Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary Information

Luminescent iminophosphorane gold, palladium and platinum complexes as potential anticancer agents‡

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Contents:

1. Crystallographic Data for Compounds 3 and 4

Single crystals of **3a** and **3d** (see details below) were mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Kappa CCD diffractometer using graphite monochromated Mo-Ka radiation (l=0.71073 Å). Space group assignments were based on systematic absences, E statistics and successful refinement of the structures. The structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 6.1 software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the crystallographic data are given in Table S1 (below). These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. (CCDC 977990 for compound **3**, and 977991 for compound **4**).

3: Crystals of **3** (purple prisms with approximate dimensions 0.25 x 0.23 x 0.23mm) were obtained from a solution of **3** in CH_3CN by slow diffusion of Et_2O at RT. **4**: Crystals of **4** (orange prisms with approximate dimensions 0.25 x 0.24 x 0.22mm) were obtained from a solution of **4** in CH_2Cl_2 by slow diffusion of Et_2O at RT.

Table S1. Crystal Data and Structure Refinement for Complexes **3** and **4**.

Compound	**3**	**4**
formula	$C_{27}H_{20}Cl_2N_2PAu.\ CH_3COCH_3.\ ClO_4^-$	$C_{27}H_{21}Cl_2N_2PPd.3CHCl_3$
fw	828.81	939.83
T [K]	293(2)	293(2)
λ ($Mo_{K\alpha}$)[Å]	0.71073	0.71073
crystal system	Triclinic	Orthorombic
space group	P-1	P2(1)2(1)2(1)
a [Å]	7.894(5)	19.497(4)
b [Å]	15.290(5)	10.517(2)
c [Å]	25.892(5)	18.232(4)
α [°]	90.028(5)	90
β [°]	90.039(5)	90
γ [°]	90.581(5)	90
V [Å]^3	3125(2)	3738.5(13)
Z	4	4
D_{calcd} (g cm^{-3})	1.762	1.670
μ (mm^{-1})	5.057	1.351
GOF	1.053	1.060
R_1[$I>2\sigma$]	0.0512	0.0483
wR_2(all data)	0.1509	0.1343

2. Luminescence Studies for Ligand **1** and compounds **2**-**7**

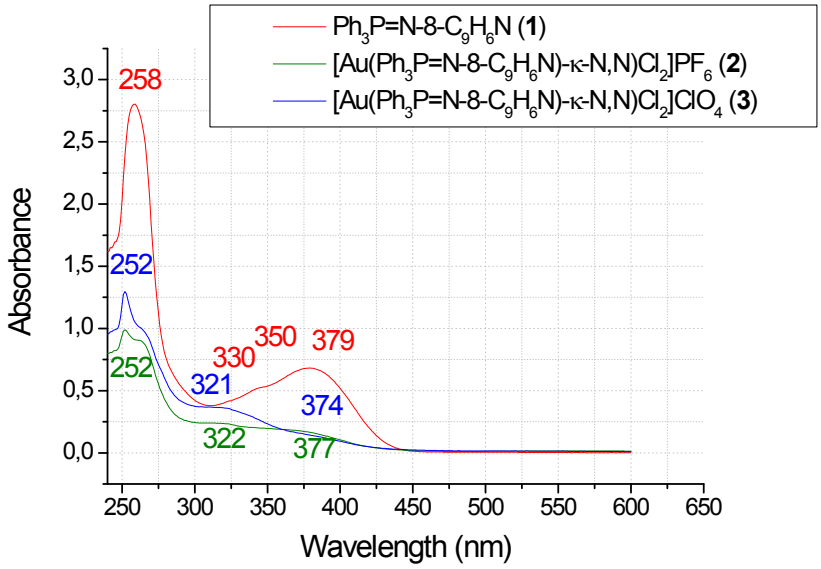

Figure S1. Absorption spectra of ligand **1** and gold compounds **2** and **3** in DMSO solution (5 x 10^{-4} M) at RT.

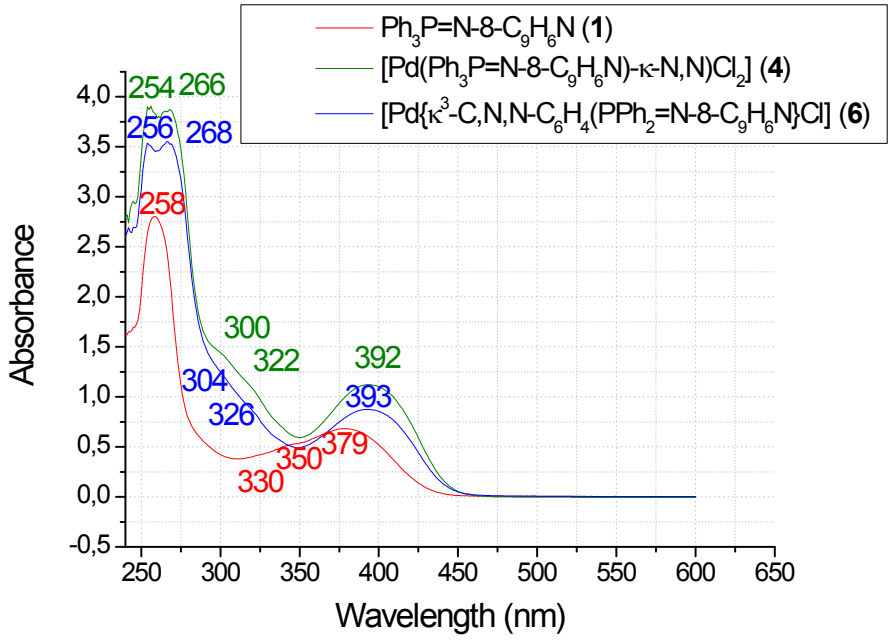

Figure S2. Absorption spectra of ligand **1** and palladium compounds **4** and **6** in DMSO solution (5 x 10^{-4} M) at RT.

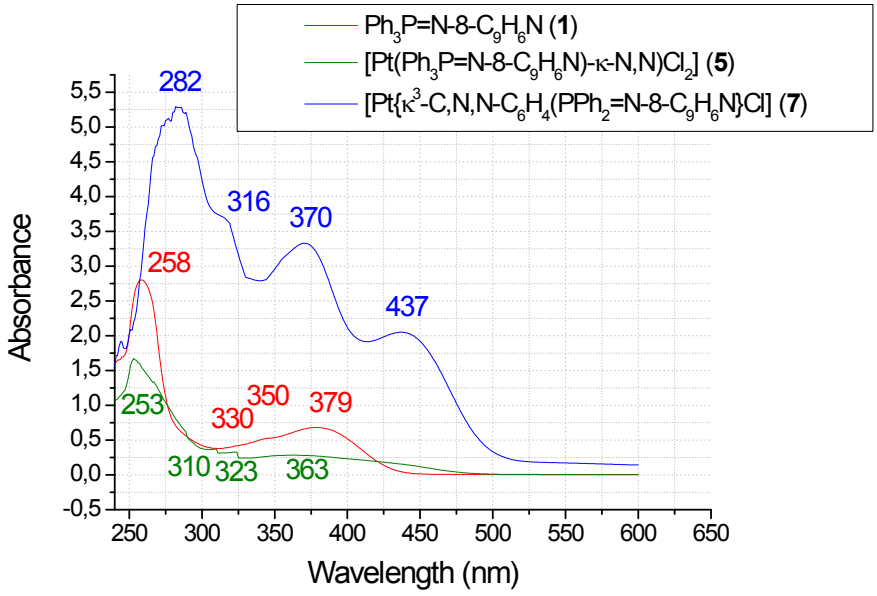

Figure S3. Absorption spectra of ligand **1** and platinum compounds **5** and **7** in DMSO solution (5 x 10^{-4} M) at RT.

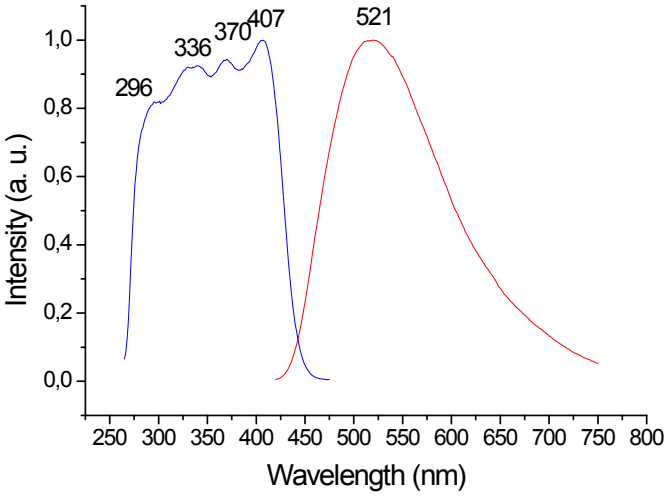

Figure S4. Excitation (blue) and emission (red) spectra of compound **1** in DMSO solution (5 x 10^{-4} M) at RT.

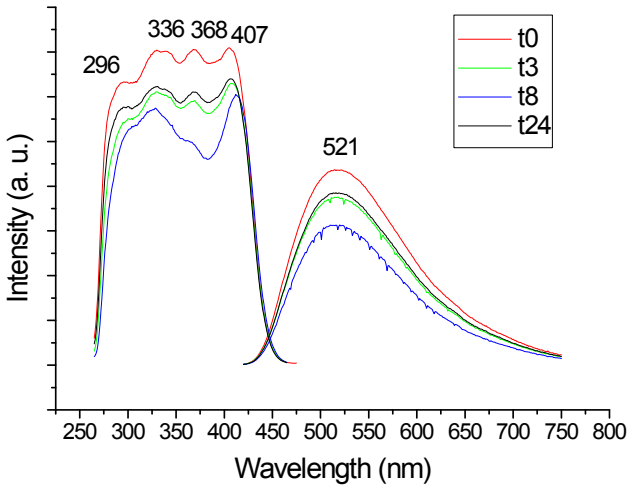

Figure S5. Luminescence of compound **1** in DMSO solution (5 x 10^{-4} M) at RT over time (24 h)

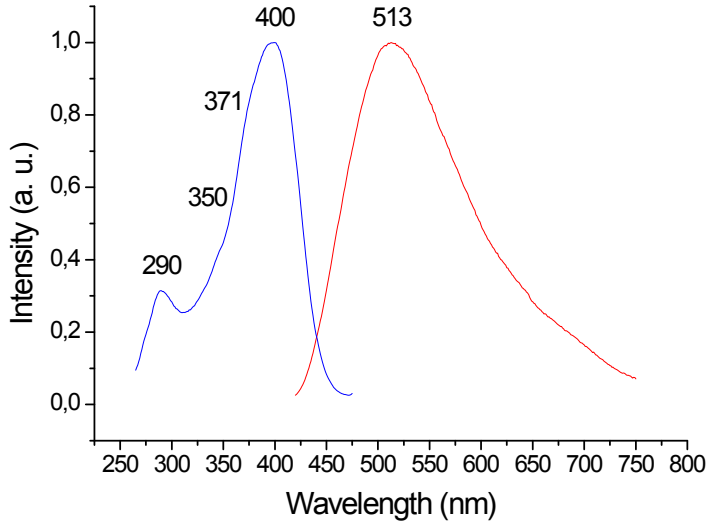

Figure S6. Excitation (blue) and emission (red) spectra of compound **2** in DMSO solution (5 x 10^{-4} M) at RT.

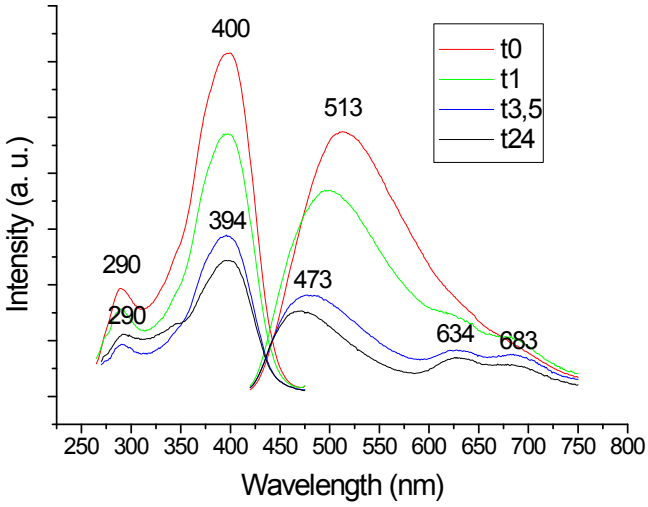

Figure S7. Luminescence of compound **2** in DMSO solution (5 x 10^{-4} M) at RT over time (24 h).

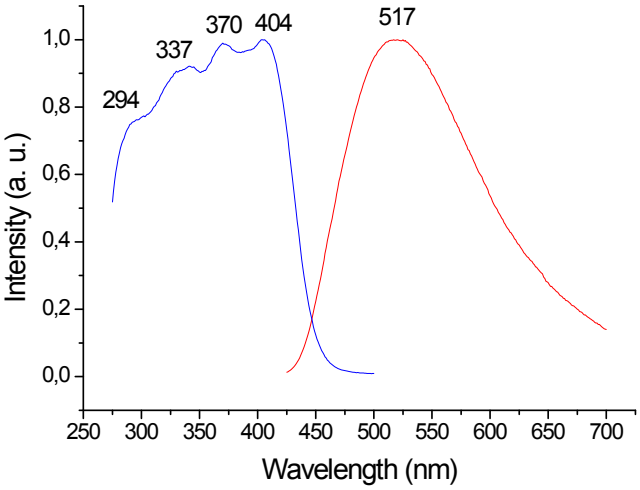

Figure S8. Excitation (blue) and emission (red) spectra of compound **3** in DMSO solution (5 x 10^{-4} M) at RT.

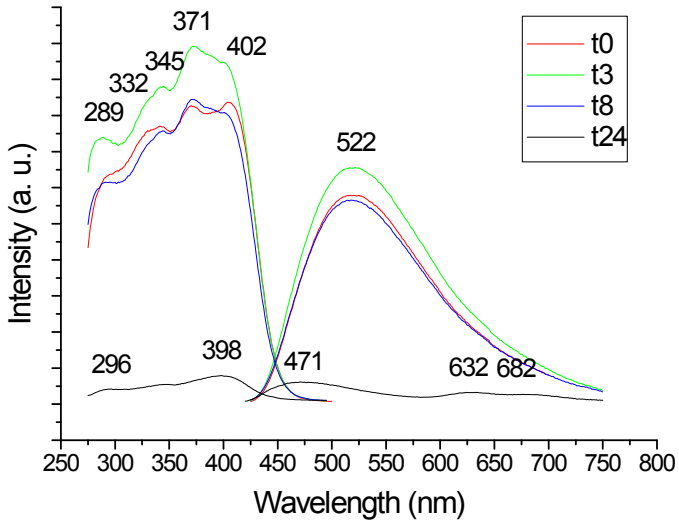

Figure S9. Luminescence of compound **3** in DMSO solution (5 x 10^{-4} M) at RT over time (24 h).

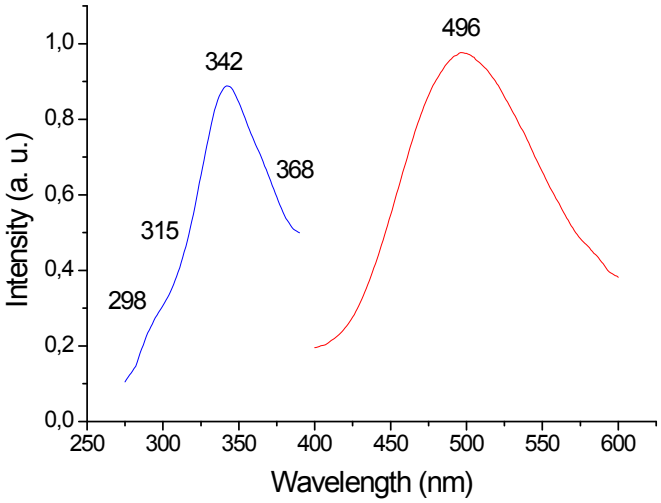

Figure S10. Excitation (blue) and emission (red) spectra of compound **4** in DMSO solution (5 x 10^{-4} M) at RT.

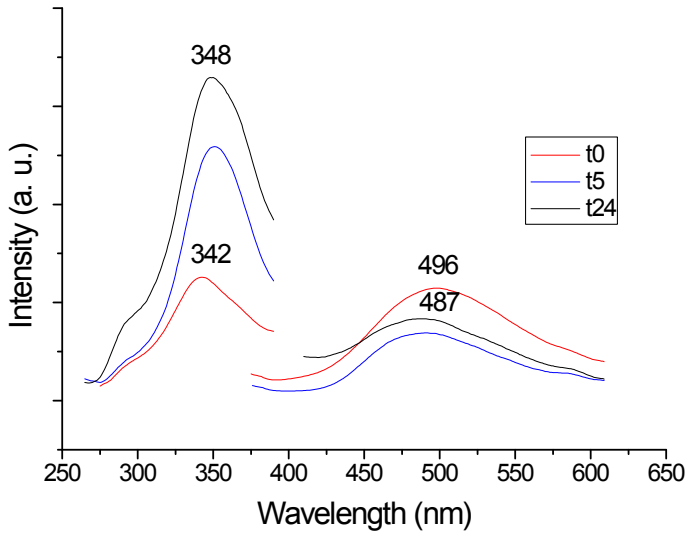

Figure S11. Luminescence of compound **4** in DMSO solution (5 x 10^{-4} M) at RT over time (24 h).

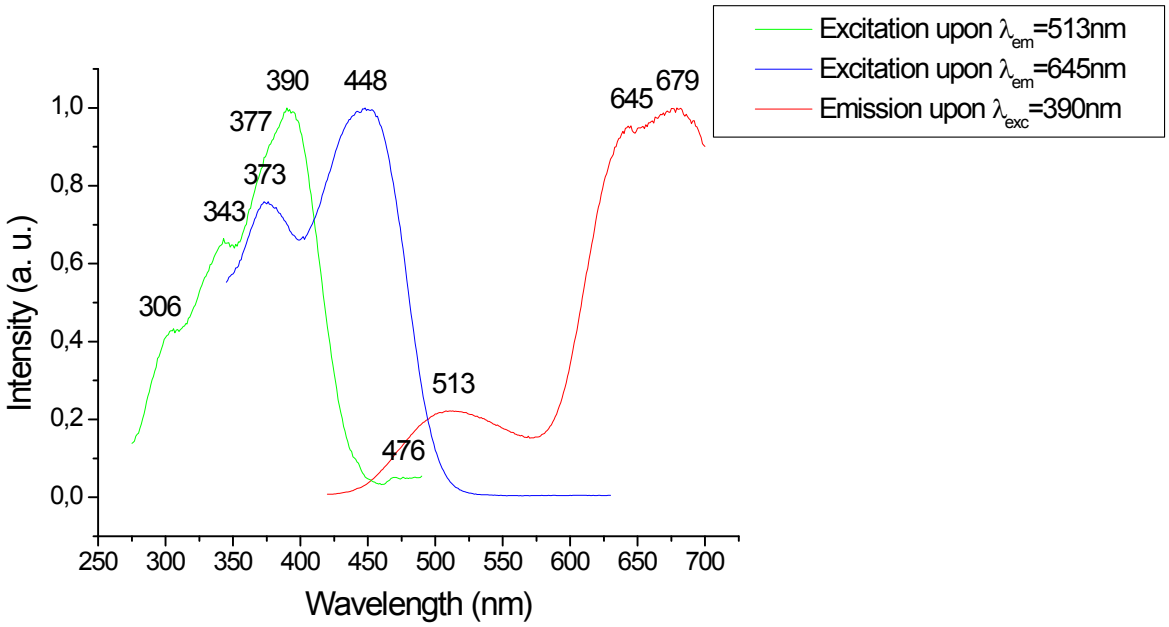

Figure S12. Excitation (blue and green) and emission (red) spectra of compound **5** in DMSO solution (5 x 10^{-4} M) at RT.

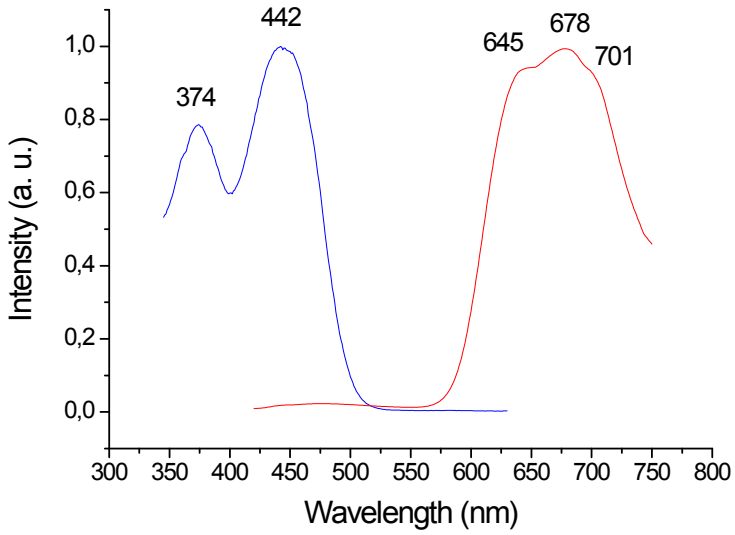

Figure S13. Excitation (blue) and emission (red) spectra of compound **5** in DMSO solution (5 x 10^{-4} M) at RT immediately after the first measurement of luminescence.

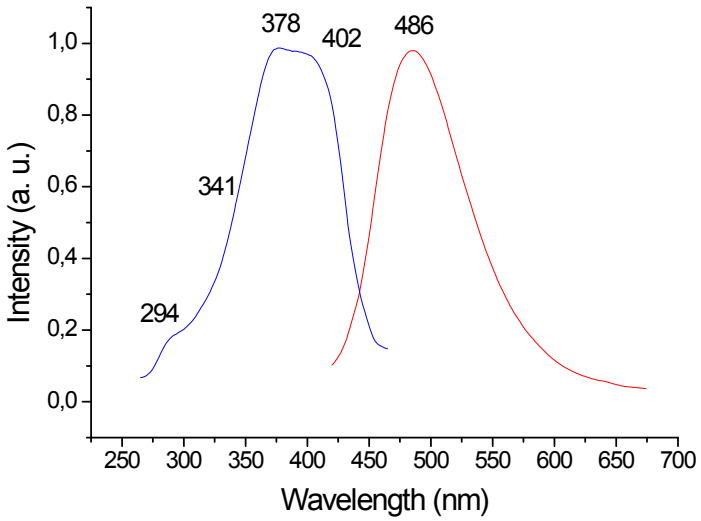

Figure S14. Excitation (blue) and emission (red) spectra of compound **6** in DMSO solution (5 x 10^{-4} M) at RT.

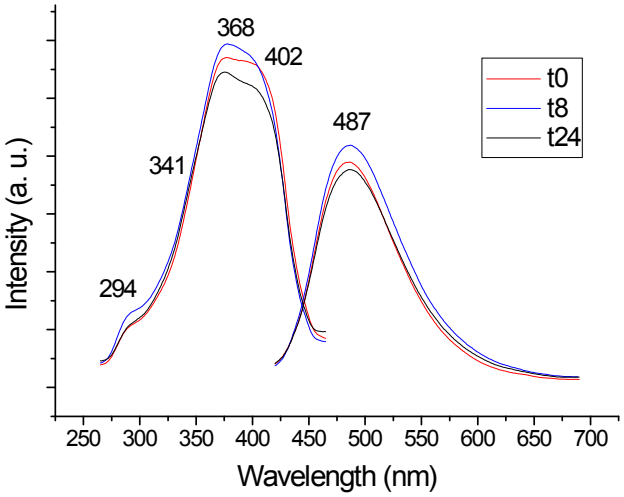

Figure S15. Luminescence of compound **6** in DMSO solution (5 x 10^{-4} M) at RT over time (24 h).

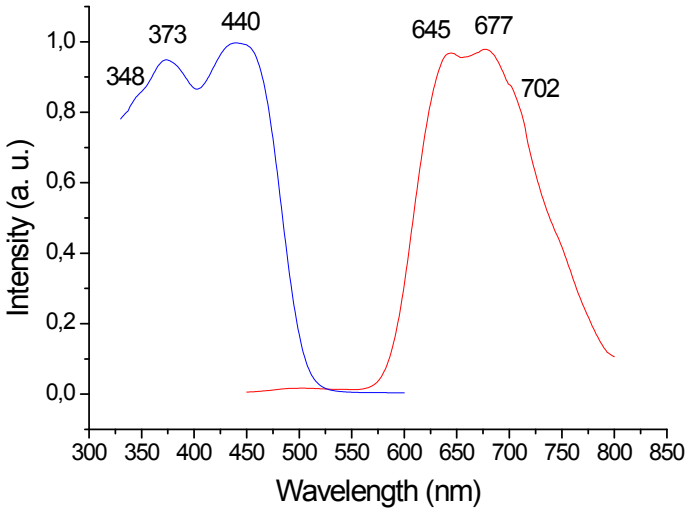

Figure S16. Excitation (blue) and emission (red) spectra of compound **7** in DMSO solution (5 x 10^{-4} M) at RT.

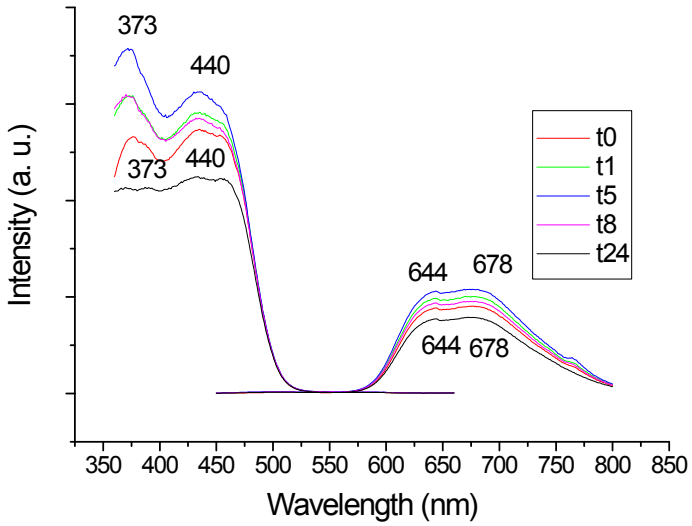

Figure S17. Luminescence of compound **7** in DMSO solution (5 x 10^{-4} M) at RT over time (24 h).

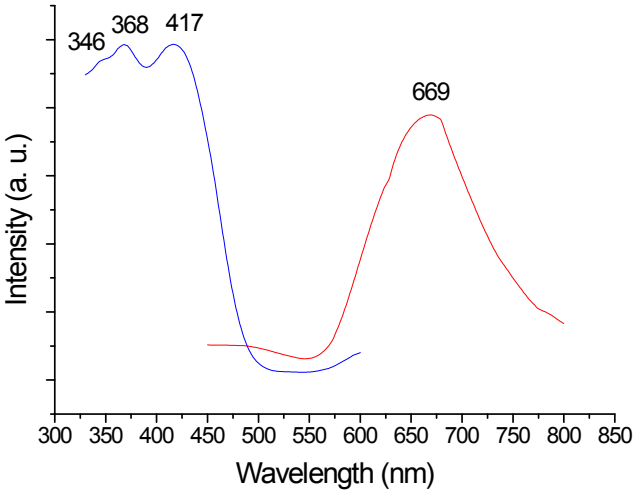

Figure S15. Excitation (blue) and emission (red) spectra of compound **7** in DMSO:H_2O (50:50) solution (5 x 10^{-4} M) at RT.

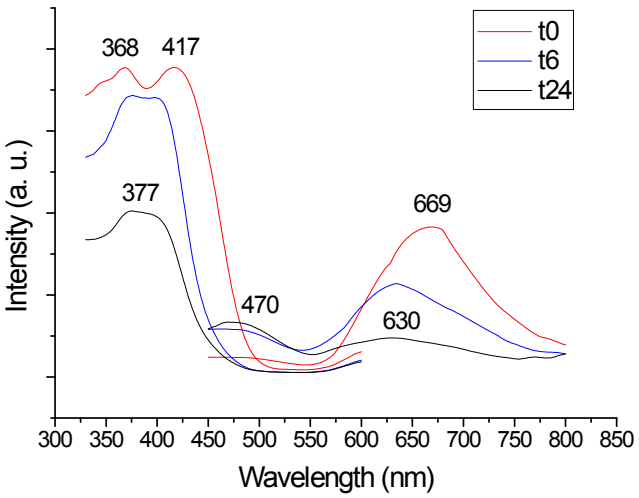

Figure S16. Luminescence of compound **7** in DMSO:H_2O (50:50) solution (5 x 10^{-4} M) at RT over time (24h).

3. Stability of compounds **2**-**7** in d^6-DMSO solution overtime assessed by $^{31}P\{^1H\}$ NMR spectroscopy. Selected $^{31}P\{^1H\}$ NMR spectra for compounds **4** and **7**.

	d^6-DMSO						
	4 hr	1 day	2 days	4 days	1 week	2 weeks	Half life (50%)
2	53%	13%		0%			**4 h**
3	73%	31%		0%			**6 h**
4	4%	0%					**1.5 h**
5	41%	9%		9%	9%		**2 h**
6	>99%	>99%	>99%	>99%	>99%	>99%	**weeks**
7	>99%	>99%	>99%	>99%	>99%	>99%	**weeks**

% of decomposition of initial compound determined by integration of all the signals appearing in the $^{31}P\{^1H\}$ NMR spectra, the sum being set to 100%.

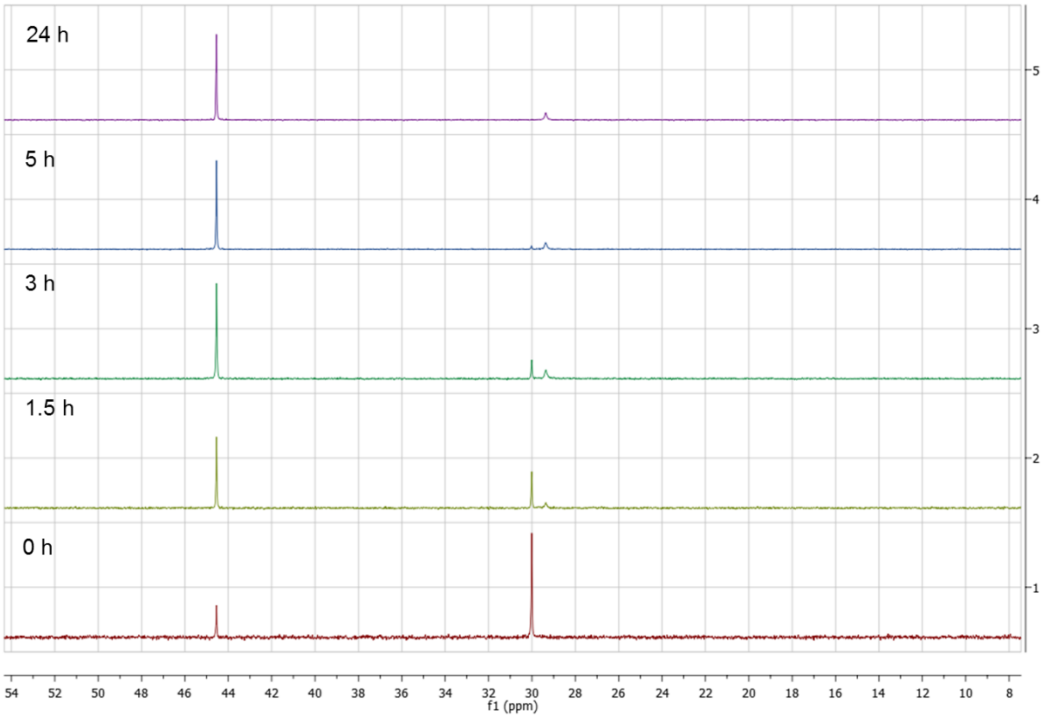

Figure S17. Conversion of coordination palladium compound [Pd((Ph$_3$P=N-8-C$_9$H$_6$N)-κ-N,N)Cl$_2$] **4** (δ = 30.0 ppm) into cyclometalated [Pd{κ^3-C,N,N-C$_6$H$_4$(PPh$_2$=N-8-C$_9$H$_6$N}Cl] **6** (δ = 44.6 ppm) in d^6-DMSO solution over time. Small peak at δ = 29.4 ppm corresponds to PPh$_3$=O.

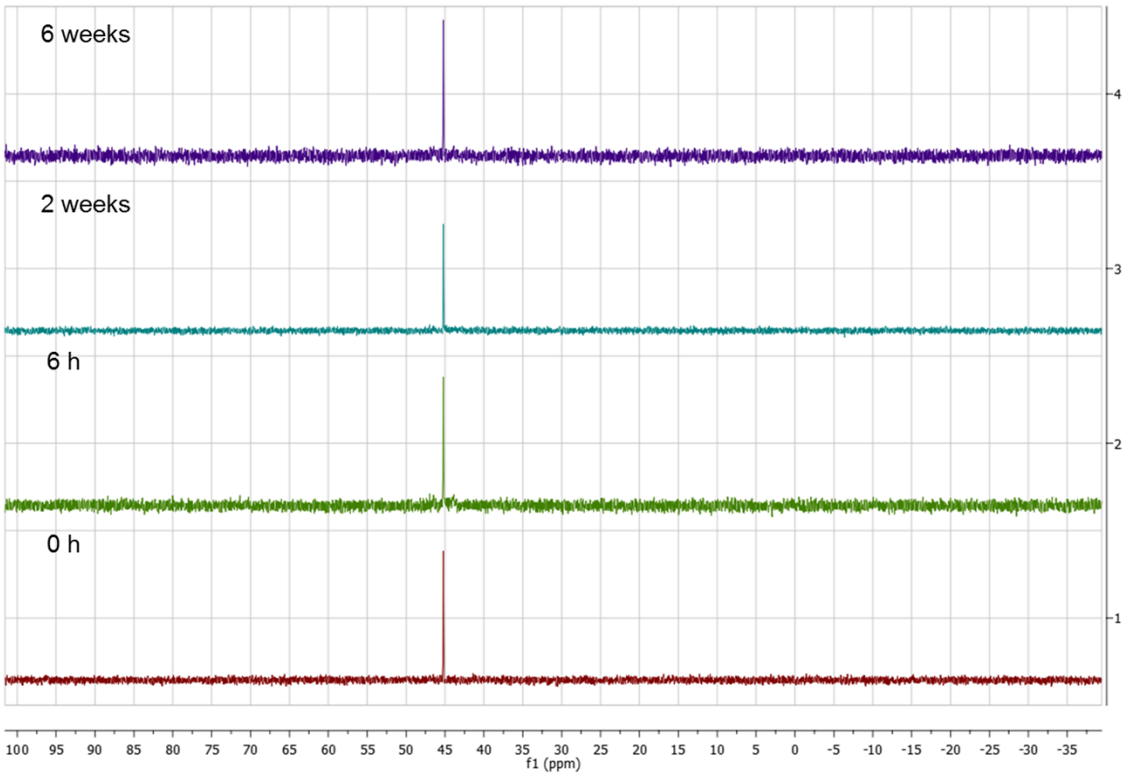

Figure S18. Study of the stability of cycloplatinated compound [Pt{κ^3-C,N,N-C_6H_4(PPh_2=N-8-C_9H_6N}Cl] **7** (δ = 45.2 ppm) by $^{31}P\{^1H\}$ NMR spectroscopy in d^6-DMSO solution over time.