Di-, tri- and tetraphosphine-substituted Fe/Se carbonyls: Synthesis, Characterization and electrochemical properties

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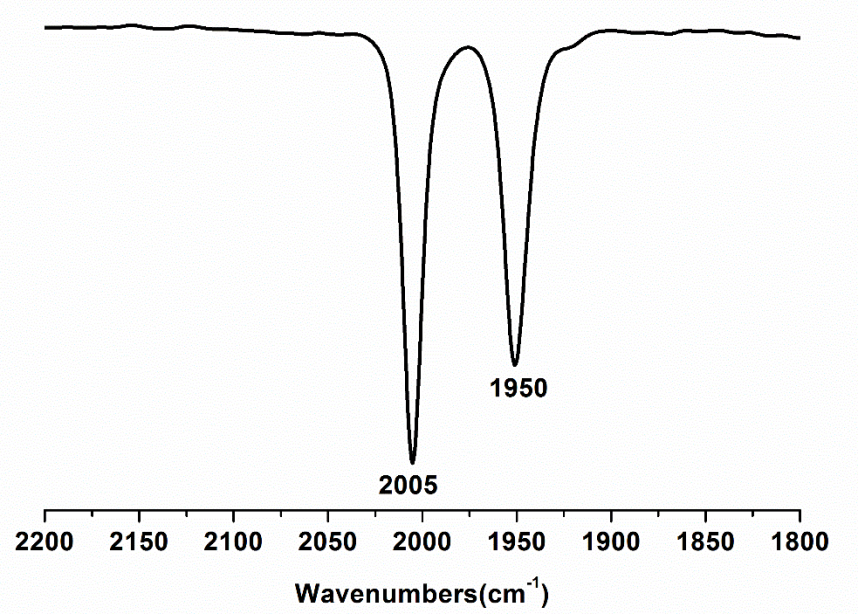


Figure S1. FT-IR (CH_2Cl_2, 25ºC) spectrum of **1**. *Assignments:* ν_{CO} = 2005, 1950 cm^{-1}.

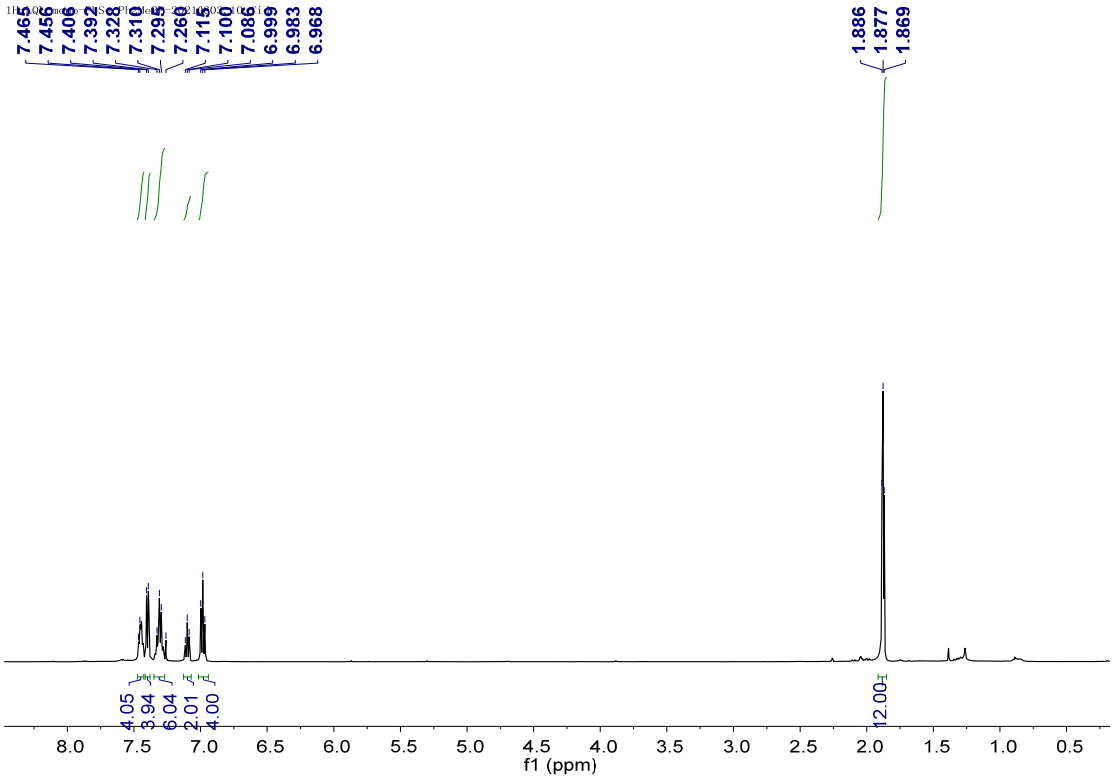


Figure S2. ^1H NMR (500 MHz, $CDCl_3$, 25 ºC) spectrum of **1**. *Assignments:* δ = 7.47-6.97 (m, 20H, $4C_6H_5$), 1.87 (t, $^2J_{P\text{-}H}$ = 4.5 Hz, 12H, $4CH_3$) ppm.

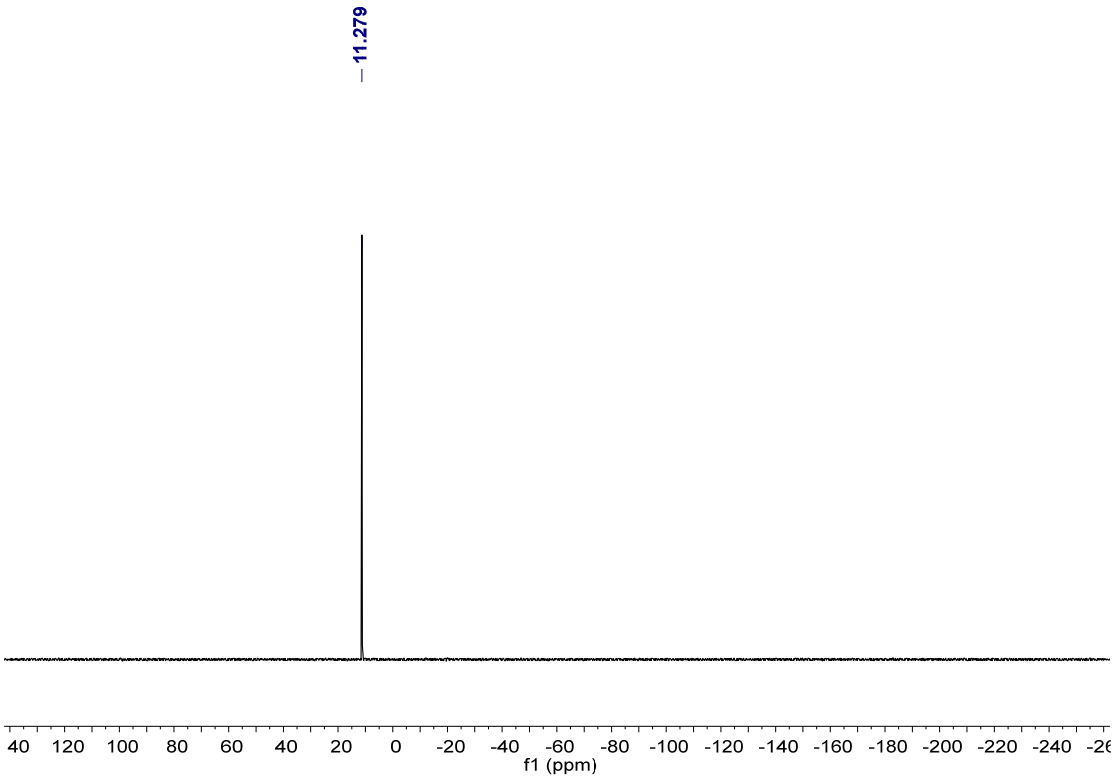


Figure S3. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C) spectrum of **1**.

Assignments: δ =11.28 (s) ppm

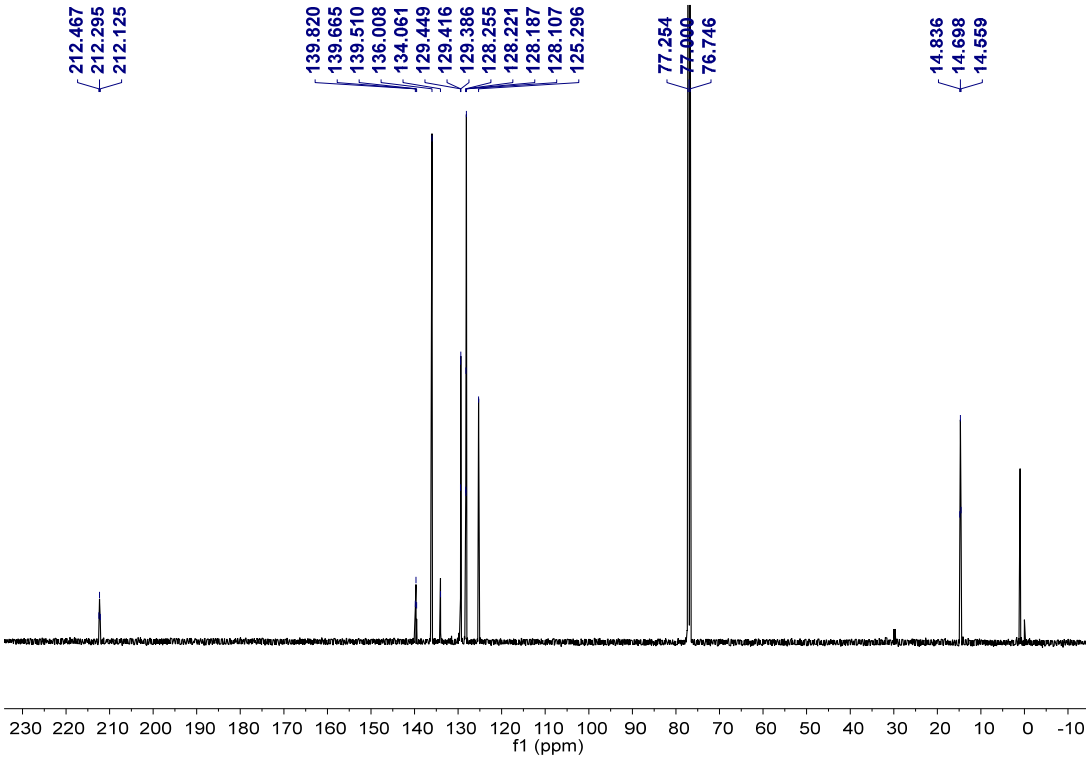


Figure S4. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) spectrum of **1**.

Assignments: δ = 212.3 (t, $^2J_{P\text{-}C}$ = 21.4, $Fe(CO)_2$), 139.8-125.3 (C_6H_5), 14.7 (t, $J_{P\text{-}C}$ = 17.4 Hz, PCH_3) ppm

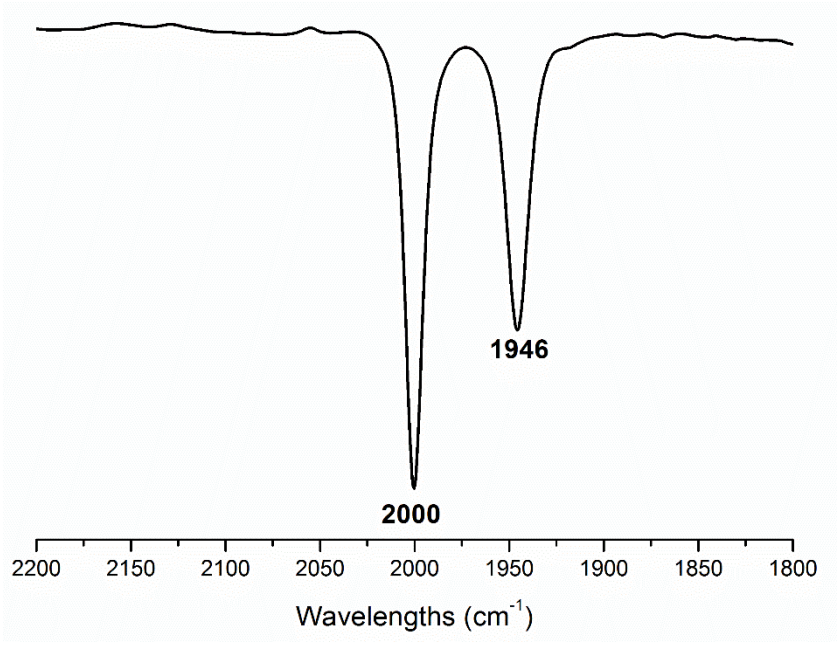


Figure S5. FT-IR (CH_2Cl_2, 25ºC) spectrum of **2**. *Assignments:* ν_{CO} = 2000, 1946 cm^{-1}.

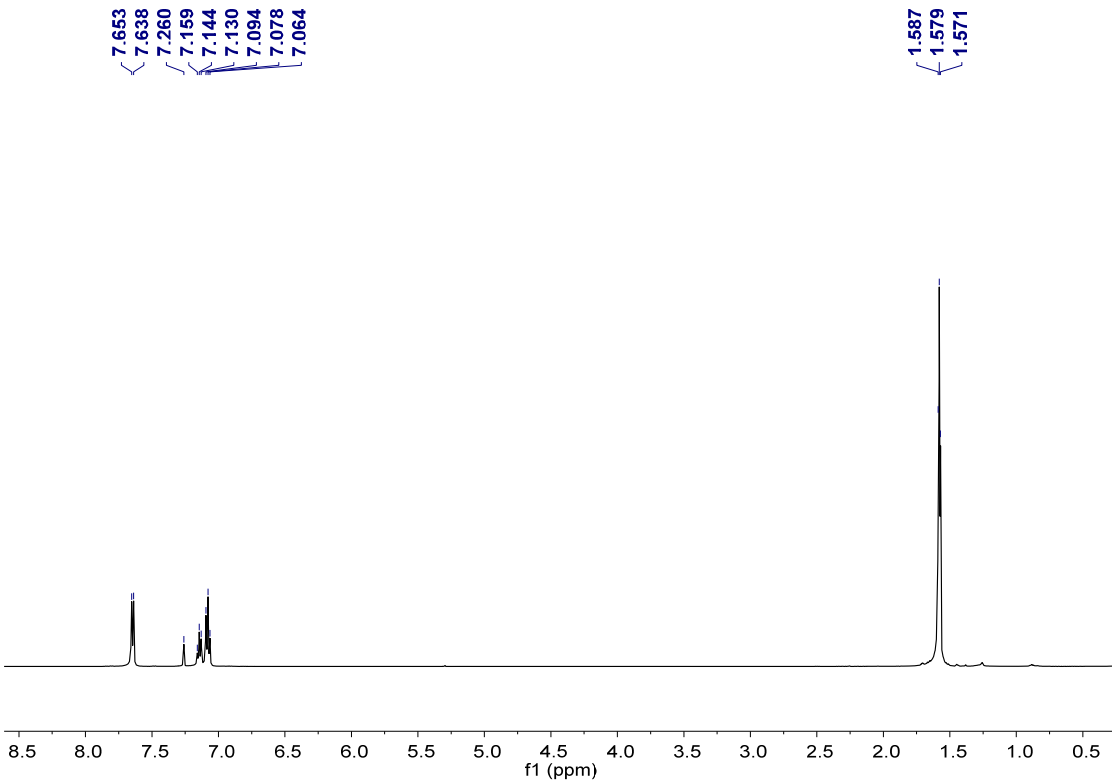


Figure S6. ^1H NMR (500 MHz, $CDCl_3$, 25 ºC) spectrum of **2**. *Assignments:* δ = 7.65, 7.14, 7.08 (d, t, t, $^3J_{H-H}$ = 7.5 Hz, 10H, $2C_6H_5$), 1.58 (t, $^2J_{P-H}$ = 4Hz, 18H, $6CH_3$) ppm.

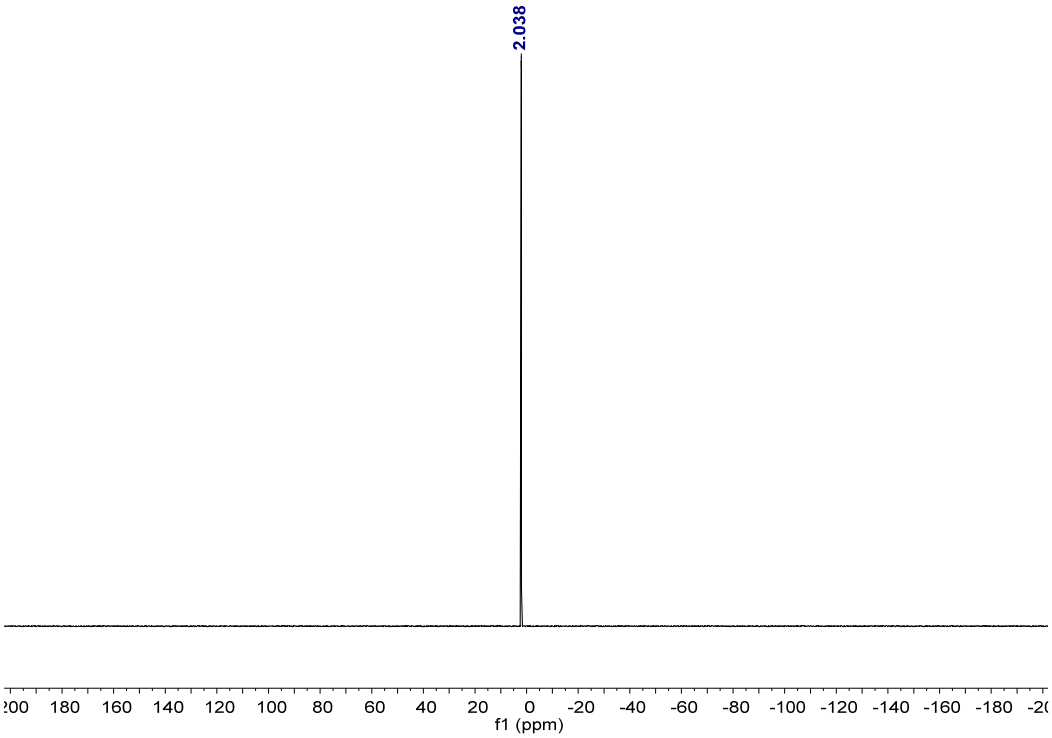


Figure S7. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C) spectrum of **2**.

Assignments: δ = 2.04 (s) ppm

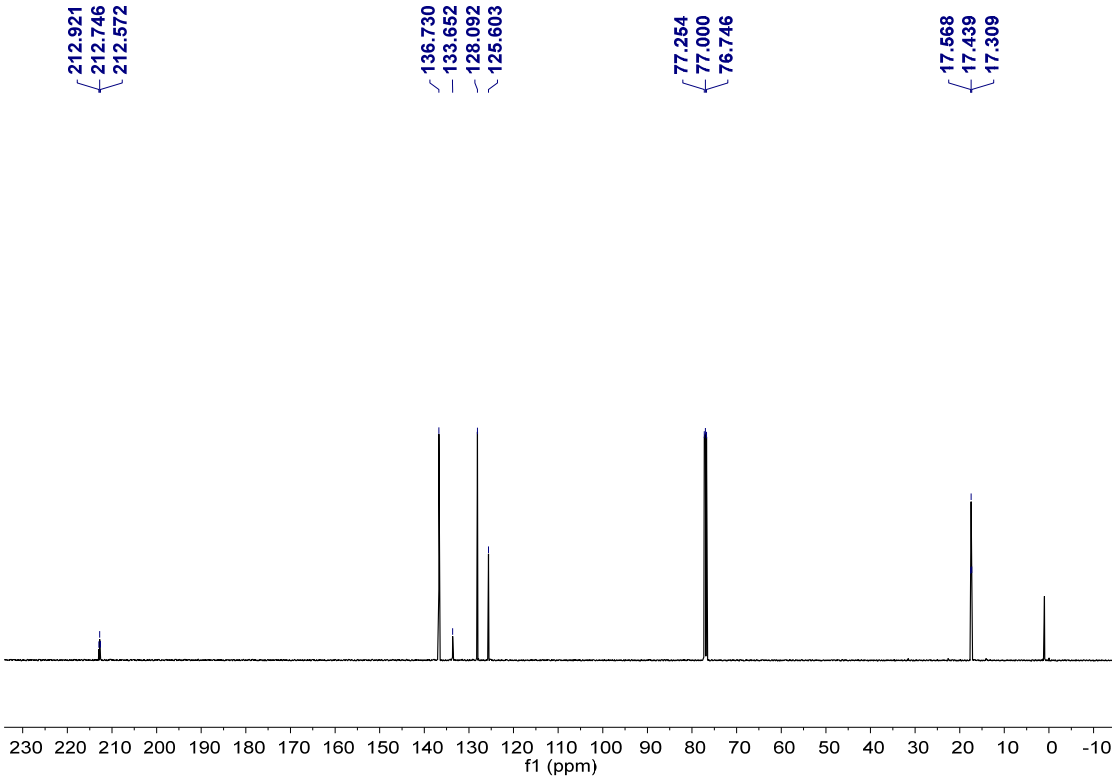


Figure S8. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) spectrum of **2**. *Assignments:* δ= 212.7 (t, $^2J_{P\text{-}C}$ = 22.0, $Fe(CO)_2$), 136.7, 133.6, 128.1, 125.6 (C_6H_5), 17.4 (t, $J_{P\text{-}C}$ = 16.2 Hz, PCH_3) ppm.

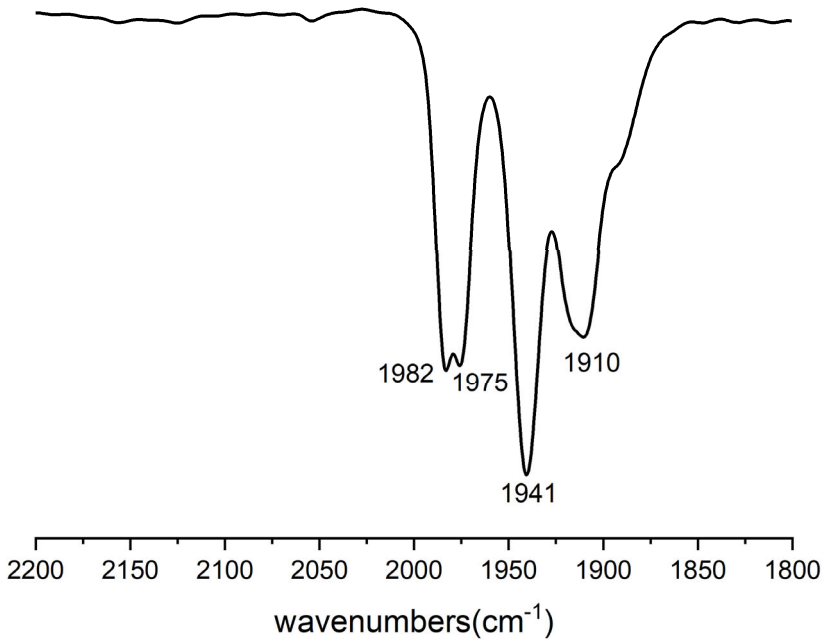


Figure S9. FT-IR (CH_2Cl_2, 25°C) spectrum of **3-anti**.

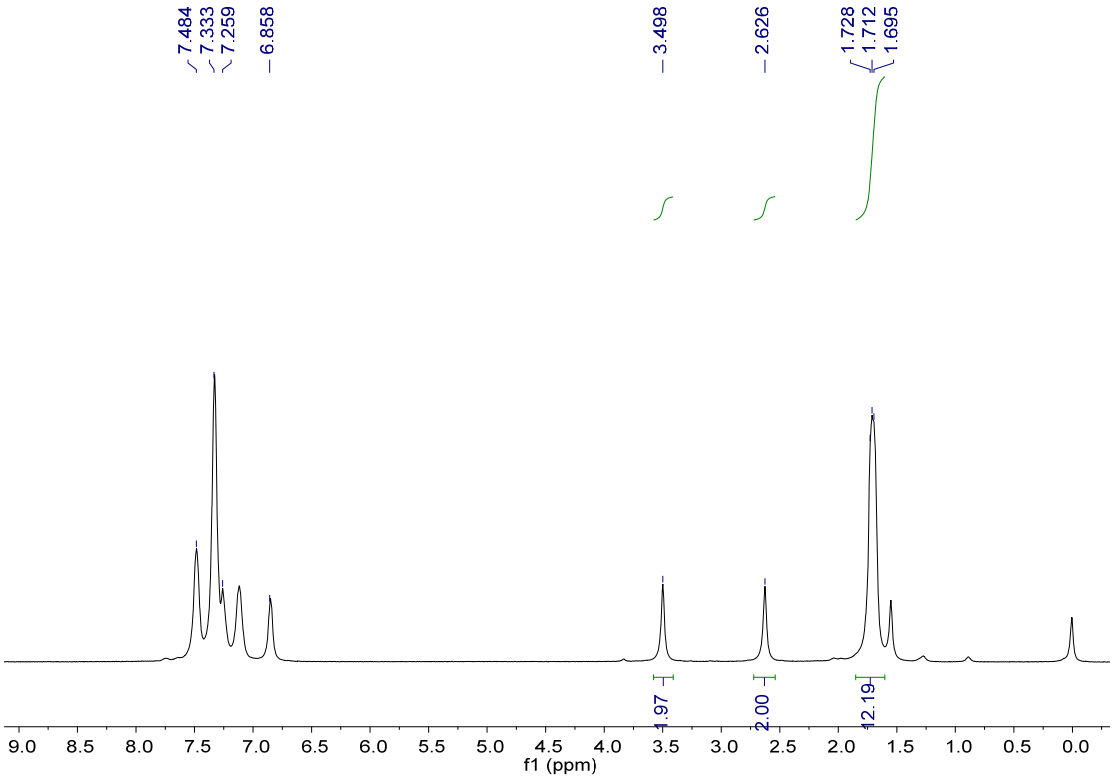


Figure S10. ^1H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of **3-anti**.
Assignments: δ = 7.48-6.86 (m, 20H, $4C_6H_5$), 3.50, 2.63 (2s, 4H, $2PhCH_2$), 1.71 (t, J = 8.0 Hz, 12H, $4PCH_3$) ppm.

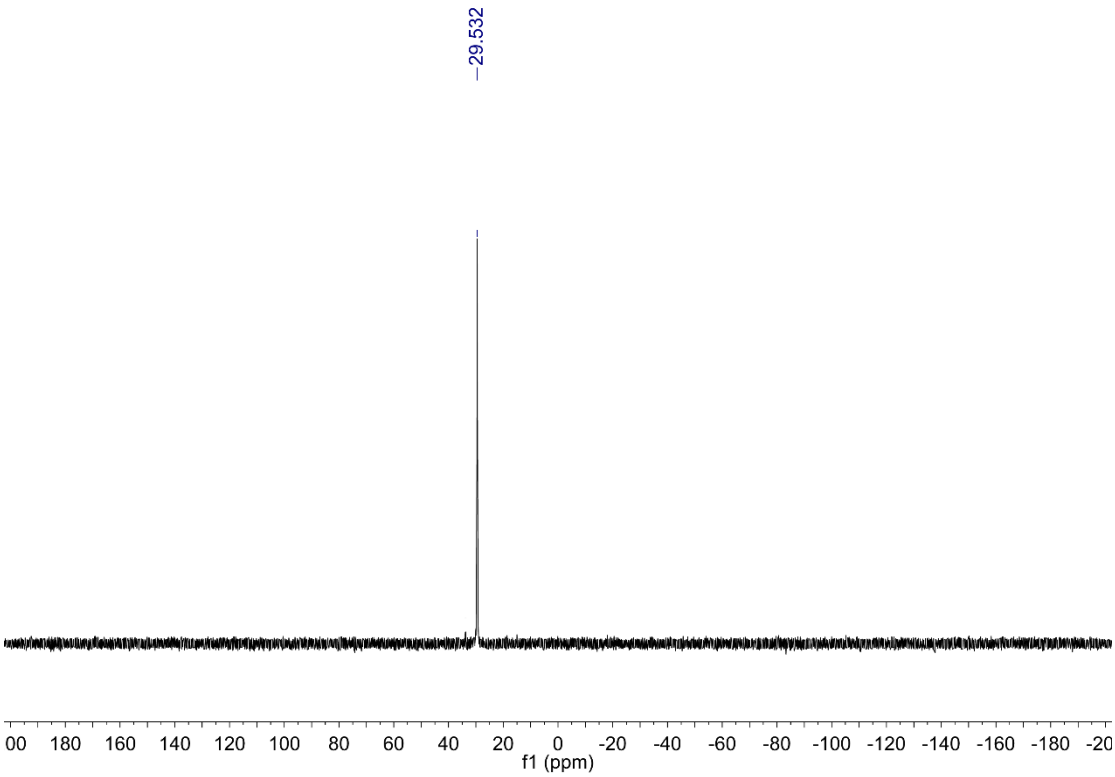


Figure S11. ^{31}P NMR (202 MHz, $CDCl_3$, 25 ºC) spectrum of **3-anti**.

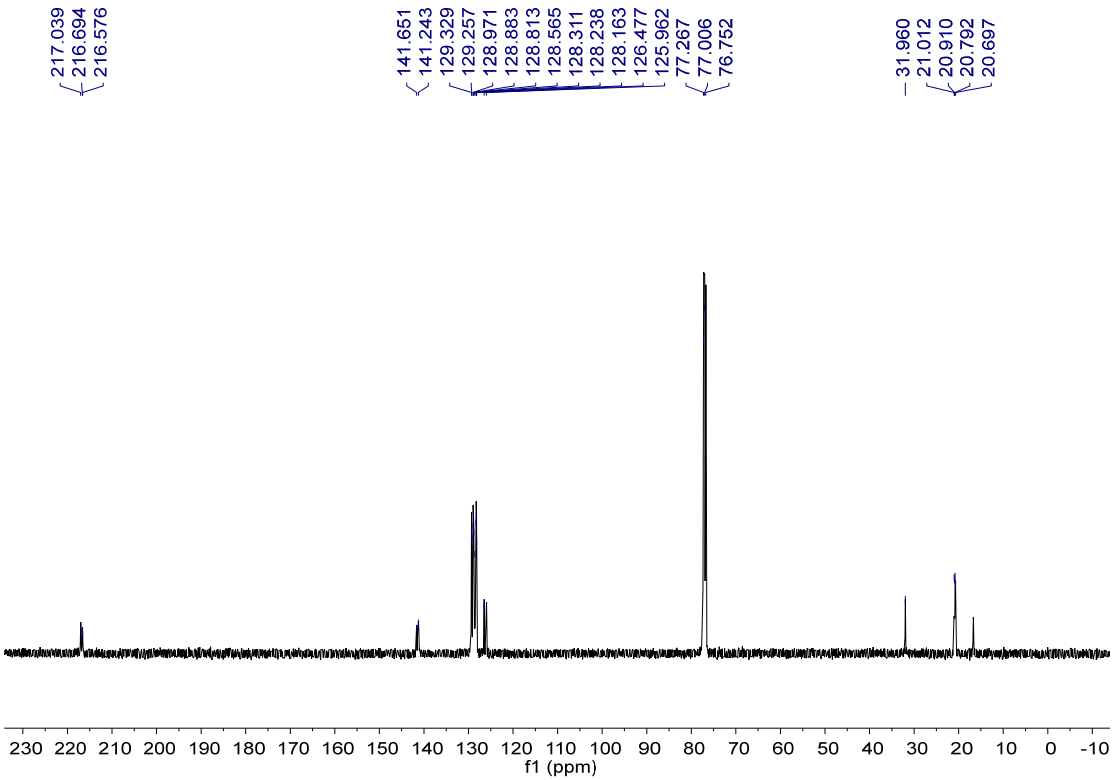


Figure S12. ^{13}C NMR (126 MHz, $CDCl_3$, 25 ºC) spectrum of **3-anti**.

Assignments: δ = 216.7, (t, $^2J_{P\text{-}C}$ = 3.2 Hz, $PFe(CO)_2$), 126.0-141.6 (m, C_6H_5), 32.0 (s, Ph*C*H_2), 20.9 (d, $J_{P\text{-}C}$ = 12.8 Hz, PCH_3), 20.7 (d, $J_{P\text{-}C}$ = 11.9 Hz, PCH_3).

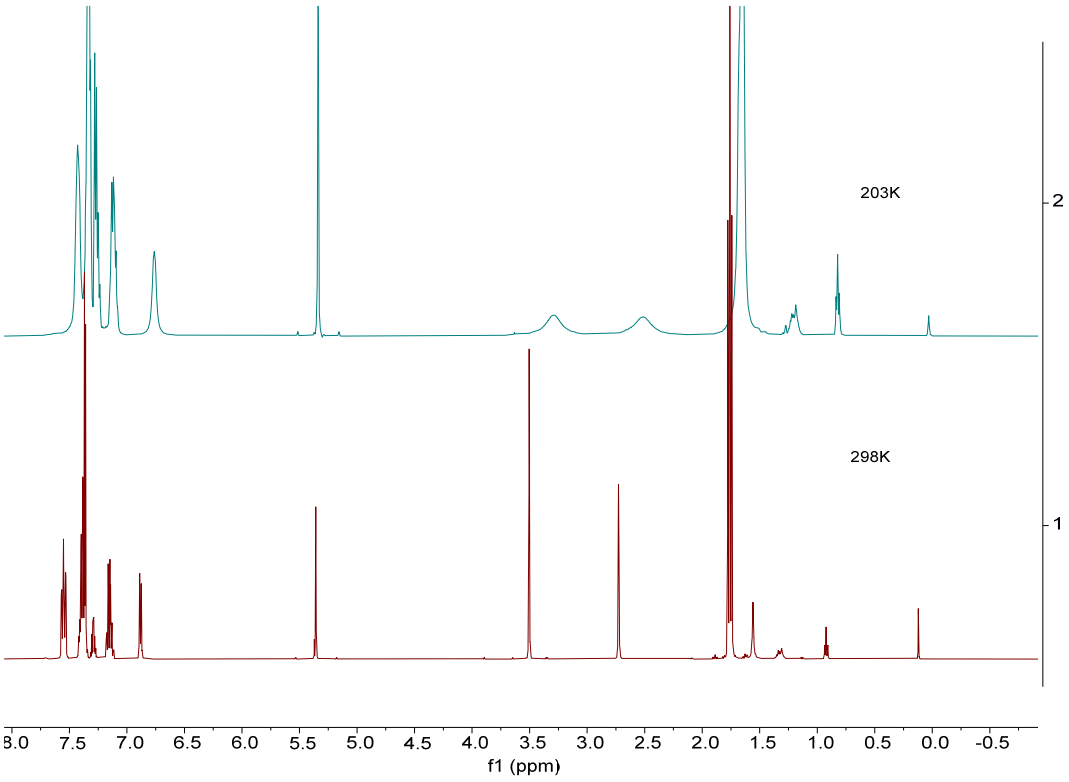


Figure S13. VT-^{1}HNMR spectrum of **3-anti** in CD_2Cl_2.

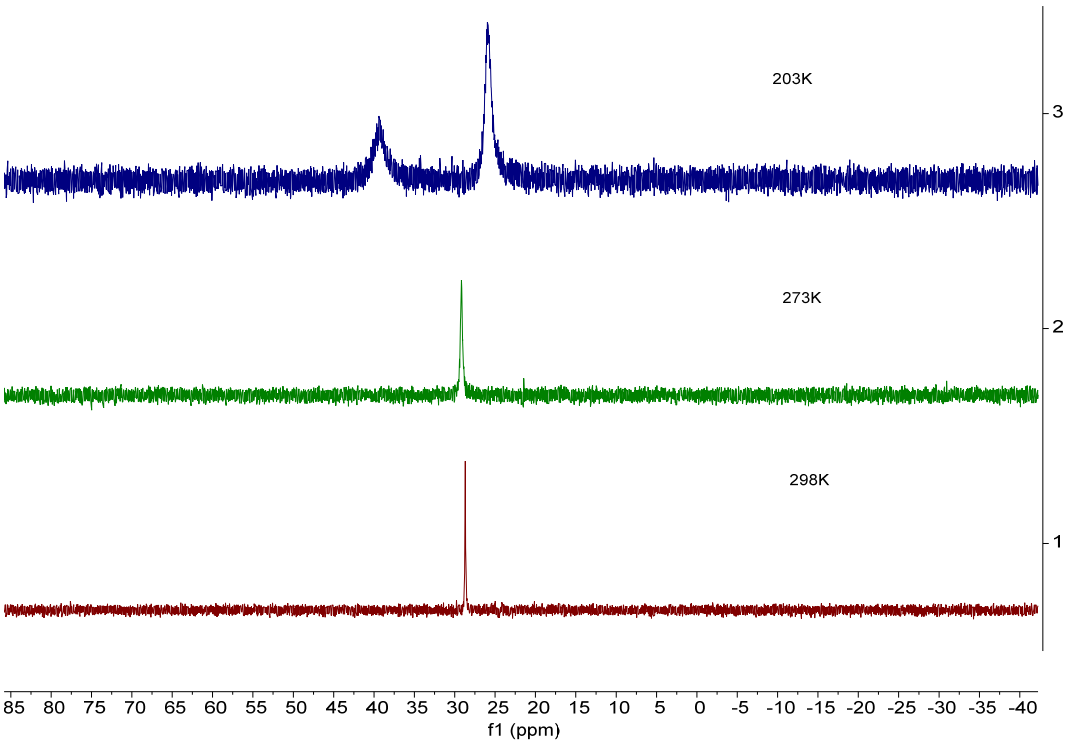


Figure S14. VT-^{31}PNMR spectra of **3-anti** in CD_2Cl_2.

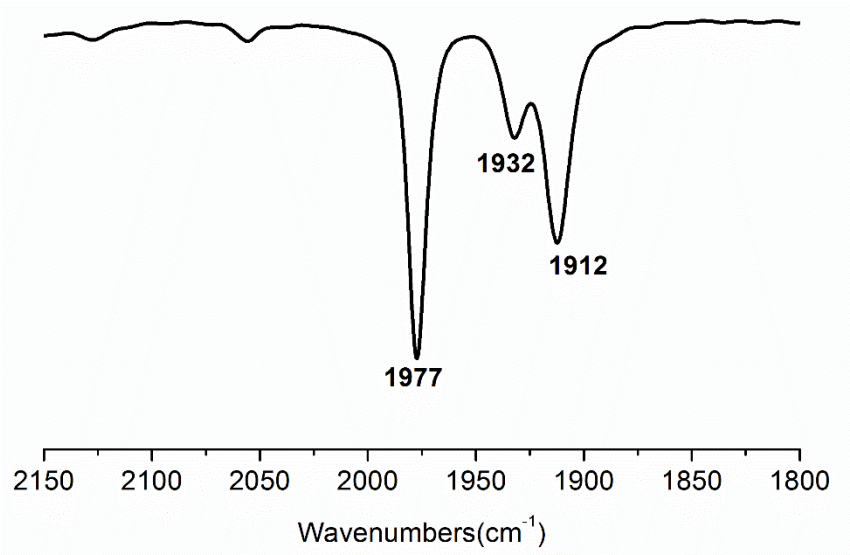


Figure S15. FT-IR (CH_2Cl_2, 25ºC) spectrum of **3-syn**.
Assignments: ν_{CO} = 1977, 1932, 1912 cm^{-1}.

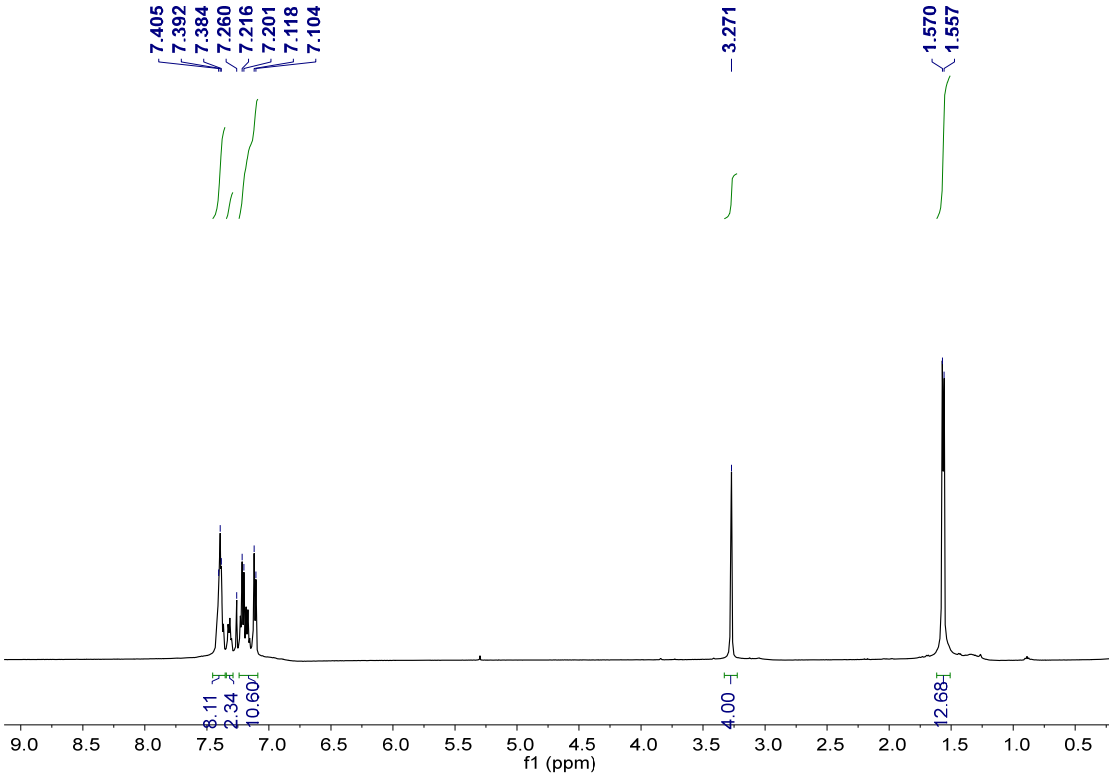


Figure S16. ^1H NMR (500 MHz, $CDCl_3$, 25 ºC) spectrum of **3-syn**.
Assignments: δ = 7.41-7.10 (m, 20H, $4C_6H_5$), 3.27 (s, 4H, $2PhCH_2$), 1.56 (d, J = 6.5 Hz, 12H, $4PCH_3$) ppm.

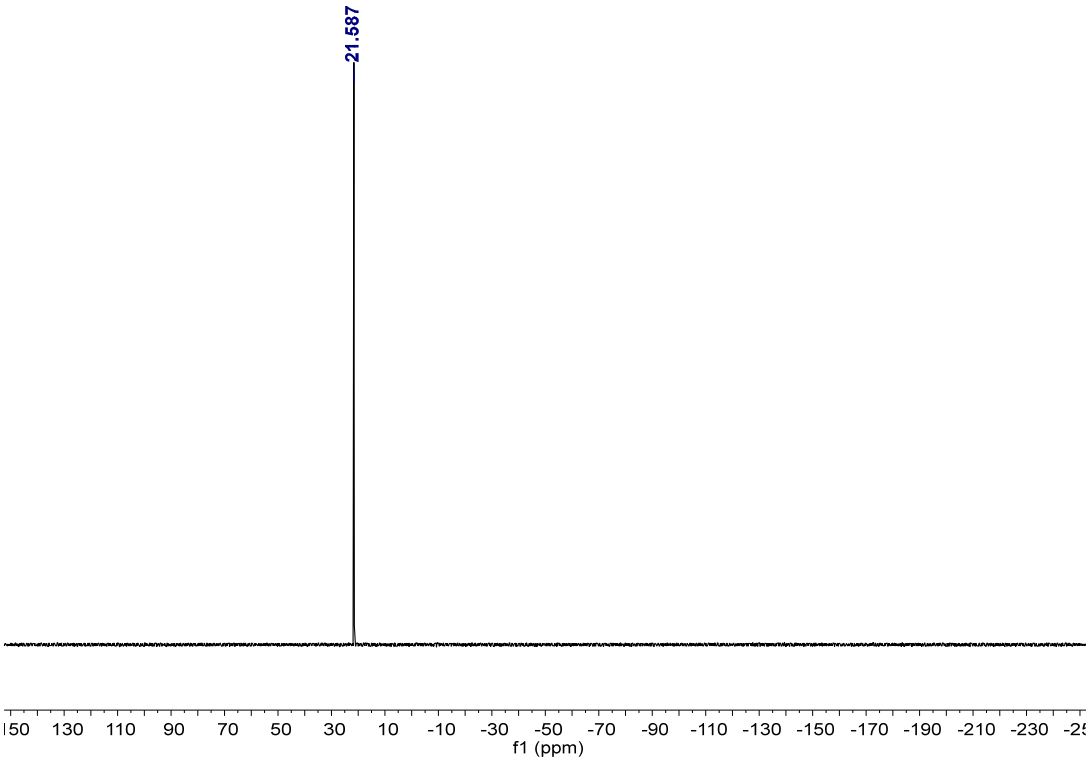


Figure S17. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C) spectrum of **3-syn**.

Assignments: δ = 21.58 (s) ppm

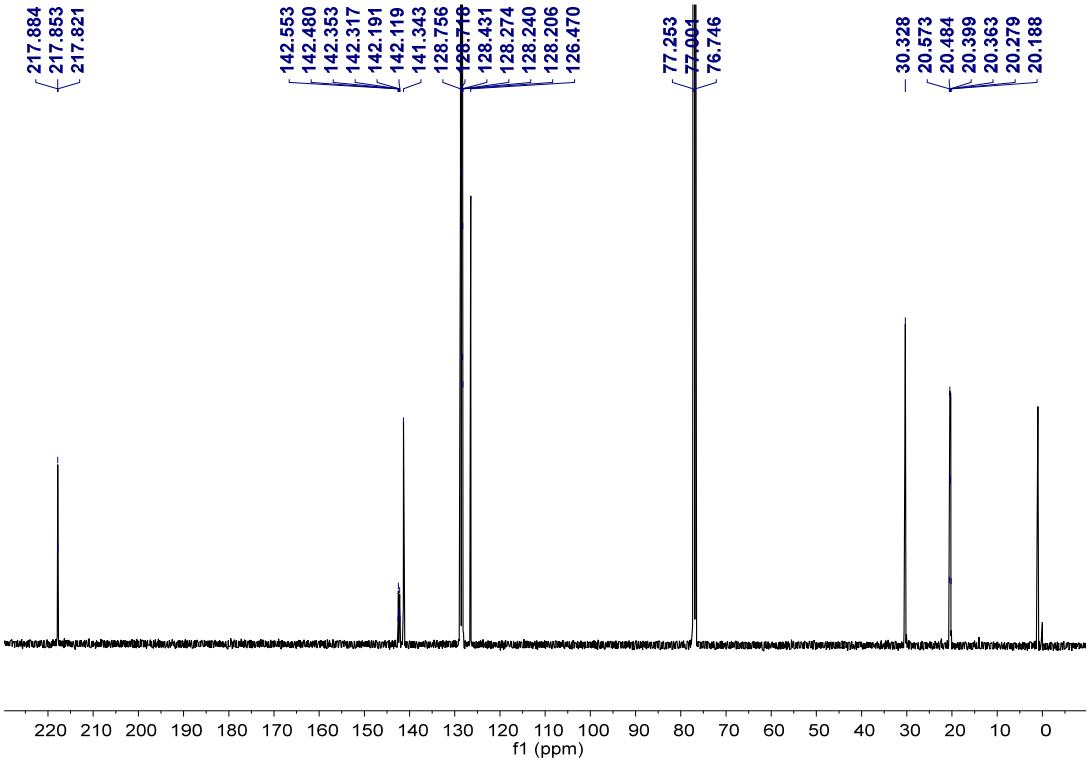


Figure S18. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) spectrum of **3-syn**.

Assignments: δ = 217.8, (t, $^2J_{P\text{-}C}$ = 3.2 Hz, $PFe(CO)_2$), 126.5-142.5 (m, C_6H_5), 30.3 (s, Ph*C*H_2), 20.5, 20.3 (2t, $J_{P\text{-}C}$ = 11.2 Hz, PCH_3).

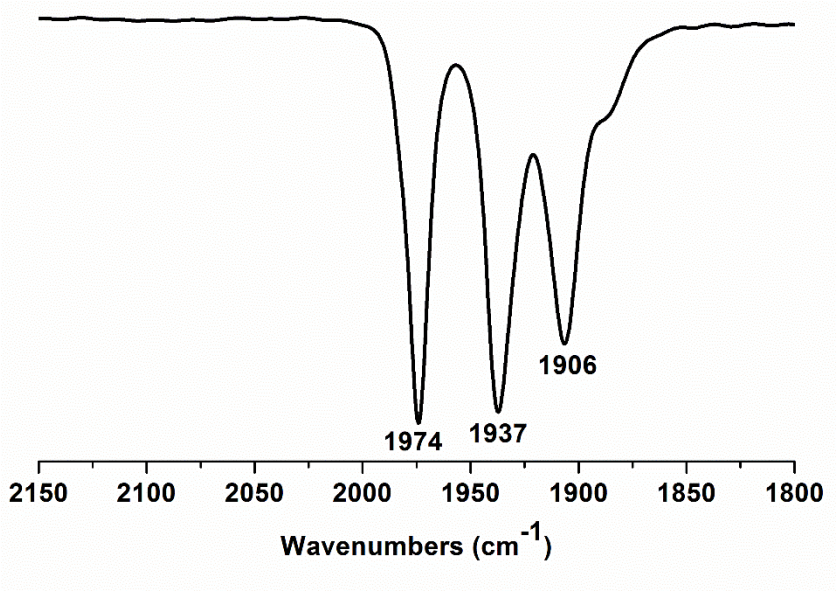


Figure S19. FT-IR (in CH_2Cl_2, 25ºC) spectrum of **4-anti**.
Assignments: ν_{CO} = 1974, 1937, 1906 cm^{-1}.

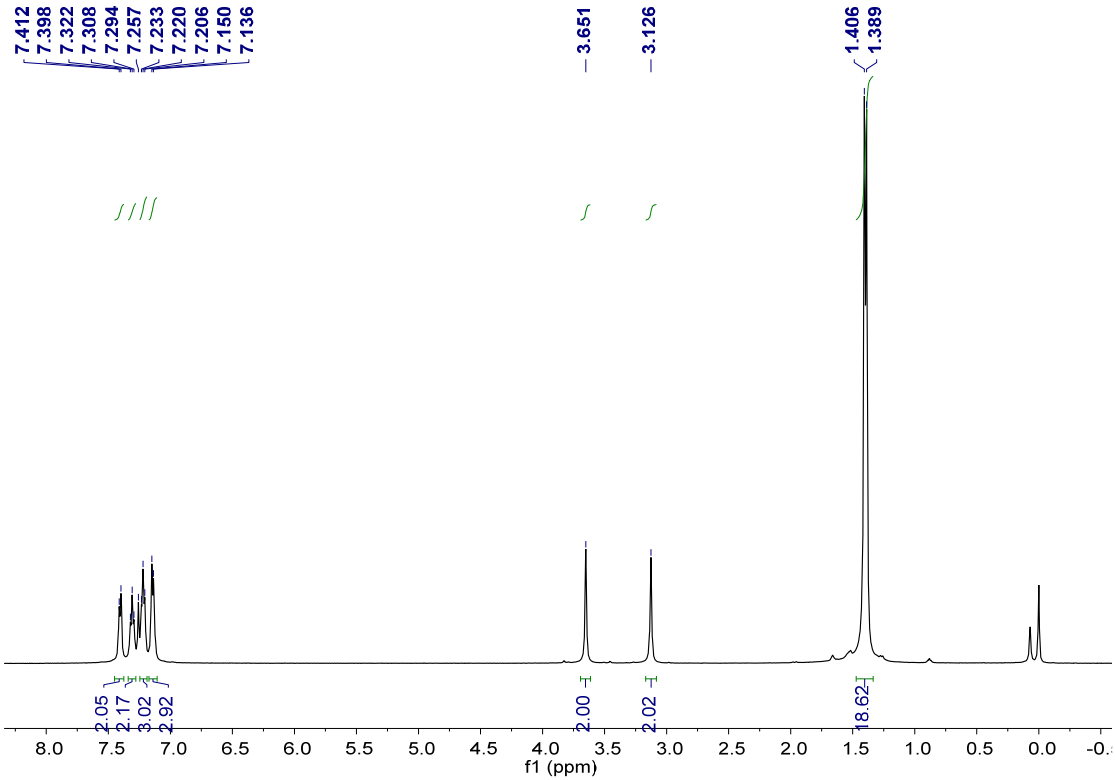


Figure S20. ^1H NMR (500 MHz, $CDCl_3$, 25 ºC) spectrum of **4-anti**. *Assignments:* δ = 7.14-7.41(m, 10H, $2C_6H_5$), 3.65, 3.13 (2s, 4H, $2CH_2$), 1.39 (d, $^2J_{P\text{-}H}$ = 8.5Hz, 18H, $6CH_3$) ppm.

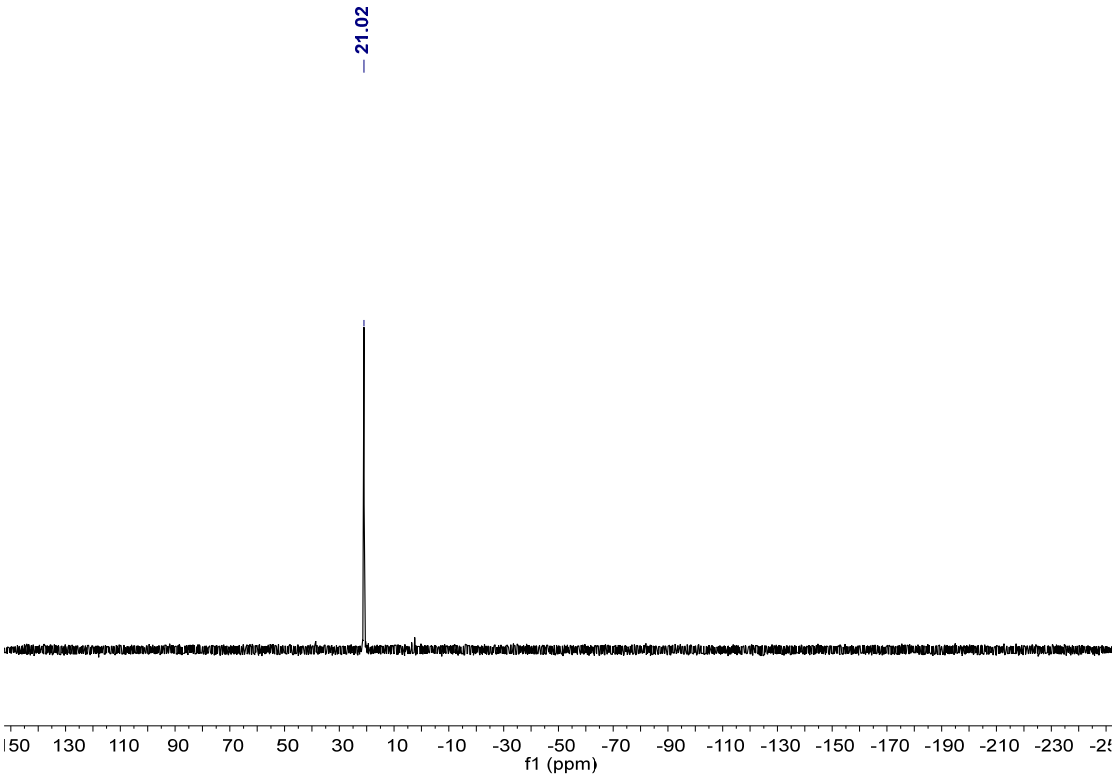


Figure S21. ^{31}P NMR (202 MHz, $CDCl_3$, 25 ºC) spectrum of **4-anti**.
Assignments: δ = 21.02 (s) ppm.

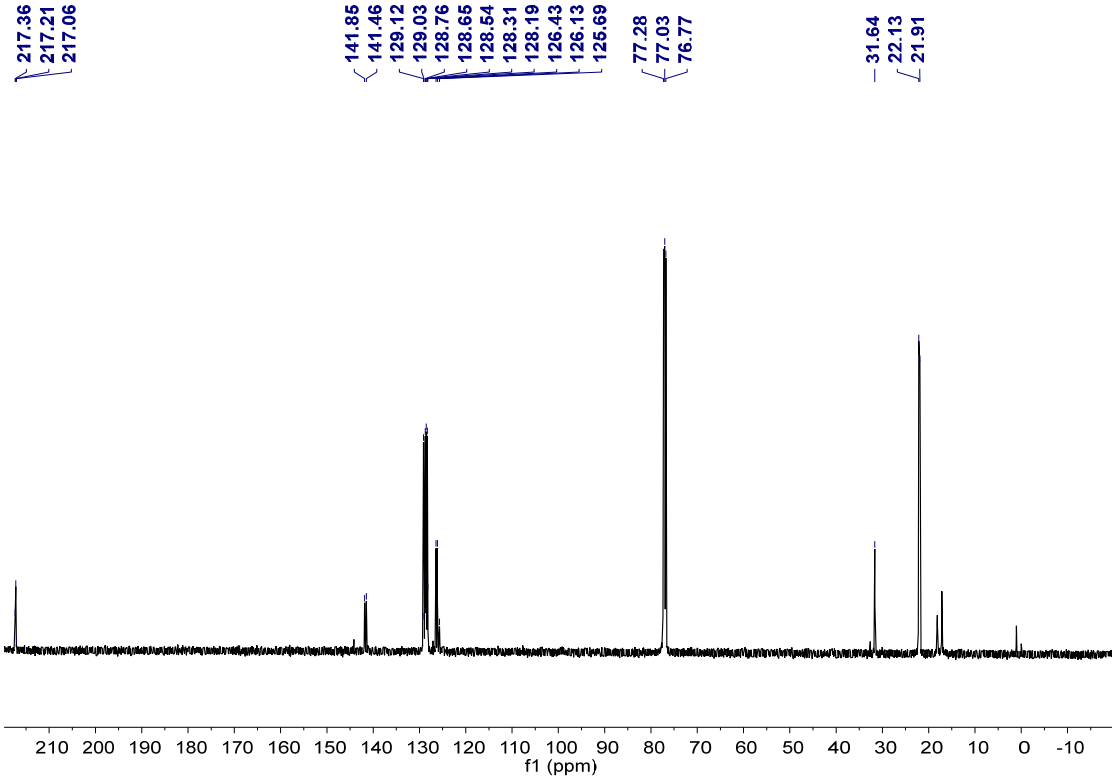


Figure S22. ^{13}C NMR (126 MHz, $CDCl_3$, 25 ºC) spectrum of **4-anti**.

Assignments: δ = 217.2 (t, $^2J_{P\text{-}C}$ = 18.9, $Fe(CO)_2$), 141.8-125.7 (m, C_6H_5), 31.6 (s, CH_2), 22.0 (d, $J_{P\text{-}C}$ = 27.7 Hz, PCH_3) ppm.

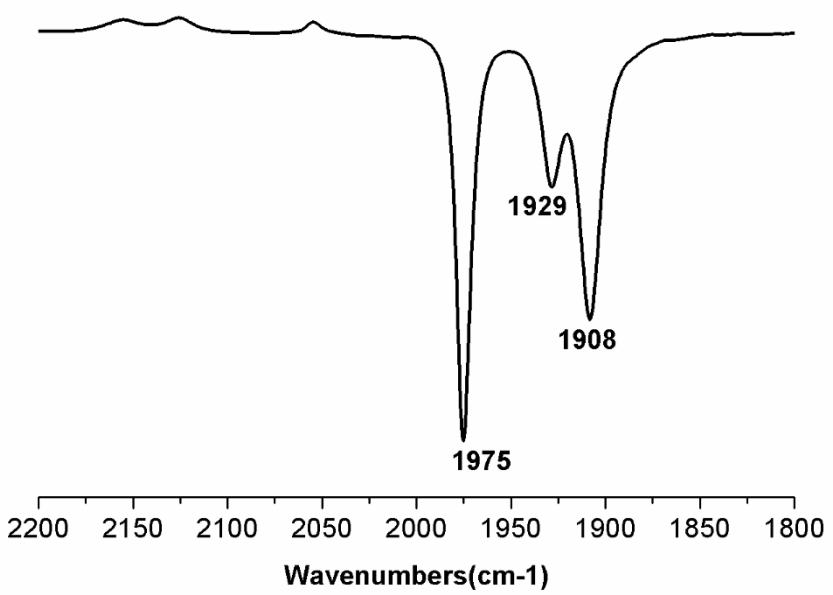


Figure S23. FT-IR (in CH_2Cl_2, 25°C) spectrum of **4-syn**.
Assignments: ν_{CO} = 1975, 1929, 1908 cm^{-1}.

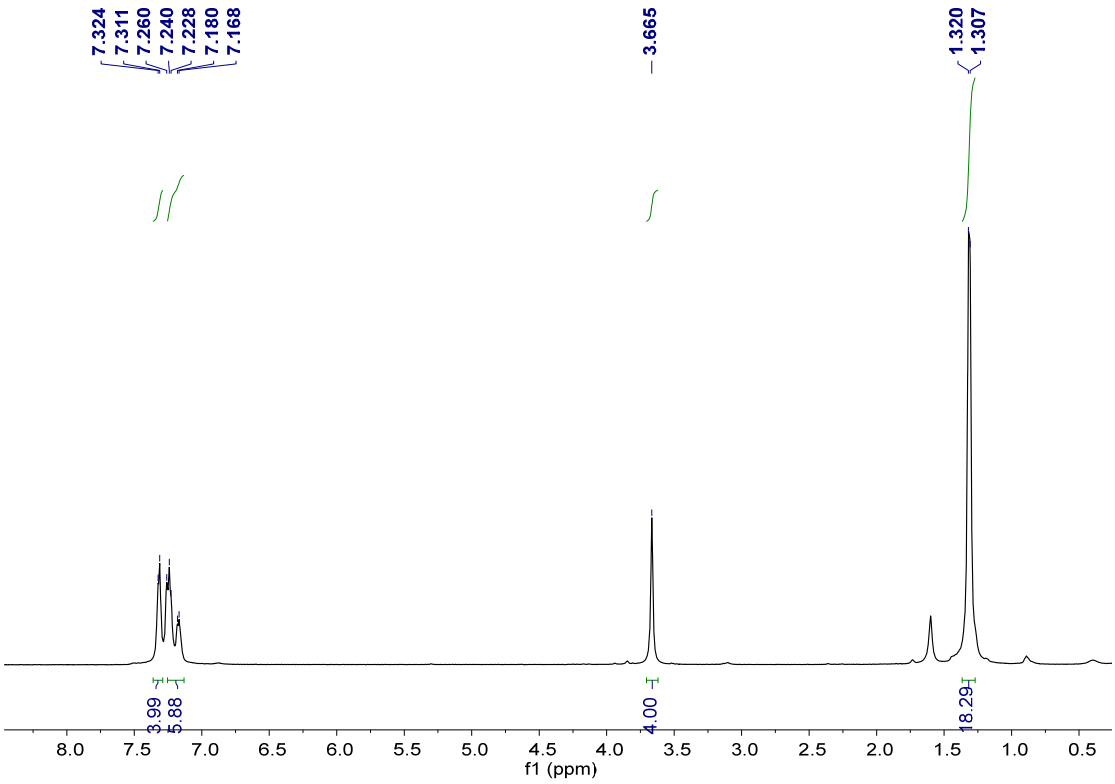


Figure S24. ^1H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of **4-syn**.
Assignments: δ = 7.17-7.32 (m, 10H, $2C_6H_5$), 3.67 (s, 4H, $2PhCH_2$), 1.31 (d, J = 4.5 Hz, 18H, $6CH_3$) ppm

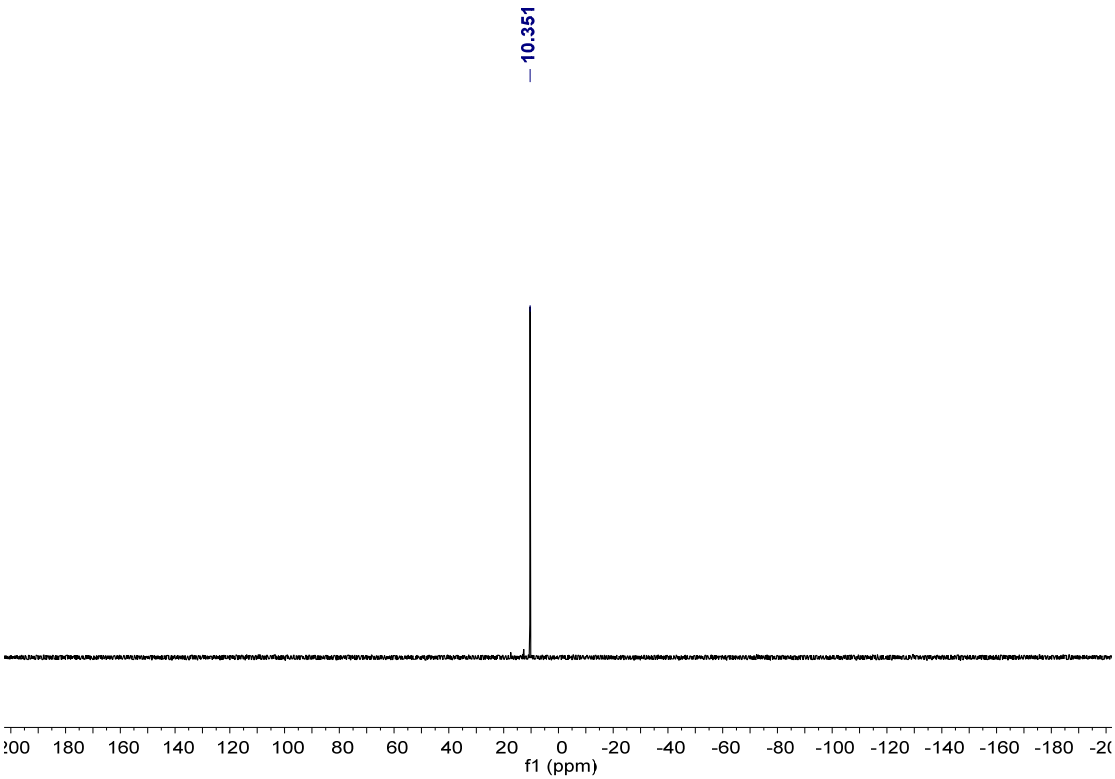


Figure S25. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C) spectrum of **4-syn**. *Assignments:* δ = 10.35 (s) ppm

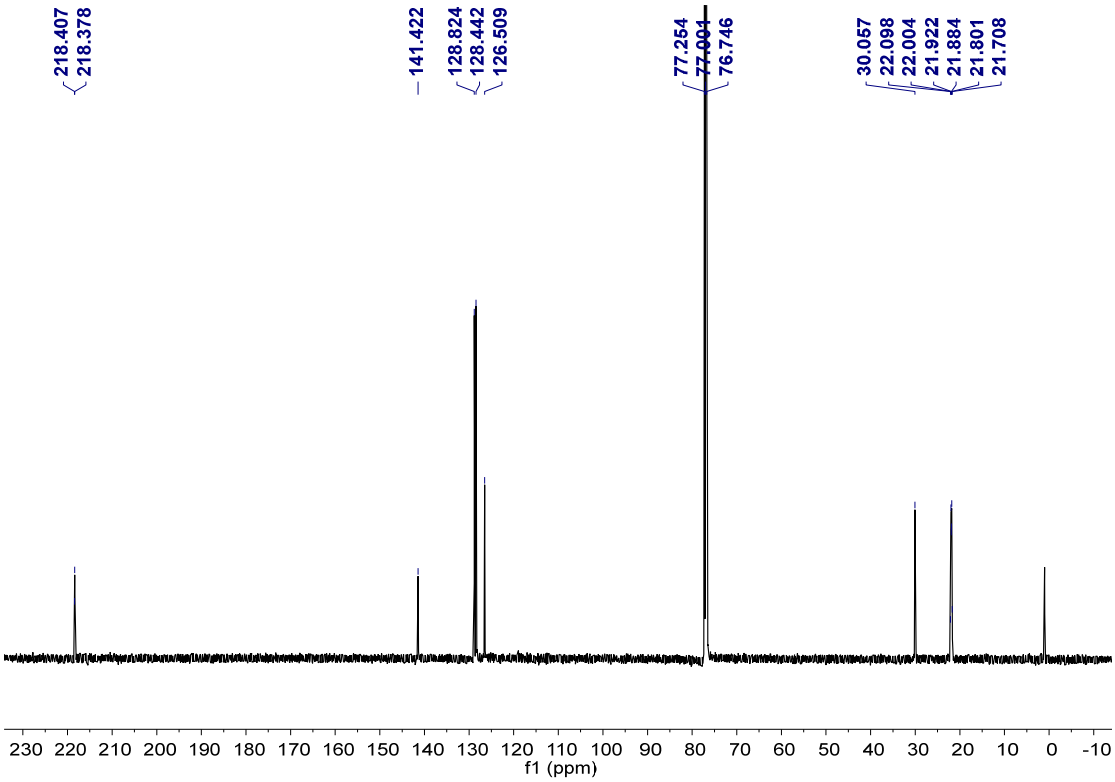
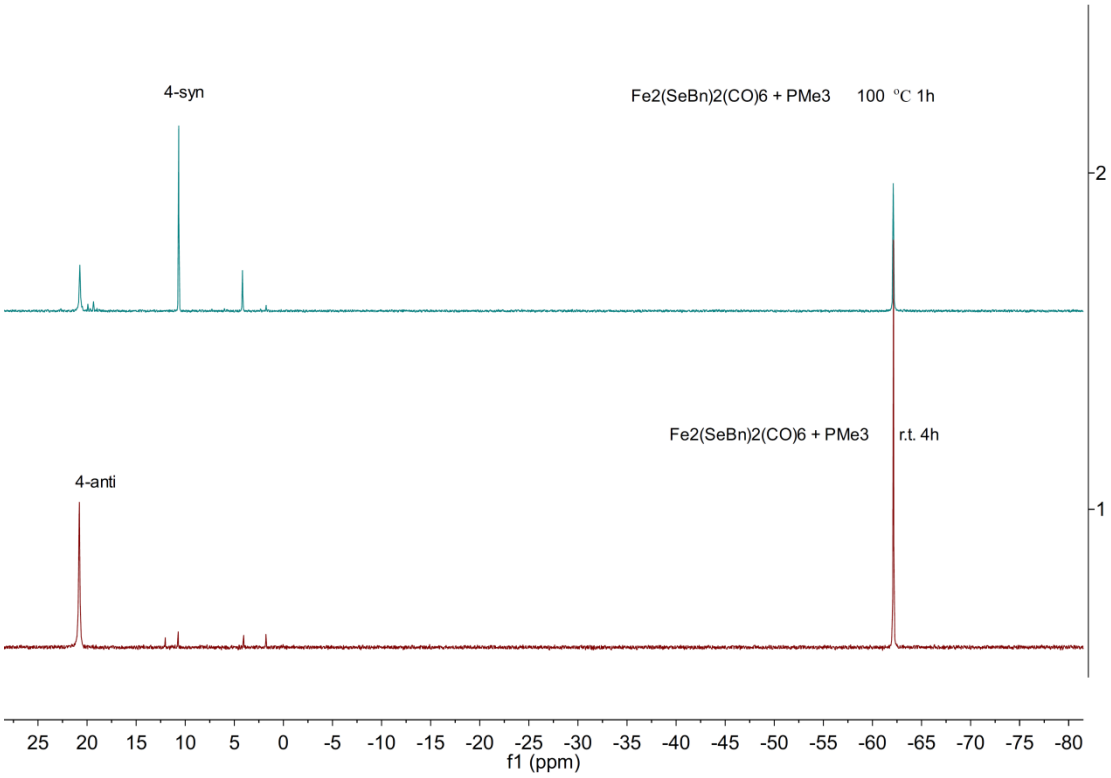


Figure S26. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) spectrum of **4-syn**.

Assignments: δ= 218.4 (t, $^2J_{P-C}$ = 3.7, $Fe(CO)_2$), 141.4, 128.8, 128.4, 126.5 (s, C_6H_5), 30.1 (s, CH_2), 22.1-21.7 (m, PCH_3).



FigureS27 ^{31}P NMR spectra in the reaction of 5 equivalents of PMe_3 with $Fe(\mu\text{-}SeCH_2Ph)_2(CO)_6$ in toluene (stirred at room temperature for 4h (1), then heated to 100ºC for 1h (2)).

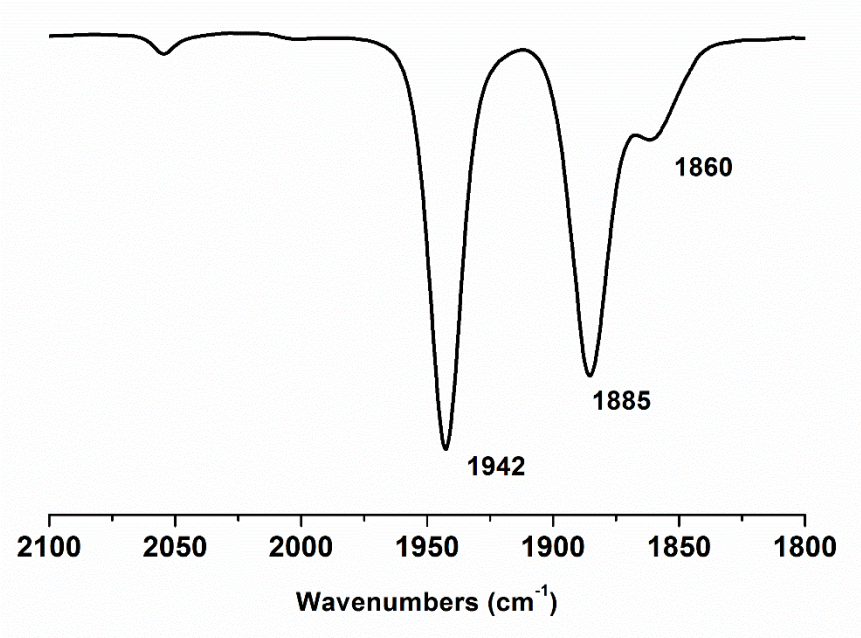


Figure S28. FT-IR (in CH_2Cl_2, 25ºC) spectrum of **5**.
Assignments: ν_{CO} = 1942, 1885, 1660 cm^{-1}.

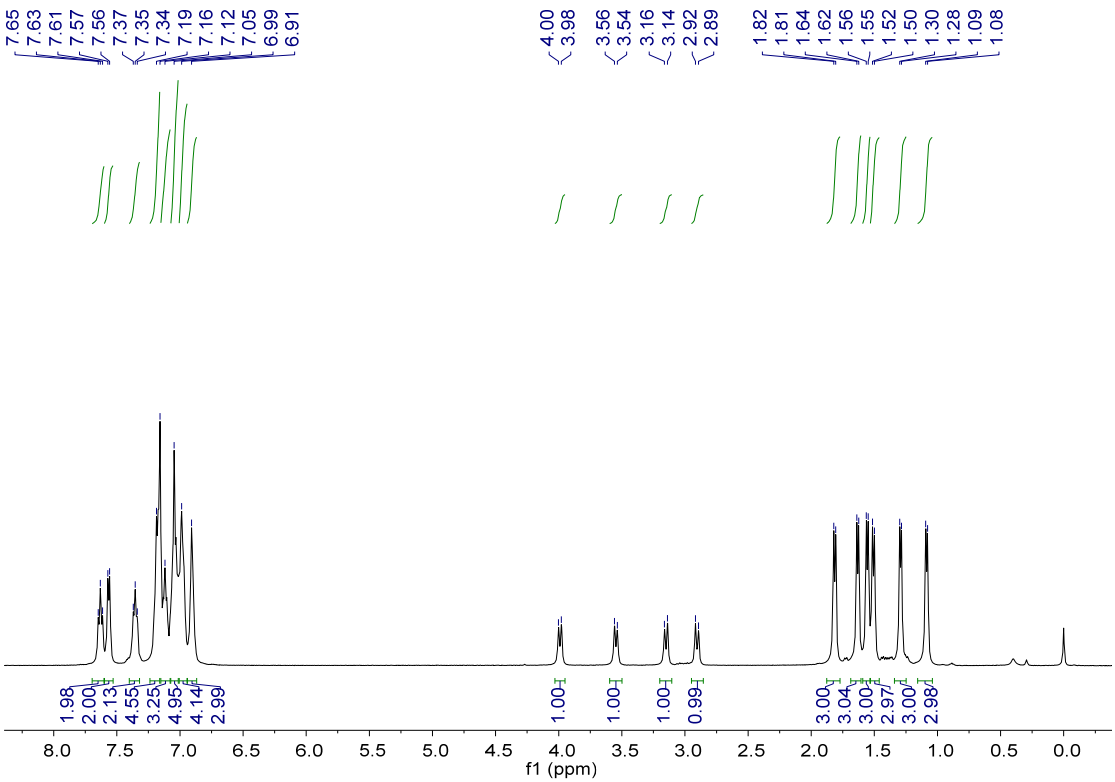


Figure S29. ^{1}H NMR (500 MHz, C_6D_6, 25 ºC) spectrum of **5**. *Assignments:* δ = 6.91-7.65 (m, 25H, $4C_6H_5$), 3.99, 3.55, 3.15, 2.90 (ABq, $^{2}J_{H\text{-}H}$ = 11.5Hz, 4H, $2C_6H_5CH_2$), 1.81, 1.63, 1.56, 1.51, 1.29, 1.09 (6d, $^{2}J_{P\text{-}H}$ = 8.0 Hz, 18H, $6CH_3$) ppm.

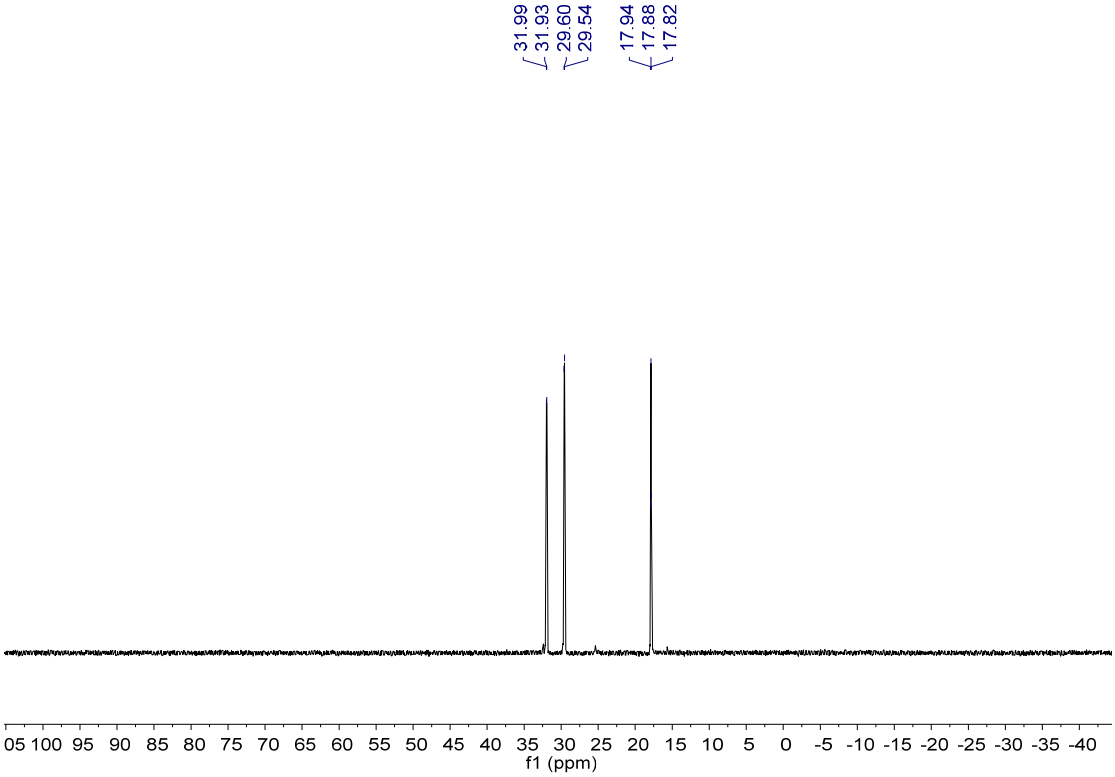


Figure S30. ^{31}P NMR (202 MHz, C_6D_6, 25 ºC) spectrum of **5**.
Assignments: δ = 32.0 (d, J = 11.7 Hz, *apical*-Fe(CO)$(PPhMe_2)_2$), 29.6 (d, J = 11.6 Hz, *apical*-Fe$(CO)_2PPhMe_2$), 17.9 (t, J = 12.1 Hz, *basal*-Fe(CO)$(PPhMe_2)_2$) ppm.

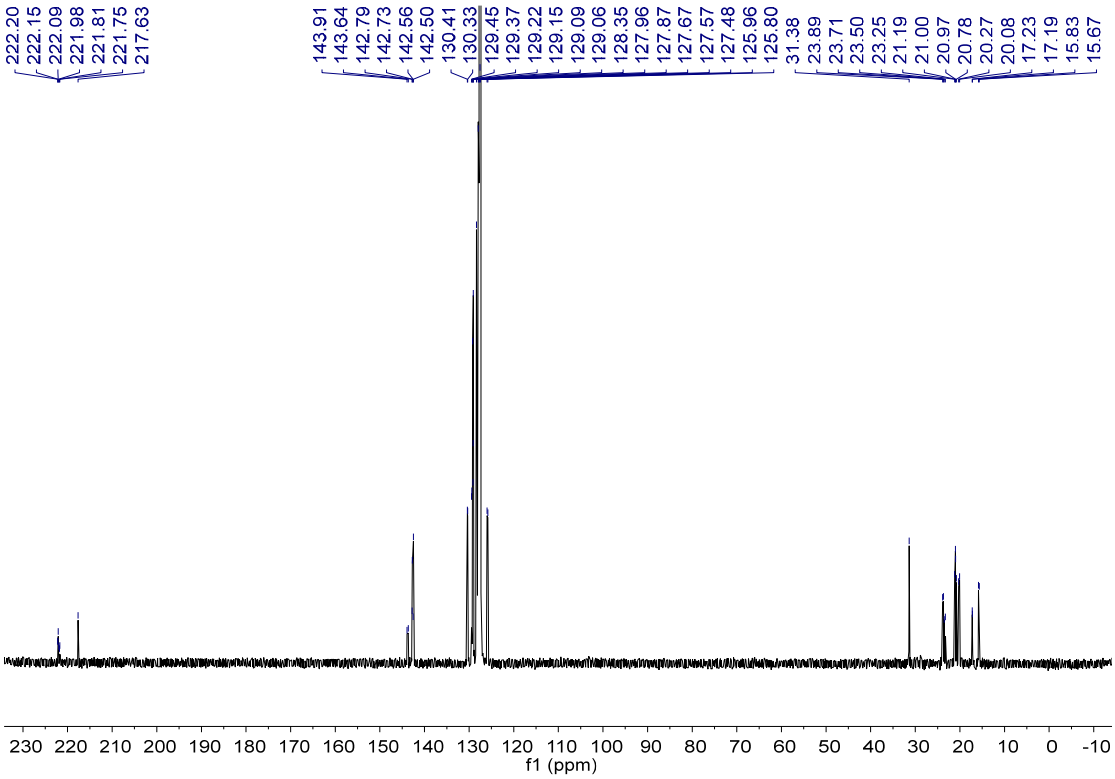


Figure S31. ^{13}C NMR (126 MHz, C_6D_6, 25 °C) spectrum of **5**. *Assignments:* δ = 221.8-222.2 (m, Fe(CO), 217.6 (s, Fe(CO)), 143.9-125.8 (m, C_6H_5), 31.4(s, CH_2), 23.9-15.7 (m, PCH_3) ppm.

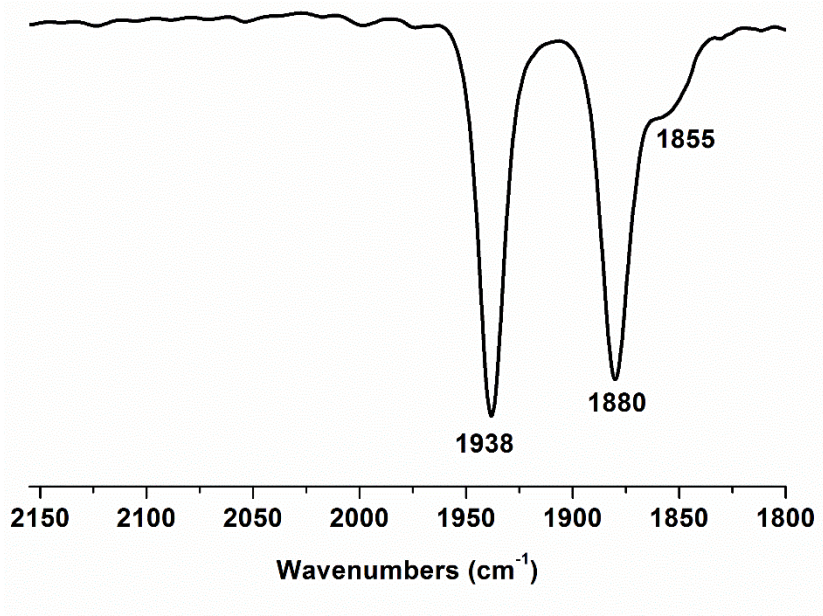


Figure S32. FT-IR (in CH_2Cl_2, 25°C) spectrum of **6**.
Assignments: ν_{CO} = 1938, 1880, 1855 cm^{-1}.

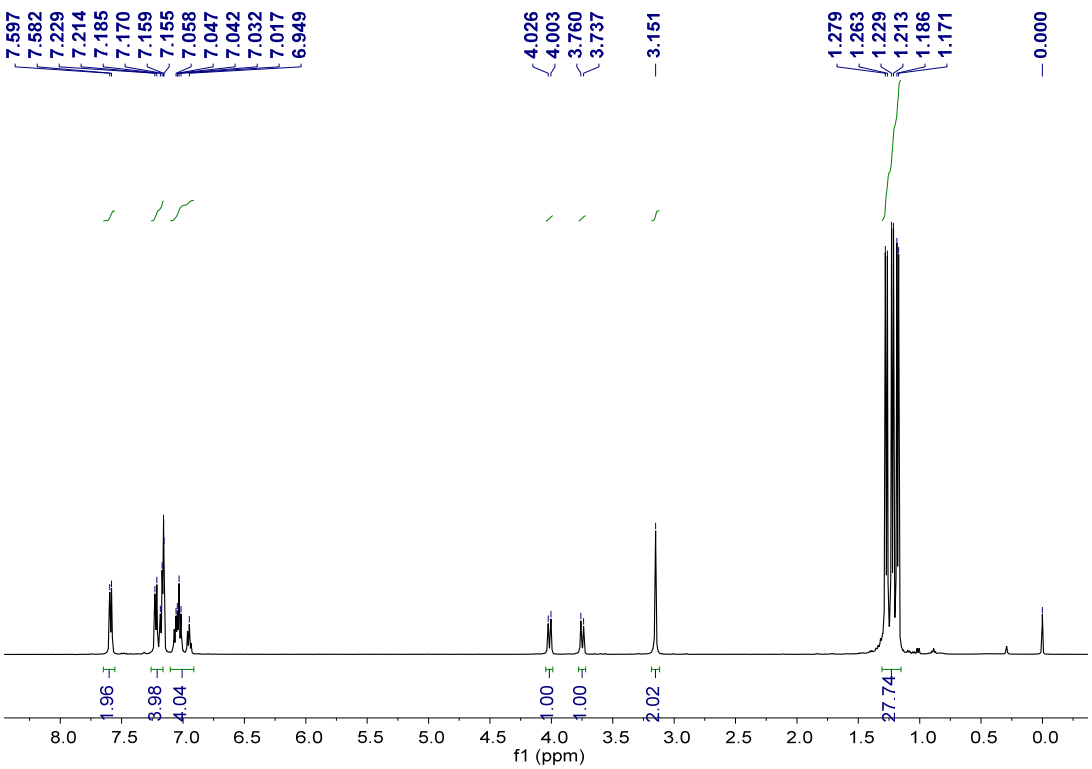


Figure S33. ^{1}H NMR (500 MHz, C_6D_6, 25 °C) spectrum of **6**. *Assignments:* δ = 6.95-7.60 (m, 10H, $2C_6H_5$), 4.01, 3.75 (2d, $^{2}J_{H\text{-}H}$ = 11.5Hz, 2H, *e*-$C_6H_5CH_2$), 3.15 (s, 2H, *a*-$C_6H_5CH_2$), 1.27, 1.22, 1.18 (3d, $^{2}J_{P\text{-}H}$ = 8.0 Hz, 27H, $9CH_3$) ppm.

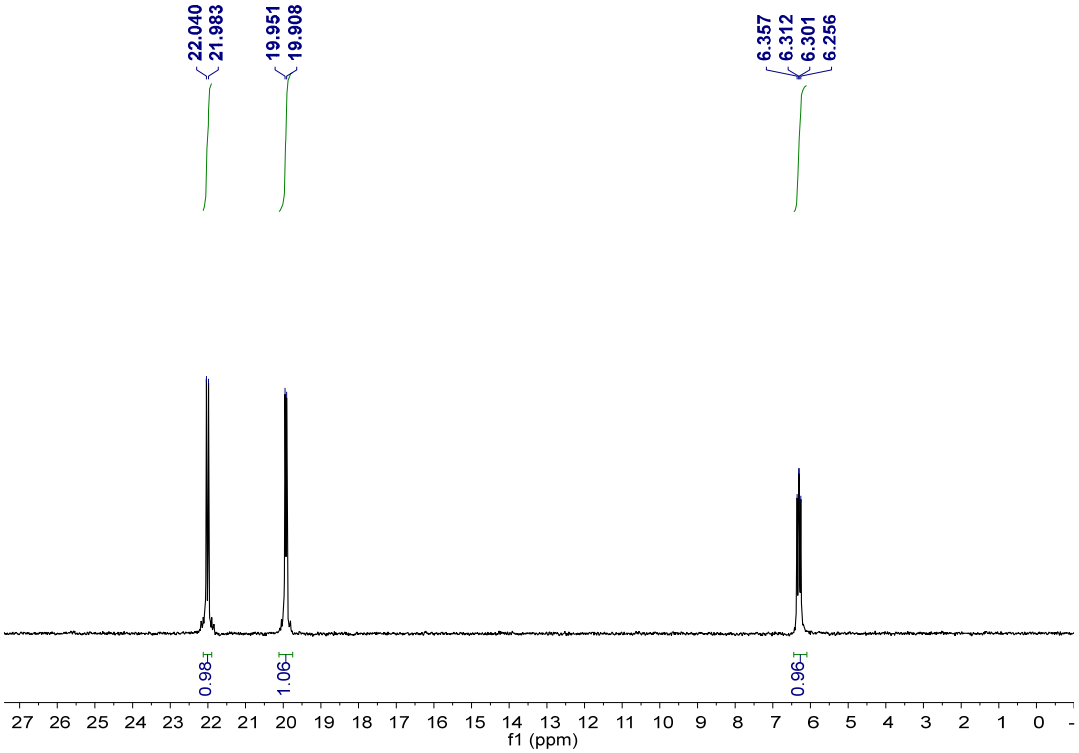


Figure S34. ^{31}P NMR (202 MHz, C_6D_6, 25 °C) spectrum of **6**. *Assignments:* δ = 22.0 (d, $J_{P\text{-}P}$ = 11.5 Hz, *apical*-Fe(CO)$(PMe_3)_2$), 19.9 (d, $J_{P\text{-}P}$ = 8.7 Hz, *apical*-$Fe(CO)_2PMe_3$), 22.0 (dd, $J_{P\text{-}P}$ = 11.3, 9.1Hz, *basal*-Fe(CO)$(PMe_3)_2$).

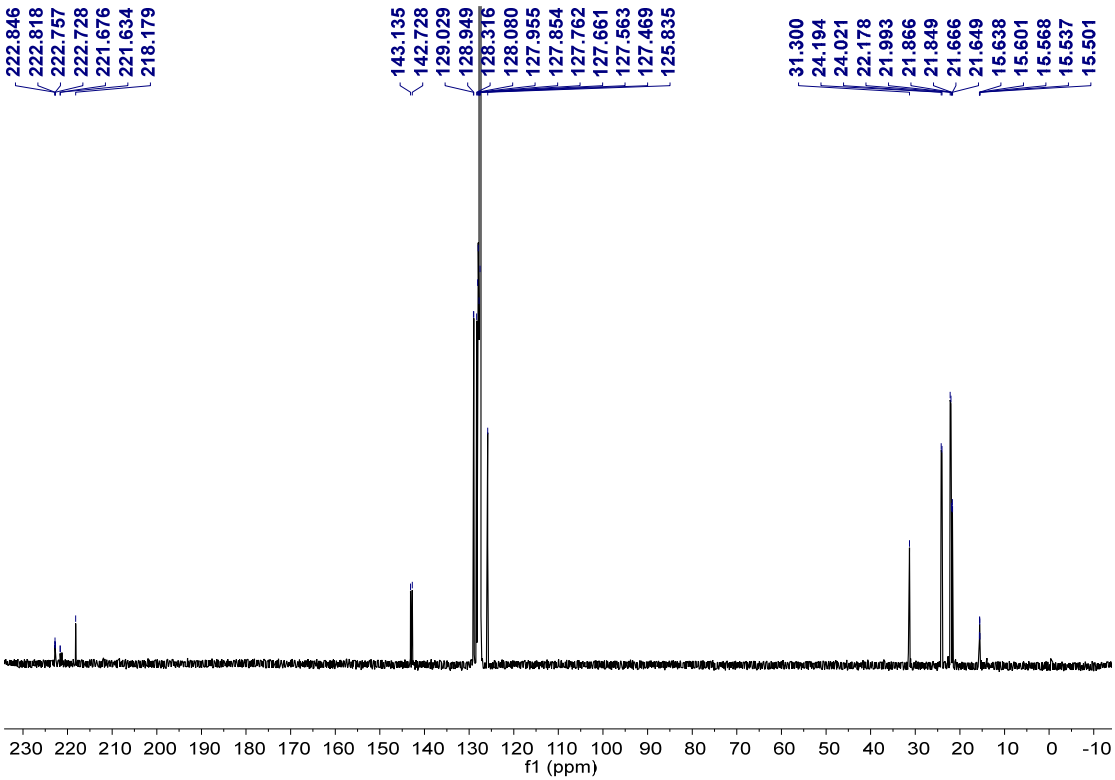


Figure S35. ^{13}C NMR (126 MHz, C_6D_6, 25 ^oC) spectrum of **6**. *Assignments:* δ = 221.3-222.8 (m, Fe(CO), 218.2 (s, Fe(CO)), 143.1-125.8 (m, C_6H_5), 31.3 (s, CH_2), 24.2-15.5 (m, PCH_3) ppm.

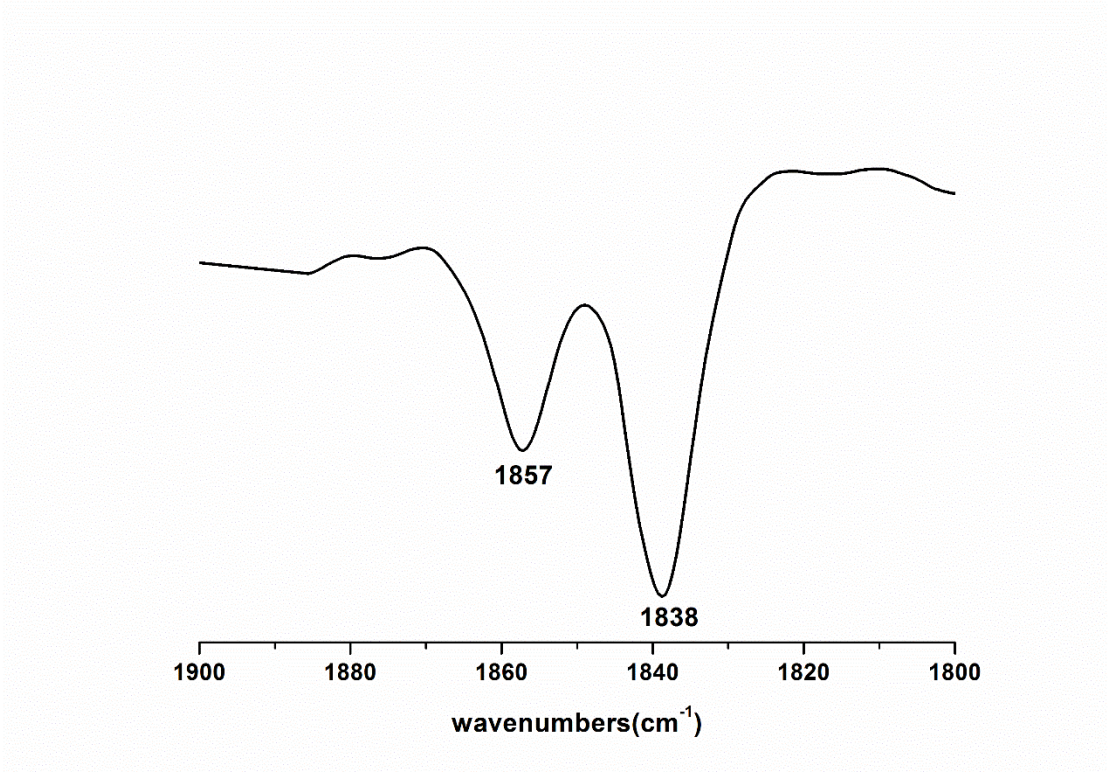


Figure S36. FT-IR (in toluene, 25ºC) spectrum of **7**.
Assignments: ν_{CO} = 1938, 1880, 1855 cm^{-1}.

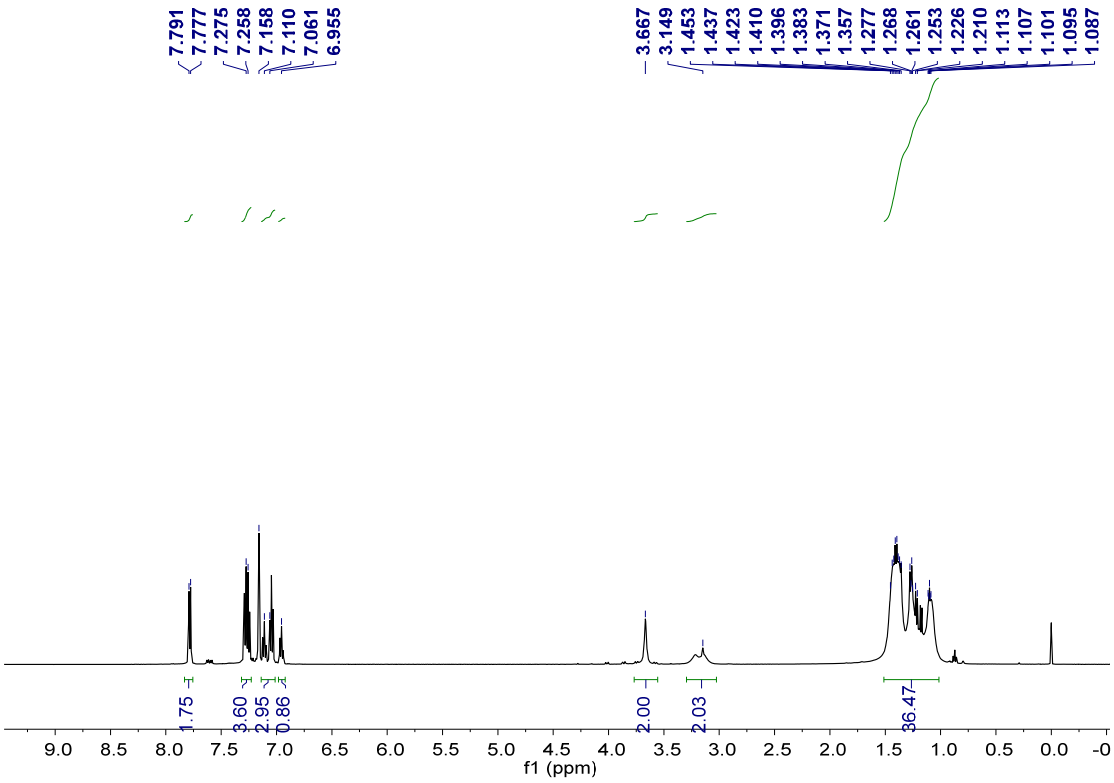


Figure S37. ^{1}H NMR (500 MHz, C_6D_6, 25 ºC) spectrum of **7**. *Assignments:* δ = 6.96-7.79 (m, 10H, $2C_6H_5$), 3.67 (d, 2H, *e*-$C_6H_5CH_2$), 3.15 (s, 2H, *a*-$C_6H_5CH_2$), 1.09-1.45 (m, 36H, $12CH_3$) ppm.

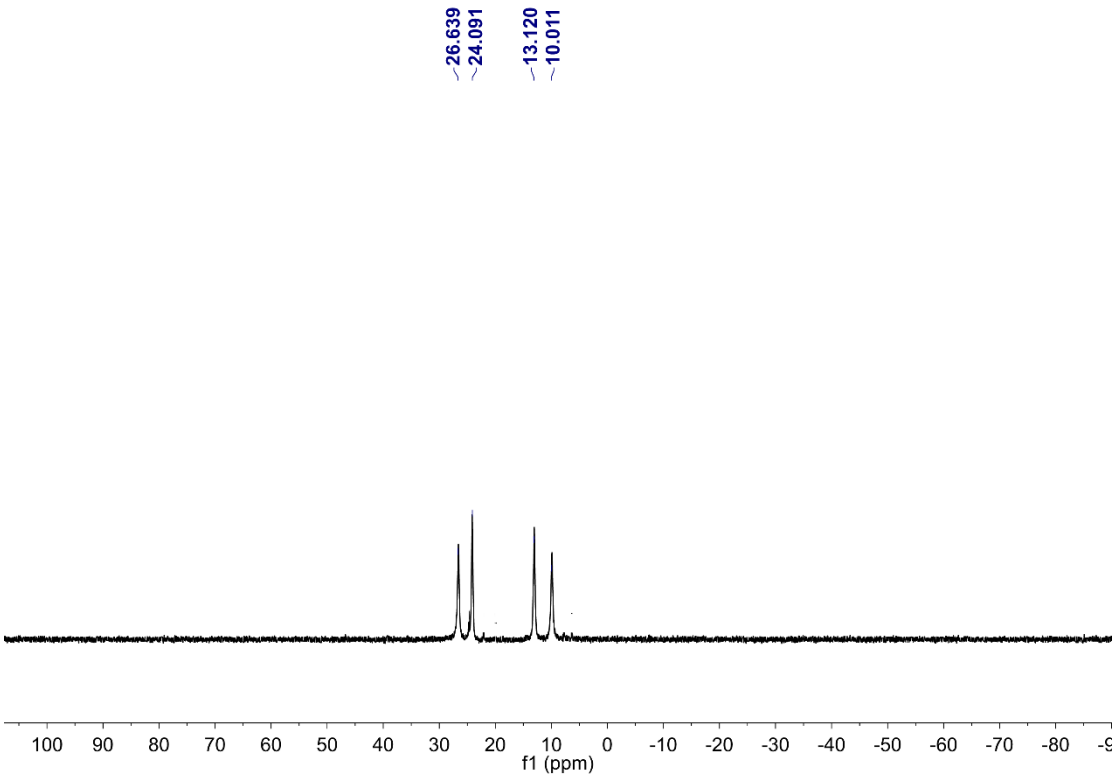


Figure S38. ^{31}P NMR (202 MHz, C_6D_6, 25 °C) spectrum of **7**. *Assignments:* δ = 26.6 (s), 24.1 (s), 13.1 (s), 10.0 (s).

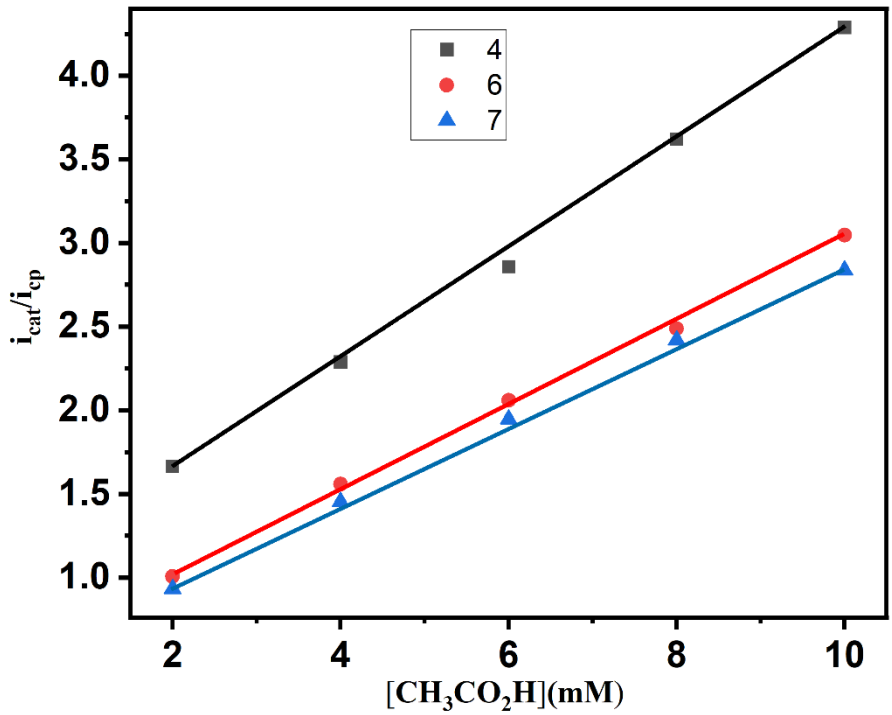


Figure S39. Plots of i_{cat} (μA) vs [HOAc] (mM) for a solution of **4**, **6** and **7** (1.0 mM) with 0.1 M n-Bu_4NPF_6/MeCN at a scan rate of 0.1 V s^{-1}.

Table S1. Crystal data and structure refinement parameters for compounds **1-3**.

Compound	**1**	**2**	**3-syn**	**3-anti**
Mol formula	$C_{30}H_{32}FeO_2P_2Se_2$	$C_{20}H_{28}FeO_2P_2Se_2$	$C_{34}H_{36}Fe_2O_4P_2Se_2$	$C_{34}H_{36}Fe_2O_4P_2Se_2$
Mol wt	700.26	576.13	840.19	840.19
Wavelength (Å)	0.71073	0.71073	1.54178	0.71073
Cryst syst	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	P21/c	P 21/n
a /Å	9.5662(8)	11.7653(12)	21.2567(5)	9.1562(9)
b /Å	10.8574(9)	14.8573(15)	20.1481(5)	18.9496(16)
c /Å	15.7815(13)	15.8567(16)	17.2656(5)	20.2164(18)
α /deg	76.313(2)	112.254(5)	90	90
β /deg	88.635(3)	92.185(2)	90.004(2)	97.088(2)
γ/deg	77.739(2)	96.229(3)	90	90
V/Å^3	1555.7(2)	2540.7(5)	7394.5(3)	3480.9(5)
Z	2	4	8	4
D_c/gcm^{-3}	1.495	1.506	1.509	1.603
abs coeff/mm^{-1}	2.952	3.596	9.635	8.130
F(000)	704	1152	3376	1688
index ranges	-11≤ h ≤ 10 -12≤ k ≤12 -17≤ l ≤18	-13 ≤ h ≤ 13 -17 ≤ k ≤ 17 -18 ≤ l ≤ 12	-25≤ h ≤25 -23≤ k ≤23 -20≤ l ≤ 19	-10 ≤ h ≤ 10 -22 ≤ k ≤ 22 -16 ≤ l ≤ 24
no. of reflns	7877	12842	48505	17475
no. of indepreflns	5374	8768	12916	6093
Goodness of fit	1.048	1.066	1.073	0.977
R	0.0522	0.0574	0.0635	0.0522
R_w	0.1310	0.1344	0.1756	0.1089

Table S2. Crystal data and structure refinement parameters for compounds **4-7**.

Compound	**4-syn**	**4-anti**	**5**	**6**	**7**
Mol formula	$C_{24}H_{32}Fe_2O_4P_2Se_2$	$C_{24}H_{32}Fe_2O_4P_2Se_2$	$C_{41}H_{47}Fe_2O_3P_3Se_2$	$C_{26}H_{41}Fe_2O_3P_3Se_2$	$C_{28}H_{50}Fe_2O_2P_4Se_2$
Mol wt	716.05	716.05	950.31	764.12	812.18
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Cryst syst	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Orthorhombic
Space group	P21/n	P2(1)2(1)2(1)	P-1	P21/n	Pbca
a /Å	10.6496(9)	11.5785(11)	9.4986(9)	23.261(3)	15.6555(15)
b /Å	13.5686(12)	15.9720(13)	10.0483(11)	12.4950(13)	11.3257(12)
c /Å	20.9799(18)	16.1003(14)	24.425(2)	25.607(3)	42.587(4)
α /deg	90	90	94.422(2)	90	90
β /deg	103.421(3)	90	96.009(2)	106.916(3)	90
γ/deg	90	90	105.156(3)	90	90
V/Å^3	2948.8(4)	2977.5(5)	2224.5(4)	7120.8(13)	7551.1(13)
Z	4	4	2	8	8
D_c/gcm^{-3}	1.613	1.597	1.419	1.426	1.429
abs coeff/mm^{-1}	3.587	3.553	2.430	3.017	2.888
F(000)	1432	1432	964	3088	3312
index ranges	-12≤ h ≤ 12 -15≤ k ≤16 -15≤ l ≤24	-13 ≤ h ≤ 13 -18 ≤ k ≤ 13 -19 ≤ l ≤ 19	-10≤ h ≤11 -11≤ k ≤8 -26≤ l ≤ 29	-21 ≤ h ≤ 27 -14 ≤ k ≤ 13 -30 ≤ l ≤ 21	-18 ≤ h ≤ 18 -13 ≤ k ≤ 13 -50 ≤ l ≤ 41
no. of reflns	14423	14350	10744	34977	34800
no. of indepreflns	5167	5244	7577	12525	6660
Goodness of fit	1.008	0.859	1.067	1.058	1.163
R	0.0620	0.0331	0.0892	0.0730	0.0808
R_w	0.1712	0.0592	0.1946	0.1857	0.1771

Table S3

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

Compound **1**			
Se(1)-C(19)	1.939(6)	Fe(1)-C(1)	1.766(6)
Se(1)-Fe(1)	2.4891(9)	Fe(1)-C(2)	1.792(7)
Se(2)-C(25)	1.950(6)	Fe(1)-P(1)	2.2989(15)
Se(2)-Fe(1)	2.5062(9)	Fe(1)-P(2)	2.3119(16)
C(1)-Fe(1)-C(2)	90.6(2)	P(1)-Fe(1)-Se(1)	83.86(4)
C(1)-Fe(1)-P(1)	91.07(17)	P(2)-Fe(1)-Se(1)	88.31(5)
C(2)-Fe(1)-P(1)	93.76(18)	C(1)-Fe(1)-Se(2)	176.77(17)
C(1)-Fe(1)-P(2)	90.29(17)	C(2)-Fe(1)-Se(2)	87.73(16)
C(2)-Fe(1)-P(2)	93.94(18)	P(1)-Fe(1)-Se(2)	91.80(4)
P(1)-Fe(1)-P(2)	172.17(6)	P(2)-Fe(1)-Se(2)	87.07(5)
C(1)-Fe(1)-Se(1)	97.91(17)	Se(1)-Fe(1)-Se(2)	83.87(3)
C(2)-Fe(1)-Se(1)	171.19(16)		

Table S4

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

Compound **2**			
Fe(1)-C(2)	1.758(7)	Fe(1)-C(2)	1.758(7)
Fe(1)-C(1)	1.779(8)	Fe(1)-C(1)	1.779(8)
Fe(1)-P(2)	2.299(2)	Fe(1)-P(2)	2.299(2)
Fe(1)-P(1)	2.310(2)	Fe(1)-P(1)	2.310(2)
C(2)-Fe(1)-C(1)	93.5(3)	C(1)-Fe(1)-Se(1)	169.6(2)
C(2)-Fe(1)-P(2)	89.5(2)	P(2)-Fe(1)-Se(1)	84.61(6)
C(1)-Fe(1)-P(2)	93.3(2)	P(1)-Fe(1)-Se(1)	89.58(6)
C(2)-Fe(1)-P(1)	91.1(2)	C(2)-Fe(1)-Se(2)	178.3(2)
C(1)-Fe(1)-P(1)	92.4(2)	C(1)-Fe(1)-Se(2)	87.5(2)
P(2)-Fe(1)-P(1)	174.18(8)	P(2)-Fe(1)-Se(2)	91.76(7)
C(2)-Fe(1)-Se(1)	96.7(2)	P(1)-Fe(1)-Se(2)	87.50(6)

Table S5

Selected bond lengths (Å) and angles (º) for **3-syn**.

Compound **3-syn**			
Se(1)-C(21)	1.985(6)	Fe(1)-C(2)	1.741(7)
Se(1)-Fe(2)	2.3778(10)	Fe(1)-C(1)	1.759(7)
Se(1)-Fe(1)	2.3961(11)	Fe(1)-P(1)	2.2239(18)
Se(2)-C(28)	1.995(7)	Fe(1)-Fe(2)	2.5517(13)
Se(2)-Fe(2)	2.4027(11)	Fe(2)-C(4)	1.749(7)
Se(2)-Fe(1)	2.4066(11)	Fe(2)-P(2)	2.2225(19)

C(2)-Fe(1)-C(1)	91.1(3)	C(4)-Fe(2)-C(3)	92.6(3)
C(2)-Fe(1)-P(1)	98.0(2)	C(4)-Fe(2)-P(2)	95.7(3)
C(1)-Fe(1)-P(1)	98.1(2)	C(3)-Fe(2)-P(2)	99.9(2)
C(2)-Fe(1)-Se(1)	94.3(2)	C(4)-Fe(2)-Se(1)	92.3(2)
C(1)-Fe(1)-Se(1)	160.9(2)	C(3)-Fe(2)-Se(1)	159.1(2)
P(1)-Fe(1)-Se(1)	99.30(5)	P(2)-Fe(2)-Se(1)	99.80(5)
C(2)-Fe(1)-Se(2)	156.3(2)	C(4)-Fe(2)-Se(2)	158.4(3)
C(1)-Fe(1)-Se(2)	92.7(2)	C(3)-Fe(2)-Se(2)	92.8(2)
P(1)-Fe(1)-Se(2)	104.60(6)	P(2)-Fe(2)-Se(2)	103.93(6)
Se(1)-Fe(1)-Se(2)	75.30(3)	Se(1)-Fe(2)-Se(2)	75.70(3)
C(2)-Fe(1)-Fe(2)	98.5(2)	C(4)-Fe(2)-Fe(1)	100.4(3)
C(1)-Fe(1)-Fe(2)	103.7(2)	C(3)-Fe(2)-Fe(1)	101.1(2)
P(1)-Fe(1)-Fe(2)	152.25(6)	P(2)-Fe(2)-Fe(1)	152.82(6)
Se(1)-Fe(1)-Fe(2)	57.34(3)	Se(1)-Fe(2)-Fe(1)	58.04(3)
Se(2)-Fe(1)-Fe(2)	57.88(3)	Se(2)-Fe(2)-Fe(1)	58.03(3)

Table S6

Selected bond lengths (Å) and angles (º) for **3-anti**.

Compound **3-anti**			
Se(1)-C(21)	1.982(4)	Fe(1)-C(2)	1.739(5)
Se(1)-Fe(2)	2.3657(10)	Fe(1)-P(1)	2.2046(14)
Se(1)-Fe(1)	2.3674(8)	Fe(1)-Fe(2)	2.5622(10)
Se(2)-C(28)	1.957(5)	Fe(2)-C(3)	1.715(6)
Se(2)-Fe(1)	2.3542(10)	Fe(2)-C(4)	1.746(6)
Se(2)-Fe(2)	2.3707(8)	Fe(2)-P(2)	2.2063(16)
Fe(1)-C(1)	1.707(7)		
C(1)-Fe(1)-C(2)	95.2(3)	C(3)-Fe(2)-C(4)	99.8(3)
C(1)-Fe(1)-P(1)	93.4(2)	C(3)-Fe(2)-P(2)	86.71(18)
C(2)-Fe(1)-P(1)	100.17(17)	C(4)-Fe(2)-P(2)	99.98(19)
C(1)-Fe(1)-Se(2)	165.32(19)	C(3)-Fe(2)-Se(1)	162.28(19)
C(2)-Fe(1)-Se(2)	92.50(19)	C(4)-Fe(2)-Se(1)	97.63(19)
P(1)-Fe(1)-Se(2)	97.57(5)	P(2)-Fe(2)-Se(1)	93.55(5)
C(1)-Fe(1)-Se(1)	85.65(19)	C(3)-Fe(2)-Se(2)	91.00(18)
C(2)-Fe(1)-Se(1)	149.71(17)	C(4)-Fe(2)-Se(2)	105.50(19)
P(1)-Fe(1)-Se(1)	110.03(5)	P(2)-Fe(2)-Se(2)	154.44(5)
Se(2)-Fe(1)-Se(1)	81.43(3)	Se(1)-Fe(2)-Se(2)	81.13(3)
C(1)-Fe(1)-Fe(2)	109.33(19)	C(3)-Fe(2)-Fe(1)	105.18(18)
C(2)-Fe(1)-Fe(2)	94.54(17)	C(4)-Fe(2)-Fe(1)	149.16(18)
P(1)-Fe(1)-Fe(2)	151.68(5)	P(2)-Fe(2)-Fe(1)	99.26(5)
Se(2)-Fe(1)-Fe(2)	57.47(3)	Se(1)-Fe(2)-Fe(1)	57.26(3)
Se(1)-Fe(1)-Fe(2)	57.19(3)	Se(2)-Fe(2)-Fe(1)	56.85(3)

Table S7

Selected bond lengths (Å) and angles (º) for **4-syn**.

Compound **4-syn**			
Se(1)-Fe(1)	2.3695(13)	Fe(1)-C(1)	1.738(9)
Se(1)-Fe(2)	2.3710(13)	Fe(1)-P(1)	2.204(2)
Se(2)-C(18)	1.961(8)	Fe(1)-Fe(2)	2.5422(14)
Se(2)-Fe(1)	2.3624(13)	Fe(2)-C(4)	1.718(9)
Se(2)-Fe(2)	2.3719(13)	Fe(2)-C(3)	1.740(9)
Fe(1)-C(2)	1.723(10)	Fe(2)-P(2)	2.201(2)
C(2)-Fe(1)-C(1)	89.0(4)	C(4)-Fe(2)-C(3)	91.6(4)
C(2)-Fe(1)-P(1)	99.9(3)	C(4)-Fe(2)-P(2)	98.4(3)
C(1)-Fe(1)-P(1)	98.9(3)	C(3)-Fe(2)-P(2)	97.9(3)
C(2)-Fe(1)-Se(2)	160.5(3)	C(4)-Fe(2)-Se(1)	161.4(3)
C(1)-Fe(1)-Se(2)	95.0(3)	C(3)-Fe(2)-Se(1)	93.1(3)
P(1)-Fe(1)-Se(2)	98.25(8)	P(2)-Fe(2)-Se(1)	98.78(8)
C(2)-Fe(1)-Se(1)	92.8(3)	C(4)-Fe(2)-Se(2)	92.3(3)
C(1)-Fe(1)-Se(1)	161.5(3)	C(3)-Fe(2)-Se(2)	159.8(3)
P(1)-Fe(1)-Se(1)	98.95(8)	P(2)-Fe(2)-Se(2)	101.03(7)
Se(2)-Fe(1)-Se(1)	77.51(4)	Se(1)-Fe(2)-Se(2)	77.30(4)
C(2)-Fe(1)-Fe(2)	102.8(3)	C(4)-Fe(2)-Fe(1)	103.8(3)
C(1)-Fe(1)-Fe(2)	104.1(3)	C(3)-Fe(2)-Fe(1)	102.5(3)
P(1)-Fe(1)-Fe(2)	147.72(9)	P(2)-Fe(2)-Fe(1)	149.13(8)
Se(2)-Fe(1)-Fe(2)	57.70(4)	Se(1)-Fe(2)-Fe(1)	57.54(4)
Se(1)-Fe(1)-Fe(2)	57.60(4)	Se(2)-Fe(2)-Fe(1)	57.34(4)

Table S8

Selected bond lengths (Å) and angles (º) for **4-anti**.

Compound **4-anti**			
Se(1)-C(11)	1.965(6)	Fe(1)-C(2)	1.735(8)
Se(1)-Fe(1)	2.3598(11)	Fe(1)-P(1)	2.189(2)
Se(1)-Fe(2)	2.3694(11)	Fe(1)-Fe(2)	2.5746(12)
Se(2)-C(18)	1.973(6)	Fe(2)-C(3)	1.724(8)
Se(2)-Fe(1)	2.3481(11)	Fe(2)-C(4)	1.730(8)
Se(2)-Fe(2)	2.3607(11)	Fe(2)-P(2)	2.207(2)
Fe(1)-C(1)	1.721(8)		
C(1)-Fe(1)-C(2)	104.9(4)	C(3)-Fe(2)-C(4)	90.4(3)
C(1)-Fe(1)-P(1)	90.2(2)	C(3)-Fe(2)-P(2)	96.2(2)
C(2)-Fe(1)-P(1)	90.7(3)	C(4)-Fe(2)-P(2)	97.4(2)
C(1)-Fe(1)-Se(2)	94.1(2)	C(3)-Fe(2)-Se(2)	95.4(2)
C(2)-Fe(1)-Se(2)	96.1(3)	C(4)-Fe(2)-Se(2)	162.9(2)
P(1)-Fe(1)-Se(2)	170.71(7)	P(2)-Fe(2)-Se(2)	97.97(7)
C(1)-Fe(1)-Se(1)	142.6(2)	C(3)-Fe(2)-Se(1)	158.6(2)
C(2)-Fe(1)-Se(1)	112.5(2)	C(4)-Fe(2)-Se(1)	86.6(2)
P(1)-Fe(1)-Se(1)	88.93(6)	P(2)-Fe(2)-Se(1)	105.21(6)

Se(2)-Fe(1)-Se(1)	82.66(4)	Se(2)-Fe(2)-Se(1)	82.19(4)
C(1)-Fe(1)-Fe(2)	89.8(2)	C(3)-Fe(2)-Fe(1)	104.2(2)
C(2)-Fe(1)-Fe(2)	150.8(3)	C(4)-Fe(2)-Fe(1)	106.3(2)
P(1)-Fe(1)-Fe(2)	114.78(7)	P(2)-Fe(2)-Fe(1)	148.34(7)
Se(2)-Fe(1)-Fe(2)	57.09(3)	Se(2)-Fe(2)-Fe(1)	56.62(3)
Se(1)-Fe(1)-Fe(2)	57.19(3)	Se(1)-Fe(2)-Fe(1)	56.84(3)

Table S9

Selected bond lengths (Å) and angles (º) for **5**.

Compound **5**			
Se(1)-Fe(2)	2.4311(19)	Fe(1)-P(2)	2.245(4)
Se(1)-Fe(1)	2.4509(18)	Fe(1)-P(1)	2.256(3)
Se(2)-C(35)	2.011(11)	Fe(1)-Fe(2)	2.620(2)
Se(2)-Fe(1)	2.4058(17)	Fe(2)-C(3)	1.746(13)
Se(2)-Fe(2)	2.4182(19)	Fe(2)-C(2)	1.762(13)
Fe(1)-C(1)	1.753(12)	Fe(2)-P(3)	2.253(3)
C(1)-Fe(1)-P(2)	98.8(4)	C(3)-Fe(2)-C(2)	92.1(5)
C(1)-Fe(1)-P(1)	88.2(3)	C(3)-Fe(2)-P(3)	93.5(4)
P(2)-Fe(1)-P(1)	101.01(12)	C(2)-Fe(2)-P(3)	100.9(4)
C(1)-Fe(1)-Se(2)	93.4(3)	C(3)-Fe(2)-Se(2)	166.7(4)
P(2)-Fe(1)-Se(2)	101.11(10)	C(2)-Fe(2)-Se(2)	93.2(4)
P(1)-Fe(1)-Se(2)	157.30(11)	P(3)-Fe(2)-Se(2)	97.39(10)
C(1)-Fe(1)-Se(1)	160.8(4)	C(3)-Fe(2)-Se(1)	88.9(4)
P(2)-Fe(1)-Se(1)	100.14(11)	C(2)-Fe(2)-Se(1)	147.0(4)
P(1)-Fe(1)-Se(1)	91.23(9)	P(3)-Fe(2)-Se(1)	111.97(11)
Se(2)-Fe(1)-Se(1)	79.89(6)	Se(2)-Fe(2)-Se(1)	80.04(6)
C(1)-Fe(1)-Fe(2)	104.1(4)	C(3)-Fe(2)-Fe(1)	110.9(4)
P(2)-Fe(1)-Fe(2)	149.04(11)	C(2)-Fe(2)-Fe(1)	91.2(4)
P(1)-Fe(1)-Fe(2)	100.31(10)	P(3)-Fe(2)-Fe(1)	152.37(11)
Se(2)-Fe(1)-Fe(2)	57.33(5)	Se(2)-Fe(2)-Fe(1)	56.88(5)
Se(1)-Fe(1)-Fe(2)	57.18(5)	Se(1)-Fe(2)-Fe(1)	57.91(5)

Table S10

Selected bond lengths (Å) and angles (º) for **6**.

Compound **6**			
Se(1)-Fe(2)	2.4206(15)	Se(3)-Fe(4)	2.4136(16)
Se(1)-Fe(1)	2.4216(15)	Se(3)-Fe(3)	2.4171(16)
Se(2)-Fe(2)	2.4529(15)	Se(4)-Fe(3)	2.4265(17)
Se(2)-Fe(1)	2.4702(14)	Se(4)-Fe(4)	2.4553(16)
Fe(1)-C(1)	1.726(10)	Fe(3)-P(6)	2.268(3)
Fe(1)-P(2)	2.239(3)	Fe(3)-Fe(4)	2.6290(19)
Fe(1)-P(1)	2.248(3)	Fe(4)-C(27)	1.772(10)
Fe(1)-Fe(2)	2.6342(17)	Fe(4)-P(5)	2.247(3)
Fe(2)-C(3)	1.793(10)	Fe(4)-P(4)	2.247(3)

Fe(2)-C(2)	1.796(11)	Fe(3)-C(28)	1.772(12)
Fe(2)-P(3)	2.259(3)	Fe(3)-C(29)	1.772(11)
C(1)-Fe(1)-P(2)	85.9(3)	C(3)-Fe(2)-C(2)	91.9(4)
C(1)-Fe(1)-P(1)	96.5(3)	C(3)-Fe(2)-P(3)	100.2(3)
P(2)-Fe(1)-P(1)	101.04(11)	C(2)-Fe(2)-P(3)	92.9(3)
C(1)-Fe(1)-Se(1)	94.5(3)	C(3)-Fe(2)-Se(1)	93.0(3)
P(2)-Fe(1)-Se(1)	156.40(9)	C(2)-Fe(2)-Se(1)	166.9(3)
P(1)-Fe(1)-Se(1)	102.36(9)	P(3)-Fe(2)-Se(1)	98.10(9)
C(1)-Fe(1)-Se(2)	162.7(3)	C(3)-Fe(2)-Se(2)	151.1(3)
P(2)-Fe(1)-Se(2)	92.58(8)	C(2)-Fe(2)-Se(2)	89.4(3)
P(1)-Fe(1)-Se(2)	100.76(8)	P(3)-Fe(2)-Se(2)	108.58(8)
Se(1)-Fe(1)-Se(2)	80.06(5)	Se(1)-Fe(2)-Se(2)	80.42(5)
C(1)-Fe(1)-Fe(2)	105.9(3)	C(3)-Fe(2)-Fe(1)	94.8(3)
P(2)-Fe(1)-Fe(2)	100.13(9)	C(2)-Fe(2)-Fe(1)	110.5(3)
P(1)-Fe(1)-Fe(2)	150.10(9)	P(3)-Fe(2)-Fe(1)	151.76(9)
Se(1)-Fe(1)-Fe(2)	57.02(4)	Se(1)-Fe(2)-Fe(1)	57.06(4)
Se(2)-Fe(1)-Fe(2)	57.33(4)	Se(2)-Fe(2)-Fe(1)	57.97(4)

Table S11

Selected bond lengths (Å) and angles (º) for **7**.

Compound **7**			
Se(1)-C(15)	2.013(9)	Fe(1)-P(1)	2.232(3)
Se(1)-Fe(1)	2.4039(15)	Fe(1)-P(2)	2.243(3)
Se(1)-Fe(2)	2.4319(15)	Fe(1)-Fe(2)	2.7197(17)
Se(2)-C(22)	2.022(9)	Fe(2)-C(2)	1.712(10)
Se(2)-Fe(1)	2.4214(15)	Fe(2)-P(3)	2.234(3)
Se(2)-Fe(2)	2.4365(15)	Fe(2)-P(4)	2.240(3)
Fe(1)-C(1)	1.745(11)		
C(1)-Fe(1)-P(1)	86.1(3)	C(2)-Fe(2)-P(3)	90.0(3)
C(1)-Fe(1)-P(2)	96.4(3)	C(2)-Fe(2)-P(4)	94.2(4)
P(1)-Fe(1)-P(2)	101.89(11)	P(3)-Fe(2)-P(4)	97.72(11)
C(1)-Fe(1)-Se(1)	94.9(3)	C(2)-Fe(2)-Se(1)	159.2(3)
P(1)-Fe(1)-Se(1)	156.19(10)	P(3)-Fe(2)-Se(1)	97.56(9)
P(2)-Fe(1)-Se(1)	101.65(9)	P(4)-Fe(2)-Se(1)	103.83(9)
C(1)-Fe(1)-Se(2)	163.4(3)	C(2)-Fe(2)-Se(2)	87.7(3)
P(1)-Fe(1)-Se(2)	91.89(8)	P(3)-Fe(2)-Se(2)	164.02(10)
P(2)-Fe(1)-Se(2)	100.10(8)	P(4)-Fe(2)-Se(2)	98.22(9)
Se(1)-Fe(1)-Se(2)	80.48(5)	Se(1)-Fe(2)-Se(2)	79.63(5)
C(1)-Fe(1)-Fe(2)	108.0(3)	C(2)-Fe(2)-Fe(1)	104.0(3)
P(1)-Fe(1)-Fe(2)	100.80(9)	P(3)-Fe(2)-Fe(1)	109.76(9)
P(2)-Fe(1)-Fe(2)	147.57(9)	P(4)-Fe(2)-Fe(1)	146.71(9)
Se(1)-Fe(1)-Fe(2)	56.27(4)	Se(1)-Fe(2)-Fe(1)	55.29(4)
Se(2)-Fe(1)-Fe(2)	56.22(4)	Se(2)-Fe(2)-Fe(1)	55.69(4)