Supporting Information

Dithiolato- and halogenido-bridged nickel-iron complexes related to the active site of [NiFe]-H_2ases: preparation, structures, and electrocatalytic H_2 production

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1. IR and ^{1}H (^{31}P) NMR spectra of 3a

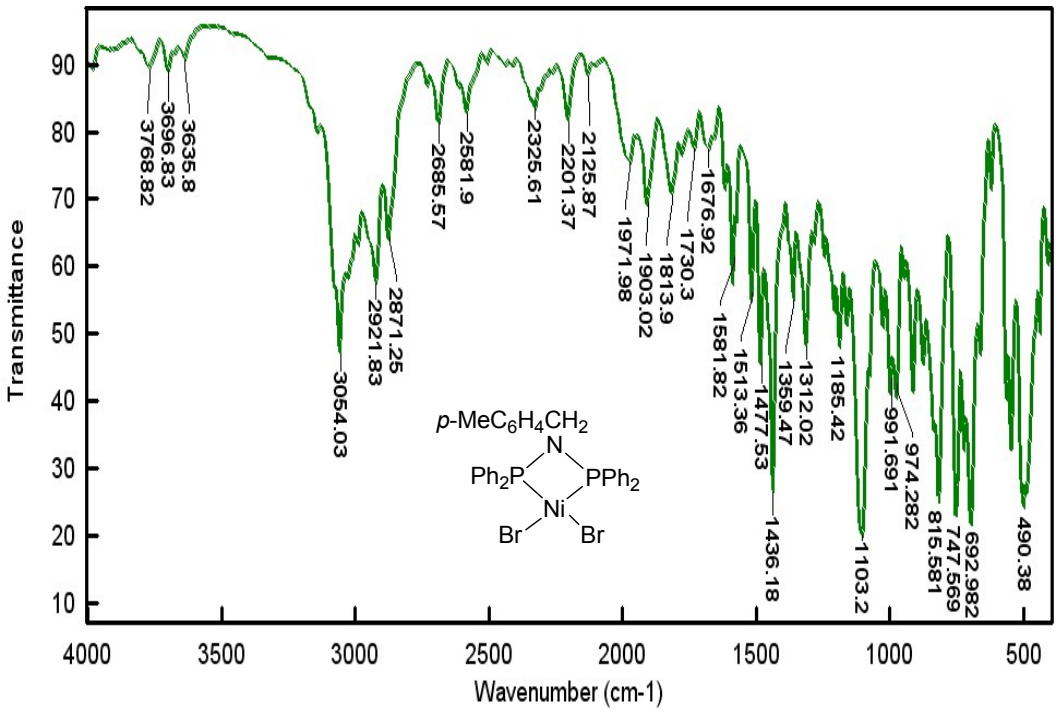

Fig. S1 IR spectrum of **3a**.

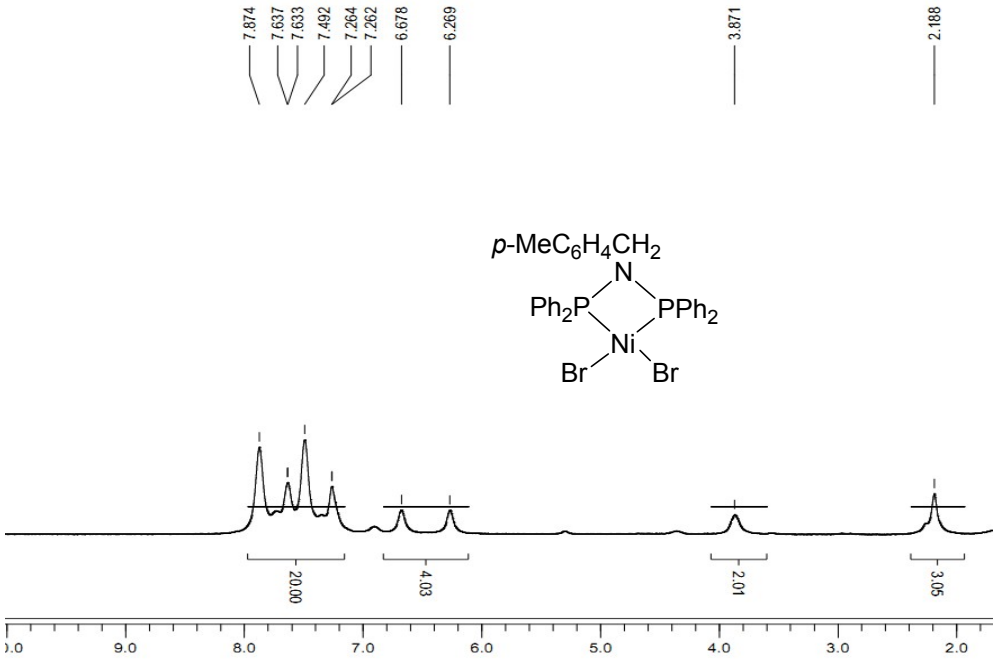

Fig. S2 ^{1}H NMR spectrum of **3a**.

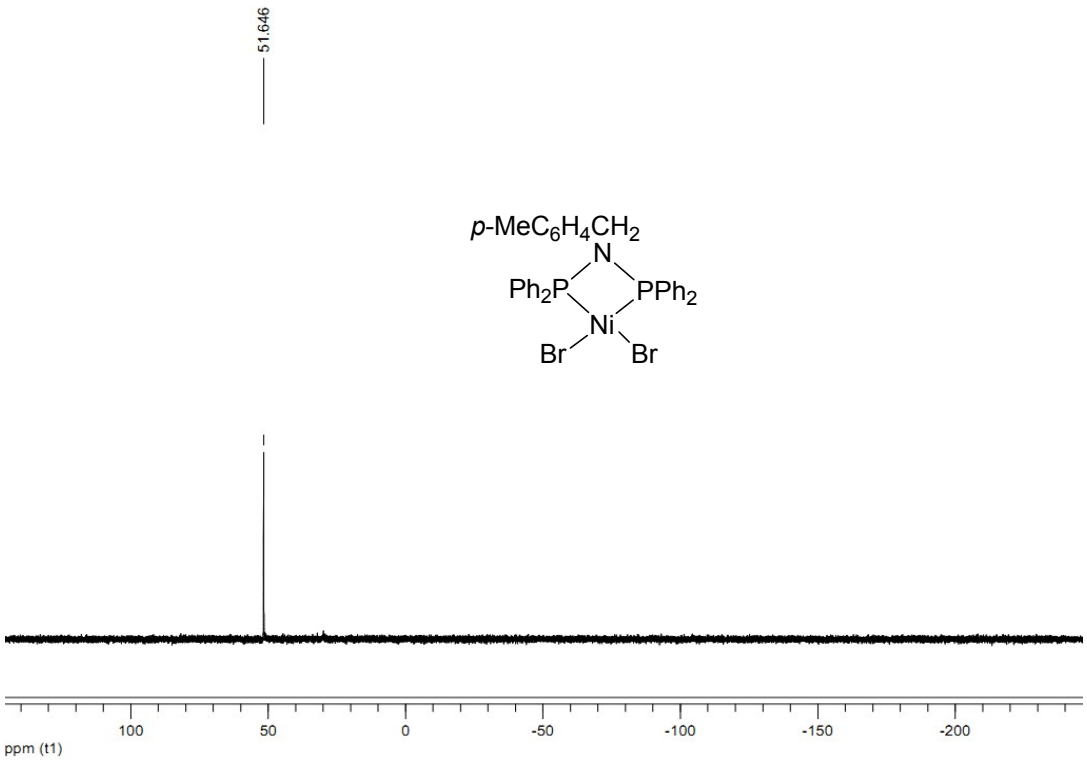

Fig. S3 ^{31}P NMR spectrum of **3a**.

2. IR and ^{1}H (^{31}P) NMR spectra of 4b

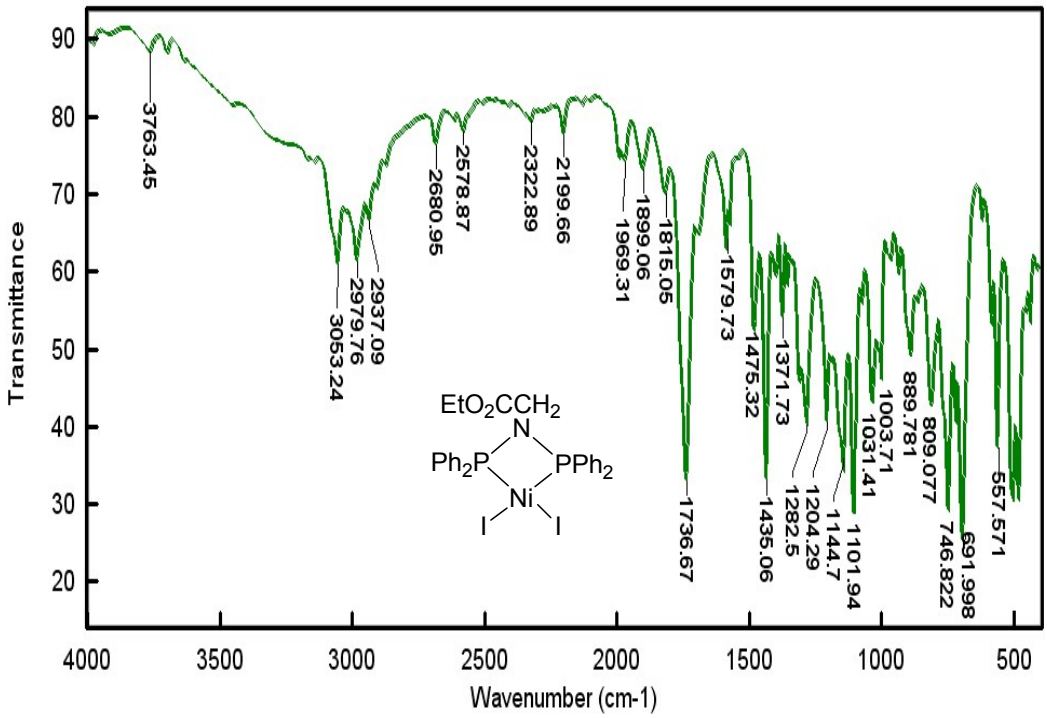

Fig. S4 IR spectrum of **4b**.

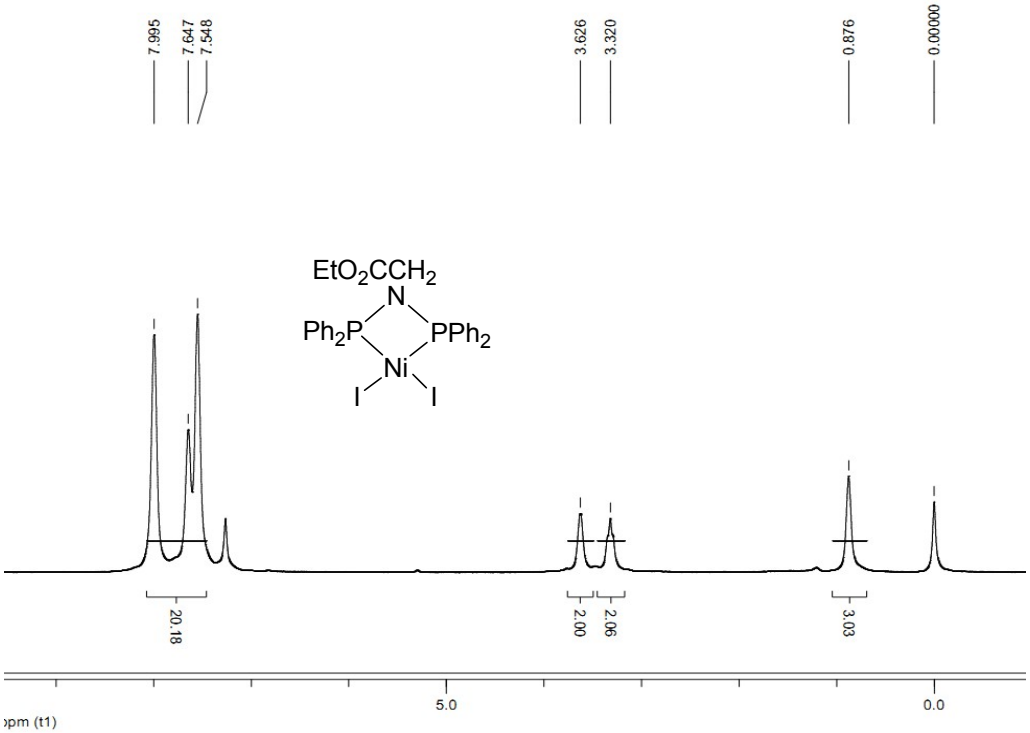

Fig. S5 ^{1}H NMR spectrum of **4b**.

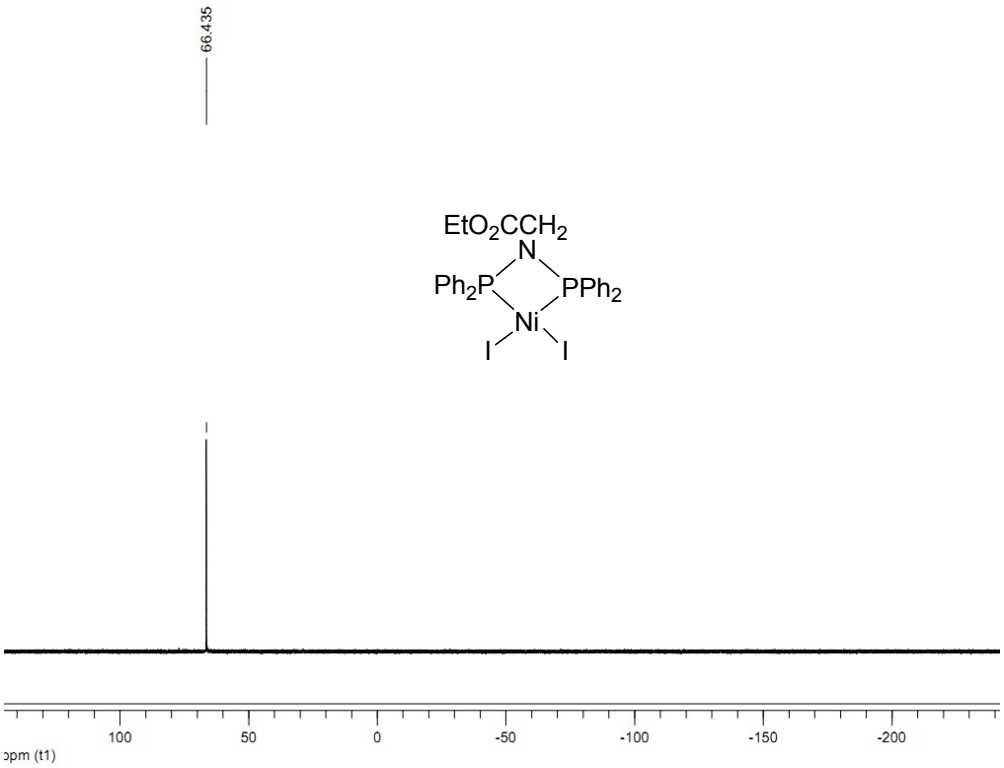

Fig. S6 ^{31}P NMR spectrum of **4b**.

3. Molecular structure of 3b and 4b.

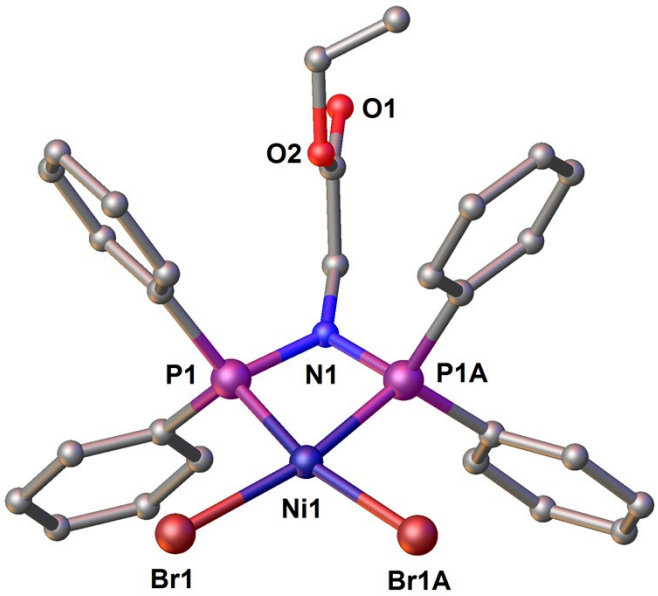

Fig. S7 Molecular structure of **3b**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°) : Ni1–P1 2.1257 (8), Ni1–Br1 2.3393(5), P1–N1 1.698(2); P1–Ni1–P1A 73.75(4), P1–Ni1–Br1 93.23(2), Br1–Ni1–Br1A 99.80(3), P1–N1–P1A 97.36(17).

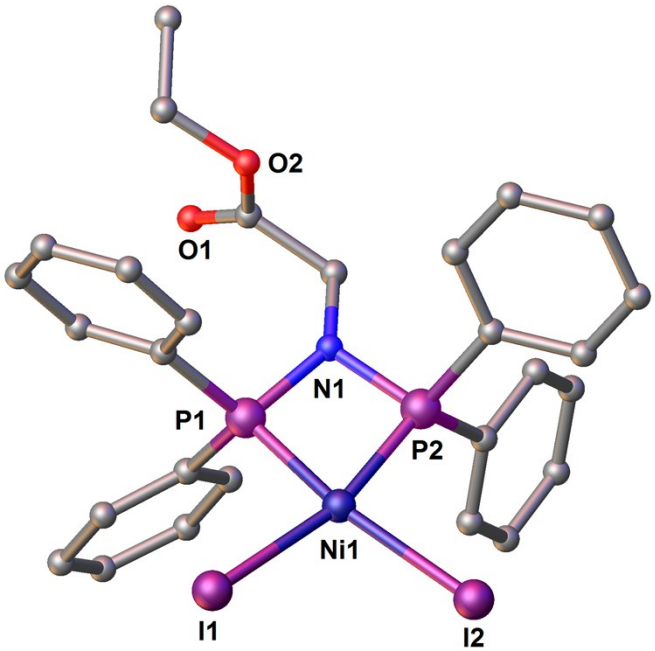

Fig. S8 Molecular structure of **4b**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°) : Ni1–P1 2.1366(8), Ni1–P2 2.1285(8), Ni1–I1 2.5150(5), Ni1–I2 2.5094(5), P1–N1 1.699(2), P2–N1 1.699(2); P1–Ni1–P2 74.00(3), P1–Ni1–I1 92.66(3), I1–Ni1–I2 100.178(18), P1–N1–P2 98.12(10).

4. IR and ^{1}H (^{31}P, ^{11}B, ^{19}F) NMR spectra of **5b**.

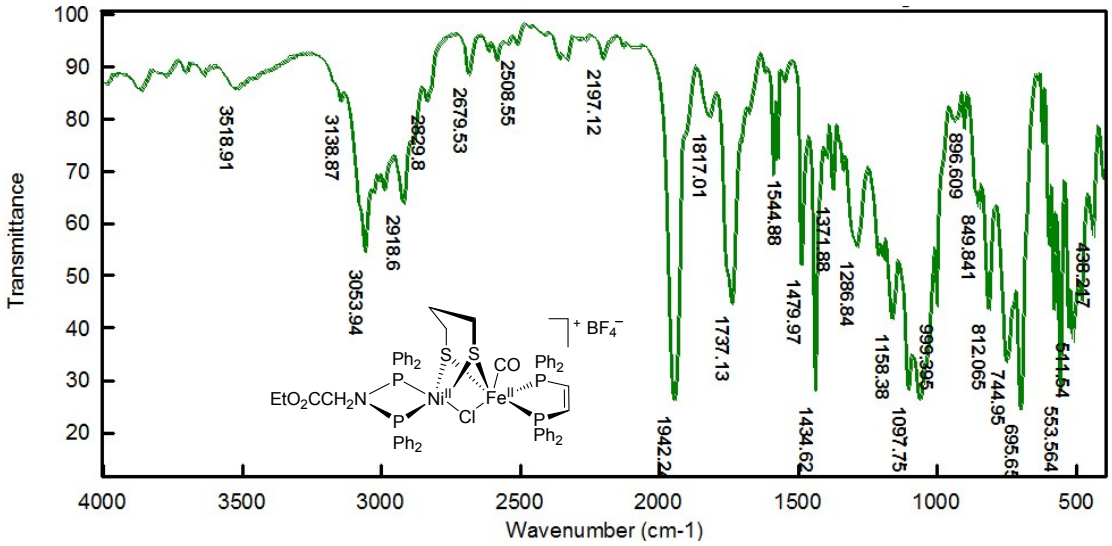

Fig. S9 IR spectrum of **5b**

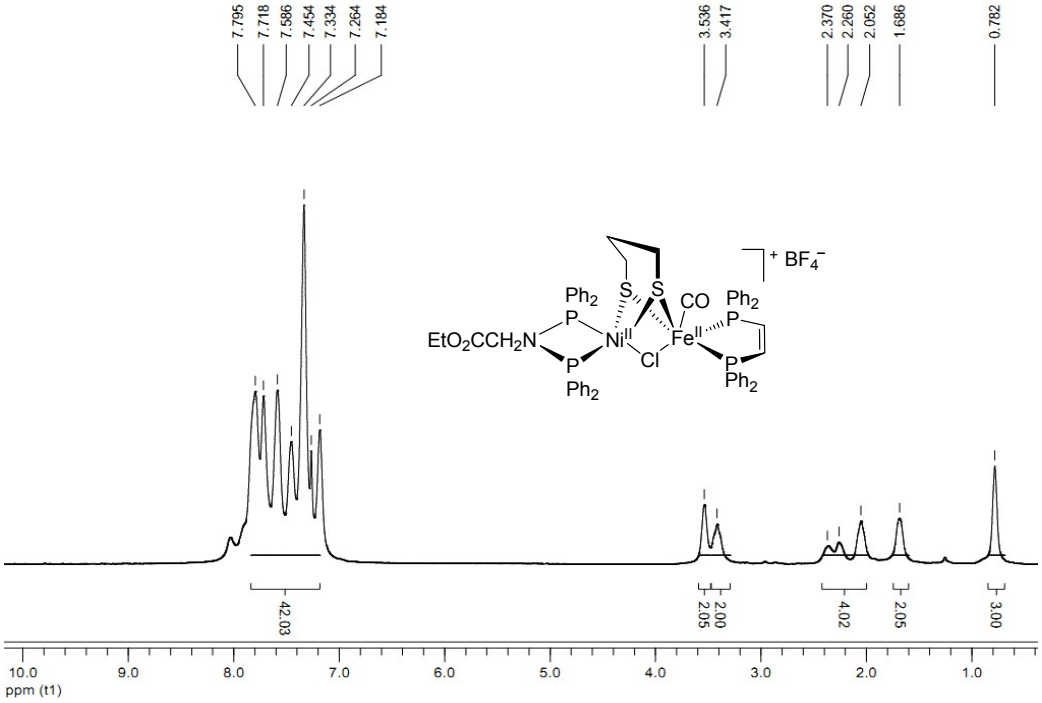

Fig. S10 ^{1}H NMR spectrum of **5b**.

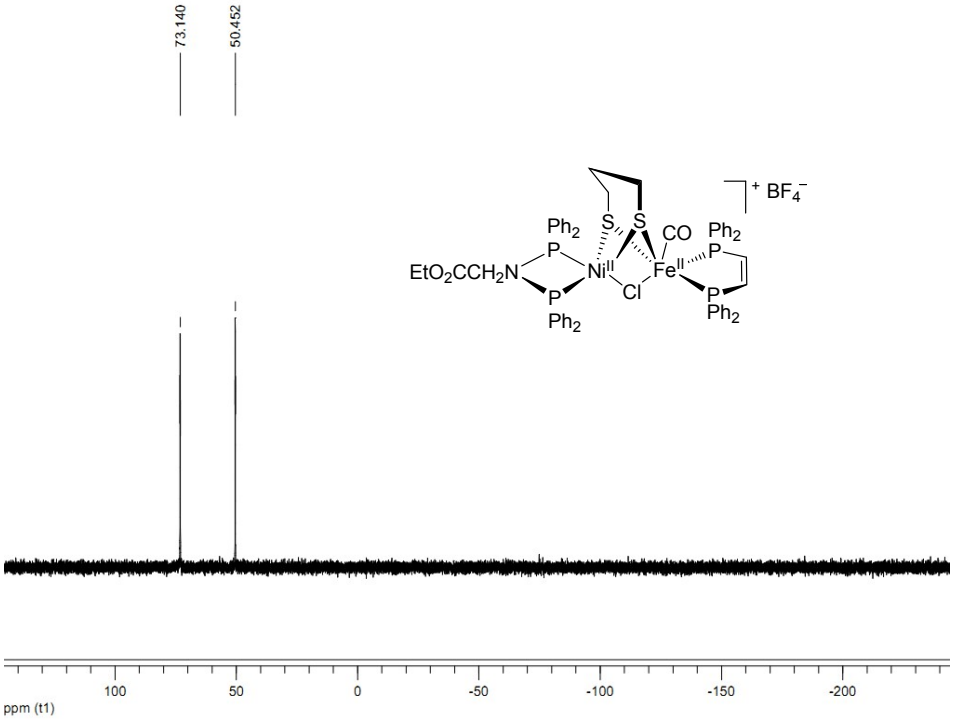

Fig. S11 ^{31}P NMR spectrum of **5b**.

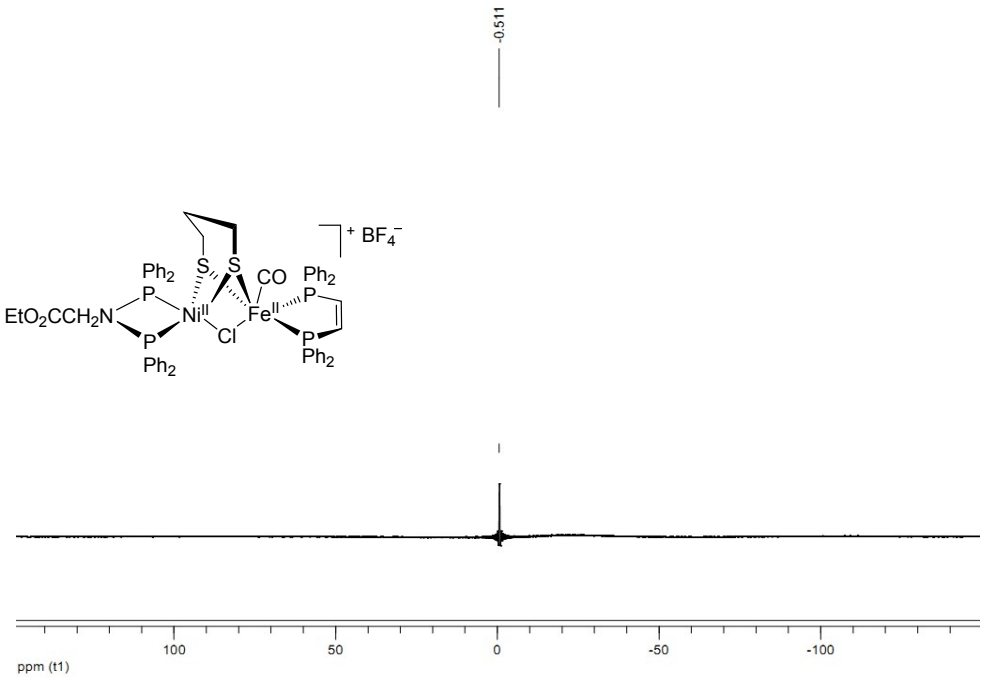

Fig. S12 ^{11}B NMR spectrum of **5b**.

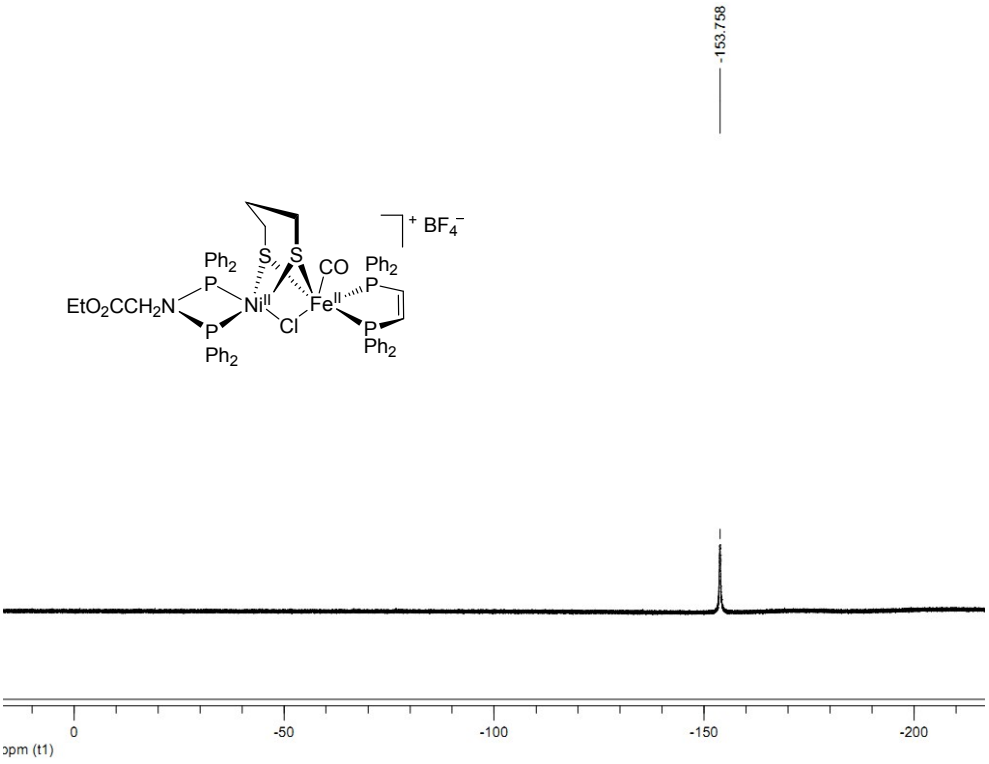

Fig. S13 ^{19}F NMR spectrum of **5b**.

5. IR and ^{1}H (^{31}P, ^{11}B, ^{19}F) NMR spectra of 6a

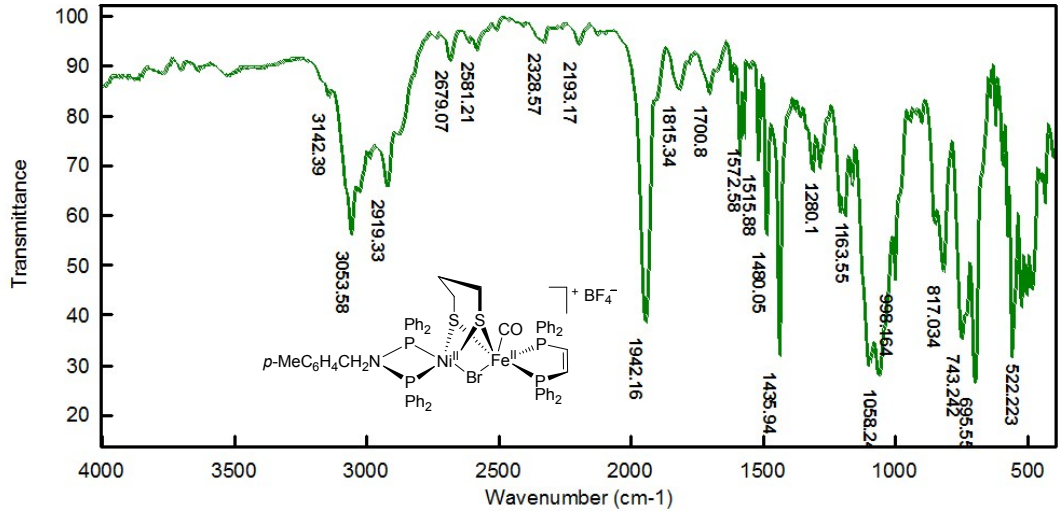

Fig. S14 IR spectrum of **6a**.

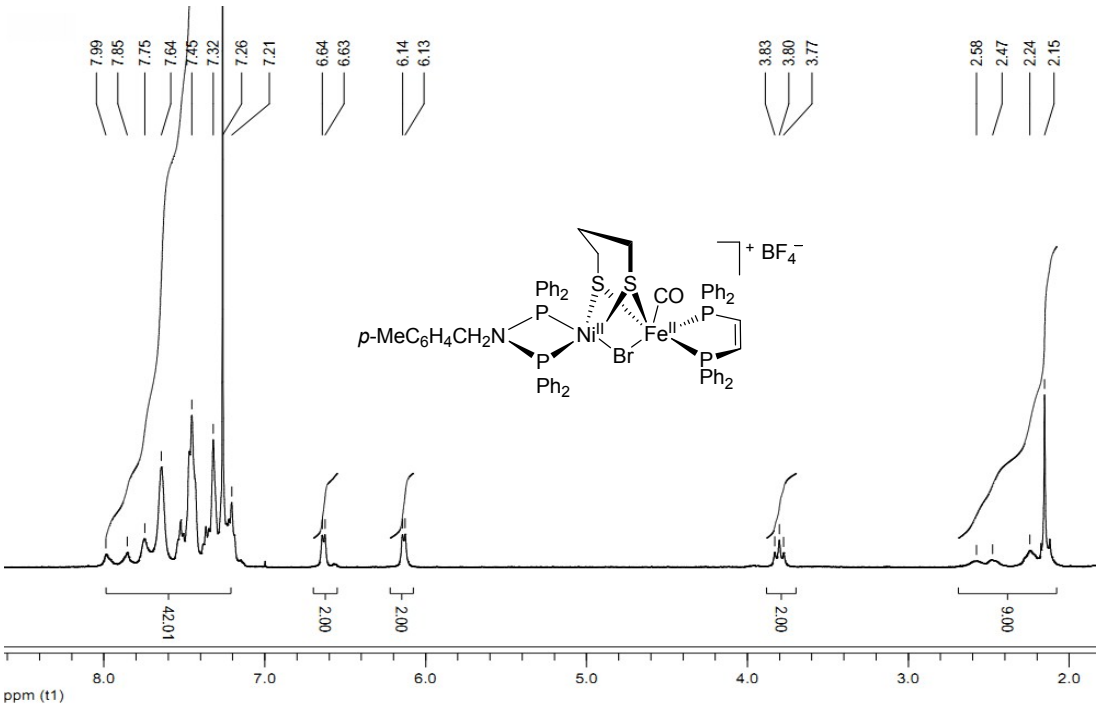

Fig. S15 ^{1}H NMR spectrum of **6a**.

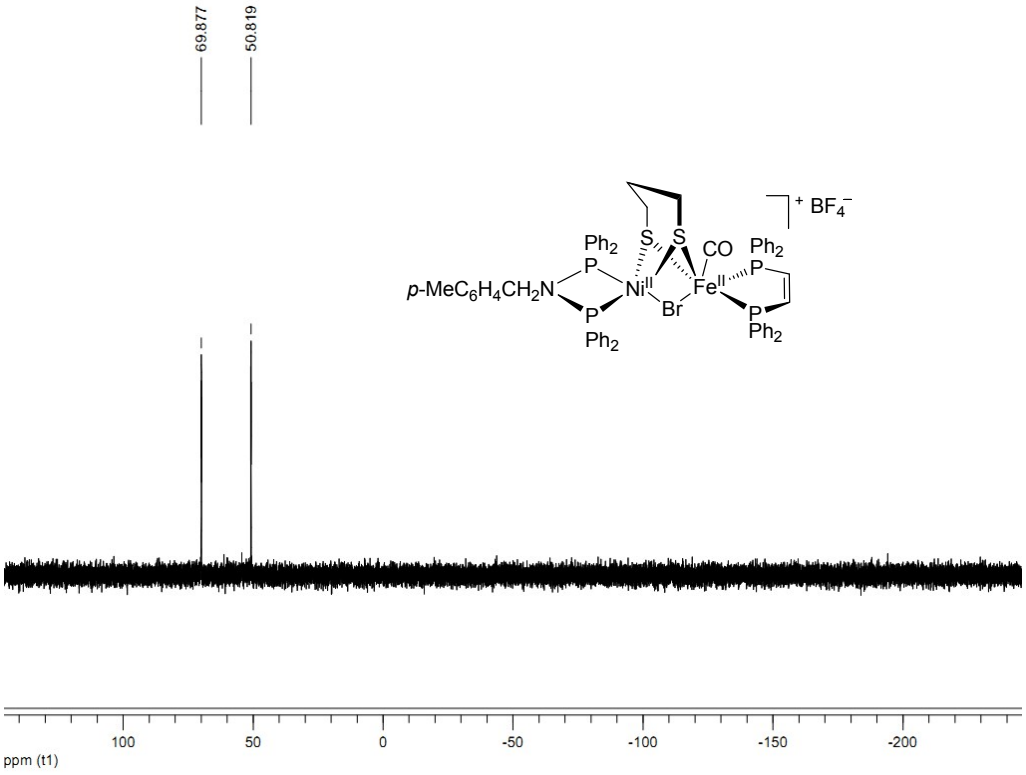

Fig. S16 ^{31}P NMR spectrum of **6a**.

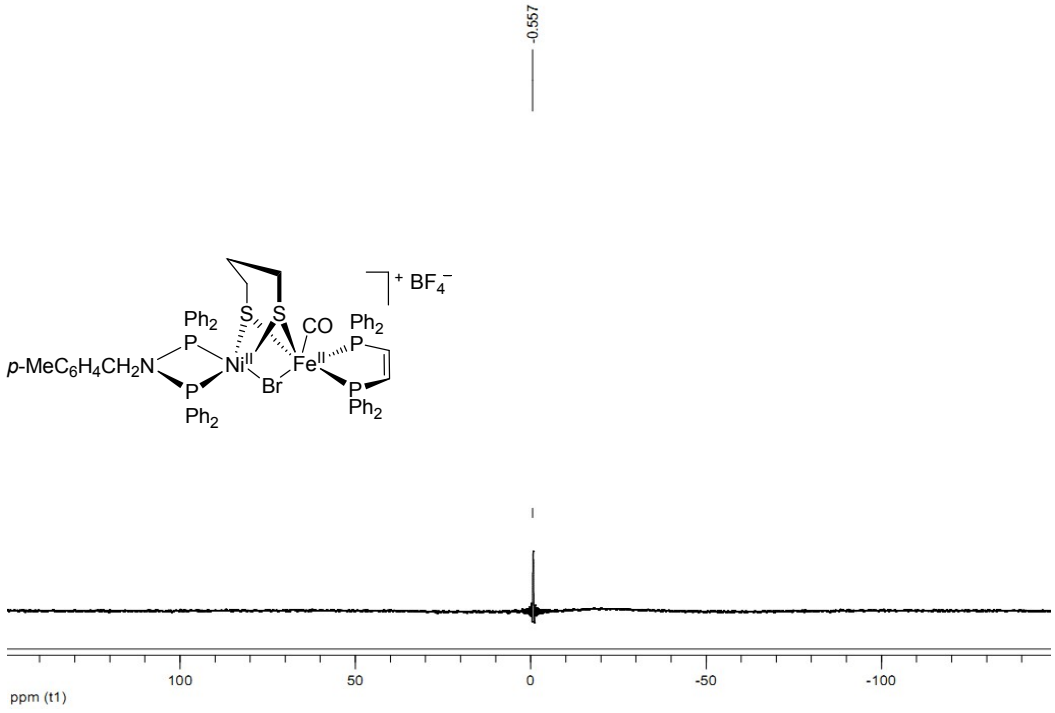

Fig. S17 ^{11}B NMR spectrum of **6a**.

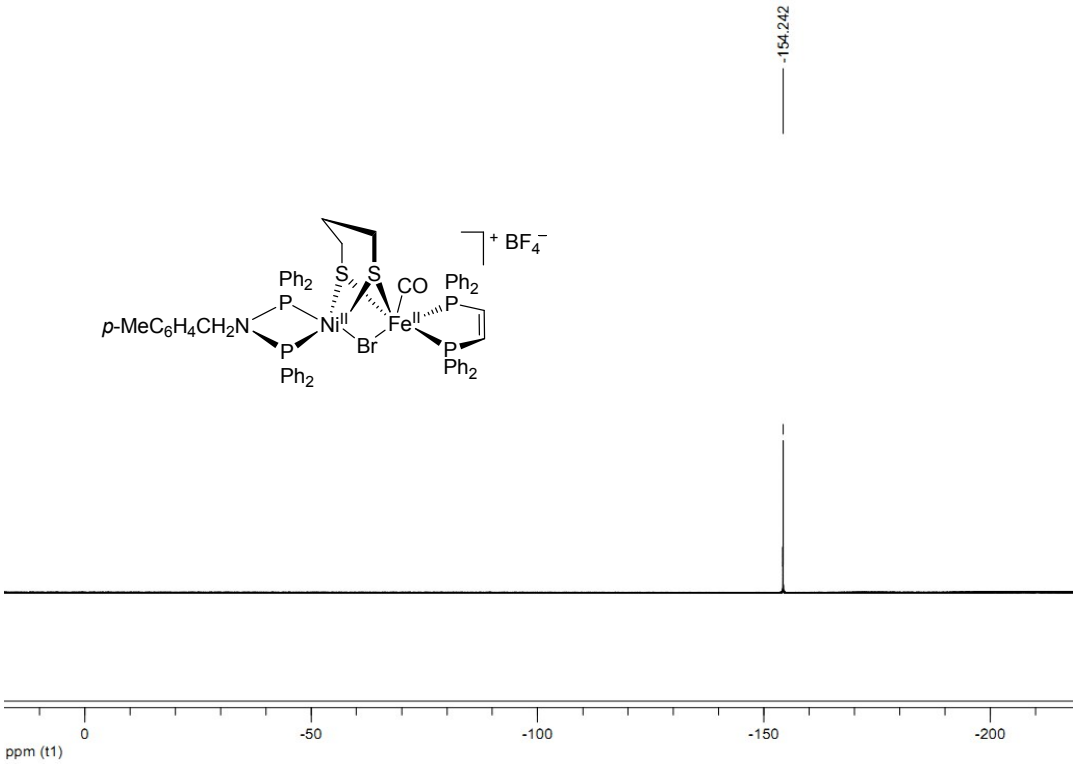

Fig. S18 ^{19}F NMR spectrum of **6a**.

6. IR and ^{1}H (^{31}P, ^{11}B, ^{19}F) NMR spectra of 7a

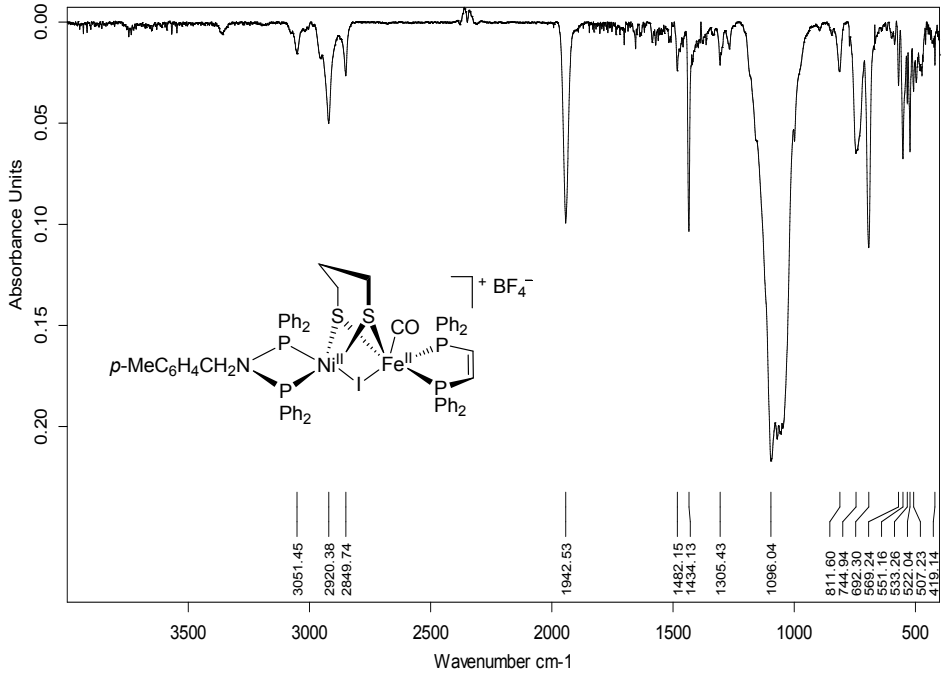

Fig. S19 IR spectrum of **7a**.

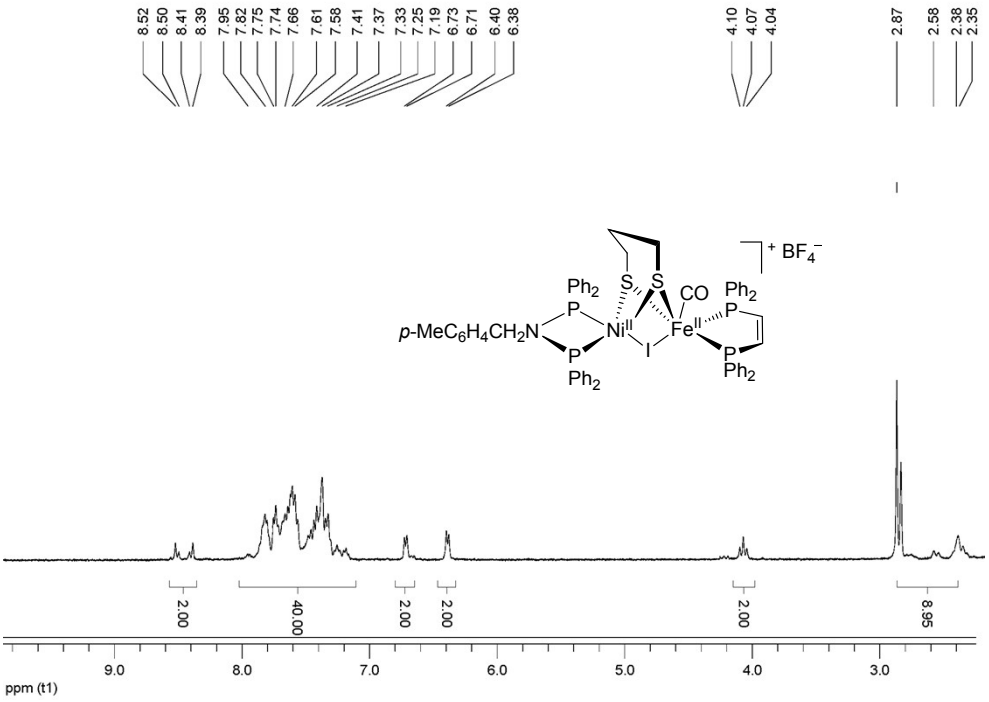

Fig. S20 ^{1}H NMR spectrum of **7a**.

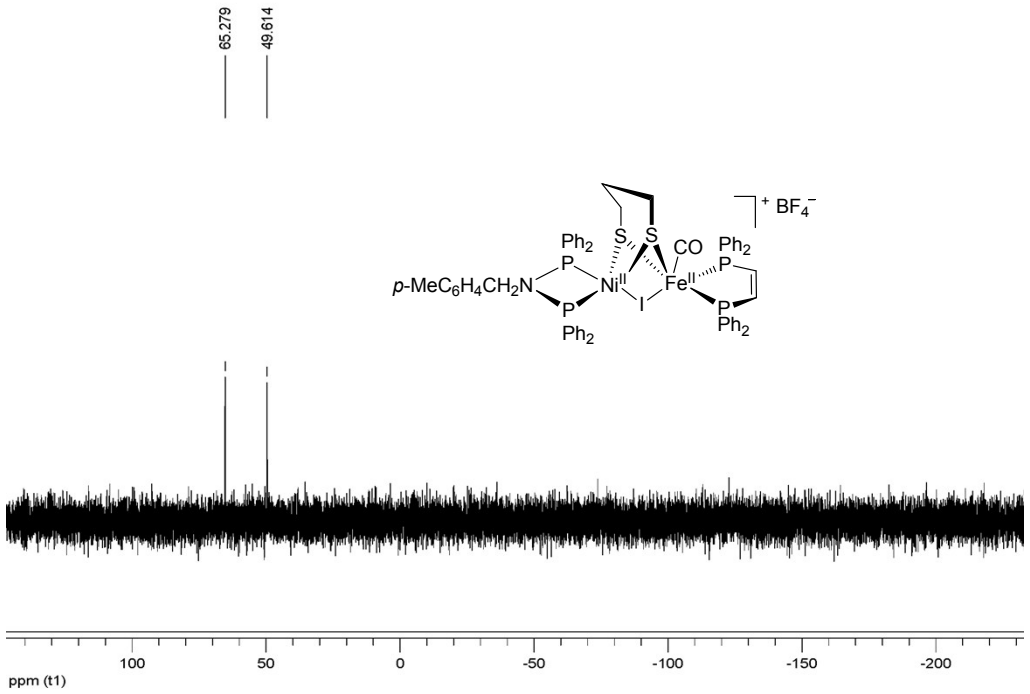

Fig. S21 ^{31}P NMR spectrum of **7a**.

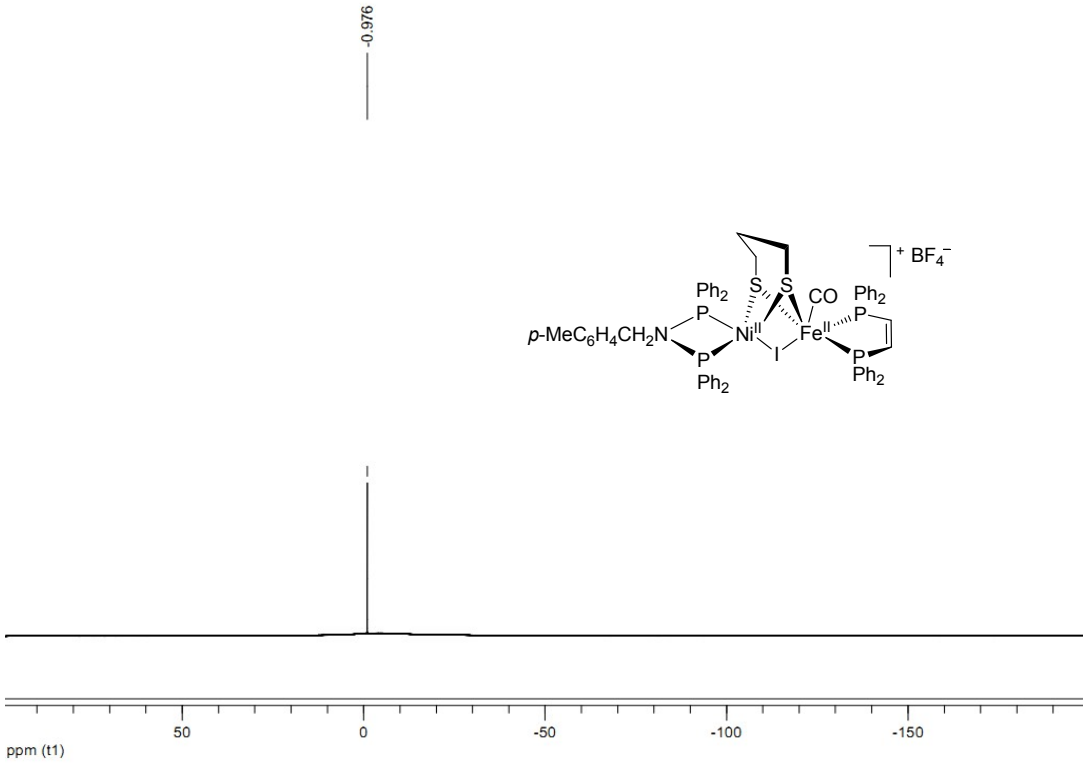

Fig. S22 ^{11}B NMR spectrum of **7a**.

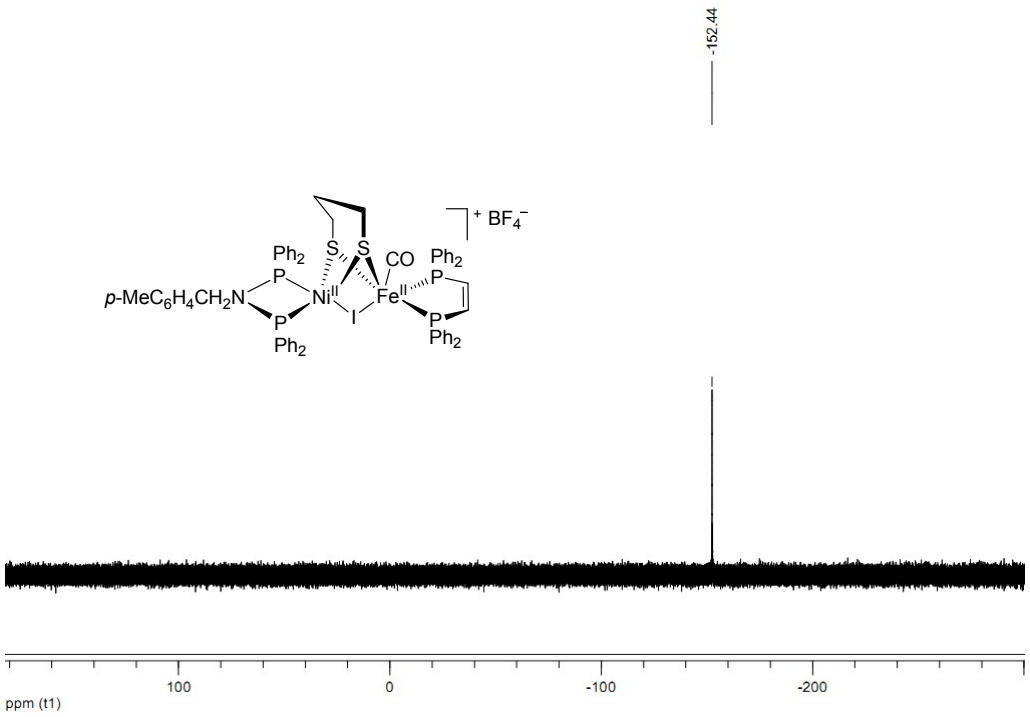

Fig. S23 ^{19}F NMR spectrum of **7a**.

7. Bulk electrolysis for the two-electron reduction of $[CpFe(CO)_2]_2$ and the one-electron reductions of 5a–7a.

The reduction events for **5a–7a** is a one-electron process since their final Q values determined by bulk electrolysis are close to half that of the known two-electron reduction process of dimer $[CpFe(CO)_2]_2$.[1,2]

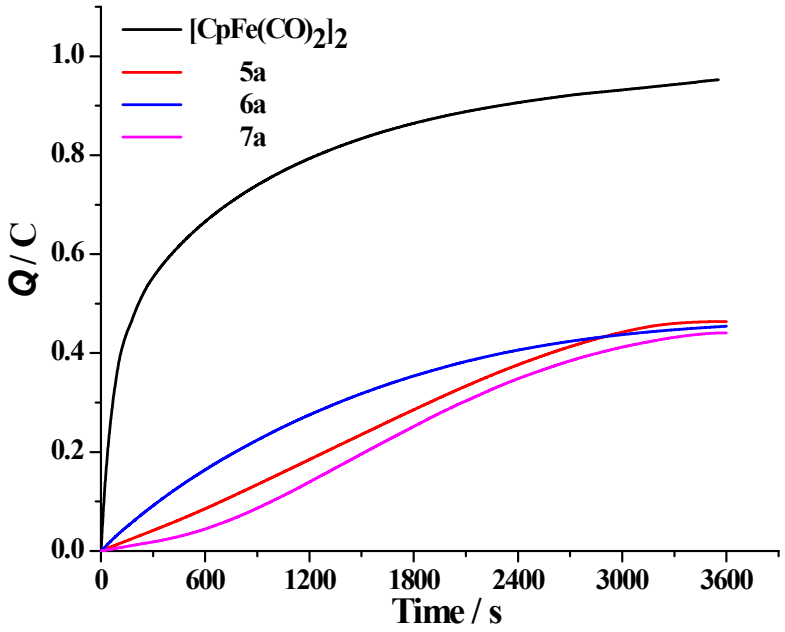

Fig. S24 Bulk electrolysis for the two-electron reduction of $[CpFe(CO)_2]_2$ and the one-electron reductions of **5a–7a**.

8. Bulk electrolysis for the two-electron reduction of $[CpFe(CO)_2]_2$ and the one-electron oxidations of 5a–7a.

The oxidation events for **5a–7a** are also a one-electron process since the final Q values determined by bulk electrolysis are close to half that of the known two-electron reduction of dimer $[CpFe(CO)_2]_2$.[1,2]

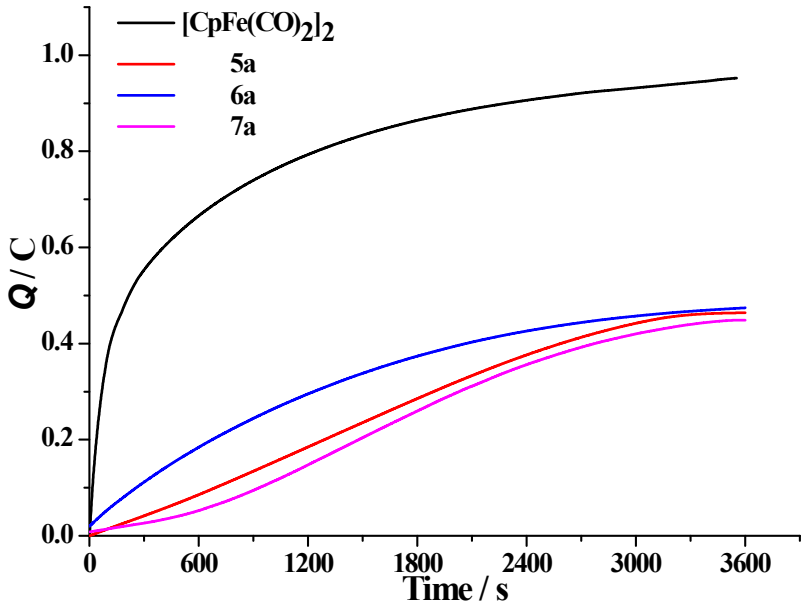

Fig. S25 Bulk electrolysis for the two-electron reduction of $[CpFe(CO)_2]_2$ and the one-electron oxidations of **5a–7a**.

9. Plots of i_p versus $\nu^{1/2}$ for the reduction peaks of 5a–7a.

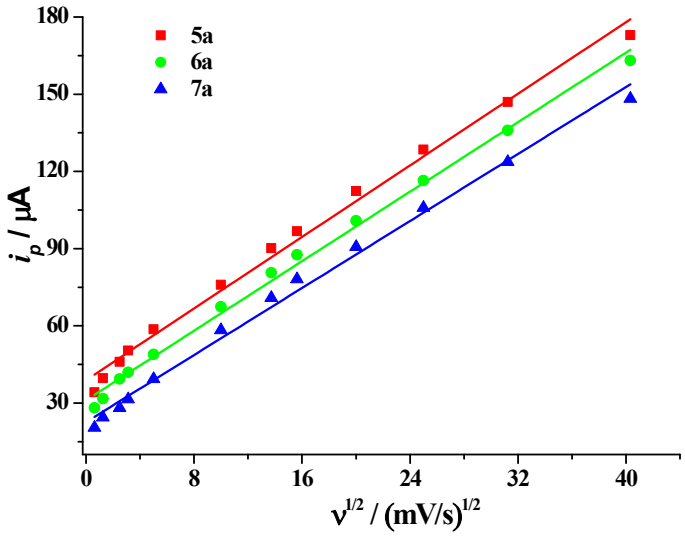

Fig. S26 Plots of i_p versus $\nu^{1/2}$ for the reduction peaks of **5a** (▪), **6a**(●)and **7a**(▲).

10. Cyclic voltammograms and overpotential determinations of 6a,b and 7a,b with Cl_2CHCO_2H in MeCN.

Since the pK_a and the standard redox potential of Cl_2CHCO_2H in MeCN (pK_a^{MeCN} = 13.2, $E^0_{H^+/H2}$ = –0.14 V)[3] are known, the equilibrium potential (E^0_{HA} = –0.92 V vs Fc/Fc$^+$) can be calculated according to eq.S1 using Evans′ relationship.[3] The overpotentials of the electrocatalytic proton reductions catalyzed by **6a,b** and **7a,b** were measured using eq.S2 from the potential at 0.5 (i_{pc}), where i_{pc} is the cathodic peak current in the cyclic voltammogram recorded after addition of 40 mM or 68 mM of Cl_2CHCO_2H.

$$E^0_{HA} = E^0_{H^+/H2} - (2.303RT/F)pK_{a,HA} \qquad \text{eq.S1}$$

$$\text{overpotential} = |E^0_{HA} - E_{cat/2}| \qquad \text{eq.S2}$$

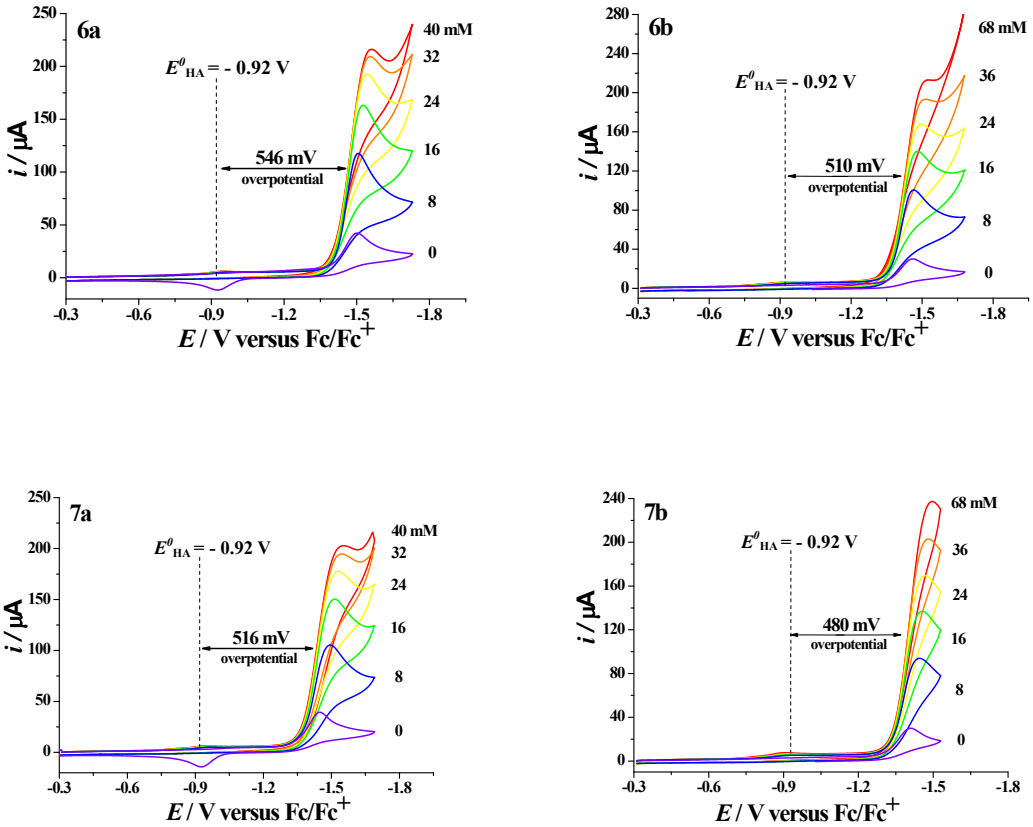

Fig. S27 Cyclic voltammograms of **6a**,**b** and **7a,b** (1.0 mM) with varying amount of Cl_2CHCO_2H (denoted on right) in 0.1 M *n*-Bu_4NPF_6/MeCN at a scan rate of 0.1 Vs^{-1}.

11. TOF calculations

The turnover frequency (TOF) was calculated using a ratio of i_{cat}/i_p (eqs. S3 and S4), where i_{cat} is the peak current of the reduction wave in the presence of acid and i_p is the peak current in the absence of acid. The value of i_{cat}/i_p is in the regime where the catalytic rate is independent of $[H]^+$.[4]

$i_{cat}/i_p = (n/0.446)(RTk/Fv)^{1/2}$ eq. S3

$TOF = 1.94v(i_{cat}/i_p)^2$ eq. S4

n = number of electrons transfered R = ideal gas constant in $K^{-1}mol^{-1}$

T = temperature in K k = rate constant

v = scan rate in V/ s

$TOF_{\mathbf{5a}} = 1.94v(i_{cat}/i_p)^2 = 1.94\ (V^{-1}) \times 0.1\ (Vs^{-1}) \times (7.0)^2 = 9.5$

$TOF_{\mathbf{5b}} = 1.94v(i_{cat}/i_p)^2 = 1.94\ (V^{-1}) \times 0.1\ (Vs^{-1}) \times (9.3)^2 = 16.8$

$TOF_{\mathbf{6a}} = 1.94v(i_{cat}/i_p)^2 = 1.94\ (V^{-1}) \times 0.1\ (Vs^{-1}) \times (6.0)^2 = 7.0$

$TOF_{\mathbf{6b}} = 1.94v(i_{cat}/i_p)^2 = 1.94\ (V^{-1}) \times 0.1\ (Vs^{-1}) \times (8.1)^2 = 12.7$

$TOF_{\mathbf{7a}} = 1.94v(i_{cat}/i_p)^2 = 1.94\ (V^{-1}) \times 0.1\ (Vs^{-1}) \times (5.4)^2 = 5.7$

$TOF_{\mathbf{7b}} = 1.94v(i_{cat}/i_p)^2 = 1.94\ (V^{-1}) \times 0.1\ (Vs^{-1}) \times (7.9)^2 = 12.1$

12.References

1 L.-C. Song, B. Gai, Z.-H. Feng, Z.-Q. Du, Z.-J. Xie, X.-J. Sun and H.-B. Song, *Organometallics*, 2013, **32**, 3673-3684.

2 L.-C. Song, Y.-X. Wang, X.-K. Xing, S.-D. Ding, L.-D. Zhang, X.-Y. Wang and H.-T. Zhang, *Chem. Eur. J.*, 2016, **22**, 16304-16314.

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4 M. E. Carroll, B. E. Barton, D. L. Gray, A. E. Mack and T. B. Rauchfuss, *Inorg. Chem.*, 2011, **50**, 9554-9563.