



SUPPLEMENTARY MATERIAL TO
**Synthesis, characterization and biological activity of Pt(II) complexes
with steroidal thiosemicarbazones**

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ISOLATED YIELDS AND SPECTROSCOPIC DATA OF SYNTHESIZED COMPOUNDS

19-Norandrost-4-ene-3,17-dione 3-thiosemicarbazone (2a) (E/Z=7:3). Yield: 63 %; R_f = 0.66 (toluene/EtOAc, 6:4, double development); m.p.: > 219 °C (decomp.); IR (ATR, cm^{-1}): 3422 & 3246 (NH), 1732 (C=O), 1586, 1497 (C=N), 1285 (C=S), 754 (C–S). ESI-TOF-MS (m/z): calcd. for $\text{C}_{19}\text{H}_{27}\text{N}_3\text{OS}$ [$\text{M} + \text{H}$]⁺: 346.19476. Found: 346.19388.

(2a-E). ¹H-NMR (500 MHz, DMSO- d_6): 0.72 (1H, *m*, H-9), 0.86 (3H, *s*, H₃C-18), 0.98 (1H, *qd*, $J = 12.4$ Hz, H α -7), 1.12–1.33 (4H, *m*, H α -1, H α -11, H α -12 & H-14), 1.42–1.56 (2H, *m*, H-8 & H β -15), 1.64 (1H, *d*, $J = 11.5$ Hz, H β -12), 1.76–1.92 (3H, *m*, H β -1, H β -7 & H α -15), 1.96–2.09 (3H, *m*, H-10, H β -11 & H α -16), 2.21 (1H, *td*, $J = 11$ & 4 Hz, H α -6), 2.25 (1H, *m*, H β -2), 2.37–2.45 (2H, *m*, H β -6 & H β -16), 2.82 (1H, *dt*, $J = 16.5$ & 3.5 Hz, H α -2), 5.87 (1H, *s*, H-4), 7.51 & 8.03 (2H, *2brs*, NH₂), 10.07 (1H, *s*, NH); ¹³C-NMR (125 MHz, DMSO- d_6 , δ / ppm): 219.7 (*s*, C-17), 178.2 (*s*, C=S), 152.0 (*s*, C-5), 150.9 (*s*, C-3), 121.6 (*s*, C-4), 49.5 (*d*, C-14), 49.1 (*d*, C-9), 47.2 (*s*, C-13), 40.9 (*d*, C-10), 39.2 (*d*, C-8, overlapped with DMSO), 35.3 (*t*, C-16), 34.3 (*t*, C-6), 31.2 (*t*, C-12), 29.7 (*t*, C-7), 25.8 (*t*, C-11), 25.3 (*t*, C-1), 23.3 (*t*, C-2), 21.3 (*t*, C-15), 13.5 (*q*, C-18).

(2a-Z). ¹H-NMR (500 MHz, DMSO- d_6 , δ / ppm): 0.72 (1H, *m*, H-9), 0.86 (3H, *s*, H₃C-18), 0.98 (1H, *qd*, $J = 12$ & 4 Hz, H α -7), 1.12–1.33 (4H, *m*, H α -1, H α -11, H α -12 & H-14), 1.42–1.56 (2H, *m*, H-8 & H β -15), 1.64 (1H, *d*, $J = 11.5$ Hz, H β -12), 1.76–1.92 (3H, *m*, H β -1, H β -7 & H α -15), 1.96–2.09 (3H, *m*, H-10,

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H β -11 & H α -16), 2.21 (1H, *td*, $J = 11$ & 4 Hz, H α -6), 2.25 (1H, *m*, H β -2), 2.31 (1H, *dt*, $J = 15$ & 3.5 Hz, H α -2), 2.37–2.45 (2H, *m*, H β -6 & H β -16), 6.70 (1H, *s*, H-4), 7.51 & 7.95 (2H, *brs*, NH₂), 10.32 (1H, *s*, NH); ¹³C-NMR (125 MHz, DMSO-*d*₆, δ / ppm): 219.7 (*s*, C-17), 178.0 (*s*, C=S), 156.2 (*s*, C-5), 148.2 (*s*, C-3), 113.2 (*s*, C-4), 49.4 (*d*, C-14), 48.9 (*d*, C-9), 47.2 (*s*, C-13), 42.1 (*d*, C-10), 39.2 (*d*, C-8, overlapped with DMSO), 35.3 (*t*, C-16), 34.9 (*t*, C-6), 31.2 (*t*, C-12), 30.0 (*t*, C-7), 27.1 (*t*, C-2), 25.8 (*t*, C-11), 25.1 (*t*, C-1), 21.3 (*t*, C-15), 13.5 (*q*, C-18).

Androsta-4,9(11)-diene-3,17-dione 3-thiosemicarbazone (2b) (*E/Z*=8:2). Yield: 53 %, $R_f = 0.44$ (toluene/EtOAc, 6:4, double development), m.p.: > 198 °C (decomp.); IR (ATR, cm⁻¹): 3425 & 3256 (NH), 3142, 2928, 1737 (C=O), 1585, 1502 (C=N), 1297 (C=S), 1087, 877; ESI-TOF-MS (*m/z*): calcd. for C₂₀H₂₇N₃OS [M + H]⁺: 358.19476. Found 358.19350.

(2b-E). ¹H-NMR (500 MHz, DMSO-*d*₆, δ / ppm): 0.79 (3H, *s*, H₃C-18), 0.98 (1H, *qd*, $J = 13$, 3 Hz, H α -7), 1.20 (3H, *s*, H₃C-19), 1.45 (1H, *m*, H-14), 1.58 (1H, *d*, *brs*, *d*, $J = 11$ Hz, H α -15), 1.69 (1H, *td*, $J = 13.5$ & 4.5 Hz, H β -1), 1.91 (1H, *dd*, $J = 17$ & 5 Hz, H α -12), 1.96–2.05 (4H, *m*, H α -1, H β -7, H β -12 & H β -15), 2.11 (1H, *dd*, $J = 19$ & 9.5 Hz, H β -16), 2.20–2.37 (3H, *m*, H β -2, H β -6 & H-8), 2.41 (1H, *dd*, $J = 20$ & 11 Hz, H α -16), 2.51 (1H, *m*, H α -6), 2.88 (1H, *dt*, $J = 17.4$ & 3.5 Hz, H α -2), 5.49 (1H, *d*, $J = 5.5$ Hz, H-11), 5.81 (1H, *s*, H-4), 7.54 & 8.07 (2H, *brs* & *m*, NH₂), 10.09 (1H, *s*, NH); ¹³C-NMR (125 MHz, DMSO-*d*₆, δ / ppm): 220.3 (*s*, C-17), 178.3 (*s*, C=S), 154.5 (*s*, C-5), 150.0 (*s*, C-3), 146.1 (*s*, C-9), 121.0 (*d*, C-4), 116.5 (*d*, C-11), 47.3 (*d*, C-14), 45.2 (*s*, C-13), 39.9 (*s*, C-10, overlapped with DMSO), 36.5 (*d*, C-8), 35.8 (*t*, C-16), 33.1 (*t*, C-12), 32.6 (*t*, C-1), 31.6 (*t*, C-6), 31.1 (*t*, C-7), 26.2 (*q*, C-19), 22.3 (*t*, C-15), 21.2 (*t*, C-2), 13.6 (*q*, C-18).

(2b-Z). ¹H-NMR (500 MHz, DMSO-*d*₆): 0.79 (3H, *s*, H₃C-18), 0.98 (1H, *qd*, $J = 13$ & 3 Hz, H α -7), 1.20 (3H, *s*, H₃C-19), 1.56 (1H, *m*, H-14), 1.58 (1H, *d*, *brs*, *d*, $J = 11$ Hz, H α -15), 1.80 (1H, *td*, $J = 13.5$ & 4 Hz, H β -1), 1.91 (1H, *dd*, $J = 17$ & 5 Hz, H α -12), 1.96–2.05 (4H, *m*, H α -1, H β -7, H β -12 & H β -15), 2.11 (*dd*, $J = 19$, 9.5 Hz, 1H, H β -16), 2.20–2.35 (*m*, 3H, H β -2, H β -6, H-8), 2.41 (1H, *dd*, $J = 20$ & 11 Hz, H α -16), 2.47 (1H, *m*, H α -2), 2.51 (1H, *m*, H α -6), 5.47 (1H, *m*, H-11), 6.65 (1H, *s*, H-4), 7.53 & 7.98 (2H, *brs* & *s*, NH₂), 10.36 (1H, *s*, NH); ¹³C-NMR (125 MHz, DMSO-*d*₆, δ / ppm): 220.3 (*s*, C-17), 178.3 (*s*, C=S), 158.7 (*s*, C-5), 147.5 (*s*, C-3), 146.1 (*s*, C-9), 116.6 (*d*, C-11), 112.6 (*d*, C-4), 47.3 (*d*, C-14), 45.2 (*s*, C-13), 41.1 (*s*, C-10), 36.2 (*d*, C-8), 35.8 (*t*, C-16), 34.2 (*t*, C-1), 33.1 (*t*, C-12), 32.0 (*t*, C-6), 31.5 (*t*, C-7), 27.5 (*t*, C-2), 26.5 (*q*, C-19), 22.3 (*t*, C-15), 13.8 (*q*, C-18).

Complex 4 [Pt(2a)₂]. Yield: 19.4 %; m.p.: >200 °C (decomp.); IR (ATR, cm⁻¹): 3448, 3306, 3116, 2922, 2852, 1736, 1607, 1528, 1447, 1419, 1320, 1006, 879; Anal. calcd. for C₃₈H₅₂N₆O₂PtS₂: C, 51.63; H, 5.93; N, 9.51; S, 7.25 %.

Found: C, 50.96; H, 6.16; N, 10.24; S 7.52 %; A_M (DMSO, $\mu\text{S cm}^{-1}$): 3.4; $^1\text{H-NMR}$ (500 MHz, DMSO- d_6 , δ / ppm): 0.62 (1H, *qd*, $J = 10$ & 4 Hz, H-9), 0.83 (3H, *s*, CH₃-18), 0.87–0.99 (2H, *m*, H α -7 & H α -12), 1.00–1.12 (2H, *m*, H α -1 & H-14), 1.25 (1H, *qd*, $J = 13$ & 2.5 Hz, H α -11), 1.49–1.58 (2H, *m*, H-8 & H β -15), 1.65 (1H, *dt*, $J = 12.5$ & 2.5 Hz, H β -12), 1.73 (1H, *brd*, $J = 11.5$ Hz, H β -11), 1.81–1.90 (3H, *m*, H β -2, H β -7 & H α -15), 1.95 (1H, *m*, H α -16), 2.02 (1H, *m*, H β -1), 2.07 (1H, *m*, H-10), 2.20–2.30 (2H, *m*, H α -6 & H β -6), 2.39 (1H, *dd*, $J = 19$ & 10 Hz, H β -16), 3.40 (1H, *m*, H α -2, overlapped with DMSO), 6.52 (1H, *s*, H-4), 6.70 (2H, *brs*, NH₂); $^{13}\text{C-NMR}$ (125 MHz, DMSO- d_6 , δ / ppm): 219.3 (*s*, C-17), 172.3 (*s*, C=S), 161.3 (*s*, C-3), 153.3 (*s*, C-5), 122.1 (*d*, C-4) 50.4 (*d*, C-14), 49.7 (*d*, C-9), 47.1 (*s*, C-13), 41.4 (*d*, C-10), 38.8 (*d*, C-8), 35.1 (*t*, C-16), 34.9 (*t*, C-6), 31.4 (*t*, C-12), 29.8 (*t*, C-7), 26.3 (*t*, C-11), 25.7 (*t*, C-1), 24.8 (*t*, C-2), 21.2 (*t*, C-15), 13.5 (*q*, C-18).

Complex 5 [*Pt(2b)*]₂. Yield: 23.9%; m.p.; >200 °C (decomp.); IR (ATR, cm^{-1}): 3455, 3343, 3289, 3197, 2931, 2900, 2843, 1739, 1720, 1608, 1518, 1322, 1017, 826; Anal. calcd. for C₄₀H₅₂N₆O₂PtS₂: C, 52.91; H, 5.77; N, 9.25; S, 7.06 %. Found: C, 52.83; H, 5.80; N, 9.21; S, 7.01 %; A_M (DMSO, $\mu\text{S cm}^{-1}$): 1.9; $^1\text{H-NMR}$ (500 MHz, DMSO- d_6 , δ / ppm): 0.75 (3H, *s*, H₃C-18), 0.85 (1H, *qd*, $J = 13$ & 2.5 Hz, H α -7), 1.16 (3H, *s*, H₃C-19), 1.24 (1H, *m*, H-14), 1.49–1.63 (2H, *m*, H β -1 & H α -15), 1.79 (1H, *brd*, $J = 18$ Hz, H α -12), 1.84–1.92 (2H, *m*, H α -1 & H β -12), 1.95–2.09 (4H, *m*, H β -6, H β -7, H β -15 & H β -16), 2.24 (1H, *td*, $J = 16.5$ & 4.5 Hz, H β -2), 2.34 (1H, *m*, H-8), 2.44 (1H, *dd*, $J = 17.5$ & 9 Hz, H α -16), 2.55 (1H, *m*, H α -6, overlapped with DMSO), 3.36 (1H, *m*, H α -2, partially overlapped with H₂O from DMSO), 5.31 (1H, *d*, $J = 5$ Hz, H-11), 6.38 (1H, *s*, H-4), 6.78 (2H, *brs*, NH₂); $^{13}\text{C-NMR}$ (125 MHz, DMSO- d_6 , δ / ppm): 220.0 (*s*, C-17), 172.9 (*s*, C=S), 160.6 (*s*, C-3), 156.5 (*s*, C-5); 146.1 (*s*, C-9), 121.3 (*d*, C-4), 116.1 (*d*, C-11), 47.7 (*d*, C-14), 45.1 (*s*, C-13), 40.4 (*s*, C-10), 36.2 (*d*, C-8), 35.6 (*t*, C-16), 33.5 (*t*, C-12), 32.6 (*t*, C-6), 32.5 (*t*, C-1), 30.9 (*t*, C-7), 25.9 (*q*, C-19), 24.3 (*t*, C-2), 22.1 (*t*, C-15), 13.7 (*q*, C-18).