$. – **HRMS** (EI, $C_{27}H_{39}ON$): calc. = 393.3026 found = 393.3027.

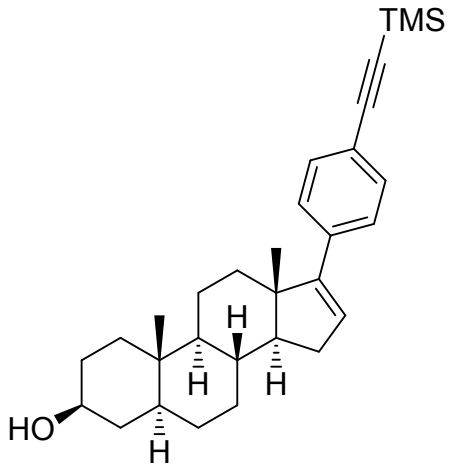
(3*β*, 5*α*)-17-(1‘,3‘-Benzodioxol-5-yl)-5*a*-androst-16-en-3-ol (**4j**)



The synthesis followed the **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), ^{t}BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and 5-bromo-1,3-benzodioxole (31 µL, 52.0 mg, 257 µmol, 1.30 equiv.). After column chromate-graphy (silica gel, CH/EtOAc, 4:1) the product **4j** was obtained as a colourless solid (28 mg, 71.0 µmol, 36%).

***R**$_f$* = 0.25 (EtOAc/CH, 1:3). - **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 6.90 – 6.80 (m, 2H, 4’ and 6’-C*H*), 6.74 (d, *J* = 8.0 Hz, 1H, 7’-C*H*), 5.93 (s, 2H, 2’-CH_2), 5.78 (dd, *J* = 3.3, 1.8 Hz, 1H, C_q=C*H*), 3.60 (tt, *J* = 10.2, 4.3 Hz, 1H, C*H*OH), 2.22 – 2.13 (m, 1H, =CHCH_2^a), 2.05 – 1.91 (m, 2H, =CHCH_2^b + CH_2), 1.84 – 1.57 (m, 7H, 4 different CH_2 + 8-C*H* + C*H*), 1.40 – 1.21 (m, 6H, 5 different CH_2), 1.21 – 1.09 (m, 1H, 5- C*H*), 1.03 – 0.94 (m, 2H, 2 different CH_2), 0.98 (s, 3H, 18- CH_3), 0.86 (s, 3H, 19-CH_3), 0.77 – 0.66 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 154.3 (C_q=CH), 147.2 (3a‘ or 7a‘-C_q), 146.2 (3a‘ or 7a‘-C_q), 131-4 (5‘-C_q), 126.1 (+, C_q=*C*H), 119.9 (+, 6‘-*C*H), 107.8 (+, 7‘-*C*H), 107.2 (+,4‘-*C*H), 100.7 (–, OCH_2O), 71.2 (+, *C*HOH), 57.4 (+, *C*H), 54.5 (+, *C*H), 47.3 (13-C_q), 44.9 (+, 5-*C*H), 38.1 (–, *C*H_2), 36.7 (–, *C*H_2), 35.5 (–, *C*H_2), 35.4 (10-C_q), 33.9 (+, 8-*C*H), 31.7 (–, *C*H_2), 31.4 (–, *C*H_2), 31.2 (–, *C*H_2), 28.5 (–, *C*H_2), 21.1 (–, *C*H_2), 16.6 (+, 18-*C*H_3), 12.2 (+, 12-*C*H_3) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3309 (br), 2921 (w), 2847 (w), 1707 (vw), 1500 (w), 14488 (w), 1442 (vw), 1372 (vw), 1344 (vw), 1262 (vw), 1243 (w), 1217 (vw), 1078 (vw), 1031 (w), 932 (vw), 858 (vw), 802 (vw), 748 (vw), 692 (vw), 570 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 394 (100) $[M]^{\bullet+}$, 379 (9) $[M - CH_3]^+$, 367 (17), 214 (20). – **HRMS** (EI, $C_{26}H_{34}O_3$): calc. = 394.2502, found = 394.2504.

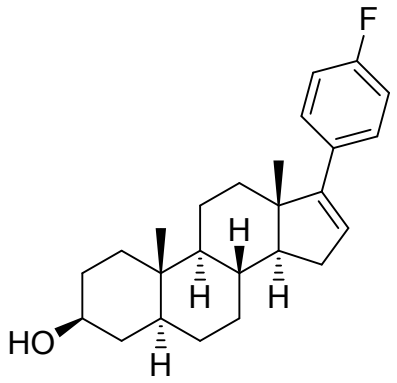
(3*β*, 5*α*)-17-(((4‘-Trimethylsilyl)ethynyl)phenyl)androst-16-en-3-ol (**4k**)



The synthesis followed the **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), ^{t}BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and (4-bromophenylethynyl)trimethylsilane (65 mg, 257 µmol, 1.30 equiv.). After column chromatography (silica gel, CH/EtOAc, 4:1) the product **4k** was obtained as a colourless solid (in mixture with **5**, 30%).

R_f = 0.38 (EtOAc/CH, 1:4). – **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.5 Hz, 2H, 3‘,5‘-C*H*), 7.21 (d, *J* = 8.4 Hz, 2H, 2‘,6‘-C*H*), 5.85 (dd, *J* = 3.4, 1.8 Hz, 1H, =C*H*), 3.59 – 3.41 (tt, *J* = 10.6, 1.8 Hz, 1H, C*H*OH), 2.11 (ddd, *J* = 15.8, 6.5, 3.3 Hz, 1H, =CHCH_2^a), 1.96 – 1.89 (m, 2H, =CHCH_2^b, CH_2), 1.78 – 1.58 (m, 3H, 3 different CH_2), 1.56 – 1.37 (m, 4H, 2 different CH_2, C*H*, 8-C*H*), 1.31 – 1.12 (m, 6H, 5 different CH_2), 1.12 – 1.00 (m, 1H, 5-C*H*), 0.92 (s, 3H, CH_3), 0.92 – 0.86 (m, 2H, 2 different CH_2), 0.77 (s, 3H, CH_3), 0.68 – 0.65 (m, 1H, C*H*), 0.16 (s, 9H, Si(CH_3)$_3$) ppm. – **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 154.1 (C_q=CH), 137.4 ($C_{q,Ar}$), 131.5 (+, *C*H$_{Ar}$), 128.1 (+, C_q=*C*H), 126.2 (+, *C*H$_{Ar}$), 121.0 ($C_{q,Ar}$), 105.1 (C_q), 94.1 (C_q), 71.1 (+, *C*HOH), 57.4 (+, *C*H), 54.5 (+, *C*H), 47.2 (13-C_q), 44.9 (+, 5-*C*H), 38.0 (–, *C*H$_2$), 36.6 (–, *C*H$_2$), 35.5 (10-C_q), 35.3 (–, *C*H$_2$), 33.9 (+, 8-*C*H), 31.7 (–, *C*H$_2$), 31.4 (–, *C*H$_2$), 31.3 (–, *C*H$_2$), 28.5 (–, *C*H$_2$), 21.1 (–, *C*H$_2$), 16.6 (+, 18-*C*H$_3$), 12.2 (+, 19-*C*H$_3$), -0.15 (Si(*C*H$_3$)$_3$). – **IR** (ATR): $\tilde{\nu}$ = 3294 (br), 2921 (w), 2849 (w), 2154 (vw), 1503 (vw), 1444 (vw), 1370 (vw), 1247 (w), 1106 (vw), 1079 (vw), 1039 (vw), 862 (w), 840 (w), 810 (w), 758 (w), 699 (vw), 675 (vw), 622 (vw), 585 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 446 (14) [M]$^{\bullet+}$, 346 (22), 274 [defunctionalized steroid] (100), 259 (63), 241 (35), 148 (67). – **HRMS** (EI, $C_{30}H_{42}OSi$): calc. = 446.2999; found = 446.2998.

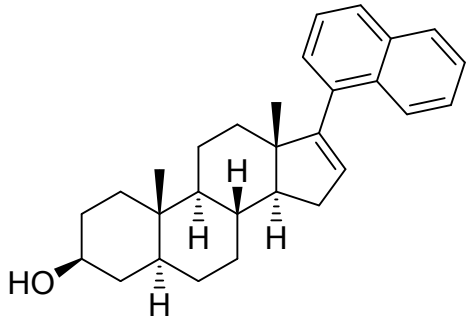
(3*β*, 5*α*)-17-(4'-Fluorophenyl)androst-16-en-3-ol (**4l**)



The synthesis followed the **GP-1** using vinylbromide **2-Br** (65 mg, 184 µmol, 1.00 equiv.), ^{t}BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.30 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and 1-bromo-4-fluorobenzene (26µL, 48 mg, 257 µmol, 1.40 equiv.). After column chromatography (silica gel, CH/EtOAc, 4:1) the product **4l** was obtained as a colourless solid (18 mg, 49.1 µmol, 27%).

***R**$_f$* = 0.41 (EtOAc/CH, 1:3) – **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.30 (m, 2H, C*H*$_{Ar}$), 6.97 (m, 2H, C*H*$_{Ar}$), 5.83 (dd, ^3J = 3.3 = 1.8 Hz, 1H, C*H*=CH$_2$), 3.60 (tt, ^3J = 11.1, 4.8 Hz, 1H, C*H*OH), 2.19 (ddd, *J* = 15.5, 6.5, 3.3 Hz, 1H, CH=C*H*$_2^a$), 2.05 – 1.89 (m, 2H, CH=C*H*$_2^b$, C*H*$_2$), 1.84 – 1.77 (m, 1H, C*H*$_2$), 1.75 – 1.50 (m, 7H, 8-C*H* + C*H* + 5 different C*H*$_2$), 1.46 – 1.25 (m, 5H, 4 different C*H*$_2$), 1.20 – 1.18 (m, 1H, 5-C*H*), 1.05 – 0.93 (m, 2H, 2 different C*H*$_2$), 0.98 (s, 3H, C*H*$_3$), 0.86 (s, 3H, C*H*$_3$), 0.81 – 0.68 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (100 MHz, $CDCl_3$): δ = 161.7 (d, ^1J = 245.4Hz, *C*F), 153.7(*C*$_q$=CH), 133.2 (d, *J* = 3.3 Hz, *C*$_q$=CH$_{Ar}$), 128.0 (+, d, *J* = 7.7 Hz, 2 × *C*H$_{Ar}$), 126.9 (+, *J* = 1.4 Hz, C$_q$=*C*H), 114.7 (+, d, *J* = 21.2 Hz, 2 × *C*H$_{Ar}$), 71.1 (+, *C*H, *C*HOH), 57.4 (+, *C*H), 54.5 (+, *C*H), 47.2 (13-*C*$_q$), 44.9 (+, 5-*C*H), 38.0 (–, *C*H$_2$), 36.6 (–, *C*H$_2$), 35.5 (10-*C*$_q$), 35.3 (–, *C*H$_2$), 33.9 (+, 8-*C*H), 31.7 (–, *C*H$_2$), 31.3 (–, 2 × *C*H$_2$), 28.5 (–, *C*H$_2$), 21.0 (–, 11-*C*H$_2$), 16.4 (+, 18-*C*H$_3$), 12.1 (+, 19-*C*H$_3$) ppm. – ^{19}F-NMR (375 MHz, $CDCl_3$): δ = -120.5 (s, 1F) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3329 (vw), 2922 (w), 2848 (vw), 1599 (vw), 1505 (w), 1443 (vw), 1370 (vw), 1259 (w), 1223 (vw), 1157 (vw), 1224 (vw), 1158 (vw), 1079 (vw), 1029 (vw), 800 (w), 696 (vw), 623 (vw), 574 (vw), 503 (vw), 402 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 368 $[M]^{\bullet+}$, 353 (12), 166 (57), 82 (100). – **HRMS** (EI, $C_{25}H_{33}O_1F_1$): calc. = 368.2510; found = 368.2510.

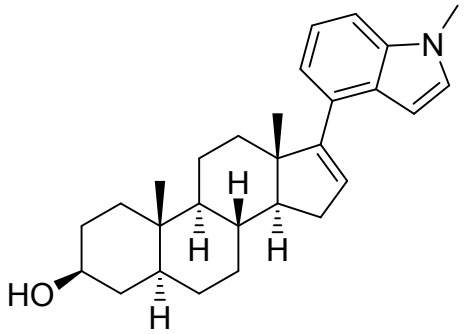
(3*β*, 5*α*)-17-(4‘-Naphtyl)androst-16-en-3-ol (**4m**)



The synthesis followed the **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), *t*BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and 1-bromonaphthalene (35 µL, 53 mg, 257 µmol, 1.30 equiv.). After column chromatography (silica gel, CH/EtOAc, 4:1) the product **4m** was obtained as a colourless solid (43 mg, 106 µmol, 54%).

***R*f** = 0.29 (EtOAc/CH, 1:4). – **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.98 – 7.88 (m, 1H, C*H*$_{Ar}$), 7.72 – 7.66 (m, 1H, C*H*$_{Ar}$), 7.60 (d, *J* = 8.2 Hz, 1H, C*H*$_{Ar}$), 7.35 – 7.26 (m, 3H, C*H*$_{Ar}$), 7.14 – 7.07 (m, 1H, C*H*$_{Ar}$), 5.60 (dd, *J* = 3.2, 1.6 Hz, 1H, =C*H*), 3.46 (tt, *J* = 10.6, 5.0 Hz, 1H, C*H*OH), 2.23 (ddd, *J* = 15.2, 6.4, 3.1 Hz, 1H, =CHC*H*$_2^a$), 2.03 (ddd, *J* = 15.2, 11.0, 1.6 Hz, 1H, =CHC*H*$_2^b$), 1.71 – 1.50 (m, 5H, C*H* + 8-C*H* + 3 different C*H*$_2$), 1.47 – 1.33 (m, 3H, 3 different C*H*$_2$), 1.26 – 1.10 (m, 6H, 5 different C*H*$_2$), 1.07 – 0.91 (m, 2H, 5-C*H* + C*H*$_2$), 0.82 (s, 3H, C*H*$_3$), 0.90 – 0.77 (m, 1H, C*H*$_2$), 0.71 (s, 3H, C*H*$_3$), 0.76 – 0.62 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 153.7 (*C*$_q$=CH), 144.9 (+, =*C*H), 137.0 (*C*$_{q,Ar}$), 134.6 (*C*$_{q,Ar}$), 133.7 (*C*$_{q,Ar}$), 130.5 (+, *C*H$_{Ar}$), 128.9 (+, *C*H$_{Ar}$), 127.8 (+, *C*H$_{Ar}$), 127.7 (+, *C*H$_{Ar}$), 126.4 (+, *C*H$_{Ar}$), 126.3 (+, *C*H$_{Ar}$), 125.8 (+, *C*H$_{Ar}$), 72.2 (+, *C*HOH), 58.3 (+, *C*H), 55.8 (+, *C*H), 50.7 (13-*C*$_q$), 46.1 (+, 5-*C*H), 39.1 (–, *C*H$_2$), 37.8 (–, *C*H$_2$), 36.7 (10-*C*$_q$), 36.1 (–, *C*H$_2$), 35.5 (+, 8-*C*H), 33.1 (–, *C*H$_2$), 33.0 (–, *C*H$_2$), 32.4 (–, *C*H$_2$), 29.6 (–, *C*H$_2$), 22.1 (–, *C*H$_2$), 17.4 (+, 18-*C*H$_3$), 13.3 (+, 19-*C*H$_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3338 (br), 3040 (vw), 2919 (w), 2847 (w), 1505 (vw), 1443 (w), 1367 (w), 1261 (vw), 1131 (vw), 1077 (vw), 1036 (w), 951 (vw), 922 (vw), 834 (vw), 798 (w), 775 (m), 735 (w), 678 (vw), 657 (vw), 605 (vw), 493 (vw), 427 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 400 (16) [M]$^{\bullet+}$, 274 [defunctionalized steroid] (60), 259 (41), 181 (66). – **HRMS** (EI, $C_{29}H_{36}O$): calc. = 400.2761; found = 400.2762.

(3*β*, 5*α*)-17-(1'-Methyl-1*H*-indol-4'-yl)-5-androst-16-en-3-ol (**4n**)

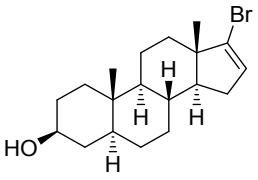


The synthesis followed **GP-1** using vinylbromide **2-Br** (70 mg, 198 µmol, 1.00 equiv.), ^{t}BuLi in *n*-pentane (1.9 M, 0.32 mL, 614 µmol, 3.10 equiv.), $Pd_2(dba)_3$ (9 mg, 9.90 µmol, 5 mol%), XPhos (19 mg, 39.6 µmol, 20 mol%) and 5-bromo-1-methyl-*1H*-indole (54 mg, 257 µmol, 1.30 equiv.). After column chromate-graphy (silica gel, CH/EtOAc, 4:1) the product **4n** was obtained as a colourless solid (20 mg, 50.3 µmol, 25%).

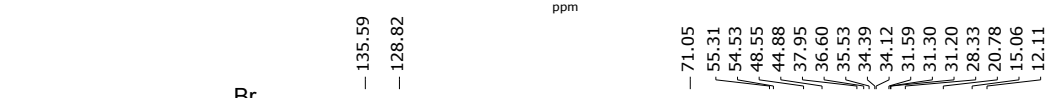
***R**f* = 0.34 (EtOAc/CH, 1:2) – **^{1}H-NMR** (400 MHz, $CDCl_3$ + d_3-MeOD): δ = 7.62 (m, 1H, C*H*$_{Ar}$), 7.17 (m, 2H, 2 × C*H*$_{Ar}$), 7.03 (d, *J* = 3.1 Hz, 1H, 2'-C*H*$_{Ar}$), 6.46 (d, *J* = 3.1 Hz, 1H, 3'-C*H*$_{Ar}$), 5.84 (dd, *J* = 3.0, 1.7 Hz, 1H, C_q=C*H*), 3.78 (s, 3H, NC*H*$_3$), 3.60 (tt, *J* = 10.6, 4.6 Hz, 1H, C*H*OH), 2.12 (ddd, *J* = 15.2, 6.3, 3.2 Hz, 1H, =CHC*H*$_2$[a]), 2.06 – 2.01 (m, 1H, C*H*$_2$), 1.92 (ddd, *J* = 15.4, 11.0, 1.9 Hz, 1H, =CHC*H*$_2$[b]), 1.69 – 1.18 (m, 13H, 7 different C*H*$_2$ + 8-C*H* + C*H*), 1.10 – 1.03 (m, 1H, 5-C*H*), 0.97 (s, 3H, C*H*$_3$), 0.94 – 0.87 (m, 2H, 2 different C*H*$_2$), 0.79 (s, 3H, C*H*$_3$), 0.73 – 0.66 (m, 1H, C*H*) ppm. – **^{13}C-NMR** (101 MHz, $CDCl_3$ + d_3-MeOD): δ = 155.6 (*C*$_q$=CH), 135.6 (*C*$_{q,Ar}$N), 128.7 (+, 2'-N*C*H$_{Ar}$), 128.5 (*C*$_{q,Ar}$), 128.0 (*C*$_{q,Ar}$), 124.9 (+, C_q=*C*H), 121.1 (+, *C*H$_{Ar}$), 118.4 (+, *C*H$_{Ar}$), 108.5 (+, 7'-*C*H$_{Ar}$), 100.8 (+, 3'-*C*H$_{Ar}$), 70.8 (+, *C*HOH), 57.4 (+, *C*H), 54.5 (+, *C*H), 47.3 (13-*C*$_q$), 44.8 (+, 5-*C*H), 37.6(–, *C*H$_2$), 36.6 (–, *C*H$_2$), 35.5 (–, *C*H$_2$), 35.4 (10-*C*$_q$), 33.9 (+, 8-*C*H), 32.5 (+, NC*H*$_3$), 31.7 (–, *C*H$_2$), 31.2 (–, *C*H$_2$), 30.9 (–, *C*H$_2$), 28.5 (–, *C*H$_2$), 21.1(–, *C*H$_2$), 16.5 (+, *C*H$_3$), 12.1 (+, *C*H$_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3266 (br), 2923 (w), 2857 (w), 1510 (vw), 1487 (vw), 1441 (vw), 1357 (w), 1333 (w), 1272 (vw), 1248 (vw), 1154 (vw), 1115 (vw), 1078 (vw), 1045 (w), 956 (vw), 908 (vw), 875 (vw), 796 (w), 759 (vw), 719 (w), 673 (vw), 652 (vw), 632 (vw), 576 (vw), 541 (vw) 498 (vw) cm^{-1}. – **MS** (EI, eV): *m/z* (%) = 403 (100) [M]$^{\bullet+}$, 367 (14), 278 (20), 214 (30). – **HRMS** (EI, $C_{28}H_{37}ON$): calc. = 403.2870 found = 403.2870.

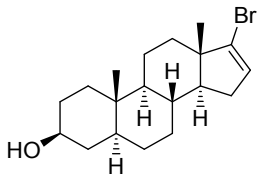
2.3. ^{1}H and ^{13}C NMR spectra of the steroids

(3*β*, 5*α*)-17-Bromoandrost-16-en-3-ol (**1a-Br**)

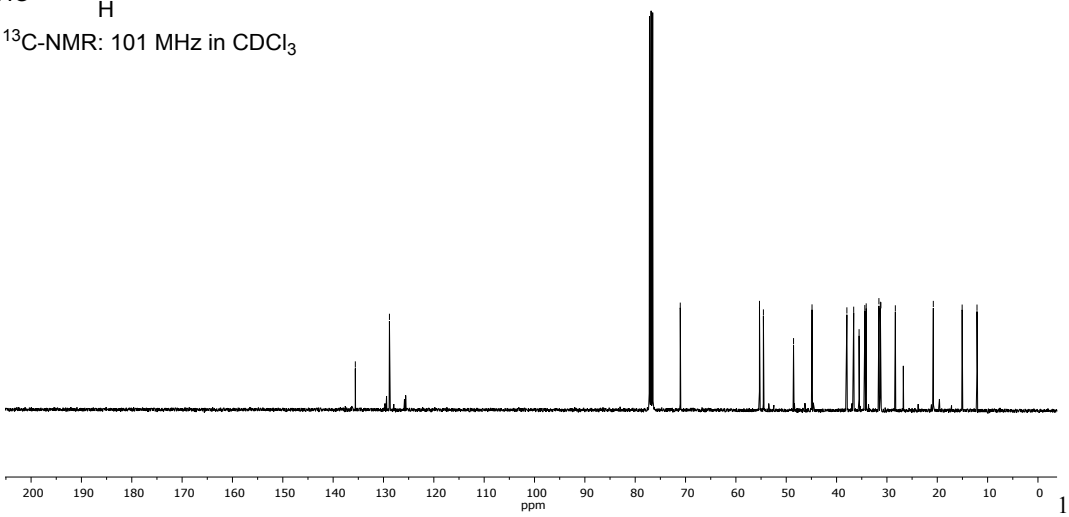


^{1}H-NMR: 400 MHz in $CDCl_3$



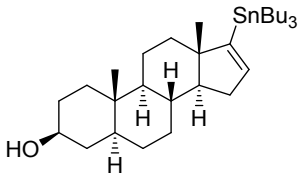


^{13}C-NMR: 101 MHz in $CDCl_3$

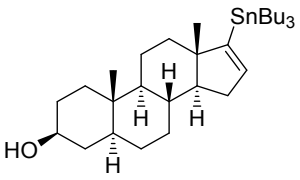


1H-NMR contains traces of DCM.

(3*β*, 5*α*)-17-Tributyltinandrost-16-en-3-ol (**1a-SnBu$_3$**)

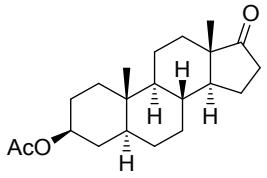


^{1}H-NMR: 400 MHz in $CDCl_3$

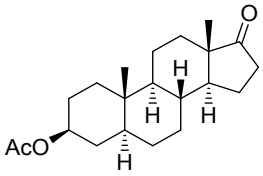


^{13}C-NMR: 101 MHz in $CDCl_3$

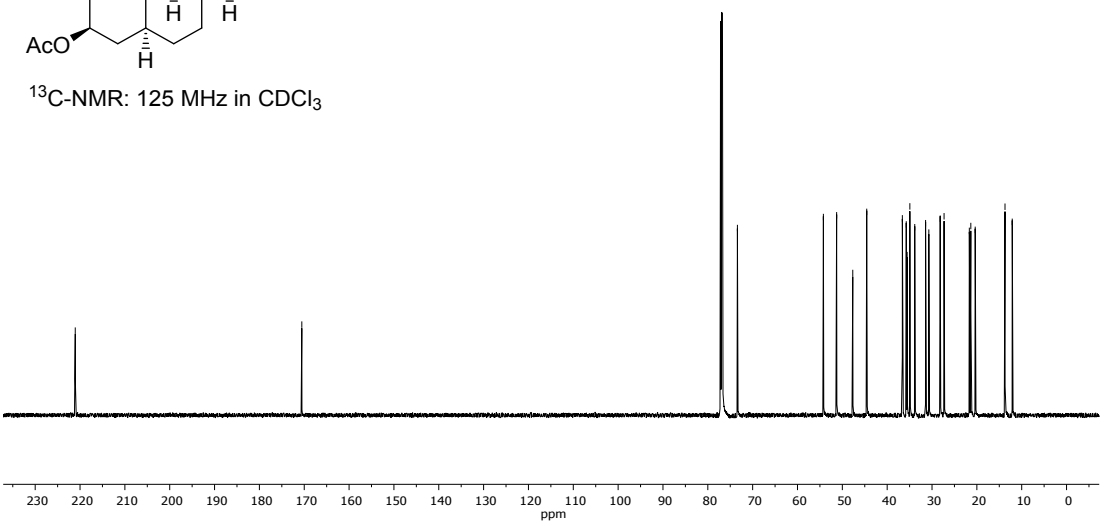
3*β*-Acetyloxy-5*α*-androstan-17-on



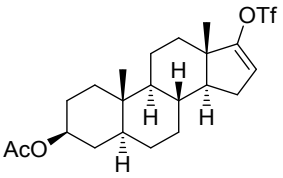
^{1}H-NMR: 600 MHz in $CDCl_3$



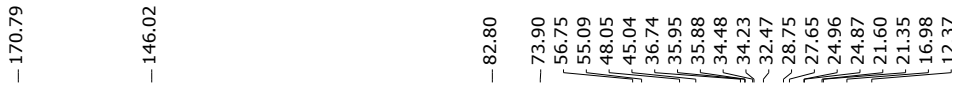
^{13}C-NMR: 125 MHz in $CDCl_3$

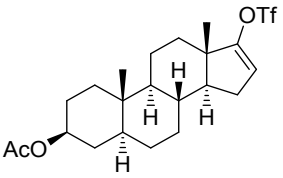


3*β*-Acetyloxy-5*α*-androst-16-en-17-triflate (**1b-OTf**)

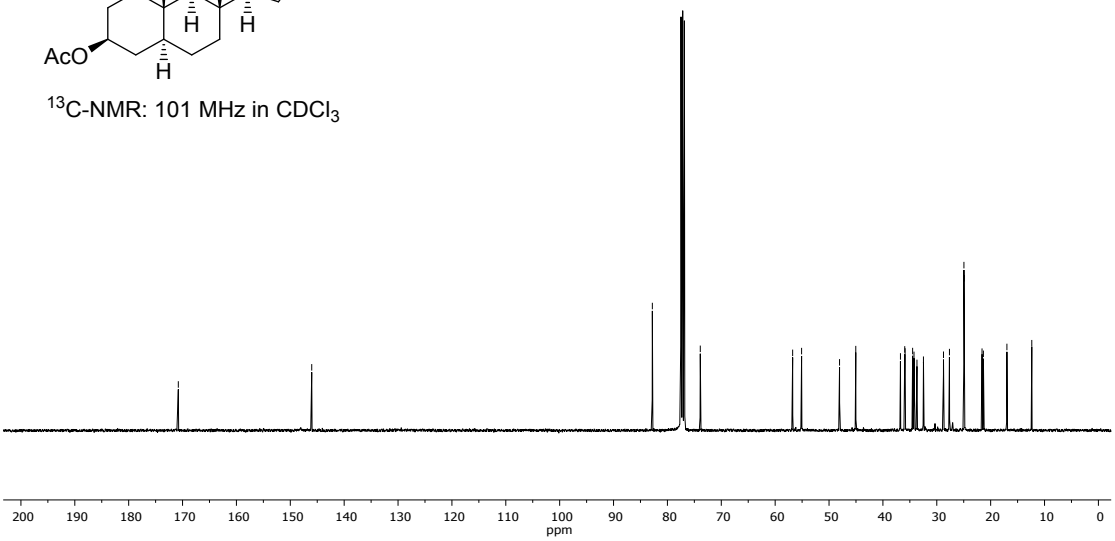


^{1}H-NMR: 300 MHz in $CDCl_3$

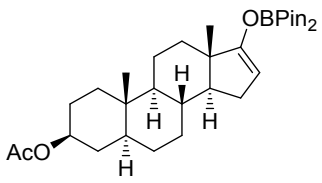




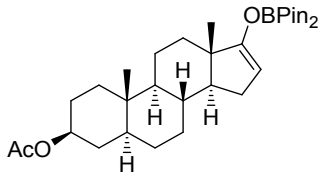
^{13}C-NMR: 101 MHz in $CDCl_3$



3*β*-Acetyloxy-17-(4',4',5',5'-Tetramethyl-1',3',2'-dioxaborolan-2-yl)-5*α*-androst-16-en (**1b-Pin$_2$**)

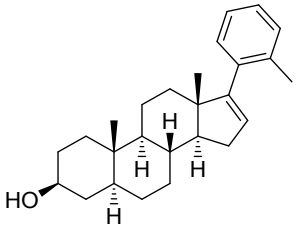


^{1}H-NMR: 300 MHz in $CDCl_3$

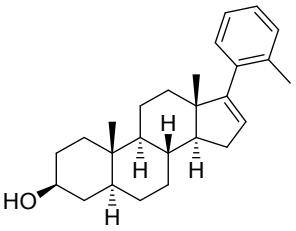


^{13}C-NMR: 101 MHz in $CDCl_3$

(3*β*, 5*α*)-17-(2'-Methylphenyl)-5*a*-androst-16-en-3-ol (**4a**)



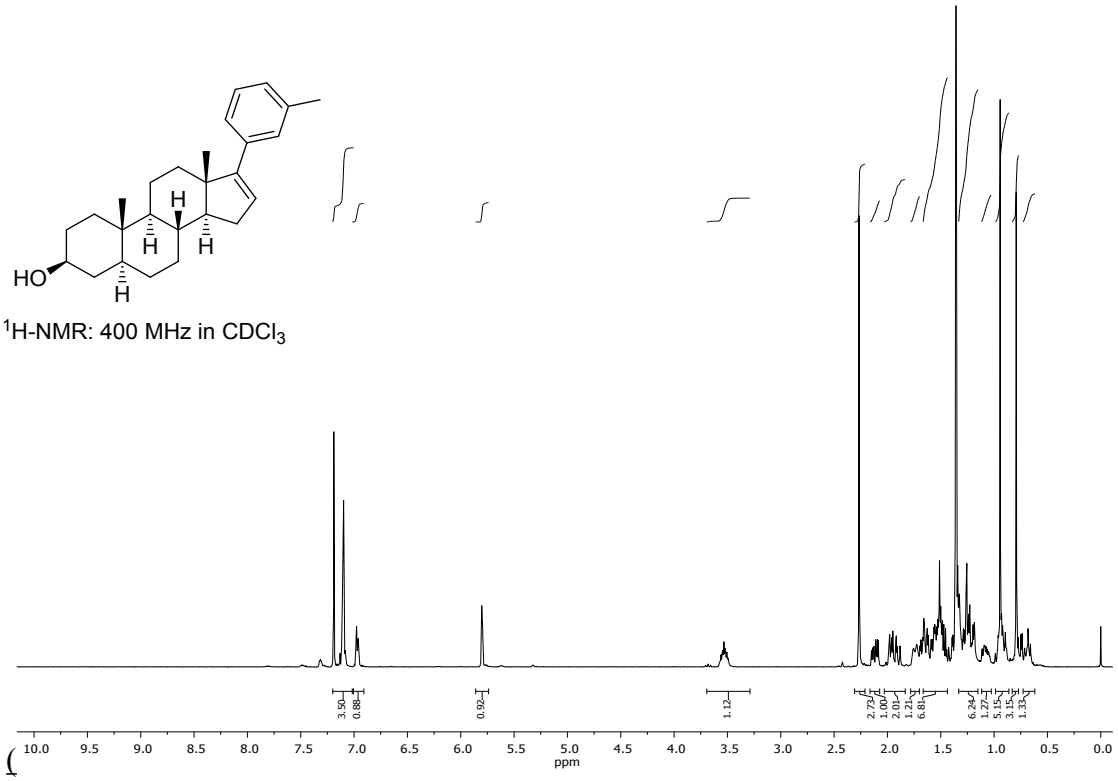
^{1}H-NMR: 400 MHz in $CDCl_3$



^{13}C-NMR: 101 MHz in $CDCl_3$

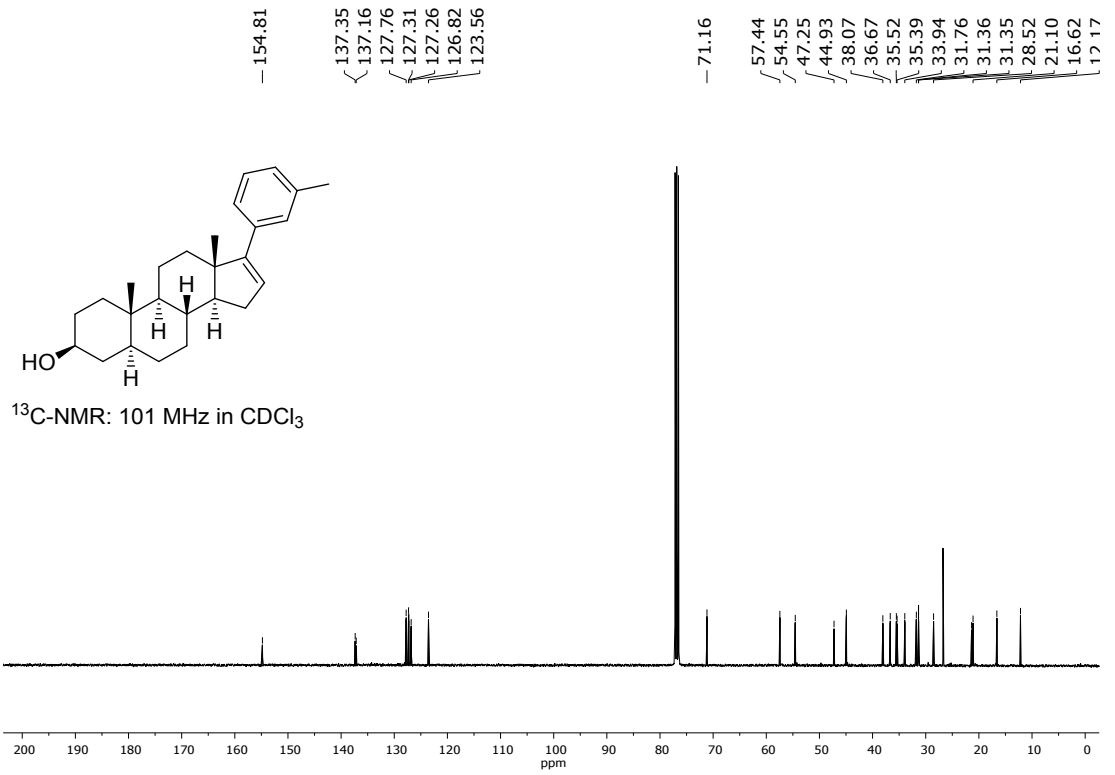
* slightly impured by CH

(3*β*, 5*α*)-17-(3'-Methylphenyl)-5*a*-androst-16-en-3-ol (**4b**)



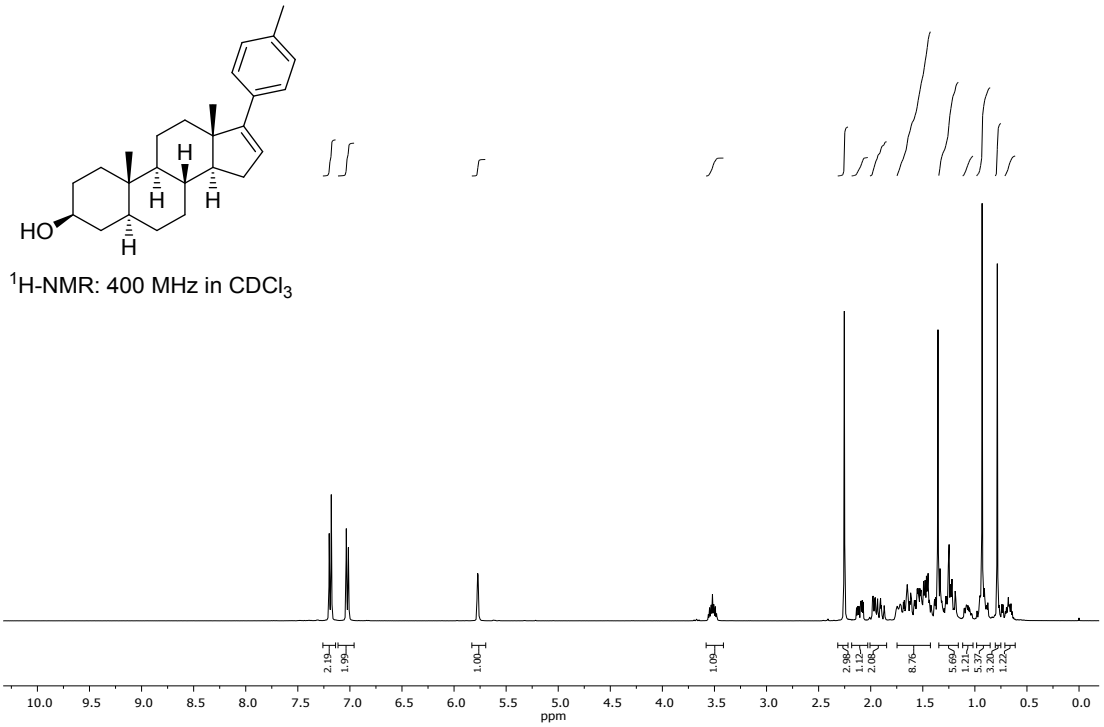
^{1}H-NMR: 400 MHz in $CDCl_3$

(

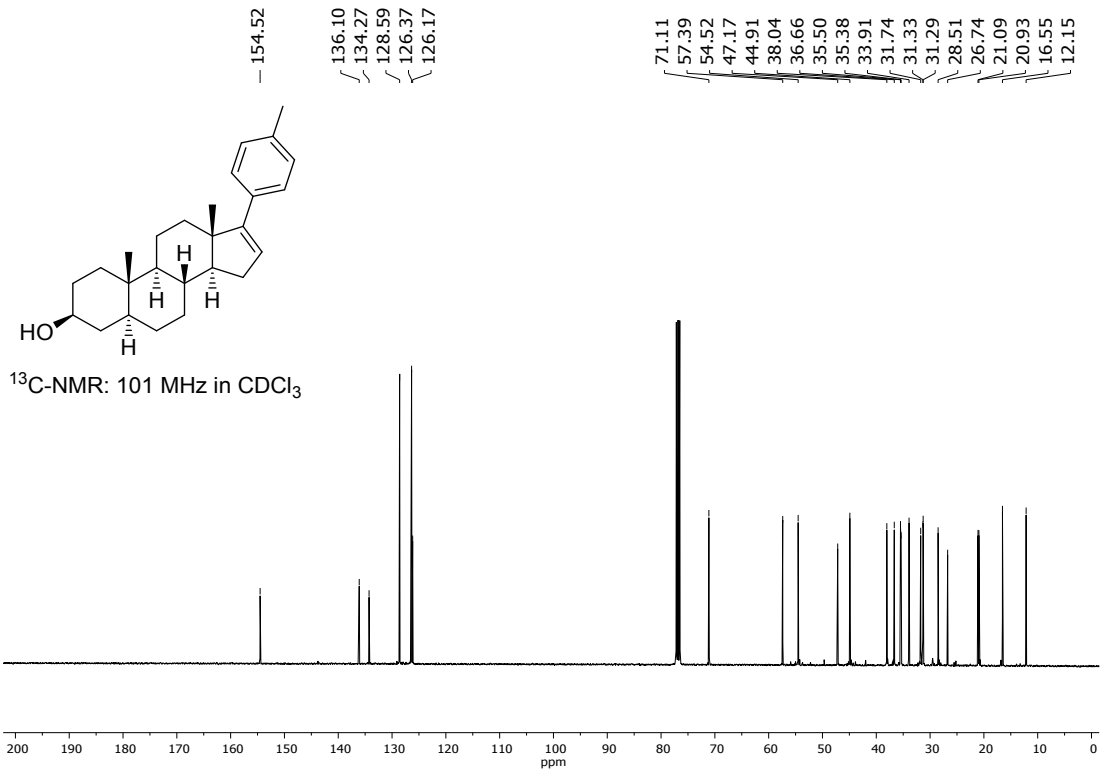


^{13}C-NMR: 101 MHz in $CDCl_3$

(3*β*, 5*α*)-17-(4'-Methylphenyl)-5*a*-androst-16-en-3-ol (**4c**)



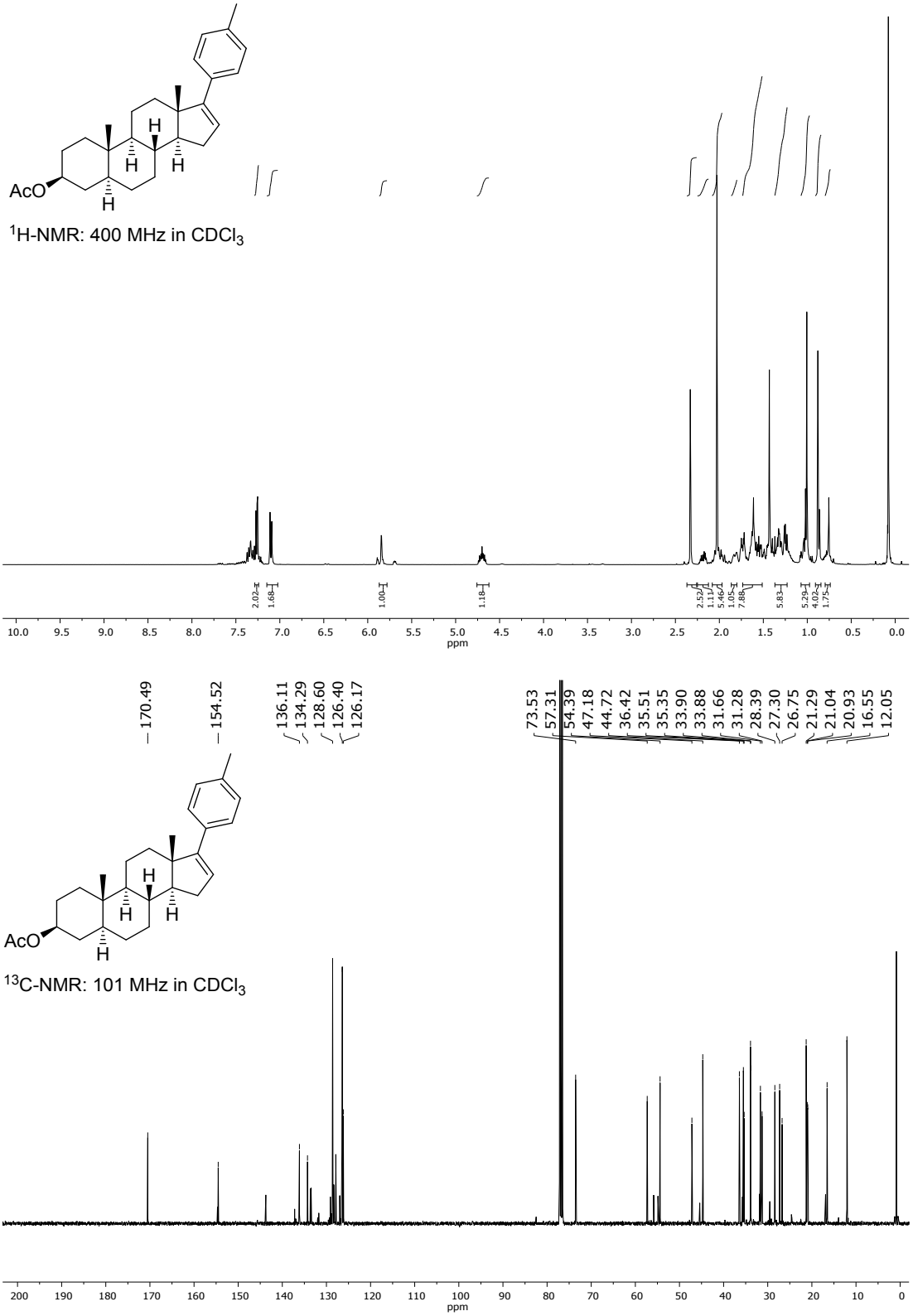
^{1}H-NMR: 400 MHz in $CDCl_3$



^{13}C-NMR: 101 MHz in $CDCl_3$

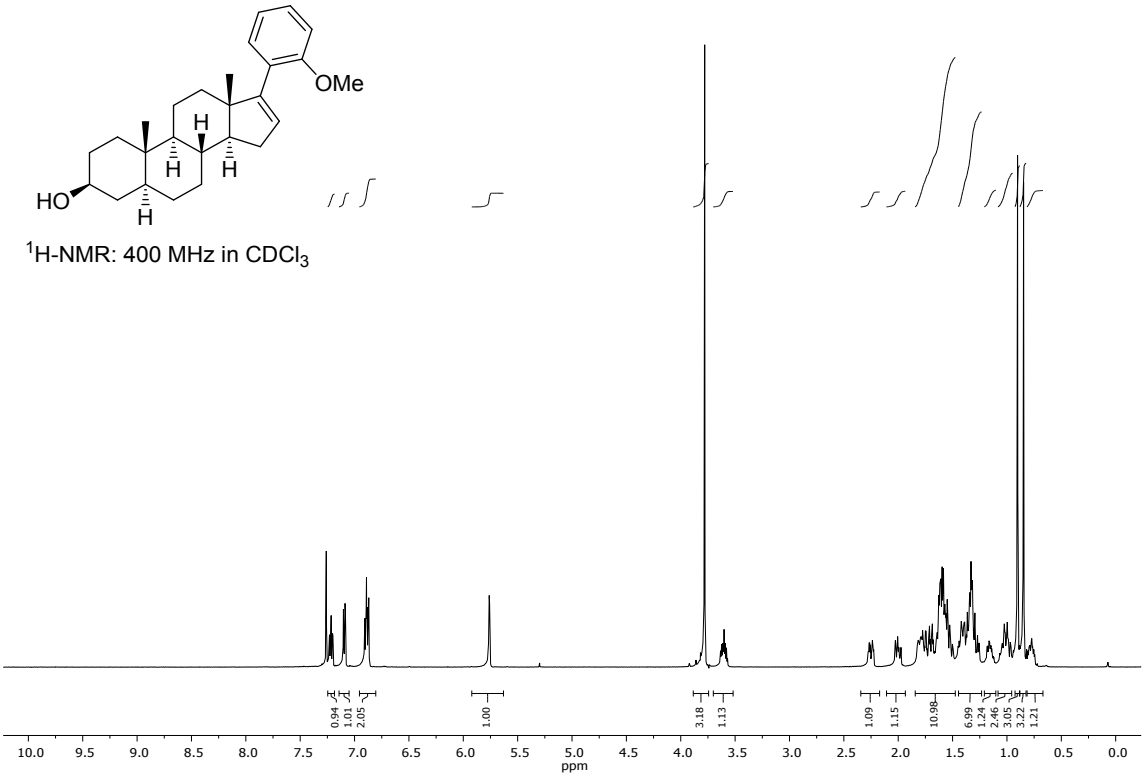
* slightly impured by CH

3*β*-Acetyloxy-17-(4'-methylphenyl)-5*α*-androst-16-en (**4c-OAc**)

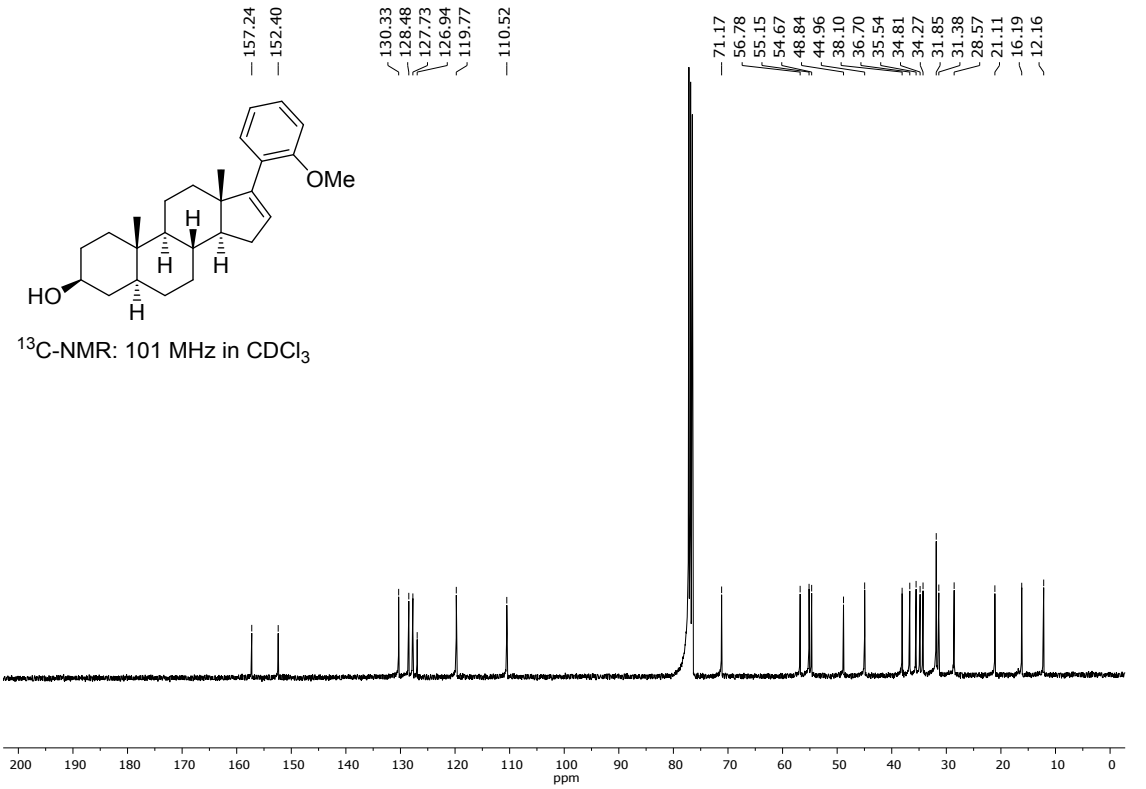


NMR spectra contain not completely separable rests of the defunctionalized steroid (ratio of the product to the defunctionalized according 1H NMR spectrum: 1 : 0.17.)

(3β, 5α)-17-(2'-Methoxyphenyl)androst-16-en-3-ol (**4d**)



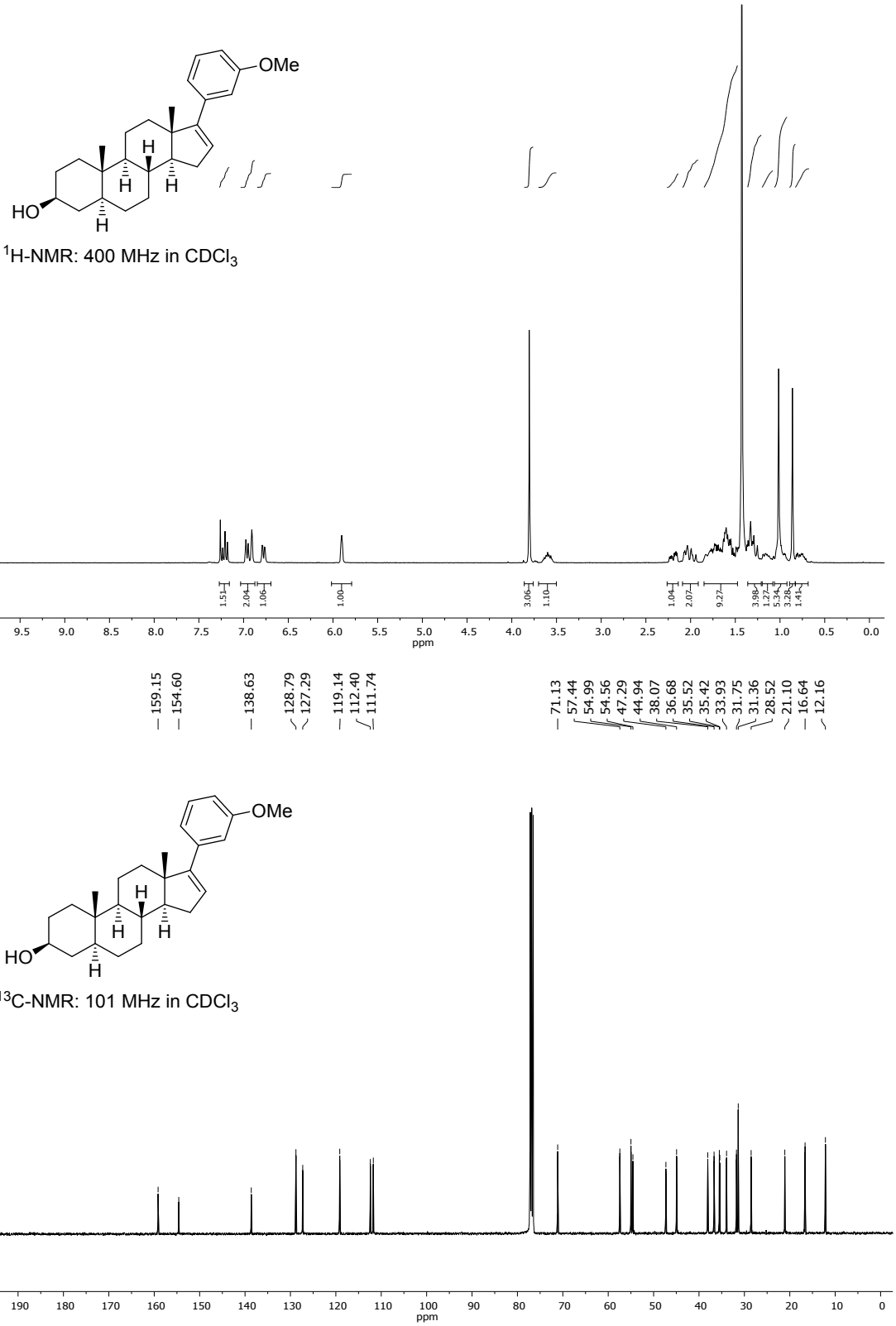
^{1}H-NMR: 400 MHz in $CDCl_3$



^{13}C-NMR: 101 MHz in $CDCl_3$

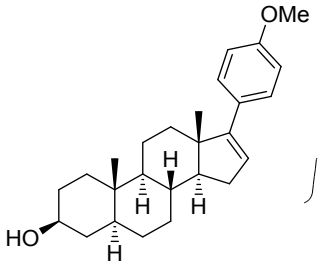
* slightly impured by CH

(3*β*, 5*α*)-17-(3'-Methoxyphenyl)androst-16-en-3-ol (**4e**)

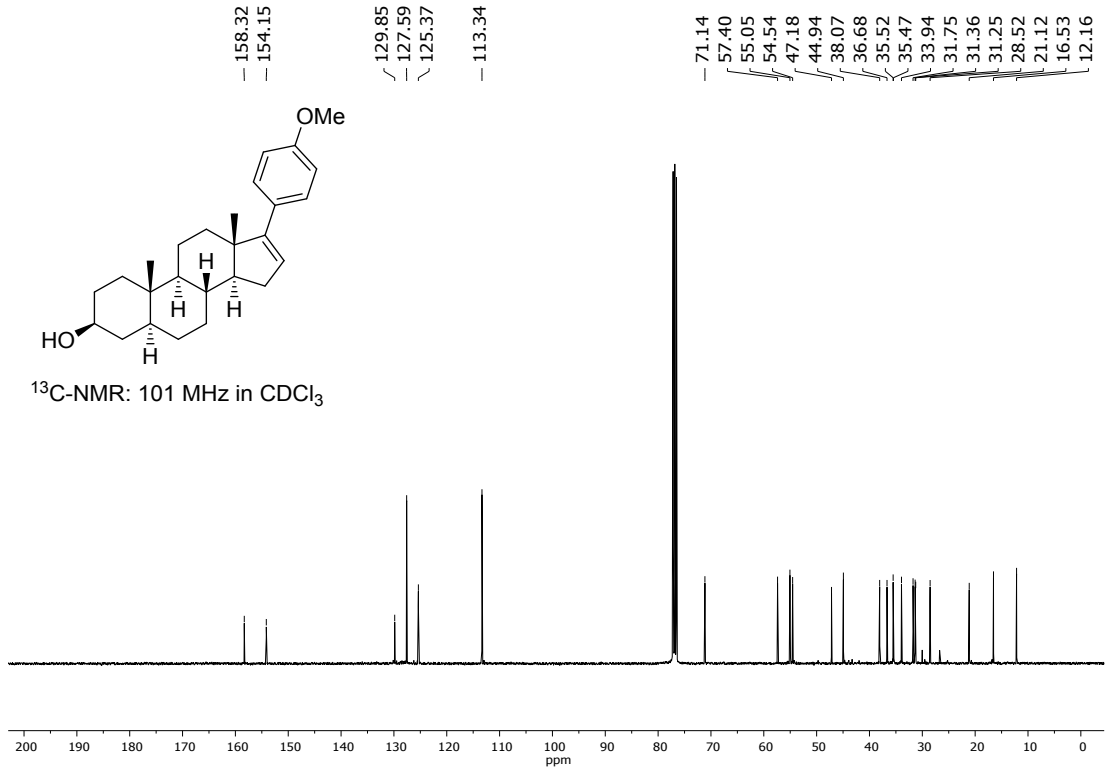


* slightly impured by CH

(3*β*, 5*α*)-17-(4'-Methoxyphenyl)androst-16-en-3-ol (**4f**)

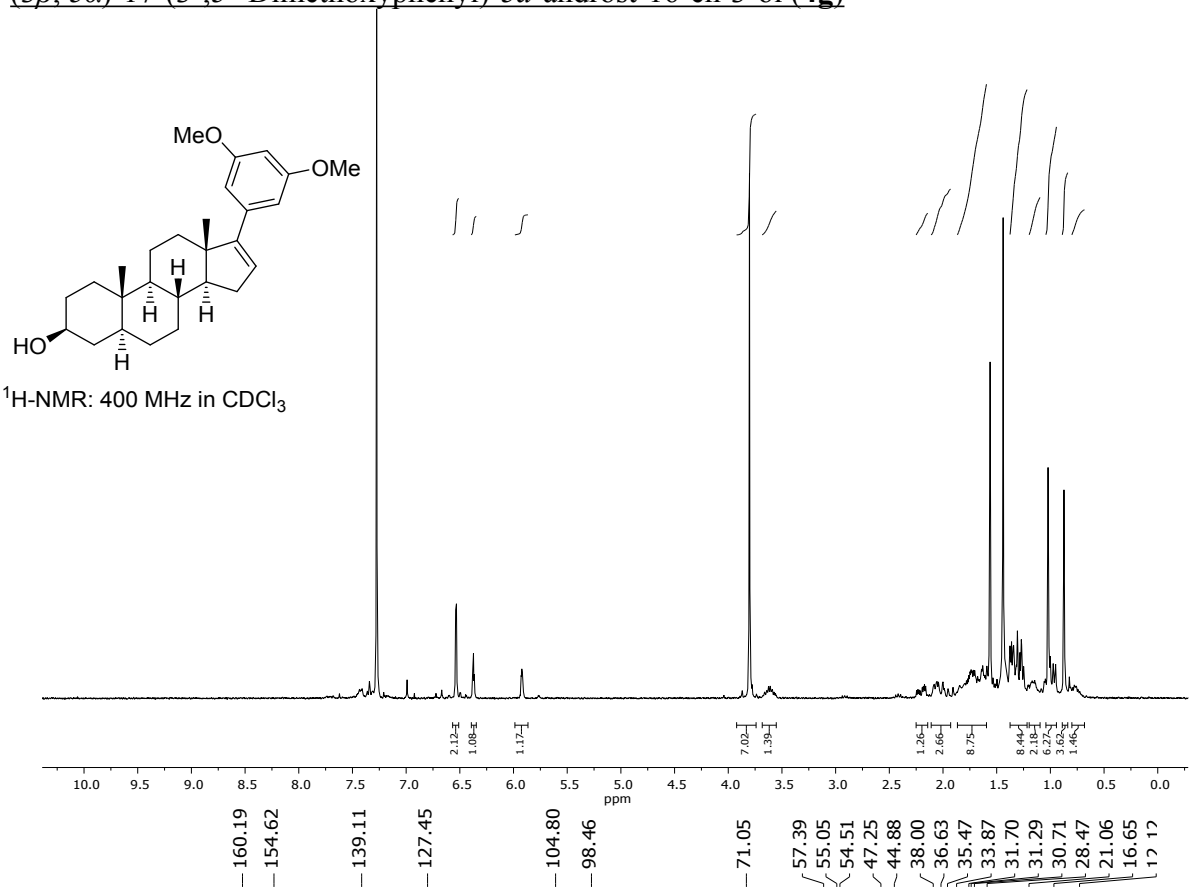


^{1}H-NMR: 400 MHz in $CDCl_3$

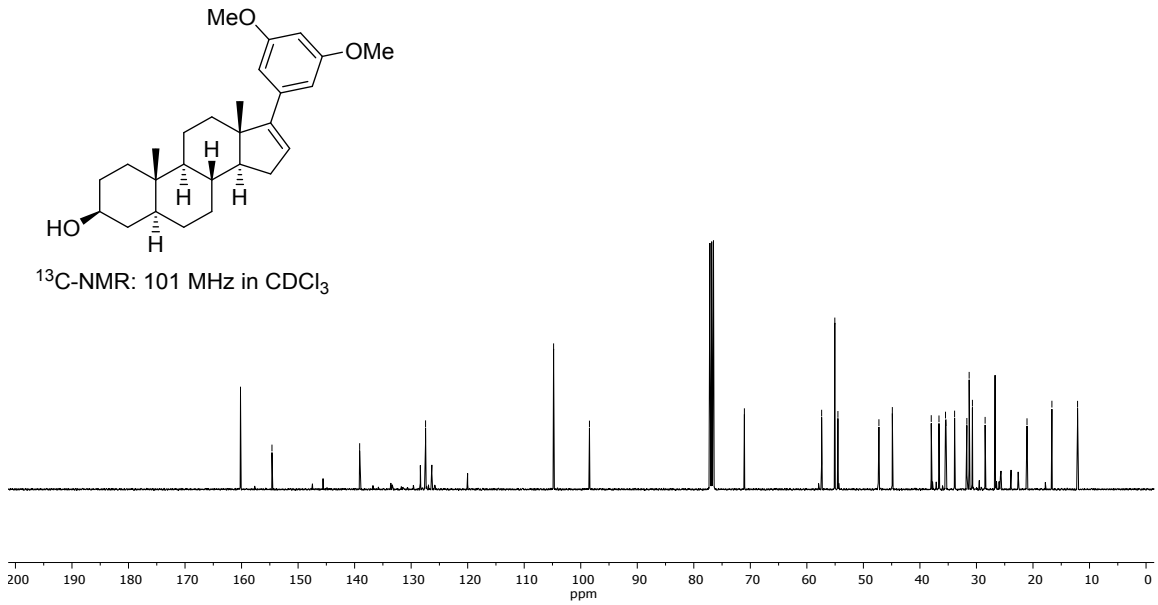


^{13}C-NMR: 101 MHz in $CDCl_3$

(3*β*, 5*α*)-17-(3',5'-Dimethoxyphenyl)-5*a*-androst-16-en-3-ol (**4g**)



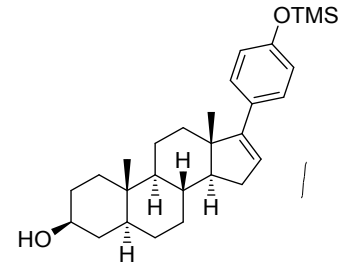
^{1}H-NMR: 400 MHz in $CDCl_3$



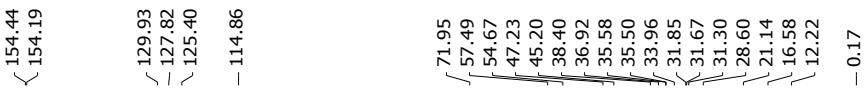
^{13}C-NMR: 101 MHz in $CDCl_3$

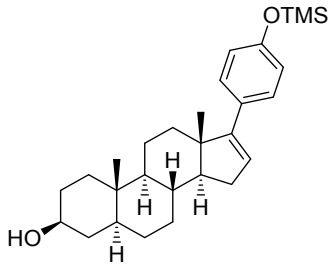
* spectra show impurities of CH and an aromatic impuritie

(3*β*, 5*α*)-17-(4‘-Trimethylsilylphenyl)androst-16-en-3-ol (**4h**)

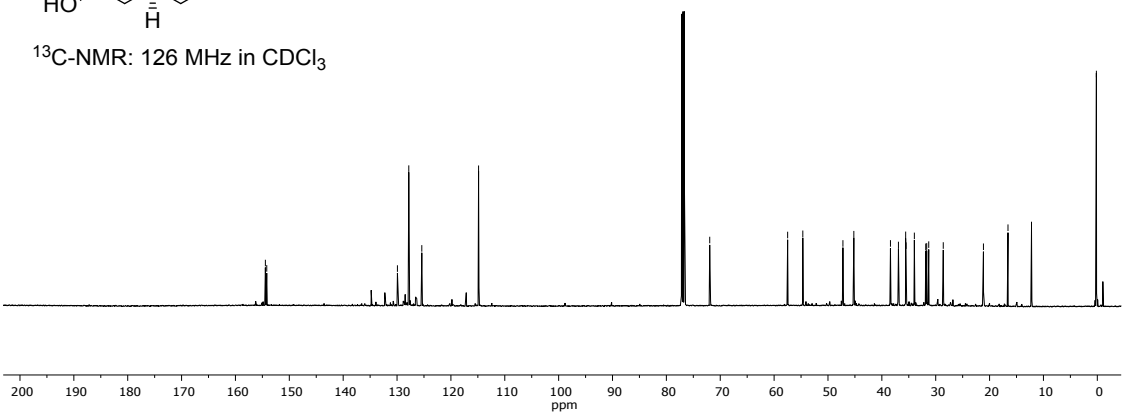


^{1}H-NMR: 500 MHz in $CDCl_3$

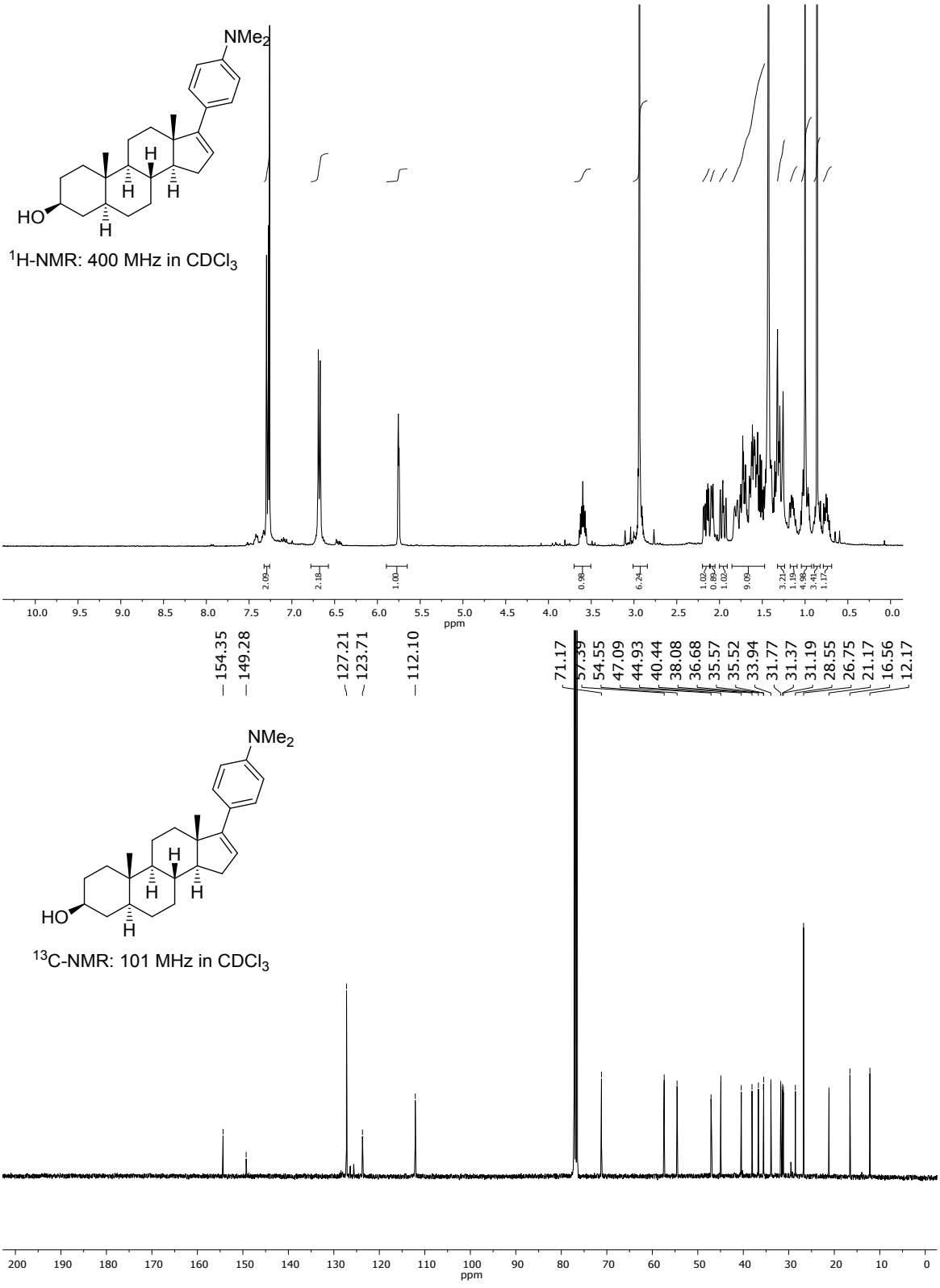




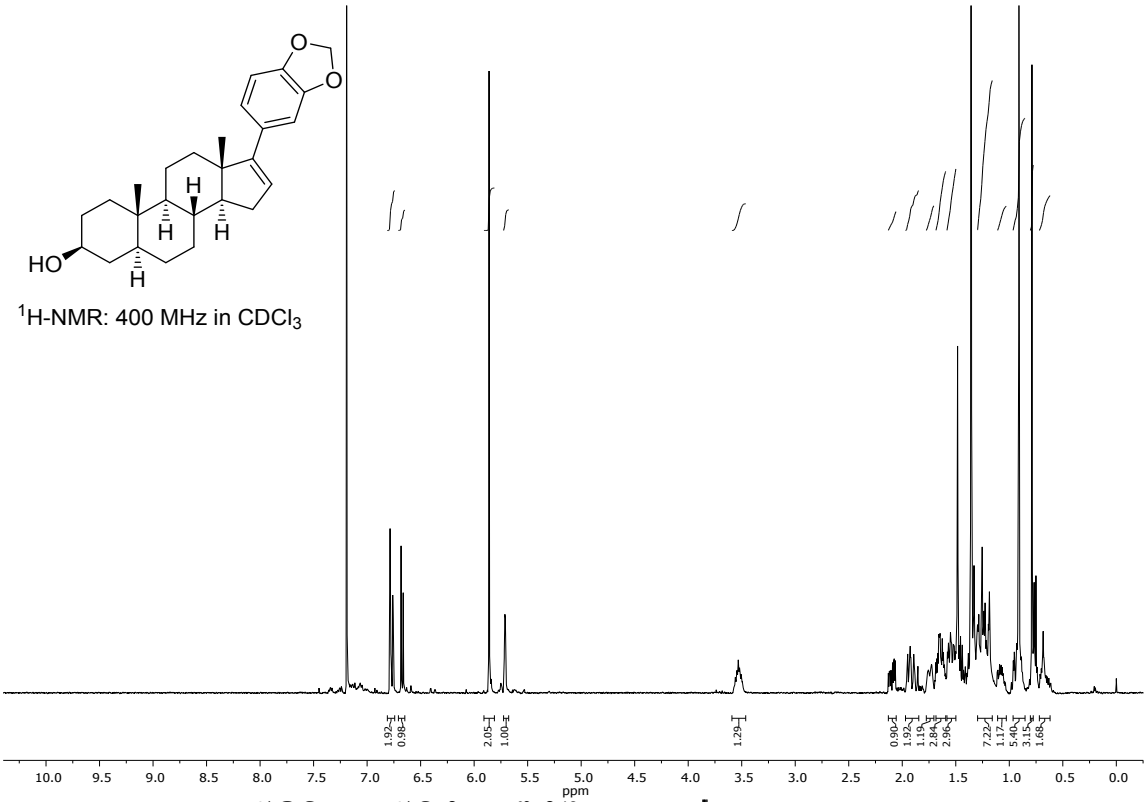
^{13}C-NMR: 126 MHz in $CDCl_3$



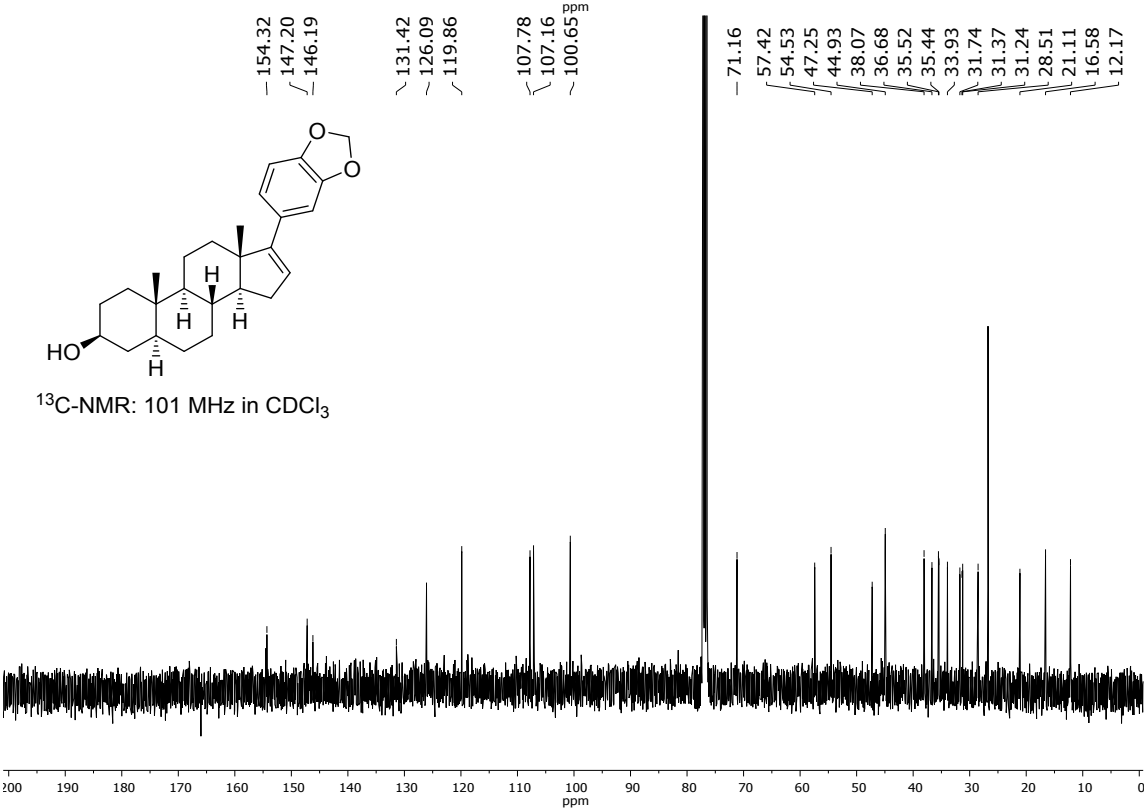
(3*β*, 5*α*) 17-(4'-(Dimethylamino)phenyl)-5*a*-androst-16-en-3-ol (**4i**)



(3*β*, 5*α*)-17-(1‘,3‘-Benzodioxol-5-yl)-5*a*-androst-16-en-3-ol (**4m**)



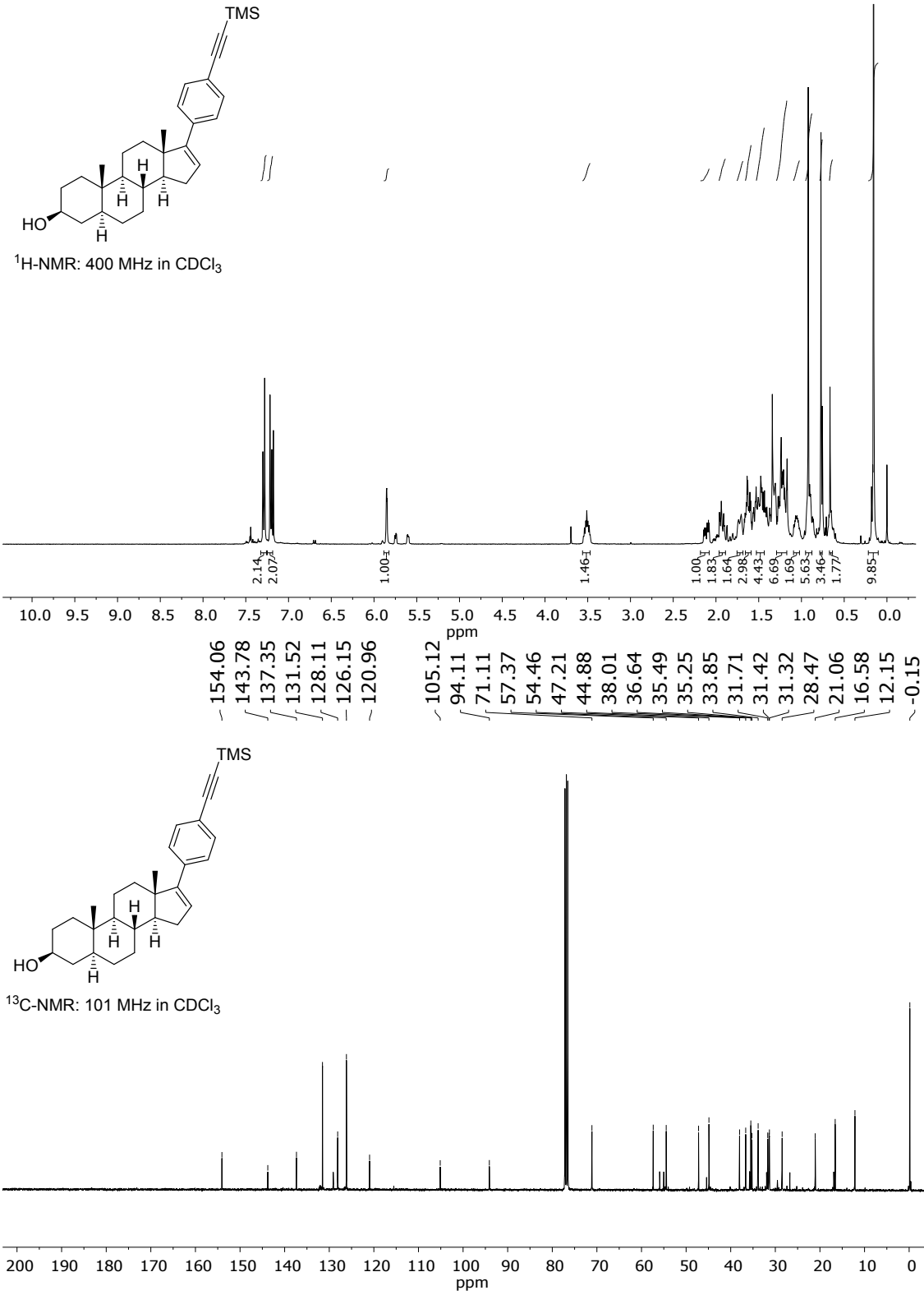
^{1}H-NMR: 400 MHz in $CDCl_3$



^{13}C-NMR: 101 MHz in $CDCl_3$

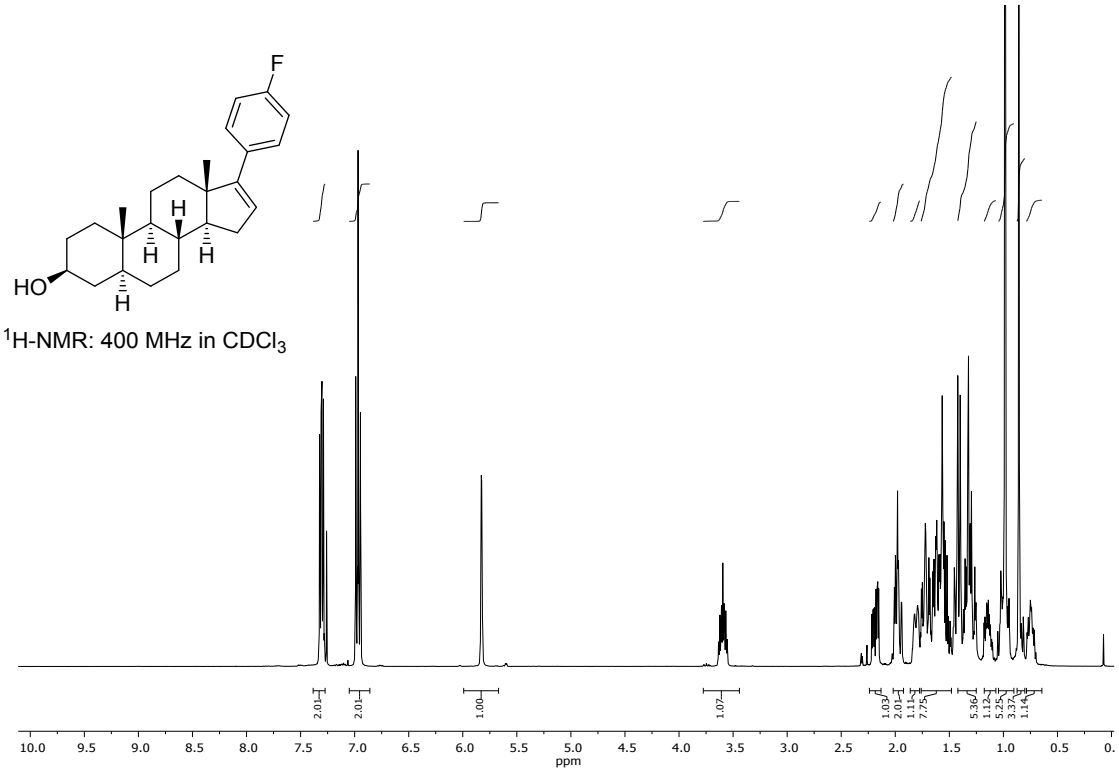
* slightly impured by CH

(3*β*, 5*α*)-17-(((4‘-Trimethylsilyl)ethynyl)phenyl)androst-16-en-3-ol (**h**)

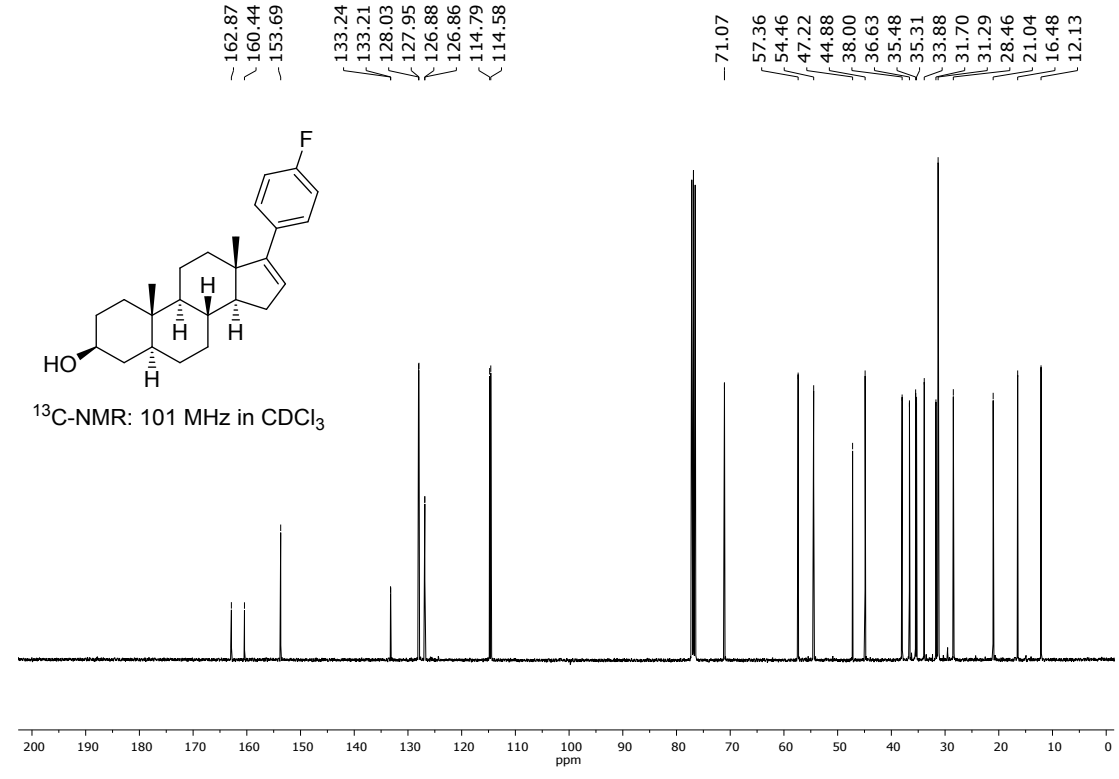


*impured by defunctionalized steroid **5**

(3β, 5α)-17-(4'-Fluorophenyl)androst-16-en-3-ol (**4l**)

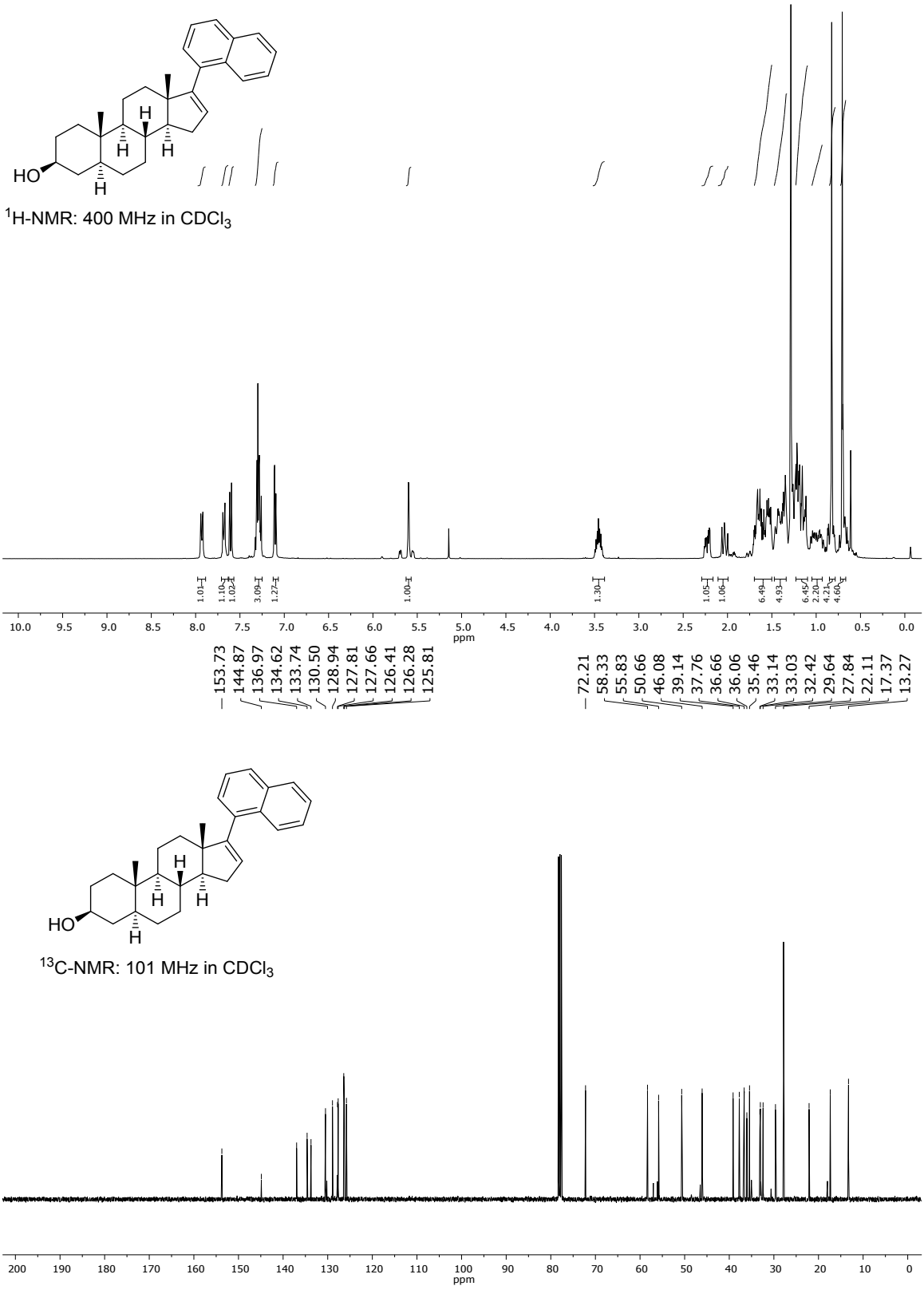


^{1}H-NMR: 400 MHz in $CDCl_3$



^{13}C-NMR: 101 MHz in $CDCl_3$

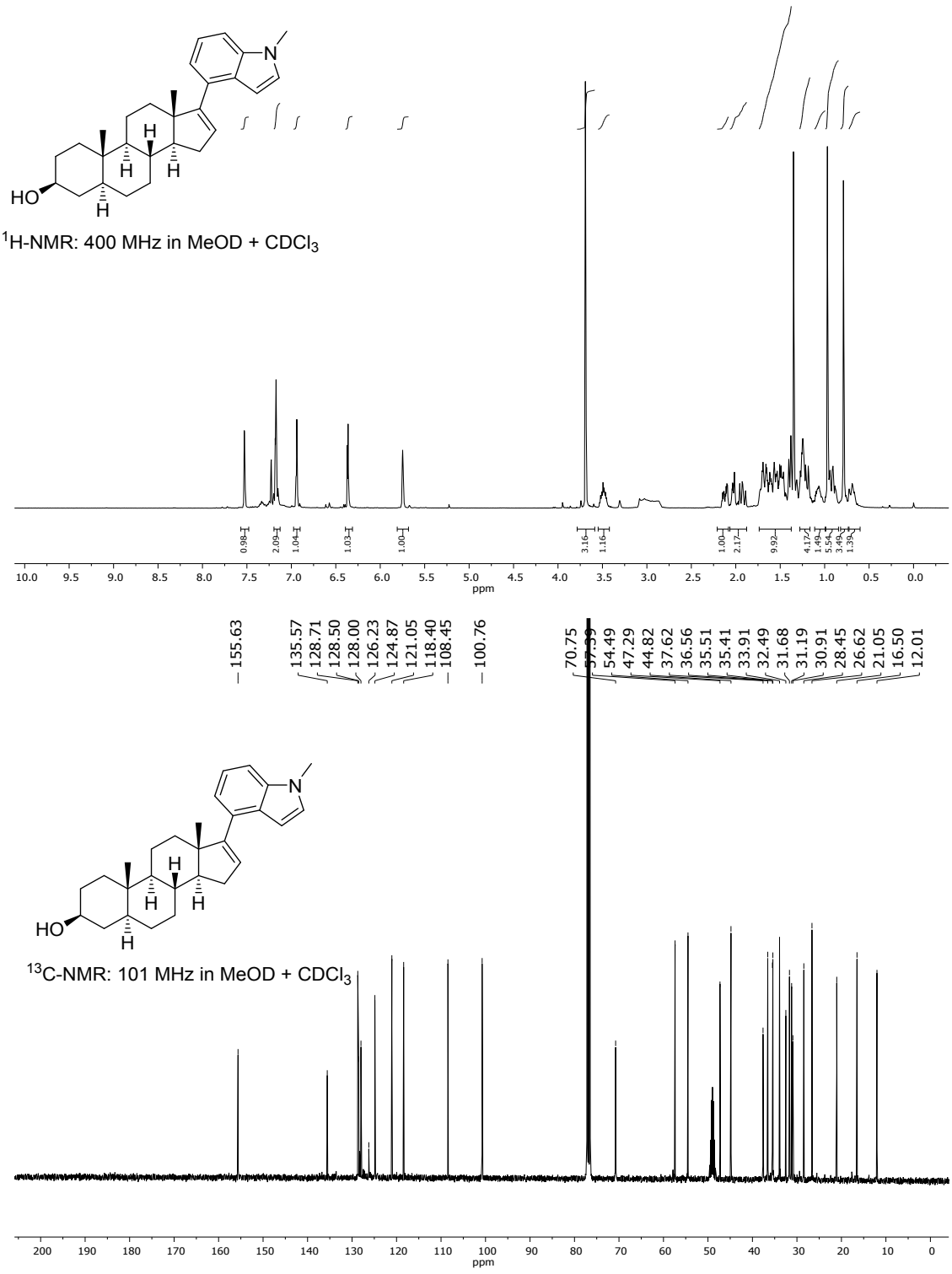
(3*β*, 5*α*)-17-(4‘-Naphtyl)androst-16-en-3-ol (**4m**)



^{1}H-NMR: 400 MHz in $CDCl_3$

^{13}C-NMR: 101 MHz in $CDCl_3$

(3*β*, 5*α*)-17-(1'-Methyl-1*H*-indol-4'-yl)-5-androst-16-en-3-ol (**4n**)



3. References

[1] W. C. Still, M. Kahn, A. Mitra, *The Journal of Organic Chemistry* **1978**, *43*, 2923-2925.
[2] H. Mori, K. Tsuneda, *Chemical & pharmaceutical bulletin* **1963**, *11*, 1413-1417.
[3] aZ. Li, M. Alyamani, J. Li, K. Rogacki, M. Abazeed, S. K. Upadhyay, S. P. Balk, M.-E. Taplin, R. J. Auchus, N. Sharifi, *Nature* **2016**, *533*, 547-551; bW. Harnisch, E. Morera, G. Ortar, *The Journal of Organic Chemistry* **1985**, *50*, 1990-1992.
[4] L. S. Liebeskind, J. Wang, *Tetrahedron* **1993**, *49*, 5461-5470.