

Supporting Information

Synthesis, Characterization and Biological Properties of Steroidal Ruthenium(II) and Iridium(III) Complexes based on the Androst-16-en-3-ol Framework

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1. General Remarks

NMR spectra were recorded on a *Bruker* Avance 400, *Bruker* Avance III HD, 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 ^1H NMR and ^{13}C NMR were the residual solvent peaks of d_1 -chloroform (^1H : $\delta = 7.26$ ppm; ^{13}C : $\delta = 77.0$ ppm). All coupling constants (J) are absolute values and are given in Hertz (Hz). The description of signals includes: s = singlet, d = doublet, t = triplet, q = quartet, 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 ^1H 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 DEPT-signal). Furthermore, 2D NMR experiments such as COSY (COSY = correlation spectroscopy) HSQC (HSQC = heteronuclear single-quantum correlation), HMBC (HMBC = heteronuclear multiple-bond correlation) or NOESY (NOESY = nuclear Overhauser effect spectroscopy) were performed in order to uniquely assign all H and C atoms. The sum of H-atoms does not add up to the number of H atoms in the sum formula for the presented steroids, since the proton of the OH is in most cases not visible in the ^1H NMR spectrum.

IR spectra were recorded on a *Bruker* alpha-p and a FT-IR IFS 88 spectrometer. The compounds were measured 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} between 3600 cm^{-1} and 500 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) or FAB-MS (fast atom bombardement) 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 $[\text{M}]^+$ and characteristic fragment peaks are given as $[\text{M}-\text{fragment}]^+$ or $[\text{fragment}]^+$. 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, F₂₅₄), detected under UV-light at 254 nm or stained with “Seebach staining solution” (mixture of phosphomolybdic acid, cerium(IV)-sulfate tetrahydrate, sulfuric acid and water).

Solvent mixtures are understood as volume/volume. Solvents, reagents and chemicals were purchased from *Aldrich*, *Fluka*, *Carbolution*, *ChemPur*, *ABCR*, *TCI* and *Fisher Scientific*. All solvents, reagents and chemicals were used as purchased unless stated otherwise. Solvents were removed at 40 °C at the rotavapor.

Dichloromethane (DCM) was distilled from CaH_2 under argon atmosphere and tetrahydrofuran (THF) was distilled from Na/benzophenone under argon atmosphere before prior use. Methanol (MeOH,

99.9%) and *N,N*-Dimethylformamid (DMF, 99.8%) were purchased as acroseal bottles from ACROS OrganicsTM.

Air- or moisture-sensitive reactions were carried out under argon atmosphere in oven-dried and previously evacuated and heated glass ware. Liquids were transferred with plastic syringes and steel cannula. Solids were used as powder.

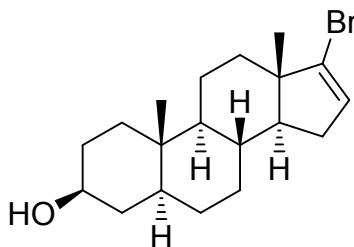
Reaction control was performed by thin layer chromatography. If not stated otherwise, crude products were purified by flash chromatography on silica gel by the procedure of Still.¹ Silica gel 60 (0.040 × 0.063 mm, Geduran[®], Merck) was used as stationary phase and solvents of *p.a.* quality as mobile phase were used.

2. Experimental Section

2.1. Synthetic procedures for the steroidal ligands

Please note that the protocols for the synthesis of the steroidal ligands are already published in *Adv. Synth. Catal.* **2017**, *359*, 832-840.²

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

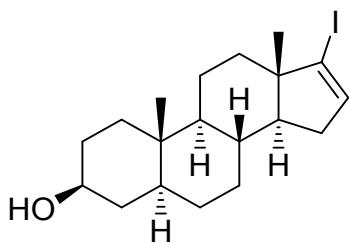


The synthesis of (3 β ,5 α)-17-bromoandrost-16-en-3-ol (**4a**) followed a modified, reported procedure.³ A solution of *epi*-androsterone **3** (500 mg, 1.72 mmol, 1.00 equiv.), hydrazine monohydrate (1.10 mL, 34.4 mmol, 20.0 equiv.) and NEt₃ (4.80 mL, 34.4 mmol, 20.0 equiv.) in EtOH (25 mL) was heated under argon atmosphere for 16 h to 50 °C.

After cooling, the solvents were removed and the obtained colorless powder was dissolved in dry pyridine (7.0 mL) under argon atmosphere. NBS (918 mg, 5.16 mmol, 3.00 equiv.) in dry pyridine (7.0 mL) was added slowly at 0 °C. The mixture was stirred for 1 h 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 NaHCO₃ (40 mL) and brine (40 mL). The organic phase was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (cyclohexane/ethyl acetate, 5:1) to afford the title compound **4a** (461 mg, 1.30 mmol, 76%) as a colorless powder.

R_f = 0.22 (cHex/EtOAc, 3:1). – **1H NMR** (400 MHz, CDCl₃): δ = 5.81 (dd, *J* = 3.3, 1.7 Hz, 1H, =CH), 3.59 (tt, *J* = 15.9, 11.1, 4.8 Hz, 1H, CHOH), 2.11 (ddd, *J* = 14.8, 6.2, 3.3 Hz, 1H, =CHCH₂^b), 1.87 (ddd, *J* = 14.8, 11.1, 1.8 Hz, 1H, =CHCH₂^a), 1.83–1.77 (m, 1H, CH₂), 1.73 – 1.21 (m, 12H, 8-CH + 7 different CH₂), 1.18–1.06 (m, 1H, 5-CH), 1.02–0.88 (m, 2H, 2 different CH₂), 0.83 (s, 3H, CH₃), 0.82 (s, 3H, CH₃), 0.72 (ddd, *J* = 12.3, 10.0, 4.6 Hz, 1H, 9-CH) ppm. – **13C NMR** (101 MHz, CDCl₃): δ = 135.6 (=CH), 128.8 (17-C_qBr), 71.1 (+, CHOH), 55.3 (+, CH), 54.5 (+, CH), 48.6 (13-C_q), 44.9 (+, 5-CH), 38.0 (–, CH₂), 36.6 (–, CH₂), 35.5 (10-C_q), 34.4 (–, CH₂), 34.1 (+, 8-CH), 31.6 (–, CH₂), 31.3 (–, CH₂), 31.2 (–, CH₂), 28.3 (–, 6-CH₂), 21.1 (–, 11-CH₂), 15.1 (+, 18-CH₃), 12.1 (+, 19-CH₃) ppm. – **IR** (ATR): ν = 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, 70 eV, 100 °C): *m/z* (%) = 354 (17) + 352 (17) [M]⁺, 339 (38) + 337 (40) [M-CH₃]⁺, 321 (17) + 319 (18), 273 (100) [M-Br]⁺, 255 (23), 239 (28). – **HRMS** (EI, C₁₉H₂₉O⁷⁹Br): calc. = 352.1396; found = 352.1398.

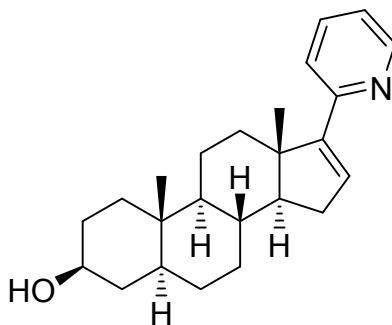
(3 β ,5 α)-17-Iodoandrostan-16-en-3-ol (4b**)²**



A solution of *epi*-androsterone **3** (1.00 g, 3.44 mmol, 1.00 equiv.), hydrazine monohydrate (2.1 mL, 68.9 mmol, 20.0 equiv.) and NEt₃ (9.6 mL, 68.9 mmol, 20.0 equiv.) in EtOH (50 mL) was heated under argon atmosphere for 18 h to 50 °C. After cooling, the solvents were removed and the obtained colorless powder was dissolved in dry THF (60 mL) and dry NEt₃ (10 mL) under argon atmosphere. At 0 °C, I₂ (1.75 g, 6.89 mmol, 2.00 equiv.) in dry THF (10 mL) was added slowly *via* cannulation. The mixture was stirred for 1 h at room temperature and afterwards quenched with saturated aqueous solutions of Na₂S₂O₃ (30 mL) and NaHCO₃ (50 mL). The product was extracted with ethyl acetate (3 × 100 mL) and the combined organic layers were washed with brine (40 mL). The organic phase was dried over Na₂SO₄ and the solvent was evaporated. The residue was purified by flash chromatography on silica (cyclohexane/ethyl acetate, 5:1) to afford the title compound **4b** (1.25, 3.13 mmol, 91%) as a colorless, light sensitive powder.

R_f = 0.67 (cHex/EtOAc, 1:1). – **1H NMR** (500 MHz, CDCl₃): δ = 6.10 (dd, *J* = 3.4, 1.7 Hz, 1H, =CH), 3.59 (tt, *J* = 10.4, 4.6 Hz, 1H, CHOH), 2.11 (ddd, *J* = 15.0, 6.4, 3.2 Hz, 1H, =CHCH₂^a), 1.91 (ddd, *J* = 15.0, 11.0, 1.7 Hz, 1H, =CHCH₂^b), 1.85–1.78 (m, 1H, CH₂), 1.74–1.54 (m, 6H, 5 different CH₂ + 8-CH), 1.49–1.24 (m, 6H, 4 different CH₂ + CH), 1.21–1.08 (m, 2H, CH₂ + 5-CH), 1.06–0.91 (m, 2H, 2 different CH₂), 0.82 (s, 3H, CH₃), 0.71 (s, 3H, CH₃), 0.74–0.68 (m, 1H, CH) ppm. – **13C NMR** (101 MHz, CDCl₃): δ = 137.3 (+, =CH), 112.7 (C_qI), 71.1 (+, CHOH), 54.6 (+, CH), 54.5 (+, CH), 49.9 (13-C_q), 44.8 (+, 5-CH), 37.9 (–, CH₂), 36.6 (–, CH₂), 36.1 (–, CH₂), 35.5 (10-C_q), 34.40 (+, 8-CH), 33.5 (–, CH₂), 31.4 (–, CH₂), 31.3 (–, CH₂), 28.4 (–, 6-CH₂), 21.5 (–, 11-CH₂), 15.1 (+, 18-CH₃), 12.1 (+, 19-CH₃) ppm. – **IR** (ATR): ν = 3306 (br), 2921 (w), 2846 (w), 1574 (vw), 1447 (w), 1369 (w), 1244 (vw), 1231 (vw), 1133 (vw), 1079 (vw), 1039 (w), 988 (w), 949 (vw), 917 (vw), 871 (vw), 850 (vw), 834 (vw), 811 (w), 735 (vw), 705 (vw), 656 (w), 609 (vw), 582 (vw), 562 (vw), 495 (vw) cm^{−1}. – **MS** (EI, 70 eV, 100 °C): *m/z* (%) = 400 (93) [M]⁺, 385 (88) [M-CH₃]⁺, 255 (26), 161 (27), 148 (35), 107 (26). – **HRMS** (EI, C₁₉H₂₉O₁¹²⁷I₁): calc. = 400.1258; found = 400.1259.

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

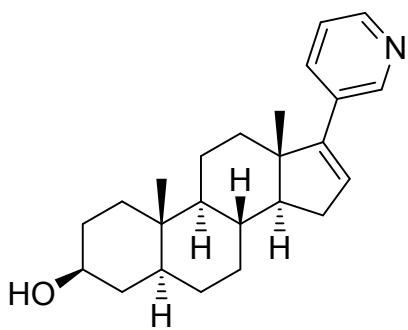


In a Schlenk tube, alkenyl iodide **4a** (150 mg, 375 μ mol, 1.00 equiv.), 2-tributylstannylpyridine^{2, 4} (420 mg, 1.14 mmol, 3.04 equiv.), LiCl (53 mg, 1.25 mmol, 0.30 equiv.) and CuCl (186 mg, 1.88 mmol, 5.00 equiv.) were dissolved in dry DMF (6.0 mL) under argon atmosphere. The reaction mixture was degassed using three freeze-pump-thaw cycles. Then, Pd(PPh₃)₄ (130 mg, 113 μ mol, 30 mol%) was added and the reaction mixture

was stirred at 80 °C for 60 h. After cooling to room temperature, an aqueous solution of KF (3 M, 4.00 equiv.) was added and stirred for 30 min, followed by filtration over Celite® (dichloromethane as eluent). The organic phase was washed with aqueous saturated NH₄Cl solution (100 mL) and extracted with dichloromethane (2×100 mL). The combined organic layers were washed with brine (100 mL), dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure and the title compound **5a** was obtained as a colorless solid (98 mg, 278 μ mol, 74%) after flash column chromatography on silica gel (cyclohexane/ethyl acetate, 4:1). For the biological tests the compound was washed multiple times with *n*-hexane.

R_f = 0.32 (cHex/EtOAc, 2:1). – **1H NMR** (400 MHz, CDCl₃): δ = 8.55 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H, NCH_{Ar}), 7.58 (td, *J* = 7.7, 1.9 Hz, 1H, CH_{Ar}), 7.37 (dt, *J* = 8.1, 1.1 Hz, 1H, CH_{Ar}), 7.09 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H, CH_{Ar}), 6.39 (dd, *J* = 3.5, 1.9 Hz, 1H, C_q=CH), 3.60 (tt, *J* = 11.0, 4.7 Hz, 1H, CHOH), 2.39 (ddd, *J* = 12.1, 3.8, 2.2 Hz, 1H, CH₂), 2.24 (ddd, *J* = 16.1, 6.4, 3.4 Hz, 1H, CH=CH₂^a), 2.04 (ddd, *J* = 16.1, 11.4, 1.9 Hz, 1H, CH=CH₂^b), 1.85–1.79 (m, 1H, CH₂), 1.76 – 1.46 (m, 8H, 4 different CH₂ + 8-CH + CH), 1.40–1.23 (m, 5H, 4 different CH₂), 1.21 – 1.10 (m, 1H, 5-CH), 1.11 (s, 3H, CH₃), 1.06–0.96 (m, 2H, 2 different CH₂), 0.87 (s, 3H, CH₃), 0.83–0.69 (m, 1H, CH) ppm. – **13C MR** (101 MHz, CDCl₃): δ = 155.5 (C_q), 154.1 (C_q), 148.8 (6'-CHN), 135.7 (+, 4'-CH_{Ar}), 131.5 (C_q=CH), 121.1 (+, 3'- or 4'-CH_{Ar}), 120.7 (+, 3' or 4'-CH_{Ar}), 71.2 (+, CHOH), 57.2 (+, CH), 54.6 (+, CH), 47.0 (13-C_q), 44.9 (+, 5-CH), 38.1 (–, CH₂), 36.7 (–, CH₂), 35.5 (10-C_q), 35.1 (–, CH₂), 33.8 (+, 8-CH), 31.8 (–, CH₂), 31.5 (–, CH₂), 31.4 (–, CH₂), 28.5 (–, 6-CH₂), 21.0 (–, 11-CH₂), 16.2 (+, 18-CH₃), 12.2 (+, 19-CH₃) ppm. – **IR** (ATR): ν = 3282 (br), 2913 (w), 2848 (w), 1584 (vw), 1462 (w), 1448 (w), 1366 (vw), 1148 (vw), 1036 (w), 1006 (vw), 957 (vw), 923 (vw), 772 (w), 739 (vw), 692 (w), 604 (vw), 487 (vw), 403 (vw) cm⁻¹. – **MS** (EI, 70 eV, 70 °C): *m/z* (%) = 351 (100) [M]⁺, 336 (82) [M-CH₃]⁺, 269 (52). – **HRMS** (EI, C₂₄H₃₃ON): calc. = 351.2557; found = 351.2555.

(3 β ,5 α)-17-(3'-Pyridinyl)androst-16-en-3-ol (5b**)²**

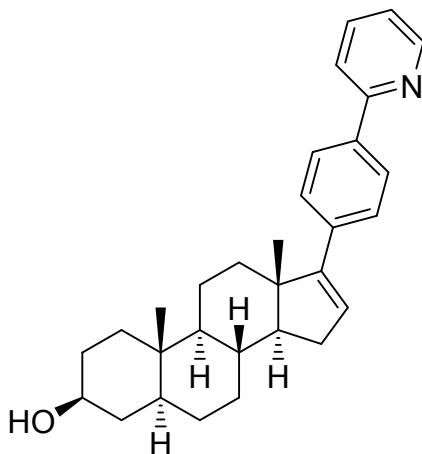


In a Schlenk tube, vinyl iodide **1-I** (50 mg, 125 μ mol, 1.00 equiv.), crude 3-tributylstannylpypyridine², ⁴ (140 mg, 375 μ mol, 3.00 equiv.), LiCl (53 mg, 1.25 mmol, 10.0 equiv.) and CuCl (124 mg, 1.25 mmol, 10.0 equiv.) were dissolved in dry DMF (3.0 mL) under argon atmosphere. The reaction mixture was degassed using three freeze-pump-thaw cycles. Then Pd(PPh₃)₄ (29 mg, 25 μ mol, 20 mol%) was added and the reaction mixture

was stirred at 80 °C for 60 h. After cooling to room temperature an aqueous solution of KF (3 M, 4.00 equiv.) was added and stirred for 30 min, followed by filtration over Celite® (dichloromethane as eluent). The organic phase was washed with aqueous saturated NH₄Cl solution (50 mL) and extracted with dichloromethane (2×50 mL). The combined organic layers were washed with brine (100 mL), dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure and, after flash column chromatography on silica gel (cyclohexane/ethyl acetate, 4:1), the title compound **5b** was obtained as a colorless solid (27 mg, 75.7 μ mol, 60%). For the biological tests the compound was washed multiple times with *n*-hexane.

R_f = 0.18 (cHex/EtOAc, 3:2). – **1H NMR** (400 MHz, CDCl₃): δ = 8.59 (s, 1H, 2'-CH_{Pyr}), 8.43 (d, *J* = 3.2 Hz, 1H, 4'-CH_{Pyr}), 7.63 (dt, *J* = 8.0, 2.0 Hz, 1H, 6'-CH_{Ar}), 7.20 (dd, *J* = 7.8, 4.8 Hz, 1H, 5'-CH_{Ar}), 5.96 (dd, *J* = 3.3 Hz, 1.8 Hz, 1H, C_q=CH), 3.60 (tt, *J* = 15.9, 11.0, 4.8 Hz, 1H, CHOH), 2.22 (ddd, *J* = 15.7, 6.4, 3.3 Hz, 1H, =CHCH₂^a), 2.05–1.97 (m, 2H, =CHCH₂^b + CH₂), 1.82 – 1.79 (m, 1H, CH₂), 1.82–1.51 (m, 6H, 4 different CH₂ + 8-CH + CH), 1.45–1.24 (m, 6H, 5 different CH₂), 1.17–1.10 (m, 1H, 5-CH), 1.05–0.89 (m, 2H, 2 different CH₂), 0.99 (s, 3H, CH₃), 0.85 (s, 3H, CH₃), 0.78–0.72 (m, 1H, CH) ppm. – **13C NMR** (101 MHz, CDCl₃): δ = 151.6 (C_q=CH_{Ar}), 147.6 (+, 2'-CH_{Pyr} or 4'-CH_{Pyr}), 147.5 (+, 2'-CH_{Pyr} or 4'-CH_{Pyr}), 134.5 (+, 6'-CH_{Pyr}), 133.9 (C_q, Pyr), 129.0 (+, CH=C_q), 122.8 (+, 5'-CH_{Pyr}), 71.0 (+, 3-CHOH), 57.3 (+, CH), 54.4 (+, CH), 47.4 (13-C_q), 44.9 (+, 5-CH), 38.0 (–, CH₂), 36.7 (–, CH₂), 35.5 (10-C_q), 35.2 (–, CH₂), 33.9 (+, 8-CH), 31.7 (–, CH₂), 31.5 (–, CH₂), 31.3 (–, CH₂), 28.4 (–, 6-CH₂), 21.0 (–, 11-CH₂), 16.5 (+, 18-CH₃), 12.1 (+, 19-CH₃) ppm. – **IR** (ATR): ν = 3314 (br), 2922 (w), 2850 (w), 1597 (vw), 1438 (w), 1416 (w), 1224 (vw), 1190 (w), 1119 (w), 1080 (w), 1049 (w), 1025 (w), 855 (vw), 802 (w), 754 (vw), 720 (w), 695 (w), 629 (vw), 540 (m), 503 (vw), 406 (vw) cm⁻¹. – **MS** (EI, 70 eV, 130 °C): *m/z* (%) = 351 (65) [M]⁺, 336 (100) [M – CH₃]⁺, 277 (71). – **HRMS** (EI, C₂₄H₃₃ON): calc. = 351.2557; found = 351.2556.

(3 β ,5 α)-17-(4'-Pyridin-2'-yl)phenyl)androst-16-en-3-ol (5c**)²**



In a Schlenk tube, alkenyl iodide **4b** (50 mg, 125 μ mol, 1.00 equiv.), crude 2-(4-tributylstannylphenyl)pyridine² (83 mg, 187 μ mol, 1.50 equiv.), LiCl (53 mg, 1.25 mmol, 10.0 equiv.) and CuCl (124 mg, 1.25 mmol, 10.0 equiv.) were dissolved in dry DMF (3.0 mL) under argon atmosphere. The reaction mixture was degassed using three freeze-pump-thaw cycles. Then Pd(PPh₃)₄ (29 mg, 25 μ mol, 20 mol%) was added and the reaction mixture was stirred at 80 °C for 60 h. After cooling to room temperature an aqueous solution of KF (3 M, 4.00 equiv.) was added and stirred for 30 min, followed by filtration over Celite® (dichloromethane as eluent). The organic phase was washed with aqueous saturated NH₄Cl solution (50 mL) and extracted with dichloromethane (2×50 mL). The combined organic layers were washed with brine (100 mL), dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure and, after flash column chromatography on silica gel (cyclohexane/ethyl acetate, 4:1), the title compound **5c** was obtained as a colorless solid (34 mg, 80.0 μ mol, 64%). For biological tests the compound was washed multiple times with *n*-hexane.

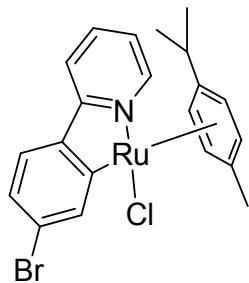
R_f = 0.14 (cHex/EtOAc, 3:1). – **1H NMR** (400 MHz, CDCl₃): δ = 8.61 (dt, *J* = 4.8, 1.6 Hz, 1H, N=CH_{Pyr}), 7.85 (d, *J* = 8.5 Hz, 2H, CH_{Ph}), 7.70–7.74 (m, 1H, CH_{Pyr}), 7.67–7.64 (m, 2H, CH_{Pyr}), 7.41 (d, *J* = 8.5 Hz, 2H, CH_{Ph}), 7.14 (ddd, *J* = 6.1, 4.8, 2.4 Hz, 1H, CH_{Pyr}), 5.92 (dd, *J* = 3.3, 1.8 Hz, 1H, =CH), 3.52 (tt, *J* = 9.6, 4.3 Hz, 1H, CHOH), 2.15 (ddd, *J* = 15.7, 6.4, 3.3 Hz, 1H, =CHCH₂), 2.07–1.89 (m, 2H, =CHCH₂ + CH₂), 1.75–1.37 (m, 9H, 5 different CH₂, 8-CH + 14-CH), 1.32–1.17 (m, 4H, 3 different CH₂), 1.17–1.11 (m, 1H, 5-CH), 1.00–0.88 (m, 2H, 2 different CH₂), 0.98 (s, 3H, CH₃), 0.80 (s, 3H, CH₃), 0.61–0.77 (m, 1H, 9-CH) ppm. – **13C NMR** (100 MHz, CDCl₃): δ = 157.1(C_q=N), 154.3 (C_q=CH), 149.5 (+, CH_{Pyr}), 137.9 (C_q=CH_{Ar}), 137.4 (C_q=CH_{Ar}), 136.5 (+, CH_{Pyr}), 127.7 (+, =CH), 126.8 (+, 2 × CH_{Ph}), 126.4 (+, 2 × CH_{Ph}), 121.7 (+, CH_{Pyr}), 120.1 (+, CH_{Pyr}), 71.1 (+, CHOH), 57.4 (+, CH), 54.5 (+, CH), 47.3 (13-C_q), 44.9 (+, 5-CH), 38.2 (−, CH₂), 36.7 (−, CH₂), 35.5 (10-C_q), 35.4 (−, CH₂), 33.9 (+, 8-CH), 31.8 (−, CH₂), 31.5 (−, CH₂), 31.4 (−, CH₂), 28.5 (−, CH₂), 21.1 (−, CH₂), 16.6 (+, CH₃), 12.2 (+, CH₃) ppm. – **IR** (ATR): ν = 3412 (vw), 2919 (w), 2847 (w), 1584 (w), 1463 (w), 1434 (w), 1378 (w), 1299 (w), 1157 (vw), 1135 (vw), 1039 (w), 989 (vw), 846 (w), 781 (m), 751 (w), 631 (w), 494 (w), 407 (w) cm^{−1}. – **MS** (EI, 70 eV, 200 °C): *m/z* (%) = 427 (20) [M]⁺, 412 (13) [M-CH₃]⁺, 308 (100). – **HRMS** (EI, C₃₀H₃₇ON): calc. = 427.2870; found = 427.2870.

2.2. Synthetic procedures for the ruthenium(II) and iridium(III) complexes

General procedure for the cyclometalation

Under argon atmosphere, the ligand (2.00 equiv.), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (1.00 equiv.) or $[\text{Ir Cp}^*\text{Cl}_2]_2$ and KOAc (4.00 equiv.) were dissolved in dry MeOH or CH_2Cl_2 and stirred at room temperature for 24 h. The suspension was concentrated and the residue was purified by flash column chromatography on silica gel (cyclohexane/ethyl acetate) to obtain the corresponding cyclometalated complex as a yellow to orange solid.

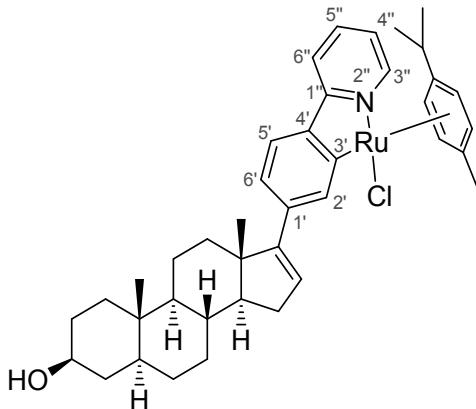
[5-Bromo-2-(2-pyridinyl- κN)phenyl- κC]chlorido(η^6 -*para*-cymene) ruthenium(II) (**6**)



Following the general procedure, $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (306 mg, 0.50 mmol, 1.00 equiv.), 2-(4-bromophenyl)pyridine (234 mg, 1.00 mmol, 2.00 equiv.) and KOAc (196 mg, 2.00 mmol, 4.00 equiv.) were dissolved in dry MeOH (10 mL) and stirred 24 h at room temperature. The suspension was concentrated and then purified *via* flash column chromatography on silica gel (cyclohexane/ethyl acetate, 1:1) to afford the title compound **6** as a yellow solid (336 mg, 0.667 mmol, 67%).

$R_f = 0.14$ (cHex/EtOAc, 1:1). – **1H NMR** (500 MHz, CDCl_3): $\delta = 9.13$ (d, $J = 5.7$ Hz, 1H, 3- CH_{Pyrr}), 8.21 (d, $J = 1.9$ Hz, 1H, 6- CH_{Ar}), 7.67 – 7.56 (m, 2H, CH_{Ar}), 7.39 (d, $J = 8.2$ Hz, 1H, CH_{Ar}), 7.09 (dd, $J = 8.2$, 1.9 Hz, 1H, CH_{Ar}), 7.04 – 6.98 (m, 1H, CH_{Ar}), 5.51 (d, $J = 6.0$ Hz, 2H, CH_{cymene}), 5.14 (d, $J = 6.0$ Hz, 1H, CH_{cymene}), 4.93 (d, $J = 5.9$ Hz, 1H, CH_{cymene}), 2.36 (hept, $J = 6.9$ Hz, 1H, $CH(\text{CH}_3)_2$), 2.00 (s, 3H, $C_{\text{q,cymene}}\text{CH}_3$), 0.91 (d, $J = 6.9$ Hz, 3H, $CH\text{CH}_3$), 0.81 (d, $J = 6.9$ Hz, 3H, $CH\text{CH}_3$) ppm. – **13C NMR** (126 MHz, CDCl_3): $\delta = 183.4$ ($C_{\text{q}}\text{--Ru}$), 164.5 ($C_{\text{q}}\text{N}$), 154.7 (+, CH_{aryl}), 142.1 (C_{q}), 141.3 (+, CH_{aryl}), 136.9 (+, CH_{aryl}), 125.6 (+, CH_{aryl}), 125.0 (+, CH_{aryl}), 124.3 (C_{q}), 121.8 (+, CH_{aryl}), 119.0 (+, CH_{aryl}), 101.4 (C_{q}), 100.8 (C_{q}), 91.0 (+, CH_{cymene}), 89.4 (+, CH_{cymene}), 84.8 (+, CH_{cymene}), 82.1 (+, CH_{cymene}), 30.8 (+, $CH(\text{CH}_3)_2$), 22.5 (+, $CH\text{CH}_3$), 21.8 (+, $CH\text{CH}_3$), 18.8 (+, $C_{\text{q,Ar}}\text{CH}_3$) ppm. – **IR** (ATR): $\nu = 2953$ (vw), 1732 (vw), 1601 (w), 1566 (w), 1533 (w), 1470 (w), 1414 (w), 1380 (w), 1293 (vw), 1257 (w), 1095 (vw), 1067 (vw), 1045 (w), 1007 (w), 860 (w), 768 (m), 712 (vw), 683 (w), 566 (vw) cm^{-1} . – **MS** (FAB, 3-NBA): m/z (%) = 510/509/508/507/506/505/504/503/502/501/500/499 [$M]^+$, 472/471/470/469/468/467/466/465/464/463/462 [$M\text{--Cl}]^+$. – **HRMS** (FAB, $\text{C}_{21}\text{H}_{21}\text{N}^{79}\text{Br}^{35}\text{Cl}^{102}\text{Ru}$, $[M]^+$): calc. = 502.9589; found = 502.9590.

Chlorido(η^6 -*para*-cymene)[17-(4'-pyridin-2''-yl- κ N-phenyl-3' κ C)-(5 α ,3 β)-androst-16-enolido]-ruthenium(II) (7)

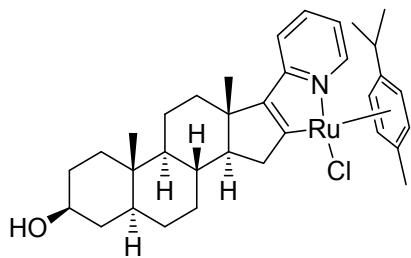


According to the general procedure (3 β ,5 α)-17-(4'-pyridin-2''-ylphenyl)androst-16-en-3-ol (**5c**) (100 mg, 234 μ mol), [Ru(*p*-cymene)Cl₂]₂ (72 mg, 117 μ mol) and KOAc (46 mg, 468 μ mol) stirred in dry methanol (10 mL) for 20 h at room temperature. After flash column chromatography on silica gel (cHex/EtOAc/ NEt₃, 200:200:1 → 0:200:1) the ruthenium(II) complex **7** was obtained as a yellow solid (48 mg, 83.0 μ mol, 35%) consisting of an inseparable mixture of its diastereomers (*dr* = 1:1.). An unambiguous assignment of the signals in order to definite diastereomer was not possible even with 2D NMR experiments. Therefore, the signals for the diastereomeric mixture are given, same signals are stated with “and” if clearly distinguishable.

*R*_f = 0.31 (EtOAc/NEt₃, 200:1). – **1H NMR** (600 MHz, CDCl₃): δ = 9.20 (d, *J* = 5.6 Hz, 1H, 3''-CH_{Ar}N), 8.16 (s, 1H, 2'-CH_{Ar}), 7.68–7.59 (m, 2H, 5''-CH_{Ar} + 6''-CH_{Ar}) 7.52 (d, *J* = 8.0 Hz, 1H, 5'-CH_{Ar}), 7.04 (d, *J* = 8.2 Hz, 1H, 6'-CH_{Ar}), 7.01 (ddd, *J* = 7.1, 5.7, 1.7 Hz, 1H, 4''-CH_{Ar}), 6.03 (ddd, *J* = 10.3, 3.3, 1.8 Hz, 1H, =CH), 5.57 (d, *J* = 5.9 Hz, 1H, CH_{cymene}), 5.49 (dd, *J* = 17.1, 5.8 Hz, 1H, CH_{cymene}), 5.17 (dd, *J* = 5.2 Hz, 1H, CH_{cymene}), 5.00 (dd, *J* = 8.2, 6.4 Hz, 1H, CH_{cymene}), 3.60 (tt, *J* = 10.6, 4.8 Hz, 1H, CHOH), 2.48 (hep, *J* = 6.9 Hz, 1H, CH(CH₃)₂), 2.23 (dtd, *J* = 15.6, 6.2, 3.3 Hz, 1H, CH₂), 2.21–2.13 (m, 1H, CH₂), 2.08–2.02 (m, 1H, CH₂), 2.01 and 1.99 each (s, 3H, C_{q,cymene}CH₃), 1.83–1.23 (m, 13H, 7 different CH₂ + 8-CH + 14-CH), 1.21–1.13 (m, 1H, 5-CH), 1.12 and 1.08 each (s, 3H, 18-CH₃), 1.06–1.00 (m, 2H, 2 different CH₂), 1.01 (dd, *J* = 6.9 Hz, 3H, CH(CH₃)₂), 0.92 and 0.90 each (d, *J* = 6.9 Hz, 1.5H, CH(CH₃)₂), 0.88 (s, 3H, 19-CH₃), 0.83–0.73 (m, 1H, 9-CH) ppm. – **13C NMR** (151 MHz, CDCl₃): δ = 180.5 (C_q-Ru), 165.1 (1''-C_qN), 155.7 and 155.5 each (17-C_q), 154.4 (+, 3''-CH_{Ar}), 141.9 and 141.9 each (4'-C_q), 137.9 (1'-C_q), 137.4 and 137.3 each (+, 2'-CH_{Ar}), 136.4 (+, 5''-CH_{Ar}), 127.3 (+, =CH), 123.2 and 123.1 each (+, 5'-CH_{Ar}), 121.4 and 121.2 each (+, 6'- or 4''-CH_{Ar}), 120.9 and 120.9 each (+, 6'- or 4''-CH_{Ar}), 118.5 and 118.5 each (+, 6''-CH_{Ar}), 100.9 and 100.8 each (C_{q,cymene}CH(CH₃)₂), 99.7 and 99.2 each (C_{q,cymene}CH₃), 90.2 and 90.1 each (+, CH_{cymene}), 89.9 and 89.8 each (+, CH_{cymene}), 83.7 and 83.6 each (+, CH_{cymene}), 83.1 and 82.6 each (+, CH_{cymene}), 71.3 and 71.2 each (+, 3-CHOH), 57.6 and 57.6 each (+, CH), 54.7 and 54.6 each (+, CH), 47.6 and 47.4 (13-C_q), 45.0 and 45.0 each (+, CH), 38.2 (–, CH₂), 36.8 (–, CH₂), 35.9 and 35.6 each (–, CH₂ + 10-C_q), 34.1 and 34.0 each (+, CH), 31.9 and 31.9 each (–, CH₂), 31.6 and 31.6 each (–, CH₂), 31.5 (–, CH₂), 30.7 (+, CH(CH₃)₂), 28.7 (–, CH₂), 22.6 and 22.5 each (+, CH(CH₃)₂), 21.6 and 21.6 each (+, CH(CH₃)₂), 21.3 (–, 11-CH₂), 18.6 and 18.6 each (+, C_{q,cymene}CH₃), 17.0 and 17.0 each (+, 18-CH₃)₂, 12.3 (+, 19-CH₃)₂) ppm. – **IR** (ATR): ν = 3401 (br), 2917 (w), 2848 (w), 1601 (vw), 1576 (vw), 1558 (vw), 1471 (w), 1378 (vw), 1316 (vw), 1158 (vw), 1079 (vw), 1037 (vw), 1007 (vw), 957 (vw), 918 (vw), 828 (vw), 810 (vw), 774 (w), 724 (w), 642 (vw),

498 (vw) cm^{-1} . – **MS** (FAB, 3-NBA): m/z (%) = 694/695/696/697/698/699/700 [M]⁺, 658/659/660/662/663/664/665 [M–Cl]⁺, 599/600/601/602/603/604/605, 154 (100). – **HRMS** (FAB, C₄₀H₅₀ON³⁵Cl¹⁰²Ru, [M+H]⁺): calc = 697.2619; found = 697.2620.

Chlorido(η^6 -*para*-cymene)[(5 α)-17-(2'-pyridinyl- κ N)androst-16-en-3 β -ol-16 κ C]ruthenium(II) (8**)**



According to the general procedure, (3 β ,5 α)-17-(2'-pyridinyl)androst-16-en-3-ol (**5a**) (33 mg, 94.4 μmol), [Ru(*p*-cymene)Cl₂]₂ (29 mg, 47.2 μmol) and KOAc (19 mg, 189 μmol) in dry methanol (1.0 mL) were stirred 20 h at room temperature. After flash column chromatography on silica gel (*c*Hex/EtOAc/NEt₃, 1:1:0.05 → 0:1:0.05) the two diastereomeric ruthenium(II) complexes **8** were obtained as yellow solids (F1 = (**R-Ru**)-**8**: 16 mg, 25.7 μmol , 27%; F2 = (**S-Ru**)-**8**: 14 mg, 22.5 μmol , 24%).

(R-Ru)-8*

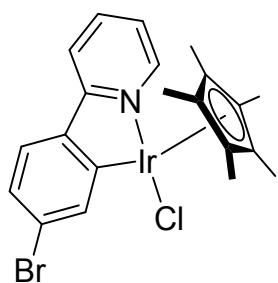
R_f = 0.63 (EtOAc/NEt₃, 200:1). – **1H NMR** (500 MHz, CDCl₃): δ = 9.09 (dd, J = 5.8, 1.5 Hz, 1H, 3'-CHN), 7.42 (td, J = 7.8, 1.6 Hz, 1H, 5'-CH), 7.09 (d, J = 8.1 Hz, 1H, 6'-CH), 6.68 (t, J = 6.5 Hz, 1H, 4'-CH), 5.54 (d, J = 5.9 Hz, 1H, CH_{cymene}), 5.51 (d, J = 5.9 Hz, 1H, CH_{cymene}), 5.21 (d, J = 5.9 Hz, 1H, CH_{cymene}), 4.93 (d, J = 5.7 Hz, 1H, CH_{cymene}), 3.60 (tt, J = 10.6, 4.6 Hz, 1H, CHOH), 3.11 (dd, J = 16.2 Hz, J = 4.8 Hz, 1H, 15-CH₂^a), 2.50 (dd, J = 16.3, 11.4 Hz, 1H, 15-CH₂^b), 2.41 (p, J = 6.9 Hz, 1H, CH(CH₃)₂), 2.19 (dd, J = 8.1, 2.7 Hz, 1H, CH₂), 2.01 (s, 3H, C_{q,cymene}CH₃), 2.19 (dd, J = 8.1, 2.7 Hz, 1H, CH₂), 1.89 – 1.80 (m, 2H, 2 different CH₂), 1.76–1.57 (m, 5H, 3 different CH₂ + CH + CH), 1.52–1.28 (m, 6H, 5 different CH₂), 1.22–1.11 (m, 2H, CH₂ + CH), 1.00 (d, J = 5.1 Hz, 3H, CH(CH₃)₂), 0.98 (d, J = 5.3 Hz, 3H, CH(CH₃)₂), 0.86 (s, 3H, 19-CH₃), 0.85–0.78 (m, 1H, CH), 0.84 (s, 3H, 18-CH₃) ppm. – **13C NMR** (126 MHz, CDCl₃): δ = 208.7 (16-C_q-Ru), 163.4 (1'-C_qN), 154.7 (+, 3'-CH_{Ar}N), 150.4 (17-C_q), 135.8 (+, 5'-CH_{Ar}), 117.8 (+, 6'-CH_{Ar}), 116.4 (+, 4'-CH_{Ar}), 99.7 (C_{q,cymene}), 99.1 (C_{q,cymene}), 90.0 (+, CH_{cymene}), 87.3 (+, CH_{cymene}), 85.5 (+, CH_{cymene}), 81.2, (+, CH_{cymene}), 71.3 (+, 3-CHOH), 58.5 (+, 14-CH), 55.2 (+, 9-CH), 45.1 (+, 5-CH), 44.9 (13-C_q), 44.8 (–, CH₂), 38.2 (–, CH₂), 36.8 (–, CH₂), 36.2 (–, CH₂), 35.7 (10-C_q), 33.8 (+, 8-CH), 32.2 (–, CH₂), 31.4 (–, CH₂), 30.9 (+, CH(CH₃)₂), 28.7 (–, CH₂), 22.2 (+, CH(CH₃)₂), 22.1 (+, CH(CH₃)₂), 21.3 (–, CH₂), 18.7 (+, C_{q,cymene}(CH₃)₂), 16.6 (+, 18-CH₃), 12.3 (+, 19-CH₃) ppm. – **IR** (ATR): ν = 3367 (vw), 2918 (m), 2849 (m), 1736 (w), 1662 (w), 1596 (w), 1501 (w), 1465 (m), 1376 (w), 1241 (w), 1151 (w), 1080 (w), 1040 (w), 961 (w), 842 (vw), 776 (w), 745 (w) cm^{-1} . – **MS** (+FAB, 3-NBA): m/z (%) = 618/619/620/621/622/623/624/ 625 [M+H]⁺, 581/582/583/584/585/586/587/588 [M–Cl]⁺. – **HRMS** (+FAB, C₃₄H₄₇O₁N₁³⁵Cl₁¹⁰²Ru₁, [M+H]⁺): calc = 622.2384; found = 622.2385.

(S-Ru)-8*

$R_f = 0.51$ (EtOAc/NEt₃, 200:1). – **1H NMR** (500 MHz, CDCl₃): $\delta = 9.07$ (d, $J = 5.8$ Hz, 1H, 3'-CHN), 7.41 (t, $J = 7.6$ Hz, 1H, 5'-CH), 7.07 (d, $J = 8.0$ Hz, 1H, 6'-CH), 6.68 (t, $J = 6.5$ Hz, 1H, 4'-CH), 5.57 (d, $J = 6.0$ Hz, 1H, CH_{cymene}), 5.47 (d, $J = 5.7$ Hz, 1H, CH_{cymene}), 5.17 (d, $J = 6.0$ Hz, 1H, CH_{cymene}), 4.88 (d, $J = 5.7$ Hz, 1H, CH_{cymene}), 3.57 (tt, $J = 10.5, 4.7$ Hz, 1H, CHOH), 2.98 (dd, $J = 16.1, 6.4$ Hz, 1H, 15-CH₂^a), 2.84 (dd, $J = 16.1, 11.3$ Hz, 1H, 15-CH₂^b), 2.41–2.29 (m, 1H, CH(CH₃)₂), 2.11 (dd, $J = 11.1, 4.1$ Hz, 1H, CH₂), 2.03 (s, 3H, C_{q,cymene}CH₃), 1.84–1.53 (m, 8H, 6 different CH₂ + 8-CH + 14-CH), 1.49–1.25 (m, 5H, 4 different CH₂), 1.18–1.27 (m, 2H, CH₂ + 5-CH), 1.00–0.95 (m, 1H, CH₂), 0.93 (s, 3H, 18-CH₃), 0.91 (d, $^3J = 6.8$ Hz, 3H, CH(CH₃)₂), 0.89 (d, 3H, CH(CH₃)₂), 0.87 (s, 3H, 19-CH₃), 0.80–0.72 (m, 1H, 9-CH) ppm. – **13C NMR** (126 MHz, CDCl₃): $\delta = 209.7$ (16-C_q-Ru), 163.2 (1'-C_qN), 154.6 (+, 3'-CH_{Ar}N), 150.7 (17-C_q), 135.9 (+, 5'-CH_{Ar}), 117.6 (+, 6'-CH_{Ar}), 116.6 (+, 4'-CH_{Ar}), 100.8 (C_{q, cymene}), 98.4 (C_{q, cymene}), 91.8(+, CH_{cymene}), 85.7 (+, CH_{cymene}), 85.6 (+, CH_{cymene}), 80.3 (+, CH_{cymene}), 71.0 (+, 3-CHOH), 58.3 (+, 14-CH), 54.6 (+, 9-CH), 44.8 (+, 5-CH), 44.5 (13-C_q), 44.3 (–, CH₂), 38.0 (–, CH₂), 36.7 (–, CH₂), 35.6 (10-C_q), 35.3 (–, CH₂), 34.1 (+, 8-CH), 31.8 (–, CH₂), 31.3 (–, CH₂), 30.9 (+, CH(CH₃)₂), 28.7 (–, CH₂), 22.2 (+, CH(CH₃)), 21.8 (+, CH(CH₃)), 21.2 (–, CH₂), 18.8 (+, C_{q,cymene}CH₃), 17.4 (+, 18-CH₃), 12.2 (+, 19-CH₃) ppm. – **IR** (ATR): $\nu = 3323$ (br), 2919 (w), 2849 (w), 1663 (vw), 1595 (vw), 1502 (vw), 1465 (w), 1376 (vw), 1151 (vw), 1080 (vw), 1039 (w), 960 (vw), 921 (vw), 842 (vw), 776 (vw), 725 (vw) cm⁻¹. – **MS** (+FAB, 3-NBA): m/z (%) = 618/619/620/621/622/623/624/625 [M+H]⁺, 581/582/583/584/585/586/587/588 [M-Cl]⁺. – **HRMS** (+FAB, C₃₄H₄₇O₁N₁³⁵Cl₁¹⁰²Ru₁, [M+H]⁺): calc. = 622.2384; found = 622.2383.

* NMR spectra contain traces of the other diastereomer.

[5-Bromo-2-(2-pyridinyl- κ N)phenyl- κ C]chlorido(η^5 -pentamethylcyclopentadienyl)iridium(III) (9**)**

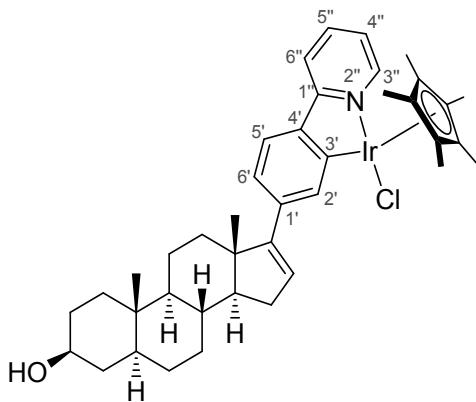


Following the general procedure, [IrCp^{*}Cl₂]₂ (50 mg, 62.8 μ mol, 1.00 equiv.), 2-(4-bromophenyl)pyridine (29 mg, 0.125 mmol, 2.00 equiv.) and KOAc (49 mg, 0.502 mmol, 4.00 equiv.) were dissolved in dry CH₂Cl₂ (3.0 mL) and stirred 24 h at room temperature. The suspension was concentrated and then purified *via* flash column chromatography on silica gel (cyclohexane/ethyl acetate, 2:1→1:3) to afford the title compound **9** as yellow solid (50 mg, 85.1 μ mol, 68%).

$R_f = 0.34$ (cHex/EtOAc, 2:3). – **1H NMR** (500 MHz, CDCl₃): $\delta = 8.67$ (d, $J = 5.6$ Hz, 1H, 3'-CH), 7.91 (d, $J = 2.0$ Hz, 1H, 6-CH), 7.76 (d, $J = 8.1$ Hz, 1H, 6'-CH), 7.66 (t, $J = 8.0$ Hz, 1H, 5'-CH), 7.52 (d, $J = 8.2$ Hz, 1H, 3-CH), 7.16 (dd, $J = 8.2, 2.0$ Hz, 1H, 4-CH), 7.13 – 7.06 (m, 1H, 4'-CH), 1.67 (s, 15H, CH₃, Cp^{*}) ppm. – **13C NMR** (126 MHz, CDCl₃): $\delta = 166.2$ (1'-C_q), 165.4 (1-C_q), 151.3 (+, 3'-CH), 142.9 (2-C_q), 137.8 (+, 6-CH), 137.1 (+, 5'-CH), 125.8 (5-C_q-Br), 125.0 (+, 3- or 4-CH), 124.9 (+, 3- or 4-CH),

122.5 (+, 4'-CH), 118.9 (+, 6'-CH), 88.6 ($5\times C_q$, Cp*), 8.76 (+, 5 $\times CH_3$, Cp*) ppm. – **IR** (ATR): $\nu = 2961$ (w), 1731 (vw), 1601 (w), 1567 (w), 1528 (w), 1467 (w), 1416 (w), 1368 (w), 1294 (w), 1258 (m), 1160 (vw), 1070 (m), 1015 (m), 877 (w), 796 (m), 774 (m), 690 (w), 613 (w), 567 (vw), 516 (w) cm⁻¹. – **MS** (FAB, 3-NBA): m/z (%) = 595 [M]⁺. – **HRMS** (FAB, C₂₁H₂₂N⁷⁹Br³⁵Cl¹⁹³Ir, [M]⁺): calc. = 595.0254; found = 595.0255.

Chlorido(η^5 -pentamethylcyclopentadienyl)[17-(4'-pyridin-2''-yl- κ N-phenyl-3' κ C)-(5 α ,3 β)androst-16-enolido]iridium(III) (10)



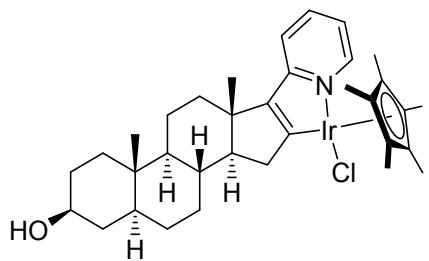
According to the general procedure (3 β ,5 α)-17-(4'-pyridin-2'-ylphenyl)androst-16-en-3-ol (**5c**) (25 mg, 58.5 μ mol, 2.00 equiv.), [IrCp*Cl₂]₂ (23 mg, 29.2 μ mol, 1.00 equiv.) and KOAc (9 mg, 87.7 μ mol, 3.00 equiv.) stirred in dry CH₂Cl₂ (3.0 mL) at room temperature for 20 h. After flash column chromatography on silica gel (cHex/EtOAc 1:1→1:3) the iridium(III) complex **10** was obtained as a yellow solid (16 mg, 20.5 μ mol, 70%) in an inseparable mixture of its diastereomers (*dr* = 1:1.15). An unambiguous

assignment of the signals to the diastereomers was not possible even with 2D NMR experiments. Therefore, the signals for the diastereomeric mixture are given, same signals are stated with “and” if clearly distinguishable.

¹H NMR (500 MHz, CDCl₃): $\delta = 8.66$ (d, $J = 5.5$ Hz, 1H, NCH_{Ar}), 7.88 – 7.80 (m, 1H, CH_{Ar}), 7.76 (d, $J = 8.1$ Hz, 1H, CH_{Ar}), 7.62 (td, $J = 7.7$, 1.6 Hz, 1H, CH_{Ar}), 7.58 (d, $J = 8.0$ Hz, 1H, CH_{Ar}), 7.10 – 6.95 (m, 2H, 2 \times CH_{Ar}) 5.99 (ddd, $J = 7.4$, 3.4, 1.8 Hz, 1H, =CH), 3.67–3.50 (m, 1H, CHOH), 2.27–2.12 (m, 2H, 2 different CH₂), 2.09–1.98 (m, 1H, CH₂), 1.85–1.60 (m, 5H, 4 different CH₂ + CH), 1.62 (s, 7.5H, 5 CH₃, Cp*), 1.61 (s, 7.5H, 5 CH₃, Cp*), 1.62–1.52 (m, 2H, CH₂ + CH), 1.53–1.24 (m, 6H, 5 different CH₂), 1.21–1.10 (m, 1H, CH), 1.10 (s, 1.5H, 18-CH₃), 1.09 (s, 1.5H, 18-CH₃), 1.07–0.95 (m, 2H, 2 different CH₂), 0.87 (s, 3H, 19-CH₃), 0.83–0.72 (m, 1H, CH) ppm. – **¹³C NMR** (126 MHz, CDCl₃): $\delta = 167.2$ (C_q -Ir), 162.9 and 162.8 each (C_q), 155.8 and 155.5 each (C_q) 151.2 and 151.2 each (+, NCH_{Ar}), 142.8 and 142.7 each ($C_{q,Ar}$), 139.6 and 139.5 each ($C_{q,Ar}$), 136.8 (+, CH_{Ar}), 134.0 and 133.6 each (+, CH_{Ar}), 127.4 and 127.3 each (+, 16-CH), 123.5 and 123.3 each (+, CH_{Ar}), 121.9 and 121.9 each (+, CH_{Ar}), 121.3 and 120.8 each (+, CH_{Ar}), 118.8 and 118.7 each (+, CH_{Ar}), 88.4 and 88.4 each (+, 5 \times C_q, Cp*), 71.3 and 71.3 each (+, CHOH), 57.6 and 57.6 each (+, CH), 54.7 and 54.7 each (+, CH), 47.5 and 47.5 each (13-C_q), 45.1 and 45.1 each (+, CH), 38.2 (–, CH₂), 36.8 (–, CH₂), 35.7 (–, CH₂ + 10-C_q), 34.2 and 34.1 each (+, CH), 32.0 and 32.0 each (–, CH₂), 31.7 and 31.6 each (–, CH₂), 31.5 (–, CH₂), 28.7 (–, CH₂), 21.4 and 21.3 each (–, CH₂), 17.1 and 17.0 each (+, 18-CH₃), 12.4 (+, 19-CH₃), 9.01 and 8.99 each (+, 5 \times CH₃, Cp*) ppm. – **IR** (ATR): $\nu = 3408$ (br), 2914 (w), 2848 (vw), 1604 (vw), 1579 (vw),

1560 (vw), 1470 (vw), 1376 (vw), 1316 (vw), 1265 (vw), 1157 (vw), 1030 (vw), 885 (vw), 810 (vw), 773 (w), 727 (vw), 613 (vw), 500 (vw), 434 (vw) cm^{-1} . – **MS** (FAB, 3-NBA): m/z (%) = 793/792/791/790/789/788/787 [M]⁺, 756/755/754/753/752/751/750 [M–Cl]⁺, 363 [IrCp^{*}Cl]⁺. – **HRMS** (FAB, C₄₀H₅₁ON³¹⁵Cl¹⁹³Ir, [M]⁺): calc. = 789.3289; found = 789.3291.

Chlorido(η^5 -pentamethylcyclopentadienyl)[(5 α ,3 β)-17-((2'-pyridinyl- κ N)androst-16-en-ol-16 κ Cido] iridium(III) (**11**)



According to the general procedure (3 β ,5 α)-17-(2'-pyridinyl)-androst-16-en-3-ol (**5a**) (77 mg, 218 μmol , 2.00 equiv.), [IrCp^{*}Cl₂]₂ (87 mg, 109 μmol , 1.00 equiv.) and KOAc (32 mg, 327 μmol , 3.00 equiv.) in dry CH₂Cl₂ (5.0 mL) were stirred at room temperature for 26 h. After flash column chromatography on silica gel (*c*Hex/EtOAc, 2:1→1:1) the iridium(III) complex **10**

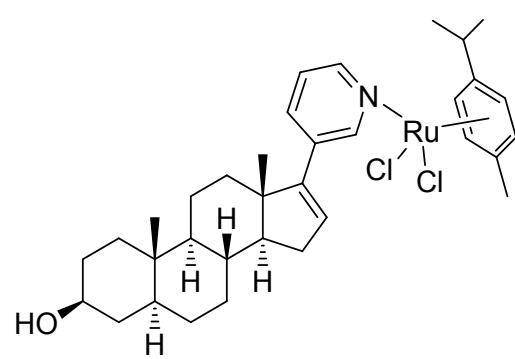
was obtained as a yellow solid (76 mg, 0.107 mmol, 48%) as a mixture of its diastereomers (*dr* = 1:1.15). An unambiguous assignment of the signals to the diastereomers was not possible even with 2D NMR experiments. Therefore, the signals for the diastereomeric mixture are given, same signals are stated with “and” if clearly distinguishable.

¹H NMR (500 MHz, CDCl₃): δ = 8.51 (dd, *J* = 5.8, 1.5 Hz, 0.64H, 3-CHN, major) and 8.44 (dd, *J* = 5.8, 1.5 Hz, 0.36 H, 3-CHN), 7.44–7.32 (m, 1H, 5-CH, both), 7.22–7.15 (m, 1H, 6-CH, both), 6.70 (td, *J* = 6.5, 5.8, 1.3 Hz, 1H, 4-CH, both) 3.60 (tt, *J* = 10.6, 4.7 Hz, 1H, CHOH, both) 2.86 (dd, *J* = 16.3, 6.1 Hz, 0.64H, 15-CH₂^a, major) and 2.73 (dd, *J* = 16.2, 6.4 Hz, 0.36H, 15-CH₂^a, minor), 2.59 (dd, *J* = 16.2, 11.3 Hz, 0.36H, 15-CH₂^b, minor), 2.28–2.17 (m, 2H, CH₂, both + 15-CH₂^b, major), 1.87–1.74 (m, 2H, 2 different CH₂, both), 1.71 (s, 10H, 5×CH₃(Cp^{*}), major), 1.68 (s, 5H, 5×CH₃(Cp^{*}), minor), 1.70–1.43 (m, 7H, different CH₂ + CH + CH, both), 1.35–1.27 (m, 3.36H, 2 different CH₂, both + CH, minor), 1.19–0.98 (m, 4H, 2 different CH₂, both + CH, major), 0.97 (s, 1H, 18-CH₃, minor), 0.87 and 0.86 (two s, 5H, 18-CH₃, major + 19-CH₃, major + 19-CH₃, minor), 0.83–0.71 (m, 1H, CH, both) ppm.

– **¹³C NMR** (126 MHz, CDCl₃): δ = 187.9 and 187.2 each (16-C_q-Ir), 165.1 and 164.9 each (1-C_qN), 153.2 and 151.9 each (17-C_q), 151.6 and 151.5 (+, CH_{pyr}), 136.7 and 136.5 each (+, CH_{pyr}), 117.8 and 117.6 each (+, CH_{pyr}), 117.4 and 116.9 each (+, CH_{pyr}), 88.5 and 88.5 each (C_{q,Ar}, 5×Cp^{*}), 71.4 and 71.2 each (+, CHOH), 59.1 and 58.7 each (+, CH), 55.3 and 54.7 each (+, CH), 45.5 and 45.3 (13-C_q), 45.2 and 45.0 (–, CH₂), 39.3 and 39.1 each (–, CH₂), 38.3 and 38.2 each (–, CH₂), 37.0 and 36.8 each (–, CH₂), 36.3 and 35.3 each (–, CH₂), 35.8 and 35.7 each (10-C_q), 34.4 and 34.1 each (+, CH), 32.3 and 31.9 each (–, CH₂), 31.6 and 31.5 each (–, CH₂), 28.8 (–, CH₂), 21.6 and 21.4 each (–, CH₂), 18.4 and 16.5 each (+, 18-CH₃), 12.4 and 12.4 each (+, 19-CH₃), 9.2 and 9.1 each (+, 5×CH₃, Cp^{*}) ppm. – **IR** (ATR): ν = 3410 (br), 2914 (w), 2848 (vw), 1597 (vw), 1500 (vw), 1466 (w), 1375 (vw), 1242 (vw), 1080 (vw), 1026 (w), 961 (vw), 776 (w), 726 (m), 643 (vw) cm^{-1} . – **MS** (FAB, 3-NBA): m/z

(%) = 717/716/715/714/713/712/711 [M]⁺, 680/679/678/677/676/675/674 [M-Cl]⁺, 663/662/661/660/659/658 [M-Cl-OH/H₂O]⁺, 363 [IrCp^{*}Cl]⁺. – **HRMS** (FAB, C₃₄H₄₇ON³⁵Cl¹⁹³Ir, [M]⁺): calc. = 713.2976; found = 713.2974.

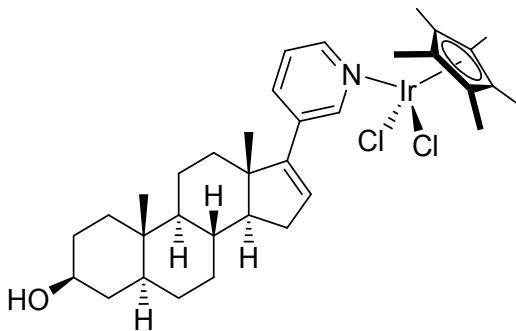
Dichlorido(η^6 -*para*-cymene)[(5 α ,3 β)-17-((3'-pyridinyl- κ N)-androst-16-en-3-olido]ruthenium(II) (**12**)



Under argon atmosphere, (3 β ,5 α)-17-(3'-pyridinyl)-androst-16-en-3-ol (**5b**) (22 mg, 62.6 μ mol, 2.00 equiv.) and [Ru(*p*-cymene)Cl₂]₂ (19 mg, 31.1 μ mol, 1.00 equiv.) were in dry CH₂Cl₂ (1.5 mL). The solution was stirred 24 h at room temperature then, a mixture of *n*-hexane and ethyl acetate (10 mL, 4:1) was added. The precipitate was washed with *n*-hexane (ca. 30 mL) and the title compound **12** was obtained as an orange solid (14 mg, 21.7 μ mol, 70%).

¹H NMR (500 MHz, CDCl₃): δ = 9.02 (d, *J* = 2.0 Hz, 1H, 2'-CH), 8.84 (d, *J* = 5.3 Hz, 1H, 4'-CH), 7.67 (dt, *J* = 8.0, 1.7 Hz, 1H, 6'-CH), 7.21 (dd, *J* = 7.9, 5.6 Hz, 1H, 5'-CH), 6.05 (d, *J* = 1.6 Hz, 1H, =CH), 5.50–5.37 (m, 2H, 2×CH_{cymene}), 5.21 (d, *J* = 5.9 Hz, 2H, 2×CH_{cymene}), 3.60 (tt, *J* = 10.5, 4.5 Hz, 1H, CHOH), 2.23 (ddd, *J* = 6.1, 6.5, 3.4 Hz, 1H, 15-CH₂^a), 2.12 (s, 3H, C_{q,cymene}CH₃), 2.08–1.92 (m, 2H, 15-CH₂^b + CH₂), 1.83–1.78 (m, 1H, CH₂), 1.76–1.50 (m, 6H, 6H, 4 different CH₂+ CH + CH), 1.49–1.39 (m, 3H, 3 different CH₂), 1.31 (s, 3H, CHCH₃), 1.30 (s, 3H, CHCH₃), 1.30–1.23 (m, 4H, 2 different CH₂ + CH(CH₃)₂), 1.19–1.09 (m, 1H, CH), 1.02–0.95 (m, 2H, 2 different CH₂), 1.00 (s, 3H, 18-CH₃), 0.85 (s, 3H, 19-CH₃), 0.80–0.70 (m, 1H, CH) ppm. – **¹³C NMR** (126 MHz, CDCl₃): δ = 152.6 (+, 2',4'-CH), 150.2 (1'-C_q), 134.8 (+, 6'-CH), 133.9 (17-C_q), 131.2 (+, 16-CH), 123.7 (+, 5'-CH), 103.5 (C_{q,cymene}), 96.8 (C_{q,cymene}), 82.4 (+, CH_{cymene}), 82.3 (+, 2×CH_{cymene}), 82.3 (+, CH_{cymene}), 71.1 (+, 3-CHOH), 57.3 (+, CH), 54.4 (+, CH), 47.4 (13-C_q), 44.9 (+, CH), 38.0 (–, CH₂), 36.7 (–, CH₂), 35.5 (10-C_q), 35.1 (–, CH₂), 33.8 (+, CH), 31.8 (–, CH₂), 31.7 (–, CH₂), 31.4 (–, CH₂), 30.5 (+, CH(CH₃)₂), 28.5 (–, CH₂), 22.2 (+, CHCH₃), 22.1 (+, CHCH₃), 21.1 (–, CH₂), 18.1 (+, C_{q,cymene}CH₃), 16.7 (+, 18-CH₃), 12.2 (+, 19-CH₃) ppm. – **IR** (ATR): ν = 3416 (br), 2919 (w), 2848 (w), 1601 (vw), 1443 (vw), 1413 (vw), 1376 (vw), 1262 (vw), 1079 (vw), 1039 (w), 923 (vw), 867 (vw), 800 (w), 730 (vw), 698 (vw), 667 (vw) cm⁻¹. – **MS** (FAB, 3-NBA): *m/z* (%) = 662/661/660/659/658/657/656/655 [M]⁺, 626/625/624/623/622/621/620/619 [M-Cl]⁺. – **HRMS** (FAB, C₃₄H₄₇ON³⁵Cl¹⁰²Ru, [M]⁺): calc. = 657.2078; found = 657.2079.

Dichlorido(η^5 -pentamethylcyclopentadienyl)[(5 α ,3 β)-17-((3'-pyridinyl- κ N)androst-16-en-3-ol)ido]-iridium(III) (**13**)



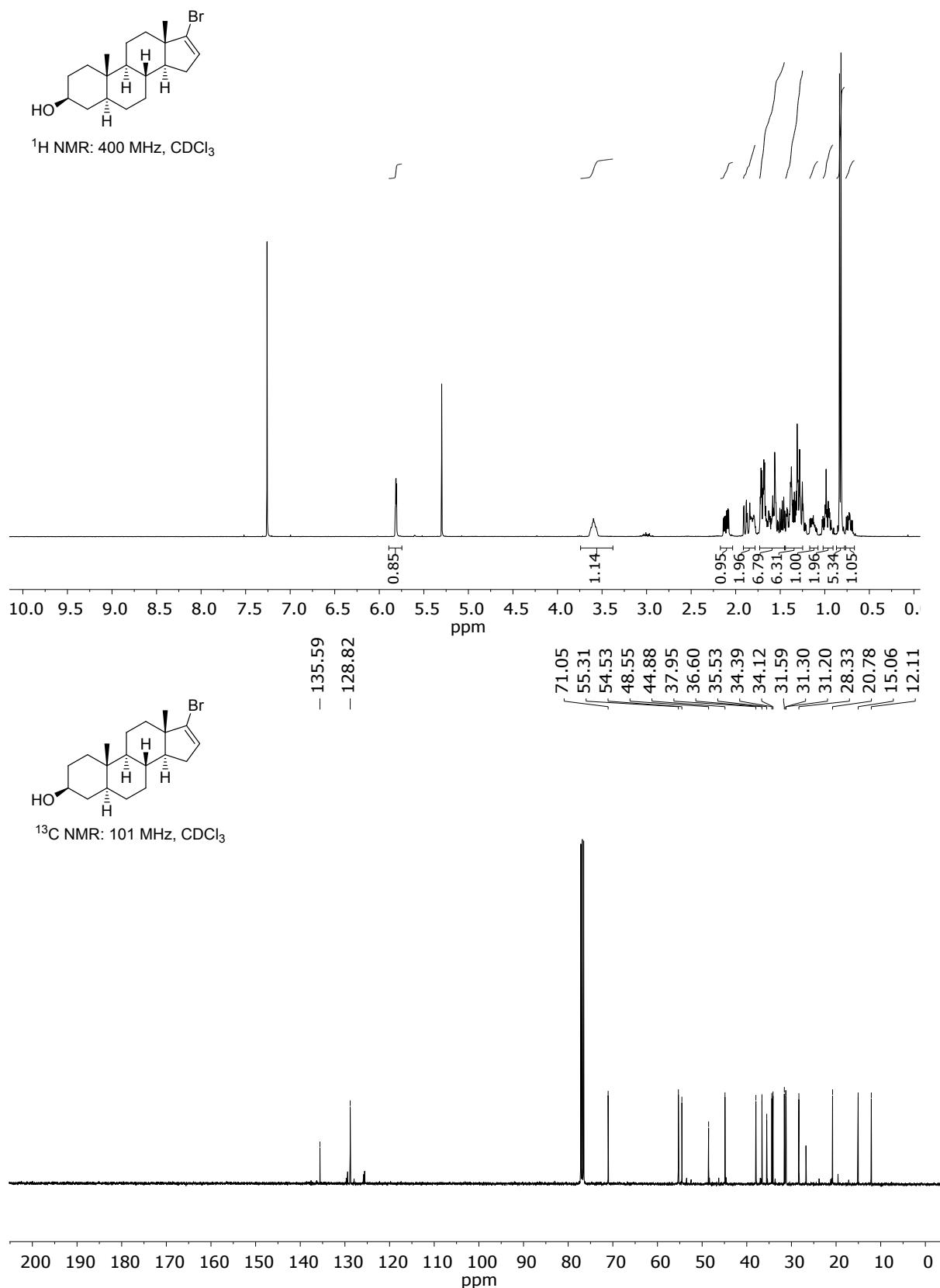
Under argon atmosphere, (3 β ,5 α)-17-(3'-pyridinyl)androst-16-en-3-ol (**5b**) (32 mg, 91.0 μ mol, 2.00 equiv.) and [IrCp*Cl₂]₂ (36 mg, 45.5 μ mol, 1.00 equiv.) were in dry CH₂Cl₂ (3.0 mL). The solution was stirred 24 h at room temperature. A mixture of *n*-hexane and ethyl acetate (10 mL, 4:1) was added. The precipitate was washed with *n*-hexane (ca. 30 mL) and

the title compound **13** was obtained as a yellow solid (52 mg, 68.8 μ mol, 76%).

¹H NMR (500 MHz, CDCl₃): δ = 8.99 (d, *J* = 1.9 Hz, 1H, 2'-CH_{pyr}), 8.77 (d, *J* = 5.6 Hz, 1H, 4'-CH_{pyr}), 7.67 (d, *J* = 7.8 Hz, 1H, 5'-CH_{pyr}), 7.26 – 7.15 (m, 1H, 6'-CH_{pyr}), 6.14 – 6.06 (m, 1H, 16-CH), 3.67 – 3.49 (m, 1H, 3-CHOH), 2.24 (ddd, *J* = 16.1, 6.4, 3.3 Hz, 1H, 15-CH₂^a), 2.10–1.97 (m, 2H, 15-CH₂^b + CH₂), 1.85–1.77 (m, 1H, CH₂), 1.74–1.55 (m, 6H, 4 different CH₂ + CH + CH), 15.3 (m, 15H, 5×CH₃, Cp*) 1.46–1.20 (m, 6H, 5 different CH₂), 1.19–1.07 (m, 1H, CH), 1.07–0.98 (m, 2H, 2 different CH₂), 1.01 (s, 3H, 18-CH₃), 0.85 (s, 3H, 19-CH₃), 0.81–0.71 (m, 1H, CH) ppm. – **¹³C NMR** (126 MHz, CDCl₃): δ = 151.2 (+, 2'- or 4'-CH_{pyr}), 151.0 (+, 2'- or 4'-CH_{pyr}), 150.1 (17-C_q), 135.0 (+, 5'-CH_{pyr}), 134.8 (1'-C_q), 131.3 (+, 16-CH), 124.6 (+, 6'-CH_{pyr}), 85.5 (5×C_q, Cp*), 71.1 (+, CHOH), 57.2 (+, CH), 54.4 (+, CH), 47.4 (13-C_q), 44.9 (+, CH), 38.0 (–, CH₂), 36.7 (–, CH₂), 35.6 (10-C_q), 35.2 (–, CH₂), 33.8 (+, CH), 31.8 (–, CH₂), 31.7 (–, CH₂), 31.4 (–, CH₂), 28.5 (–, CH₂), 21.1 (–, CH₂), 16.7 (+, 18-CH₃), 12.2 (+, 19-CH₃), 8.4 (+, 5×CH₃, Cp*) ppm. – **IR** (ATR): ν = 3402 (br), 2925 (w), 2852 (w), 1599 (vw), 1445 (w), 1422 (vw), 1375 (w), 1291 (vw), 1224 (vw), 1193 (vw), 1117 (vw), 1082 (w), 1049 (w), 1029 (w), 922 (vw), 841 (vw), 804 (w), 732 (w), 703 (w), 611 (vw), 538 (vw) cm⁻¹. – **MS** (FAB, 3-NBA): *m/z* (%) = 752/751/750/749/748/747/747/746 [M]⁺, 718/717/716/715/714/713/712 [M-Cl]⁺, 398 [IrCp*Cl₂]⁺, 363 [IrCp*Cl]⁺. – **HRMS** (FAB, C₃₄H₄₈ON³⁵Cl₂¹⁹³Ir, [M]⁺): calc. = 749.2742; found = 749.2741.

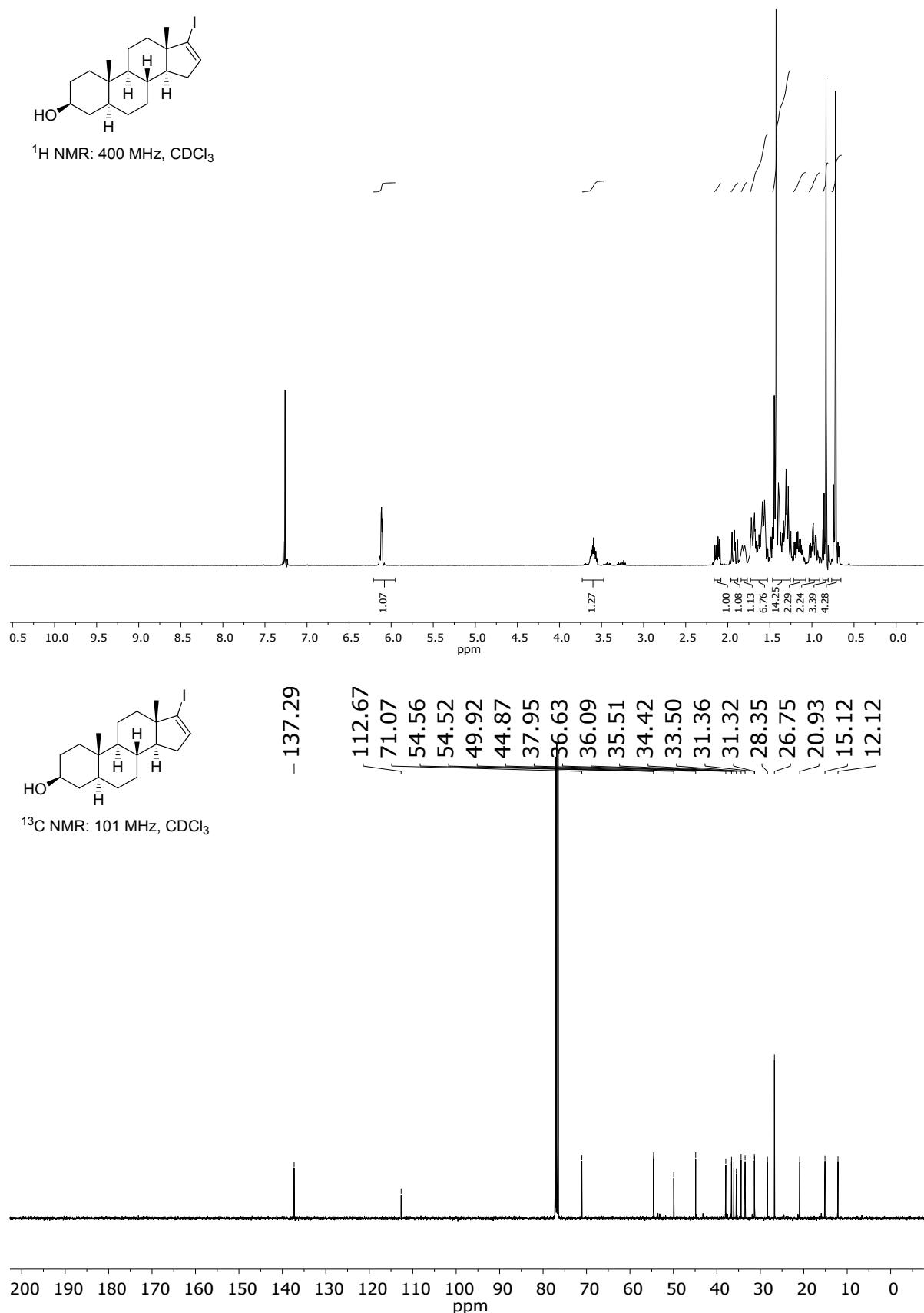
2.3. NMR spectra of the synthesized compounds

(3 β ,5 α)-17-Bromoandrost-16-en-3-ol (4a)²



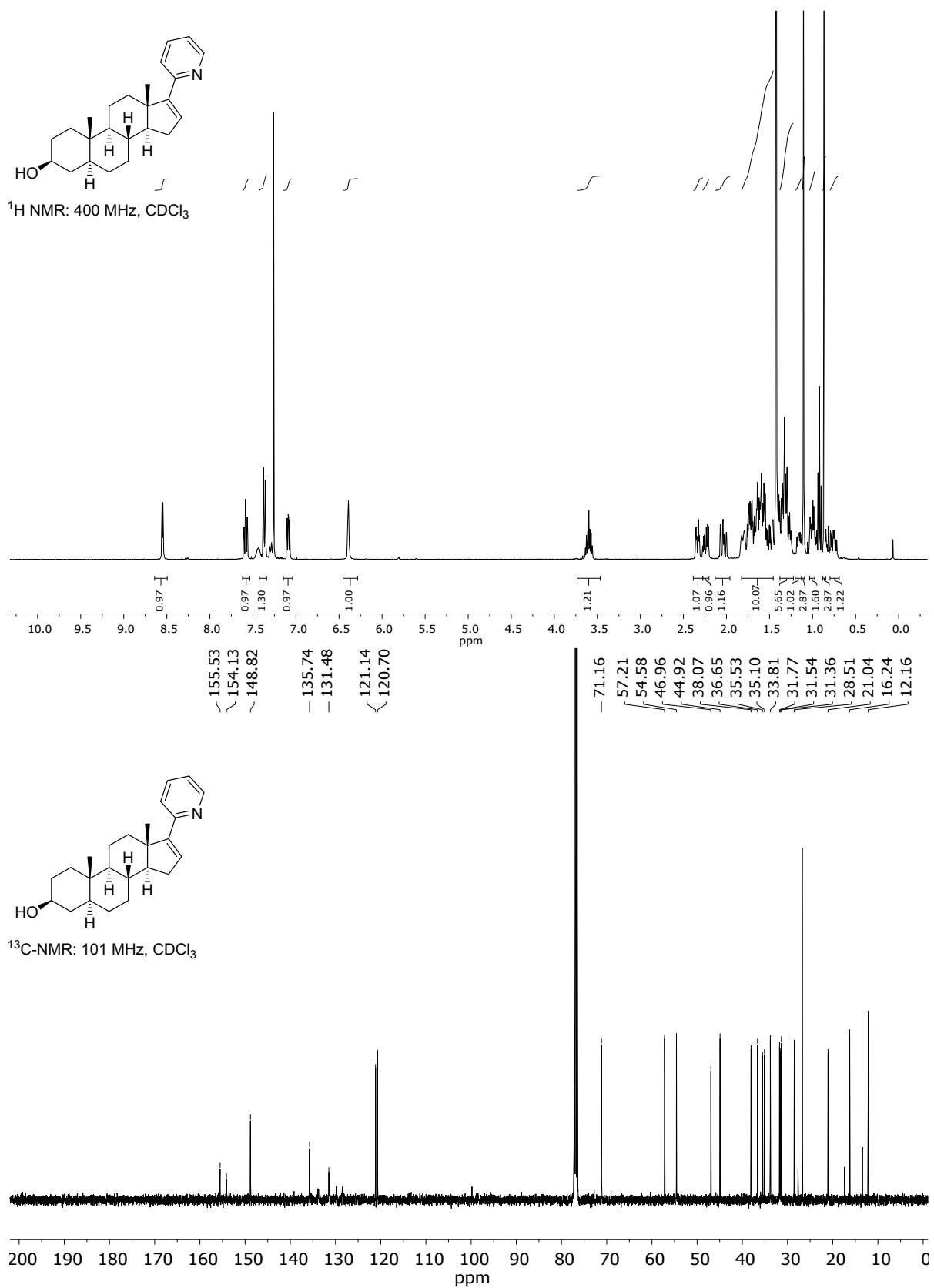
NMR spectra contain traces of dichloromethane.

*(3 β ,5 α)-17-Iodoandrostan-16-en-3-ol (**4b**)²*

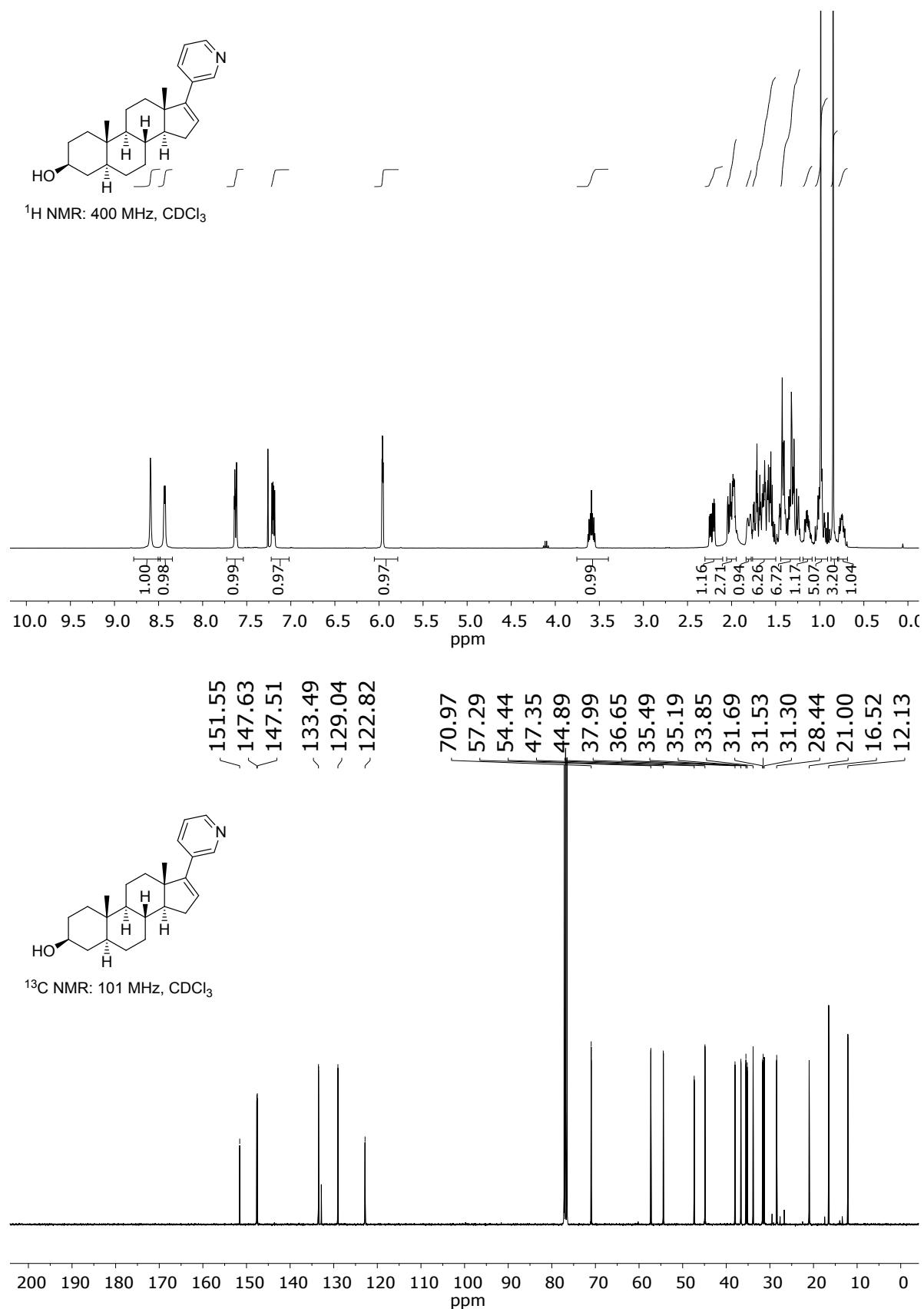


NMR spectra contain traces of cyclohexane.

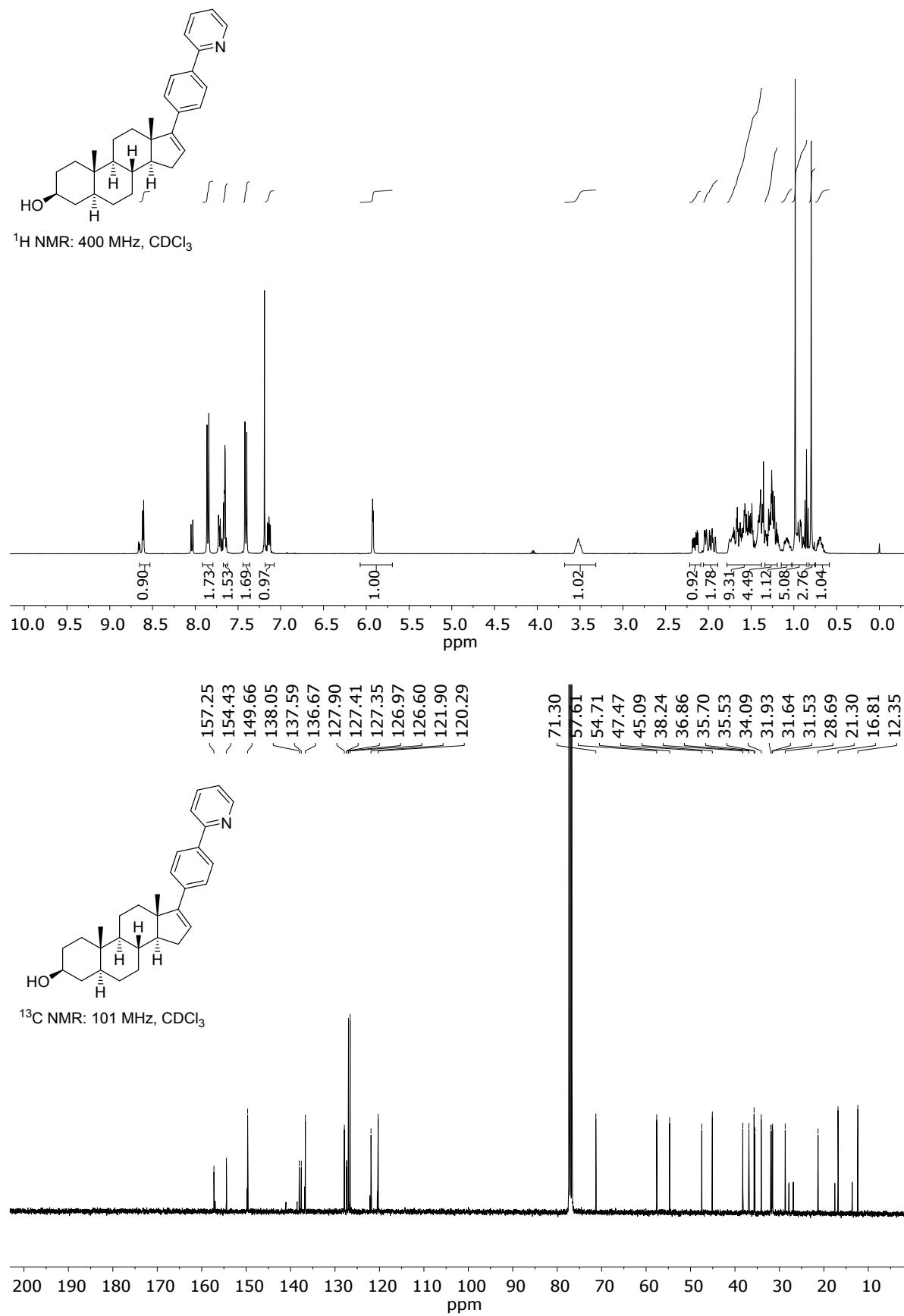
(3 β , 5 α)-17-(2'-Pyridyl)-5 α -androst-16-en-3-ol (5a**)²**



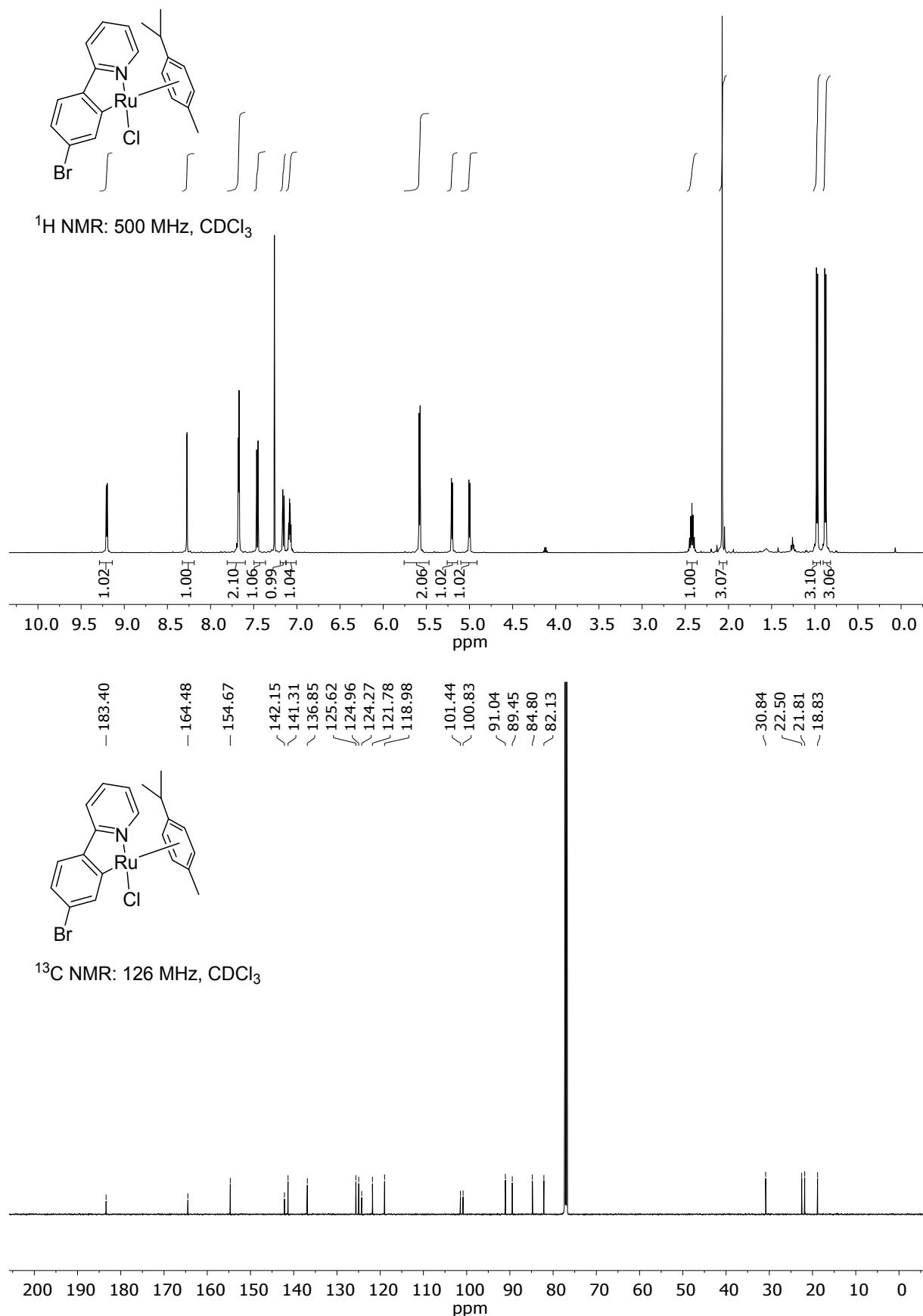
*(3 β , 5 α)-17-(3'-Pyridinyl)-5 α -androst-16-en-3-ol (**5b**)²*



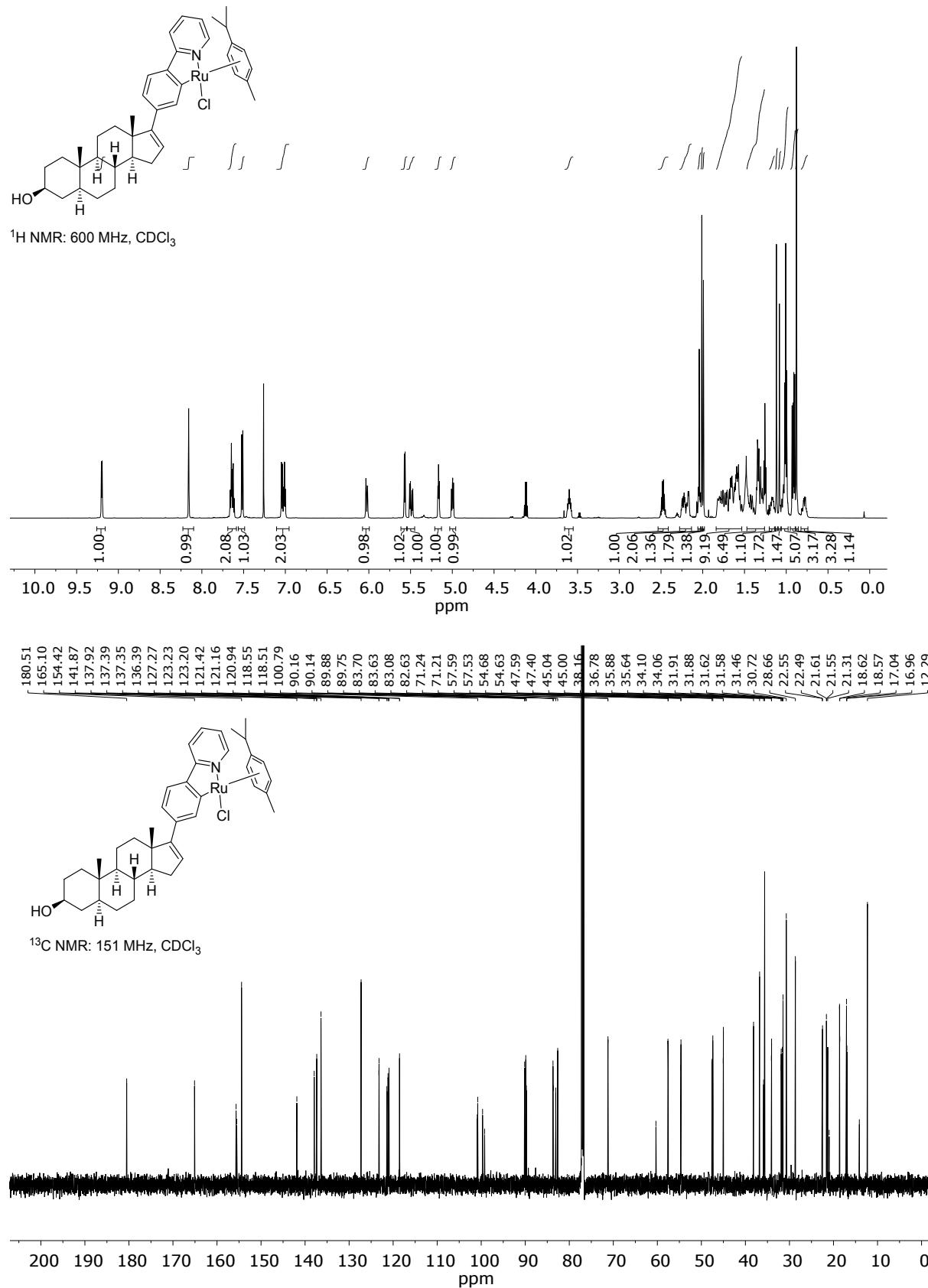
*3 β , 5 α)-17-(4'-Pyridin-2'-ylphenyl)androst-16-en-3-ol (**5c**)²*



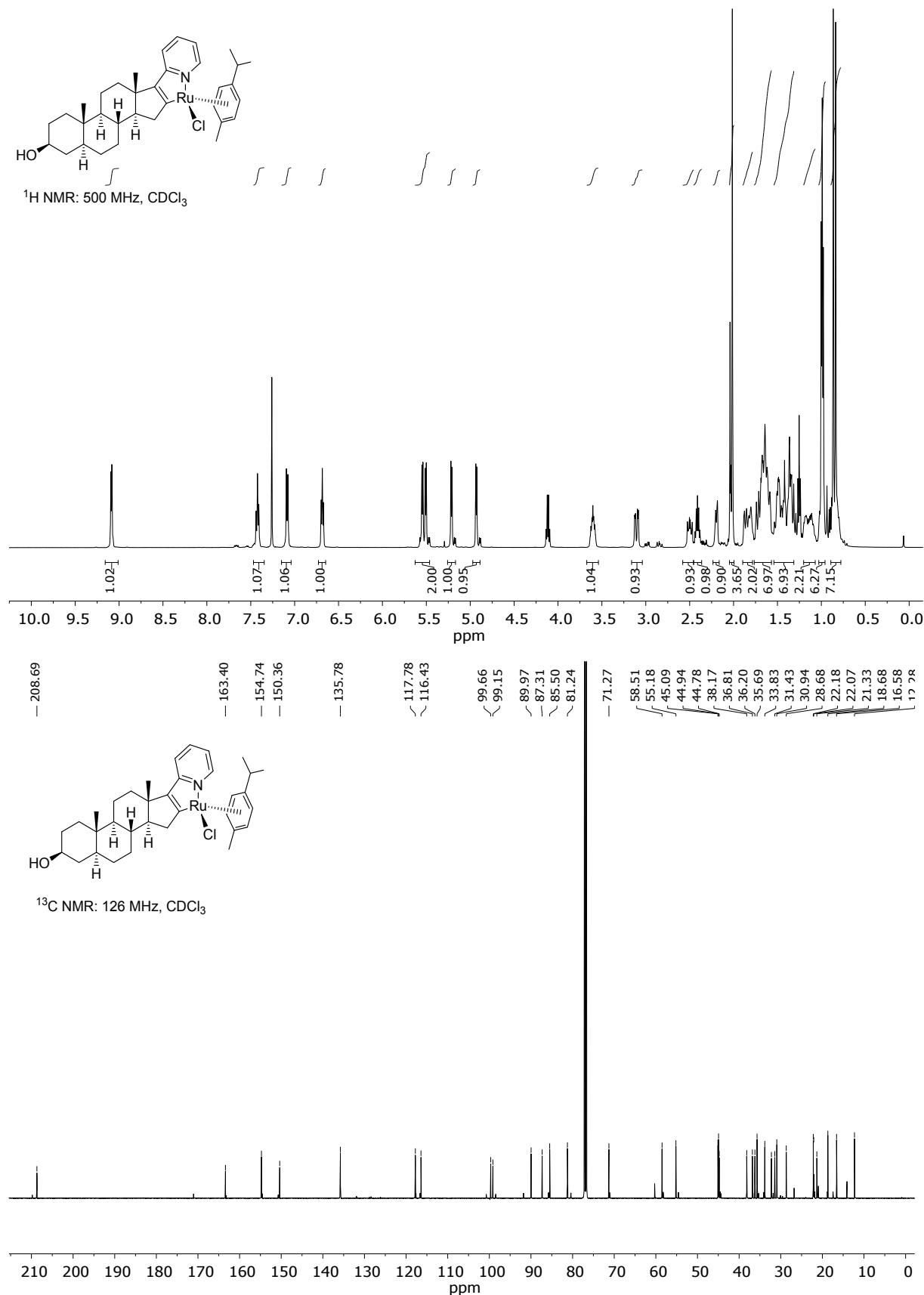
[5-Bromo-2-(2-pyridinyl- κ N)phenyl- κ C¹]chlorido(η^6 -*para*-cymene) ruthenium(II) (**6**)



Chlorido(η^6 -*para*-cymene)[17-(4'-pyridin-2''-yl- κ N-phenyl-3' κ C)-(5 α ,3 β)-androst-16-enolido]-ruthenium(II) (7)

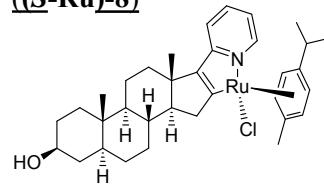


Chlorido(η^6 -*para*-cymene)[(5 α)-17-(2'-pyridinyl- κ N)androst-16-en-3 β -ol-16 κ C¹⁶]ruthenium(II)
(*R*-Ru)-8)

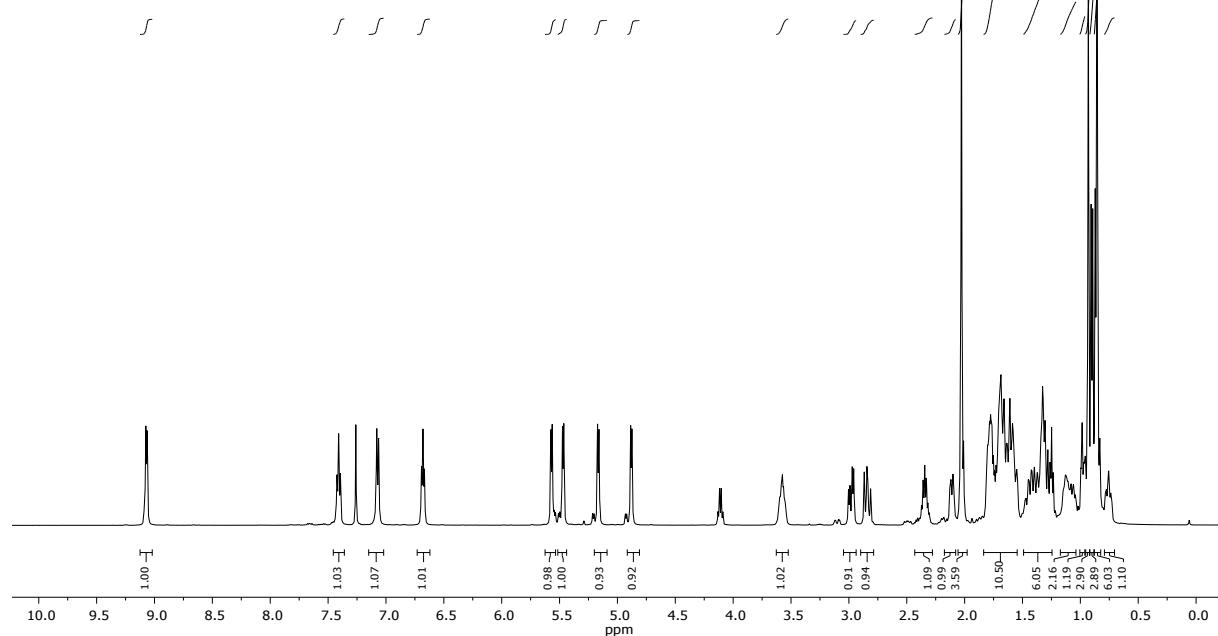


Chlorido(η^6 -*para*-cymene)[(5 α)-17-(2'-pyridinyl- κ N)androst-16-en-3 β -ol-16 κ C¹⁶]ruthenium(II)

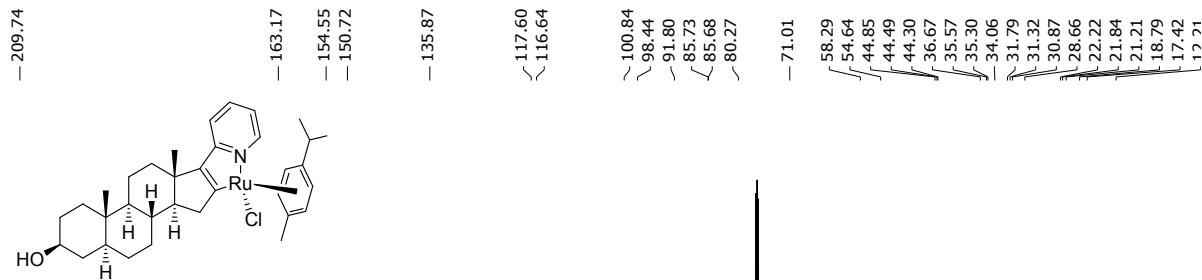
(*S*-Ru)-8)



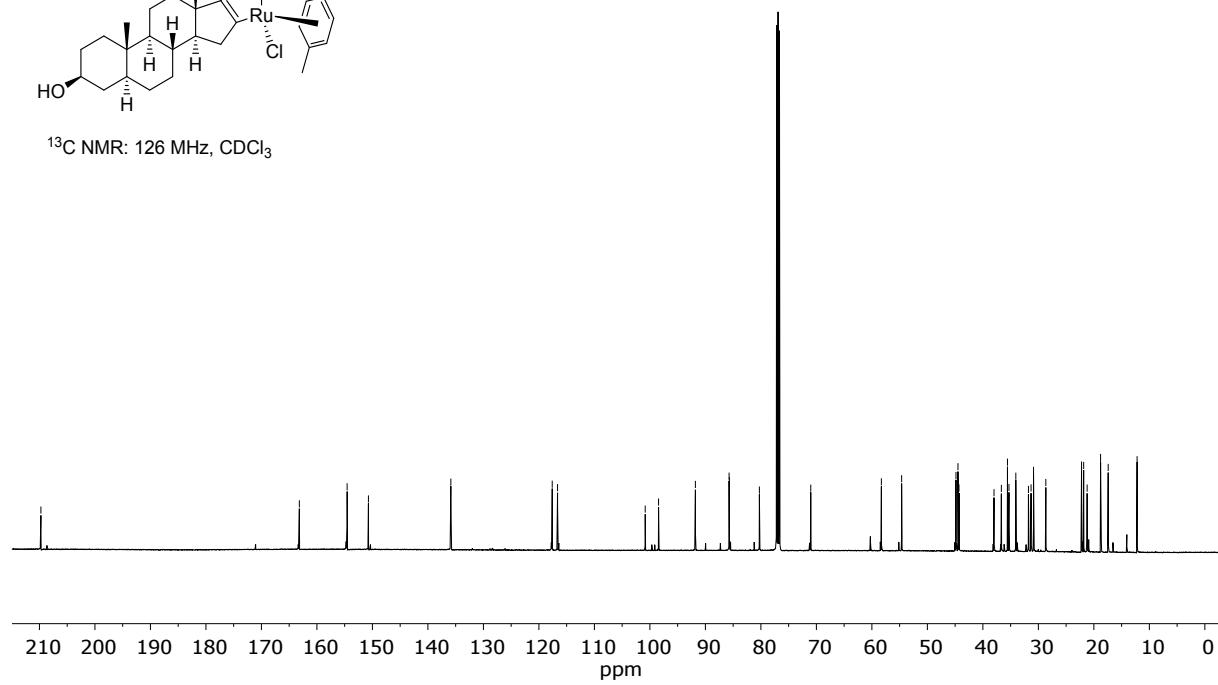
¹H NMR: 500 MHz, CDCl₃



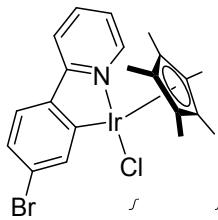
-209.74



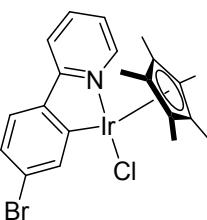
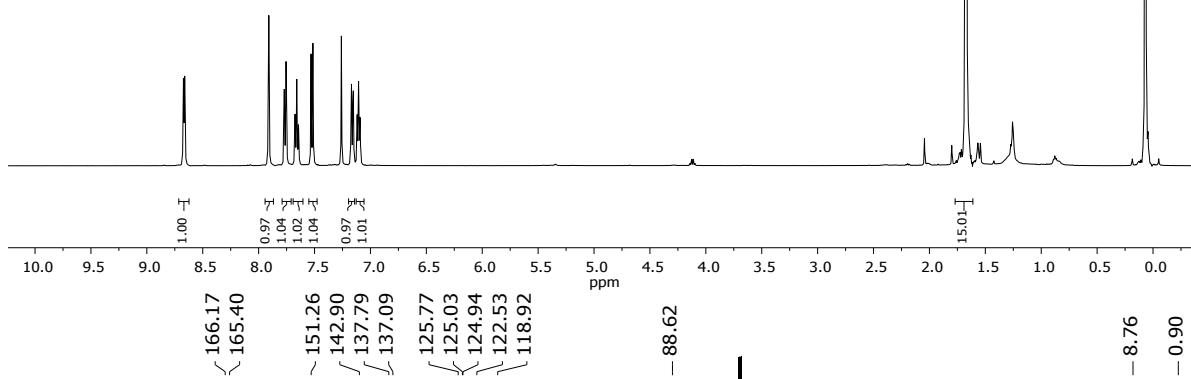
¹³C NMR: 126 MHz, CDCl₃



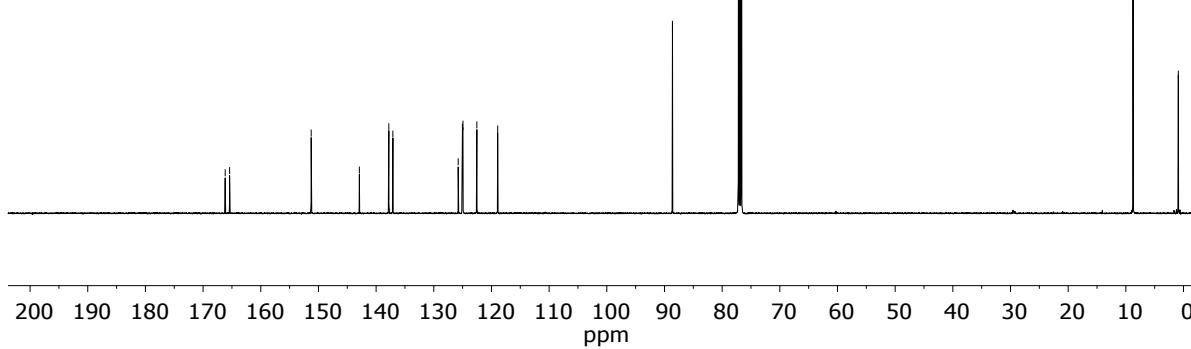
[5-Bromo-2-(2-pyridinyl- κ N)phenyl- κ C¹]chlorido(η^5 -pentamethylcyclopentadienyl)iridium(III) (**9**)



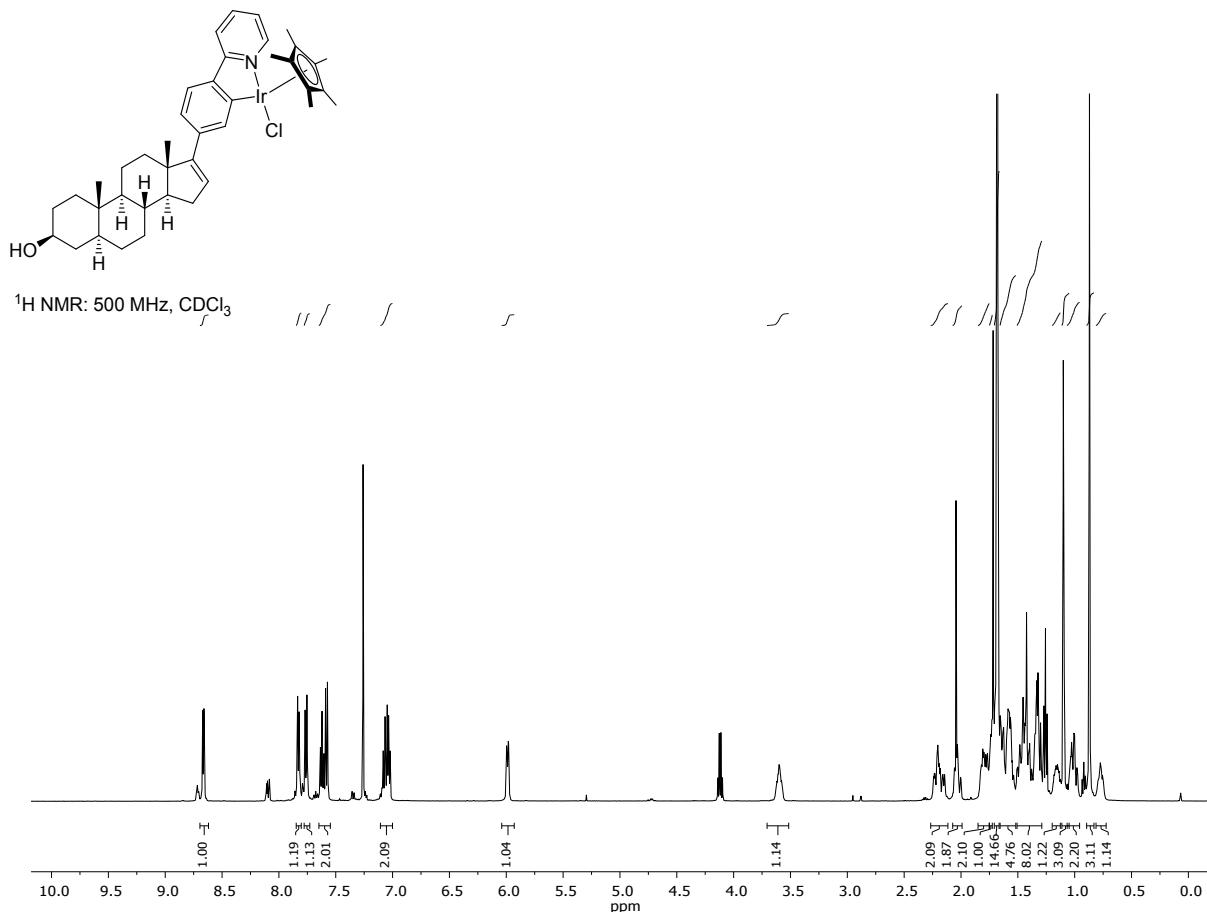
¹H NMR (500 MHz, CDCl₃)



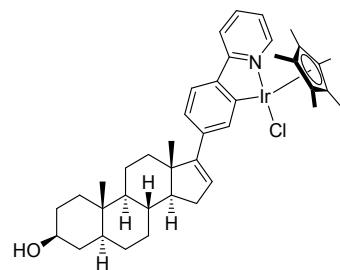
¹³C NMR (126 MHz, CDCl₃)



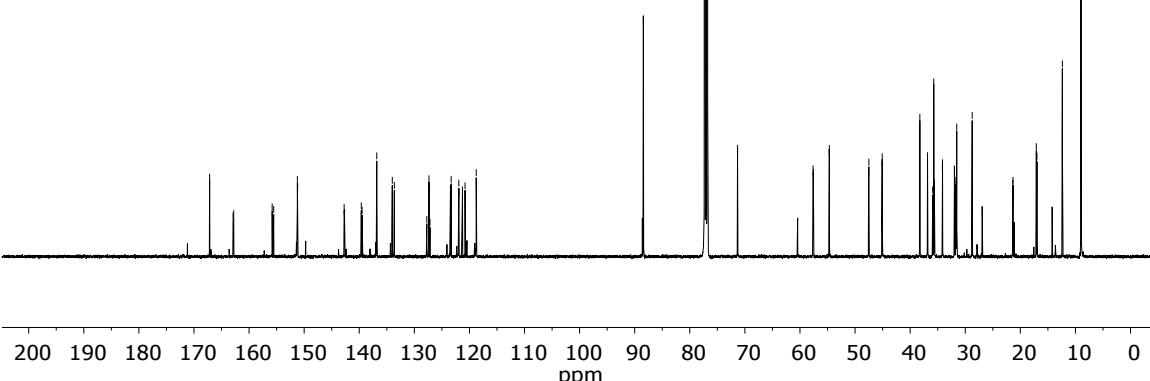
Chlorido(η^5 -pentamethylcyclopentadienyl)[17-(4'-pyridin-2''-yl- κ N-phenyl-3' κ C)-(5 α ,3 β)androst-16-enolido]iridium(III) (**10**)



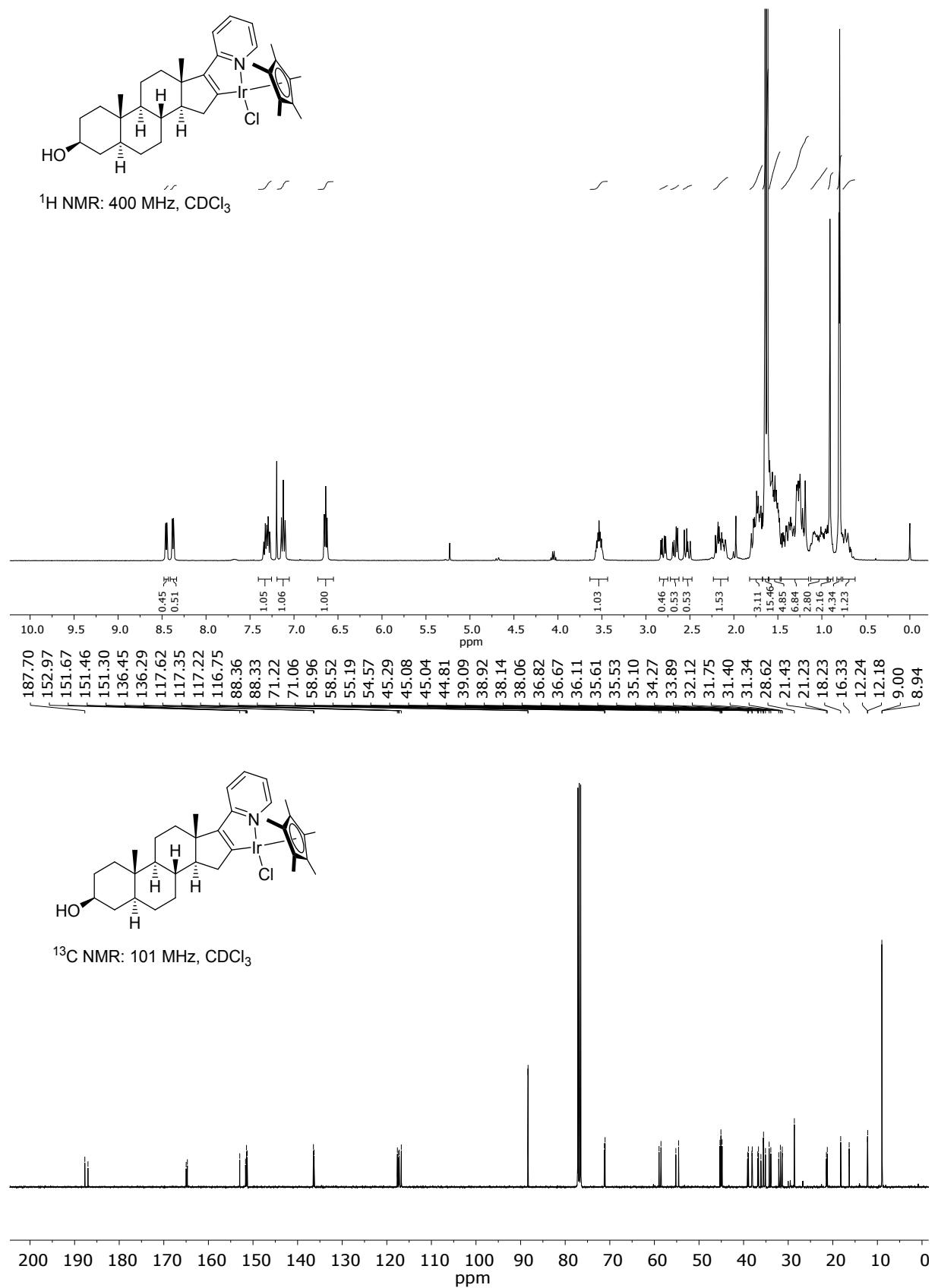
167.16	36.84
151.23	35.91
151.18	35.71
136.82	35.61
134.00	34.15
133.63	31.97
127.35	31.70
127.30	31.64
123.45	31.55
123.31	28.74
121.90	21.37
121.26	21.33
120.79	17.10
118.77	16.98
118.74	12.37
88.43	9.01
88.41	8.99
71.34	
71.33	
57.63	
57.57	
54.68	
54.67	
47.54	
47.50	
45.11	
45.08	
38.24	



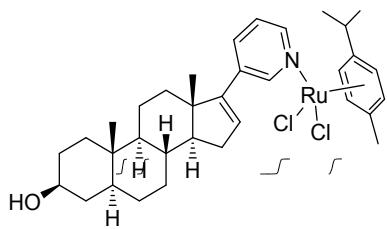
¹³C NMR: 151 MHz, CDCl₃



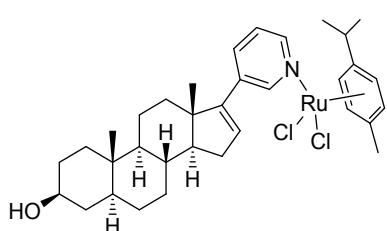
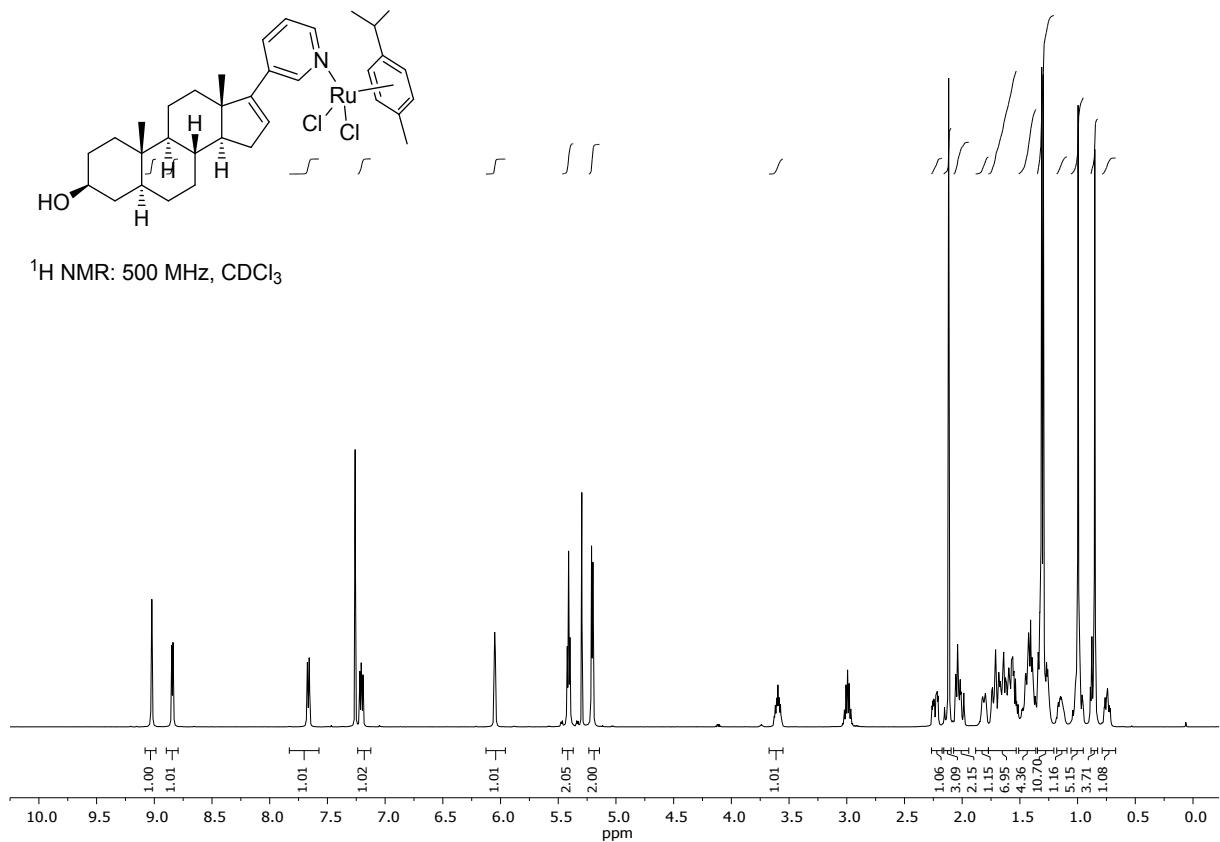
Chlorido(η^5 -pentamethylcyclopentadienyl)[(5 α ,3 β)-17-((2'-pyridinyl- κ N)androst-16-en-ol-16 κ Cido]iridium(III) (**11**)



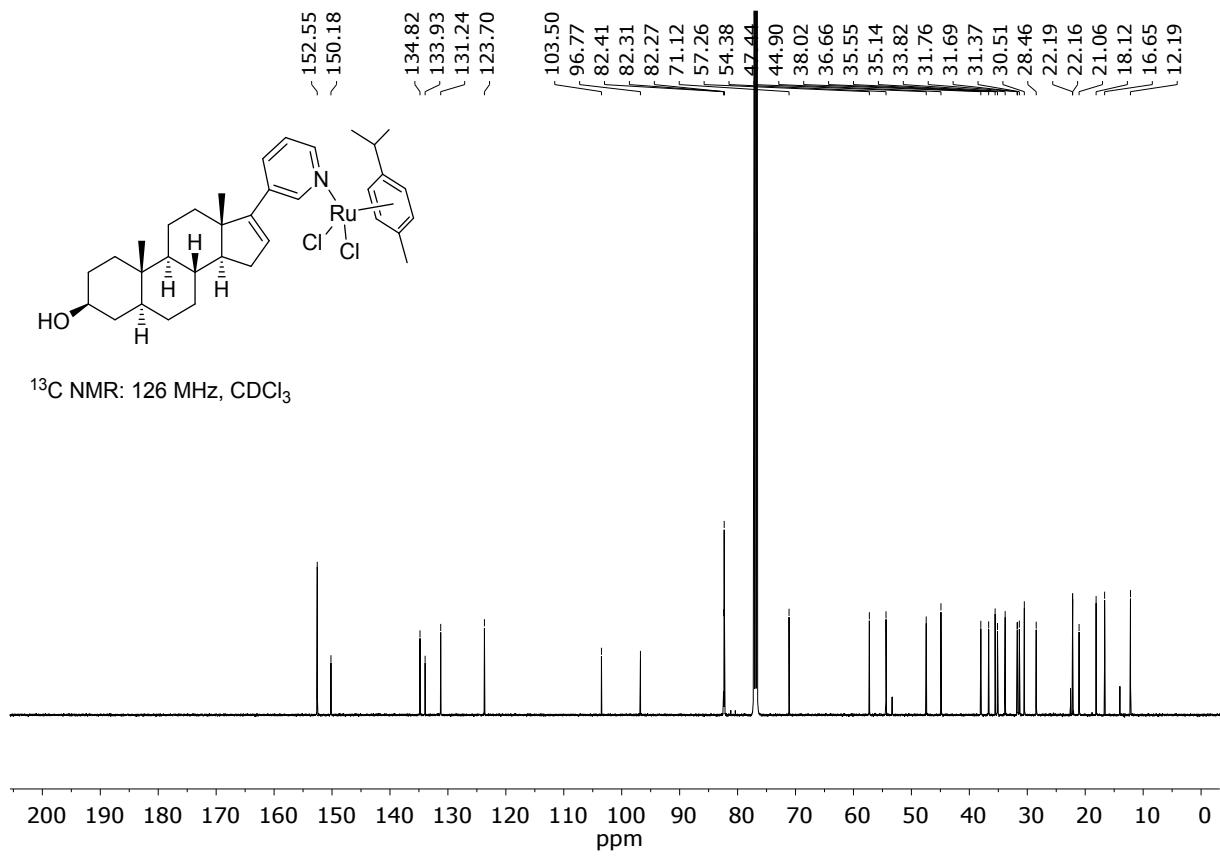
Dichlorido(η^6 -*para*-cymene)[(5*a*,3*B*)-17-((3'-pyridinyl- κ N)-androst-16-en-3-ol)ido]ruthenium(II) (12)



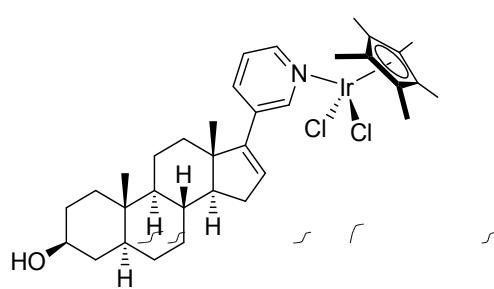
^1H NMR: 500 MHz, CDCl_3



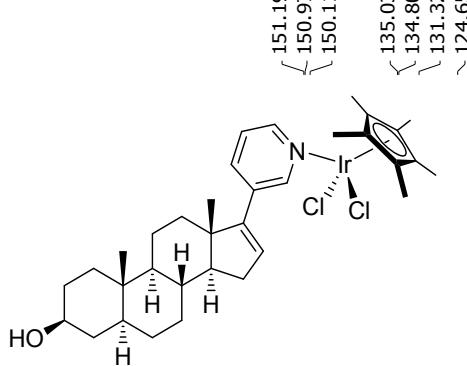
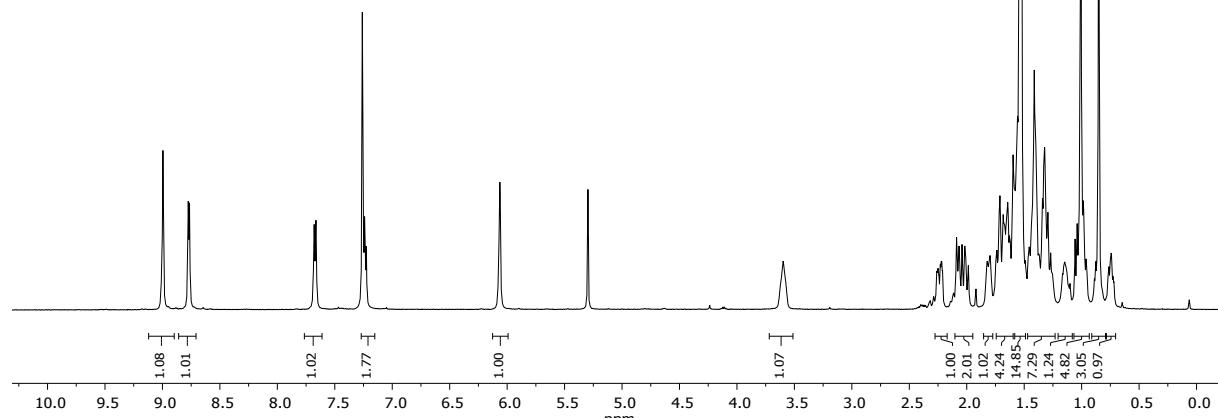
¹³C NMR: 126 MHz, CDCl₃



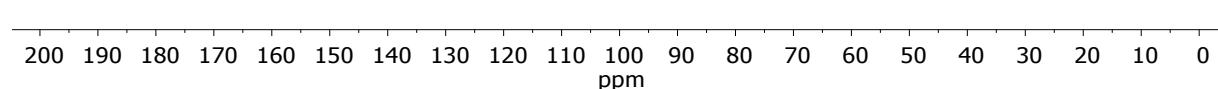
Dichlorido(η^5 -pentamethylcyclopentadienyl)[(5 α ,3 β)-17-((3'-pyridinyl- κ N)androst-16-en-3-ol)ido]iridium(III) (**13**)



¹H NMR (500 MHz, CDCl₃)

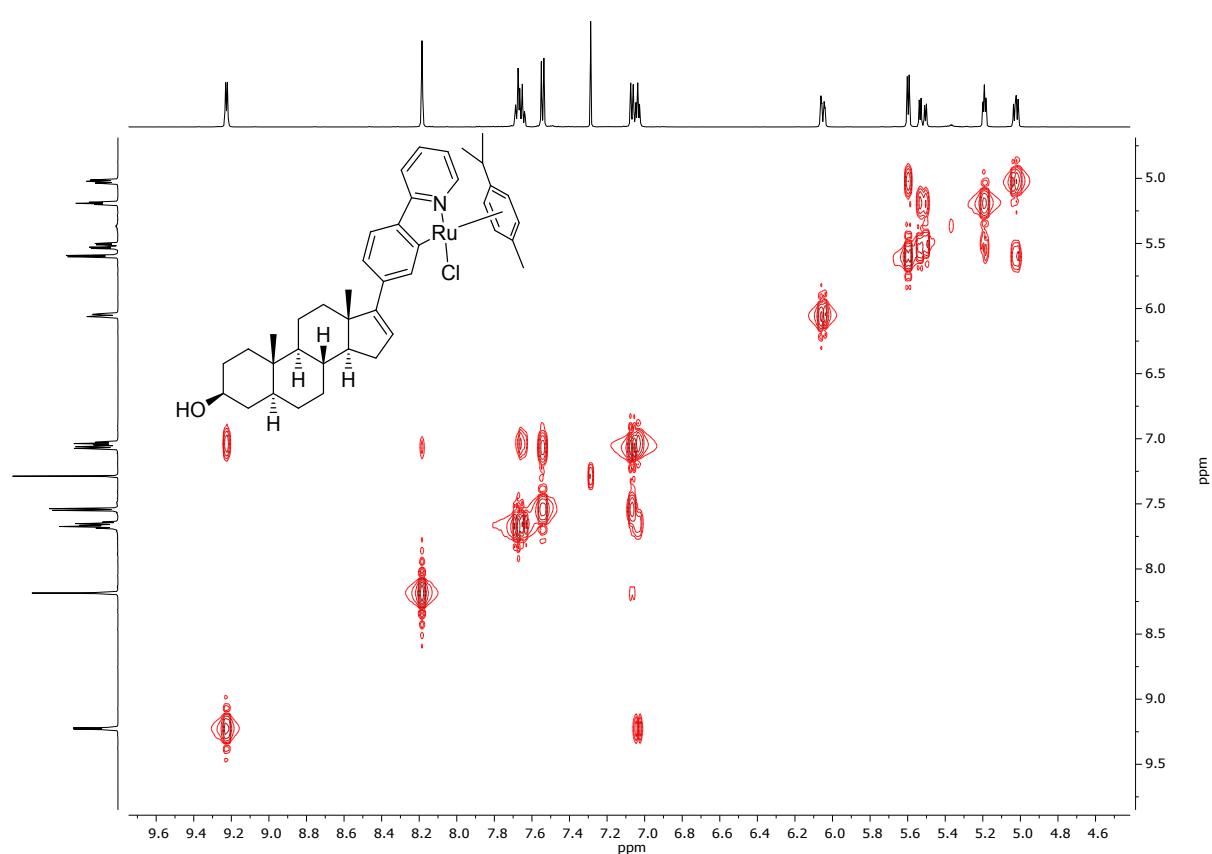
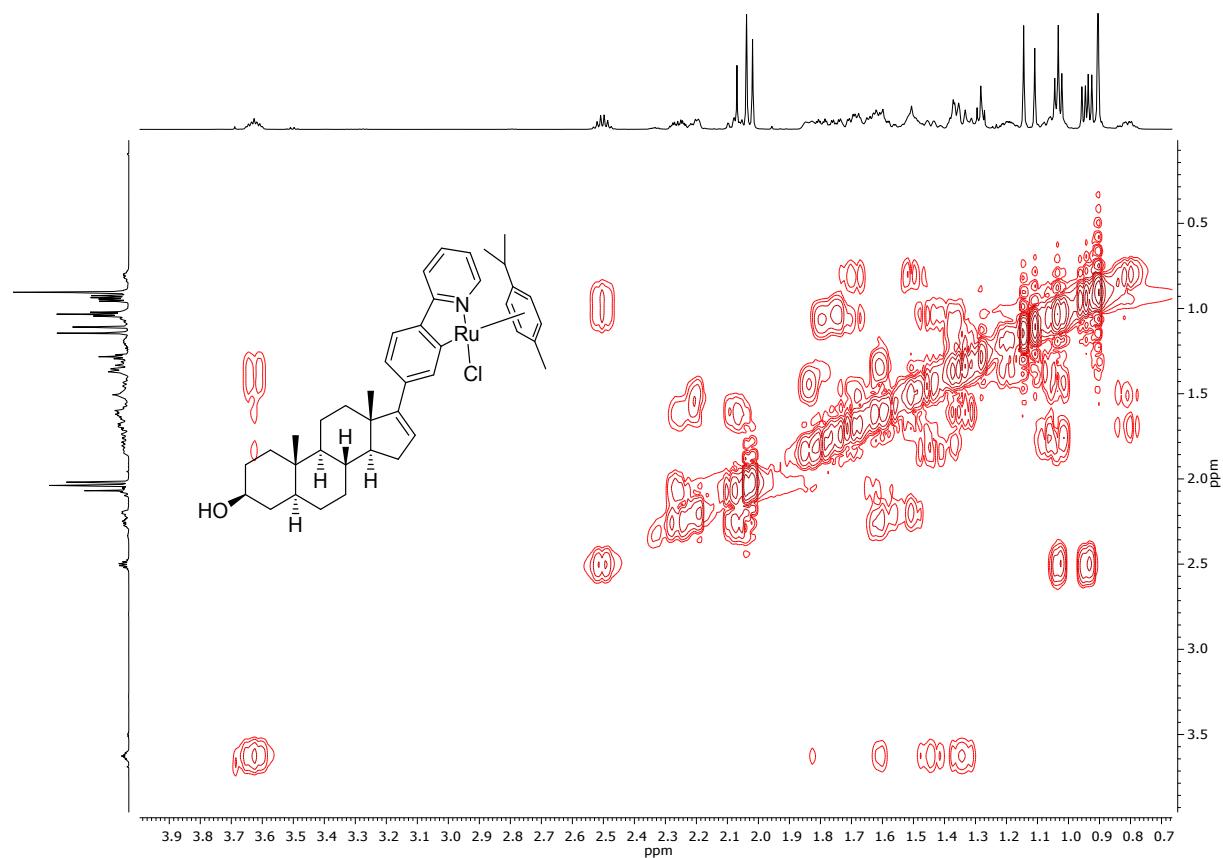


¹³C NMR (126 MHz, CDCl₃)

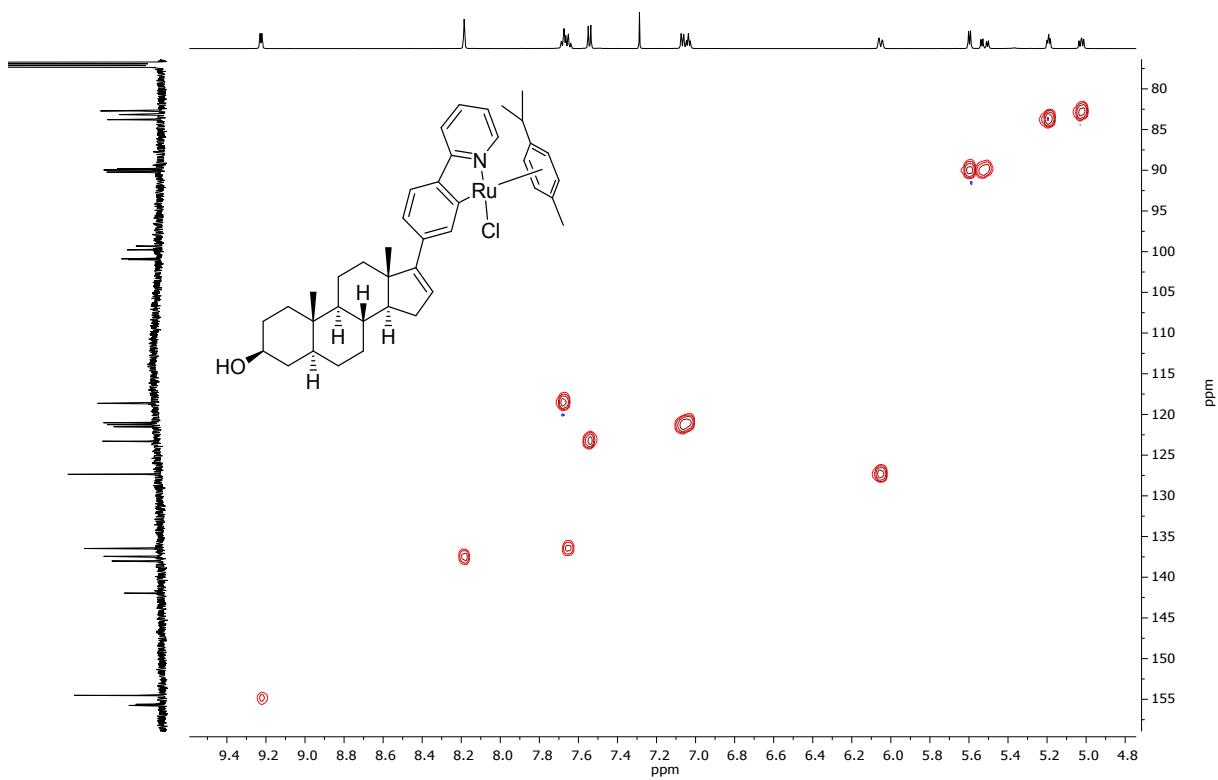
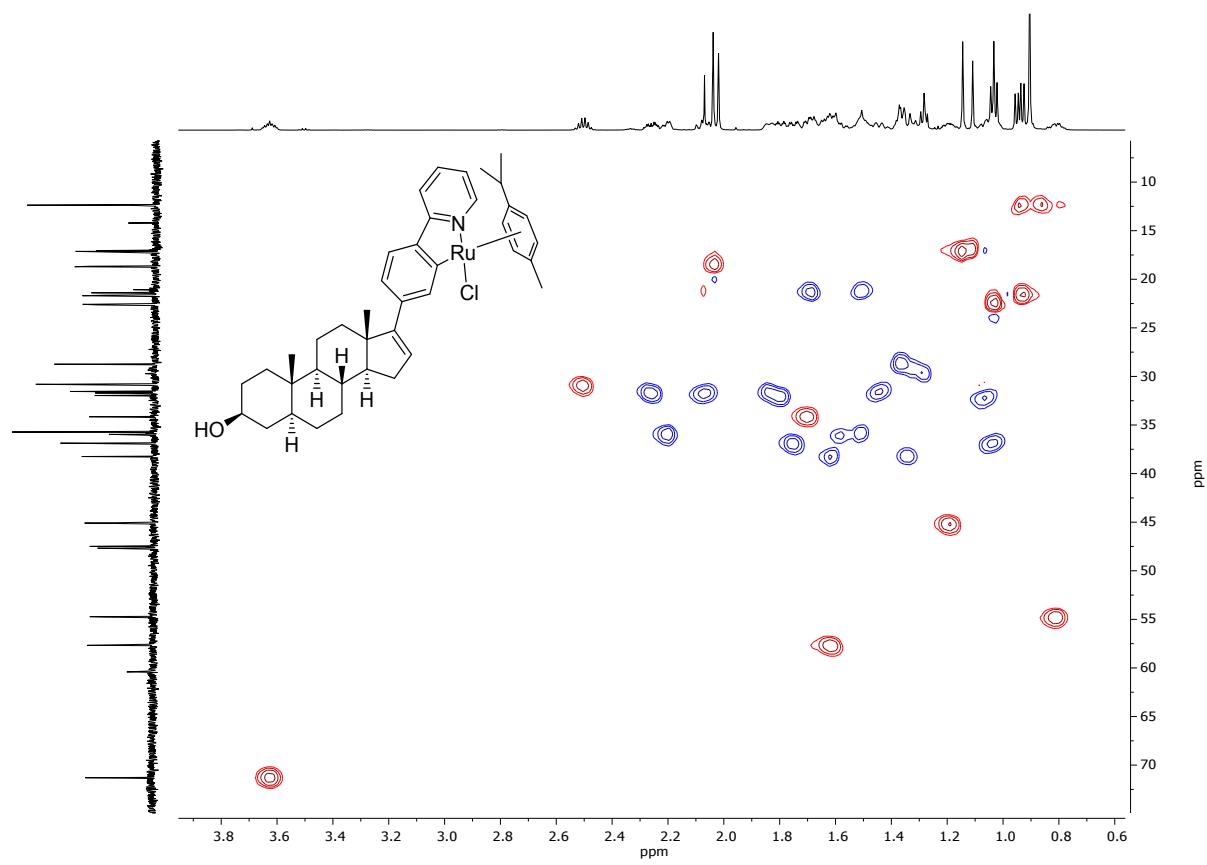


2.4 Additional 2D NMR spectra for selected compounds

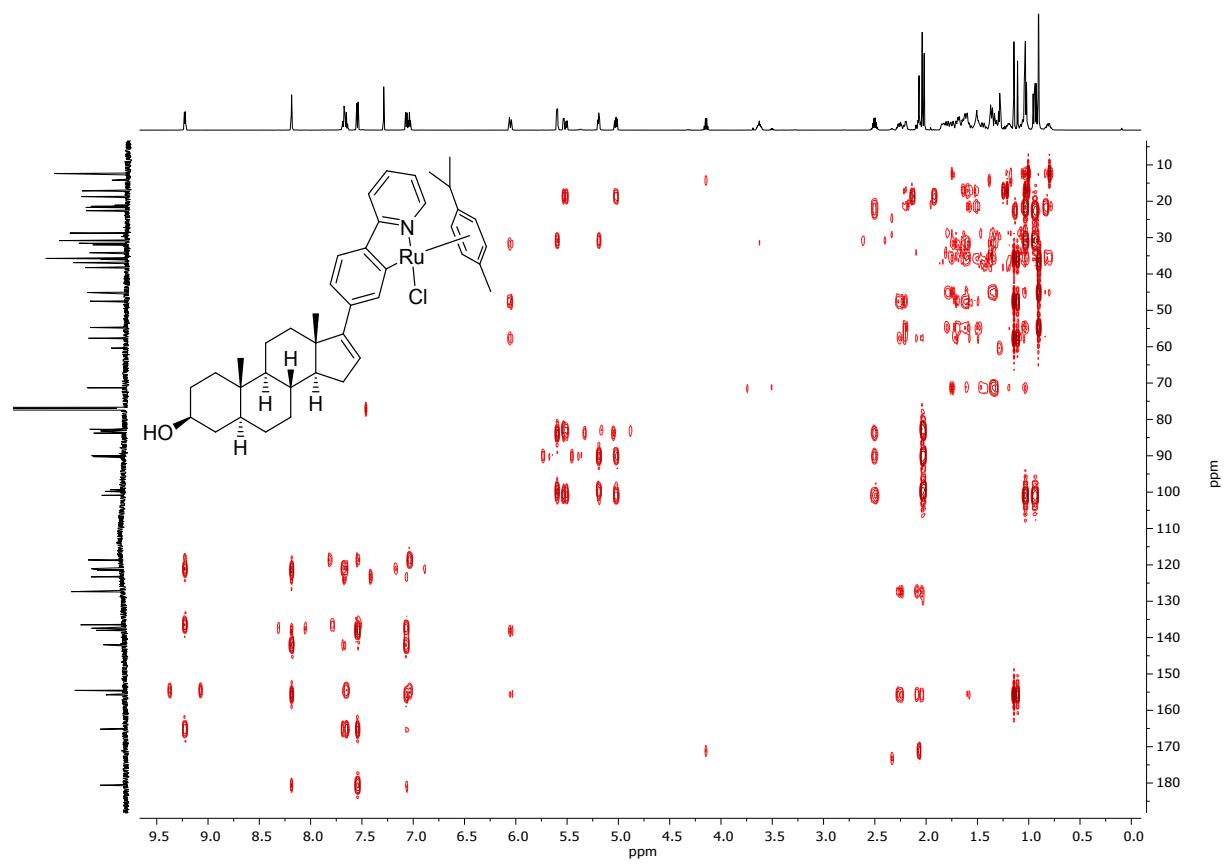
COSY spectra of Ru-complex 7:



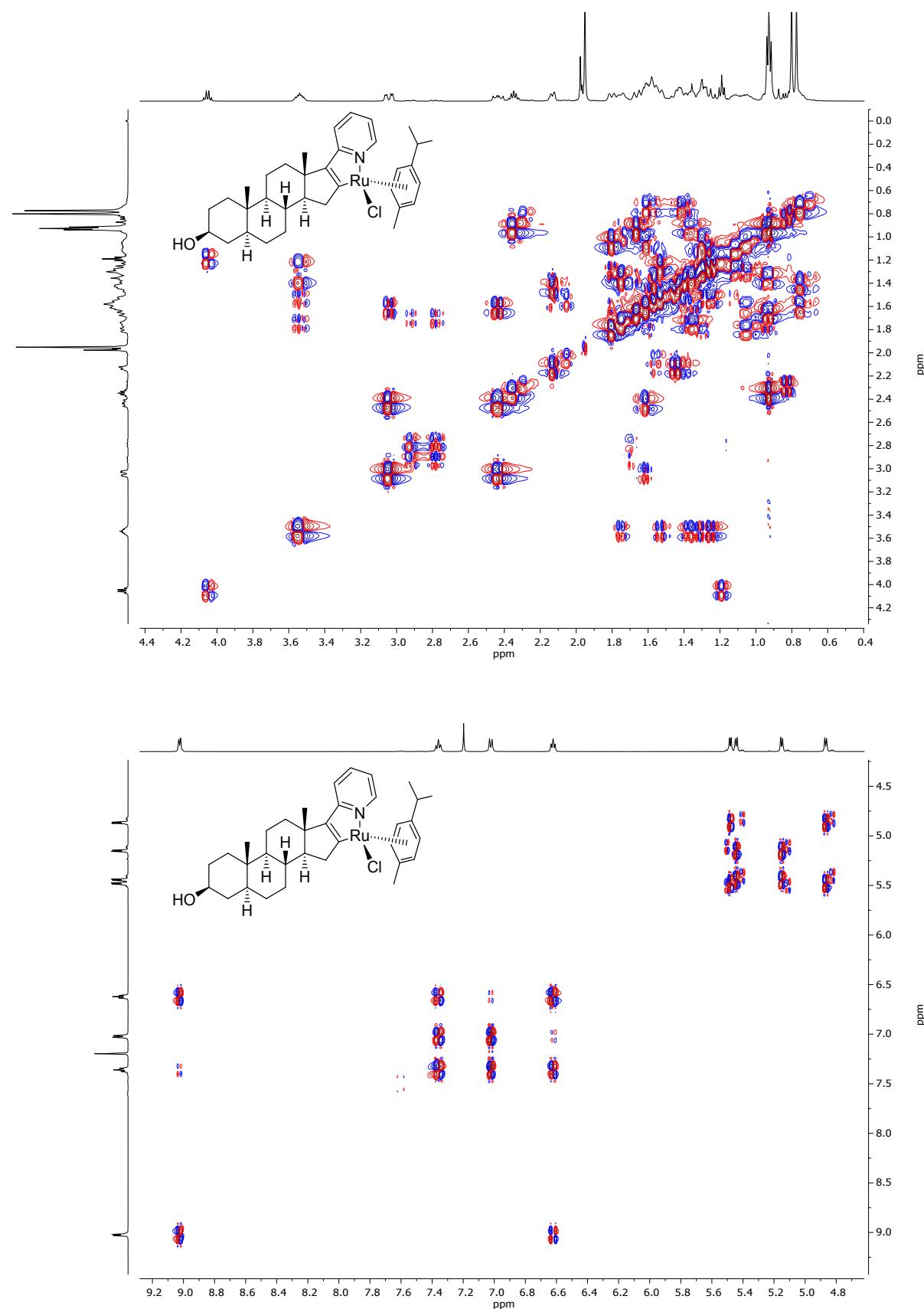
HSQC spectra of Ru-complex 7:



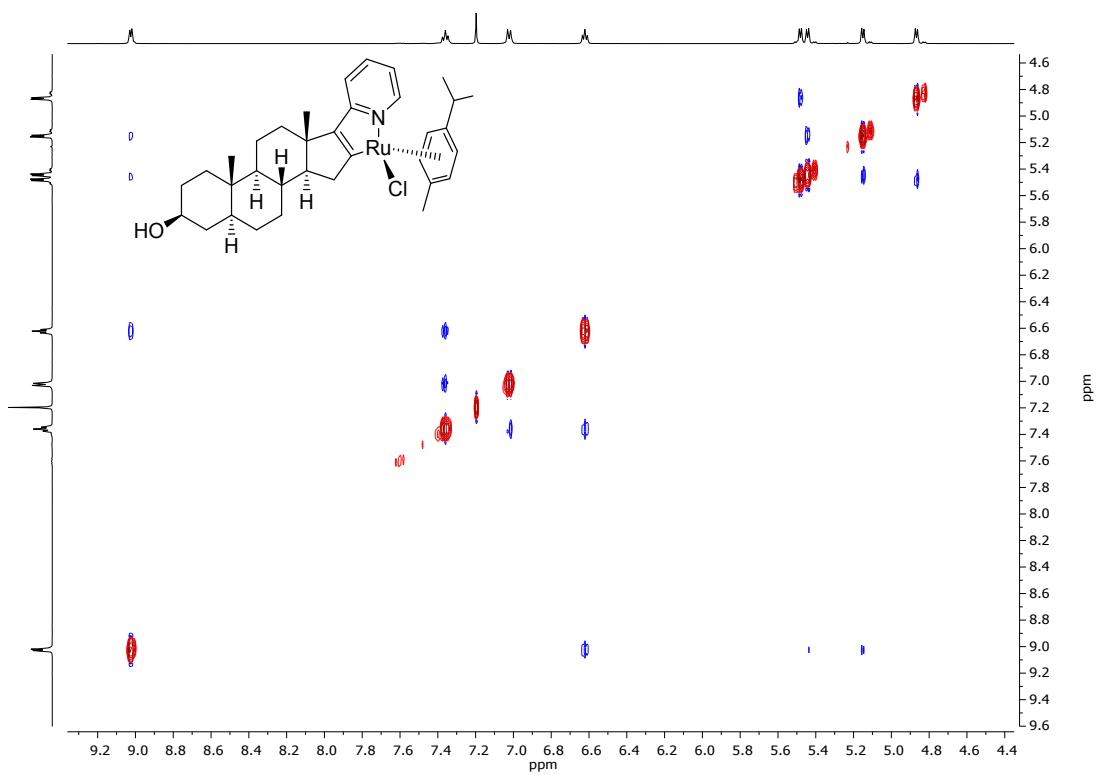
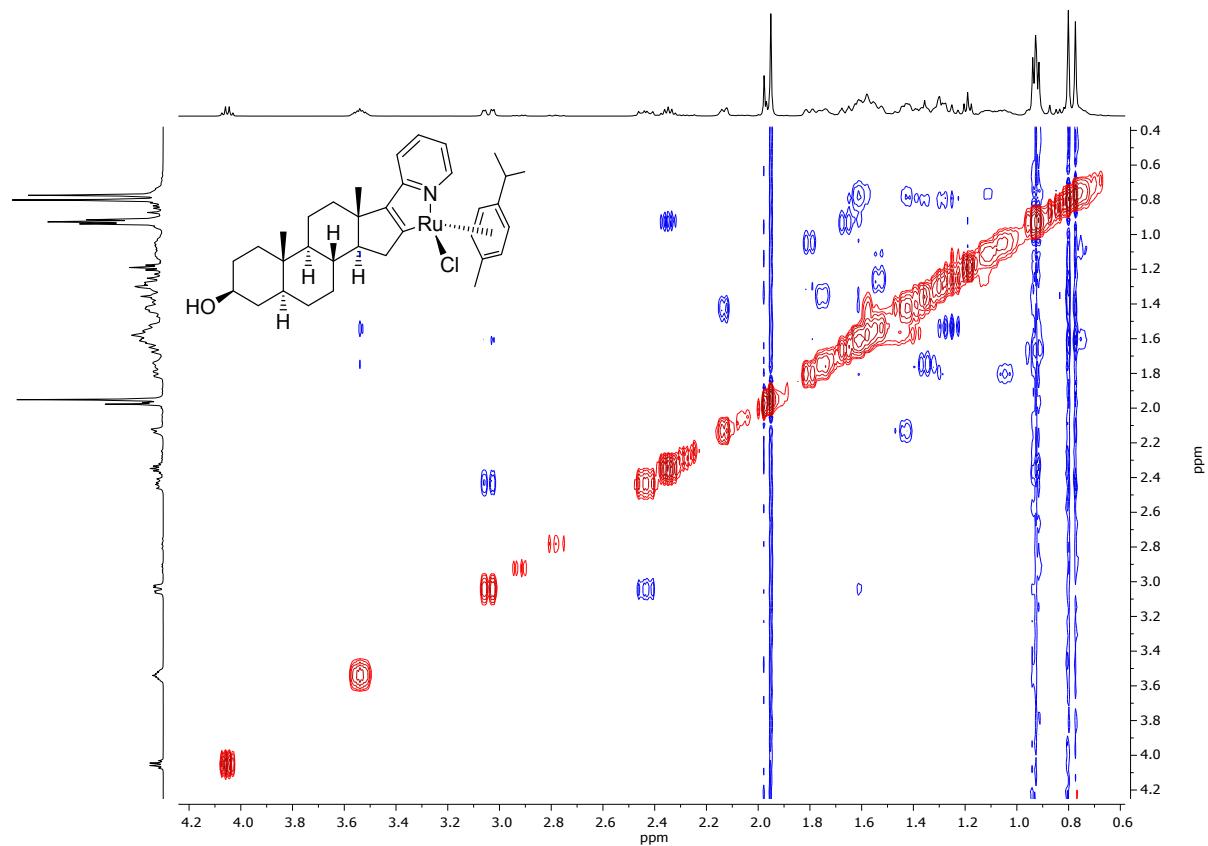
HMBC spectrum of Ru-complex 7:



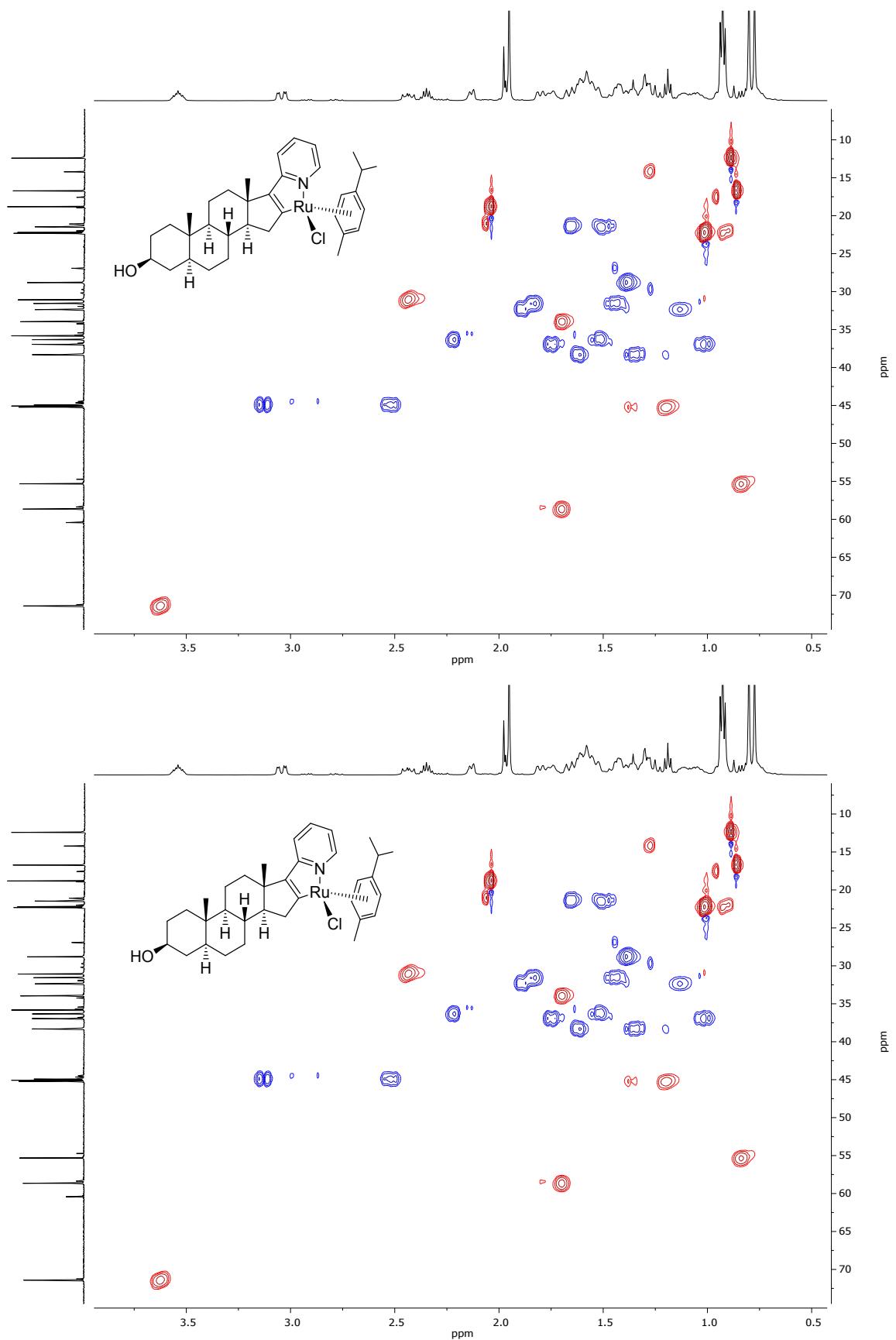
COSY spectra of Ru-complex (*R*-Ru)-8:



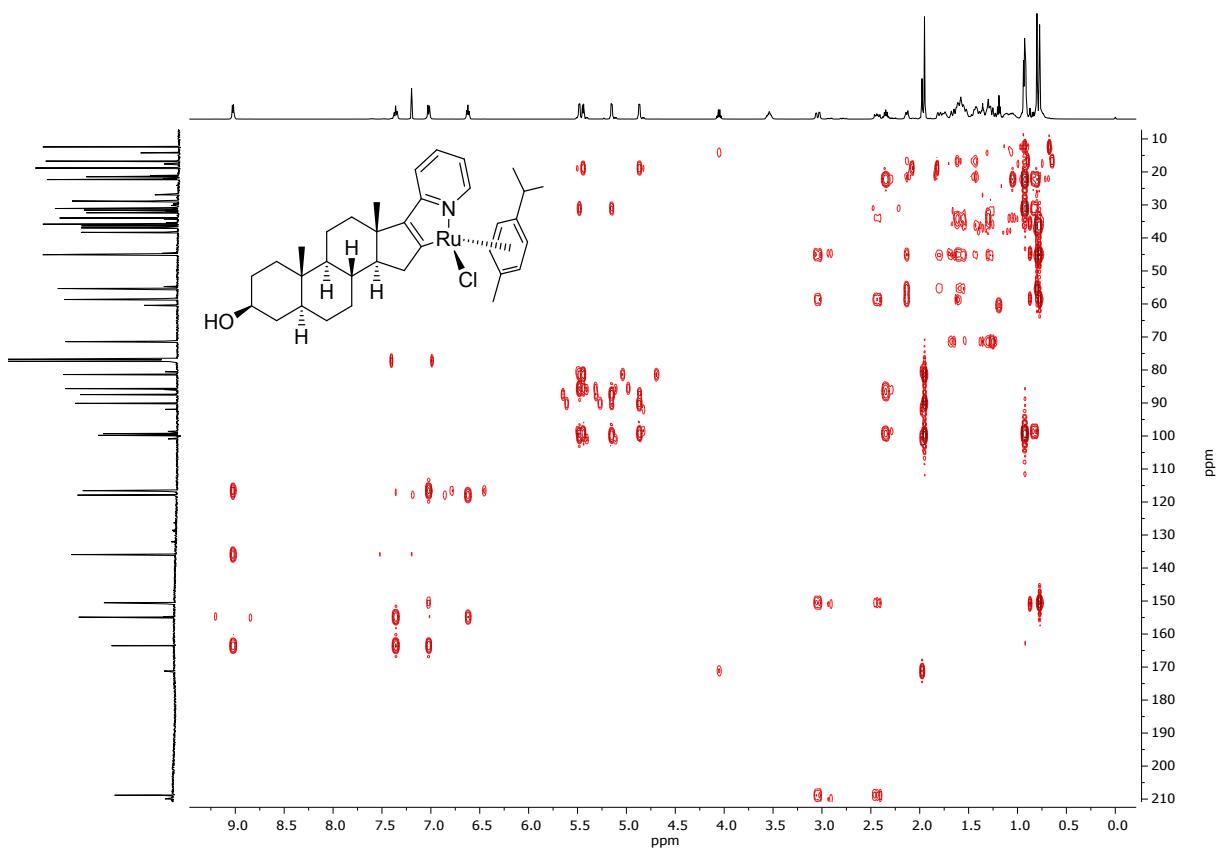
NOESY spectra of Ru-complex (*R*-Ru)-8:



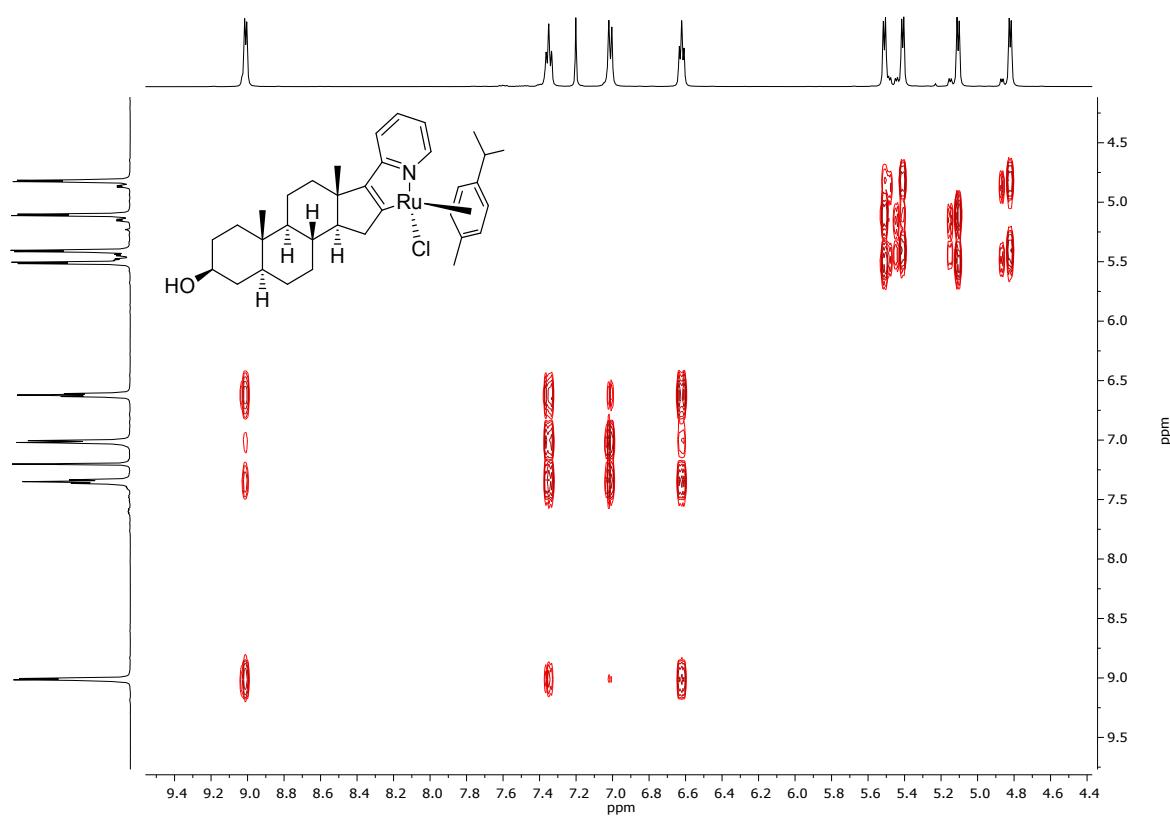
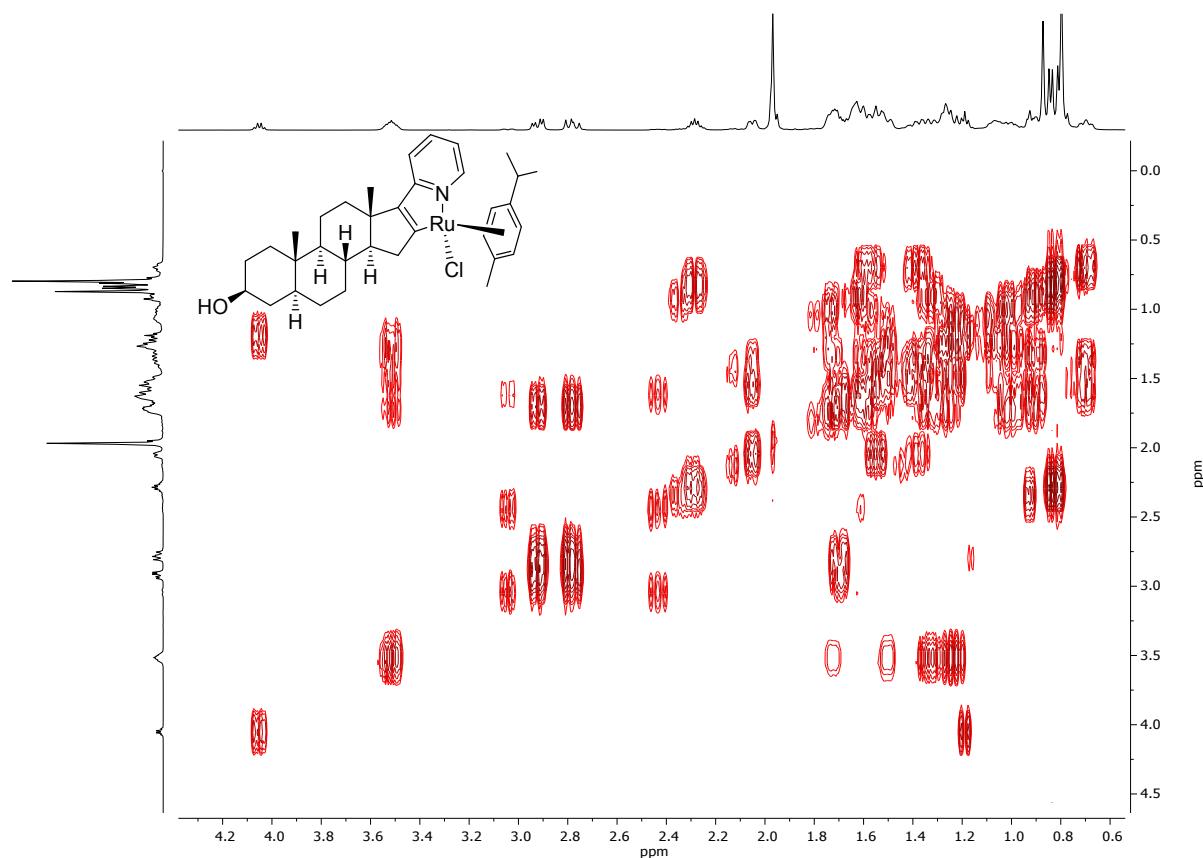
HSQC spectra of Ru-complex (*R*-Ru)-8:



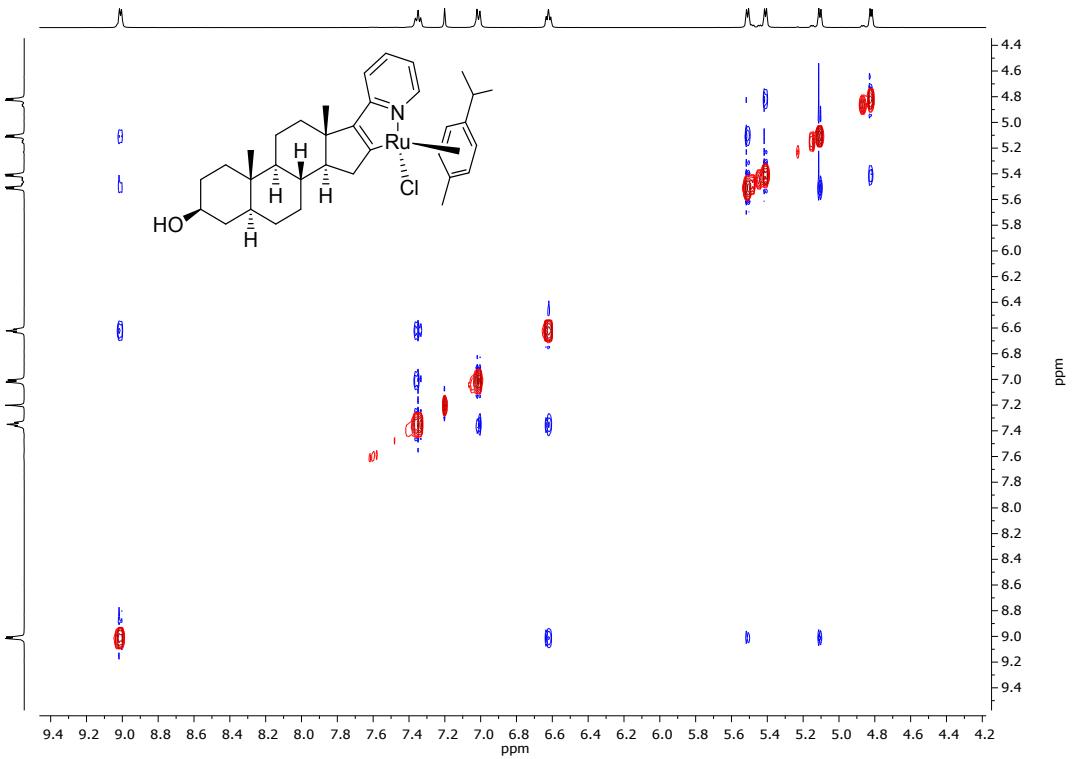
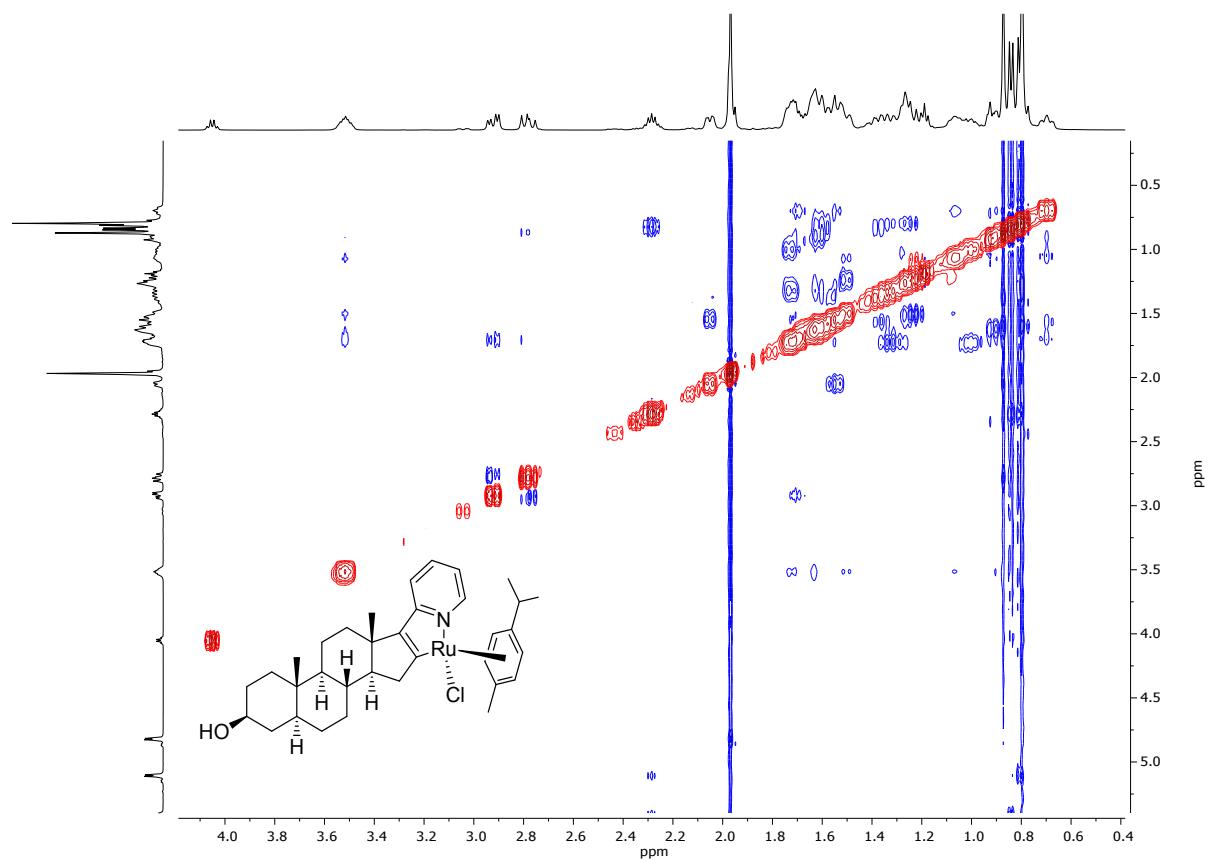
HMBC spectrum of Ru-complex (*R*-Ru)-8:



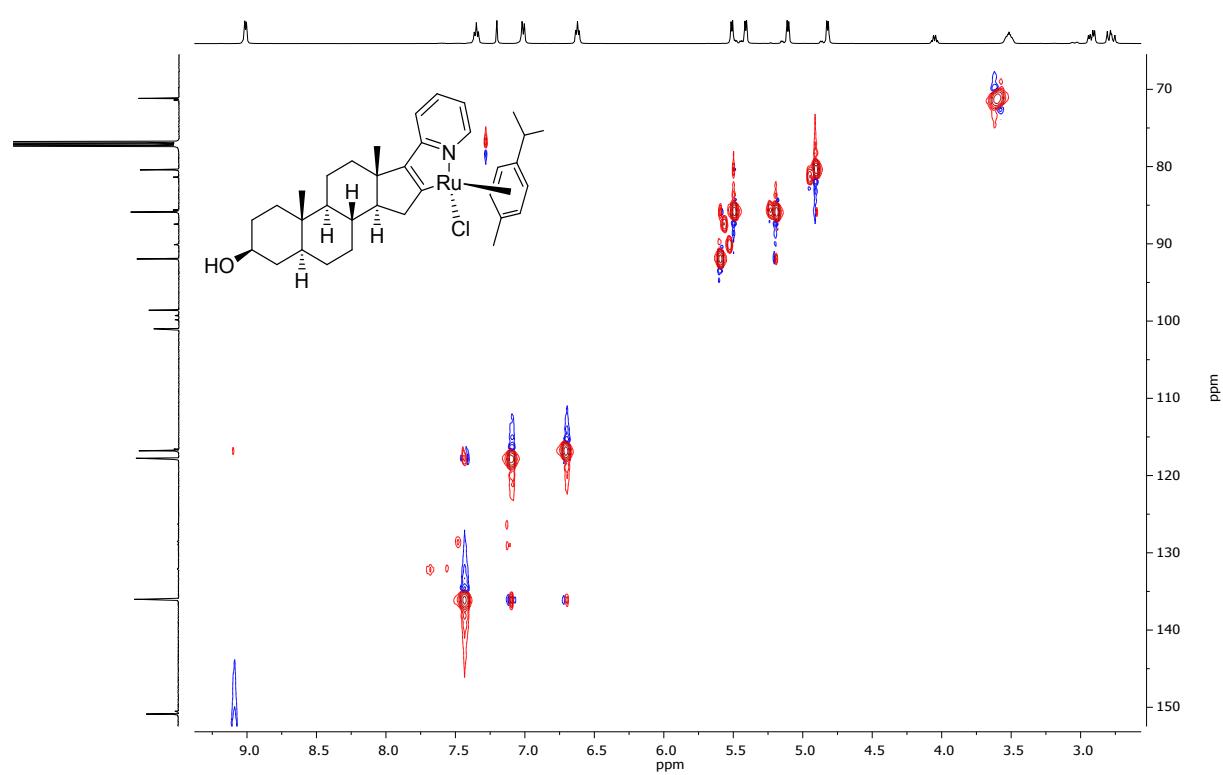
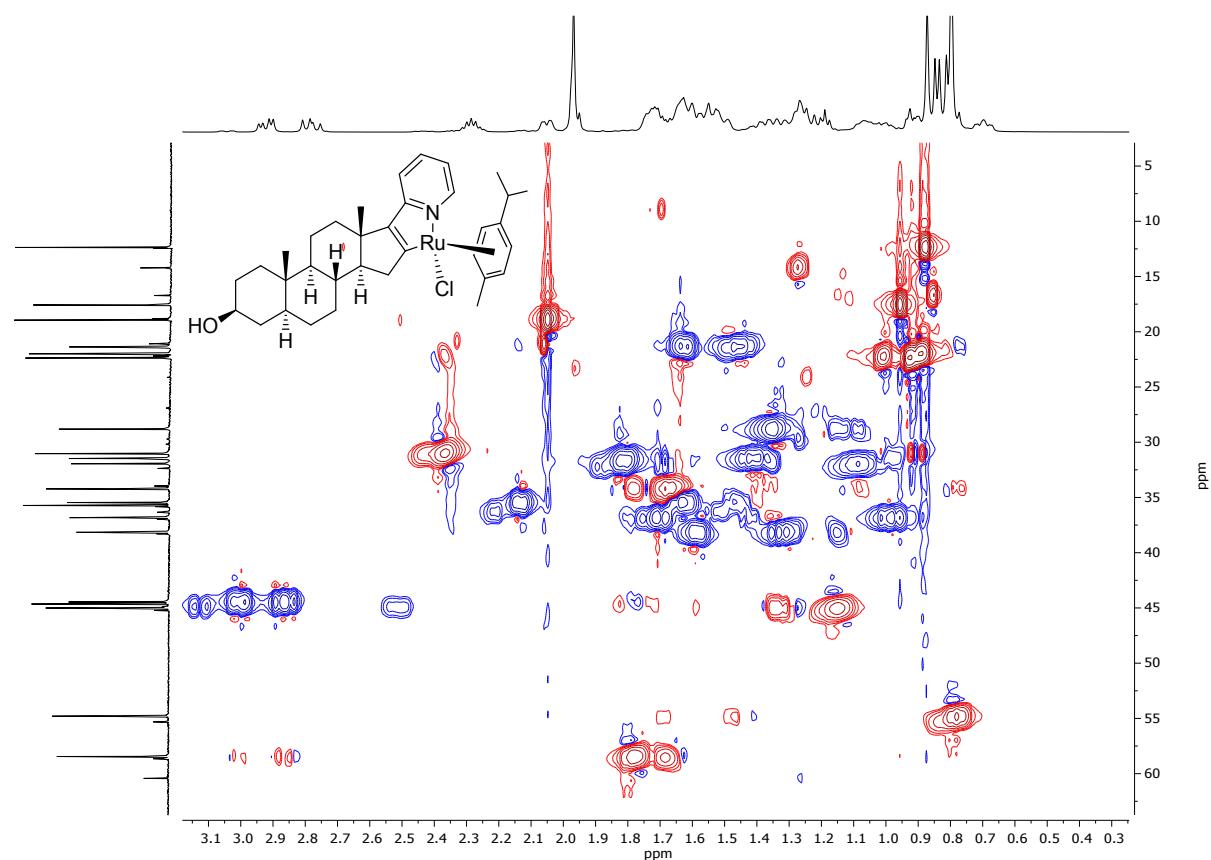
COSY spectra of Ru-complex (**S-Ru**-8):



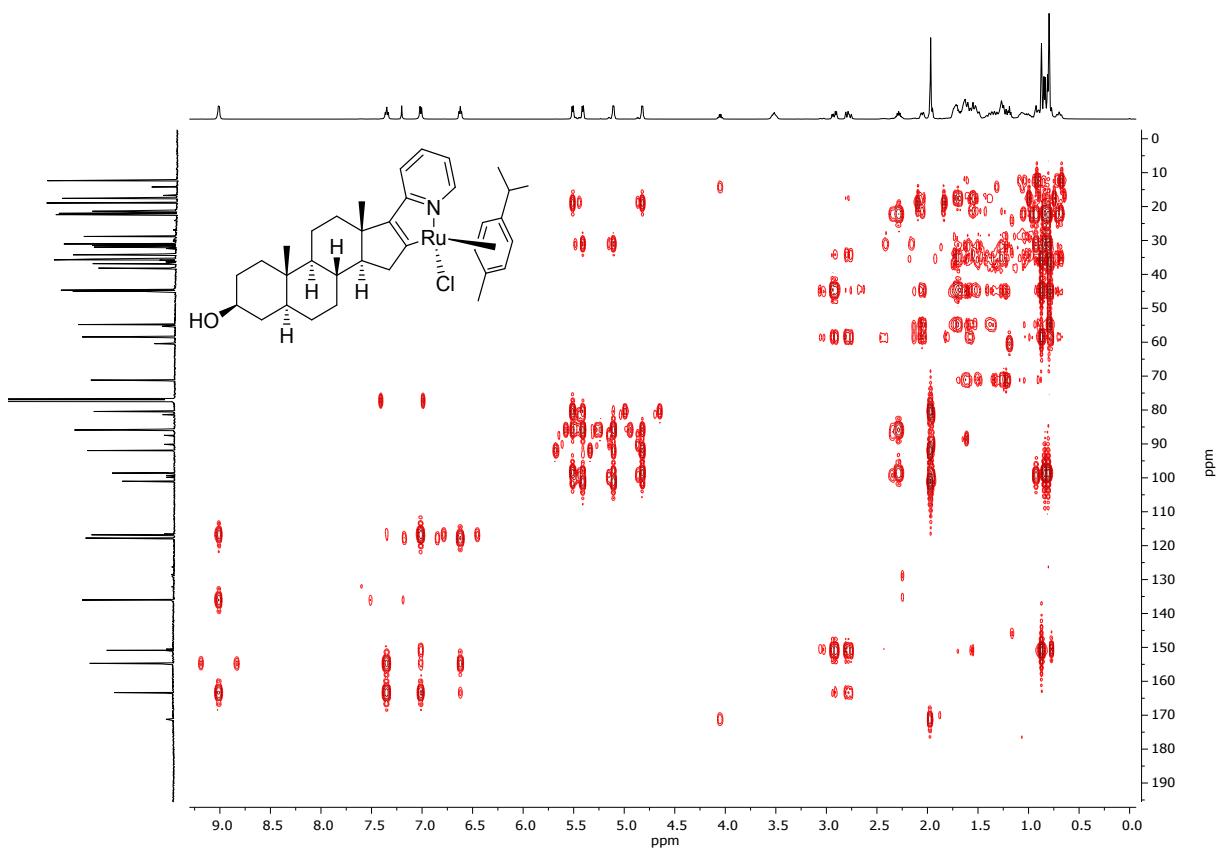
NOESY spectra of Ru-complex (*S*-Ru)-8:



HSQC spectra of Ru-complex (**S-Ru**-8):



HMBC spectrum of Ru-complex (*S*-Ru)-8:



2.5. X-ray crystallography

The single-crystal X-ray diffraction were carried out by Dr. Martin Nieger (**5b**, **7**) and Dr. Olaf Fuhr ((*R*-Ru)-**8**, **12** and **13**).

The single-crystal X-ray diffraction study of **5b** [V. Koch, M. Nieger, S. Bräse, *Adv. Synth. Catal.* 2017, **359**, 832-840]² and **7** was carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). Direct Methods (SHELXS-97)⁵ was used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2)⁶. Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(O) free). A semi-empirical absorption corrections were applied. The absolute configuration were determined by refinement of Parsons' x-parameter⁷.

CCDC 1521243 (**5b**) and 1859054 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

($3\beta,5\alpha$)-17-(3'-Pyridinyl)-5 α -androst-16-en-3-ol (5b**)**

Crystal data

C ₂₄ H ₃₃ NO	$D_x = 1.214 \text{ Mg m}^{-3}$
$M_r = 351.51$	Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$
Orthorhombic, $P2_12_12_1$ (no.19)	Cell parameters from 9909 reflections
$a = 6.1607 (4) \text{ \AA}$	$\theta = 3.8\text{--}72.2^\circ$
$b = 13.4846 (9) \text{ \AA}$	$\mu = 0.55 \text{ mm}^{-1}$
$c = 23.1554 (15) \text{ \AA}$	$T = 123 \text{ K}$
$V = 1923.6 (2) \text{ \AA}^3$	Rods, colourless
$Z = 4$	$0.20 \times 0.06 \times 0.04 \text{ mm}$
$F(000) = 768$	

Data collection

Bruker D8 VENTURE diffractometer with Photon100 detector	3801 independent reflections
Radiation source: INCOATEC microfocus sealed tube	3681 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	$R_{\text{int}} = 0.028$
rotation in ϕ and ω , 1° , shutterless scans	$\theta_{\text{max}} = 72.2^\circ$, $\theta_{\text{min}} = 3.8^\circ$
Absorption correction: multi-scan <i>SADABS</i> (Sheldrick, 2014)	$h = -7 \rightarrow 7$
$T_{\text{min}} = 0.869$, $T_{\text{max}} = 0.971$	$k = -16 \rightarrow 16$
17442 measured reflections	$l = -28 \rightarrow 27$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.080$	$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.5125P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3801 reflections	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
238 parameters	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
0 restraints	Absolute structure: Flack x determined using 1508 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons, Flack and Wagner, <i>Acta Cryst. B</i> 69 (2013) 249-259).
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.04 (9)

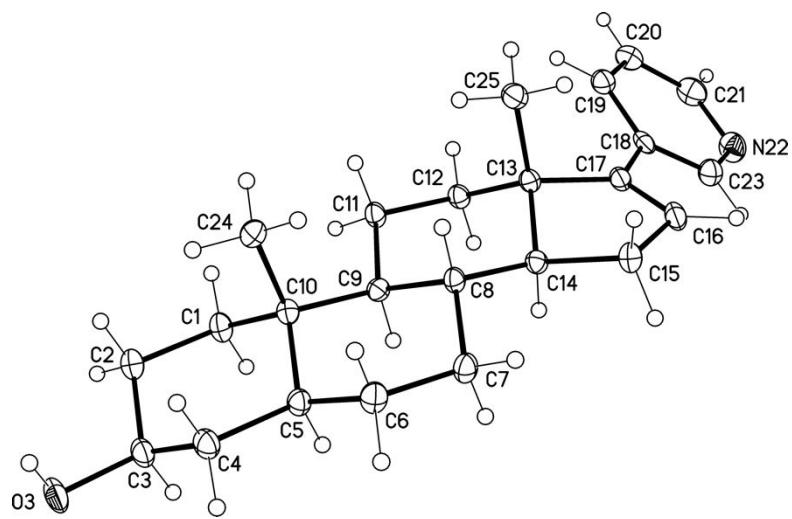
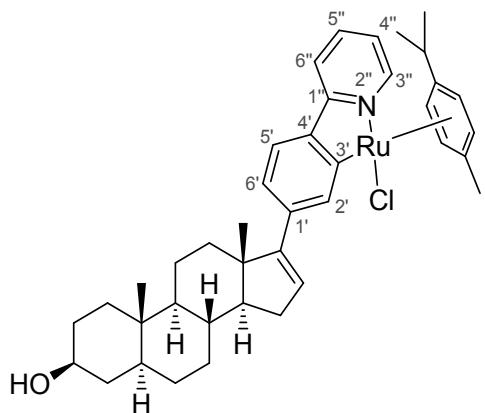


Figure 1: Molecular structure of **5b** (displacement parameters are drawn at 50% probability level).

Chlorido(η^6 -*para*-cymene)[17-(4'-pyridin-2''-yl- κ N-phenyl-3' κ C)-(5 α ,3 β)-androst-16-enolido]-ruthenium(II) (7)



Crystal data

$C_{40}H_{50}ClNORu$	$D_x = 1.391 \text{ Mg m}^{-3}$
$M_r = 697.33$	$Cu K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$
Orthorhombic, $P2_12_12_1$ (no.19)	Cell parameters from 9783 reflections
$a = 8.1509 (2) \text{ \AA}$	$\theta = 4.4\text{--}72.0^\circ$
$b = 10.2164 (3) \text{ \AA}$	$\mu = 4.79 \text{ mm}^{-1}$
$c = 39.9845 (10) \text{ \AA}$	$T = 123 \text{ K}$
$V = 3329.62 (15) \text{ \AA}^3$	Plates, orange
$Z = 4$	$0.16 \times 0.14 \times 0.04 \text{ mm}$
$F(000) = 1464$	

Data collection

Bruker D8 VENTURE diffractometer with Photon100 detector	6513 independent reflections
Radiation source: INCOATEC microfocus sealed tube	6455 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	$R_{\text{int}} = 0.020$
rotation in ϕ and ω , 0.5°, shutterless scans	$\theta_{\text{max}} = 72.1^\circ$, $\theta_{\text{min}} = 4.4^\circ$
Absorption correction: multi-scan SADABS (Sheldrick, 2014)	$h = -10 \rightarrow 10$
$T_{\text{min}} = 0.687$, $T_{\text{max}} = 0.829$	$k = -12 \rightarrow 12$
22924 measured reflections	$l = -42 \rightarrow 49$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.024$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.061$	$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 1.3266P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{\max} = 0.002$
6513 reflections	$\Delta\rho_{\max} = 0.68 \text{ e \AA}^{-3}$
401 parameters	$\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$
1 restraint	Absolute structure: Flack x determined using 2704 quotients $[(I+)-(I-)]/[(I+)+(I-)]$ (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: -0.011 (2)

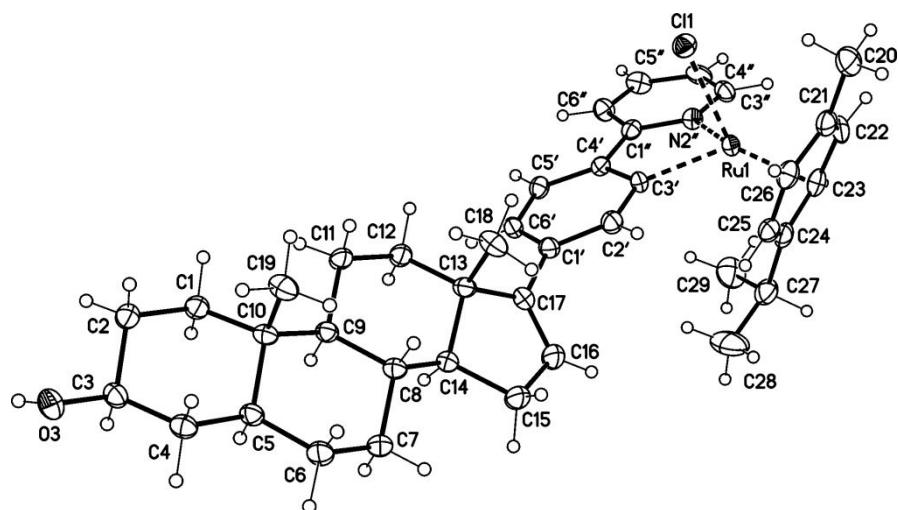


Figure 2: Molecular structure of 7 (displacement parameters are drawn at 50% probability level).

For single crystal X-ray analysis suitable crystals were selected and (*R*)-**8**, **12** and **13** were investigated on a *Stoe StadiVari* diffractometer using Ga-K α radiation ($\lambda = 1.34143 \text{ \AA}$) generated by an Metaljet X-ray source. The crystals were kept at 180.15 K during data collection. Using Olex2⁸, the structures were solved with the ShelXS⁵ structure solution program using Direct Methods and refined with the ShelXL⁶ refinement package using Least Squares minimization. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were modelled on idealized positions.

(R)-Chlorido(η^6 -*para*-cymene)[(5*a*)-17-(2'-pyridinyl- κN)androst-16-en-3*β*-ol-16*κ*C¹⁶]

ruthenium(II) ((R-Ru)-8)

Empirical formula	C ₃₄ H ₄₆ ClNORu
Formula weight	621.24
Temperature/K	180.15
Crystal system	hexagonal
Space group	P6 ₅
a/Å	31.5730(9)
b/Å	31.5730(9)
c/Å	10.3106(2)
α/°	90
β/°	90
γ/°	120
Volume/Å ³	8901.1(5)
Z	6
ρ _{calcd} /cm ³	0.695
μ/mm ⁻¹	1.788
F(000)	1956.0
Crystal size/mm ³	0.27 × 0.05 × 0.04
Radiation	GaKα (λ = 1.34143)
2Θ range for data collection/°	7.442 to 118.8
Index ranges	-40 ≤ h ≤ 39, -37 ≤ k ≤ 40, -12 ≤ l ≤ 6
Reflections collected	50192
Independent reflections	8931 [R _{int} = 0.0829, R _{sigma} = 0.0764]
Indep. refl. with I>=2σ (I)	3717
Data/restraints/parameters	8931/1/350
Goodness-of-fit on F ²	0.803
Final R indexes [I>=2σ (I)]	R ₁ = 0.0940, wR ₂ = 0.2189
Final R indexes [all data]	R ₁ = 0.1274, wR ₂ = 0.2277
Largest diff. peak/hole / e Å ⁻³	0.77/-0.44
Flack parameter	0.05(2)

Dichlorido(η^6 -*para*-cymene)[(5 α ,3 β)-17-((3'-pyridinyl- κ N)-androst-16-en-3-ol)ido]ruthenium(II) (**12**)

Empirical formula	C ₃₄ H ₄₇ Cl ₂ NORu
Formula weight	657.69
Temperature/K	180.15
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/ \AA	7.0251(2)
b/ \AA	15.6281(5)
c/ \AA	28.6301(12)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	3143.27(19)
Z	4
ρ_{calc} g/cm ³	1.390
μ/mm^{-1}	3.844
F(000)	1376.0
Crystal size/mm ³	0.1 × 0.08 × 0.03
Radiation	GaK α ($\lambda = 1.34143$)
2 Θ range for data collection/ $^\circ$	11.832 to 118.208
Index ranges	-8 ≤ h ≤ 8, -19 ≤ k ≤ 8, -35 ≤ l ≤ 35
Reflections collected	23083
Independent reflections	6440 [$R_{\text{int}} = 0.0255$, $R_{\text{sigma}} = 0.0339$]
Indep. refl. with $I \geq 2\sigma(I)$	5586
Data/restraints/parameters	6440/0/352
Goodness-of-fit on F ²	1.045
Final R indexes [I $\geq 2\sigma(I)$]	$R_1 = 0.0342$, $wR_2 = 0.0832$
Final R indexes [all data]	$R_1 = 0.0397$, $wR_2 = 0.0848$
Largest diff. peak/hole / e \AA^{-3}	0.47/-0.52
Flack parameter	-0.035(7)

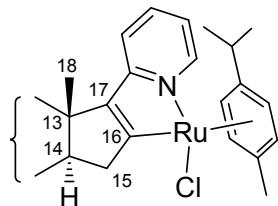
Dichlorido(η^5 -pentamethylcyclopentadienyl)[(5 α ,3 β)-17-((3'-pyridinyl- κ N)androst-16-en-3-ol)ido]-iridium(III) (13)

Empirical formula	C ₃₄ H ₄₈ Cl ₂ IrNO
Formula weight	749.83
Temperature/K	180.15
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/ \AA	6.9313(2)
b/ \AA	17.0346(7)
c/ \AA	32.1445(13)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	3795.4(2)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.312
μ/mm^{-1}	5.488
F(000)	1512.0
Crystal size/mm ³	0.24 \times 0.2 \times 0.02
Radiation	GaK α ($\lambda = 1.34143$)
2 Θ range for data collection/ $^\circ$	6.578 to 105.986
Index ranges	-8 \leq h \leq 4, -20 \leq k \leq 20, -38 \leq l \leq 22
Reflections collected	11444
Independent reflections	6364 [$R_{\text{int}} = 0.0569$, $R_{\text{sigma}} = 0.0594$]
Indep. refl. with $I \geq 2\sigma$ (I)	5200
Data/restraints/parameters	6364/60/307
Goodness-of-fit on F ²	1.099
Final R indexes [$I \geq 2\sigma$ (I)]	$R_1 = 0.0922$, $wR_2 = 0.2578$
Final R indexes [all data]	$R_1 = 0.1020$, $wR_2 = 0.2639$
Largest diff. peak/hole / e \AA^{-3}	2.67/-2.79
Flack parameter	0.18(5)

3. Quantum Chemical Calculations

3.1 Calculated Chemical Shifts

Table S1: Selected chemical Shift differences $\Delta_{\delta} = \delta_S - \delta_R$ of diastereomer (**R-Ru**)-**8** and (**S-Ru**)-**8** calculated in the def2-TZVPP⁹ level of theory applying different exchange-correlation functionals. All functionals reproduce the experimental observed trends in chemical shift differences of the two diastereomers except for the ¹³C shift of carbon 14. The shift difference of Carbon 15 is not correctly predicted by the M06 and M06-2X functionals¹⁰. The hybrid functionals including exact Hartree-Fock exchange (B3LYP¹¹, TPSSh¹²) are closer to the experimental ¹³C shifts than their GGA (bp86¹³⁻¹⁴) counterpart. However, in case of ¹H chemical shift differences BP86 performs equally well like TPSSh. Interestingly, the *meta*-GGA hybrids M06 (27% HF-exchange) and M06-2X (54% Hartree-Fock exchange) compare worse to the experimental values for both ¹H and ¹³C chemical shifts. Nevertheless, one should keep in mind that the chemical shift differences of the present study are very small compared to the general accuracy of DFT chemical shift predictions. In addition, for all NMR shift predictions the bp86/def2-TZVPP structures were used throughout. A more thorough comparison would require optimizations using all functionals discussed. Hence, the presented discussion should not be interpreted as a general functional benchmark for NMR shift calculations. MAE: Mean Absolute Error.

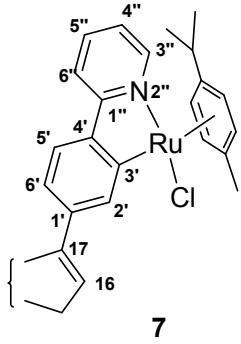


8

	B3LYP	BP86	M06	M06-2X	TPSSh	Exp.
C	13-C _q	-0.16	-0.12	-0.36	-0.21	-0.50
	14-CH	0.90	1.05	0.63	0.57	-0.20
	15-CH ₂	-0.09	-0.23	0.34	0.02	-0.50
	16-C _q -Ru	0.71	0.49	1.29	0.21	1.00
	17-C _q -Pyr	0.30	0.20	1.11	0.79	0.15
	18-CH ₃	1.85	1.72	2.15	2.31	0.80
MAE	0.53	0.57	0.71	0.73	0.54	--
H	14-CH	-0.04	0.00	-0.19	-0.18	n.d.
	15 α -CH ₂	-0.29	-0.28	-0.39	-0.41	-0.13
	15 β -CH ₂	0.36	0.34	0.42	0.56	0.34
	18-CH ₃	0.13	0.12	0.16	0.24	0.09
MAE	0.08	0.06	0.14	0.22	0.06	--

Table S2: Selected chemical Shift differences $\Delta_{\delta} = \delta_S - \delta_R$ of diastereomer (*R*)-7 and (*S*)-7 calculated in the def2-TZVPP basis using different exchange-correlation functionals.

		B3LYP	BP86	M06	M06-2X	TPSSh
H	6'	0.00	0.00	0.01	0.48	0.01
	5'	0.03	0.03	0.13	0.63	0.03
	2'	-0.01	-0.03	-0.05	1.29	-0.02
	6''	0.01	0.01	-0.03	0.47	0.01
	5'''	0.00	-0.01	-0.02	0.62	-0.01
	4'''	0.01	0.01	0.10	0.57	0.00
	3'''	0.02	0.00	0.15	1.04	0.01
	14	-0.01	-0.01	0.03	0.48	-0.02
	1'	-0.95	-1.10	-1.00	16.10	-1.04
	6'	0.00	-0.03	-0.05	16.32	0.00
C	5'	0.37	0.46	1.14	16.98	0.38
	4'	-1.45	-1.42	-2.50	16.82	-1.37
	3'	-1.55	-1.67	-1.48	34.29	-1.36
	2'	0.39	0.60	0.30	21.44	0.37
	1''	0.15	0.17	-0.15	24.92	0.18
	6''	-0.05	0.03	-0.63	15.26	0.11
	5'''	-0.07	-0.09	-0.77	22.06	-0.01
	4'''	-0.05	0.00	-0.11	14.92	-0.02
	3'''	-0.17	-0.24	-0.08	22.13	-0.23
	17	0.37	0.34	0.36	18.84	0.33
N	16	0.35	0.34	0.23	18.51	0.31
	2''	-0.40	-0.66	1.24	47.60	-0.41



3.2 Computational Studies

XYZ-Coordinates (Ångström) of optimized structures (bp86/def2-TZVPP).

(R-Ru)-7

C	-3.569295	0.641060	-4.861566
H	-4.276180	0.280617	-4.101449
H	-3.185688	1.610888	-4.500056
C	-4.321272	0.856599	-6.181824
H	-4.802104	-0.077740	-6.510462
H	-5.126777	1.594016	-6.035227
C	-3.384292	1.329811	-7.290799
H	-2.987457	2.327490	-7.017775
O	-4.057222	1.421355	-8.563710
H	-4.814791	2.019600	-8.452000
C	-2.209578	0.376361	-7.454556
H	-1.520926	0.770857	-8.217081
H	-2.581736	-0.589453	-7.831744
C	-1.460622	0.193903	-6.129535
H	-1.139778	1.202336	-5.803055
C	-0.187168	-0.639045	-6.289373
H	-0.446044	-1.664172	-6.600114
H	0.425349	-0.216167	-7.100877
C	0.612598	-0.670583	-4.986473
H	1.501510	-1.309790	-5.094680
H	0.981968	0.347088	-4.766029
C	-0.230692	-1.150011	-3.800460
H	-0.489187	-2.207773	-3.972717
C	-1.535515	-0.318366	-3.673469
H	-1.203700	0.731644	-3.547351
C	-2.377037	-0.335853	-4.986229
C	-2.343479	-0.681166	-2.409948
H	-3.168957	0.033405	-2.288788
H	-2.815325	-1.665441	-2.544404
C	-1.518327	-0.695532	-1.108908
H	-1.192867	0.327947	-0.861597
H	-2.155963	-1.032749	-0.279115
C	-0.274641	-1.577898	-1.266761
C	0.520498	-1.029184	-2.481993
H	0.627489	0.054983	-2.285010
C	1.932798	-1.605619	-2.289908
H	2.026798	-2.631416	-2.691559
H	2.716236	-1.007090	-2.776367
C	2.031955	-1.589981	-0.783356
Ru	2.567795	0.384927	4.728719
C	0.818440	-1.503493	-0.187889
C	0.121004	-1.095854	5.479725
C	-0.867056	-1.645978	6.310357
H	-1.691937	-2.197578	5.863339
C	-0.780043	-1.497487	7.688354
H	-1.544922	-1.922213	8.337469
C	0.312443	-0.808728	8.229667
C	1.263215	-0.282002	7.366458
N	1.166012	-0.396659	6.025588
C	-2.904461	-1.751572	-5.283299
H	-2.099985	-2.495798	-5.312221
H	-3.621161	-2.065868	-4.512954
H	-3.425129	-1.797840	-6.247245
C	-0.666606	-3.063165	-1.450659
H	-1.391051	-3.202807	-2.262103
H	0.215377	-3.676385	-1.676571
H	-1.118503	-3.461487	-0.533331
C1	3.779939	-1.664820	5.083430
H	2.137362	0.249570	7.734878
H	0.433166	-0.682448	9.303612
C	2.086614	2.427262	5.237095
C	2.045705	2.292895	3.817824
C	3.231922	1.786386	3.183824
C	4.357674	1.413977	3.946603
C	4.424147	1.658695	5.370739
C	3.288655	2.190237	5.992247
C	0.835986	2.643579	2.980622

H	3.226112	1.602529	2.110689
H	5.193705	0.918363	3.456167
C	5.637294	1.238048	6.140687
H	3.281047	2.335264	7.072013
H	5.828056	0.167515	5.972783
H	6.524052	1.794863	5.804966
H	5.504451	1.404148	7.216047
C	-0.491502	2.470041	3.721730
H	0.837602	1.942734	2.130161
C	0.991224	4.070915	2.427705
H	1.188053	2.731170	5.770741
H	-0.583854	1.455203	4.128398
H	-0.593519	3.188723	4.547317
H	-1.329011	2.640900	3.032742
H	0.157966	4.315550	1.754720
H	0.995959	4.804715	3.246885
H	1.928860	4.183061	1.866531
H	2.978021	-1.671732	-0.247663
C	0.583836	-1.413023	1.256505
C	1.536375	-0.775729	2.079749
C	-0.585118	-1.927524	1.861156
C	-0.765017	-1.840611	3.235250
C	0.198011	-1.207496	4.038043
C	1.363063	-0.633396	3.458585
H	-1.341444	-2.422309	1.256548
H	-1.662758	-2.269029	3.683634
H	2.423356	-0.363170	1.599955

(S-Ru)-7

Ru	-3.513723	0.354745	0.407982
C1	-3.492517	-0.562880	2.636610
O	8.616396	1.160843	-1.330255
H	8.767100	2.119486	-1.280117
N	-3.432267	-1.623488	-0.216453
C	5.455362	-0.880527	-1.519345
H	5.331140	-1.972192	-1.520729
H	5.032642	-0.514799	-2.471271
C	6.953067	-0.552020	-1.474614
H	7.421054	-1.001658	-0.585042
H	7.460581	-0.982075	-2.350424
C	7.192961	0.950181	-1.434512
H	6.829545	1.390998	-2.383774
C	6.427756	1.594198	-0.280548
H	6.569564	2.687513	-0.305136
H	6.851795	1.239445	0.672081
C	4.930357	1.275789	-0.366639
H	4.585069	1.632436	-1.356717
C	4.107700	2.028634	0.680983
H	4.400325	1.703166	1.692401
H	4.339948	3.103682	0.623673
C	2.610759	1.800118	0.468224
H	2.309325	2.259305	-0.490603
H	2.027654	2.303560	1.253742
C	2.250291	0.311535	0.428390
H	2.434555	-0.111553	1.429724
C	3.118712	-0.442662	-0.614765
H	2.916343	0.058767	-1.582293
C	4.645812	-0.255789	-0.359161
C	2.691536	-1.915976	-0.783195
H	3.230762	-2.355374	-1.633389
H	3.001707	-2.492227	0.100571
C	1.180044	-2.120031	-1.004624
H	0.967484	-3.199905	-1.030062
H	0.885557	-1.711592	-1.985089
C	0.371318	-1.409525	0.087735
C	0.791505	0.088602	0.056085
H	0.695096	0.384480	-1.006718
C	-0.357903	0.825492	0.771013
H	-0.433086	1.885824	0.492575
H	-0.264621	0.796968	1.872029
C	-1.550526	-0.000782	0.350569
C	-1.131818	-1.238010	-0.076706

C	0.609374	-2.073652	1.464118
H	0.111089	-1.506996	2.261300
H	1.673554	-2.160558	1.716887
H	0.181702	-3.086162	1.463935
C	5.066313	-0.910424	0.969247
H	4.478251	-0.541607	1.817934
H	6.122257	-0.723761	1.198002
H	4.934076	-1.999506	0.921297
C	-2.172154	-2.175765	-0.349648
C	-4.521049	-2.397612	-0.383250
H	-5.480738	-1.907033	-0.233798
C	-4.440295	-3.742105	-0.722583
H	-5.352724	-4.318964	-0.858212
C	-3.171733	-4.320038	-0.876147
H	-3.072478	-5.373766	-1.135954
C	-2.042060	-3.537631	-0.683581
H	-1.045601	-3.963611	-0.778734
C	-5.477429	1.523272	0.851863
C	-4.281950	2.289285	1.129996
H	-4.130138	2.675391	2.136750
C	-3.295693	2.523007	0.149057
H	-2.415400	3.111760	0.400971
C	-3.388616	1.891200	-1.136903
C	-4.522697	1.054267	-1.366492
H	-4.583605	0.499733	-2.302599
C	-5.594846	0.937335	-0.413435
H	-6.447786	0.305784	-0.652248
C	-6.487032	1.331822	1.959506
H	-5.902696	1.287886	2.892479
C	-7.417358	2.556405	2.029619
H	-6.846375	3.488981	2.134604
H	-8.096358	2.472788	2.889149
H	-8.026039	2.631724	1.116915
C	-7.275091	0.025844	1.848817
H	-7.922437	0.012613	0.960085
H	-7.922131	-0.097513	2.727221
H	-6.592488	-0.833121	1.803311
C	-2.324595	2.071506	-2.178832
H	-1.342425	2.229178	-1.716832
H	-2.547246	2.946974	-2.807373
H	-2.261711	1.190370	-2.828644

(R-Ru)-8

Ru	-3.513723	0.354745	0.407982
C1	-3.492517	-0.562880	2.636610
O	8.616396	1.160843	-1.330255
H	8.767100	2.119486	-1.280117
N	-3.432267	-1.623488	-0.216453
C	5.455362	-0.880527	-1.519345
H	5.331140	-1.972192	-1.520729
H	5.032642	-0.514799	-2.471271
C	6.953067	-0.552020	-1.474614
H	7.421054	-1.001658	-0.585042
H	7.460581	-0.982075	-2.350424
C	7.192961	0.950181	-1.434512
H	6.829545	1.390998	-2.383774
C	6.427756	1.594198	-0.280548
H	6.569564	2.687513	-0.305136
H	6.851795	1.239445	0.672081
C	4.930357	1.275789	-0.366639
H	4.585069	1.632436	-1.356717
C	4.107700	2.028634	0.680983
H	4.400325	1.703166	1.692401
H	4.339948	3.103682	0.623673
C	2.610759	1.800118	0.468224
H	2.309325	2.259305	-0.490603
H	2.027654	2.303560	1.253742
C	2.250291	0.311535	0.428390
H	2.434555	-0.111553	1.429724
C	3.118712	-0.442662	-0.614765
H	2.916343	0.058767	-1.582293
C	4.645812	-0.255789	-0.359161

C	2.691536	-1.915976	-0.783195
H	3.230762	-2.355374	-1.633389
H	3.001707	-2.492227	0.100571
C	1.180044	-2.120031	-1.004624
H	0.967484	-3.199905	-1.030062
H	0.885557	-1.711592	-1.985089
C	0.371318	-1.409525	0.087735
C	0.791505	0.088602	0.056085
H	0.695096	0.384480	-1.006718
C	-0.357903	0.825492	0.771013
H	-0.433086	1.885824	0.492575
H	-0.264621	0.796968	1.872029
C	-1.550526	-0.000782	0.350569
C	-1.131818	-1.238010	-0.076706
C	0.609374	-2.073652	1.464118
H	0.111089	-1.506996	2.261300
H	1.673554	-2.160558	1.716887
H	0.181702	-3.086162	1.463935
C	5.066313	-0.910424	0.969247
H	4.478251	-0.541607	1.817934
H	6.122257	-0.723761	1.198002
H	4.934076	-1.999506	0.921297
C	-2.172154	-2.175765	-0.349648
C	-4.521049	-2.397612	-0.383250
H	-5.480738	-1.907033	-0.233798
C	-4.440295	-3.742105	-0.722583
H	-5.352724	-4.318964	-0.858212
C	-3.171733	-4.320038	-0.876147
H	-3.072478	-5.373766	-1.135954
C	-2.042060	-3.537631	-0.683581
H	-1.045601	-3.963611	-0.778734
C	-5.477429	1.523272	0.851863
C	-4.281950	2.289285	1.129996
H	-4.130138	2.675391	2.136750
C	-3.295693	2.523007	0.149057
H	-2.415400	3.111760	0.400971
C	-3.388616	1.891200	-1.136903
C	-4.522697	1.054267	-1.366492
H	-4.583605	0.499733	-2.302599
C	-5.594846	0.937335	-0.413435
H	-6.447786	0.305784	-0.652248
C	-6.487032	1.331822	1.959506
H	-5.902696	1.287886	2.892479
C	-7.417358	2.556405	2.029619
H	-6.846375	3.488981	2.134604
H	-8.096358	2.472788	2.889149
H	-8.026039	2.631724	1.116915
C	-7.275091	0.025844	1.848817
H	-7.922437	0.012613	0.960085
H	-7.922131	-0.097513	2.727221
H	-6.592488	-0.833121	1.803311
C	-2.324595	2.071506	-2.178832
H	-1.342425	2.229178	-1.716832
H	-2.547246	2.946974	-2.807373
H	-2.261711	1.190370	-2.828644

(S-Ru)-8

Ru	-3.350581	-1.895227	0.464603
C1	-4.437879	-0.117773	-0.734549
O	5.287950	6.762770	-0.566295
H	5.000231	7.420480	0.088560
N	-2.755420	-2.609750	-1.391996
C	3.586154	3.715439	-1.984893
H	3.970945	2.971867	-2.696364
H	2.702349	4.176152	-2.459188
C	4.657207	4.791024	-1.764231
H	5.589755	4.337696	-1.393407
H	4.901509	5.281975	-2.717532
C	4.198991	5.835668	-0.757150
H	3.330955	6.377914	-1.181140
C	3.764380	5.178653	0.551040
H	3.382450	5.947089	1.243622

H	4.644598	4.724750	1.033062
C	2.672394	4.130815	0.305535
H	1.839057	4.652301	-0.204506
C	0.919654	2.632354	1.323059
H	0.088044	3.225313	0.902347
H	0.545443	2.188337	2.257702
C	1.277865	1.523406	0.328405
H	2.018899	0.861350	0.806955
C	1.885190	2.119174	-0.970189
H	1.109975	2.803131	-1.369032
C	3.127613	3.017067	-0.683535
C	2.130075	1.048421	-2.053753
H	2.404439	1.541980	-2.996009
H	2.997399	0.433412	-1.773027
C	0.928260	0.121536	-2.322490
H	1.235942	-0.655057	-3.039495
H	0.111842	0.691036	-2.794693
C	0.411017	-0.489440	-1.014272
C	0.062099	0.699229	-0.070502
H	-0.579490	1.361999	-0.681029
C	-0.893921	0.096257	0.978280
H	-1.567263	0.836781	1.430799
H	-0.352086	-0.390451	1.811105
C	-1.631419	-0.934560	0.154974
C	-0.932039	-1.206484	-0.994597
C	1.461829	-1.450094	-0.411952
H	1.161402	-1.778385	0.591731
H	2.458753	-0.998406	-0.336103
H	1.546321	-2.347184	-1.041564
C	4.290169	2.183899	-0.113315
H	3.998124	1.621814	0.781715
H	5.145118	2.813102	0.161408
H	4.648000	1.461072	-0.858484
C	-1.543734	-2.148278	-1.874883
C	-3.498188	-3.445329	-2.141945
H	-4.457344	-3.737517	-1.718671
C	-3.075290	-3.919486	-3.377455
H	-3.708044	-4.605779	-3.936330
C	-1.832162	-3.495789	-3.868678
H	-1.468133	-3.852412	-4.831993
C	-1.074046	-2.605716	-3.120859
H	-0.117070	-2.242450	-3.488603
C	-2.570788	-3.111690	2.098189
C	-3.068597	-1.873323	2.625437
H	-2.392176	-1.210499	3.163440
C	-4.391576	-1.451216	2.365073
H	-4.711343	-0.462214	2.687456
C	-5.329593	-2.304105	1.669780
C	-4.867452	-3.528200	1.172736
H	-5.534697	-4.171148	0.600676
C	-3.478522	-3.877078	1.304452
H	-3.119312	-4.775905	0.806264
C	-1.144418	-3.541349	2.361662
H	-0.556554	-2.616874	2.479438
C	-1.078169	-4.317559	3.688493
H	-1.657415	-5.249770	3.618298
H	-1.486530	-3.726117	4.519151
H	-0.038900	-4.578574	3.931114
C	-0.530939	-4.344369	1.211632
H	0.534041	-4.526140	1.406816
H	-0.620172	-3.800931	0.263015
H	-1.015450	-5.324721	1.100605
C	-6.718993	-1.812111	1.407325
H	-6.674256	-0.867577	0.844680
H	-7.245669	-1.617161	2.352525
H	-7.296288	-2.537827	0.823187
C	2.101452	3.560727	1.605477
H	1.785960	4.388947	2.259295
H	2.888066	3.017086	2.153596

4. References

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