Supporting information

Synthesis and magnetic properties of manganese carbonyl complexes with different coordination modes of 3,4,5-triaryl-1,2-diphospholide ligand

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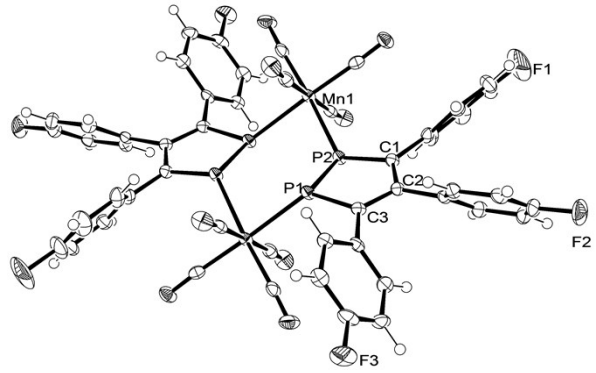

Figure 1S. ORTEP drawing of bis-(μ,η^1:η^1-3,4,5-tris-(*para*-fluorophenyl)-1,2-diphosphacyclopentadienide)-bis-(tetracarbonylmanganese(I)) (**2b**). Selected bond lengths (Å) and angles (°): Mn1-P1 2.3661(8); Mn1-P2 2.3675(8); P1-P2 2.112(1); P1-C3 1.750(3); P2-C1 1.750(3); C1-C2 1.416(3); C2-C3 1.396(4); C3-P1-P2 94.6(1); P2-P1-Mn1 123.11(3); C3-P1-Mn1 125.72(9); C1-P2-P1 94.59(9); P1-P2-Mn1 122.42(4); C1-P2-Mn1 125.51(9).

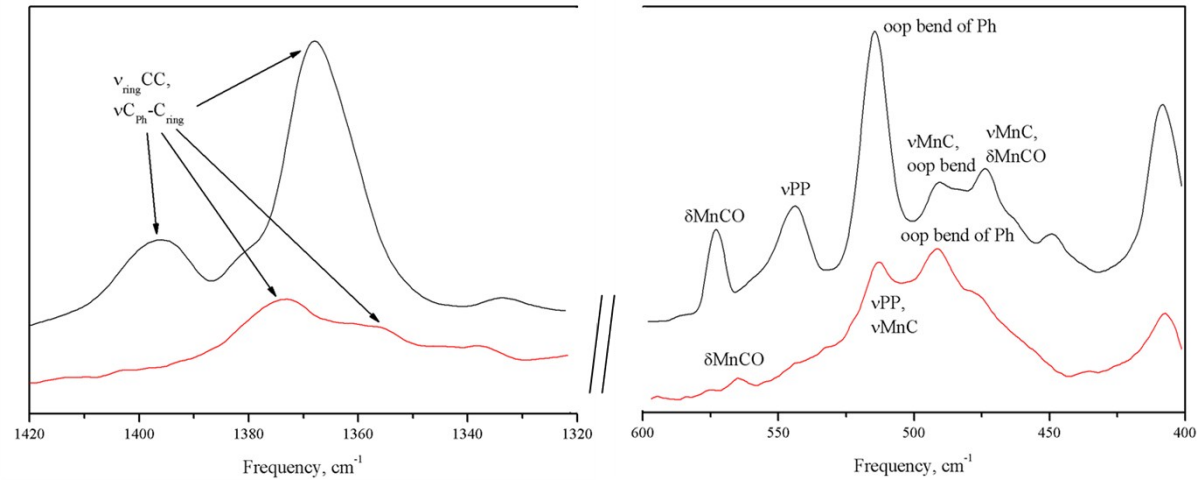

Figure 2S. Comparison of experimental Raman spectra of **2a** (black) and **3a** (red). The bands are assigned on the basis of DFT spectra simulations: ν (stretching), δ (bending), oop bend (out-of-plane bending) vibrations.

Table 1S: Scaling factors for the force fields of compounds **2a** and **3a**.

scaling factor		value
stretch	CC, CO	0.9207 [a]
stretch	CH	0.915 [b]
stretch	CP, PP	1.040 [c]
stretch	CMn, MnP	1.0
bend	CCC, PCC	1.0144 [a]
bend	PPC	1.070 [c]
bend	CCH	0.950 [a]
torsion	all	0.9523 [a]
out of plane	ring-H, ring-C	0.976 [a]

[a] Baker, J.; Jarzecki, A.; Pulay, P. *J. Phys. Chem. A* **1998**, *102*, 1412-1424.
[b] Katsyuba, S. A.; Grunenberg, J.; Schmutzler, R. *J. Mol. Struct*. **2001**, *559*, 315-320.
[c] Katsyuba, S. A.; Vandyukova, E. E. *Chem. Phys. Lett.* **2003**, *377*, 658-662

Table 2S: Calculated and experimental vibrational spectra of **2a.**

Experiment		**Computations**		
IR, solid	Raman, solid		I_{IR}	Assignment[c]
ν (cm^{-1}), I[a]	ν (cm^{-1}), I[a]	ν (cm^{-1})[b]	km/mole	
3078 sh				Ph: ν_{ar}CH
3057 vw	3061 m	3079; 3079; 3079; 3079; 3072; 3072; 3069; 3069; 3069; 3069; 3066; 3066; 3060; 3060; 3060; 3060; 3060; 3060; 3051; 3051; 3051; 3051; 3050; 3050	5; 19; 10; 8; 0; 48; 0; 45; 68; 0; 32; 15; 0; 49; 34; 0; 10; 53; 4; 10; 5; 0; 5; 4	Ph: ν_{ar}CH
3026 vw	3024 sh vw	3044; 3044; 3044; 3044; 3042; 3042	0; 5; 7; 0; 0; 3	Ph: ν_{ar}CH
2135 vvw	2140 w			
	2115 vw			
2092 sh	2088 m	2073	0	ν_sCO
2077 s	2076 w	2066	1221	ν_sCO
2047 s, sh	2023 w	2022; 2020; 2018;	0;1230; 1145;	ν_{as}CO
2010 vs	2014 vw	2012; 2008; 2007	0; 1074; 0	ν_{as}CO
	2004 w			
1985 vs, sh	1990 w			
1954 sh;	1979 w			
1914 s, sh				
1646 vvw	1634 sh			
1597 vw	1598 vs	1604; 1604; 1601; 1601; 1600; 1600	0; 26; 0; 5; 8; 0	Ph: νCC, δCCH
1575 vvw	1577 vw	1580; 1580;	4; 0;	Ph: νCC, δ CCH
1556 vvw		1576; 1576; 1575; 1575	0; 1; 9; 0	
1538 vw				
1520 vvw				
1490 w	1492 w	1505; 1505; 1502; 1502; 1500; 1500	0; 34; 0; 0; 35; 0	Ph: νCC, δCCH, $\nu C_{Ph}C_{lig}$
1444 w	1446 vw	1455; 1455; 1455; 1455; 1451; 1451	3; 0; 0; 3; 14; 0	Ph: νCC, δCCH
1411 vw	1396 vw	1378; 1378	0; 4	$\nu C_{Ph}C_{lig}$, ν_sCC (ligand)
	1368 m	1356; 1356	46; 0	$\nu C_{Ph}C_{lig}$, ν_{as}CC (ligand)
	1334 vw	1328; 1328; 1327; 1327	3; 0; 0; 0	Ph: δCCH, νCC
	1312 vw	1324; 1324	2; 0	Ph: δCCH, νCC
	1293 w	1286; 1286; 1284; 1284; 1279; 1279	0; 0; 2; 0; 11; 0	Ph: νCC, $\nu C_{Ph}C_{lig}$
1260 m	1275 vw	1270; 1270	0; 0	Ph: νCC, $\nu C_{Ph}C_{lig}$
1179 w	1183 w	1183; 1182; 1182; 1181; 1180; 1179; 1179; 1178	33; 0; 1; 0; 15; 0; 2; 0	Ph: νCC, δCCH, $\nu C_{Ph}C_{lig}$, ligand: ν_{as}CC
1154 w	1159 vw	1160; 1160; 1160; 1159; 1159; 1159	0; 0; 0; 0; 0; 0	Ph: δCCH, νCC
	1146 w	1148; 1148	1; 2	$\nu C_{Ph}C_{lig}$,

				Ph: νCC, δCCC, ligand: νCC, νPC
1095 m	1109 vvw	1089; 1089	16; 0	Ph: νCC, δCCH,
1078 m	1076 vvw	1083; 1083; 1083; 1083	3; 0; 0; 1	Ph: νCC, δCCH
1028 m	1033 w	1038; 1038;	0; 0;	Ph: νCC, δCCH
		1033; 1033; 1032; 1032	20; 0; 0; 10	
	1003 s	1006; 1006;	0; 7;	Ph: δCCC
	990 sh	999; 999; 998; 998	0; 4; 0; 5	
	971 vw	979; 979; 979; 979;	1; 0; 0; 1;	Ph: out-of-plane
		978; 978	0; 0	
	962 vw	967; 966; 966; 965;	0; 1; 19; 0;	Ligand: ν_sPC, ν_{as}PC
		955; 955; 954; 954;	0; 0; 6; 0;	Ph: δCCC, νCC
		953; 953	0; 0	Ph: out-of-plane
	929 vvw, br	917; 917; 915; 915	2; 0; 0; 11	Ph: out-of-plane
913 vw	915 vvw	910; 909	20; 0	Ph: out-of-plane H, Ligand: ν_{as}PC
867 vw		849; 849; 847; 847;	0; 0; 0; 0;	$\nu C_{Ph}C_{lig}$,
		845; 845;	5; 0;	Ph: out-of-plane, νCC
	841 w	843; 842	0; 1	Ligand: ν_sPC
797 m	791 vvw	794; 793	51; 0	Ph: out-of-plane, $\nu C_{Ph}C_{lig}$
	769 vw	772; 772	9; 0	Ph: out-of-plane
757 w	757 sh vvw	763; 762	0; 59	Ph: out-of-plane
727 vw		734; 733	65; 0	Ph: out-of-plane, $\nu C_{Ph}C_{lig}$
				Ligand: ν_{as}PC
698 m	692 vvw	706; 706; 700; 700;	21; 0; 0; 58;	Ph: out-of-plane,
		699; 699;	54; 0;	Ligand: out-of-plane
		697; 697	2; 0	
		682; 677	0; 370	δMnCO, δCMnC ν_sMnC
	663 vvw	670; 670	0; 0	Ph: δCCC
				Ligand: ν_sPC
648 m	652 sh	657; 656; 652; 644;	0; 121; 407; 0;	δCMnC, δMnCO,
		642; 642	0; 5	νMnC
				Ph: δCCC, Ligand: νPC, δCCC
627 s	622 vw	630; 630; 630; 630;	1; 0; 0; 2;	Ph: δCCC, δCCH,
		626; 626	0; 0	out-of-plane
575 vvw	573 vw	588; 586;	2; 0;	Ph: δCCC, Ligand δPCC
		583; 582;	0; 0;	δCMnC, δMnCO
		580; 576;	0; 0;	Out-of-plane lig ν_sPP, ν_{as}PP
		569; 568	0; 11	δMnCO, δCMnC
542 vw	544 vw	547; 541	0, 19	ν_sPP, ν_{as}PP
511 vw	514 w	520; 519; 511; 510	5; 0; 3; 0	Out-of-plane lig-Ph ν_{as}PC,
				Ph: tors CC
491 vw	491 vw	495; 495;	0; 29;	Out-of-plane lig-Ph Ph: tors CC,
				νPC, νMnC
		494; 489	0; 6	νMnC, δMnCO

		482; 481	18; 0	νMnC
	474 vw	470; 466	37; 0	νMnC, δMnCO, δPMnC
	449 vvw	457; 455; 453; 446	0; 2; 1; 0	νMnC, δMnCO
				νPC, $\delta_{Ph\text{-}lig}$CCC, δCPP, νMnP
423 vvw		426; 425; 424; 424	5; 0; 0; 3	νMnC, δMnCO
	408 w	410; 410; 410; 409; 408; 408	0; 2; 0; 0; 0; 0	Ph: tors CC
	385 vw	400; 399	0; 8	ν_sMnC
	357 vvw	367; 364	5; 0	[c]
		350	0	[c]
		344	0	[c]
	300 vw	313; 297	16; 0	[c]
	261 w	267; 265; 257; 254	0; 0; 0; 30	[c]
	241 w	236; 236; 235; 231	0; 0; 0; 34	[c]
	220 w	210; 210	0; 5	[c]
	176 w	185	2	[c]
	160 w	167; 165; 162	0; 0; 0	[c]

[a]w, weak; m, medium; s, strong; v, very; sh, shoulder; br, broad.
[b]ν, stretch; δ, bend; s, symmetrical; as, antisymmetrical.
[c]complex vibration involving the whole molecule

Table 3S: Calculated and experimental vibrational spectra of **3a.**

Experiment		**Computations**		
IR, solid	Raman, solid		I_{IR}	Assignment[c]
ν (cm^{-1}), I[a]	ν (cm^{-1}), I[a]	ν (cm^{-1})[b]	km/mole	
3057 m	3060 s	3058;	2;	Ph: ν_{ar}CH
3025 m	3025 w sh	3040; 3036; 3030; 3029; 3028; 3022; 3021; 3020; 3012; 3012; 3011; 3003; 3003; 3003	4; 7; 13; 27; 28; 32; 21; 22; 5; 9; 6; 2; 0; 1	Ph: ν_{ar}CH
2020 vs	2023 w	2007	996	ν_sCO
1951 vs br	1956 w br	1968; 1949	639; 650	ν_{as}CO
1598 w	1599 vs	1605; 1604; 1603	2; 2; 1	Ph: νCC, δCCH
1577 vw sh	1578 w	1582; 1580; 1579	3; 1; 4	Ph: νCC, δCCH
1490 m	1494 w	1507; 1504; 1503	9; 4; 12	Ph: νCC, δCCH, $\nu C_{Ph}C_{lig}$
1443 m	1443 vw	1457; 1455; 1454	2; 1; 12	Ph: νCC, δCCH
1370vw	1373 w	1369	11	ν_{lig}CC, $\nu C_{Ph}C_{lig}$
	1359 vw	1344; 1331; 1329	6; 4; 1	ν_{lig}CC, $\nu C_{Ph}C_{lig}$,
	1338 vw			Ph: νCC, δCCH
	1311 vw	1325	2	ν_{lig}CC, $\nu C_{Ph}C_{lig}$, Ph: νCC, δCCH
	1287 w	1288; 1284; 1282	1; 2; 2	Ph: νCC
1261 m	1272 w	1255	1	$\nu C_{Ph}C_{lig}$
	1203 w			
	1194 w	1186; 1185; 1184;	1; 3; 2	Ph: νCC, δCCH,
1177 vw	1184 w	1172;	3	$\nu C_{Ph}C_{lig}$, ν_{ligas}CC
	1159 w	1161; 1161; 1161	0; 0; 0	Ph: δCCH, νCC
	1142 vw	1132	0	$\nu C_{Ph}C_{lig}$, ν_{lig}CC, Ph: νCC
	1128 vw			
1096 m		1092; 1088; 1085	10; 0; 1	Ph: νCC, δCCH
1079 m				
1027 m	1033 w	1038; 1034; 1032	0; 5; 3	Ph: νCC, δCCH
	1003 s	1004; 1000; 999	2; 0; 3	Ph: νCC, δCCC
	990 vw	983; 982; 981	0; 0; 0	Ph: out-of-plane, tors: CC
	968 vvw	964; 957; 956; 956; 954	2; 0; 1; 0; 5	Ph: νCC, δCCC, Ligand: νPC, δCCC
913 vw	935 vvw	923; 921; 913	1; 1; 0	Ph: out-of-plane, tors: CC
	909 vvw			
867 vw	869 vvw	847; 846; 845; 835	0; 0; 1; 1	Ligand: νPC, Ph: δCCC
	842 vw			
802 m	787 vvw	794	10	Ph: out-of-plane, $\nu C_{Ph}C_{lig}$
756 w	766 vvw	770; 764	5; 24	Ph: out-of-plane
	754 vvw			
	729 vvw	735	29	Ph: out-of-plane
698 s	710 vvw	702; 700; 700	24; 15; 32	Ph: out-of-plane, tors
652 m	659 vw	682; 666; 661; 649	114; 12; 0; 40	δMnCO, νMnC; $\delta PC_{lig}C_{Ph}$, $\delta MnC_{lig}C_{Ph}$, $\delta C_{lig}C_{Ph}C_{Ph}$, Ph: δCCC

	635 vvw	639; 636; 631; 629	48; 11; 5; 1	δMnCO, νMnC, Ph: δCCC
618 m	621 vw	623; 592; 572	2; 11; 10	$\delta MnC_{lig}C_{Ph}$, νMnC, Ph: δCCC
	560 vvw	553	10	νMnC, Ph: out-of-plane
527 w		538; 532	25; 26	Ph: out-of-plane, tors, νPP, νMnC
	513 w	512; 506	0; 7	Ph: out-of-plane, tors, νPP, νMnC
494 vw	491 w	498; 493	1; 4	νMnC, νPP, νPC, Ph: out-of-plane
462 vw	478 vw sh 457 vvw sh	477; 476; 463	2; 2; 4	νMnC, δMnCO, $\delta MnC_{lig}C_{Ph}$
	408 vvw	418; 411; 409; 405	0; 0; 0; 0	δMnCO, Ph: tors
	343 vw	366; 335	1; 2	$\delta C_{lig}C_{lig}C_{Ph}$, $\delta MnC_{lig}C_{Ph}$, $\nu C_{lig}C_{Ph}$
	260 w	281; 262; 255	1; 0; 0	$\delta PC_{lig}C_{Ph}$, $\delta C_{lig}C_{Ph}C_{Ph}$, $\nu C_{lig}C_{Ph}$, Ligand: δPCC
	238 w	239; 231	0; 0	νMnP, Ph: out-of-plane
	220 w	225; 214	0; 0	νMnP, $\nu C_{lig}C_{Ph}$
	201 w	192	1	νMnC

[a,b,c]See footnotes for Table 2S.

Table 4S. Selected bond lengths and angles in **2a**.

Bond lengths (Å)					
P2-C1	1.741[a]	1.764[b]	P2-C3	1.733[a]	1.764[b]
C2-C3	1.408[a]	1.418[b]	C1-C2	1.420[a]	1.418[b]
Mn1-P2	2.367[a]	2.462[b]	Mn1-P1’	2.349[a]	2.462[b]
P1-P2	2.095[a]	2.136[b]			
Angles (°)					
C1-C2-C3	117.49[a]	118.07[b]	C2-C3-P1	115.70[a]	115.82[b]
C2-C1-P2	115.49[a]	115.82[b]	C3-P1-P2	95.46[a]	94.50[b]
C1-P2-P1	94.69[a]	94.53[b]	C3-P1-Mn2	125.17[a]	125.89[b]
C1-P2-Mn1	125.50[a]	125.90[b]	P2-P1-Mn2	122.13[a]	119.54[b]
P1-P2-Mn1	124.68[a]	119.72[b]	P2-Mn1-P1’	84.28[a]	84.88[b]

[a]X-ray
[b] B3LYP/basis set II

Table 5S. Selected bond lengths (Å) and angles (°) computed for **3a.**

Bond lengths (Å)			
P2-C1	1.784	P1-C3	1.803
C1-C2	1.441	C2-C3	1.427
Mn1-P2	2.491	Mn1-P1	2.501
P1-P2	2.167		
Angles (°)			
C1-C2-C3	115.54	C2-C3-P1	118.25
C2-C1-P2	117.79	C1-P2-P1	94.67
C3-P1-P2	93.61	C1-P2-Mn1	60.63
C3-P1-Mn1	61.83	P1-P2-Mn1	64.50
P2-P1-Mn1	64.05	P2-Mn1-P1	51.45

Table 6S. Mulliken charges computed for complexes **2** and **3.**

	2a	**2b**	**2c**	**3a**	**3b**	**3c**
Mn	-0.552	-0.545	-0.540	-0.407	-0.403	-0.398
P	0.211	0.209	0.211	0.184, 0.218	0.186, 0.221	0.190, 0.225
P2-Cp	0.034	0.031	0.037	-0.018	-0.016	-0.008

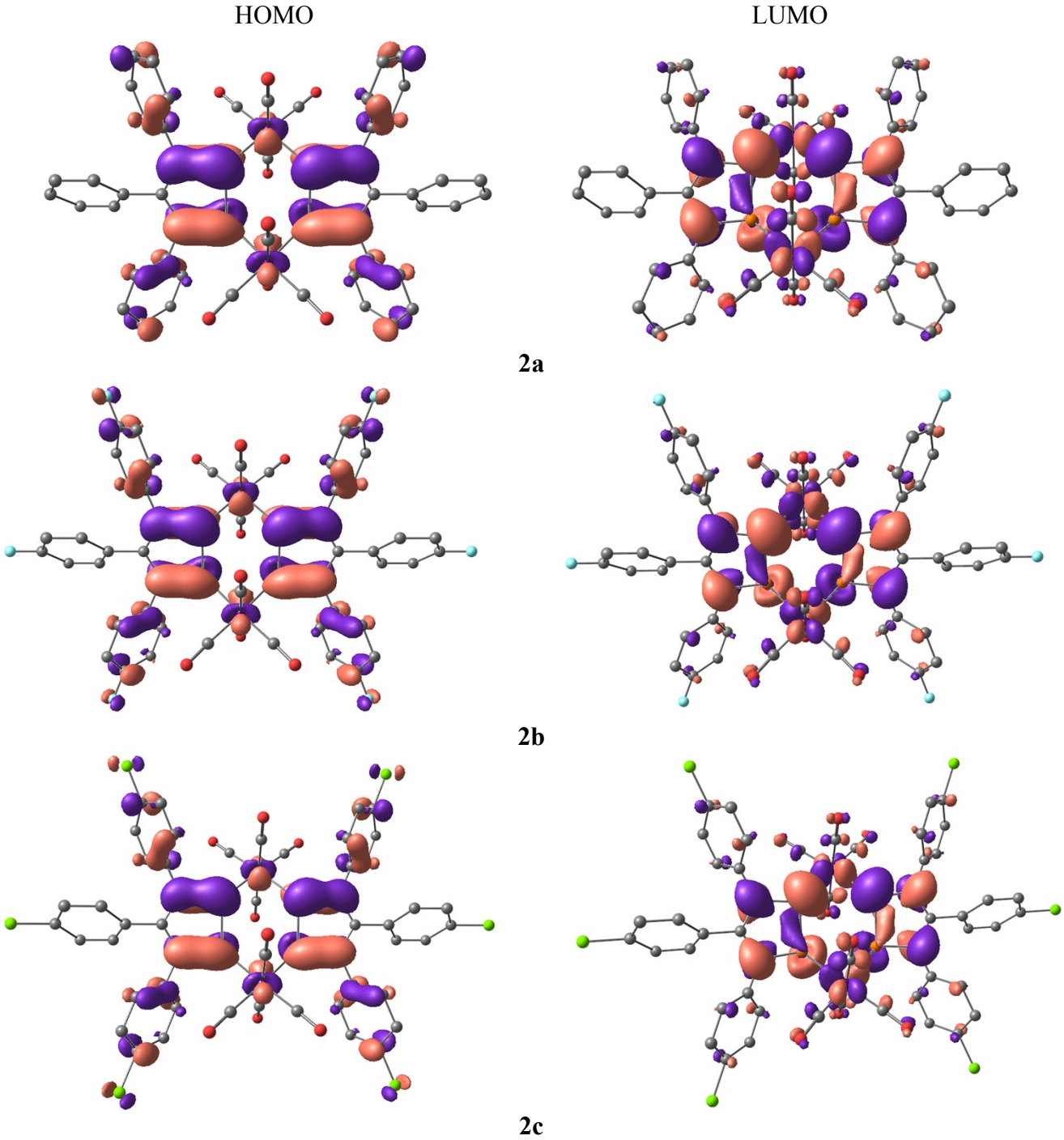

Figure 3S. Frontier molecular orbitals of complexes **2**.

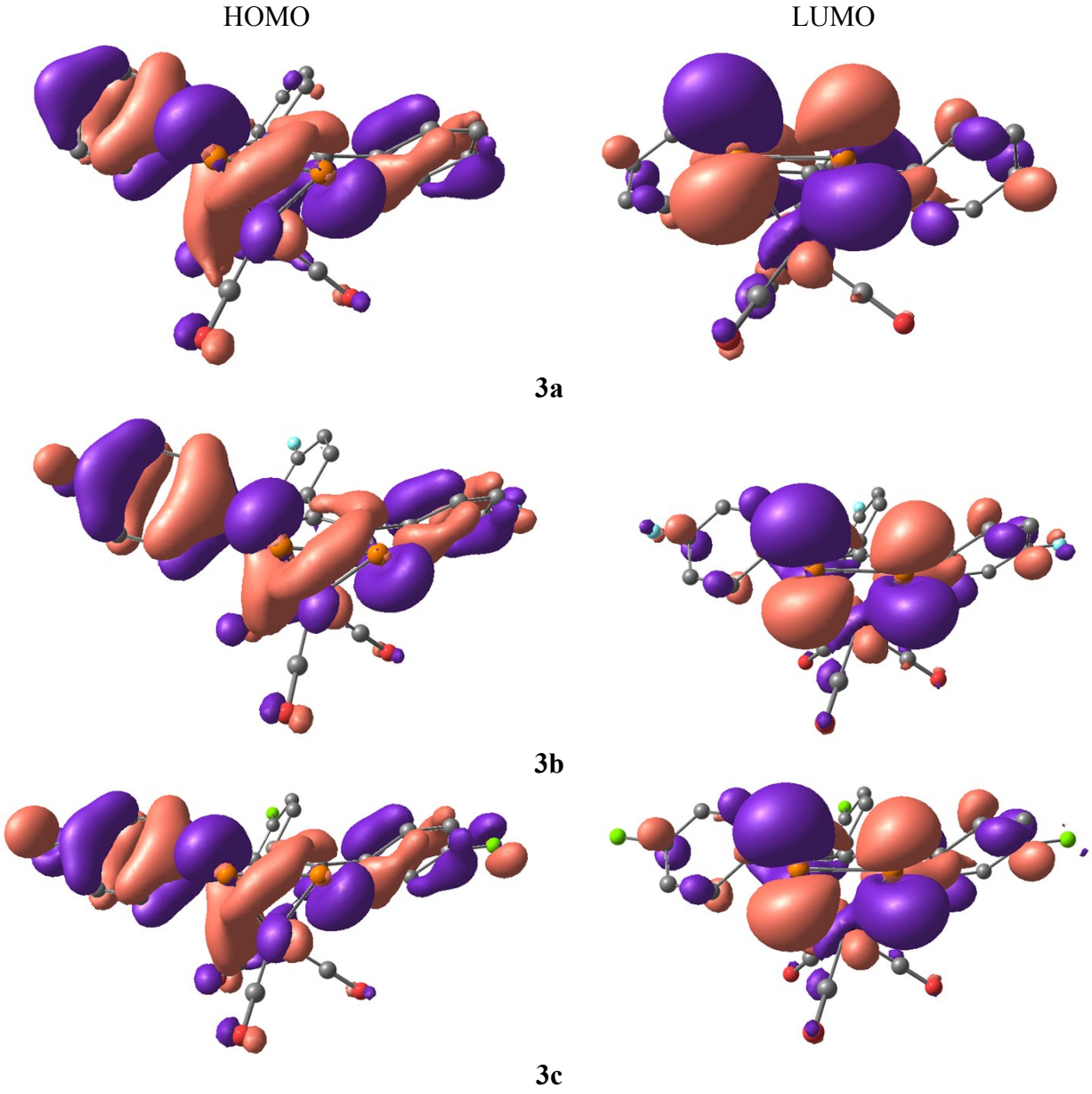

Figure 4S. Frontier molecular orbitals of complexes **3**.

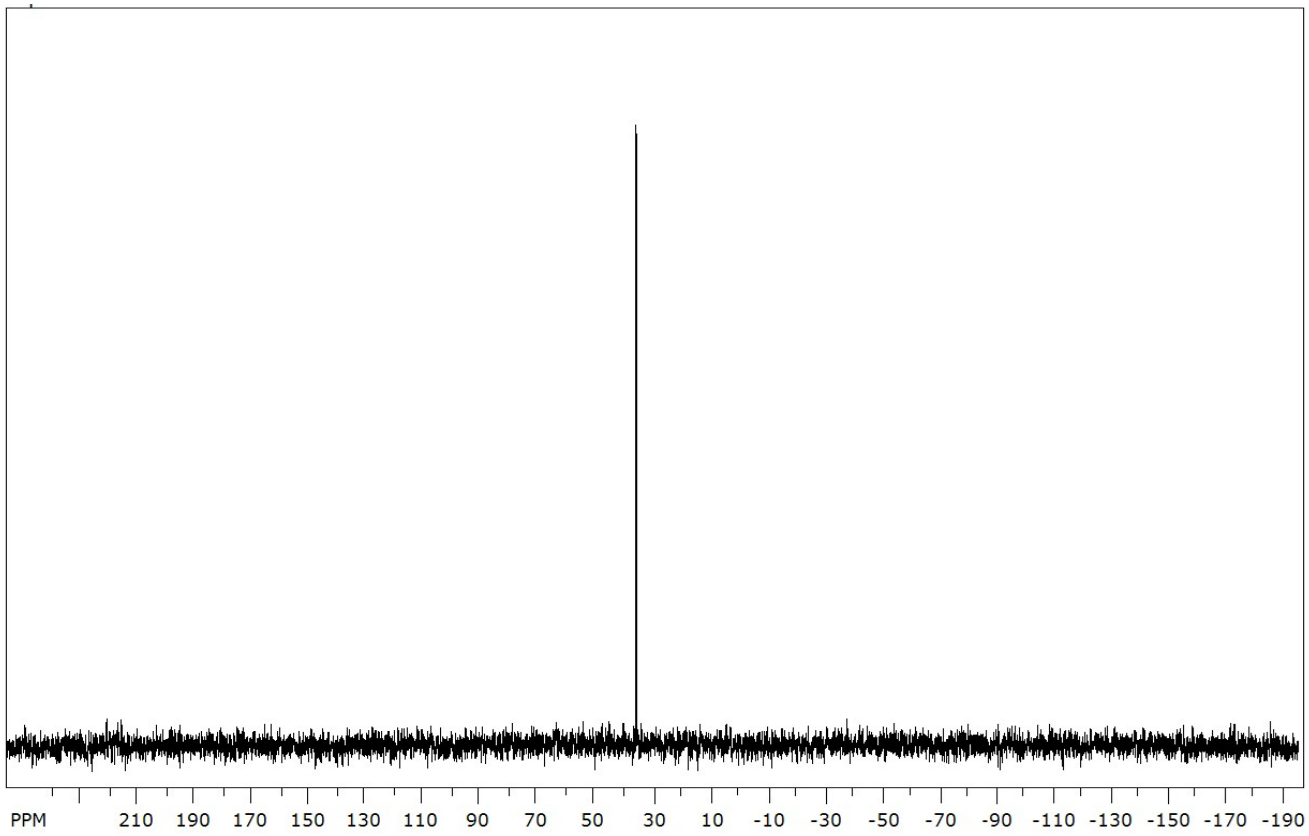

Figure 5S. ^{31}P NMR spectrum of complex **3a**.

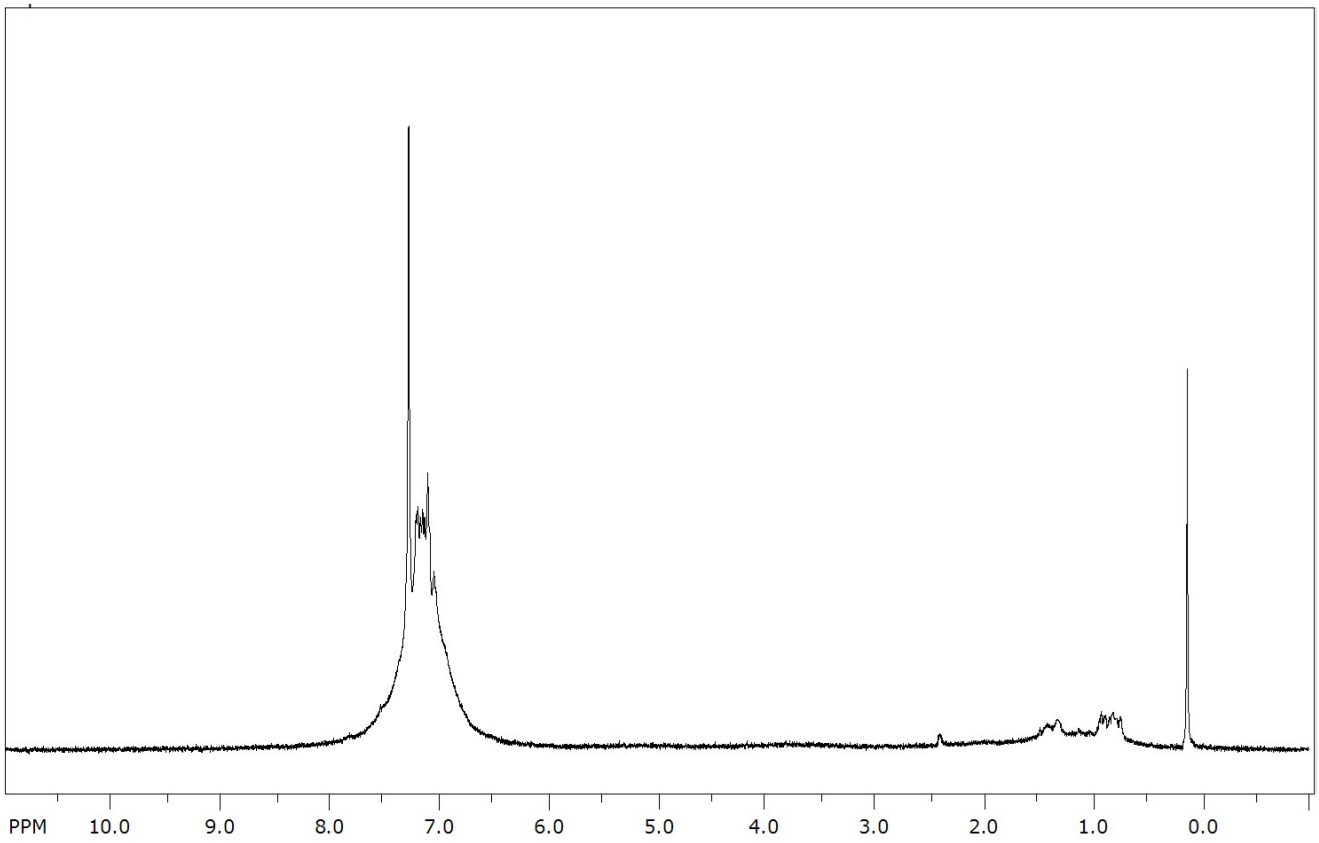

Figure 6S. ^{1}H NMR spectrum of complex **3a**.

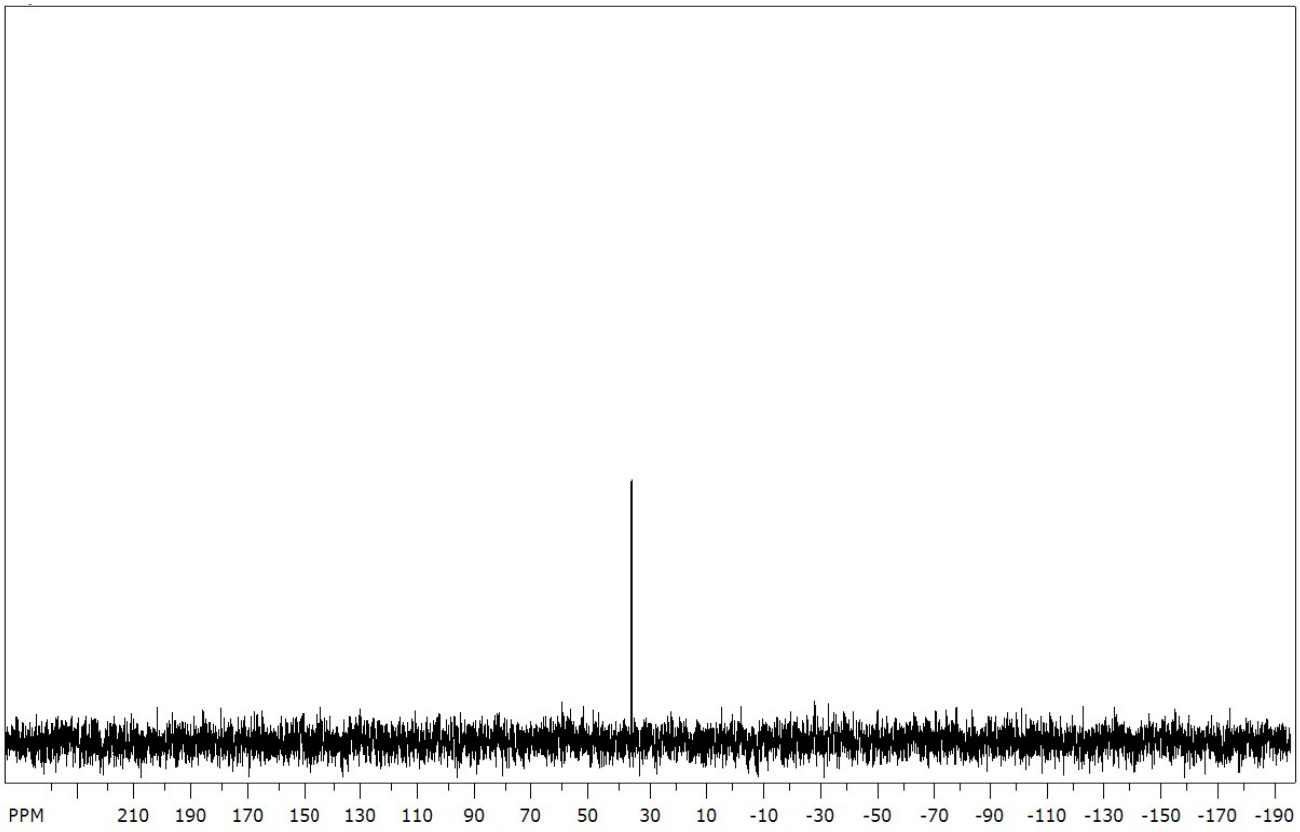

Figure 7S. ^{31}P NMR spectrum of complex **3b**.

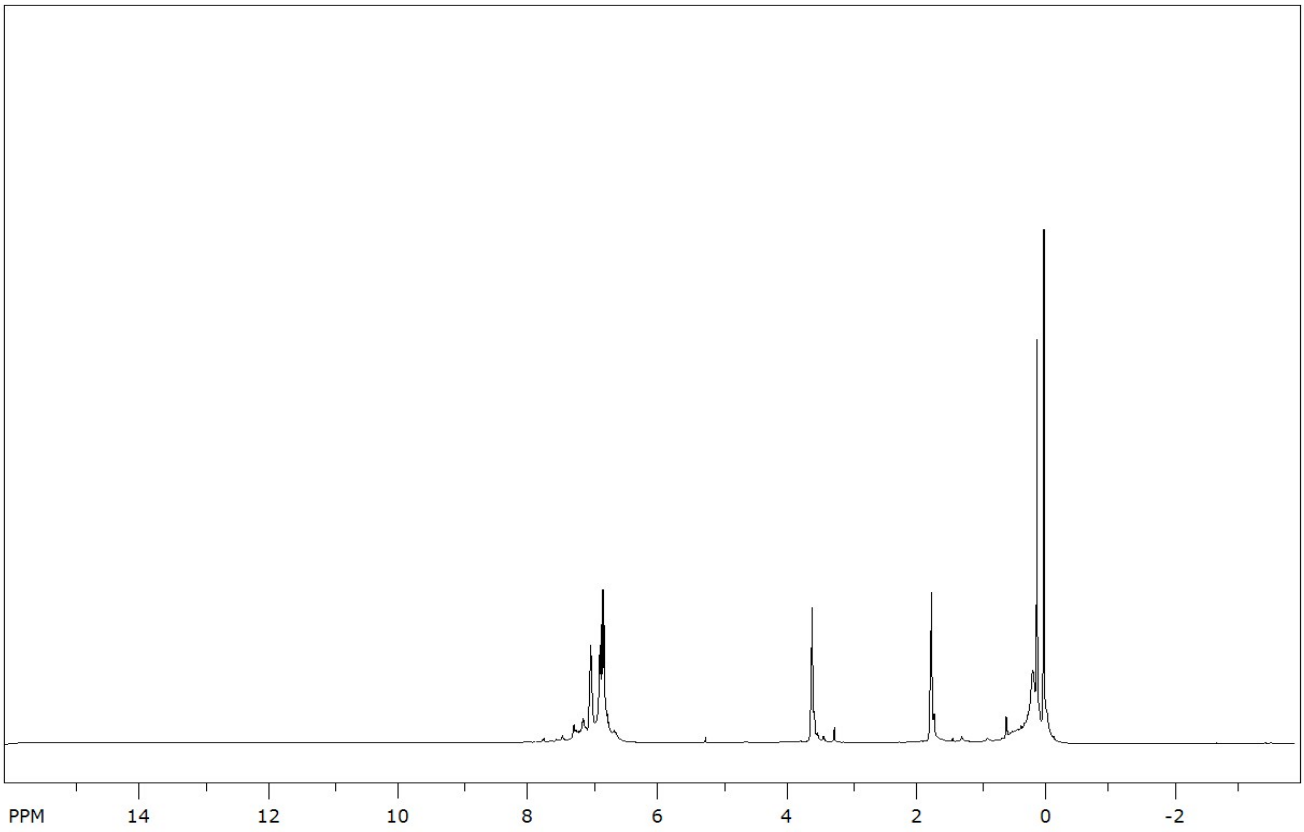

Figure 8S. ^{1}H NMR spectrum of complex **3b**.

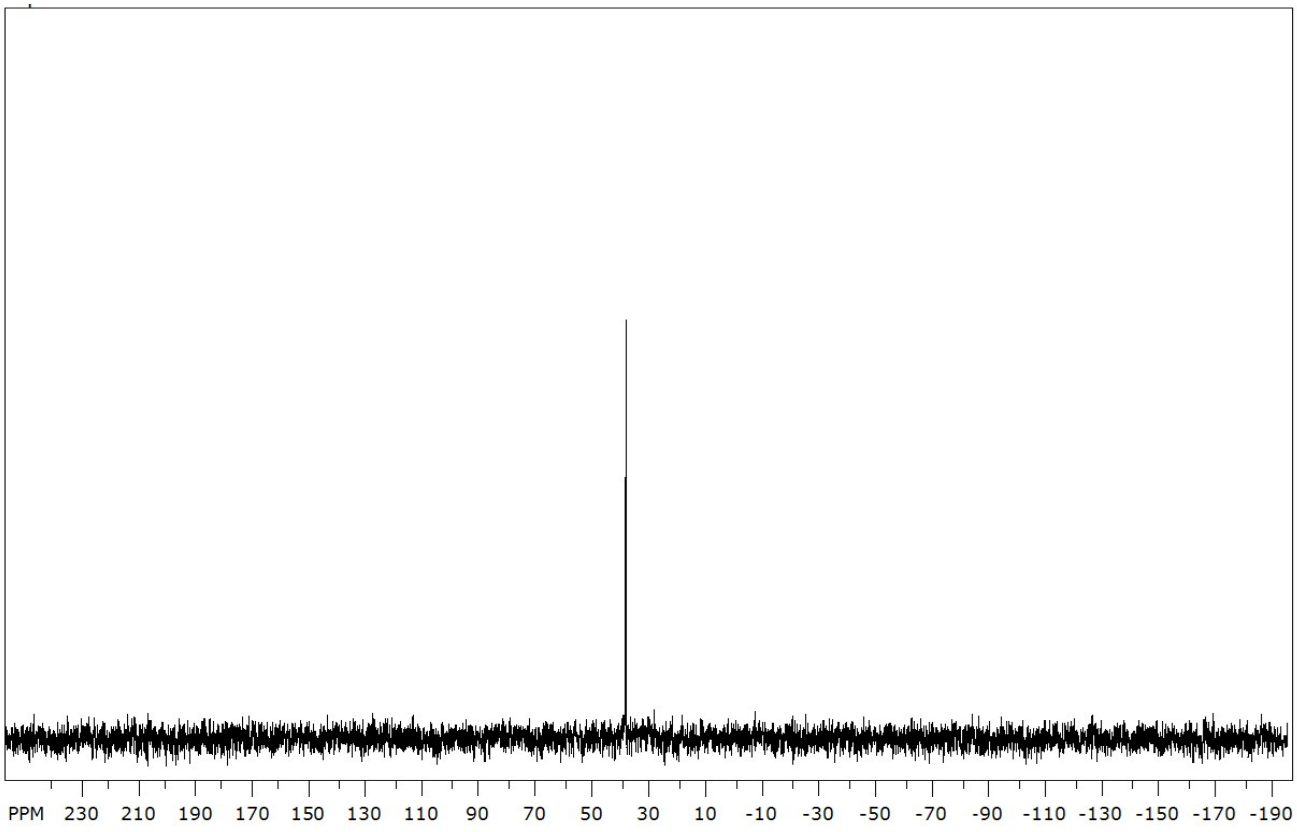

Figure 9S. ^{31}P NMR spectrum of complex **3c**.

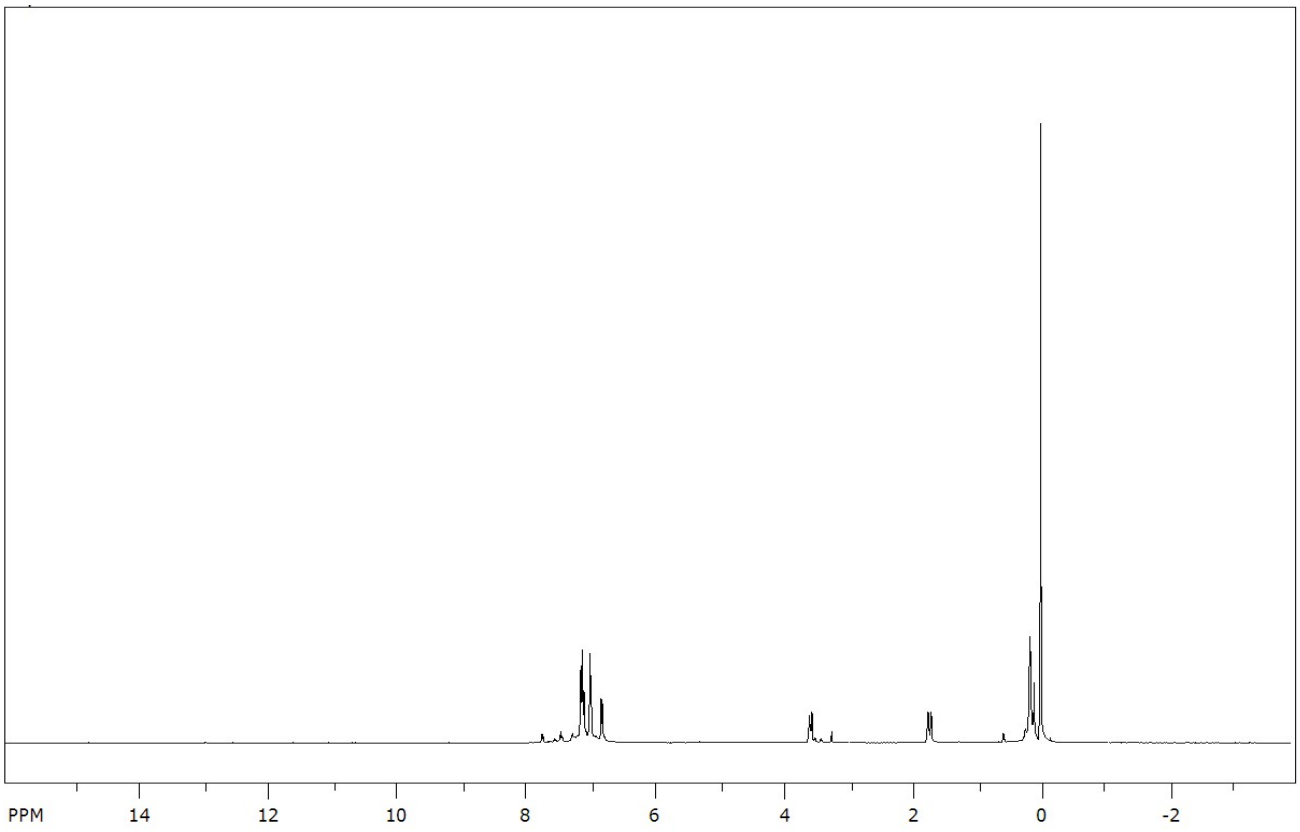

Figure 10S. ^{1}H NMR spectrum of complex **3c**.