Half-sandwich arene ruthenium(II) and osmium(II) thiosemicarbazone complexes: solution behavior and antiproliferative activity

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Supporting Information

Table S1

Figures S1-S7

Table S1. X-ray crystallographic data for complexes **1**, **2·acetone**, **3**, and **4·acetone.**

Identification code	**1**	**2·acetone**	**3**	**4·acetone**
Empirical formula	$C_{19}H_{25}Cl_2N_3O_2OsS$	$C_{27}H_{33}Cl_2N_3O_3OsS$	$C_{19}H_{25}Cl_2N_3O_2RuS$	$C_{27}H_{33}Cl_2N_3O_3RuS$
Formula weight	620.58	740.72	531.45	651.59
Temperature/K	150(2)	150(2)	150(2)	150(2)
Crystal system	orthorhombic	triclinic	orthorhombic	triclinic
Space group	$P2_12_12_1$	P-1	$P2_12_12_1$	P-1
a/Å	10.7744(2)	9.86196(14)	10.73778(14)	9.84609(16)
b/Å	11.5150(3)	11.23953(13)	11.50758(15)	11.2583(2)
c/Å	17.3324(4)	13.4752(2)	17.3192(2)	13.4517(2)
α/°	90	82.5065(11)	90	82.4504(14)
β/°	90	77.9531(12)	90	78.0644(13)
γ/°	90	84.5370(11)	90	84.4095(14)
Volume/$Å^3$	2150.39(9)	1444.71(4)	2140.07(5)	1442.44(4)
Z	4	2	4	2
$\rho_{calc}g/cm^3$	1.917	1.703	1.649	1.500
μ/mm^{-1}	6.296	4.703	9.308	0.834
F(000)	1208.0	732.0	1080.0	668.0
Crystal size/mm^3	0.2 × 0.16 × 0.1 yellow block	0.16 × 0.16 × 0.08 yellow block	0.12 × 0.08 × 0.06 orange block	0.28 × 0.18 × 0.06 orange block
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.686 to 75.388	6.774 to 60.63	9.226 to 155.996	5.07 to 73.418
Index ranges	$-16 \le h \le 18$, $-12 \le k \le 19$, $-27 \le l \le 29$	$-13 \le h \le 14$, $-15 \le k \le 15$, $-19 \le l \le 18$	$-10 \le h \le 13$, $-14 \le k \le 12$, $-21 \le l \le 21$	$-16 \le h \le 16$, $-18 \le k \le 18$, $-21 \le l \le 22$
Reflections collected	19836	68684	10573	65958
Independent reflections	10741 [R_{int} = 0.0361, R_{sigma} = 0.0615]	8088 [R_{int} = 0.0409, R_{sigma} = 0.0253]	4363 [R_{int} = 0.0311, R_{sigma} = 0.0377]	13758 [R_{int} = 0.0399, R_{sigma} = 0.0305]
Data/restraints/parameters	10741/0/258	8088/6/357	4363/0/258	13758/36/381
Goodness-of-fit on F^2	1.016	1.036	1.043	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0615	R_1 = 0.0202, wR_2 = 0.0417	R_1 = 0.0269, wR_2 = 0.0693	R_1 = 0.0278, wR_2 = 0.0608
Final R indexes [all data]	R_1 = 0.0439, wR_2 = 0.0646	R_1 = 0.0234, wR_2 = 0.0428	R_1 = 0.0276, wR_2 = 0.0699	R_1 = 0.0371, wR_2 = 0.0644
Largest diff. peak/hole / e $Å^{-3}$	1.84/-1.15	1.21/-0.73	1.18/-0.43	0.52/-0.66
Flack parameter	-0.016(5)		-0.024(6)	

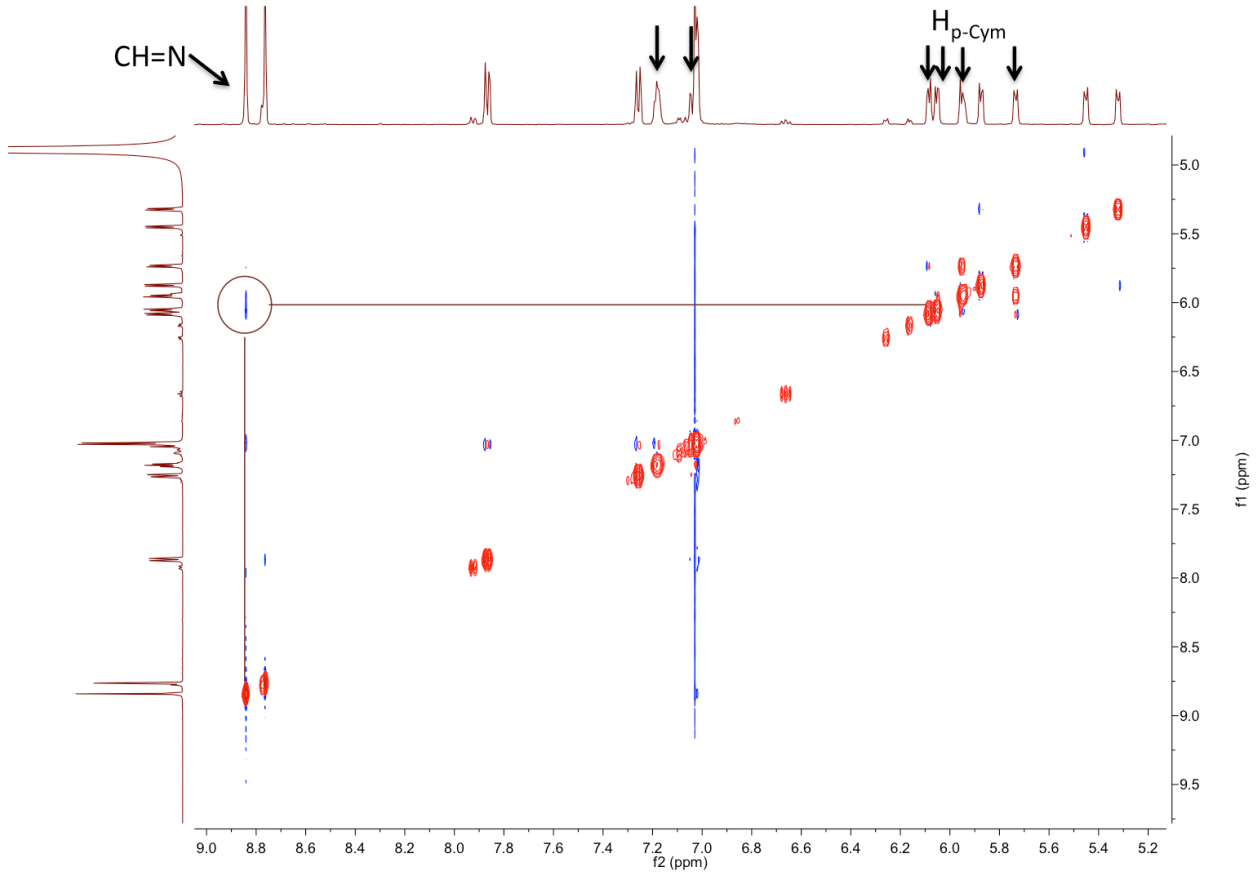

Figure S1. ^{1}H-^{1}H 2D NMR NOESY spectrum of complex **1** in MeOD-d_4 at T = 298 K showing the interaction between the iminic and the aromatic p-cymene protons for the *Z* isomer of coordinated ligand **L1**.

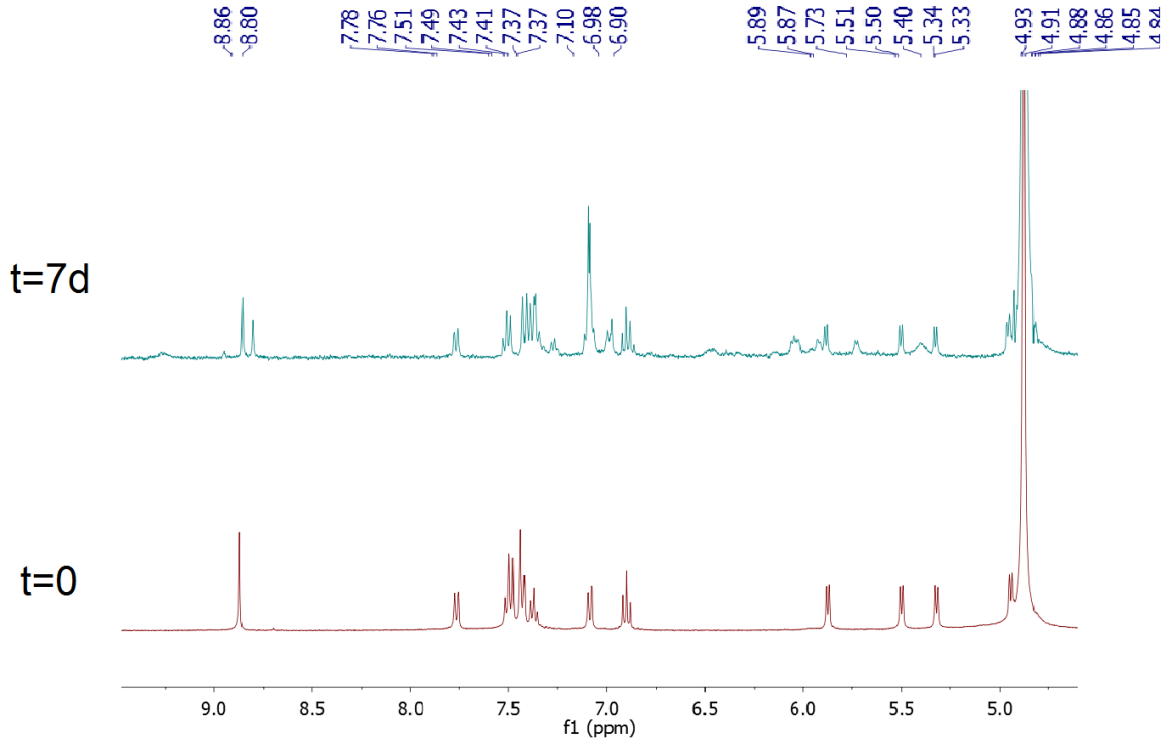

Figure S2. ^{1}H-NMR spectrum of complex **2** in MeOD at 298 K at t=0 and t= 7 days.

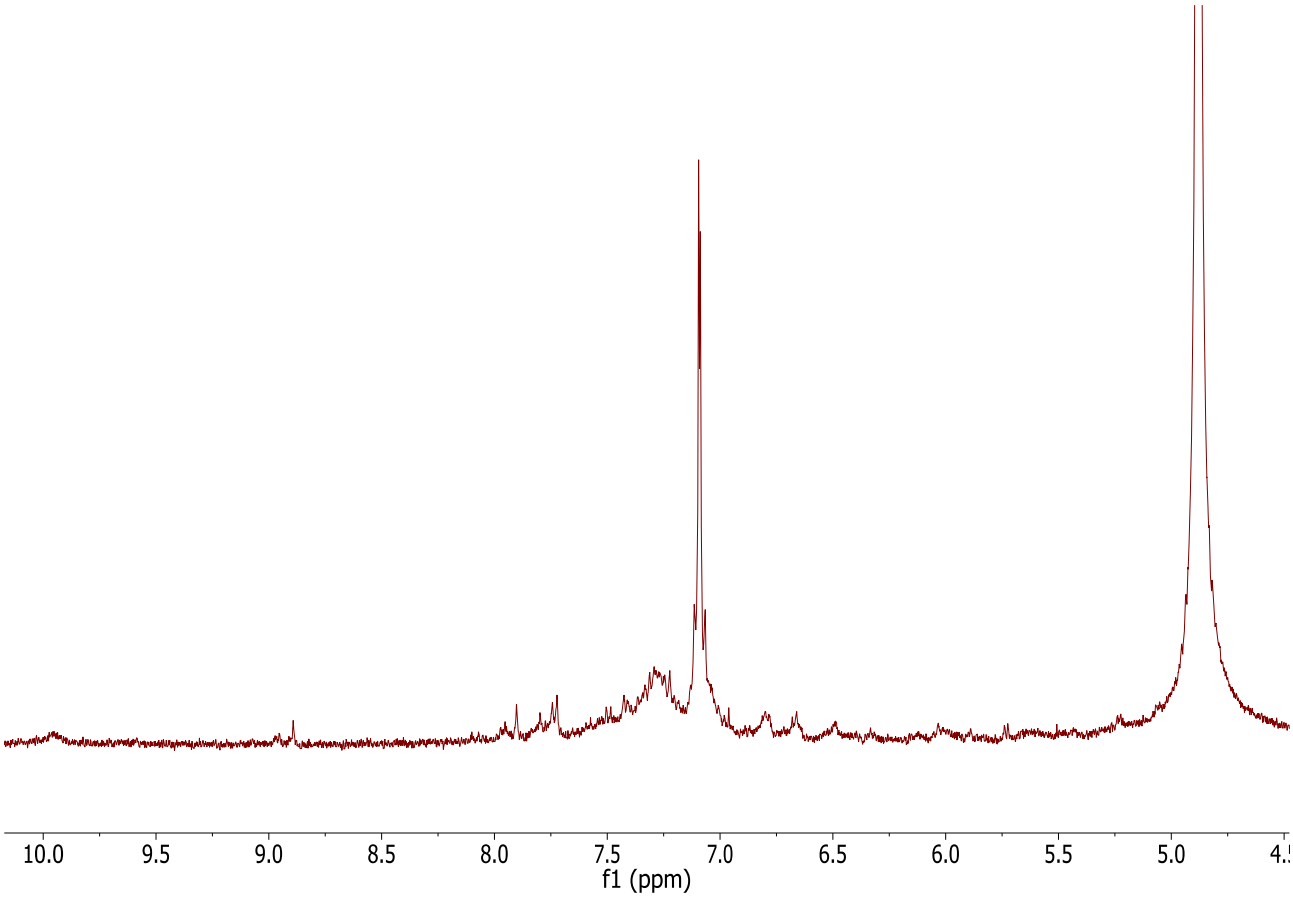

Figure S3. ^{1}H-NMR spectrum of complex **4** after 7 days in MeOD at 298 K.

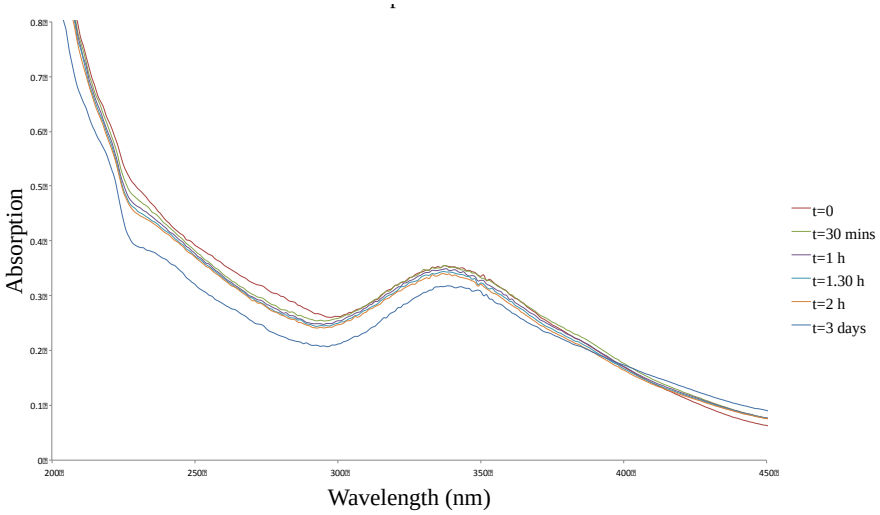

Figure S4. UV-visible spectra of complex **2** in methanol at T=298 K over time (1, 0.5, 1, 1.5, 2 h and 3 d).

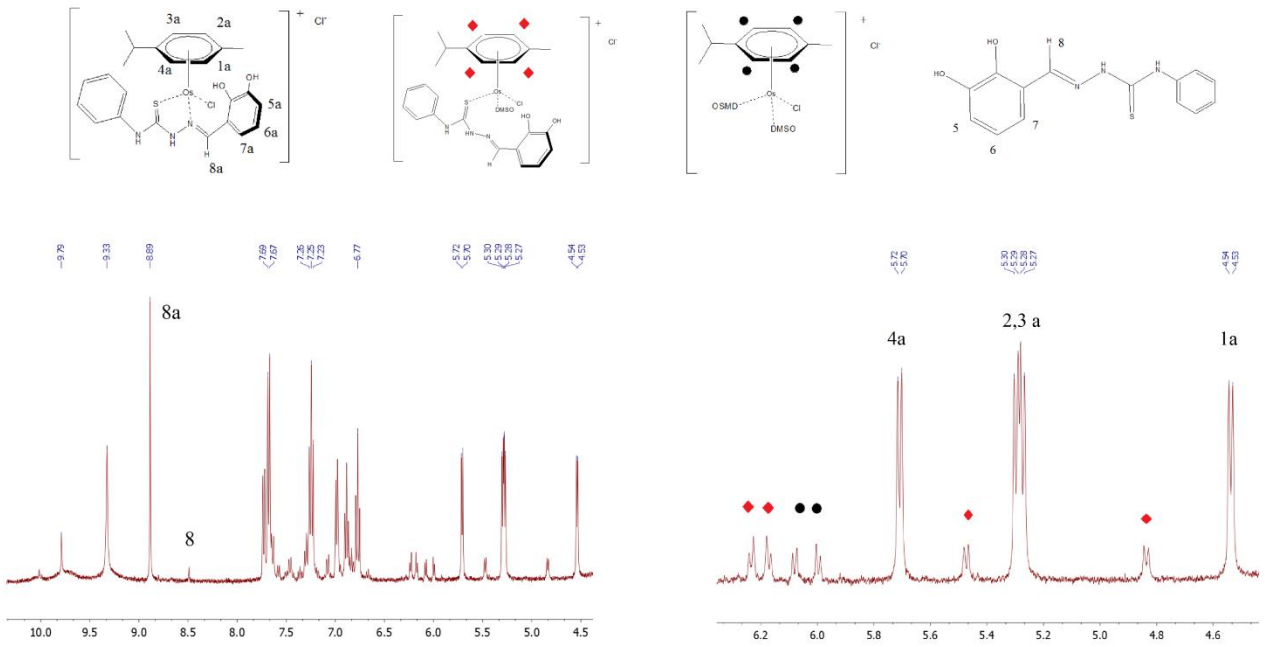

Figure S5. A) ^{1}H-NMR spectrum of complex **2** in d_6-DMSO. **B)** Expansion of the p-cymene region.

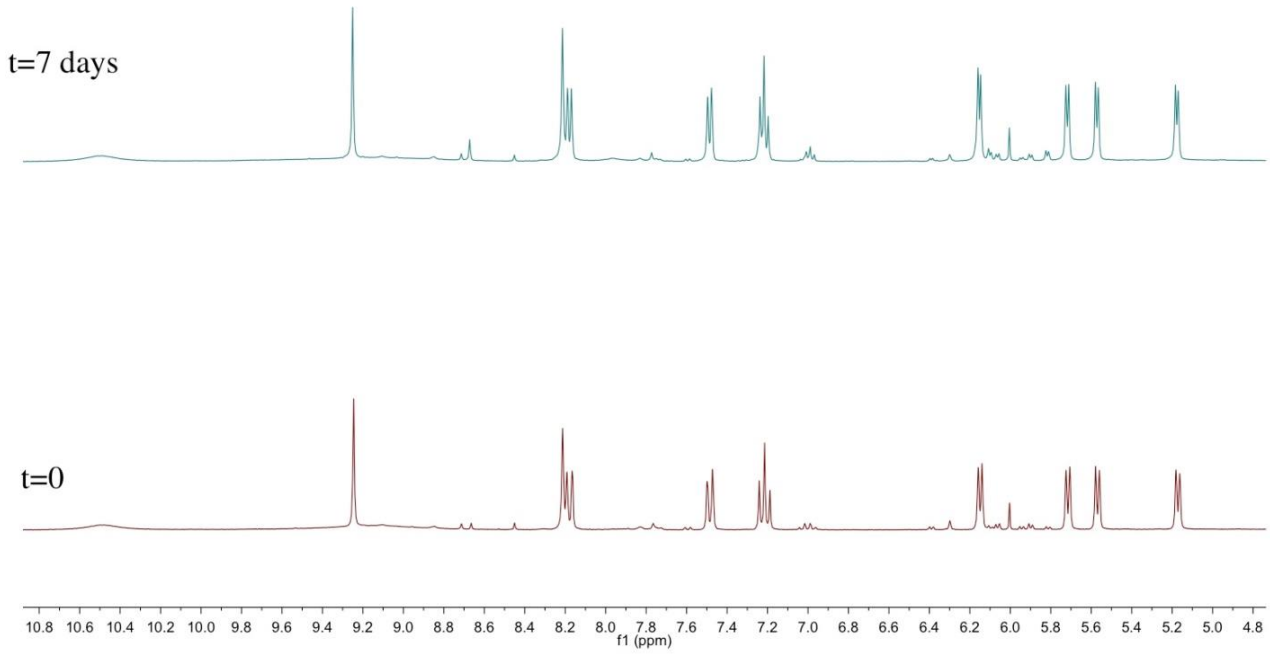

Figure S6. ^{1}H-NMR of complex **1** in DMF-d_7 after dissolution and after 7 days at 298 K.

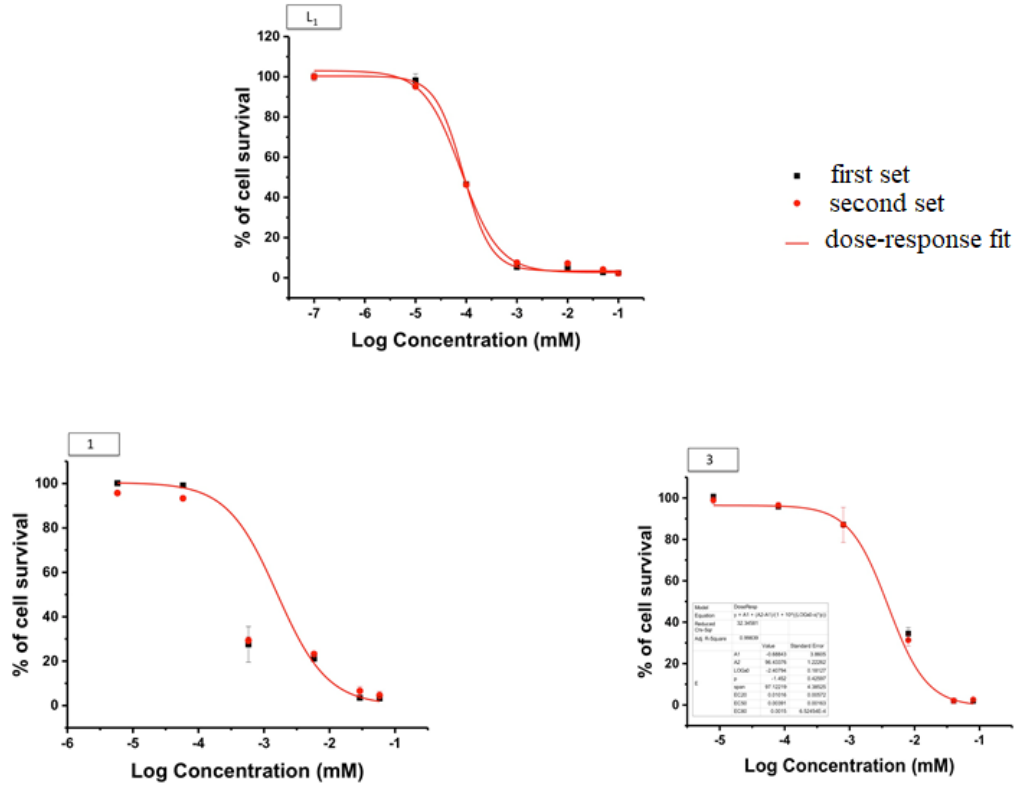

Figure S7. Examples of dose response curves for ligand **L**$_1$ and related osmium **1** and ruthenium **3** complexes in the A2780 human ovarian cancer cell line. Experiments included 48 h of pre-incubation time, 24 h of drug exposure and 72 h of recovery time in drug-free medium. IC_{50} values, as the inflection point of the dose-response curves, were obtained from triplicates of duplicates (black and red data sets) and their standard deviations were calculated.