Supplementary Information

1,4-Dihydrophosphinolines and Their Complexes with Group 10 Metals

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Crystal data and structure refinement for *2b*, *trans*-5, *cis*-6, *trans*-7, *trans*-8 and *cis*-8

Table S1. Summary of crystal data, data collection and structure refinement for the X-ray diffraction study of complexes *2b*, *trans*-5, *cis*-6, *trans*-7, *trans*-8, and *cis*-8.

	2b	***trans-5***	***cis-6***	***trans-7***	***trans-8***	***cis-8***
CCD number	1426280	1432271	1432270	1432267	1432269	1432268
dentification code	asb598	KP_4	KP3	km868last	kp1_new	KMA-805
Empirical formula	$C_{34}H_{32}P_2Br_2$	$C_{34}H_{34}Cl_2P_2Pd$	$C_{34}H_{34}Cl_2P_2Pt$	$C_{18}H_{18}BrCl_3PPd_{0.5}$	$C_{18}H_{18}BrCl_3PPt_{0.5}$	$C_{34}H_{32}Br_2Cl_2P_2Pt$
Formula weight	662.36	681.92	770.54	504.75	549.10	928.34
Temperature/K	100.01(10)	100(2)	100.01(10)	293(2)	100.01(10)	100.00(10)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	P-1	P-1	$P2_1/n$
a/Å	20.3791(3)	12.2369(4)	11.9317(6)	8.7824(4)	8.7628(3)	11.3816(3)
b/Å	10.08862(14)	8.2187(2)	15.5172(6)	11.1066(6)	11.1119(5)	18.9270(4)
c/Å	15.5172(2)	15.0367(5)	16.9442(8)	11.4473(6)	11.4634(5)	16.0478(4)
α/°	90.00	90	90	103.246(5)	103.369(4)	90
β/°	110.0486(17)	91.105(3)	100.854(5)	106.855(5)	106.943(3)	109.582(3)
γ/°	90.00	90	90	107.784(5)	107.517(3)	90
Volume/Å^3	2996.96(8)	1511.98(8)	3081.0(2)	953.72(9)	953.98(7)	3257.08(15)
Z	4	2	4	2	2	4
ρ_{calc}g/cm^3	1.468	1.4977	1.661	1.758	1.912	1.893
μ/mm^{-1}	4.596	7.741	11.258	3.112	14.199	7.048
F(000)	1344.0	700.4	1520.0	500.0	532.0	1792.0
Crystal size/mm^3	0.15 × 0.12 × 0.07	0.23 × 0.16 × 0.10	0.1042 × 0.0925 × 0.0773	0.24 × 0.16 × 0.10	0.12 × 0.10 × 0.08	0.2 × 0.2 × 0.2
Radiation	Cu *Kα* (λ = 1.54184)	Cu *Kα* (λ = 1.54184)	Cu *Kα* (λ = 1.54184)	Mo *Kα* (λ = 0.71073)	Cu*Kα* (λ = 1.54184)	Mo*Kα* (λ = 0.71073)
2Θ range for data collection/°	9.24 to 152.7°	9.24 to 152.42	7.79 to 144.992	5.24 to 54.98	8.606 to 144.92	5.344 to 55

Index ranges	-25 ≤ h ≤ 25, -12 ≤ k ≤ 12, -19 ≤ l ≤ 19	-14 ≤ h ≤ 15, -10 ≤ k ≤ 10, -18 ≤ l ≤ 18	-14 ≤ h ≤ 14, -11 ≤ k ≤ 19, -20 ≤ l ≤ 20	-10 ≤ h ≤ 11, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14	-9 ≤ h ≤ 10, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	-13 ≤ h ≤ 14, -24 ≤ k ≤ 24, -20 ≤ l ≤ 12
Reflections collected	38236	18145	21352	7578	13901	25858
Independent reflections	6269[R_{int} = 0.0349]	3166 [R_{int} = 0.0462, R_{sigma} = 0.0271]	6094 [R_{int} = 0.0746, R_{sigma} = 0.0582]	4114 [R_{int} = 0.0263, R_{sigma} = 0.0454]	3786 [R_{int} = 0.0406, R_{sigma} = 0.0335]	7480 [R_{int} = 0.0271, R_{sigma} = 0.0242]
Data/restraints/parameters	6269/0/347	3166/0/179	6094/0/356	4114/0/198	3786/0/216	7480/0/374
Goodness-of-fit on F^2	1.016	1.187	1.077	1.045	1.103	1.123
Final R indexes [I>=2σ (I)]	R_1 = 0.0275, wR_2 = 0.0735	R_1 = 0.0398, wR_2 = 0.1346	R_1 = 0.0565, wR_2 = 0.1454	R_1 = 0.0511, wR_2 = 0.1245	R_1 = 0.0209, wR_2 = 0.0492	R_1 = 0.0238, wR_2 = 0.0538
Final R indexes [all data]	R_1 = 0.0305, wR_2 = 0.0765	R_1 = 0.0452, wR_2 = 0.1434	R_1 = 0.0743, wR_2 = 0.1692	R_1 = 0.0631, wR_2 = 0.1339	R_1 = 0.0253, wR_2 = 0.0507	R_1 = 0.0282, wR_2 = 0.0556
Largest diff. peak/hole / e $Å^{-3}$	0.49/-0.39	1.48/-0.71	3.98/-2.15	2.65/-0.50	1.00/-0.52	1.77/-0.77

Table S2. Distance from selected atom to plane P1−Cl1−Cl2−P1A−Pt1 (Å) for complexes *cis*-6 and *cis*-8.

Selected atom	Distance from selected atom to plane P1−Cl1−Cl2−P1A−Pt1 (Å)	
	***cis*-6**	***cis*-8**
Pt1	−0.0143(9)	0.0130(4)
P1	−0.0253(11)	0.2131(4)
P1A	0.0350(11)	−0.2234(4)
Cl1	0.0341(11)	−0.2317(4)
Cl2	−0.0296(12)	0.2290(4)

NMR spectra

2a

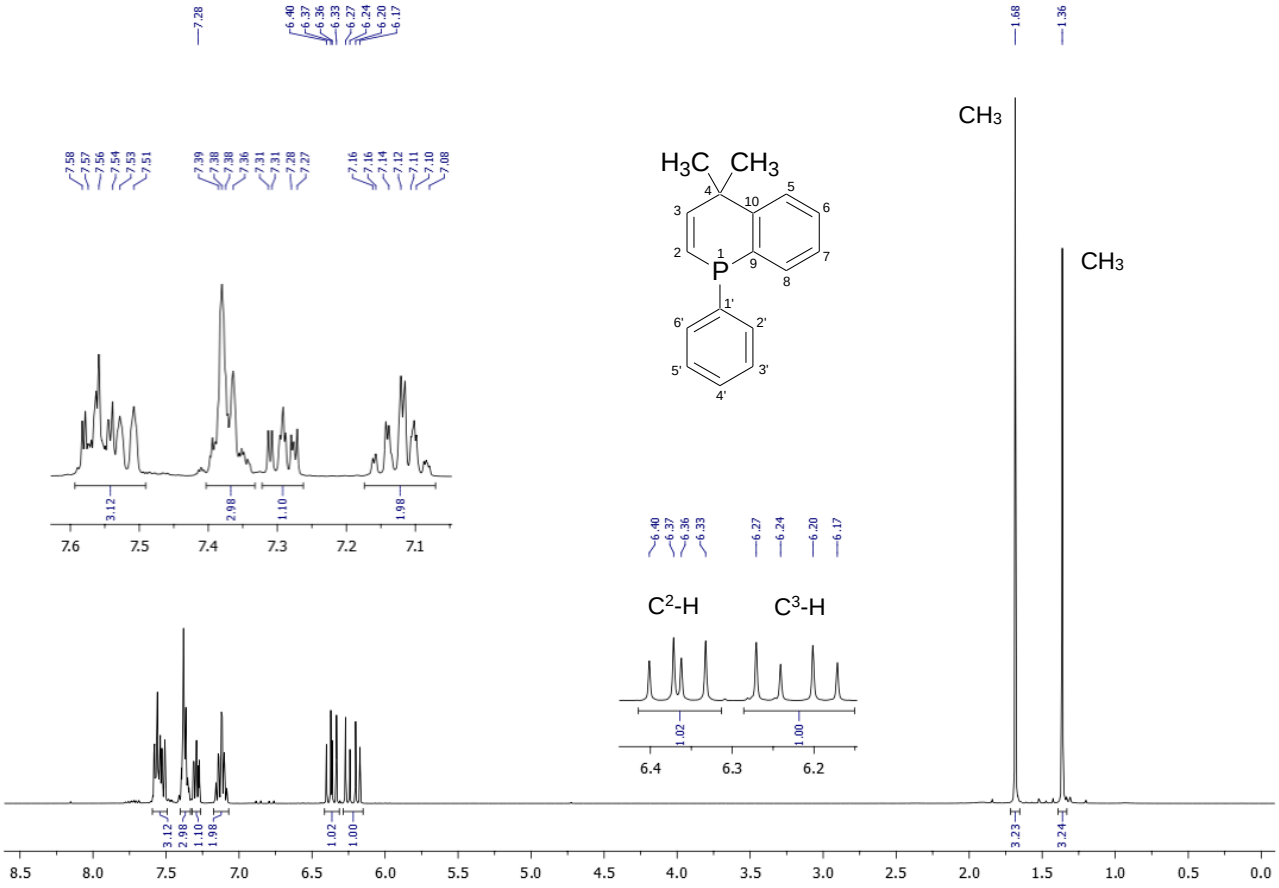

Fig. S1. ^{1}H NMR spectrum of the compound **2a** ($CDCl_3$).

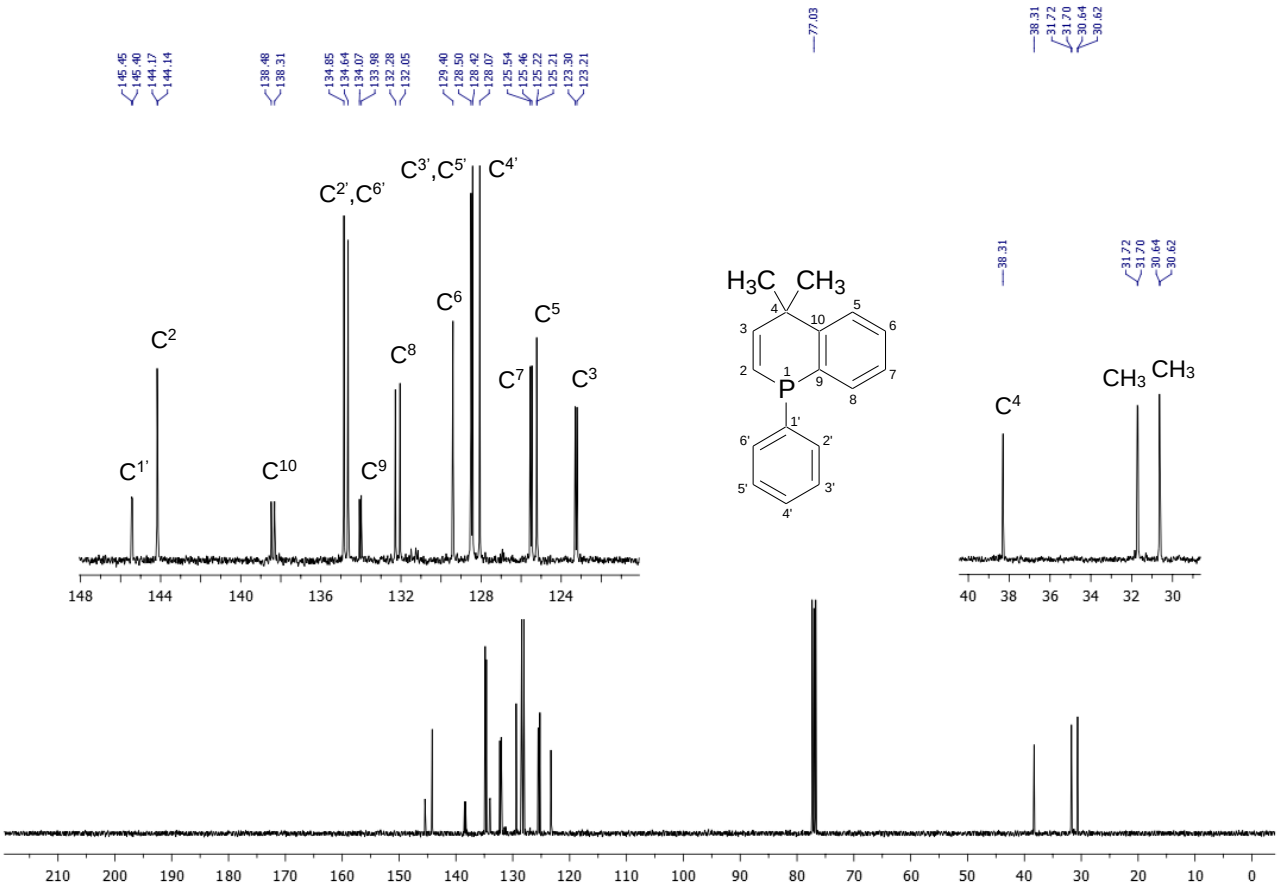

Fig. S2. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2a** ($CDCl_3$).

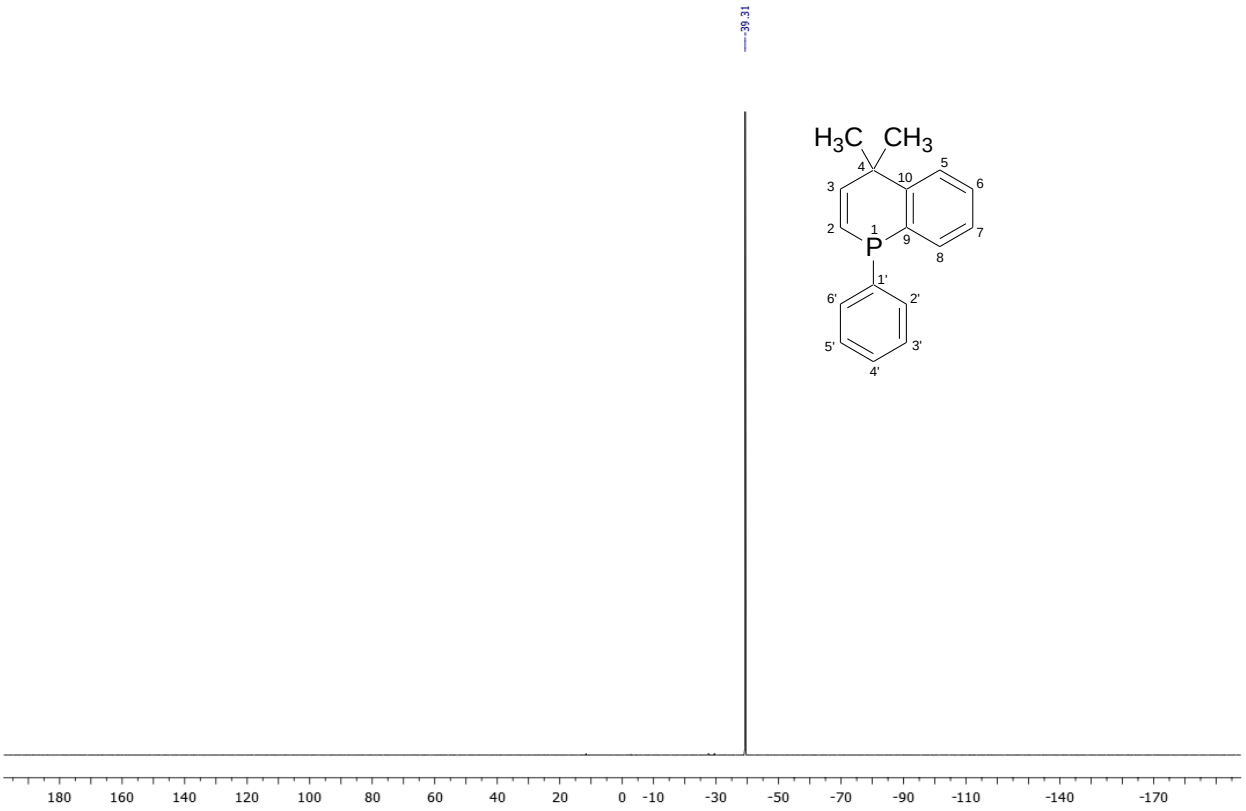

Fig. S3. $^{31}P\{^{1}H\}$ NMR spectrum of the compound **2a** ($CDCl_3$).

2b

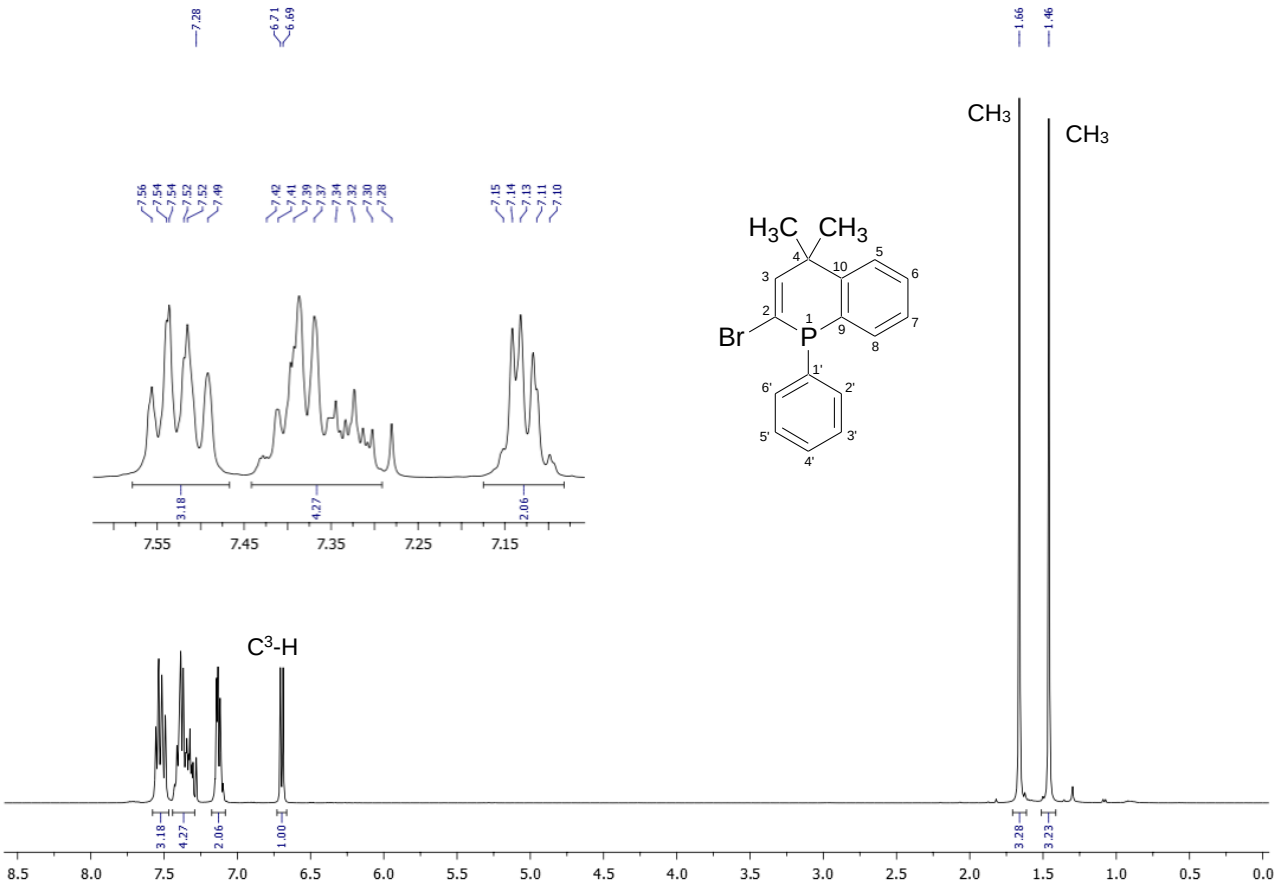

Fig. S4. ^{1}H NMR spectrum of the compound **2b** ($CDCl_3$).

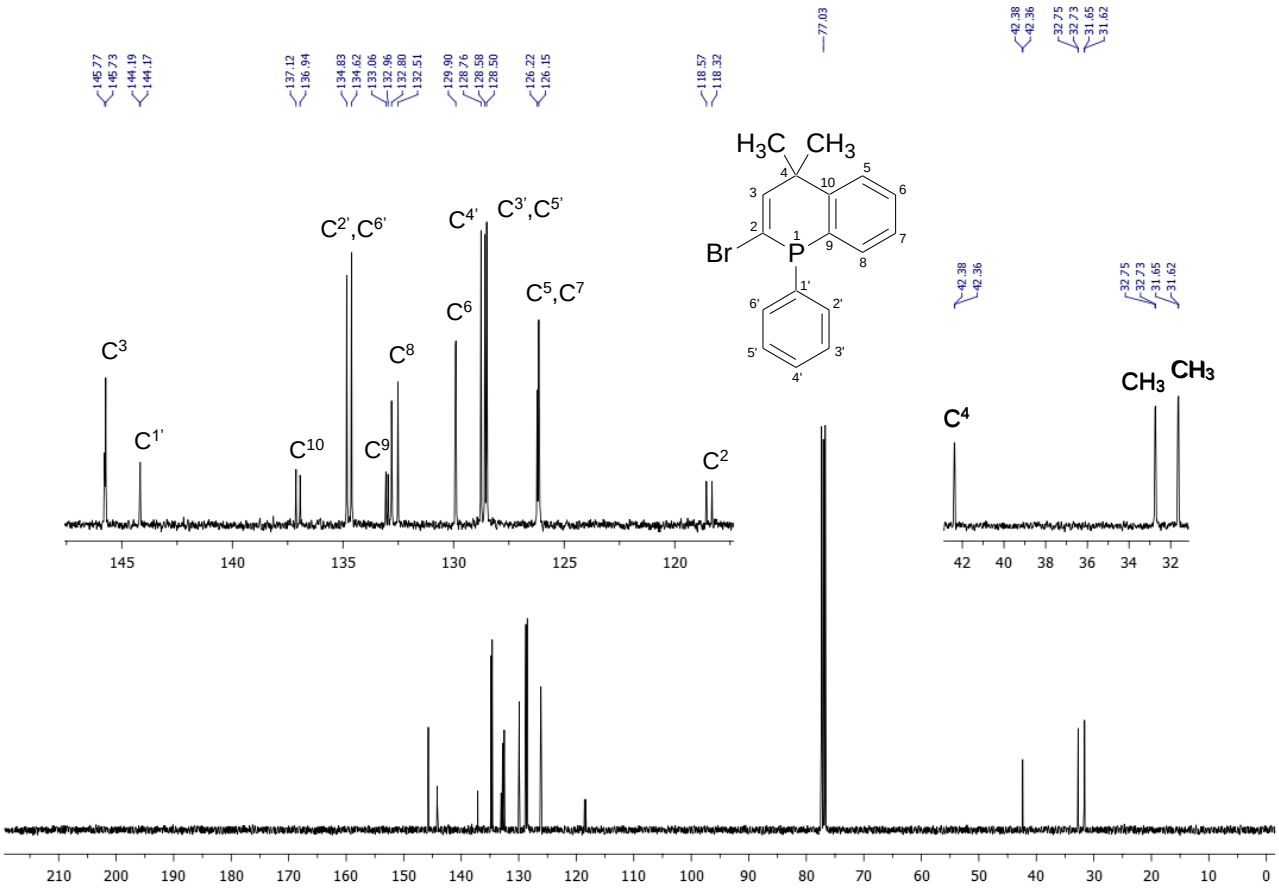

Fig. S5. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2b** ($CDCl_3$).

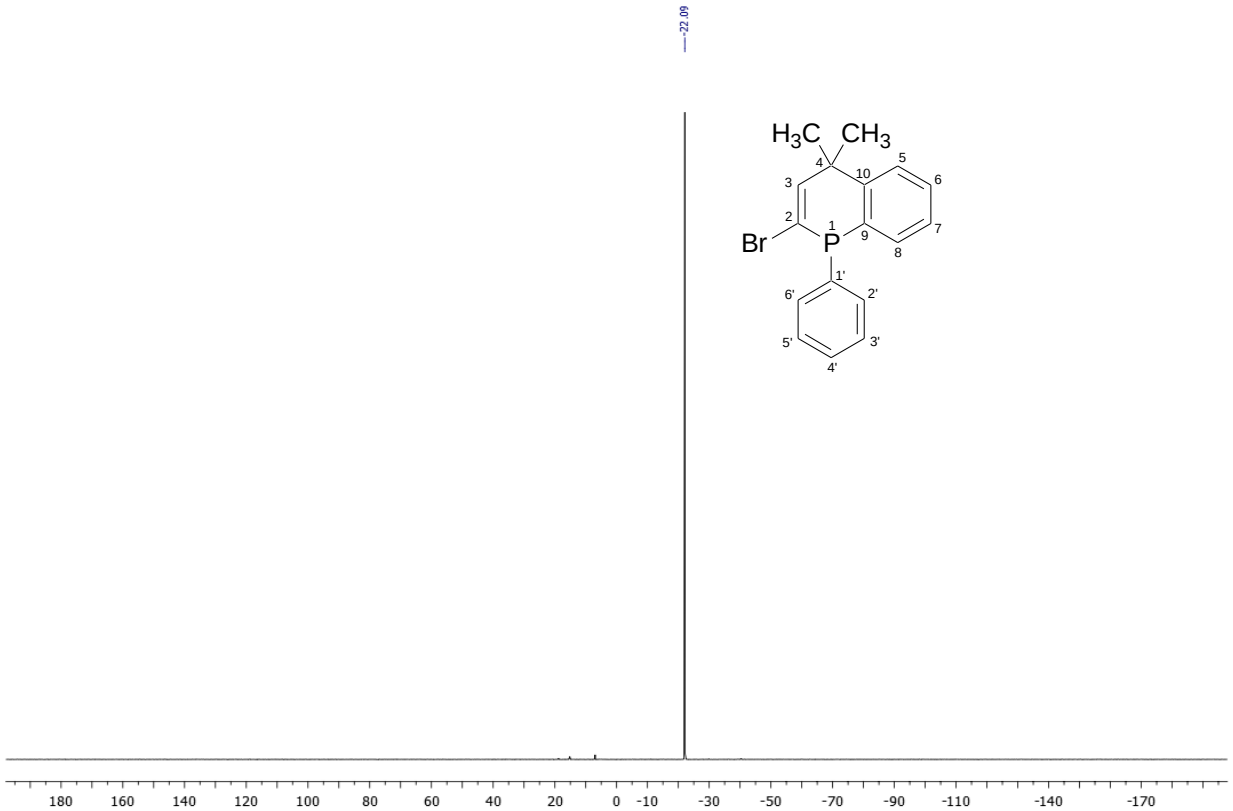

Fig. S6. $^{31}P\{^{1}H\}$ NMR spectrum of the compound **2b** ($CDCl_3$).

***trans*-5**

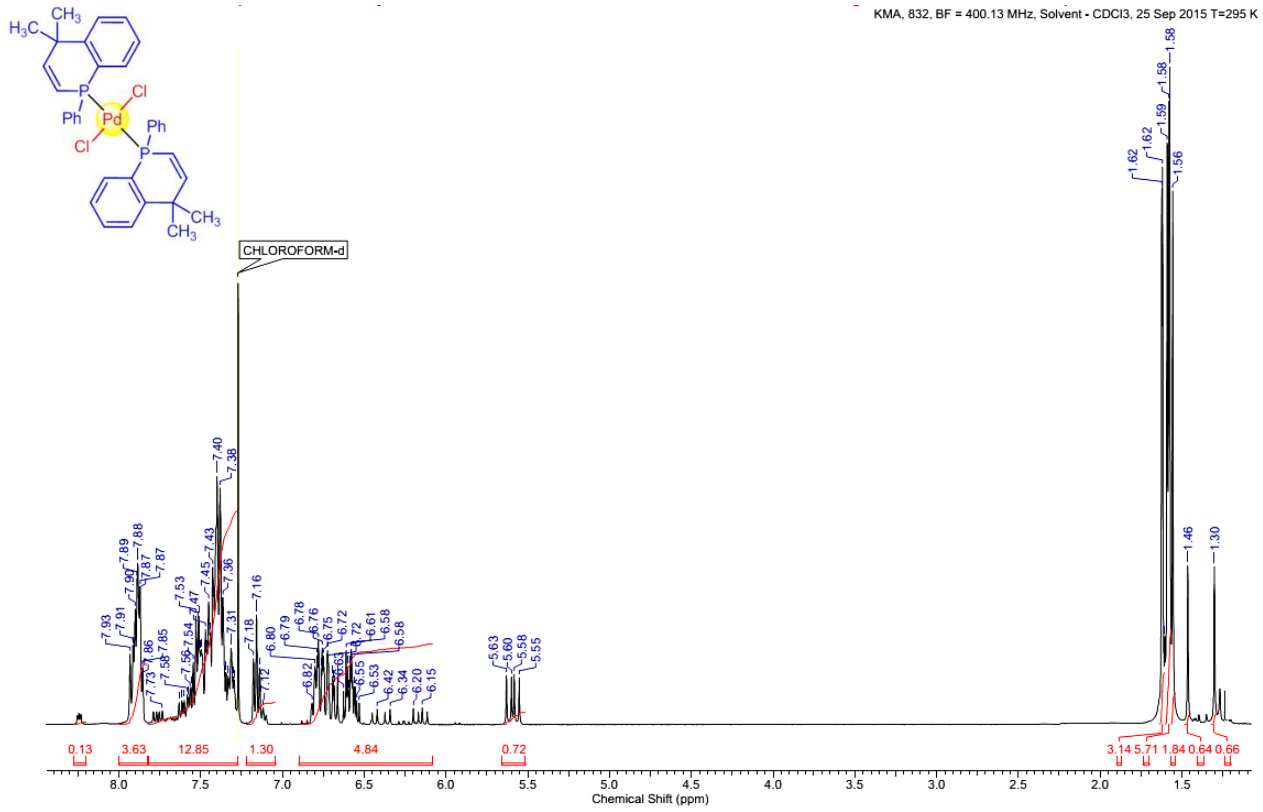

Fig. S7. ^{1}H NMR spectrum of the compound **5** ($CDCl_3$, mixture of *cis*-and *trans*- isomers).

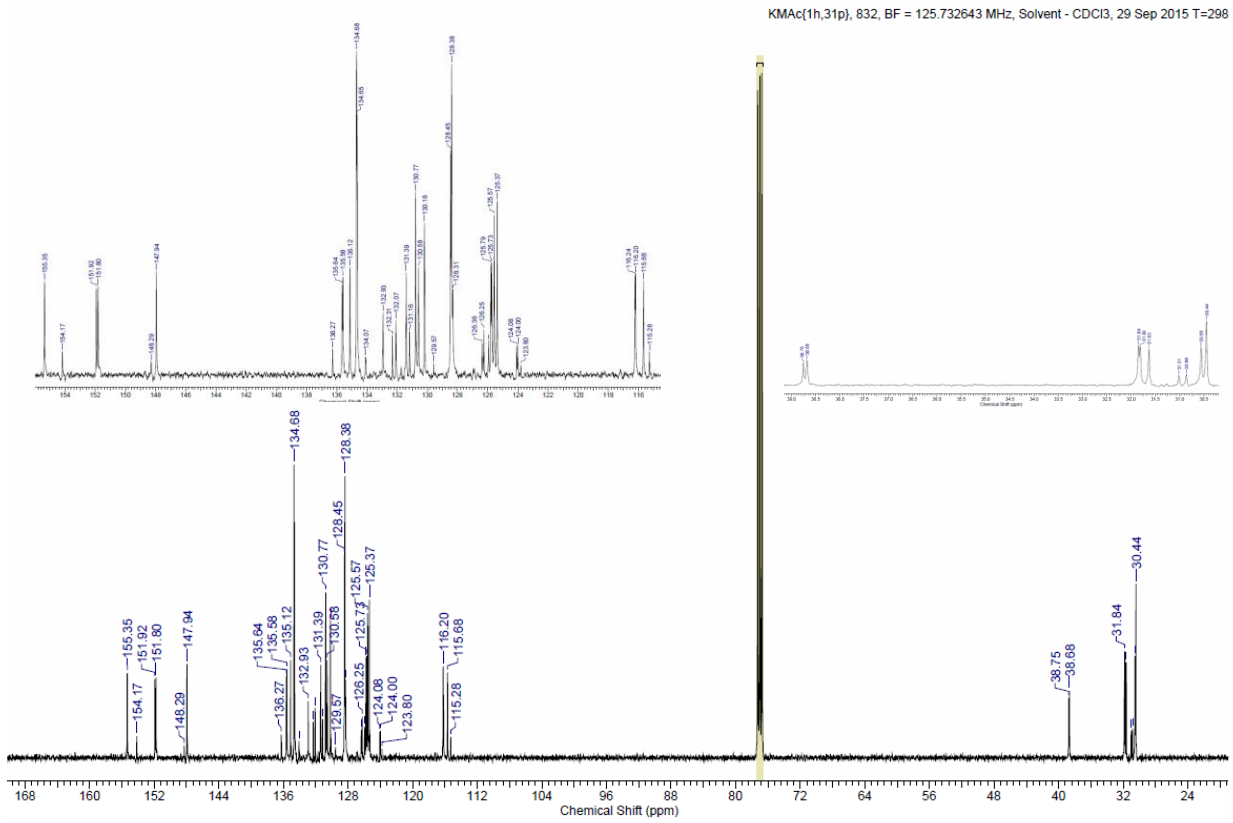

Fig. S8. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of the compound **5** ($CDCl_3$, mixture of *cis*-and *trans*- isomers).

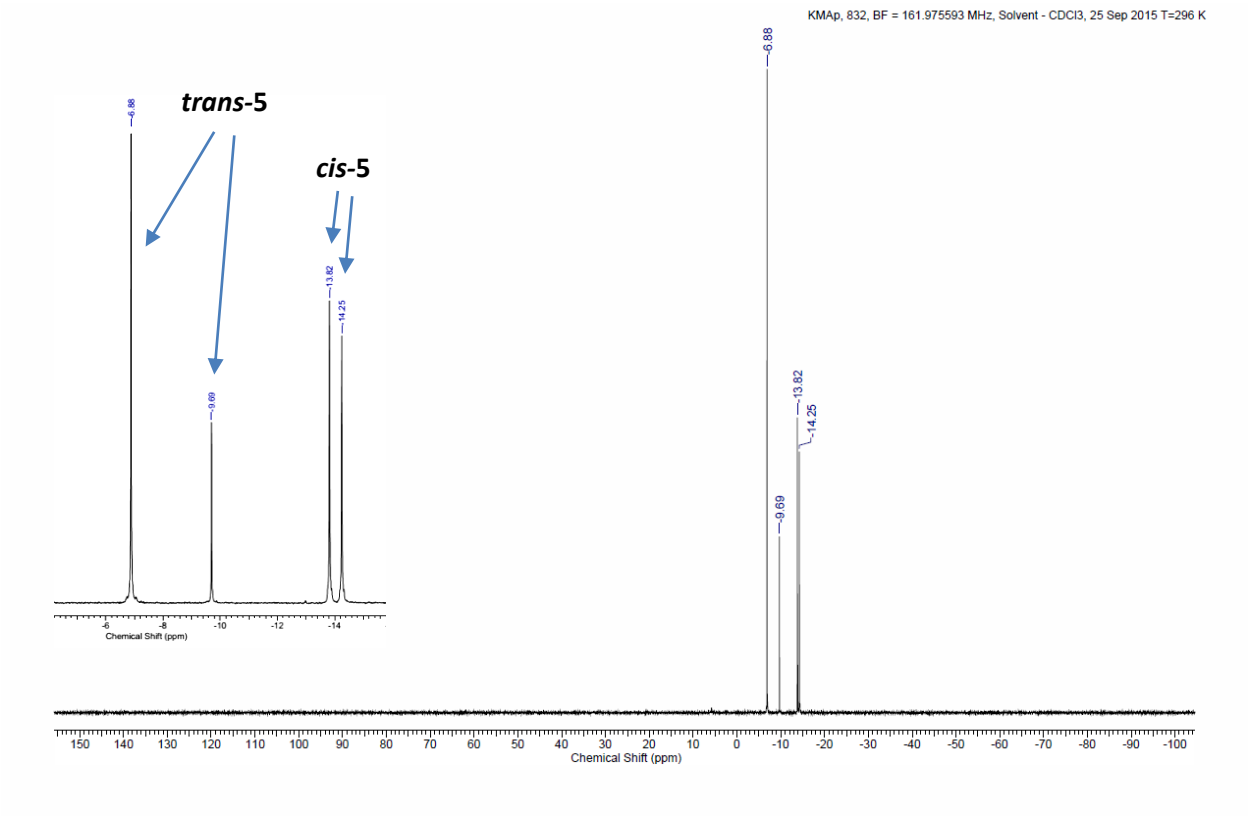

Fig. S9. $^{31}P\{^{1}H\}$ NMR spectrum of the compound **5** ($CDCl_3$, mixture of *cis*-and *trans*- isomers).

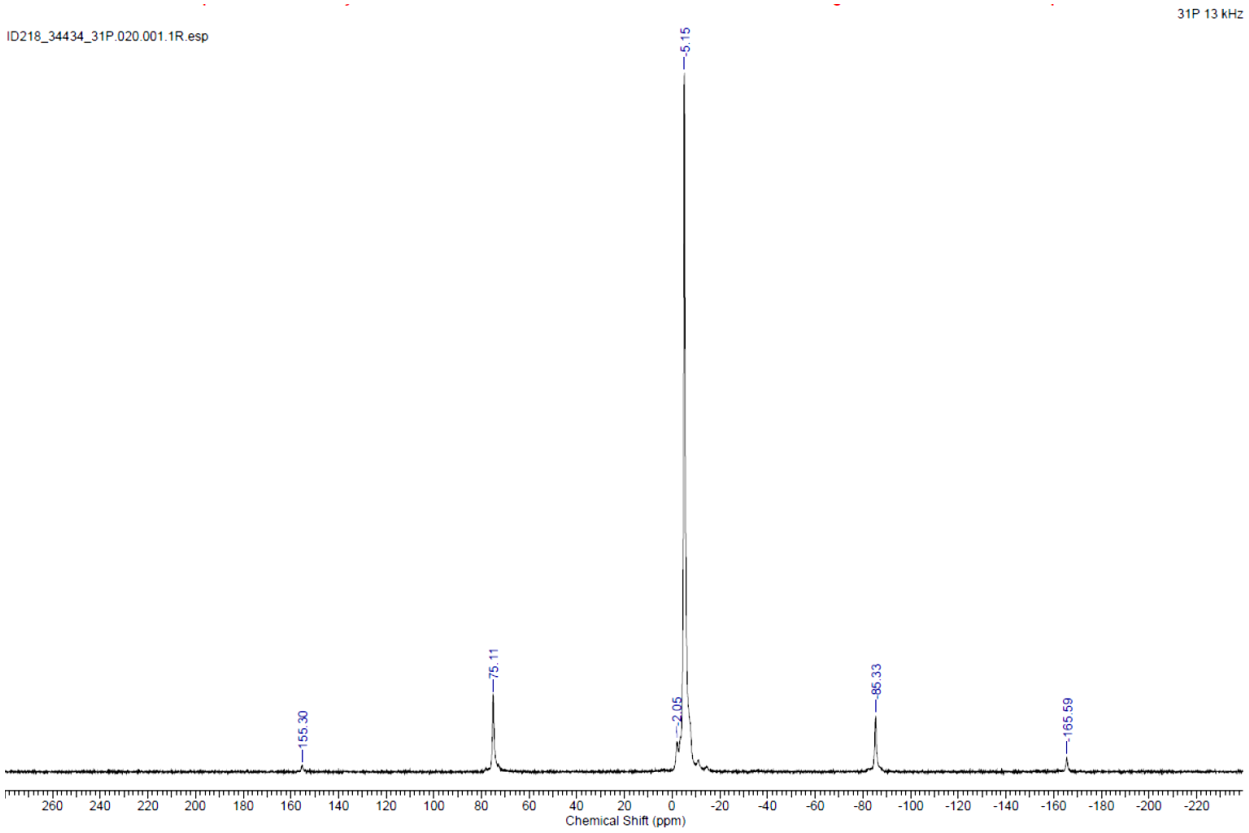

Fig. S10. ^{31}P MAS NMR spectrum of the compound ***trans*-5**.

***cis*-6**

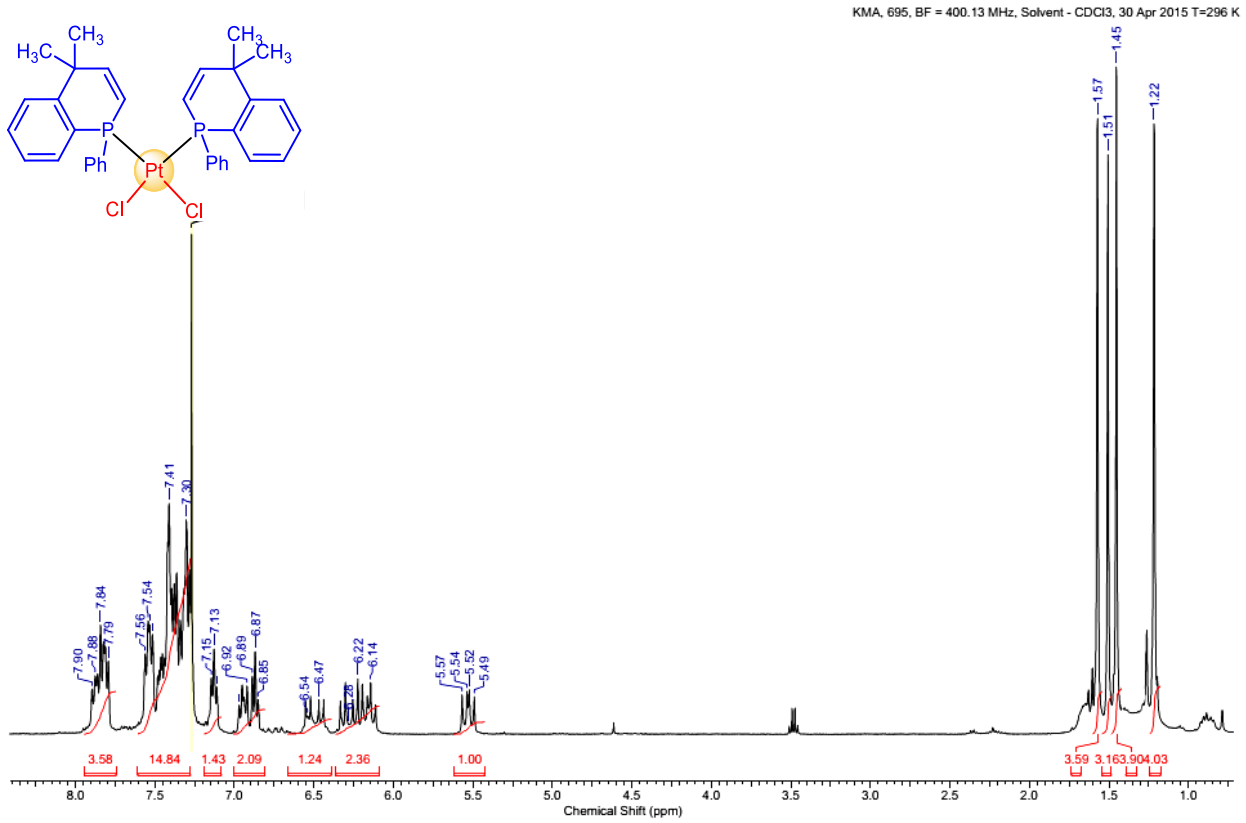

Fig. S11. ^{1}H NMR spectrum of the compound ***cis*-6** ($CDCl_3$).

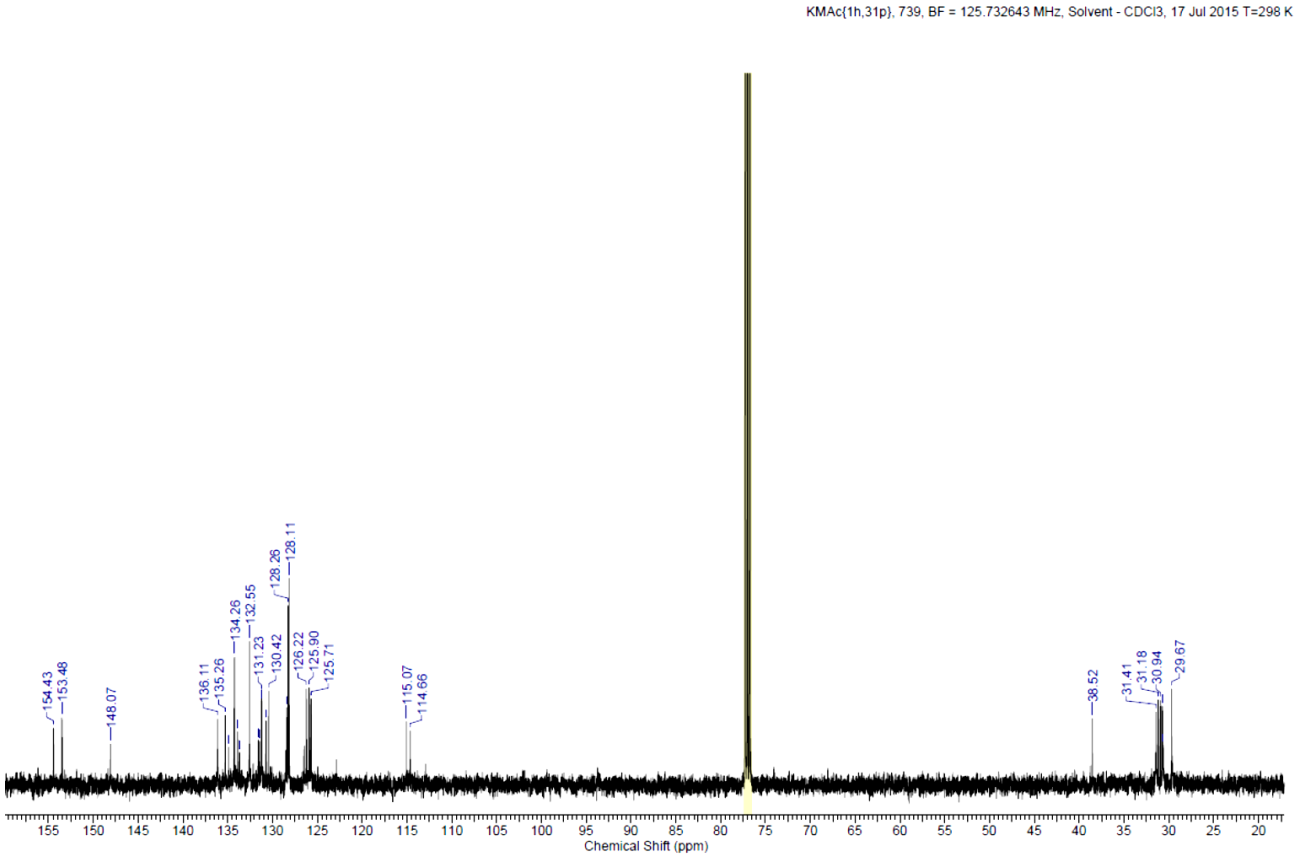

Fig. S12. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of the compound ***cis*-6** ($CDCl_3$).

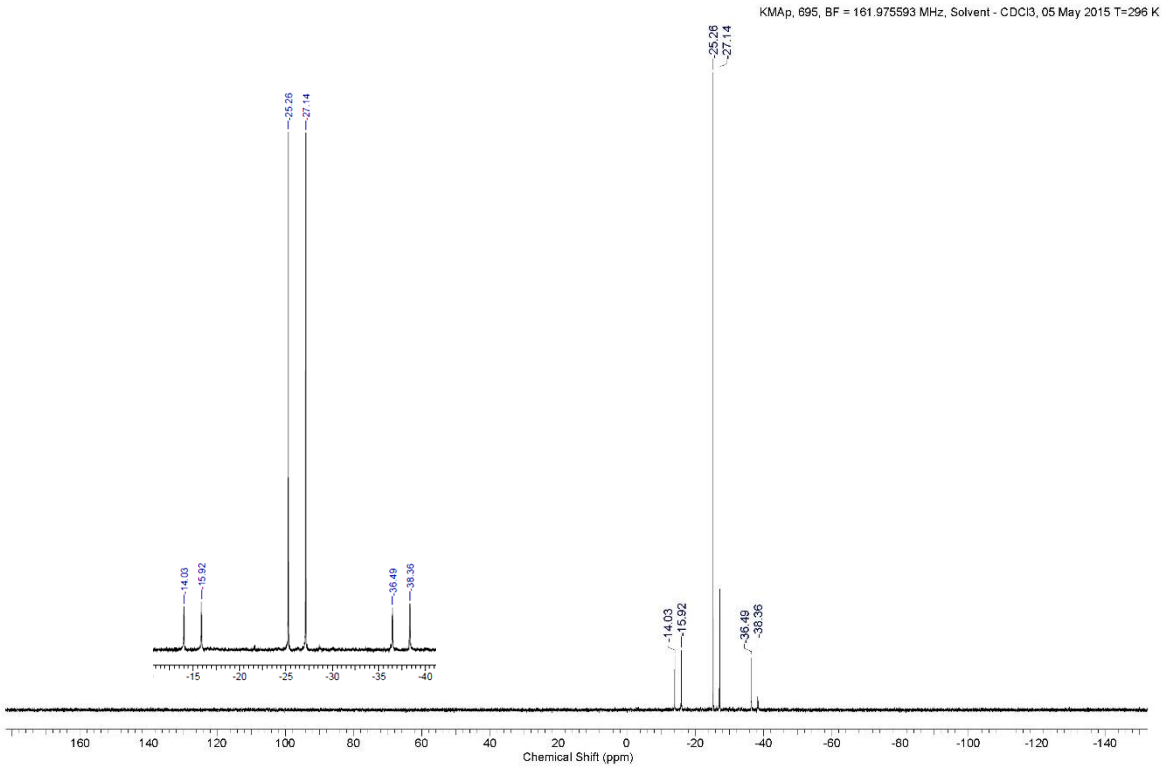

Fig. S13. $^{31}P\{^{1}H\}$ NMR spectrum of the compound ***cis*-6** ($CDCl_3$).

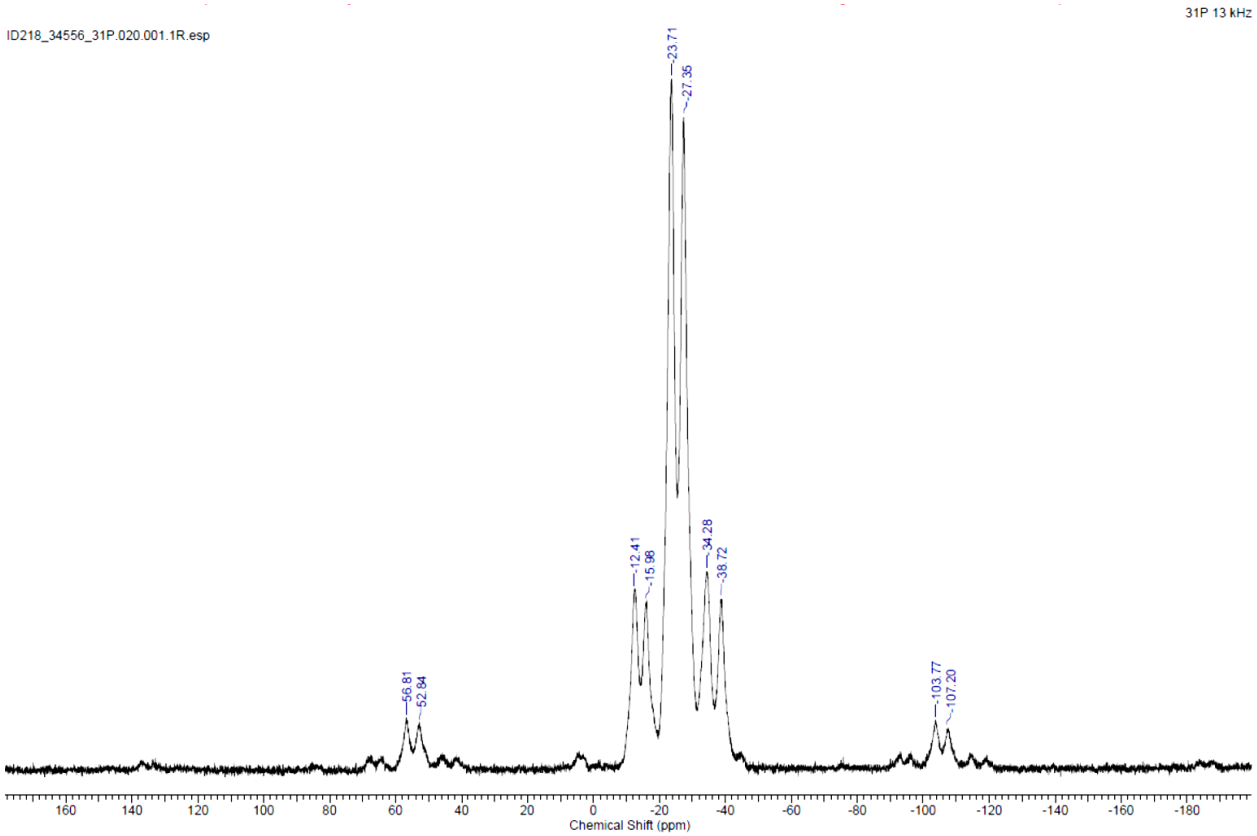

Fig. S14. ^{31}P MAS NMR spectrum of the compound ***cis*-6**.

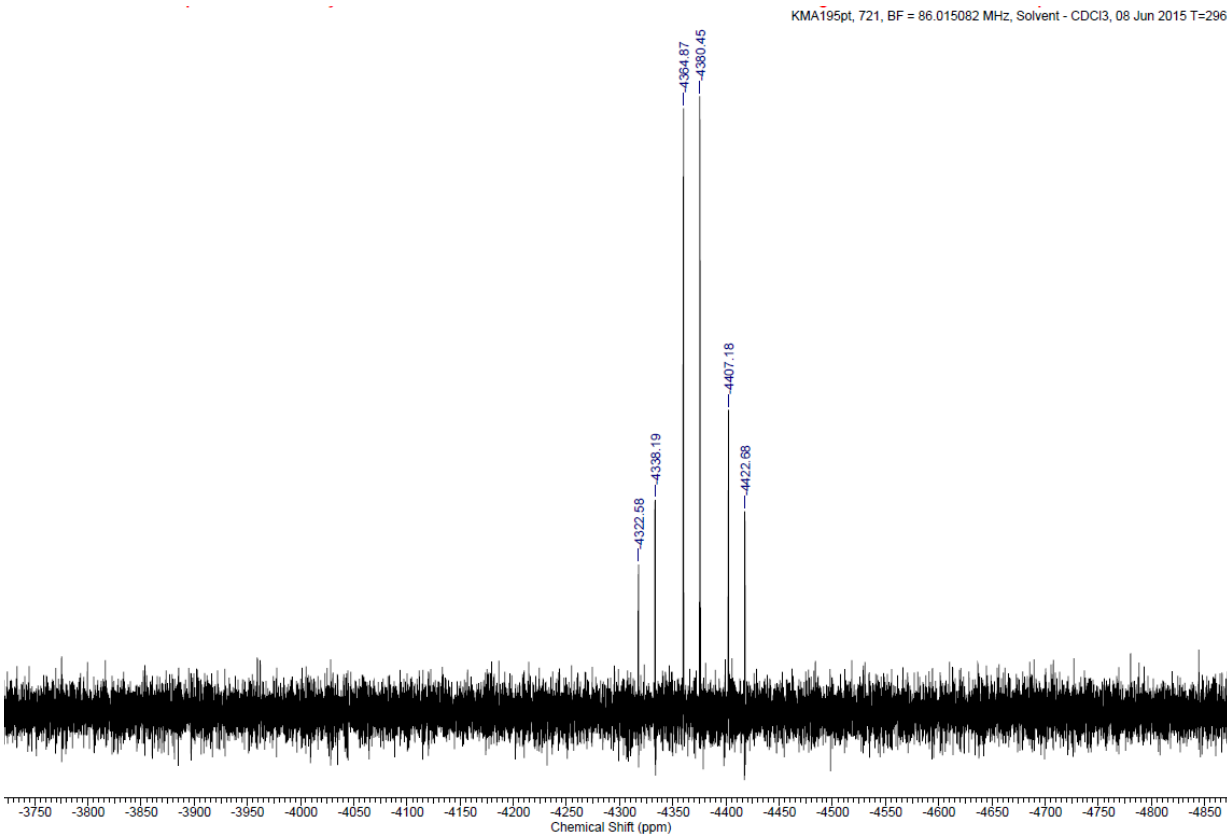

Fig. S15. ^{195}Pt NMR spectrum of the compound ***cis*-6** ($CDCl_3$).

***trans*-7**

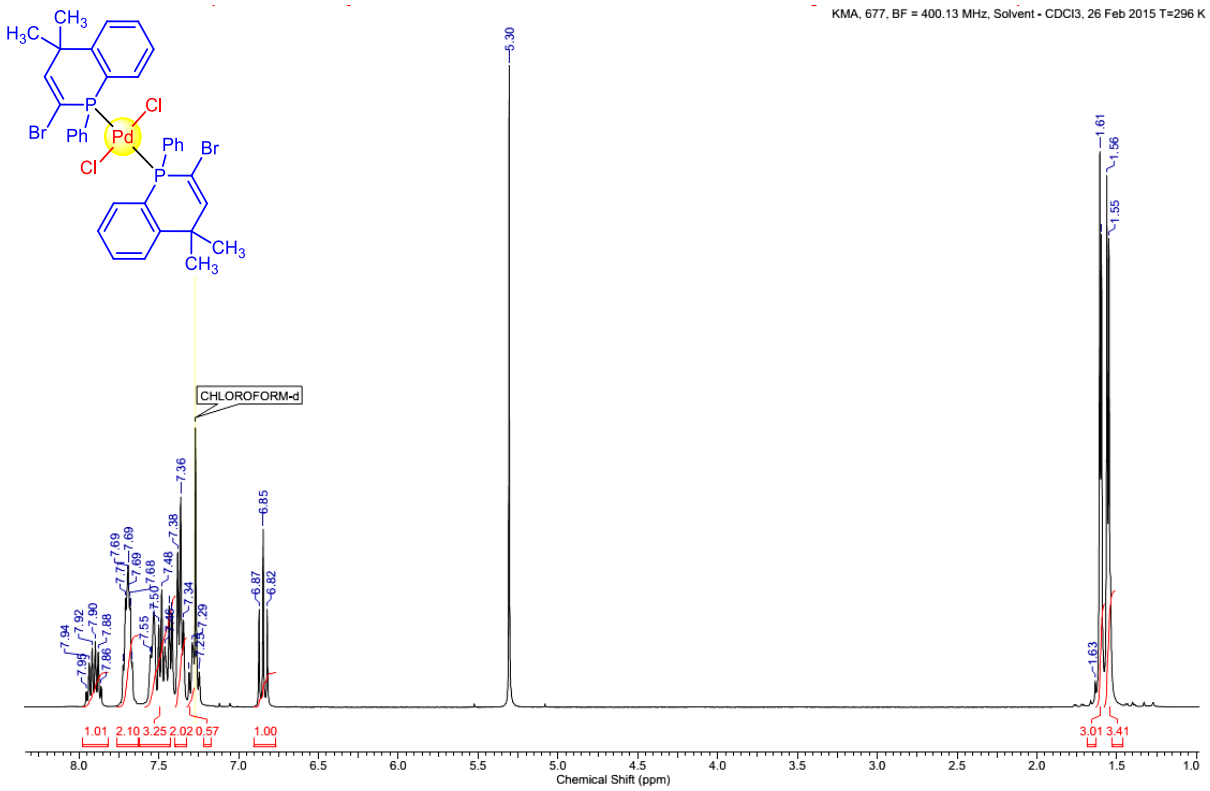

Fig. S16. ^{1}H NMR spectrum of the compound ***trans*-7** ($CDCl_3$).

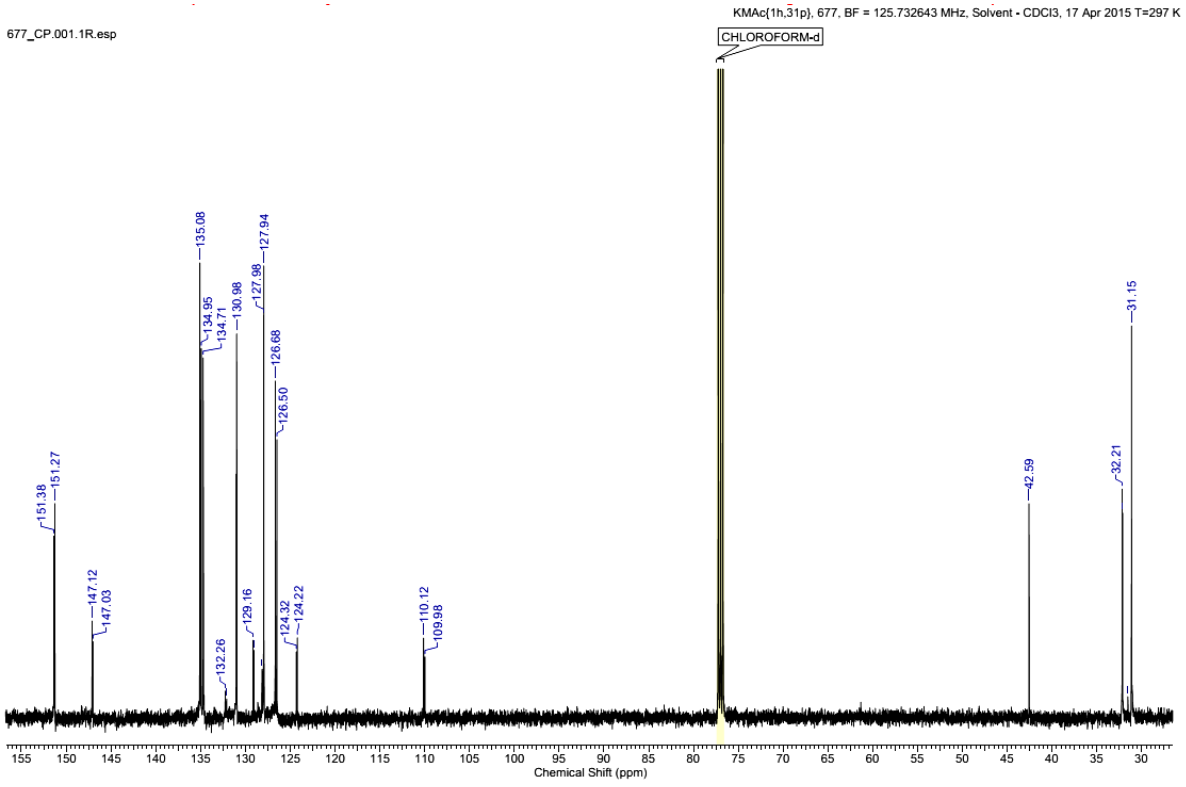

Fig. S17. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of the compound ***trans*-7** ($CDCl_3$).

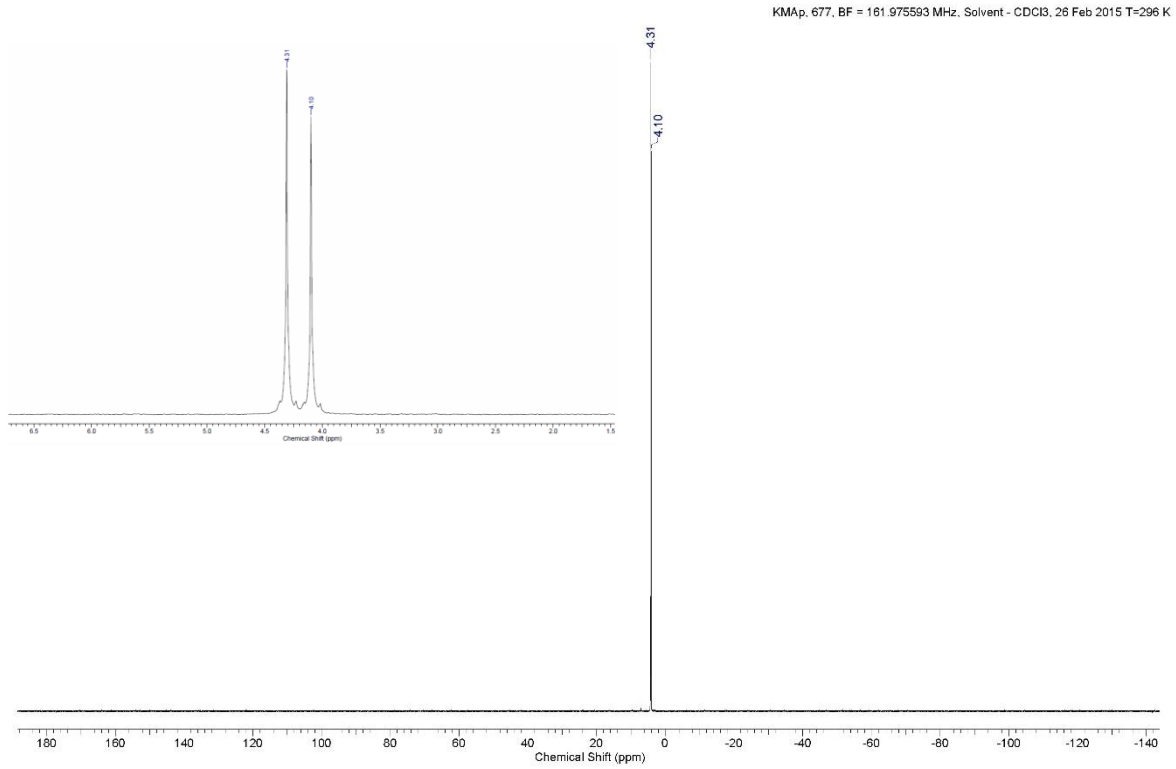

Fig. S18. $^{31}P\{^{1}H\}$ NMR spectrum of the compound ***trans*-7** ($CDCl_3$).

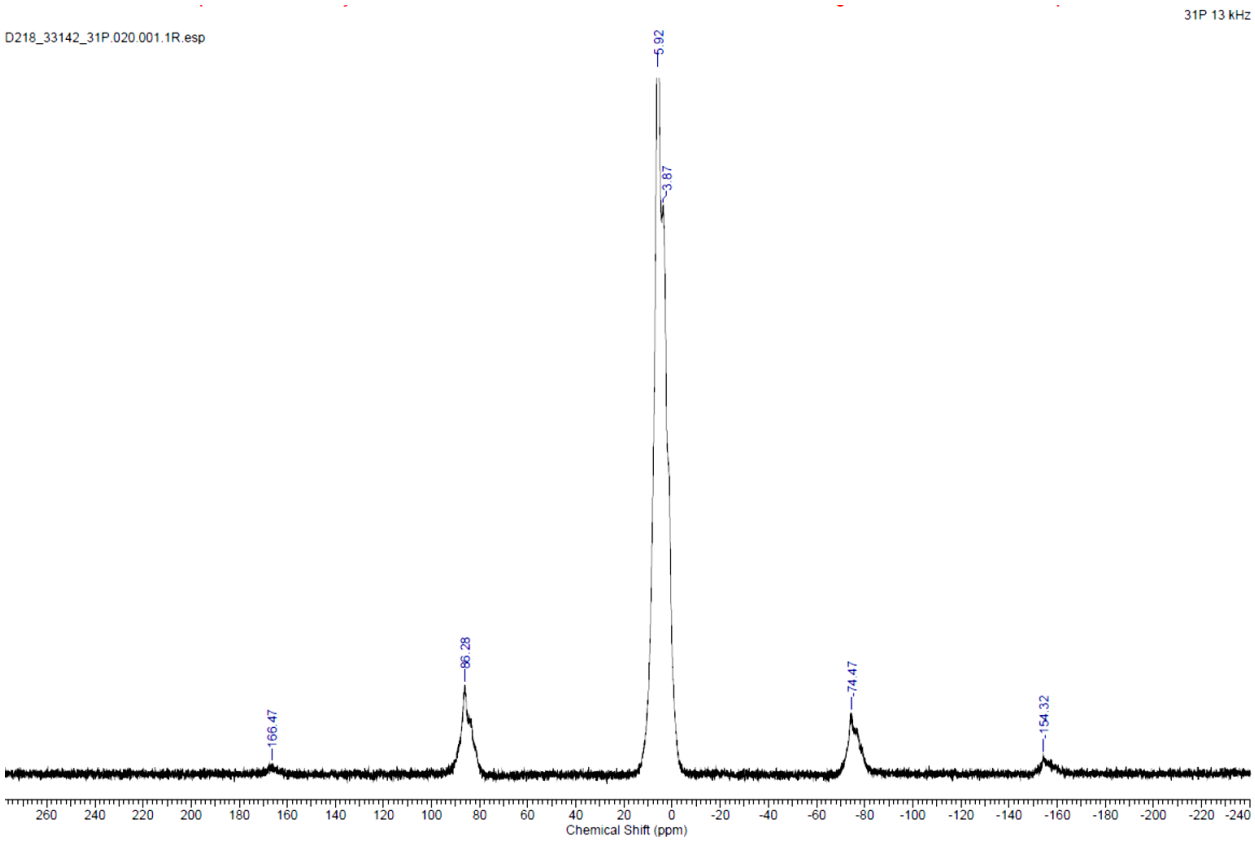

Fig. S19. ^{31}P MAS NMR spectrum of the compound ***trans*-7**.

***trans*-8**

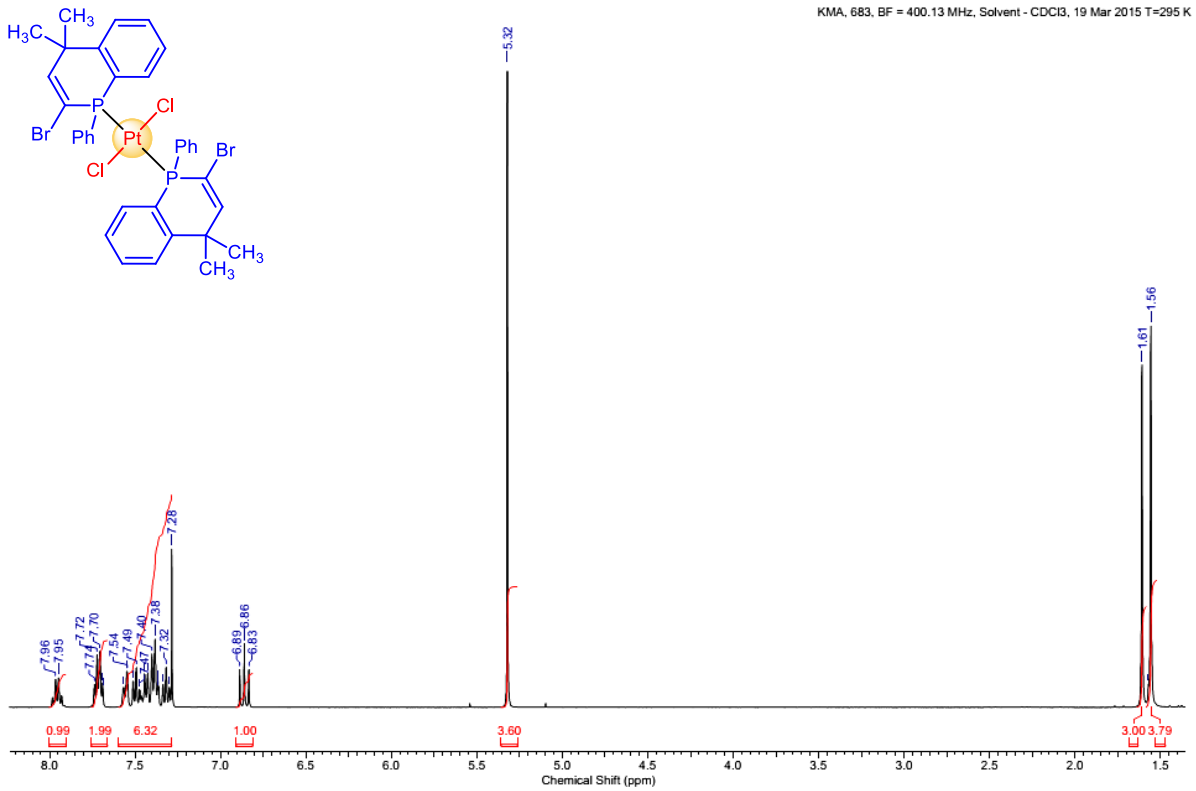

Fig. S20. ^{1}H NMR spectrum of the compound ***trans*-8** ($CDCl_3$).

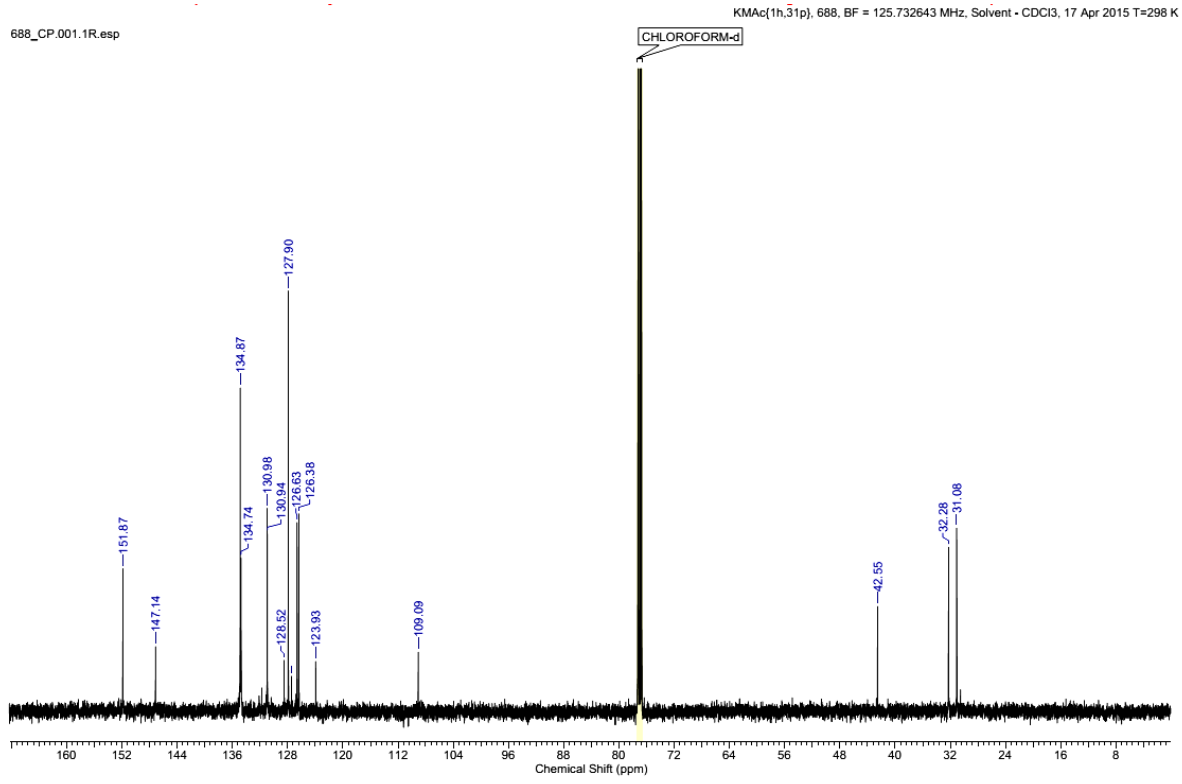

Fig. S21. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of the compound ***trans*-8** ($CDCl_3$).

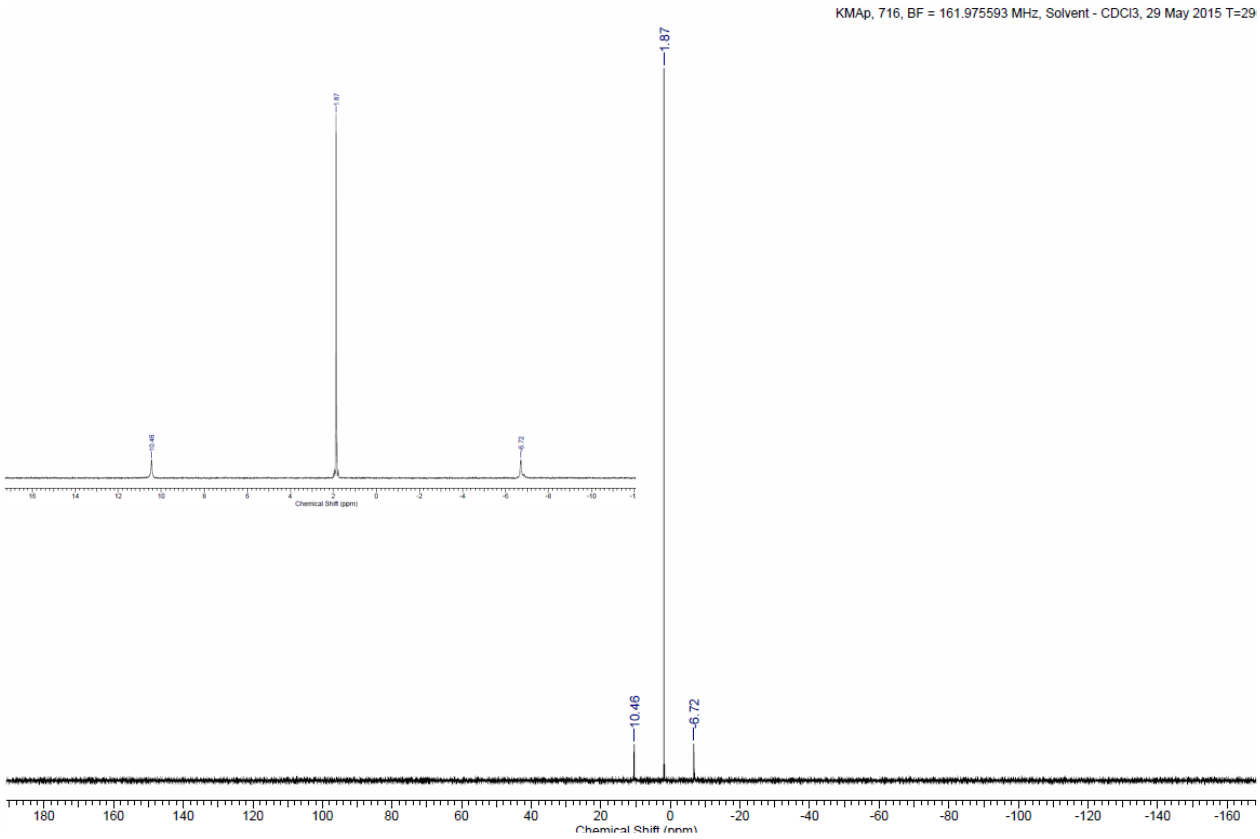

Fig. S22. $^{31}P\{^{1}H\}$ NMR spectrum of the compound ***trans*-8** ($CDCl_3$).

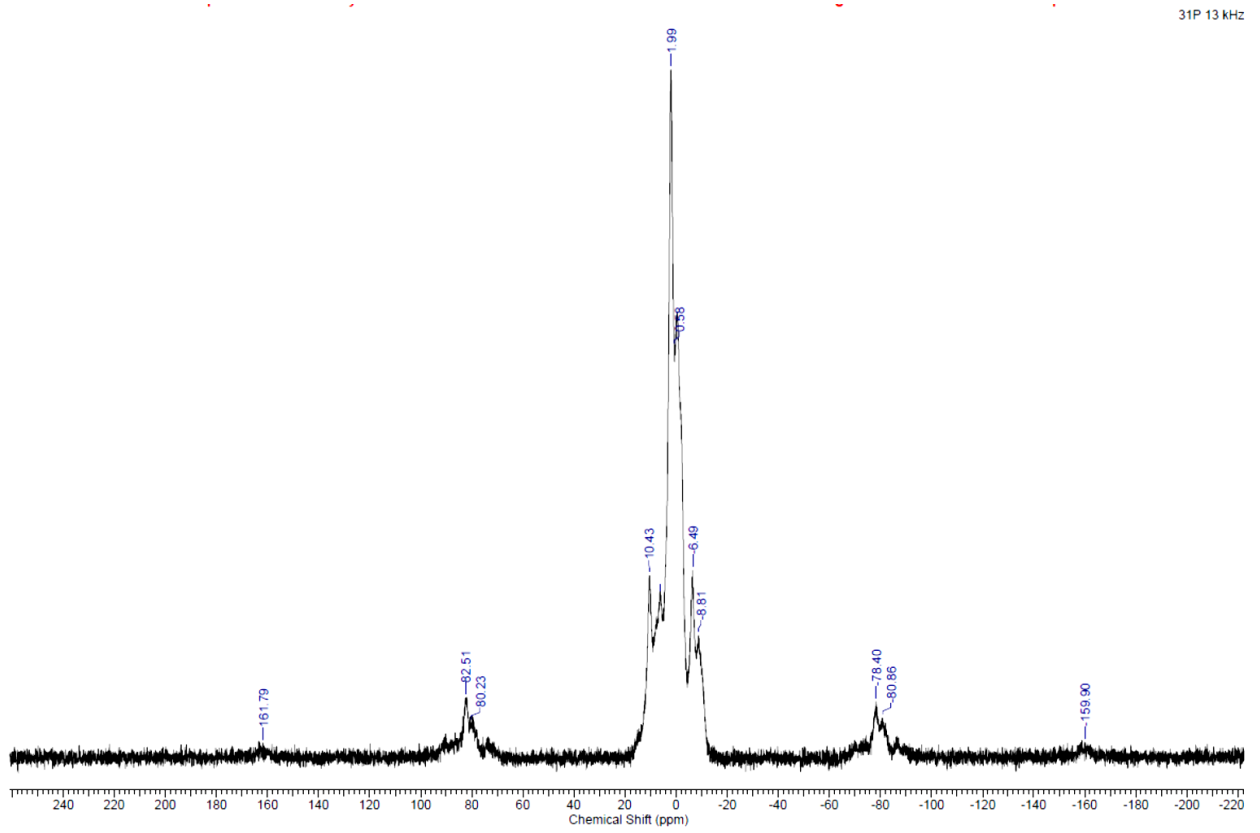

Fig. S23. ^{31}P MAS NMR spectrum of the compound ***trans*-8**.

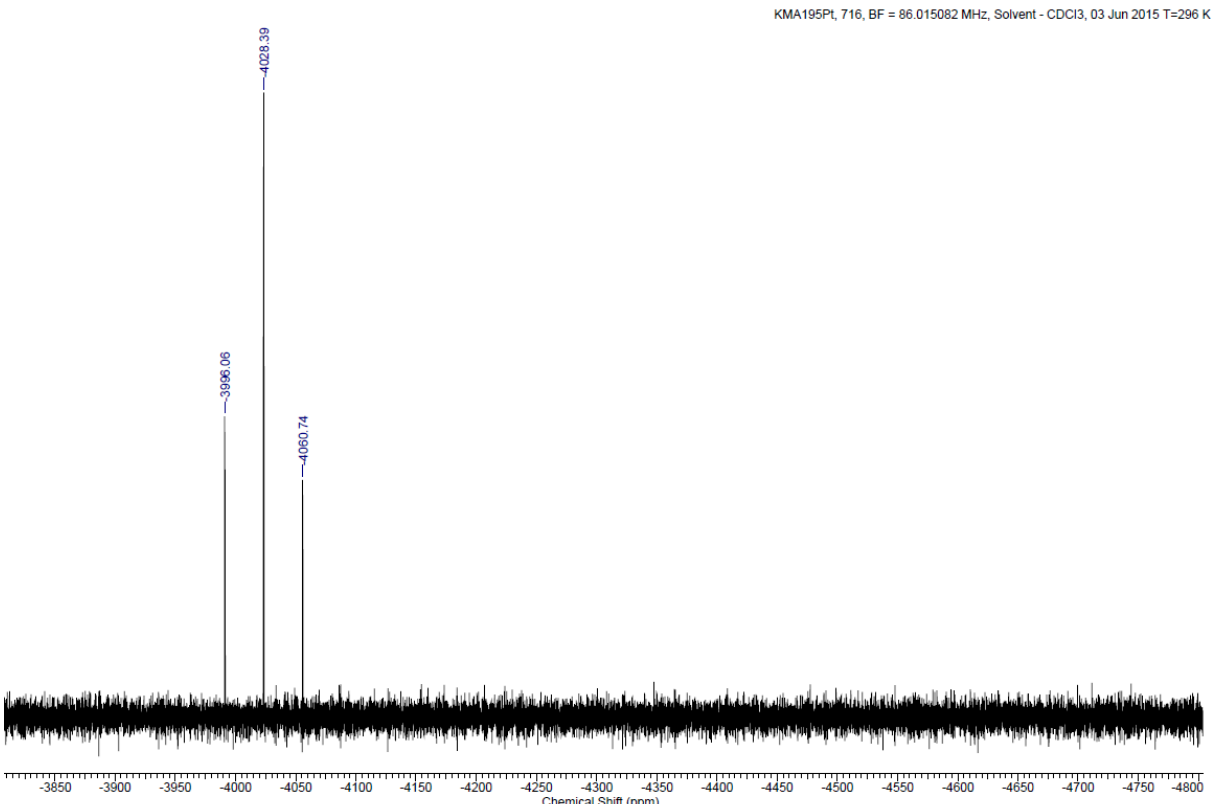

Fig. S24. ^{195}Pt NMR spectrum of the compound ***trans*-8** ($CDCl_3$).

***cis*-8**

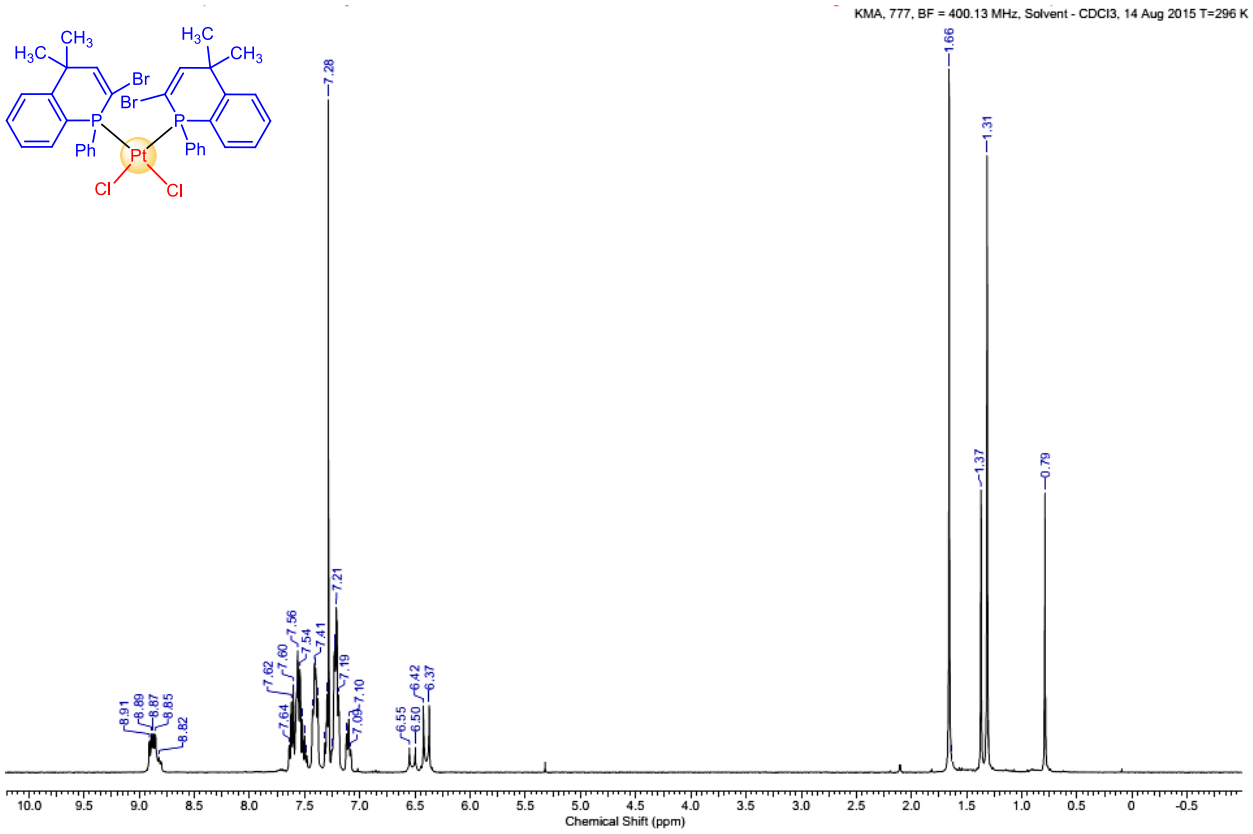

Fig. S25. ^{1}H NMR spectrum of the compound ***cis*-8** ($CDCl_3$).

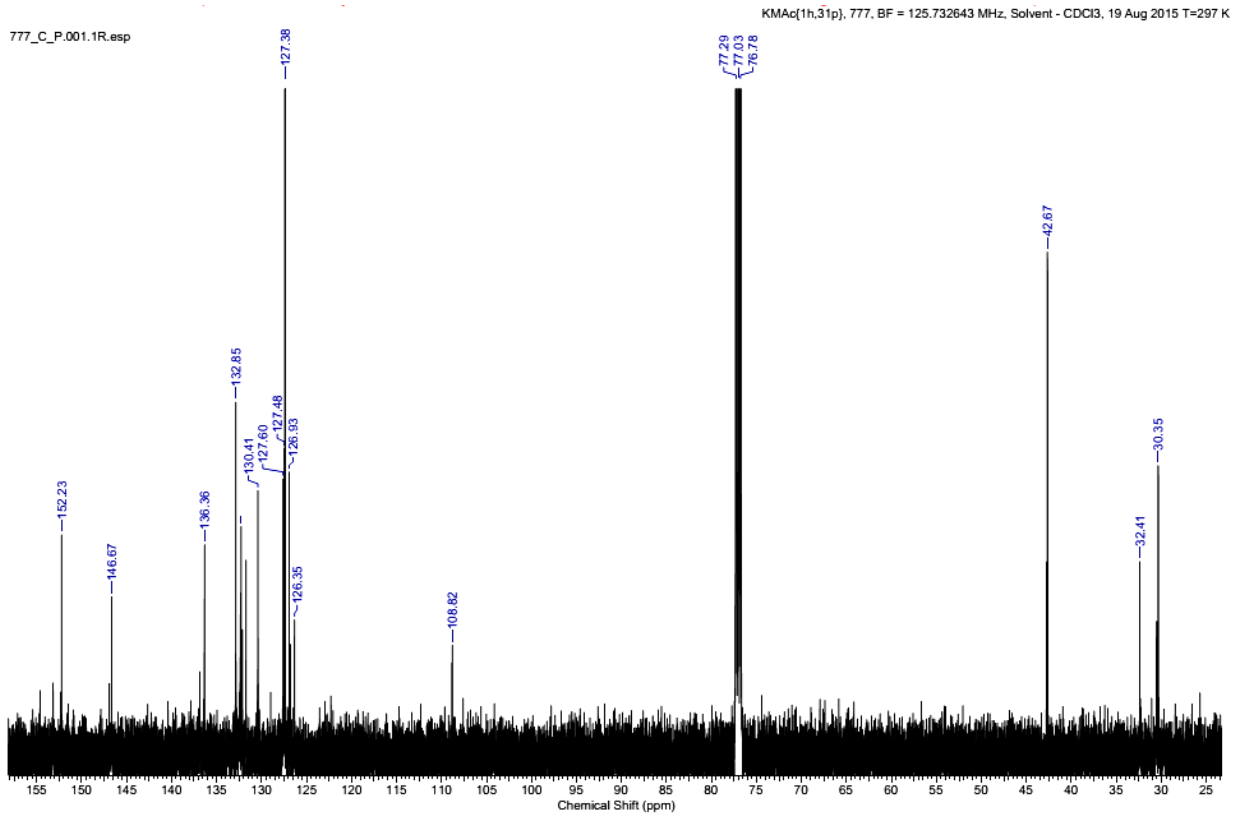

Fig. S26. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of the compound ***cis*-8** ($CDCl_3$).

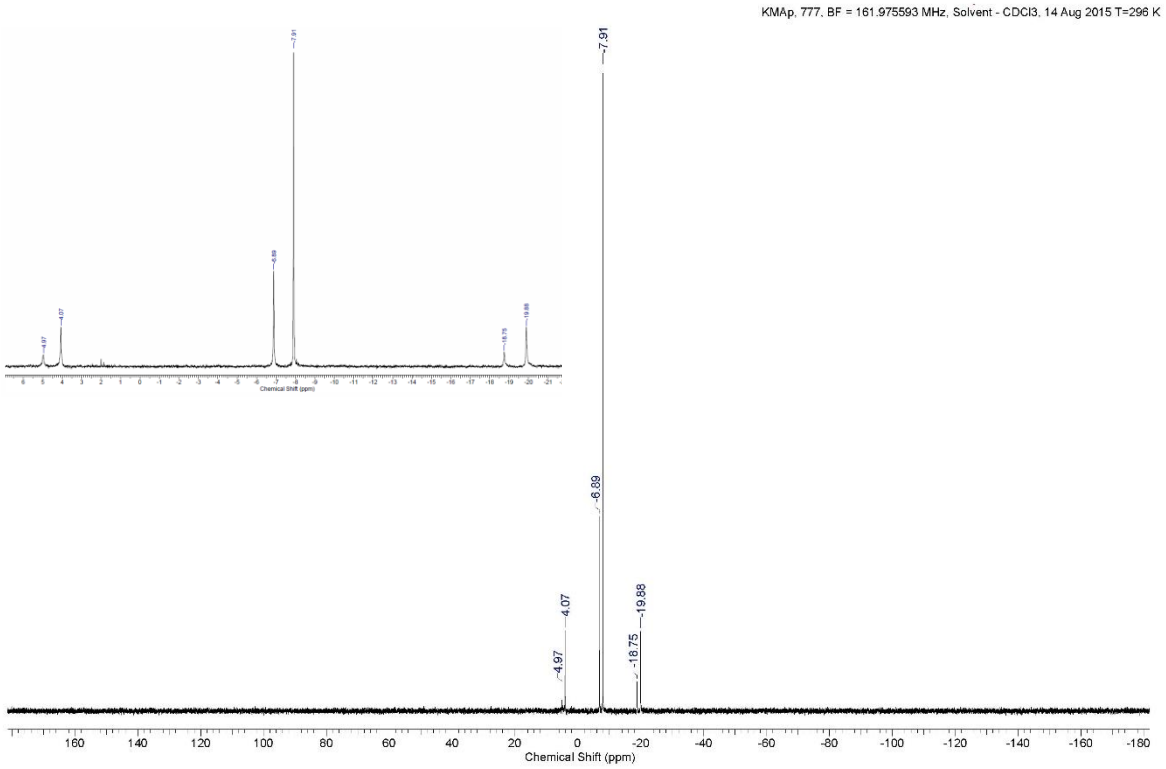

Fig. S27. $^{31}P\{^{1}H\}$ NMR spectrum of the compound ***cis*-8** ($CDCl_3$).

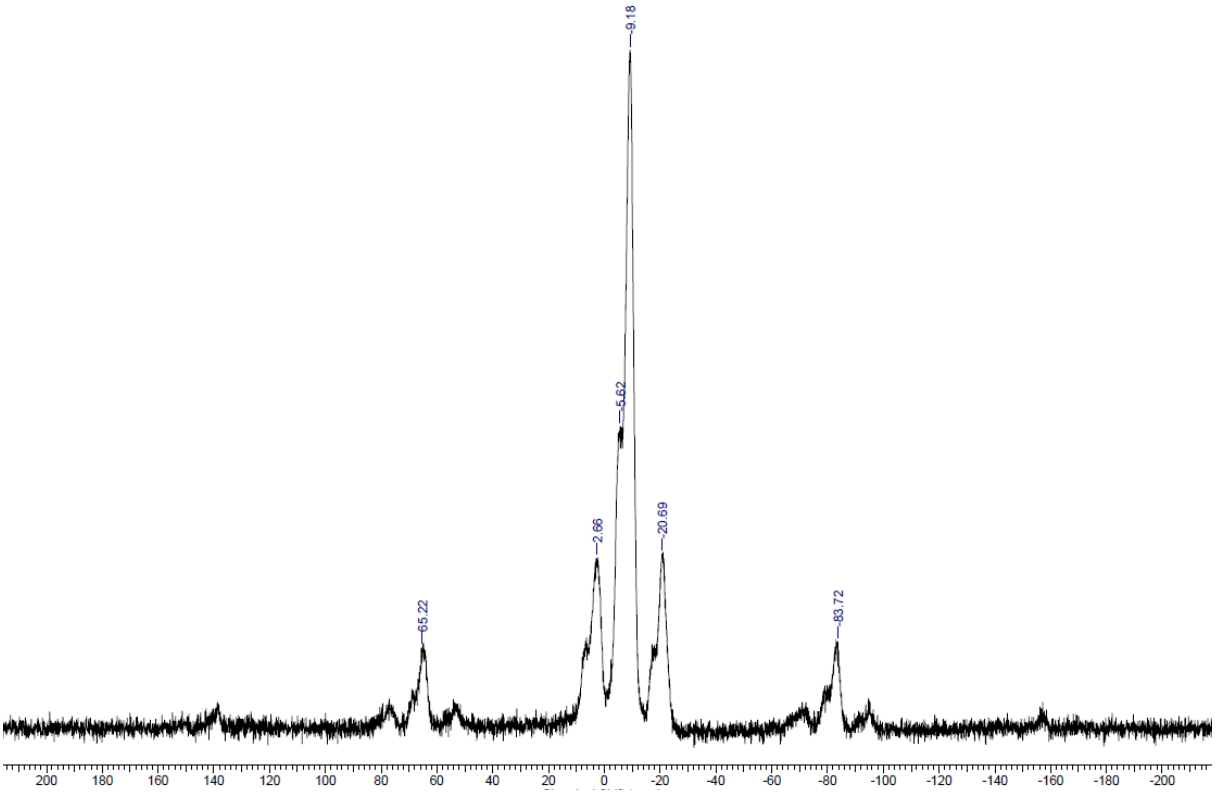

Fig. S28. ^{31}P MAS NMR spectrum of the compound ***cis*-8**.

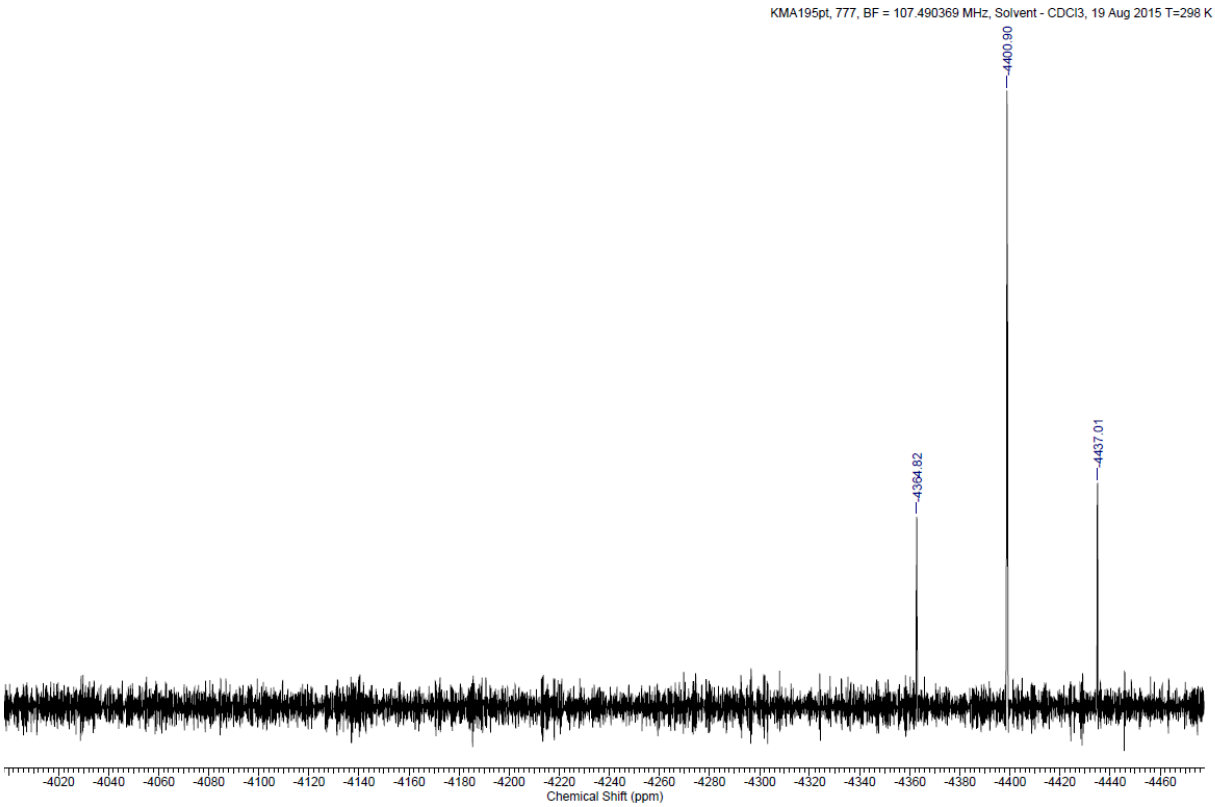

Fig. S29. ^{195}Pt NMR spectrum of the compound ***cis*-8** ($CDCl_3$).