Supporting Information

Synthesis, properties, and electrochemistry of bis(iminophosphorane)pyridine iron(II) pincer complexes

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Contents

S1. General Considerations 2

S2. Synthesis of **PyN3** 2

S3. Synthesis of **ImPh** [2] 4

S4. Characterization of **ImBu** 6

S5. Characterization of **ImMe** 8

S6. Characterization of **FeImPh** 10

S7. Characterization of **FeImBu** 13

S8. Characterization of **FeImMe** 15

S9. Characterization of **FeImPh(Br)** 17

S10. Crystallographic details 19

S11. Stability studies 21

S12. NMR spectra of **[Fe(tpy)$_2$]Cl$_2$** and triphenylphosphine oxide from the reaction between **FeImPh** and terpyridine 23

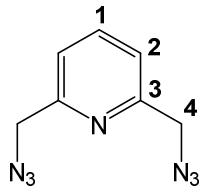
S13. Cyclic voltammogram of ferrocene 24

S1. General Considerations

All reactions were carried out under nitrogen atmosphere using Schlenk techniques. THF and Et_2O were distilled over sodium prior to use. Pyridine-2,6-dicarboxylic acid, Na_2CO_3, $NaBH_4$ and PBr_3 were purchased from Sigma-Aldrich and NaN_3 was purchased from MCF chemicals. All purchased reagents were used as received. The precursor $FeCl_2py_4$ was prepared according to the literature [1].

^1H, ^{13}C NMR and 31P spectra were carried out in $CDCl_3$ on a JEOL GX 300 spectrometer (300.5296 MHz for ^1H, 75.5682 MHz for ^{13}C and 121.5 MHz for ^{31}P). The δ scale is used throughout; chemical shifts are in ppm, and the coupling constants are in Hz. The samples of the iron complexes were prepared in an inert atmosphere and transferred to an NMR tube coupled to a J Young valve. FAB+ mass spectra were obtained using a JEOL JMS-SX102A instrument with m-nitrobenzyl alcohol as matrix. DART mass spectra were obtained using Joel AccuTOF JMS-T100LC instrument. Infrared spectra were performed on a Bruker Alpha ATR spectrometer with neat samples of the compounds.

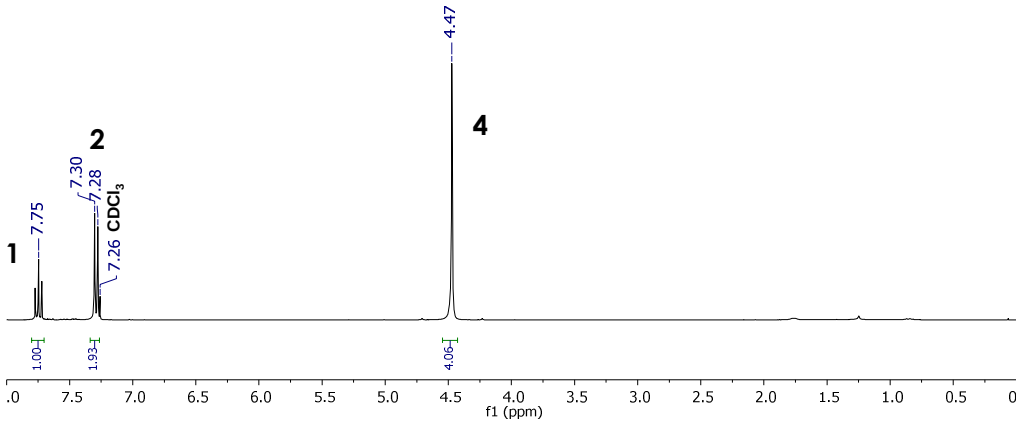
S2. Synthesis of PyN3



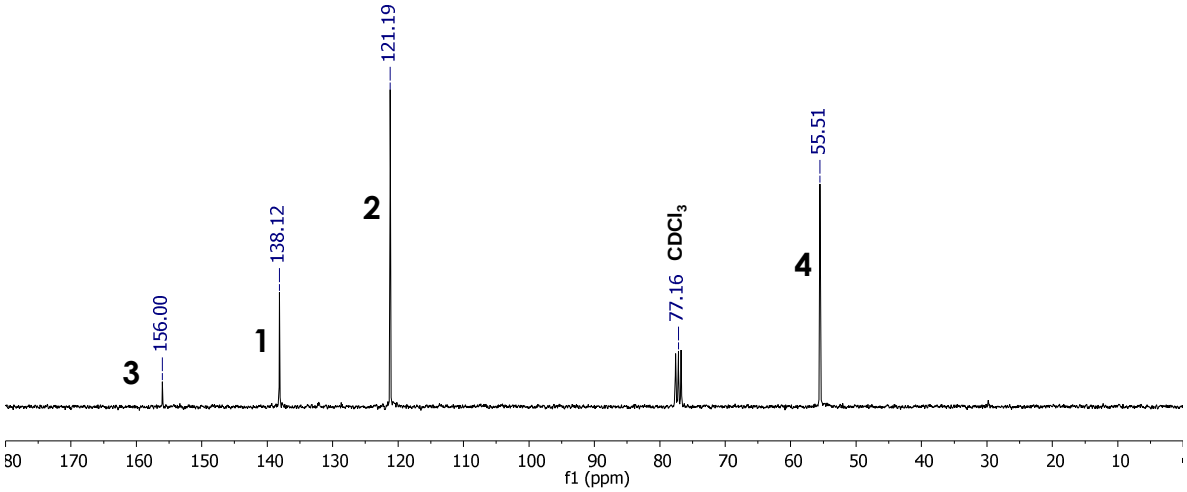
PyN3

In a Schlenk flask, 0.305 g (4.69 mmol) of NaN_3 were slowly added to a solution of 0.50 g (1.88 mmol) of PyBr in 10 mL of DMSO. The reaction mixture was left in agitation for 12 hours followed by the addition of 10 mL of water. Extractions were performed with 3 x 20 mL of diethylether. The organic phase was washed with 40 mL of a saturated NaCl solution, then dried over Na_2SO_4, and the solvent was evaporated to dryness under vacuum. A yellow oil corresponding to **PyN3** was obtained in 65 % yield (0.230 g, 1.22 mmol).

^1H NMR ($CDCl_3$, 300 MHz) 7.76 (t, J_{HH} = 8.0, 1H, H1), 7.30 (d, J_{HH} = 8.0, 2H, H2), 4.48 (s, 4H, H4). ^{13}C {^1H} NMR ($CDCl_3$, 75 MHz) δ = 155.9 (C3), 138.0 (C1), 121.1 (C2), 55.4 (C4).

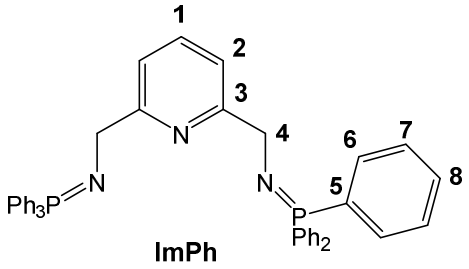


^{1}H NMR spectrum for **PyN3** ($CDCl_3$, 300 MHz, 298 K).



^{13}C {^{1}H} NMR spectrum for **PyN3** ($CDCl_3$, 75 MHz, 298 K).

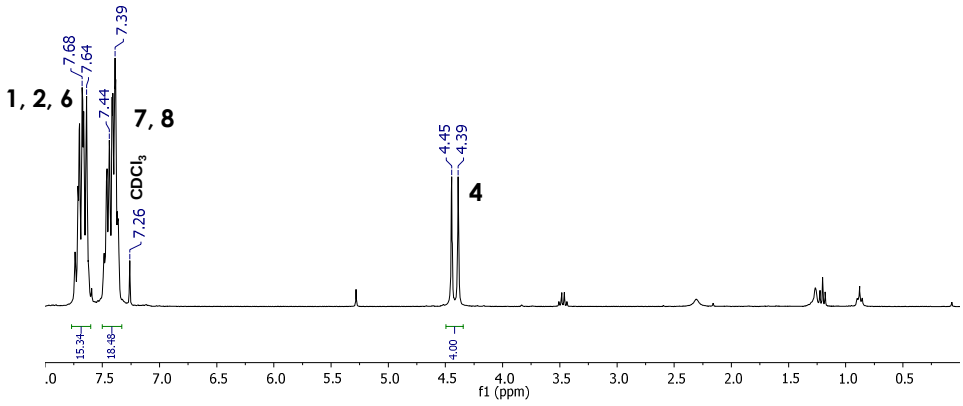
S3. Synthesis of ImPh [2]



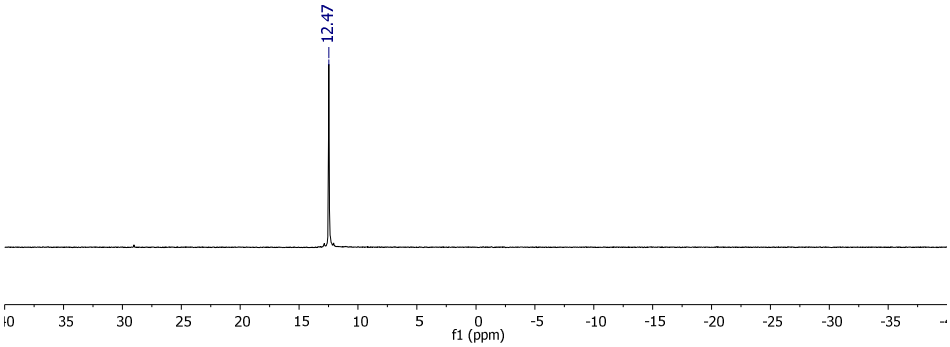
ImPh

In a Schlenk flask, 0.277 g (1.056 mmol) of PPh_3 were slowly added to solution of 0.10 g (0.528 mmol) of **PyN3** in 10 mL of diethylether, and the reaction mixture was stirred at room temperature for 12 hours. The solvent was concentrated under vacuum to about 5 mL, and the white precipitate was filtered off through a canula fitted with filter paper, then washed with 30 mL of cold diethylether, and dried under vacuum. The white solid corresponding to **ImPh** was obtained in 65 % yield (0.225 g, 0.343 mmol).

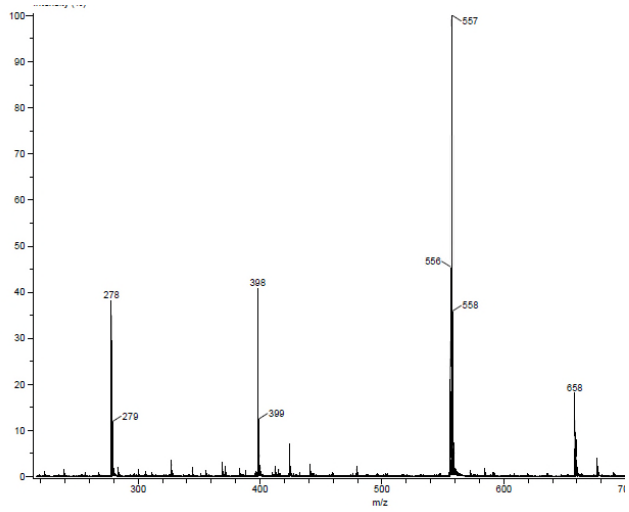
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) 12.0 (s). ^{1}H NMR ($CDCl_3$, 300 MHz) 7.79–7.59 (m, 15H, H1, H2, H6), 7.57–7.30 (m, 18H, H7, H8), 4.30 (d, J_{PH} = 18.0, 4H, H4). MS (DART): *m/z*, 657. IR (ν cm^{-1}): 1105 ($\nu_{N=P}$).



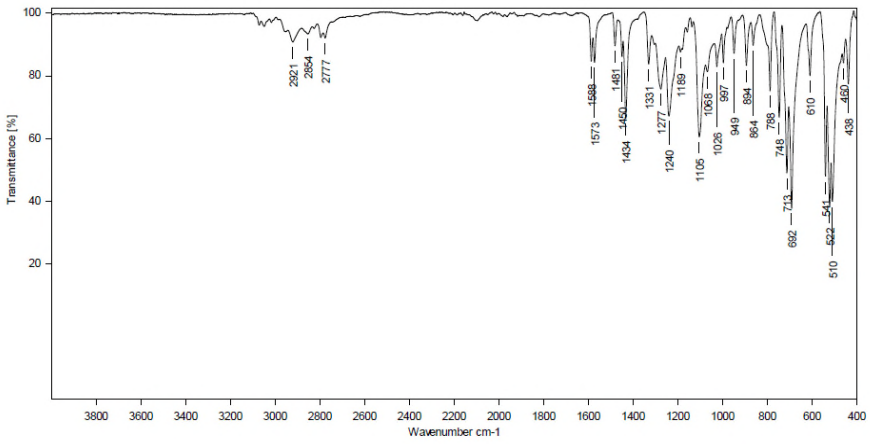
^{1}H NMR spectrum for **ImPh** ($CDCl_3$, 300 MHz, 298 K).



^{31}P $\{^{1}H\}$ NMR spectrum for **ImPh** ($CDCl_3$, 121 MHz, 298 K).

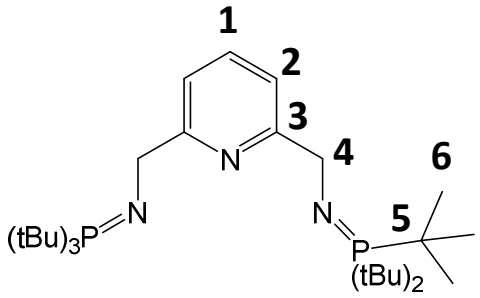


MS(DART) for **ImPh.**



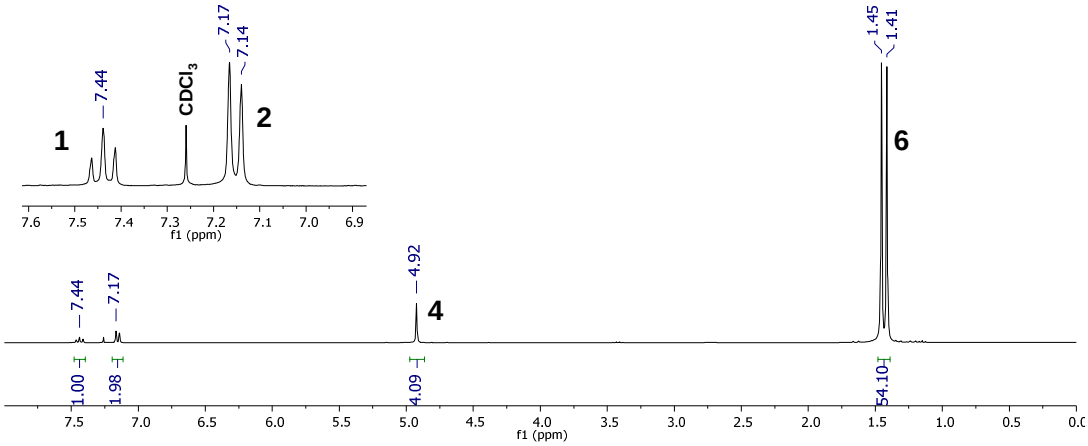
ATR-IR spectrum for **ImPh**.

S4. Characterization of ImBu

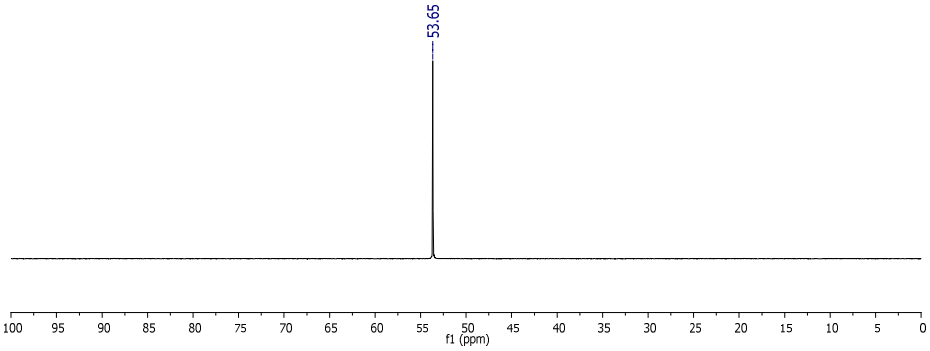


ImBu

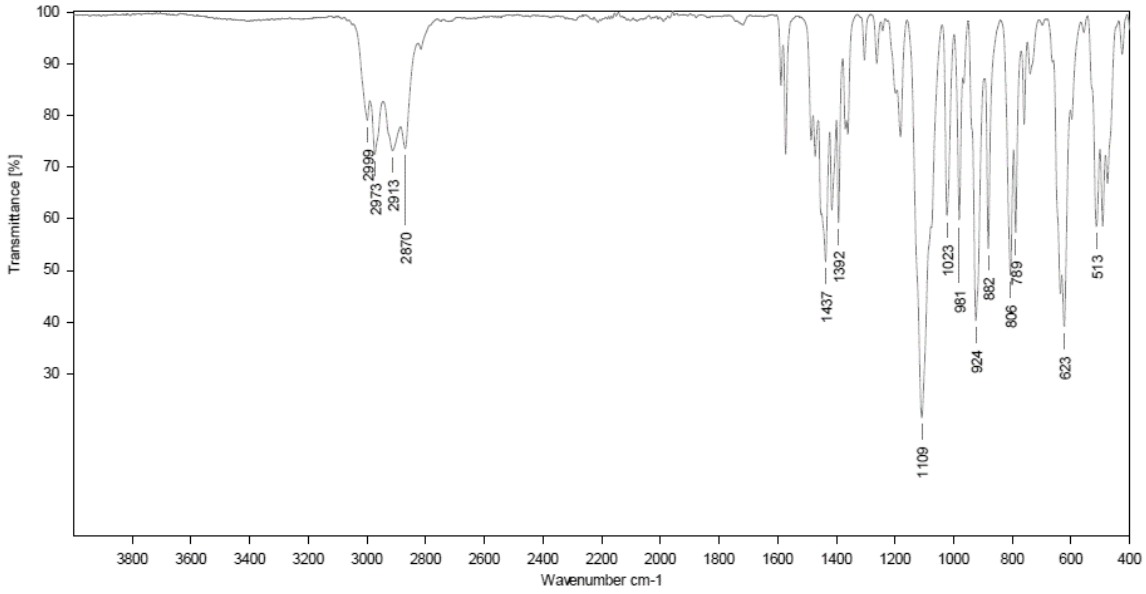
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) 53.65 (s). ^{1}H NMR ($CDCl_3$, 300 MHz) 7.44 (t, J_{HH} = 8.6 Hz, 1H, H1), 7.17 (d, J_{HH} = 9.0, 2H, H2), 4.92 (s, 4H, H4), 1.43 (d, J_{PH} = 12.0, 54H, H6). IR (ν cm^{-1}): 1109 ($\nu_{N=P}$).



^{1}H NMR spectrum for **ImBu** ($CDCl_3$, 300 MHz, 298 K).

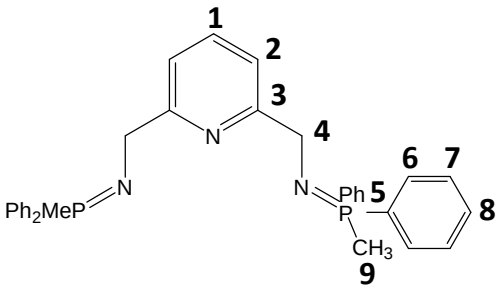


$^{31}P\{^{1}H\}$ NMR spectrum for **ImBu** ($CDCl_3$, 121 MHz, 298 K).



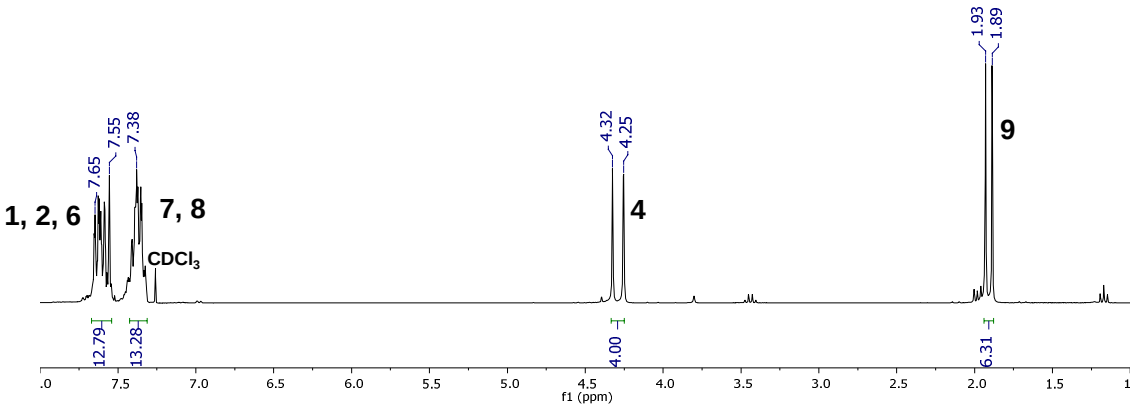
ATR-IR spectrum for **ImBu**.

S5. Characterization of ImMe

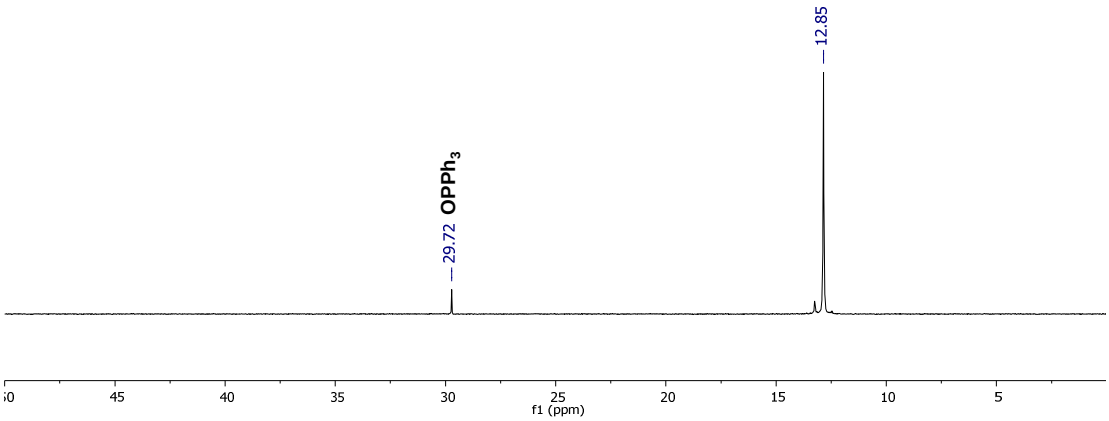


ImMe

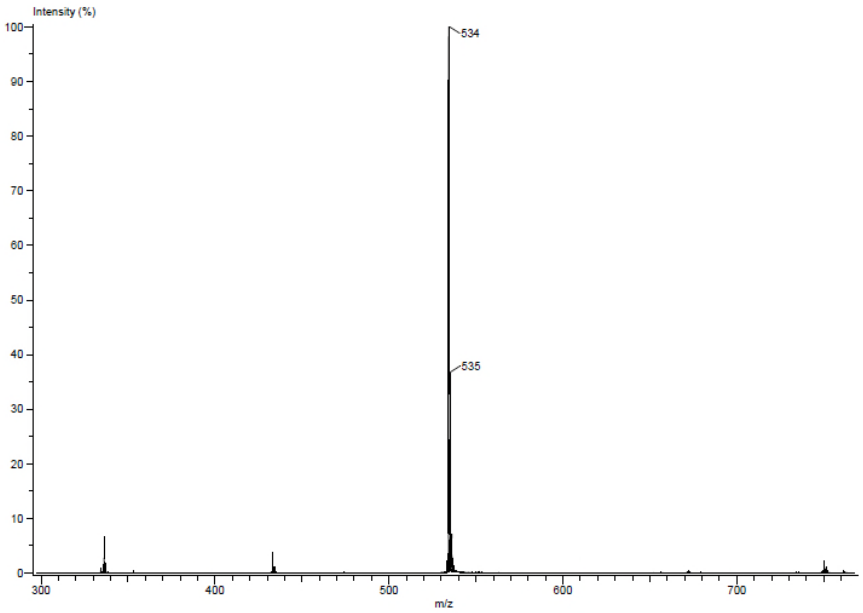
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) 12.85 (s). ^{1}H NMR ($CDCl_3$, 300 MHz) 7.66–7.54 (m, 12H, H1, H2, H6), 7.42–7.31 (m, 13H, H7, H8), 4.28 (d, J_{PH} = 21.0, 4H, H4) 1.91 (d, J_{PH} = 12.0, 6H, H9). MS (DART): *m/z*, 534.



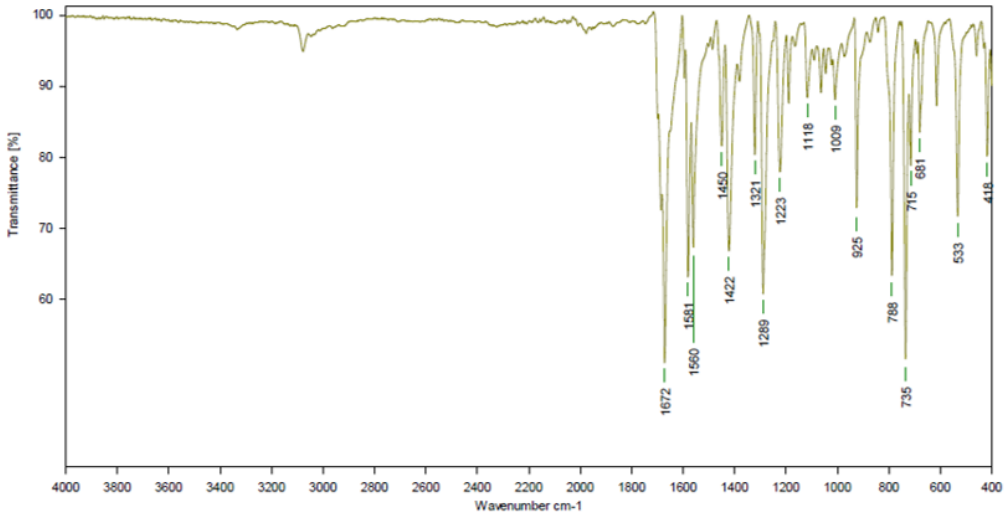
^{1}H NMR spectrum for **ImMe** ($CDCl_3$, 300 MHz, 298 K).



$^{31}P\{^{1}H\}$ NMR spectrum for **ImMe** ($CDCl_3$, 121 MHz, 298 K).

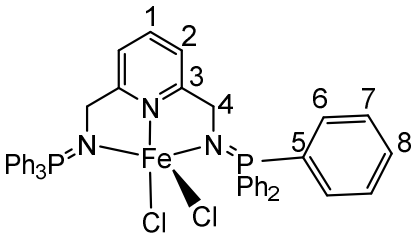


MS(DART) for **ImMe.**



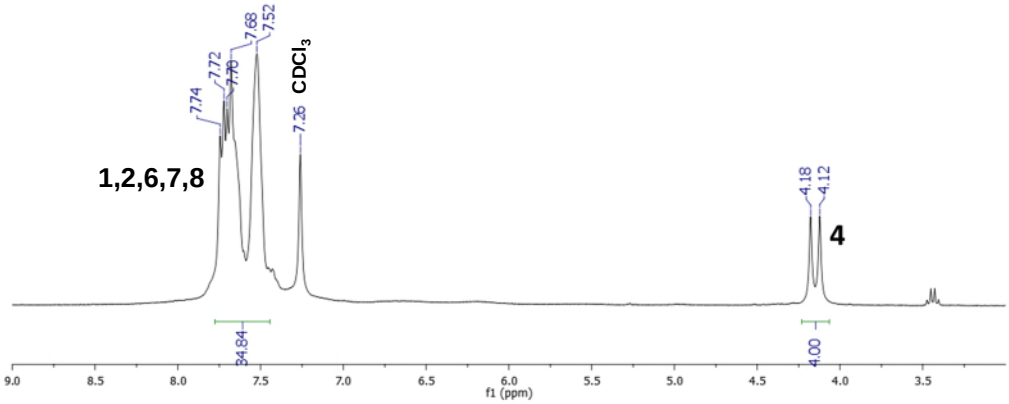
ATR-IR spectrum for **ImMe**.

S6. Characterization of FeImPh

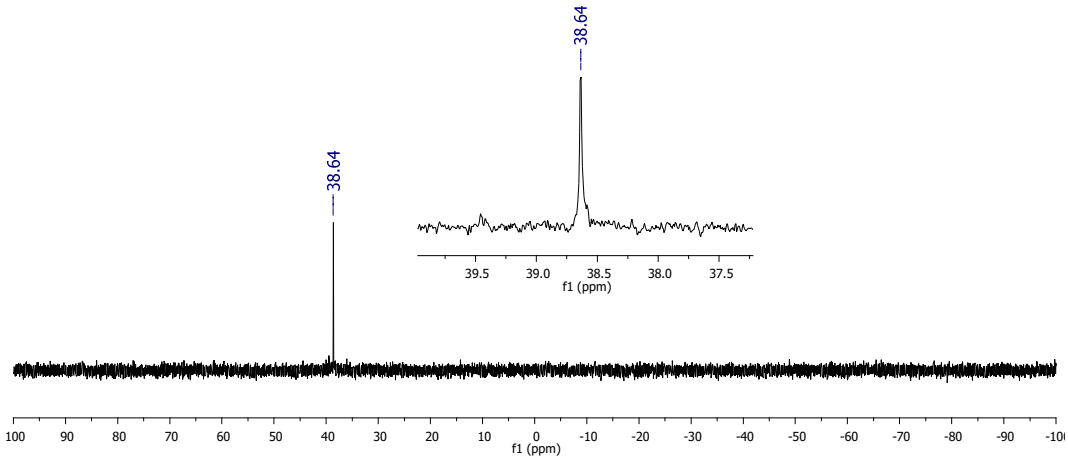


FeImPh

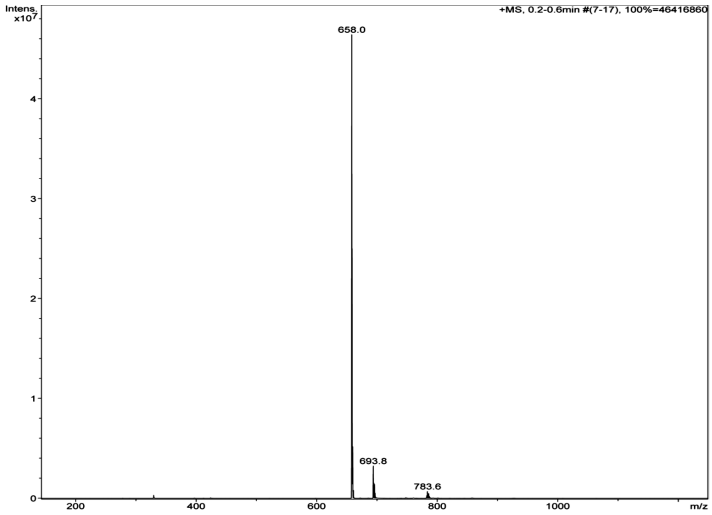
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) 38.64 (s). ^{1}H NMR ($CDCl_3$, 300 MHz) 7.45-7.90 (m, 34H, H1, H2, H6, H7, H8), 4.15 (d, J_{PH} = 18, 4H, H4). MS (ESI+): m/z, 783.6. IR (ν cm^{-1}): 1113 ($\nu_{N=P}$). Anal Calcd for $C_{43}H_{37}Cl_2FeN_3P_2 \cdot 0.75\ CH_2Cl_2$: N, 5.00; C, 62.36; H, 4.59. Found: N, 5.21; C, 62.03; H, 4.69.



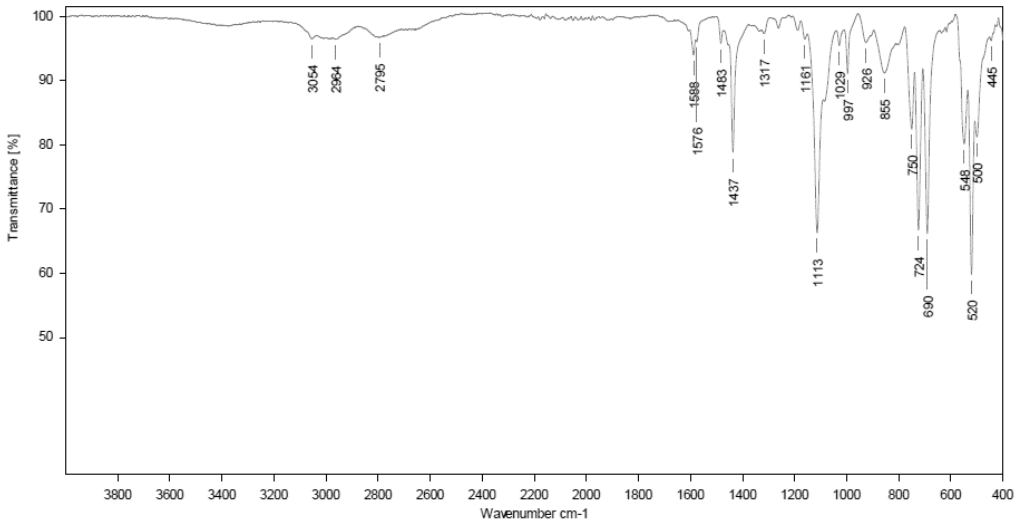
^{1}H NMR spectrum for **FeImPh** ($CDCl_3$, 300 MHz, 298 K).



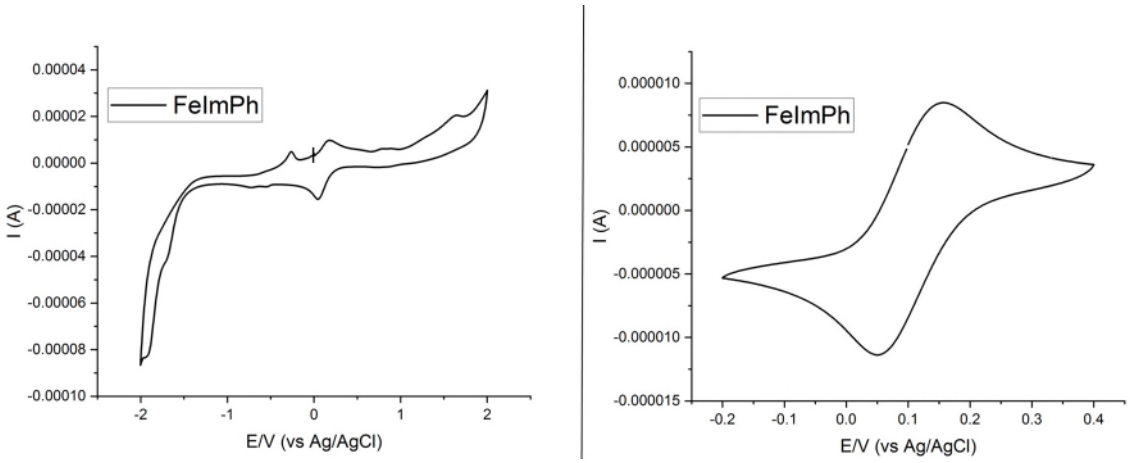
$^{31}P\{^{1}H\}$ NMR spectrum for **FeImPh** ($CDCl_3$, 121 MHz, 298 K).



MS(ESI) for **FeImPh.**

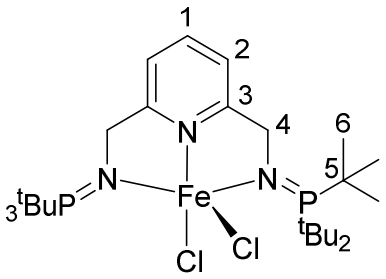


ATR-IR spectrum for **FeImPh.**



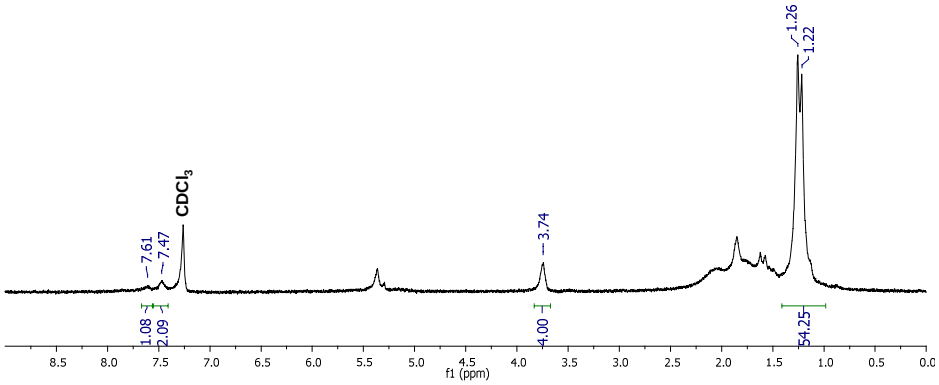
Cyclic voltammetry of complex **FeImPh** (0.1 M nBu$_4$NPF$_6$, 100 mVs^{-1}, glassy carbon, Ag/AgCl, 25 °C, 1×10^{-4} M in CH_2Cl_2).

S7. Characterization of FeImBu

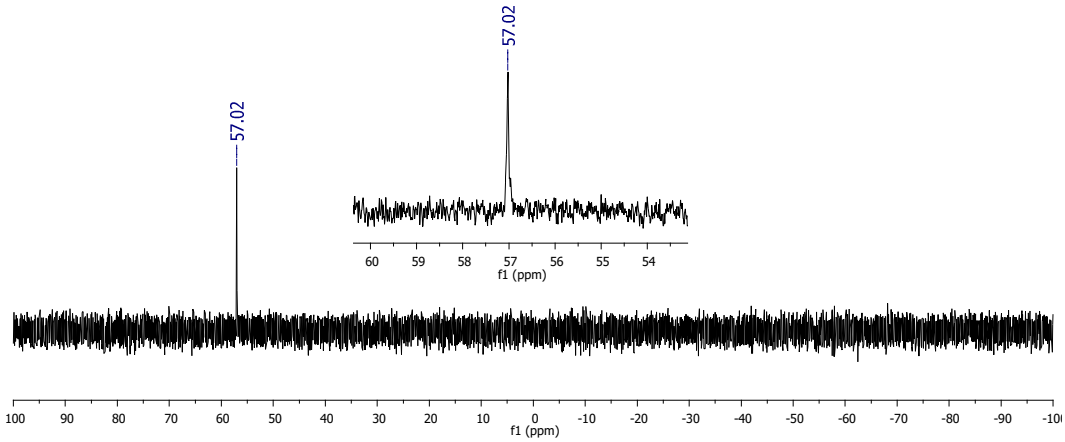


FeImBu

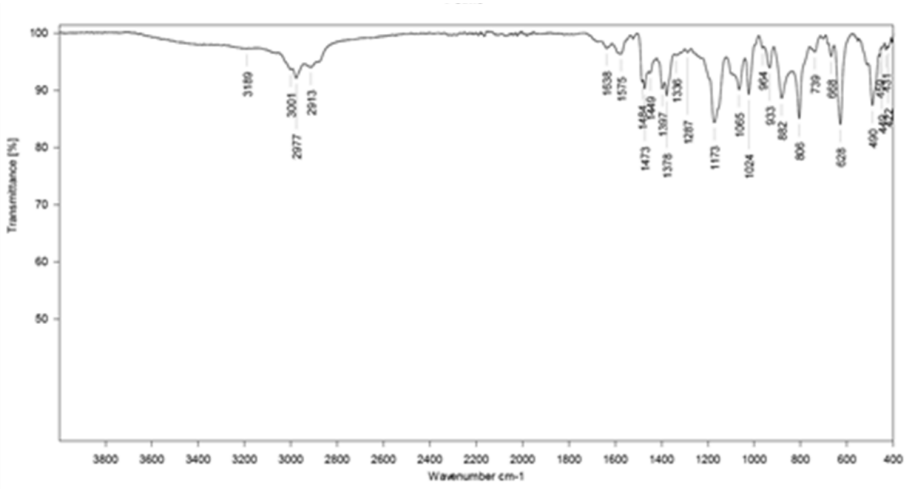
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) 69.75 (s).^{1}H NMR ($CDCl_3$, 300 MHz) 7.61 (s, 1H, H1), 7.47 (s, 2H, H2), 3.74 (s, 4H, H4), 1.26-1.22 (m, 54H, H6). IR (ν cm^{-1}): 1173 ($\nu_{N=P}$).



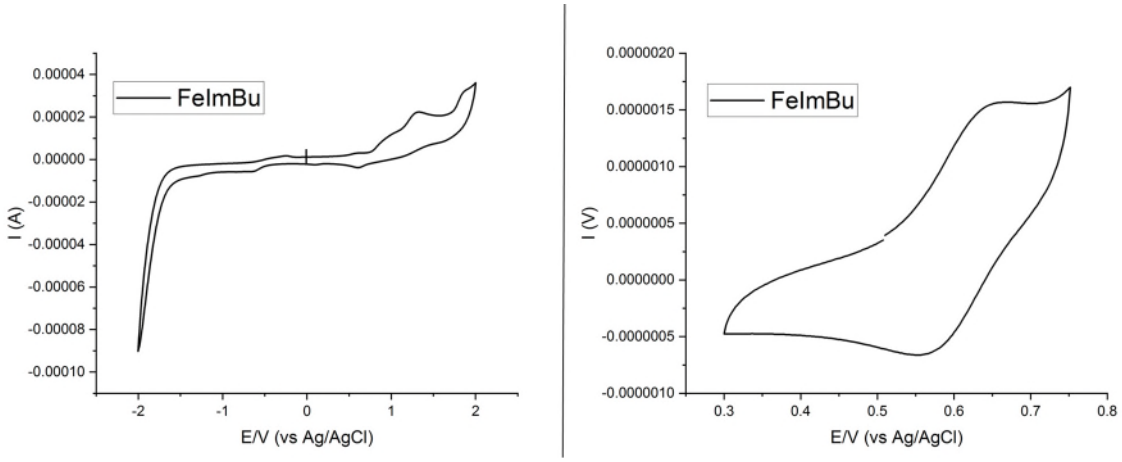
^{1}H NMR spectrum for **FeImBu** ($CDCl_3$, 300 MHz, 298 K).



$^{31}P\{^{1}H\}$NMR spectrum for **FeImBu** ($CDCl_3$, 300 MHz, 298 K).

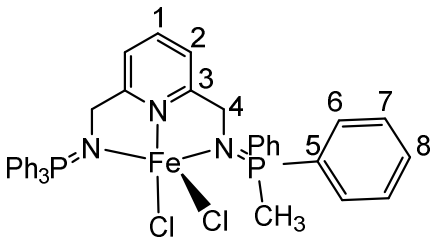


ATR-IR spectrum for **FeImBu**.



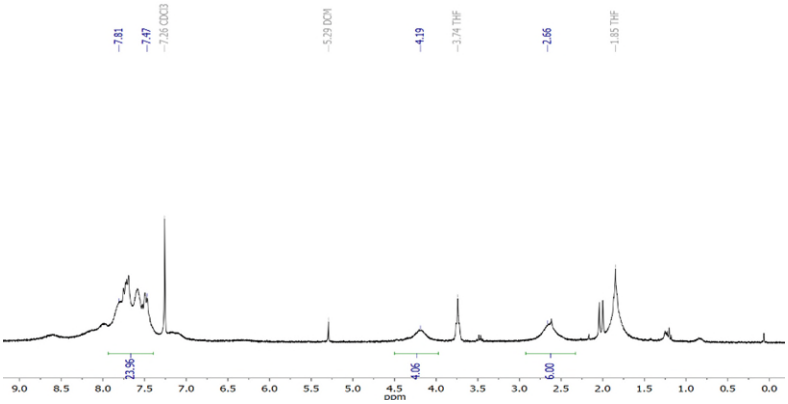
Cyclic voltammetry of complex **FeImBu** (0.1 M nBu$_4$NPF$_6$, 100 mVs^{-1}, glassy carbon, Ag/AgCl, 25 °C, 1×10^{-4} M in CH_2Cl_2).

S8. Characterization of FeImMe

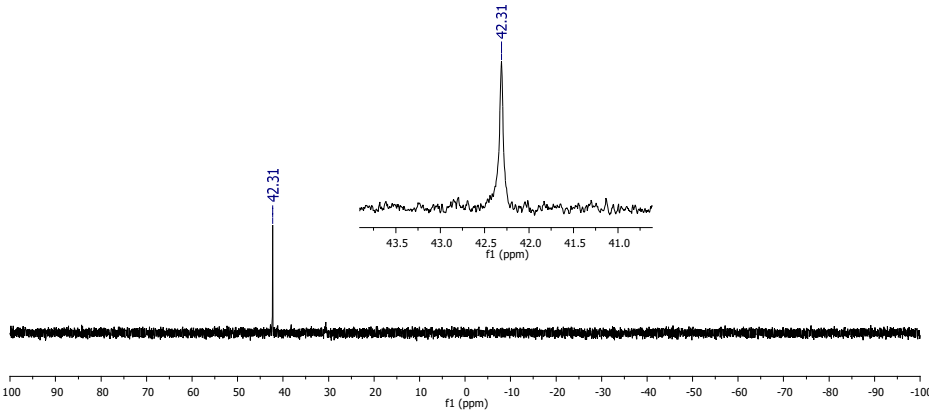


FeImMe

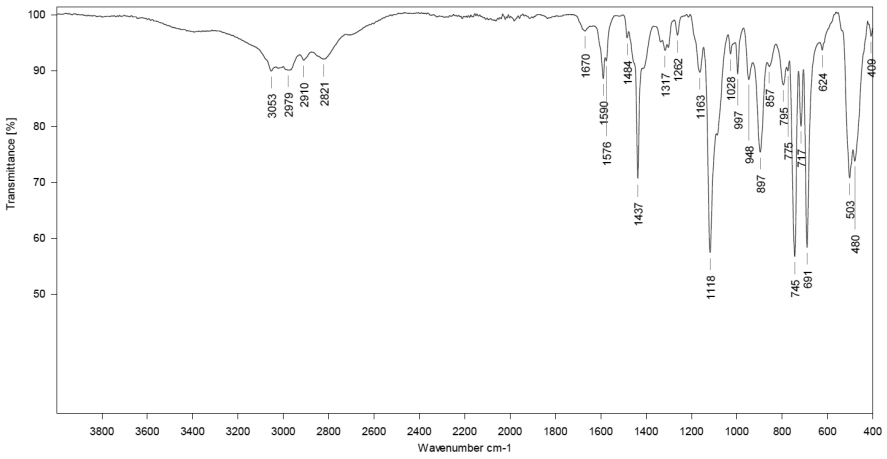
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) 42.31 (s). ^{1}H NMR ($CDCl_3$, 300 MHz) 7.81-7.47 (m, 23H, H1, H2, H3, H6, H7, H8), 4.19 (m, 4H, H4), 2.66 (m, 6H, CH_3). MS (DART): *m/z*, 660. IR (ν cm^{-1}): 1118 ($\nu_{N=P}$).



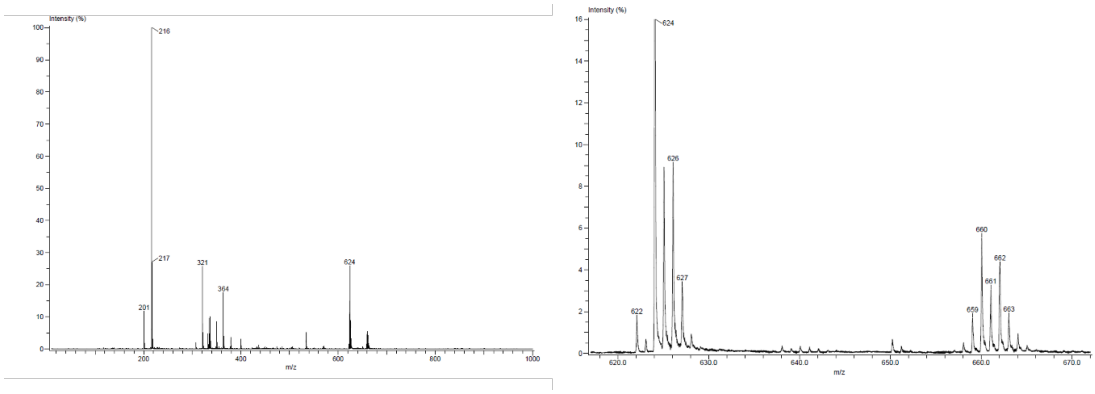
^{1}H NMR spectrum for **FeImMe** ($CDCl_3$, 121 MHz, 298 K).



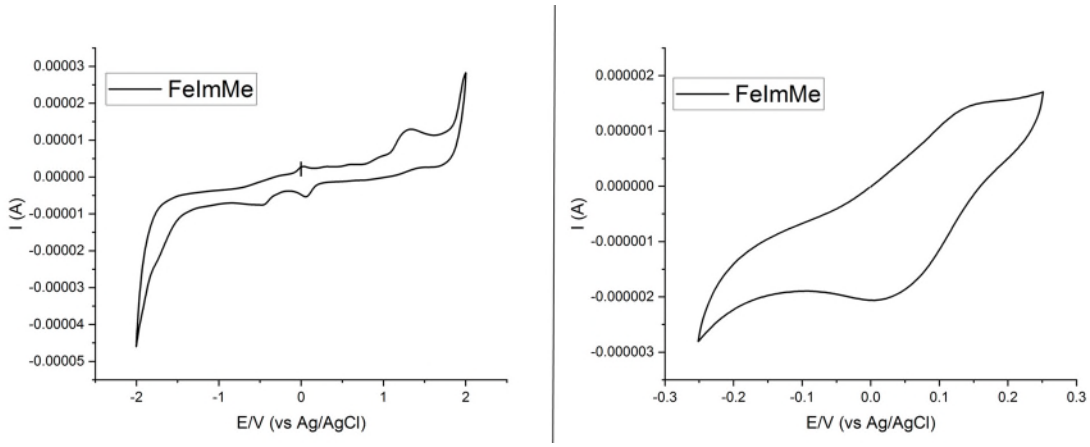
$^{31}P\{H\}$ NMR spectrum for **FeImMe** ($CDCl_3$, 121 MHz, 298 K).



ATR-IR spectrum for **FeImMe**.

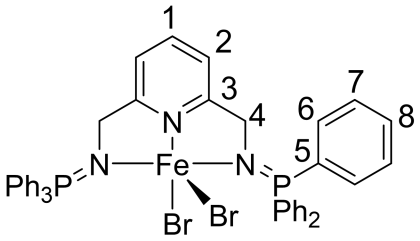


MS(DART) for **FeImMe.**



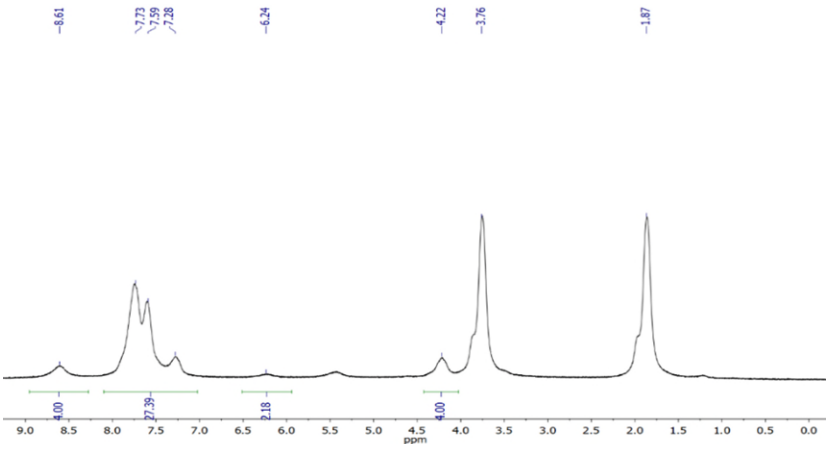
Cyclic voltammetry of complex **FeImMe** (0.1 M nBu$_4$NPF$_6$, 100 mVs^{-1}, glassy carbon, Ag/AgCl, 25 °C, 1×10^{-4} M in CH_2Cl_2).

S9. Characterization of FeImPh(Br)

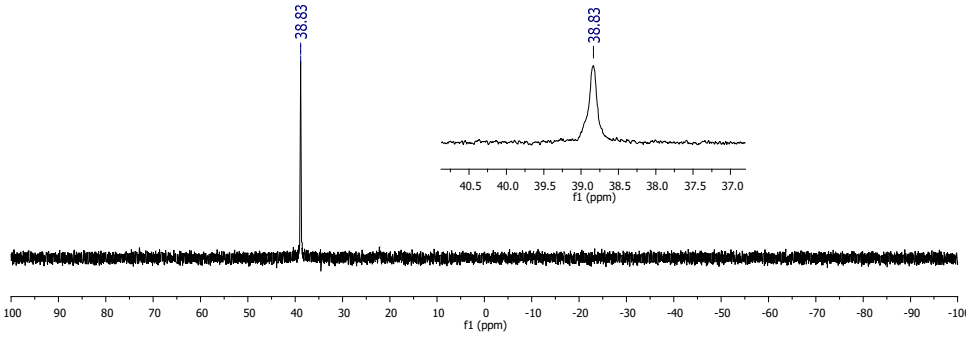


FeImPh(Br)

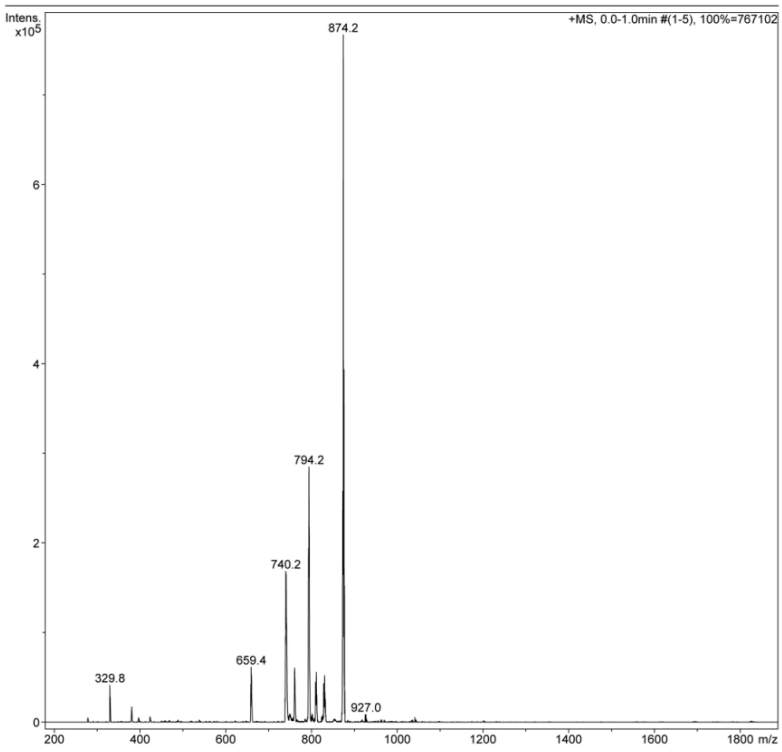
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) 42.31 (s). ^{1}H NMR ($CDCl_3$, 300 MHz) 8.61 (s, 4H) 7.73-7.28 (m, 27H), 6.24 (s, 2H), 4.22 (s, 4H). MS(ESI^+) *m/z* Calcd for $C_{43}H_{37}Br_2FeN_3P_2$ $[M+H]^+$: 874.02; found: 874.2. IR (ν cm^{-1}): 1116 ($\nu_{N=P}$).



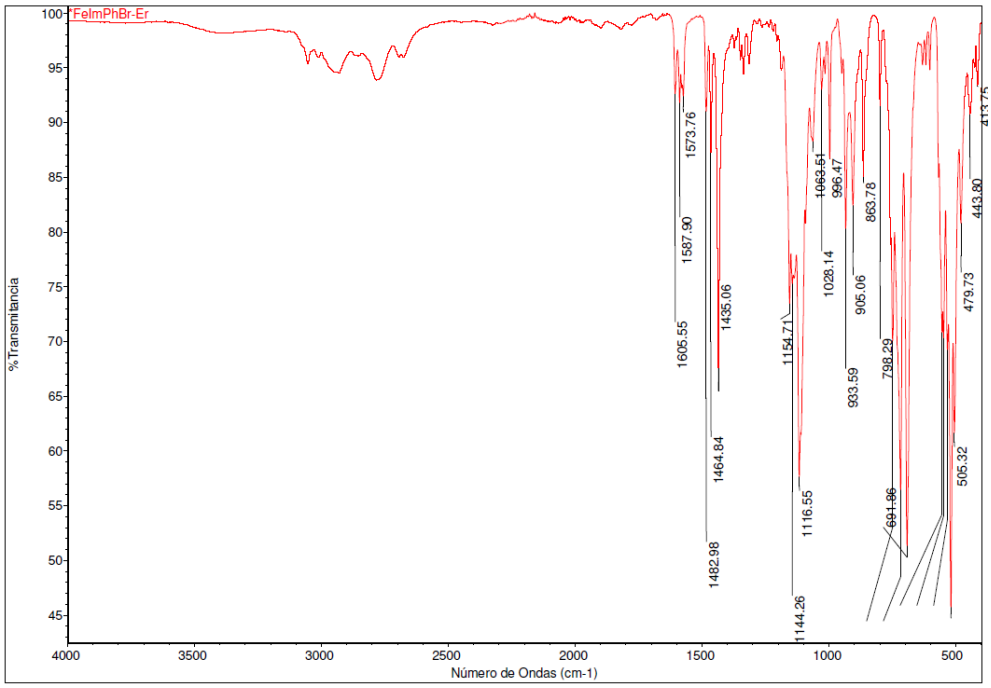
^{1}H NMR spectrum of **FeImPhBr** ($CDCl_3$, 300 MHz, 298 K).



$^{31}P\{^{1}H\}$ NMR spectrum of **FeImPhBr** ($CDCl_3$, 121 MHz, 298 K).



MS(ESI) of **FeImPhBr**

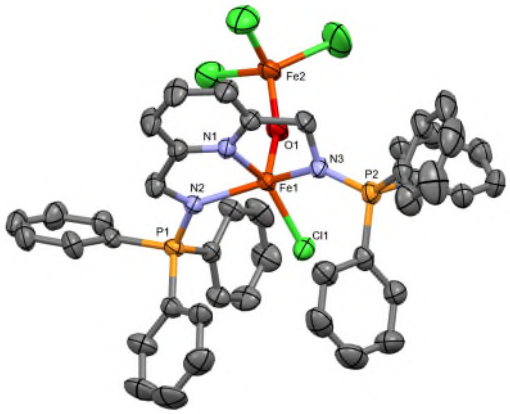


ATR-IR spectrum of **FeImPhBr**

S10. Crystallographic Details

Crystallographic Data for **Fe2ImPh.**

Empirical formula	$C_{43}H_{37}Cl_4Fe_2N_3OP_2$
Formula weight	927.19
Temperature (k)	298
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions (in å and °)	a =13.361(6) α = 105.615(14) b =14.758(7) β = 96.300(14) c = 16.070(8) γ = 111.913(13)
Volume ($Å^3$)	2752(2)
Z	2
Density (g/cm^3, calculated)	1.119
Absorption coeff. (mm^{-1})	0.808
F(000)	948.0
Crystal size (mm)	0.411 × 0.273 × 0.252
Θ range for data collection (°)	2.30 to 28.39
Index ranges	*–17 ≤ h ≤ 17* *–19 ≤ k ≤ 19* *–21 ≤ l ≤ 21*
Reflections collected	13654
Independent reflections	9594
Absorption correction	None
Refinement method	Full-matrix least-squares on f^2
Data/restrains/parameters	13654/0/496
Goodness of fit on f^2	0.960
Final r indices [i > 2σ(i)]	R1 = 0.0739, wr2 = 0.1972
R indices (all data)	R1 = 0.1541 , wr2 = 0.1927
Largest diff. Peak and hole ($e \cdot Å^{-3}$)	0.651 to -0.476



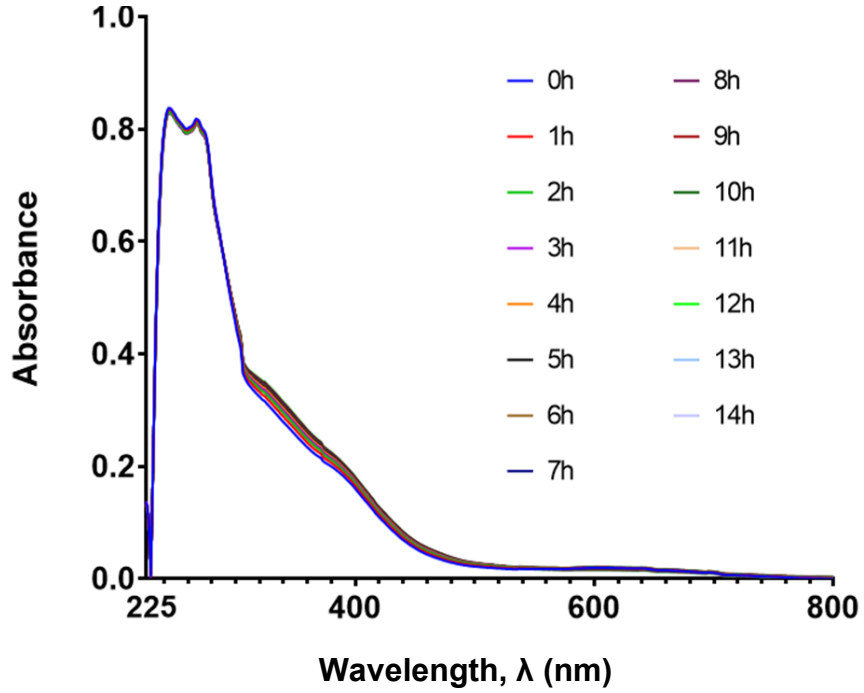
Bond lengths	(Å)
Fe1-O1	1.776(3)
Fe1-N1	2.096(4)
Fe1-N3	2.132(4)
Fe1-N2	2.136(3)
Fe1-Cl1	2.2421(16)
Fe2-O1	1.764(3)
P1-N2	1.612(3)
P2-N3	1.594(4)

Table S1. Select bond lengths (Å) of complex **Fe2ImPh**.

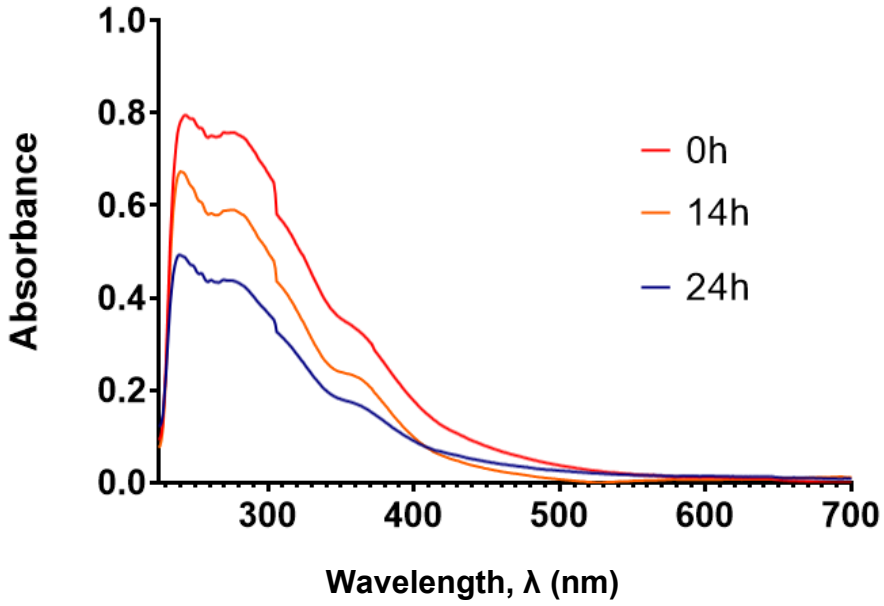
Bond angles	(°)
O1-Fe1-N1	100.28(14)
O1-Fe1-N3	100.34(14)
O1-Fe1-N2	106.73(13)
N1-Fe1-N3	75.06(14)
N1-Fe1-N2	76.11(14)
N3-Fe1-N2	143.32(14)
Fe2-O1-Fe1	158.3(2)
P1-N2-Fe1	128.6(2)
P2-N3-Fe1	127.5(2)
N1-Fe1-Cl1	147.91(11)
N3-Fe1-Cl1	95.39(11)
N2-Fe1-Cl1	97.10(10)
O1-Fe1-Cl1	111.63(12)

Table S2. Select bond angles (°) of complex **Fe2ImPh**.

S11. Stability studies



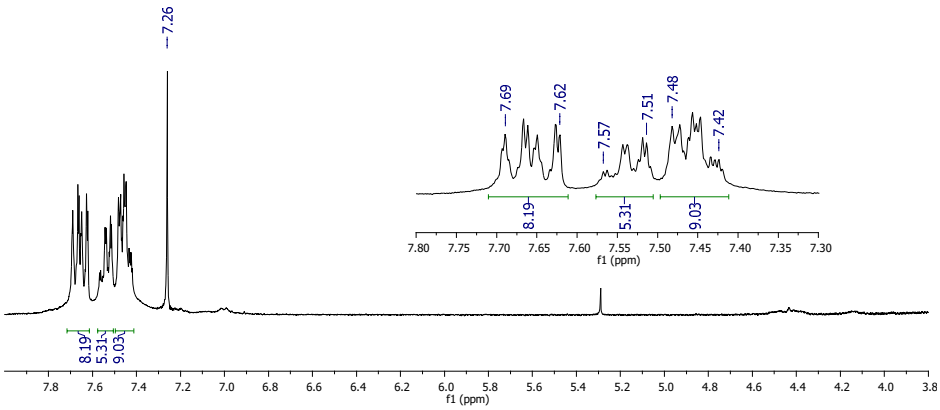
Electronic absorption spectra of **FeImPh** in CH_2Cl_2 solution, 9.63×10^{-5} M at 25 °C.



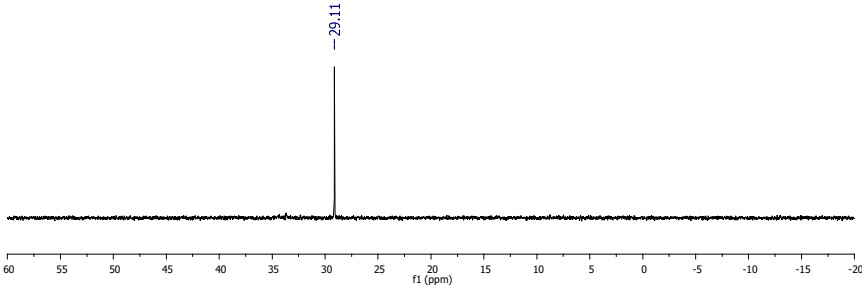
Electronic absorption spectra of **FeImBu** in CH_2Cl_2 solution, 9.63×10^{-5} M at 25 °C.

FeImBu in $CDCl_3$ solution upon contact with atmospheric conditions, 30 minutes (left) and 4 hours (right)

S12. Characterization of $[Fe(tpy)_2]Cl_2$ and triphenylphosphine oxide from the reaction between FeImPh and terpyridine

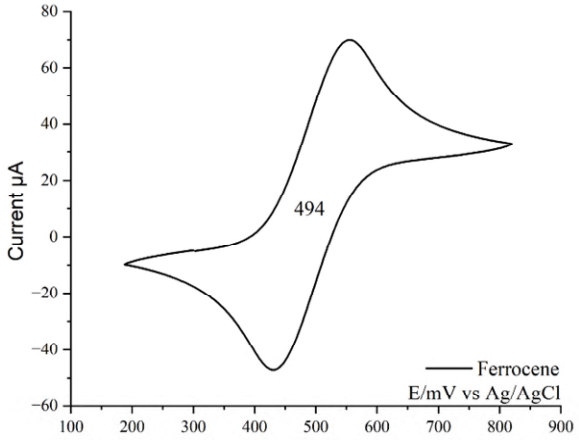


^{1}H NMR spectrum of **$[Fe(tpy)_2]Cl_2$** ($CDCl_3$, 300 MHz, 298 K).



^{31}P $\{^{1}H\}$ NMR spectrum for **$OPPh_3$** ($CDCl_3$, 121 MHz, 298 K).

S13. Cyclic voltammogram of ferrocene



Cyclic voltammetry of ferrocene (0.1 M *n*Bu_4NPF_6, 100 mVs^{-1}, glassy carbon, Ag/AgCl, 25 °C, 1×10^{-3} M in CH_2Cl_2).

References

1. Wu, J.Y.; Stanzl, B.N.; Ritter, T. A strategy for the synthesis of well-defined iron catalysts and application to regioselective diene hydrosilylation. *J Am Chem Soc* **2010**, *132*, 13214-13216, doi:10.1021/ja106853y.
2. Cheisson, T.; Auffrant, A. Versatile coordination chemistry of a bis(methyliminophosphoranyl)pyridine ligand on copper centres. *Dalton Trans* **2014**, *43*, 13399-13409, doi:10.1039/c4dt01794c.