Electronic Supplementary Information (ESI) for the manuscript:

Cytotoxic gold(III) complexes incorporating 2,2′:6′,2″-terpyridine ligand framework – the impact of the substituent in 4′-position of terpy ring

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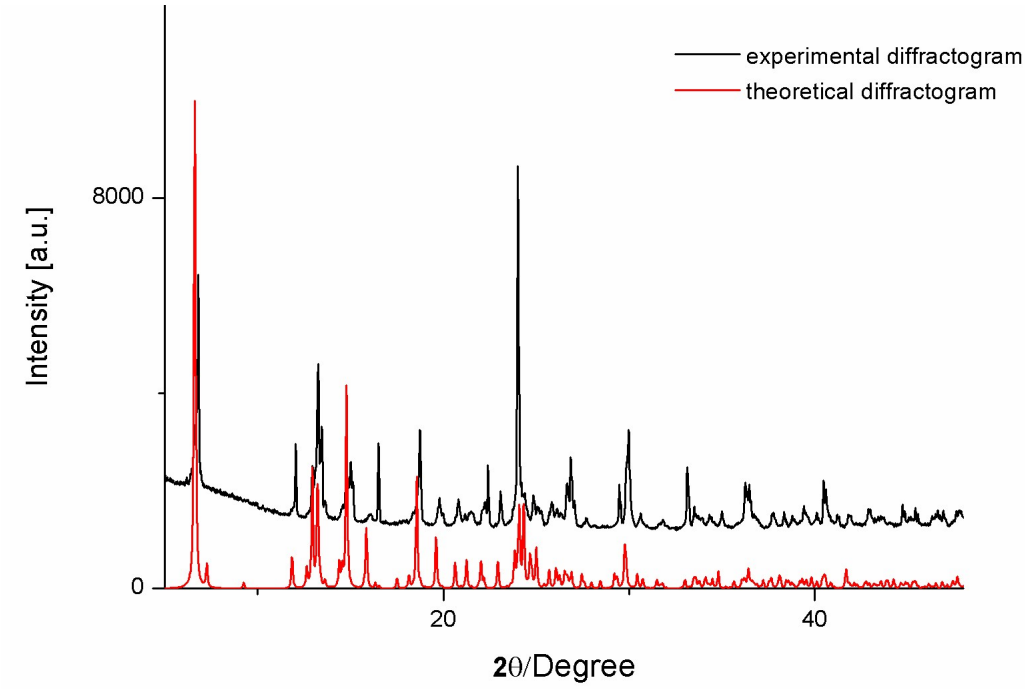


Figure S1. XRPD pattern of **1** (experimental - black) and the simulation of its powder pattern from the crystal structure (red).

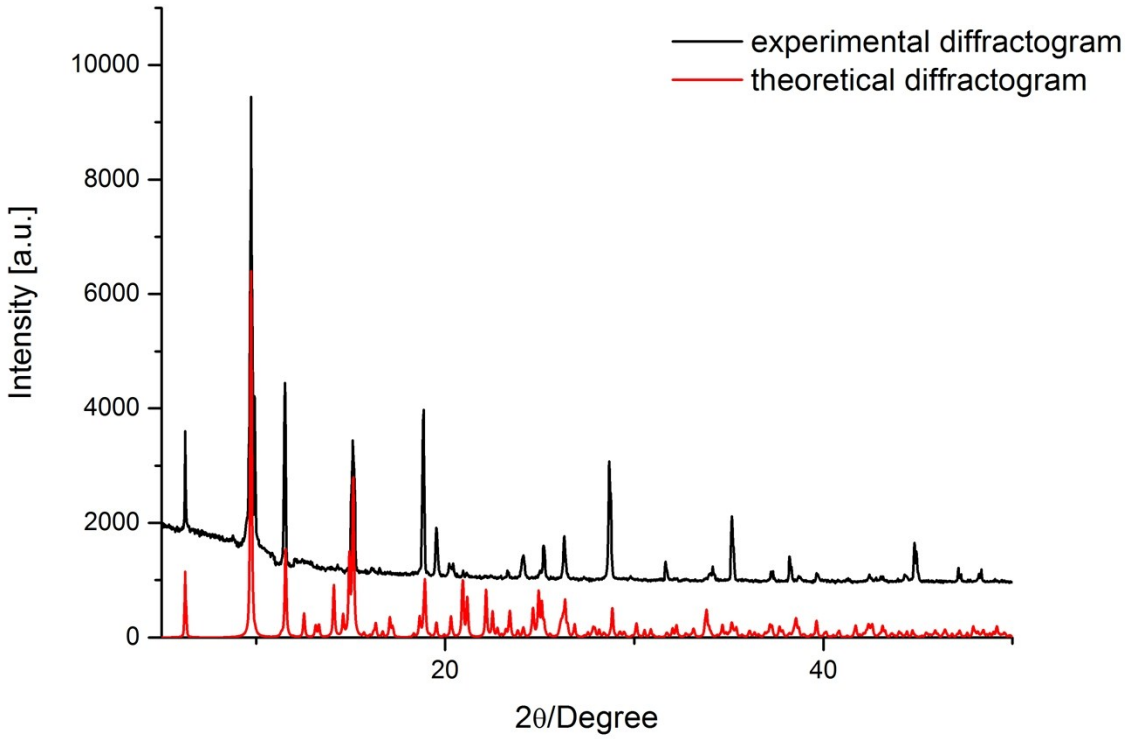


Figure S2. XRPD pattern of **2** (experimental - black) and the simulation of its powder pattern from the crystal structure (red).

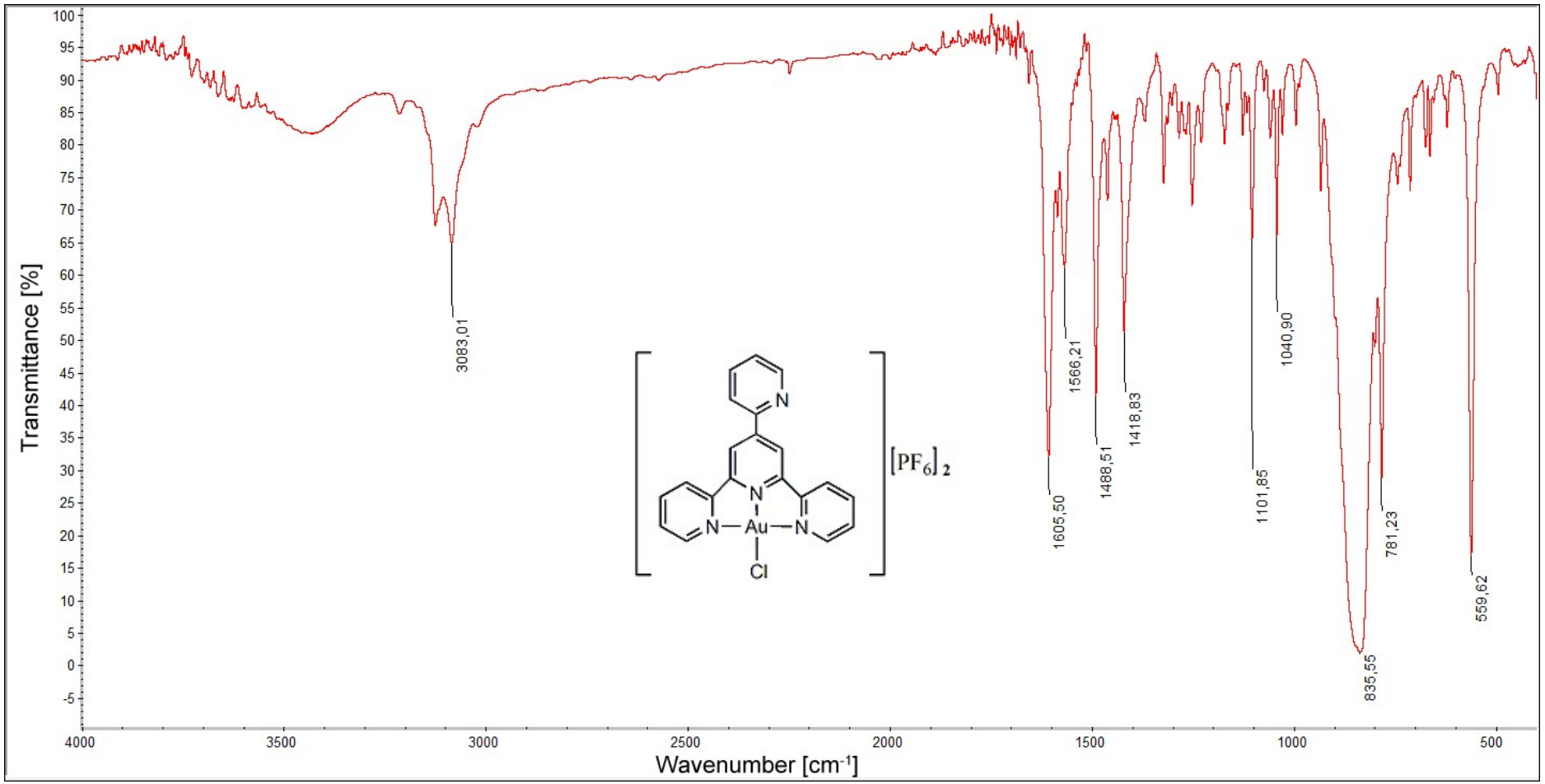


Figure S3. IR spectrum of **1**.

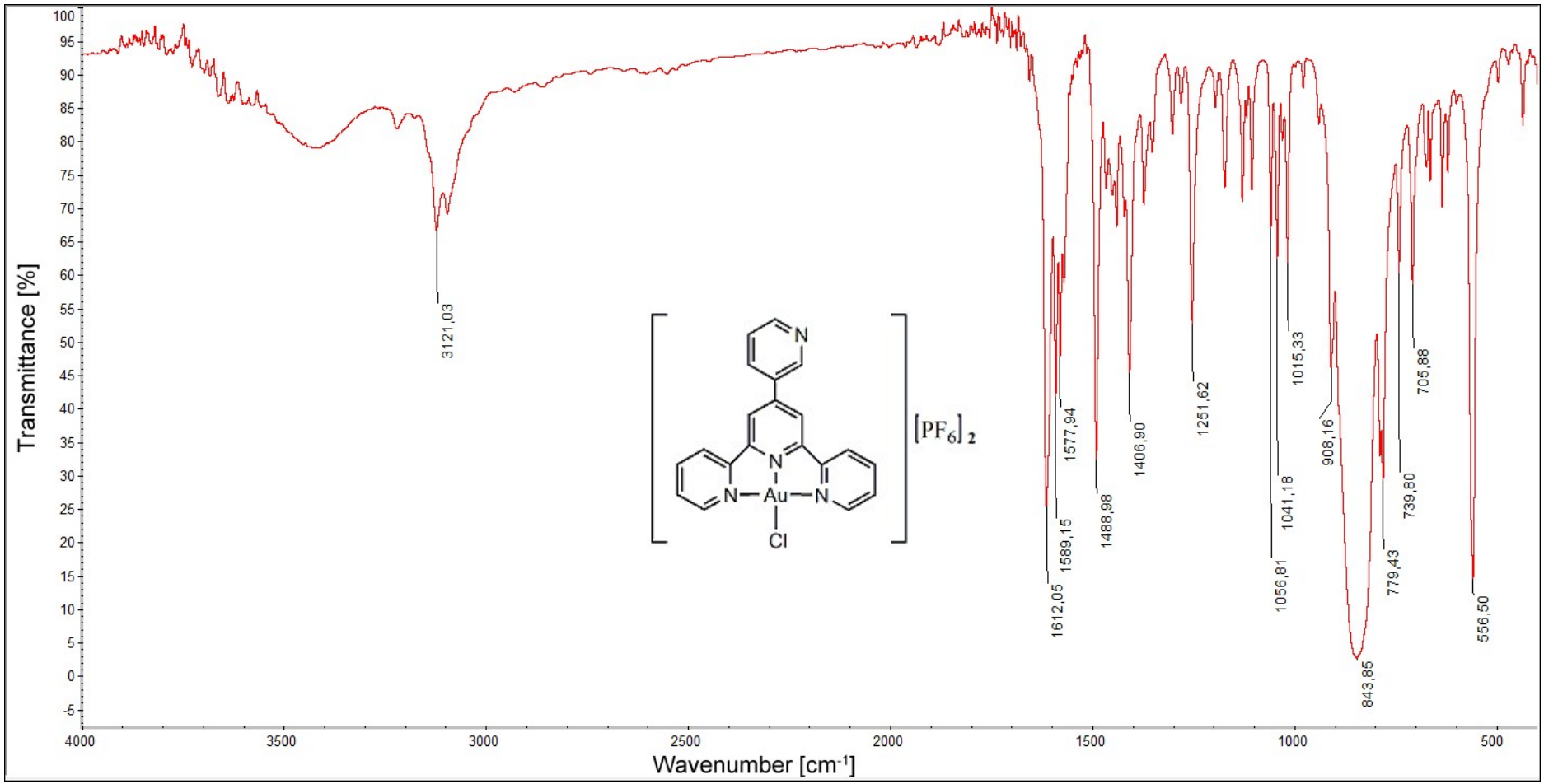


Figure S4. IR spectrum of **2**.

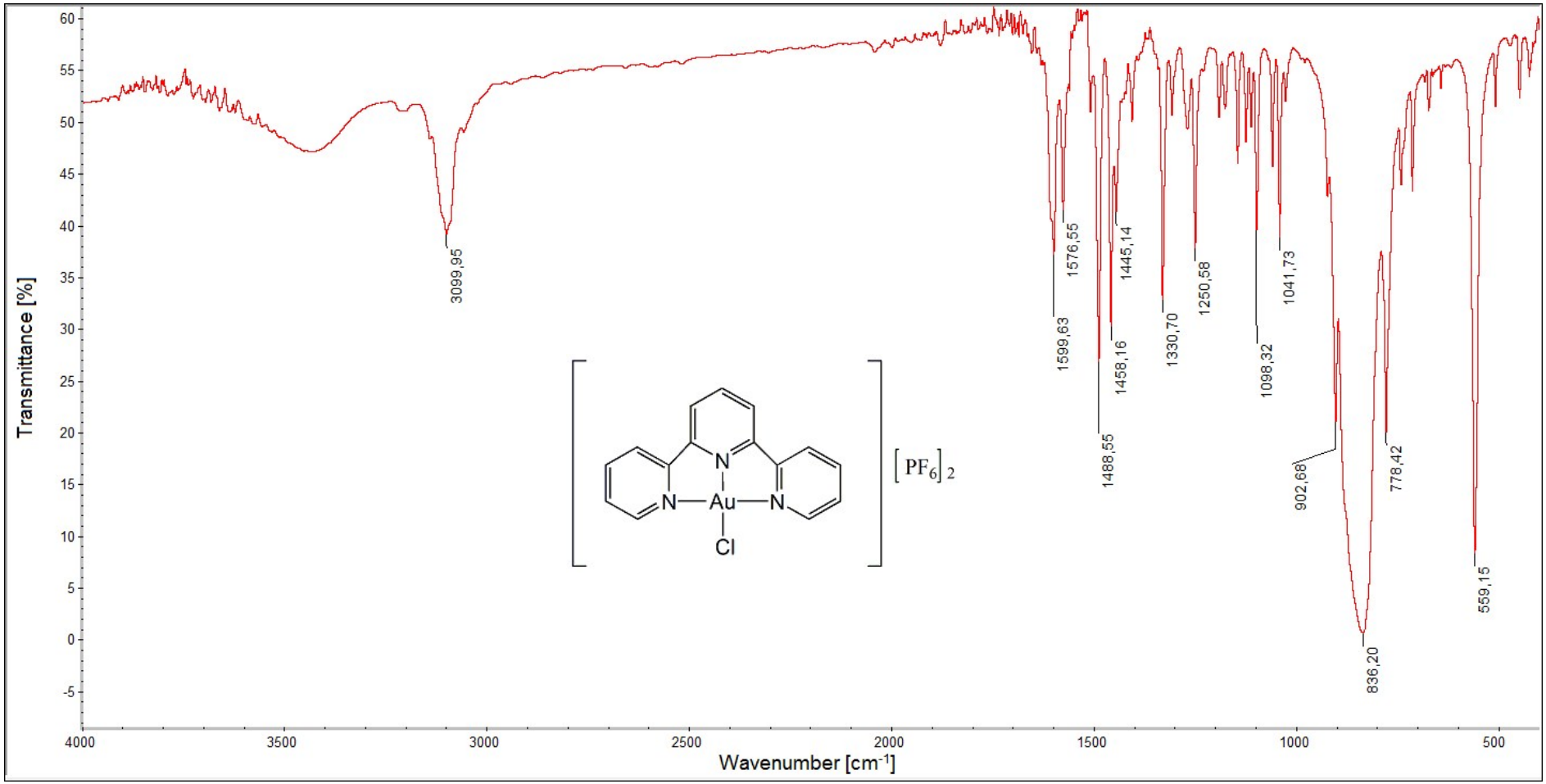
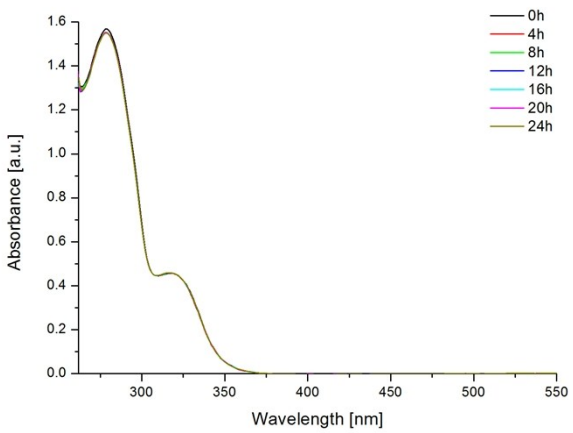
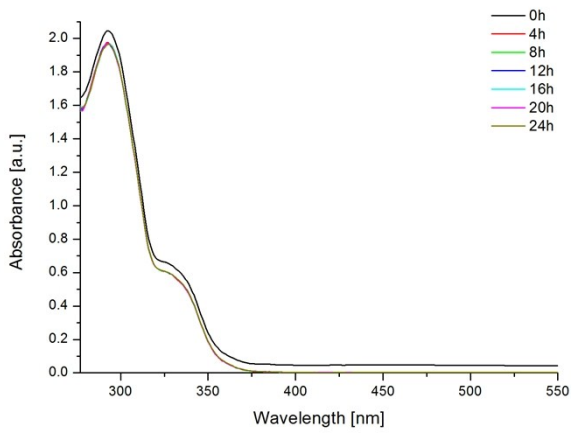


Figure S5. IR spectrum of $[AuCl(terpy)](PF_6)_2$.

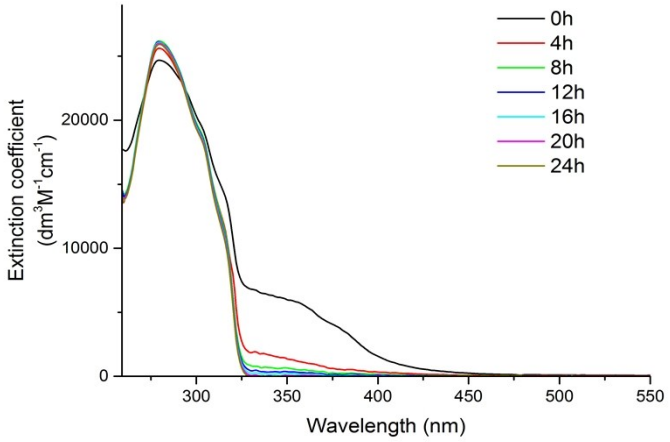


R^1-terpy in DMSO

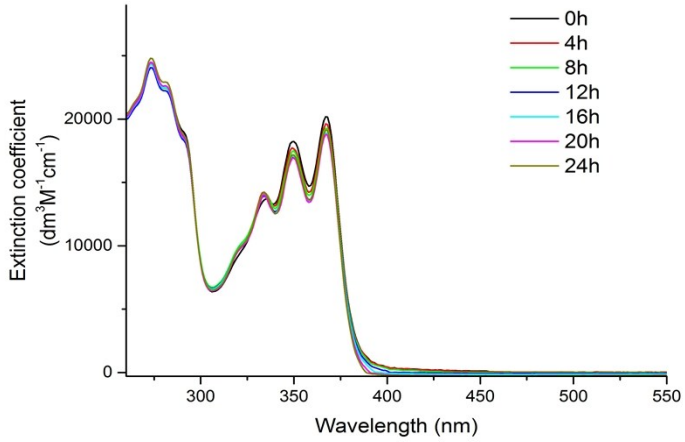


R^2-terpy in DMSO

Figure S6. UV-Vis spectra of the free ligands in DMSO over 24 h.



[AuCl(terpy)]$(PF_6)_2$ in DMSO



[AuCl(terpy)]$(PF_6)_2$ in PBS

Figure S7. UV-Vis spectra of [AuCl(terpy)]$(PF_6)_2$ in DMSO and 10 mM phosphate-buffered saline (PBS) over 24h.

Table S1. The selected structural data for Au(III) coordination compounds incorporating 2,2′:6′,2″-terpyridine derivatives.

Compound[a]	Au-N_c (Å)	Au-N_d (Å)	Au-Cl (Å)	Au-F (Å)	N_c[b]-Au-N_d[c] [°]	N_d–Au–N_d [°]	C–N_d–C [°]	C–N_c–C [°]	Ref.
1	1.938(8)	2.020(8) 2.027(8)	2.257(3)	3.075(14) 3.061(17)[d]	81.6(3) 81.3(3)	162.9(3)	120.0(9) 121.3(9)	124.2(8)	–
2	1.971(7)	2.047(8) 2.017(8)	2.257(3)	3.11(1) 2.885(6)	79.8(3) 82.1(3)	161.8(3)	121.6(9) 121.4(9)	125.9(8)	
$[AuCl(terpy)](PF_6)_2$	1.935(9)	2.014(9) 2.032(9)	2.253(3)	3.03(3) 3.16(2)	81.0(4) 81.9(4)	162.7(4)	122.3(10) 120.9(10)	124.2(10)	
$[AuCl(terpy)]Cl_2 \cdot 3H_2O$	1.931(7)	2.029(6) 2.018(6)	2.269(2)	–	81.4 (3) 81.4 (3)	162.7(3)	121.5(7) 121.1(7)	123.4(7)	1
$[AuCl(terpy)]_2[AuCl_2]_3[AuCl_4]$	1.941(8)	2.022(9) 2.030(8)	2.271(3)	–	81.3(4) 81.4(4)	162.6(4)	120.1 (9) 121.0(9)	124.5(9)	
$[Au(4\text{-}MeOPh\text{-}terpy)Cl](ClO_4)_2$	1.924(6)	2.020(7) 2.047(7)	2.2559(24)	–	80.1(3) 82.5(3)	162.6(3)	120.3(7) 122.2(7)	123.1(7)	2
$[AuCl(S\text{-}8)] (SO_3CF_3)_2$	1.945(7)	2.025(8) 2.018(8)	2.259(3)	–	81.4(3) 81.2(3)	162.5(3)	119.6(8) 120.6(9)	124.4(8)	3
$[Au(terpy)(OH)](ClO_4)_2$	1.949(4)	2.009(5) 2.008(4)	–	–	81.2(2) 81.5(2)	162.6(2)	121.4(5) 120.7(5)	125.4(4)	4
$[AuCl(terpy)]Cl_2 \cdot 3H_2O$	1.950 (3)	2.021 (4) 2.025 (4)	2.2686 (11)	–	81.39 (15) 81.25 (15)	162.64 (15)	121.1 (4) 120.7 (4)	125.6 (4)	5
$[AuCl(terpy)](BF_4)_2$	1.947(3)	2.014(3) 2.028(3)	2.2574(10)	2.915(3) 3.130(2)	80.88(16) 81.53(16)	162.94(12)	120.0(5) 121.3(6)	125.2(3)	6
$[AuCl(terpy)](SO_3CF_3)_2$	1.954(4)	2.014(4) 2.026(4)	2.2711(12)	–	81.69(13) 81.36(13)	162.37(17)	119.5(4) 120.7(4)	124.3(4)	
$[Au(4\text{-}DMAP)(terpy)](SO_3CF_3)_2$	1.934(5)	2.015(5) 2.013(4)	–	–	81.38(19) 81.53(19)	162.9(2)	120.1(5) 121.5(5)	124.3(5)	7
$[Au(terpy)(OH)](SO_3CF_3)_2$	1.963(4)	2.020(5) 2.015(5)	–	–	81.2(2) 82.0(2)	163.2(2)	120.9(5) 120.9(5)	126.3(5)	
$[Au(terpy)(NHpyCl)](ClO_4)_2$	1.960(5)	2.031(5) 2.032(5)	–	–	80.9(2) 80.85(19)	161.7(2)	120.0(5) 121.3(6)	123.4(5)	8
$[Au(terpy)(NHpymCl)](ClO_4)_2$	1.947(11)	2.001(10) 2.014(11)	–	–	81.4(5) 81.5(5)	162.5(5)	119.3(10) 122.0(12)	124.2(12)	
$[Au(terpy)(NHpym)](ClO_4)_2$	1.940(10)	2.023(10) 2.053(11)	–	–	80.8(4) 80.4(4)	161.1(4)	119.3(10) 123.4(10)	123.4(10)	
$[Au(C_6F_5)(\eta 3\text{-}terpy)](PF_6)_2$	1.985(3)	2.028(3) 2.025(3)	–	3.148(2) 3.040(3)	80.88(11) 80.60(11)	161.45(11)	120.2(3) 120.2(3)	124.9(3)	9

[a] Abbreviation for the ligands: terpy – 2,2':6',2"-terpyridine, S-8 – 4'-(methylthio)-2,2':6',2''-terpyridinyl, 4-MeOPh-terpy –4'-(4-methoxyphenyl)-2,2',6',2''-terpyridine, 4-DMAP- 4-dimethylamoniopyridine, NH_2pyCl – 2-amino-5-chloropyridine, NH_2pymCl – 2-amino-4-chloro-pyrimidine, NH_2pym – 2-aminopyrimidine.

[b] N_c – central nitrogen atom of terpyridine ligand

[c] N_d – distal nitrogen atoms of terpyridine ligand

[d] Symmetry code: (d) = -1/2+x,1/2-y,-1/2+z

Table S2. X—Y•••Cg(J)(π-ring) interactions for **1**, **2** and [AuCl(terpy)]$(PF_6)_2$.

Y-X(I)•••Cg(J)	X(I)•••Cg(J) [Å]	X-Perp [Å]	γ [°]	Y-X(I)•••Cg(J) [°]
1				
P(1)-F(2)•••Cg(1)[a]	3.06(3)	-3.010	9.73	118.2(11)
P(1)-F(4)•••Cg(2)	3.36(4)	2.970	27.64	118.0(16)
P(1)-F(6)•••Cg(2)	3.19(2)	3.150	8.66	125.1(10)
2				
Au(1)-Cl(1)•••Cg(3)[b]	3.819(5)	-3.449	25.45	104.74(11)
P(1)-F(5)•••Cg(4)	3.175(11)	-2.771	29.20	150.7(6)
P(2)-F(10)•••Cg(4)	2.936(7)	2.867	12.49	138.6(3)
P(2)-F(12)•••Cg(3)[c]	3.118(7)	3.114	3.07	121.0(3)
[AuCl(terpy)]$(PF_6)_2$				
P(1)-F(2)•••Cg(4)	3.038(6)	2.784	23.60	152.9(7)
P(1)-F(5)•••Cg(2)	3.012(9)	-2.919	14.31	132.5(9)
P(2)-F(9)•••Cg(4)	2.981(9)	-2.956	7.55	132.5(4)

γ = angle X(I)→Cg(J) vector and normal to plane J.

Cg1 is the centroid of atoms N(1)/C(1)/C(2)/C(3)/C(4)/C(5); Cg2 is the centroid of atoms N(3)/C(11)/C(12)/C(13)/C(14)/C(15); Cg3 is the centroid of atoms N(4)/C(19)/C(18)/C(17)/C(16)/C(20); Cg4 is the centroid of atoms N(2)/C(6)/C(7)/C(8)/C(9)/C(10);

Symmetry codes: (a) = 1/2+x,1/2-y,1/2+z; (b) = 1/2-x, 1/2+y, z; (c) = -x,1-y, 1-z.

Table S3. Short π•••π interactions for **1.**

Cg(I)•••Cg(J)	Cg(I)•••Cg(J) [Å]	α[°]	β[°]	γ [°]	Cg(I)-Perp [Å]	Cg(J)-Perp [Å]
1						
Cg(2)•••Cg(5)[a]	3.736(5)	9.0(4)	22.26	17.92	3.555(4)	-3.457(4)

α = dihedral angle between *Cg*(I) and *Cg*(J); *Cg*(I)-Perp = Perpendicular distance of *Cg*(I) on ring J; *Cg*(J)-Perp = perpendicular distance of *Cg*(J) on ring I; β = angle *Cg*(I)→*Cg*(J) vector and normal to ring I; γ = angle *Cg*(I) →*Cg*(J) vector and normal to plane J;

Cg2 is the centroid of atoms N(3)/C(11)/C(12)/C(13)/C(14)/C(15); Cg5 is the centroid of atoms N(4)/C(16)/C(17)/C(18)/C(19)/C(20);

Symmetry codes: (a) = -1+x, y, z.

Table S4. Short intra- and intermolecular hydrogen bonds detected in structures **1**, **2** and $[AuCl(terpy)](PF_6)_2$**.**

D–H•••A	D–H [Å]	H•••A [Å]	D–A [Å]	D–H•••A[°]
1				
C(1)–H(1)•••Cl(1)	0.93	2.82	3.380(12)	119.4
C(2)–H(2)•••F(11) [a]	0.93	2.39	3.204(15)	146.3
C(3)–H(3)•••F(7) [b]	0.93	2.53	3.23(2)	132.0
C(7)–H(7)•••N(4)	0.93	2.36	2.711(14)	101.7
C(15)–H(15)•••Cl(1)	0.93	2.79	3.356(11)	120.4
C(19)–H(19)•••F(8) [c]	0.93	2.55	3.222(18)	129.8
C(19)–H(19)•••F(9) [c]	0.93	2.43	3.348(17)	170.1
2				
C(2)–H(2)•••F(8) [d]	0.93	2.50	3.270(13)	140.00
C(2)–H(2)•••F(3) [e]	0.93	2.54	3.069(14)	116.20
C(4)–H(4)•••F(7) [f]	0.93	2.45	3.316(13)	155.50
C(4)–H(4)•••F(9) [f]	0.93	2.54	3.299(13)	139.30
C(7)–H(7)•••F(7) [f]	0.93	2.51	3.405(12)	161.40
C(9)–H(9)•••F(3) [g]	0.93	2.44	3.278(12)	149.50
C(12)–H(12)•••F(3) [g]	0.93	2.50	3.280(13)	141.80
C(13)–H(13)•••F(2) [h]	0.93	2.49	3.395(14)	163.40
C(14)–H(14)•••F(4) [h]	0.93	2.49	3.139(14)	127.30
C(15)–H(15)•••Cl(1)	0.93	2.79	3.352(11)	120.20
C(15)–H(15)•••F(5) [i]	0.93	2.55	3.264(14)	134.00
C(18)–H(18)•••F(11) [j]	0.93	2.51	3.254(13)	137.10
C(19)–H(19)•••F8) [j]	0.93	2.49	3.357(13)	154.30
C(20)–H(20)•••F(2) [g]	0.93	2.45	3.248(13)	143.60
$[AuCl(terpy)](PF_6)_2$				
C(1)–H(1)•••Cl(1)	0.93	2.75	3.331(13)	121.4
C(9)–H(9)•••F(8) [k]	0.93	2.47	3.310(13)	151.0
C(14)–H(14)•••F(4) [d]	0.93	2.49	3.251(11)	140.0
C(15)–H(15)•••Cl(1)	0.93	2.83	3.382(14)	119.2

Symmetry codes: (a) = -1/2+x,1/2-y,1/2+z; (b) = 1/2+x,1/2-y,1/2+z; (c) = 1+x,y,z; (d) = 1-x,1-y,1-z; (e) = 1/2+x,y,1/2-z; (f) = 1/2-x,-1/2+y,z; (g) = -1/2+x,y,1/2-z; (h) = -x,1/2+y,1/2-z; (i) = 1/2-x,1/2+y,z; (j) = -1/2+x,1/2-y; (k) = -1+x,y,z;

Table S5. Crystal data and structure refinement for $[AuCl(terpy)](PF_6)_2$.

$[AuCl(terpy)](PF_6)_2$	
Empirical formula	$C_{15}H_{11}AuClF_{12}N_3P_2$
Formula weight	755.62
Temperature [K]	295.0(2)
Wavelength [Å]	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions [Å,°]	a =7.6686(5) b = 8.4908(6) c = 17.6734(10) α = 92.649(5) β = 95.322(5) γ = 112.313(7)
Volume [$Å^3$]	1055.86(13)
Z	2
Density (calculated) [Mg/m^3]	2.377
Absorption coefficient [mm^{-1}]	7.360
F(000)	712
Crystal size [mm]	0.16×0.042×0.025
θ range for data collection [°]	3.309 to 25.048
Index ranges	-6≤ h ≤9 -10≤ k ≤10 -21≤ l≤20
Reflections collected	9141
Independent reflections	3717 (R_{int} = 0.0600)
Completeness to 2theta	99.7%
Min. and max. transm.	0.60729 and 1.000
Data / restraints / parameters	3717 / 0 / 307
Goodness-of-fit on F^2	1.018
Final R indices [I>2σ(I)]	R1 = 0.0602 wR2 = 0.1340
R indices (all data)	R1 = 0.0807 wR2 = 0.1432
Largest diff. peak and hole [e $Å^{-3}$]	2.21 and -1.76

Table S6. The bond lengths [Å] and angles [°] for $[AuCl(terpy)](PF_6)_2$

Bond lengths	
Au(1)–N(1)	2.032(9)
Au(1)–N(2)	1.935(9)
Au(1)–N(3)	2.014(9)
Au(1)–Cl(1)	2.253(3)
Bond angles	
N(1)–Au(1)–N(2)	81.9(4)
N(2)–Au(1)–N(3)	81.0(4)
N(1)–Au(1)–N(3)	162.7(4)
Cl(1)–Au(1)–N(1)	98.1(3)
Cl(1)–Au(1)–N(2)	178.1(3)
Cl(1)–Au(1)–N(3)	99.1(3)
C(1)–N(1)–C(5)	122.3(10)
C(6)–N(2)–C(10)	124.2(10)
C(11)–N(3)–C(15)	120.9(10)

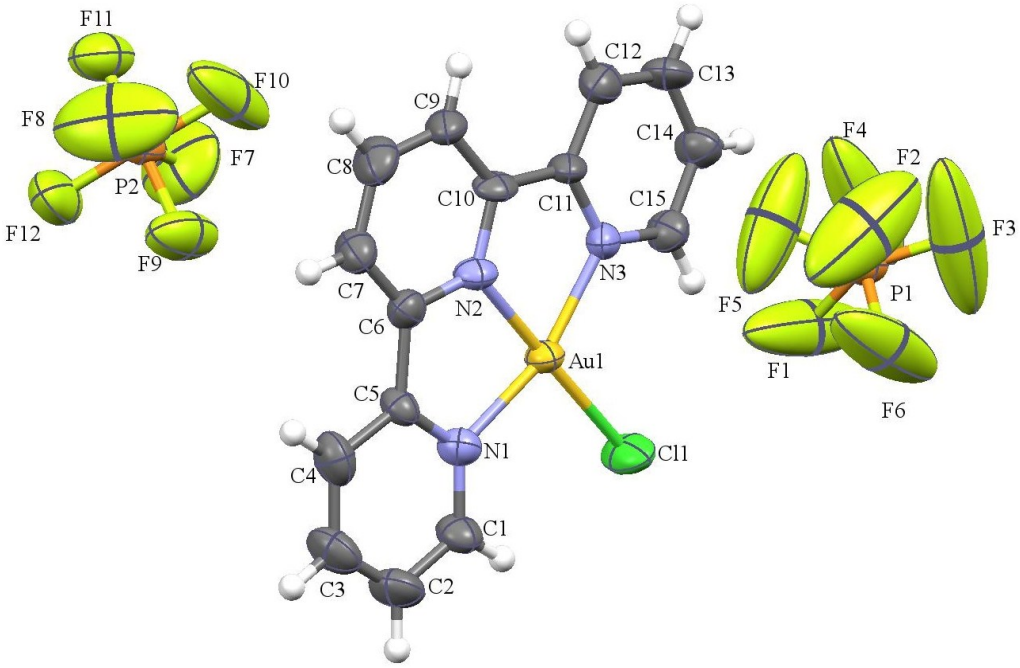


Figure S8. Molecular structure of [AuCl(terpy)]$(PF_6)_2$ together with the atom numbering. Displacement ellipsoids are drawn at 50% probability level.

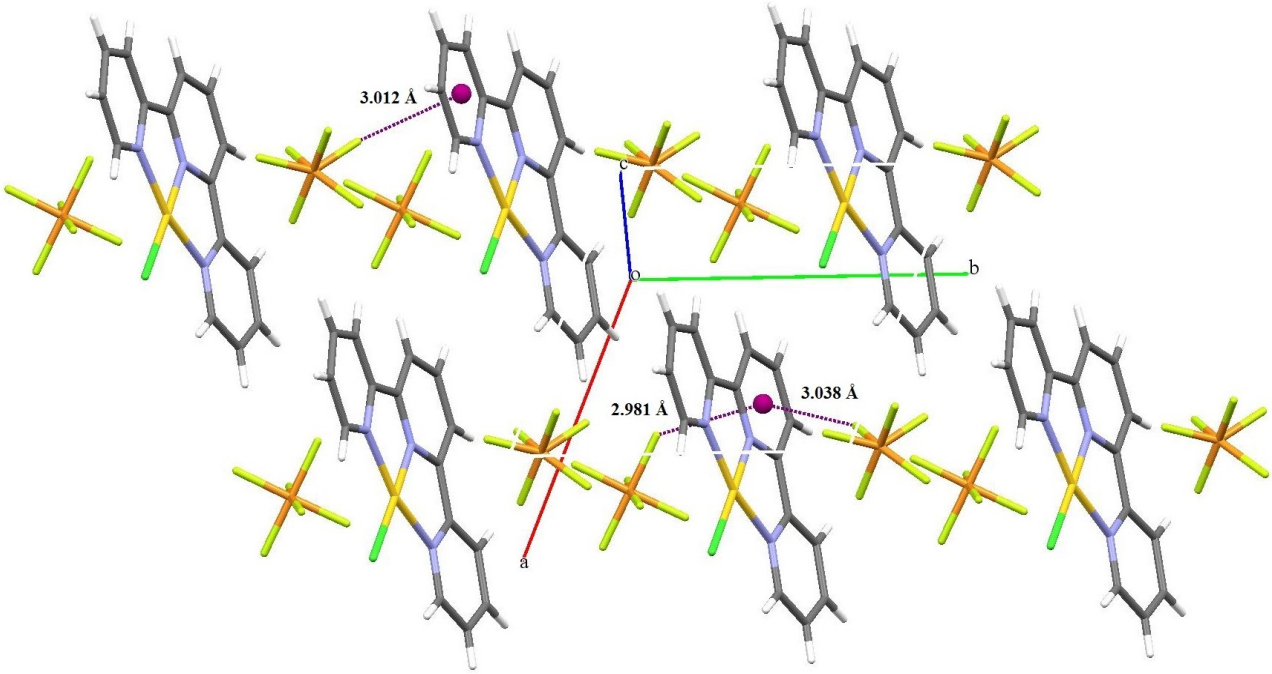


Figure S9. View of the supramolecular packing of [AuCl(terpy)]$(PF_6)_2$ arising from weak F•••π type interactions.

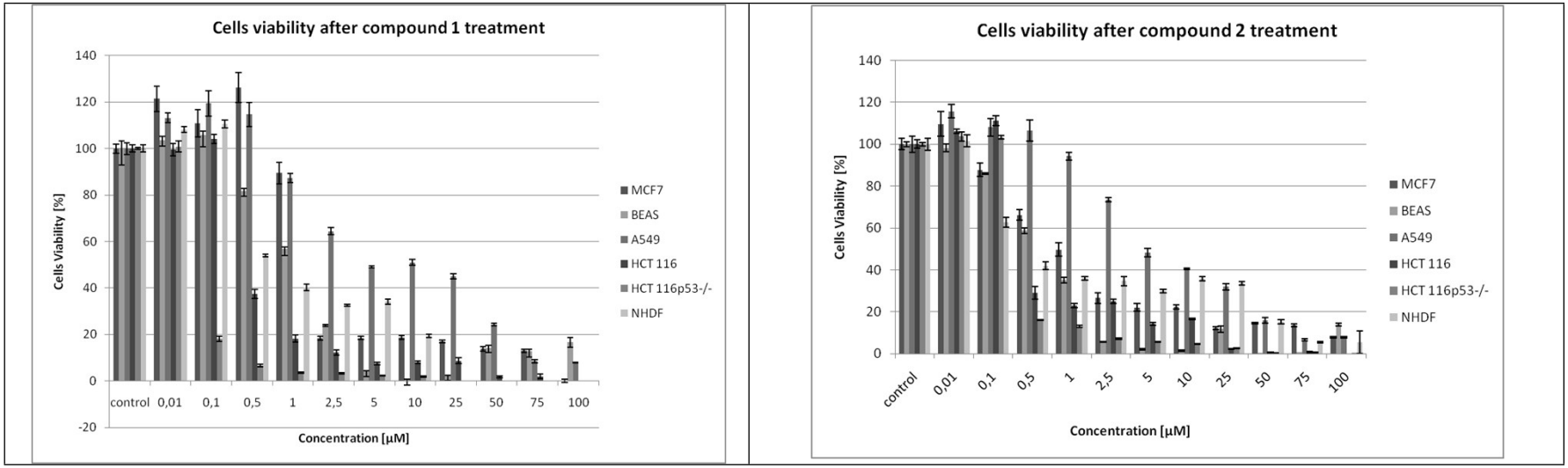


Figure S10. Cells viability after compounds **1** and **2** treatment

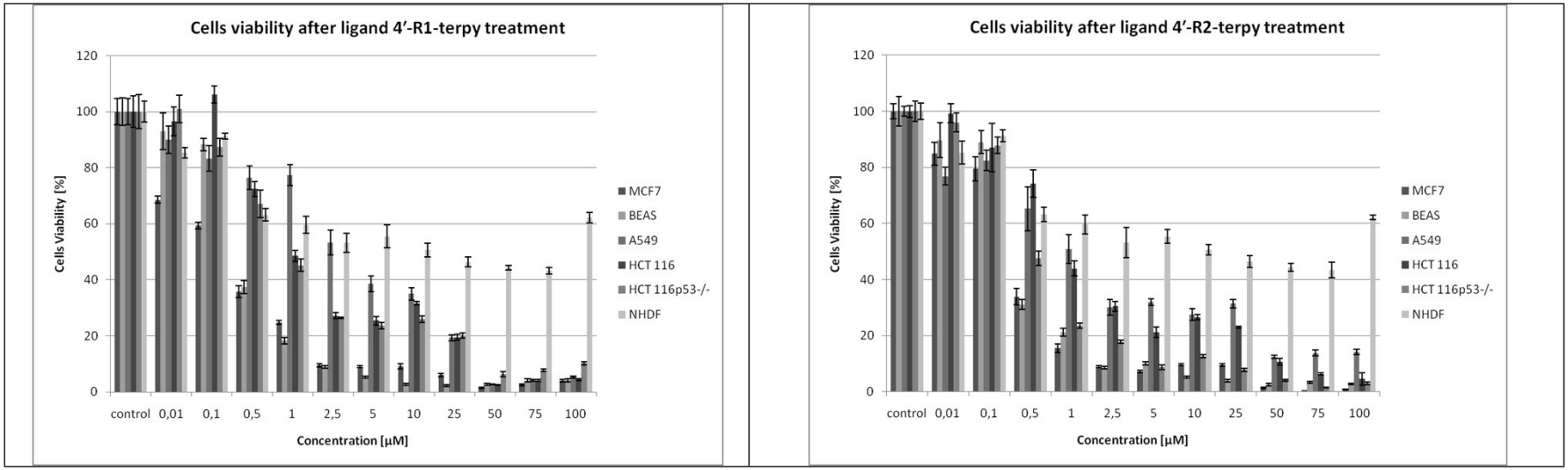


Figure S11. Cells viability after ligands 4'-R^1-terpy and 4'-R^2-terpy treatment

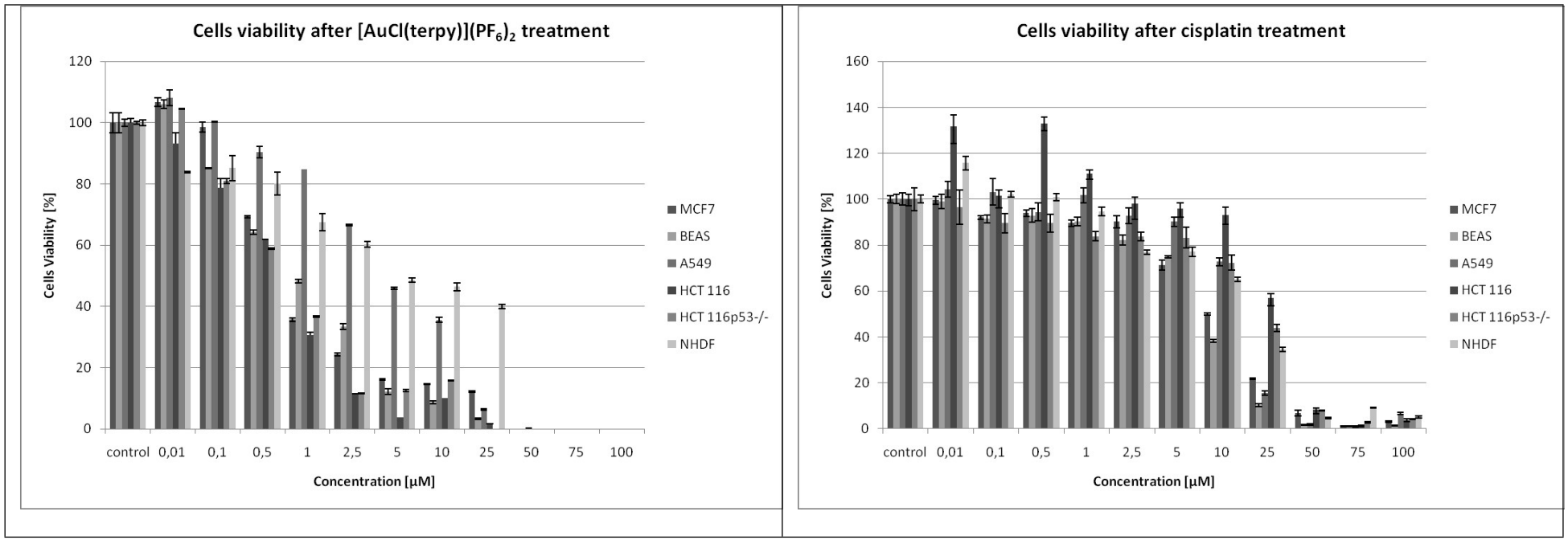
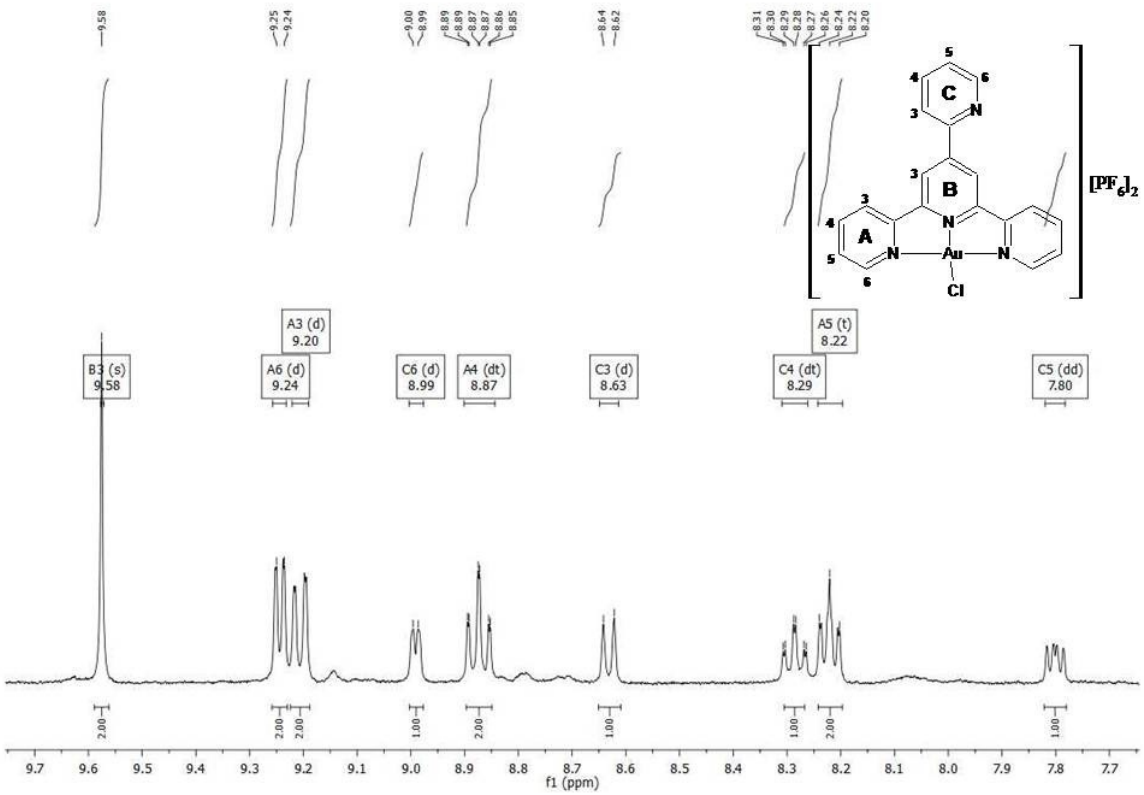
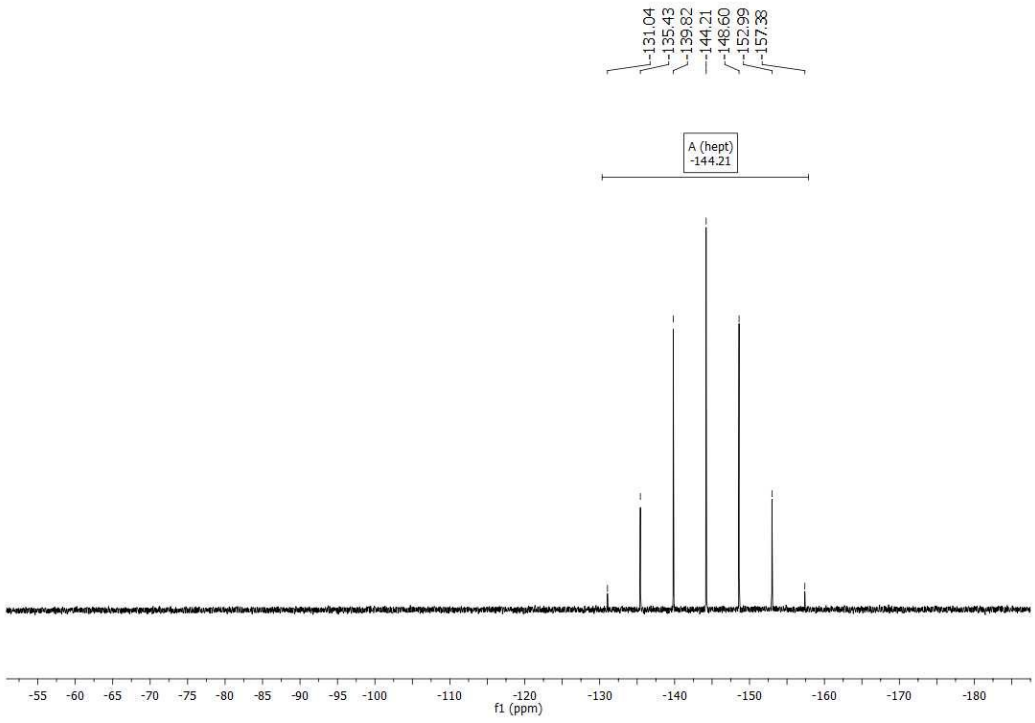


Figure S12. Cells viability after [AuCl(terpy)]$(PF_6)_2$ and cisplatin treatment



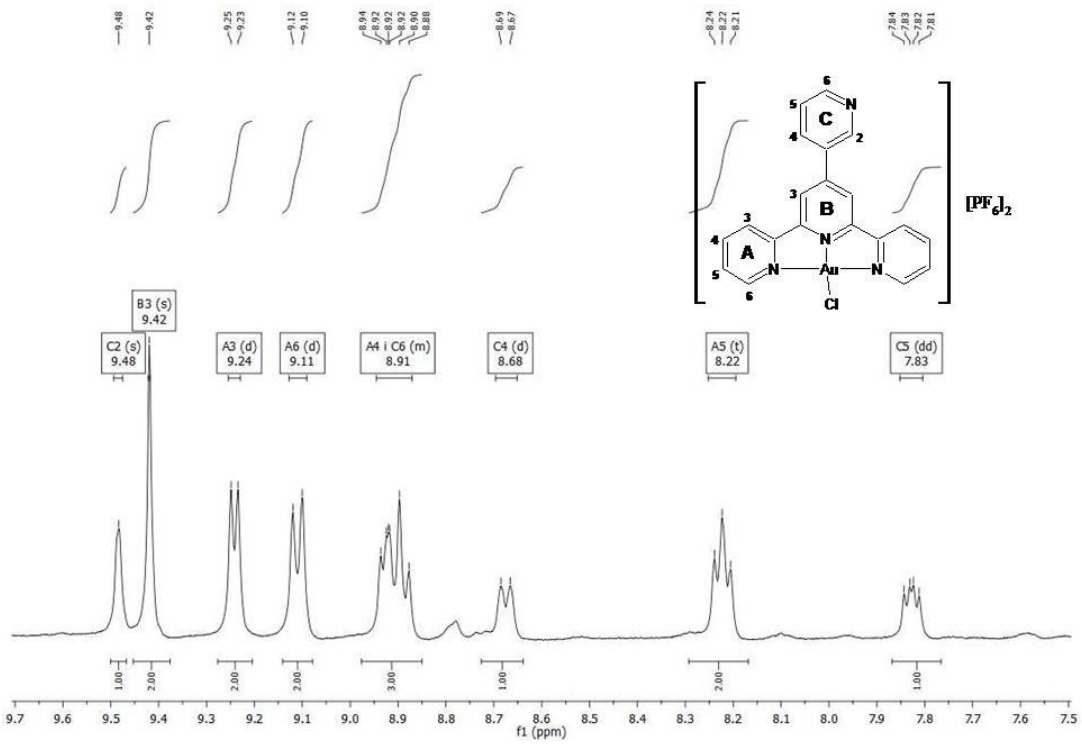
(a)



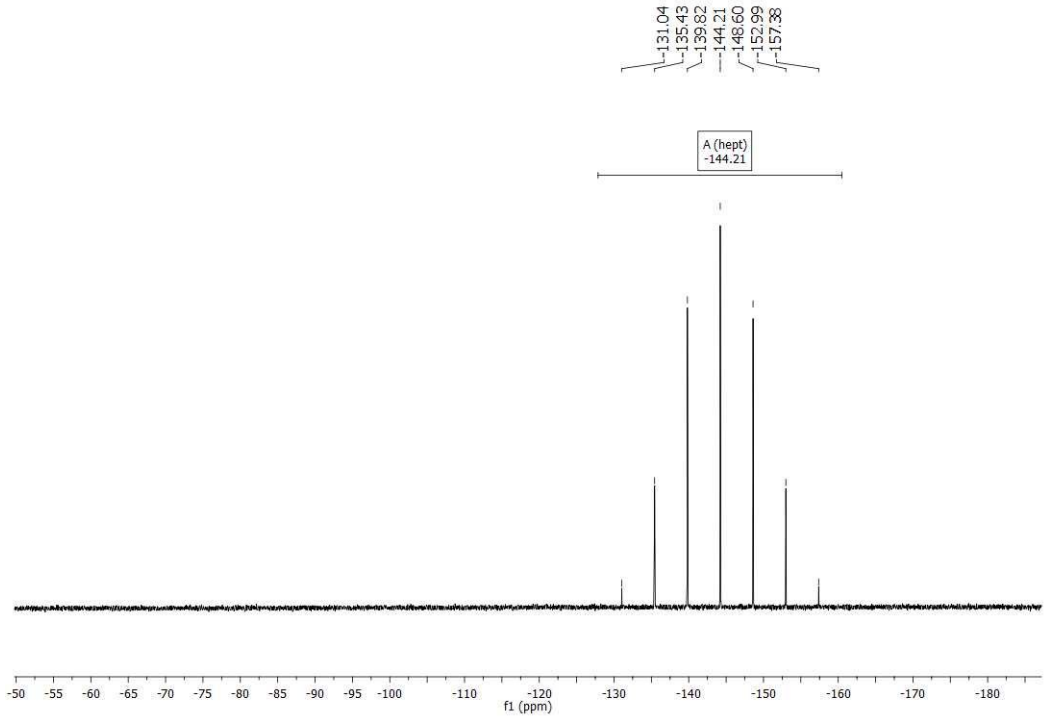
(b)

Figure S13. (a) ^{1}H (400 MHz, DMSO-d_6) and (b) ^{31}P (162 MHz, DMSO-d_6) NMR spectra of **1.** The assignment has been made on the basis of the literature data for the related complexes $[Au(terpy)C1]^{2+}$ [1, 4], $[AuCl(\mathbf{S\text{-}8})](O_3SCF_3)_2$ [2] (**S-8** = 4′-methylsulfanyl-2,2′:6′,2″-terpyridine), $[Au(C_6F_5)(\eta^3\text{-terpy})](PF_6)_2$ [9] as well as ^{1}H NMR spectra of the free ligands [10, 11] were taken into consideration.

Presence of the low intensity signals in ^{1}H NMR are due to instability of **1** in DMSO (evidenced by Uv-Vis monitoring)

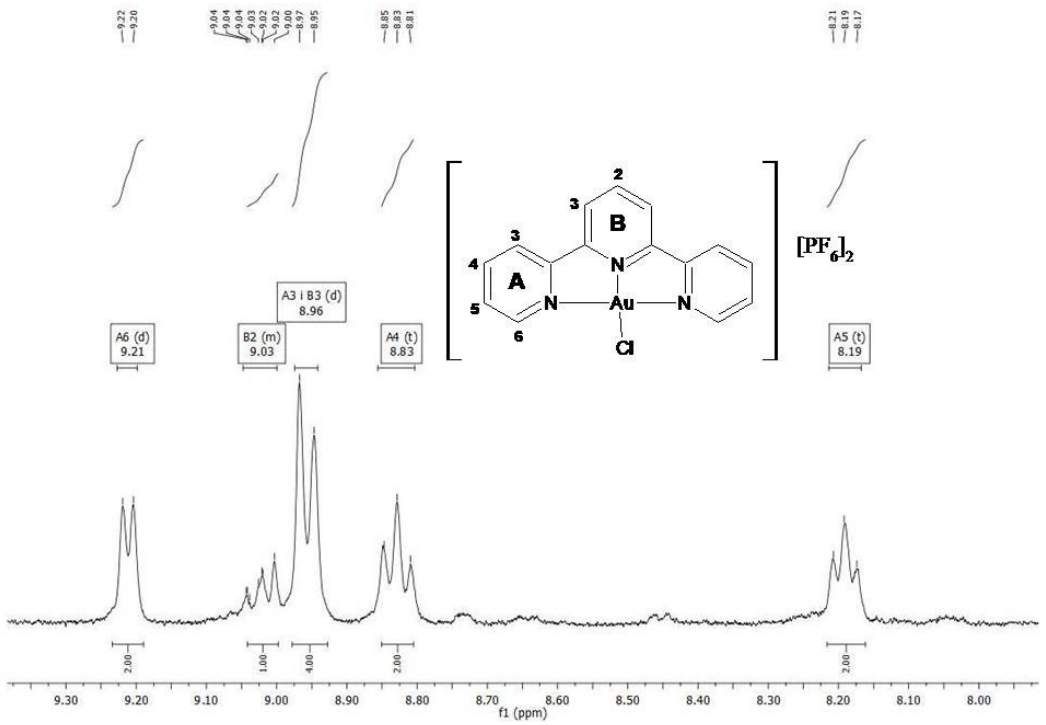


(a)

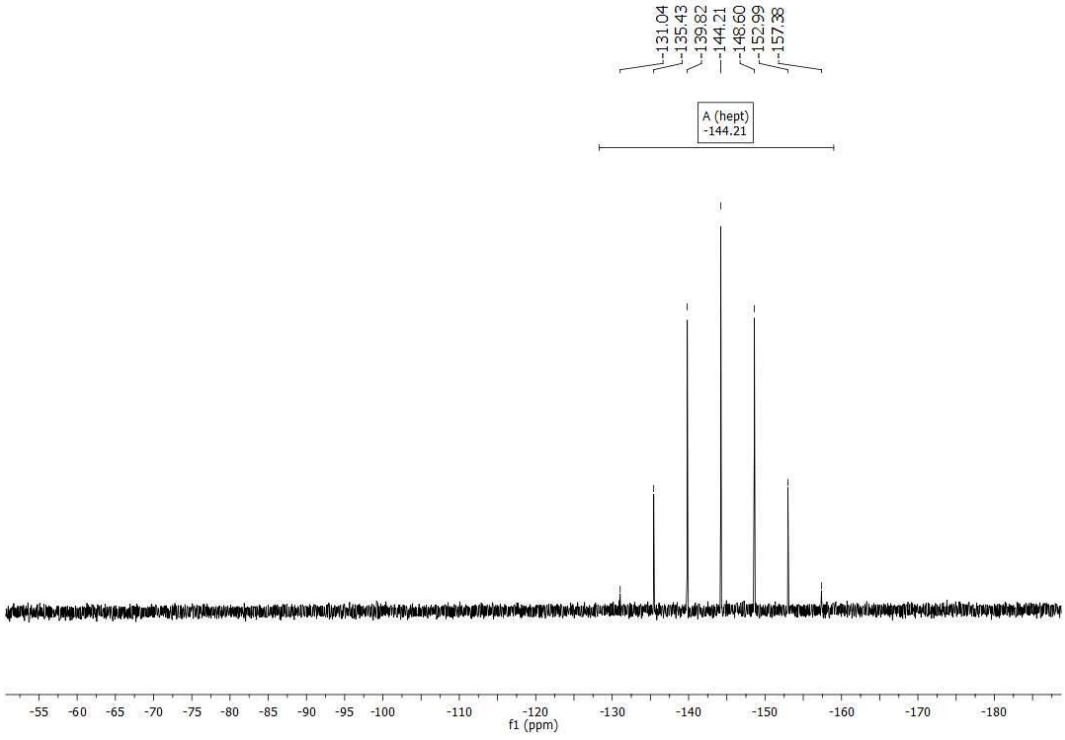


(b)

Figure S14. (a) ^{1}H (400 MHz, DMSO-d_6) and (b) ^{31}P (162 MHz, DMSO-d_6) NMR spectra of **2.** The assignment has been based on the literature data for the related complexes [Au(terpy)C1]$^{2+}$ [1, 4], [AuCl(**S-8**)]$(O_3SCF_3)_2$ [2] (**S-8** = 4′-methylsulfanyl-2,2′:6′,2′′-terpyridine), [Au(C_6F_5)(η^3-terpy)]$(PF_6)_2$ [9] as well as ^{1}H NMR spectra of the free ligands [10, 11] were taken into consideration.
Presence of the low intensity signals in ^{1}H NMR are due to instability of **2** in DMSO (evidenced by Uv-Vis monitoring)



(a)



(b)

Figure S15. (a) ^{1}H (a) (400 MHz, DMSO-d_6) and (b) ^{31}P (162 MHz, DMSO-d_6) NMR spectra of [AuCl(terpy)]$(PF_6)_2$. The assignment has been made on the basis of the literature data for the related complexes $[Au(terpy)C1]^{2+}$ [1, 4], [AuCl(**S-8**)]$(O_3SCF_3)_2$ [2] (**S-8** = 4′-methylsulfanyl-2,2′:6′,2″-terpyridine), $[Au(C_6F_5)(\eta^3\text{-terpy})](PF_6)_2$ [9] as well as ^{1}H NMR spectra of the free ligands [10, 11] were taken into consideration.
Presence of the low intensity signals in ^{1}H NMR are due to instability of [AuCl(terpy)]$(PF_6)_2$ in DMSO-d_6 (evidenced by Uv-Vis monitoring)

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