Supplementary data for

Diacylthioureas – an overlooked class of ligands; the coordination chemistry of diacylated thiourea with platinum(II) palladium(II) and gold(III).

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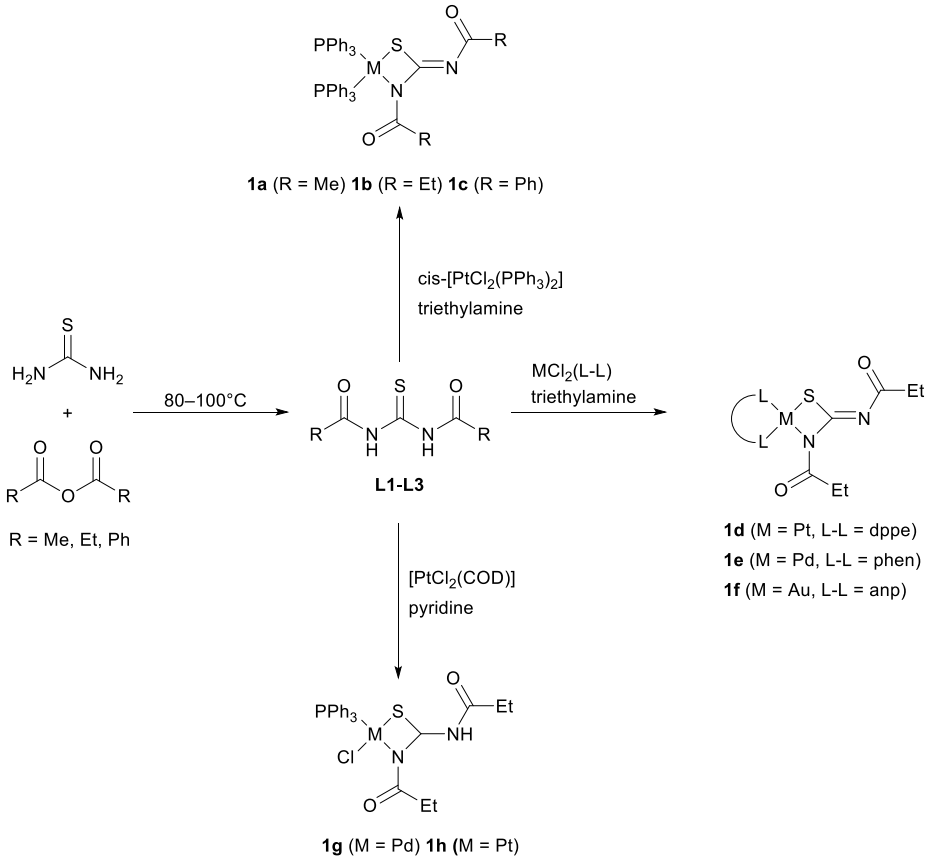

Scheme S1: Full reaction scheme for the complexes and ligands prepared in this study.

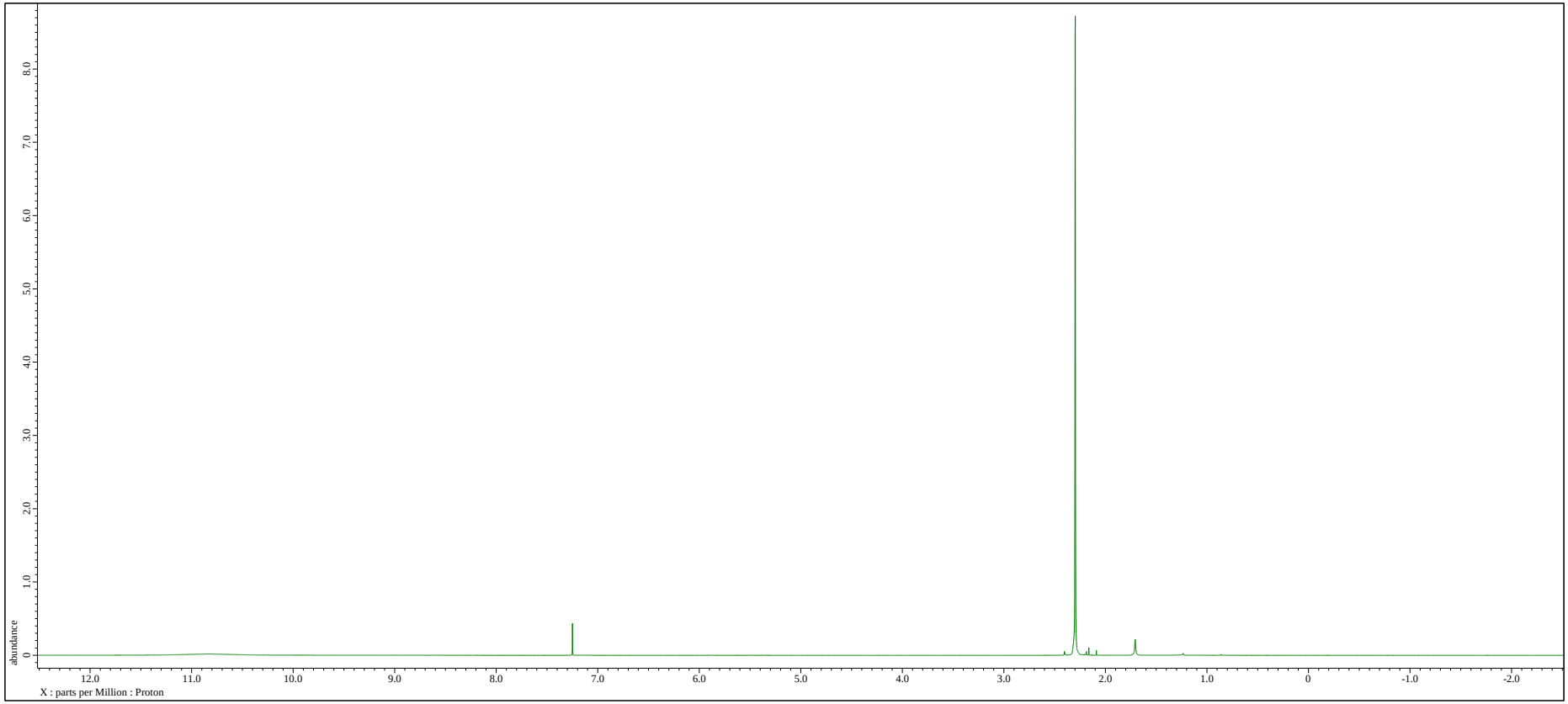

Figure S1: ^{1}H NMR spectrum of ligand **L1**

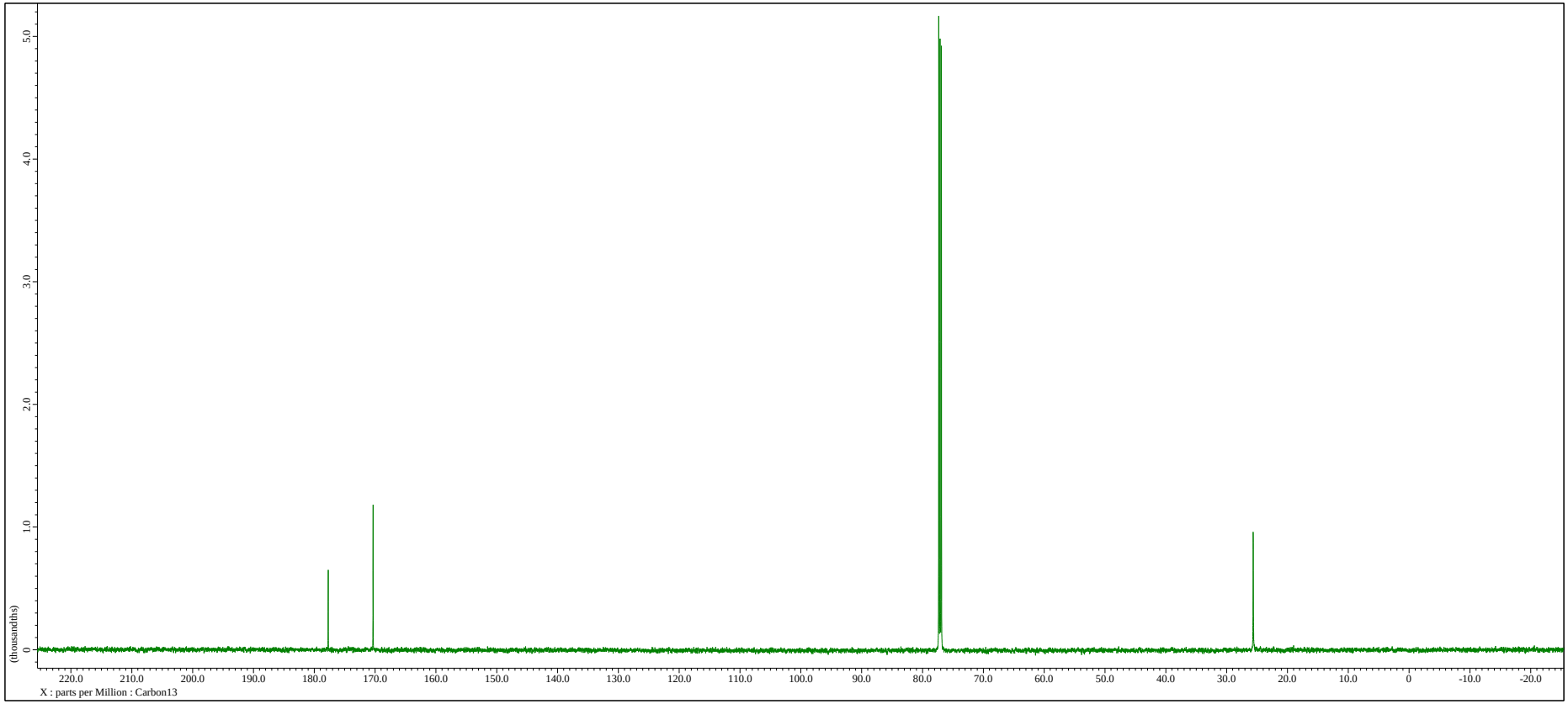

Figure S2: ^{13}C NMR spectrum of ligand **L1**

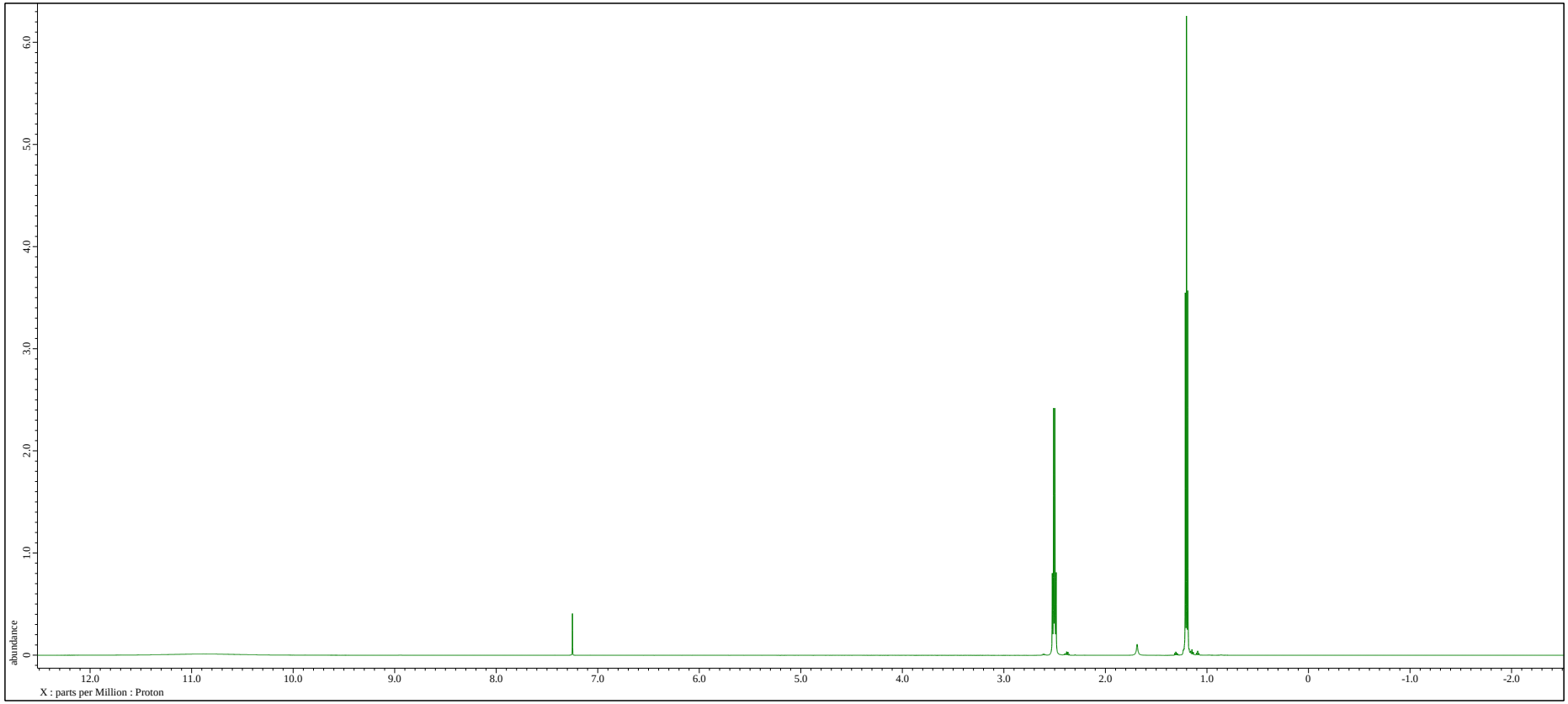

Figure S3: ^{1}H NMR spectrum of ligand **L2**

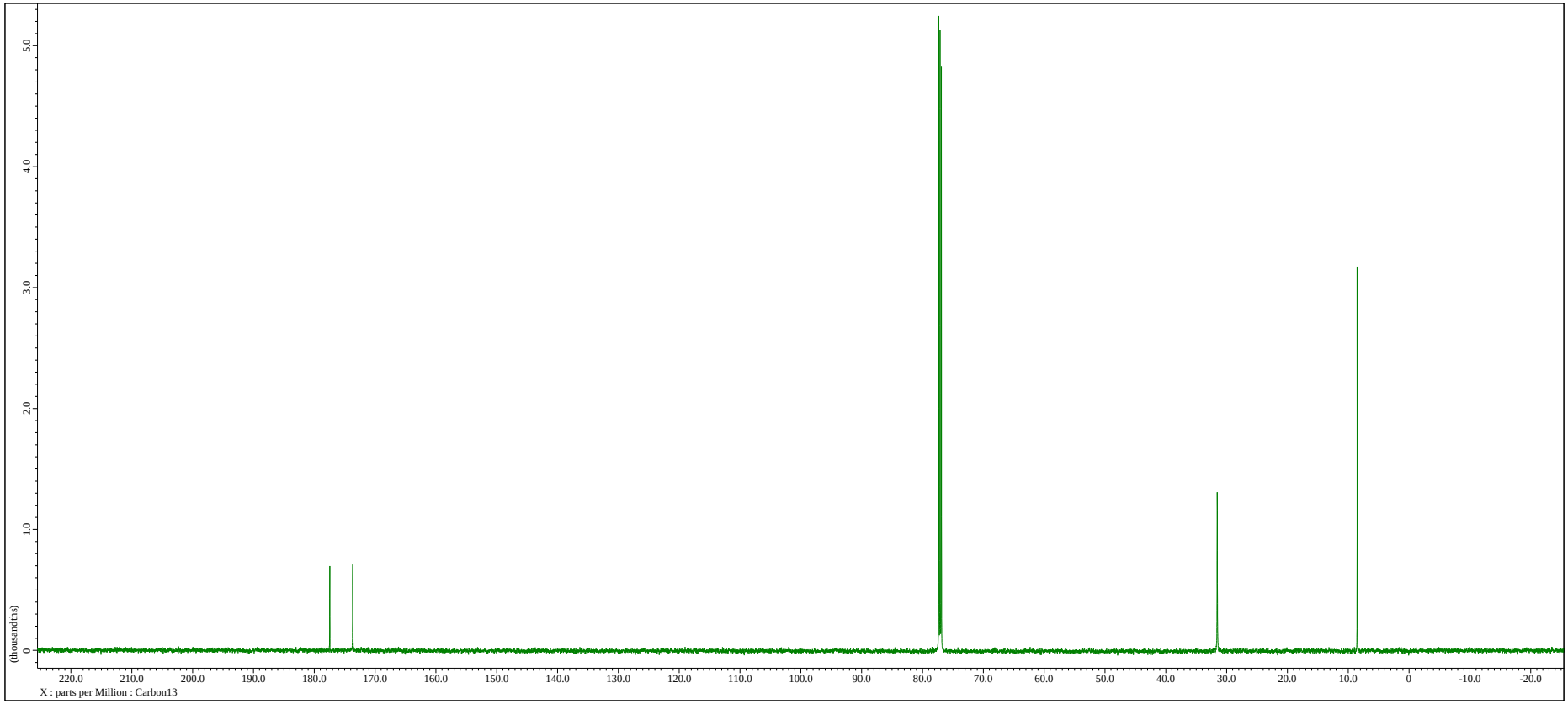

Figure S4: ^{13}C NMR spectrum of ligand **L2**

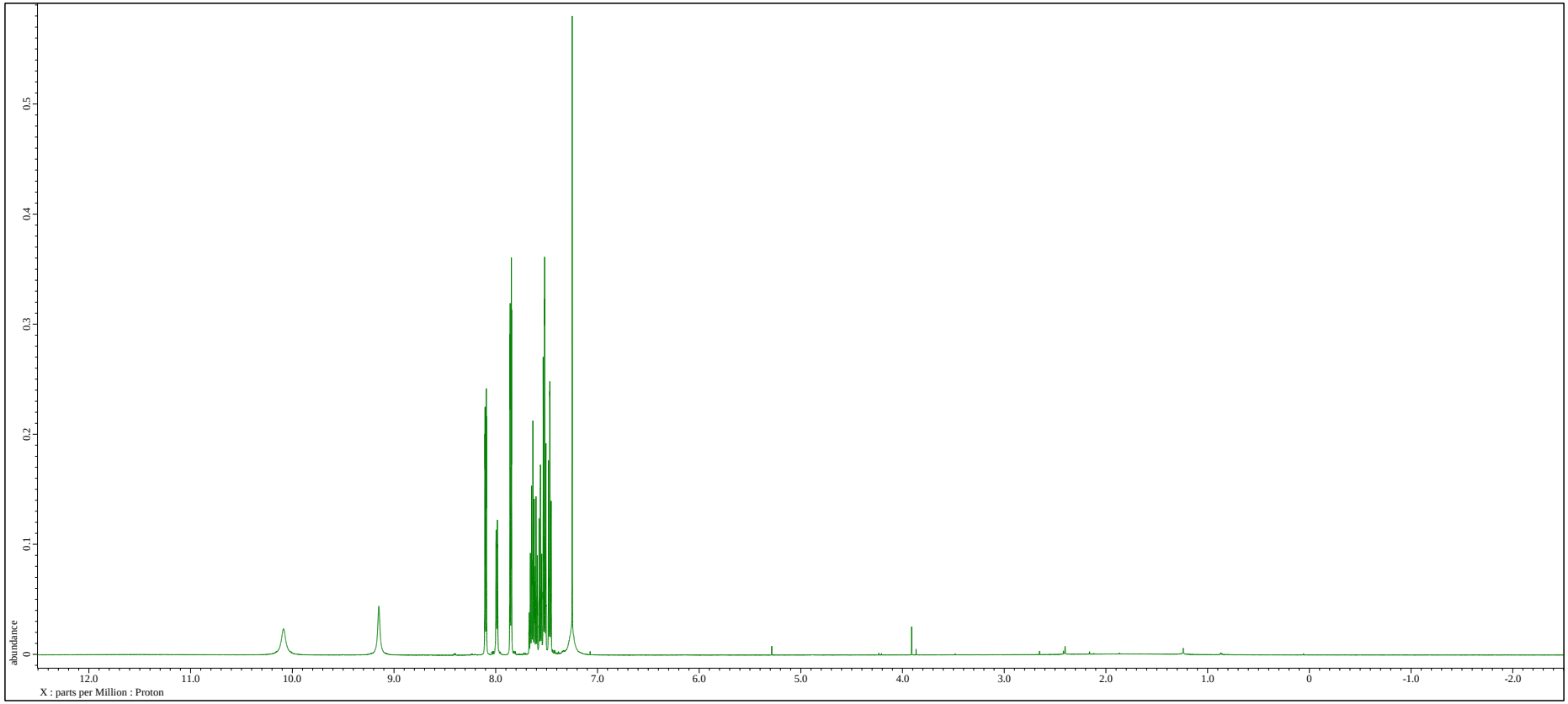

Figure S5: ^{1}H NMR spectrum of ligand **L3**

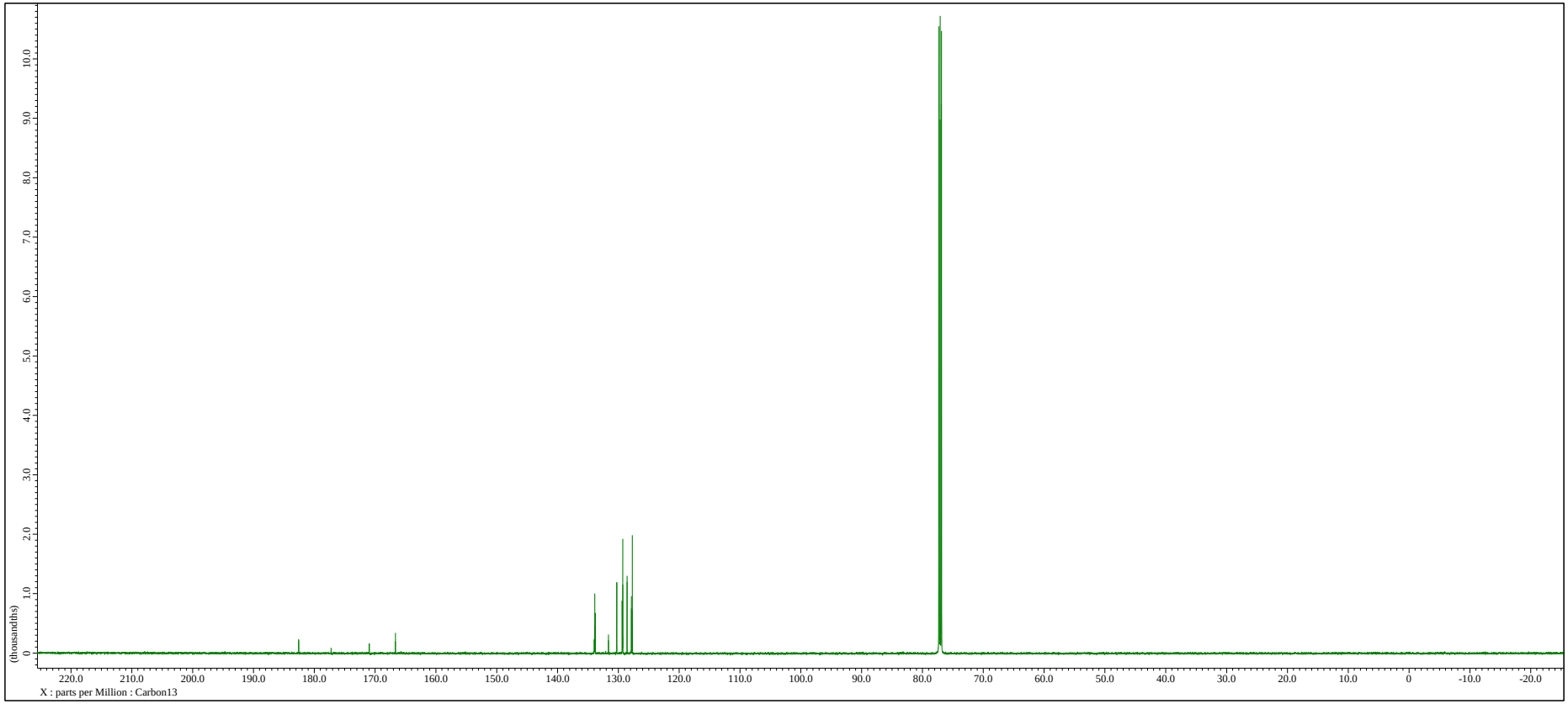

Figure S6: ^{13}C NMR spectrum of ligand **L3**

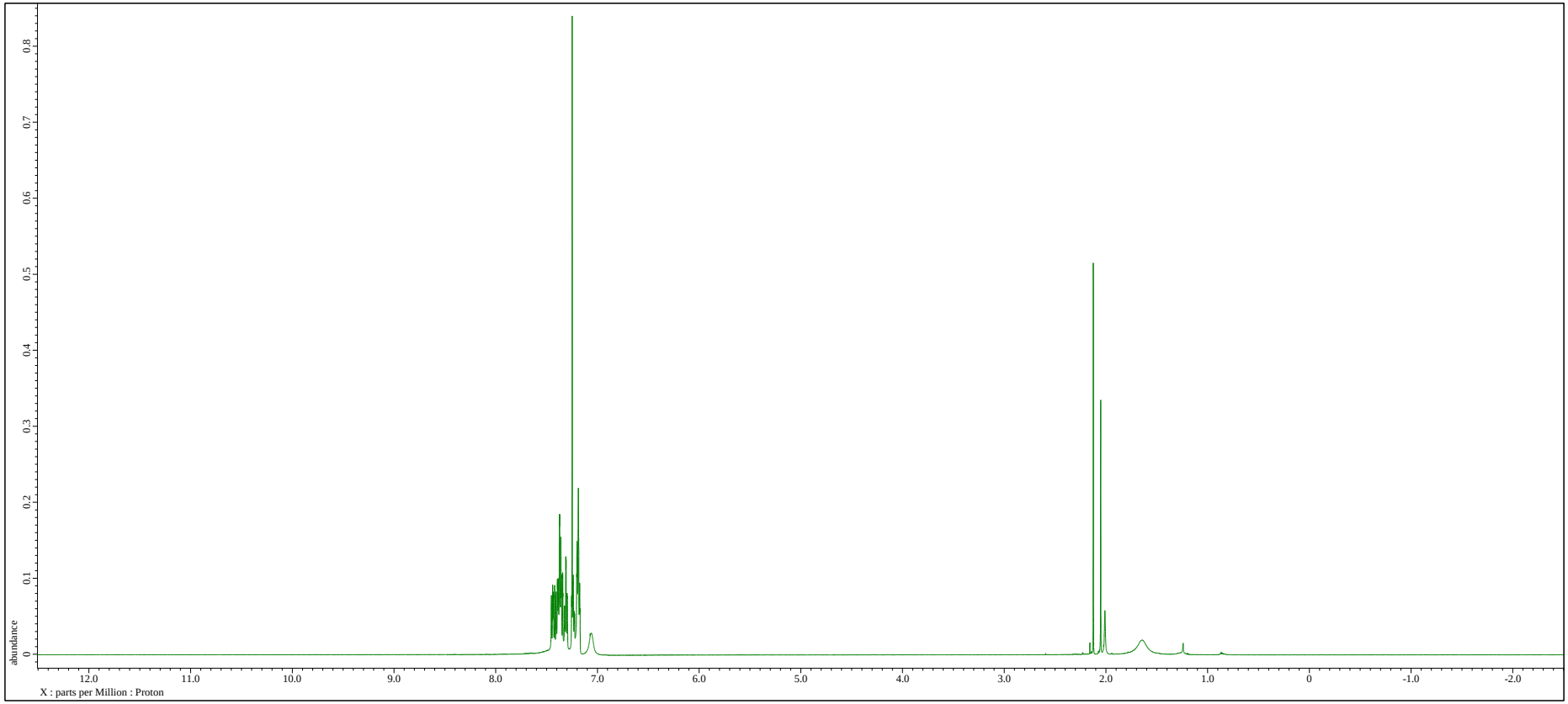

Figure S7: ^{1}H NMR spectrum of complex **1a**

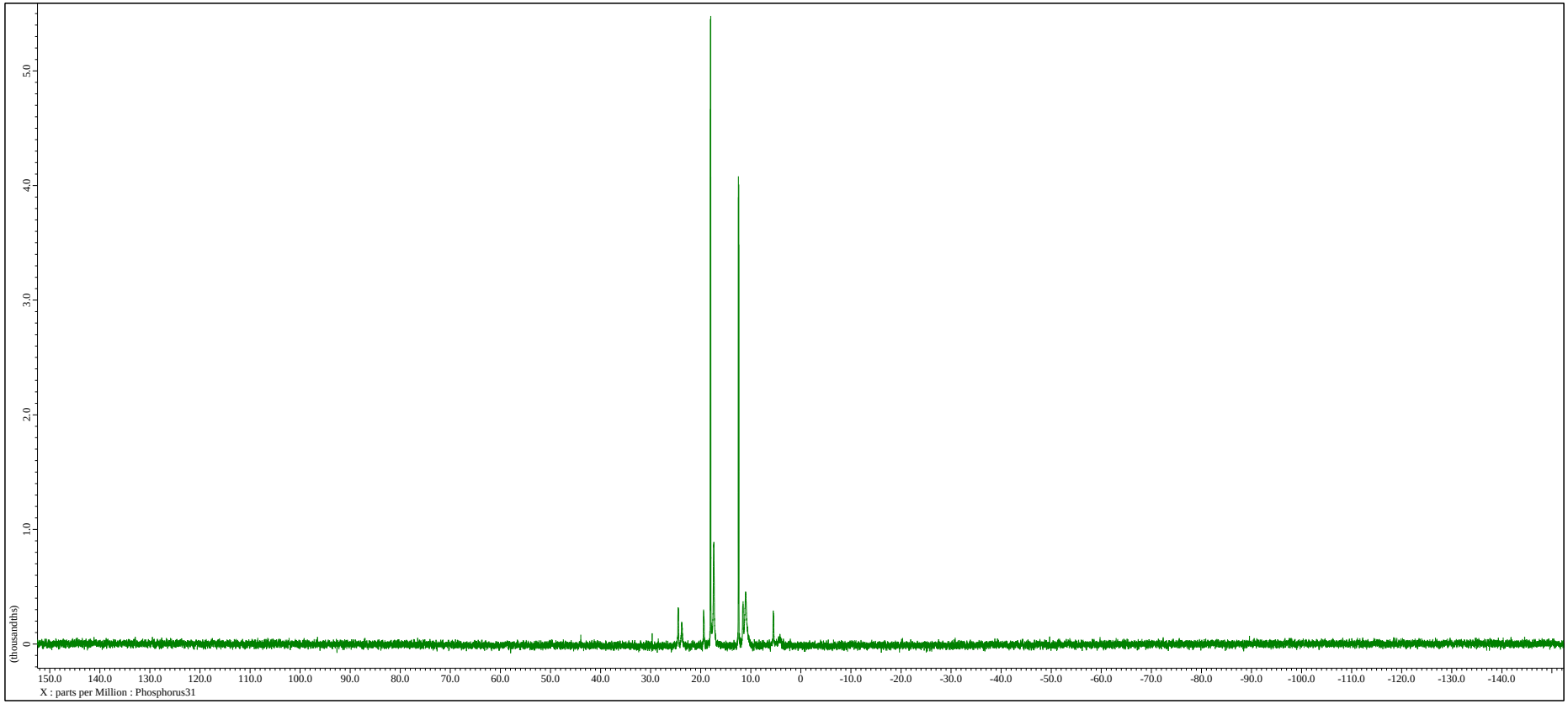

Figure S8: $^{31}P\{^{1}H\}$ NMR spectrum of complex **1a**

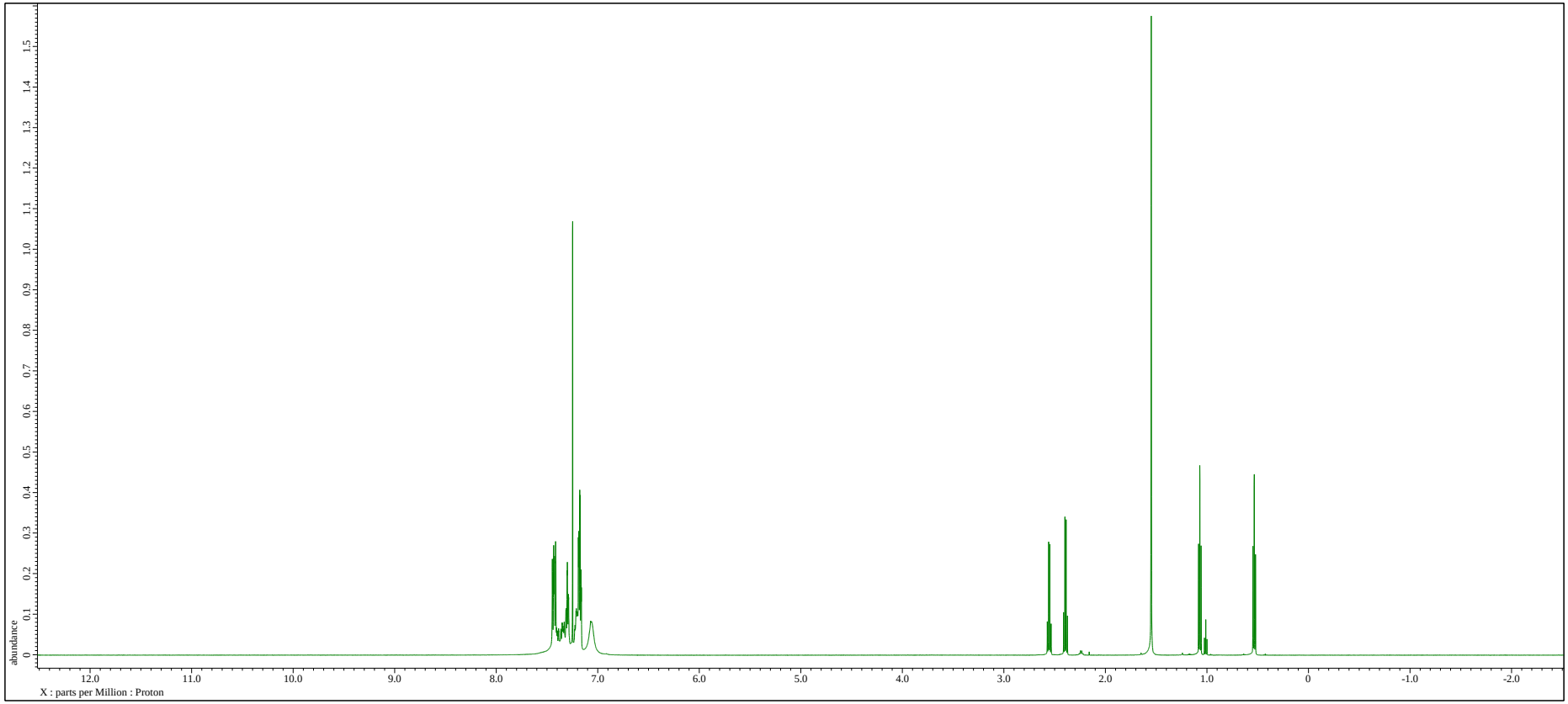

Figure S9: ^{1}H NMR spectrum of complex **1b**

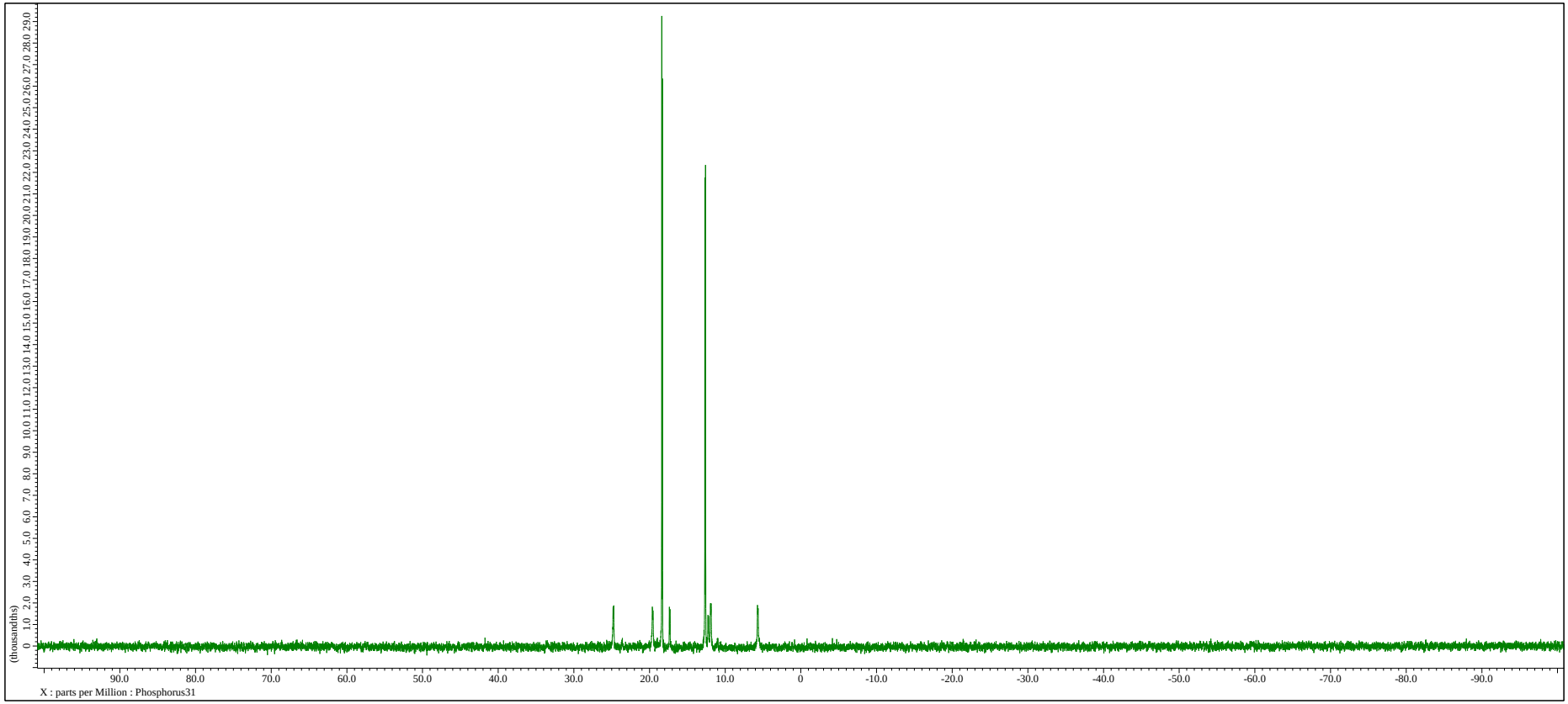

Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum of complex **1b**

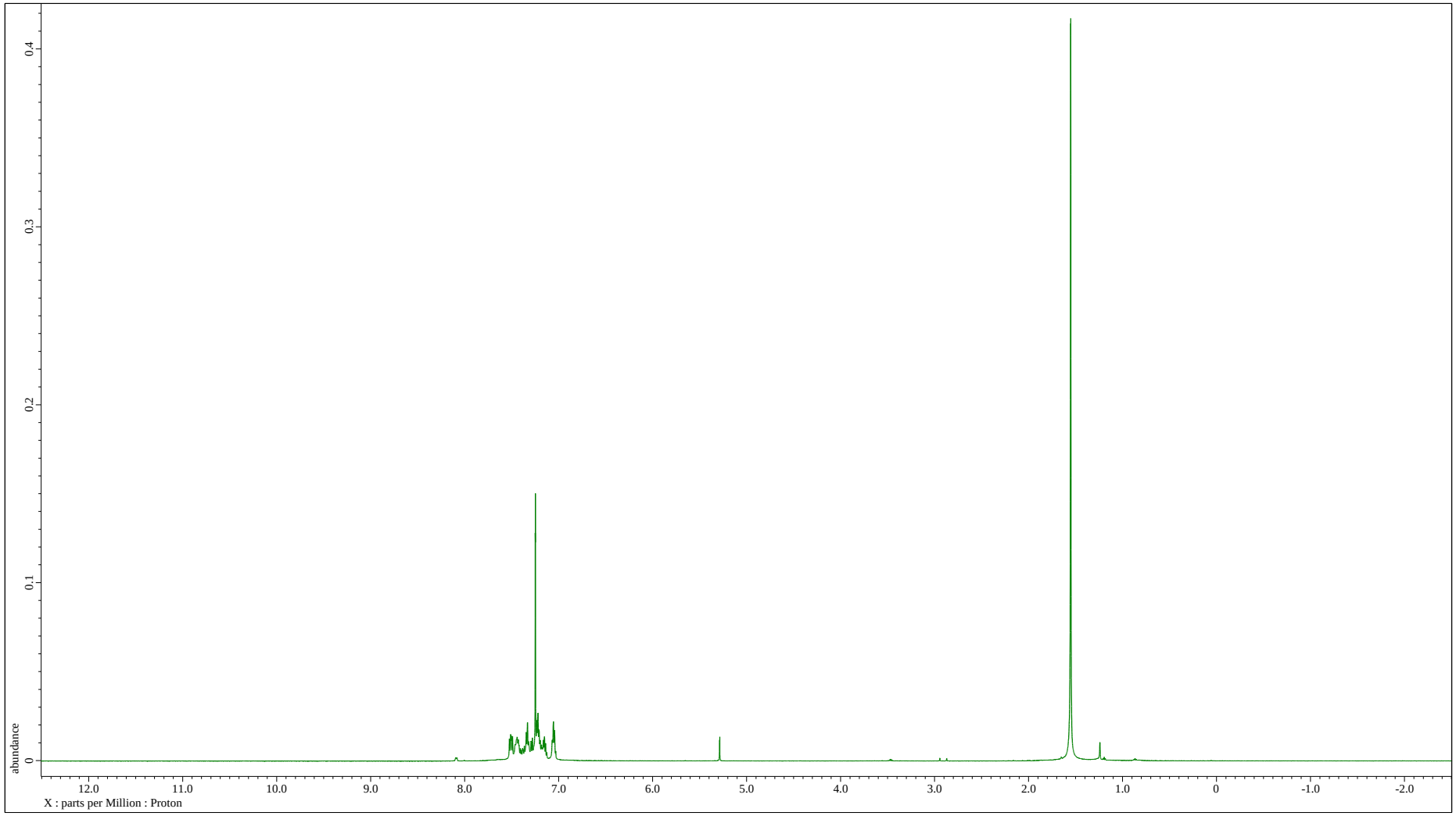

Figure S11: ^{1}H NMR spectrum of complex **1c**

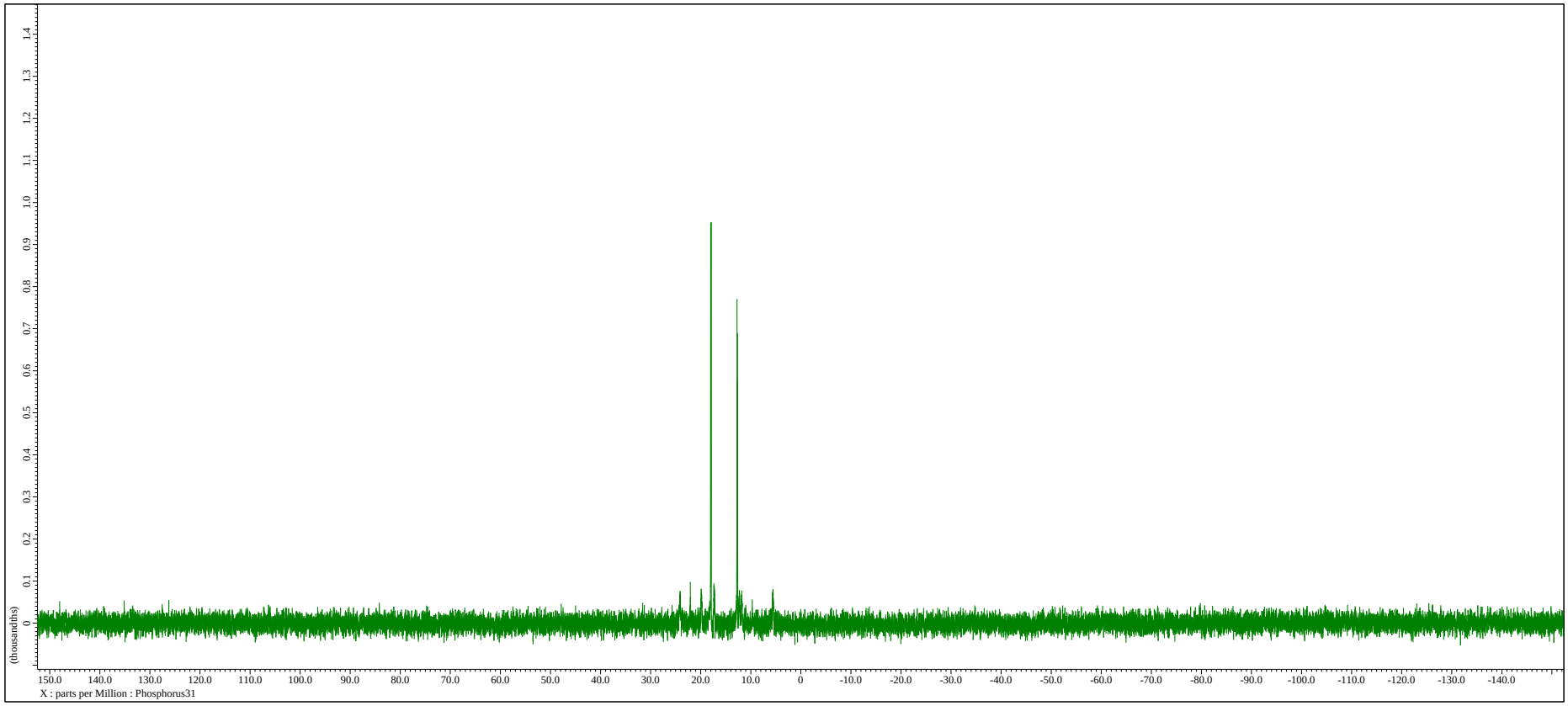

Figure S12: $^{31}P\{^{1}H\}$ NMR spectrum of complex **1c**

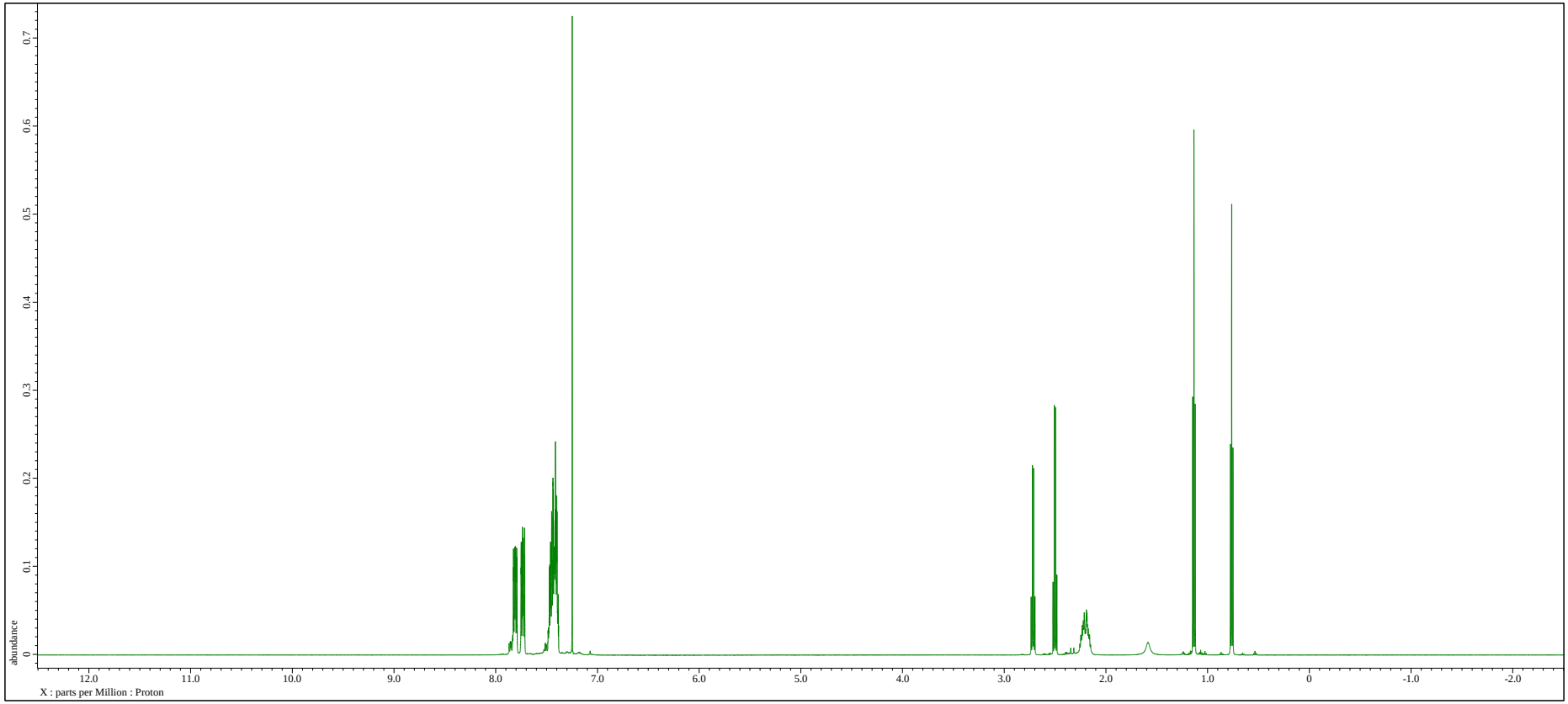

Figure S13: ^{1}H NMR spectrum of complex **1d**

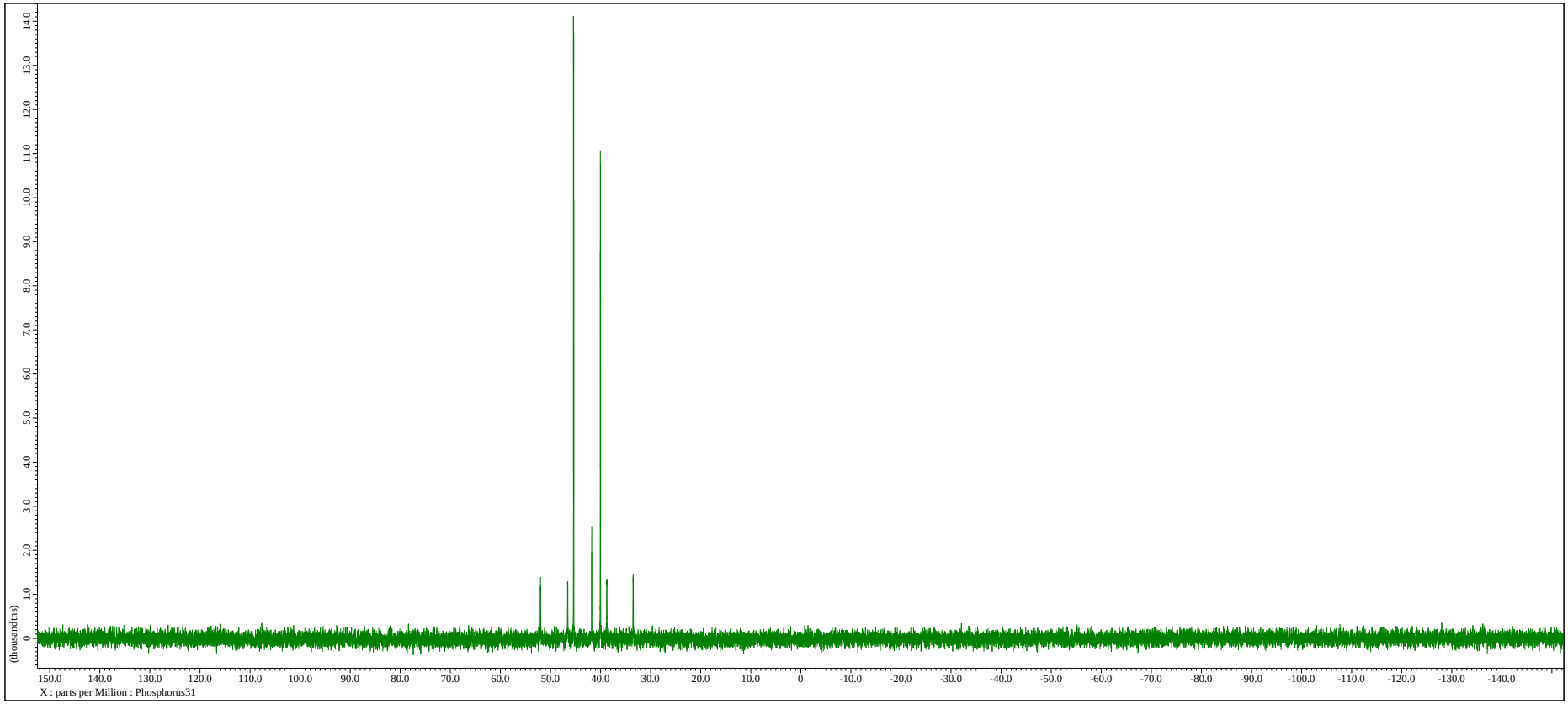

Figure S14: $^{31}P\{^{1}H\}$ NMR spectrum of complex **1d**

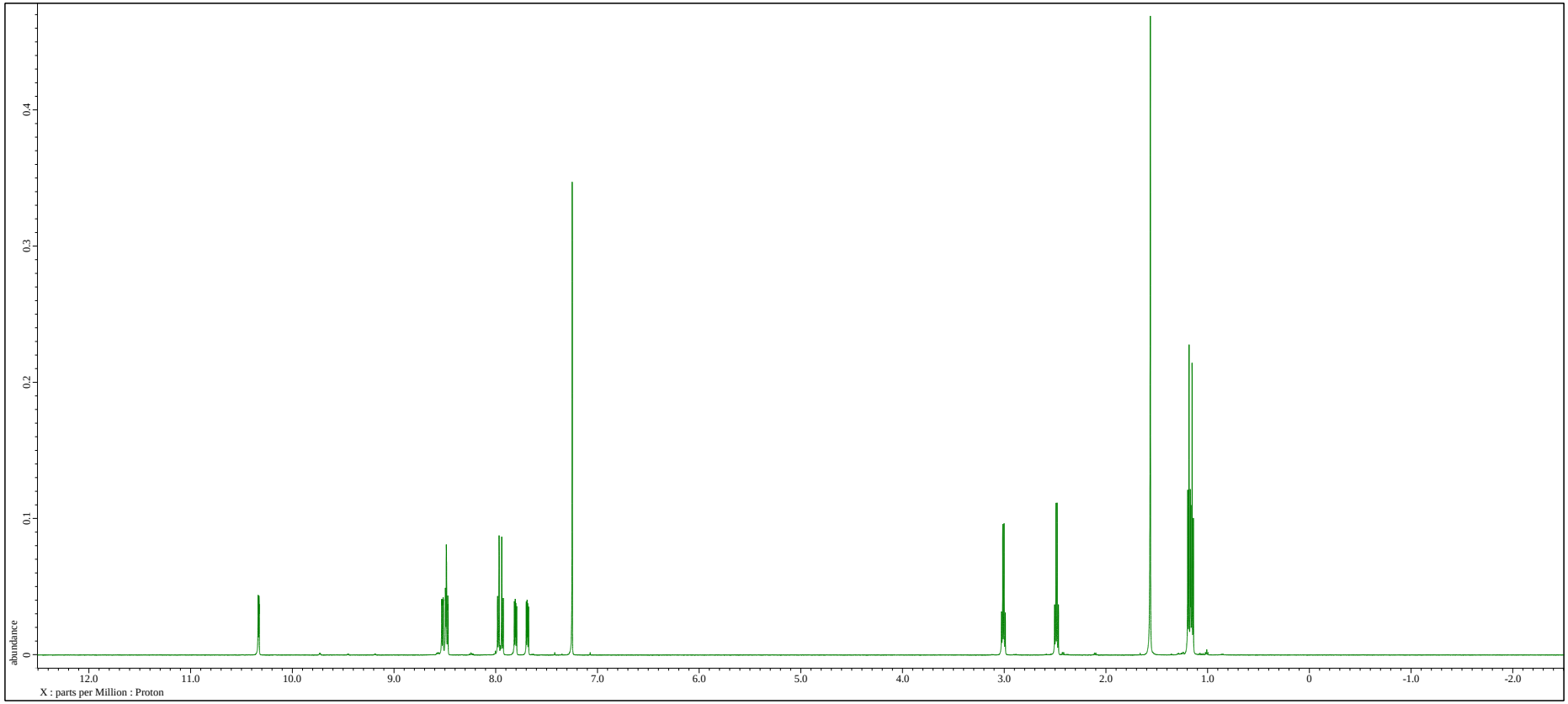

Figure S15: ^{1}H NMR spectrum of complex **1e**

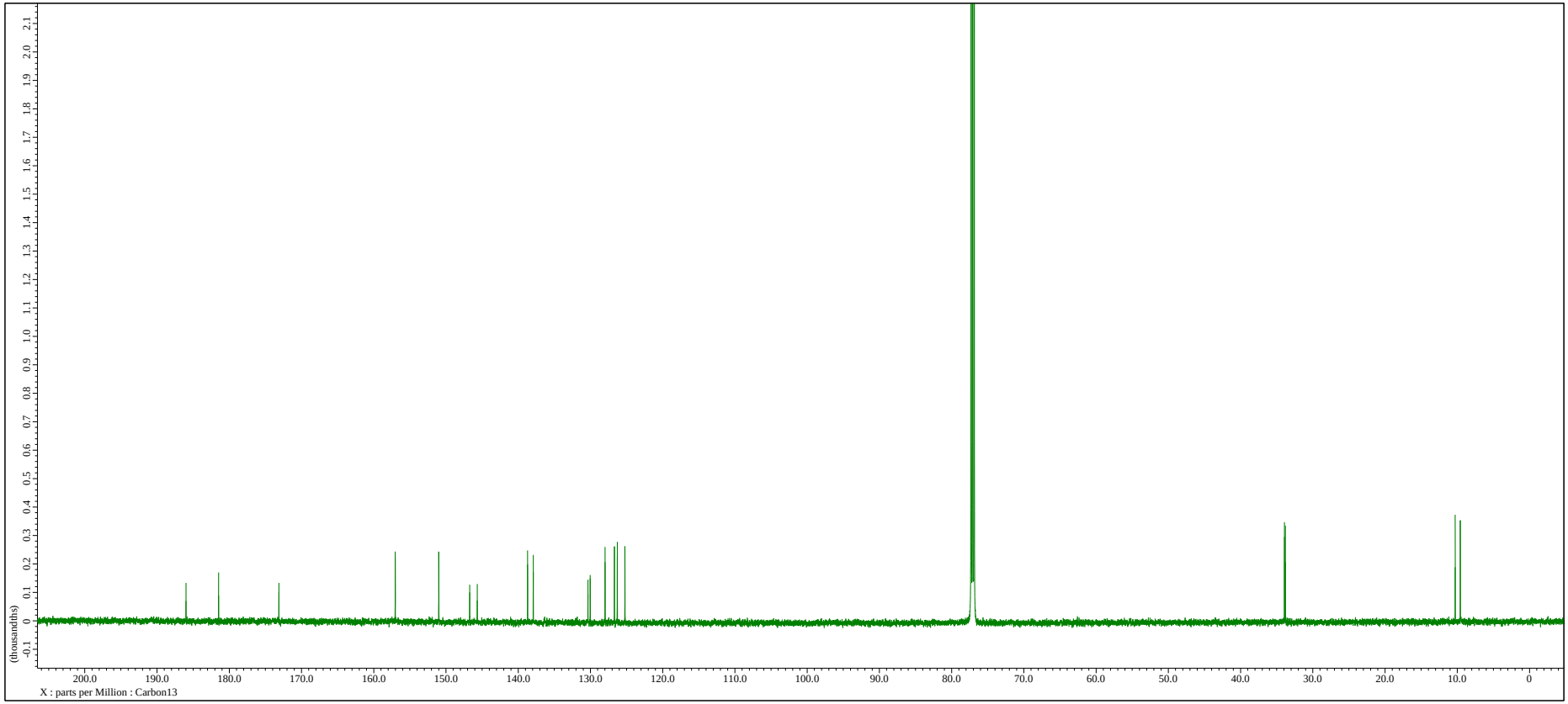

Figure S16: ^{13}C NMR spectrum of complex **1e**

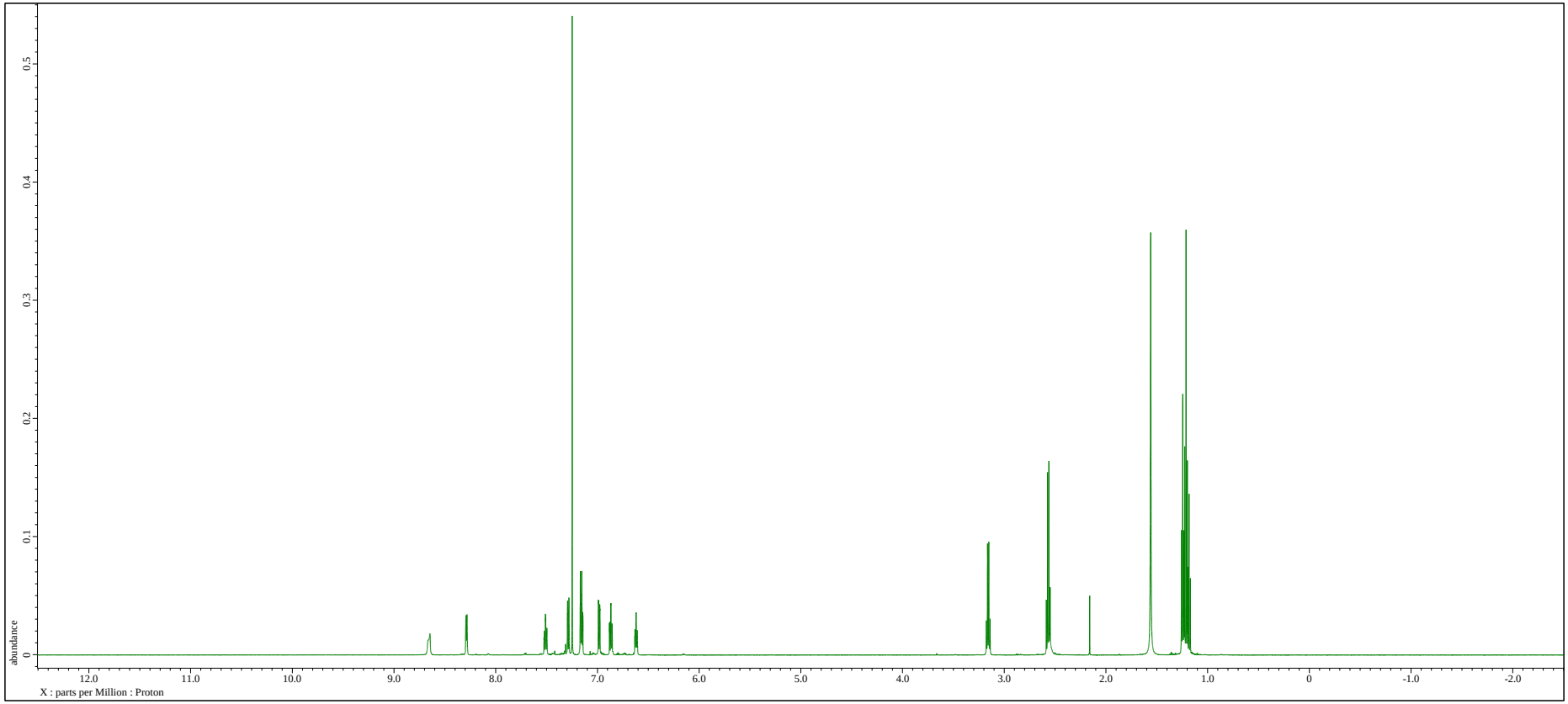

Figure S17: ^{1}H NMR spectrum of complex **1f**

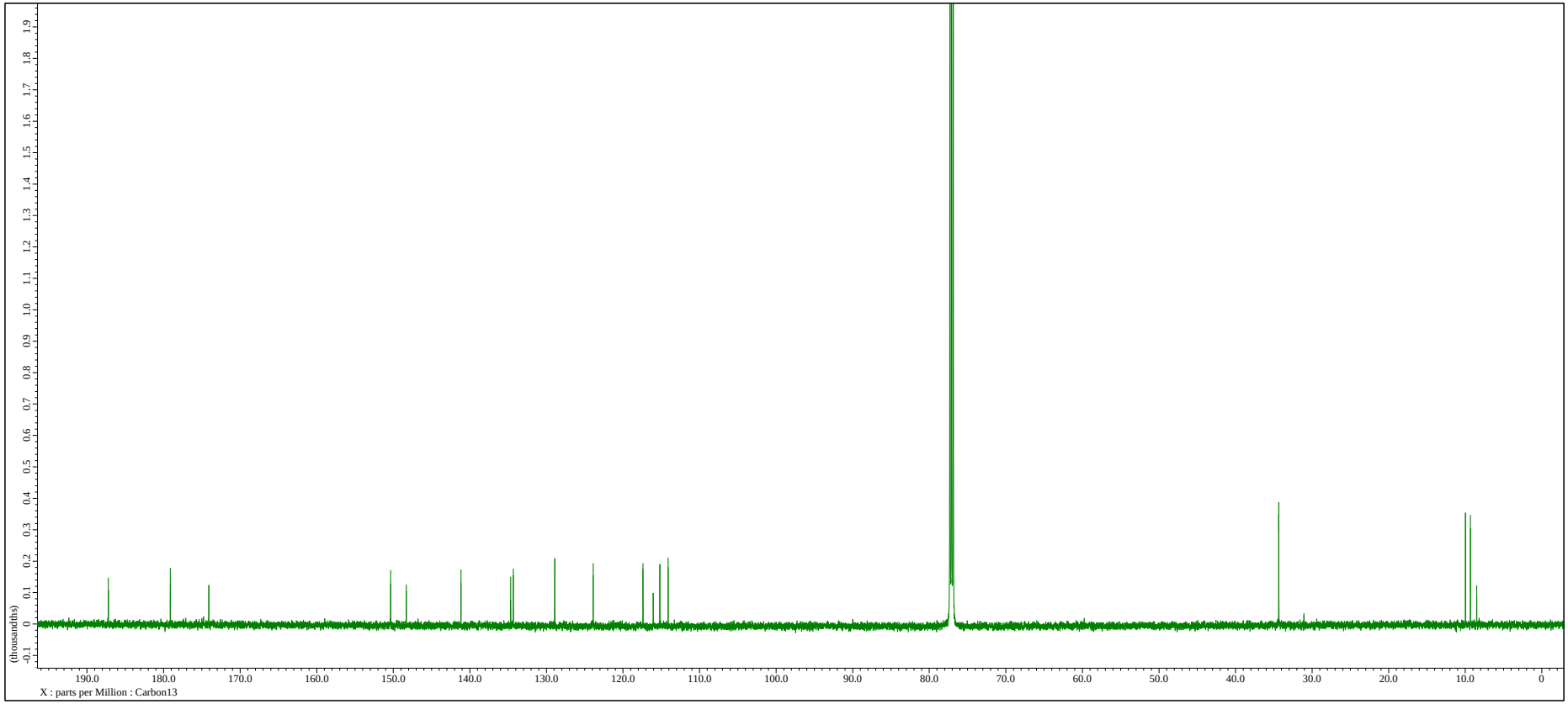

Figure S18: ^{13}C NMR spectrum of complex **1f**

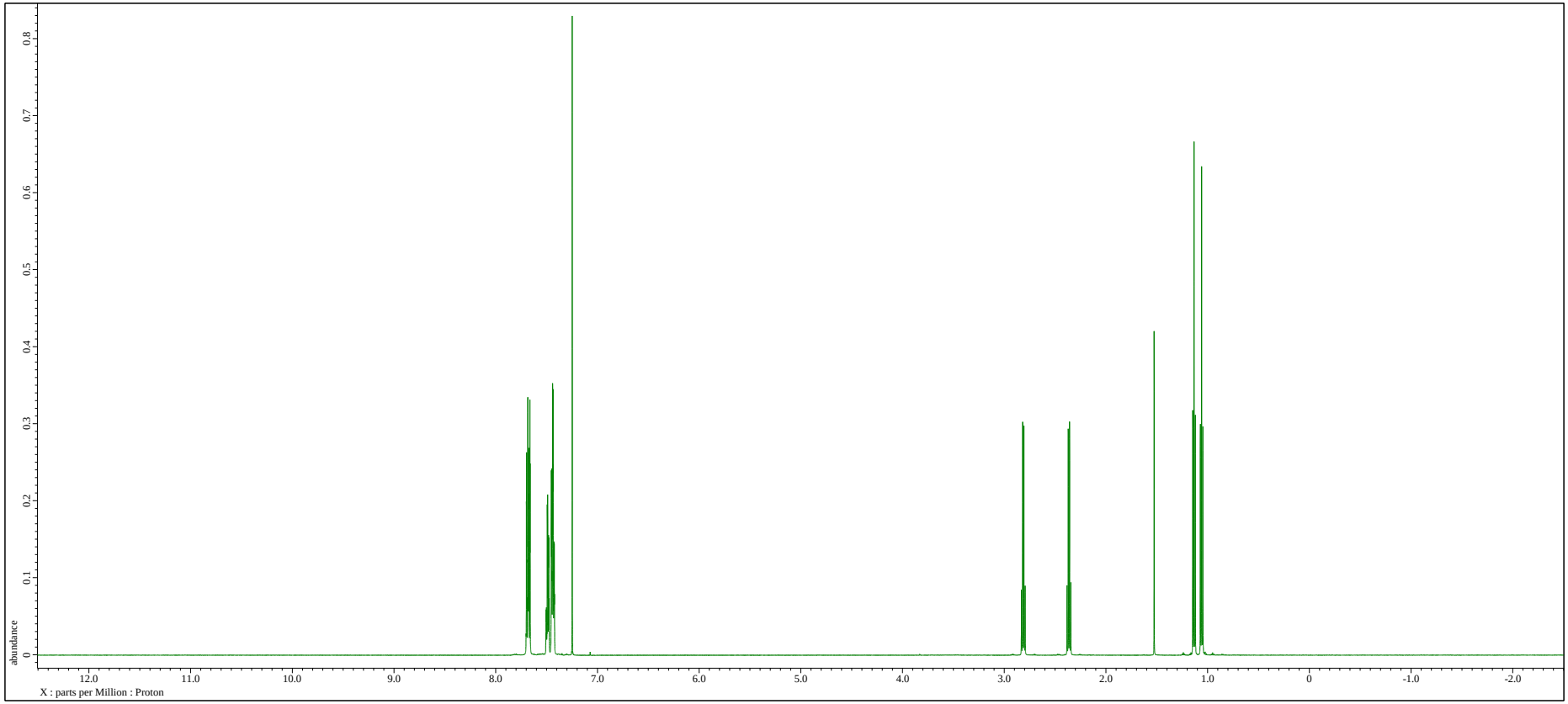

Figure S19: ^{1}H NMR spectrum of complex **1g**

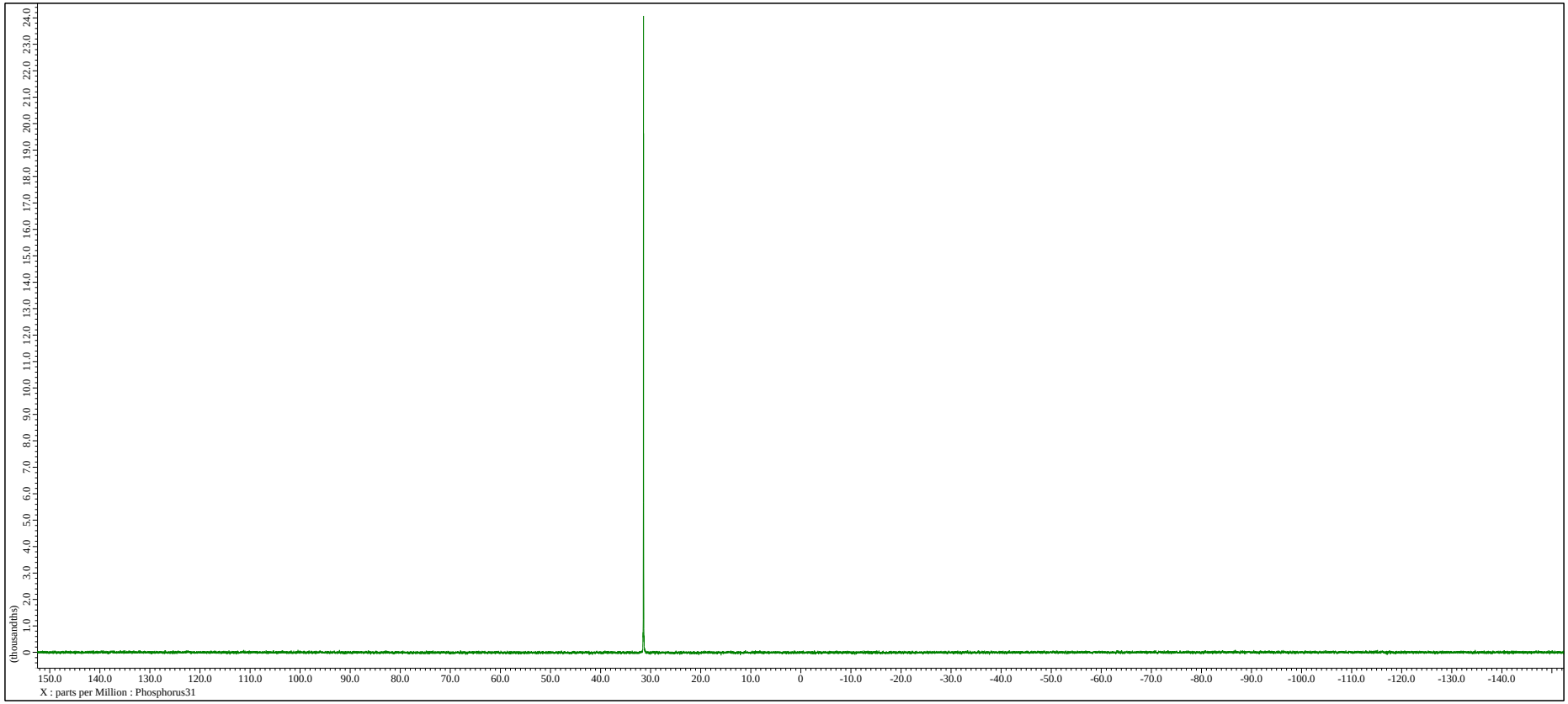

Figure S20: $^{31}P\{^{1}H\}$ NMR spectrum of complex **1g**

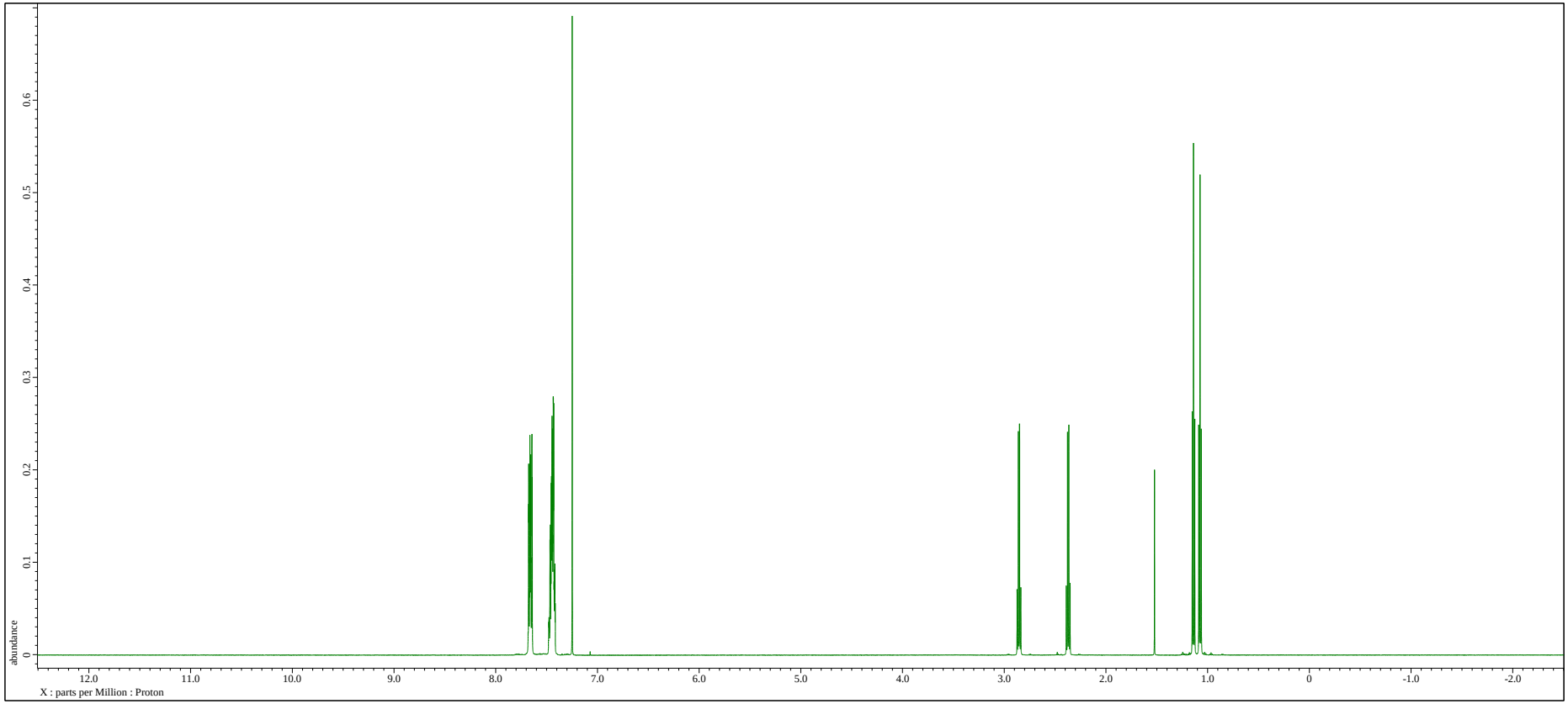

Figure S21: ^{1}H NMR spectrum of complex **1g**

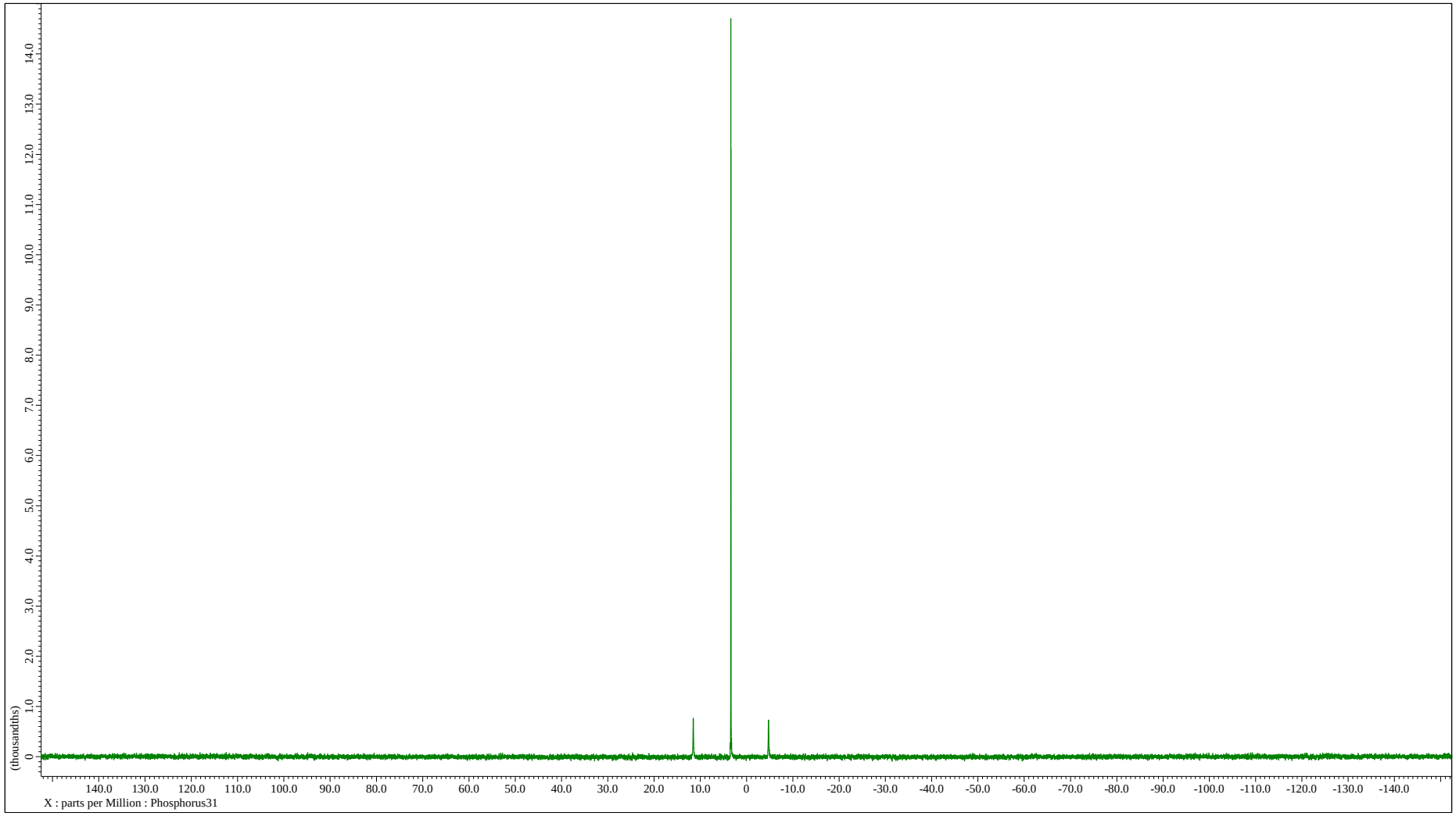

Figure S22: $^{31}P\{^{1}H\}$ NMR spectrum of complex **1g**

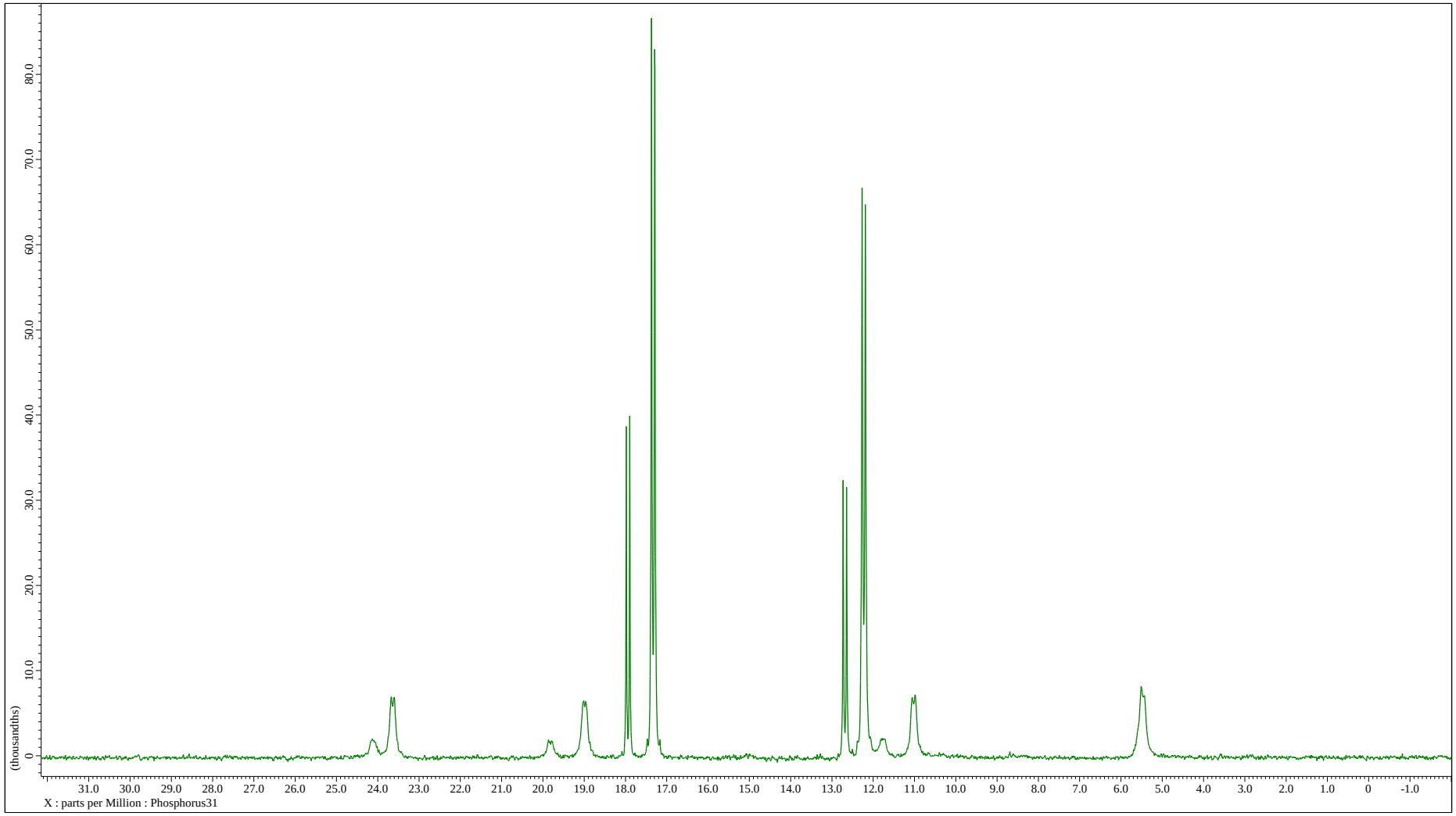

Figure S23: $^{31}P\{^{1}H\}$ NMR spectrum of complex **1c** showing a second set of resonances due to decomposition.

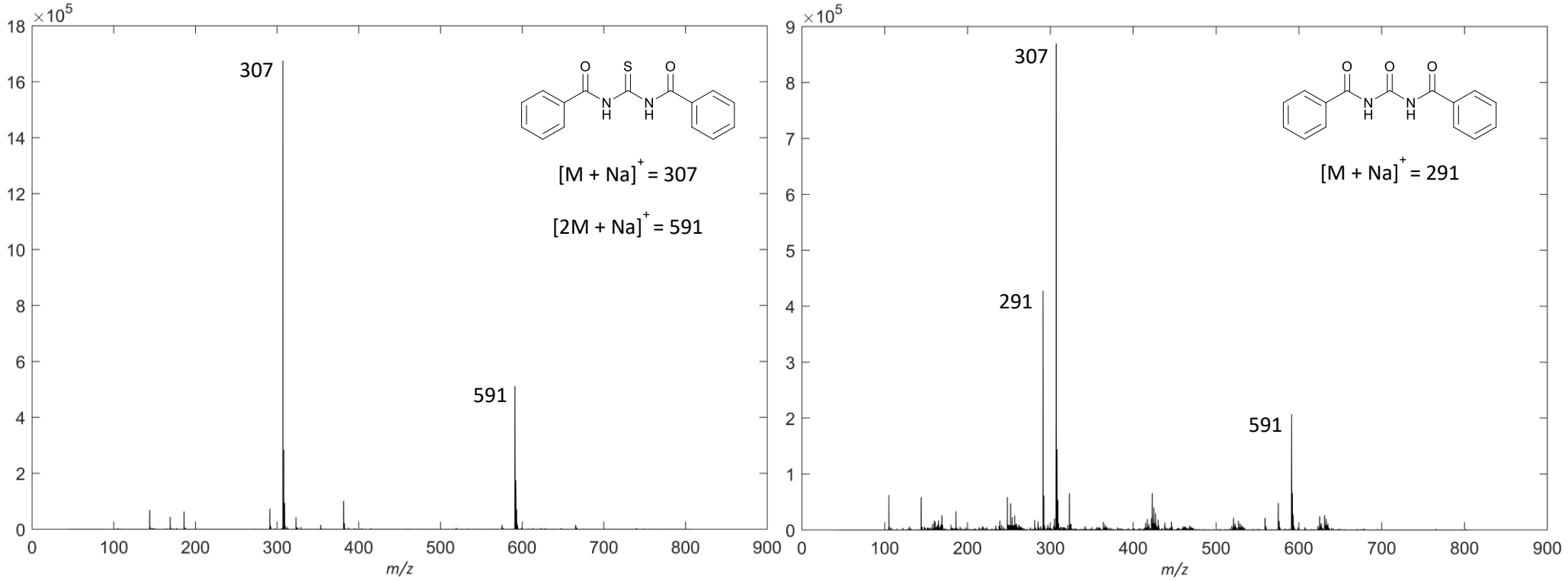

Figure S24: ESI-MS comparison of crude samples of ligand **L3** before (Left) and after (Right) boiling in water for approximately 5 minutes showing the formation of a new peak corresponding to the urea product.

Crystallographic information:

Table 1: Selected bond lengths in the molecular structure of molecular structures of complexes **1a**, **1b**, **1f**, **1g**, and **1h** and the molecular structure of **L2**

Bond	**Bond length (Å)**		**Bond**	
	1a	**1b**		**1f**
Pt – P1	2.307(8)	2.306(5)	**Au -N3**	2.081(4)
Pt – P2	2.255(9)	2.249(5)	**Au – C20**	2.018(5)
Pt - S1	2.331(9)	2.325(5)	**Au – S1**	2.290(1)
Pt - N1	2.073(4)	2.083(2)	**Au – N1**	2.105(4)
S1- C1	1.784(4)	1.738(2)	**S1 – C1**	1.773(4)
C1 - N1	1.390(5)	1.382(3)	**C1 – N1**	1.368(5)
C1 - N2	1.269(5)	1.276(3)	**C1 – N2**	1.305(5)

	1g	**1h**		**L2**
M-P1	2.246(6)	2.227(6)	**S1 - C1**	1.952(2)
M – Cl	2.320(9)	2.326(8)	**C1 - N1**	1.382(3)
M – S1	2.287(7)	2.290(7)	**C1 - N2**	1.370(3)
M – N1	2.139(2)	2.142(2)	**N1 - C2**	1.381(3)
S1 – C1	1.727(3)	1.722(3)	**C2 - O1**	1.224(2)
C1 – N1	1.331(4)	1.344(4)	**N2 - C5**	1.396(3)
C1 – N2	1.352(3)	1.347(3)	**C5 - O2**	1.206(2)

Table 2: Crystallographic details for the diacylthiourea molecule **L2** and complexes **1a** and **1b**.

Complex	**L2**	**1a**	**1b**
Identification code	MCR4	MCR3	MCR2
Empirical formula	$C_7H_{12}N_2O_2S$	$C_{41}H_{36}N_2O_2P_2PtS$	$C_{44}H_{42}Cl_2N_2O_2P_2PtS$
Formula weight	188.25	877.85	990.83
Temperature/K	100.0(2)	100.0(2)	100.0(2)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a/Å	5.17400(10)	14.7870(2)	12.81780(10)
b/Å	9.3578(2)	11.88550(10)	21.7252(2)
c/Å	19.0340(4)	20.6357(2)	14.81870(10)
α/°	90	90	90
β/°	90	94.9210(10)	103.0940(10)
γ/°	90	90	90
Volume/Å^3	921.57(3)	3613.37(7)	4019.26(6)
Z	4	4	4
ρ_{calc}g/cm^3	1.3567	1.6136	1.6373
μ/mm^{-1}	2.848	8.943	9.310
F(000)	402.5	1734.3	1969.5
Crystal size/mm^3	0.12 × 0.05 × 0.01	0.18 × 0.18 × 0.14	1.12 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.3 to 148.16	6 to 148.62	7.08 to 148.46
Index ranges	-6 ≤ h ≤ 6, -11 ≤ k ≤ 7, -23 ≤ l ≤ 22	-18 ≤ h ≤ 18, -14 ≤ k ≤ 14, -25 ≤ l ≤ 24	-16 ≤ h ≤ 15, -26 ≤ k ≤ 26, -18 ≤ l ≤ 18
Reflections collected	5339	56816	64158
Independent reflections	1799 [R_{int} = 0.0395, R_{sigma} = 0.0387]	7283 [R_{int} = 0.0460, R_{sigma} = 0.0256]	8104 [R_{int} = 0.0451, R_{sigma} = 0.0244]
Data/restraints/parameters	1799/0/111	7283/0/445	8104/0/490
Goodness-of-fit on F^2	1.030	1.039	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0290, wR_2 = 0.0774	R_1 = 0.0316, wR_2 = 0.0752	R_1 = 0.0190, wR_2 = 0.0425
Final R indexes [all data]	R_1 = 0.0318, wR_2 = 0.0788	R_1 = 0.0352, wR_2 = 0.0771	R_1 = 0.0209, wR_2 = 0.0432
Largest diff. peak/hole / e Å^{-3}	0.39/-0.20	1.81/-1.75	0.60/-0.61

Table 3: Crystallographic details for the complexes **1f**, **1g** and **1h**

Complex	**1f**	**1g**	**1h**
Identification code	MCR103_auto	MCR105_auto	MCR106_auto
Empirical formula	$C_{18}H_{19}AuN_4O_2S$	$C_{25}H_{26}ClN_2O_2PPdS$	$C_{25}H_{26}ClN_2O_2PPtS$
Formula weight	552.41	591.41	680.07
Temperature/K	100.00(10)	100.00(10)	100.0(3)
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	P-1	P-1
a/Å	12.94247(16)	9.70784(19)	9.69560(14)
b/Å	19.2338(2)	10.9768(3)	11.01772(16)
c/Å	7.50278(9)	12.7313(3)	12.69262(16)
α/°	90	68.297(2)	68.3323(13)
β/°	104.5517(12)	85.0358(17)	85.0689(11)
γ/°	90	81.1443(18)	81.4341(12)
Volume/Å^3	1807.77(4)	1244.81(5)	1245.30(3)
Z	4	2	2
ρ_{calc}g/cm^3	2.0295	1.5777	1.8135
μ/mm^{-1}	16.548	8.597	13.122
F(000)	1051.9	603.7	658.8
Crystal size/mm^3	0.05 × 0.05 × 0.02	0.05 × 0.04 × 0.03	0.05 × 0.05 × 0.04
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.42 to 144.68	7.48 to 144.26	7.5 to 144.72
Index ranges	-15 ≤ h ≤ 15, -23 ≤ k ≤ 21, -9 ≤ l ≤ 9	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -15 ≤ l ≤ 14
Reflections collected	48018	33325	35228
Independent reflections	3476 [R_{int} = 0.0556, R_{sigma} = 0.0211]	4736 [R_{int} = 0.0675, R_{sigma} = 0.0332]	4735 [R_{int} = 0.0509, R_{sigma} = 0.0258]
Data/restraints/parameters	3476/0/240	4736/0/300	4735/0/300
Goodness-of-fit on F^2	1.063	1.028	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0304, wR_2 = 0.0790	R_1 = 0.0335, wR_2 = 0.0908	R_1 = 0.0178, wR_2 = 0.0429
Final R indexes [all data]	R_1 = 0.0344, wR_2 = 0.0846	R_1 = 0.0357, wR_2 = 0.0922	R_1 = 0.0188, wR_2 = 0.0432
Largest diff. peak/hole / e Å^{-3}	3.08/-1.73	1.49/-1.40	0.58/-1.05

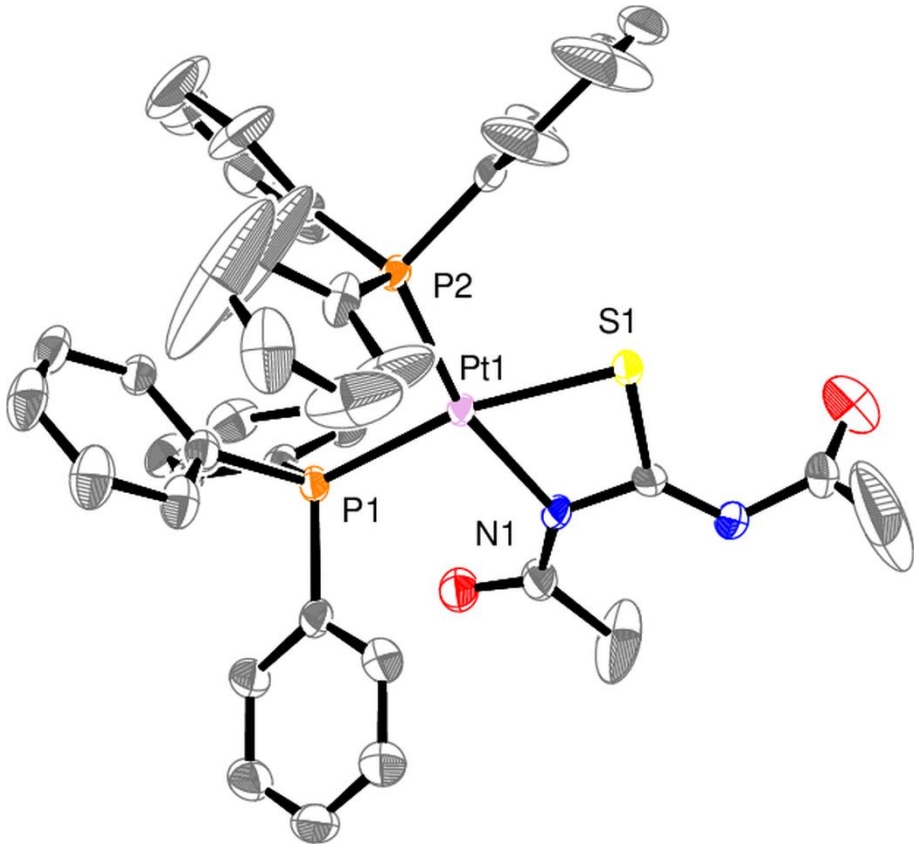

*Figure S24: Molecular structure of the complex [Pt{EtC(O)NC(S)NC(O)Et}(PPh$_3$)$_2$] **1a** showing a partial atom numbering scheme. Hydrogen atoms and a molecule of dichloromethane of crystallisation are omitted for clarity and ellipsoids are shown at the 50% probability level.*

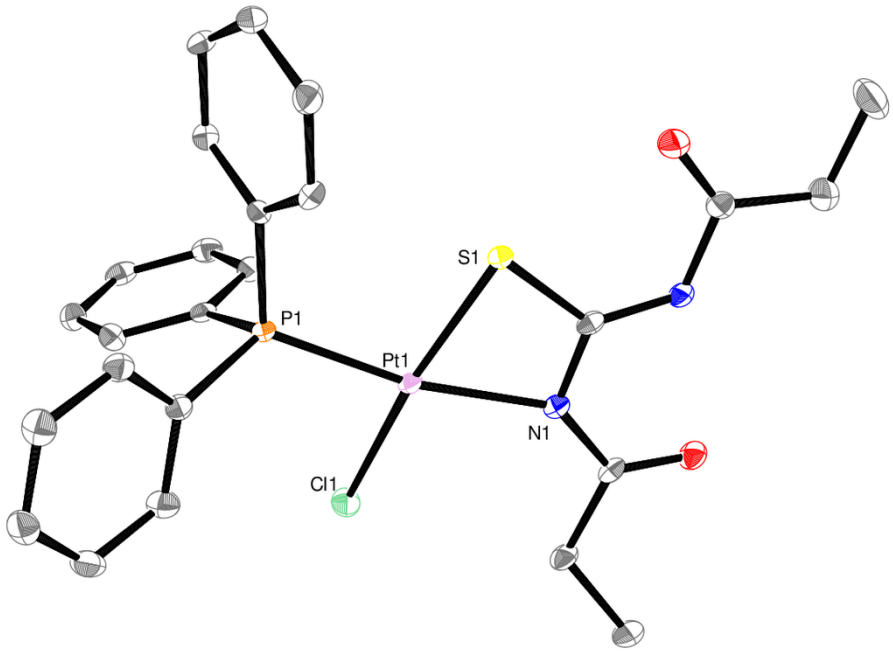

Figure S25: Molecular structure of the complex [Pd{EtC(O)NC(S)NHC(O)Et}(PPh_3)Cl] ***1f*** *showing a partial atom numbering scheme. Hydrogen atoms and a molecule of dichloromethane of crystallisation are omitted for clarity and ellipsoids are shown at the 50% probability level.*

Computational information:

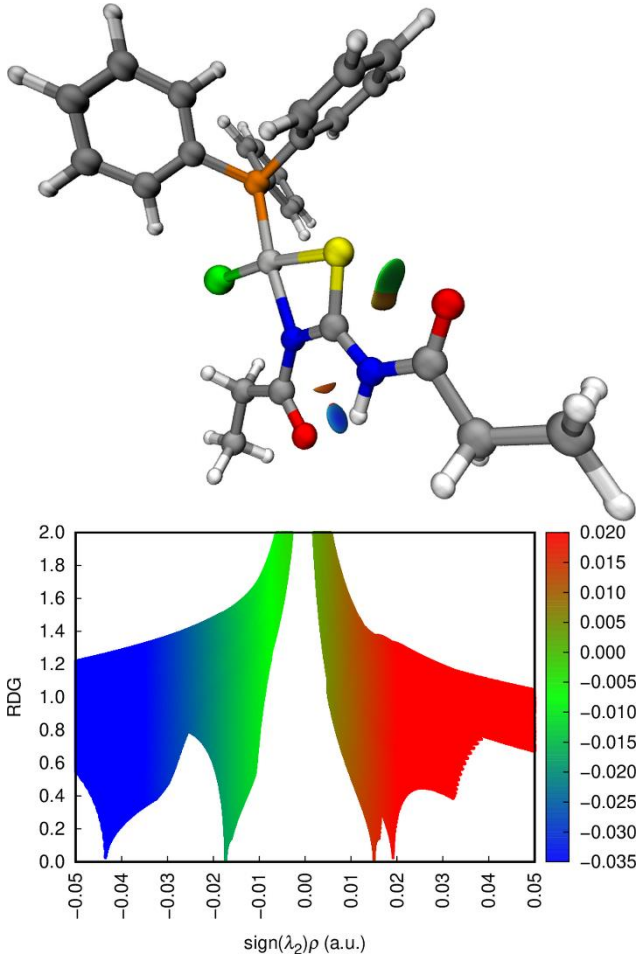

Figure S26: Plot of RDG verses sign(λ_2)ρ for **1f** showing troughs related to chalcogen interactions and NCI isosurfaces using a blue-green-red colour scale. Isovalue = 0.5 for clarity.

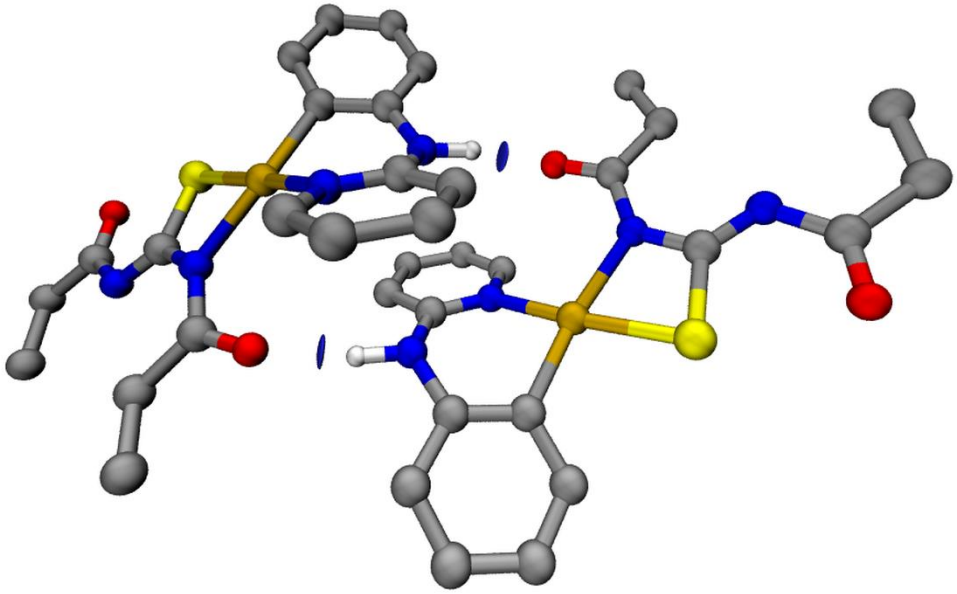

Figure S27: NCI isosurfaces of H bonded interactions of the Au dimer of 1f in the solid state using a blue-green-red colour scale. Isovalue = 0.4 for clarity.

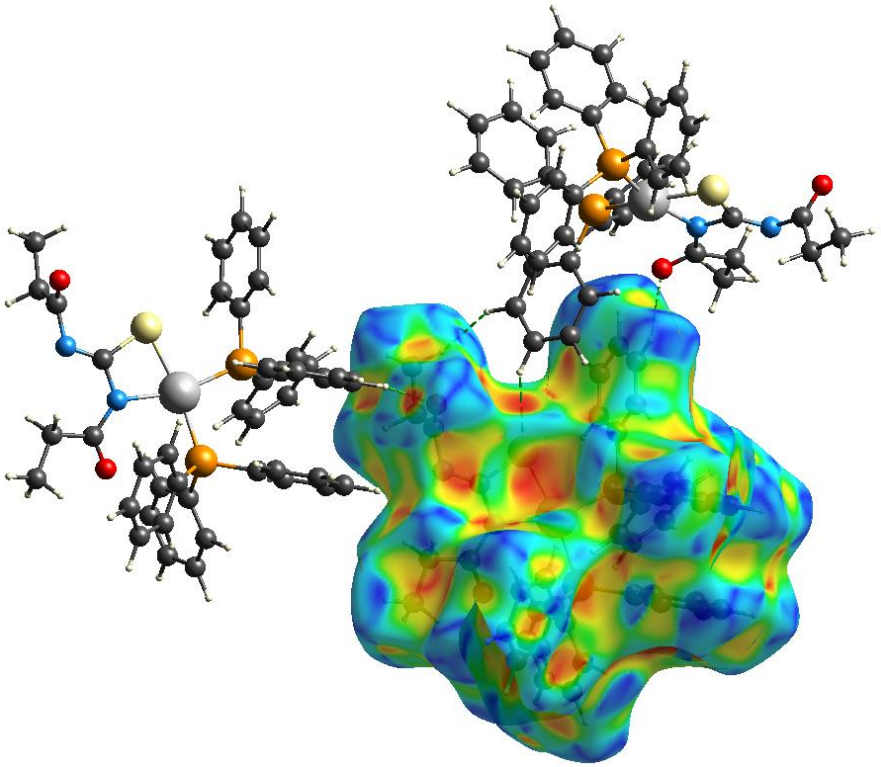

Figure S28: Hirshfeld surface index of complex **1a**