Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Facile access to tetra-substituted $Fe^{II}Fe^{II}$ biomimetics for the oxidized state active site of [FeFe]-hydrogenases

Xin-Ping Gao, [a] Shu-Fen Bai, [a] Yan-Lan Wang, [a] Shuang Lü,*[b] and Qian-Li Li *[a]

[a] Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, P.R. China

[b] State Key Laboratory for Macromolecule Drugs and Large-scale Manufacturing, School of Pharmaceutical Sciences, Liaocheng 252059, P.R. China

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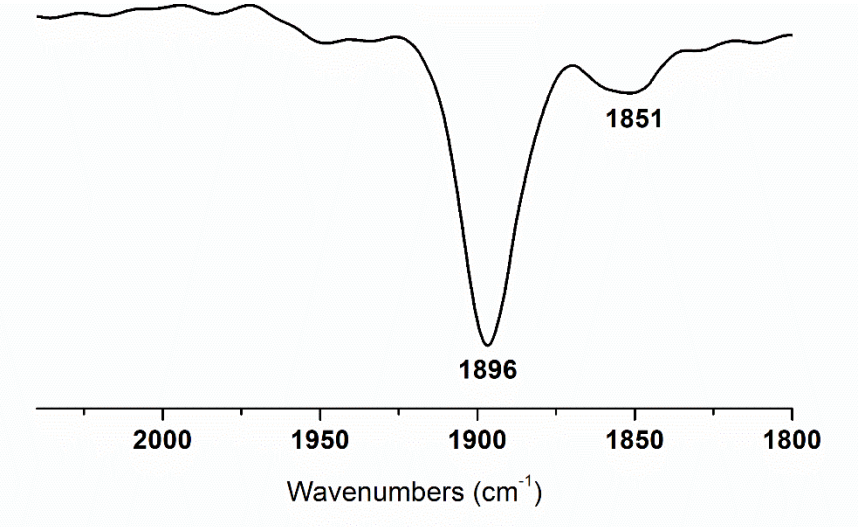

Figure S1. FT-IR (CH_2Cl_2, 25ºC) spectrum of **1**. *Assignments:* ν_{CO} = 1896, 1851 cm^{-1}.

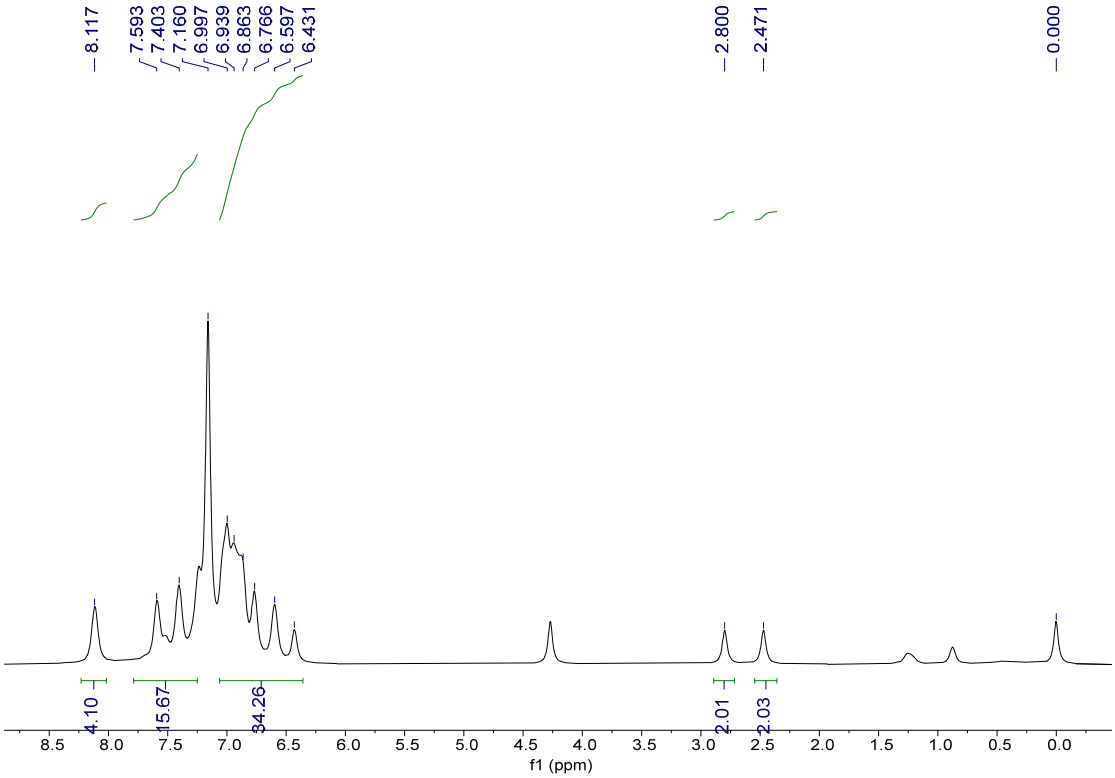

Figure S2. ^1H NMR (500 MHz, C_6D_6, 25 ºC) spectrum of **1**. *Assignments:* δ = 6.43-8.12 (m, 54H, $10C_6H_5$ and 2CH=CH), 2.80, 2.47 (s, 4H, $2CH_2$).

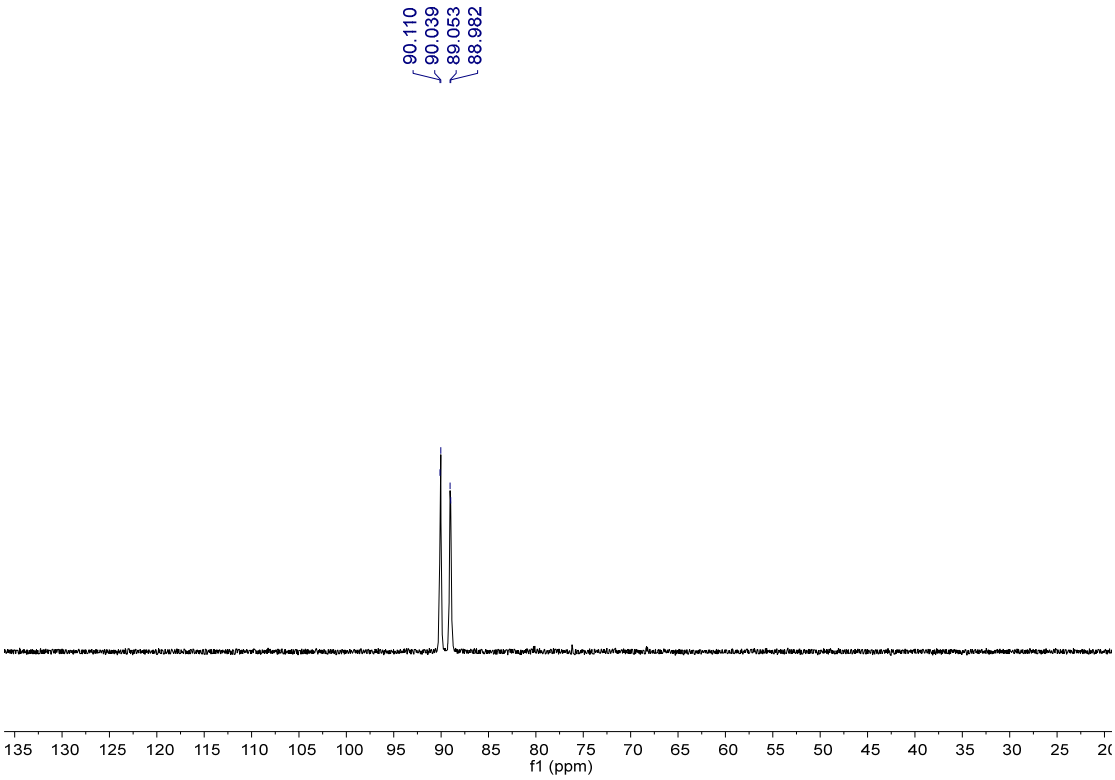

Figure S3. ^{31}P NMR (202 MHz, C_6D_6, 25 ºC) spectrum of **1**. *Assignments:* δ = 90.1 (d, $J_{P\text{-}P}$ = 11.1 Hz), 89.0 (d, $J_{P\text{-}P}$ = 11.1 Hz).

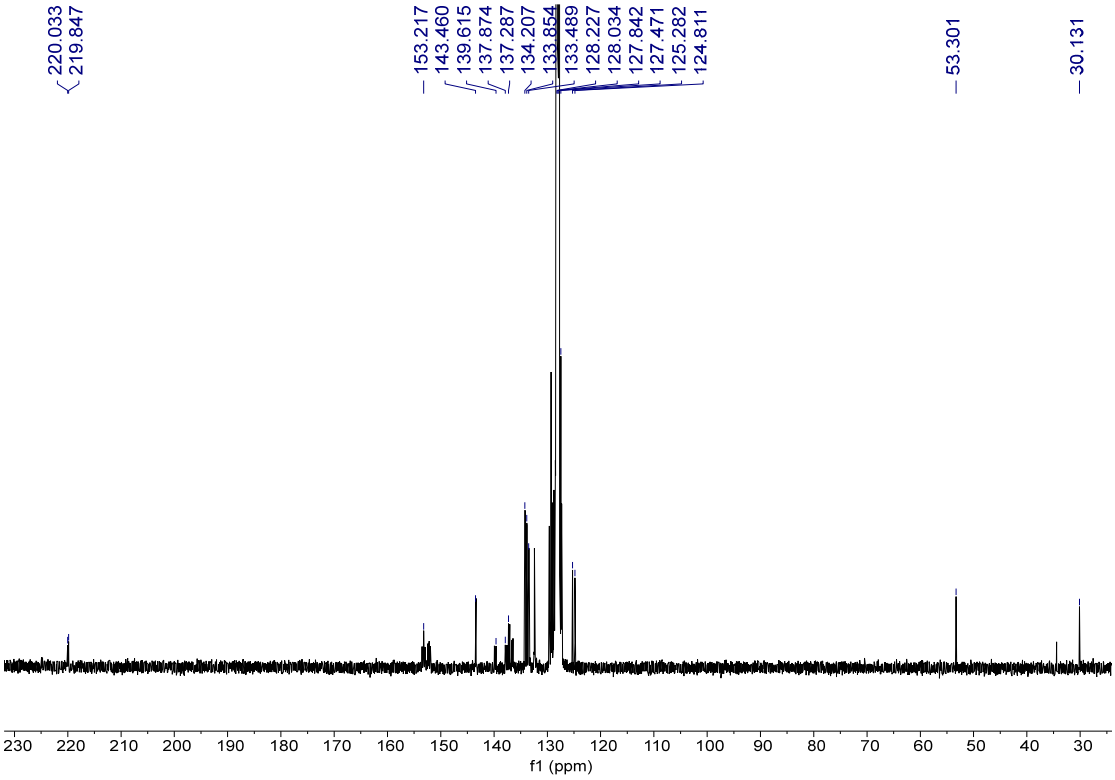

Figure S4. ^{13}C NMR (126 MHz, C_6D_6, 25 ºC) spectrum of **1**. *Assignments:* δ = 220.1 (t, $^2J_{P\text{-}C}$ = 3.4 Hz, PFeCO), 219.8 (t, $^2J_{P\text{-}C}$ = 3.2 Hz, PFeCO), 153.2-124.8 (m, C_6H_5 and PCH=CHP), 30.1 (s, CH_3).

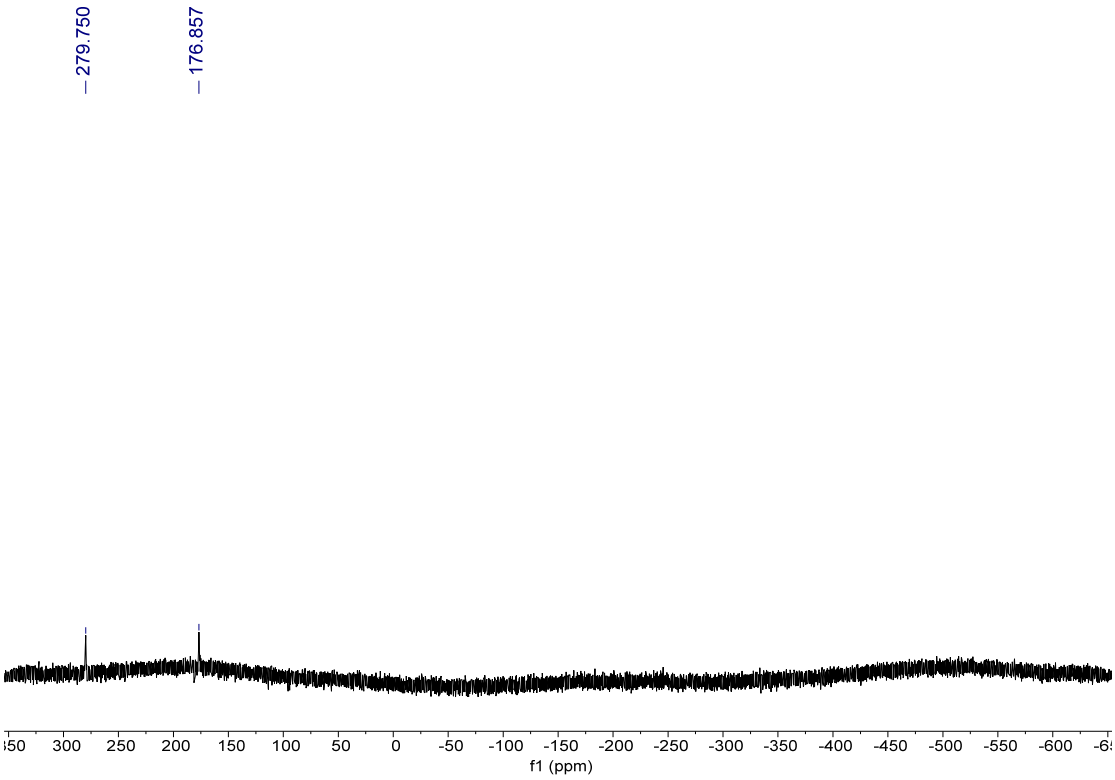

Figure S5. ^{77}Se NMR (95 MHz, C_6D_6, 25 ºC) spectrum of **1**. *Assignments:* δ = 279.8 (s), 176.9 (s).

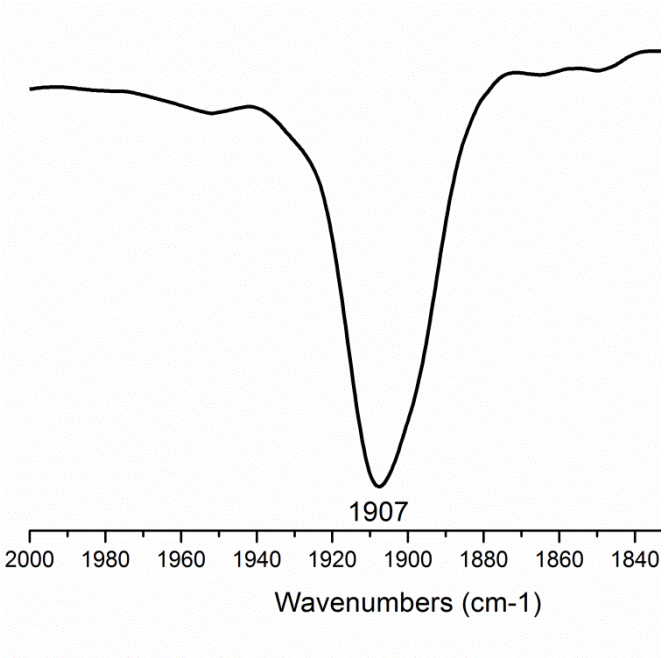

Figure S6. FT-IR (C_6D_6, 25 ºC) spectrum of **2**. *Assignments:* ν_{CO} = 1907 cm^{-1}.

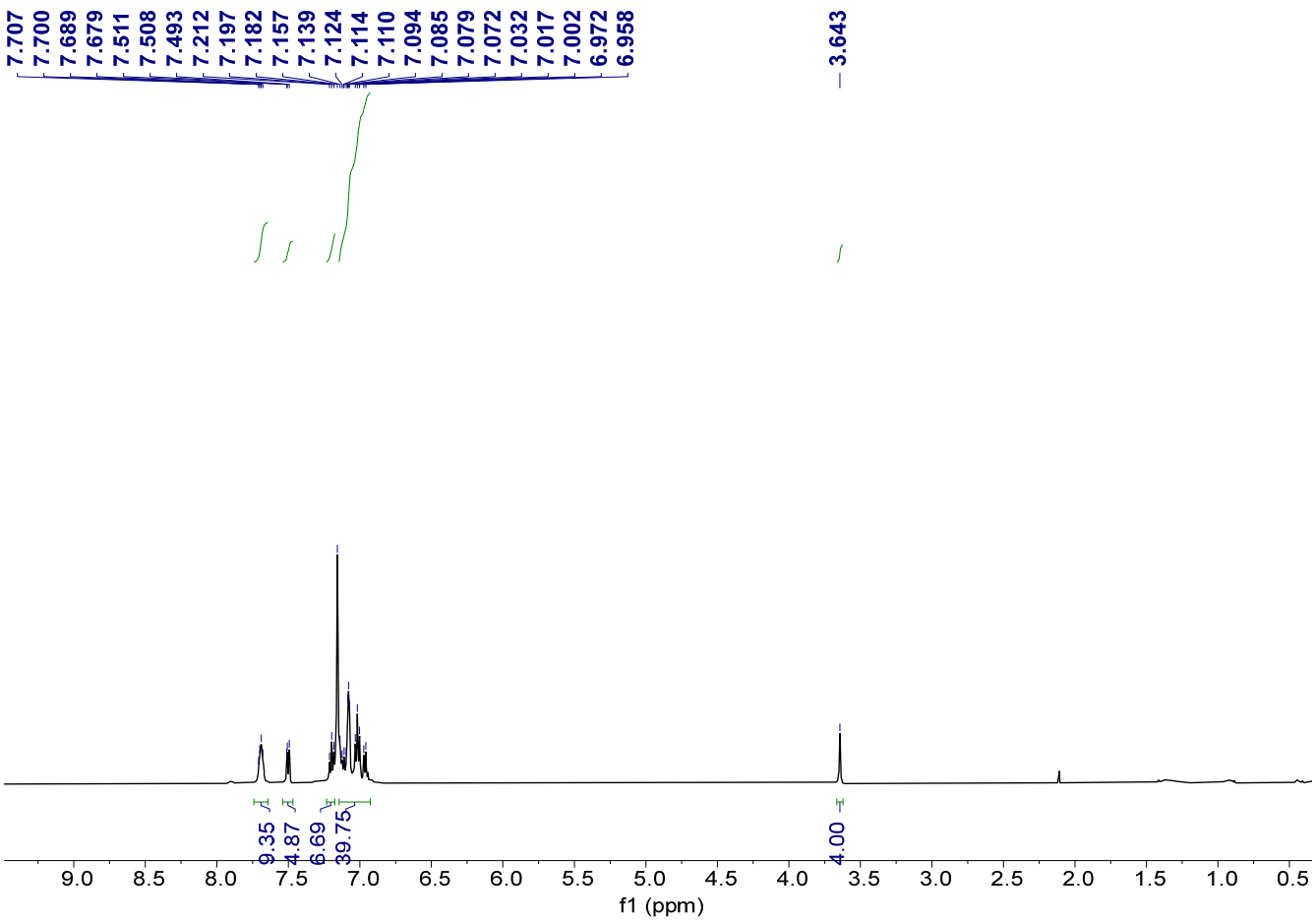

Figure S7. ^{1}H NMR (500 MHz, C_6D_6, 25 ^{o}C) spectrum of **2**. *Assignments:* δ = 6.96-7.70 (m, 54H, $10C_6H_5$ and 2CH=CH), 3.64 (s, 4H, $2CH_2$).

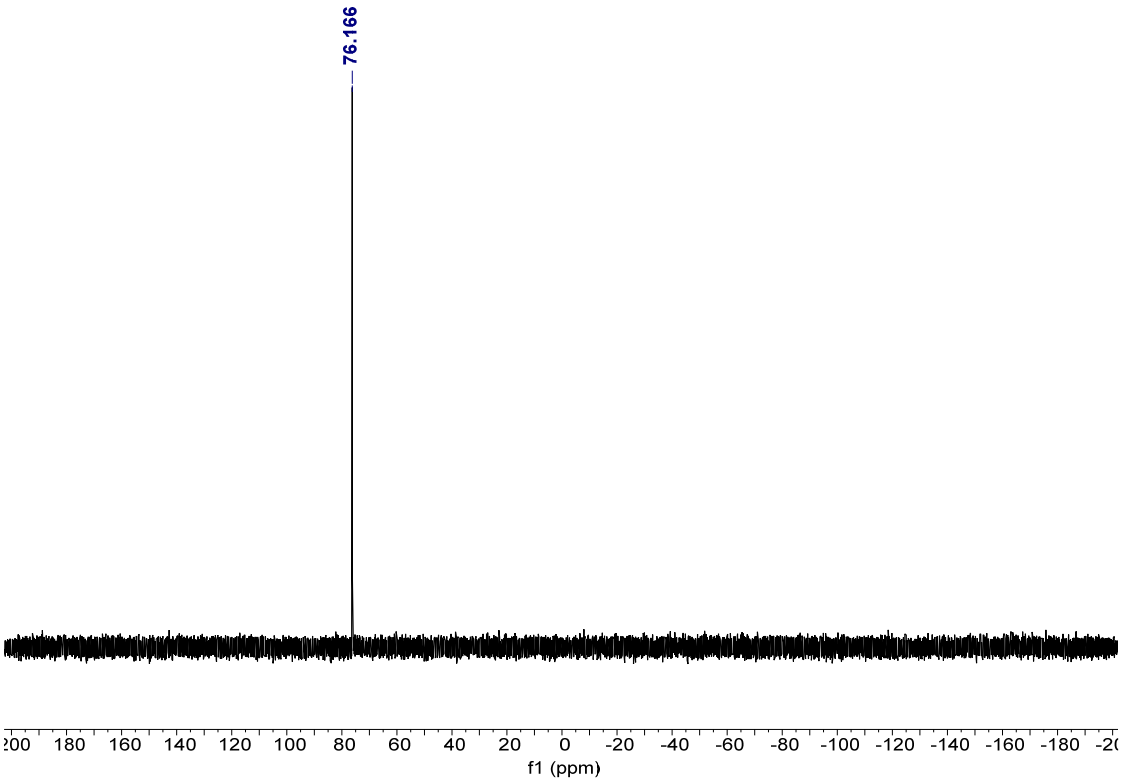

Figure S8. ^{31}P NMR (202 MHz, C_6D_6, 25 ºC) spectrum of **2**. *Assignments:* δ = 76.2(s).

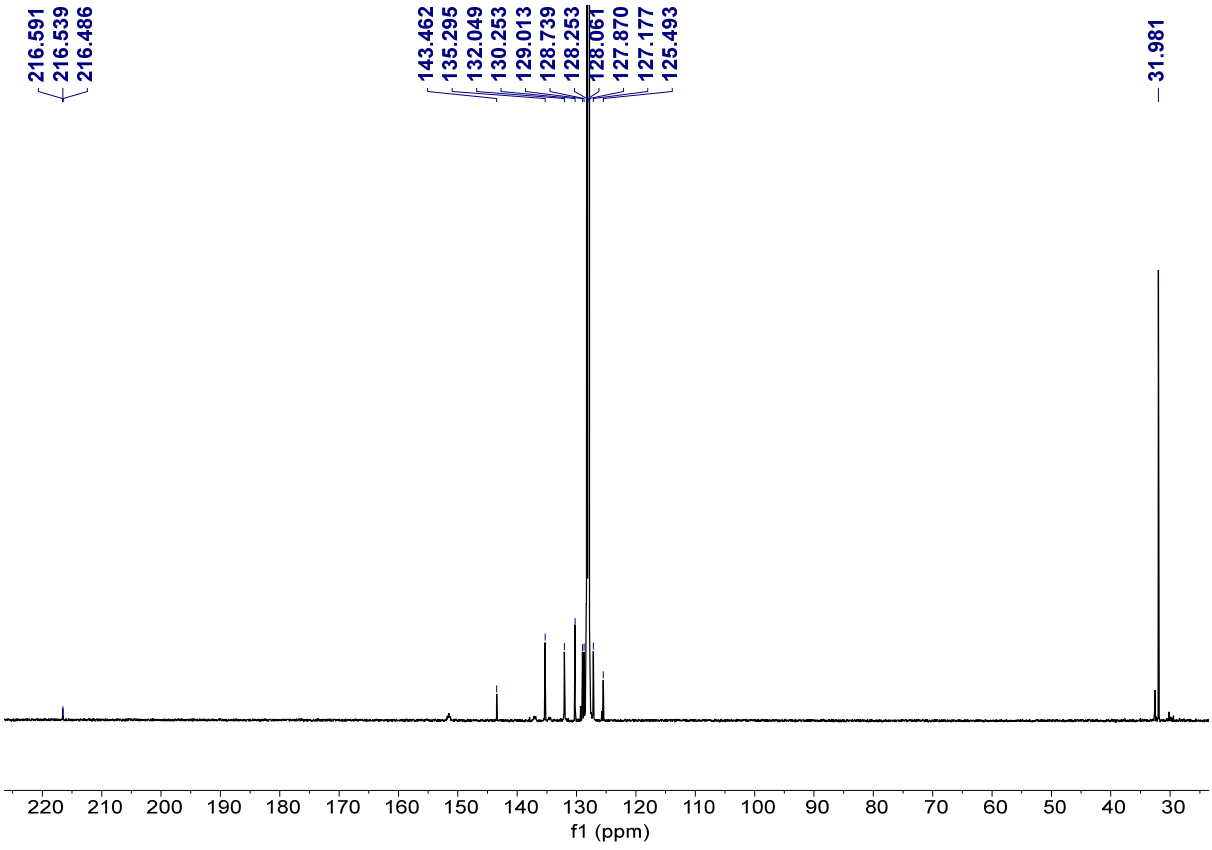

Figure S9. ^{13}C NMR (126 MHz, C_6D_6, 25 ºC) spectrum of **2**. *Assignments:* δ = 216.5 (t, $^2J_{P\text{-}C}$ = 6.5 Hz, PFeCO), 151.5-125.5 (m, C_6H_5 and PCH=CHP), 32.0 (s, CH_3).

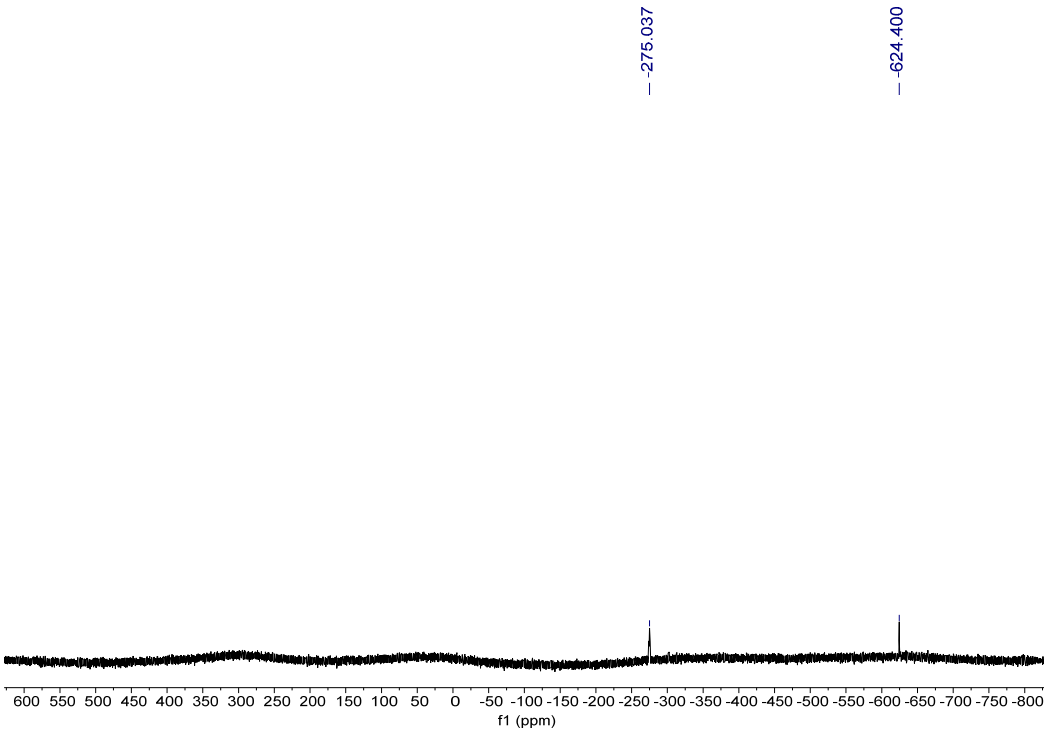

Figure S10. ^{77}Se NMR (95 MHz, C_6D_6, 25 ºC) spectrum of **2**. *Assignments:* δ = -275.0 (s), -624.4 (s).

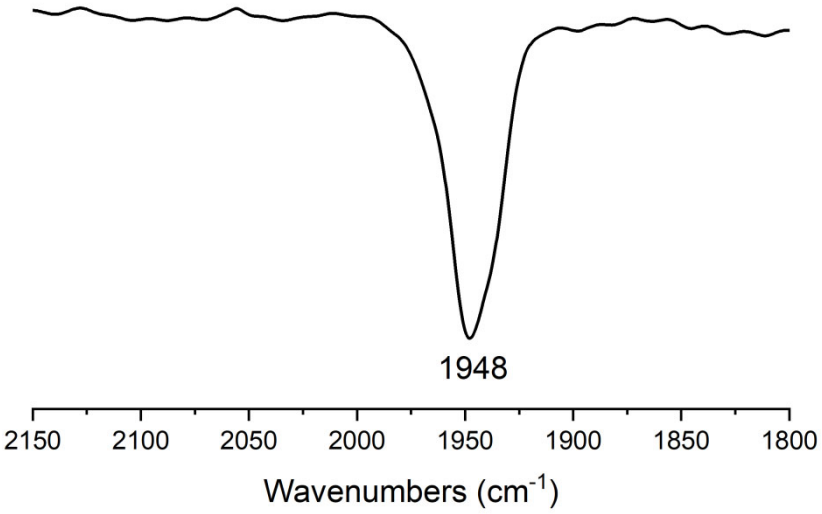

Figure S11. FT-IR (CH_2Cl_2, 25 ºC) spectrum of **[3]Cl**. *Assignments:* ν_{CO} = 1948 cm^{-1}.

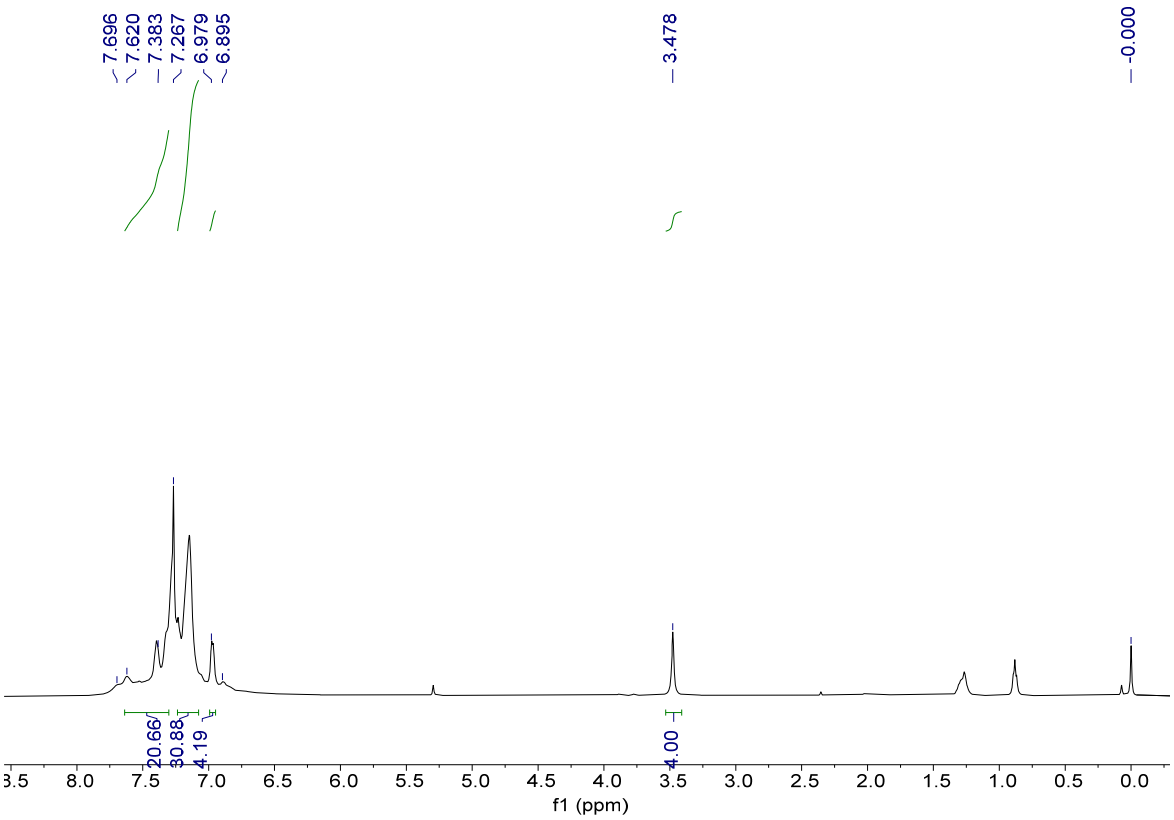

Figure S12. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) spectrum of **[3]Cl**. *Assignments:* δ = 6.89-7.69 (m, 54H, $10C_6H_5$ and 2CH=CH), 3.48 (s, 4H, $2CH_2$).

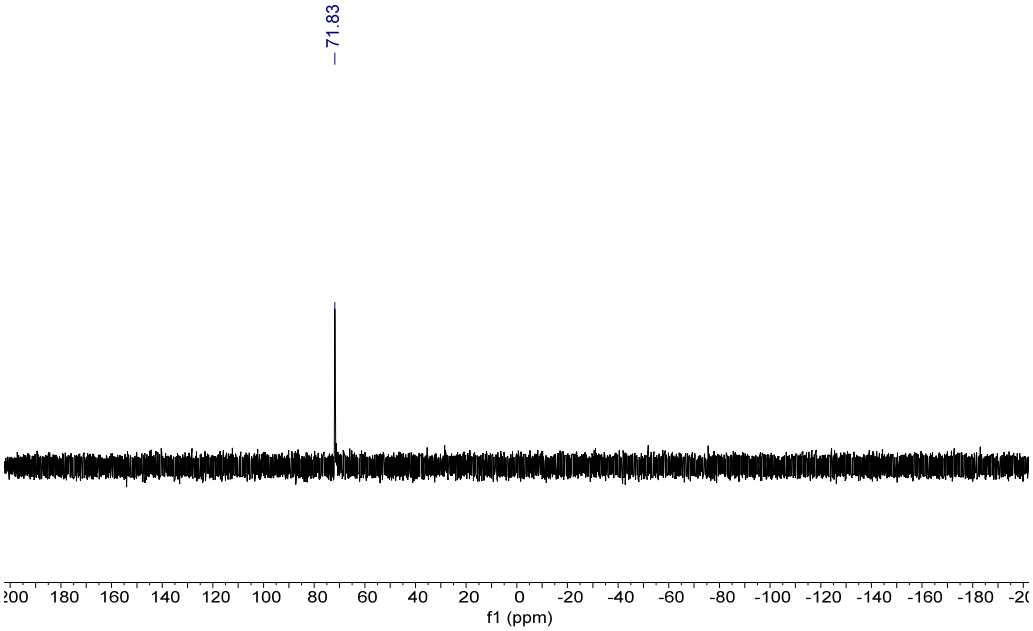

Figure S13. ^{31}P NMR (202 MHz, $CDCl_3$, 25 ºC) spectrum of **[3]Cl**. *Assignments:* δ = 71.8 (s).

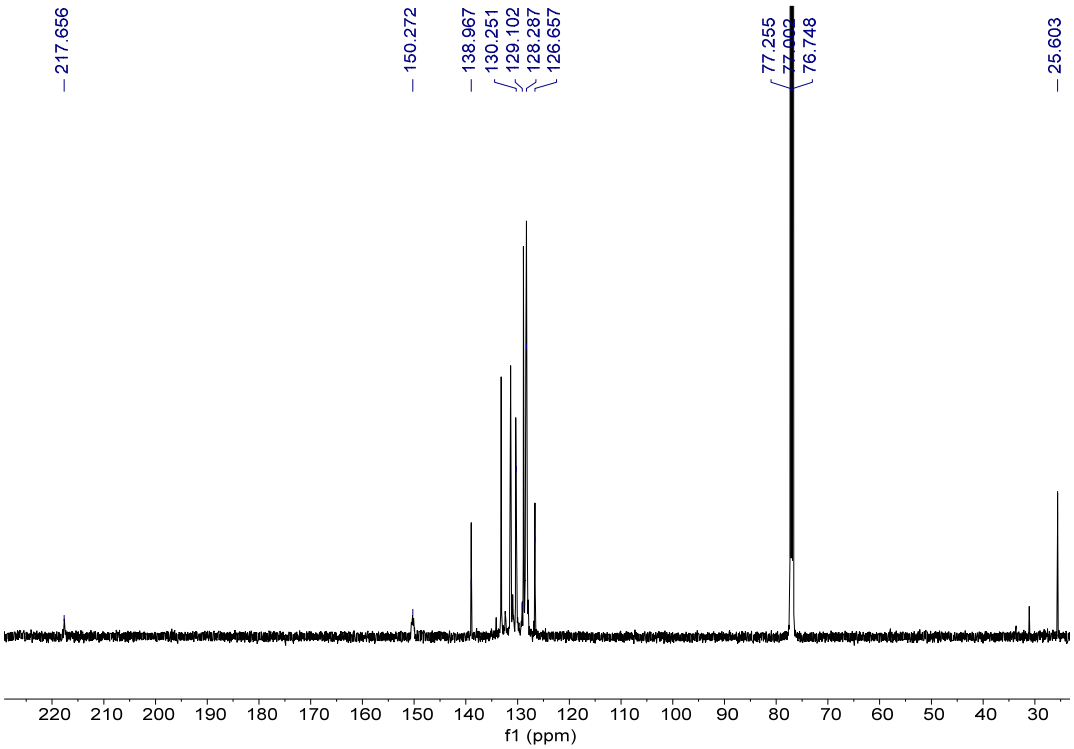

Figure S14. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) spectrum of **[3]Cl**. *Assignments:* δ = 217.7 (t, $^{2}J_{P\text{-}C}$ = 10.6 Hz, PFeCO), 150.3-126.7 (m, C_6H_5 and PCH=CHP), 25.6 (s, CH_2).

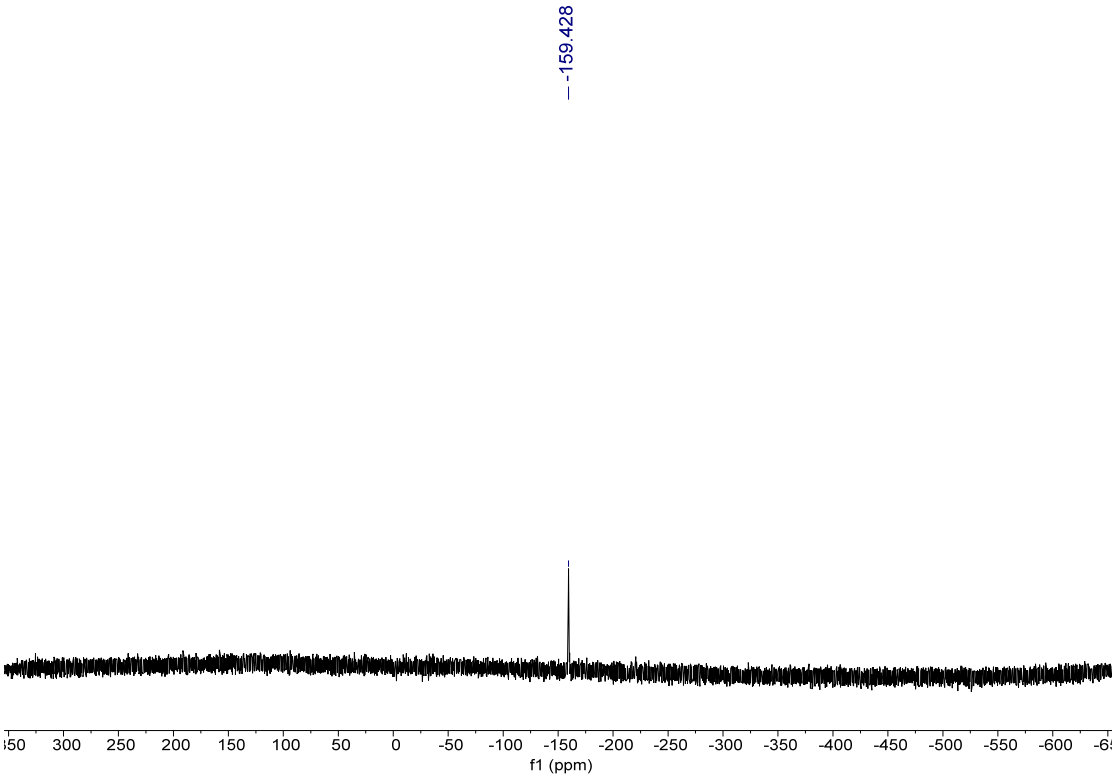

Figure S15. ^{77}Se NMR (95 MHz, $CDCl_3$, 25 °C) spectrum of **[3]Cl**. *Assignments:* δ = -159.4 (s).

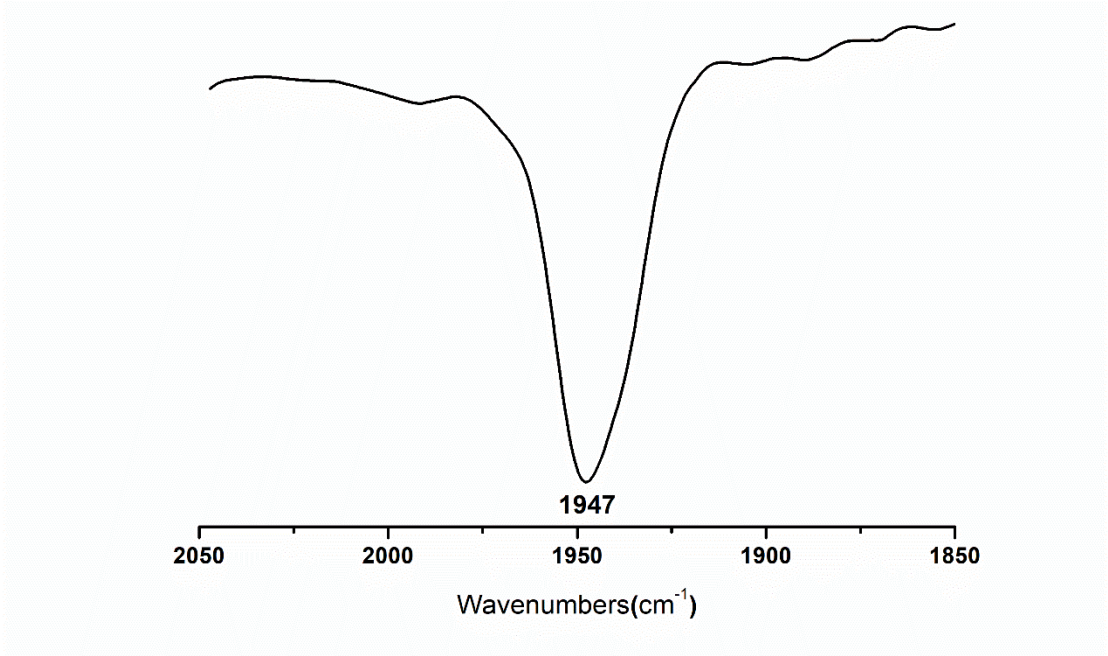

Figure S16. FT-IR (CH_2Cl_2, 25 ºC) spectrum of [**4**]**Br**. *Assignments:* ν_{CO} = 1947cm^{-1}.

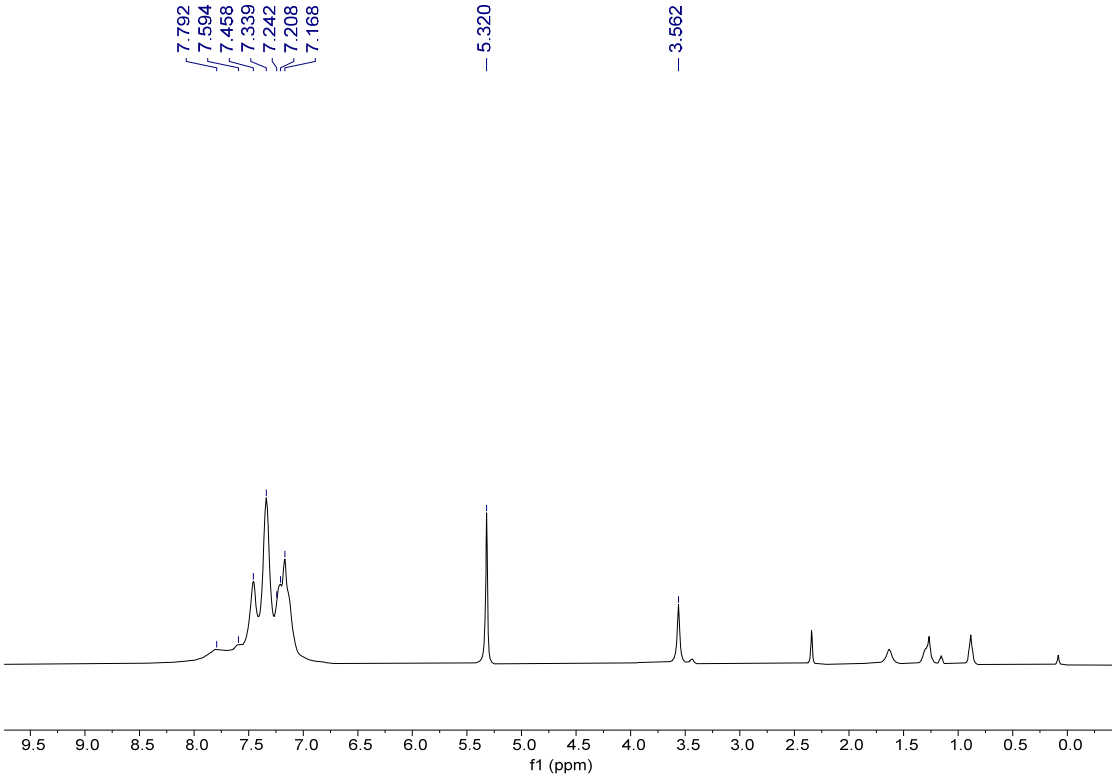

Figure S17. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 ºC) spectrum of [**4**]**Br**. *Assignments:* δ = 7.16-7.79 (m, 54H, 10C_6H_5, 2CH=CH), 3.56(s, 4H, 2CH_2).

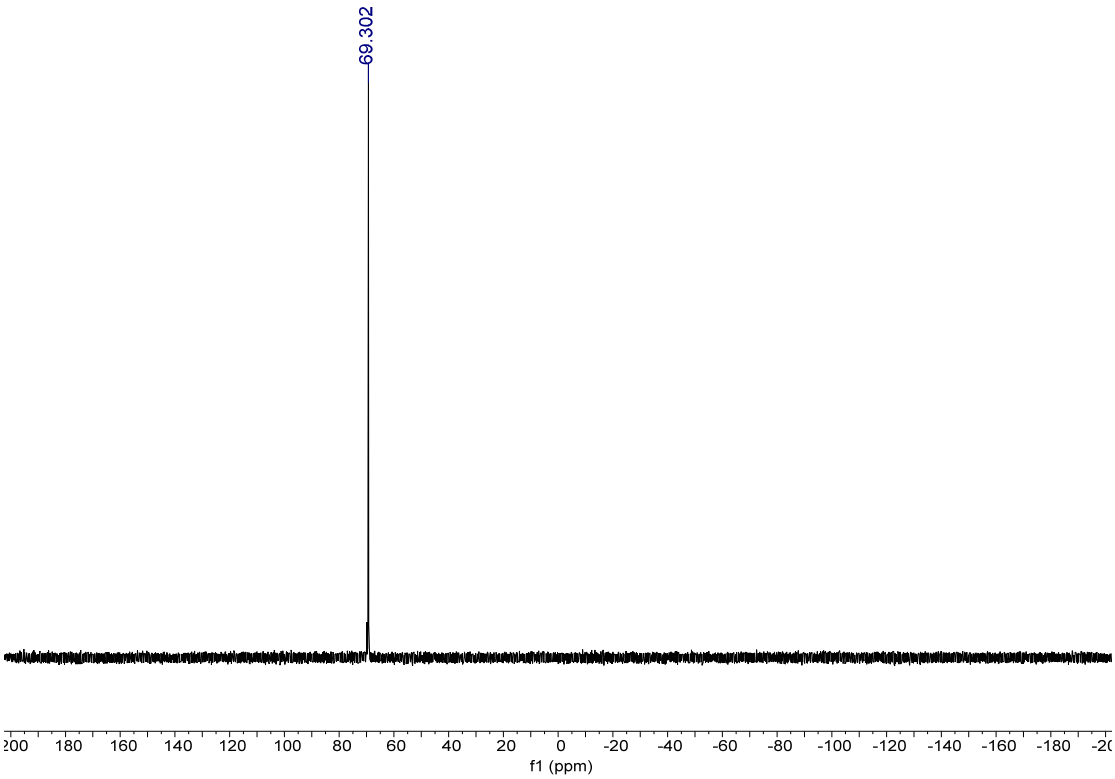

Figure S18. ^{31}P NMR (202 MHz, CD_2Cl_2, 25 ºC) spectrum of [**4**]**Br**. *Assignments:* δ = 69.3

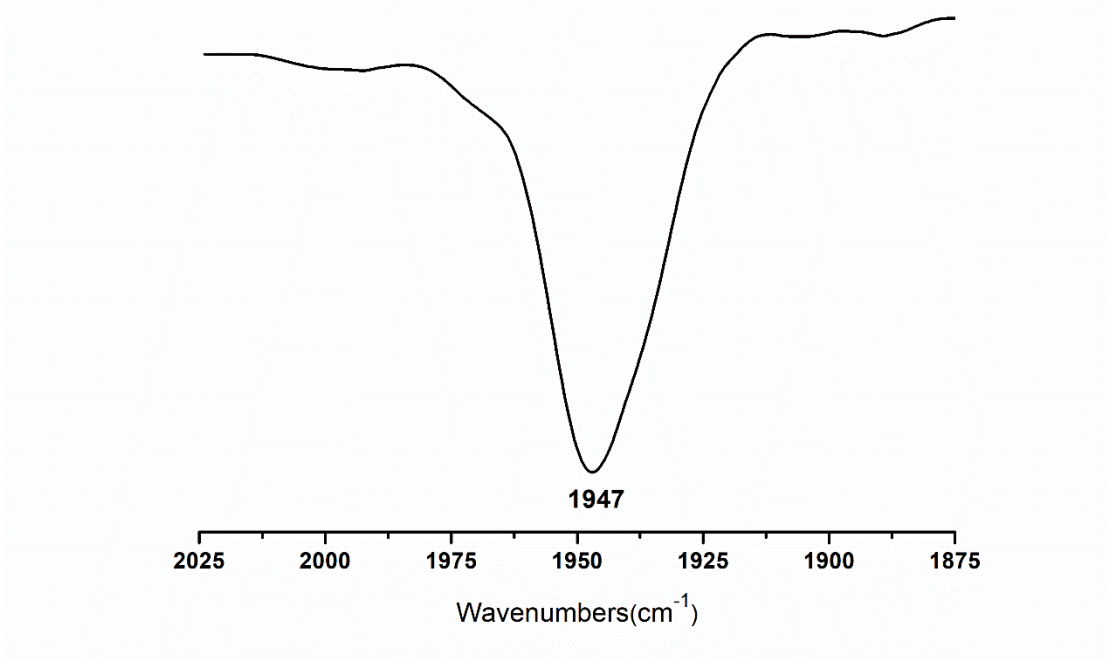

Figure S19. FT-IR (CH_2Cl_2, 25ºC) spectrum of [**5**]$\mathbf{I_3}$. *Assignments:* ν_{CO} = 1947 cm^{-1}.

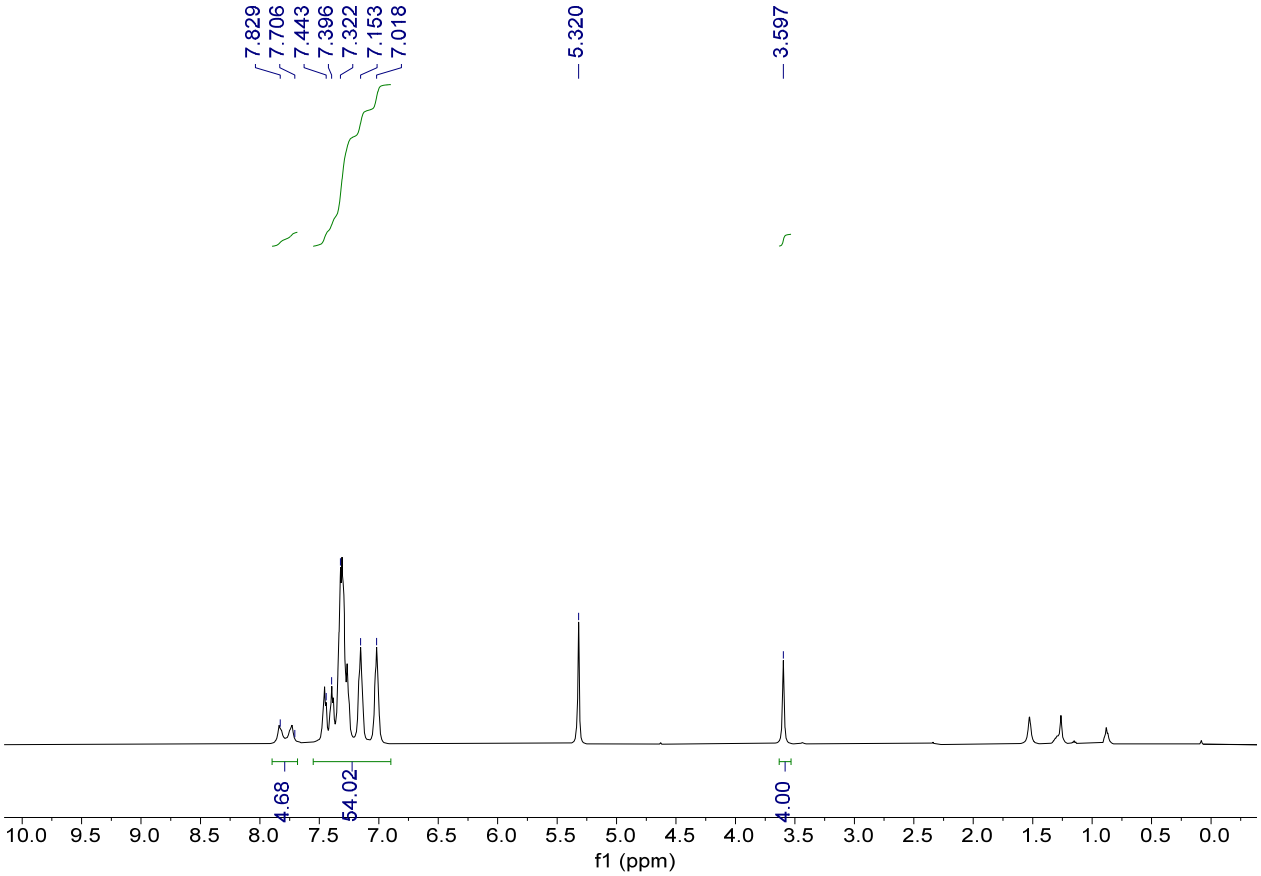

Figure S20. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 ºC) spectrum of [**5**]$\mathbf{I_3}$. *Assignments:* δ = 7.01-7.83 (m, 54H, $10C_6H_5$, 2CH=CH), 3.60 (s, 4H, $2CH_2$).

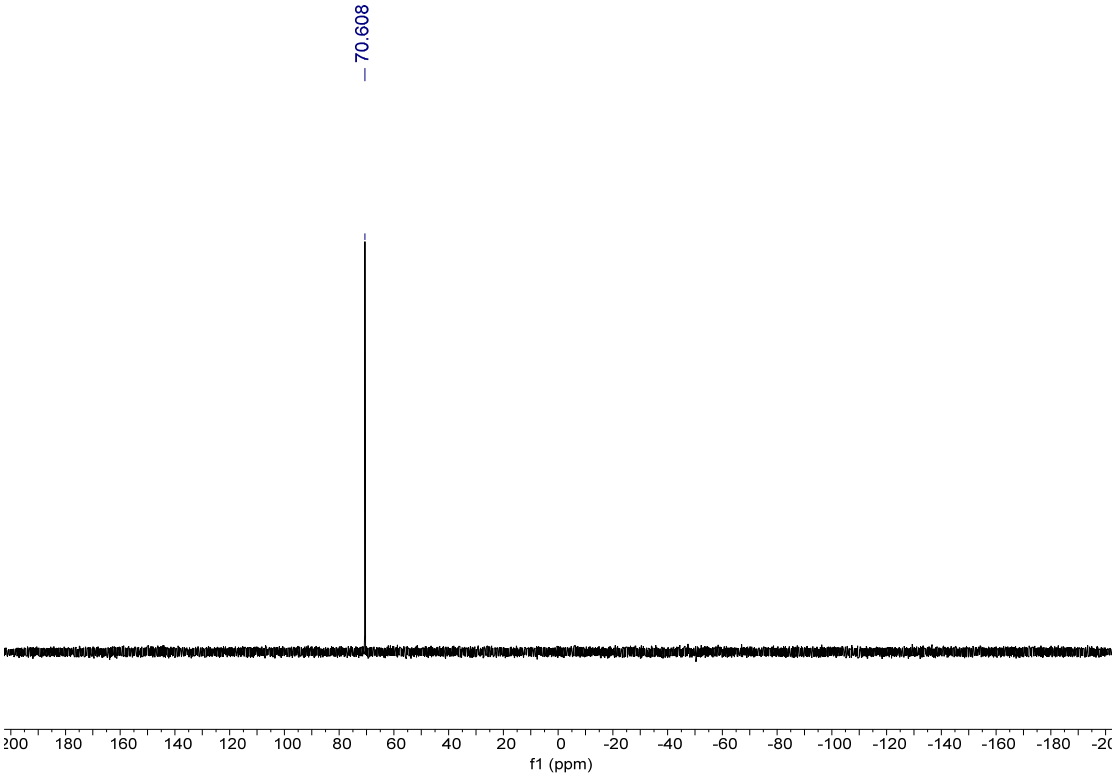

Figure S21. ^{31}P NMR (202 MHz, CD_2Cl_2, 25 ºC) spectrum of [**5**]$\mathbf{I_3}$. *Assignments:* δ = 70.6 ppm

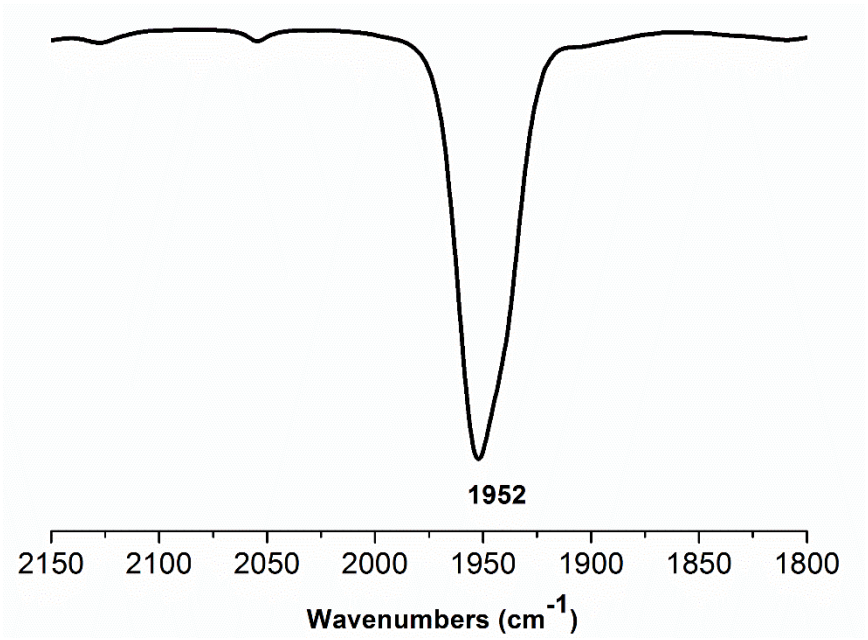

Figure S22. FT-IR (CH_2Cl_2, 25ºC) spectrum of **[6]Cl**. *Assignments:* ν_{CO} = 1952 cm^{-1}.

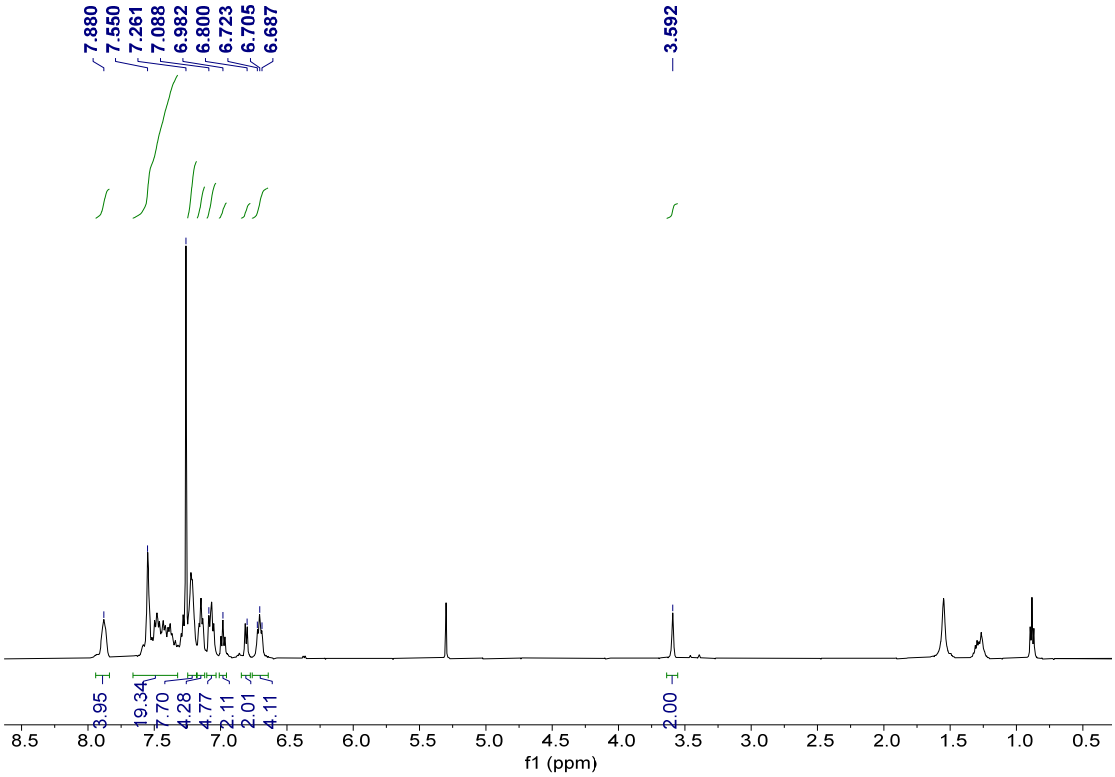

Figure S23. ^1H NMR (500 MHz, $CDCl_3$, 25 ºC) spectrum of **[6]Cl**. *Assignments:* δ = 6.69-7.88 (m, 49H, $9C_6H_5$, 2CH=CH), 3.59 (s, 2H, CH_2).

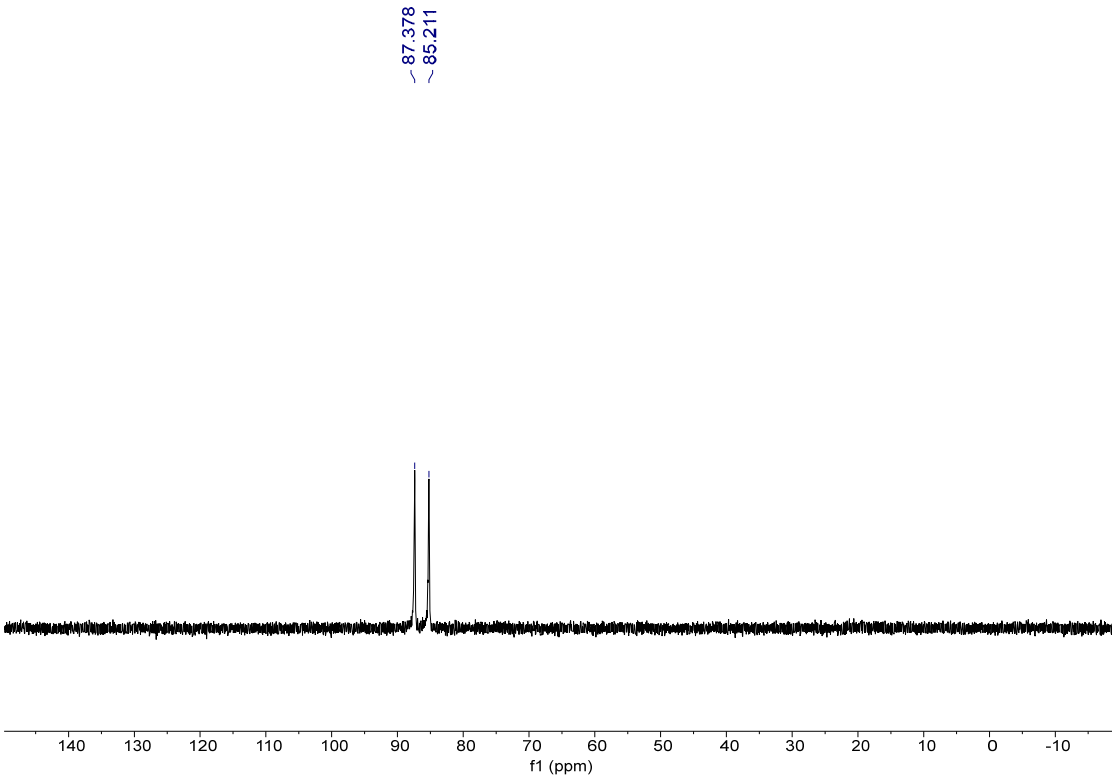

Figure S24. ^{31}P NMR (202 MHz, $CDCl_3$, 25 ºC) spectrum of **[6]Cl**. *Assignments:* δ = 87.3 (s), 85.2 (s)

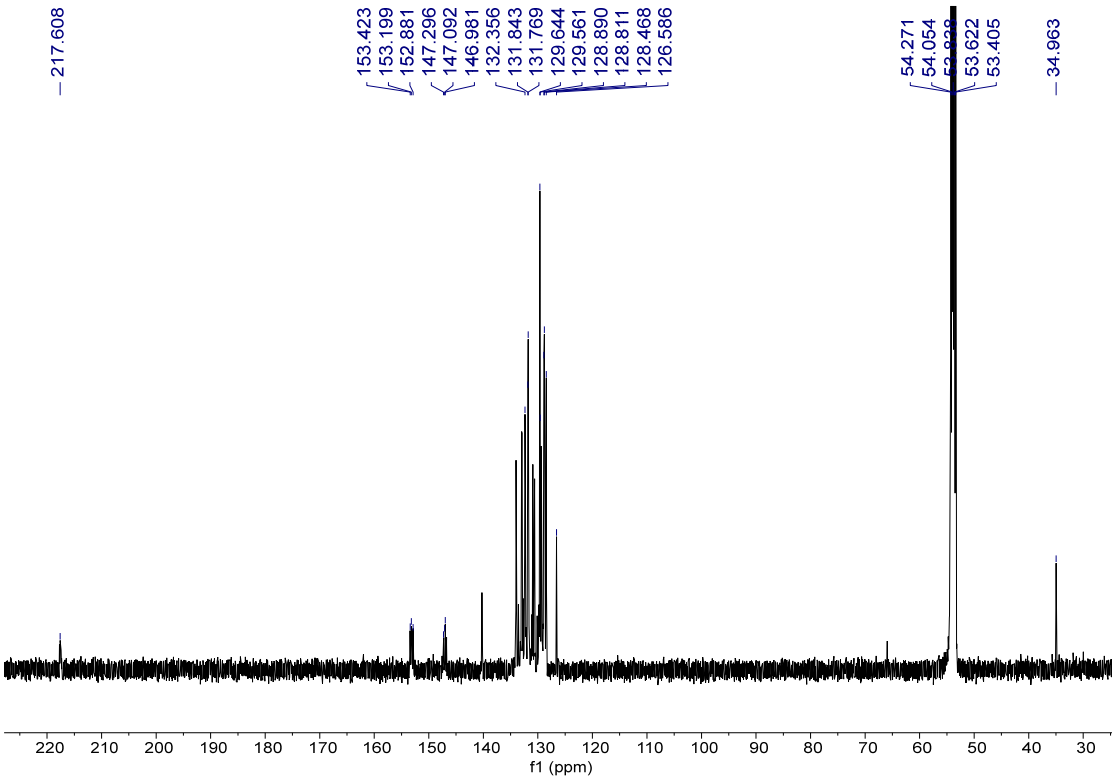

Figure S25. ^{13}C NMR (126 MHz, CD_2Cl_2, 25 ºC) spectrum of **[6]Cl**. *Assignments:* δ = 217.6 (t, $^2J_{P\text{-}C}$ = 15.8 Hz, PFeCO), 153.4-126.6 (m, C_6H_5 and PCH=CHP), 34.9 (s, CH_2).

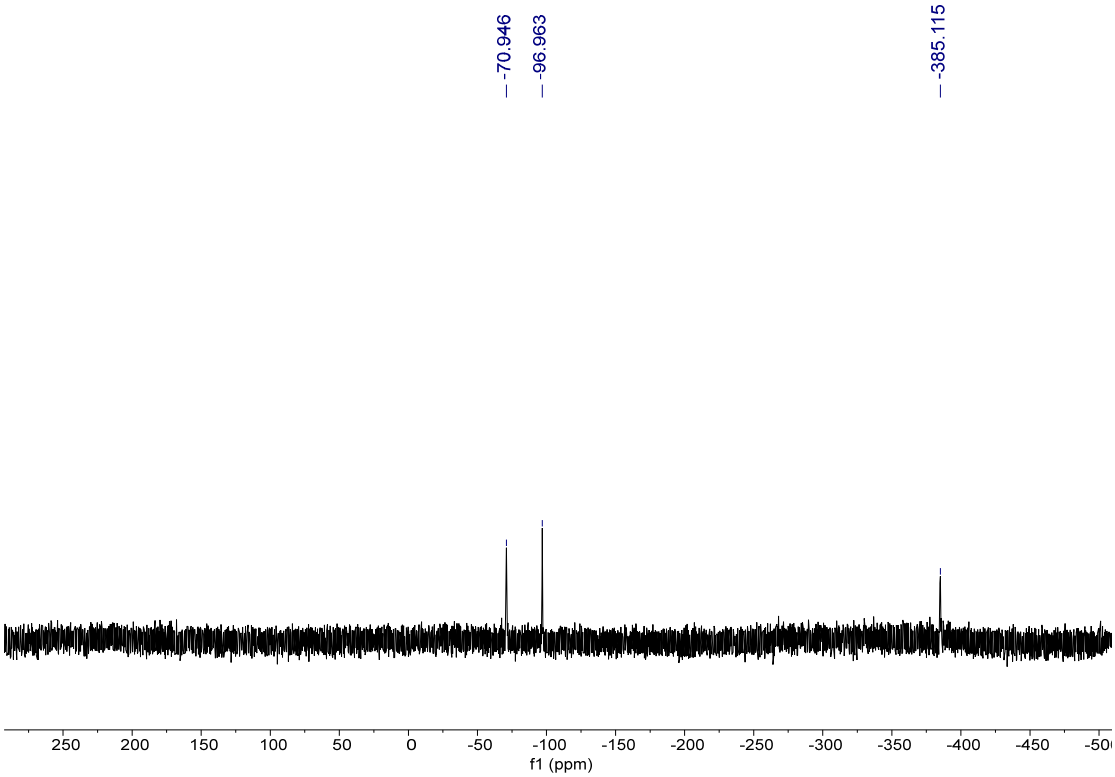

Figure S26. ^{77}Se NMR (95 MHz, CD_2Cl_2, 25 °C) spectrum of **[6]Cl**. *Assignments:* δ = -70.9 (s), -97.0 (s) -385.1 (s).

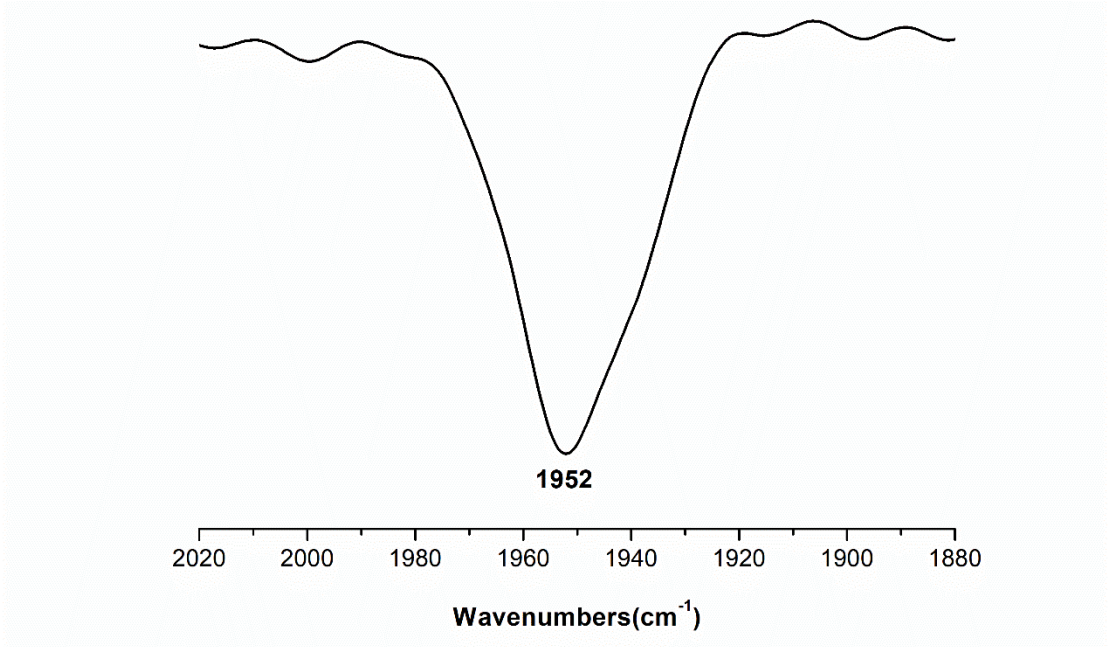

Figure S27. FT-IR (CH_2Cl_2, 25°C) spectrum of **[6]Br**. *Assignments:* ν_{CO} = 1952 cm^{-1}.

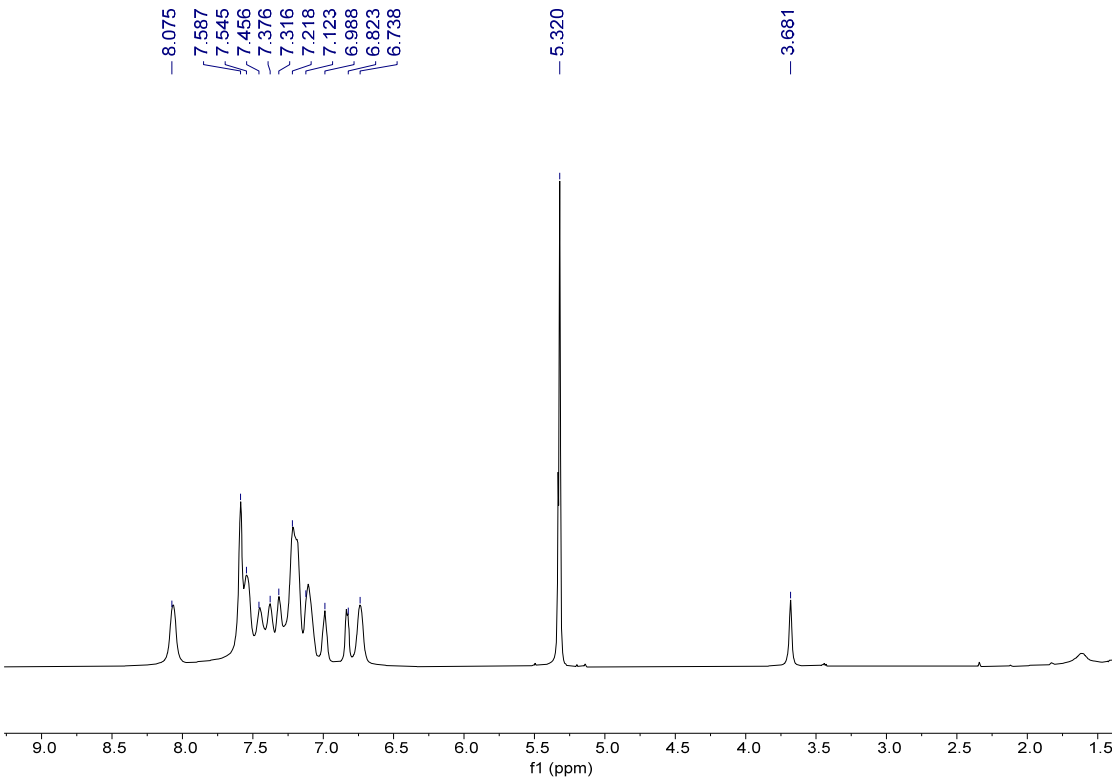

Figure S28. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) spectrum of **[6]Br**. *Assignments:* δ = 6.74-8.07 (m, 49H, $9C_6H_5$, 2CH=CH), 3.68 (s, 2H, CH_2).

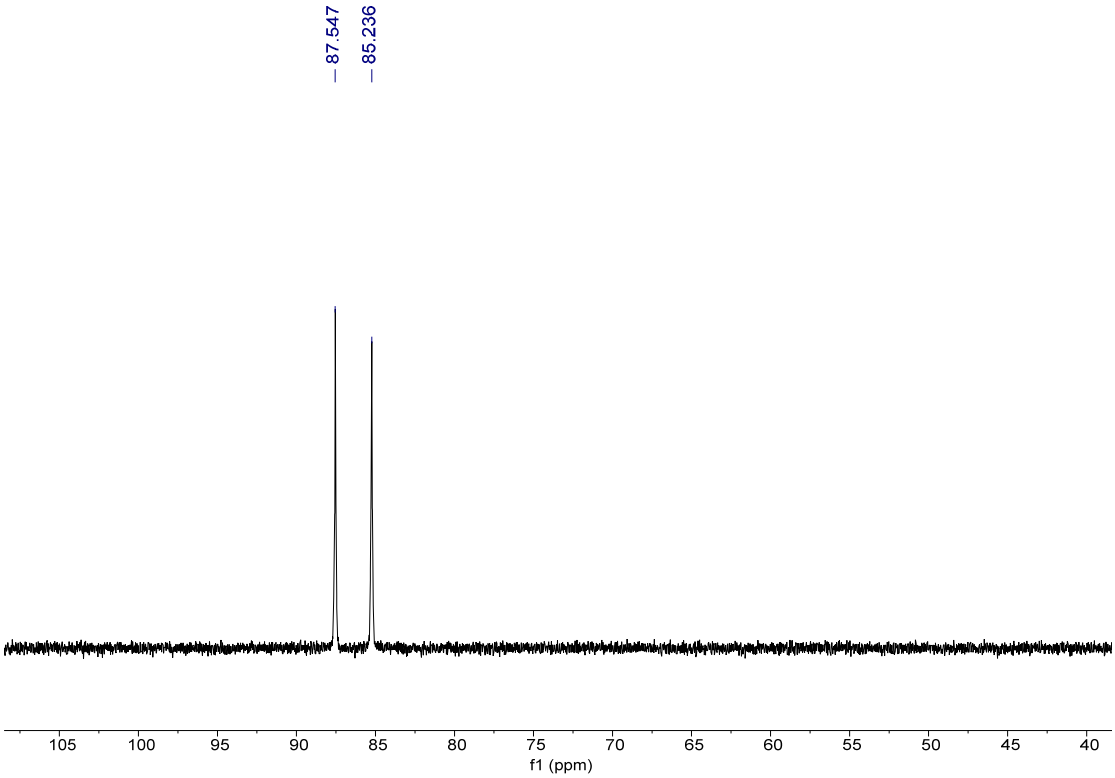

Figure S29. ^{31}P NMR (202 MHz, CD_2Cl_2, 25 °C) spectrum of **[6]Br**. *Assignments:* δ = 87.5(s), 85.2 (s).

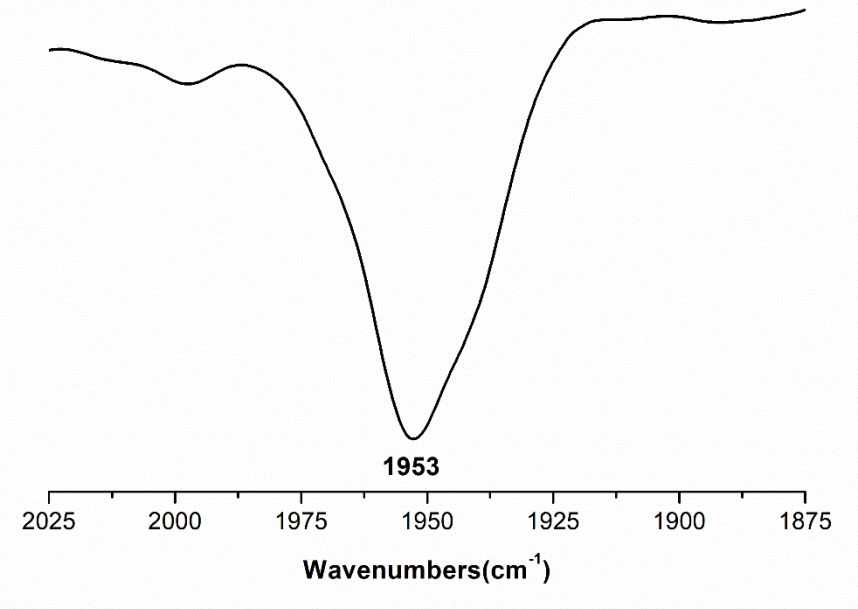

Figure S30. FT-IR (CH_2Cl_2, 25ºC) spectrum of **[6]I_3**. *Assignments:* ν_{CO} = 1953 cm^{-1}.

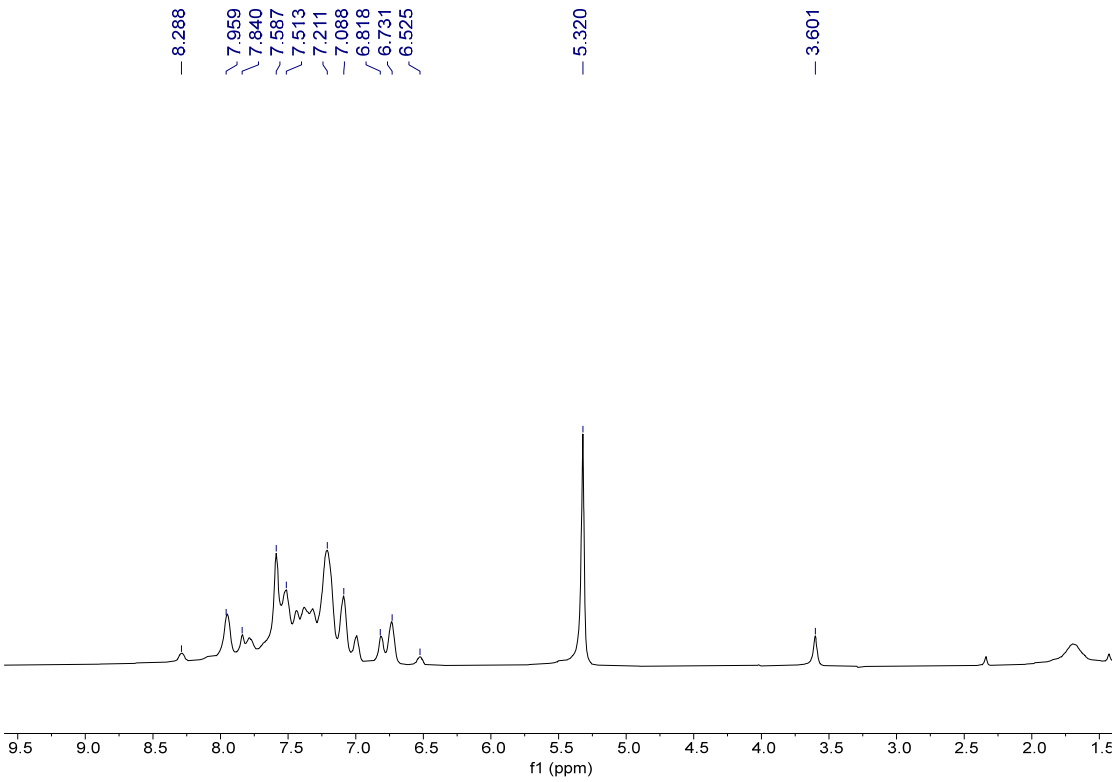

Figure S31. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 ºC) spectrum of **[6]I_3**. *Assignments:* δ = 6.53-8.29 (m, 49H, 9C_6H_5, 2CH=CH), 3.60 (s, 2H, CH_2).

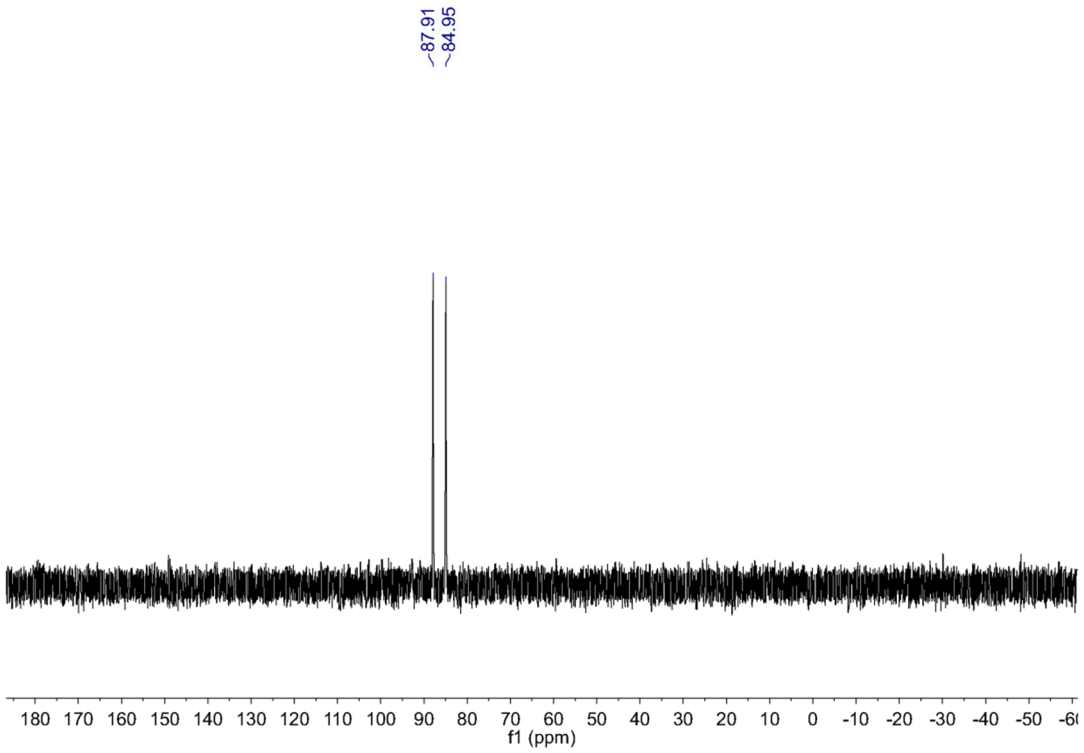

Figure S32. ^{31}P NMR (202 MHz, CD_2Cl_2, 25 °C) spectrum of **[6]$^+$I$_3^-$**. *Assignments:* δ = 87.9 (s), 85.0(s).

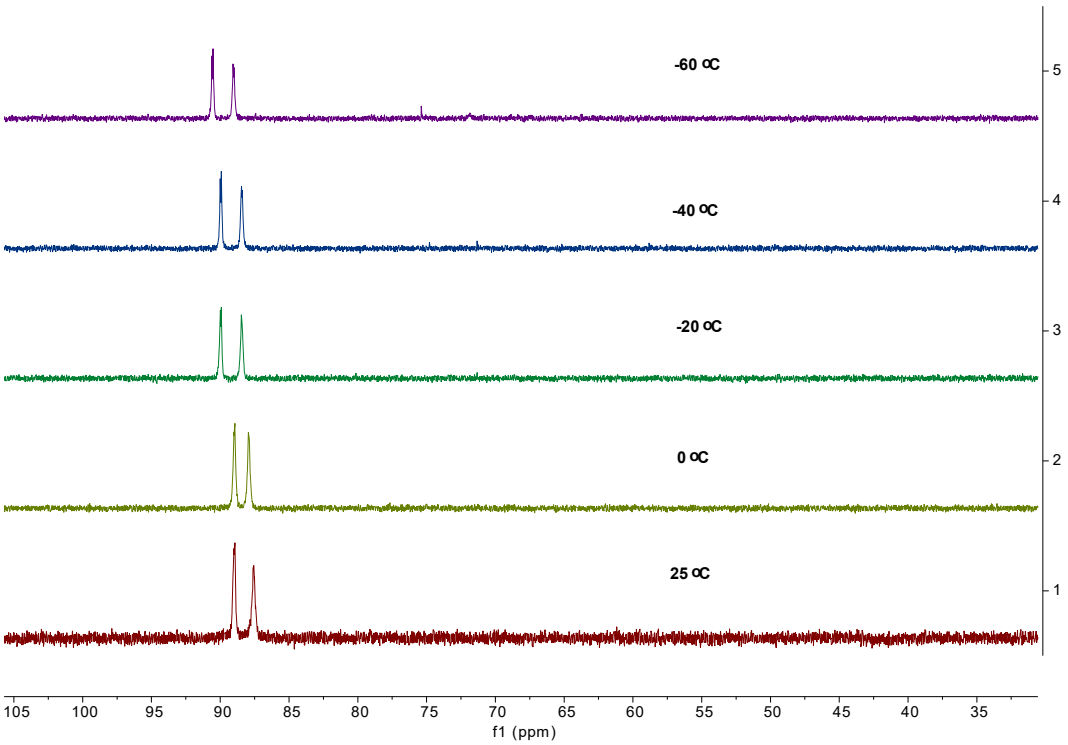

Figure S33. Variable-temperature ^{31}P NMR spectra of a CH_2Cl_2 solution of **1**.

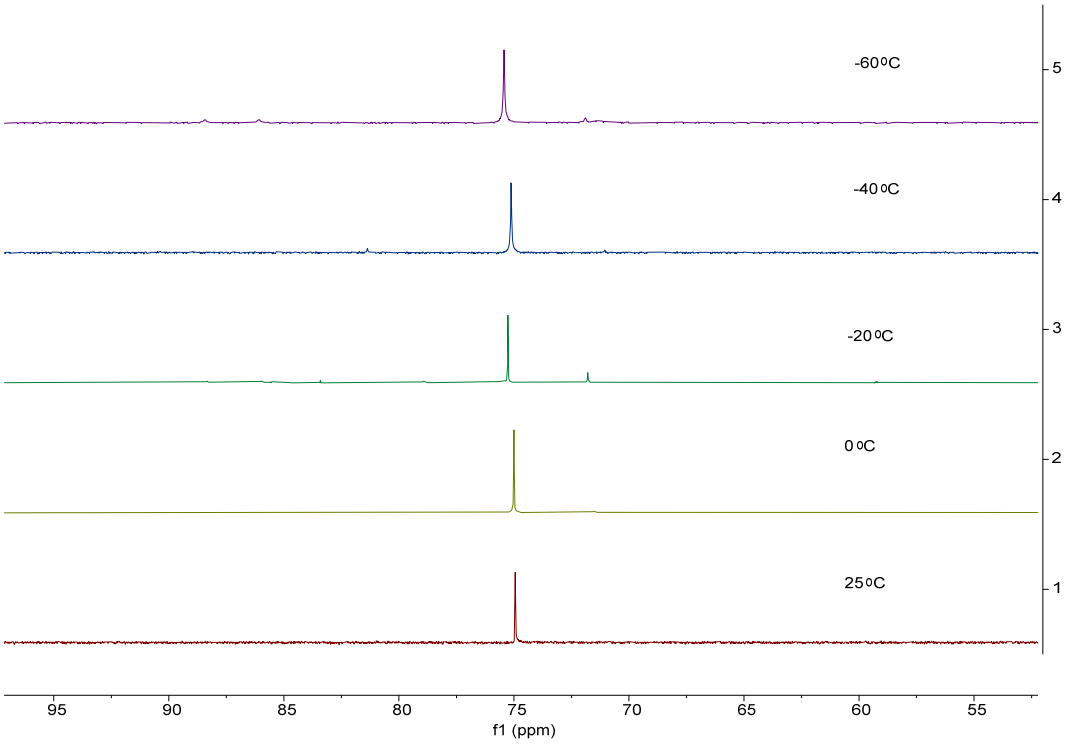

Figure S34. Variable-temperature ^{31}P NMR spectra of a CH_2Cl_2 solution of **2**.

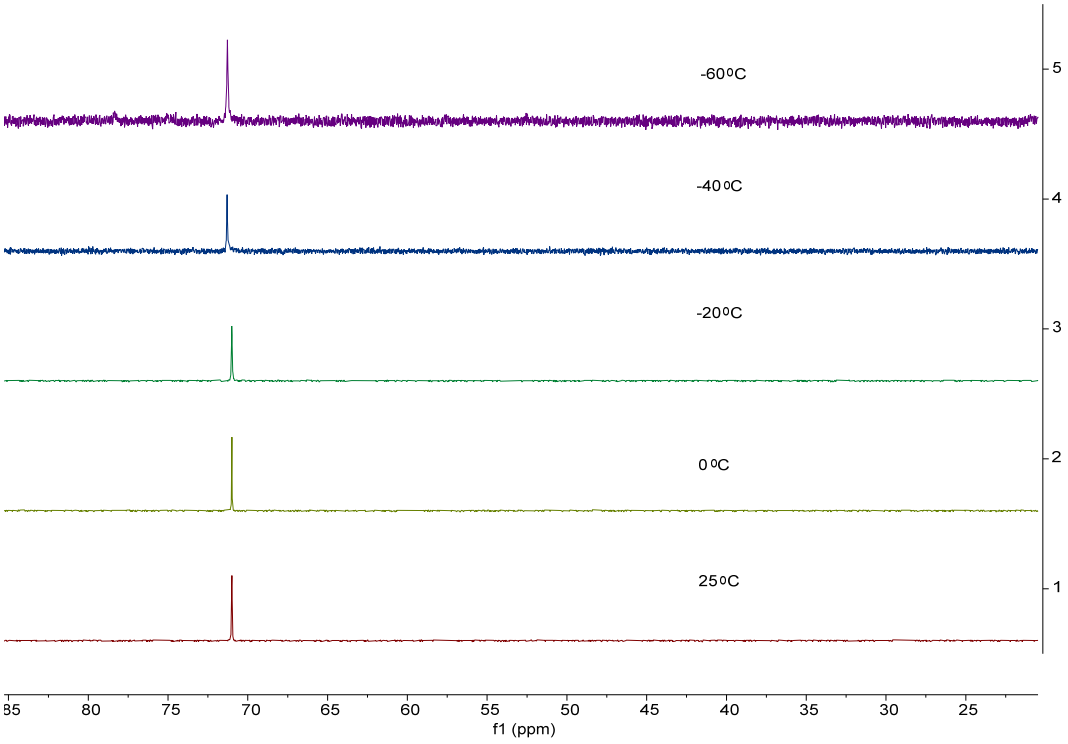

Figure S35. Variable-temperature ^{31}P NMR spectra of a CH_2Cl_2 solution of [**3**]**Cl**.

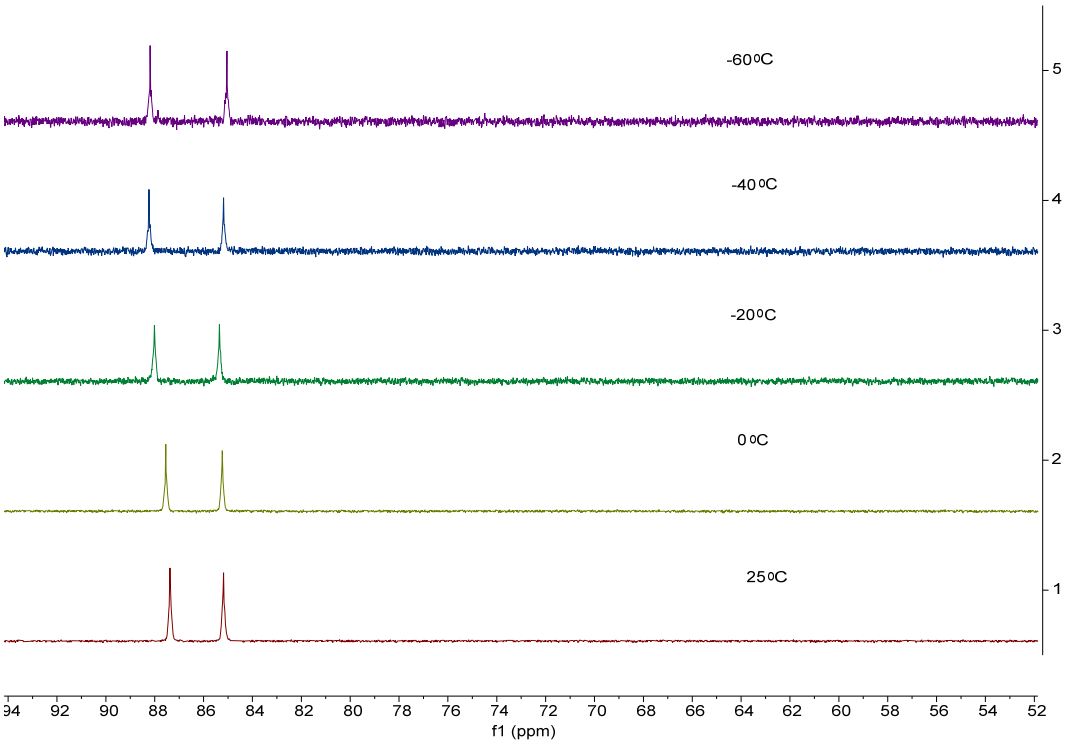

Figure S36. Variable-temperature ^{31}P NMR spectra of a CH_2Cl_2 solution of [**6**]**Cl**.

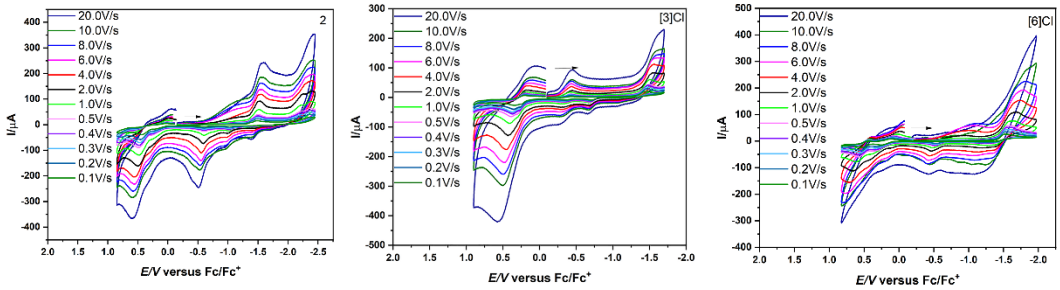

Figure S37. Cyclic voltammogram of complexes **2**, **[3]Cl** and **[6]Cl** (1.0 mM) in 0.1 M *n*-Bu_4NPF_6/MeCN at a scan rate of 0.1-20 V s^{-1} (Scan direction was towards negative potential).

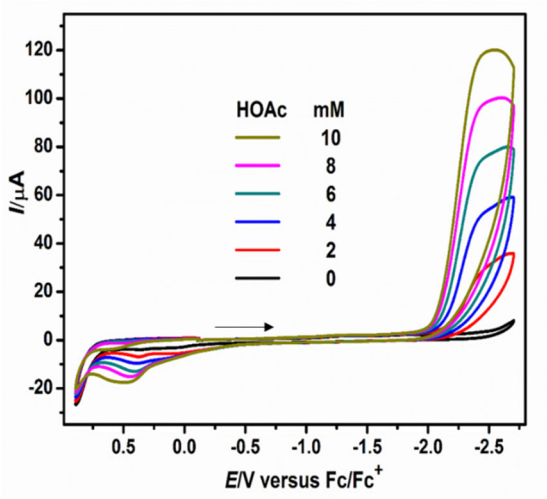

Figure S38. Cyclic voltammogram of CH_3CO_2H (0-10 mM) in 0.1M n-Bu_4NPF_6/MeCN at a scan rate of 0.1 V s^{-1} (Scan direction was towards negative potential).

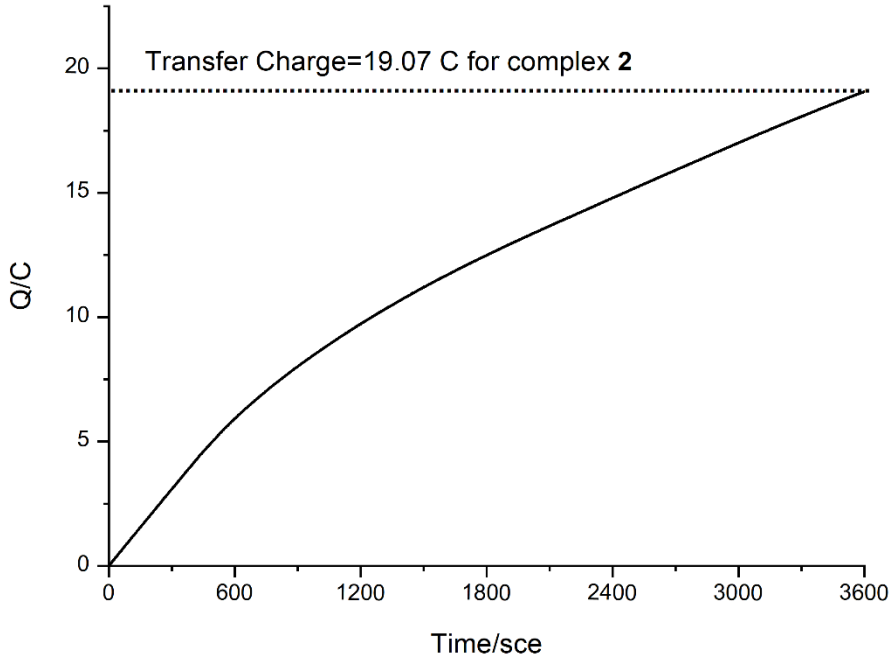

Figure S39. Bulk electrolysis experiment (Q-t curve) of complex **2** (0.5 mM) in 30 mM CH_3CO_2H/MeCN solution for 1 h

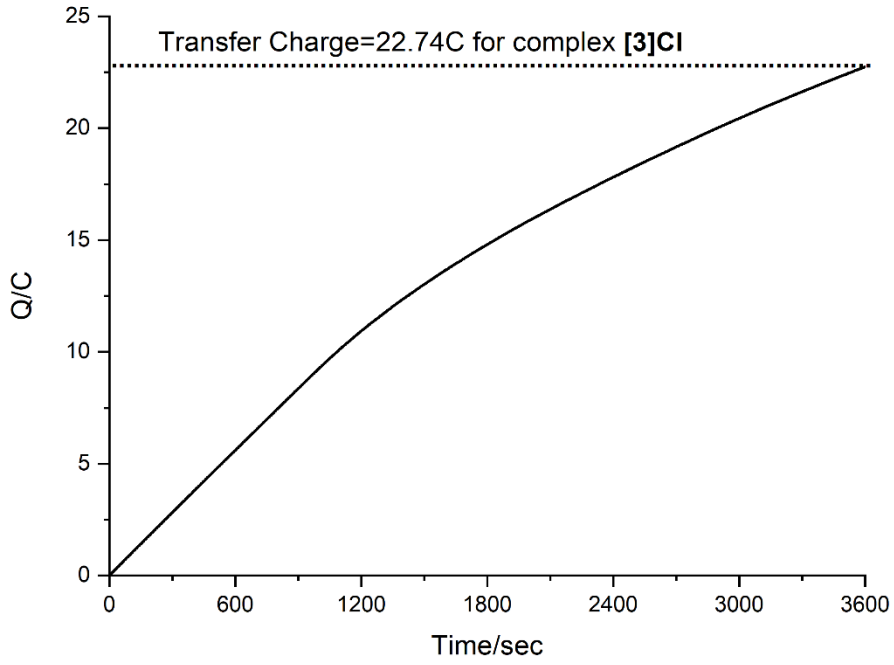

Figure S40. Bulk electrolysis experiment (Q-t curve) of complex **[3]Cl** (0.5 mM) in 30 mM CH_3CO_2H/MeCN solution for 1 h

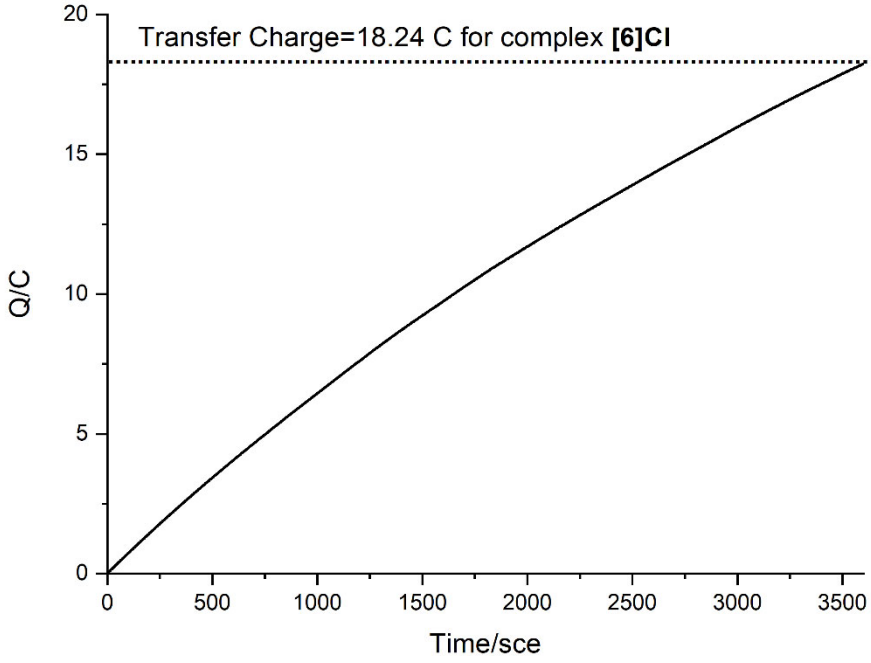

Figure S41. Bulk electrolysis experiment (Q-t curve) of complex **[6]Cl** (0.5 mM) in 30 mM CH_3CO_2H/MeCN solution for 1 h

Table S1. Crystal data and structure refinement parameters for complexes **1, 2** [**3**]**Cl** and [**4**]**Br**.

Complex	**1**	**2**	[**3**]**Cl**	[**4**]**Br**
Mol formula	$C_{69}H_{60}Cl_2Fe_2O_2P_4Se_2$	$C_{68}H_{58}Fe_2O_2P_4Se_3$	$C_{73}H_{63}Cl_{17}Fe_2O_2P_4Se_2$	$C_{68}H_{58}Br_2Fe_2O_2P_4Se_2$
Mol wt	1385.57	1379.6	1968.38	1460.46
Wavelength (Å)	0.71073	0.71073	1.54178	0.71073
Crystal systerm	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	P -1	C c	P -1	P n m a
a (Å)	13.0628(11)	23.121(2)	11.1715(4)	20.426(2)
b (Å)	13.2184(13)	14.3052(11)	19.6825(7)	18.0567(19)
c (Å)	21.5736(18)	20.9130(16)	19.9482(7)	21.292(2)
a (°)	85.832(3)	90	87.753(2)	90
b (°)	73.911(2)	116.972(4)	76.726(2)	90
g (°)	61.5680(10)	90	75.410(2)	90
V/Å^3	3139.7(5)	6164.7(9)	4130.6(3)	7853.0(13)
Z	2	4	2	4
Dcalc (Mg/m^3)	1.466	1.486	1.583	1.235
abs coeff/mm^{-1}	1.853	2.39	9.965	2.431
F(000)	1408	2784	1972	2928
index ranges	-15<=h<=8 -15<=k<=12 -25<=l<=25	-27<=h<=23 -17<=k<=15 -24<=l<=24	-13<=h<=13 -23<=k<=23 -23<=l<=23	0<=h<=24 0<=k<=21 0<=l<=25
no. of reflns	15562	15163	42965	7075
no. of indepreflns	10822	7744	14336	7075
Goodness of fit	0.964	0.969	1.079	0.751
R	0.0652	0.0309	0.0915	0.0846
Rw	0.1906	0.0597	0.2498	0.1667

Table S2. Crystal data and structure refinement parameters for complexes **[5]I_3, [6]Cl [6]Br and [6]I_3**.

Complex	**[5]I_3**	**[6]Cl**	**[6]Br**	**[6]I_3**
Mol formula	$C_{68}H_{58}Fe_2I_4O_2P_4Se_2$	$C_{62}H_{53}Cl_3Fe_2O_2P_4Se_3$	$C_{61}H_{51}BrFe_2O_2P_4Se_3$	$C_{61}H_{51}Fe_2I_3O_2P_4Se_3$
Mol wt	1808.24	1408.85	1368.38	1669.17
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal systerm	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	P n m a	P 21/n	P 21/n	P 21/n
a (Å)	20.5995(19)	11.5638(9)	11.8315(11)	23.086(3)
b (Å)	18.8685(16)	25.932(2)	27.630(3)	12.1078(15)
c (Å)	21.390(2)	20.0938(18)	19.418(2)	27.073(3)
a (°)	90	90	90	90
b (°)	90	92.552(2)	93.403(3)	111.492(5)
g (°)	90	90	90	90
V/Å^3	8313.9(13)	6019.7(9)	6336.6(11)	7041.3(14)
Z	4	4	4	4
Dcalc (Mg/m^3)	1.445	1.555	1.434	1.575
abs coeff/mm^{-1}	2.821	2.578	2.951	3.405
F(000)	3496	2824	2728	3224
	0<=h<=24	-13<=h<=11	-8<=h<=14	-27<=h<=27
index ranges	0<=k<=22	-30<=k<=30	-30<=k<=32	-14<=k<=6
	0<=l<=25	-18<=l<=23	-23<=l<=23	-28<=l<=32
no. of reflns	7530	29270	29883	33012
no. of indepreflns	7530	10600	11122	12374
Goodness of fit	1.085	0.905	1.014	0.795
R	0.0861	0.0625	0.0838	0.0943
Rw	0.1857	0.1141	0.2062	0.2635

Table S3 Selected bond lengths (Å) and angles (º) for **1**.

Complex **1**			
Se(1)-Fe(2)	2.4131(10)	Fe(1)-P(1)	2.2298(17)
Se(1)-Fe(1)	2.4146(10)	Fe(1)-Fe(2)	2.6781(11)
Se(2)-Fe(2)	2.3864(9)	Fe(2)-C(2)	1.756(7)
Se(2)-Fe(1)	2.3915(9)	Fe(2)-P(4)	2.1922(17)
Fe(1)-C(1)	1.756(7)	Fe(2)-P(3)	2.2264(17)
Fe(1)-P(2)	2.2157(17)		
C(55)-Se(1)-Fe(2)	108.09(18)	P(1)-Fe(1)-Fe(2)	151.39(6)
C(55)-Se(1)-Fe(1)	114.6(2)	Se(2)-Fe(1)-Fe(2)	55.82(3)
Fe(2)-Se(1)-Fe(1)	67.38(3)	Se(1)-Fe(1)-Fe(2)	56.28(3)
C(62)-Se(2)-Fe(2)	112.7(2)	C(2)-Fe(2)-P(4)	89.9(2)
C(62)-Se(2)-Fe(1)	116.3(2)	C(2)-Fe(2)-P(3)	88.2(2)
Fe(2)-Se(2)-Fe(1)	68.18(3)	P(4)-Fe(2)-P(3)	86.21(6)
C(1)-Fe(1)-P(2)	91.7(2)	C(2)-Fe(2)-Se(2)	90.4(2)
C(1)-Fe(1)-P(1)	102.5(2)	P(4)-Fe(2)-Se(2)	102.52(5)
P(2)-Fe(1)-P(1)	86.02(6)	P(3)-Fe(2)-Se(2)	171.15(6)
C(1)-Fe(1)-Se(2)	94.82(19)	C(2)-Fe(2)-Se(1)	163.8(2)
P(2)-Fe(1)-Se(2)	172.69(6)	P(4)-Fe(2)-Se(1)	104.64(5)
P(1)-Fe(1)-Se(2)	95.82(5)	P(3)-Fe(2)-Se(1)	99.80(5)
C(1)-Fe(1)-Se(1)	137.2(2)	Se(2)-Fe(2)-Se(1)	79.59(3)
P(2)-Fe(1)-Se(1)	93.49(5)	C(2)-Fe(2)-Fe(1)	107.5(2)
P(1)-Fe(1)-Se(1)	120.24(5)	P(4)-Fe(2)-Fe(1)	151.31(6)
Se(2)-Fe(1)-Se(1)	79.46(3)	P(3)-Fe(2)-Fe(1)	116.28(5)
C(1)-Fe(1)-Fe(2)	85.26(19)	Se(2)-Fe(2)-Fe(1)	56.00(3)
P(2)-Fe(1)-Fe(2)	121.62(5)	Se(1)-Fe(2)-Fe(1)	56.34(3)

Table S4 Selected bond lengths (Å) and angles (º) for **2**.

Complex **2**			
Se(1)-Fe(2)	2.4099(11)	Fe(1)-C(1)	1.741(8)
Se(1)-Fe(1)	2.4215(11)	Fe(1)-P(1)	2.2116(17)
Se(2)-Fe(1)	2.4007(10)	Fe(1)-P(2)	2.225(2)
Se(2)-Fe(2)	2.4360(10)	Fe(2)-C(2)	1.736(7)
Se(3)-Fe(2)	2.4605(11)	Fe(2)-P(3)	2.215(2)
Se(3)-Fe(1)	2.4883(11)	Fe(2)-P(4)	2.2183(18)
C(3)-Se(1)-Fe(2)	114.1(2)	P(3)-Fe(2)-Se(1)	166.92(7)
C(3)-Se(1)-Fe(1)	107.63(19)	P(4)-Fe(2)-Se(1)	90.25(6)
Fe(2)-Se(1)-Fe(1)	85.59(3)	C(2)-Fe(2)-Se(2)	98.7(2)
C(10)-Se(2)-Fe(1)	109.01(18)	P(3)-Fe(2)-Se(2)	93.35(5)
C(10)-Se(2)-Fe(2)	115.0(2)	P(4)-Fe(2)-Se(2)	160.30(6)
Fe(1)-Se(2)-Fe(2)	85.47(3)	Se(1)-Fe(2)-Se(2)	86.91(3)
Fe(2)-Se(3)-Fe(1)	83.10(3)	C(2)-Fe(2)-Se(3)	169.1(2)
C(1)-Fe(1)-P(1)	91.1(2)	P(3)-Fe(2)-Se(3)	90.51(6)
C(1)-Fe(1)-P(2)	90.1(2)	P(4)-Fe(2)-Se(3)	87.49(6)
P(1)-Fe(1)-P(2)	84.28(7)	Se(1)-Fe(2)-Se(3)	77.06(3)
C(1)-Fe(1)-Se(2)	95.4(2)	Se(2)-Fe(2)-Se(3)	72.87(3)
P(1)-Fe(1)-Se(2)	173.54(7)	C(19)-P(1)-Fe(1)	115.3(2)
P(2)-Fe(1)-Se(2)	95.32(6)	P(2)-Fe(1)-Se(3)	101.38(6)
C(1)-Fe(1)-Se(1)	92.8(2)	Se(2)-Fe(1)-Se(3)	72.98(3)
P(1)-Fe(1)-Se(1)	92.61(6)	Se(1)-Fe(1)-Se(3)	76.32(3)
P(2)-Fe(1)-Se(1)	175.75(7)	C(2)-Fe(2)-P(3)	97.0(2)
Se(2)-Fe(1)-Se(1)	87.44(4)	C(2)-Fe(2)-P(4)	101.0(2)
C(1)-Fe(1)-Se(3)	164.2(2)	P(3)-Fe(2)-P(4)	85.10(7)
P(1)-Fe(1)-Se(3)	100.76(6)	C(2)-Fe(2)-Se(1)	95.9(2)

Table S5 Selected bond lengths (Å) and angles (º) for [**3**]**Cl**.

Complex [**3**]**Cl**			
Fe(1)-C(1)	1.735(6)	Fe(2)-C(2)	1.743(8)
Fe(1)-P(1)	2.2376(17)	Fe(2)-P(4)	2.2282(16)
Fe(1)-P(2)	2.2450(17)	Fe(2)-P(3)	2.2300(17)
Fe(1)-Cl(17)	2.4092(13)	Fe(2)-Cl(17)	2.3670(16)
Fe(1)-Se(2)	2.4176(10)	Fe(2)-Se(2)	2.4363(9)
Fe(1)-Se(1)	2.4560(10)	Fe(2)-Se(1)	2.4380(10)
C(1)-Fe(1)-P(1)	90.12(19)	P(4)-Fe(2)-Se(1)	92.86(5)
C(1)-Fe(1)-P(2)	87.9(2)	P(3)-Fe(2)-Se(1)	172.48(6)
P(1)-Fe(1)-P(2)	83.79(6)	Cl(17)-Fe(2)-Se(1)	81.88(4)
C(1)-Fe(1)-Cl(17)	166.4(2)	Se(2)-Fe(2)-Se(1)	87.83(3)
P(1)-Fe(1)-Cl(17)	98.29(5)	C(55)-Se(1)-Fe(2)	108.5(2)
P(2)-Fe(1)-Cl(17)	103.58(6)	C(55)-Se(1)-Fe(1)	107.44(19)
C(1)-Fe(1)-Se(2)	91.91(19)	Fe(2)-Se(1)-Fe(1)	80.10(3)
P(1)-Fe(1)-Se(2)	93.42(5)	C(62)-Se(2)-Fe(1)	109.8(2)
P(2)-Fe(1)-Se(2)	177.20(6)	C(62)-Se(2)-Fe(2)	118.2(2)
Cl(17)-Fe(1)-Se(2)	76.96(4)	Fe(1)-Se(2)-Fe(2)	80.90(3)
C(1)-Fe(1)-Se(1)	91.19(19)	C(2)-Fe(2)-Cl(17)	173.4(2)
P(1)-Fe(1)-Se(1)	178.14(6)	P(4)-Fe(2)-Cl(17)	91.29(6)
P(2)-Fe(1)-Se(1)	94.95(5)	P(3)-Fe(2)-Cl(17)	90.65(6)
Cl(17)-Fe(1)-Se(1)	80.66(4)	C(2)-Fe(2)-Se(2)	98.41(19)
Se(2)-Fe(1)-Se(1)	87.84(4)	P(4)-Fe(2)-Se(2)	168.45(7)
C(2)-Fe(2)-P(4)	93.1(2)	P(3)-Fe(2)-Se(2)	91.41(5)
C(2)-Fe(2)-P(3)	94.6(2)	Cl(17)-Fe(2)-Se(2)	77.39(4)
P(4)-Fe(2)-P(3)	86.39(6)	C(2)-Fe(2)-Se(1)	92.9(2)

Table S6 Selected bond lengths (Å) and angles (º) for [**4**]**Br**.

Complex [**4**]**Br**			
Br(1)-Fe(1)	2.531(2)	Fe(1)-P(1)	2.281(3)
Br(1)-Fe(2)	2.570(2)	Fe(2)-C(2)	1.77(2)
Se(1)-Fe(1)	2.4565(16)	Fe(2)-P(2)	2.273(3)
Se(1)-Fe(2)	2.4572(16)	Fe(1)-C(1)	1.793(18)
Fe(1)-Br(1)-Fe(2)	78.47(7)	P(2)-Fe(2)-Br(1)	101.50(10)
C(29)-Se(1)-Fe(1)	117.7(3)	Se(1)-Fe(2)-Br(1)	78.10(6)
C(29)-Se(1)-Fe(2)	109.1(3)	P(1)-Fe(1)-Br(1)	92.63(9)
Fe(1)-Se(1)-Fe(2)	82.07(6)	Se(1)-Fe(1)-Br(1)	78.87(6)
C(1)-Fe(1)-P(1)	96.8(3)	C(2)-Fe(2)-P(2)	91.6(3)
C(1)-Fe(1)-Se(1)	92.1(3)	C(2)-Fe(2)-Se(1)	89.4(3)
P(1)-Fe(1)-Se(1)	92.69(7)	C(2)-Fe(2)-Br(1)	162.4(4)
C(1)-Fe(1)-Br(1)	167.3(5)		

Table S7 Selected bond lengths (Å) and angles (º) for [**5**]$\mathbf{I_3}$.

Complex **[5]$\mathbf{I_3}$**			
Se(1)-Fe(2)	2.4933(18)	Fe(1)-I(1)	2.772(2)
Se(1)-Fe(1)	2.4937(17)	Fe(2)-C(2)	1.722(16)
Fe(1)-C(1)	1.780(17)	Fe(2)-P(2)	2.285(3)
Fe(1)-P(1)	2.312(3)	Fe(2)-I(1)	2.779(2)
C(29)-Se(1)-Fe(2)	108.8(3)	C(2)-Fe(2)-Se(1)	92.2(3)
C(29)-Se(1)-Fe(1)	114.3(3)	P(2)-Fe(2)-Se(1)	93.92(8)
Fe(2)-Se(1)-Fe(1)	84.72(6)	C(2)-Fe(2)-I(1)	166.5(4)
C(1)-Fe(1)-P(1)	95.5(4)	P(2)-Fe(2)-I(1)	100.72(10)
C(1)-Fe(1)-Se(1)	94.2(4)	Se(1)-Fe(2)-I(1)	78.18(6)
P(1)-Fe(1)-Se(1)	93.35(7)	Fe(1)-I(1)-Fe(2)	74.51(6)
C(1)-Fe(1)-I(1)	169.4(5)	Se(1)-Fe(1)-I(1)	78.30(6)
P(1)-Fe(1)-I(1)	92.33(9)	C(2)-Fe(2)-P(2)	89.2(3)

Table S8 Selected bond lengths (Å) and angles (º) for [**6**]**Cl**.

Complex [**6**]**Cl**			
Fe(1)-C(60)	1.736(9)	Fe(2)-C(61)	1.719(9)
Fe(1)-P(1)	2.204(2)	Fe(2)-P(4)	2.202(2)
Fe(1)-P(2)	2.235(2)	Fe(2)-P(3)	2.218(2)
Fe(1)-Se(2)	2.3874(13)	Fe(2)-Se(2)	2.3992(13)
Fe(1)-Se(1)	2.4344(12)	Fe(2)-Se(1)	2.4440(13)
Fe(1)-Se(3)	2.4567(14)	Fe(2)-Se(3)	2.4557(12)
C(60)-Fe(1)-P(1)	92.3(3)	P(4)-Fe(2)-Se(3)	109.16(7)
C(60)-Fe(1)-P(2)	92.8(3)	P(3)-Fe(2)-Se(3)	94.91(7)
P(1)-Fe(1)-P(2)	86.28(8)	Se(2)-Fe(2)-Se(3)	57.23(3)
C(60)-Fe(1)-Se(2)	105.6(3)	Se(1)-Fe(2)-Se(3)	82.75(4)
P(1)-Fe(1)-Se(2)	162.06(8)	C(1)-Se(1)-Fe(1)	110.7(3)
P(2)-Fe(1)-Se(2)	91.85(7)	C(1)-Se(1)-Fe(2)	102.2(2)
C(60)-Fe(1)-Se(1)	91.7(3)	Fe(1)-Se(1)-Fe(2)	87.53(4)
P(1)-Fe(1)-Se(1)	94.39(7)	Se(2)-Se(3)-Fe(2)	60.16(4)
P(2)-Fe(1)-Se(1)	175.50(8)	Se(2)-Se(3)-Fe(1)	59.82(4)
Se(2)-Fe(1)-Se(1)	86.14(4)	Fe(2)-Se(3)-Fe(1)	86.77(4)
C(60)-Fe(1)-Se(3)	162.3(3)	Se(3)-Se(2)-Fe(1)	62.82(4)
P(1)-Fe(1)-Se(3)	104.86(7)	Se(3)-Se(2)-Fe(2)	62.61(4)
P(2)-Fe(1)-Se(3)	92.60(7)	Fe(1)-Se(2)-Fe(2)	89.66(4)
Se(2)-Fe(1)-Se(3)	57.36(4)	P(3)-Fe(2)-Se(2)	93.30(7)
Se(1)-Fe(1)-Se(3)	82.92(4)	C(61)-Fe(2)-Se(1)	93.9(3)
C(61)-Fe(2)-P(4)	90.5(3)	P(4)-Fe(2)-Se(1)	94.85(7)
C(61)-Fe(2)-P(3)	88.4(3)	P(3)-Fe(2)-Se(1)	177.64(7)
P(4)-Fe(2)-P(3)	85.64(9)	Se(2)-Fe(2)-Se(1)	85.67(4)
C(61)-Fe(2)-Se(2)	103.2(3)	C(61)-Fe(2)-Se(3)	160.2(3)
P(4)-Fe(2)-Se(2)	166.26(7)		

Table S9 Selected bond lengths (Å) and angles (º) for [**6**]**Br**.

Complex [**6**]**Br**			
Fe(1)-C(1)	1.732(13)	Fe(2)-C(2)	1.697(13)
Fe(1)-P(1)	2.188(3)	Fe(2)-P(3)	2.194(3)
Fe(1)-P(2)	2.205(3)	Fe(2)-P(4)	2.217(3)
Fe(1)-Se(2)	2.3883(18)	Fe(2)-Se(2)	2.3729(18)
Fe(1)-Se(1)	2.4212(18)	Fe(2)-Se(1)	2.4210(18)
Fe(1)-Se(3)	2.4399(17)	Fe(2)-Se(3)	2.4487(18)
C(1)-Fe(1)-P(1)	89.9(4)	P(4)-Fe(2)-Se(3)	92.61(10)
C(1)-Fe(1)-P(2)	87.6(4)	Se(2)-Fe(2)-Se(3)	57.44(5)
P(1)-Fe(1)-P(2)	86.02(12)	Se(1)-Fe(2)-Se(3)	81.92(6)
C(1)-Fe(1)-Se(2)	102.9(4)	C(55)-Se(1)-Fe(2)	111.6(4)
P(1)-Fe(1)-Se(2)	167.10(11)	C(55)-Se(1)-Fe(1)	101.6(4)
P(2)-Fe(1)-Se(2)	93.16(10)	Fe(2)-Se(1)-Fe(1)	87.88(6)
C(1)-Fe(1)-Se(1)	95.1(4)	Se(2)-Se(3)-Fe(1)	60.20(5)
P(1)-Fe(1)-Se(1)	94.27(10)	Se(2)-Se(3)-Fe(2)	59.64(5)
P(2)-Fe(1)-Se(1)	177.23(11)	Fe(1)-Se(3)-Fe(2)	86.83(6)
Se(2)-Fe(1)-Se(1)	85.94(6)	Se(3)-Se(2)-Fe(2)	62.93(5)
C(1)-Fe(1)-Se(3)	160.1(4)	Se(3)-Se(2)-Fe(1)	62.44(5)
P(1)-Fe(1)-Se(3)	109.85(10)	Fe(2)-Se(2)-Fe(1)	89.77(6)
P(2)-Fe(1)-Se(3)	95.21(9)	P(4)-Fe(2)-Se(2)	91.51(10)
Se(2)-Fe(1)-Se(3)	57.36(5)	C(2)-Fe(2)-Se(1)	91.3(4)
Se(1)-Fe(1)-Se(3)	82.10(6)	P(3)-Fe(2)-Se(1)	94.96(10)
C(2)-Fe(2)-P(3)	92.7(4)	P(4)-Fe(2)-Se(1)	174.47(11)
C(2)-Fe(2)-P(4)	94.1(4)	Se(2)-Fe(2)-Se(1)	86.28(6)
P(3)-Fe(2)-P(4)	85.77(12)	C(2)-Fe(2)-Se(3)	159.8(4)
C(2)-Fe(2)-Se(2)	103.4(4)	P(3)-Fe(2)-Se(3)	106.76(10)
P(3)-Fe(2)-Se(2)	163.89(11)		

Table S10 Selected bond lengths (Å) and angles (º) for [**6**]$\mathbf{I_3}$.

Complex [**6**]$\mathbf{I_3}$			
Se(1)-Fe(1)	2.394(2)	Fe(1)-C(1)	1.755(18)
Se(1)-Fe(2)	2.403(2)	Fe(1)-P(1)	2.251(4)
Se(2)-Se(3)	2.332(2)	Fe(1)-P(2)	2.273(4)
Se(2)-Fe(1)	2.403(2)	Fe(2)-C(2)	1.679(13)
Se(2)-Fe(2)	2.429(2)	Fe(2)-P(4)	2.236(4)
Se(3)-Fe(2)	2.369(2)	Fe(2)-P(3)	2.268(4)
Se(3)-Fe(1)	2.381(2)		
C(55)-Se(1)-Fe(1)	110.4(4)	P(4)-Fe(2)-Se(2)	108.57(11)
C(55)-Se(1)-Fe(2)	103.8(3)	P(3)-Fe(2)-Se(2)	94.15(11)
Fe(1)-Se(1)-Fe(2)	80.60(7)	Se(3)-Fe(2)-Se(2)	58.16(7)
Se(3)-Se(2)-Fe(1)	60.36(7)	Se(1)-Fe(2)-Se(2)	86.59(7)
Se(3)-Se(2)-Fe(2)	59.63(6)	C(1)-Fe(1)-Se(2)	163.2(5)
Fe(1)-Se(2)-Fe(2)	79.90(7)	P(1)-Fe(1)-Se(2)	95.76(12)
Se(2)-Se(3)-Fe(2)	62.22(6)	P(2)-Fe(1)-Se(2)	95.51(13)
Se(2)-Se(3)-Fe(1)	61.28(7)	Se(3)-Fe(1)-Se(2)	58.36(7)
Fe(2)-Se(3)-Fe(1)	81.56(8)	Se(1)-Fe(1)-Se(2)	87.37(8)
C(1)-Fe(1)-P(1)	101.1(5)	C(2)-Fe(2)-P(4)	91.7(4)
C(1)-Fe(1)-P(2)	86.5(5)	C(2)-Fe(2)-P(3)	90.7(4)
P(1)-Fe(1)-P(2)	83.97(15)	P(4)-Fe(2)-P(3)	84.85(14)
C(1)-Fe(1)-Se(3)	105.0(5)	C(2)-Fe(2)-Se(3)	101.7(4)
P(1)-Fe(1)-Se(3)	152.84(13)	P(4)-Fe(2)-Se(3)	166.34(12)
P(2)-Fe(1)-Se(3)	90.10(12)	P(3)-Fe(2)-Se(3)	92.57(12)
C(1)-Fe(1)-Se(1)	91.9(5)	C(2)-Fe(2)-Se(1)	91.6(4)
P(1)-Fe(1)-Se(1)	91.51(12)	P(4)-Fe(2)-Se(1)	86.73(11)
P(2)-Fe(1)-Se(1)	174.86(13)	P(3)-Fe(2)-Se(1)	171.33(13)
Se(3)-Fe(1)-Se(1)	95.03(8)		