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Monomeric Nickel Hydroxide Stabilized by a Sterically Demanding Phosphorus-Nitrogen PN^3P-Pincer Ligand: Synthesis, Reactivity and Catalysis

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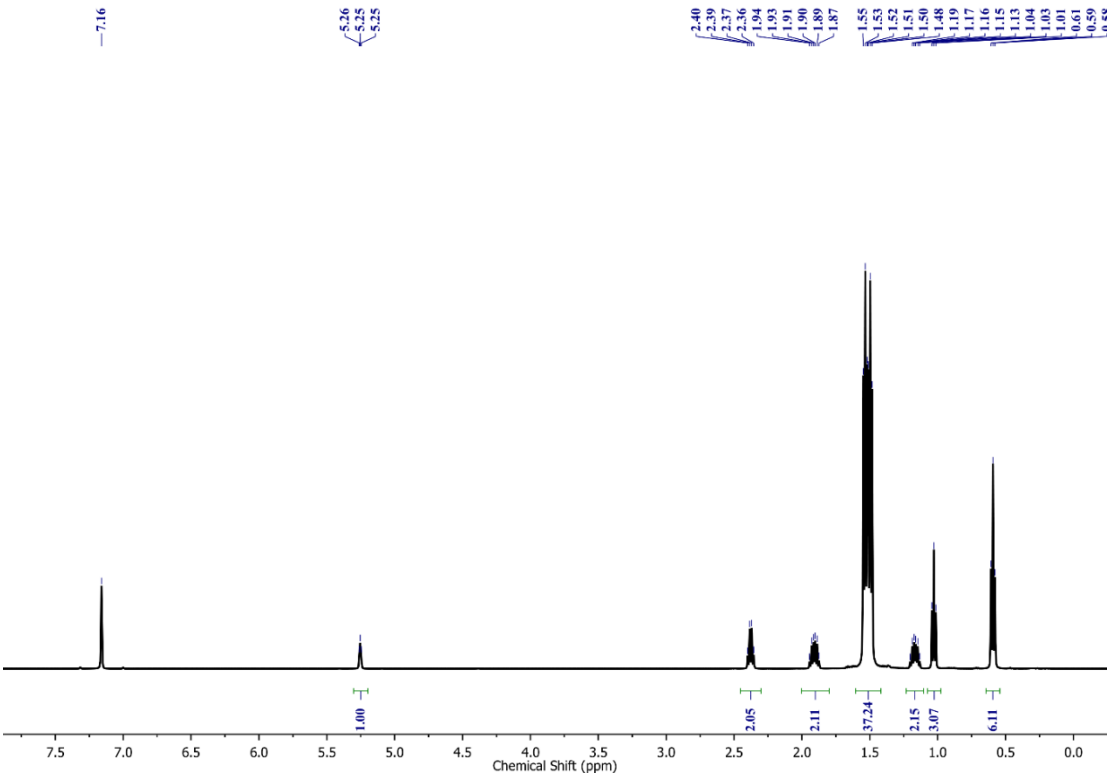

Fig. S1 ^{1}H NMR spectrum of complex **2** (500 MHz, C_6D_6, 25 °C).

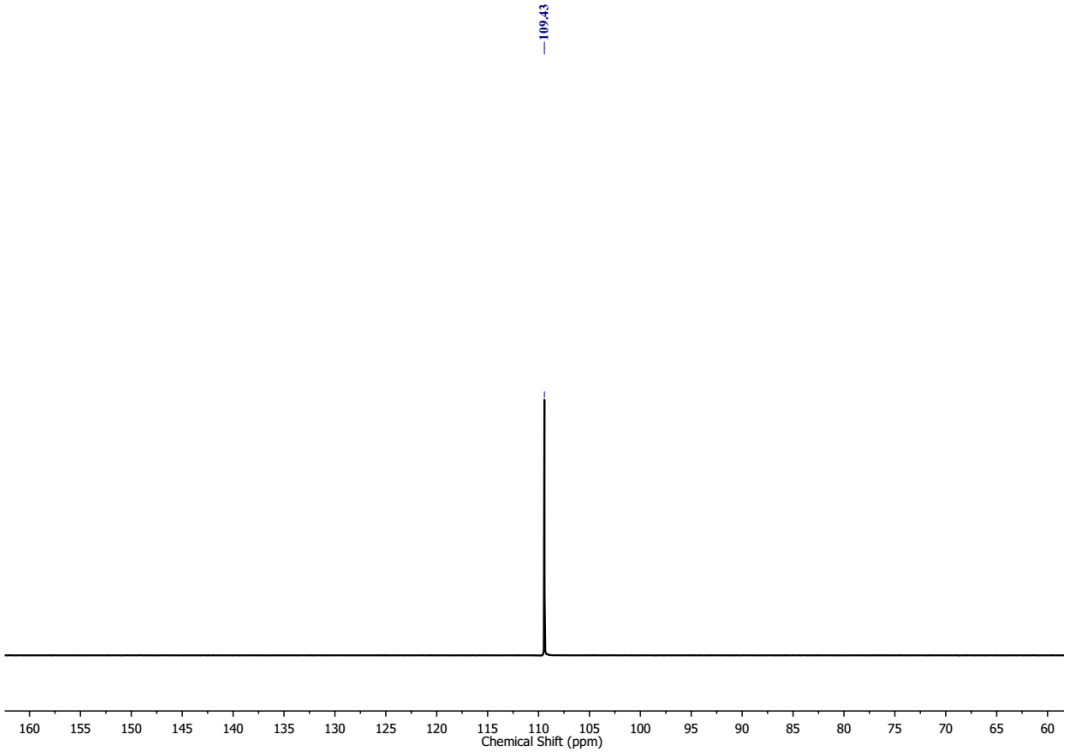

Fig. S2 ^{31}P{^{1}H} NMR spectrum of complex **2** (202 MHz, C_6D_6, 25 °C).

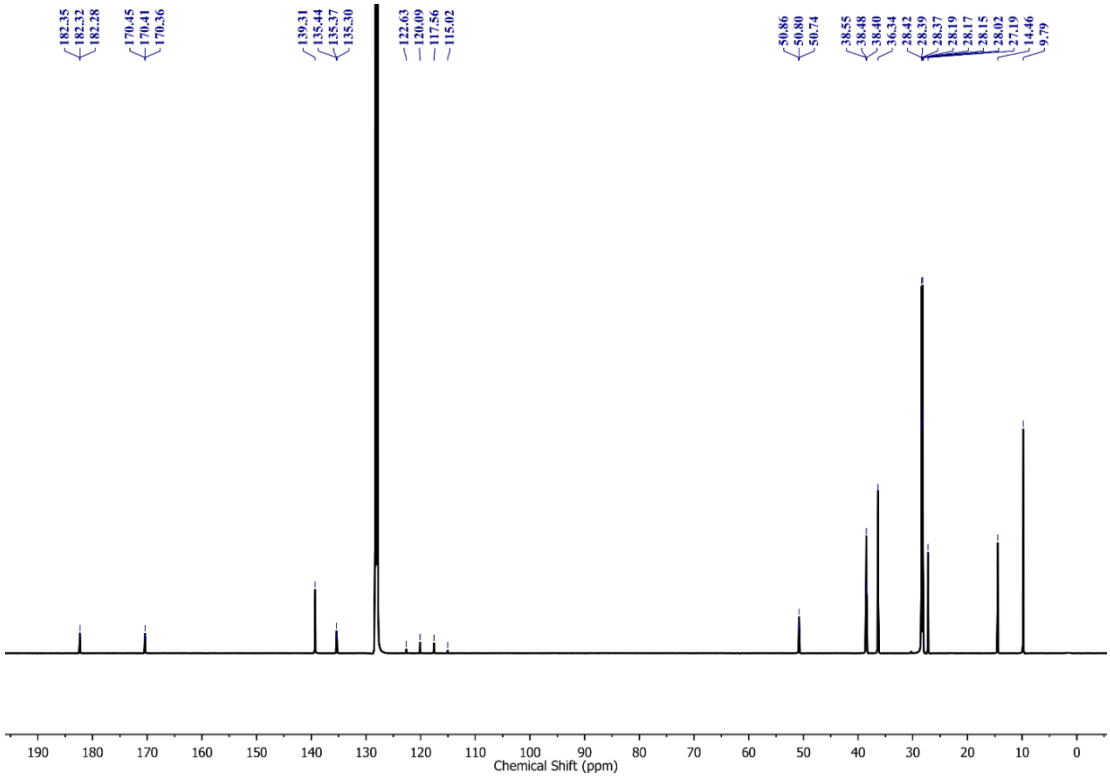

Fig. S3 ^{13}C NMR spectrum of complex **2** (126 MHz, C_6D_6, 25 °C).

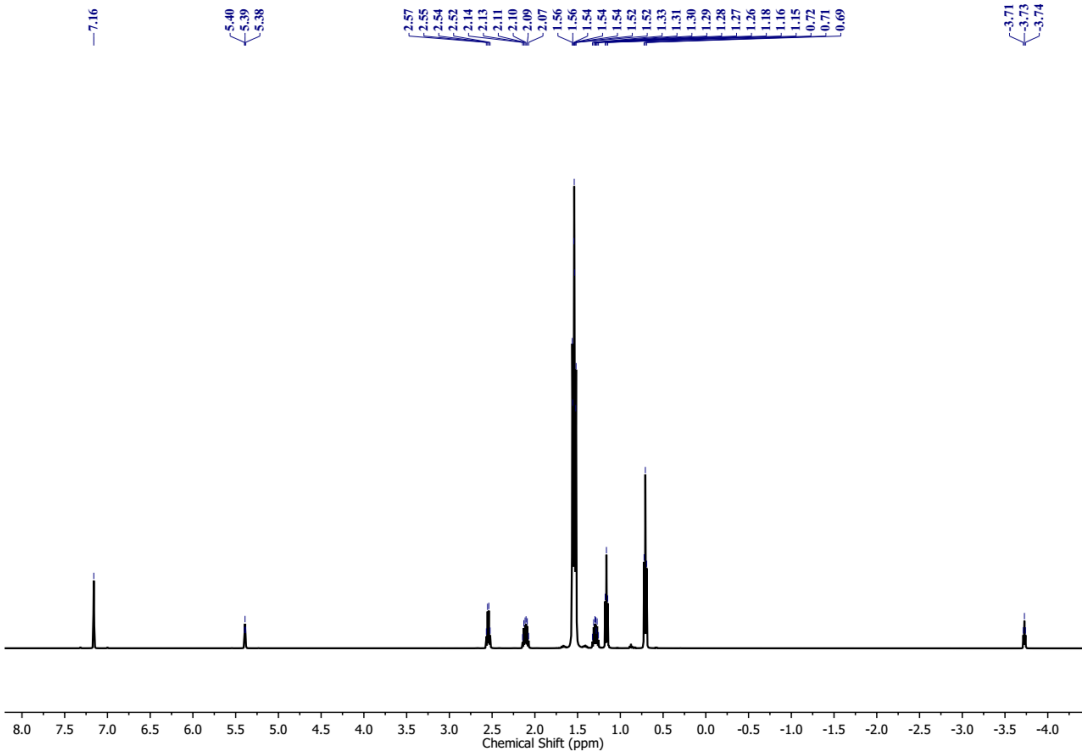

Fig. S4 ^{1}H NMR spectrum of complex **3** (500 MHz, C_6D_6, 25 °C).

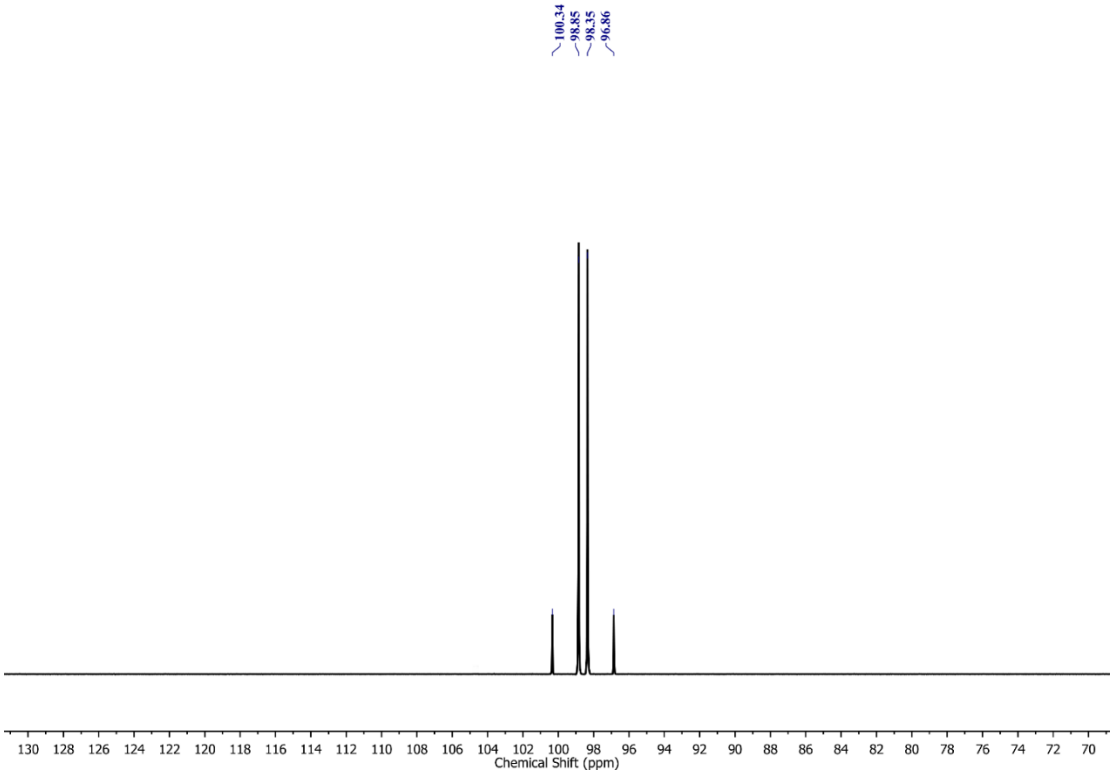

Fig. S5 $^{31}P\{^{1}H\}$ NMR spectrum of complex **3** (202 MHz, C_6D_6, 25 °C).

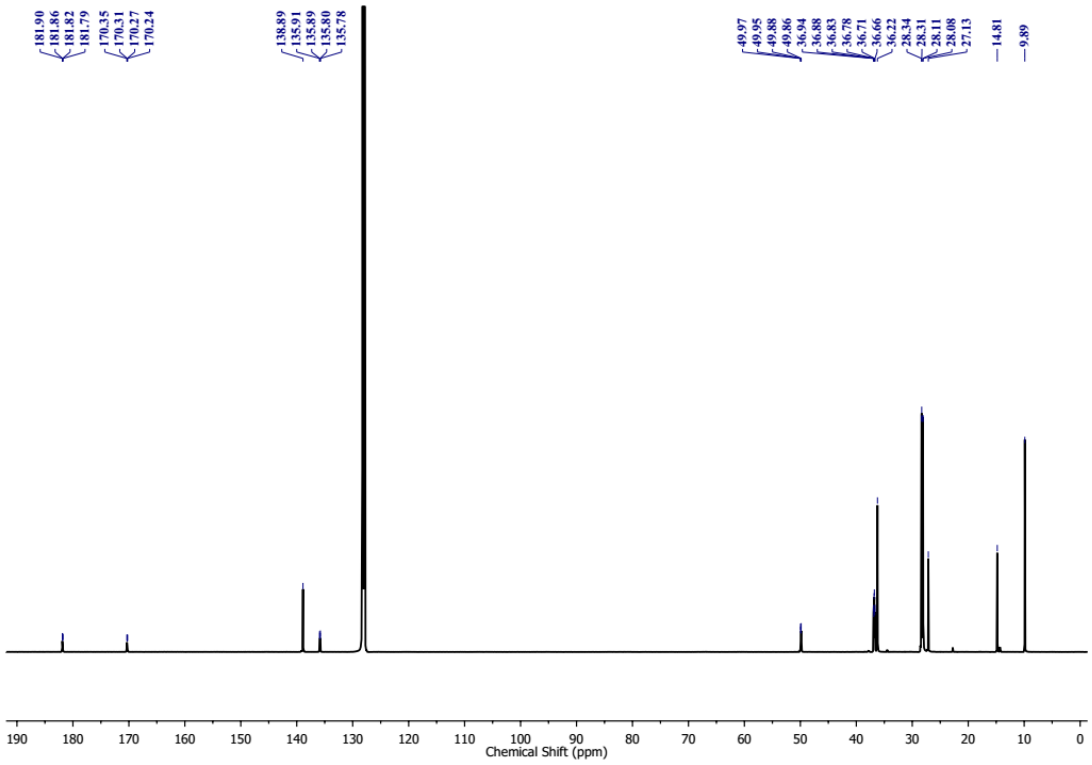

Fig. S6 ^{13}C NMR spectrum of complex **3** (126 MHz, C_6D_6, 25 °C).

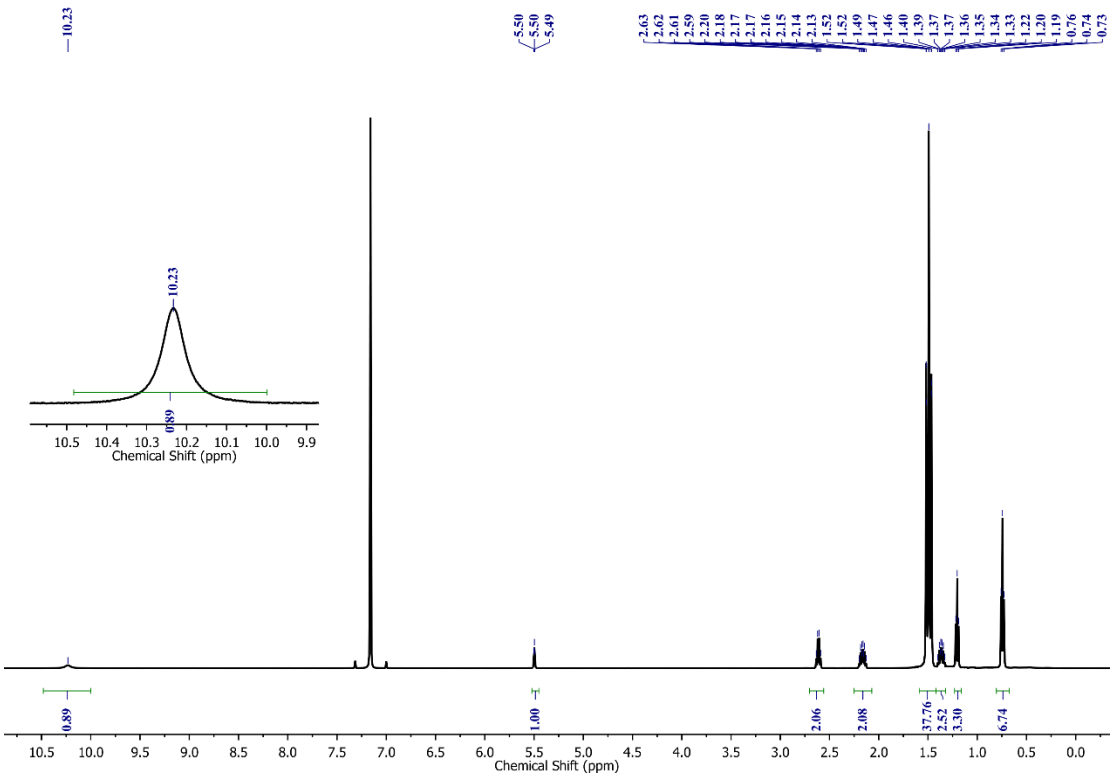

Fig. S7 ^{1}H NMR spectrum of complex **4** (500 MHz, C_6D_6, 25 °C).

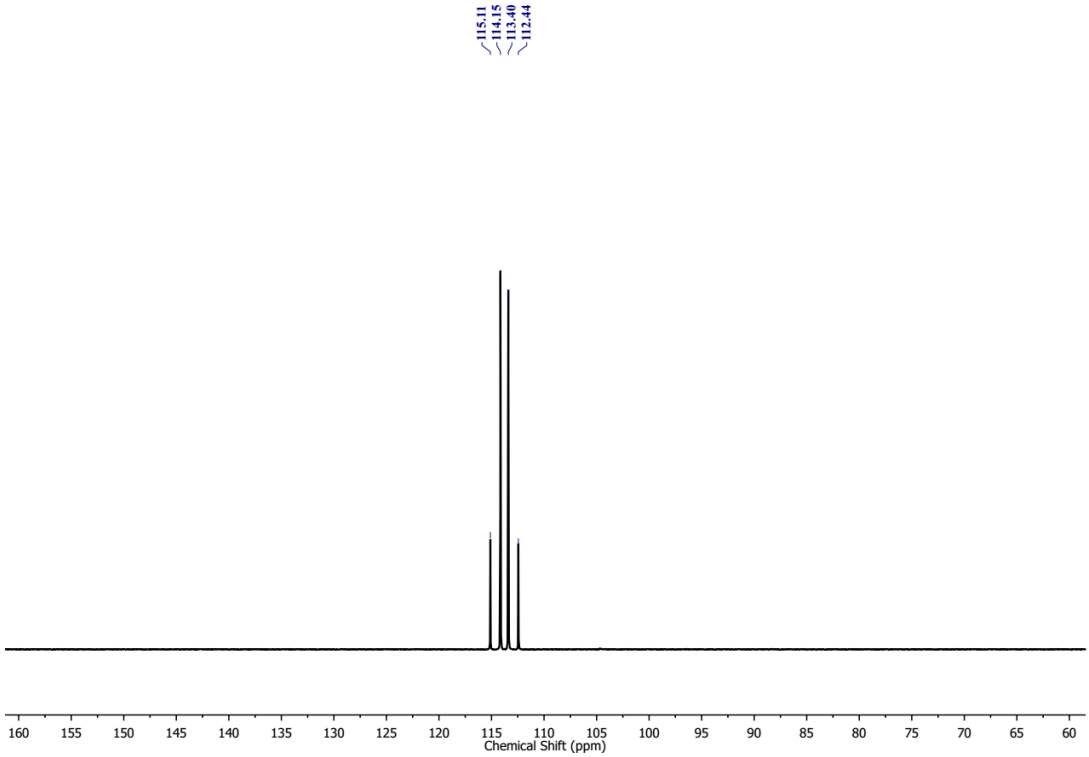

Fig. S8 ^{31}P{^{1}H} NMR spectrum of complex **4** (202 MHz, C_6D_6, 25 °C).

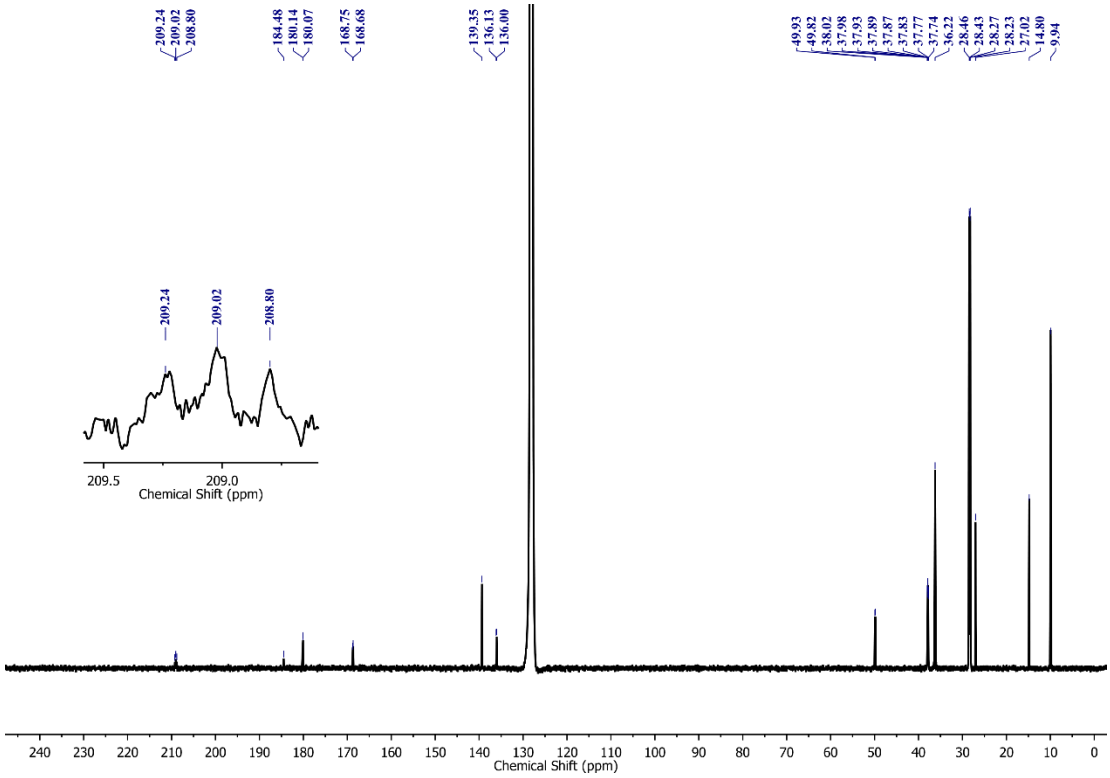

Fig. S9 ^{13}C NMR spectrum of complex **4** (126 MHz, C_6D_6, 25 °C).

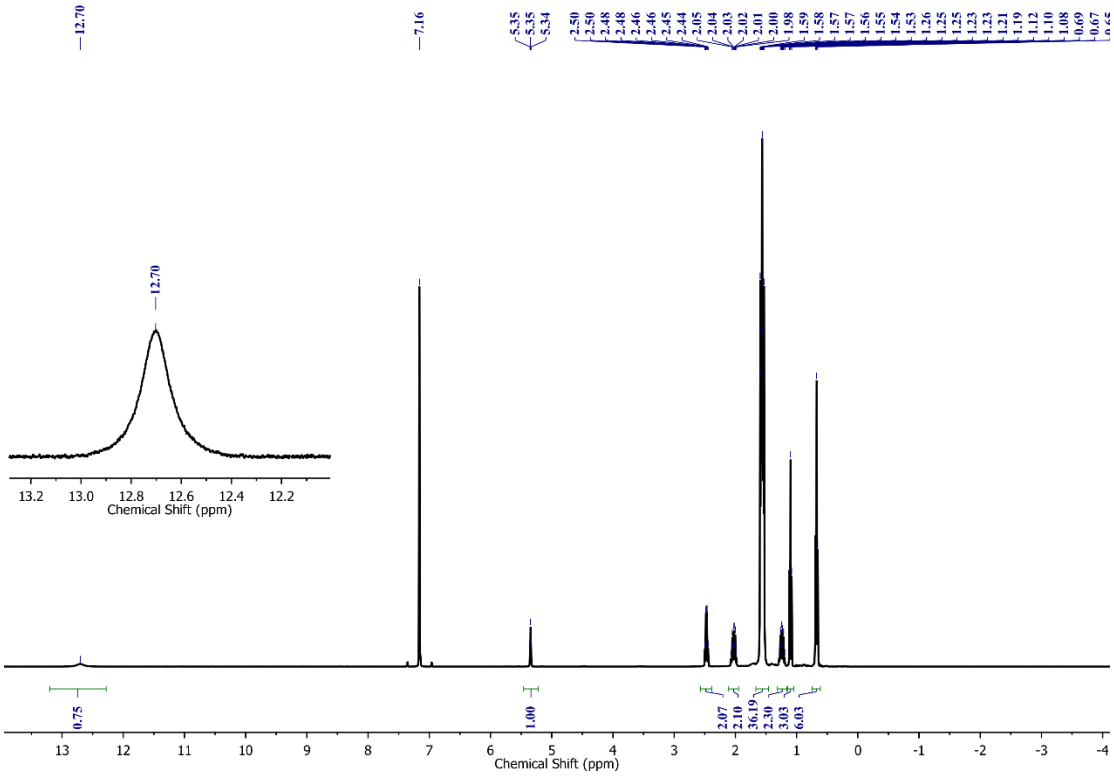

Fig. S10 ^{1}H NMR spectrum of complex **5** (400 MHz, C_6D_6, 25 °C).

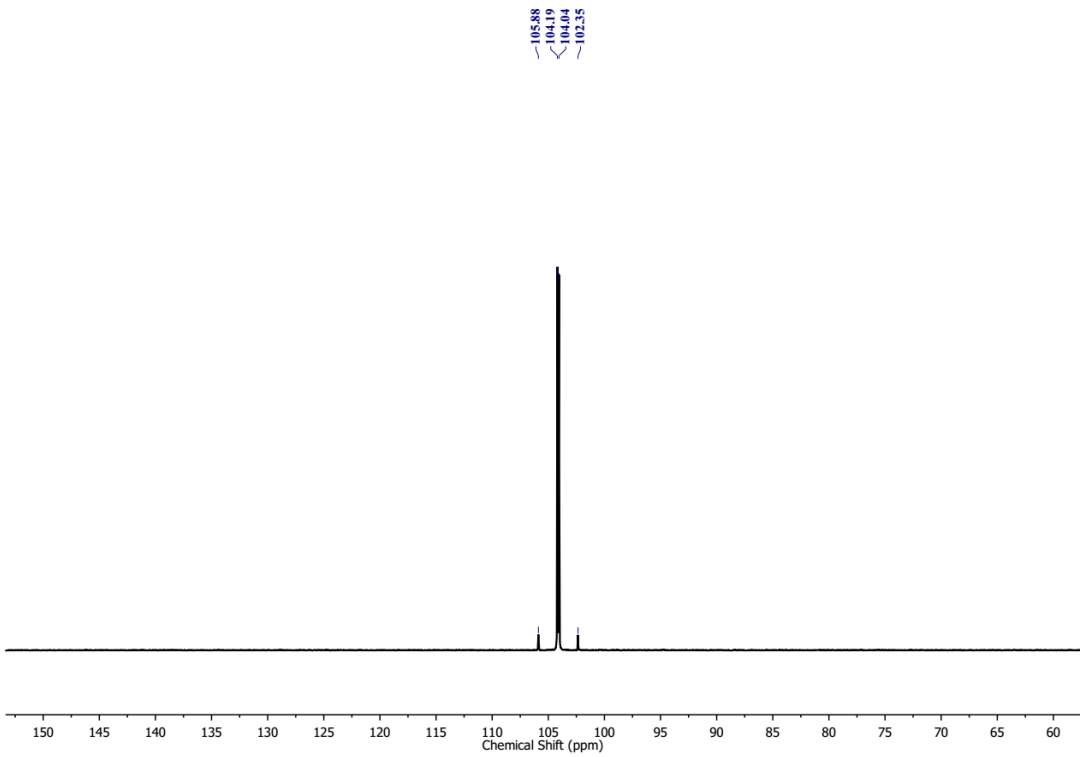

Fig. S11 $^{31}P\{^{1}H\}$ NMR spectrum of complex **5** (162 MHz, C_6D_6, 25 °C).

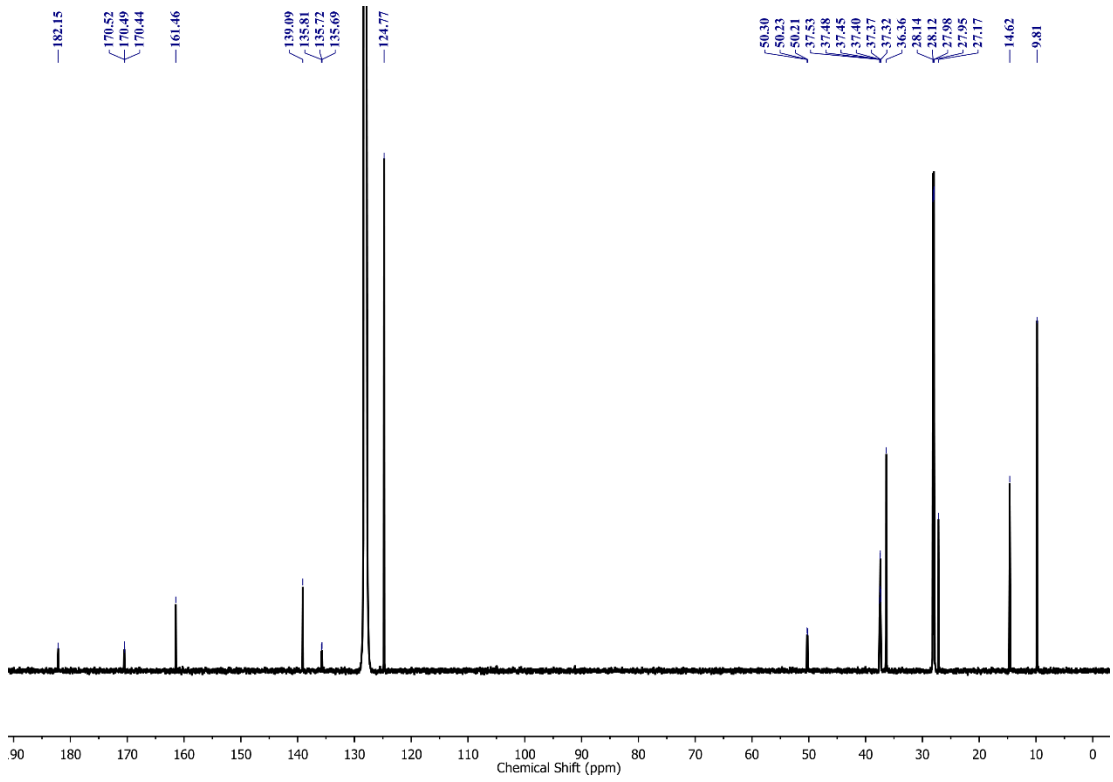

Fig. S12 ^{13}C NMR spectrum of complex **5** (101 MHz, C_6D_6, 25 °C).

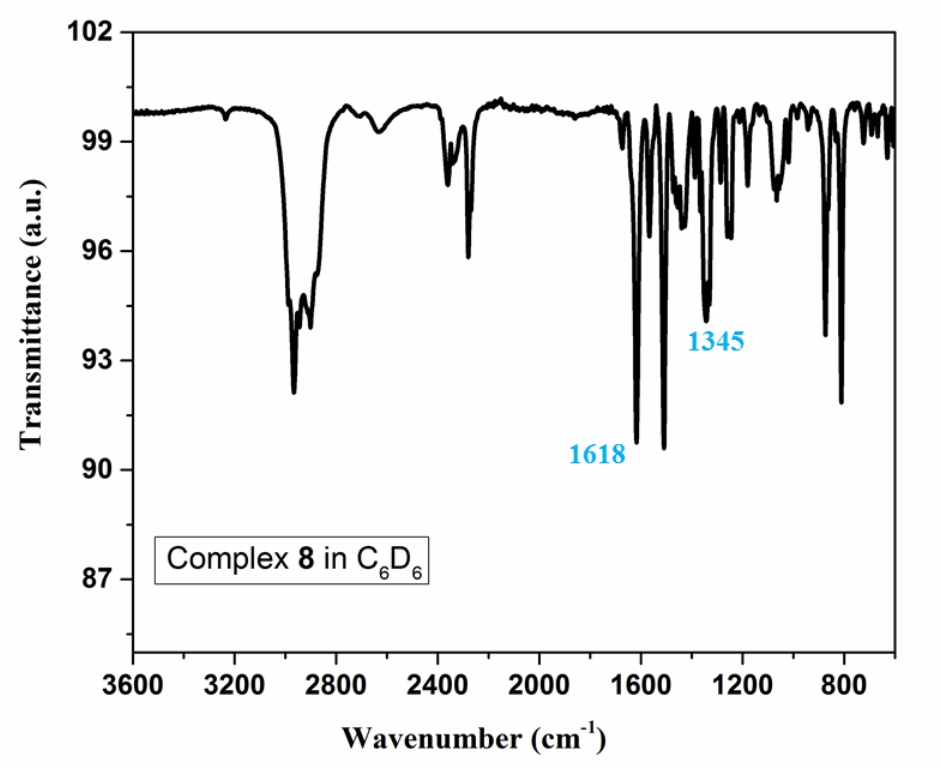

Fig. S13 FT-IR spectrum of complex **5**.

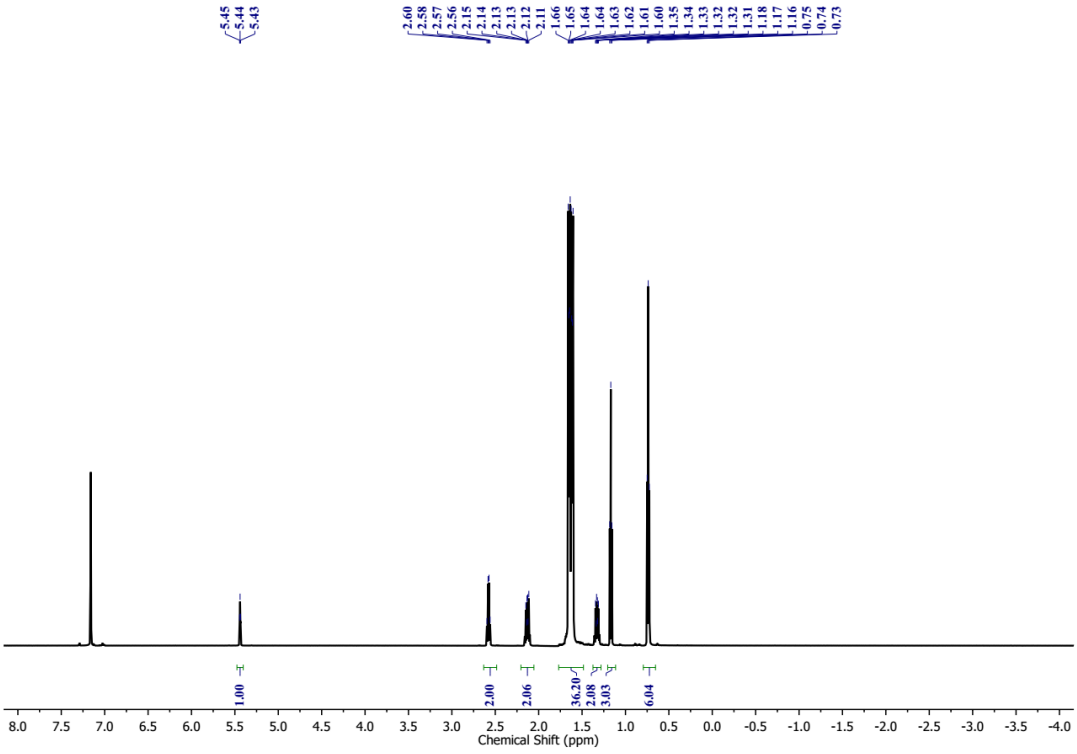

Fig. S14 ^{1}H NMR spectrum of complex **6** (600 MHz, C_6D_6, 25 °C).

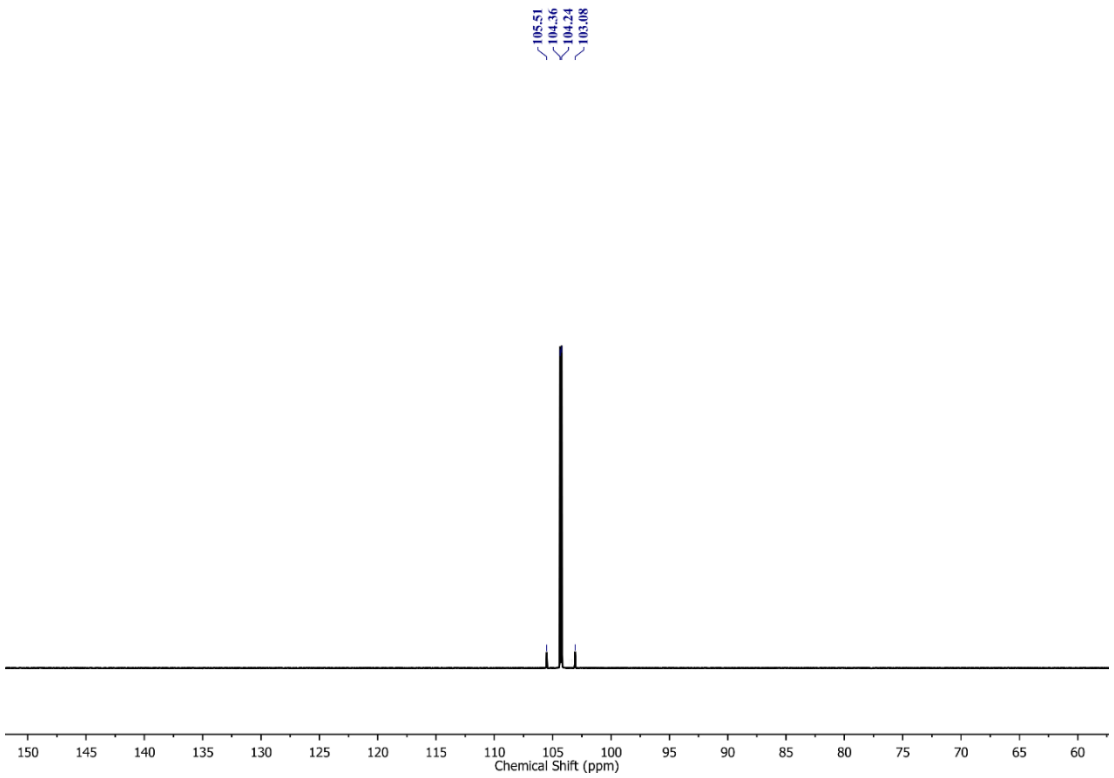

Fig. S15 $^{31}P\{^{1}H\}$ NMR spectrum of complex **6** (243 MHz, C_6D_6, 25 °C).

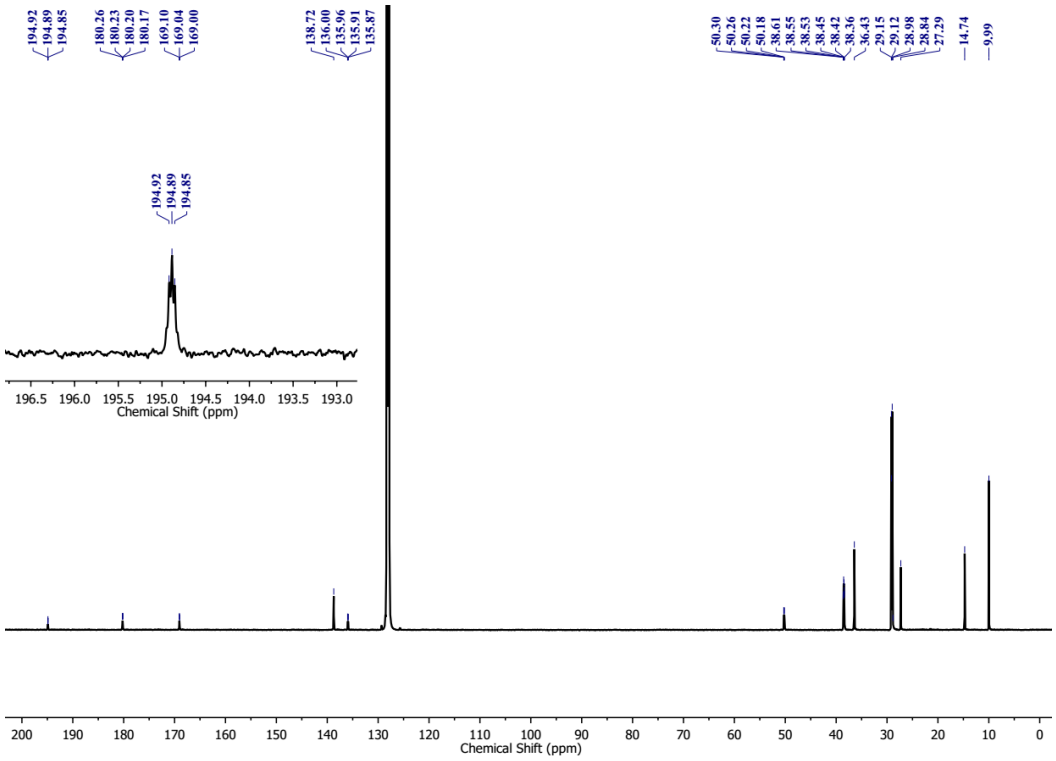

Fig. S16 ^{13}C NMR spectrum of complex **6** (126 MHz, C_6D_6, 25 °C).

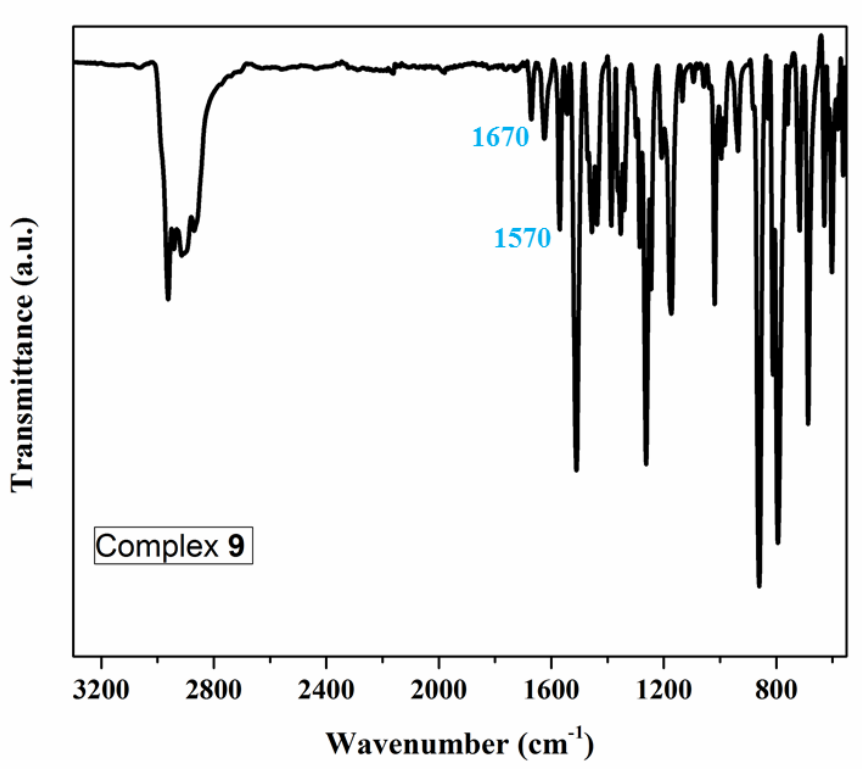

Fig. S17 FT-IR spectrum of complex **6.**

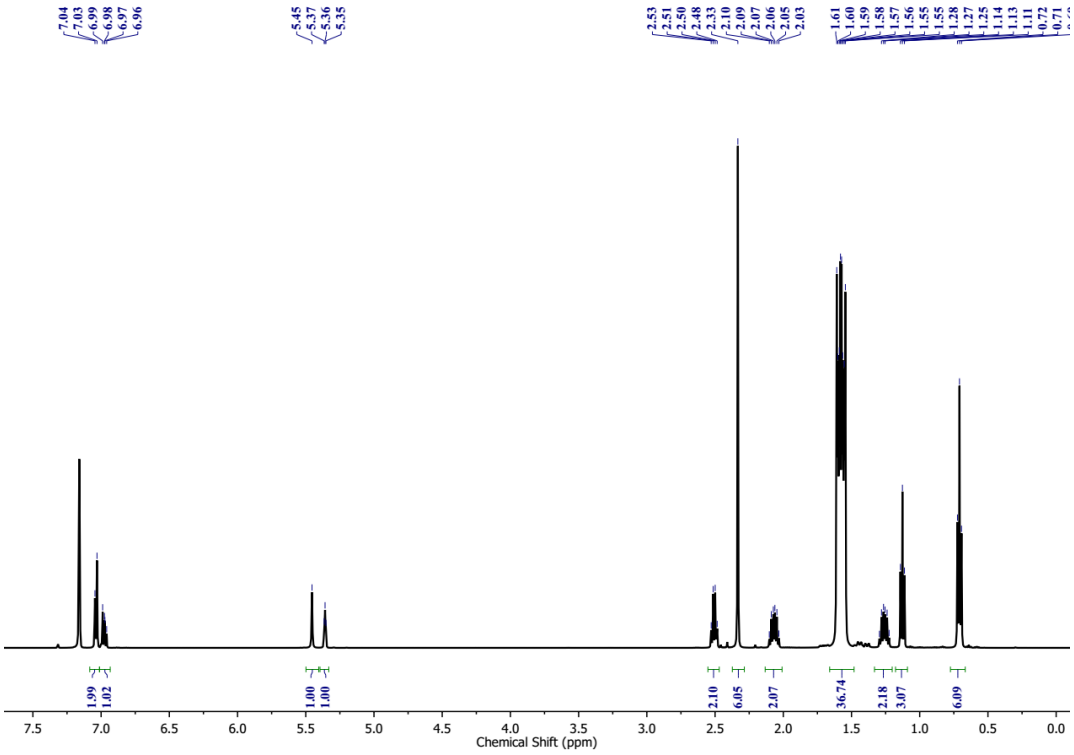

Fig. S18 ^{1}H NMR spectrum of complex **7** (500 MHz, C_6D_6, 25 °C).

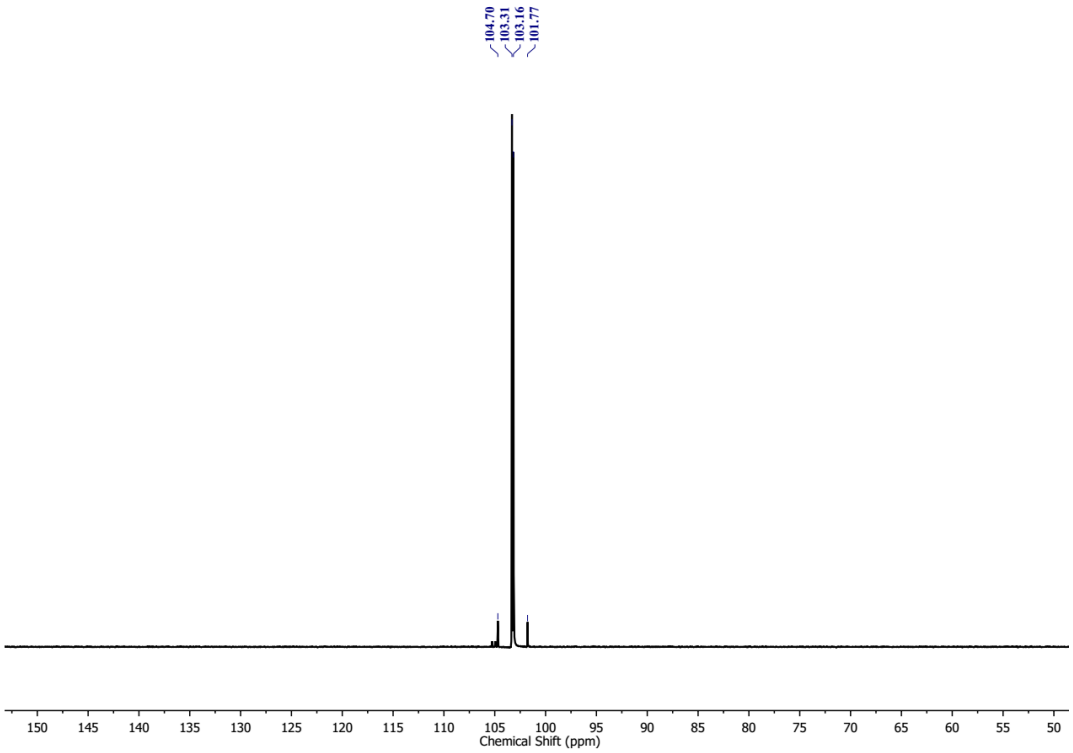

Fig. S19 $^{31}P\{^{1}H\}$ NMR spectrum of complex **7** (202 MHz, C_6D_6, 25 °C).

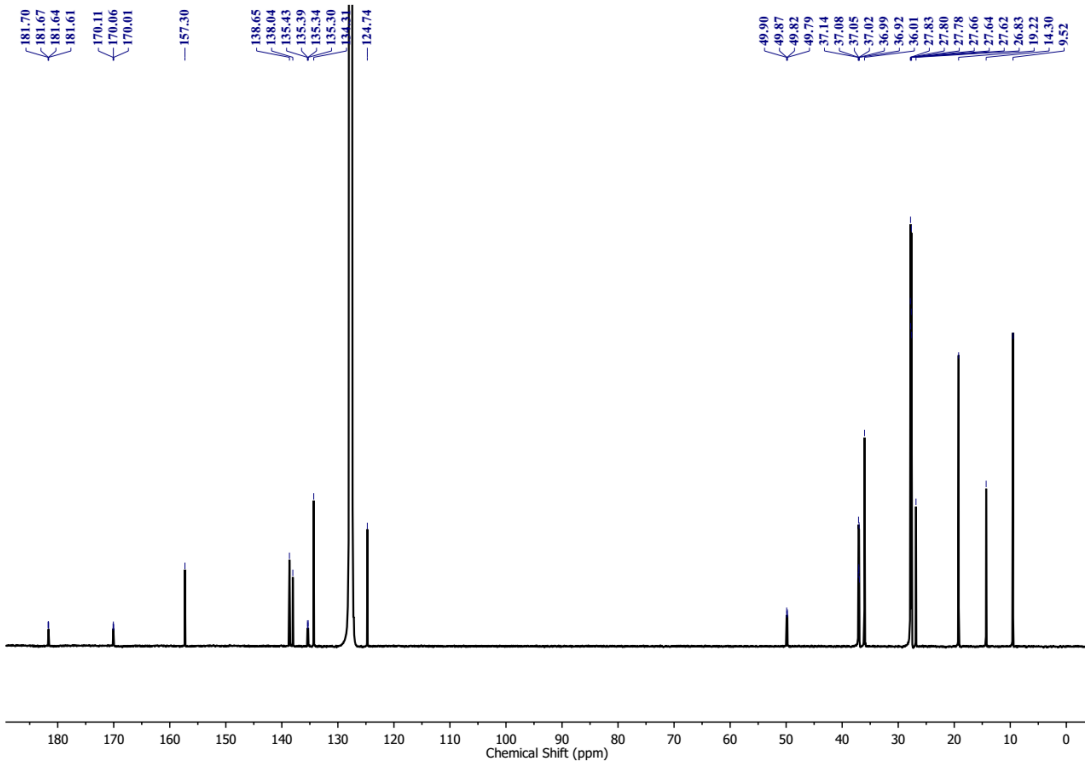

Fig. S20 ^{13}C NMR spectrum of complex **7** (126 MHz, C_6D_6, 25 °C).

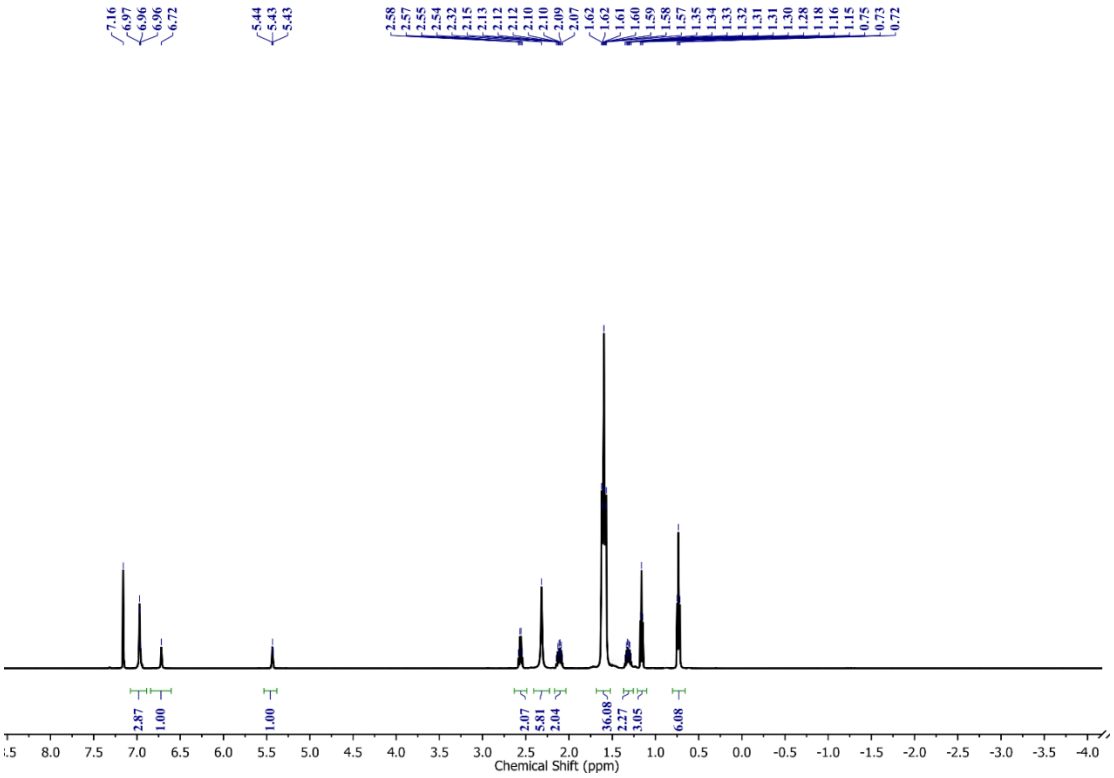

Fig. S21 ^{1}H NMR spectrum of complex **8** (500 MHz, C_6D_6, 25 °C).

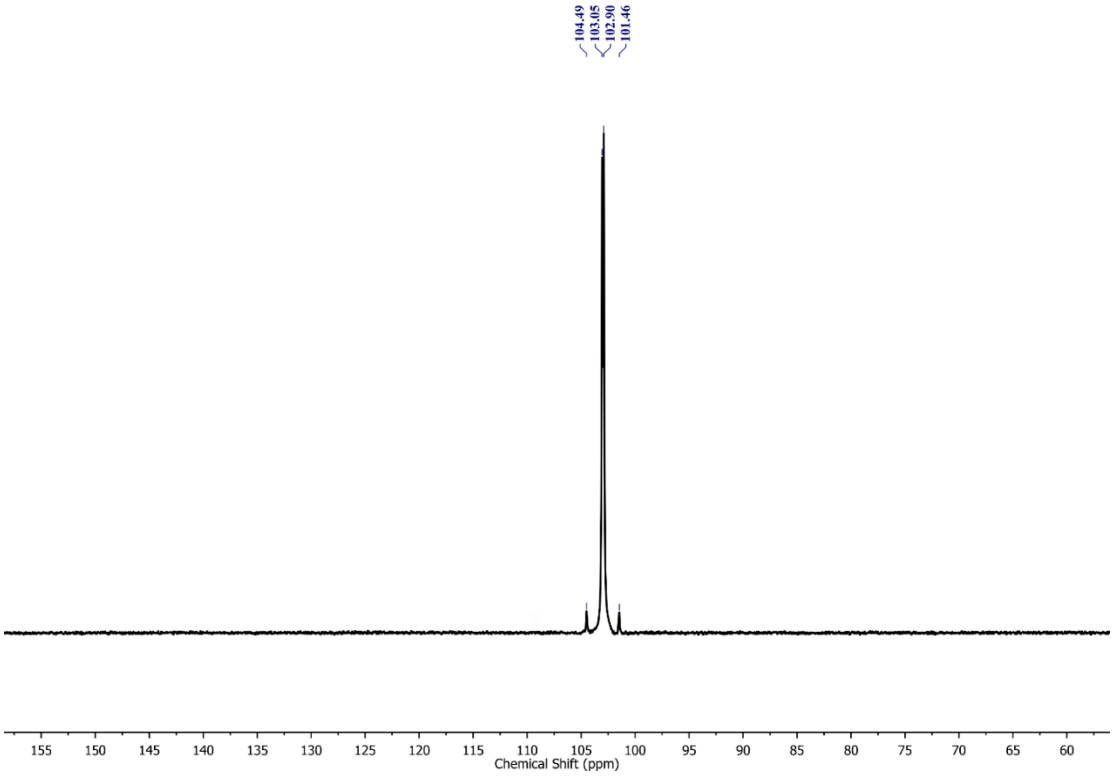

Fig. S22 $^{31}P\{^{1}H\}$ NMR spectrum of complex **8** (202 MHz, C_6D_6, 25 °C).

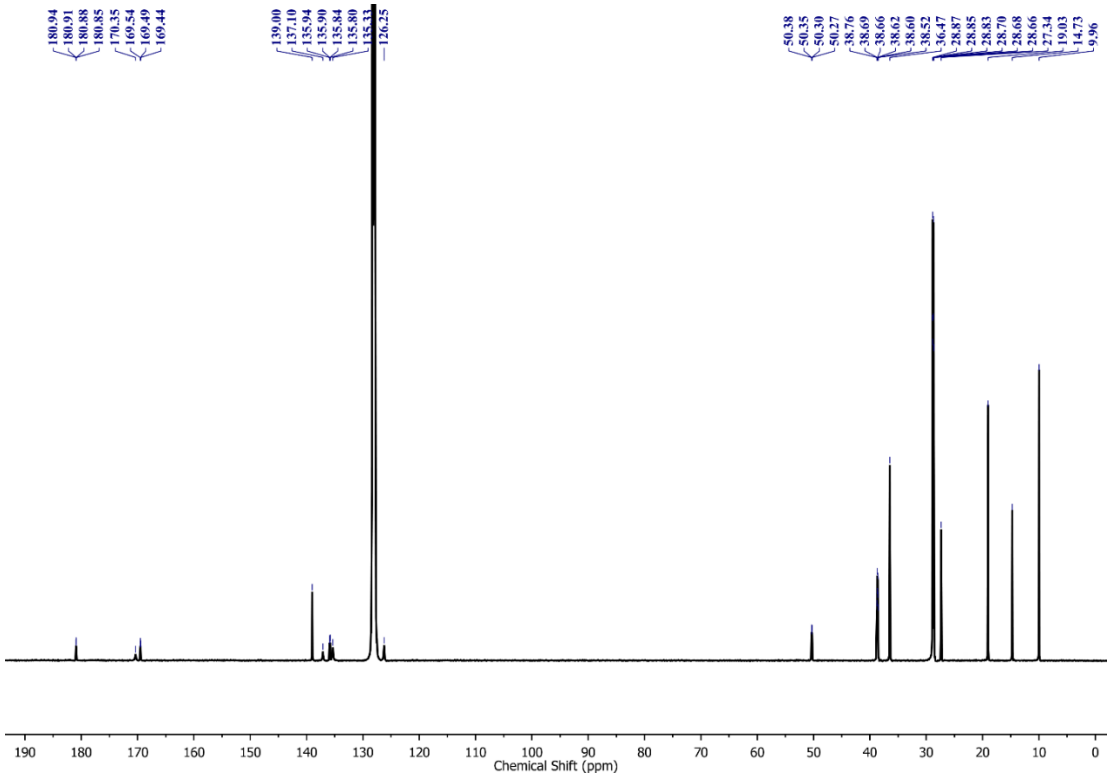

Fig. S23 ^{13}C NMR spectrum of complex **8** (126 MHz, C_6D_6, 25 °C).

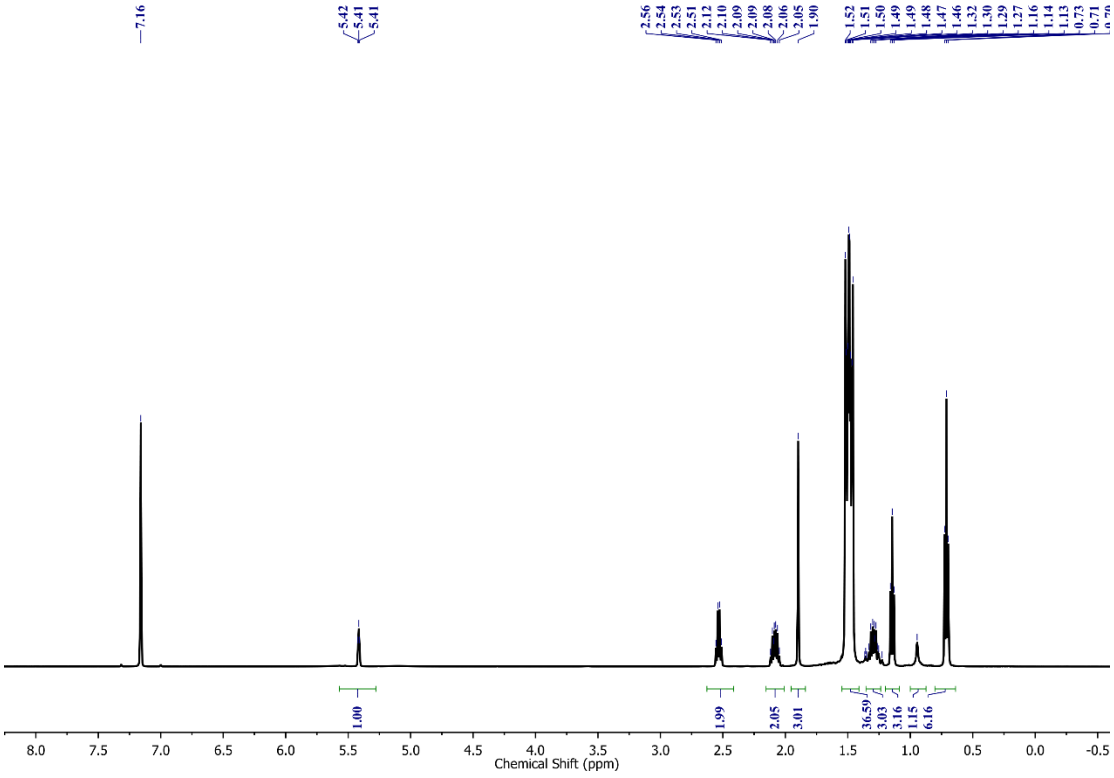

Fig. S24 ^{1}H NMR spectrum of complex **9** (500 MHz, C_6D_6, 25 °C).

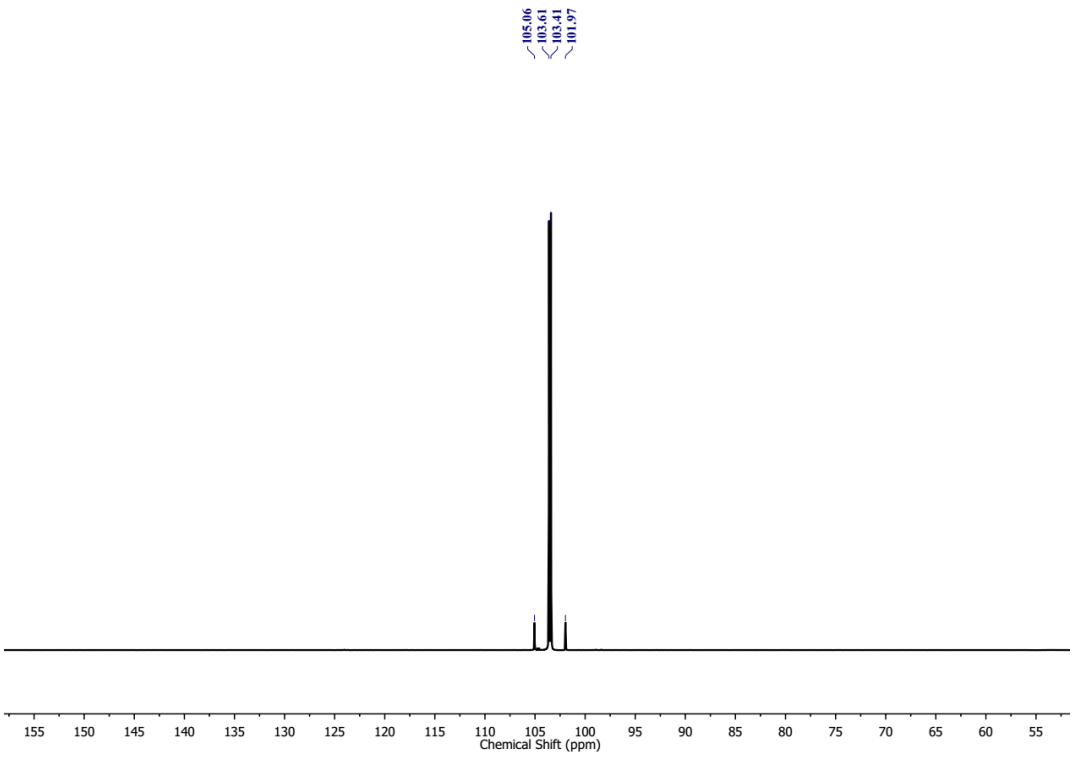

Fig. S25 $^{31}P\{^{1}H\}$ NMR spectrum of complex **9** (202 MHz, C_6D_6, 25 °C).

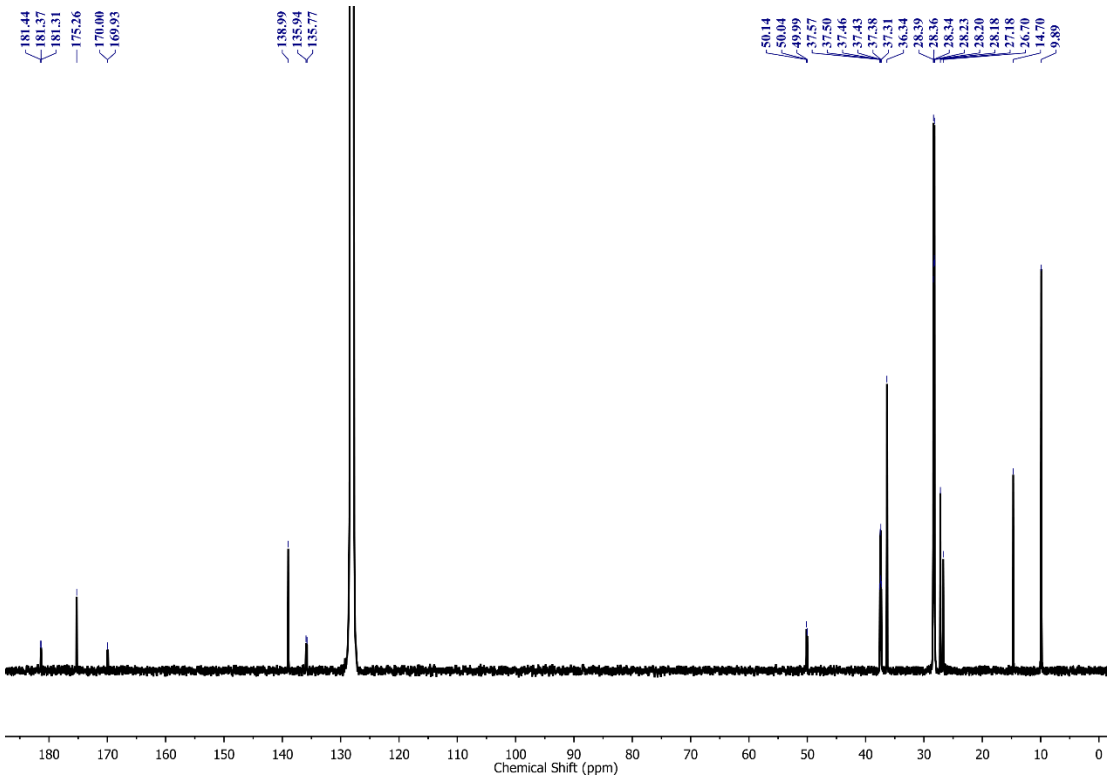

Fig. S26 ^{13}C NMR spectrum of complex **9** (101 MHz, C_6D_6, 25 °C).

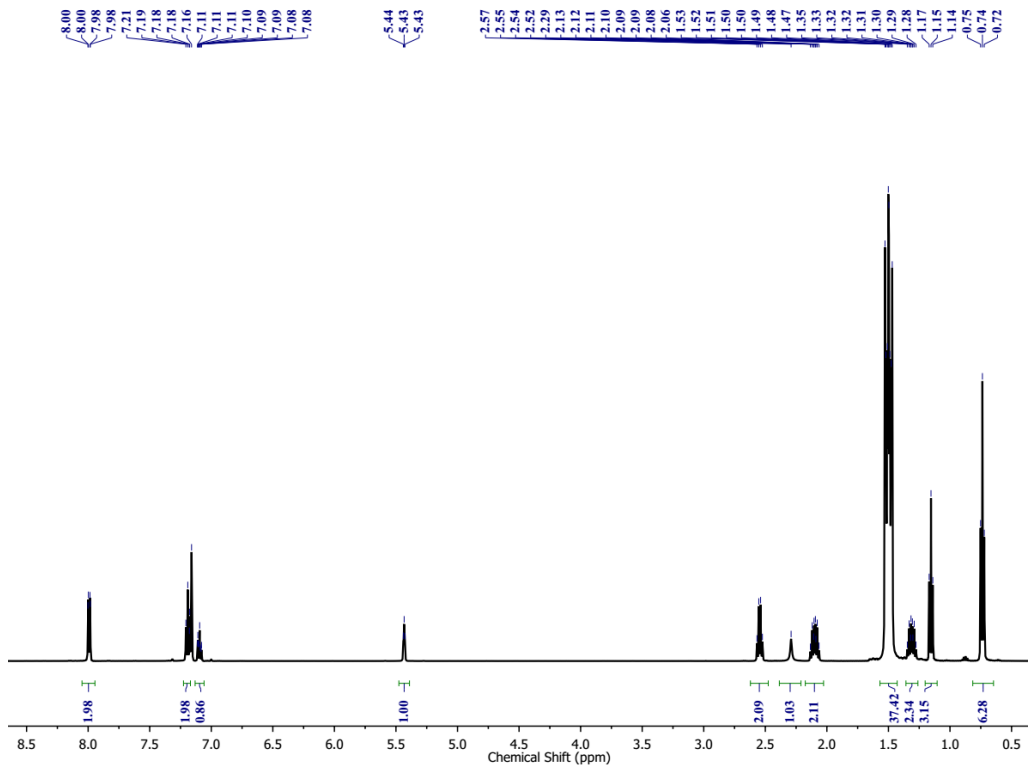

Fig. S27 ^{1}H NMR spectrum of complex **10** (500 MHz, C_6D_6, 25 °C).

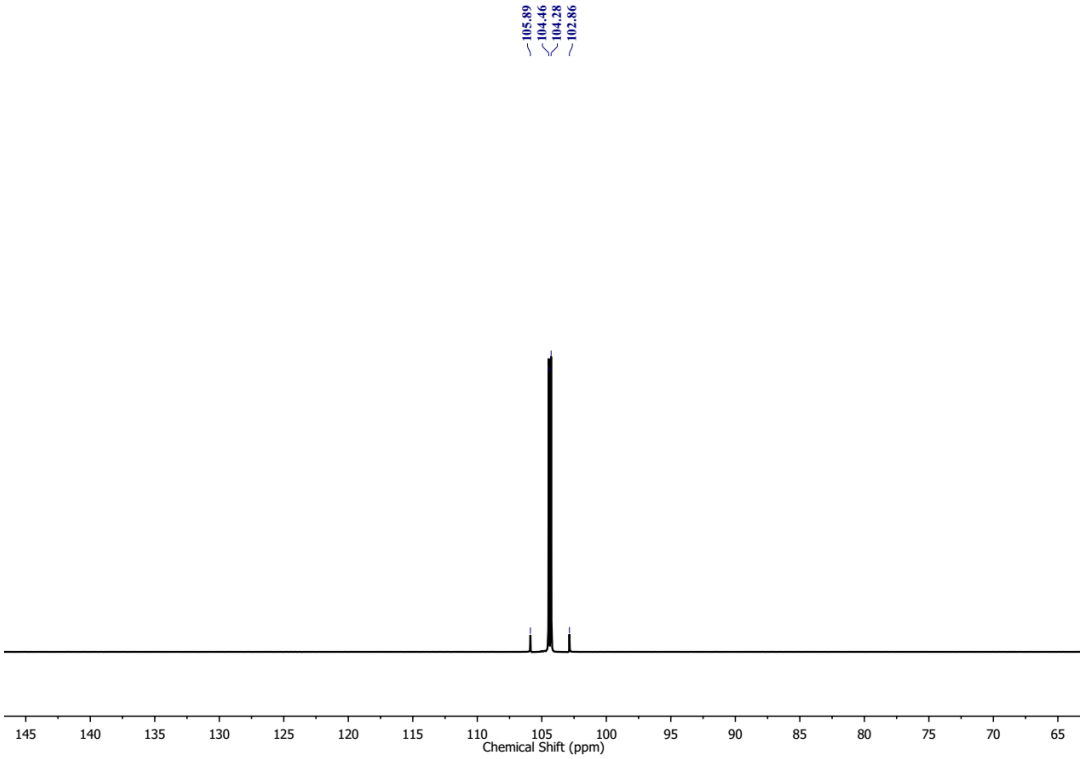

Fig. S28 ^{31}P{^{1}H} NMR spectrum of complex **10** (202 MHz, C_6D_6, 25 °C).

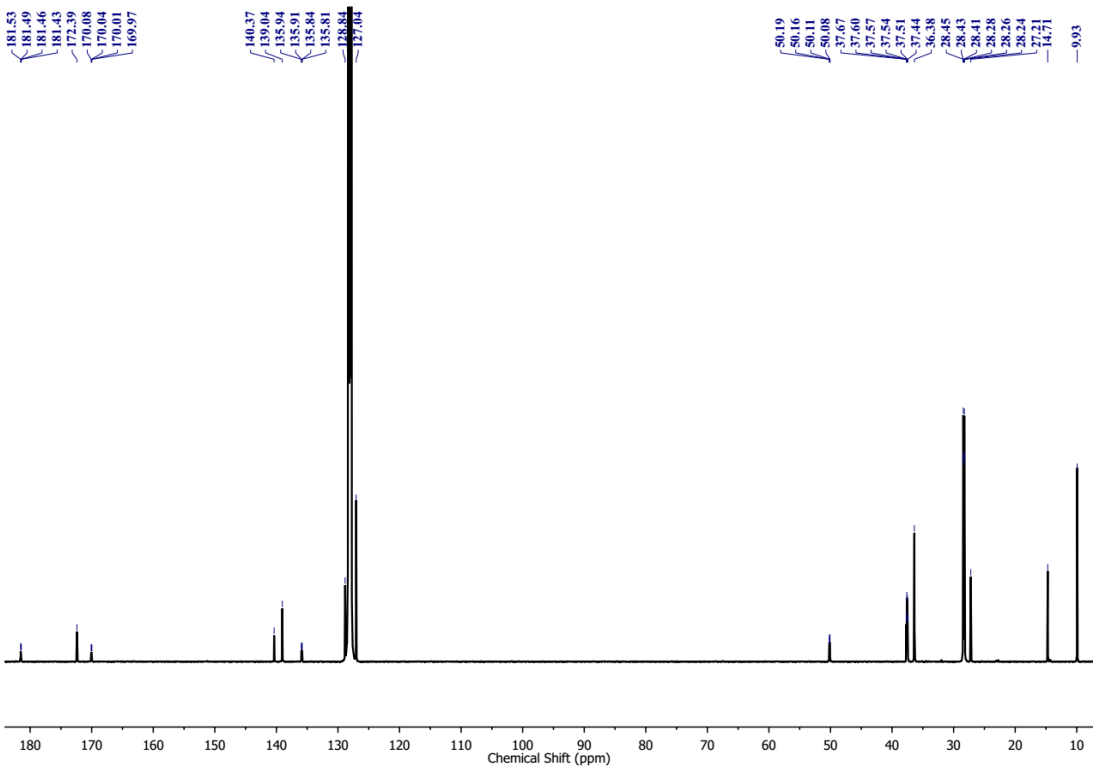

Fig. S29 ^{13}C NMR spectrum of complex **10** (126 MHz, C_6D_6, 25 °C).

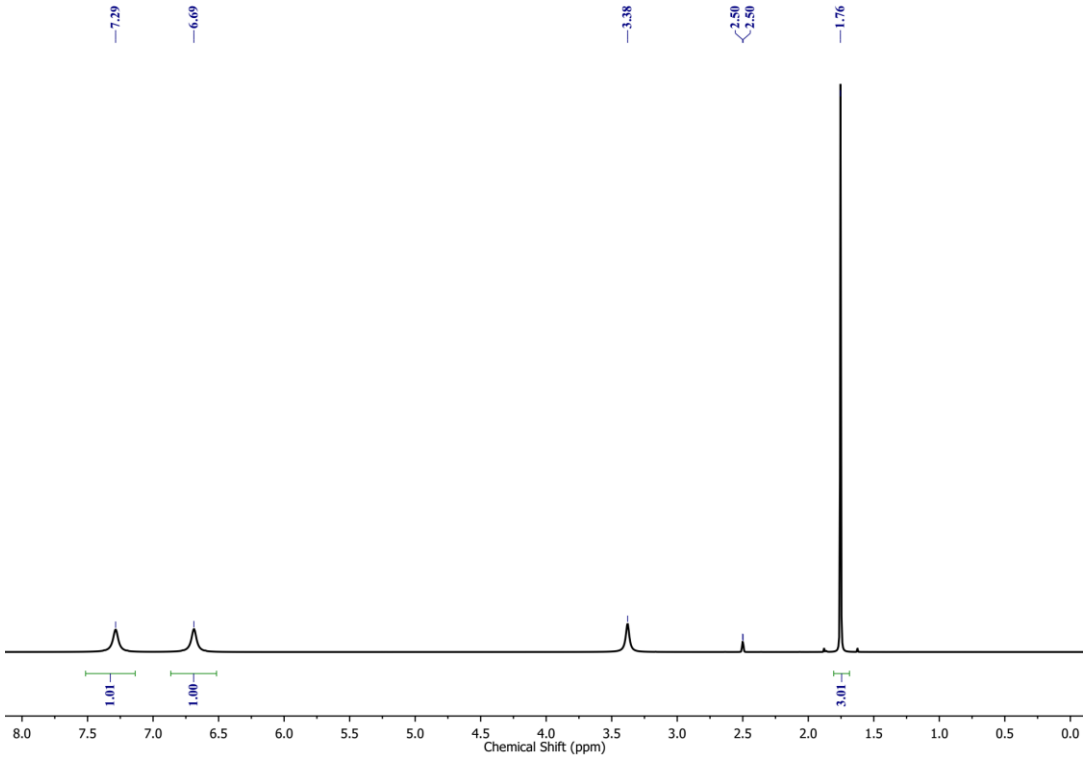

Fig. S30 ^{1}H NMR spectrum of compound **12a** (500 MHz, DMSO-d_6, 25 °C).

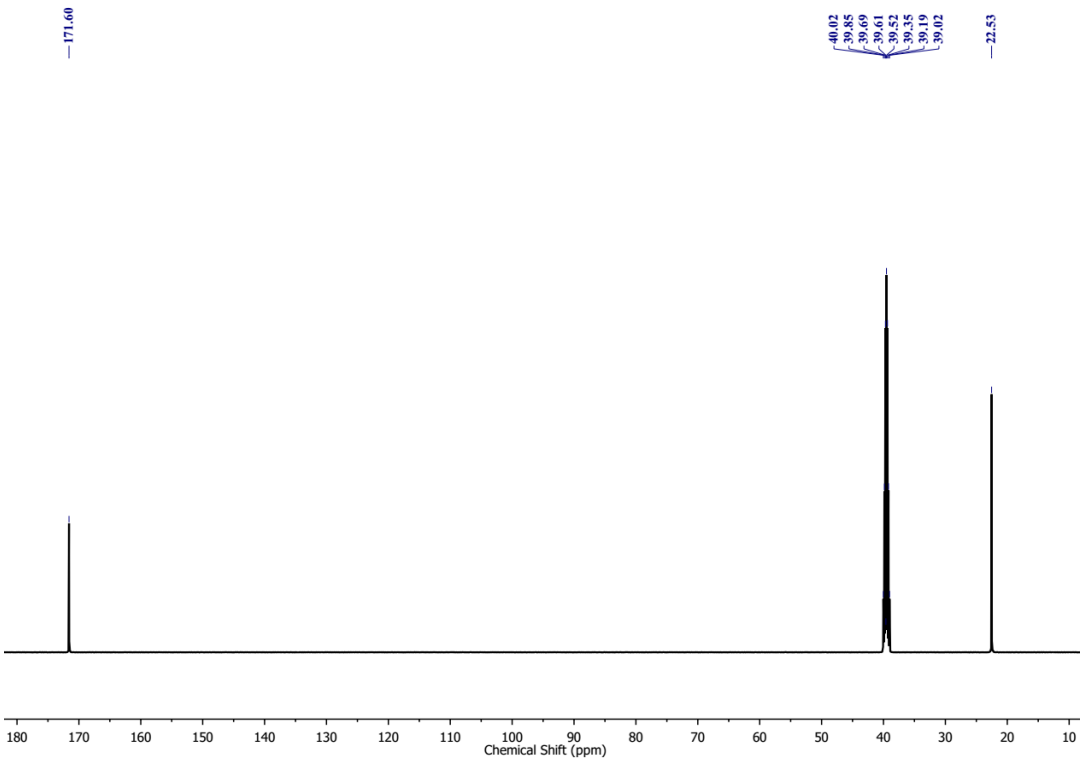

Fig. S31 ^{13}C NMR spectrum of compound **12a** (126 MHz, DMSO-d_6, 25 °C).

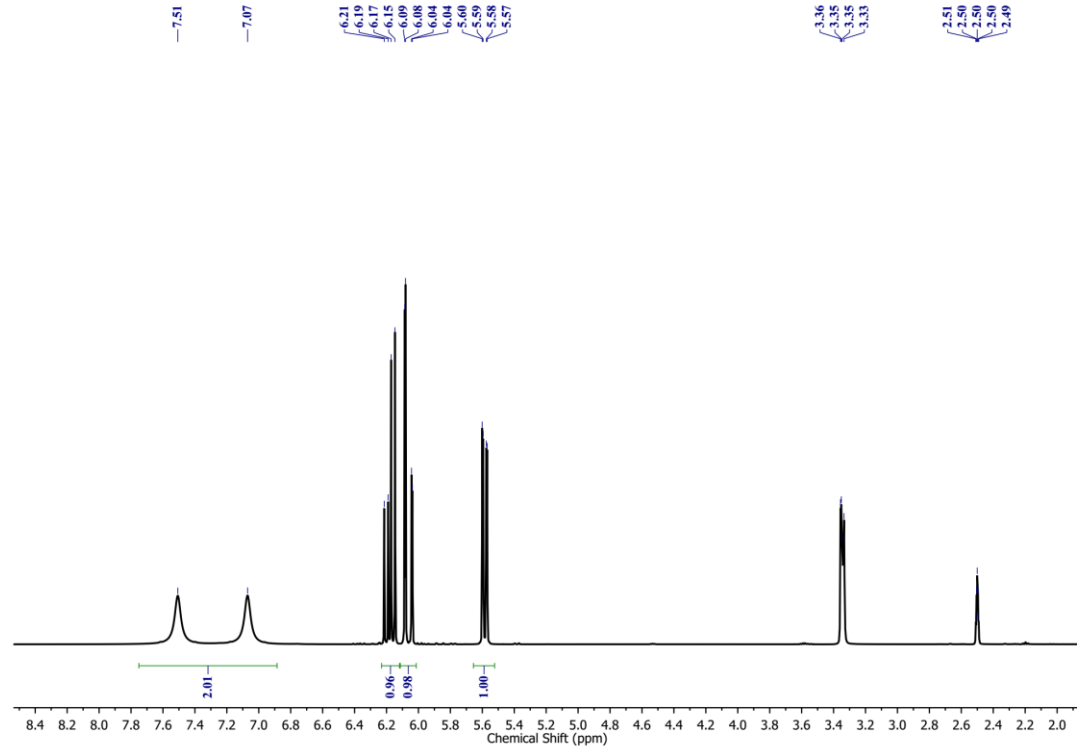

Fig. S32 ^{1}H NMR spectrum of compound **12b** (400 MHz, DMSO-d_6, 25 °C).

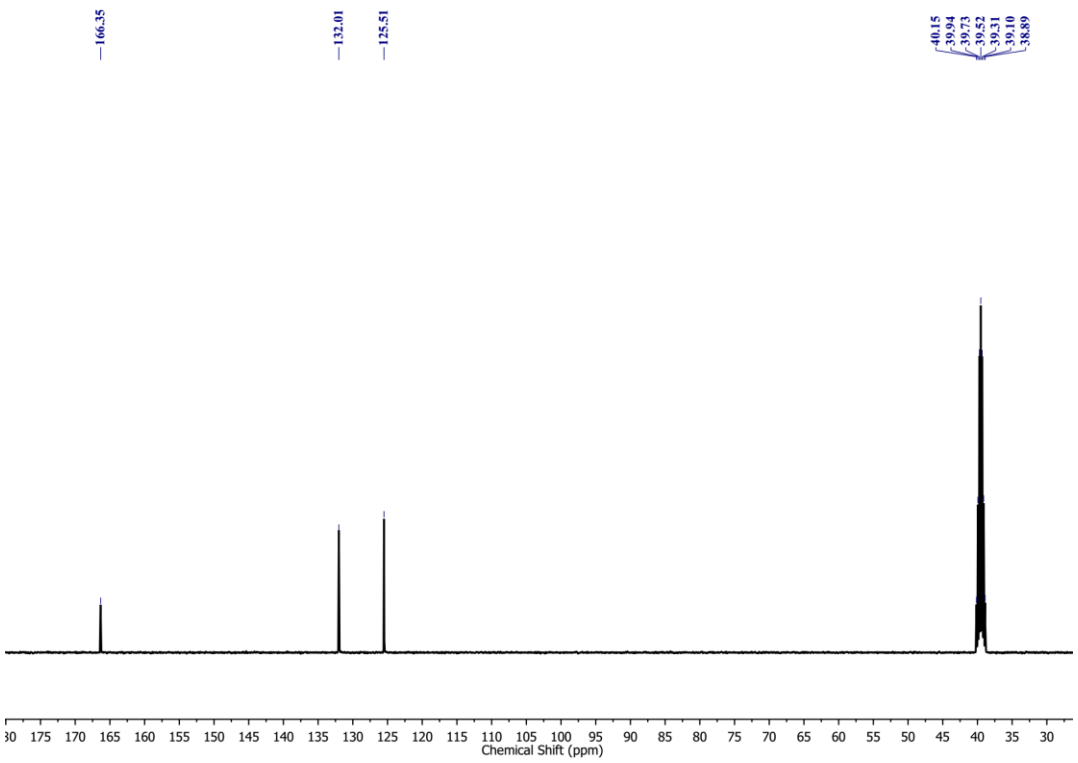

Fig. S33 ^{13}C NMR spectrum of compound **12b** (101 MHz, DMSO-d_6, 25 °C).

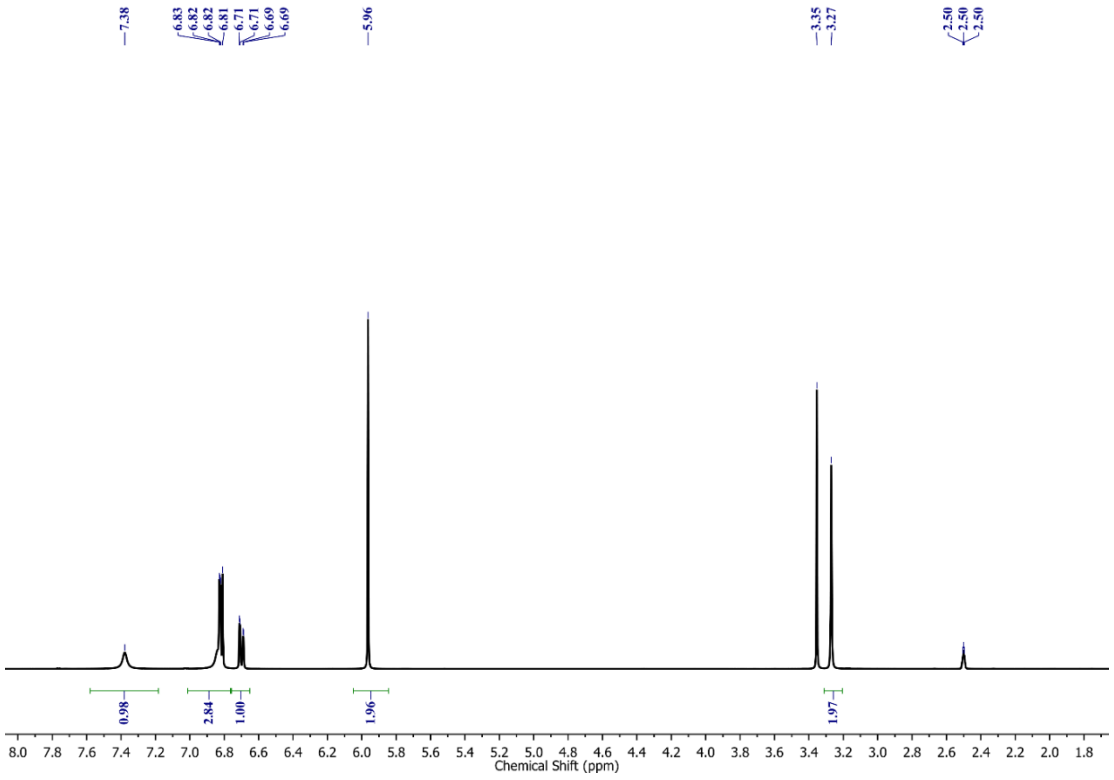

Fig. S34 ^{1}H NMR spectrum of compound **12c** (400 MHz, DMSO-d_6, 25 °C).

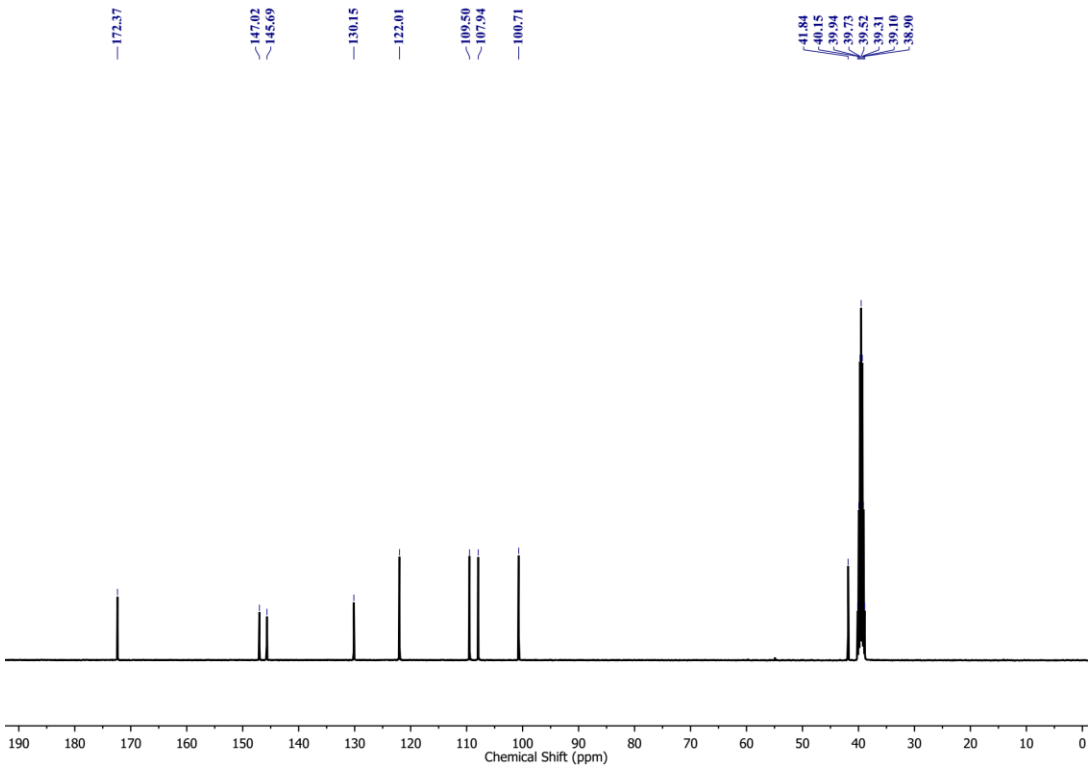

Fig. S35 ^{13}C NMR spectrum of compound **12c** (101 MHz, DMSO-d_6, 25 °C).

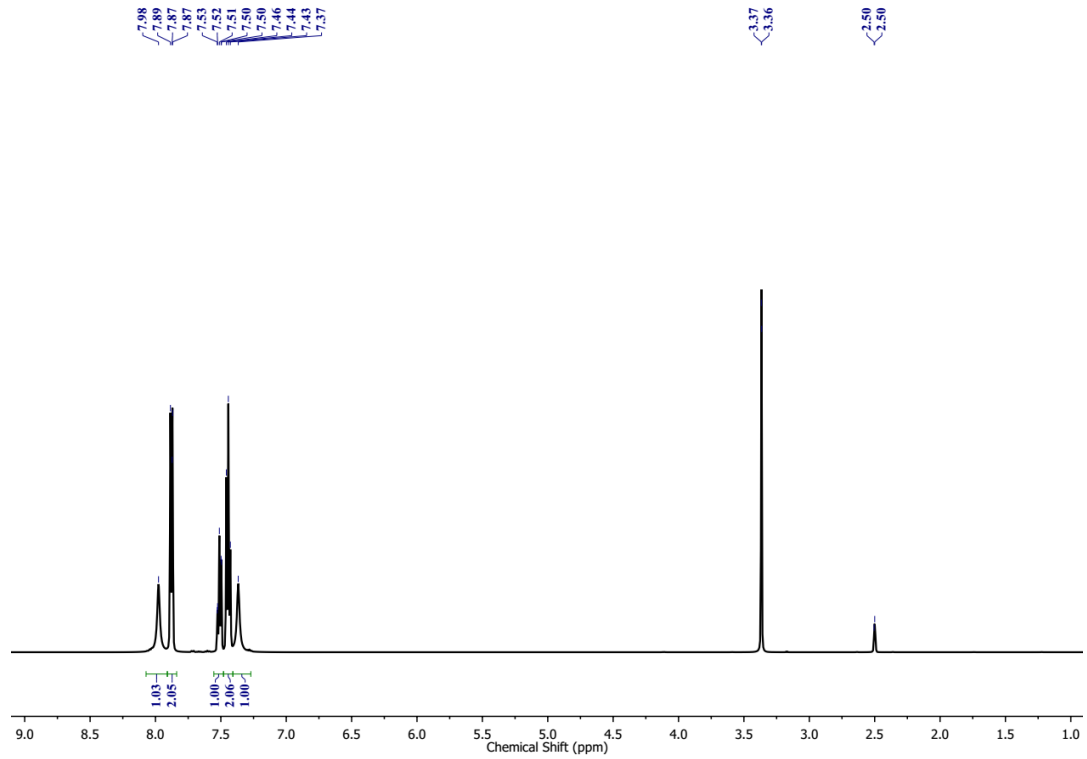

Fig. S36 ^{1}H NMR spectrum of compound **12d** (500 MHz, DMSO-d_6, 25 °C).

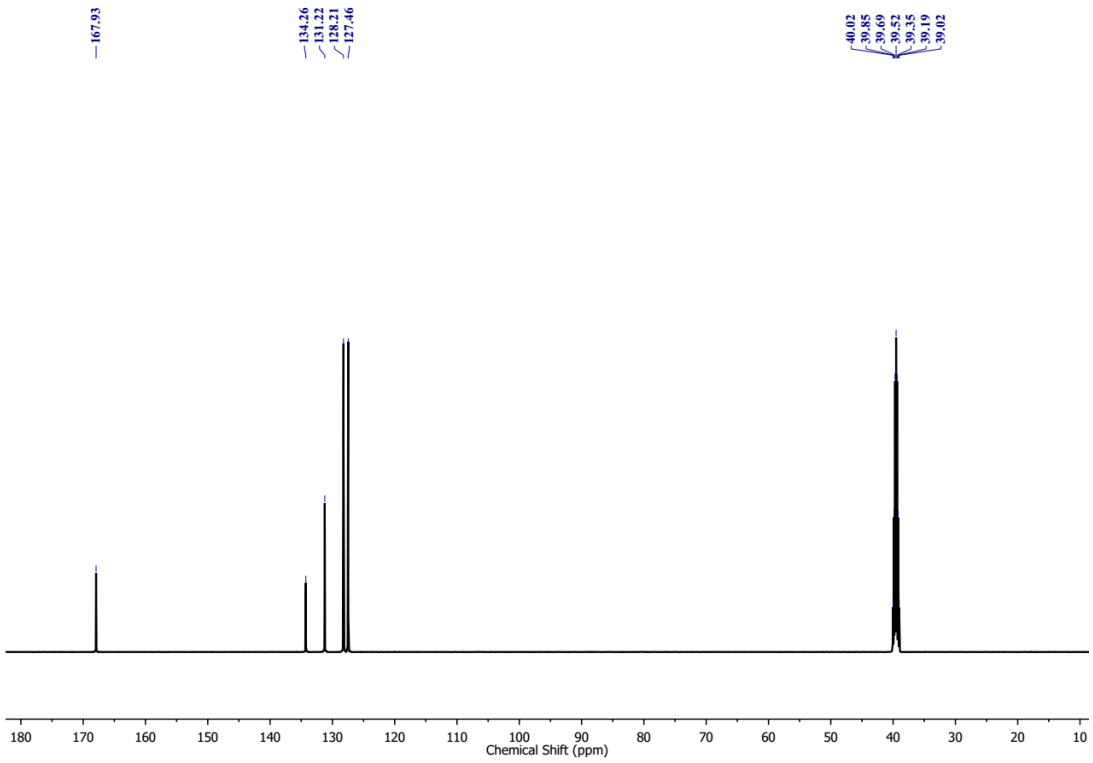

Fig. S37 ^{13}C NMR spectrum of compound **12d** (126 MHz, DMSO-d_6, 25 °C).

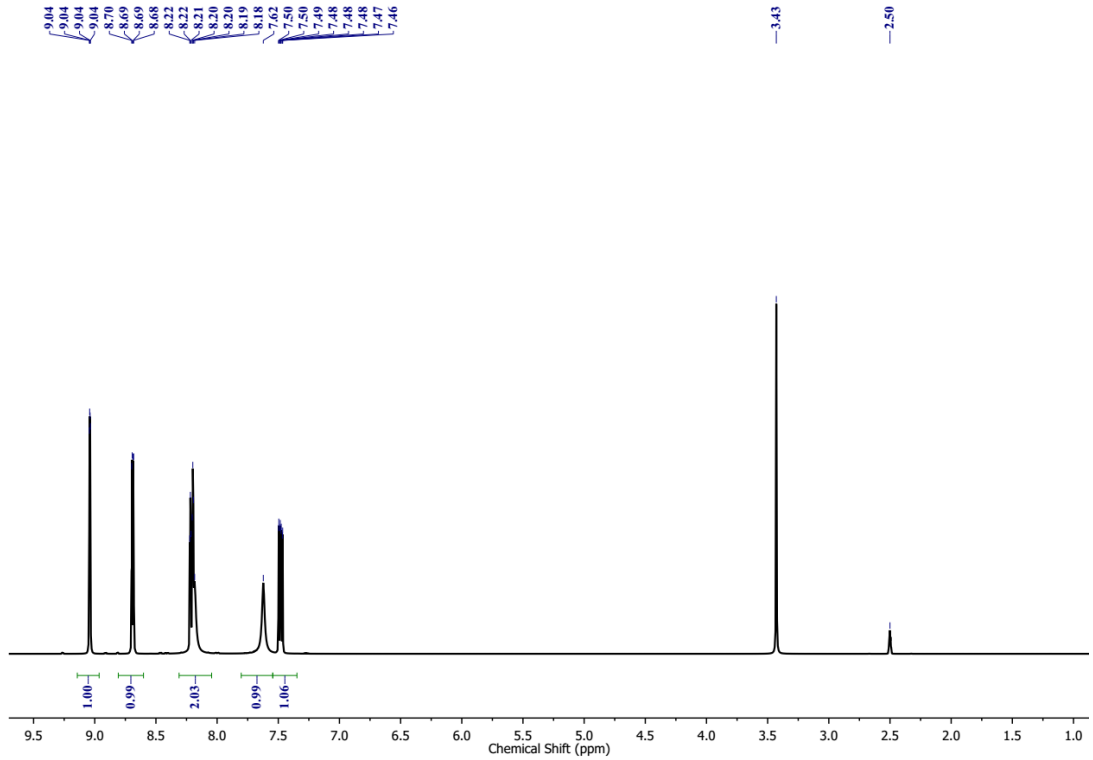

Fig. S38 ^{1}H NMR spectrum of compound **12e** (400 MHz, DMSO-d_6, 25 °C).

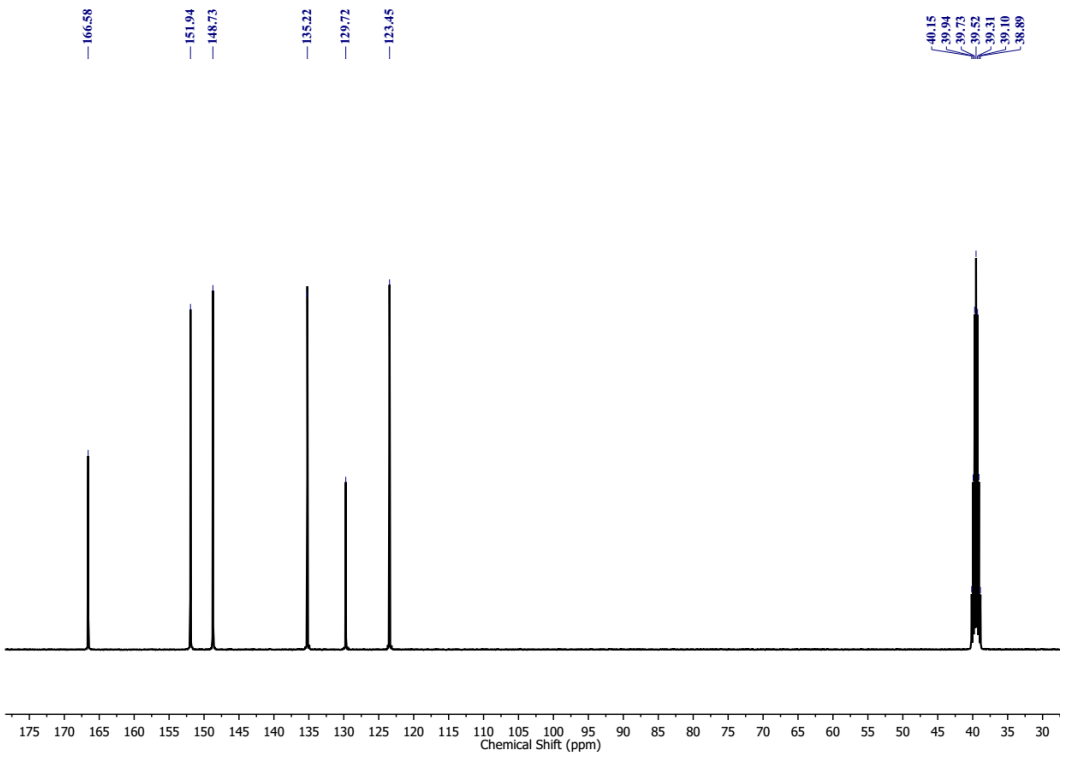

Fig. S39 ^{13}C NMR spectrum of compound **12e** (101 MHz, DMSO-d_6, 25 °C).

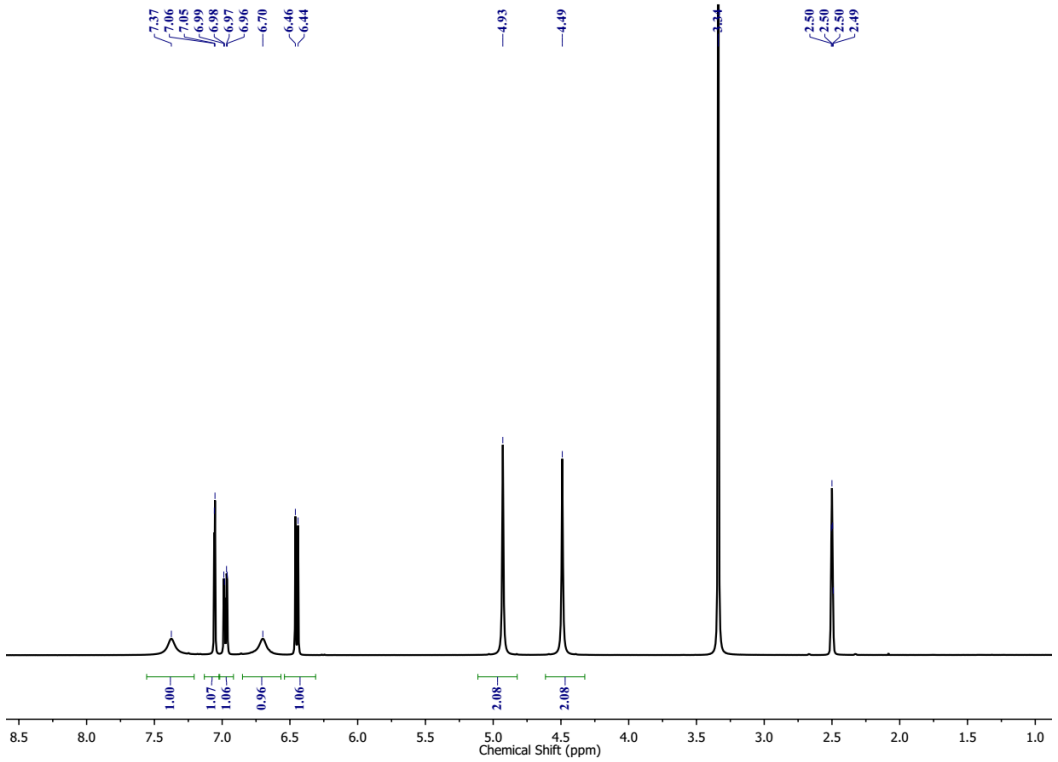

Fig. S40 ^{1}H NMR spectrum of compound **12f** (400 MHz, DMSO-d_6, 25 °C).

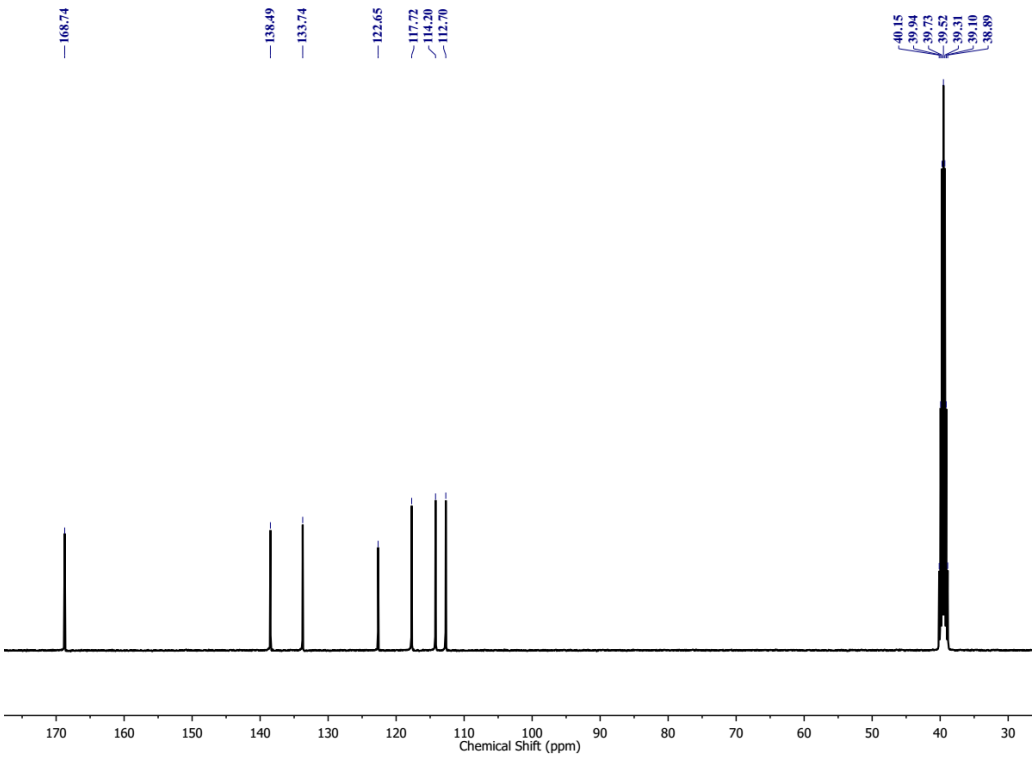

Fig. S41 ^{13}C NMR spectrum of compound **12f** (101 MHz, DMSO-d_6, 25 °C).

Table S1 Summary of Crystallographic Data for complexes 3, 6, 7.

Entry	**3**	**6**	**7**
Formula	$C_{27}H_{53}N_3NiOP_2$	$C_{55}H_{104}N_6Ni_2OP_4S_2$	$C_{36}H_{62}N_4NiO_2P_2$
F. W.	556.37	1170.86	703.54
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/c	P-1	P21
a (Å)	18.929(7)	8.677(4)	10.937(4)
b (Å)	10.157(3)	11.612(5)	11.634(4)
c (Å)	16.116(6)	18.416(8)	15.984(6)
α (deg)	90	74.030(15)	90
β (deg)	93.702(13)	80.855(16)	109.214(10)
γ (deg)	90	68.967(14)	90
V (Å^3)	3092.0(19)	1661.2(13)	1920.6(13)
Z	4	1	2
D_{calcd} (g/cm^3)	1.195	1.170	1.217
radiation (λ), Å	Mo K (0.71073)	Mo K (0.71073)	Mo K (0.71073)
θ range (°)	2.28 to 29.66	2.48 to 28.72	2.73 to 40.49
μ (mm^{-1})	0.754	0.764	0.623
F(000)	1208	632	760
no. of reflns collcd	65694	50327	67266
no. of reflns unique	8697	8536	24054
R(int)	0.0760	0.0541	0.0834
GOF	1.059	1.343	0.878
R_1 [I> 2σ(I)]	0.0488	0.0514	0.0598
wR_2 [I> 2σ(I)]	0.1466	0.1687	0.1528
R_1 [all data]	0.0724	0.0580	0.0786
wR_2 [all data]	0.1636	0.1747	0.1690
Δρmax, min/e Å^{-3}	0.064, -0.626	1.389, -1.027	0.902, -0.630

Table S2 Summary of Crystallographic Data for complexes 8-10.

Entry	**8**	**9**	**10**
Formula	$C_{36}H_{49}N_4NiOP_2S$	$C_{29}H_{56}N_4NiOP_2$	$C_{34}H_{58}N_4NiOP_2$
F. W.	706.50	597.42	659.49
Crystal system	Triclinic	orthorhombic	Monoclinic
Space group	P-1	P 21 21 21	P2(1)/c
a (Å)	11.653(5)	11.7380(11)	8.821(3)
b (Å)	13.249(6)	15.611(2)	27.389(8)
c (Å)	14.083(7)	18.0809(18)	15.683(5)
α (deg)	72.813(13)	90	90
β (deg)	87.034(14)	90	106.055(13)
γ (deg)	74.527(13)	90	90
V (Å^3)	2001.0(16)	3313.2(6)	3641(2)
Z	2	4	4
D_{calcd} (g/cm^3)	1.173	1.198	1.203
radiation (λ), Å	Mo K (0.71073)	Mo K (0.71073)	Mo K (0.71073)
θ range (°)	2.12 to 29.97	2.07 to 33.17	2.52 to 29.58
μ (mm^{-1})	0.647	0.709	0.651
F(000)	750	1296	1424
no. of reflns collcd	76590	64229	60711
no. of reflns unique	11428	12629	10185
R(int)	0.0996	0.1340	0.0804
GOF	1.142	0.918	1.044
R_1 [I> 2σ(I)]	0.0701	0.0557	0.0593
wR_2 [I> 2σ(I)]	0.1863	0.1311	0.1535
R_1 [all data]	0.2076	0.1058	0.0956
wR_2 [all data]	0.2171	0.1700	0.1740
Δρmax, min/e Å^{-3}	0.913, - 0.754	0.598, -0.551	0.937, -0.812