Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information File

Bulky 1,1'-bisphosphanoferrocenes and their coordination behaviour towards Cu(I)

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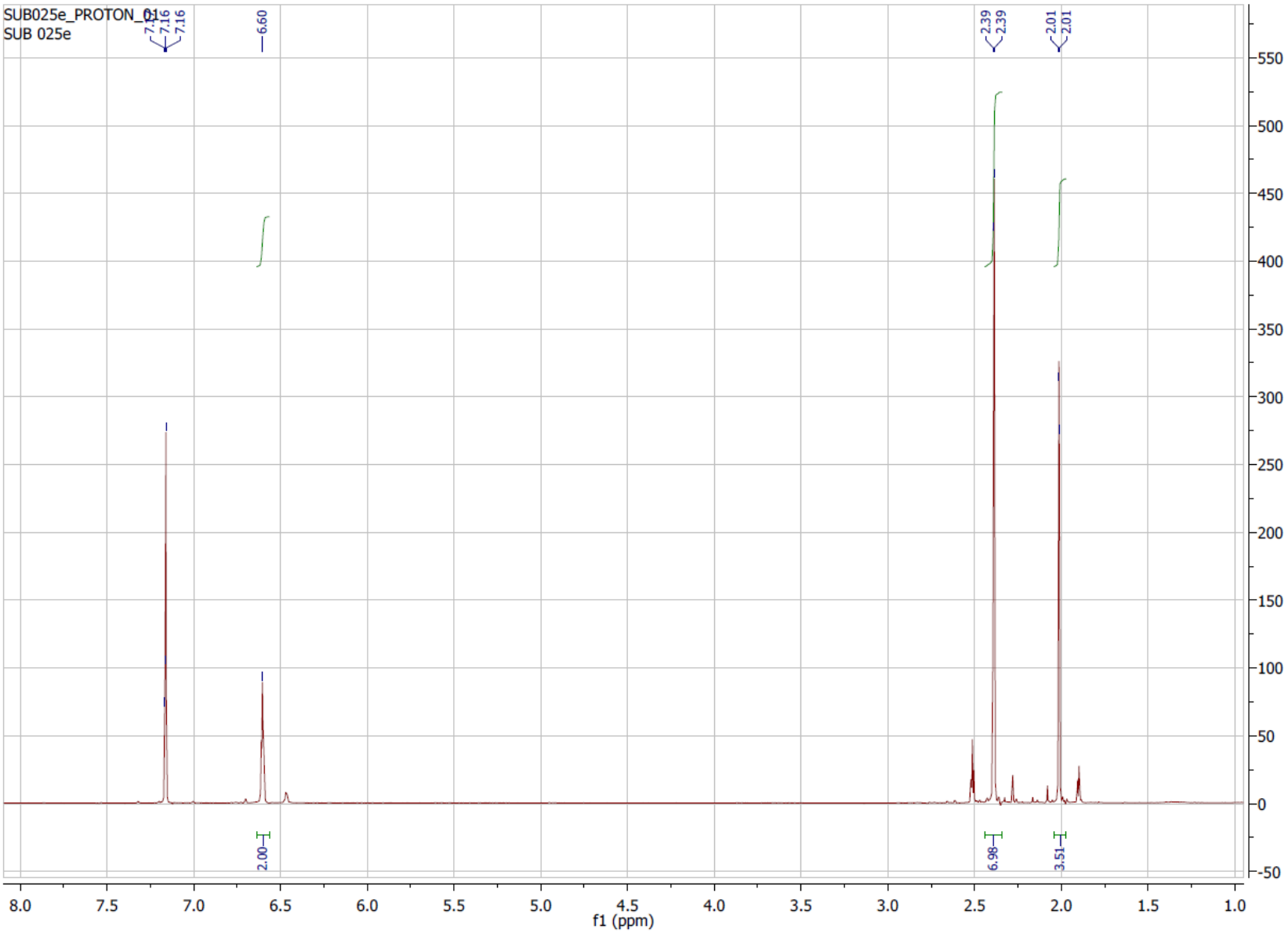


Fig S1. ^{1}H NMR of Mes_2PX (X = Cl/Br, 48%/52%) in C_6D_6.

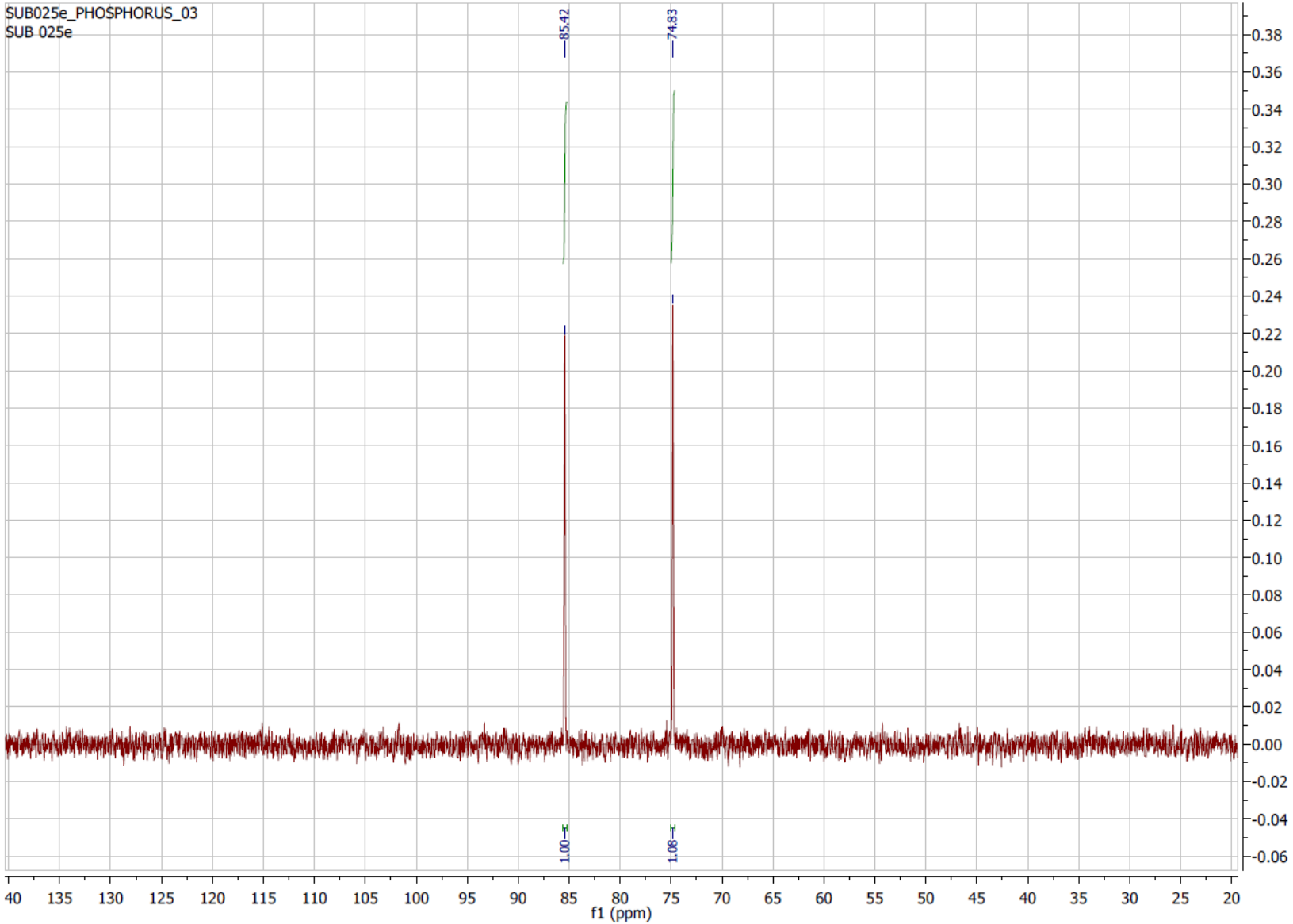


Fig S2. Proton coupled ^{31}P NMR of Mes_2PX (X = Cl/Br, 48%/52%) in C_6D_6.

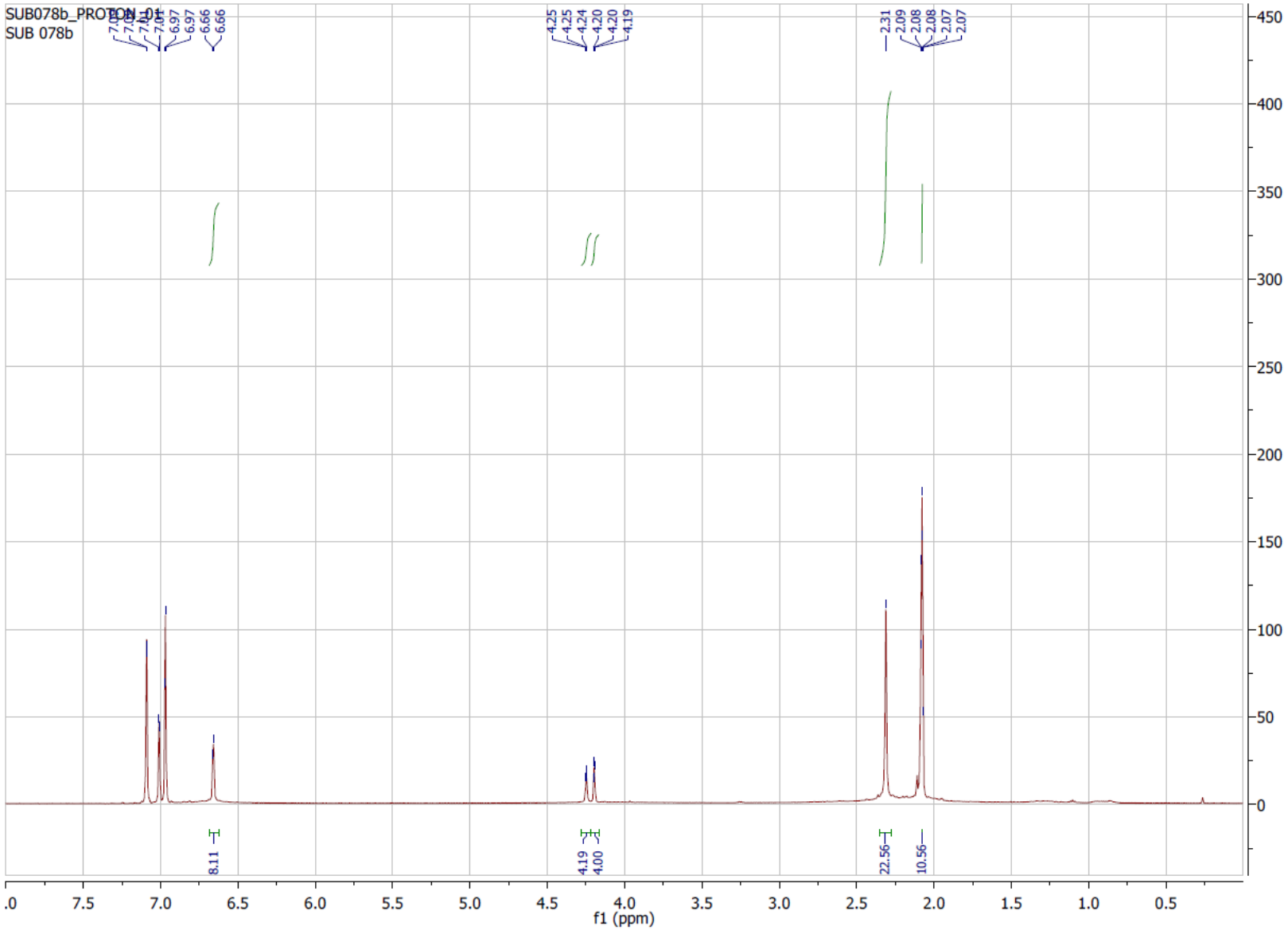


Fig S3. ^{1}H NMR of Fc'($PMes_2$)$_2$ (**1**) in toluene-d8.

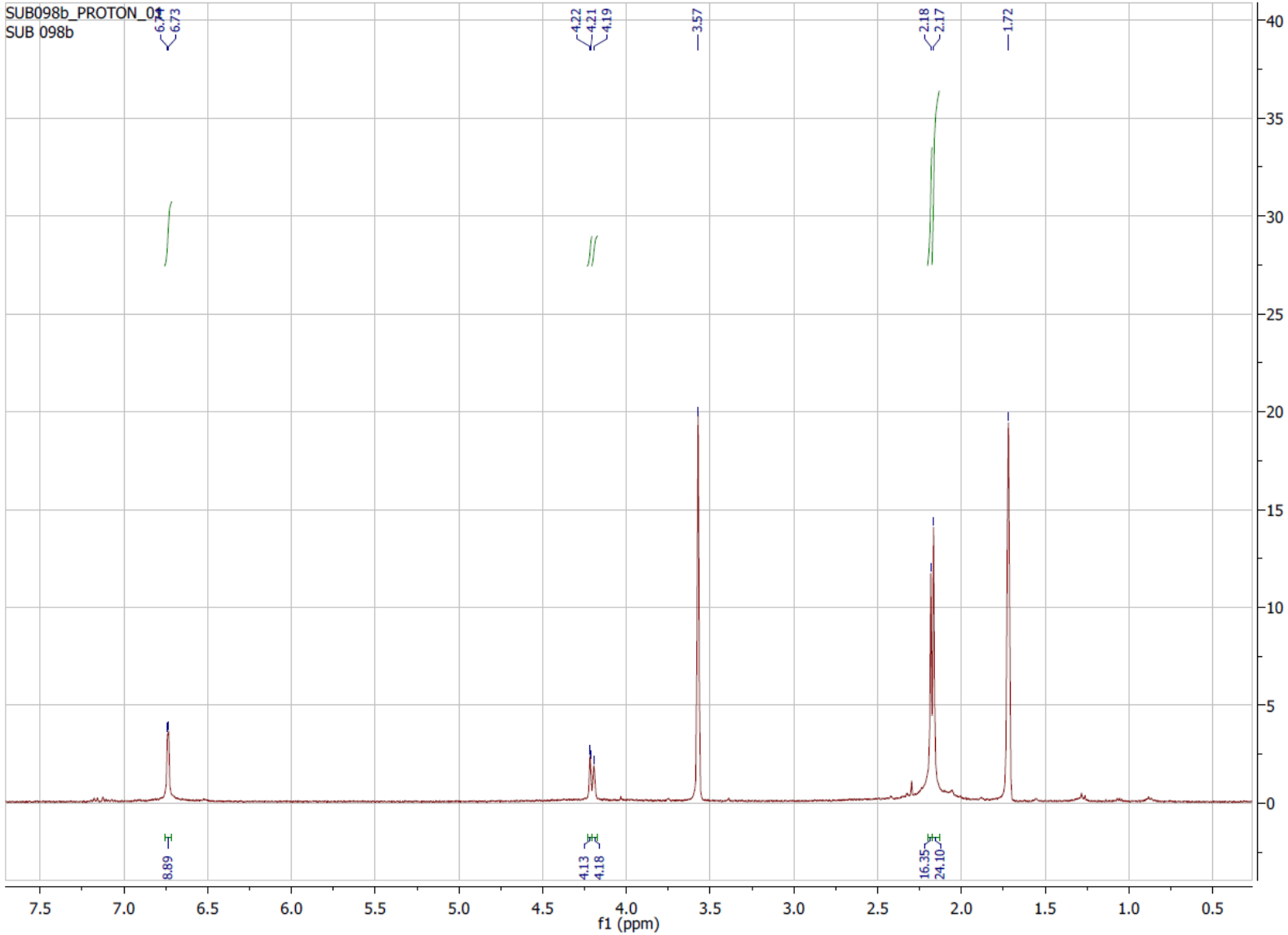


Fig S4. ^{1}H NMR of Fc'($PMes_2$)$_2$ (**1**) in thf-d8.

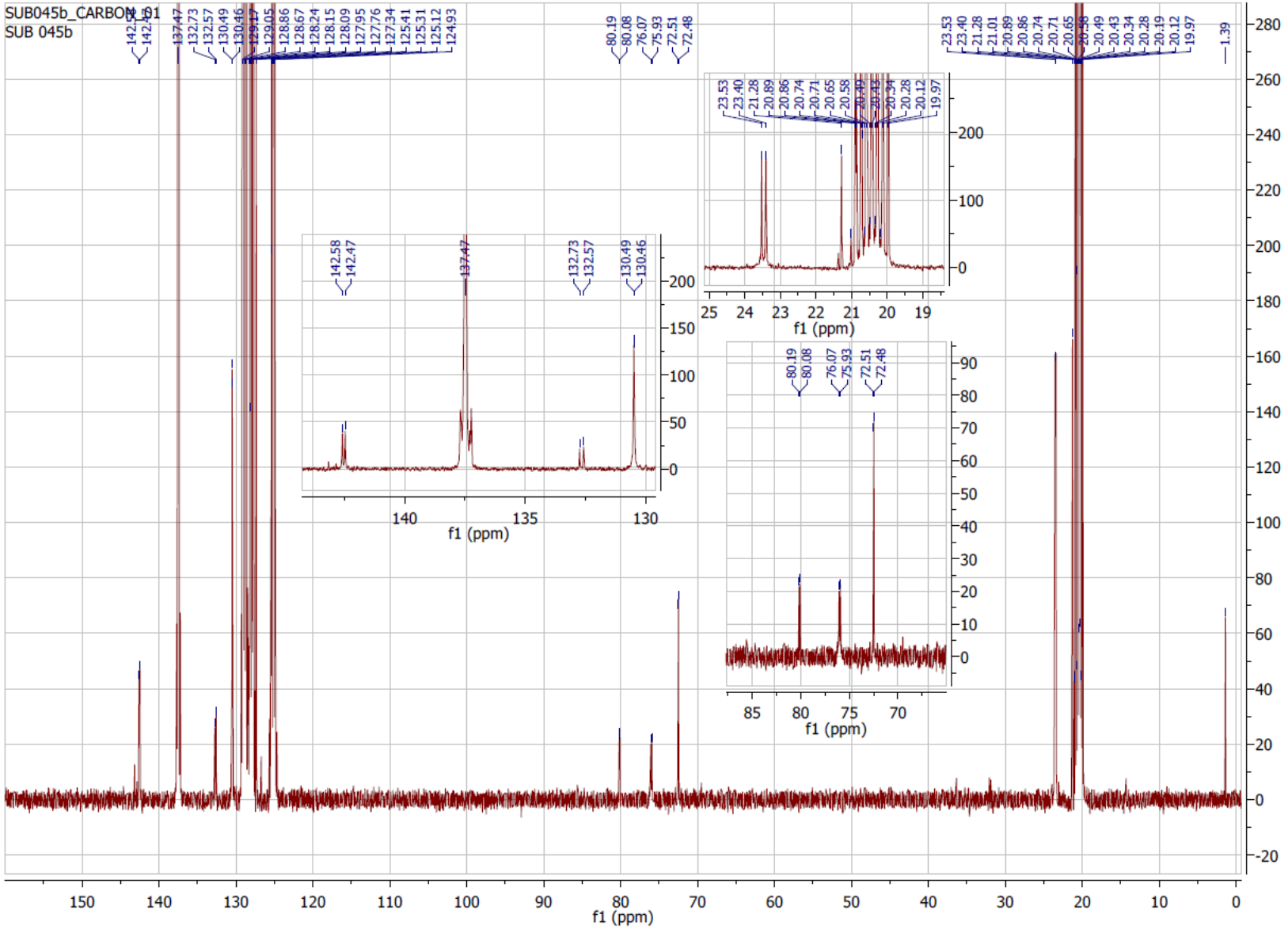


Fig S5. ^{13}C NMR of Fc'(PMes$_2$)$_2$ (**1**) in toluene-d8.

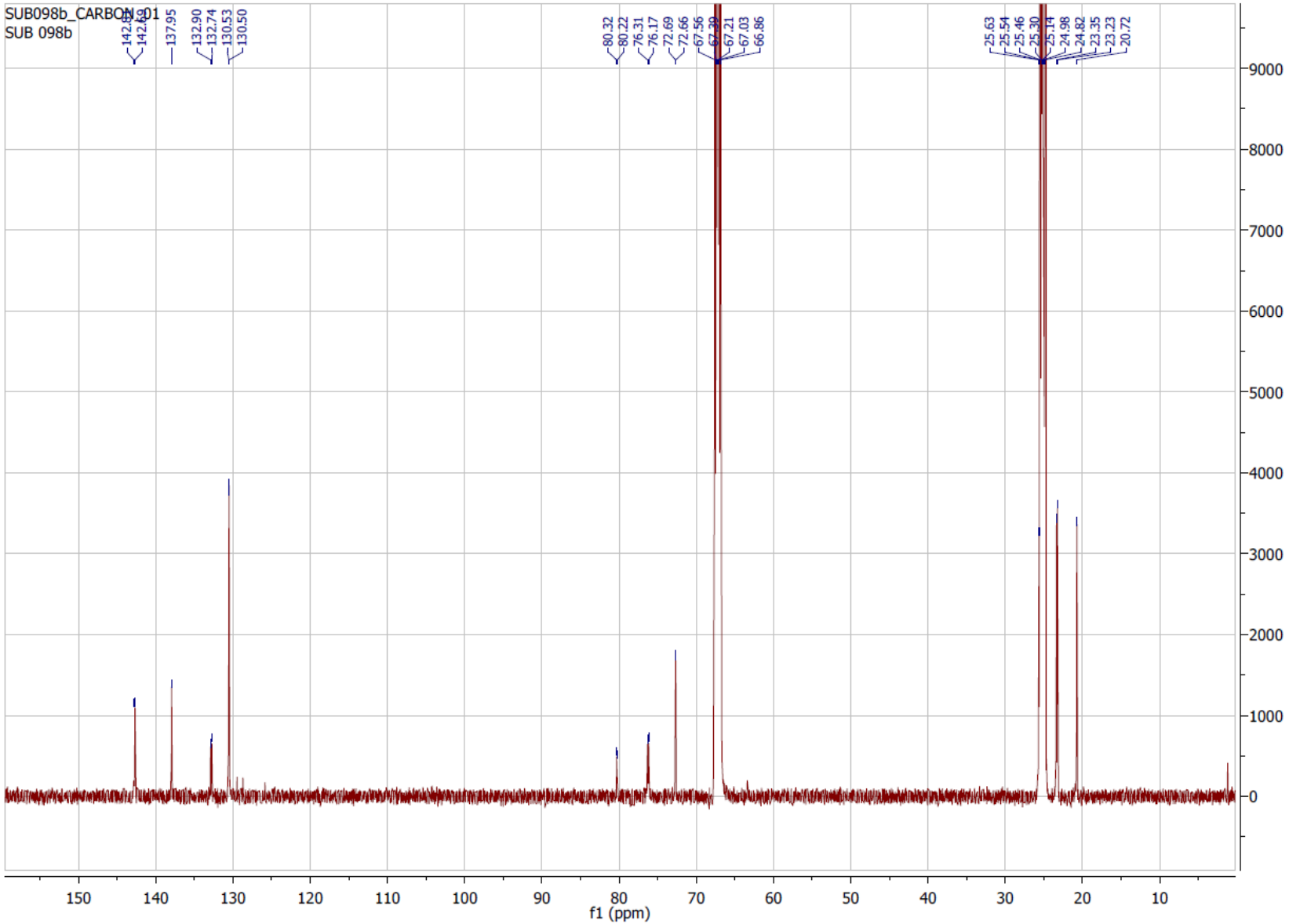


Fig S6. ^{13}C NMR of Fc'($PMes_2$)$_2$ (**1**) in thf-d8.

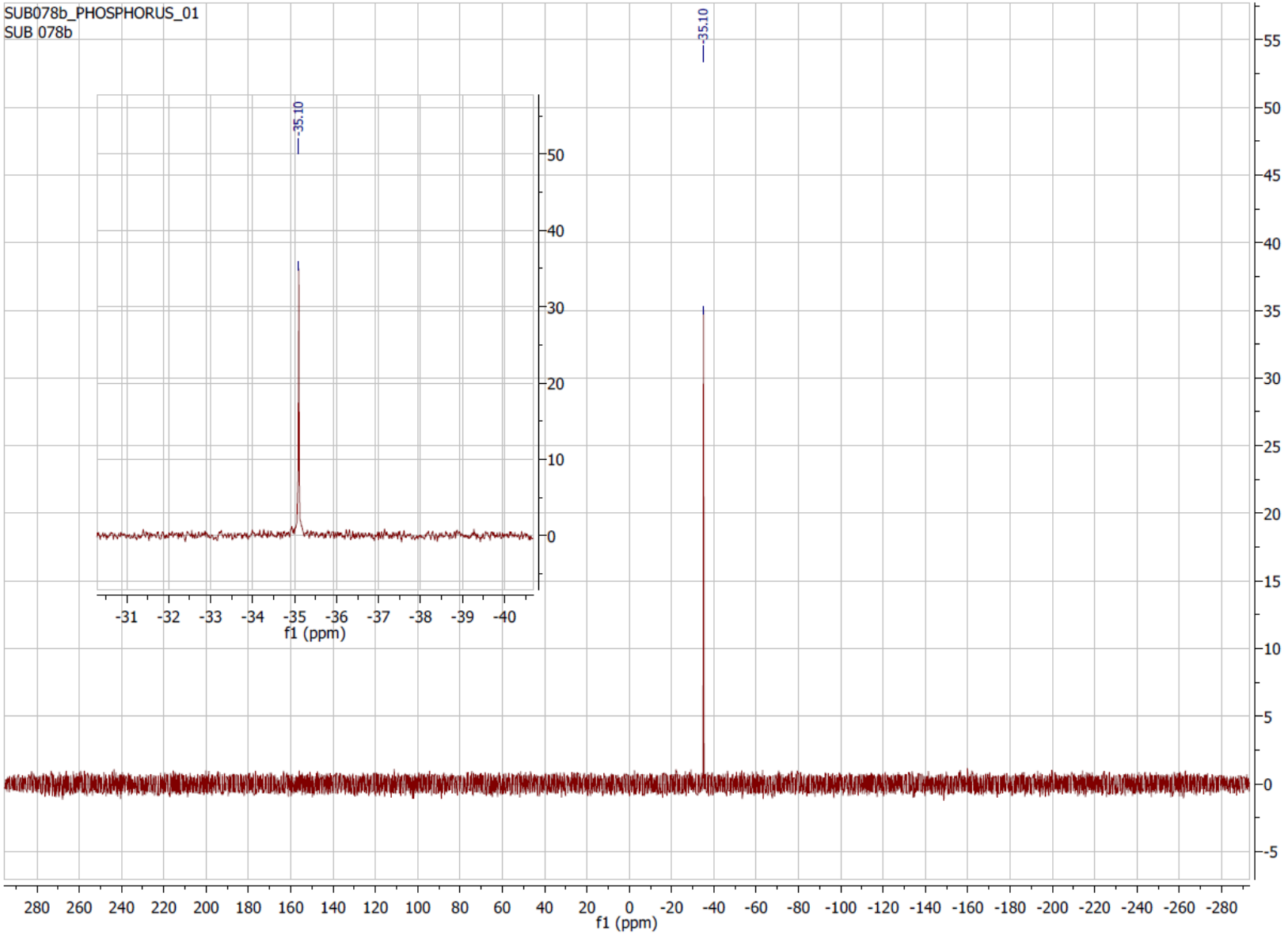


Fig S7. ^{31}P NMR of Fc'($PMes_2$)$_2$ (**1**) in toluene-d8.

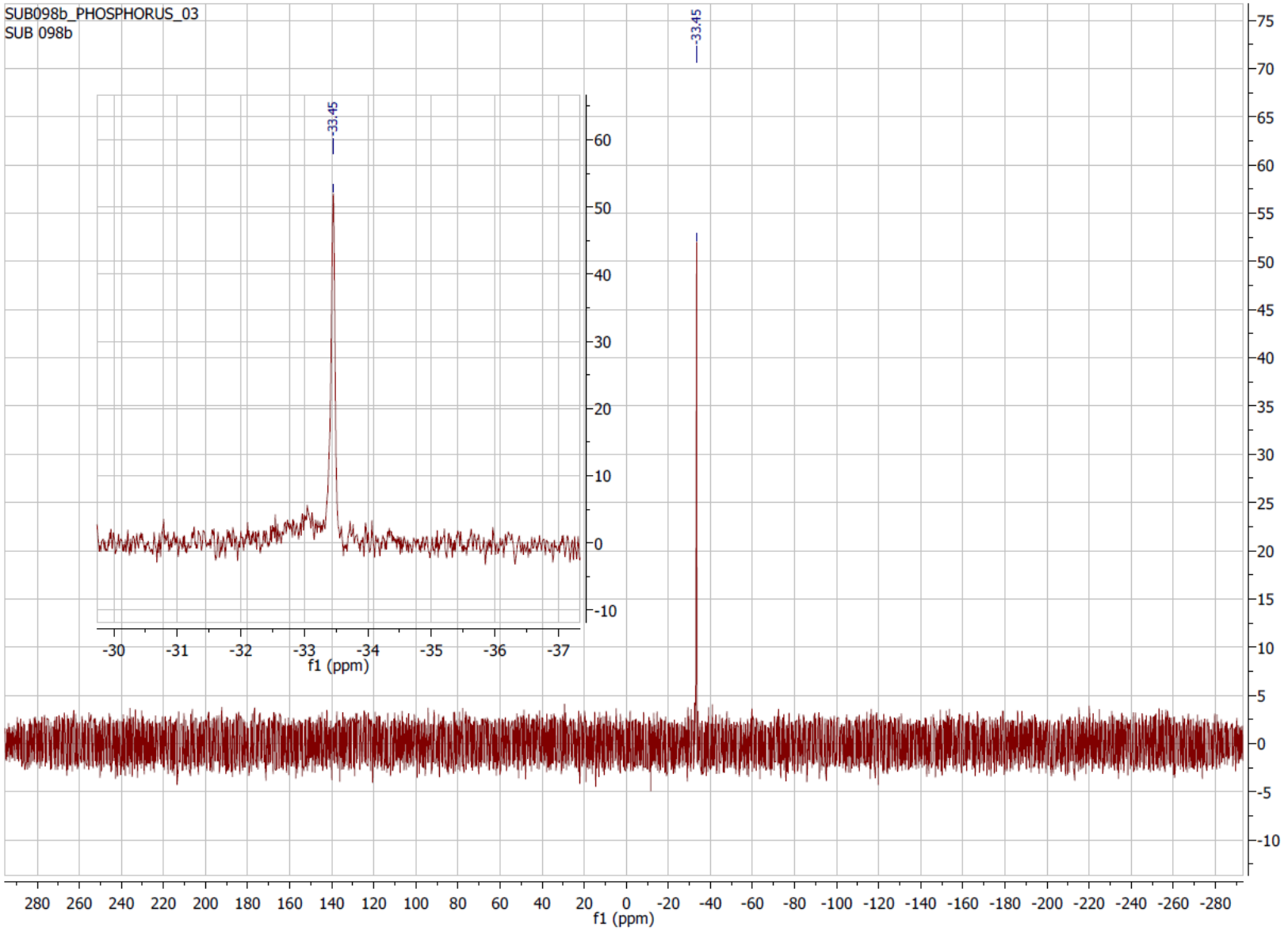


Fig S8. ^{31}P NMR of Fc'($PMes_2$)$_2$ (**1**) in thf-d8.

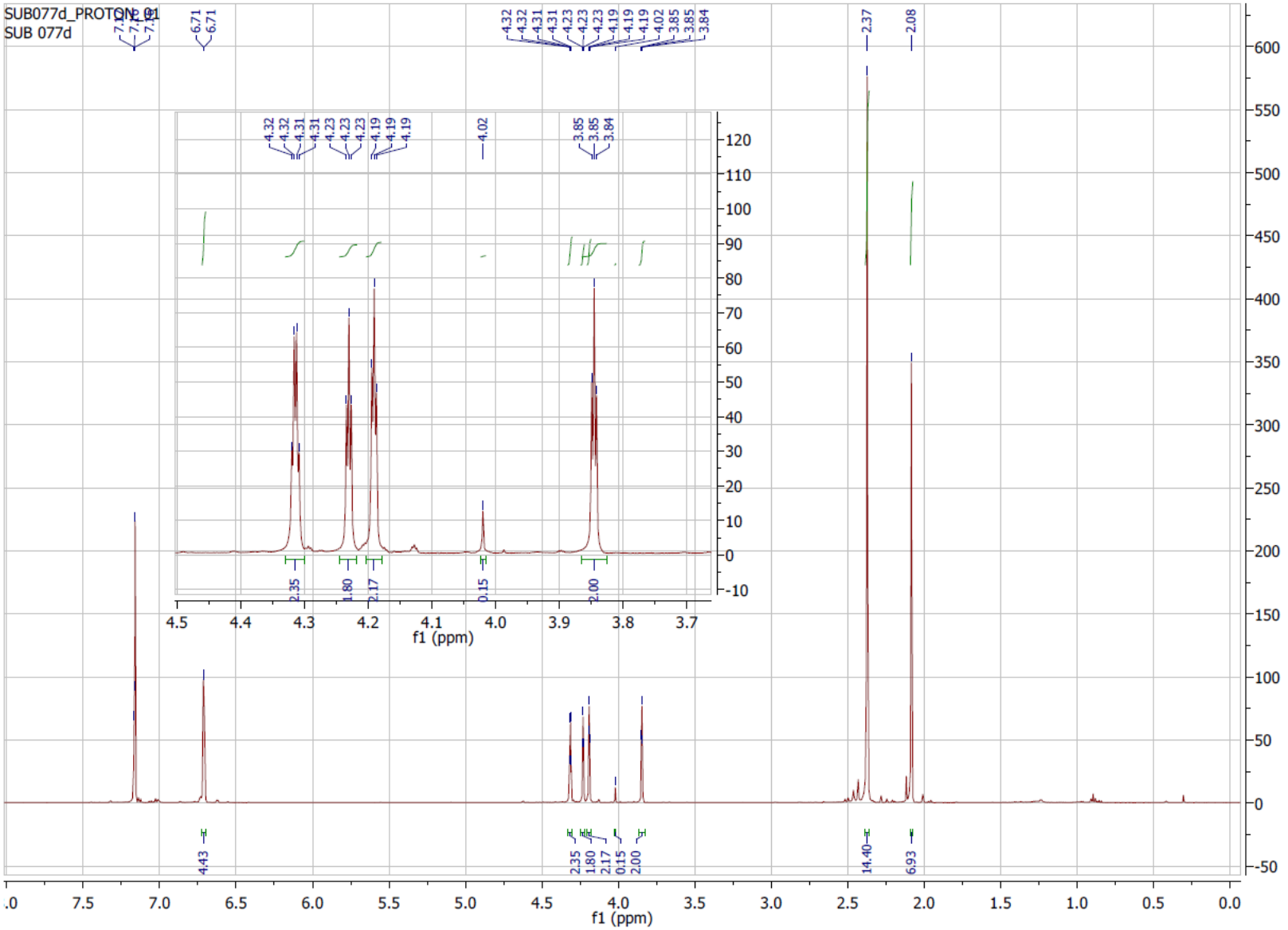


Fig S9. ^{1}H NMR of Fc'(PMes$_2$)Br (**4**) in C_6D_6. The peak at δ 4.02 is resulting from the free Cp of Fc(PMes$_2$) (2-3%).

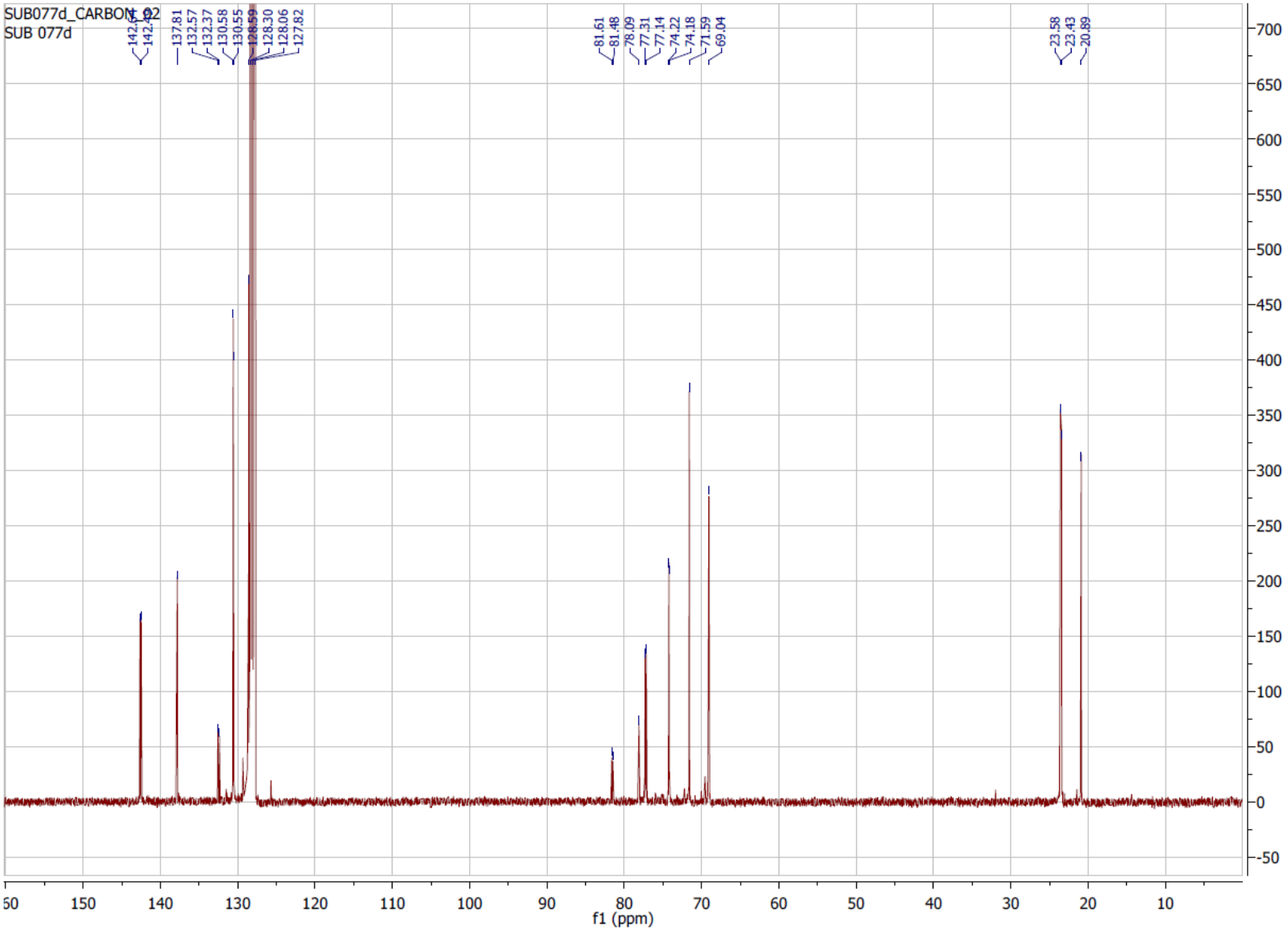


Fig S10. ^{13}C NMR of Fc'($PMes_2$)Br (**4**) in C_6D_6.

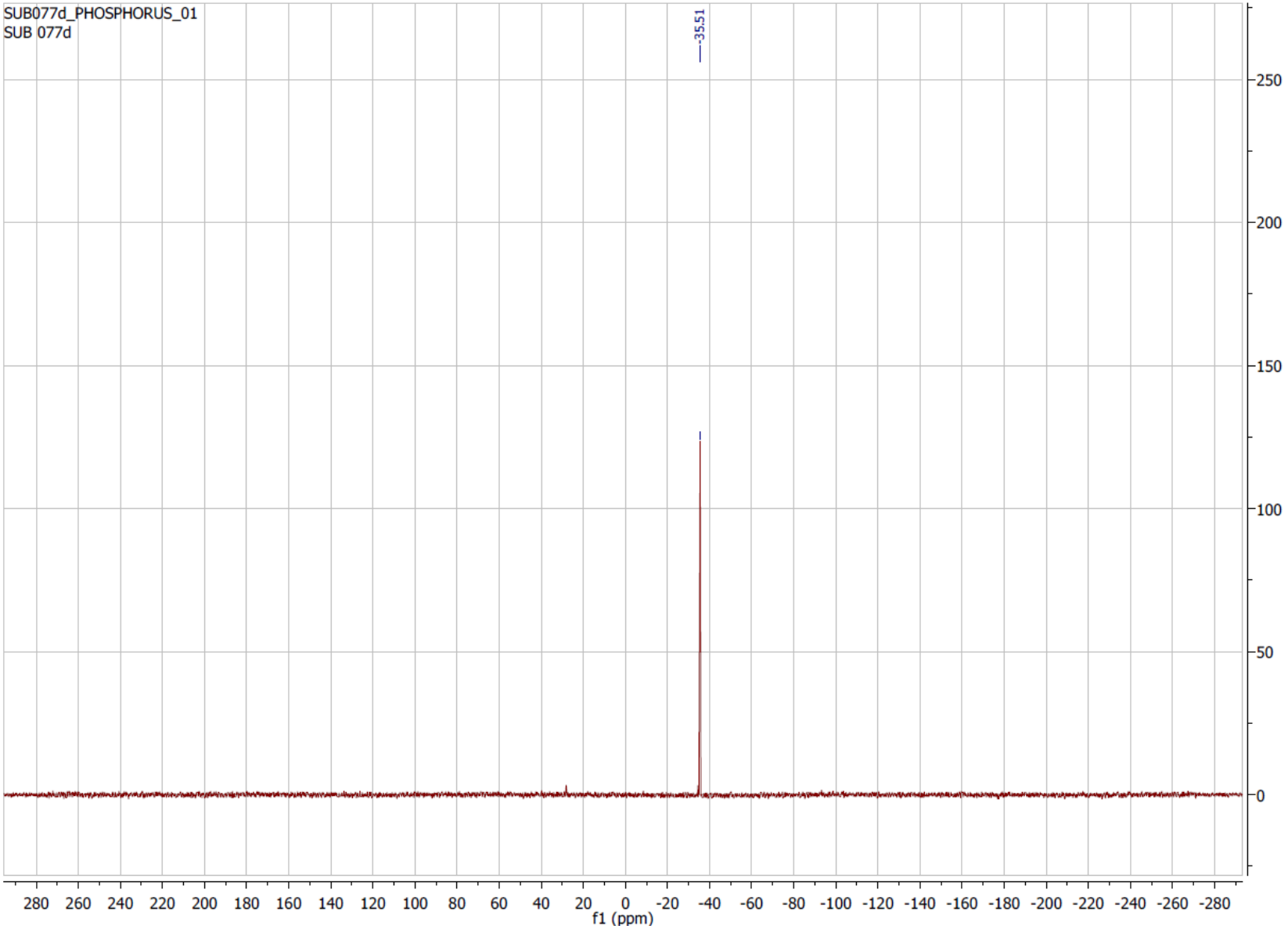


Fig S11. ^{31}P NMR of Fc'($PMes_2$)Br (**4**) in C_6D_6.

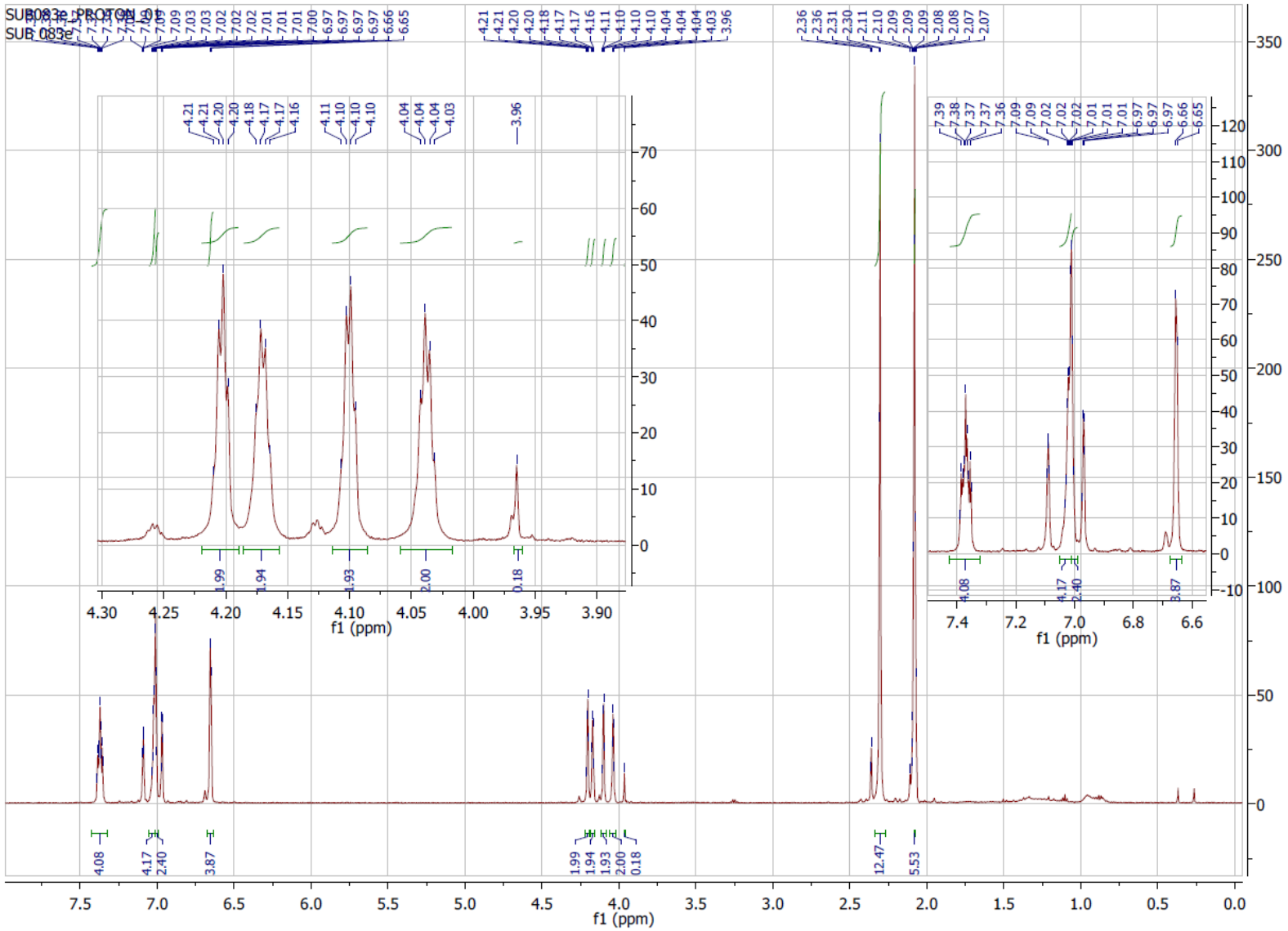


Fig S12. ^{1}H NMR of Fc'(PMes$_2$)(PPh$_2$) (**3**) in toluene-d8. The peak at δ 3.96 is resulting from the free Cp of Fc(PMes$_2$) (3-4%).

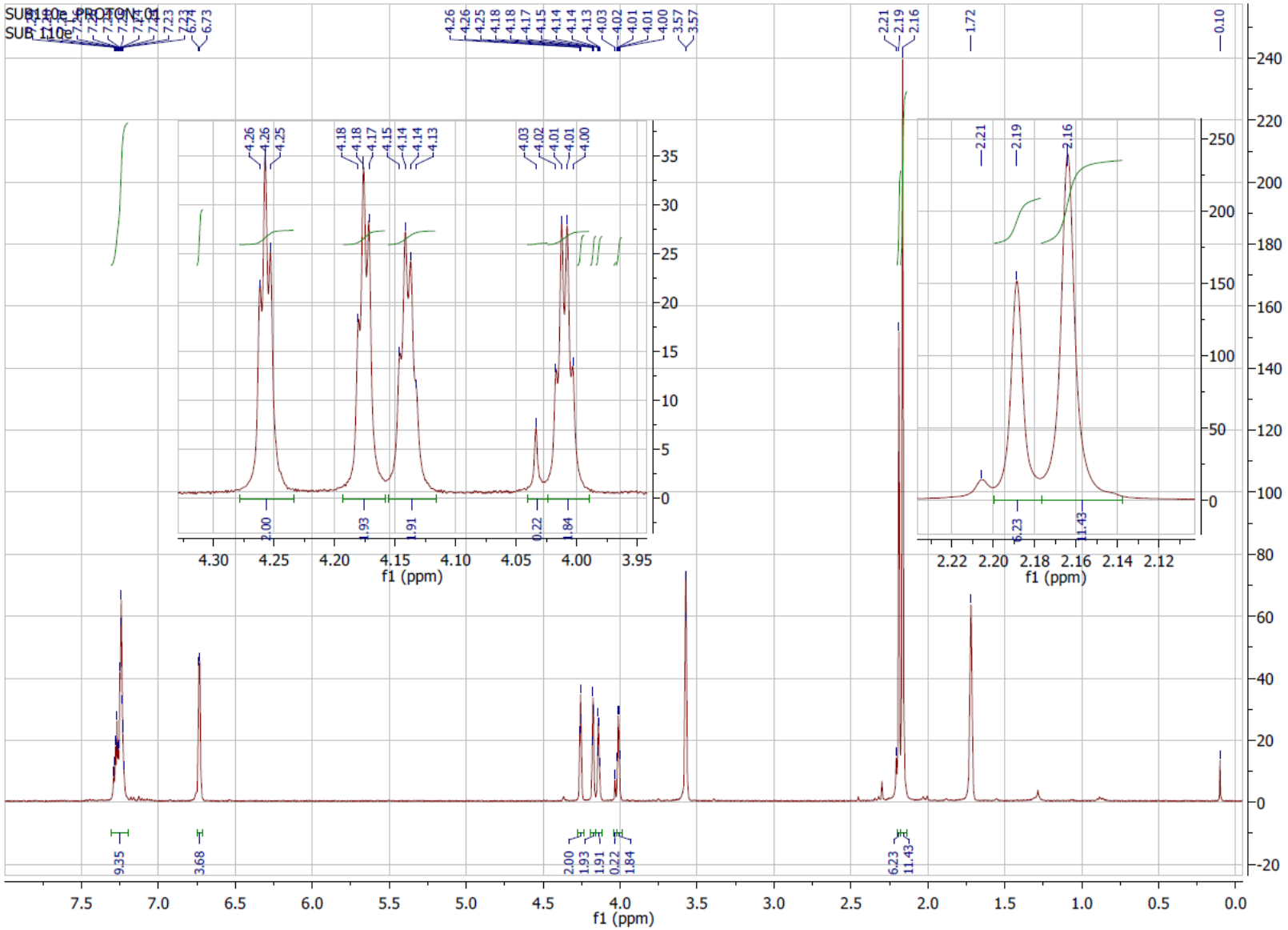


Fig S13. ^{1}H NMR of Fc'(PMes$_2$)(PPh$_2$) (**3**) in thf-d8. The peak at δ 4.03 is resulting from the free Cp of Fc(PMes$_2$) (3-4%).

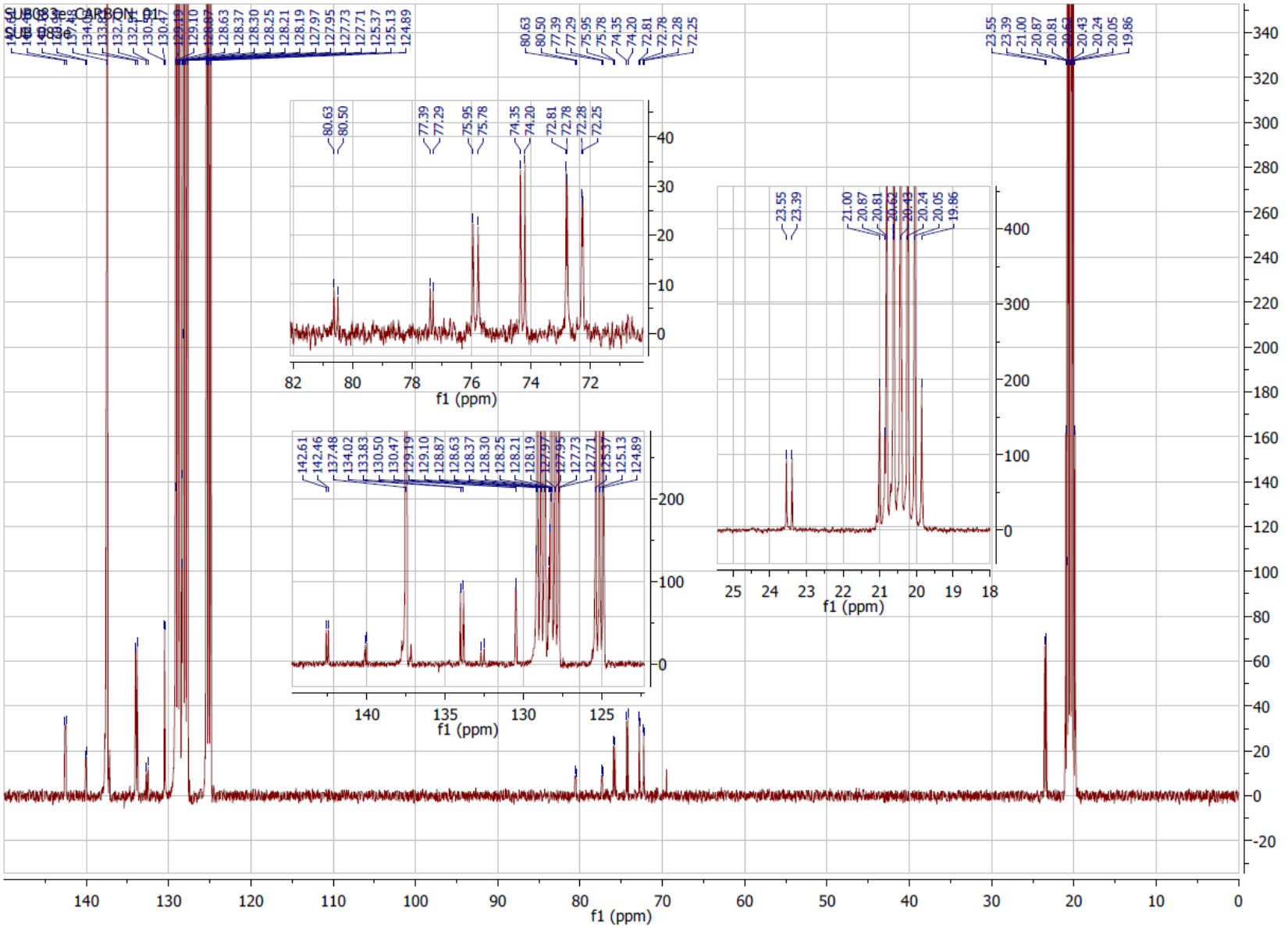


Fig S14. ^{13}C NMR of Fc'($PMes_2$)(PPh_2) (**3**) in toluene-d8.

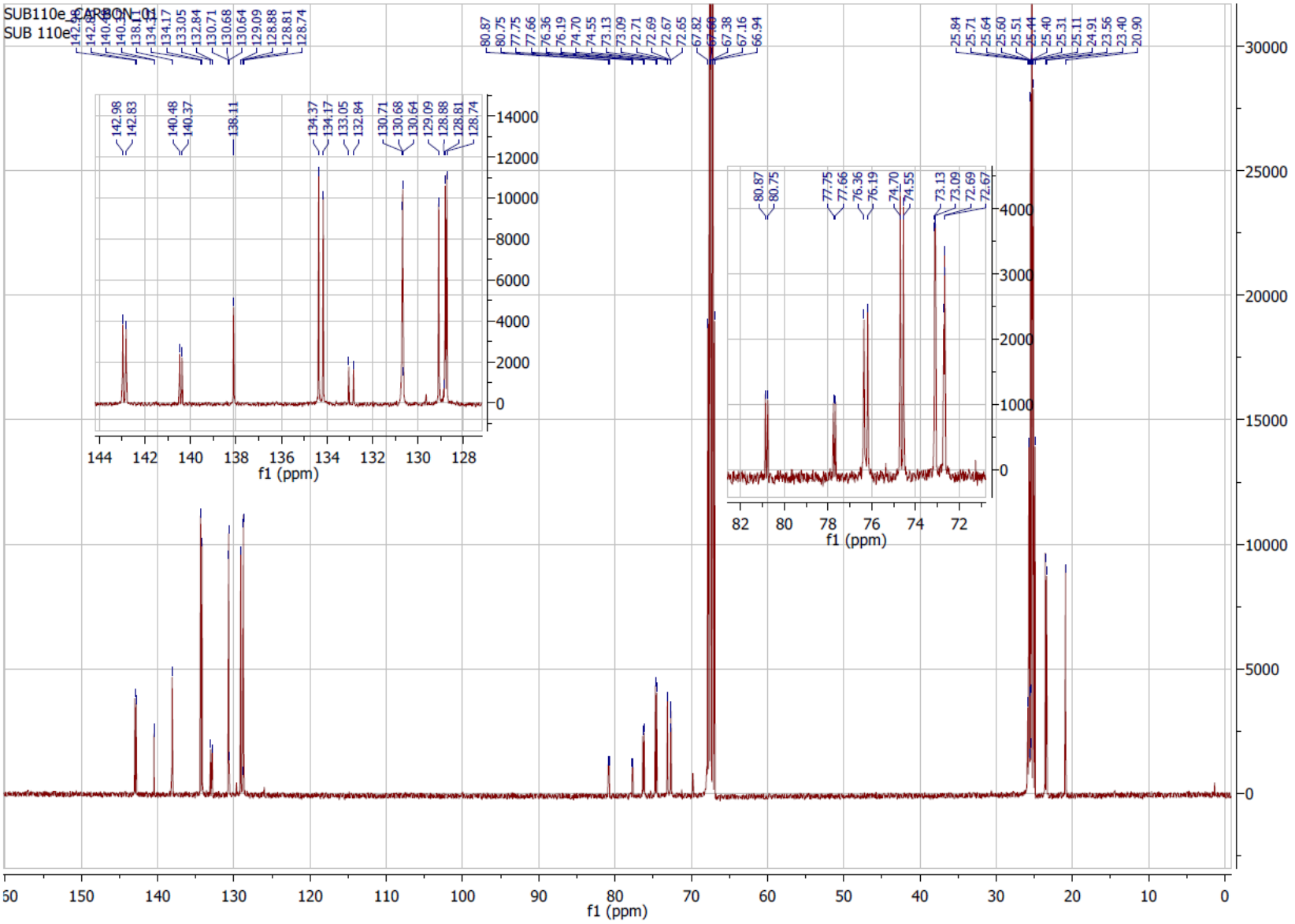


Fig S15. ^{13}C NMR of Fc'($PMes_2$)(PPh_2) (**3**) in thf-d8.

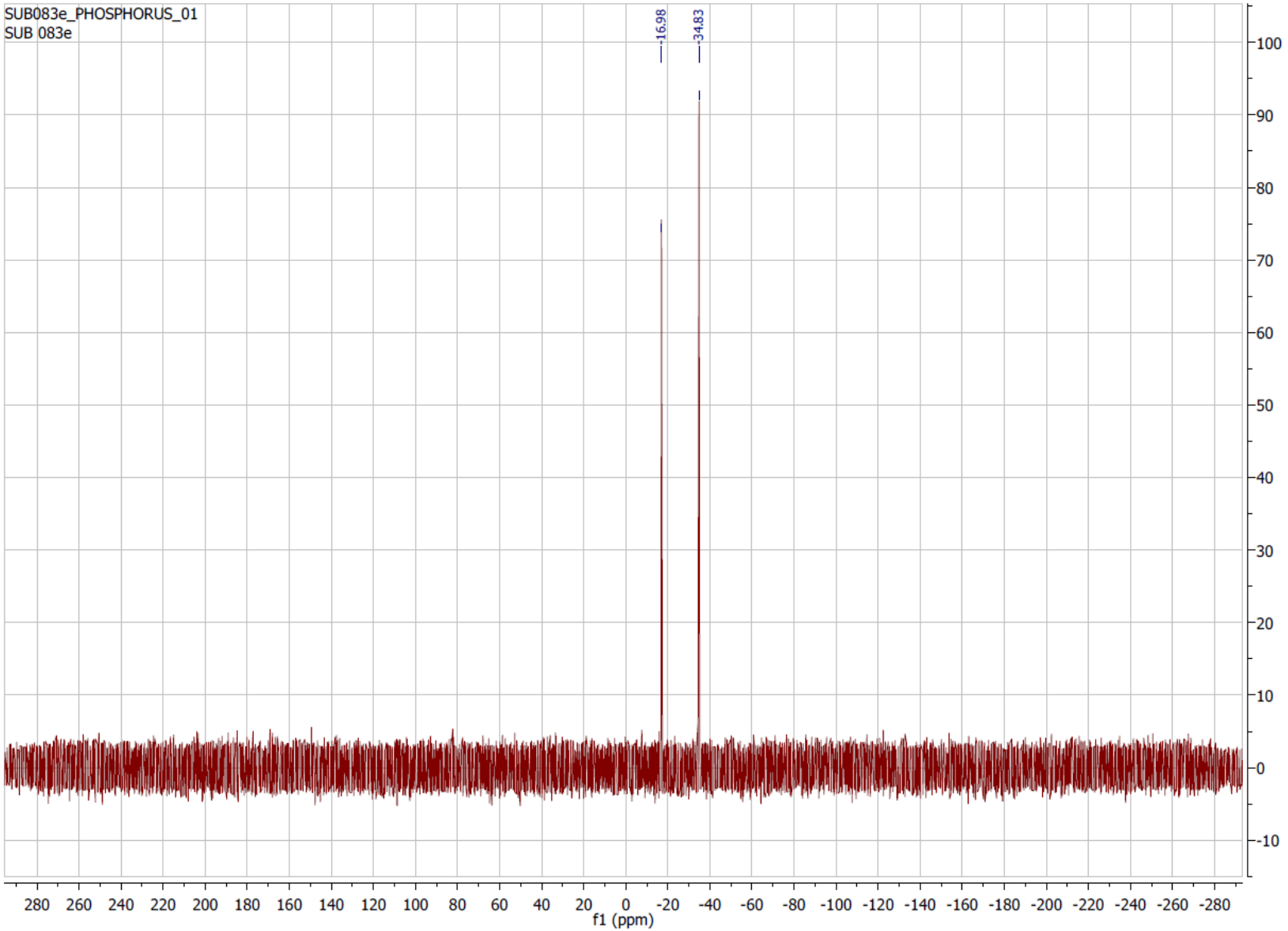


Fig S16. ^{31}P NMR of Fc'($PMes_2$)(PPh_2) (**3**) in toluene-d8.

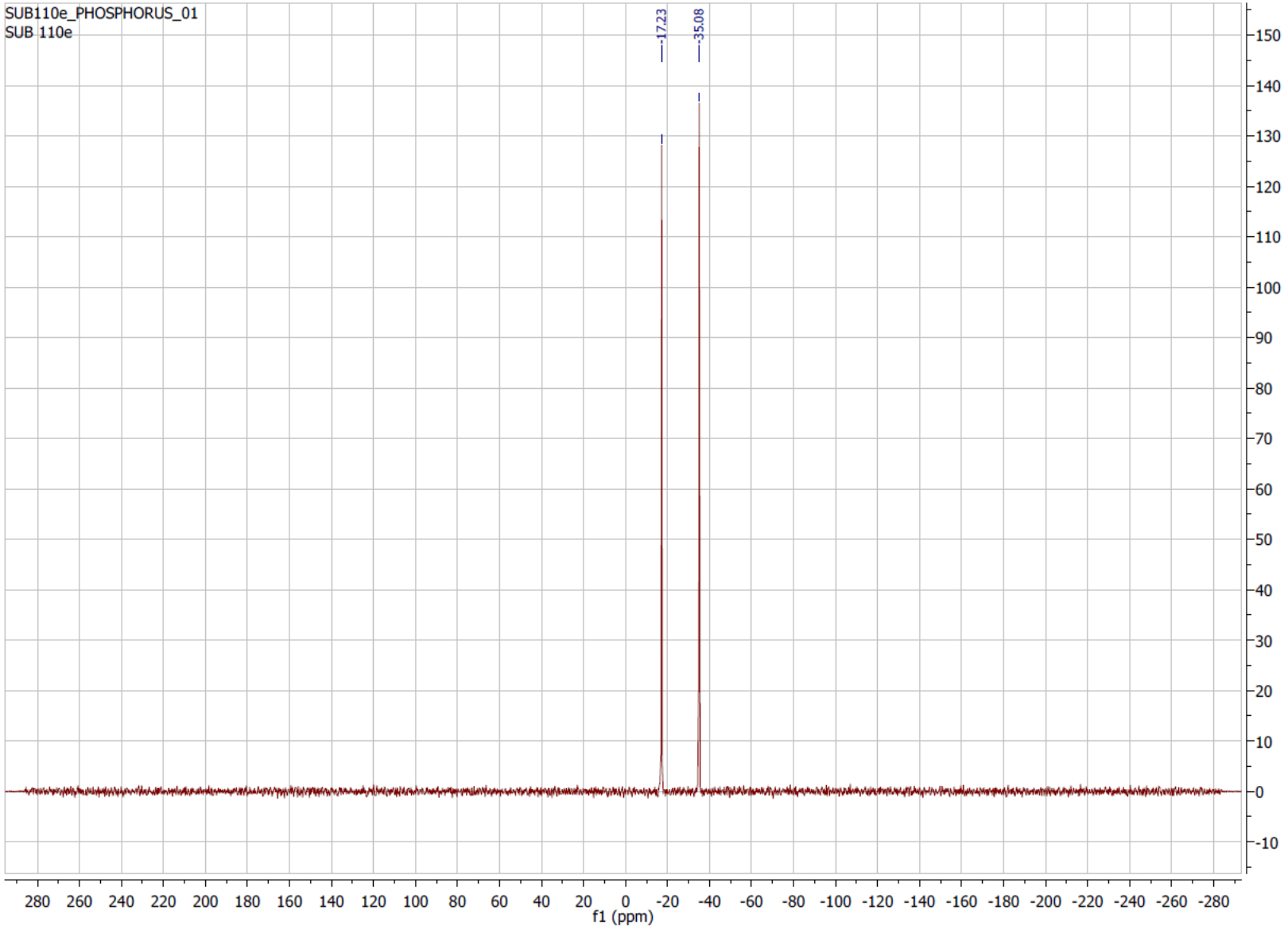


Fig S17. ^{31}P NMR of Fc'($PMes_2$)(PPh_2) (**3**) in thf-d8.

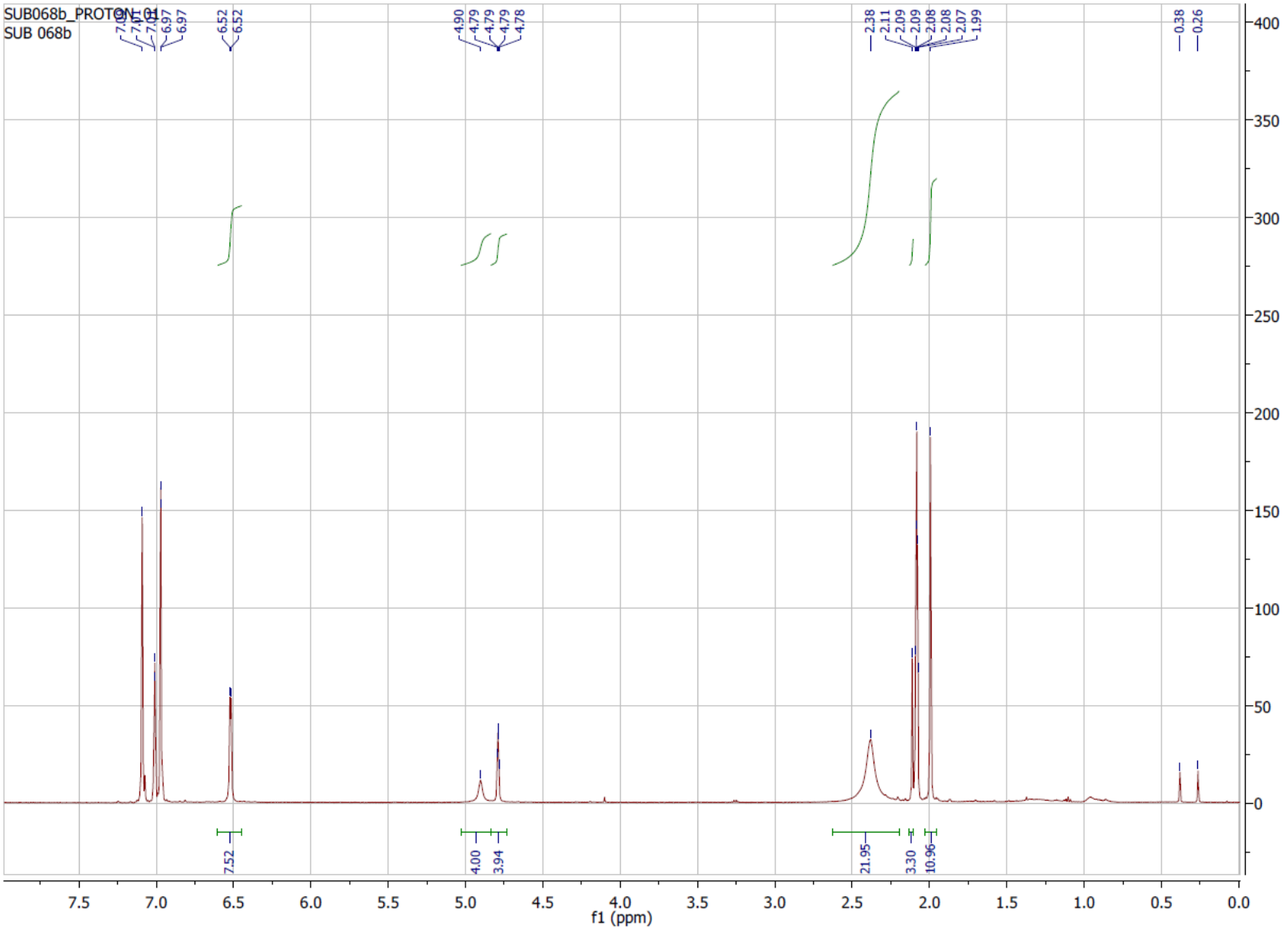


Fig S18. ^{1}H NMR of Fc'($PSeMes_2$)$_2$ (**5**) in toluene-d8.

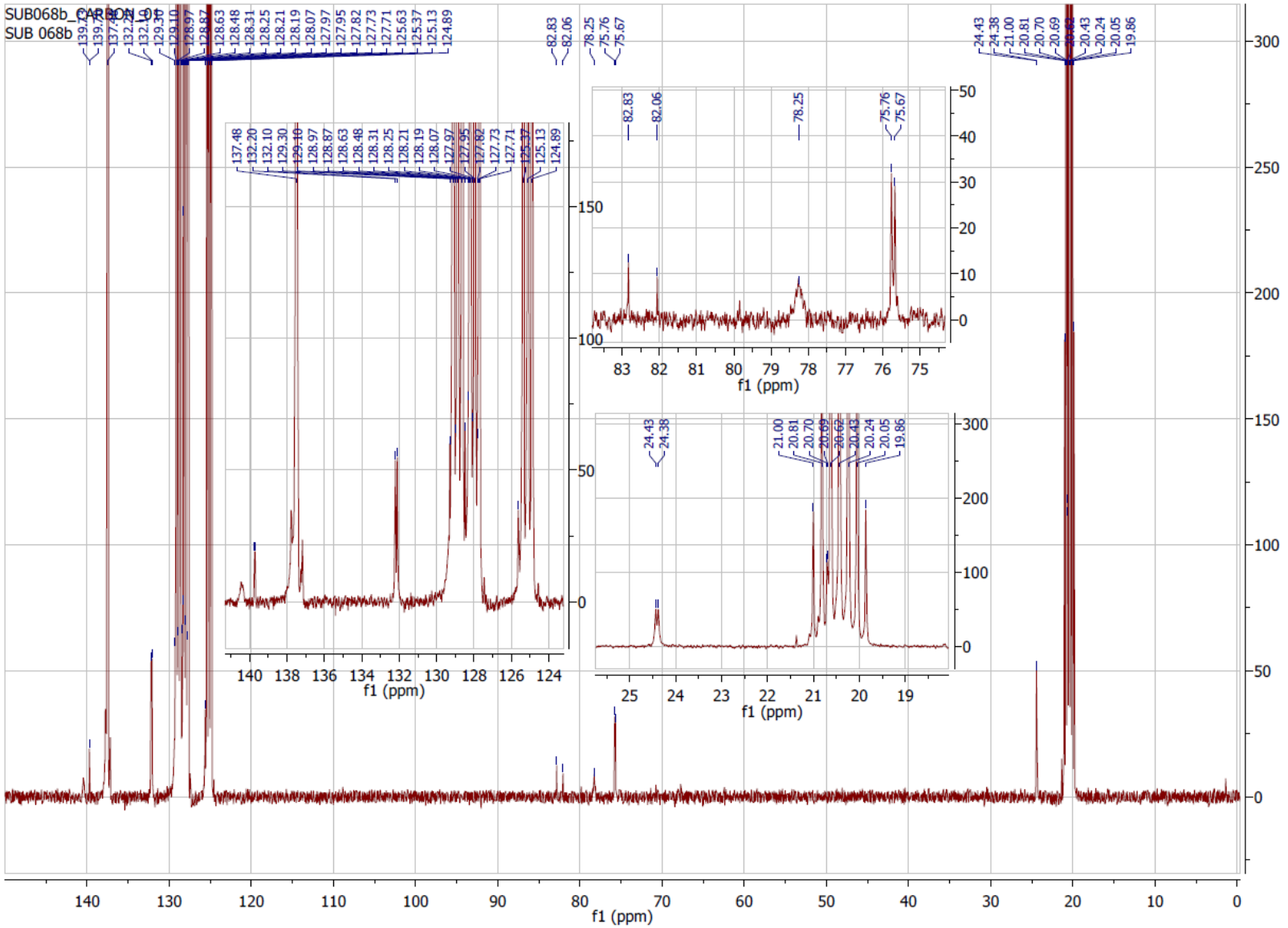


Fig S19. ^{13}C NMR of Fc'$(PSeMes_2)_2$ (**5**) in toluene-d8.

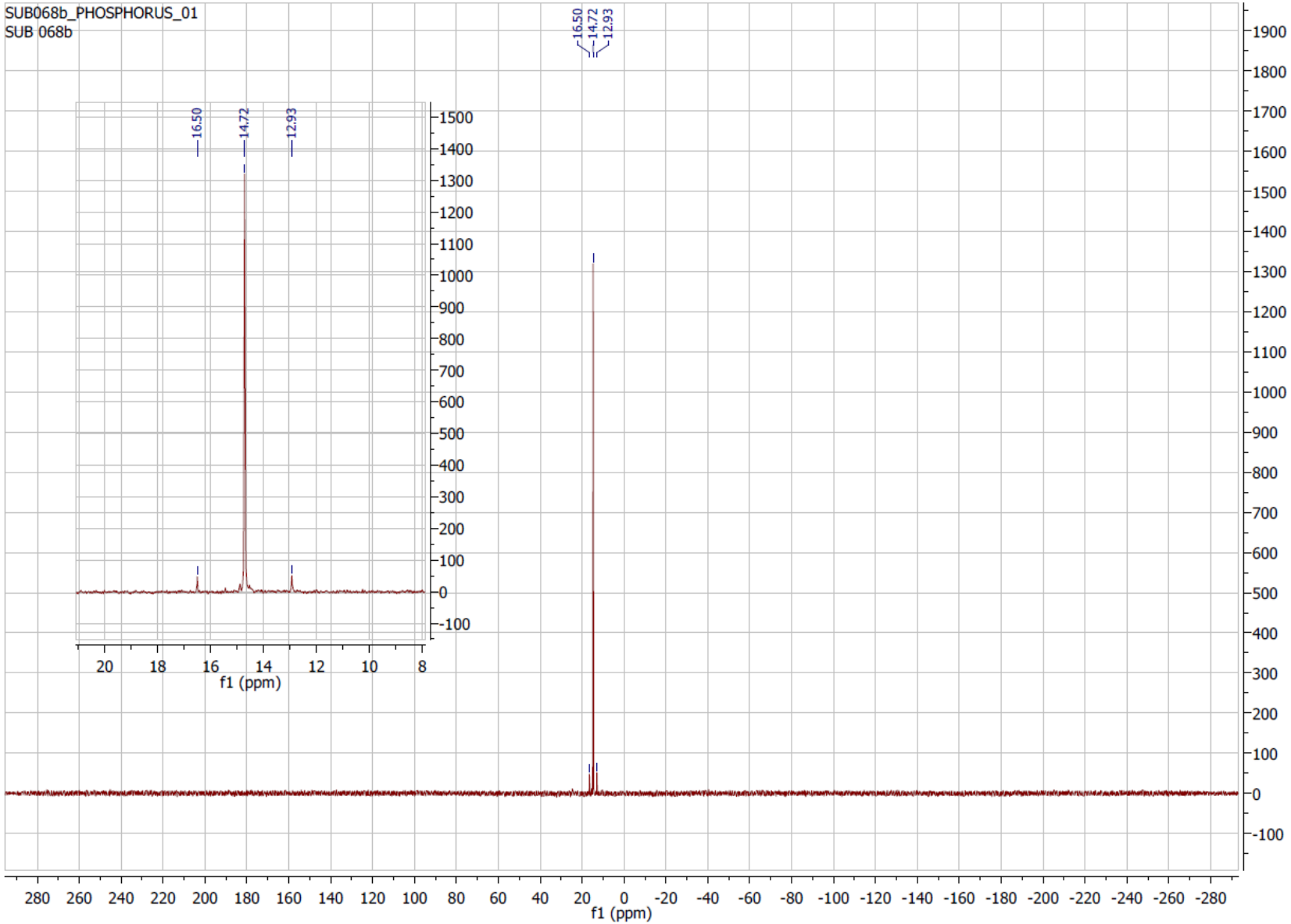


Fig S20. ^{31}P NMR of Fc'(PSeMes$_2$)$_2$ (**5**) in toluene-d8.

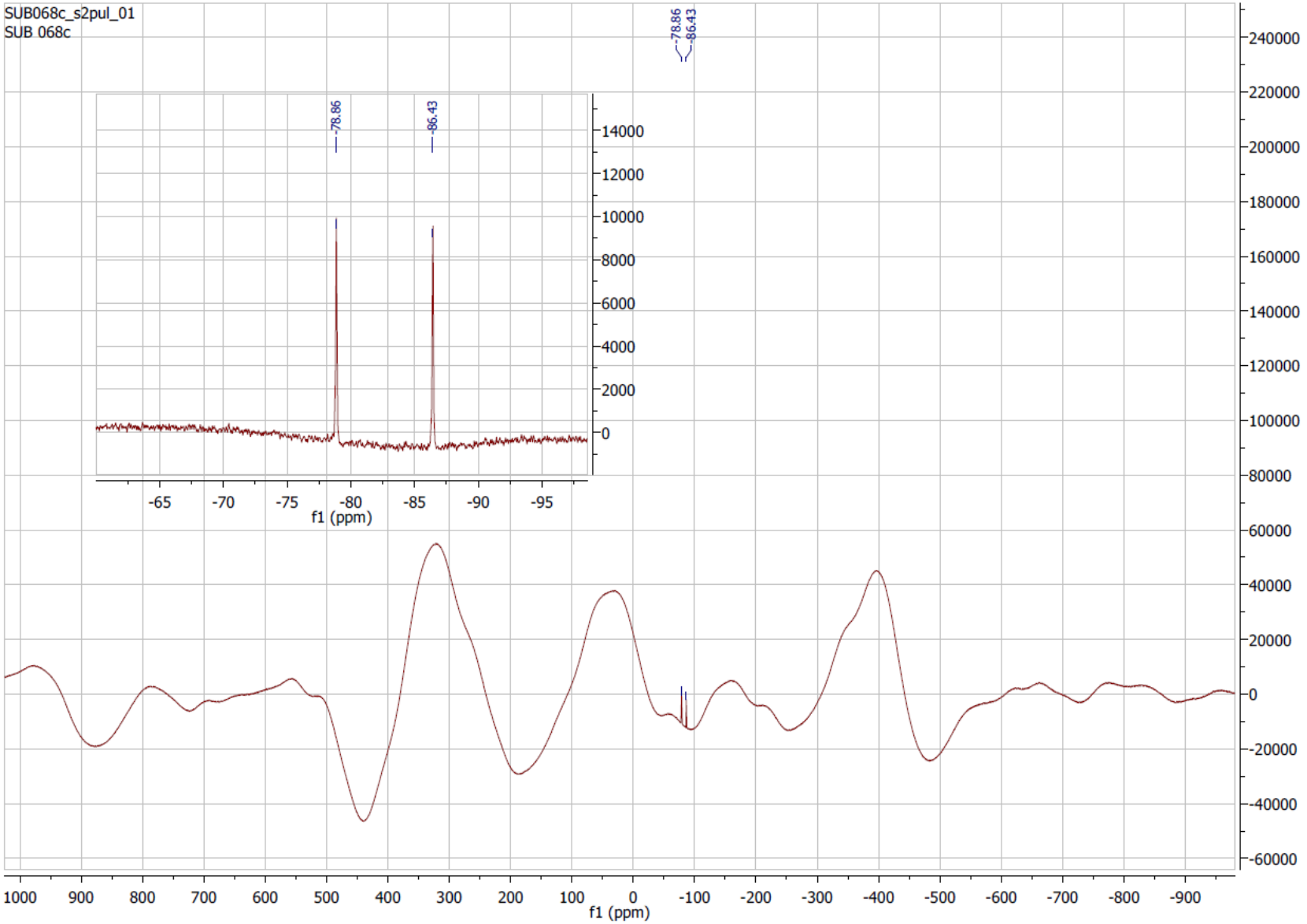


Fig S21. ^{31}P NMR of Fc'($PSeMes_2$)$_2$ (**5**) in toluene-d8.

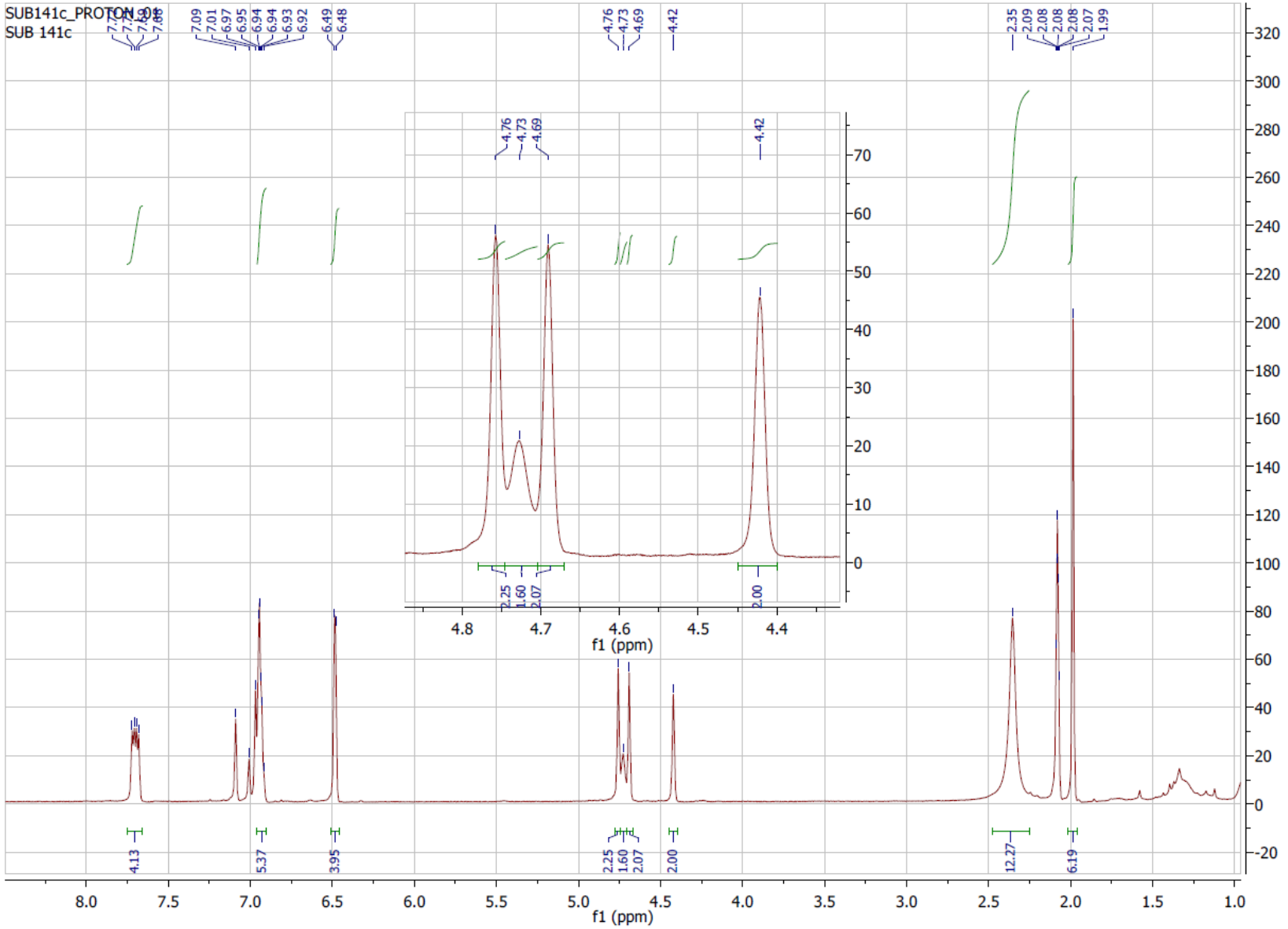


Fig S22. ^{1}H NMR of Fc'($PSeMes_2$)($PSePh_2$) (**6**) in toluene-d8.

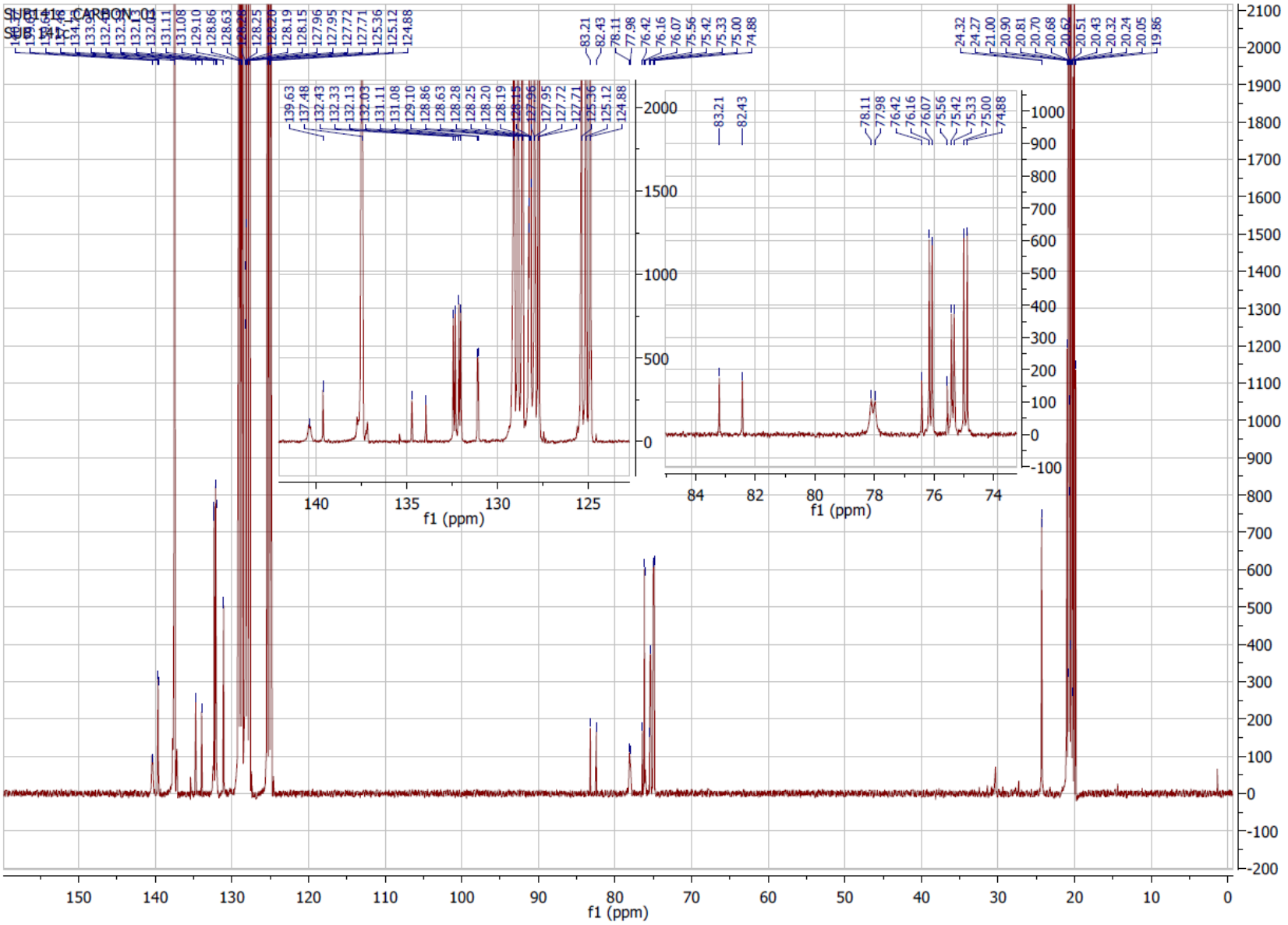


Fig S23. ^{13}C NMR of Fc'($PSeMes_2$)($PSePh_2$) (**6**) in toluene-d8.

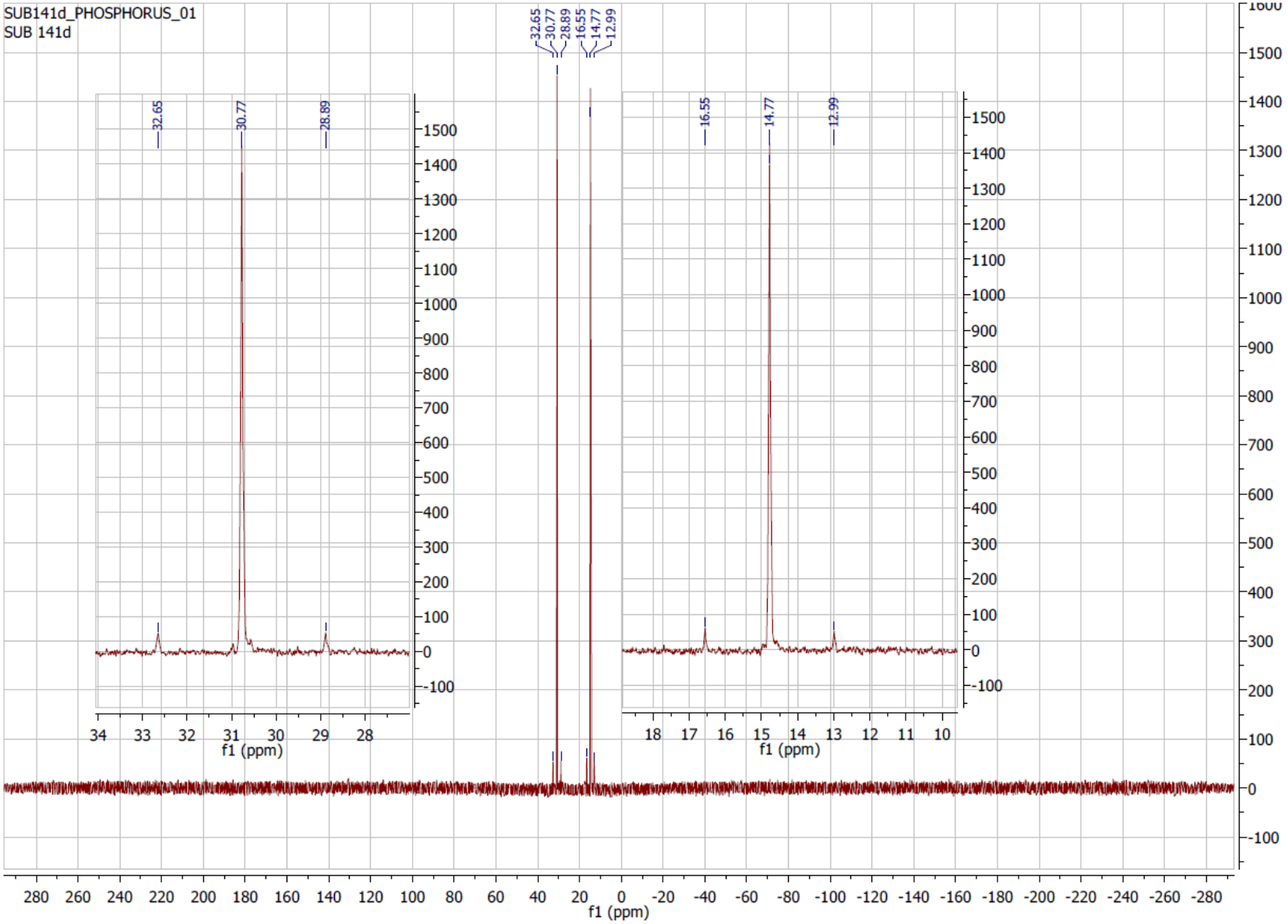


Fig S24. ^{31}P NMR of Fc'($PSeMes_2$)($PSePh_2$) (**6**) in toluene-d8.

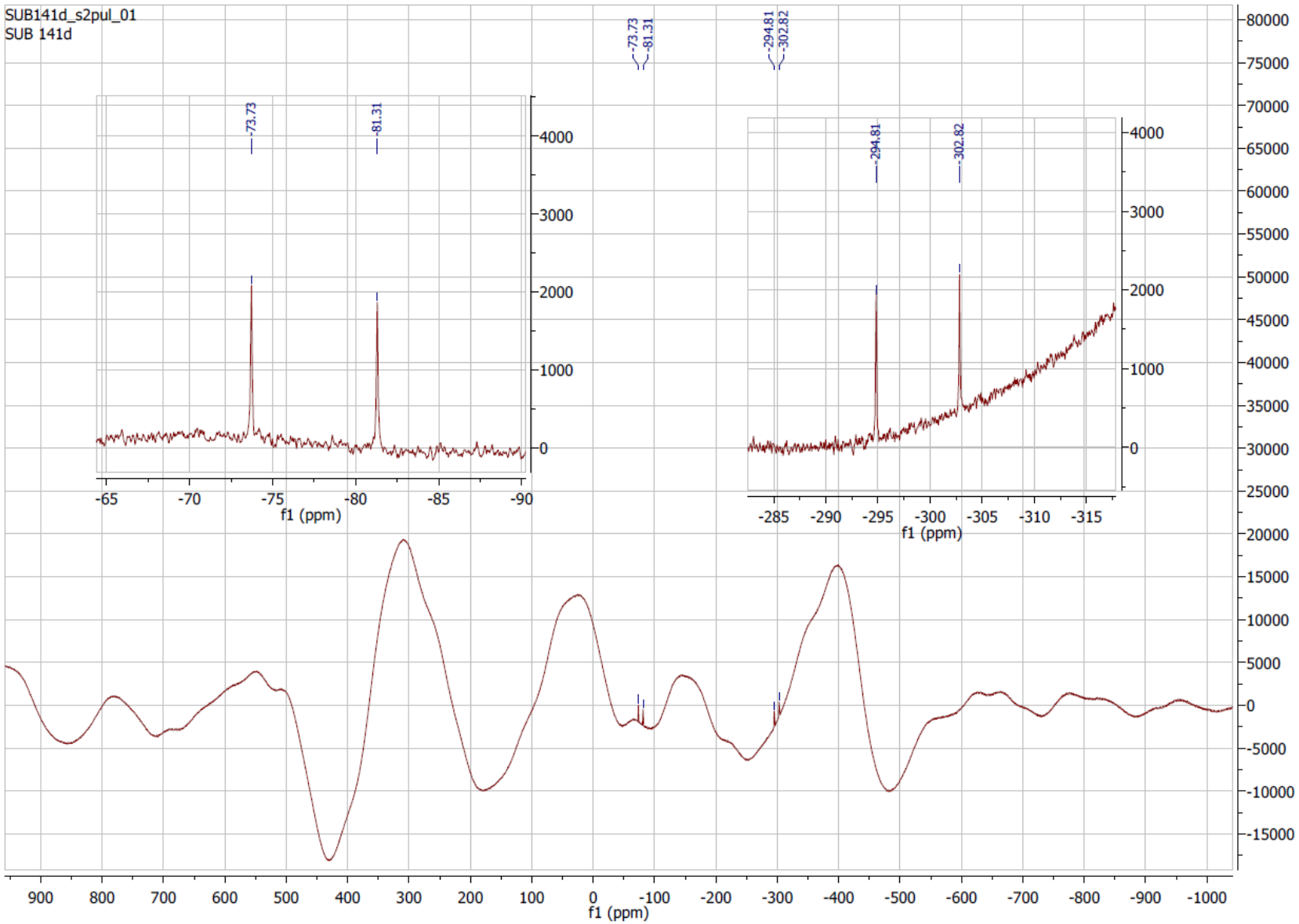


Fig S25. ^{77}Se NMR of Fc'($PSeMes_2$)($PSePh_2$) (**6**) in toluene-d8.

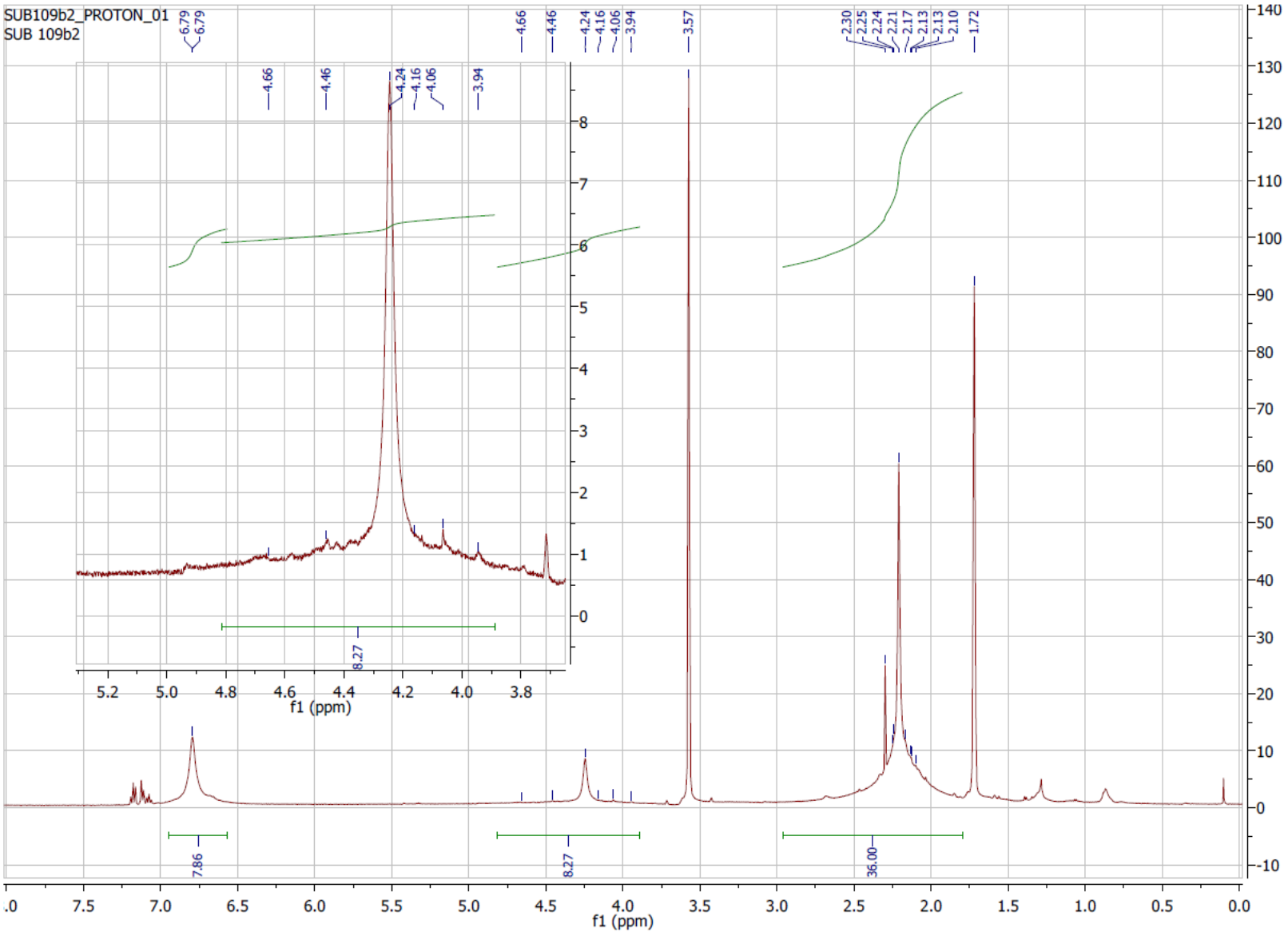


Fig S26. ^{1}H NMR of Fc'($PMes_2$)$_2$.CuBr (**7**) in thf-d8.

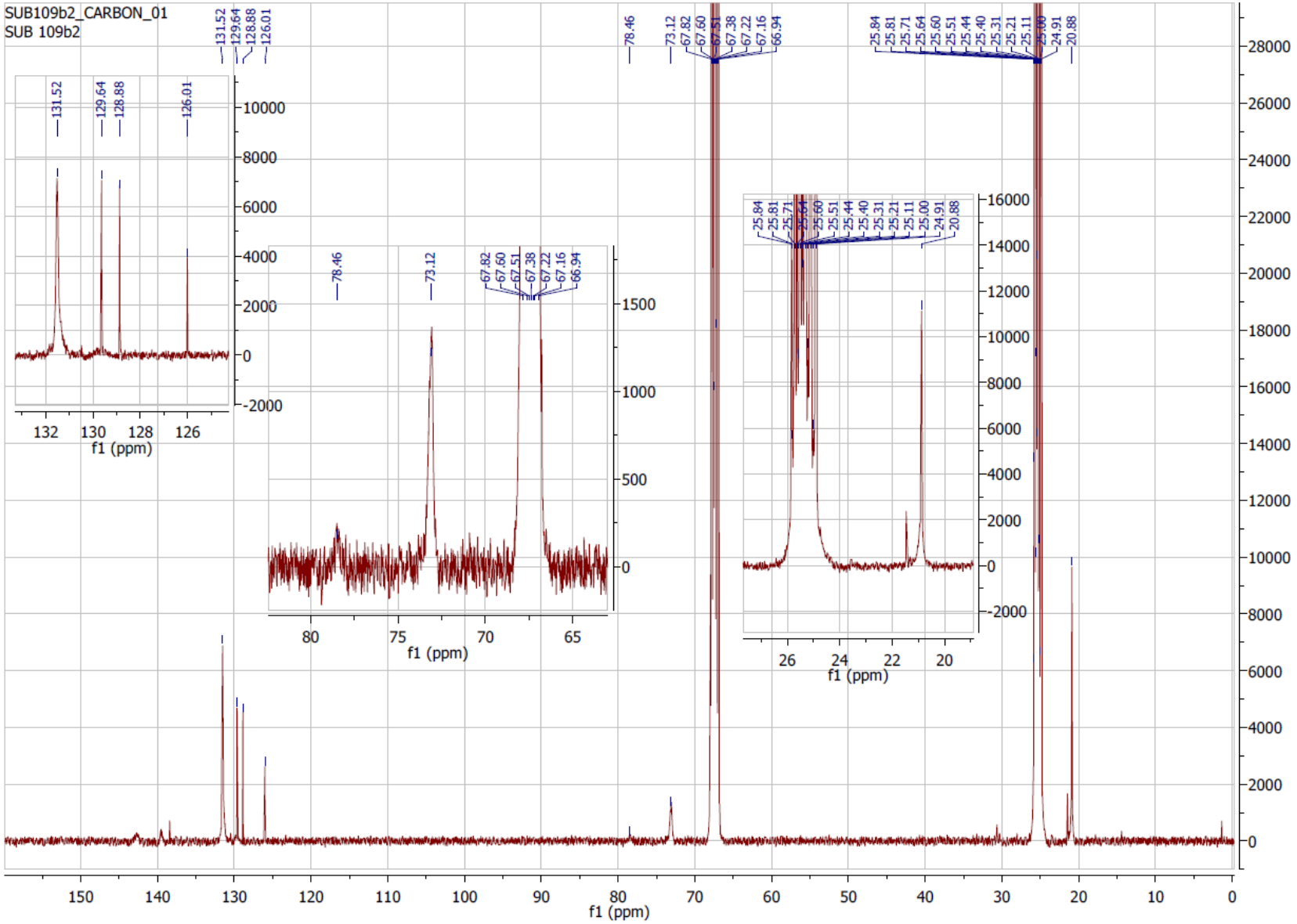


Fig S27. ^{13}C NMR of Fc'(PMes$_2$)$_2$.CuBr (**7**) in thf-d8.

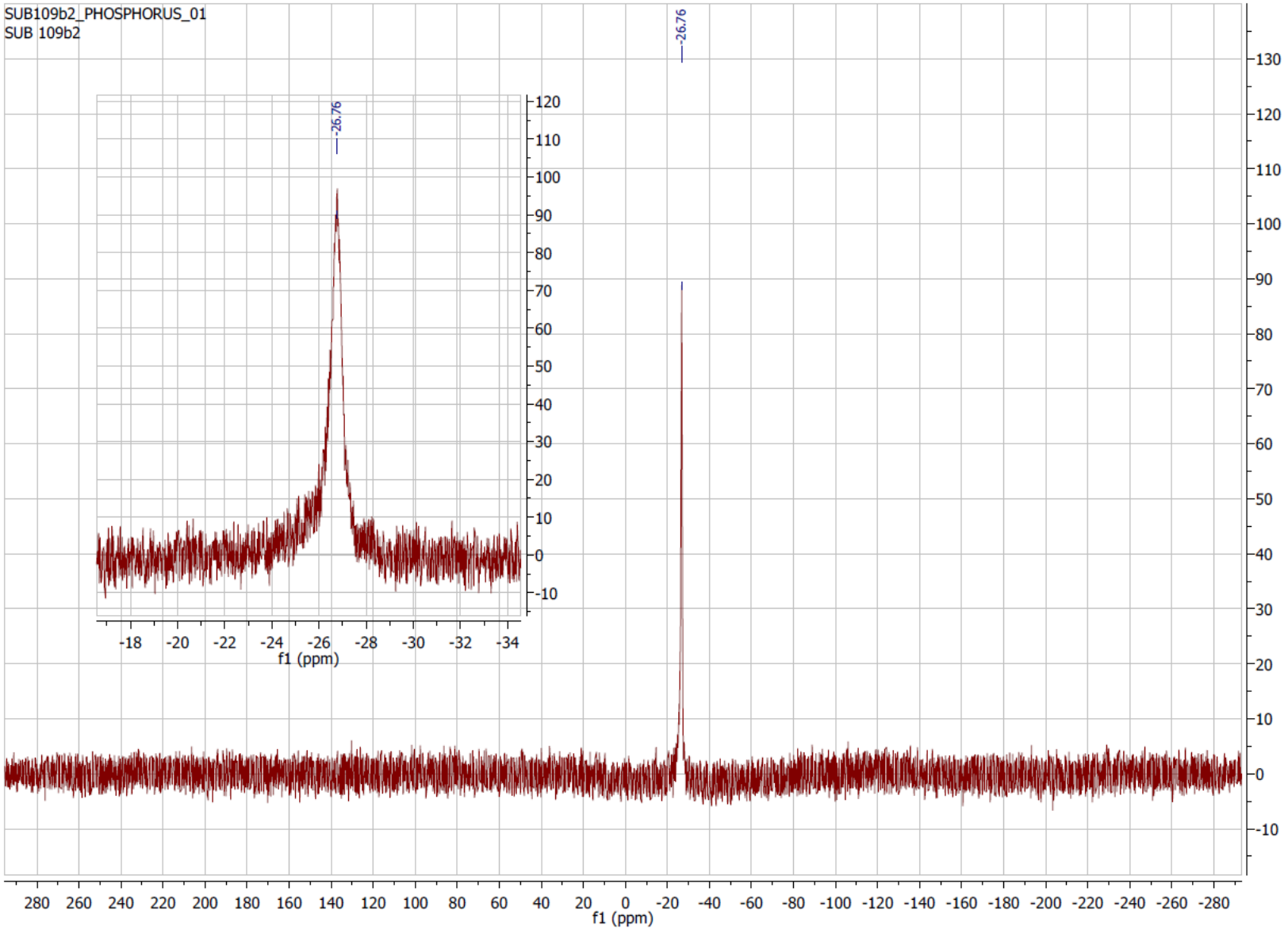


Fig S28. ^{31}P NMR of Fc'($PMes_2$)$_2$.CuBr (**7**) in thf-d8.

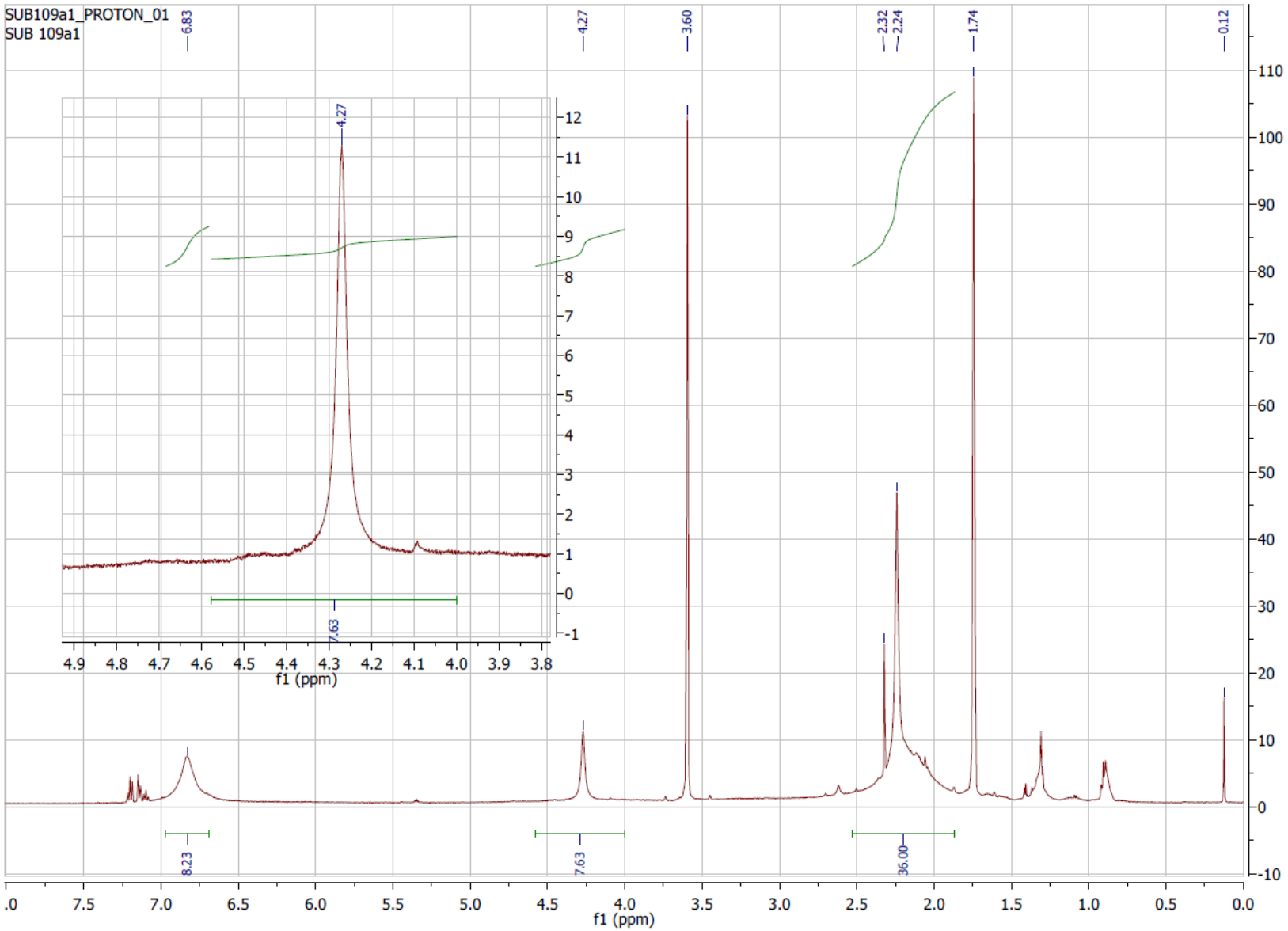


Fig S29. ^{1}H NMR of Fc'($PMes_2$)$_2$.CuI (**8**) in thf-d8.

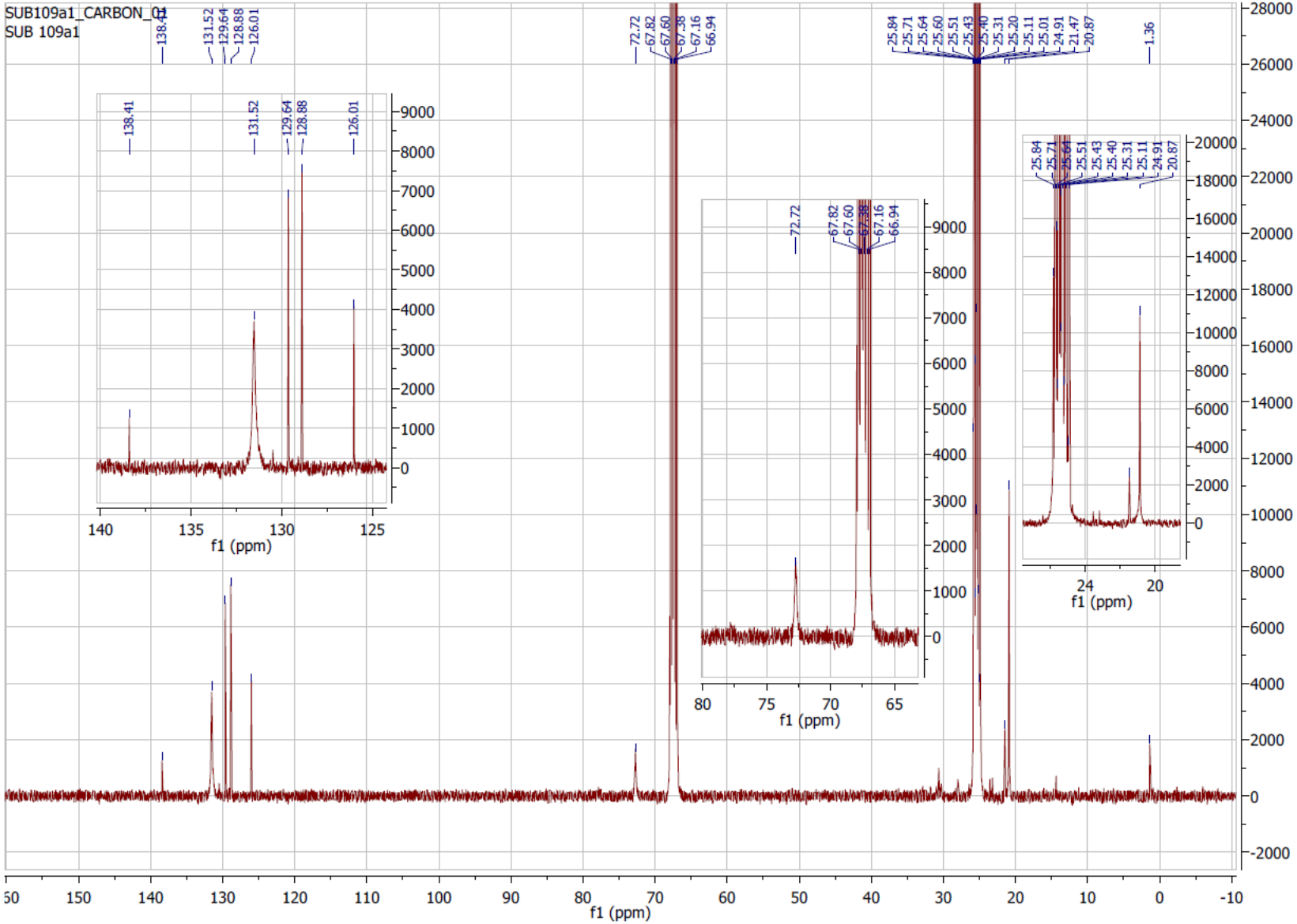


Fig S30. ^{13}C NMR of Fc'(PMes$_2$)$_2$.CuI (**8**) in thf-d8.

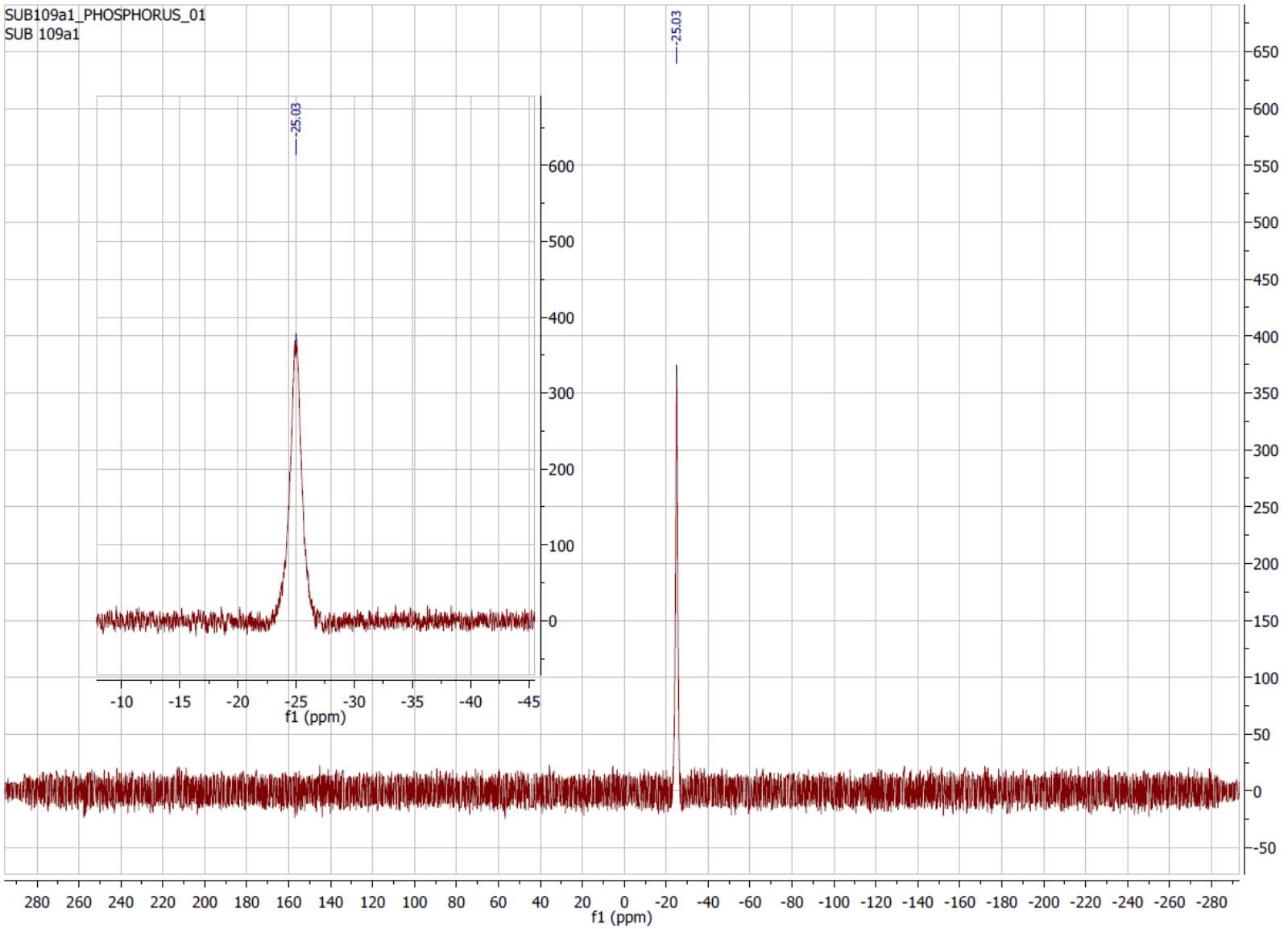


Fig S31. ^{31}P NMR of Fc'($PMes_2$)$_2$.CuI (**8**) in thf-d8.

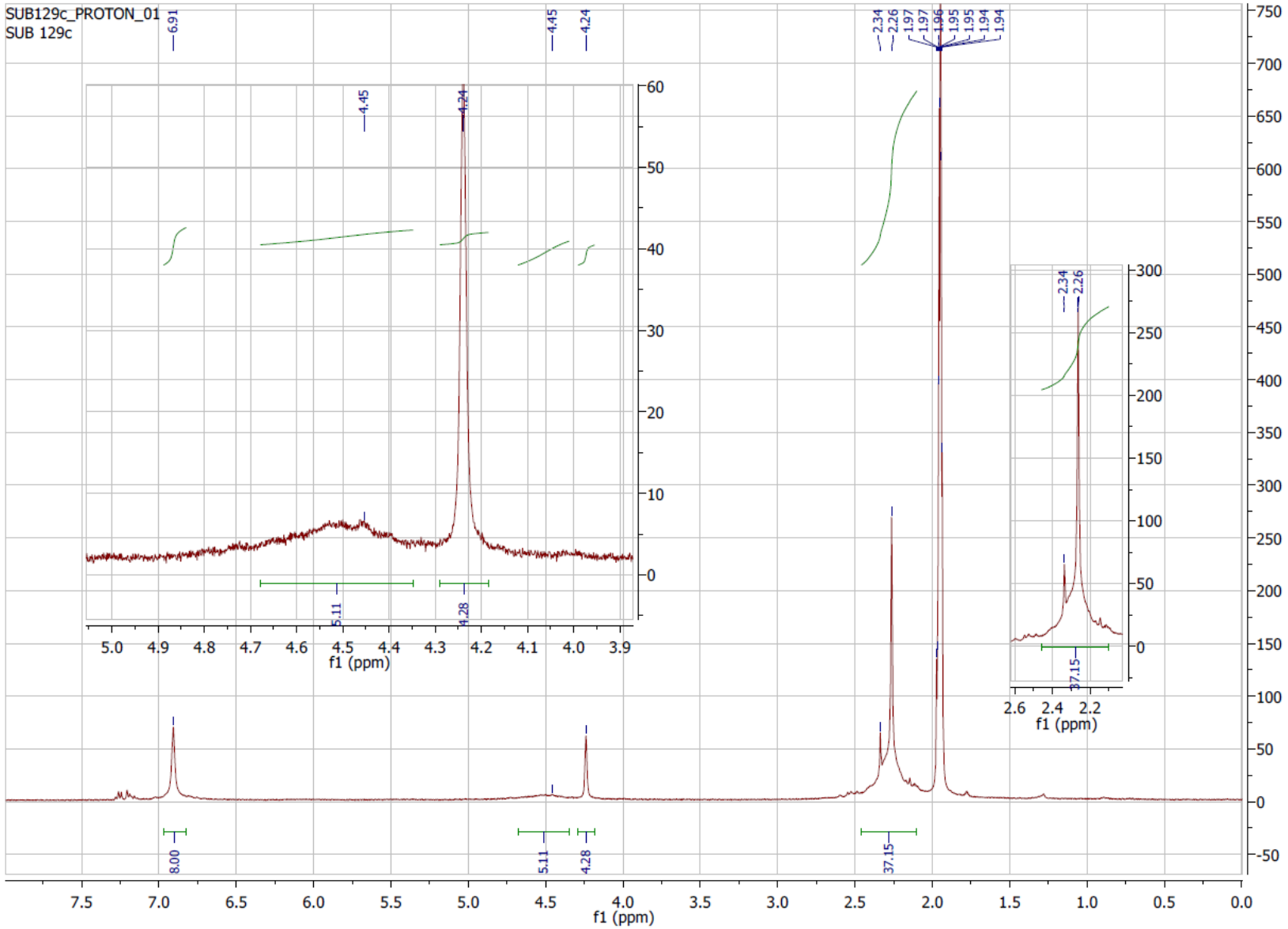


Fig S32. ^{1}H NMR of Fc'$(PMes_2)_2$.$CuBF_4$ (**9**) in CD_3CN.

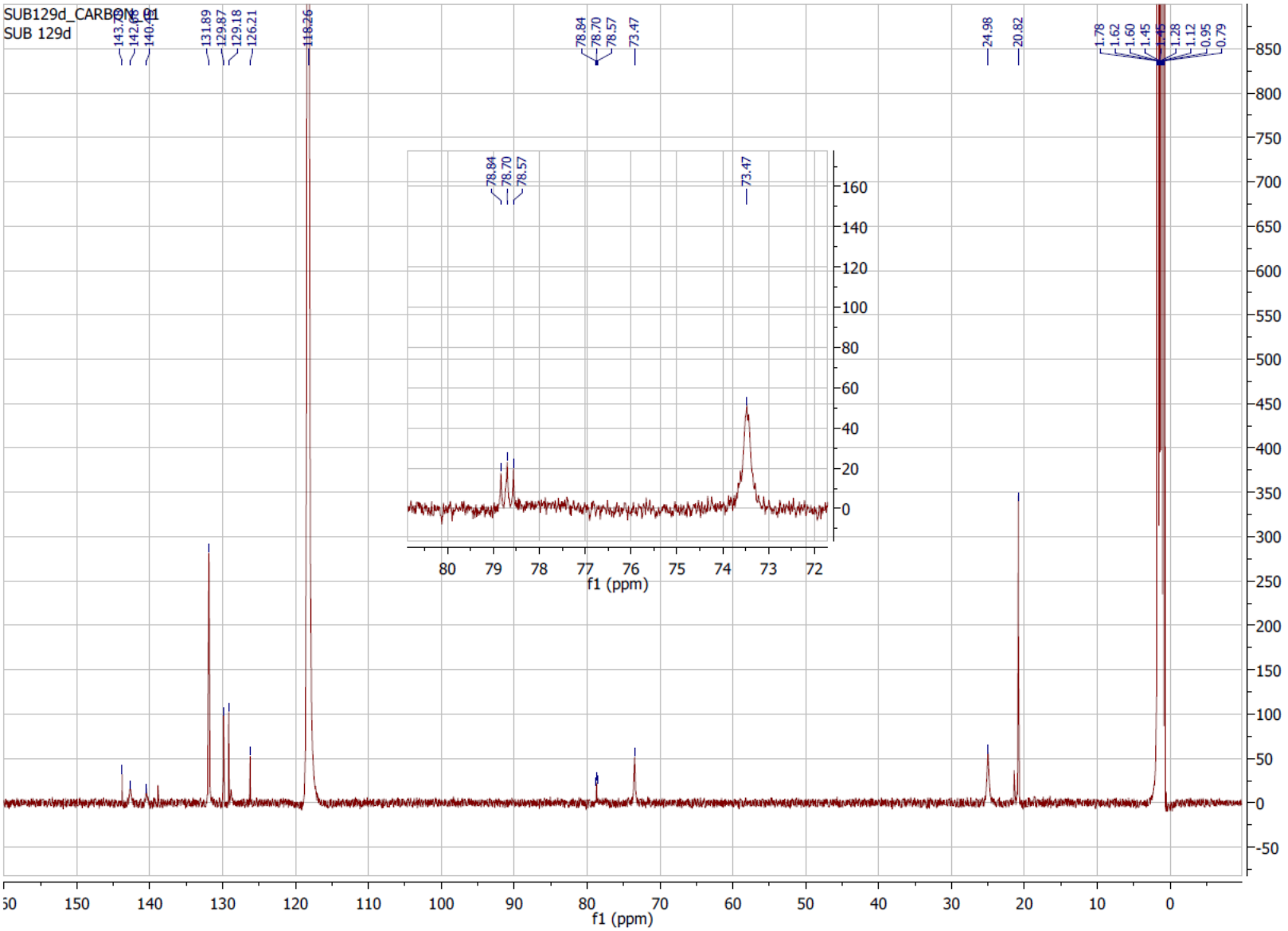


Fig S33. ^{13}C NMR of Fc'$(PMes_2)_2$.$CuBF_4$ (**9**) in CD_3CN.

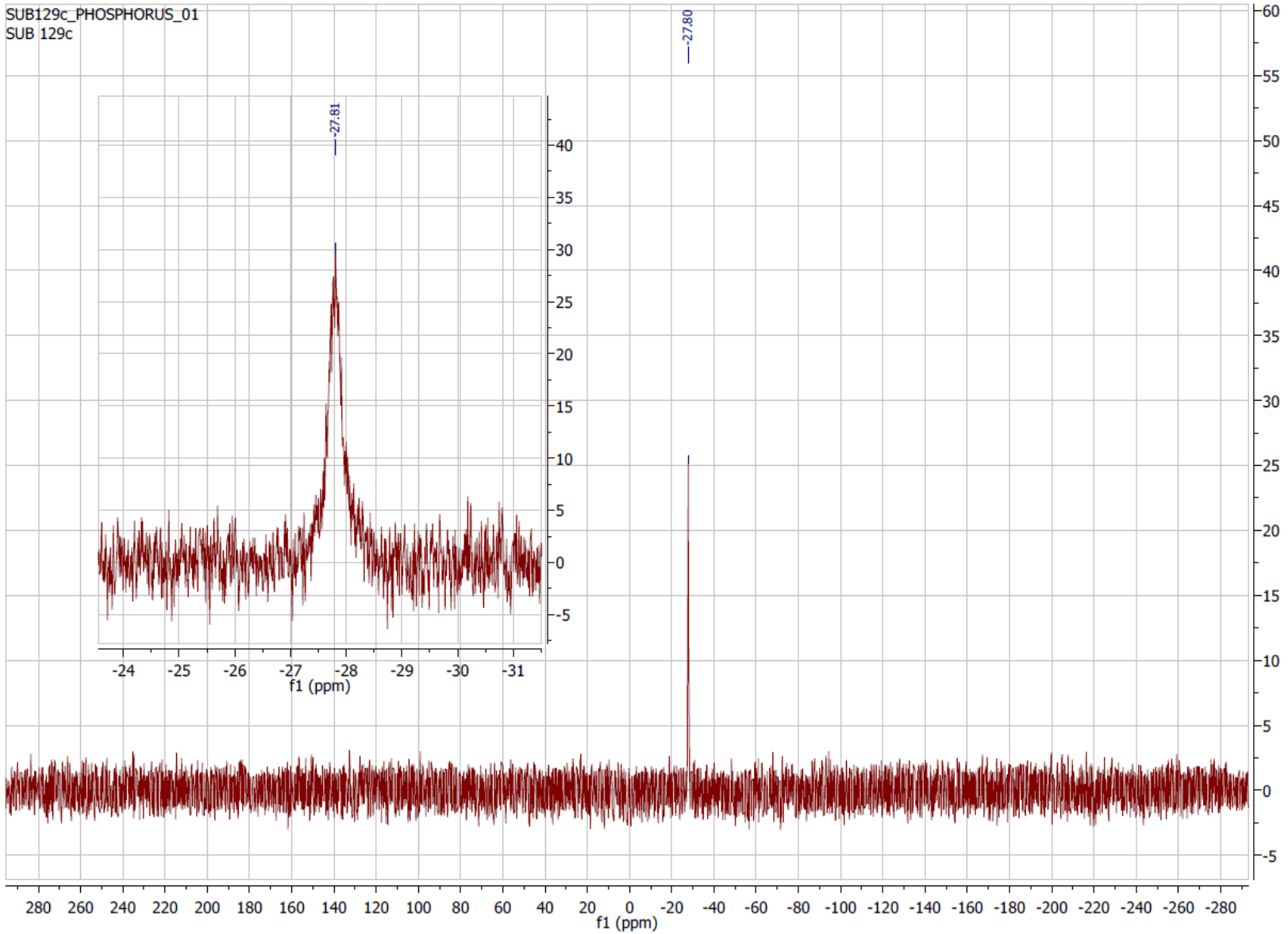


Fig S34. ^{31}P NMR of Fc'$(PMes_2)_2$.$CuBF_4$ (**9**) in CD_3CN.

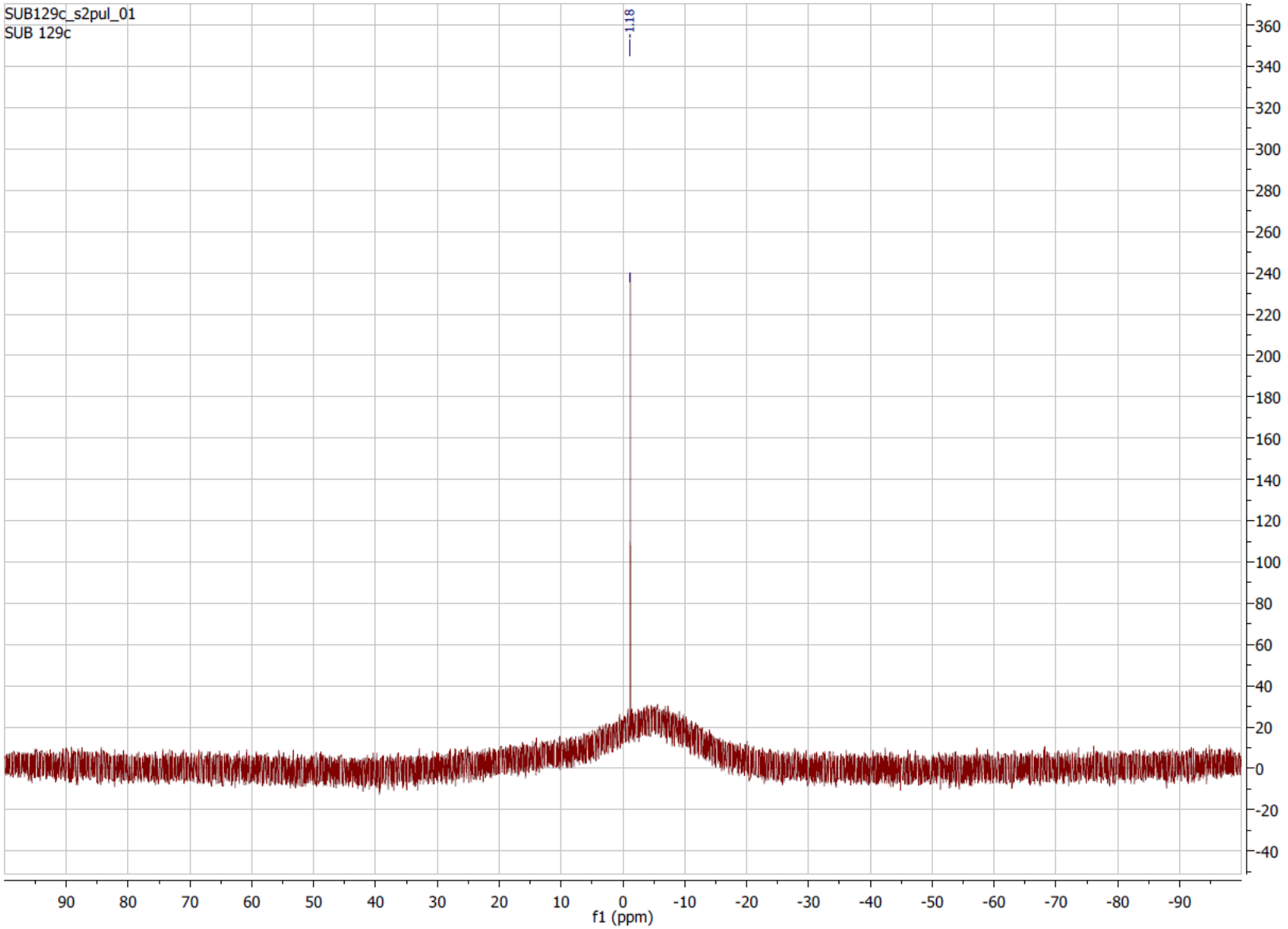


Fig S35. ^{11}B NMR of Fc'$(PMes_2)_2$.$CuBF_4$ (**9**) in CD_3CN.

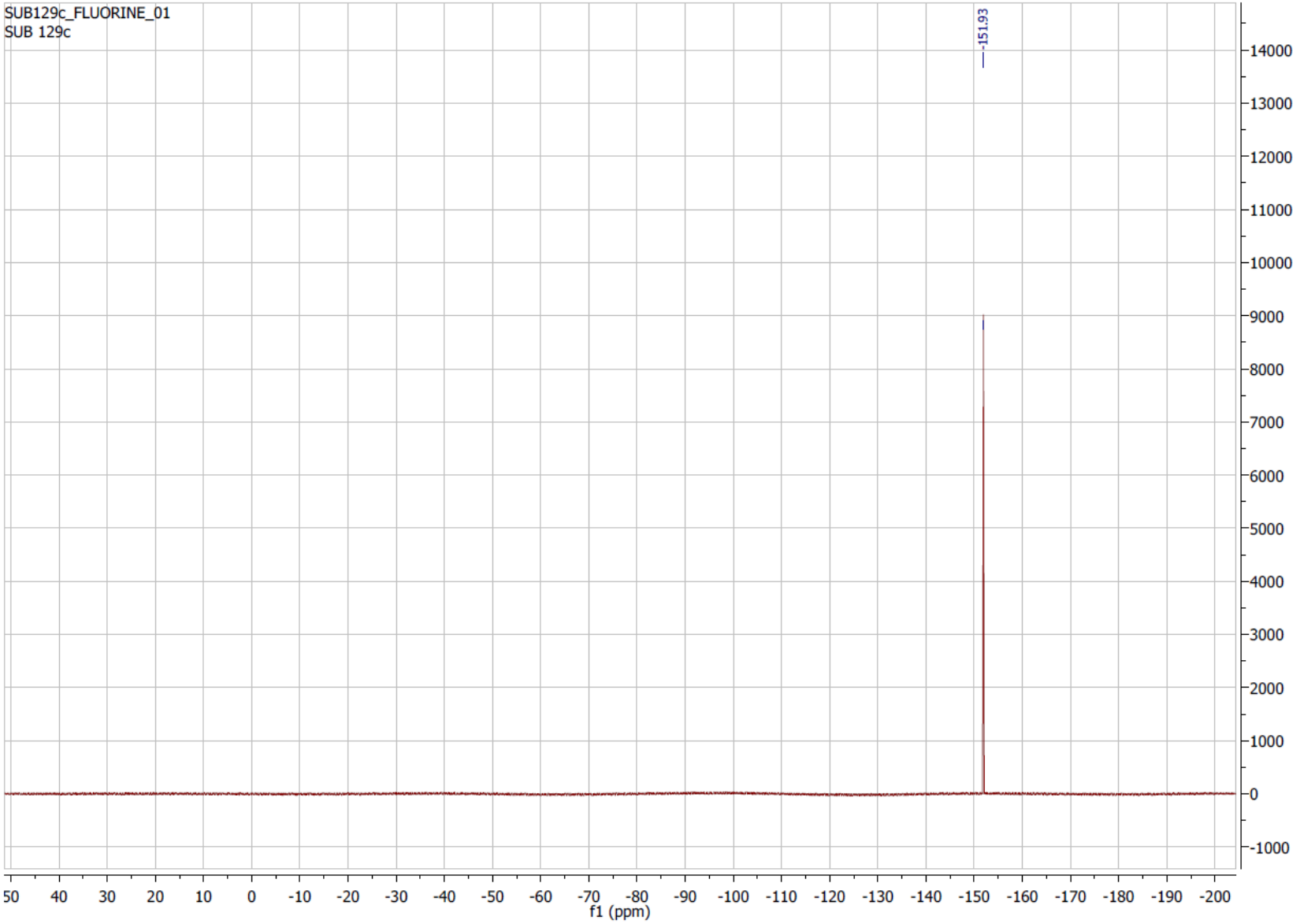


Fig S36. ^{19}F NMR of Fc'$(PMes_2)_2$.$CuBF_4$ (**9**) in CD_3CN.

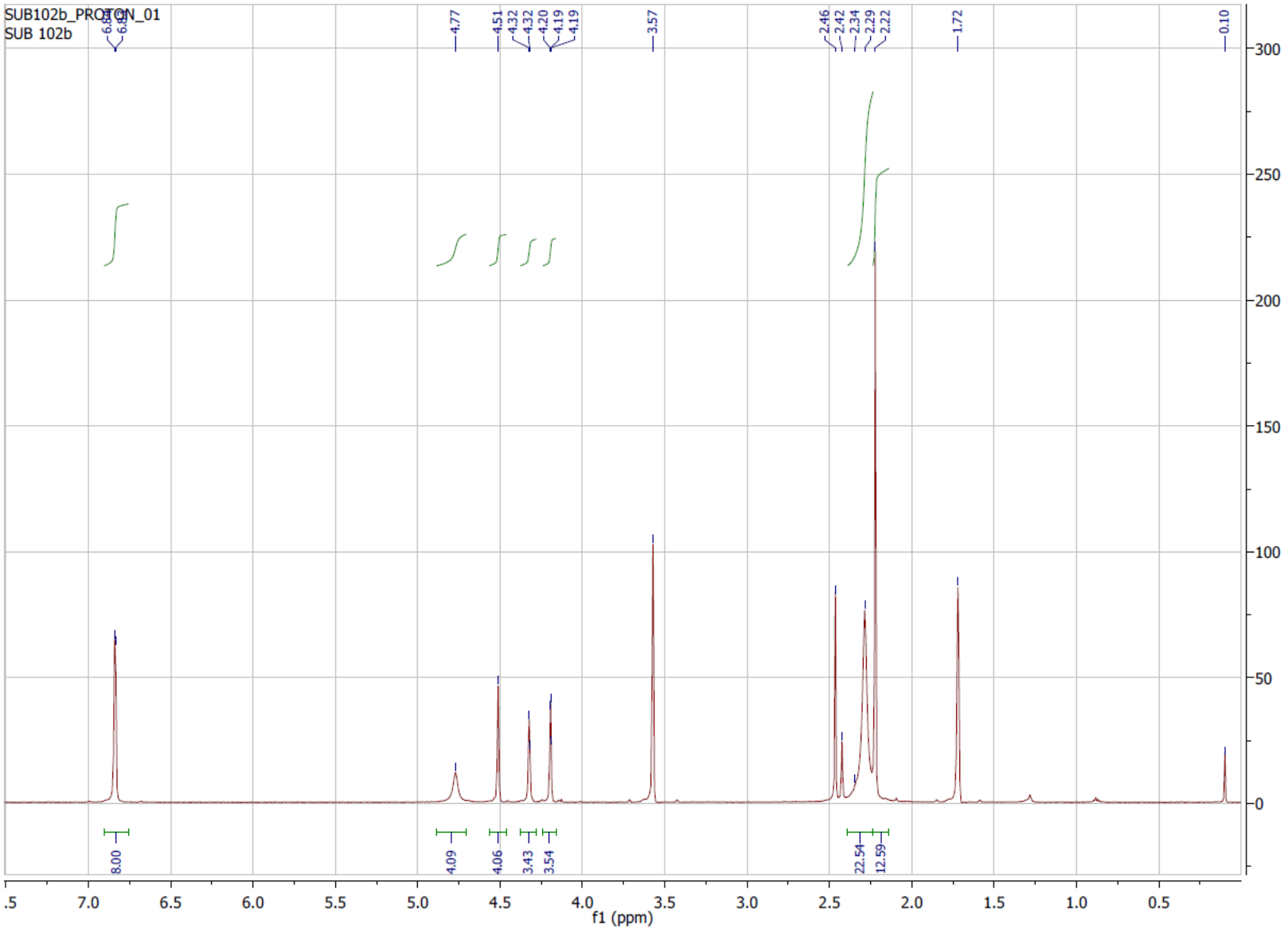


Fig S37. ^{1}H NMR of [Fc'(PMes$_2$)Br.CuBr]$_2$ (**14**) in thf-d8. The peak at δ 2.46 is resulting from water dissolved in NMR solvent.

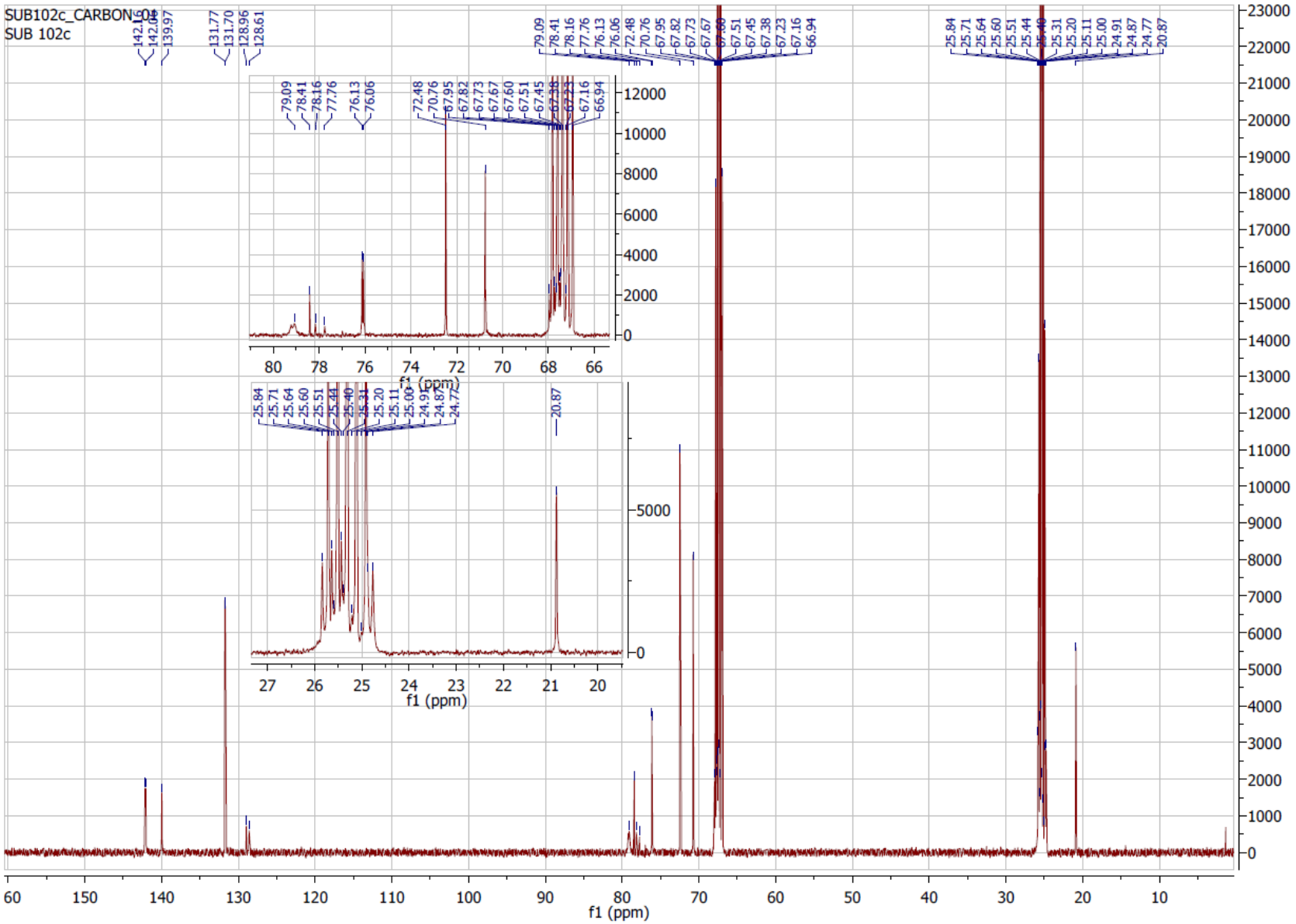


Fig S38. ^{13}C NMR of [Fc'(PMes$_2$)Br.CuBr]$_2$ (**14**) in thf-d8.

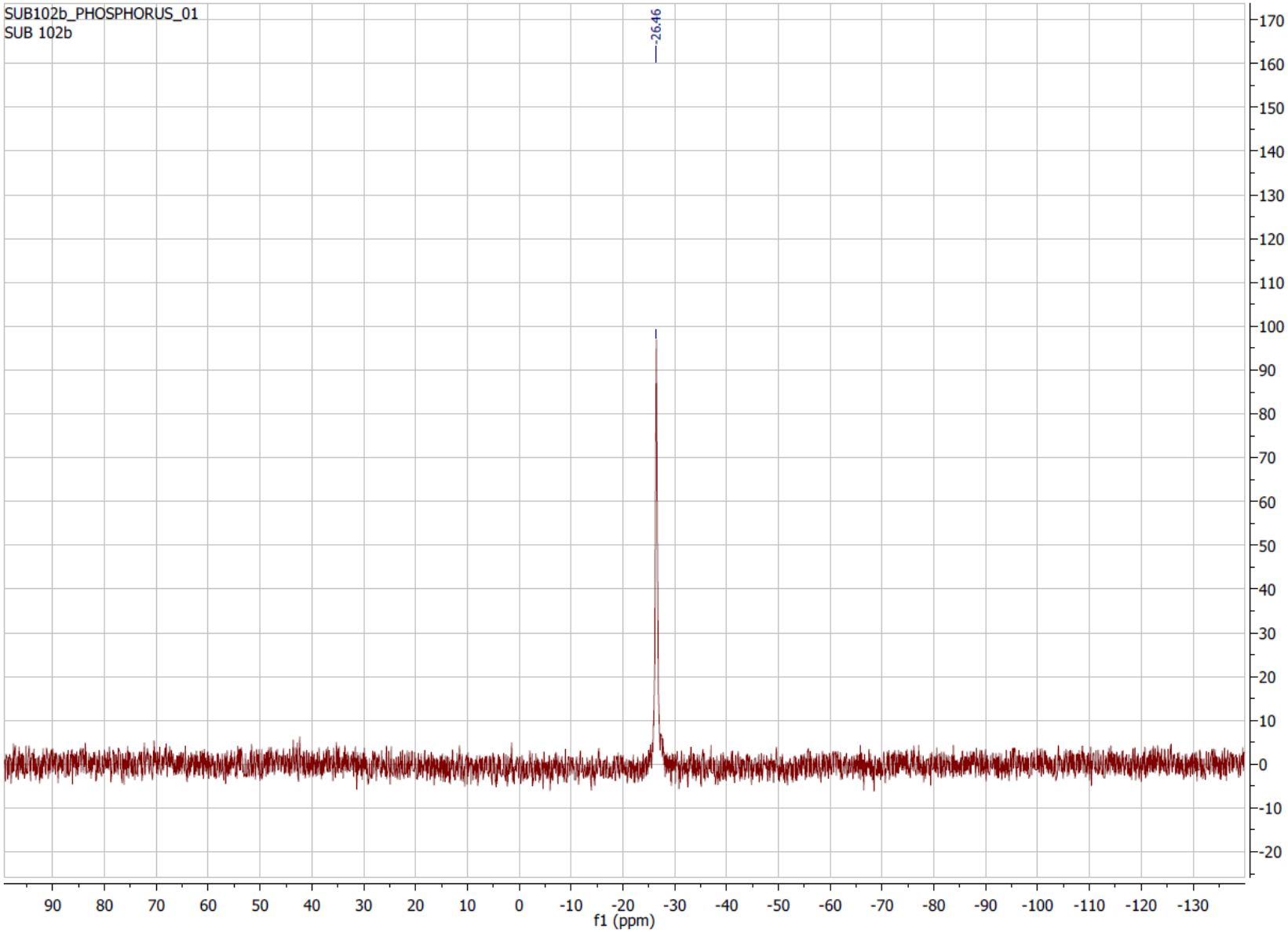


Fig S39. ^{31}P NMR of [Fc'($PMes_2$)Br.CuBr]$_2$ (**14**) in thf-d8.

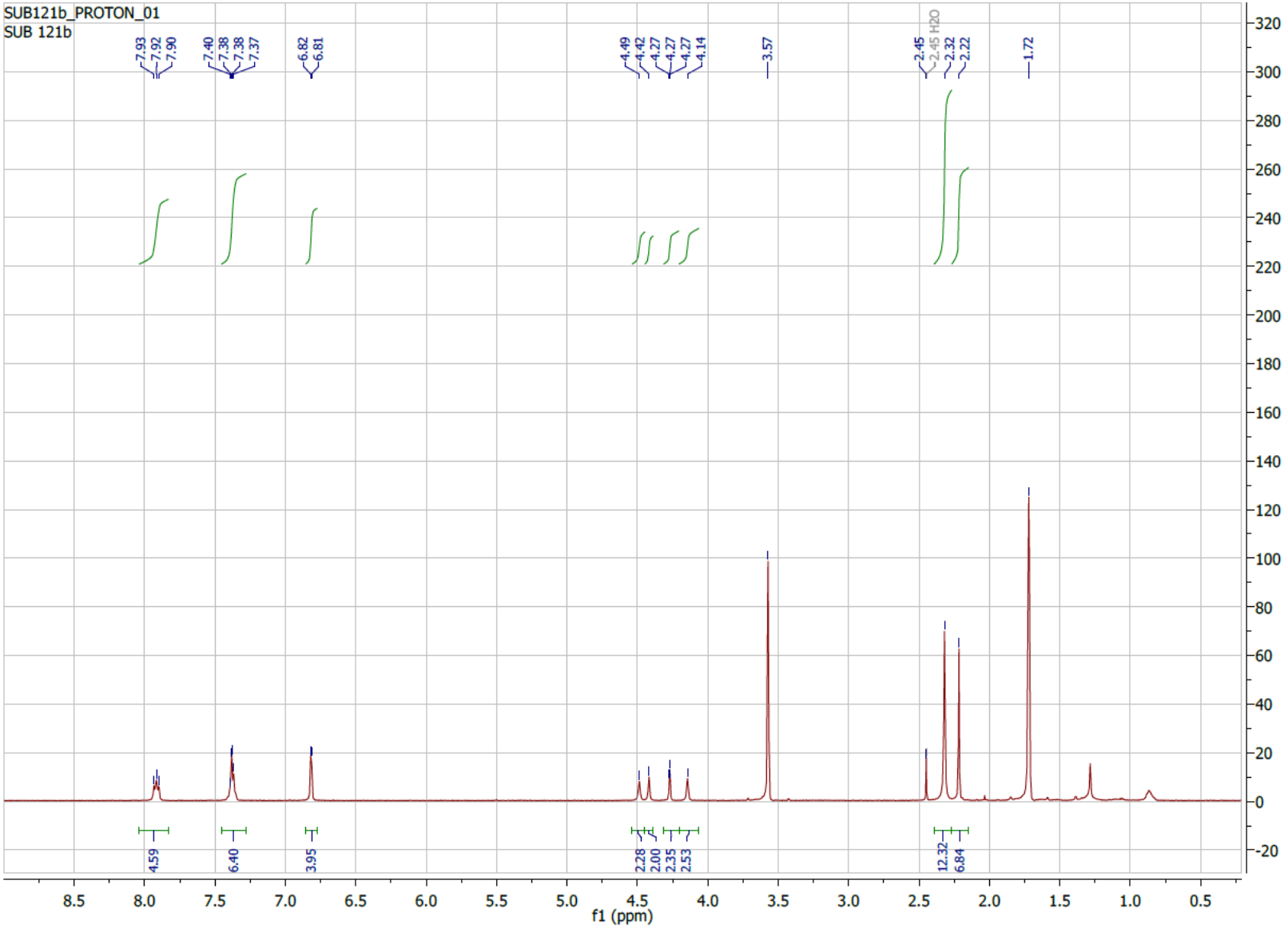


Fig S40. ^{1}H NMR of Fc'($PMes_2$)(PPh_2).CuBr (**10**) in thf-d8. The peak at δ 2.45 is resulting from water dissolved in NMR solvent.

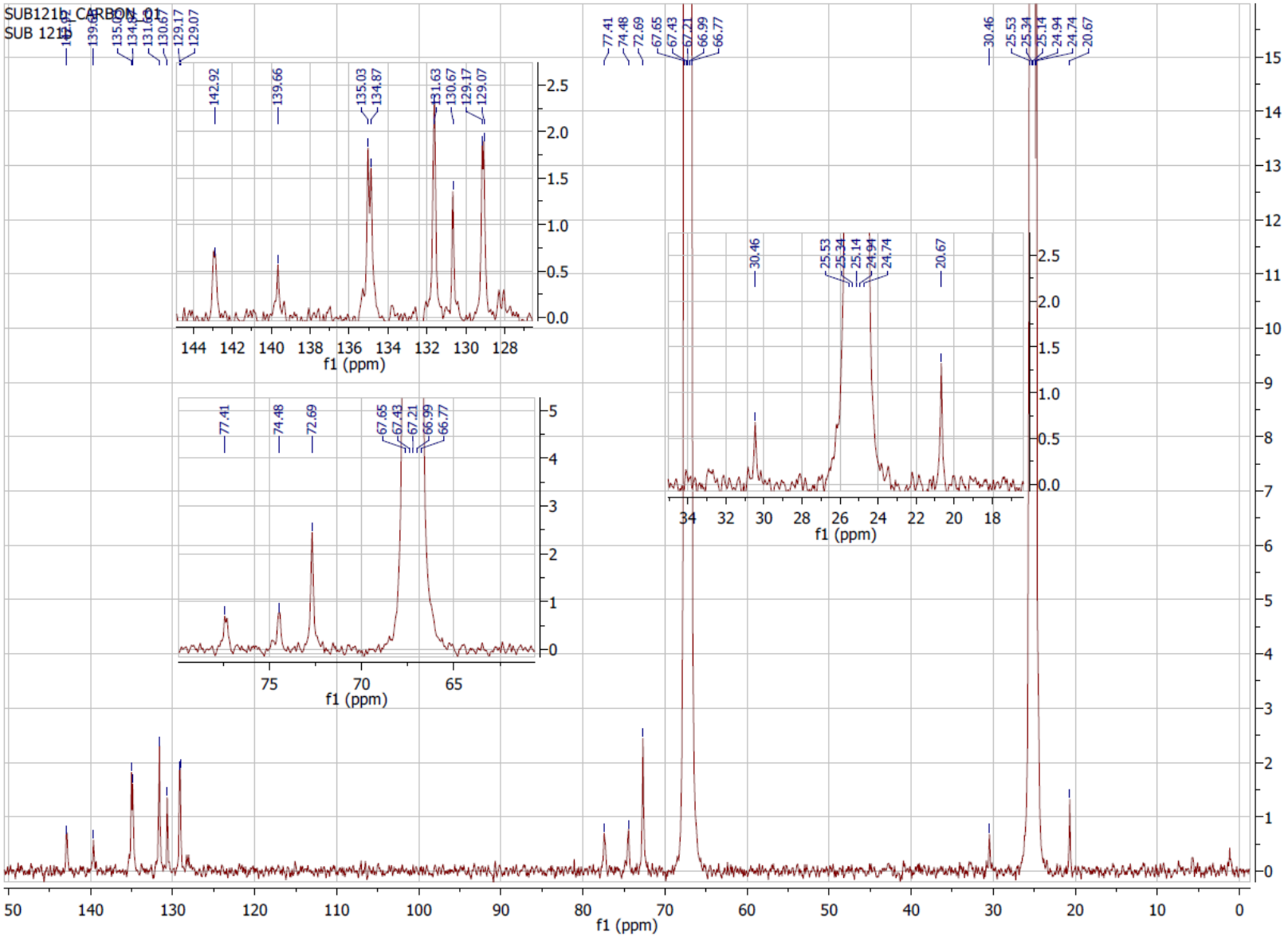


Fig S41. ^{13}C NMR of Fc'($PMes_2$)(PPh_2).CuBr (**10**) in thf-d8.

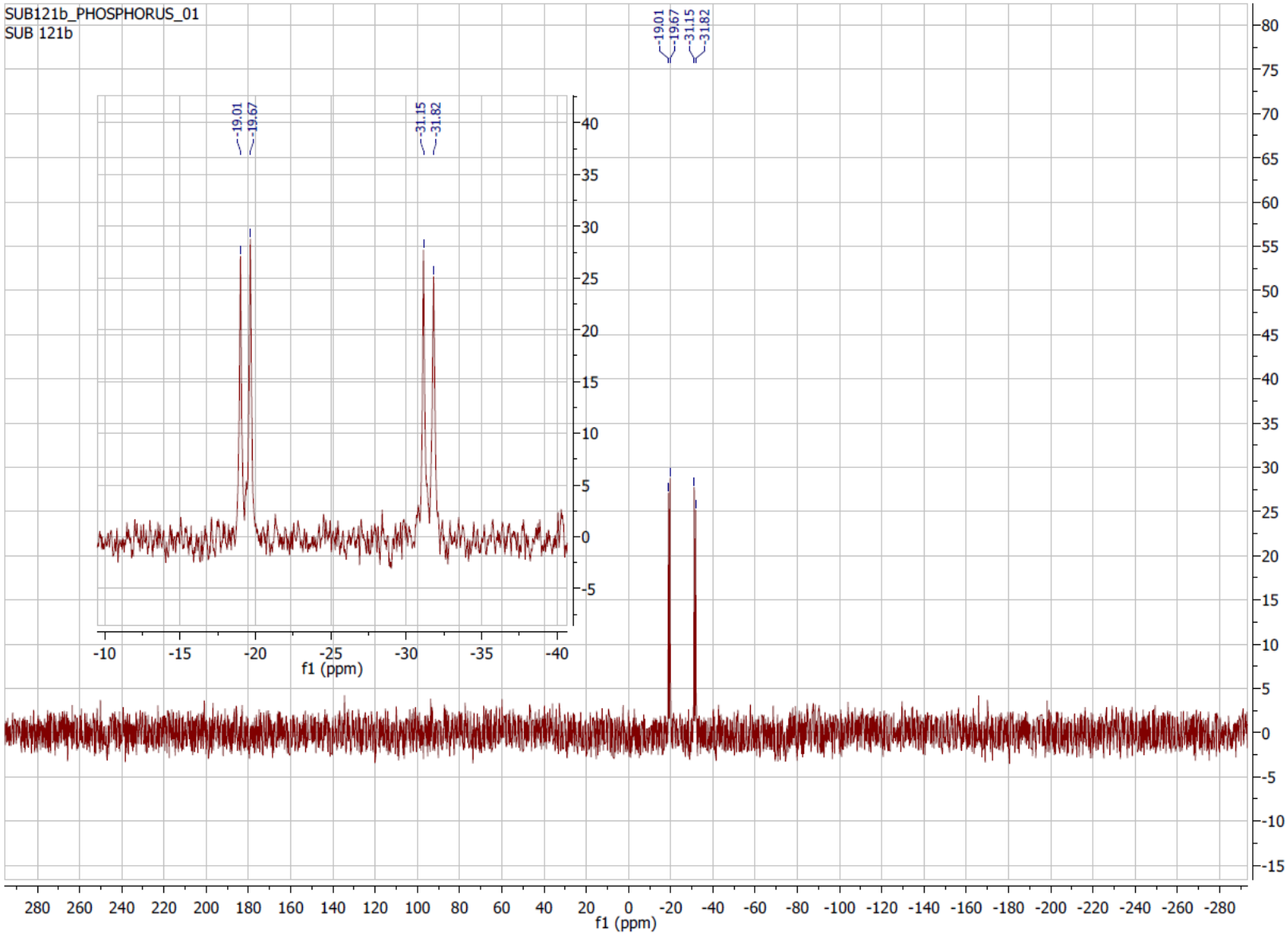


Fig S42. ^{31}P NMR of Fc'($PMes_2$)(PPh_2).CuBr (**10**) in thf-d8.

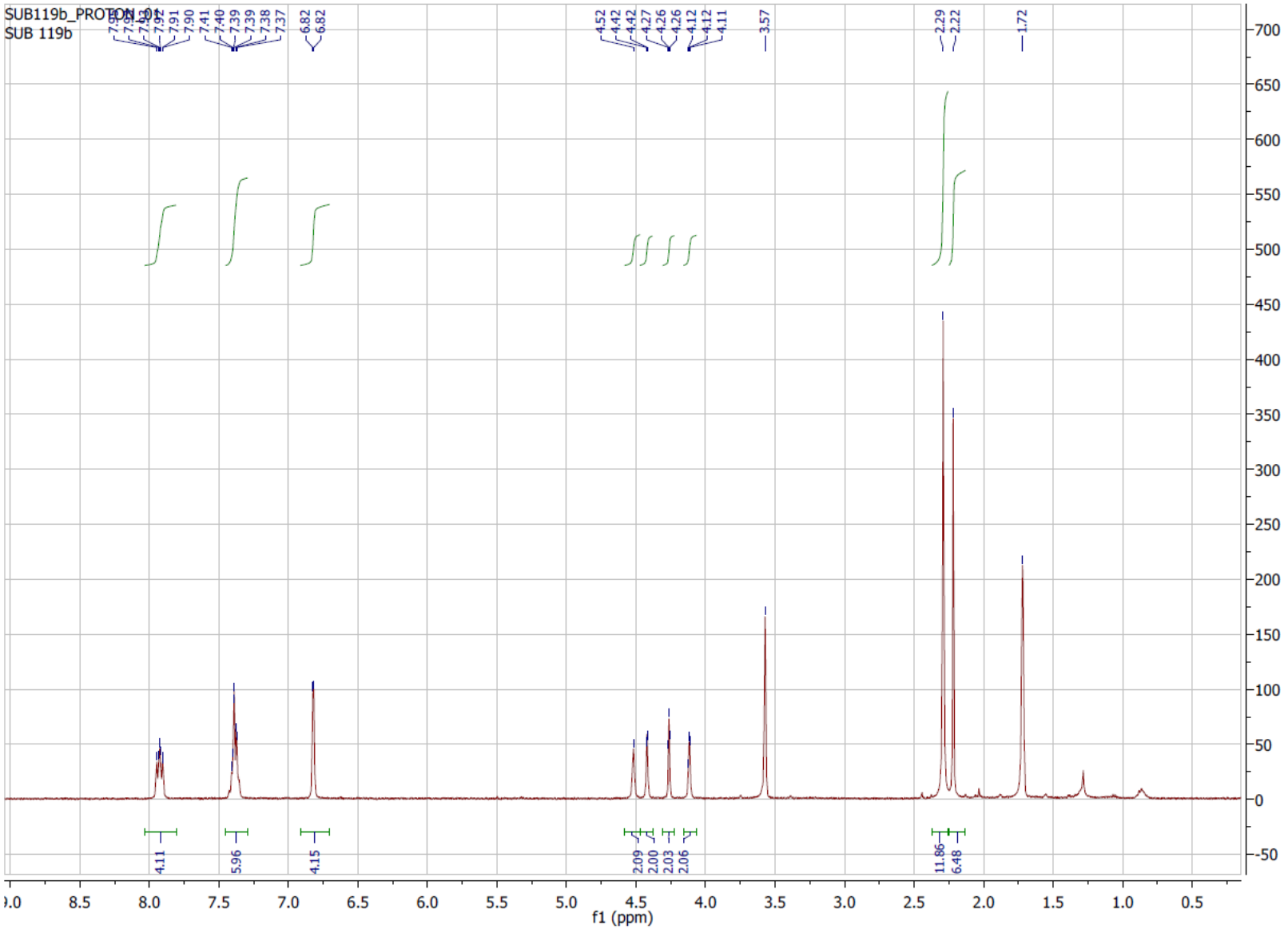


Fig S43. ^{1}H NMR of Fc'($PMes_2$)(PPh_2).CuI (**11**) in thf-d8.

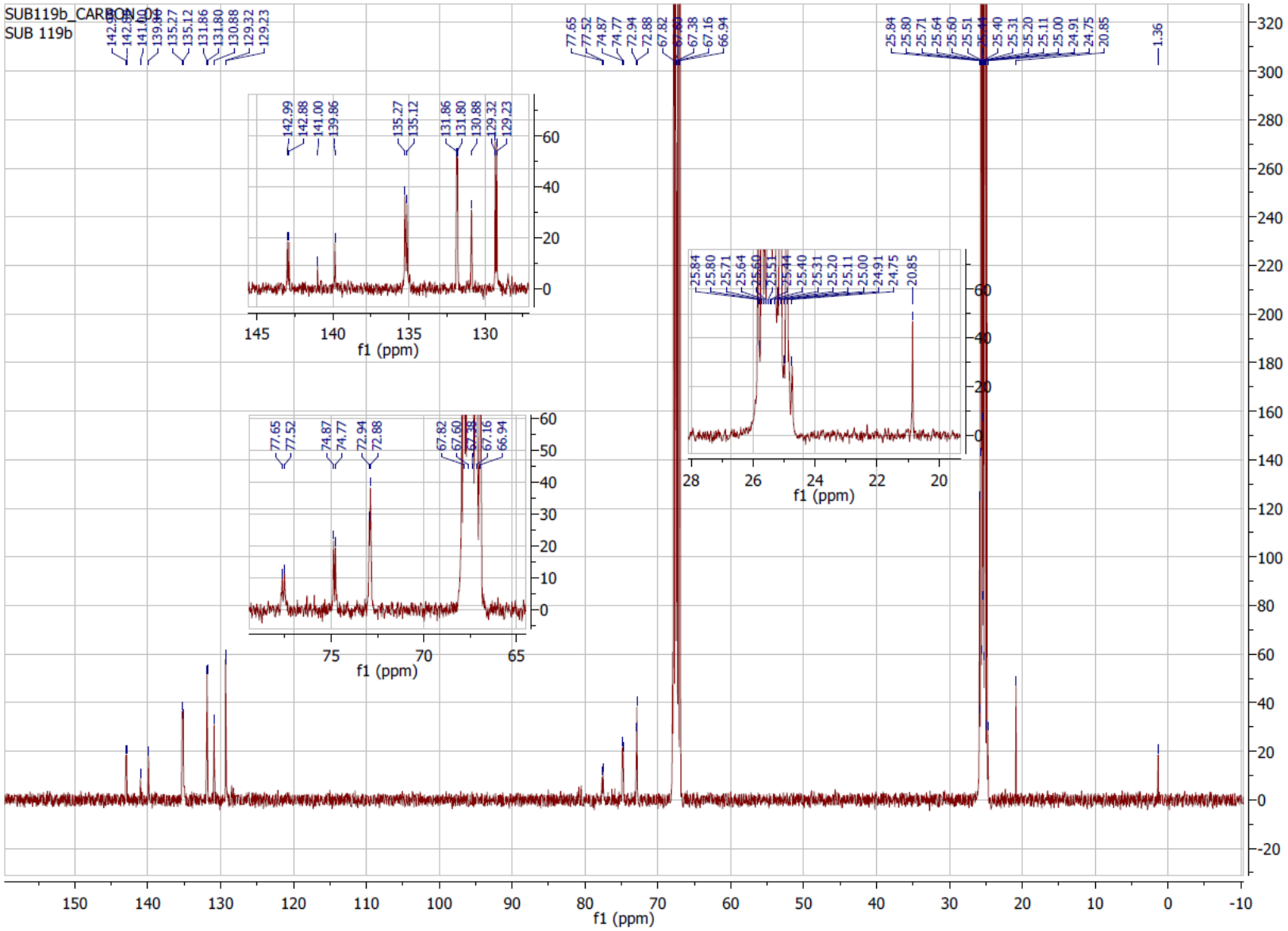


Fig S44. ^{13}C NMR of Fc'($PMes_2$)(PPh_2).CuI (**11**) in thf-d8.

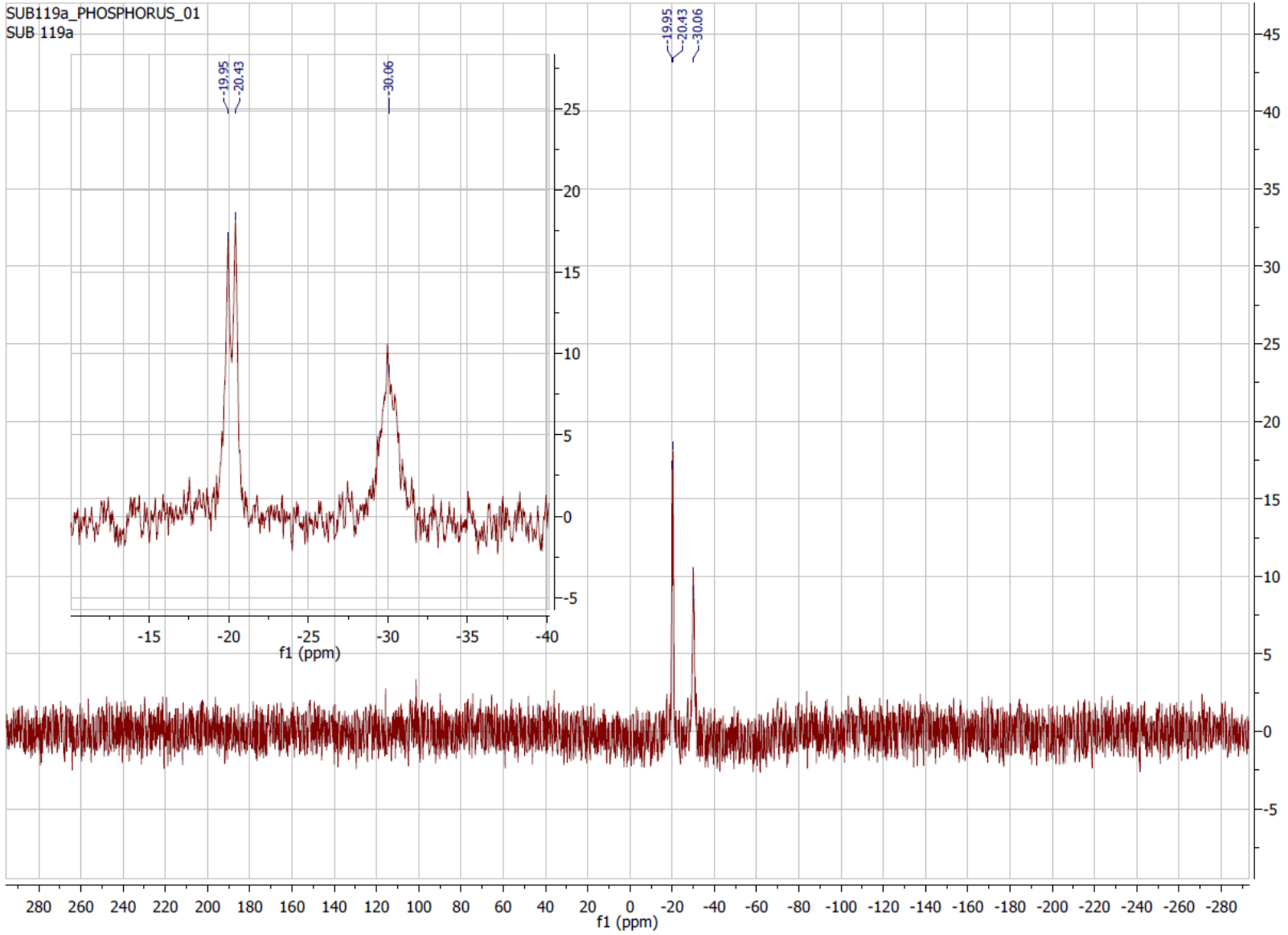


Fig S45. ^{31}P NMR of Fc'(PMes$_2$)(PPh$_2$).CuI (**11**) in thf-d8.

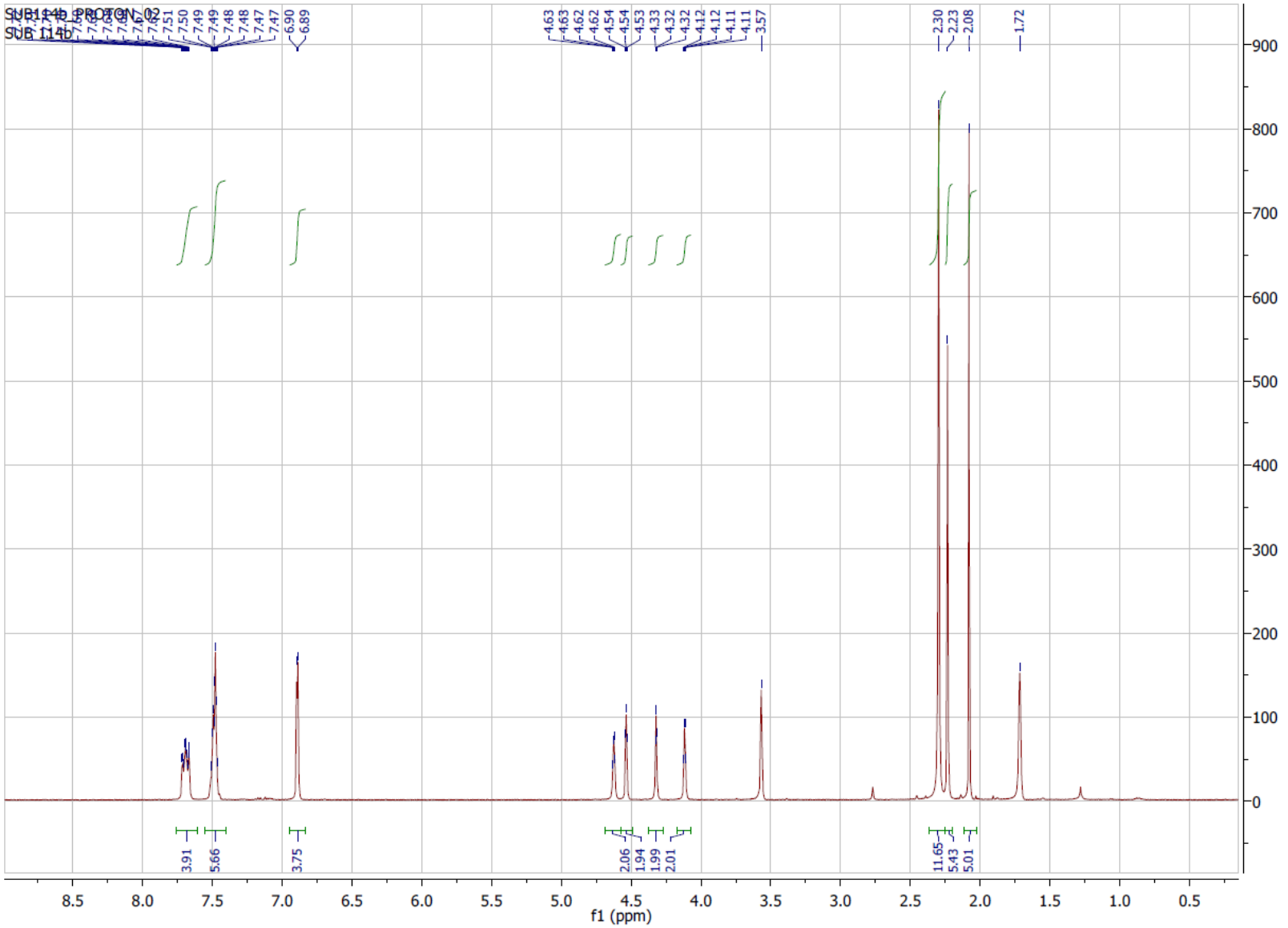


Fig S46. ^{1}H NMR of Fc'($PMes_2$)(PPh_2).Cu($MeCN)_2BF_4$ (**12**) in thf-d8.

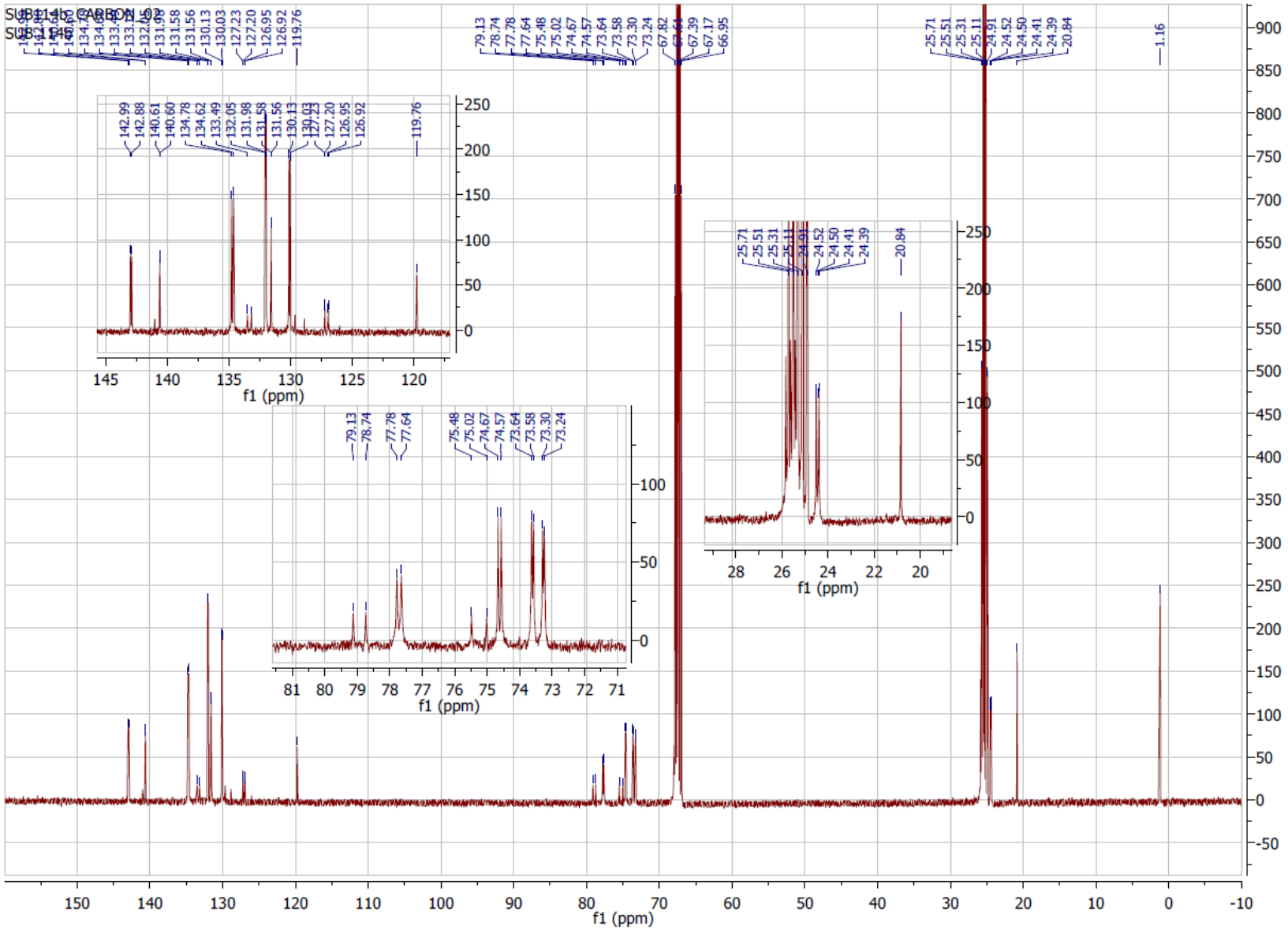


Fig S47. ^{13}C NMR of Fc'($PMes_2$)(PPh_2).Cu($MeCN)_2BF_4$ (**12**) in thf-d8.

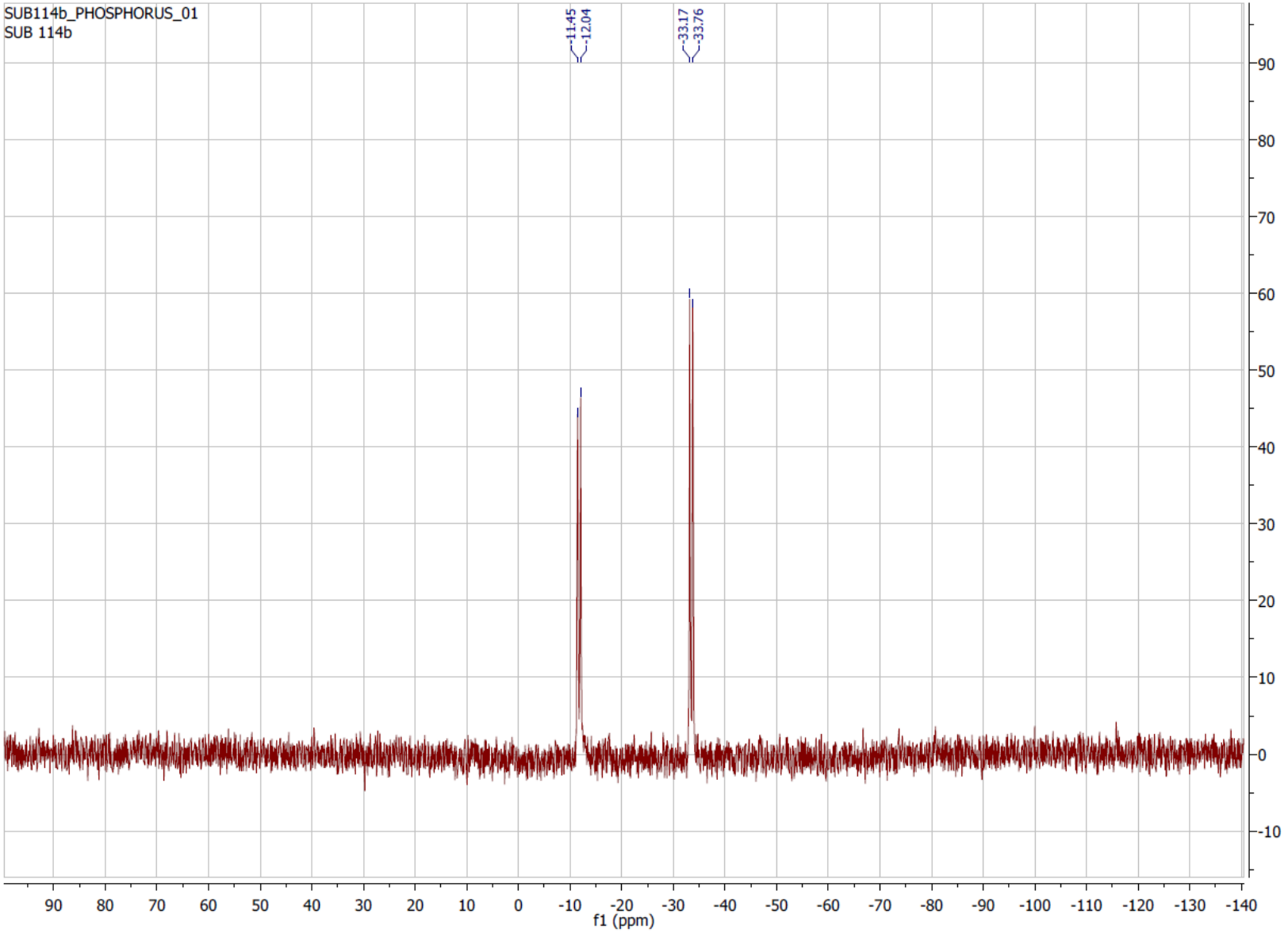


Fig S48. ^{31}P NMR of Fc'($PMes_2$)(PPh_2).Cu($MeCN)_2BF_4$ (**12**) in thf-d8.

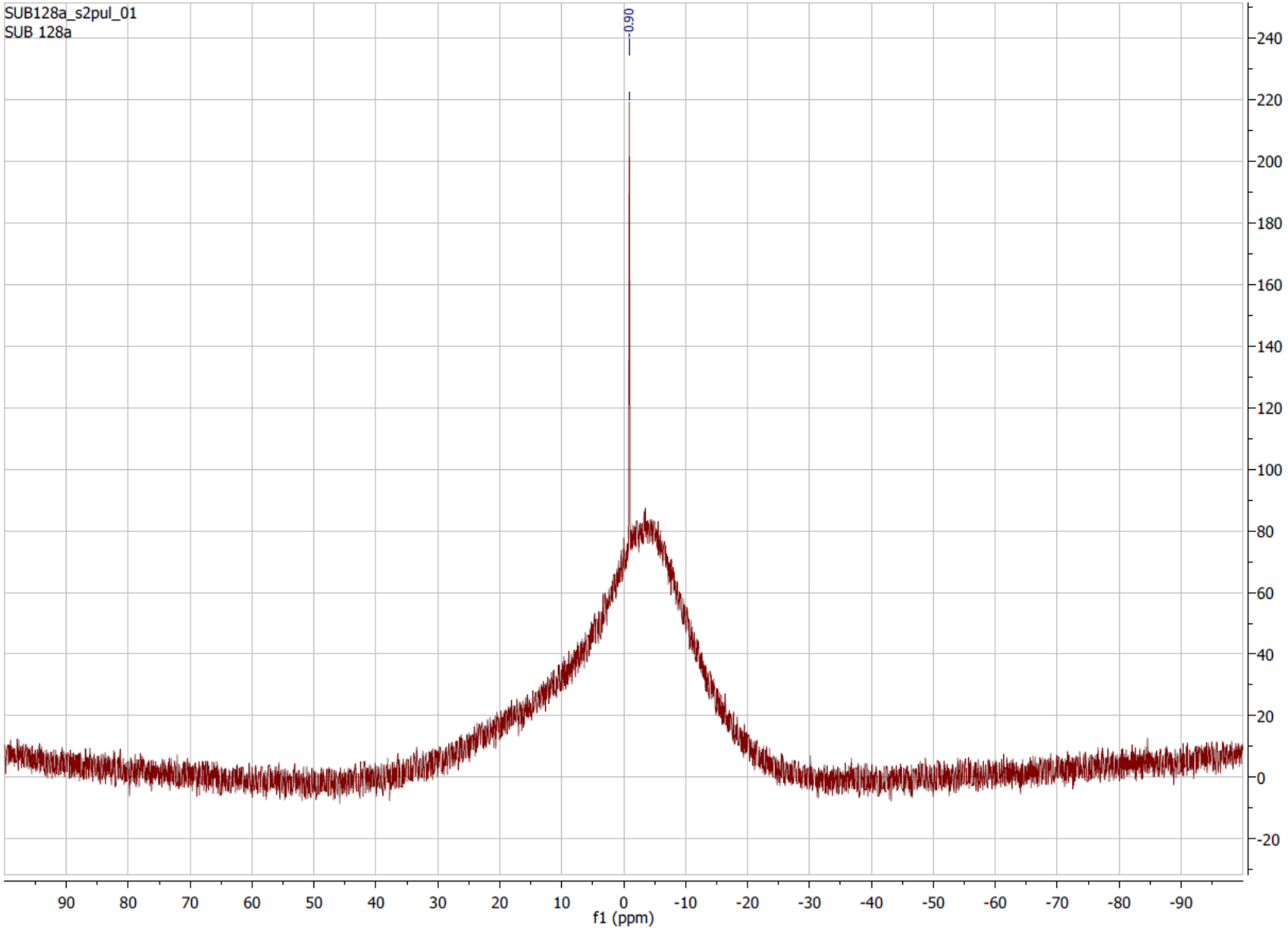


Fig S49. ^{11}B NMR of Fc'($PMes_2$)(PPh_2).Cu($MeCN)_2BF_4$ (**12**) in thf-d8.

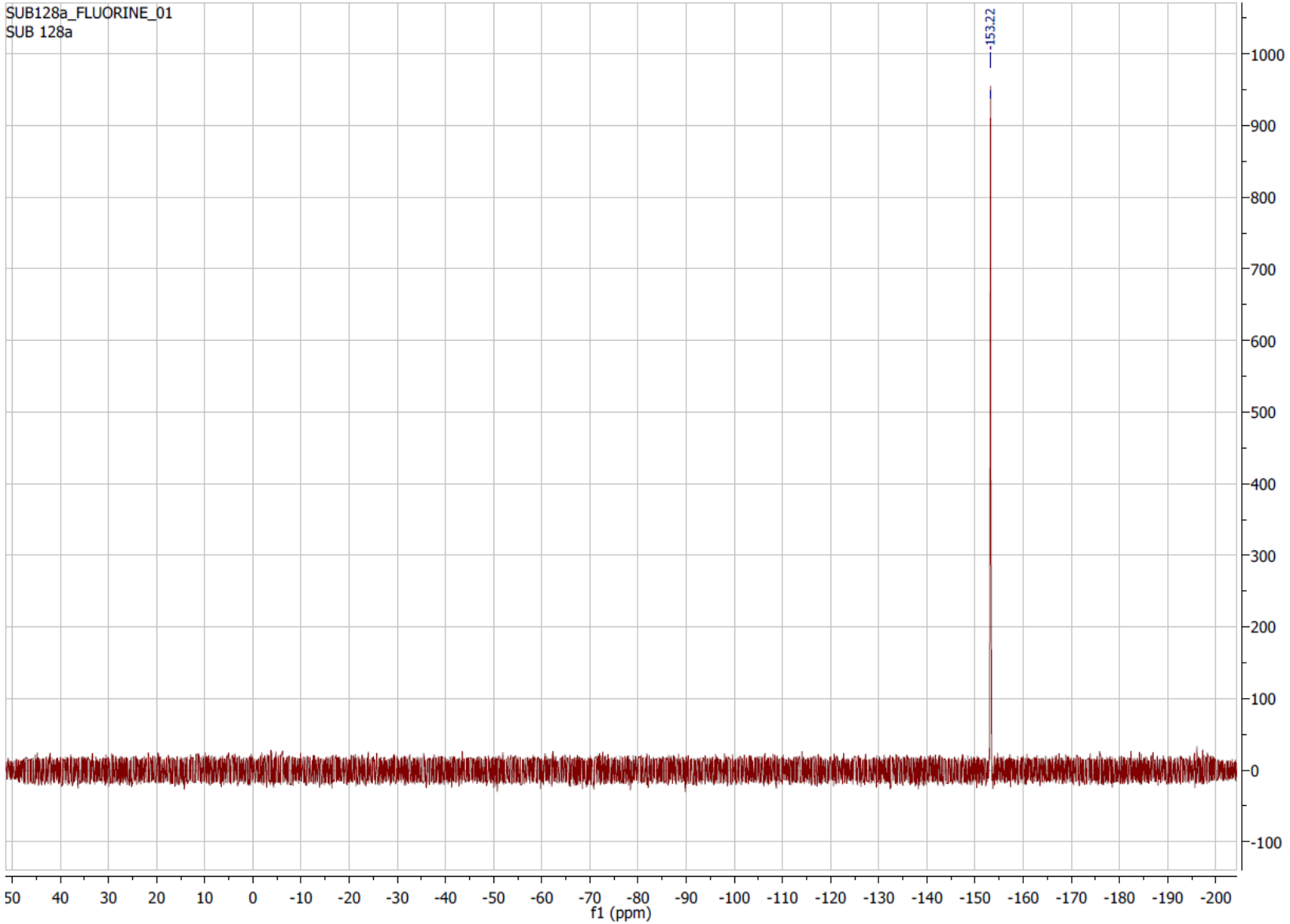


Fig S50. ^{19}F NMR of Fc'($PMes_2$)(PPh_2).Cu($MeCN)_2BF_4$ (**12**) in thf-d8.

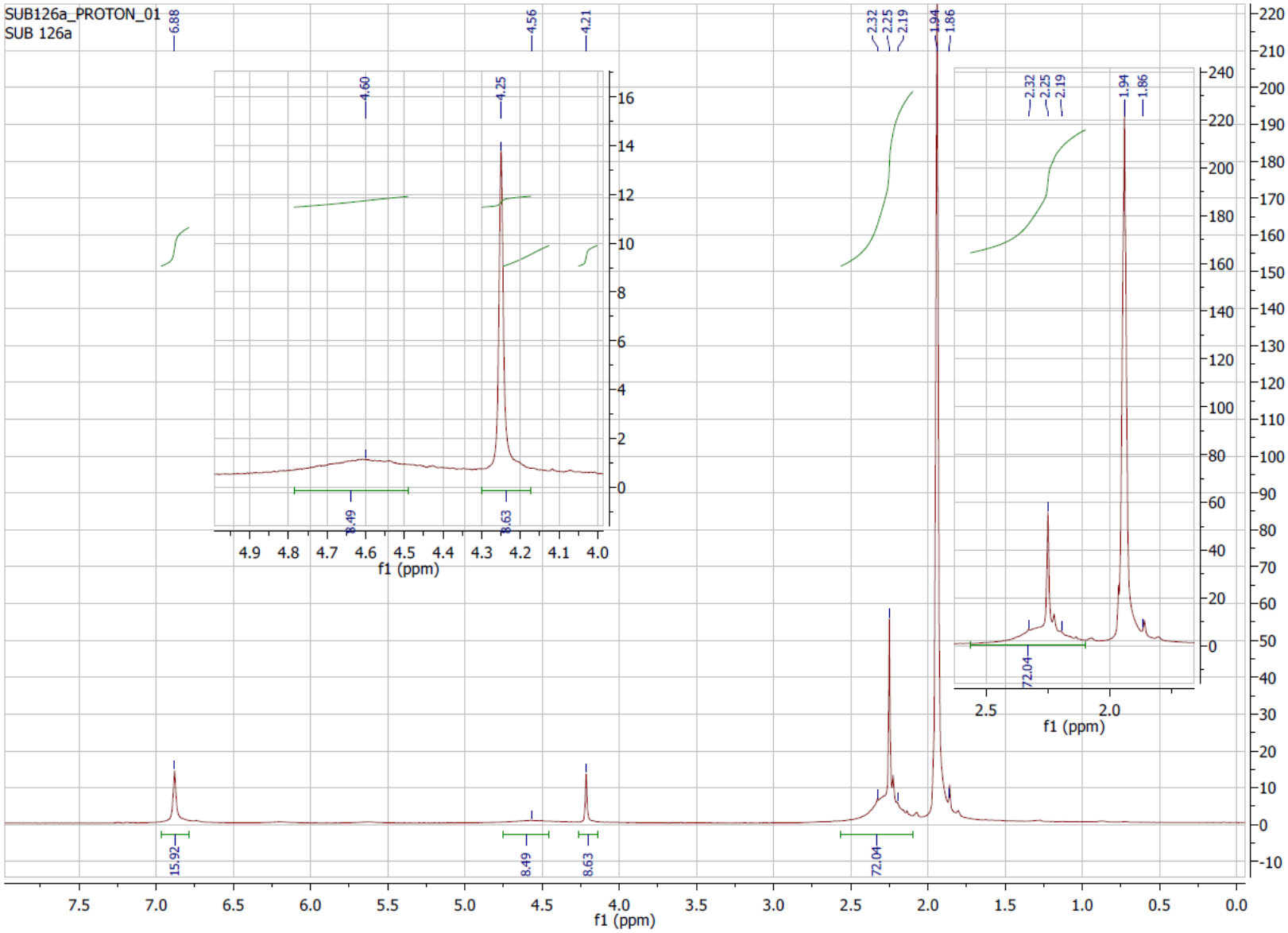


Fig S51. ^{1}H NMR of [Fc'($PMes_2$)$_2$.($CuBr$)$_2$]$_2$ (**13**) in CD_3CN.

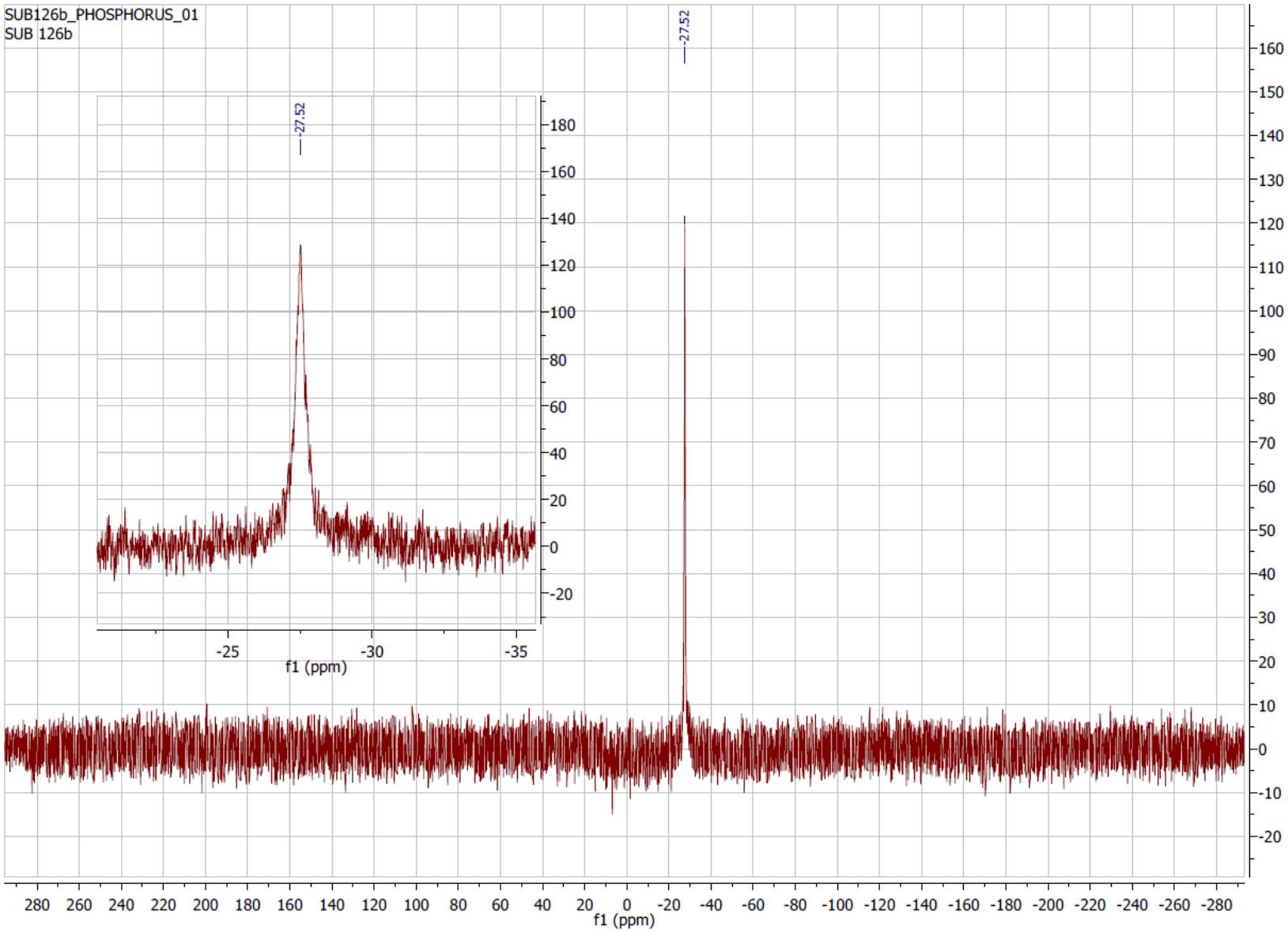


Fig S52. $^{31}P\{^{1}H\}$ NMR of $[Fc'(PMes_2)_2.(CuBr)_2]_2$ (**13**) in CD_3CN.

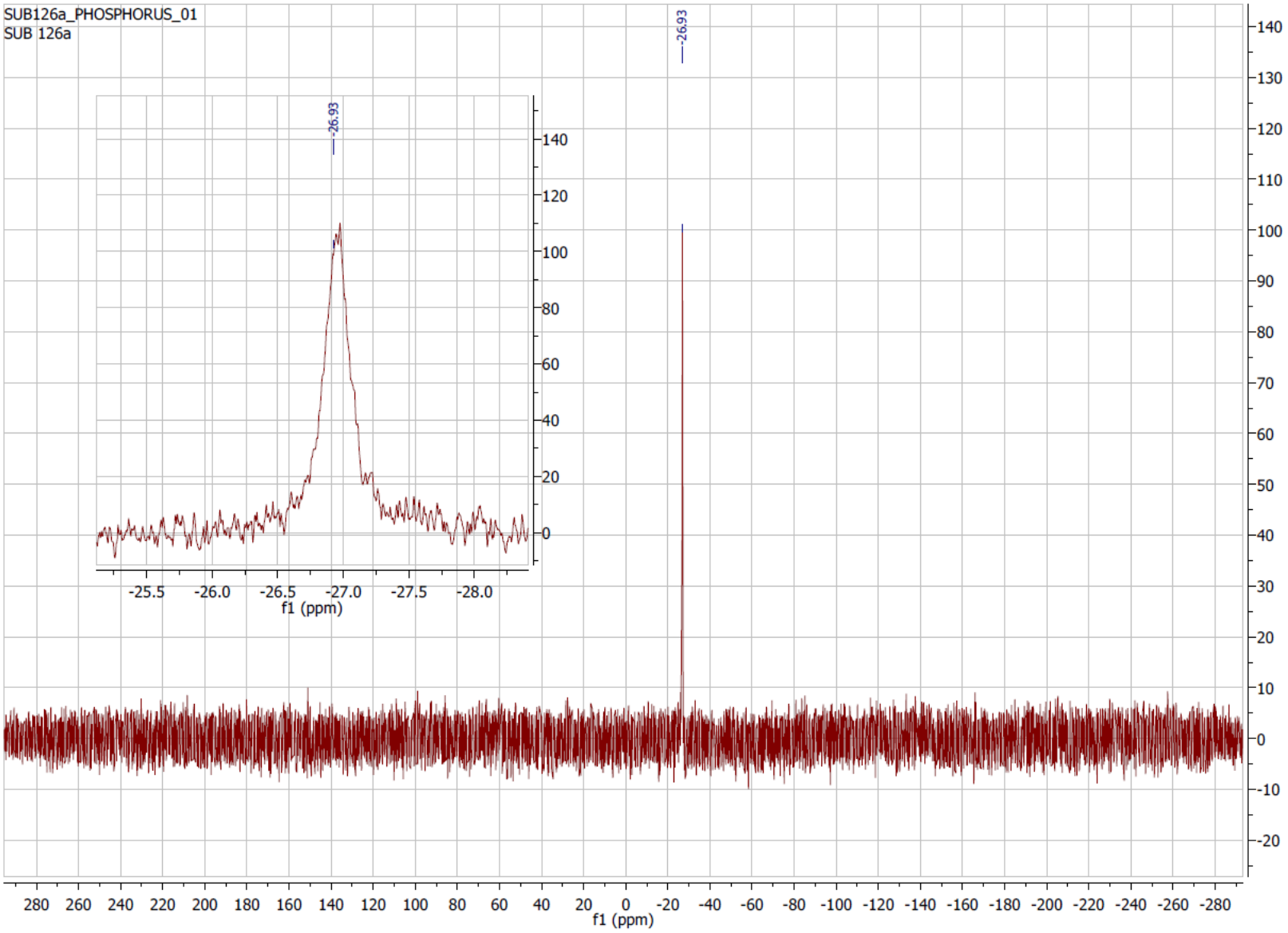


Fig S53. $^{31}P\{^{1}H\}$ NMR of $[Fc'(PMes_2)_2.(CuBr)_2]_2$ (**13**) in thf-d8.

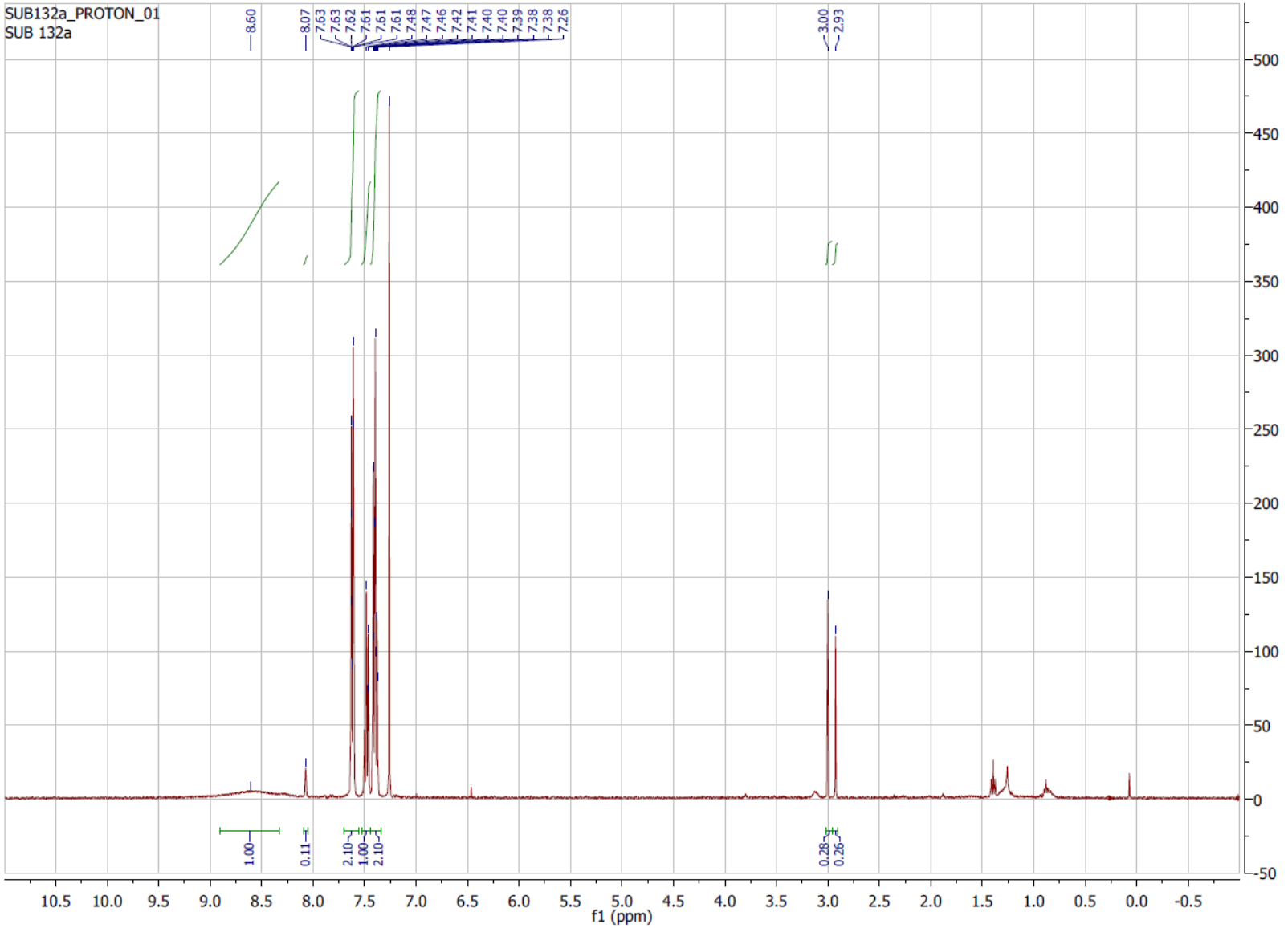


Fig S54. ^{1}H NMR of Ph–C≡C–COOH in $CDCl_3$. The peaks at δ 2.93 and 3.00 are resulting from residual DMF (~8%).

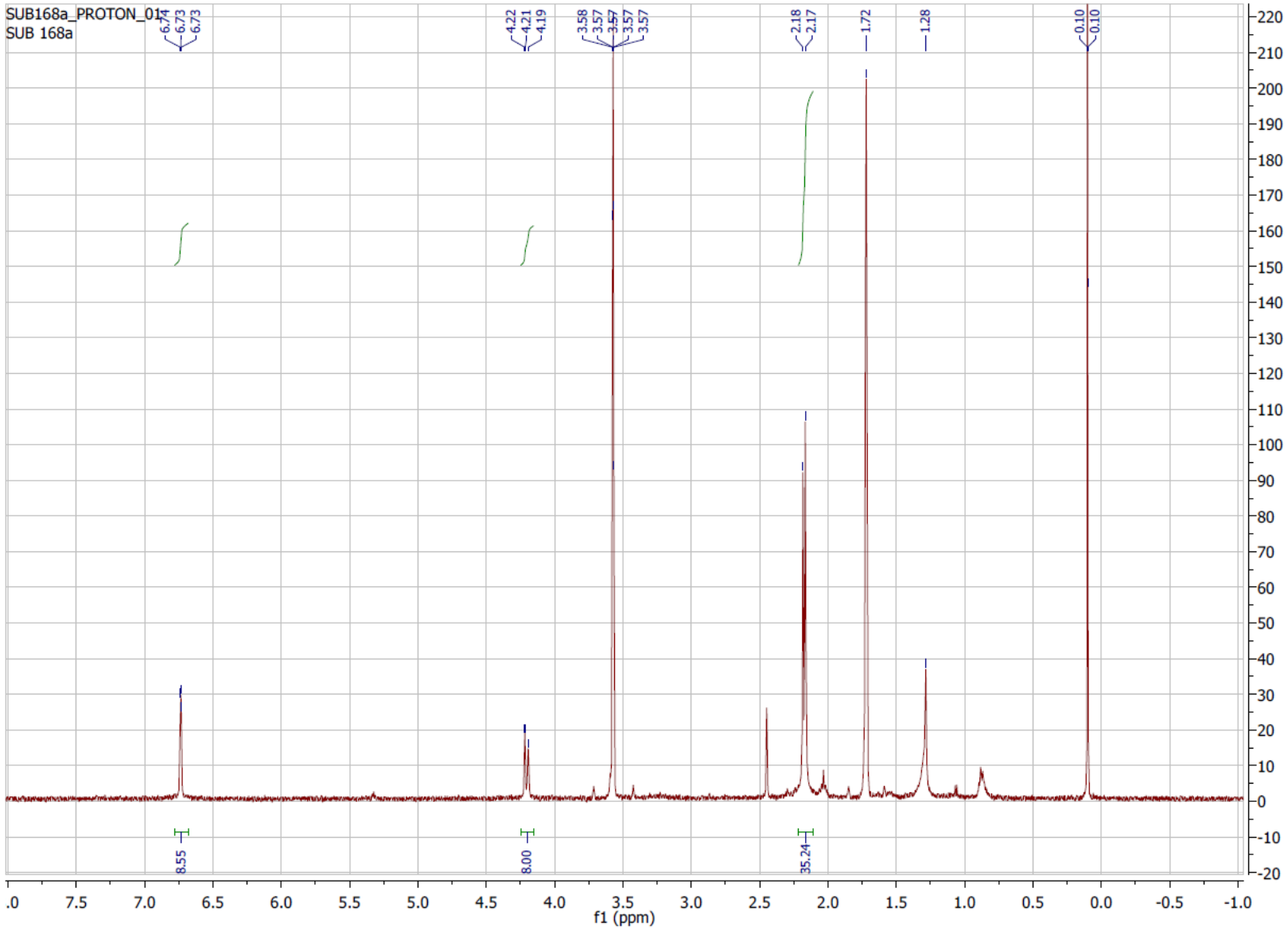


Fig S55. ^{1}H NMR of remaining part of $Fc(PMes_2)_2$.CuI (after catalysis) in thf-d8.

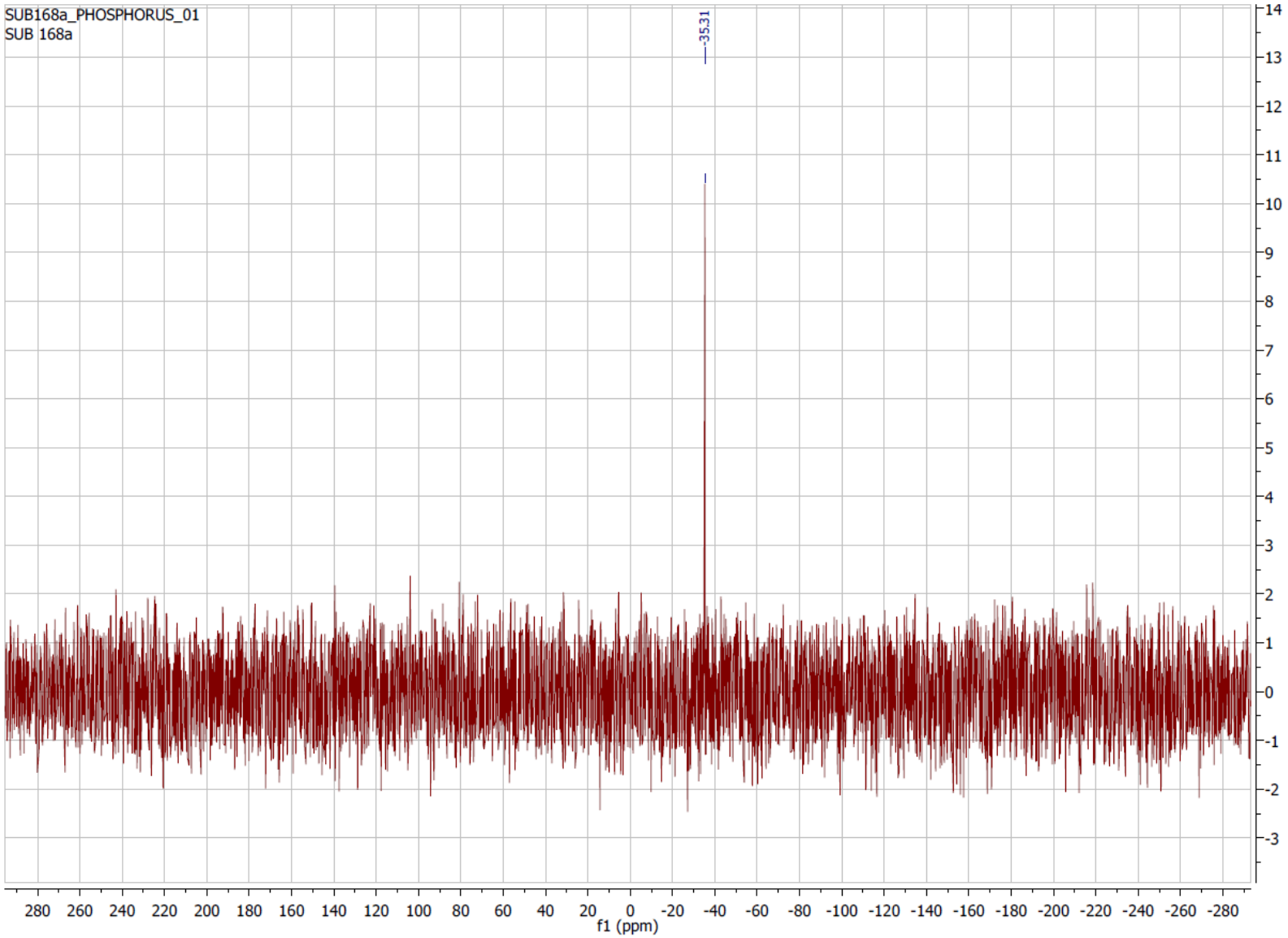


Fig S56. ^{31}P NMR of remaining part of Fc'$(PMes_2)_2$.CuI (after catalysis) in thf-d8.

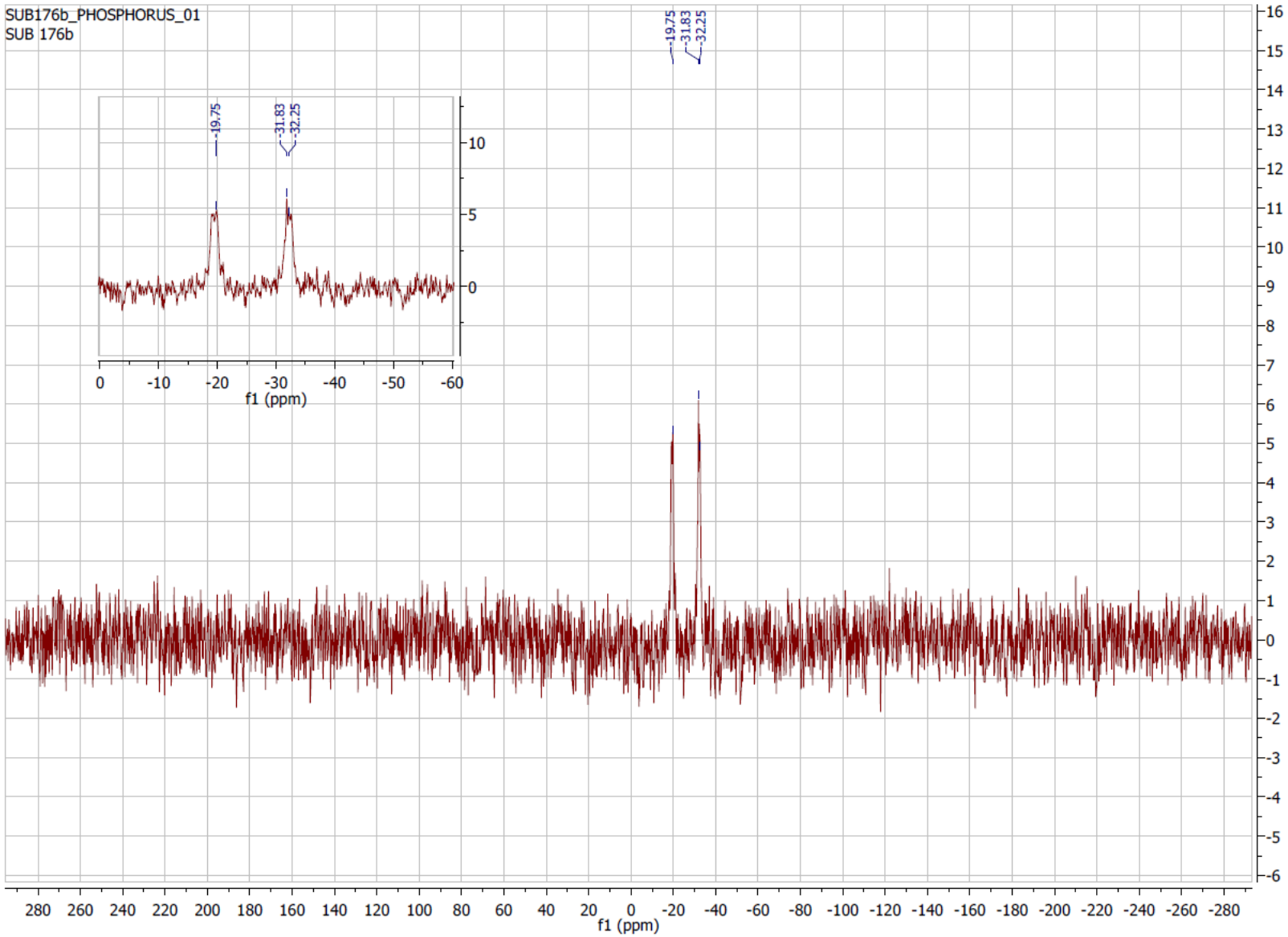


Fig S57. ^{31}P NMR of remaining part of Fc'($PMes_2$)(PPh_2).CuI (after catalysis) in thf-d8.

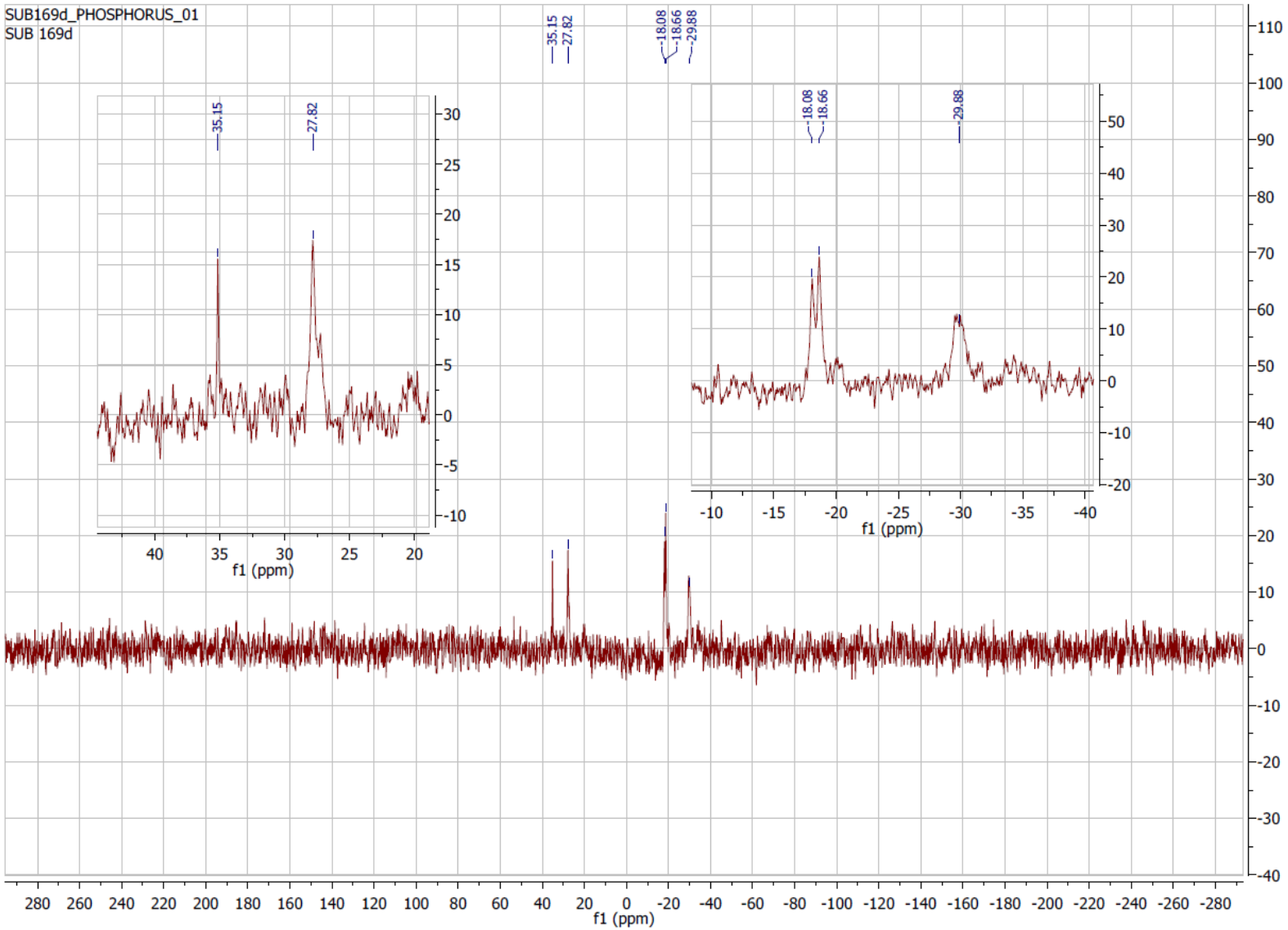


Fig S58. ^{31}P NMR of remaining part of Fc'($PMes_2$)(PPh_2).CuBr (after catalysis) in thf-d8. The peaks at δ 2.93 and 3.00 are probably resulting from Fc($POMes_2$)($POPh_2$).

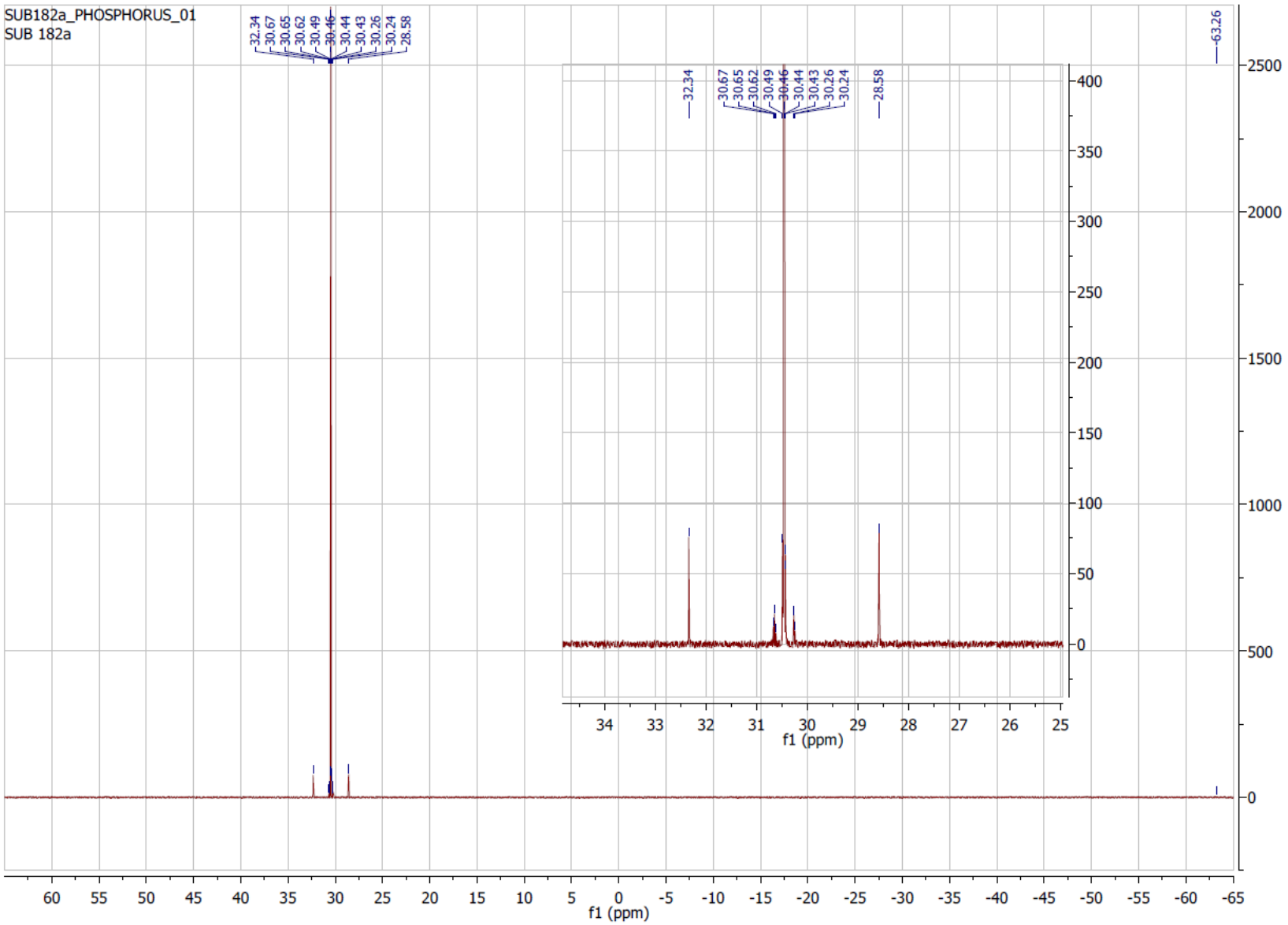


Fig S59. ^{31}P NMR of dppf[Se]$_2$ in toluene-d8.

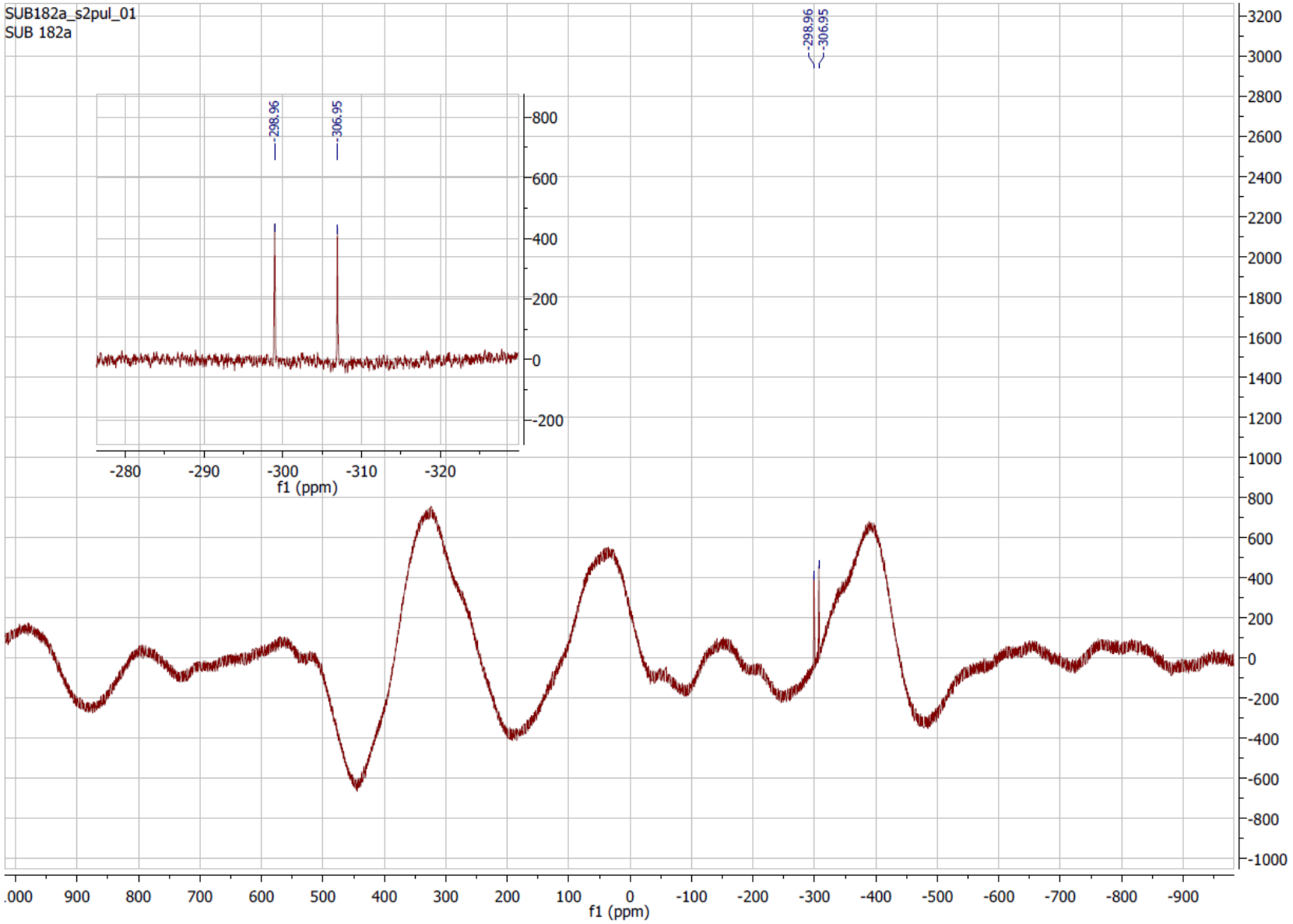


Fig S60. ^{77}Se NMR of dppf[Se]$_2$ in toluene-d8.

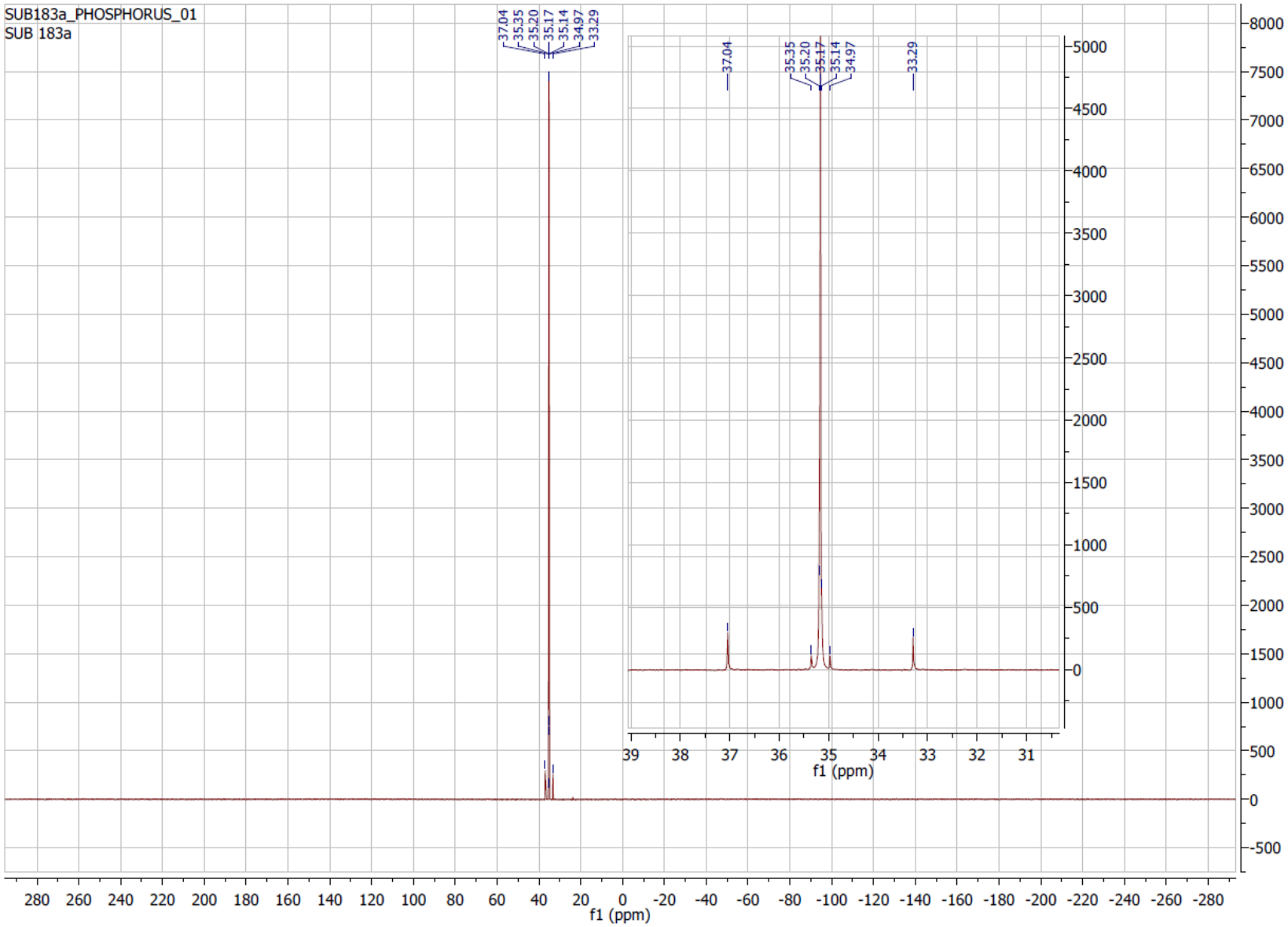


Fig S61. ^{31}P NMR of $Ph_3P[Se]$ in toluene-d8.

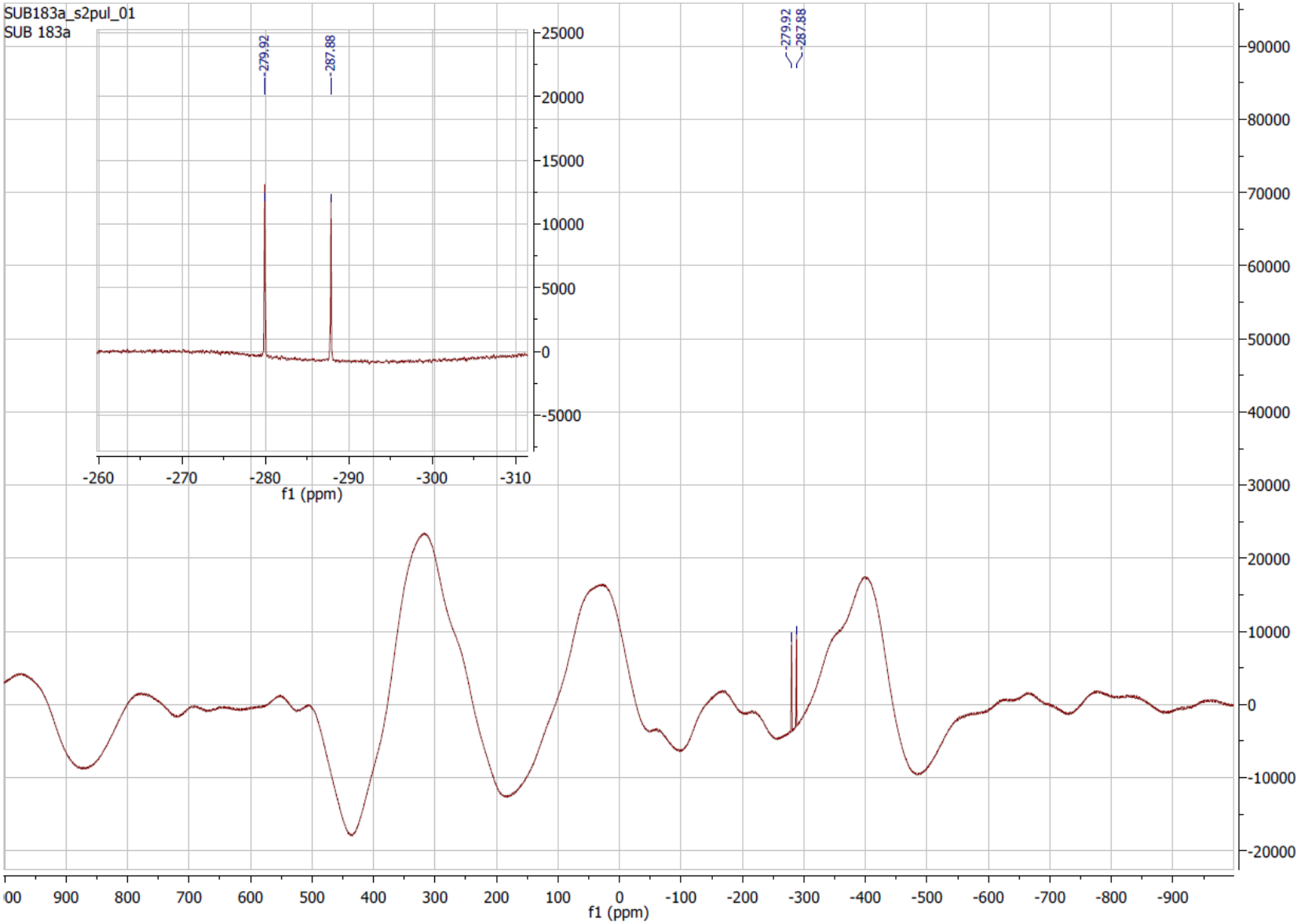


Fig S62. ^{77}Se NMR of $Ph_3P[Se]$ in toluene-d8.

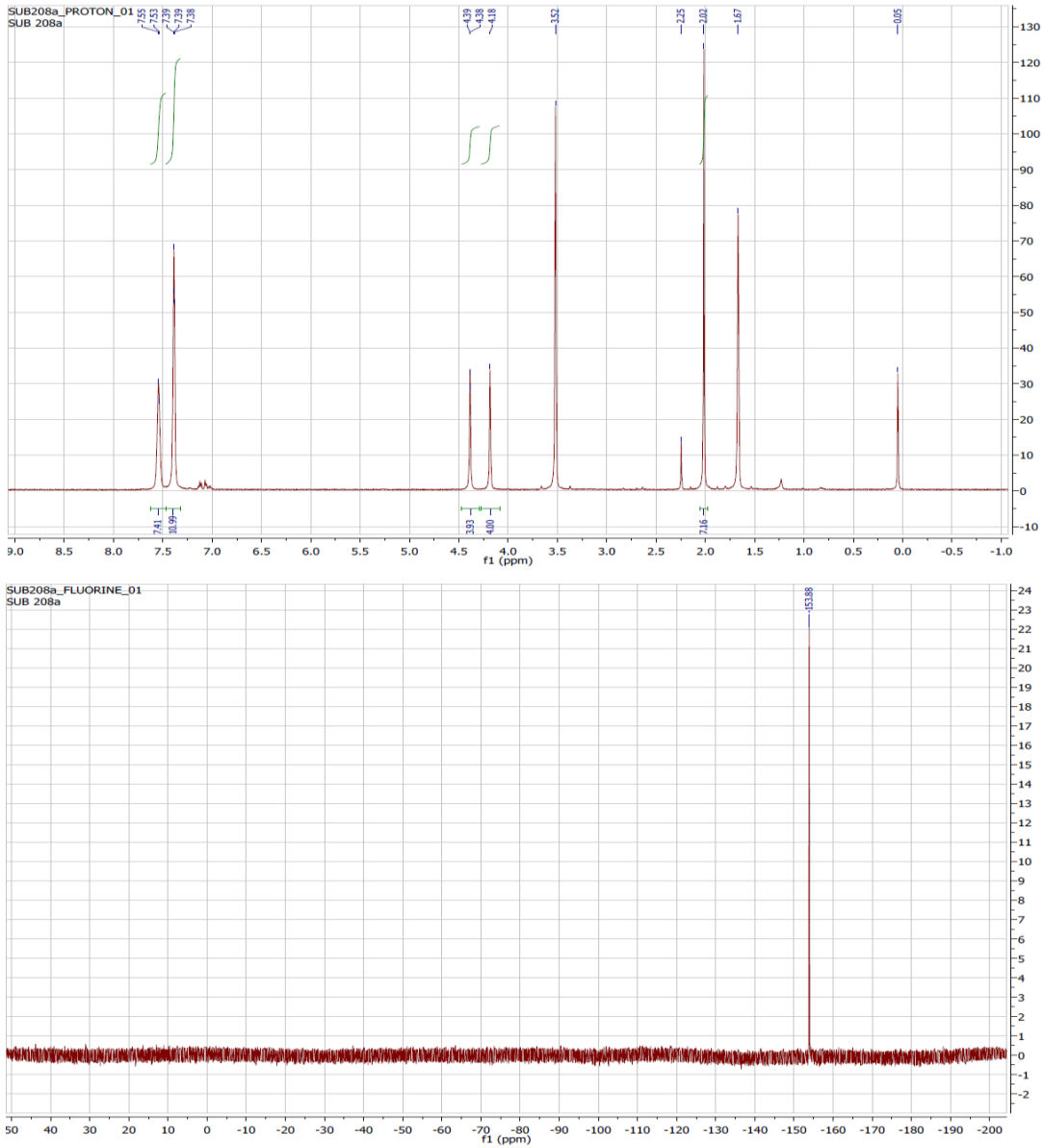


Fig S63. ^{1}H (top) and ^{19}F (bottom) NMR spectra of Fc'(PPh_2).Cu($MeCN)_2BF_4$ in thf-d8.

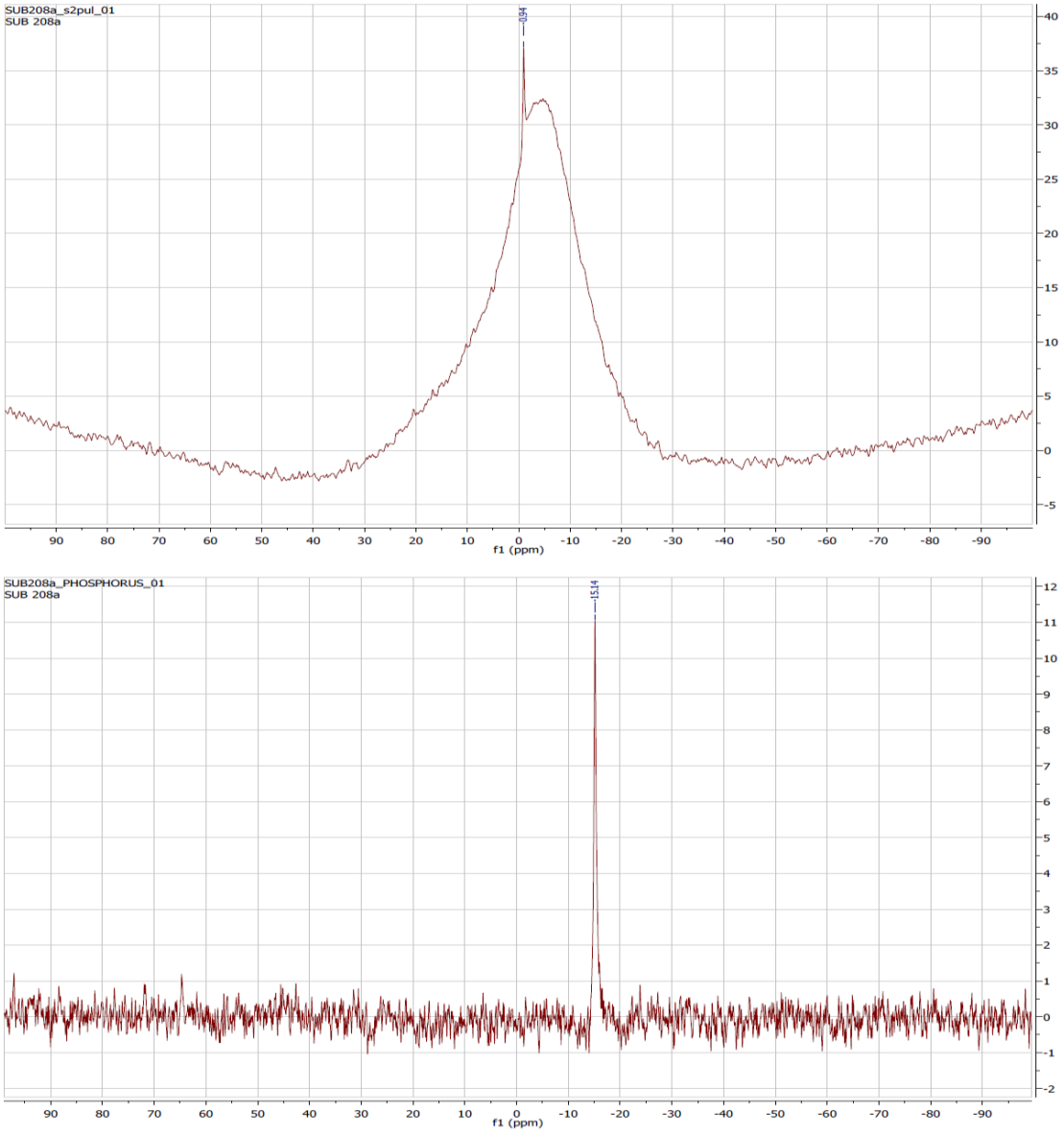


Fig S64. ^{11}B (top) and ^{31}P (bottom) NMR spectra of $Fc'(PPh_2)_2.Cu(MeCN)_2BF_4$ in thf-d8.

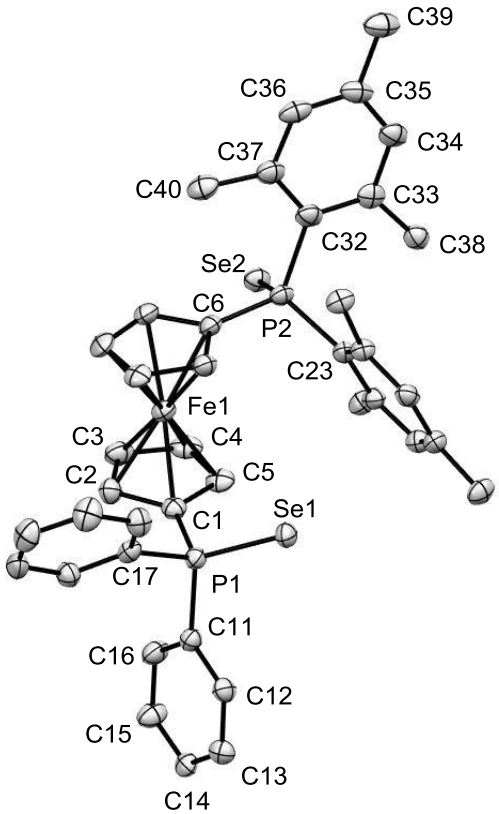


Fig S65. Ortep plots of the molecular structures of **6** in the solid state with ellipsoids drawn at the 50% probability level.
Labels for some selected atoms and H atoms are omitted for clarity. The refinement data for this structure can be found in table S1 (SI file). Selected bond lengths [Å] and angles [°]: C(1)-P(1) 1.783(5), P(1)-C(11) 1.822(5), P(1)-Se(1) 2.0971(13), C(1)-C(5) 1.441(7), C(1)-Fe(1) 2.023(5), C(1)-C(2) 1.441(7), P(2)-C(32) 1.836(5), P(2)-Se(2) 2.1246(14), P(2)-C(6) 1.801(5), C(32)-C(33) 1.413(7), C(38)-C(33) 1.520(7), C(1)-P(1)-Se(1) 112.90(16), C(1)-P(1)-C(11) 103.4(2), C(1)-P(1)-C(17) 105.8(2), Se(1)-P(1)-C(17) 114.21(18), Se(1)-P(1)-C(11) 113.64(15), C(32)-P(2)-C(23) 104.6(2), C(23)-P(2)-C(6) 102.5(2), C(6)-P(2)-Se(2) 106.85(18), Se(2)-P(2)-C(32) 105.05(17), Se(2)-P(2)-C(23) 123.63(18).

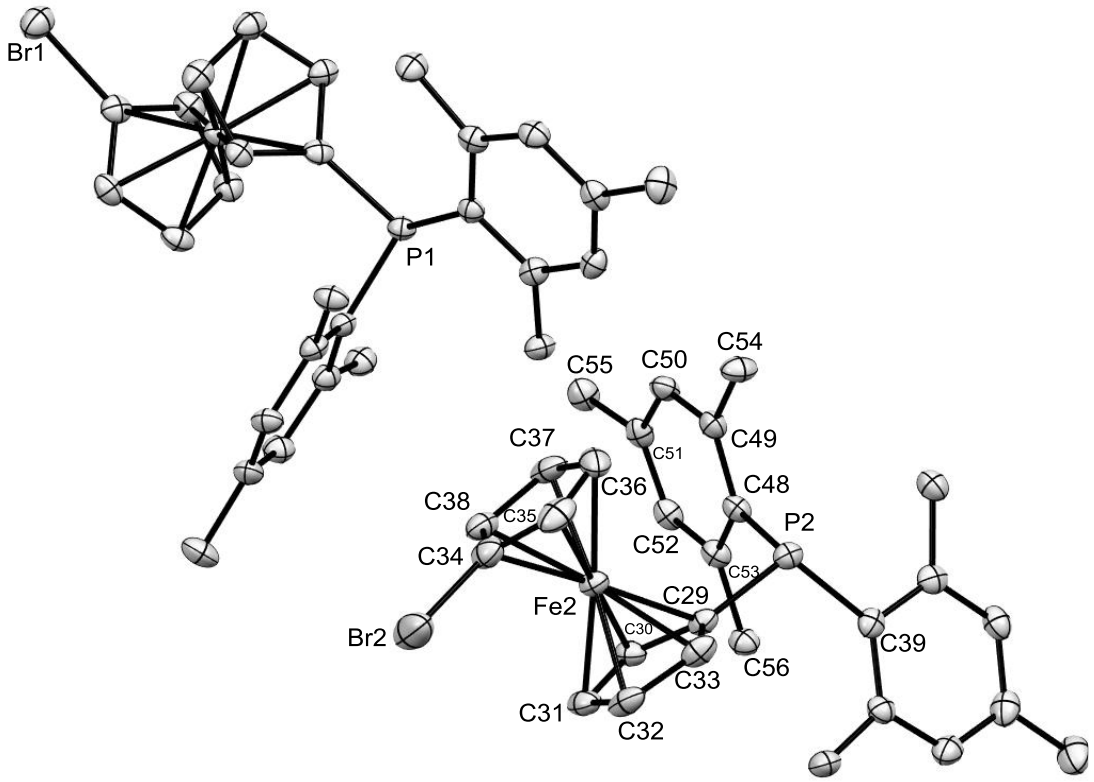


Fig S66. Ortep plots of the molecular structures of **4** in the solid state with ellipsoids drawn at the 50% probability level.
Labels for some selected atoms and H atoms are omitted for clarity. The refinement data for this structure can be found in table S1 (SI file). Selected bond lengths [Å] and angles [°]: P(2)-C(29) 1.815(5), P(2)-C(48) 1.850(5), Fe(2)-C(29) 2.068(4), Br(2)-C(34) 1.882(5), C(29)-C(33) 1.438(6), C(48)-C(49) 1.401(6), C(49)-C(54) 1.503(6), C(29)-P(2)-C(48) 99.8(2), C(29)-P(2)-C(39) 108.7(2), C(48)-P(2)-C(39) 103.9(2), P(2)-C(48)-C(49) 116.8(3), C(54)-C(48)-C(49) 123.3(4), C(38)-C(34)-Br(2) 123.7(4), Br(2)-C(34)-Fe(2) 124.6(3).

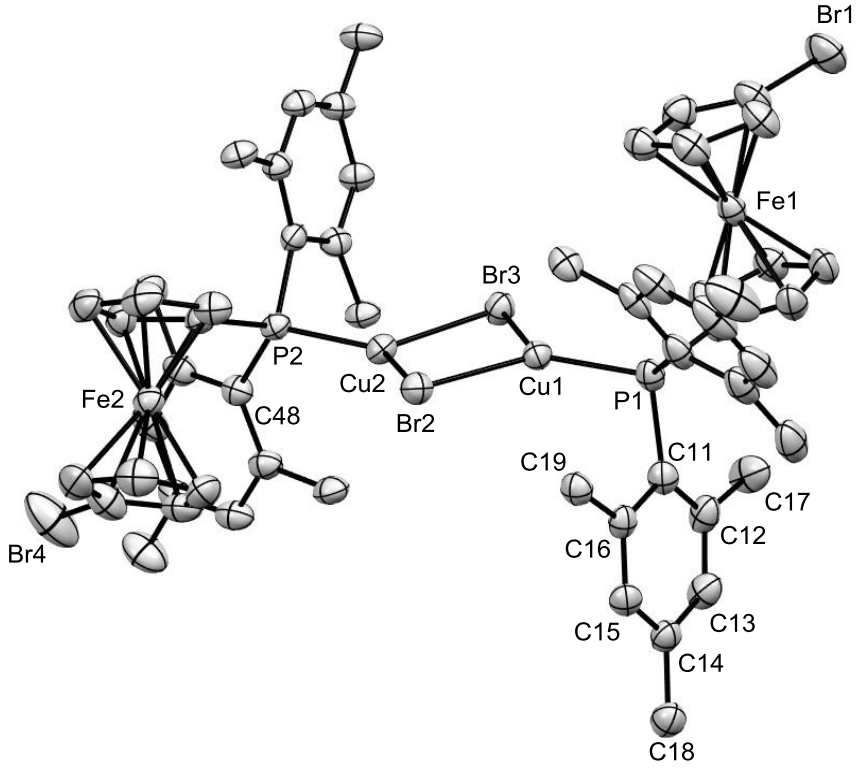


Fig S67. The sidewise view of complex **14**.
Labels for some selected atoms and H atoms are omitted for clarity.

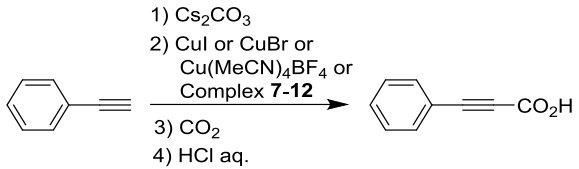
Table S1. Crystal Refinement data of Compounds **3-6**.

Identification code	**3**	**4**	**5**	**6**
CCDC deposition number	1980151	1980152	1980153	1980154
Empirical formula	$C_{40}H_{40}FeP_2$	$C_{28}H_{30}BrFeP$	$C_{46}H_{52}FeP_2Se_2$	$C_{40}H_{40}FeP_2Se_2$
Formula weight	638.51	533.25	880.58	796.43
Temperature/K	100.(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	C2/c
a/Å	8.5144(4)	8.4912(4)	10.4268(4)	31.3894(12)
b/Å	25.1345(8)	23.5605(7)	13.3560(5)	14.2794(4)
c/Å	15.3247(6)	23.4724(9)	16.4319(7)	26.1071(11)
α/°	90	90	90	90
β/°	98.919(3)	90.731(3)	103.866(3)	143.827(2)
γ/°	90	90	90	90
Volume/$Å^3$	3239.9(2)	4695.4(3)	2221.63(15)	6906.7(5)
Z	4	8	4	8
$\rho_{calc}g/cm^3$	1.309	1.509	1.316	1.532
μ/mm^{-1}	0.592	2.426	2.079	2.666
F(000)	1344.0	2192.0	904.0	3232.0
Crystal size/mm^3	0.15 × 0.09 × 0.03	0.25 × 0.12 × 0.04	0.14 × 0.113 × 0.06	0.17 × 0.1 × 0.04
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.14 to 53.692	2.45 to 51.996	3.978 to 53.684	3.252 to 53.612
Index ranges	$-10 \le h \le 10$, $-29 \le k \le 31$, $-19 \le l \le 19$	$-9 \le h \le 10$, $-29 \le k \le 29$, $-28 \le l \le 28$	$-13 \le h \le 13$, $-16 \le k \le 16$, $-20 \le l \le 20$	$-39 \le h \le 38$, $-17 \le k \le 18$, $-24 \le l \le 33$
Reflections collected	14949	28237	14224	15330
Independent reflections	6884 [R_{int} = 0.0343, R_{sigma} = 0.0417]	9214 [R_{int} = 0.0286, R_{sigma} = 0.0270]	4710 [R_{int} = 0.0253, R_{sigma} = 0.0211]	7312 [R_{int} = 0.0438, R_{sigma} = 0.0496]
Data/restraints/parameters	6884/0/394	9214/0/571	4710/0/238	7312/0/412
Goodness-of-fit on F^2	1.076	1.025	1.049	1.034
Final R indexes [I≥2σ (I)]	R_1 = 0.0543, wR_2 = 0.1119	R_1 = 0.0541, wR_2 = 0.1310	R_1 = 0.0316, wR_2 = 0.0795	R_1 = 0.0452, wR_2 = 0.1050
Final R indexes [all data]	R_1 = 0.0820, wR_2 = 0.1302	R_1 = 0.0705, wR_2 = 0.1470	R_1 = 0.0378, wR_2 = 0.0829	R_1 = 0.0746, wR_2 = 0.1441
Largest diff. peak/hole / e $Å^{-3}$	0.52/-0.62	2.19/-2.63	0.53/-0.31	1.17/-1.44

Table S2. Crystal Refinement data of Compounds **10** and **12-14**.

Identification code	**10**	**12**	**13**	**14**
CCDC deposition number	1980155	1980156	1980157	1980158
Empirical formula	$C_{40}H_{40}BrCuFeP_2$	$C_{44}H_{46}BCuF_4FeN_2P_2$	$C_{104}H_{116}Br_4Cu_4Fe_2P_4$	$C_{56}H_{60}Br_4Cu_2Fe_2P_2$
Formula weight	781.96	870.97	2175.34	1353.40
Temperature/K	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	C2/c
a/Å	12.6946(6)	12.8168(4)	12.8345(3)	33.3874(12)
b/Å	15.4310(5)	19.2843(5)	15.7867(4)	9.2825(2)
c/Å	17.5511(8)	16.9754(5)	25.8517(6)	34.0895(11)
α/°	90	90	90	90
β/°	98.194(4)	97.048(3)	103.724(2)	92.551(3)
γ/°	90	90	90	90
Volume/$Å^3$	3403.0(3)	4164.0(2)	5088.4(2)	10554.5(6)
Z	4	4	2	8
$\rho_{calc}g/cm^3$	1.526	1.389	1.420	1.703
μ/mm^{-1}	6.659	0.987	5.897	9.624
F(000)	1600.0	1800.0	2216.0	5408.0
Crystal size/mm^3	0.170 × 0.130 × 0.030	0.295 × 0.232 × 0.093	0.290 × 0.210 × 0.120	0.32 × 0.2 × 0.03
Radiation	Cu Kα (λ = 1.54186)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54186)	CuKα (λ = 1.54186)
2Θ range for data collection/°	7.036 to 139.976	3.21 to 51	6.614 to 137.992	7.252 to 141.7
Index ranges	$-15 \le h \le 14$, $-18 \le k \le 15$, $-10 \le l \le 21$	$-13 \le h \le 15$, $-23 \le k \le 23$, $-20 \le l \le 20$	$-15 \le h \le 15$, $-16 \le k \le 19$, $-18 \le l \le 31$	$-40 \le h \le 36$, $-4 \le k \le 10$, $-41 \le l \le 36$
Reflections collected	14141	17948	18470	17748
Independent reflections	6254 [R_{int} = 0.0566, R_{sigma} = 0.0448]	7743 [R_{int} = 0.0169, R_{sigma} = 0.0173]	9224 [R_{int} = 0.0277, R_{sigma} = 0.0216]	9419 [R_{int} = 0.0303, R_{sigma} = 0.0242]
Data/restraints/parameters	6254/0/412	7743/0/504	9224/0/514	9419/0/607
Goodness-of-fit on F^2	1.094	1.063	1.024	1.063
Final R indexes [I≥2σ (I)]	R_1 = 0.0634, wR_2 = 0.1718	R_1 = 0.0414, wR_2 = 0.1086	R_1 = 0.0711, wR_2 = 0.2122	R_1 = 0.0631, wR_2 = 0.1763
Final R indexes [all data]	R_1 = 0.0722, wR_2 = 0.1828	R_1 = 0.0494, wR_2 = 0.1216	R_1 = 0.0767, wR_2 = 0.2210	R_1 = 0.0671, wR_2 = 0.1814
Largest diff. peak/hole / e $Å^{-3}$	1.15/-1.09	1.70/-0.47	3.19/-1.19	3.20/-2.50

Table S3. Synthesis of phenylpropiolic acid from phenylacetylene.[a]



Entry	Catalyst	Amount of Catalyst (mol%)	Percentage Yield[b]
1	Blank	0	0
2	CuI	2	34
3	CuI	3	58
4	CuI	4	59
5	CuBr	3	41
6	$Cu(MeCN)_4(BF_4)$	3	29
7	**7**	3	62
8	**8**	3	69
9	**9**	3	59
10	**10**	3	88
11	**11**	3	86
12	**12**	3	76
13	dppf. $Cu(MeCN)_2(BF_4)$[c]	3	33

[a] Reaction conditions: phenylacetylene (1 mmol), catalyst (1-4%, as indicated in the table), Cs_2CO_3 (1.5 mmol), dry CO_2 (1 atm in balloon), dry DMF (10 mL), 24 h, and room temperature. [b] Yield of the crystalline product is reported. From some initial studies, it was noticed that the yield of this reaction can significantly be improved by increasing the catalyst loading (Entry 1-3). However, no substantial increase in the yield could be found when the catalyst loading changed from 3 mol% to 4 mol% (Entry 3 and 4). Therefore, the 3 mol% catalyst loading was used for the rest of our investigation.

[c] Wu, X.; Zhang, W.; Zhang, X.; Ding, N.; Hor, T. S. A. Pyrididine-Carboxylate Ligands as Double-Bridge Spacers in CuI Metallacycles. *Eur. J. Inorg. Chem.* **2015**, 876-881.

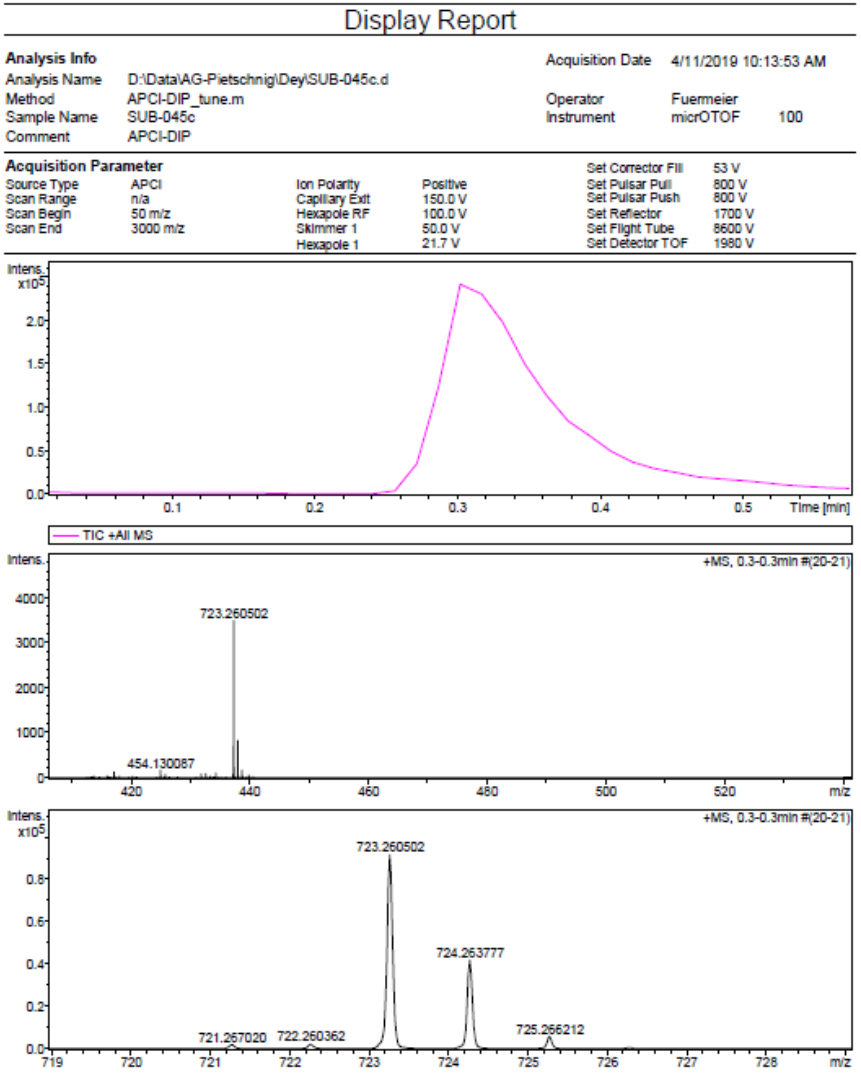


Fig S68. APCI-MS report of Fc'($PMes_2$)$_2$ (**1**).

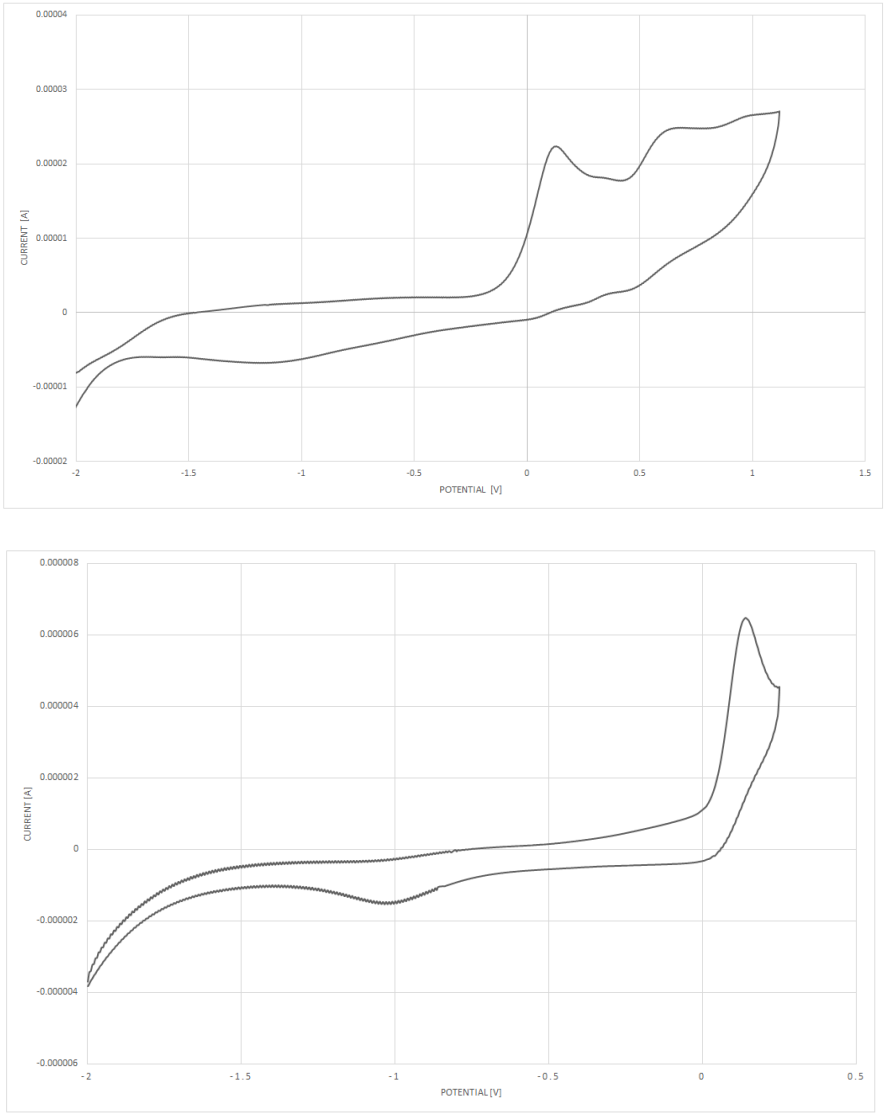


Fig S69. Cyclic voltammetry of **1** (referenced vs Fc^{+}/Fc) measured with voltage sweep 100 mV/s.

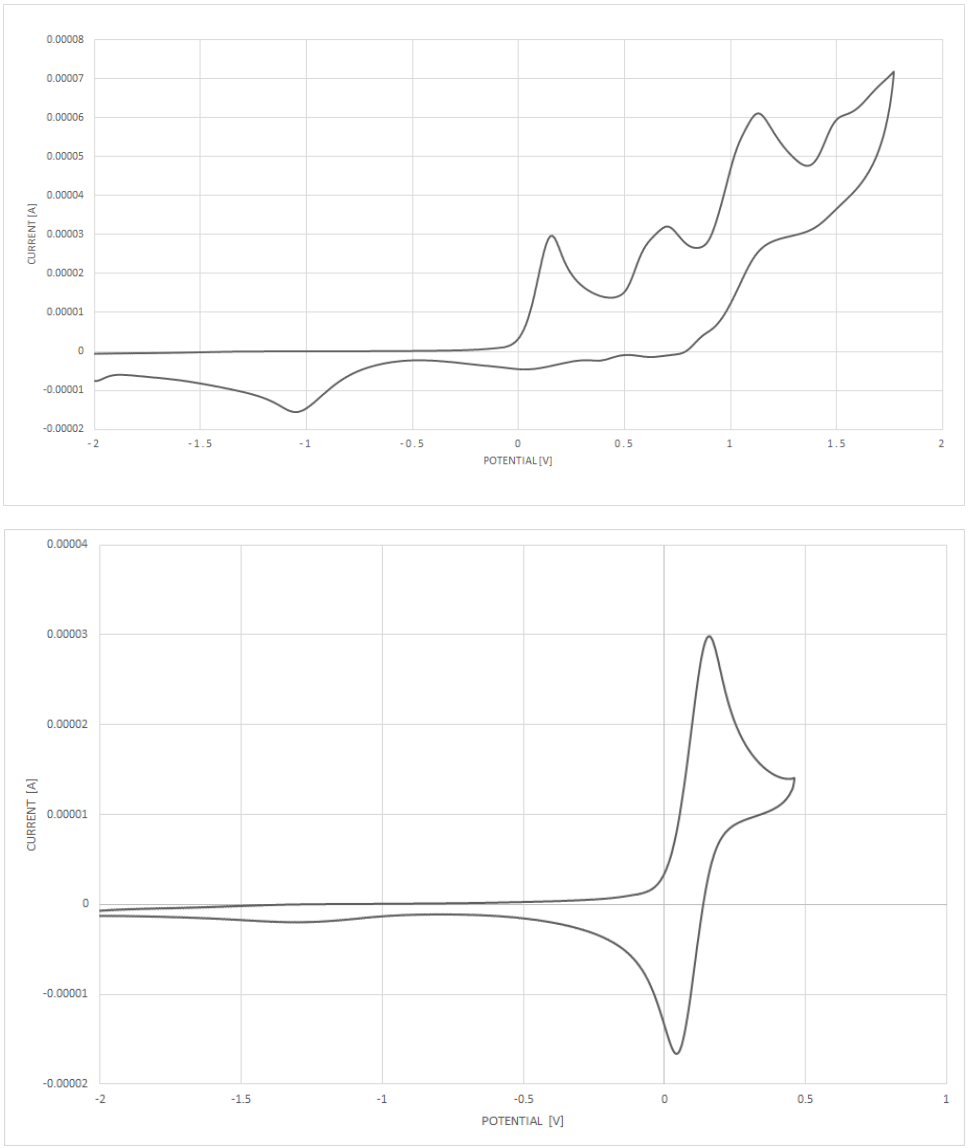
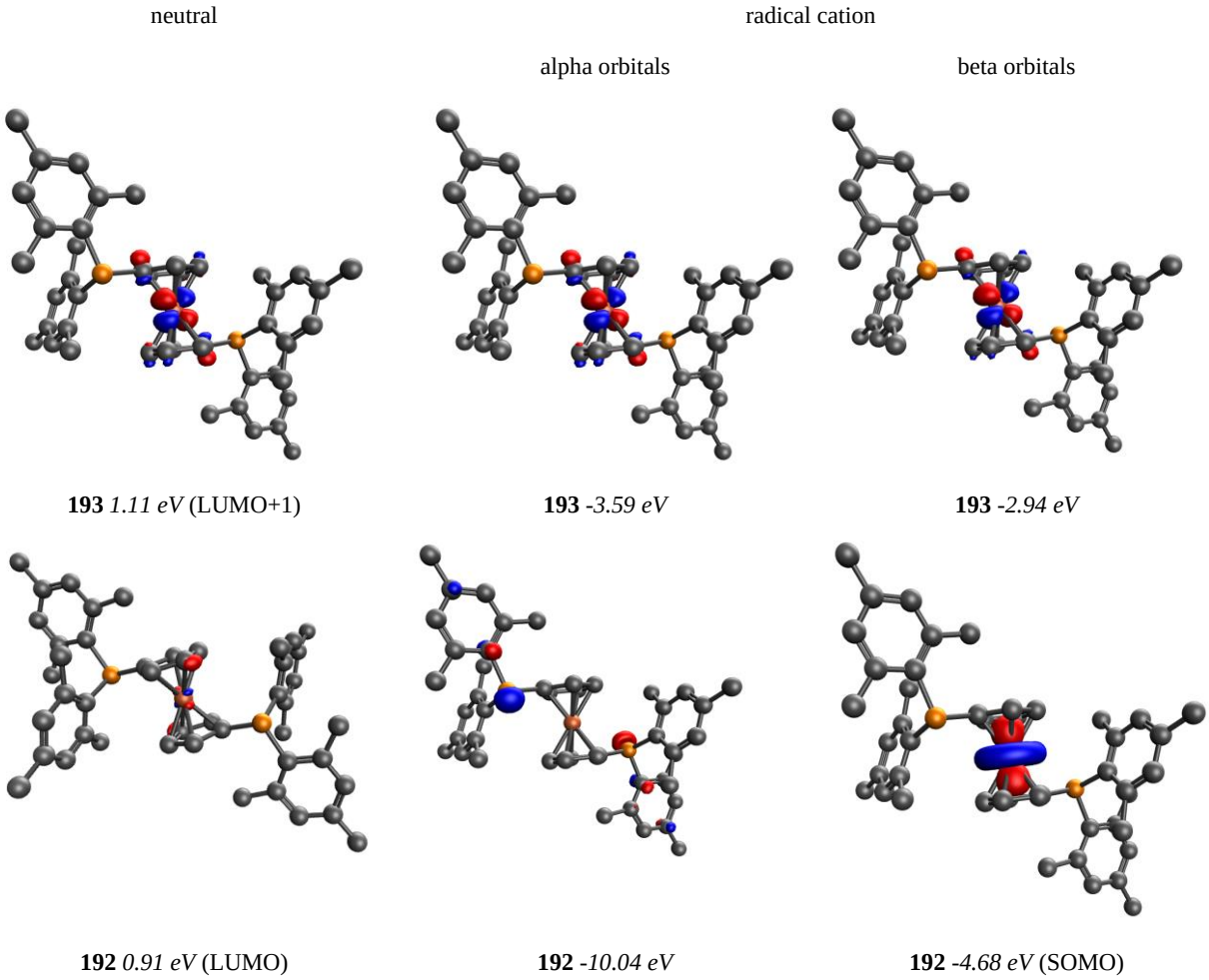


Fig S70. Cyclic voltammetry of **3** (referenced vs Fc^{+}/Fc) measured with voltage sweep 100 mV/s.

Computational details

All calculations were carried out with the Gaussian 09 quantum chemistry program package.[1] Full geometry optimization was performed for all molecules at the ω-B97X-D/6-31G*[2] or ω-B97X-D/6-311+G** level of theory, followed by calculation of harmonic vibrational frequencies at the same levels to establish the nature of the stationary points obtained. Minima are characterised by only positive eigenvalues and transition structures by a single negative eigenvalue of the Hessian. Subsequent IRC calculations were carried out to identify the minima connected with each transition structure. The depicted energies were calculated on these geometries at the higher 6-311+G** basis set. The IQmol[3] program was used for visualization of molecules and molecular orbitals.



[1] G. M. J. Frisch and others, 'Gaussian 09, Revision E.01', *Gaussian, Inc.: Wallingford, CT*, 2009 <https://doi.org/111>.

[2] Jeng-Da Chai and Martin Head-Gordon, 'Long-Range Corrected Hybrid Density Functionals with Damped Atom–Atom Dispersion Corrections', *Physical Chemistry Chemical Physics*, 10.44 (2008), 6615 <https://doi.org/10.1039/b810189b>.

[3] A. T. B. Gilbert, *IQmol Molecular Viewer. Available at: Http://Iqmol.Org (Accessed October, 2012).*

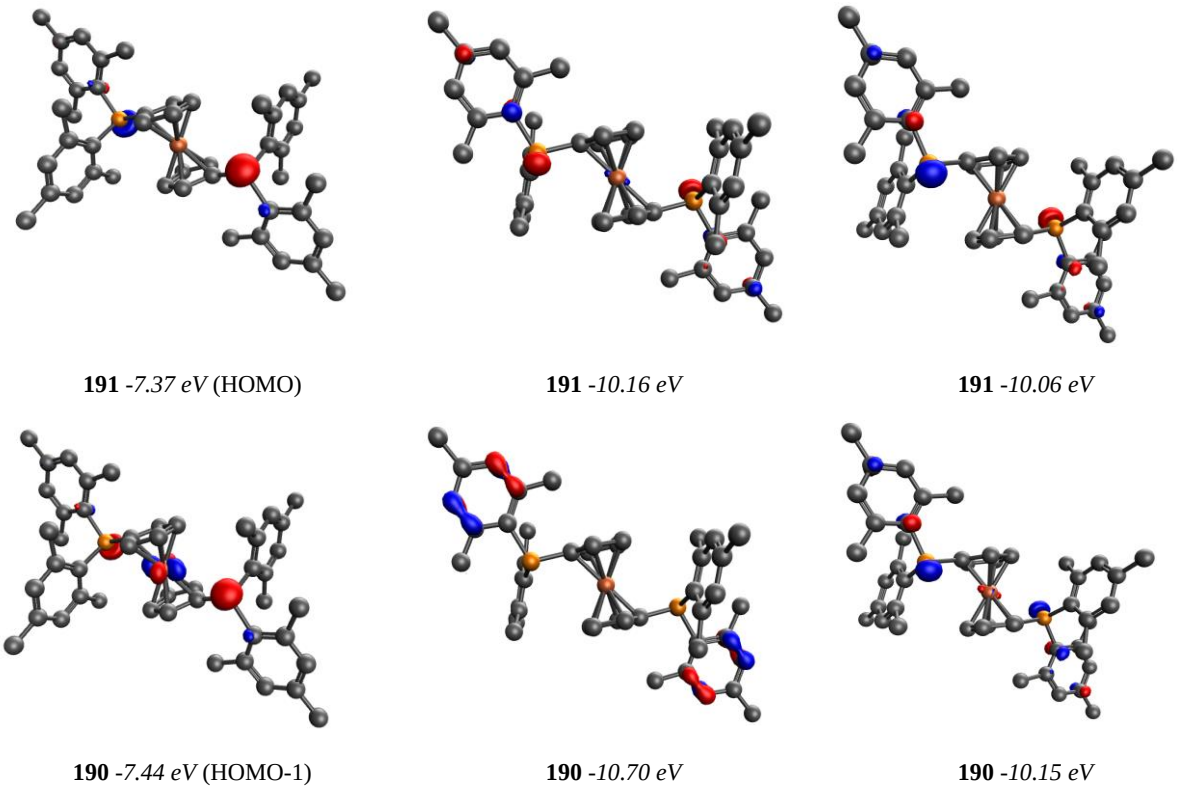


Fig S71. Important Kohn-Sham (ω-B97X-D/6-311+G**//ω-B97X-D/6-31G*) orbitals of compound **1** and its radical cation.
The numbering of the orbitals (in **bold**) is presented together with their energies (in eV presented *in italics*, in parentheses). Hydrogen atoms were omitted for clarity.

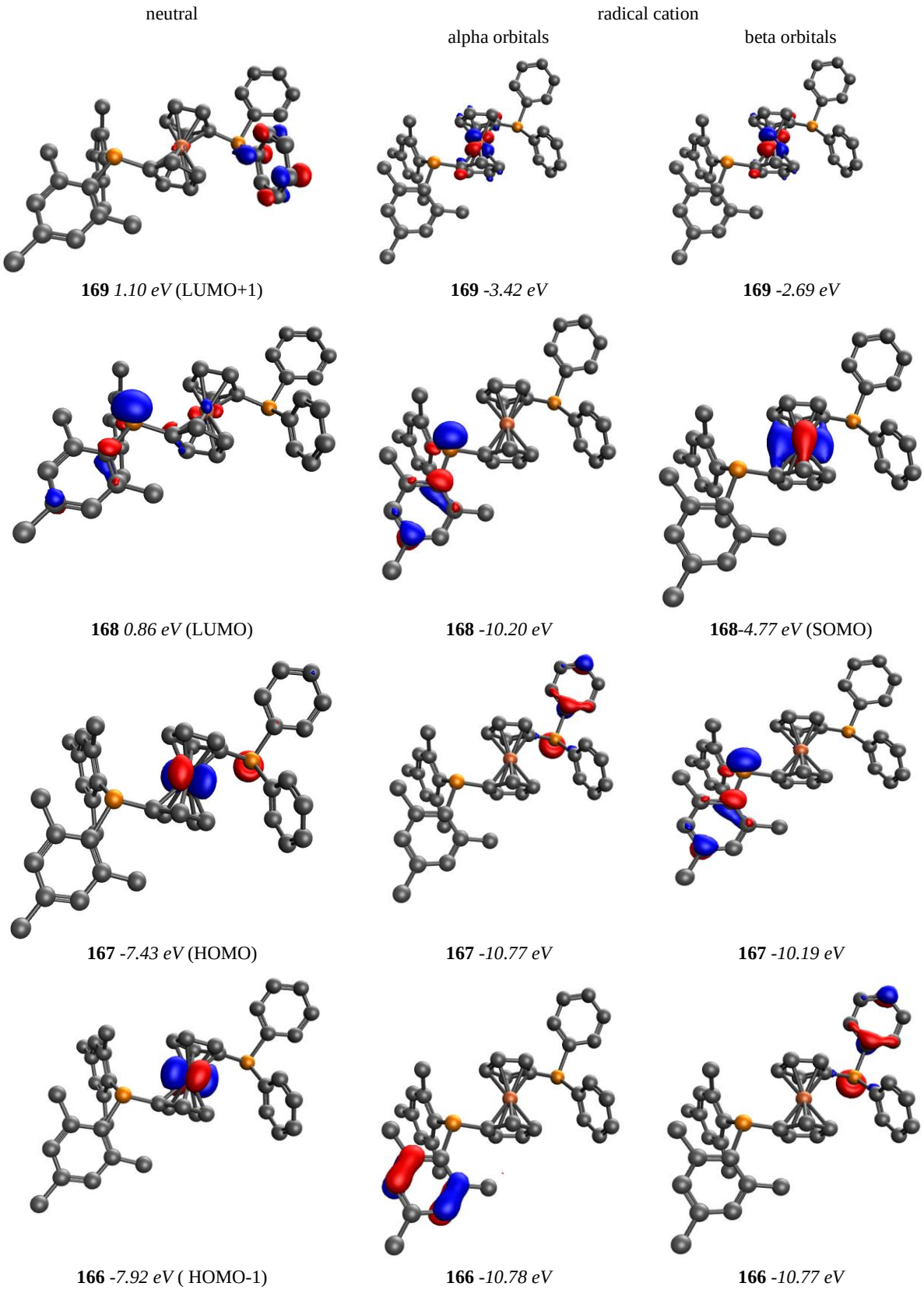


Fig S72. Important Kohn-Sham (ω-B97X-D/6-311+G**//ω-B97X-D/6-31G*) orbitals of compound **3** and its radical cation.
The numbering of the orbitals (in **bold**) is presented together with their energies (in eV presented *in italics*, in parentheses). Hydrogen atoms were omitted for clarity.

1 **3**

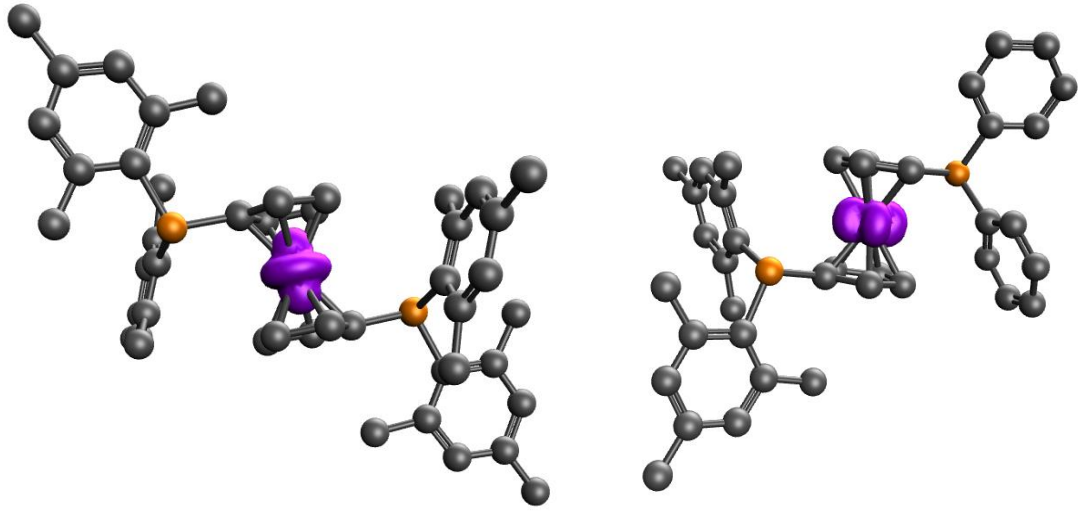


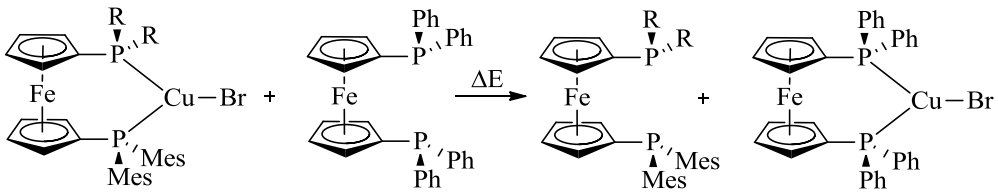
Fig S73. ωB97X-D/6-311+G** spin density distribution of the radical cations of compound **1** and **3**. Hydrogen atoms were omitted for clarity.

Table S4. Calculated parameters for **dppf**, **1** and **3**

compounds Fc (subst-1) (subst-2)*	Subst-1			Subst-2			ν(CO)** [cm^{-1}]
	Character (%)		Sum of bond angles around P	Character (%)		Sum of bond angles around P	
	s	p		s	p		
dppf Fc(PPh_2)(PPh_2)	46.6	53.4	303.1	46.9	53.1	304.2	2102.1
3 Fc($PMes_2$)(PPh_2)	44.4	55.6	313.8	46.6	53.4	304.2	2096.7
1 rotamer-1 Fc($PMes_2$)($PMes_2$)	44.7	55.3	313.2	44.7	55.3	313.2	2090.9
1 rotamer-2 Fc($PMes_2$)($PMes_2$)	44.35	55.65	313.0	44.35	55.65	313.0	

*calculated at ω-B97XD/6-311+G**

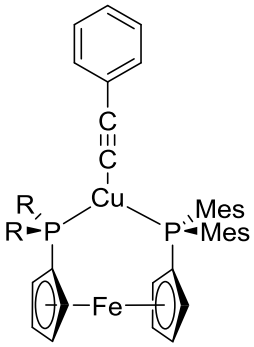
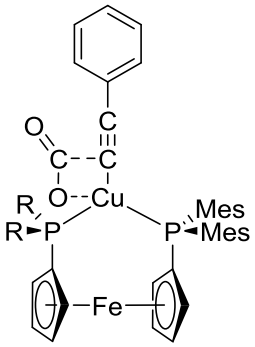
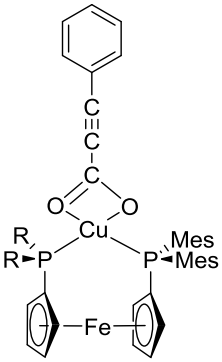
ν(CO) in the chelate complex Fc(subst-1)(subst-2)Pd-CO. Calculated on equilibrium structure obtained at ω-B97XD/6-311+G level of theory with ω-B97XD method and the following basis set:: 6-311+G** for H, C, P, O and def-2-TZVP for Pd



ligand	isodesmic reaction energy (kcal/mol)
1	-8.4
3	-4.0

Fig S74. Isodesmic reaction for the comparison of the stability of CuBr complexes with compound **1** and **3** (at the ω-B97X-D/6-311+G**//ω-B97X-D/6-31G* level of theory). The reaction energy of the **7+3→10+1** isodesmic reaction is the difference between the isodesmic reaction energies of **3** and **1**.

Table S5. The calculated barrier of the CO_2 insertion at various levels of theory

level of theory	R		 transition state	
		ΔE_{rel} (kcal/mol)		
ω-B97X-D/6-31G*	Ph	0.0	10.5	-3.6
	Mes	0.0	13.1	-0.7
ω-B97X-D/6-311+G**//ω-B97X-D/6-31G*	Ph	0.0	14.0	-5.1
	Mes	0.0	15.2	-1.3
B3LYP-D3/6-31G*	Ph	0.0	9.8	-2.0
	Mes	0.0	12.4	1.2
M06-2X-D3/6-31G*	Ph	0.0	8.3	-6.7
	Mes	0.0	10.2	-3.4

XYZ coordinates and total energies of the investigated systems

Table S6. dppf gauche neutral

E(RwB97XD) = -3258.36080539
E+ZPE= -3257.835324
E+E(thermal)= -3257.804426
E+H(thermal)= -3257.803481
E+G(thermal)= -3257.900394
P 1.98620200 -0.18304900 -0.88267900
P -1.98613900 0.18318100 -0.88274200
C 3.74298400 -0.73587900 -0.98710200
C -2.20251700 -1.64714800 -0.88008100
C -1.17913000 -2.42496600 -1.43013300
C -1.26279200 -3.81565300 -1.42076000
C -2.37765300 -4.44305200 -0.87261100
C -3.41256200 -3.67636000 -0.34130100
C -3.32687800 -2.28774700 -0.34783600
C 4.41909100 -1.38511000 0.04864100
C 5.73428100 -1.81291300 -0.12417400
C 6.39174400 -1.59346000 -1.32960400
C 5.72586900 -0.94787400 -2.36974000
C 4.41117900 -0.53102400 -2.20121800
C -1.62731400 0.50645700 0.87432200
C -2.01470300 -0.23441100 2.03560600
C -1.57438800 0.47195900 3.18655500
C -0.90813400 1.65196000 2.75155400
C -0.93617100 1.67468500 1.33263500
C -3.74281300 0.73643000 -0.98683000
C -4.41905200 1.38469000 0.04943000
C -5.73419100 1.81275200 -0.12318300
C -6.39147900 1.59449100 -1.32892100
C -5.72548100 0.94985600 -2.36957400
C -4.41084600 0.53278100 -2.20124600
Fe 0.00012200 -0.00034900 1.99133700
C 0.90798400 -1.65310800 2.75099400
C 1.57442200 -0.47339900 3.18653700
C 2.01499100 0.23334900 2.03591600
C 1.62760400 -0.50699000 0.87430800
C 0.93617500 -1.67527000 1.33207500
C 2.20230400 1.64731600 -0.87952000
C 3.32648100 2.28789900 -0.34686300
C 3.41199200 3.67651900 -0.33988100
C 2.37709100 4.44323700 -0.87117400
C 1.26243200 3.81586400 -1.41975800
C 1.17893200 2.42516800 -1.42955400
H -0.30759500 -1.93595000 -1.85819000
H -2.44670400 -5.52708400 -0.86853000
H -4.14327200 -1.69472300 0.05581200
H -3.89751300 0.03623300 -3.02182600

H -7.41710900 1.92671100 -1.46068100
H -3.92131200 1.55521700 0.99918700
H -1.68699200 0.14633400 4.21231400
H 4.14288800 1.69484900 0.05672500
H 2.44599200 5.52727800 -0.86672800
H 0.30753200 1.93617500 -1.85790900
H 0.48683200 -2.42889100 0.69891600
H 0.42690500 -2.38430900 3.38682300
H 1.68706900 -0.14822900 4.21243500
H 2.52634200 1.18627200 2.02989800
H -2.52576300 -1.18748900 2.02913100
H -0.42726900 2.38299200 3.38773900
H -0.48693600 2.42868300 0.69984800
H 0.45809900 4.40713600 -1.84794200
H 4.28957600 4.16091400 0.07865800
H -6.24563800 2.31490500 0.69322800
H -6.22938100 0.77771900 -3.31627200
H -0.45843300 -4.40688900 -1.84894100
H -4.29029600 -4.16077100 0.07690600
H 3.92120100 -1.55652200 0.99816000
H 6.24565500 -2.31579800 0.69183200
H 7.41742300 -1.92547300 -1.46150000
H 6.22989300 -0.77480300 -3.31620200
H 3.89797300 -0.03369300 -3.02140500

Table S7. dppf trans neutral

E(RwB97XD) = -3258.35857354
E+ZPE= -3257.832957
E+E(thermal)= -3257.802091
E+H(thermal)= -3257.801147
E+G(thermal)= -3257.898764
C -4.39522300 2.20703400 -0.04757100
C -4.60066100 0.95971000 -0.64185500
C -5.91468400 0.54128800 -0.88889100
C -6.99467100 1.33999800 -0.53362600
C -6.77924000 2.58100600 0.06248200
C -5.47870200 3.01181300 0.30027800
P -3.22441600 -0.13761500 -1.19518500
C -3.56761000 -1.63362700 -0.17536700
C -4.05677500 -1.58181600 1.13493800
C -4.26346400 -2.75076700 1.85949900
C -3.99599000 -3.98983000 1.28033300
C -3.53021800 -4.05594700 -0.02907400
C -3.32272000 -2.88300100 -0.75190300
H -4.28931900 -0.61972300 1.58343900
H -4.16165500 -4.90247300 1.84524900
H -2.96019300 -2.93659500 -1.77568800
C -1.81093700 0.62323700 -0.33515000
C -0.85699600 1.43499000 -1.02938700
C 0.07781900 1.94176600 -0.09231200

C -0.28399500 1.44895700 1.19345400
C -1.44238400 0.63919500 1.04854100
Fe 0.06979000 -0.09802600 -0.07691100
C 1.62780900 -0.81237900 -1.15244100
C 1.92817800 -0.85764100 0.24824600
C 0.93037700 -1.68159100 0.85949100
C 0.03576300 -2.13389000 -0.14221300
C 0.46895200 -1.59890800 -1.38922400
P 3.32042300 -0.15940400 1.19701700
C 3.42488400 1.56949600 0.56964800
C 3.76577100 1.90595700 -0.74554100
C 3.73821000 3.23081400 -1.16671000
C 3.38202400 4.24182000 -0.27450500
C 3.06899400 3.92334900 1.04288800
C 3.09515600 2.59411700 1.46049400
C 4.75294600 -0.93737400 0.33519800
C 4.64594900 -2.16874200 -0.31769500
C 5.76826600 -2.77220800 -0.87991100
C 7.01268900 -2.15636100 -0.79742500
C 7.13141700 -0.93196400 -0.14408100
C 6.01272000 -0.33158300 0.42235100
H -6.09421900 -0.42567400 -1.35340700
H -3.38566900 2.55357300 0.15211100
H -7.62199400 3.20797600 0.33870300
H -0.84211800 -2.74258400 0.02177300
H 0.86217600 -1.89387300 1.91844300
H 2.17945700 -0.25889600 -1.89965500
H -1.94275800 0.09962500 1.84085300
H 0.25557800 1.62657400 2.11417000
H 0.93401700 2.56053500 -0.32170300
H -0.84301200 1.60261000 -2.09858600
H -5.30175600 3.97765000 0.76487000
H -8.00675200 0.99457700 -0.72398700
H -3.33460500 -5.01896500 -0.49144000
H -4.64093500 -2.69575000 2.87653200
H -0.02472700 -1.73071200 -2.34307900
H 4.06523300 1.12647200 -1.44032200
H 3.99583000 3.47668200 -2.19283300
H 3.35862400 5.27592700 -0.60560500
H 2.80324900 4.70676500 1.74630200
H 2.85051900 2.34728700 2.49054800
H 6.11846700 0.62655000 0.92537700
H 8.09858900 -0.44270700 -0.07327900
H 7.88620600 -2.62637400 -1.23953400
H 5.66509300 -3.72717900 -1.38716300
H 3.68011400 -2.65886100 -0.39766000

Table S8. Compound **1** *gauche* neutral

E(ω-B97X-D/6-31G*) = -3730.00741179
E(ω-B97X-D/6-311+G**)= -3730.56009505
E(ω-B97X-D/6-31G*) +ZPE= -3729.141457
E(ω-B97X-D/6-31G*) +E(thermal)= -3729.092628
E(ω-B97X-D/6-31G*) +H(thermal)= -3729.091684
E(ω-B97X-D/6-31G*) +G(thermal)= -3729.222377
C -4.31414400 -1.46693700 -1.21495700
C -3.02085600 -1.47517200 -0.63495800
C -2.44839900 -2.72517700 -0.30885400
C -3.21214400 -3.89117100 -0.39285300
C -4.52052600 -3.87969000 -0.85146200
C -5.03056300 -2.66100400 -1.29184700
P -1.88548900 -0.01693700 -0.41858400
C -2.78194200 1.56612000 -0.72739400
C -3.82259700 2.07628600 0.07530800
C -4.30778400 3.36008600 -0.17632000
C -3.79962100 4.15721200 -1.19665500
C -2.79013700 3.62996200 -1.99837400
C -2.27347000 2.35234300 -1.78624300
C -4.47677700 1.29742900 1.19354600
C -4.31785600 5.55341400 -1.42976800
C -1.20575000 1.84439800 -2.73160500
C -0.99225900 -2.91049200 0.06384000
C -5.35473800 -5.13345500 -0.90521500
C -4.97320700 -0.25523700 -1.83810100
C -1.70506200 0.13216200 1.40889900
C -1.40412400 1.36682800 2.06947800
C -1.40151700 1.14875600 3.47325400
C -1.67185100 -0.22810200 3.69702900
C -1.85200600 -0.85111000 2.43101400
Fe -0.00007900 -0.00245800 2.57139500
C 1.40473200 -1.37173200 2.07169500
C 1.70593000 -0.13694500 1.41126300
C 1.85243600 0.84628200 2.43325500
C 1.67049600 0.22362900 3.69917600
C 1.40041000 -1.15326100 3.47541100
P 1.88574000 0.01278600 -0.41560900
C 2.78670200 -1.56713400 -0.72675800
C 3.82773500 -2.07688000 0.07568600
C 4.31753900 -3.35813600 -0.18005000
C 3.81378900 -4.15301700 -1.20430700
C 2.80334300 -3.62636300 -2.00521100
C 2.28182700 -2.35149200 -1.78870100
C 4.47800800 -1.30013400 1.19767600
C 4.33721200 -5.54651500 -1.44194100
C 1.21126700 -1.84456800 -2.73138100
C 3.01557000 1.47509400 -0.63292500
C 2.43647000 2.72403000 -0.31409400
C 3.19634900 3.89278700 -0.39790100

C 4.50743800 3.88498100 -0.84825700
C 5.02426700 2.66695400 -1.28282800
C 4.31186200 1.47060300 -1.20694800
C 0.97883100 2.90624300 0.05403300
C 4.97796700 0.26082100 -1.82645600
C 5.33717000 5.14172000 -0.90137800
H -1.70825600 -0.72629800 4.65674700
H 1.25504800 -2.32473700 1.58494000
H 1.19467300 -1.89803000 4.23258300
H 1.70586400 0.72198800 4.65884500
H 2.08465300 1.88964600 2.27648200
H -2.08252400 -1.89492500 2.27448500
H -1.19653900 1.89368700 4.23047300
H -1.25334700 2.31942900 1.58247800
H 2.72861500 4.83665900 -0.12238000
H 6.02327000 2.64611000 -1.71456200
H -5.11601900 3.74395400 0.44382000
H -2.39581200 4.22881400 -2.81710700
H -2.74999400 -4.83585500 -0.11081100
H -6.02748200 -2.63737400 -1.72821900
H 5.12615000 -3.74164300 0.43982100
H 2.41187600 -4.22359500 -2.82649100
H -5.79060900 -0.58040400 -2.48828300
H -5.39548200 0.42622600 -1.09561000
H -4.27830500 0.32841000 -2.44573100
H -5.87023700 -5.22803200 -1.86693500
H -4.74241600 -6.02846400 -0.75985400
H -6.12306300 -5.12575000 -0.12314700
H -0.88639400 -3.43596500 1.01924800
H -0.48994400 -3.51737900 -0.69839600
H -0.44471200 -1.97191200 0.14299600
H -0.92997000 2.62406800 -3.44809900
H -0.30228500 1.52049600 -2.20528100
H -1.56033900 0.97827100 -3.30204400
H -4.45787800 5.75197600 -2.49743100
H -5.27527800 5.71455300 -0.92562300
H -3.61121100 6.30052600 -1.04899600
H -5.54215100 1.54474500 1.24954500
H -4.38343800 0.21765200 1.06320600
H -4.02548500 1.54356400 2.16039300
H 0.49214100 3.56084300 -0.67815900
H 0.41973100 1.97076000 0.07199900
H 0.86674400 3.37821300 1.03618100
H 4.72110600 6.03461600 -0.75887600
H 6.10341800 5.13782800 -0.11725800
H 5.85491100 5.23693700 -1.86183800
H 5.79658100 0.58874900 -2.47372600
H 5.40020200 -0.41855600 -1.08210400
H 4.28767300 -0.32580200 -2.43641100
H 5.54382100 -1.54525400 1.25495500
H 4.38254100 -0.22014900 1.07065600
H 4.02543100 -1.55034300 2.16287600

H 5.29534100 -5.70568600 -0.93851300
H 3.63341000 -6.29737400 -1.06328400
H 4.47766900 -5.74128700 -2.51024100
H 0.93902400 -2.62237300 -3.45128300
H 0.30676400 -1.52794600 -2.20230000
H 1.56067400 -0.97389500 -3.29804900

Table S9. Compound **1** *gauche* radical cation

E(ω-B97X-D/6-31G*) = -3729.80607664
E(ω-B97X-D/6-311+G**) = -3730.35229960
E(ω-B97X-D/6-31G*) +ZPE= -3728.940066
E(ω-B97X-D/6-31G*) +E(thermal)= -3728.890771
E(ω-B97X-D/6-31G*) +H(thermal)= -3728.889827
E(ω-B97X-D/6-31G*) +G(thermal)= -3729.021441
C -4.31979300 -1.36616800 -1.14198900
C -3.01710800 -1.40177800 -0.58302600
C -2.44139500 -2.65846900 -0.28691000
C -3.21226700 -3.81808700 -0.39069200
C -4.52567900 -3.78828400 -0.83496600
C -5.03832700 -2.55603800 -1.23756100
P -1.89809200 0.04602500 -0.32005200
C -2.64941300 1.66197500 -0.74315500
C -3.66297000 2.30720700 -0.00481600
C -4.03231800 3.60541100 -0.35846300
C -3.44458500 4.27957600 -1.42431100
C -2.47086400 3.61195700 -2.16637900
C -2.06246200 2.31895700 -1.85118600
C -4.41268400 1.66758700 1.14258000
C -3.84369900 5.68923500 -1.77305200
C -1.02944000 1.65436400 -2.73383500
C -0.98754400 -2.86390200 0.08866500
C -5.36419200 -5.03620500 -0.91600800
C -4.97934700 -0.13450800 -1.72180900
C -1.81576700 0.20339200 1.49929200
C -1.42770900 1.39741500 2.18642100
C -1.40459500 1.14320600 3.58699000
C -1.70890600 -0.23357100 3.77333300
C -1.93941500 -0.80524800 2.49113300
Fe 0.00015200 -0.00002500 2.67769100
C 1.42795700 -1.39748000 2.18625900
C 1.81595100 -0.20343800 1.49912900
C 1.93970800 0.80517300 2.49098200
C 1.70931100 0.23346100 3.77318800
C 1.40496600 -1.14330700 3.58683500
P 1.89809900 -0.04602100 -0.32021600
C 2.64941900 -1.66195500 -0.74336300
C 3.66303600 -2.30714800 -0.00507900
C 4.03231400 -3.60539200 -0.35865400
C 3.44444800 -4.27962800 -1.42438500

C 2.47063700 -3.61206000 -2.16637900
C 2.06228700 -2.31903100 -1.85123500
C 4.41281700 -1.66744600 1.14223100
C 3.84347600 -5.68933000 -1.77305100
C 1.02906700 -1.65452900 -2.73371900
C 3.01705900 1.40182100 -0.58318100
C 2.44129900 2.65846800 -0.28697800
C 3.21211300 3.81812500 -0.39072800
C 4.52551600 3.78840400 -0.83504000
C 5.03821400 2.55620000 -1.23770000
C 4.31973800 1.36629100 -1.14215500
C 0.98744300 2.86381500 0.08863000
C 4.97935100 0.13467300 -1.72199800
C 5.36396600 5.03637000 -0.91604000
H -1.75543000 -0.76021000 4.71729300
H 1.24879600 -2.35402900 1.71528900
H 1.18565500 -1.86587200 4.36133600
H 1.75592600 0.76007300 4.71715900
H 2.19071000 1.83969200 2.30209900
H -2.19041600 -1.83976200 2.30222600
H -1.18522800 1.86575200 4.36149200
H -1.24860000 2.35398400 1.71547000
H 2.75294000 4.77223600 -0.13950400
H 6.03992700 2.52073700 -1.66006500
H -4.81836400 4.09781100 0.21024900
H -2.02339100 4.11153800 -3.02252000
H -2.75313100 -4.77223100 -0.13952400
H -6.04004600 -2.52051400 -1.65990800
H 4.81839500 -4.09777100 0.21002700
H 2.02302200 -4.11171600 -3.02240200
H -5.83246100 -0.43439100 -2.33556400
H -5.35588700 0.54581500 -0.95492000
H -4.30197900 0.43926400 -2.35788600
H -5.86156600 -5.11689600 -1.88774700
H -4.76177300 -5.93642300 -0.76690700
H -6.14696800 -5.02667800 -0.14923700
H -0.88719500 -3.30993400 1.08544900
H -0.51728900 -3.55630900 -0.61783600
H -0.40385900 -1.94174300 0.06298500
H -0.70321600 2.33974300 -3.52051000
H -0.14673200 1.33485700 -2.17013200
H -1.43561100 0.76106500 -3.22228000
H -3.96730000 5.81057900 -2.85353900
H -4.78216500 5.97196000 -1.28864200
H -3.07463600 6.40059200 -1.45064800
H -5.47082300 1.94303600 1.09446900
H -4.35418400 0.57672300 1.13681800
H -4.03585000 2.01668600 2.11097000
H 0.51708800 3.55608400 -0.61794200
H 0.40382400 1.94161300 0.06309900
H 0.88711700 3.30997500 1.08535800
H 4.76150100 5.93655300 -0.76691500

H 6.14673100 5.02685900 -0.14925700
H 5.86135000 5.11711700 -1.88776800
H 5.83233200 0.43461900 -2.33590800
H 5.35610600 -0.54553600 -0.95511400
H 4.30195700 -0.43923000 -2.35792800
H 5.47093600 -1.94297200 1.09412800
H 4.35439000 -0.57657800 1.13631300
H 4.03598200 -2.01639100 2.11067600
H 4.78199500 -5.97204300 -1.28873500
H 3.07443300 -6.40063700 -1.45049100
H 3.96693800 -5.81077000 -2.85354300
H 0.70264500 -2.33999200 -3.52023700
H 0.14650100 -1.33494600 -2.16983400
H 1.43513600 -0.76128900 -3.22235800

Table S10. Compound **1** *trans* neutral

E(ω-B97X-D/6-31G*) = -3730.02012219
E(ω-B97X-D/6-311+G**)= -3730.57119914
E(ω-B97X-D/6-31G*)+ZPE= -3729.152600
E (ω-B97X-D/6-31G*)+E(thermal)= -3729.104370
E (ω-B97X-D/6-31G*)+H(thermal)= -3729.103426
E (ω-B97X-D/6-31G*)+G(thermal)= -3729.232330
C -4.94156800 2.21968300 0.36318100
C -4.86582400 1.06488900 -0.44587800
C -6.04831000 0.60757800 -1.07988600
C -7.26096300 1.25125500 -0.84394200
C -7.35529000 2.36540700 -0.01767100
C -6.18199000 2.83414600 0.55821700
P -3.35127000 0.08181400 -0.89488000
C -3.68935400 -1.58652600 -0.14948100
C -4.21752300 -1.79807400 1.14545700
C -4.36325300 -3.10278600 1.61755400
C -4.02243400 -4.21560500 0.85405700
C -3.54090700 -3.99547700 -0.43031000
C -3.38228700 -2.70857200 -0.94933500
C -4.68527800 -0.68737900 2.05699400
C -4.19529800 -5.60801400 1.40457200
C -2.93105900 -2.59184700 -2.38805800
C -6.06569200 -0.57479600 -2.02128500
C -8.67942400 3.04625200 0.21657900
C -3.76359800 2.86837000 1.05254600
C -1.94466700 0.63786300 0.12713200
C -1.06774000 1.68806700 -0.29384800
C -0.09210500 1.90223100 0.71388200
C -0.33361100 0.96206200 1.75652600
C -1.45991300 0.17800200 1.39211600
Fe 0.00006600 -0.00018000 0.00023800
C 1.45974900 -0.17832400 -1.39192400
C 1.94483800 -0.63811600 -0.12705000
C 1.06806200 -1.68834700 0.29419700

C 0.09220000 -1.90261800 -0.71328900
C 0.33341100 -0.96247700 -1.75603200
P 3.35152300 -0.08208400 0.89487000
C 3.68929500 1.58646900 0.14980600
C 4.21717300 1.79842000 -1.14518800
C 4.36245700 3.10325400 -1.61703400
C 4.02155600 4.21586300 -0.85322600
C 3.54041000 3.99531800 0.43120900
C 3.38218900 2.70825300 0.94998000
C 4.68508400 0.68802100 -2.05699300
C 4.19397100 5.60836300 -1.40350900
C 2.93125400 2.59112300 2.38876000
C 4.86611000 -1.06489400 0.44541300
C 4.94185000 -2.21957000 -0.36383100
C 6.18231400 -2.83381600 -0.55923000
C 7.35567400 -2.36500400 0.01648000
C 7.26136800 -1.25099200 0.84293500
C 6.04867600 -0.60750500 1.07921700
C 3.76382300 -2.86831000 -1.05306600
C 6.06610400 0.57478300 2.02072200
C 8.67985200 -3.04562700 -0.21816900
H -0.72017900 -2.61461200 -0.66281500
H 1.14274100 -2.22364500 1.23217000
H 1.85952600 0.65237300 -1.95648600
H -1.85986900 -0.65270900 1.95653100
H 0.26013900 0.82407500 2.65010800
H 0.72032000 2.61418900 0.66361700
H -1.14211200 2.22343400 -1.23180700
H -6.22624600 3.71614900 1.19399400
H -8.15804000 0.87022900 -1.32855800
H -3.28773300 -4.84880500 -1.05619800
H -4.76307200 -3.25360100 2.61868200
H -0.26057200 -0.82453300 -2.64947000
H 4.76196900 3.25436900 -2.61824500
H 3.28720500 4.84844000 1.05737000
H 8.15849900 -0.86991300 1.32741100
H 6.22655900 -3.71571000 -1.19516000
H -4.10356600 3.72137800 1.64655300
H -3.23412200 2.18696600 1.72306100
H -3.02605000 3.23822400 0.33529300
H -8.59832600 3.82700800 0.97866500
H -9.05138000 3.51350800 -0.70265800
H -9.43929400 2.32964300 0.54710700
H -7.01788700 -0.61938400 -2.55733100
H -5.26392400 -0.50392300 -2.76522300
H -5.93489300 -1.52486000 -1.49238000
H -2.55489900 -3.55256500 -2.75209200
H -3.76777300 -2.29505400 -3.03105900
H -2.15068500 -1.84398300 -2.52709900
H -4.78565400 -1.05740200 3.08174300
H -4.00303600 0.16297500 2.07262400
H -5.66121900 -0.30640300 1.73881700

H -3.81405400 -6.36279400 0.71068800
H -3.66695800 -5.72535400 2.35698000
H -5.25304200 -5.82670400 1.59065700
H 8.59865500 -3.82639800 -0.98023000
H 9.43951300 -2.32890000 -0.54892500
H 9.05215300 -3.51281900 0.70096000
H 7.01845800 0.61953600 2.55646400
H 5.93492800 1.52487800 1.49195700
H 5.26457600 0.50365200 2.76489600
H 4.10376300 -3.72135700 -1.64702700
H 3.02632300 -3.23810400 -0.33574200
H 3.23430200 -2.18697000 -1.72361100
H 3.81280200 6.36298800 -0.70940400
H 5.25162000 5.82733500 -1.58987500
H 3.66535500 5.72583800 -2.35575800
H 2.55510700 3.55171600 2.75313100
H 2.15094600 1.84317700 2.52772500
H 3.76811300 2.29420300 3.03151400
H 4.78570000 1.05836000 -3.08161400
H 5.66095700 0.30694900 -1.73871900
H 4.00285300 -0.16233000 -2.07305500

Table S11. Compound **1** *trans* radical cation

E(ω-B97X-D/6-31G*) = -3729.77971873
E(ω-B97X-D/6-311+G**)=-3730.32502219
E(ω-B97X-D/6-31G*)+ZPE= -3728.913269
E(ω-B97X-D/6-31G*)+E(thermal)= -3728.864271
E(ω-B97X-D/6-31G*)+H(thermal)= -3728.863327
E(ω-B97X-D/6-31G*)+G(thermal)= -3728.995379
C -4.96245300 2.18828900 0.39738000
C -4.86143900 1.04786500 -0.42656500
C -6.02036600 0.57572100 -1.09070900
C -7.24383100 1.20265600 -0.86867400
C -7.36853400 2.30552400 -0.03045800
C -6.21314700 2.78307200 0.57629100
P -3.34817700 0.07409600 -0.85821500
C -3.62971000 -1.60527900 -0.13535600
C -4.13320000 -1.83584700 1.16897000
C -4.22360500 -3.14446800 1.63874300
C -3.86141600 -4.24520900 0.86300500
C -3.41490000 -4.00596700 -0.43045500
C -3.30867900 -2.71292400 -0.95070300
C -4.63931200 -0.74230000 2.08097300
C -3.98869400 -5.64281300 1.40923800
C -2.91834400 -2.59973200 -2.40944500
C -6.00421400 -0.60324900 -2.03687000
C -8.70521400 2.96508100 0.18482700
C -3.80333200 2.84395200 1.11093200
C -1.95564000 0.64663400 0.20630400
C -1.08037700 1.70956500 -0.19083300
C -0.07091800 1.87661600 0.79654700

C -0.28821800 0.89365100 1.80500400
C -1.43176900 0.12916800 1.43538000
Fe -0.00003400 0.00003100 -0.00042300
C 1.43195900 -0.12907300 -1.43596600
C 1.95552600 -0.64671000 -0.20682600
C 1.08010200 -1.70962100 0.19000100
C 0.07084200 -1.87647900 -0.79760800
C 0.28842600 -0.89341900 -1.80591300
P 3.34782700 -0.07425500 0.85804600
C 3.62959400 1.60515900 0.13534800
C 4.13332600 1.83571800 -1.16889600
C 4.22399500 3.14434400 -1.63860300
C 3.86185300 4.24511200 -0.86287900
C 3.41512600 4.00588000 0.43050100
C 3.30862500 2.71282600 0.95068100
C 4.63944400 0.74217400 -2.08091200
C 3.98935500 5.64272300 -1.40905700
C 2.91803800 2.59977200 2.40936800
C 4.86128000 -1.04788000 0.42678400
C 4.96254000 -2.18840600 -0.39698300
C 6.21331300 -2.78311700 -0.57558200
C 7.36854400 -2.30538000 0.03131100
C 7.24358800 -1.20241000 0.86935900
C 6.02003100 -0.57555000 1.09109700
C 3.80359500 -2.84425000 -1.11064900
C 6.00363300 0.60355600 2.03708600
C 8.70531400 -2.96487600 -0.18360800
H -0.75614700 -2.57245500 -0.74636300
H 1.16456000 -2.27206700 1.11109800
H 1.81627200 0.73205400 -1.96597300
H -1.81592400 -0.73191500 1.96557600
H 0.34445700 0.71138500 2.66345700
H 0.75602600 2.57263300 0.74509900
H -1.16508700 2.27189200 -1.11198000
H -6.28255600 3.65685800 1.21985200
H -8.12654500 0.81710600 -1.37394200
H -3.15851800 -4.84921800 -1.06830700
H -4.60592700 -3.31346600 2.64313100
H -0.34406100 -0.71097100 -2.66446700
H 4.60651100 3.31331600 -2.64292100
H 3.15876700 4.84913000 1.06836800
H 8.12617500 -0.81672900 1.37475000
H 6.28290800 -3.65699400 -1.21899900
H -4.16199800 3.67753300 1.71942500
H -3.27331200 2.16126600 1.78171000
H -3.07031400 3.25198200 0.40764400
H -8.64972400 3.74506000 0.94890000
H -9.06685200 3.42655100 -0.74069300
H -9.45765300 2.23478800 0.49997700
H -6.93344200 -0.63915900 -2.61081800
H -5.17778300 -0.54041600 -2.75471400
H -5.90694000 -1.55536600 -1.50406400

H -2.25510900 -3.41960200 -2.70196200
H -3.81407400 -2.66911100 -3.03820300
H -2.43788200 -1.65263700 -2.65577700
H -4.75360600 -1.12079700 3.10019800
H -3.98203500 0.12839300 2.11936600
H -5.61609600 -0.38013500 1.74480400
H -3.58437900 -6.38466900 0.71548200
H -3.46206400 -5.74422800 2.36388200
H -5.04007300 -5.89107700 1.59095200
H 8.65006400 -3.74485000 -0.94770400
H 9.45781400 -2.23455500 -0.49854200
H 9.06671100 -3.42634400 0.74200600
H 6.93246300 0.63917500 2.61170100
H 5.90711700 1.55562200 1.50404700
H 5.17667900 0.54120300 2.75436600
H 4.16240700 -3.67798700 -1.71884300
H 3.07041000 -3.25211400 -0.40743500
H 3.27374800 -2.16173400 -1.78173300
H 3.58503600 6.38459600 -0.71532200
H 5.04077500 5.89088700 -1.59066300
H 3.46282100 5.74421300 -2.36374700
H 2.25344700 3.41875700 2.70131300
H 2.43896800 1.65206900 2.65603200
H 3.81352900 2.67091700 3.03827600
H 4.75365000 1.12067100 -3.10014700
H 5.61628300 0.38009700 -1.74481000
H 3.98224100 -0.12857700 -2.11926400

Table S12. Compound **3** *gauche* neutral

E(ω-B97X-D/6-31G*) = -3494.18712894
E(ω-B97X-D/6-311+G**)= -3494.68433035
E(ω-B97X-D/6-31G*) +ZPE= -3493.491604
E(ω-B97X-D/6-31G*) +E(thermal)= -3493.452503
E(ω-B97X-D/6-31G*) +H(thermal)= -3493.451559
E(ω-B97X-D/6-31G*) +G(thermal)= -3493.562805
C -3.27567800 1.43760300 -1.12743600
C -2.66599200 1.30049100 0.12586600
C -1.78732100 2.29672100 0.55682500
C -1.48730000 3.38729200 -0.25807800
C -2.07355700 3.49426600 -1.51348800
C -2.97722200 2.52192000 -1.94372100
P -2.85787400 -0.17263700 1.21200000
C -4.67921100 -0.45029200 1.12444000
C -5.21491900 -1.74280300 1.10936800
C -6.59199800 -1.94131200 1.14466900
C -7.45769100 -0.85291800 1.20017500
C -6.93537800 0.43713200 1.22577800
C -5.55908800 0.63641600 1.19270100
C -2.26276100 -1.56263500 0.18200900
C -1.28867300 -2.49387500 0.65882900

C -1.14102400 -3.53201500 -0.29938600
C -2.02765900 -3.25670000 -1.37910400
C -2.71363400 -2.04730800 -1.08878100
Fe -0.71378500 -1.72727800 -1.13783400
C -0.03679700 0.13550100 -1.54633800
C 0.99780800 -0.61087000 -0.90211800
C 1.24576900 -1.75644100 -1.71665800
C 0.38356000 -1.70658500 -2.84756600
C -0.40579800 -0.52823400 -2.74510800
P 1.75380000 -0.08548200 0.69016900
C 1.94667100 1.72751800 0.38909700
C 2.27039800 2.32450600 -0.84669600
C 2.25915400 3.71628400 -0.95375500
C 1.96745100 4.54248200 0.12573900
C 1.69199600 3.94102700 1.35147900
C 1.66799000 2.55538000 1.50091300
C 2.69718700 1.55162300 -2.07431300
C 1.93252000 6.04169000 -0.02588400
C 1.37801100 1.99281100 2.87518400
C 3.42384800 -0.90984800 0.67537800
C 3.37172500 -2.30351000 0.92410000
C 4.53772300 -3.06797000 0.88475000
C 5.78327400 -2.49544200 0.66596600
C 5.83521700 -1.11230400 0.53738900
C 4.69674800 -0.30266600 0.55239300
C 2.09295800 -3.01105300 1.30922700
C 4.95408000 1.18793400 0.49431700
C 7.04018200 -3.32534000 0.61358900
H -1.30724800 2.20498600 1.52700400
H -1.83098700 4.33421600 -2.15797500
H -3.99022600 0.69192200 -1.46345600
H -5.16645100 1.64974200 1.20792800
H -8.53216900 -1.00904500 1.22527000
H -4.55268700 -2.60275000 1.06060600
H -2.13620500 -3.84655200 -2.27960700
H -0.44469700 1.06900800 -1.19244900
H -1.17621900 -0.20431600 -3.43154600
H 0.32834500 -2.45008100 -3.63146600
H 1.97896600 -2.52710800 -1.52050700
H -3.45210600 -1.57331200 -1.72046500
H -0.46101900 -4.37076000 -0.23204900
H -0.75050900 -2.39241900 1.59184700
H 4.46596400 -4.13995900 1.05628800
H 6.80640100 -0.63325700 0.42741600
H -6.98928400 -2.95222700 1.12501300
H -7.60176800 1.29401300 1.26925900
H -0.77768500 4.13299700 0.08426300
H -3.44846100 2.61115500 -2.91845500
H 2.51045100 4.16735400 -1.91206900
H 1.48615000 4.56853100 2.21645500
H 1.18790500 2.80190000 3.58669100
H 0.51095900 1.32476100 2.86991800

H 2.22106000 1.40574700 3.25601100
H 2.54258300 6.37258800 -0.87178600
H 0.90805600 6.39306000 -0.20166600
H 2.29835000 6.54244700 0.87595300
H 3.46714500 2.11354900 -2.61397900
H 3.10206900 0.56707200 -1.83295800
H 1.85868300 1.39636500 -2.76048800
H 6.01055700 1.38089800 0.70183600
H 4.73322100 1.61591100 -0.48614500
H 4.36569300 1.74285500 1.22706100
H 6.83180600 -4.38069000 0.81235600
H 7.51518100 -3.25702700 -0.37179300
H 7.77304000 -2.98112000 1.35173800
H 2.27766200 -4.07843200 1.46220400
H 1.69492200 -2.59931600 2.24418700
H 1.30665200 -2.91252900 0.56021100

Table S13. Compound **3** *gauche* radical cation

E(ω-B97X-D/6-31G*) = -3493.97427868
E(ω-B97X-D/6-311+G**)= -3494.46467580
E(ω-B97X-D/6-31G*) +ZPE= -3493.279299
E(ω-B97X-D/6-31G*) +E(thermal)= -3493.238676
E(ω-B97X-D/6-31G*) +H(thermal)= -3493.237732
E(ω-B97X-D/6-31G*) +G(thermal)= -3493.355183
C -4.14963200 0.71927200 -1.11027700
C -2.94792500 0.92228300 -0.42253200
C -2.22777400 2.10135200 -0.64592200
C -2.67455000 3.03765600 -1.57555100
C -3.85633600 2.81249900 -2.27549100
C -4.59786300 1.65655800 -2.03529400
P -2.25468800 -0.27003400 0.79310300
C -3.74893900 -0.92239500 1.63409600
C -4.51471000 -2.00861400 1.19820700
C -5.64441800 -2.40282500 1.90964800
C -6.02392900 -1.71411700 3.05831900
C -5.26609000 -0.63400200 3.50195300
C -4.13021400 -0.24736200 2.79950600
C -1.84291600 -1.69866100 -0.29541800
C -0.94338600 -2.73309700 0.11398200
C -0.85293900 -3.70304300 -0.91333500
C -1.68689800 -3.28685800 -1.98006200
C -2.29392200 -2.05650400 -1.60969400
Fe -0.26684300 -1.79029400 -1.60382400
C 0.29221100 0.13281700 -2.00364000
C 1.34268300 -0.42524600 -1.20891200
C 1.79638700 -1.58243000 -1.90403300
C 1.08460100 -1.70037300 -3.13287300
C 0.15919100 -0.62381400 -3.20119400
P 1.72029500 0.07242000 0.50751400
C 1.43548300 1.88187400 0.43998800

C 1.63693600 2.70990100 -0.68412300
C 1.14340500 4.01630400 -0.65513000
C 0.49939000 4.54486900 0.45849700
C 0.38454000 3.73769800 1.59049100
C 0.83341700 2.42069300 1.60401700
C 2.39861000 2.30984700 -1.92835900
C -0.05854600 5.94342700 0.45104500
C 0.67137700 1.61445100 2.87116900
C 3.47783100 -0.43438300 0.74145500
C 3.64480900 -1.81466100 1.01614700
C 4.92950900 -2.34353300 1.13272800
C 6.06374500 -1.54396100 1.05128600
C 5.87561700 -0.17480800 0.88931900
C 4.61533000 0.40634700 0.74639800
C 2.48644900 -2.75960400 1.26272400
C 4.57349100 1.91514200 0.66796000
C 7.44525700 -2.12284400 1.20438800
H -1.31829300 2.29663400 -0.08245000
H -4.21076500 3.54405300 -2.99503100
H -4.74918200 -0.16392400 -0.90394100
H -3.53340800 0.58645400 3.16139800
H -6.90657200 -2.02278700 3.60951400
H -4.23432200 -2.55662100 0.30262100
H -1.80135300 -3.79099000 -2.93096000
H -0.30230200 0.99679700 -1.74087000
H -0.54366200 -0.42437900 -3.99892100
H 1.22963500 -2.47299700 -3.87619300
H 2.57763900 -2.24952100 -1.56463300
H -2.96306900 -1.46764800 -2.22346100
H -0.21783200 -4.57947500 -0.90713900
H -0.39745300 -2.74267500 1.04828400
H 5.04490700 -3.40797800 1.32293400
H 6.74727700 0.47589700 0.88273000
H -6.22980900 -3.24953900 1.56452400
H -5.55347900 -0.09888200 4.40148400
H -2.10271900 3.94647300 -1.73855100
H -5.53415400 1.49277800 -2.55995300
H 1.29378600 4.64700700 -1.52904400
H -0.07590000 4.14616200 2.48680100
H 0.31071300 2.25172400 3.68284000
H -0.04707000 0.79955200 2.73109200
H 1.61807200 1.17068000 3.19802800
H 0.37506400 6.54595700 -0.35167900
H -1.14514000 5.92240600 0.30485300
H 0.13086100 6.45143000 1.40129100
H 3.11208600 3.09851400 -2.18783400
H 2.96027100 1.38133200 -1.81183500
H 1.73078800 2.19116600 -2.78918100
H 5.53860100 2.32461600 0.97643400
H 4.38198500 2.27562600 -0.34503800
H 3.81038500 2.34337000 1.32046700
H 7.44340900 -3.20707200 1.06288600

H 8.14069600 -1.68542700 0.48138800
H 7.84250000 -1.91809900 2.20502200
H 2.85817400 -3.71867200 1.63254400
H 1.80376000 -2.35058700 2.01527300
H 1.89399200 -2.96860700 0.36557500

Table S14. Compound **3** *trans*

E(ω-B97X-D/6-31G*) = -3494.18982984
E(ω-B97X-D/6-311+G**)= -3494.68720769
E(ω-B97X-D/6-31G*) +ZPE= -3493.494012
E(ω-B97X-D/6-31G*) +E(thermal)= -3493.454110
E(ω-B97X-D/6-31G*) +H(thermal)= -3493.453166
E(ω-B97X-D/6-31G*) +G(thermal)= -3493.567313
C 5.25120000 -0.52543800 -1.15355300
C 4.04396000 -1.06686600 -0.64535900
C 4.08401000 -2.33959300 -0.03543500
C 5.31343900 -2.98999700 0.10420900
C 6.50995500 -2.44561500 -0.34327100
C 6.45083800 -1.21253800 -0.98267300
P 2.54688900 -0.01724300 -0.98740200
C 2.87266900 1.52295700 -0.00545400
C 3.36903700 1.54549200 1.31757200
C 3.51716900 2.77054500 1.96898400
C 3.21075100 3.98266500 1.35764800
C 2.75702600 3.94875200 0.04428700
C 2.59531100 2.74811000 -0.64961500
C 3.80786600 0.31278600 2.07396900
C 3.39195700 5.28454400 2.09519100
C 2.16598800 2.83428900 -2.09824100
C 2.87525500 -3.07958800 0.48936200
C 7.82406000 -3.16098600 -0.16064800
C 5.31030900 0.79299900 -1.89045300
C 1.10688500 -0.70662600 -0.10534000
C 0.60836000 -0.52147400 1.22416900
C -0.54413500 -1.33669600 1.38958600
C -0.78692200 -2.01775300 0.16367400
C 0.21361500 -1.61637500 -0.75703700
Fe -0.81645300 0.00041000 -0.11263800
C -1.73574200 1.69627800 0.51812600
C -2.69779600 0.74544500 0.04963500
C -2.37404600 0.46528000 -1.31729400
C -1.23318400 1.23125600 -1.67437700
C -0.83820100 1.99345200 -0.53704200
P -4.06918800 0.16033800 1.09931700
C -4.18939300 -1.62327400 0.65251900
C -4.55728400 -2.08599700 -0.61647800
C -4.54410800 -3.44582600 -0.90557500
C -4.17665100 -4.36652000 0.07516300
C -3.83957000 -3.92189200 1.34947000
C -3.85177900 -2.55804800 1.63459600

C -5.51833200 0.84906900 0.19126600
C -6.77838700 0.26723400 0.37878200
C -7.90821300 0.80715100 -0.22469300
C -7.80041600 1.94737300 -1.01758900
C -6.55523800 2.53948100 -1.20165600
C -5.42150400 1.99517200 -0.60297200
H 0.01467700 2.65299200 -0.46508300
H -1.69020400 2.09496700 1.52320000
H -2.89260700 -0.23280100 -1.95939600
H 1.01528900 0.15285900 1.96460400
H -1.16143300 -1.38810200 2.27640800
H -1.61435500 -2.68233100 -0.04396200
H 0.29701100 -1.93524500 -1.78821700
H 5.32961100 -3.96490700 0.58709100
H 7.36610600 -0.76994000 -1.37167800
H 2.52805300 4.88405800 -0.46241400
H 3.89089700 2.77570100 2.99151900
H -0.73393700 1.20728100 -2.63392900
H -4.86874000 -1.37632000 -1.37770800
H -4.82428100 -3.79049100 -1.89685900
H -4.16528900 -5.42850700 -0.15191100
H -3.56658500 -4.63474500 2.12174200
H -3.58974000 -2.21293300 2.63165000
H -6.87536700 -0.62594500 0.99134500
H -8.87554100 0.33625000 -0.07501200
H -8.68270000 2.37169100 -1.48760000
H -6.46103300 3.42905000 -1.81795300
H -4.45494300 2.46445800 -0.76247500
H 3.18314200 -4.03556900 0.92219500
H 2.33968400 -2.52273100 1.26272800
H 2.15077800 -3.29276700 -0.30122100
H 6.26792200 0.89593000 -2.40849900
H 4.51286800 0.86937100 -2.63826000
H 5.20288500 1.64661900 -1.21264600
H 7.68516300 -4.13753700 0.31250000
H 8.32473000 -3.32041800 -1.12223900
H 8.50583500 -2.57707100 0.46826500
H 3.82428700 0.51382900 3.14952100
H 3.16134300 -0.54727000 1.90112100
H 4.81774000 0.01403000 1.77224100
H 1.78070200 3.83314400 -2.32387600
H 3.01646000 2.64625000 -2.76405200
H 1.39969500 2.10297600 -2.35865700
H 2.96779300 6.12425000 1.53720600
H 2.90907000 5.25224100 3.07771000
H 4.45472500 5.49524400 2.26173800

Table S15. Compound **3** *trans* radical cation

E(ω-B97X-D/6-31G*) = -3493.94640344
E(ω-B97X-D/6-311+G**)= -3494.45972118

E(ω-B97X-D/6-31G*) +ZPE= -3493.249846
E(ω-B97X-D/6-31G*) +E(thermal)= -3493.210067
E(ω-B97X-D/6-31G*) +H(thermal)= -3493.209123
E(ω-B97X-D/6-31G*) +G(thermal)= -3493.323733
C 5.14013300 -0.52879100 -1.35487400
C 3.97115500 -1.06677300 -0.76181800
C 4.03409100 -2.34427900 -0.16647000
C 5.25938300 -3.01336000 -0.13162400
C 6.42580000 -2.47992200 -0.66628500
C 6.33702600 -1.23676500 -1.28343100
P 2.50126500 0.03975800 -0.96444700
C 2.86306400 1.53029400 0.06898000
C 3.39272000 1.48552800 1.38151800
C 3.53551100 2.67523200 2.09436600
C 3.20325100 3.91616300 1.55409300
C 2.73368800 3.94846300 0.24597300
C 2.57400700 2.78570800 -0.51175300
C 3.87588200 0.22040600 2.05228700
C 3.38553100 5.17657200 2.35783500
C 2.15977500 2.96169900 -1.95800400
C 2.86072800 -3.07397100 0.44548800
C 7.73771500 -3.21556900 -0.59200000
C 5.16042500 0.80447800 -2.06642800
C 1.10154600 -0.67923800 -0.00489000
C 0.62191700 -0.41513100 1.31819700
C -0.53563200 -1.21303600 1.55334800
C -0.80230000 -1.96343200 0.37221100
C 0.18579500 -1.61626200 -0.58722300
Fe -0.83906100 0.04278900 -0.01570500
C -1.77930900 1.75883400 0.56090800
C -2.73640000 0.81340600 0.07295500
C -2.36380600 0.51423200 -1.27859700
C -1.19996100 1.26439900 -1.60789900
C -0.83501900 2.03506200 -0.46539100
P -4.18320300 0.25306300 1.08223000
C -4.14463200 -1.56335900 0.79695100
C -4.36938200 -2.16817500 -0.44643100
C -4.23827800 -3.54471400 -0.59470500
C -3.89497700 -4.33686800 0.50198700
C -3.70239400 -3.75060700 1.74933400
C -3.83166900 -2.37017400 1.89533200
C -5.53896200 0.79936300 -0.03320000
C -6.75450000 0.10526800 -0.01119700
C -7.83337400 0.55063300 -0.76706400
C -7.71691800 1.69874400 -1.54578700
C -6.51682000 2.40256200 -1.56194500
C -5.43454500 1.95924300 -0.80732800
H 0.03731500 2.66701600 -0.36576300
H -1.76060900 2.16197500 1.56542400
H -2.86471100 -0.19165100 -1.92665300
H 1.04457300 0.30721000 2.00386400
H -1.14440300 -1.20666200 2.44772300

H -1.64016100 -2.62968200 0.21571800
H 0.23661500 -1.97978900 -1.60577400
H 5.30002800 -3.99359900 0.33709900
H 7.22716500 -0.80219300 -1.73270700
H 2.50272400 4.90823900 -0.21055900
H 3.93616000 2.63292800 3.10496900
H -0.65471500 1.21130100 -2.54108600
H -4.67601300 -1.56349400 -1.29564300
H -4.41546900 -4.00431300 -1.56217700
H -3.79675300 -5.41145400 0.38472800
H -3.46094700 -4.36626100 2.61014100
H -3.69507400 -1.91587700 2.87375100
H -6.86088100 -0.79437100 0.58907800
H -8.76825700 -0.00049300 -0.74509800
H -8.56005800 2.04588800 -2.13439100
H -6.42079700 3.30299900 -2.16065600
H -4.50882900 2.52858000 -0.82714400
H 3.19550000 -4.01864800 0.88053700
H 2.37438800 -2.50789600 1.24547900
H 2.09677300 -3.31752100 -0.29968800
H 6.08827700 0.91816100 -2.63203500
H 4.32850200 0.89848900 -2.77442500
H 5.09572600 1.64276700 -1.36384600
H 7.61791000 -4.20486400 -0.14232300
H 8.17346000 -3.34635800 -1.58807600
H 8.46338400 -2.65783700 0.01012000
H 4.03059100 0.39264200 3.12067300
H 3.18549300 -0.61866500 1.94782300
H 4.82887300 -0.10478300 1.62318200
H 1.68076400 3.93373500 -2.10675300
H 3.04167100 2.93102800 -2.60845000
H 1.48484500 2.18310300 -2.31664900
H 2.94805100 6.04284100 1.85475200
H 2.92214100 5.08491100 3.34556000
H 4.44979100 5.38258700 2.51633800

Table S16. CuBr complex of dppf

E(ω-B97X-D/6-31G*) = -7470.52747849
E(ω-B97X-D/6-311+G**) = -7473.61388326
E(ω-B97X-D/6-31G*) +ZPE = -7469.998713
E(ω-B97X-D/6-31G*) +E(thermal)=- -7469.964168
E(ω-B97X-D/6-31G*) +H(thermal)=--7469.963224
E(ω-B97X-D/6-31G*) +G(thermal)=- -7470.069057
C -3.23970600 1.86560000 1.64409800
C -3.07669200 0.51984200 1.29637200
C -3.88133400 -0.45043600 1.90140800
C -4.84095200 -0.07887400 2.83778200
C -5.00726700 1.26275400 3.17177000
C -4.20557700 2.23235200 2.57557100
P -1.82131400 0.12573000 0.03263100

Cu 0.00641600 1.33940300 0.09869700
P 1.85208000 0.16899400 0.03400600
C 3.23485400 0.87024300 -0.92753900
C 4.11195900 0.08720300 -1.68442800
C 5.16786300 0.68170300 -2.36815400
C 5.35693400 2.05958200 -2.29753500
C 4.48115100 2.84481800 -1.55293500
C 3.41928900 2.25604000 -0.87375100
C 2.56695400 -0.24063800 1.66440100
C 3.84895100 -0.78019800 1.80468700
C 4.34127000 -1.10617100 3.06355600
C 3.56011700 -0.88805400 4.19663000
C 2.28962600 -0.33548600 4.06856700
C 1.79733900 -0.00912600 2.80800300
C 1.62530900 -1.45389600 -0.73749300
C 2.06442800 -2.74564500 -0.31168700
C 1.58602400 -3.70714500 -1.24280400
C 0.85500900 -3.02102200 -2.25235500
C 0.87574800 -1.63547300 -1.94366600
Fe 0.04163000 -2.66790400 -0.41731800
C -0.76111900 -3.60790400 1.20325300
C -0.81299600 -2.19716200 1.35430500
C -1.57039600 -1.65435900 0.26780900
C -1.98204500 -2.75129300 -0.55067300
C -1.48003800 -3.95037800 0.02451700
C -2.70834000 0.20148200 -1.56258100
C -3.98423600 -0.34601200 -1.73094600
C -4.61520300 -0.29075200 -2.96810400
C -3.98022900 0.31977700 -4.04826500
C -2.71900300 0.88307200 -3.88531900
C -2.08728600 0.82882400 -2.64561200
H 0.81078000 0.44051100 2.71530200
H 3.94807800 -1.13753400 5.17971500
H 4.46813500 -0.93682900 0.92549600
H 3.96260000 -0.98710600 -1.75119300
H 2.71223500 2.87571800 -0.32688300
H 6.18231500 2.52209000 -2.83101700
H -4.48753000 -0.81090500 -0.88724100
H -4.47553500 0.36656400 -5.01352900
H -1.11444100 1.29847900 -2.51851000
H -0.33951900 -1.62591000 2.14169200
H -0.23491600 -4.29373200 1.85316100
H -1.59701500 -4.94498900 -0.38449800
H -2.54174700 -2.67279600 -1.47262900
H 2.62678900 -2.95390600 0.58846600
H 1.72611100 -4.77762100 -1.17440500
H 0.34202400 -3.47551500 -3.08894800
H 0.38066900 -0.84943700 -2.50001400
H -2.22837000 1.37583200 -4.71902400
H -5.60560900 -0.71928900 -3.08952800
H 5.84106800 0.06794000 -2.95952200
H 4.61560800 3.92114700 -1.50730200

H 1.68408400 -0.14657200 4.94963800
H 5.33808600 -1.52552200 3.16225000
H -3.74968500 -1.49964700 1.65103800
H -5.45920000 -0.83848200 3.30731300
H -5.75669500 1.55130300 3.90297000
H -4.32496200 3.27877000 2.83905700
H -2.59654900 2.62157200 1.19837000
Br -0.09254900 3.59994900 0.14300000

Table S17. Compound **7**

E(ω-B97X-D/6-31G*)= -7942.18445655
E(ω-B97X-D/6-311+G**) =-7945.36954770
E(ω-B97X-D/6-31G*) +ZPE =-7941.316168
E(ω-B97X-D/6-31G*) +E(thermal)=-7941.263312
E(ω-B97X-D/6-31G*) +H(thermal)=-7941.262368
E(ω-B97X-D/6-31G*) +G(thermal)= -7941.401405
C 2.55056600 2.77189500 -0.38537200
C 2.98050100 1.44133000 -0.57721500
C 4.17183700 1.22394200 -1.30478000
C 4.98773600 2.31491300 -1.60618500
C 4.65219900 3.62128200 -1.26925900
C 3.40423200 3.82840300 -0.69657500
P 1.85263600 0.09410000 0.00882100
C 1.72162800 0.32967600 1.82779000
C 1.80875200 1.52253000 2.60546300
C 1.67985100 1.18598400 3.97870300
C 1.51801100 -0.22103200 4.07314900
C 1.53788900 -0.74794500 2.75560600
Fe 0.02540900 0.58402200 2.95309400
C -1.74946000 -0.41642800 3.02643500
C -1.65194700 0.32598000 1.81095200
C -1.47774500 1.69999700 2.18727700
C -1.47767600 1.79356500 3.60156400
C -1.63911500 0.48263700 4.12143800
P -1.89115800 0.01844700 0.01670400
C -2.29319000 -1.71691700 -0.47298600
C -1.76885200 -2.86198000 0.14896200
C -2.15639200 -4.12805200 -0.29198200
C -3.00478400 -4.30349200 -1.37577700
C -3.40178300 -3.16183100 -2.06809200
C -3.04980000 -1.87700900 -1.66180700
C -0.69436100 -2.81369300 1.20179600
C -3.45058200 -5.67438500 -1.81297500
C -3.46140400 -0.73432800 -2.56272300
C 4.58990800 -0.10863000 -1.88523000
C 5.58298700 4.77022900 -1.55602700
C 1.13305000 3.15373700 -0.02525900
C 2.73847200 -1.51764200 0.00546500
C 2.25524600 -2.56338000 -0.80999300
C 2.84383400 -3.82603000 -0.71598400

C 3.90517300 -4.08856700 0.14222400
C 4.40648600 -3.03160300 0.89573300
C 3.85495800 -1.75314000 0.84066000
C 1.15622100 -2.38759900 -1.82861700
C 4.53972400 -0.68434800 1.66376000
C 4.49802200 -5.46927500 0.25213300
Cu -0.05409600 0.39450000 -1.09037100
C -3.51274000 0.90536800 -0.07766000
C -3.57923700 2.16774200 -0.70482100
C -4.79689000 2.84523300 -0.74762800
C -5.95794300 2.32341700 -0.18769100
C -5.87267800 1.08503200 0.43561100
C -4.67845000 0.36595700 0.50759700
C -2.39633600 2.83269300 -1.36185000
C -7.25196000 3.09452300 -0.22842300
C -4.74550100 -0.98147900 1.18933600
H -2.66346000 3.83880100 -1.69727600
H 1.47031200 -1.79591500 2.50309100
H 1.37470300 -0.78994100 4.98188000
H 1.68005700 1.88869000 4.80107100
H 1.96177100 2.52126200 2.22767700
H -1.87439200 -1.48438800 3.11608300
H -1.64336100 0.20450900 5.16686000
H -1.34114000 2.69923900 4.17652500
H -1.38968900 2.53303100 1.50398900
H 3.05784400 4.84542100 -0.52199500
H 5.91314900 2.13225200 -2.14818700
H -6.76571400 0.65624400 0.88576000
H -4.83683000 3.81480800 -1.23941100
H -1.54594200 2.93141300 -0.68225100
H -2.03168300 2.27765100 -2.23134800
H -5.61850700 -1.02294400 1.84706500
H -4.83773900 -1.79123600 0.45774200
H -3.86484000 -1.19256700 1.79655800
H -7.39014100 3.58820000 -1.19566100
H -8.11217100 2.44167900 -0.05265200
H -7.26452600 3.87440200 0.54216700
H -1.74653600 -4.99977100 0.21521000
H -3.99117000 -3.27234700 -2.97584600
H -1.02375200 -3.25098000 2.15146400
H 0.17391000 -3.39115400 0.86446200
H -0.34878700 -1.80169600 1.39312900
H -2.68434400 0.03324400 -2.63044000
H -3.62655000 -1.11336600 -3.57489900
H -4.38414500 -0.25219700 -2.22712600
H -3.57361400 -5.72753500 -2.89916300
H -2.73200800 -6.44291900 -1.51234300
H -4.41609300 -5.93053900 -1.36048200
H 2.46468800 -4.62501600 -1.34914800
H 5.26795700 -3.20031100 1.53912200
H 0.99392600 -3.31958200 -2.37672900
H 0.20264000 -2.12632600 -1.36209200

H 1.38779800 -1.60439600 -2.55741400
H 5.57722600 -5.42606000 0.42886400
H 4.04997100 -6.01821000 1.08908200
H 4.32313500 -6.05186800 -0.65720600
H 4.42718300 0.31424700 1.23872100
H 4.14390100 -0.65247800 2.68404000
H 5.61054600 -0.90047800 1.72861500
H 5.32296700 0.06023400 -2.67885400
H 5.04204400 -0.78313800 -1.15418900
H 3.73712800 -0.62456300 -2.33372400
H 1.10405400 4.02568000 0.63772300
H 0.61713100 3.41787300 -0.95591100
H 0.55793300 2.35880500 0.45029900
H 5.02995500 5.66837600 -1.84887800
H 6.17375200 5.02389800 -0.66727400
H 6.28427800 4.52482300 -2.35914200
Br 0.35864100 1.12857800 -3.23030200

Table S18. Compound **10**

E(ω-B97X-D/6-31G*)= -7706.35802973
E(ω-B97X-D/6-311+G**)= -7709.49260864
E(ω-B97X-D/6-31G*) +ZPE = -7705.658193
E(ω-B97X-D/6-31G*) +E(thermal)= -7705.615018
E(ω-B97X-D/6-31G*) +H(thermal)=-7705.614074
E(ω-B97X-D/6-31G*) +G(thermal)= -7705.734801
C -3.90453000 -1.40565200 -0.59425800
C -2.65195100 -1.39174400 0.05786900
C -2.22791000 -2.56181300 0.72475300
C -3.11970800 -3.61744200 0.90374400
C -4.40717000 -3.58917300 0.38370900
C -4.75775600 -2.49123400 -0.39398700
P -1.43363600 -0.00722800 -0.04889500
C -1.10594500 0.49748400 1.68744600
C -1.28916300 -0.20745500 2.91382700
C -0.98635900 0.66615100 3.99258900
C -0.60976700 1.92297800 3.44806400
C -0.66991900 1.81775200 2.03369100
Fe 0.63789000 0.47465500 2.78224200
C 1.95994400 -1.05060400 2.50035100
C 2.24063500 0.02981100 1.60631500
C 2.50346200 1.18412100 2.40377200
C 2.38152800 0.81794000 3.77138600
C 2.04842900 -0.56360500 3.83042900
P 2.25358600 -0.12211800 -0.20187500
C 2.71037500 1.57247700 -0.72283600
C 3.99732400 1.93716600 -1.12088600
C 4.26858900 3.24955500 -1.50089300
C 3.26147900 4.20945800 -1.48553800
C 1.97240000 3.85270200 -1.09637700
C 1.70047900 2.54229900 -0.72298500
C -0.79932800 -2.81241200 1.14929300

C -5.37330600 -4.71966500 0.62403400
C -4.36257000 -0.35993100 -1.58550400
C -2.22569100 1.54517600 -0.63726500
C -3.19177600 2.22956100 0.13520900
C -3.61785200 3.49268400 -0.27044000
C -3.13615200 4.10173900 -1.42524200
C -2.24477200 3.38258000 -2.21304400
C -1.78990600 2.11209200 -1.85513600
C -3.84187200 1.65328200 1.37307400
C -0.89265700 1.40343400 -2.84355000
C -3.57594400 5.48856100 -1.81695000
Cu 0.37084200 -0.77506700 -1.05876000
C 3.74008400 -1.13553000 -0.49241400
C 4.87140500 -1.07050700 0.32952300
C 5.98798700 -1.84761100 0.04412200
C 5.98270700 -2.69496300 -1.06318000
C 4.85750300 -2.77038600 -1.87750500
C 3.73520900 -1.99590700 -1.59400200
H -0.98980600 1.86715000 -3.82928100
H 4.79044800 1.19647200 -1.13966600
H 3.47750800 5.23118300 -1.78326200
H 0.68781400 2.26774000 -0.44250900
H 1.74020300 -2.06904000 2.21055300
H 1.86719500 -1.13706700 4.72942700
H 2.48762600 1.48485600 4.61654100
H 2.72502000 2.17178800 2.02246000
H -1.62386700 -1.22933700 3.01464200
H -1.01524500 0.40633700 5.04228000
H -0.29588900 2.79529600 4.00525900
H -0.45348200 2.61803000 1.34055600
H 1.17311200 4.58787300 -1.09587800
H 5.27345500 3.51994300 -1.81161000
H -4.36157400 4.01044400 0.33213400
H -1.89942400 3.81375300 -3.15026800
H 0.16649600 1.47589100 -2.56816400
H -1.13459900 0.34391300 -2.95535900
H -4.86591000 2.02999600 1.45809200
H -3.88922000 0.56250400 1.35554100
H -3.30521300 1.94391100 2.28186500
H -3.65820200 5.59027800 -2.90346700
H -4.54515900 5.73911400 -1.37559400
H -2.85266800 6.23682800 -1.47113200
H -2.77690700 -4.50281100 1.43589500
H -5.72704300 -2.48378600 -0.88759100
H -0.75464000 -3.34672700 2.10499500
H -0.31057000 -3.43361300 0.38934000
H -0.20614500 -1.90647100 1.25818200
H -3.57291700 -0.12989800 -2.30596900
H -5.21674300 -0.74497600 -2.14903300
H -4.66947100 0.57873400 -1.11839500
H -6.13303600 -4.76971100 -0.16158100
H -4.85707000 -5.68412700 0.66087400

H -5.89409000 -4.58937600 1.58043100
H 4.87356800 -0.41406200 1.19610700
H 6.86184900 -1.79582700 0.68706300
H 6.85555800 -3.30271000 -1.28390400
H 4.84344900 -3.44151100 -2.73076000
H 2.84087600 -2.08345000 -2.20723800
Br 0.00230600 -2.33919100 -2.68090100

ATR-IR spectra

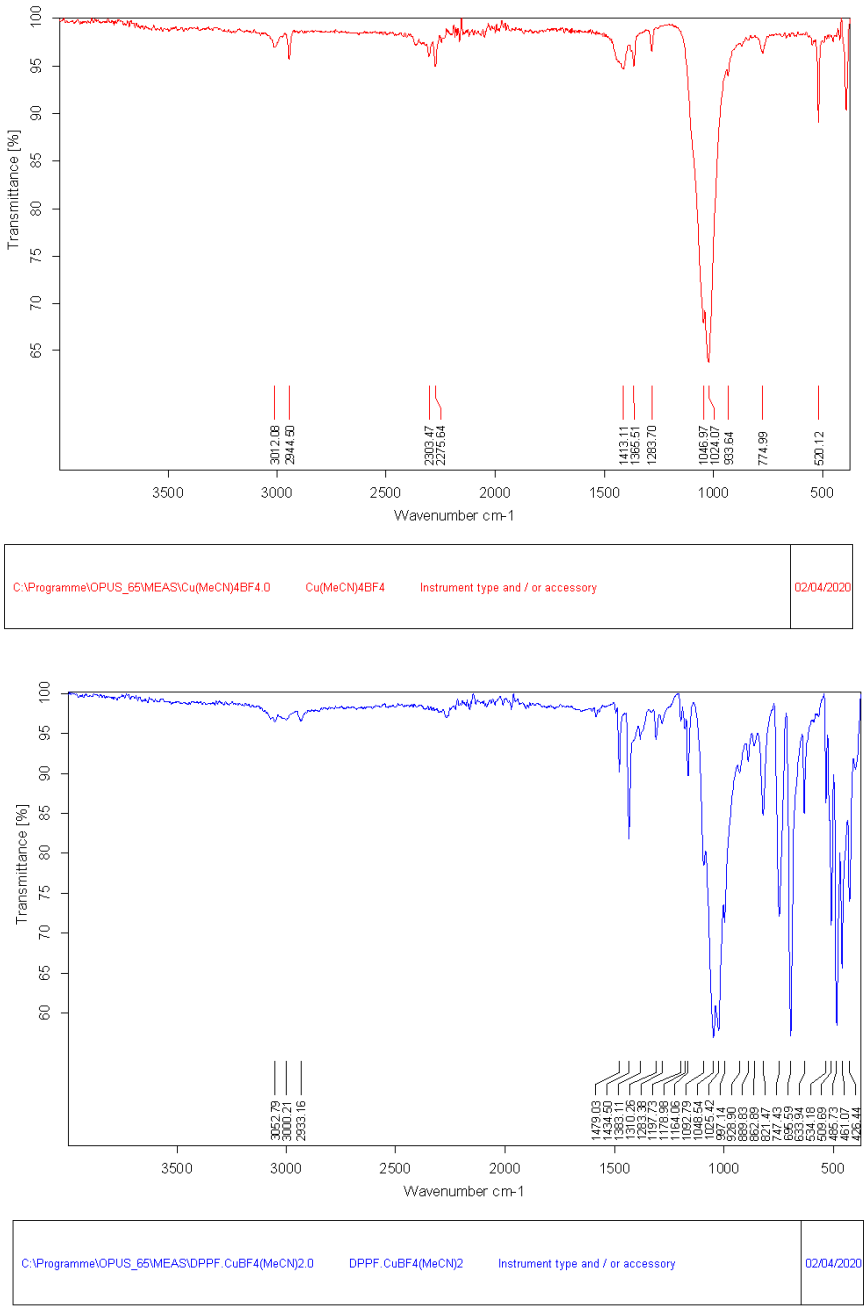
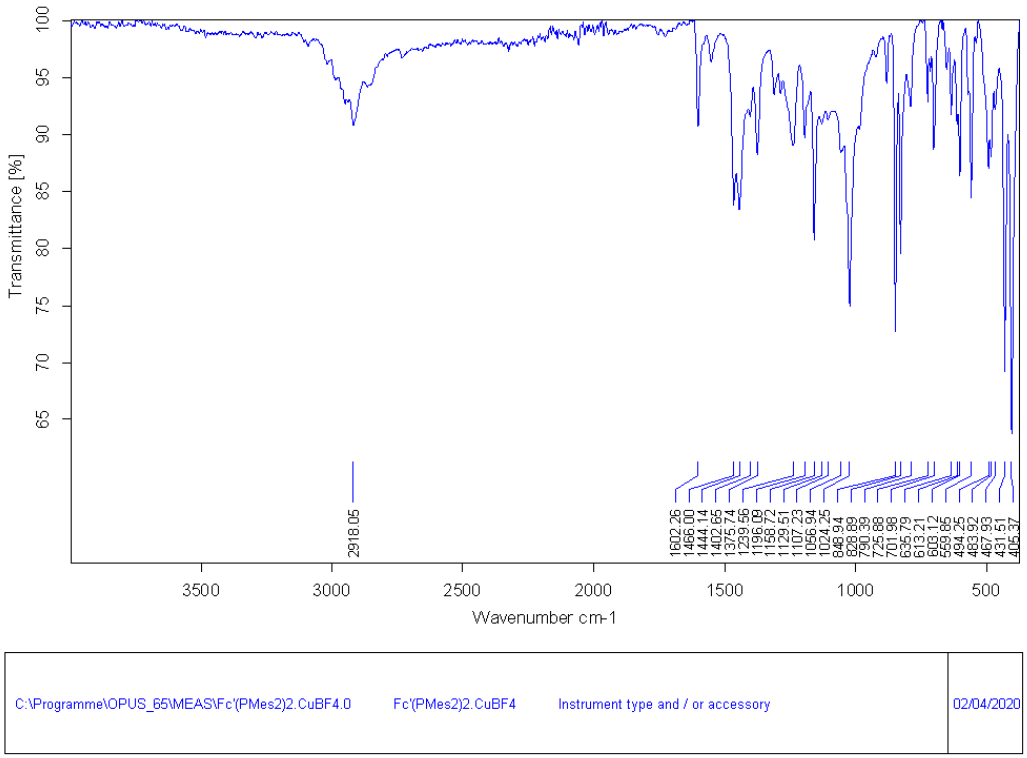


Fig S75. Solid state IR spectra of $Cu(MeCN)_4BF_4$ (top) and dppf·$Cu(MeCN)_2BF_4$ (bottom).



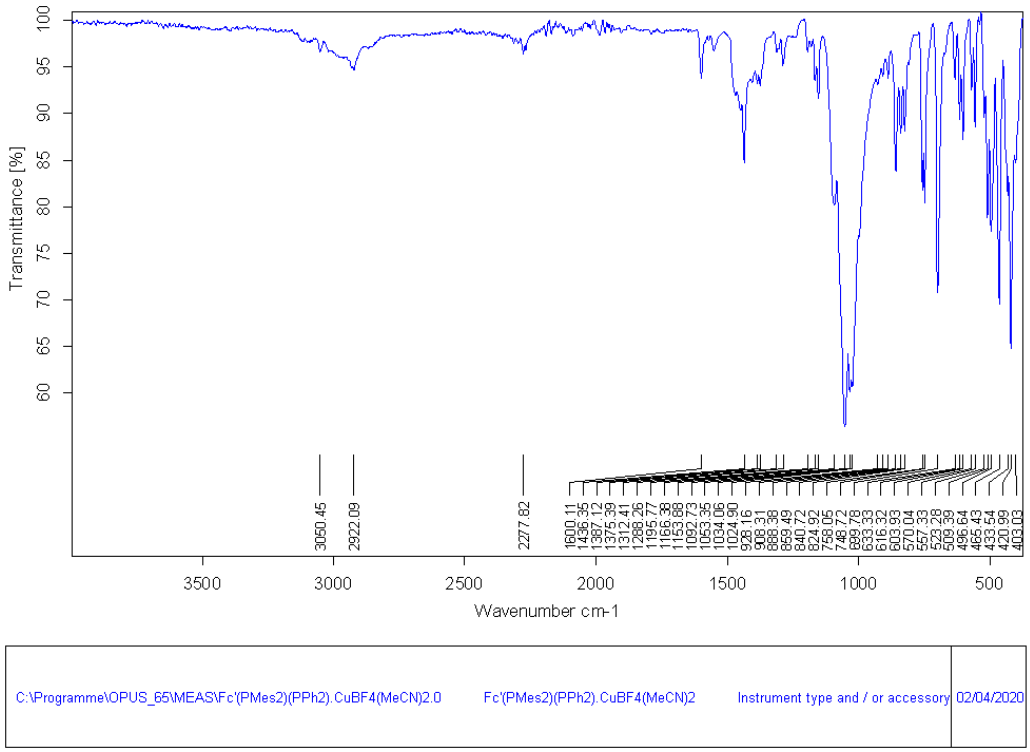


Fig S76. Solid state IR spectra of **9** (top) and **12** (bottom).