Supporting Information for:

A Nontrigonal Tricoordinate Phosphorus Ligand Exhibiting Reversible 'Nonspectator' L/X–Switching

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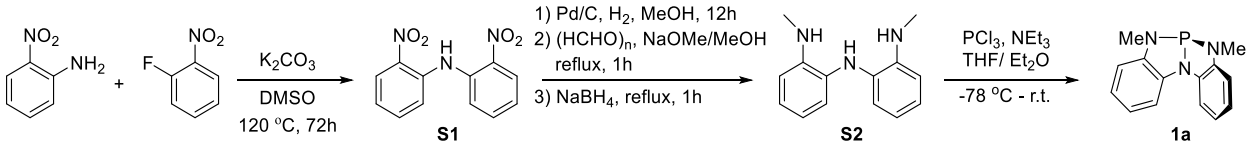
Contents

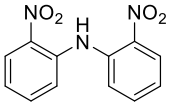
I. General Materials and Methods.

All reagents were purchased from Sigma-Aldrich, Alfa Aesar, ACROS, TCI, or Oakwood Chemicals, and used as received unless otherwise noted. Diethyl ether (Et_2O), methylene chloride (CH_2Cl_2), tetrahydrofuran (THF), acetonitrile (MeCN) and pentane were dried according to the method of Grubbs[1] as modified by Bergman[2] using a Glass Contour Solvent Purification System. All glassware was oven-dried at 120 °C prior to use. All reactions were carried out under a dry nitrogen atmosphere (Schlenk line or glovebox) unless otherwise noted. Solution NMR spectra other than $^{57}Fe/^{31}P$ 2-D spectra were recorded on a JEOL 500 MHz NMR and processed with the MestraNova software. $^{57}Fe/^{31}P$ 2-D spectra were recorded on a Bruker 600 MHz NMR and processed with the MestraNova software. ^{1}H NMR chemical shifts are given in ppm with respect to solvent residual peaks ($CDCl_3$, 7.26 ppm; CD_2Cl_2, 5.32 ppm; CD_3CN, 1.94 ppm; C_6D_6, 7.16 ppm), $^{13}C\{^{1}H\}$ NMR shifts are given in ppm with respect to solvent residual peaks ($CDCl_3$, 77.16 ppm; CD_2Cl_2, 53.84 ppm; CD_3CN, 1.32, 118.26 ppm; C_6D_6, 128.06 ppm), $^{31}P\{^{1}H\}$ NMR shifts are given in ppm with respect to 85% phosphoric acid (0 ppm), ^{19}F NMR shifts are given in ppm with respect to $CFCl_3$ (0 ppm), ^{57}Fe NMR shifts are given in ppm with respect to $Fe(CO)_5$ (0 ppm). Coupling constants are reported as *J*-values in Hz. High resolution ESI Mass spectrometry spectra were obtained from the Mass Spectrometry Laboratory at the School of Chemical Sciences, University of Illinois at Urbana-Champagne. X-ray diffraction data was collected on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073 Å). Raw data integration and reduction were performed with the SAINT[3] and SADABS[4] programs. Structures were solved using direct methods using SHELXT[5] and refined using least-squares methods on F^2 using the SHELXL software package. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were fixed in their ideal geometries. Graphical representation was done using the XP program.

II. Synthetic Procedures.

*Synthesis of **1a**:*



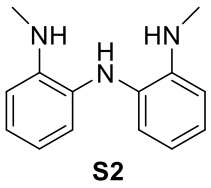


Bis(2-nitrophenyl)amine **(S1)**: Synthesized according to a modified literature procedure.[6] 1-Fluoro-2-nitrobenzene (15.8 mL, 150 mmol, 1 equiv) was added to a solution of 2-nitroaniline (20.7 g, 150 mmol, 1 equiv) and potassium carbonate (24.9 g, 180 mmol, 1.2 equiv) in DMSO (400 mL). The reaction mixture was heated with stirring at 120 ºC for 72h. The reaction mixture was cooled and H_2O (400 mL) was added to generate an orange precipitate. The solid was collected by filtration, washed with H_2O (1000 mL), and dried under vacuum to give the product as an orange solid (35.8 g, 92.1%). The product was used in the next step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.01 (s, 1H, NH), 8.18 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.58-7.53 (m, 4H), 7.09 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.6, 137.3, 135.0, 126.9, 122.0, 119.9.

HRMS calculated for $C_{12}H_{10}N_3O_4$ $[M+H]^+$ 260.0671. Found 260.0670.



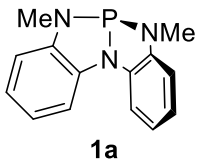
Bis(2-methylaminophenyl)amine **(S2)**: Synthesized according to a modified literature procedure.[6] Palladium on carbon (300 mg, 10% by weight) was added to a suspension of **S1** (3.00 g, 11.5 mmol, 1 equiv) in MeOH (50 mL). The reaction mixture was placed in a high-pressure reactor and charged with hydrogen (400 psi). The reaction was stirred for 12 h. Following venting of the reactor, the reaction mixture was quickly filtered over celite and diluted with MeOH (150 mL). Paraformaldehyde (3.44 g, 115 mmol, 10 equiv) and then sodium methoxide (25% in MeOH, 7.80 mL) were added and the reaction mixture was heated to reflux for 1 h. The red solution was cooled to ambient temperature and then placed in an ice bath. Sodium borohydride (4.34 g, 115 mmol, 10 equiv) was then added slowly in small portions. The reaction mixture was subsequently heated to reflux and stirred for 1

h to give a colorless solution. The mixture was cooled and aqueous sodium hydroxide (150 mL, 1 M) was added to precipitate a solid. The flask was stored in a freezer for several hours and then the solid was collected on a glass frit. The solid was dried under vacuum overnight at 40 ºC to afford the product as a light purple solid (1.90 g, 72.7%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (m, 2H), 6.68 (m, 6H), 4.87 (s 1H), 3.74 (q, *J* = 5.4 Hz, 2H), 2.87 (d, *J* = 5.4 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.9, 130.8, 123.8, 119.8, 118.0, 110.8, 30.9.

HRMS calculated for $C_{14}H_{18}N_3$ $[M+H]^+$ 228.1501. Found 228.1504.



1a

1a: Synthesized according to a modified literature procedure.[6] Phosphorus trichloride (.64 mL, 7.3 mmol, 1 equiv) was added to Et_2O (80 mL) in a flame-dried, nitrogen filled flask and cooled to -78 ºC. **S2** (1.7 g, 7.3 mmol, 1.2 equiv) was dissolved in THF (10 mL) and added dropwise via syringe. Triethylamine (7.1 mL, 51 mmol, 7.0 equiv) in Et_2O (15 mL) was added dropwise via syringe. The reaction was stirred at -78 ºC for 1 h and then warmed to room temperature and stirred for 4 h. The volatiles were removed, and the resulting solid residue was brought into a nitrogen filled glovebox. The solid was triturated with pentane and passed over a plug of celite. The filtrate was evaporated to give a slightly pink solid. This solid was dissolved in minimal Et_2O and cooled to -35 ºC to induce crystallization of the title product as colorless crystals (1.2 g, 62%).

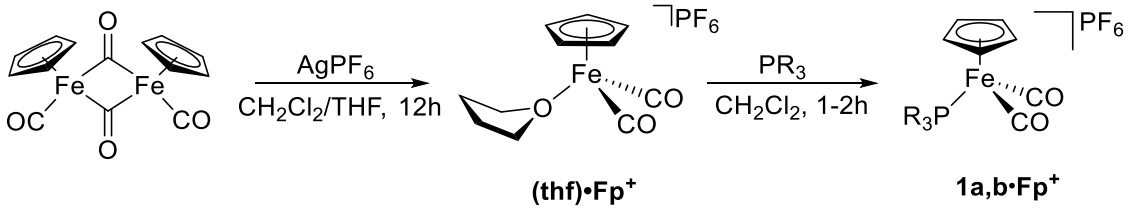
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.8, 1.1 Hz, 2H), 7.02 (td, *J* = 7.7, 1.2 Hz, 2H), 6.83 (td, *J* = 7.7, 1.2 Hz, 2H), 6.60 (d, *J* = 7.7 Hz, 2H), 3.08 (d, *J* = 8.4 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.3 (d, *J* = 7.1 Hz), 139.6, 124.4, 119.0, 117.1 (d, *J* = 6.0 Hz), 108.7, 29.9 (d, *J* = 30.7 Hz).

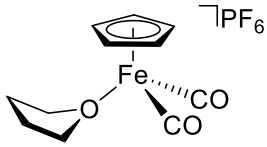
^{31}P{^{1}H} NMR (203 MHz, $CDCl_3$) δ 160.4.

HRMS calculated for $C_{14}H_{15}N_3P$ $[M+H]^+$ 256.1004. Found 256.1003.

Synthesis of iron cyclopentadienyl dicarbonyl complexes:



(thf)•Fp$^+$ **1a,b•Fp$^+$**



(thf)•Fp$^+$

Ironcyclopentadienyldicarbonyl(tetrahydrofuran)hexafluorophosphate (**(thf)•**Fp$^+$): Synthesized according to a modified procedure. [7] Cyclopentadienyliron dicarbonyl dimer (1.00 g, 2.83 mmol, 0.5 eq) was dissolved in a 2:1 mixture of CH_2Cl_2 (50 mL) and THF (25 mL). Silver hexafluorophosphate (1.43 g, 5.65 mmol, 1.0 eq) was added and the reaction was stirred overnight to produce a red solution with a grey precipitate. The reaction was filtered through a plug of celite and the filtrate was evaporated to give a light red solid, which was washed further with ether and dried under vacuum to give the product as a light red solid (1.02 g, 45.7%).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 5.38 (s, 5H), 3.45 (s, 4H), 1.83 (s, 4H).

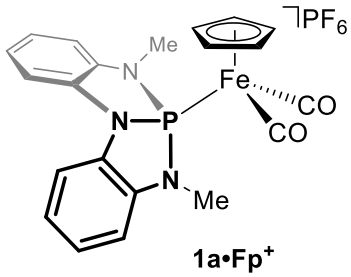
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 208.9, 85.8, 82.3, 26.6.

^{31}P{^{1}H} NMR (203 MHz, CD_2Cl_2) δ -144.0 (sept, J = 708 Hz, **P**F_6^-).

^{19}F NMR (471 MHz, CD_2Cl_2) δ -72.9 (d, *J* = 707 Hz, P**F$_6$**$^-$).

FTIR (ATR) ν(cm^{-1}): 2030, 2073.

HRMS calculated for $C_{11}H_{13}O_3Fe$ $[M]^+$ 249.0214. Found 249.0221.



1a•Fp$^+$

1a•Fp$^+$: **(thf)•**Fp$^+$ (126 mg, 0.327 mmol, 1 equiv) was dissolved in CH_2Cl_2 (3 mL). **1a** (100 mg, 0.392 mmol, 1.2 equiv) in CH_2Cl_2 (3 mL) was added and the reaction was stirred for 2 h. The solvent was removed, and the resulting solid was washed with ether and dried to give the product as a golden yellow solid (163 mg, 81.8%). Single crystals for X-ray diffraction were obtained by adding THF to the solid and passing the suspension through a syringe filter to give a saturated solution, to which pentane was then slowly added via vapor diffusion at room temperature overnight.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.03 (t, *J* = 7.7 Hz, 2H), 6.83 (d, *J* = 7.8 Hz, 2H), 5.37 (s, 5H), 3.16 (d, *J* = 10.7 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 207.8 (d, *J* = 32.5 Hz), 139.0, 138.9, 137.3, 126.0, 121.6, 109.2 (d, *J* = 6.1 Hz), 88.7, 28.9 (d, *J* = 9.0 Hz).

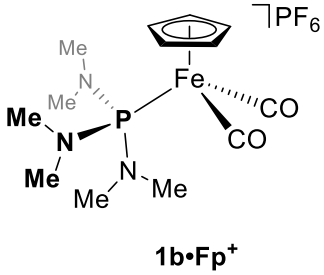
^{31}P{^{1}H} NMR (203 MHz, CD_3CN) δ 183.5, -144.0 (sept, J = 708 Hz, **P**F_6^-).

^{19}F NMR (471 MHz, CD_3CN) δ -72.9 (d, *J* = 707 Hz, P**F$_6^-$**).

^{57}Fe NMR (16 Hz, CD_3CN) δ 616 (d, *J* = 59.5 Hz).

FTIR (ATR) ν(cm^{-1}): 2017, 2061.

HRMS calculated for $C_{21}H_{19}N_3O_2PFe$ $[M]^+$ 432.0564. Found 432.0565.



1b•Fp$^+$

1b•Fp^+: Complex (thf)•Fp^+ (0.13 mg, 0.33 mmol, 1 equiv) was dissolved in CH_2Cl_2 (3 mL). **1b** (0.71 mL, 0.39 mmol, 1.2 equiv) in CH_2Cl_2 (3 mL) was added and the reaction was stirred for 1 h. The volatiles were removed, and the resulting solid was washed with ether and dried to give the product as a brown solid (0.13 g, 85%). Single crystals for X-ray diffraction were obtained by adding THF to the solid and passing the suspension through a syringe filter to give a saturated solution, to which pentane was then added slowly via vapor diffusion at room temperature overnight.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.41 (s, 5H), 2.64 (d, *J* = 9.8 Hz, 18H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 212.2 (d, *J* = 34.0 Hz), 87.9, 38.5 (d, *J* = 4.5 Hz).

^{31}P{^{1}H} NMR (203 MHz, CD_3CN) δ 141.4, -144.0 (sept, J = 708 Hz, **P**F_6^-).

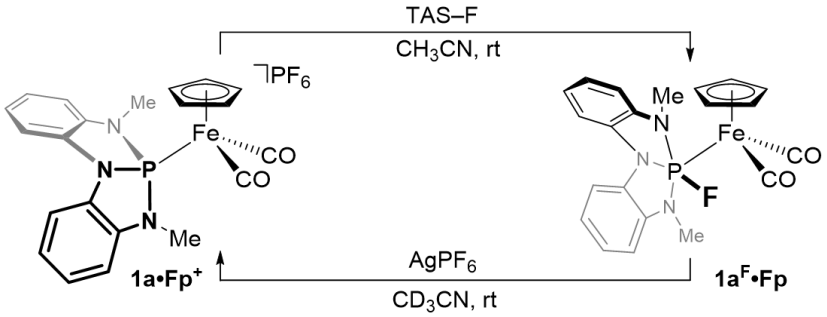
^{19}F NMR (471 MHz, CD_3CN) δ -72.9 (d, *J* = 707 Hz, P**F$_6^-$**).

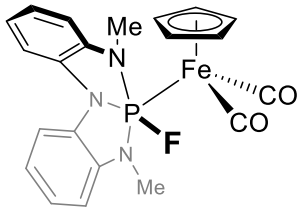
^{57}Fe NMR (16 Hz, CD_3CN) δ 688 (d, *J* = 50.4 Hz).

FTIR (ATR) ν(cm^{-1}): 2000, 2045.

HRMS calculated for $C_{13}H_{23}N_3O_2PFe$ $[M]^+$ 340.0877. Found 340.0881.

Fluorination of [Fp(PR$_3$)]PF$_6$ complexes:





1a^F•Fp: **1a**•Fp$^+$ (40 mg, 0.069 mmol, 1 equiv) was dissolved in MeCN (4.5 mL). Tris(dimethylamino)sulfonium trimethyldifluorosilicate (19 mg, 0.069 mmol, 1 equiv) in MeCN (1.5 mL) was added slowly, immediately causing a color change from yellow to orange. After stirring for 1 h, the volatiles were removed to give an orange residue. This residue was triturated with ether (15 mL), filtered through a syringe filter, and evaporated to give the product as an orange solid (20 mg, 44%). A single crystal of suitable quality for X-ray diffraction was obtained by slow evaporation of a saturated solution of **1a^F•**Fp in CH_2Cl_2 at –30 ºC over the course of 2 weeks.

^{1}H NMR (500 MHz, C_6D_6) δ 7.20 (d, *J* = 8.7 Hz, 2H), 6.87-6.94 (m, 4H), 6.54 (d, *J* = 7.5 Hz, 2H), 3.99 (s, 5H), 3.11 (d, *J* = 7.6 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 213.3 (dd, *J* = 44.4, 5.5 Hz), 137.7 (d, *J* = 20.3 Hz), 133.8 (d, *J* = 11.0 Hz), 120.8, 119.3, 110.2 (d, *J* = 4.0 Hz), 108.9 (dd, *J* = 7.9, 2.2 Hz), 83.8, 34.1 (dd, *J* = 16.6, 5.6 Hz).

^{31}P{^{1}H} NMR (203 MHz, C_6D_6) δ -3.0 (d, *J* = 971 Hz).

^{19}F NMR (471 MHz, C_6D_6) δ 27.4 (d, *J* = 971 Hz).

^{57}Fe NMR (16 Hz, C_6D_6) δ 1013 (d, *J* = 53.5 Hz).

FTIR (ATR) ν(cm^{-1}): 1952, 2007.

HRMS calculated for $C_{21}H_{19}N_3O_2PFe$ [M-F]$^+$ 432.0564. Found 432.0568.

Fluoride abstraction was performed by adding $AgPF_6$ (5.6 mg, .022 mmol, 1 equiv) to a solution of **1a^F•**Fp (10 mg, .022 mmol, 1 equiv) in CD_3CN (1 mL), causing immediate precipitation of a solid and changing the color from orange to yellow. This solution was passed through a syringe filter and immediately analyzed by NMR showing regeneration of **1a**•Fp$^+$.

III. Crystallographic Procedures and Data

Compound **1a**•Fp^+**:**

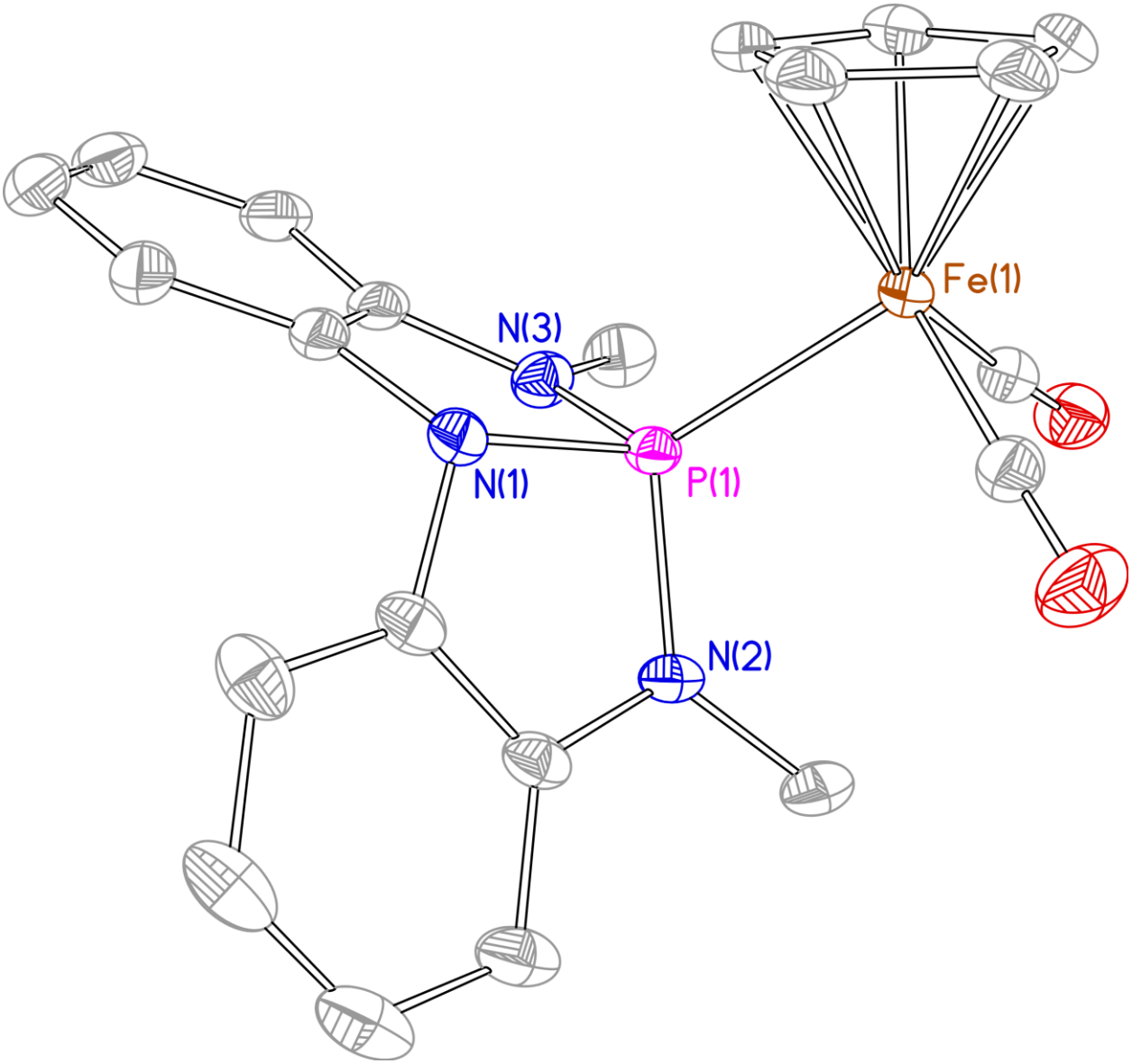


Table S1. Crystal data and structure refinement for **1a**•Fp+.

Identification code	fpnnnp_10	
Empirical formula	C25 H27 F6 Fe N3 O3 P2	
Formula weight	649.28	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.7202(6) Å	α= 90°.
	b = 18.7967(10) Å	β= 105.406(2)°.
	c = 13.6423(8) Å	γ = 90°.
Volume	2650.2(3) $Å^3$	
Z	4	
Density (calculated)	1.627 Mg/m^3	
Absorption coefficient	0.767 mm^{-1}	
F(000)	1328	
Crystal size	0.270 x 0.060 x 0.030 mm^3	
Theta range for data collection	2.167 to 32.618°.	
Index ranges	-16<=h<=16, -28<=k<=28, -20<=l<=20	
Reflections collected	269152	
Independent reflections	9682 [R(int) = 0.0542]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7464 and 0.6843	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9679 / 714 / 392	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0381, wR2 = 0.1046	
R indices (all data)	R1 = 0.0463, wR2 = 0.1102	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.010 and -0.552 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	6892(1)	3762(1)	6290(1)	18(1)
P(1)	7251(1)	3108(1)	5073(1)	17(1)
O(2)	4378(1)	4318(1)	5143(1)	32(1)
N(1)	8598(1)	2583(1)	5248(1)	20(1)
O(1)	8461(2)	4935(1)	5863(1)	37(1)
N(2)	7566(1)	3554(1)	4106(1)	21(1)
N(3)	6236(1)	2414(1)	4764(1)	22(1)
C(16)	6895(2)	1766(1)	5015(1)	23(1)
C(26)	8742(1)	3343(1)	3924(1)	20(1)
C(21)	9355(2)	2800(1)	4579(1)	22(1)
C(7)	5368(2)	4101(1)	5566(1)	24(1)
C(11)	8240(2)	1850(1)	5282(1)	22(1)
C(4)	6415(2)	3917(1)	7674(1)	27(1)
C(15)	6349(2)	1096(1)	5022(1)	30(1)
C(5)	7770(2)	3938(1)	7845(1)	29(1)
C(25)	9303(2)	3629(1)	3205(1)	28(1)
C(3)	5982(2)	3232(1)	7271(1)	25(1)
C(23)	11108(2)	2827(1)	3809(1)	34(1)
C(6)	7839(2)	4481(1)	6012(1)	25(1)
C(27)	6880(2)	4177(1)	3593(1)	27(1)
C(22)	10543(2)	2538(1)	4537(1)	28(1)
C(2)	7068(2)	2838(1)	7197(1)	26(1)
C(24)	10500(2)	3362(1)	3161(1)	34(1)
C(12)	9068(2)	1272(1)	5520(1)	31(1)
C(1)	8183(2)	3270(1)	7536(1)	28(1)
C(17)	4828(2)	2461(1)	4528(1)	28(1)
C(14)	7184(2)	512(1)	5244(1)	37(1)
C(13)	8511(2)	596(1)	5479(1)	37(1)
P(1S)	3416(1)	3812(1)	1702(1)	22(1)
F(6S)	3094(1)	3727(1)	490(1)	32(1)
F(5S)	4321(1)	4481(1)	1650(1)	31(1)

F(4S)	2190(1)	4329(1)	1564(1)	34(1)
F(3S)	4640(1)	3293(1)	1836(1)	34(1)
F(2S)	3722(1)	3896(1)	2909(1)	38(1)
F(1S)	2504(1)	3142(1)	1744(1)	39(1)
C(1S)	2305(2)	3695(1)	6305(2)	38(1)
C(4S)	2911(2)	4235(1)	7901(1)	34(1)
O(1S)	3316(2)	4068(2)	6992(3)	40(1)
C(2S)	1224(3)	3582(2)	6793(2)	34(1)
C(3S)	1461(9)	4168(6)	7592(8)	36(1)
O(1SB)	3355(12)	3783(10)	7305(11)	46(3)
C(2SB)	1098(12)	3938(11)	6505(11)	41(3)
C(3SB)	1400(40)	4150(30)	7700(30)	41(5)

Table S3. Bond lengths [Å] and angles [°] for 2a.

Fe(1)-C(7)	1.7879(17)
Fe(1)-C(6)	1.7893(16)
Fe(1)-C(1)	2.1003(16)
Fe(1)-C(4)	2.1038(15)
Fe(1)-C(3)	2.1054(16)
Fe(1)-C(5)	2.1052(16)
Fe(1)-C(2)	2.1130(15)
Fe(1)-P(1)	2.1809(4)
P(1)-N(2)	1.6713(12)
P(1)-N(3)	1.6790(13)
P(1)-N(1)	1.7131(13)
O(2)-C(7)	1.140(2)
N(1)-C(21)	1.4329(19)
N(1)-C(11)	1.4338(19)
O(1)-C(6)	1.135(2)
N(2)-C(26)	1.406(2)
N(2)-C(27)	1.458(2)
N(3)-C(16)	1.404(2)
N(3)-C(17)	1.460(2)
C(16)-C(15)	1.390(2)
C(16)-C(11)	1.399(2)
C(26)-C(25)	1.388(2)
C(26)-C(21)	1.400(2)
C(21)-C(22)	1.381(2)
C(11)-C(12)	1.386(2)
C(4)-C(5)	1.409(3)
C(4)-C(3)	1.429(2)
C(4)-H(4)	0.9500
C(15)-C(14)	1.398(3)
C(15)-H(15)	0.9500
C(5)-C(1)	1.431(3)
C(5)-H(5)	0.9500
C(25)-C(24)	1.395(3)
C(25)-H(25)	0.9500

C(3)-C(2)	1.406(2)
C(3)-H(3)	0.9500
C(23)-C(24)	1.383(3)
C(23)-C(22)	1.402(3)
C(23)-H(23)	0.9500
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(22)-H(22)	0.9500
C(2)-C(1)	1.418(3)
C(2)-H(2)	0.9500
C(24)-H(24)	0.9500
C(12)-C(13)	1.398(3)
C(12)-H(12)	0.9500
C(1)-H(1)	0.9500
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(14)-C(13)	1.381(3)
C(14)-H(14)	0.9500
C(13)-H(13)	0.9500
P(1S)-F(2S)	1.5982(12)
P(1S)-F(5S)	1.6007(11)
P(1S)-F(6S)	1.6053(11)
P(1S)-F(4S)	1.6053(11)
P(1S)-F(1S)	1.6057(12)
P(1S)-F(3S)	1.6066(11)
C(1S)-O(1S)	1.416(3)
C(1S)-C(2SB)	1.465(13)
C(1S)-C(2S)	1.497(3)
C(1S)-O(1SB)	1.530(12)
C(1S)-H(1S1)	0.9900
C(1S)-H(1S2)	0.9900
C(4S)-O(1SB)	1.347(12)
C(4S)-O(1S)	1.453(3)
C(4S)-C(3SB)	1.57(5)

C(4S)-C(3S)	1.504(10)
C(4S)-H(4S1)	0.9900
C(4S)-H(4S2)	0.9900
C(2S)-C(3S)	1.522(10)
C(2S)-H(2S1)	0.9900
C(2S)-H(2S2)	0.9900
C(3S)-H(3S1)	0.9900
C(3S)-H(3S2)	0.9900
C(2SB)-C(3SB)	1.62(4)
C(2SB)-H(2S3)	0.9900
C(2SB)-H(2S4)	0.9900
C(3SB)-H(3S3)	0.9900
C(3SB)-H(3S4)	0.9900

C(7)-Fe(1)-C(6)	95.77(7)
C(7)-Fe(1)-C(1)	155.99(7)
C(6)-Fe(1)-C(1)	102.44(7)
C(7)-Fe(1)-C(4)	92.44(7)
C(6)-Fe(1)-C(4)	111.88(7)
C(1)-Fe(1)-C(4)	66.38(7)
C(7)-Fe(1)-C(3)	90.57(7)
C(6)-Fe(1)-C(3)	151.30(7)
C(1)-Fe(1)-C(3)	66.04(7)
C(4)-Fe(1)-C(3)	39.70(6)
C(7)-Fe(1)-C(5)	126.83(7)
C(6)-Fe(1)-C(5)	88.18(7)
C(1)-Fe(1)-C(5)	39.80(7)
C(4)-Fe(1)-C(5)	39.12(7)
C(3)-Fe(1)-C(5)	65.97(7)
C(7)-Fe(1)-C(2)	122.89(7)
C(6)-Fe(1)-C(2)	141.06(7)
C(1)-Fe(1)-C(2)	39.33(7)
C(4)-Fe(1)-C(2)	66.00(6)
C(3)-Fe(1)-C(2)	38.95(6)
C(5)-Fe(1)-C(2)	65.98(7)
C(7)-Fe(1)-P(1)	95.75(5)

C(6)-Fe(1)-P(1)	92.28(5)
C(1)-Fe(1)-P(1)	98.99(5)
C(4)-Fe(1)-P(1)	153.56(5)
C(3)-Fe(1)-P(1)	114.95(5)
C(5)-Fe(1)-P(1)	137.17(5)
C(2)-Fe(1)-P(1)	88.58(4)
N(2)-P(1)-N(3)	116.39(7)
N(2)-P(1)-N(1)	93.42(6)
N(3)-P(1)-N(1)	93.04(7)
N(2)-P(1)-Fe(1)	115.53(5)
N(3)-P(1)-Fe(1)	113.34(5)
N(1)-P(1)-Fe(1)	122.13(4)
C(21)-N(1)-C(11)	119.82(12)
C(21)-N(1)-P(1)	110.24(10)
C(11)-N(1)-P(1)	109.59(10)
C(26)-N(2)-C(27)	120.20(12)
C(26)-N(2)-P(1)	112.14(10)
C(27)-N(2)-P(1)	126.85(11)
C(16)-N(3)-C(17)	121.98(13)
C(16)-N(3)-P(1)	111.23(11)
C(17)-N(3)-P(1)	124.84(11)
C(15)-C(16)-C(11)	120.47(15)
C(15)-C(16)-N(3)	127.03(16)
C(11)-C(16)-N(3)	112.50(13)
C(25)-C(26)-C(21)	121.00(15)
C(25)-C(26)-N(2)	126.42(15)
C(21)-C(26)-N(2)	112.57(12)
C(22)-C(21)-C(26)	121.03(15)
C(22)-C(21)-N(1)	127.54(15)
C(26)-C(21)-N(1)	111.43(13)
O(2)-C(7)-Fe(1)	176.91(14)
C(12)-C(11)-C(16)	121.63(15)
C(12)-C(11)-N(1)	126.89(16)
C(16)-C(11)-N(1)	111.46(13)
C(5)-C(4)-C(3)	107.71(15)
C(5)-C(4)-Fe(1)	70.49(9)

C(3)-C(4)-Fe(1)	70.21(9)
C(5)-C(4)-H(4)	126.1
C(3)-C(4)-H(4)	126.1
Fe(1)-C(4)-H(4)	124.8
C(16)-C(15)-C(14)	117.78(19)
C(16)-C(15)-H(15)	121.1
C(14)-C(15)-H(15)	121.1
C(4)-C(5)-C(1)	108.22(15)
C(4)-C(5)-Fe(1)	70.38(9)
C(1)-C(5)-Fe(1)	69.92(9)
C(4)-C(5)-H(5)	125.9
C(1)-C(5)-H(5)	125.9
Fe(1)-C(5)-H(5)	125.4
C(26)-C(25)-C(24)	117.91(17)
C(26)-C(25)-H(25)	121.0
C(24)-C(25)-H(25)	121.0
C(2)-C(3)-C(4)	108.17(15)
C(2)-C(3)-Fe(1)	70.82(9)
C(4)-C(3)-Fe(1)	70.09(9)
C(2)-C(3)-H(3)	125.9
C(4)-C(3)-H(3)	125.9
Fe(1)-C(3)-H(3)	124.8
C(24)-C(23)-C(22)	121.03(16)
C(24)-C(23)-H(23)	119.5
C(22)-C(23)-H(23)	119.5
O(1)-C(6)-Fe(1)	178.07(15)
N(2)-C(27)-H(27A)	109.5
N(2)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
N(2)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(21)-C(22)-C(23)	117.90(17)
C(21)-C(22)-H(22)	121.0
C(23)-C(22)-H(22)	121.0
C(3)-C(2)-C(1)	108.46(14)

C(3)-C(2)-Fe(1)	70.23(9)
C(1)-C(2)-Fe(1)	69.85(9)
C(3)-C(2)-H(2)	125.8
C(1)-C(2)-H(2)	125.8
Fe(1)-C(2)-H(2)	125.7
C(23)-C(24)-C(25)	121.13(16)
C(23)-C(24)-H(24)	119.4
C(25)-C(24)-H(24)	119.4
C(11)-C(12)-C(13)	117.54(19)
C(11)-C(12)-H(12)	121.2
C(13)-C(12)-H(12)	121.2
C(2)-C(1)-C(5)	107.42(15)
C(2)-C(1)-Fe(1)	70.82(9)
C(5)-C(1)-Fe(1)	70.29(9)
C(2)-C(1)-H(1)	126.3
C(5)-C(1)-H(1)	126.3
Fe(1)-C(1)-H(1)	124.2
N(3)-C(17)-H(17A)	109.5
N(3)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
N(3)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(13)-C(14)-C(15)	121.41(17)
C(13)-C(14)-H(14)	119.3
C(15)-C(14)-H(14)	119.3
C(14)-C(13)-C(12)	121.05(17)
C(14)-C(13)-H(13)	119.5
C(12)-C(13)-H(13)	119.5
F(2S)-P(1S)-F(5S)	90.45(7)
F(2S)-P(1S)-F(6S)	179.48(7)
F(5S)-P(1S)-F(6S)	89.92(6)
F(2S)-P(1S)-F(4S)	89.96(7)
F(5S)-P(1S)-F(4S)	90.40(6)
F(6S)-P(1S)-F(4S)	89.67(6)
F(2S)-P(1S)-F(1S)	90.03(7)

F(5S)-P(1S)-F(1S)	179.52(7)
F(6S)-P(1S)-F(1S)	89.60(6)
F(4S)-P(1S)-F(1S)	89.57(7)
F(2S)-P(1S)-F(3S)	90.25(7)
F(5S)-P(1S)-F(3S)	89.75(6)
F(6S)-P(1S)-F(3S)	90.12(6)
F(4S)-P(1S)-F(3S)	179.74(8)
F(1S)-P(1S)-F(3S)	90.28(7)
O(1S)-C(1S)-C(2S)	108.8(2)
C(2SB)-C(1S)-O(1SB)	106.1(7)
O(1S)-C(1S)-H(1S1)	109.9
C(2S)-C(1S)-H(1S1)	109.9
O(1S)-C(1S)-H(1S2)	109.9
C(2S)-C(1S)-H(1S2)	109.9
H(1S1)-C(1S)-H(1S2)	108.3
O(1SB)-C(4S)-C(3SB)	109.8(17)
O(1S)-C(4S)-C(3S)	105.2(4)
O(1S)-C(4S)-H(4S1)	110.7
C(3S)-C(4S)-H(4S1)	110.7
O(1S)-C(4S)-H(4S2)	110.7
C(3S)-C(4S)-H(4S2)	110.7
H(4S1)-C(4S)-H(4S2)	108.8
C(1S)-O(1S)-C(4S)	108.8(2)
C(1S)-C(2S)-C(3S)	102.4(4)
C(1S)-C(2S)-H(2S1)	111.3
C(3S)-C(2S)-H(2S1)	111.3
C(1S)-C(2S)-H(2S2)	111.3
C(3S)-C(2S)-H(2S2)	111.3
H(2S1)-C(2S)-H(2S2)	109.2
C(4S)-C(3S)-C(2S)	103.1(5)
C(4S)-C(3S)-H(3S1)	111.2
C(2S)-C(3S)-H(3S1)	111.2
C(4S)-C(3S)-H(3S2)	111.2
C(2S)-C(3S)-H(3S2)	111.2
H(3S1)-C(3S)-H(3S2)	109.1
C(4S)-O(1SB)-C(1S)	108.2(8)

C(1S)-C(2SB)-C(3SB)	108.1(19)
C(1S)-C(2SB)-H(2S3)	110.1
C(3SB)-C(2SB)-H(2S3)	110.1
C(1S)-C(2SB)-H(2S4)	110.1
C(3SB)-C(2SB)-H(2S4)	110.1
H(2S3)-C(2SB)-H(2S4)	108.4
C(4S)-C(3SB)-C(2SB)	97(2)
C(4S)-C(3SB)-H(3S3)	112.3
C(2SB)-C(3SB)-H(3S3)	112.3
C(4S)-C(3SB)-H(3S4)	112.3
C(2SB)-C(3SB)-H(3S4)	112.3
H(3S3)-C(3SB)-H(3S4)	109.9

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 2a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	24(1)	17(1)	13(1)	1(1)	6(1)	2(1)
P(1)	21(1)	17(1)	13(1)	1(1)	5(1)	-1(1)
O(2)	30(1)	38(1)	29(1)	7(1)	8(1)	9(1)
N(1)	23(1)	20(1)	15(1)	-1(1)	5(1)	2(1)
O(1)	45(1)	28(1)	36(1)	3(1)	7(1)	-11(1)
N(2)	24(1)	22(1)	16(1)	4(1)	8(1)	0(1)
N(3)	24(1)	20(1)	20(1)	0(1)	5(1)	-4(1)
C(16)	36(1)	19(1)	14(1)	0(1)	7(1)	-2(1)
C(26)	23(1)	24(1)	15(1)	-3(1)	6(1)	-5(1)
C(21)	24(1)	26(1)	14(1)	-4(1)	5(1)	-2(1)
C(7)	30(1)	24(1)	21(1)	2(1)	10(1)	3(1)
C(11)	34(1)	19(1)	13(1)	1(1)	7(1)	2(1)
C(4)	40(1)	27(1)	17(1)	-1(1)	12(1)	5(1)
C(15)	50(1)	22(1)	18(1)	0(1)	12(1)	-7(1)
C(5)	40(1)	31(1)	14(1)	-1(1)	4(1)	-3(1)
C(25)	33(1)	32(1)	19(1)	-2(1)	11(1)	-10(1)
C(3)	34(1)	28(1)	17(1)	3(1)	10(1)	-1(1)
C(23)	23(1)	51(1)	29(1)	-11(1)	11(1)	-4(1)
C(6)	32(1)	22(1)	20(1)	0(1)	5(1)	-1(1)
C(27)	34(1)	27(1)	21(1)	9(1)	8(1)	3(1)
C(22)	23(1)	38(1)	23(1)	-8(1)	4(1)	2(1)
C(2)	42(1)	22(1)	15(1)	4(1)	10(1)	5(1)
C(24)	32(1)	47(1)	26(1)	-8(1)	15(1)	-12(1)
C(12)	47(1)	27(1)	18(1)	3(1)	9(1)	11(1)
C(1)	31(1)	36(1)	17(1)	7(1)	6(1)	7(1)
C(17)	25(1)	30(1)	30(1)	1(1)	6(1)	-7(1)
C(14)	74(1)	18(1)	21(1)	1(1)	16(1)	-3(1)
C(13)	68(1)	22(1)	23(1)	5(1)	15(1)	12(1)
P(1S)	26(1)	21(1)	19(1)	-1(1)	7(1)	0(1)
F(6S)	38(1)	38(1)	20(1)	-4(1)	8(1)	-2(1)
F(5S)	31(1)	24(1)	35(1)	1(1)	6(1)	-4(1)

F(4S)	29(1)	35(1)	38(1)	-4(1)	10(1)	7(1)
F(3S)	36(1)	28(1)	39(1)	2(1)	10(1)	10(1)
F(2S)	47(1)	48(1)	19(1)	-2(1)	8(1)	3(1)
F(1S)	46(1)	31(1)	43(1)	-1(1)	19(1)	-12(1)
C(1S)	38(1)	39(1)	39(1)	-13(1)	14(1)	-9(1)
C(4S)	40(1)	33(1)	26(1)	-1(1)	2(1)	0(1)
O(1S)	31(1)	47(2)	45(1)	-23(1)	15(1)	-8(1)
C(2S)	38(1)	33(1)	35(1)	-12(1)	17(1)	-10(1)
C(3S)	38(2)	39(2)	35(3)	-12(2)	18(2)	-4(2)
O(1SB)	41(4)	58(7)	37(5)	-17(5)	5(4)	3(5)
C(2SB)	35(4)	55(9)	36(5)	-17(5)	12(4)	-18(5)
C(3SB)	45(6)	49(12)	28(7)	-22(7)	9(7)	-11(7)

Compound **1b•**Fp^{+}**:**

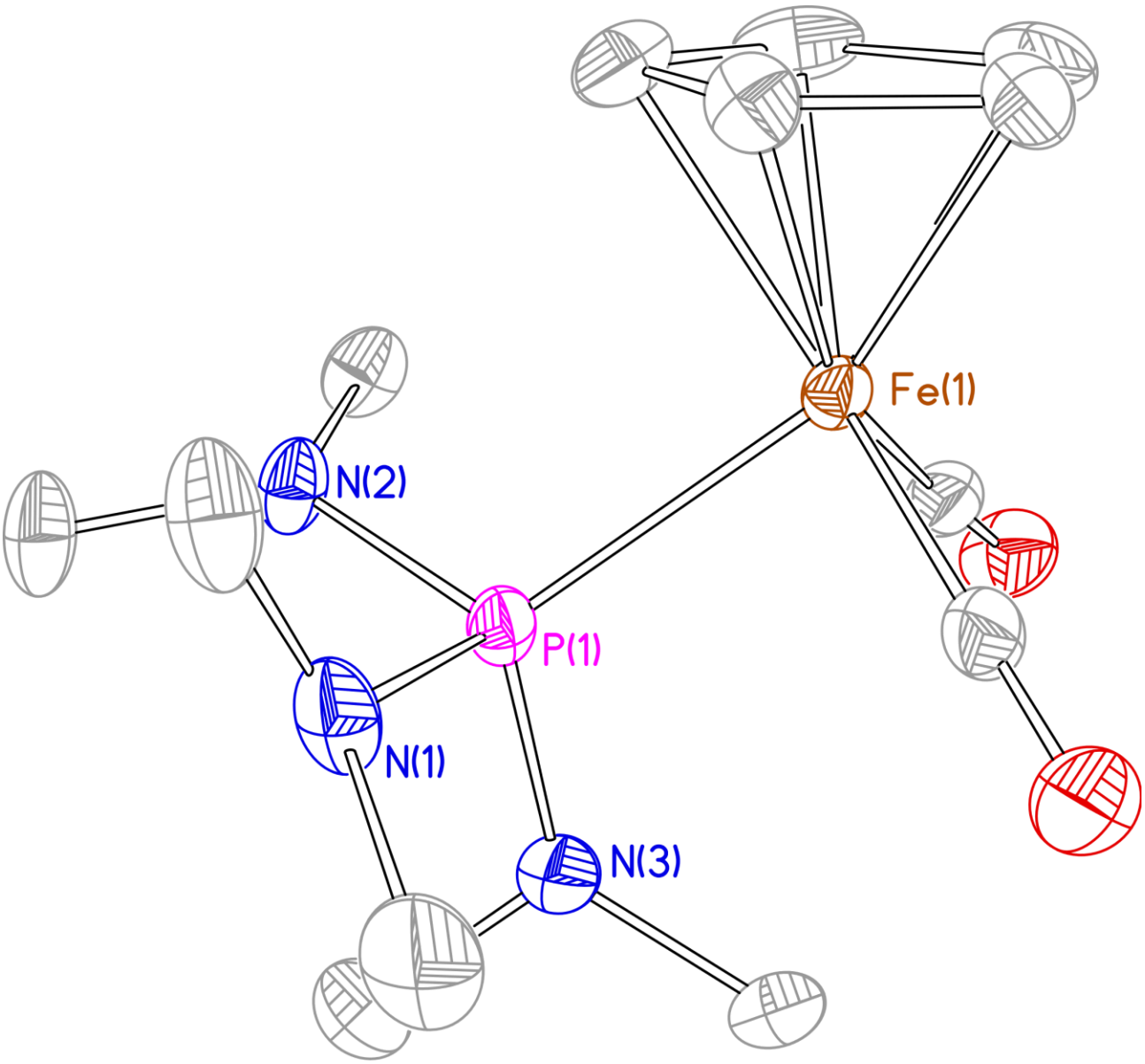


Table S5. Crystal data and structure refinement for **1b**•Fp^+.

Identification code	fppnme2_7	
Empirical formula	C13 H23 F6 Fe N3 O2 P2	
Formula weight	485.13	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.0704(6) Å	α= 90°.
	b = 19.2166(9) Å	β= 90.417(2)°.
	c = 15.4820(7) Å	γ = 90°.
Volume	3888.5(3) $Å^3$	
Z	8	
Density (calculated)	1.657 Mg/m^3	
Absorption coefficient	1.009 mm^{-1}	
F(000)	1984	
Crystal size	0.230 x 0.130 x 0.030 mm^3	
Theta range for data collection	2.292 to 33.204°.	
Index ranges	-20<=h<=20, -29<=k<=29, -23<=l<=23	
Reflections collected	429575	
Independent reflections	14863 [R(int) = 0.0462]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	.7465 and .6786	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14863 / 0 / 499	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1162	
R indices (all data)	R1 = 0.0519, wR2 = 0.1253	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.971 and -1.354 e.$Å^{-3}$	

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	2667(1)	5656(1)	4332(1)	16(1)
Fe(2)	2408(1)	4170(1)	-94(1)	17(1)
P(2)	3006(1)	3453(1)	-1103(1)	17(1)
P(3)	4984(1)	5828(1)	7382(1)	22(1)
P(1)	2104(1)	6754(1)	4419(1)	18(1)
P(4)	43(1)	4245(1)	2341(1)	22(1)
F(31)	6199(1)	5840(1)	7288(1)	34(1)
F(32)	3762(1)	5804(1)	7479(1)	40(1)
F(33)	5082(1)	6139(1)	8344(1)	45(1)
F(41)	-94(1)	4679(1)	1464(1)	37(1)
F(34)	4899(1)	6602(1)	7014(1)	51(1)
F(42)	-1156(1)	4088(1)	2337(1)	45(1)
F(43)	1241(1)	4403(1)	2344(1)	45(1)
F(44)	178(1)	3827(1)	3231(1)	48(1)
F(45)	-159(1)	4938(1)	2884(1)	46(1)
F(35)	5060(1)	5067(1)	7786(1)	44(1)
F(36)	4874(1)	5522(1)	6432(1)	53(1)
O(11)	4800(1)	6073(1)	4530(1)	32(1)
O(12)	2569(2)	5760(1)	2455(1)	41(1)
O(21)	271(1)	3910(1)	-501(1)	39(1)
F(46)	254(2)	3561(1)	1793(1)	60(1)
N(11)	970(1)	6907(1)	3946(1)	28(1)
N(12)	1867(1)	7002(1)	5424(1)	22(1)
N(13)	2912(2)	7336(1)	4002(1)	29(1)
N(21)	4203(1)	3168(1)	-971(1)	26(1)
N(22)	3061(1)	3808(1)	-2075(1)	25(1)
O(22)	2675(2)	3105(1)	1231(1)	48(1)
N(23)	2293(1)	2731(1)	-1193(1)	30(1)
C(21)	3313(1)	4992(1)	-570(1)	22(1)
C(11)	2199(2)	4609(1)	4230(1)	26(1)
C(122)	2635(1)	6868(1)	6095(1)	26(1)

C(12)	1374(1)	5023(1)	4544(1)	24(1)
C(22)	2286(2)	5218(1)	-470(1)	26(1)
C(15)	3017(2)	4663(1)	4821(2)	31(1)
C(23)	2037(2)	5149(1)	430(1)	28(1)
C(25)	3683(1)	4774(1)	248(1)	24(1)
C(121)	1126(2)	7531(1)	5679(1)	32(1)
C(111)	61(2)	6540(1)	4232(2)	36(1)
C(13)	1690(2)	5326(1)	5337(1)	27(1)
C(14)	2703(2)	5113(1)	5510(1)	32(1)
C(131)	3636(2)	7228(1)	3299(1)	31(1)
C(16)	2606(2)	5719(1)	3186(1)	26(1)
C(26)	1114(1)	3998(1)	-345(1)	26(1)
C(221)	2217(2)	4241(1)	-2389(1)	35(1)
C(132)	2707(2)	8079(1)	4140(2)	45(1)
C(24)	2899(2)	4879(1)	864(1)	27(1)
C(17)	3961(1)	5922(1)	4444(1)	23(1)
C(231)	1708(2)	2388(1)	-520(2)	32(1)
C(112)	941(2)	7058(2)	3013(1)	46(1)
C(27)	2562(2)	3511(1)	705(1)	31(1)
C(211)	4393(2)	2588(1)	-375(2)	41(1)
C(212)	5068(2)	3640(1)	-1012(2)	34(1)
C(222)	3765(2)	3610(2)	-2756(1)	40(1)
C(232)	2518(3)	2256(2)	-1905(2)	66(1)

Table S7. Bond lengths [Å] and angles [°] for 2b.

Fe(1)-C(17)	1.7739(19)
Fe(1)-C(16)	1.7792(18)
Fe(1)-C(14)	2.1022(18)
Fe(1)-C(15)	2.1026(19)
Fe(1)-C(11)	2.1086(19)
Fe(1)-C(12)	2.1108(18)
Fe(1)-C(13)	2.1177(18)
Fe(1)-P(1)	2.2381(5)
Fe(2)-C(26)	1.7640(19)
Fe(2)-C(27)	1.781(2)
Fe(2)-C(25)	2.0957(18)
Fe(2)-C(22)	2.1015(18)
Fe(2)-C(23)	2.1060(19)
Fe(2)-C(21)	2.1089(17)
Fe(2)-C(24)	2.1092(19)
Fe(2)-P(2)	2.2305(5)
P(2)-N(22)	1.6538(16)
P(2)-N(21)	1.6676(16)
P(2)-N(23)	1.6766(17)
P(3)-F(36)	1.5897(16)
P(3)-F(35)	1.5946(15)
P(3)-F(31)	1.5961(13)
P(3)-F(34)	1.5963(16)
P(3)-F(32)	1.6064(13)
P(3)-F(33)	1.6078(15)
P(1)-N(12)	1.6592(15)
P(1)-N(13)	1.6715(18)
P(1)-N(11)	1.6742(16)
P(4)-F(46)	1.5903(17)
P(4)-F(43)	1.5954(14)
P(4)-F(42)	1.5957(14)
P(4)-F(45)	1.5970(15)
P(4)-F(41)	1.6014(14)
P(4)-F(44)	1.6035(14)

O(11)-C(17)	1.141(2)
O(12)-C(16)	1.135(2)
O(21)-C(26)	1.139(2)
N(11)-C(111)	1.455(3)
N(11)-C(112)	1.473(3)
N(12)-C(121)	1.460(2)
N(12)-C(122)	1.462(2)
N(13)-C(131)	1.462(3)
N(13)-C(132)	1.470(3)
N(21)-C(212)	1.451(3)
N(21)-C(211)	1.467(3)
N(22)-C(222)	1.456(3)
N(22)-C(221)	1.461(3)
O(22)-C(27)	1.137(3)
N(23)-C(231)	1.455(3)
N(23)-C(232)	1.463(3)
C(21)-C(25)	1.415(3)
C(21)-C(22)	1.420(3)
C(21)-H(21)	0.9500
C(11)-C(15)	1.406(3)
C(11)-C(12)	1.428(3)
C(11)-H(11)	0.9500
C(122)-H(12A)	0.9800
C(122)-H(12B)	0.9800
C(122)-H(12C)	0.9800
C(12)-C(13)	1.417(3)
C(12)-H(12)	0.9500
C(22)-C(23)	1.439(3)
C(22)-H(22)	0.9500
C(15)-C(14)	1.436(3)
C(15)-H(15)	0.9500
C(23)-C(24)	1.407(3)
C(23)-H(23)	0.9500
C(25)-C(24)	1.420(3)
C(25)-H(25)	0.9500
C(121)-H(12D)	0.9800

C(121)-H(12E)	0.9800
C(121)-H(12F)	0.9800
C(111)-H(11A)	0.9800
C(111)-H(11B)	0.9800
C(111)-H(11C)	0.9800
C(13)-C(14)	1.410(3)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(131)-H(13A)	0.9800
C(131)-H(13B)	0.9800
C(131)-H(13C)	0.9800
C(221)-H(22A)	0.9800
C(221)-H(22B)	0.9800
C(221)-H(22C)	0.9800
C(132)-H(13D)	0.9800
C(132)-H(13E)	0.9800
C(132)-H(13F)	0.9800
C(24)-H(24)	0.9500
C(231)-H(23A)	0.9800
C(231)-H(23B)	0.9800
C(231)-H(23C)	0.9800
C(112)-H(11D)	0.9800
C(112)-H(11E)	0.9800
C(112)-H(11F)	0.9800
C(211)-H(21A)	0.9800
C(211)-H(21B)	0.9800
C(211)-H(21C)	0.9800
C(212)-H(21D)	0.9800
C(212)-H(21E)	0.9800
C(212)-H(21F)	0.9800
C(222)-H(22D)	0.9800
C(222)-H(22E)	0.9800
C(222)-H(22F)	0.9800
C(232)-H(23D)	0.9800
C(232)-H(23E)	0.9800
C(232)-H(23F)	0.9800

C(17)-Fe(1)-C(16)	96.58(9)
C(17)-Fe(1)-C(14)	92.43(8)
C(16)-Fe(1)-C(14)	154.10(9)
C(17)-Fe(1)-C(15)	91.20(8)
C(16)-Fe(1)-C(15)	115.40(9)
C(14)-Fe(1)-C(15)	39.94(10)
C(17)-Fe(1)-C(11)	123.90(8)
C(16)-Fe(1)-C(11)	88.83(8)
C(14)-Fe(1)-C(11)	66.14(8)
C(15)-Fe(1)-C(11)	39.00(8)
C(17)-Fe(1)-C(12)	156.16(8)
C(16)-Fe(1)-C(12)	99.44(9)
C(14)-Fe(1)-C(12)	65.88(8)
C(15)-Fe(1)-C(12)	65.97(8)
C(11)-Fe(1)-C(12)	39.57(7)
C(17)-Fe(1)-C(13)	126.42(8)
C(16)-Fe(1)-C(13)	136.87(9)
C(14)-Fe(1)-C(13)	39.03(8)
C(15)-Fe(1)-C(13)	66.05(9)
C(11)-Fe(1)-C(13)	65.96(8)
C(12)-Fe(1)-C(13)	39.17(7)
C(17)-Fe(1)-P(1)	92.14(6)
C(16)-Fe(1)-P(1)	89.05(6)
C(14)-Fe(1)-P(1)	114.89(7)
C(15)-Fe(1)-P(1)	154.75(7)
C(11)-Fe(1)-P(1)	143.90(6)
C(12)-Fe(1)-P(1)	105.62(5)
C(13)-Fe(1)-P(1)	92.14(6)
C(26)-Fe(2)-C(27)	97.06(10)
C(26)-Fe(2)-C(25)	156.82(8)
C(27)-Fe(2)-C(25)	97.66(9)
C(26)-Fe(2)-C(22)	92.77(8)
C(27)-Fe(2)-C(22)	151.89(9)
C(25)-Fe(2)-C(22)	66.29(7)
C(26)-Fe(2)-C(23)	91.70(8)

C(27)-Fe(2)-C(23)	113.17(9)
C(25)-Fe(2)-C(23)	66.03(8)
C(22)-Fe(2)-C(23)	40.00(8)
C(26)-Fe(2)-C(21)	127.06(8)
C(27)-Fe(2)-C(21)	135.60(9)
C(25)-Fe(2)-C(21)	39.32(7)
C(22)-Fe(2)-C(21)	39.41(8)
C(23)-Fe(2)-C(21)	66.25(8)
C(26)-Fe(2)-C(24)	124.24(9)
C(27)-Fe(2)-C(24)	86.51(9)
C(25)-Fe(2)-C(24)	39.48(7)
C(22)-Fe(2)-C(24)	66.32(8)
C(23)-Fe(2)-C(24)	39.00(8)
C(21)-Fe(2)-C(24)	66.04(7)
C(26)-Fe(2)-P(2)	94.00(7)
C(27)-Fe(2)-P(2)	90.47(7)
C(25)-Fe(2)-P(2)	103.68(5)
C(22)-Fe(2)-P(2)	115.11(6)
C(23)-Fe(2)-P(2)	154.80(6)
C(21)-Fe(2)-P(2)	91.00(5)
C(24)-Fe(2)-P(2)	141.73(6)
N(22)-P(2)-N(21)	101.59(8)
N(22)-P(2)-N(23)	107.09(9)
N(21)-P(2)-N(23)	105.03(9)
N(22)-P(2)-Fe(2)	113.54(6)
N(21)-P(2)-Fe(2)	116.74(6)
N(23)-P(2)-Fe(2)	111.83(6)
F(36)-P(3)-F(35)	91.64(11)
F(36)-P(3)-F(31)	90.25(8)
F(35)-P(3)-F(31)	89.41(8)
F(36)-P(3)-F(34)	90.49(11)
F(35)-P(3)-F(34)	177.77(11)
F(31)-P(3)-F(34)	91.24(8)
F(36)-P(3)-F(32)	89.50(9)
F(35)-P(3)-F(32)	89.70(8)
F(31)-P(3)-F(32)	179.07(9)

F(34)-P(3)-F(32)	89.65(9)
F(36)-P(3)-F(33)	179.33(9)
F(35)-P(3)-F(33)	88.41(9)
F(31)-P(3)-F(33)	90.42(8)
F(34)-P(3)-F(33)	89.45(10)
F(32)-P(3)-F(33)	89.83(8)
N(12)-P(1)-N(13)	107.03(9)
N(12)-P(1)-N(11)	100.92(8)
N(13)-P(1)-N(11)	105.85(10)
N(12)-P(1)-Fe(1)	113.01(6)
N(13)-P(1)-Fe(1)	113.44(6)
N(11)-P(1)-Fe(1)	115.48(7)
F(46)-P(4)-F(43)	89.12(11)
F(46)-P(4)-F(42)	90.93(11)
F(43)-P(4)-F(42)	179.90(11)
F(46)-P(4)-F(45)	179.20(12)
F(43)-P(4)-F(45)	90.30(10)
F(42)-P(4)-F(45)	89.66(10)
F(46)-P(4)-F(41)	89.80(10)
F(43)-P(4)-F(41)	90.39(8)
F(42)-P(4)-F(41)	89.52(8)
F(45)-P(4)-F(41)	89.66(9)
F(46)-P(4)-F(44)	91.50(11)
F(43)-P(4)-F(44)	89.49(8)
F(42)-P(4)-F(44)	90.60(8)
F(45)-P(4)-F(44)	89.03(10)
F(41)-P(4)-F(44)	178.69(10)
C(111)-N(11)-C(112)	112.30(19)
C(111)-N(11)-P(1)	120.22(14)
C(112)-N(11)-P(1)	118.70(16)
C(121)-N(12)-C(122)	112.57(14)
C(121)-N(12)-P(1)	125.59(13)
C(122)-N(12)-P(1)	118.93(12)
C(131)-N(13)-C(132)	111.40(18)
C(131)-N(13)-P(1)	127.42(14)
C(132)-N(13)-P(1)	118.55(16)

C(212)-N(21)-C(211)	111.91(18)
C(212)-N(21)-P(2)	121.36(14)
C(211)-N(21)-P(2)	118.75(14)
C(222)-N(22)-C(221)	112.77(17)
C(222)-N(22)-P(2)	125.64(16)
C(221)-N(22)-P(2)	120.01(13)
C(231)-N(23)-C(232)	111.48(18)
C(231)-N(23)-P(2)	127.61(14)
C(232)-N(23)-P(2)	117.65(15)
C(25)-C(21)-C(22)	108.12(16)
C(25)-C(21)-Fe(2)	69.84(10)
C(22)-C(21)-Fe(2)	70.01(10)
C(25)-C(21)-H(21)	125.9
C(22)-C(21)-H(21)	125.9
Fe(2)-C(21)-H(21)	125.8
C(15)-C(11)-C(12)	108.10(18)
C(15)-C(11)-Fe(1)	70.27(11)
C(12)-C(11)-Fe(1)	70.30(11)
C(15)-C(11)-H(11)	126.0
C(12)-C(11)-H(11)	126.0
Fe(1)-C(11)-H(11)	125.1
N(12)-C(122)-H(12A)	109.5
N(12)-C(122)-H(12B)	109.5
H(12A)-C(122)-H(12B)	109.5
N(12)-C(122)-H(12C)	109.5
H(12A)-C(122)-H(12C)	109.5
H(12B)-C(122)-H(12C)	109.5
C(13)-C(12)-C(11)	107.88(16)
C(13)-C(12)-Fe(1)	70.68(10)
C(11)-C(12)-Fe(1)	70.14(11)
C(13)-C(12)-H(12)	126.1
C(11)-C(12)-H(12)	126.1
Fe(1)-C(12)-H(12)	124.7
C(21)-C(22)-C(23)	107.35(16)
C(21)-C(22)-Fe(2)	70.57(10)
C(23)-C(22)-Fe(2)	70.17(11)

C(21)-C(22)-H(22)	126.3
C(23)-C(22)-H(22)	126.3
Fe(2)-C(22)-H(22)	124.6
C(11)-C(15)-C(14)	107.91(17)
C(11)-C(15)-Fe(1)	70.73(11)
C(14)-C(15)-Fe(1)	70.02(11)
C(11)-C(15)-H(15)	126.0
C(14)-C(15)-H(15)	126.0
Fe(1)-C(15)-H(15)	124.8
C(24)-C(23)-C(22)	108.05(17)
C(24)-C(23)-Fe(2)	70.63(11)
C(22)-C(23)-Fe(2)	69.83(10)
C(24)-C(23)-H(23)	126.0
C(22)-C(23)-H(23)	126.0
Fe(2)-C(23)-H(23)	125.2
C(21)-C(25)-C(24)	108.33(17)
C(21)-C(25)-Fe(2)	70.84(10)
C(24)-C(25)-Fe(2)	70.77(11)
C(21)-C(25)-H(25)	125.8
C(24)-C(25)-H(25)	125.8
Fe(2)-C(25)-H(25)	124.2
N(12)-C(121)-H(12D)	109.5
N(12)-C(121)-H(12E)	109.5
H(12D)-C(121)-H(12E)	109.5
N(12)-C(121)-H(12F)	109.5
H(12D)-C(121)-H(12F)	109.5
H(12E)-C(121)-H(12F)	109.5
N(11)-C(111)-H(11A)	109.5
N(11)-C(111)-H(11B)	109.5
H(11A)-C(111)-H(11B)	109.5
N(11)-C(111)-H(11C)	109.5
H(11A)-C(111)-H(11C)	109.5
H(11B)-C(111)-H(11C)	109.5
C(14)-C(13)-C(12)	108.25(18)
C(14)-C(13)-Fe(1)	69.89(11)
C(12)-C(13)-Fe(1)	70.15(10)

C(14)-C(13)-H(13)	125.9
C(12)-C(13)-H(13)	125.9
Fe(1)-C(13)-H(13)	125.7
C(13)-C(14)-C(15)	107.86(17)
C(13)-C(14)-Fe(1)	71.08(11)
C(15)-C(14)-Fe(1)	70.05(11)
C(13)-C(14)-H(14)	126.1
C(15)-C(14)-H(14)	126.1
Fe(1)-C(14)-H(14)	124.4
N(13)-C(131)-H(13A)	109.5
N(13)-C(131)-H(13B)	109.5
H(13A)-C(131)-H(13B)	109.5
N(13)-C(131)-H(13C)	109.5
H(13A)-C(131)-H(13C)	109.5
H(13B)-C(131)-H(13C)	109.5
O(12)-C(16)-Fe(1)	179.9(3)
O(21)-C(26)-Fe(2)	177.67(18)
N(22)-C(221)-H(22A)	109.5
N(22)-C(221)-H(22B)	109.5
H(22A)-C(221)-H(22B)	109.5
N(22)-C(221)-H(22C)	109.5
H(22A)-C(221)-H(22C)	109.5
H(22B)-C(221)-H(22C)	109.5
N(13)-C(132)-H(13D)	109.5
N(13)-C(132)-H(13E)	109.5
H(13D)-C(132)-H(13E)	109.5
N(13)-C(132)-H(13F)	109.5
H(13D)-C(132)-H(13F)	109.5
H(13E)-C(132)-H(13F)	109.5
C(23)-C(24)-C(25)	108.13(17)
C(23)-C(24)-Fe(2)	70.38(11)
C(25)-C(24)-Fe(2)	69.75(10)
C(23)-C(24)-H(24)	125.9
C(25)-C(24)-H(24)	125.9
Fe(2)-C(24)-H(24)	125.5
O(11)-C(17)-Fe(1)	177.85(17)

N(23)-C(231)-H(23A)	109.5
N(23)-C(231)-H(23B)	109.5
H(23A)-C(231)-H(23B)	109.5
N(23)-C(231)-H(23C)	109.5
H(23A)-C(231)-H(23C)	109.5
H(23B)-C(231)-H(23C)	109.5
N(11)-C(112)-H(11D)	109.5
N(11)-C(112)-H(11E)	109.5
H(11D)-C(112)-H(11E)	109.5
N(11)-C(112)-H(11F)	109.5
H(11D)-C(112)-H(11F)	109.5
H(11E)-C(112)-H(11F)	109.5
O(22)-C(27)-Fe(2)	177.9(2)
N(21)-C(211)-H(21A)	109.5
N(21)-C(211)-H(21B)	109.5
H(21A)-C(211)-H(21B)	109.5
N(21)-C(211)-H(21C)	109.5
H(21A)-C(211)-H(21C)	109.5
H(21B)-C(211)-H(21C)	109.5
N(21)-C(212)-H(21D)	109.5
N(21)-C(212)-H(21E)	109.5
H(21D)-C(212)-H(21E)	109.5
N(21)-C(212)-H(21F)	109.5
H(21D)-C(212)-H(21F)	109.5
H(21E)-C(212)-H(21F)	109.5
N(22)-C(222)-H(22D)	109.5
N(22)-C(222)-H(22E)	109.5
H(22D)-C(222)-H(22E)	109.5
N(22)-C(222)-H(22F)	109.5
H(22D)-C(222)-H(22F)	109.5
H(22E)-C(222)-H(22F)	109.5
N(23)-C(232)-H(23D)	109.5
N(23)-C(232)-H(23E)	109.5
H(23D)-C(232)-H(23E)	109.5
N(23)-C(232)-H(23F)	109.5
H(23D)-C(232)-H(23F)	109.5

H(23E)-C(232)-H(23F) 109.5

Symmetry transformations used to generate equivalent atoms:

Table S8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 2b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	16(1)	20(1)	13(1)	1(1)	0(1)	3(1)
Fe(2)	16(1)	16(1)	18(1)	1(1)	4(1)	0(1)
P(2)	18(1)	16(1)	17(1)	-1(1)	1(1)	0(1)
P(3)	16(1)	29(1)	20(1)	7(1)	-1(1)	-1(1)
P(1)	20(1)	22(1)	13(1)	-1(1)	-1(1)	6(1)
P(4)	17(1)	25(1)	24(1)	3(1)	-2(1)	0(1)
F(31)	17(1)	45(1)	40(1)	10(1)	2(1)	-1(1)
F(32)	17(1)	68(1)	35(1)	11(1)	1(1)	-1(1)
F(33)	39(1)	64(1)	30(1)	-10(1)	-6(1)	9(1)
F(41)	31(1)	54(1)	26(1)	13(1)	-4(1)	-2(1)
F(34)	40(1)	43(1)	70(1)	29(1)	2(1)	6(1)
F(42)	21(1)	64(1)	49(1)	19(1)	-5(1)	-12(1)
F(43)	18(1)	77(1)	39(1)	13(1)	-4(1)	-6(1)
F(44)	35(1)	62(1)	47(1)	34(1)	-2(1)	4(1)
F(45)	59(1)	41(1)	38(1)	-13(1)	-11(1)	12(1)
F(35)	40(1)	33(1)	60(1)	18(1)	-1(1)	-4(1)
F(36)	38(1)	96(1)	26(1)	-15(1)	-4(1)	4(1)
O(11)	20(1)	40(1)	37(1)	7(1)	3(1)	0(1)
O(12)	73(1)	33(1)	16(1)	-5(1)	2(1)	6(1)
O(21)	20(1)	30(1)	65(1)	1(1)	-2(1)	-4(1)
F(46)	68(1)	38(1)	72(1)	-19(1)	-4(1)	11(1)
N(11)	28(1)	35(1)	21(1)	-5(1)	-9(1)	14(1)
N(12)	21(1)	31(1)	16(1)	-7(1)	-1(1)	5(1)
N(13)	38(1)	22(1)	26(1)	2(1)	8(1)	3(1)
N(21)	20(1)	27(1)	32(1)	1(1)	4(1)	4(1)
N(22)	26(1)	31(1)	17(1)	2(1)	4(1)	0(1)
O(22)	71(1)	42(1)	32(1)	15(1)	1(1)	3(1)
N(23)	34(1)	23(1)	32(1)	-8(1)	9(1)	-8(1)
C(21)	27(1)	20(1)	20(1)	0(1)	0(1)	-8(1)
C(11)	29(1)	20(1)	29(1)	0(1)	0(1)	2(1)
C(122)	25(1)	36(1)	15(1)	-4(1)	-3(1)	-1(1)

C(12)	19(1)	26(1)	28(1)	-1(1)	-3(1)	-1(1)
C(22)	28(1)	16(1)	33(1)	2(1)	-10(1)	-2(1)
C(15)	23(1)	29(1)	41(1)	16(1)	-4(1)	3(1)
C(23)	25(1)	24(1)	36(1)	-7(1)	3(1)	4(1)
C(25)	23(1)	25(1)	24(1)	-4(1)	-4(1)	-1(1)
C(121)	28(1)	39(1)	30(1)	-17(1)	-1(1)	9(1)
C(111)	21(1)	43(1)	43(1)	-14(1)	-11(1)	10(1)
C(13)	28(1)	31(1)	22(1)	0(1)	6(1)	-8(1)
C(14)	34(1)	40(1)	21(1)	13(1)	-9(1)	-13(1)
C(131)	39(1)	31(1)	24(1)	6(1)	7(1)	0(1)
C(16)	38(1)	22(1)	18(1)	-2(1)	1(1)	6(1)
C(26)	21(1)	20(1)	38(1)	0(1)	3(1)	-1(1)
C(221)	41(1)	43(1)	20(1)	4(1)	-4(1)	6(1)
C(132)	62(2)	24(1)	51(1)	2(1)	15(1)	6(1)
C(24)	33(1)	28(1)	21(1)	-6(1)	1(1)	2(1)
C(17)	21(1)	27(1)	22(1)	5(1)	3(1)	4(1)
C(231)	28(1)	23(1)	44(1)	1(1)	7(1)	-4(1)
C(112)	52(1)	62(2)	24(1)	-1(1)	-16(1)	25(1)
C(27)	40(1)	28(1)	24(1)	4(1)	6(1)	3(1)
C(211)	30(1)	40(1)	53(1)	15(1)	5(1)	13(1)
C(212)	18(1)	30(1)	54(1)	-3(1)	1(1)	0(1)
C(222)	44(1)	50(1)	25(1)	-5(1)	13(1)	-1(1)
C(232)	80(2)	50(2)	69(2)	-39(2)	41(2)	-36(2)

Compound **1a^{F}•Fp:**

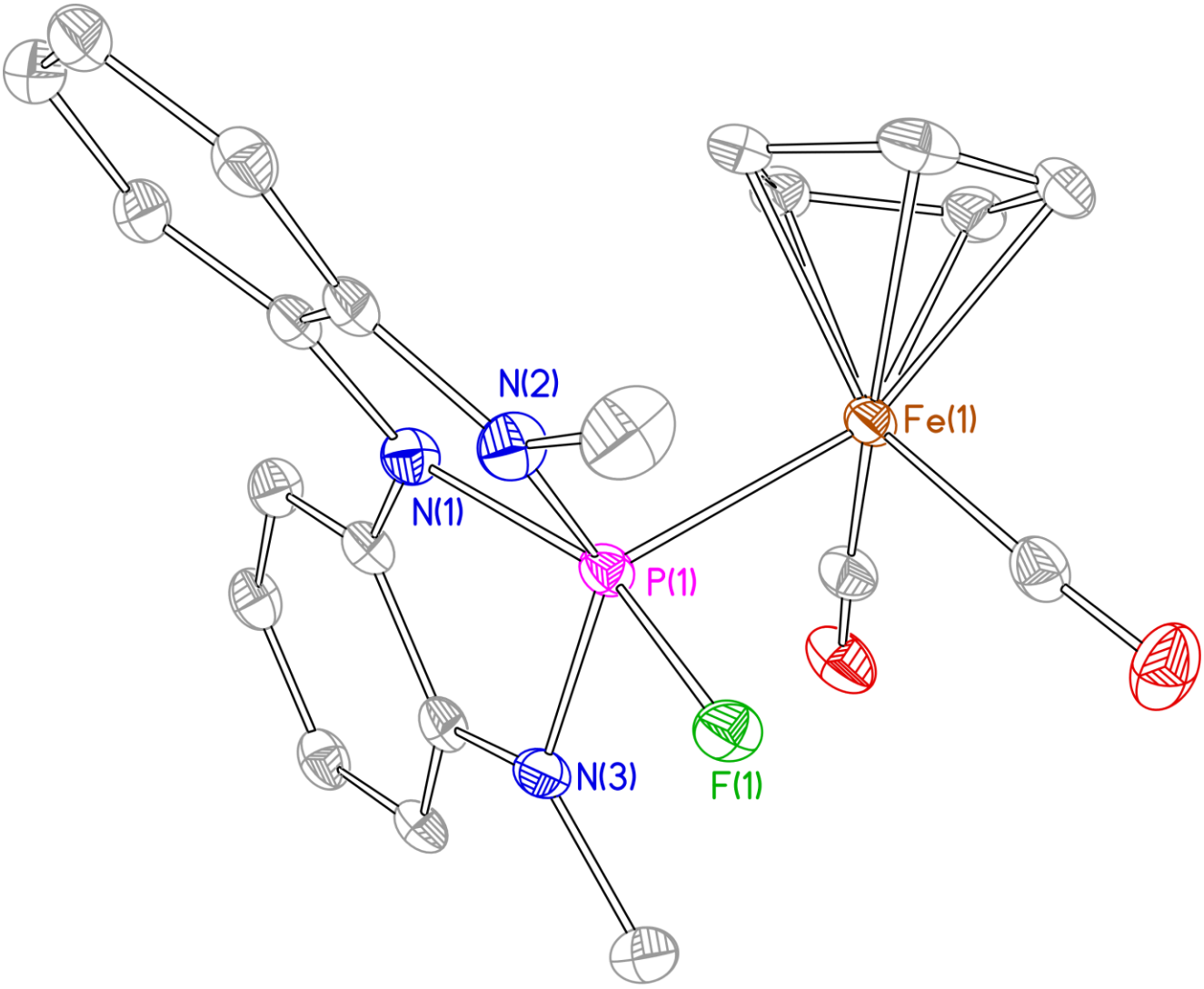


Table S9. Crystal data and structure refinement for **1a^{F}**•Fp.

Identification code	FpNNNPF5x	
Empirical formula	C21 H19 F Fe N3 O2 P	
Formula weight	451.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
Unit cell dimensions	a = 20.512(2) Å	α= 90°.
	b = 7.2560(8) Å	β= 90°.
	c = 12.6618(13) Å	γ = 90°.
Volume	1884.5(3) Å^3	
Z	4	
Density (calculated)	1.590 Mg/m^3	
Absorption coefficient	0.919 mm^{-1}	
F(000)	928	
Crystal size	0.200 x 0.110 x 0.080 mm^3	
Theta range for data collection	1.986 to 31.503°.	
Index ranges	-30<=h<=30, -10<=k<=10, -12<=l<=18	
Reflections collected	65006	
Independent reflections	5534 [R(int) = 0.0617]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7463 and 0.6680	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5534 / 1 / 265	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0802	
R indices (all data)	R1 = 0.0418, wR2 = 0.0826	
Absolute structure parameter	0.03(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.592 and -0.446 e.Å^{-3}	

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	6375(1)	3610(1)	3663(1)	14(1)
P(1)	5812(1)	4860(1)	5067(1)	14(1)
F(1)	6046(1)	7049(2)	4929(2)	18(1)
O(2)	7423(1)	2377(3)	5039(2)	27(1)
O(1)	6973(1)	7139(3)	3150(2)	28(1)
N(1)	5399(1)	2902(3)	5628(2)	16(1)
N(2)	5043(1)	5611(3)	4731(2)	19(1)
N(3)	6274(1)	4836(3)	6230(2)	16(1)
C(12)	4732(1)	2816(4)	5455(2)	15(1)
C(3M)	6039(2)	928(4)	3348(3)	21(1)
C(25)	6600(2)	766(5)	7958(3)	20(1)
C(11)	4529(1)	4403(4)	4907(2)	15(1)
C(4M)	5524(2)	2188(5)	3191(3)	21(1)
C(13)	4282(2)	1481(4)	5751(3)	19(1)
C(16)	3879(1)	4627(4)	4640(3)	18(1)
C(22)	5756(1)	1989(4)	6400(2)	16(1)
C(24)	6094(2)	-344(4)	7621(3)	19(1)
C(26)	6701(1)	2507(4)	7504(2)	17(1)
C(21)	6268(1)	3136(4)	6739(2)	16(1)
C(5M)	5710(2)	3440(5)	2397(3)	24(1)
C(23)	5672(2)	244(4)	6825(3)	18(1)
C(15)	3428(2)	3259(4)	4918(3)	21(1)
C(2)	7001(2)	2886(4)	4519(3)	19(1)
C(14)	3625(2)	1729(5)	5474(3)	22(1)
C(1)	6727(2)	5776(4)	3377(3)	19(1)
C(2M)	6550(2)	1378(5)	2624(3)	23(1)
C(27)	6828(2)	6034(5)	6459(3)	21(1)
C(17)	4924(2)	7199(5)	4036(3)	28(1)
C(1M)	6346(2)	2923(5)	2044(3)	26(1)

Table 11. Bond lengths [Å] and angles [°] for 3.

Fe(1)-C(2)	1.761(3)
Fe(1)-C(1)	1.767(3)
Fe(1)-C(3M)	2.103(3)
Fe(1)-C(5M)	2.109(3)
Fe(1)-C(1M)	2.112(3)
Fe(1)-C(4M)	2.114(3)
Fe(1)-C(2M)	2.118(3)
Fe(1)-P(1)	2.3047(9)
P(1)-F(1)	1.6687(18)
P(1)-N(2)	1.723(3)
P(1)-N(3)	1.750(3)
P(1)-N(1)	1.800(3)
O(2)-C(2)	1.147(4)
O(1)-C(1)	1.146(4)
N(1)-C(12)	1.388(4)
N(1)-C(22)	1.389(4)
N(2)-C(11)	1.389(4)
N(2)-C(17)	1.471(4)
N(3)-C(21)	1.392(4)
N(3)-C(27)	1.460(4)
C(12)-C(13)	1.389(4)
C(12)-C(11)	1.407(4)
C(3M)-C(4M)	1.411(5)
C(3M)-C(2M)	1.431(5)
C(3M)-H(3M)	0.9500
C(25)-C(24)	1.381(5)
C(25)-C(26)	1.403(4)
C(25)-H(25)	0.9500
C(11)-C(16)	1.385(4)
C(4M)-C(5M)	1.407(5)
C(4M)-H(4M)	0.9500
C(13)-C(14)	1.405(4)
C(13)-H(13)	0.9500
C(16)-C(15)	1.402(4)

C(16)-H(16)	0.9500
C(22)-C(23)	1.386(4)
C(22)-C(21)	1.406(4)
C(24)-C(23)	1.396(4)
C(24)-H(24)	0.9500
C(26)-C(21)	1.392(4)
C(26)-H(26)	0.9500
C(5M)-C(1M)	1.430(5)
C(5M)-H(5M)	0.9500
C(23)-H(23)	0.9500
C(15)-C(14)	1.376(5)
C(15)-H(15)	0.9500
C(14)-H(14)	0.9500
C(2M)-C(1M)	1.404(5)
C(2M)-H(2M)	0.9500
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(1M)-H(1M)	0.9500

C(2)-Fe(1)-C(1)	95.37(15)
C(2)-Fe(1)-C(3M)	94.57(14)
C(1)-Fe(1)-C(3M)	156.64(14)
C(2)-Fe(1)-C(5M)	157.27(14)
C(1)-Fe(1)-C(5M)	99.23(14)
C(3M)-Fe(1)-C(5M)	65.76(13)
C(2)-Fe(1)-C(1M)	123.22(15)
C(1)-Fe(1)-C(1M)	91.26(14)
C(3M)-Fe(1)-C(1M)	65.67(13)
C(5M)-Fe(1)-C(1M)	39.60(14)
C(2)-Fe(1)-C(4M)	129.12(14)
C(1)-Fe(1)-C(4M)	135.50(14)
C(3M)-Fe(1)-C(4M)	39.10(13)

C(5M)-Fe(1)-C(4M)	38.91(14)
C(1M)-Fe(1)-C(4M)	65.57(13)
C(2)-Fe(1)-C(2M)	91.76(14)
C(1)-Fe(1)-C(2M)	118.90(14)
C(3M)-Fe(1)-C(2M)	39.63(13)
C(5M)-Fe(1)-C(2M)	65.93(14)
C(1M)-Fe(1)-C(2M)	38.78(14)
C(4M)-Fe(1)-C(2M)	65.82(13)
C(2)-Fe(1)-P(1)	90.47(11)
C(1)-Fe(1)-P(1)	90.75(10)
C(3M)-Fe(1)-P(1)	110.26(9)
C(5M)-Fe(1)-P(1)	106.58(10)
C(1M)-Fe(1)-P(1)	145.87(11)
C(4M)-Fe(1)-P(1)	89.84(9)
C(2M)-Fe(1)-P(1)	149.88(10)
F(1)-P(1)-N(2)	86.33(11)
F(1)-P(1)-N(3)	86.69(11)
N(2)-P(1)-N(3)	134.91(13)
F(1)-P(1)-N(1)	158.11(12)
N(2)-P(1)-N(1)	85.18(12)
N(3)-P(1)-N(1)	85.12(12)
F(1)-P(1)-Fe(1)	98.61(7)
N(2)-P(1)-Fe(1)	113.12(10)
N(3)-P(1)-Fe(1)	111.96(9)
N(1)-P(1)-Fe(1)	103.28(9)
C(12)-N(1)-C(22)	127.5(3)
C(12)-N(1)-P(1)	116.0(2)
C(22)-N(1)-P(1)	113.9(2)
C(11)-N(2)-C(17)	117.7(3)
C(11)-N(2)-P(1)	117.1(2)
C(17)-N(2)-P(1)	123.2(2)
C(21)-N(3)-C(27)	116.3(3)
C(21)-N(3)-P(1)	113.2(2)
C(27)-N(3)-P(1)	125.6(2)
N(1)-C(12)-C(13)	130.1(3)
N(1)-C(12)-C(11)	109.4(2)

C(13)-C(12)-C(11)	120.5(3)
C(4M)-C(3M)-C(2M)	108.0(3)
C(4M)-C(3M)-Fe(1)	70.87(18)
C(2M)-C(3M)-Fe(1)	70.73(18)
C(4M)-C(3M)-H(3M)	126.0
C(2M)-C(3M)-H(3M)	126.0
Fe(1)-C(3M)-H(3M)	124.0
C(24)-C(25)-C(26)	120.7(3)
C(24)-C(25)-H(25)	119.7
C(26)-C(25)-H(25)	119.7
C(16)-C(11)-N(2)	128.1(3)
C(16)-C(11)-C(12)	120.0(3)
N(2)-C(11)-C(12)	111.8(2)
C(5M)-C(4M)-C(3M)	108.5(3)
C(5M)-C(4M)-Fe(1)	70.34(19)
C(3M)-C(4M)-Fe(1)	70.04(18)
C(5M)-C(4M)-H(4M)	125.8
C(3M)-C(4M)-H(4M)	125.8
Fe(1)-C(4M)-H(4M)	125.5
C(12)-C(13)-C(14)	118.7(3)
C(12)-C(13)-H(13)	120.6
C(14)-C(13)-H(13)	120.6
C(11)-C(16)-C(15)	119.4(3)
C(11)-C(16)-H(16)	120.3
C(15)-C(16)-H(16)	120.3
C(23)-C(22)-N(1)	130.0(3)
C(23)-C(22)-C(21)	121.0(3)
N(1)-C(22)-C(21)	109.0(3)
C(25)-C(24)-C(23)	120.7(3)
C(25)-C(24)-H(24)	119.6
C(23)-C(24)-H(24)	119.6
C(21)-C(26)-C(25)	119.1(3)
C(21)-C(26)-H(26)	120.5
C(25)-C(26)-H(26)	120.5
C(26)-C(21)-N(3)	127.4(3)
C(26)-C(21)-C(22)	119.7(3)

N(3)-C(21)-C(22)	113.0(3)
C(4M)-C(5M)-C(1M)	107.6(3)
C(4M)-C(5M)-Fe(1)	70.75(19)
C(1M)-C(5M)-Fe(1)	70.31(19)
C(4M)-C(5M)-H(5M)	126.2
C(1M)-C(5M)-H(5M)	126.2
Fe(1)-C(5M)-H(5M)	124.3
C(22)-C(23)-C(24)	118.8(3)
C(22)-C(23)-H(23)	120.6
C(24)-C(23)-H(23)	120.6
C(14)-C(15)-C(16)	120.4(3)
C(14)-C(15)-H(15)	119.8
C(16)-C(15)-H(15)	119.8
O(2)-C(2)-Fe(1)	176.9(3)
C(15)-C(14)-C(13)	120.9(3)
C(15)-C(14)-H(14)	119.6
C(13)-C(14)-H(14)	119.6
O(1)-C(1)-Fe(1)	176.5(3)
C(1M)-C(2M)-C(3M)	107.4(3)
C(1M)-C(2M)-Fe(1)	70.4(2)
C(3M)-C(2M)-Fe(1)	69.64(18)
C(1M)-C(2M)-H(2M)	126.3
C(3M)-C(2M)-H(2M)	126.3
Fe(1)-C(2M)-H(2M)	125.3
N(3)-C(27)-H(27A)	109.5
N(3)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
N(3)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
N(2)-C(17)-H(17A)	109.5
N(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
N(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

C(2M)-C(1M)-C(5M)	108.5(3)
C(2M)-C(1M)-Fe(1)	70.8(2)
C(5M)-C(1M)-Fe(1)	70.1(2)
C(2M)-C(1M)-H(1M)	125.8
C(5M)-C(1M)-H(1M)	125.8
Fe(1)-C(1M)-H(1M)	124.9

Symmetry transformations used to generate equivalent atoms:

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 3. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	19(1)	13(1)	11(1)	0(1)	-1(1)	-1(1)
P(1)	18(1)	12(1)	11(1)	0(1)	-1(1)	-1(1)
F(1)	25(1)	12(1)	18(1)	1(1)	-1(1)	-1(1)
O(2)	26(1)	35(1)	18(1)	-4(1)	-3(1)	10(1)
O(1)	32(1)	18(1)	36(2)	1(1)	10(1)	-3(1)
N(1)	19(1)	15(1)	14(1)	3(1)	-2(1)	0(1)
N(2)	20(1)	16(1)	19(1)	3(1)	-2(1)	0(1)
N(3)	20(1)	15(1)	12(1)	-2(1)	-1(1)	-1(1)
C(12)	19(1)	17(1)	10(1)	-1(1)	1(1)	0(1)
C(3M)	30(2)	16(1)	17(1)	-1(1)	-1(1)	-6(1)
C(25)	20(1)	26(2)	14(1)	2(1)	0(1)	5(1)
C(11)	19(1)	16(1)	10(1)	0(1)	1(1)	1(1)
C(4M)	22(1)	26(2)	15(2)	-6(1)	-2(1)	-5(1)
C(13)	21(1)	22(1)	15(1)	3(1)	1(1)	-2(1)
C(16)	20(1)	21(1)	14(1)	1(1)	0(1)	2(1)
C(22)	19(1)	18(1)	12(1)	-1(1)	0(1)	1(1)
C(24)	25(1)	19(1)	15(1)	4(1)	1(1)	3(1)
C(26)	21(1)	21(1)	11(1)	-1(1)	-1(1)	2(1)
C(21)	19(1)	17(1)	11(1)	1(1)	1(1)	1(1)
C(5M)	30(2)	24(2)	19(2)	-3(1)	-9(1)	-1(1)
C(23)	21(1)	17(1)	18(1)	3(1)	1(1)	1(1)
C(15)	18(1)	28(2)	15(2)	-1(1)	0(1)	0(1)
C(2)	22(1)	18(1)	17(2)	-4(1)	1(1)	1(1)
C(14)	20(1)	27(2)	18(2)	0(1)	1(1)	-4(1)
C(1)	22(1)	19(1)	16(1)	-2(1)	3(1)	2(1)
C(2M)	24(1)	22(2)	22(2)	-9(1)	2(1)	-2(1)
C(27)	21(1)	21(1)	22(2)	-3(1)	-3(1)	-3(1)
C(17)	28(2)	22(2)	34(2)	12(1)	-7(1)	1(1)
C(1M)	36(2)	28(2)	12(2)	-2(1)	1(1)	-9(1)

IV. DFT Calculations

A. General Computational Information

Geometries were optimized in Orca 4.0.0[8] using the M06-L[9] density functional with the def2-TZVP basis set.[10] Functional choice was based on a survey of several functionals and comparing optimized geometries with experimental crystallographic structures, specifically with regards to metrics involving the Fe and P local environment (See **Table S13** below). Its accuracy for reproducing bond lengths in **1a^{F}•**Fp in comparison to other functionals led to its usage. Calculations were carried out in the gas phase without symmetry constraint unless otherwise noted. Stationary points were characterized by frequency calculations to confirm their identity as local minima (zero imaginary frequencies). Natural bond order (NBO) analysis was performed with the NBO 6.0 program[11] through Orca. NLMOs were visualized using the Jmol software.[12]

Table S13. Collected bond metrics for the phosphorus and iron local environments with different functionals for **1a•**Fp^{+} and **1a^{F}•**Fp in comparison with experimental crystallographic data.

1a•Fp^{+}:

Functional	d(P-Fe)	d(P-N_{mid})	d(P-$N_{side,mean}$)	d(Fe-$(CO)_{mean}$)	∠(N_2-P-N_3)
X-Ray Diffraction	2.181	1.713	1.675	1.789	116.4
BP86	2.226	1.719	1.699	1.769	118.5
TPSS	2.232	1.716	1.694	1.781	118.8
PBE	2.219	1.718	1.698	1.766	118.5
B97D	2.197	1.711	1.691	1.772	118.4
M06L	2.205	1.705	1.682	1.788	117.5

1a^{F}•Fp:

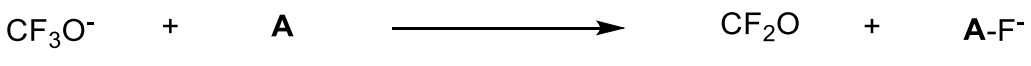
Functional	d(P-Fe)	d(P-N_{mid})	d(P-$N_{side,mean}$)	d(Fe-$(CO)_{mean}$)	d(P-F)
X-Ray Diffraction	2.305	1.800	1.737	1.764	1.668
BP86	2.372	1.827	1.754	1.751	1.686
TPSS	2.366	1.823	1.745	1.763	1.682
PBE	2.365	1.823	1.753	1.749	1.686
B97D	2.348	1.822	1.754	1.753	1.676
M06L	2.329	1.809	1.735	1.761	1.665

Energy decomposition analysis (EDA-NOCV)[13] was performed, analyzed, and visualized using a trial version of the ADF modeling suite[14] with the BP86[15] density functional and a frozen core treatment. Fragments were defined as the Fe(Cp)$(CO)_2^{+}$ metal center and the appropriate phosphorus ligand.

For topological analysis of the electron density (QTAIM),[16] an all-electron single point calculation was conducted. Coordinates obtained from the above geometry optimization were used as the input, and analysis and visualization of the QTAIM data was performed with the Multiwfn program.[17]

B. Method for Calculating Fluoride Ion Affinity

Fluoride ion affinities (FIA) were calculating using Christe's method.[18] Briefly, this is done by measuring the enthalpy of reaction for the following reaction, where **A** is the molecule of interest to be studied. A known value for the FIA of CF_2O (-49.8 kcal/mol) is added to the calculated value to give the final FIA. Solvent corrections (CPCM(CH_2Cl_2)) were applied to the calculations to account for charge neutralization.[19]



$$FIA = \Delta H_{rxn} - 49.8 \text{ kcal/mol}$$

Compound	Computed Total Enthalpy (Eh)	Computed Total Enthalpy (kcal/mol)
CF_2O	-313.10169285	-196474.1302
CF_3O^-	-413.12358904	-259238.7702
1a•Fp^+	-2731.29635077	-1713913.042
1a^F•Fp	-2831.33339594	-1776687.188
1b•Fp^+	-2428.76981290	-1524074.917
1b^F•Fp	-2528.76475665	-1586822.644

C. Cartesian Coordinates for Stationary Points

Cartesian coordinates of the M06-L/def2-TZVP stationary points in Å units and the absolute thermochemical data in Hartrees.

1a•Fp^+

Temperature = 298.150 K
Pressure = 1.0000 Atm
Electronic Energy = -2731.68354853
Total Thermal Energy = -2731.29729498
Enthalpy = -2731.29635077
Free Energy = -2731.37208436

Fe	5.30180233927635	7.17809079486311	8.13996341584950
P	5.79822016423460	5.66458672155575	6.61621952674889
O	3.25888234915385	8.60494217447179	6.58792662762768
N	7.16275696480110	4.67315226263149	6.84767802700012
O	7.59418094633389	8.85443714507702	7.37935127450114
N	6.43490654056998	6.33127684972016	5.18440943250371
N	4.75457812380467	4.37156065474302	6.47136429150928
C	5.43736113554392	3.14166321438853	6.52146707865113
C	7.83700736957748	6.21125249497039	5.23510968524033
C	8.26703892914803	5.26082761363313	6.17114943429931
C	4.07763569037560	8.03761071896756	7.15881980705511
C	6.80834473195583	3.30520286152233	6.74516515772027

C	4.29174822827166	7.63571802109186	9.93705545542127
H	3.61450543031092	8.46608762871882	10.05874671093913
C	4.88300812623635	1.87904833301205	6.40548051032849
H	3.82218442984896	1.75341754501250	6.23196396207792
C	5.68156007845184	7.66006606613155	10.16002592326031
H	6.25918302075808	8.51294822845344	10.48012940015282
C	8.76333695885702	6.94311750526932	4.50985788516703
H	8.44410403673908	7.69755881288185	3.80262587657508
C	3.93753791282175	6.32411177542930	9.49343144854574
H	2.94374528118126	5.98360458277786	9.24905905165313
C	10.53800045575277	5.73078036925434	5.63278635215050
H	11.59450126183304	5.55419476689211	5.78508236425712
C	6.69383471848915	8.19421750891606	7.64286208533761
C	5.80888856822935	7.43291103063570	4.47105001547702
H	6.05237853045094	8.40762441475779	4.90706260158740
H	4.72927528899561	7.29871817744730	4.47403591472095
H	6.13933596565857	7.42989740298438	3.43388410168421
C	9.60750947336880	5.01245850379076	6.38164799173965
H	9.92322797422774	4.28988360707742	7.12275996623129
C	5.11770122307120	5.54463438336338	9.47263982049157
H	5.18483615730016	4.50499183288072	9.18691754512526
C	10.11690145287316	6.68471548596018	4.71688460261053
H	10.85105415002251	7.25148847669631	4.15865919093357
C	7.64677746628355	2.21153390690201	6.83980725889695
H	8.70758962673446	2.34130640617172	7.00717665393055
C	6.20491351982413	6.36687263207297	9.85386637954023
H	7.23824372529089	6.06368117231086	9.91864434105620
C	3.30187449262724	4.43186208133354	6.51344739916023
H	2.86929227733957	4.03709930030449	5.59423271544574
H	2.98269798386694	5.46604025193568	6.62605535195024
H	2.92437642921099	3.85324853131458	7.35877048495763
C	5.73021029658094	0.77629876668920	6.49973248738885
H	5.31500292609740	-0.21875790738011	6.40540491932697
C	7.09264180013227	0.93977154531043	6.70539091252562
H	7.73739544748631	0.07279534705535	6.76800856064663

1a^{F}•Fp

Temperature = 298.150 K
Pressure = 1.0000 Atm
Electronic Energy = -2831.72272823
Total Thermal Energy = -2831.33434015
Enthalpy = -2831.33339594

Free Energy = -2831.40603176

Fe	5.08663446815943	6.93955536002039	8.21398825401729
P	5.48632782117047	5.89852250098078	6.16947338780497
O	2.23825250396543	6.49000982582239	7.82391527570712
N	6.85980167629974	4.76787044060991	6.49972090359946
O	5.06873676303350	9.49970514987651	6.83145907914972
N	6.61147384155726	6.72234835127760	5.13653926248371
N	4.56122846698555	4.45677647520393	5.89677551363588
C	5.13412280133296	3.29421430776186	6.39136410261067
C	7.94359587711220	6.41083951985448	5.36559458889863
C	8.10067878803850	5.26368697793338	6.15923997617316
C	3.36864975596425	6.65963346743285	7.94412251794324
C	6.48301118528615	3.46374223414877	6.74107830564912
C	5.25510166121675	7.43156193711632	10.26241709461601
H	4.64492893409904	8.15792710462590	10.77230073323994
C	4.51956124955004	2.06148230941574	6.53774476095556
H	3.48228360839509	1.92784237717790	6.26478168322942
C	6.48532552657093	7.67868213599394	9.60343400063636
H	6.96940305450834	8.63809490108123	9.51149745813522
C	9.05103493654572	7.09200384103154	4.88799762258784
H	8.93203913186940	7.97244198172633	4.27235420241780
C	4.97558419589741	6.04900573863721	10.11842067186847
H	4.09980125135754	5.54112092433689	10.49043003805597
C	10.47891962790044	5.48803541635962	5.97995429624113
H	11.47039681018599	5.12677629433361	6.21691843459934
C	5.07425239372396	8.47310087522974	7.34831198441097
C	6.35327178553490	7.87173352615979	4.28941550959211
H	6.75212182048402	8.78951962742291	4.72986368692356
H	5.29476726542331	7.99967592329015	4.12198899923847
H	6.84307185968043	7.72573819514659	3.32474885916016
C	9.37065819899312	4.80330072236984	6.47117363224109
H	9.51020145501929	3.92768743224304	7.08544169793023
C	6.01833460571413	5.44894290143798	9.37451659793801
H	6.08264680879725	4.40861480912173	9.10088326397565
C	10.32202008078112	6.61890616098690	5.20073785345572
H	11.19033939342428	7.14603284588526	4.82923377716838
C	7.21267360401131	2.39223459207760	7.23289859283048
H	8.24929294401956	2.50450464917825	7.50880008901424
C	6.95899692299266	6.46435078984638	9.05315319633835
H	7.86950775075177	6.33721043728111	8.49102206568141
C	3.17214563822960	4.36781191327333	5.48679231372483
H	3.06759429825032	3.58646645516943	4.73163529344968
H	2.83139826758439	5.30107526183216	5.06522956125284

H	2.52492252432634	4.10600901351337	6.32845102641028
C	5.26100951221977	0.99042274035149	7.02790714720974
H	4.78651345130076	0.02522424017251	7.14236269243072
C	6.59091422086574	1.15384629784865	7.36747310362552
H	7.16053217666110	0.31563356439115	7.74512607997606
F	4.27103908420865	6.74568745301144	5.40921081176546

CF_2O

Temperature = 298.150 K
Pressure = 1.0000 Atm
Electronic Energy = -313.11969618
Total Thermal Energy = -313.10263706
Enthalpy = -313.10169285
Free Energy = -313.13072472

C	-0.42133741418179	0.47734087977204	-0.00008835993986
O	-0.48069139616926	1.65523975071994	0.00004722650399
F	-1.19734196216790	-0.33105425065643	0.68137918112219
F	0.43162077251896	-0.24922637983555	-0.68133804768633

CF_3O^-

Temperature = 298.150 K
Pressure = 1.0000 Atm
Electronic Energy = -413.14387409
Total Thermal Energy = -413.12453325
Enthalpy = -413.12358904
Free Energy = -413.15490981

C	-2.37812881844211	-0.22230805235799	-0.00003185935012
O	-1.15904665023943	-0.22233590037019	0.00000628171387
F	-3.02047900066111	0.63715561068676	0.91903165323811
F	-3.02063129856707	-1.44810278914832	0.28477572676222
F	-3.02051423209027	0.14369113118974	-1.20378180236408

1b•Fp^+

Temperature = 298.150 K
Pressure = 1.0000 Atm
Electronic Energy = -2529.14681029
Total Thermal Energy = -2528.76570086
Enthalpy = -2528.76475665
Free Energy = -2528.84051461

Fe	3.11607495068511	7.97027165640346	-0.07945805949463
P	3.89740201343032	6.60853852670720	-1.74109139250948

O	0.30214407097707	7.57864537780691	-0.79909011390107
N	5.49818351123349	6.10179226753124	-1.56125606904259
N	3.98647057240838	7.35562450001503	-3.22691266859868
O	3.39647849368379	5.92542788088735	2.00475264902199
N	3.01281051609953	5.19522989383665	-1.87573139618266
C	4.42540626648898	9.47844842066298	-0.79875681792647
H	5.01095412300398	9.39893714554214	-1.70123825209770
C	3.10656674371866	9.98004466467568	-0.72074390283761
H	2.52536718261754	10.37383613888581	-1.53939447831110
C	2.68955148657316	9.90841980178049	0.64335456767825
H	1.72980397541012	10.21460154573477	1.02847854951652
C	4.82260586409364	9.06512022965380	0.49535139255934
H	5.77668920790001	8.64659673439066	0.77355418187791
C	1.41146154701120	7.69316551111441	-0.51818947460100
C	2.91419906724410	8.23564323924668	-3.67579391122151
H	3.33183232900123	9.16794322293778	-4.06511754715978
H	2.23989604122322	8.47875877058812	-2.85991600307616
H	2.32947078983930	7.76395192299086	-4.46998362341447
C	3.74385487438552	9.34920626074018	1.38859866513664
H	3.73491958433011	9.14824218653566	2.44858971792834
C	2.18530471196612	4.59048475436285	-0.83972544166442
H	1.35748653347650	4.06376075170380	-1.31549887202135
H	1.75961134702949	5.33611510314167	-0.17791110163951
H	2.74283358821326	3.86987551181105	-0.23123692354923
C	3.27434461501687	6.68565691287372	1.15023799000977
C	5.76982340860646	5.10555492717236	-0.52851546966651
H	6.64288337785335	4.51863048861700	-0.81636894833170
H	4.92836055762361	4.42723360272575	-0.40859563621921
H	5.98269648196759	5.57277577096597	0.44034430410396
C	6.61490867196323	7.03159952107921	-1.71912857754079
H	6.89615775431460	7.49837768751735	-0.76992334858619
H	6.37940485148699	7.81282940903387	-2.43585128898990
H	7.48458454952775	6.48442050091775	-2.08784434395787
C	4.87720118531577	6.96943710544052	-4.32220295555367
H	4.30066692111242	6.55158790472111	-5.15209474426938
H	5.60239905850584	6.23051366312444	-3.99577283111410
H	5.41325288478269	7.84812638210813	-4.69033774930478
C	3.41585590554193	4.22443721925381	-2.89504568168585
H	4.05711252762984	3.44359852280802	-2.47370332427448
H	3.95378871119997	4.71116337812560	-3.70239797781267
H	2.52480914550732	3.75175498382826	-3.30933309127623

1b^{F}•Fp

Temperature = 298.150 K

Pressure = 1.0000 Atm
Electronic Energy = -2529.14681029
Total Thermal Energy = -2528.76570086
Enthalpy = -2528.76475665
Free Energy = -2528.84051461

Fe	3.31788364566214	8.16732232841299	0.06090458867345
P	3.92371592646721	6.28859065892481	-1.37976895743103
O	0.67985470046451	6.96167721993102	0.38201186204476
N	5.57456046258212	5.84261573866126	-1.34603173150078
N	4.09635230425402	7.18300865977865	-2.89408266665512
O	4.73282168385849	6.91711833198382	2.30030310299899
N	2.92388623752643	5.09937546862518	-2.06484828740710
C	4.11733160025370	9.67728253832777	-1.22866994665943
H	4.60526166695163	9.45776033287690	-2.16393433820898
C	2.73170785736965	9.88679089902582	-1.04557319974566
H	1.98177181854050	9.91845922775851	-1.81891740510723
C	2.50682921538760	10.10908180192022	0.34722579666274
H	1.55028219838114	10.29469799098602	0.81032186298397
C	4.74742967949693	9.73240844380353	0.03115122666207
H	5.80174486481574	9.60870240546027	0.22325509712511
C	1.74541307685679	7.39163761430112	0.24457614025989
C	2.89484162038801	7.76967206419147	-3.43165015626581
H	3.04646056629231	8.81406730175551	-3.73797790606652
H	2.09257226058971	7.75204058963975	-2.69321061787491
H	2.53899937661026	7.22722794618350	-4.31990312310566
C	3.74166556539443	10.01387143479668	1.01091415412045
H	3.90351611285868	10.11507425090191	2.07263671328014
C	1.95191407809072	4.28371268304656	-1.34975827206031
H	1.10165619292816	4.10156832192336	-2.01281588838418
H	1.58782983355755	4.78030332784880	-0.45971983340150
H	2.36227556962700	3.31161734588189	-1.05354360501676
C	4.15831927549953	7.32300974466501	1.38564208046025
C	5.96537096891763	4.57787492902866	-0.75312636737008
H	6.93613275933287	4.28642666522422	-1.16284435610648
H	5.23781233074602	3.80763212318312	-1.00086269204177
H	6.05344430678484	4.62440590800631	0.33891624756373
C	6.53603646168636	6.90245059617584	-1.08823338870171
H	6.68025385147480	7.09141878523838	-0.01493321935387
H	6.21480685681049	7.83296091737627	-1.55291876482493
H	7.50741071315117	6.63222421438479	-1.51157362259877
C	5.16905856147100	7.18054476597397	-3.86132784642374
H	4.81888604261523	6.82297948411433	-4.84140451250922
H	5.98446411402849	6.53528072823813	-3.54814726891285

H	5.57346867376328	8.19107089339249	-4.02386248738192
C	3.10049389485258	4.62521500632940	-3.42833435386666
H	3.23117751038394	3.53819660172548	-3.41573425882835
H	3.98019154362661	5.05233843624565	-3.89531571728044
H	2.22871619320100	4.84309477649393	-4.05558760161266
F	3.66327782644868	5.32338049725677	0.17463351986887

VI. Multinuclear NMR Spectra

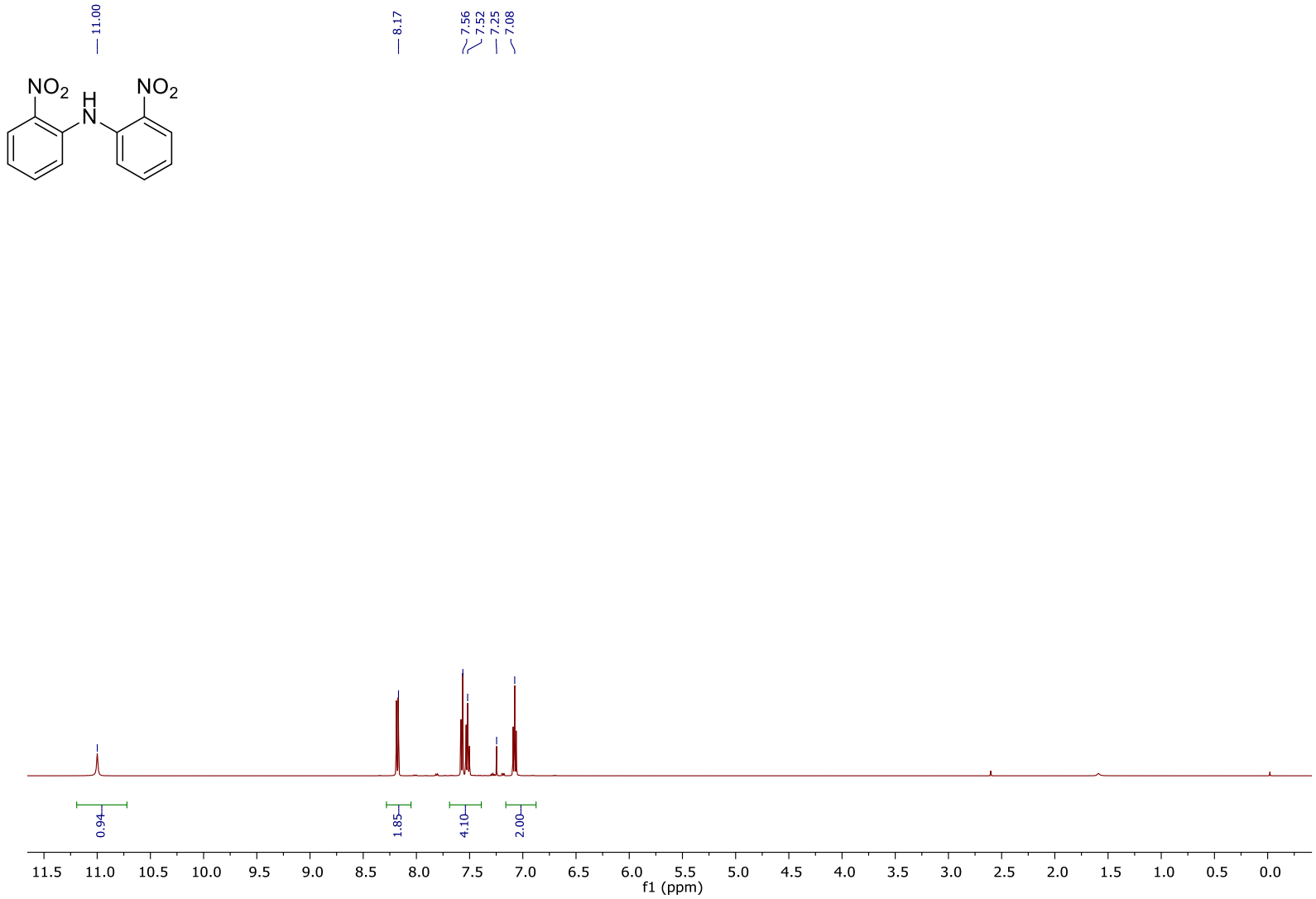


Figure S1. ^{1}H NMR of **S1**.

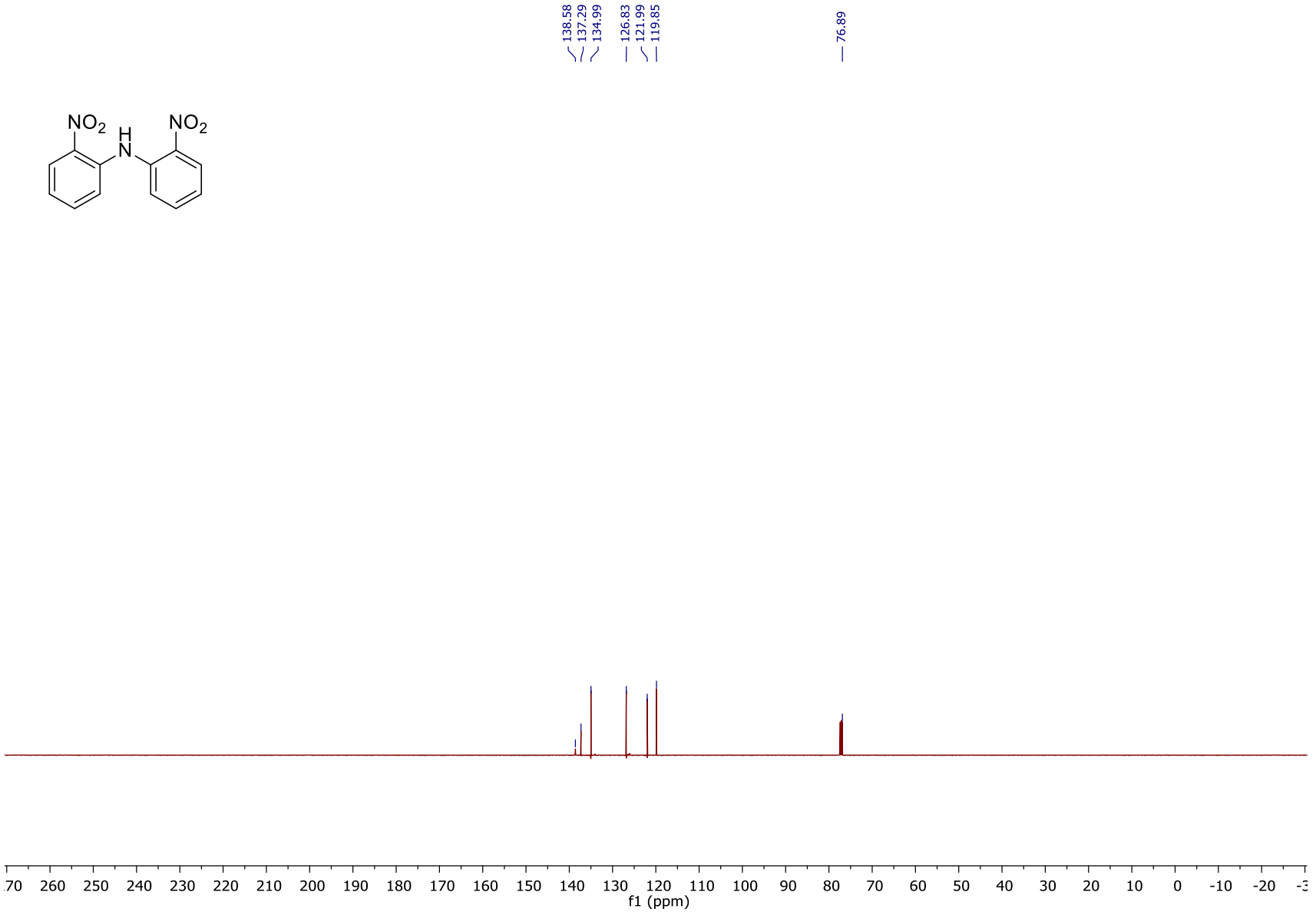


Figure S2. $^{13}C\{^{1}H\}$ NMR of **S1**.

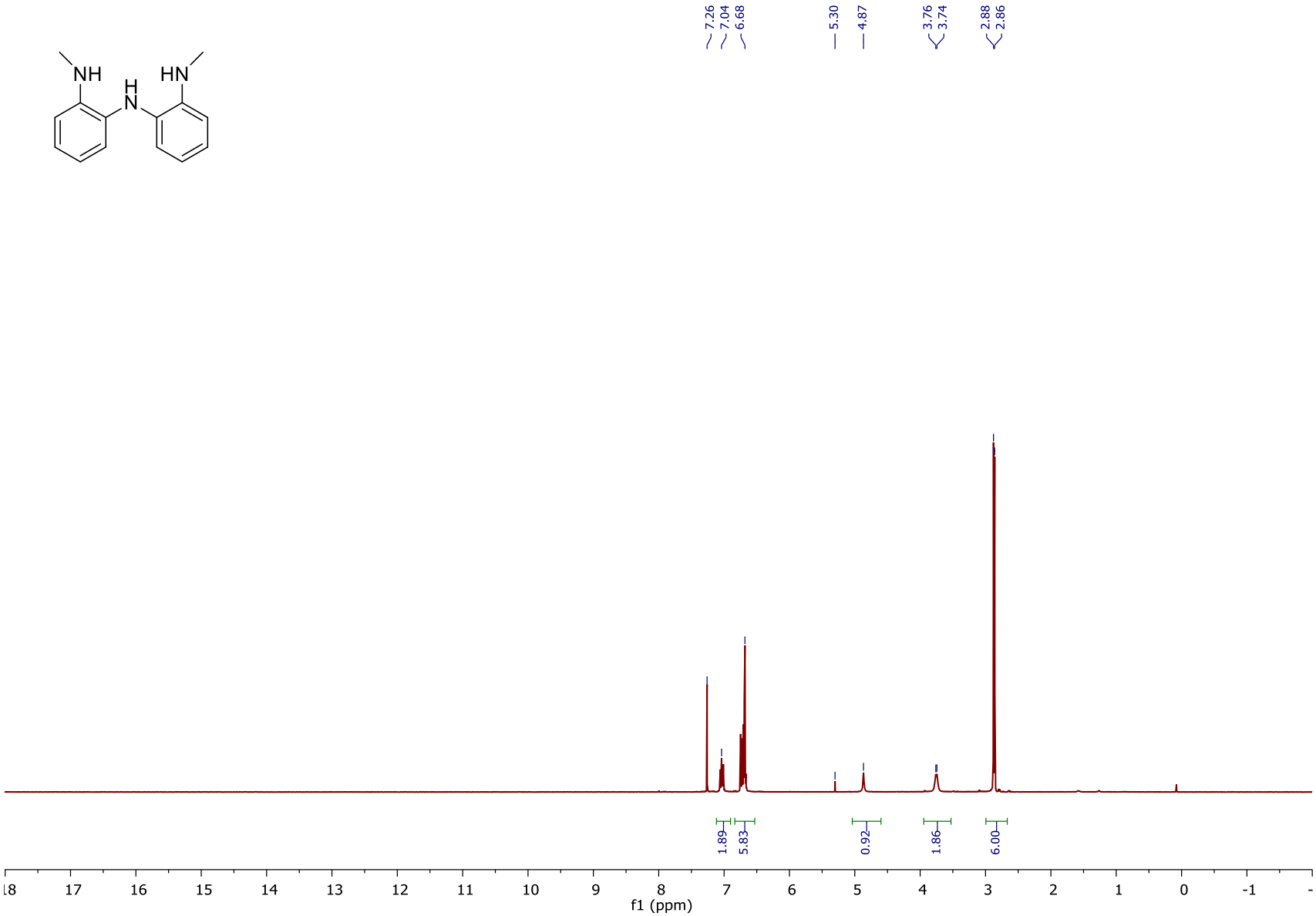


Figure S3. ^{1}H NMR of **S2**.

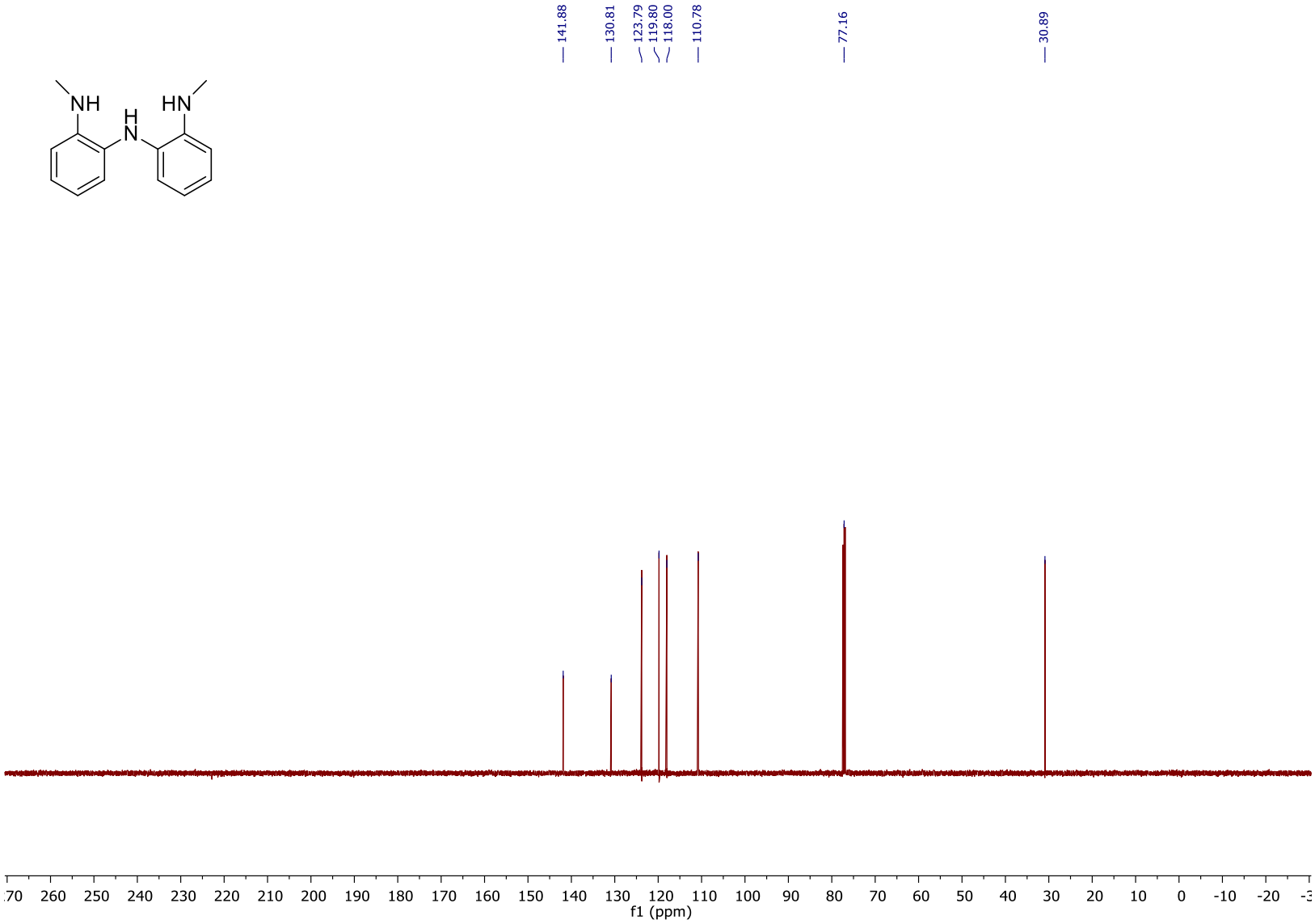


Figure S4. $^{13}C\{^{1}H\}$ NMR of **S2**.

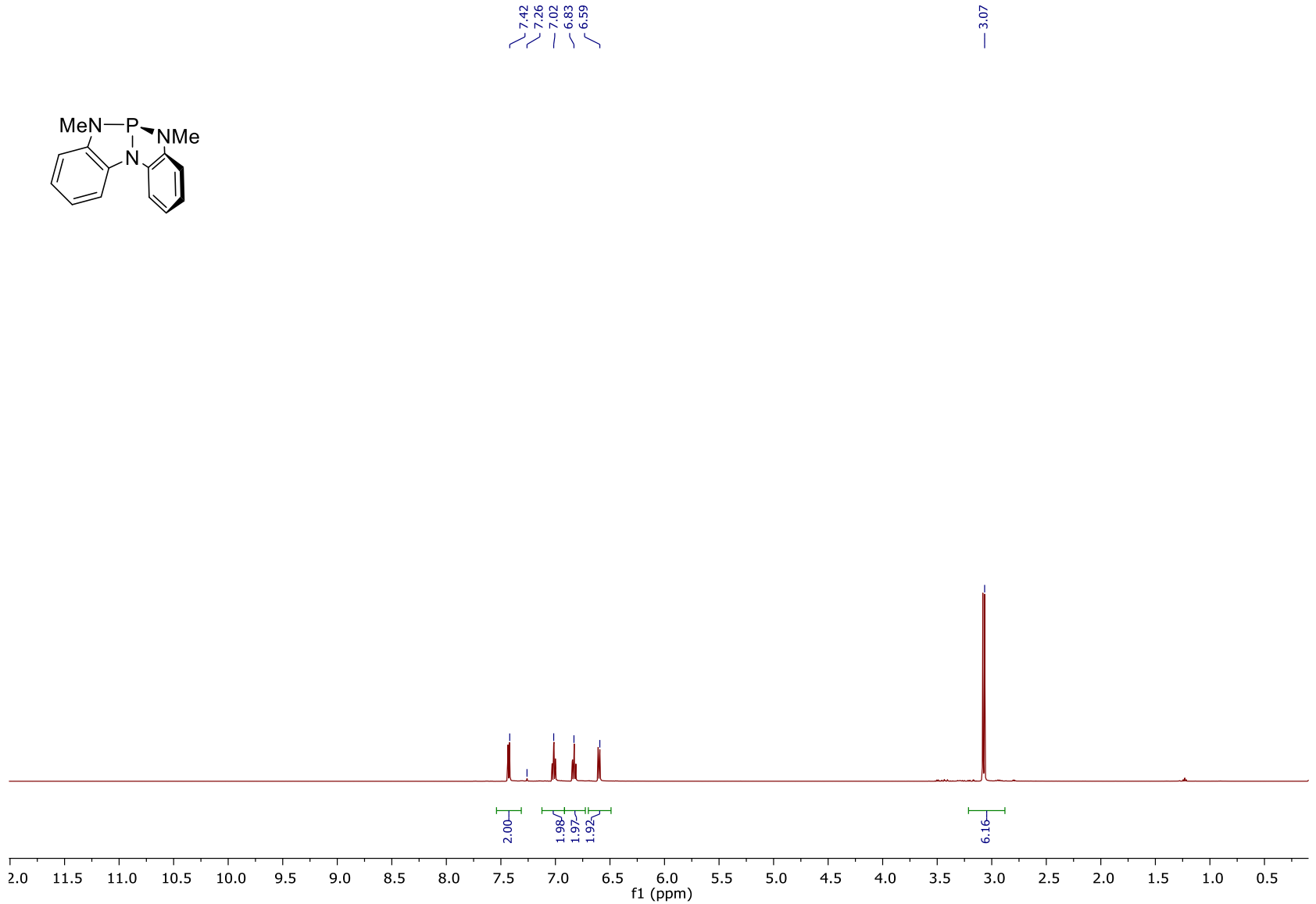


Figure S5. ^{1}H NMR of **1a**.

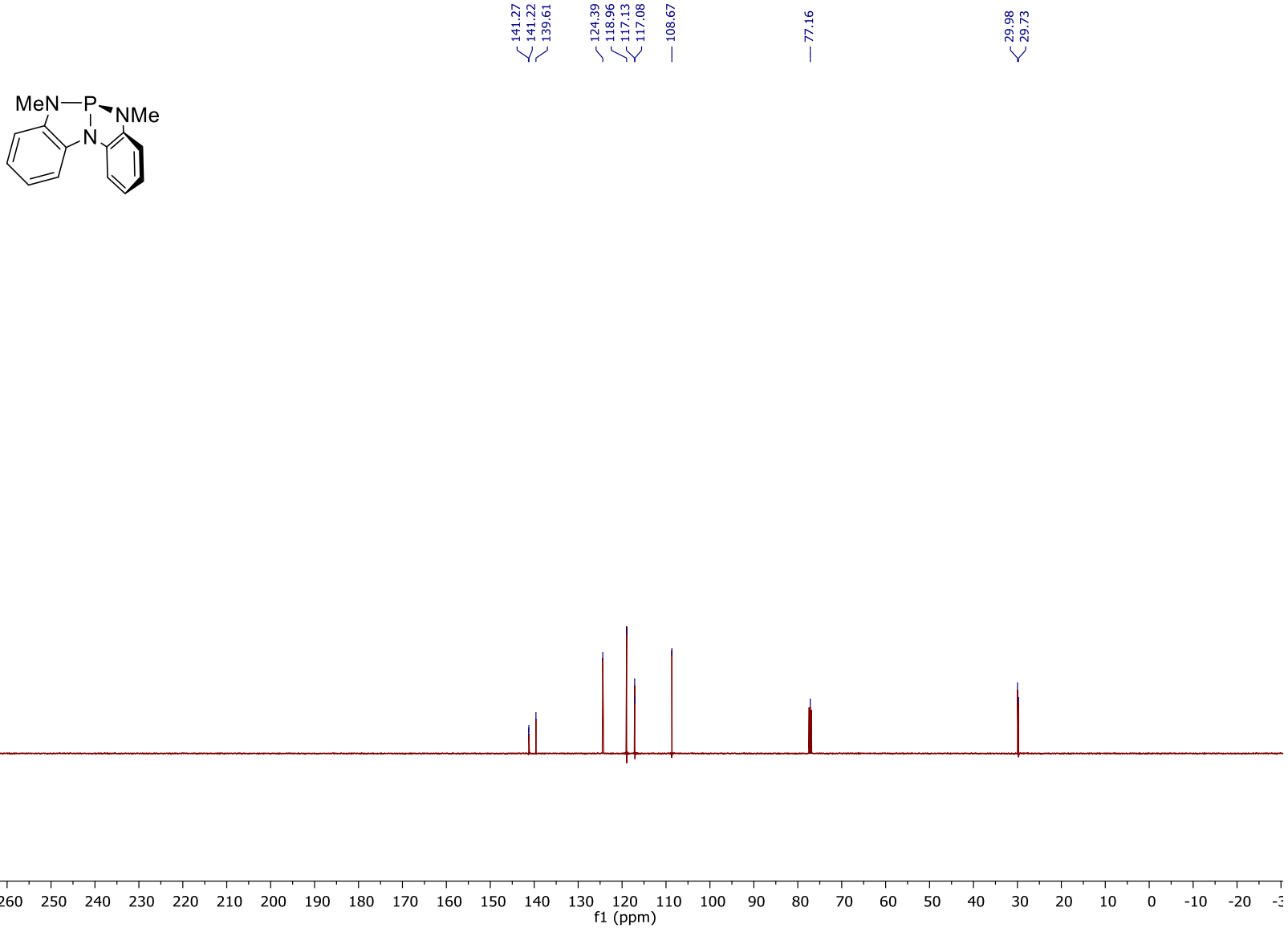


Figure S6. $^{13}C\{^{1}H\}$ NMR of **1a**.

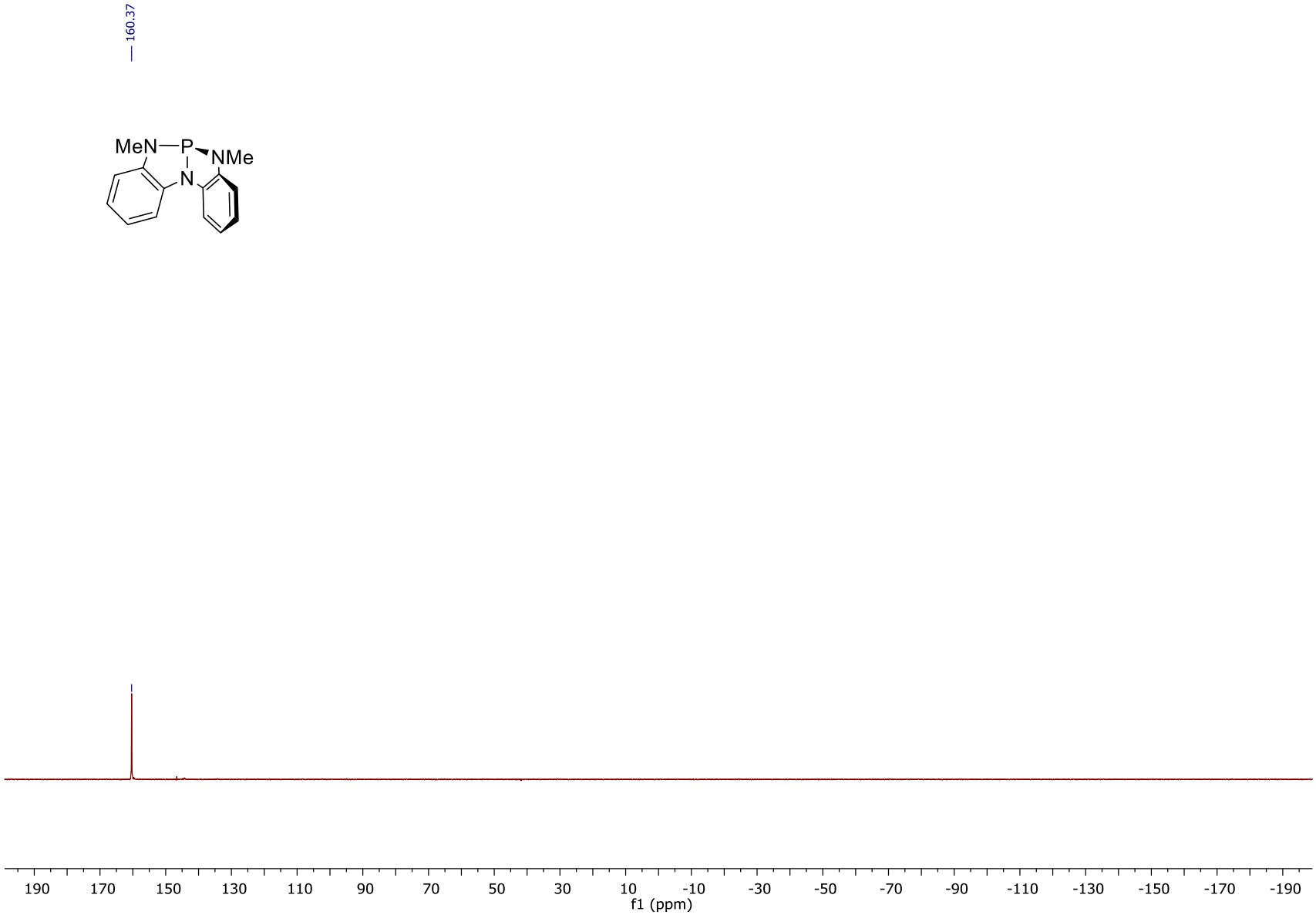


Figure S7. $^{31}P\{^{1}H\}$ NMR of **1a**.

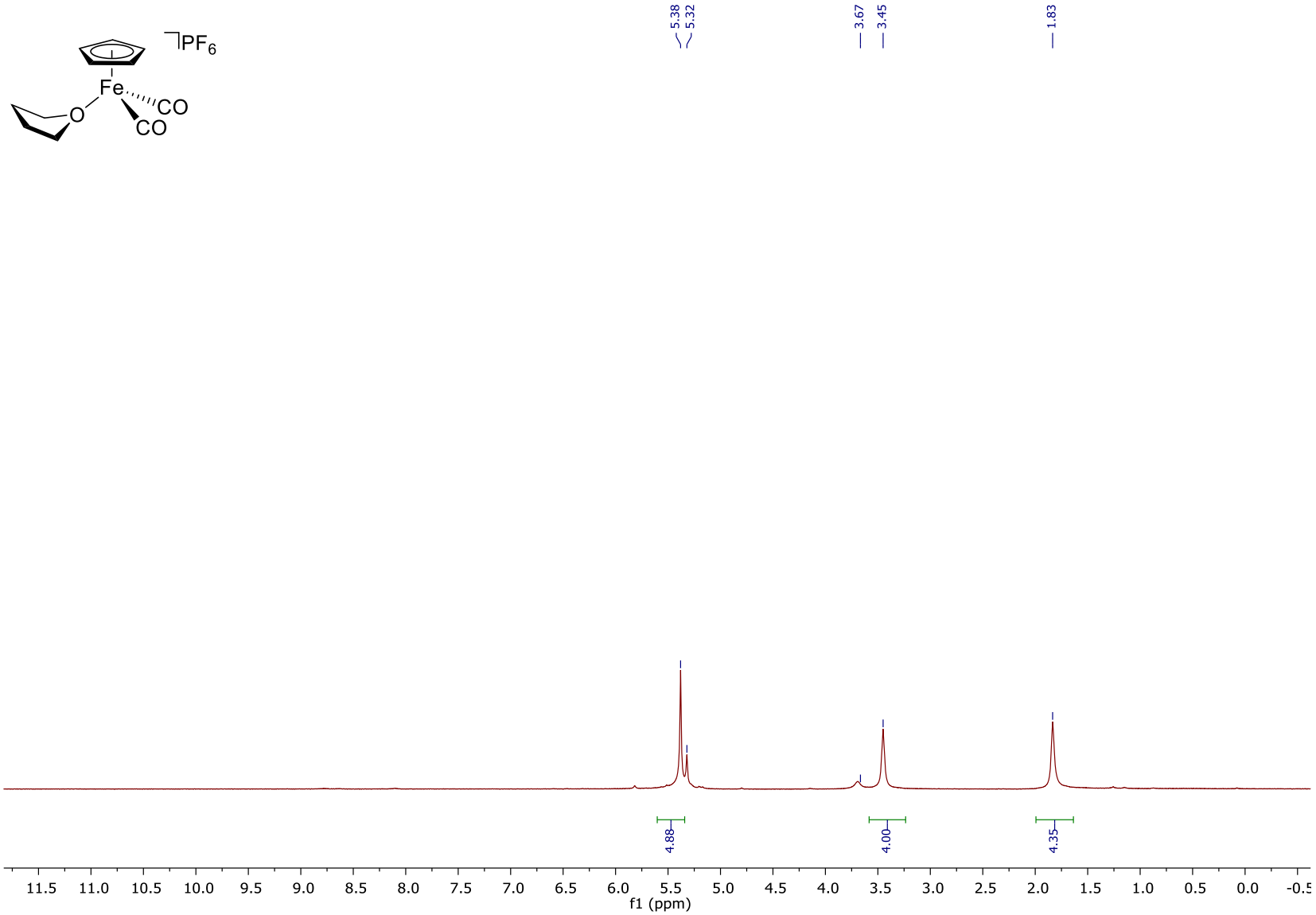


Figure S8. ^{1}H NMR of **(thf)**•Fp^{+}.

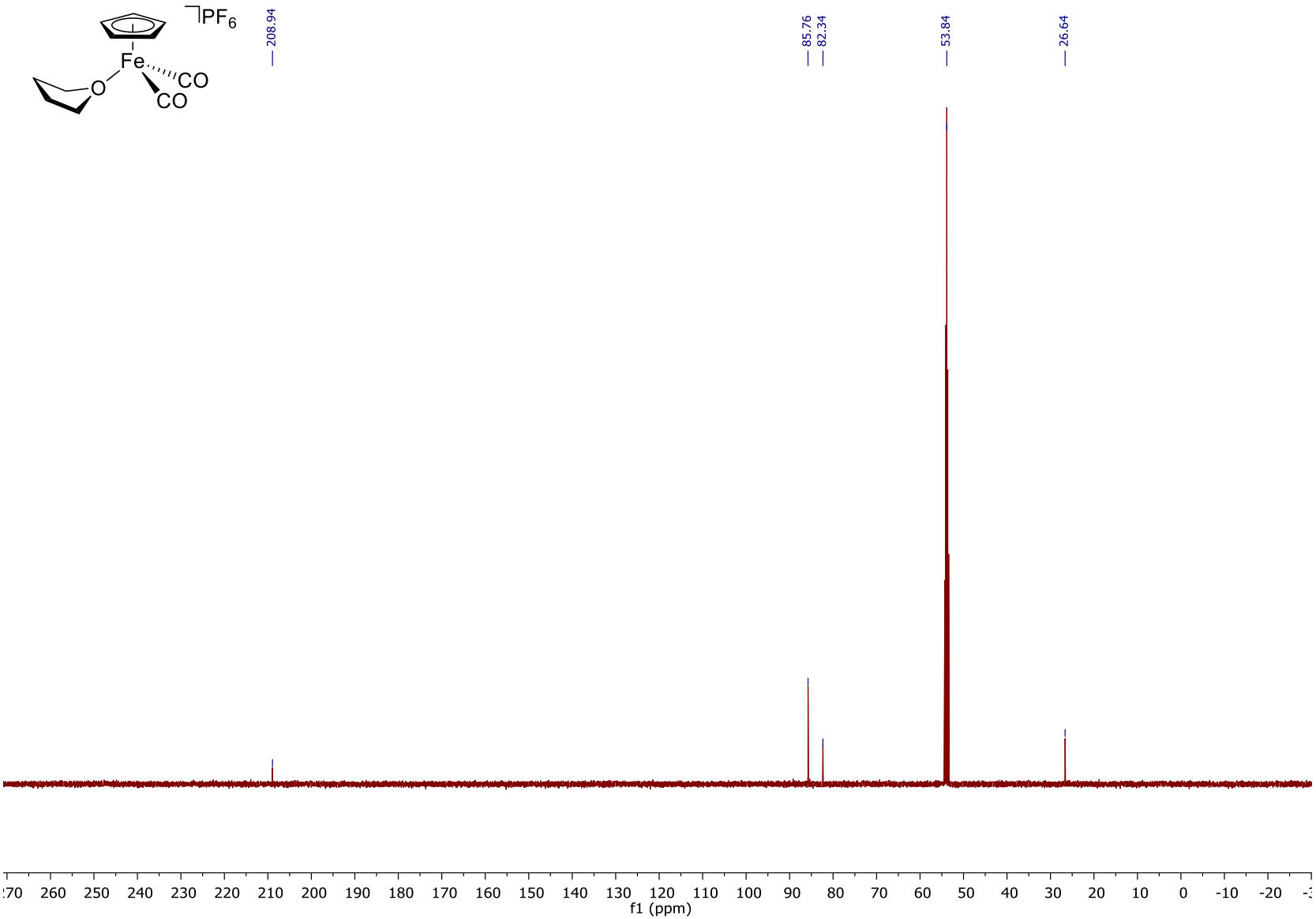


Figure S9. $^{13}C\{^{1}H\}$ NMR of **(thf)•**Fp^{+}.

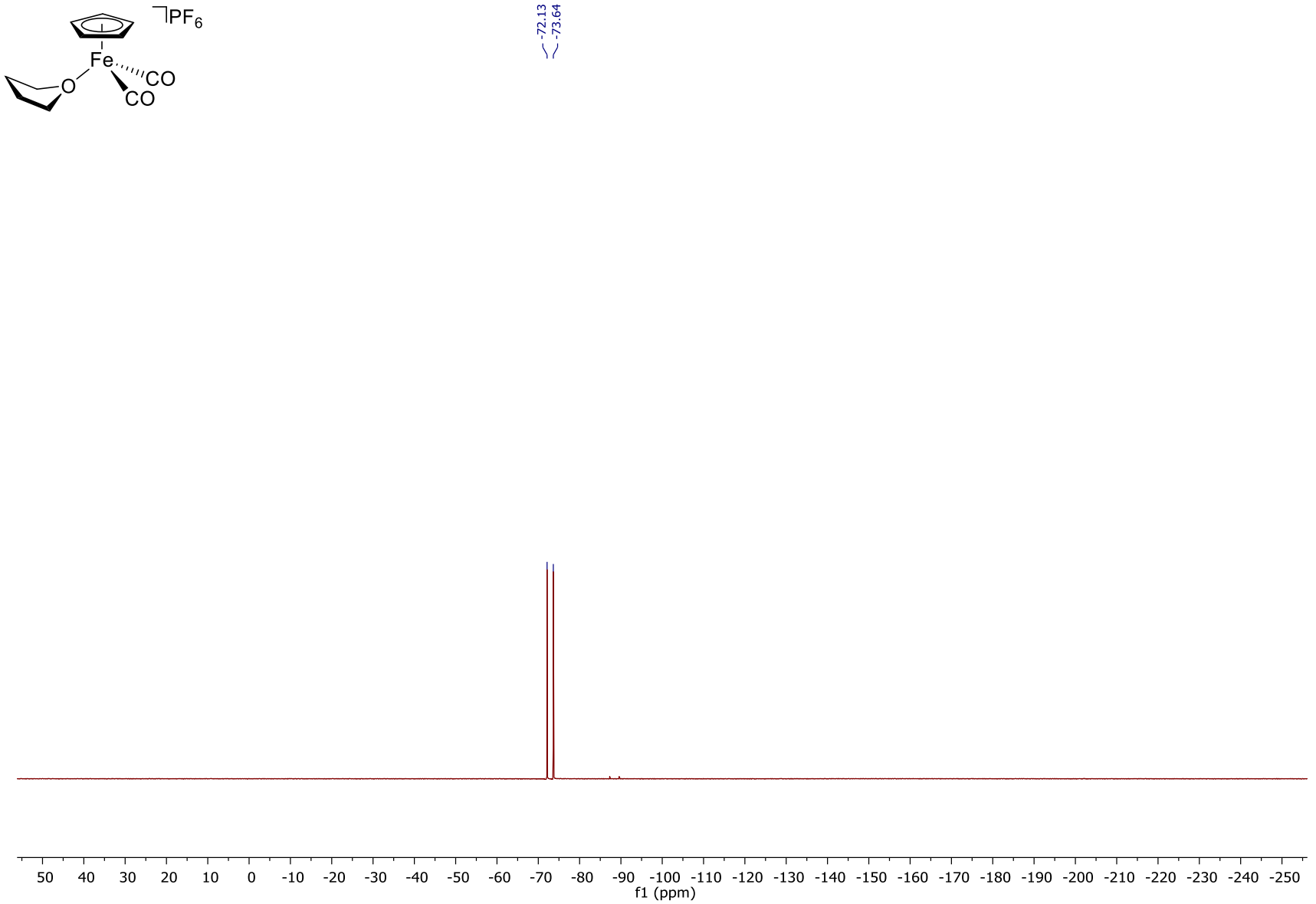


Figure S10. ^{19}F NMR of **(thf)•**Fp^{+}.

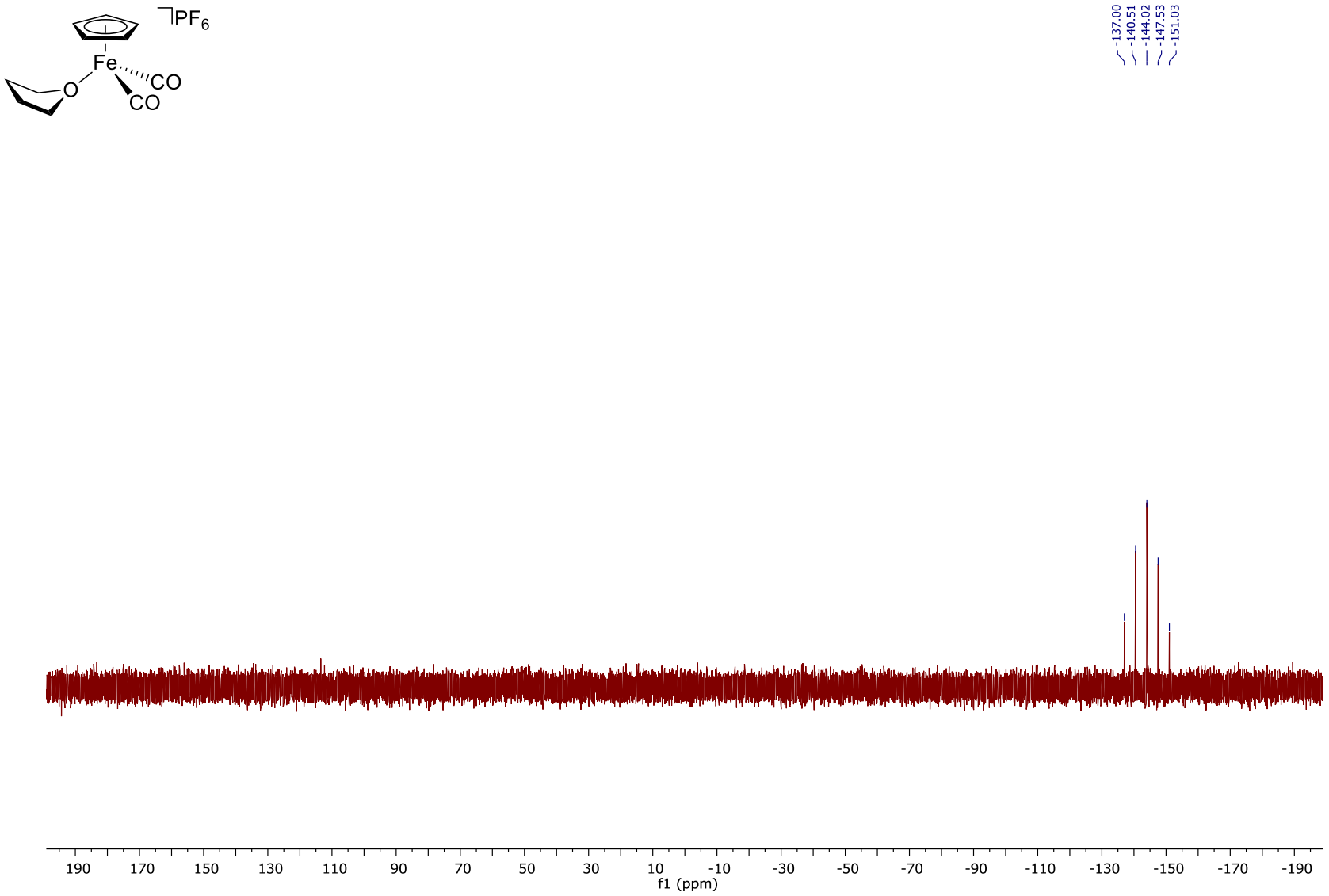


Figure S11. $^{31}P\{^{1}H\}$ NMR of **(thf)•**Fp^{+}.

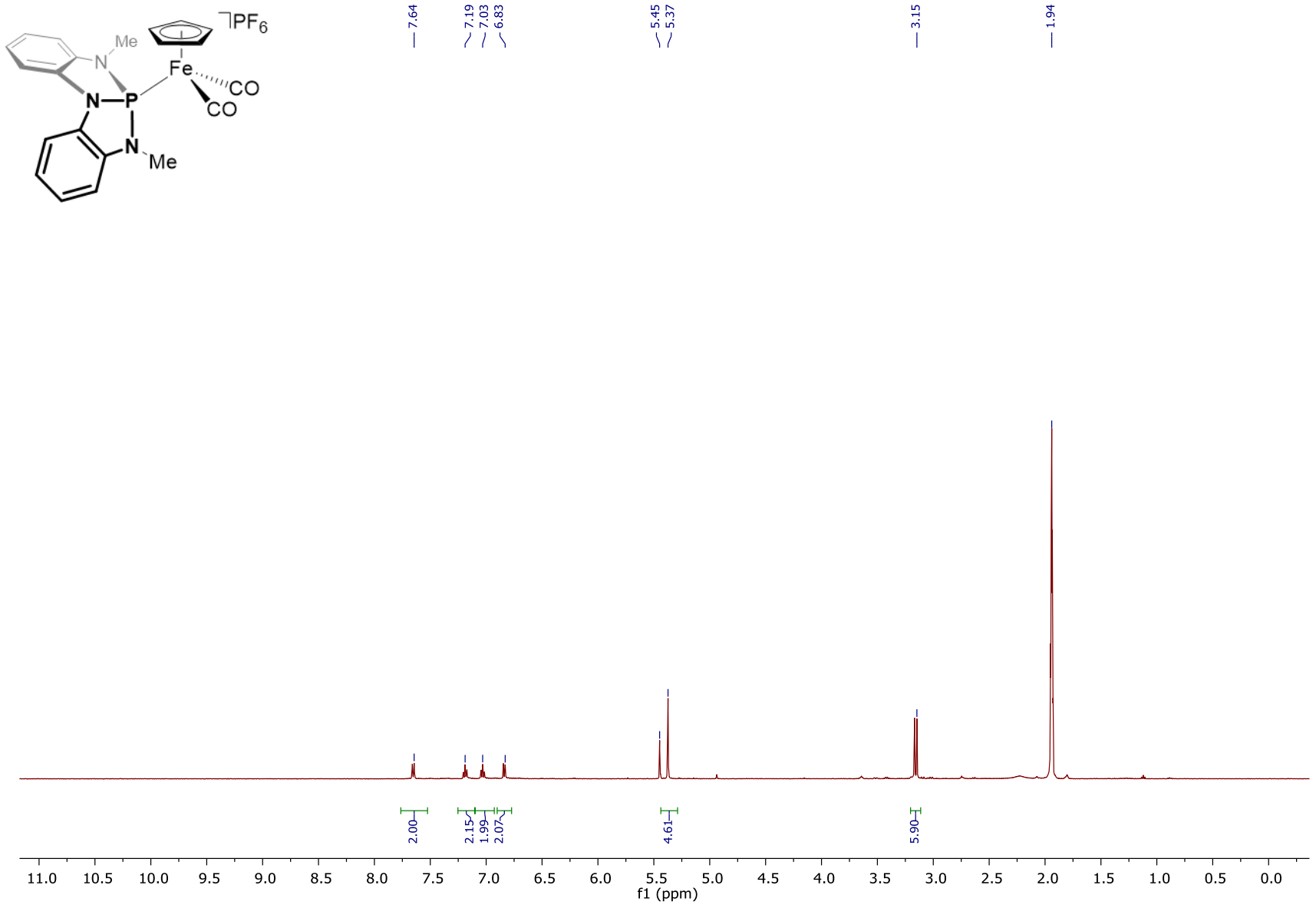


Figure S12. ^{1}H NMR of **1a**•Fp^{+}.

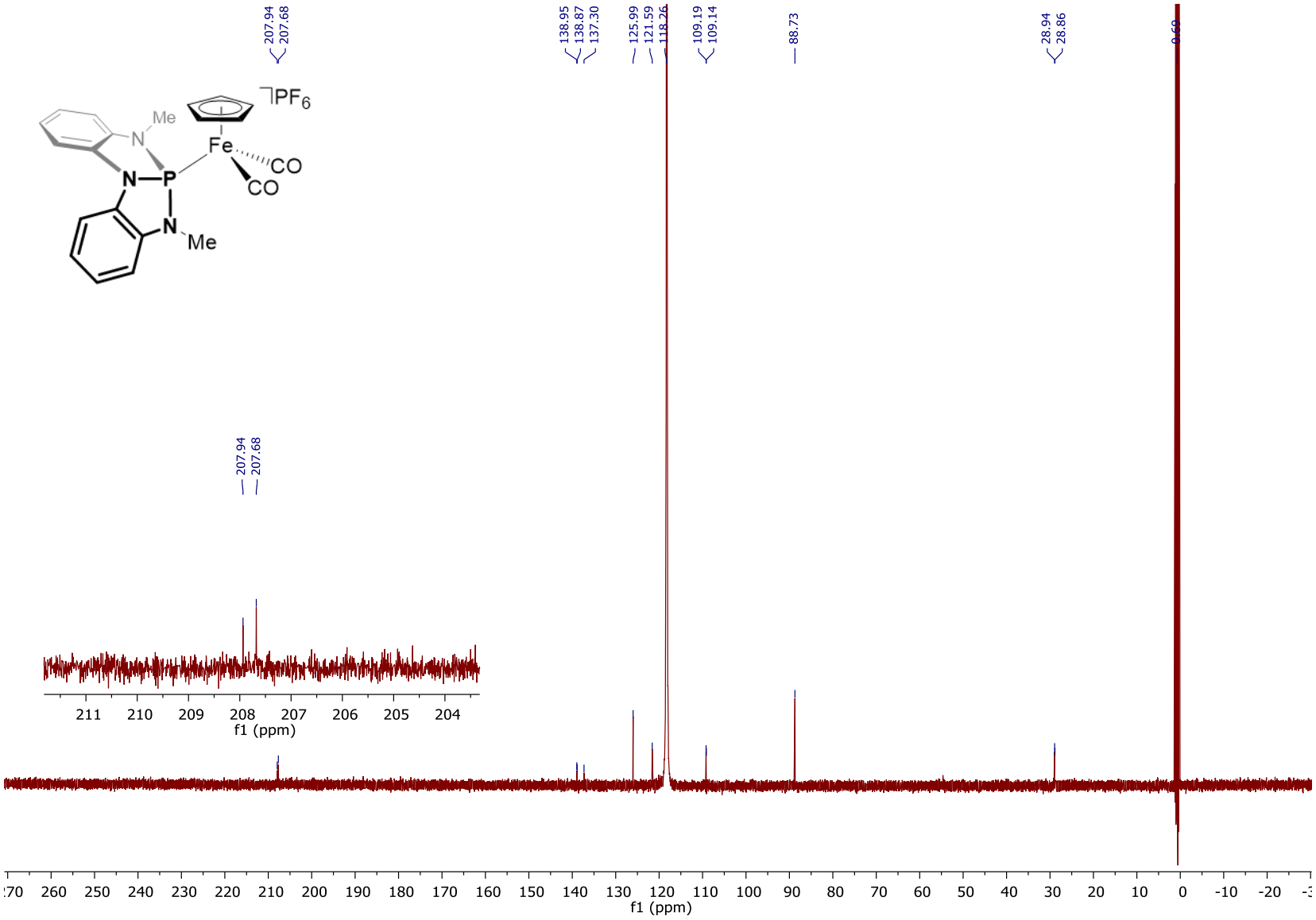


Figure S13. $^{13}C\{^{1}H\}$ NMR of **1a**•Fp^{+}.

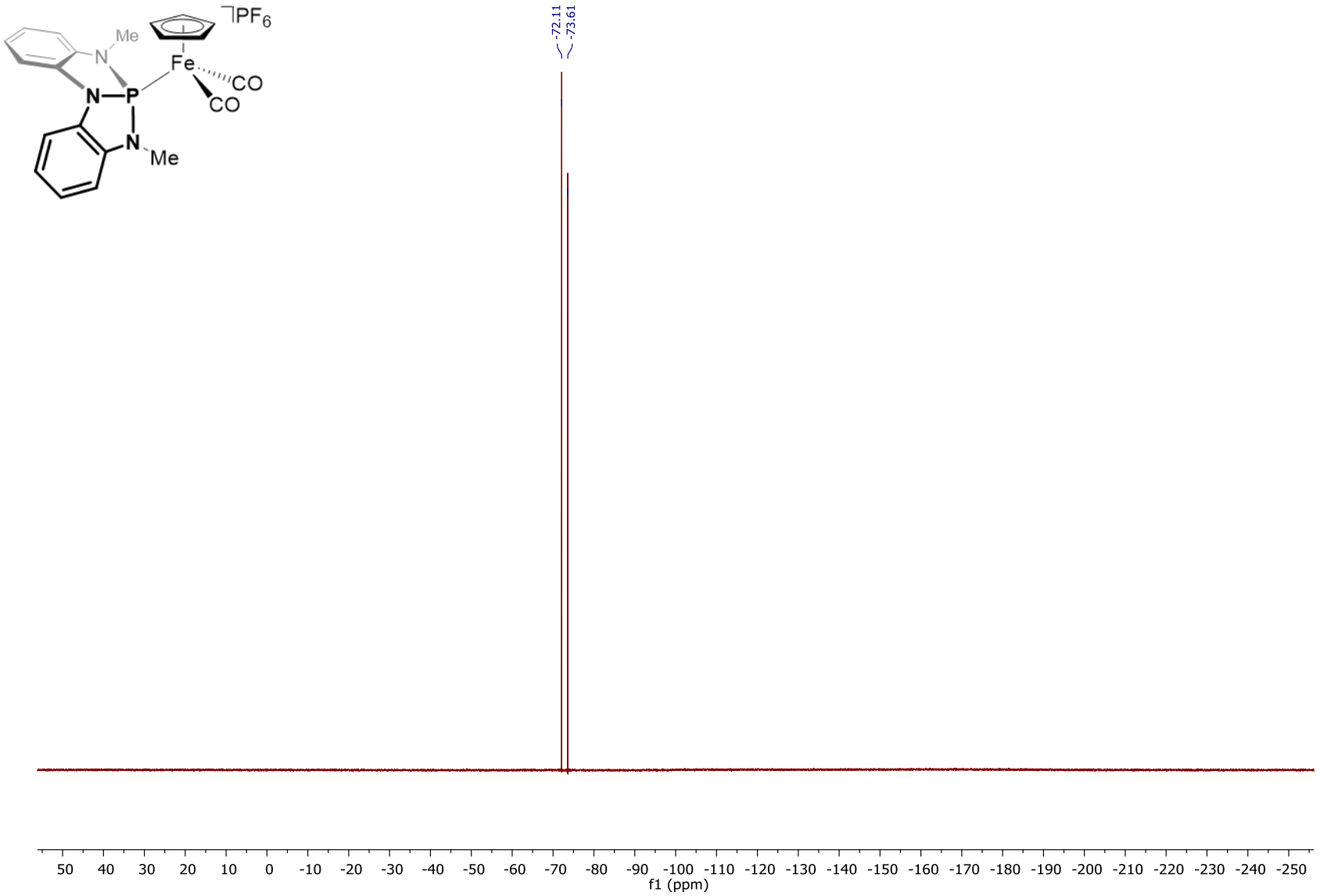


Figure S14. ^{19}F NMR of **1a**•Fp^{+}.

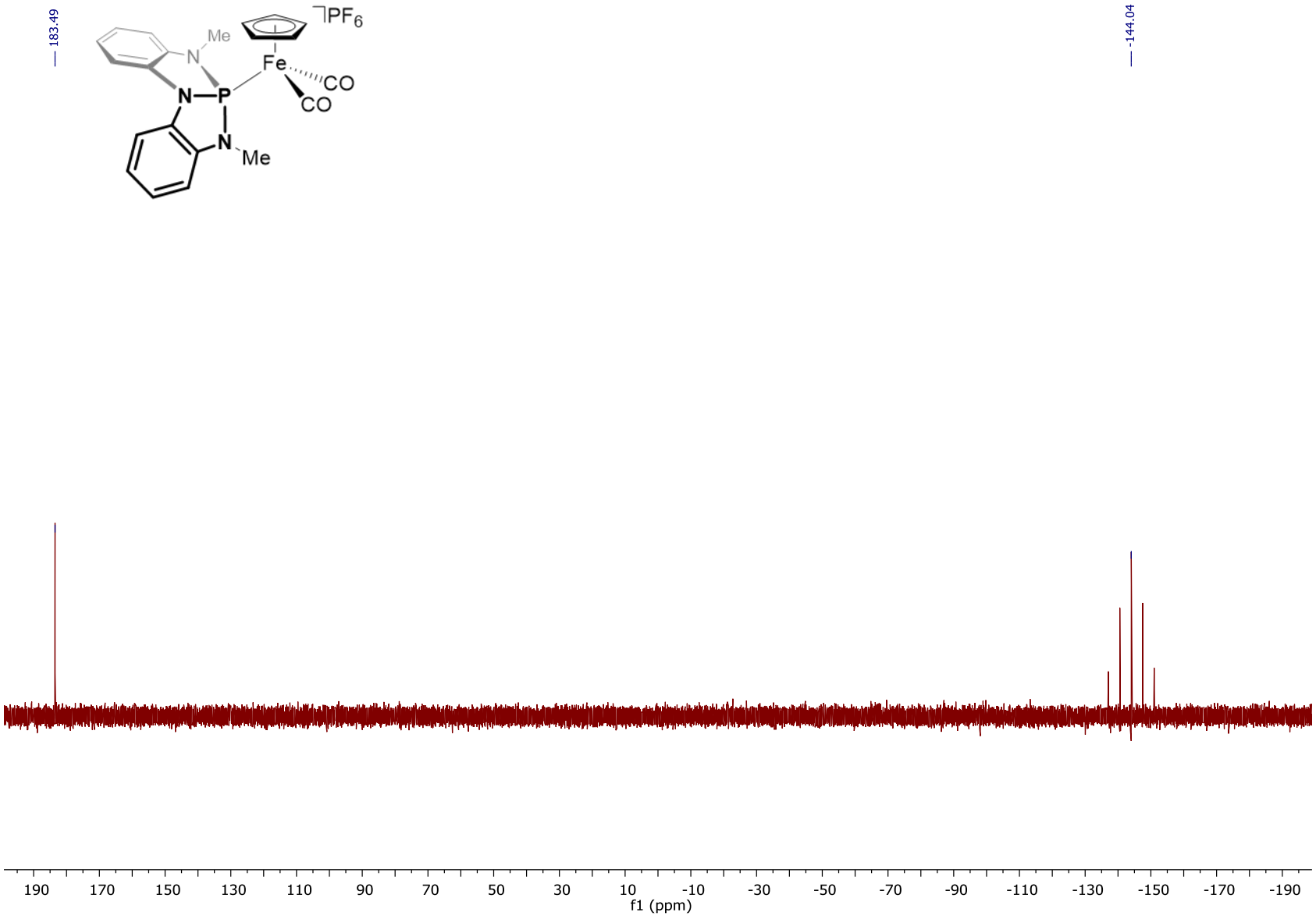


Figure S15. $^{31}P\{^{1}H\}$ NMR of **1a**•Fp^{+}.

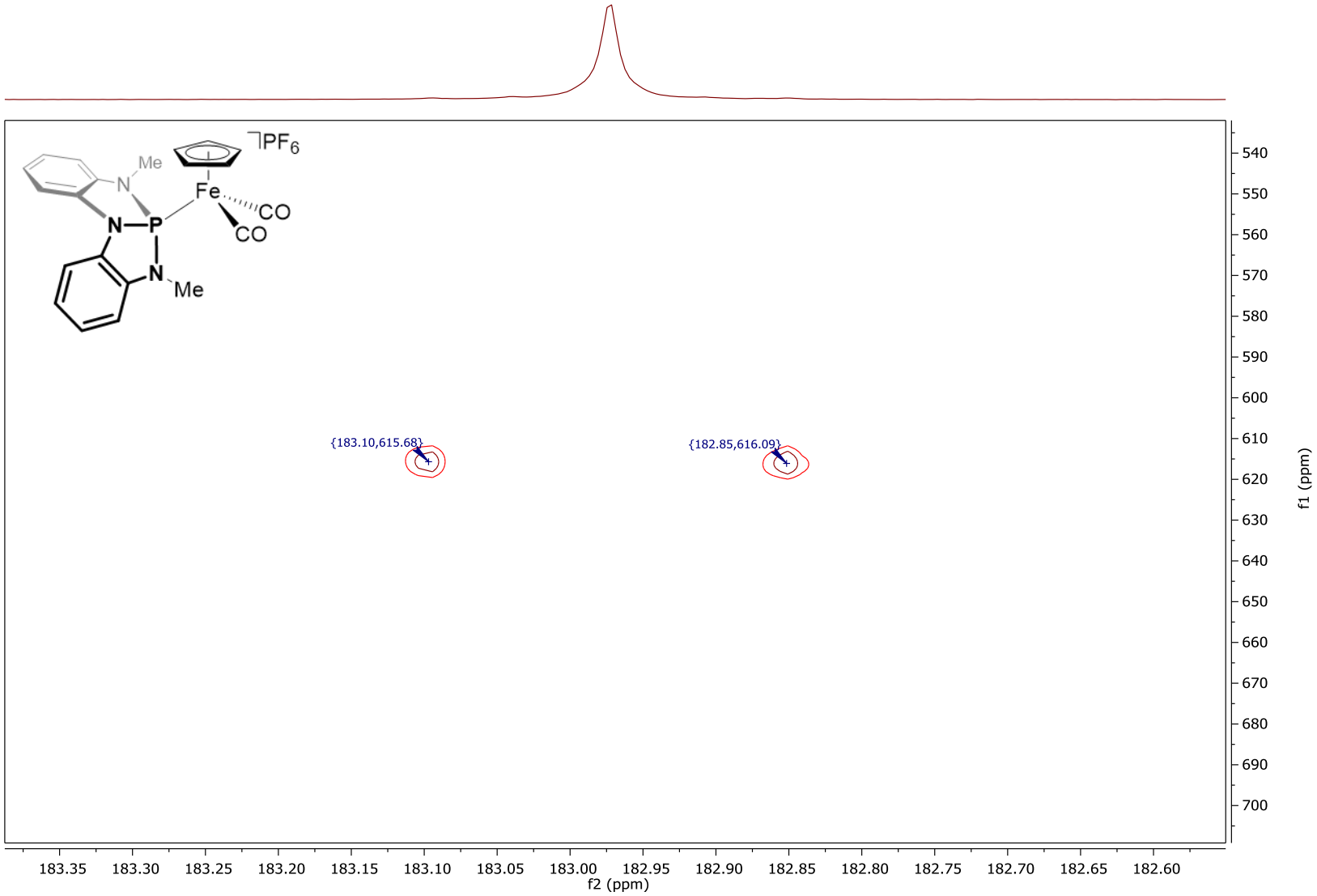


Figure S16. ^{31}P-^{57}Fe 2D NMR of **1a**•Fp^{+}. f1 is ^{57}Fe and f2 is ^{31}P. 1-D ^{31}P{^{1}H} NMR shown along top horizontal axis

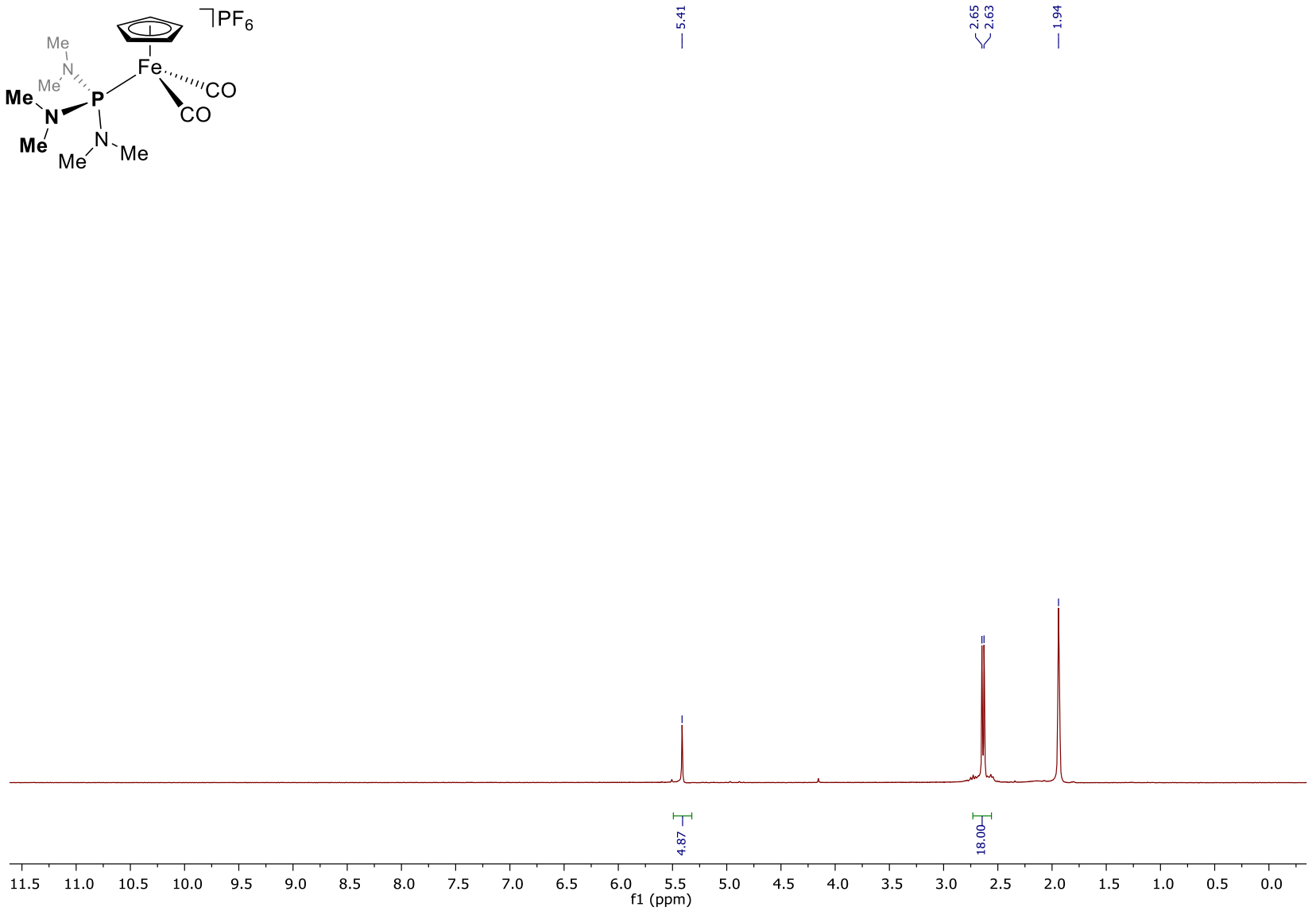


Figure S17. ^{1}H NMR of **1b**•Fp^{+}.

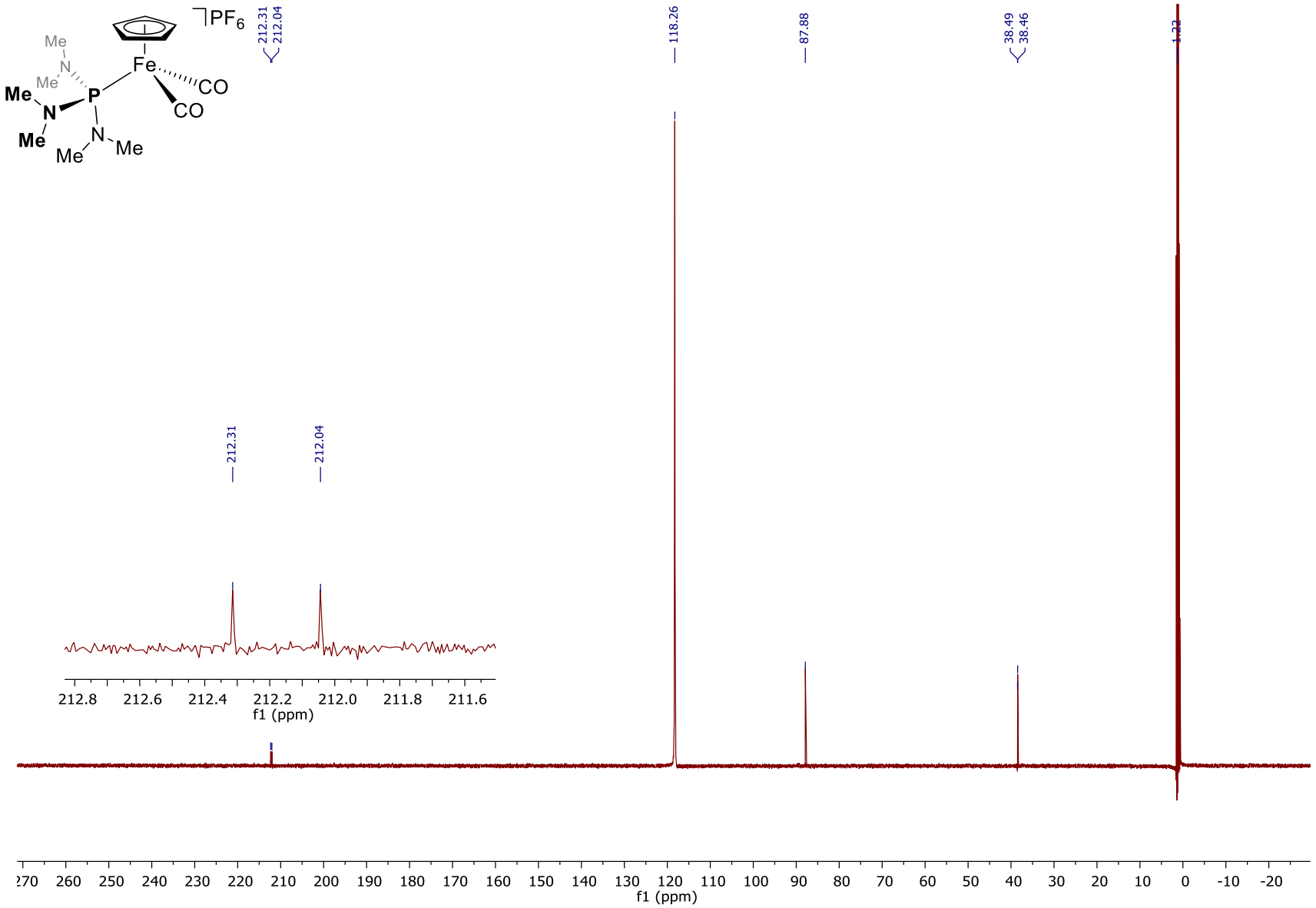


Figure S18. $^{13}C\{^{1}H\}$ NMR of **1b**•Fp^{+}.

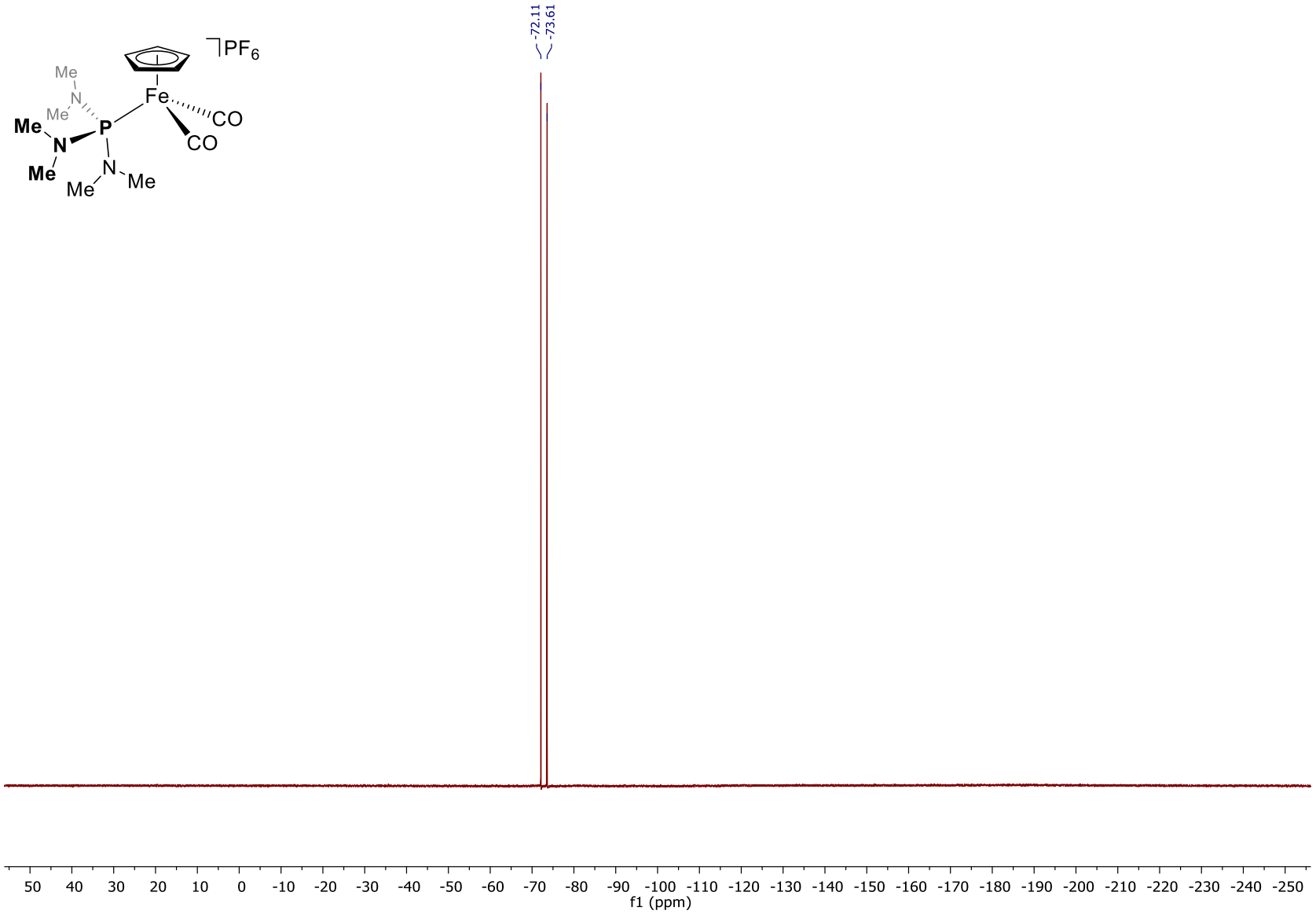


Figure S19. ^{19}F NMR of **1b**•Fp^{+}.

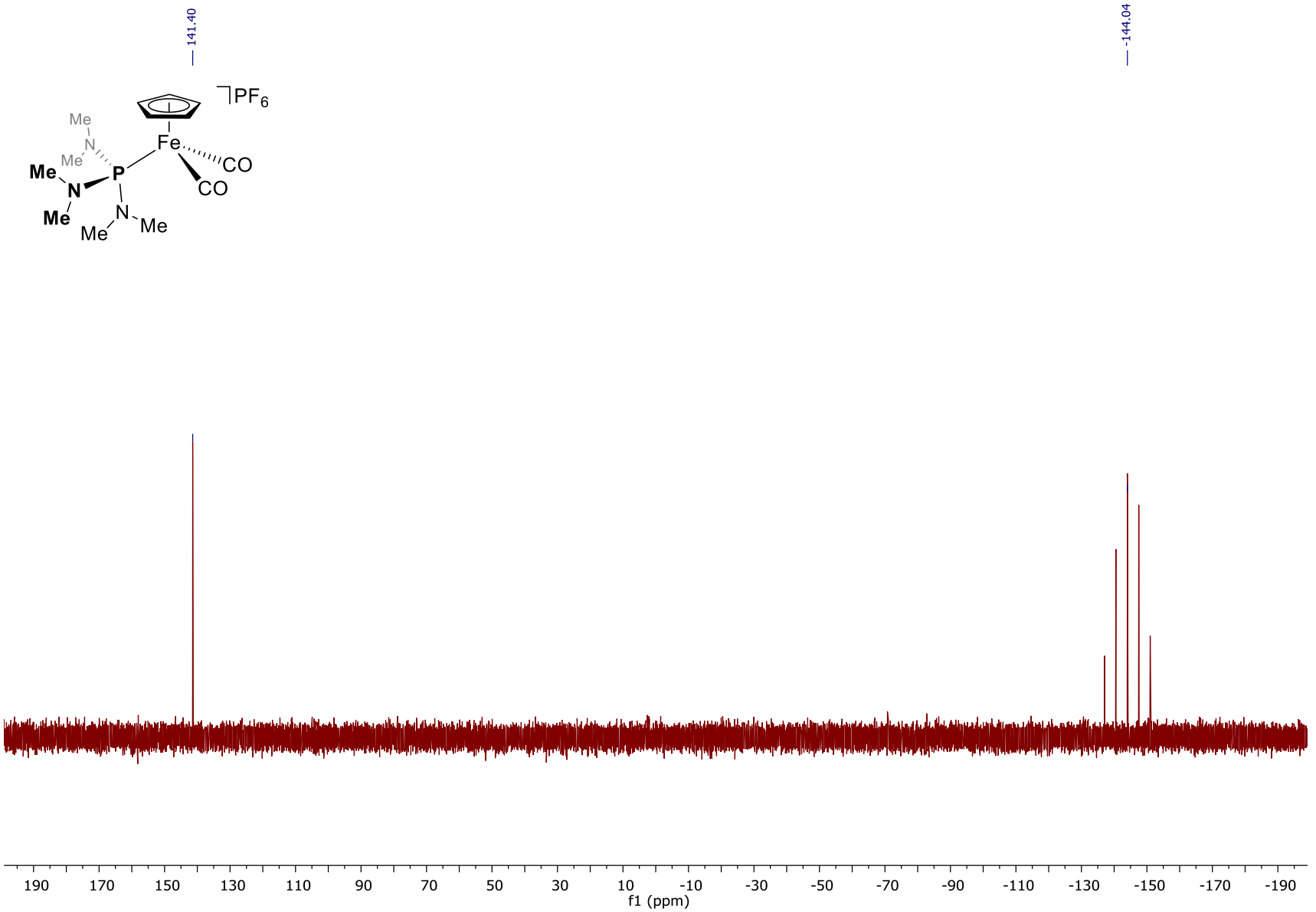


Figure S20. $^{31}P\{^{1}H\}$ NMR of **1b**•Fp^{+}.

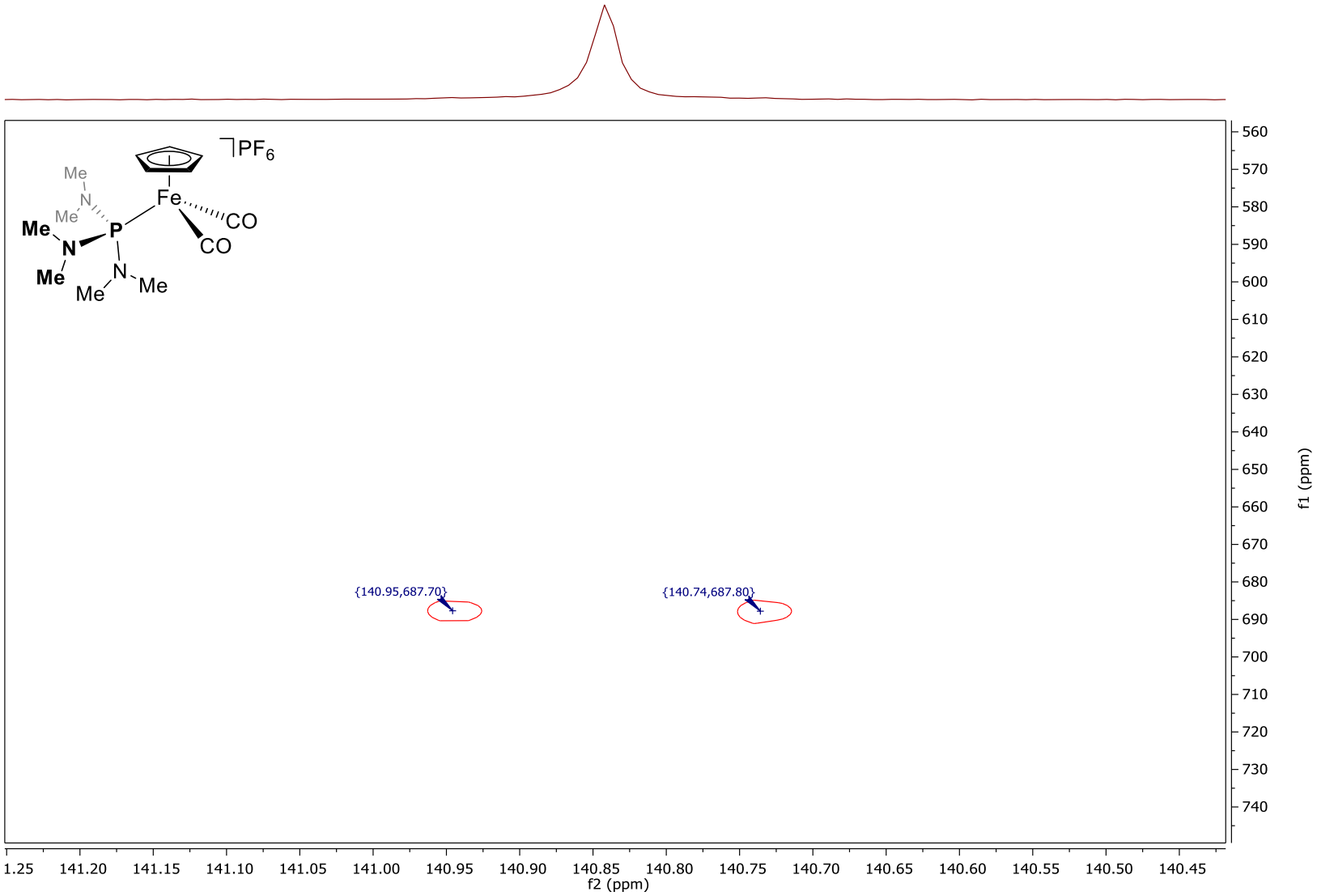


Figure S21. ^{31}P-^{57}Fe 2D NMR of **1b**•Fp^{+}. f1 is ^{57}Fe and f2 is ^{31}P. 1-D ^{31}P{^{1}H} NMR shown along top horizontal axis

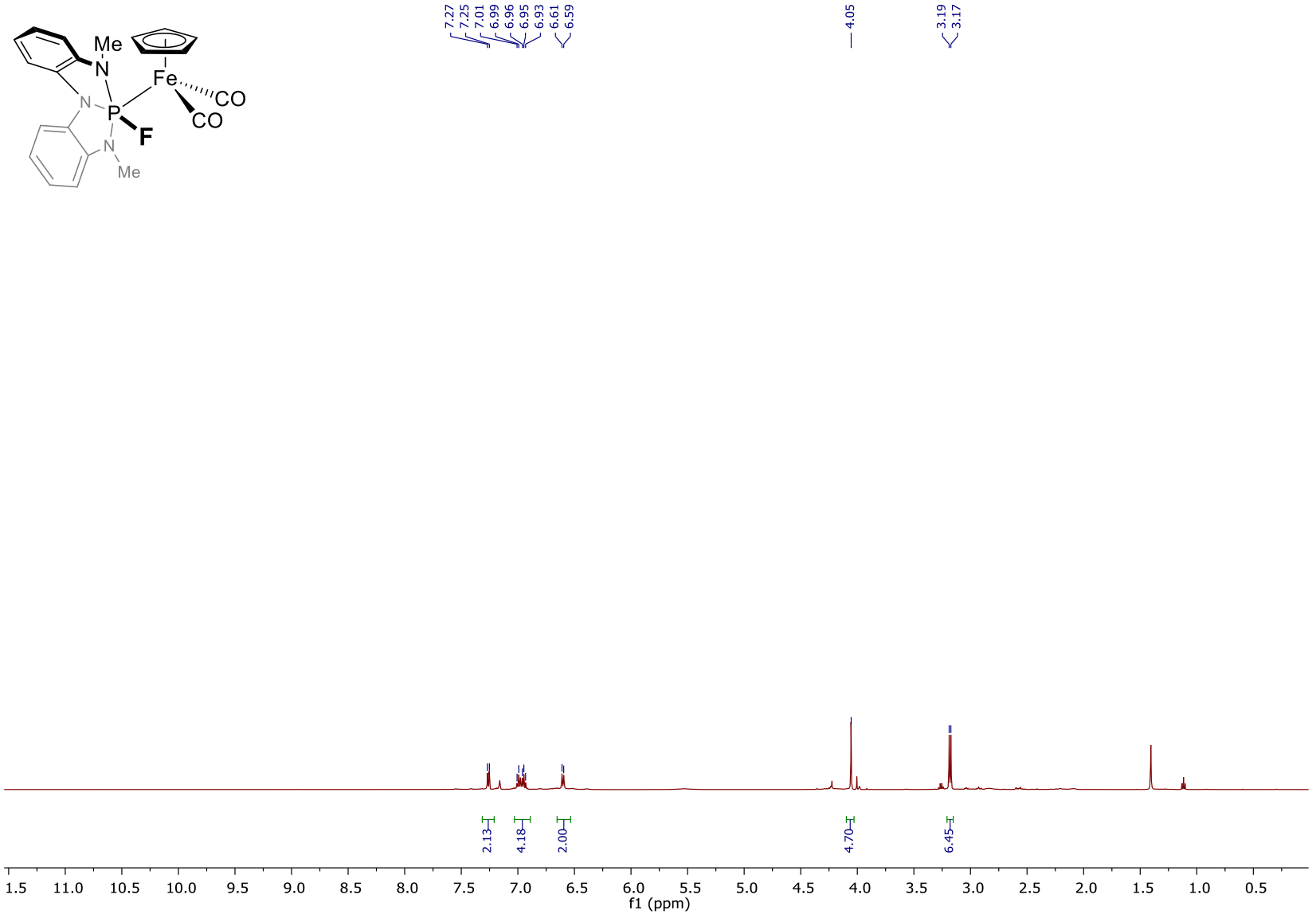


Figure S22. ^{1}H NMR of **1a^{F}**•Fp.

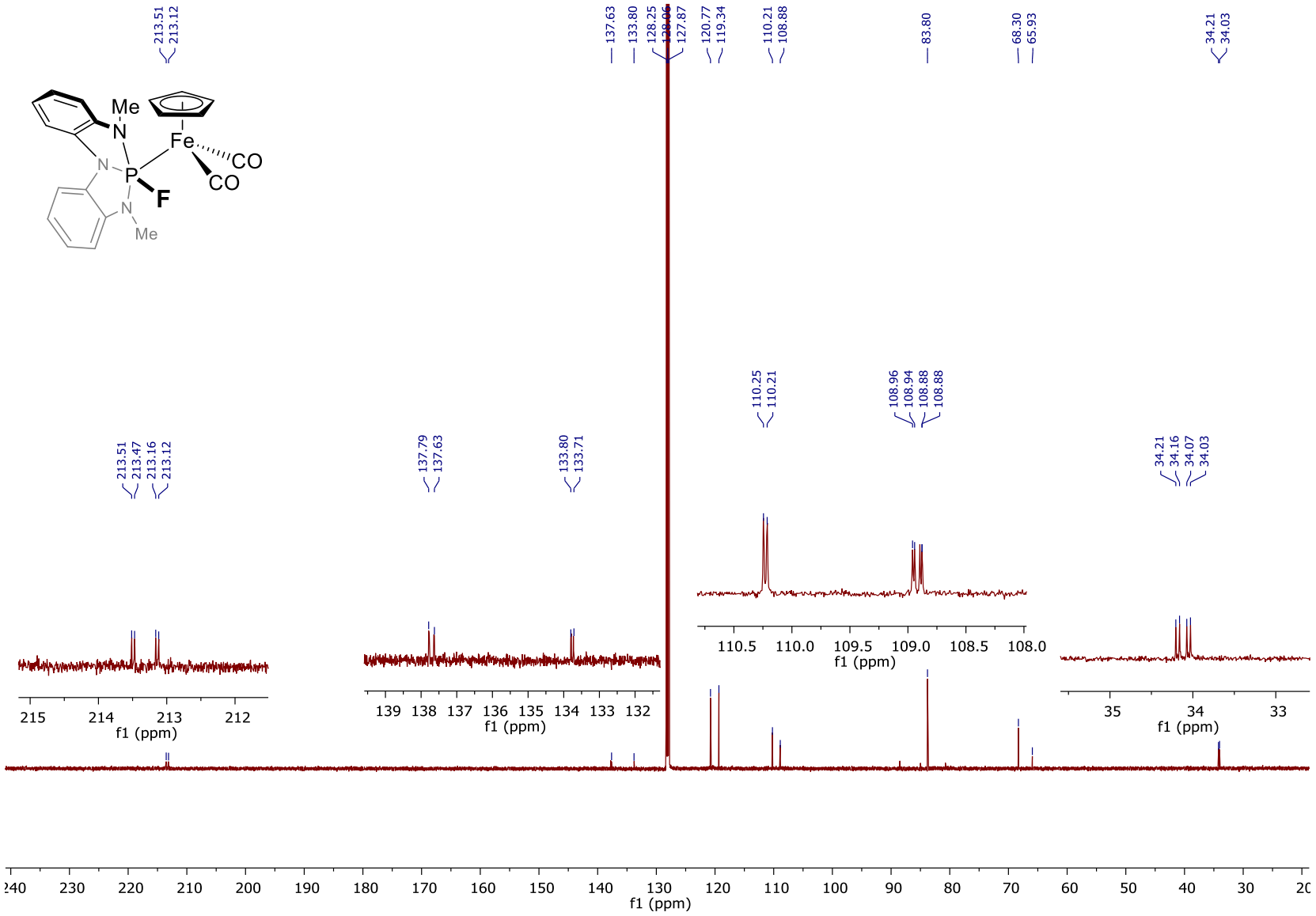


Figure S23. $^{13}C\{^{1}H\}$ NMR of **1a^{F}**•Fp.

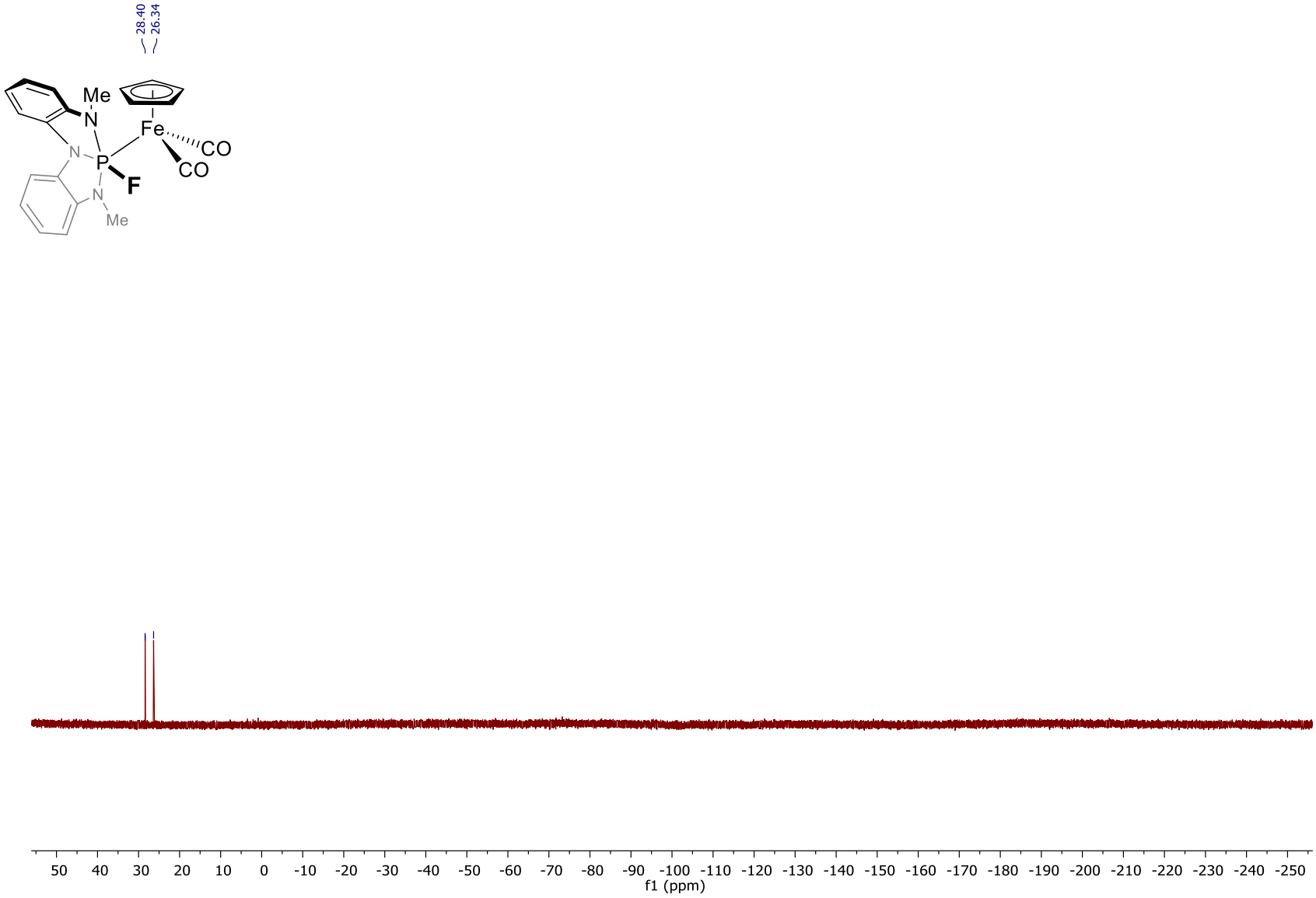


Figure S24. ^{19}F NMR of **1a^{F}**•Fp.

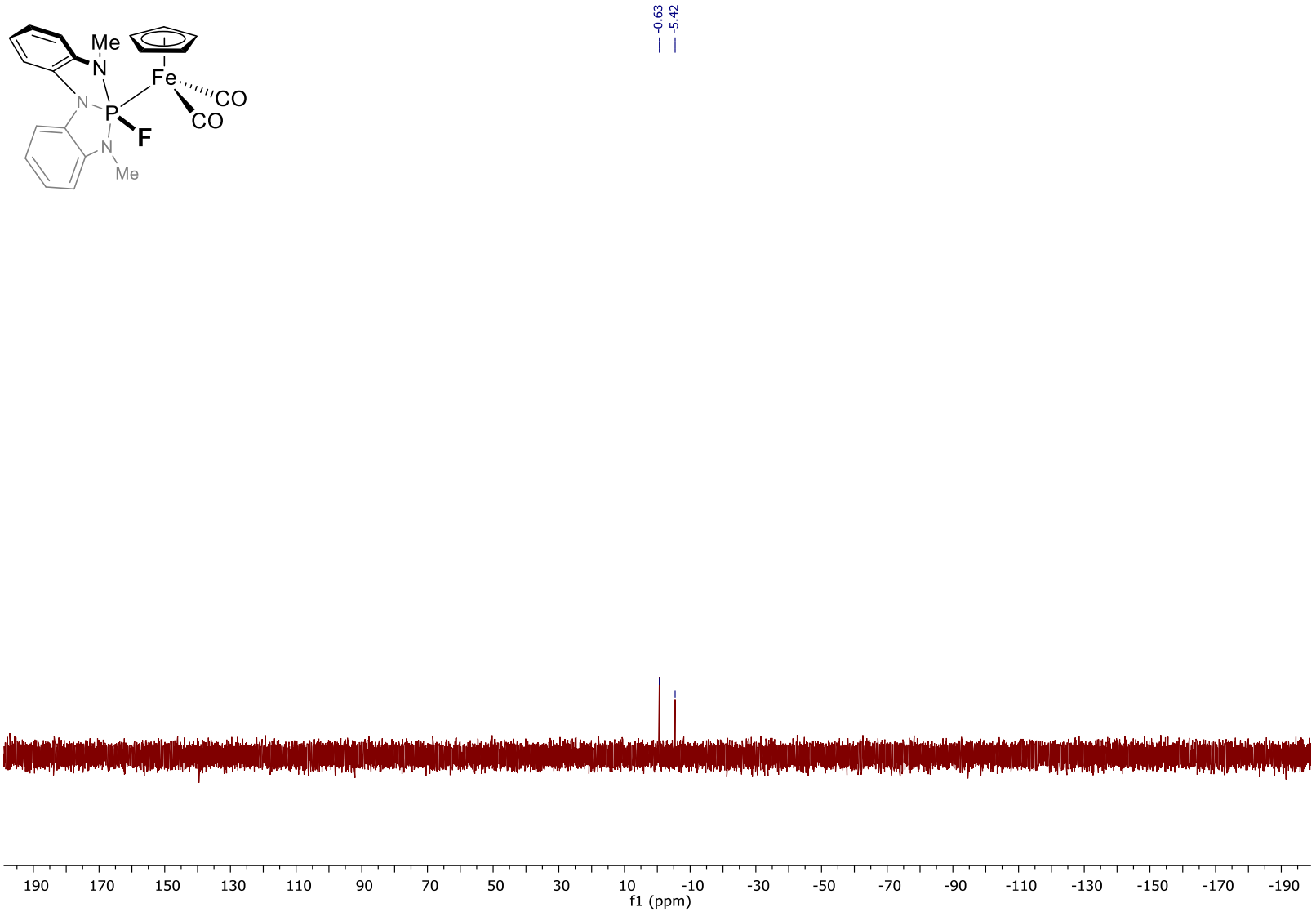


Figure S25. $^{31}P\{^{1}H\}$ NMR of **1a^{F}**•Fp.

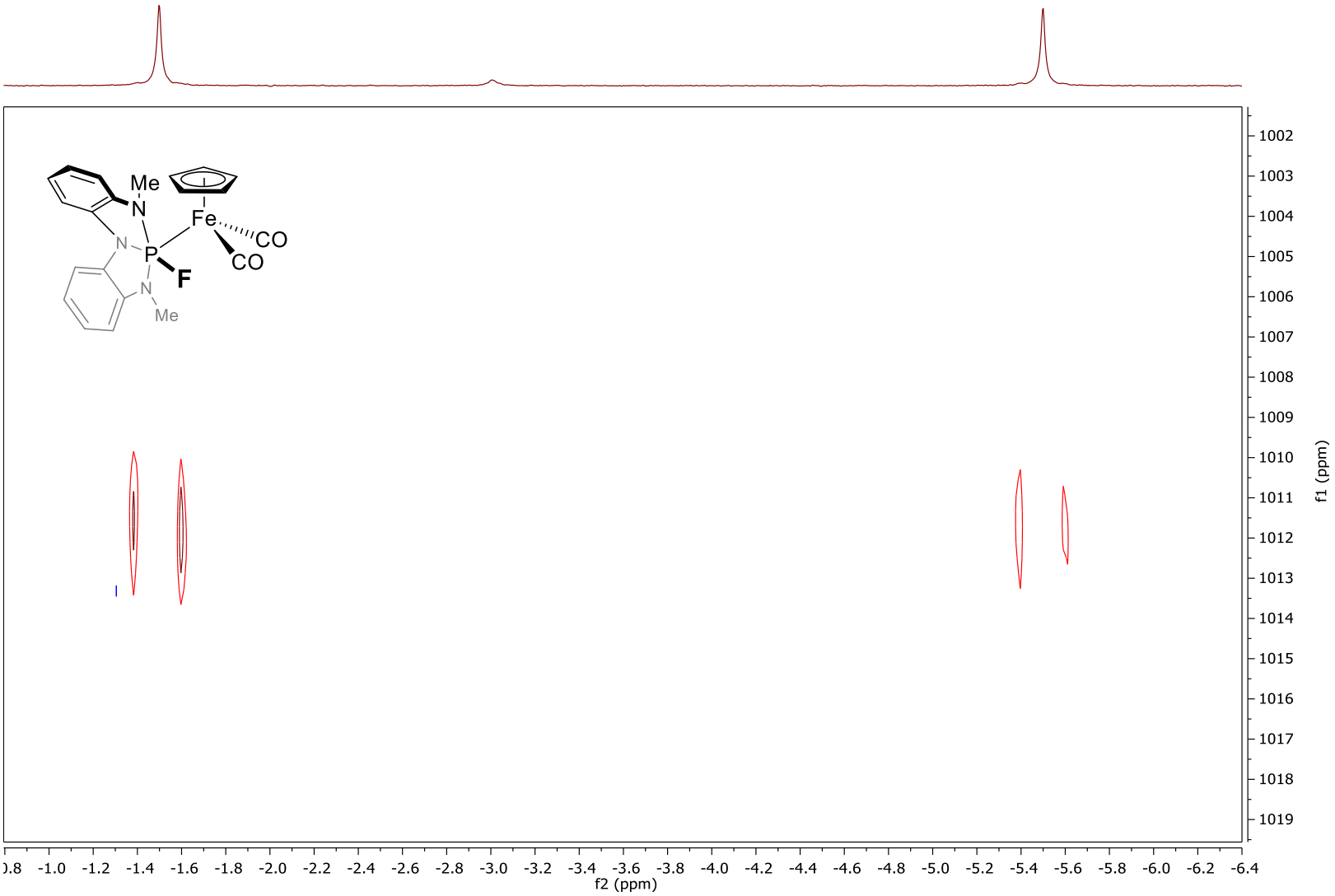


Figure S26. ^{31}P-^{57}Fe 2D NMR of **1a^{F}**•Fp. f1 is ^{57}Fe and f2 is ^{31}P. 1-D ^{31}P{^{1}H} NMR shown along top horizontal axis

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