Coordination behaviour of a hybrid phosphinoguanidine ligand

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Supporting Information

Optimisation of the synthesis of 2-(diphenylphosphino)aniline (2)

General procedure. An oven-dried Schlenk flask equipped with a stirring bar was charged successively with a solid catalyst ($Pd(OAc)_2$ was dosed in the form of a toluene solution containing 1 mg $Pd(OAc)_2$ per 1 mL), a base and 2-iodoaniline (438 mg, 2.0 mmol), flushed with nitrogen, and sealed with a rubber septum. Dry toluene (up to 5 mL total volume) was introduced, followed by neat diphenylphosphine (348 μL, 2.0 mmol) and amine additive. The reaction vessel was transferred to a preheated oil bath and stirred at constant temperature for the given reaction time. Conversion was determined by integrating the ^1H NMR spectra of small aliquots withdrawn from a cooled reaction mixture and diluted with dmso-d_6. The results are outlined in Table S1.

Table S1 Summary of the catalytic experiments[a]

Entry	T/°C	Time/h	Catalyst [mol.%]	Base [equiv.]	Amine [mol.%][c]	NMR yield/%
1	110	24	$Pd(OAc)_2$ [0.1]/CuI [5]	Cs_2CO_3 [2]	DMEDA [35]	>99
2	110	24	$Pd(OAc)_2$ [0.1]/CuI **[2]**	Cs_2CO_3 **[1]**	DMEDA **[10]**	>99
3	110	24	$Pd(OAc)_2$ [0.1]/CuI [2]	**K_2CO_3** [1]	DMEDA [10]	>99
4	110	24	**CuI** [2]	K_2CO_3 [1]	DMEDA [10]	9
5	110	24	$Pd(OAc)_2$ [1]	Cs_2CO_3 [2]	DMEDA [35]	>99
6	110	24	$Pd(OAc)_2$ **[0.1]**	Cs_2CO_3 **[1]**	DMEDA **[10]**	>99
7	110	24	$Pd(OAc)_2$ [0.1]	**K_2CO_3** [1]	DMEDA [10]	>99
8	110	24	$Pd(OAc)_2$ [0.1]	K_2CO_3 [1]	DMEDA **[5]**	97
9	110	24	$Pd(OAc)_2$ [0.1]	K_2CO_3 [1]	**Et_2NH** [10]	59
10	110	24	$Pd(OAc)_2$ [0.1]	K_2CO_3 [1]	**Et_3N** [10]	68
11	110	24	$Pd(OAc)_2$ **[0.5]**	**Cs_2CO_3** [1]	**none**	40
12	110	**4**	$Pd(OAc)_2$ [0.1]	K_2CO_3 [1]	DMEDA [10]	>99
13	110	**2**	$Pd(OAc)_2$ [0.1]	K_2CO_3 [1]	DMEDA [10]	>99
14	**100**	2	$Pd(OAc)_2$ [0.1]	K_2CO_3 [1]	DMEDA [10]	45
15	100	**12**	$Pd(OAc)_2$ [0.1]	K_2CO_3 [1]	DMEDA [10]	>99
16	**90**	2	$Pd(OAc)_2$ [0.1]	K_2CO_3 [1]	DMEDA [10]	0
17[b]	100	12	$Pd(OAc)_2$ [0.1]	K_2CO_3 [1]	DMEDA [10]	0

[a] The change from a previous entry is highlighted in bold. [b] DMEDA = *N*,*N*'-dimethylethylenediamine. [c] Reaction using 2-bromoaniline (2.0 mmol) as the starting material

Additional structural diagrams

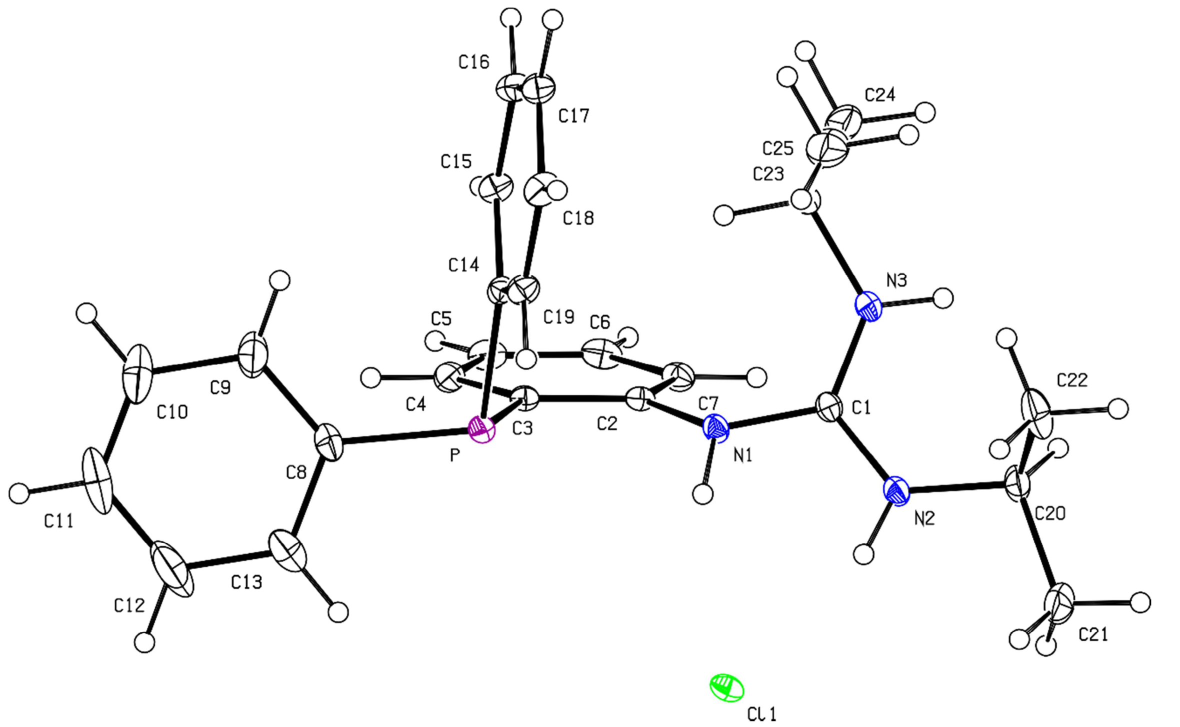

Figure S1. PLATON plot of the structure of (**1H**)Cl showing 30% probability ellipsoids

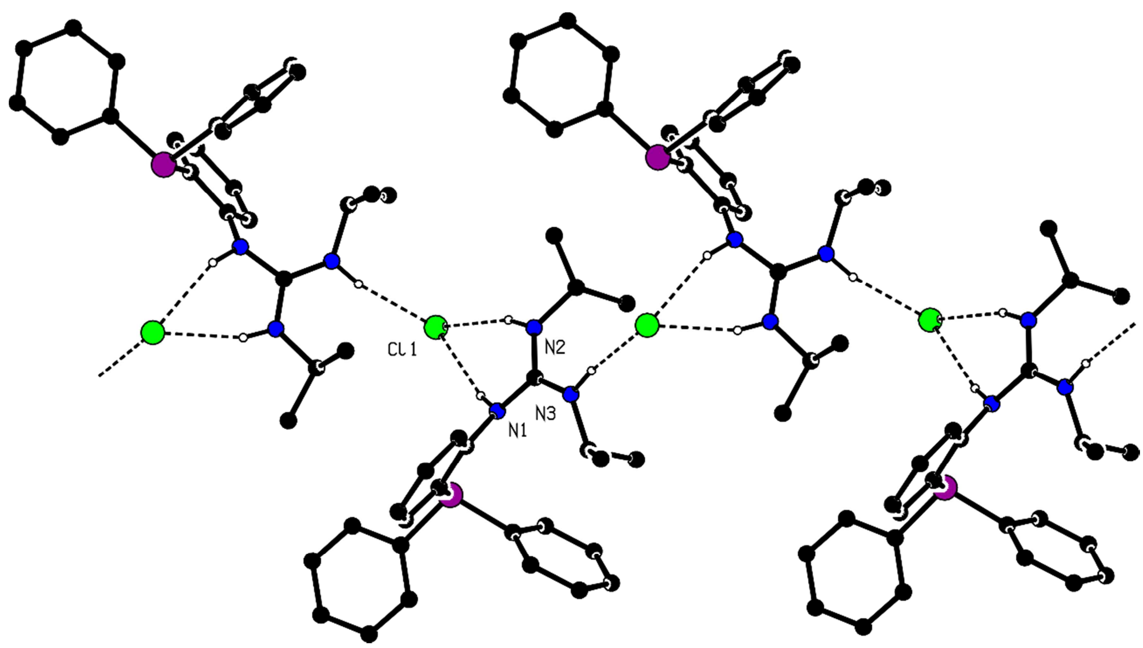

Figure S2. Simplified packing diagram of (**1H**)Cl (only NH hydrogens are shown for clarity). Hydrogen bond parameters: N1···Cl1 = 3.200(1) Å, N2···Cl1 = 3.133(1), N3···Cl1 = 3.175(1) Å

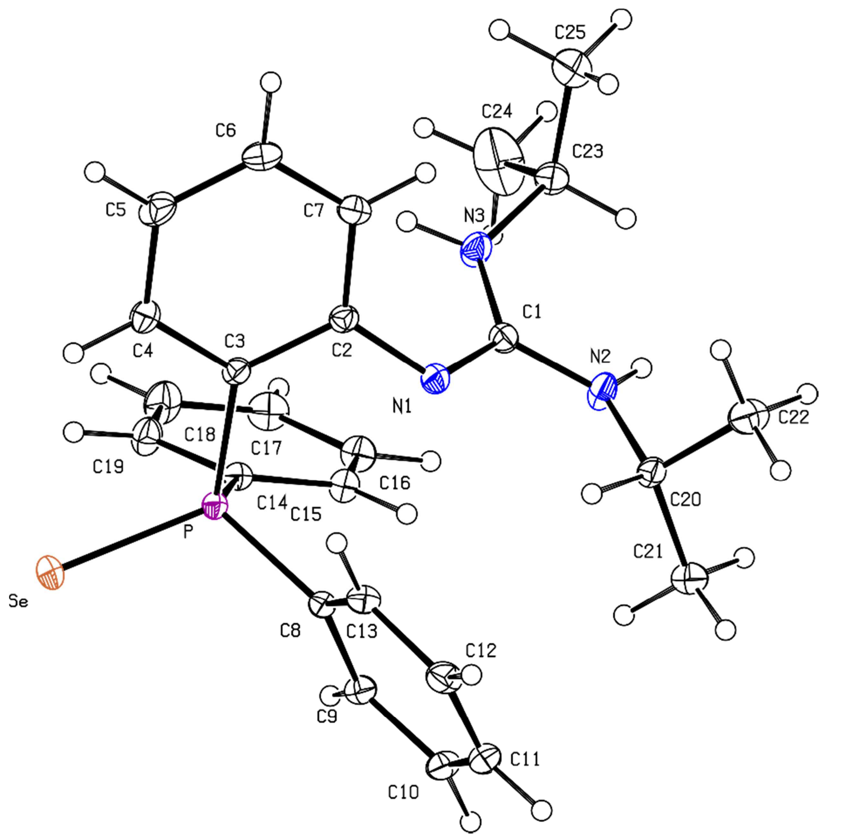

Figure S3. PLATON plot of the structure of **3** showing 30% probability ellipsoids

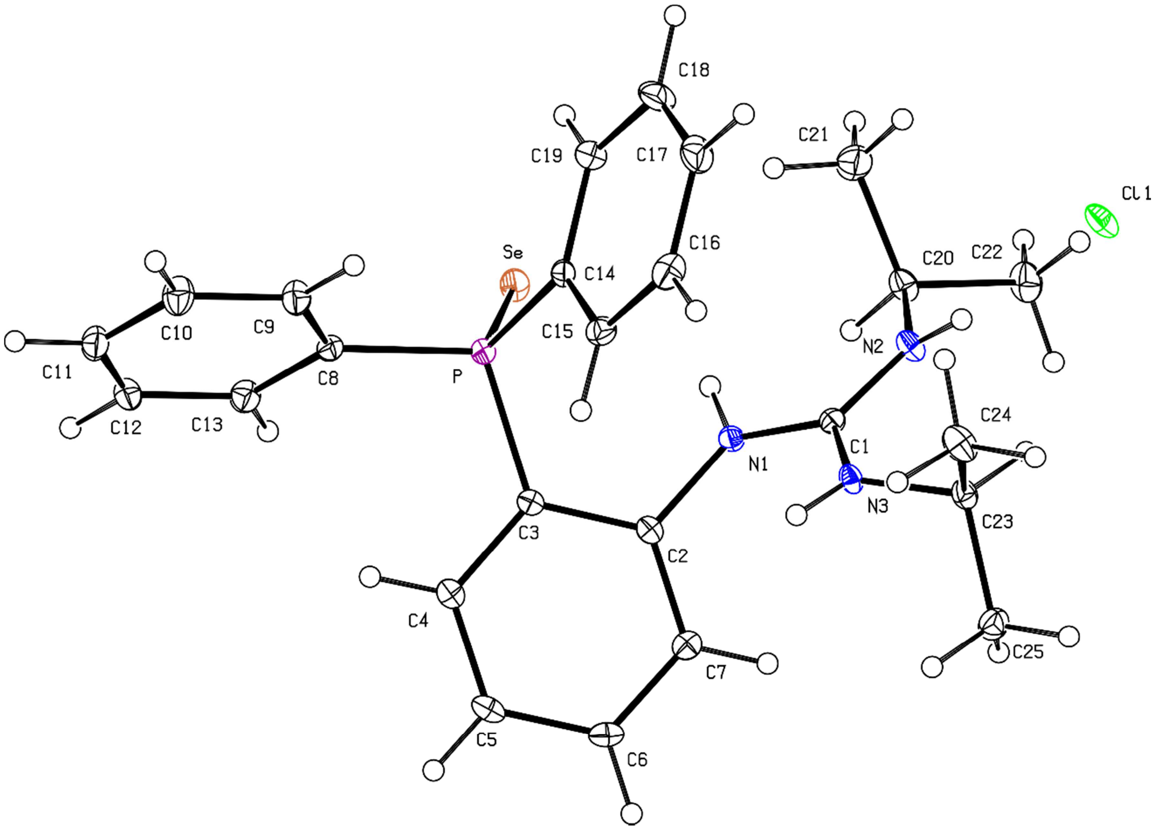

Figure S4. PLATON plot of the structure of (**3H**)Cl showing 30% probability ellipsoids

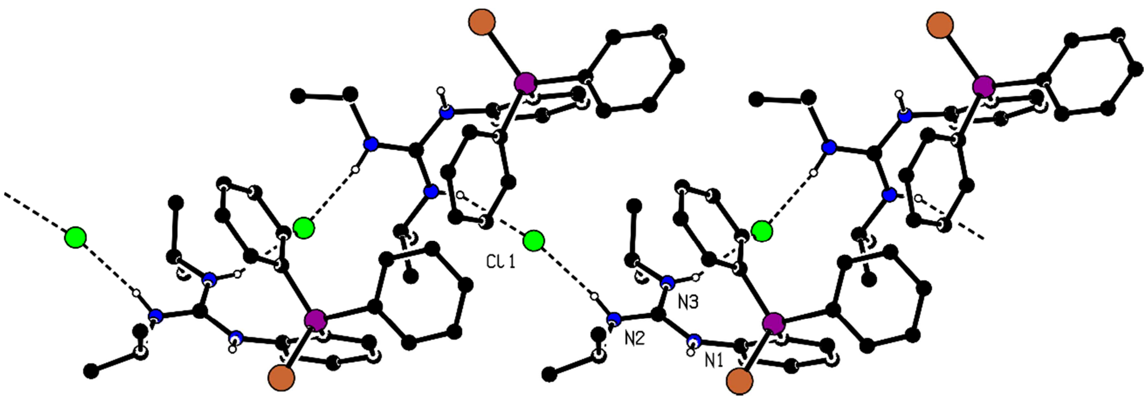

Figure S5. Simplified packing diagram of (**3H**)Cl (only NH hydrogens are shown for clarity). Hydrogen bond parameters: N1···Se = 3.450(1) Å (intramolecular; not indicated in the figure); N2···Cl1 = 3.139(1) Å, N3···Cl1 = 3.198(1) Å

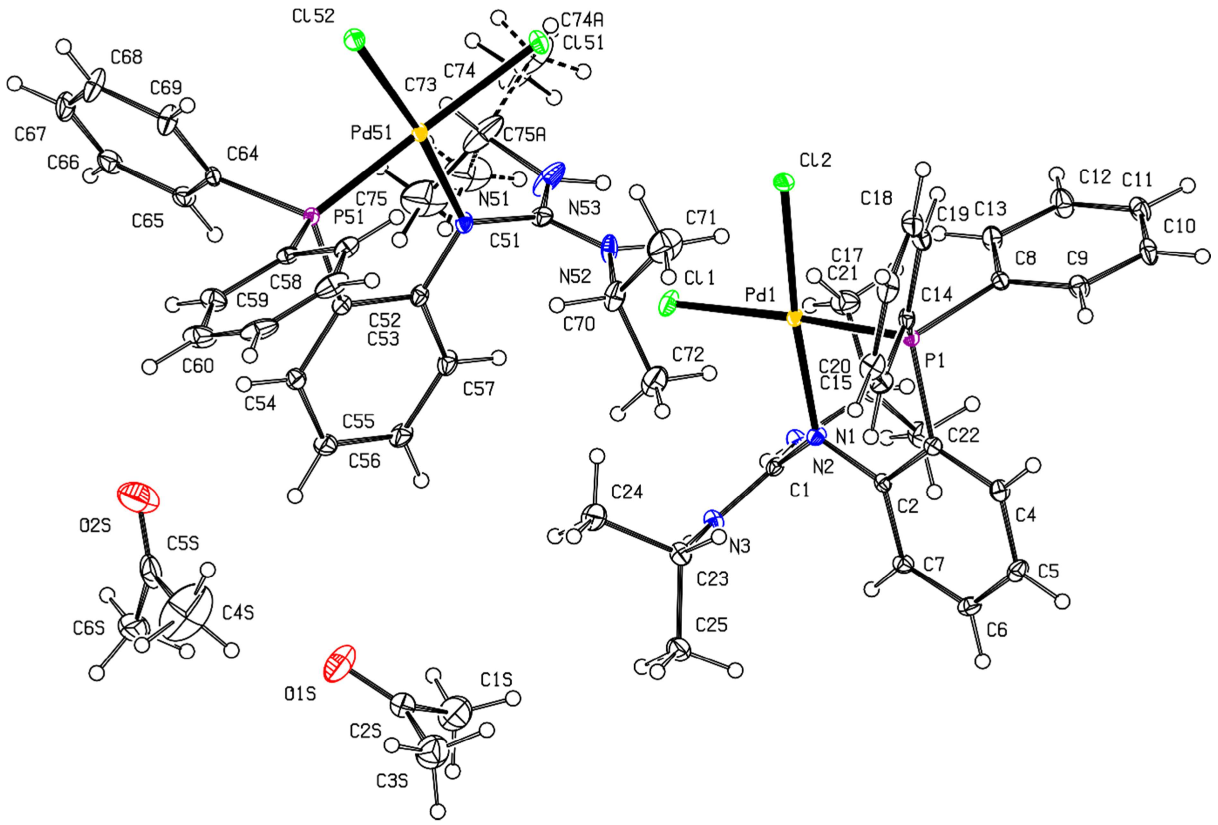

Figure S6. Full PLATON plot of the structure of **4**·Me_2CO showing 30% probability ellipsoids

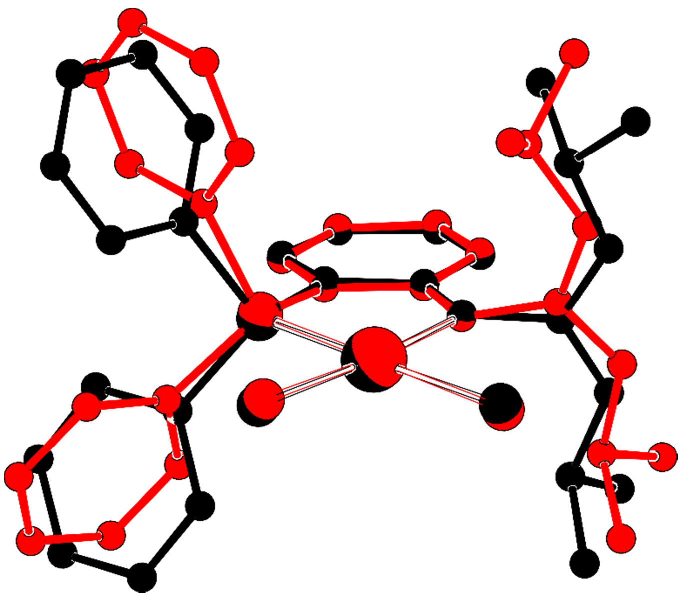

Figure S7. Overlap of the two crystallographically complex molecules in the structure of **4**·Me_2CO (molecule 1 in red, molecule 2 in black); only one position of the disordered isopropyl group is shown to avoid complicating the figure.

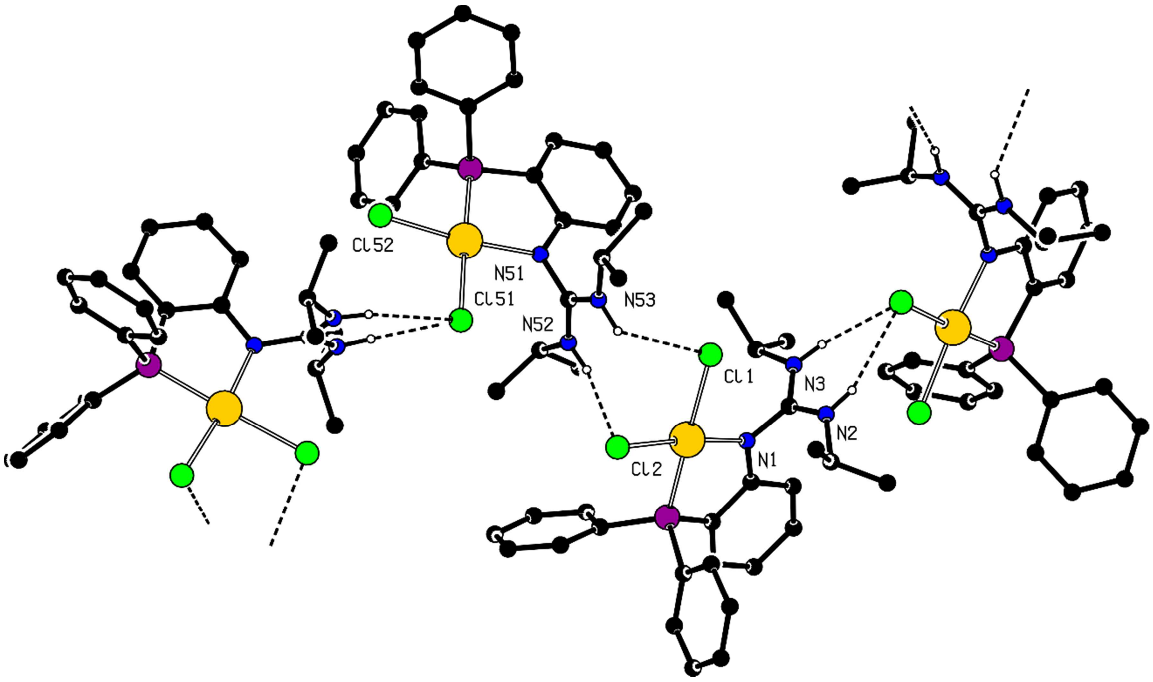

Figure S8. Simplified packing diagram of **4**·Me_2CO (only NH hydrogens and one position of the disordered isopropyl group are shown for clarity). Note that the NH groups of the molecule 1 (Pd1) form hydrogen bonds with the same chloride ligand, Cl51, in molecule 2 (Pd51), while the NH groups in molecule 2 interact with the different chlorides in molecule 1. These interactions give rise to zig-zag chains oriented along the crystallographic *c* axis. Hydrogen bond parameters: N2···Cl51 = 3.460(2) Å, N3···Cl51 = 3.305(2) Å, N52···Cl2 = 3.299(2) Å, N53···Cl1 = 3.278(2) Å

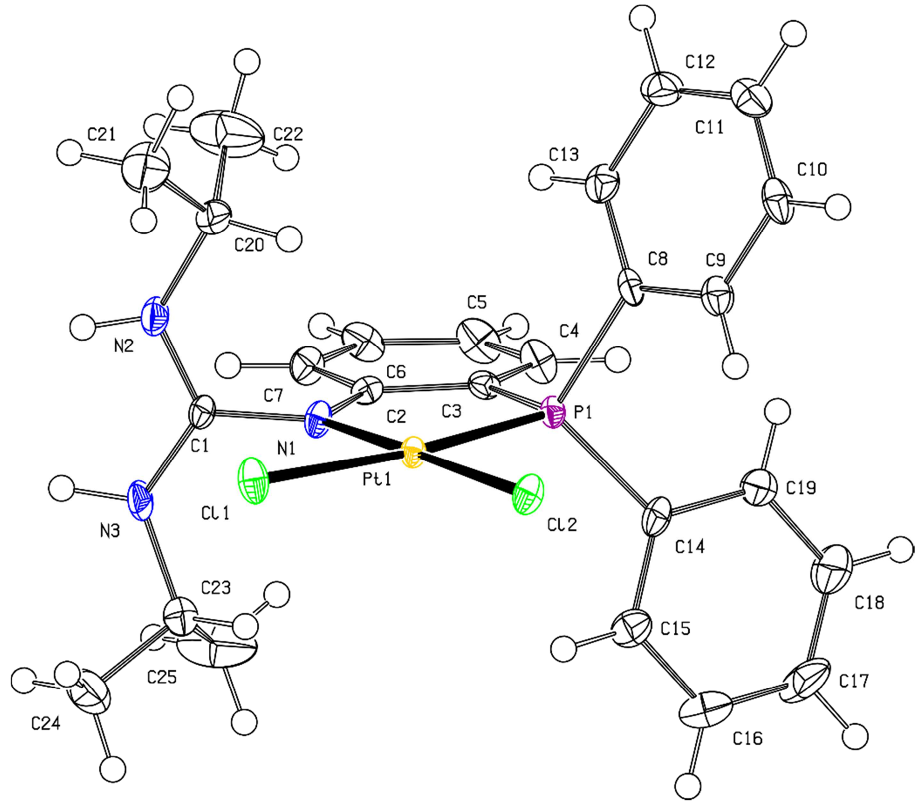

Figure S9. PLATON plot of the structure of **7** showing 30% probability ellipsoids

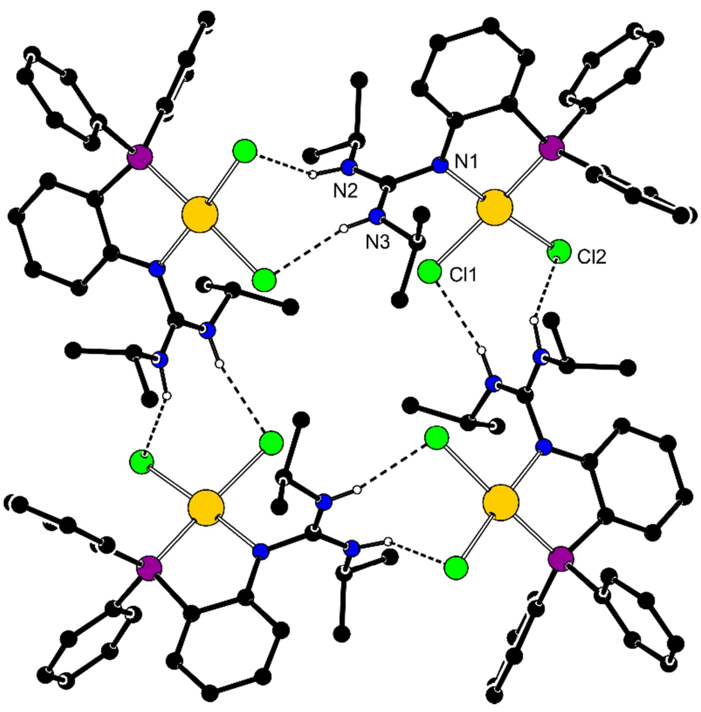

Figure S10. Simplified packing diagram of **7** (only NH hydrogens are shown for clarity). The complex molecules assemble into closed cyclic arrays around the crystallographic four-fold axis. Hydrogen bond parameters: N2···Cl1 = 3.250(4) Å, N3···Cl2 = 3.452(4) Å

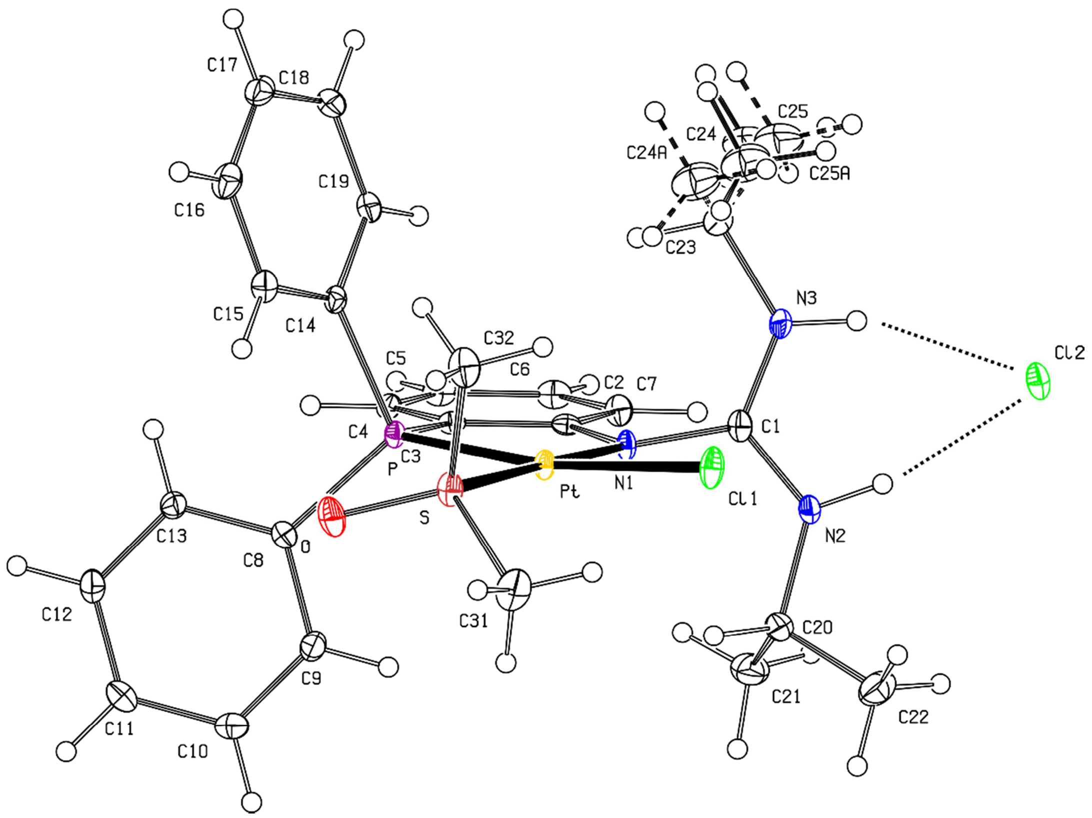

Figure S11. PLATON plot of the structure of **5** showing 30% probability ellipsoids; the N-H···Cl hydrogen bonds are indicated by dotted lines (N2···Cl2 = 3.180(2) Å, N3···Cl2 = 3.214(2) Å).

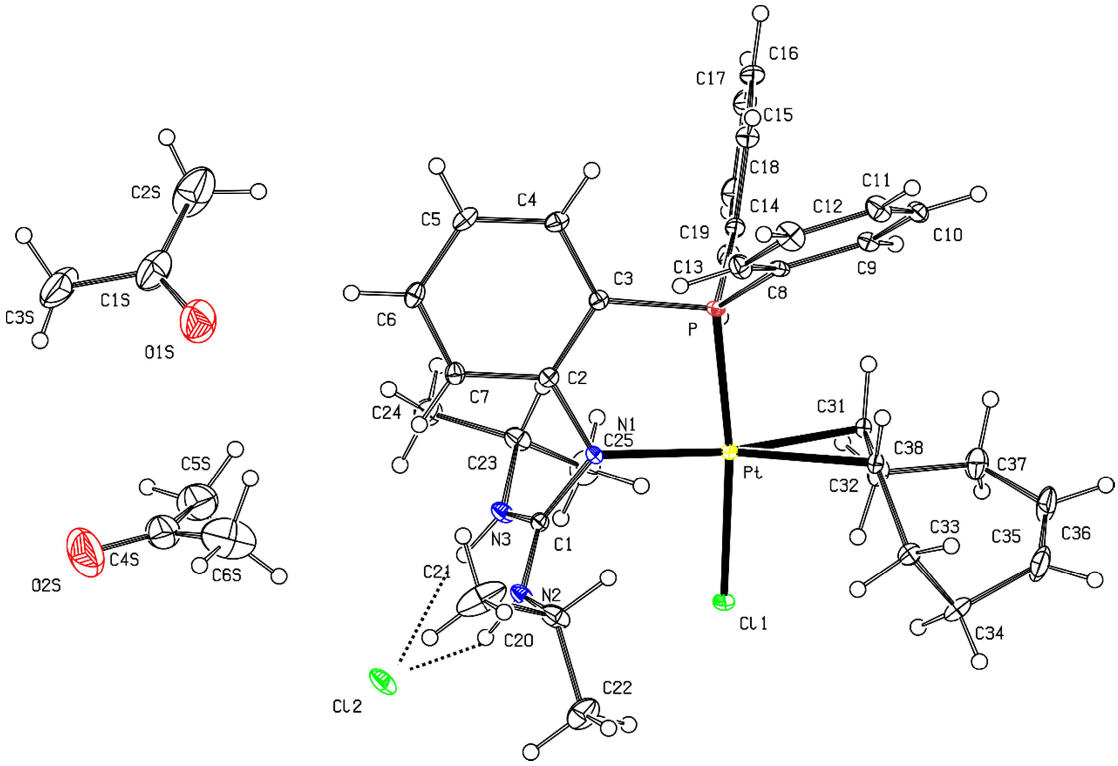

Figure S12. PLATON plot of the structure of **6**·$2Me_2CO$ showing 30% probability ellipsoids; the N-H···Cl hydrogen bonds are shown as dotted lines (N2···Cl2 = 3.180(2) Å, N3···Cl2 = 3.096(3) Å).

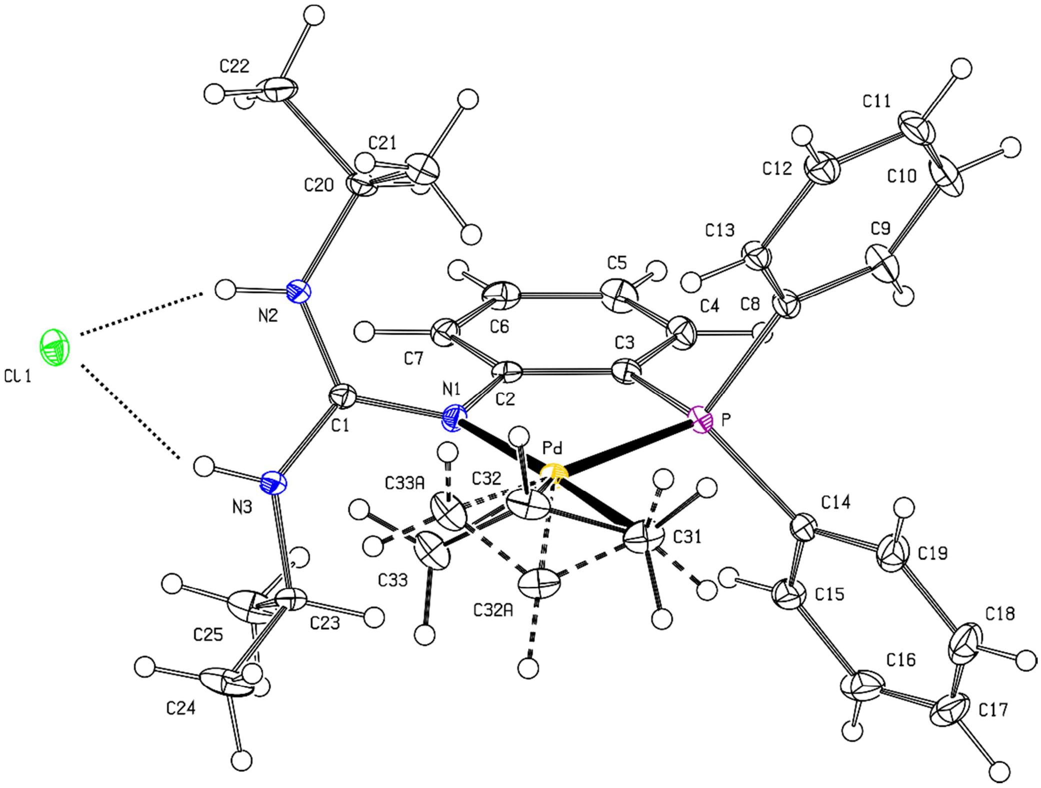

Figure S13. PLATON plot of the structure of **8** showing 30% probability ellipsoids. The N-H···Cl hydrogen bonds are shown as dotted lines (N2···Cl2 = 3.178(2) Å, N3···Cl2 = 3.182(2) Å).

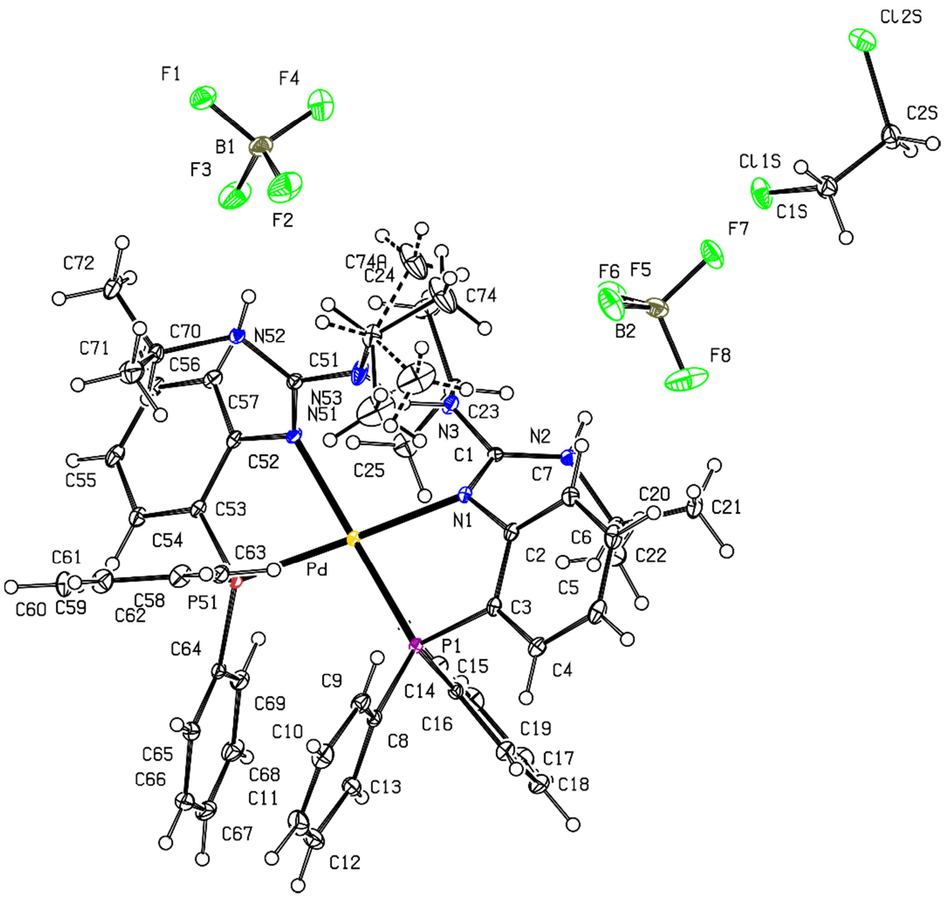

Figure S14. PLATON plot of the structure of **9**·$C_2H_4Cl_2$ showing 30% probability ellipsoids

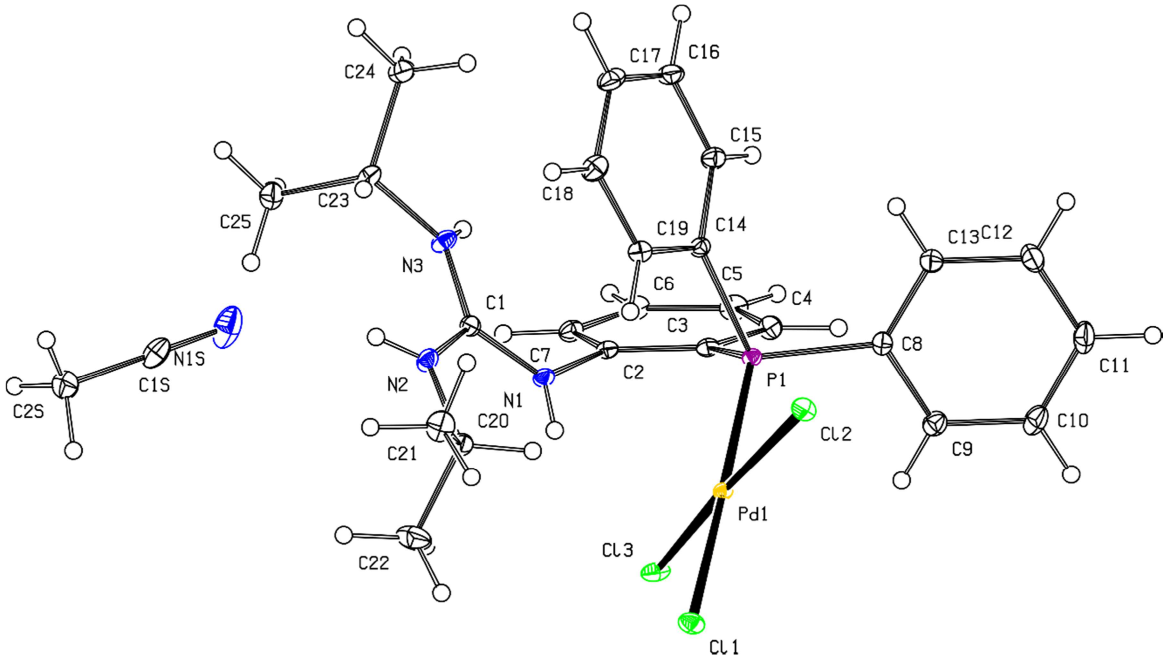

Figure S15. PLATON plot of the structure of **9**·MeCN showing 30% probability ellipsoids

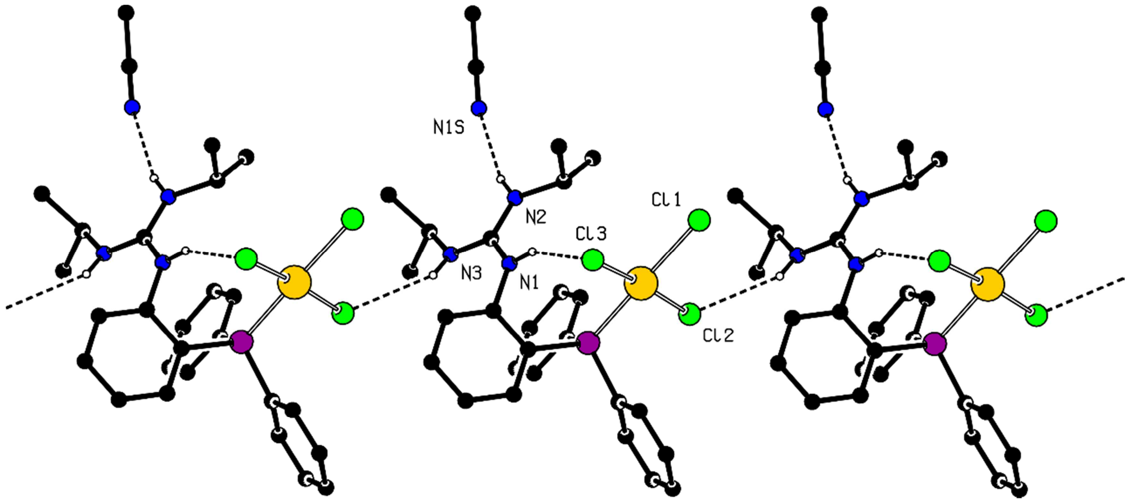

Figure S16. Simplified packing diagram of **10**·MeCN (only NH hydrogens are shown for clarity); Hydrogen bond parameters: N1···Cl3 = 3.107(1) Å, N2···N1S = 2.995(2) Å, N3···Cl3 = 3.387(1) Å

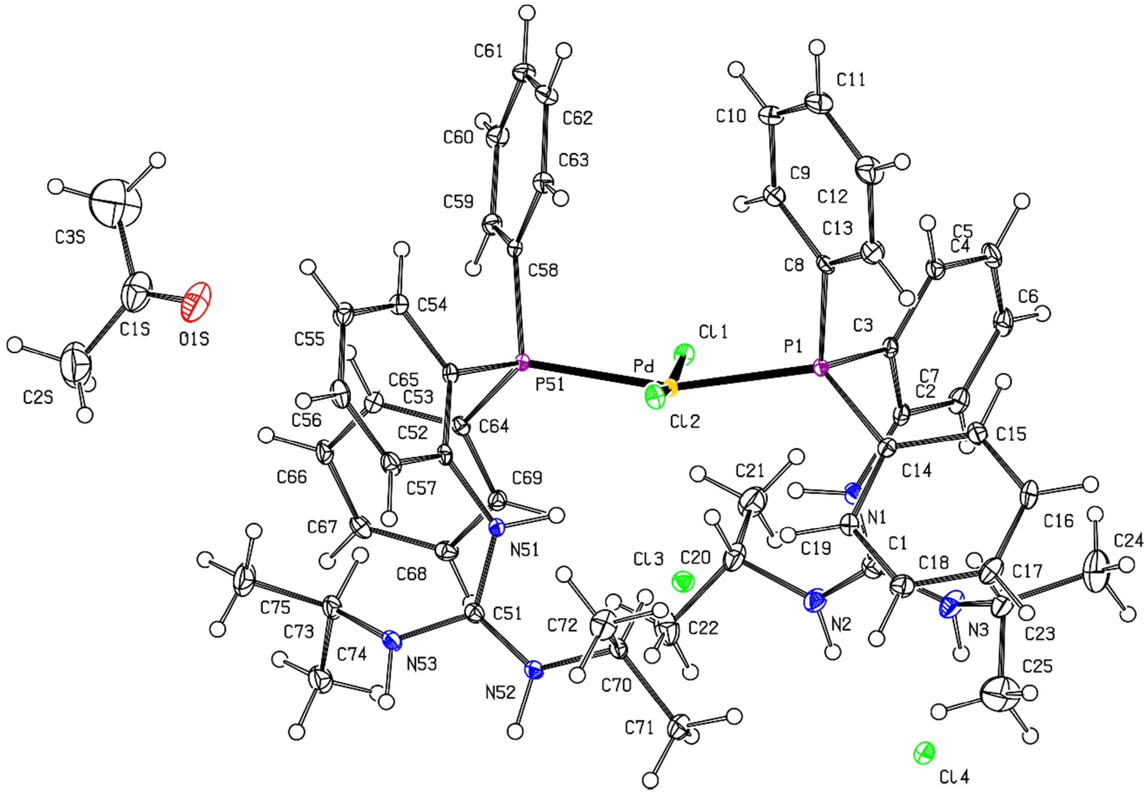

Figure S17. PLATON plot of the structure of **11**·Me_2CO showing 30% probability ellipsoids

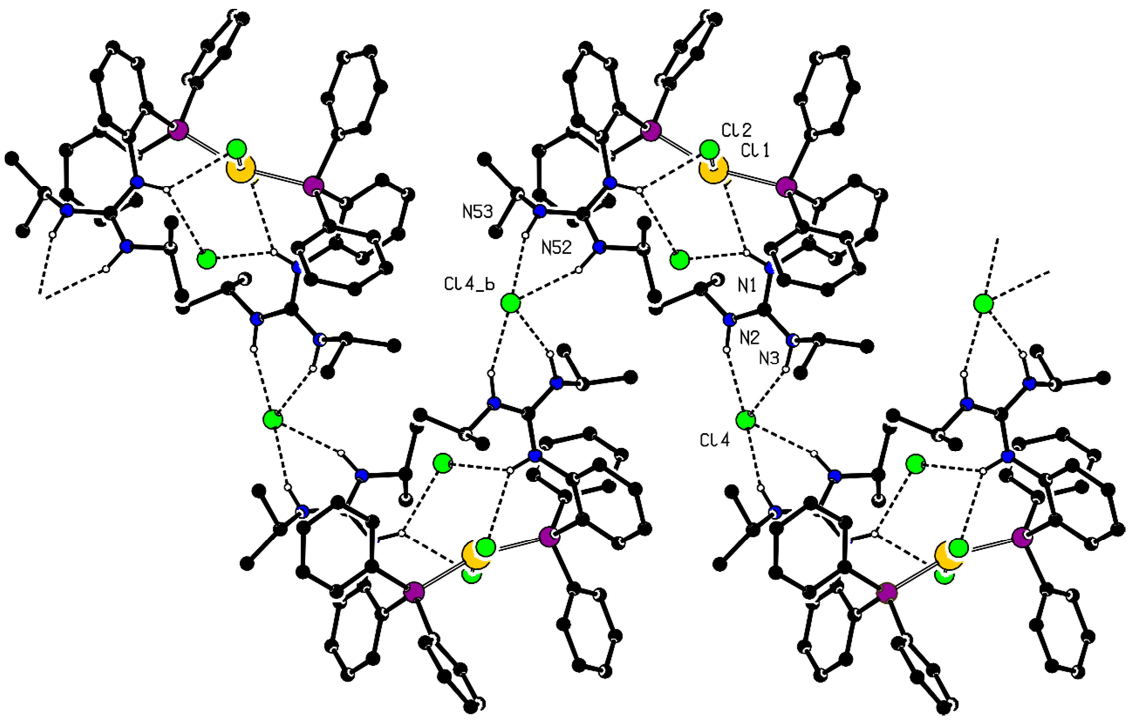

Figure S18. Simplified packing diagram of **11**·Me_2CO (only NH hydrogens are shown for clarity); Hydrogen bond parameters: N1···Cl1 (intramolecular) = 3.337(2) Å; N1···Cl3 = 3.233(2) Å, N2···Cl4 = 3.201(2) Å, N3···Cl4 = 3.340(2) Å, N51···Cl2 (intramolecular) = 3.259(2) Å, N51···Cl3 = 3.496(2) Å, N52···Cl4 = 3.2508(2) Å, and N53···Cl4 = 3.203(2) Å

Table S2. Selected crystallographic data and structure refinement parameters[a]

Compound	(**1H**)Cl	**3**	(**3H**)Cl
Formula	$C_{25}H_{31}ClN_3P$	$C_{25}H_{30}N_3PSe$	$C_{25}H_{31}ClN_3PSe$
M	439.95	482.45	518.91
T [K]	130(2)	150(2)	120(2)
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$ (no. 19)[c]	$P2_1/c$ (no. 14).	*Pbca* (no. 61)
a [Å]	10.1489(4)	14.1735(4)	11.1802(2)
b [Å]	12.9048(4)	9.6026(3)	13.5729(2)
c [Å]	19.8932(8)	17.3982(5)	33.3512(7)
α [°]	90	90	90
β [°]	90	96.210(1)	90
γ [°]	90	90	90
V [Å]^3	2605.4(2)	2354.0(1)	5061.0(2)
Z	4	4	8
μ(Mo Kα) [mm^{-1}]	0.223	1.680	1.670
Diffrns collected	26308	60794	43114
Independent diffrns	5970	6856	5797
Observed[a] diffrns	5772	6451	5070
R_{int}[b] [%]	2.12	2.09	3.70
No. of parameters	276	275	284
R[b] obsd diffrns [%]	2.42	2.74	2.50
R, *wR*[b] all data [%]	2.57, 5.99	2.95, 6.82	3.14, 6.24
Δρ [e Å^{-3}]	0.19, –0.15	0.76, –0.49	0.33, –0.31
CCDC deposition no.	2119578	2119579	2119580

[a] Diffractions with $I > 2\sigma(I)$. [b] Definitions: $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$, where $F_o^2(\text{mean})$ is the average intensity of symmetry-equivalent diffractions. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$. [c] Flack's enantiomorph parameter: –0.02(1).

Table S2 continued

Compound	**4**·Me_2CO	**5**	**6**·2Me_2CO
Formula	$C_{28}H_{36}Cl_2N_3OPPd$	$C_{27}H_{36}Cl_2N_3OPPtS$	$C_{39}H_{54}Cl_2N_3O_2PPt$
M	638.87	747.61	893.81
T [K]	120(2)	120(2)	120(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a [Å]	8.5730(5)	13.5803(2)	10.7829(5)
b [Å]	32.934(2)	10.3485(2)	27.718(2)
c [Å]	21.093(1)	21.2730(4)	13.6704(7)
α [°]	90	90	90
β [°]	96.416(3)	96.195(1)	94.110(2)
γ [°]	90	90	90
V [Å]^3	5918.1(7)	2972.16(9)	4075.2(4)
Z	8	4	4
μ(Mo Kα) [mm^{-1}]	0.887	5.050	3.649
Diffrns collected	108792	20069	67396
Independent diffrns	13609	6828	9374
Observed[a] diffrns	11895	5928	8089
R_{int}[b] [%]	3.27	2.39	4.12
No. of parameters	670	340	441
R[b] obsd diffrns [%]	2.24	2.03	2.33
R, *wR*[b] all data [%]	2.96, 5.18	2.65, 4.37	3.19, 5.36
Δρ [e Å^{-3}]	0.81, –0.64	0.84, –0.58	1.52, –0.68
CCDC deposition no.	2119581	2119582	2119583

Table S2 continued

Compound	**7**·0.4CH_2Cl_2	**8**	**9**·$C_2H_4Cl_2$
Formula	$C_{25.4}H_{30.8}Cl_{2.8}N_3PPt$	$C_{28}H_{35}ClN_3PPd$	$C_{52}H_{64}B_2Cl_2F_8N_6P_2Pd$
M	703.45	586.41	1185.95
T [K]	120(2)	120(2)	120(2)
Crystal system	tetragonal	monoclinic	monoclinic
Space group	*P*4/*n* (no. 85)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a [Å]	25.143(1)	8.6425(6)	12.9302(5)
b [Å]	25.143(1)	13.5124(7)	18.6083(8)
c [Å]	8.4349(4)	24.174(2)	22.976(1)
α [°]	90	90	90
β [°]	90	97.545(2)	92.540(2)
γ [°]	90	90	90
V [Å]^3	5332.1(6)	2798.6(3)	5522.8(4)
Z	8	4	4
μ(Mo Kα) [mm^{-1}]	5.623	0.836	0.559
Diffrns collected	57467	50649	109514
Independent diffrns	6354	6418	12720
Observed[a] diffrns	6032	5819	11477
R_{int}[b] [%]	2.36	2.97	2.81
No. of parameters	293	324	675
R[b] obsd diffrns [%]	3.28	2.28	2.57
R, *wR*[b] all data [%]	3.47, 7.25	2.73, 5.19	3.07, 6.24
Δρ [e Å^{-3}]	1.77, –1.34	0.53, –0.42	0.54, –0.67
CCDC deposition no.	2119584	2119585	2119586

Table S2 continued

Compound	**10**·MeCN	**11**·Me$_2$CO
Formula	$C_{27}H_{34}Cl_3N_4PPd$	$C_{53}H_{68}Cl_4N_6OP_2Pd$
M	658.30	1115.27
T [K]	120(2)	130(2)
Crystal system	triclinic	monoclinic
Space group	*P*–1 (no. 2)	$P2_1/c$ (no. 14)
a [Å]	9.3439(4)	21.5183(8)
b [Å]	10.3772(4)	14.4903(5)
c [Å]	16.5278(7)	19.5743(8)
α [°]	91.699(1)	90
β [°]	97.475(1)	115.795(1)
γ [°]	110.848(1)	90
V $[Å]^3$	1479.9(1)	5495.2(4)
Z	2	4
μ(Mo Kα) [mm^{-1}]	0.975	0.633
Diffrns collected	73450	76236
Independent diffrns	6778	11437
Observed[a] diffrns	6694	9766
R_{int}[b] [%]	1.78	3.68
No. of parameters	333	614
R[b] obsd diffrns [%]	1.56	2.84
R, *wR*[b] all data [%]	1.58, 4.05	3.82, 6.52
Δρ [e $Å^{-3}$]	0.37, –0.41	0.47,–0.63
CCDC deposition no.	2119587	2119588

Copies of the NMR spectra

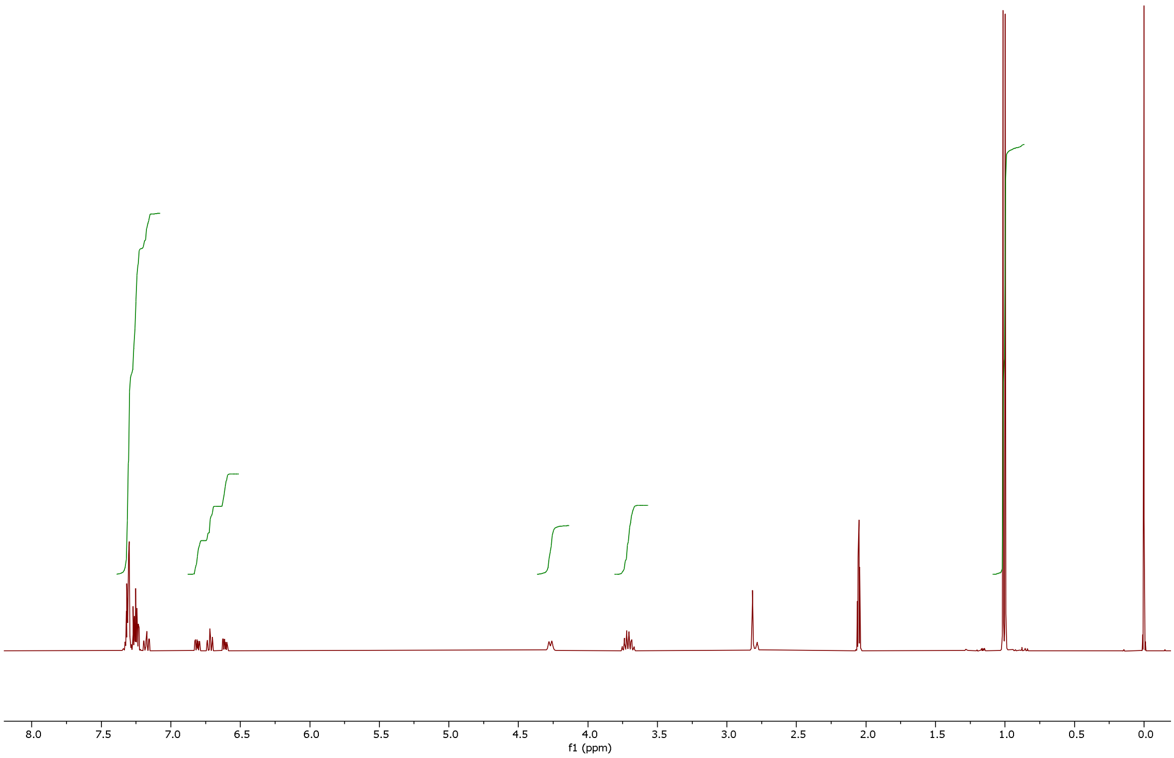

Figure S19. ^{1}H NMR spectrum (acetone-d_6, 400 MHz) of **1**

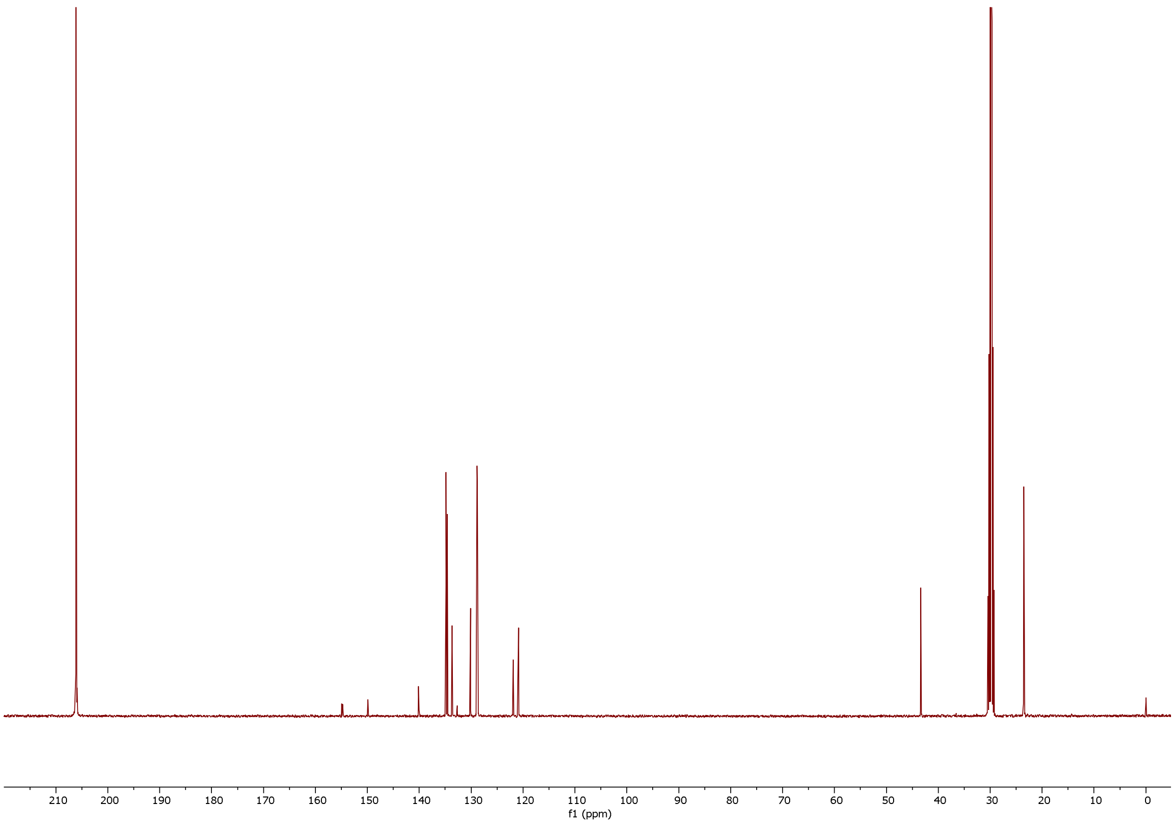

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (acetone-d_6, 101 MHz) of **1**

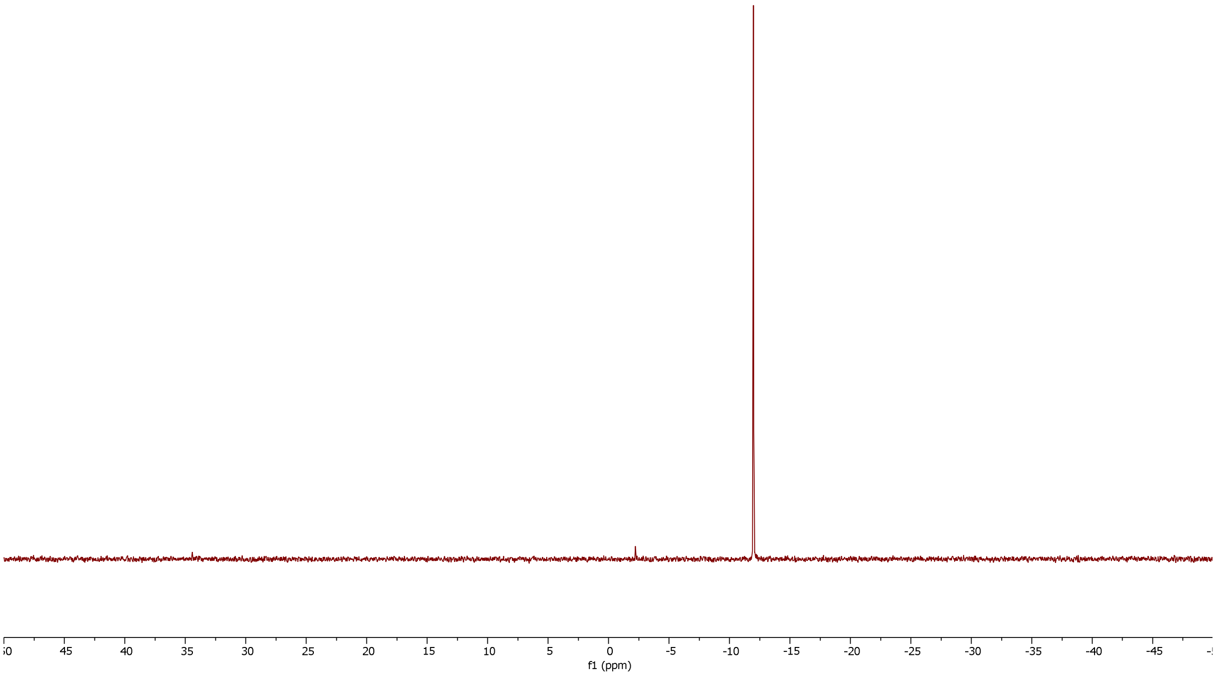

Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum (acetone-d_6, 162 MHz) of **1**

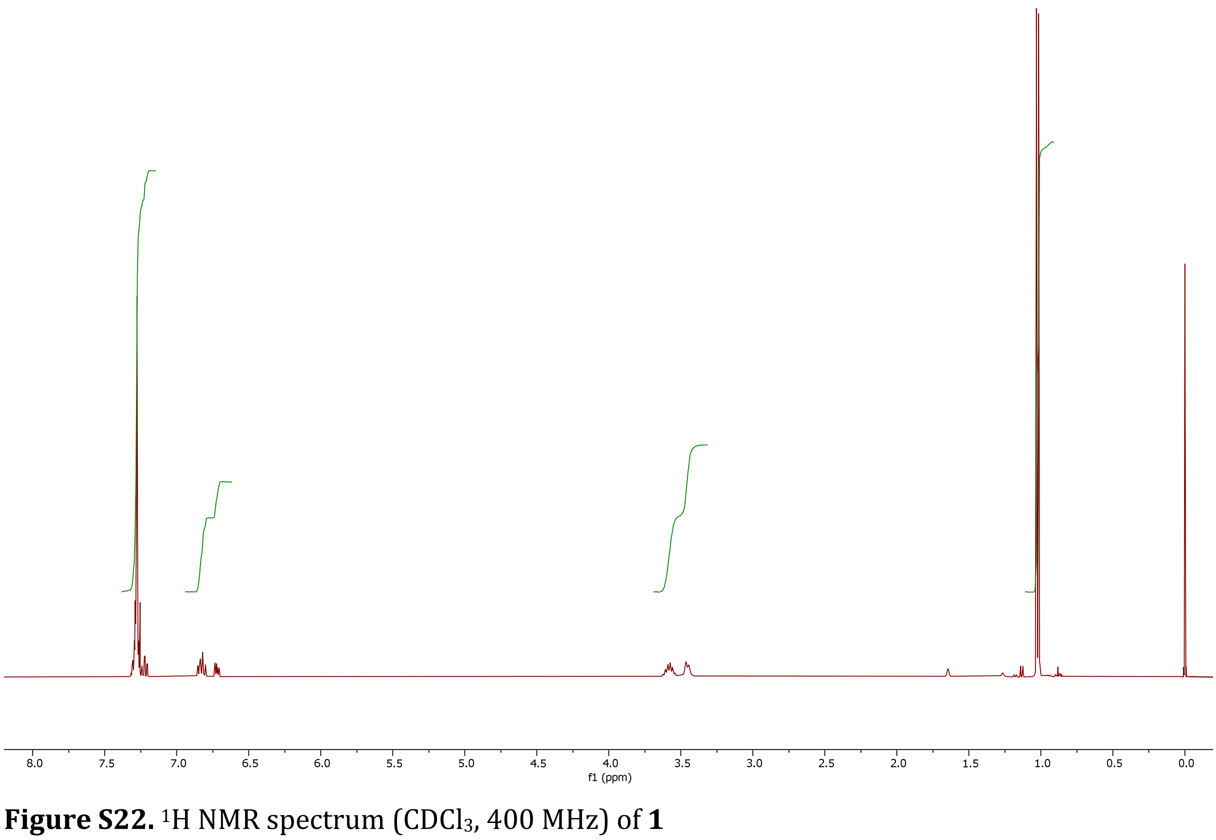

Figure S22. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1**

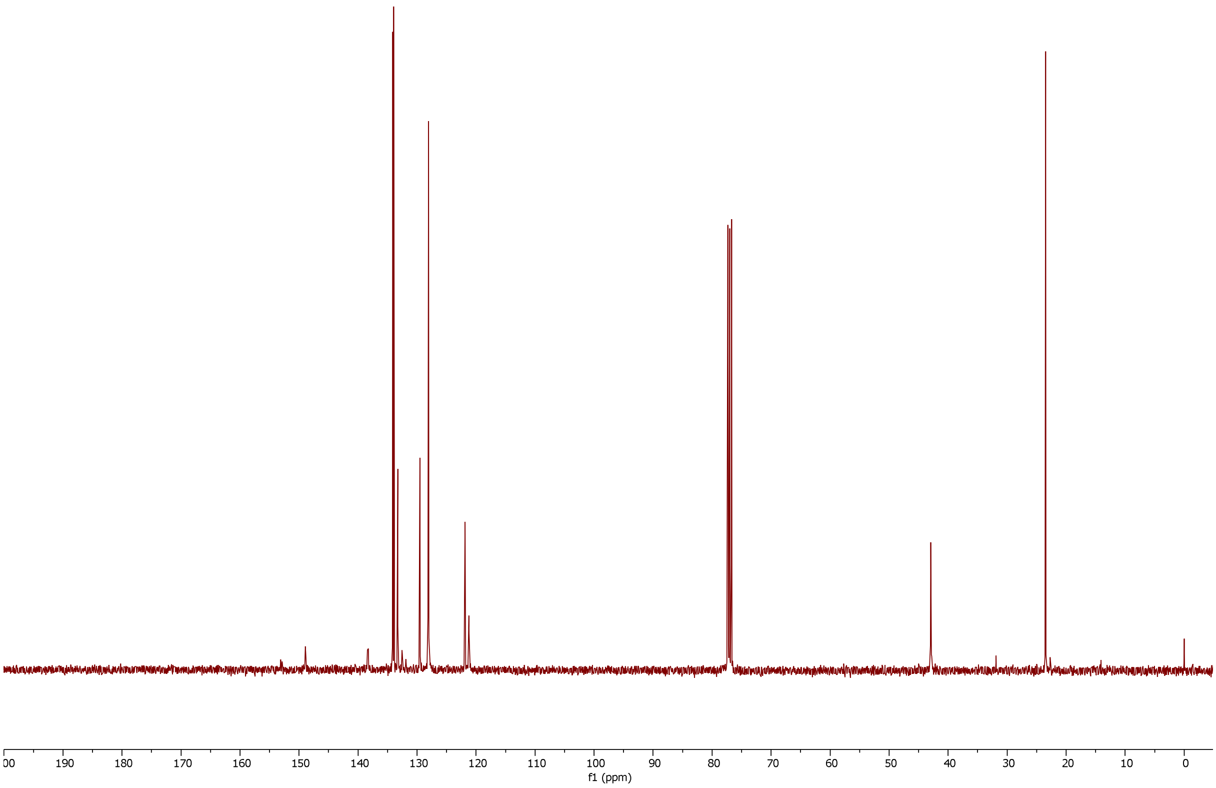

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **1**

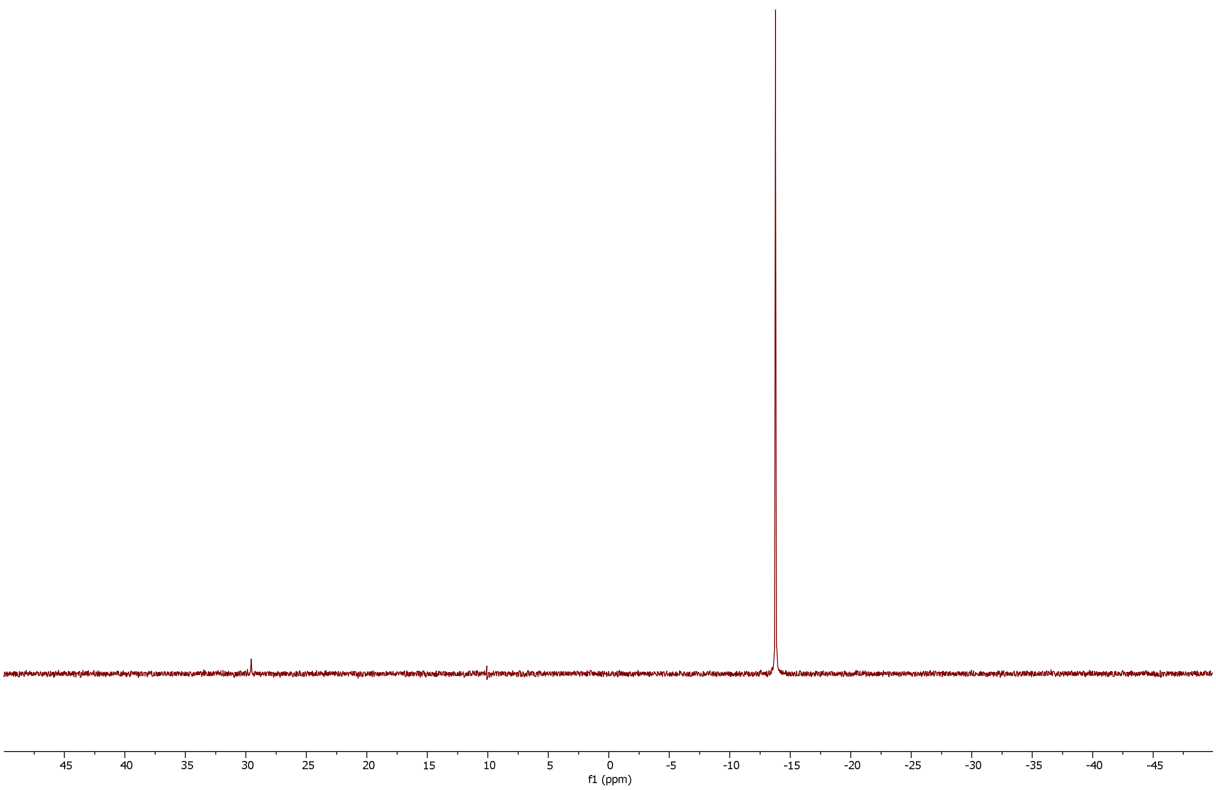

Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **1**

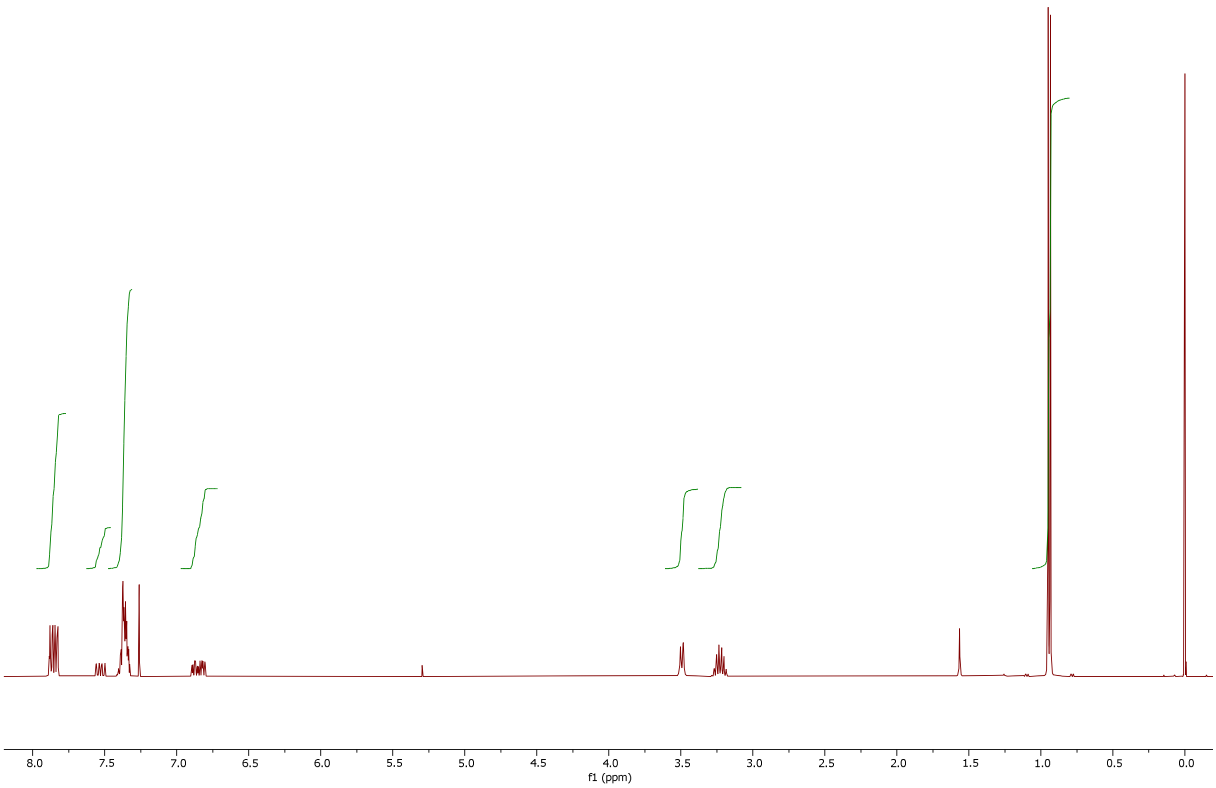

Figure S25. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3**

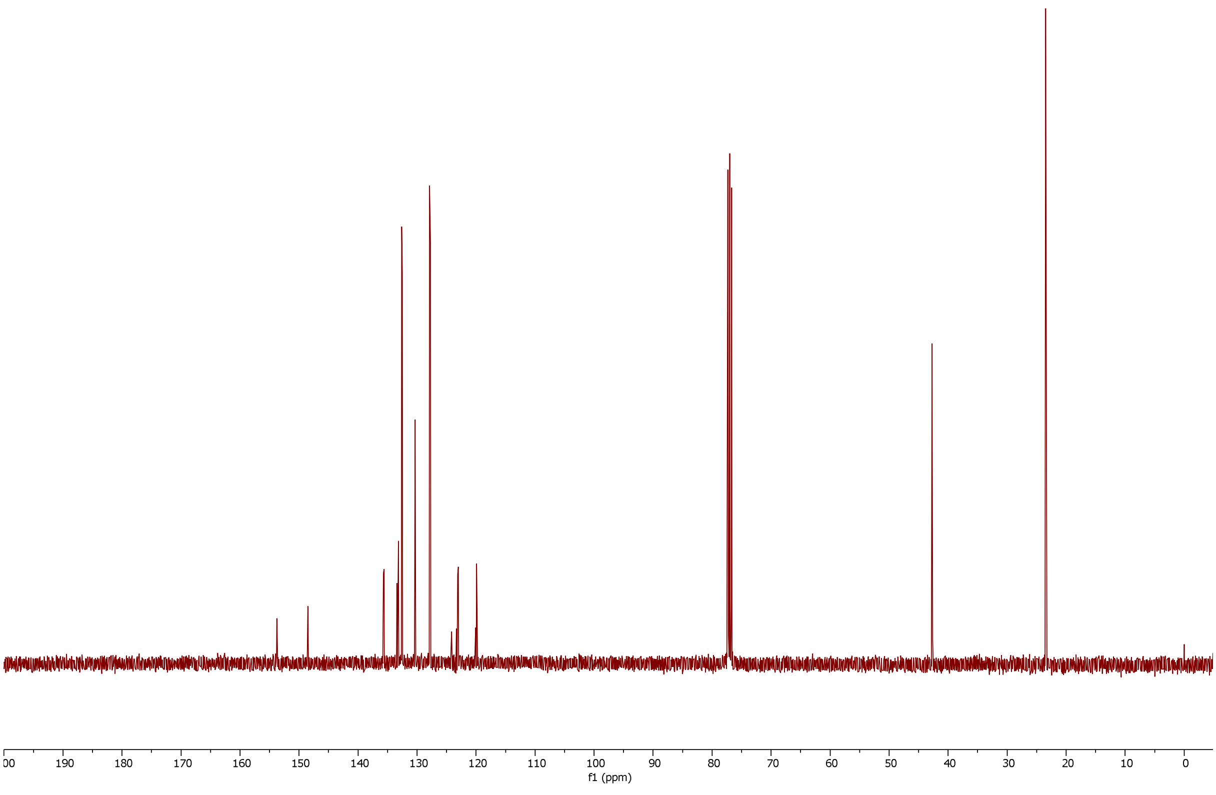

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **3**

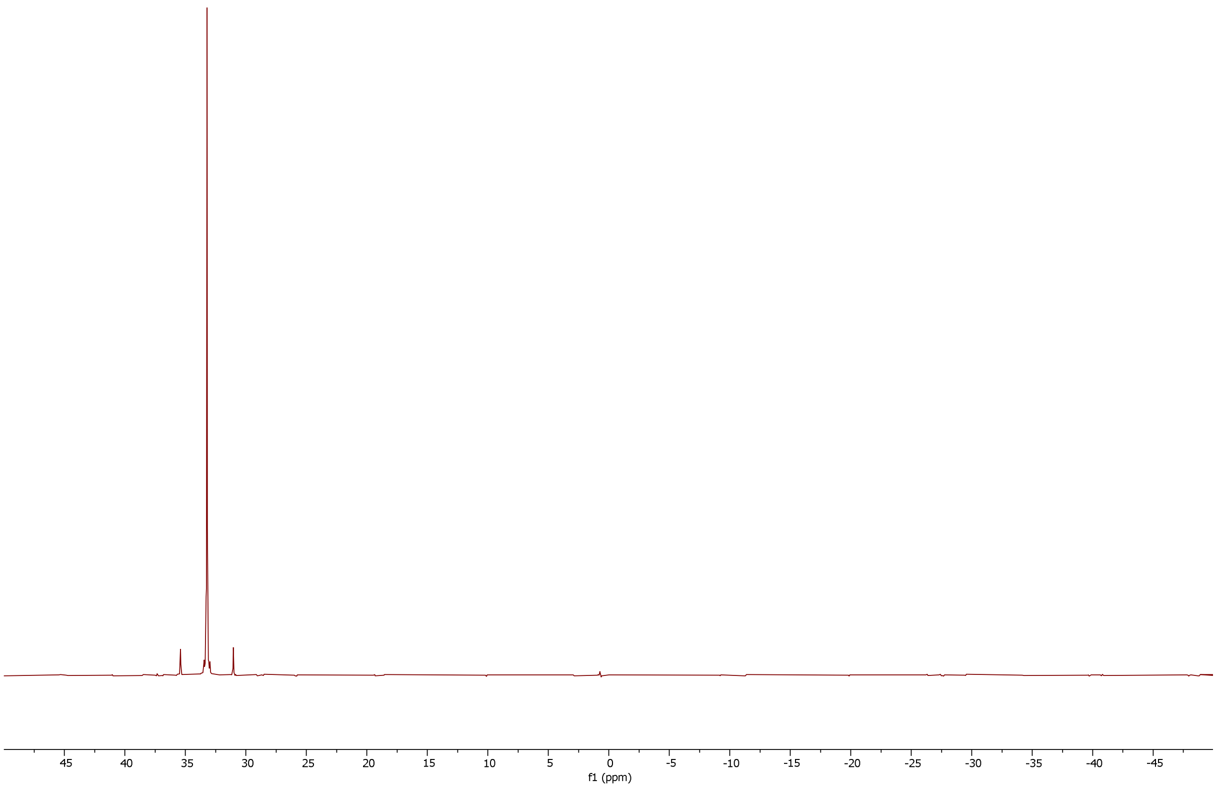

Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **3**

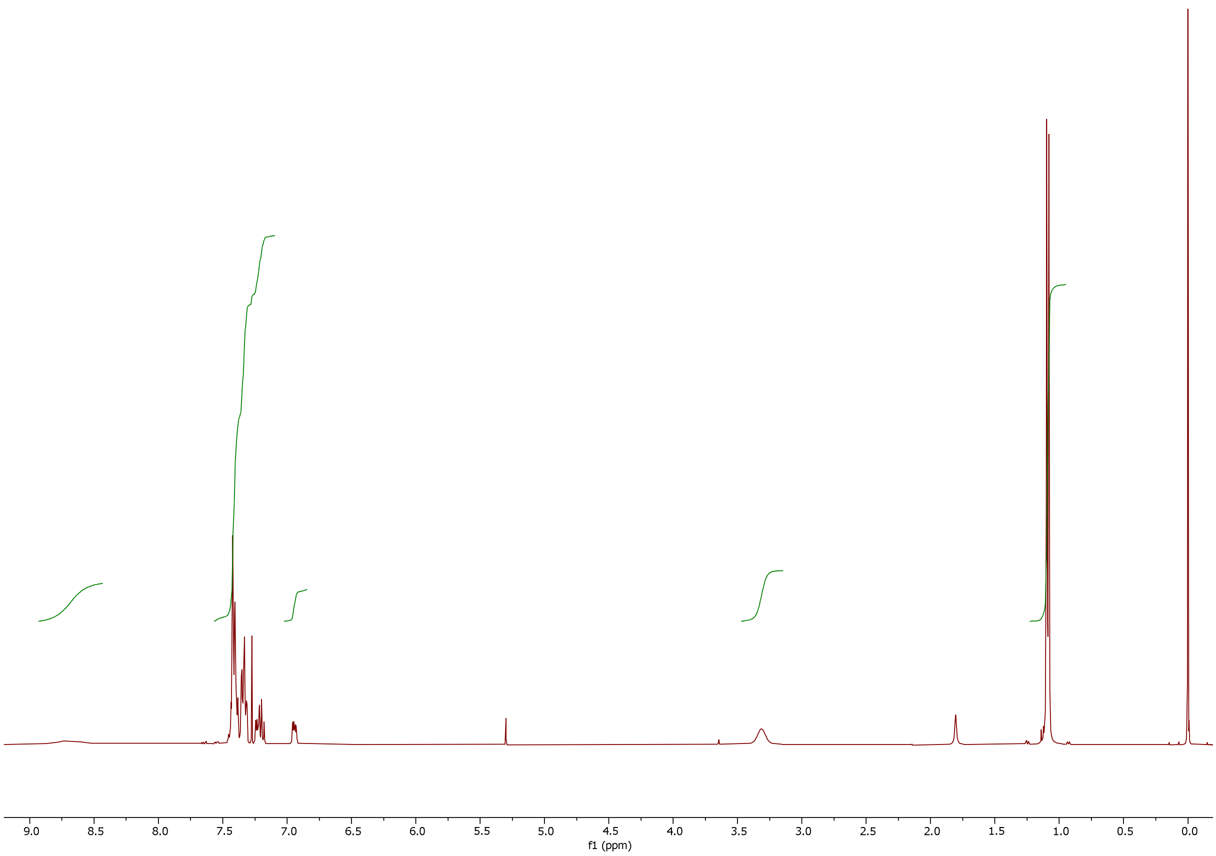

Figure S28. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (**1H**)Cl

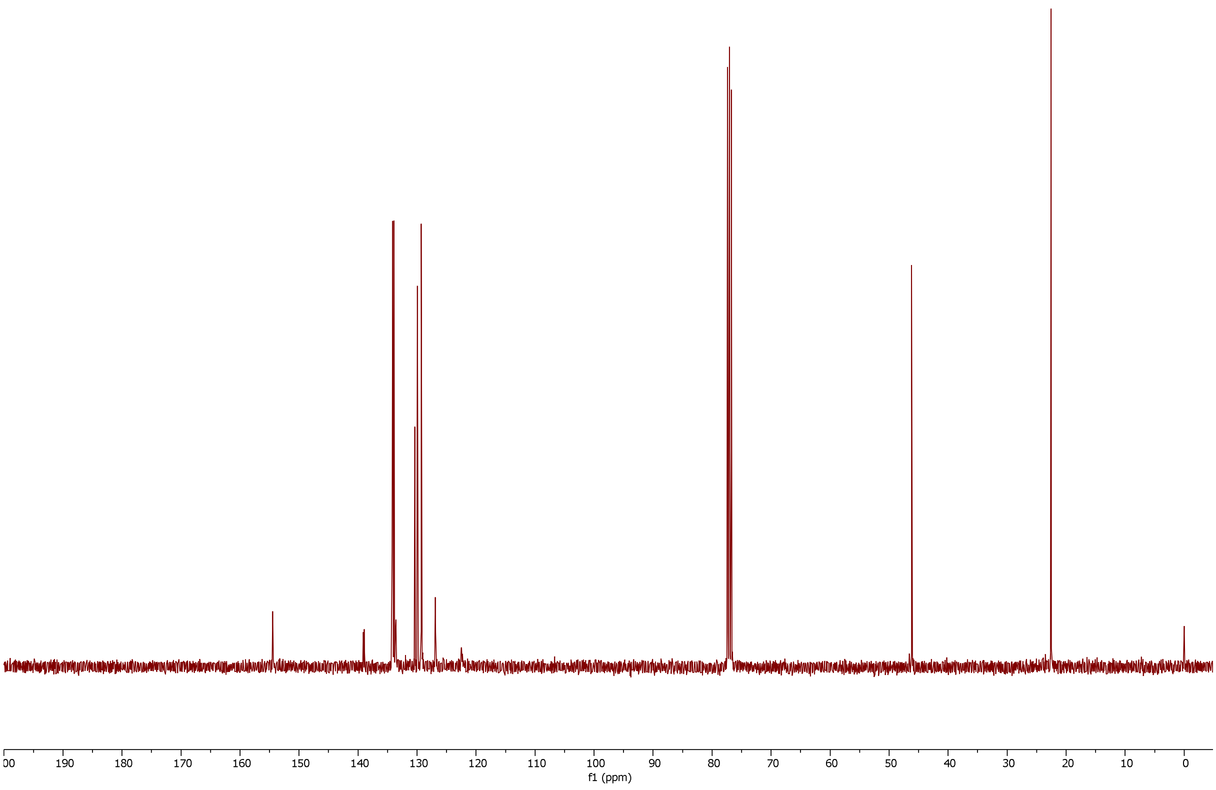

Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of (**1H**)Cl

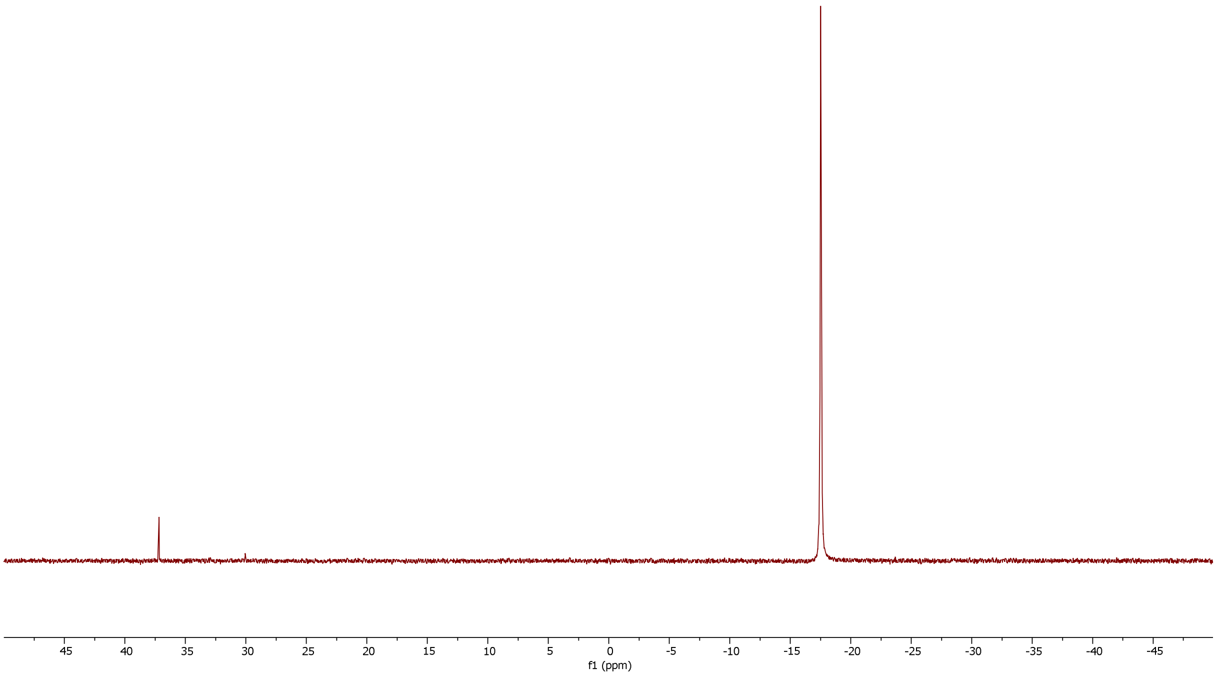

Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of (**1H**)Cl; the signal at δ_P 37.2 is due to traces of the corresponding phosphine oxide

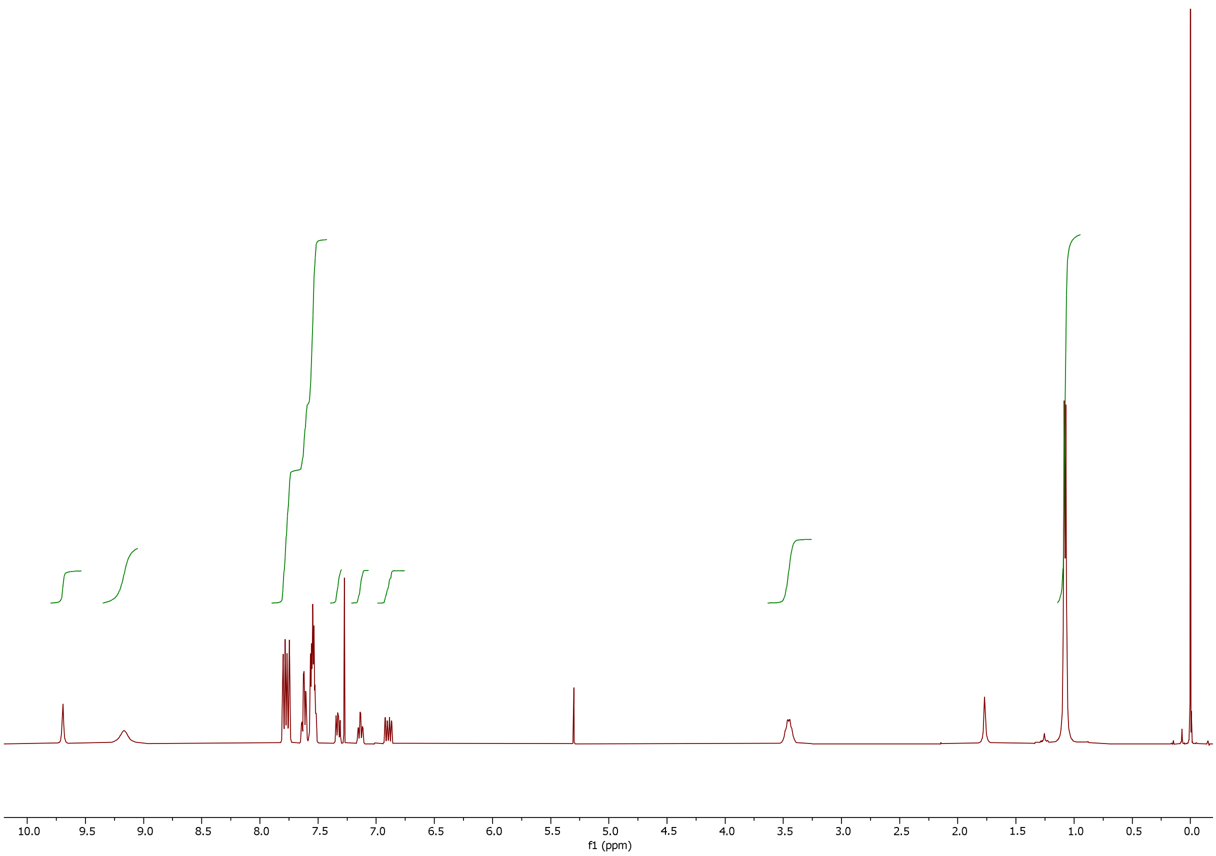

Figure S31. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (**3H**)Cl

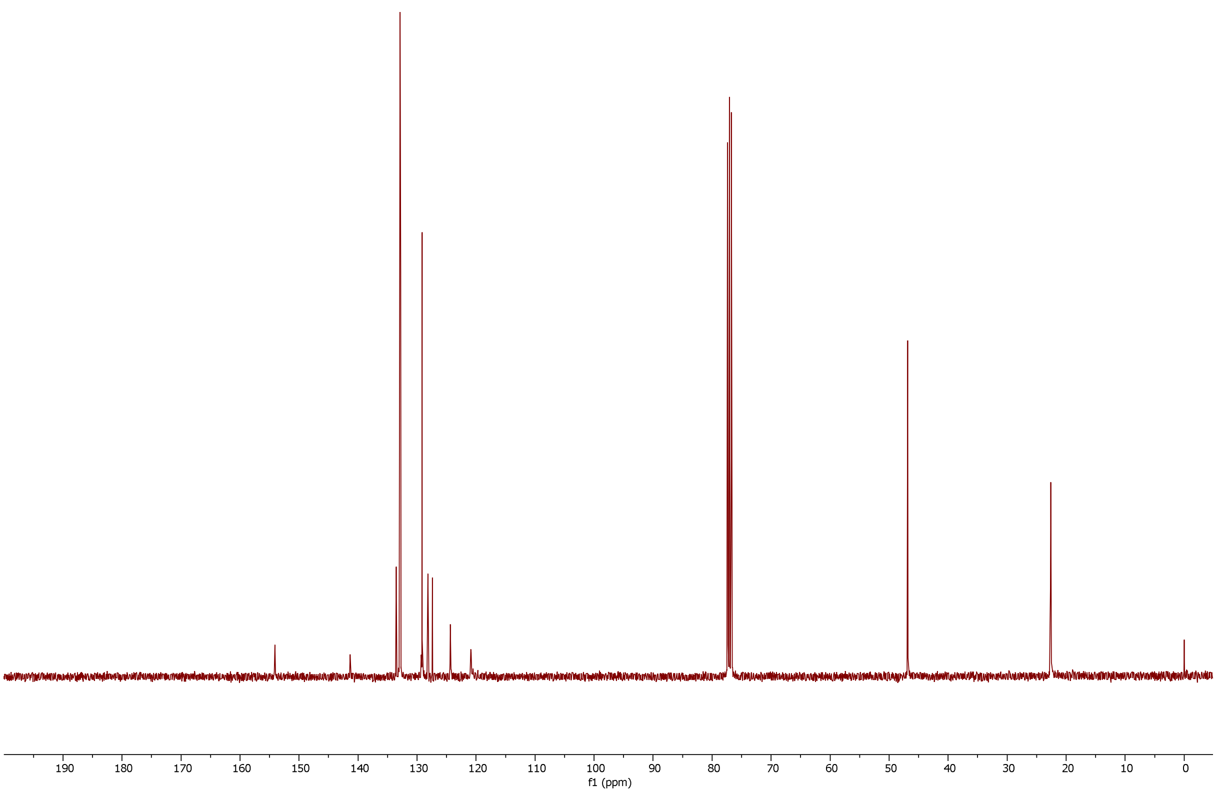

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of (**3H**)Cl

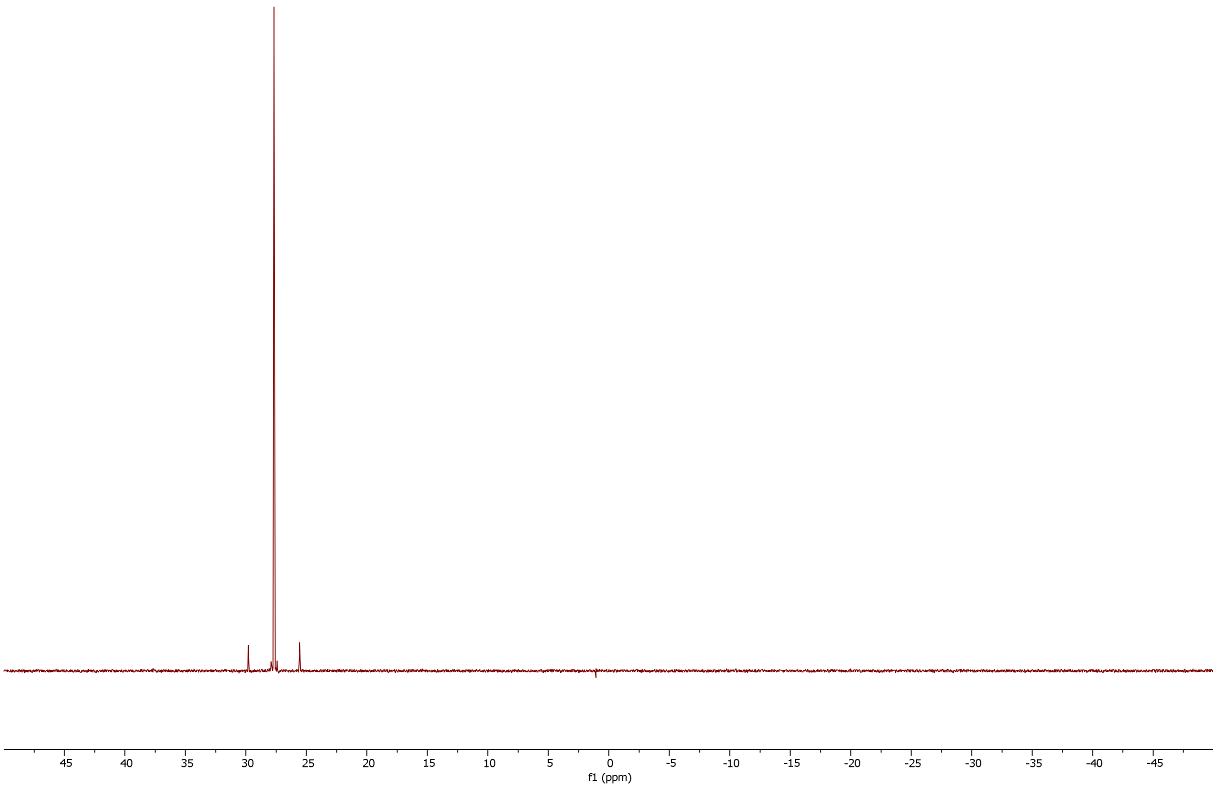

Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of (**3H**)Cl

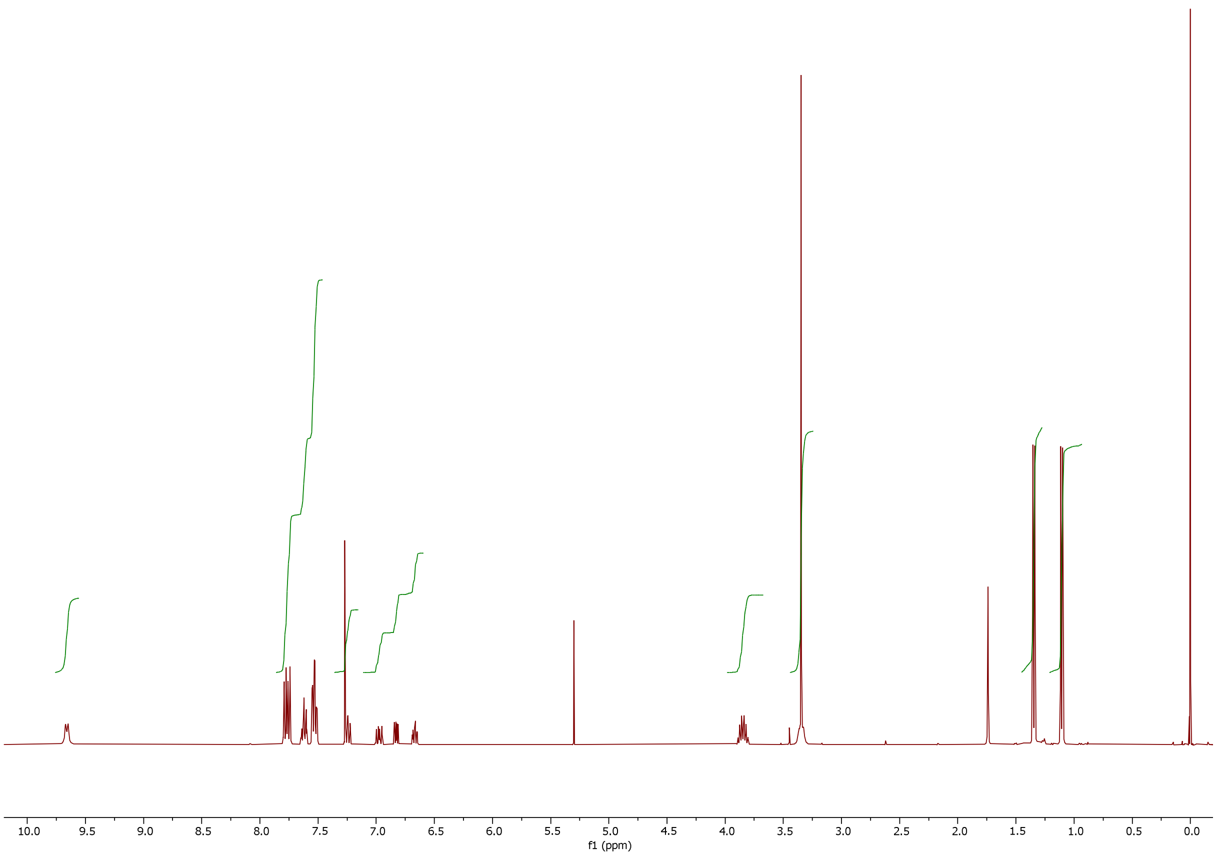

Figure S34. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5**

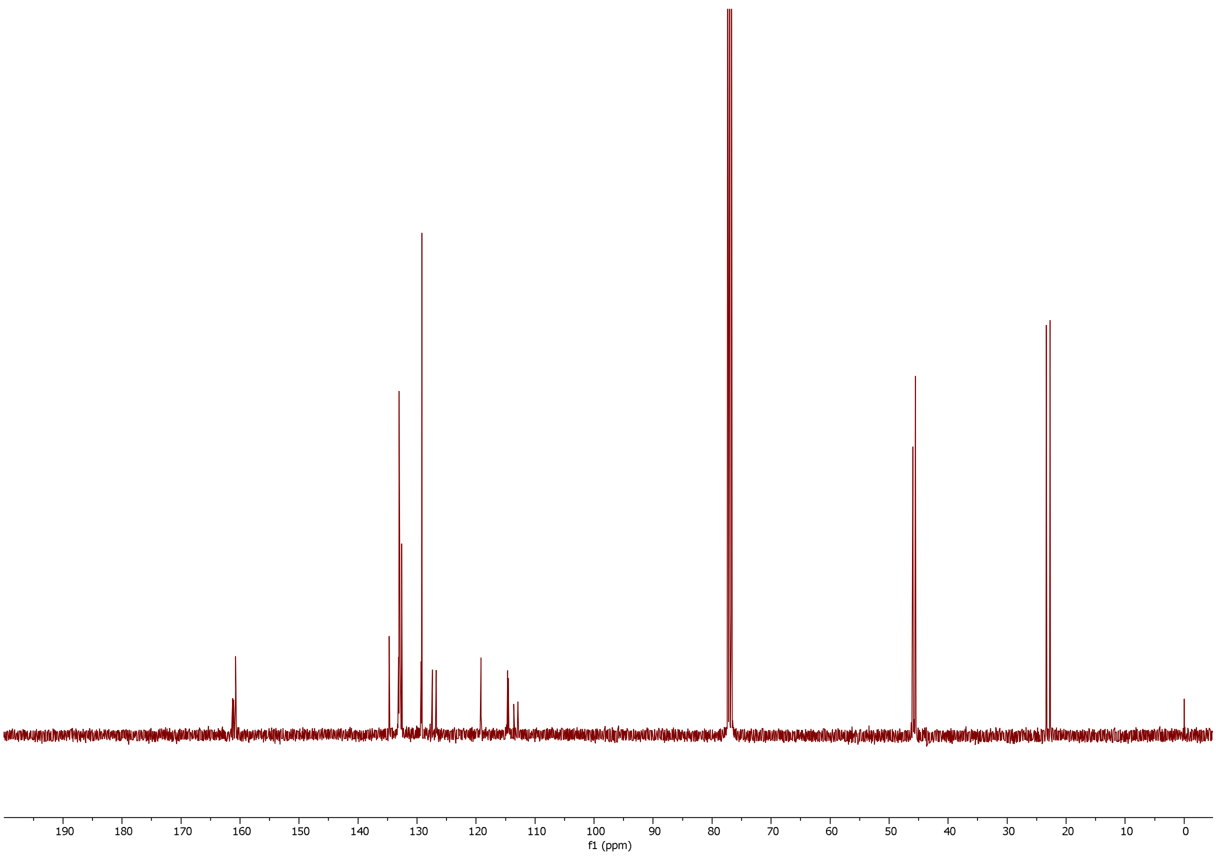

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **5**

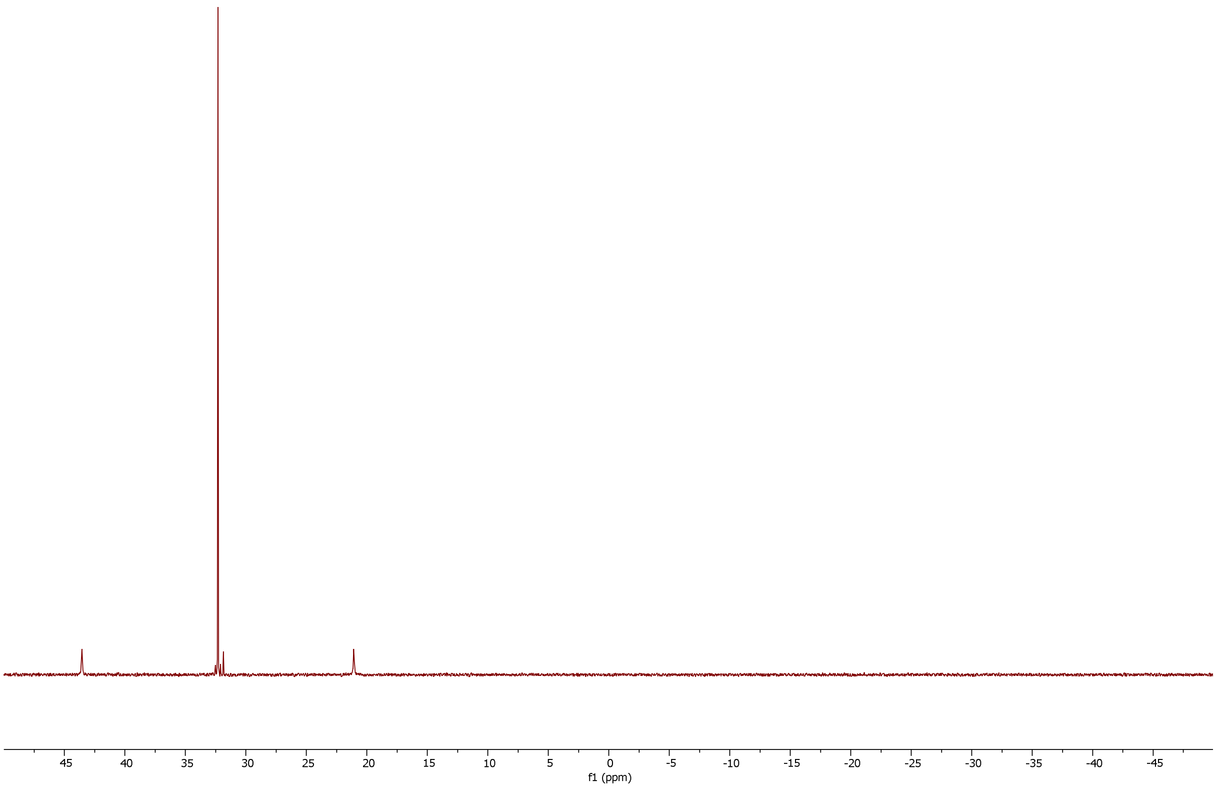

Figure S36. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **5**

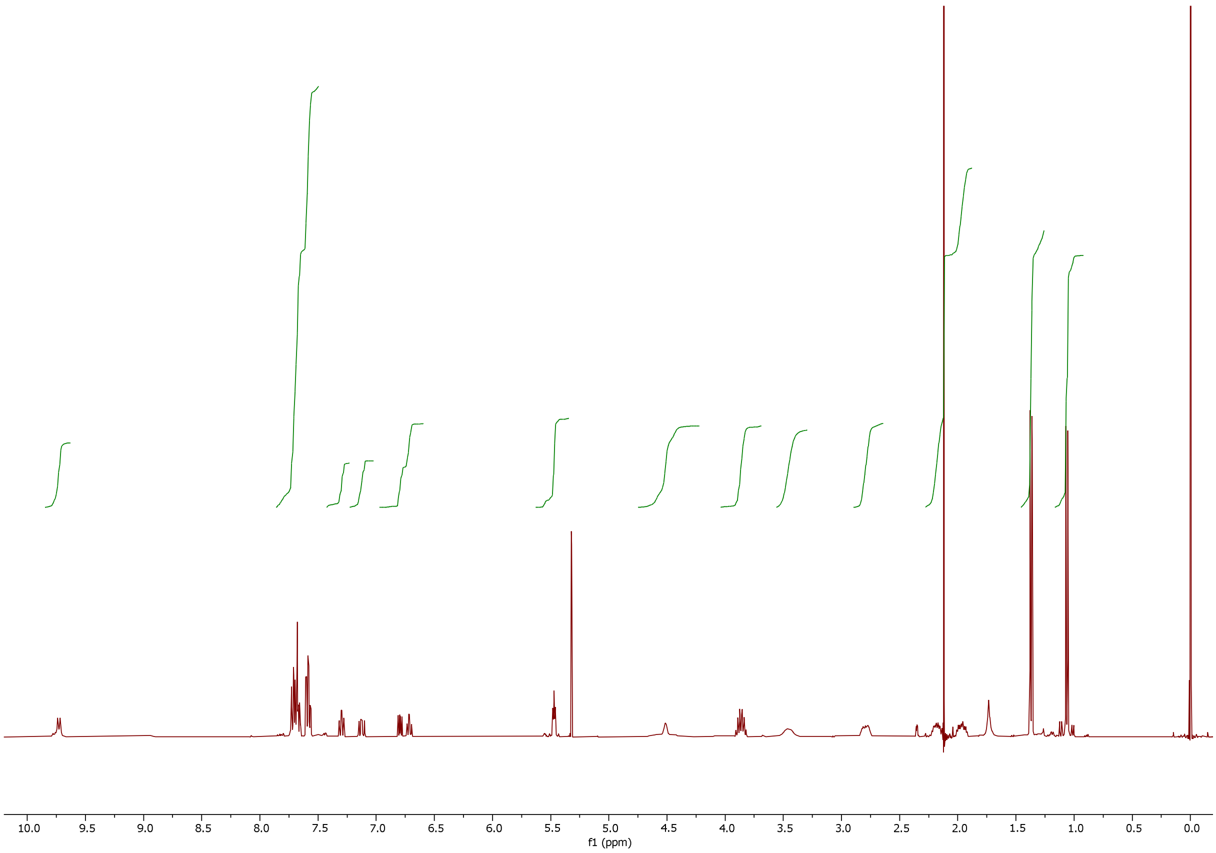

Figure S37. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **6**

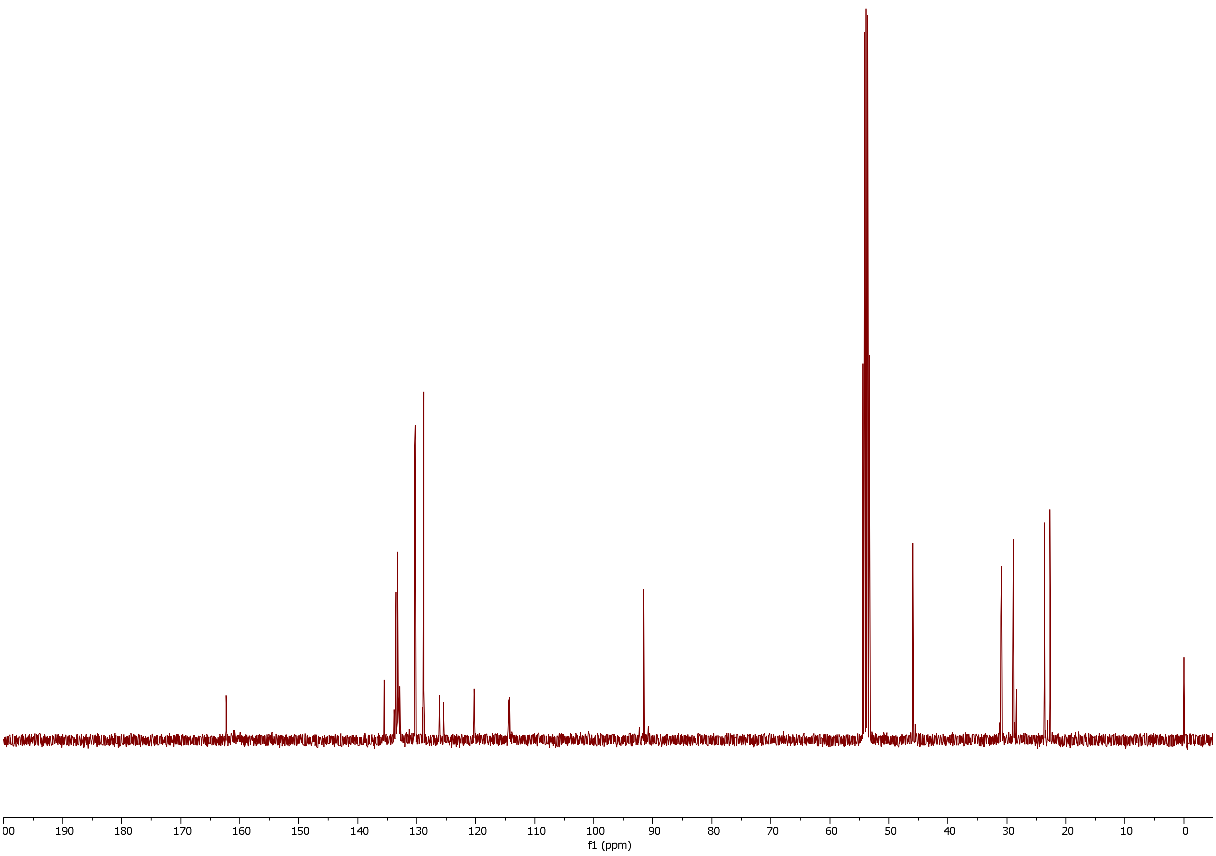

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 101 MHz) of **6**

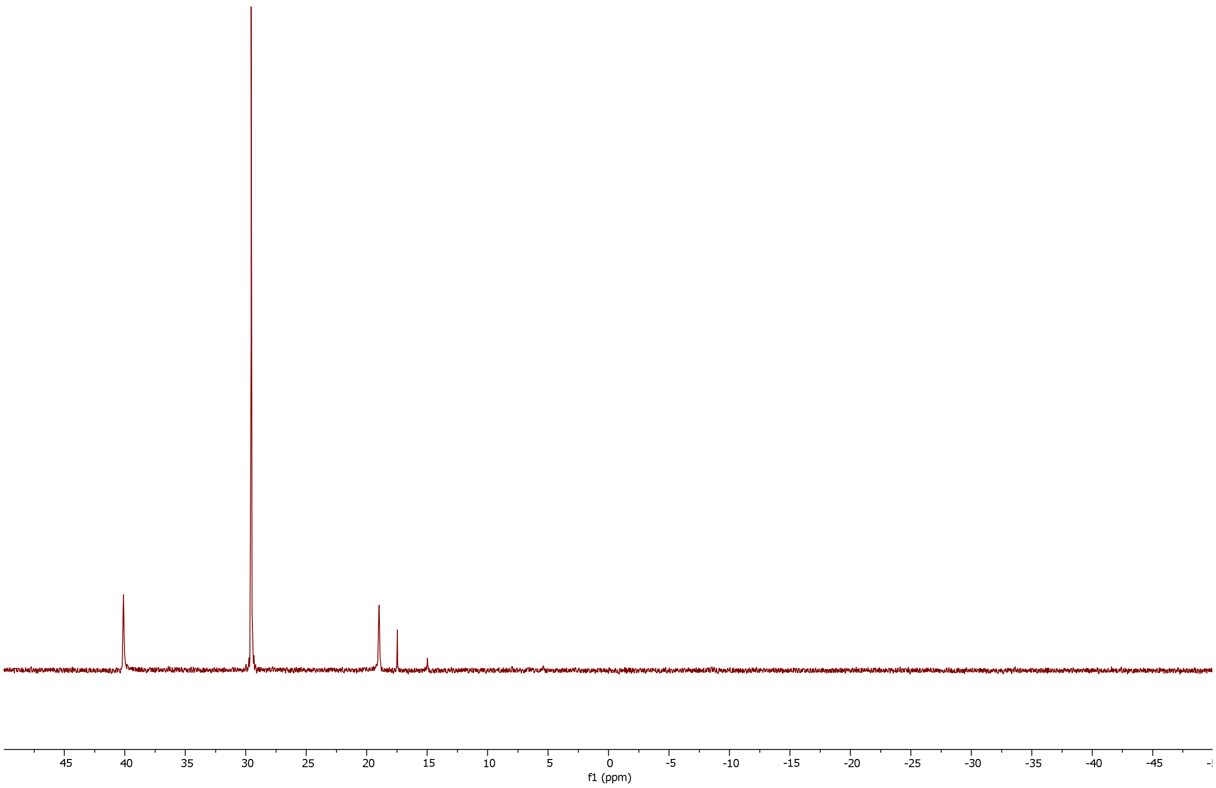

Figure S39. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 162 MHz) of **6**

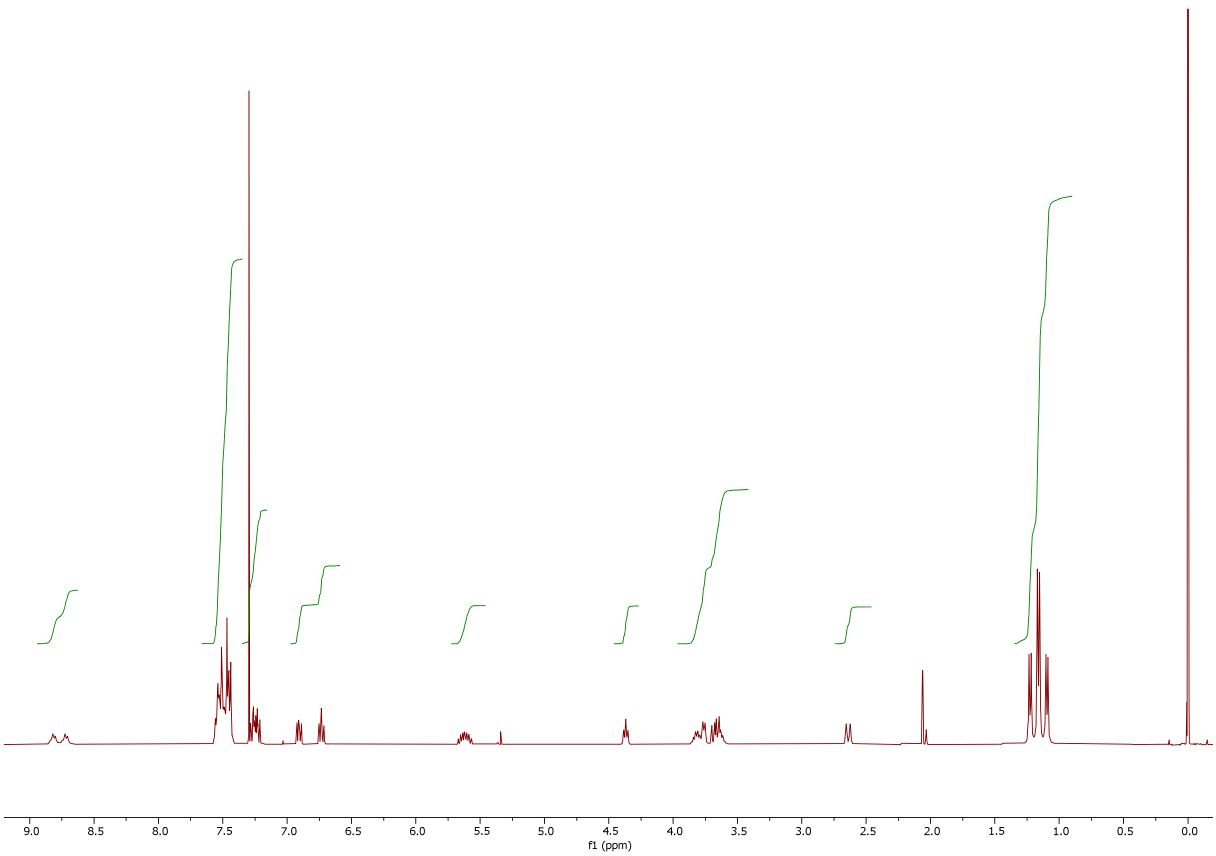

Figure S40. ^{1}H NMR spectrum (**–25°C**, $CDCl_3$, 400 MHz) of **8**

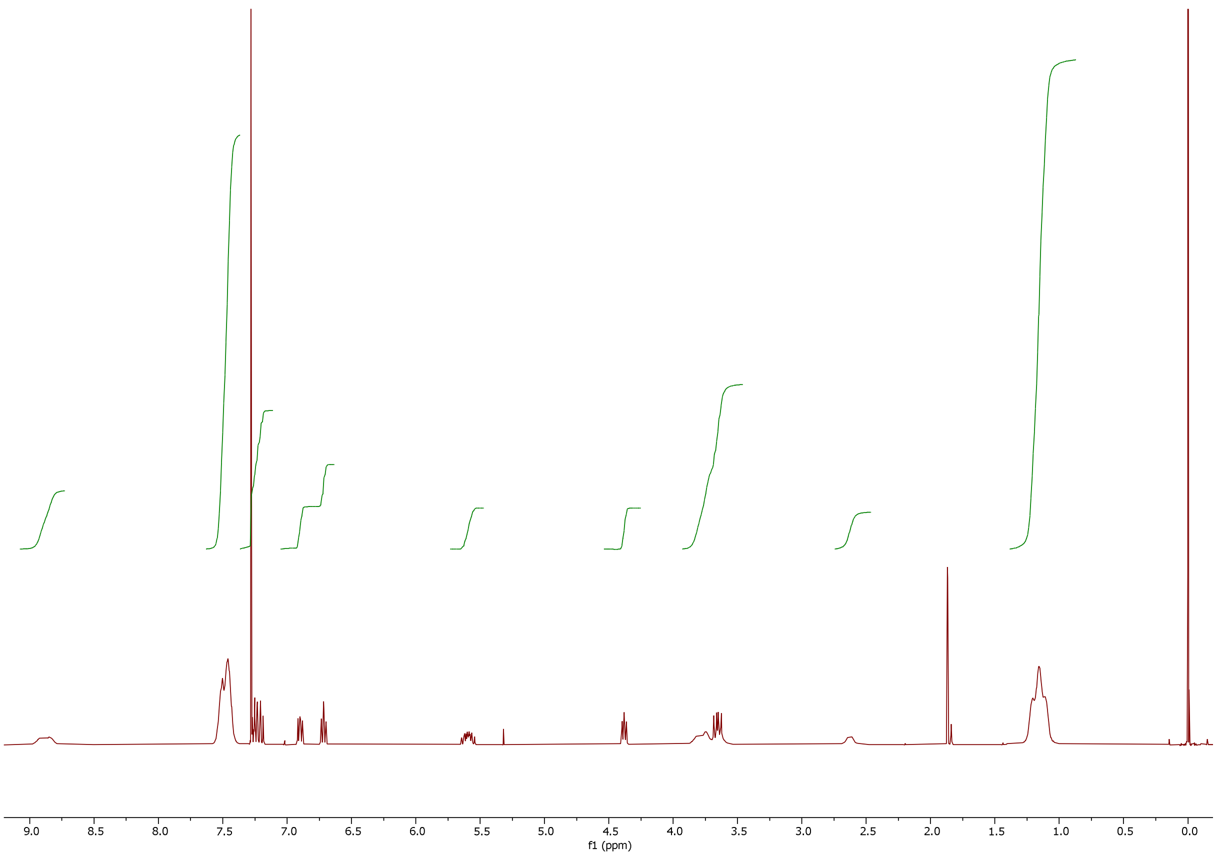

Figure S41. ^{1}H NMR spectrum (**0°C**, $CDCl_3$, 400 MHz) of **8**

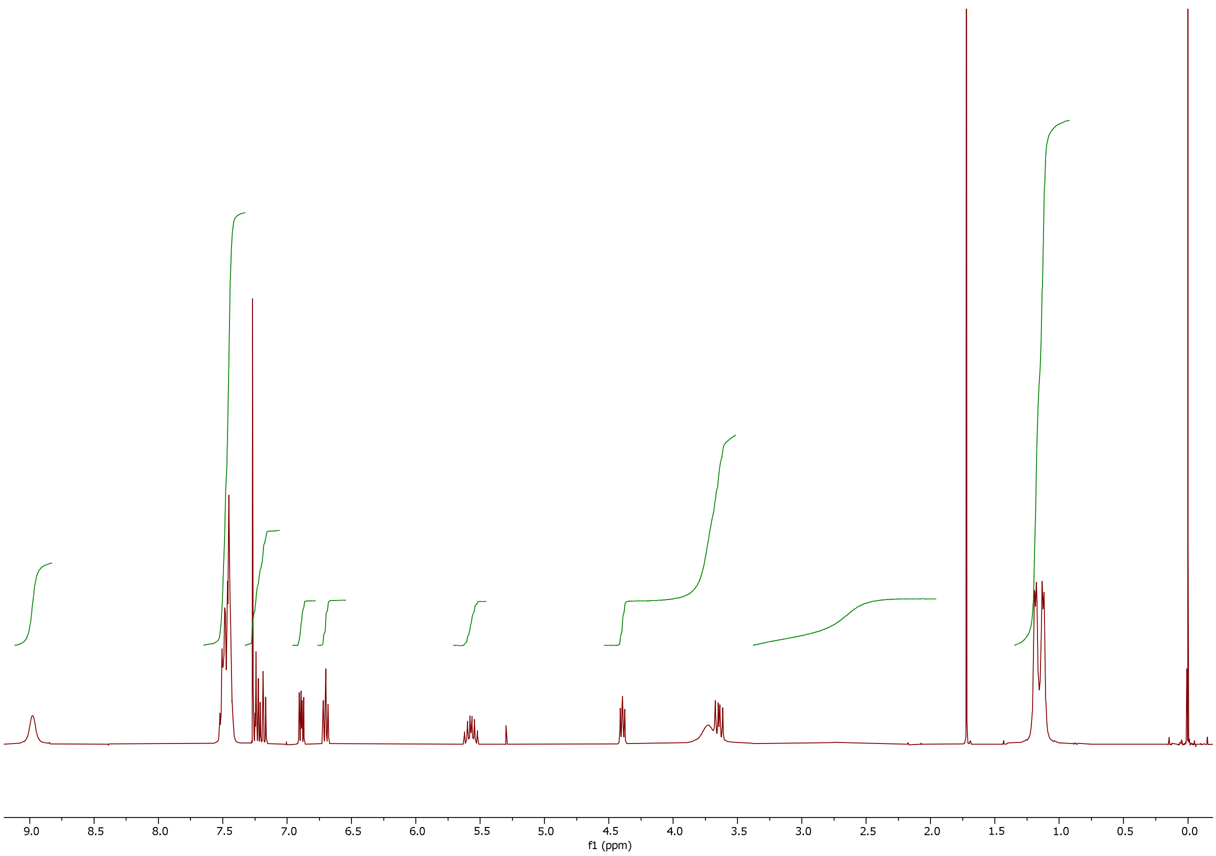

Figure S42. ^{1}H NMR spectrum (**25°C**, $CDCl_3$, 400 MHz) of **8**

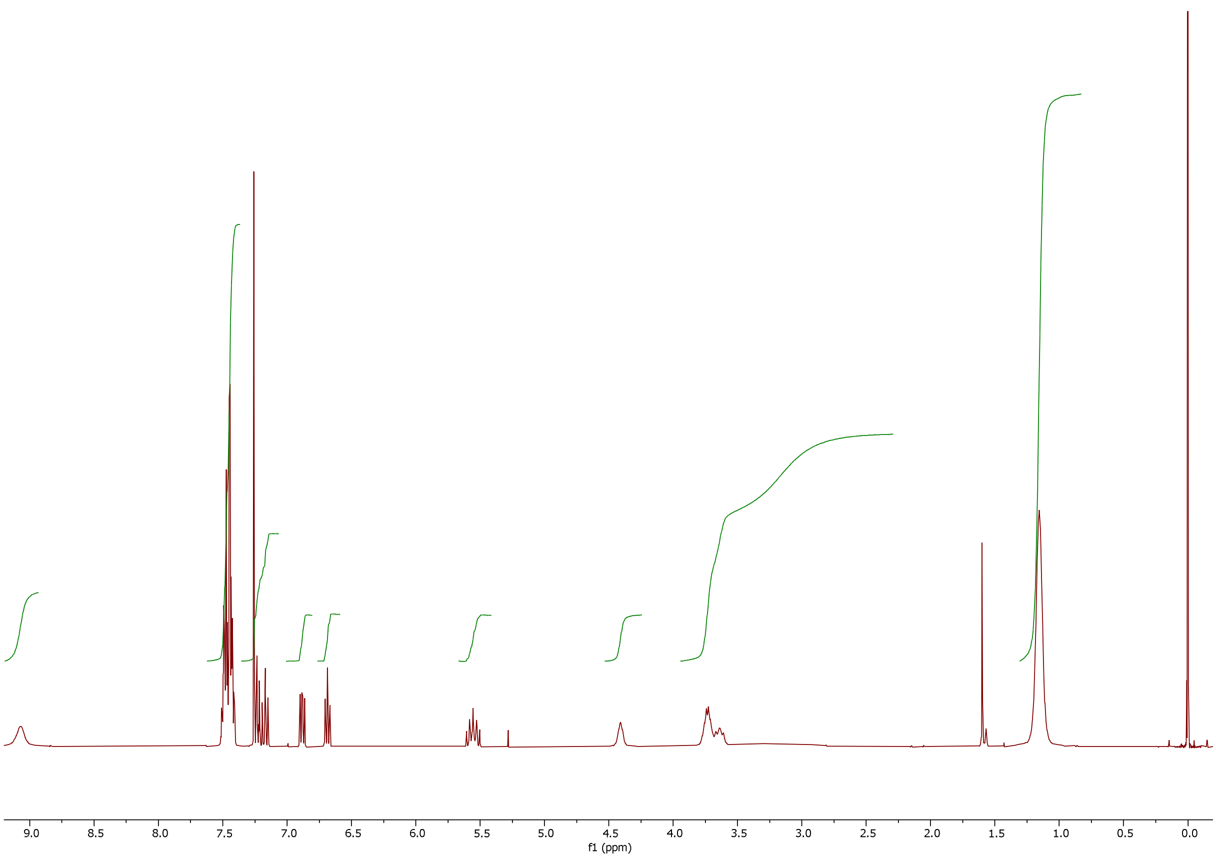

Figure S43. ^{1}H NMR spectrum (**50°C**, $CDCl_3$, 400 MHz) of **8**

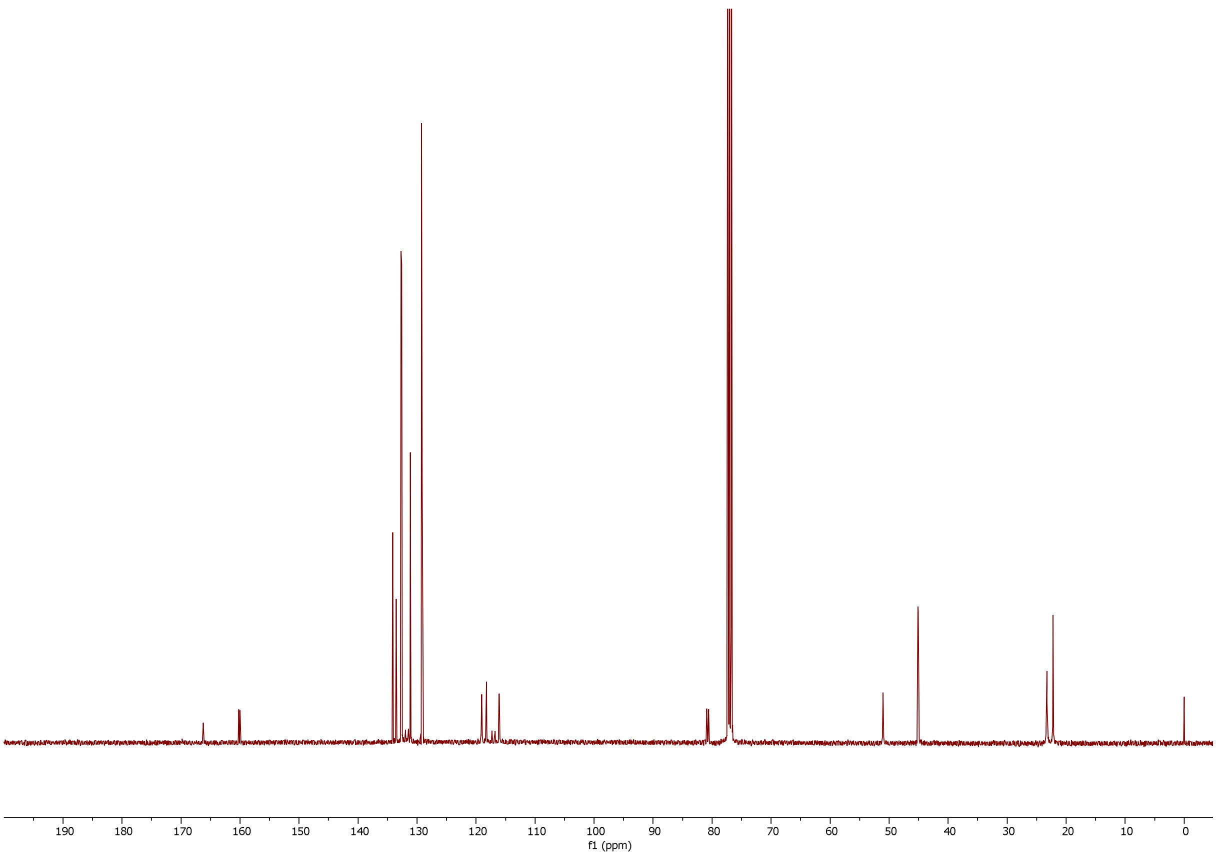

Figure S44. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **8**

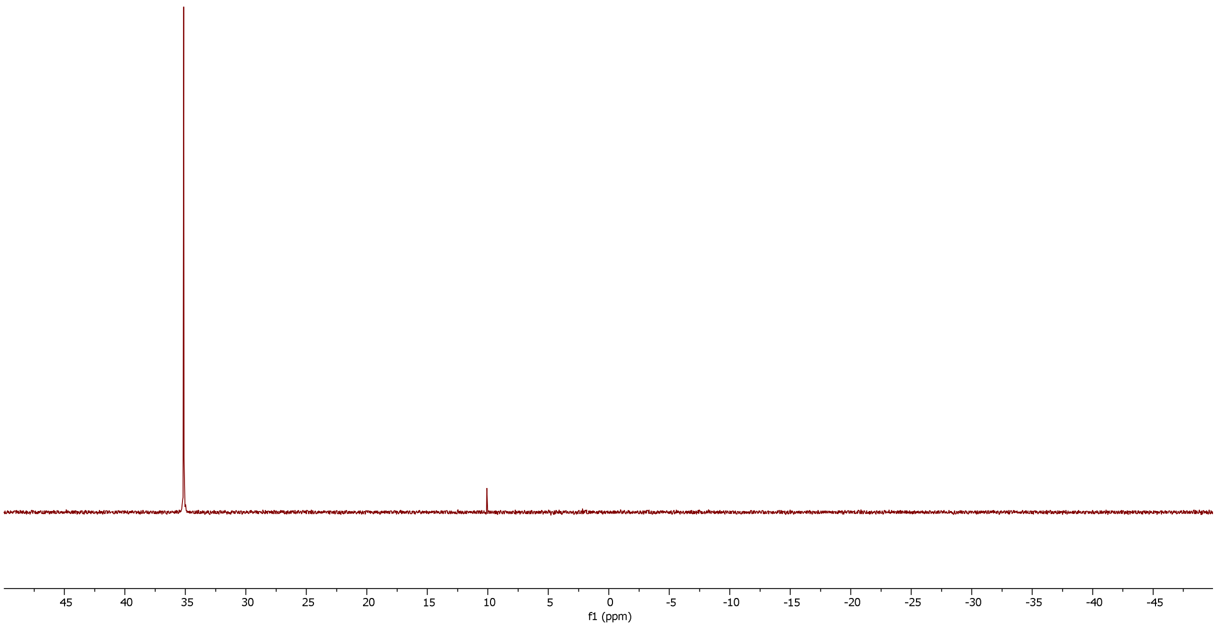

Figure S45. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **8**

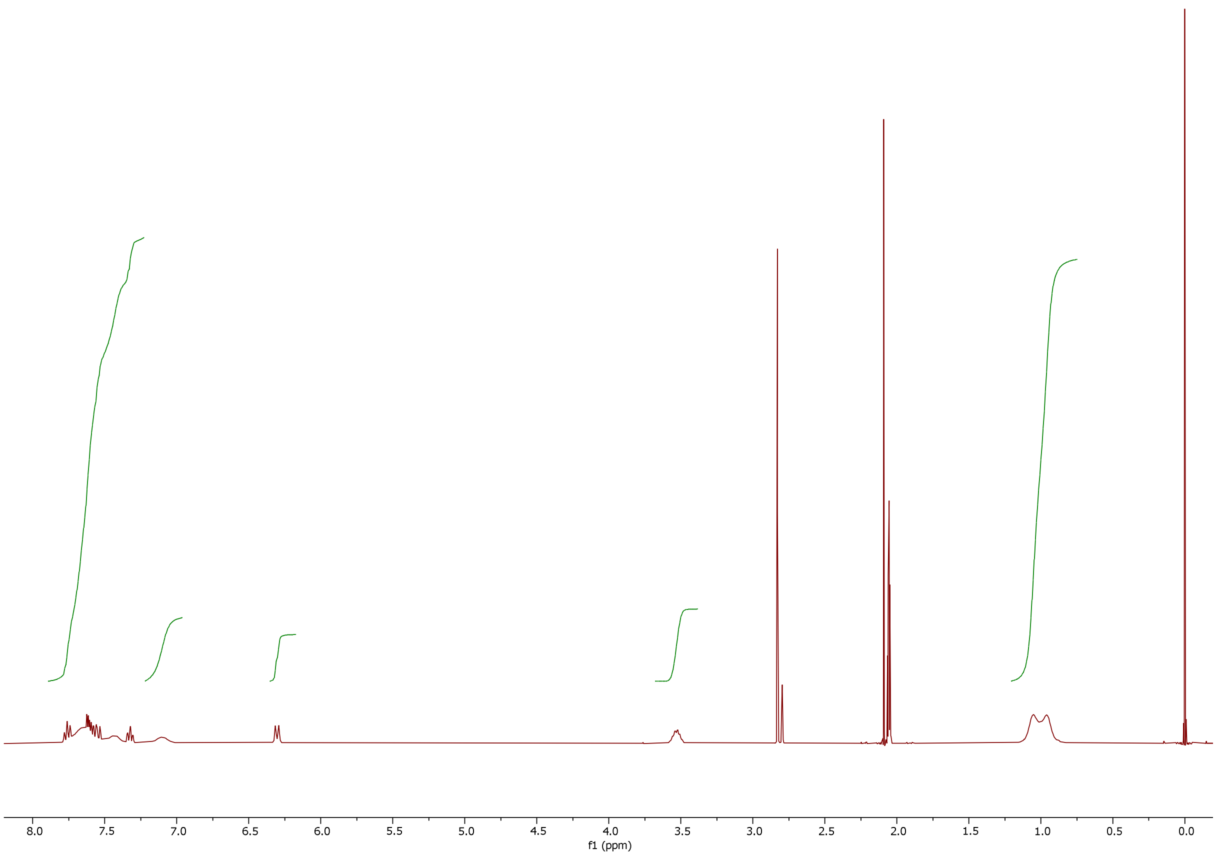

Figure S46. ^{1}H NMR spectrum (acetone-d_6, 400 MHz) of **9**

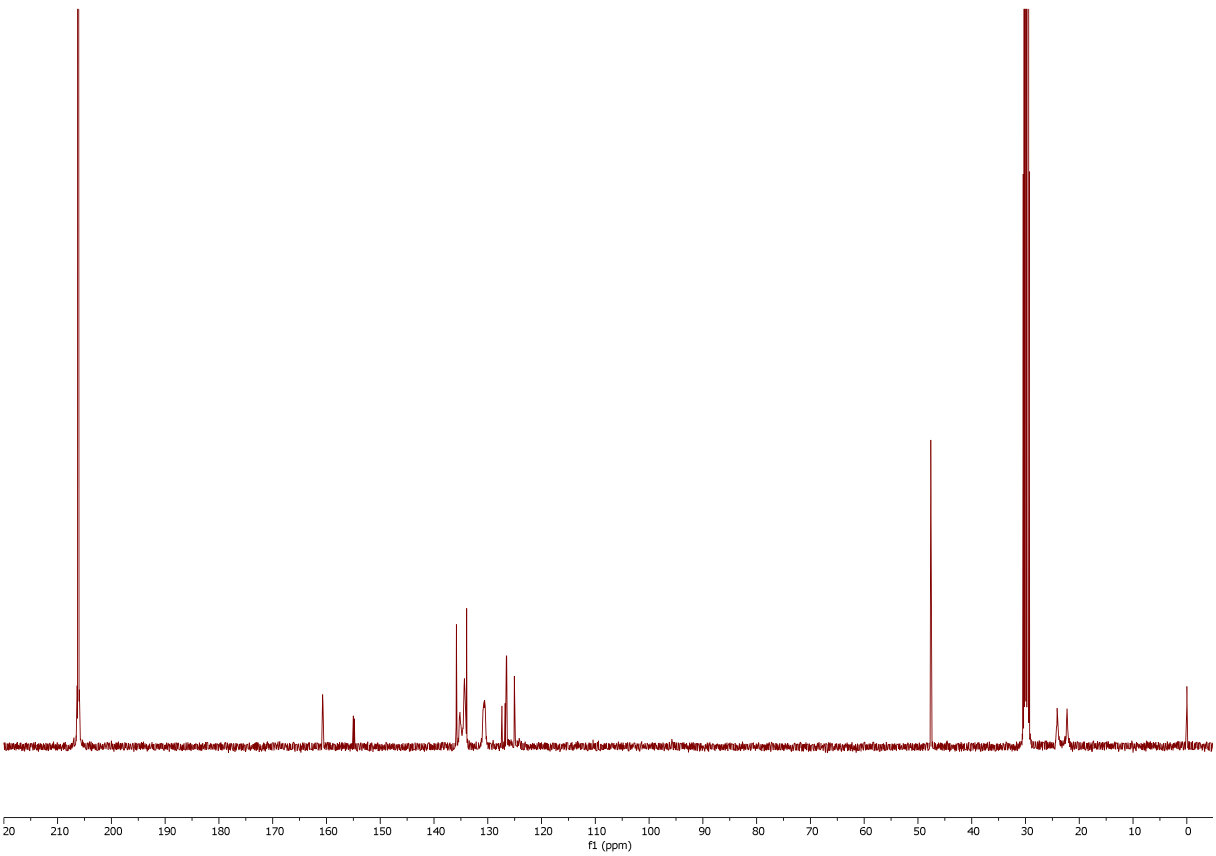

Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum (acetone-d_6 101 MHz) of **9**

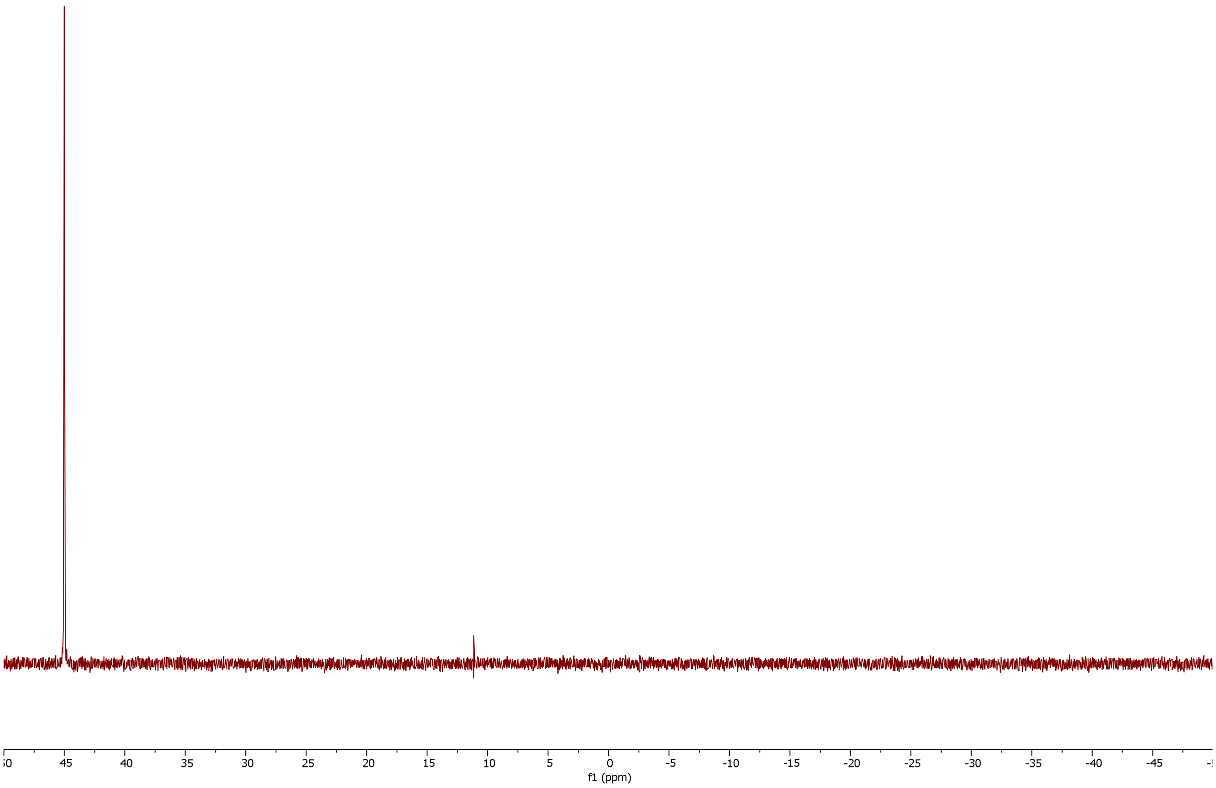

Figure S48. $^{31}P\{^{1}H\}$ NMR spectrum (acetone-d_6, 162 MHz) of **9**