Electronic Supplementary Material (ESI) for Dalton Transactions.

Deactivation of the coordinating ability of the iminophosphorane group by effect of *ortho*-carborane.

Pablo Crujeiras, José Luis Rodríguez-Rey, Antonio Sousa-Pedrares*[a]

[a]*Departamento de Química Inorgánica, Facultad de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain. E-mail: antonio.sousa.pedrares@usc.es*

Index

Secondary interactions involving the iminophosphorane nitrogen atom………….....2

Figure S1. Supramolecular dimers found in the crystal structure of **L1H**..……….........4

Figure S2. Selected intramolecular interactions for **PtL2**……………………………....5

Table S1. Summary of crystal data and refinement for the organic carborane derivatives………………………………..……...6

Table S2. Summary of crystal data and refinement for the metal complexes.................7

Table S3. Intramolecular C-H…N interactions……...8

Tabla S4. Selected bond lengths (Å) for **PdL3**…..8

Table S5. Selected angles (º) for **PdL3**…...8

Figures S3-S16. ^{1}H NMR spectra………………………...……………………9

Figures S17-S27. ^{11}B{^{1}H} NMR spectra…………………………...………………16

Figures S28-S41. ^{31}P{^{1}H} NMR spectra…….…………………..…...……………19

Secondary interactions involving the iminophosphorane nitrogen atom.

The deactivation of the donor ability of the nitrogen atom of the iminophosphorane group by the *o*-carborane moiety is also reflected in the secondary interactions that involve this atom. In all compounds presented in this work (organic derivatives and coordination compounds), the nitrogen atom is not involved in intermolecular interactions. This atom only engages in an intramolecular C-H…N interaction with a CH group of a phenyl ring of the iminophosphorane moiety. An example of this interaction is shown in Figure S1 for the thiol **L1H** (C20-H20…N1). This particular case of the thiol **L1H** is especially interesting, as the thiol group (-SH) does not establish an S-H…N hydrogen bond interaction with the nitrogen atom, neither intramolecular nor intermolecular. Instead, the thiol group establishes an S-H…H-B dihydrogen bond interaction with the hydridic hydrogen atom of a BH group of a vicinal carborane cage [S1-H1…H11$^{\#1}$-B11$^{\#1}$, #1: 1-x, 1-y, 1-z]. This interaction is the strongest directional interaction found in the crystal packing of **L1H** [d(H…H): 2.283 Å; S1-H1-H11: 173.94º, B11-H11-H1: 135.96º] and leads to the formation of supramolecular dimers, with both molecules related by an inversion center (see Figure S1).

The same intramolecular C-H…N interaction is also found for the rest of the organic derivatives, where is also the only secondary interaction that involves the nitrogen atom. The C-H…N intramolecular interactions for the organic derivatives show N…H contacts in the range 2.372-2.575 Å and (CHN) angles in the range 106.11-111.18º (see data in Table S3), which show that the intramolecular interactions are weak [D-H…A, distance (H…A) > 2.2 Å, angle (DHA) > 90º].[1]

In the case of the metal complexes, the situation is very similar. The nitrogen atom of the iminophosphorane group does not coordinate the metal atom in any of the metal complexes. The only interactions that involve the nitrogen atom are the same C-H…N intramolecular interactions found in the organic carboranes, which show H…N contacts in the range 2.473-2.752 Å, and (CHN) angles in the range 106.12-111.88º (see data in Table S3). These values show that the intramolecular interactions are weak[1] and of similar strength as the ones found in the organic carboranes (Table S3). Incidentally, in the case of complex **PtL2**, the thioether group establishes an intramolecular C-H…S interaction that changes the conformation of the complex, allowing a more directional C-H…N intramolecular interaction with a CH group of a triphenylphosphine coligand (see Figure S2 and data in Table S3). This different pattern of C-H...N interactions for **PtL2** is reflected in a slightly longer PN bond distance, as discussed in the paper (See "Crystal structures of the metal complexes").

1. T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48-76.

Figure S1. Supramolecular dimers found in the crystal structure of **L1H**. Thermal ellipsoids are shown at the 40% probability level. Symmetry transformation used to generate equivalent atoms #1: 1-x, 1-y, 1-z. Data for the intermolecular interaction S1-H1…[H11-B11]$^{\#1}$ d(H1…H11$^{\#1}$): 2.283 Å; (S1-H1-H11$^{\#1}$): 173.94º; (B11#1-H11#1-H1): 135.96º. Data for the C-H…N intramolecular interaction in Table S3.

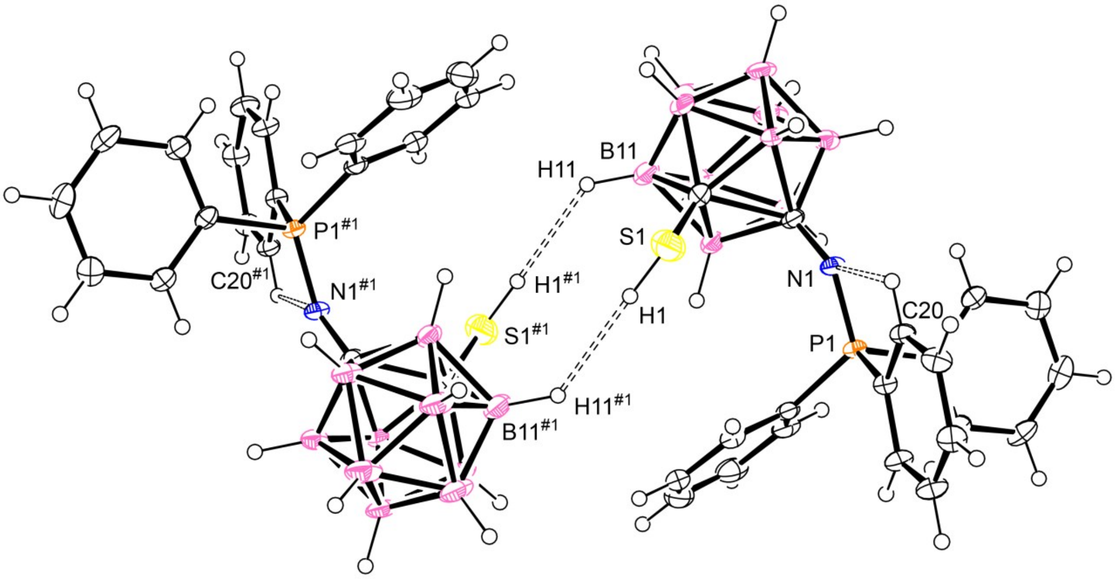

Figure S2. Selected intramolecular interactions for **PtL2**. Thermal ellipsoids are shown at the 40% probability level. Data for the C-H…S interaction: C17-H17…S2 d(H17…S2): 2.650 Ǻ; (C17-H17-S2): 119.63º. Data for the C-H…N intramolecular interactions in Table S3.

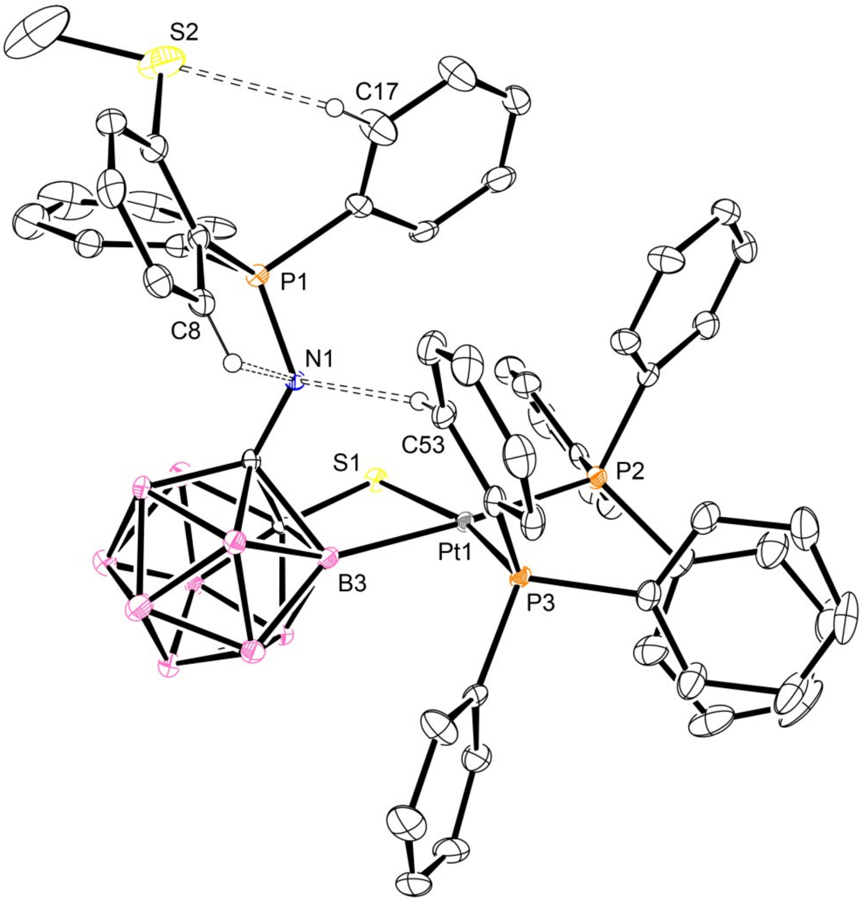

Table S1. Summary of crystal data and refinement for the organic carborane derivatives.

	I1	**I2**	**L1H**	**L1L1**	**L1SL1**	**L2L2**
Empirical Formula	$C_{20}H_{26}B_{10}NP$	$C_{21}H_{28}B_{10}NPS$	$C_{20}H_{26}B_{10}NPS$	$C_{40}H_{50}B_{20}N_2P_2S_2$	$C_{40}H_{50}B_{20}N_2P_2S_3$	$C_{42}H_{54}B_{20}N_2P_2S_4$
Formula weight	419.49	465.57	451.55	901.08	933.14	993.25
Temperature (K)	100(2)	100(2)	100(2)	100(2)	Q	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystalline system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P 2(1)/c	P -1	P -1	P -1	P -1	P -1
Cell Constants (Å, °)	a = 11.1751(9)	a = 8.9531(8)	a = 9.2362(5)	a = 12.3152(14)	a = 11.3649(19)	a = 11.9947(12)
	b = 14.4422(9)	b = 9.3607(9)	b = 9.3086(6)	b = 13.2930(14)	b = 13.447(3)	b = 15.9662(15)
	c = 14.0860(13)	c = 16.1914(16)	c = 15.2904(11)	c = 16.4955(17)	c = 17.662(4)	c = 16.0932(16)
	α = 90	α = 99.553(6)	α = 101.023(4)	α = 105.459(6)	α = 92.371(10)	α = 108.061(5)
	β = 90.479(4)	β = 104.144(5)	β = 96.990(4)	β = 106.507(7)	β = 91.565(9)	β = 108.609(5)
	γ = 90	γ = 105.200(5)	γ = 107.852(4)	γ = 99.016(7)	γ = 91.256(9)	γ = 105.405(5)
Volume (Å^3)	2273,3(3)	1230.8(2)	1205.14(14)	2415.2(5)	2695.2(9)	2539.5(4)
Z	4	2	2	2	2	2
Absorption coefficient (mm^{-1})	0.131	0.209	0.211	0.211	0.228	0.286
F(000)	872	484	468	932	964	1028
Theta range for data collection (°)	2.02-26.43	1.33-26.37	1.38-26.43	1.36-25.34	1.15-26.53	1.46-26.37
Index ranges	$-13 \leq h \leq 13$	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$	$-14 \leq h \leq 13$	$-14 \leq h \leq 14$	$-14 \leq h \leq 13$
	$0 \leq k \leq 18$	$-11 \leq k \leq 11$	$-11 \leq k \leq 11$	$-16 \leq k \leq 15$	$-16 \leq k \leq 16$	$-19 \leq k \leq 18$
	$0 \leq l \leq 17$	$-20 \leq l \leq 20$	$0 \leq l \leq 19$	$0 \leq l \leq 19$	$0 \leq l \leq 22$	$0 \leq l \leq 20$
Size (mm)	0.36 x 0.23 x 0.13	0.43 x 0.23 x 0.14	0.35 x 0.20 x 0.12	0.50 x 0.25 x 0.20	0.20 x 0.16 x 0.10	0.31 x 0.10 x 0.07
Collected reflections	30186	52853	33886	60623	81208	54384
Independent reflections	4665 [R(int) = 0.0754]	4989 [R(int) = 0.0309]	4869 [R(int) = 0.0609]	8780 [R(int) = 0.1019]	11090 [R(int) = 0.0646]	10369 [R(int) = 0.0397]
Data/ restraints/ parameters	4665 / 0 / 289	4989 / 0 / 312	4869 / 0 / 299	8780 / 0 / 595	11090 / 0 / 604	10369 / 0 / 633
Goodness-on-fit (F^2)	1.031	1.065	1.094	1.043	1.024	1.030
Final R indices [I>2s(I)][a]	R_1 = 0.0505	R_1 = 0.0452	R_1 = 0.0719	R_1 = 0.0566	R_1 = 0.0659	R_1 = 0.0378
	wR_2 = 0.1124	wR_2 = 0.1160	wR_2 = 0.1689	wR_2 = 0.1274	wR_2 = 0.1491	wR_2 = 0.0874
R indices (all data)	R_1 = 0.0779	R_1 = 0.0507	R_1 = 0.1260	R_1 = 0.0984	R_1 = 0.0900	R_1 = 0.0507
	wR_2 = 0.1280	wR_2 = 0.1200	wR_2 = 0.1873	wR_2 = 0.1476	wR_2 = 0.1604	wR_2 = 0.0941
Largest diff. peak and hole (e· Å^{-3})	0.319 and -0.371	1.153 and -0.491	0.783 and -0.526	0.708 and -0.422	1.977 and -0.689	0.902 and -0.649

[a] $R_1 = \sum[|F_o|- |F_c|/\sum|F_o|]$; $wR_2 = [|\sum(F_o^2-F_c^2)/\sum(F_o^2)]^{1/2}$

Table S2. Summary of crystal data and refinement for the metal complexes.

	PdL1·(CH_2Cl_2)	**PtL1**	**PtL2**	**PdL1dppm**	**PdL1dppe·2($CHCl_3$)**	**PdL3**
Empirical Formula	$C_{59}H_{67}B_{20}Cl_2N_2P_3S_2Pd$	$C_{56}H_{54}B_{10}NP_3SPt$	$C_{57}H_{56}B_{10}NP_3S_2Pt$	$C_{65}H_{72}B_{20}N_2P_4S_2Pd$	$C_{68}H_{76}B_{20}Cl_6N_2P_4S_2Pd$	$C_{42}H_{33}NP_2SPd$
Formula weight	1354.67	1169.16	1215.24	1391.84	1644.60	752.09
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystalline system	Triclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	P -1	P 21/n	P na21	P bca	P 2(1)/c	P 2(1)/n
Cell Constants (Å, °)	a = 12.3514(8)	a = 14.7193(13)	a = 20.8339(8)	a = 19.5245(11)	a = 13.0843(5)	a = 13.2739(15)
	b = 14.7100(9)	b = 18.0109(16)	b = 12.4463(5)	b = 17.5596(11)	b = 20.6736(7)	b = 14.8318(14)
	c = 20.6311(13)	c = 19.5680(16)	c = 20.9452(8)	c = 44.352(3)	c = 29.9704(9)	c = 18.650(2)
	α = 71.407(2)	α = 90	α = 90	α = 90	α = 90	α = 90
	β = 87.315(3)	β = 97.773(5)	β = 90	β = 90	β = 91.598(2)	β = 100.915(3)
	γ = 67.325(2)	γ = 90	γ = 90	γ = 90	γ = 90	γ = 90
Volume (Å^3)	3265.8(4)	5140.0(8)	5431.2(4)	15205.9(16)	8103.8(5)	3605.3(7)
Z	2	4	4	8	4	4
Absorption coefficient (mm^{-1})	0.545	2.905	2.789	0.422	0.599	0.692
F(000)	1384	2344	2440	5712	3352	1536
Theta range for data collection (°)	1.58-28.28	1.54-25.34	1.90-27.48	1.39-25.35	1.55-28.28	1.73-21.26
Index ranges	-16≤ h ≤ 16	-17 ≤ h ≤ 17	-27 ≤ h ≤ 27	-23 ≤ h ≤ 17	-17 ≤ h ≤ 17	-13 ≤ h ≤ 13
	-17≤ k ≤ 19	0 ≤ k ≤ 21	-16 ≤ k ≤ 15	-21 ≤ k ≤ 16	-27 ≤ k ≤ 27	0 ≤ k ≤ 15
	-27≤ l ≤ 27	0 ≤ l ≤ 23	-27 ≤ l ≤ 27	-53 ≤ l ≤ 53	-39≤ l ≤ 39	0 ≤ l ≤ 19
Size (mm)	0.35 x 0.11 x 0.07	0.13 x 0.09 x 0.05	0.20 x 0.12 x 0.08	0.24 x 0.10 x 0.08	0.40 x 0.18 x 0.10	0.10 x 0.07 x 0.04
Collected reflections	66475	86346	89412	105801	151268	18354
Independent reflections	16189 [R(int) = 0.0588]	9374 [R(int) = 0.0565]	12439 [R(int) = 0.0443]	13928 [R(int) = 0.1668]	20112 [R(int) = 0.0571]	3983 [R(int) = 0.1331]
Data/ restraints/ parameters	16189 / 0 / 805	9374 / 0 / 649	12439 / 18 / 686	13928 / 0 / 847	20112 / 0 / 928	3983 / 806 / 424
Goodness-on-fit (F^2)	1.015	1.026	1.035	1.011	1.039	1.015
Final R indices [I>2s(I)][a]	R_1 = 0.0388	R_1 = 0.0260	R_1 = 0.0282	R_1 = 0.0641	R_1 = 0.0652	R_1 = 0.0549
	wR_2 = 0.0726	wR_2 = 0.0564	wR_2 = 0.0620	wR_2 = 0.1283	wR_2 = 0.1687	wR_2 = 0.1012
R indices (all data)	R_1 = 0.0673	R_1 = 0.0397	R_1 = 0.0350	R_1 = 0.1311	R_1 = 0.0874	R_1 = 0.1131
	wR_2 = 0.0806	wR_2 = 0.0610	wR_2 = 0.0640	wR_2 = 0.1519	wR_2 = 0.1855	wR_2 = 0.1251
Largest diff. peak and hole (e· Å^{-3})	0.583 and -0.664	1.064 and -0.966	1.795 and -0.714	0.500 and -0.805	2.716 and -1.753	0.556 and -0.461

[a] $R_1 = \sum[|F_o|- |F_c|/\Sigma|F_o|]$; $wR_2 = [|\Sigma(F_o^2-F_c^2)/\Sigma(F_o^2)]^{1/2}$

Table S3. Intramolecular C-H…N interactions.

	C-H-N (labels)	**N…H (Å)**	**C-H-N (º)**
I1	C10-H10a…N1	2.534	106.11
I2	C21-H21…N1	2.510	108.53
L1H	C20-H20…N1	2.546	107.24
L1L1	C14-H14…N1 C114-H114…N2 C116-H116…N2	2.515 2.575 2.558	107.13 108.71 108.02
L1SL1	C20-H20…N1 C114-H114…N2	2.476 2.518	108.06 107.83
L2L2	C8-H8a…N1 C108-H10d…N2	2.384 2.372	110.58 111.18
PdL1	C4-H4a…N1 C24-H24…N2	2.514 2.582	107.52 106.24
PtL1	C20-H20…N1	2.473	107.25
PtL2	C8-H8a…N1 C53-H53…N1*	2.595 2.410	111.88 152.29
PdL1dppm	C4-H4a…N1 C20-H20…N1 C24-H24…N2 C40-H40…N2	2.526 2.624 2.628 2.555	107.79 109.52 108.96 107.67
PdL1dppe	C4-H4a…N1 C24-H24…N2 C40-H40…N2	2.752 2.627 2.525	106.12 108.52 107.66

All the interactions involve an adjacent CH group of the iminophosphorane ligand except (*) that involves a CH group of a thiphenylphosphine coligand (see **Figure S2**).

Tabla S4. Selected bond lengths (Å) for **PdL3**.

	Pd-C8	**Pd-N1**	**Pd-S1**	**M-P2**	**P1-N1**	**C1-N1**	**C6-S1**
PdL3	2.061(8)	2.071(6)	2.321(2)	2.236(2)	1.595(7)	1.428(10)	1.752(8)

Table S5. Selected angles (º) for **PdL3**.

	C8-Pd-N1	**N1-Pd-S1**	**S1-Pd-P2**	**P2-Pd-C8**	**C8-Pd-S1**	**P2-Pd-N1**	**P1-N1-C1**
PdL3	87.1(3)	84.8(2)	93.39(9)	94.7(2)	171.9(2)	178.2(2)	125.3(6)

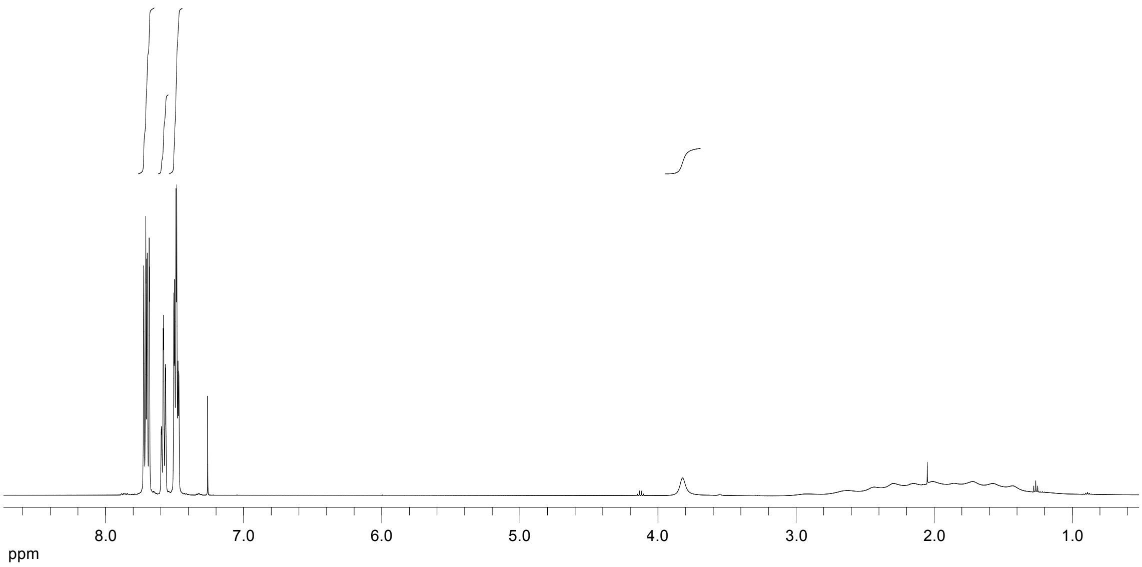

Figure S.3. ^{1}H NMR spectrum (CDCl$_3$) of **I1.**

Figure S.4. ^{1}H NMR spectrum (CDCl$_3$) of **I2.**

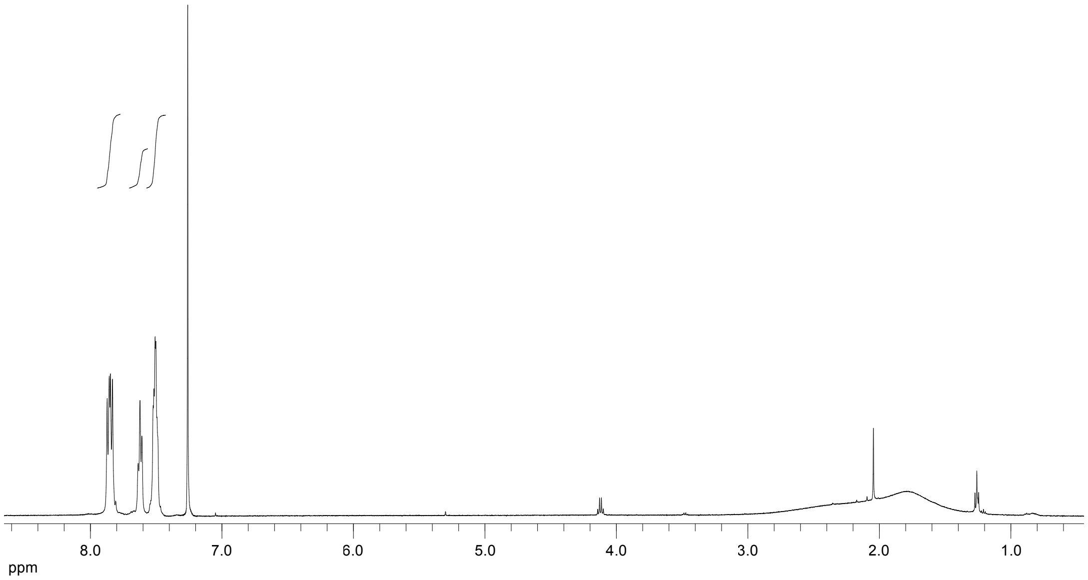

Figure S.5. ^{1}H NMR spectrum ($CDCl_3$) of **L1H.**

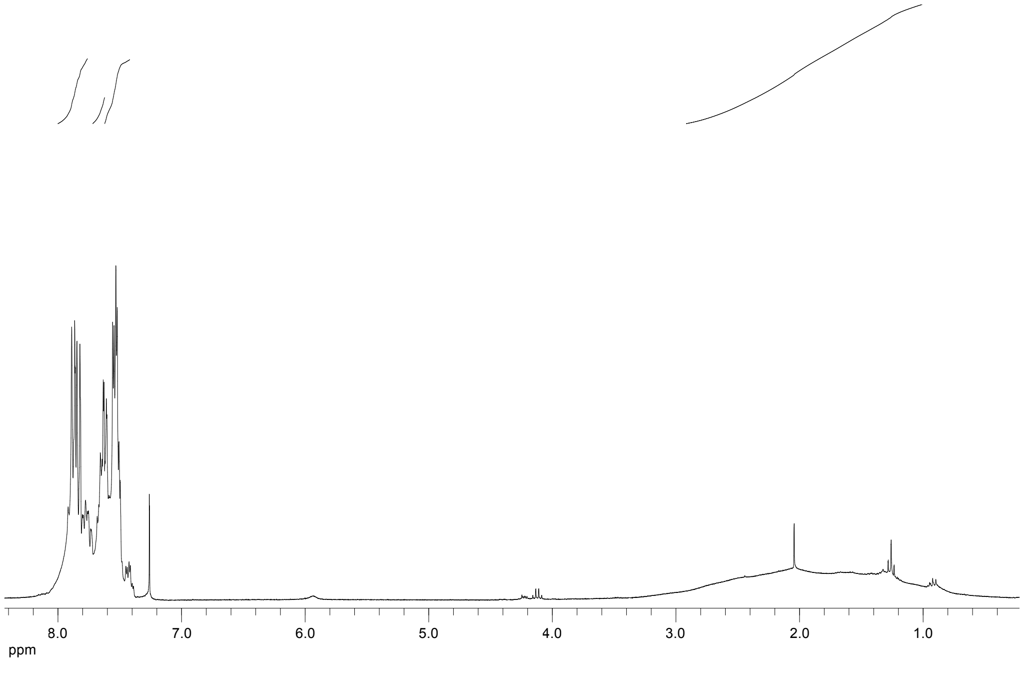

Figure S.6. ^{1}H NMR spectrum ($CDCl_3$) of **L1L1.**

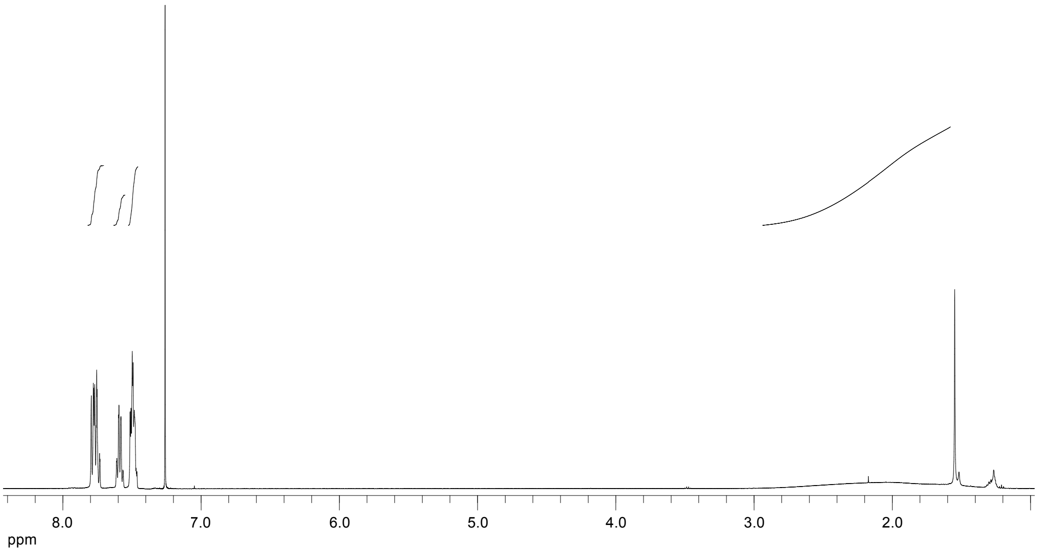

Figure S.7. ^{1}H NMR spectrum ($CDCl_3$) of **L1SL1.**

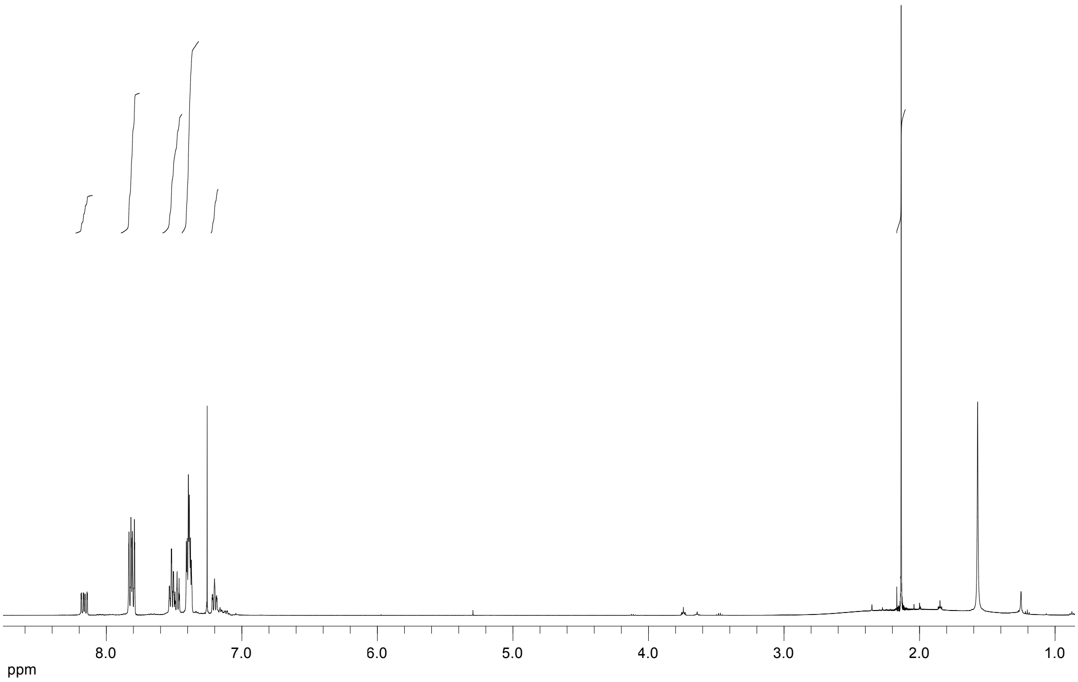

Figure S.8. ^{1}H NMR spectrum ($CDCl_3$) of **L2L2.**

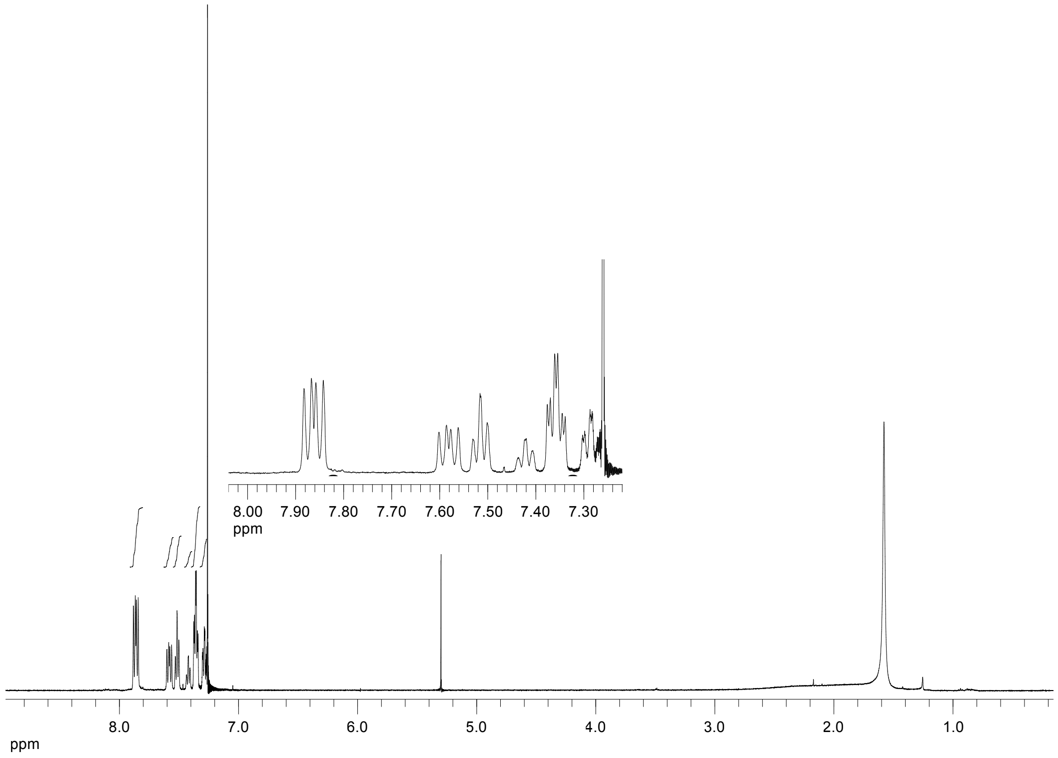

Figure S.9. ^{1}H NMR spectrum ($CDCl_3$) of **PdL1.**

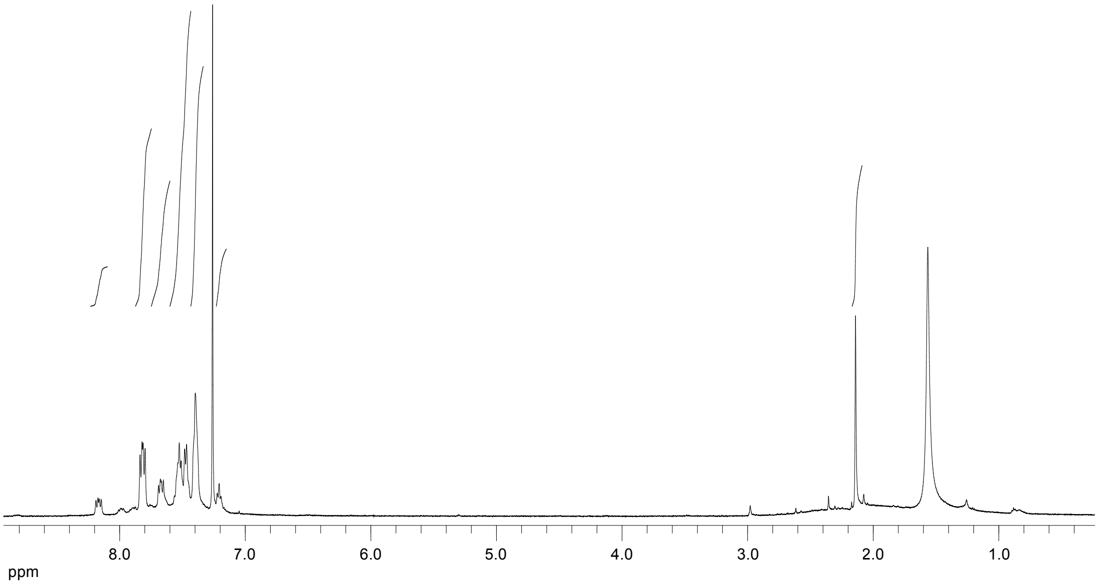

Figure S.10. ^{1}H NMR spectrum ($CDCl_3$) of **PdL2.**

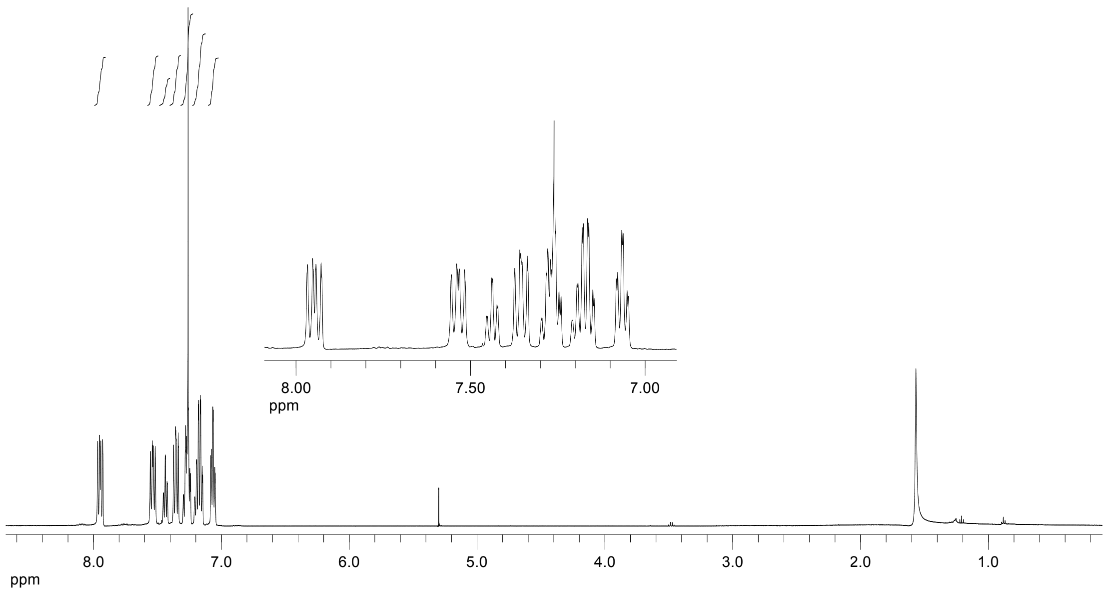

Figure S.11. ^{1}H NMR spectrum ($CDCl_3$) of **PtL1.**

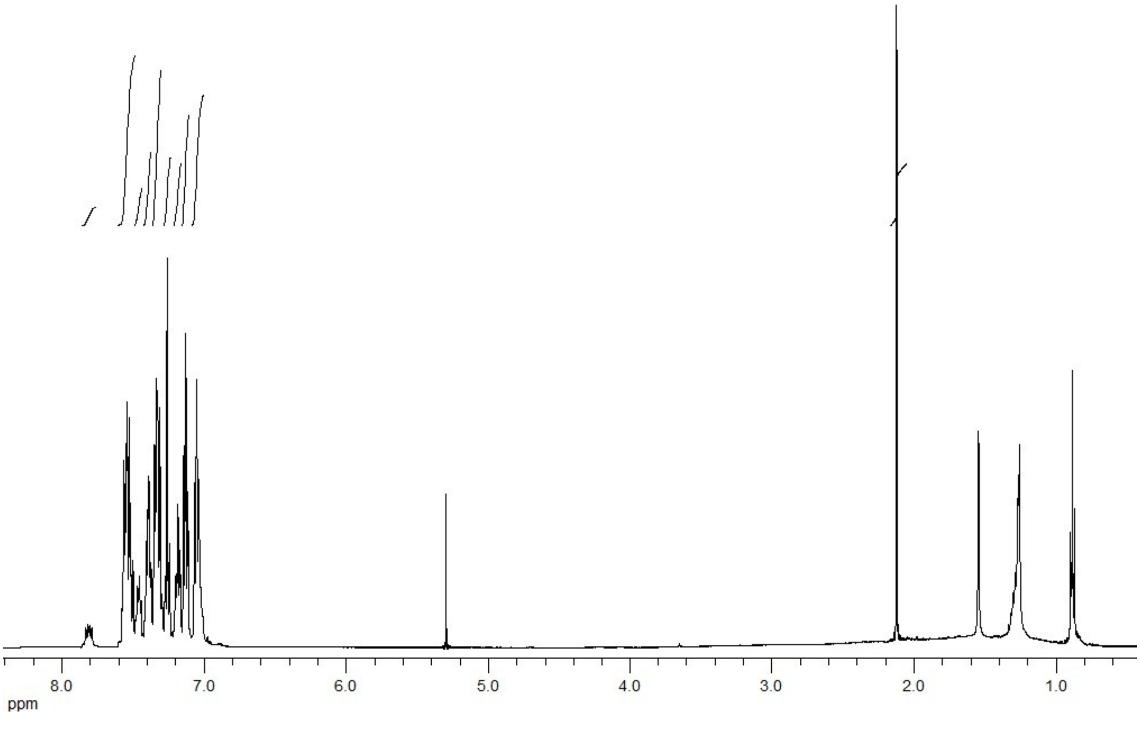

Figure S.12. ^{1}H NMR spectrum ($CDCl_3$) of **PtL2.**

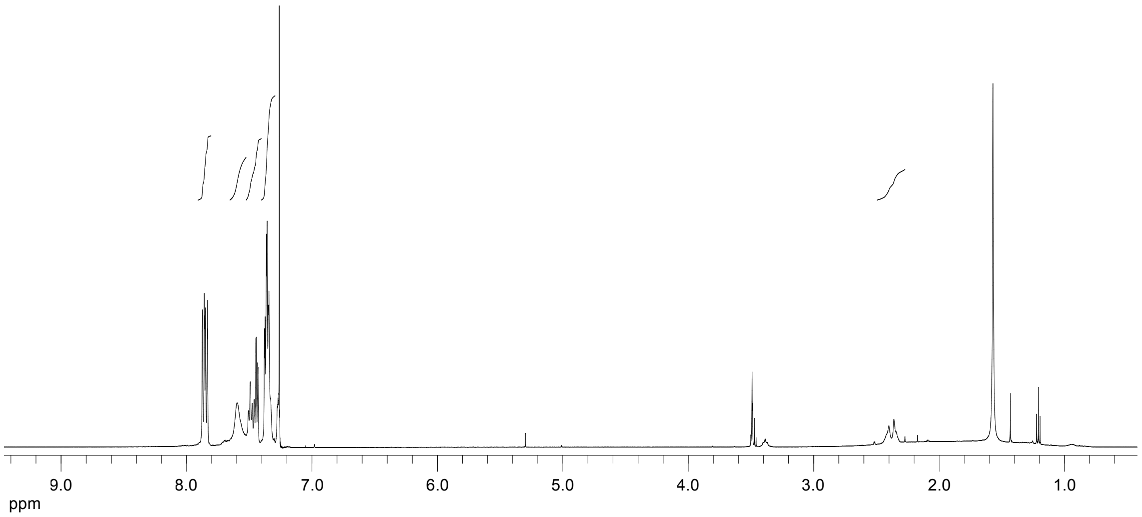

Figure S.13. ^{1}H NMR spectrum ($CDCl_3$) of **PdL1dppe.**

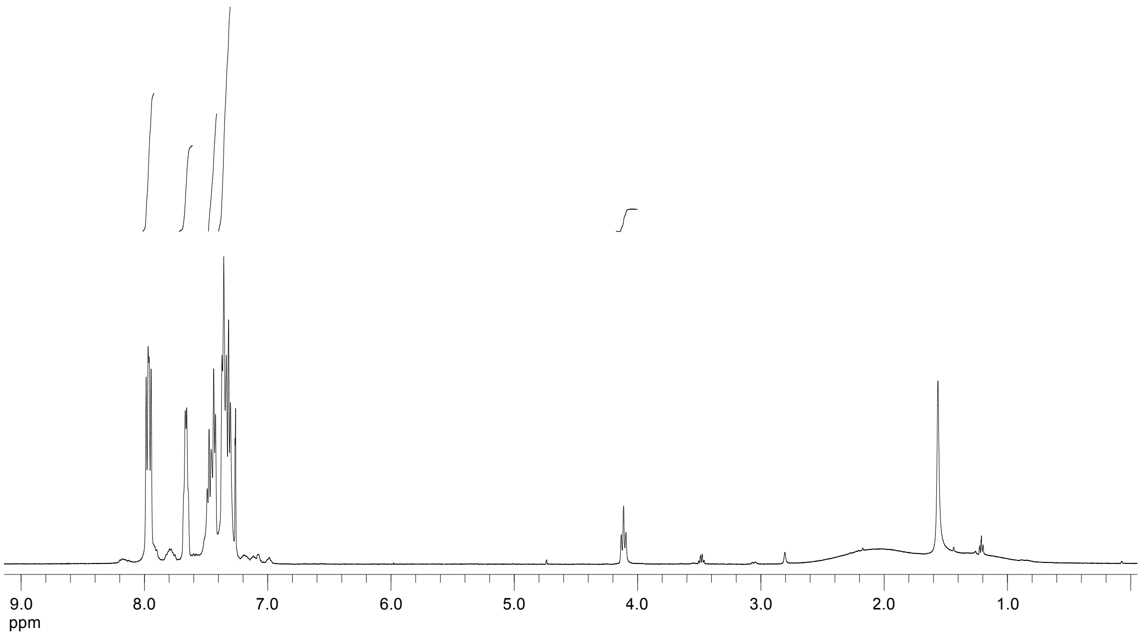

Figure S.14. ^{1}H NMR spectrum ($CDCl_3$) of **PdL1dppm.**

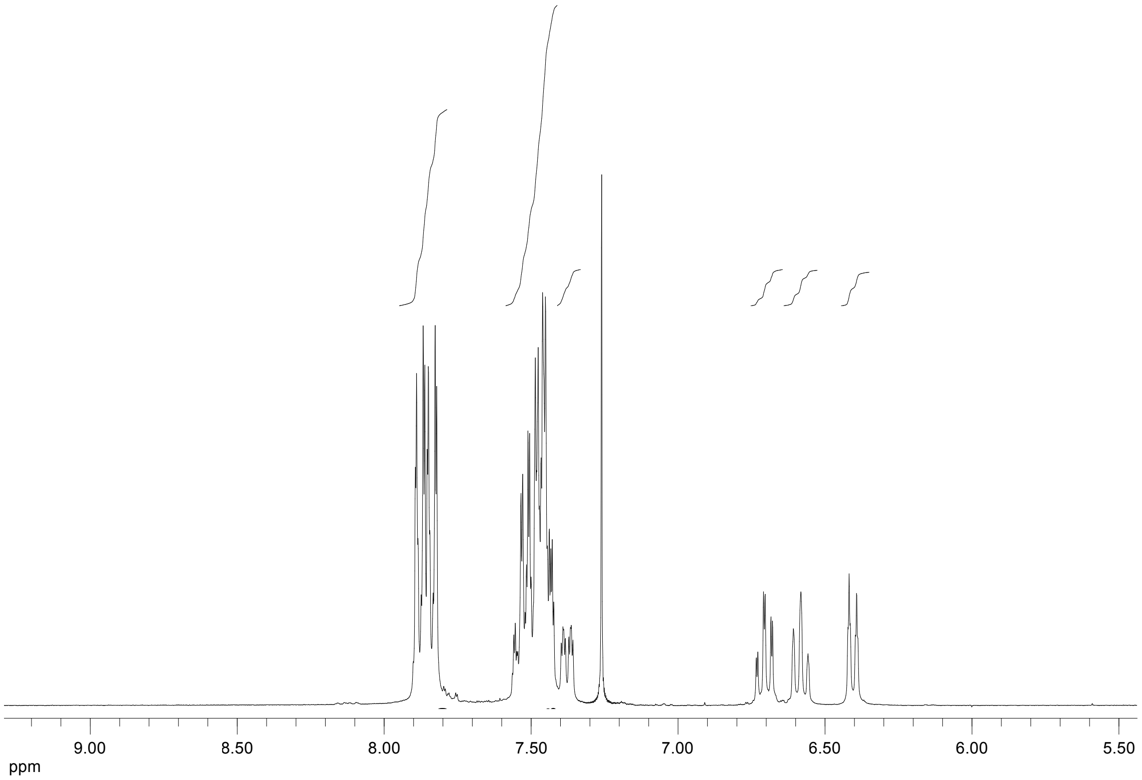

Figure S.15. ^{1}H NMR spectrum ($CDCl_3$) of **L3L3.**

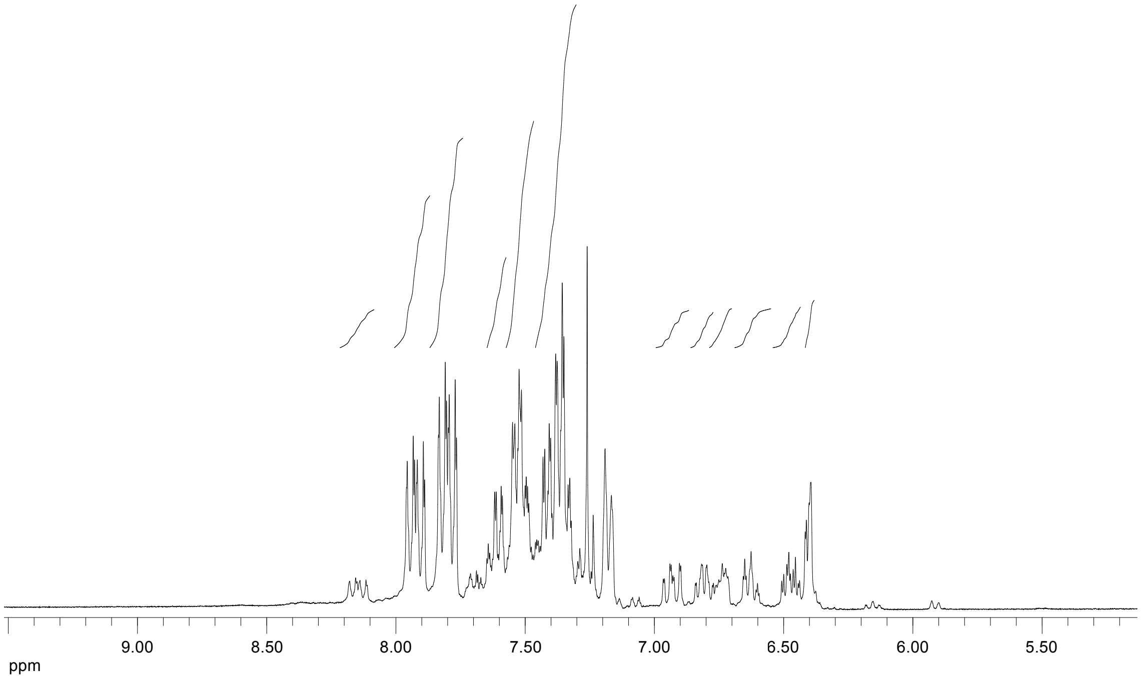

Figure S.16. ^{1}H NMR spectrum ($CDCl_3$) of **PdL3.**

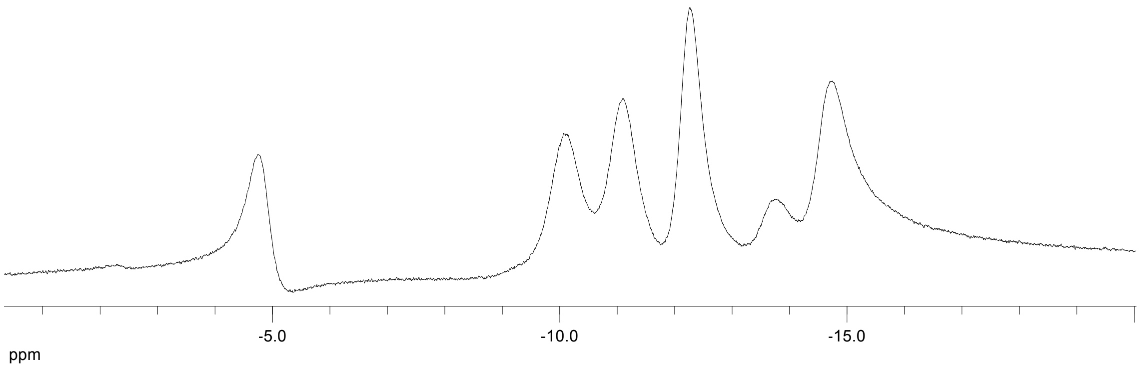

Figure S.17. $^{11}B\{^1H\}$ NMR spectrum ($CDCl_3$) of **I1.**

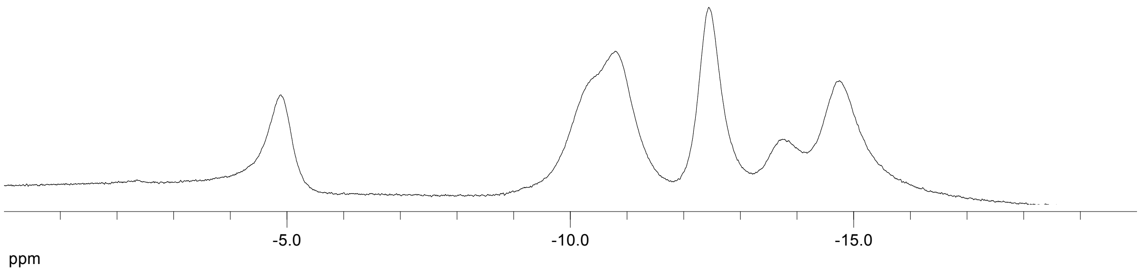

Figura S.18. $^{11}B\{^1H\}$ NMR spectrum ($CDCl_3$) of **I2.**

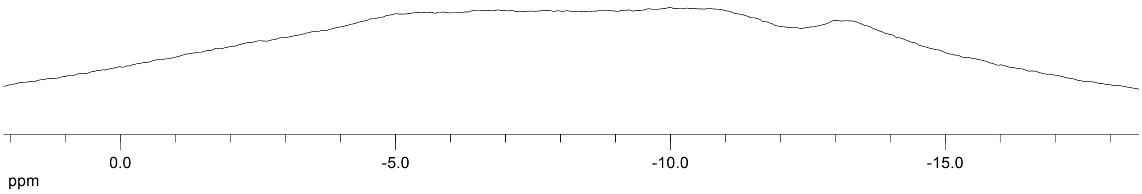

Figure S.19. $^{11}B\{^1H\}$ NMR spectrum ($CDCl_3$) of **L1H.**

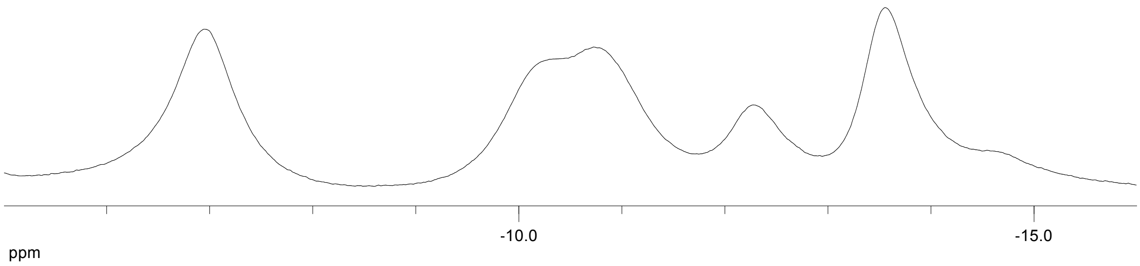

Figure S.20. $^{11}B\{^1H\}$ NMR spectrum ($CDCl_3$) of **L1L1.**

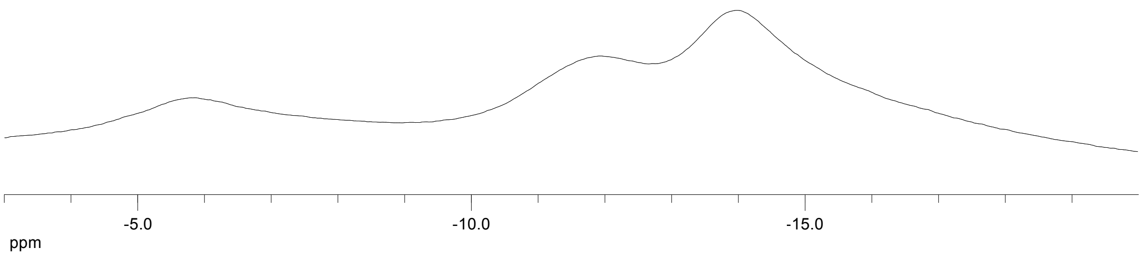

Figure S.21. $^{11}B\{^1H\}$ NMR spectrum ($CDCl_3$) of **L1SL1.**

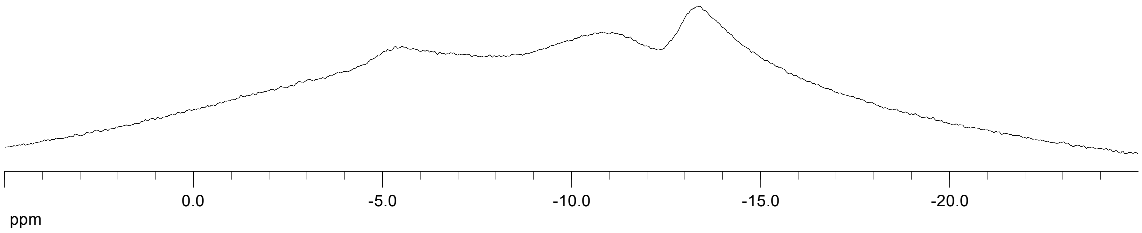

Figure S.22. $^{11}B\{^1H\}$ NMR spectrum ($CDCl_3$) of **L2L2.**

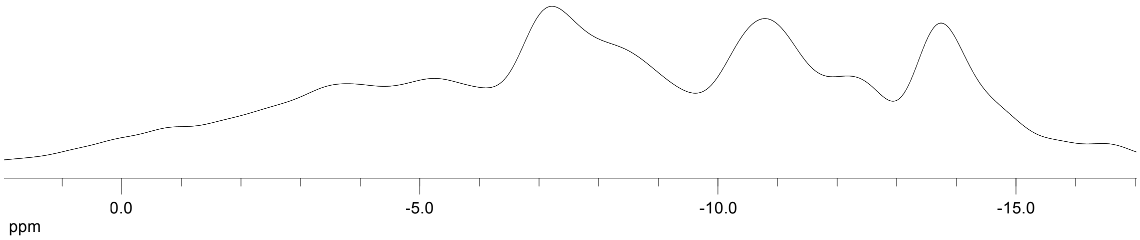

Figure S.23. $^{11}B\{^1H\}$ NMR spectrum ($CDCl_3$) of **PdL1.**

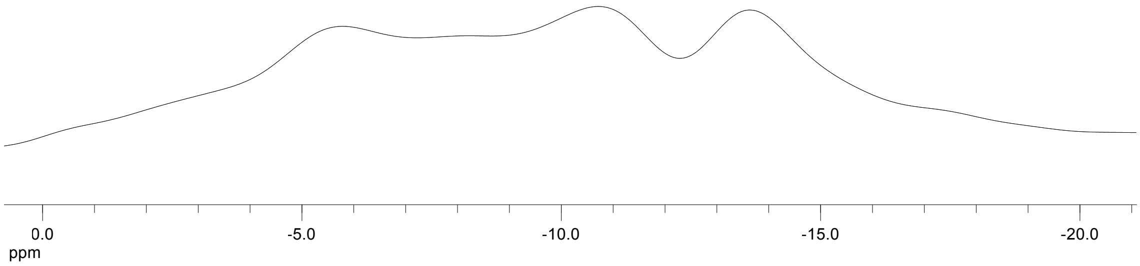

Figure S.24. $^{11}B\{^1H\}$ NMR spectrum ($CDCl_3$) of **PdL2.**

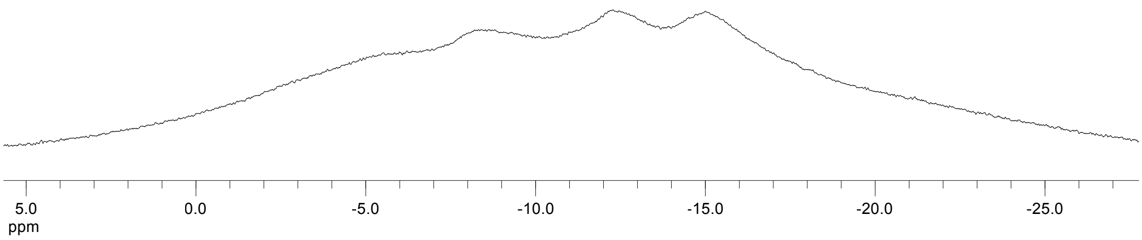

Figure S.25. $^{11}B\{^1H\}$ NMR spectrum ($CDCl_3$) of **PtL2.**

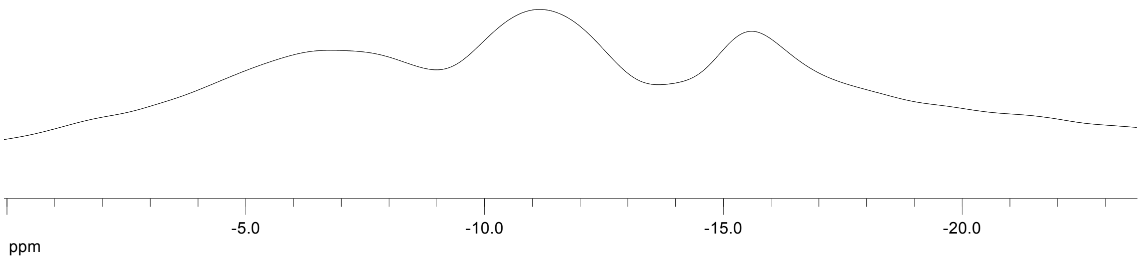

Figure S.26. $^{11}B\{^1H\}$ NMR spectrum ($CDCl_3$) of **PdL1dppe.**

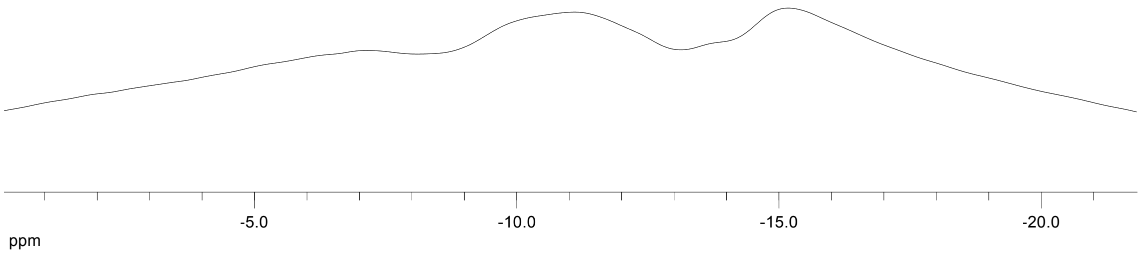

Figure S.27. $^{11}B\{^1H\}$ NMR spectrum ($CDCl_3$) of **PdL1dppm.**

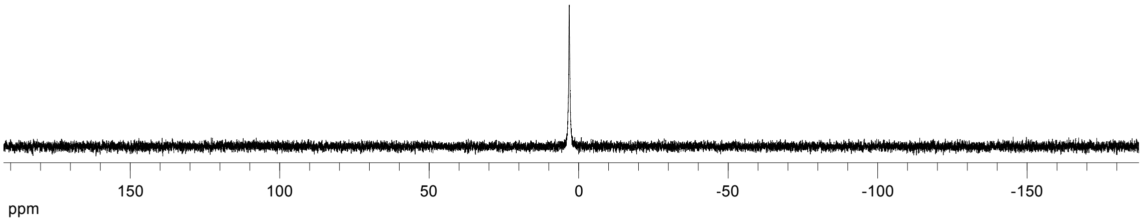

Figure S.28. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **I1.**

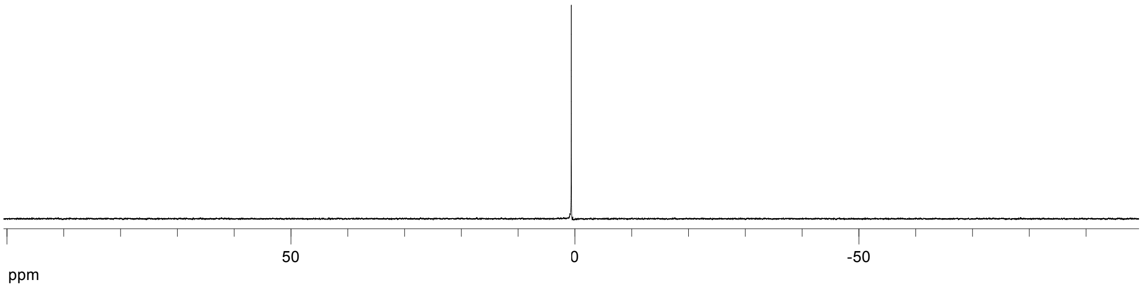

Figure S.29. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **I2.**

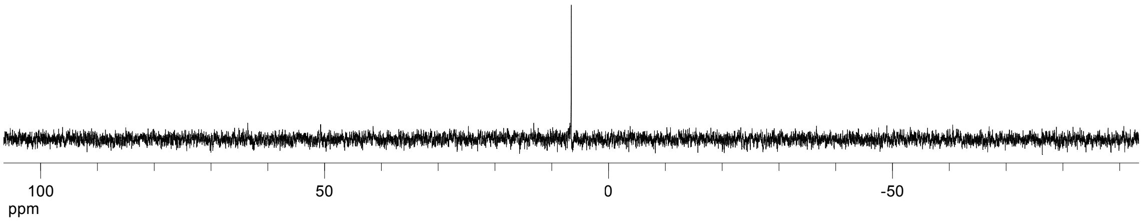

Figure S.30. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **L1H.**

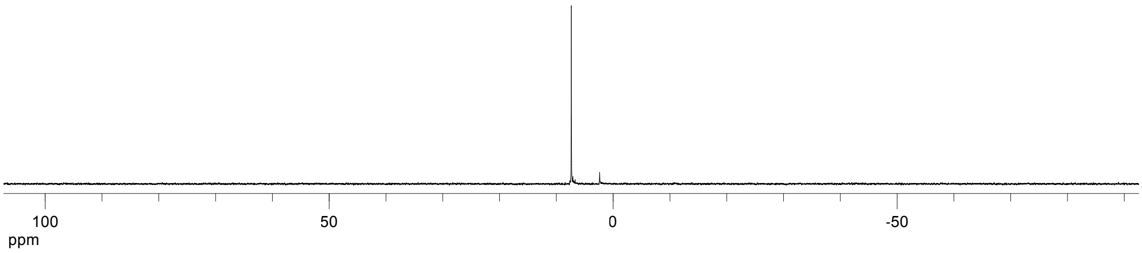

Figure S.31. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **L1L1.**

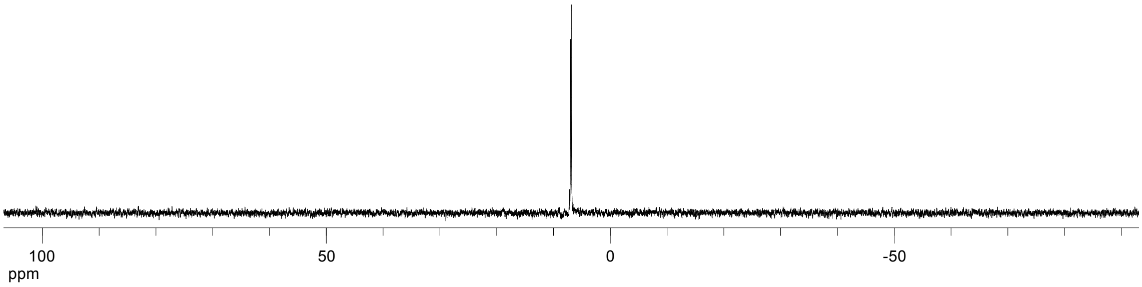

Figure S.32. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **L1SL1.**

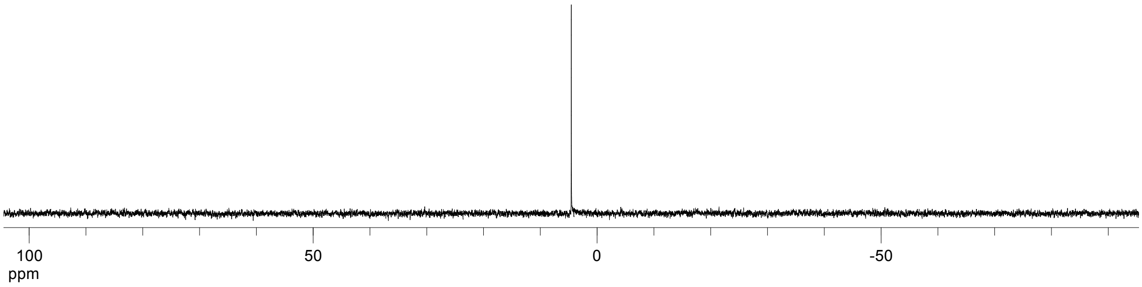

Figure S.33. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **L2L2.**

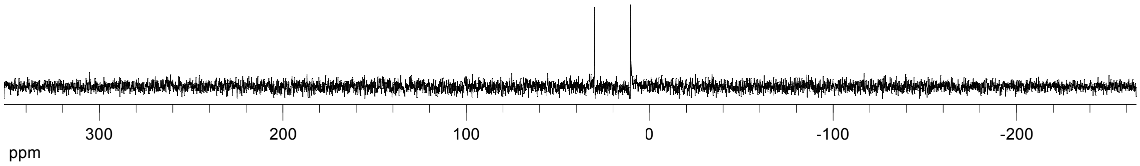

Figure S.34. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **PdL1.**

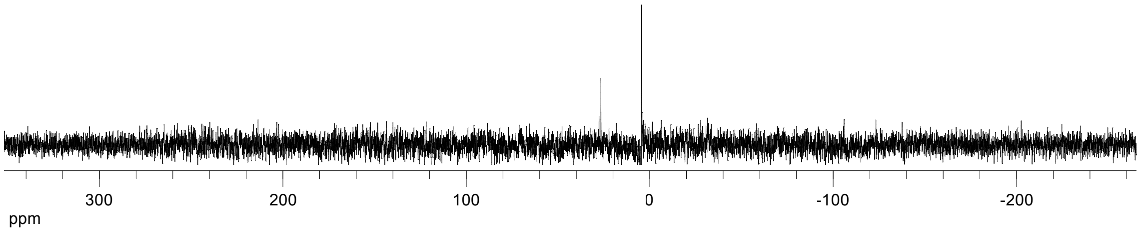

Figure S.35. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **PdL2.**

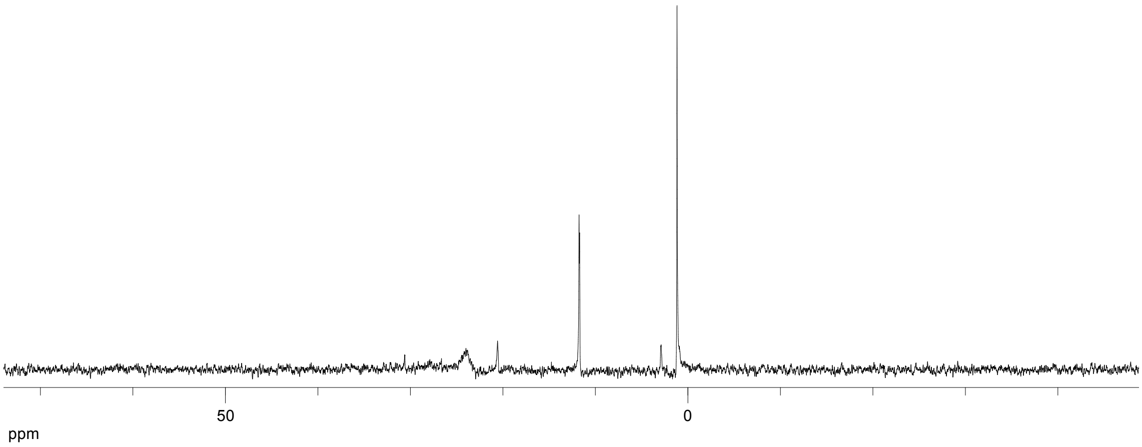

Figure S.36. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **PtL1.**

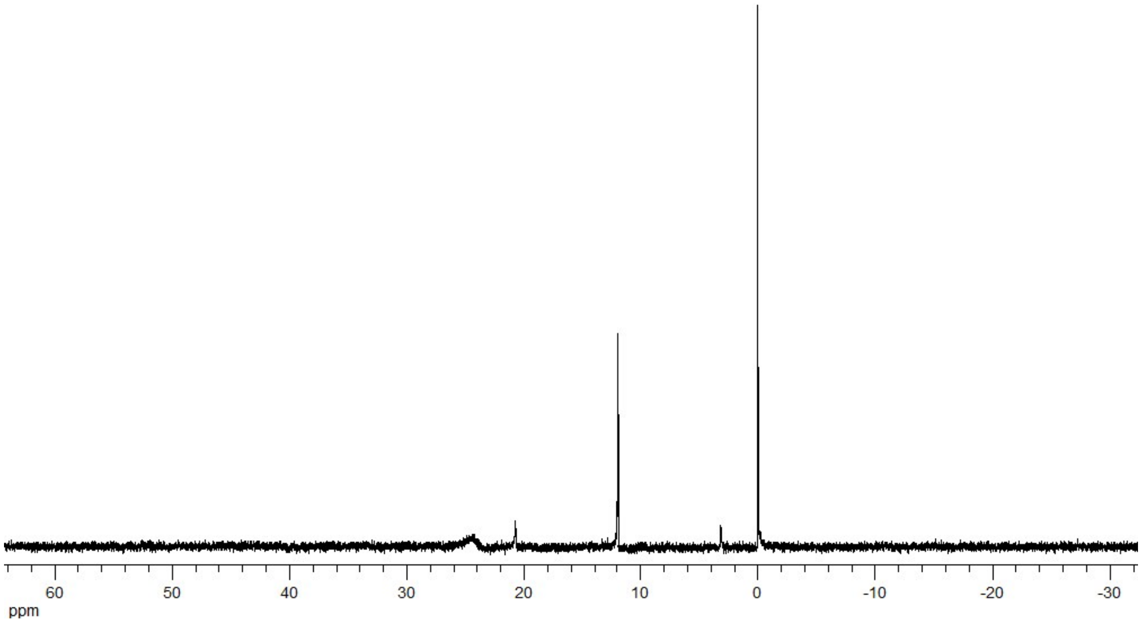

Figure S.37. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **PtL2.**

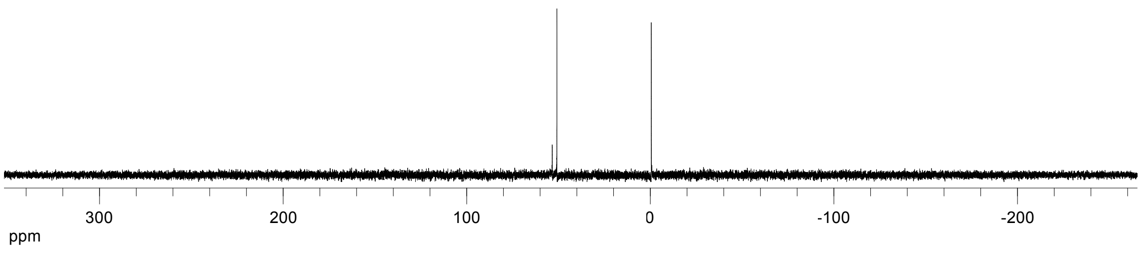

Figure S.38. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **PdL1dppe.**

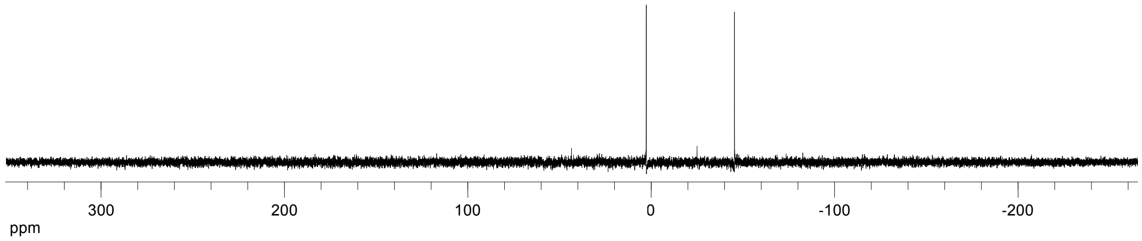

Figure S.39. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **PdL1dppm.**

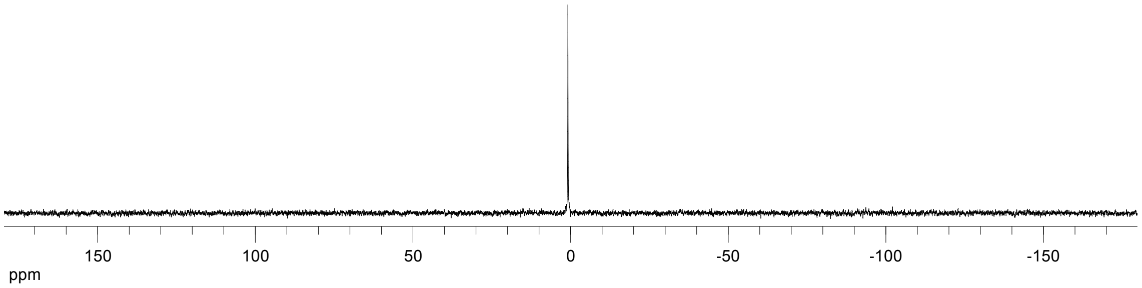

Figure S.40. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **L3L3.**

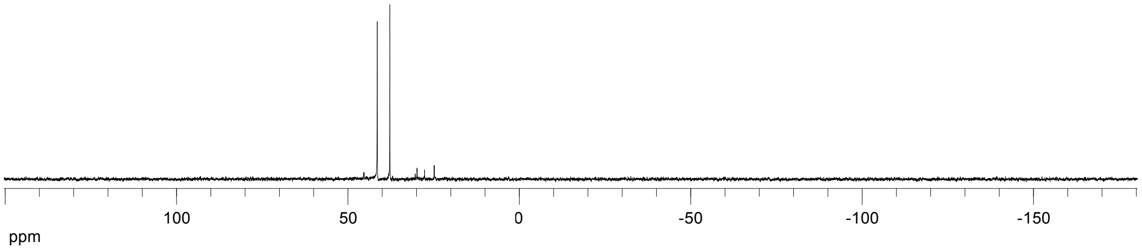

Figure S.41. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **PdL3.**