Electronic Supplementary Material (ESI) for Dalton Transactions

Synthesis and structural characterisation of Pd(II) and Pt(II) complexes with a flexible, ferrocene-based P,S-donor amidophosphine ligand

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Supporting Information

Contents

Description of the crystal packing for 1 and 1O

In the crystal, the molecules of **1** assemble into infinite chains by means of cooperative N–H···O=C and C–H···O=C hydrogen bonds formed between the molecules associated around the crystallographic glide planes (space group $P2_1/c$; Figure S1). Phosphine oxide **1O** forms an intramolecular N–H···O=C hydrogen bond (see main text) and its solid-state assembly is based on the soft C–H···X (X = O, S, N) interactions.

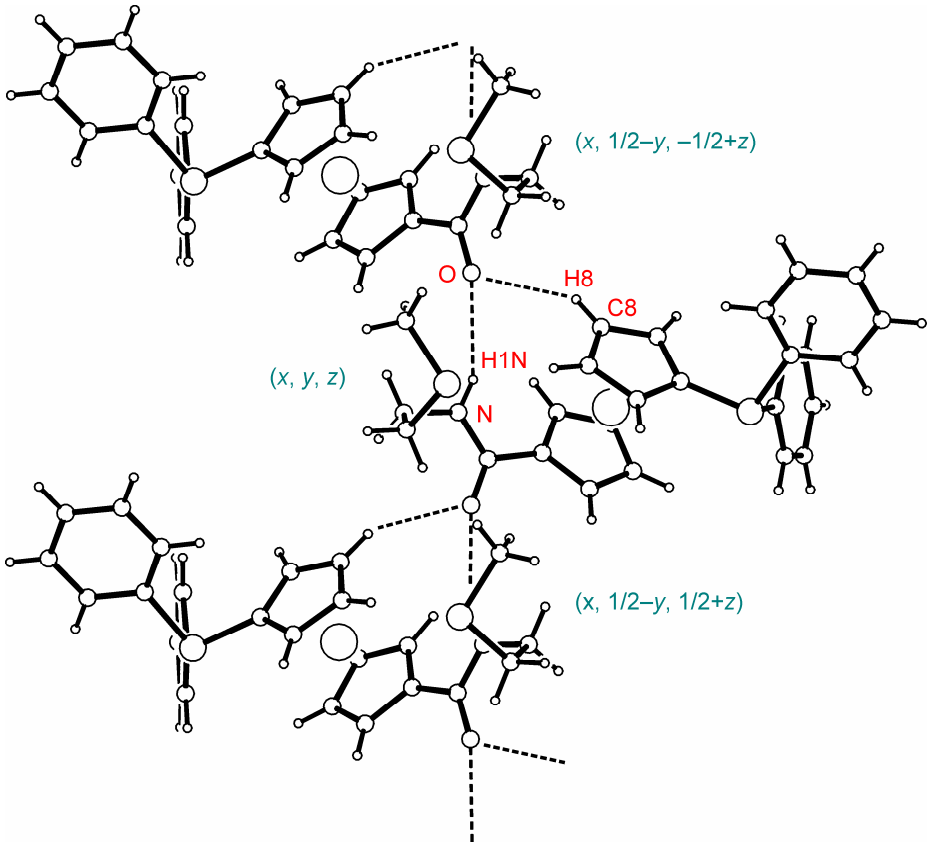


Figure S1 Section of the infinite hydrogen bonded chain in the structure of phosphine **1** showing the cooperating hydrogen bonds as dashed lined. The H-bond parameters are as follows: N–H1N···O, N···O = 3.339(2) Å, angle at H1N = 153°; C8–H8···O, C8···O = 3.392(2) Å, angle at H8 = 144°.

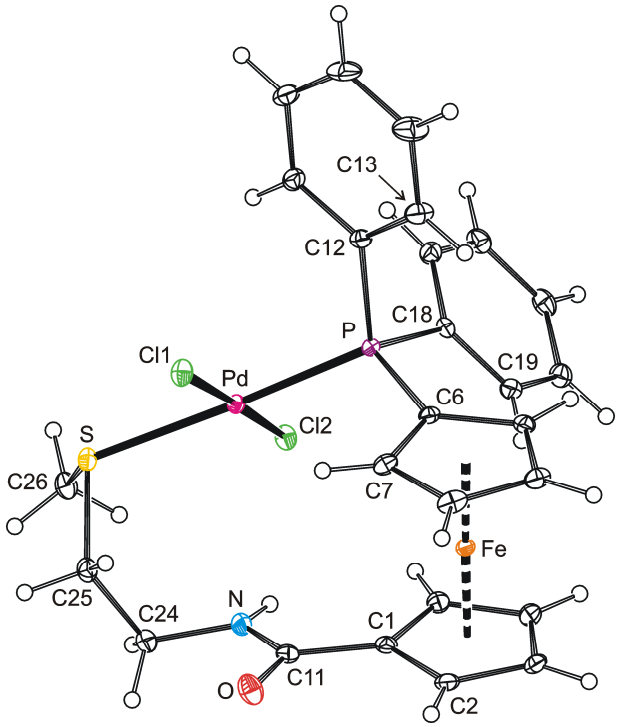
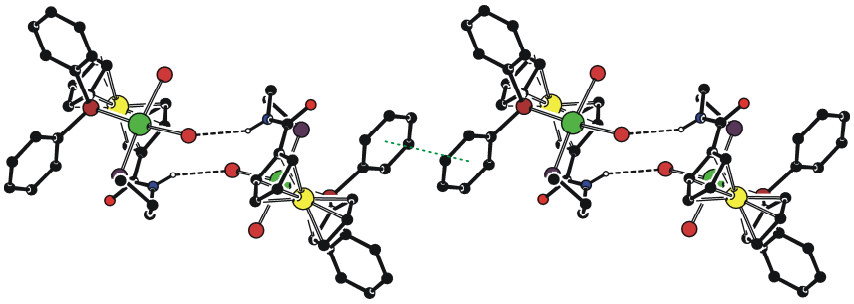


Figure S2 View of complex molecule in the crystal structure of *trans*-**2**·½H_2O with atomic labels and displacement ellipsoids at the 30% probability level.

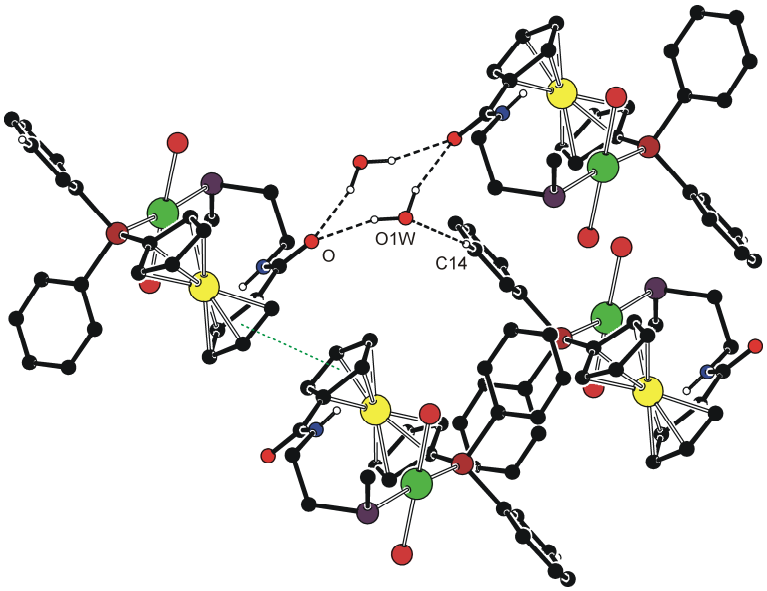
Description of the crystal packing of *cis*-3, *trans*-2·½H_2O and *trans*-3·½CH_3CO_2Et

In the crystal state, the molecules of *cis*-**3** associate into centrosymmetric dimers via N–H1N···Cl1 hydrogen bonds (N···Cl = 3.258(2) Å). These dimers further assemble into infinite via offset π···π stacking interactions of the inversion-related phenyl rings C(18-23) at the centroid-centroid distance of 3.860(1) Å. Chlorine atom Cl2 forms some additional intermolecular C-H···Cl contacts.



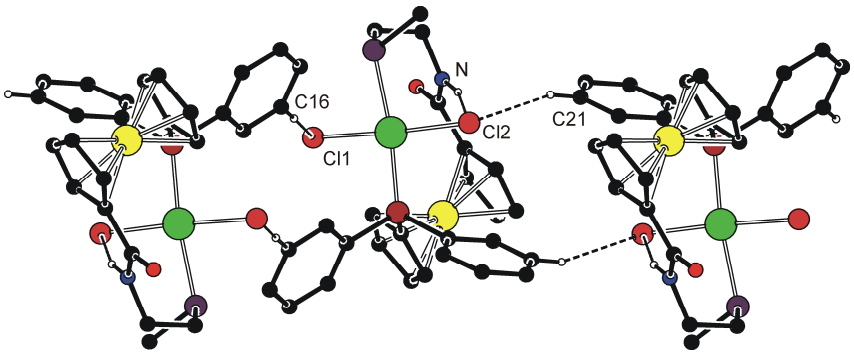
H-bonds (black dashed lines) and π···π interactions (green dashed lines) in the structure of *cis*-**3**.

The structure of *trans*-**2**·½H_2O contains water molecules that are disordered over two equally populated positions in structural voids. These molecules play an important role in the crystal array, linking two adjacent complex molecules via the O1W–H1W···O and O1W–H2W···O hydrogen bonds (O···O1W: 2.917(4) and 2.816(4) Å). In addition, the water oxygen act as a H-bond acceptor for an aromatic CH group (C14-H14···O1W, C14···O1W = 3.441(4) Å). A π···π interaction is detected between the proximal cyclopentadienyl rings C(1-5) (centroid distance: 3.940(1) Å). The NH proton does not enter into any intermolecular interactions.



H-bonds (black dashed lines) and π···π interactions (green dashed lines) in the structure of *tran*-**2**·½H_2O. Note that the water molecules have 50% occupancies, lying across the crystallographic inversion centres.

The molecules of complex *trans*-**3**·½CH_3CO_2Et form hydrogen bonds in which the Cl2 atom behaves as a bifurcate H-bond acceptor, namely in the *intra*molecular N–H1N···Cl2 and *inter*molecular C20-H20····Cl2 interactions. Atom Cl1 is involved in hydrogen bonding towards C16-H16. H-bond lengths are as follows: N···Cl2 = 3.535(2) Å, C20···Cl2 = 3.707(3) Å, C16···Cl1 = 3.751(3) Å. The solvating ethyl acetate is disordered in structural voids left between the bulky complex molecules.



The principal hydrogen bonding interactions in the structure of *trans*-**3**·½CH_3CO_2Et.

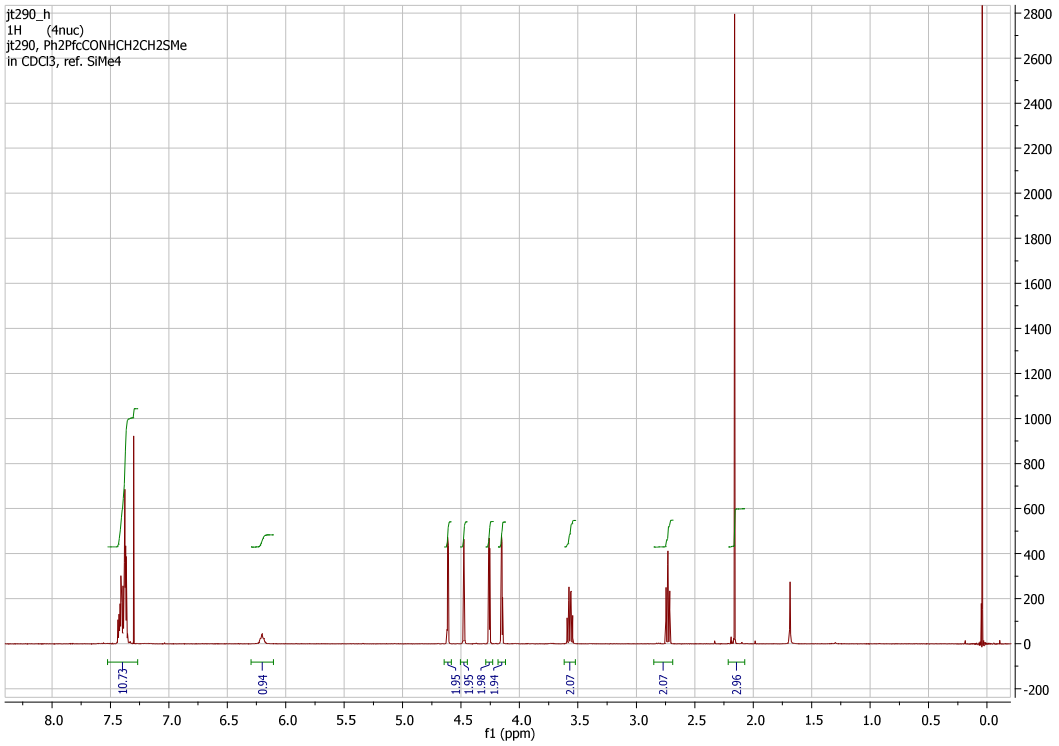
Table S1 Summary of crystallographic data and structure refinement parameters.[a]

Compound	**1**	**1O**	*trans*-**2**·½H_2O	*trans*-**3**·½CH_3CO_2Et	*cis*-**3**
Formula	$C_{26}H_{26}FeNOPS$	$C_{26}H_{26}FeNO_2PS$	$C_{26}H_{27}Cl_2FeNO_{1.5}PPdS$	$C_{28}H_{30}Cl_2FeNO_2PPtS$	$C_{26}H_{26}Cl_2FeNOPPtS$
M	487.36	503.36	673.67	797.40	753.35
Crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	8.3665(2)	10.5814(4)	9.4362(3)	9.397(1)	8.7438(2)
b/Å	24.8131(6)	11.0866(4)	10.7177(3)	10.905(1)	10.5637(2)
c/Å	11.1353(3)	11.8118(4)	14.0579(4)	15.384(2)	14.1431(3)
α/°	90	69.962(1)	109.416(1)	95.995(4)	91.953(1)
β/°	99.135(1)	64.830(1)	107.291(1)	102.319(4)	90.081(1)
γ/°	90	81.931(1)	90.302(1)	113.710(4)	99.957(1)
V/Å^3	2282.4(1)	1178.16(7)	1271.70(6)	1377.9(3)	1285.89(5)
Z	4	2	2	2	2
D_c/g mL^{-1}	1.418	1.419	1.759	1.922	1.946
μ(Mo Kα)/mm^{-1}	0.841	0.820	1.656	5.953	6.370
Diffractions collected	39428	16356	19504	20413	21895
Independent/obsd[b] diffrns	5253/4635	5129/4407	5815/5447	6309/5977	5907/5621
R_{int}[c]/%	2.88	3.21	1.81	1.97	1.98
R[c] observed diffrns/%	3.39	3.87	1.89	1.64	1.51
R, *wR*[c] all data/%	4.03, 8.81	4.77, 11.5	2.11, 4.59	1.85, 3.47	1.67, 3.22
Δρ/e Å^{-3}	1.19,[e] –0.66	1.11,[f] –0.55	0.35,–0.57	0.76, –0.54	0.57, –0.38
CCDC reference no.	962382	962383	962384	962386	962385

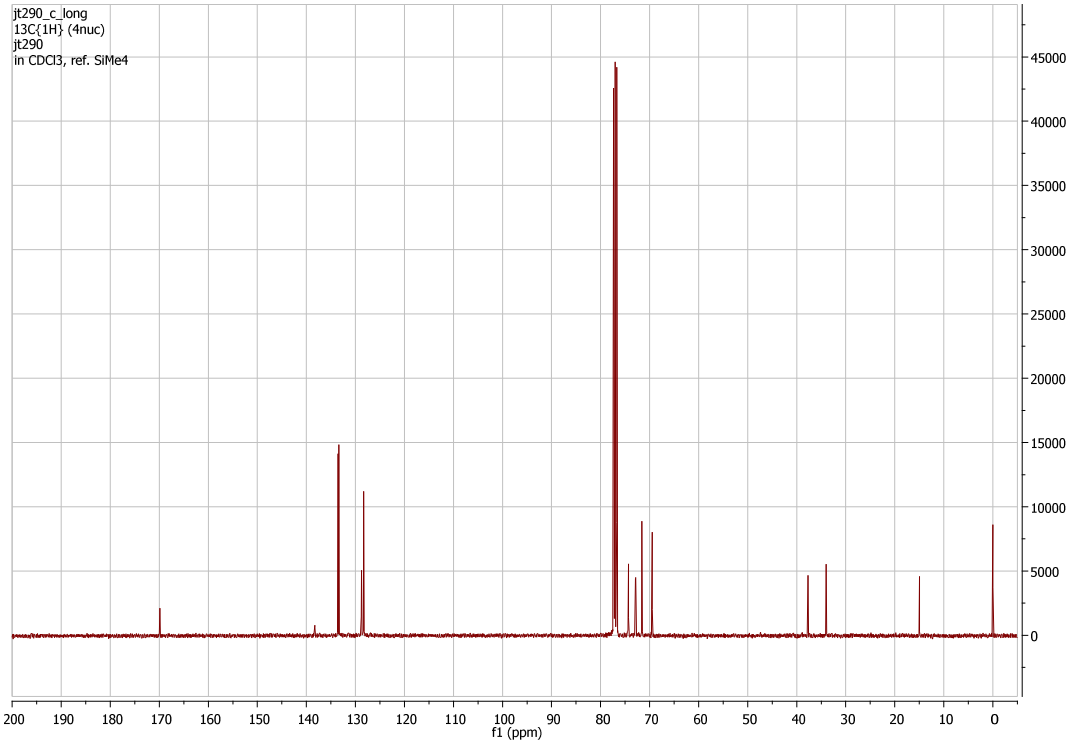
[a] Common details: $T = 150(2)$ K. [b] Diffractions with $I > 2\sigma(I)$. [c] Definitions: $R_{int} = \Sigma\left|F_o^2 - F_o^2(\text{mean})\right|/\Sigma F_o^2$, where F_o^2(mean) is the average intensity of symmetry-equivalent diffractions. $R = \Sigma\left|\left|F_o\right| - \left|F_c\right|\right|/\Sigma\left|F_o\right|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\, w(F_o^2)^2]^{1/2}$. [e] Residual electron density attributable to the lone electron pair at phosphorus atom. [f] Residual electron density near the iron atom.

NMR spectra

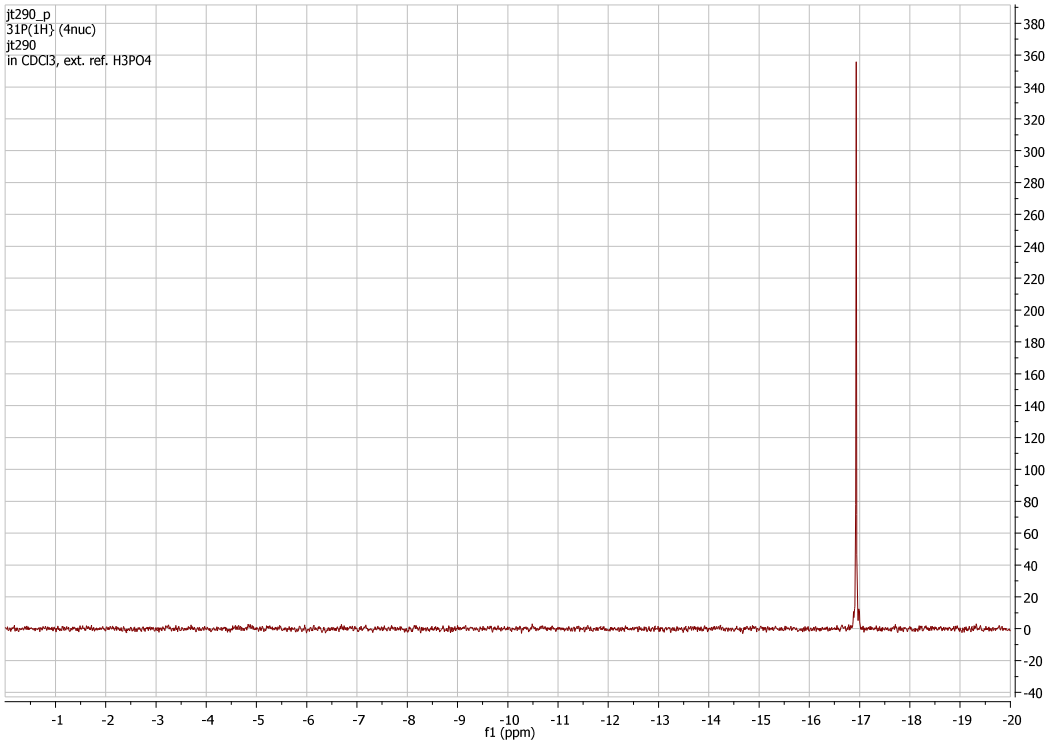
^{1}H NMR spectrum of **1**



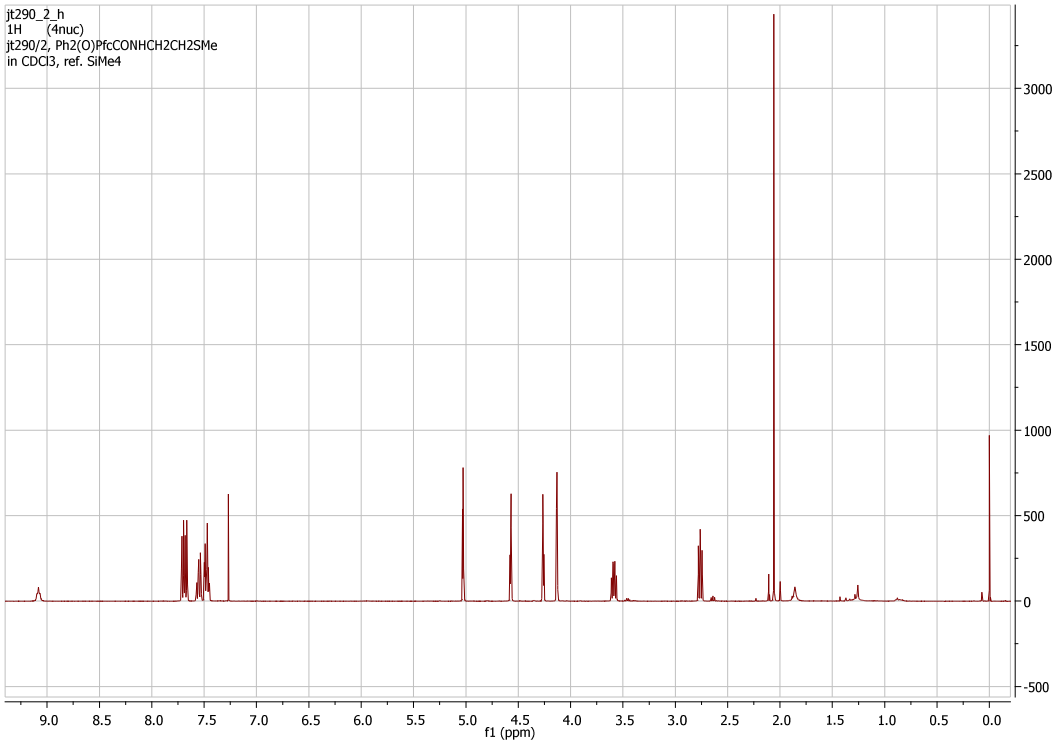
^{13}C{^{1}H} NMR spectrum of **1**



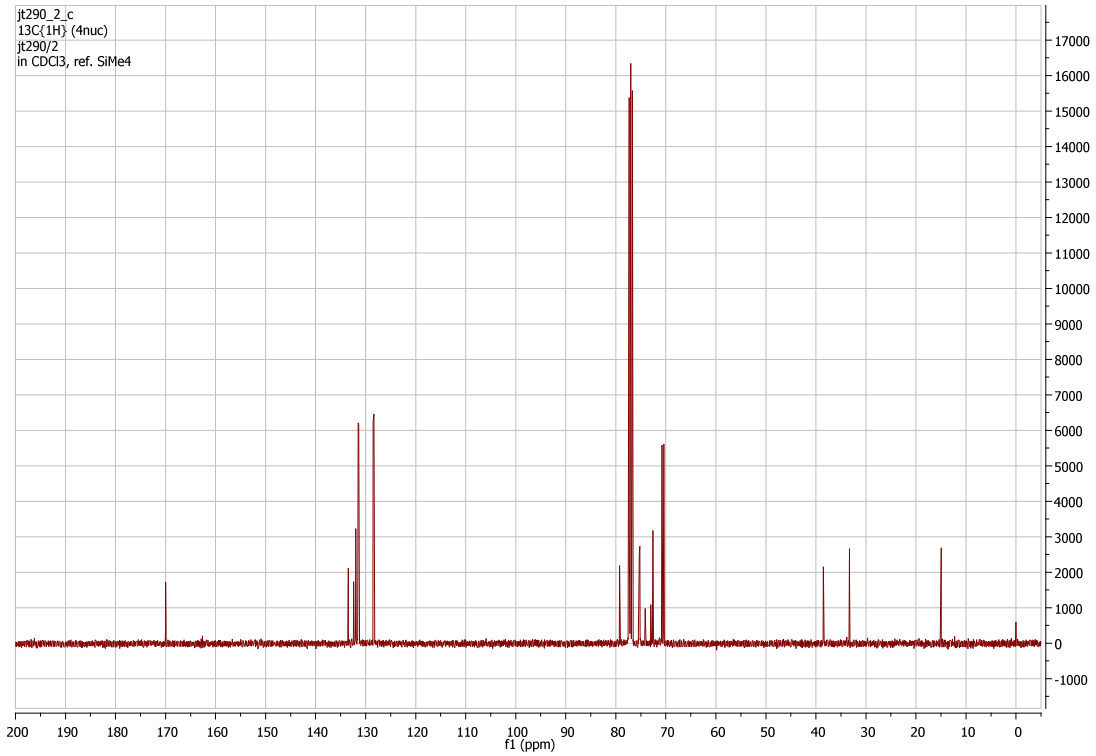
$^{31}P\{^{1}H\}$ NMR spectrum of **1**



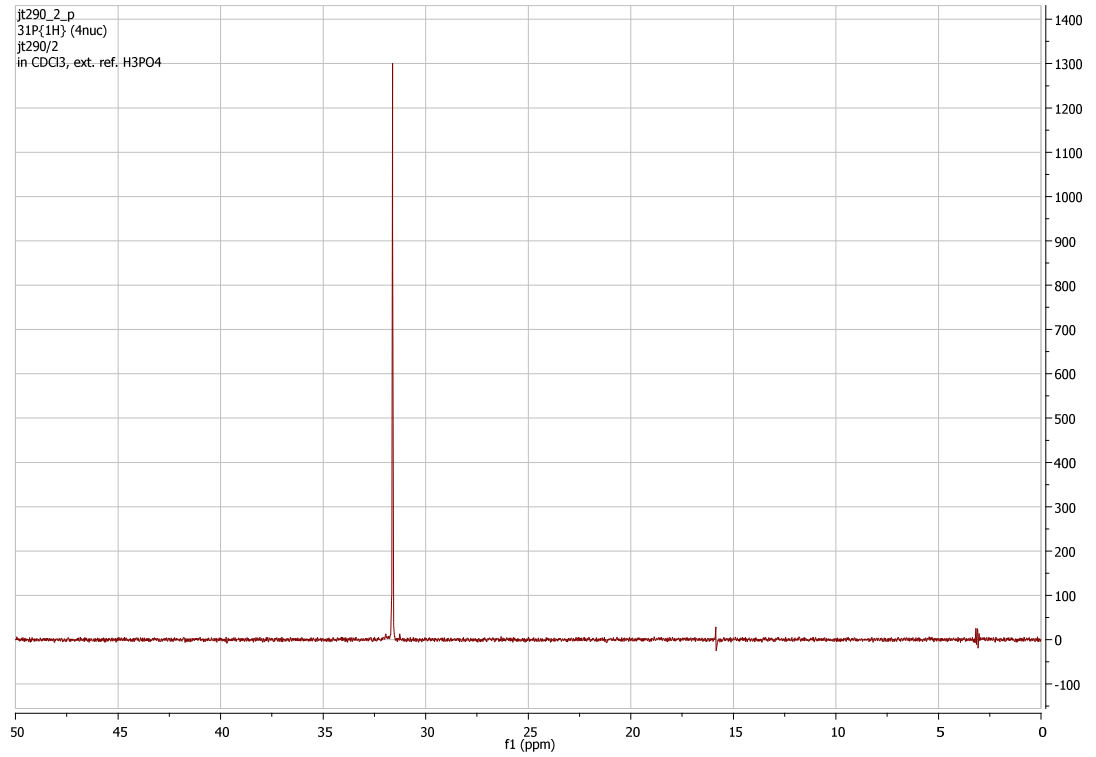
^{1}H NMR spectrum of **1O**



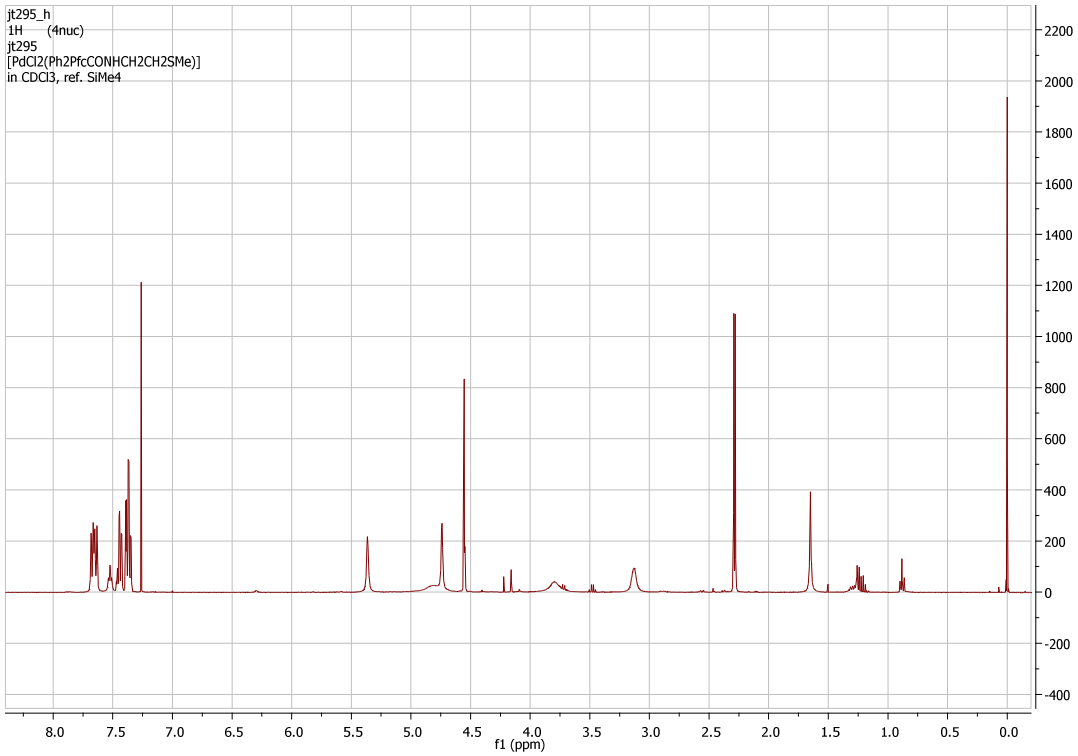
$^{13}C\{^{1}H\}$ NMR spectrum of **1O**



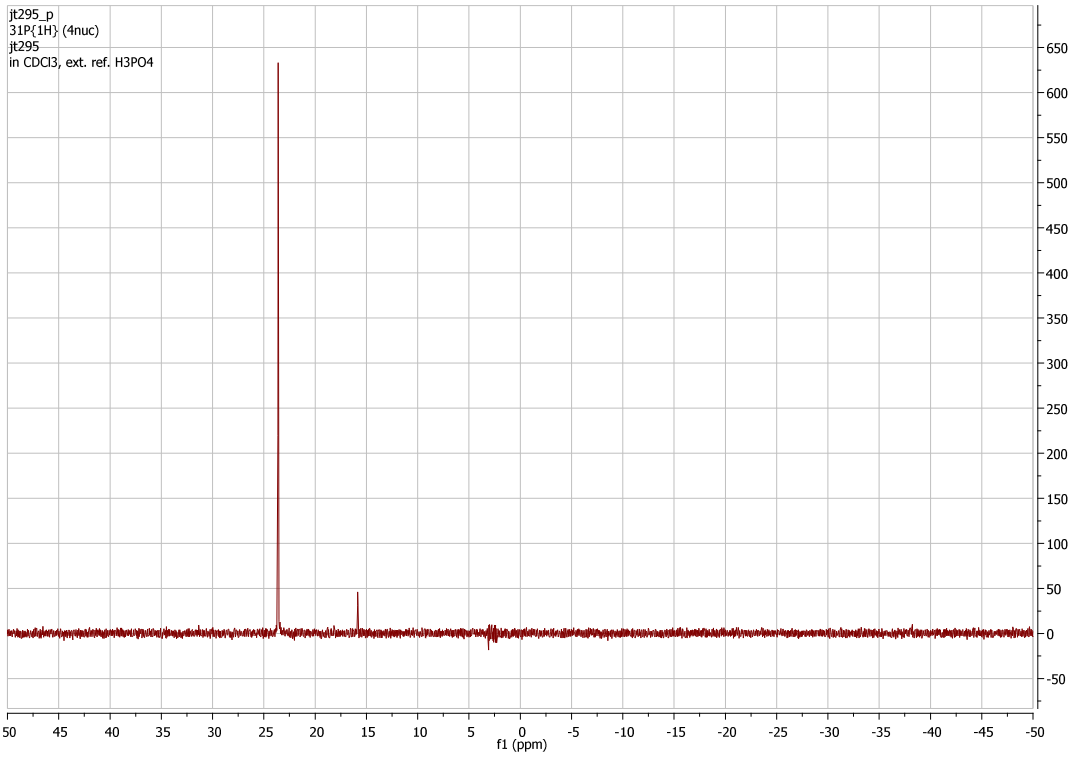
$^{31}P\{^{1}H\}$ NMR spectrum of **1O**



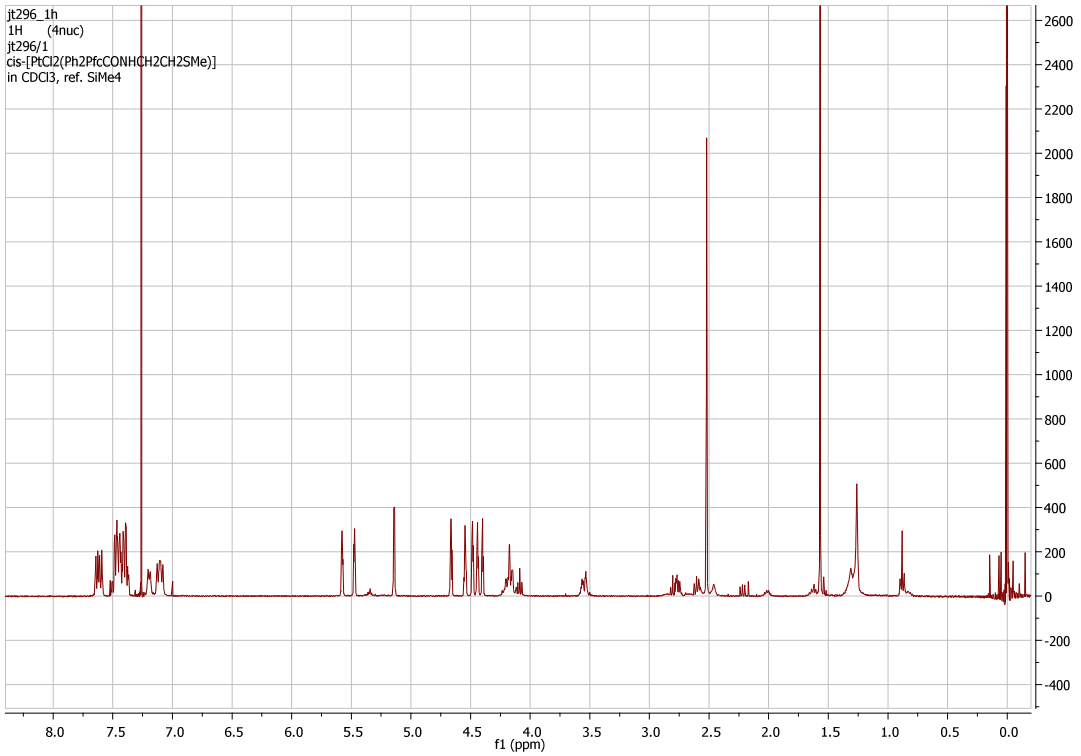
^{1}H NMR spectrum of *trans*-**2**



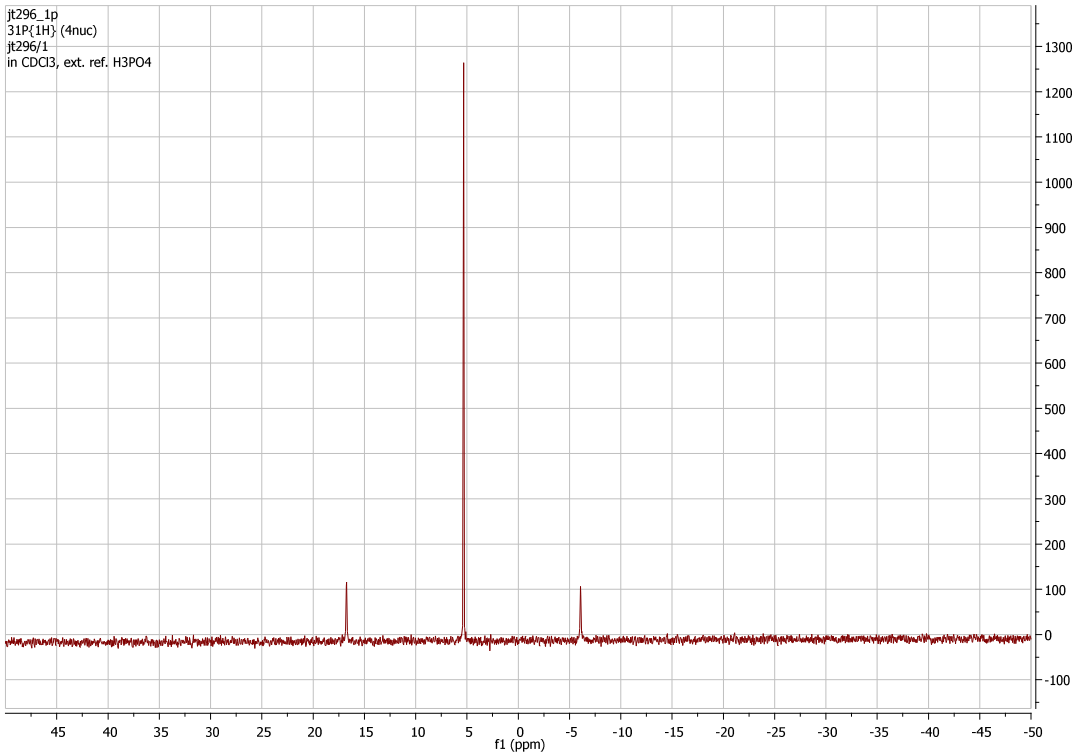
^{31}P{^{1}H} NMR spectrum of *trans*-**2**



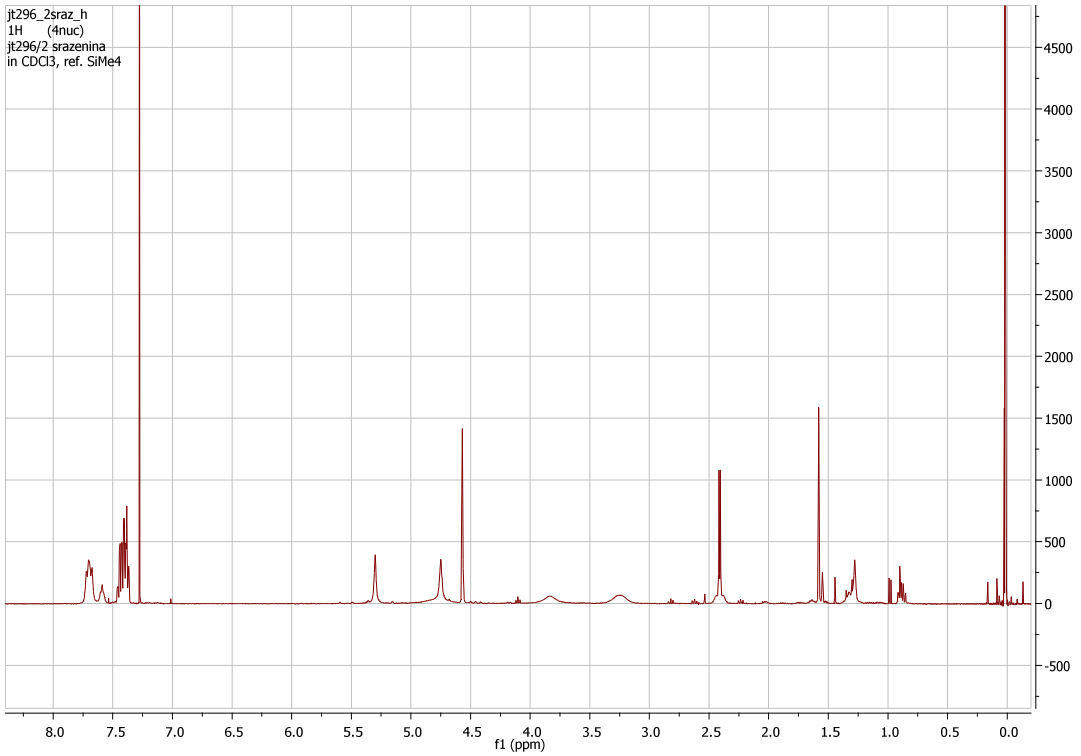
^{1}H NMR spectrum of *cis*-**3**



^{31}P{^{1}H} NMR spectrum of *cis*-**3**



^{1}H NMR spectrum of *trans*-**3**



^{31}P{^{1}H} NMR spectrum of *trans*-**3**