Supporting Information

Structural and functional biomimetics of [Fe]-hydrogenase featuring a mono-, di- or tetrasubstituted pyridine ligand with a *fac*-C, N, S ligation

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1. IR and ^{1}H (^{13}C) NMR spectra of model **1** (Fig. S1–S3)

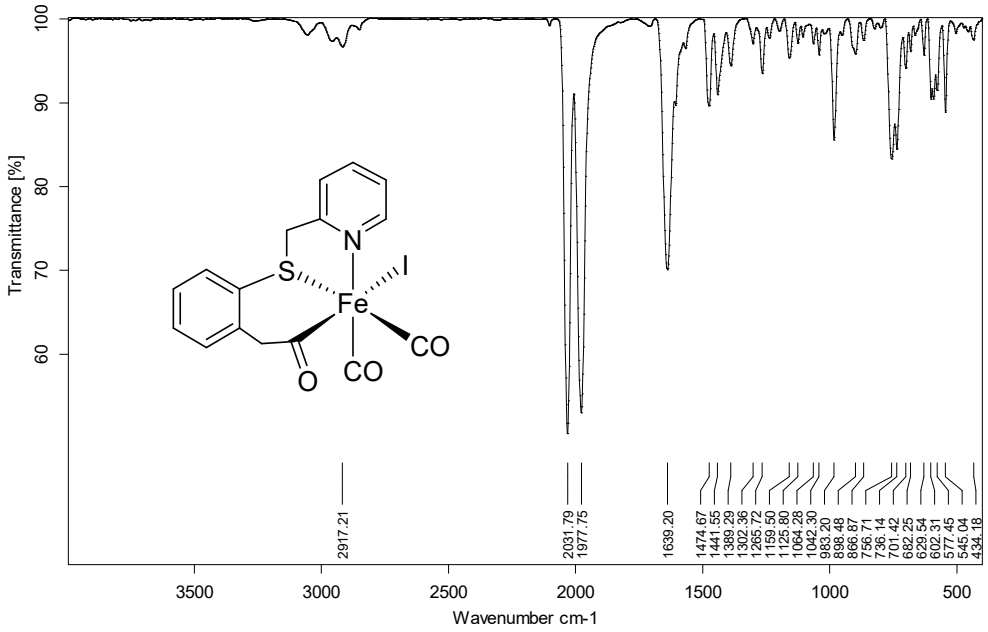

Fig. S1 IR spectrum of model **1**.

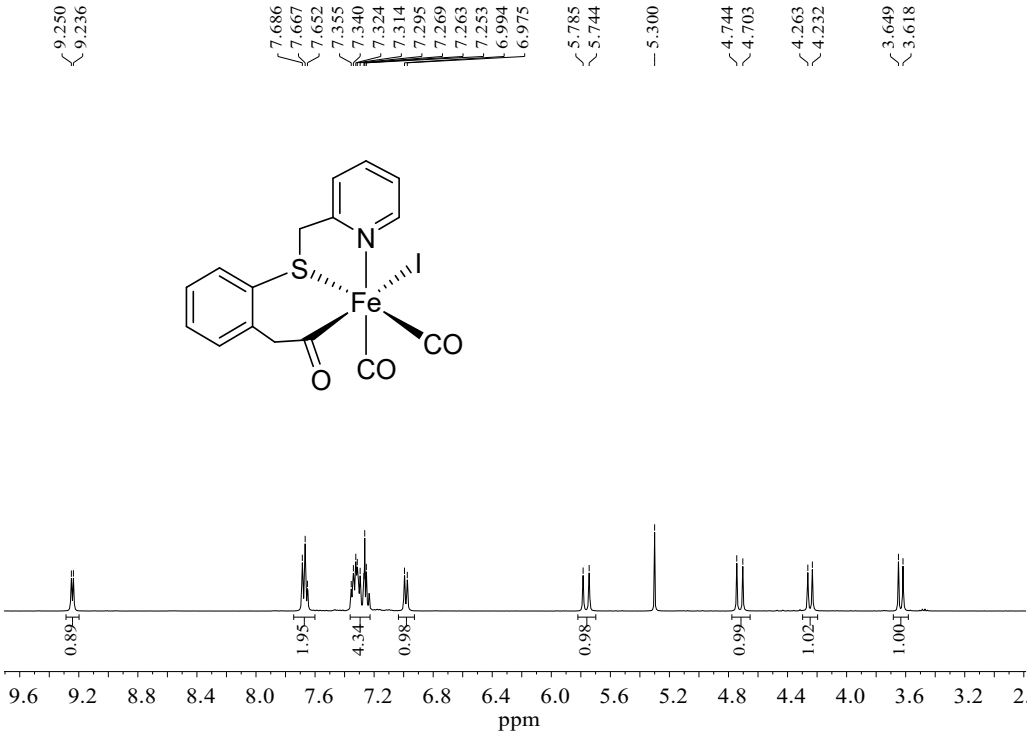

Fig. S2 ^{1}H NMR spectrum of model **1** in $CDCl_3$.

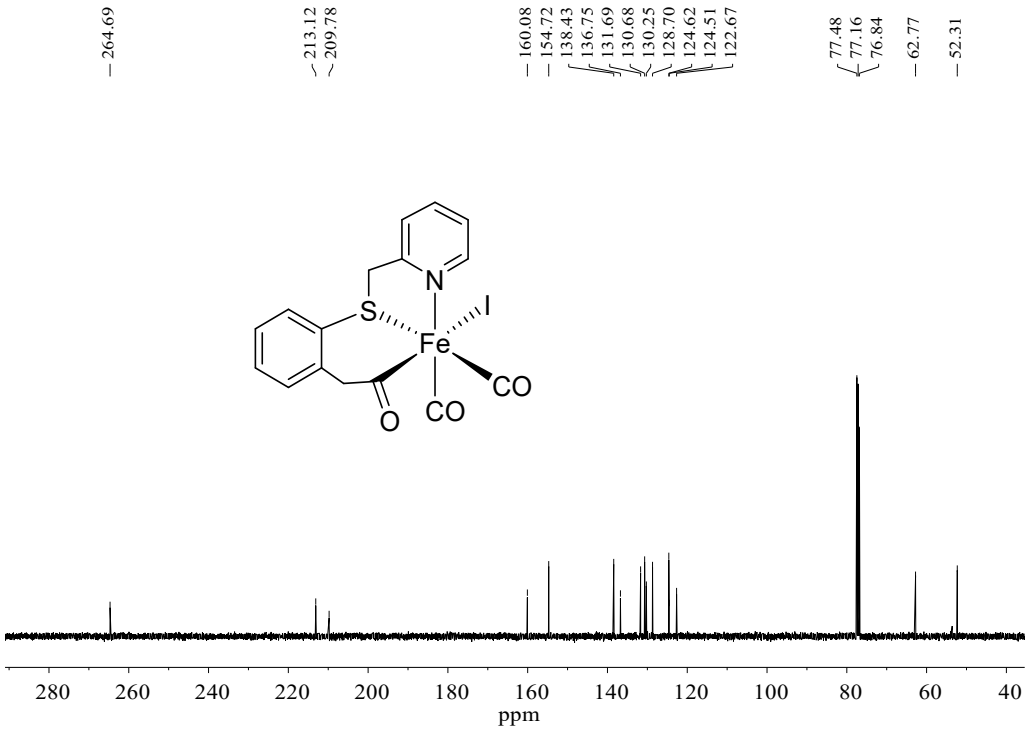

Fig. S3 ^{13}C NMR spectrum of model **1** in $CDCl_3$.

2. IR and ^{1}H (^{13}C) NMR spectra of model **2** (Fig. S4–S6)

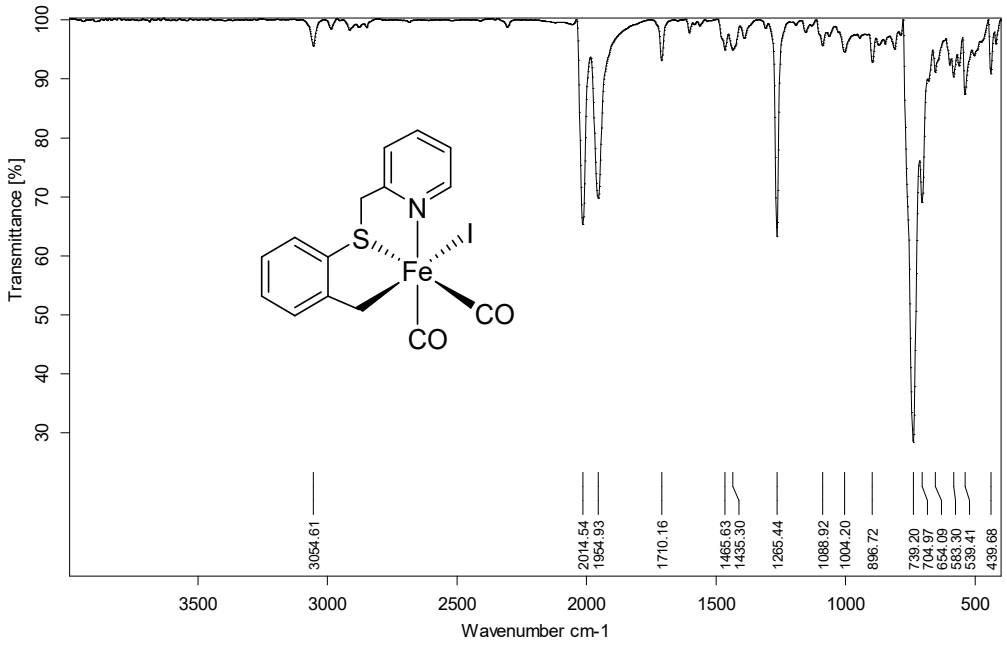

Fig. S4 IR spectrum of model **2**.

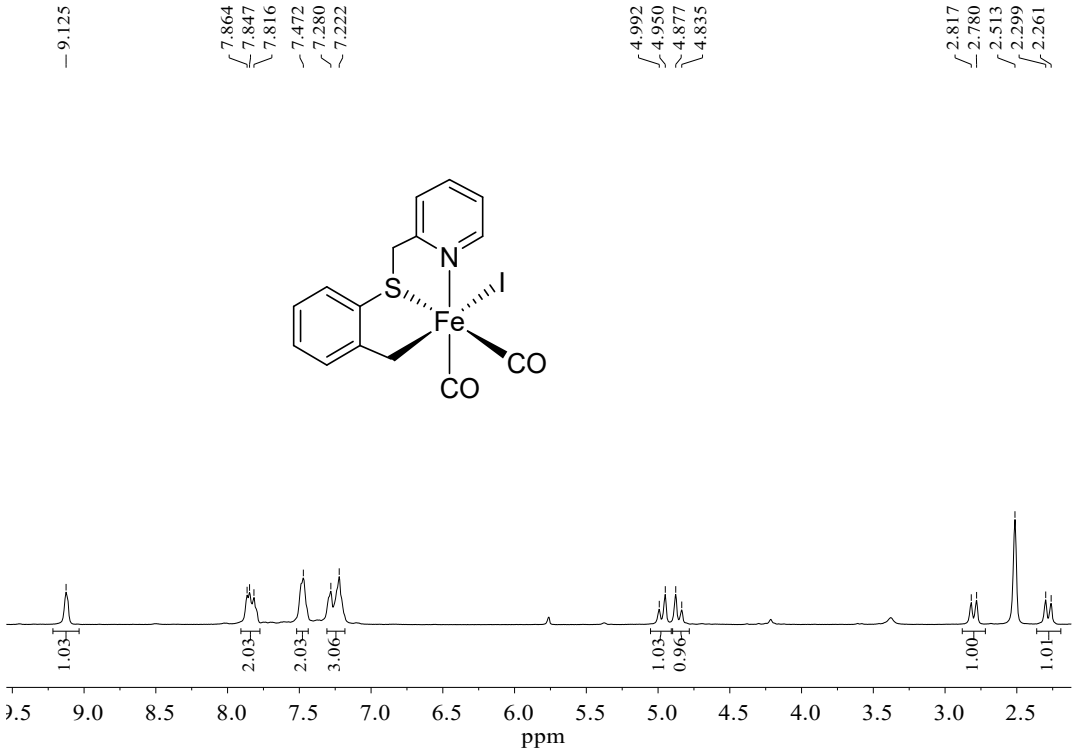

Fig. S5 ^{1}H NMR spectrum of model **2** in d^{6}-DMSO.

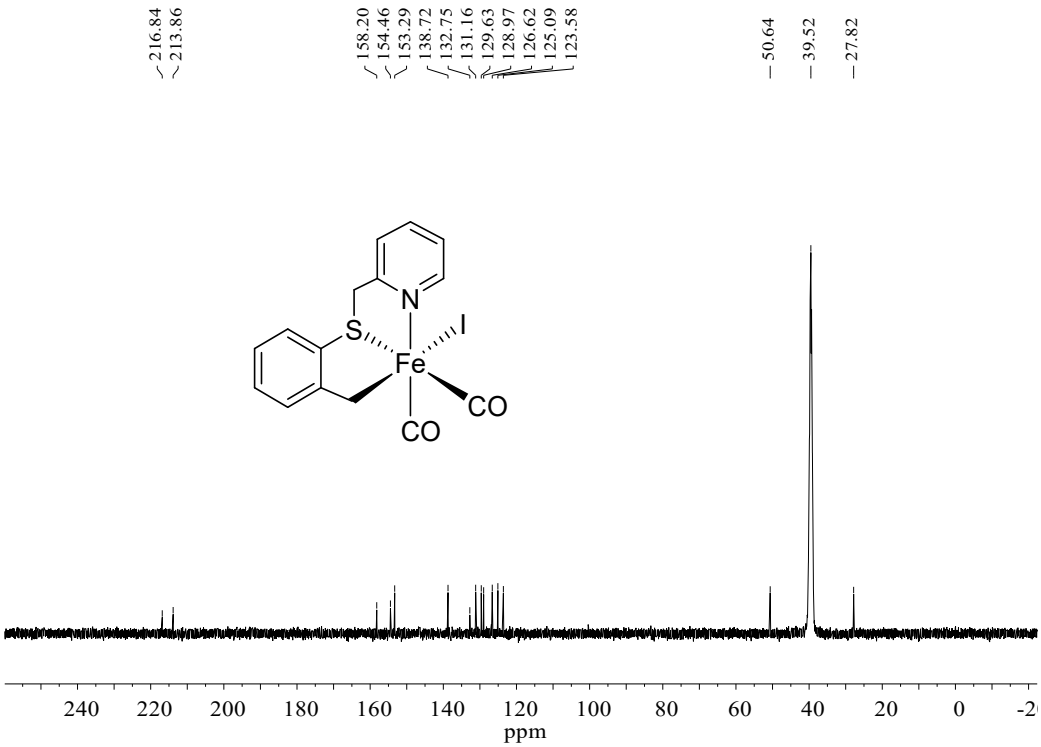

Fig. S6 ^{13}C NMR spectrum of model **2** in d^6-DMSO.

3. IR and ^{1}H (^{13}C) NMR spectra of model **3** (Fig. S7–S9)

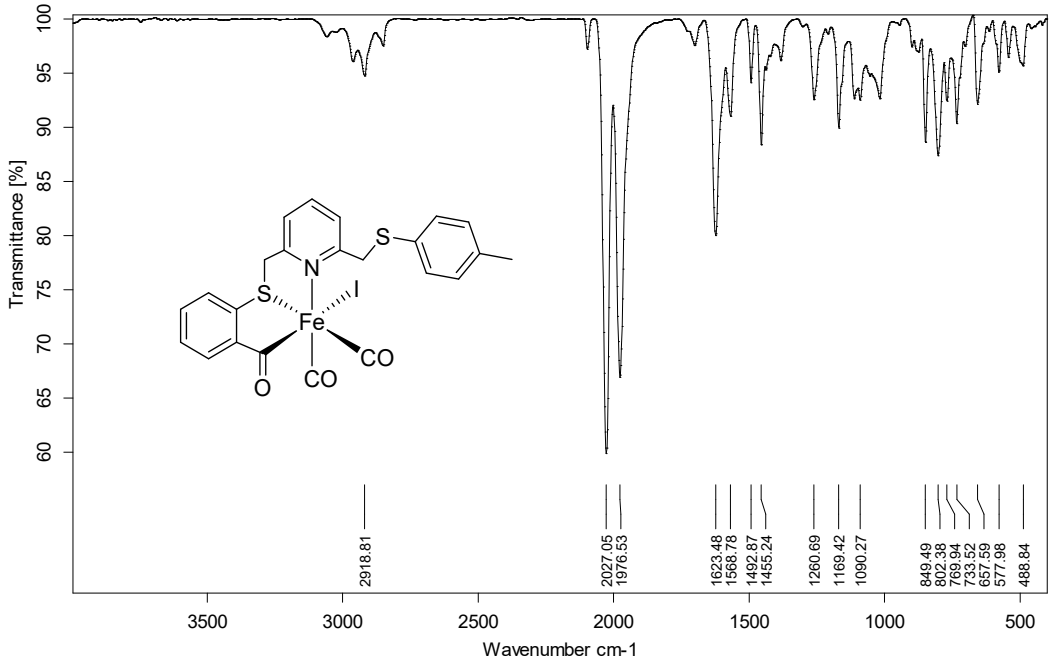

Fig. S7 IR spectrum of model **3**.

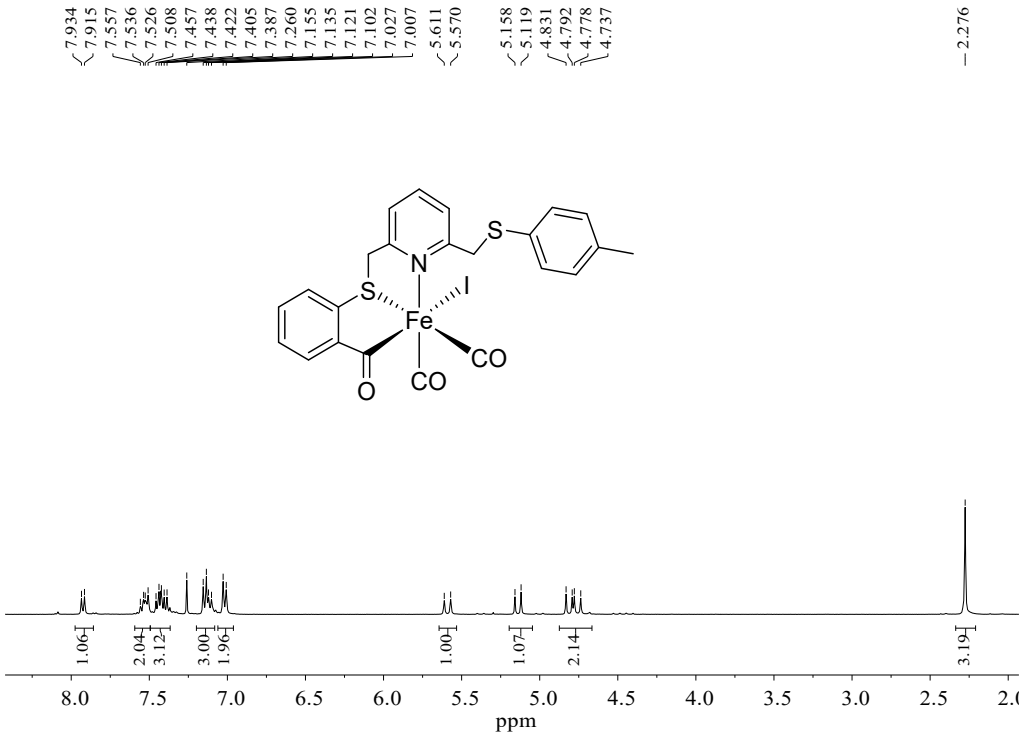

Fig. S8 ^{1}H NMR spectrum of model **3** in $CDCl_3$.

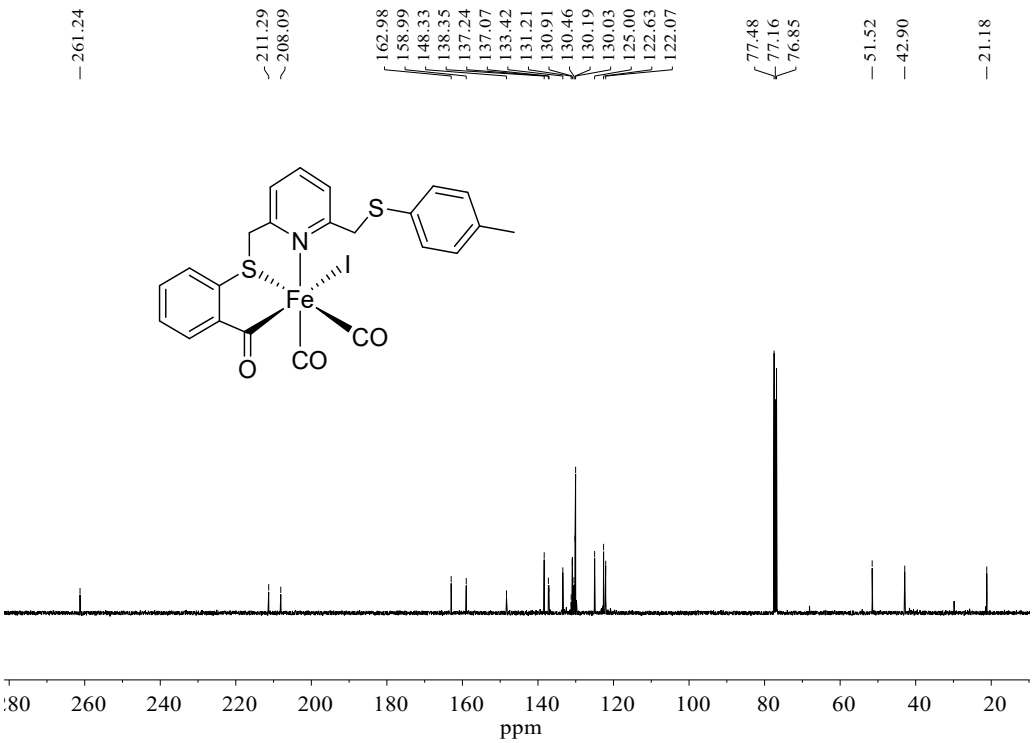

Fig. S9 ^{13}C NMR spectrum of model **3** in $CDCl_3$.

4. IR and ^{1}H (^{13}C) NMR spectra of model **4** (Fig. S10–S12)

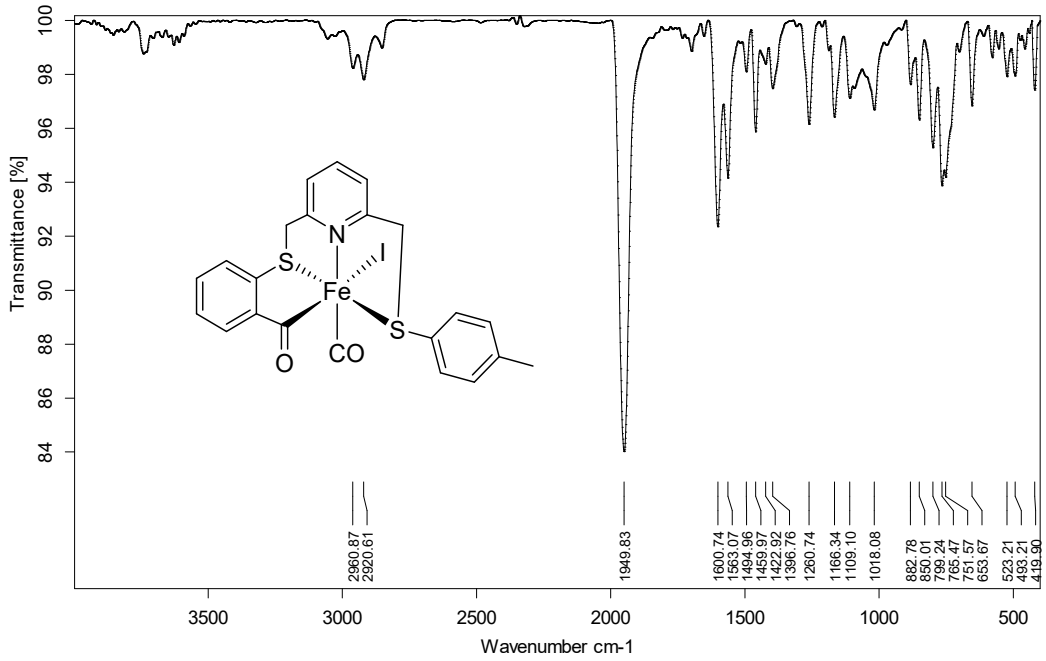

Fig. S10 IR spectrum of model **4**.

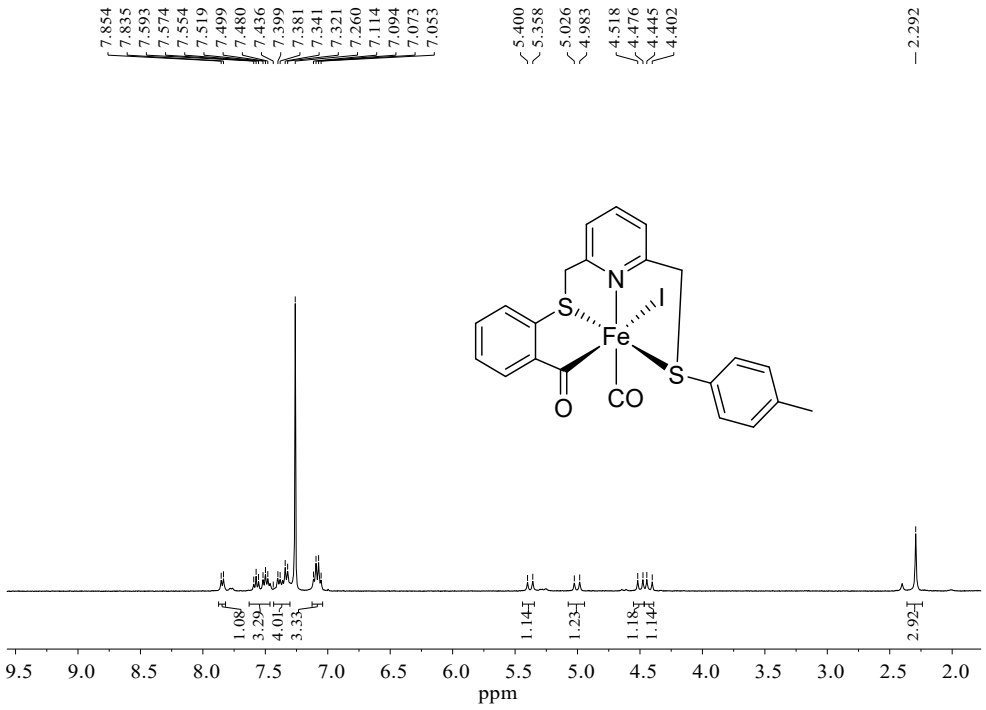

Fig. S11 ^{1}H NMR spectrum of model **4** in $CDCl_3$.

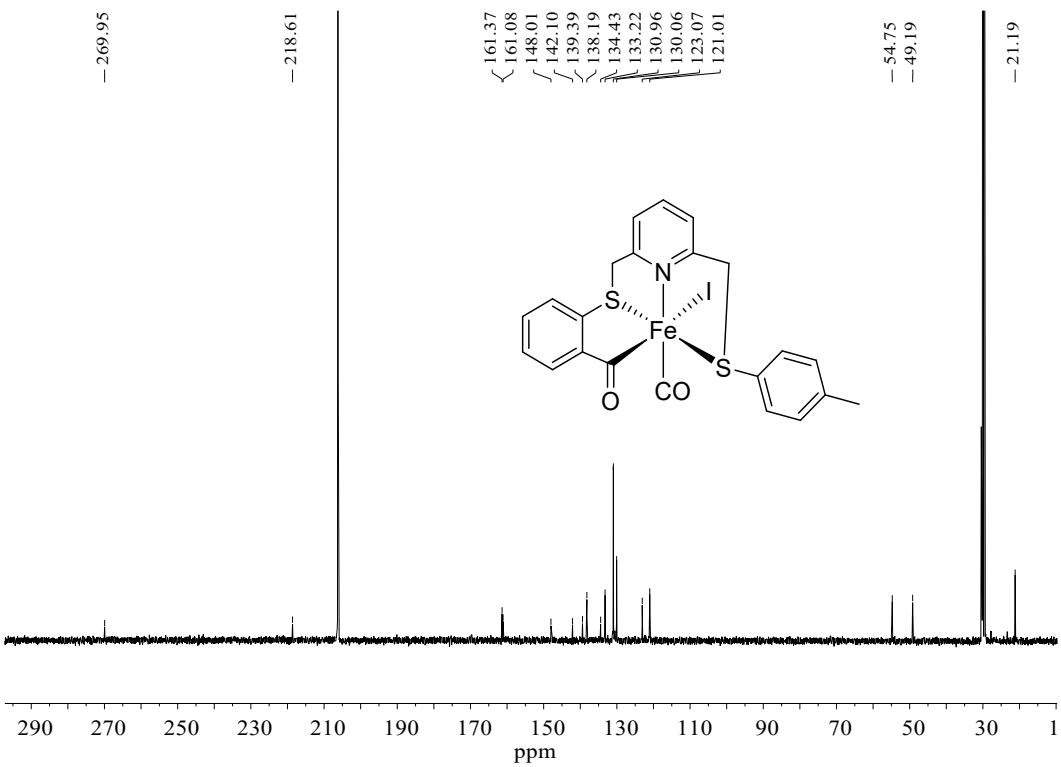

Fig. S12 ^{13}C NMR spectrum of model **4** in acetone-d_6

5. IR and ^{1}H (^{13}C) NMR spectra of model **5** (Fig. S13–S15)

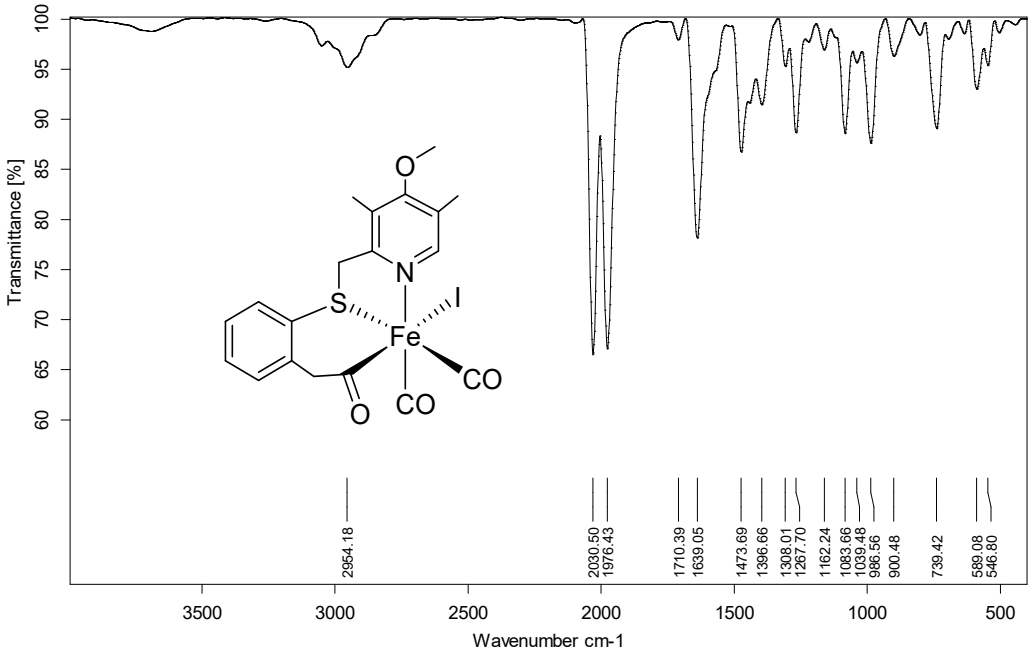

Fig. S13 IR spectrum of model **5**.

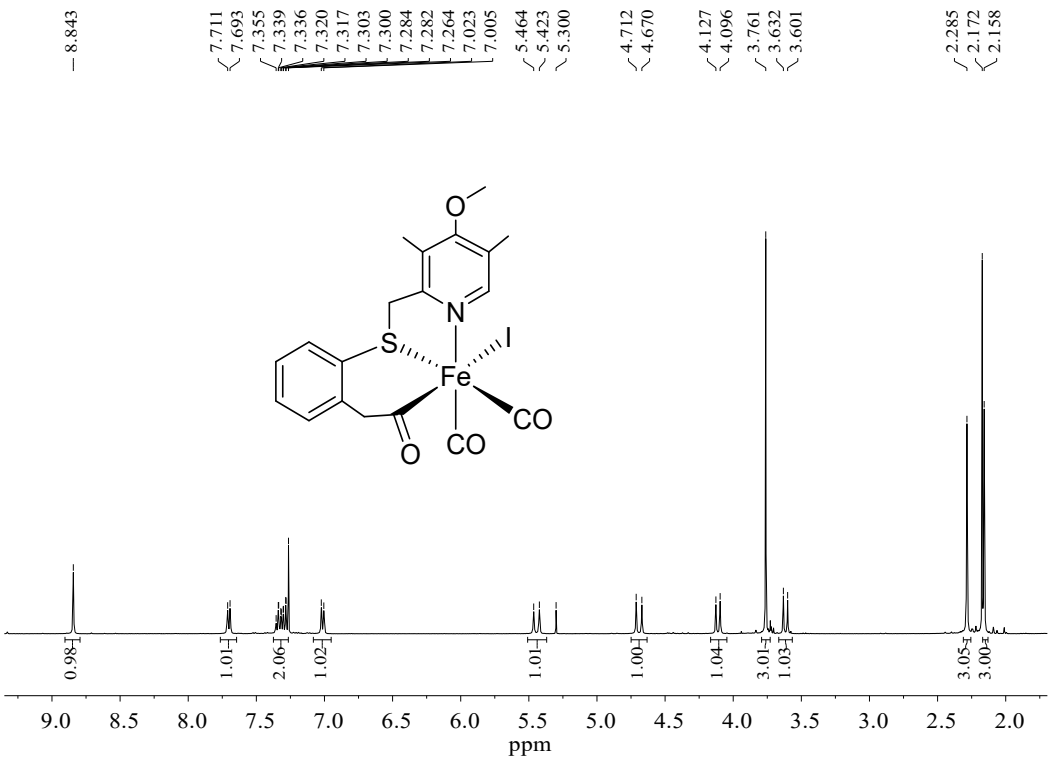

Fig. S14 ^{1}H NMR spectrum of model **5** in $CDCl_3$.

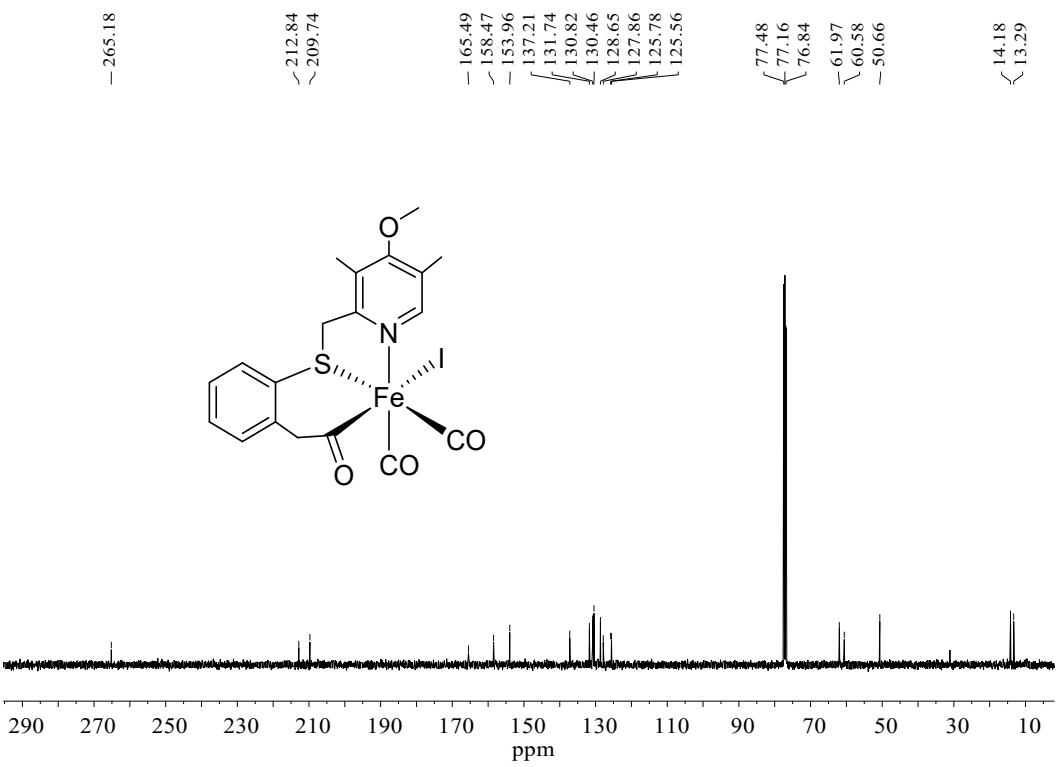

Fig. S15 ^{13}C NMR spectrum of model **5** in $CDCl_3$.

6. IR and ^{1}H (^{13}C) NMR spectra of model **6** (Fig. S16–S18)

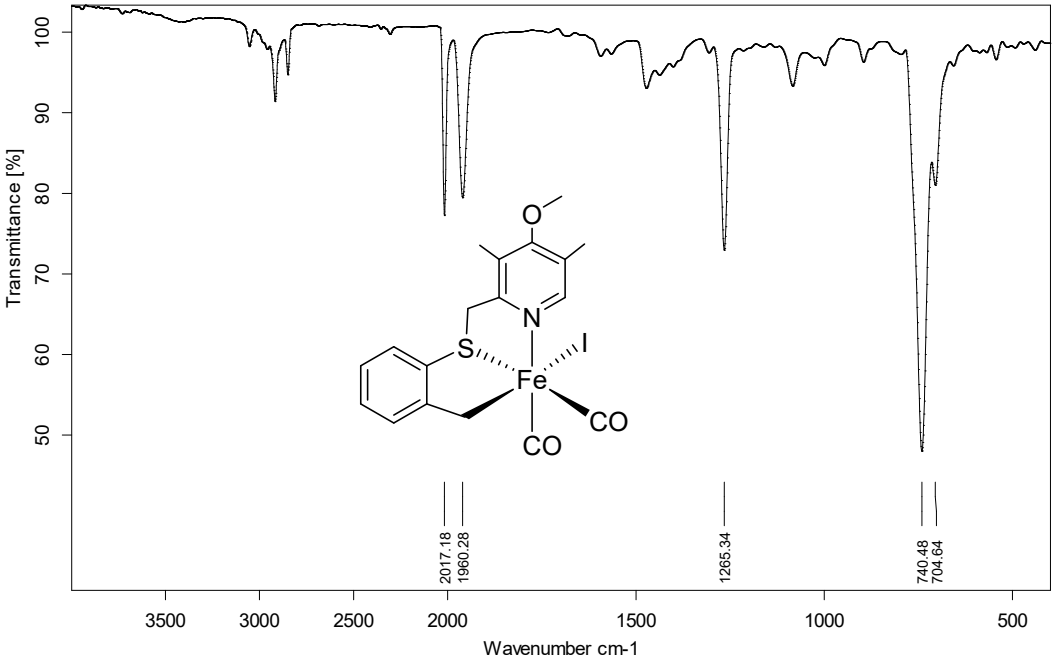

Fig. S16 IR spectrum of model **6**.

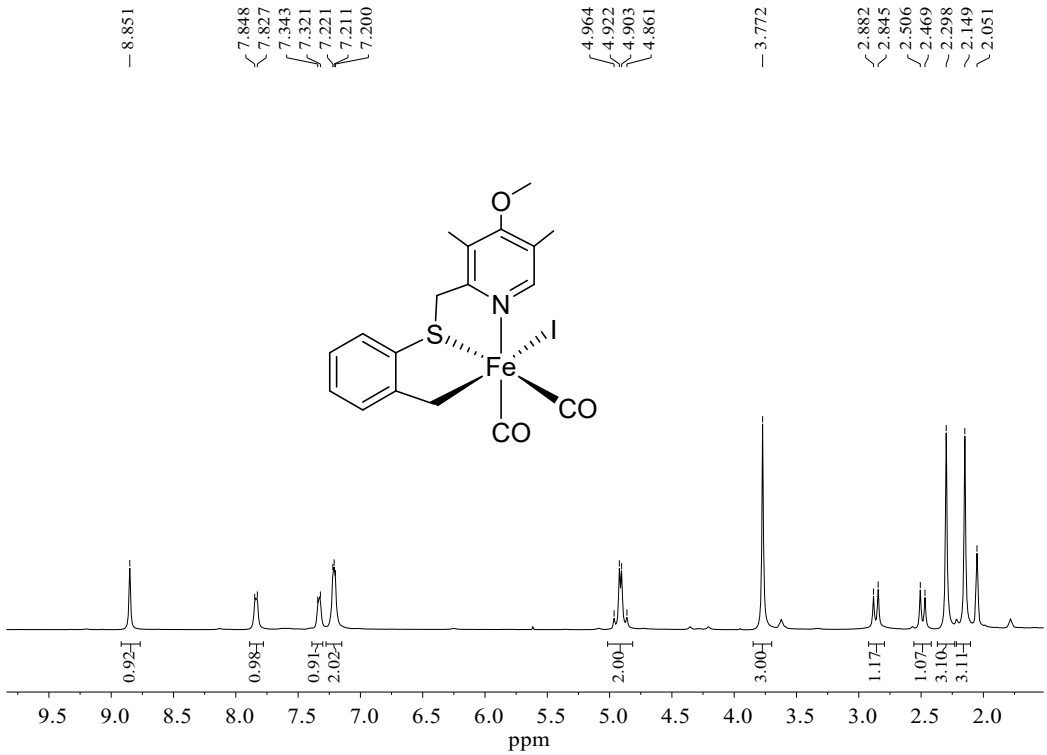

Fig. S17 ^{1}H NMR spectrum of model **6** in acetone-d_6.

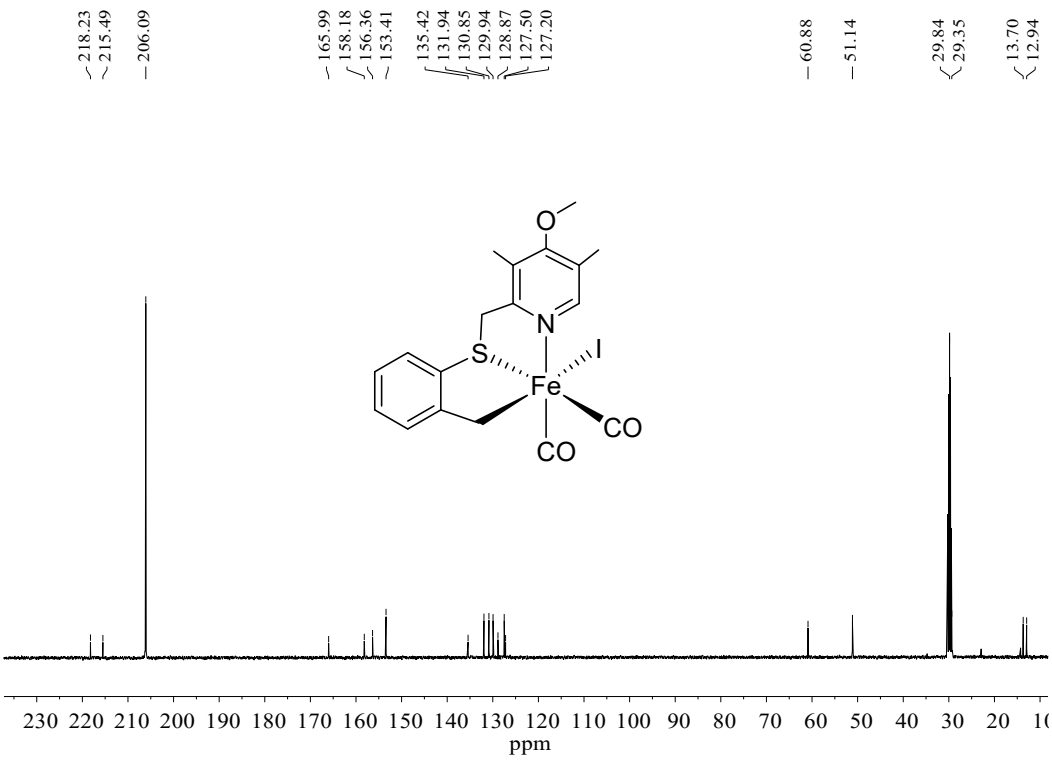

Fig. S18 ^{13}C NMR spectrum of model **6** in acetone-d_6.

7. IR and ^{1}H (^{13}C) NMR spectra of complex **7** (Fig. S19–S21)

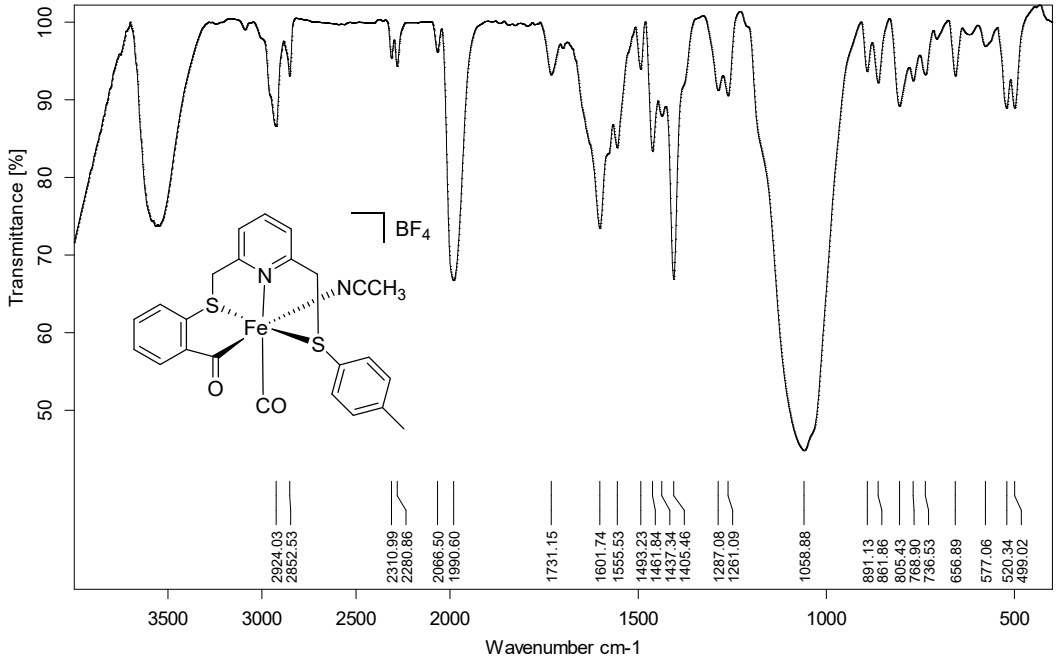

Fig. S19 IR spectrum of complex **7**.

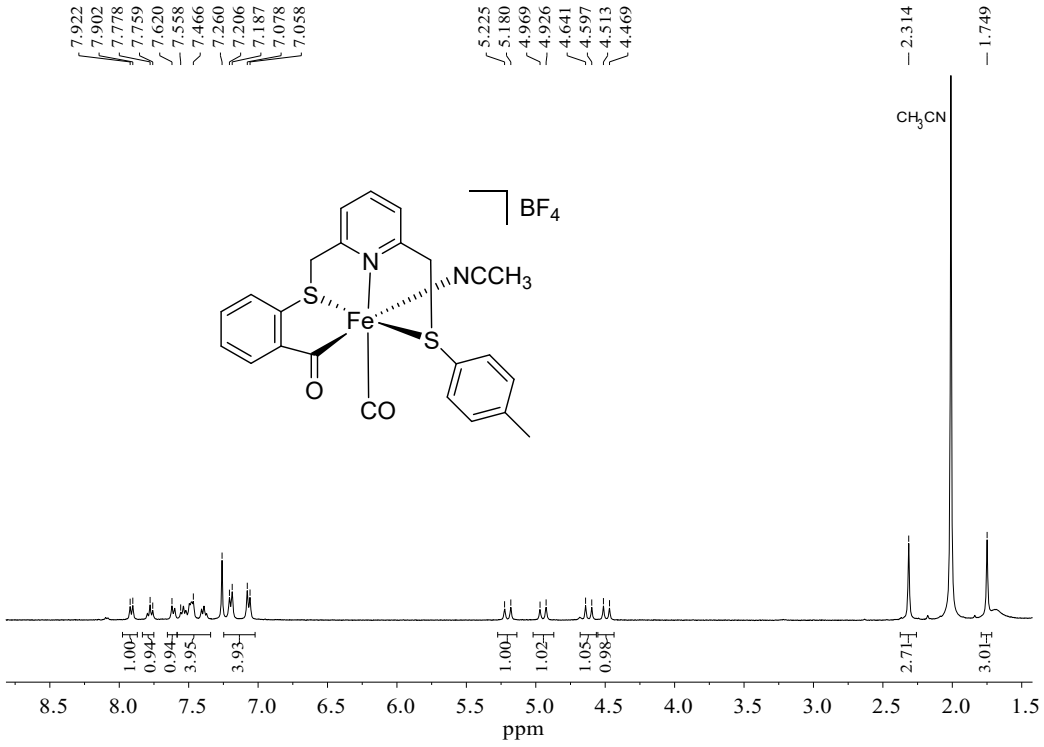

Fig. S20 ^{1}H NMR spectrum of complex **7** in $CDCl_3$.

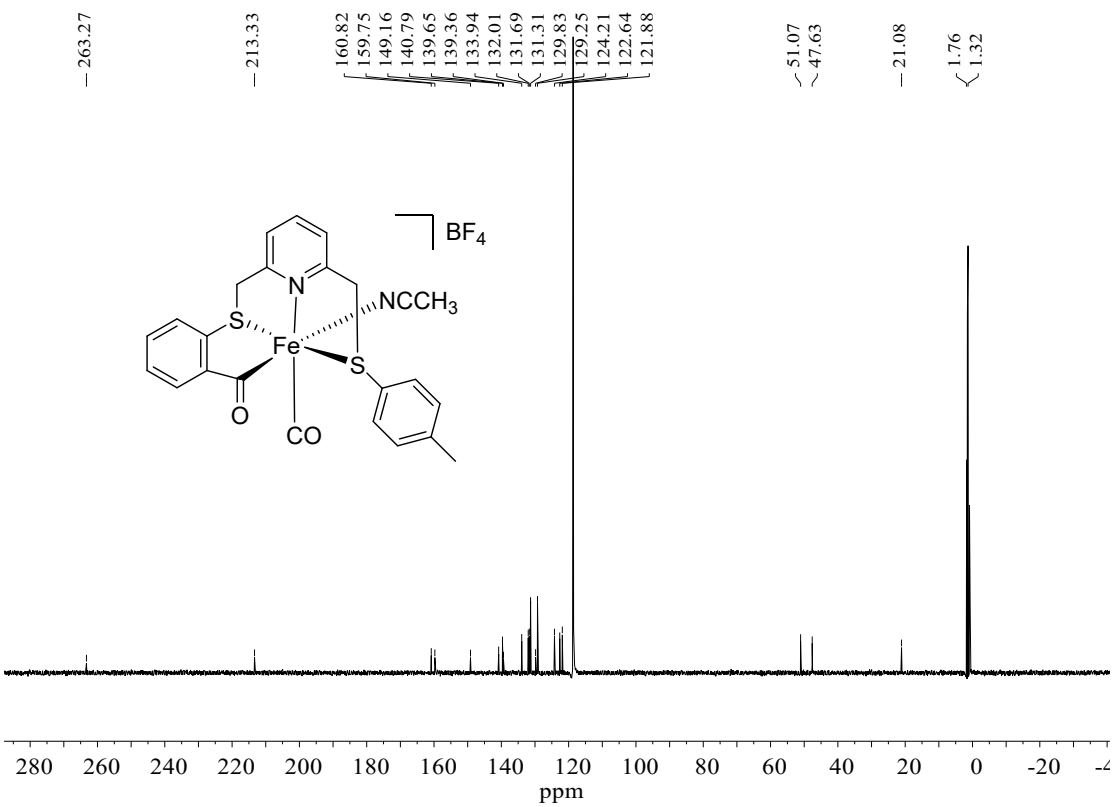

Fig. S21 ^{13}C NMR spectrum of complex **7** in acetonitril-d_3.

8. IR and ^{1}H (^{13}C) NMR spectra of complex **8** (Fig. S22–S24)

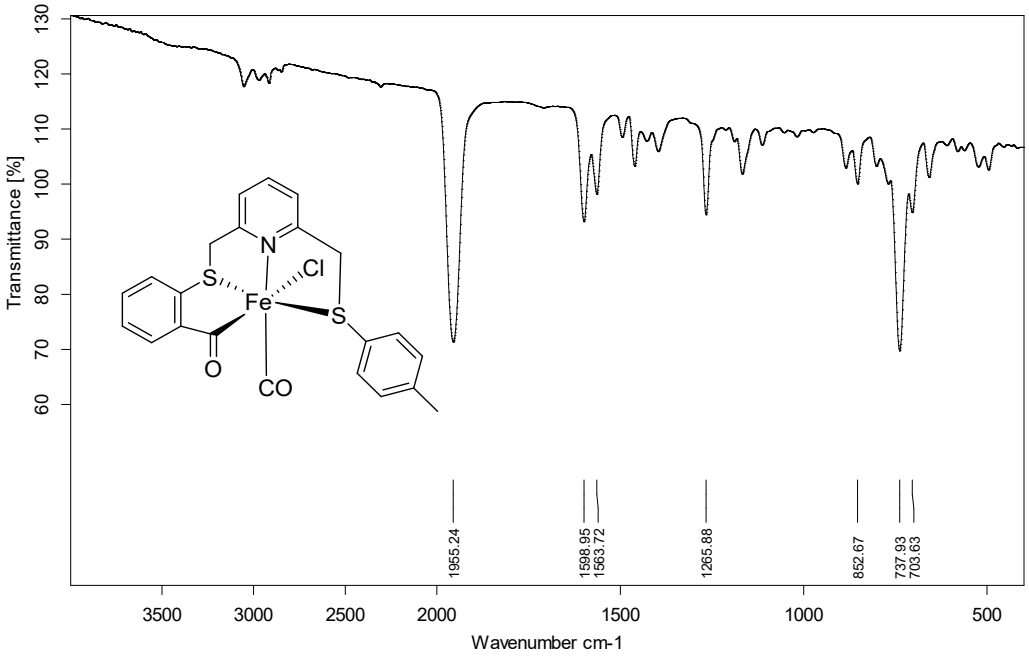

Fig. S22 IR spectrum of complex **8**.

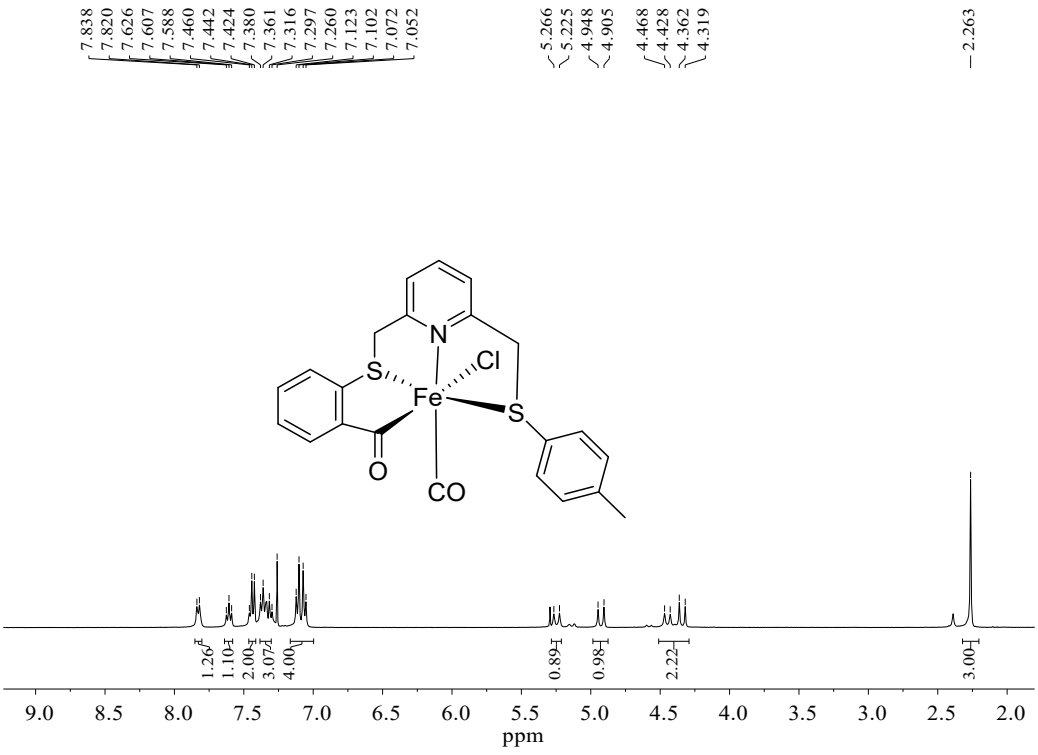

Fig. S23 ^{1}H NMR spectrum of complex **8** in $CDCl_3$.

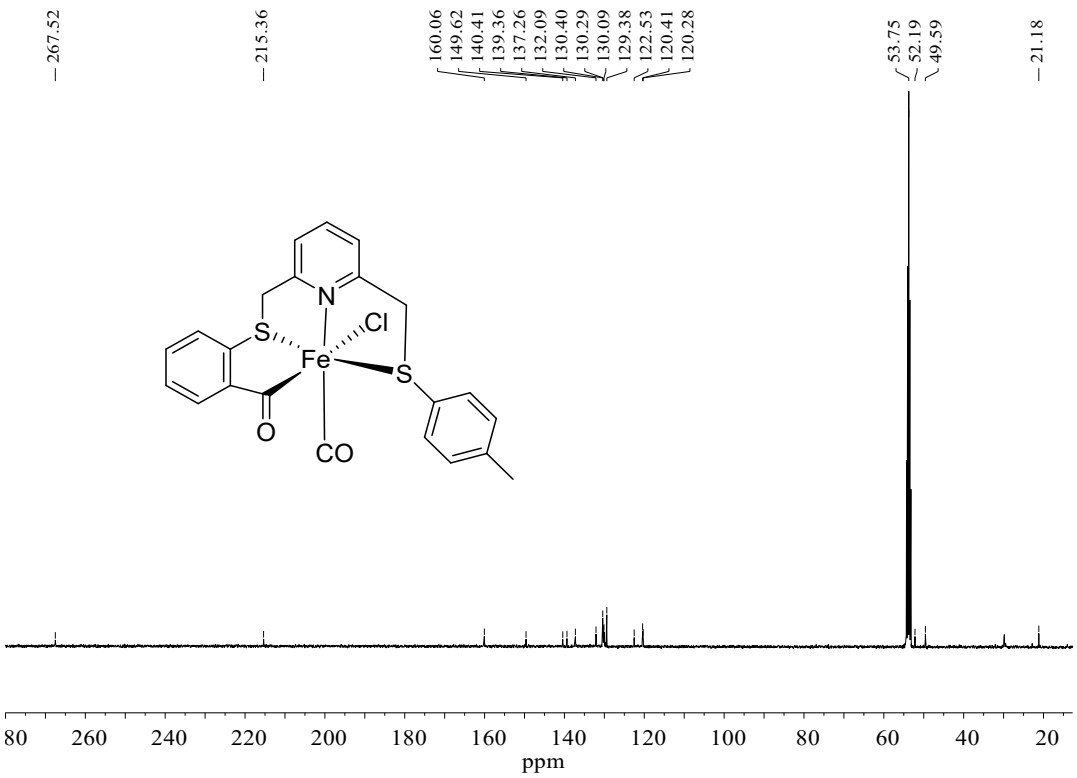

Fig. S24 ^{13}C NMR spectrum of complex **8** in CD_2Cl_2.

9. Product Im-H isolated from reactions of $ImBF_4$ with H_2 in the presence of $AgBF_4$ and Et_3N catalyzed by models **1–6** in a synthetic scale

(i) Product Im-H isolated from reaction of $ImBF_4$ with H_2 catalyzed by model **1**

In an argon-filled glove box, a mixture of model **1** (12 mg, 25 μmol), $AgBF_4$ (5 mg, 25 μmol), $ImBF_4$ (77.5 mg, 250 μmol), Et_3N (35 μL, 250 μmol) and $CHCl_3$ (3.0 mL) was added to a 30 mL autoclave's inner sleeve (made of PTFE) containing a magnetic stir-bar. The inner sleeve was put to the autoclave and then the autoclave was sealed. After 1.0 MPa of H_2 was filled and released three times, the mixture was stirred under 1.0 MPa H_2 at room temperature for 8. Solvent was removed at reduced pressure to give a residue, which was subjected to silica gel column chromatography. Elution with CH_2Cl_2/hexane (v/v = 4:1) developed a colorless band, from which product Im-H (51 mg, 91%) was obtained as a white solid (note that Im-H was separated by column chromatography and monitored by thin layer chromatography (TLC) using the fluorescent TLC plates covered with silica gel GF 254 under UV irradiation).

(ii) Product Im-H isolated from reaction of $ImBF_4$ with H_2 catalyzed by model **2**

The same procedure as that described in (i) was followed, but model **2** (11 mg, 25 μmol) was used instead of model **1**. Product Im-H (49 mg, 87%) was obtained as a white solid.

(iii) Product Im-H isolated from reaction of $ImBF_4$ with H_2 catalyzed by model **3**

The same procedure as that described in (i) was followed, but model **3** (15 mg, 25 μmol) was used instead of model **1**. Product Im-H (36 mg, 64%) was obtained as a white solid.

(iv) Product Im-H isolated from reaction of $ImBF_4$ with H_2 catalyzed by model **4**

The same procedure as that described in (i) was followed, but model **4** (14.5 mg, 25 μmol) was used instead of model **1**. Product Im-H (53 mg, 95%) was obtained as a white solid.

(v) Product Im-H isolated from reaction of $ImBF_4$ with H_2 catalyzed by model **5**

The same procedure as that described in (i) was followed, but model **5** (13.5 mg, 25 μmol) was used instead of model **1**. Product Im-H (38 mg, 68%) was obtained as a white solid.

(vi) Product Im-H isolated from reaction of $ImBF_4$ with H_2 catalyzed by model **6**

The same procedure as that described in (i) was followed, but model **6** (13 mg, 25 μmol) was used instead of model **1**. Product Im-H (50 mg, 89%) was obtained as a white solid.

10. Reactions of $ImBF_4$ with H_2 in the presence of $AgBF_4$ and Et_3N catalyzed by models **1–6** and their *in situ* ^1H NMR spectra of the resulting reaction solutions (Fig. S25–S30)

(i) Reaction of $ImBF_4$ with H_2 catalyzed by model **1** and its *in situ* ^1H NMR spectrum of the resulting reaction solution

In an argon-filled glove box, a mixture of model **1** (2.4 mg, 5 μmol), $AgBF_4$ (1.0 mg, 5 μmol), $ImBF_4$ (15.5 mg, 50 μmol), Et_3N (7.0 μL, 50 μmol) and 0.6 mL of $CDCl_3$ was added to a 5 mL test tube containing a magnetic stir-bar. The test tube was put to a 30 mL inner sleeve of the autoclave and then the autoclave was sealed. After 1.0 MPa H_2 was filled and released three times, the mixture was stirred under 1.0 MPa H_2 at room temperature for 8 h and then an equimolar Ph_3CH (12.2 mg, 50 μmol) was added as internal standard. The resulting grey-black suspensions was filtered through a microfilter to give a yellowish solution, which was determined *in situ* by ^1H NMR spectroscopy to calculate its ^1H NMR yield (Fig. S25).

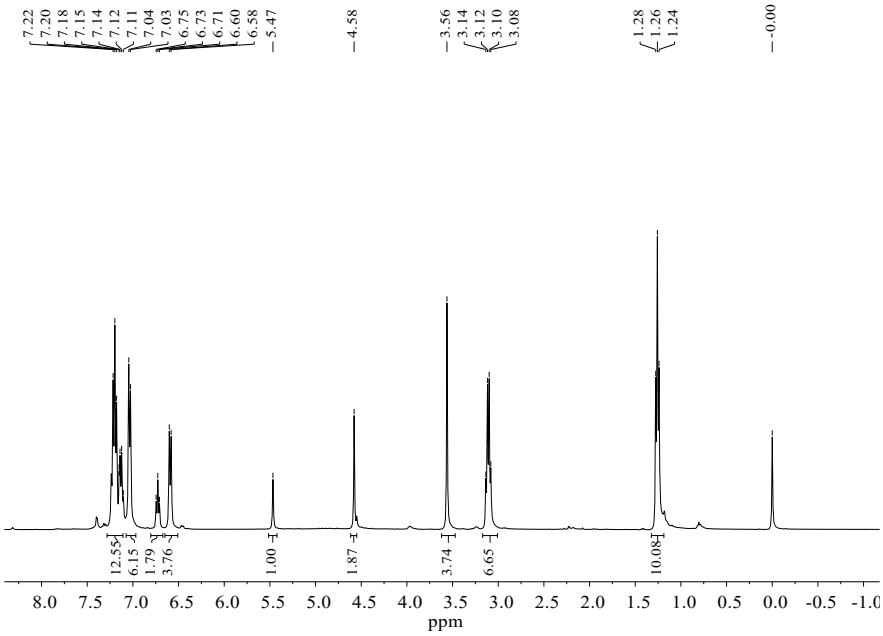

Fig. S25 ^1H NMR spectrum of the resulting solution originated from reaction of $ImBF_4$ with 1.0 MPa H_2 catalyzed by model **1** in the presence of $AgBF_4$ and Et_3N.

The ^1H NMR yield of product Im-H :

$$\frac{\text{integrated value of } NCH_2N \text{ group in Im-H}}{2} = \frac{1.87}{2} \times 100\% = 94\%$$

(ii) Reaction of $ImBF_4$ with H_2 catalyzed by model **2** (2.3 mg, 5 μmol) and its *in situ* ^1H NMR spectrum of the resulting reaction solution.

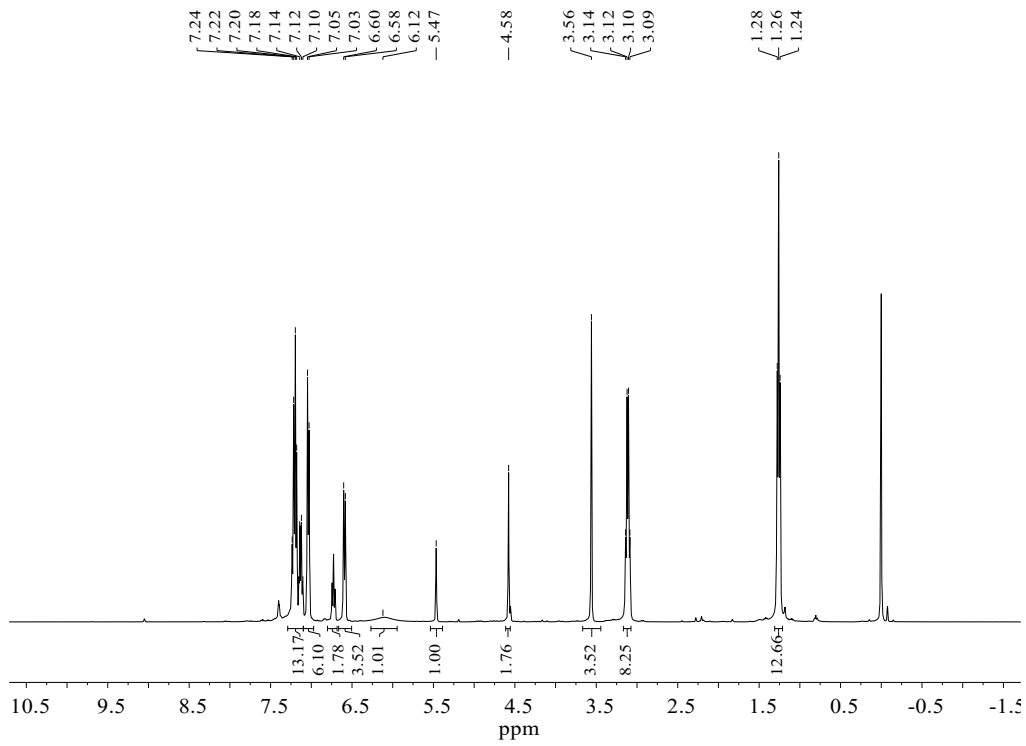

Fig. S26 ^1H NMR spectrum of the resulting solution originated from reaction of $ImBF_4$ with 1.0 MPa H_2 catalyzed by model **2** in the presence of $AgBF_4$ and Et_3N.

The ^1H NMR yield of product Im-H = $\frac{1.76}{2}$ x 100% = 88%

(iii) Reaction of $ImBF_4$ with H_2 catalyzed by model **3** (3.0 mg, 5 μmol) and its *in situ* ^1H NMR spectrum of the resulting reaction solution.

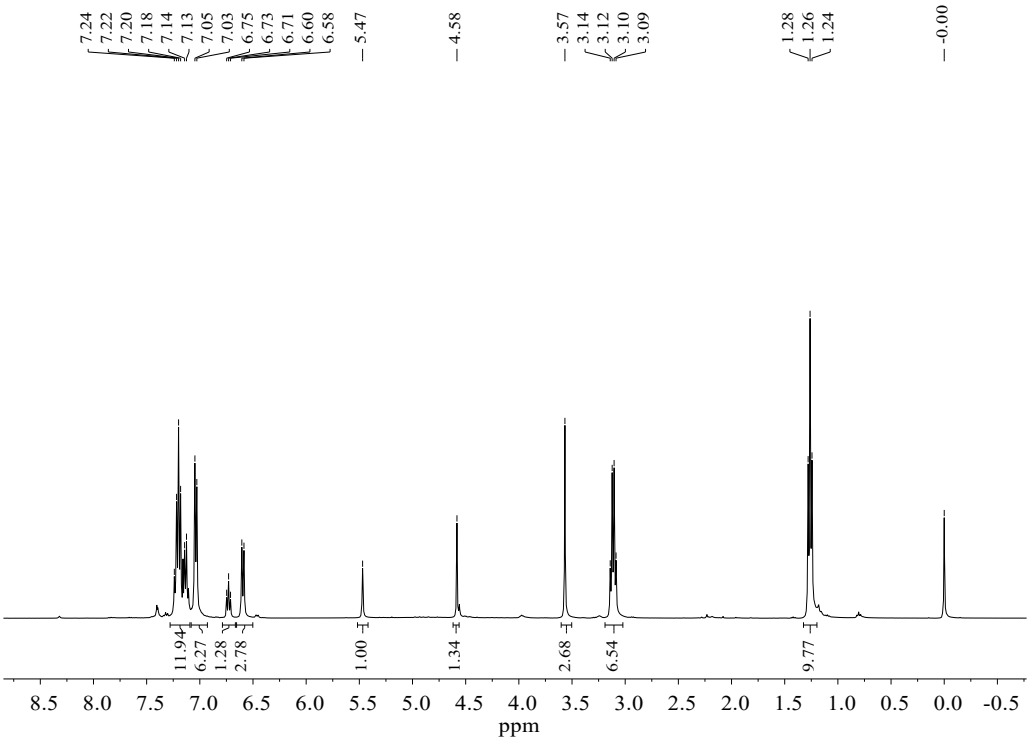

Fig. S27 ^1H NMR spectrum of the resulting solution originated from reaction of $ImBF_4$ with 1.0 MPa H_2 catalyzed by model **3** in the presence of $AgBF_4$ and Et_3N.

The ^1H NMR yield of product Im-H = $\frac{1.34}{2}$ x 100% = 67%

(iv) Reaction of $ImBF_4$ with H_2 catalyzed by model **4** (2.8 mg, 5 μmol) and its *in situ* ^1H NMR spectrum of the resulting reaction solution

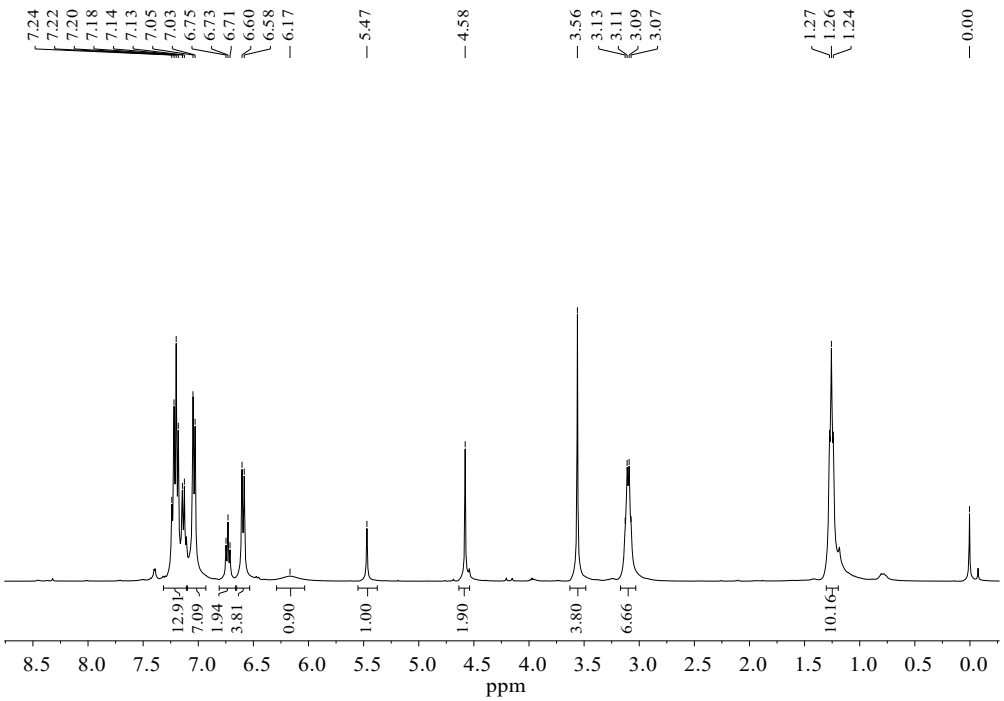

Fig. S28. ^1H NMR spectrum of the resulting solution originated from reaction of $ImBF_4$ with 1.0 MPa H_2 catalyzed by model **4** in the presence of $AgBF_4$ and Et_3N.

The ^1H NMR yield of product Im-H = $\frac{1.90}{2}$ x 100% = 95%

(v) Reaction of $ImBF_4$ with H_2 catalyzed by model **5** (2.7 mg, 5 μmol) and its *in situ* ^1H NMR spectrum of the resulting reaction solution.

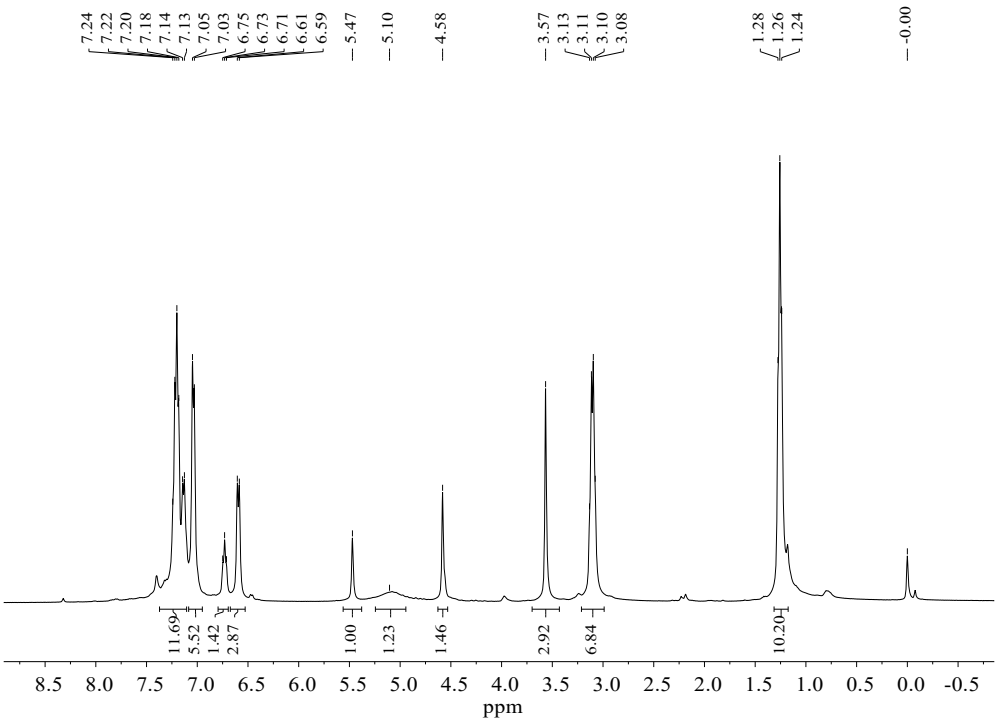

Fig. S29 ^1H NMR spectrum of the resulting solution originated from reaction of $ImBF_4$ with 1.0 MPa H_2 catalyzed by model **5** in the presence of $AgBF_4$ and Et_3N.

The ^1H NMR yield of product Im-H = $\frac{1.46}{2}$ x 100% = 73%

(vi) Reaction of $ImBF_4$ with H_2 catalyzed by model **6** (2.6 mg, 5 μmol) and its *in situ* ^1H NMR spectrum of the resulting reaction solution.

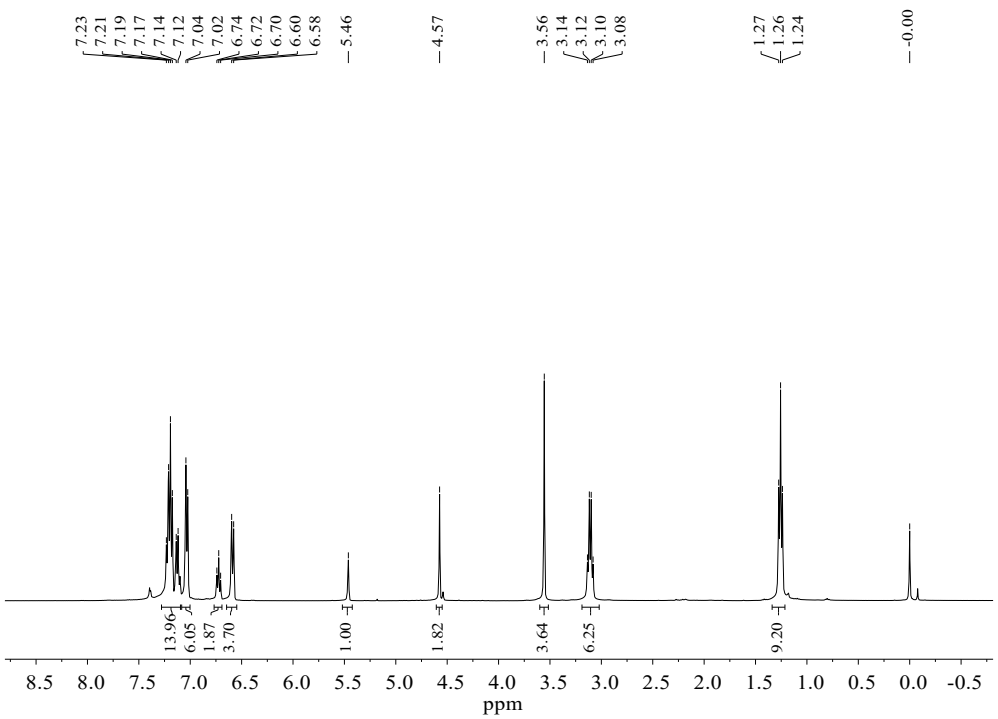

Fig. S30. ^1H NMR spectrum of the resulting solution originated from reaction of $ImBF_4$ with 1.0 MPa H_2 catalyzed by model **6** in the presence of $AgBF_4$ and Et_3N.

The ^1H NMR yield of product Im-H = $\frac{1.82}{2}$ x 100% = 91%