Amine-catalyzed substitution of iodide in $CpFe(CO)_2I$ by phosphine and bisphosphine ligands

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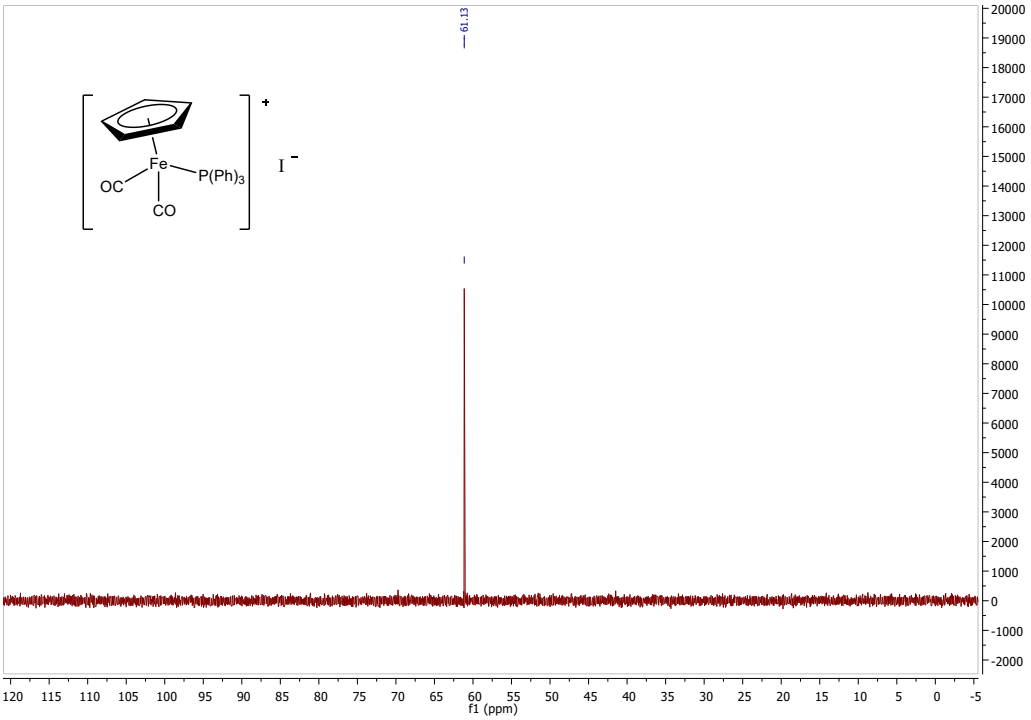

Figure S1. 243 MHz ^{31}P NMR spectrum of **2** in $CDCl_3$

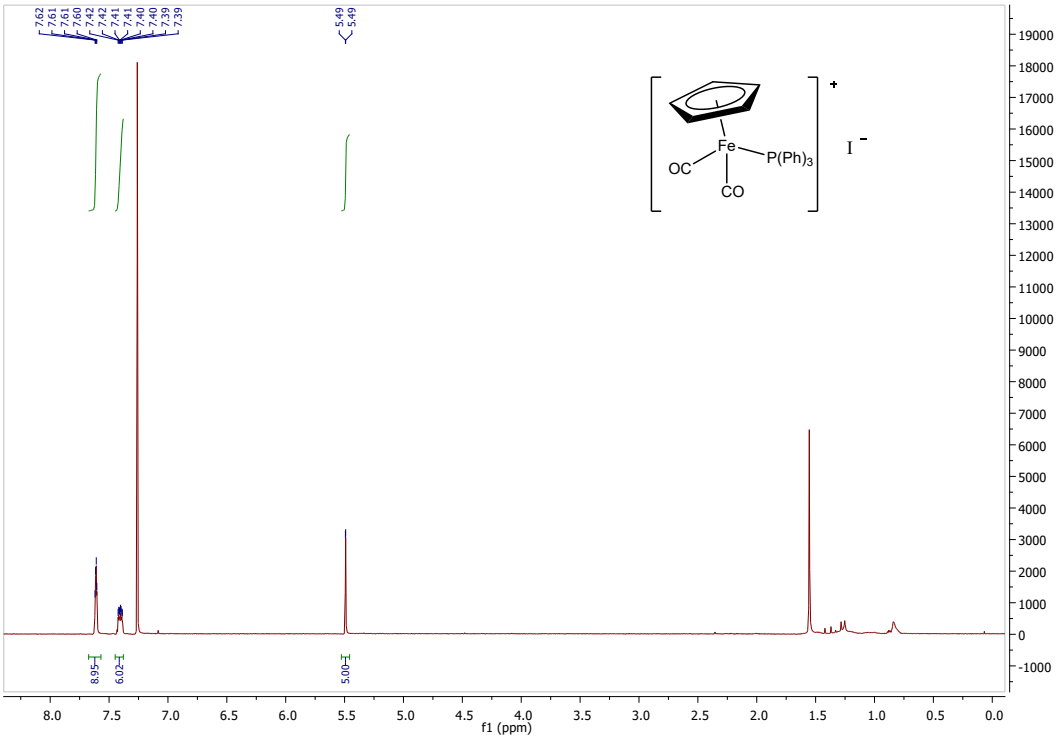

Figure S2. 600 MHz ^{1}H NMR spectrum of **2** in $CDCl_3$

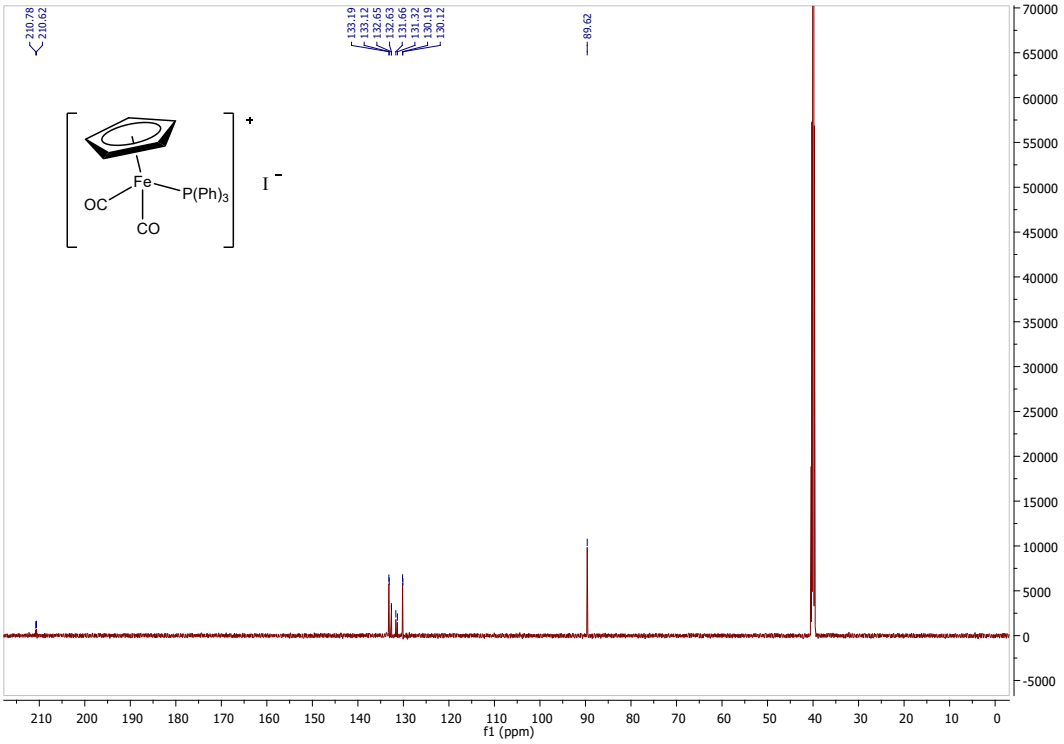

Figure S3. 151 MHz ^{13}C NMR spectrum of **2** in DMSO

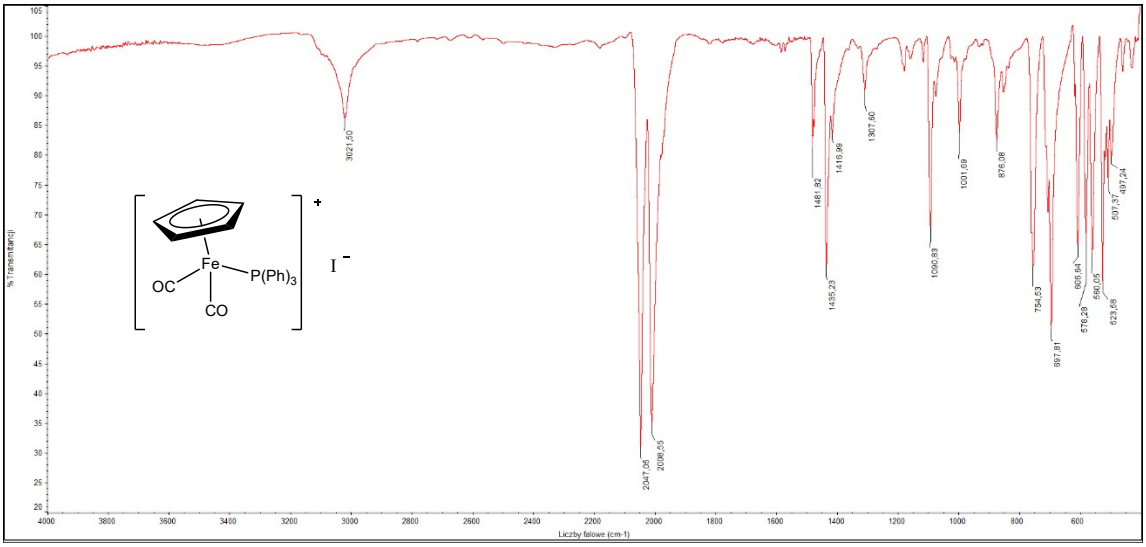

Figure S4. IR spectrum of **2** (KBr, cm^{-1})

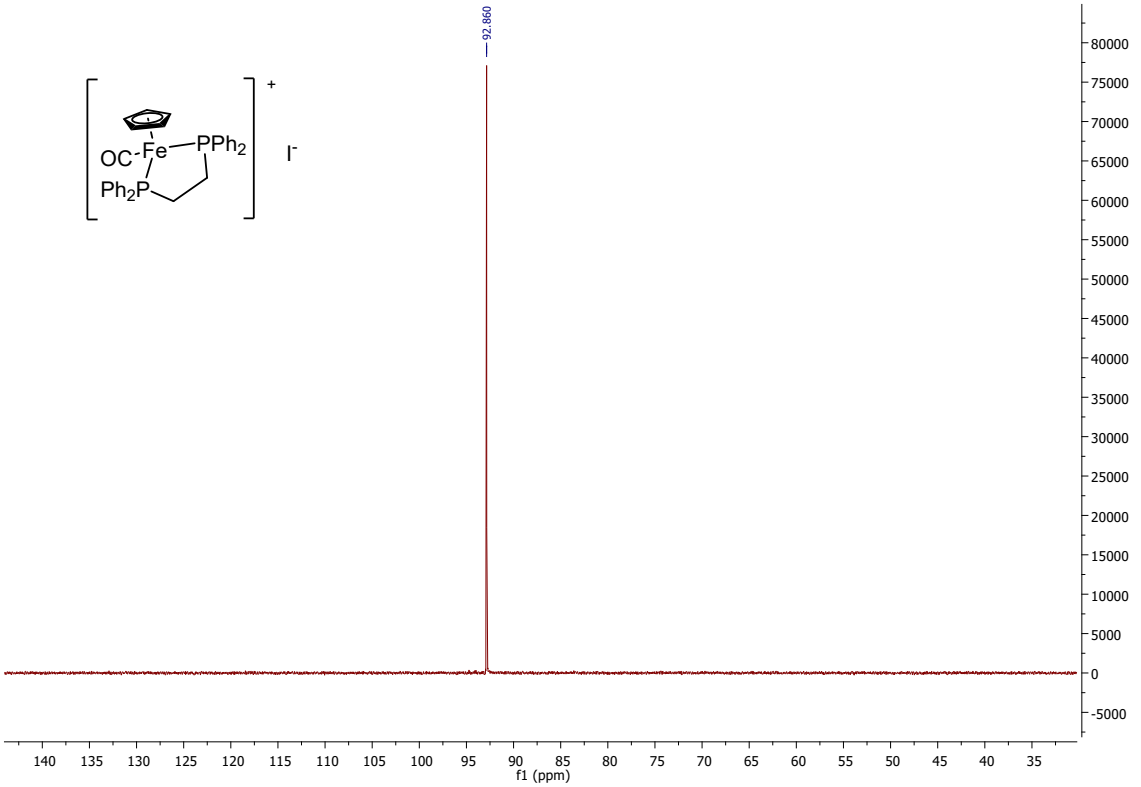

Figure S5. 243 MHz ^{31}P NMR spectrum of **4** in DMSO

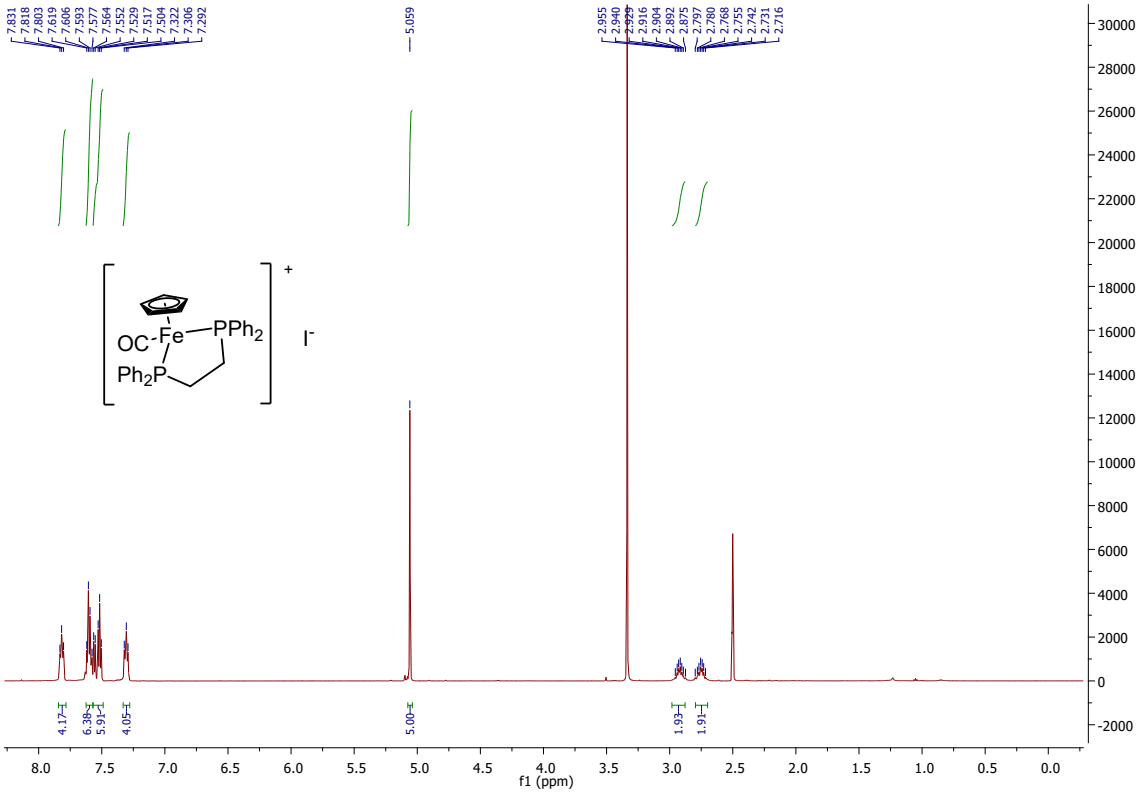

Figure S6. 600 MHz ^{1}H NMR spectrum of **4** in DMSO

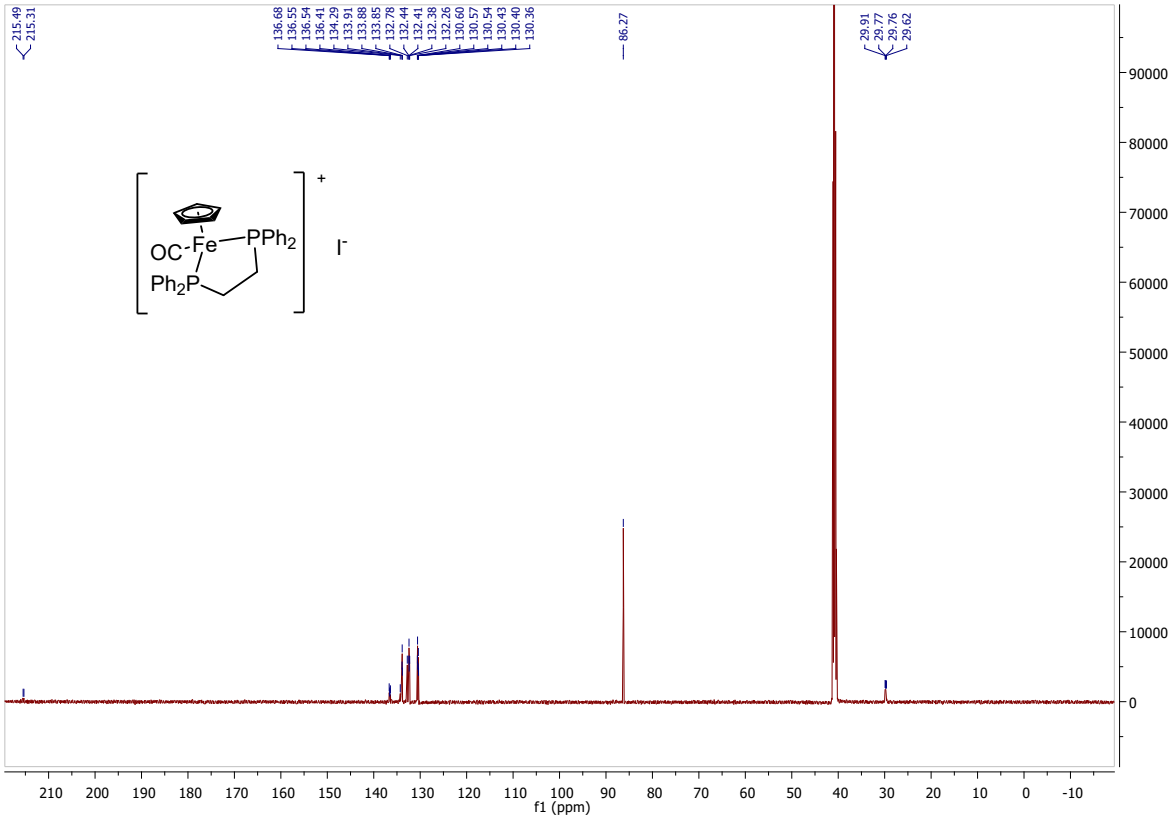

Figure S7. 151 MHz ^{13}C NMR spectrum of **4** in MeOD

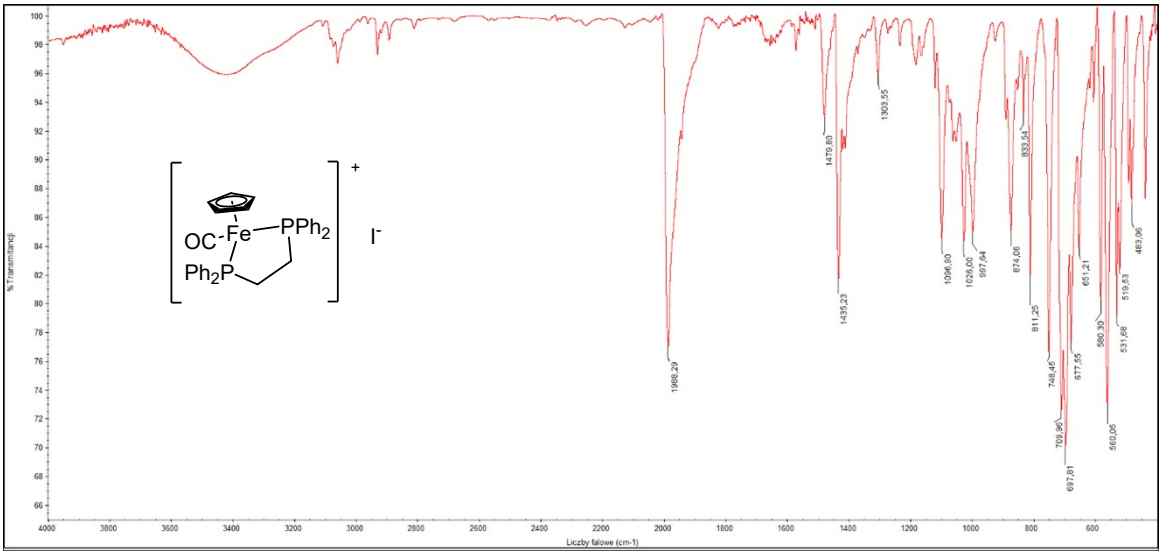

Figure S8. IR spectrum of **4** (KBr, cm^{-1})

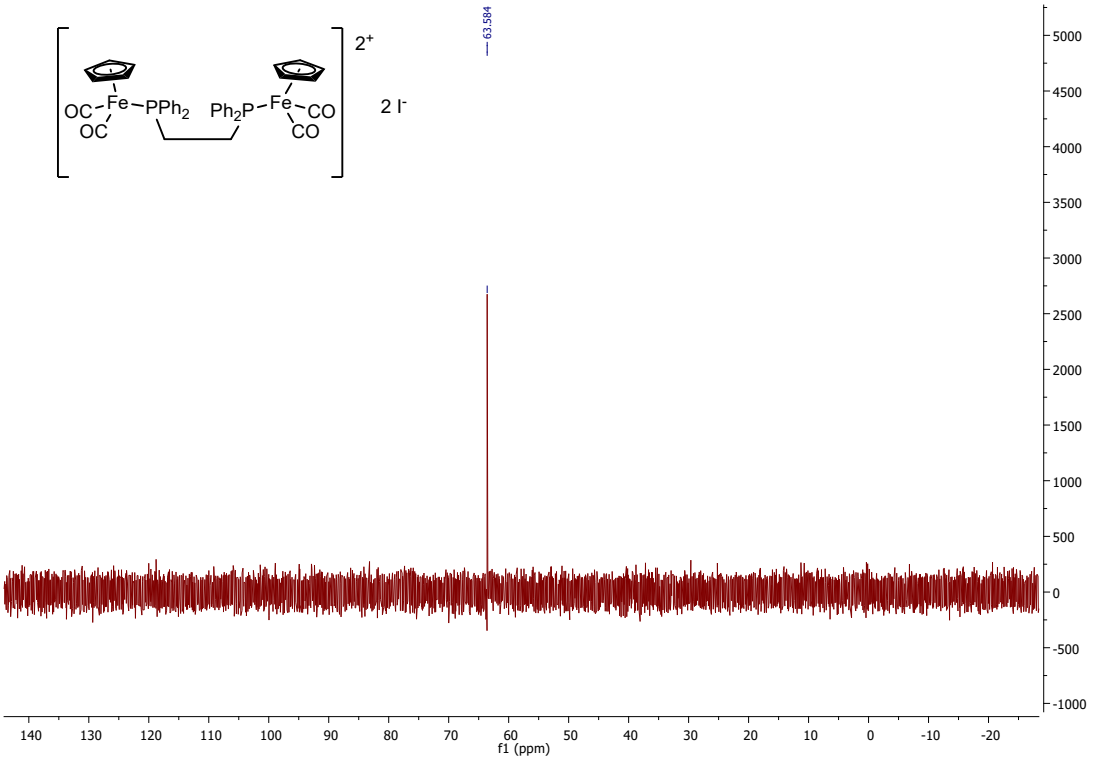

Figure S9. 243 MHz ^{31}P NMR spectrum of **5** in DMSO

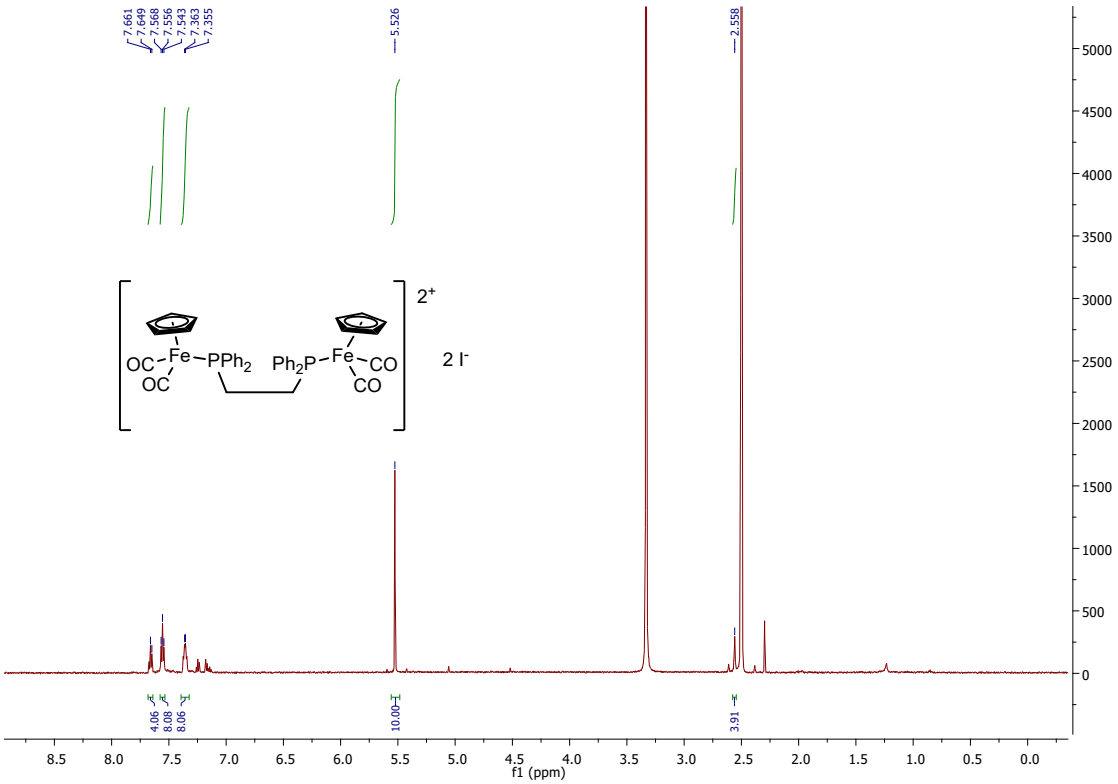

Figure S10. 600 MHz ^{1}H NMR spectrum of **5** in DMSO

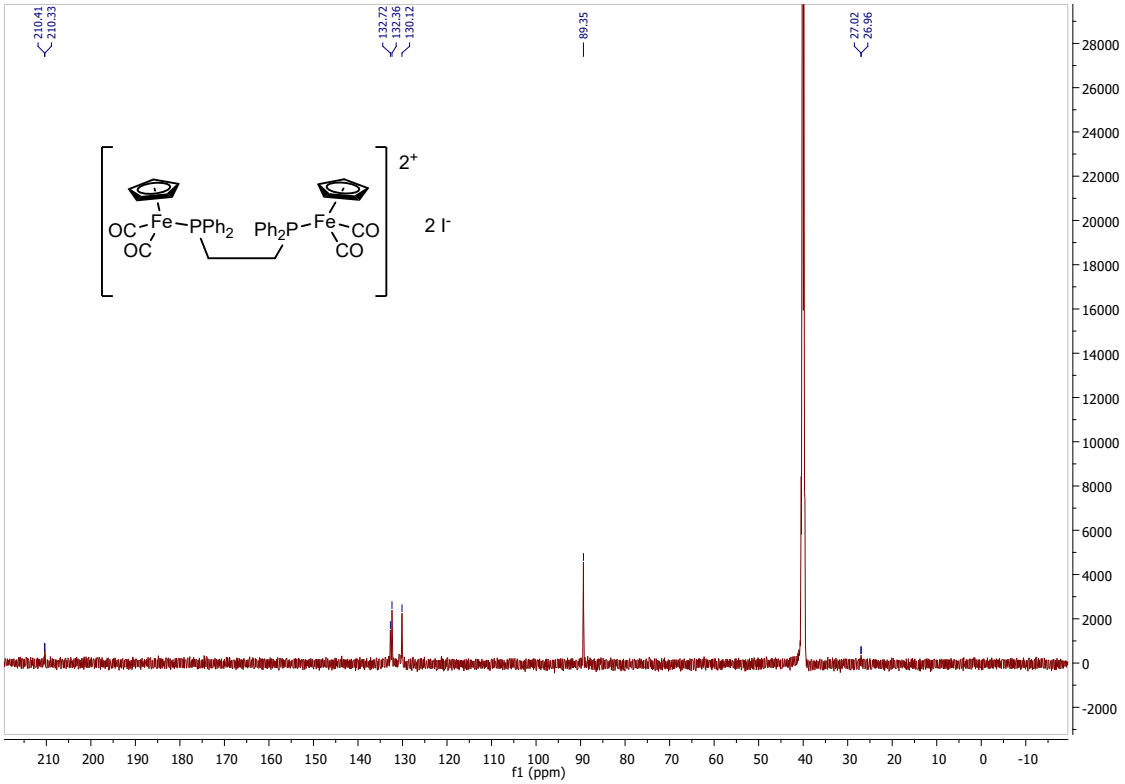

Figure S11. 151 MHz ^{13}C NMR spectrum of **5** in DMSO

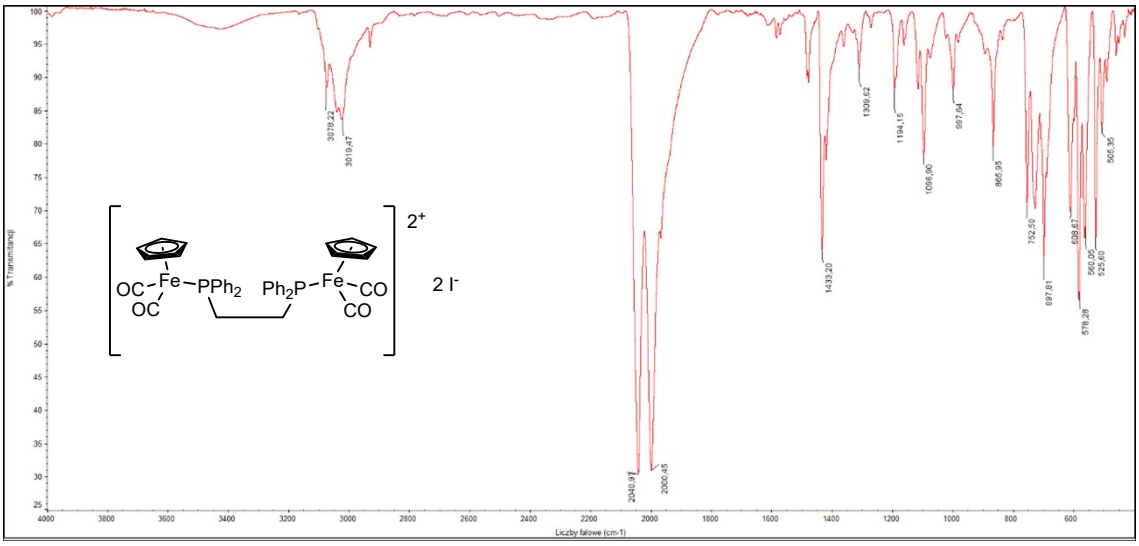

Figure S12. IR spectrum of **5** (KBr, cm^{-1})

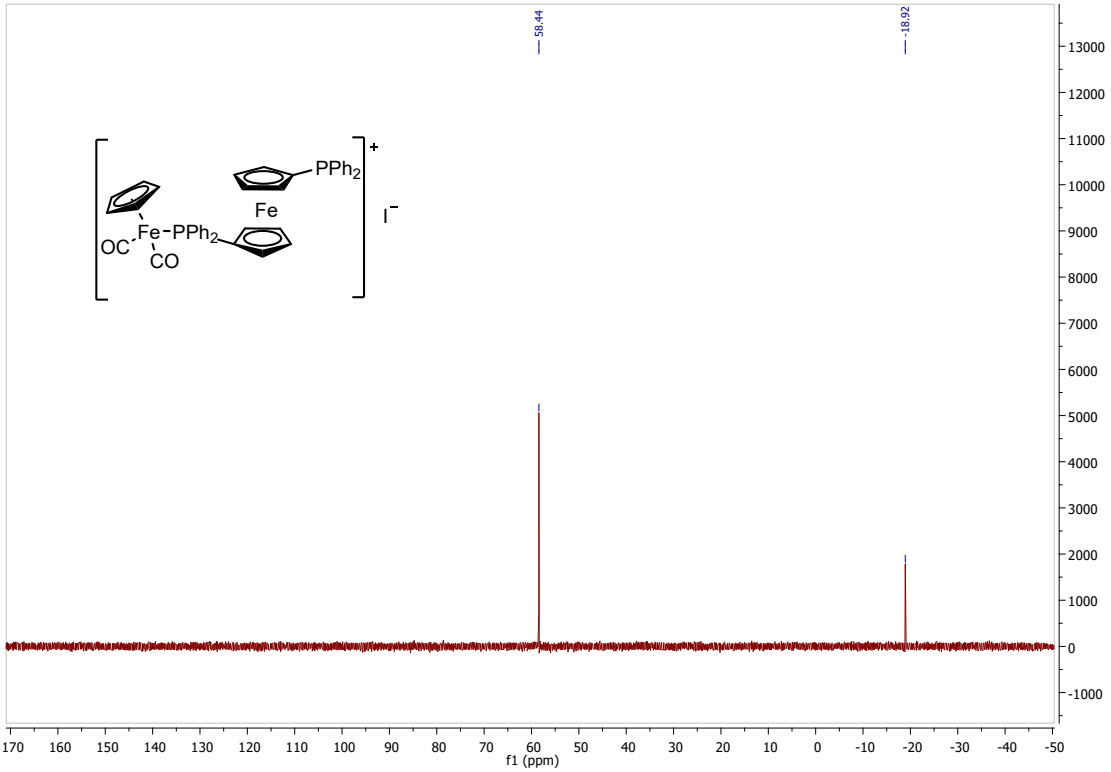

Figure S13. 243 MHz ^{31}P NMR spectrum of **8** in $CDCl_3$

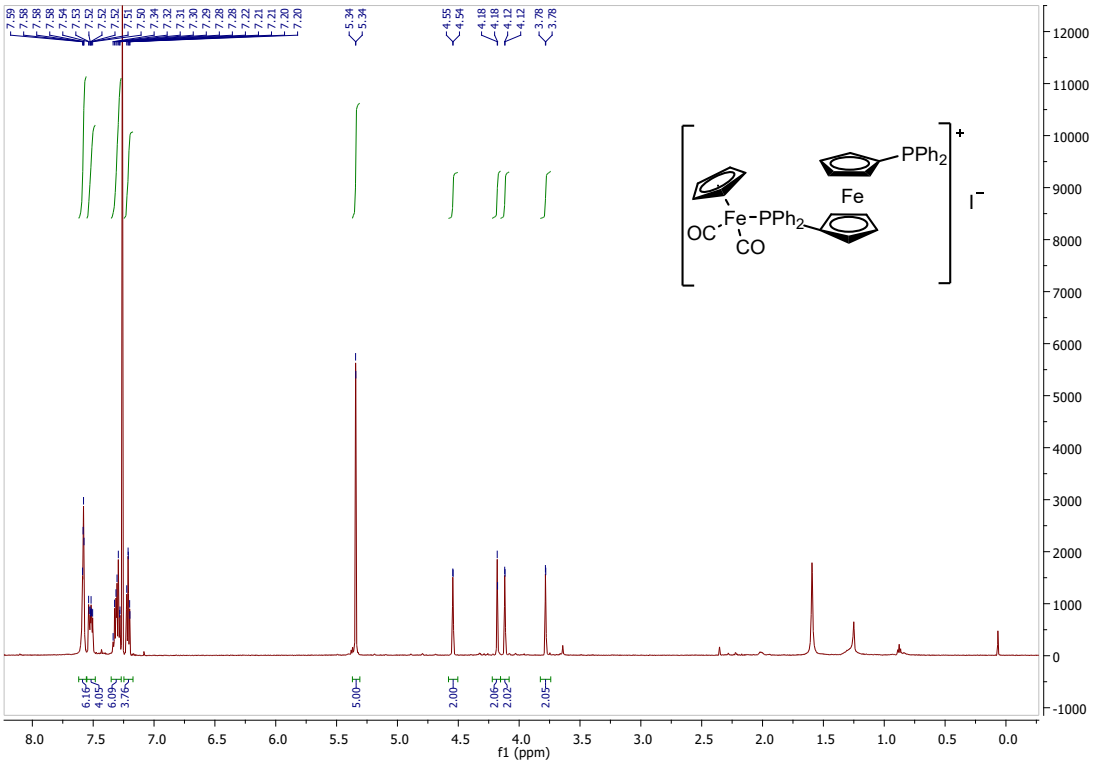

Figure S14. 600 MHz ^{1}H NMR spectrum of **8** in $CDCl_3$

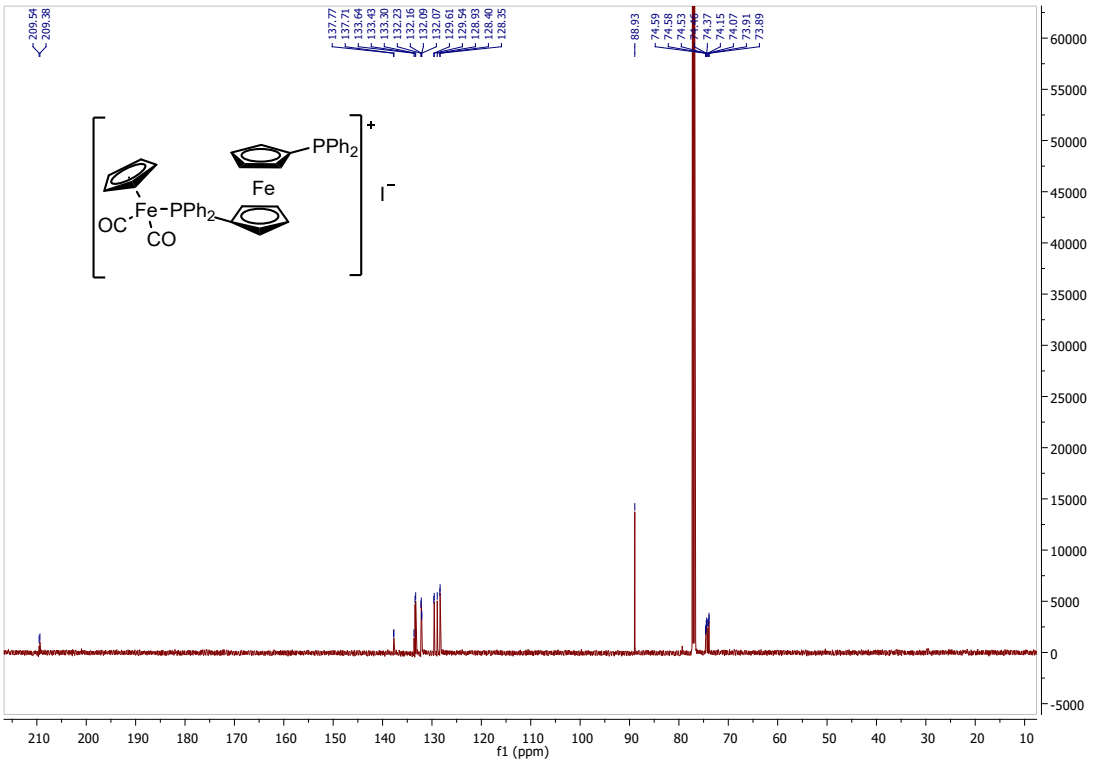

Figure S15. 151 MHz ^{13}C NMR spectrum of **8** in $CDCl_3$

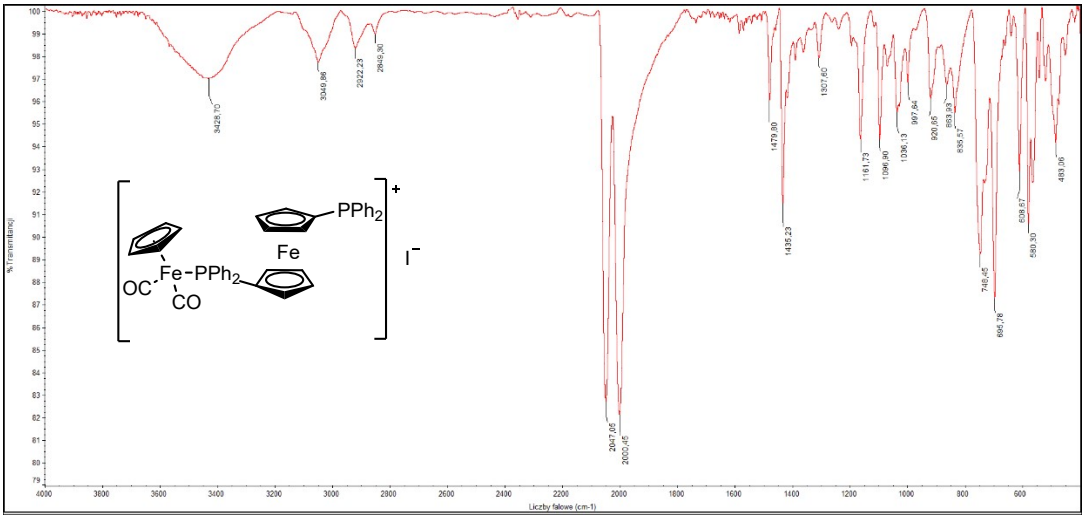

Figure S16. IR spectrum of **8** (KBr, cm^{-1})

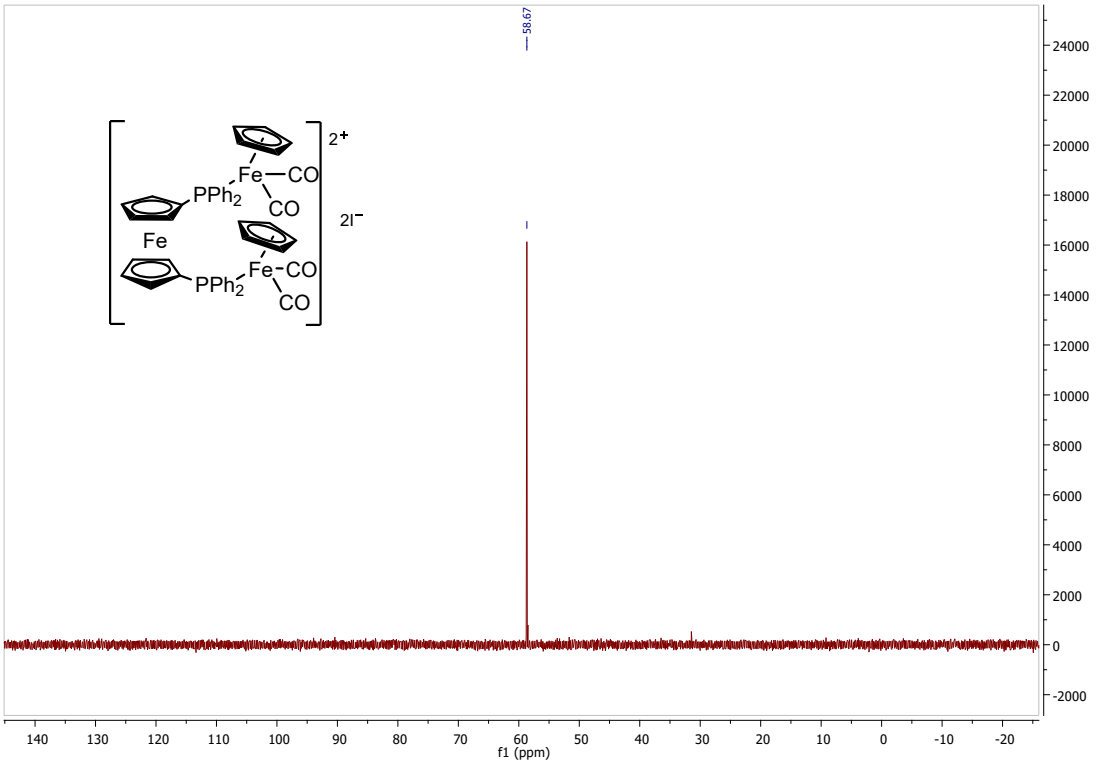

Figure S17. 243 MHz ^{31}P NMR spectrum of **9** in MeOD

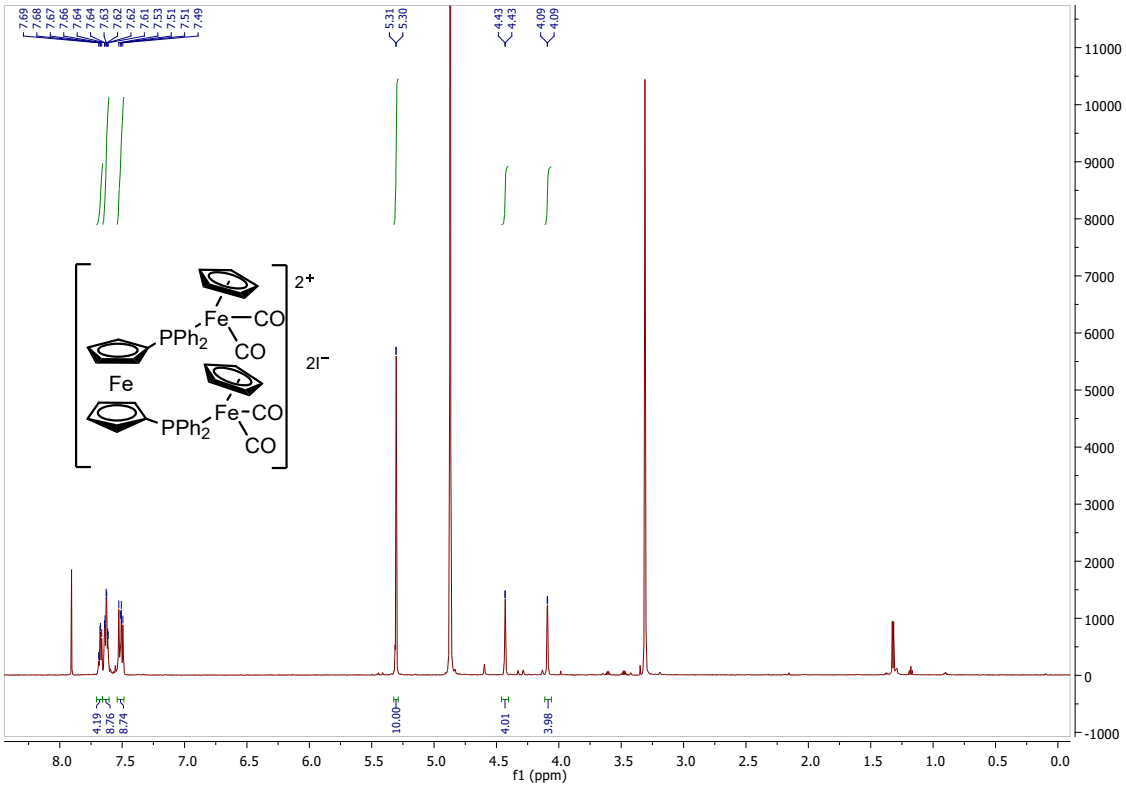

Figure S18. 600 MHz ^{1}H NMR spectrum of **9** in MeOD

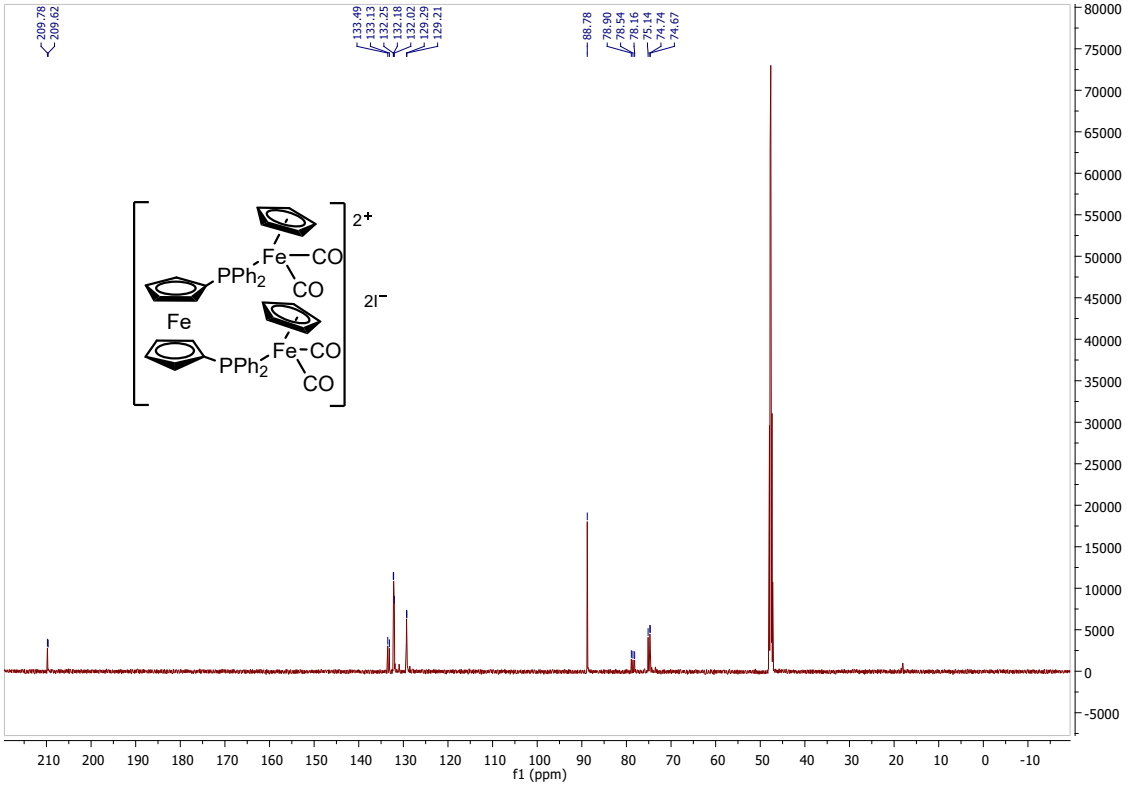

Figure S19. 151 MHz ^{13}C NMR spectrum of **9** in MeOD

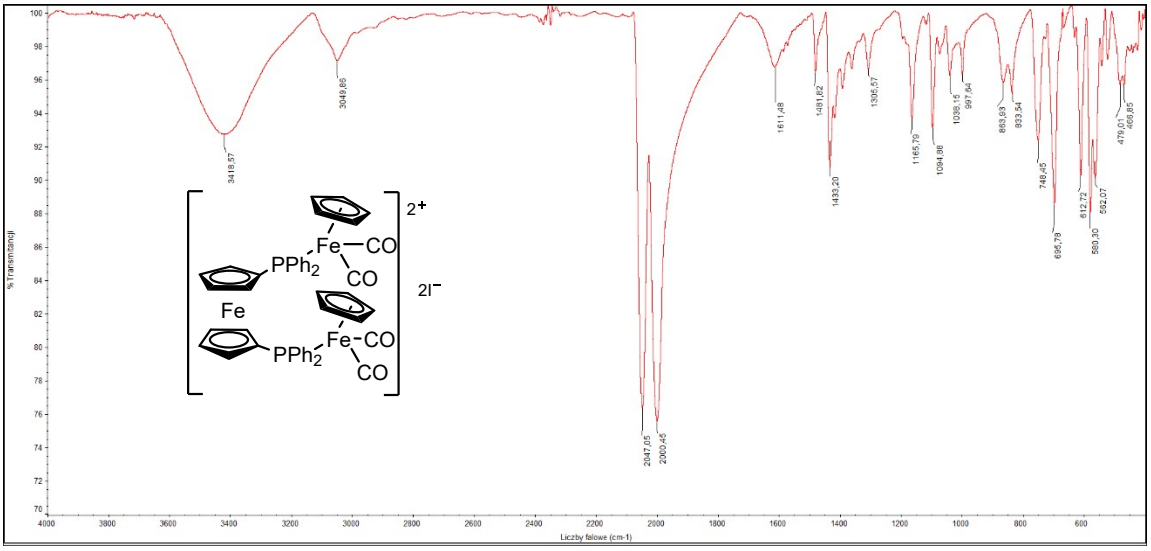

Figure S20. IR spectrum of **9** (KBr, cm^{-1})

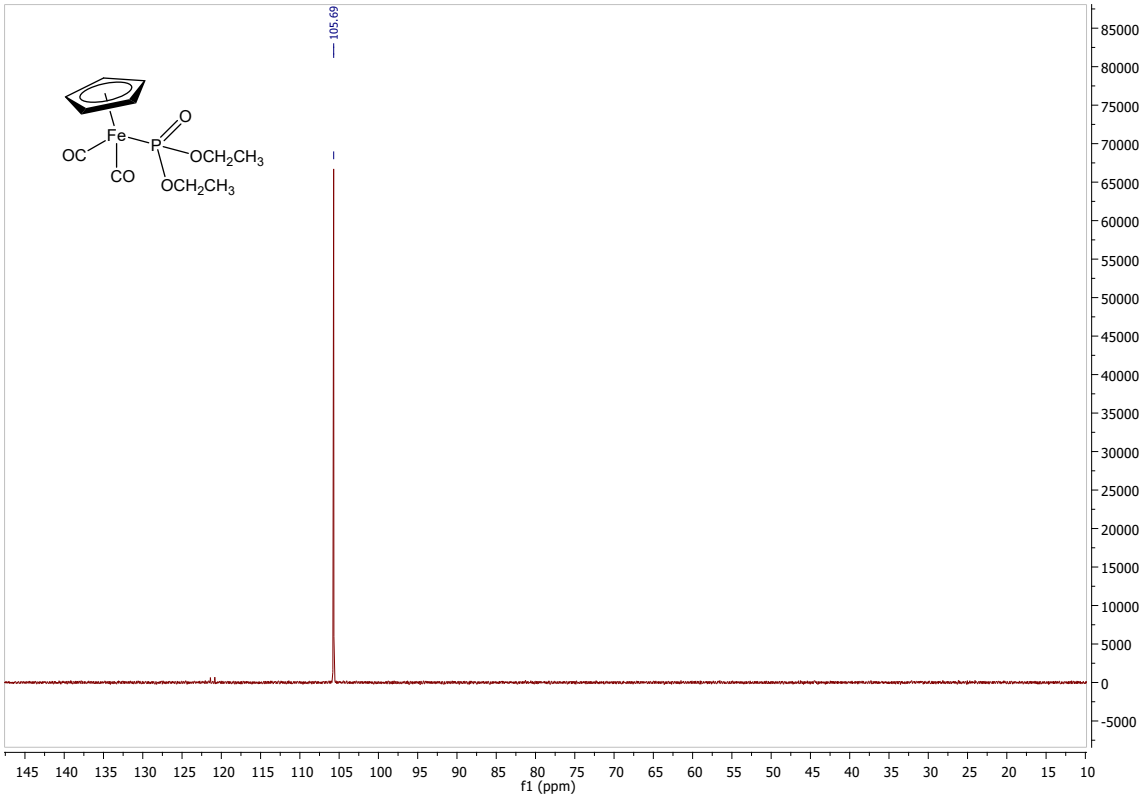

Figure S21. 243 MHz ^{31}P NMR spectrum of **11** in $CDCl_3$

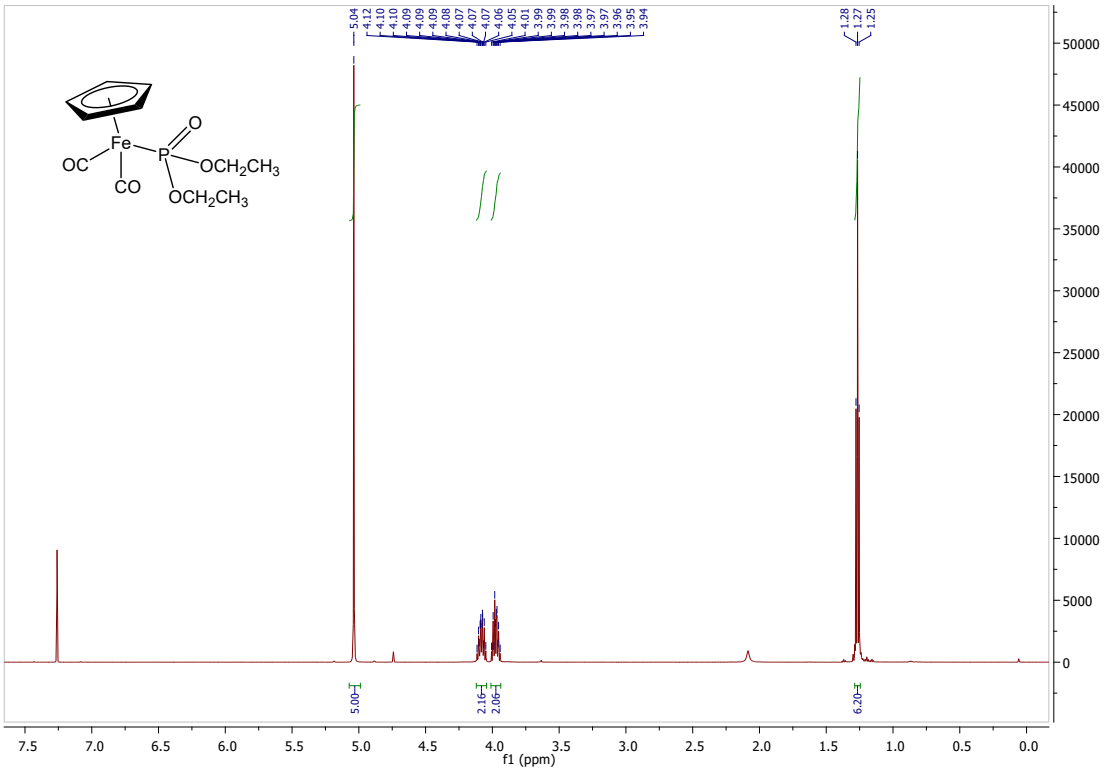

Figure S22. 600 MHz ^{1}H NMR spectrum of **11** in $CDCl_3$

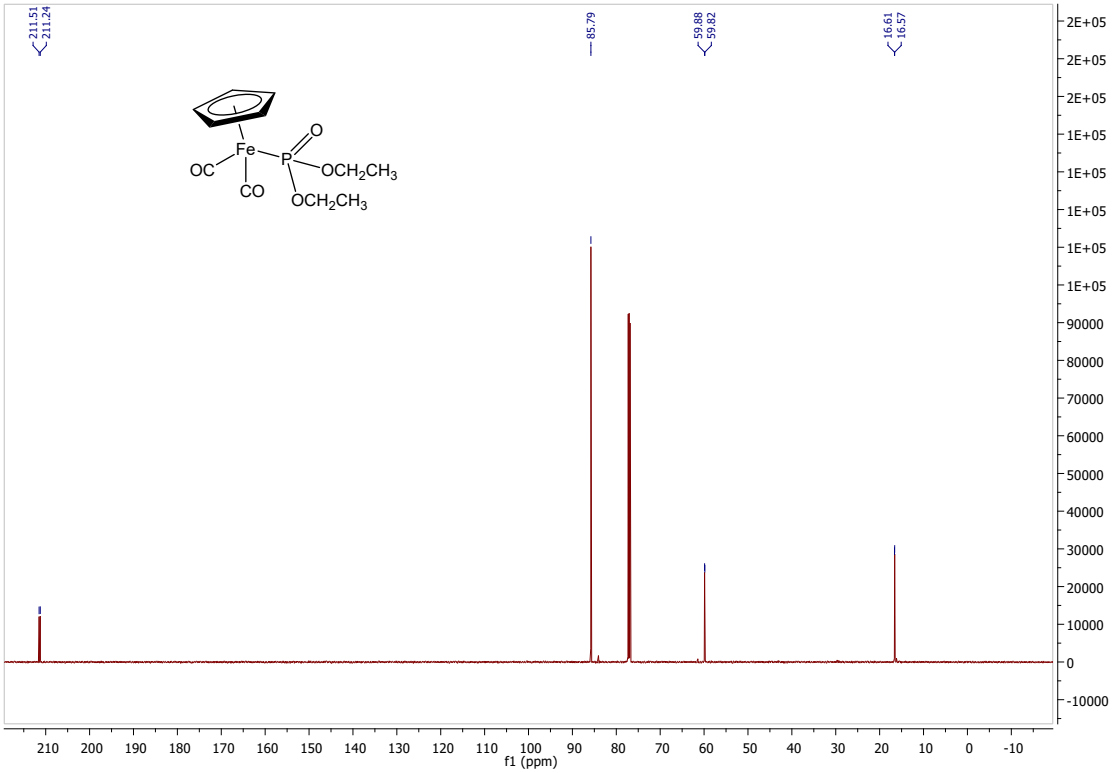

Figure S23. 151 MHz ^{13}C NMR spectrum of **11** in $CDCl_3$

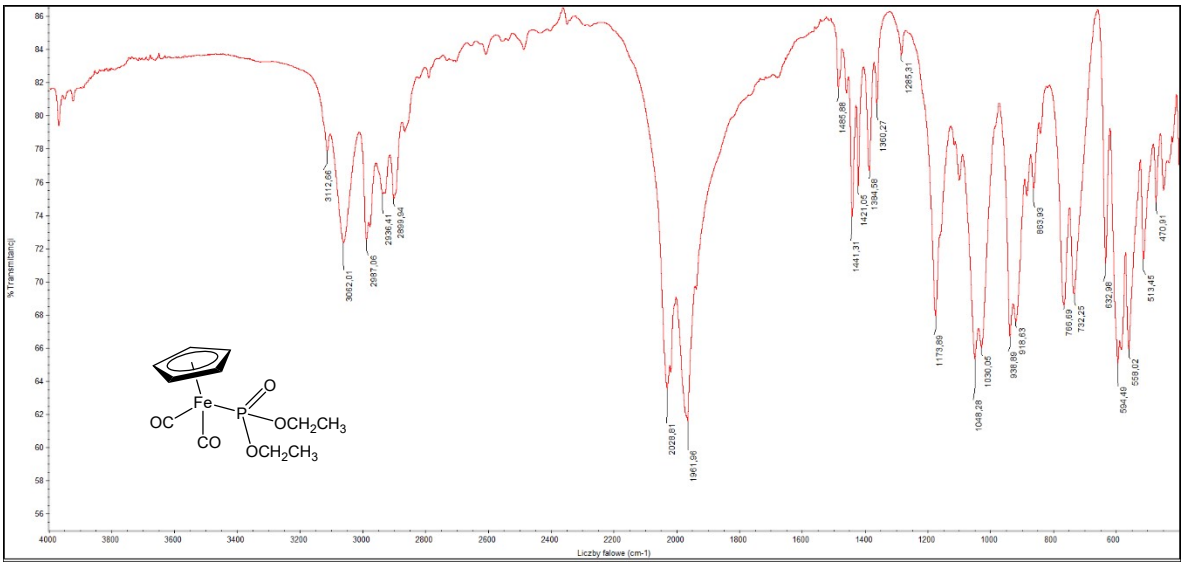

Figure S24. IR spectrum of **11** (KBr, cm^{-1})

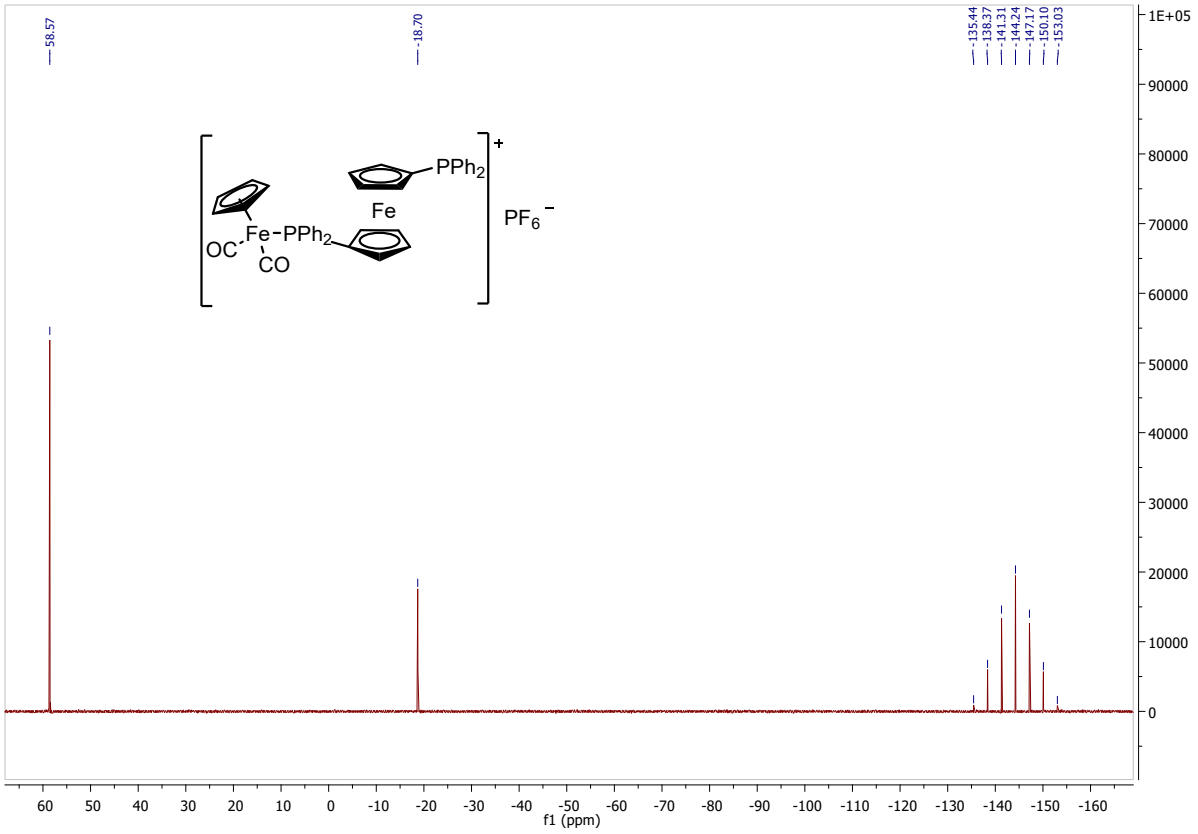

Figure S25. 243 MHz ^{31}P NMR spectrum of **8a** in $CDCl_3$

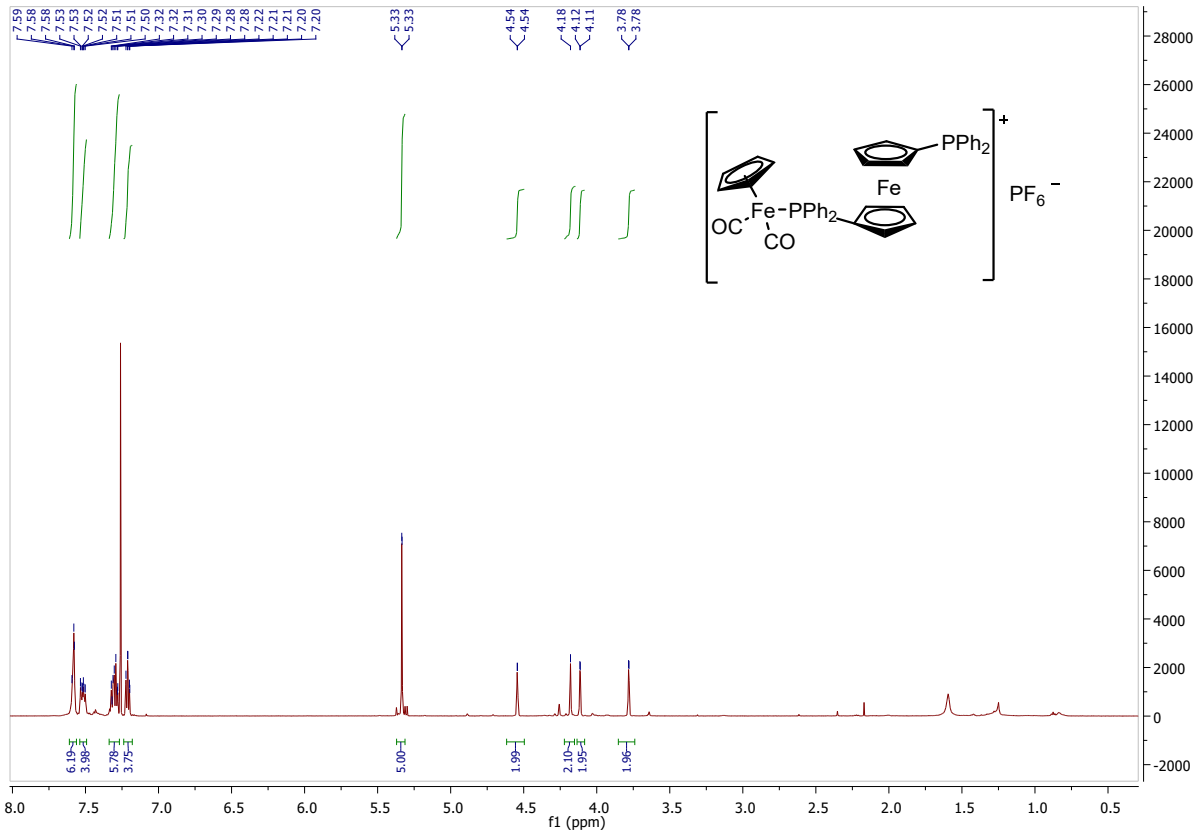

Figure S26. 600 MHz ^{1}H NMR spectrum of **8a** in $CDCl_3$

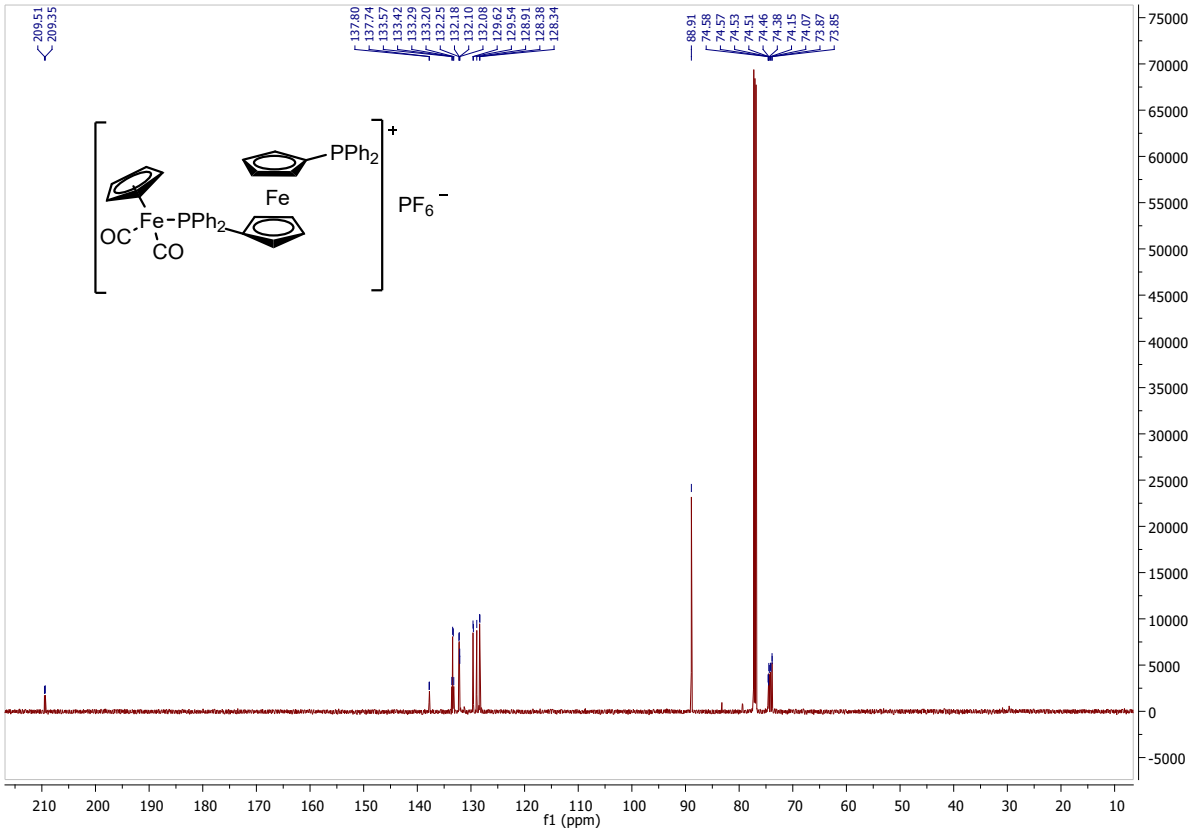

Figure S27. 151 MHz ^{13}C NMR spectrum of **8a** in $CDCl_3$

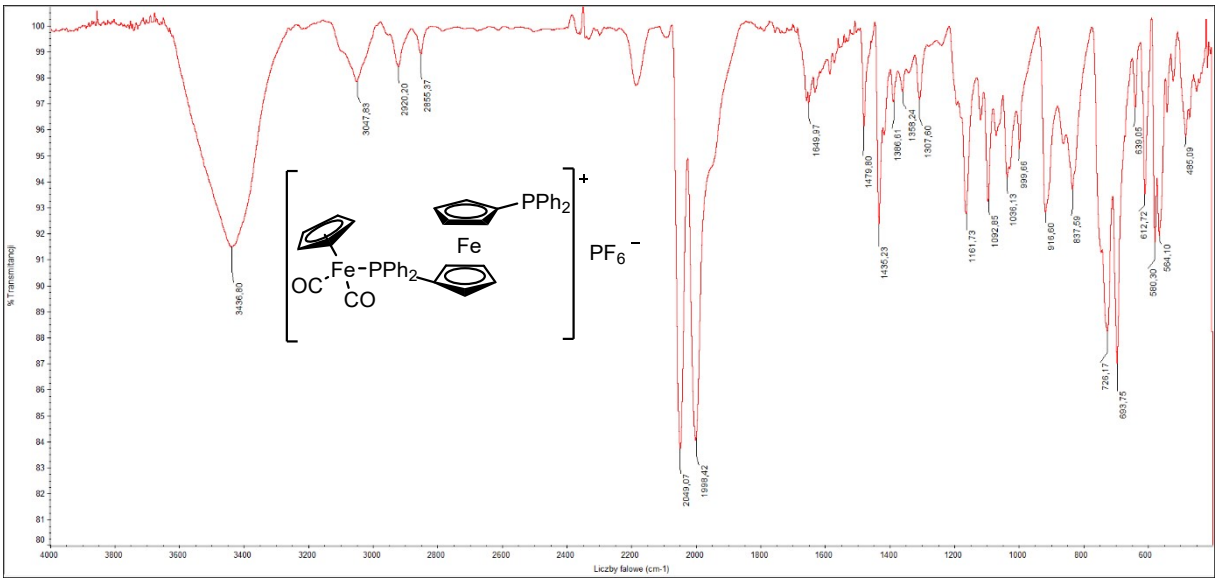

Figure S28. IR spectrum of **8a** (KBr, cm^{-1})

Table S1. Crystal data and structure refinement details for **4**, **8a**, and **9**.

	4	**8a**	**9**
Empirical formula	$[C_{32}H_{29}FeOP_2]^+ I^-$	$[C_{41}H_{33}Fe_2O_2P_2]^+ [PF_6]^- \cdot CH_2Cl_2$	$[C_{48}H_{38}Fe_3O_4P_2]^{2+} 2I^-$
Formula weight / g·mol^{-1}	674.24	961.21	1162.07
Crystal habit, colour	yellow plate	orange prism	yellow block
Crystal size/mm	0.107 × 0.065 × 0.057	0.7374 x 0.1169 x 0.0655	0.123 × 0.074 × 0.046
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$	tetragonal / $I\bar{4}2d$
a/Å	9.7064(2)	13.2746(9)	21.4111(2)
b/Å	14.0307(2)	10.8531(7)	21.4111(2)
c/Å	23.7668(5)	27.8509(18)	19.0714(3)
β/°	118.778(3)	91.081(7)	90
Volume/Å^3	2836.98(12)	4011.8(5)	8743.0(2)
Z / ρ_x Mg/m^3	4 / 1.579	4 / 1.591	8 / 1.766
μ /mm^1	14.052	1.041	20.013
F(000)	1352	1952	4576
Radiation/Å	Cu Kα (λ = 1.54184)	MoKα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2θ range /completeness	7.596 – 152.964 / 99.8%	2.654 – 25.000°/ 99.99%	8.26 – 153.22 / 99.5%
Index ranges	-12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -21 ≤ l ≤ 29	-8 ≤ h ≤ 15 -11 ≤ k ≤ 12 -33 ≤ l ≤ 33	-26 ≤ h ≤ 18 -26 ≤ k ≤ 26 -24 ≤ l ≤ 23
Reflections collected	40468 [R_{int} = 0.0307]	16129 [R_{int} = 0.0827]	37237 [R_{int} = 0.0518]
Data/restraints/parameters	5952 / 0 / 334	7045 / 6 / 515	4570 / 0 /281
Goodness-of-fit on F^2	1.014	1.072	1.042
Final R indices [I≥2σ (I)]	R_1 = 0.0208 / wR_2 = 0.0499	R_1 = 0.1159 / wR_2 = 0.3093	R_1 = 0.0413, wR_2 = 0.1075
Final R indices [all data]	R_1 = 0.0238 / wR_2 = 0.0517	R_1 = 0.1719 / wR_2 = 0.3366	R_1 = 0.0426, wR_2 = 0.1086
Largest diff. peak/hole / e·Å^{-3}	0.31 / -0.68	2.41 / -1.45	0.62/-1.02
Flack parameter	-	-	-0.002(3)
CCDC number	2269767	2176904	2269863

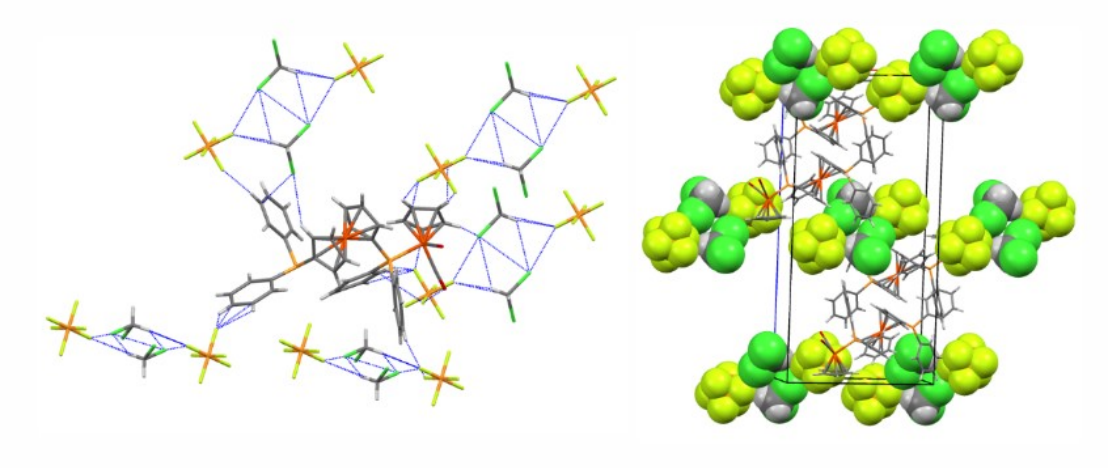

Figure S29. A single **8a** cation surrounded by PF_6^- hexafluorophosphate anions and solvent molecules (left). Dotted blue lines indicate intermolecular contacts of C-H…Cl, C-H…F hydrogen bonds and C-Cl…F halogen bonds. Crystal packing in unit cell (right). Tetramers of hexafluorophosphate anions and dichloromethane molecules are presented in space-fill style (atoms are presented as spheres corresponding to van der Waals atomic radii).

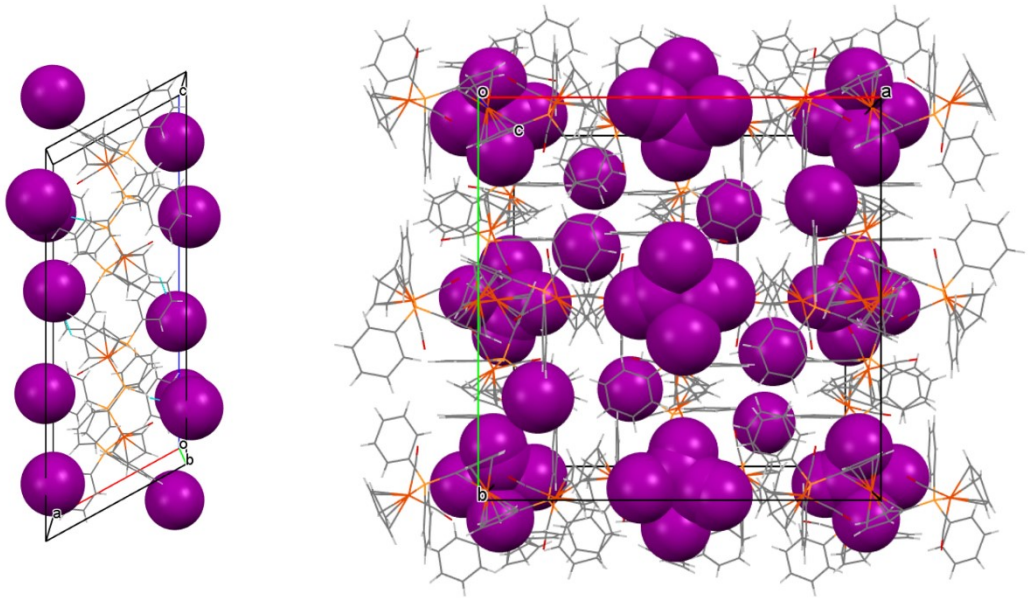

Figure S30. Crystal packing in unit cell (**4** left, **9** right). Iodine anions are presented in space-fill style (atoms are presented as spheres corresponding to van der Waals atomic radii).

Interatomic distances shorter than sum of corresponding van der Waalsa radii are presented in Hirshfeld molecular surface as red spots (compare **Figure S30** left). In turn, white areas show where molecules stick each other with distance equal to sum of van der Waals radii. As seen in the picture, all these areas results mainly from hydrogens contacts. The most numerus are H…H and H…C what is obvious (terminal atoms of molecules), but also large group represents H…F/Cl contacts for the **8a** cation and H…I for the **4** cation and **9** cation. These contacts are due to formation of C-H…F, C-H…Cl and C-H…I hydrogen bonds. The colored blue points in fingerprint plots (**Figure S32** right) indicate that in the case of the **8a** C-H…F are evidently shorter (peak about 1.4Å) than C-H…Cl (peak about 1.8 Å). In the case of H…I contacts for the **4** and **9** (**Figure S31** right and **Figure S33** right), the

peak for the former is about 1.9 Å, while for the latter the two peaks can be observed: one about 1.9 Å and one about 1.6 Å. This double peak on the histogram for the H…I contacts is easy to explain. In the crystal structure of **9** are two I^- anions. The longer distance is for the iodine anion I1 which forms two C-H…I hydrogen bonds with the shortest H…I contact of 3.014 Å. The shorter peak is for the I2 anion which is engaged in four hydrogen bonds with the shortest H…I contact of 2.219 Å, and additionally the position of this atom is disordered.

The corresponding plots also asymmetric as there are typical intermolecular contacts between various species: cation…anion (H…F and H…I) , cation…solvent molecule (H…Cl).

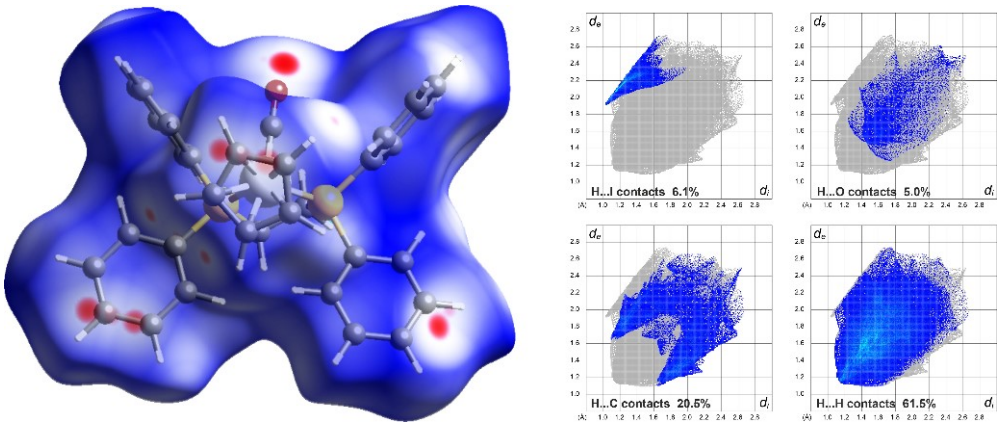

Figure S31. Hirshfeld surface of **4** cation by d_{norm} parameter (left) and fingerprint plot of hydrogen intermolecular contacts H…I, H…O, H…C and H…H with indicated percentage (right).

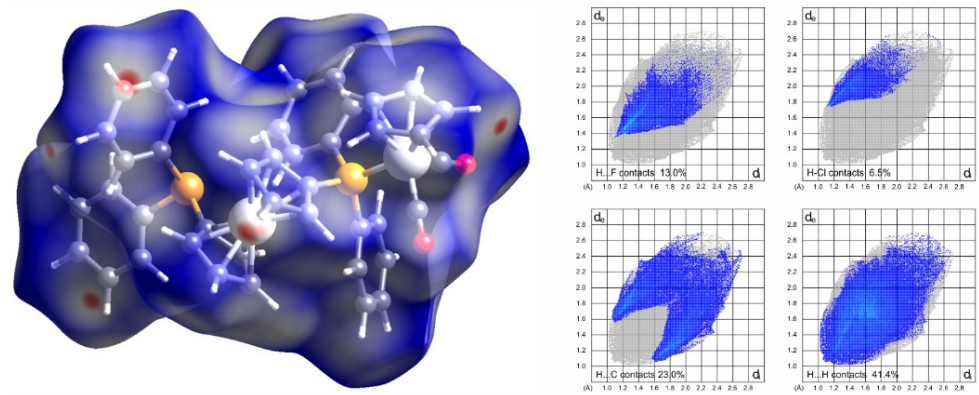

Figure S32. Hirshfeld surface of **8a** cation by d_{norm} parameter (left) and fingerprint plot of hydrogen intermolecular contacts H…F, H…Cl, H…C and H…H with indicated percentage (right).

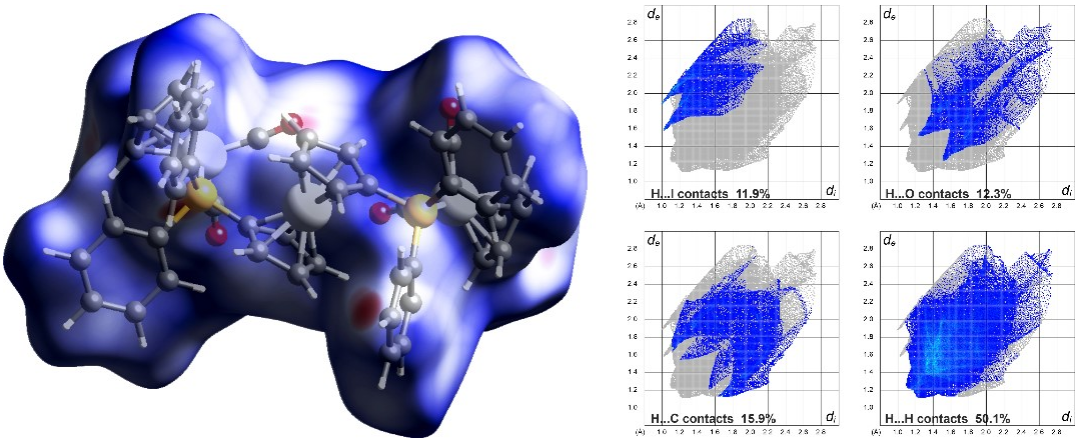

Figure S33. Hirshfeld surface of **9** cation by d_{norm} parameter (left) and fingerprint plot of hydrogen intermolecular contacts H…I, H…O, H…C and H…H with indicated percentage (right).

Table S2. Selected bond lengths [Å] and angles [°] for **8a**

cation		**anion**	
Fe1-C1	2.100(13)	F1-P10	1.564(9)
Fe1-C2	2.117(12)	F2-P10	1.587(8)
Fe1-C3	2.112(11)	F3-P10	1.590(9)
Fe1-C4	2.092(11)	F4-P10	1.559(9)
Fe1-C5	2.106(11)	F5-P10	1.580(9)
Fe1-Cg1 (C1-C2-C3-C4-C5)		F6-P10	1.560(8)
Fe2-C11	2.063(10)	F6-P10-F4	89.0(6)
Fe2-C12	2.067(10)	F6-P10-F1	90.4(6)
Fe2-C13	2.046(11)	F4-P10-F1	89.0(6)
Fe2-C14	2.066(11)	F6-P10-F5	179.0(6)
Fe2-C15	2.061(11)	F4-P10-F5	91.5(6)
Fe2-Cg2 (C11-C12-C13-C14-C15)		F1-P10-F5	88.8(6)
Fe2-C16	2.061(10)	F6-P10-F2	90.4(5)
Fe2-C17	2.037(11)	F4-P10-F2	177.5(6)
Fe2-C18	2.037(11)	F1-P10-F2	88.6(5)
Fe2-C19	2.059(12)	F5-P10-F2	89.0(5)
Fe2-C20	2.042(11)	F6-P10-F3	90.1(5)
Fe2-Cg2 (C16-C17-C18-C19-C20)		F4-P10-F3	92.3(5)
Fe1-C6	1.792(14)	F1-P10-F3	178.6(5)
O6-C6	1.123(14)	F5-P10-F3	90.7(5)
Fe1-C7	1.744(19)	F2-P10-F3	90.2(5)
C7-O7	1.200(18)		

Fe1-P1	2.228(3)	**solvent**	
P1-C11	1.805(10)	Cl1-C10	1.818(18)
P1-C21	1.825(11)	Cl2-C10	1.809(19)
P1-C31	1.823(12)	Cl2-C10-Cl1	106.8(9)
P2-C16	1.827(12)		
P2-C41	1.834(12)		
P2-C51	1.819(10)		
C7-Fe1-C6	93.3(6)		
C7-Fe1-P1	91.7(4)		
C6-Fe1-P1	90.8(3)		
C11-P1-C21	105.0(5)		
C11-P1-C31	109.3(5)		
C21-P1-C31	103.8(5)		
C11-P1-Fe1	107.6(3)		
C21-P1-Fe1	117.0(4)		
C31-P1-Fe1	113.6(4)		
C51-P2-C16	101.2(5)		
C51-P2-C41	102.4(5)		
C16-P2-C41	101.9(5)		

Table S3. Selected bond lengths [Å] and angles [°] for **4**

4 - cation	
Fe1-C1	2.095(2)
Fe1-C2	2.104(2)
Fe1-C3	2.113(2)
Fe1-C4	2.105(2)
Fe1-C5	2.094(2)
Fe1-Cg1 (C1-C2-C3-C4-C5)	
Fe1-C6	1.756(2)
O6-C6	1.146(3)
Fe1-P1	2.2077(6)
P1-C7	1.843(2)
P1-C9	1.825(2)
P1-C15	1.829(2)
Fe1-P2	2.2062(6)
P2-C8	1.842(2)
P2-C21	1.825(2)
P2-C27	1.825(2)
P1-Fe1-P2	87.76(2)

P1-Fe1-C6	90.63(6)
P2-Fe1-C6	86.27(6)
Fe1-P1-C7	107.82(6)
Fe1-P1-C9	113.53(6)
Fe1-P1-C15	121.05(6)
C7-P1-C9	107.41(9)
C7-P1-C15	104.06(9)
C9-P1-C15	101.94(9)
Fe1-P2-C8	106.63(6)
Fe1-P2-C21	113.88(6)
Fe1-P2-C27	119.66(6)
C8-P2-C21	104.69(9)
C8-P2-C27	106.11(9)
C21-P2-C27	104.69(9)

Table S4. Selected bond lengths [Å] and angles [°] for **9**

9 - cation	
Fe1-C1	2.104(8)
Fe1-C2	2.103(7)
Fe1-C3	2.110(7)
Fe1-C4	2.091(6)
Fe1-C5	2.104(7)
Fe1-Cg1 (C1-C2-C3-C4-C5)	
Fe2-C8	2.045
Fe2-C9	2.039
Fe2-C10	2.054
Fe2-C11	2.077
Fe2-C12	2.07
Fe2-Cg2 (C8-C9-C10-C11-C12)	
Fe1-C6	1.786(8)
O6-C6	1.10(1)
Fe1-C7	1.799(9)
O7-C7	1.05(1)
Fe1-P1	2.241(2)
P1-C8	1.792(7)
P1-C13	1.823(6)
P1-C19	1.822(7)
P1-Fe1-C6	96.3(2)
P1-Fe1-C7	89.5(3)
C6-Fe1-C7	95.9(4)
Fe1-P1-C8	114.4(2)

Fe1-P1-C13	118.1(2)
Fe1-P1-C19	110.7(2)
C13-P1-C8	105.1(3)
C19-P1-C8	102.2(3)
C19-P1-C13	104.8(3)

Table S5. Geometric parameters of hydrogen and halogen bonds in crystal structure **8a, 4** and **9.**

hydrogen bonds	**D-H**	**H...A**	**D...A**	**D-H.....A**	**symmetry code**
			8a		
C4-H4...Cl2	0.93	3.01	3.673(15)	129.7(8)	-x,-y,-z
C10-H101... Cl2	0.93	3.15	3.786(16)	124.9(8)	-x,2-y,-z
C17-H17... Cl1	0.93	3.05	3.857(15)	145.6(7)	x,y,z
C24-H24...Cl1	0.93	3.00	3.858(13)	154.4(8)	x,+y-1,+z
C35-H35...O6	0.93	2.79	3.429(15)	126.9(8)	-x+1/2+1,+y-1/2,-z+1/2
C55-H55...O7	0.93	2.92	3.470(16)	119.1(8)	x-1,+y,+z
C56-H56...O7	0.93	2.67	3.342(15)	130.3(7)	x-1,+y,+z
C1-H1...F3	0.93	2.63	3.373(15)	137.7(8)	-x+1,-y+1,-z
C1-H1...F6	0.93	2.91	3.352(15)	110.7(7)	x-1,+y,+z
C2-H2...F6	0.93	2.70	3.333(14)	126.4(7)	x,y,z
C3-H3...F1	0.93	2.77	3.575(16)	145.3(8)	x,y,z
C3-H3...F4	0.93	2.72	3.449(16)	135.3(8)	x,y,z
C5-H5...F3	0.93	2.59	3.507(15)	167.2(8)	x,+y-1,+z
C10-H101 ...F5	0.93	2.37	3.324(21)	168.6(9)	x-1,+y,+z
C12-H12...F4	0.93	2.71	3.197(14)	113.4(7)	x-1,+y,+z
C25-H25...F6	0.93	2.93	3.664(15)	136.3(8)	x,+y-1,+z
C25-H25...F3	0.93	2.84	3.405(15)	119.9(8)	x,+y-1,+z
C26-H26...F3	0.93	2.68	3.326(14)	127.2(7)	x,+y-1,+z
C26-H26...F2	0.93	2.87	3.350(14)	112.9 (7)	x,+y-1,+z
C34-H34...F1	0.93	2.82	3.725(16)	165.9(8)	-x+1/2+1,+y-1/2,-z+1/2
C43-H43...F1	0.93	2.61	3.540(16)	175.4(8)	x-1,+y,+z
C45-H45...F4	0.93	2.91	3.393(17)	114.1(8)	x-1,+y,+z
C45-H45...F5	0.93	2.91	3.750(16)	151.5(8)	x-1,+y,+z
C53-H53...F2	0.93	2.69	3.306(14)	124.4(7)	-x+1/2,+y-1/2,-z+1/2
C54-H54...F2	0.93	2.71	3.318(13)	123.7(7)	-x+1/2,+y-1/2,-z+1/2
halogen bonds	**R-X**	**X...Y**		**R-X.....Y**	**symmetry code**
C10-Cl2....F5	1.808(14)	3.012(12)		159.7(7)	
hydrogen bonds	**D-H**	**H...A**	**D...A**	**D-H.....A**	**symmetry code**

			4		
C4-H4…I1	0.95	3.158	3.849(2)	131.0	x,y,z
C3-H3…I1	0.95	3.162	4.073(2)	161.1	2-x,1-y,1-z
C8-H8B…I1	0.99	3.03	3.847(2)	140.7	1+x,1.5-y,1/2+z
			9		
C15-H15…I1	0.95	3.164	3.837	129.2	x,y,z
C17-H17…I2	0.95	2.719	3.470(8)	136.5	x,y,z
C5-H5…I1	0.95	3.014	3.938	164.1	y,1-x,1-z
C9-H9…I2	0.95	3.162	3.751(8)	121.8	1-y,x,2-z
C20-H20…I2	0.95	2.846	3.495(7)	126.3	1.5-x,y,1.75-z
C21-H21…I2	0.95	3.175	4.012(9)	148.1	1/2+y,x,-1/4+z