Three Bonding Modes of Bis(2-picolyl)phenylphosphine at Iron: Isolation of a Dinuclear Iron Complex Featuring Dearomatized Pyridine Moieties.

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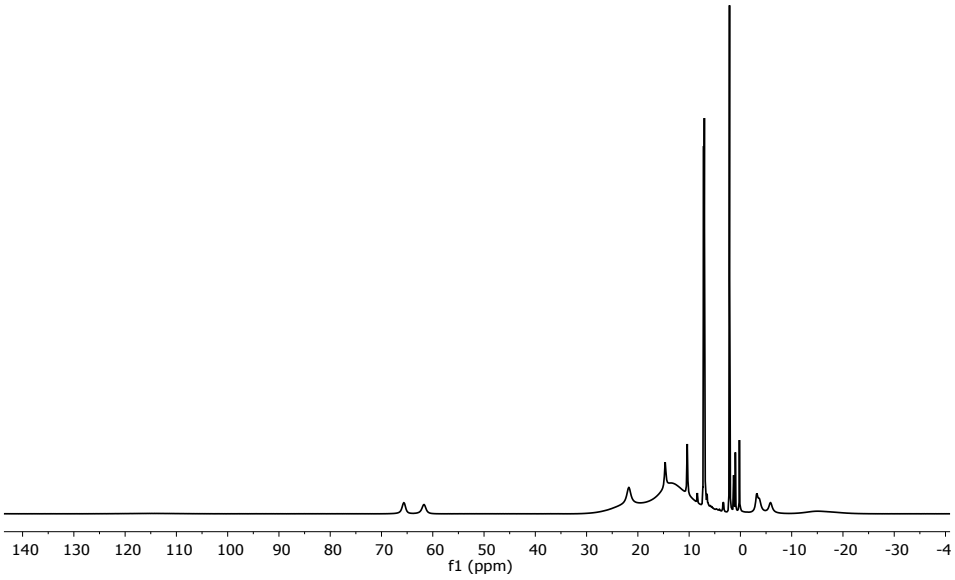

Figure S1.[1]H NMR spectrum (500.4 MHz, 230 K, Tol-D_8) of complex **1**

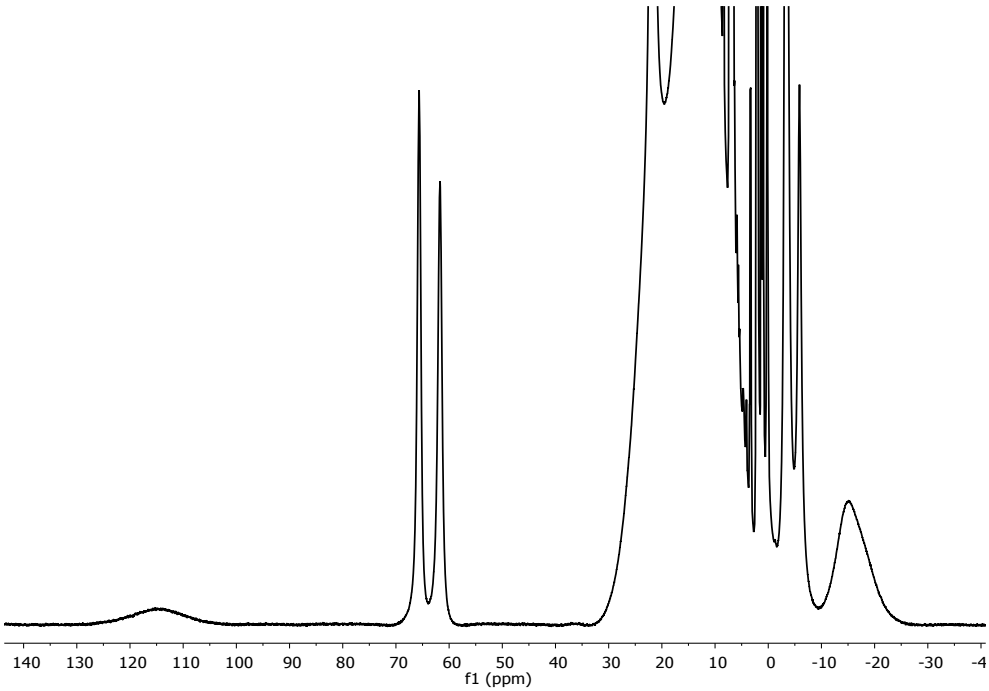

Figure S2. [1]H NMR spectrum (500.4 MHz, 230 K, Tol-D_8) of complex **1** (increased intensity)

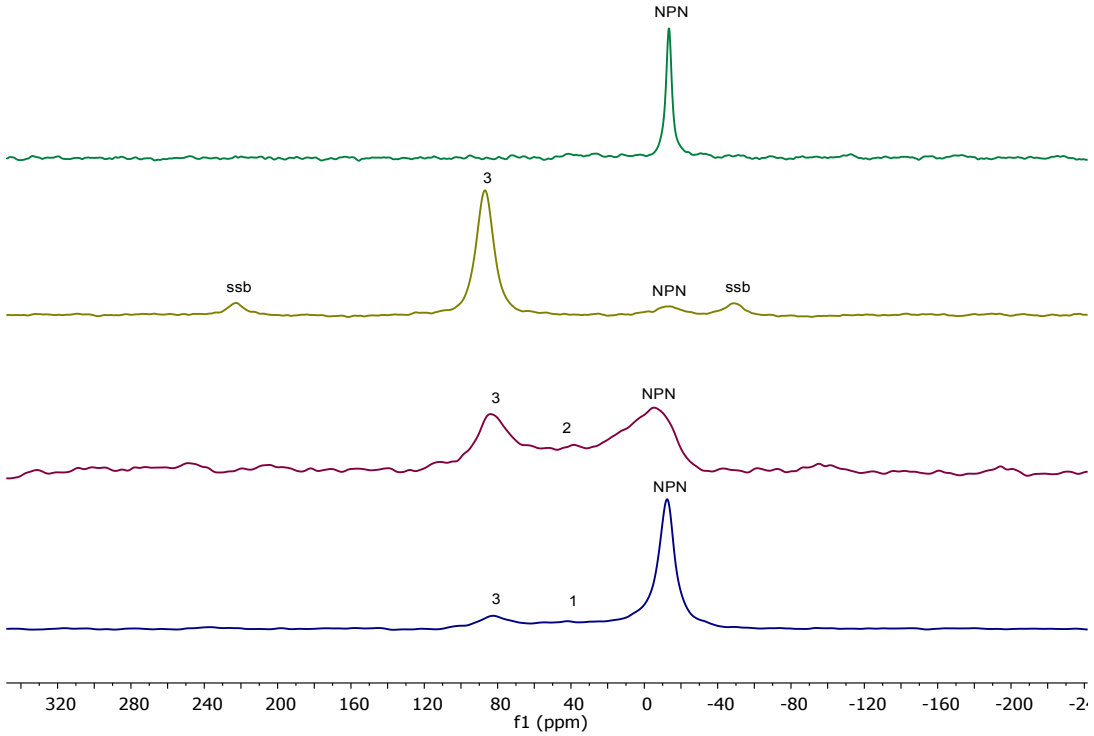

Figure S3. MAS ^{31}P NMR spectra (161.8 MHz) of NPN (280 K), compounds **3** (280 K), **2** (289 K), and **1** (289 K) (from top to bottom) in the solid state

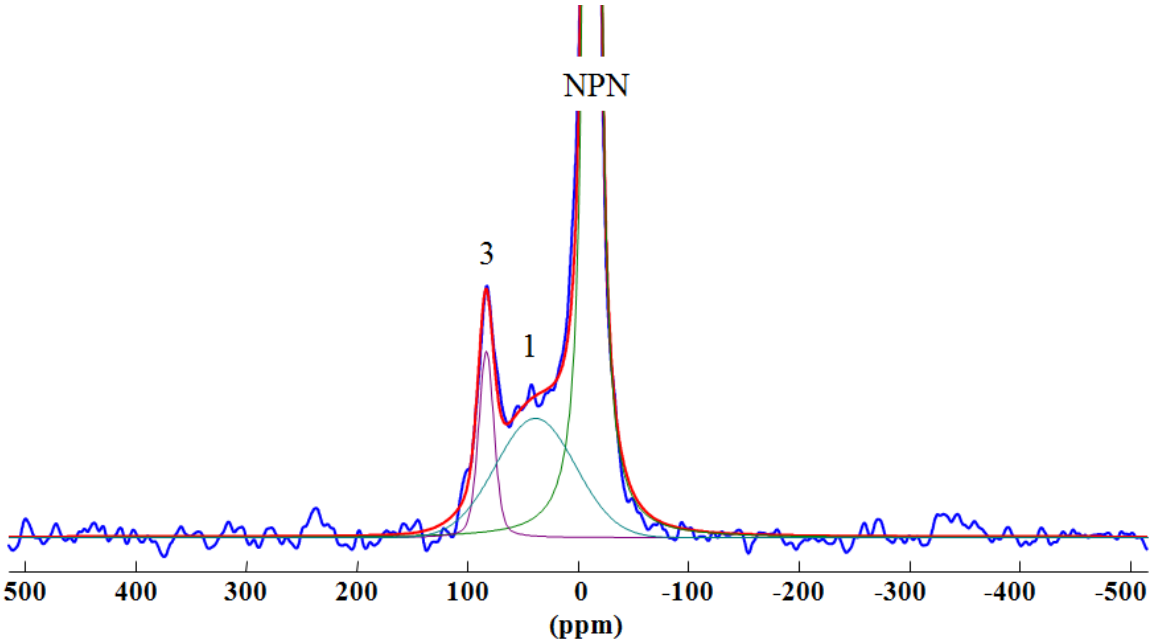

Figure S4. MAS ^{31}P NMR spectrum (161.8 MHz, 289 K) of **1** in the solid state, the peak for **1** is at 39 ppm, linewidth is 13.7 KHz

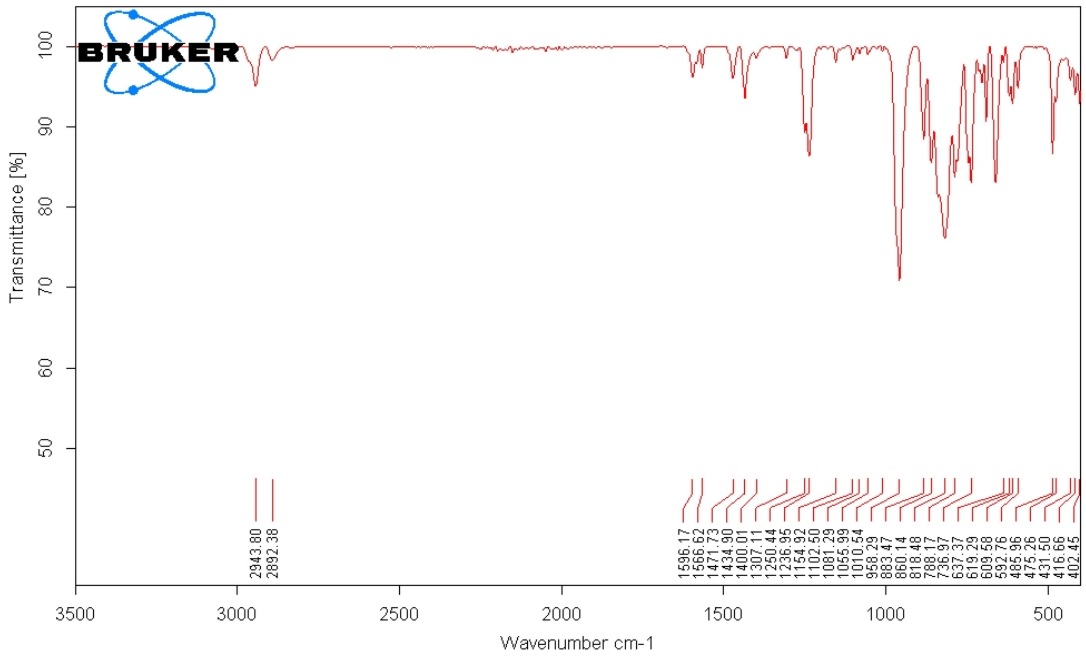

Figure S5. ATR IR spectrum of **1**

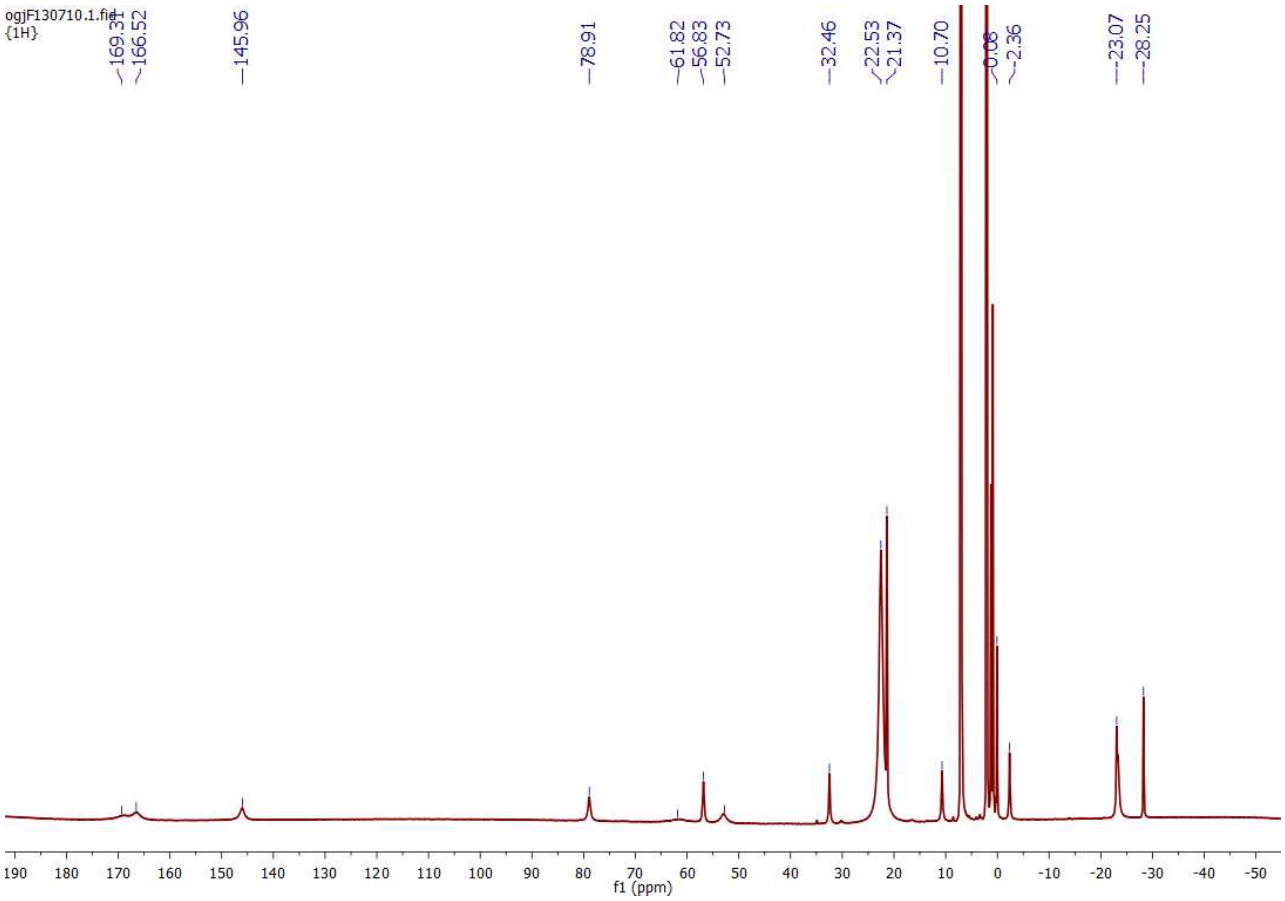

Figure S6. ^{1}H NMR spectrum (500.4 MHz, Tol-D_8, 301 K) of complex **2**

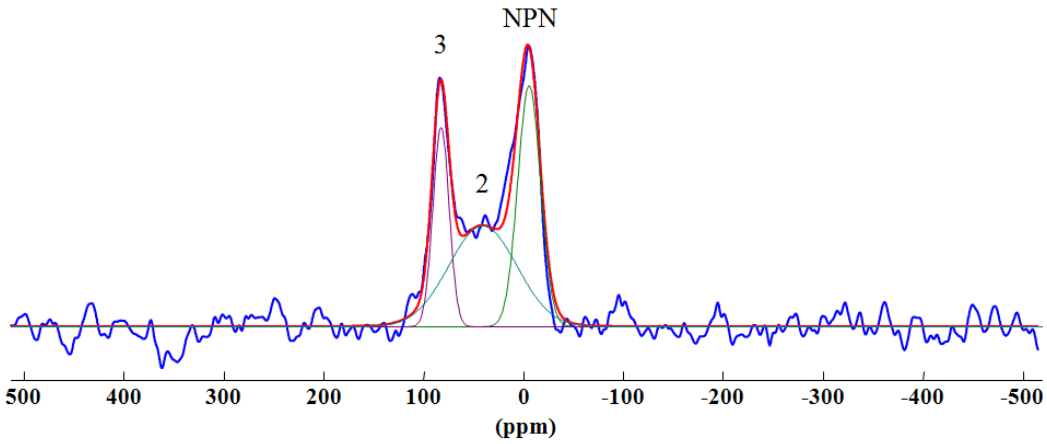

Figure S7. MAS ^{31}P NMR spectrum (161.8 MHz, 289 K) of **2** in the solid state, the peak for **2** is at 41.4 ppm, linewidth is 13.0 KHz

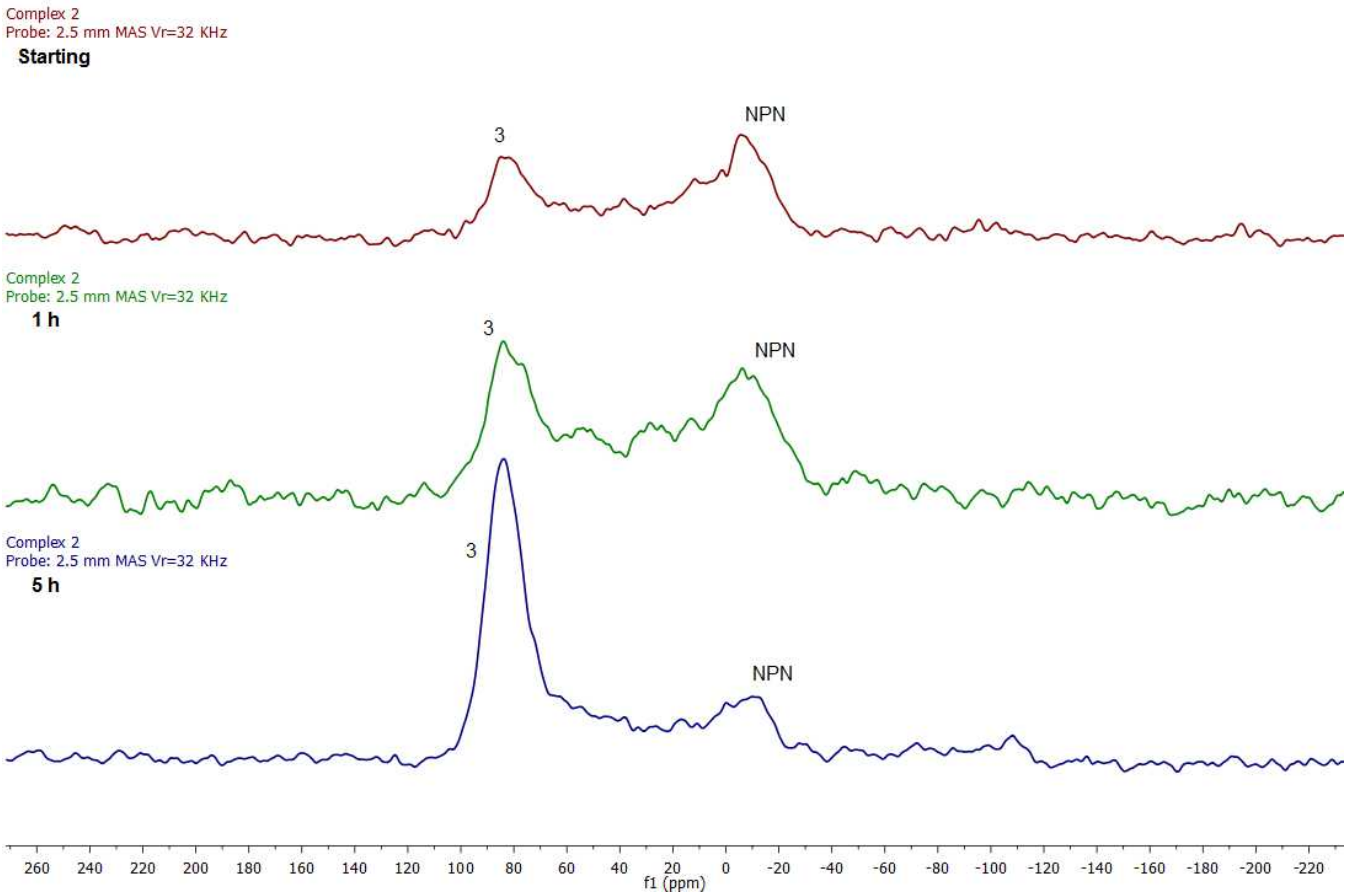

Figure S8. Time dependence of MAS ^{31}P NMR spectra (161.8 MHz, 289 K) of **2** in the solid state. Within 5 hours, the signal for free NPN decreased while the signal for compound **3** increased

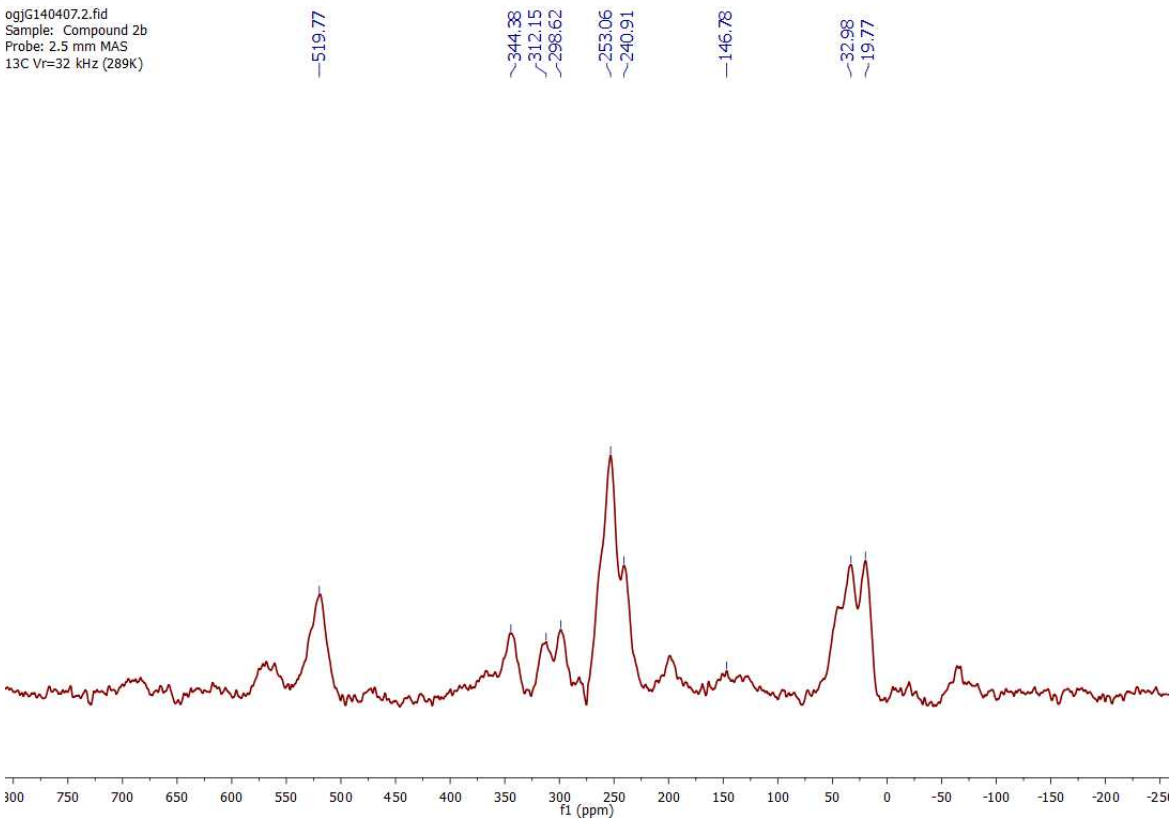

Figure S9. MAS ^{13}C NMR spectrum (100.5 MHz, 289 K) for **2** in the solid state

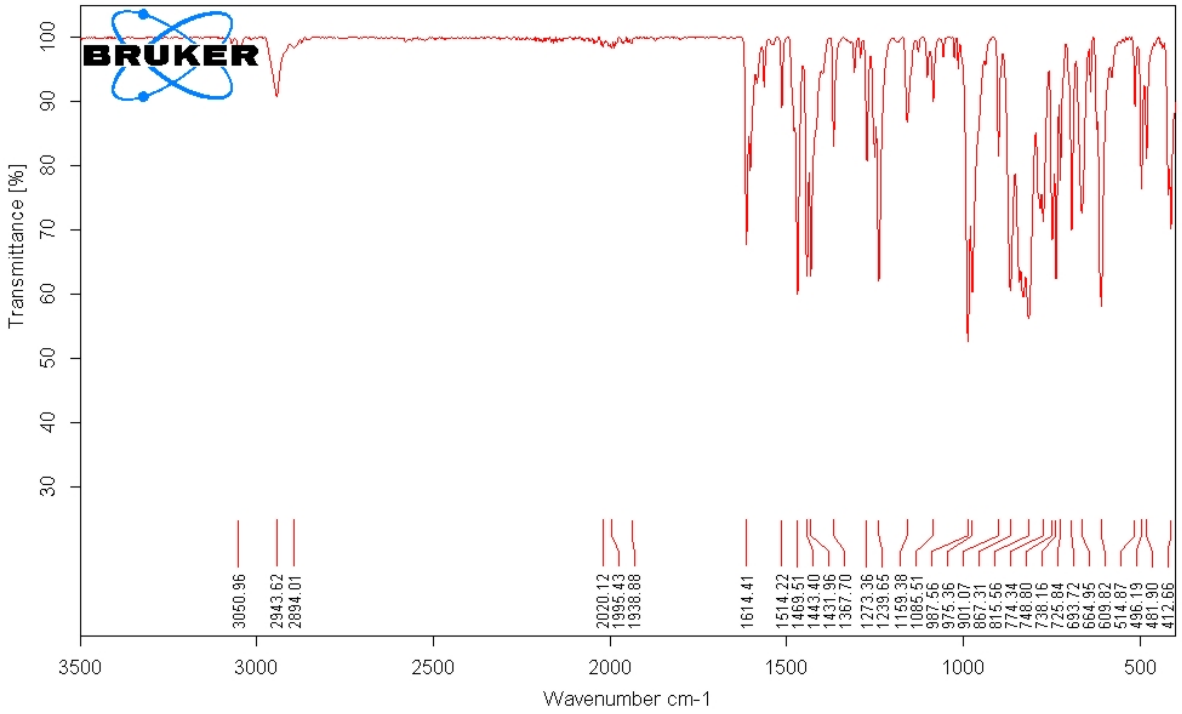

Figure S10. ATR IR spectrum of **2**

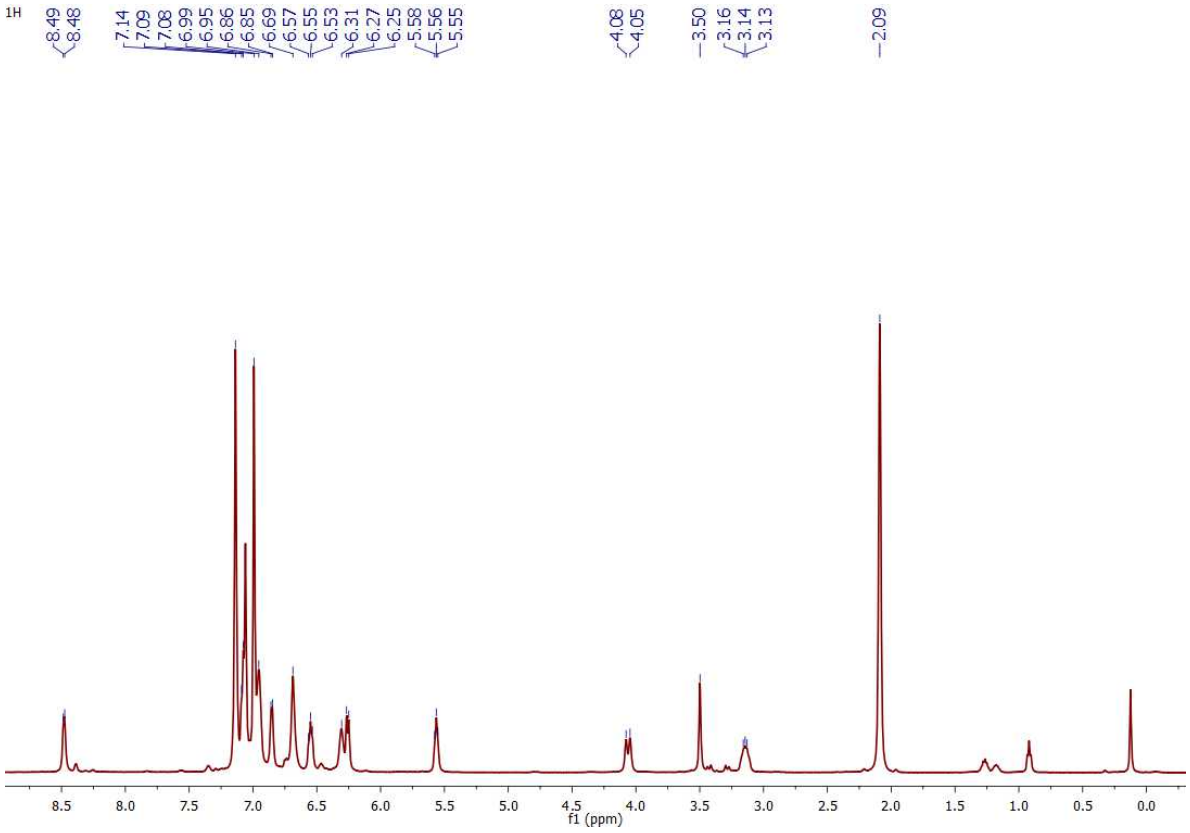

Figure S11. ^{1}H NMR spectrum (500.3 MHz, Tol-D_8, 240K) of complex **3**

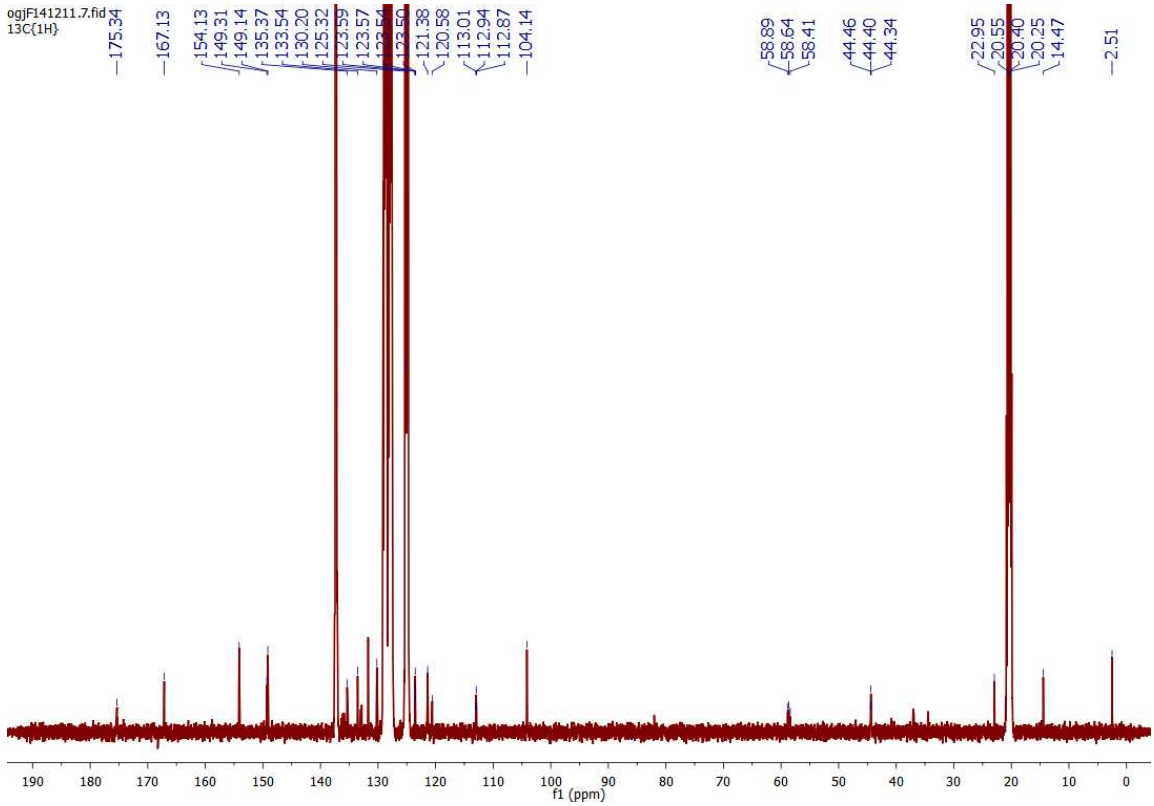

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz) of complex **3**, in Tol-D_8, at 240 K

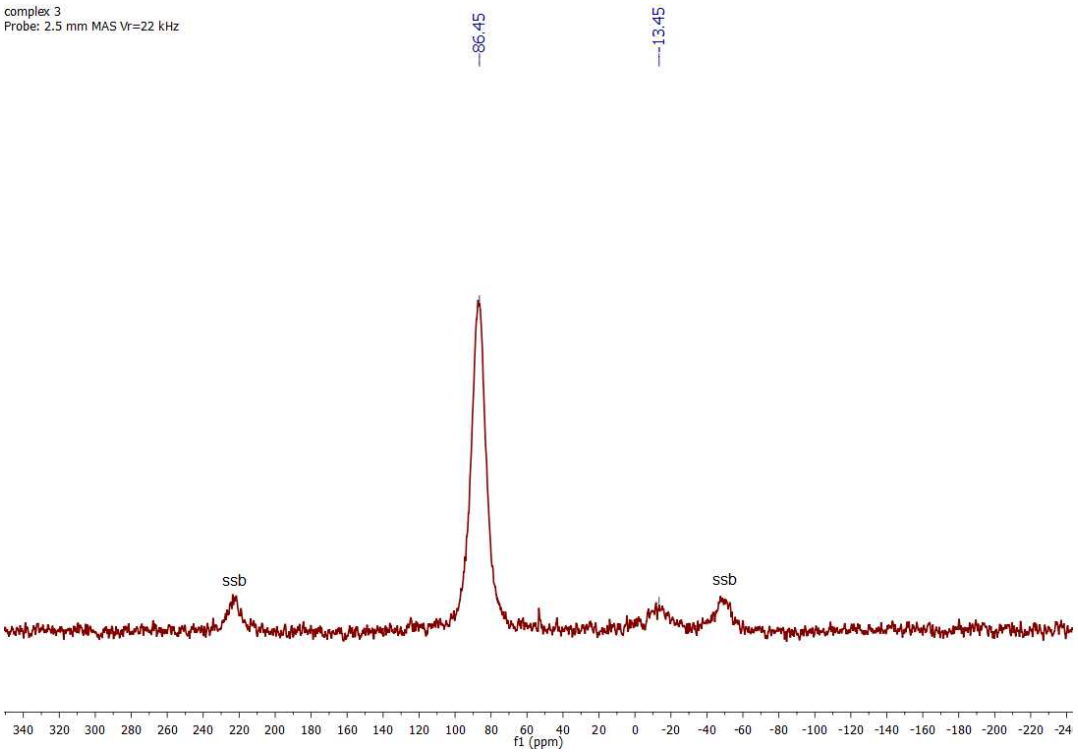

Figure S13. MAS $^{31}P\{^{1}H\}$ NMR spectrum (161.8 MHz, 280K) of **3** in the solid state

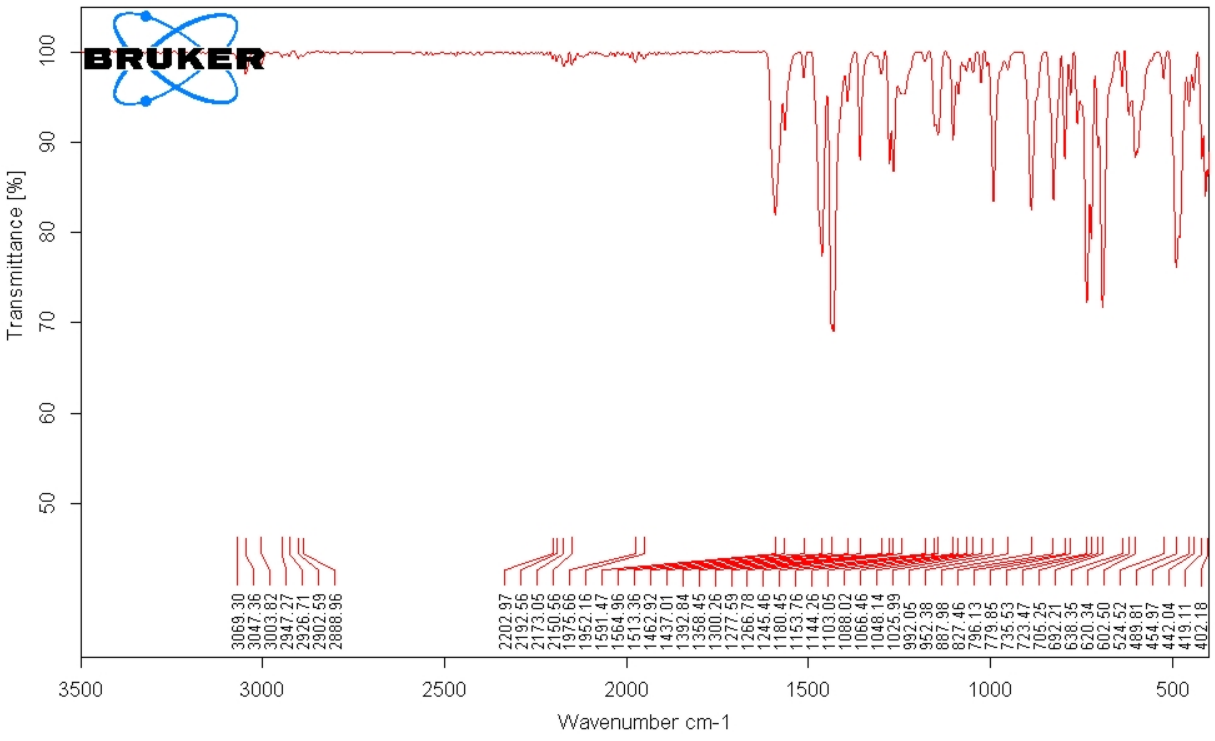

Figure S14. ATR IR spectrum of **3**

X-Ray Data

Table 1. Selected bond lengths (Å) and angles (deg) for complexes **1**, **2**[a], and **3**.

Complex**1**			
Fe(1)-N(1)	2.2236(12)	Fe(1)-N(2)	1.9663(11)
Fe(1)-N(3)	1.9799(11)	Fe(1)-P(1)	2.5579(4)
C(1)-C(2)	1.500(2)	C(7-C(8)	1.498(2)
N(1)-Fe(1)-N(2)	122.52(5)	N(1)-Fe(1)-N(3)	99.66(5)
N(1)-Fe(1)-P(1)	75.03(3)	N(2)-Fe(1)-N(3)	124.28(5)
N(2)-Fe(1)-P(1)	100.73(3)	N(3)-Fe(1)-P(1)	125.98(4)
C(2)-C(1)-P(1)	109.04(10)	C(8)-C(7)-P(1)	116.36(10)
Complex **2**			
Fe(1)-N(1)	2.0654(15)	Fe(1)-N(2)	2.1548(15)
Fe(1)-N(3)	1.9499(15)	Fe(1)-P(1)	2.4387(5)
C(5)-C(6)	1.389(3)	C(6)-P(1)	1.7524(19)
C(17)-C(18)	1.502(2)	C(18)-P(1)$^{\#1}$	1.8530(18)
N(1)-Fe(1)-N(2)	101.50(6)	N(1)-Fe(1)-N(3)	132.71(6)
N(1)-Fe(1)-P(1)	82.49(4)	N(2)-Fe(1)-N(3)	105.72(6)
N(2)-Fe(1)-P(1)	121.53(4)	N(3)-Fe(1)-P(1)	113.30(5)
C(5)-C(6)-P(1)	119.47(14)	C(17)-C(18)-P(1)$^{\#1}$	113.51(12)
Complex **3**			
Fe(1)-P(1)	2.1564(9)	P(2)-Fe(1)	2.1547(9)
N(1)-Fe(1)	2.046(2)	N(2)-Fe(1)	2.011(2)
N(3)-Fe(1)	2.013(2)	N(4)-Fe(1)	2.058(2)
C(1)-C(2)	1.499(4)	C(7)-C(8)	1.396(4)
C(19)-C(20)	1.399(4)	C(25)-C(26)	1.491(4)
P(2)-Fe(1)-P(1)	96.80(3)	N(1)-Fe(1)-P(1)	82.28(7)
N(2)-Fe(1)-P(1)	84.75(7)	N(3)-Fe(1)-P(1)	93.34(8)
N(4)-Fe(1)-P(1)	177.73(8)	N(1)-Fe(1)-P(2)	179.07(8)
N(2)-Fe(1)-P(2)	93.50(7)	N(3)-Fe(1)-P(2)	85.12(8)

N(4)-Fe(1)-P(2)	81.13(7)	N(2)-Fe(1)-N(1)	86.27(10)
N(3)-Fe(1)-N(1)	95.07(10)	N(1)-Fe(1)-N(4)	99.79(10)
N(2)-Fe(1)-N(3)	177.51(10)	N(2)-Fe(1)-N(4)	96.30(10)
N(3)-Fe(1)-N(4)	85.56(10)		

[a]Symmetry codes: #1 –x+1, -y, -z