Electronic Supplementary Information

Reactivity of a half-lantern $Pt_2(II,II)$ complex with triphenylphosphine: Selectivity in protonation reaction

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Table S1. Composition (%) of frontier MOs for complex **2** in acetone solution.

MO	**Energies(ev)**	**Pt**	**Spy**	**ppy**	**PPh_3**
LUMO+4	-0.73	1	2	2	95
LUMO+3	-0.95	9	5	20	66
LUMO+2	-1.01	5	2	71	22
LUMO+1	-1.06	25	3	11	61
LUMO	-1.72	6	2	86	6
HOMO	-5.22	12	80	6	2
HOMO-1	-5.88	34	24	40	2
HOMO-2	-6.17	68	11	14	7
HOMO-3	-6.35	15	36	46	3
HOMO-4	-6.54	8	25	61	6

Table S2. TD-DFT computed and experimental wavelengths (nm) for the lower energy band in complex **2** in acetone solution.

λ_{cal} (nm)	f^a	λ_{exp} (nm)	Transition (Percentage Contribution)	Character	Assignment L = ppy, L' = Spy
433	0.018	420	HOMO→LUMO (70%)	d(Pt)/π(spy)→ π*(ppy)	^{1}L'LCT/^{1}MLCT

[a] Oscillator strength

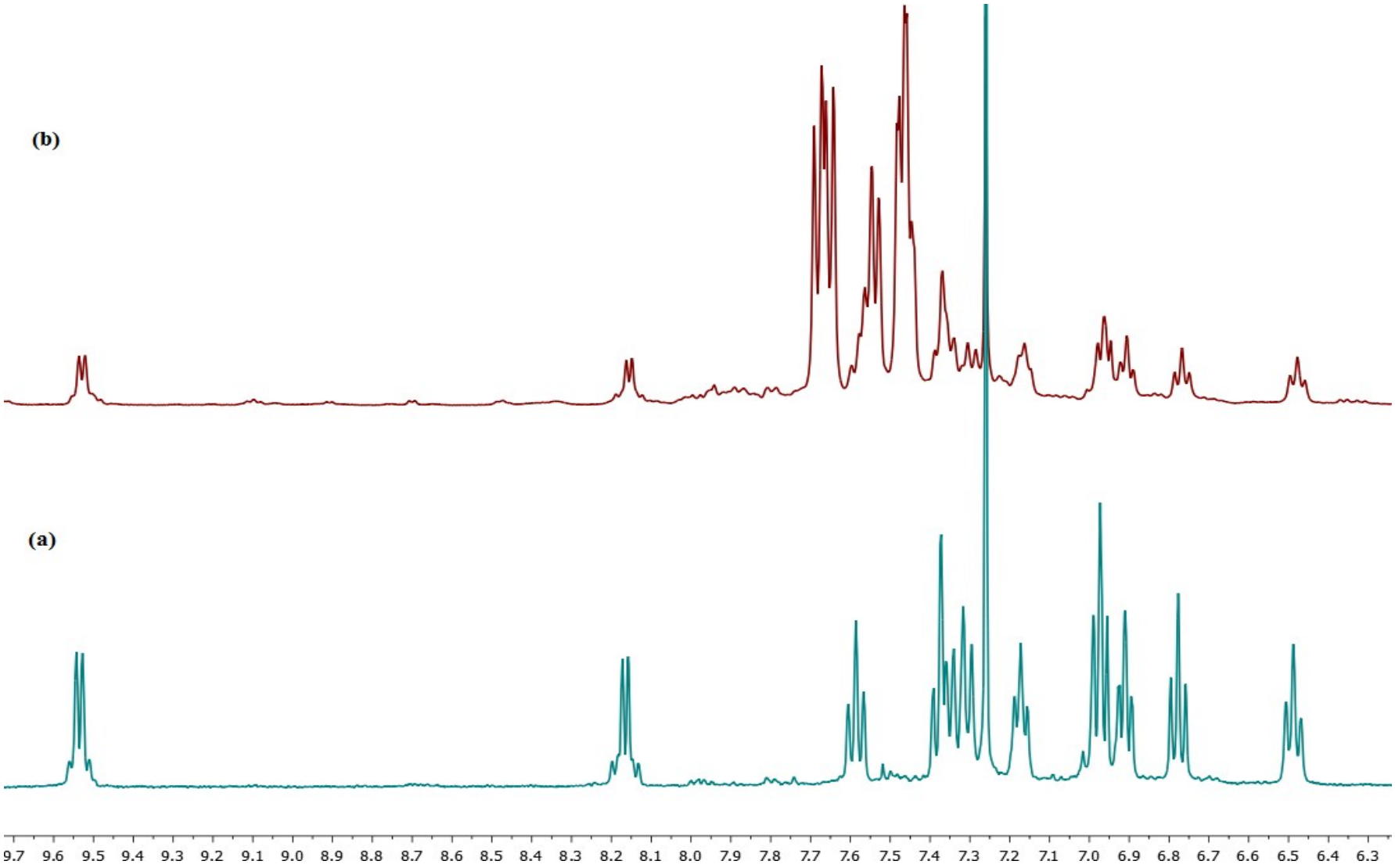

Figure S1. ^{1}H NMR spectra of complex (a) **1a** and (b) reaction mixture of complex **1a** with PPh_3 in CD_2Cl_2 at room temperature.

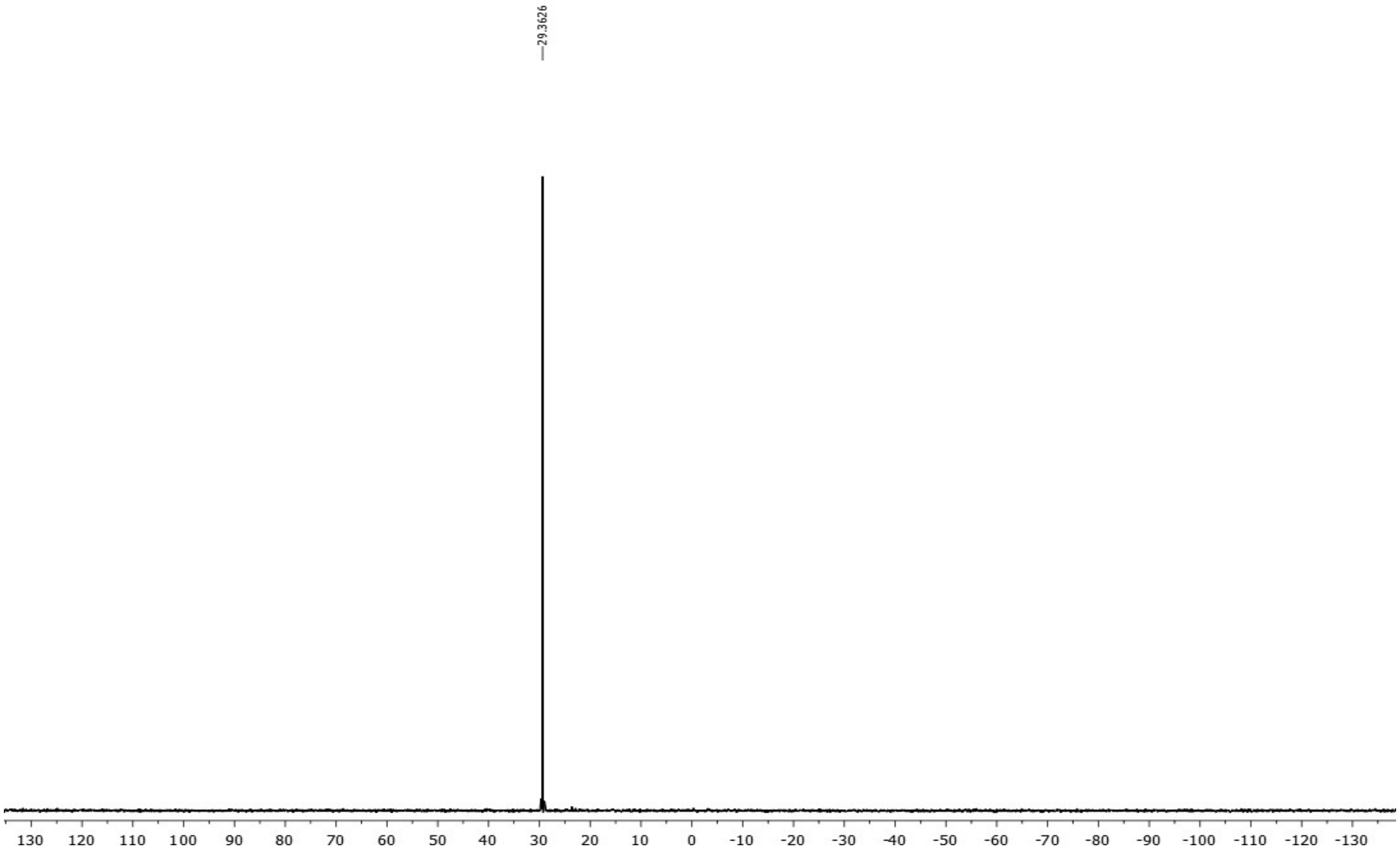

Figure S2. ^{31}P $\{^{1}H\}$ NMR spectra of reaction mixture of complex **1a** with PPh_3 in CD_2Cl_2 at room temperature and formed triphenylphosphine oxide.

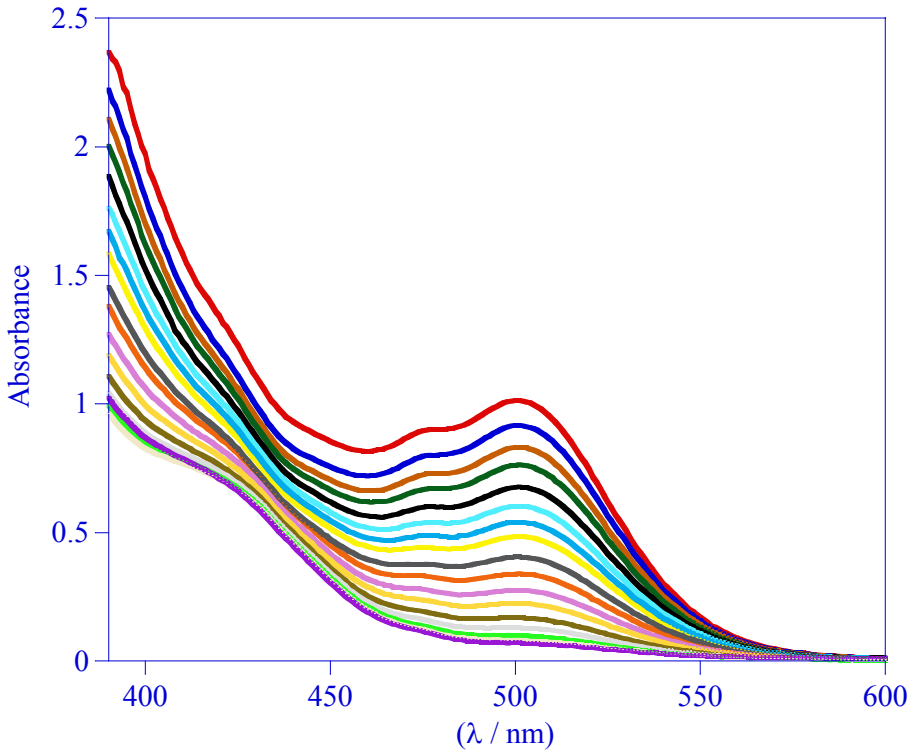

Figure S3. Change in the absorbance spectra of complex [{Pt(ppy)(μ_2-Spy)}$_2$], **1**, with an excess of PPh_3 in acetone at T = 25 °C as function of wavelength; successive spectra recorded at intervals of 3 min.

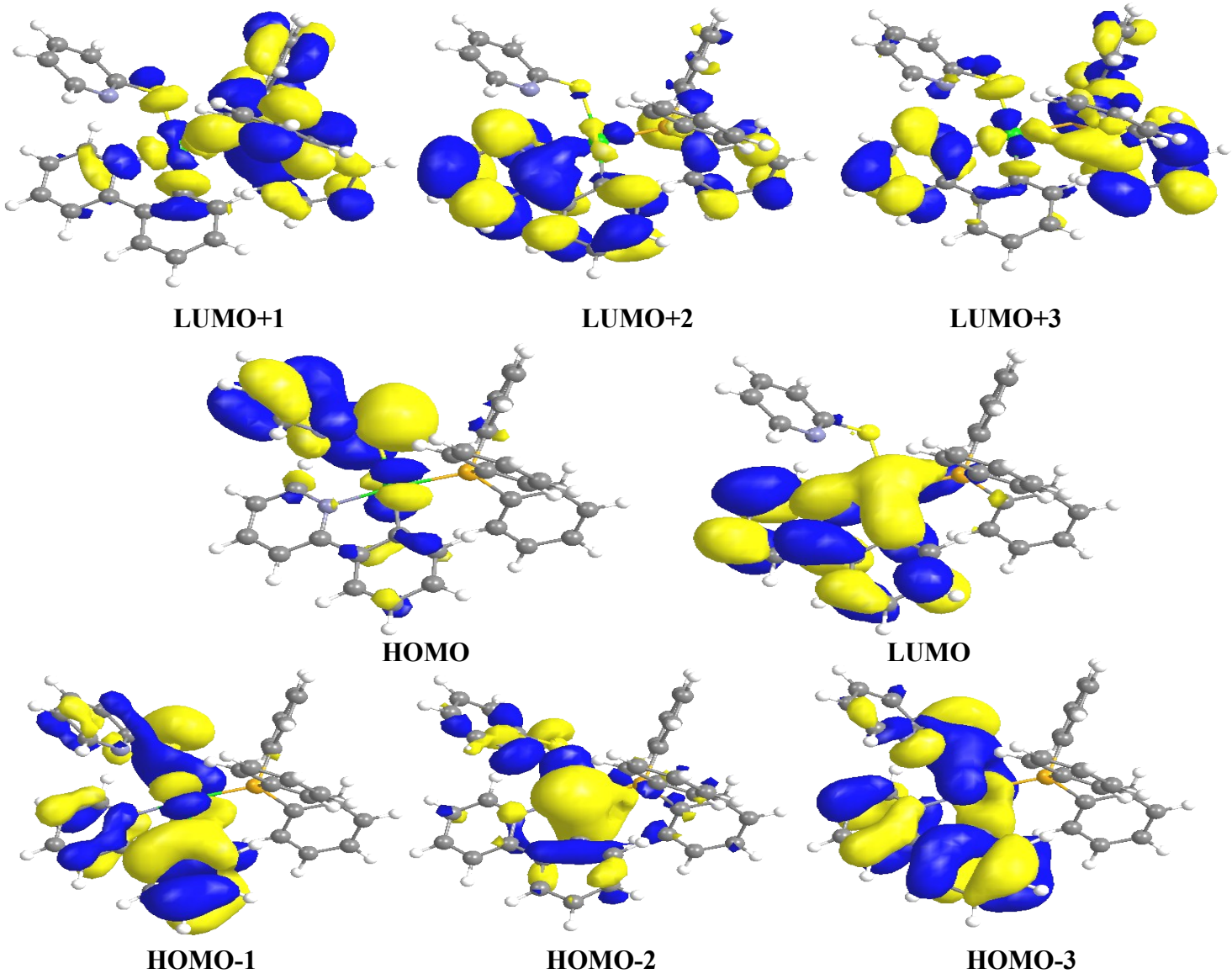

Figure S4. Representative frontier orbitals involved in the absorption of complex **2**.

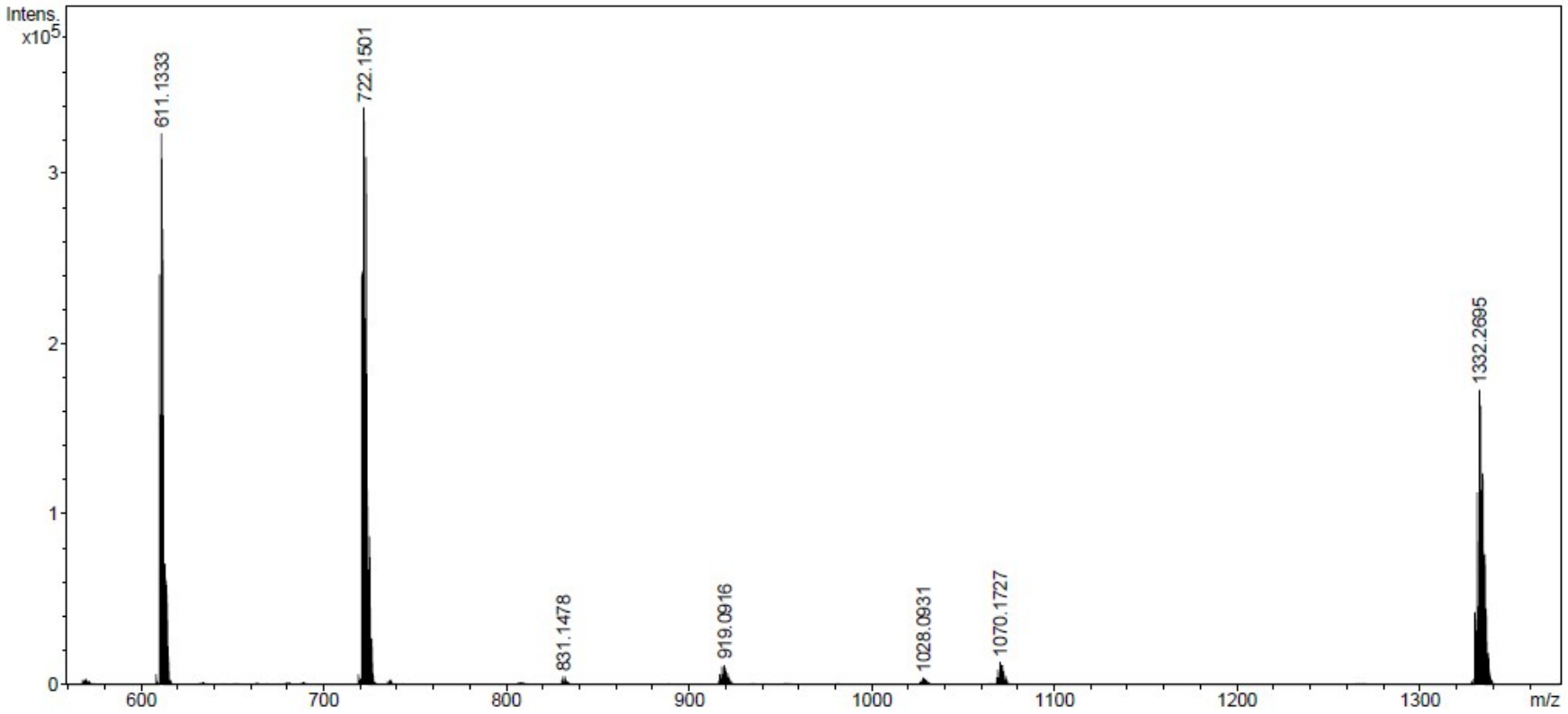

Figure S5. ESI-Mass spectrum of complex **2** in cationic mode.

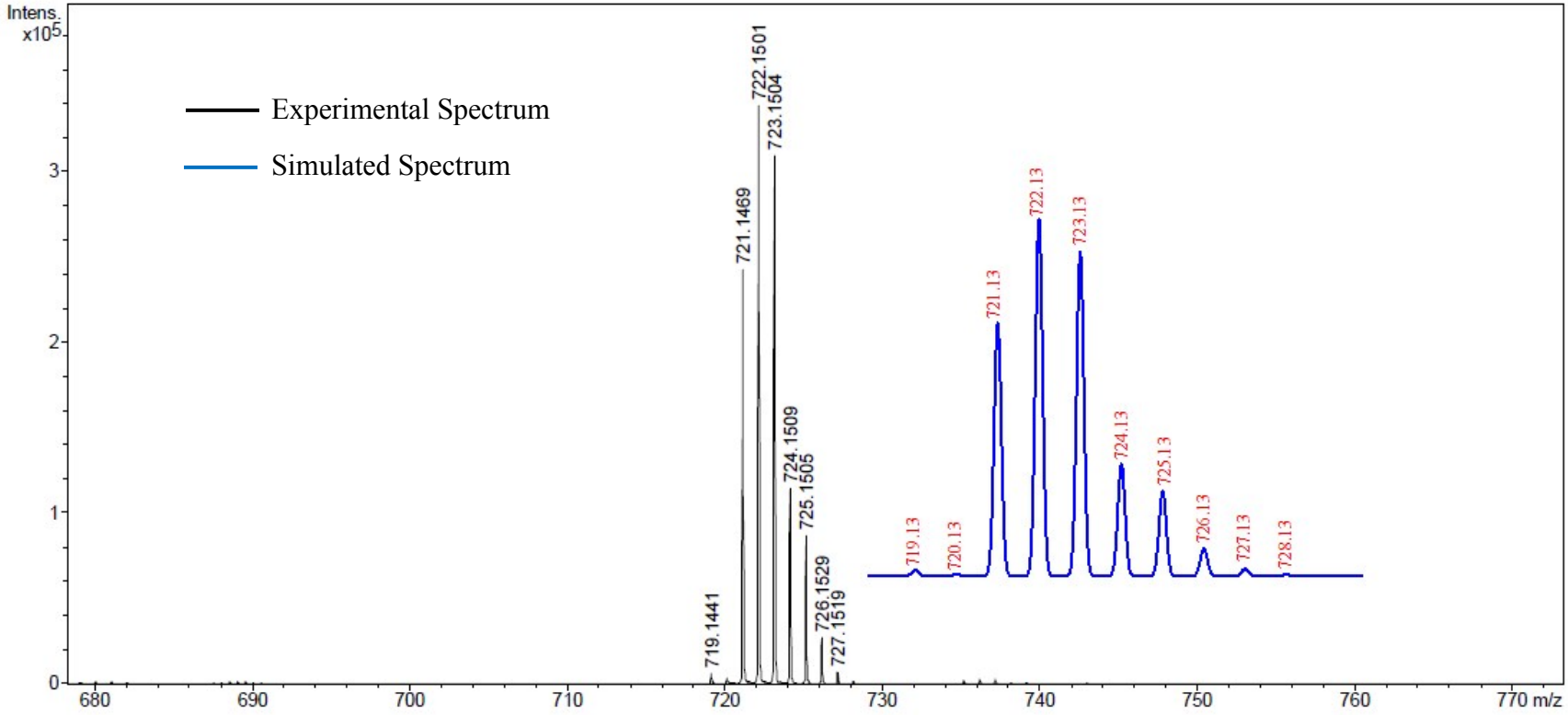

Figure S6. ESI-Mass spectrum of complex **2**, peak corresponding to $[Pt(ppy)(\eta^1\text{-S-Spy})(PPh_3)]^+$, $[\mathbf{2}]^+$ (experimental, black; simulated, blue).

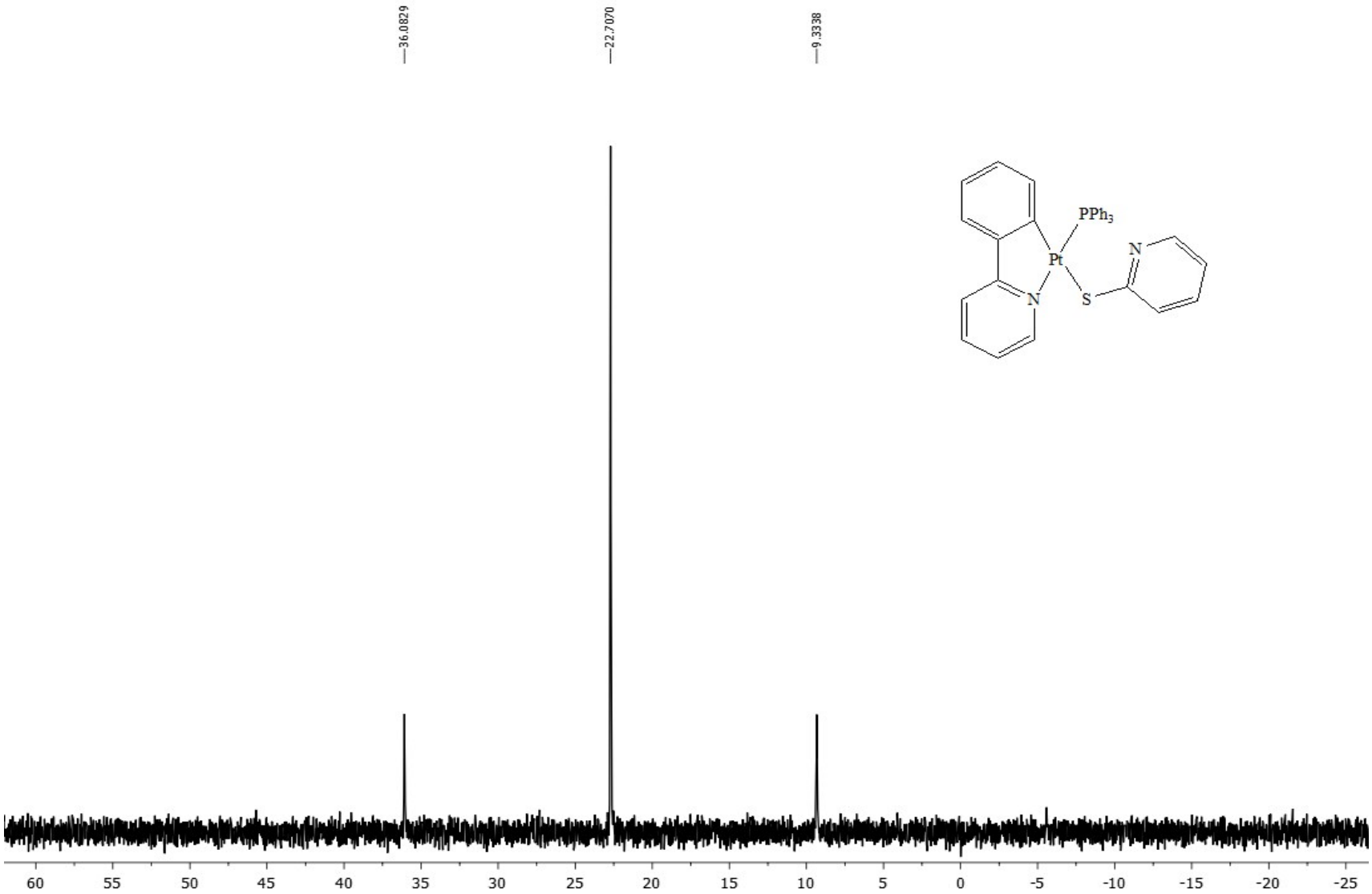

Figure S7. ^{31}P $\{^{1}H\}$ NMR spectrum of complex **2** in CD_2Cl_2 at room temperature.

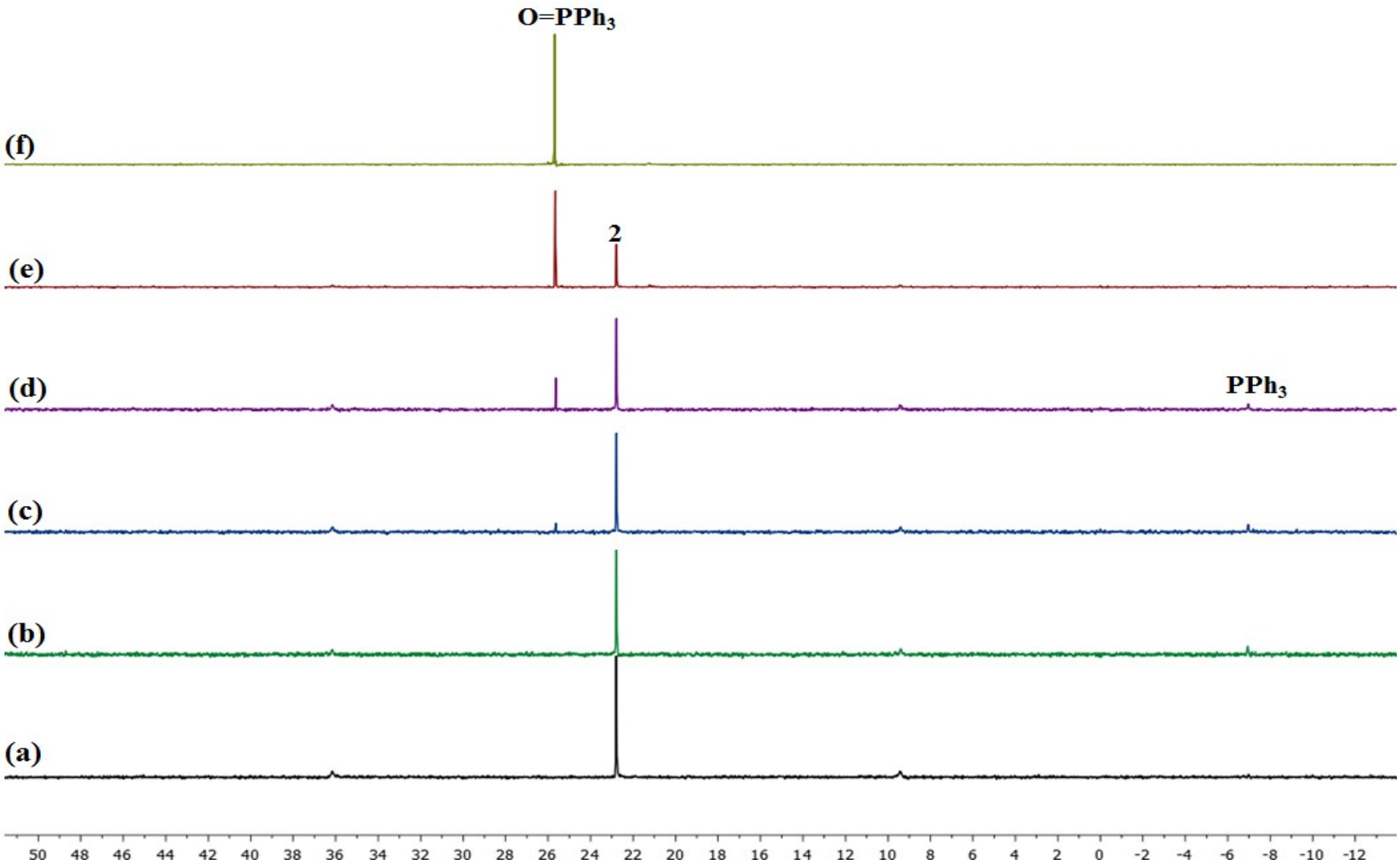

Figure S8. Complex **2** as monitored by ^{31}P $\{^{1}H\}$ NMR spectroscopy in dmso-d_6 at room temperature. (a) complex **2**, (b) after 6h in the dry and deoxygenated solvent; (c) 6 h (d) 12 h, (e) 24 h and (f) 48 h in the hydrated (hydrous and aerated) solvent. The signal assignments are depicted.

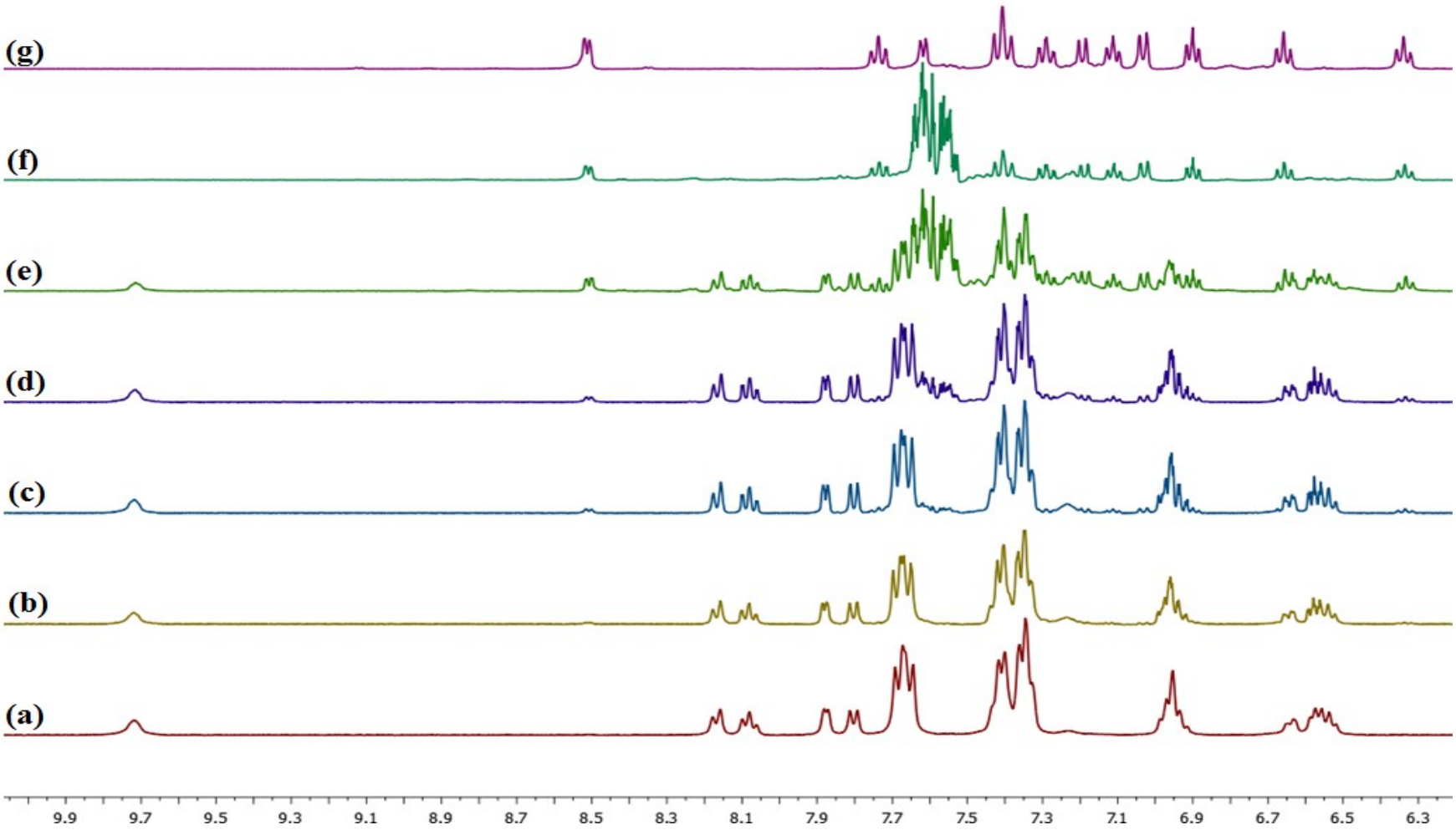

Figure S9. Complex **2** as monitored by ^{1}H NMR spectroscopy in dmso-d_6 at room temperature. (a) complex **2**, (b) 6 h, (c) 12 h, (d) 24 h, (e) 48 h, (f) 72 h in the hydrous and aerated solvent and (g) complex **1**.

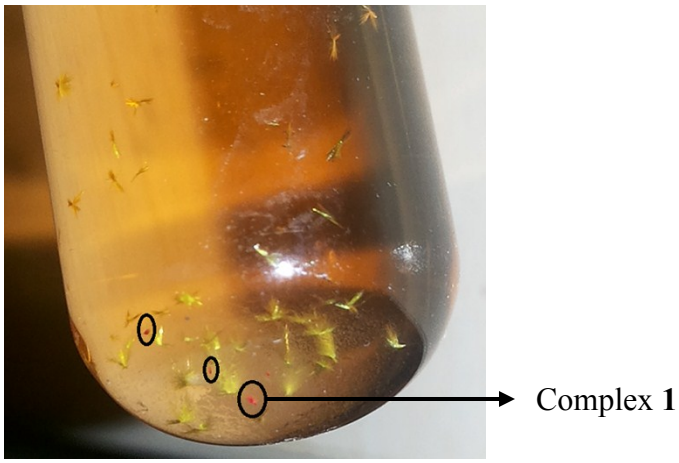

Figure S10. Photograph of transformation of complex **2** to complex **1**.

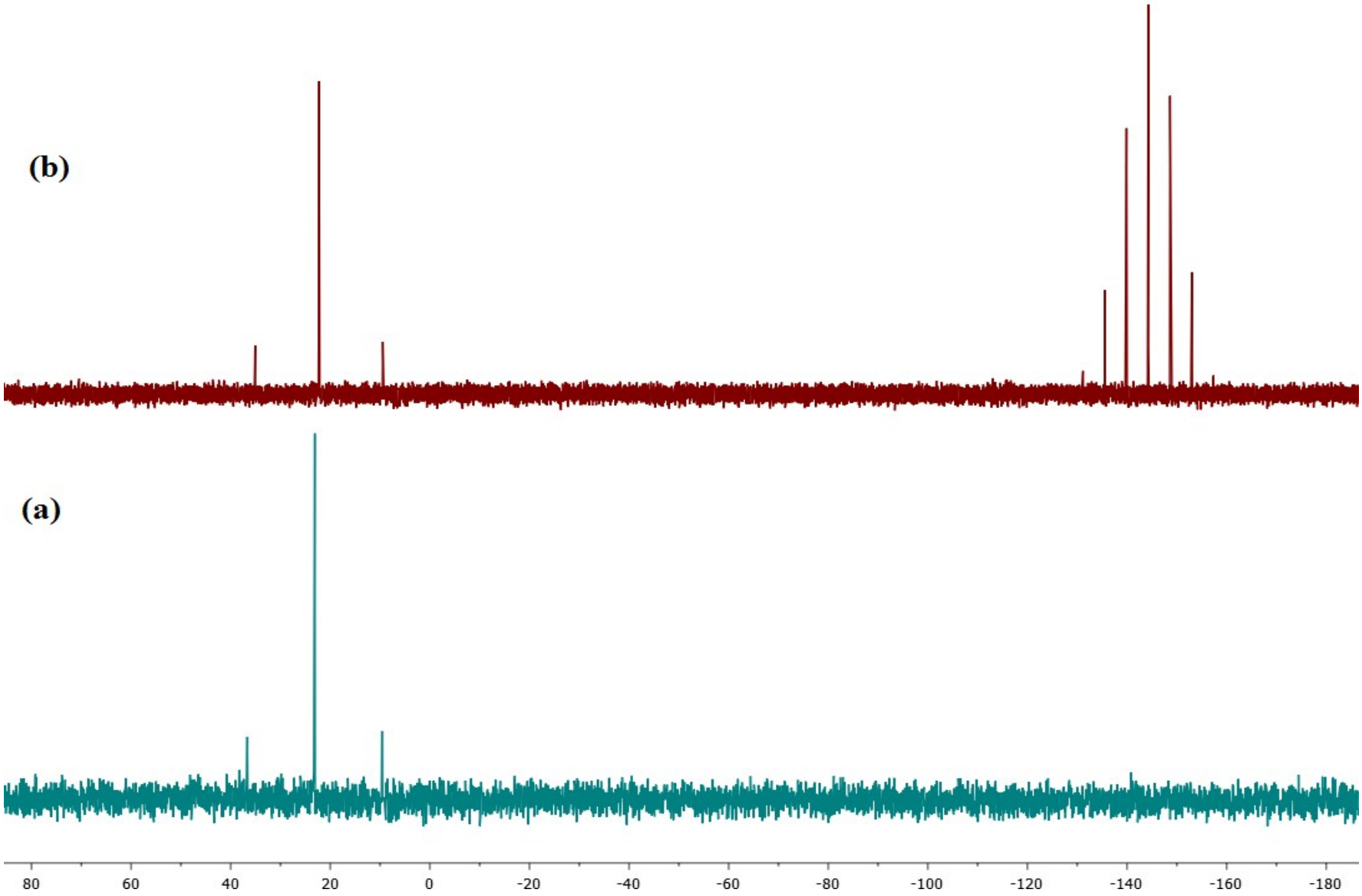

Figure S11. ^{31}P $\{^{1}H\}$ NMR spectra of (a) complex **2** and (b) complex **5** in acetone-d_6 at room temperature.

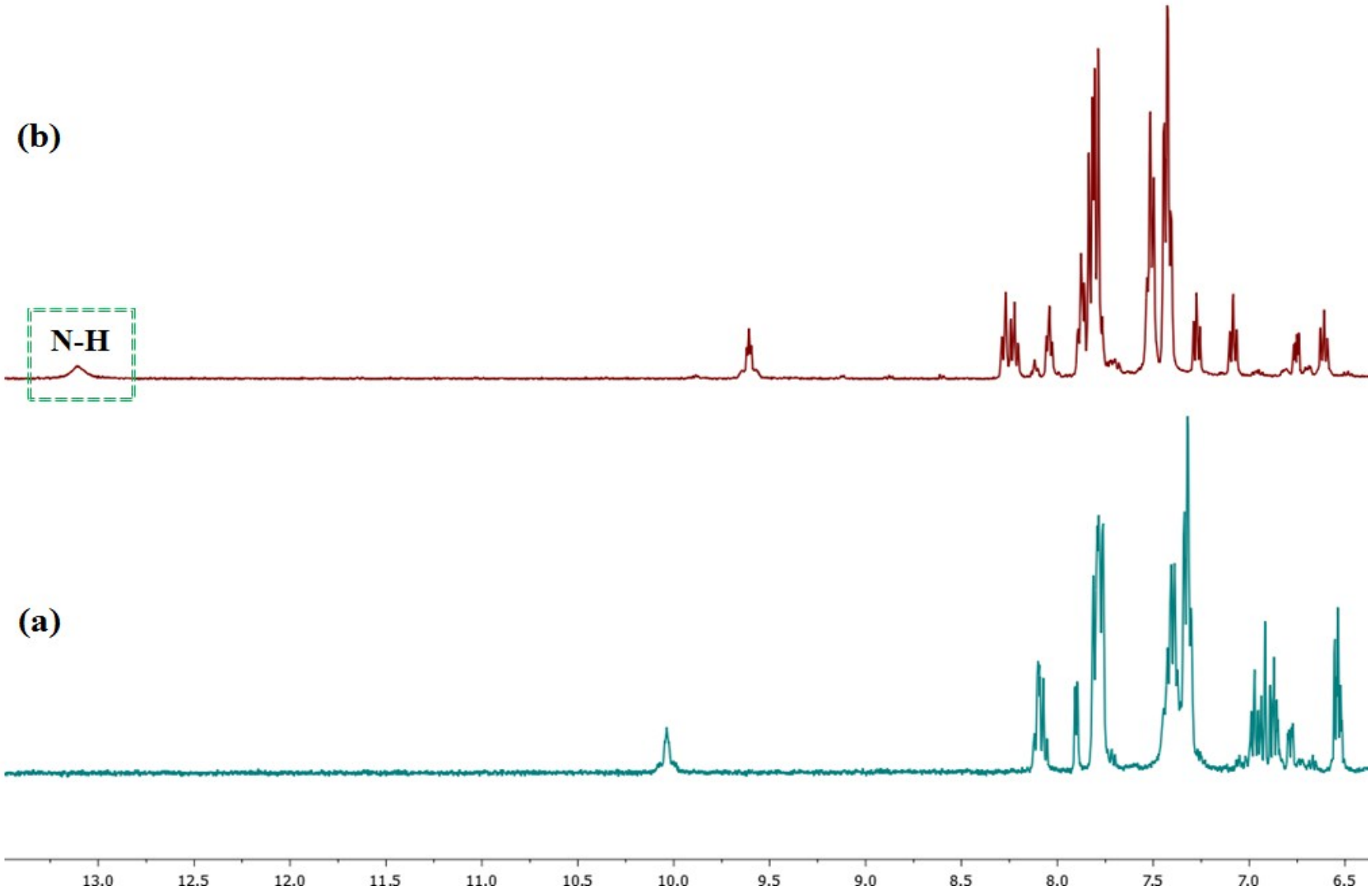

Figure S12. ^{1}H NMR spectra of (a) complex **2** and (b) complex **5** in acetone-d_6 at room temperature.

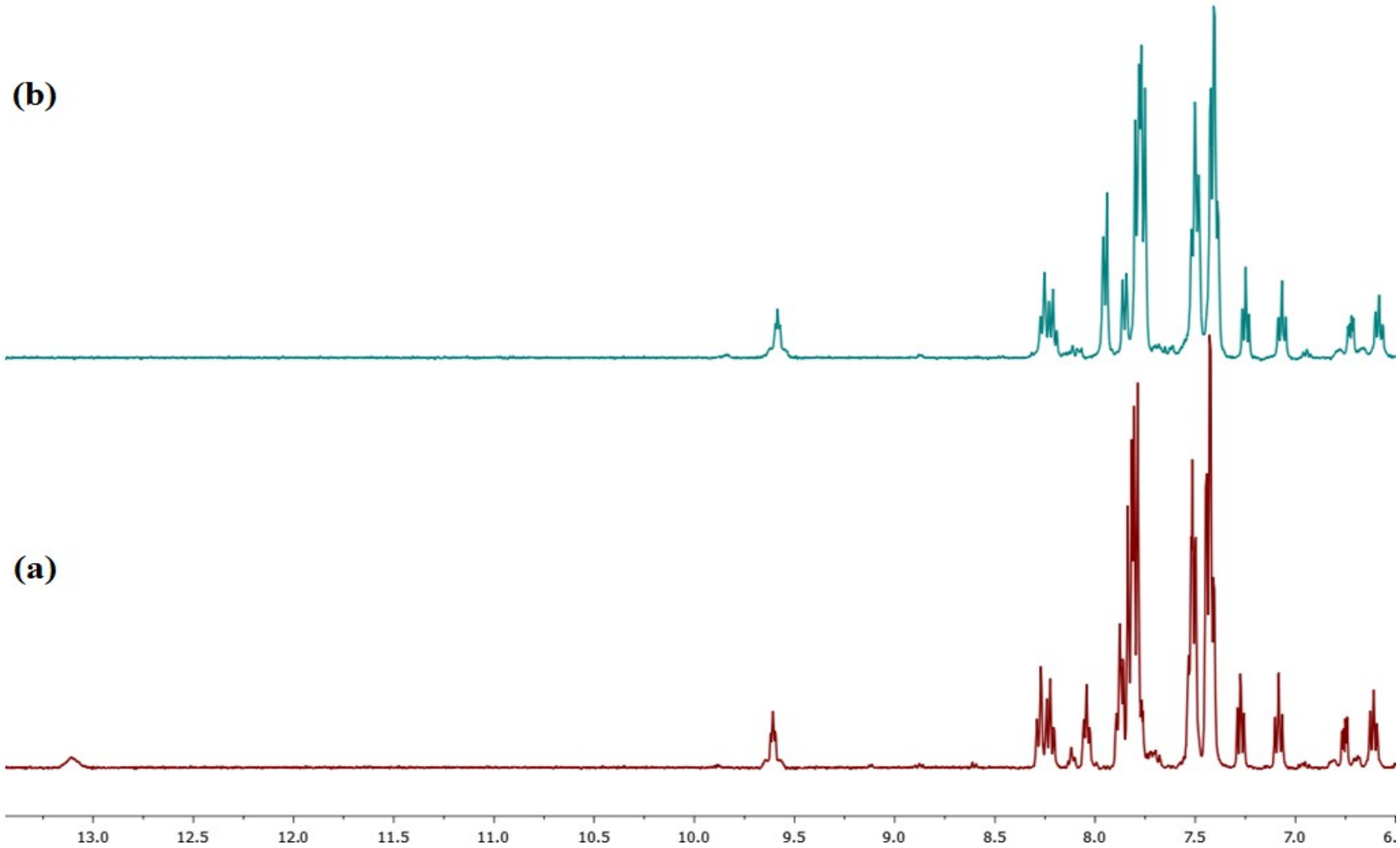

Figure S13. ^{1}H NMR spectra of (a) complex **5** (b) complex **5** + D_2O in acetone-d_6 at room temperature.

Table S3. Crystallographic and structure refinement data for complex **4**.

Formula	$C_{35}H_{28}NPPtS$
Formula weight	720.69
T (K)	298(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space Group	$P2_1/c$
Crystal size(mm)	0.25×0.15×0.12
a (Å)	17.452(4)
b (Å)	8.2580(17)
c (Å)	20.121(4)
α (°)	90
β (°)	90.95(3)
γ (°)	90
V (Å^3)	2899.4(10)
Z	4
D_{calc} (g cm^{-1})	1.651
θ_{min}, θ_{max} (°)	2.32-25.00
F_{000}	1416
μ (mm^{-1})	4.992
Index ranges	$-20 \le h \le 20$
	$-9 \le k \le 9$
	$-23 \le l \le 23$
Data collected	15434
Unique data	5090
R_1[a], wR_2[b] (I > 2σ (I))	0.0542, 0.1014
R_1[a], wR_2[b] (all data)	0.1170, 0.1142
GOF on F^2 (S)	0.803

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b]$wR_2 = [\Sigma(w(F_o^{5}-F_c^{2})^2)/\Sigma w(F_o^{2})^2]^{1/2}$

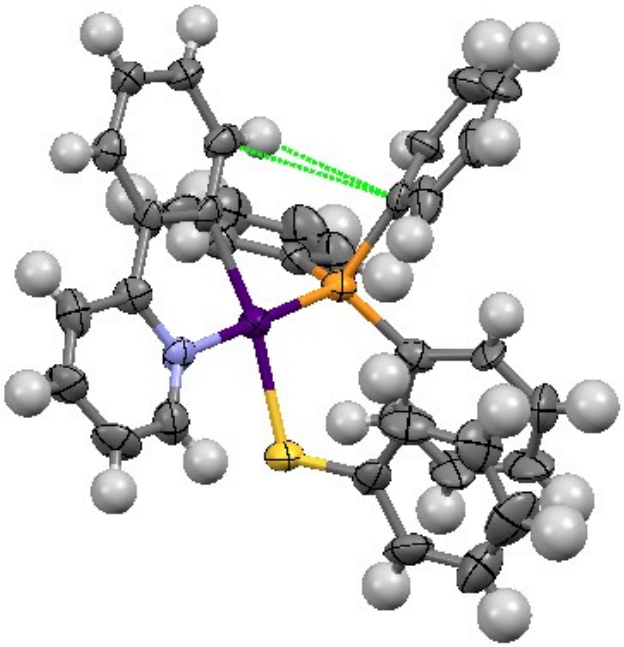

Figure S14. C–H···π interaction between C–H group adjacent to metalated carbon atom of the ppy ligand and the phenyl ring of PPh_3 ligand in complex **4** (green lines).

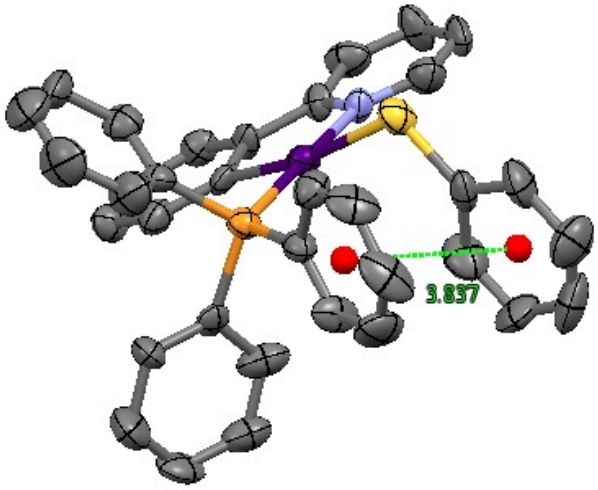

Figure S15. Intramolecular π···π contact between the SPh and phenyl ring of PPh_3 in complex **4**.