Supporting Information

for

Synthesis and characterisation of Group 11 metal complexes with a guanidine-tagged triphenylphosphine and evaluation of the isolated Au(I) complexes in gold-mediated organic reactions

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Contents

X-ray crystallography

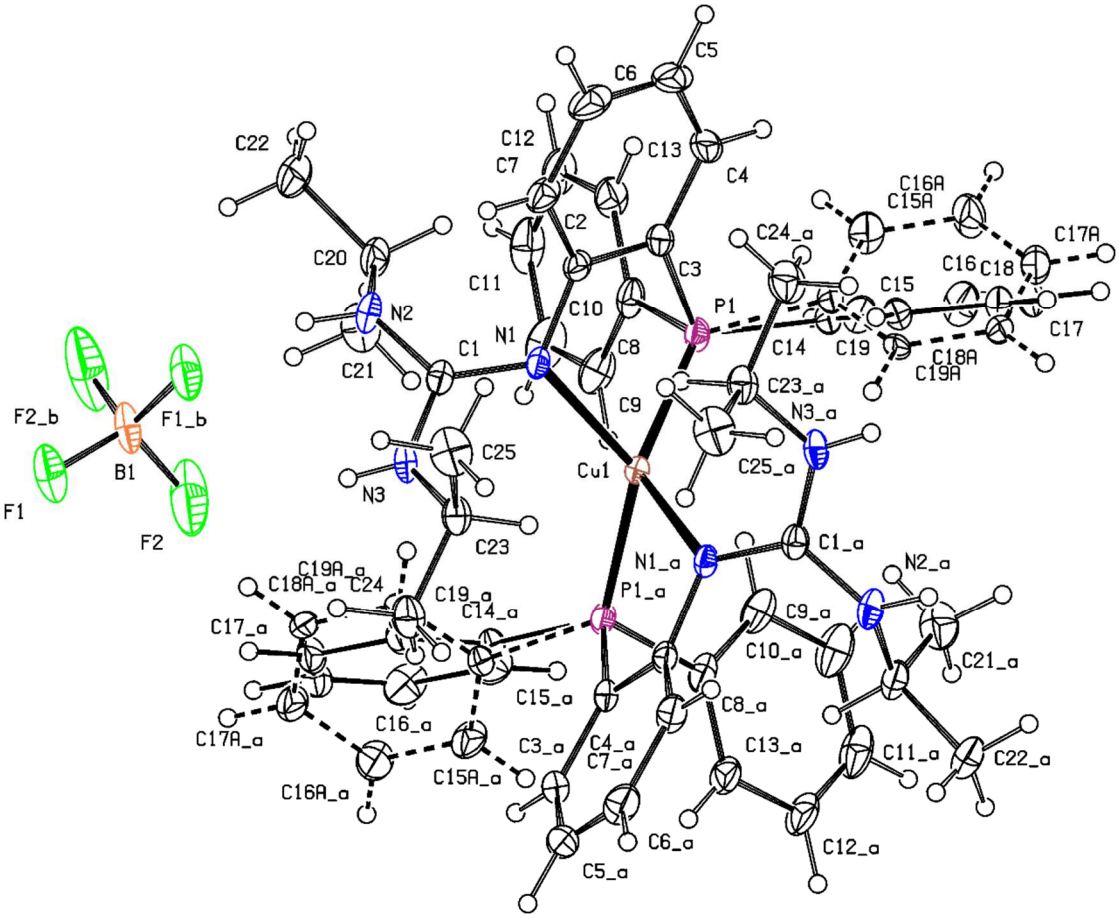

Figure S1 PLATON plot of the structure of **2a**·$C_2H_4Cl_2$ with displacement ellipsoids at the 30% probability level (symmetry operations: a = 1−x, y, 1−z; b = 2−x, y, 2−z)

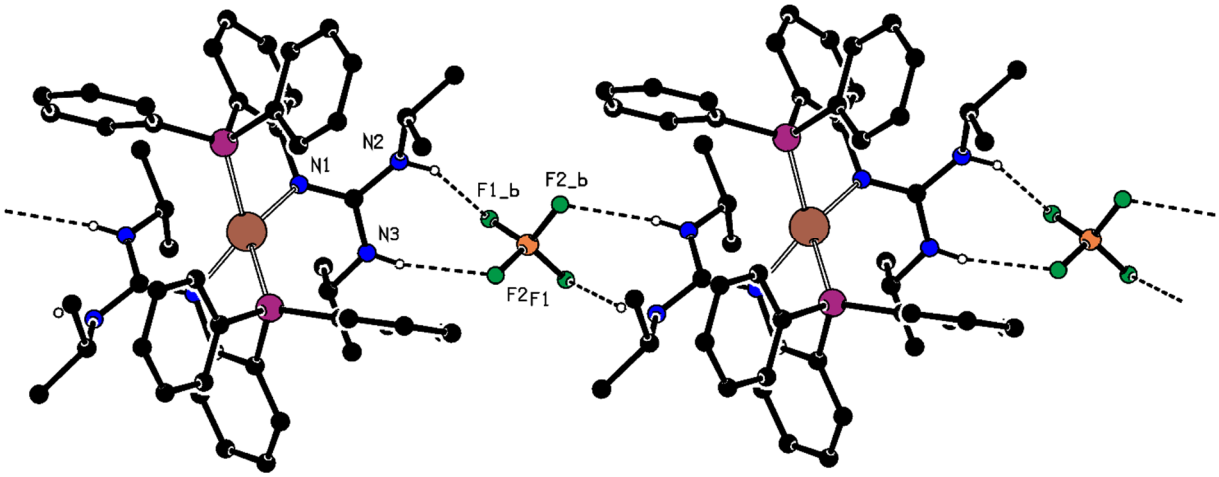

Figure S2 Simplified packing diagram for **2a**·$C_2H_4Cl_2$ showing the N–H···F hydrogen bonds (N2···F1 = 3.043(4) Å, N3···F2 = 3.024(5) Å; the chains propagate along the [1 0 1] direction)

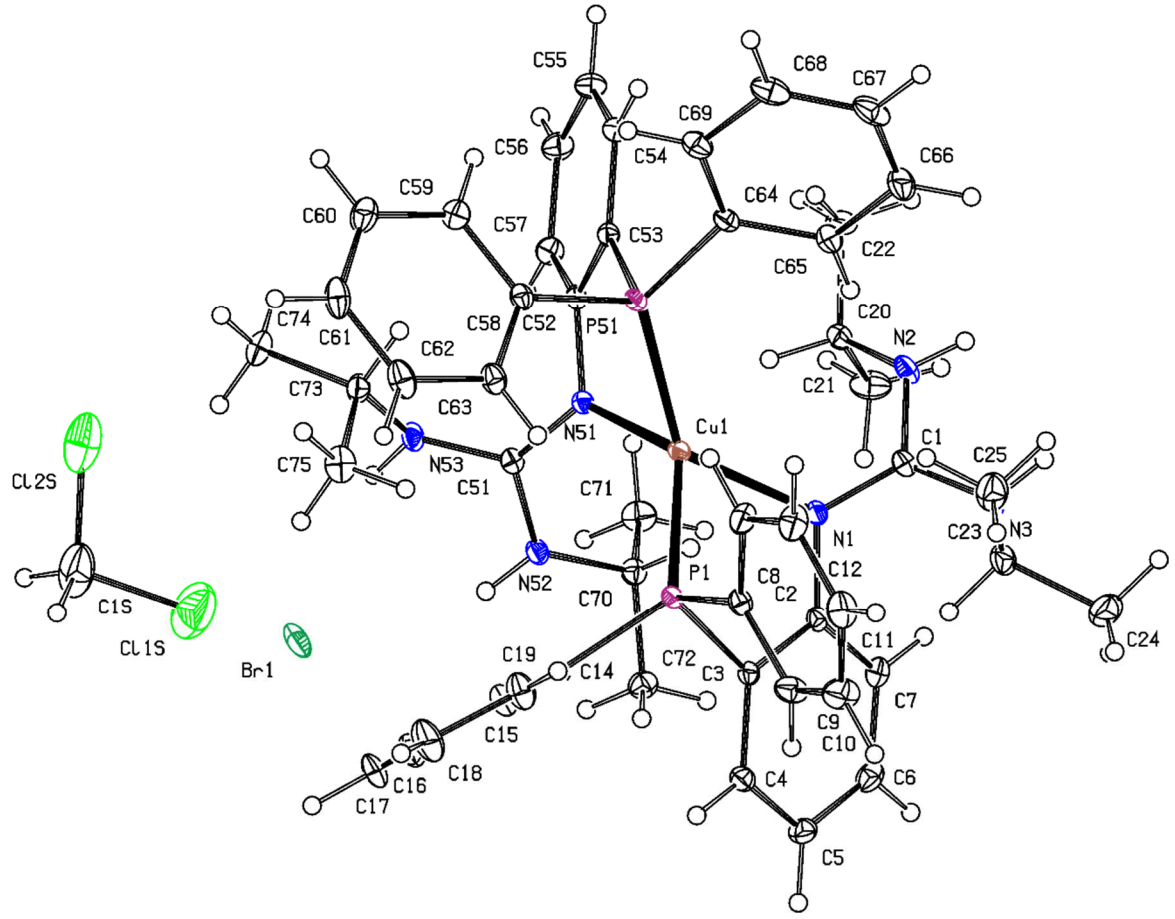

Figure S3 PLATON plot of the structure of **2b**·CH_2Cl_2 showing displacement ellipsoids at the 30% probability level

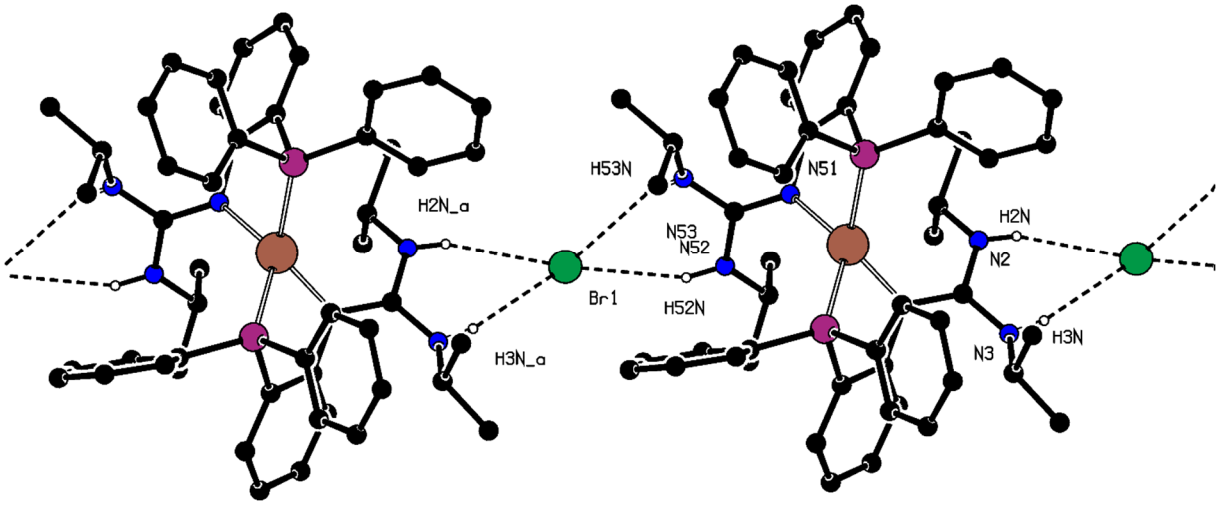

Figure S4 Simplified packing diagram for **2b**·CH_2Cl_2 illustrating the cooperative N–H···Br hydrogen bonds (N2···Br1 = 3.525(2) Å, N3···Br1 = 3.460(2) Å; N52···Br1 = 3.527(2) Å, and N53···Br1 = 3.420(2) Å)

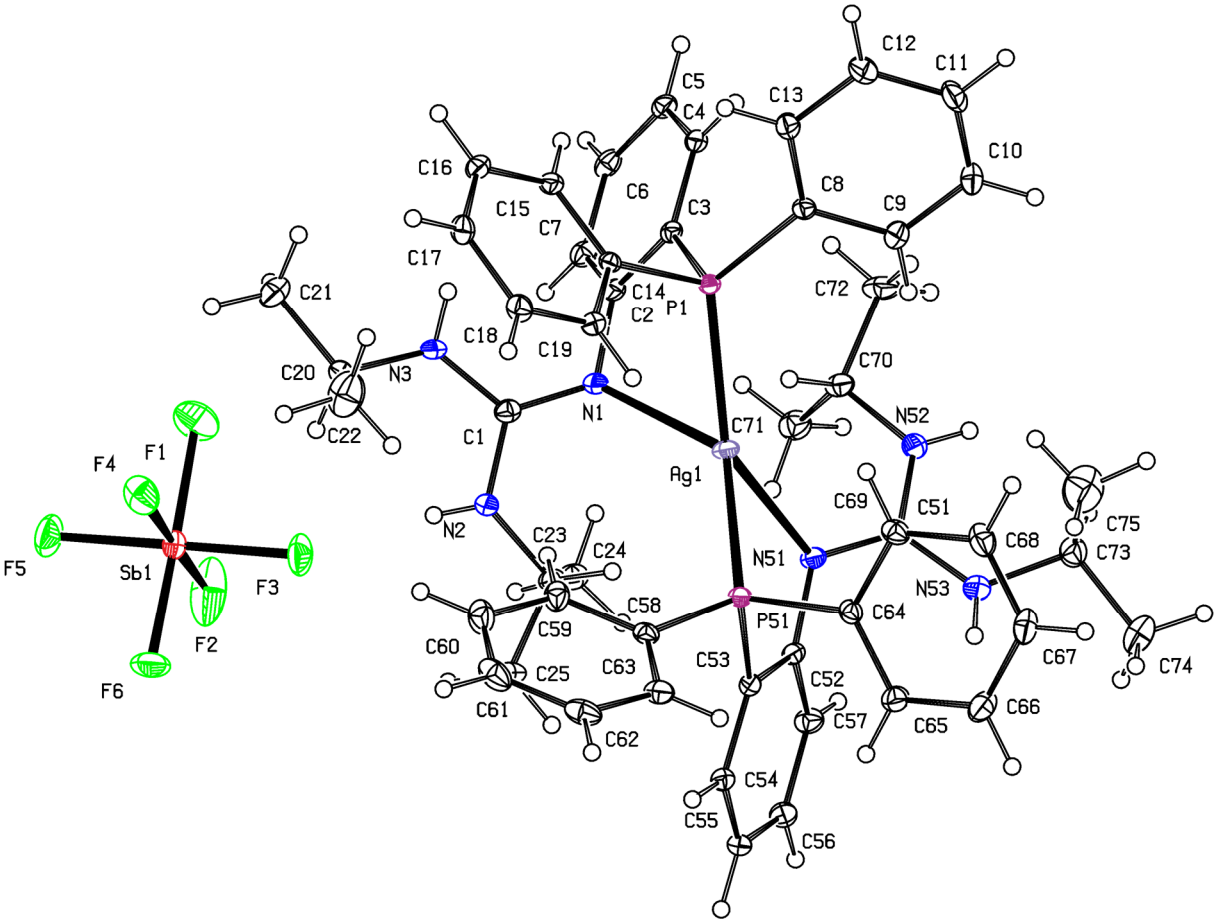

Figure S5 PLATON plot of **3a** with displacement ellipsoids at the 30% probability level

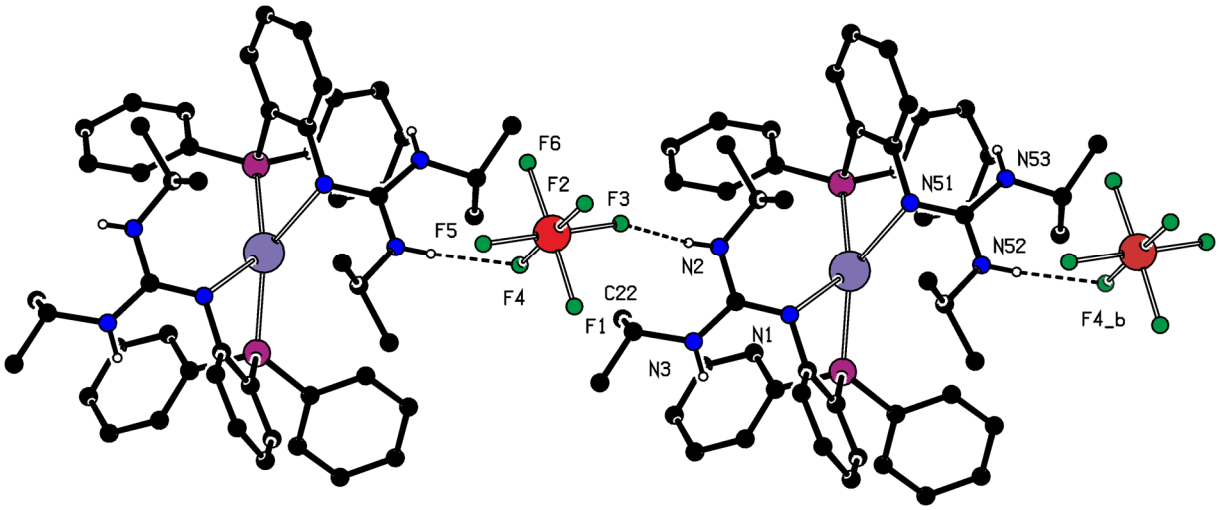

Figure S6 Simplified packing diagram for **3a** (N2···F3 = 3.089(3) Å, N52···F4 = 3.106(3) Å; the chains are oriented along the crystallographic *b* axis)

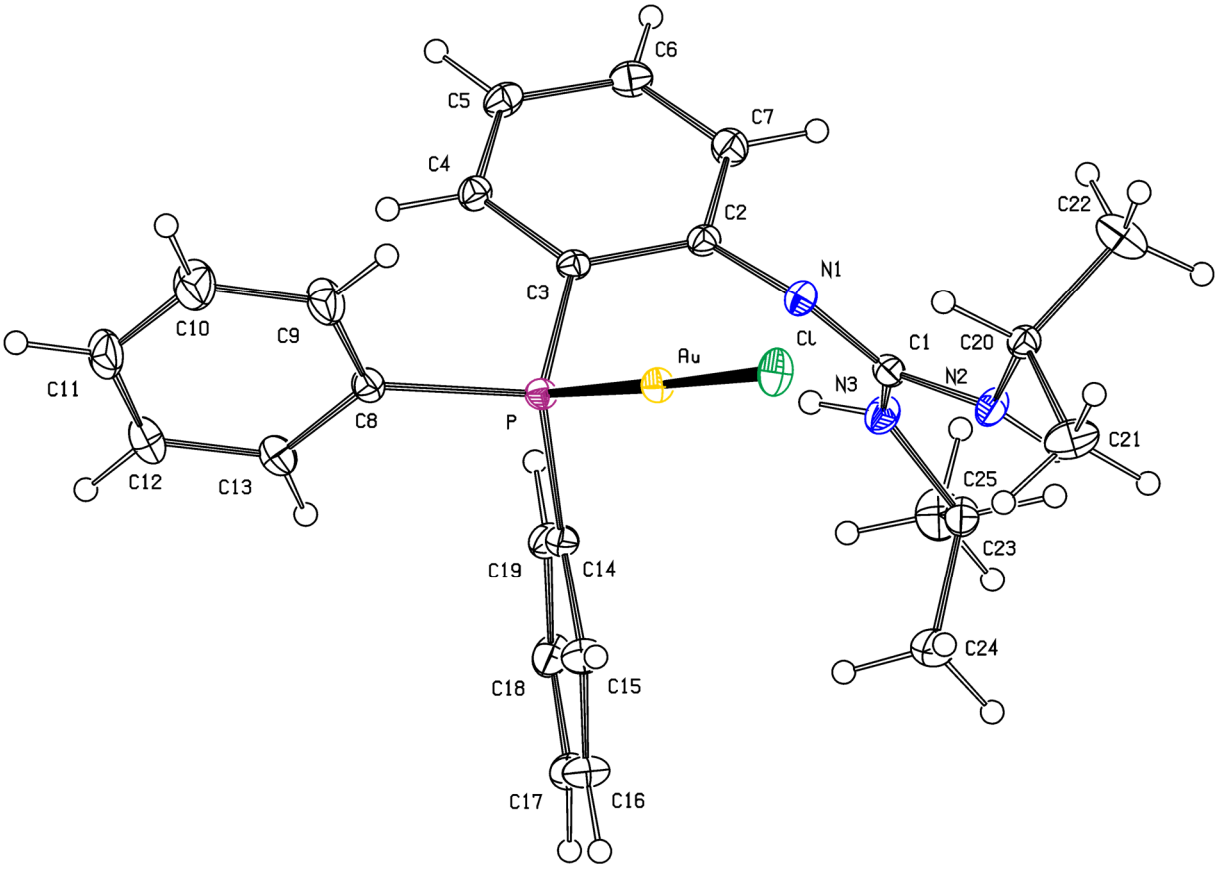

Figure S7 PLATON plot of **4** with displacement ellipsoids at 30% probability level

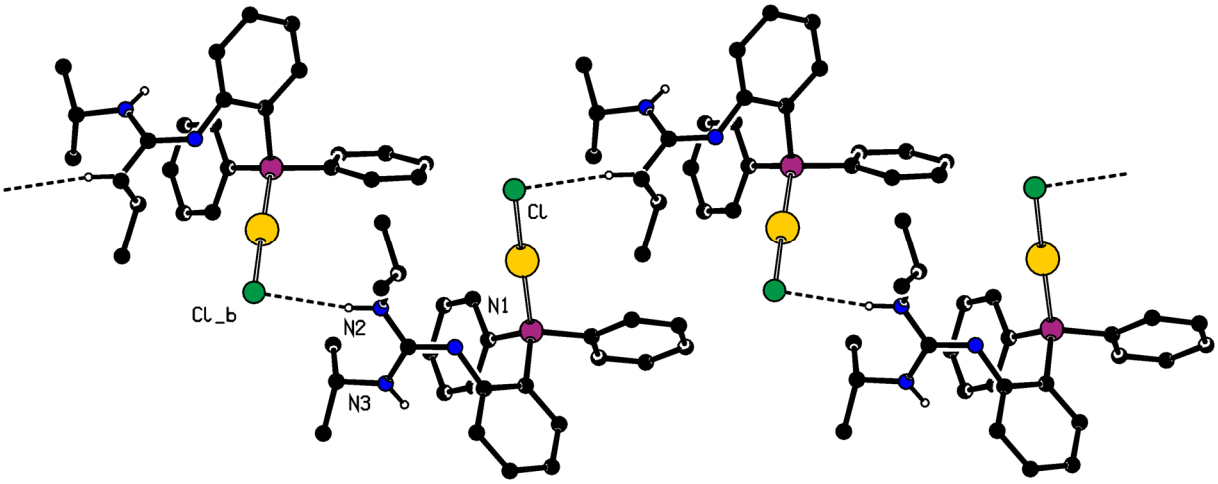

Figure S8 Section of the infinite hydrogen-bonded chains in the structure of **4** (N2···Cl = 3.487(1) Å; the chains are oriented parallel to the crystallographic *c* axis)

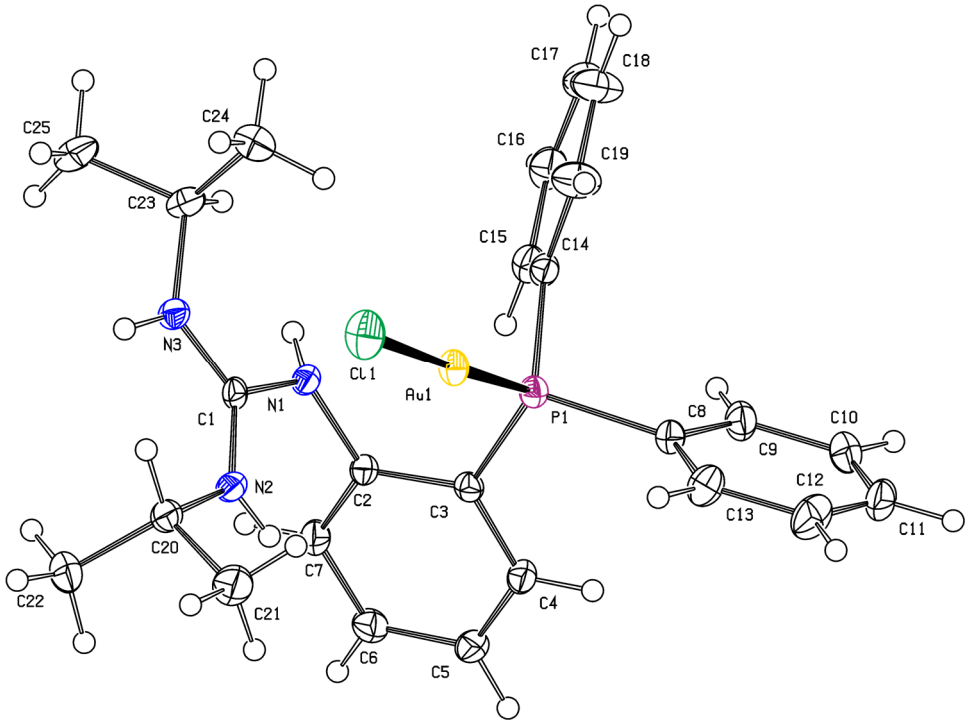

Figure S9 PLATON plot of the complex molecule in the structure **7a**·H_2O·CH_2Cl_2 showing displacement ellipsoids at the 30% probability level

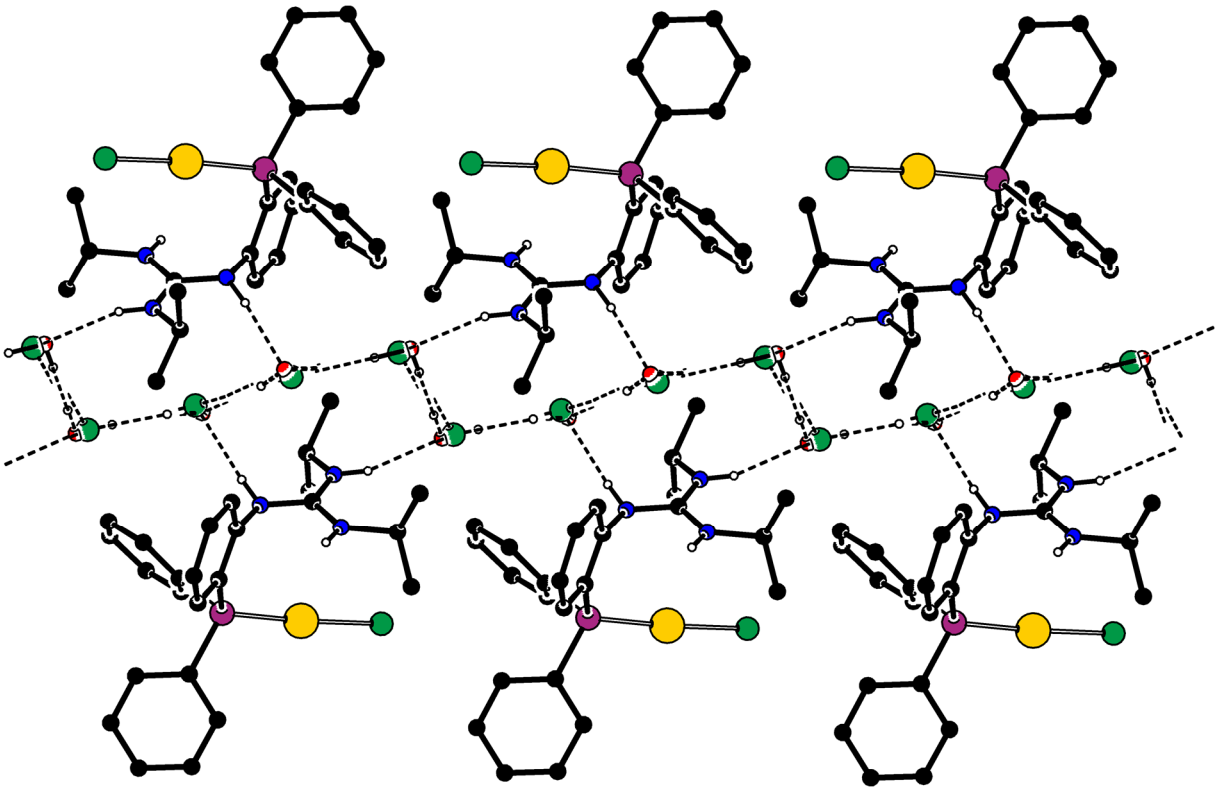

Figure S10 Section of the hydrogen-bonded ribbon in the structure of **7a**·H_2O·CH_2Cl_2. Note that the water molecules and chloride anions, interconnected by HO–H···Cl^- hydrogen bonds into a chain in the centre, are alternating in their positions (50:50).

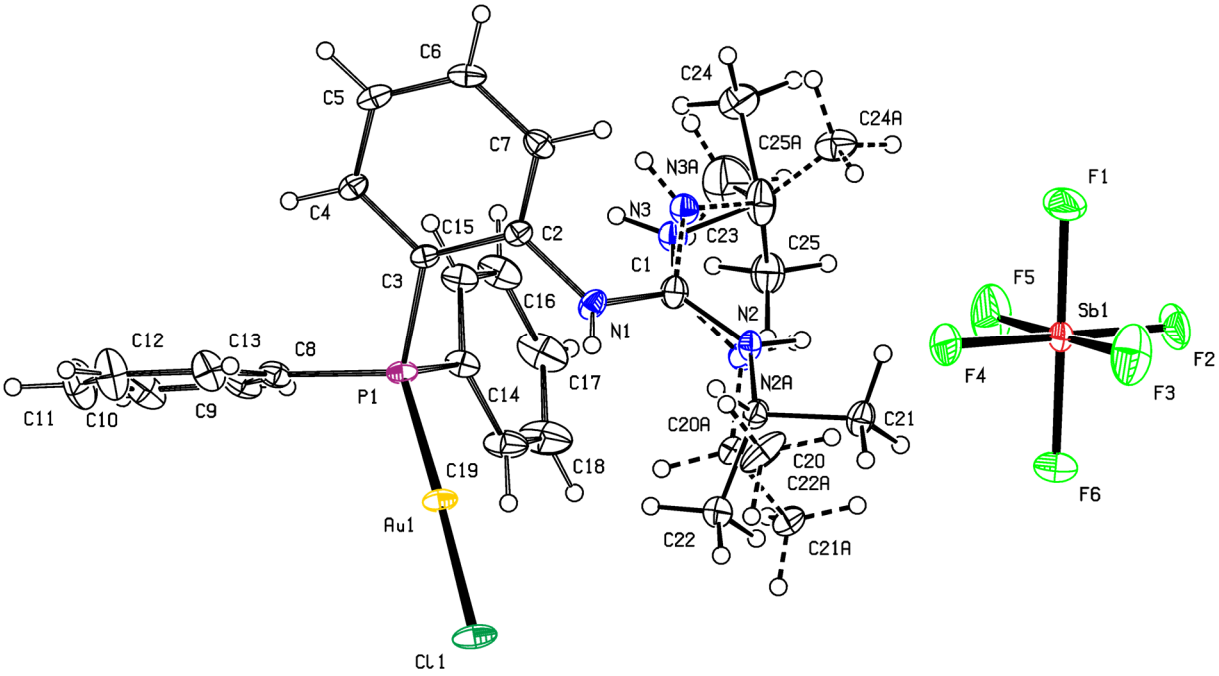

Figure S11 PLATON plot of the molecular structure of **7b**·½$C_2H_4Cl_2$ with displacement ellipsoids at the 30% probability level

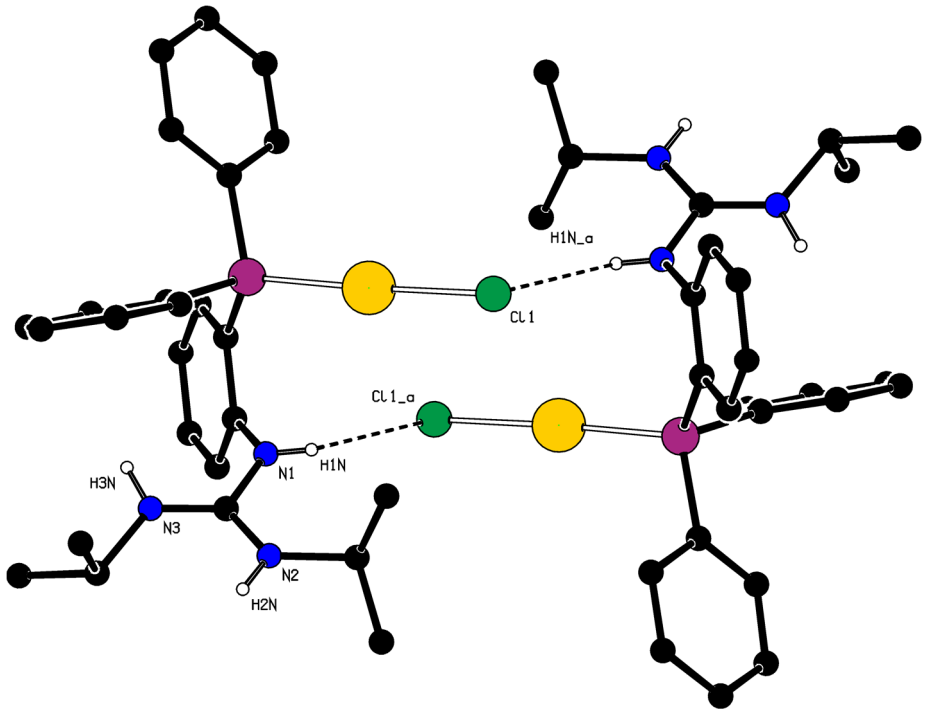

Figure S12 Simplified packing diagram for **7b**·½$C_2H_4Cl_2$ (N1···Cl1 = 3.221(3) Å; a = 2−x, 1−y, 2−z; additional contacts are seen between the guanidine NH and the $[SbF_6]^-$ anion)

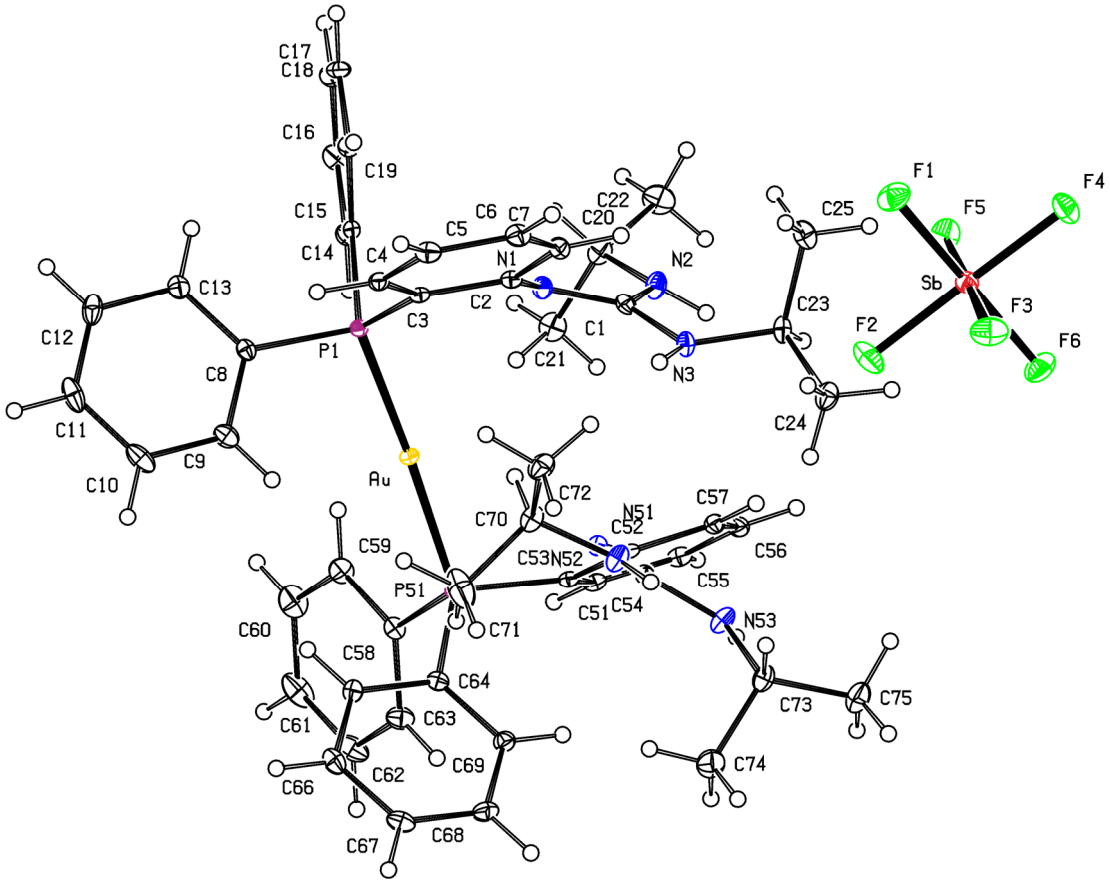

Figure S13 PLATON plot of the structure of compound **5** with displacement ellipsoids at the 30% probability level

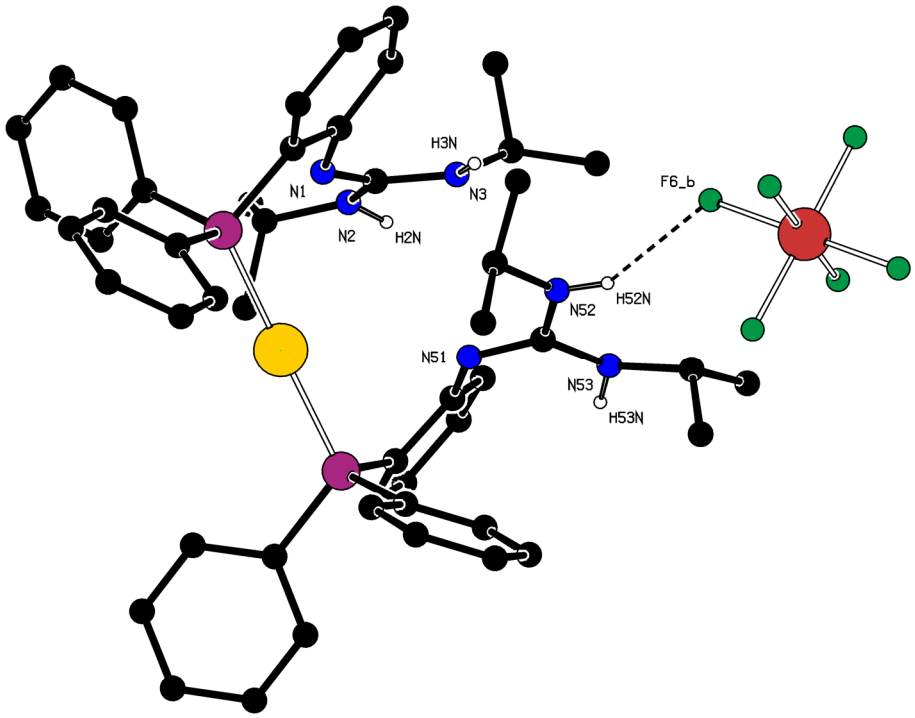

Figure S14 Simplified diagram showing the N–H···F hydrogen bonds in the structure of **5** (N52···F6 = 3.253(2) Å, b = ½−x, ½+y, ½−z)

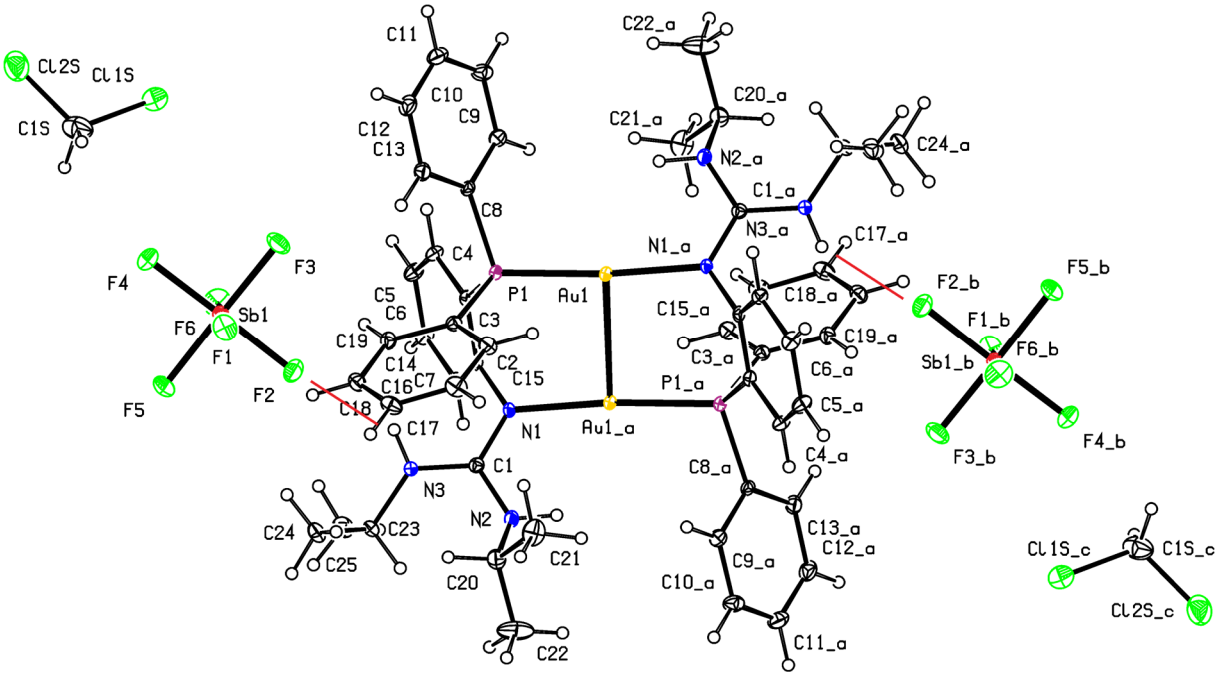

Figure S15 PLATON plot of the structure of **6**·2CH_2Cl_2 with displacement ellipsoids at 30% probability level. The N–H···F hydrogen bond is indicated by red lines (N3···F2 = 3.143(3) Å).

Table S1. Selected crystallographic data and structure refinement parameters.[a]

Compound	**2a**·$C_2H_4Cl_2$	**2b**·CH_2Cl_2	**3a**
Formula	$C_{52}H_{64}BCl_2CuF_4N_6P2$	$C_{51}H_{62}BrCl_2CuN_6P_2$	$C_{50}H_{60}AgF_6N_6P_2Sb$
M	1056.28	1035.35	1150.60
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2 (no. 5)	*Cc* (no. 9)	$P2_1/c$ (no. 14)
T [K]	120(2)	120(2)	120(2)
a [Å]	11.4909(6)	11.3528(5)	9.0246(3)
b [Å]	20.768(1)	22.421(1)	13.8102(4)
c [Å]	12.5771(7)	20.7154(8)	41.589(1)
α [°]	90	90	90
β [°]	115.248(2)	101.490(2)	94.617(1)
γ [°]	90	90	90
V [Å]^3	2714.7(3)	5167.3(4)	5166.4(3)
Z	2	4	4
μ(Mo Kα) [mm^{-1}]	0.613	1.401	1.025
Diffrns collected	62555	92033	76434
Independent diffrns	6241	15051	11855
Observed[a] diffrns	6219	14486	11298
R_{int}[b] [%]	2.40	3.40	2.28
No. of parameters	321	577	603
R[b] obsd diffrns [%]	3.12	2.59	3.72
R, *wR*[b] all data [%]	3.14, 7.95	2.82, 6.01	3.94, 7.35
Δρ [e Å^{-3}]	0.51, −0.30	0.55, −0.54	1.69, −1.24

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

Table S1 continued

Compound	**4**	**7a**·H_2O·CH_2Cl_2	**7b**·½$C_2H_4Cl_2$
Formula	$C_{25}H_{30}AuClN_3P$	$C_{26}H_{35}AuCl_4N_3OP$	$C_{26}H_{32}AuCl_2F_6N_3PSb$
M	635.90	775.30	921.13
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
T [K]	150(2)	150(2)	120(2)
a [Å]	8.9997(3)	8.5896(3)	9.8737(3)
b [Å]	20.4818(7)	9.5972(3)	11.1820(3)
c [Å]	14.2314(4)	19.1254(5)	15.0194(5)
α [°]	90	85.717(1)	75.100(1)
β [°]	107.334(1)	81.756(1)	86.198(1)
γ [°]	90	84.901(1)	85.197(1)
V [Å]^3	2504.1(1)	1551.09(8)	1595.15(8)
Z	4	2	2
μ(Mo Kα) [mm^{-1}]	6.062	5.162	5.714
Diffrns collected	72057	29187	32034
Independent diffrns	5764	7106	7286
Observed[a] diffrns	5601	6974	6966
R_{int}[b] [%]	2.37	2.27	1.90
No. of parameters	284	309	410
R[b] obsd diffrns [%]	1.11	1.93	2.27
R, *wR*[b] all data [%]	1.17, 2.71	1.98, 4.72	2.42, 5.19
Δρ [e Å^{-3}]	0.42, −0.42	1.06, −1.22	1.66, −1.77

Table S1 continued

Compound	**5**	**6**·2CH_2Cl_2
Formula	$C_{50}H_{60}AuF_6N_6P_2Sb$	$C_{52}H_{64}Au_2Cl_4F_{12}N_6P_2Sb_2$
M	1239.69	1842.26
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
T [K]	120(2)	120(2)
a [Å]	11.2205(2)	8.1541(4)
b [Å]	20.5943(4)	16.2447(8)
c [Å]	21.9857(5)	23.836(2)
α [°]	90	90
β [°]	91.710(1)	97.106(2)
γ [°]	90	90
V [Å]^3	5078.2(2)	3133.1(3)
Z	4	2
μ(Mo Kα) [mm^{-1}]	3.543	5.818
Diffrns collected	54360	38524
Independent diffrns	11660	7172
Observed[a] diffrns	10688	6751
R_{int}[b] [%]	2.91	2.41
No. of parameters	603	365
R[b] obsd diffrns [%]	1.81	1.91
R, *wR*[b] all data [%]	2.20, 3.76	2.10, 4.39
Δρ [e Å^{-3}]	0.45, −0.40	1.16, −0.77

Copies of the NMR spectra

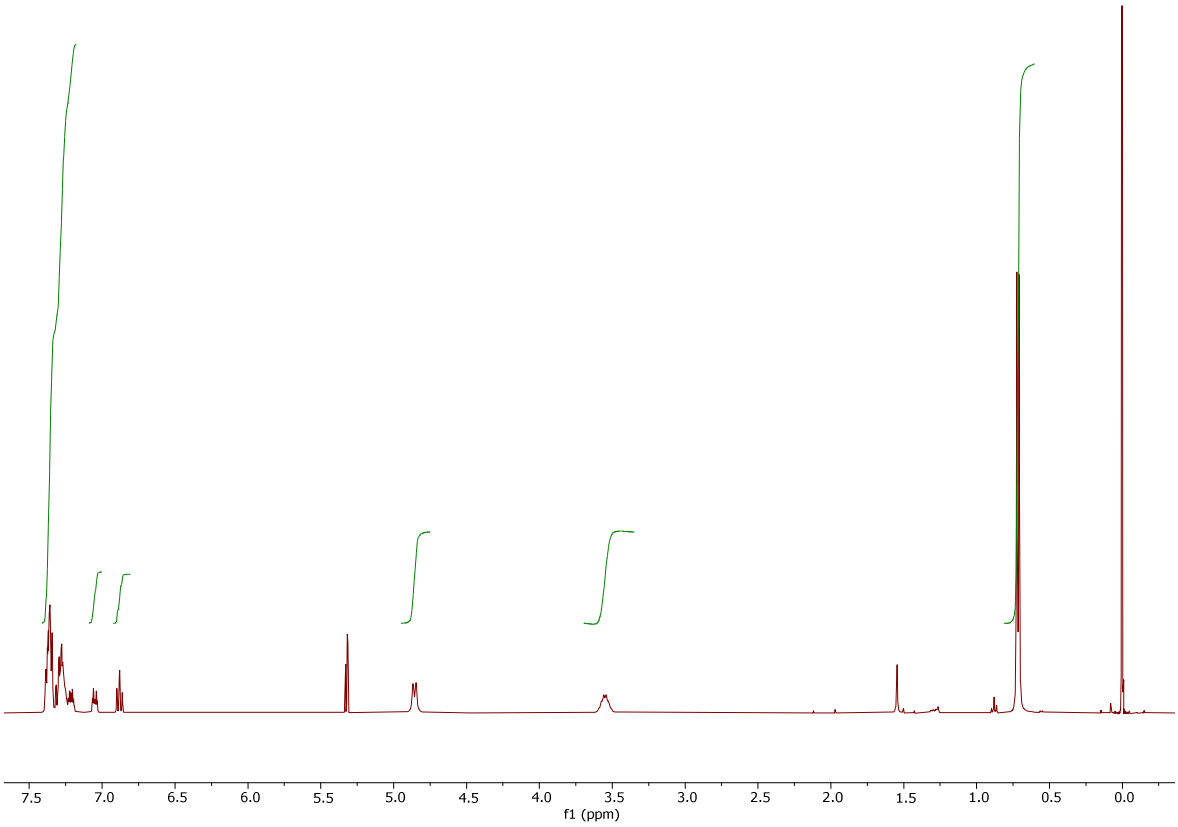

Figure S16 ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **2a**

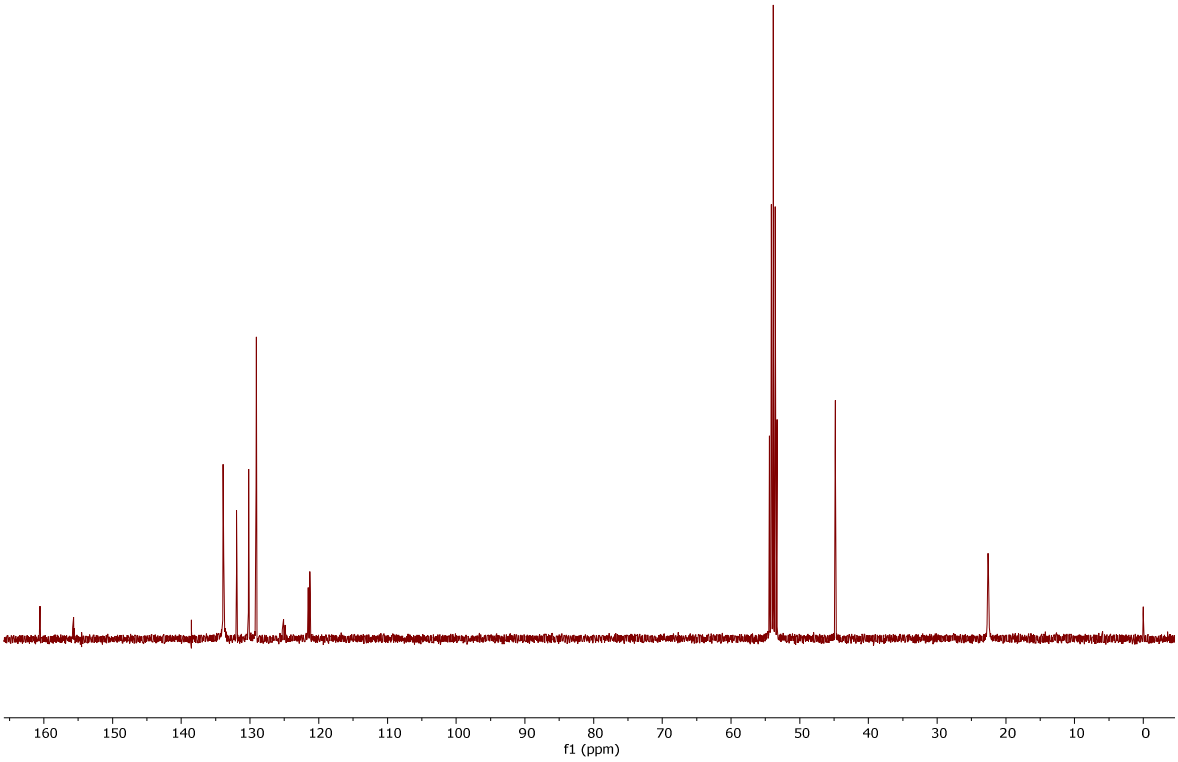

Figure S17 $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 101 MHz) of **2a**

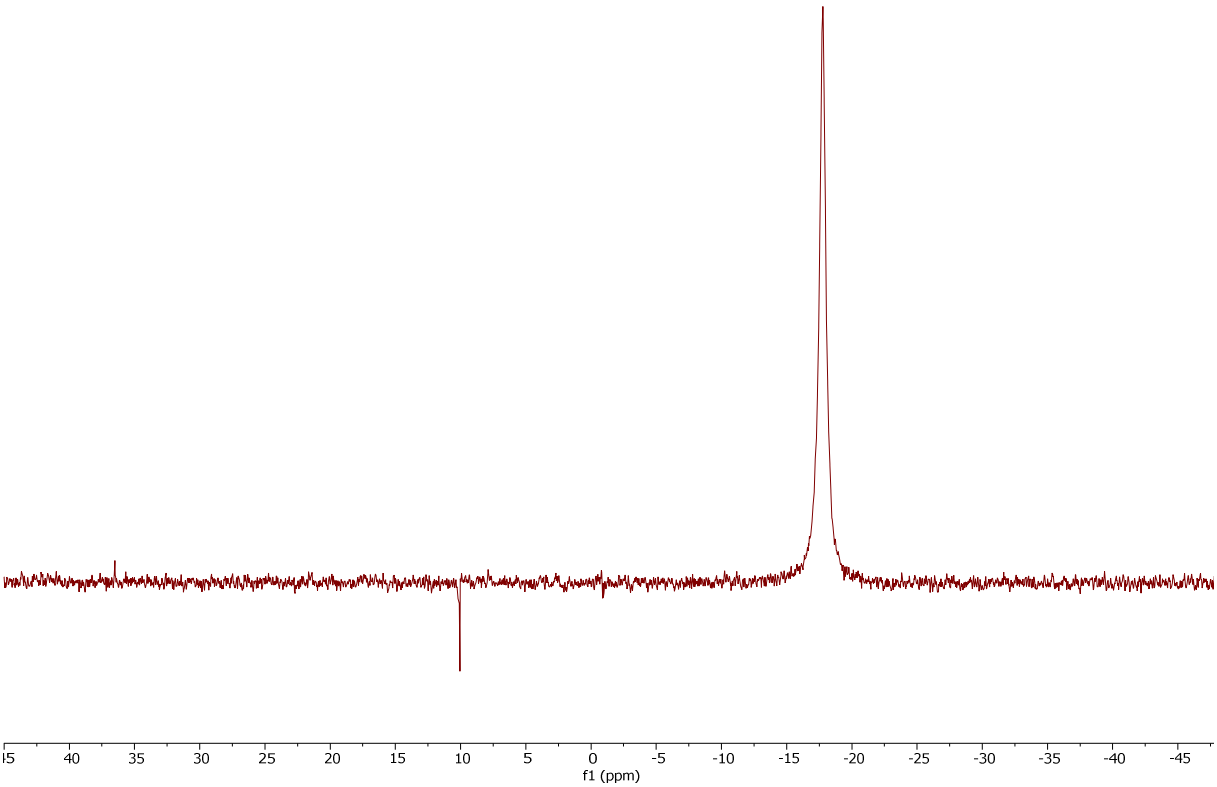

Figure S18 $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 162 MHz) of **2a** (the "signal" at $\delta_P \approx 10$ is a spike)

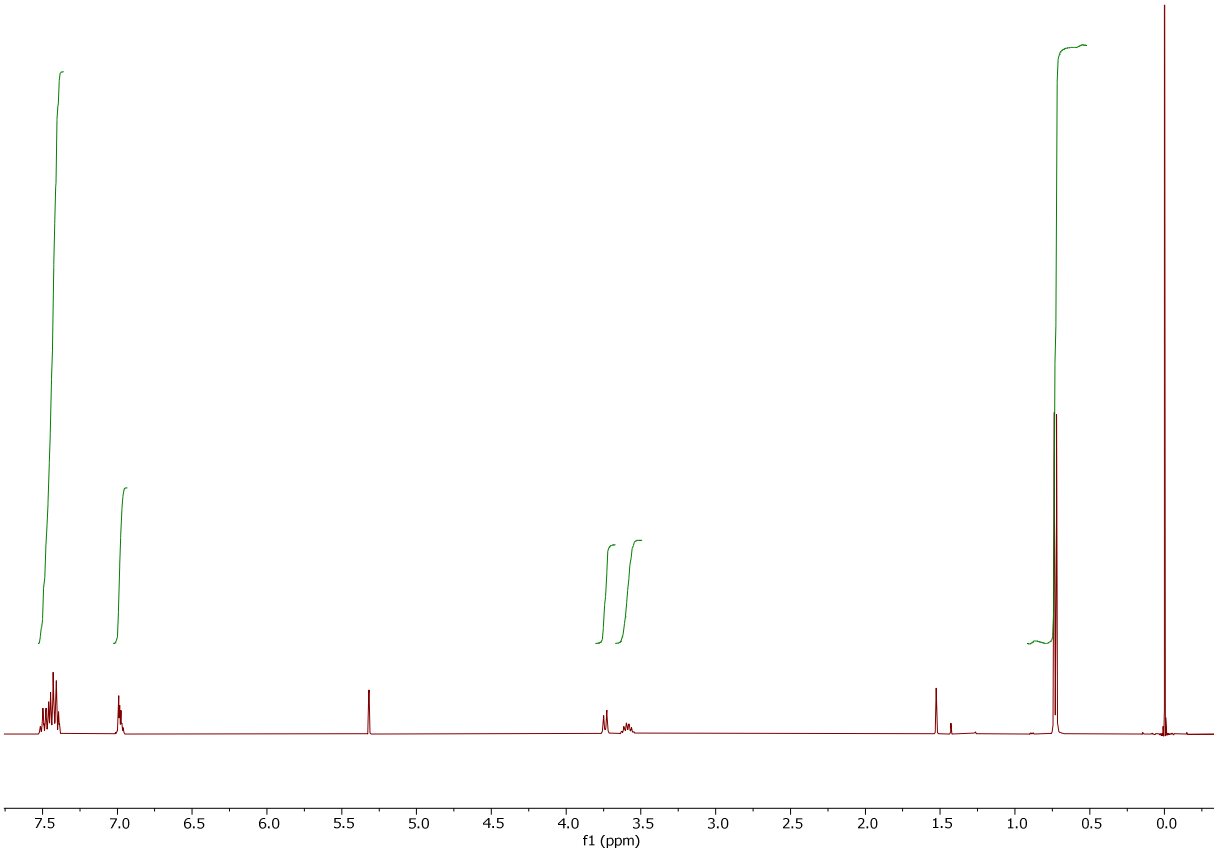

Figure S19 ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **3a**

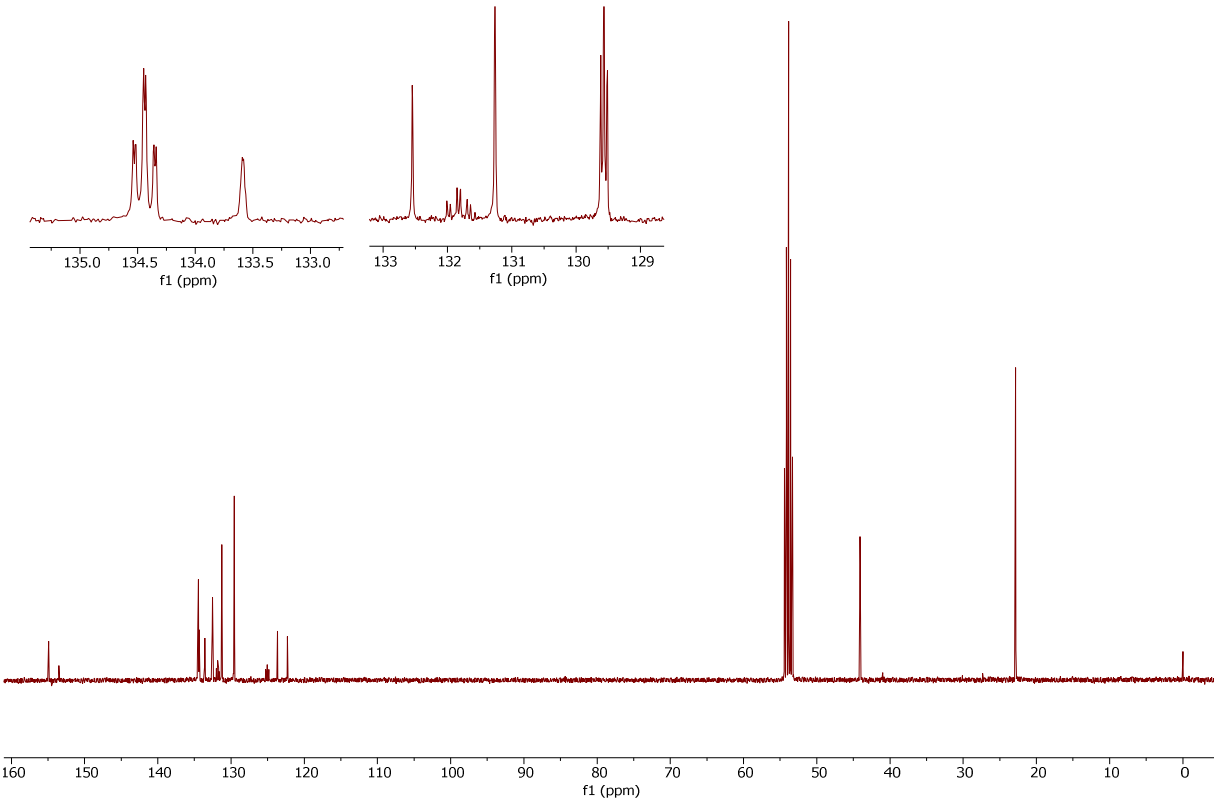

Figure S20 $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 101 MHz) of **3a**

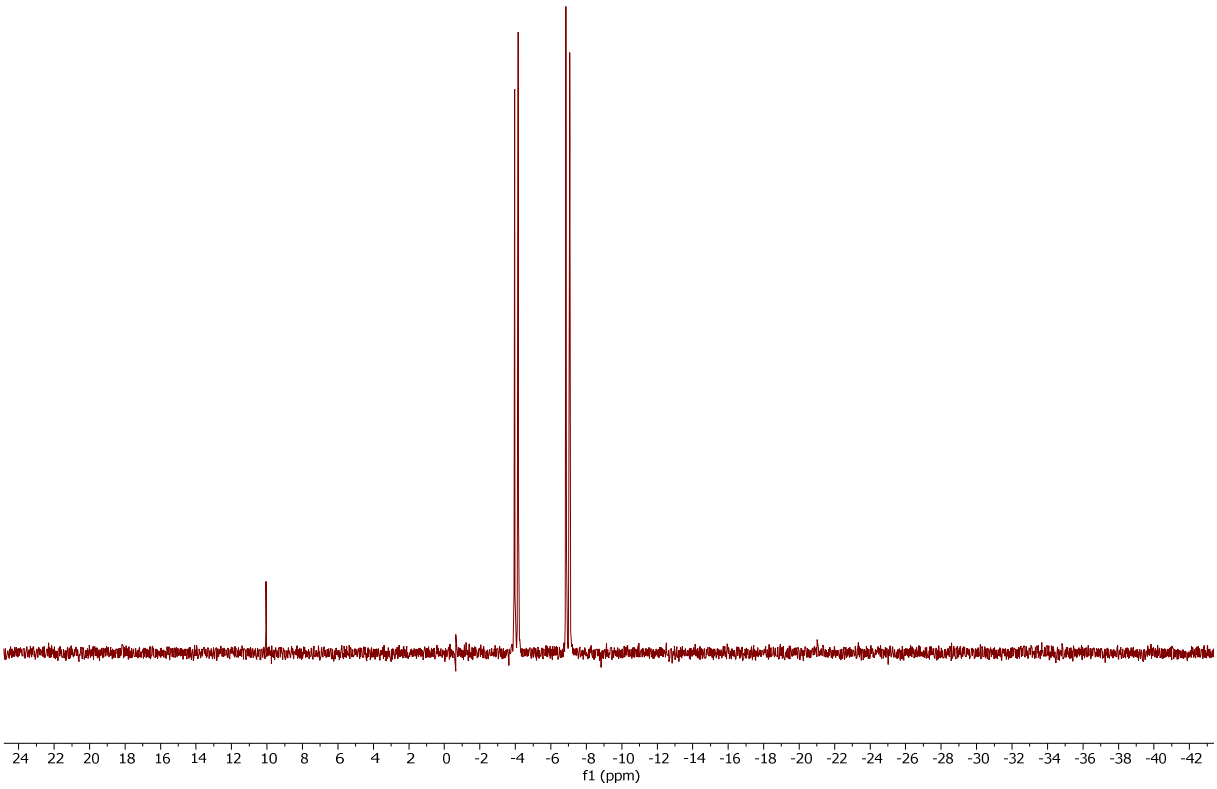

Figure S21 $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 162 MHz) of **3a** (the "signal" at $\delta_P \approx 10$ is a spike)

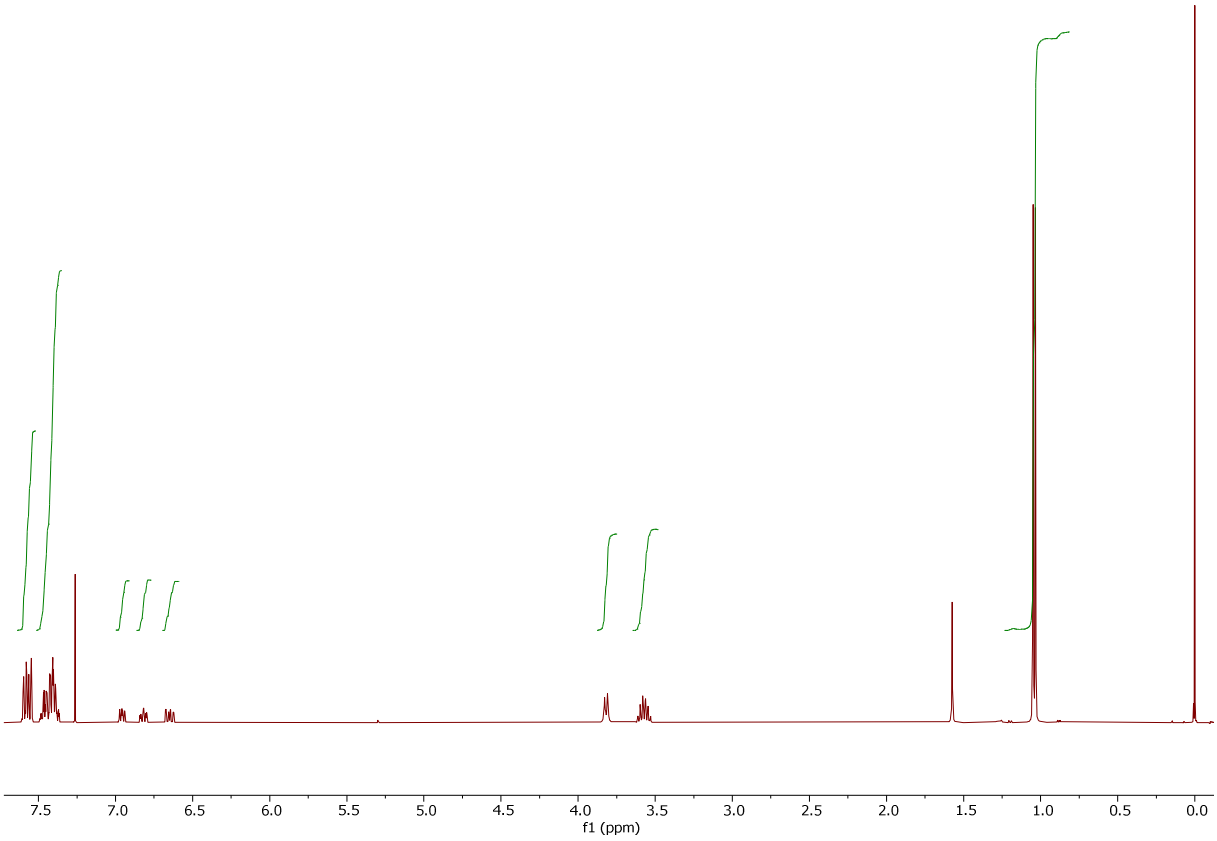

Figure 22 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4**

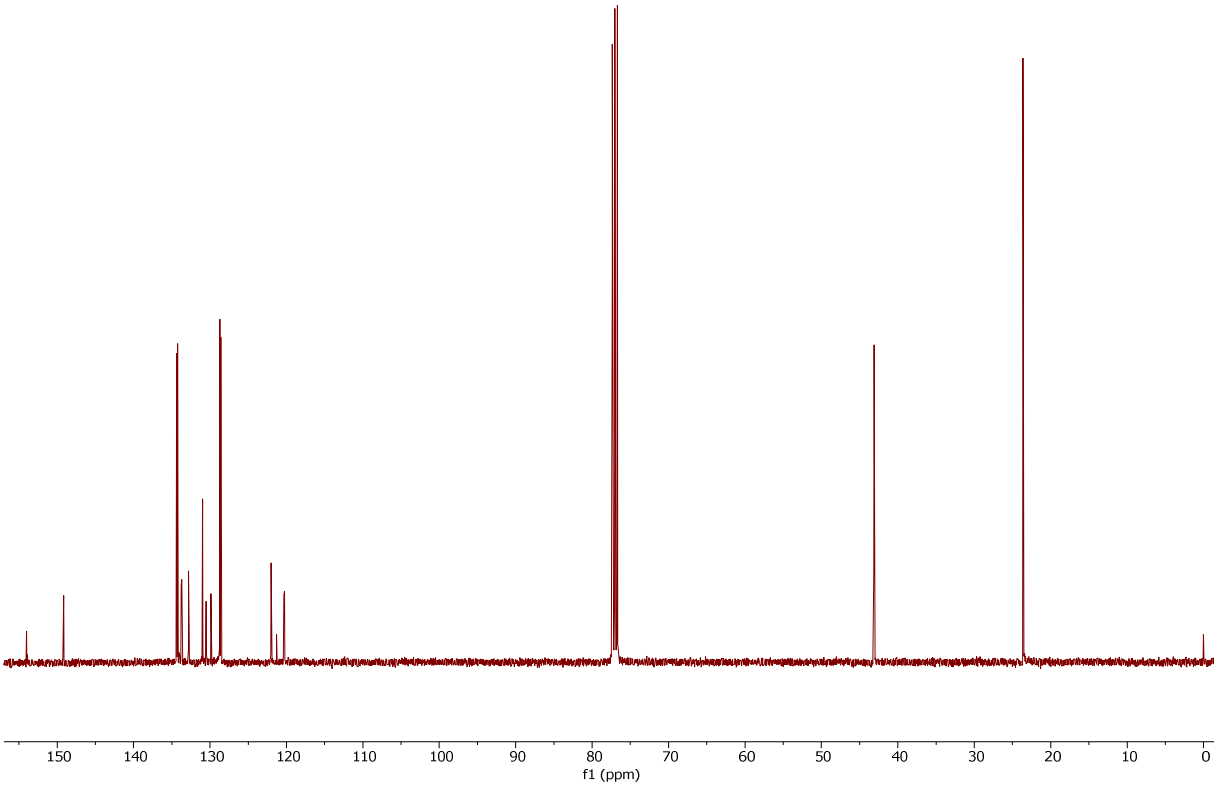

Figure S23 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **4**

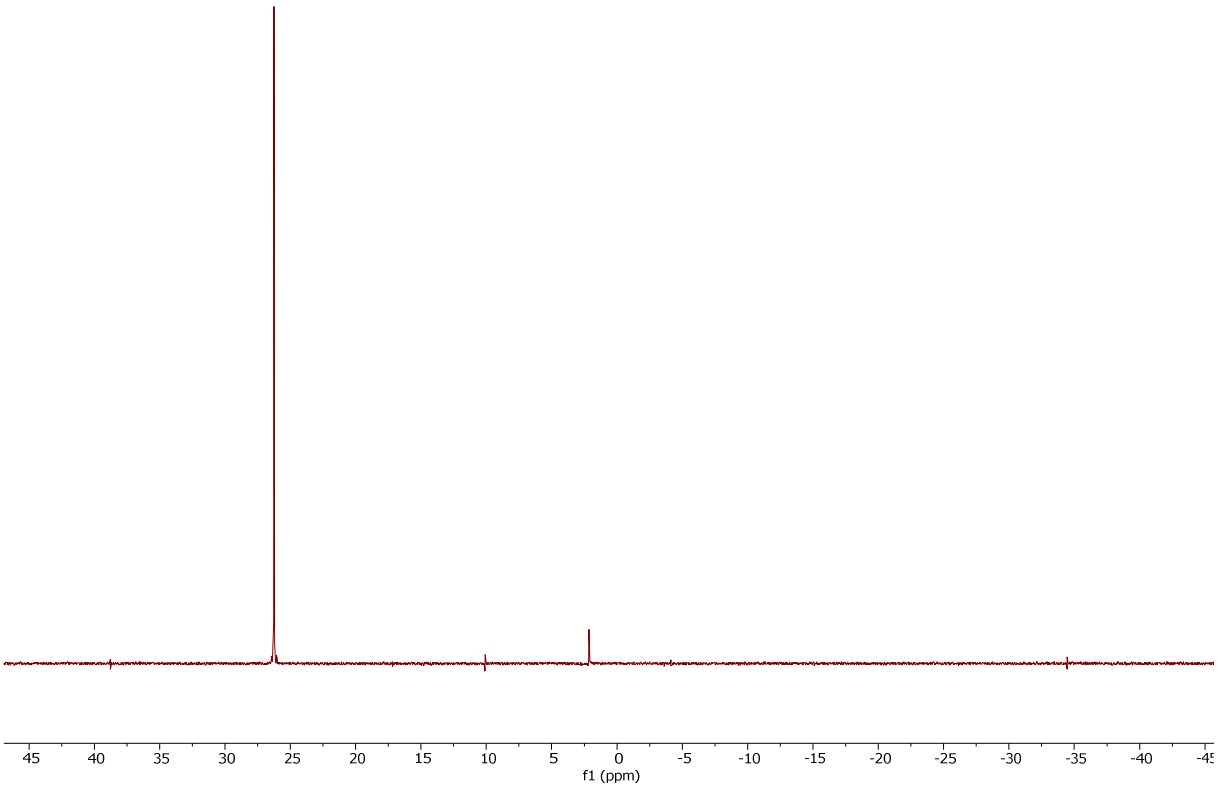

Figure S24 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **4**

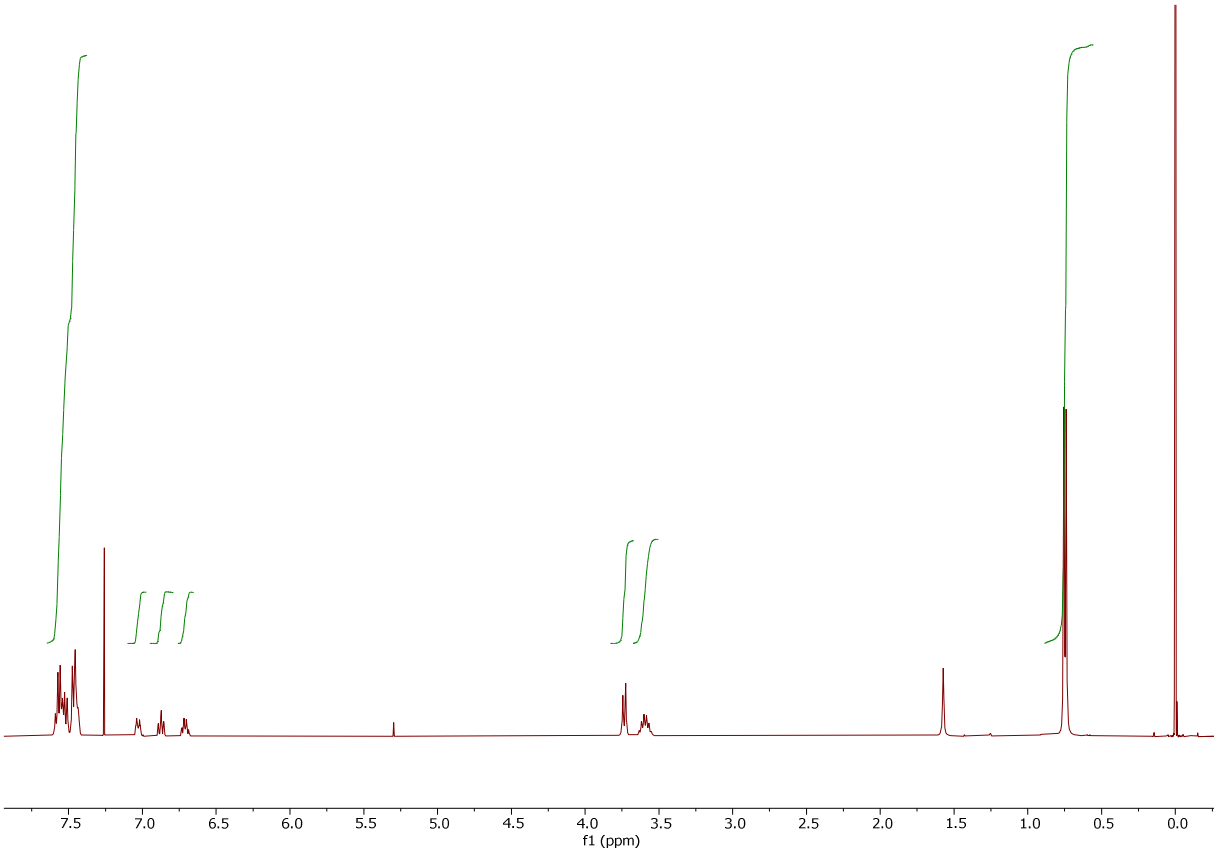

Figure S25 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5**

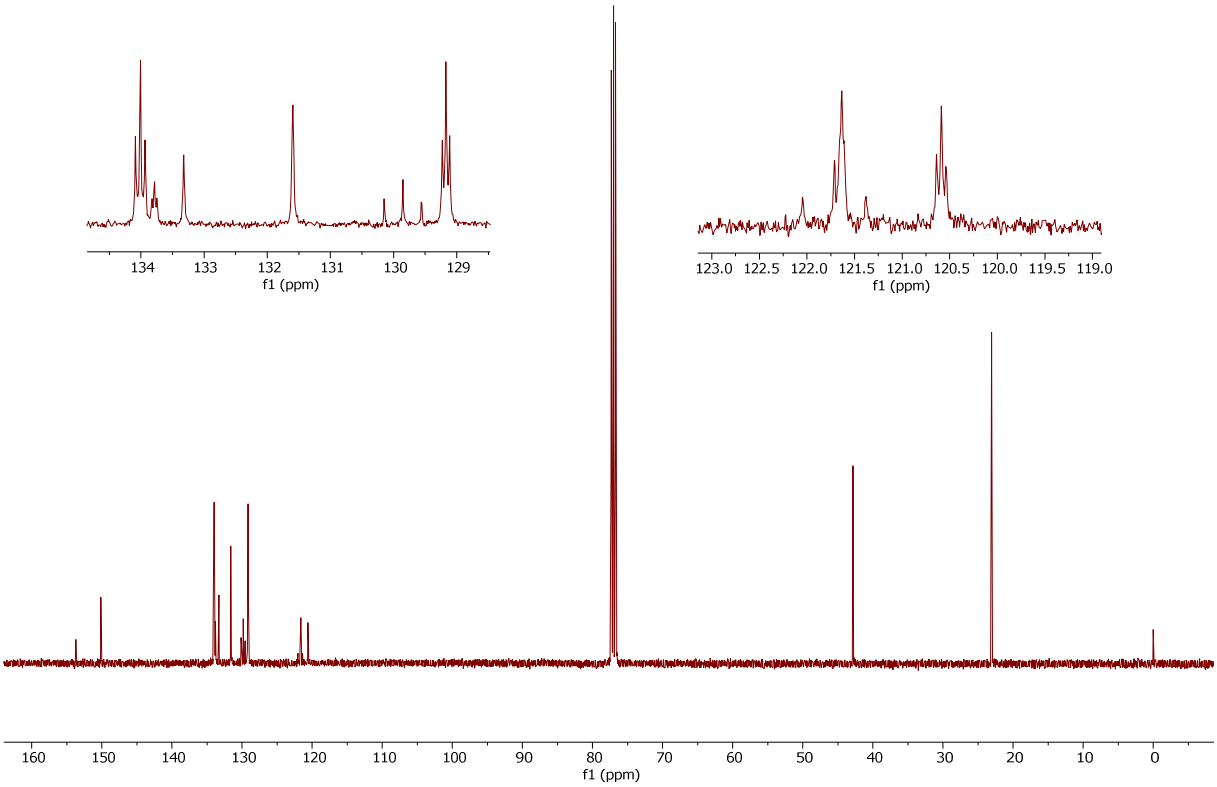

Figure S26 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **5**

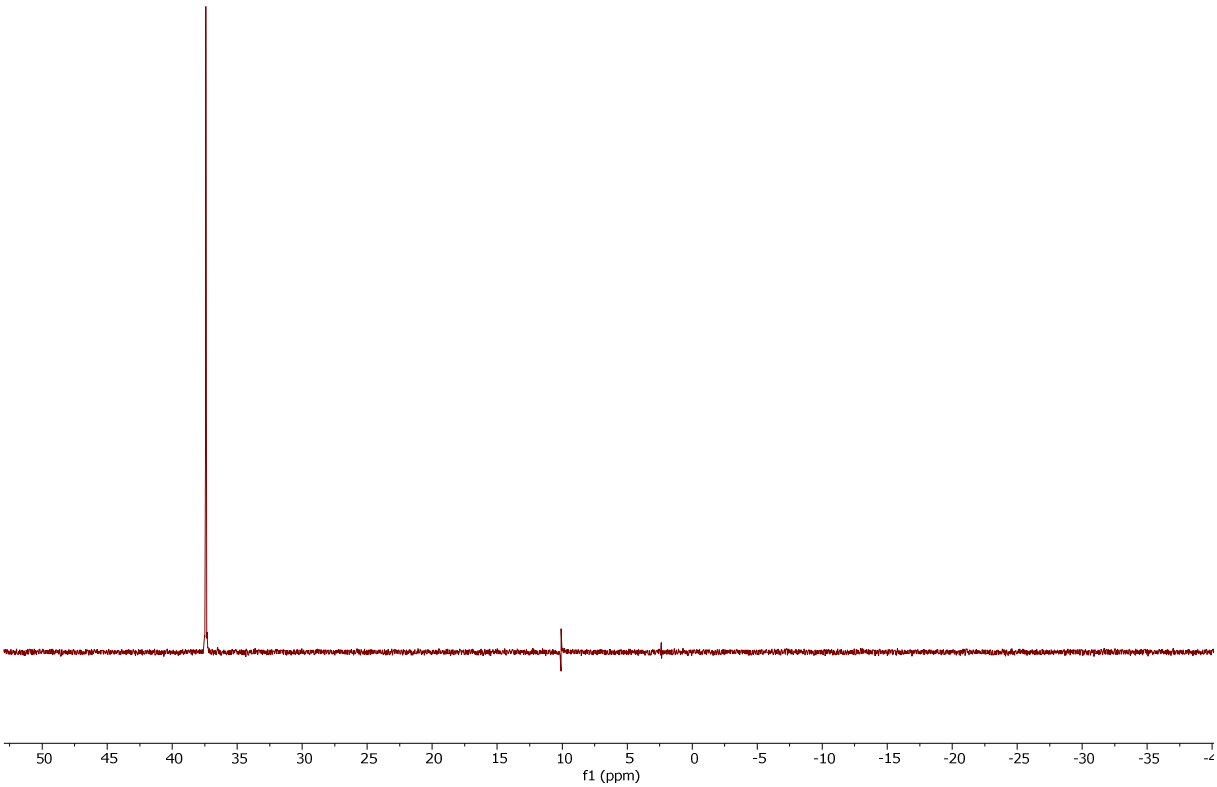

Figure S27 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **5**

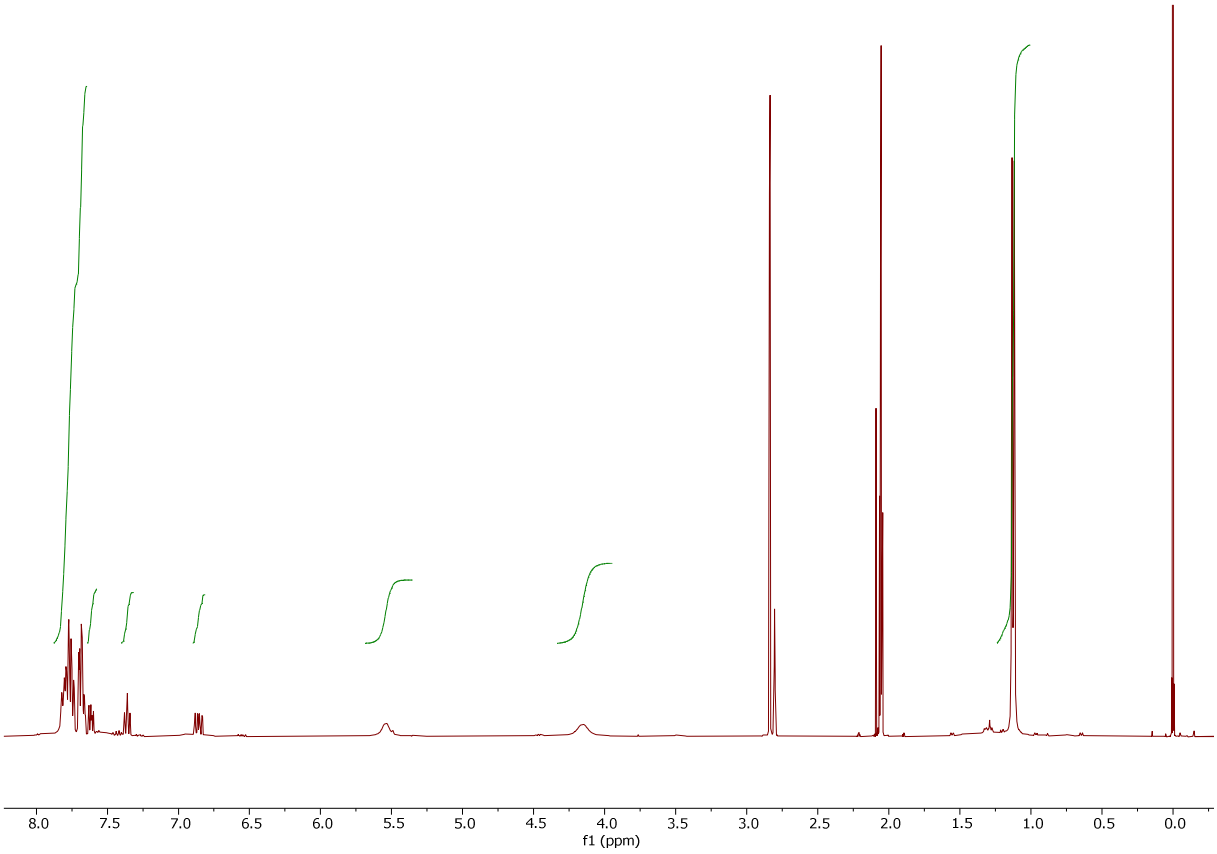

Figure S28 ^{1}H NMR spectrum (acetone-d_6, 400 MHz) of **6**

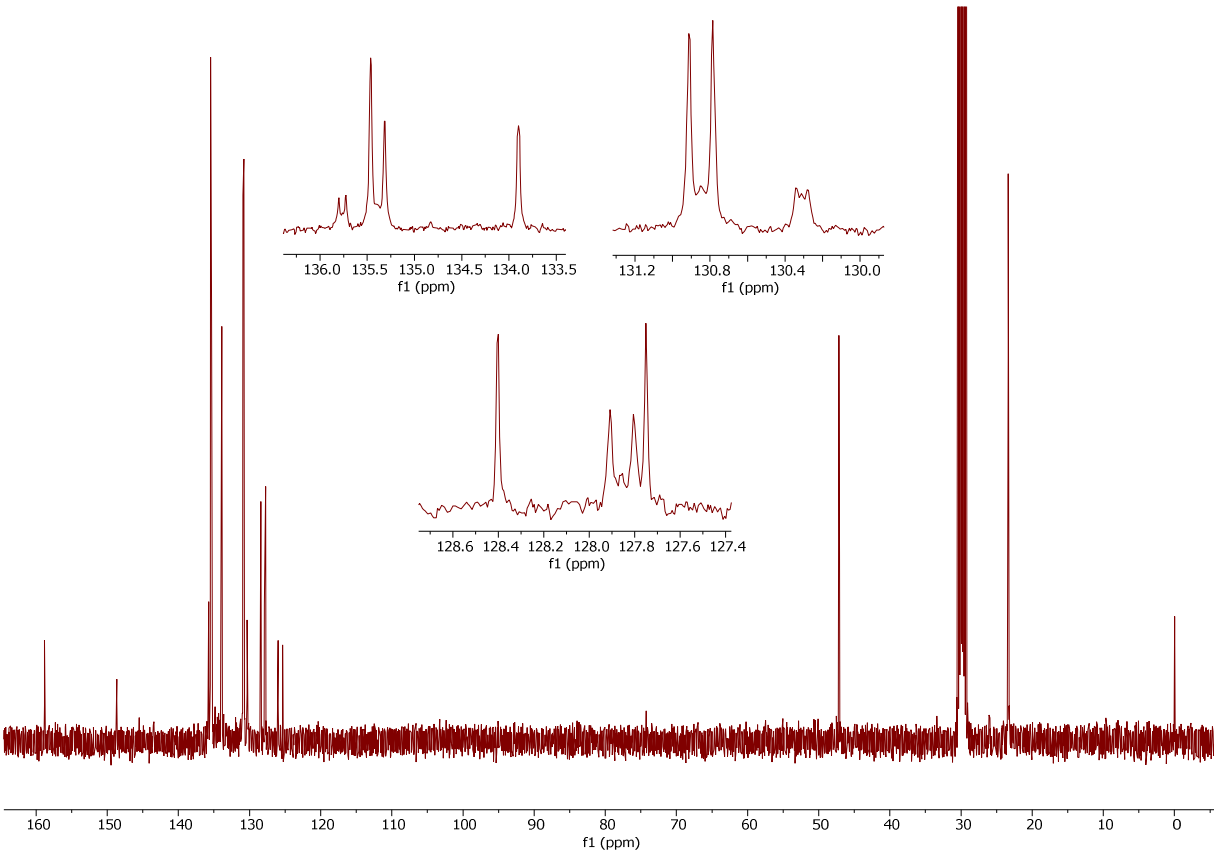

Figure S29 ^{13}C{^{1}H} NMR spectrum (acetone-d_6, 101 MHz) of **6**

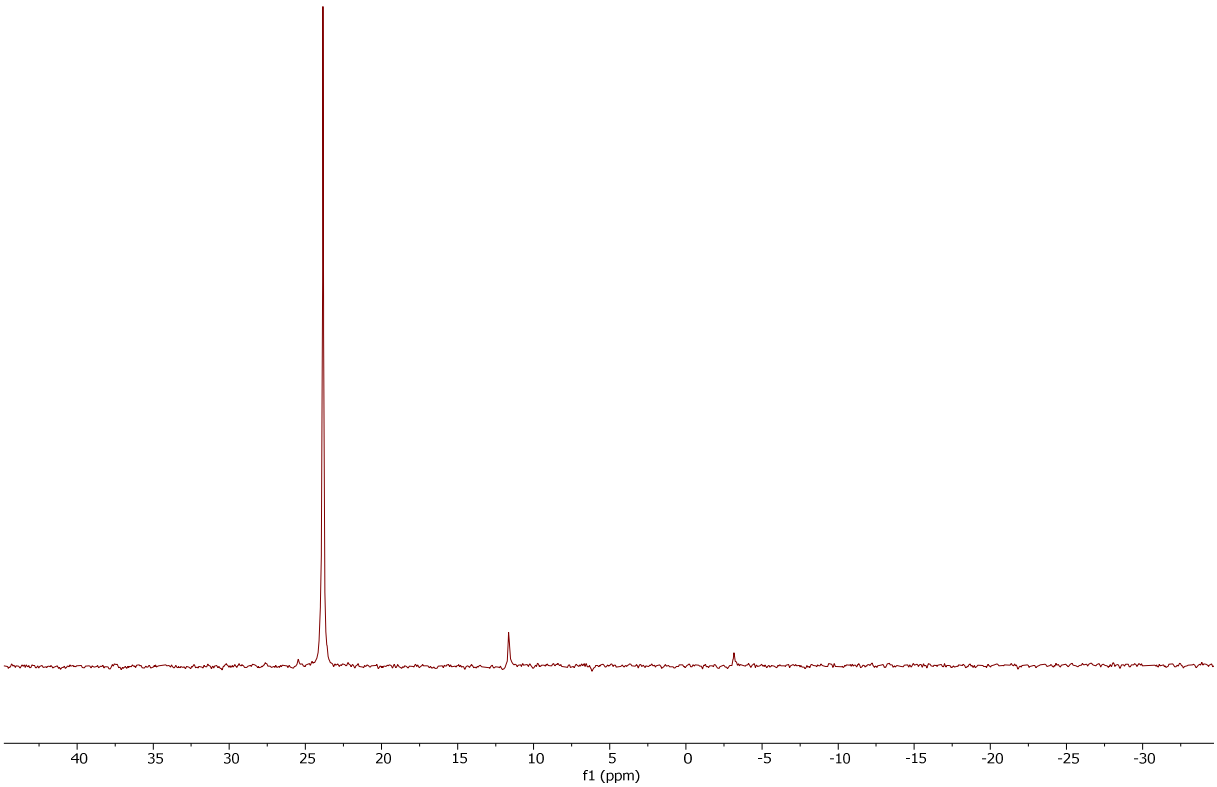

Figure S30 $^{31}P\{^{1}H\}$ NMR spectrum (acetone-d_6, 162 MHz) of **6**

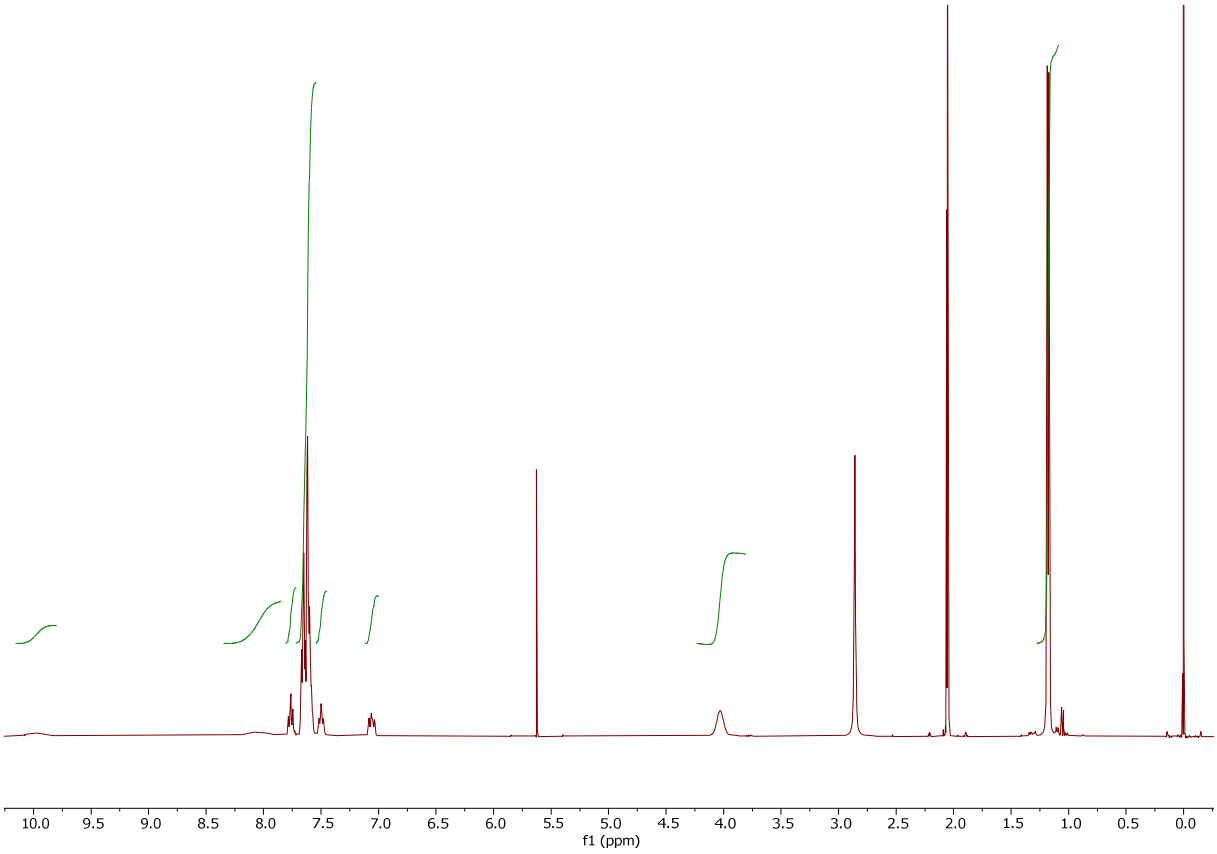

Figure S31 ^{1}H NMR spectrum (acetone-d_6, 400 MHz) of **7a**

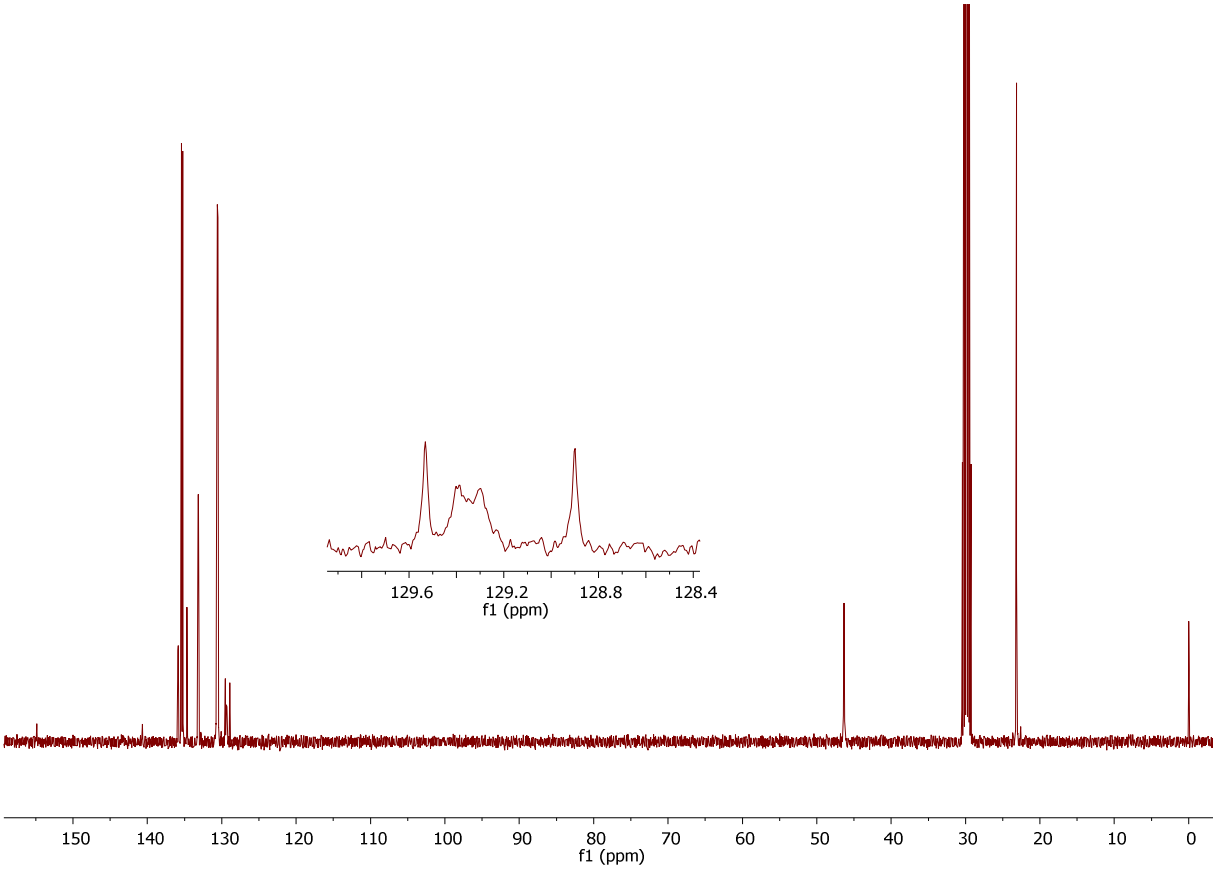

Figure S32 ^{13}C{^{1}H} NMR spectrum (acetone-d_6, 101 MHz) of **7a**

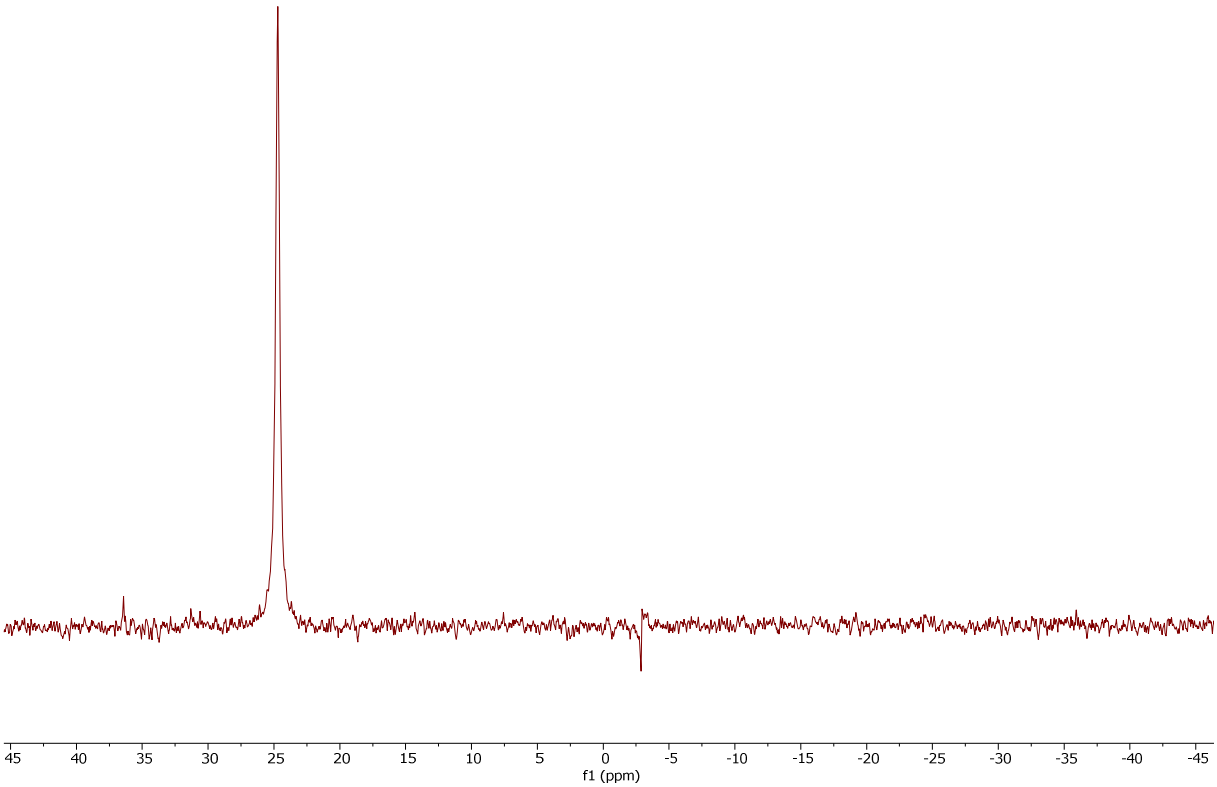

Figure S33 $^{31}P\{^{1}H\}$ NMR spectrum (acetone-d_6, 162 MHz) of **7a**

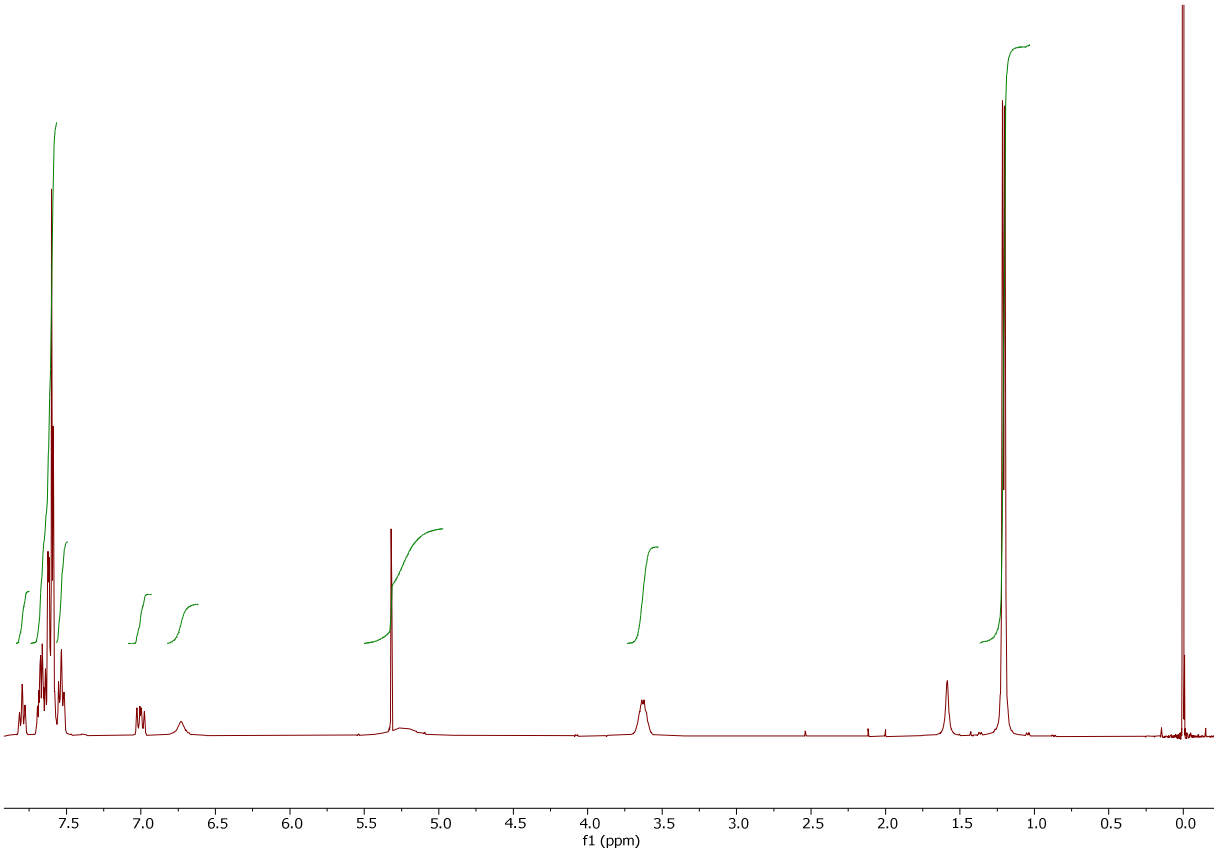

Figure S34 ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **7b**

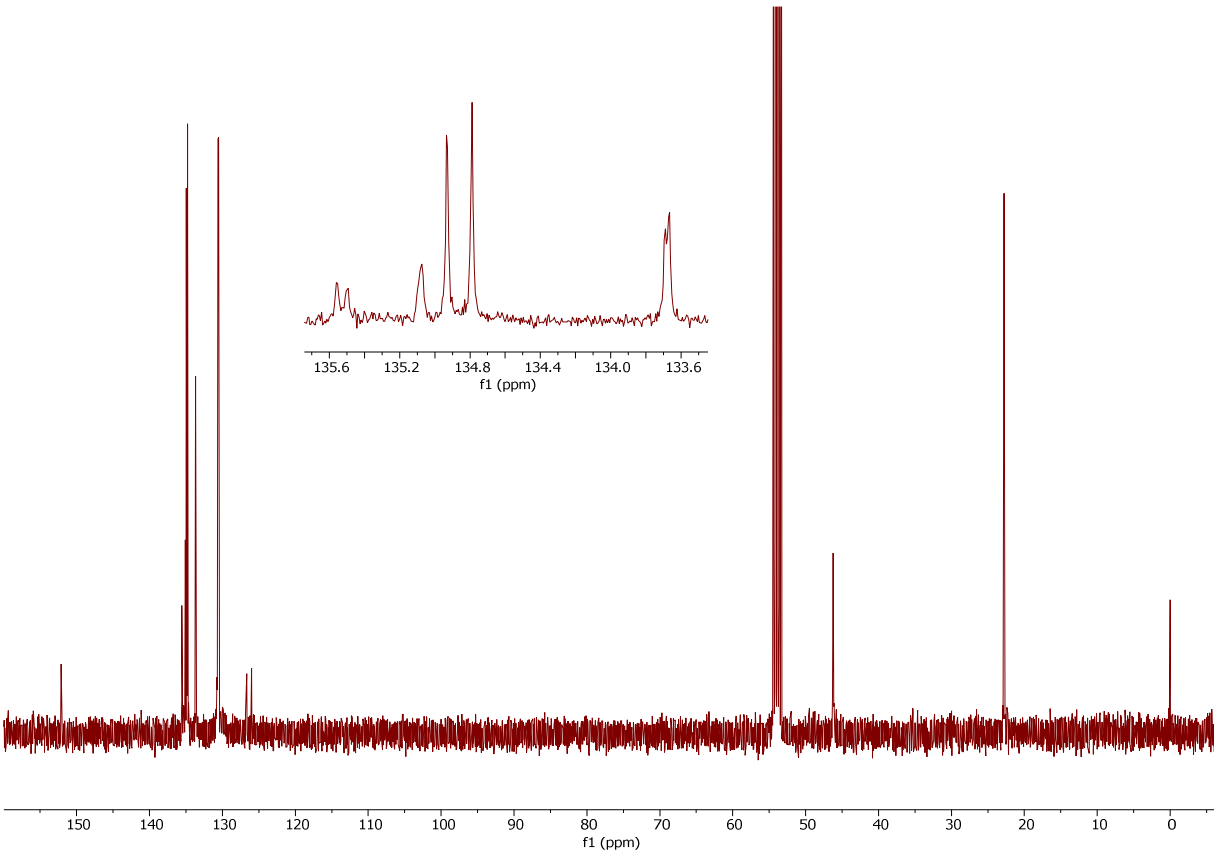

Figure S35 $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 101 MHz) of **7b**

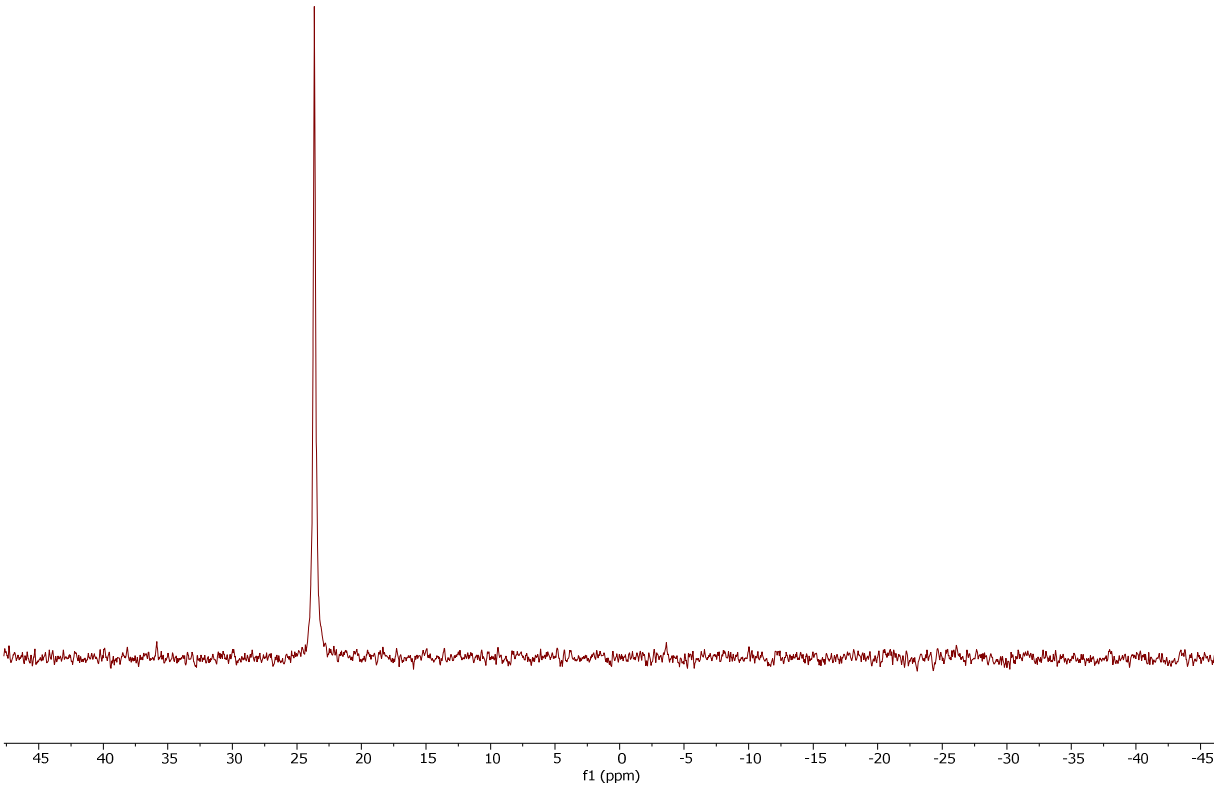

Figure S36 $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 162 MHz) of **7b**