Supporting Information

Biomimetic Models of [Fe]-Hydrogenase Featuring a 2-Acylphenylthiomethyl-6-R-pyridine (R = H or OMe) Ligand

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1. Synthesis and Spectroscopic Characterization Data

1.1 General comments

All reactions were carried out using standard Schlenk and vacuum-line techniques under an atmosphere of highly purified nitrogen or argon. $Na_2Fe(CO)_4 \cdot (1,4\text{-dioxane})_{1.5}$ must be kept under a dry inert atmosphere at all times since it is very pyrophoric. MeCN, CH_2Cl_2, Et_3N were purified by distillation under N_2 from CaH_2. Tetrahydrofuran (THF) and *n*-hexane were distilled from Na/benzophenone ketyl under nitrogen. Trifluoroacetic acid, iodine, thionyl chloride, *p*-$MeC_6H_4SO_2Cl$ (TsCl), $AgBF_4$, 2-$HOCH_2$-6-$MeOC_5H_3N$, H_2 and D_2 were available commercially and used as received. Disodium thiosalicylate,[1] 1,3-diphenylimidazolium tetrafluoroborate ($ImBF_4$),[2] $Na_2Fe(CO)_4 \cdot (1,4\text{-dioxane})_{1.5}$,[3] 2-$TsOCH_2C_5H_4N$,[4] were prepared according to the published methods. IR spectra were recorded on a Bruker Vector 22 or Bruker Tensor 27 FT-IR infrared spectrophotometer, while ^1H, ^2H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker Avance 400 NMR and 600 NMR spectrometers, respectively. Elemental analyses were performed on an Elementar Vario EL analyzer. Melting points were determined on an SGW X-4 microscopic melting point apparatus and are uncorrected.

1.2 Synthesis and characterization data of precursors 1a,b, 2a,b and models 3a,b

1.2.1 2-$HO_2CC_6H_4SCH_2C_5H_4N$ (1a)

To a stirred solution of 2-$TsOCH_2C_5H_4N$ (2.63 g, 10.0 mmol) in THF (50 mL) was added disodium thiosalicylate (1.98 g, 10.0 mmol) and then the mixture was stirred at room temperature for 6 h. After trifluoroacetic acid (0.74 mL, 10.0 mmol) was added and the new mixture was stirred at this temperature for 0.5 h, volatiles were removed at reduced pressure and then water (100 mL) was added to the resulting residue to give a white suspension. The suspension was extracted with CH_2Cl_2 (3×50 mL) and then the combined extracts were dried over anhydrous $MgSO_4$. Removal of $MgSO_4$ and CH_2Cl_2 produced **1a** (2.20 g, 90%) as a white solid. M.p. 179 °C (dec); Anal. Calcd. for $C_{13}H_{11}NO_2S$: C, 63.65; H, 4.52; N, 5.71. Found: C, 63.45; H, 4.76; N, 5.75. ^1H NMR

(400 MHz, DMSO-d_6): δ 4.33 (s, 2H, CH_2), 7.18−8.52 (m, 8H, C_5H_4N, C_6H_4), 13.13 (s, 1H, CO_2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 38.3 (s, CH_2), 122.8, 123.8, 124.5, 126.2, 128.2, 131.4, 132.8, 137.4, 141.4, 149.5, 157.6 (11s, C_5H_4N, C_6H_4), 167.9 (s, C=O) ppm. IR (KBr disk): $\nu_{C=O}$ 1685 (s) cm^{-1}.

1.2.2 2-$HO_2CC_6H_4SCH_2$-6-$MeOC_5H_3N$ (1b)

(i) 2-$TsOCH_2$-6-$MeOC_5H_3N$

The stirred mixture consisting of 2-$HOCH_2$-6-$MeOC_5H_3N$ (0.557 g, 4.0 mmol) in THF (15 mL) and NaOH (1.20 g, 30.0 mmol) in water (15 mL) was cooled to 0 °C and then *p*-toluenesulfonyl chloride (1.14 g, 6.0 mmol) was added. The new mixture was warmed to room temperature and stirred at this temperature for 5 h. To the resulting mixture was added water (30 mL) and then the aqueous solution was extracted with CH_2Cl_2 (3×30 mL). After the combined extracts were washed with water (2×50 mL) and dried over anhydrous Na_2SO_4, removal of Na_2SO_4 and CH_2Cl_2 afforded **2-$TsOCH_2$-6-$MeOC_5H_3N$** (0.610 g, 52%) as a yellow solid. M.p. 73−74 °C; Anal. Calcd. for $C_{14}H_{15}NO_4S$: C, 57.32; H, 5.15; N, 4.78. Found: C, 57.33; H, 5.14; N, 4.78. ^1H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H, $CH_3C_6H_4$), 3.83 (s, 3H, CH_3O), 5.03 (s, 2H, CH_2), 6.63−7.84 (m, 7H, C_5H_3N, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.7 (s, $CH_3C_6H_4$), 53.4 (s, CH_3O), 71.6 (s, CH_2), 110.7, 114.5, 128.1, 129.9, 133.1, 139.2, 144.9, 151.1, 163.7 (9s, C_5H_3N, C_6H_4), ppm. IR (KBr disk): ν 1321(m), 1176 (m), 753 (s) cm^{-1}.

(ii) 2-$HO_2CC_6H_4SCH_2$-6-$MeOC_5H_3N$ (1b)

The same procedure was followed as preparation of **1a**, except that 2-$TsOCH_2$-6-$MeOC_5H_3N$ (2.94 g, 10.0 mmol) was used in place of 2-$TsOCH_2C_5H_4N$. **1b** (1.55 g, 56%) was obtained as a white solid. M.p. 164−165 °C; Anal. Calcd. for $C_{14}H_{13}NO_3S$: C, 61.08; H, 4.76; N, 5.09. Found: C, 60.73; H, 4.76; N, 5.08. ^1H NMR (400 MHz, DMSO-d_6): δ 3.84 (s, 3H, CH_3O), 4.23 (s, 2H, CH_2), 6.69−7.89 (m, 7H, C_5H_3N, C_6H_4), 13.04 (s, 1H, CO_2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 37.4 (s, CH_2), 53.0

(CH_3O), 108.8, 116.1, 124.0, 126.0, 127.8, 130.9, 132.3, 139.7, 140.9, 154.9, 163.0 (11s, C_5H_3N, C_6H_4), 167.4 (s, C=O) ppm. IR (KBr disk): $\nu_{C=O}$ 1672 (s) cm^{-1}.

1.2.3 [2-ClC(O)C_6H_4S$CH_2C_5H_4$N]·HCl (2a)

To a stirred solution of **1a** (1.23 g, 5.0 mmol) in CH_2Cl_2 (30 mL) was slowly added thionyl chloride (0.73 mL, 10.0 mmol) and then the mixture was refluxed for 4 h. Removal of volatiles at reduced pressure gave rise to **2a** (1.43 g, 95%) as a pale yellow solid. M.p. 150–151 °C; Anal. Calcd. for $C_{13}H_{11}Cl_2NOS$: C, 52.01; H, 3.69; N 4.67. Found: C, 51.96; H, 3.81; N, 4.56. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.86 (s, 2H, CH_2), 7.30–8.63 (m, 8H, C_5H_4N, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 33.0 (s, CH_2), 125.3, 126.3, 127.4, 127.6, 131.3, 135.3, 135.5, 140.8, 145.4, 154.1 (10s, C_5H_4N, C_6H_4), 167.1 (s, C=O) ppm. IR (KBr disk): $\nu_{C=O}$ 1750 (s) cm^{-1}.

1.2.4 [2-ClC(O)C_6H_4SCH_2-6-MeOC_5H_3N]·HCl (2b)

The same procedure was followed as preparation of **2a**, except that **1b** (1.38 g, 5.0 mmol) was utilized instead of **1a**. **2b** (1.62 g, 98%) was obtained as a pale yellow solid. M.p. 96–97 °C; Anal. Calcd. for $C_{14}H_{13}Cl_2NO_2S$: C, 50.92; H, 3.97; N, 4.24. Found: C, 51.29; H, 3.67; N, 4.48. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.05 (s, 3H, CH_3O), 4.47 (s, 2H, CH_2), 6.80–8.33 (m, 7H, C_5H_3N, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 36.8 (s, CH_2), 55.2 (s, CH_3O), 109.2, 116.5, 124.8, 126.1, 126.7, 128.9, 130.1, 134.6, 135.2, 141.8, 142.8, 153.4, 162.9 (13s, C_5H_3N, C_6H_4), 166.6 (s, C=O) ppm. IR (KBr disk): $\nu_{C=O}$ 1722 (s) cm^{-1}.

1.2.5 η^3-[2-C(O)C_6H_4S$CH_2C_5H_4$N]Fe$(CO)_2$I (3a)

At room temperature, Et_3N (139 μL, 1.0 mmol) was added to a suspension of **2a** (0.300 g, 1.0 mmol) in THF (10 mL) and then the mixture was sonicated for 2 min. After the insoluble [Et_3NH]Cl salt was removed by centrifugation, the resulting solution was added dropwise to a stirred suspension of $Na_2Fe(CO)_4$·(1,4-dioxane)$_{1.5}$ (0.346 g, 1.0 mmol) in MeCN (10 mL) at −78 °C. The resulting mixture was warmed slowly to 0 °C and stirred at this temperature for 0.5 h. After the mixture was cooled to −30 °C, I_2 (0.254 g, 1.0 mmol) was added. The new mixture was warmed to room temperature and

stirred at this temperature for 5 h. Solvent was removed at reduced pressure and the residue was subjected to column chromatography on silica gel. Elution with CH_2Cl_2/acetone (v/v = 10:1) developed a yellow band, from which **3a** (0.252 g, 54%) was obtained as a yellow solid. M.p. 132 °C (dec); Anal. Calcd. for $C_{15}H_{10}FeINO_3S$: C, 38.57; H, 2.16; N, 3.00. Found: C, 38.53; H, 2.35; N, 2.87. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.52, 5.26 (dd, J = 16.0 Hz, 2H, CH_2), 7.17−9.01 (m, 8H, C_5H_4N, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 51.3 (s, CH_2), 122.6, 123.9, 124.8, 131.1, 131.2, 133.4, 137.8, 138.6, 147.8, 153.7, 158.8 (11s, C_5H_4N, C_6H_4), 209.3, 210.6 (2s, C≡O), 262.0 (s, FeC=O) ppm. IR (KBr disk): $\nu_{C\equiv O}$ 2033 (vs), 1979 (vs); $\nu_{FeC=O}$ 1626 (s) cm^{-1}.

1.2.6 η^3-[2-C(O)C_6H_4SCH_2-6-MeOC_5H_3N]Fe$(CO)_2$I (3b)

The same procedure was followed as preparation of complex **3a**, except that **2b** (0.330 g, 1.0 mmol) was employed in place of **2a**. Elution with CH_2Cl_2/acetone (v/v = 40:1) developed a yellow band, from which **3a** (0.250 g, 50%) was obtained as a yellow solid. M.p. 132 °C (dec); Anal. Calcd. for $C_{16}H_{12}FeINO_4S$: C, 38.66; H, 2.43; N, 2.82. Found: C, 38.94; H, 2.56; N, 2.63. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.09 (s, 3H, CH_3O), 4.63, 5.34 (dd, J = 16.0 Hz, 2H, CH_2), 6.64−7.92 (m, 7H, C_5H_3N, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 50.9 (s, CH_2), 56.6 (s, CH_3O), 105.6, 116.3, 122.3, 130.6, 130.7, 132.9, 137.5, 141.0, 148.0, 157.7, 166.1 (11s, C_5H_3N, C_6H_4), 208.4, 212.0 (2s, C≡O), 259.8 (s, FeC=O) ppm. IR (KBr disk): $\nu_{C\equiv O}$ 2033 (vs), 1975 (vs); $\nu_{FeC=O}$ 1626 (s) cm^{-1}.

1.3 IR and ^{1}H (^{13}C) NMR spectra of models 3a,b

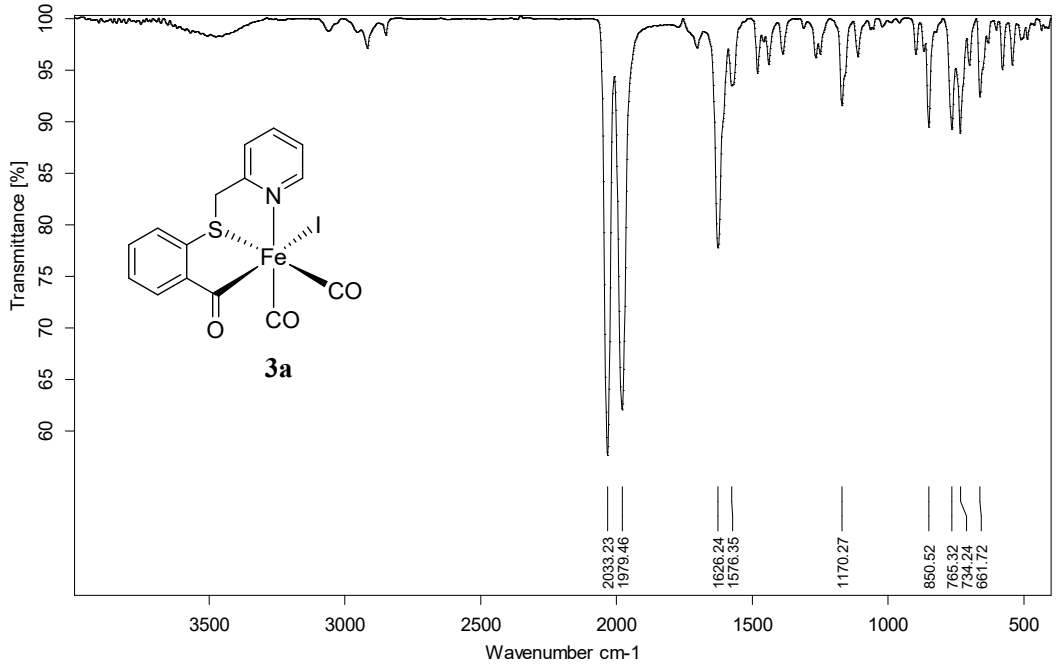

Figure S1. IR spectrum of model **3a**.

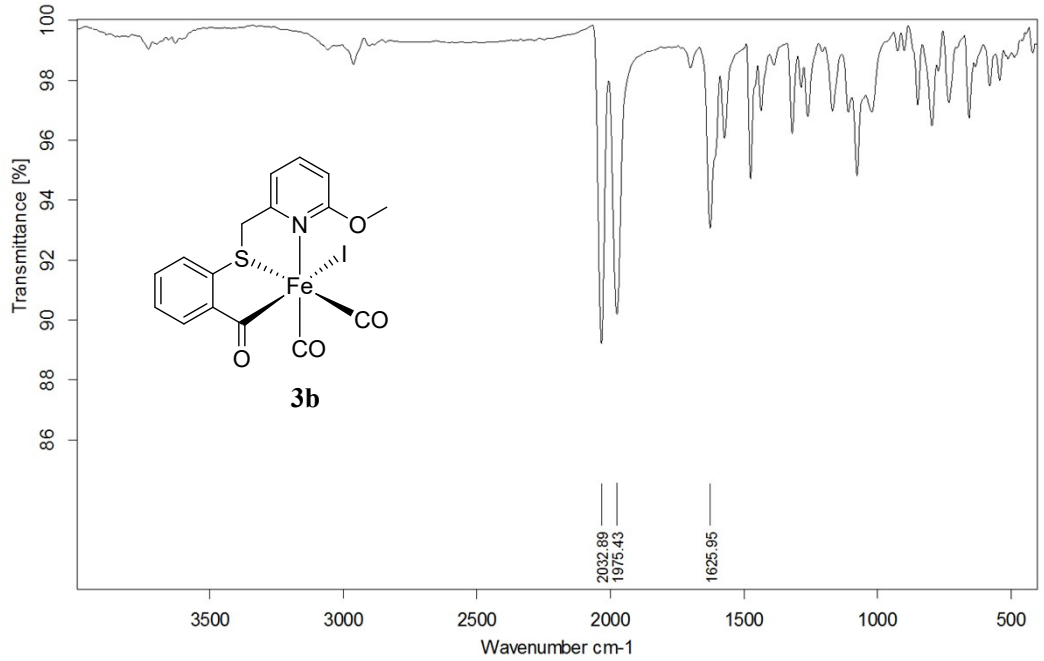

Figure S2. IR spectrum of model **3b**.

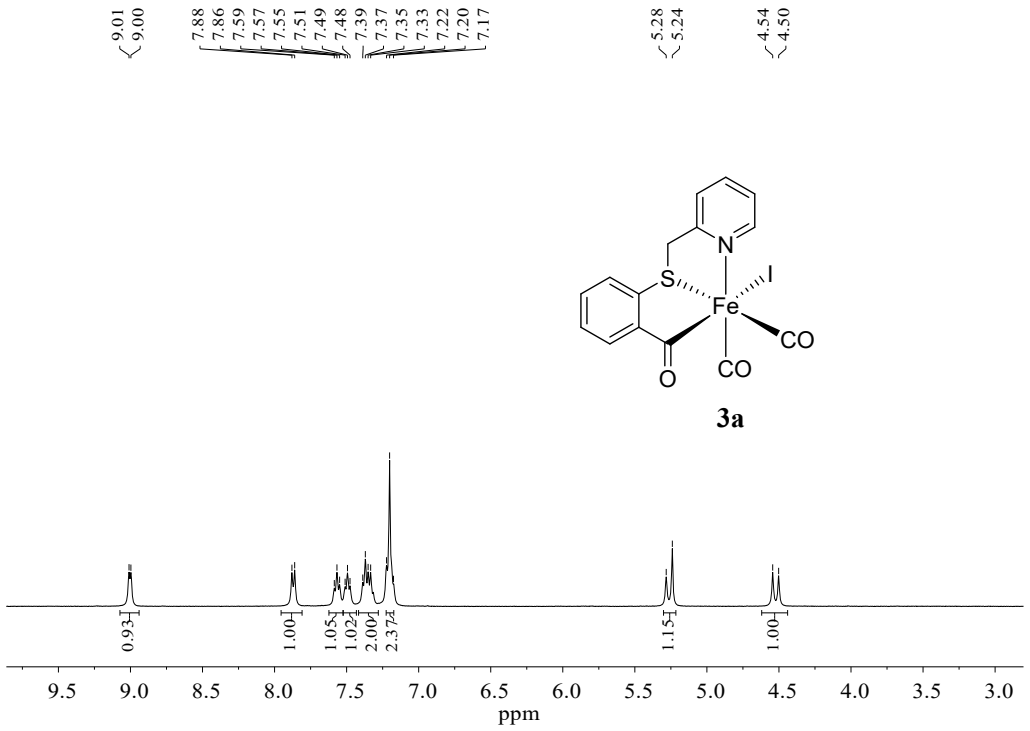

Figure S3. ^{1}H NMR spectrum of model **3a** in $CDCl_3$.

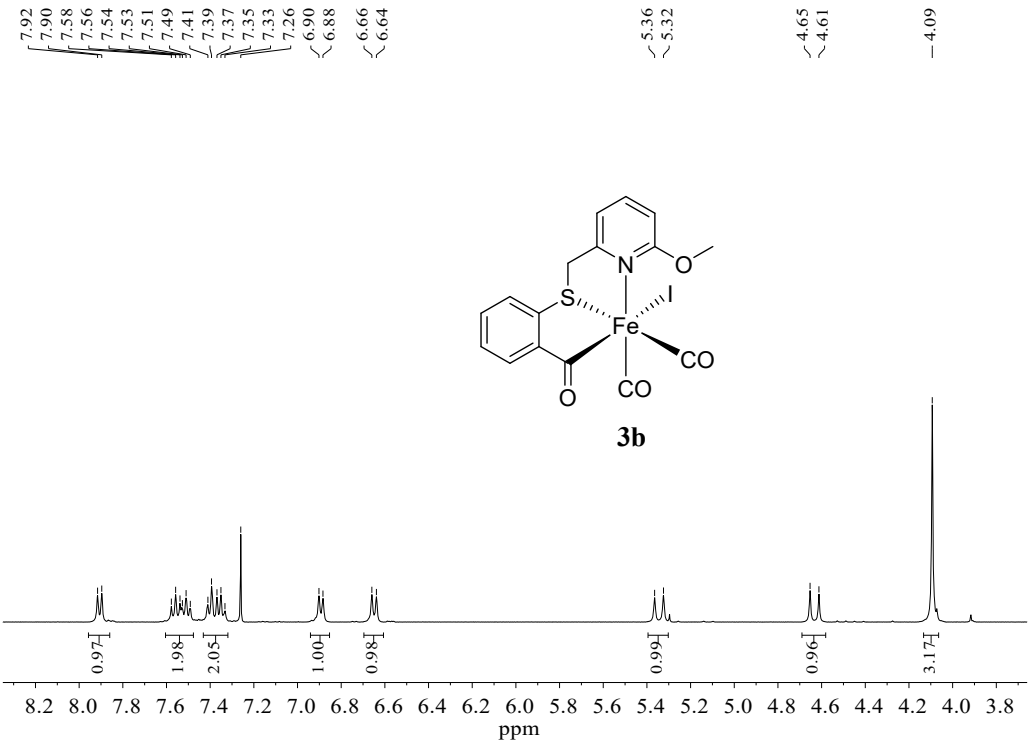

Figure S4. ^{1}H NMR spectrum of model **3b** in $CDCl_3$.

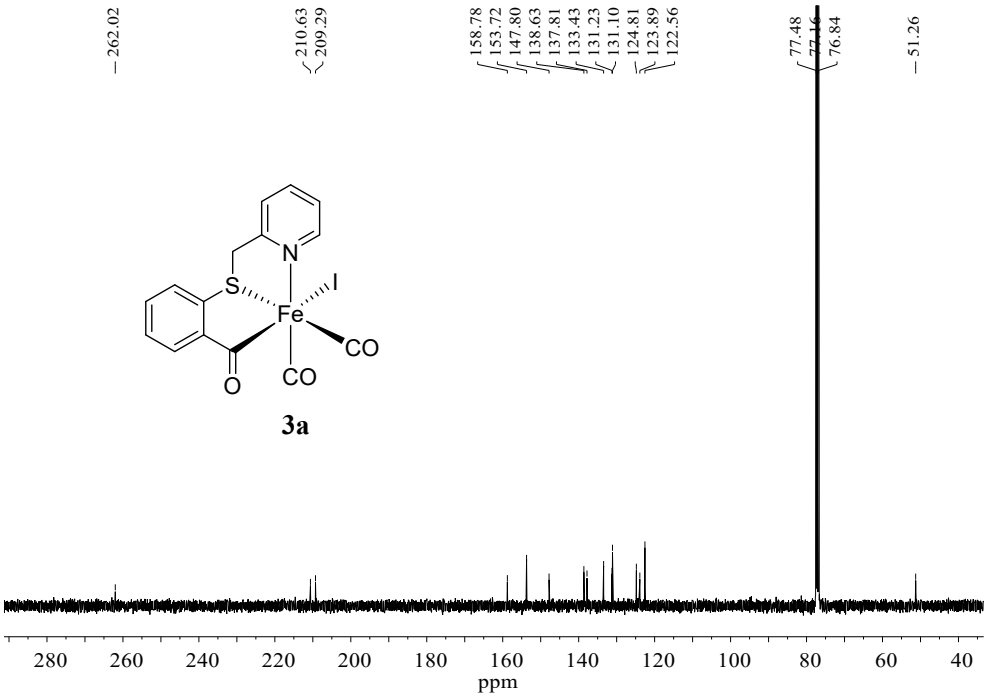

Figure S5. ^{13}C NMR spectrum of model **3a** in $CDCl_3$.

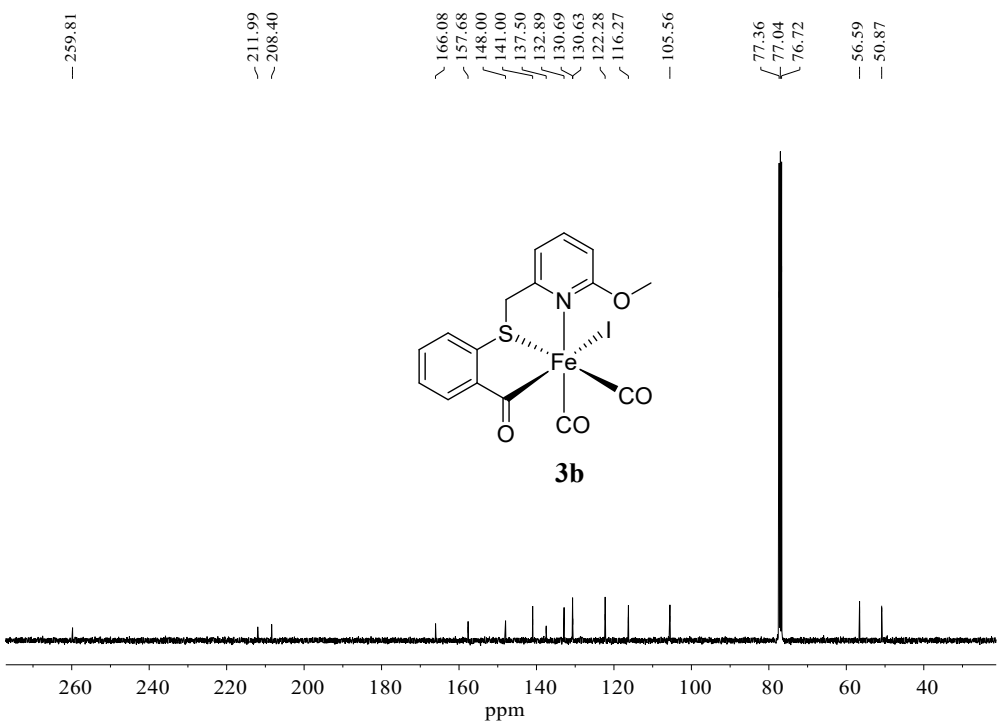

Figure S6. ^{13}C NMR spectrum of model 3b **in $CDCl_3$.**

2. Experiments for H_2 Activation and Hydride Transfer Reactions

2.1 Product Im-H isolated from reaction of $ImBF_4$ with H_2 catalyzed by model 3a or 3b (Figure S7)

In an argon-filled glove box, a mixture of model **3a** (11.7 mg, 25 μmol) or **3b** (12.4 mg, 25 μmol), $AgBF_4$ (10 mg, 50 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 14 h to give a grey suspension in the case of **3a** or **3b** (see Figure S7). 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 = 1:4) developed a colorless band, from which product Im-H (26.3 mg, 47% in the case of **3a** or 19.7 mg, 35% in the case of **3b**) 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). M.p. 124–125 °C (lit[5] 127 °C); Anal. Calcd. for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.37; H, 7.20; N, 12.64. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.68 (s, 4H, NCH_2CH_2N), 4.69 (s, 2H, NCH_2N), 6.69–7.33 (m, 10H, $2C_6H_5$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 46.7 (s, NCH_2CH_2N), 66.1 (s, NCH_2N), 112.7, 117.9, 129.5, 146.5 (4s, C_6H_5) ppm. IR (KBr disk): *ν* 1603, 1574, 1501, 1347, 1239, 1187, 1158, 994, 868, 744, 693 cm^{-1}.

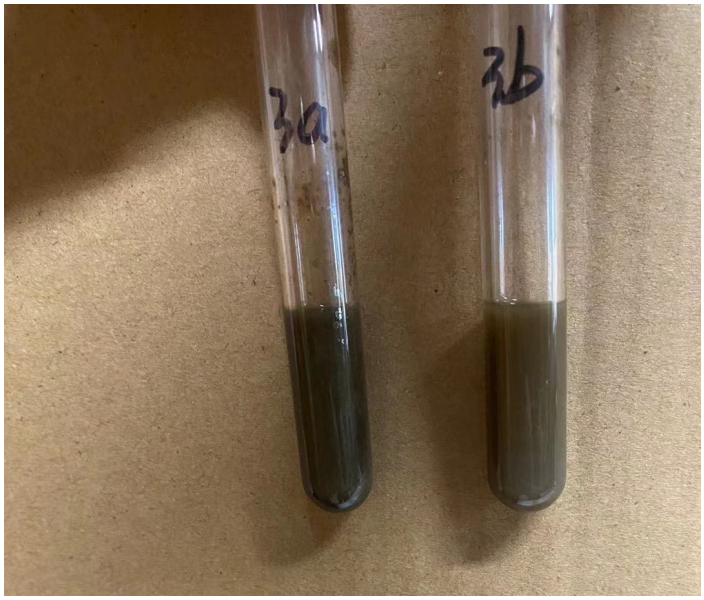

Figure S7. A photo showing the two grey suspensions originated in the cases of **3a,b**.

2.2 Reaction of $ImBF_4$ with H_2 catalyzed by model 3a or 3b and the *in situ* ^1H NMR spectra (Figures S8 and S9)

The same reaction of $ImBF_4$ with H_2 in the presence of **3a** or **3b**, $AgBF_4$, Et_3N was carried out as described in 2.1 except that $CHCl_3$ was replaced by $CDCl_3$. The resulting grey suspension originated in the case of **3a** or **3b** was filtered through a microfilter to give the corresponding yellow $CDCl_3$ solutions, which were determined *in situ* by ^1H NMR spectroscopy (Figures S8 and S9) to prove the formation of product Im-H and concomitant product $[Et_3NH]BF_4$.[6]

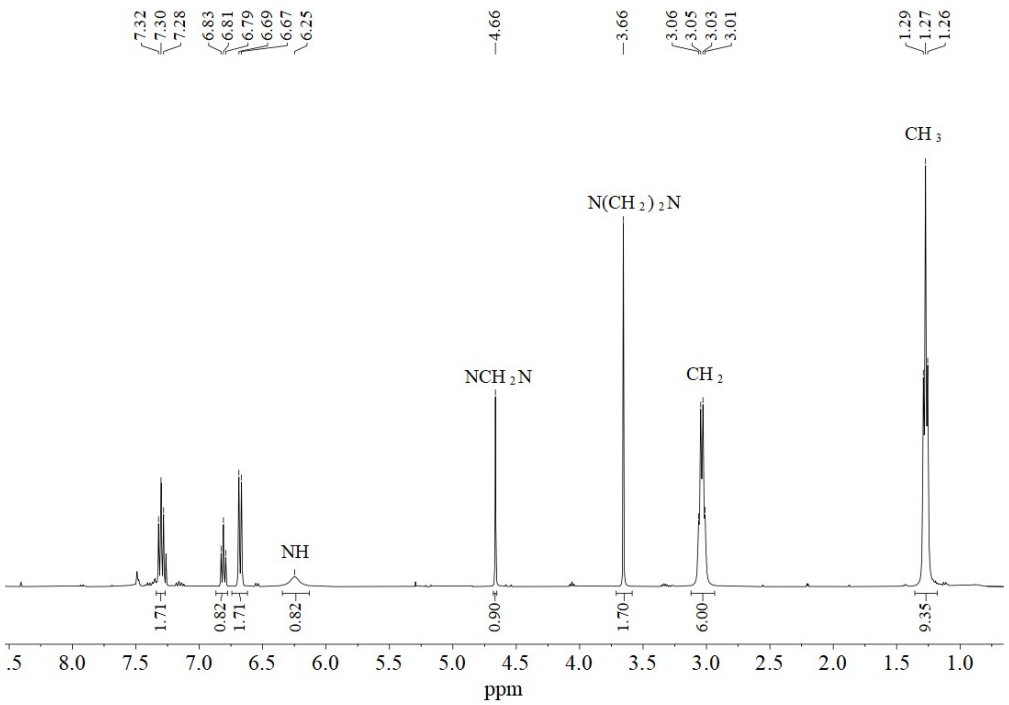

Figure S8. ^{1}H NMR spectrum of the resulting solution originated from reaction of $ImBF_4$ with 1.0 MPa H_2 catalyzed by model **3a** in the presence of $AgBF_4$ and Et_3N.

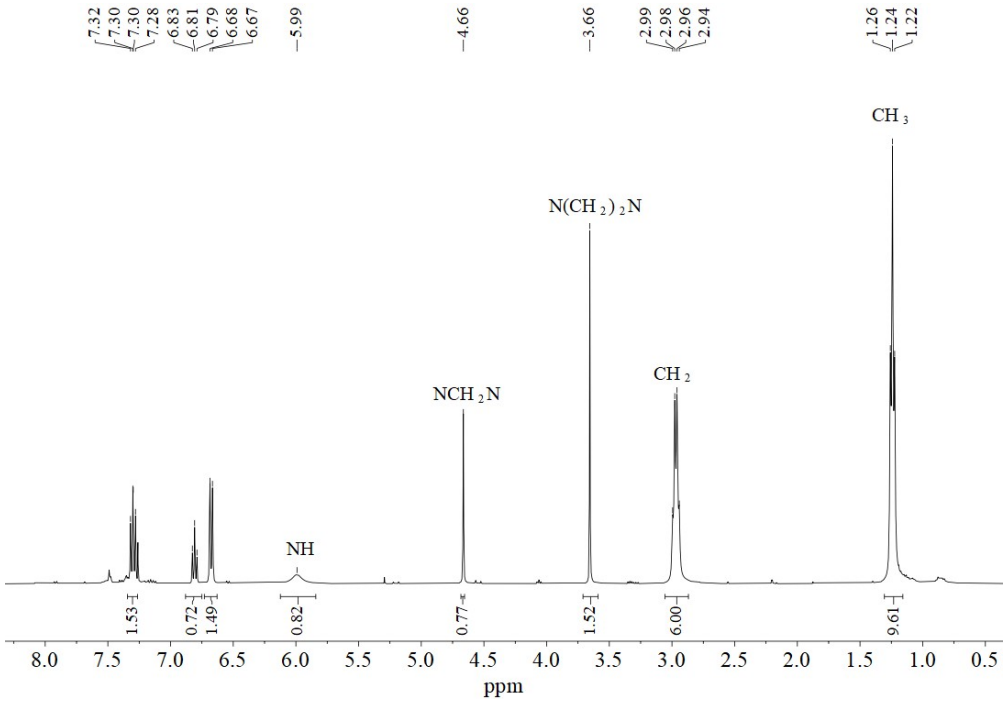

Figure S9. ^{1}H NMR spectrum of the resulting solution originated from reaction of $ImBF_4$ with 1.0 MPa H_2 catalyzed by model **3b** in the presence of $AgBF_4$ and Et_3N.

3. Experiments for D_2 Activation and Deuteride Transfer Reactions

3.1 Product Im-D isolated from reaction of $ImBF_4$ with D_2 catalyzed by model 3a or 3b

In an argon-filled glove box, a mixture of model **3a** (11.7 mg, 25 μmol) or **3b** (12.4 mg, 25 μmol), $AgBF_4$ (10 mg, 50 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 containing a magnetic stir-bar. The same procedure was followed as that for the aforementioned H_2 activation except that 1.0 MPa H_2 was replaced by 1.0 MPa D_2. New product Im-D (24.8 mg, 44% in the case of **3a** or 18.6 mg, 33% in the case of **3b**) was obtained as a white solid. M.p. 119−120 °C; Anal. Calcd. for $C_{15}H_{15}DN_2$: C, 79.96; H, 7.60; N, 12.43. Found: C, 79.99; H, 7.43; N, 12.26. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67 (s, 4H, NCH_2CH_2N), 4.66 (s, 1H, NCHDN), 6.68−7.34 (m, 10H, $2C_6H_5$) ppm. ^{2}H NMR (600 MHz, $CHCl_3$): δ 4.71 (NCHDN) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 46.6 (s, NCH_2CH_2N), 65.4, 65.6, 65.9 (3s, NCHDN), 112.5, 117.7, 129.5, 146.5 (4s, C_6H_5) ppm. IR (KBr disk): *ν* 1604, 1577, 1508, 1347, 1239, 1187, 1159, 994, 868, 744, 693 cm^{-1}.

3.2 Reaction of $ImBF_4$ with D_2 catalyzed by model 3a or 3b and the *in situ* ^2H NMR spectra (Figures S10 and S11)

The same reaction of $ImBF_4$ with D_2 in the presence of $AgBF_4$, Et_3N was carried out as described in 3.1, except that the resulting suspension originated in the case of **3a** or **3b** was filtered through a microfilter to give the corresponding two yellow $CHCl_3$ solutions, which were determined *in situ* by ^2H NMR spectroscopy to prove the formation Im-D and concomitant product $[Et_3ND]BF_4$.

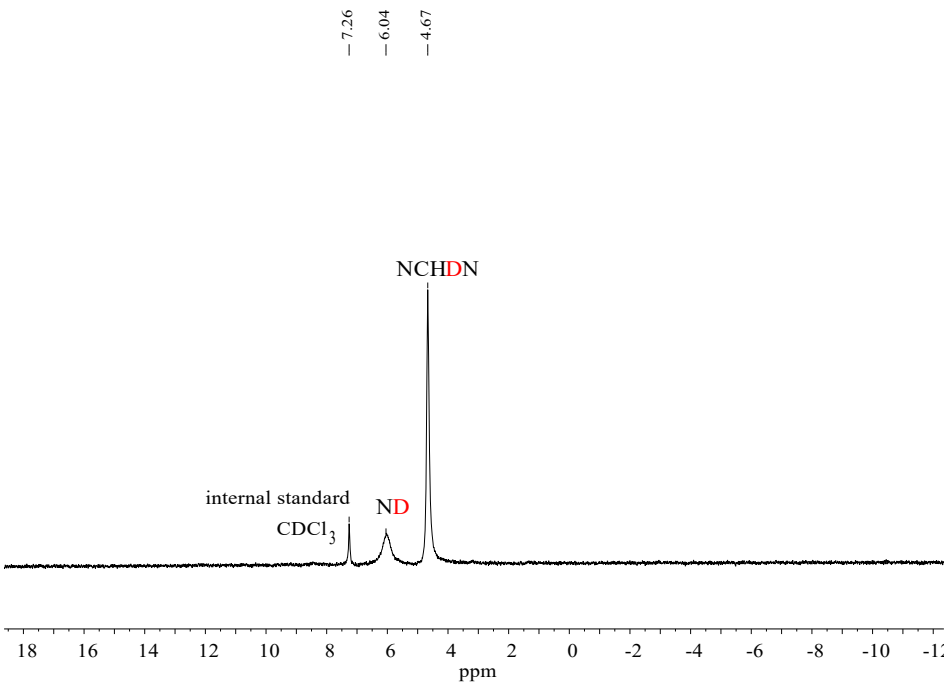

Figure S10. ^{2}H NMR spectrum of the resulting $CHCl_3$ solution originated from reaction of $ImBF_4$ with 1.0 MPa D_2 catalyzed by model **3a** in the presence of $AgBF_4$ and Et_3N.

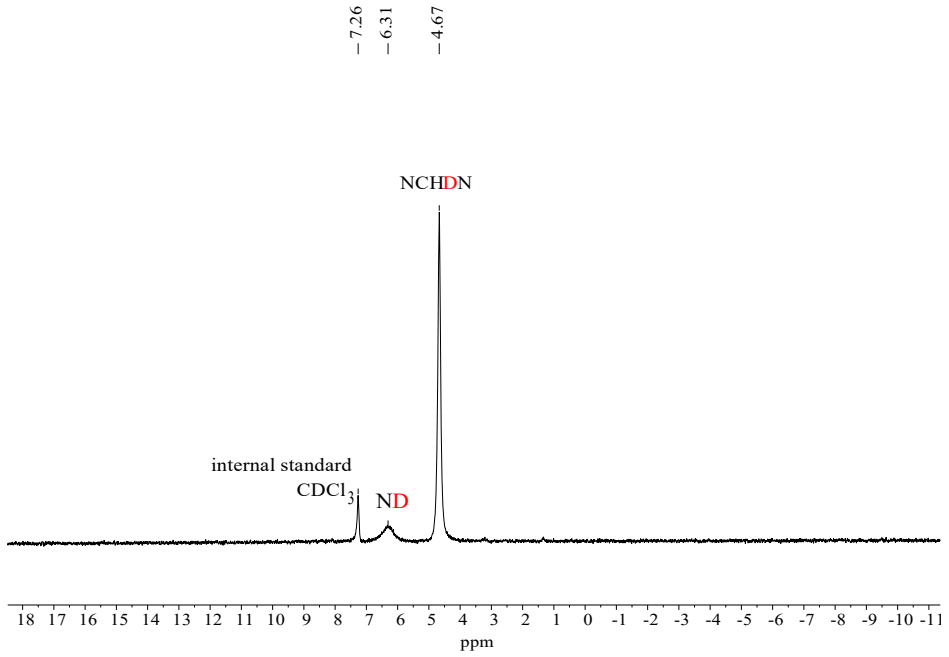

Figure S11. ^{2}H NMR spectrum of the resulting $CHCl_3$ solution originated from reaction of $ImBF_4$ with 1.0 MPa D_2 catalyzed by model **3b** in the presence of $AgBF_4$ and Et_3N.

4. *In situ* IR and ^{1}H NMR Spectra of the 5-Coordinate Intermediate $\{\eta^3$-[2-C(O)$C_6H_4SCH_2$-6-RC_5H_3N]Fe$(CO)_2\}^+$ (M_3, R = H) Suggested in the Mechanistic Pathway

(1) In a nitrogen-filled glove box, model **3a** (4.7 mg, 10 μmol), $AgBF_4$ (4.0 mg, 20 μmol) and 0.6 mL of $CDCl_3$ were placed in a 25 mL flask containing a magnetic stir-bar. The mixture was stirred at room temperature for 1 h and then was filtered. The IR spectrum of the resulting solution was determined in order to prove formation of the 5-coordinated cationic intermediate **M_3** (R = H) (Figure S12).

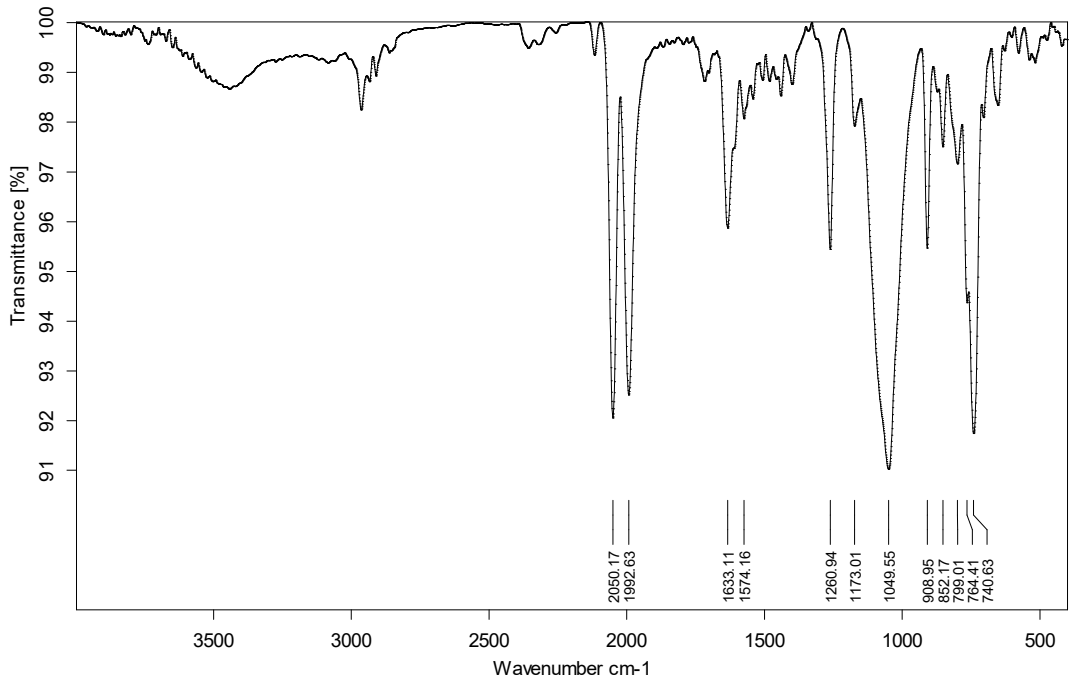

Figure S12. *In situ* IR spectrum of the 5-coordinate intermediate $\{\eta^3$-[2-C(O)$C_6H_4SCH_2$-6-RC_5H_3N]Fe$(CO)_2\}^+$ (**M_3**, R = H) formed from reaction of model **3a** with $AgBF_4$ in $CDCl_3$.

(2) In a nitrogen-filled glove box, model **3a** (9.3 mg, 20 μmol), $AgBF_4$ (8.0 mg, 40 μmol) and 0.6 mL of $CDCl_3$ were placed in a 25 mL flask containing a magnetic stir-bar. The mixture was stirred at room temperature for 1 h and then was filtered. The ^1H NMR spectrum of the resulting solution was determined in order to prove formation of the 5-coordinated cationic intermediate $\mathbf{M_3}$ (R = H) (Figure S13).

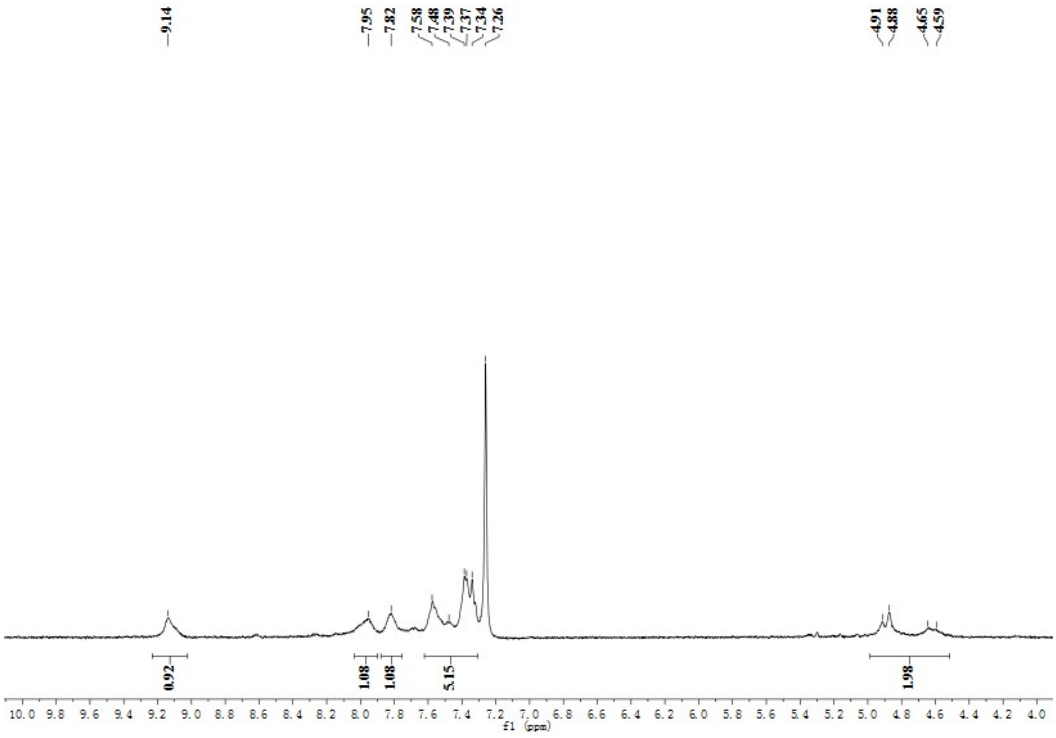

Figure S13. *In situ* ^1H NMR spectrum of the 5-coordinate intermediate $\{\eta^3$-[2-$C(O)C_6H_4SCH_2$-6-$RC_5H_3N]Fe(CO)_2\}^+$ ($\mathbf{M_3}$, R = H) formed from reaction of model **3a** with $AgBF_4$ in $CDCl_3$.

5. *In situ* IR Spectrum of the Fe–H Intermediate η^3-[2-C(O)$C_6H_4SCH_2$-6-RC_5H_3N]Fe(CO)$_2$H ($\mathbf{M_5}$, R = H) Suggested in the Mechanistic Pathway

(1) In an argon-filled glove box, model **3a** (18.7 mg, 40 μmol), $AgBF_4$ (15.6 mg, 80 μmol), Et_3N (28.0 μL, 0.20 mmol) and 0.6 mL of $CDCl_3$ were 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 of H_2 was filled and released three times, the mixture was stirred under 1.0 MPa H_2 at room temperature for 1 h. The resulting grey suspension was filtered through a microfilter to give a yellowish solution. The IR spectrum of the solution was determined in order to prove formation of the Fe–H intermediate $\mathbf{M_5}$ (R = H) (Figure S14)

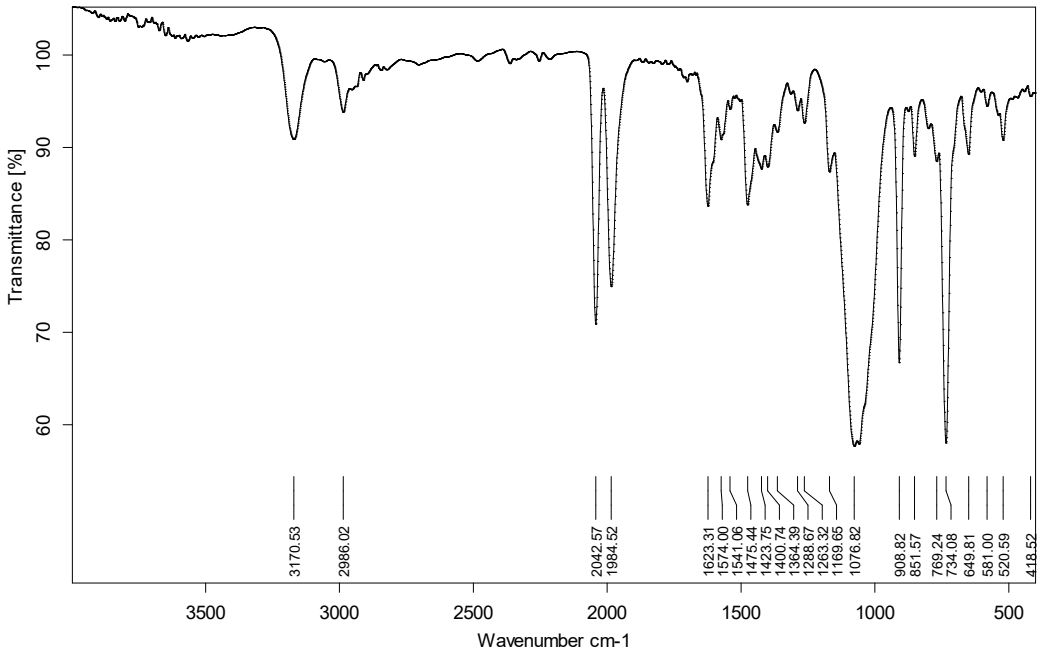

Figure S14. *In situ* IR spectrum of the Fe–H intermediate η^3-[2-C(O)$C_6H_4SCH_2$-6-RC_5H_3N]Fe(CO)$_2$H ($\mathbf{M_5}$, R = H) generated from reaction of model **3a** with H_2 in the presence of $AgBF_4$ and Et_3N in $CDCl_3$.

(2) In an argon-filled glove box, model **3a** (18.7 mg, 40 μmol), $AgBF_4$ (15.6 mg, 80 μmol), Et_3N (28.0 μL, 0.20 mmol) and 0.6 mL of $CDCl_3$ were 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 of H_2 was filled and released three times, the mixture was stirred under 1.0 MPa H_2 at room temperature for 1 h. The resulting grey suspension was filtered through a microfilter to give a yellowish solution. The ^1H NMR spectrum of the solution was determined in order to prove formation of the Fe–H intermediate $\mathbf{M_5}$ (R = H) (see Figure 5 in the text).

6. X-Ray Crystal Structure

6.1 Crystal structure determinations of models 3a,b

The single crystals of **3a,b** were grown by slow evaporation of their CH_2Cl_2/*n*-hexane solutions at −30 °C for **3a** and at room temperature for **3b**, respectively. A single crystal of **3a** was mounted on a Bruker P4 diffractometer, whereas a single crystal of **3b** was mounted on a Rigaku-D diffractometer. The crystal data of **3a,b** were collected using a confocal monochromator with Mo Kα radiation (λ = 0.71073 Å) in the ω scanning mode at 113 K. The data collection, reduction, and absorption correction were performed by the CRYSTALCLEAR program,[7] whereas the structures were solved by direct methods using the SHELXT program[8,9] and refined by full-matrix least-squares techniques (SHELXL)[9] on F^2. Hydrogen atoms were located by using the geometric method. Details of crystal data, data collections, and structure refinements are summarized in Table S1. CCDC 2167104 and 2167105 contain the supplementary crystallographic data of **3a,b** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6.2 Crystal data and structure refinement details for models 3a,b

Table S1. Crystal data and structure refinement details for models **3a,b**.

	3a	**3b**
mol formula	$C_{15}H_{10}FeINO_3S$	$C_{16}H_{12}FeINO_4S$
mol wt	467.05	497.08
cryst syst	triclinic	orthorhombic
space group	P-1	$P2_12_12_1$
a /Å	8.2779(17)	7.7561(2)
b /Å	8.2797(17)	12.2662(3)
c /Å	13.137(3)	18.2643(6)
α /deg	91.00(3)	90
β /deg	94.52(3)	90
γ /deg	119.13(3)	90
V/Å^3	782.5(3)	1737.68(8)
Z	2	4
*D*c/g·cm^{-3}	1.982	1.900
abs coeff/mm^{-1}	3.079	2.784
F(000)	452	968.0
index ranges	$-10 \le h \le 10$	$-9 \le h \le 10$
	$-10 \le k \le 10$	$-16 \le k \le 16$
	$-17 \le l \le 17$	$-24 \le l \le 22$
no. of reflns	9225	17781
no. of indep reflns	3661	4507
$2\theta_{max}$ /deg	55.70	57.398
Final R indexes [I>=2σ (I)]	$R_1 = 0.0400$, $wR_2 = 0.0845$	$R_1 = 0.0337$, $wR_2 = 0.0812$
Final R indexes [all data]	$R_1 = 0.0473$, $wR_2 = 0.0867$	$R_1 = 0.0365$, $wR_2 = 0.0839$
GOF	0.786	1.070
largest diff peak and hole/eÅ^{-3}	1.092 and −1.938	1.566 and −1.017

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