A) Stability studies of the *trans*-[PtI_2(amine)(PPh_3)] in DMSO solution

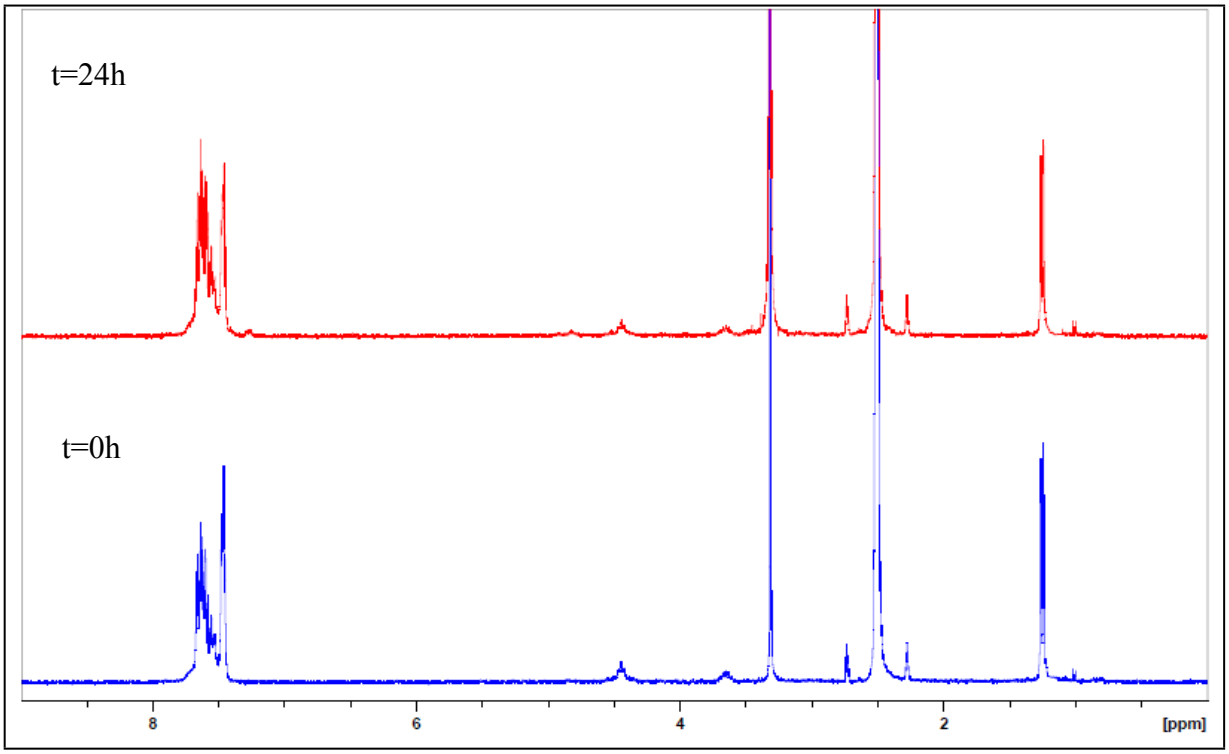

Figure SM-A1. NMR spectra of the complex *trans*-[PtI_2(ipa)(PPh_3)] at t: 0 and 24h.

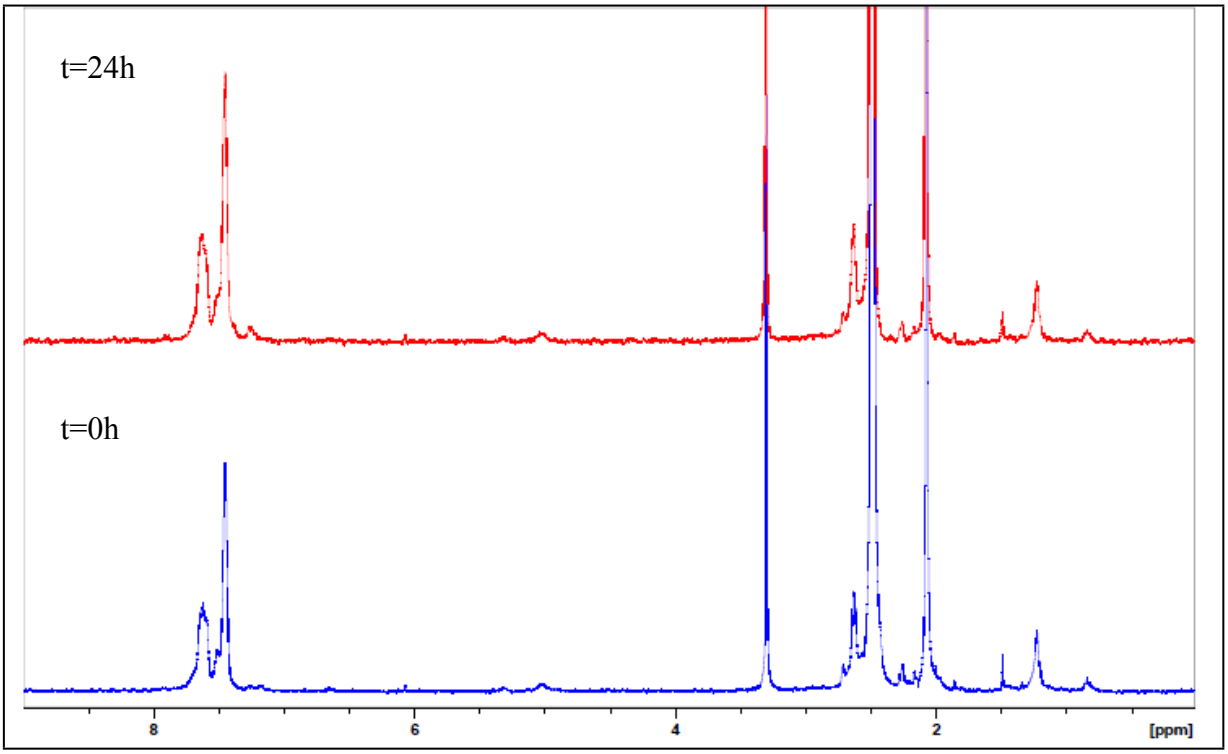

Figure SM-A2. NMR spectra of the complex *trans*-[PtI_2(dma)(PPh_3)] at t: 0 and 24h.

B) NMR studies of 9EtG and the most active complex: 1.

Experimental part of the binding studies of *trans*-[PtI_2(amine)(PPh_3)] with 9-EtG:

Samples of complex **1** were prepared by mixing 0.5 mL of complex solution (2 mg) in H_2O:Acetone-d_6 (1:2) with 9-EtG (1 mg) into a NMR tube. The temperature of the tube was maintained at 37 ºC with slight stirring during the entire experiment (24 hours). ^1H spectra were acquired at various times to monitor the reactivity.

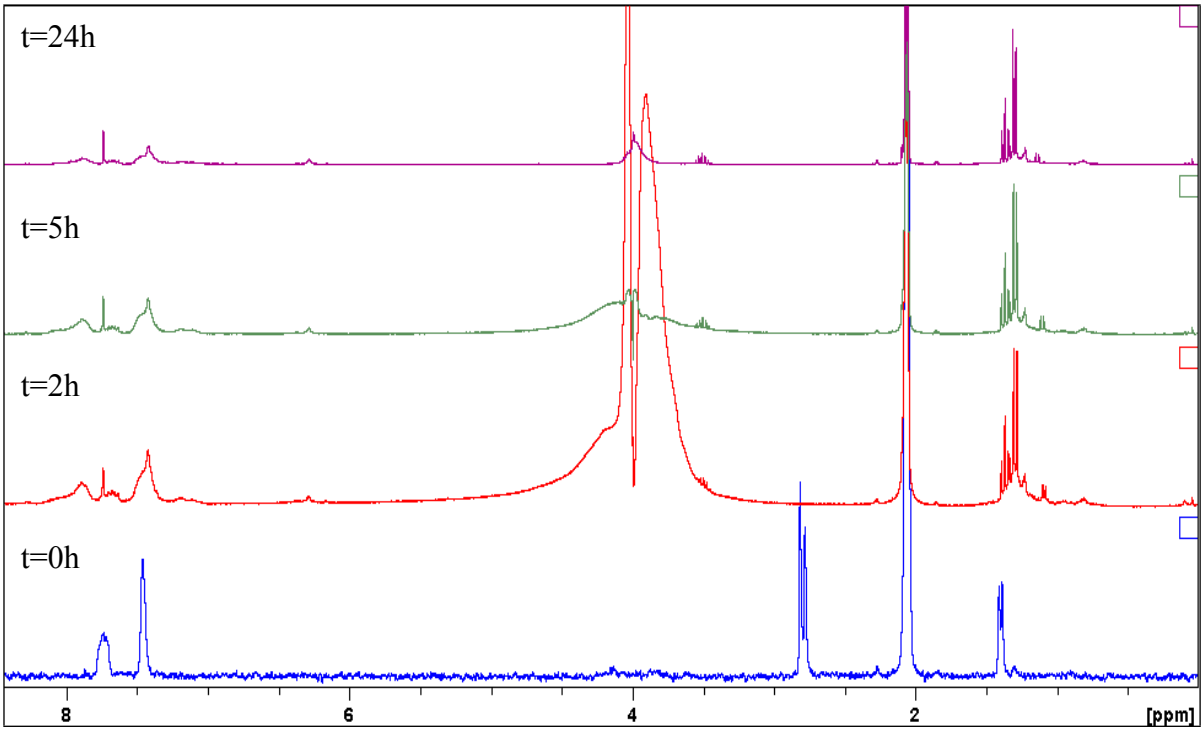

Figure SM-B1. NMR spectra of the complex *trans*-[PtI_2(ipa)(PPh_3)] at t: 0 and its monitoring reaction with 9EtG at t:2h, 5h and 24h.

C) Single crystal data from *trans*-[PtI_2(ipa)(PPh_3)]:

A light orange prismatic-like specimen of $C_{21}H_{24}I_2NPPt$, approximate dimensions 0.10 mm x 0.19 mm x 0.22 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.A total of 4079 frames were collected in a Bruker Kappa Apex II difractometer using graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) and operating at 50 kV and 30 mA. The total exposure time was 11.33 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 51025 reflections to a maximum θ angle of 28.35° (0.75 Å resolution), of which 5847 were independent (average redundancy 8.727, completeness = 99.1%, R_{int} = 4.00%, R_{sig} = 2.28%) and 4953 (84.71%) were greater than $2\sigma(F^2)$. The final cell constants of *a* = 9.5189(7) Å, *b* = 10.9327(10) Å, *c* = 11.5197(10) Å, α = 84.048(4)°, β = 81.976(4)°, γ = 86.335(4)°, volume = 1179.20(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9235 reflections above 20 σ(I) with 4.935° < 2θ < 55.65°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of

minimum to maximum apparent transmission was 0.644. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2523 and 0.4787. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{21}H_{24}I_2NPPt$. The final anisotropic full-matrix least-squares refinement on F^2 with 237 variables converged at R_1 = 2.81%, for the observed data and wR_2 = 11.29% for all data. The goodness-of-fit was 1.000. The largest peak in the final difference electron density synthesis was 1.103 $e^-/Å^3$ and the largest hole was -1.964 $e^-/Å^3$ with an RMS deviation of 0.414 $e^-/Å^3$. On the basis of the final model, the calculated density was 2.169 g/cm^3 and F(000), 712 e^-.

Table SM-C1. Sample and crystal data for *trans*-[PtI_2(ipa)(PPh_3)].

Chemical formula	$C_{21}H_{24}I_2NPPt$	
Formula weight	770.27	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.10 x 0.19 x 0.22 mm	
Crystal habit	light orange prismatic	
Crystal system	triclinic	
Space group	*P* -1	
Unit cell dimensions	*a* = 9.5189(7) Å	α = 84.048(4)°
	b = 10.9327(10) Å	β = 81.976(4)°
	c = 11.5197(10) Å	γ = 86.335(4)°
Volume	1179.20(17) Å^3	
Z	2	
Density (calculated)	2.169 Mg/cm^3	
Absorption coefficient	8.641 mm^{-1}	
F(000)	712	

Table SM-A2. Data collection and structure refinement for *trans*-[PtI_2(ipa)(PPh_3)].

Theta range for data collection	1.79 to 28.35°	
Index ranges	-12<=h<=12, -14<=k<=14, -15<=l<=15	
Reflections collected	51025	
Independent reflections	5847 [R(int) = 0.0400]	
Coverage of independent reflections	99.1%	
Absorption correction	multi-scan	
Max. and min. transmission	0.4787 and 0.2523	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5847 / 0 / 237	
Goodness-of-fit on F^2	1.000	
Δ/σ_{max}	0.001	
Final R indices	4953 data; I>2σ(I)	R_1 = 0.0281, wR_2 = 0.0924

	all data $R_1 = 0.0394$, $wR_2 = 0.1129$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0827P)^2+0.3094P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.103 and -1.964 eÅ^{-3}
R.M.S. deviation from mean	0.414^{-3}