Supporting Information

Rhenium(I) tricarbonyl complexes with (2-hydroxyphenyl)diphenylphosphine as PO bidentate ligand

Antonio Shegani[†], Charalampos Triantis[†], Berthold A. Nock[†], Theodosia Maina[†], Christos Kiritsis[†], Vassilis Psycharis[‡], Catherine Raptopoulou[‡], Ioannis Pirmettis[†], Francesco Tisato[¥], Minas S. Papadopoulos[†*]

[†]*Institute of Nuclear & Radiological Sciences & Technology, Energy & Safety, National Center for Scientific Research "Demokritos", 15310 Athens, Greece*

[‡]*Institute of Nanoscience and Nanotechnology, National Center for Scientific Research "Demokritos", 15310 Athens, Greece*

[¥]*Consiglio Nazionale delle Ricerche - Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia, 35127 Padova, Italy*

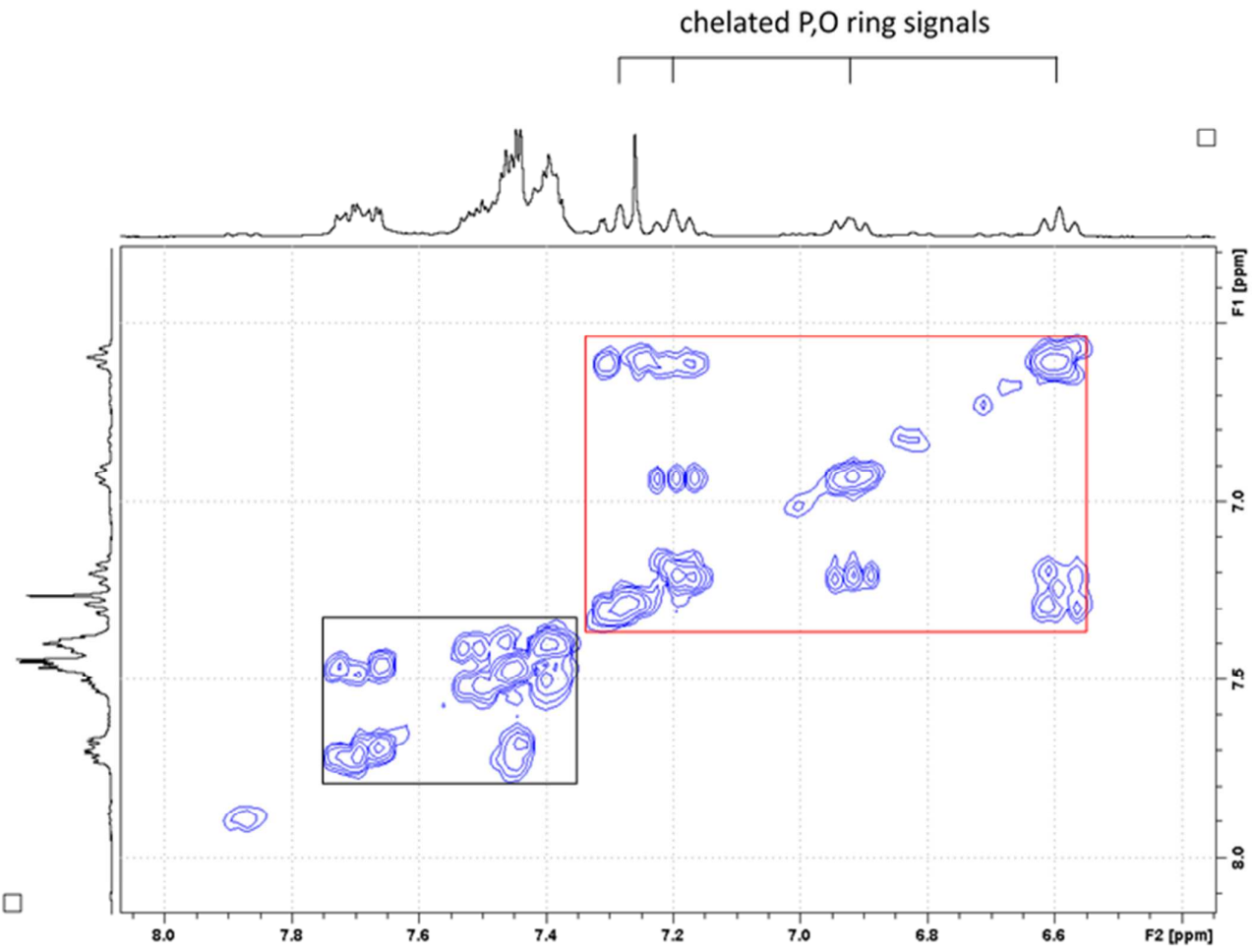

Figure S1. ^{1}H-^{1}H contour COSY map of the aromatic region of complex **6**.

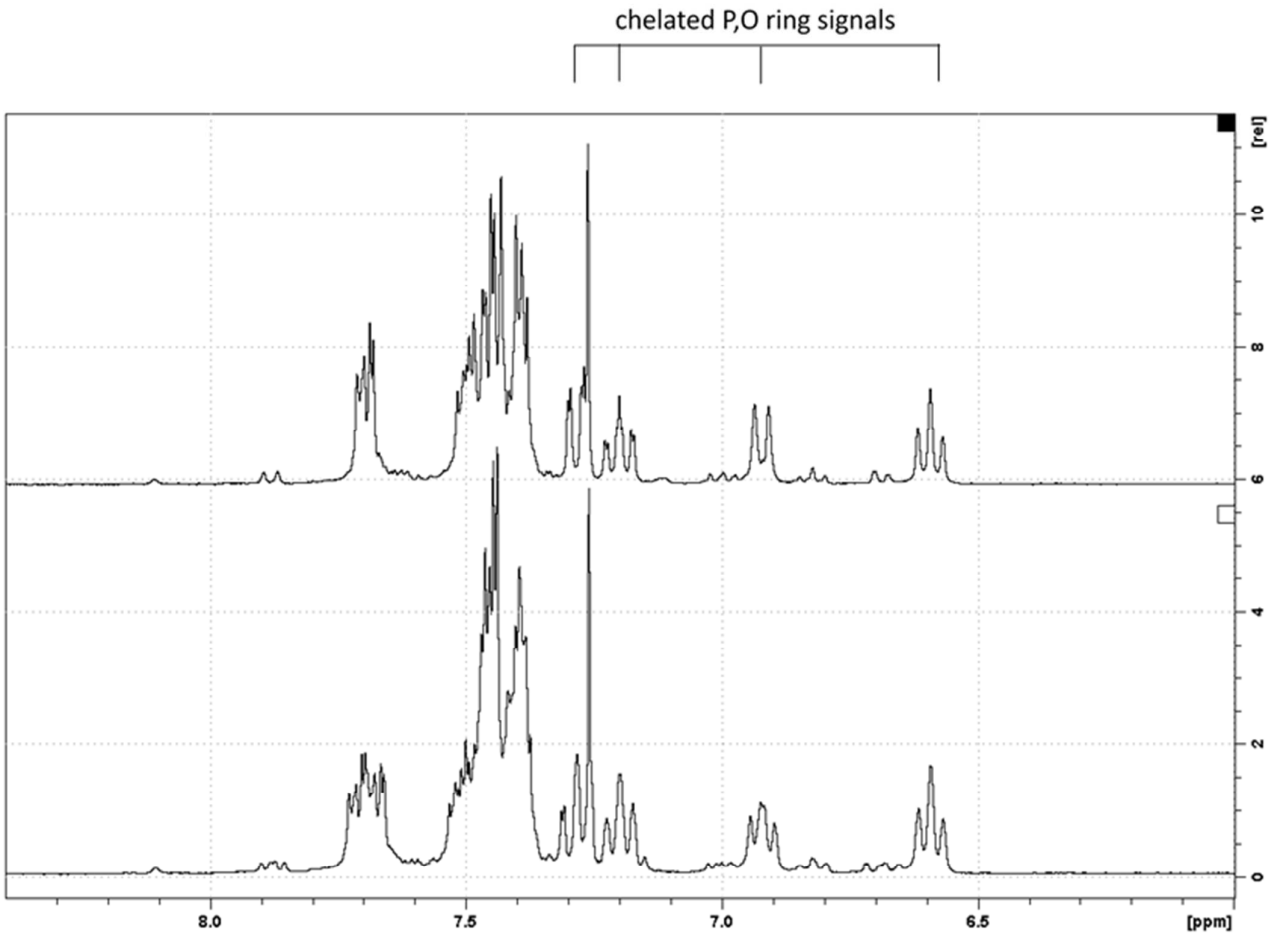

Figure S2. ^{1}H spectrum (bottom trace) and $^{1}H\{^{31}P\}$ spectrum (top trace) of the aromatic region of complex **6**

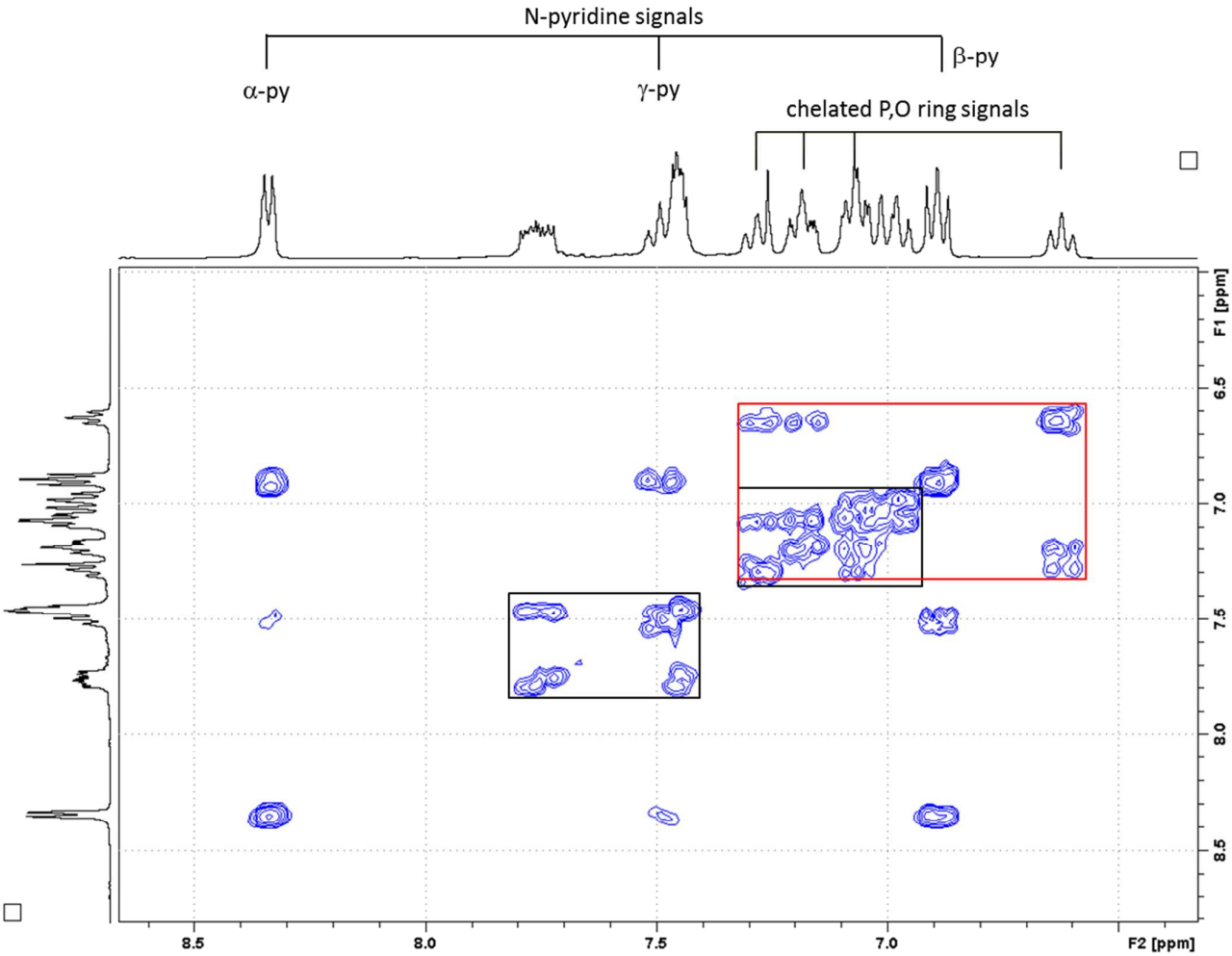

Figure S3. ^{1}H-^{1}H contour COSY map of the aromatic region of complex **5**

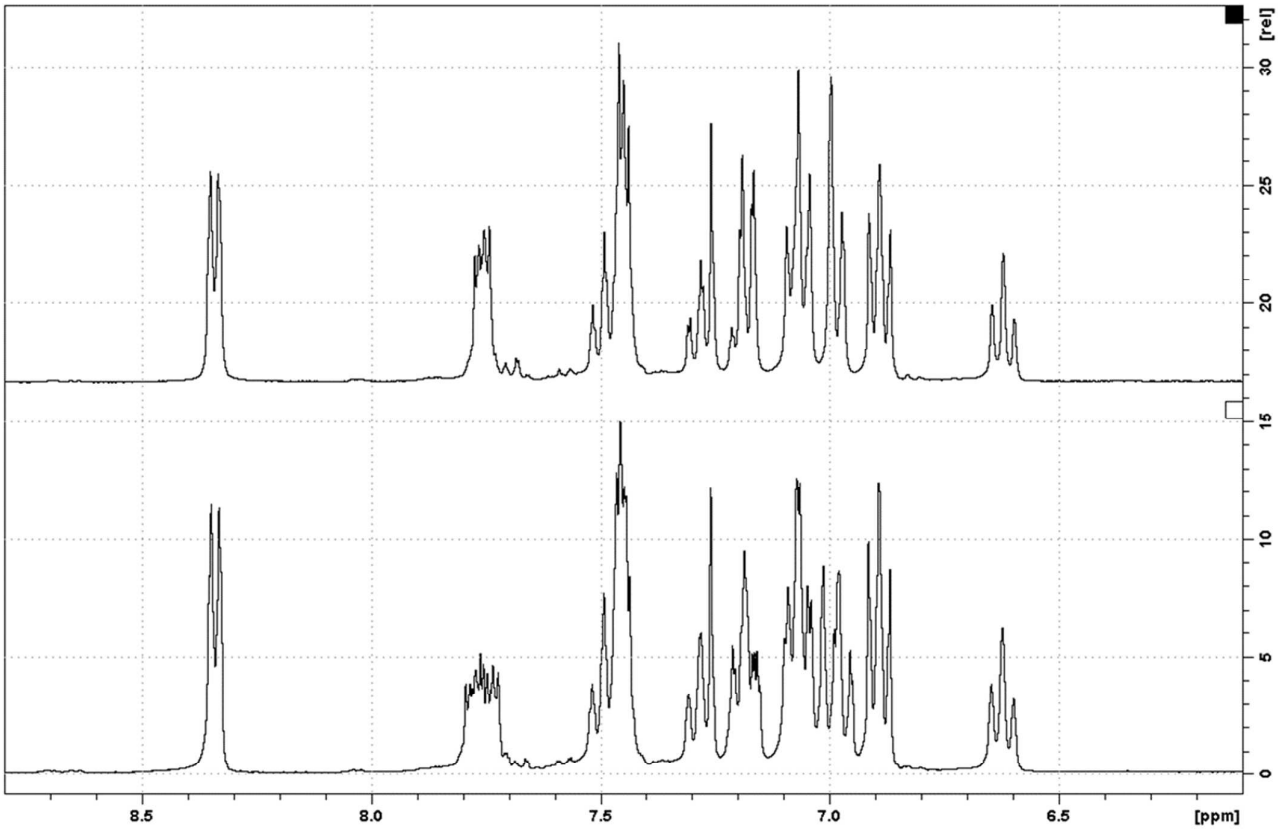

Figure S4. ^{1}H spectrum (bottom trace) and $^{1}H\{^{31}P\}$ spectrum (top trace) of the aromatic region of complex **5**.

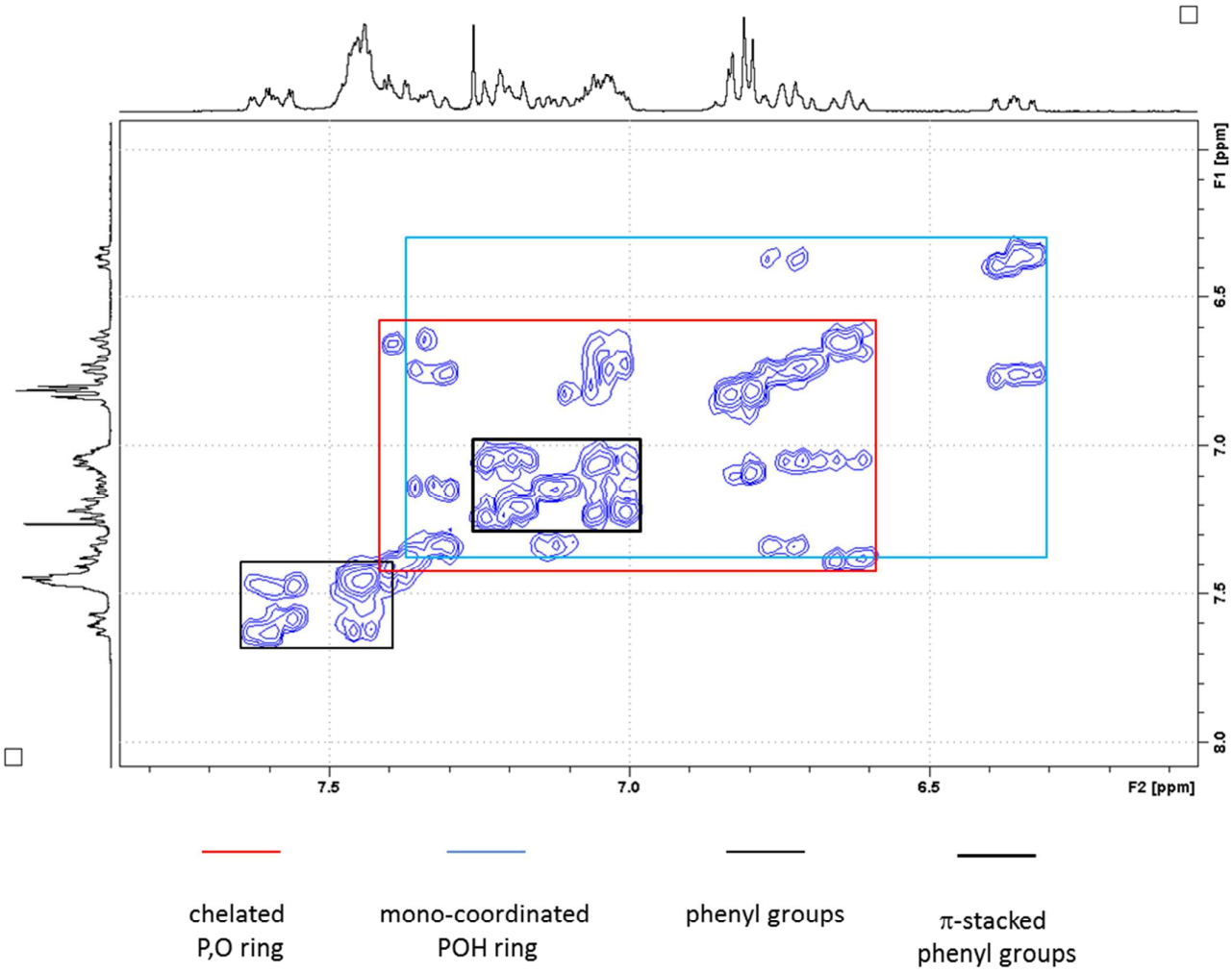

Figure S5. ^{1}H-^{1}H contour COSY map of the aromatic region of complex **2**

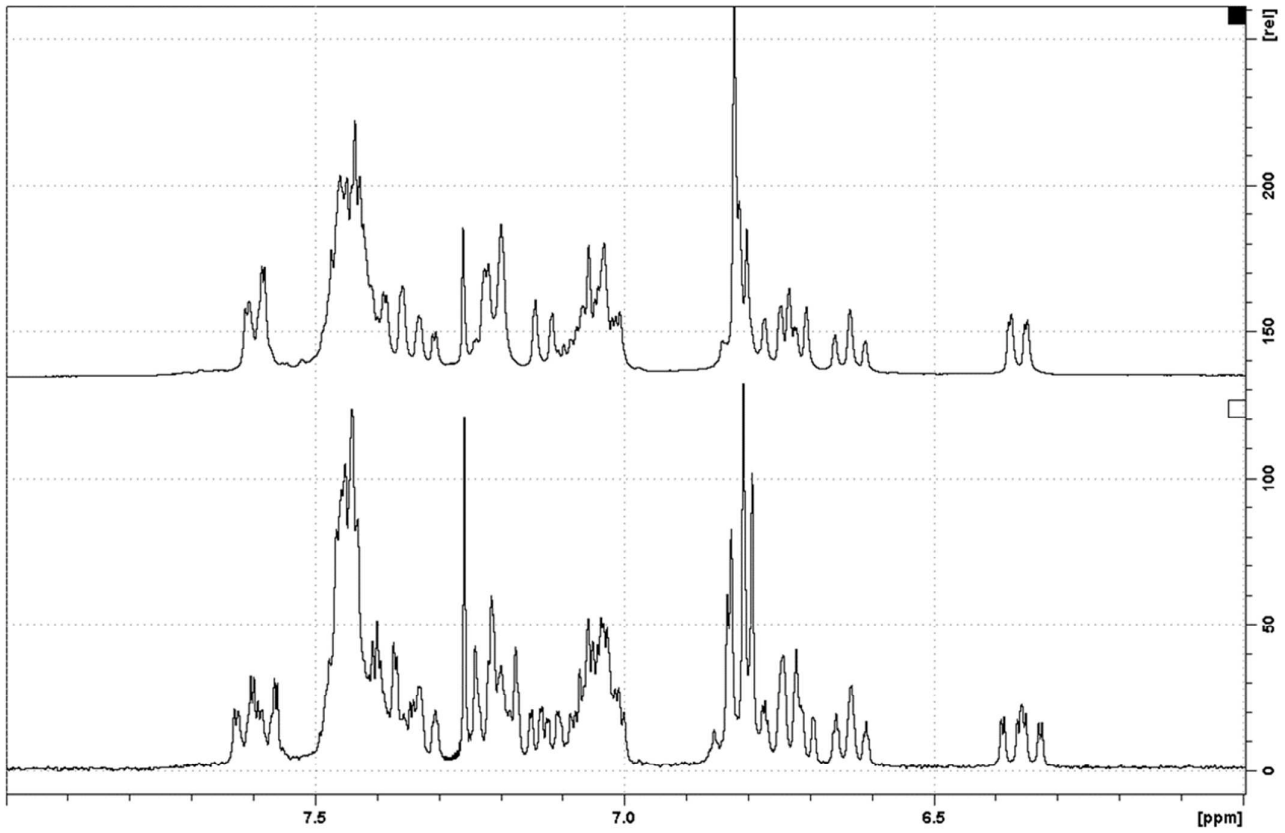

Figure S6. ^{1}H spectrum (bottom trace) and $^{1}H\{^{31}P\}$ spectrum (top trace)of the aromatic region of complex **2**

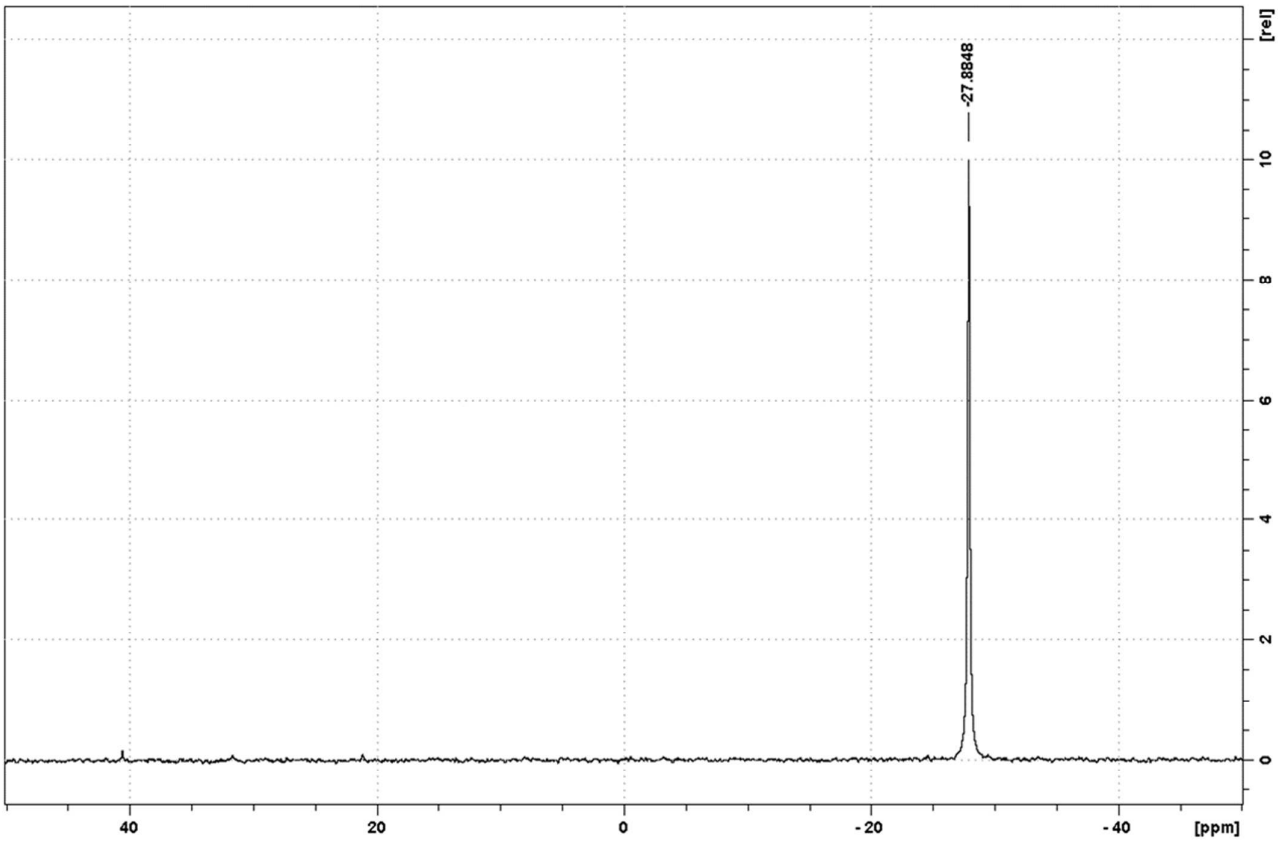

Figure S7. $^{31}P\{^{1}H\}$ spectrum of uncoordinated POH.

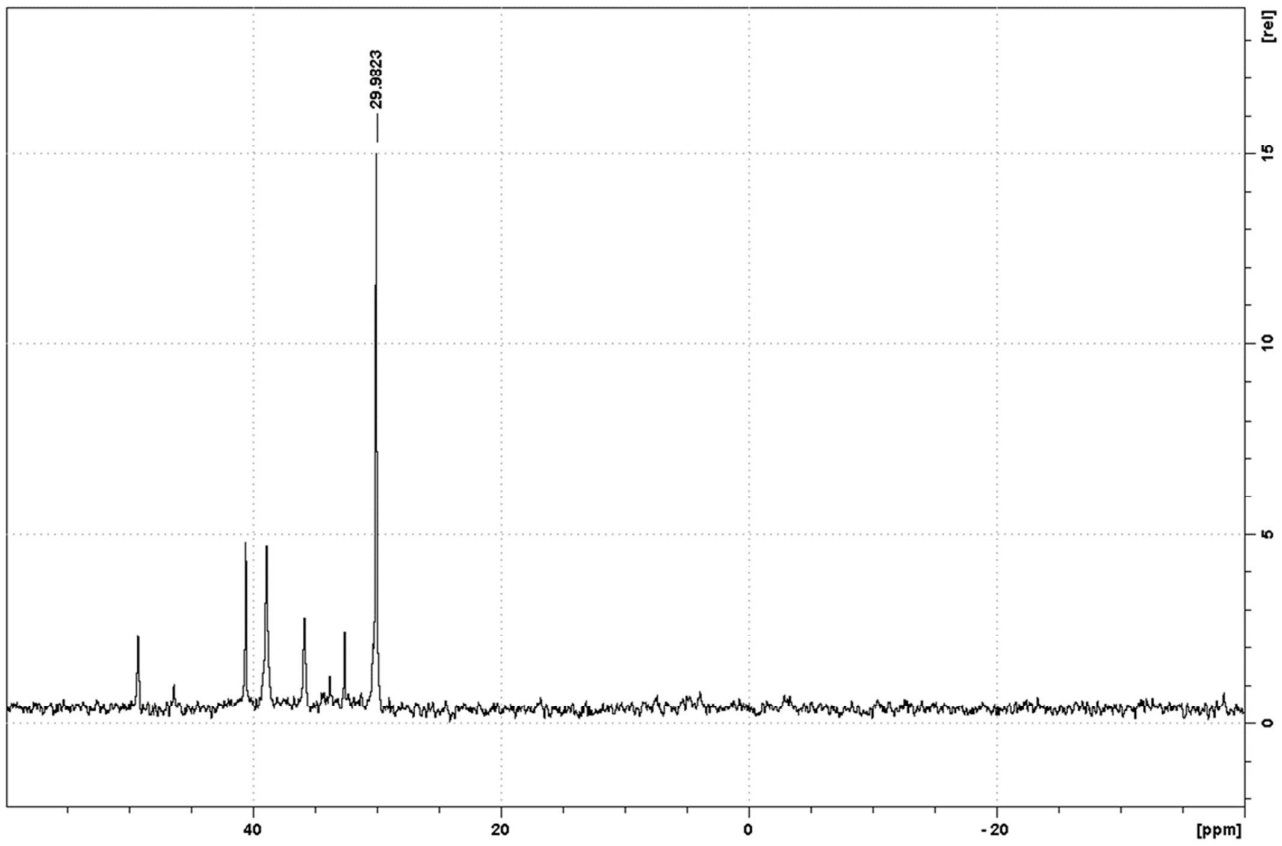

Figure S8. $^{31}P\{^{1}H\}$ spectrum of complex **1**

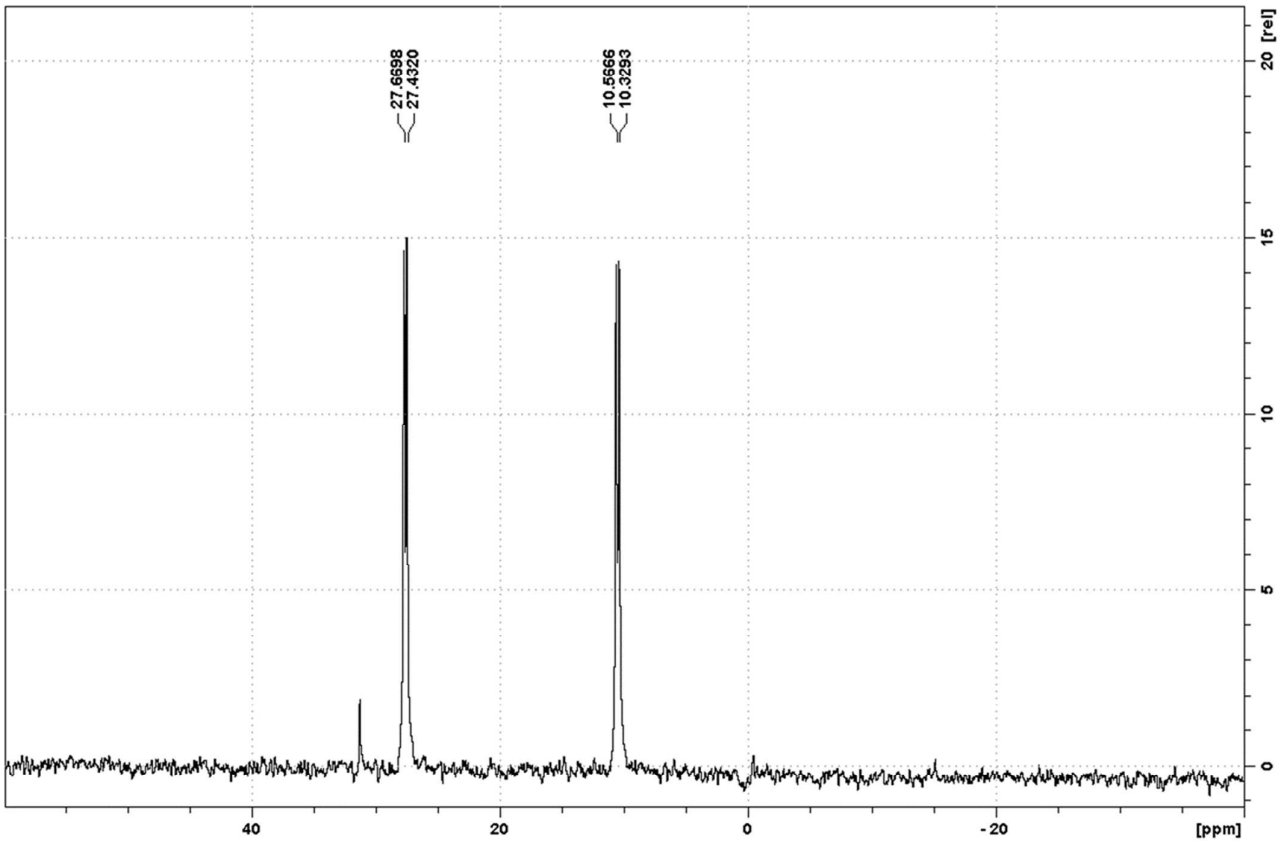

Figure S9. $^{31}P\{^{1}H\}$ spectrum of complex **2**

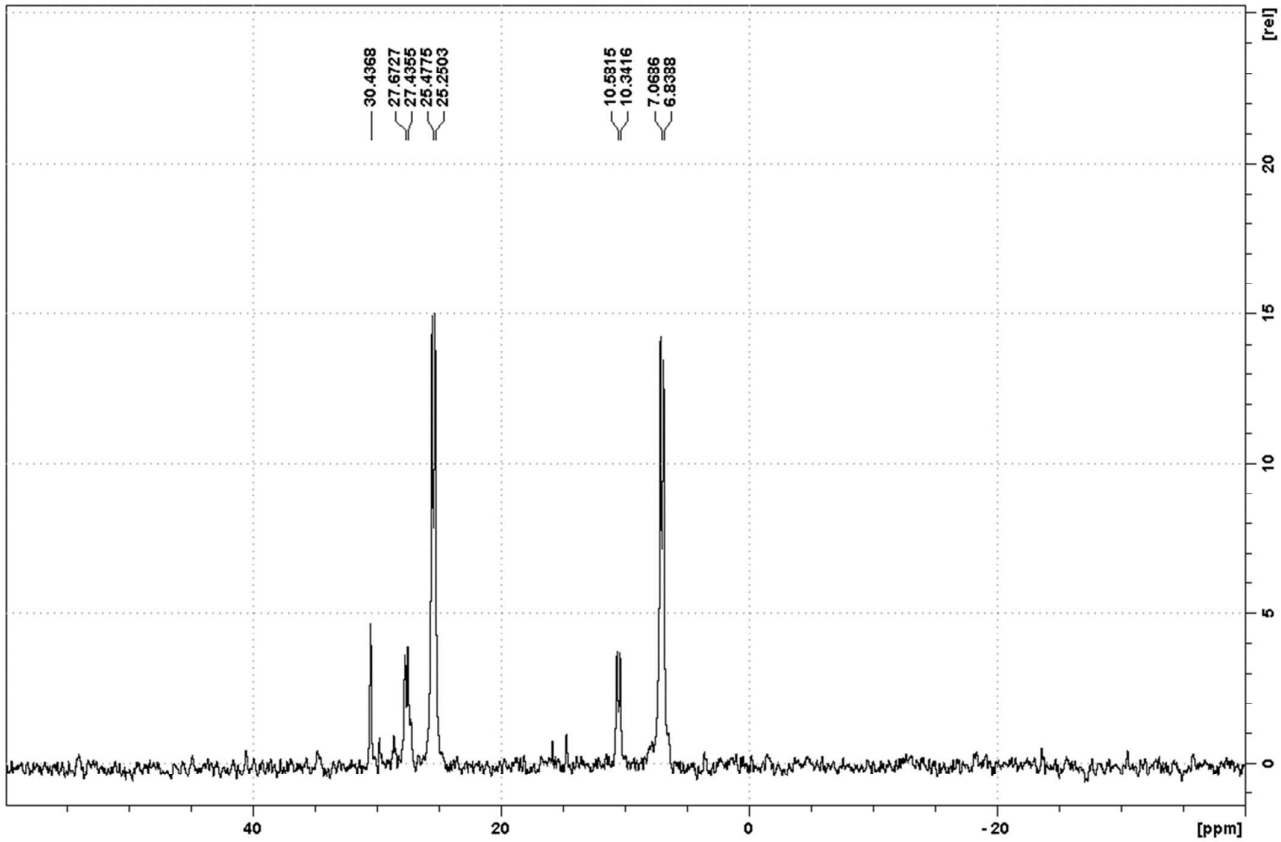

Figure S10. $^{31}P\{^{1}H\}$ spectrum of complex **3**

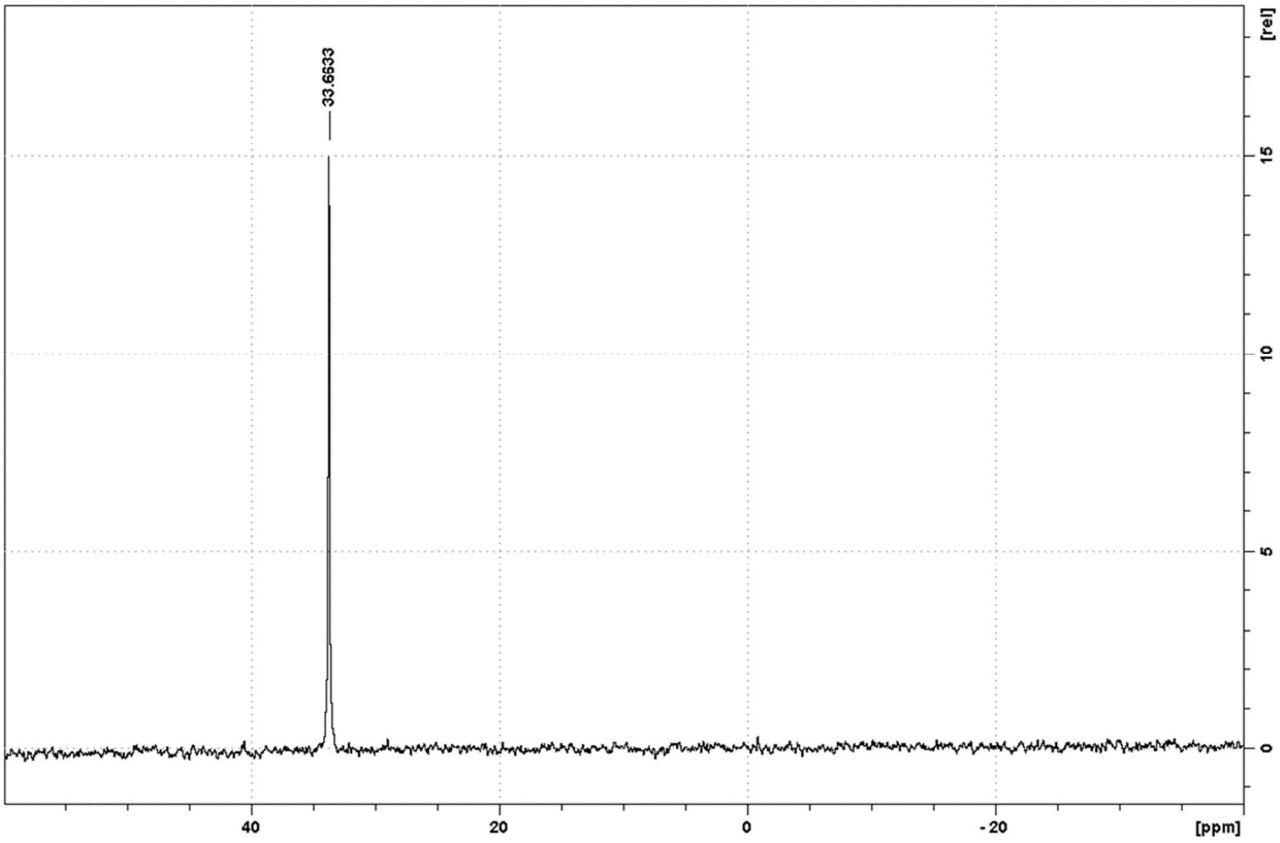

Figure S11. $^{31}P\{^{1}H\}$ spectrum of complex **4**

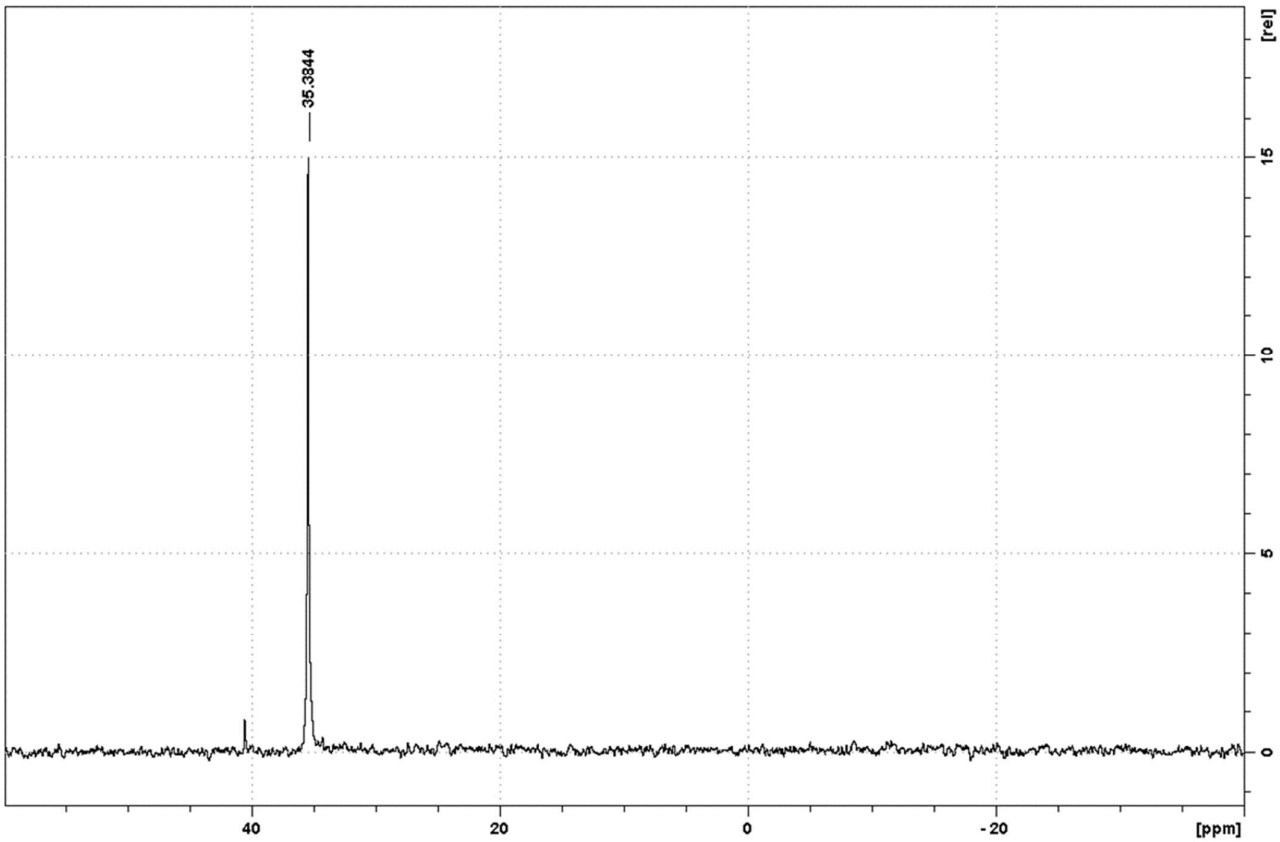

Figure S12. $^{31}P\{^{1}H\}$ spectrum of complex **5**

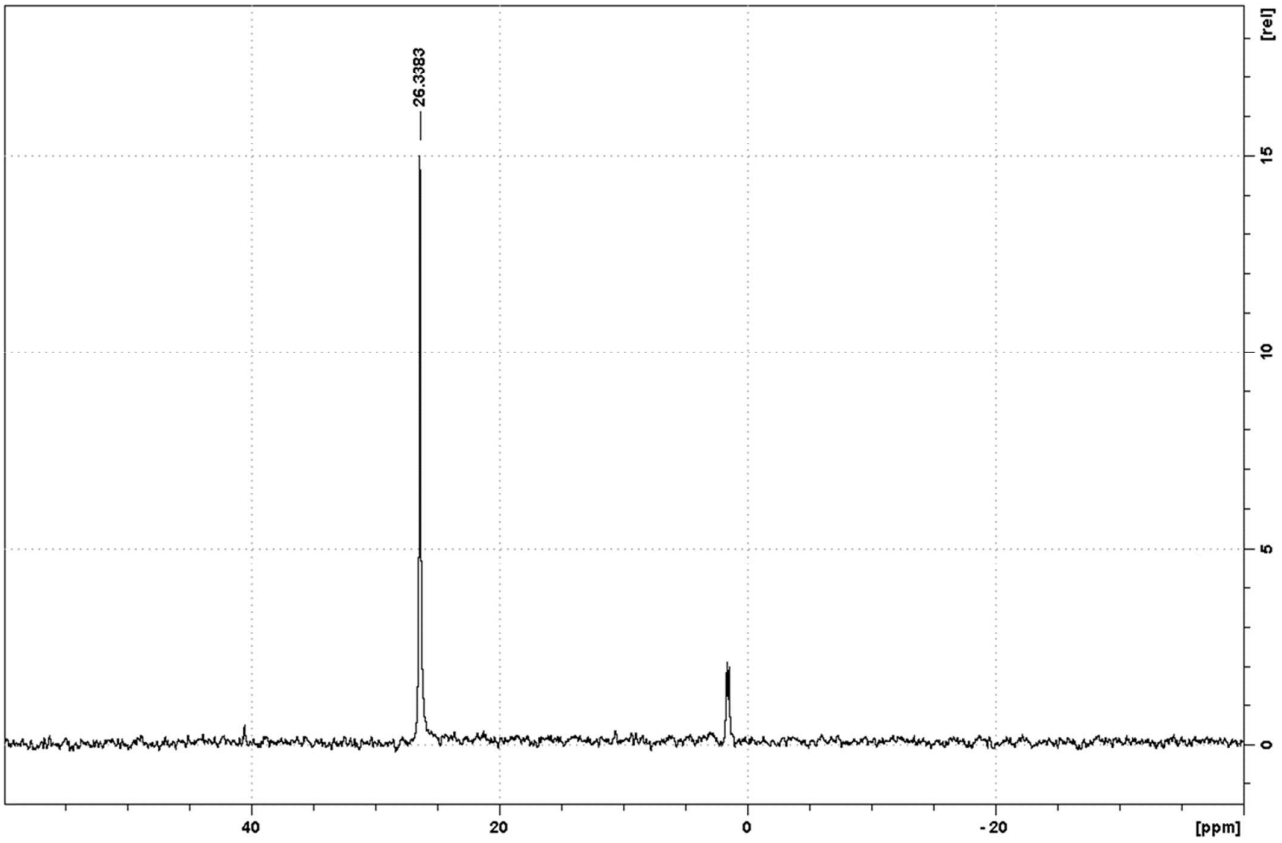

Figure S13. $^{31}P\{^{1}H\}$ spectrum of complex **6**

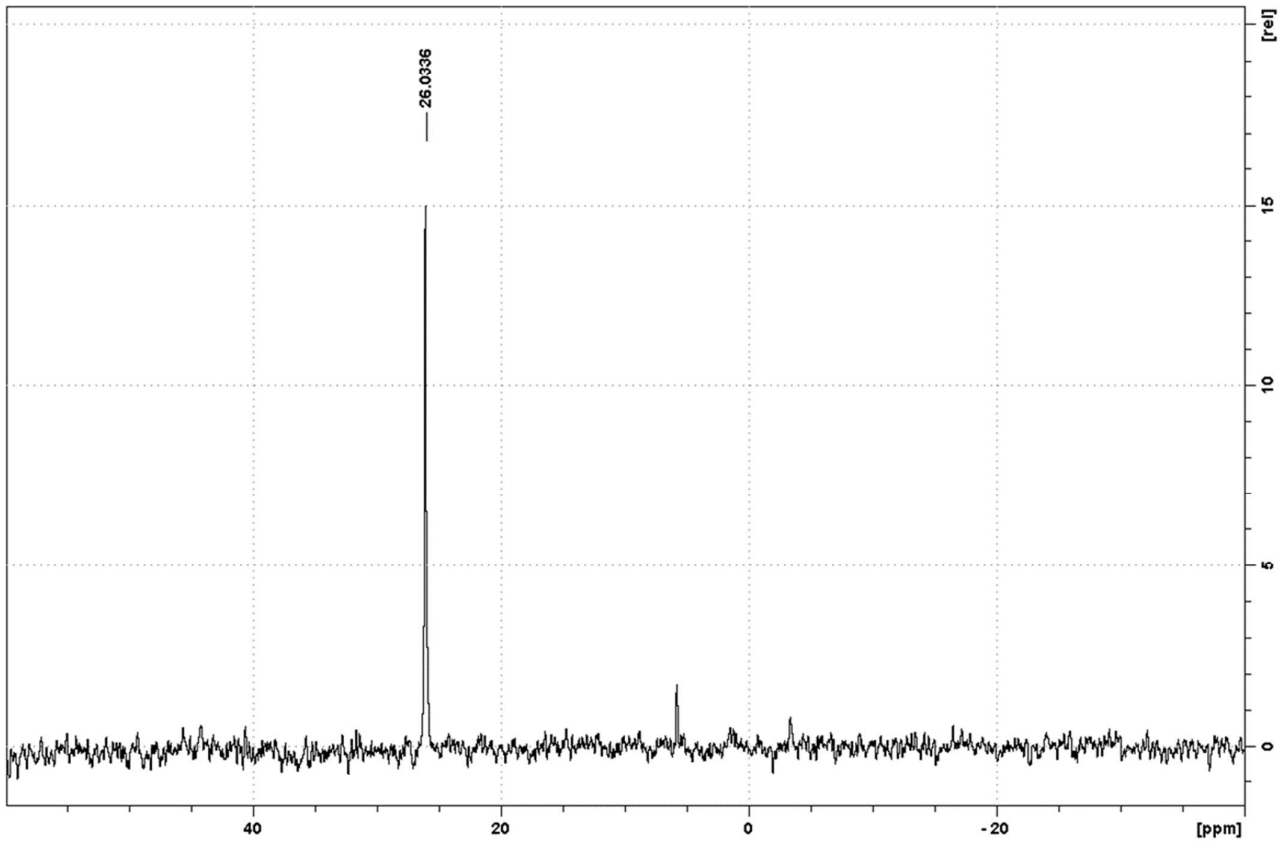

Figure S14. $^{31}P\{^{1}H\}$ spectrum of complex **7**

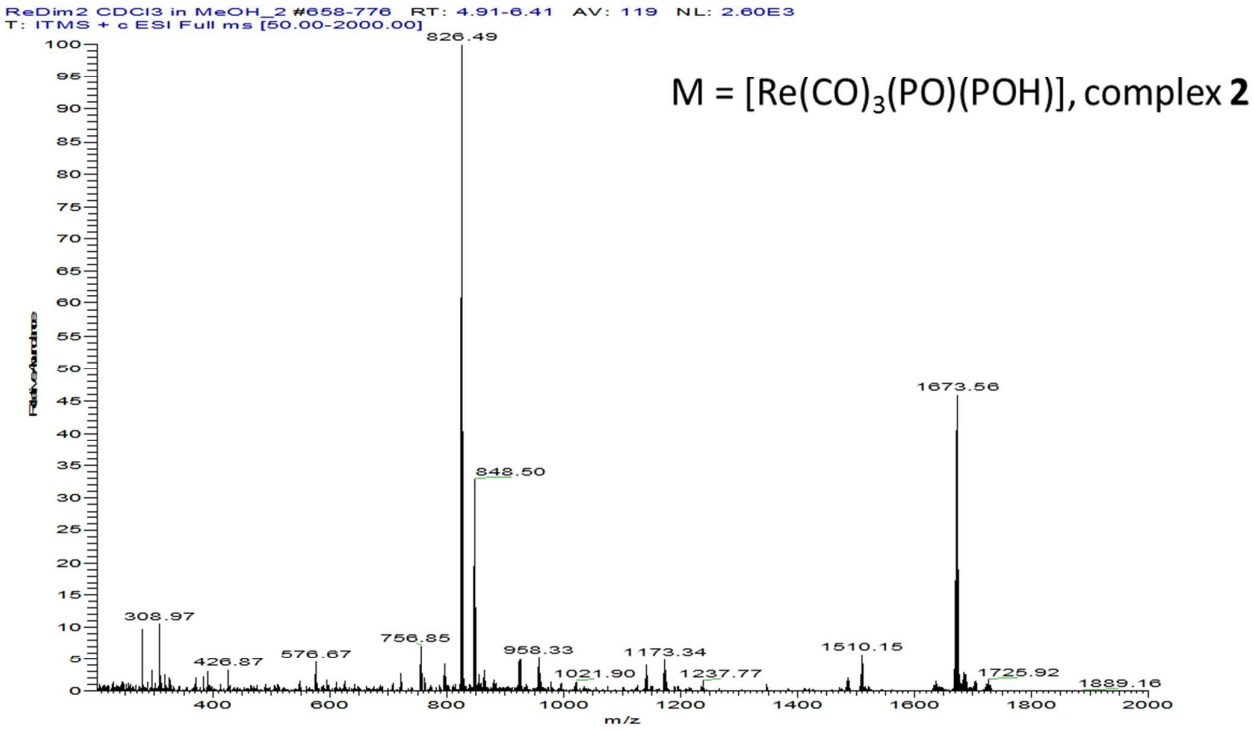

Figure S15. ESI(+)MS spectrum of complex **2**

M = $[Re(CO)_3(PO)(PPh_3)]$, complex **3**

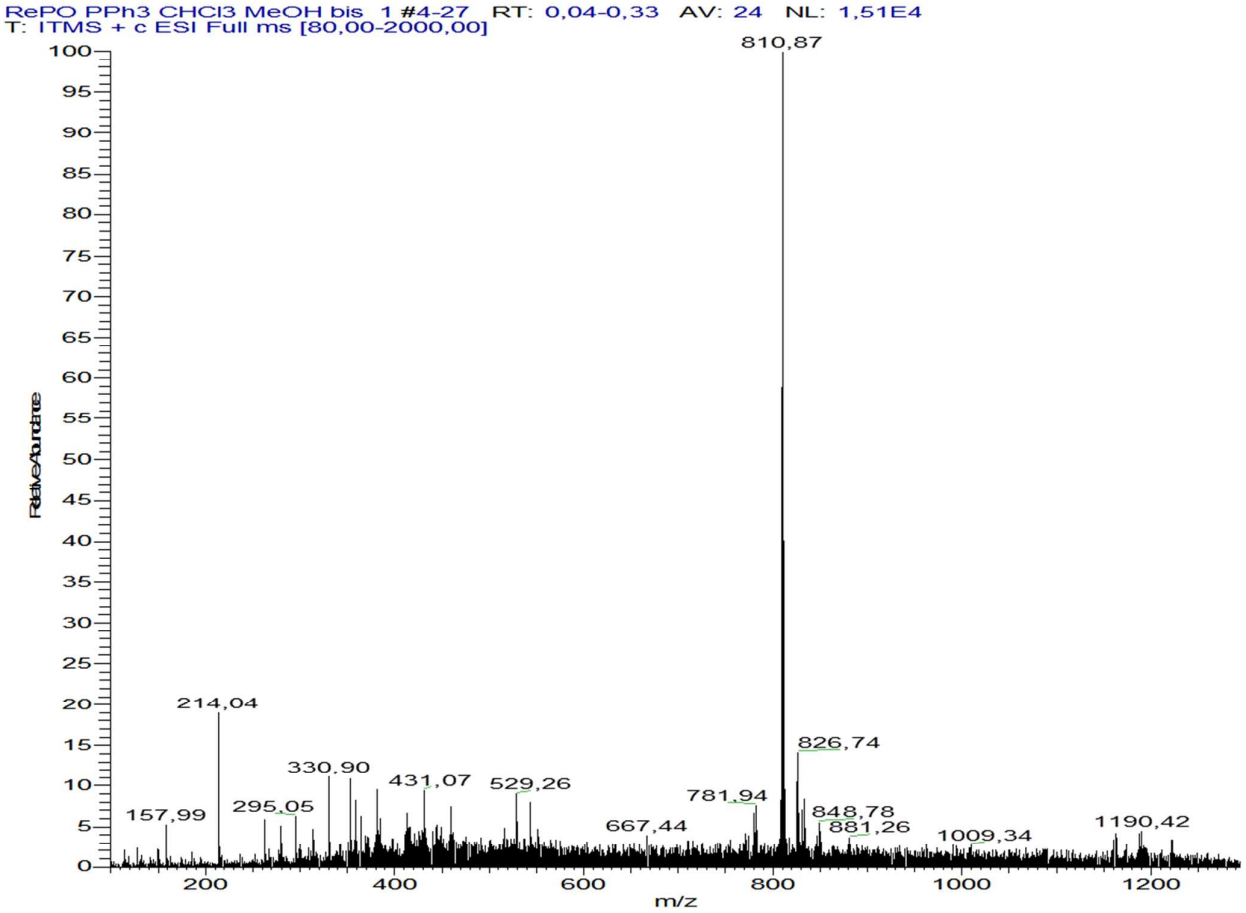

Figure S16. ESI(+)MS spectrum of complex **3**

M = [Re(CO)$_3$(PO)(im)], complex **4**

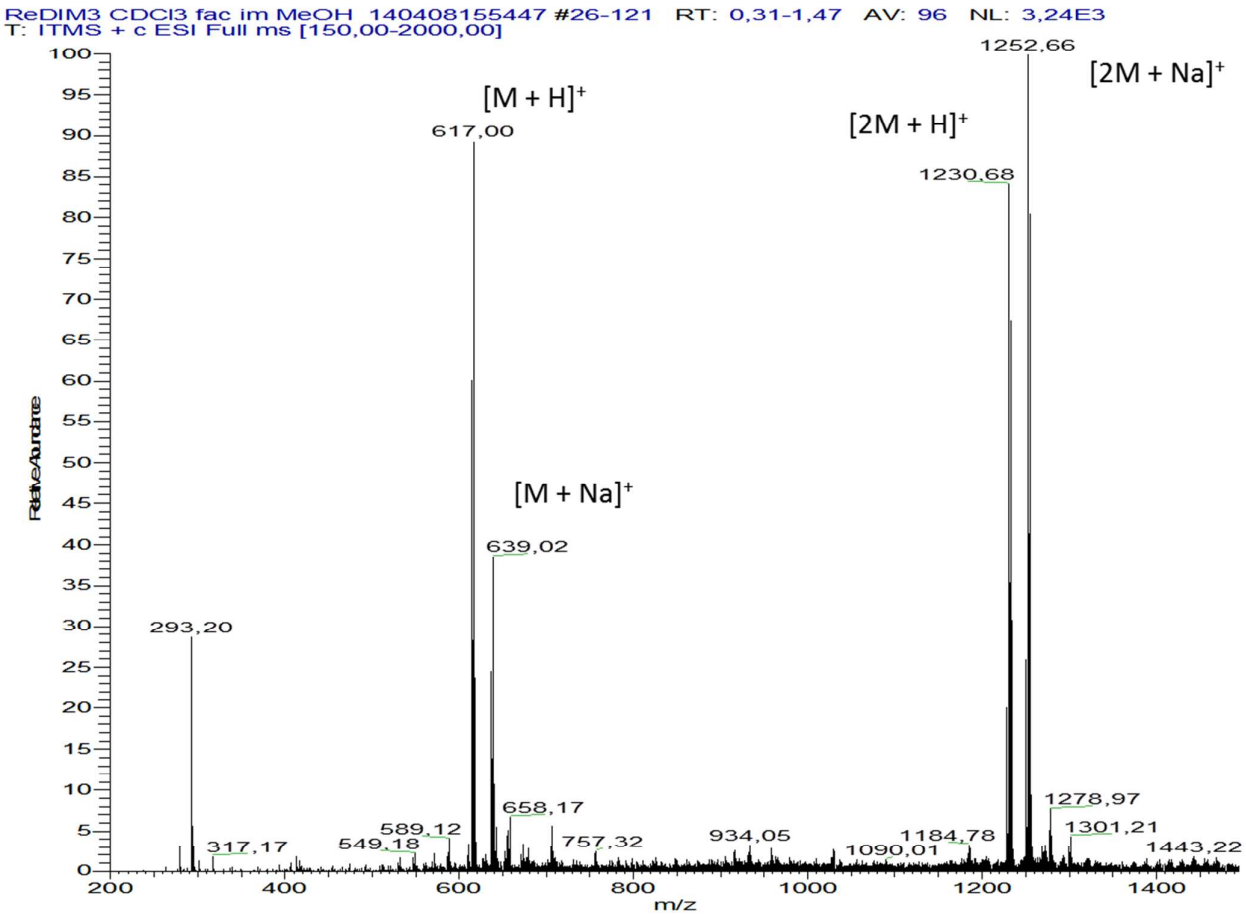

Figure S17. ESI(+)MS spectrum of complex **4**

M = [Re(CO)$_3$(PO)(py)], complex **5**

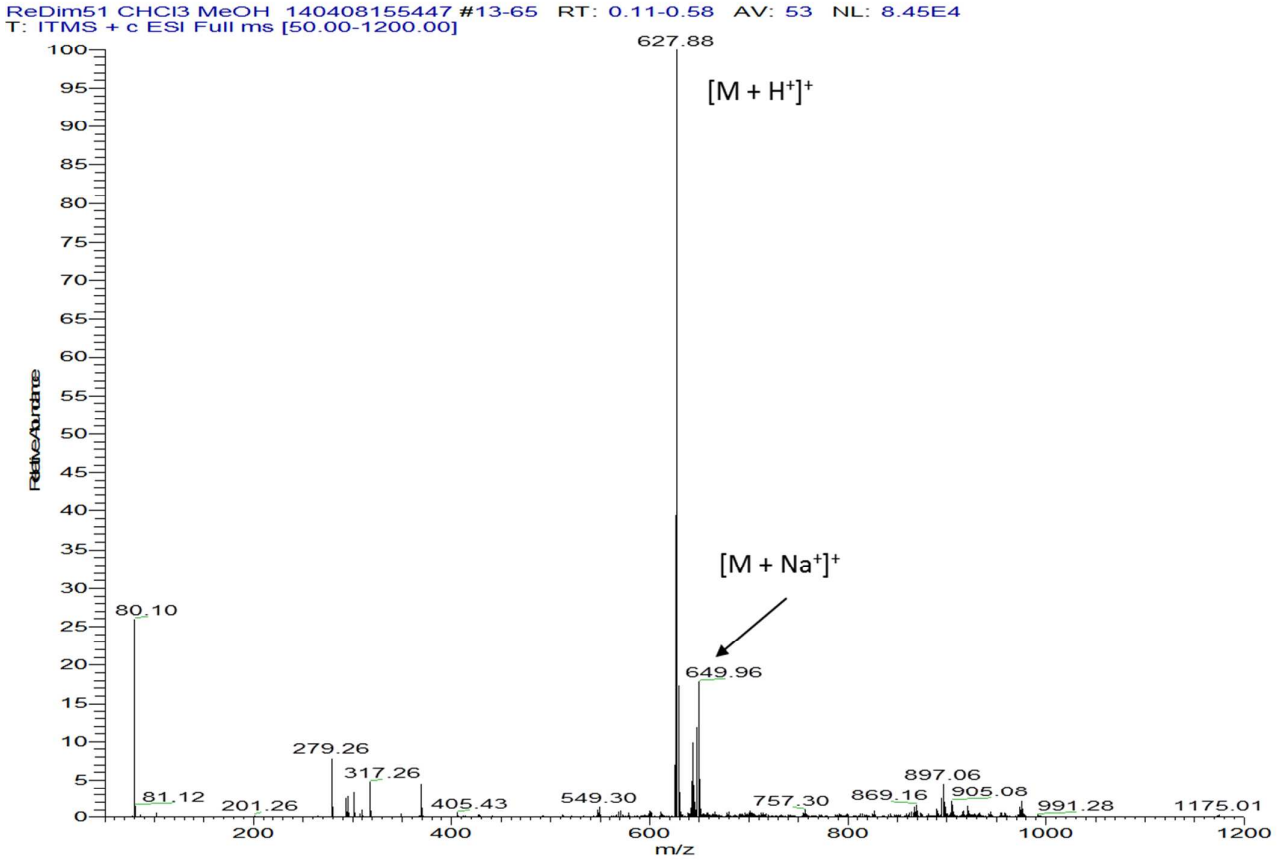

Figure S18. ESI(+)MS spectrum of complex **5**

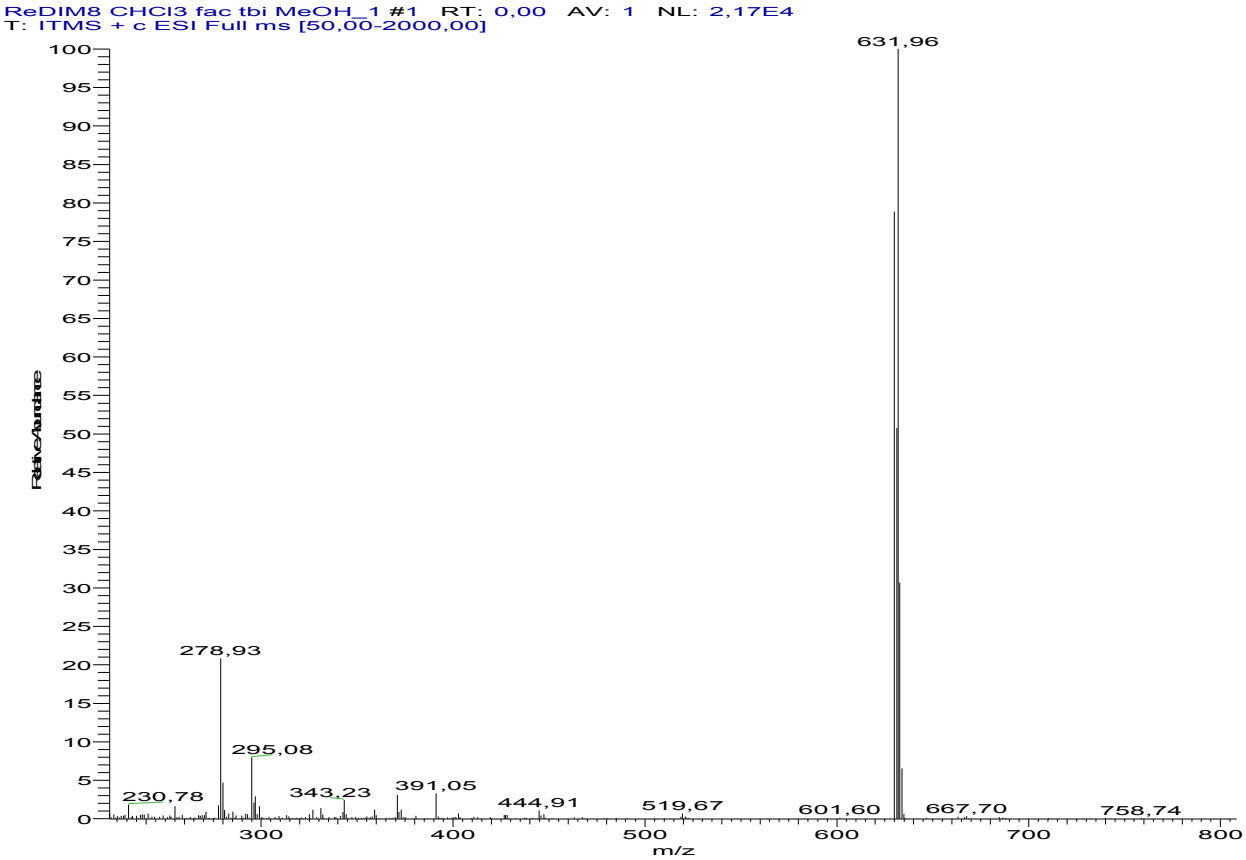

Figure S19. ESI(+)MS spectrum of complex **7**

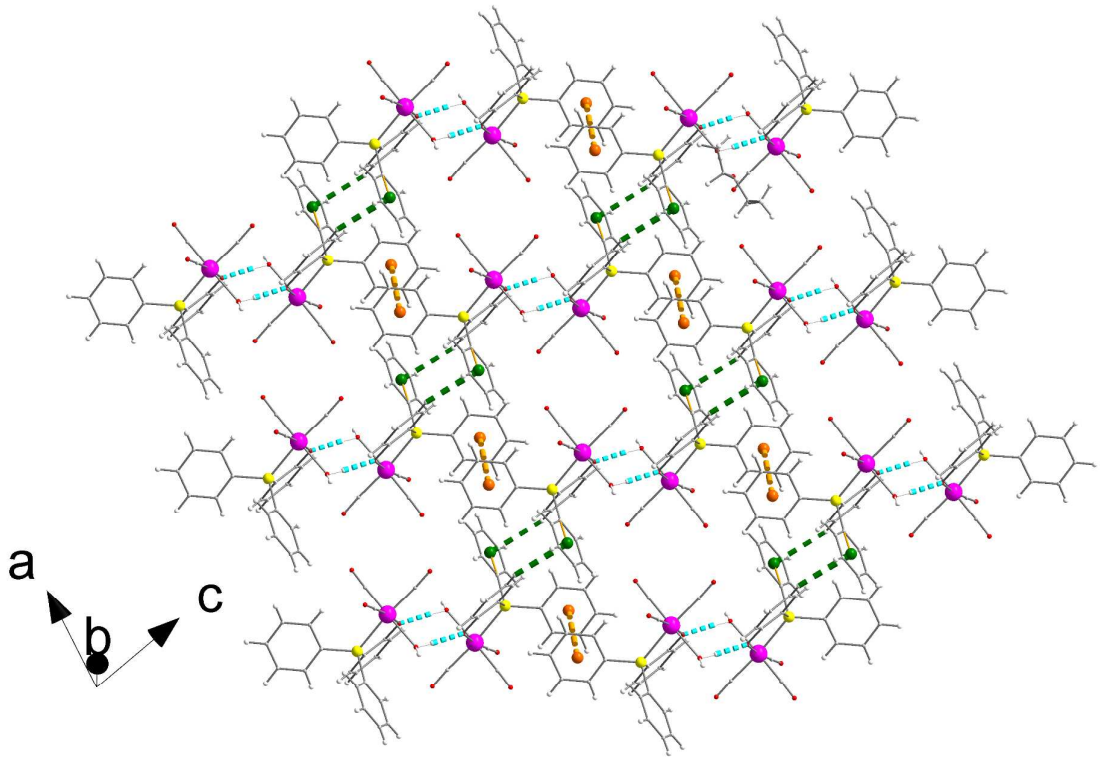

Figure S20. Layers of clusters in **1** parallel to the (010) plane. Dashed cyan, green and orange lines represent O1W-H1WA···O1, C15-H15···Cg1 (C-H···π) and π ···π intermolecular interactions between C7···C12 phenyl rings respectively.

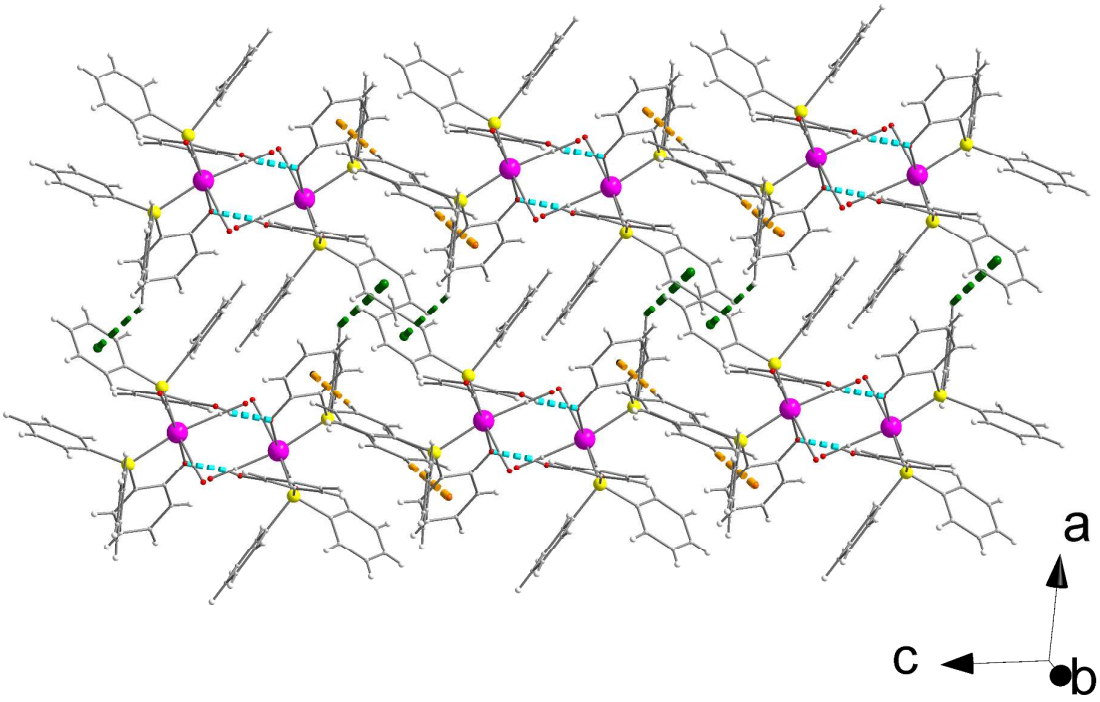

Figure S21. Layers of clusters in **2** parallel to the (010) plane. Dashed cyan, green and orange lines represent O2-H2O···O1, C3-H3···Cg1 and C11-H11···Cg2 (C-H···π) intermolecular interactions respectively.

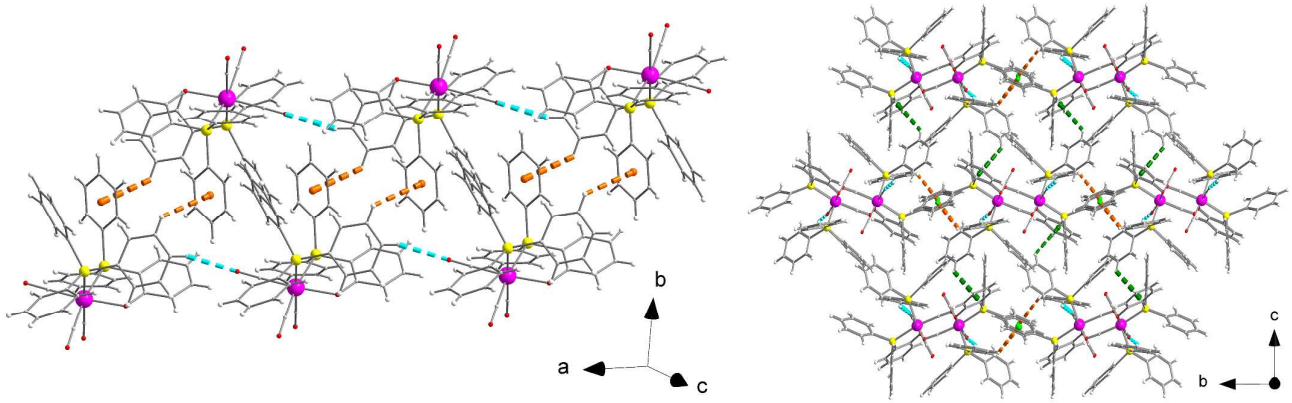

Figure S22. a) Chains of clusters in **3** parallel to the a axis. Dashed cyan and orange lines represent C22-H22···O3 hydrogen bond and C23-H23···Cg1 C-H···π intermolecular interactions. b) View of the structure down the a-axis where the packing of chain is shown, which interact through the C33-H33···Cg2 (dashed green lines) C-H-π type of intermolecular interactions and built the 3D structure.

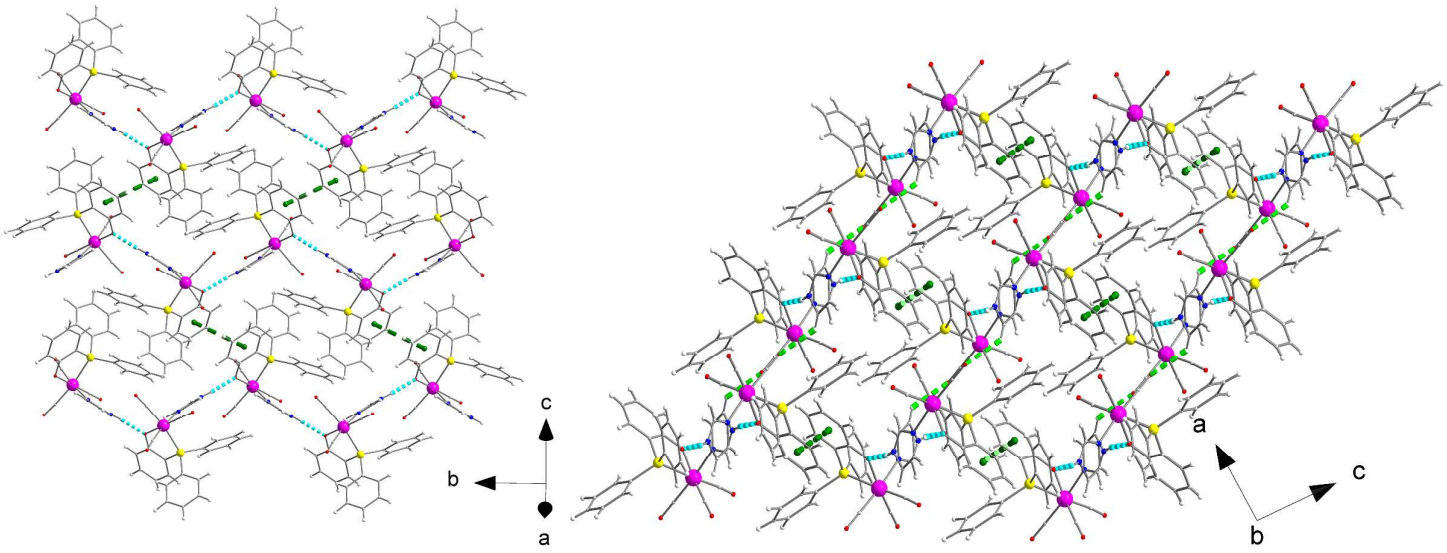

Figure S23. a) layers of clusters in **4** parallel to the (101) plane. Dashed cyan and green lines represent N2-H2N···O1 and π··· π intermolecular interactions of centrosymetrically related C13..C18 penyl rings . b) View of the structure down to –b axis where the packing of layers is shown which interact through the C20-H20···O2 (dashed light green lines) type of intermolecular interactions and built a 3D structure.

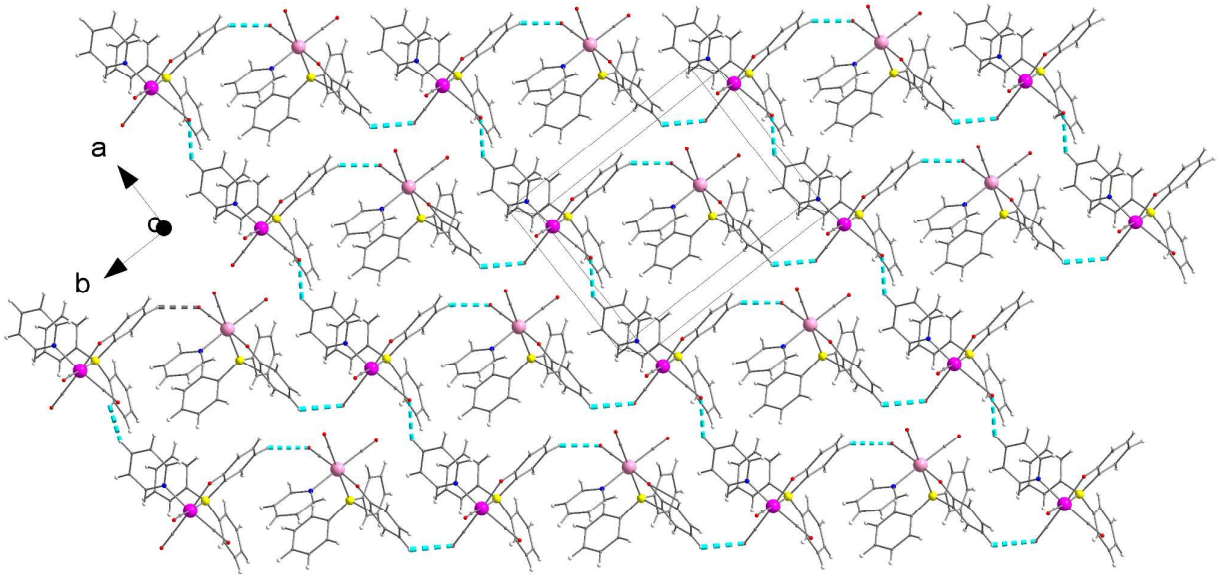

Figure S24. a) layers of clusters in 5 parallel to the (001) plane. Dashed cyan lines indicate C30-H30···O4, C4-H4···O7′ and C47-H47···O6″ hydrogen bond intermolecular interactions.

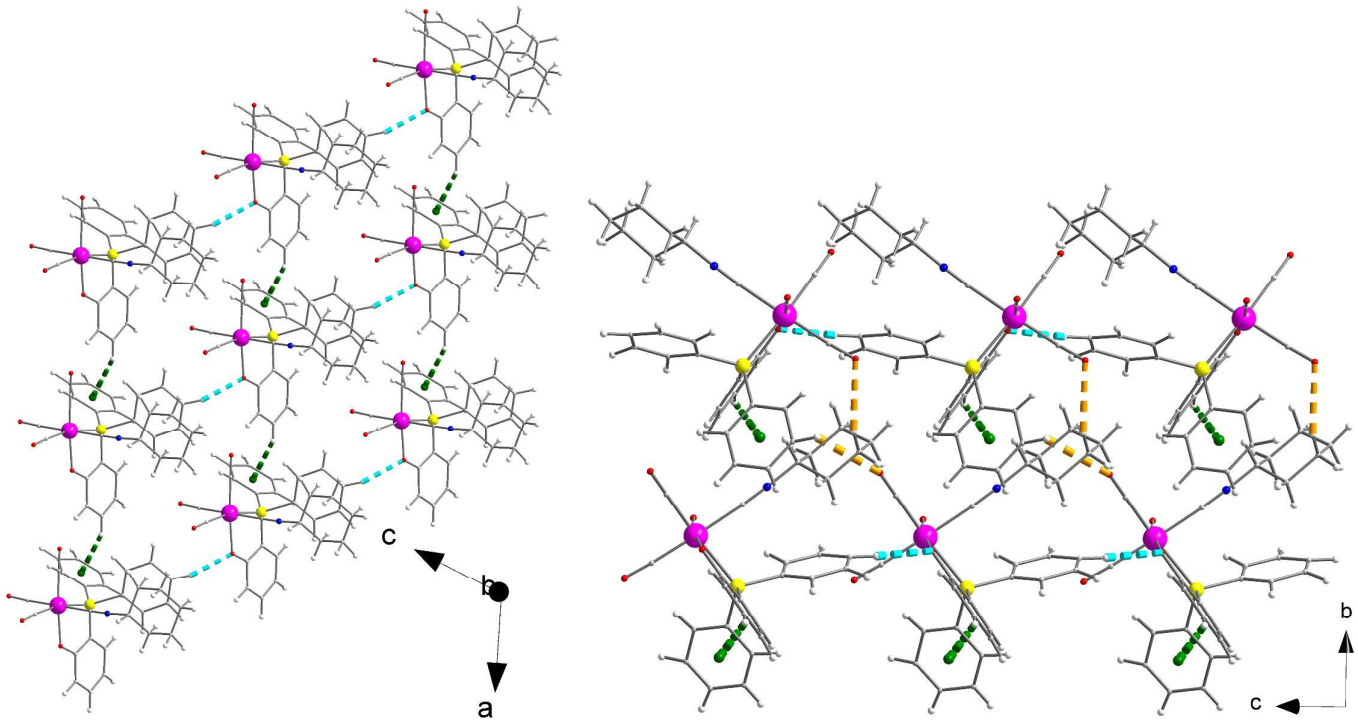

Figure S25. a) layers of clusters in **6** parallel to the (010) plane. Dashed cyan and green lines represent C10-H10···O1 hydrogen bond and C16-H16··· Cg1 C-H···π intermolecular interactions respectivelly. b) View of the structure down to –b axis where the packing of layers is shown which interact through the C3-H3···O4 and C22-H22A···O2 (dashed orange lines) hydrogen bond interactions and built a 3D structure.

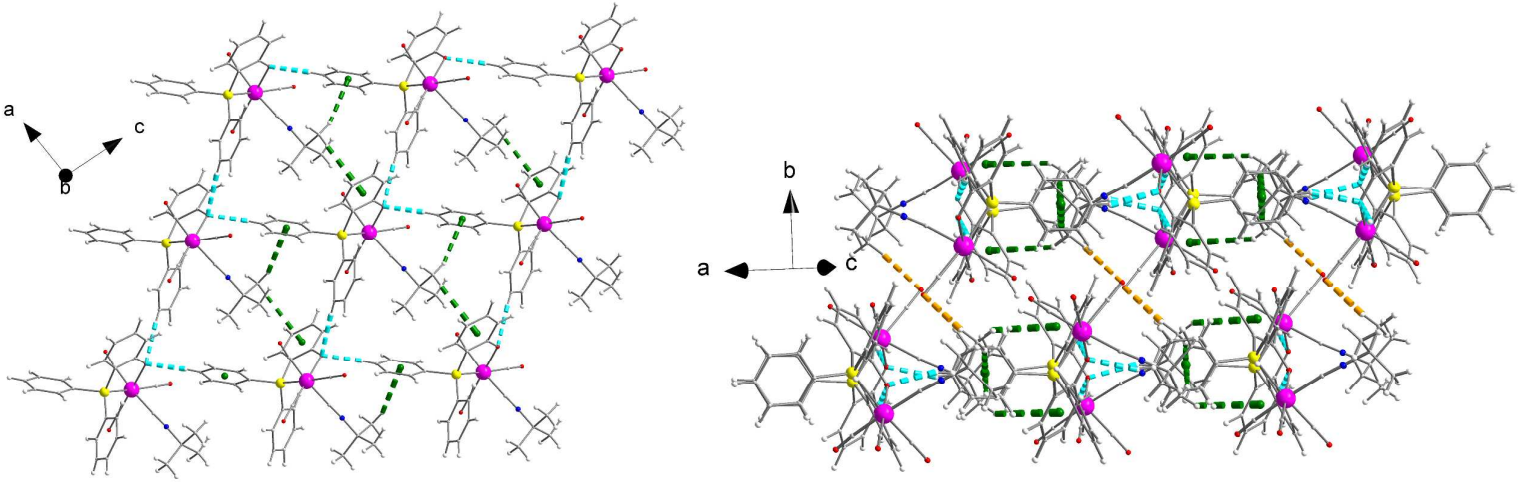

Figure S26. a) layers of clusters in **7** parallel to the (010) plane. Dashed cyan and green lines represent C10-H10···O1, C15-H15···O1 hydrogen bonds and C23-H23C··· Cg1 , C23-H23A···Cg2 C-H···π intermolecular interactions. b) View of the structure along [101] direction where the packing of layers is shown which interact through the C23-H23B···O4 (dashed orange lines) hydrogen bond interactions and built a 3D structure.

	1·Et$_2$O	**2**	**3**	**4**
Formula	$C_{25}H_{26}O_6PRe$	$C_{39}H_{29}O_5P_2Re$	$C_{39}H_{29}O_4P_2Re$	$C_{24}H_{18}N_2O_4PRe$
Fw	639.63	825.76	809.76	615.57
Space group	*P*-1	*P*-1	$P2_1/c$	$P2_1/n$
a (Å)	9.8210(2)	10.7557(2)	11.7525(4)	9.7316(2)
b (Å)	11.5130(2)	11.7493(2)	13.5609(4)	12.8414(2)
c (Å)	12.9106(2)	12.9340(2)	21.0785(8)	17.3759(3)
α (^{o})	70.140(1)	94.423(1)	90.0	90.0
β (^{o})	76.997(1)	97.438(1)	98.856(1)	93.226(1)
γ (^{o})	70.219(1)	92.536(1)	90.0	90.0
V (Å^3)	1281.93(4)	1613.48(5)	3319.3(2)	2167.98(7)
Z	2	2	4	4
T (ºC)	25	-113	-113	-103
Radiation	Cu Kα	Cu Kα	Mo Kα	Cu Kα
$2\theta_{max}$ (^{o})	130	130	54	130
Reflections collected/unique/used	34585/4126 [R_{int} = 0.0260]/4126	40015/5197 [R_{int} = 0.0717]/5197	34025/7199 [R_{int} = 0.0613]/7199	17325/3520 [R_{int} = 0.0425]/3520
ρ_{calcd} (g cm^{-3})	1.657	1.700	1.620	1.886
μ (mm^{-1})	10.167	8.678	3.798	11.958
Reflections with $I>2\sigma(I)$	4035	5028	5698	3388
Parameters refined	357	540	515	349
$(\Delta/\sigma)_{max}$	0.005	0.005	0.003	0.002
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ (e/Å^3)	1.089/-0.943	1.132/-1.443	2.931/-1.417	1.636/-0.833
R_1/wR_2 (for all data)	0.0244/0.0609	0.0292/0.0668	0.0568/0.0971	0.0323/0.0764
R_1/wR_2[a] (for $I>2\sigma(I)$)	0.0237/0.0604	0.0284/0.0662	0.0418/0.0903	0.0310/0.0753

Table S1a. Crystallographic data for **1 – 4**

[a] $w=1/[\sigma^2(F_o^2)+(\alpha P)^2+bP]$ and $P = [\max(F_o^2,0)+2F_c^2]/3$; $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S1b. Crystallographic data for **5** – **7**

	5	**6**	**7**
Formula	$C_{26}H_{19}NO_4PRe$	$C_{28}H_{25}NO_4PRe$	$C_{26}H_{23}NO_4PRe$
Fw	626.59	656.66	630.62
Space group	$P2_12_12_1$	$P2_1$	$P2_1/n$
a (Å)	10.8416(2)	9.1368(2)	10.3645(2)
b (Å)	14.0100(3)	16.4414(3)	14.9455(3)
c (Å)	30.9594(6)	9.3599(2)	16.3314(3)
α (^{o})	90.0	90.0	90.0
β (^{o})	90.0	113.620(1)	95.448(1)
γ (^{o})	90.0	90.0	90.0
V (Å^3)	4702.45(16)	1288.26(5)	2518.35(8)
Z	8	2	4
T (ºC)	-93	-113	-113
Radiation	Cu Kα	Cu Kα	Cu Kα
$2\theta_{max}$ (^{o})	130	134	130
Reflections collected/unique/used	60110/7735 [R_{int} = 0.0574]/7735	20165/4366 [R_{int} = 0.0949]/4366	33198/4195 [R_{int} = 0.0687]/4195
ρ_{calcd} (g cm^{-3})	1.770	1.693	1.663
μ (mm^{-1})	11.027	10.091	10.296
Reflections with $I>2\sigma(I)$	7617	4324	4040
Parameters refined	703	317	368
$(\Delta/\sigma)_{max}$	0.010	0.001	0.005
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ (e/Å^3)	1.075/-1.520	2.378/-1.292	1.498/-1.229
R_1/wR_2 (for all data)	0.0288/0.0658	0.0468/0.1126	0.0314/0.0731
R_1/wR_2[a] (for $I>2\sigma(I)$)	0.0281/0.0654	0.0466/0.1123	0.0302/0.0721

[a] $w=1/[\sigma^2(F_o^2)+(\alpha P)^2+bP]$ and P = [max $(F_o^2,0)+2F_c^2]/3$; $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)$

Table S2. Retention times (t_R) of Re and ^{99m}Tc complexes

Complex	**M = Re (t_R min)**	**M = ^{99m}Tc (t_R min)**
fac-[M(CO)$_3$(PO)(H$_2$O)]	26.9	28.0
fac-[M(CO)$_3$(PO)(POH)]	41.5	42.0
fac-[M(CO)$_3$(PO)(PPh$_3$)]	42.9	43.3
fac-[M(CO)$_3$(PO)(im)]	29.3	30.0
fac-[M(CO)$_3$(PO)(py)]	34.4	35.0
fac-[M(CO)$_3$(PO)(cisc)]	38.4	39.6
fac-[M(CO)$_3$(PO)(tbi)]	37.2	38.0

Table S3. Stability of **1´ - 7´** complexes during histidine and cysteine challenge assays

Complex	**Histidine (% intact)**			**Cysteine (% intact)**		
	1 h	**3 h**	**6 h**	**1 h**	**3 h**	**6 h**
***fac*-[^{99m}Tc(CO)$_3$(PO)(H$_2$O)], 1´**	97 ± 2	97 ± 2	96 ± 1	98 ± 2	97 ± 1	96 ± 1
***fac*-[^{99m}Tc(CO)$_3$(PO)(POH)], 2´**	98 ± 2	97 ± 2	97 ± 2	98 ± 1	98 ± 1	97 ± 2
***fac*-[^{99m}Tc(CO)$_3$(PO)(PPh$_3$)], 3´**	97 ± 2	97 ± 1	96 ± 1	98 ± 1	97 ± 2	97 ± 1
***fac*-[^{99m}Tc(CO)$_3$(PO)(im)], 4´**	97 ± 2	97 ± 1	96 ± 1	98 ± 2	98 ± 2	96 ± 1
***fac*-[^{99m}Tc(CO)$_3$(PO)(py)], 5´**	98 ± 1	97 ± 2	96 ± 1	96 ± 1	96 ± 1	96 ± 1
***fac*-[^{99m}Tc(CO)$_3$(PO)(cisc)], 6´**	98 ± 1	98 ± 1	98 ± 1	98 ± 2	98 ± 1	97 ± 2
***fac*-[^{99m}Tc(CO)$_3$(PO)(tbi)], 7´**	98 ± 1	97 ± 2	97 ±	98 ± 1	97 ± 2	97 ± 1